UNIVERSITY OF CALIFORNIA SAN DIEGO

Oh, Where Electrons Will Go

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Chemistry

by

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Committee in charge:

Professor Guy Bertrand, Chair
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Professor Clifford P. Kubiak
Professor Robert S. Pomeroy
Professor Alina M. Schimpf

2021

The dissertation of Glen Paxton Junor is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2021

DEDICATION

This dissertation is dedicated to my wife Victoria Junor who has wholeheartedly supported my development as a scientist and a father. Together we moved to San Diego with our eight-month-old daughter to begin my work towards a PhD. While I was teaching, taking classes, and doing research she was teaching our daughter how to sleep, eat, and use the toilet. Over the years at UC San Diego, our marriage has grown deeper and increasingly fulfilling, and our daughter has grown to be curious, independent, and self-confident. I cannot be prouder of Victoria. Though invisible, her contributions to the work done in this document are enormous.

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LIST OFABBREVIATIONS

NaOH: Sodium Hydroxide

NHC: N-heterocyclic carbene

CAAC: Cyclic(alkyl)(amino) carbene

CAArC: Cyclic(amino)(aryl) carbene

DAC: Diamidocarbene

***py*NHC:** pyramidalized N-heterocyclic carbene

***a*NHC:** abnormal N-heterocyclic carbene

MIC: mesoionic carbene

BiCAAC: Bicyclic(alkyl)(amino) carbene

Ad: adamantyl

Cy: cyclohexyl

Mes: 2,4,6-trimethylphenyl

***i*Pr:** isopropyl

***t*Bu:** tert-butyl

Dipp: 2,6-diisopropylphenyl

Me: methyl

IAd: 1,3-bis(adamantyl)-imidazol-2-ylidene

I^{t}Bu: 1,3-bis(tert-butyl)-imidazol-2-ylidene

I^{i}Pr: 1,3-bis(isopropyl)-imidazol-2-ylidene

ICy: 1,3-bis(cyclohexyl)-imidazol-2-ylidene

IMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene

SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene

I^{i}PrMe$_2$: 1,3-bis(isopropyl)-4,5-dimethyl-imidazol-2-ylidene

DFT: Density Functional Theory

NCHB: Non-Classical Hydrogen Bond

QTAIM: Quantum Theory of Atoms in Molecules

BCP: Bond path critical point

NMR: Nuclear Magnetic Resonance

TEP: Tolman Electronic Parameter

IR: Infrared

CO: carbon monoxide

HEP: Huynh Electronic Parameter

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

***bz*NHC:** benzimidazol-2-ylidene

CBA: Cyclic-bentallene

sNHC: imidazolin-2-ylidene

MAC: monoamido carbene

***thio*NHC:** thiazolylidene

DMSO: dimethylsulfoxide

THF: Tetrahydrofuran

9-BBN: 9-borabicyclononane

BPin: pinacolboryl

Ph: phenyl

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I am also immensely grateful for my undergraduate research advisor at UC Irvine, Prof. Matt Law. I emailed you May 13th 2013 as a student at a local community college (Orange Coast College), expressing my desire to join your group, after reading three papers you recently published on nanocrystal semiconductors. At the time, I did not understand what a volt was, yet I was asking you to accept me into your research on electronics! You offered to meet with me and discuss a summer research position. I remember coming to the interview in an ill-fitting suit, barely

able to contain my excitement about all of the projects you presented to me. I worked in your group for more than three years and loved it! It is hard to explain the scale of the transformation I went through in those years. I remember the look of horror in the guidance councilor's eyes when I signed up for 21 units of only math, physics, and chemistry in my very first quarter at UCI. I felt I was barely keeping my head above water, and I needed a guide, so I watched everything you did! I carefully observed how you analyzed results, navigated interpersonal conflict in your group, sought funding, applied for tenure, and how you did it all while raising your two baby girls! When my wife became pregnant in 2015, we needed to consider our plans for the future and my career trajectory. We had complete confidence that I would be able to successfully pursue my PhD and find a career in science because of my experience in your group. When I started community college, I was a psychology major with zero experience in physical science. As I began to learn my deep interest in chemistry and physics, I was repeatedly met with rejection. Two of the most memorable were from guidance counselors saying, "no psychologist successfully switches to chemistry, only the other way" and "you will never be a chemist." However, you did not seem to care about my pedigree, only that I was interested in your work, and you decided to let me try. It is amazing what can come out of such a simple kindness. Thank you for giving me a chance!

I must also thank my General Chemistry professor at Orange Coast College, Prof. Helen Maughan. I was so excited when I started your class, but I was also riddled with fear. I had just rejected my offer to transfer out of community college and get my bachelor's degree in psychology because I wanted to study chemistry. I was so scared that I would fail and prove that my dreams of studying chemistry were a huge mistake, but your lectures were so engaging and your explanations in the lab were so interesting that my wonder and passion were able to overcome my fear. You noticed that I was genuinely interested in what we were studying and would give me papers to read, or extra experiments to do to keep my excitement going. In fact, it was you that suggested I join a research group at UCI! I wanted to join one, but only planned to try after one or two years of classwork there. You told me to start in the summer before I even began classes!

You were the catalyst that began my journey to the PhD in chemistry. I think it was crucial that I got to spend three years in research before starting grad school. I think it was critical that I learned fundamental physics and chemistry while being able to directly apply my lessons in a research lab. You are a phenomenal teacher. You saw something in me that I did not know myself, and you pushed me to explore it. Without such guidance and support, I have no idea where I would be today.

I think perhaps one of the best project managers around is Dr. Rodolphe Jazzar. I always have plenty of ideas and I am happy running reactions and carefully analyzing the results. However, as the mountain of data grows it becomes difficult to remember what the point is! While troubleshooting a reaction, optimizing conditions, and trying to isolate and understand byproducts and impurities, I often found myself overwhelmed. On multiple occasions I even wanted to quit! You would sit me down and help sift through the data, pulling out all the little (and sometimes big!) discoveries I already made. Many of my publications are a direct result of such project management. I would pursue some large overarching idea, but you would help me publish the discoveries we made along the way. Through you, I have become much better at finding and valuing the important incremental progress that pushes science forward.

I must also thank my wife Victoria Junor for the work she has put towards both editing this dissertation and the years of listening to my near constant thoughts on the chemical natures of everything around us. You listened to me practice every scientific presentation, from Law group meetings at UCI to my thesis defense at UCSD. You were there when I mixed an iron bar, bleach, and vinegar in an attempt to create a large amount of “rust” for a thermite reaction (before I understood chemistry enough to know better…). You have heard many repetitions of the selenophenol story, which I often repeat to entertain guests, and you listen to my musings on the chemical composition of all the foods we eat. You have patiently supported my ever-growing love for the scientific principles that underlie the world around us, and gently steered the conversations to more important topics when I went on too long. For this dissertation, you thoroughly read the

first two chapters and provided excellent, detailed comments. Of course, this all pales in comparison to the enormous contributions you have made to both mine and our daughter's lives on a daily basis. I love you with all my heart and I am grateful you are in my life!

After my wife, Prof. Cory Windorff has been the most critical source of emotional support I have had. I met you in Irvine after you arrived in the summer to begin your PhD in chemistry. I had just taken my first chemistry course and was considering switching my major from psychology, which was an emotional decision. We were talking late one night over coffee and you posed the fateful question: "want to see me dispose of Uranium waste?" I have never been the same since! Your unbridled passion for chemistry has been nothing short of a constant inspiration for me. In the beginning, you showed me how to use a Schlenk line and helped me understand my first inorganic chemistry courses. Now, you commiserate with me on paper and grant rejections and the challenges of being a professional chemist. With you, I have a friend that can relate to nearly every aspect of my professional and personal life, a rare privilege. I look forward to being close friends with you for many years into the future!

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There has also been a number of mentors in the lab that have helped shape the direction I have travelled to the completion of my PhD. Dr. Jesse Peltier, I am grateful for your willingness to share your job search experience, partake in intense personal-finance discussions, and send daily gratitude lists with me! Prof. Erik Romero, thank you for staying friends and sharing your insights with me as you moved from senior grad student to postdoc and “finally” to professor at UCSD! Dr. Mohand Melaimi and Dr. Cory Weinstein, you were my earliest mentors in the Bertrand group (when I was an undergraduate summer student!). You both played a large part in my ultimate decision to join UCSD for my PhD.

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None of the work I did would be possible without the facility managers of UCSD. Dr. Robert Konecny, you are always available to help me utilize and navigate computational resources, which have been critical for the theoretical discussions found throughout this dissertation. Dr. Anthony Mrse, not only do you keep the NMR facility running, but you are always available to sit and discuss both the simple and more advanced experiments. Dr. Milan Gembicky, you have built a phenomenal X-ray facility and you have taken a lot of time to teach and mentor me over the years. Of course, you also have solved many nearly impossible crystal structures for me!

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Chapter 2, in part, has been adapted from Cory. M. Weinstein, Glen. P. Junor, Daniel R. Tolentino, Rodolphe Jazzar, Mohand Melaimi, and Guy Bertrand "Highly Ambiphilic Room Temperature Stable Six-Membered Cyclic (Alkyl)(amino)carbenes" *Journal of the American Chemical Society*, 2018, *140*, 9255-9260. The dissertation author was co-author of this paper.

Chapter 3, in part, has been adapted from Glen P. Junor, Jan Lorkowski, Cory M. Weinstein, Rodolphe Jazzar, Cezary Pietraszuk, and Guy Bertrand "The influence of C(sp^3)H-Selenium Interactions on the ^{77}Se NMR Quantification of the π-Accepting Properties of Carbenes" *Angewandte Chemie International Edition*, 2020, *59*, 22028-22033. The dissertation author was the primary investigator and author of this paper.

Chapter 4, in part, is currently being prepared for submission for publication of the material Francois Vermersch, Sima Yazdani, Glen P. Junor, Douglas B Grotjahn, Rodolphe Jazzar, and Guy Bertrand "Experimental Comparison of Carbene Brønsted Basicity, a Proxy for σ-Donating Properties." The dissertation author was co-author of this paper.

Chapter 5, in part, has been adapted from Glen P. Junor, Erik A. Romero, Xi Chen, Rodolphe Jazzar, and Guy Bertrand "Readily Available Primary Aminoboranes as Powerful Reagents for Aldimine Synthesis" *Angewandte Chemie International Edition*, 2019, *58*, 2875-2878. The dissertation author was the primary investigator and author of this paper.

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G. P. Junor[#], J. Lorkowski[#], C. M. Weinstein, R. Jazzar, C. Pietraszuk, G. Bertrand. The influence of C(sp^3)H-Selenium Interactions on the ^{77}Se NMR Quantification of the π-Accepting Properties of Carbenes. *Angew. Chem. Int. Ed.* **2020**, *59*, 22028-22033 and *Angew. Chem.* **2020**, *132*, 22212-22217. DOI: 10.1002/anie.202010744 and DOI: 10.1002/ange.202010744.
[#]Authors Contributed Equally

S. Yazdani, G. P. Junor, J. L. Peltier, M. Gembicky, R. Jazzar, D. B. Grotjahn, G. Bertrand. Influence of Carbene and Phosphine Ligands on the Catalytic Activity of Gold Complexes in the Hydroamination and Hydrohydrazination of Alkynes. *ACS Catal*. **2020**, *10*, 5190-5201.

G. P. Junor, E.A. Romero, X. Chen, R. Jazzar, G. Bertrand, Readily Available Primary Aminoboranes as Powerful Reagents for Aldimine Synthesis. *Angew. Chem. Int. Ed*. **2019**, *58*, 2875-2878. and *Angew. Chem.* **2019**, *131*, 2901-2904. DOI: 10.1002/anie.201814081 and DOI: 10.1002/ange.201814081
Very Important Paper (VIP)

D. Pichon, M. Soleilhavoup, J. Morvan, G. P. Junor, T. Vives, C. Crevisy, V. Lavallo, J.-M. Campagne, M. Mauduit, R. Jazzar, G. Bertrand. The Debut of Chiral Cyclic (Alkyl)(amino)carbenes (CAACs) in Enantioselective Catalysis. *Chem. Sci.* **2019**, *10*, 7807-7811. DOI: 10.1039/C9SC02810B
Highlighted In: Chemistry Views and l'Institut de Chimie

F. N. Stappen, K. Enemark-Rasmussen, G. P. Junor, M. H. Clausen, J. Zhang, C. Engelbrekt. Implications of Byproduct Chemistry in Nanoparticle Synthesis. *J. Phys. Chem. C.* **2019**, *123*, 25402-25411. DOI: 10.1021/acs.jpcc.9b03193
Journal Cover

C. M. Weinstein, G. P. Junor, D. Tolentino, R. Jazzar, M. Melaimi, G. Bertrand, Highly Ambiphilic Room Temperature Stable Six-Membered Cyclic (Alkyl)(amino)carbenes. *J. Am. Chem. Soc*. **2018**, *140*, 9255-9260. DOI: 10.1021/jacs.8b05518

FELLOWSHIPS, SCHOLARSHIPS & AWARDS

National science foundation graduate research fellowship	*2018*
Strategic enhancement of excellence through diversity fellowship	*2016-17*
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Harold c. urey graduate studies award	*2016*
Chancellor's Award of Distinction	*2016*
Rose Hills Foundation Undergraduate Science and Engineering Scholarship	*2015-2016*
Pitts Undergraduate Achievement Award	*2016*
University of California Leadership Excellence through Advanced Degrees	*2014-2016*
UCI Alumni Association Distinguished Anteater Award	*2015-2016*
American Chemical Society Award for Outstanding Research Presentation	*2015*
UC LEADs Symposium- 1ST Prize Research Poster in Physical Sciences and Math	*2015*
Robert Doedens Undergraduate Achievement Award	*2015*
Maria Rebecca and Maureen Bellettini Award	*2014*
Frank and Sara McKnight Prize in Undergraduate Chemistry- Semifinalist	*2014*

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Implications of Byproduct Chemistry in Nanoparticle Synthesis
2016-19

Collaboration between myself (UC San Diego) and the Clausen, Zhang, and Engelbrekt groups (Technical University of Denmark) focused on understanding the causes of unusual spectral features in Au-nanoparticle solutions.

Products of Collaboration:

Peer-reviewed Publications:

1. F. N. Stappen, K. Enemark-Rasmussen, G. P. Junor, M. H. Clausen, J. Zhang, C. Engelbrekt, *J. Phys. Chem. C.* **2019**, *123*, 25402. DOI: 10.1021/acs.jpcc.9b03193

Free Dissemination of Knowledge to the Public:

2. Data from: Implications of Byproduct Chemistry in Nanoparticle Synthesis F. N. Stappen, K. Enemark-Rasmussen, G. P. Junor, M. H. Clausen, J. Zhang, C. Engelbrekt, *UCSD Library Digital Collections* **2018**, DOI: 10.6075/J0GB228D

Artistic Works:

3. Front-cover of the Journal of Physical Chemistry C Volume 123, Issue 41 (Artist: Nedjeljko Seselj)

PRESS & HIGHLIGHTS

Les debuts des alkylaminocarbenes cycliques (CAACs) chiraux en catalyse asymetrique *July 2019*
http://www.inc.cnrs.fr/fr/cnrsinfo/les-debuts-des-alkylaminocarbenes-cycliques-caacs-chiraux-en-catalyse-asymetrique

First Chiral CAACs in Asymmetric Catalysis *June 2019*
https://www.chemistryviews.org/details/news/11169033/First_Chiral_CAACs_in_Asymmetric_Catalysis.html

Chemistry in pictures: just add borane *March 2018*
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Taking the back road *September 2016*

Junor, G. Taking the Back Road. *Composite*, September 2016, pp 13-14. https://issuu.com/composite/docs/issue_02 Accessed December 16, 2016.

FREE DISSEMINATION OF KNOWLEDGE TO THE PUBLIC

DATA FROM: THE INFLUENCE OF C(SP^3)H-SELENIUM INTERACTIONS ON THE ^{77}SE NMR QUANTIFICATION OF THE π-ACCEPTING PROPERTIES OF CARBENES

G. P. Junor, J. Lorkowski, C. M. Weinstein, R. Jazzar, C. Pietraszuk, G. Bertrand; *UC San Diego Library Digital Collections* **2020,** DOI: 10.6075/J06M357V

DATA FROM: INFLUENCE OF CARBENE AND PHOSPHINE LIGANDS ON THE CATALYTIC ACTIVITY OF GOLD COMPLEXES IN THE HYDROAMINATION AND HYDROHYDRAZINATION OF ALKYNES

S. Yazdani, G. P. Junor, J. L. Peltier, M. Gembicky, R. Jazzar, D. B. Grotjahn, G. Bertrand; *UC San Diego Library Digital Collections* **2020,** DOI: 10.6075/J0GB22FN

DATA FROM: READILY AVAILABLE PRIMARY AMINOBORANES AS POWERFUL REAGENTS FOR ALDIMINE SYNTHESIS

G. P. Junor, E.A. Romero, X. Chen, R. Jazzar, G. Bertrand, *UC San Diego Library Digital Collections* **2019**, DOI: 10.6075/J00Z71HW

DATA FROM: IMPLICATIONS OF BYPRODUCT CHEMISTRY IN NANOPARTICLE SYNTHESIS

F. N. Stappen, K. Enemark-Rasmussen, G. P. Junor, M. H. Clausen, J. Zhang, C. Engelbrekt, *UCSD Library Digital Collections* **2018**, DOI: 10.6075/J0GB228D

FIELDS OF STUDY

Major Fields: Inorganic Chemistry, Organic Chemistry, Main-group Chemistry

Professor Guy Bertrand

ABSTRACT OF THE DISSERTATION

Oh, Where Electrons Will Go

by

Glen Paxton Junor

Doctor of Philosophy in Chemistry

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Professor Guy Bertrand, Chair

This dissertation involves the study and manipulation of molecular orbitals on ambiphilic molecules to obtain unusual properties and develop new applications. Carbenes, which can simultaneously serve as powerful Brønsted bases and Lewis acids, undergo further amplification of those properties as the bond angle at the carbene center changes (chapter 2). Such profound reactivity fluctuations from seemingly simple geometric modifications highlight the need for

accurate measurement of carbene frontier orbitals. However, X-ray and NMR studies show that carbene-selenium adducts are susceptible to H-Se non-classical hydrogen bonds which cause large downfield shifts in ^{77}Se NMR, disrupting a commonly used technique for assessing carbene π-acidity (chapter 3). Furthermore, common techniques used to characterize carbene donor abilities are unable to avoid the confounding of carbene basic and acidic orbitals. To directly see how carbene lone pairs compare to each other, we ranked different carbene families by basicity through a proton exchange method (chapter 4). The basicity ranking highlights several surprising qualitative errors that occur throughout many theoretical calculations. Finally, exploring the reactivity of aminoboranes, a class of 1,2-ambiphiles, we developed a new methodology for the synthesis of aldimines (chapter 5). Preliminary mechanistic studies suggest that the mechanism is orthogonal to traditional condensation methods and allows access to products that are conventionally difficult to obtain. This dissertation will hopefully serve as another example of how we can advance main-group synthetic chemistry by taking a molecular orbital perspective.

Chapter 1- Introduction: Predicting Reactivity with Molecular Orbitals

One of the most startling features of quantum mechanics is the importance of symmetry when predicting the interactions between objects. Symmetry-related selection rules are borne out of the wave nature of small particles and the concepts of constructive and destructive interference.[1-3] One can approach this concept by adopting a macroscale perspective with two waves on a long string. The waves first approach one another, eventually interacting, and finally pass through each other (Figure 1.1). The observed interaction will vary depending on the relative phases of the two waves. If they are in phase, the interaction will result in constructive interference and amplification (Figure 1.1, left). If the waves are of opposite phase, there will be destructive interference and they will cancel out at the point of interaction (Figure 1.1, right). The phenomena of constructive and destructive interference hold true whether the waves are big or small, but phase can be generally ignored for "non-wave" objects, like when a ball strikes a bat.

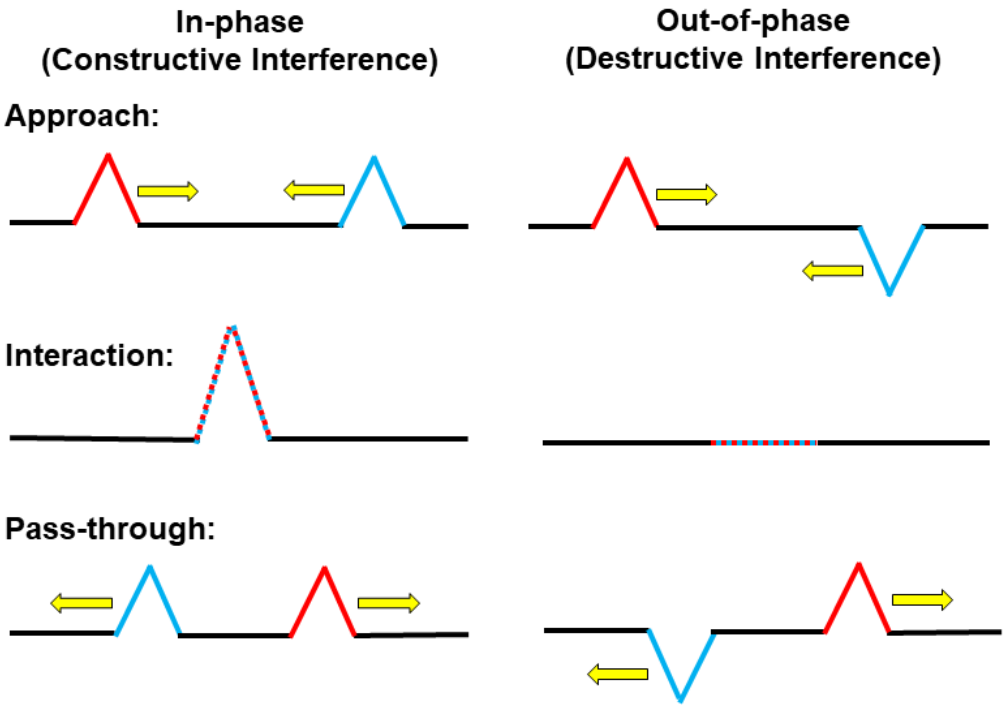


Figure 1.1: Interaction of waves propagating on a string. Two in-phase waves constructively interfere leading to an increase in magnitude (left). Two out-of-phase waves destructively interfere, leading to a magnitude of zero when interacting (right).

A common surprise for new students in the physical sciences is that very small objects exhibit wave-particle duality.[1-3] Thus, in the quantum regime, the phase of an interaction between

two particles matters. For example, if two electrons occupy the same region while in phase the electron density is amplified. However, if those two electrons are out-of-phase the electron density of that region drops to zero. To accommodate such constructive and destructive interference, both the native symmetry of an object and the overall symmetry of an interaction must be accounted for.

In chemistry (excluding nuclear chemistry), the primary concern is the behavior of electrons. Synthetic chemists work to build molecules by creating conditions that favor particular interactions of electrons over others. To design a new reaction, chemists must understand the nature of the electrons involved, particularly their shape and energy, and the three-dimensional manner in which they are likely to interact. To understand the shape and energy of individual electrons, one must turn to quantum mechanics and the Schrodinger equation.[1]

Solutions to the Schrodinger equation for a system containing one electron and one nucleus give the so-called “hydrogenic orbitals” (Figure 1.2). The names most commonly used by chemists are s, p, d, and f orbitals. In fact, the periodic table of elements is essentially organized by the type of orbital that occupies the highest-energy position for a given element. The highest occupied orbital of alkali and alkaline earth metals are s-orbitals.[2] The highest occupied orbitals of the transition metals are the d-orbitals.[4-5] The highest occupied for the main-group species and noble gases are the p-orbitals. The highest occupied orbitals of lanthanides and actinides[6-7] are the f-orbitals.

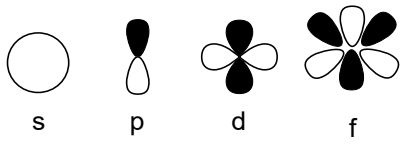


Figure 1.2: A few (of many) representations of hydrogenic orbitals most commonly encountered in synthetic chemistry

To predict the three-dimensional interaction of multiple electrons, particularly during a chemical reaction, one must turn to molecular orbital theory and the various quantitative

derivatives.[4, 8-12] A qualitative understanding can be gained by considering the interaction of two electrons exhibiting the p-orbital configuration (Figure 1.3). If the two orbitals approach each other anti-symmetrically (dark phases pointed in opposite directions), then the interaction will be constructive and form a bond (Figure 1.3, top left). If the two orbitals approach each other symmetrically (dark phases pointed in the same direction) then destructive interference occurs and electron density rapidly drops to zero between the two original orbitals, forming an anti-bonding interaction (Figure 1.3, top right). If one p-orbital approaches the other side-on, then it experiences equal parts constructive and destructive interference and leads to no net interaction, referred to as a non-bonding situation (Figure 1.3, bottom). These are but a few examples of the possible three-dimensional interactions of two electrons, and there are many more depending on the number of electrons involved and whether they occupy s, p, d, or f orbitals (or some combination of them). Real chemical systems are designed with such considerations.

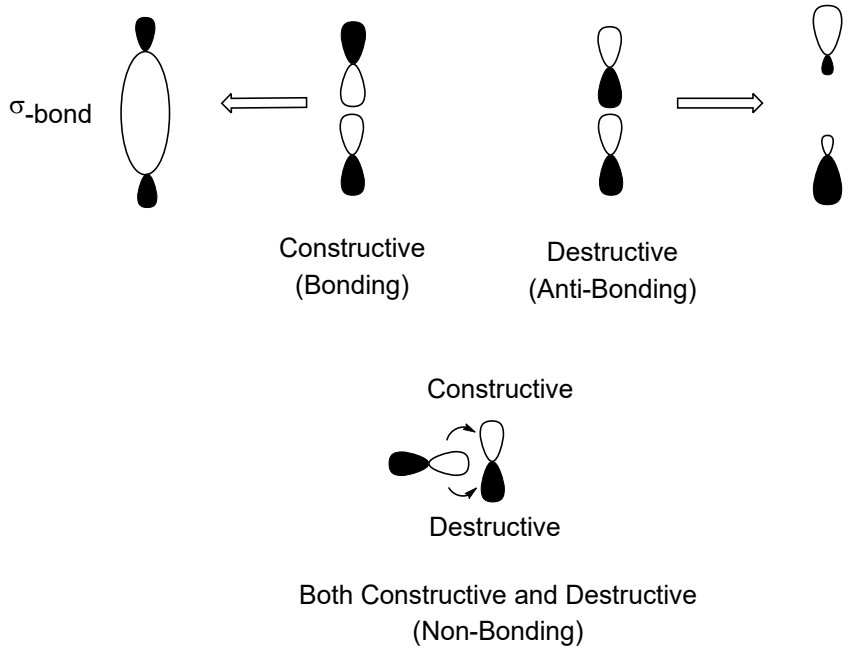


Figure 1.3: Examples of important phase interactions between electrons

The foundational concept that allows chemists to account for symmetry effects during chemical design is the fact that the energy of electrons is quantized, as described by Quantum

Mechanics. [1-3] The quantization of energy forces electrons to adopt only certain shapes.[1-3] Since chemical reactions transform one molecule into another through the movement of electrons, the shape of both the initial and final resting place of said electrons must be considered. Thus, both an electron and its final (empty) resting place, a.k.a electron-hole ("hole" for short), must obey the same quantum mechanical laws that give rise to symmetry-related selection rules. For example, ammonia features a pair of electrons in a nitrogen-centered sp^3-orbital, which has a good symmetry match to borane's empty (hole-containing) p-orbital (Figure 1.4). Unsurprisingly, a reaction occurs when these two reagents are mixed together. The two low-density gaseous reagents transform into an energy-dense fuel source, ammonia borane, which is considered a good candidate for hydrogen storage for a greener combustion economy.[13] Thus, understanding the orbitals of reagent molecules can lead to the design of more desirable products.

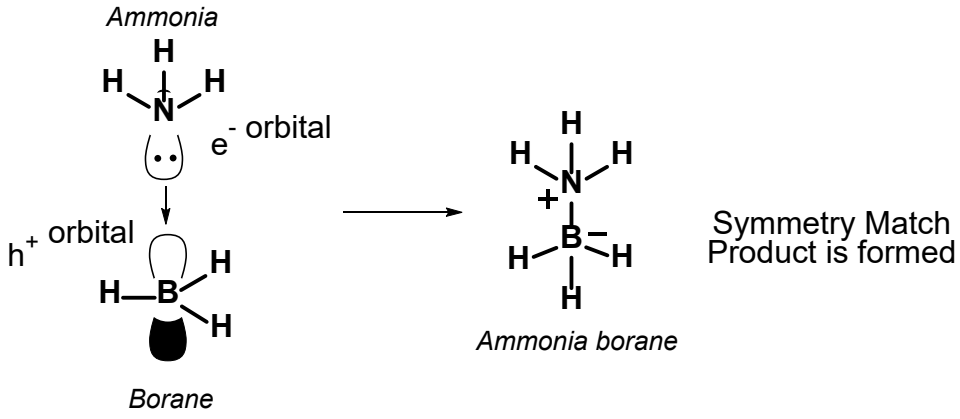


Figure 1.4: Electron-containing orbital from ammonia reacts with the hole (h^+)-containing orbital on borane.

In addition to the development of valuable products, understanding the orbitals of a molecule allows the design of ancillary features that prevent degradation. For example, iminiums are valuable precursors and catalysts,[14-16] but they are highly water sensitive. In fact, many iminiums will hydrolyze (decompose through reaction with water) upon exposure to moist air. A lone-pair of electrons on the water oxygen atom has the proper symmetry to attack the empty orbital on the iminium (Figure 1.5). The reaction often proceeds quickly.

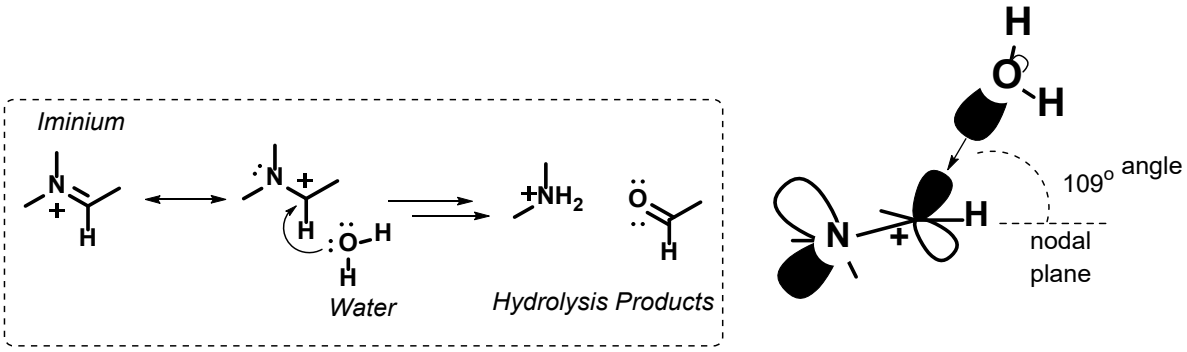


Figure 1.5: Hydrolysis of an iminium: reaction (left) and orbital considerations (right).

However, to attack the empty orbital on the iminium, water must approach from a 109° angle from the nodal plane (Figure 1.5, right).[17] Knowing this weakness to nucleophiles, the Bertrand group designs their iminium precursors with large diisopropylphenyl (dipp) groups attached to the nitrogen (Figure 1.6).[15-16, 18-19] The large substituent blocks the required approach angle, and prevents the orbital overlap required by symmetry. The only available angle of approach is on the iminium orbital's nodal plane. Since this plane includes equal in-phase and out-of-phase contributions, no reaction occurs even if the molecule is completely surrounded by pure water. In fact, these iminiums are manufactured on the metric ton scale every year and they are isolated and purified by ion exchange in enormous quantities of water.

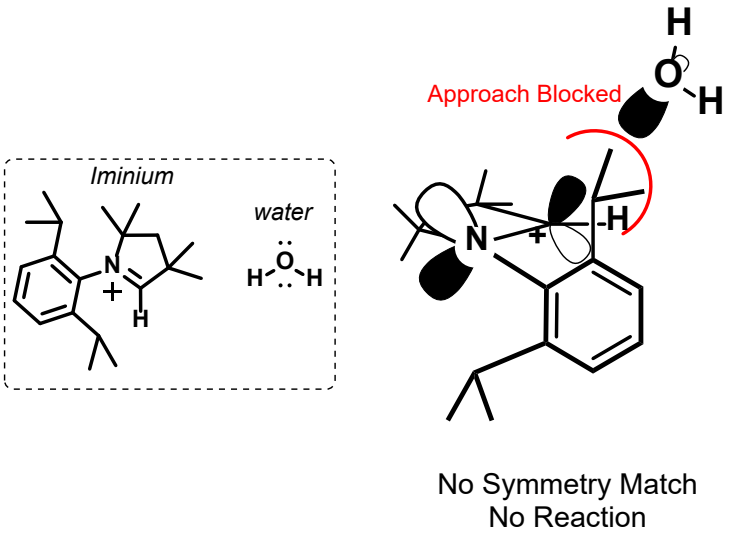


Figure 1.6: Effects of orbital symmetry requirements on reaction. Water does not react with the bulky iminium.

Of course, there are ways to force this reaction to occur. The application of heat will cause the dipp group to rotate, opening up the avenue of attack for water. Also, deprotonating the water, or including sodium hydroxide (NaOH) in the solution, will lead to addition on the iminium. Likely, the strong force caused by electrostatic attraction between the positively charged iminium and negatively charged hydroxide ion allows the $^{-}$OH to "blow past" the steric encumbrance of the isopropyl group. From these iminiums, we see that by designing appropriate symmetry around a reaction site, one can protect from unwanted side-reactions while still allowing easy access to desired products. Whereas, from the aminoborane example we learned that, if done properly, new reactions can be designed to give high yields of pure product without the input of additional energy (heat, electricity) or expensive catalysts.

The selection rules imparted by constructive and destructive interference of matter waves have profound effects on chemical reactivity and stability. In the case of iminiums, a simple structural change transformed something highly fragile into a product with nearly indefinite shelf-life. Utilization of strategic orbital combinations in ammonia and borane changed the two low-density gases into an energy-dense fuel. These are but two simple examples of the power of molecular orbital thinking. The remainder of this dissertation will continue to demonstrate, in detail, the use of such thinking to design molecules with unusual properties, solve spectroscopic mysteries, and discover new chemical reactions.

Chapter 2- Influencing the Orbitals of Carbenes:

Changing Bond Angle

As the preceding chapter suggests, my scientific interests have centered on how molecular structure influences electron symmetry and energy, and how these parameters ultimately govern chemical reactivity. Such interests naturally draw my attention towards molecules with weird electronic structures. The first family of molecules to grab my attention in such a manner are the carbenes.

Carbenes are unusual chemical species, regularly behaving as sources of surprising and useful chemistry. [20-25] These peculiar molecules have intrigued chemists since the early 1800s.[26-29] Yet, despite such long standing curiosity, the first stable carbene was not isolated until 1988 by the Bertrand group.[30-31] To understand the challenges inherent to their synthesis, one must consider the bizarre electronic structure of carbenes.

All carbenes have two bonds and two frontier electrons (Figure 2.1). In the ground state, the two electrons can be separate, occupying all orbitals (Figure 2.1, left); or paired together, leaving one orbital empty (Figure 2.1, right). The choice has enormous implications on the stability and reactivity of the resulting carbene, and neither option aligns well with the conventional "rules" of organic chemistry taught to early chemistry students (i.e. the octet rule).[32]

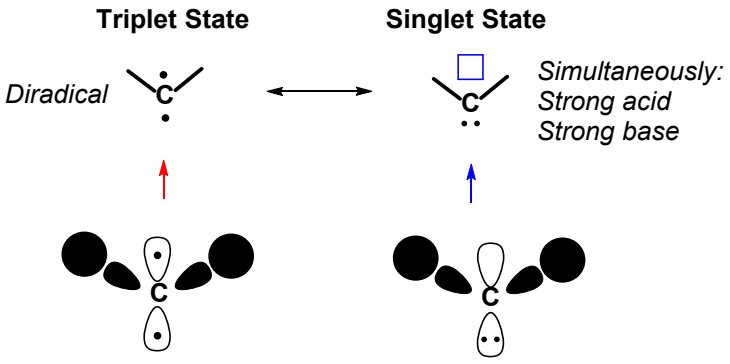


Figure 2.1: Possible electron configurations of carbenes with reactivity challenges highlighted (top). The blue square signifies an empty orbital. More detailed view of the orbitals involved (bottom).

If the two electrons are kept in separate orbitals, the carbene is termed a triplet carbene (Figure 2.1, left).[20] Triplet carbenes count the earliest known carbenes amongst their members and behave as diradicals. For comparison, organic monoradicals (some examples are given in Figure 2.2, top left) are highly reactive species, known to cleave even inert C-H and C-C bonds,

and are powerful tools for synthetic chemists.[33-34] Organic biradicals (two radicals, centered on different atoms) are even more reactive than monoradicals, but several have been isolated and crystallographically characterized (some examples are in Figure 2.2, bottom).[22-23, 35-37]

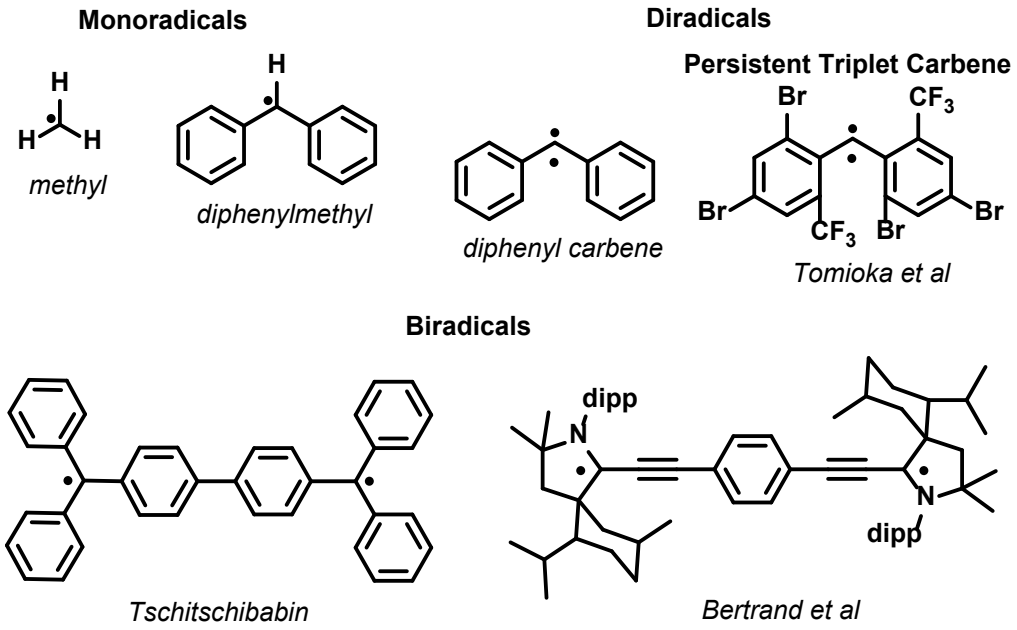


Figure 2.2: Examples of a triplet carbene, mono and biradicals

Triplet carbenes are diradicals, with both unpaired electrons residing on the same atom, and are particularly unstable. Diphenylcarbene, for example, has a room temperature lifetime two orders of magnitude lower than diphenylmethyl radical, and is even more short-lived than methyl radical.[20] However, despite the challenges inherent to the isolation of these species, triplet carbenes were harnessed for selective chemical reactions in the late 1800s[28] and early 1900s[27, 29] and are still involved in useful transformations, particularly when coordinated to transition metals (though transition metals change the electronic structure of these fragments quite a bit).[38-43] The most stable triplet carbene synthesized to date can survive for almost a day in solution (Figure 2.2, top right).[44]

Carbenes favor the singlet state (Figure 2.1, right) when the carbene bond angle is acute and when heteroatoms are adjacent to the carbene carbon, particularly if the heteroatom features a π-donating lone-pair of electrons.[25] Singlet carbenes are ambiphilic, featuring both a highly

acidic empty orbital and a strongly basic lone pair on the same carbon atom (Figure 2.1, right). To make the first stable singlet carbene, the phosphino(silyl)carbene (Figure 2.3), Bertrand *et al* sought to tame both of these properties simultaneously.[30-31]

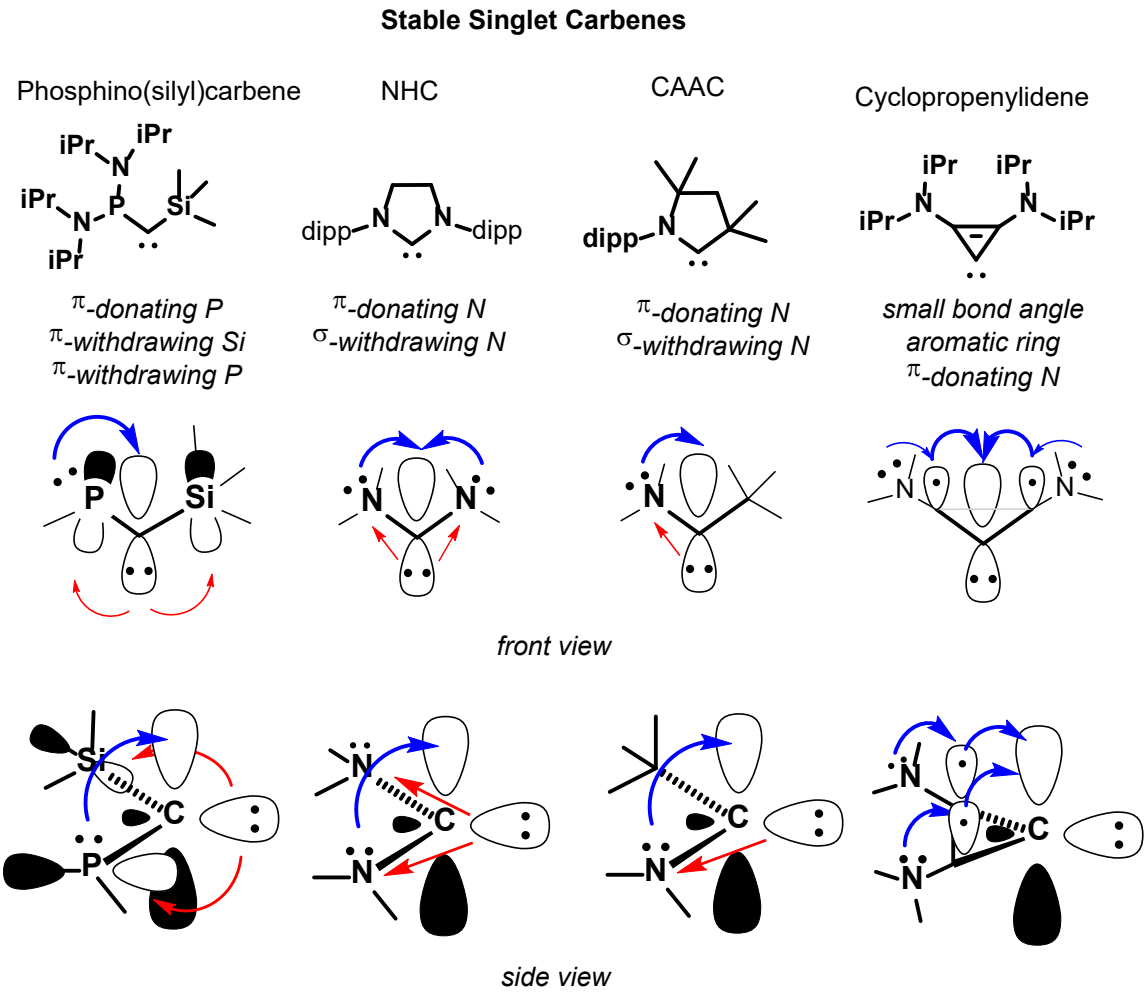


Figure 2.3: Some examples of stable singlet carbenes chosen to demonstrate important modes of stabilization. Blue arrows signify electron donation, red arrows depict withdrawal. Curved arrows highlight the π-symmetry of an interaction while straight arrows show inductive σ effects.

In the phosphino(silyl)carbene, the phosphorus atom adjacent to the carbene center features a π-donating lone pair, to reduce the acidity of the carbene empty orbital (blue arrow). To reduce the basicity of the carbene lone-pair, both the phosphorus and silicon anti-bonding σ* orbitals are available to withdraw excess electron density (red arrows). The resulting carbene is astonishingly stable despite its impressive reactivity. The phosphino(silyl)carbene is an oil that can be distilled at 250°C and isolated in 80% yield,[30-31] most carbenes are not stable at such high

temperatures. Despite such excellent thermal stability, the phosphino(silyl)carbene readily inserts into strong N-H bonds[30] and is even capable of cyclopropanation with alkenes,[31, 45] a reaction typically reserved for only the most reactive[21] or unstable[20] carbenes. In fact, it is the only stable carbene capable of coordinating dinitrogen, to date, as evidenced by the stability of the diazo precursor from which it is made.[30-31]

Spurred by the isolation of the first carbene by the Bertrand group in 1988, numerous carbene scaffolds have been developed to tune the properties of both the acidic empty orbital and the basic lone pair on the carbene center. A few such carbene families are shown in Figures 2.3 and 2.4.[25] N-heterocyclic carbenes (NHC)[40] and cyclic(alkyl)(amino)carbenes (CAAC)[24, 46-48] have emerged as the most popular and are important to numerous fields, partly due to their ease of synthesis and high modularity. NHCs use two π-donating nitrogen atoms to heavily quench the acidity of the empty orbital (Figure 2.3, blue arrows). Simultaneously, those same nitrogen atoms are electronegative and pull electron density away from the carbene, reducing the basicity (Figure 2.3, red arrows). CAACs follow a similar stability pattern, but with only one nitrogen atom, making the carbene empty orbital much more acidic and the lone pair more basic (Figure 2.3). Additional carbene families (Figure 2.4) have been developed to tune these properties in various fashions including, but not limited to, the cyclic(amino)(aryl)carbenes (CAArC),[15] diamidocarbenes (DAC),[49-50] and pyramidalized NHCs (*py*NHC).[51] Carbenes in these categories often have strongly acidic empty orbitals on the carbene center. Recently, other carbene scaffolds[15, 52-55] have also been rising in importance.[25]

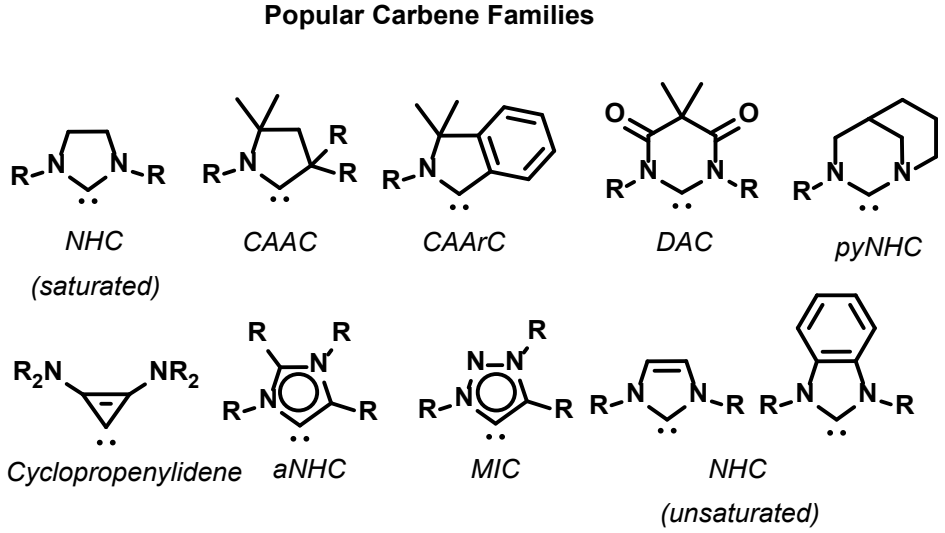


Figure 2.4: Some popular families of carbenes.

When strongly acidic empty orbitals are less desired the carbene empty orbital can be inserted into an aromatic network, shown in detail for cyclopropenylidenes in Figure 2.3. Cyclopropenylidenes,[56] abnormal NHCs,[54] mesoionic carbenes (MIC),[52, 55] and unsaturated NHCs[57-58] use this strategy to focus on the properties of the carbene lone pair (Figure 2.4).

Aside from heteroatom effects and aromatic stabilization, it has been known for many years that reducing the bond angle at the carbene center favors the singlet state.[20, 59] For a carbene to have a triplet ground state, the two available orbitals must be degenerate (equal). As the carbene angle changes, the orbitals can lose their degeneracy and favor the singlet state. A close look at methylene can be instructive, starting from the dissection of methane (Figure 2.5).

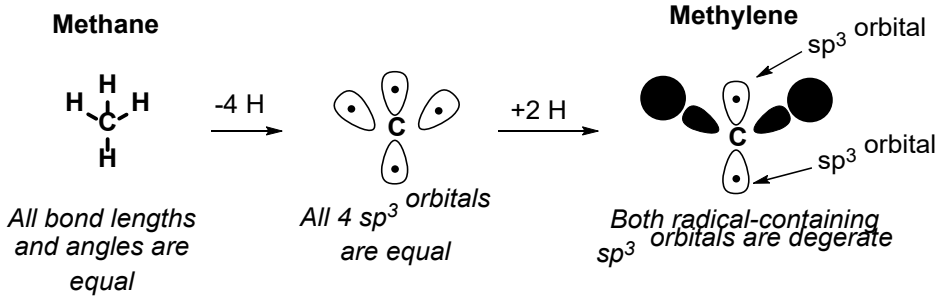


Figure 2.5: Dissecting methane to understand the methylene triplet ground state.

Methane, CH_4, is a tetrahedral molecule with four degenerate bonds between hydrogen and carbon (Figure 2.5, left). The bonds are classic examples of covalent interactions with electrons that are evenly shared between the two atoms. For accounting purposes, one can imagine that carbon "owns" four of these electrons, one from each bond. If hydrogens are removed to provide a closer look at carbon's orbitals, four equivalent sp^3 orbitals can be seen (Figure 2.5, middle). All orbitals are equivalent, so the electrons separate evenly between them, to reduce overall electrostatic repulsion. If two of the orbitals combine with a hydrogen atom each, again in a symmetric fashion, methylene (the simplest carbene) is created (Figure 2.5, right). Thus, it becomes quite easy to see why methylene adopts the triplet ground state, with the two electrons in separate degenerate orbitals.

However, from the perspective of hybridization theory, sp^3 orbitals are created by the hybridization of one s and three p orbitals. An s orbital has a single phase that constructively interferes with half of each p orbital and destructively interferes with the other half, leading to a large lobe of one phase and a small lobe of the other (Figure 2.6, top). As a consequence of this holdover from the p orbitals, every sp^3 orbital has two phases. A side view of methylene highlights the close overlap of both C-H bonds with the small lobes of radical-containing orbitals. If the radical orbitals remain degenerate, they can avoid the destabilizing electrostatic repulsion caused by placing both electrons in the same orbital. However, one may notice that the small lobes of the sp^3 orbitals are in-phase with the C-H σ-bonds. Strong overlap between in-phase orbitals leads to significant constructive interference and can lead to improved stability. However, the sp^3 orbitals are orthogonal to the C-H bond plane (more clearly represented in Figure 2.6 middle-bottom) and thus overlap is minimal.

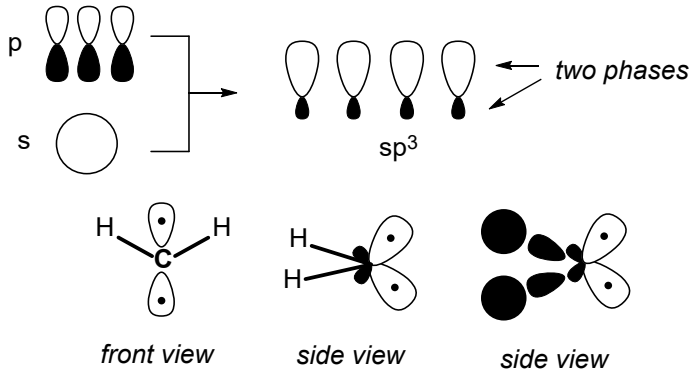


Figure 2.6: Closer look at methylene orbitals.

Thus, methylene is in a bit of a conundrum. It can maintain maximum distance between the two electrons with an sp^3 configuration (Figure 2.7, left), or it could change its orbital hybridization to sp^2 and maximize the stabilizing effect of orbital overlap with the C-H bonds (Figure 2.7, right). At small angles, up to around 104°, methylene favors pairing the electrons and taking advantage of the increased orbital overlap.[20] At larger angles, reducing the electrostatic repulsion becomes more important and methylene adopts the triplet state.[20, 59]

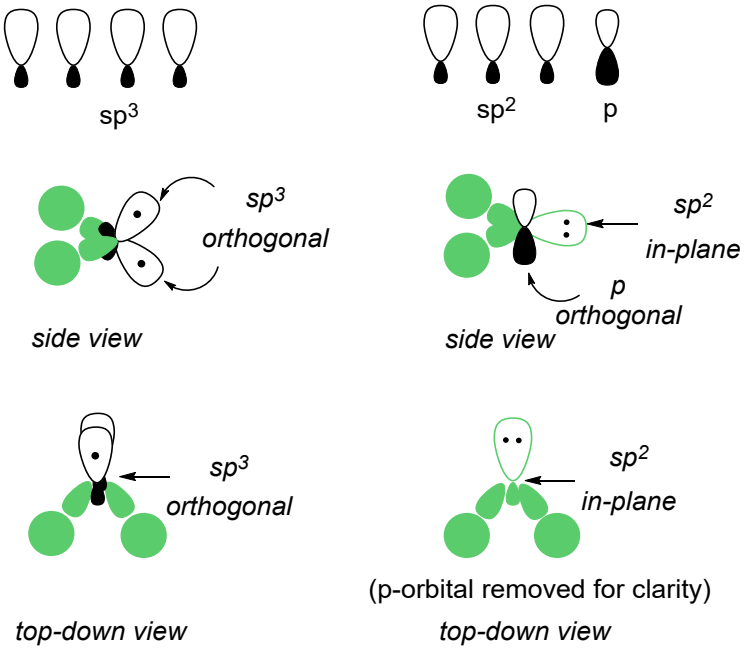
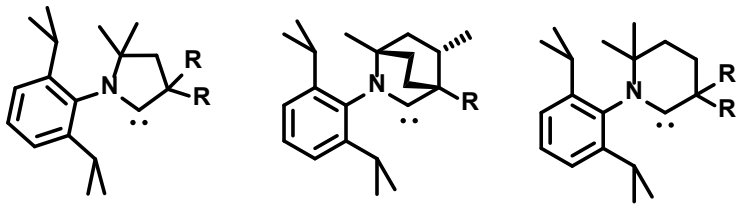


Figure 2.7: Effects of rehybridization on methylene. Green orbitals are in the same plane.

For carbenes without heteroatom stabilization, like methylene, shrinking the bond angle has been one avenue to find stable carbenes.[20, 59] However, I wondered how increasing the bond angle would change the properties of heteroatom stabilized carbenes, and if it would lead to new reactivity.

In search of new physical properties and chemical reactivity, I wanted to take a carbene with minimal stabilization factors built into its structure. An ideal candidate would be stable and readily synthesized, but would feature high ambiphilicity (having both the highly acidic empty orbital and the strongly basic lone pair that are characteristic of carbenes). Working with Dr. Cory Weinstein, we imagined that experimental modification of the bond angles of such a family would truly highlight the breadth and impressiveness of carbene reactivity. The carbenes that satisfy all such requirements are the CAACs (Figure 2.8).

Cyclic(alkyl)(amino)carbenes (CAACs)



CAAC-5 *BiCAAC* *CAAC-6*

Bond Angle: 106.5° 108.3° 117.9°

Figure 2.8: Members of the CAAC family and their carbene bond angles

The first CAAC was synthesized in 2005[18, 60] by the Bertrand group and has since unleashed a dazzling array of new chemical transformations.[15, 19, 24-25, 37, 61-70] To widen the bond angle, the Bertrand group sought to expand the ring size from five (CAAC-5) to six. The first attempt at such an expansion created the bicyclic(alkyl)(amino)carbene (BiCAAC, Figure 2.8) in 2017.[71] Though the carbene bond angle is only marginally widened compared to CAAC-5, the improved ambiphilicity, the rigidity of the backbone, and the unique and tunable steric properties of the new ligand were rapidly utilized in a number of applications.[15, 53, 72]

Seeking a deeper understanding of the orbital changes likely to occur upon widening the CAAC bond angle, I turned to the type of molecular orbital theory called Symmetry Adapted Linear Combination of Atomic Orbitals.[4, 8-10, 12] In Figure 2.9, the orbital configurations of CAACs are compared between an acute and, albeit extreme, linear carbene bond angle.

At acute bond angles, the favorable overlap of the lone-pair orbital with the substituent σ-bonds occurs, similar to the methylene example in Figure 2.7. The overlap between the carbene lone pair and the substituents forms a bonding interaction (highlighted in blue, Figure 2.9) which is stabilizing and lowers the energy (and reactivity) of the lone pair.

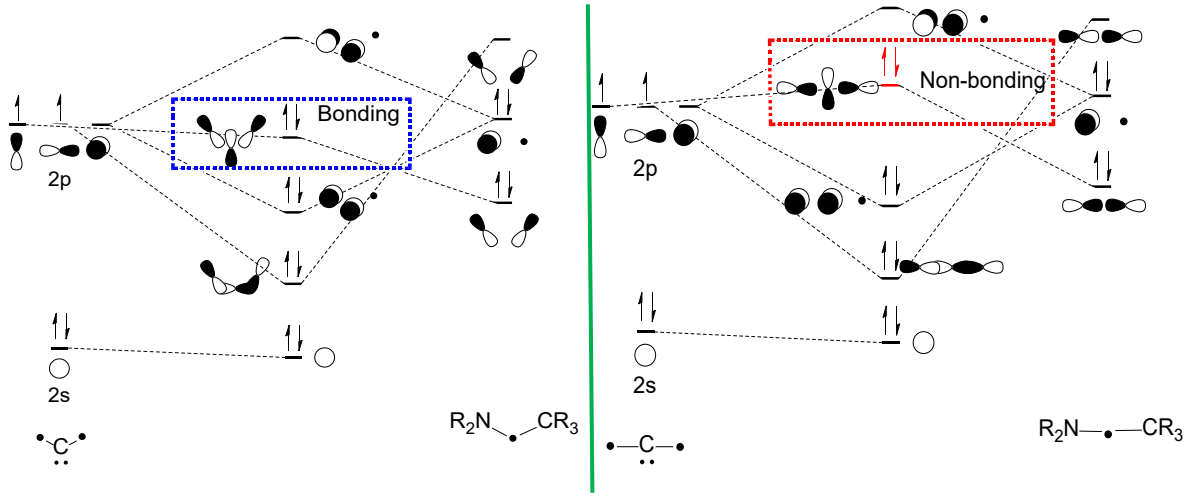


Figure 2.9: Truncated molecular orbital diagrams of CAACs at acute (left) and linear (right) bond angles. Relative energies of the orbitals are not to scale.

When the angle is widened completely to 180°, the orbital overlap with the substituents is completely eliminated (highlighted in red, Figure 2.9). The substituents in the linear example point directly at the lone pair node and experience equal parts constructive and destructive interference, like shown in Chapter 1 at the bottom of Figure 1.3. The resulting non-bonding situation does not provide the stabilizing interaction present at acute angles, raising the energy and overall reactivity of the carbene lone pair. Additionally, no obvious changes occur in the carbene empty orbital between the two systems. In both scenarios, the empty orbitals (highest shown in Figure 2.9) do not change in phase or degree of overlap between acute and linear bond angles. Overall, this

qualitative depiction suggests that a CAAC will become more ambiphilic through the destabilization of the carbene lone pair as the angle widens.

I found that Density functional theory (DFT),[73-74] one quantitative variant of molecular orbital theory, strongly agrees with the conclusions drawn from the qualitative picture (Figure 2.10).[75] In NHCs, changing from a five to six membered ring widens the bond angle and is predicted to raise the energy of the lone pair from -5.62 to -5.15 eV, a significant change. Similarly, moving from CAAC-5 to BiCAAC and eventually to CAAC-6 moves the lone pair from -5.20 to -4.82 eV. As predicted by the qualitative description, changing the ring size for both NHCs and CAACs is predicted to have a rather large effect on the energy of the carbene lone pair, but a smaller effect on the empty orbital position. Furthermore, optimization of the triplet state highlights an increased flexibility of the CAAC-6 backbone, compared to CAAC-5 and BiCAAC; which allows for major conformational changes, leading to a small singlet-triplet gap; and hints at the possibility of novel reactivity and exceptional π-acidity.[75-76]

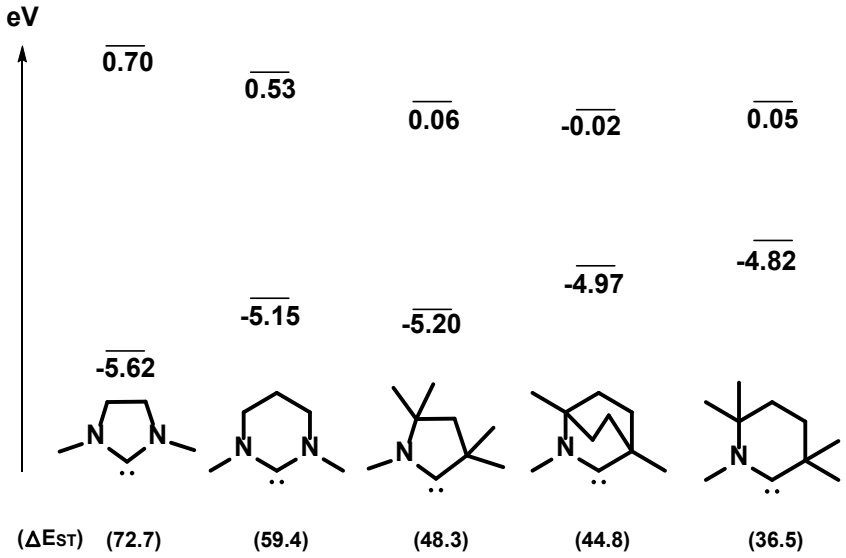


Figure 2.10: Frontier orbital energies and singlet-triplet gaps (ΔE_{st}) of NHCs and CAACs calculated by DFT at the B3LYP/def2-TZVPP level of theory with a fine integration grid.[75]

In 2018, seeking to experimentally validate my theoretical predictions on the effect of widening the carbene bond angle, Dr. Cory Weinstein synthesized several room-temperature stable CAAC-6 derivatives, and our hopes for new physical properties and reactivity were

realized.[75] The crystal structure showed a 117.8° bond angle - a major increase from the 106.5° angle found in CAAC-5. Rhodium carbonyl complexes were made for measurement of the overall donor ability (Tolman Electronic Parameter[77]) of CAAC-6 and showed it to be the most donating member of the CAAC family, validating the molecular orbital prediction. Simultaneously, ^{77}Se and ^{31}P NMR of selenium and phenylphosphinidine adducts, respectively, showed that the carbene is more π-accepting than CAAC-5 derivates. In fact, when a menthyl substituent is brought into close proximity of the carbene center, rapid cleavage of a C-H bond was observed.[75] Also, pure CAAC-6 is a bright yellow compound, even in the crystalline state, whereas CAAC-5 is colorless. To see if this color was due to the closeness of the nucleophilic HOMO and electrophilic LUMO, responsible for the high degree of ambiphilicity exhibited by CAAC-6, I sought to model the UV-Vis spectrum by time-dependent density functional theory (TD-DFT).[78-81]

To rapidly test the performance of a number of DFT methods, I chose a truncated CAAC-6 molecular model based on the crystal structure of the full carbene (Figure 2.12). I surveyed the hybrid functionals B3LYP,[82] M06-2X,[83] and ωB97X-D[84] both with and without the Tamm-Dancoff approximation[85] (TDA and TD-DFT, respectively).

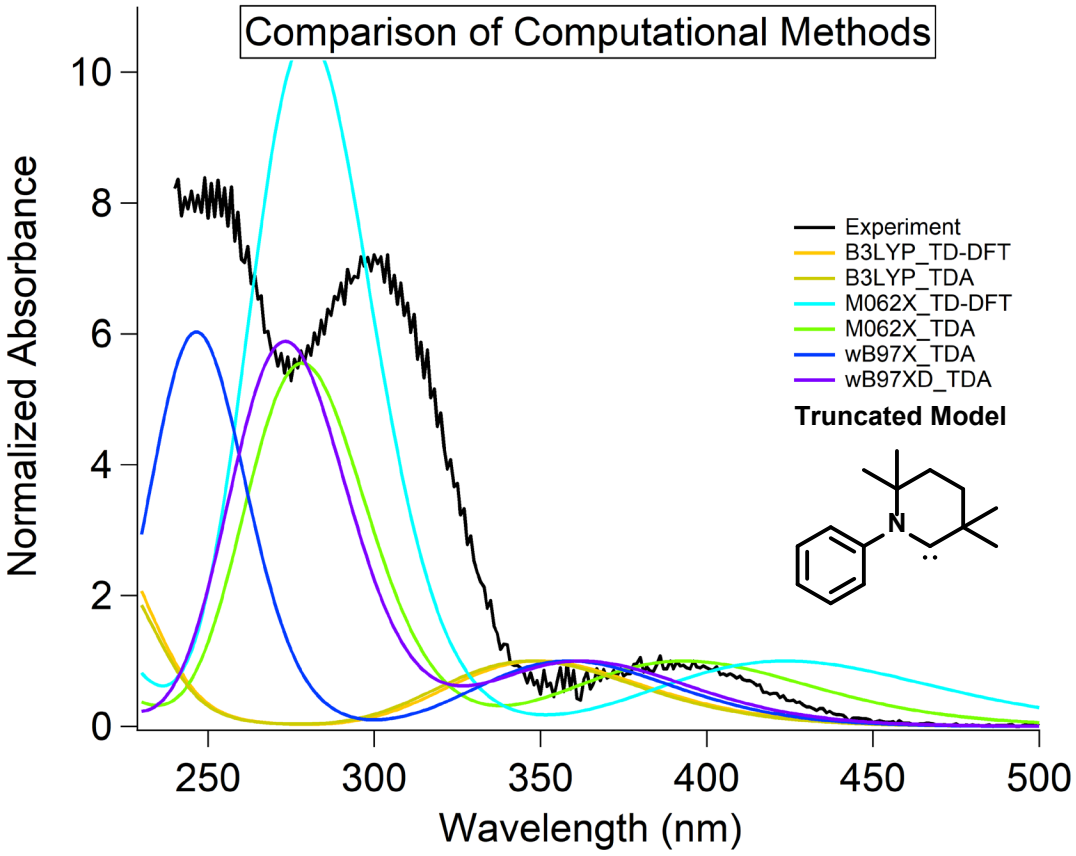


Figure 2.11: Comparison of computational methods on truncated CAAC-6. All simulations use the def2-TZVPP basis set.

Ultimately, TD-DFT using the M06-2X functional, the def2-TZVPP basis set, and the Tamm-Dancoff approximation provided the best fit to experimental data and the method was used to model the full molecule measured experimentally. Since the UV-Vis of CAAC-6 was measured in pentane solution, the TD-DFT calculation was performed in a polarizable continuum of that solvent. The simulated spectrum is in good agreement with the experimental UV-Vis spectrum (Figure 2.13, left). Further, the TD-DFT results assign the peak responsible for the molecule's color to a transition from the carbene lone pair to the empty orbital, as hypothesized (Figure 2.13, right).

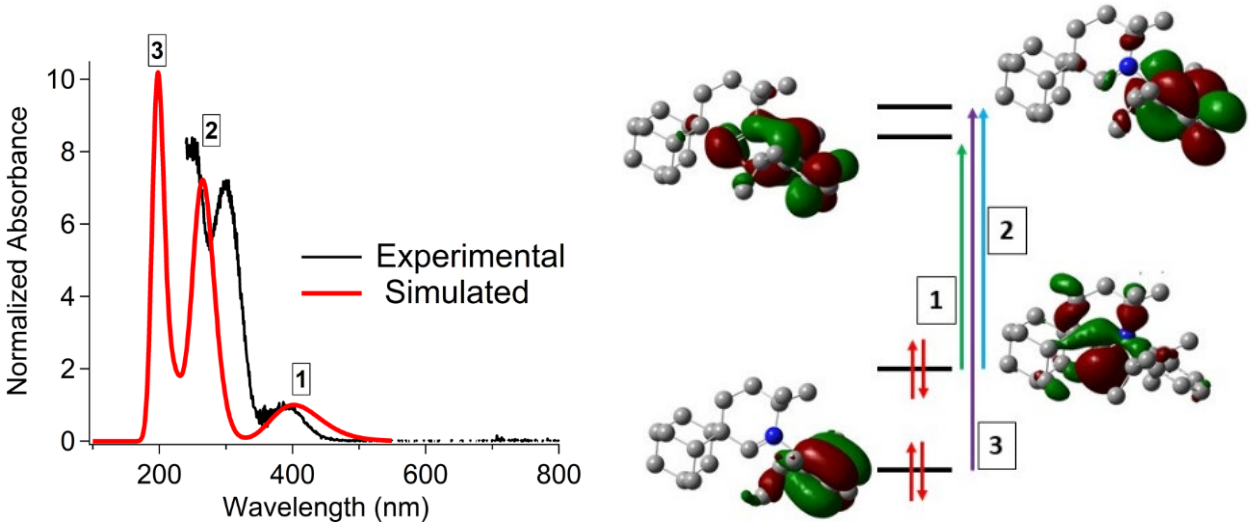


Figure 2.12: Experimental versus simulated UV-Vis spectra (left), and molecular orbitals and corresponding electronic transitions for CAAC-6 (right).

In conclusion, as shrinking the carbene bond angle leads to stabilization of a singlet configuration in methylene, widening the bond angle destabilizes it in CAAC. The resultant closeness of the lone pair and empty orbital energies instills a new degree of ambiphilicity that can be measured with the Tolman Electronic Parameter, ^{77}Se NMR, ^{31}P NMR, and even UV-Vis spectroscopy. In fact, this ambiphilicity makes CAAC-6 capable of reactivity never before seen in stable carbenes, like the intramolecular activation of inert C-H bonds.[75] CAAC-6 is an example of how a simple conceptual change like bond angle widening, as understood through a molecular orbital perspective, can be used to profoundly change the reactivity and physical properties of a chemical system.

Acknowledgments

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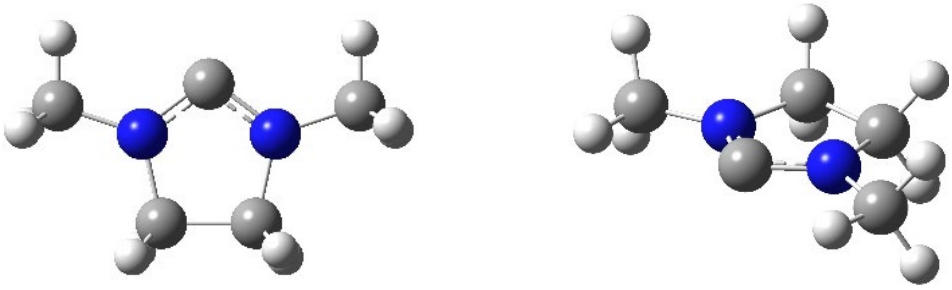
Temperature Stable Six-Membered Cyclic (Alkyl)(amino)carbenes" *Journal of the American Chemical Society*, 2018, *140*, 9255-9260. The dissertation author was co-author of this paper.

Supporting Information

All density functional theory (DFT)[73-74] calculations were performed with the Gaussian09 program package.[86] All optimizations were performed with the B3LYP functional and employing Weigend's def2-TZVPP basis set.[87] Ground states were fully optimized without constraints at the corresponding level of theory and uniquely characterized by occurrence of no imaginary frequencies and verified by the corresponding frequency calculation. Gibbs free reaction energies and enthalpies were calculated for standard conditions (p = 1 atm, T = 298 K) and are unscaled. For the visualization of frontier molecular orbitals and optimized structures, GaussView5 was used.

Optimized x,y,z-coordinates:

NHC-5-singlet

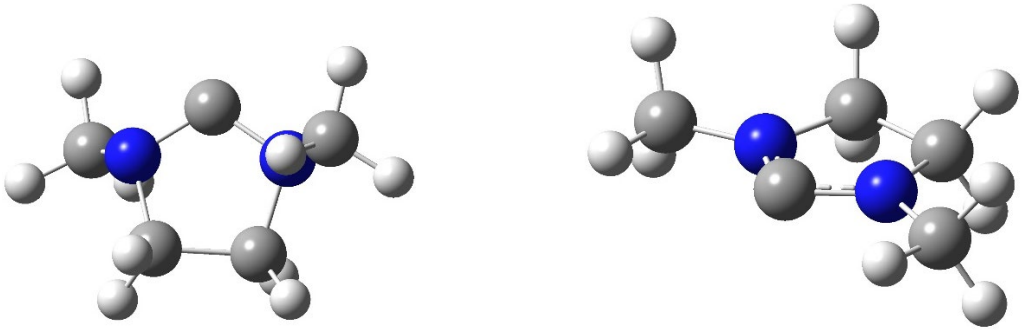


Electronic energy= -306.121215487 hartree/particle
Zero-point correction= 0.148771 (Hartree/Particle)
Thermal correction to Energy= 0.156579
Thermal correction to Enthalpy= 0.157524
Thermal correction to Gibbs Free Energy= 0.116409
Sum of electronic and zero-point Energies= -305.972444
Sum of electronic and thermal Energies= -305.964636
Sum of electronic and thermal Enthalpies= -305.963692
Sum of electronic and thermal Free Energies= -306.004807

N	1.07256800	0.20730300	-0.03549100
C	0.00000200	1.01233500	-0.00006100
C	-0.76599300	-1.23284700	-0.03345500
H	-1.22900800	-1.77362700	0.79482300

H	-1.14600100	-1.66294600	-0.96530600
N	-1.07256800	0.20730100	0.03538300
C	-2.43855100	0.66335500	0.00281700
H	-2.43758100	1.74874000	0.04768500
H	-2.94430600	0.34594200	-0.91594400
H	-3.00681000	0.27077800	0.85199100
C	2.43855500	0.66335800	-0.00272800
H	2.43756400	1.74873600	-0.04775500
H	2.94412200	0.34609300	0.91618400
H	3.00696900	0.27066300	-0.85173700
C	0.76599400	-1.23287400	0.03346700
H	1.14600600	-1.66286100	0.96536100
H	1.22900100	-1.77370800	-0.79477400

NHC-5-triplet

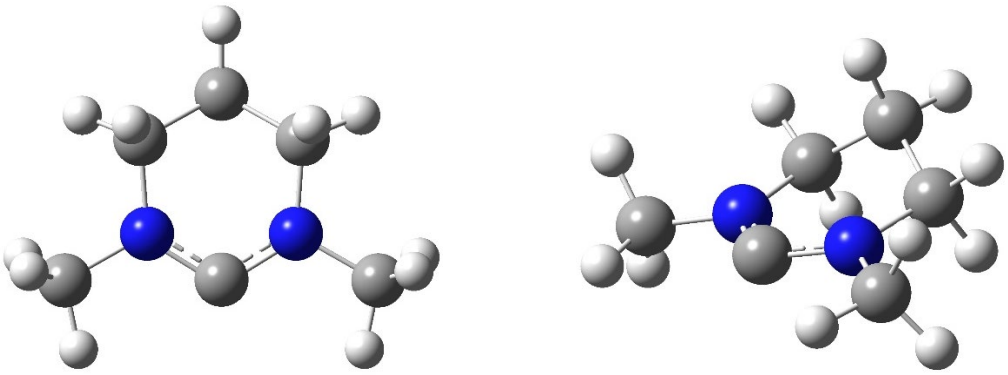


Electronic energy= -306.003837515 hartree/particle
Zero-point correction= 0.147275 (Hartree/Particle)
Thermal correction to Energy= 0.155044
Thermal correction to Enthalpy= 0.155988
Thermal correction to Gibbs Free Energy= 0.113813
Sum of electronic and zero-point Energies= -305.856563
Sum of electronic and thermal Energies= -305.848793
Sum of electronic and thermal Enthalpies= -305.847849
Sum of electronic and thermal Free Energies= -305.890024

N	1.08692900	-0.29445100	0.44910700
C	0.00000800	-1.02998100	-0.00009700
C	2.36850600	-0.48271000	-0.23090300
H	2.61278100	-1.54269800	-0.23199000
H	2.35231100	-0.13353000	-1.27329700
H	3.15194400	0.04668500	0.31206300
C	0.57604800	1.09462100	0.51711500
H	1.36988800	1.80402400	0.28830500
H	0.20175300	1.30510800	1.52114700
C	-0.57607600	1.09464900	-0.51708200
H	-1.36991900	1.80403700	-0.28823500
H	-0.20178000	1.30518300	-1.52110200
N	-1.08695200	-0.29443000	-0.44914900
C	-2.36847300	-0.48274100	0.23095800

H	-3.15195200	0.04671900	-0.31188600
H	-2.61276100	-1.54272600	0.23196000
H	-2.35218100	-0.13366600	1.27338500

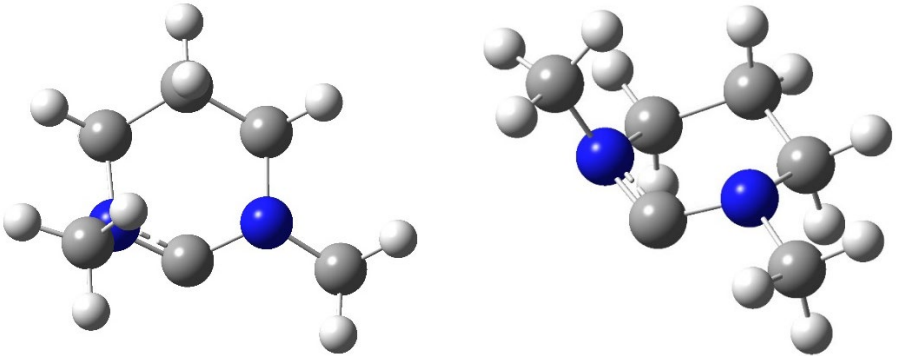
NHC-6-singlet



Electronic energy= -345.448568811
Zero-point correction= 0.178511 (Hartree/Particle)
Thermal correction to Energy= 0.186872
Thermal correction to Enthalpy= 0.187816
Thermal correction to Gibbs Free Energy= 0.146068
Sum of electronic and zero-point Energies= -345.270058
Sum of electronic and thermal Energies= -345.261697
Sum of electronic and thermal Enthalpies= -345.260753
Sum of electronic and thermal Free Energies= -345.302501

N	1.14019700	-0.39113400	0.00089600
C	0.00001600	-1.09479400	-0.09208500
C	-1.24324200	1.05701800	0.20521700
H	-1.38168600	1.27783800	1.27073000
H	-2.13383400	1.41996800	-0.31262100
C	-2.40290000	-1.10626200	-0.02034900
H	-3.04157000	-0.75272200	-0.83620800
H	-2.19136400	-2.16202300	-0.15820900
H	-2.94899100	-0.96854400	0.91922400
C	0.00003200	1.75024900	-0.32976400
H	0.00000200	2.80324400	-0.04685900
H	0.00017900	1.70157600	-1.42071600
C	1.24315000	1.05699500	0.20553200
H	2.13391400	1.42006900	-0.31191000
H	1.38118200	1.27761400	1.27114100
N	-1.14017900	-0.39114000	0.00087400
C	2.40294200	-1.10620700	-0.02044600
H	3.04146600	-0.75275300	-0.83645800
H	2.94917800	-0.96835400	0.91901900
H	2.19141500	-2.16198800	-0.15816300

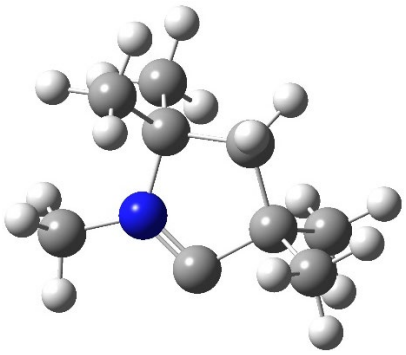
NHC-6-triplet

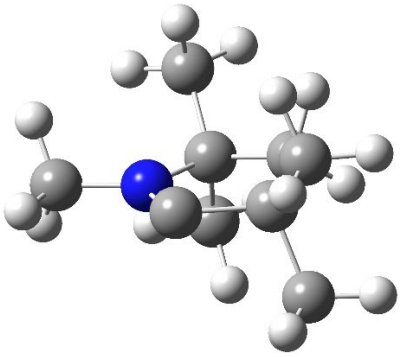


Electronic energy= -345.352401976 hartree/particle
Zero-point correction= 0.176936 (Hartree/Particle)
Thermal correction to Energy= 0.185277
Thermal correction to Enthalpy= 0.186221
Thermal correction to Gibbs Free Energy= 0.143583
Sum of electronic and zero-point Energies= -345.175466
Sum of electronic and thermal Energies= -345.167125
Sum of electronic and thermal Enthalpies= -345.166181
Sum of electronic and thermal Free Energies= -345.208819

N	-1.15833800	-0.58323100	-0.46634200
C	0.15731200	-0.90075500	-0.61393900
C	1.02591400	1.15614400	0.17969800
H	1.39983500	1.54995900	-0.77858700
H	1.66323500	1.55202800	0.97336700
C	2.49546800	-0.79300700	-0.00603800
H	3.14328000	-0.37852800	0.76726100
H	2.51229300	-1.87883100	0.07031000
H	2.89847700	-0.50902200	-0.98867500
C	-0.42342000	1.59987800	0.38784500
H	-0.49505100	2.67992000	0.24126300
H	-0.72196900	1.39345600	1.41810800
C	-1.37033800	0.87029200	-0.57930900
H	-2.41469300	1.10310600	-0.36648400
H	-1.16033400	1.16605900	-1.60881500
C	-1.93222100	-1.26774900	0.57438900
H	-2.99605700	-1.07354400	0.43101100
H	-1.76169200	-2.33825100	0.48699000
H	-1.64747700	-0.95534800	1.58680000
N	1.13889000	-0.31674400	0.19656800

CAAC-5-singlet

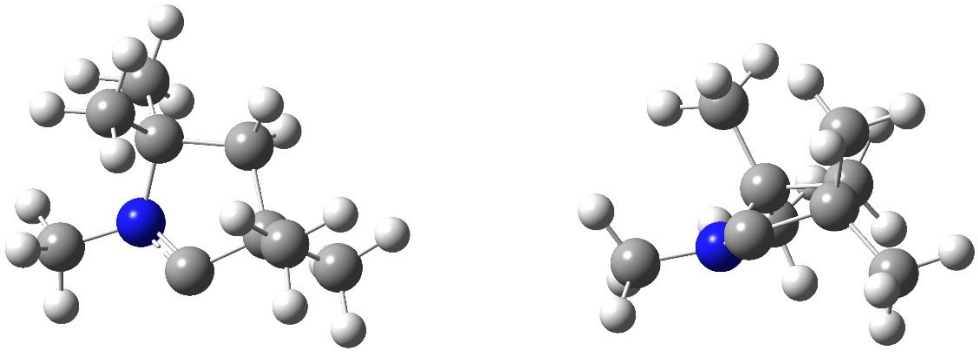




Electronic energy= -408.047144738
Zero-point correction= 0.243600 (Hartree/Particle)
Thermal correction to Energy= 0.255255
Thermal correction to Enthalpy= 0.256199
Thermal correction to Gibbs Free Energy= 0.207666
Sum of electronic and zero-point Energies= -407.803544
Sum of electronic and thermal Energies= -407.791890
Sum of electronic and thermal Enthalpies= -407.790946
Sum of electronic and thermal Free Energies= -407.839478

N	-0.64861500	0.90511900	0.04811300
C	0.59902800	1.28088100	0.08315400
C	0.44778200	-1.12521400	-0.38583200
H	0.52303200	-1.37880400	-1.44420100
H	0.64752200	-2.03763100	0.17653000
C	1.44244900	0.02170800	-0.04238700
C	-1.74666000	1.85888100	0.17533200
H	-2.36422600	1.86487300	-0.72347900
H	-2.38031800	1.61239400	1.02837100
H	-1.31006400	2.84104700	0.32062700
C	2.49819700	0.21124100	-1.13935900
H	3.15843500	1.04291300	-0.89416800
H	3.10338000	-0.69203900	-1.25098100
H	2.03329700	0.42810100	-2.10267600
C	2.15189300	-0.20344100	1.30589300
H	2.78942900	-1.08908700	1.25344400
H	2.77337600	0.65594800	1.55666500
H	1.44144800	-0.34703100	2.12126200
C	-0.95787200	-0.57256700	-0.08449700
C	-1.94155200	-0.82732400	-1.22953300
H	-2.04243700	-1.90117200	-1.39359700
H	-2.93630400	-0.43624200	-1.01192500
H	-1.58711000	-0.37676000	-2.15736500
C	-1.53590500	-1.10599700	1.23294100
H	-2.48799900	-0.63310800	1.47683900
H	-1.71567500	-2.17887700	1.15110400
H	-0.84964200	-0.93936000	2.06248800

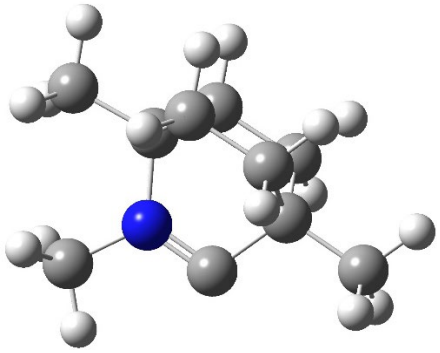
CAAC-5-triplet

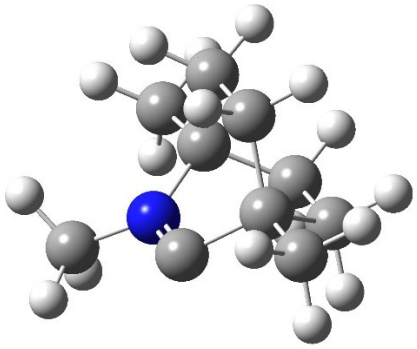


Electronic energy -407.968728698 hartree/particle
Zero-point correction= 0.242130 (Hartree/Particle)
Thermal correction to Energy= 0.253958
Thermal correction to Enthalpy= 0.254902
Thermal correction to Gibbs Free Energy= 0.204980
Sum of electronic and zero-point Energies= -407.726599
Sum of electronic and thermal Energies= -407.714771
Sum of electronic and thermal Enthalpies= -407.713827
Sum of electronic and thermal Free Energies= -407.763748

N	-1.38847600	-0.17891100	-0.34478600
C	-0.23653300	-0.92432600	-0.15621400
C	0.45191800	1.28453100	-0.27955700
H	0.96336900	2.05130800	0.30210400
H	0.57157100	1.52002400	-1.33736700
C	1.03360900	-0.14433800	-0.00130700
C	-2.66785700	-0.70180600	0.08511500
H	-2.74821900	-0.76236600	1.18120900
H	-3.46844500	-0.06310600	-0.28918100
H	-2.80766300	-1.70147700	-0.32383500
C	1.61083300	-0.23964700	1.42611500
H	1.88120100	-1.26981600	1.66076500
H	2.50850600	0.37758200	1.52229600
H	0.88576700	0.09029100	2.17067500
C	2.11893800	-0.52609300	-1.01761300
H	2.98034500	0.14172900	-0.93668400
H	2.46926600	-1.54434900	-0.84170300
H	1.73468500	-0.47381300	-2.03617700
C	-1.04187600	1.19126000	0.05812900
H	-1.21423000	1.33130200	1.13544900
H	-1.65101600	1.91759100	-0.48206000

BiCAAC-singlet

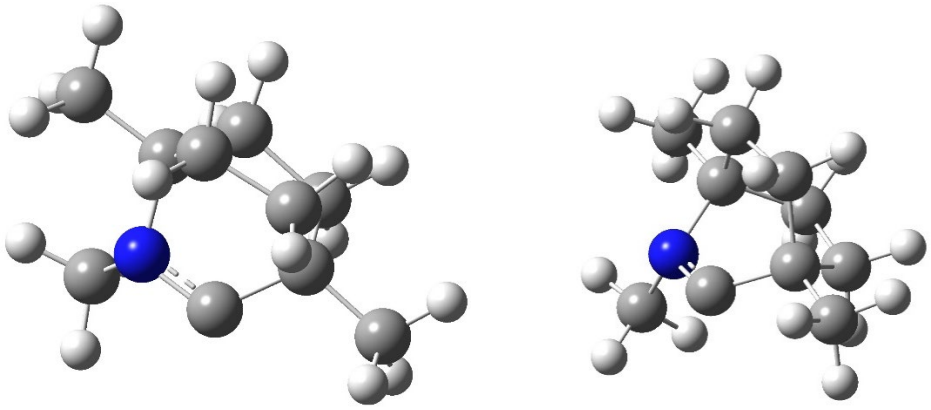




Electronic energy= -446.157959276 hartree/particle
Zero-point correction= 0.252917 (Hartree/Particle)
Thermal correction to Energy= 0.263703
Thermal correction to Enthalpy= 0.264647
Thermal correction to Gibbs Free Energy= 0.218133
Sum of electronic and zero-point Energies= -445.905043
Sum of electronic and thermal Energies= -445.894256
Sum of electronic and thermal Enthalpies= -445.893312
Sum of electronic and thermal Free Energies= -445.939827

C	-1.13001600	-0.67070900	1.25950500
C	0.35634000	-1.07595700	1.25019200
C	1.04517800	-0.49300300	0.00001500
C	-0.52925600	1.37164100	-0.00016100
C	-1.45775200	0.17302100	0.00000700
H	0.86925300	-0.71364100	2.14271500
H	0.47544800	-2.16114800	1.23428400
H	-1.36446900	-0.08215400	2.14756700
H	-1.78097900	-1.54769200	1.28314400
C	-2.92073100	0.60781200	-0.00001500
H	-3.14004200	1.21520800	-0.87892200
H	-3.59274100	-0.25452100	0.00008500
H	-3.14001400	1.21538900	0.87877400
C	-1.13007100	-0.67102000	-1.25930400
H	-1.78102500	-1.54801700	-1.28264700
H	-1.36459800	-0.08271900	-2.14751400
C	0.35628500	-1.07628000	-1.24997900
H	0.47539400	-2.16146500	-1.23381600
H	0.86915100	-0.71417800	-2.14261800
N	0.71956300	0.97559900	-0.00016700
C	1.79404000	1.96893500	-0.00020200
H	2.42329400	1.87092700	-0.88581800
H	1.31526300	2.94255300	-0.00031300
H	2.42318900	1.87106900	0.88551500
C	2.53683100	-0.79851700	0.00003500
H	3.03860600	-0.40709800	-0.88496800
H	3.03872500	-0.40620000	0.88458400
H	2.67352200	-1.88104300	0.00055500

BiCAAC-triplet

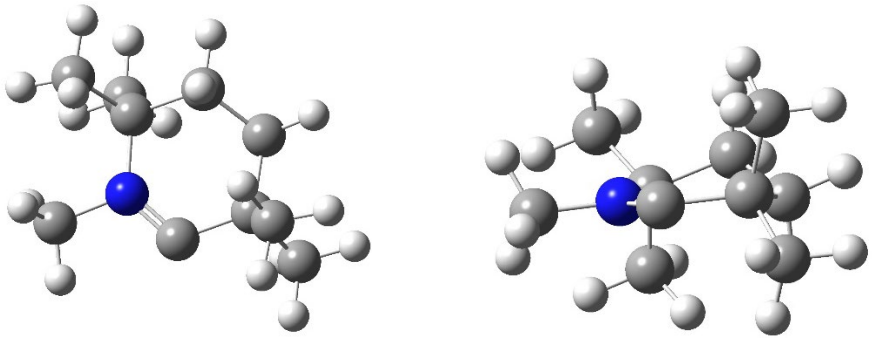


Electronic energy= -446.085100866 hartree/particle
Zero-point correction= 0.251454 (Hartree/Particle)
Thermal correction to Energy= 0.262400
Thermal correction to Enthalpy= 0.263344
Thermal correction to Gibbs Free Energy= 0.215448
Sum of electronic and zero-point Energies= -445.833647
Sum of electronic and thermal Energies= -445.822701
Sum of electronic and thermal Enthalpies= -445.821756
Sum of electronic and thermal Free Energies= -445.869653

C	1.24827000	-1.26861700	-0.66764000
C	-0.27330200	-1.52728800	-0.77566400
C	-1.07685700	-0.47580200	0.01816400
C	0.53090100	1.03216200	-0.78899200
C	1.47626200	0.13939800	-0.05186600
H	-0.59760300	-1.48879600	-1.81597100
H	-0.52731700	-2.51733200	-0.39362300
H	1.71636500	-1.31668100	-1.65042300
H	1.73562000	-2.01991200	-0.03784000
C	2.93226100	0.57676500	-0.13977300
H	3.07869600	1.54862000	0.33384200
H	3.58254200	-0.14562100	0.35817500
H	3.24885100	0.65907100	-1.18033800
C	0.97435600	0.07191500	1.41787300
H	1.61933900	-0.60105100	1.98959700
H	1.06668300	1.06176800	1.86686400
C	-0.49670500	-0.41206300	1.45317400
H	-0.57232200	-1.40569400	1.90030600
H	-1.10815800	0.24783300	2.07059600
N	-0.82591500	0.84371600	-0.65120800
C	-1.61849300	1.99891300	-0.23182900
H	-1.49588500	2.24615100	0.83186300
H	-1.29365100	2.85844900	-0.81440300
H	-2.67496500	1.83339800	-0.43571800
C	-2.56094800	-0.82020700	0.01468900
H	-2.95722200	-0.81311100	-1.00161000

H	-2.70810300	-1.81793500	0.43027800
H	-3.14593500	-0.12622900	0.61803800

CAAC-6-singlet

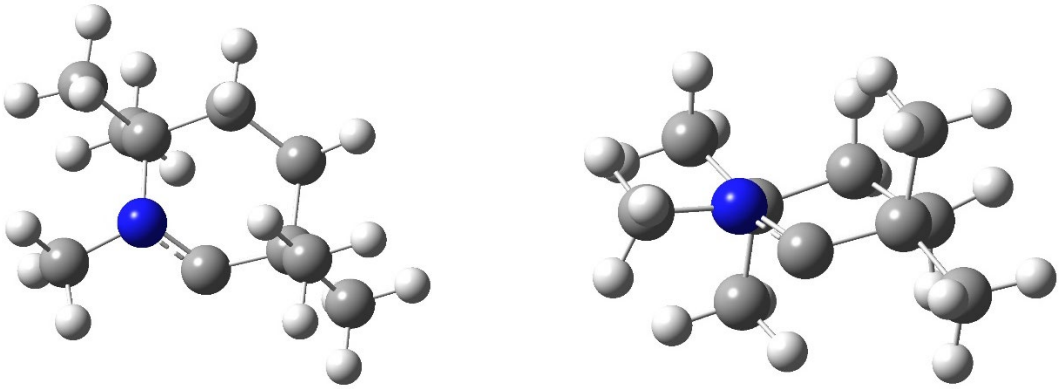


Electronic energy -447.366084081 hartree/particle
Zero-point correction= 0.273037 (Hartree/Particle)
Thermal correction to Energy= 0.285395
Thermal correction to Enthalpy= 0.286340
Thermal correction to Gibbs Free Energy= 0.236543
Sum of electronic and zero-point Energies= -447.093047
Sum of electronic and thermal Energies= -447.080689
Sum of electronic and thermal Enthalpies= -447.079744
Sum of electronic and thermal Free Energies= -447.129541

N	-0.62495300	0.92458300	0.00862100
C	0.65297500	1.19903600	0.02707800
C	1.05203600	-1.34167100	0.27141900
H	0.92264500	-1.48636800	1.34694800
H	1.74425200	-2.12153100	-0.05758900
C	1.64708200	0.05369400	0.00978100
C	2.71522600	0.36839000	1.07177700
H	3.49062500	-0.40238500	1.06998100
C	2.31917400	0.10787300	-1.37998100
H	3.15465800	-0.59509000	-1.41573900
H	1.62514400	-0.14930600	-2.18141900
H	3.17724300	1.33520700	0.87618500
H	2.27777500	0.40414200	2.07130300
H	2.69720800	1.10987200	-1.57935400
C	-0.28518900	-1.49568200	-0.43492600
H	-0.71688600	-2.48196800	-0.25056500
H	-0.14109900	-1.41943700	-1.51549600
C	-1.54554900	2.07543300	0.02611200
H	-2.29431300	1.96809700	0.81138400
H	-0.94318400	2.95686900	0.21124300
H	-2.05802300	2.18112700	-0.92991400
C	-1.30646000	-0.43699200	-0.00054700
C	-2.46687400	-0.44561600	-1.00422500
H	-2.84921900	-1.46373200	-1.09511300
H	-3.29693300	0.18780700	-0.69497700

H	-2.13490900	-0.12513900	-1.99246900
C	-1.83922600	-0.73638100	1.40894700
H	-2.57196100	0.00383000	1.72886600
H	-2.33120200	-1.71065400	1.41960400
H	-1.03631200	-0.75192300	2.14415900

CAAC-6-triplet

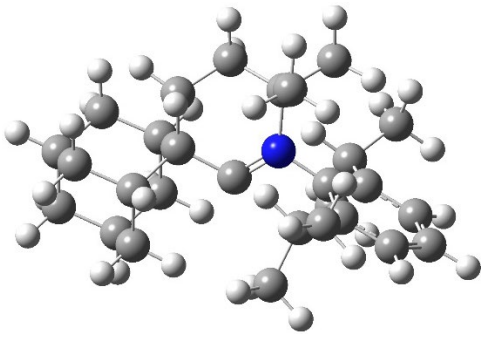


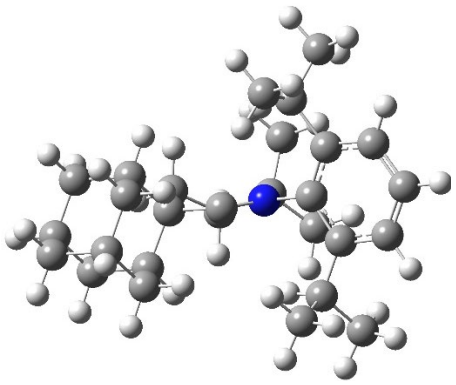
Electronic energy= -447.306306688 hartree/particle
Zero-point correction= 0.271355 (Hartree/Particle)
Thermal correction to Energy= 0.284047
Thermal correction to Enthalpy= 0.284991
Thermal correction to Gibbs Free Energy= 0.233532
Sum of electronic and zero-point Energies= -447.034952
Sum of electronic and thermal Energies= -447.022259
Sum of electronic and thermal Enthalpies= -447.021315
Sum of electronic and thermal Free Energies= -447.072774

N	-0.67092200	0.91508100	-0.02912300
C	0.58205700	0.92519400	0.52816900
C	1.08064200	-1.36579800	-0.00786000
H	1.04294900	-1.74291600	1.01594800
H	1.74813800	-2.03095600	-0.56462600
C	1.69520200	0.06862300	0.02704700
C	2.88783700	0.09417700	0.98942800
H	3.66370300	-0.59965600	0.65822900
C	2.16457200	0.49877400	-1.38081300
H	2.92867500	-0.18417500	-1.76162700
H	1.33659200	0.51705300	-2.08879000
H	3.32573300	1.09224400	1.03664900
H	2.58138700	-0.18608900	1.99753600
H	2.59416600	1.50061100	-1.34616400
C	-0.31854600	-1.41142900	-0.62917300
H	-0.72066700	-2.42401600	-0.54604100
H	-0.24940300	-1.19155800	-1.69713800
C	-1.47464300	2.11469600	0.15147700
H	-2.26047200	2.16987600	-0.59935400
H	-1.93552500	2.17365100	1.14561600

H	-0.82547600	2.98045200	0.03415400
C	-1.34205100	-0.42657500	-0.01373200
C	-2.58430300	-0.40043600	-0.90882200
H	-2.96270800	-1.41597100	-1.03251500
H	-3.38888900	0.19689000	-0.48016200
H	-2.34568500	-0.00554600	-1.89717500
C	-1.74029700	-0.83684200	1.41293600
H	-2.46602600	-0.13691300	1.83015600
H	-2.19814900	-1.82755700	1.41388200
H	-0.87470900	-0.85329800	2.07334000

Optimized structure of Singlet **CAAC-6**





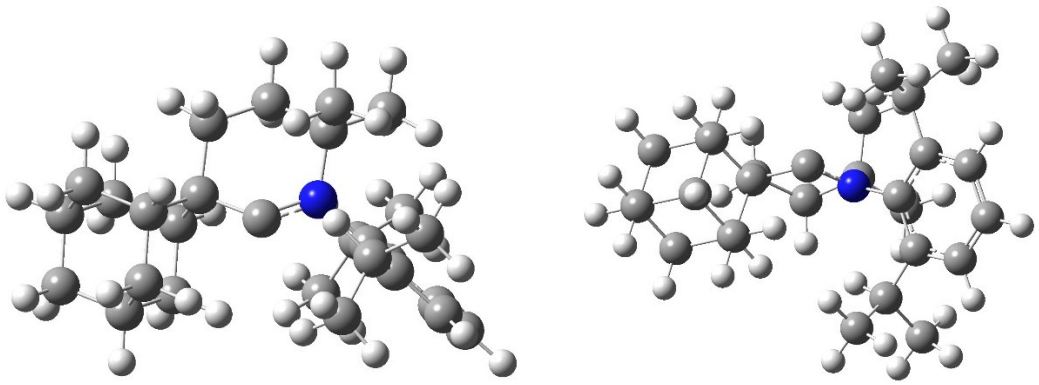
Electronic energy= -1146.79199504 hartree/particle
Zero-point correction= 0.633320 (Hartree/Particle)
Thermal correction to Energy= 0.660540
Thermal correction to Enthalpy= 0.661484
Thermal correction to Gibbs Free Energy= 0.578456
Sum of electronic and zero-point Energies= -1146.158675
Sum of electronic and thermal Energies= -1146.131456
Sum of electronic and thermal Enthalpies= -1146.130511
Sum of electronic and thermal Free Energies= -1146.213539

N	0.73111400	-0.04552400	0.60780800
C	2.54196600	1.28662000	-0.45180500
C	1.99261900	0.02925700	-0.13478200
C	2.60948900	-1.15981100	-0.57099200
C	-1.71454500	-0.22612300	0.50854400
C	3.77942100	1.32251200	-1.09461800
H	4.22072400	2.27878300	-1.34095600
C	1.92674500	-2.52116200	-0.51430600
H	1.08673200	-2.45333300	0.16987100
C	-0.34498100	-0.07296100	-0.13601000
C	3.84782500	-1.06452000	-1.20734000
H	4.34066400	-1.96670100	-1.54251200
C	0.84508600	-0.11137200	2.14796100
C	1.79303900	2.59773700	-0.24812100
H	0.93201100	2.40352400	0.38731700

C	-2.51342600	-1.29330700	-0.32242400
H	-1.99296500	-2.25213200	-0.23665700
C	-2.50567100	1.12509700	0.32685900
H	-1.98795500	1.91907600	0.87186300
C	-2.59957800	1.51846100	-1.16192400
H	-3.12737300	2.47417900	-1.24175400
H	-1.60556900	1.65357500	-1.58212500
C	4.44640100	0.16076400	-1.44469100
H	5.41079900	0.21143600	-1.93319800
C	1.80169700	0.95655600	2.68452400
H	2.82015800	0.81664400	2.32726100
H	1.81828500	0.88502500	3.77361300
H	1.47437600	1.96097400	2.42796100
C	-3.94338700	0.99419100	0.86798500
H	-3.95640500	0.78994100	1.93938600
H	-4.45327600	1.95314400	0.73582600
C	-4.77920200	0.28761400	-1.38449800
H	-5.32983500	-0.47363800	-1.94523600
H	-5.33068500	1.22632600	-1.49477100
C	2.63463900	3.69244400	0.42210300
H	3.05851800	3.35899800	1.36919100
H	2.01763900	4.57145400	0.61781100
H	3.46006200	4.01457000	-0.21427100
C	-3.35709400	0.43490000	-1.94717400
H	-3.40593000	0.71878600	-3.00188000
C	-4.69835900	-0.10417600	0.09977900
H	-5.70641800	-0.21026100	0.50998700
C	-2.60994800	-0.90077000	-1.80774500
H	-3.14617600	-1.68589100	-2.34988700
H	-1.61365200	-0.81791700	-2.23594300
C	-1.62635700	-0.65249800	1.98678400
H	-2.57285300	-0.53740000	2.51027700
H	-1.39409000	-1.72046100	2.03193600
C	-3.94360800	-1.43927600	0.23385700
H	-4.46667900	-2.21622200	-0.33121400
H	-3.93534900	-1.77042100	1.27401400
C	-0.55252400	0.13978400	2.71462800
H	-0.53837000	-0.10792400	3.77835900
H	-0.77795400	1.20725300	2.65053100
C	2.83779000	-3.65321100	-0.02048500
H	3.65068300	-3.85466800	-0.71921900
H	2.26399800	-4.57630400	0.07976100
H	3.28250500	-3.42731800	0.94916500
C	1.37185100	-1.48113700	2.59403200
H	0.71108100	-2.29693100	2.30792400
H	1.45897500	-1.48764100	3.68197900
H	2.36002900	-1.67770400	2.18385900
C	1.34239700	-2.86117900	-1.89745400
H	0.65476600	-2.08259000	-2.22515200
H	0.80019100	-3.80851700	-1.86005200
H	2.13344500	-2.95553500	-2.64381000

C	1.24292500	3.09396700	-1.59732300
H	2.05547600	3.33889300	-2.28396000
H	0.63954700	3.99309800	-1.45620300
H	0.62181600	2.33208000	-2.06594600

Optimized structure of Triplet **CAAC-6**



Electronic energy= -1146.74075255 hartree/particle
Zero-point correction= 0.631658 (Hartree/Particle)
Thermal correction to Energy= 0.659100
Thermal correction to Enthalpy= 0.660044
Thermal correction to Gibbs Free Energy= 0.576275
Sum of electronic and zero-point Energies= -1146.109095
Sum of electronic and thermal Energies= -1146.081653
Sum of electronic and thermal Enthalpies= -1146.080709
Sum of electronic and thermal Free Energies= -1146.164478

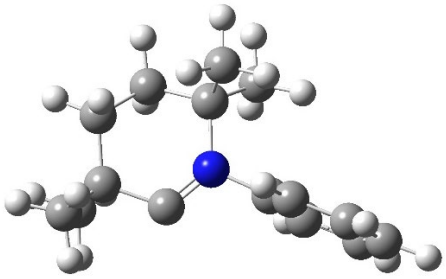
N	0.78298400	-0.09390200	0.69238600
C	2.31985600	1.38161400	-0.55599700
C	1.91863000	0.07709100	-0.18520500
C	2.59921400	-1.04724400	-0.70549400
C	-1.75543200	-0.28408600	0.59366500
C	3.43053000	1.53170900	-1.38577500
H	3.74818500	2.52584500	-1.67076400
C	2.17226500	-2.48485400	-0.44159600
H	1.33898300	-2.46491600	0.25356800
C	-0.36204600	-0.66382800	0.19613900
C	3.69984300	-0.83727600	-1.53757800
H	4.22872900	-1.69170600	-1.93857700
C	0.89235600	-0.13060600	2.19908500
C	1.56054000	2.63759600	-0.14757900
H	0.80105100	2.34202900	0.57330200
C	-2.76252900	-1.38985500	0.15966200
H	-2.45687700	-2.32908100	0.62774500
C	-2.23901400	1.04921600	-0.08048400
H	-1.56594900	1.85847500	0.21005300
C	-2.21073700	0.88361900	-1.61140400
H	-2.49835700	1.82540700	-2.08805400

H	-1.19756300	0.64895200	-1.94368000
C	4.12603600	0.43655900	-1.86822600
H	4.98593000	0.57544100	-2.51079500
C	2.07085400	0.70179900	2.69931200
H	3.01780500	0.34029200	2.29951900
H	2.11767800	0.62636800	3.78650400
H	1.96641500	1.75276800	2.44479700
C	-3.67948700	1.40559500	0.33742000
H	-3.74872500	1.59049800	1.41104200
H	-3.97129200	2.33965300	-0.15267700
C	-4.60126900	0.11169500	-1.60113100
H	-5.29404500	-0.67595300	-1.91200300
H	-4.92968300	1.03515500	-2.08745500
C	2.45657100	3.69794200	0.51149800
H	3.02429900	3.29318900	1.34884500
H	1.84905200	4.52564100	0.88259700
H	3.17246500	4.11506600	-0.19859500
C	-3.17020200	-0.23854000	-2.03976800
H	-3.13576600	-0.35212500	-3.12663800
C	-4.64018100	0.27809100	-0.07328400
H	-5.65617000	0.52710900	0.24482400
C	-2.73693400	-1.55215900	-1.36926900
H	-3.40944300	-2.36327000	-1.66419500
H	-1.73256200	-1.83119800	-1.69467800
C	-1.69207500	-0.18942000	2.15324200
H	-2.56325300	0.33906900	2.53984000
H	-1.75412200	-1.20581800	2.54777100
C	-4.19599500	-1.03452500	0.59445400
H	-4.86960600	-1.84601500	0.30411000
H	-4.26637100	-0.94952600	1.68107400
C	-0.43165900	0.48959000	2.69718200
H	-0.44826600	0.45024900	3.78946000
H	-0.43411500	1.54797400	2.42492000
C	3.29582600	-3.32474000	0.18486700
H	4.13076200	-3.46270400	-0.50431100
H	2.92312200	-4.31616500	0.44936100
H	3.69057800	-2.86081200	1.08962200
C	1.05598000	-1.56484000	2.73307200
H	0.30081700	-2.23596400	2.32819200
H	0.96596300	-1.56645400	3.82094100
H	2.03806300	-1.96284000	2.48323800
C	1.65357600	-3.15012000	-1.72709700
H	0.82097600	-2.58696900	-2.14820800
H	1.30497700	-4.16303000	-1.51590000
H	2.43425400	-3.21717100	-2.48720300
C	0.83245000	3.25083100	-1.35617100
H	1.54503800	3.59184100	-2.10943900
H	0.23690700	4.11232900	-1.04683600
H	0.16743600	2.53056200	-1.82924900

TD-DFT and corresponding population analyses

To choose the appropriate functional and computation method (Tamm-Dancoff approximation or formal TD-DFT), [78-81] we simulated the UV-Vis spectrum of **CAAC-6** with a model compound **M**. M was created from the optimized structure of singlet **CAAC-6** (B3LYP/def2-TZVPP) followed by deletion of the unnecessary atoms. The structure was not re-optimized, in order to better mimic the geometry and molecular orbital structure of **CAAC-6**.

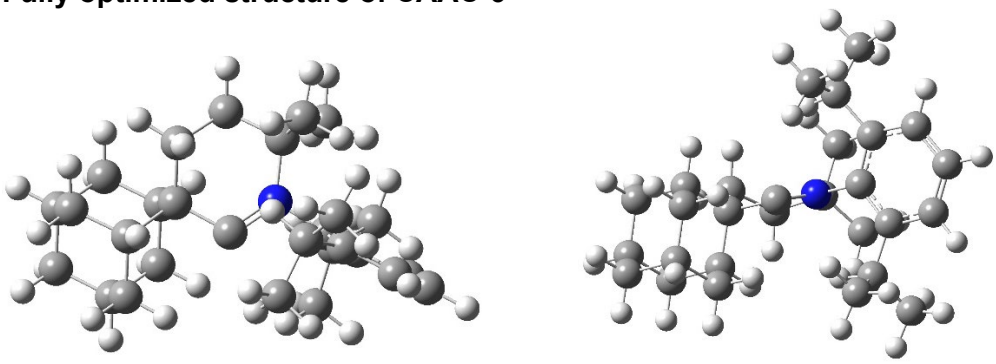
Model M:



N	0.73111400	-0.04552400	0.60780800
C	1.99261900	0.02925700	-0.13478200
C	-1.71454500	-0.22612300	0.50854400
C	3.77942100	1.32251200	-1.09461800
H	4.22072400	2.27878300	-1.34095600
C	-0.34498100	-0.07296100	-0.13601000
C	3.84782500	-1.06452000	-1.20734000
H	4.34066400	-1.96670100	-1.54251200
C	0.84508600	-0.11137200	2.14796100
C	4.44640100	0.16076400	-1.44469100
H	5.41079900	0.21143600	-1.93319800
C	1.80169700	0.95655600	2.68452400
H	2.82015800	0.81664400	2.32726100
H	1.81828500	0.88502500	3.77361300
H	1.47437600	1.96097400	2.42796100
C	-1.62635700	-0.65249800	1.98678400
H	-2.57285300	-0.53740000	2.51027700
H	-1.39409000	-1.72046100	2.03193600
C	-0.55252400	0.13978400	2.71462800
H	-0.53837000	-0.10792400	3.77835900
H	-0.77795400	1.20725300	2.65053100
C	1.37185100	-1.48113700	2.59403200
H	0.71108100	-2.29693100	2.30792400
H	1.45897500	-1.48764100	3.68197900
H	2.36002900	-1.67770400	2.18385900
C	2.60948900	-1.15981100	-0.57099200
H	2.14795593	-2.11364300	-0.42235908
C	2.54196600	1.28662000	-0.45180500
H	2.03041963	2.19467376	-0.20960946
C	-2.49773188	-1.27234203	-0.30609952
H	-2.48451518	-1.00131288	-1.34112055
H	-2.04330783	-2.23322299	-0.18319077
H	-3.50953474	-1.30940831	0.03999446

C	-2.48745813	1.09398995	0.33104165
H	-2.56538032	1.32433478	-0.71096094
H	-3.46756842	0.99229864	0.74810604
H	-1.96644946	1.88255742	0.83265038

Fully optimized structure of CAAC-6



Electronic energy= -1146.30207423 hartree/particle
Zero-point correction= 0.639804 (Hartree/Particle)
Thermal correction to Energy= 0.666165
Thermal correction to Enthalpy= 0.667109
Thermal correction to Gibbs Free Energy= 0.586935
Sum of electronic and zero-point Energies= -1145.662270
Sum of electronic and thermal Energies= -1145.635909
Sum of electronic and thermal Enthalpies= -1145.634965
Sum of electronic and thermal Free Energies= -1145.715139

N	0.70873900	-0.15474900	0.54472800
C	2.39113700	1.42972200	-0.30515400
C	1.97869600	0.10562400	-0.11583900
C	2.73322900	-0.97059200	-0.59943900
C	-1.67945100	-0.49666100	0.36598700
C	3.64593000	1.65266800	-0.86528700
H	3.98678000	2.66911700	-1.01526600
C	2.17657800	-2.37973500	-0.67313300
H	1.30170800	-2.43852900	-0.03043500
C	-0.32235400	-0.22586800	-0.25473000
C	3.97984800	-0.69909800	-1.15691900
H	4.58209100	-1.51550400	-1.53400800
C	0.79633200	-0.32269900	2.05810900
C	1.47099700	2.61282800	-0.07083600
H	0.58511800	2.26575100	0.45866400
C	-2.52873000	-1.34261000	-0.62628800
H	-2.02784100	-2.30614700	-0.76594600
C	-2.40932500	0.87668800	0.51177100
H	-1.83166100	1.52543200	1.17526300
C	-2.54967700	1.57722700	-0.84997200
H	-3.05200200	2.53778300	-0.69955800
H	-1.56809200	1.77790400	-1.27817000
C	4.45080600	0.59856700	-1.26160600

H	5.42650100	0.78926400	-1.68886500
C	1.47662700	0.88501600	2.69778100
H	2.50728500	1.00130800	2.36392400
H	1.48426400	0.73494800	3.77851800
H	0.93046500	1.80447300	2.49459700
C	-3.81572100	0.66768600	1.08866100
H	-3.77647300	0.23119200	2.08857000
H	-4.30234800	1.64181600	1.19276800
C	-4.76765300	0.48385700	-1.21374600
H	-5.37030300	-0.12636000	-1.89233300
H	-5.28001200	1.44269900	-1.09194400
C	2.11665300	3.73340800	0.74259100
H	2.49640400	3.37304200	1.69848900
H	1.38715800	4.52102700	0.93671100
H	2.94830100	4.18619300	0.20108900
C	-3.37159700	0.70574600	-1.80500500
H	-3.45745300	1.20594700	-2.77231100
C	-4.63956100	-0.21762300	0.14291900
H	-5.63218200	-0.37963800	0.56930300
C	-2.66661200	-0.64256200	-1.98437500
H	-3.25159300	-1.27882500	-2.65514400
H	-1.68266200	-0.49449600	-2.42675500
C	-1.53028700	-1.23425300	1.70189200
H	-2.48441900	-1.40452500	2.19519100
H	-1.11149300	-2.22619400	1.49742400
C	-3.93917600	-1.56848700	-0.05816700
H	-4.51475000	-2.17305600	-0.76466100
H	-3.90940200	-2.12868400	0.87727600
C	-0.61325600	-0.46159700	2.62829900
H	-0.53237700	-0.95046200	3.60106900
H	-1.03468500	0.52786900	2.81572600
C	3.16821700	-3.45323800	-0.22960600
H	4.01307000	-3.52377100	-0.91589700
H	2.67891700	-4.42800100	-0.21745400
H	3.56152800	-3.25704300	0.76824900
C	1.61492100	-1.56963200	2.39903700
H	1.11593500	-2.48508500	2.08354100
H	1.74266400	-1.61105000	3.48115400
H	2.60440100	-1.53358200	1.94599500
C	1.69289600	-2.64402900	-2.10324400
H	0.94601900	-1.90395500	-2.39204200
H	1.25049300	-3.63895700	-2.17791500
H	2.52731100	-2.58795700	-2.80503300
C	0.99692900	3.13820100	-1.43078400
H	1.83677000	3.54561000	-1.99703400
H	0.25694100	3.92941400	-1.29894600
H	0.55007800	2.33296400	-2.01439500

TD-DFT Calculated Transitions

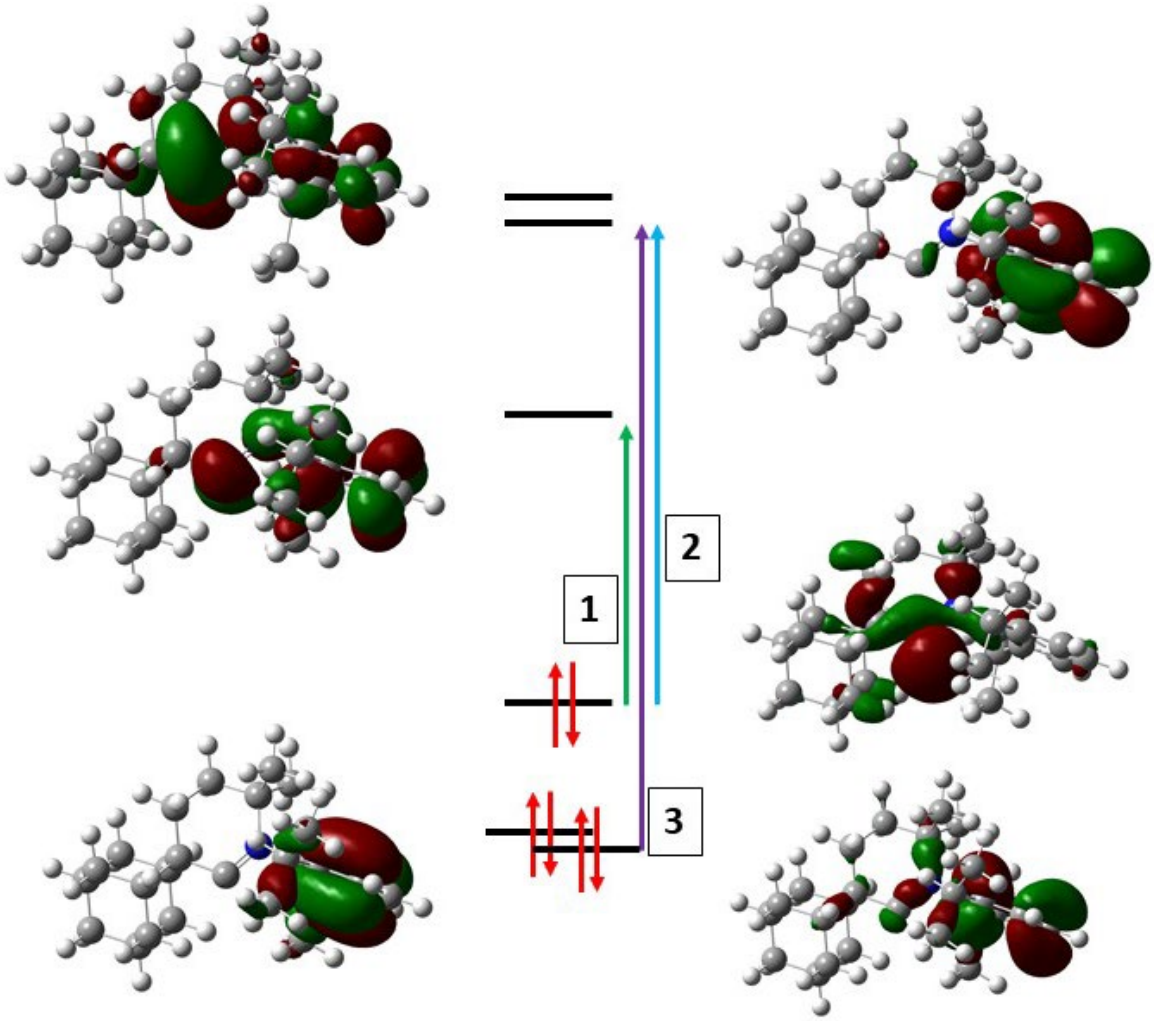


Figure 2.13: Calculated MOs and corresponding electronic transitions for **CAAC-6**.

	Energy (eV)	Oscillator Strength	Kohn-Sham orbitals involved
1	3.0854	0.0070	HOMO → LUMO
2	4.6662	0.0452	HOMO → LUMO+1
3	4.8003	0.0058	HOMO-1 → LUMO+1
4	5.5046	0.0069	HOMO-2 → LUMO
5	5.5450	0.0035	HOMO-1 → LUMO+1
6	5.9097	0.0021	HOMO → LUMO+2
7	6.2322	0.0221	HOMO-2 → LUMO+1
8	6.2942	0.0484	HOMO-2 → LUMO+1

Table 2.1. Calculated transitions involved in simulated spectrum with respective energies and oscillator strengths. Major Kohn-Sham orbitals involved in the transitions are noted. Major Transitions: **1**, **2**, **7**, **8** (**7** and 8 are essentially identical transitions)

Closer look at 7 and 8:

Excited State 7: Singlet-A 6.2322 eV 198.94 nm f=0.0221 <S**2>=0.000
106 -> 110 -0.34454
107 -> 109 0.54059
108 -> 114 0.11215
108 -> 115 0.10198
108 -> 116 0.11943

Excited State 8: Singlet-A 6.2942 eV 196.98 nm f=0.0484 <S**2>=0.000
106 -> 110 0.11049
107 -> 109 -0.22035
108 -> 114 0.33856
108 -> 115 0.30158
108 -> 116 0.27987
108 -> 117 0.14173
108 -> 118 0.22274
108 -> 119 0.21548

Chapter 3- Problems Measuring Empty Orbitals: The influence of C(sp^3)H-Selenium Interactions on the ^{77}Se NMR Quantification of the π-Accepting Properties of Carbenes

In Chapter 2, I discussed the profound changes in carbene properties that can stem from seemingly simple structural modifications, like the widening of a carbene bond angle.[75] Our discovery further emphasized how choosing the best carbene for a given application is not an easy task;[88] it requires a thorough understanding of carbene stereoelectronic properties. Thus, careful measurement of carbene properties is critical for the further progression of the field, especially as carbenes become increasingly ubiquitous in chemical science.[15-16, 30-31, 50, 54-55, 57, 89-105]

To evaluate the electronic properties of carbenes, several techniques have been developed, including calorimetric measurements of ruthenium complexes,[106] the ^{13}C NMR chemical shifts of palladium complexes,[107] the electrochemical E_0 value for the Ru(III)/Ru(II) redox couples,[108-111] and the Tolman Electronic Parameter (TEP), which is the most popular.[77] Although all of these techniques provide a convenient way to evaluate the overall donor abilities of carbenes, they fail to deconvolute the σ-donating and π-accepting properties. To determine their π-accepting character, the $^{31}P\{^1H\}$ NMR[112] and $^{77}Se\{^1H\}$ NMR[113] chemical shifts of phenylphosphinidene- and selenium-carbene-adducts, respectively, have been exploited. The latter, developed by Ganter, relies on the ability of carbenes to engage in backbonding with the selenium lone pair (Figure 3.1). The more π-accepting carbenes favor resonance form **I**, which results in a downfield $^{77}Se\{^1H\}$ NMR signal, whereas the less π-accepting ones favor resonance form **II** resulting in an upfield shift. Compared with the phosphinidene scale (~400 ppm),[112] the selenium scale covers a wider spectral range (~1200 ppm) which should allow for a greater delineation of the π-accepting properties of closely matching carbenes. Moreover, it benefits from a simple experimental protocol *i.e.* addition of elemental selenium to an *in-situ* generated free carbene.

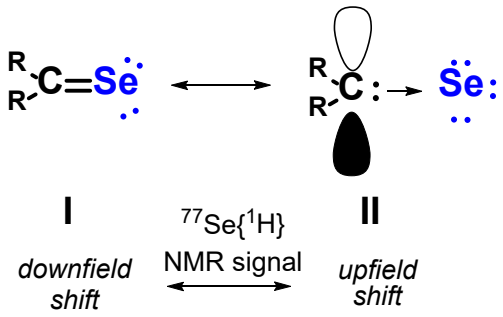


Figure 3.1: Canonical Structures of Carbene-Se adducts and their relation to $^{77}Se\{^{1}H\}$ NMR Spectroscopy.

Despite the popularity of this method,[71, 114-125] careful examination of the literature reveals several inconsistencies in $^{77}Se\{^{1}H\}$ NMR data. For example, it appears that the chemical shift for the selenium adduct of NHCs bearing tertiary *N*-alkyl substituents such as **IAd** (197 ppm) and **I^{t}Bu** (183 ppm) display unexpectedly downfield signals with respect to secondary alkyl analogues such as **ICy** (−22 ppm) and **I^{i}PrMe$_2$** (−18 ppm) (Figure 3.2).[125]

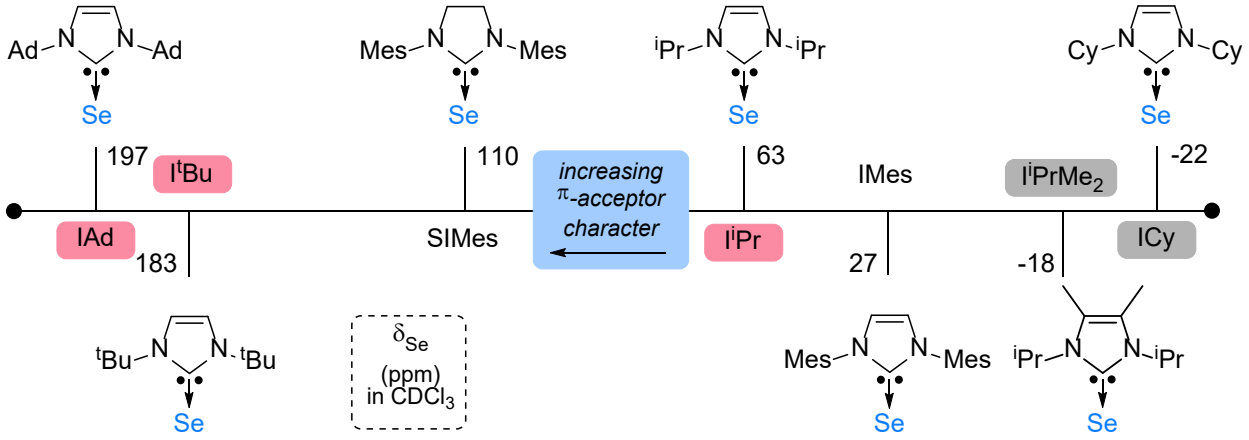


Figure 3.2: Non-linear behavior of the $^{77}Se\{^{1}H\}$ NMR chemical shifts in NHC-Se adducts

As mentioned by Cavallo, Nolan *et al*,[125] such "difference amongst N,N-dialkylimidazol-2-ylidenes was very intriguing" since these data support, counterintuitively, a much stronger π-accepting character for tertiary *N*-alkyl substituted NHCs. Similar observations were recently highlighted by Huynh across several other carbene families,[126] stating caution should be taken when analyzing $^{77}Se\{^{1}H\}$ NMR data of carbene-selenium adducts.

Rather short intramolecular Se–H distances, which are close to or within the sum of Van der Waals radii, were previously noted across several Se-NHC adducts by Cavallo and co-workers.[125] We hypothesized that non-classical hydrogen bonding (NCHB)[127-129] interactions resulting from negative hyperconjugation trigger a non-linear behavior of the $^{77}Se\{^{1}H\}$ NMR scale in carbene-selenium adducts. NCHB is well established with O and S, but is less common for selenium, which is less electronegative.[130] These interactions have been proposed with acidic protons in some oxazolylidene-selenium adducts[131-132] but are much more surprising with unactivated alkyl protons.

To begin testing our hypothesis, we first considered the five-membered cyclic (alkyl)(amino) carbenes (CAAC-5).[18-19, 60, 62, 133] We previously reported that the $^{77}Se\{^{1}H\}$ NMR signal of the selenium adduct of ^{Et}CAAC-5 **3.1a** is at 481 ppm.[71] As observed with the NHC series, we found that the $^{77}Se\{^{1}H\}$ NMR chemical shift of the selenium adducts of the more sterically hindered ^{Menth}CAAC-5 (635 ppm) **3.1b** and ^{Ad}CAAC-5 (683 ppm) **3.1c** (Figure 3.3) appeared considerably downfield. Going further, we synthesized the adducts of six-membered cyclic (alkyl)(amino)carbenes (CAAC-6), which provide more steric crowding than CAAC-5s as a result of a larger C-C_{carb}-N angle.[75] Here also, we observed marked differences in the chemical shift of the small ^{Et}CAAC-6 (715 ppm) **3.2a** and the large ^{Ad}CAAC-6 (863 ppm) **3.2b**. Altogether, these results suggest, counterintuitively, that the bulkier CAACs **3.1**(**b,c**) and **3.2b** could be more π-accepting than their smaller variants **3.1a** and **3.2a**, respectively. Intrigued by these results, we verified by DFT that within the same family, these carbenes have comparable HOMO-LUMO gaps and should therefore display similar electronic properties (Figure 3.4).[134] Furthermore, the X-ray crystallographic analysis showed short intramolecular Se···H distances for the adamantyl variants **3.1c** and **3.2b** (Figure 3.5), which are not present in **3.1a**[71] and **3.2a**.[75]

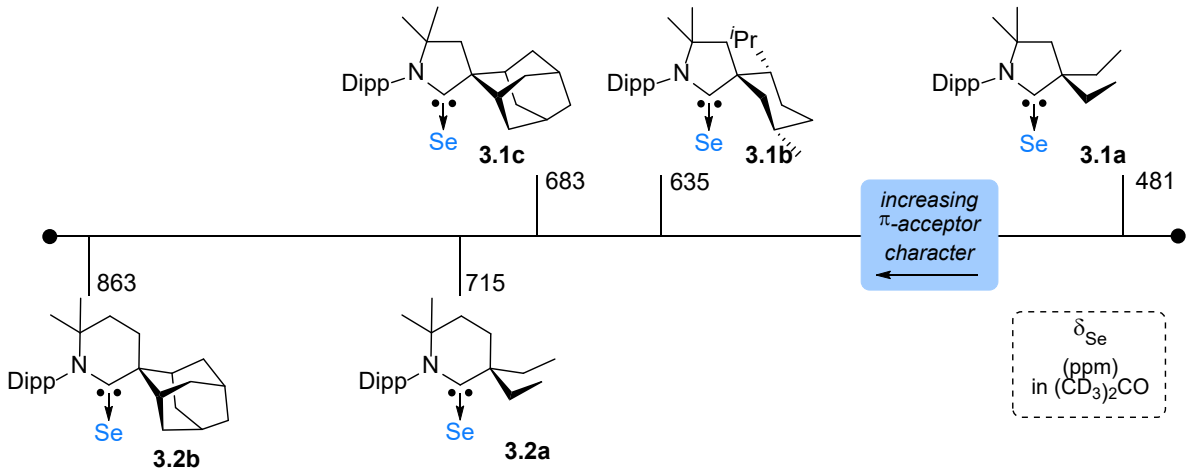


Figure 3.3: Non-linear behavior of the $^{77}Se\{^{1}H\}$ NMR chemical shifts in CAAC-Se adducts.

Free carbene	^{X}**CAAC-5**		^{X}**CAAC-6**	
X	*Et*	***Ad***	*Et*	***Ad***
LUMO[a]	-0.44	**-0.47**	-0.41	**-0.44**
HOMO[a]	-5.26	**-5.16**	-4.85	**-4.72**

[a] values in *eV*

Figure 3.4: Differences in $^{77}Se\{^{1}H\}$ NMR chemical shifts of **3.1a,c** and **3.2a,b** are not expected since the carbene HOMO-LUMO gaps are similar within each CAAC family.

Thus, it appears, that the same phenomenon is present in both CAACs and NHCs, although the substituent involved is attached to nitrogen for NHCs and on carbon for CAACs. To make a direct comparison, N-alkyl substituted CAACs were desirable, but until now they were hardly available using current synthetic methodologies. We found that they are readily accessible upon using a monomethylated instead of a dimethylated backbone (Scheme 3.1). Several CAAC-6^{Me} iminium salts **3.3a-e** with various substituents on the nitrogen were prepared.[61] Contrary to the well-known dimethylated CAAC derivatives, the corresponding free CAAC-6^{Me} **3.4a-e** are not stable at room temperature. However, using variable temperature $^{13}C\{^{1}H\}$ NMR, we confirmed that they can be generated at -80 °C and are persistent until -60 °C. Adducts **3.5a-e** were prepared by deprotonation of **3.3a-e** with KHMDS at –78 °C in the presence of excess elemental selenium.

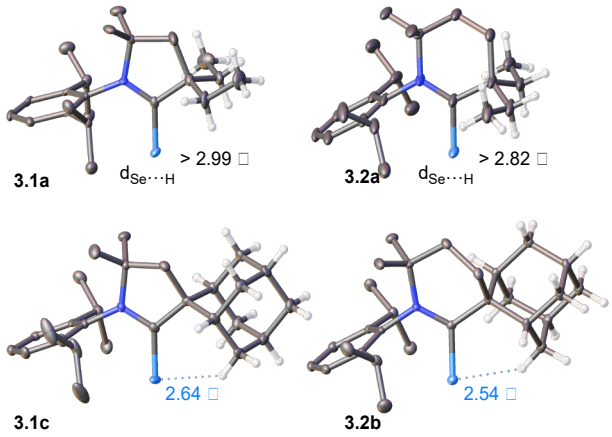
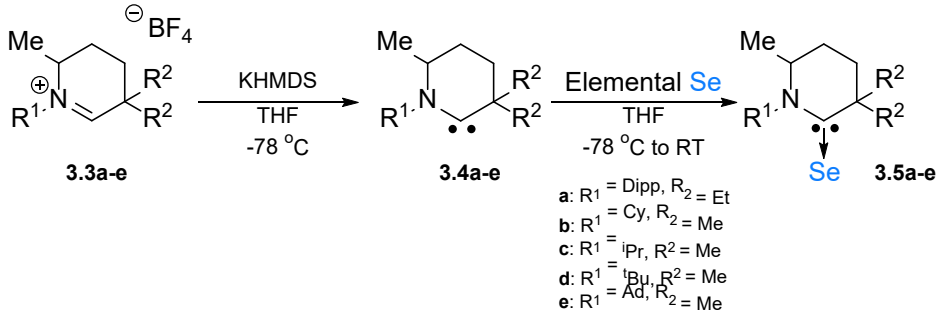


Figure 3.5: Short intramolecular Se-H distances are observed in **3.1c** and **3.2b** but not in **3.1a** and **3.2a**.



Scheme 3.1: Synthesis of CAAC-6 Se adducts **3.5a-e**.

The $^{77}Se\{^1H\}$ NMR chemical shifts for the room temperature stable **3.5a-e** were explored to confirm the substitution pattern that leads to NCHB (Figure 3.6). Compared to the N-aryl substituted **3.5a (**669 ppm), an upfield shift is observed for the N-alkyl substituted derivatives (**3.5b:** 521; **3.5c**: 526 ppm). This is in good agreement with alkyl substituents increasing electron density on the nitrogen, thus raising the LUMO and reducing the carbene π-acidity. This should also be the case with *N*-^{t}Bu **3.5d** and *N*-Ad **3.5e** but their signals (777 and 789 ppm, respectively), were downshifted by over 268 ppm compared **3.5b,c**. As a reference, this range is larger than the difference between the DAC-Se adducts (846-856 ppm),[121] and Alder's acyclic diaminocarbene-Se (593 ppm),[135-136] which are two very distinct families of carbenes. Interestingly, DFT predicted that the π-accepting properties of N-alkyl carbenes **4b-e** are within the same range, which conflicted with the ^{77}Se NMR data.[134]

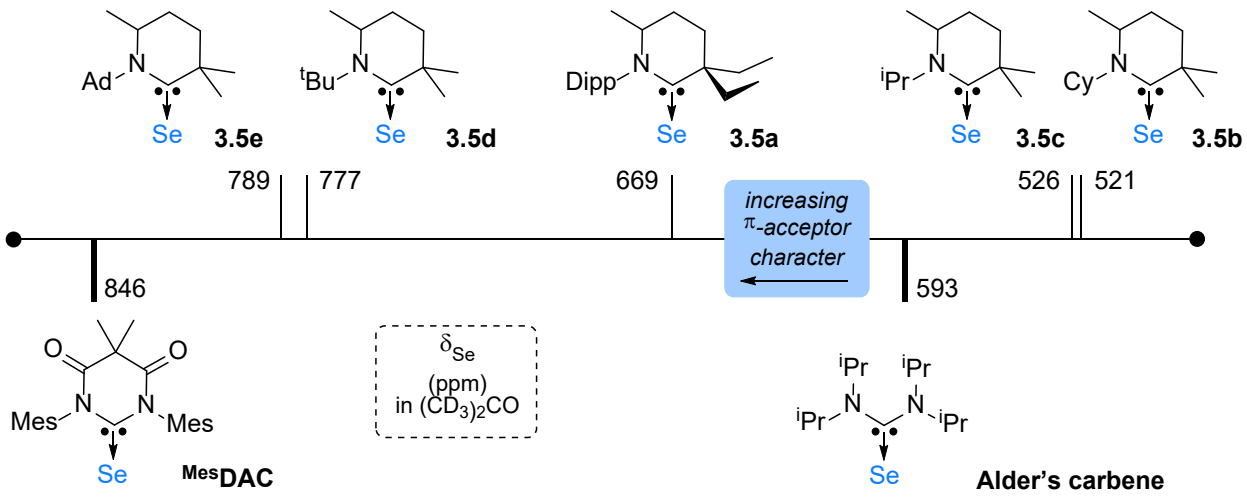


Figure 3.6: Non-linear behaviour of the $^{77}Se\{^{1}H\}$ NMR chemical shifts in CAAC-Se adducts. DAC- and Alder carbene-Se adducts included for comparison.

Upon comparing the ^{1}H NMR of aldiminium **3.3b** and carbene-selenium adduct **3.5b**, we noticed a marked downfield shift of the exocyclic N-C-**H_a** hydrogen from 3.75 ppm to 5.85 ppm (Figure 3.7). This is an additional indication of the participation of C(sp^3)-H bonds in non-classical C-H···Se interactions. Note that recording the ^{1}H NMR of **3.5b** up to 100°C did not show a coalescence of the signal suggesting the presence of a rather strong Se-H interaction.

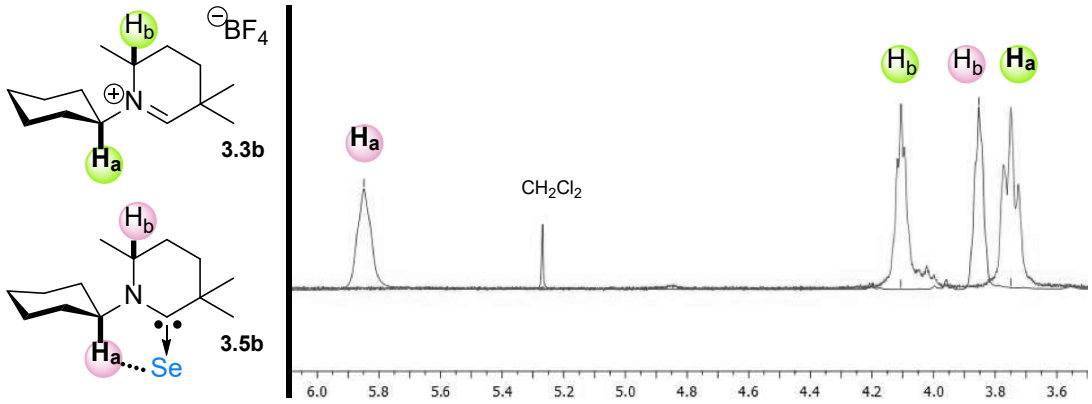


Figure 3.7: Comparison of the ^{1}H NMR of **3.3b** and **3.5b** highlights NHCB Se-H interactions.

The solid-state structures of compounds **3.5b-e** also display short intramolecular Se-H distances, which is not the case for **3.5a** (Figure 3.8). Note, that these distances (2.46-2.66 Å) are well within the range of intramolecular hydrogen bonding in Silks' crystalline selenourea adduct [Se-H 2.51-2.60 Å], and in line with their proposed NCHB interactions.[131-132] Following geometry

optimizations of **3.5c** and **3.5d**, based on the X-ray crystal structure data,[75] at the BP98/def2tzvpp level of theory, and quantum theory of atoms in molecules (QTAIM) analysis we confirmed the existence of bond paths in both compounds (Figure 3.9).[137-138] Comparison of the electron density ρ(r) at the Se-H bond path critical points (BCP) showed that NHCB interactions are stronger when involving a β-hydrogen (**3.5c)** than a γ-hydrogen to nitrogen (**3.5d**).[139] Thus, the strength of these interactions does not rationalize the observed upfield chemical shift of **3.5c** compared to **3.5d**.

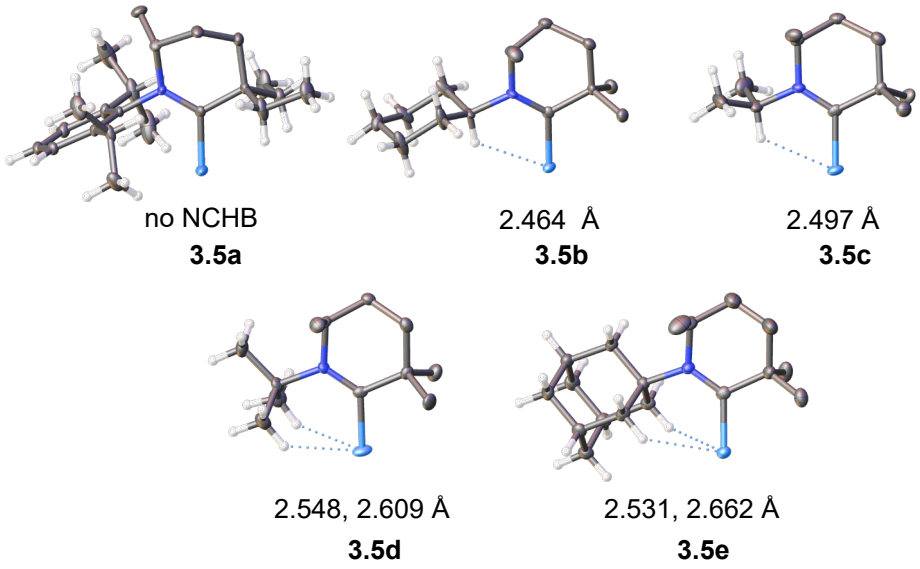


Figure 3.8: Solid state structures of selenoamides **3.5a-e** indicating NCHB Se-H interactions or absence thereof.

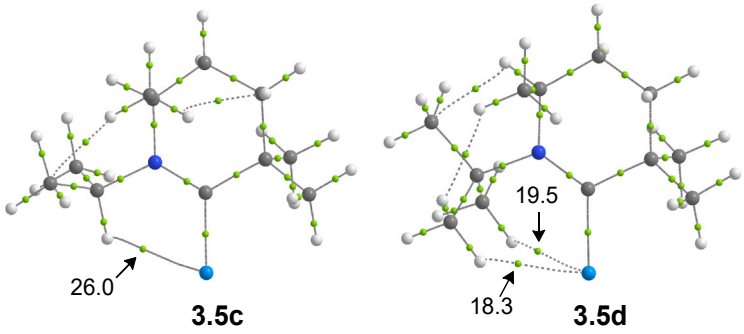


Figure 3.9: QTAIM analysis highlighting the Se-H bond paths and the electron density ρ(r) at the bond path critical points (BCP) (values in 10^{-3} a.u.)

To investigate further, ^{77}Se NMR chemical shifts of **3.1c**, **3.2b** and **3.5b-e** were calculated by DFT (Figure 3.10). The experimental value was well reproduced in the case of the

conformationally rigid **3.1c** and **3.2b**. For the N-alkyl substituted **3.5b-e**, which allow for a higher degree of rotation at nitrogen, calculations predicted upfield selenium NMR chemical shifts compared to those observed experimentally. We wondered, if in these cases, the accessibility of other conformational isomers, also stabilized through NCHB interactions, could explain the discrepancies. As an example, we considered **3.5c** and its conformer **3.5c'**. We confirmed that **3.5c'** is energetically accessible (+2.3 kcal.mol^{-1}) and more importantly predicts a significant downfield shift (+74 ppm) of the Se NMR signal. Consequently, we propose that the deshielding of the selenium atom in **3.5c'** is favored by the formation of a quasi-cyclic 6-membered conformation stabilized by NCHB C(sp^3)-H-Se interaction. In this case, the NCHB is better described as a negative hyperconjugative interaction between the lone pair of the Se atom (H-bond acceptor) and the $\sigma^*_{C\text{-}H}$ orbital of the C(sp^3)-H (H-bond donor); orbital overlap is maximized in a quasi 6-membered ring and facilitates electron transfer.[140-141] Note that the directionality of this type of interaction has already been shown to be a critical parameter for maximizing orbital overlap.[140-141] This effect is more pronounced in more constrained systems such as **3.5d-e**, which have a higher probability of such 6-membered ring conformations than **3.5b,c**. Moreover, it is particularly well exemplified in **3.1c** and **3.2b** in which the unusual distortion of the backbone, observed by X-ray, places the C-H bond in the right position with respect to the selenium atom (Figure 3.11).

	(CAAC)Se	^{77}Se{^{1}H} in ppm Experimental	Predicted[c]
rigid	**3.1c**[a]	683	688
	3.2b[a]	863	883
flexible	**3.5b**[b]	521	425
	3.5c[a]	526	**427**
	3.5d[a]	777	688
	3.5e[a]	789	694

[a] $CDCl_3$. [b] $(CD_3)_2CO$. [c] Using X-ray data

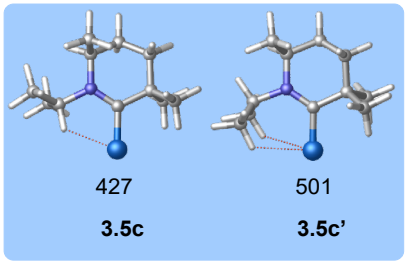


Figure 3.10: Experimental and predicted ^{77}Se{^{1}H} NMR chemical shift of **3.1c**, **3.2b** and **3.5b-e** (left). Significant downfield-shift of ^{77}Se{^{1}H} NMR signal caused by rotation of substituent and formation of quasi 6-membered ring (right).

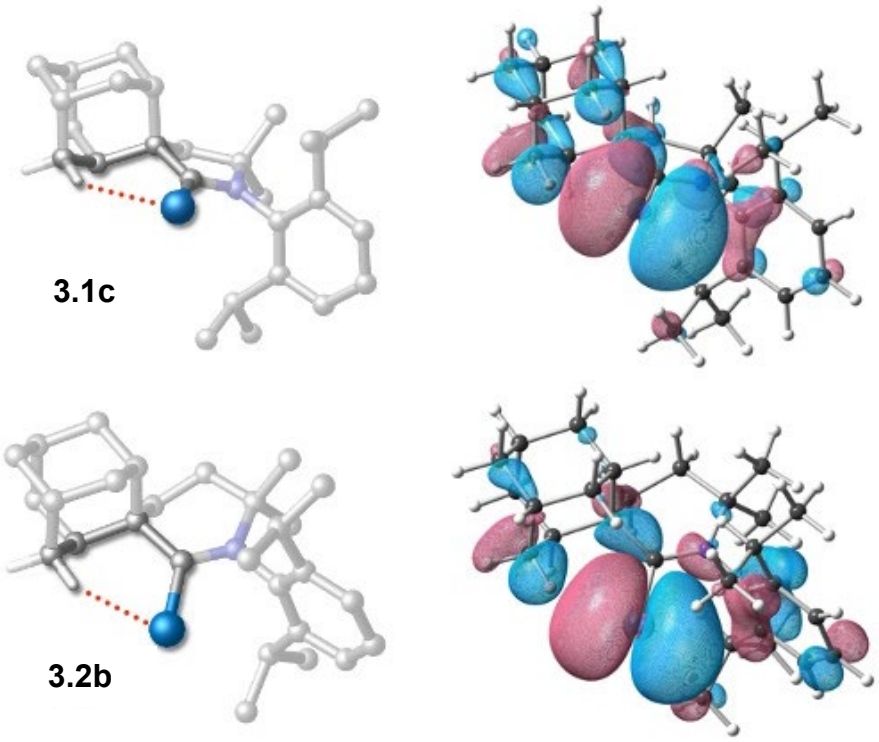


Figure 3.11: Quasi-cyclic 6-membered conformation stabilized by NCHB C(sp^3)-H-Se interaction in **3.1c** and **3.2b** maximizes orbital overlap with a significant backbone distortion.

In conclusion, we have provided experimental and computational evidence for the existence of non-classical hydrogen bonding interactions in CAAC-selenium adducts, causing major deviations from the expected trend in ^{77}Se NMR chemical shifts. Since the same reasoning can also be applied to **I^{t}Bu** and **IAd**, it is likely that this phenomenon is also found in other carbene motifs not considered in the present study. These findings encourage caution when probing π-accepting properties within a carbene family, especially when bulky substituents are in proximity to the carbene center.

Acknowledgements

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Supporting Information

I. General Considerations

All manipulations were performed under an Argon atmosphere in either an MBraun glovebox or using standard Schlenk techniques, unless otherwise mentioned. Glassware was dried in an oven overnight at 150 ºC or flame dried before use. Benzene, THF, Et_2O, and toluene were freshly distilled over Na metal. Hexanes, *n*-pentane, DCM, and $CHCl_3$ were freshly distilled over CaH_2. Acetonitrile was distilled over P_2O_5. Additionally, benzene (C_6D_6) and chloroform ($CDCl_3$) used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried according to published methods.

NMR: Multinuclear NMR data were recorded on a Varian INOVA 500MHz and 400MHz, Jeol 500 MHz, or Bruker 300 MHz spectrometers. NMR signals are listed in ppm, relative to residual solvent signals (^{1}H and ^{13}C), H_3PO_4 (^{31}P), and $SeMe_2$ (^{77}Se). Coupling constants are in Hertz (Hz). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet, br = broad. All spectra were recorded at 25 ºC unless otherwise noted.

Melting Points: Melting points were measured with an electrothermal MEL-TEMP apparatus. Pure crystals of each compound were added to a capillary tube which was then sealed from air with vacuum grease.

Mass Spectrometry: High resolution mass spectrometry data was collected on an Agilent 6230 TOF-MS at the UC San Diego Mass Spectrometry Laboratory.

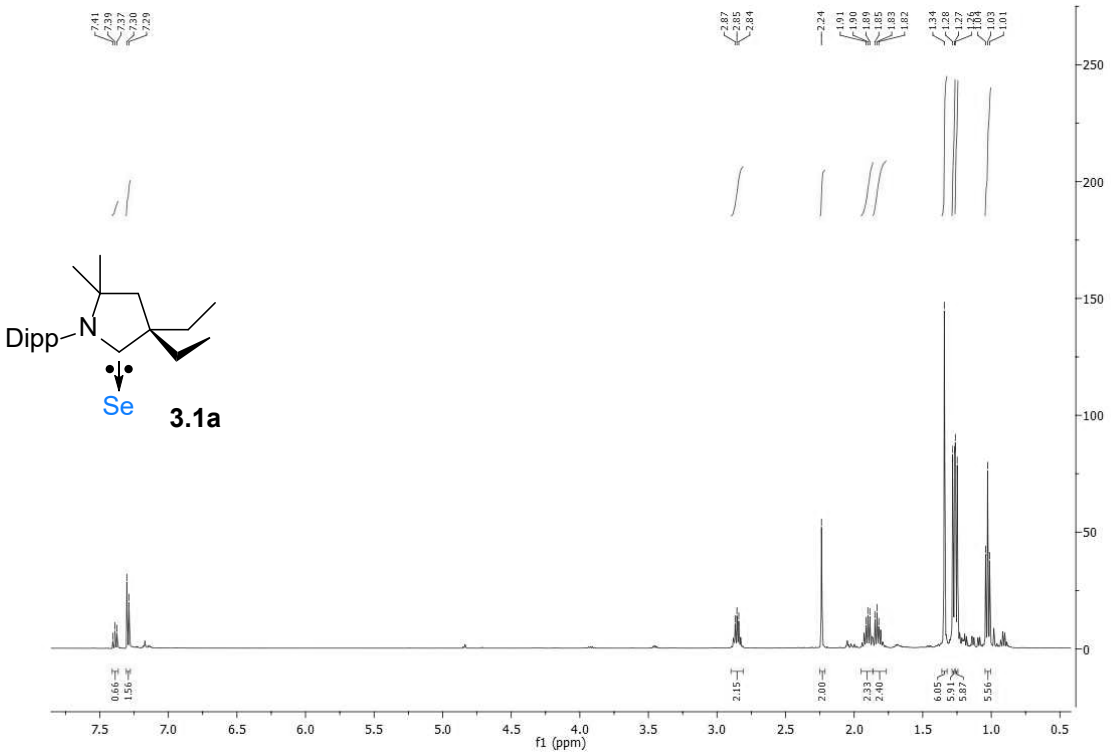
X-Ray Crystallography: Single crystal X-Ray diffraction data were collected on Bruker Apex II diffractometers using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2. Olex2 software was employed for the resolution,[142] refinement, and generation of crystallographic information files of every structure. The structures were solved with the ShelXS9[143] structure solution program using Direct Methods and refined with the ShelXL9 refinement package using Least Squares minimization. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and their coordinates were refined riding on their parent atoms.

II. Synthetic methods

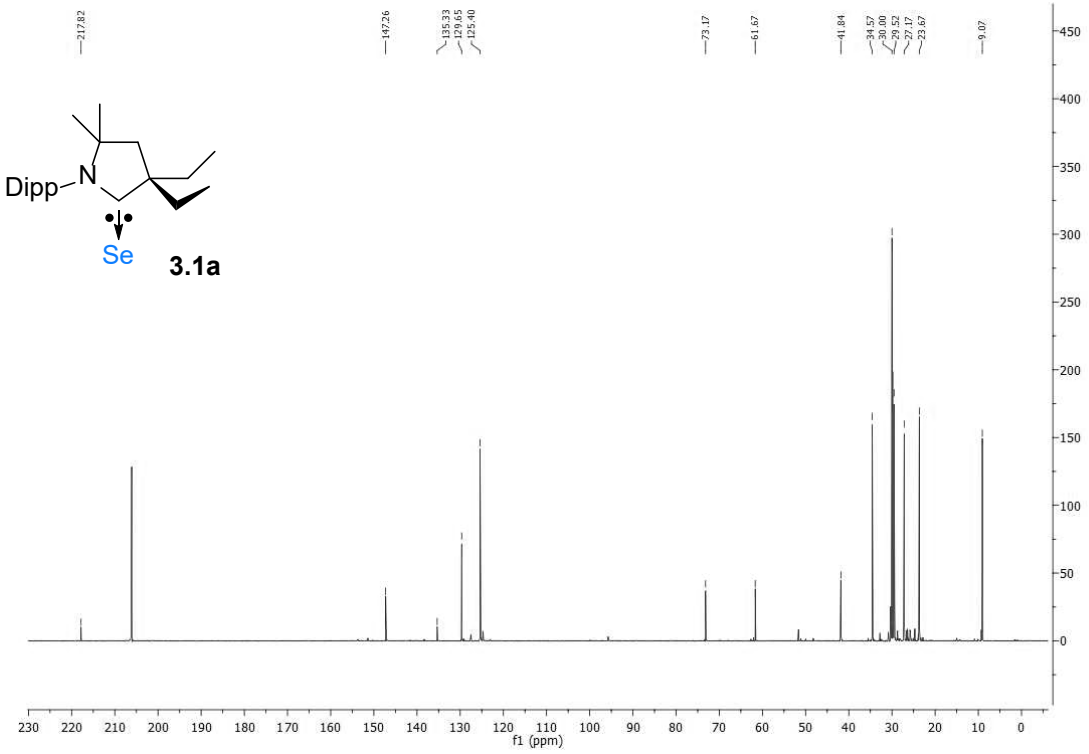
II.1. Preparation of compound 3.1a-b

*Synthesis of **3.1a**:* Prepared following the reported procedure using ^{Et}CAAC5.HBF$_4$ (296 mg, 1 eq), KHMDS (162 mg, 1.05 eq) and Se (116 mg, 2 eq) resulting in 107 mg of **3.1a** in 37% yield.^{1}H NMR and ^{13}C{^{1}H} NMR were found to match those reported in the literature.[71] **^{1}H NMR** (500 MHz, (C_6D_6) δ = 7.18-7.23 (m, 1H), 7.11 (d, J = 7.7 Hz, 2H), 2.90 (sept, J = 6.7 Hz, 2H), 2.05 (dq, J S10 = 14.8, 7.4 Hz, 2H), 1.85 (dq, J = 14.7, 7.4 Hz, 2H), 1.73 (s, 2H), 1.48 (d, J = 6.7 Hz, 6H), 1.20 (d, J = 6.8 Hz, 6H), 0.99 (s, 6H), 0.98 (t, J = 7.4 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 217.5, 147.0, 134.9, 129.3, 125.0, 71.7, 61.2, 41.9, 34.4, 29.8, 29.1, 27.3, 23.6, 9.1. **^{77}Se NMR** (57 MHz, acetone-d_6) δ 481.5

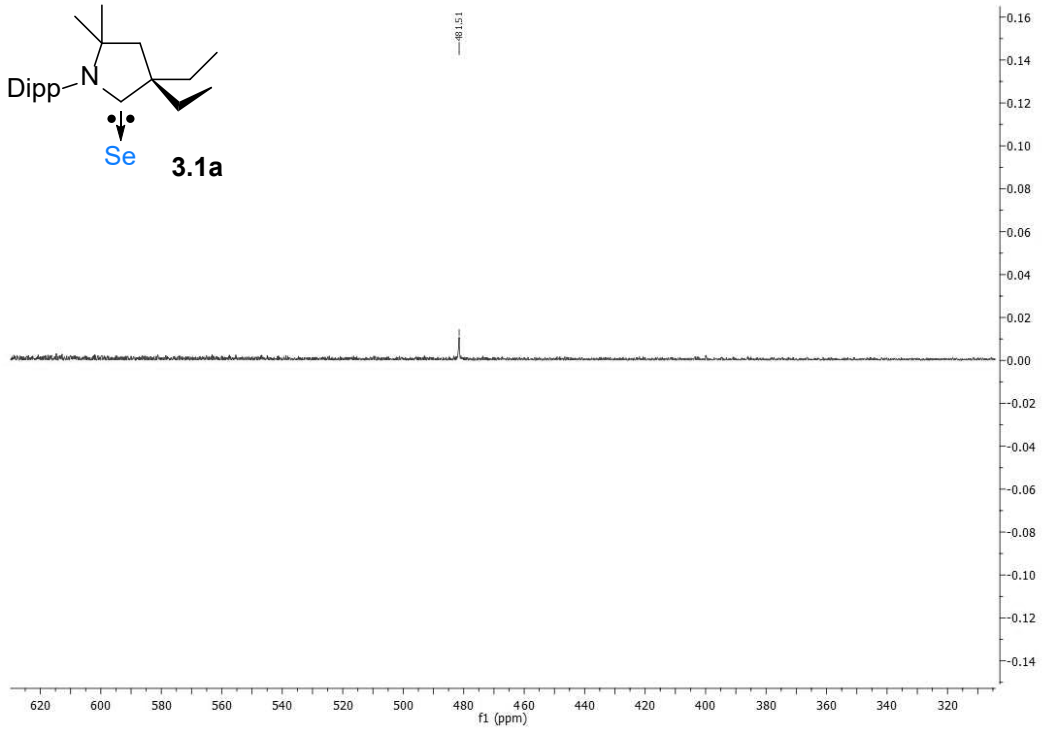
^{1}H NMR for 3.1a (C_6D_6)



$^{13}C\{^{1}H\}$ NMR for 3.1a (C_6D_6)



$Se\{^{1}H\}$ NMR for 3.1a (acetone-d_6)

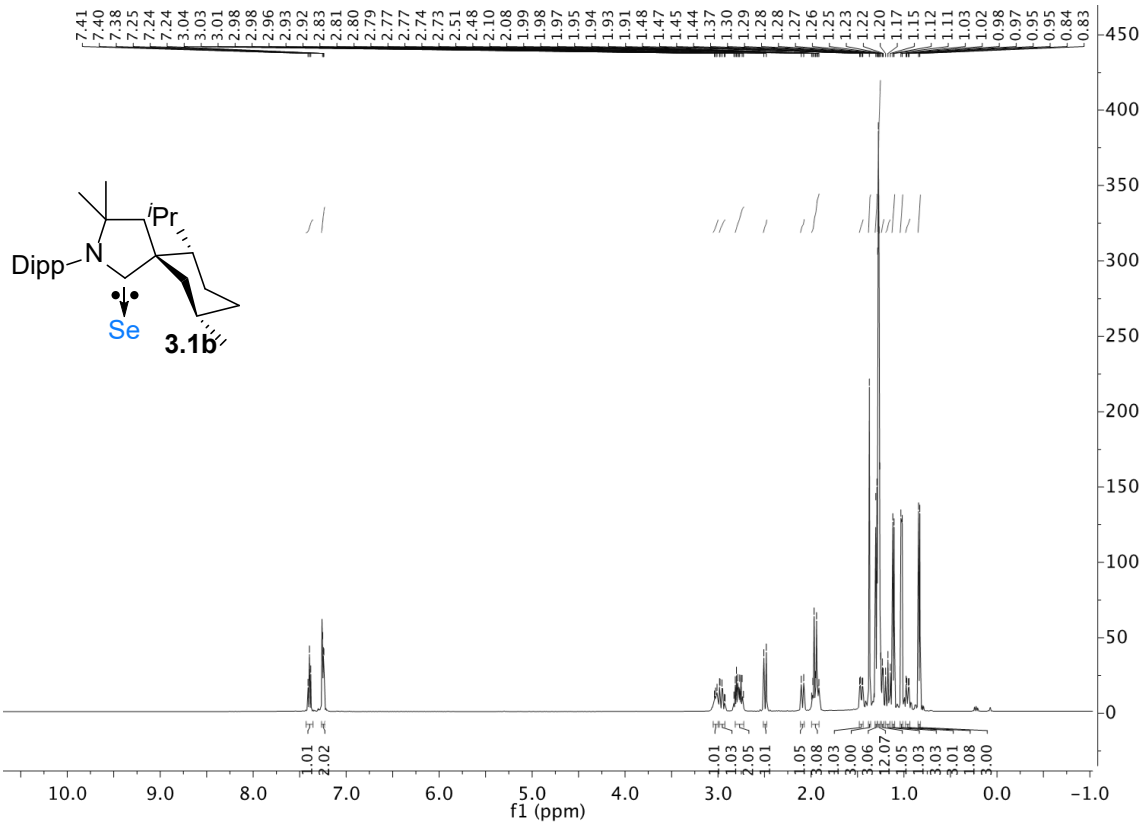


*Standard procedure for the one pot preparation of Se-adducts **3.1b-c***: The corresponding iminium salt[19, 62] (1 eq), KHMDS (1.05 eq), and Se black (2 eq) were all combined in a Schlenk with a stir bar. The Schlenk was cooled to -78 ˚C and Et_2O (10 mL) was slowly added. The resulting slurry was warmed to room temperature and stirred for 24h. Et_2O was then removed *in vacuo* and the product was purified in air by column chromatography with DCM as eluent. After purification, products were moved into an argon glovebox for long-term storage.

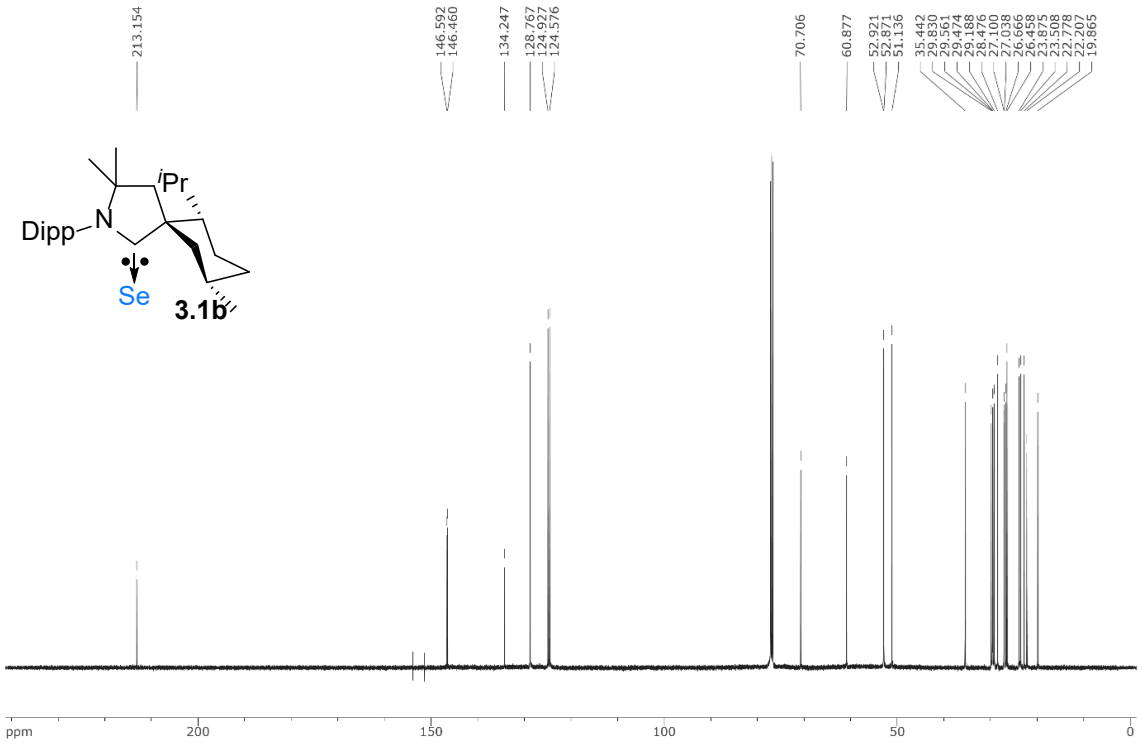
*Synthesis of **3.1b**:* Prepared following the standard procedure using ^{Menth}CAAC5.HBF_4 (310 mg, 1 eq), KHMDS (149 mg, 1.13 eq) and Se (104 mg, 2 eq) gave 240 mg of **3.1c** as a yellow solid (yield = 79%). Single crystals of **3.1c** were grown through slow evaporation of DCM. **MP**: 172-174 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.7 Hz ,1H), 7.25-7.24 (m, 2H), 3.05-3.01 (m, 1H), 2.98-2.92 (m, 1H), 2.93-2.73(m, 2H), 2.49 (d, *J* = 13.5 Hz, 1H), 2,10 - 2.08 (m, 1H), 1.99-1.91 (m, 3H), 1.48 -1.44 (m, 1H), 1.37 (s, 3H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.28 -1.25 (m, 12H), 1.23-1.22 (d, *J* =4,4 Hz, 1H), 1.17 (t, J = 12.7 Hz, 1H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.9

Hz, 3H), 0.98 – 0.95 (m, 1H), 0.84 (d, J = 6.7 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 213.4, 146.7, 134.5, 129.0, 125.1, 124.8, 70.9, 61.1, 53.1, 53.1, 51.4, 35.7, 30.1, 29.8, 29.7, 29.4, 28.7, 27.3, 27.3, 26.9, 26.7, 24.1, 23.7, 23.0, 22.4, 20.1. **$^{77}Se\{^{1}H\}$ NMR** (95 MHz, $CDCl_3$) 635.1. HRMS: *m/z* calculated for $C_{27}H_{44}NSe$ $[M+H]^+$ 462.2635, found 462.2633

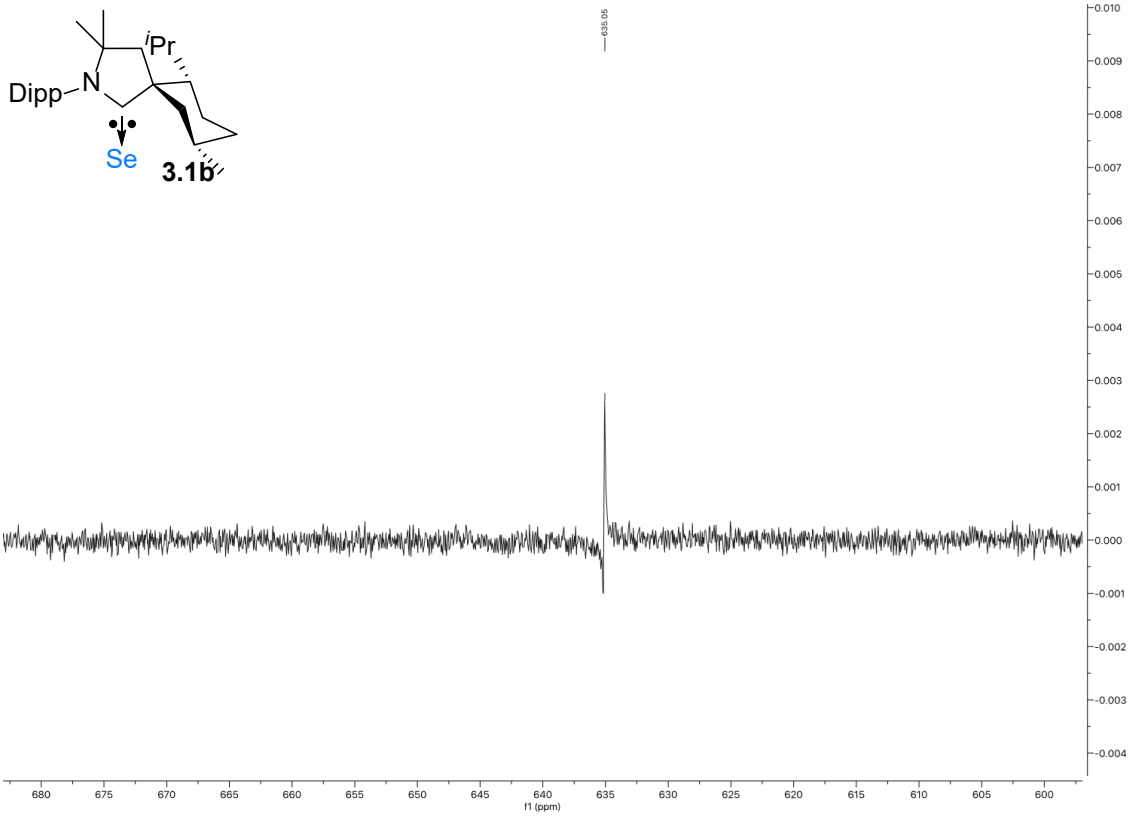
^{1}H NMR for 3.1b ($CDCl_3$)



$^{13}C\{^{1}H\}$ NMR for 3.1b ($CDCl_3$)

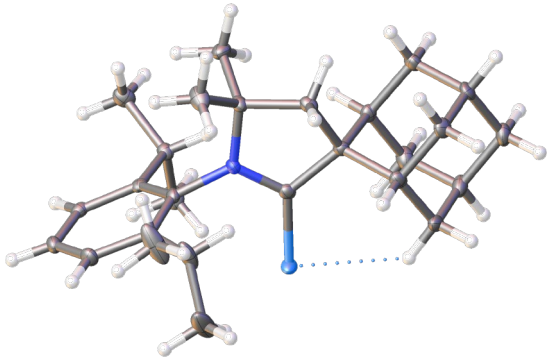


Se{^{1}H} NMR for 3.1b ($CDCl_3$)



*Synthesis of **3.1c**:* Prepared following the standard procedure using ^{Ad}CAAC5.HBF$_4$ (290 mg, 1 eq), KHMDS (130 mg, 1.05eq) and Se (101 mg, 2 eq) gave 220 mg of **3.1b** as a yellow solid (yield = 77%) Single crystals of **3.1b** were grown through slow evaporation of DCM. 222-223 C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 4.04 (d, *J* = 13.0 Hz, 2H), 2.72 (hept, *J* = 6.7 Hz, 2H), 2.52 (s, 2H), 2.14 (d, *J* = 9.9 Hz, 2H), 2.06 – 2.01 (m, 2H), 2.01 – 1.94 (m, 1H), 1.94 – 1.88 (m, 1H), 1.79 – 1.73 (m, 3H), 1.74 - 1.72 (m, 1H), 1.54 (d, *J* = 14.1 Hz, 2H), 1.29 – 1.28 (m, overlaping, 12H), 1.25 (d, *J* = 6.7 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 215.4, 146.5, 135.2, 128.9, 125.1, 69.5, 61.4, 50.1, 39.7, 37.2, 35.2, 32.1, 29.4, 28.8, 27.6, 27.0, 24.0. **^{77}Se NMR** (95 MHz, $CDCl_3$) δ 683.0; (95 MHz, acetone-d_6) 688.4. HRMS: *m/z* calculated for $C_{27}H_{40}NSe$ $[M+H]^+$ 458.2322, found 458.2320.

Crystal data and structure refinement for 3.1b CCDC# 2020768



Ellipsoid shown at 50% probability

Empirical formula	$C_{27}H_{39}NSe$
Formula weight	456.55
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	8.4785(5)
b/Å	17.1820(11)
c/Å	18.1533(10)

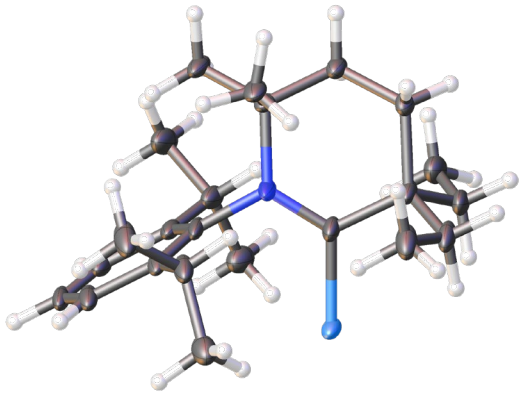
α/°	111.343(2)
β/°	101.938(2)
γ/°	98.532(3)
Volume/Å^3	2336.2(2)
Z	4
ρ_{calc}g/cm^3	1.298
μ/mm^{-1}	1.620
F(000)	968.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.512 to 50.848
Index ranges	-10 ≤ h ≤ 7, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21
Reflections collected	15067
Independent reflections	8502 [R_{int} = 0.0478, R_{sigma} = 0.0674]
Data/restraints/parameters	8502/0/535
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0981
Largest diff. peak/hole / e Å^{-3}	0.40/-0.32

II.2. Preparation of compound 3.2a-b

*Standard procedure for the one pot preparation of Se-adducts **3.2a-b***: The corresponding iminium salt[75] (1 eq), KHMDS (1.05 eq), and Se black (2 eq) were all combined in a Schlenk with a stir bar. The Schlenk was cooled to -78 °C and THF (20 mL) was slowly added over 5 minutes. The resulting slurry was slowly warmed to room temperature while stirring over 12h. THF was then removed *in vacuo* and the product was extracted with pentane.

*Synthesis of **3.2a**:* Prepared following the standard procedure using ^{Et}CAAC6.HBF$_4$ (50 mg, 1 eq) and Se (15 mg, 2 eq). **^{1}H NMR** and **^{13}C{^{1}H} NMR** were found to match those reported in the literature.[75] **^{1}H NMR** (500 MHz, C_6D_6) δ 7.21 – 7.16 (m, 1H), 7.13 – 7.05 (m, 2H), 2.84 (sept, *J* = 6.6 Hz, 2H), 2.47 – 2.34 (m, 2H), 2.03 – 1.94 (m, 2H), 1.70 – 1.63 (m, 2H), 1.60 – 1.54 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 6H), 1.24 (d, *J* = 6.6 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 6H), 0.97 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ 220.83 (CSe), 145.25 (C_{Ar}), 141.85 (C_{Ar}), 125.14 (C_{Ar}), 63.03 (C_q), 53.60 (C_q), 38.07, 36.05, 29.73, 29.06, 27.08, 24.38, 23.29, 9.18, 3.74, 3.48. **^{77}Se NMR** (57 MHz, $(CD_3)_2CO$) δ 714.91.

Crystal data and structure refinement for 3.2a CCDC# 2020773



Ellipsoid shown at 30% probability

Empirical formula	$C_{23}H_{37}NSe$
Formula weight	406.49
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	7.8515(3)
b/Å	15.0372(7)
c/Å	8.8766(3)
α/°	90

β/°	90.3040(10)
γ/°	90
Volume/Å^3	1048.00(7)
Z	2
ρ_{calc}g/cm^3	1.288
μ/mm^{-1}	2.436
F(000)	432.0
Crystal size/mm^3	0.06 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.964 to 136.642
Index ranges	-9 ≤ h ≤ 9, -18 ≤ k ≤ 17, -10 ≤ l ≤ 10
Reflections collected	10244
Independent reflections	2004 [R_{int} = 0.0317, R_{sigma} = 0.0230]
Data/restraints/parameters	2004/0/151
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1045
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1059
Largest diff. peak/hole / e Å^{-3}	0.31/-0.43

One level B error was detected by the IUCr checkCIF in this structure. Despite several attempts we were not able to obtain better crystals for this compound.

_vrf_PLAT250_gb_rj_fv_20200729b_0m_a

;

PROBLEM: Large U3/U1 Ratio for Average U(i,j) Tensor ....

RESPONSE: The structure is modulated.

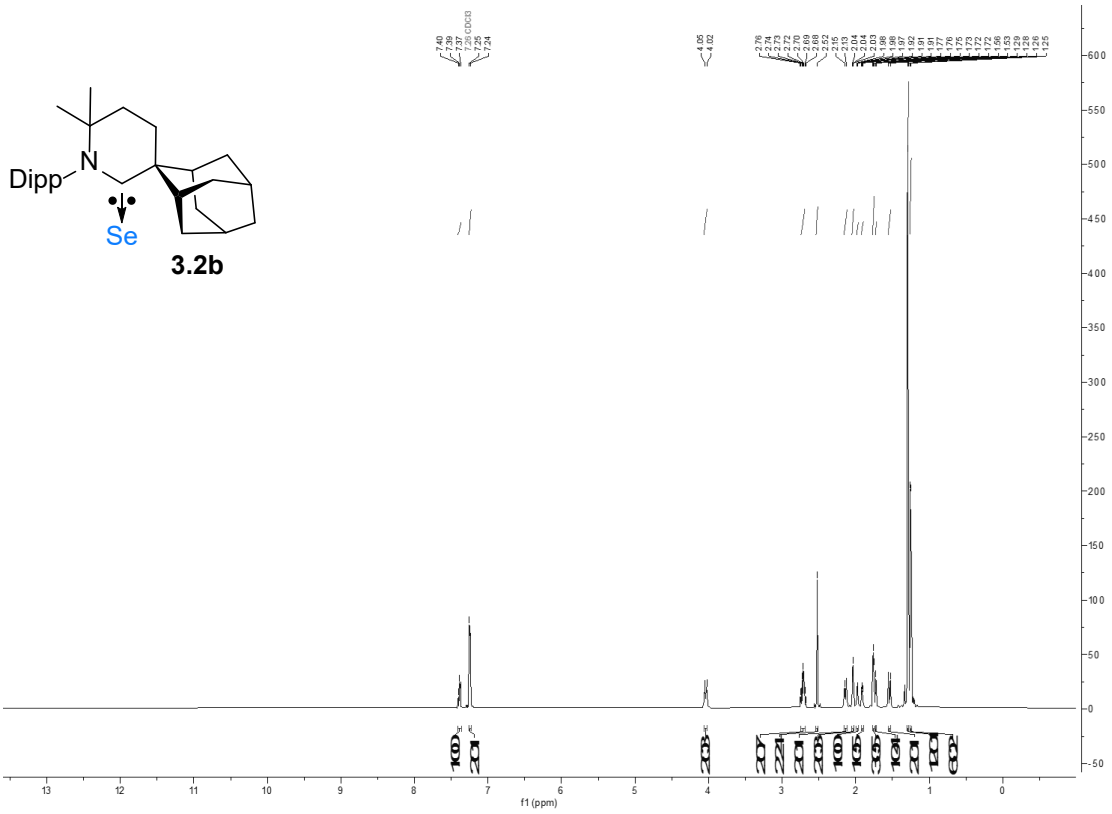
;

end Validation Reply Form

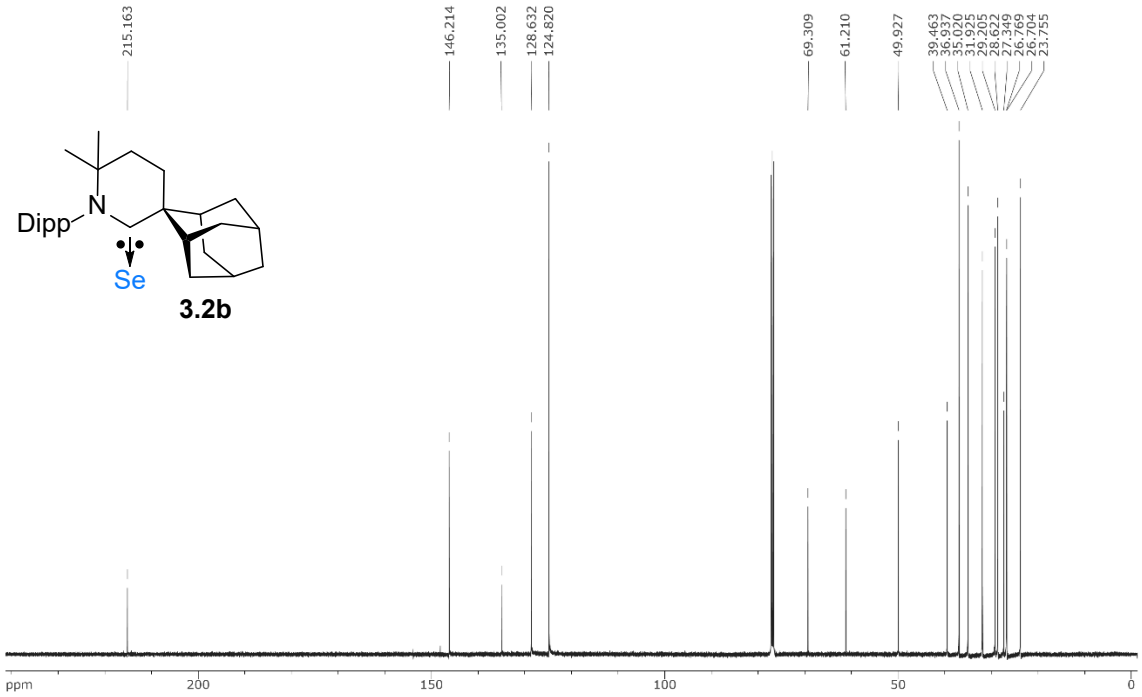
*Synthesis of **3.2b**:* Prepared following the standard procedure using ^{Ad}CAAC6.HBF$_4$ (48 mg, 1 eq) and Se (20 mg, 2 eq). Single crystals of **3.2b** were grown in at -20 °C in a concentrated

pentane solution overnight. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 3.66 (d, *J* = 13.3 Hz, 2H), 2.73 (sept, *J* = 6.6 Hz, 2H), 2.27 – 2.19 (br s, 4H), 2.16 (s, 4H), 2.04 – 1.38 (m, 14H), 1.30 (d, *J* = 6.6 Hz, 12H), 1.28 (s, 3H), 1.23 – 1.09 (m, 4H), 0.82 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 221.41 (CSe), 146.06 (C_{Ar}), 140.84 (C_{Ar}), 127.82 (C_{Ar}), 124.73 (C_{Ar}), 64.70 (C_q), 53.40 (C_q), 40.05, 36.16, 34.54, 33.86, 32.99, 32.10, 29.56, 28.00, 27.53, 27.43, 26.85, 24.02. **^{77}Se NMR** (57 MHz, $CDCl_3$) δ 863.29.

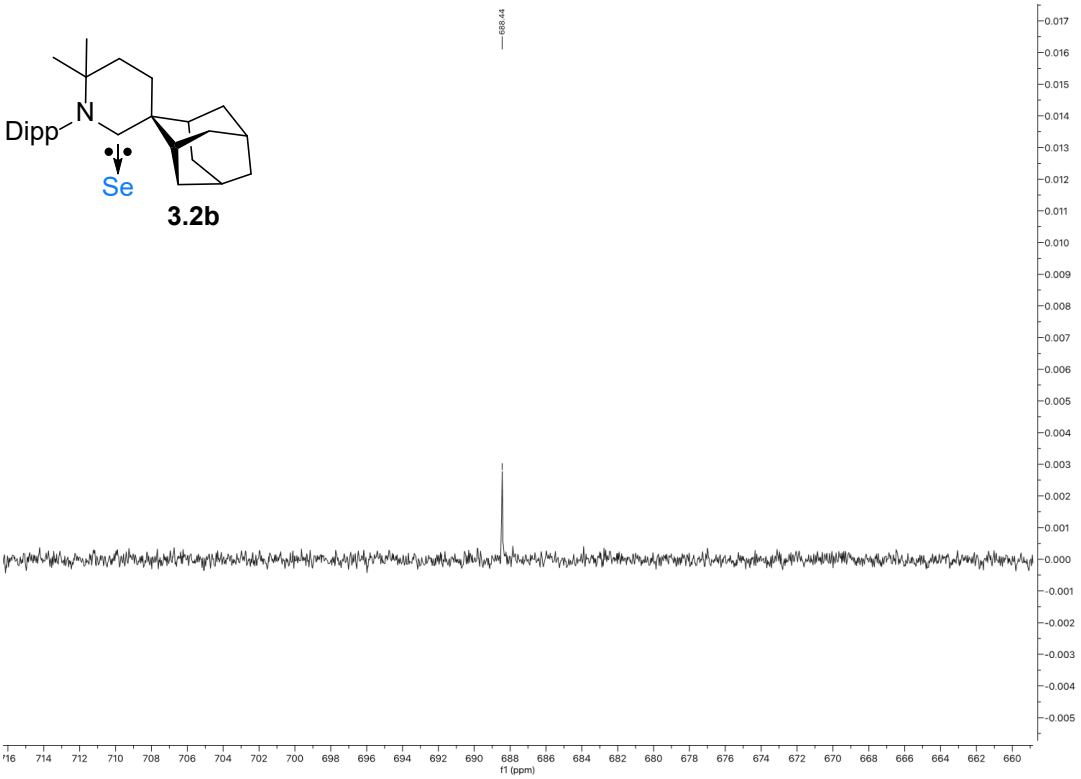
^{1}H NMR for 3.2b ($CDCl_3$)



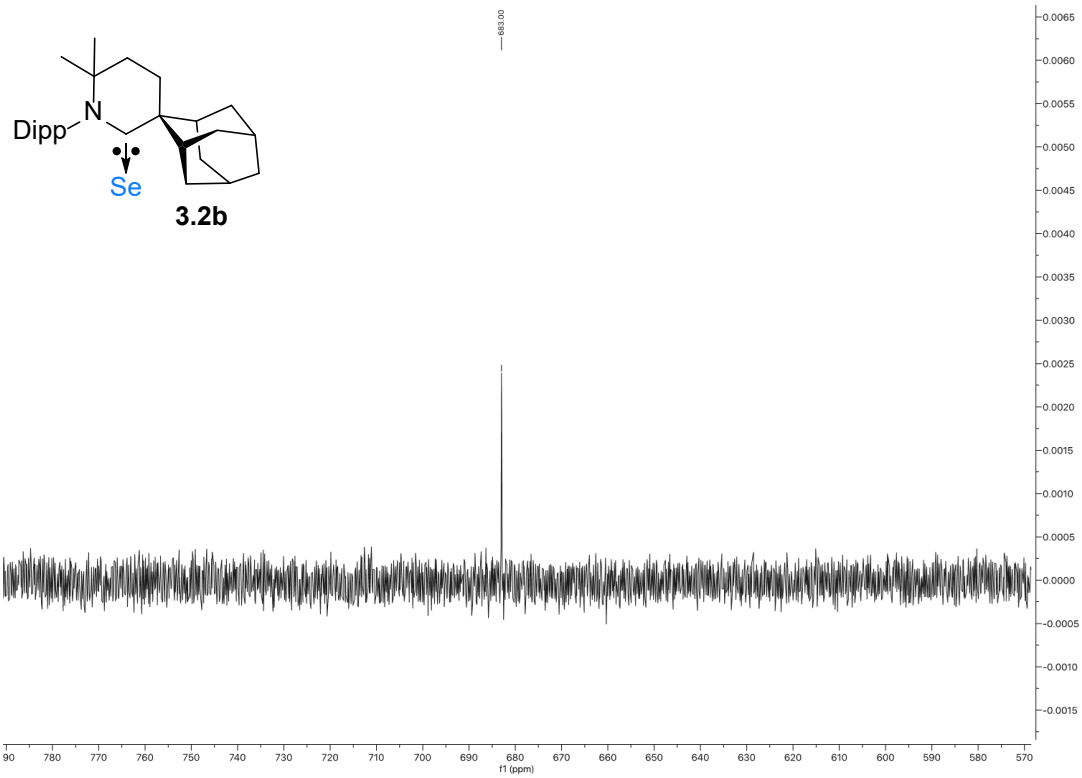
^{13}C{^{1}H} NMR for 3.2b ($CDCl_3$)



Se{^{1}H} NMR for 3.2b (acetone-d_6)

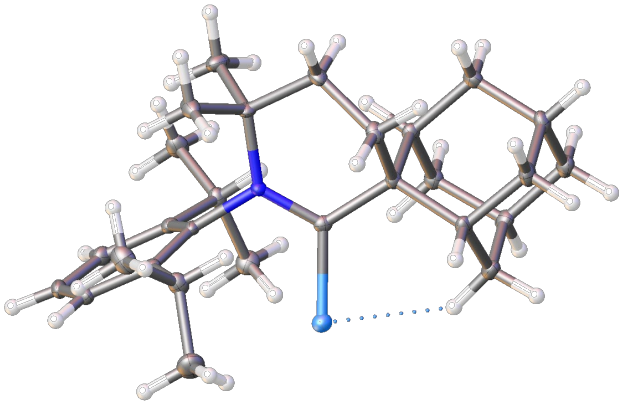


Se{^{1}H} NMR for 3.2b ($CDCl_3$)



3.2b

Crystal data and structure refinement for 3.2b CCDC# 2020770



Ellipsoid shown at 50% probability

Empirical formula	$C_{28}H_{41}NSe$
Formula weight	470.58
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.4245(2)

b/Å	15.9264(4)
c/Å	13.2465(4)
α/°	90
β/°	99.4230(10)
γ/°	90
Volume/Å^3	2377.69(10)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	1.594
F(000)	1000.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.032 to 52.744
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -16 ≤ l ≤ 11
Reflections collected	14170
Independent reflections	4858 [R_{int} = 0.0241, R_{sigma} = 0.0251]
Data/restraints/parameters	4858/0/277
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0922
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0941
Largest diff. peak/hole / e Å^{-3}	0.97/-0.42

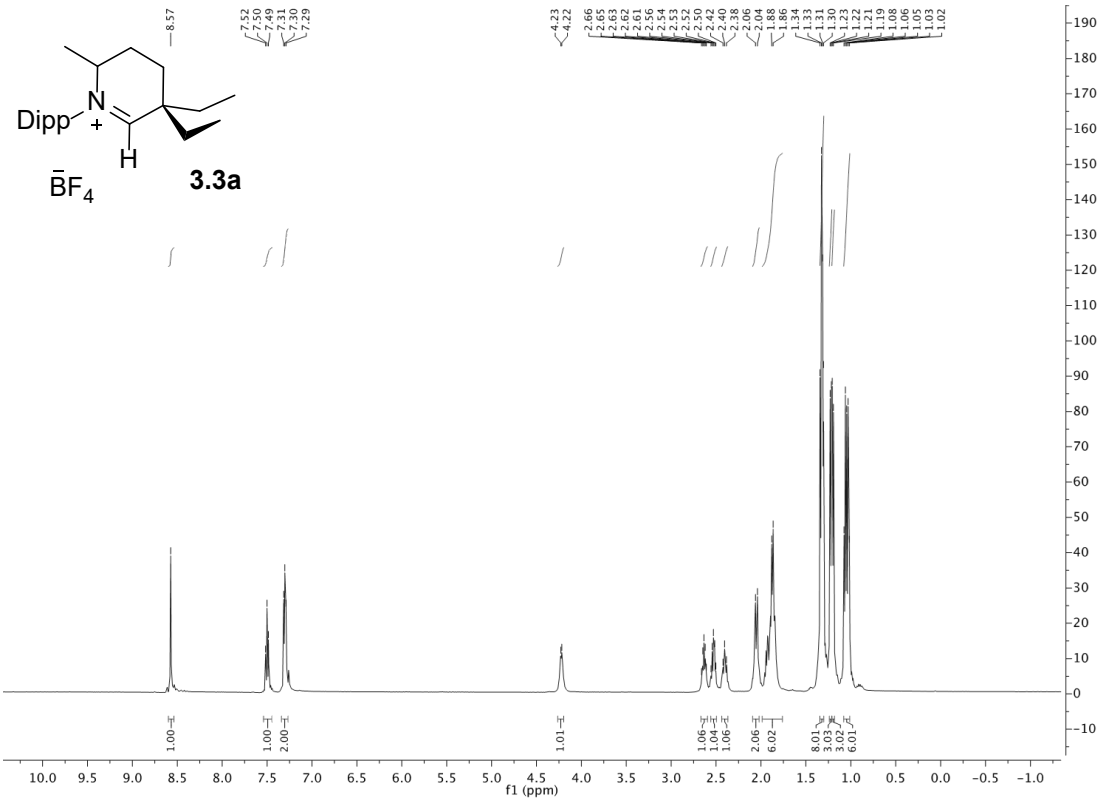
II.3. Preparation of compound 3.3a-e, 3.4a and 3.5a-e

*Standard procedure for the preparation of 3.**3a-e**:* **3.3a-e** were prepared from a modified procedure.[61] In a Schlenk, the corresponding imine (1 eq) was dissolved in THF (60 mL) and cooled to -78 °C. Freshly prepared LDA in THF (1.1 eq) was then slowly added to the imine generating a slightly yellow coloured solution. The solution was stirred while gradually warmed to room temperature over 2h. The solution was then cooled back to -78 °C and 1,3-dibromobutane

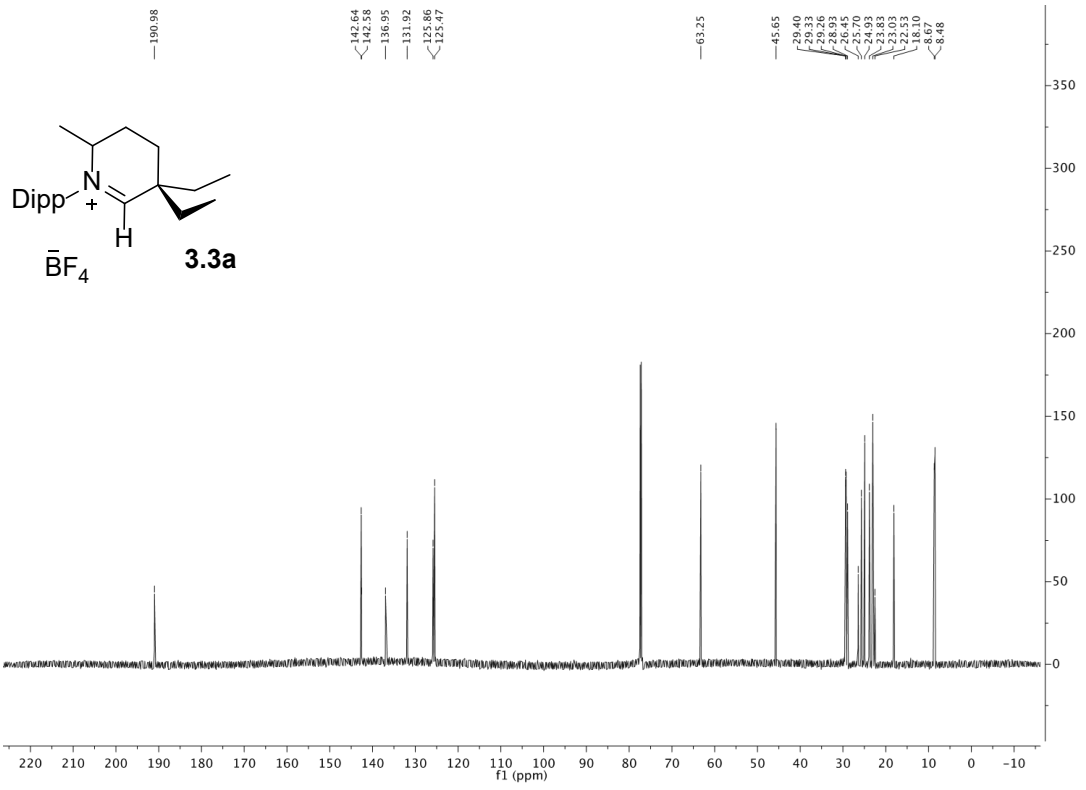
(1.05 eq) was added in one portion. The solution was stirred and warmed to room temperature over 12h. THF was removed *in vacuo* and the resulting slurry was dissolved in Et_2O, washed with H_2O (3 x 100 mL), dried over $MgSO_4$ and filtered. The Et_2O was removed *in vacuo* and the resulting oily solid was dissolved in dry CH_3CN (50 mL) and heated to 70 °C under an Argon atmosphere for 12h. The CH_3CN was removed *in vacuo* and the resulting oily solid was washed with additional Et_2O (2 x 200 mL) and pentane (2 x 200 mL) to enforce precipitation of the corresponding bromo-iminium salts. Subsequent anion exchange was achieved by treating a dichloromethane solution of the corresponding bromo-iminium salts with an aqueous solution of $NaBF_4$ (2 eq). Separation of the organic phase, drying over magnesium sulfate and evaporation of the solvent *in vacuo* afforded the corresponding bromo-iminiums salts as a white microcrystalline solid.

*Synthesis of **3.3a**:* Prepared following the standard procedure using imine (**R^1** = Dipp; **R^2** Et) (4.3 g, 1 eq), LDA (2.0 g, 1.1 eq), 1,3-dibromobutane (3.8 g, 1.05 eq), and $NaBF_4$ (2.8 g, 1.5 eq) gave **3.3a** as a white microcrystalline solid (4.8 g, 72% yield). **MP**: 227-229°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* = 7.6 Hz, 2H), 4.26 – 4.18 (m, 1H), 2.63 (sept, *J* = 7.0 Hz, 1H), 2.53 (sept, *J* = 7 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.10 – 2.00 (m, 2H), 1.97 – 1.80 (m, 6H), 1.35 – 1.28 (m, 8H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.08–1.02 (m, overlapping, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 191.0 (C*C*HN), 142.6 (C_{Ar}), 142.6 (C_{Ar}), 137.0 (C_{Ar}), 131.9 (C_{Ar}), 125.9 (C_{Ar}), 125.5 (C_{Ar}), 63.2 (N*C*HMe), 45.6 (C_q), 29.4, 29.3, 29.4, 28.9, 26.5, 25.7, 24.93, 23.8, 23.0, 18.1, 8.7, 8.5. **HRMS**: *m/z* calculated for $C_{22}H_{36}N$ $[M\text{-}BF_4^-]^+$ 314.2848, found 314.2843.

^{1}H NMR spectra of 3.3a ($CDCl_3$)

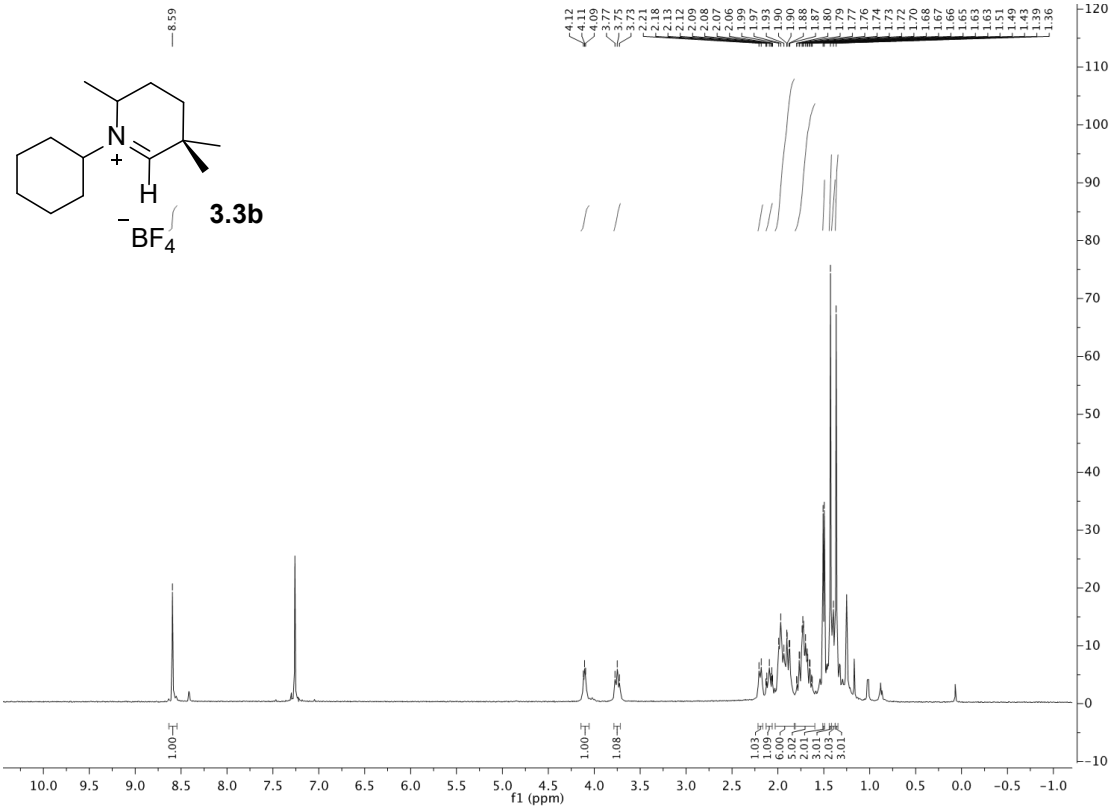


$^{13}C\{^1H\}$ NMR spectra of 3.3a ($CDCl_3$)

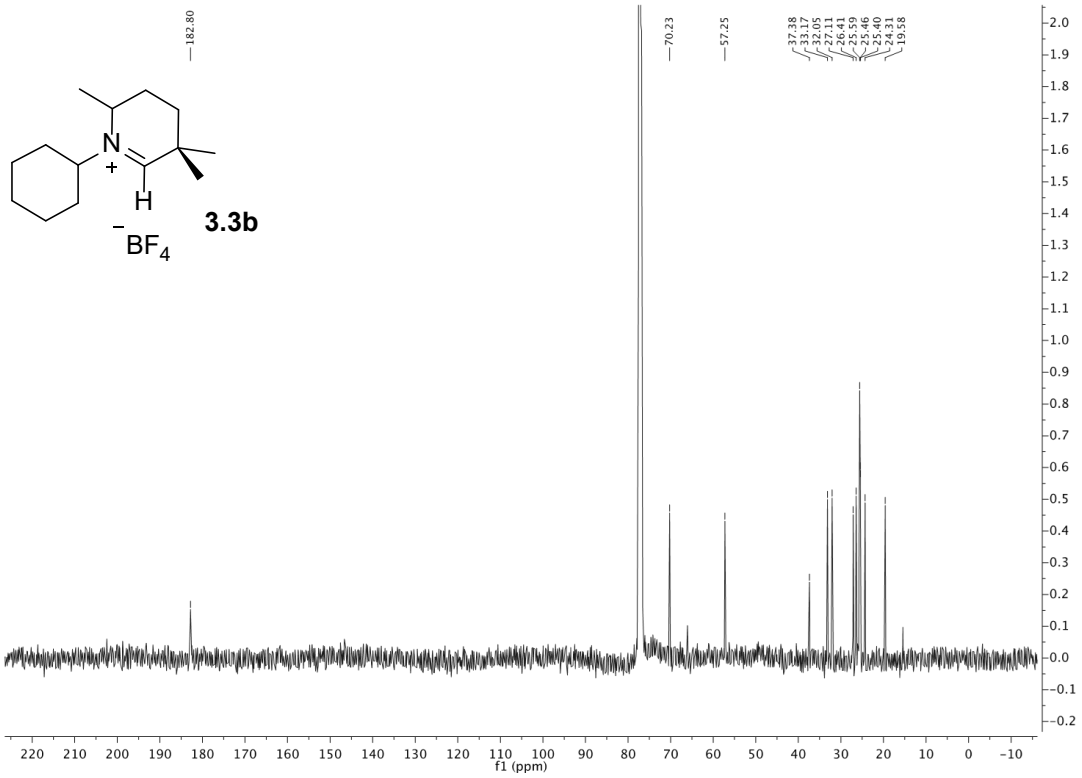


*Synthesis of **3.3b**:* Prepared following the standard procedure using imine (**R^1** = Cy; **R^2** Me) (11.7 g, 1 eq), LDA (8.6 g, 1.1 eq), 1,3-dibromobutane (16.4 g, 1.05 eq), and $NaBF_4$ (12.5 g, 1.5 eq) gave **3.3b** as a white microcrystalline solid (8.7 g, 55% yield). **MP**: 245-248ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 4.14 – 4.06 (m, 1H), 3.80 – 3.70 (m, 1H), 2.21-218 (m, broad, 1H), 2.13-2.06 (m, 1H), 1.99-1.87 (m, 6H), 1.80-1.63(m, 5H), 1.50 (d, *J* = 7.0 Hz, 2H), 1.43 (s, 3H), 1.42 – 1.38 (m, 2H), 1.36 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 182.8 (C*C*HN), 70.2 (N*C*Cy), 57.25 (N*C*HCH3), 37.4 (Cq), 33.2, 32.0, 27.1, 26.41, 25.6, 25.5, 25.4, 24.3, 19.6. **HRMS:** *m/z* calculated for $C_{14}H_{26}N$ $[M\text{-}BF_4^-]^+$ 208.2065, found 208.2060.

^{1}H NMR spectra of 3.3b ($CDCl_3$)

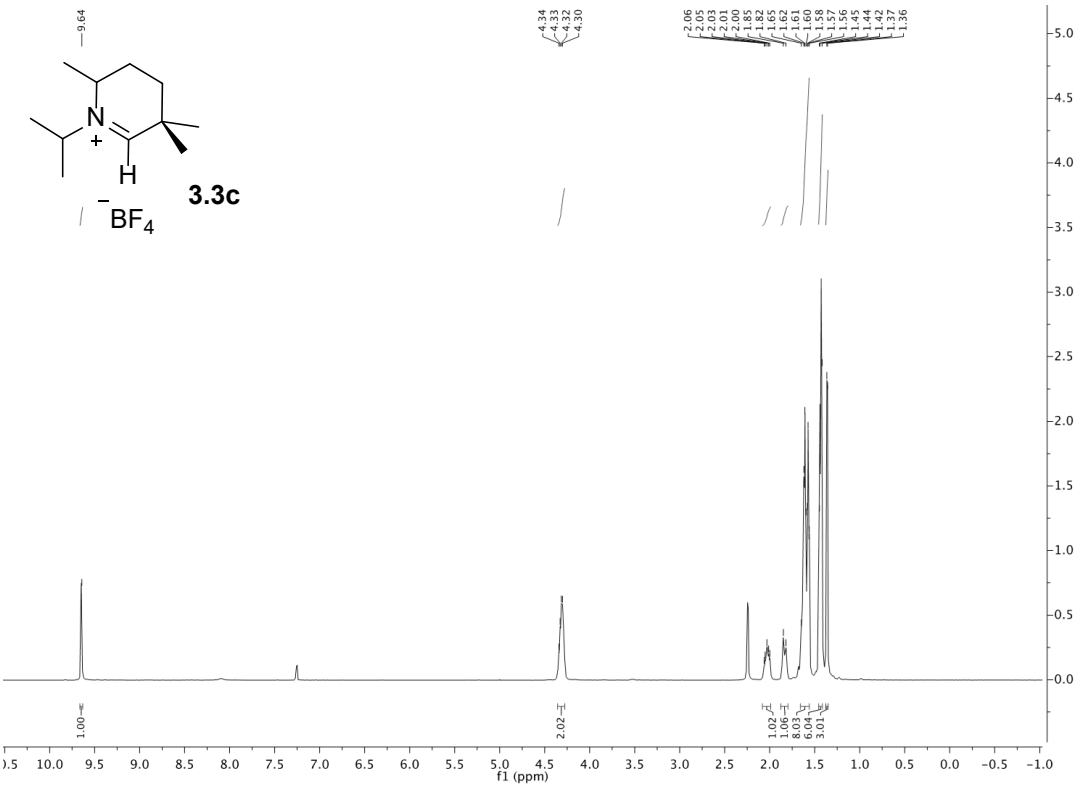


^{13}C{^{1}H} NMR spectra of 3.3b ($CDCl_3$)

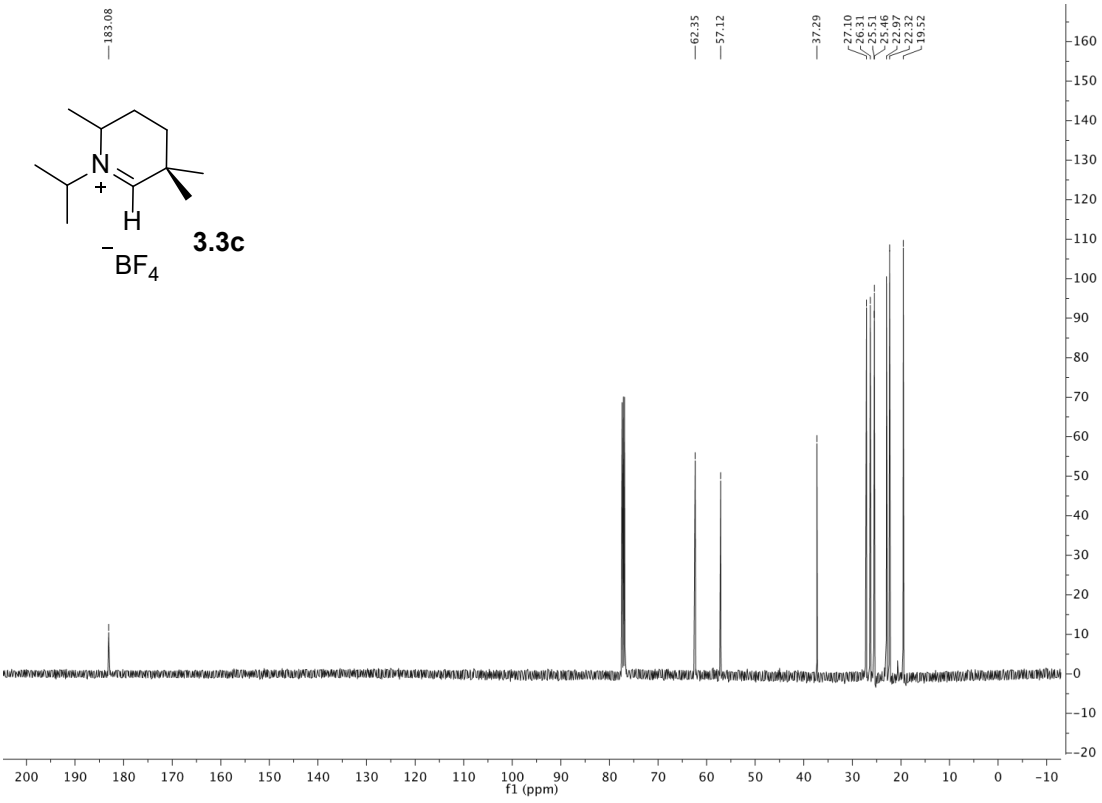


*Synthesis of **3.3c**:* Prepared following the standard procedure using imine (**R**[1] = iPr; **R**[2] Me) (8.1 g, 1 eq), LDA (1.1 eq), 1,3-dibromobutane (16.2 g, 1.05 eq), and NaBF4 (1.5 eq) gave **3.3c** as a white microcrystalline solid (2.60 g, 15% yield). **MP**: 211-213ºC; **^{1}H NMR** (300 MHz, CDCl3) δ 9.56 (s, 1H), 4.26 – 4.16 (m, 2H), 2.08 – 1.98 (m, 1H), 1.85 – 1.82 (m, 1H), 1.66 – 1.56 (m, 8H), 1.46 – 1.40 (m, 6H), 1.36 (d, *J* = 3.8 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CDCl3) δ 183.1 (C*C*HN), 62.4 (N*C*i-Pr), 57.1 (N*C*HCH3), 37.3 (Cq), 27.1, 26.3, 25.5, 25.5, 22.9, 22.3, 19.5. **HRMS:** *m/z* calculated for C11H22N $[M\text{-}BF_4^-]^+$ 168.1747, found 168.1748.

^{1}H NMR for 3.3c ($CDCl_3$)

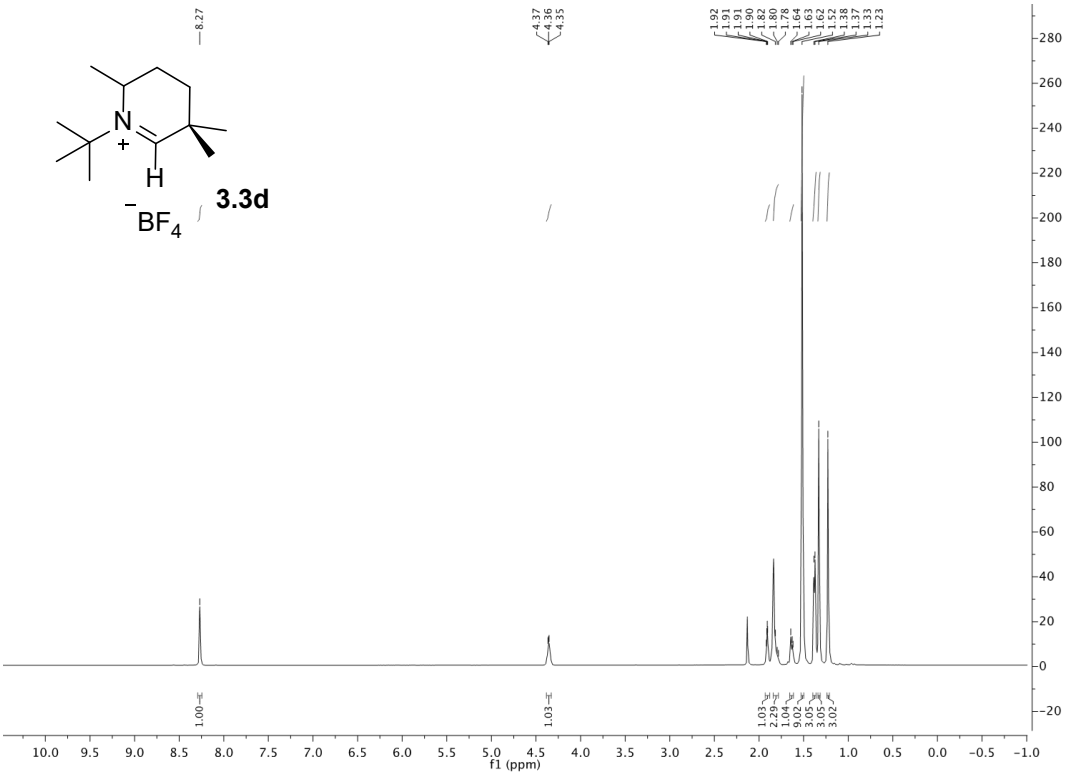


$^{13}C\{^{1}H\}$ NMR for 3.3c ($CDCl_3$)

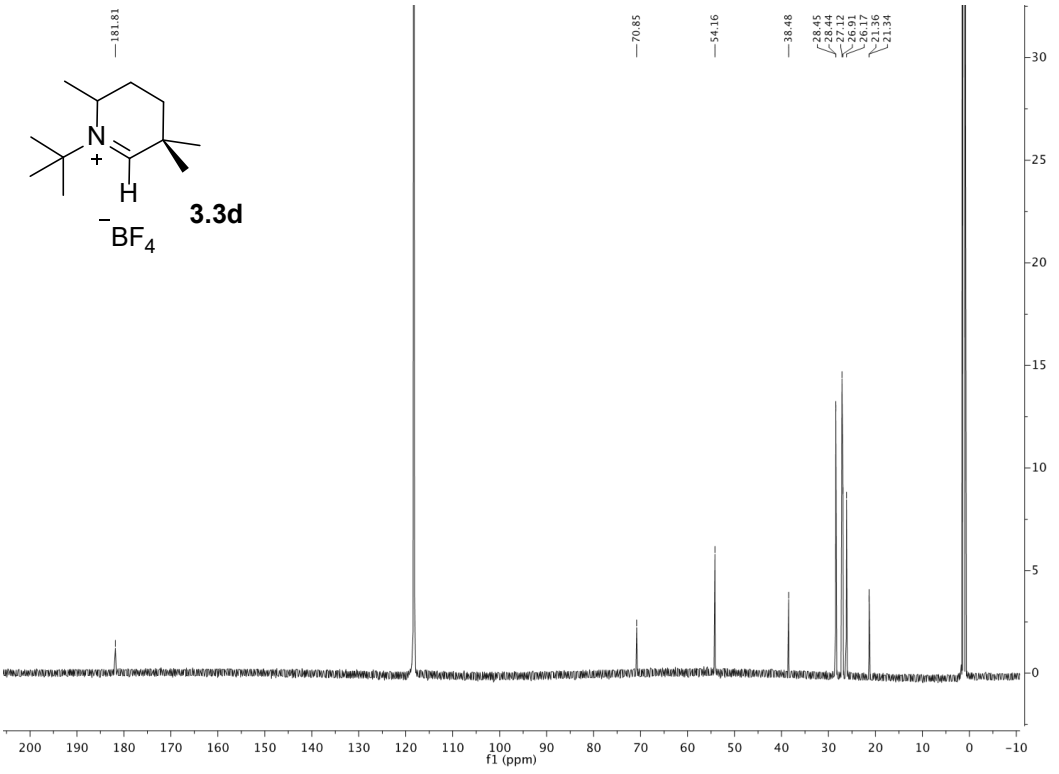


*Synthesis of **3.3d**:* Prepared following the standard procedure using imine (**R^1** = tBu; **R^2** Me) (13.6 g, 1 eq), LDA (12.0 g, 1.1 eq), 1,3-dibromobutane (23.0 g, 1.05 eq), and $NaBF_4$ (17.5 g, 1.5 eq) gave **3.3d** as a white microcrystalline solid (10.6 g, 43% yield). **MP**: 243-245°C; **^{1}H NMR** (500 MHz, CD_3CN) δ 8.27 (s, 1H), 4.37-4.35 (m, 1H), 1.92-1.90 (m, 1H), 1.82-1.78 (m, 2H, overlapping with solvent signal), 1.64-1.62 (m, 1H), 1.52 (s, 9H), 1.38 (d, *J* = 6.7 Hz, 3H), 1.33 (s, 3H), 1.23 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN) δ 181.8 (C*C*HN), 70.8 (N*C*-*t*-Bu), 54.2 (N*C*HCH$_3$), 38.5 (Cq), 28.5, 28.4, 27.1, 26.9, 26.2, 21.4, 21.3. **HRMS:** *m/z* calculated for $C_{12}H_{24}N^+$ $[M\text{-}BF_4^-]^+$ 182.1904, found 182.1900.

^{1}H NMR for 3.3d (CD_3CN)

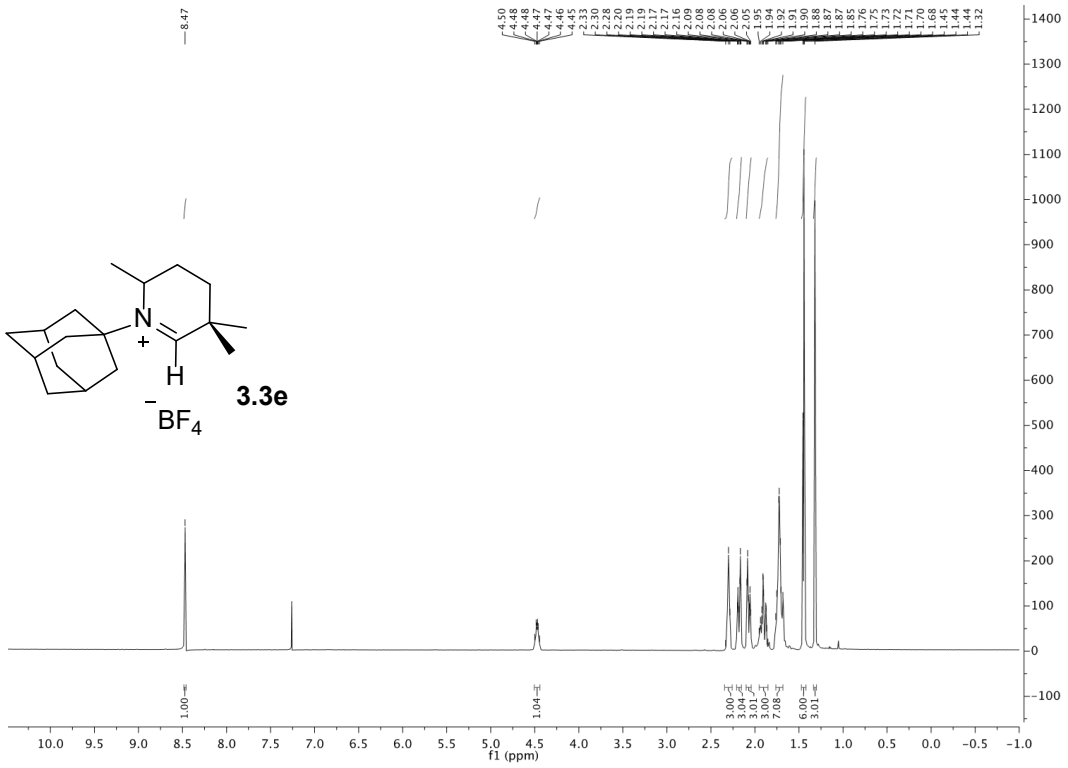


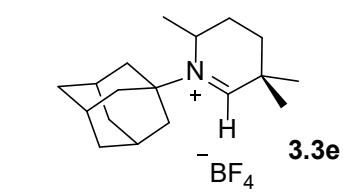
^{13}C{^{1}H} NMR for 3.3d (CD_3CN)



*Synthesis of **3.3e**:* Following the standard procedure using imine (**R**[1] = Ad; **R**[2] Me) (6.5 g, 1 eq), LDA (3.6 g, 1.1 eq), 1,3-dibromobutane (6.8 g, 1.05 eq), and NaBF4 (5.2 g, 1.5 eq) gave **3.3e** as a white microcrystalline solid (4.2 g, 38% yield). **MP**: 280-282 oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 4.51 – 4.44 (m, 1H), 2.33 – 2.28 (m, 3H), 2.20 – 2.16 (m, 3H), 2.09 – 2.05 (m, 3H), 1.95 – 1.85 (m, 3H), 1.76 – 1.68 (m, 7H), 1.45 (d, *J* = 8.0 Hz), 1.44 (s, 3H), 1.32 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.3 (C*C*HN), 71.0 (N*C*Ad), 52.0 (N*C*HCH3), 40.5, 37.9 (C_q), 35.0, 29.9, 27.2, 26.8, 26.5, 26.4, 21.9. **HRMS**: *m/z* calculated for $[C_{13}H_{30}N]^+$ $[M]^+$ 260.2373, found 260.2374.

^{1}H NMR for 3.3e ($CDCl_3$)



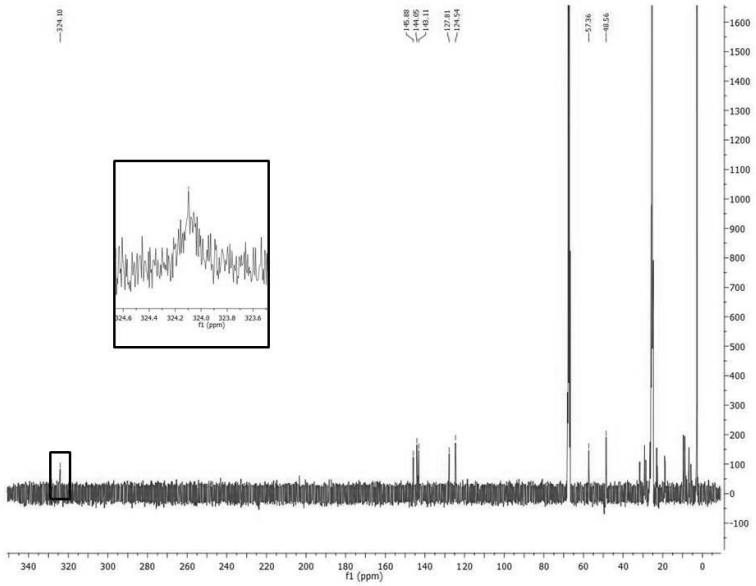


3.3e

$^{13}C\{^{1}H\}$ NMR for 3.3e ($CDCl_3$)

3.3e

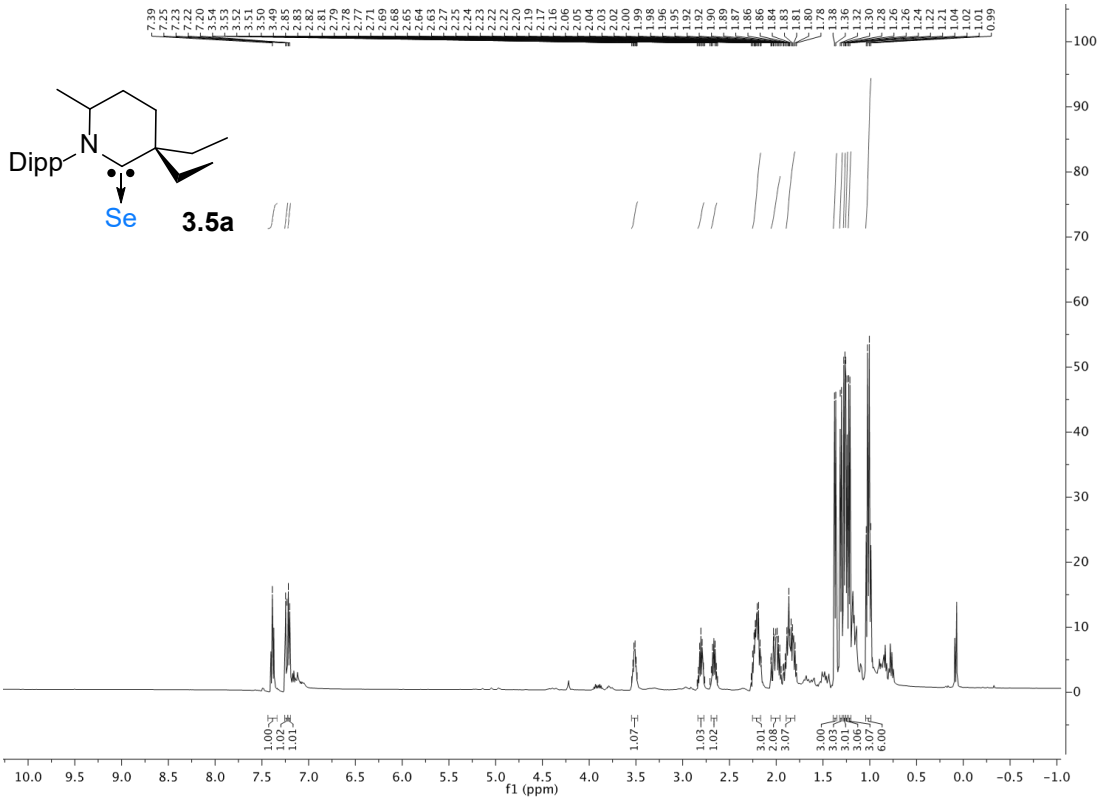
*Deprotonation of **3.3a** to generate **3.4a** at low temperature*: THF (1 mL) was added to an NMR tube containing a solid mixture of iminium **3.3a** (40 mg, 1 eq) and KHMDS (21 mg, 1.05 eq) slowly at -78 °C. The NMR tube was carefully shaken to retain cold temperature, and transferred quickly to an NMR machine precooled to -80 °C. **$^{13}C\{^{1}H\}$ VT-NMR** (75 MHz, THF, -80 °C) δ 324.10 (br s, C_{carb}), 145.88 (C_{Ar}), 145.05 (C_{Ar}), 143.11 (C_{Ar}), 127.81 (C_{Ar}), 124.54 (C_{Ar}), 57.36, 48.56, and other alkyl signals appearing around the THF solvent signal.



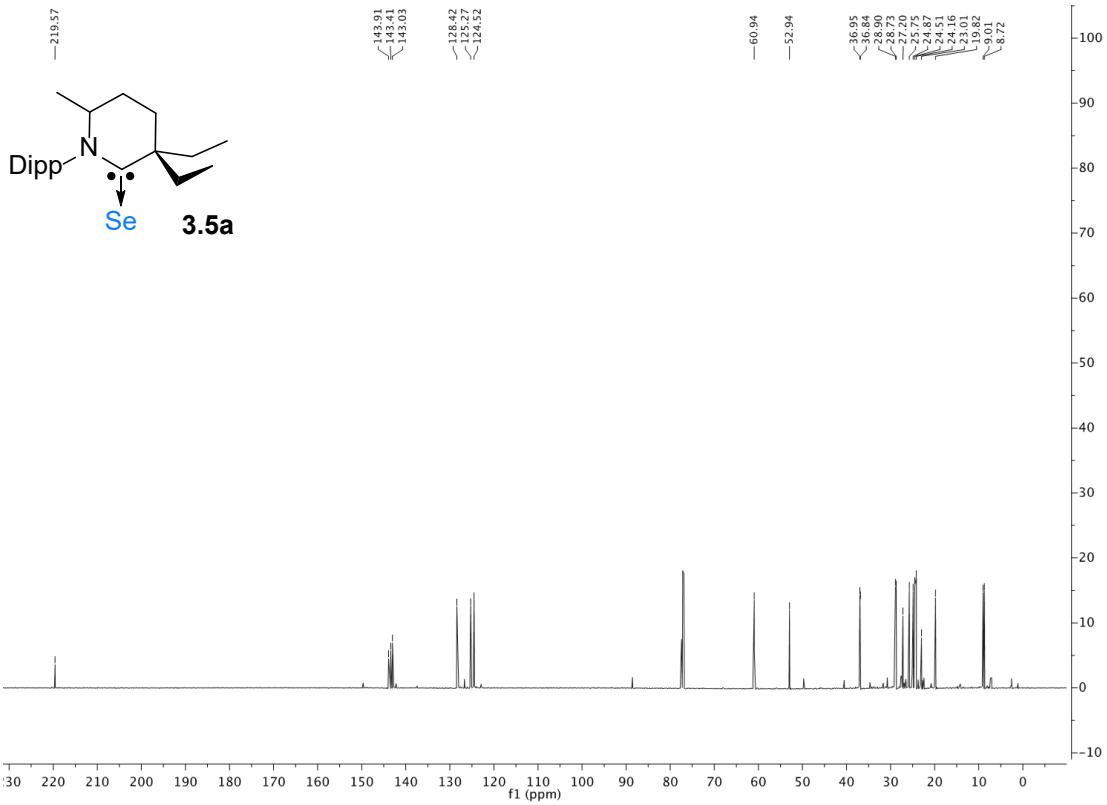
*Standard procedure for the one pot preparation of Se-adducts **3.5a-e***: Iminium salt **3.3** (1 eq), KHMDS (1.05 eq), and Se black (2 eq) were all combined in a Schlenk with a stir bar. The Schlenk was cooled to -78 °C and THF (20 mL) was slowly added over 5 minutes. The resulting slurry was slowly warmed to room temperature while stirring over 12h. THF was then removed *in vacuo* and the product was extracted with pentane. The solution was concentrated to ¼ volume and stored at -20 °C overnight giving yellow-orange crystals of compound **3.5**. **Note**: All compounds **3.5a-e** were found to be too sensitive to be purified by column chromatography and where characterized upon crystallization.

Synthesis of **3.5a**: Prepared following the standard procedure using iminium salt **3.3a** (240 mg, 1 eq), KHMDS (125 mg, 1.05 eq), and Se black (188 mg, 2 eq) gave **3.5a** as orange crystals (108 mg, 46% yield). **MP**: 184-186 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 3.56 – 3.48 (m, 1H), 2.81 (sept, *J* = 6.5, 1H), 2.67 (sept, *J* = 6.5 Hz, 1H), 2.27 – 2.14 (m, 3H), 2.06 – 1.95 (m, 2H), 1.92-1.78 (m, 3H), 1.37 (d, *J* = 6.5 Hz, 3H), 1.31 (d, *J* = 6.5 Hz, 3H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.25 (d, *J* = 6.5 Hz, 3H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.01 (q, *J* = 7.5 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 219.6 (C_{carb}), 143.9 (C_{Ar}), 143.4 (C_{Ar}), 143.0 (C_{Ar}), 128.4 (C_{Ar}), 125.3(C_{Ar}), 124.5 (C_{Ar}), 61.0 ($NCHCH_3$), 52.9 (C_q), 36.9, 36.8, 28.9, 28.7, 27.20, 25.7, 24.9, 24.5, 24.2, 23.01, 19.82, 9.01, 8.72. **^{77}Se{^{1}H} NMR** (95 MHz, $(CD_3)_2CO$) δ 672.9. **HRMS**: *m/z* calculated for $C_{22}H_{36}NSe$ $[M+H]^+$ 394.2013, found 394.2011.

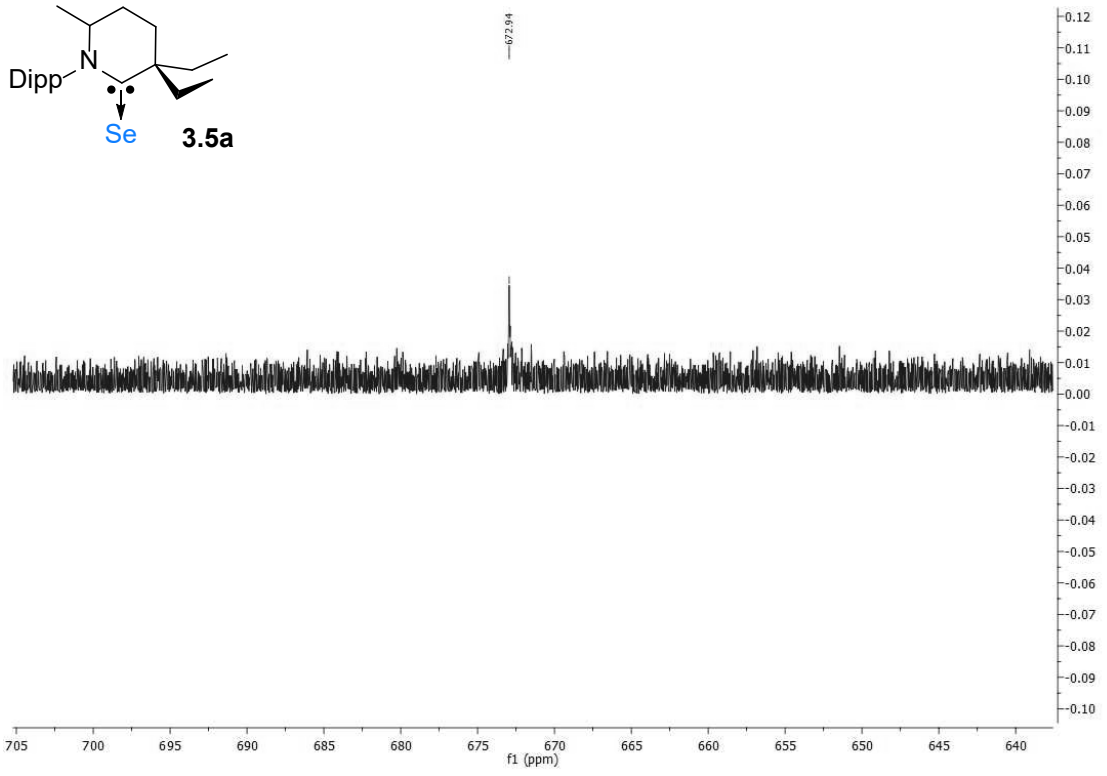
^{1}H NMR for 3.5a ($CDCl_3$)



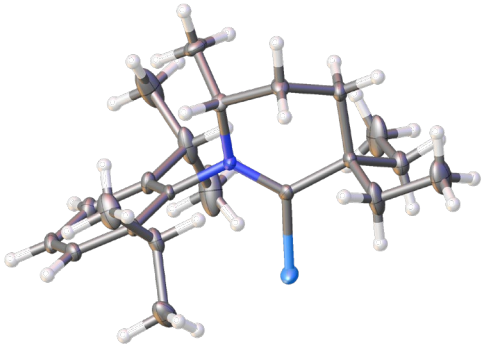
^{13}C{^{1}H} NMR for 3.5a ($CDCl_3$)



$^{77}Se\{^{1}H\}$ NMR for 3.5a (acetonde-d_6)



Crystal data and structure refinement for 3.5a CCDC# 2020772



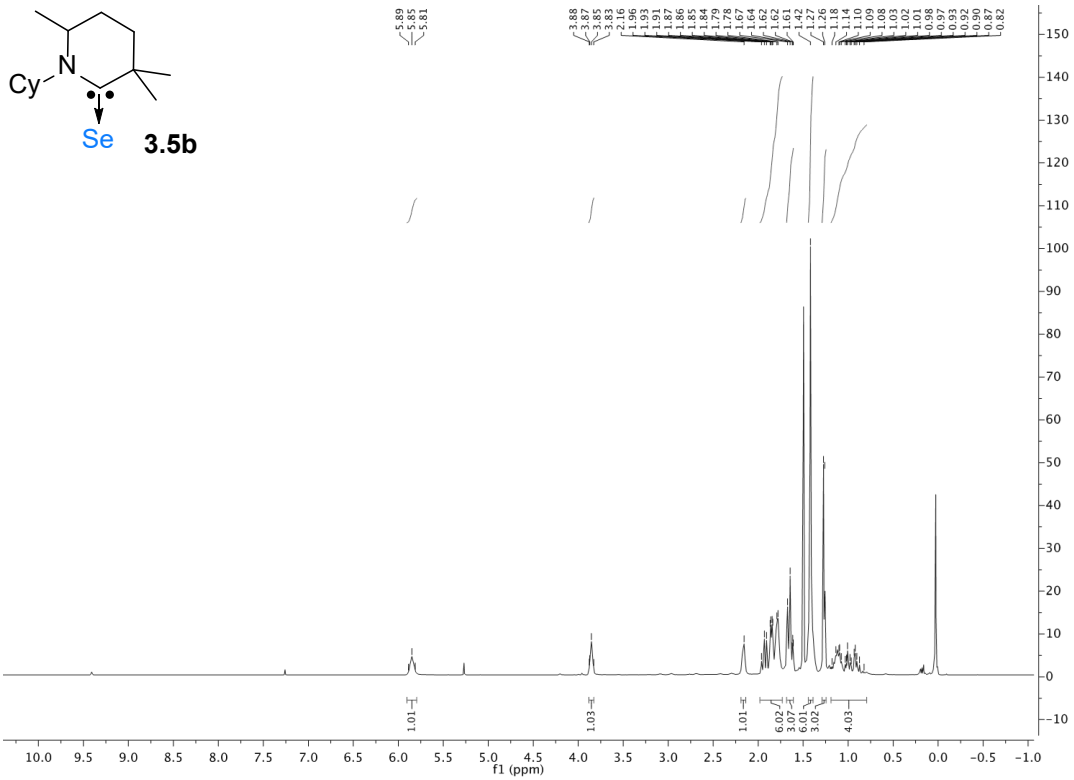
Ellipsoid shown at 30% probability

Empirical formula	$C_{22}H_{35}NSe$
Formula weight	392.47
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9113(16)
b/Å	14.1348(19)
c/Å	13.955(2)
α/°	90
β/°	99.086(5)
γ/°	90
Volume/Å^3	2125.3(5)
Z	4
ρ_{calc}g/cm^3	1.227
μ/mm^{-1}	1.770
F(000)	832.0
Crystal size/mm^3	0.34 × 0.21 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.754 to 48.232
Index ranges	-12 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 12

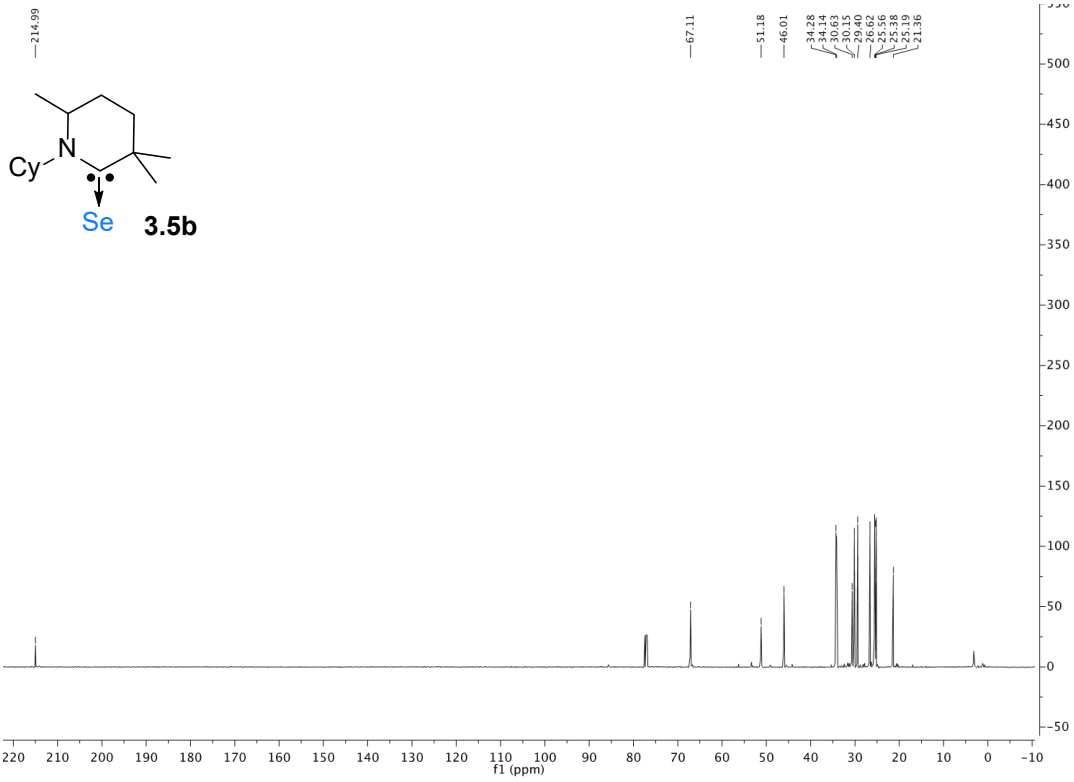
Reflections collected	10295
Independent reflections	3220 [R_{int} = 0.0446, R_{sigma} = 0.0606]
Data/restraints/parameters	3220/60/262
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.0999
Final R indexes [all data]	R_1 = 0.0896, wR_2 = 0.1108
Largest diff. peak/hole / e $Å^{-3}$	1.06/-1.08

Synthesis of **3.5b**: Prepared following the standard procedure using iminium salt **3.3b** (330 mg, 1 eq), KHMDS (245 mg, 1.05 eq), and Se black (176 mg, 2 eq) gave **3.5b** as orange crystals (78 mg, 47% yield). **MP**: 155-157^{O}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.90 – 5.80 (m, 1H), 3.90 – 3.80 (m, 1H), 2.20 – 2.13 (m, 1H), 1.97 – 1.75 (m, 6H), 1.67 – 1.61 (m, 3H), 1.42 (s, 6H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.18 – 0.82 (m, 4H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 215.0 (C_{Carb}), 67.1, 51.2, 46.0, 34.3, 34.1, 30.6, 30.1, 29.4, 26.6, 25.6, 25.4, 25.2, 21.4. **^{77}Se{^{1}H} NMR** (95 MHz, $(CD_3)_2CO$) δ 522.7. **HRMS**: *m/z* calculated for $C_{14}H_{26}NSe$ $[M+H]^+$ 288.1230, found 288.1223.

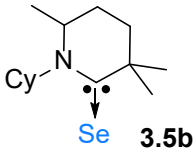
^{1}H NMR for 3.5b ($CDCl_3$)



$^{13}C\{^{1}H\}$ NMR for 3.5b ($CDCl_3$)

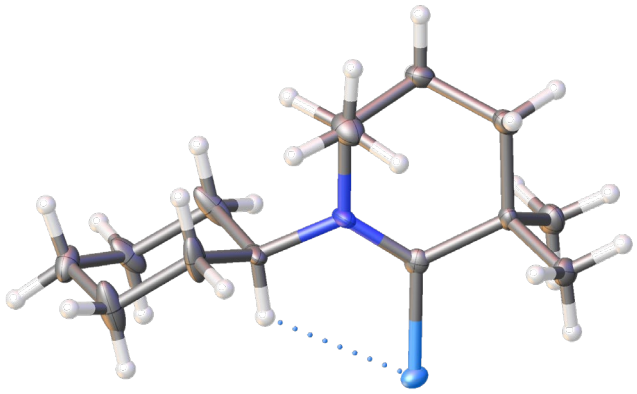


$^{77}Se\{^{1}H\}$ NMR for 3.5b (acetone-d_6)



3.5b

Crystal data and structure refinement for 3.5b CCDC# 2020774



Ellipsoid shown at 30% probability

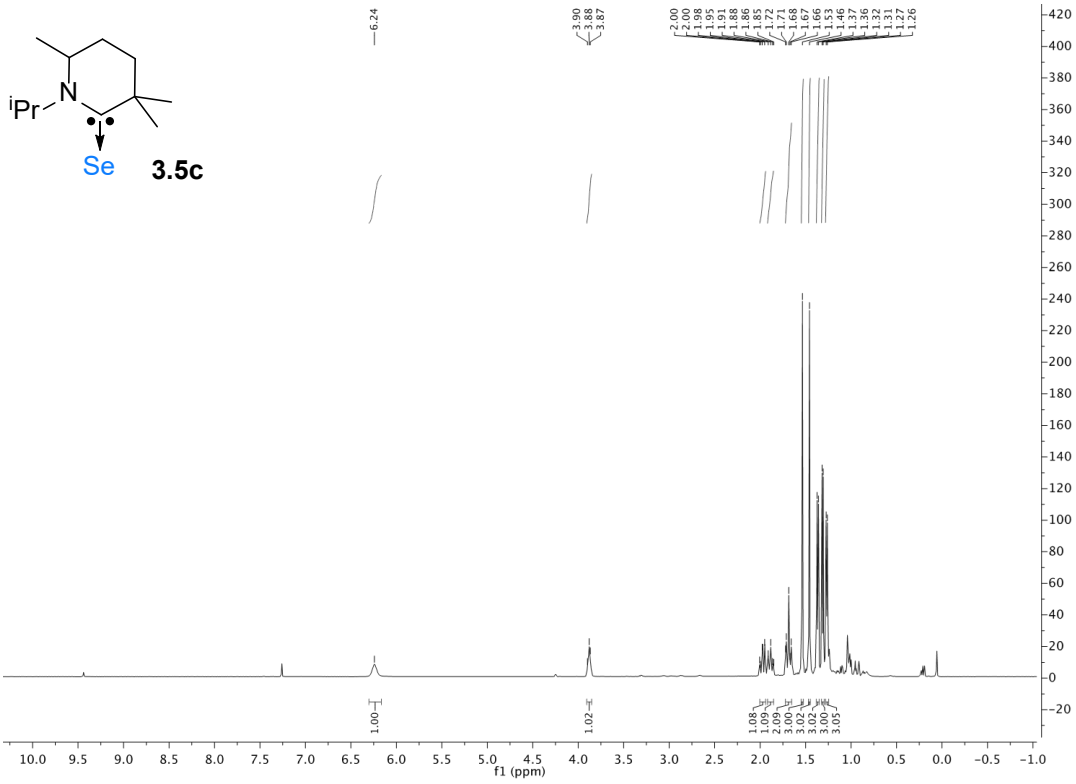
Empirical formula	$C_{14}H_{25}NSe$
Formula weight	286.31
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.8542(6)

b/Å	12.9039(14)
c/Å	18.9035(18)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1428.0(3)
Z	4
$\rho_{calc}g/cm^3$	1.332
μ/mm^{-1}	2.607
F(000)	600.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.822 to 50.838
Index ranges	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -22 ≤ l ≤ 16
Reflections collected	8453
Independent reflections	2613 [R_{int} = 0.0556, R_{sigma} = 0.0685]
Data/restraints/parameters	2613/0/149
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0718
Final R indexes [all data]	R_1 = 0.0567, wR_2 = 0.0764
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.42
Flack parameter	0.40(2)

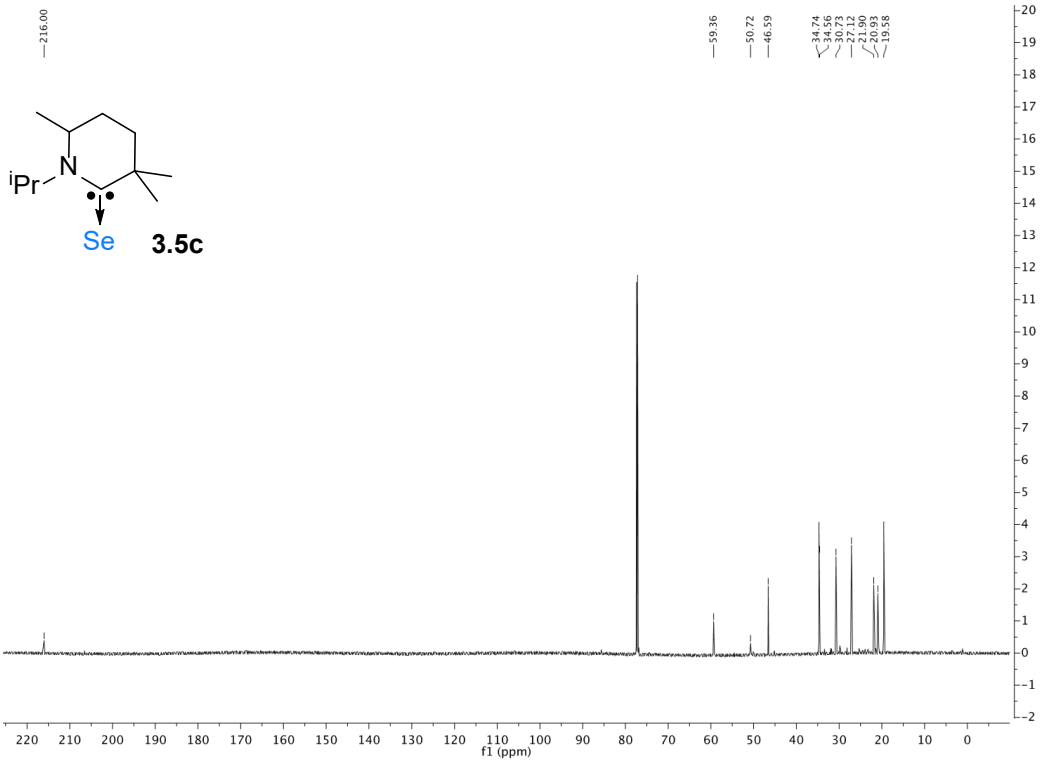
Synthesis of **3.5c**: Prepared following the standard procedure using iminium salt **3.3c** (222mg, 1 eq), KHMDS (196 mg, 1.05 eq), and Se black (141 mg, 2 eq) giving **3.5a** as yellow-orange crystals (60 mg, 28% yield). **MP**: 152-155^{O}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.24 (br s, 1H), 3.88 (m, 1H), 2.00 – 1.98 (m, 1H), 1.91 – 1.85 (m, 1H), 1.72 – 1.66 (m, 2H), 1.53 (s, 3H),

1.46 (s, 3H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.31 (d, *J* = 6.5 Hz, 3H), 1.27 (d, *J* = 6.5 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 216.00 (CCarb), 59.4 (N*C*HCH3), 50.7 (N*Ci*-Pr) , 46.6 (Cq), 34.7, 34.6, 30.7, 27.1, 21.9, 20.9, 19.6; **$^{77}Se\{^{1}H\}$ NMR** (95 MHz, $(CD_3)_2CO$) δ 526.5 **HRMS**: *m/z* calculated for $C_{11}H_{22}NSe$ $[M+H]^+$ 248.0917, found 248.0911.

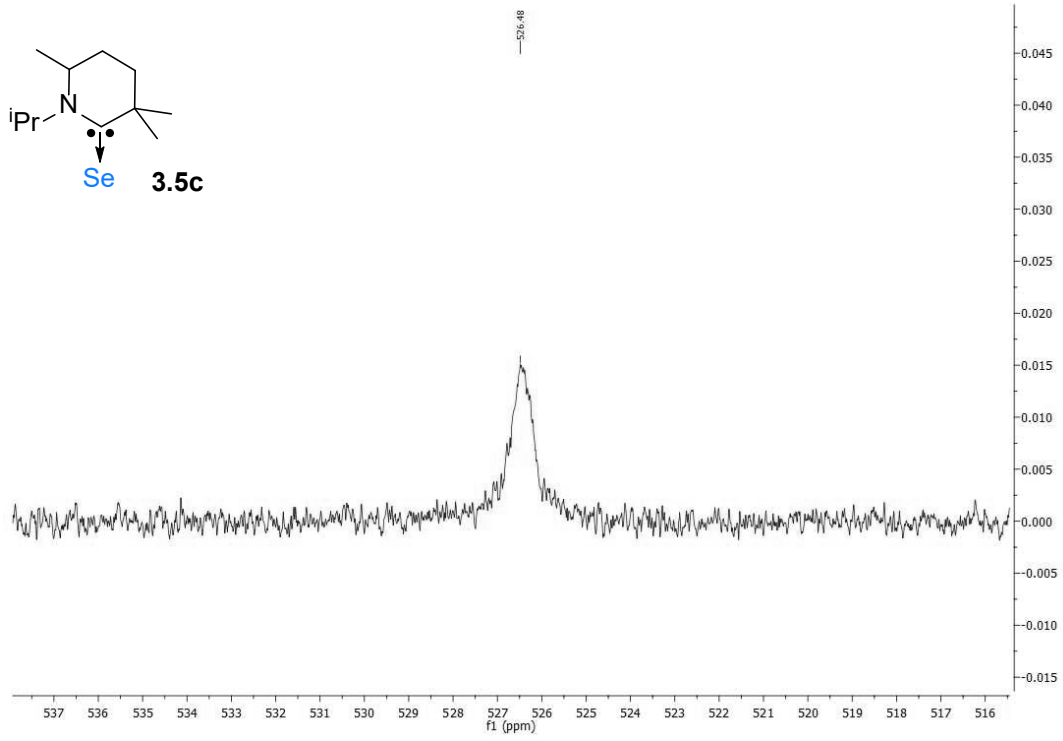
^{1}H NMR for 3.5c ($CDCl_3$)



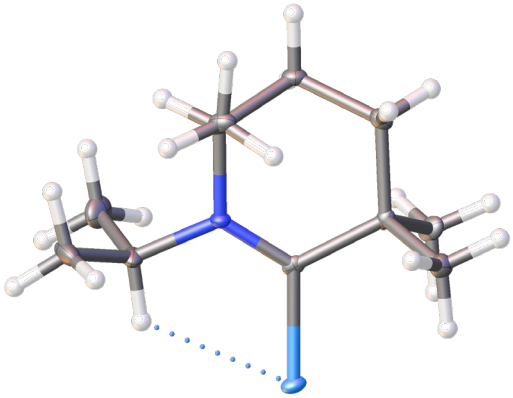
$^{13}C\{^{1}H\}$ NMR for 3.5c ($CDCl_3$)



^{77}Se{^{1}H} NMR for 3.5c (acetone-d_6)



Crystal data and structure refinement for 3.5c CCDC# 2020769



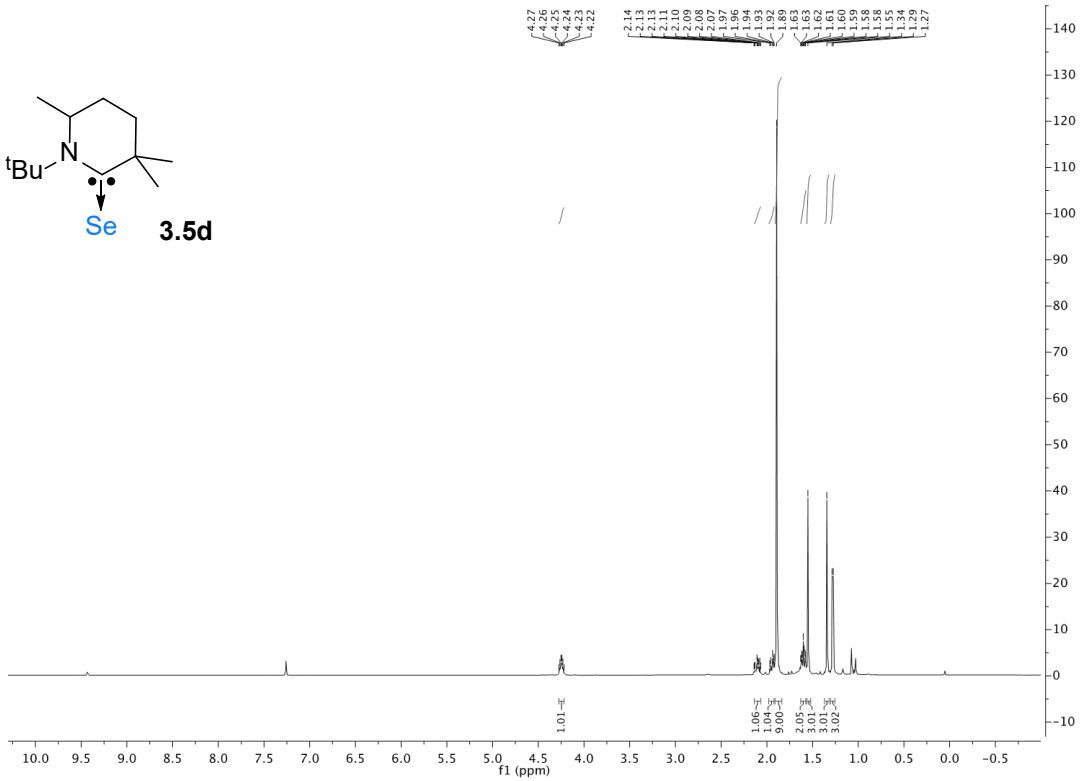
Ellipsoid shown at 30% probability

Empirical formula	$C_{11}H_{21}NSe$
Formula weight	246.05
Temperature/K	100.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.9043(7)
b/Å	13.8065(15)
c/Å	14.6027(17)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1190.4(2)
Z	4
ρ_{calc}g/cm^3	1.373
μ/mm^{-1}	3.107
F(000)	512.0
Crystal size/mm^3	0.95 × 0.13 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.58 to 51.396
Index ranges	-7 ≤ h ≤ 7, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17

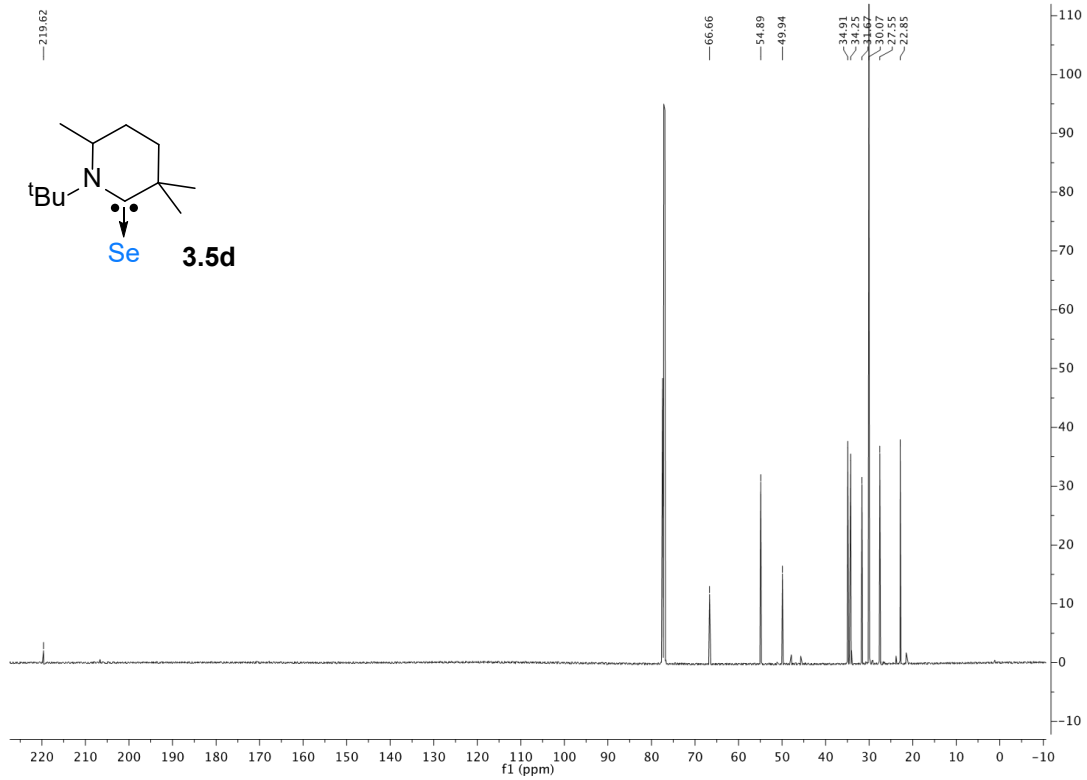
Reflections collected	8131
Independent reflections	2262 [R_{int} = 0.0508, R_{sigma} = 0.0576]
Data/restraints/parameters	2262/0/125
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0320, wR_2 = 0.0567
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0596
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.28
Flack parameter	0.19(2)

Synthesis of **3.5d**: Prepared following the standard procedure using iminium salt **3.3d** (170 mg, 1 eq), KHMDS (139 mg, 1.05 eq), and Se black (100 mg, 2 eq) gave **3.5d** as orange crystals. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.27 – 4.22 (m, 1H), 2.14 – 2.07 (m, 1H), 1.97 – 1.92 (m, 1H), 1.89 (s, 9H), 1.63 – 1.58 (m, 2H), 1.55 (s, 3H), 1.34 (s, 3H), 1.28 (d, *J* = 6.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 219.6 (C_{Carb}), 66.6 (N*C*(*t*-Bu)), 54.9 (N*C*HCH$_3$), 49.9 (C_q), 34.9, 34.2, 31.7, 30.1, 27.5, 22.9; **^{77}Se{^{1}H} NMR** (95 MHz, $(CD_3)_2CO$) δ 779.6. **HRMS**: *m/z* calculated for $C_{12}H_{24}NSe$ $[M+H]^+$ 262.1069, found 262.1063.

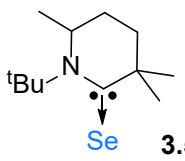
^{1}H NMR for 3.5d ($CDCl_3$)



$^{13}C\{^{1}H\}$ NMR for 3.5d ($CDCl_3$)

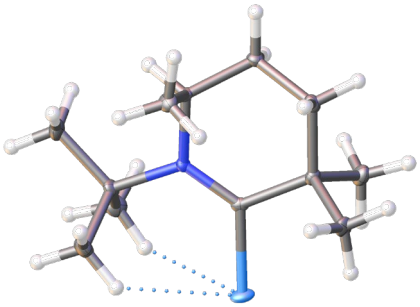


$^{77}Se\{^{1}H\}$ NMR for 3.5d (acetone-d_6)



3.5d

Crystal data and structure refinement for 3.5d CCDC# 2020771



Ellipsoid shown at 30% probability

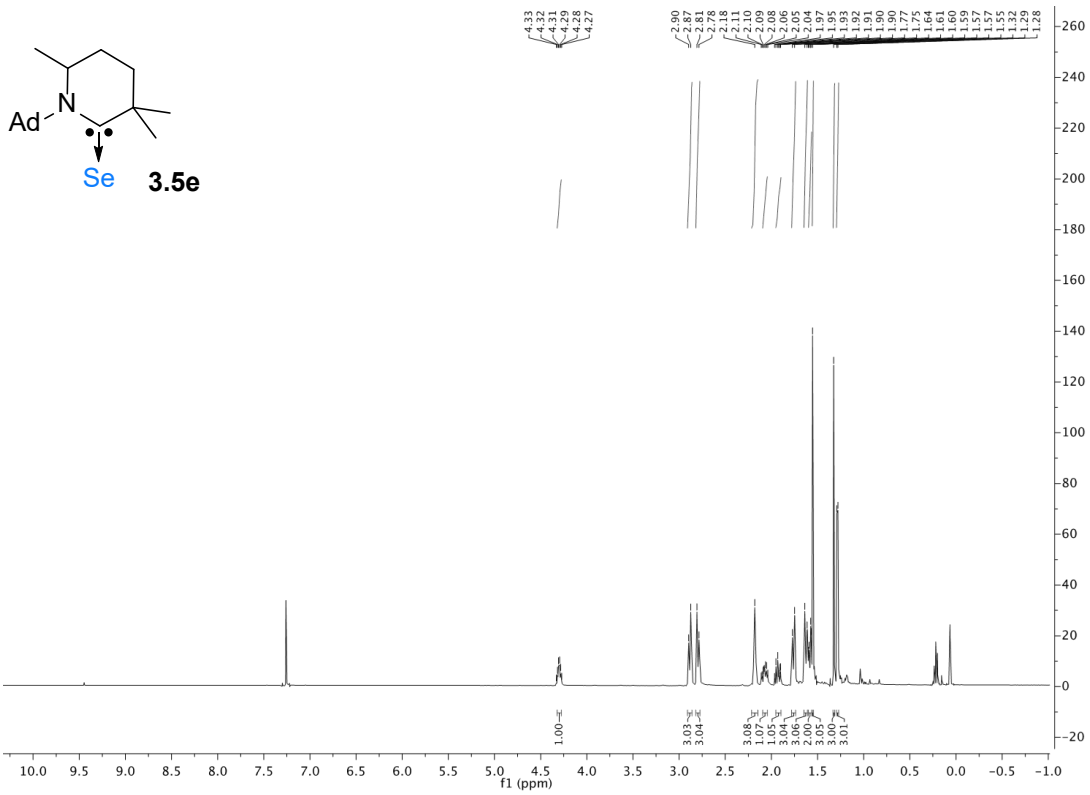
Empirical formula	$C_{12}H_{23}NSe$
Formula weight	260.27
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.9560(6)
b/Å	15.3956(17)

c/Å	14.0328(14)
α/°	90
β/°	101.375(5)
γ/°	90
Volume/Å^3	1261.5(2)
Z	4
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	2.943
F(000)	544.0
Crystal size/mm^3	0.28 × 0.195 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.97 to 50.666
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 18, -16 ≤ l ≤ 16
Reflections collected	8197
Independent reflections	2296 [R_{int} = 0.0353, R_{sigma} = 0.0386]
Data/restraints/parameters	2296/0/133
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0657
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.0696
Largest diff. peak/hole / e Å^{-3}	0.51/-0.33

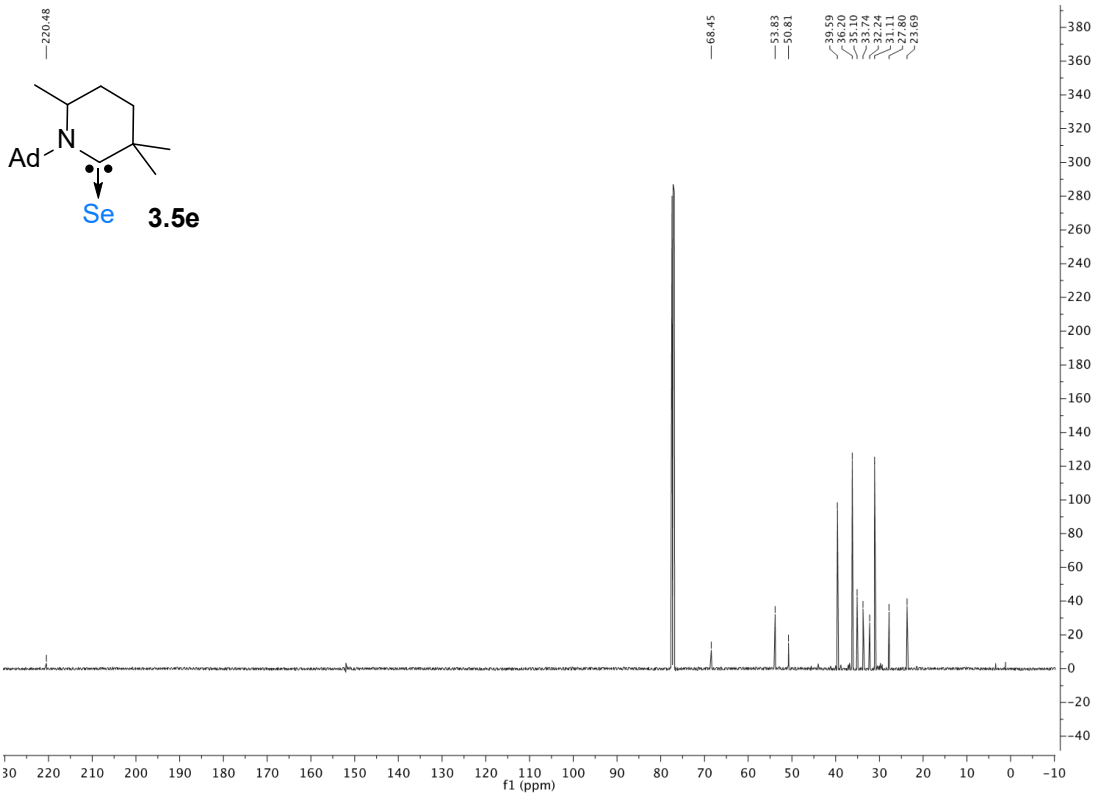
Synthesis of **3.5e**: Prepared following the standard procedure using iminium salt **3.3e** (155 mg, 1 eq), KHMDS (102 mg, 1.05 eq), and Se black (73 mg, 2 eq) gave **3.5e** as orange crystals (63 mg, 42% yield). **MP**: 165-167 ^{O}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.33-4.27 (m, 1H), 2.88 (d, *J* = 11.5 Hz, 3H), 2.80 (d, *J* = 11.5 Hz, 3H), 2.18 (s broad, 1H), 2.11 – 2.04 (m, 1H), 1.97-1.90 (m, 1H), 1.76 (d, *J* = 12.0 Hz, 3H), 1.63 (d, *J* = 12.0 Hz, 3H), 1.61 – 1.57 (m, 2H), 1.55 (s. 3H), 1.32 (s, 3H), 1.29 (d, *J* = 6.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 220.5 (CC_{arb}), 68.5 (NC_{Ad}),

53.8 (N*C*HCH3), 50.8 (Cq), 39.6, 36.2, 35.1, 33.7, 32.2, 31.1, 27.8 23.7. **^{77}Se{^{1}H} NMR** (95 MHz, (CD3)2CO) δ 792.2. **HRMS**: *m/z* calculated for C18H30NSe $[M+H]^+$ 340.1538, found 340.1540.

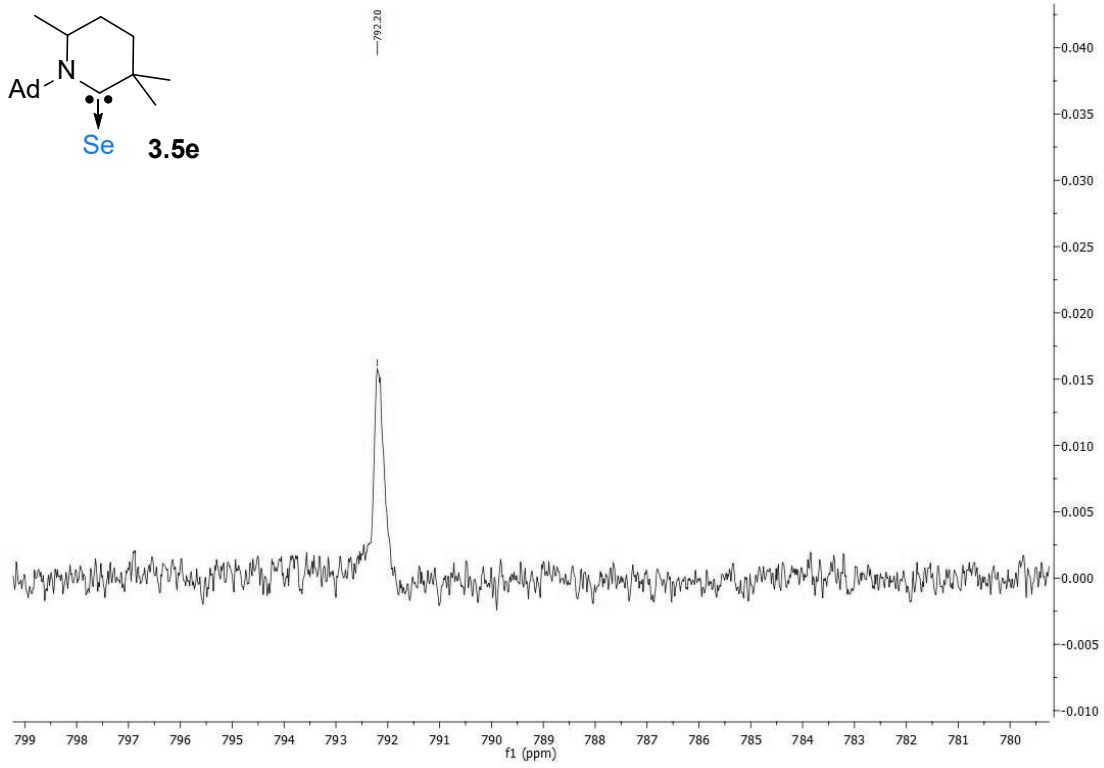
^{1}H NMR for 3.5e ($CDCl_3$)



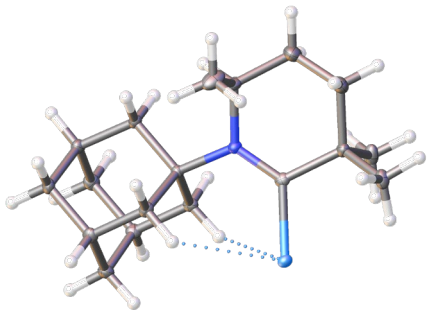
^{13}C{^{1}H} NMR for 3.5e ($CDCl_3$)



$^{77}Se\{^{1}H\}$ NMR for 3.5e (acetone-d_6)



Crystal data and structure refinement for 3.5e CCDC# 2020775



Ellipsoid shown at 30% probability

Empirical formula	$C_{18}H_{29}NSe$
Formula weight	338.38
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.9264(9)
b/Å	10.9686(7)
c/Å	19.7127(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3227.4(4)
Z	8
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	2.319
F(000)	1424.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.132 to 52.812
Index ranges	-16 ≤ h ≤ 18, -13 ≤ k ≤ 13, -21 ≤ l ≤ 24
Reflections collected	22527

Independent reflections	3307 [R_{int} = 0.0441, R_{sigma} = 0.0303]
Data/restraints/parameters	3307/0/184
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0846
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.0927
Largest diff. peak/hole / e $Å^{-3}$	1.06/-0.41

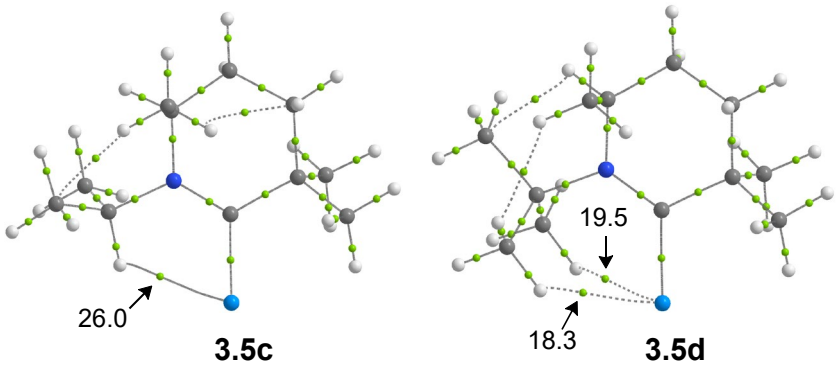
V. Computational methods

V.1. General Considerations

All calculations were done with the Gaussian09 program suite, with ultrafine integration grids.[86, 144] All files (.chk, .fchk, .log) pertaining to the computational data discussed in this article are available for download free of charge from the UC San Diego Library Digital Collections.[134] Geometry optimizations, frequency and population analyses for the free carbenes were performed at the B3LYP[82]/def2-TZVPP[87] level of theory, to match other literature.[21, 47, 53, 71] Geometry optimizations, frequency and population analyses for the selenium adducts were performed at the BP86[145-146]/def2-TZVPP level of theory, to resemble other reports.[125] The NMR calculations, through the gauge-independent atomic orbital method (GIAO),[147-151] on the Se adducts were done at the BP86/def2-TZVPP level of theory with a polarizable continuum model[152] of the experimentally used solvent, assuming Bondi atomic radii.[153-154] Optimization and NMR calculation of the ^{77}Se NMR standard SeMe2 was performed at the same level of theory as the carbene-Se adducts to allow for calculation of computed chemical shifts and comparison to experimental NMR spectra. All calculated structures were confirmed to be minima by the presence of zero imaginary frequencies calculated at the same level of theory as the optimization. 2D representation of the computational results was performed using CYLview.[155]

V.2. QTAIM

The quantum theory of atoms in molecules (QTAIM) was performed with the AIMII software package using the corresponding .fchk files.[156]



3.5c **3.5d**

Se···H		D[a]	ρ_{bcp}[b]	∇^2_{bcp}[c]	ε[d]
5c		4.596515	0.026006	0.058426	0.250760
5d	(i)	4.860944	0.019545	0.045235	0.100169
	(ii)	4.943183	0.018355	0.041827	0.093635

[a] Bond path length. [b] Electron density at the bond critical path (bcp).
[c] Laplacian of the electron density at the bcp. [c] Ellipticity at the bcp.

All values are reported in atomic units (bohr) [a.u.]

VI. DFT calculated XYZ coordinates and relevant data

The XYZ coordinates, energetics, and DFT-computed Se NMR shielding tensors pertaining to the manuscript are included hereafter. Note that the corresponding files are also accessible free of charge from UCSD Library Digital Collections.[134]

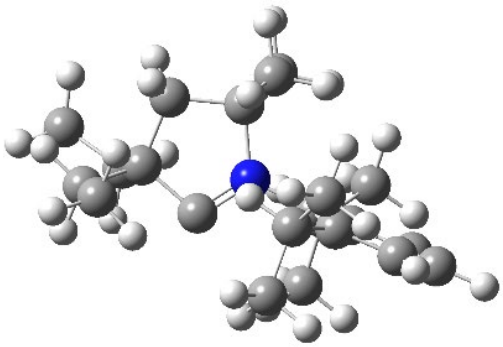
To compare an experimental ^{77}Se{H} chemical shift to a DFT NMR-GIAO calculation, apply the following formula: DFT-computed chemical shift (ppm) = $IST_{Me2Se} - IST_{Adduct}$

Where IST_{Me2Se} is the Isotropic value of the NMR Shielding tensor for Me_2Se calculated and IST_{Adduct} is the Isotropic value of the NMR Shielding tensor for the Carbene-Selenium adduct calculated in the same solvent as experiment (either chloroform or acetone).

VI.1. Free Carbenes:

Level of theory for optimizations, frequencies, population analyses – B3LYP/def2-TZVPP

EtCAAC-5:



Electronic energy: -914.465816338 Hartree/particle
Zero-point correction= 0.521777 (Hartree/Particle)
Thermal correction to Energy= 0.547698
Thermal correction to Enthalpy= 0.548642
Thermal correction to Gibbs Free Energy= 0.468274
Sum of electronic and zero-point Energies= -913.944040
Sum of electronic and thermal Energies= -913.918119
Sum of electronic and thermal Enthalpies= -913.917175
Sum of electronic and thermal Free Energies= -913.997542

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C	1.74100500	1.41040400	-0.16614600
C	0.89028600	2.65680200	-0.37059600
H	-0.13053900	2.42080800	-0.08723400
C	-0.87224100	-0.05694900	1.56585700
C	-0.72088800	1.29691200	2.26698600
H	0.32775300	1.56460800	2.39375900
H	-1.16852000	1.23594100	3.25998400
H	-1.22119000	2.09812900	1.72706100
C	0.85553200	3.02165500	-1.86556900
H	1.85309500	3.27184400	-2.23170100
H	0.20977200	3.88677100	-2.03053800
H	0.47201600	2.18975900	-2.45538900
C	1.19060400	0.12251700	-0.01597600
C	2.00358300	-1.02572000	-0.07601600
C	3.38469100	-0.85093800	-0.16662000
H	4.02701100	-1.71992300	-0.20933400
C	1.43755600	-2.43522700	-0.18213400
H	0.38264500	-2.39720000	0.07355800
C	3.12866700	1.52617300	-0.25435600
H	3.57224100	2.50609600	-0.36540400
C	1.33917700	3.85562100	0.47521900
H	1.38095700	3.61023300	1.53692800
H	0.64013800	4.68419800	0.34829300
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H	5.02391800	0.52503500	-0.29119000
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H	-2.99622300	1.34328100	-1.76602900
C	-3.24484900	-1.31810000	-1.03002600
H	-4.24156700	-1.38653800	-0.58702400
H	-3.38586200	-1.03246000	-2.07532000
C	-0.24216500	-1.13153400	2.45221300
H	-0.36420300	-2.12811500	2.03362000
H	-0.73326100	-1.11953700	3.42650800
H	0.81996200	-0.94851400	2.61512700
C	1.51774000	-2.91659500	-1.64195800
H	0.99221100	-2.23000300	-2.30522100
H	1.06629400	-3.90583300	-1.74202400
H	2.55477800	-2.98511300	-1.97583900
C	-2.58388700	-2.69522900	-0.98803700
H	-3.20761800	-3.43272100	-1.49575700
H	-2.43399700	-3.05201200	0.03295600
H	-1.61506200	-2.67870700	-1.48672200
C	2.10912500	-3.44156000	0.76157600
H	3.15592900	-3.60641100	0.50289700
H	1.60552500	-4.40778600	0.69698000
H	2.07183000	-3.11040500	1.79967500
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H	-3.02029400	0.25833400	1.76270800
H	-2.56530600	-1.40533700	1.47664900
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C	-4.60308600	1.33705700	-0.33022700
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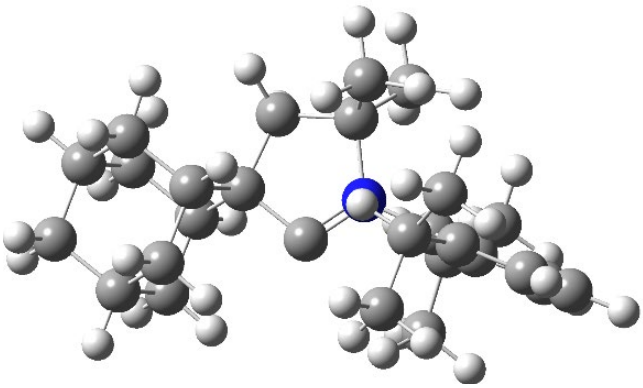
AdCAAC-5:



Electronic energy: -1107.48025611 Hartree/particle
Zero-point correction= 0.603872 (Hartree/Particle)
Thermal correction to Energy= 0.630311
Thermal correction to Enthalpy= 0.631256
Thermal correction to Gibbs Free Energy= 0.549615
Sum of electronic and zero-point Energies= -1106.876384
Sum of electronic and thermal Energies= -1106.849945
Sum of electronic and thermal Enthalpies= -1106.849000
Sum of electronic and thermal Free Energies= -1106.930641

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H	0.08712600	2.00212400	2.13324500
C	0.33613100	-0.07553200	-0.45346200
C	3.82335100	-1.45679000	0.56727900
H	3.61407900	-1.68753300	1.61500400
H	4.41748800	-2.28862900	0.17814700
C	-0.31516900	-0.13532200	1.89298500
C	1.62756100	-0.20190700	0.34390300
C	1.17019500	-0.51357500	1.80041100
H	1.28514100	-1.58128000	1.99658500
H	1.74749900	0.00979100	2.55964000
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C	2.51922300	-1.33968500	-0.24350700
H	1.96402400	-2.28048100	-0.17924600
C	2.45816600	1.12115700	0.21818600
H	1.86782900	1.95347300	0.61124000
C	-1.14704700	-1.18305000	2.63241800
H	-0.99590800	-2.18234800	2.23098400
H	-2.21149500	-0.95042900	2.59871100
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C	2.80942700	1.40234500	-1.25633700
H	1.89979500	1.51282800	-1.84511000
H	3.36225600	2.34488200	-1.31878700
C	4.96499800	0.13296000	-1.00850500
H	5.58533900	-0.67372500	-1.41038700
H	5.54930400	1.05462500	-1.08864300
C	-3.95525500	1.35096800	-0.64176500
H	-4.42410400	2.31188000	-0.80407000
C	-2.61069600	1.30040100	-0.27111400
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H	-0.88822300	3.94493000	-1.68246100
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H	-4.65026000	-1.93452500	-0.91119000
C	3.77196800	1.00920700	1.01484900
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H	3.90068000	0.45723700	-2.86655700
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H	-2.71494300	3.41524100	1.56939300
H	-3.41358300	4.04900800	0.08212600
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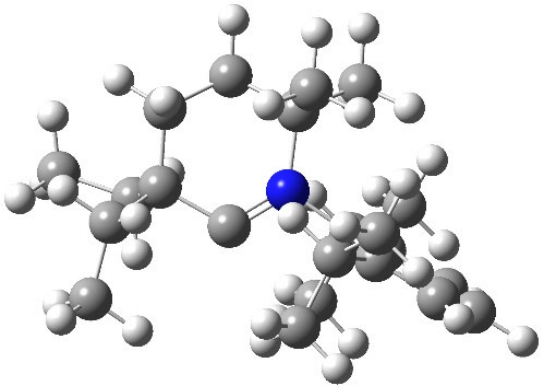
H	-2.32427700	-4.54029800	0.38355900
H	-3.83467200	-3.81467500	-0.14056500
C	-1.79323500	-2.92780000	-1.81578000
H	-1.16736600	-2.18353200	-2.30726500
H	-2.71885000	-3.02683700	-2.38598300
H	-1.27459600	-3.88834000	-1.84640700

EtCAAC-6:



Electronic energy: -953.782174792 Hartree/particle
Zero-point correction= 0.550851 (Hartree/Particle)
Thermal correction to Energy= 0.577631

Thermal correction to Enthalpy= 0.578575
Thermal correction to Gibbs Free Energy= 0.496555
Sum of electronic and zero-point Energies= -953.231324
Sum of electronic and thermal Energies= -953.204544
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Sum of electronic and thermal Free Energies= -953.285620

C	-0.30786500	0.06930200	1.96041500
C	-2.45448400	-0.30641100	-0.12662700
C	-2.71976600	-0.46770800	1.38176100
H	-3.75848500	-0.23423500	1.62372700
H	-2.58121400	-1.51481400	1.66192000
C	-1.78278200	0.40930700	2.19743400
H	-1.94780500	1.46068300	1.94911000
H	-1.98696300	0.31073900	3.26597500
N	-0.09110300	-0.01323600	0.43163200
C	-0.98813800	-0.18740600	-0.50437500
C	0.05293200	-1.26885700	2.61795500
H	-0.12980000	-1.19739700	3.69163600
H	-0.53885500	-2.09631400	2.23209800
H	1.10562100	-1.50573700	2.47941200
C	-3.01167900	-1.56177400	-0.85833900
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H	-4.02712400	-1.74164900	-0.49216100
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H	1.62663800	0.96153400	2.46740800
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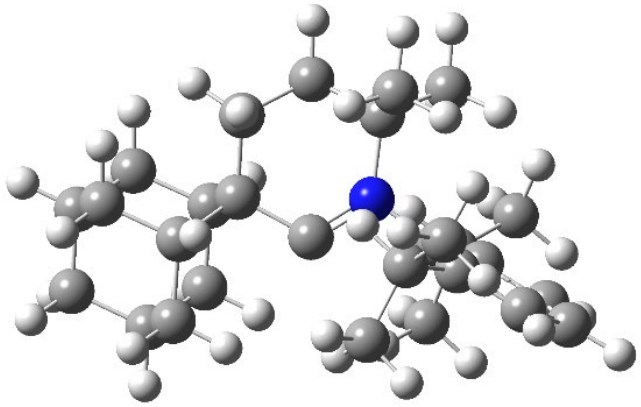
C	-3.10759400	0.99773300	-0.67551700
H	-2.68983900	1.85168400	-0.13598600
H	-2.78587900	1.12298000	-1.70942100
C	-3.01428000	-1.53187200	-2.38551000
H	-3.71113900	-0.79148300	-2.78036000
H	-2.02321100	-1.29725400	-2.76936300
H	-3.31695400	-2.50342100	-2.78041200
C	-4.63397000	1.07261800	-0.60374500
H	-5.00677800	1.02358600	0.42014300
H	-4.97819300	2.01818200	-1.02606200
H	-5.11222300	0.27178200	-1.16797400
C	1.28825400	0.10075000	-0.04724800
C	2.06328800	-1.05859200	-0.23425800
C	1.79433400	1.37360500	-0.37530700
C	3.39217300	-0.90292700	-0.63378900
C	3.12628400	1.47002600	-0.77526400
C	3.93177200	0.34760800	-0.87844800
H	4.00748700	-1.78053000	-0.77786700
H	3.53614200	2.43849200	-1.02704800

H	4.96609000	0.44521700	-1.18171100
C	1.48640600	-2.46697600	-0.16635300
H	0.51534000	-2.41477100	0.31614000
C	0.91784000	2.61861700	-0.43707300
H	-0.00060400	2.41588300	0.10877500
C	1.56278700	3.86230700	0.18899300
H	2.43282800	4.19812600	-0.37663100
H	0.84861700	4.68770700	0.19876200
H	1.88482000	3.68143800	1.21506200
C	0.51098800	2.89162600	-1.89634600
H	1.38684300	3.11453200	-2.50873500
H	0.00706700	2.02484300	-2.32250900
H	-0.16475500	3.74793200	-1.95056800
C	1.24075100	-2.99373300	-1.59178900
H	0.77258700	-3.97989100	-1.55802200
H	0.58572600	-2.31930000	-2.14194500
H	2.17860900	-3.08575000	-2.14277400
C	2.35008900	-3.45111300	0.63400100
H	1.84057600	-4.41272000	0.71794200
H	3.30991900	-3.63667900	0.15008200
H	2.55357200	-3.08948400	1.64257100

AdCAAC-6:



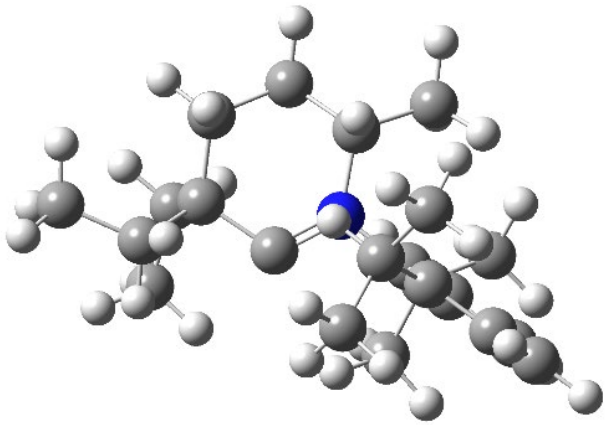
Electronic energy: -1146.79211264 Hartree/particle
Zero-point correction= 0.633279 (Hartree/Particle)
Thermal correction to Energy= 0.660453
Thermal correction to Enthalpy= 0.661397
Thermal correction to Gibbs Free Energy= 0.578919
Sum of electronic and zero-point Energies= -1146.158834
Sum of electronic and thermal Energies= -1146.131660
Sum of electronic and thermal Enthalpies= -1146.130716
Sum of electronic and thermal Free Energies= -1146.213193

N	0.73037600	-0.05031100	0.60485300
C	2.53150300	1.29515100	-0.45136600
C	1.99233800	0.03273200	-0.13608400

C	2.62021800	-1.15056200	-0.57154600
C	-1.71481800	-0.23357000	0.50717500
C	3.76800200	1.34273600	-1.09478900
H	4.20064100	2.30316000	-1.33991800
C	1.95280000	-2.51935000	-0.51331200
H	1.10188400	-2.45618400	0.15802000
C	-0.34504700	-0.09324600	-0.13915400
C	3.85718400	-1.04346000	-1.20932400
H	4.35834000	-1.94092300	-1.54530300
C	0.84362200	-0.10757600	2.14560400
C	1.77210400	2.59989300	-0.24443100
H	0.91866200	2.39955600	0.39907200
C	-2.52421500	-1.30805500	-0.30395900
H	-2.01085100	-2.26934600	-0.20453700
C	-2.49332300	1.12166600	0.30210000
H	-1.96654700	1.92075500	0.83039100
C	-2.59194400	1.48922200	-1.19307200
H	-3.11253700	2.44758600	-1.28667200
H	-1.59971800	1.60915100	-1.62193300
C	4.44429000	0.18706200	-1.44743900
H	5.40748600	0.24646400	-1.93732700
C	1.80780600	0.95465800	2.67990400
H	2.82336000	0.81397000	2.31503800
H	1.83155300	0.87774800	3.76850600
H	1.48185100	1.96146700	2.43104200
C	-3.92984600	1.01283100	0.85162800
H	-3.94007000	0.82921400	1.92688200
H	-4.43280500	1.97302200	0.70342000
C	-4.78361500	0.27332100	-1.38263100
H	-5.34343900	-0.49282400	-1.92732800
H	-5.32743800	1.21482500	-1.50624100
C	2.60891100	3.70465300	0.41584100
H	3.04201400	3.37933800	1.36166000
H	1.98556700	4.57906700	0.61195600
H	3.42698700	4.03093100	-0.22759800
C	-3.36283500	0.39858000	-1.95477000
H	-3.41455600	0.66386200	-3.01416800
C	-4.69736400	-0.09367000	0.10744100
H	-5.70392600	-0.18407500	0.52502300
C	-2.62485300	-0.93965600	-1.79516000
H	-3.16851400	-1.73035100	-2.32169000
H	-1.62996600	-0.87113200	-2.22953200
C	-1.63090400	-0.63719500	1.99248600
H	-2.57722600	-0.50659200	2.51240000
H	-1.40755400	-1.70620500	2.05344200
C	-3.95413700	-1.43300400	0.25965200
H	-4.48606700	-2.21334200	-0.29219900

H	-3.94541700	-1.74844800	1.30449700
C	-0.55211100	0.15657000	2.71093500
H	-0.53875100	-0.08071100	3.77710200
H	-0.77154700	1.22473600	2.63684700
C	2.87016000	-3.63561700	0.00400700
H	3.69800700	-3.83123200	-0.67880800
H	2.30725800	-4.56568200	0.10149400
H	3.29524600	-3.39669200	0.97925500
C	1.35979300	-1.48004900	2.59509000
H	0.69911800	-2.29221300	2.29916400
H	1.43534700	-1.48971100	3.68380800
H	2.35152700	-1.68026700	2.19534600
C	1.39250500	-2.87895300	-1.90132000
H	0.70344500	-2.11003700	-2.24815800
H	0.85757200	-3.83027500	-1.86152500
H	2.19536300	-2.97519500	-2.63466500
C	1.20748400	3.08706800	-1.59100100
H	2.01326800	3.34090900	-2.28227900
H	0.59332200	3.97858000	-1.44832800
H	0.59422600	2.31618900	-2.05516700

3.4a:



Electronic energy: -914.460462379 Hartree/particle
Zero-point correction= 0.522795 (Hartree/Particle)
Thermal correction to Energy= 0.548515
Thermal correction to Enthalpy= 0.549460
Thermal correction to Gibbs Free Energy= 0.468430
Sum of electronic and zero-point Energies= -913.937667
Sum of electronic and thermal Energies= -913.911947
Sum of electronic and thermal Enthalpies= -913.911003
Sum of electronic and thermal Free Energies= -913.992033

N	0.10545300	0.06148000	0.42842200
C	1.04149000	-0.09242200	-0.47281500
C	2.70493100	0.56312400	1.39127000

H	2.61142800	1.65413600	1.39709200
H	3.71469800	0.33967400	1.74248800
C	2.49632800	0.03939000	-0.04636800
C	3.12202300	1.03434700	-1.06131900
C	3.14148600	-1.37541000	-0.17695500
H	4.15515800	-1.31464800	0.22848600
H	2.60261500	-2.06086600	0.48226100
H	2.90952000	0.67699900	-2.06832600
H	2.58719800	1.98447500	-0.96918100
C	1.67457900	-0.01832600	2.34653400
H	1.82999100	0.35182500	3.36212900
H	1.76628700	-1.10695700	2.39563800
C	0.26434100	0.34655200	1.91086100
H	0.12910300	1.42597600	2.02848600
C	-0.78229800	-0.35664500	2.76936100
H	-1.79826700	-0.06445200	2.51382500
H	-0.70322900	-1.44040800	2.68465500
H	-0.60975400	-0.09250400	3.81409900
C	-1.26960200	0.05193100	-0.06024800
C	-1.89431600	1.27976000	-0.33166300
C	-1.93135600	-1.17133800	-0.26074700
C	-3.21725900	1.26015200	-0.77520500
C	-3.24959200	-1.13417700	-0.71357900
C	-3.89575500	0.06725700	-0.95870100
H	-3.71795500	2.19407400	-0.99419100
H	-3.77904500	-2.06218300	-0.88230000
H	-4.92106100	0.07215000	-1.30510000
C	-1.24942900	-2.51825500	-0.06806000
H	-0.31020800	-2.34655600	0.45438500
C	-1.17244900	2.61709000	-0.22821000
H	-0.16785600	2.43327700	0.14672000
C	-2.07531800	-3.49557200	0.78048300
H	-1.50484800	-4.40857700	0.96075800
H	-2.34155500	-3.06664000	1.74729100
H	-3.00076100	-3.78601700	0.28131500
C	-0.89794200	-3.13819700	-1.43084900
H	-1.80115100	-3.35567200	-2.00450000
H	-0.27989000	-2.45662300	-2.01348000
H	-0.35211500	-4.07445700	-1.29688100
C	-1.86076200	3.58085200	0.74976300
H	-1.28753900	4.50552900	0.83958500
H	-2.86340800	3.84729400	0.41179400
H	-1.95416000	3.14302100	1.74479600
C	-1.00864100	3.25919100	-1.61553600
H	-0.48498500	2.58655800	-2.29452500
H	-1.97603300	3.50069000	-2.05907400
H	-0.43584000	4.18577000	-1.54094300

C	3.19754000	-1.98633100	-1.57740100
H	3.85638100	-1.42380100	-2.23955100
H	3.58402100	-3.00596500	-1.52560300
H	2.21180700	-2.01510100	-2.03686600
C	4.62130200	1.29427000	-0.90262800
H	4.95917600	2.00873100	-1.65500800
H	4.86767000	1.71209300	0.07456400
H	5.21064500	0.38535300	-1.03172500

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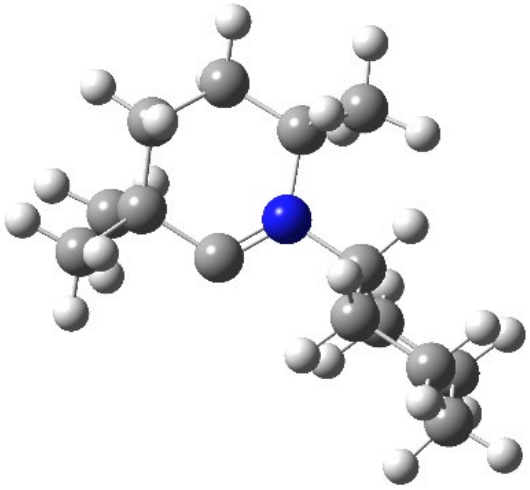
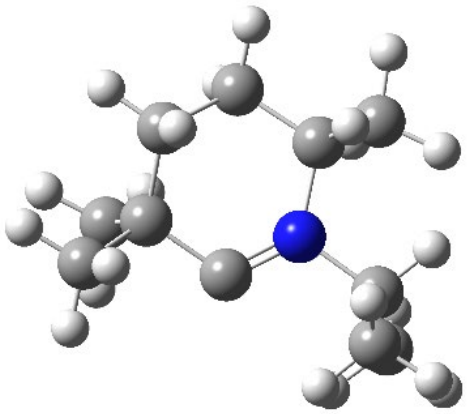


Electronic energy: -603.474273182 Hartree/particle
Zero-point correction= 0.367599 (Hartree/Particle)
Thermal correction to Energy= 0.383119
Thermal correction to Enthalpy= 0.384063
Thermal correction to Gibbs Free Energy= 0.325712
Sum of electronic and zero-point Energies= -603.106674
Sum of electronic and thermal Energies= -603.091154
Sum of electronic and thermal Enthalpies= -603.090210
Sum of electronic and thermal Free Energies= -603.148561

N	0.24829400	0.29355100	-0.13786900
C	0.79481900	-0.82158700	0.25428800
C	2.95442300	0.06094200	-0.78134200
H	2.71790100	-0.23351100	-1.80877600
H	4.04406100	0.03434900	-0.69407000
C	2.30562900	-0.94557700	0.18488300
C	2.61727000	-2.37651600	-0.28771900
H	3.69776800	-2.53796500	-0.33603900
C	2.84552400	-0.78818800	1.62130600
H	3.91826900	-0.99400300	1.64143800
H	2.68430600	0.21322300	2.02108500
H	2.18046900	-3.10673200	0.39257800
H	2.20325000	-2.55952000	-1.28078200

H	2.34824100	-1.49193900	2.28867100
C	2.43785200	1.46540200	-0.52086000
H	2.86999100	2.18312000	-1.22138600
H	2.74727000	1.78998200	0.47538100
C	0.91538400	1.55653100	-0.62171700
H	0.63007600	1.65772800	-1.67430600
C	-1.25029700	0.33185400	-0.20434900
C	-1.79022500	-0.77441800	-1.11458700
C	-1.87538700	0.25647800	1.19002600
H	-1.51836500	1.28839300	-0.65568000
C	-3.31971500	-0.74016000	-1.18614000
H	-1.44602000	-1.73094400	-0.71858100
H	-1.35854500	-0.66874200	-2.11366900
C	-3.40580200	0.27737200	1.12349100
H	-1.52483000	-0.66704300	1.65581700
H	-1.51125500	1.08210000	1.80597700
C	-3.94847400	-0.82235200	0.20727800
H	-3.67632000	-1.56040600	-1.81310200
H	-3.64713700	0.18491000	-1.67455300
H	-3.81853100	0.17253700	2.12939100
H	-3.74392900	1.25196800	0.75307300
H	-5.03653500	-0.75309400	0.13707500
H	-3.72386100	-1.79984700	0.64577800
C	0.42835800	2.79320700	0.13831100
H	-0.63387700	2.99172500	0.01221800
H	0.63431400	2.69171300	1.20472400
H	0.96908100	3.66920000	-0.22439000

3.4c:

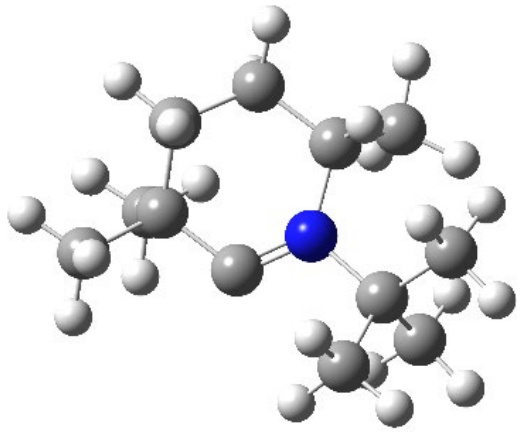


Electronic energy: -486.697478866 Hartree/particle
Zero-point correction= 0.301283 (Hartree/Particle)
Thermal correction to Energy= 0.315171
Thermal correction to Enthalpy= 0.316115
Thermal correction to Gibbs Free Energy= 0.262055

Sum of electronic and zero-point Energies= -486.396196
Sum of electronic and thermal Energies= -486.382308
Sum of electronic and thermal Enthalpies= -486.381363
Sum of electronic and thermal Free Energies= -486.435424

N	-0.65367100	-0.01527300	-0.10763500
C	0.23462800	-0.91053900	0.21220300
C	1.95932900	0.67293800	-0.80231300
H	1.79951000	0.36772500	-1.84134000
H	3.00106700	0.99748800	-0.73122500
C	1.70154600	-0.53550100	0.11488200
C	2.44421400	-1.76327200	-0.44074000
H	3.51683600	-1.56296900	-0.51262600
C	2.20519500	-0.28068900	1.55057900
H	3.28670400	-0.12637300	1.54463300
H	1.73998300	0.59288200	2.00784700
H	2.28807200	-2.62760700	0.20373600
H	2.08118300	-2.02260800	-1.43675000
H	1.98428600	-1.13958700	2.18413900
C	1.02438500	1.81947100	-0.45723100
H	1.17918300	2.67121800	-1.12290600
H	1.24293100	2.17887800	0.55108600
C	-0.44822900	1.41597700	-0.53163900
H	-0.78323900	1.46828200	-1.57318700
C	-2.08966300	-0.46708500	-0.14582000
H	-2.66426600	0.37016000	-0.53996000
C	-1.28608500	2.39030000	0.30096500
H	-2.35878700	2.24008400	0.19866300
H	-1.02748800	2.30994500	1.35770900
H	-1.06777800	3.41055300	-0.01943000
C	-2.58990600	-0.79694000	1.25618100
H	-3.63142200	-1.11995200	1.22030700
H	-1.98460900	-1.59916900	1.67668200
H	-2.52391100	0.06728900	1.91811400
C	-2.25615500	-1.64055500	-1.10623700
H	-1.68288400	-2.49566200	-0.75354700
H	-3.30961100	-1.91689500	-1.17668700
H	-1.90561300	-1.38140200	-2.10679400

3.4d:

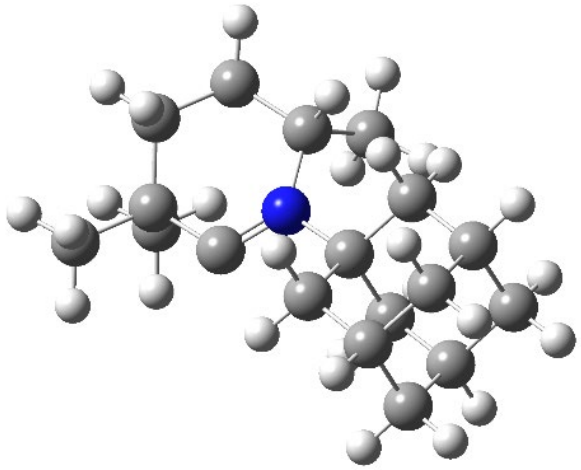


Electronic energy: -526.014437405 Hartree/particle
Zero-point correction= 0.329226 (Hartree/Particle)
Thermal correction to Energy= 0.344250
Thermal correction to Enthalpy= 0.345195
Thermal correction to Gibbs Free Energy= 0.288911
Sum of electronic and zero-point Energies= -525.685212
Sum of electronic and thermal Energies= -525.670187
Sum of electronic and thermal Enthalpies= -525.669243
Sum of electronic and thermal Free Energies= -525.725526

N	-0.44228300	-0.05689300	-0.06798400
C	0.48595100	-0.92269800	0.22361900
C	2.11172300	0.60806100	-0.96484400
H	1.85106000	0.21869500	-1.95386300
H	3.15522100	0.92998700	-1.02167600
C	1.93809100	-0.51792300	0.06503700
C	2.70590500	-1.76411800	-0.40985000
H	3.77035800	-1.54091200	-0.52494300
C	2.47705100	-0.12874600	1.45681000
H	3.54997100	0.06921600	1.40063400
H	1.99013900	0.75602000	1.86649900
H	2.59017500	-2.57838600	0.30469400
H	2.32659600	-2.11253600	-1.37187300
H	2.31757000	-0.94598300	2.16051000
C	1.22123300	1.78427900	-0.61347100
H	1.27111400	2.55990900	-1.38042000
H	1.59111400	2.24557900	0.30386300
C	-0.25739000	1.40325800	-0.42024500
H	-0.77568200	1.55593500	-1.36600200
C	-1.88883500	-0.58321500	-0.02128800
C	-0.85921600	2.34535300	0.62898200
H	-1.93726000	2.26439500	0.72985000
H	-0.41072500	2.16231700	1.60630000
H	-0.63285500	3.37540800	0.34636900
C	-1.90571300	-2.04001300	-0.50549400

H	-2.93774400	-2.39567000	-0.51340200
H	-1.50742700	-2.11698500	-1.51800500
H	-1.30498500	-2.67425000	0.13659400
C	-2.81884500	0.20773700	-0.95475100
H	-2.47230900	0.16361600	-1.98820200
H	-3.80460900	-0.25591800	-0.92479100
H	-2.94869600	1.25058500	-0.67763300
C	-2.38543200	-0.54164600	1.42934400
H	-1.69739400	-1.10318400	2.06091600
H	-2.46326000	0.47199500	1.81802600
H	-3.37152600	-1.00355000	1.49936400

3.4e:



Electronic energy: -758.357890412 Hartree/particle
Zero-point correction= 0.440313 (Hartree/Particle)
Thermal correction to Energy= 0.457256
Thermal correction to Enthalpy= 0.458200
Thermal correction to Gibbs Free Energy= 0.397442
Sum of electronic and zero-point Energies= -757.917577
Sum of electronic and thermal Energies= -757.900635
Sum of electronic and thermal Enthalpies= -757.899691
Sum of electronic and thermal Free Energies= -757.960449

N	0.84542600	0.18420300	-0.09053500
C	1.51423700	-0.88946300	0.21905600
C	3.45683100	0.12172400	-1.02039700
H	3.07667000	-0.24609000	-1.97816800
H	4.54613500	0.15495400	-1.11004400
C	3.02396600	-0.86054400	0.07828800
C	3.47497900	-2.28089900	-0.30369400
H	4.56273100	-2.32774800	-0.40738500
C	3.63737600	-0.52024700	1.45162500
H	4.72623500	-0.59602900	1.40494000

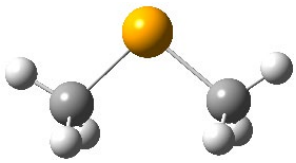
H	3.38291400	0.48241500	1.79333900
H	3.16100700	-2.99675200	0.45547600
H	3.02970800	-2.58883600	-1.25104000
H	3.28037300	-1.22408400	2.20410300
C	2.91838100	1.51379500	-0.74091700
H	3.10210800	2.17731000	-1.58811900
H	3.46896000	1.94058500	0.09869800
C	1.40946500	1.54687500	-0.41556900
H	0.87831800	1.89246400	-1.29971500
C	1.17033100	2.54787400	0.72140900
H	0.11970200	2.71318700	0.94242100
H	1.65814000	2.20844100	1.63582800
H	1.60642000	3.51044500	0.44652800
C	-0.68550500	0.04748300	-0.06445500
C	-2.94180300	0.94169600	-0.78194800
C	-1.07478200	-1.30282900	-0.70574600
C	-1.17058000	0.05093900	1.39819100
H	-3.42826500	1.75235400	-1.33065300
C	-3.31512900	-0.40783000	-1.40896600
C	-3.39431900	0.96902500	0.68721400
H	-0.54118200	-2.09627300	-0.18928900
H	-0.73301000	-1.31431500	-1.74516100
C	-2.59456600	-1.52412800	-0.64117600
H	-0.90852700	0.99266300	1.88474200
H	-0.64423800	-0.74546600	1.92748200
C	-2.69262800	-0.16013400	1.45965000
H	-3.02575500	-0.42680100	-2.46361400
H	-4.39850700	-0.55357800	-1.37214200
H	-3.15793500	1.93767100	1.13783300
H	-4.47973000	0.84935700	0.74443500
H	-2.82656000	-2.49285500	-1.09099900
C	-3.05062900	-1.51378500	0.82678600
H	-3.01204300	-0.14510700	2.50493100
H	-4.12929500	-1.68481400	0.88815600
H	-2.56528400	-2.32433700	1.37637100
C	-1.41524800	1.15207600	-0.85948800
H	-1.10087100	1.12569500	-1.90632400
H	-1.18846100	2.14635500	-0.47806100

VI.2. Carbene Se adducts:

Level of theory for optimizations, frequencies, population analyses – BP86/def2-TZVPP

Level of theory for NMR calculations– gauge-independent atomic orbital method (GIAO), solvent = polarizable continuum model (PCM), atomic radii= Bondi, BP86/def2-TZVPP

Me_2Se:



Solvent = Both Chloroform and Acetone PCM calculations were performed
Electronic energy: -2481.68029941 Hartree/particle
Zero-point correction= 0.072011 (Hartree/Particle)
Thermal correction to Energy= 0.077323
Thermal correction to Enthalpy= 0.078268
Thermal correction to Gibbs Free Energy= 0.043309
Sum of electronic and zero-point Energies= -2481.608288
Sum of electronic and thermal Energies= -2481.602976
Sum of electronic and thermal Enthalpies= -2481.602032
Sum of electronic and thermal Free Energies= -2481.636990

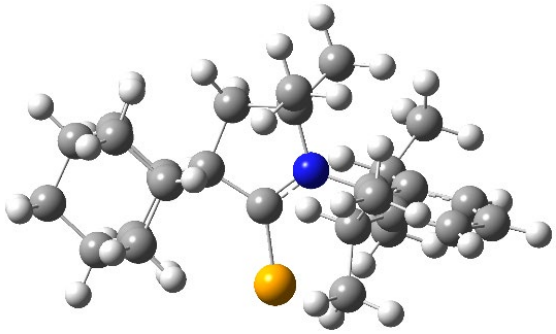
Se	0.00000000	0.47545100	0.00000000
C	1.47693400	-0.82440800	0.00000000
H	1.43741800	-1.44715800	-0.90126800
H	2.40582900	-0.24193500	-0.00002800
H	1.43745200	-1.44712800	0.90129100
C	-1.47693400	-0.82440800	0.00000000
H	-1.43743800	-1.44714100	0.90128100
H	-2.40582900	-0.24193500	-0.00000400
H	-1.43743200	-1.44714500	-0.90127800

NMR Calculation (Chloroform)
SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1714.3944 Anisotropy = 654.9491
XX= 2151.0272 YX= 0.0000 ZX= -0.0003
XY= 0.0000 YY= 1530.9937 ZY= -0.0008
XZ= -0.0007 YZ= -0.0002 ZZ= 1461.1625
Eigenvalues: 1461.1625 1530.9937 2151.0272

NMR Calculation (Acetone)
SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1724.5492 Anisotropy = 655.3795
XX= 2161.4689 YX= 0.0000 ZX= -0.0003

XY= 0.0000 YY= 1546.7987 ZY= -0.0009
XZ= -0.0007 YZ= -0.0002 ZZ= 1465.3801
Eigenvalues: 1465.3801 1546.7987 2161.4689

3.1c:



Solvent = Chloroform
Electronic energy: -3509.32972197 Hartree/particle
Zero-point correction= 0.588487 (Hartree/Particle)
Thermal correction to Energy= 0.617099
Thermal correction to Enthalpy= 0.618043
Thermal correction to Gibbs Free Energy= 0.532204
Sum of electronic and zero-point Energies= -3508.741235
Sum of electronic and thermal Energies= -3508.712623
Sum of electronic and thermal Enthalpies= -3508.711679
Sum of electronic and thermal Free Energies= -3508.797518

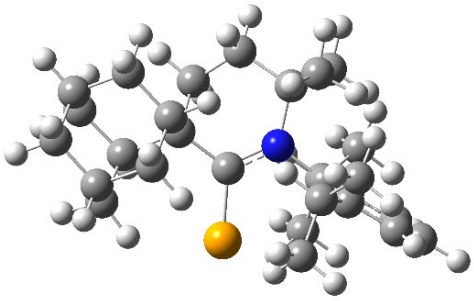
N	0.69621300	0.06985900	0.60035500
C	0.33289700	-1.25598700	2.71621200
H	-0.03262900	-1.17000900	3.74975600
H	1.36419100	-1.62922600	2.75737300
H	-0.28711700	-1.99712700	2.19779400
C	-0.32920600	0.15025900	-0.28549400
C	-3.83761000	1.47782900	0.97091500
H	-3.48552100	1.75357600	1.97726300
H	-4.50723400	2.28996700	0.64269100
C	0.27631300	0.12888300	2.04783400
C	-1.67081800	0.26674600	0.47680500
C	-1.15900700	0.65279400	1.89524400
H	-1.14268600	1.75234100	1.96602000
H	-1.79396200	0.28794100	2.70926400
C	2.08831300	-0.06863900	0.21248700
C	-2.66305900	1.37013000	-0.03520000
H	-2.11820300	2.32856700	-0.07448400
C	-2.48488000	-1.08792800	0.45819800
H	-1.82189400	-1.91473000	0.75960400
C	1.14170000	1.08934200	2.87130200
H	1.10163400	2.11133000	2.47770200
H	2.19023700	0.76311100	2.90610600

H	0.76071300	1.11013500	3.90268200
C	-3.05748000	-1.38888000	-0.94500200
H	-2.24532600	-1.48344200	-1.67937200
H	-3.58439200	-2.35767300	-0.90670000
C	-5.19291200	-0.16882900	-0.37424500
H	-5.89472600	0.62295100	-0.68679100
H	-5.76311900	-1.11314100	-0.34207300
C	4.02791300	-1.45226000	-0.20840200
H	4.47758800	-2.43858500	-0.33483400
C	2.65163100	-1.36000500	0.04667500
C	-3.26900000	1.06448200	-1.42002200
H	-3.95951900	1.88341800	-1.68656200
H	-2.48079500	1.03078800	-2.18263200
C	2.29734700	2.51398400	0.00733400
H	1.24224600	2.45752300	0.31118200
C	1.78812300	-3.23247300	-1.40136200
H	1.40151200	-2.49251700	-2.11455100
H	1.13609600	-4.11856900	-1.42949300
H	2.79157200	-3.54212700	-1.73060100
C	4.24252300	0.94235600	-0.22834200
H	4.86059800	1.83064700	-0.36946200
C	-3.67698400	-0.99782100	1.44061600
H	-4.22188800	-1.95649600	1.41548800
H	-3.34339300	-0.86425400	2.48084900
C	2.87367900	1.09987000	0.03025800
C	-4.62115000	0.14737300	1.02146100
H	-5.44206700	0.23297400	1.75247300
C	-4.03013300	-0.27359500	-1.37884500
H	-4.42223700	-0.50386800	-2.38279300
C	1.83237600	-2.64807200	0.02694800
H	0.79983100	-2.39937900	0.30626100
C	4.82526900	-0.31800600	-0.32716900
H	5.89478600	-0.41552400	-0.52176500
C	2.35755800	-3.71088800	1.01066800
H	2.42693000	-3.33248100	2.03979300
H	3.35819800	-4.06316600	0.71989900
H	1.69198900	-4.58681300	1.01408000
C	3.02745300	3.47559100	0.96494600
H	3.06105800	3.09552100	1.99495600
H	2.52432600	4.45396100	0.97574200
H	4.06460100	3.64790600	0.64176700
C	2.32599100	3.08305200	-1.42752600
H	1.79638900	2.41848700	-2.12264100
H	3.36154500	3.20258600	-1.78066500
H	1.84464600	4.07237000	-1.45397800
Se	-0.03113300	0.10435700	-2.09116400

NMR Calculation (Chloroform)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1026.0059 Anisotropy = 1082.9860
XX= 995.7255 YX= 100.9579 ZX= 155.5497
XY= 164.4799 YY= 1722.7124 ZY= 43.8256
XZ= -24.4098 YZ= 34.7179 ZZ= 359.5798
Eigenvalues: 352.4031 977.6180 1747.9965

3.2b:



Solvent = Chloroform
Electronic energy: -3548.62669286 Hartree/particle
Zero-point correction= 0.616813 (Hartree/Particle)
Thermal correction to Energy= 0.646249
Thermal correction to Enthalpy= 0.647193
Thermal correction to Gibbs Free Energy= 0.559797
Sum of electronic and zero-point Energies= -3548.009880
Sum of electronic and thermal Energies= -3547.980444
Sum of electronic and thermal Enthalpies= -3547.979500
Sum of electronic and thermal Free Energies= -3548.066896

Se	-0.07955000	-0.23038600	-2.03244900
N	-0.70801800	-0.17640700	0.65982900
C	-2.03181200	0.21467700	0.15109300
C	1.73182000	-0.65236200	0.30126700
C	-2.35197500	1.59602200	0.05850000
C	-3.66835400	1.95272900	-0.27071900
H	-3.92636100	3.01074300	-0.34148400
C	2.44316900	0.64114900	0.86109000
H	1.76501700	1.16555000	1.55051400
C	0.31503000	-0.33155800	-0.23937500
C	-2.99746600	-0.77568600	-0.18078100
C	2.75529600	-1.26638600	-0.73260600
H	2.28765900	-2.14744100	-1.20088400
C	-4.29355200	-0.35310800	-0.50563700
H	-5.04380600	-1.10334500	-0.76105900
C	3.73049600	0.24161900	1.62037000
H	4.19266600	1.15378700	2.03483900

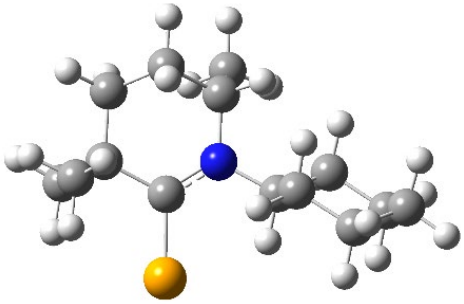
H	3.50602800	-0.40777400	2.48046800
C	4.05700400	-1.68205200	0.00808600
H	3.88949800	-2.47088500	0.75522900
H	4.74556600	-2.11650800	-0.73523300
C	1.45140300	-1.68241100	1.43087000
H	0.86817000	-2.51607200	1.00485200
H	2.37758400	-2.12263400	1.81344800
C	-1.32342000	2.72280600	0.16487000
H	-0.37391100	2.28970300	0.50807800
C	3.85785600	0.96421300	-1.21824200
H	4.12492600	1.67747100	-2.01513900
C	-4.64216300	0.99454500	-0.53078900
H	-5.66150500	1.29613500	-0.77775600
C	3.22171700	-0.28797200	-1.84126900
H	3.96161400	-0.81497200	-2.46841100
H	2.38415700	-0.01051400	-2.48806900
C	-0.62882600	-0.37362600	2.18075800
C	2.82621300	1.61397700	-0.27546700
H	1.93244100	1.90794400	-0.84684000
H	3.24346000	2.53173400	0.17313500
C	4.72148000	-0.44750400	0.66063200
H	5.61608700	-0.76516500	1.22136000
C	-2.69600200	-2.27096600	-0.30628700
H	-1.66645400	-2.44228700	0.04045800
C	-1.72950300	3.83753700	1.14815100
H	-2.62716400	4.36904900	0.79963400
H	-0.92320900	4.58201500	1.22668500
H	-1.93932400	3.45739600	2.15651800
C	-1.76180200	-1.30061800	2.65680700
H	-2.75410800	-0.92313400	2.38580200
H	-1.70951400	-1.35946100	3.75328900
H	-1.64354300	-2.31626100	2.26080900
C	0.71404200	-1.02878500	2.58464700
H	1.36633900	-0.27436100	3.04637400
H	0.50957200	-1.77090000	3.37026300
C	-0.79226700	0.96651000	2.91601000
H	-0.02469900	1.69487300	2.62541800
H	-0.69403800	0.78544700	3.99650600
H	-1.78227100	1.40351000	2.73704300
C	5.11904600	0.56341100	-0.43166300
H	5.59205700	1.44872500	0.02771100
H	5.86124100	0.11666300	-1.11427900
C	-1.06839300	3.34024400	-1.22820200
H	-0.77283200	2.57092000	-1.95345500
H	-0.26784000	4.09325600	-1.16981600
H	-1.97365600	3.84024100	-1.60468200
C	-3.65135200	-3.15872200	0.51796100

H	-3.69327100	-2.87660000	1.57741100
H	-3.33377100	-4.21041400	0.45617400
H	-4.67586000	-3.10781100	0.12097000
C	-2.76258600	-2.71571900	-1.78417800
H	-3.78914400	-2.62921200	-2.17143600
H	-2.45683600	-3.76898400	-1.87580300
H	-2.10074600	-2.10423100	-2.40956200

NMR Calculation (Chloroform)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 830.8330 Anisotropy = 1239.2496
XX= 891.8060 YX= 161.6297 ZX= 134.9353
XY= 244.7654 YY= 1554.4619 ZY= 384.8152
XZ= -19.7607 YZ= 143.3051 ZZ= 46.2311
Eigenvalues: 0.7385 834.7611 1656.9993

3.5b:



Solvent = Acetone
Electronic energy: -3005.34169515 Hartree/particle
Zero-point correction= 0.359846 (Hartree/Particle)
Thermal correction to Energy= 0.377207
Thermal correction to Enthalpy= 0.378151
Thermal correction to Gibbs Free Energy= 0.314946
Sum of electronic and zero-point Energies= -3004.981849
Sum of electronic and thermal Energies= -3004.964489
Sum of electronic and thermal Enthalpies= -3004.963544
Sum of electronic and thermal Free Energies= -3005.026750

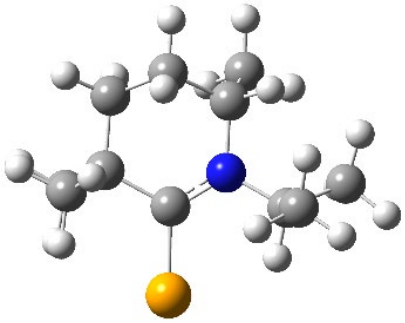
Se	-0.83308900	-2.09958600	-0.39022700
N	0.05227200	0.56250800	-0.09521900
C	1.43879200	0.01276600	-0.10994600
H	1.31506100	-1.01435700	-0.48868800
C	-2.43535200	0.25353000	0.20492400
C	-1.01014400	-0.27933300	-0.10452700
C	-0.06135200	2.03811800	0.07550800
H	0.86016200	2.34601200	0.59247800
C	-2.51825600	1.79373300	0.34878100

H	-2.69059600	2.25045900	-0.63781200
H	-3.40369800	2.04026100	0.95393900
C	1.98047000	-0.08329400	1.32802700
H	1.26488700	-0.65581800	1.93748600
H	2.05915400	0.92613500	1.77122700
C	-1.25623300	2.37867300	0.96533500
H	-1.33122400	3.47192300	1.06735300
H	-1.08969200	1.97032500	1.97462400
C	4.35092100	-0.05485100	0.41405600
H	5.31595800	-0.58498100	0.40905300
H	4.55498600	0.96289400	0.79252700
C	3.36075100	-0.75885200	1.35128400
H	3.74887500	-0.77819800	2.38148200
H	3.24734800	-1.81088800	1.03884400
C	-3.42254500	-0.17908300	-0.90003800
H	-3.11899700	0.21786600	-1.87997100
H	-4.42379400	0.21454300	-0.66535800
H	-3.47174100	-1.27191500	-0.97440500
C	-2.88469100	-0.38403200	1.54753400
H	-2.85741800	-1.47788600	1.47975100
H	-3.91180100	-0.05945100	1.77414100
H	-2.23540600	-0.07686900	2.38076000
C	-0.12028000	2.77274200	-1.27692900
H	0.78442000	2.60621500	-1.87111400
H	-0.21761800	3.85488900	-1.10357400
H	-0.97753900	2.44322000	-1.87776000
C	2.41944600	0.74114500	-1.03836500
H	2.55898200	1.79133600	-0.72750000
H	2.02570200	0.75182800	-2.06602800
C	3.78874000	0.03787200	-1.01077700
H	3.68149300	-0.97806000	-1.42773700
H	4.49003300	0.57406800	-1.66864600

NMR Calculation (Acetone)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1299.7763 Anisotropy = 949.2339
XX= 961.4960 YX= -86.4854 ZX= 58.9800
XY= -141.4729 YY= 1007.5531 ZY= -29.9311
XZ= 14.0046 YZ= 97.2863 ZZ= 1930.2798
Eigenvalues: 865.9337 1100.7964 1932.5989

3.5c:



Solvent = Acetone
Electronic energy: -2888.56889433 Hartree/particle
Zero-point correction= 0.295658 (Hartree/Particle)
Thermal correction to Energy= 0.311197
Thermal correction to Enthalpy= 0.312141
Thermal correction to Gibbs Free Energy= 0.253468
Sum of electronic and zero-point Energies= -2888.273236
Sum of electronic and thermal Energies= -2888.257698
Sum of electronic and thermal Enthalpies= -2888.256754
Sum of electronic and thermal Free Energies= -2888.315426

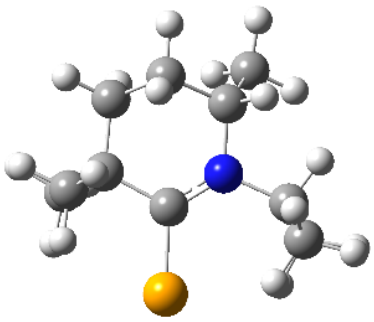
Se	-1.23334600	-1.78859700	-0.25678700
N	0.89398300	0.04554800	-0.00434300
C	-0.44909300	-0.12292800	-0.07225100
C	-1.39888500	1.09603500	0.08067900
C	1.56029700	1.37438000	0.08264800
H	2.47957100	1.20597700	0.66417200
C	-0.67133300	2.46238600	0.14432000
H	-0.52707600	2.85442100	-0.87409100
H	-1.32766900	3.18333900	0.65463800
C	-2.40638900	1.14248100	-1.08776000
H	-1.88873700	1.23660300	-2.05375600
H	-3.06415100	2.01684700	-0.96411300
H	-3.01648800	0.23181700	-1.11456700
C	1.79180900	-1.14134100	0.13900500
H	1.16304300	-1.98533400	-0.18044500
C	0.67583100	2.36105800	0.84438400
H	1.17820300	3.33929800	0.88741200
H	0.55104800	2.01536500	1.88268600
C	-2.18549900	0.90337700	1.40556000
H	-2.72974400	-0.04818500	1.39286500
H	-2.90249200	1.73047000	1.52162600
H	-1.51680800	0.90332800	2.27911000
C	1.96268500	1.91110200	-1.30403300
H	2.68032500	1.25251500	-1.80420800
H	2.43100800	2.90051800	-1.19372100
H	1.09191800	2.01565300	-1.96373000

C	2.14010500	-1.34290400	1.61912500
H	2.73287400	-0.50811100	2.02502500
H	2.73473000	-2.25962400	1.73960900
H	1.22482800	-1.45168300	2.21672000
C	3.03222700	-1.10531100	-0.75430500
H	2.76543100	-1.00944100	-1.81530900
H	3.56797000	-2.05756200	-0.63258400
H	3.73756800	-0.30275400	-0.49041100

NMR Calculation (Acetone)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1297.9956 Anisotropy = 954.5808
XX= 861.6662 YX= -16.5963 ZX= -19.3811
XY= -47.9001 YY= 1104.7393 ZY= 15.5340
XZ= 3.7891 YZ= 133.5197 ZZ= 1927.5814
Eigenvalues: 857.4572 1102.1469 1934.3828

3.5c':



Solvent = Acetone
Electronic energy: -2888.56544105 Hartree/particle
Zero-point correction= 0.295451 (Hartree/Particle)
Thermal correction to Energy= 0.311097
Thermal correction to Enthalpy= 0.312041
Thermal correction to Gibbs Free Energy= 0.253606
Sum of electronic and zero-point Energies= -2888.269990
Sum of electronic and thermal Energies= -2888.254344
Sum of electronic and thermal Enthalpies= -2888.253400
Sum of electronic and thermal Free Energies= -2888.311836

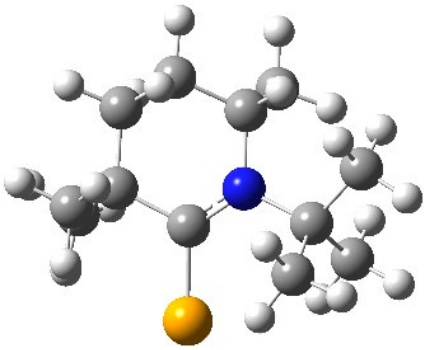
Se	1.29206800	-1.61609600	-0.08734500
N	0.14339400	0.96200600	0.11052900
C	-2.23554600	1.35186100	0.79008100
H	-2.11632800	1.01058500	1.83012900
H	-3.02211300	2.12129100	0.79390100
C	-1.52095100	-0.92389800	-0.04257000
C	-0.93473400	1.98208800	0.30477600
H	-0.55556500	2.64458700	1.10118300

C	-0.06783000	-0.36838900	-0.00440300
C	1.50328000	1.60995300	0.14279400
C	-2.59590300	0.18213500	-0.11010200
H	-2.70556300	0.53064700	-1.14956700
H	-3.56731100	-0.25187300	0.17090200
C	-1.70289300	-1.83173800	-1.27952400
H	-1.50256300	-1.27895600	-2.20906000
H	-2.74294700	-2.19247500	-1.31088600
H	-1.02256300	-2.69018500	-1.23881300
C	-1.12895400	2.83074000	-0.96308800
H	-0.18612300	3.28066600	-1.30131000
H	-1.83441100	3.64864000	-0.75684700
H	-1.52820900	2.22998800	-1.79103900
C	-1.75078100	-1.77607200	1.23115500
H	-1.00696100	-2.57981400	1.28755700
H	-2.75826500	-2.21805100	1.19577100
H	-1.67044500	-1.17502500	2.14870700
C	2.26392300	1.30759300	1.44086100
H	1.64755700	1.54122400	2.32138600
H	3.16384600	1.93881500	1.48102800
H	2.56626900	0.25552900	1.48905400
C	2.33662000	1.40366900	-1.12749200
H	2.72908900	0.38416700	-1.19889200
H	3.17957000	2.11085900	-1.10504900
H	1.74180800	1.61312300	-2.02779400
H	1.25977600	2.68184000	0.17072300

NMR Calculation (Acetone)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1223.3401 Anisotropy = 895.8040
XX= 977.1919 YX= 187.9554 ZX= 31.3066
XY= -93.5587 YY= 888.7334 ZY= -150.6535
XZ= 5.1503 YZ= -95.6536 ZZ= 1804.0951
Eigenvalues: 852.9614 996.5161 1820.5428

3.5d:



Solvent = Acetone
Electronic energy: -2927.87701637 Hartree/particle
Zero-point correction= 0.322314 (Hartree/Particle)
Thermal correction to Energy= 0.339132
Thermal correction to Enthalpy= 0.340076
Thermal correction to Gibbs Free Energy= 0.279410
Sum of electronic and zero-point Energies= -2927.554702
Sum of electronic and thermal Energies= -2927.537884
Sum of electronic and thermal Enthalpies= -2927.536940
Sum of electronic and thermal Free Energies= -2927.597607

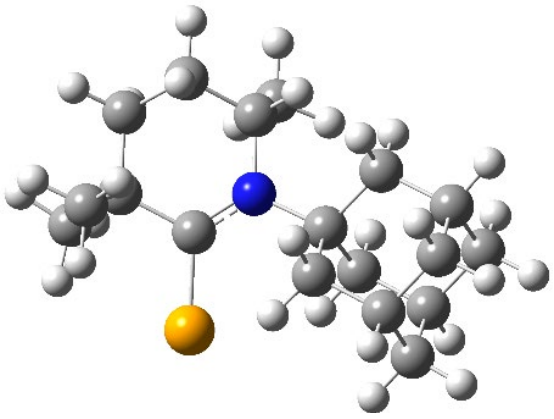
Se	-0.69265700	-2.00555500	-0.28796900
N	0.70956400	0.45717700	0.11310600
C	-0.39933100	2.65469200	0.58731700
H	-0.37582600	2.48935400	1.67582700
H	-0.28962200	3.73853400	0.42717000
C	-1.81980200	0.60491800	0.17039600
C	0.78978100	1.94618300	-0.05427600
H	1.67713400	2.27274400	0.49147400
C	-0.48252400	-0.18876500	-0.02131400
C	2.06357200	-0.27503400	0.24782700
C	-1.69054100	2.13257500	-0.00825900
H	-1.73289000	2.38090700	-1.08058700
H	-2.56693500	2.61530100	0.45096700
C	-2.92179900	0.13467000	-0.80031700
H	-2.60163800	0.24667200	-1.84622700
H	-3.81650600	0.75831700	-0.64534200
H	-3.18396000	-0.91604200	-0.63863000
C	0.98049600	2.31847400	-1.53479300
H	1.90530800	1.88746600	-1.93976600
H	1.04278700	3.41173900	-1.64194200
H	0.14991500	1.95562100	-2.15442200
C	-2.28537600	0.30460100	1.62253500
H	-2.43116500	-0.77423000	1.75720300
H	-3.23927700	0.82067200	1.81141400
H	-1.55522800	0.64724100	2.36981800
C	2.01276200	-1.22837100	1.45900300
H	1.80166900	-0.66339300	2.37867200
H	2.99610900	-1.70711500	1.57121900
H	1.25956000	-2.01285800	1.34032500
C	3.21669700	0.70829300	0.54667100
H	3.40349000	1.42943700	-0.26024500
H	4.12681400	0.10199700	0.64852400
H	3.08290700	1.24727600	1.49565300
C	2.42569900	-1.00749400	-1.05999500
H	1.65555300	-1.73421600	-1.33904700
H	3.37631200	-1.54235200	-0.91735900

H	2.56107600	-0.29288500	-1.88429500

NMR Calculation (Acetone)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1035.9800 Anisotropy = 1118.8363
XX= 796.7715 YX= -4.2155 ZX= 94.2998
XY= -274.4507 YY= 537.3756 ZY= 7.0457
XZ= -78.0849 YZ= -202.8628 ZZ= 1773.7930
Eigenvalues: 470.9455 855.1237 1781.8709

3.5e:



Solvent = Acetone
Electronic energy: -3160.21815453 Hartree/particle
Zero-point correction= 0.429842 (Hartree/Particle)
Thermal correction to Energy= 0.448796
Thermal correction to Enthalpy= 0.449740
Thermal correction to Gibbs Free Energy= 0.384283
Sum of electronic and zero-point Energies= -3159.788312
Sum of electronic and thermal Energies= -3159.769358
Sum of electronic and thermal Enthalpies= -3159.768414
Sum of electronic and thermal Free Energies= -3159.833871

Se	-1.19884200	-2.06198700	-0.36634100
N	-0.50067100	0.69241500	0.01616000
C	1.86611000	1.65240200	0.29016400
H	1.71984400	2.38814400	-0.51581000
H	1.58262700	2.12925500	1.24320700
C	1.48632700	-0.23374800	-1.29728000
H	0.88481600	-1.12145100	-1.52820100
H	1.32528900	0.50005000	-2.10442600
C	-1.47255200	-0.26145500	-0.04191200
C	1.01153900	0.37622100	0.04633700
C	3.64852700	0.32677800	1.50112000
H	4.72307400	0.08143000	1.54102400
H	3.38596400	0.78941500	2.46747400

C	3.37492200	1.30515000	0.34666200
H	3.92843800	2.24420400	0.51147800
C	2.98170800	-0.60561400	-1.21917200
H	3.27549300	-1.07447700	-2.17231600
C	1.31251100	-0.56710700	1.23912700
H	1.02793800	-0.05197600	2.17228000
H	0.70727500	-1.47759100	1.16201000
C	-2.95178000	0.12214200	0.30641600
C	2.80838500	-0.94088900	1.27419400
H	2.97040500	-1.65224000	2.10024400
C	-3.97755600	-0.64678000	-0.54978700
H	-3.81692400	-0.46096600	-1.62148200
H	-4.98792900	-0.29529200	-0.28667800
H	-3.91911800	-1.72729800	-0.38308800
C	3.20898700	-1.59976100	-0.06188700
H	4.26895000	-1.90282500	-0.02841000
H	2.61316600	-2.51137300	-0.22627700
C	3.81541900	0.66600900	-0.98231500
H	4.89089400	0.42471000	-0.94431300
H	3.67277100	1.37475400	-1.81563100
C	-0.86310700	2.14119100	-0.13561100
H	-0.05697600	2.71430200	0.32529200
C	-3.15002700	-0.28734900	1.79286000
H	-2.97099200	-1.36266600	1.91580000
H	-4.18350500	-0.06042600	2.09695700
H	-2.46735900	0.25251000	2.46458300
C	-2.13585300	2.49415800	0.62794400
H	-1.96151400	2.35660100	1.70663300
H	-2.35189700	3.56295000	0.47409600
C	-3.27924700	1.62247500	0.15141300
H	-3.49844500	1.84127800	-0.90572500
H	-4.20553000	1.83862000	0.70589000
C	-0.92840500	2.52945500	-1.62272700
H	0.03829000	2.37012100	-2.11830600
H	-1.18800300	3.59413400	-1.72198900
H	-1.67716800	1.93708900	-2.16512400

NMR Calculation (Acetone)

SCF GIAO Magnetic shielding tensor (ppm):
Se Isotropic = 1030.1804 Anisotropy = 1174.9221
XX= 855.2580 YX= 50.0159 ZX= 191.7657
XY= -194.6498 YY= 451.5225 ZY= 56.2884
XZ= 66.3083 YZ= -295.4040 ZZ= 1783.7607
Eigenvalues: 431.9238 845.1557 1813.4618

Chapter 4- Evaluating Lone Pair Strength: Experimental Comparison of Carbene Brønsted Basicity, a Proxy for σ-Donating Properties

In Chapter 2, I developed a qualitative understanding of carbene electronic structure and used it (in combination with Density Functional Theory calculations) to predict the effect of changing carbene geometry on the important frontier orbitals - the nucleophilic lone pair and acidic empty orbital, summarized in Figure 4.1. In chapter 3, we sought to improve the measurement of the acidic carbene empty orbital by identifying the source of a problem with the selenium scale. Now, in chapter 4, we will test some assumptions frequently invoked by carbene chemists when attempting to predict, and ultimately measure, the nucleophilic carbene lone pair.

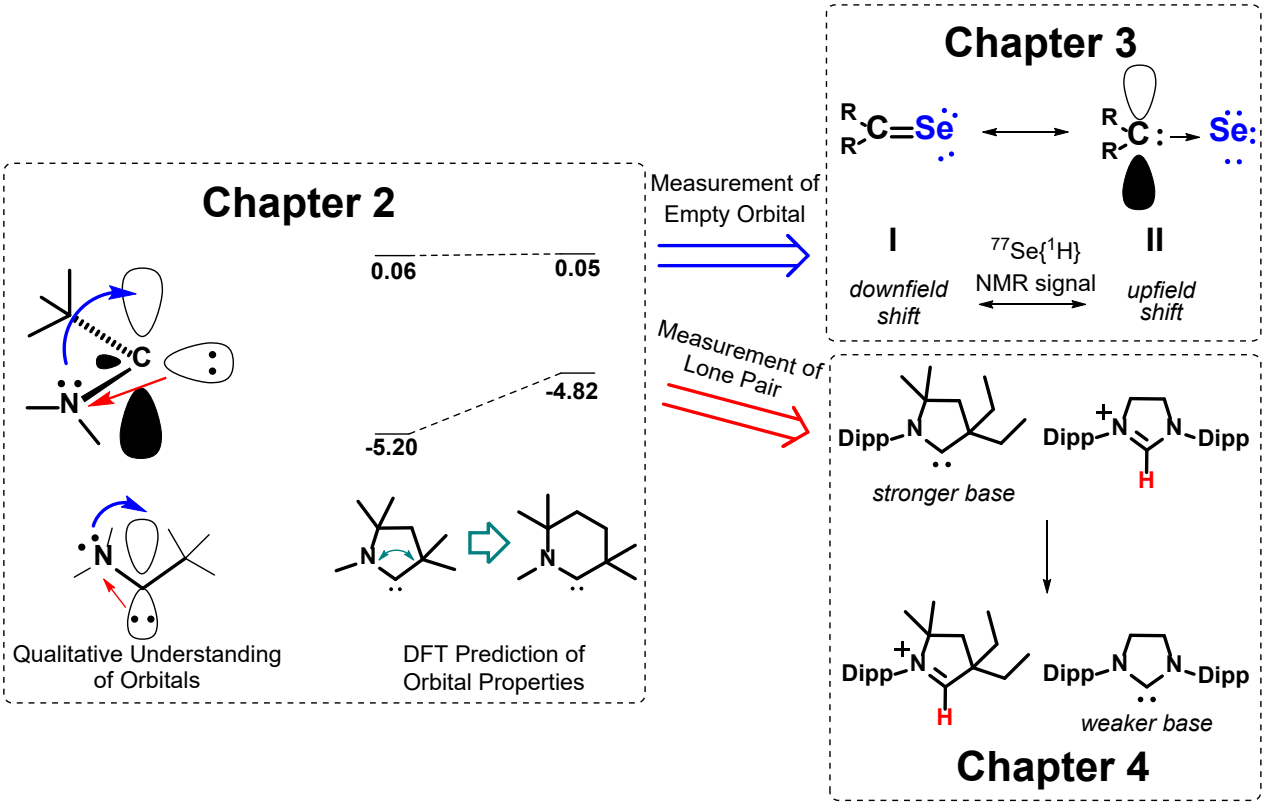


Figure 4.1: Graphical representation of how carbene properties are predicted then ultimately measured.

The most popular tool for measuring carbene donor properties (lone pair "strength") is the Tolman Electronic Parameter (TEP),[77] Figure 4.2. A carbene is coordinated to a bis(carbonyl)rhodium chloride complex and an IR spectrum is taken. A strongly donating carbene will donate electron density into the rhodium allowing for increased back-donation from the rhodium into the carbonyl ligands, causing a strong red-shift of the CO stretching frequency. Thus,

the carbonyl IR stretching frequency is a measure of the electron-richness of the rhodium metal center, and by proxy the donor strength of the carbene lone pair (Figure 4.2, emphasized in blue).

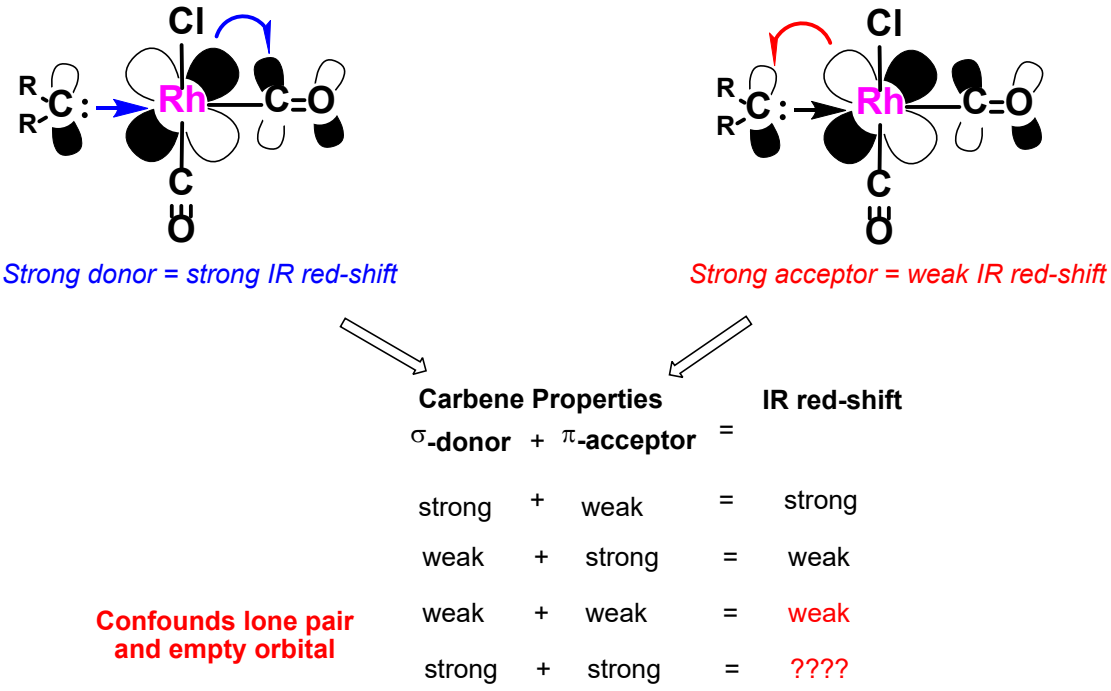


Figure 4.2: Measuring the carbene lone pair through TEP, highlighting the problem of confounded orbitals.

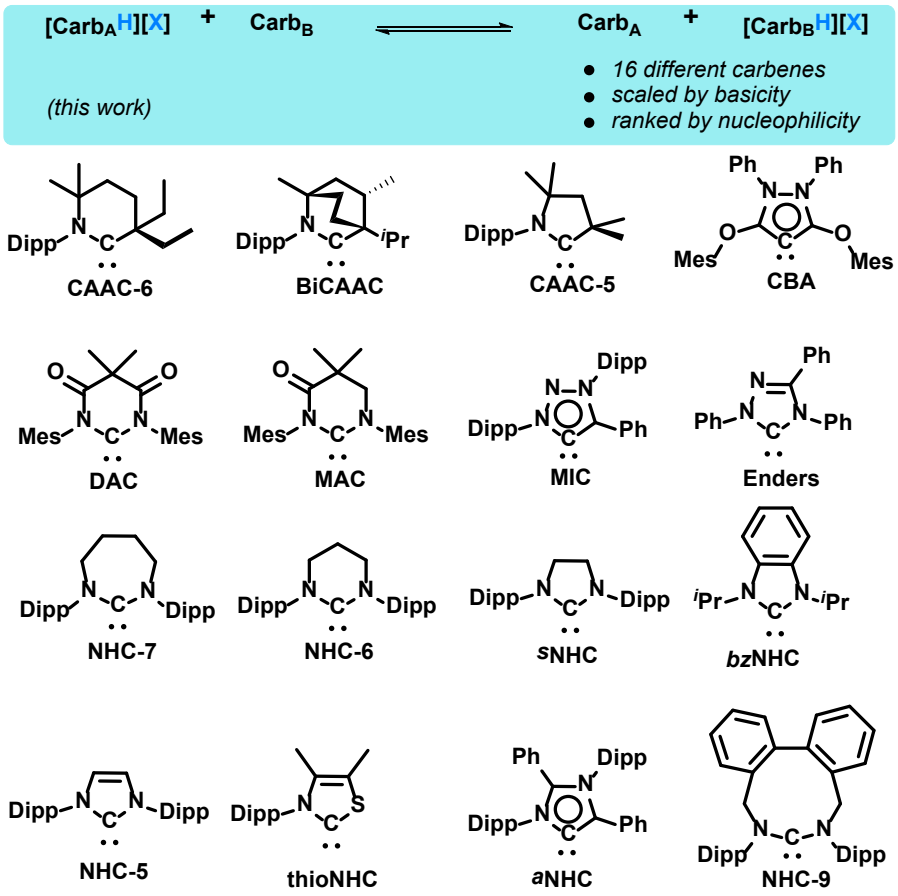
However, if the carbene simultaneously features a strongly acidic empty orbital, the carbene competes with the carbonyl ligand for back-donation of rhodium electron density. A strongly acidic empty orbital will deplete the density on rhodium and lead to a blue shift of the IR stretching frequency, or at least lessen the red shift expected from the effect of lone pair strength alone (Figure 4.2, emphasized in red). Unfortunately for the TEP, many interesting carbenes feature strongly acidic empty orbitals and thus TEP confounds the carbene lone pair and empty orbital. As a result, the TEP is now widely considered a measure of a carbene's "overall" or "net" donor ability.

In light of such problems, a number of techniques have been developed in competition with TEP. For example, the Huynh Electronic Parameter (HEP) involves the preparation of transition-metal bis-carbene adducts.[107, 126] However this method is still largely restricted to NHCs, and has recently shown some limitations.[157] Alternatively, one could envisage "adjusting" the

Tolman Electronic Parameter (TEP) by “subtracting” the acidic nature of the empty orbital using ^{31}P or ^{77}Se NMR data. However, this merely emphasizes the need for a method to evaluate the nucleophilicity of a carbene lone pair independently.

In the absence of broadly applicable and practical experimental methods, carbene HOMO energies or gas-phase proton affinities obtained from DFT calculations are frequently used to predict the lone pair’s properties.[21, 88, 158-165] However, these assumptions have seldomly been explored experimentally.[166-168] Perhaps foreshadowing the need for significant experimental validation, the relationship between HOMO energies and basicity has been shown for families of compounds, but often requires the use of additional quantum parameters (dipole moments, bond orders, atomic charges on hydrogen, and bond lengths) to fit true experimental trends.[165, 169-170]

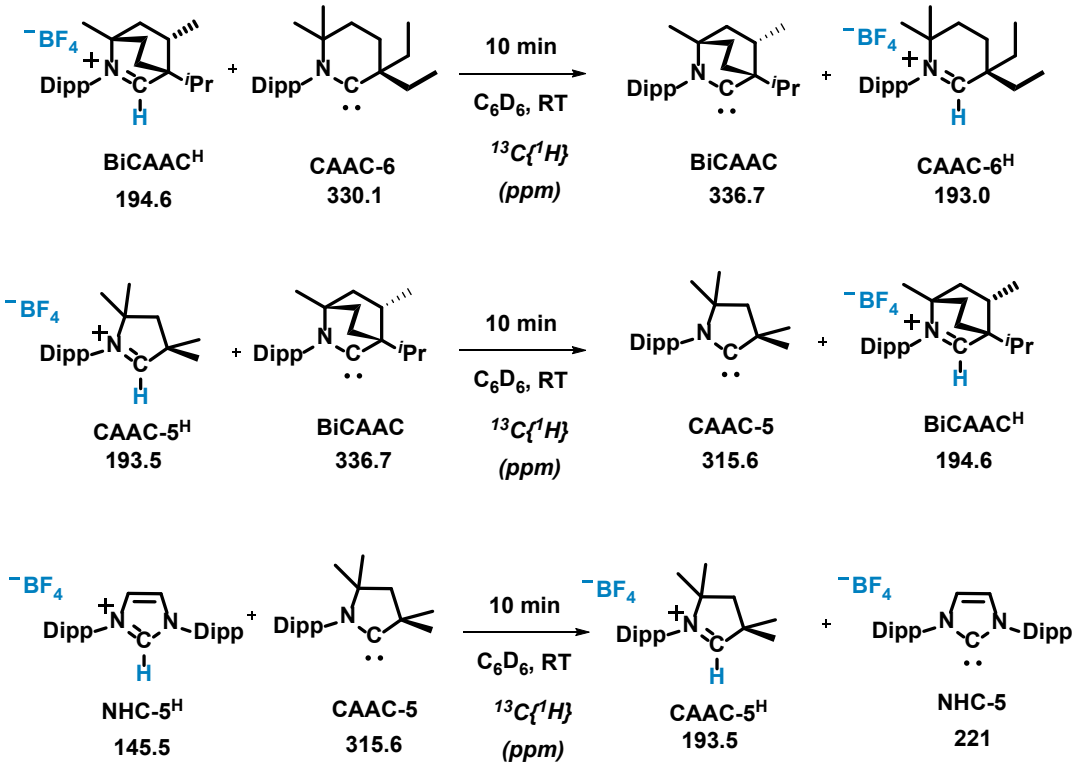
Though DFT is immensely valuable, it is critical to have experimental validation of computational predictions. However, many carbenes are extremely strong bases and accurate experimental measurement of carbene pKa has thus far been limited.[104, 162, 165] To find an easy way to evaluate the donor strength of a new carbene, Bertrand *et al* reported bromine exchange between two carbenes in 2017.[71] One problem is that bromine is a large atom with many lone pairs of electrons, which may be susceptible to unintended interactions with the carbene empty orbital or substituents, as found with carbene-selenium adducts.[76] However, the use of proton rather than bromine exchange between two carbenes could avoid such issues due to the small size of the hydrogen atom and its lack of lone-pairs. The qualitative ranking of carbenes this way would also avoid the challenges found when trying to measure pKa of extremely strong bases.[104, 162, 165] In such a manner, a qualitative framework to understand carbene lone pair properties can be created while the quantitative measurements (i.e. pKa) are still being pursued. The qualitative ranking is possible by using the reaction between a given carbene conjugate acid [$\mathbf{Carb_A}$.H][X] and free carbene candidate $\mathbf{Carb_B}$, (Scheme 4.1).



Scheme 4.1. Scaling of carbenes Brønsted basicity, an experimental marker for their nucleophilic nature (*This work*).

To begin our experimental exploration, we looked at this process using free carbenes and BF_4 conjugate acids from the CAAC family of carbenes meaning **CAAC-5**,[60] **BiCAAC**[71] and **CAAC-6**.[75] Computationally, I confirmed that the thermodynamics of these reactions are exergonic in favor of the most basic carbenes (**CAAC-5^H** reacting with **BiCAAC: -**3.7 kcal/mol, **BiCAAC^H** reacting with **CAAC-6 :** -4.9 kcal/mol). Francois Vermersch then probed these predictions experimentally. **BiCAAC^H** was reacted with **CAAC-6** in benzene at room temperature (Scheme 4.2), and the quantitative formation of free **BiCAAC** and **CAAC-6^H** iminium was observed with their characteristic $^{13}C\{^1H\}$ NMR signals at 336.76 ppm and 193.0 ppm, respectively. Next, **CAAC-5^H** was reacted with **BiCAAC**, which showed the rapid formation of free **CAAC-5** along with **BiCAAC^H**, with their characteristic signals at 315.6 ppm and 194.6 ppm,

respectively. Concerned that differences in solubility of the partners could shift the equilibrium, Francois checked that these reactions occurred equally in THF.



Scheme 4.2: Demonstrating carbene-to-carbene proton exchange.

To confirm that this strategy could be applicable to other carbene motifs, we next considered the unsaturated 5-membered **NHC-5**. The reaction of **NHC-5^H** with free **CAAC-5** led to a complete exchange affording free **NHC-5** and **CAAC-5^H** within 10 minutes at room temperature.[171-172] From these preliminary results, we determined that these carbenes are best ranked by decreasing basicity in the order **CAAC-6** > **BiCAAC** > **CAAC-5** > **NHC-5**, in good correlation with their respective HOMO energies.

To expand the scope of this strategy, Francois compared fifteen structurally diverse popular carbenes featuring a broad range of electronic properties, including the CAACs (**CAAC-5**,[60] **BiCAAC**,[71] **CAAC-6**[75]), the amido carbenes (**DAC**,[173] **MAC**[174]), the N-heterocyclic carbenes (**NHC-5**, ***bz*NHC**,[175] ***s*NHC**,[176] **NHC-6**,[177] **NHC-7**[178]), the cyclic-bentallenes (**CBA**[179]), the abnormal NHCs (***a*NHC**[180]), the mesoionic carbenes (**MIC**[55]), the Enders carbenes (**Enders**[181]) and the thio-

amino carbenes (***thio*NHC**[182]). Given the number of carbenes considered and ensuing possible permutations, the list was first organized by predicted HOMO energies (Figure 4.4), prior to being evaluated for proton exchange with their immediate neighbors.

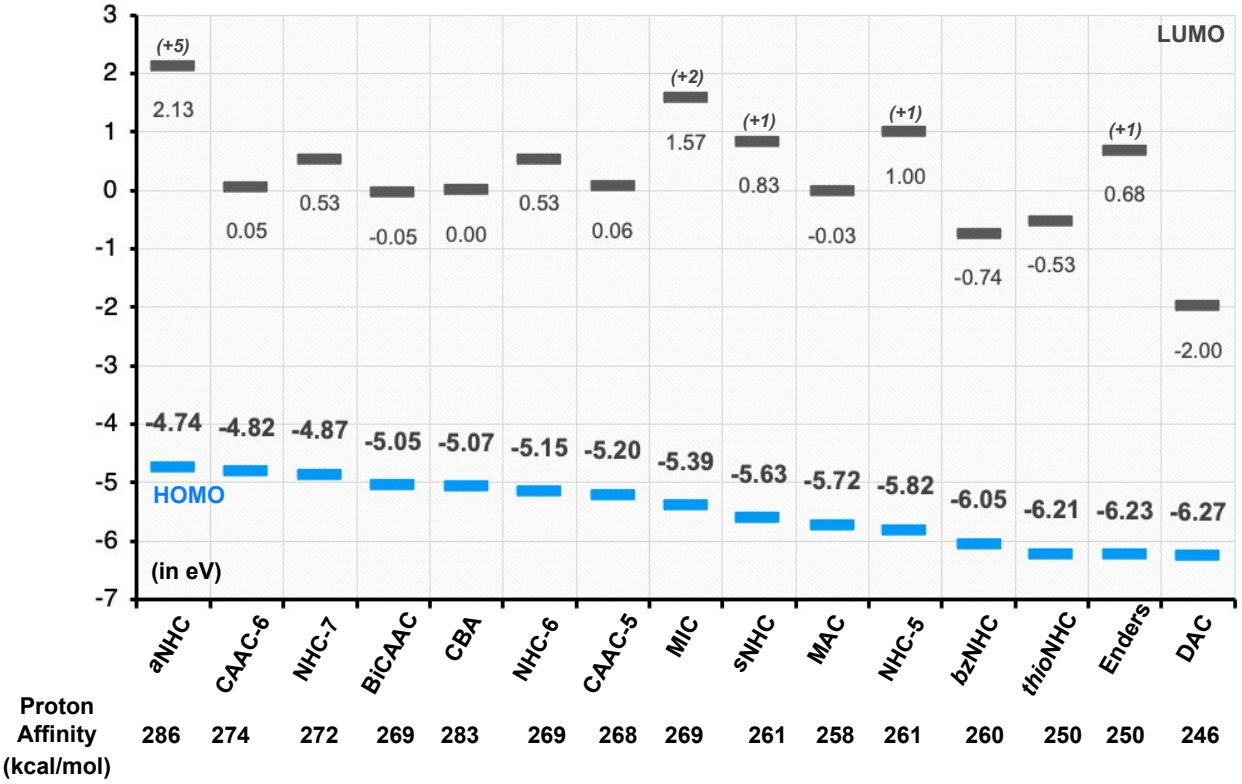


Figure 4.3: Proposed theoretical scale as a blueprint for studying the carbene-to-carbene Brønsted basicity.

Following this blueprint, and as shown in Figure 4.5 (left), an unsorted experimental map was established. A grid was constructed showing the reaction between carbene conjugate acids [**Carb**$_{\mathbf{A}}$.H][X] (y-axis) and free carbenes **Carb**$_{\mathbf{B}}$ (x-axis), Figure 4.5. The grid provides a visual map for the direction of reaction with various combinations of [**Carb**$_{\mathbf{A}}$.H][X] and **Carb**$_{\mathbf{B}}$, with blue squares indicating a forward reaction, pink showing no reaction, and green indicating an equilibrium mixture.

Interestingly, during this study two sets of three-way equilibria were uncovered. The first one involved the **NHC-7**, **CAAC-5** and **NHC-6**, whereas the later involved **MAC**, ***s*NHC** and **NHC-**

5. Fortunately, the direction of these equilibria allowed us to rank these carbenes unambiguously by decreasing basicity in the order **NHC-7** > **CAAC-5** > **NHC-6** and ***s*NHC** > **NHC-5** > **MAC**.

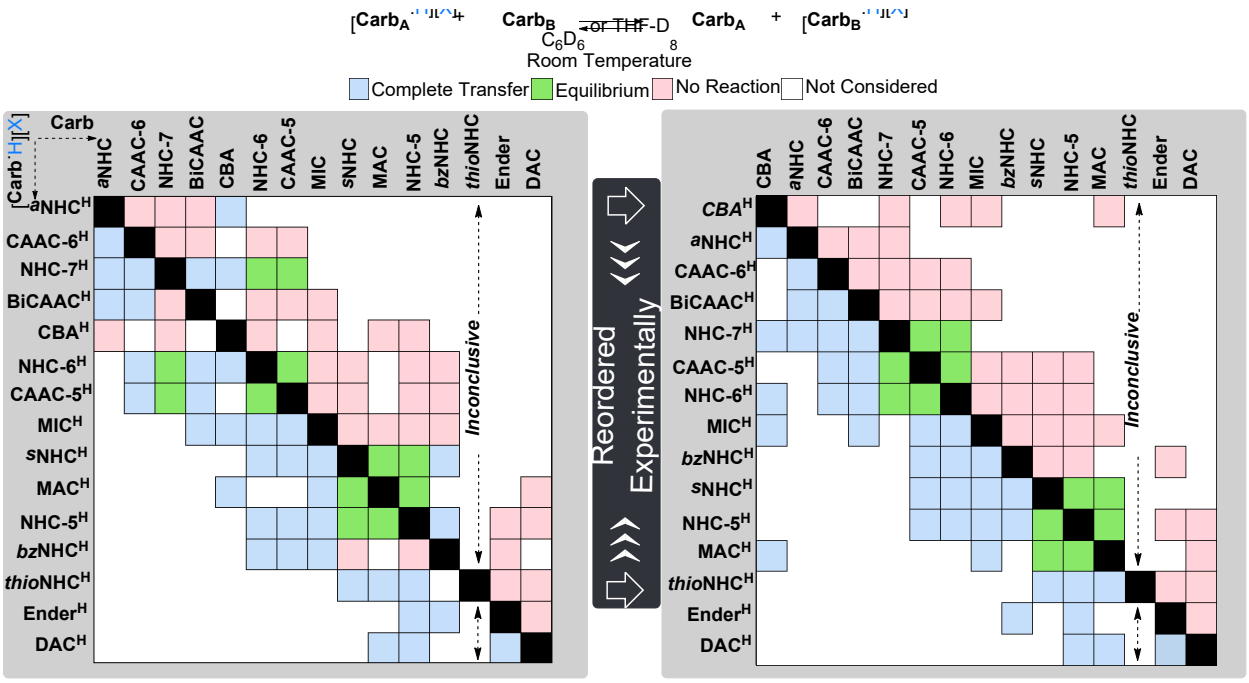


Figure 4.4: Experimental ranking of carbene-to-carbene Brønsted basicity: unsorted (left), sorted (right).

Note also that the ranking of the ***thio*NHC** proved somewhat challenging given the tendency of the free carbene to dimerize under acidic conditions.[182] However, reaction of the ***thio*NHC^H** with the **MAC** leading to the ***thio*NHC** dimer along with **MAC^H** supports the transient formation of the ***thio*NHC** free carbene. In contrast, the lack of reaction between the ***thio*NHC^H** and **Enders** carbene places the ***thio*NHC** between the **MAC** and the **Enders.** Altogether, sorting of these experimental results (Figure 4.5, right) allowed us to unambiguously rank these fifteen carbene motifs by decreasing basicities in the order **CBA** > ***a*NHC** > **CAAC-6** > **BiCAAC** > **NHC-7** > **CAAC-5** > **NHC-6** > **MIC** > ***bz*NHC** > ***s*NHC** > **NHC-5** > **MAC** > ***thio*NHC** > **Enders** > **DAC** (Figure 4.6). To the best of our knowledge, this is first direct experimental ranking of carbene-to-carbene basicity.

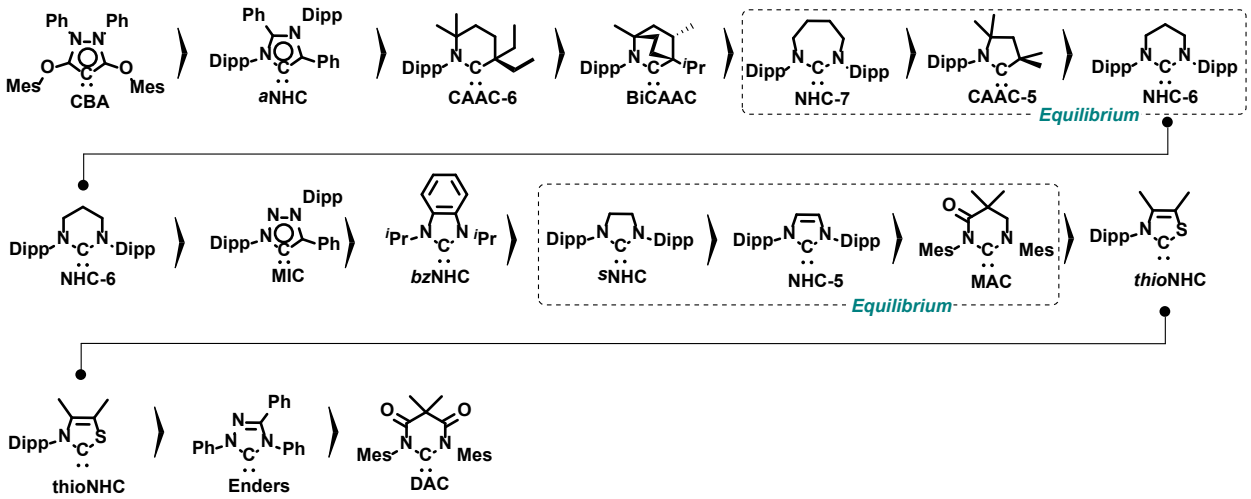


Figure 4.5: Experimental ranking of carbene-to-carbene Brönsted basicity.

There are a number of striking differences between the experimental ranking of carbene basicity and the predicted trends from DFT, as highlighted by the need to re-sort the reaction grid in Figure 4.5. Possibly most alarmingly, the most basic carbene according to experiment (**CBA**) is predicted to be only moderately basic by DFT. Also, **NHC-7** is predicted to be significantly more basic than **BiCAAC** and nearly equivalent to **CAAC-6**, yet it actually forms an equilibrium with **CAAC-5**, experimentally confirmed to be much less basic than **BiCAAC** and **CAAC-6**. DFT also gets the ordering of 4 different NHCs (***bz*NHC**, ***s*NHC**, **NHC-5**, **MAC**) wrong. Together, these data suggest that DFT prediction of carbene properties at the popular B3LYP/def2-TZVPP level of theory is not adequate for drawing general conclusions. Though calculations at this level often prove adequate for predicting trends within a carbene family (like the basicity trend of **CAAC-5**, **BiCAAC**, and **CAAC-6**)[71, 75] it seems inadequate for comparing between families. Furthermore, the use of predicted gas-phase proton affinity instead of HOMO often results in the same erroneous predictions (Figure 4.4). Proton affinity predicts **BiCAAC** is less basic than **NHC-7**, even though it is much more basic in reality, **CBA** is still predicted to be too low, and several equilibria would be expected that do not occur in actual experiment.

DFT on abbreviated carbene structures has proven ubiquitous[15, 21, 47, 53, 71, 75-76, 88, 163, 183-185] for prediction of carbene properties, and thus I hoped the failure to match experimental basicity

trends was only due to the choice of B3LYP as a functional. Thus, I began my search for a functional to match experiment with the M06-2X functional on abbreviated carbene structures (Figure 4.7). Just as found with B3LYP when comparing the HOMO position, the relative ordering of carbene basicity is generally wrong (Figure 4.7). Just as found with B3LYP, M06-2X/def2-TZVPP predicts that **NHC-7** is more basic than **BiCAAC** and **NHC-6** is more basic than **CAAC-5**, in conflict with experiment. Furthermore, a nearly identical erroneous trend is found in predictions of proton affinity; which is often considered a better estimation of basicity than HOMO alone.[163, 186]

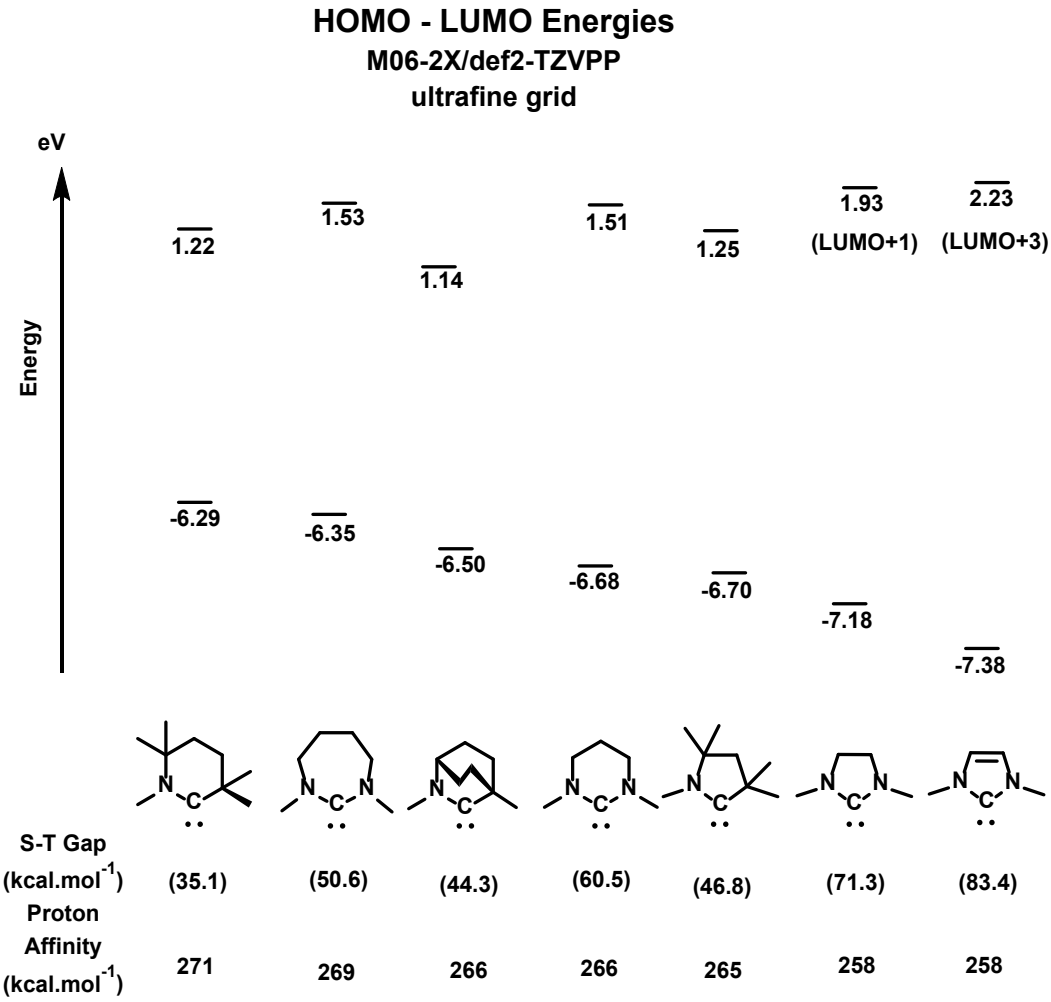


Figure 4.6: M06-2X/def2-TZVPP calculations of several carbenes.

Continuing the survey of popular functionals, I focused my attention on the problematic predictions of **BiCAAC** and **NHC-7** with the hybrids PBE ("PBE1PBE"), and ωB97X-D and the pure functionals PBE ("PBEPBE"), PW91 ("PW91PW91", "mPWPW91"), TPSS, and revTPSS. No method predicted the correct ordering, whether by HOMO position or proton affinity (Figure 4.8).

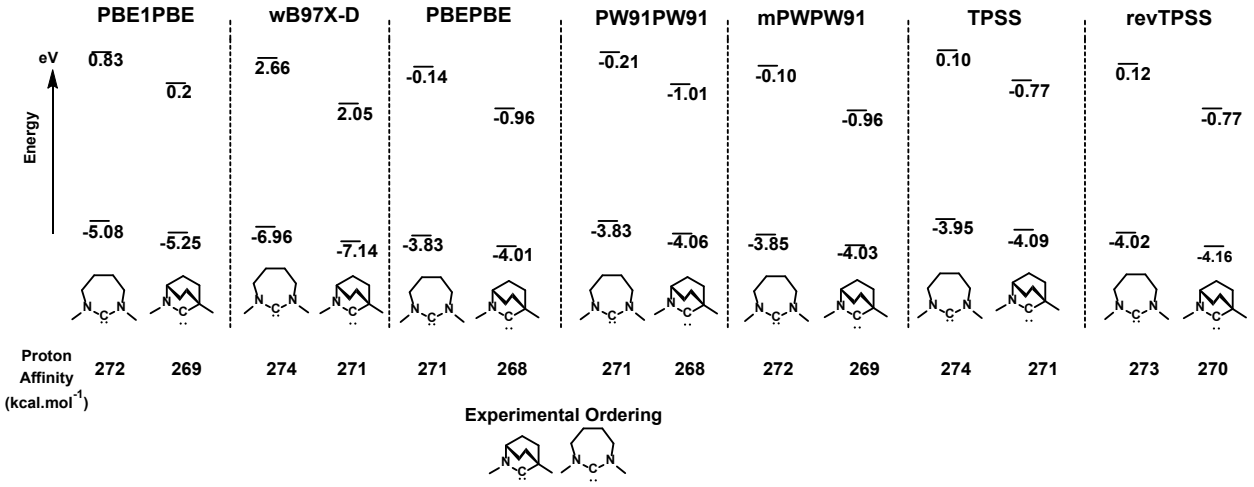


Figure 4.7: Different functionals at the def2-TZVPP level of theory.

Until this point, all calculations were done in the gas phase. Wondering if including a solvent model could improve the results, I repeated the revTPSS calculations with THF modelled as a polarizable continuum (Figure 4.9). Finally, the correct ordering is observed with the HOMO position (though the difference is likely less than the margin of error). However, the incorrect ordering persists for proton affinity. Clearly, solvent can have important effects, though the proton affinity, normally considered a better analogue to basicity, seems to be less sensitive to this than the HOMO position. At best, it seems that proton affinity is better than HOMO only randomly, which equally impairs its ability to serve as a predictive computational exercise. Furthermore, inclusion of solvent effects in this way still completely misses the fact that **NHC-7** forms an equilibrium with **CAAC-5**, and is thus much less basic than **BiCAAC**.

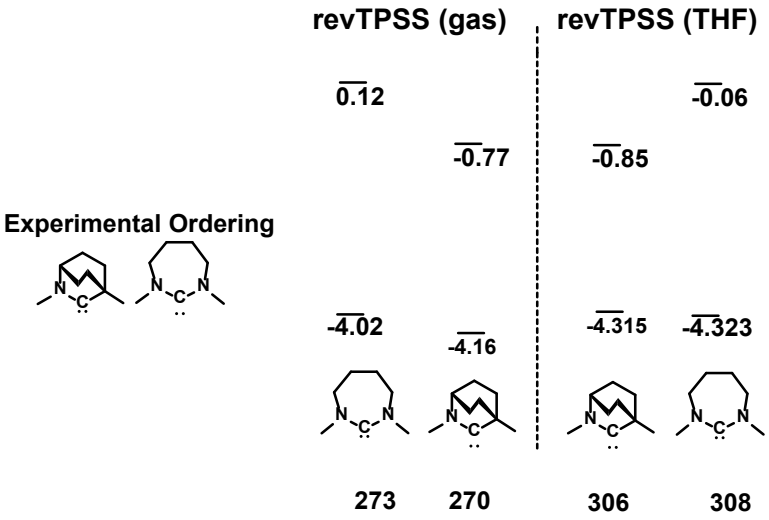


Figure 4.8: revTPSS/def2-TZVPP calculations in the gas phase and THF polarizable continuum.

After such dismal performance of a number of popular methods on truncated carbenes, I again turned to the literature, seeking accurate prediction of pKa with full carbene structures. Recently, Ji and coworkers published a study of DFT-predicted pKa on a very large number of carbene core and substituent combinations following a procedure they developed for a variety of organic acids.[160-161, 164-165] Their publication correctly predicts the experimental basicity scale for all carbenes they studied (Figure 4.10). I used their methodology on the few specific core-substituent combinations that they did not include, but we used in our experimental comparisons (Figure 4.11). Note, their method uses fine rather than ultrafine integration grids and the value of -268.34 kcal/mol for ΔG_{soln} H^+.

$$pKa = \frac{\Delta G^*_{soln}(Carb) + \Delta G^*_{soln}(H^+) - \Delta G^*_{soln}(CarbH^+)}{RT \ln(10)}$$

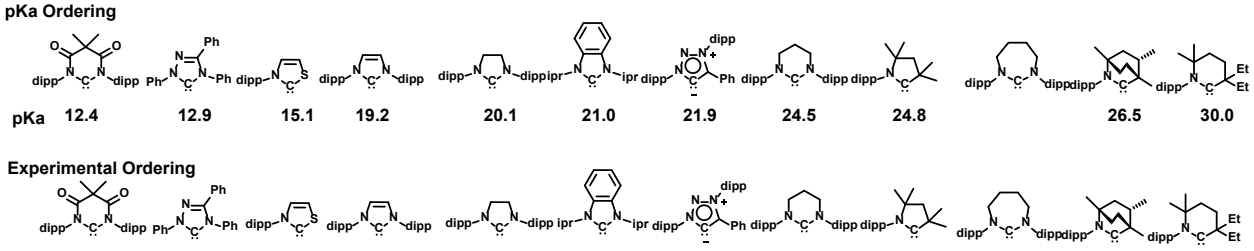


Figure 4.9: Ordering by pKa values calculated by Ji et al.

Despite using the same methods as Ji et al,[165] my predicted pKa values were consistently off by ~3 pKa units (Figure 4.11). I hoped to prevent such discrepancies by using the same method with the identical integration grid described by Ji et al. Perhaps the error is due to the integration grid choice,[144] unfortunately we do not have the computational resources necessary for the ultrafine grid. Nevertheless, the general trend and qualitative ordering was largely preserved between their study and ours except for the placement of **NHC-5**, and **DAC** giving us confidence to model carbenes not described in their paper. Though this computational method presents a significant improvement over the methods already discussed, several discrepancies remain. The **CBA** and ***a*NHC** are predicted to be much less basic than experiment shows and ***s*NHC-5** and **DAC** are predicted to be stronger bases than they actually are. Further, the carbenes that demonstrate equilibria are not predicted with this method. For example, **NHC-7** and **CAAC-5** are predicted to be within 1.2 pKa units of each other. However, **BiCAAC** and **NHC-7** are within 1 pKa unit, but do not show an equilibrium in experiment. Thus, the relative difference between the pKa of two different species as computed here cannot be taken too seriously.

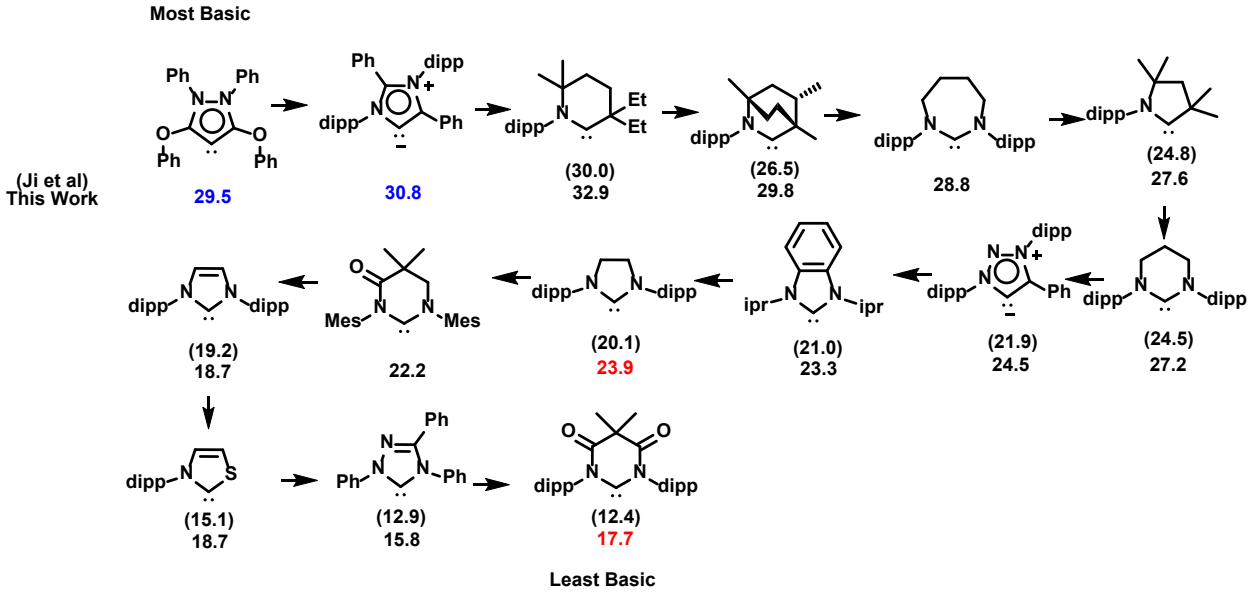


Figure 4.10: Experimental ordering of relative basicity with complete set of predicted pKa values. Red shows a predicted basicity is too high. Blue shows a predicted basicity too low.

To summarize the computational investigations, some simplistic calculations commonly employed in the literature to characterize the various donor abilities of carbenes fail to capture the *qualitative* ordering of different carbene basicities. It seems that trends *within* a family (**NHC-7**>**NHC-6**>**NHC-5**) are adequately predicted by the simplistic methods, but more care must be taken when comparing different carbenes. The full substituents must be used (major differences are extensively documented by Ji et al[164-165]) and solvent must be well-modeled before analysis can be believed (Figures 4.9 and 4.11).[187] Unfortunately, even after such considerations, major qualitative errors can sometimes persist. This is the case for the **CBA, *a*NHC**, and ***bz*NHC** that DFT forecasts to be less basic and σ-donating than found experimentally. Similarly, the pKa of **DAC** is overestimated by calculations. These observations recommend caution when relying solely on theoretical methods as a proxy for determining the σ-donating ability of a carbene lone-pair.

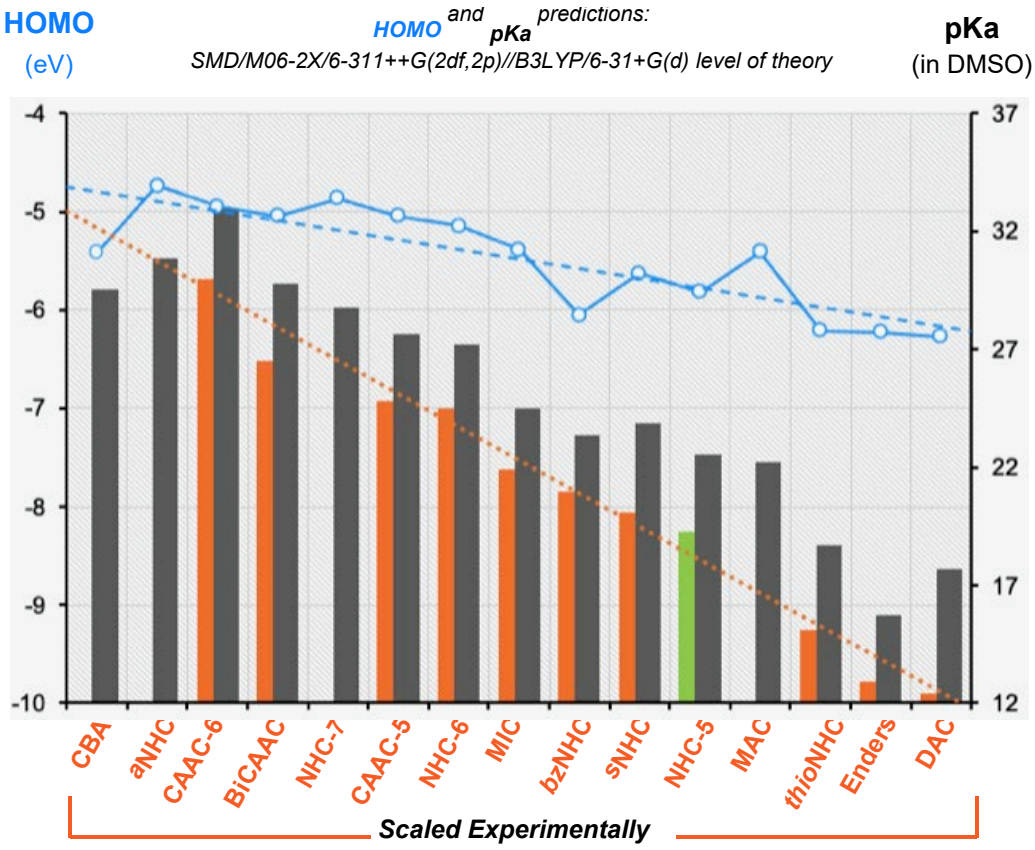
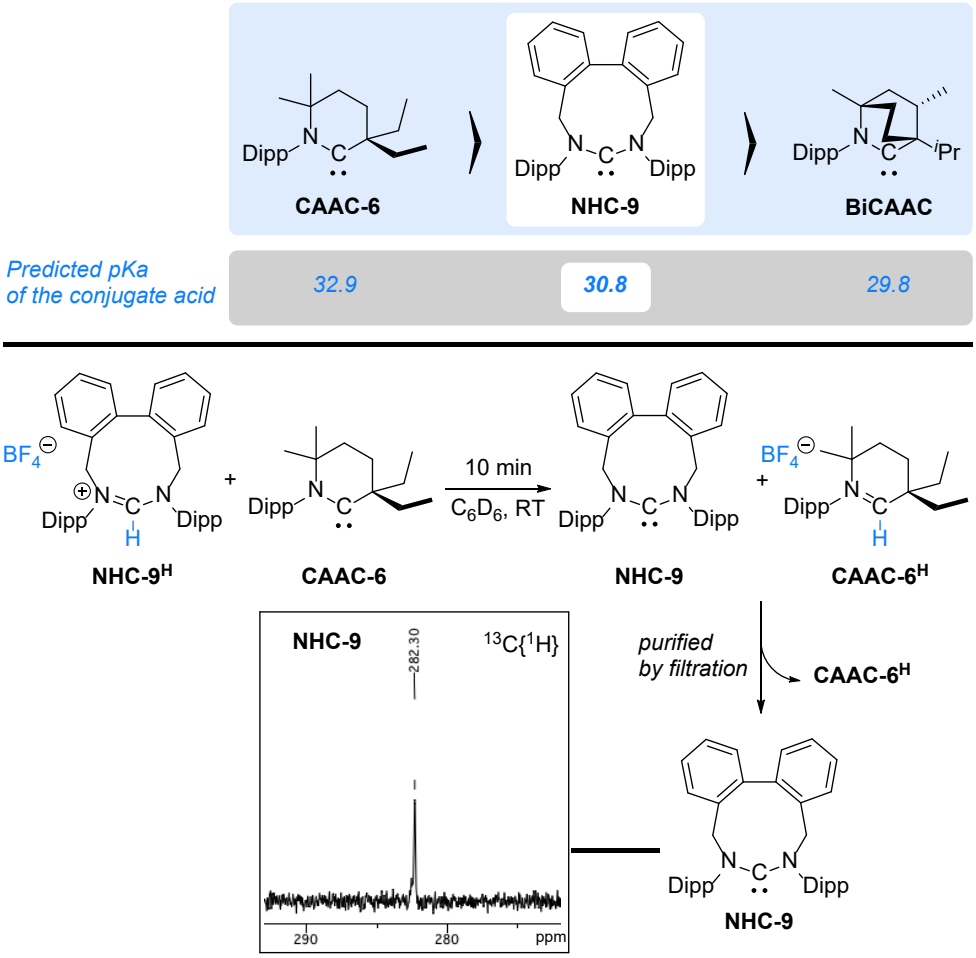


Figure 4.11: Predicted pKa and HOMO energies vs. experimental carbene Brønsted basicity.

To illustrate the synthetic usefulness of the carbene-carbene proton exchange, we targeted **NHC-9**, which had so far eluded spectroscopic characterization.[188] Using DFT, I predicted the pKa of **NHC-9^{H}** to be between those of **CAAC-6^{H}** and **BiCAAC^{H}** (Scheme 4.3). Accordingly, Francois reacted **NHC-9^{H}** with **CAAC-6** (1:1) to afford the corresponding free **NHC-9** along with **CAAC-6^{H}**. Gratifyingly, **NHC-9** was isolated in nearly quantitative yield by a simple filtration and fully characterized by NMR spectroscopy. Note also that this exchange reaction allows for the complete recycling of the sacrificial iminium.



Scheme 4.3: Using carbenes as neutral non nucleophilic bases

In conclusion, a simple experimental procedure for scaling the lone pair properties of carbenes according to their respective basicity is described. It is shown that this scale correlates with the predicted HOMO energies of the respective carbenes, although some inconsistencies

have been observed. We are confident that these results will help further our understanding of carbene electronic properties. It is also demonstrated that the carbene-carbene proton exchange reaction provides a practical route for the preparation of carbenes sensitive to classical alkali bases. Along this line, the use of the most basic carbene, **CBA**, which is readily available in large quantities, is under current investigation to replace expensive non-nucleophilic neutral bases, such as the Schwesinger and the Verkade bases.[189-190]

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Catalysis Science Program, under Award No. DE-SC0009376 (GB). Thanks are due to the Alfred P. Sloan Foundations University Centre for Exemplary Mentoring (G.P.J.). This material is based upon work supported by the National Science Foundation Graduate Research Fellowship Program under Grant No. (DGE-1650112; G.P.J.). We also acknowledge the Keck Foundation as well as the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number TG-CHE190107 for provided computational resources. We also acknowledge Dr. R. Konecny for valued discussions on computation.

Chapter 4, in part, is currently being prepared for submission for publication of the material Francois Vermersch, Sima Yazdani, Glen P. Junor, Douglas B Grotjahn, Rodolphe Jazzar, and Guy Bertrand “Experimental Comparison of Carbene Brønsted Basicity, a Proxy for σ-Donating Properties.” The dissertation author was co-author of this paper.

Supporting Information

All calculations used the Gaussian09[86] program suite with ultrafine[144] (99,590) integration grids (“integral=ultrafinegrid”). With the def2-TZVPP[87, 191] basis set, hybrid functionals B3LYP[82], M06-2X[83], PBE (“PBE1PBE”[192-193]), and ωB97X-D[84, 194] were compared in addition to the pure functionals PBE (“PBEPBE[195-196]”), PW91 (“PW91PW91”, “mPWPW91”)[197-199], TPSS[200], and revTPSS[201]. HOMO/LUMO and proton affinity calculations were done in the gas phase, with the

exclusion of one PCM[152] calculation with THF as solvent. Predictions of molecule pKa were done with the SMD[202] solvent model.

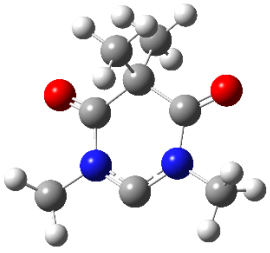
For completeness, the XYZ coordinates and energetics are included as pertaining to various calculations used for this manuscript. However, for convenience, the reader is recommended to download the files directly from UCSD Library Digital Collections.[187] The data is organized here in a manner that resembles the structure of the Digital Collection. First, the various levels of theory used for the sake of attaining HOMO/LUMO positions, singlet-triplet gaps, and proton affinities are grouped together. At the end, the results for pKa calculations at the M06-2X/6-311++G(2df,2p) level of theory using DMSO as solvent, modelled by the SMD method, are denoted accordingly.

For clarity, DFT functionals that have separate, changeable exchange and correlation functionals in the Gaussian09 program are given a name that specifies each. For example, the PW91 pure functional is noted as “PW91PW91” to emphasize that the PW91 exchange and PW91 correlation functionals were chosen for the specific calculation. In contrast, some functionals like B3LYP or M06-2X do not have the option for different exchange and correlation functionals, and thus receive the simpler name format. We found that calculations of HOMO/LUMO or proton affinity at the various [functional]/def2-TZVPP levels of theory had the same qualitative errors in the ordering of carbene basicity, leading us to pursue a more rigorous type of calculation used for the prediction of pKa.

HOMO/LUMO, Singlet-Triplet Gap, Proton Affinity

B3LYP/def2-TZVPP

Diamidocarbene (DAC)

Singlet: 

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Thermal correction to Enthalpy= 0.210079
Thermal correction to Gibbs Free Energy= 0.158237
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Sum of electronic and thermal Energies= -572.023148
Sum of electronic and thermal Enthalpies= -572.022204
Sum of electronic and thermal Free Energies= -572.074047

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H	3.05728300	-1.50954900	0.79034900
H	2.15570500	-2.89006600	0.10024500
H	2.93703400	-1.68645800	-0.96052200
C	0.00001600	1.65334600	1.51042200
H	0.88870100	2.26199400	1.66849000
H	-0.88858400	2.26213000	1.66844300
H	-0.00006400	0.84138300	2.23865100
C	0.00005400	2.29636400	-0.93755900
H	-0.88948900	2.90200500	-0.78390700
H	0.88962500	2.90196400	-0.78389800
H	0.00005400	1.94430600	-1.96938500
N	-1.15067000	-1.08845100	-0.00625100
C	-1.27496700	0.30545300	-0.10936900
O	-2.35635100	0.82260600	-0.26357700
C	-2.41222800	-1.84405200	-0.01983800
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H	-2.15582900	-2.88996500	0.10056600
H	-3.05739600	-1.50929800	0.79039000
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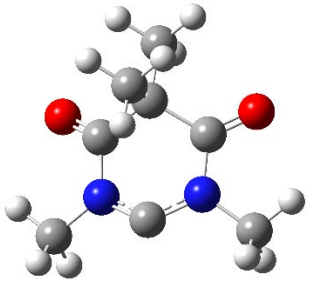

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Zero-point correction= 0.194686 (Hartree/Particle)
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H	-0.88519800	1.93206700	1.96331500
H	0.00000800	0.42700000	2.25015500
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H	-0.88936200	3.01469400	-0.33310800
H	0.88940000	3.01467400	-0.33314600
H	-0.00002200	2.29315100	-1.67247600
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H	-2.47220600	-2.54411400	0.75514700
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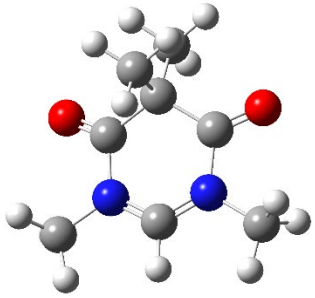
O	2.29789200	0.84323400	-0.60006500



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Sum of electronic and thermal Enthalpies= -572.414010

Sum of electronic and thermal Free Energies= -572.466302

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H	-0.88675900	2.17672500	1.77847100
H	0.00007000	0.71839400	2.24991300
C	-0.00000500	2.41676800	-0.82272200
H	-0.88665100	3.01019400	-0.61705900
H	0.88666100	3.01018300	-0.61710800
H	-0.00003400	2.15027800	-1.87887800
N	-1.17026800	-1.07018500	-0.00870800
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C	-2.43041400	-1.84127500	-0.02260300
H	-2.93481800	-1.69078600	-0.97313200
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N	1.17024300	-1.07020300	-0.00872500
C	1.27492000	0.36792100	-0.14653000
O	2.35018100	0.83776200	-0.35429900
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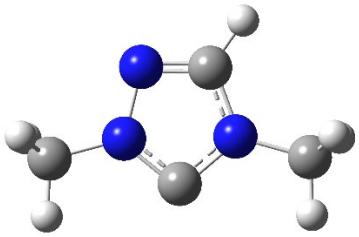
H	-0.00002400	-2.75649500	0.09981100

Enders NHC



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N	1.03808100	-0.13452000	-0.00003200
N	-1.05249800	-0.11992300	-0.00001300
C	2.44120300	-0.49177000	0.00002700
H	2.93108400	-0.09058900	0.88649100
H	2.50534400	-1.57509700	0.00016300
H	2.93112800	-0.09080800	-0.88651300
C	-2.44743200	-0.52316000	0.00002000
H	-2.47509500	-1.60821100	-0.00001400
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H	-2.95850900	-0.15072300	-0.88804800
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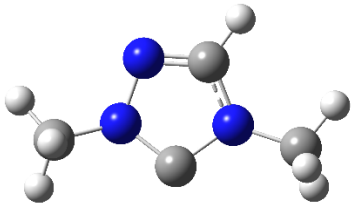
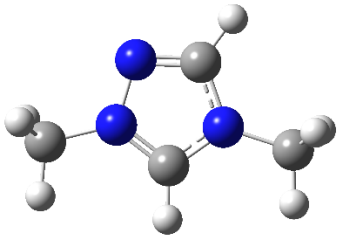
H	-1.22255300	2.04556600	0.00002400

Triplet:



Electronic energy: -320.823201193 Hartree/particle
Zero-point correction= 0.111913 (Hartree/Particle)
Thermal correction to Energy= 0.119149
Thermal correction to Enthalpy= 0.120093
Thermal correction to Gibbs Free Energy= 0.079687
Sum of electronic and zero-point Energies= -320.711289
Sum of electronic and thermal Energies= -320.704053
Sum of electronic and thermal Enthalpies= -320.703108
Sum of electronic and thermal Free Energies= -320.743515

C	-0.00818100	-0.95538200	-0.03715800
N	-0.70494900	1.17695100	0.00843600
N	-1.12823600	-0.13197600	-0.31564500
N	1.11521200	-0.10650800	-0.13779800
C	-2.44658400	-0.48975800	0.16595500
H	-3.14947400	0.27020100	-0.16654200
H	-2.72455300	-1.44993600	-0.26552900
H	-2.48000400	-0.56459000	1.25902600
C	2.47613700	-0.51809300	0.09776000
H	2.75857400	-1.29008900	-0.61857300
H	3.13534100	0.33751800	-0.03420900
H	2.60516000	-0.91776000	1.10888500
C	0.59147800	1.13590300	0.04445500
H	1.20366300	2.00936700	0.20593300

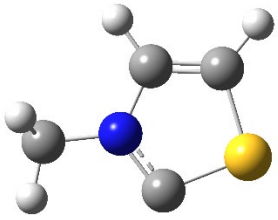


Carbene-H^+:

Electronic energy: -321.369691113 Hartree/particle
Zero-point correction= 0.128265 (Hartree/Particle)
Thermal correction to Energy= 0.135366
Thermal correction to Enthalpy= 0.136311
Thermal correction to Gibbs Free Energy= 0.095924
Sum of electronic and zero-point Energies= -321.241426
Sum of electronic and thermal Energies= -321.234325
Sum of electronic and thermal Enthalpies= -321.233381
Sum of electronic and thermal Free Energies= -321.273767

N	0.70659000	1.21246100	0.00000100
N	1.06558000	-0.09382900	0.00000700
N	-1.07744000	-0.08322100	-0.00000500
C	2.47973000	-0.46918300	0.00000600
H	2.95007500	-0.05883800	0.88961700
H	2.55310100	-1.55261800	0.00009600
H	2.95004100	-0.05898600	-0.88969200
C	-2.48717700	-0.50062200	-0.00000300
H	-2.53188900	-1.58521300	-0.00003000
H	-2.97701900	-0.11698000	0.89132800
H	-2.97703300	-0.11693500	-0.89130600
C	-0.59504600	1.19917100	-0.00000500
H	-1.21885500	2.07699300	-0.00000800
C	0.00098100	-0.87645300	-0.00000200
H	-0.00246200	-1.95278400	-0.00000200

Thiazolylidene (*thio*NHC)

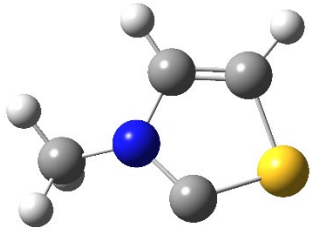


Singlet:

Electronic energy: -608.427192132 Hartree/particle
Zero-point correction= 0.082667 (Hartree/Particle)
Thermal correction to Energy= 0.088256
Thermal correction to Enthalpy= 0.089200
Thermal correction to Gibbs Free Energy= 0.053223
Sum of electronic and zero-point Energies= -608.344525
Sum of electronic and thermal Energies= -608.338936

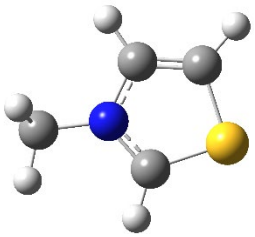
Sum of electronic and thermal Enthalpies= -608.337992
Sum of electronic and thermal Free Energies= -608.373969

C	-0.08570800	-1.15193000	-0.00002500
N	-0.89840000	-0.08047100	0.00000000
C	-2.35306100	-0.23543500	-0.00000100
H	-2.78340100	0.22734200	-0.88849200
H	-2.57109200	-1.29772500	-0.00003900
H	-2.78339500	0.22727700	0.88852700
C	1.02010900	1.14728100	0.00002300
H	1.69973300	1.98221000	0.00003900
C	-0.32430900	1.19094600	0.00003000
H	-0.95575500	2.06565900	0.00005200
S	1.50878300	-0.52166500	-0.00001600



Triplet:
Electronic energy: -608.321319320 Hartree/particle
Zero-point correction= 0.080535 (Hartree/Particle)
Thermal correction to Energy= 0.086682
Thermal correction to Enthalpy= 0.087626
Thermal correction to Gibbs Free Energy= 0.049345
Sum of electronic and zero-point Energies= -608.240785
Sum of electronic and thermal Energies= -608.234638
Sum of electronic and thermal Enthalpies= -608.233693
Sum of electronic and thermal Free Energies= -608.271974

C	-0.01309200	-1.00095000	0.50081700
N	-1.00071500	-0.04480100	0.30409800
C	-2.29266600	-0.34456200	-0.30198800
H	-2.95051600	0.51550200	-0.18370300
H	-2.19708400	-0.57711700	-1.36793700
H	-2.73965900	-1.19594900	0.20695700
C	0.94472600	1.13828600	-0.06572100
H	1.61801900	1.97726200	-0.12996900
C	-0.38555400	1.19213500	0.14046400
H	-0.98158400	2.09128600	0.20123500
S	1.54595900	-0.52542700	-0.15604400

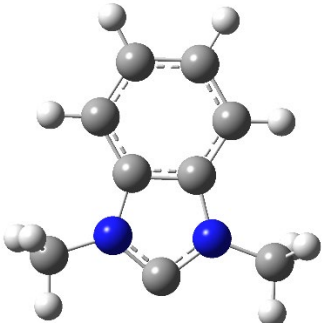


Carbene-H^+:

Electronic energy: -608.839211122 Hartree/particle
Zero-point correction= 0.096266 (Hartree/Particle)
Thermal correction to Energy= 0.101916
Thermal correction to Enthalpy= 0.102861
Thermal correction to Gibbs Free Energy= 0.066581
Sum of electronic and zero-point Energies= -608.742945
Sum of electronic and thermal Energies= -608.737295
Sum of electronic and thermal Enthalpies= -608.736351
Sum of electronic and thermal Free Energies= -608.772631

N	-0.92359300	-0.02691500	-0.00000100
C	-2.38739700	-0.20854200	0.00000100
H	-2.61281000	-1.26988800	-0.00000300
H	-2.80297500	0.25588000	0.89113300
H	-2.80297700	0.25588500	-0.89112800
C	-0.32775800	1.21830900	-0.00001300
H	-0.94137700	2.10435300	-0.00002300
C	1.02251800	1.14647700	-0.00001100
H	1.72698600	1.96116400	-0.00001900
C	-0.05238600	-1.02430900	0.00001000
H	-0.34635300	-2.06138100	0.00002000
S	1.54467500	-0.49057600	0.00000700

Benzannulated NHC (*bz*NHC)

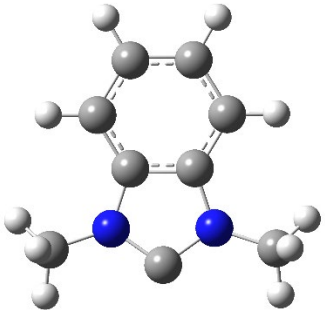


Singlet:

Electronic energy: -458.623833611 Hartree/particle
Zero-point correction= 0.173602 (Hartree/Particle)
Thermal correction to Energy= 0.182950
Thermal correction to Enthalpy= 0.183894
Thermal correction to Gibbs Free Energy= 0.139399
Sum of electronic and zero-point Energies= -458.450232
Sum of electronic and thermal Energies= -458.440884

Sum of electronic and thermal Enthalpies= -458.439939
Sum of electronic and thermal Free Energies= -458.484434

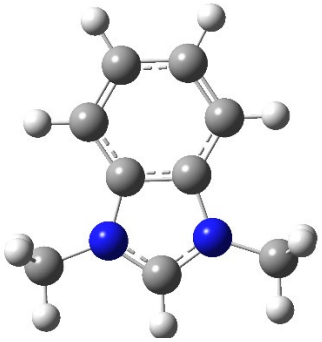
C	-0.17037300	0.70037500	-0.00002000
C	-0.17034400	-0.70038300	-0.00001600
C	-1.35672200	-1.42256600	-0.00003300
C	-2.54565100	-0.69929700	-0.00002000
C	-2.54567300	0.69917800	0.00002100
C	-1.35676400	1.42250000	0.00004000
H	-1.36245100	-2.50379900	-0.00004800
H	-3.48857600	-1.22916300	-0.00003200
H	-3.48860300	1.22902900	0.00003700
H	-1.36259500	2.50373300	0.00010600
C	1.63270300	2.44522000	-0.00004700
H	1.28049800	2.97453300	0.88732200
H	2.71810300	2.42664900	-0.00056400
H	1.27962400	2.97460100	-0.88702100
C	1.63288000	-2.44511800	0.00002700
H	2.71827500	-2.42633800	0.00014000
H	1.28028200	-2.97452900	0.88719500
H	1.28040300	-2.97457700	-0.88714200
C	2.01040700	0.00005700	0.00000500
N	1.16874000	1.07343200	0.00007400
N	1.16872700	-1.07342300	-0.00003600



Triplet:
Electronic energy: -458.497313812 Hartree/particle
Zero-point correction= 0.170339 (Hartree/Particle)
Thermal correction to Energy= 0.180448
Thermal correction to Enthalpy= 0.181392
Thermal correction to Gibbs Free Energy= 0.133956
Sum of electronic and zero-point Energies= -458.326974
Sum of electronic and thermal Energies= -458.316866
Sum of electronic and thermal Enthalpies= -458.315922
Sum of electronic and thermal Free Energies= -458.363358

C	-0.14942300	-0.70879500	-0.07628500
C	-0.14952700	0.70876700	-0.07637400
C	-1.33636500	1.42207800	0.00783500

C	-2.53482000	0.69382900	0.03173600
C	-2.53471400	-0.69423400	0.03180000
C	-1.33614300	-1.42229600	0.00797000
H	-1.34335900	2.50228500	0.03904800
H	-3.47481500	1.22793300	0.06291900
H	-3.47462700	-1.22848000	0.06301800
H	-1.34296000	-2.50250000	0.03931200
C	1.61295200	-2.48379800	0.07987500
H	0.99540100	-3.17289100	-0.49451000
H	2.64363900	-2.58199700	-0.25625400
H	1.56156000	-2.76119300	1.13934100
C	1.61245400	2.48404400	0.08004100
H	2.64331200	2.58241200	-0.25549900
H	0.99514000	3.17311600	-0.49463500
H	1.56043200	2.76136000	1.13950200
C	1.96083200	0.00015800	0.10379700
N	1.16900300	-1.13332700	-0.15166500
N	1.16882500	1.13353200	-0.15185100



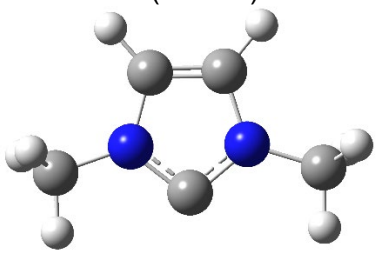
Carbene-H^+:

Electronic energy: -459.052307199 Hartree/particle
Zero-point correction= 0.187561 (Hartree/Particle)
Thermal correction to Energy= 0.197076
Thermal correction to Enthalpy= 0.198021
Thermal correction to Gibbs Free Energy= 0.153060
Sum of electronic and zero-point Energies= -458.864746
Sum of electronic and thermal Energies= -458.855231
Sum of electronic and thermal Enthalpies= -458.854287
Sum of electronic and thermal Free Energies= -458.899248

C	-0.20861900	0.70037700	-0.00000700
C	-0.20861800	-0.70037800	0.00000300
C	-1.39171700	-1.43211400	0.00001200
C	-2.56837700	-0.70260600	0.00001500
C	-2.56837800	0.70260200	0.00000900
C	-1.39171900	1.43211200	0.00000000
H	-1.39948400	-2.51234000	0.00001900
H	-3.51333900	-1.22696400	0.00002300

H	-3.51334100	1.22695900	0.00001300
H	-1.39948700	2.51233800	-0.00000100
C	1.61456800	2.47468800	-0.00002600
H	1.25762300	2.98898100	0.88992100
H	2.70056500	2.46820300	-0.00033600
H	1.25713100	2.98912700	-0.88968900
C	1.61457300	-2.47468600	0.00002200
H	2.70057000	-2.46819800	0.00004900
H	1.25736200	-2.98904900	0.88982000
H	1.25740500	-2.98905600	-0.88979000
N	1.12754100	1.09658700	-0.00002200
N	1.12754200	-1.09658600	0.00000600
C	1.88321100	0.00000100	-0.00001100
H	2.95986100	0.00000100	-0.00001700

Unsaturated NHC5 (NHC-5)

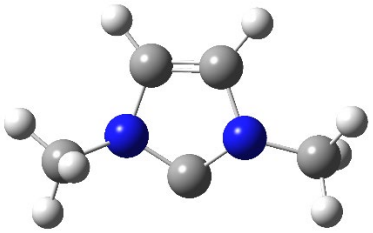


Singlet:

Electronic energy: -304.916823118 Hartree/particle
Zero-point correction= 0.126295 (Hartree/Particle)
Thermal correction to Energy= 0.133303
Thermal correction to Enthalpy= 0.134248
Thermal correction to Gibbs Free Energy= 0.095285
Sum of electronic and zero-point Energies= -304.790528
Sum of electronic and thermal Energies= -304.783520
Sum of electronic and thermal Enthalpies= -304.782575
Sum of electronic and thermal Free Energies= -304.821538

C	0.00008500	0.97669200	-0.00001300
N	1.06075100	0.12142700	-0.00000800
N	-1.06085600	0.12129700	0.00000300
C	2.43953700	0.57091600	-0.00000500
H	2.96435400	0.21386600	-0.88748300
H	2.43247000	1.65655900	-0.00008800
H	2.96430900	0.21400400	0.88755600
C	-2.43953400	0.57092600	0.00000100
H	-2.43232100	1.65657100	0.00000900
H	-2.96443100	0.21404200	-0.88750400
H	-2.96443800	0.21402800	0.88749600
C	-0.67581700	-1.21025100	0.00001300
H	-1.37485700	-2.02791000	0.00002300
C	0.67576300	-1.21041300	0.00000600

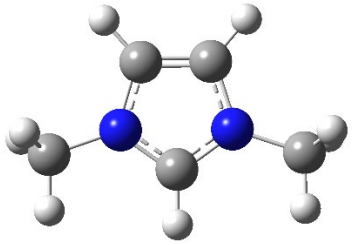
H	1.37544400	-2.02744300	0.00001200



Triplet:

Electronic energy: -304.781699920 Hartree/particle
Zero-point correction= 0.123164 (Hartree/Particle)
Thermal correction to Energy= 0.130573
Thermal correction to Enthalpy= 0.131517
Thermal correction to Gibbs Free Energy= 0.090876
Sum of electronic and zero-point Energies= -304.658535
Sum of electronic and thermal Energies= -304.651127
Sum of electronic and thermal Enthalpies= -304.650183
Sum of electronic and thermal Free Energies= -304.690824

C	0.01941500	-0.88097900	-0.43173400
N	1.05690000	-0.16287500	0.22126300
N	-1.15817800	-0.12515800	-0.39473000
C	2.44590600	-0.52677800	0.05443700
H	3.06603000	0.13783000	0.65445800
H	2.59595700	-1.54660500	0.40595500
H	2.76636000	-0.47100500	-0.99322300
C	-2.33870700	-0.60332900	0.32737900
H	-2.63717800	-1.56769500	-0.07819900
H	-2.14615600	-0.71293800	1.40210400
H	-3.15777700	0.10091300	0.18238000
C	-0.69459400	1.19323700	-0.17328200
H	-1.34628200	2.04456800	-0.27441000
C	0.61372800	1.15945900	0.15692600
H	1.29349700	1.98150400	0.31284900



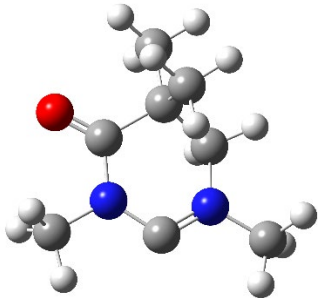
Carbene-H^+:

Electronic energy: -305.346165136 Hartree/particle
Zero-point correction= 0.140336 (Hartree/Particle)
Thermal correction to Energy= 0.147518
Thermal correction to Enthalpy= 0.148462
Thermal correction to Gibbs Free Energy= 0.108747

Sum of electronic and zero-point Energies= -305.205829
Sum of electronic and thermal Energies= -305.198647
Sum of electronic and thermal Enthalpies= -305.197703
Sum of electronic and thermal Free Energies= -305.237418

N	1.08483700	0.08382300	-0.00000600
N	-1.08483800	0.08381800	0.00000200
C	2.47488900	0.55169000	-0.00000600
H	2.98057400	0.18582200	-0.89032500
H	2.48277500	1.63743600	-0.00008200
H	2.98053600	0.18594500	0.89038400
C	-2.47488800	0.55168900	-0.00000200
H	-2.48277100	1.63743500	0.00000500
H	-2.98055300	0.18588900	-0.89036000
H	-2.98056000	0.18588000	0.89034900
C	-0.67890000	-1.23337000	0.00001500
H	-1.37933300	-2.04876200	0.00002500
C	0.67890200	-1.23337000	0.00000900
H	1.37934200	-2.04875700	0.00001500
C	-0.00000100	0.85859100	-0.00001000
H	-0.00000900	1.93423900	-0.00002200

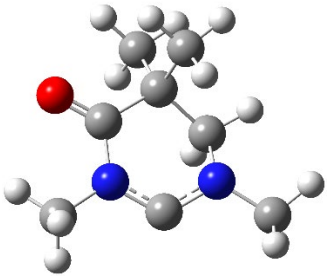
Monoamidocarbene (MAC)



Singlet:
Electronic energy: -498.172714661 Hartree/particle
Zero-point correction= 0.215428 (Hartree/Particle)
Thermal correction to Energy= 0.227237
Thermal correction to Enthalpy= 0.228181
Thermal correction to Gibbs Free Energy= 0.178819
Sum of electronic and zero-point Energies= -497.957287
Sum of electronic and thermal Energies= -497.945478
Sum of electronic and thermal Enthalpies= -497.944534
Sum of electronic and thermal Free Energies= -497.993896

C	-1.15668200	1.28753100	0.10167200
C	-0.87844300	-1.06503800	-0.58691100
C	0.52314200	-1.07708300	0.01931900
H	-1.40382500	-1.98657400	-0.33026000
H	-0.81867200	-1.01956200	-1.68064900
C	0.46622400	-1.41822800	1.52304800

H	0.08008900	-2.43040300	1.65790500
H	1.46368800	-1.37299500	1.95886700
H	-0.17875500	-0.73131600	2.07083600
C	1.40207300	-2.09071300	-0.71698200
H	2.41106500	-2.08705100	-0.31147400
H	0.98639100	-3.09443000	-0.61130700
H	1.47049900	-1.85795400	-1.78034900
N	0.21560200	1.37919400	-0.03971000
C	1.12369700	0.32329000	-0.10310500
O	2.31920500	0.52181500	-0.16745900
C	0.80161400	2.72248000	0.03083100
H	1.35318700	2.94394600	-0.88175800
H	-0.01787300	3.42121000	0.15434100
H	1.49421900	2.79495800	0.86866300
C	-3.09972500	-0.10461000	-0.04332300
H	-3.35564900	-0.87708700	0.68545700
H	-3.54903200	0.83861000	0.24936300
H	-3.49185200	-0.40764200	-1.01824100
N	-1.65682000	0.08166100	-0.10872100

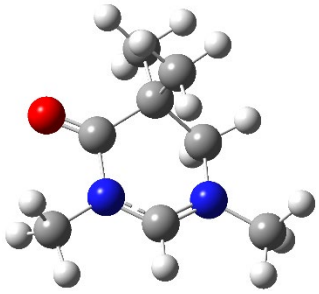


Triplet:

Electronic energy: -498.081374459 Hartree/particle
Zero-point correction= 0.213284 (Hartree/Particle)
Thermal correction to Energy= 0.225622
Thermal correction to Enthalpy= 0.226566
Thermal correction to Gibbs Free Energy= 0.174258
Sum of electronic and zero-point Energies= -497.868090
Sum of electronic and thermal Energies= -497.855753
Sum of electronic and thermal Enthalpies= -497.854809
Sum of electronic and thermal Free Energies= -497.907116

C	-1.07937600	1.26594800	-0.12330500
C	-0.94833100	-1.02123100	-0.57652700
C	0.49334300	-1.08182500	-0.03421900
H	-1.45736600	-1.96281500	-0.36295700
H	-0.94716700	-0.87763000	-1.66557100
C	-3.13416400	0.00474000	0.06440100
H	-3.46606000	-0.95396500	0.46083700
H	-3.53485900	0.80028000	0.69115300
H	-3.53843400	0.12595700	-0.94904500

C	0.50145300	-1.68598900	1.38321000
H	0.16862100	-2.72590200	1.34885500
H	1.50789600	-1.66107500	1.79875200
H	-0.16182100	-1.13562800	2.05027500
C	1.34994200	-1.94581100	-0.97063000
H	2.37267300	-1.99721400	-0.60439000
H	0.94503100	-2.95828100	-1.02436300
H	1.37460400	-1.53401400	-1.98063900
N	0.27817100	1.40465600	-0.01683100
C	1.13503500	0.31752000	0.05166100
O	2.34545000	0.46708700	0.16998600
C	0.83308800	2.75645400	-0.04620900
H	1.88773500	2.68525500	-0.29114500
H	0.30563900	3.34191800	-0.79807600
H	0.72087600	3.23782400	0.92585800
N	-1.68487300	0.05530800	0.09544200



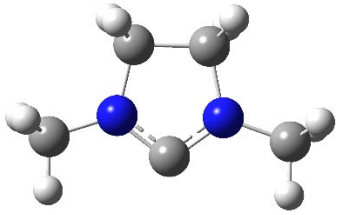
Carbene-H^+:

Electronic energy: -498.596824082 Hartree/particle
Zero-point correction= 0.229354 (Hartree/Particle)
Thermal correction to Energy= 0.241420
Thermal correction to Enthalpy= 0.242364
Thermal correction to Gibbs Free Energy= 0.192367
Sum of electronic and zero-point Energies= -498.367470
Sum of electronic and thermal Energies= -498.355405
Sum of electronic and thermal Enthalpies= -498.354460
Sum of electronic and thermal Free Energies= -498.404457

C	-0.74455300	-1.20706000	-0.55458100
C	0.66055600	-1.04492100	0.03919800
H	-1.17696600	-2.15351400	-0.23519500
H	-0.71353700	-1.20707800	-1.64806700
C	-3.09213700	-0.42014200	-0.06666200
H	-3.27610000	-1.15925700	0.71128800
H	-3.64463500	0.48756300	0.16002200
H	-3.42738700	-0.81664600	-1.02441900
C	0.65414800	-1.33246500	1.55878900
H	0.36527200	-2.36988400	1.72846100
H	1.64926300	-1.18697200	1.97521400
H	-0.03930000	-0.69384000	2.10774700

C	1.62381000	-1.99539100	-0.68042000
H	2.62800500	-1.89482000	-0.27655800
H	1.30005700	-3.02707300	-0.54283300
H	1.66963700	-1.78632500	-1.74909500
N	0.09981300	1.39598600	-0.02290800
C	1.13037300	0.39424500	-0.13698300
O	2.26188200	0.75127200	-0.27474300
C	0.53222400	2.80373000	0.06008800
H	1.02895300	3.08496400	-0.86460800
H	-0.33902900	3.43315500	0.21669600
H	1.23064400	2.92108300	0.88395300
C	-1.19040100	1.07227900	0.04873100
H	-1.89379400	1.86604700	0.26551700
N	-1.65699300	-0.12873400	-0.13696800

Saturated NHC5 (*s*NHC)

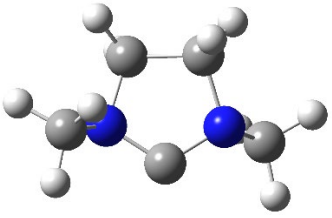


Singlet:

Electronic energy: -306.121209099 Hartree/particle
Zero-point correction= 0.148724 (Hartree/Particle)
Thermal correction to Energy= 0.156549
Thermal correction to Enthalpy= 0.157494
Thermal correction to Gibbs Free Energy= 0.116264
Sum of electronic and zero-point Energies= -305.972485
Sum of electronic and thermal Energies= -305.964660
Sum of electronic and thermal Enthalpies= -305.963716
Sum of electronic and thermal Free Energies= -306.004945

N	1.07211700	0.20721000	-0.03547900
C	0.00000500	1.01241300	-0.00002300
C	-0.76587600	-1.23311000	-0.03402900
H	-1.22943400	-1.77444400	0.79357800
H	-1.14523800	-1.66264000	-0.96639300
N	-1.07211400	0.20721000	0.03540900
C	-2.43794500	0.66351300	0.00309900
H	-2.43629800	1.74884200	0.04881100
H	-2.94395200	0.34737900	-0.91600000
H	-3.00634000	0.27079800	0.85212800
C	2.43795300	0.66350600	-0.00306000
H	2.43632300	1.74883000	-0.04890800
H	2.94384200	0.34748300	0.91614200
H	3.00643900	0.27067500	-0.85197000
C	0.76586400	-1.23311900	0.03404600
H	1.14522900	-1.66258500	0.96643500

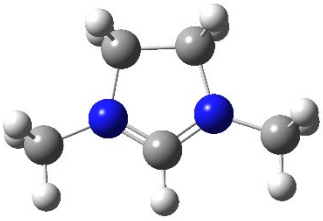
H	1.22941000	-1.77449400	-0.79353600



Triplet:

Electronic energy: -306.003832236 Hartree/particle
Zero-point correction= 0.147259 (Hartree/Particle)
Thermal correction to Energy= 0.155031
Thermal correction to Enthalpy= 0.155975
Thermal correction to Gibbs Free Energy= 0.113766
Sum of electronic and zero-point Energies= -305.856573
Sum of electronic and thermal Energies= -305.848802
Sum of electronic and thermal Enthalpies= -305.847857
Sum of electronic and thermal Free Energies= -305.890067

N	-1.08746300	0.29374000	0.44762800
C	-0.00000800	1.02921200	-0.00007200
C	-2.36944000	0.48430900	-0.23074100
H	-2.61269300	1.54453600	-0.22974900
H	-2.35543100	0.13693400	-1.27381500
H	-3.15278000	-0.04510700	0.31229900
C	-0.57775600	-1.09567200	0.51548200
H	-1.37102600	-1.80461700	0.28351200
H	-0.20644700	-1.30744800	1.52031600
C	0.57778400	-1.09567800	-0.51549000
H	1.37105700	-1.80461700	-0.28351200
H	0.20647300	-1.30746500	-1.52032100
N	1.08748300	0.29373600	-0.44765600
C	2.36940900	0.48433000	0.23080900
H	3.15279000	-0.04511300	-0.31214600
H	2.61266500	1.54455600	0.22979000
H	2.35531600	0.13700000	1.27389600



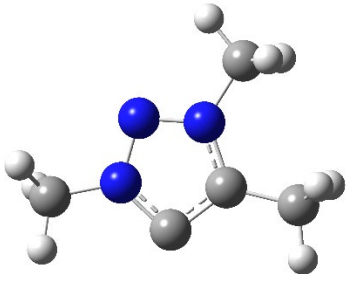
Carbene-H^+:

Electronic energy: -306.552066076 Hartree/particle
Zero-point correction= 0.163573 (Hartree/Particle)
Thermal correction to Energy= 0.171503
Thermal correction to Enthalpy= 0.172447

Thermal correction to Gibbs Free Energy= 0.131296
Sum of electronic and zero-point Energies= -306.388493
Sum of electronic and thermal Energies= -306.380563
Sum of electronic and thermal Enthalpies= -306.379619
Sum of electronic and thermal Free Energies= -306.420770

N	1.10284300	0.16611200	-0.00015200
C	-0.77383900	-1.27494200	0.00020600
H	-1.19677100	-1.74948300	0.88472600
H	-1.19725400	-1.74970200	-0.88395800
N	-1.10284400	0.16611200	0.00014600
C	-2.46934400	0.66619700	-0.00009200
H	-2.45933600	1.75311800	-0.00027900
H	-2.99432000	0.31402500	-0.88782900
H	-2.99453600	0.31432600	0.88763400
C	2.46934300	0.66619700	0.00010500
H	2.45933500	1.75311900	0.00030000
H	2.99431300	0.31402000	0.88784300
H	2.99454300	0.31433300	-0.88761900
C	0.77384000	-1.27494200	-0.00020700
H	1.19725300	-1.74969700	0.88396000
H	1.19677400	-1.74948800	-0.88472400
C	0.00000000	0.87626300	-0.00001200
H	-0.00000100	1.95721900	-0.00001300

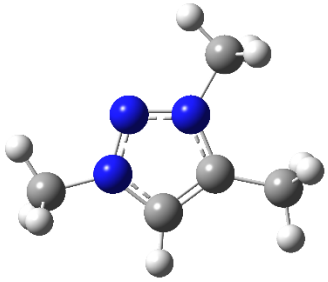
Mesoionic carbene (MIC)



Singlet:
Electronic energy: -360.248438739 Hartree/particle
Zero-point correction= 0.141915 (Hartree/Particle)
Thermal correction to Energy= 0.150625
Thermal correction to Enthalpy= 0.151569
Thermal correction to Gibbs Free Energy= 0.107438
Sum of electronic and zero-point Energies= -360.106524
Sum of electronic and thermal Energies= -360.097814
Sum of electronic and thermal Enthalpies= -360.096869
Sum of electronic and thermal Free Energies= -360.141001

C	0.57896400	-1.28324700	-0.00884800
N	1.32075200	-0.13309400	-0.01193600
C	2.77319600	-0.06208400	0.00851600

H	3.11823000	0.68122200	-0.70724700
H	3.12441800	0.20782500	1.00418100
H	3.14556300	-1.04578500	-0.25466800
C	-2.02888800	-1.42354800	0.00416200
H	-2.62436300	-1.17866300	0.88795500
H	-2.63006800	-1.17666200	-0.87522700
H	-1.85430400	-2.49640500	0.00230700
C	-0.70752300	-0.73511300	0.00078100
C	-1.65080100	1.62803900	0.00104000
H	-2.26495700	1.52304400	-0.89232700
H	-2.28037900	1.50880300	0.88161500
H	-1.18694700	2.60885500	0.01283200
N	-0.59792200	0.62765500	0.00316400
N	0.65761600	1.02308000	-0.00456100



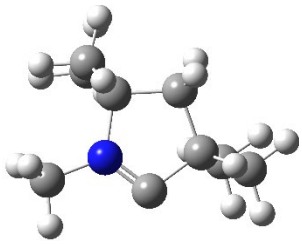
Carbene-H^+:

Electronic energy: -360.692385564 Hartree/particle
Zero-point correction= 0.155681 (Hartree/Particle)
Thermal correction to Energy= 0.164380
Thermal correction to Enthalpy= 0.165325
Thermal correction to Gibbs Free Energy= 0.121917
Sum of electronic and zero-point Energies= -360.536705
Sum of electronic and thermal Energies= -360.528005
Sum of electronic and thermal Enthalpies= -360.527061
Sum of electronic and thermal Free Energies= -360.570469

N	-1.33350100	-0.07158600	-0.00000500
C	-2.79800700	-0.00700900	0.00004000
H	-3.08116300	1.03999100	-0.00034400
H	-3.17737700	-0.49987400	-0.89173000
H	-3.17730800	-0.49920000	0.89221300
C	2.05266700	-1.42708300	0.00001800
H	2.64138300	-1.17341100	-0.88270200
H	2.64152600	-1.17313600	0.88256100
H	1.88753400	-2.50142300	0.00019600
C	0.75106400	-0.71261000	0.00000800
C	1.68053200	1.65483400	-0.00001500
H	2.29256400	1.53613400	0.89114400
H	2.29295100	1.53572200	-0.89085000
H	1.20687500	2.63047300	-0.00034200

N	0.61945000	0.64647400	-0.00002200
N	-0.63634000	1.03450200	-0.00004800
C	-0.54265700	-1.17272600	0.00000800
H	-0.93585500	-2.17343500	0.00002500

CAAC-5

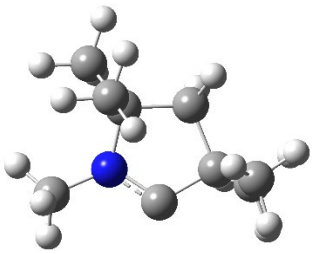


Singlet:

Electronic energy: -408.047168370 Hartree/particle
Zero-point correction= 0.243596 (Hartree/Particle)
Thermal correction to Energy= 0.255241
Thermal correction to Enthalpy= 0.256185
Thermal correction to Gibbs Free Energy= 0.207706
Sum of electronic and zero-point Energies= -407.803572
Sum of electronic and thermal Energies= -407.791928
Sum of electronic and thermal Enthalpies= -407.790984
Sum of electronic and thermal Free Energies= -407.839462

N	-0.64838600	0.90485400	0.04986000
C	0.59932600	1.28008600	0.08478000
C	0.44810600	-1.12932300	-0.37214900
H	0.52698000	-1.39851900	-1.42633200
H	0.64546900	-2.03347000	0.20411200
C	1.44287500	0.02121300	-0.04023700
C	-1.74587600	1.85991400	0.17232900
H	-2.35924600	1.86645800	-0.72937400
H	-2.38393200	1.61484900	1.02255400
H	-1.30864000	2.84154700	0.31934500
C	2.48948800	0.20815800	-1.14649400
H	3.15098000	1.04156900	-0.91065400
H	3.09477100	-0.69483900	-1.26010800
H	2.01583200	0.42046800	-2.10659000
C	2.16219700	-0.19797300	1.30351300
H	2.80180800	-1.08204300	1.24967600
H	2.78263700	0.66396900	1.54798300
H	1.45726500	-0.34159700	2.12368200
C	-0.95871800	-0.57278000	-0.08205800
C	-1.54577600	-1.10359200	1.23226500
H	-2.50330400	-0.63649500	1.46595500
H	-1.71750900	-2.17805200	1.15372800
H	-0.86797100	-0.92880800	2.06713300
C	-1.93453500	-0.82789800	-1.23361900

H	-2.03991500	-1.90191300	-1.39349500
H	-2.92877200	-0.43027100	-1.02593000
H	-1.57028300	-0.38365400	-2.16068000

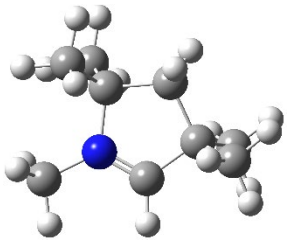


Triplet:

Electronic energy: -407.968714482 Hartree/particle
Zero-point correction= 0.242063 (Hartree/Particle)
Thermal correction to Energy= 0.253899
Thermal correction to Enthalpy= 0.254844
Thermal correction to Gibbs Free Energy= 0.204883
Sum of electronic and zero-point Energies= -407.726651
Sum of electronic and thermal Energies= -407.714815
Sum of electronic and thermal Enthalpies= -407.713871
Sum of electronic and thermal Free Energies= -407.763832

N	0.77673600	0.92750000	-0.14916400
C	-0.51239300	1.16271100	0.28258200
C	-0.46907100	-1.04487500	-0.44117700
H	-0.68570600	-1.99226700	0.05247800
H	-0.55253000	-1.20457900	-1.51631200
C	-1.48963100	0.07200700	-0.01075900
C	1.83755400	1.82542200	0.25433300
H	2.03749400	1.80141500	1.33409100
H	2.75623900	1.58079300	-0.27704400
H	1.55484100	2.84389100	-0.01104700
C	-2.31655100	-0.33334500	1.22095700
H	-2.93067000	0.50233200	1.55977200
H	-2.98402900	-1.16512800	0.98174600
H	-1.67680500	-0.63385300	2.05006300
C	-2.44728900	0.41436900	-1.16946300
H	-3.05873200	-0.45088700	-1.44082300
H	-3.11986100	1.22437600	-0.88359000
H	-1.89028000	0.73244600	-2.05082000
C	0.96950500	-0.55519000	-0.10985900
C	1.42782400	-1.03635600	1.27483000
H	1.45929200	-2.12656700	1.30715100
H	2.42858900	-0.67081300	1.51041800
H	0.74795300	-0.69010200	2.05322400
C	1.96904200	-0.99086600	-1.18050600
H	1.99983100	-2.08028200	-1.24243400

H	1.68331200	-0.59731700	-2.15581300
H	2.97996100	-0.64922500	-0.95253600



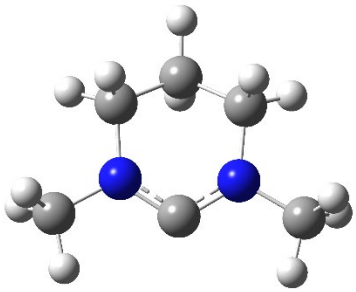
Carbene-H^+:

Electronic energy: -408.488740504 Hartree/particle
Zero-point correction= 0.257800 (Hartree/Particle)
Thermal correction to Energy= 0.269563
Thermal correction to Enthalpy= 0.270507
Thermal correction to Gibbs Free Energy= 0.221664
Sum of electronic and zero-point Energies= -408.230940
Sum of electronic and thermal Energies= -408.219177
Sum of electronic and thermal Enthalpies= -408.218233
Sum of electronic and thermal Free Energies= -408.267076

N	-0.69220800	0.88424700	0.03669700
C	0.43994700	-1.17143700	-0.32137600
H	0.52767800	-1.49355000	-1.35749800
H	0.62928100	-2.03920000	0.30592900
C	1.45720900	-0.02971900	-0.03817100
C	-1.75852000	1.88241800	0.13769800
H	-2.36216800	1.85941600	-0.76655000
H	-2.38901400	1.65432400	0.99391400
H	-1.32069200	2.86862800	0.25999800
C	2.47375500	0.16441700	-1.17887400
H	3.14140900	1.00268400	-0.97891500
H	3.08460400	-0.73362800	-1.26892900
H	1.98120700	0.33365500	-2.13652200
C	2.20466000	-0.19584700	1.30512500
H	2.85060500	-1.07112400	1.24077800
H	2.83384600	0.66815900	1.51944700
H	1.52119200	-0.34016900	2.14132000
C	-0.98335800	-0.60854100	-0.06914400
C	0.55707900	1.14988900	0.05919600
H	0.89748900	2.17500000	0.15903900
C	-1.59012300	-1.08200300	1.25428400
H	-2.56275500	-0.62959600	1.44449000
H	-1.73949000	-2.15972900	1.20222000
H	-0.93512200	-0.87424300	2.09986400
C	-1.93364200	-0.86694300	-1.23628300
H	-2.03110100	-1.94361500	-1.37148100
H	-2.93212400	-0.47224200	-1.05135000

H	-1.55143600	-0.44790600	-2.16736400

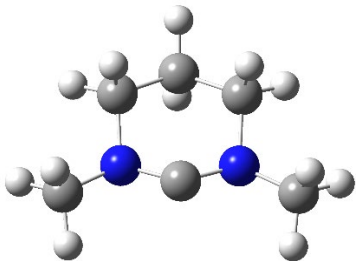
NHC-6



Singlet:

Electronic energy: -345.448554654 Hartree/particle
Zero-point correction= 0.178420 (Hartree/Particle)
Thermal correction to Energy= 0.186808
Thermal correction to Enthalpy= 0.187752
Thermal correction to Gibbs Free Energy= 0.145921
Sum of electronic and zero-point Energies= -345.270134
Sum of electronic and thermal Energies= -345.261747
Sum of electronic and thermal Enthalpies= -345.260803
Sum of electronic and thermal Free Energies= -345.302634

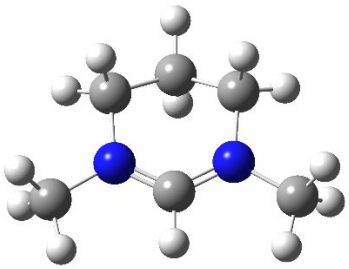
N	1.07211700	0.20721000	-0.03547900
C	0.00000500	1.01241300	-0.00002300
C	-0.76587600	-1.23311000	-0.03402900
H	-1.22943400	-1.77444400	0.79357800
H	-1.14523800	-1.66264000	-0.96639300
N	-1.07211400	0.20721000	0.03540900
C	-2.43794500	0.66351300	0.00309900
H	-2.43629800	1.74884200	0.04881100
H	-2.94395200	0.34737900	-0.91600000
H	-3.00634000	0.27079800	0.85212800
C	2.43795300	0.66350600	-0.00306000
H	2.43632300	1.74883000	-0.04890800
H	2.94384200	0.34748300	0.91614200
H	3.00643900	0.27067500	-0.85197000
C	0.76586400	-1.23311900	0.03404600
H	1.14522900	-1.66258500	0.96643500
H	1.22941000	-1.77449400	-0.79353600



Triplet:

Electronic energy: -345.349222426 Hartree/particle
Zero-point correction= 0.176691 (Hartree/Particle)
Thermal correction to Energy= 0.185131
Thermal correction to Enthalpy= 0.186076
Thermal correction to Gibbs Free Energy= 0.143148
Sum of electronic and zero-point Energies= -345.172531
Sum of electronic and thermal Energies= -345.164091
Sum of electronic and thermal Enthalpies= -345.163147
Sum of electronic and thermal Free Energies= -345.206074

N	-1.08746300	0.29374000	0.44762800
C	-0.00000800	1.02921200	-0.00007200
C	-2.36944000	0.48430900	-0.23074100
H	-2.61269300	1.54453600	-0.22974900
H	-2.35543100	0.13693400	-1.27381500
H	-3.15278000	-0.04510700	0.31229900
C	-0.57775600	-1.09567200	0.51548200
H	-1.37102600	-1.80461700	0.28351200
H	-0.20644700	-1.30744800	1.52031600
C	0.57778400	-1.09567800	-0.51549000
H	1.37105700	-1.80461700	-0.28351200
H	0.20647300	-1.30746500	-1.52032100
N	1.08748300	0.29373600	-0.44765600
C	2.36940900	0.48433000	0.23080900
H	3.15279000	-0.04511300	-0.31214600
H	2.61266500	1.54455600	0.22979000
H	2.35531600	0.13700000	1.27389600



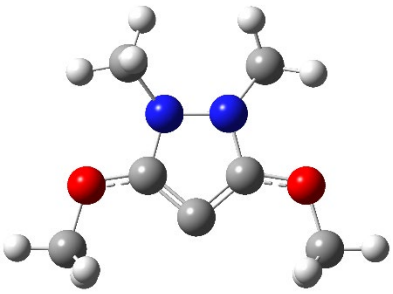
Carbene-H^+:

Electronic energy: -345.892742358 Hartree/particle
Zero-point correction= 0.193532 (Hartree/Particle)
Thermal correction to Energy= 0.202048

Thermal correction to Enthalpy= 0.202992
Thermal correction to Gibbs Free Energy= 0.160796
Sum of electronic and zero-point Energies= -345.699210
Sum of electronic and thermal Energies= -345.690694
Sum of electronic and thermal Enthalpies= -345.689750
Sum of electronic and thermal Free Energies= -345.731947

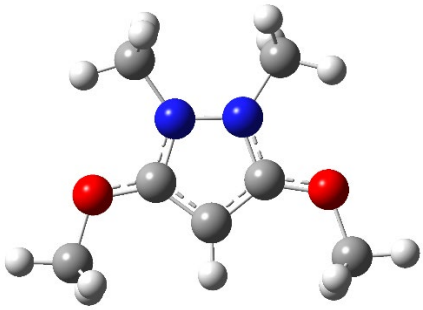
N	1.16717400	-0.35659300	0.02362100
C	-1.25375700	1.10205100	0.20250300
H	-1.39905900	1.31525200	1.26418500
H	-2.13995900	1.44688200	-0.32772400
C	-2.41870600	-1.11357000	-0.02900600
H	-3.01159800	-0.78990900	-0.88374000
H	-2.20754100	-2.17555100	-0.12256100
H	-2.98902100	-0.94497900	0.88421600
C	-0.00000200	1.77400700	-0.34035500
H	0.00000000	2.82638600	-0.06260900
H	-0.00001300	1.72564000	-1.43020700
C	1.25376400	1.10205300	0.20247900
H	2.13995200	1.44687000	-0.32778100
H	1.39909900	1.31527000	1.26415300
N	-1.16717600	-0.35659200	0.02361900
C	2.41870300	-1.11357400	-0.02899600
H	3.01158600	-0.78993800	-0.88374500
H	2.98902600	-0.94495600	0.88421500
H	2.20753600	-2.17555700	-0.12251600
C	-0.00000100	-0.95643800	-0.05322800
H	0.00000000	-2.03029400	-0.18694500

Cyclicbentallene (CBA)



Singlet:
Electronic energy: -534.008536517 Hartree/particle
Zero-point correction= 0.191019 (Hartree/Particle)
Thermal correction to Energy= 0.203475
Thermal correction to Enthalpy= 0.204419
Thermal correction to Gibbs Free Energy= 0.152541
Sum of electronic and zero-point Energies= -533.817517
Sum of electronic and thermal Energies= -533.805062
Sum of electronic and thermal Enthalpies= -533.804118
Sum of electronic and thermal Free Energies= -533.855996

C	0.00000000	1.18700800	0.00000000
N	0.68813600	-1.04966400	-0.12308600
C	-1.04483700	0.28772100	0.09223700
C	1.04483800	0.28772000	-0.09223700
O	-2.36419400	0.50122800	0.13968700
O	2.36419500	0.50122600	-0.13968800
N	-0.68813700	-1.04966400	0.12308300
C	2.77025600	1.87623200	-0.12192500
H	2.38731100	2.37360400	0.76723800
H	3.85690900	1.85679800	-0.12261500
H	2.39225000	2.39451700	-1.00141300
C	-2.77025400	1.87623400	0.12192600
H	-3.85690700	1.85680100	0.12262600
H	-2.39223900	2.39452000	1.00140900
H	-2.38731600	2.37360400	-0.76724100
C	-1.48462500	-2.11400000	-0.46551600
H	-1.39510000	-2.13137600	-1.55549600
H	-1.18103000	-3.07930600	-0.06309600
H	-2.52032800	-1.93716000	-0.19255900
C	1.48462300	-2.11399900	0.46551900
H	1.39510100	-2.13136800	1.55549800
H	1.18102400	-3.07930700	0.06310500
H	2.52032500	-1.93716400	0.19255800



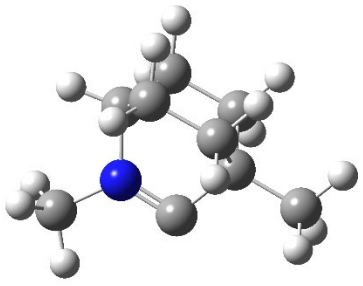
Carbene-H^+:

Electronic energy: -534.472542861 Hartree/particle
Zero-point correction= 0.204676 (Hartree/Particle)
Thermal correction to Energy= 0.217431
Thermal correction to Enthalpy= 0.218375
Thermal correction to Gibbs Free Energy= 0.165655
Sum of electronic and zero-point Energies= -534.267867
Sum of electronic and thermal Energies= -534.255112
Sum of electronic and thermal Enthalpies= -534.254167
Sum of electronic and thermal Free Energies= -534.306888

N	0.68937400	-1.01192200	-0.03587300
C	-1.10480200	0.27157000	0.02723600

C	1.10480100	0.27156900	-0.02724700
O	-2.39846300	0.49917900	0.02805000
O	2.39846300	0.49917800	-0.02806400
N	-0.68937500	-1.01192200	0.03587400
C	2.84238400	1.87492200	-0.03691300
H	2.48980700	2.38637200	0.85749900
H	3.92514500	1.82676600	-0.03715000
H	2.48887600	2.37505900	-0.93726200
C	-2.84238300	1.87492300	0.03691500
H	-3.92514400	1.82676800	0.03714900
H	-2.48887700	2.37504800	0.93727100
H	-2.48980400	2.38638400	-0.85749000
C	-1.48574800	-2.21854600	-0.12686700
H	-1.34271200	-2.64692100	-1.11850200
H	-1.23043700	-2.94776300	0.63861400
H	-2.52506300	-1.93078900	-0.00716600
C	1.48574700	-2.21854500	0.12687200
H	1.34271500	-2.64691700	1.11850900
H	1.23043400	-2.94776500	-0.63860500
H	2.52506200	-1.93078900	0.00716700
C	0.00000000	1.12097300	0.00001300
H	0.00000100	2.19341200	0.00002600

BiCAAC

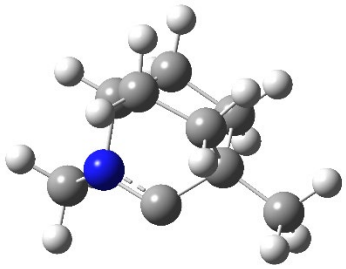


Singlet:

Electronic energy: -406.830061568 Hartree/particle
Zero-point correction= 0.225453 (Hartree/Particle)
Thermal correction to Energy= 0.234815
Thermal correction to Enthalpy= 0.235759
Thermal correction to Gibbs Free Energy= 0.192013
Sum of electronic and zero-point Energies= -406.604608
Sum of electronic and thermal Energies= -406.595247
Sum of electronic and thermal Enthalpies= -406.594303
Sum of electronic and thermal Free Energies= -406.638048

C	1.00120100	0.52792200	1.26002500
C	-0.34680100	1.28196800	1.25422300
C	-1.12360300	0.85921800	0.00002200
C	-0.07497700	-1.32324000	-0.00007200
C	1.11579900	-0.37441700	0.00000400

H	-2.13643400	1.25927300	0.00002100
H	-0.93191000	1.05103000	2.14522100
H	-0.20397000	2.36364000	1.23634000
H	1.09008000	-0.09738200	2.14936900
H	1.84404500	1.22245100	1.27820300
C	2.43229000	-1.14538900	-0.00001000
H	2.49966100	-1.78776900	-0.87885000
H	3.29130900	-0.46919400	0.00004600
H	2.49962200	-1.78786600	0.87876300
C	1.00126000	0.52806500	-1.25992000
H	1.84409800	1.22260400	-1.27797100
H	1.09019200	-0.09713400	-2.14933200
C	-0.34674900	1.28209800	-1.25410300
H	-0.20392900	2.36377100	-1.23611000
H	-0.93181700	1.05124100	-2.14514800
N	-1.17994400	-0.62261600	-0.00005800
C	-2.49533500	-1.25229300	-0.00012300
H	-3.06130000	-0.95605900	-0.88630300
H	-2.34718300	-2.32777400	-0.00014800
H	-3.06136400	-0.95610700	0.88603300

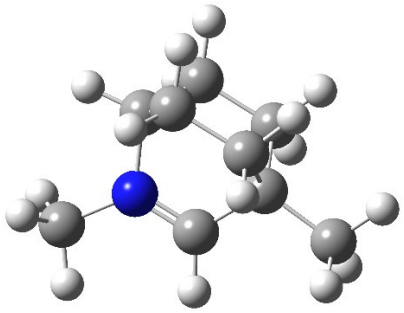


Triplet:

Electronic energy: -406.755426336 Hartree/particle
Zero-point correction= 0.223927 (Hartree/Particle)
Thermal correction to Energy= 0.233480
Thermal correction to Enthalpy= 0.234424
Thermal correction to Gibbs Free Energy= 0.189032
Sum of electronic and zero-point Energies= -406.531500
Sum of electronic and thermal Energies= -406.521947
Sum of electronic and thermal Enthalpies= -406.521002
Sum of electronic and thermal Free Energies= -406.566394

C	-1.27729500	1.01726500	-0.72617800
C	0.10958900	1.71058600	-0.76904500
C	1.12573500	0.89021300	0.03424600
C	0.03888200	-1.01979800	-0.73516400
C	-1.13092400	-0.38140000	-0.05706900
H	2.10145600	1.37851000	0.03677500
H	0.46474700	1.80134900	-1.79536500
H	0.05820600	2.71786300	-0.35258700

H	-1.67782500	0.89684300	-1.73225200
H	-2.00008300	1.60999800	-0.15694500
C	-2.41390300	-1.19630100	-0.15724300
H	-2.30472700	-2.15972400	0.34278100
H	-3.24547500	-0.66370300	0.30883400
H	-2.67206700	-1.38583200	-1.19984300
C	-0.71786600	-0.12877100	1.42193800
H	-1.52551700	0.40079100	1.93511300
H	-0.59546800	-1.08942200	1.92333400
C	0.59935100	0.68856200	1.46975500
H	0.44182500	1.66713400	1.92780600
H	1.35015000	0.18152900	2.07673200
N	1.27895800	-0.42738600	-0.63375000
C	2.41582200	-1.24369900	-0.22642200
H	2.34476800	-1.60303200	0.80980300
H	2.47563700	-2.11288100	-0.87930700
H	3.33532100	-0.66767000	-0.33754100



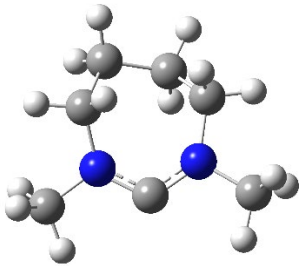
Carbene-H^+:

Electronic energy: -407.272766142 Hartree/particle
Zero-point correction= 0.239785 (Hartree/Particle)
Thermal correction to Energy= 0.249236
Thermal correction to Enthalpy= 0.250180
Thermal correction to Gibbs Free Energy= 0.206235
Sum of electronic and zero-point Energies= -407.032981
Sum of electronic and thermal Energies= -407.023530
Sum of electronic and thermal Enthalpies= -407.022586
Sum of electronic and thermal Free Energies= -407.066532

C	-1.02585300	-0.56963700	1.25686600
C	0.33404600	-1.29896700	1.26290300
C	1.12014300	-0.90291600	0.00002200
C	-1.13988900	0.35637100	0.00000700
H	2.12955500	-1.30431300	0.00002100
H	0.91345700	-1.05079600	2.15150900
H	0.21182800	-2.38091000	1.25552900
H	-1.15733900	0.02393400	2.16041700
H	-1.85728500	-1.27224600	1.21374500

C	-2.41924400	1.18594400	-0.00000800
H	-2.48334500	1.82079900	-0.88442400
H	-3.28980400	0.53128300	0.00004600
H	-2.48330500	1.82089300	0.88434400
C	-1.02591100	-0.56977200	-1.25675800
H	-1.85734000	-1.27237800	-1.21352100
H	-1.15744200	0.02370100	-2.16036700
C	0.33398800	-1.29910000	-1.26278000
H	0.21177200	-2.38104300	-1.25528700
H	0.91335800	-1.05102200	-2.15143900
N	1.21736200	0.57980600	-0.00005900
C	2.52647900	1.23513000	-0.00012400
H	3.07898700	0.92874200	-0.88697300
H	2.39628900	2.31369800	-0.00017000
H	3.07903500	0.92882300	0.88672400
C	0.08787000	1.19352500	-0.00006600
H	0.08026800	2.27872800	-0.00012300

NHC-7

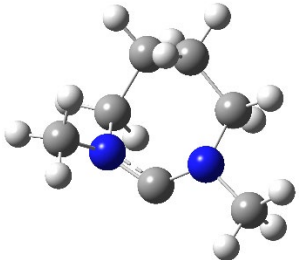


Singlet:

Electronic energy: -384.760646960 Hartree/particle
Zero-point correction= 0.207220 (Hartree/Particle)
Thermal correction to Energy= 0.216721
Thermal correction to Enthalpy= 0.217665
Thermal correction to Gibbs Free Energy= 0.173224
Sum of electronic and zero-point Energies= -384.553427
Sum of electronic and thermal Energies= -384.543926
Sum of electronic and thermal Enthalpies= -384.542982
Sum of electronic and thermal Free Energies= -384.587423

C	0.17739100	-1.26731600	-0.15426500
C	1.36119600	0.98446100	0.20721400
C	-1.06489600	1.77705300	-0.03488100
C	0.34448100	1.74616400	-0.64021200
H	1.31925600	1.29747400	1.25564100
H	-1.16596900	2.62347600	0.65036500
H	2.36166200	1.24179500	-0.14310100
H	-1.80276500	1.92660500	-0.82603500
H	0.70605500	2.76630100	-0.78607200
H	0.31552700	1.28344100	-1.62775500

N	-1.04721100	-0.73566200	0.00015100
C	-2.18728600	-1.59173200	-0.30045300
H	-2.72585200	-1.87261700	0.61138500
H	-2.88996000	-1.08555100	-0.96828000
H	-1.81735500	-2.48910200	-0.78545700
C	2.54842900	-1.15746800	0.05150600
H	3.09137800	-1.00016200	0.98852400
H	2.38118300	-2.21999700	-0.08864600
H	3.16794200	-0.77417900	-0.76653300
N	1.25072500	-0.49228700	0.08544800
C	-1.36879600	0.49940800	0.73761200
H	-0.80615900	0.48833700	1.67474200
H	-2.42265800	0.46639300	1.01290500

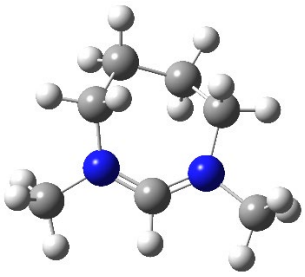


Triplet:

Electronic energy: -384.679277087 Hartree/particle
Zero-point correction= 0.205384 (Hartree/Particle)
Thermal correction to Energy= 0.215193
Thermal correction to Enthalpy= 0.216138
Thermal correction to Gibbs Free Energy= 0.169814
Sum of electronic and zero-point Energies= -384.473893
Sum of electronic and thermal Energies= -384.464084
Sum of electronic and thermal Enthalpies= -384.463139
Sum of electronic and thermal Free Energies= -384.509463

C	0.47192500	-1.04119000	-0.51514100
C	-1.62133400	0.05733400	-0.93139100
C	-0.26141900	1.56930700	0.71314500
C	-1.50925100	1.40511800	-0.17588500
H	-1.22401800	0.16475700	-1.93989300
H	-0.22099100	2.61642200	1.02330500
H	-2.66946500	-0.23915900	-1.02366400
H	-0.37916500	0.99010100	1.63144900
H	-1.54013600	2.21163400	-0.91323400
H	-2.38577100	1.54903900	0.46037600
N	1.40061000	-0.23336600	0.14806400
C	2.78949600	-0.53982700	-0.15527400
H	3.07322200	-0.24757000	-1.17626000
H	3.43996800	-0.01745500	0.54724400
H	2.94965800	-1.61138800	-0.05228600

C	-1.46939600	-1.70284100	0.83875900
H	-2.47627800	-2.04041800	0.58295700
H	-0.86411400	-2.57004800	1.09151800
H	-1.53835900	-1.06081400	1.72561700
N	-0.86454900	-1.02272200	-0.30204300
C	1.10262200	1.21030300	0.11385900
H	1.18733400	1.59958900	-0.91361900
H	1.87983100	1.69870000	0.70590300



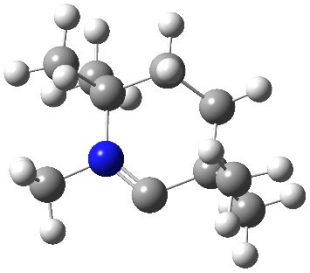
Carbene-H^+:

Electronic energy: -385.209125301 Hartree/particle
Zero-point correction= 0.222456 (Hartree/Particle)
Thermal correction to Energy= 0.232083
Thermal correction to Enthalpy= 0.233028
Thermal correction to Gibbs Free Energy= 0.188212
Sum of electronic and zero-point Energies= -384.986669
Sum of electronic and thermal Energies= -384.977042
Sum of electronic and thermal Enthalpies= -384.976098
Sum of electronic and thermal Free Energies= -385.020913

C	1.35924500	1.04830500	0.19938300
C	-1.10289300	1.77817500	-0.05858500
C	0.31919400	1.77907000	-0.64389300
H	1.31696300	1.32738000	1.25368900
H	-1.23929500	2.63025300	0.60944700
H	2.35471200	1.31095000	-0.15299500
H	-1.82784300	1.90004800	-0.86380300
H	0.65768100	2.80728500	-0.77048200
H	0.32016600	1.34113500	-1.64387200
N	-1.06329800	-0.73836000	0.06442300
C	-2.16750600	-1.62533400	-0.31946200
H	-2.76293800	-1.87604700	0.55762000
H	-2.80253200	-1.12704900	-1.05099900
H	-1.77790200	-2.53797700	-0.76243800
C	2.57869600	-1.12807900	0.06492400
H	3.08969300	-0.95954700	1.01251100
H	2.43066000	-2.19684300	-0.06288500
H	3.19908600	-0.74811000	-0.74574400
N	1.28496300	-0.43202200	0.07198500

C	-1.41392800	0.52586200	0.75060600
H	-0.88116800	0.53342600	1.70223500
H	-2.47378700	0.47101100	0.98572400
C	0.18158600	-1.13152800	-0.09666700
H	0.31848700	-2.16206200	-0.40070400

CAAC-6

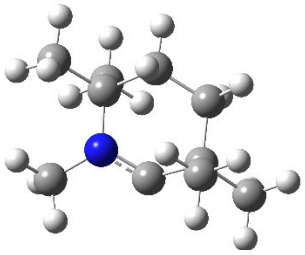


Singlet:

Electronic energy: -447.366030887 Hartree/particle
Zero-point correction= 0.272928 (Hartree/Particle)
Thermal correction to Energy= 0.285323
Thermal correction to Enthalpy= 0.286268
Thermal correction to Gibbs Free Energy= 0.236383
Sum of electronic and zero-point Energies= -447.093103
Sum of electronic and thermal Energies= -447.080707
Sum of electronic and thermal Enthalpies= -447.079763
Sum of electronic and thermal Free Energies= -447.129648

N	-0.62579800	0.92475900	0.00577500
C	0.65226200	1.19877200	0.02264400
C	1.05138200	-1.34341700	0.26370600
H	0.92201800	-1.49363700	1.33840400
H	1.74361300	-2.12156300	-0.06924300
C	1.64668600	0.05362700	0.00888800
C	2.70651100	0.36821000	1.07926600
H	3.48185900	-0.40265200	1.08423500
C	2.32910500	0.11004900	-1.37573400
H	3.16549800	-0.59207200	-1.40549400
H	1.64183900	-0.14713000	-2.18306400
H	3.17012500	1.33489000	0.88683300
H	2.26106500	0.40465300	2.07522800
H	2.70771300	1.11254500	-1.57127400
C	-0.28611300	-1.49379500	-0.44256800
H	-0.71752100	-2.48114300	-0.26314900
H	-0.14284700	-1.41110800	-1.52279300
C	-1.54637600	2.07555900	0.02338400
H	-2.29269200	1.96960500	0.81125600
H	-0.94345900	2.95734900	0.20477500
H	-2.06185000	2.17919300	-0.93125900
C	-1.30632700	-0.43727800	-0.00075000

C	-2.47289400	-0.44579100	-0.99719800
H	-2.85500800	-1.46410400	-1.08593600
H	-3.30100900	0.18717100	-0.68210500
H	-2.14737300	-0.12457200	-1.98729600
C	-1.83111400	-0.73844600	1.41142300
H	-2.55579300	0.00631800	1.73900000
H	-2.33069100	-1.70887300	1.42172300
H	-1.02363000	-0.76311800	2.14136500

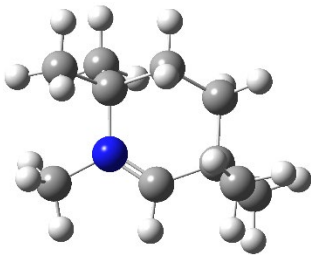


Triplet:

Electronic energy: -447.306347250 Hartree/particle
Zero-point correction= 0.271279 (Hartree/Particle)
Thermal correction to Energy= 0.283981
Thermal correction to Enthalpy= 0.284925
Thermal correction to Gibbs Free Energy= 0.233453
Sum of electronic and zero-point Energies= -447.035068
Sum of electronic and thermal Energies= -447.022366
Sum of electronic and thermal Enthalpies= -447.021422
Sum of electronic and thermal Free Energies= -447.072895

N	0.77673600	0.92750000	-0.14916400
C	-0.51239300	1.16271100	0.28258200
C	-0.46907100	-1.04487500	-0.44117700
H	-0.68570600	-1.99226700	0.05247800
H	-0.55253000	-1.20457900	-1.51631200
C	-1.48963100	0.07200700	-0.01075900
C	1.83755400	1.82542200	0.25433300
H	2.03749400	1.80141500	1.33409100
H	2.75623900	1.58079300	-0.27704400
H	1.55484100	2.84389100	-0.01104700
C	-2.31655100	-0.33334500	1.22095700
H	-2.93067000	0.50233200	1.55977200
H	-2.98402900	-1.16512800	0.98174600
H	-1.67680500	-0.63385300	2.05006300
C	-2.44728900	0.41436900	-1.16946300
H	-3.05873200	-0.45088700	-1.44082300
H	-3.11986100	1.22437600	-0.88359000
H	-1.89028000	0.73244600	-2.05082000
C	0.96950500	-0.55519000	-0.10985900
C	1.42782400	-1.03635600	1.27483000

H	1.45929200	-2.12656700	1.30715100
H	2.42858900	-0.67081300	1.51041800
H	0.74795300	-0.69010200	2.05322400
C	1.96904200	-0.99086600	-1.18050600
H	1.99983100	-2.08028200	-1.24243400
H	1.68331200	-0.59731700	-2.15581300
H	2.97996100	-0.64922500	-0.95253600



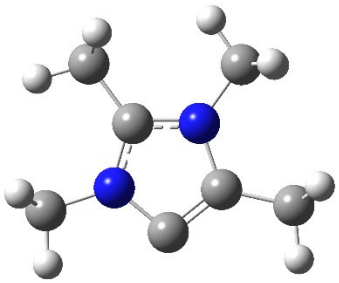
Carbene-H^+:

Electronic energy: -447.816853980 Hartree/particle
Zero-point correction= 0.287515 (Hartree/Particle)
Thermal correction to Energy= 0.300025
Thermal correction to Enthalpy= 0.300969
Thermal correction to Gibbs Free Energy= 0.250837
Sum of electronic and zero-point Energies= -447.529339
Sum of electronic and thermal Energies= -447.516829
Sum of electronic and thermal Enthalpies= -447.515885
Sum of electronic and thermal Free Energies= -447.566017

N	-0.66112200	0.90460400	-0.00807200
C	1.03743400	-1.38524300	0.24166400
H	0.92320200	-1.55497200	1.31320200
H	1.72057900	-2.15416400	-0.11815400
C	1.66046600	-0.00123600	0.00565800
C	2.66994000	0.35509900	1.11961400
H	3.45223400	-0.40328300	1.13984800
C	2.37848900	0.08176500	-1.36740600
H	3.23309400	-0.59392000	-1.35088700
H	1.72628300	-0.20999300	-2.18945900
H	3.14494700	1.32015200	0.94072400
H	2.19810000	0.37615000	2.10218400
H	2.75265100	1.08612300	-1.56794100
C	-0.30971000	-1.51071600	-0.45776100
H	-0.74116300	-2.49483200	-0.27766300
H	-0.18043400	-1.42583100	-1.53889700
C	-1.53384500	2.09515700	-0.00106500
H	-2.26623900	2.00420500	0.79599900
H	-0.93019700	2.98154200	0.16599100
H	-2.04934300	2.17831600	-0.95384400
C	-1.33703800	-0.46518800	0.00085500

C	0.61396300	1.05762600	-0.00304700
H	0.96540000	2.08564500	-0.01216800
C	-2.51347500	-0.44649200	-0.98030300
H	-2.90882000	-1.45877100	-1.05101800
H	-3.32845400	0.19536700	-0.65179100
H	-2.20143900	-0.14463500	-1.98023700
C	-1.83037000	-0.72879700	1.43016000
H	-2.55445100	0.01607000	1.75674700
H	-2.32946700	-1.69659900	1.45410300
H	-1.01375400	-0.75064500	2.14955800

Abnormal NHC (*a*NHC)

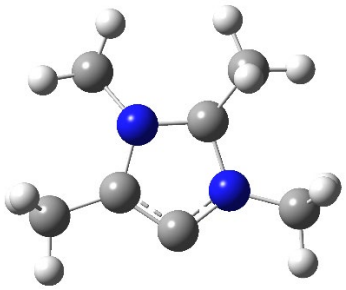


Singlet:

Electronic energy: -383.554814983 Hartree/particle
Zero-point correction= 0.180864 (Hartree/Particle)
Thermal correction to Energy= 0.191574
Thermal correction to Enthalpy= 0.192518
Thermal correction to Gibbs Free Energy= 0.143390
Sum of electronic and zero-point Energies= -383.373951
Sum of electronic and thermal Energies= -383.363241
Sum of electronic and thermal Enthalpies= -383.362297
Sum of electronic and thermal Free Energies= -383.411425

C	0.02209300	-1.62969600	0.00074500
N	-1.06242400	-0.73215800	0.00037400
C	-2.44176000	-1.19196800	0.00048200
H	-2.97647000	-0.84997700	0.88818800
H	-2.97517000	-0.85434800	-0.88968100
H	-2.40114900	-2.27610200	0.00311200
C	2.55148600	-1.08790100	-0.00037700
H	3.07364100	-0.70548300	-0.88371900
H	3.07513100	-0.69948700	0.87940700
H	2.65277000	-2.17074600	0.00299000
C	1.09594000	-0.76643800	-0.00022000
C	1.49333700	1.74584400	0.00149600
H	2.10398400	1.77500800	0.90414900
H	2.15625100	1.73853500	-0.86341500
H	0.88424100	2.64493300	-0.03552700
N	0.65019100	0.56504200	-0.00170700
C	-0.69200300	0.56013100	-0.00082700

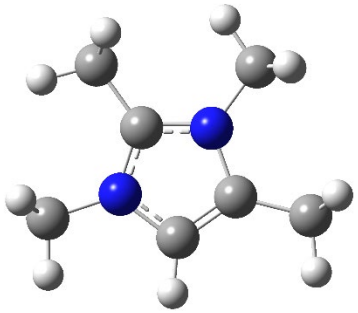
C	-1.57302400	1.75997200	-0.00044200
H	-1.41422800	2.38463000	0.88229900
H	-1.41288500	2.38608000	-0.88194300
H	-2.61688700	1.45710400	-0.00166800



Triplet:

Electronic energy: -383.459472347 Hartree/particle
Zero-point correction= 0.177758 (Hartree/Particle)
Thermal correction to Energy= 0.188478
Thermal correction to Enthalpy= 0.189422
Thermal correction to Gibbs Free Energy= 0.141295
Sum of electronic and zero-point Energies= -383.281714
Sum of electronic and thermal Energies= -383.270994
Sum of electronic and thermal Enthalpies= -383.270050
Sum of electronic and thermal Free Energies= -383.318177

C	0.08742700	-1.51482100	0.13088900
N	1.11312300	-0.71050400	-0.24026200
C	2.51007500	-1.07380300	-0.18009800
H	3.04389400	-0.64747200	-1.03206000
H	2.99410000	-0.73030200	0.73950900
H	2.57994300	-2.15672000	-0.22376200
C	-2.47346900	-1.22247400	0.20262900
H	-2.97439300	-0.84994400	1.10346900
H	-3.07208200	-0.89595700	-0.65287200
H	-2.48439700	-2.30948200	0.23785100
C	-1.07128600	-0.75073500	0.11435300
C	-1.61834000	1.64962100	-0.36837400
H	-1.70201300	1.70273300	-1.46244400
H	-2.60738800	1.48572800	0.05396500
H	-1.25980000	2.61368100	-0.00893900
N	-0.72234700	0.59740000	0.05643400
C	0.68090800	0.66588400	-0.26778600
C	1.49250300	1.69095600	0.46384000
H	1.07845600	2.68515100	0.29330500
H	1.49789500	1.52054200	1.55249000
H	2.52345200	1.70599700	0.11357100



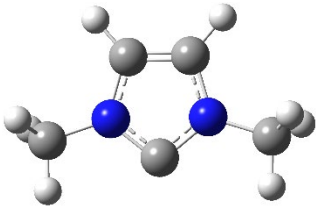
Carbene-H^+:

Electronic energy: -384.026332273 Hartree/particle
Zero-point correction= 0.195373 (Hartree/Particle)
Thermal correction to Energy= 0.206065
Thermal correction to Enthalpy= 0.207009
Thermal correction to Gibbs Free Energy= 0.158728
Sum of electronic and zero-point Energies= -383.830959
Sum of electronic and thermal Energies= -383.820267
Sum of electronic and thermal Enthalpies= -383.819323
Sum of electronic and thermal Free Energies= -383.867604

N	-1.09533800	-0.67939800	0.00058500
C	-2.48545500	-1.14373400	0.00013100
H	-3.00316700	-0.79137600	0.88920200
H	-3.00055100	-0.79767800	-0.89295300
H	-2.47853600	-2.22887000	0.00406500
C	2.56038200	-1.08990600	-0.00061000
H	3.07093400	-0.70666900	-0.88574200
H	3.07382100	-0.69741600	0.87870900
H	2.66693200	-2.17198300	0.00470100
C	1.11945100	-0.72834100	-0.00024100
C	1.52491900	1.76274300	0.00148600
H	2.12863500	1.77635200	0.90661400
H	2.17787900	1.74200100	-0.86826600
H	0.91819200	2.66069000	-0.03352000
N	0.65956700	0.58422800	-0.00141900
C	-0.68537000	0.59567000	-0.00059700
C	-1.55421100	1.79913000	-0.00048500
H	-1.37372500	2.41410500	0.88226600
H	-1.37438600	2.41376100	-0.88364400
H	-2.60234900	1.51462500	-0.00023300
C	0.00921200	-1.50923200	0.00079400
H	-0.08685500	-2.57933400	0.00175600

M06-2X/def2-TZVPP

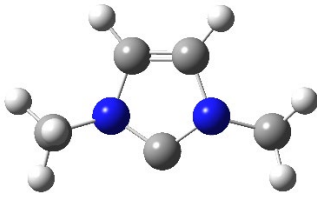
Unsaturated NHC-5 (NHC-5)



Singlet:

Electronic energy: -304.780038920 Hartree/particle
Zero-point correction= 0.127936 (Hartree/Particle)
Thermal correction to Energy= 0.134867
Thermal correction to Enthalpy= 0.135812
Thermal correction to Gibbs Free Energy= 0.097000
Sum of electronic and zero-point Energies= -304.652103
Sum of electronic and thermal Energies= -304.645172
Sum of electronic and thermal Enthalpies= -304.644227
Sum of electronic and thermal Free Energies= -304.683039

C	0.00001400	0.97786100	-0.00001500
N	1.05602700	0.12245700	-0.00000700
N	-1.05605700	0.12240600	0.00000200
C	2.43315200	0.56560400	-0.00000500
H	2.95243200	0.20502900	-0.88763900
H	2.42692700	1.65090500	-0.00007900
H	2.95239200	0.20515300	0.88770400
C	-2.43315600	0.56560400	0.00000000
H	-2.42687500	1.65090400	0.00000500
H	-2.95244600	0.20512900	-0.88767300
H	-2.95245100	0.20512100	0.88766600
C	-0.67431500	-1.20454000	0.00001400
H	-1.37805400	-2.01806800	0.00002400
C	0.67432200	-1.20456800	0.00000800
H	1.37818500	-2.01798200	0.00001400

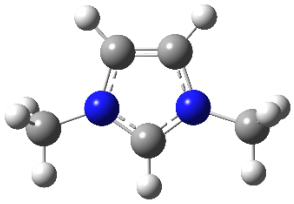


Triplet:

Electronic energy: -304.642286741 Hartree/particle
Zero-point correction= 0.125170 (Hartree/Particle)
Thermal correction to Energy= 0.132578
Thermal correction to Enthalpy= 0.133522
Thermal correction to Gibbs Free Energy= 0.092101
Sum of electronic and zero-point Energies= -304.517117
Sum of electronic and thermal Energies= -304.509709
Sum of electronic and thermal Enthalpies= -304.508765

Sum of electronic and thermal Free Energies= -304.550186

C	0.00761600	-0.93983600	-0.10554700
N	1.08886900	-0.16845200	0.34321400
N	-1.11738700	-0.16009700	-0.38672600
C	2.42701200	-0.51063600	-0.10325700
H	3.14093500	0.17169600	0.35512900
H	2.66188500	-1.52279200	0.21883600
H	2.51510800	-0.45654300	-1.19442900
C	-2.39709100	-0.53105800	0.20228000
H	-2.66108800	-1.53384600	-0.12565500
H	-2.35867400	-0.51195100	1.29727800
H	-3.16327600	0.15954300	-0.14695900
C	-0.65277400	1.16203100	-0.19393600
H	-1.31548900	1.99852700	-0.33794300
C	0.62937600	1.15461400	0.18199100
H	1.29539100	1.98451300	0.34914400



Carbene-H^+:

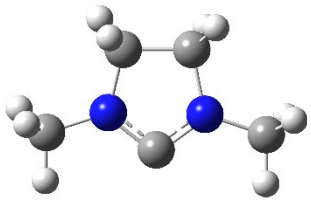
Electronic energy: -305.204183997 Hartree/particle
Zero-point correction= 0.141814 (Hartree/Particle)
Thermal correction to Energy= 0.148916
Thermal correction to Enthalpy= 0.149860
Thermal correction to Gibbs Free Energy= 0.110370
Sum of electronic and zero-point Energies= -305.062370
Sum of electronic and thermal Energies= -305.055268
Sum of electronic and thermal Enthalpies= -305.054324
Sum of electronic and thermal Free Energies= -305.093813

N	1.07999200	0.08452000	-0.00000600
N	-1.07999400	0.08451500	0.00000200
C	2.46730700	0.54892200	-0.00000600
H	2.96828000	0.18057000	-0.89101900
H	2.47276700	1.63443800	-0.00008300
H	2.96824200	0.18069500	0.89108000
C	-2.46730700	0.54892100	-0.00000200
H	-2.47276400	1.63443700	0.00000500
H	-2.96826000	0.18063800	-0.89105500
H	-2.96826700	0.18062800	0.89104400
C	-0.67770100	-1.22945800	0.00001500
H	-1.38302700	-2.04112400	0.00002500

C	0.67770500	-1.22945600	0.00000900
H	1.38304000	-2.04111500	0.00001500
C	-0.00000200	0.85676700	-0.00001000
H	-0.00001000	1.93340800	-0.00002100

*s*NHC-5

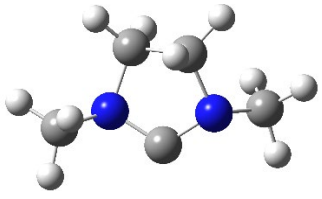
Singlet:



Electronic energy: -305.975822255 Hartree/particle
Zero-point correction= 0.150651 (Hartree/Particle)
Thermal correction to Energy= 0.158283
Thermal correction to Enthalpy= 0.159227
Thermal correction to Gibbs Free Energy= 0.118935
Sum of electronic and zero-point Energies= -305.825171
Sum of electronic and thermal Energies= -305.817540
Sum of electronic and thermal Enthalpies= -305.816596
Sum of electronic and thermal Free Energies= -305.856888

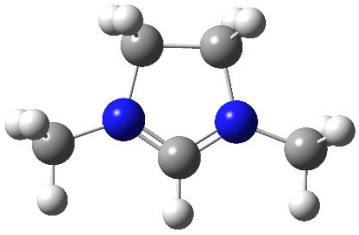
N	1.06671600	0.20574400	-0.06250600
C	0.00000000	1.01569000	0.00000300
C	-0.76166600	-1.22197200	-0.06353000
H	-1.25824200	-1.80260400	0.71468000
H	-1.09940800	-1.59659500	-1.03467500
N	-1.06671600	0.20574400	0.06250500
C	-2.43171000	0.65325200	0.00583700
H	-2.43770000	1.73631000	0.08541100
H	-2.90486200	0.36074900	-0.93685600
H	-3.01478400	0.22717500	0.82590900
C	2.43171000	0.65325300	-0.00583900
H	2.43769900	1.73631200	-0.08538400
H	2.90486800	0.36072400	0.93684300
H	3.01477900	0.22719800	-0.82592700
C	0.76166600	-1.22197100	0.06353000
H	1.09941100	-1.59659300	1.03467600
H	1.25824200	-1.80260400	-0.71468000

Triplet:



Electronic energy: -305.860357792 Hartree/particle
Zero-point correction= 0.149496 (Hartree/Particle)
Thermal correction to Energy= 0.156925
Thermal correction to Enthalpy= 0.157869
Thermal correction to Gibbs Free Energy= 0.117020
Sum of electronic and zero-point Energies= -305.710862
Sum of electronic and thermal Energies= -305.703433
Sum of electronic and thermal Enthalpies= -305.702488
Sum of electronic and thermal Free Energies= -305.743337

N	-1.07407800	0.30852300	0.48959700
C	-0.00000500	1.04371300	-0.00004000
C	-2.33069500	0.44407400	-0.24311800
H	-2.58663900	1.49915900	-0.30624200
H	-2.26284600	0.04282600	-1.26288000
H	-3.12388700	-0.07302900	0.29576300
C	-0.53941700	-1.06549600	0.55035800
H	-1.33388100	-1.79213700	0.39139300
H	-0.09254300	-1.23912800	1.53063200
C	0.53943400	-1.06549900	-0.55036400
H	1.33390100	-1.79213700	-0.39139700
H	0.09255800	-1.23913500	-1.53063600
N	1.07409100	0.30852200	-0.48961400
C	2.33067600	0.44408600	0.24315800
H	3.12389200	-0.07302800	-0.29567700
H	2.58661600	1.49917200	0.30627200
H	2.26277900	0.04285800	1.26292400

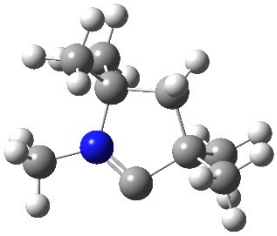


Carbene-H^+:
Electronic energy: -306.401077030 Hartree/particle
Zero-point correction= 0.165141 (Hartree/Particle)
Thermal correction to Energy= 0.173029
Thermal correction to Enthalpy= 0.173973
Thermal correction to Gibbs Free Energy= 0.132836
Sum of electronic and zero-point Energies= -306.235936
Sum of electronic and thermal Energies= -306.228048
Sum of electronic and thermal Enthalpies= -306.227104
Sum of electronic and thermal Free Energies= -306.268241

N	1.09786200	0.16753000	0.00045900

C	-0.77218300	-1.26778100	0.00042400
H	-1.19546500	-1.73807900	0.88651800
H	-1.19643400	-1.73954800	-0.88440500
N	-1.09786200	0.16753000	-0.00043200
C	-2.46362600	0.65868600	-0.00005500
H	-2.45664400	1.74529100	0.00118600
H	-2.98219500	0.30227400	-0.88884300
H	-2.98224800	0.30032000	0.88792700
C	2.46362600	0.65868600	0.00002500
H	2.45664400	1.74529100	-0.00105800
H	2.98226800	0.30215000	0.88872100
H	2.98217500	0.30044400	-0.88805000
C	0.77218300	-1.26778200	-0.00042500
H	1.19643400	-1.73956600	0.88439500
H	1.19546500	-1.73806100	-0.88652800
C	0.00000000	0.87730600	0.00001800
H	0.00000000	1.95937300	0.00002300

CAAC-5

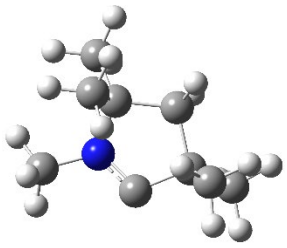


Singlet:

Electronic energy: -407.847533452 Hartree/particle
Zero-point correction= 0.246246 (Hartree/Particle)
Thermal correction to Energy= 0.257654
Thermal correction to Enthalpy= 0.258598
Thermal correction to Gibbs Free Energy= 0.210783
Sum of electronic and zero-point Energies= -407.601287
Sum of electronic and thermal Energies= -407.589879
Sum of electronic and thermal Enthalpies= -407.588935
Sum of electronic and thermal Free Energies= -407.636750

N	-0.64887800	0.89424600	0.08157000
C	0.59264400	1.28297000	0.13088300
C	0.45164800	-1.08971400	-0.46520400
H	0.51365200	-1.25446700	-1.54254400
H	0.66011100	-2.04123100	0.02549400
C	1.43543600	0.02881500	-0.04786800
C	-1.76250000	1.81778400	0.23329800
H	-2.34195200	1.87271900	-0.68843200
H	-2.42157600	1.49647000	1.04029700
H	-1.34954100	2.79366000	0.46348500

C	2.50434500	0.27174100	-1.11034700
H	3.16523700	1.08194300	-0.80373300
H	3.10128200	-0.63027300	-1.26406200
H	2.05066400	0.54873300	-2.06316400
C	2.11567600	-0.26378500	1.29384700
H	2.75315100	-1.14592800	1.20543300
H	2.73070200	0.58353000	1.59561600
H	1.38806000	-0.44663300	2.08525100
C	-0.94343700	-0.56398200	-0.10671400
C	-1.48071000	-1.15692500	1.19518000
H	-2.43251100	-0.70602900	1.47748700
H	-1.64700500	-2.22704600	1.06753300
H	-0.77420100	-1.01324500	2.01127900
C	-1.95329200	-0.77137200	-1.22972600
H	-2.03600400	-1.83612600	-1.44983400
H	-2.94531400	-0.41093000	-0.95460200
H	-1.63146200	-0.25805800	-2.13659200

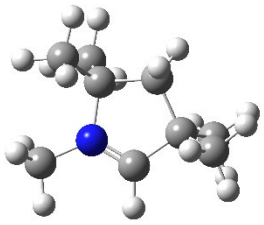


Triplet:

Electronic energy: -407.770416611 Hartree/particle
Zero-point correction= 0.244891 (Hartree/Particle)
Thermal correction to Energy= 0.256420
Thermal correction to Enthalpy= 0.257364
Thermal correction to Gibbs Free Energy= 0.208283
Sum of electronic and zero-point Energies= -407.525525
Sum of electronic and thermal Energies= -407.513996
Sum of electronic and thermal Enthalpies= -407.513052
Sum of electronic and thermal Free Energies= -407.562134

N	0.78215000	0.91275700	-0.27239600
C	-0.50644100	1.19636500	0.13181100
C	-0.47074700	-1.05591800	-0.41740800
H	-0.68942200	-1.99157300	0.09877600
H	-0.54391300	-1.23616200	-1.49090600
C	-1.47477400	0.07018000	-0.02274900
C	1.83687800	1.79974000	0.16521700
H	1.94598900	1.81576100	1.25682000
H	2.78269000	1.49835900	-0.28302800
H	1.60705300	2.81048800	-0.16900500
C	-2.22492700	-0.24548800	1.27481600
H	-2.81426500	0.61682100	1.58891900

H	-2.90514100	-1.08705600	1.12586500
H	-1.53704800	-0.49606700	2.08123500
C	-2.49148600	0.31423300	-1.14397100
H	-3.09345700	-0.58065000	-1.31983400
H	-3.16425300	1.13014900	-0.87708200
H	-1.98158000	0.57946300	-2.06993500
C	0.95375000	-0.55232800	-0.09493600
C	1.36846700	-0.89813100	1.33681400
H	1.34274000	-1.97804600	1.48622500
H	2.38415600	-0.55677300	1.54243800
H	0.69879300	-0.43005900	2.05887800
C	1.97565300	-1.09215900	-1.08447600
H	1.99685700	-2.18228500	-1.03906700
H	1.71744900	-0.78775200	-2.09813700
H	2.98005800	-0.73288100	-0.85610500



Carbene-H^+:

Electronic energy: -408.283866055 Hartree/particle

Zero-point correction= 0.260222 (Hartree/Particle)

Thermal correction to Energy= 0.271769

Thermal correction to Enthalpy= 0.272713

Thermal correction to Gibbs Free Energy= 0.224559

Sum of electronic and zero-point Energies= -408.023644

Sum of electronic and thermal Energies= -408.012097

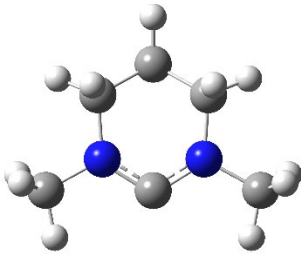
Sum of electronic and thermal Enthalpies= -408.011153

Sum of electronic and thermal Free Energies= -408.059307

N	-0.69253400	0.87561700	0.06366600
C	0.44349900	-1.13230000	-0.42761800
H	0.51260500	-1.34046100	-1.49502900
H	0.64636500	-2.05810400	0.10691900
C	1.45103700	-0.02124300	-0.04936200
C	-1.77853000	1.84095500	0.19791500
H	-2.34763200	1.86431800	-0.72856100
H	-2.42881200	1.53377300	1.01348600
H	-1.36497500	2.82320100	0.40455700
C	2.49311500	0.23680600	-1.14166800
H	3.16065800	1.05264300	-0.86471600
H	3.09587500	-0.66123700	-1.27387200
H	2.02383800	0.47447000	-2.09618000
C	2.15280400	-0.26790800	1.29701100
H	2.80388800	-1.13542800	1.19467600

H	2.76942700	0.58471800	1.58111000
H	1.44262400	-0.46613300	2.09878500
C	-0.96714800	-0.60167400	-0.09631000
C	0.54923900	1.15320000	0.09780200
H	0.88205500	2.17640900	0.24336700
C	-1.51173300	-1.13409800	1.22527100
H	-2.47803200	-0.69596100	1.47199200
H	-1.65493100	-2.20951200	1.12970900
H	-0.82013500	-0.95403800	2.04736400
C	-1.96105000	-0.81519000	-1.22739500
H	-2.04036000	-1.88486000	-1.41739900
H	-2.95542700	-0.45176900	-0.96959200
H	-1.62669600	-0.33264100	-2.14614900

NHC-6

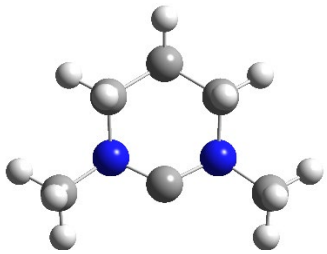


Singlet:

Electronic energy: -345.284574841 Hartree/particle
Zero-point correction= 0.180528 (Hartree/Particle)
Thermal correction to Energy= 0.188826
Thermal correction to Enthalpy= 0.189770
Thermal correction to Gibbs Free Energy= 0.148106
Sum of electronic and zero-point Energies= -345.104047
Sum of electronic and thermal Energies= -345.095749
Sum of electronic and thermal Enthalpies= -345.094805
Sum of electronic and thermal Free Energies= -345.136469

N	1.13472100	-0.39054800	0.00011500
C	0.00000000	-1.09834400	-0.09755300
C	-1.23442300	1.04993200	0.21088200
H	-1.35372200	1.26615500	1.27871100
H	-2.13217200	1.41167400	-0.29412500
C	-2.39966000	-1.09327400	-0.01965200
H	-3.02796400	-0.74006500	-0.84194900
H	-2.19693500	-2.15198600	-0.14447300
H	-2.94441400	-0.93578700	0.91612400
C	-0.00000100	1.73741400	-0.33939100
H	0.00000000	2.79409000	-0.07547800
H	-0.00000500	1.65928600	-1.42777600
C	1.23442600	1.04993300	0.21087300
H	2.13217000	1.41167200	-0.29414600
H	1.35373700	1.26616200	1.27870000

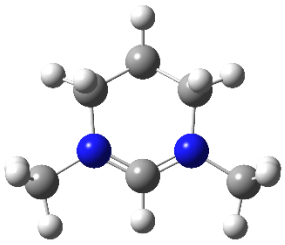
N	-1.13472200	-0.39054800	0.00011600
C	2.39965900	-1.09327600	-0.01964800
H	3.02796900	-0.74006100	-0.84193700
H	2.94440600	-0.93579700	0.91613300
H	2.19693300	-2.15198700	-0.14447800



Triplet:

Electronic energy: -345.186039821 Hartree/particle
Zero-point correction= 0.179152 (Hartree/Particle)
Thermal correction to Energy= 0.187351
Thermal correction to Enthalpy= 0.188295
Thermal correction to Gibbs Free Energy= 0.145996
Sum of electronic and zero-point Energies= -345.006888
Sum of electronic and thermal Energies= -344.998689
Sum of electronic and thermal Enthalpies= -344.997745
Sum of electronic and thermal Free Energies= -345.040044

N	1.20598000	-0.35570900	-0.29599000
C	0.00000000	-0.94541800	0.03982000
C	-1.25781200	1.01986000	0.21059600
H	-1.33400000	1.01395800	1.30951900
H	-2.15052300	1.49760900	-0.19611400
C	-2.36920300	-1.14327600	0.06092400
H	-3.26108200	-0.66048500	-0.33624900
H	-2.28180400	-2.13663900	-0.37598900
H	-2.47481000	-1.24616700	1.14967300
C	0.00000000	1.76293400	-0.22407500
H	0.00000000	2.76701400	0.20094100
H	0.00000000	1.85225300	-1.31147300
C	1.25781200	1.01986000	0.21059700
H	2.15052300	1.49760900	-0.19611200
H	1.33399900	1.01395800	1.30952000
N	-1.20598000	-0.35570900	-0.29599000
C	2.36920300	-1.14327600	0.06092300
H	3.26108200	-0.66048500	-0.33625000
H	2.47481100	-1.24616600	1.14967200
H	2.28180300	-2.13663900	-0.37598800

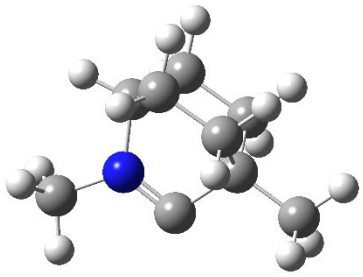


Carbene-H^+:

Electronic energy: -345.723535706 Hartree/particle
Zero-point correction= 0.195406 (Hartree/Particle)
Thermal correction to Energy= 0.203843
Thermal correction to Enthalpy= 0.204787
Thermal correction to Gibbs Free Energy= 0.162749
Sum of electronic and zero-point Energies= -345.528130
Sum of electronic and thermal Energies= -345.519693
Sum of electronic and thermal Enthalpies= -345.518749
Sum of electronic and thermal Free Energies= -345.560787

N	1.16153400	-0.35627800	0.02359100
C	-1.24618600	1.09640900	0.20774900
H	-1.37344200	1.30619300	1.27195200
H	-2.13927000	1.43929300	-0.31174800
C	-2.41421300	-1.10279600	-0.02834000
H	-2.99813300	-0.77903300	-0.88833100
H	-2.20832200	-2.16634200	-0.11110800
H	-2.98286200	-0.91795700	0.88199600
C	-0.00000200	1.76112400	-0.35040000
H	0.00000100	2.81764400	-0.09253800
H	-0.00001300	1.68339900	-1.43803900
C	1.24619400	1.09641000	0.20772500
H	2.13926400	1.43928200	-0.31180500
H	1.37348500	1.30621200	1.27192000
N	-1.16153600	-0.35627700	0.02358900
C	2.41420900	-1.10280100	-0.02832900
H	2.99812400	-0.77906000	-0.88833200
H	2.98286400	-0.91794000	0.88199800
H	2.20831700	-2.16634900	-0.11106900
C	-0.00000100	-0.95615700	-0.05668400
H	-0.00000200	-2.03059400	-0.19547800

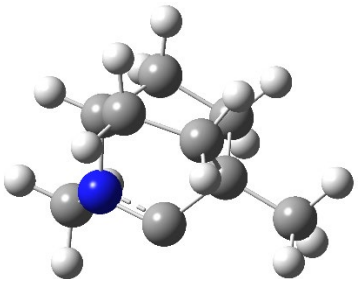
BiCAAC



Singlet:

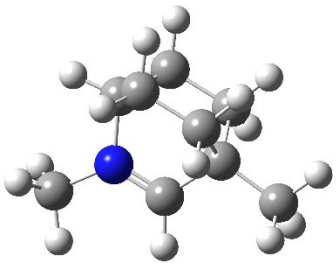
Electronic energy: -406.641851781 Hartree/particle
Zero-point correction= 0.228005 (Hartree/Particle)
Thermal correction to Energy= 0.237257
Thermal correction to Enthalpy= 0.238201
Thermal correction to Gibbs Free Energy= 0.194573
Sum of electronic and zero-point Energies= -406.413847
Sum of electronic and thermal Energies= -406.404595
Sum of electronic and thermal Enthalpies= -406.403650
Sum of electronic and thermal Free Energies= -406.447279

C	0.99764300	0.52480300	1.25386000
C	-0.34750600	1.27507200	1.25045800
C	-1.12031700	0.85152200	0.00002100
C	-0.07216200	-1.32489700	-0.00007300
C	1.11149200	-0.37179800	0.00000400
H	-2.13573500	1.24463200	0.00002000
H	-0.93303400	1.03807300	2.13868400
H	-0.20761000	2.35634100	1.23029500
H	1.08795900	-0.10341500	2.14076400
H	1.84076100	1.21864100	1.26585700
C	2.42619200	-1.13339200	-0.00000800
H	2.49275000	-1.77367800	-0.87997600
H	3.27861400	-0.44967800	0.00004800
H	2.49271100	-1.77377500	0.87989300
C	0.99770100	0.52494400	-1.25375500
H	1.84081400	1.21879200	-1.26562700
H	1.08807100	-0.10316900	-2.14072700
C	-0.34745500	1.27520200	-1.25034000
H	-0.20757000	2.35647000	-1.23006800
H	-0.93294200	1.03828200	-2.13861400
N	-1.17284600	-0.62211600	-0.00005800
C	-2.48793000	-1.24169200	-0.00012200
H	-3.04708300	-0.93679800	-0.88656300
H	-2.34659100	-2.31762900	-0.00015700
H	-3.04713900	-0.93686100	0.88630600

Triplet: 

Electronic energy: -406.568798222 Hartree/particle
Zero-point correction= 0.226596 (Hartree/Particle)
Thermal correction to Energy= 0.235908
Thermal correction to Enthalpy= 0.236852
Thermal correction to Gibbs Free Energy= 0.192081
Sum of electronic and zero-point Energies= -406.342203
Sum of electronic and thermal Energies= -406.332890
Sum of electronic and thermal Enthalpies= -406.331946
Sum of electronic and thermal Free Energies= -406.376717

C	-1.29914100	1.07802300	-0.58131700
C	0.09053500	1.74462700	-0.70203100
C	1.13034400	0.89478200	0.03007200
C	0.01700500	-0.94060200	-0.84733300
C	-1.11897900	-0.36897400	-0.06500000
H	2.10338300	1.38768800	0.03409800
H	0.38667900	1.82645700	-1.74723500
H	0.08431100	2.74873900	-0.27761800
H	-1.80148700	1.05928400	-1.54824500
H	-1.94372700	1.62242700	0.11507400
C	-2.39518300	-1.18063400	-0.17693900
H	-2.25600700	-2.17871100	0.24055300
H	-3.20624500	-0.69034500	0.36477400
H	-2.69154700	-1.28550900	-1.22112400
C	-0.62754600	-0.26346300	1.39862600
H	-1.42819700	0.14692600	2.01905300
H	-0.41283400	-1.26853700	1.76594700
C	0.63491700	0.62611300	1.46198400
H	0.41752500	1.58438700	1.93702900
H	1.41730600	0.15309600	2.05527000
N	1.26834100	-0.37851400	-0.70529400
C	2.33521300	-1.25585000	-0.24744000
H	2.15644900	-1.64626200	0.76293900
H	2.41211200	-2.10079800	-0.92899300
H	3.28091000	-0.71336300	-0.25820000

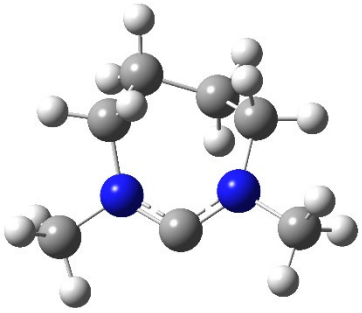


Carbene-H^+:

Electronic energy: -407.079562391 Hartree/particle
Zero-point correction= 0.242124 (Hartree/Particle)
Thermal correction to Energy= 0.251473
Thermal correction to Enthalpy= 0.252418
Thermal correction to Gibbs Free Energy= 0.208573
Sum of electronic and zero-point Energies= -406.837439
Sum of electronic and thermal Energies= -406.828089
Sum of electronic and thermal Enthalpies= -406.827145
Sum of electronic and thermal Free Energies= -406.870989

C	-1.02339000	-0.56612600	1.25020700
C	0.33408800	-1.29205900	1.25894700
C	1.11734300	-0.89659100	0.00002200
C	-1.13647500	0.35283500	0.00000700
H	2.12905800	-1.29314000	0.00002000
H	0.91317800	-1.03810500	2.14555300
H	0.21388100	-2.37377800	1.25004100
H	-1.15673500	0.02912600	2.15224400
H	-1.85434000	-1.26920300	1.20248800
C	-2.41251000	1.17655000	-0.00000800
H	-2.47527800	1.80902500	-0.88570100
H	-3.27733900	0.51435100	0.00004800
H	-2.47523700	1.80912100	0.88561900
C	-1.02344900	-0.56626200	-1.25009800
H	-1.85439300	-1.26933800	-1.20226000
H	-1.15684100	0.02889000	-2.15219300
C	0.33403100	-1.29219100	-1.25882600
H	0.21383000	-2.37391000	-1.24980500
H	0.91308000	-1.03832400	-2.14548400
N	1.21076800	0.57956000	-0.00005800
C	2.52039300	1.22479300	-0.00012300
H	3.06554400	0.90978300	-0.88799700
H	2.39500100	2.30351300	-0.00016900
H	3.06559100	0.90986400	0.88775100
C	0.08738700	1.19331500	-0.00006600
H	0.08111200	2.27962000	-0.00012400

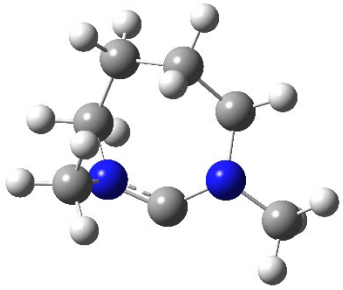
NHC-7



Singlet:

Electronic energy: -384.578725882 Hartree/particle
Zero-point correction= 0.209763 (Hartree/Particle)
Thermal correction to Energy= 0.219073
Thermal correction to Enthalpy= 0.220017
Thermal correction to Gibbs Free Energy= 0.176068
Sum of electronic and zero-point Energies= -384.368963
Sum of electronic and thermal Energies= -384.359653
Sum of electronic and thermal Enthalpies= -384.358709
Sum of electronic and thermal Free Energies= -384.402658

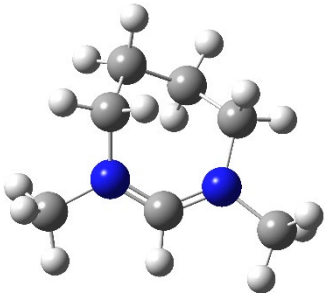
C	0.20504500	-1.26807800	-0.16417100
C	1.32956000	1.00684500	0.15885400
C	-1.09962700	1.74230800	0.00736000
C	0.26513100	1.70545600	-0.67896700
H	1.31263300	1.36162400	1.19438300
H	-1.15720500	2.58524900	0.69991600
H	2.31029700	1.27281500	-0.23795300
H	-1.88756900	1.88187900	-0.73466500
H	0.60047700	2.71895700	-0.90228500
H	0.18805900	1.17815700	-1.63052600
N	-1.01952600	-0.74531600	0.00331100
C	-2.16160700	-1.58052900	-0.32134000
H	-2.68844800	-1.89485200	0.58464300
H	-2.86600600	-1.03837900	-0.95669200
H	-1.80116700	-2.45657400	-0.85003800
C	2.56728900	-1.09261600	0.07029300
H	3.11716600	-0.86273000	0.98639600
H	2.43271200	-2.16564000	-0.00876800
H	3.15582800	-0.73326500	-0.77935400
N	1.25453800	-0.46730100	0.09617000
C	-1.32490800	0.45546200	0.78379200
H	-0.69124100	0.44238000	1.67386500
H	-2.35592000	0.38562300	1.12978400



Triplet:

Electronic energy: -384.495109539 Hartree/particle
Zero-point correction= 0.208044 (Hartree/Particle)
Thermal correction to Energy= 0.217586
Thermal correction to Enthalpy= 0.218530
Thermal correction to Gibbs Free Energy= 0.173023
Sum of electronic and zero-point Energies= -384.287066
Sum of electronic and thermal Energies= -384.277524
Sum of electronic and thermal Enthalpies= -384.276579
Sum of electronic and thermal Free Energies= -384.322087

C	0.50366200	-1.07785100	-0.44178000
C	-1.53617400	0.05007700	-0.98716500
C	-0.28198700	1.54575900	0.70750100
C	-1.53439700	1.34561300	-0.15873400
H	-1.02304100	0.21053700	-1.93473400
H	-0.25542500	2.59128400	1.01887600
H	-2.56180900	-0.25192500	-1.21392100
H	-0.36258300	0.95730500	1.62339000
H	-1.64870400	2.18737800	-0.84545000
H	-2.40606200	1.37026100	0.49873600
N	1.40241000	-0.22495900	0.19975000
C	2.78621500	-0.50228500	-0.13944300
H	3.01254100	-0.23853500	-1.18135000
H	3.44259700	0.06567700	0.51910600
H	2.98009800	-1.56450300	-0.00439600
C	-1.50403800	-1.61802900	0.83855700
H	-2.50909800	-1.94695600	0.56800600
H	-0.93181100	-2.47692900	1.18032500
H	-1.58594500	-0.90361800	1.66603800
N	-0.84422300	-1.04704200	-0.32454800
C	1.06575900	1.19829400	0.07514100
H	1.09561200	1.50807200	-0.98220300
H	1.85207200	1.74649300	0.59670600

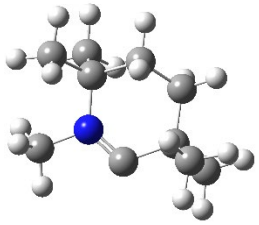


Carbene-H^+:

Electronic energy: -385.021620275 Hartree/particle
Zero-point correction= 0.224684 (Hartree/Particle)
Thermal correction to Energy= 0.234134
Thermal correction to Enthalpy= 0.235078
Thermal correction to Gibbs Free Energy= 0.190744
Sum of electronic and zero-point Energies= -384.796936
Sum of electronic and thermal Energies= -384.787486
Sum of electronic and thermal Enthalpies= -384.786542
Sum of electronic and thermal Free Energies= -384.830876

C	1.32500400	1.07329500	0.15798600
C	-1.14101000	1.74092900	-0.02353400
C	0.24191900	1.73740100	-0.68142800
H	1.29718000	1.38671200	1.20292300
H	-1.24214100	2.59310800	0.64926600
H	2.30368800	1.34934500	-0.23023400
H	-1.91175800	1.84810700	-0.78647400
H	0.55311800	2.76059400	-0.88577600
H	0.20326800	1.23297300	-1.64864900
N	-1.03484200	-0.75254000	0.07220300
C	-2.13890500	-1.61751800	-0.34061100
H	-2.72652500	-1.90157100	0.53068400
H	-2.77475600	-1.08233500	-1.04423000
H	-1.75151300	-2.50894900	-0.82589700
C	2.59849200	-1.06179100	0.08263400
H	3.10845300	-0.83596600	1.01795700
H	2.47873100	-2.13823600	0.00152200
H	3.19722400	-0.69437500	-0.74921400
N	1.28934500	-0.40586300	0.07653800
C	-1.37517300	0.48408600	0.79634400
H	-0.77411000	0.49515200	1.70639600
H	-2.41544000	0.39504600	1.10005200
C	0.20809900	-1.12903800	-0.10166100
H	0.36249700	-2.15496200	-0.41789400

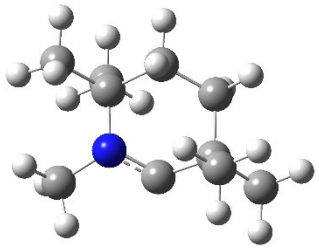
CAAC-6



Singlet:

Electronic energy: -447.149436548 Hartree/particle
Zero-point correction= 0.276062 (Hartree/Particle)
Thermal correction to Energy= 0.288168
Thermal correction to Enthalpy= 0.289112
Thermal correction to Gibbs Free Energy= 0.239740
Sum of electronic and zero-point Energies= -446.873375
Sum of electronic and thermal Energies= -446.861269
Sum of electronic and thermal Enthalpies= -446.860324
Sum of electronic and thermal Free Energies= -446.909697

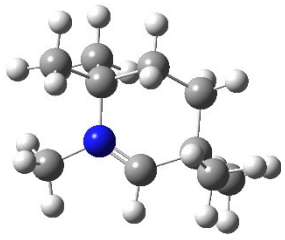
N	-0.62986400	0.91659000	0.01022300
C	0.64298600	1.20624300	0.03448400
C	1.05213500	-1.33741100	0.24349700
H	0.91597900	-1.50371500	1.31475700
H	1.75488700	-2.10092900	-0.09946900
C	1.63540900	0.06032600	0.00969900
C	2.69010400	0.36109600	1.07761900
H	3.45866800	-0.41599400	1.07507500
C	2.31086600	0.13515400	-1.36867300
H	3.14153700	-0.57265100	-1.40907600
H	1.61675000	-0.10309100	-2.17577600
H	3.15696500	1.32682800	0.88921200
H	2.23933200	0.39204900	2.07119100
H	2.69454600	1.13916300	-1.54468800
C	-0.27612500	-1.47818900	-0.47298200
H	-0.71008800	-2.46827100	-0.31973900
H	-0.13047300	-1.35929300	-1.54968800
C	-1.56667900	2.04677300	0.02994800
H	-2.32705200	1.90639700	0.79817700
H	-0.98567500	2.93625700	0.24076300
H	-2.06196400	2.15306000	-0.93458400
C	-1.28895300	-0.43699100	-0.00188700
C	-2.46934100	-0.44075200	-0.97258200
H	-2.83461500	-1.46345500	-1.07409600
H	-3.29788500	0.17453500	-0.62505200
H	-2.16133400	-0.09141100	-1.95878000
C	-1.78354600	-0.75602700	1.41050700
H	-2.52361100	-0.03050800	1.74624800
H	-2.25523300	-1.73979300	1.42048400
H	-0.96282300	-0.75664500	2.12570600



Triplet:

Electronic energy: -447.090531304 Hartree/particle
Zero-point correction= 0.274380 (Hartree/Particle)
Thermal correction to Energy= 0.286813
Thermal correction to Enthalpy= 0.287757
Thermal correction to Gibbs Free Energy= 0.236818
Sum of electronic and zero-point Energies= -446.816152
Sum of electronic and thermal Energies= -446.803718
Sum of electronic and thermal Enthalpies= -446.802774
Sum of electronic and thermal Free Energies= -446.853713

N	-0.67893300	0.91301100	-0.10566100
C	0.57423700	0.97171500	0.44840800
C	1.08387100	-1.35246700	0.06837200
H	1.01985000	-1.66287200	1.11367500
H	1.76686500	-2.04596100	-0.43033700
C	1.68250000	0.07482100	0.02277400
C	2.86018700	0.17308500	0.98714100
H	3.64182200	-0.53458900	0.70365100
C	2.15087500	0.41940900	-1.40013300
H	2.91114100	-0.28918800	-1.73734100
H	1.31858900	0.40050400	-2.10307100
H	3.28581100	1.17726400	0.97286300
H	2.54170300	-0.04785400	2.00643400
H	2.58233600	1.42073000	-1.41854800
C	-0.29740700	-1.43081600	-0.57813900
H	-0.70360900	-2.43785400	-0.46071900
H	-0.21204500	-1.24615000	-1.65187400
C	-1.51506100	2.07951200	0.11389100
H	-2.31427200	2.11956700	-0.62326500
H	-1.95523100	2.09952900	1.11774800
H	-0.89545000	2.96714200	-0.00003800
C	-1.31809000	-0.42760800	-0.01158300
C	-2.56643700	-0.45968300	-0.88709200
H	-2.92169200	-1.48711300	-0.97261700
H	-3.37581200	0.13541900	-0.46439300
H	-2.34077900	-0.08739200	-1.88726400
C	-1.69161300	-0.76715900	1.43407000
H	-2.44054300	-0.07037200	1.81272500
H	-2.11366000	-1.77166700	1.48932100
H	-0.82086000	-0.71507000	2.08642400



Carbene-H^+:

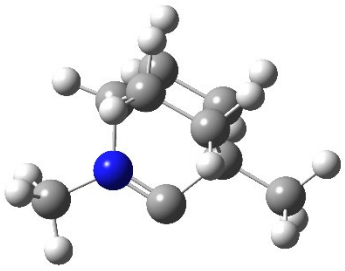
Electronic energy: -447.595699560 Hartree/particle
Zero-point correction= 0.290365 (Hartree/Particle)
Thermal correction to Energy= 0.302598
Thermal correction to Enthalpy= 0.303543
Thermal correction to Gibbs Free Energy= 0.253949
Sum of electronic and zero-point Energies= -447.305335
Sum of electronic and thermal Energies= -447.293101
Sum of electronic and thermal Enthalpies= -447.292157
Sum of electronic and thermal Free Energies= -447.341750

N	-0.66450300	0.89785800	-0.00881100
C	1.03803700	-1.38056500	0.21687600
H	0.91700600	-1.56905200	1.28448100
H	1.73020900	-2.13551300	-0.15529500
C	1.65113000	0.00447800	0.00472100
C	2.64524800	0.35049600	1.12385600
H	3.42201600	-0.41347300	1.14513800
C	2.36892200	0.10639100	-1.35680200
H	3.22924000	-0.56179800	-1.34036000
H	1.71963500	-0.18496500	-2.18141200
H	3.12386200	1.31461400	0.95052200
H	2.16020800	0.36767200	2.10005800
H	2.73263800	1.11717500	-1.54353100
C	-0.30059400	-1.49290100	-0.49247200
H	-0.73390200	-2.48133800	-0.34367800
H	-0.16882600	-1.36634200	-1.56977600
C	-1.55513000	2.06835100	0.00037500
H	-2.29712100	1.94569300	0.78451700
H	-0.97020900	2.96239800	0.18921700
H	-2.05587600	2.14814300	-0.96062900
C	-1.32105000	-0.46603200	-0.00014400
C	0.60395600	1.06089400	0.00075900
H	0.95198000	2.09156800	-0.00258200
C	-2.51680500	-0.44542600	-0.94768400
H	-2.89883100	-1.46234500	-1.02362400
H	-3.32821200	0.18266900	-0.58490500
H	-2.22806500	-0.12159700	-1.94787500
C	-1.77378200	-0.74456100	1.43302800
H	-2.51513800	-0.02145500	1.76967700

H	-2.23913000	-1.72885400	1.46430200
H	-0.93954800	-0.73495700	2.13235200

PBE1PBE/def2-TZVPP

BiCAAC

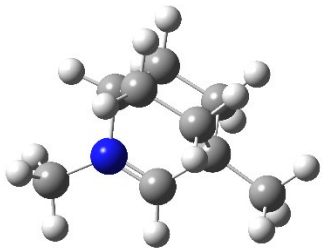


Singlet:

Electronic energy: -406.334870413 Hartree/particle
Zero-point correction= 0.226572 (Hartree/Particle)
Thermal correction to Energy= 0.235928
Thermal correction to Enthalpy= 0.236872
Thermal correction to Gibbs Free Energy= 0.193088
Sum of electronic and zero-point Energies= -406.108298
Sum of electronic and thermal Energies= -406.098943
Sum of electronic and thermal Enthalpies= -406.097999
Sum of electronic and thermal Free Energies= -406.141782

C	0.99356200	0.52368600	1.25233500
C	-0.34593000	1.27349200	1.24688400
C	-1.11821300	0.85028100	0.00002000
C	-0.07209000	-1.31897200	-0.00007200
C	1.10914800	-0.37108600	0.00000500
H	-2.13280200	1.25100700	0.00001900
H	-0.93236700	1.04373900	2.13886000
H	-0.20462600	2.35651400	1.22592300
H	1.08375500	-0.10513200	2.14097900
H	1.83960000	1.21673600	1.27059100
C	2.42160800	-1.13279600	-0.00000600
H	2.49036500	-1.77534300	-0.87983000
H	3.27802900	-0.45172200	0.00004900
H	2.49032600	-1.77543700	0.87975200
C	0.99361900	0.52382200	-1.25223300
H	1.83965700	1.21687700	-1.27037100
H	1.08385900	-0.10489800	-2.14094200
C	-0.34587500	1.27362300	-1.24676600
H	-0.20457500	2.35664400	-1.22568700
H	-0.93227100	1.04396000	-2.13879100
N	-1.17362700	-0.61831400	-0.00005900
C	-2.47941400	-1.24350500	-0.00012200
H	-3.04673600	-0.94789700	-0.88702500
H	-2.32852900	-2.32014100	-0.00016900

H	-3.04678100	-0.94798000	0.88678100

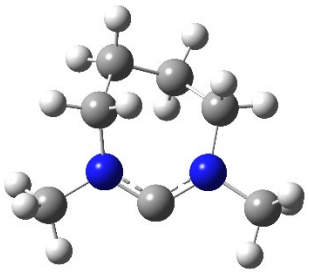


Carbene-H^+:

Electronic energy: -406.778530714 Hartree/particle
Zero-point correction= 0.240888 (Hartree/Particle)
Thermal correction to Energy= 0.250312
Thermal correction to Enthalpy= 0.251256
Thermal correction to Gibbs Free Energy= 0.207323
Sum of electronic and zero-point Energies= -406.537643
Sum of electronic and thermal Energies= -406.528219
Sum of electronic and thermal Enthalpies= -406.527274
Sum of electronic and thermal Free Energies= -406.571208

C	-1.01896700	-0.56553200	1.24795800
C	0.33399800	-1.28882400	1.25513600
C	1.11532200	-0.89295200	0.00002200
C	-1.13452500	0.35228700	0.00000700
H	2.12652500	-1.29563700	0.00002000
H	0.91377800	-1.04063900	2.14527800
H	0.21425700	-2.37250800	1.24647600
H	-1.15435500	0.02884200	2.15237900
H	-1.85164800	-1.26946000	1.20308000
C	-2.40983000	1.17307100	-0.00000700
H	-2.47714300	1.80753600	-0.88575200
H	-3.27773500	0.51283800	0.00004800
H	-2.47710300	1.80763000	0.88567300
C	-1.01902500	-0.56566600	-1.24785000
H	-1.85170300	-1.26959100	-1.20285500
H	-1.15445800	0.02861000	-2.15232900
C	0.33394000	-1.28895700	-1.25501500
H	0.21420200	-2.37264000	-1.24623700
H	0.91368000	-1.04086300	-2.14520900
N	1.21164400	0.57641300	-0.00005800
C	2.51145300	1.22505100	-0.00012300
H	3.06497000	0.91748700	-0.88764600
H	2.38404000	2.30537600	-0.00017300
H	3.06501400	0.91757500	0.88740400
C	0.08550400	1.18895200	-0.00006500
H	0.07894700	2.27597100	-0.00012300

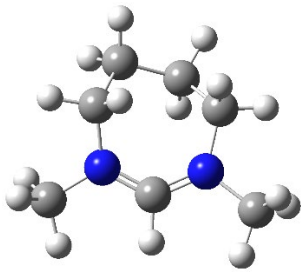
NHC-7



Singlet:

Electronic energy: -384.289628708 Hartree/particle
Zero-point correction= 0.208333 (Hartree/Particle)
Thermal correction to Energy= 0.217757
Thermal correction to Enthalpy= 0.218702
Thermal correction to Gibbs Free Energy= 0.174472
Sum of electronic and zero-point Energies= -384.081296
Sum of electronic and thermal Energies= -384.071871
Sum of electronic and thermal Enthalpies= -384.070927
Sum of electronic and thermal Free Energies= -384.115157

C	0.19017800	-1.26285100	-0.15791200
C	1.34005500	0.99016600	0.18733300
C	-1.07913500	1.75405200	-0.01863300
C	0.30693400	1.72110000	-0.65459500
H	1.30950400	1.32281400	1.23194000
H	-1.16475000	2.60025000	0.67043600
H	2.33426600	1.25518800	-0.18087200
H	-1.83981400	1.90002400	-0.79009900
H	0.65847300	2.73956000	-0.83811700
H	0.25867600	1.22812200	-1.62813800
N	-1.03148100	-0.73847400	0.00559800
C	-2.16341400	-1.58175300	-0.30907300
H	-2.71625400	-1.86107100	0.59582400
H	-2.85627900	-1.07385400	-0.98771600
H	-1.78791200	-2.48114800	-0.78990600
C	2.54556000	-1.12156900	0.05920500
H	3.08577800	-0.95636400	0.99764600
H	2.38855500	-2.18769500	-0.07856000
H	3.16373500	-0.73358400	-0.75928700
N	1.24937800	-0.47663300	0.08793700
C	-1.34414400	0.47714900	0.75421500
H	-0.74686700	0.46851600	1.67153900
H	-2.38858300	0.42723200	1.06733100



Carbene-H^+:

Electronic energy: -384.738531061 Hartree/particle
Zero-point correction= 0.223451 (Hartree/Particle)
Thermal correction to Energy= 0.233016
Thermal correction to Enthalpy= 0.233960
Thermal correction to Gibbs Free Energy= 0.189318
Sum of electronic and zero-point Energies= -384.515080
Sum of electronic and thermal Energies= -384.505515
Sum of electronic and thermal Enthalpies= -384.504571
Sum of electronic and thermal Free Energies= -384.549213

C	1.33923600	1.05303400	0.18005800
C	-1.11610100	1.75463300	-0.04324100
C	0.28397800	1.75353100	-0.65710000
H	1.30770700	1.34987400	1.23174500
H	-1.23856900	2.60691400	0.62907900
H	2.32866600	1.32458800	-0.18873100
H	-1.86252300	1.87451100	-0.83062800
H	0.61257200	2.78114000	-0.81919600
H	0.26815100	1.28831000	-1.64620900
N	-1.04913300	-0.74162200	0.06960500
C	-2.14391900	-1.61447700	-0.32781300
H	-2.74896200	-1.87114500	0.54260800
H	-2.77332600	-1.10986800	-1.06206600
H	-1.75389900	-2.52640000	-0.77560700
C	2.57478000	-1.09333200	0.07364400
H	3.08235500	-0.91532500	1.02293600
H	2.43992000	-2.16606100	-0.04824300
H	3.19615500	-0.71108200	-0.73720100
N	1.28405600	-0.41690500	0.07234000
C	-1.39177400	0.50404700	0.76671400
H	-0.82816200	0.51452600	1.70243600
H	-2.44444400	0.43557000	1.03676500
C	0.19251700	-1.12581200	-0.09922600
H	0.33759200	-2.15560500	-0.40951100

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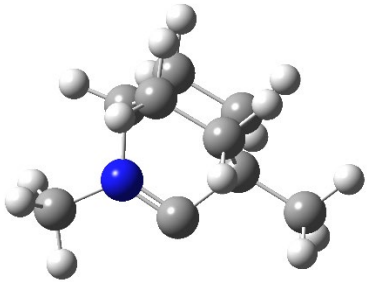
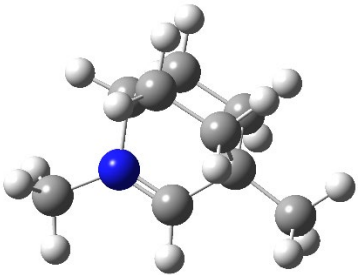
BiCAAC



Singlet:

Electronic energy: -406.706806288 Hartree/particle
Zero-point correction= 0.228072 (Hartree/Particle)
Thermal correction to Energy= 0.237301
Thermal correction to Enthalpy= 0.238245
Thermal correction to Gibbs Free Energy= 0.194694
Sum of electronic and zero-point Energies= -406.478734
Sum of electronic and thermal Energies= -406.469505
Sum of electronic and thermal Enthalpies= -406.468561
Sum of electronic and thermal Free Energies= -406.512112

C	0.99712100	0.52596600	1.25443400
C	-0.34784600	1.27368900	1.25068900
C	-1.11845400	0.84990700	0.00002000
C	-0.07342100	-1.32216700	-0.00007200
C	1.11080100	-0.37167000	0.00000500
H	-2.13162700	1.24854200	0.00001900
H	-0.93393300	1.03663000	2.13871200
H	-0.20907700	2.35519100	1.23343300
H	1.09034800	-0.09896000	2.14329200
H	1.83854500	1.22175000	1.26668600
C	2.42589000	-1.13507900	-0.00000700
H	2.49477300	-1.77600100	-0.87954500
H	3.27997300	-0.45280300	0.00004800
H	2.49473500	-1.77609400	0.87946700
C	0.99717900	0.52610400	-1.25433100
H	1.83860000	1.22189400	-1.26646200
H	1.09045500	-0.09872300	-2.14325400
C	-0.34779200	1.27381900	-1.25057100
H	-0.20903000	2.35532100	-1.23320000
H	-0.93383800	1.03684700	-2.13864300
N	-1.17447500	-0.62033200	-0.00005800
C	-2.48521400	-1.24199400	-0.00012200
H	-3.04780100	-0.94211400	-0.88675200
H	-2.34253800	-2.31841500	-0.00016700
H	-3.04784900	-0.94219400	0.88650500

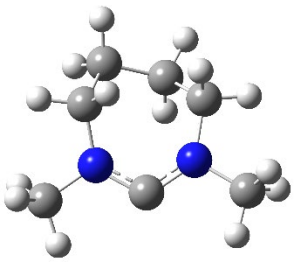


Carbene-H^+:

Electronic energy: -407.152948945 Hartree/particle
Zero-point correction= 0.242403 (Hartree/Particle)
Thermal correction to Energy= 0.251726
Thermal correction to Enthalpy= 0.252670
Thermal correction to Gibbs Free Energy= 0.208908
Sum of electronic and zero-point Energies= -406.910546
Sum of electronic and thermal Energies= -406.901223
Sum of electronic and thermal Enthalpies= -406.900279
Sum of electronic and thermal Free Energies= -406.944041

C	-1.02097700	-0.56672300	1.25183400
C	0.33618700	-1.29042700	1.25874700
C	1.11634200	-0.89354700	0.00002200
C	-1.13618800	0.35050700	0.00000700
H	2.12622900	-1.29375100	0.00002000
H	0.91605900	-1.03832900	2.14540400
H	0.21647000	-2.37199200	1.25149100
H	-1.15423700	0.02865700	2.15377200
H	-1.85052600	-1.27125200	1.20953100
C	-2.41316200	1.17427800	-0.00000700
H	-2.47798100	1.80763700	-0.88509900
H	-3.27958300	0.51436100	0.00004700
H	-2.47794200	1.80773000	0.88502100
C	-1.02103500	-0.56685900	-1.25172600
H	-1.85058100	-1.27138500	-1.20930600
H	-1.15434200	0.02842300	-2.15372200
C	0.33613000	-1.29056000	-1.25862600
H	0.21641600	-2.37212400	-1.25125400
H	0.91596100	-1.03855100	-2.14533500
N	1.21025700	0.57914400	-0.00005800
C	2.51492600	1.22645100	-0.00012300
H	3.06361000	0.91589700	-0.88753500
H	2.39122200	2.30580400	-0.00017300
H	3.06365500	0.91598500	0.88729200
C	0.08572300	1.19071700	-0.00006600
H	0.07608900	2.27586200	-0.00012400

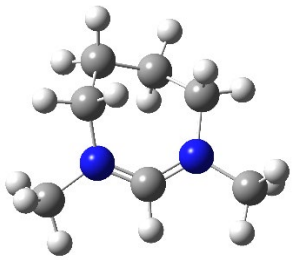
NHC-7



Singlet:

Electronic energy: -384.637923092 Hartree/particle
Zero-point correction= 0.209702 (Hartree/Particle)
Thermal correction to Energy= 0.219046
Thermal correction to Enthalpy= 0.219990
Thermal correction to Gibbs Free Energy= 0.175892
Sum of electronic and zero-point Energies= -384.428221
Sum of electronic and thermal Energies= -384.418877
Sum of electronic and thermal Enthalpies= -384.417933
Sum of electronic and thermal Free Energies= -384.462031

C	0.19403100	-1.26533900	-0.15458200
C	1.33966800	0.99388000	0.18636500
C	-1.08530700	1.75211400	-0.01833700
C	0.30270100	1.72316500	-0.65824300
H	1.30560700	1.32686400	1.22873800
H	-1.17123900	2.59776800	0.66836400
H	2.33075500	1.26132100	-0.18253600
H	-1.84619500	1.89065400	-0.78844100
H	0.65017200	2.74146300	-0.83895800
H	0.25465200	1.23079800	-1.63030100
N	-1.02983600	-0.74191200	0.00876200
C	-2.16468400	-1.58430100	-0.31400100
H	-2.70771900	-1.88210400	0.58900300
H	-2.86070600	-1.06031800	-0.97458400
H	-1.79565500	-2.47251400	-0.81702000
C	2.55476000	-1.11698300	0.05690800
H	3.10693500	-0.92158300	0.98054800
H	2.40512000	-2.18632800	-0.04946500
H	3.15411900	-0.74852000	-0.78231500
N	1.25269200	-0.47561700	0.09276100
C	-1.34753300	0.47339100	0.75900800
H	-0.75576900	0.46753000	1.67782000
H	-2.39188800	0.42211300	1.06578300



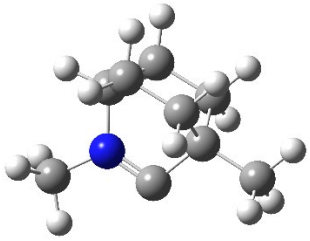
Carbene-H^+:

Electronic energy: -385.089352003 Hartree/particle
Zero-point correction= 0.224886 (Hartree/Particle)
Thermal correction to Energy= 0.234360
Thermal correction to Enthalpy= 0.235304
Thermal correction to Gibbs Free Energy= 0.190818
Sum of electronic and zero-point Energies= -384.864466
Sum of electronic and thermal Energies= -384.854992
Sum of electronic and thermal Enthalpies= -384.854048
Sum of electronic and thermal Free Energies= -384.898534

C	1.33787100	1.05706400	0.18366500
C	-1.12208900	1.75292900	-0.04604600
C	0.28158100	1.75527300	-0.66028000
H	1.29734900	1.35189900	1.23350600
H	-1.24702800	2.60603900	0.62159600
H	2.32585300	1.33143000	-0.18075000
H	-1.86663300	1.86302500	-0.83417600
H	0.60632600	2.78212800	-0.82123900
H	0.26770400	1.28769900	-1.64645900
N	-1.04620200	-0.74523400	0.07259100
C	-2.14499400	-1.61745000	-0.33117300
H	-2.73807600	-1.89257400	0.53988700
H	-2.77965800	-1.09650700	-1.04677800
H	-1.75846900	-2.51755400	-0.80199100
C	2.58359400	-1.08879000	0.06912500
H	3.10401600	-0.88133400	1.00326500
H	2.45378200	-2.16383800	-0.02150500
H	3.18491000	-0.72466500	-0.76294900
N	1.28546800	-0.41682300	0.07654500
C	-1.39550700	0.50180700	0.76985300
H	-0.83695600	0.51583400	1.70657700
H	-2.44774200	0.43179300	1.03392300
C	0.19581500	-1.12801700	-0.09528700
H	0.34213800	-2.15586400	-0.40599600

PBEPBE/def2-TZVPP

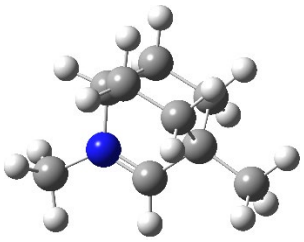
BiCAAC



Singlet:

Electronic energy: -406.272813984 Hartree/particle
Zero-point correction= 0.219088 (Hartree/Particle)
Thermal correction to Energy= 0.228748
Thermal correction to Enthalpy= 0.229693
Thermal correction to Gibbs Free Energy= 0.185394
Sum of electronic and zero-point Energies= -406.053726
Sum of electronic and thermal Energies= -406.044066
Sum of electronic and thermal Enthalpies= -406.043121
Sum of electronic and thermal Free Energies= -406.087420

C	0.99918600	0.52791000	1.26199000
C	-0.34868400	1.28362100	1.25578900
C	-1.12810900	0.86037000	0.00002100
C	-0.06908300	-1.33062600	-0.00007300
C	1.11660200	-0.37452900	0.00000500
H	-2.14950800	1.26417300	0.00002000
H	-0.93969900	1.05370200	2.15377300
H	-0.20507800	2.37378200	1.23301500
H	1.08815900	-0.10686000	2.15563000
H	1.85113300	1.22558400	1.28167000
C	2.43844700	-1.13964500	-0.00000700
H	2.50730200	-1.78663200	-0.88560400
H	3.30022500	-0.45357500	0.00004900
H	2.50726300	-1.78672700	0.88552400
C	0.99924400	0.52804900	-1.26188700
H	1.85118900	1.22573000	-1.28144600
H	1.08826600	-0.10662000	-2.15559300
C	-0.34863000	1.28375300	-1.25567000
H	-0.20503100	2.37391200	-1.23278100
H	-0.93960400	1.05392000	-2.15370300
N	-1.17945800	-0.62501600	-0.00005900
C	-2.49638600	-1.25577900	-0.00012300
H	-3.06651800	-0.95727100	-0.89342500
H	-2.34084800	-2.33940400	-0.00016500
H	-3.06656800	-0.95734700	0.89317400

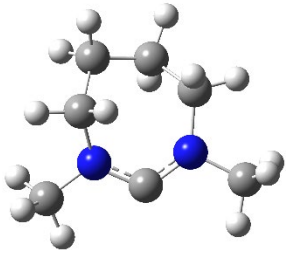


Carbene-H^+:

Electronic energy: -406.713895177 Hartree/particle
Zero-point correction= 0.233149 (Hartree/Particle)
Thermal correction to Energy= 0.242881
Thermal correction to Enthalpy= 0.243825
Thermal correction to Gibbs Free Energy= 0.199359
Sum of electronic and zero-point Energies= -406.480746
Sum of electronic and thermal Energies= -406.471015
Sum of electronic and thermal Enthalpies= -406.470070
Sum of electronic and thermal Free Energies= -406.514536

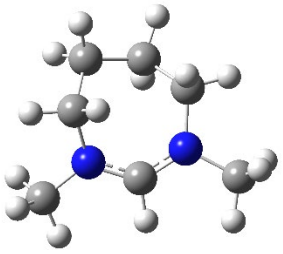
C	-1.02516800	-0.57136900	1.25720700
C	0.33563700	-1.29746600	1.26444500
C	1.12427900	-0.90012800	0.00002200
C	-1.14192700	0.35896900	0.00000700
H	2.14188300	-1.30656600	0.00002000
H	0.92031000	-1.04839700	2.16006800
H	0.21713600	-2.38877400	1.25315700
H	-1.16379700	0.02666900	2.16727800
H	-1.86400700	-1.27913000	1.20605200
C	-2.42762000	1.18055100	-0.00000700
H	-2.49715200	1.81905000	-0.89136400
H	-3.29983100	0.51410000	0.00004800
H	-2.49711100	1.81914400	0.89128600
C	-1.02522600	-0.57150300	-1.25709800
H	-1.86406200	-1.27926000	-1.20582800
H	-1.16389900	0.02643700	-2.16722700
C	0.33557900	-1.29760000	-1.26432300
H	0.21708000	-2.38890700	-1.25291500
H	0.92021000	-1.04862400	-2.15999900
N	1.22241400	0.57990300	-0.00005900
C	2.52971500	1.23493500	-0.00012400
H	3.08859000	0.92573100	-0.89307100
H	2.39931000	2.32212200	-0.00017500
H	3.08863300	0.92582100	0.89282700
C	0.08175000	1.19840400	-0.00006600
H	0.07770300	2.29250600	-0.00012400

NHC-7

Singlet: 

Electronic energy: -384.240729790 Hartree/particle
Zero-point correction= 0.201274 (Hartree/Particle)
Thermal correction to Energy= 0.211011
Thermal correction to Enthalpy= 0.211955
Thermal correction to Gibbs Free Energy= 0.167105
Sum of electronic and zero-point Energies= -384.039456
Sum of electronic and thermal Energies= -384.029719
Sum of electronic and thermal Enthalpies= -384.028775
Sum of electronic and thermal Free Energies= -384.073625

C	0.18721600	-1.27567700	-0.15812300
C	1.35698400	0.99837000	0.19277200
C	-1.08040500	1.77148000	-0.02403600
C	0.32033000	1.73846700	-0.65341700
H	1.32658400	1.32545800	1.24697100
H	-1.17224200	2.62495900	0.66739400
H	2.36023500	1.26101200	-0.17509300
H	-1.83858900	1.91998300	-0.80797400
H	0.67588200	2.76466700	-0.83129900
H	0.27707500	1.24863200	-1.63705400
N	-1.04281200	-0.74417900	0.00709500
C	-2.18434900	-1.59339100	-0.30926400
H	-2.74969600	-1.86092700	0.60088200
H	-2.87394200	-1.08838800	-1.00538500
H	-1.80186900	-2.50516700	-0.77813900
C	2.56083600	-1.14055800	0.05942300
H	3.09699900	-0.98906200	1.01131500
H	2.39503700	-2.21087800	-0.09394300
H	3.19222100	-0.74194200	-0.75427200
N	1.25713400	-0.48521800	0.08450000
C	-1.36138900	0.49015700	0.75464800
H	-0.76723700	0.47822200	1.68321300
H	-2.41604700	0.44612600	1.06020600



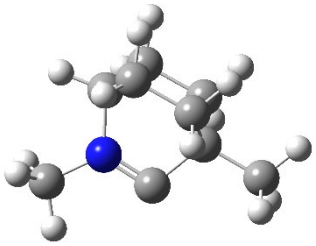
Carbene-H^+:

Electronic energy: -384.686779562 Hartree/particle
Zero-point correction= 0.216221 (Hartree/Particle)
Thermal correction to Energy= 0.226080
Thermal correction to Enthalpy= 0.227024
Thermal correction to Gibbs Free Energy= 0.181804
Sum of electronic and zero-point Energies= -384.470558
Sum of electronic and thermal Energies= -384.460700
Sum of electronic and thermal Enthalpies= -384.459755
Sum of electronic and thermal Free Energies= -384.504976

C	1.35172600	1.06392200	0.17136600
C	-1.12482500	1.76594800	-0.03802300
C	0.28241200	1.76756000	-0.66128400
H	1.33103100	1.36250100	1.23087500
H	-1.24676000	2.62247600	0.64113300
H	2.34531900	1.33534800	-0.20889300
H	-1.87845700	1.88953400	-0.82815300
H	0.61108500	2.80321200	-0.82290800
H	0.26236400	1.30396400	-1.65914000
N	-1.05909100	-0.74993200	0.07393100
C	-2.16186100	-1.62481200	-0.33472700
H	-2.78106100	-1.87574300	0.53673200
H	-2.78562500	-1.11611000	-1.08216900
H	-1.76825600	-2.54601300	-0.77784500
C	2.59626400	-1.10170800	0.08027500
H	3.09734300	-0.92672500	1.04224300
H	2.45953000	-2.18067900	-0.04833700
H	3.23039400	-0.71280700	-0.72752900
N	1.29689900	-0.41920100	0.06785600
C	-1.40286800	0.50720000	0.77646200
H	-0.83325000	0.51414300	1.71736200
H	-2.46249400	0.43822700	1.04917900
C	0.19470700	-1.13705100	-0.10111700
H	0.34084700	-2.17375000	-0.41276500

PW91PW91/def2-TZVPP

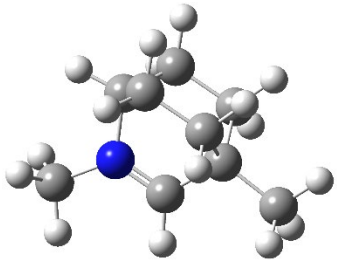
BiCAAC



Singlet:

Electronic energy: -406.645196947 Hartree/particle
Zero-point correction= 0.219570 (Hartree/Particle)
Thermal correction to Energy= 0.229214
Thermal correction to Enthalpy= 0.230158
Thermal correction to Gibbs Free Energy= 0.185891
Sum of electronic and zero-point Energies= -406.425627
Sum of electronic and thermal Energies= -406.415983
Sum of electronic and thermal Enthalpies= -406.415039
Sum of electronic and thermal Free Energies= -406.459306

C	0.99886600	0.52765600	1.26129200
C	-0.34835100	1.28315900	1.25497500
C	-1.12754700	0.86019200	0.00002100
C	-0.06934500	-1.32928500	-0.00007300
C	1.11605400	-0.37460100	0.00000500
H	-2.14748600	1.26300400	0.00002000
H	-0.93829500	1.05355000	2.15169500
H	-0.20456900	2.37162800	1.23220600
H	1.08747700	-0.10589300	2.15373900
H	1.84945500	1.22431300	1.28065800
C	2.43672400	-1.13965000	-0.00000700
H	2.50513400	-1.78560700	-0.88432500
H	3.29736600	-0.45481600	0.00004900
H	2.50509500	-1.78570200	0.88424500
C	0.99892400	0.52779500	-1.26118900
H	1.84951100	1.22445800	-1.28043400
H	1.08758400	-0.10565300	-2.15370200
C	-0.34829600	1.28329000	-1.25485600
H	-0.20452200	2.37175800	-1.23197100
H	-0.93820000	1.05376800	-2.15162500
N	-1.17888600	-0.62465500	-0.00005900
C	-2.49505900	-1.25529200	-0.00012300
H	-3.06425300	-0.95725400	-0.89210600
H	-2.33961100	-2.33722400	-0.00016500
H	-3.06430200	-0.95733100	0.89185500

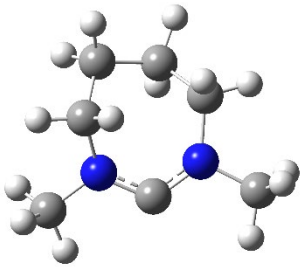


Carbene-H^+:

Electronic energy: -407.086578895 Hartree/particle
Zero-point correction= 0.233644 (Hartree/Particle)
Thermal correction to Energy= 0.243361
Thermal correction to Enthalpy= 0.244305
Thermal correction to Gibbs Free Energy= 0.199869
Sum of electronic and zero-point Energies= -406.852934
Sum of electronic and thermal Energies= -406.843218
Sum of electronic and thermal Enthalpies= -406.842274
Sum of electronic and thermal Free Energies= -406.886709

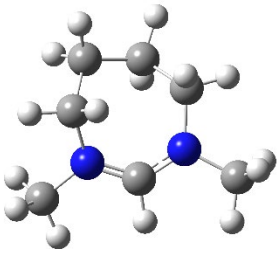
C	-1.02475400	-0.57111700	1.25654800
C	0.33532200	-1.29716800	1.26363300
C	1.12373700	-0.89999400	0.00002200
C	-1.14102000	0.35930400	0.00000700
H	2.13987900	-1.30547100	0.00002000
H	0.91895700	-1.04843500	2.15798200
H	0.21644800	-2.38677500	1.25224300
H	-1.16283300	0.02582800	2.16538800
H	-1.86233400	-1.27771600	1.20511900
C	-2.42582400	1.18033300	-0.00000700
H	-2.49498000	1.81787900	-0.89007500
H	-3.29670900	0.51484200	0.00004800
H	-2.49494000	1.81797300	0.88999600
C	-1.02481300	-0.57125200	-1.25643900
H	-1.86238900	-1.27784600	-1.20489500
H	-1.16293500	0.02559500	-2.16533700
C	0.33526400	-1.29730200	-1.26351100
H	0.21639200	-2.38690800	-1.25200100
H	0.91885700	-1.04866200	-2.15791300
N	1.22145100	0.57973400	-0.00005900
C	2.52820500	1.23442400	-0.00012400
H	3.08611800	0.92564200	-0.89176600
H	2.39777200	2.31995800	-0.00017500
H	3.08616100	0.92573200	0.89152300
C	0.08197800	1.19777700	-0.00006600
H	0.07780800	2.29018800	-0.00012300

NHC-7



Singlet:

Electronic energy: -384.588341561 Hartree/particle
Zero-point correction= 0.201734 (Hartree/Particle)
Thermal correction to Energy= 0.211458
Thermal correction to Enthalpy= 0.212402
Thermal correction to Gibbs Free Energy= 0.167575
Sum of electronic and zero-point Energies= -384.386608
Sum of electronic and thermal Energies= -384.376884
Sum of electronic and thermal Enthalpies= -384.375940
Sum of electronic and thermal Free Energies= -384.420767



Carbene-H^+:

Electronic energy: -385.034719192 Hartree/particle
Zero-point correction= 0.216695 (Hartree/Particle)
Thermal correction to Energy= 0.226539
Thermal correction to Enthalpy= 0.227483
Thermal correction to Gibbs Free Energy= 0.182290
Sum of electronic and zero-point Energies= -384.818025
Sum of electronic and thermal Energies= -384.808180
Sum of electronic and thermal Enthalpies= -384.807236
Sum of electronic and thermal Free Energies= -384.852429

mPWPW91/def2-TZVPP

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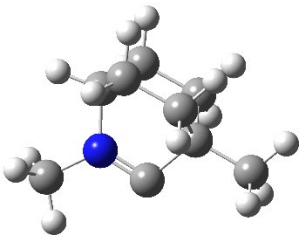
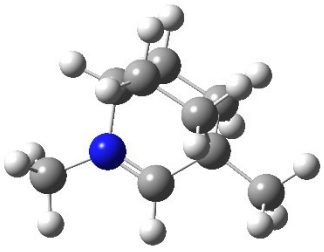


Singlet:

Electronic energy: -406.753013743 Hartree/particle
Zero-point correction= 0.219600 (Hartree/Particle)
Thermal correction to Energy= 0.229252

Thermal correction to Enthalpy= 0.230196
Thermal correction to Gibbs Free Energy= 0.185916
Sum of electronic and zero-point Energies= -406.533414
Sum of electronic and thermal Energies= -406.523762
Sum of electronic and thermal Enthalpies= -406.522818
Sum of electronic and thermal Free Energies= -406.567097

C	0.99989600	0.52867800	1.26281400
C	-0.34848200	1.28490100	1.25631300
C	-1.12834800	0.86166000	0.00002100
C	-0.06993200	-1.33033600	-0.00007300
C	1.11707400	-0.37475100	0.00000500
H	-2.14790000	1.26508500	0.00002000
H	-0.93829400	1.05559200	2.15309100
H	-0.20453700	2.37329200	1.23429900
H	1.08806700	-0.10425500	2.15559700
H	1.85000000	1.22569200	1.28321900
C	2.43867200	-1.14234400	-0.00000700
H	2.50692100	-1.78849400	-0.88414100
H	3.30058400	-0.45921700	0.00004900
H	2.50688200	-1.78858900	0.88406000
C	0.99995500	0.52881700	-1.26271000
H	1.85005600	1.22583800	-1.28299400
H	1.08817400	-0.10401500	-2.15556000
C	-0.34842700	1.28503300	-1.25619400
H	-0.20448900	2.37342300	-1.23406400
H	-0.93819800	1.05581000	-2.15302100
N	-1.18010200	-0.62494000	-0.00005900
C	-2.49730700	-1.25749200	-0.00012300
H	-3.06699300	-0.96062600	-0.89205900
H	-2.34112600	-2.33926300	-0.00016500
H	-3.06704300	-0.96070200	0.89180700

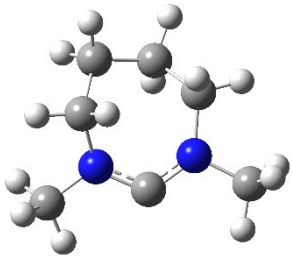


Carbene-H^+:
Electronic energy: -407.196276014 Hartree/particle
Zero-point correction= 0.233722 (Hartree/Particle)
Thermal correction to Energy= 0.243447
Thermal correction to Enthalpy= 0.244391
Thermal correction to Gibbs Free Energy= 0.199942
Sum of electronic and zero-point Energies= -406.962554
Sum of electronic and thermal Energies= -406.952829

Sum of electronic and thermal Enthalpies= -406.951885
Sum of electronic and thermal Free Energies= -406.996334

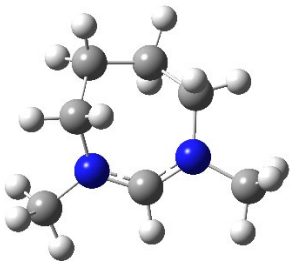
C	-1.02577000	-0.57167600	1.25824800
C	0.33513300	-1.29908700	1.26493700
C	1.12429400	-0.90182300	0.00002200
C	-1.14207700	0.35967700	0.00000700
H	2.14006000	-1.30759000	0.00002000
H	0.91875600	-1.05104000	2.15930300
H	0.21534000	-2.38846000	1.25372300
H	-1.16254500	0.02533500	2.16705000
H	-1.86321200	-1.27816900	1.20829900
C	-2.42790800	1.18314700	-0.00000700
H	-2.49652800	1.82086500	-0.88983900
H	-3.29950200	0.51885800	0.00004800
H	-2.49648800	1.82095900	0.88976100
C	-1.02582900	-0.57181100	-1.25813900
H	-1.86326800	-1.27830000	-1.20807400
H	-1.16264700	0.02510200	-2.16699900
C	0.33507500	-1.29922100	-1.26481500
H	0.21528300	-2.38859300	-1.25348100
H	0.91865600	-1.05126700	-2.15923400
N	1.22280500	0.57986400	-0.00005900
C	2.53101600	1.23660100	-0.00012400
H	3.08883800	0.92872100	-0.89188800
H	2.39936000	2.32184200	-0.00017500
H	3.08888100	0.92881000	0.89164400
C	0.08279500	1.19812600	-0.00006600
H	0.07901000	2.29028400	-0.00012400

NHC-7



Singlet:
Electronic energy: -384.688713221 Hartree/particle
Zero-point correction= 0.201754 (Hartree/Particle)
Thermal correction to Energy= 0.211491
Thermal correction to Enthalpy= 0.212435
Thermal correction to Gibbs Free Energy= 0.167571
Sum of electronic and zero-point Energies= -384.486960
Sum of electronic and thermal Energies= -384.477223
Sum of electronic and thermal Enthalpies= -384.476278
Sum of electronic and thermal Free Energies= -384.521142

C	0.18504800	-1.27545800	-0.15663900
C	1.35889100	0.99673200	0.19951800
C	-1.07747800	1.77496400	-0.02955900
C	0.32810700	1.74234300	-0.64990700
H	1.32233700	1.31790700	1.25327900
H	-1.17376000	2.62792500	0.65920800
H	2.36302700	1.25894100	-0.16041900
H	-1.82878600	1.92315600	-0.81767700
H	0.68541400	2.76758200	-0.81966200
H	0.29064500	1.25901300	-1.63499000
N	-1.04476200	-0.74354600	0.00738000
C	-2.18600300	-1.59600400	-0.30686300
H	-2.75045100	-1.86102800	0.60236900
H	-2.87450500	-1.09497500	-1.00413800
H	-1.80292600	-2.50750500	-0.77168900
C	2.55974300	-1.14624600	0.05631300
H	3.09525900	-1.00067500	1.00747800
H	2.39169200	-2.21382600	-0.10139800
H	3.19094000	-0.74675600	-0.75458600
N	1.25667600	-0.48730800	0.08412200
C	-1.36638600	0.49497700	0.74952600
H	-0.78182100	0.48428800	1.68189900
H	-2.42199900	0.45408000	1.04548800



Carbene-H^+:

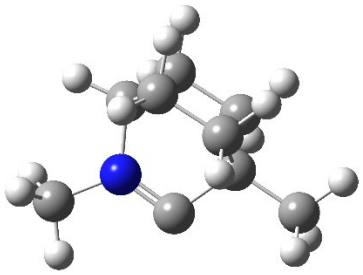
Electronic energy: -385.136917700 Hartree/particle
Zero-point correction= 0.216763 (Hartree/Particle)
Thermal correction to Energy= 0.226623
Thermal correction to Enthalpy= 0.227567
Thermal correction to Gibbs Free Energy= 0.182328
Sum of electronic and zero-point Energies= -384.920155
Sum of electronic and thermal Energies= -384.910295
Sum of electronic and thermal Enthalpies= -384.909350
Sum of electronic and thermal Free Energies= -384.954590

C	1.35512900	1.06128000	0.17755400
C	-1.11990500	1.77115000	-0.04245800
C	0.29168200	1.77200600	-0.65749900
H	1.33048200	1.35478200	1.23635700
H	-1.24438900	2.62618800	0.63532100

H	2.34948100	1.33034400	-0.19676700
H	-1.86693000	1.89638300	-0.83609800
H	0.62328000	2.80626100	-0.81055900
H	0.27601900	1.31520300	-1.65654600
N	-1.06169300	-0.74769400	0.07175100
C	-2.16497300	-1.62708100	-0.33136000
H	-2.78055500	-1.87517900	0.54121300
H	-2.78967100	-1.12314100	-1.07848500
H	-1.77101500	-2.54796600	-0.77038200
C	2.59399400	-1.10982700	0.07745700
H	3.09635500	-0.93735100	1.03711700
H	2.45351600	-2.18643900	-0.05177400
H	3.22622300	-0.72308800	-0.73041000
N	1.29546400	-0.42253100	0.06838800
C	-1.40735900	0.51277400	0.77044600
H	-0.84718800	0.51869700	1.71483100
H	-2.46776700	0.44751400	1.03329800
C	0.19149900	-1.13669600	-0.10045200
H	0.33535800	-2.17226000	-0.41022100

TPSSTPSS/def2-TZVPP

BiCAAC

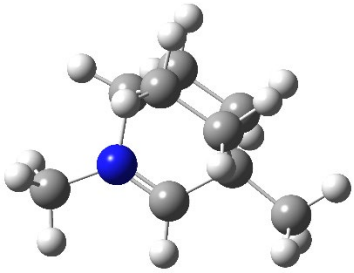


Singlet:

Electronic energy: -406.893124107 Hartree/particle
Zero-point correction= 0.221772 (Hartree/Particle)
Thermal correction to Energy= 0.231480
Thermal correction to Enthalpy= 0.232424
Thermal correction to Gibbs Free Energy= 0.187953
Sum of electronic and zero-point Energies= -406.671352
Sum of electronic and thermal Energies= -406.661644
Sum of electronic and thermal Enthalpies= -406.660700
Sum of electronic and thermal Free Energies= -406.705171

C	1.00207200	0.52852700	1.26268400
C	-0.34726100	1.28706500	1.25704900
C	-1.12798000	0.86455800	0.00002100
C	-0.07211600	-1.33510900	-0.00007300
C	1.11516300	-0.37681300	0.00000400
H	-2.14622700	1.26276900	0.00002000

H	-0.93503300	1.05703400	2.15155600
H	-0.20049500	2.37243000	1.23346700
H	1.08939500	-0.10134700	2.15413100
H	1.84921500	1.22510800	1.27849200
C	2.43845000	-1.14549700	-0.00000700
H	2.50612800	-1.78878700	-0.88330000
H	3.29661800	-0.46127100	0.00004900
H	2.50608800	-1.78888200	0.88322000
C	1.00213100	0.52866700	-1.26258000
H	1.84927000	1.22525400	-1.27826600
H	1.08950300	-0.10110700	-2.15409300
C	-0.34720700	1.28719600	-1.25692900
H	-0.20044800	2.37256000	-1.23323300
H	-0.93493800	1.05725200	-2.15148600
N	-1.18057800	-0.62375200	-0.00005900
C	-2.50146000	-1.25748000	-0.00012300
H	-3.06627300	-0.95780700	-0.89068700
H	-2.34318100	-2.33575000	-0.00016500
H	-3.06632100	-0.95788300	0.89043600



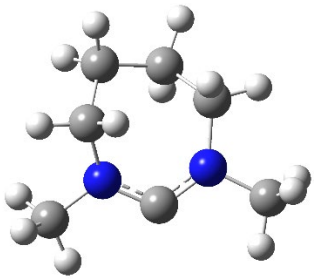
Carbene-H^+:

Electronic energy: -407.339692539 Hartree/particle
Zero-point correction= 0.236134 (Hartree/Particle)
Thermal correction to Energy= 0.245918
Thermal correction to Enthalpy= 0.246862
Thermal correction to Gibbs Free Energy= 0.202220
Sum of electronic and zero-point Energies= -407.103558
Sum of electronic and thermal Energies= -407.093775
Sum of electronic and thermal Enthalpies= -407.092831
Sum of electronic and thermal Free Energies= -407.137473

C	-1.02991300	-0.57119400	1.25791700
C	0.33200000	-1.30234300	1.26628700
C	1.12267900	-0.90808900	0.00002200
C	-1.14011600	0.36292200	0.00000700
H	2.13626500	-1.30996100	0.00002000
H	0.91347200	-1.05142600	2.15743200
H	0.20758800	-2.38814900	1.25450500
H	-1.16456300	0.02363200	2.16471700
H	-1.86420000	-1.27601300	1.20191400

C	-2.42673900	1.19130900	-0.00000700
H	-2.48990800	1.82679000	-0.88869800
H	-3.29536200	0.52763200	0.00004800
H	-2.48986700	1.82688400	0.88861900
C	-1.02997200	-0.57132900	-1.25780800
H	-1.86425500	-1.27614200	-1.20168900
H	-1.16466600	0.02339900	-2.16466600
C	0.33194200	-1.30247700	-1.26616500
H	0.20753200	-2.38828100	-1.25426300
H	0.91337300	-1.05165300	-2.15736300
N	1.22383500	0.57798800	-0.00005900
C	2.53962500	1.23692200	-0.00012400
H	3.08976000	0.92637400	-0.89150300
H	2.40099600	2.31819000	-0.00017500
H	3.08980300	0.92646300	0.89125900
C	0.08708400	1.19900800	-0.00006600
H	0.08764800	2.28798100	-0.00012400

NHC-7

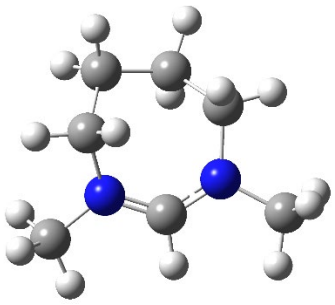


Singlet:

Electronic energy: -384.817696537 Hartree/particle
Zero-point correction= 0.203938 (Hartree/Particle)
Thermal correction to Energy= 0.213689
Thermal correction to Enthalpy= 0.214633
Thermal correction to Gibbs Free Energy= 0.169717
Sum of electronic and zero-point Energies= -384.613758
Sum of electronic and thermal Energies= -384.604007
Sum of electronic and thermal Enthalpies= -384.603063
Sum of electronic and thermal Free Energies= -384.647980

C	0.19484100	-1.28092400	-0.15831800
C	1.34823200	1.00830600	0.19673000
C	-1.09219200	1.76976700	-0.02551100
C	0.30783700	1.73424800	-0.66302400
H	1.30253500	1.33356400	1.24532400
H	-1.17897000	2.62250800	0.66035000
H	2.34831500	1.27113300	-0.16453900
H	-1.85218000	1.90817800	-0.80291700
H	0.65786500	2.75567800	-0.85219200
H	0.26206100	1.22964900	-1.63352900

N	-1.03663900	-0.74693700	0.00784600
C	-2.17900100	-1.60291800	-0.31001700
H	-2.74249300	-1.86110400	0.59799600
H	-2.86090800	-1.10128400	-1.00865600
H	-1.79054900	-2.51125500	-0.76932100
C	2.57061300	-1.12922200	0.05638300
H	3.10080900	-0.98329600	1.00696600
H	2.40788800	-2.19325600	-0.10941600
H	3.19217300	-0.71518700	-0.75051000
N	1.25863900	-0.47967500	0.08967300
C	-1.35762200	0.48741800	0.76180200
H	-0.75179400	0.47993800	1.67631100
H	-2.40500600	0.43096100	1.07322600



Carbene-H^+:

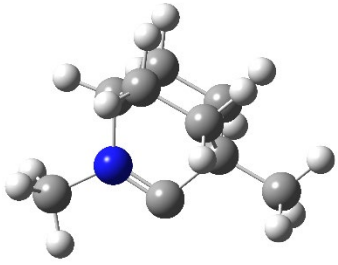
Electronic energy: -385.269008445 Hartree/particle
Zero-point correction= 0.219125 (Hartree/Particle)
Thermal correction to Energy= 0.229012
Thermal correction to Enthalpy= 0.229956
Thermal correction to Gibbs Free Energy= 0.184623
Sum of electronic and zero-point Energies= -385.049883
Sum of electronic and thermal Energies= -385.039996
Sum of electronic and thermal Enthalpies= -385.039052
Sum of electronic and thermal Free Energies= -385.084385

C	1.34760800	1.07023800	0.18837500
C	-1.12849000	1.77092100	-0.04952100
C	0.28558500	1.76789100	-0.66512700
H	1.30218700	1.35810600	1.24410200
H	-1.25101000	2.62736900	0.62195100
H	2.34258600	1.33882800	-0.17414400
H	-1.87382100	1.88394000	-0.84232200
H	0.61382700	2.79823100	-0.82964500
H	0.27200400	1.29218800	-1.65192100
N	-1.05672300	-0.74935300	0.07195900
C	-2.16179600	-1.63766000	-0.32975300
H	-2.77484600	-1.87382700	0.54365500
H	-2.77813800	-1.13899900	-1.08237100
H	-1.75717900	-2.55732100	-0.75422700
C	2.60229900	-1.10367600	0.07112300

H	3.09728000	-0.94596100	1.03324000
H	2.45816900	-2.17380100	-0.08185100
H	3.22587800	-0.69541800	-0.72827600
N	1.29522400	-0.41911400	0.07387200
C	-1.40630600	0.51465600	0.77373500
H	-0.83583500	0.52436000	1.70776600
H	-2.46194300	0.43929300	1.03956100
C	0.19589100	-1.13722100	-0.09843600
H	0.34258400	-2.16861600	-0.40870400

revTPSSrevTPSS/def2-TZVPP (gas phase)

BiCAAC

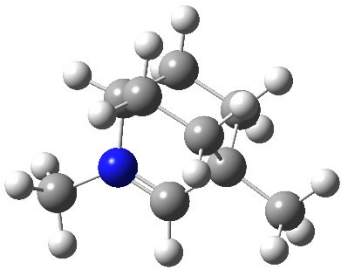


Singlet:

Electronic energy: -406.788000515 Hartree/particle
Zero-point correction= 0.221776 (Hartree/Particle)
Thermal correction to Energy= 0.231515
Thermal correction to Enthalpy= 0.232459
Thermal correction to Gibbs Free Energy= 0.187859
Sum of electronic and zero-point Energies= -406.566225
Sum of electronic and thermal Energies= -406.556485
Sum of electronic and thermal Enthalpies= -406.555541
Sum of electronic and thermal Free Energies= -406.600142

C	1.00086600	0.52587700	1.25917100
C	-0.34613300	1.28442700	1.25442700
C	-1.12575700	0.86131500	0.00002100
C	-0.07081300	-1.33706400	-0.00007300
C	1.11150400	-0.37694700	0.00000400
H	-2.14629600	1.25810500	0.00001900
H	-0.93465400	1.05284800	2.14985900
H	-0.19790500	2.37107400	1.22700100
H	1.08797200	-0.10659000	2.15076800
H	1.85006900	1.22276400	1.27014700
C	2.43495300	-1.14059000	-0.00000700
H	2.50216100	-1.78317200	-0.88586700
H	3.28988800	-0.44940200	0.00004900
H	2.50212100	-1.78326700	0.88578700
C	1.00092500	0.52601600	-1.25906800
H	1.85012400	1.22291000	-1.26992100
H	1.08808200	-0.10634900	-2.15073100

C	-0.34607900	1.28455800	-1.25430800
H	-0.19785900	2.37120300	-1.22676700
H	-0.93455800	1.05306400	-2.14978900
N	-1.17804200	-0.62271900	-0.00005900
C	-2.50019000	-1.25109800	-0.00012200
H	-3.06219800	-0.94606300	-0.89239600
H	-2.34405600	-2.33090900	-0.00016500
H	-3.06224600	-0.94613900	0.89214700



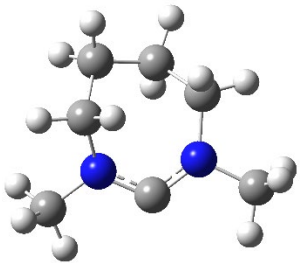
Carbene-H^+:

Electronic energy: -407.233193842 Hartree/particle
Zero-point correction= 0.236163 (Hartree/Particle)
Thermal correction to Energy= 0.245978
Thermal correction to Enthalpy= 0.246922
Thermal correction to Gibbs Free Energy= 0.202161
Sum of electronic and zero-point Energies= -406.997031
Sum of electronic and thermal Energies= -406.987216
Sum of electronic and thermal Enthalpies= -406.986271
Sum of electronic and thermal Free Energies= -407.031033

C	-1.02988400	-0.56915300	1.25371700
C	0.33018300	-1.29997700	1.26373200
C	1.12077800	-0.90515500	0.00002200
C	-1.13623200	0.36428700	0.00000700
H	2.13558500	-1.30812500	0.00002000
H	0.91178000	-1.04639000	2.15574800
H	0.20487900	-2.38702300	1.24861200
H	-1.16579200	0.02662400	2.16142900
H	-1.86552100	-1.27418500	1.19018400
C	-2.42321400	1.18884500	-0.00000700
H	-2.48495300	1.82376200	-0.89107700
H	-3.28865500	0.51846200	0.00004800
H	-2.48491200	1.82385700	0.89099900
C	-1.02994300	-0.56928800	-1.25360800
H	-1.86557600	-1.27431400	-1.18995900
H	-1.16589500	0.02639100	-2.16137800
C	0.33012500	-1.30011000	-1.26361000
H	0.20482300	-2.38715600	-1.24837100
H	0.91168000	-1.04661600	-2.15568000
N	1.22263800	0.57577100	-0.00005900
C	2.53948600	1.23096000	-0.00012400

H	3.08684100	0.91659900	-0.89338100
H	2.39961100	2.31336400	-0.00017500
H	3.08688400	0.91668900	0.89313900
C	0.08714800	1.19931500	-0.00006600
H	0.09007200	2.28931700	-0.00012400

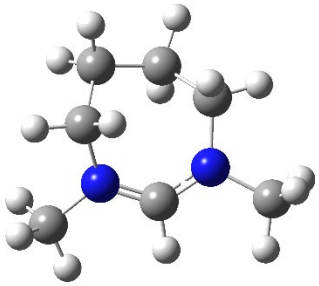
NHC-7



Singlet:

Electronic energy: -384.712862225 Hartree/particle
Zero-point correction= 0.204096 (Hartree/Particle)
Thermal correction to Energy= 0.213826
Thermal correction to Enthalpy= 0.214770
Thermal correction to Gibbs Free Energy= 0.169924
Sum of electronic and zero-point Energies= -384.508767
Sum of electronic and thermal Energies= -384.499036
Sum of electronic and thermal Enthalpies= -384.498092
Sum of electronic and thermal Free Energies= -384.542938

C	0.20161300	-1.28297000	-0.16426600
C	1.33978000	1.01390400	0.17906000
C	-1.09871900	1.76100400	-0.00809600
C	0.28316000	1.71683200	-0.67772100
H	1.30364200	1.35620900	1.22409700
H	-1.16192500	2.61186400	0.68493700
H	2.33440900	1.27565800	-0.20250400
H	-1.87840000	1.90214600	-0.76732300
H	0.62661000	2.73600500	-0.89690000
H	0.21650300	1.18495500	-1.63387200
N	-1.02925700	-0.74525000	0.00162300
C	-2.17449400	-1.59611300	-0.31331700
H	-2.72519800	-1.86539600	0.60101600
H	-2.86484700	-1.08063900	-0.99547400
H	-1.79056600	-2.49811100	-0.79135100
C	2.57461900	-1.11057100	0.06475800
H	3.10746400	-0.93737200	1.01077600
H	2.42021100	-2.18012900	-0.07929300
H	3.18594700	-0.70364000	-0.75544700
N	1.25783200	-0.47311200	0.09447600
C	-1.34019900	0.47437500	0.77667100
H	-0.70717800	0.46168000	1.67425400
H	-2.38125900	0.40655000	1.11186100



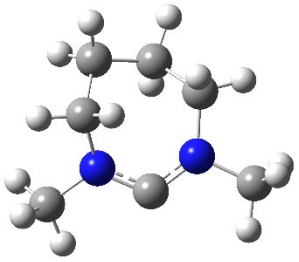
Carbene-H^+:

Electronic energy: -385.162606435 Hartree/particle
Zero-point correction= 0.219262 (Hartree/Particle)
Thermal correction to Energy= 0.229129
Thermal correction to Enthalpy= 0.230074
Thermal correction to Gibbs Free Energy= 0.184829
Sum of electronic and zero-point Energies= -384.943344
Sum of electronic and thermal Energies= -384.933477
Sum of electronic and thermal Enthalpies= -384.932533
Sum of electronic and thermal Free Energies= -384.977777

C	1.33617200	1.07911600	0.17320300
C	-1.14054700	1.75880800	-0.03608600
C	0.25808300	1.74969600	-0.68060700
H	1.29480500	1.38138300	1.22633800
H	-1.24483100	2.61579600	0.63993000
H	2.32597900	1.35142500	-0.20498300
H	-1.90412000	1.86875700	-0.81367400
H	0.57731800	2.77860100	-0.87703300
H	0.22795000	1.24348000	-1.65346700
N	-1.04776300	-0.75260600	0.07358100
C	-2.15355600	-1.63400100	-0.33623000
H	-2.76445400	-1.87753700	0.53818000
H	-2.76962000	-1.12317800	-1.08270400
H	-1.74645400	-2.54892600	-0.77185700
C	2.60923500	-1.08105700	0.07868900
H	3.09997300	-0.90948700	1.04198400
H	2.47148500	-2.15442100	-0.06670000
H	3.22825900	-0.67024200	-0.72463300
N	1.29677200	-0.40939200	0.07543300
C	-1.39124200	0.50093300	0.79079100
H	-0.79276500	0.51163400	1.70870800
H	-2.44094100	0.41371100	1.08153800
C	0.20469900	-1.13680700	-0.10124700
H	0.35728700	-2.16713800	-0.41581200

revTPSSrevTPSS/def2-TZVPP (tetrahydrofuran polarizable continuum)

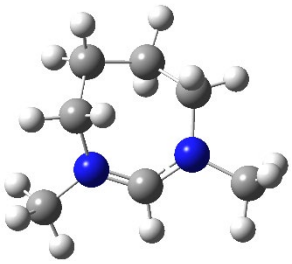
NHC-7



Singlet:

Electronic energy: -384.719336870 Hartree/particle
Zero-point correction= 0.204215 (Hartree/Particle)
Thermal correction to Energy= 0.213929
Thermal correction to Enthalpy= 0.214874
Thermal correction to Gibbs Free Energy= 0.170057
Sum of electronic and zero-point Energies= -384.515122
Sum of electronic and thermal Energies= -384.505407
Sum of electronic and thermal Enthalpies= -384.504463
Sum of electronic and thermal Free Energies= -384.549280

C	0.20440100	-1.28470400	-0.16405500
C	1.33621800	1.01353500	0.17568300
C	-1.10454100	1.75255500	-0.00822300
C	0.27729200	1.71497900	-0.67842500
H	1.29969900	1.35012100	1.22135800
H	-1.17191100	2.60381700	0.68282500
H	2.32932800	1.27704900	-0.20651200
H	-1.88671900	1.88451100	-0.76611100
H	0.61982100	2.73532000	-0.89071600
H	0.21363400	1.19026900	-1.63907700
N	-1.02669600	-0.75419400	0.01093500
C	-2.18278500	-1.58571600	-0.31875700
H	-2.74069600	-1.85446200	0.59034000
H	-2.86129400	-1.05041400	-0.99621800
H	-1.81882700	-2.49003700	-0.80844200
C	2.58567700	-1.09994300	0.06418800
H	3.11434400	-0.91265400	1.00900500
H	2.45187900	-2.17384700	-0.07094700
H	3.19209600	-0.69027300	-0.75710300
N	1.26154300	-0.47566900	0.08959200
C	-1.33552400	0.46957300	0.78400200
H	-0.69618100	0.46145700	1.67615400
H	-2.37352400	0.39651400	1.12528000

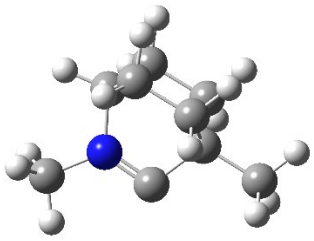


Carbene-H^+:

Electronic energy: -385.225438862 Hartree/particle
Zero-point correction= 0.219523 (Hartree/Particle)
Thermal correction to Energy= 0.229285
Thermal correction to Enthalpy= 0.230229
Thermal correction to Gibbs Free Energy= 0.185323
Sum of electronic and zero-point Energies= -385.005916
Sum of electronic and thermal Energies= -384.996154
Sum of electronic and thermal Enthalpies= -384.995210
Sum of electronic and thermal Free Energies= -385.040116

C	1.33036300	1.07957600	0.17094800
C	-1.14536200	1.75274800	-0.03450000
C	0.25024700	1.74473700	-0.68357500
H	1.28525600	1.38240900	1.22307900
H	-1.24708500	2.61025900	0.64111300
H	2.31838500	1.35568800	-0.20782500
H	-1.91255200	1.85442200	-0.80955300
H	0.56795200	2.77333000	-0.88403500
H	0.21713300	1.23147700	-1.65212100
N	-1.04331500	-0.75353700	0.07548800
C	-2.14679400	-1.63159600	-0.33789700
H	-2.75589700	-1.87968300	0.53626000
H	-2.76343000	-1.11508400	-1.07961100
H	-1.73730000	-2.54216700	-0.77896800
C	2.60878100	-1.07085700	0.08040100
H	3.09483000	-0.89481400	1.04501200
H	2.47447600	-2.14395600	-0.06473700
H	3.22759100	-0.65643100	-0.72092900
N	1.29631100	-0.40605000	0.07297000
C	-1.38633700	0.49557300	0.79513400
H	-0.78128800	0.51081000	1.70787700
H	-2.43389500	0.40505100	1.09083200
C	0.20805800	-1.13802500	-0.10204300
H	0.36111600	-2.16713500	-0.41641100

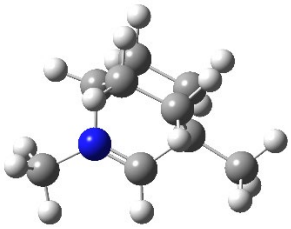
BiCAAC



Singlet:

Electronic energy: -406.795084852 Hartree/particle
Zero-point correction= 0.221927 (Hartree/Particle)
Thermal correction to Energy= 0.231636
Thermal correction to Enthalpy= 0.232580
Thermal correction to Gibbs Free Energy= 0.188026
Sum of electronic and zero-point Energies= -406.573158
Sum of electronic and thermal Energies= -406.563449
Sum of electronic and thermal Enthalpies= -406.562505
Sum of electronic and thermal Free Energies= -406.607058

C	1.00380800	0.52571100	1.25799000
C	-0.34495400	1.27964600	1.25537300
C	-1.12382200	0.85898400	0.00002000
C	-0.07270200	-1.33548000	-0.00007300
C	1.11218000	-0.38005600	0.00000400
H	-2.14372800	1.25357300	0.00001800
H	-0.93323900	1.04394100	2.14914800
H	-0.19971700	2.36597600	1.22848700
H	1.09808400	-0.10143500	2.15267600
H	1.85084900	1.22449200	1.25813400
C	2.43843800	-1.14012300	-0.00000600
H	2.51300000	-1.78034000	-0.88769500
H	3.28839900	-0.44377800	0.00005200
H	2.51295800	-1.78043600	0.88761700
C	1.00386700	0.52585000	-1.25788700
H	1.85090500	1.22463500	-1.25790900
H	1.09819300	-0.10119600	-2.15263800
C	-0.34489900	1.27977700	-1.25525500
H	-0.19966900	2.36610500	-1.22825400
H	-0.93314200	1.04415700	-2.14908000
N	-1.18084700	-0.62487900	-0.00006000
C	-2.51060100	-1.24152300	-0.00012100
H	-3.06574400	-0.92721200	-0.89183800
H	-2.37331900	-2.32374500	-0.00017100
H	-3.06578700	-0.92729900	0.89159900



Carbene-H$^+$:

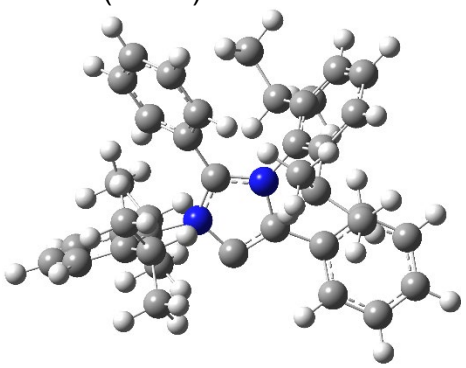
Electronic energy: -407.296912884 Hartree/particle
Zero-point correction= 0.236078 (Hartree/Particle)
Thermal correction to Energy= 0.245949
Thermal correction to Enthalpy= 0.246893
Thermal correction to Gibbs Free Energy= 0.201865
Sum of electronic and zero-point Energies= -407.060835
Sum of electronic and thermal Energies= -407.050964
Sum of electronic and thermal Enthalpies= -407.050020
Sum of electronic and thermal Free Energies= -407.095048

C	-1.03860100	0.59049800	-1.23985100
C	0.32851300	1.30643400	-1.25634400
C	1.11960600	0.90346700	0.00277700
C	-1.13390300	-0.36347800	-0.00379300
H	2.13313300	1.30686000	0.00414000
H	0.90530600	1.04029800	-2.14728100
H	0.21354400	2.39430400	-1.24202000
H	-1.19246000	0.01127500	-2.15498200
H	-1.86455900	1.30405300	-1.14893600
C	-2.42106000	-1.18535300	-0.00734200
H	-2.47483100	-1.83078100	0.87643900
H	-3.28394400	-0.51131800	0.00606600
H	-2.48516100	-1.80910700	-0.90581500
C	-1.02091300	0.54528200	1.26484200
H	-1.86429800	1.24257300	1.22678600
H	-1.13501200	-0.07275000	2.16034500
C	0.33127600	1.28929900	1.26948700
H	0.19393600	2.37457600	1.25424200
H	0.92009700	1.03725000	2.15636300
N	1.22056700	-0.57490300	-0.00888800
C	2.53640300	-1.22679000	-0.00661200
H	3.08606900	-0.89020400	0.87608800
H	2.39564800	-2.30790000	0.01875300
H	3.07377200	-0.92720200	-0.91008200
C	0.08902400	-1.20080800	-0.01886900
H	0.09272000	-2.28891000	-0.03365500

pKa Calculations

Frequencies done at: **M06-2X/6-311++G(2df,2p) (DMSO as solvent, modelled by the SMD method)**
Optimizations done at: **B3LYP/6-31+G(d) (DMSO as solvent, SMD)**

Abnormal NHC (aNHC)



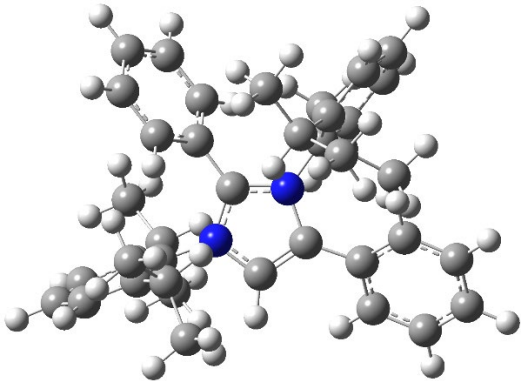
Singlet:

Electronic energy: -1621.971729 Hartree/particle
Zero-point correction= 0.728966 (Hartree/Particle)
Thermal correction to Energy= 0.766741
Thermal correction to Enthalpy= 0.767685
Thermal correction to Gibbs Free Energy= 0.662844
Sum of electronic and zero-point Energies= -1621.242763
Sum of electronic and thermal Energies= -1621.204987
Sum of electronic and thermal Enthalpies= -1621.204043
Sum of electronic and thermal Free Energies= -1621.308885

C	-0.37371700	-1.95440100	-0.16217000
N	-1.18522600	-0.81434500	-0.04460600
C	0.90494700	-1.41775300	-0.19090800
N	0.83469600	-0.00599400	-0.07251200
C	-0.47225900	0.34189900	0.01694500
C	-1.01933600	1.70523600	0.15452600
C	-2.05988900	2.13843400	-0.68746700
C	-0.52909700	2.59053500	1.13072700
C	-2.59819500	3.41880400	-0.55092000
H	-2.43743300	1.48352600	-1.46336400
C	-1.06500900	3.87326300	1.26021200
H	0.26105300	2.27430700	1.80015900
C	-2.10313800	4.29222900	0.42247400
H	-3.39909900	3.73526700	-1.21428000
H	-0.67406500	4.54095200	2.02380700
H	-2.52158500	5.29012400	0.52657600
C	2.15270500	-2.19681200	-0.32758300
C	2.20606200	-3.47622500	0.26580200
C	3.27725200	-1.76805800	-1.05831800
C	3.33027800	-4.29150900	0.13039200
H	1.35628100	-3.82476900	0.84473700
C	4.40715500	-2.58164800	-1.18531500
H	3.27418600	-0.80123800	-1.54591500
C	4.44262300	-3.84764400	-0.59412800
H	3.34066600	-5.27170500	0.60167500

H	5.25898500	-2.22285300	-1.75865300
H	5.32202700	-4.47888300	-0.69570600
C	1.94961500	0.92520100	-0.05083500
C	2.22903100	1.68438700	-1.21105300
C	2.74030400	1.01147700	1.11928200
C	3.33656300	2.54377700	-1.17134400
C	3.83769200	1.88444900	1.09511000
C	4.13681600	2.64308200	-0.03499400
H	3.57940800	3.13758100	-2.04834300
H	4.46731200	1.97089900	1.97643600
H	4.99409500	3.31220700	-0.02991700
C	-2.62468200	-0.92816800	0.08277000
C	-3.19995100	-0.87935600	1.37109000
C	-3.39361600	-1.16744800	-1.07889500
C	-4.58984300	-1.04555100	1.47028100
C	-4.77650400	-1.33488300	-0.91922700
C	-5.37309700	-1.26940300	0.33970900
H	-5.06177400	-1.01195100	2.44854200
H	-5.39556100	-1.52303200	-1.79217800
H	-6.44808400	-1.40075800	0.43975100
C	-2.37651300	-0.70955600	2.64561000
H	-1.34034600	-0.50434100	2.36411200
C	-2.77926900	-1.28343400	-2.47305700
H	-1.74071800	-0.94435700	-2.41577100
C	-3.49422600	-0.40415800	-3.51692200
H	-4.51766900	-0.74868000	-3.70817400
H	-3.54526600	0.64521100	-3.20401400
H	-2.95005200	-0.44468300	-4.46890700
C	-2.76344700	-2.75199300	-2.94500800
H	-2.27309700	-2.83030100	-3.92399300
H	-2.22205000	-3.39456800	-2.24198100
H	-3.78438000	-3.14185000	-3.04725200
C	-2.86241800	0.47365200	3.50336700
H	-2.87232700	1.40871600	2.93156500
H	-3.87381100	0.30277800	3.89202200
H	-2.19519000	0.60997500	4.36371300
C	-2.37146900	-2.01176700	3.47180700
H	-1.98860400	-2.85532200	2.88501600
H	-1.73188400	-1.89548300	4.35614100
H	-3.38098200	-2.26795000	3.81733900
C	2.46804800	0.20566300	2.39066600
H	1.55525000	-0.37832400	2.24045900
C	2.24234000	1.10925600	3.61987500
H	1.42081500	1.81812400	3.47089500
H	1.99524000	0.49077900	4.49192200
H	3.14321600	1.68435600	3.86589800
C	3.61518500	-0.78236500	2.68759200

H	4.54232700	-0.24715100	2.92839800
H	3.35637800	-1.40723800	3.55179400
H	3.81554300	-1.44306200	1.83876600
C	1.40186400	1.61111900	-2.49450700
H	0.56587600	0.92525500	-2.33208100
C	2.22034400	1.05869700	-3.67877900
H	1.58852000	1.00735200	-4.57467000
H	3.07607900	1.70517300	-3.90972300
H	2.59926500	0.05055400	-3.47862200
C	0.81224200	2.98776700	-2.86220500
H	0.13154700	2.88746200	-3.71693500
H	0.24999600	3.42449500	-2.03017600
H	1.60127500	3.69499700	-3.14683800



Carbene-H^+:

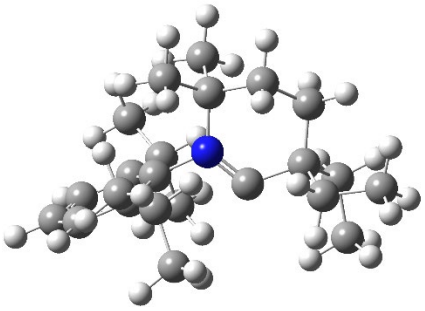
Electronic energy: -1622.482158 Hartree/particle
Zero-point correction= 0.744121 (Hartree/Particle)
Thermal correction to Energy= 0.781703
Thermal correction to Enthalpy= 0.782647
Thermal correction to Gibbs Free Energy= 0.678618
Sum of electronic and zero-point Energies= -1621.738037
Sum of electronic and thermal Energies= -1621.700456
Sum of electronic and thermal Enthalpies= -1621.699512
Sum of electronic and thermal Free Energies= -1621.803540

N	1.20368500	-0.75703600	-0.06885200
C	-0.93013900	-1.37252700	-0.23775600
N	-0.84038100	0.01877500	-0.05552200
C	0.46817600	0.37255500	0.04567900
C	1.01108800	1.72701000	0.25178300
C	0.59338500	2.50121200	1.34613100
C	1.97140700	2.24416300	-0.63418800
C	1.12820100	3.77406200	1.54996900
H	-0.13122700	2.10160600	2.04458500
C	2.50506300	3.51626200	-0.42336600
H	2.28402300	1.66658600	-1.49641100

C	2.08570500	4.28392500	0.66767500
H	0.80106800	4.36177200	2.40352200
H	3.24267300	3.90884300	-1.11817900
H	2.50247400	5.27476600	0.82895400
C	-2.14969700	-2.19012900	-0.36945100
C	-3.29190300	-1.77456000	-1.07505500
C	-2.14179300	-3.47566300	0.20720500
C	-4.39478700	-2.62290100	-1.19791700
H	-3.32337800	-0.79733000	-1.53995900
C	-3.24256300	-4.32244100	0.07488000
H	-1.27667000	-3.80604300	0.77521800
C	-4.37619200	-3.89834500	-0.62630400
H	-5.26816900	-2.28406500	-1.74936300
H	-3.21721700	-5.30933400	0.52980100
H	-5.23668300	-4.55518500	-0.72467700
C	-1.96459400	0.94756300	-0.03575500
C	-2.75619700	1.03029500	1.13233300
C	-2.23962100	1.69272700	-1.20526500
C	-3.86539600	1.88738600	1.09243300
C	-3.35907800	2.53662800	-1.17716100
C	-4.16766300	2.63061500	-0.04662000
H	-4.50215700	1.97205000	1.96832000
H	-3.60475800	3.12114200	-2.05923000
H	-5.03493500	3.28646200	-0.05247200
C	2.64764300	-0.89856400	0.04129200
C	3.39711200	-1.04638700	-1.14575500
C	3.21703200	-0.96077600	1.32959800
C	4.77880300	-1.23797600	-1.00645000
C	4.60530800	-1.14705200	1.40373800
C	5.37809500	-1.28177400	0.25210000
H	5.39383100	-1.35783800	-1.89341500
H	5.08392200	-1.20007800	2.37745100
H	6.45203400	-1.43034300	0.33513700
C	2.76010200	-1.04810800	-2.53358000
H	1.74795200	-0.63934500	-2.44584000
C	2.39777200	-0.88387900	2.61474300
H	1.36077000	-0.65268000	2.35486000
C	2.89384000	0.23032500	3.55488100
H	3.90513900	0.02500500	3.92588000
H	2.90705800	1.20480700	3.05364300
H	2.22992800	0.30587600	4.42503500
C	2.39064100	-2.24545100	3.33916500
H	1.75030200	-2.19532000	4.22873500
H	2.00804300	-3.04256900	2.69031300
H	3.39951300	-2.52756800	3.66502800
C	3.51955900	-0.16693400	-3.54244600
H	3.66225500	0.85316700	-3.16726200

H	4.50610500	-0.58024400	-3.78317000
H	2.95105500	-0.10683400	-4.47859600
C	2.63627800	-2.48859600	-3.07193000
H	2.05799300	-3.12683300	-2.39411400
H	2.13381300	-2.48571000	-4.04746000
H	3.62714300	-2.94178600	-3.20206400
C	-1.40121500	1.62492200	-2.48163300
H	-0.54672100	0.96470500	-2.30755800
C	-0.84524700	3.01247800	-2.86035500
H	-0.30317800	3.47364200	-2.02818500
H	-0.15357400	2.91872600	-3.70673900
H	-1.64923200	3.69490600	-3.16213100
C	-2.19628000	1.03655000	-3.66430600
H	-3.07168400	1.65294200	-3.90303200
H	-1.55884700	1.00012300	-4.55675600
H	-2.54242400	0.01801500	-3.45826800
C	-2.47738900	0.24292100	2.41298000
H	-1.52908800	-0.29062500	2.29353900
C	-3.57882200	-0.80285300	2.68369200
H	-3.32061100	-1.39615900	3.56995000
H	-4.54162100	-0.31377800	2.87717000
H	-3.70970800	-1.48890000	1.84180600
C	-2.33870500	1.16396500	3.64285100
H	-2.04004500	0.57043900	4.51577300
H	-1.58749900	1.94729100	3.49609300
H	-3.28951500	1.65370100	3.88511200
C	0.35673000	-1.83191000	-0.23826400
H	0.74076300	-2.83259900	-0.35787300

CAAC-6



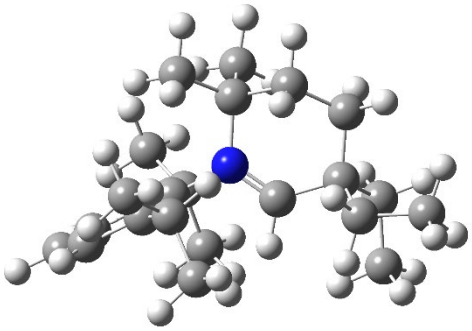
Singlet:

Electronic energy: -953.311008 Hartree/particle
Zero-point correction= 0.551691 (Hartree/Particle)
Thermal correction to Energy= 0.576765
Thermal correction to Enthalpy= 0.577709
Thermal correction to Gibbs Free Energy= 0.501504
Sum of electronic and zero-point Energies= -952.759317
Sum of electronic and thermal Energies= -952.734243
Sum of electronic and thermal Enthalpies= -952.733299

Sum of electronic and thermal Free Energies= -952.809504

C	-0.31203600	0.03703200	1.94831100
C	-2.47019600	-0.32706000	-0.14127200
C	-2.73567800	-0.46032300	1.37480200
H	-3.77531200	-0.20432700	1.61172900
H	-2.60933000	-1.50912800	1.67311700
C	-1.78210800	0.41773700	2.17843900
H	-1.92287000	1.47277400	1.90915800
H	-1.98784400	0.33540300	3.25294000
N	-0.09010400	-0.03319700	0.41631900
C	-0.99699100	-0.21300000	-0.52169900
C	0.00916200	-1.32408800	2.58980500
H	-0.23230500	-1.27084200	3.65858300
H	-0.56732700	-2.14494900	2.15510800
H	1.07255000	-1.56279900	2.50547000
C	-3.04790900	-1.59732400	-0.84357800
H	-2.44630700	-2.45820200	-0.51884900
H	-4.05419600	-1.76855200	-0.43567500
C	0.58770300	1.09159000	2.60649100
H	1.65241300	0.87498900	2.47783900
H	0.38247100	2.09910200	2.23910200
H	0.37800300	1.08589600	3.68320000
C	-3.11985600	0.97637700	-0.71423500
H	-2.67582800	1.84208600	-0.20555400
H	-2.83076100	1.06964000	-1.76771300
C	-3.13035100	-1.59953800	-2.37455800
H	-3.81420300	-0.83091200	-2.75310800
H	-2.15203000	-1.43581500	-2.83904400
H	-3.50576800	-2.57042400	-2.72421800
C	-4.64791000	1.07914500	-0.60903000
H	-4.99499900	1.10853100	0.43031800
H	-4.98656900	2.00637100	-1.08943400
H	-5.15715800	0.24694400	-1.10863900
C	1.28788700	0.10788900	-0.07306400
C	2.08763600	-1.04230300	-0.27502800
C	1.76888900	1.40081000	-0.39815500
C	3.41001200	-0.85893400	-0.71136000
C	3.09563000	1.52372500	-0.83557100
C	3.92207200	0.40949900	-0.97063500
H	4.04157700	-1.72866100	-0.87064300
H	3.48422000	2.50619000	-1.08892400
H	4.95043500	0.52740800	-1.30474200
C	1.56034600	-2.47247900	-0.16004000
H	0.56818600	-2.43984800	0.29106900
C	0.88609000	2.64977500	-0.39271100
H	-0.04128100	2.41622200	0.13477100

C	1.53654200	3.85387600	0.31477700
H	2.40022200	4.23493900	-0.24309400
H	0.81147900	4.67377100	0.39513800
H	1.87504000	3.60242700	1.32650000
C	0.50000900	3.03481300	-1.83694300
H	1.38736300	3.31021800	-2.42115600
H	-0.00245500	2.20833100	-2.35247900
H	-0.18071600	3.89619400	-1.83152400
C	1.39520800	-3.09450300	-1.56345300
H	0.95637800	-4.09773800	-1.48330300
H	0.73812600	-2.48671000	-2.19631000
H	2.36294400	-3.19039000	-2.07192400
C	2.44595500	-3.37952300	0.71499200
H	1.96252400	-4.35563300	0.84905900
H	3.42421700	-3.55906000	0.25275700
H	2.61920800	-2.95022000	1.70853400



Carbene-H^+:

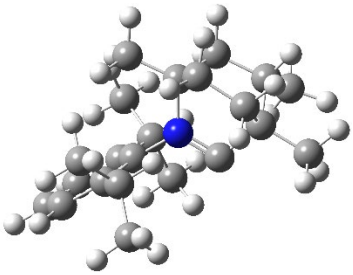
Electronic energy: -953.825073 Hartree/particle
Zero-point correction= 0.566351 (Hartree/Particle)
Thermal correction to Energy= 0.591373
Thermal correction to Enthalpy= 0.592317
Thermal correction to Gibbs Free Energy= 0.516359
Sum of electronic and zero-point Energies= -953.258722
Sum of electronic and thermal Energies= -953.233700
Sum of electronic and thermal Enthalpies= -953.232756
Sum of electronic and thermal Free Energies= -953.308714

C	-0.30305500	0.02419400	1.99449900
C	-2.48099900	-0.30046900	-0.09624600
C	-2.77409800	-0.25862300	1.41992300
H	-3.76942100	0.16335500	1.58816400
H	-2.80386700	-1.27900100	1.81719000
C	-1.73224400	0.56287900	2.17794800
H	-1.75875800	1.60974800	1.84961000
H	-1.95263800	0.55576900	3.25067200
N	-0.04844300	-0.03264800	0.47302600
C	-0.14736800	-1.38856900	2.58178900
H	-0.44629400	-1.34834300	3.63513300

H	-0.77404900	-2.12760600	2.07635000
H	0.89255600	-1.72200200	2.54316500
C	-2.99472100	-1.65318700	-0.69275100
H	-2.47077700	-2.46680000	-0.17583600
H	-4.04744300	-1.73236400	-0.39502600
C	0.70308000	0.95590300	2.67668700
H	1.73503600	0.61707900	2.54942500
H	0.61723800	1.98856600	2.33250300
H	0.47917800	0.94379600	3.74888400
C	-3.11023100	0.93564800	-0.83510400
H	-2.77357900	1.84180900	-0.31712000
H	-2.70602800	0.99389200	-1.85260400
C	-2.87811100	-1.85733400	-2.20736800
H	-3.41973000	-1.09264400	-2.77459700
H	-1.83770500	-1.85961500	-2.55170700
H	-3.30903500	-2.83048400	-2.47294800
C	-4.64158500	0.93927200	-0.91065100
H	-5.10901000	0.89393900	0.07933000
H	-4.97241000	1.87041800	-1.38696400
H	-5.03044700	0.10789700	-1.50805300
C	1.31069800	0.13410700	-0.06921900
C	2.11252600	-1.00410200	-0.29767200
C	1.73298200	1.44469900	-0.39161500
C	3.41244000	-0.78373000	-0.78068800
C	3.03986200	1.59777000	-0.87401900
C	3.88062600	0.49963300	-1.04768800
H	4.05853500	-1.63605200	-0.96855700
H	3.39892400	2.58903400	-1.13362100
H	4.89259000	0.64311000	-1.41859600
C	1.61971100	-2.44192800	-0.15210500
H	0.63900900	-2.43115300	0.32562600
C	0.80815000	2.66113900	-0.34167300
H	-0.06669100	2.41557900	0.26598200
C	1.46523800	3.90268800	0.28712000
H	2.27473600	4.29798400	-0.33727000
H	0.71798500	4.69815100	0.39731700
H	1.87768000	3.68644000	1.27958800
C	0.29430100	2.98365100	-1.76123700
H	1.12176500	3.27381800	-2.42086600
H	-0.21013500	2.12080900	-2.21163800
H	-0.41987300	3.81600600	-1.72564300
C	1.43334100	-3.08416800	-1.54314200
H	1.02245900	-4.09624500	-1.43755300
H	0.74361600	-2.50128500	-2.16534300
H	2.38843100	-3.16154400	-2.07725000
C	2.54988700	-3.30667000	0.71863100
H	2.09934800	-4.29454600	0.87538500

H	3.52477800	-3.46041200	0.24103600
H	2.72420200	-2.85401500	1.70167900
C	-1.01428800	-0.19415000	-0.37521400
H	-0.70792900	-0.21647000	-1.41826100

BiCAAC

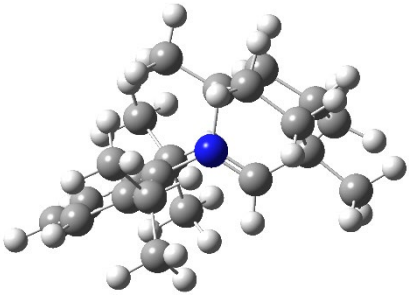


Singlet:

Electronic energy: -912.815616 Hartree/particle
Zero-point correction= 0.502100 (Hartree/Particle)
Thermal correction to Energy= 0.524585
Thermal correction to Enthalpy= 0.525529
Thermal correction to Gibbs Free Energy= 0.454610
Sum of electronic and zero-point Energies= -912.313516
Sum of electronic and thermal Energies= -912.291031
Sum of electronic and thermal Enthalpies= -912.290087
Sum of electronic and thermal Free Energies= -912.361006

N	0.31725400	-0.20253800	0.00158300
C	2.41372300	-0.90498800	-0.76343800
C	2.20894500	-2.22364700	0.04740100
H	1.66266100	-2.94086900	-0.57727500
H	3.19241500	-2.66497700	0.25308500
C	0.04390300	-0.16349000	2.53261800
H	-0.25510400	0.88920100	2.56465000
H	0.58127800	-0.38689500	3.46220900
H	-0.85918200	-0.78173900	2.51354200
C	-0.29466800	2.70345100	-0.13336600
H	0.67623200	2.22013000	-0.02613100
C	1.43720200	-1.93492500	1.35206500
H	0.58191900	-2.60736600	1.47272400
H	2.07737100	-2.07387600	2.23114800
C	-1.82842300	-2.23924300	-0.26010400
H	-0.75385500	-2.39671000	-0.16659400
C	3.15690900	0.10509300	0.18292500
H	4.04767700	-0.42877200	0.54313000
C	-2.24967600	-2.82648900	-1.62209700
H	-1.99060000	-3.89209400	-1.67022500
H	-1.74169800	-2.31660800	-2.44971300
H	-3.33144600	-2.73730400	-1.78161800
C	-3.73736100	1.06527600	-0.29716700

H	-4.77365900	1.38842400	-0.36537000
C	-0.45622300	3.68332900	1.04401800
H	0.37395600	4.40120800	1.05146300
H	-0.45802700	3.15962000	2.00740000
H	-1.38929100	4.25560800	0.96953500
C	-2.51112200	-3.00027900	0.89220300
H	-3.60451300	-2.93894500	0.82457700
H	-2.21167000	-2.60501000	1.87012900
H	-2.23536400	-4.06212300	0.85805700
C	-0.27002600	3.46605200	-1.47328600
H	-1.20754800	4.01044300	-1.64266700
H	-0.11715000	2.78381000	-2.31828600
H	0.54810900	4.19788600	-1.47634500
C	2.23627400	0.41789100	1.39256800
H	1.94782800	1.47453700	1.40169800
H	2.75501800	0.22407000	2.33897900
C	-1.36742000	1.61769200	-0.13952900
C	-3.42541100	-0.29255600	-0.29242800
H	-4.22605900	-1.02357400	-0.36968100
C	3.64293600	1.38946100	-0.50473000
H	4.38178400	1.18207100	-1.28712200
H	4.12225000	2.04747400	0.23243000
H	2.81557400	1.94844400	-0.95905400
C	1.01843800	-0.39479100	-1.09814300
C	0.96669100	-0.46043000	1.35727800
C	-2.09752100	-0.73727400	-0.20183800
C	-1.07408100	0.23437600	-0.10238800
C	-2.71240700	2.00666500	-0.23290700
H	-2.95733700	3.06518400	-0.26476100
C	3.21309700	-1.19936800	-2.03777000
H	4.23984000	-1.50883100	-1.80007500
H	2.74044800	-2.01064800	-2.60623500
H	3.26470000	-0.32484400	-2.69599500



Carbene-H^+:

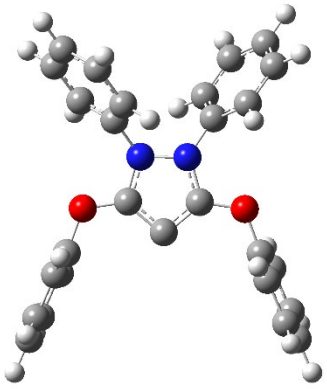
Electronic energy: -913.322275 Hartree/particle
Zero-point correction= 0.516396 (Hartree/Particle)
Thermal correction to Energy= 0.538934
Thermal correction to Enthalpy= 0.539878
Thermal correction to Gibbs Free Energy= 0.468933

Sum of electronic and zero-point Energies= -912.805879
Sum of electronic and thermal Energies= -912.783341
Sum of electronic and thermal Enthalpies= -912.782397
Sum of electronic and thermal Free Energies= -912.853343

N	0.29748800	-0.18811500	0.05223500
C	2.43006100	-0.89865200	-0.75596700
C	2.26116300	-2.20352000	0.09778800
H	1.75918900	-2.96266100	-0.51077300
H	3.26691400	-2.57437100	0.32275400
C	0.07107900	-0.12157300	2.56543900
H	-0.22785100	0.93067300	2.58428200
H	0.61818600	-0.33438700	3.49000800
H	-0.82763100	-0.74562000	2.55470700
C	-0.33750700	2.70842100	-0.12059500
H	0.64156300	2.24506000	0.00372800
C	1.46317100	-1.90662700	1.38409600
H	0.60612000	-2.57718600	1.48955100
H	2.08573400	-2.03523100	2.27531800
C	-1.80290800	-2.26420300	-0.24935600
H	-0.72580600	-2.41290500	-0.16397500
C	3.16701100	0.14610800	0.16835100
H	4.06530500	-0.37923000	0.51446600
C	-2.22903000	-2.86560400	-1.60360900
H	-1.94942200	-3.92574500	-1.64625300
H	-1.74103600	-2.35210200	-2.44097900
H	-3.31372500	-2.79858700	-1.75056100
C	-3.75461600	1.01664800	-0.30787100
H	-4.79456400	1.32450300	-0.38469500
C	-0.52939400	3.69421000	1.04697700
H	0.29287900	4.42040800	1.05976600
H	-0.53953200	3.17716300	2.01363700
H	-1.46733200	4.25472100	0.95239000
C	-2.46404800	-3.02280800	0.91683300
H	-3.55826100	-2.97207700	0.85973700
H	-2.15634000	-2.61689500	1.88761100
H	-2.17684300	-4.08126300	0.88520000
C	-0.30825800	3.45726600	-1.46812900
H	-1.25213200	3.98445000	-1.65353500
H	-0.13381100	2.77005100	-2.30500300
H	0.49819600	4.20129400	-1.46614900
C	2.25668700	0.45765200	1.38590300
H	1.96377400	1.51178700	1.39513600
H	2.78533700	0.26509200	2.32511900
C	-1.39707800	1.61075500	-0.13189700
C	-3.42734100	-0.33712800	-0.29877100
H	-4.21753300	-1.07809200	-0.38044100

C	3.61432400	1.42330700	-0.55253200
H	4.34227200	1.21229100	-1.34322200
H	4.09430700	2.09956700	0.16596700
H	2.76786800	1.96011500	-0.99868900
C	0.98880600	-0.42975500	1.39296000
C	-2.09587400	-0.76678900	-0.19728600
C	-1.10086100	0.23050000	-0.08909800
C	-2.74695900	1.97571900	-0.23872600
H	-3.00819200	3.02948000	-0.27745000
C	3.15958200	-1.18577700	-2.06907100
H	4.19366800	-1.48611700	-1.86638700
H	2.66915800	-2.00306600	-2.61087000
H	3.18100100	-0.30961200	-2.72529800
C	1.04263100	-0.41148800	-0.98355600
H	0.61228000	-0.26465800	-1.97203700

Cyclicbentallene (CBA)

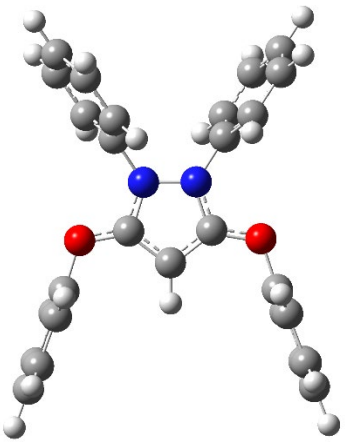


Singlet:

Electronic energy: -1300.670365 Hartree/particle
Zero-point correction= 0.401602 (Hartree/Particle)
Thermal correction to Energy= 0.424944
Thermal correction to Enthalpy= 0.425888
Thermal correction to Gibbs Free Energy= 0.348881
Sum of electronic and zero-point Energies= -1300.268763
Sum of electronic and thermal Energies= -1300.245421
Sum of electronic and thermal Enthalpies= -1300.244477
Sum of electronic and thermal Free Energies= -1300.321483

C	1.23037900	0.00003300	-0.00003700
N	-1.00175700	-0.68320000	-0.14811500
C	0.33027700	1.04643100	0.15793600
C	0.33033300	-1.04641400	-0.15804000
O	0.53376300	2.37379100	0.29289300
O	0.53389600	-2.37376900	-0.29290100
N	-1.00179500	0.68314500	0.14789100
C	1.85512900	-2.84583900	-0.30011100
C	2.40043800	-3.32622400	0.88804700

C	2.54673700	-2.91425300	-1.50766100
C	3.68487000	-3.87960300	0.86515900
H	1.82939300	-3.26685700	1.81018900
C	3.83049600	-3.46898700	-1.51801900
H	2.08900900	-2.53958400	-2.41871500
C	4.40135700	-3.95030900	-0.33446700
H	4.12174400	-4.25675900	1.78620000
H	4.38136300	-3.52558200	-2.45331600
H	5.39885800	-4.38169600	-0.34791800
C	1.85496500	2.84594200	0.30011300
C	2.40018100	3.32650200	-0.88801800
C	2.54663700	2.91425300	1.50763300
C	3.68458200	3.87995400	-0.86513800
H	1.82908400	3.26720900	-1.81013400
C	3.83036400	3.46905900	1.51798100
H	2.08898600	2.53944700	2.41866900
C	4.40113100	3.95055800	0.33445600
H	4.12138100	4.25724500	-1.78616000
H	4.38128300	3.52557100	2.45325300
H	5.39860800	4.38200000	0.34790600
C	-2.12289000	1.49814800	-0.22818000
C	-2.63177200	2.41070100	0.69972400
C	-2.68379700	1.37967300	-1.50522100
C	-3.70601900	3.22760100	0.33697700
H	-2.19308000	2.47612900	1.69084800
C	-3.77011800	2.18698500	-1.85013900
H	-2.27398900	0.66724900	-2.21536500
C	-4.27928000	3.11412300	-0.93377700
H	-4.10181200	3.94201700	1.05395500
H	-4.21218400	2.09587100	-2.83883000
H	-5.12179600	3.74341200	-1.20853500
C	-2.12277800	-1.49827000	0.22809500
C	-2.63174700	-2.41081900	-0.69975600
C	-2.68349000	-1.37984700	1.50522600
C	-3.70590000	-3.22778500	-0.33686400
H	-2.19319600	-2.47620600	-1.69094500
C	-3.76971900	-2.18721700	1.85028700
H	-2.27360900	-0.66741000	2.21531600
C	-4.27897100	-3.11436100	0.93397700
H	-4.10176300	-3.94220800	-1.05379600
H	-4.21164600	-2.09615100	2.83904600
H	-5.12141500	-3.74369700	1.20885200



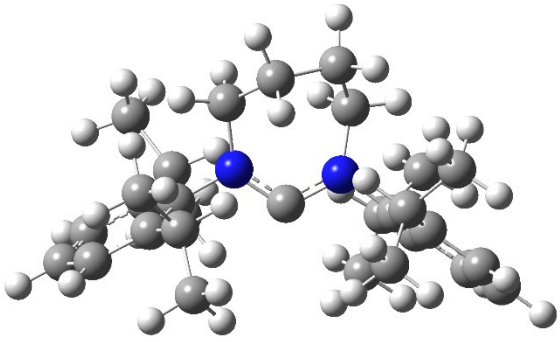
Carbene-H^+:

Electronic energy: -1301.175397 Hartree/particle
Zero-point correction= 0.414860 (Hartree/Particle)
Thermal correction to Energy= 0.438301
Thermal correction to Enthalpy= 0.439245
Thermal correction to Gibbs Free Energy= 0.362073
Sum of electronic and zero-point Energies= -1300.760537
Sum of electronic and thermal Energies= -1300.737097
Sum of electronic and thermal Enthalpies= -1300.736152
Sum of electronic and thermal Free Energies= -1300.813324

N	0.98098500	0.69647400	-0.06085900
C	-0.31108500	-1.10027200	0.05946400
C	-0.31103200	1.10027700	-0.05967300
O	-0.54811600	-2.40851100	0.08327300
O	-0.54805700	2.40851400	-0.08353600
N	0.98096200	-0.69648400	0.06120600
C	-1.90003600	2.83052300	-0.13811700
C	-2.53374000	3.17606900	1.05068300
C	-2.51288500	2.95424700	-1.38106100
C	-3.84564600	3.65714300	0.98677700
H	-2.01477500	3.07283100	1.99918300
C	-3.82491700	3.43642600	-1.42799000
H	-1.97774900	2.68346600	-2.28674300
C	-4.49053300	3.78600500	-0.24800500
H	-4.35923900	3.93229400	1.90401300
H	-4.32171300	3.54095800	-2.38872100
H	-5.50925200	4.16176900	-0.29107100
C	-1.90009800	-2.83049300	0.13801900
C	-2.53380100	-3.17646100	-1.05065600
C	-2.51295500	-2.95376800	1.38100800
C	-3.84571400	-3.65750200	-0.98658100
H	-2.01483200	-3.07356800	-1.99919000
C	-3.82499100	-3.43590900	1.42810600
H	-1.97781800	-2.68268000	2.28659800
C	-4.49060900	-3.78590600	0.24824200

H	-4.35930600	-3.93297600	-1.90372000
H	-4.32179100	-3.54009200	2.38887200
H	-5.50933300	-4.16163900	0.29144200
C	2.16280700	-1.49055500	-0.13890900
C	2.75187600	-2.10912100	0.96537700
C	2.68205900	-1.63482300	-1.42870200
C	3.88810200	-2.89790100	0.76916600
H	2.32476100	-1.97452000	1.95472400
C	3.82402200	-2.41743300	-1.60989600
H	2.19779700	-1.14453800	-2.26822600
C	4.42405000	-3.04832700	-0.51403300
H	4.35528700	-3.38807900	1.61867200
H	4.24013000	-2.53766100	-2.60626500
H	5.31095300	-3.65889400	-0.66139200
C	2.16285700	1.49051900	0.13906700
C	2.75164200	2.10928500	-0.96526600
C	2.68244900	1.63456500	1.42874800
C	3.88790900	2.89804100	-0.76921000
H	2.32428500	1.97485100	-1.95453100
C	3.82446400	2.41713800	1.60977900
H	2.19840300	1.14413300	2.26831100
C	4.42419900	3.04823400	0.51387300
H	4.35486400	3.38837500	-1.61875300
H	4.24083700	2.53718400	2.60605800
H	5.31113900	3.65877800	0.66110700
C	-1.16412400	0.00000200	-0.00024900
H	-2.24251500	0.00001900	-0.00047200

NHC-7



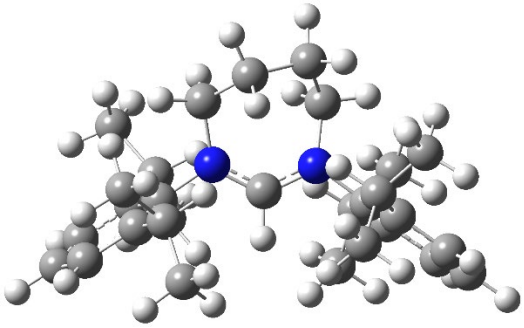
Singlet:

Electronic energy: -1239.714400 Hartree/particle
Zero-point correction= 0.649160 (Hartree/Particle)
Thermal correction to Energy= 0.680315
Thermal correction to Enthalpy= 0.681259
Thermal correction to Gibbs Free Energy= 0.590952
Sum of electronic and zero-point Energies= -1239.065241
Sum of electronic and thermal Energies= -1239.034086
Sum of electronic and thermal Enthalpies= -1239.033142

Sum of electronic and thermal Free Energies= -1239.123449

C	-0.01500000	-0.01461600	-0.04600100
C	-1.40137900	-0.44394600	2.10306700
C	0.97802200	-0.68151000	3.04355700
C	-0.35397800	-1.37582100	2.71440400
H	-1.49271300	0.48851300	2.67455200
H	0.94244400	-0.25215400	4.05407900
H	-2.37694800	-0.93502200	2.14415800
H	1.79400400	-1.41381100	3.03916400
H	-0.78078700	-1.81067500	3.62710100
H	-0.18860100	-2.21062100	2.02323300
N	1.14621200	0.10750400	0.63622700
N	-1.16711800	-0.14262900	0.65007700
C	1.28223300	0.46229100	2.07826600
H	0.61002600	1.30596000	2.27171100
H	2.30033400	0.82763900	2.23068700
C	2.36513100	0.17828900	-0.14647900
C	2.82263700	1.43637100	-0.60804500
C	3.09337400	-1.00532500	-0.40727800
C	4.01644200	1.48158500	-1.34297300
C	4.27949900	-0.90749800	-1.15226300
C	4.74155500	0.32208800	-1.61730400
H	4.38309000	2.43798300	-1.70741200
H	4.84787600	-1.80840700	-1.36954300
H	5.66370200	0.37787500	-2.19159700
C	-2.39319000	-0.06825900	-0.12285600
C	-2.92584100	-1.23983400	-0.71121900
C	-3.05991700	1.17406000	-0.22837000
C	-4.12442800	-1.13428000	-1.43224600
C	-4.25877300	1.22676100	-0.95668400
C	-4.78834200	0.08608900	-1.55803600
H	-4.54680800	-2.02163500	-1.89743900
H	-4.78464700	2.17364000	-1.05145900
H	-5.71786400	0.14616100	-2.11988200
C	2.07306100	2.73772100	-0.33116600
H	1.14028900	2.48971200	0.18246800
C	2.64336700	-2.37689900	0.08827500
H	1.71854400	-2.24029200	0.65322400
C	2.33412000	-3.33196000	-1.08106800
H	1.56717800	-2.91649500	-1.74579900
H	3.22968100	-3.53360000	-1.68239400
H	1.96516700	-4.29266400	-0.69904400
C	3.67866300	-3.00758000	1.04002600
H	3.90989000	-2.34292900	1.88142500
H	3.29161600	-3.94939600	1.45023100
H	4.61877300	-3.23258800	0.52054600

C	1.69663500	3.47319100	-1.63212800
H	1.11148000	2.83101300	-2.30119300
H	1.09514500	4.36189900	-1.40329600
H	2.58769000	3.80711600	-2.17818500
C	2.88173100	3.66692100	0.59648400
H	3.14001500	3.16944900	1.53911200
H	3.81522400	3.99120600	0.11908800
H	2.29877900	4.56538600	0.83736000
C	-2.53130500	2.44692400	0.42880900
H	-1.57772200	2.20638300	0.90700200
C	-3.48668000	2.95155500	1.52830900
H	-4.45820700	3.24488600	1.11041000
H	-3.66585000	2.18186300	2.28904600
H	-3.05921000	3.82951100	2.02989300
C	-2.25891500	3.55718500	-0.60382600
H	-1.80599400	4.42814000	-0.11300500
H	-1.57221900	3.21459500	-1.38669400
H	-3.18436900	3.89270300	-1.08860600
C	-2.25505000	-2.60445600	-0.57847300
H	-1.32636100	-2.46813800	-0.01919800
C	-3.13350300	-3.58924700	0.21878400
H	-3.37856500	-3.19543700	1.21286800
H	-4.07591300	-3.79851800	-0.30310400
H	-2.60731700	-4.54312900	0.35419600
C	-1.88592300	-3.20050600	-1.95061700
H	-2.78015600	-3.41457200	-2.54925600
H	-1.24986200	-2.51801000	-2.52680300
H	-1.33995300	-4.14342100	-1.81947800



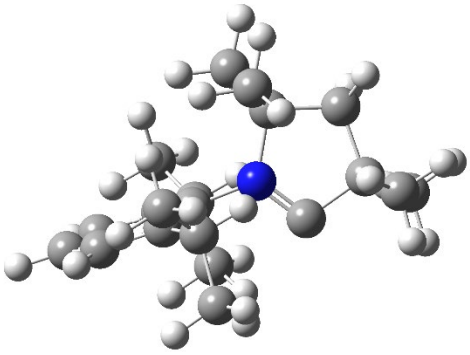
Carbene-H^+:

Electronic energy: -1240.219130 Hartree/particle
Zero-point correction= 0.663914 (Hartree/Particle)
Thermal correction to Energy= 0.695161
Thermal correction to Enthalpy= 0.696105
Thermal correction to Gibbs Free Energy= 0.605456
Sum of electronic and zero-point Energies= -1239.555216
Sum of electronic and thermal Energies= -1239.523969
Sum of electronic and thermal Enthalpies= -1239.523025
Sum of electronic and thermal Free Energies= -1239.613674

C	-1.41869300	-0.47477800	2.15719700
C	0.98175900	-0.69509300	3.08698500
C	-0.35244300	-1.39002100	2.75802300
H	-1.52070600	0.46479900	2.71094300
H	0.94585400	-0.26569900	4.09606100
H	-2.38716700	-0.97681400	2.18514700
H	1.79166900	-1.43251300	3.08317400
H	-0.77352500	-1.82200800	3.67321600
H	-0.18934000	-2.22825100	2.07077900
N	1.16891400	0.13081600	0.69560600
N	-1.19311900	-0.16930500	0.70946900
C	1.31246600	0.45869300	2.14267500
H	0.66409800	1.31876300	2.33754300
H	2.34224800	0.78860500	2.28304100
C	2.35556800	0.17113000	-0.15014800
C	2.80231500	1.42378200	-0.62872000
C	3.03800900	-1.03252300	-0.43008900
C	3.96399500	1.44122200	-1.41389800
C	4.19167800	-0.95499900	-1.22537200
C	4.65301500	0.26628300	-1.71189900
H	4.33371700	2.38857200	-1.79652500
H	4.73576700	-1.86529400	-1.46219600
H	5.55114000	0.30350100	-2.32389300
C	-2.38940000	-0.05783900	-0.11735600
C	-2.91486300	-1.22096000	-0.72193200
C	-3.00707700	1.20596000	-0.23795500
C	-4.08282900	-1.08192200	-1.48545700
C	-4.17638500	1.28464100	-1.00938100
C	-4.70880500	0.15560100	-1.62953500
H	-4.50881500	-1.95664200	-1.96943200
H	-4.67735700	2.24227100	-1.12189700
H	-5.61576900	0.23909300	-2.22365700
C	2.09014500	2.73833200	-0.31957700
H	1.16872600	2.51444000	0.22612400
C	2.58932500	-2.39180900	0.09778500
H	1.67776300	-2.24842200	0.68262600
C	2.25137500	-3.36321300	-1.04952600
H	1.47887000	-2.95110700	-1.70972700
H	3.13470900	-3.58675000	-1.66035700
H	1.87784300	-4.31124100	-0.64243000
C	3.64496900	-3.00654600	1.03756000
H	3.89093300	-2.32930700	1.86426100
H	3.26649300	-3.94259500	1.46743500
H	4.57393400	-3.23630500	0.50108400
C	1.68743700	3.48688600	-1.60490900
H	1.06530200	2.86104100	-2.25595200

H	1.11539700	4.38764100	-1.35135300
H	2.56691100	3.80262200	-2.17918100
C	2.95369300	3.63968800	0.58538300
H	3.23010600	3.12885900	1.51541200
H	3.87771100	3.94233000	0.07719500
H	2.40103900	4.55012600	0.84977700
C	-2.47581200	2.46047900	0.45043000
H	-1.53059200	2.21024200	0.94093900
C	-3.44639100	2.94506800	1.54598400
H	-4.41042200	3.24691400	1.11778900
H	-3.63681200	2.16179700	2.28951400
H	-3.02334600	3.81287800	2.06770500
C	-2.18366700	3.58976600	-0.55523900
H	-1.71976600	4.43996000	-0.03999800
H	-1.50022600	3.25650500	-1.34468300
H	-3.10227700	3.95172900	-1.03286100
C	-2.27645800	-2.59913400	-0.57383500
H	-1.37737900	-2.49741800	0.04003700
C	-3.21748800	-3.57936100	0.15404800
H	-3.51227200	-3.19717700	1.13888300
H	-4.13082100	-3.76280700	-0.42522200
H	-2.71481800	-4.54353500	0.30182500
C	-1.84364100	-3.17262300	-1.93707500
H	-2.70863200	-3.35082600	-2.58756100
H	-1.16185300	-2.49264800	-2.46170000
H	-1.32771200	-4.13043700	-1.79675100
C	-0.01589300	-0.01540500	0.11856500
H	-0.02662300	-0.00330500	-0.96705700

CAAC-5



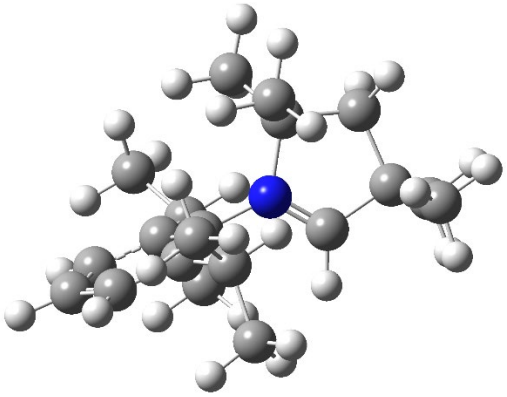
Singlet:

Electronic energy: -835.405648 Hartree/particle
Zero-point correction= 0.465243 (Hartree/Particle)
Thermal correction to Energy= 0.488556
Thermal correction to Enthalpy= 0.489500
Thermal correction to Gibbs Free Energy= 0.414568
Sum of electronic and zero-point Energies= -834.940405
Sum of electronic and thermal Energies= -834.917092

Sum of electronic and thermal Enthalpies= -834.916148
Sum of electronic and thermal Free Energies= -834.991081

C	-1.33185900	-0.07657200	-1.04386400
N	-0.61512900	-0.05367500	0.04615900
C	0.83264200	0.03790300	-0.01114100
C	1.58924200	-1.14891200	-0.06080100
C	1.45264700	1.30018100	-0.06819400
C	2.97978800	-1.04284400	-0.04779700
C	2.84736200	1.34721000	-0.05260500
C	3.60800100	0.19109200	-0.01688600
H	3.58096900	-1.94103800	-0.08153400
H	3.34552100	2.30626300	-0.09073000
H	4.68850000	0.25108800	0.00072400
C	-1.35761200	-0.10690400	1.39874900
C	-1.29686200	1.24948400	2.10895800
H	-0.26991500	1.53601100	2.33331600
H	-1.75818000	2.04149100	1.52242500
H	-1.83455900	1.18055200	3.05571200
C	-0.78243800	-1.16891300	2.33566200
H	-1.35393400	-1.16836600	3.26515000
H	-0.84753600	-2.16758800	1.90983500
H	0.25818100	-0.96363000	2.58709700
C	-2.78930500	-0.17972400	-0.62505300
C	-2.77350900	-0.45294400	0.90619400
H	-3.53001000	0.12247400	1.44003400
H	-2.98003000	-1.50726000	1.09573900
C	0.67838400	2.59342500	-0.28420800
H	-0.37108500	2.39678900	-0.08861300
C	0.77584300	3.01568000	-1.76122300
H	0.18489900	3.91680800	-1.93837900
H	1.80902000	3.23057800	-2.04072400
H	0.40128000	2.22634400	-2.41213800
C	1.11622800	3.73557800	0.64193600
H	1.06524500	3.44851500	1.69283500
H	2.13740400	4.05908400	0.43585100
H	0.46872300	4.60229900	0.49783500
C	0.95773200	-2.52047600	-0.26119400
H	-0.10452100	-2.43957100	-0.04671300
C	1.07363700	-2.93419900	-1.73928500
H	2.11913400	-3.03425400	-2.03706300
H	0.58298000	-3.89572400	-1.90472700
H	0.60329800	-2.19305300	-2.38486600
C	1.53428400	-3.60433000	0.65888800
H	0.98207400	-4.53681000	0.52888200
H	2.58021300	-3.81650700	0.43348600
H	1.47226700	-3.31852000	1.70943300

C	-3.46856700	-1.31687000	-1.40010900
H	-4.51283700	-1.41850700	-1.09410800
H	-3.43865300	-1.12160900	-2.47184900
H	-2.97059900	-2.27129800	-1.22122200
C	-3.48205500	1.14956100	-0.97913100
H	-3.39160000	1.35391100	-2.04575700
H	-4.54322400	1.09906200	-0.72506700
H	-3.04861800	1.99363000	-0.44135100



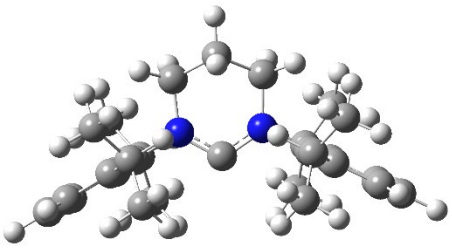
Carbene-H^+:

Electronic energy: -835.908072 Hartree/particle
Zero-point correction= 0.479444 (Hartree/Particle)
Thermal correction to Energy= 0.502840
Thermal correction to Enthalpy= 0.503784
Thermal correction to Gibbs Free Energy= 0.429313
Sum of electronic and zero-point Energies= -835.428628
Sum of electronic and thermal Energies= -835.405232
Sum of electronic and thermal Enthalpies= -835.404288
Sum of electronic and thermal Free Energies= -835.478759

N	-0.59159600	-0.03834600	0.08316200
C	0.86717600	0.02779700	-0.01849100
C	1.58118200	-1.18461600	-0.07718600
C	1.49072600	1.28771600	-0.08733400
C	2.97211700	-1.09734900	-0.10579700
C	2.88536300	1.29960100	-0.11352000
C	3.61988500	0.12654600	-0.09962400
H	3.55699000	-2.00483200	-0.14910400
H	3.40305800	2.24678500	-0.16242000
H	4.70055000	0.16573400	-0.11416900
C	-1.38350300	-0.08613000	1.41347800
C	-1.29582800	1.27247000	2.10937100
H	-0.26857700	1.52761600	2.36153700
H	-1.72501200	2.07625400	1.51539200
H	-1.85866100	1.21056300	3.04013600
C	-0.83660900	-1.16516700	2.34049300
H	-1.42730900	-1.15263000	3.25617300

H	-0.91490100	-2.16047700	1.91154900
H	0.20009200	-0.97406700	2.61335800
C	-2.82042400	-0.13241800	-0.63979100
C	-2.80608300	-0.40312400	0.88945900
H	-3.55173900	0.19406700	1.40935900
H	-3.03932800	-1.45023900	1.07679100
C	0.74575700	2.60731600	-0.24785200
H	-0.31390300	2.43506500	-0.07159900
C	0.88101100	3.11973000	-1.69399500
H	0.30480600	4.03613500	-1.82593900
H	1.92038800	3.34109800	-1.93704000
H	0.52472900	2.38777700	-2.42079200
C	1.20096600	3.68271200	0.74917200
H	1.13257200	3.33957500	1.78125500
H	2.23175600	3.98715400	0.56985600
H	0.57937400	4.57259700	0.64709900
C	0.92799800	-2.55395500	-0.22540100
H	-0.13869600	-2.45686800	-0.02838100
C	1.06911200	-3.05296800	-1.67557100
H	2.11684600	-3.19537100	-1.94098900
H	0.56021900	-4.00966100	-1.79804200
H	0.64369300	-2.34845000	-2.39231600
C	1.47698500	-3.59543400	0.76003500
H	0.91654200	-4.52622200	0.66861600
H	2.52219600	-3.82843000	0.55878800
H	1.40577700	-3.25681200	1.79326300
C	-3.45897500	-1.28024600	-1.44353500
H	-4.50895500	-1.37102900	-1.16556500
H	-3.41332600	-1.08878400	-2.51586100
H	-2.97411600	-2.23532500	-1.24129000
C	-3.49593000	1.20426200	-1.02227800
H	-3.39181500	1.41081200	-2.08762200
H	-4.56025300	1.13694900	-0.79802300
H	-3.08620300	2.04719900	-0.46747000
C	-1.36458100	-0.04429000	-0.93445700
H	-0.94368900	0.01754000	-1.93174500

NHC-6

Singlet: 

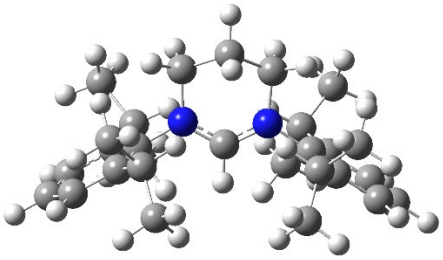
Electronic energy: -1200.421193 Hartree/particle

Zero-point correction= 0.619503 (Hartree/Particle)

Thermal correction to Energy= 0.649861
Thermal correction to Enthalpy= 0.650805
Thermal correction to Gibbs Free Energy= 0.561627
Sum of electronic and zero-point Energies= -1199.801690
Sum of electronic and thermal Energies= -1199.771332
Sum of electronic and thermal Enthalpies= -1199.770388
Sum of electronic and thermal Free Energies= -1199.859566

N	-1.14819500	-0.06034900	0.65332800
C	-0.00062600	-0.04785100	-0.06010900
C	1.24492100	-0.13783200	2.13225100
H	1.38567200	0.87845200	2.52551600
H	2.13382900	-0.72063500	2.39155600
C	-0.00935400	-0.77551000	2.71410800
H	-0.00739500	-0.67652700	3.80487000
H	-0.02593200	-1.84581000	2.47449700
C	-1.24413700	-0.10067200	2.13234500
H	-2.15115700	-0.65044400	2.40031600
H	-1.34860100	0.92344600	2.51675100
N	1.14624900	-0.08122200	0.65378400
C	-2.40929300	0.03019100	-0.04747600
C	-2.94563000	1.30307000	-0.35033700
C	-3.10665100	-1.15752400	-0.37149700
C	-4.18284600	1.36236300	-1.01076200
C	-4.33881600	-1.04540100	-1.03254300
C	-4.87494400	0.20162300	-1.35298800
H	-4.61084500	2.33116000	-1.25625800
H	-4.88619900	-1.94611900	-1.29914600
H	-5.83195300	0.26849800	-1.86577600
C	2.40836900	-0.00861900	-0.04736800
C	3.07034200	-1.20614200	-0.40713800
C	2.98116100	1.25645700	-0.31422800
C	4.30304400	-1.11046600	-1.06993800
C	4.21833900	1.29912200	-0.97588700
C	4.87485200	0.12922600	-1.35513100
H	4.82322700	-2.01852500	-1.36473600
H	4.67420800	2.26185000	-1.19390800
H	5.83198500	0.18313100	-1.86920700
C	2.31547000	2.56503600	0.10327500
H	1.35254900	2.32345900	0.56212200
C	2.49498200	-2.58527000	-0.09545900
H	1.54940100	-2.44162500	0.43421500
C	2.03281000	3.47627000	-1.10642100
H	1.41445800	2.96697500	-1.85488900
H	1.50083000	4.38008900	-0.78389500
H	2.96186700	3.79431000	-1.59576000
C	3.15719300	3.31203400	1.15721600

H	3.35206600	2.68366700	2.03493300
H	4.12491400	3.62659200	0.74611300
H	2.62880100	4.21254500	1.49608800
C	3.42452900	-3.39471300	0.83019800
H	4.37968000	-3.62466300	0.34133500
H	3.64269600	-2.85004300	1.75711200
H	2.95137100	-4.34718900	1.10182900
C	2.18890000	-3.37770000	-1.38128200
H	1.72164800	-4.33936400	-1.13310600
H	1.50303300	-2.82741900	-2.03655900
H	3.10389700	-3.58712600	-1.94953700
C	-2.24110700	2.60341000	0.02707000
H	-1.28641400	2.34716200	0.49486600
C	-2.56780700	-2.54321100	-0.02544700
H	-1.61609100	-2.41159100	0.49634300
C	-3.51483600	-3.30267800	0.92446600
H	-3.71245100	-2.72938100	1.83866500
H	-4.47869600	-3.51702300	0.44570500
H	-3.06774300	-4.26144400	1.21728900
C	-2.28831100	-3.37691800	-1.29101500
H	-3.21022300	-3.57550100	-1.85193300
H	-1.58900200	-2.86349600	-1.96181600
H	-1.84742200	-4.34452000	-1.01872400
C	-3.06022300	3.40835600	1.05572600
H	-4.01787100	3.73905600	0.63387800
H	-3.27436500	2.81418500	1.95259300
H	-2.50501000	4.30268200	1.36710500
C	-1.93102400	3.46638900	-1.21108500
H	-1.33190300	2.91307500	-1.94386200
H	-2.85048100	3.79897400	-1.70893400
H	-1.36858400	4.36190300	-0.91869600



Carbene-H^+:

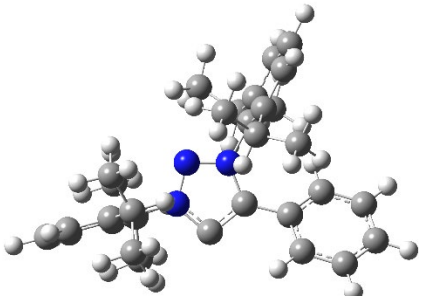
Electronic energy: -1200.923583 Hartree/particle
Zero-point correction= 0.634720 (Hartree/Particle)
Thermal correction to Energy= 0.664886
Thermal correction to Enthalpy= 0.665830
Thermal correction to Gibbs Free Energy= 0.577202
Sum of electronic and zero-point Energies= -1200.288864
Sum of electronic and thermal Energies= -1200.258697
Sum of electronic and thermal Enthalpies= -1200.257753

Sum of electronic and thermal Free Energies= -1200.346382

N	-1.17253800	-0.03653100	0.72565500
C	1.25687800	-0.07310600	2.20437200
H	1.39154300	0.95303600	2.56517900
H	2.14769300	-0.64850200	2.46461900
C	-0.00018600	-0.71239100	2.78482600
H	-0.00010900	-0.58613200	3.87152500
H	-0.00067600	-1.78693200	2.57038800
C	-1.25670300	-0.07200500	2.20439100
H	-2.14808400	-0.64633100	2.46502800
H	-1.39017700	0.95442400	2.56483300
N	1.17254900	-0.03697300	0.72566100
C	0.00001200	-0.02406700	0.11124800
H	0.00002700	-0.00110900	-0.97312900
C	2.40433500	0.01632300	-0.04165700
C	3.02916600	-1.19769300	-0.40185700
C	2.95644700	1.27755300	-0.35328000
C	4.22863300	-1.11934600	-1.12394300
C	4.15979200	1.29586900	-1.07444200
C	4.78854800	0.11284200	-1.45946900
H	4.73047100	-2.03505200	-1.42497600
H	4.61058900	2.24983100	-1.33435900
H	5.71971800	0.15096600	-2.01985400
C	-2.40430700	0.01676600	-0.04168500
C	-2.95605700	1.27801000	-0.35387100
C	-3.02948100	-1.19723200	-0.40136300
C	-4.15933600	1.29636600	-1.07514000
C	-4.22889500	-1.11885300	-1.12353600
C	-4.78841800	0.11335000	-1.45966700
H	-4.60982600	2.25034700	-1.33552100
H	-4.73097600	-2.03454600	-1.42419700
H	-5.71953500	0.15149500	-2.02013700
C	2.31544400	2.59485800	0.07387400
H	1.37113800	2.37199100	0.57965600
C	2.45933600	-2.56406700	-0.03235200
H	1.53744100	-2.40906800	0.53519600
C	3.20776000	3.34751000	1.08100200
H	3.43316600	2.72959400	1.95862000
H	4.15915700	3.64699500	0.62402800
H	2.70047600	4.25687600	1.42722300
C	1.98831500	3.49023300	-1.13636600
H	2.89871500	3.80027000	-1.66375100
H	1.34096800	2.97368300	-1.85476300
H	1.47057300	4.39808600	-0.80339900
C	3.42626700	-3.35292100	0.87233500
H	4.35880700	-3.59532000	0.34789400

H	3.68323200	-2.78703000	1.77602900
H	2.96247100	-4.29716900	1.18434000
C	2.09553900	-3.38411600	-1.28533900
H	1.63107600	-4.33407800	-0.99276300
H	1.38864300	-2.84480300	-1.92709700
H	2.98579100	-3.61607600	-1.88281000
C	-2.31471800	2.59529900	0.07280400
H	-1.37038200	2.37237800	0.57850700
C	-1.98760900	3.49026400	-1.13774100
H	-1.34048100	2.97338100	-1.85609800
H	-2.89804200	3.80031700	-1.66506000
H	-1.46964200	4.39811400	-0.80512300
C	-3.20672100	3.34841500	1.07985800
H	-4.15813300	3.64796500	0.62295300
H	-3.43210600	2.73079300	1.95768900
H	-2.69918800	4.25777300	1.42573500
C	-2.46005300	-2.56361200	-0.03125800
H	-1.53793800	-2.40863800	0.53593800
C	-3.42701400	-3.35160300	0.87414300
H	-3.68353100	-2.78512400	1.77759700
H	-4.35978000	-3.59396700	0.35008600
H	-2.96346300	-4.29584200	1.18654100
C	-2.09690700	-3.38451900	-1.28386400
H	-2.98738500	-3.61637900	-1.88103500
H	-1.38986000	-2.84590700	-1.92604300
H	-1.63285000	-4.33454600	-0.99084900

Mesoionic carbene (MIC)



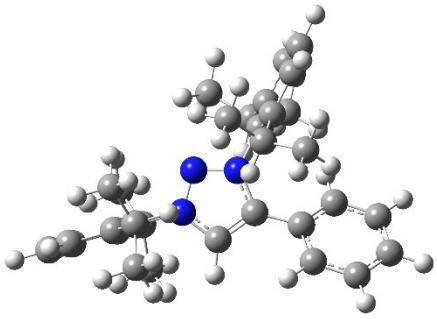
Singlet:

Electronic energy: -1406.943849 Hartree/particle
Zero-point correction= 0.636169 (Hartree/Particle)
Thermal correction to Energy= 0.669339
Thermal correction to Enthalpy= 0.670283
Thermal correction to Gibbs Free Energy= 0.573050
Sum of electronic and zero-point Energies= -1406.307680
Sum of electronic and thermal Energies= -1406.274510
Sum of electronic and thermal Enthalpies= -1406.273566
Sum of electronic and thermal Free Energies= -1406.370800

C	0.71257500	-0.27945300	1.60009400

N	1.35327500	-0.09196200	0.40240400
C	-0.62878600	-0.13287900	1.20373100
N	-0.64721000	0.11808100	-0.15507500
N	0.57566100	0.14297200	-0.66182300
C	2.78404100	-0.13639000	0.18093800
C	3.53289900	1.04062000	0.37955700
C	3.36318200	-1.36183500	-0.20473500
C	4.92014600	0.95749200	0.19014100
C	4.75403200	-1.38607500	-0.38362000
C	5.52574300	-0.24136700	-0.18592700
H	5.53250100	1.84267800	0.33925100
H	5.23712300	-2.31360500	-0.67899800
H	6.60318500	-0.28311100	-0.32739700
C	-1.82748100	-0.25309200	2.05535400
C	-1.81579700	-1.20709200	3.09167200
C	-2.96336400	0.56360800	1.90823400
C	-2.90748700	-1.34265900	3.95060900
H	-0.94744900	-1.84751500	3.21486300
C	-4.05622700	0.42265900	2.76742300
H	-2.99266300	1.32614000	1.13799400
C	-4.03509000	-0.52991200	3.79056000
H	-2.87827200	-2.08772800	4.74199100
H	-4.92214400	1.06764100	2.63955200
H	-4.88647300	-0.63550200	4.45833500
C	-1.75252600	0.28698700	-1.08069600
C	-2.40384100	-0.86804300	-1.55787900
C	-2.09590800	1.59432400	-1.48281000
C	-3.45644300	-0.67605700	-2.46471000
C	-3.15131400	1.72288400	-2.39597600
C	-3.82798900	0.60244900	-2.87824700
H	-3.98333500	-1.54001400	-2.85992100
H	-3.44507900	2.71167900	-2.73617700
H	-4.64498800	0.72651600	-3.58503900
C	-1.35184600	2.83264400	-0.99094700
H	-0.70512900	2.53758300	-0.15861300
C	-1.98864400	-2.28218600	-1.16334700
H	-1.21006600	-2.21490200	-0.39816500
C	-1.38141300	-3.03127800	-2.36602100
H	-1.03547000	-4.02482100	-2.05488200
H	-2.12111600	-3.16744400	-3.16481900
H	-0.52569600	-2.48842300	-2.78415900
C	-3.15714300	-3.08043400	-0.55536400
H	-3.95292600	-3.25544300	-1.28961100
H	-2.80044700	-4.05948700	-0.21189700
H	-3.59559700	-2.55968400	0.30395600
C	-2.30358600	3.92142100	-0.46193700
H	-1.71956000	4.74890200	-0.04033500

H	-2.93414700	4.33382800	-1.25863300
H	-2.96058400	3.53575300	0.32653300
C	-0.44605900	3.40030100	-2.10251900
H	0.12707900	4.25529400	-1.72337400
H	0.26292100	2.64778400	-2.46623700
H	-1.04292400	3.74519800	-2.95642200
C	2.89823100	2.36500300	0.79340200
H	1.81230700	2.23461400	0.81214000
C	2.54690400	-2.63274700	-0.42033100
H	1.49079600	-2.39613400	-0.26229300
C	3.33624500	2.77371000	2.21336400
H	3.08757500	1.99751400	2.94690300
H	4.41781100	2.95215700	2.26028100
H	2.82871300	3.69937800	2.51310900
C	3.20540700	3.48632800	-0.21740000
H	2.89266100	3.20867000	-1.23094600
H	2.66997800	4.40152000	0.06446900
H	4.27618800	3.72260000	-0.24569600
C	2.68743100	-3.15640400	-1.86238100
H	2.04347100	-4.03215200	-2.00958700
H	2.39629000	-2.39381600	-2.59471100
H	3.71902500	-3.45882900	-2.08067800
C	2.92896200	-3.72344900	0.59884600
H	3.97222500	-4.03948900	0.47492100
H	2.80120200	-3.36903200	1.62882800
H	2.29180400	-4.60642700	0.46246500



Carbene-H^+:

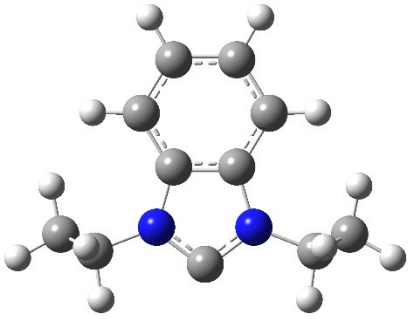
Electronic energy: -1407.440463 Hartree/particle
Zero-point correction= 0.650505 (Hartree/Particle)
Thermal correction to Energy= 0.683594
Thermal correction to Enthalpy= 0.684538
Thermal correction to Gibbs Free Energy= 0.588784
Sum of electronic and zero-point Energies= -1406.789958
Sum of electronic and thermal Energies= -1406.756868
Sum of electronic and thermal Enthalpies= -1406.755924
Sum of electronic and thermal Free Energies= -1406.851678

N	1.35928300	-0.07619200	0.33978800

C	-0.66291700	-0.13355600	1.18065300
N	-0.66631000	0.11301600	-0.17423800
N	0.55742400	0.14691200	-0.68462600
C	0.67669800	-0.25638600	1.49718600
H	1.17271100	-0.44097600	2.43804200
C	-1.78526100	0.27554100	-1.09087900
C	-2.40872800	-0.88873300	-1.58000800
C	-2.14573000	1.58377600	-1.47115400
C	-3.45946700	-0.70204000	-2.48956100
C	-3.19904000	1.70303300	-2.38743500
C	-3.84999400	0.57549400	-2.88784400
H	-3.96930900	-1.56921300	-2.89893000
H	-3.51038700	2.68974000	-2.71663100
H	-4.66465200	0.69376100	-3.59806000
C	2.79953200	-0.10990100	0.14651200
C	3.38692900	-1.34029700	-0.20505400
C	3.51936400	1.08397300	0.34382000
C	4.78028000	-1.34721400	-0.35923100
C	4.90955400	1.01090100	0.17830500
C	5.53195200	-0.18826700	-0.16801300
H	5.28034700	-2.27282900	-0.62979500
H	5.51055100	1.90372700	0.32435000
H	6.61175800	-0.21953500	-0.29056000
C	-1.83358200	-0.27181000	2.05969700
C	-1.82266800	-1.29160300	3.02921900
C	-2.93144200	0.60191100	1.98680800
C	-2.89825800	-1.43676100	3.90597800
H	-0.98154500	-1.97725900	3.08554000
C	-4.00410300	0.44917800	2.86691000
H	-2.94069000	1.41177800	1.26594700
C	-3.99241000	-0.56914900	3.82526900
H	-2.88278300	-2.23116200	4.64742000
H	-4.84642400	1.13320000	2.80641700
H	-4.83026700	-0.68369700	4.50809800
C	2.58699600	-2.62246000	-0.41175700
H	1.52493900	-2.40056900	-0.26936000
C	2.85926600	2.40211900	0.73599400
H	1.77309400	2.26960400	0.71367500
C	3.24369400	2.80430500	2.17342800
H	2.97068200	2.02465800	2.89473600
H	4.32237000	2.98393600	2.25917800
H	2.72320500	3.72744300	2.45715500
C	3.19635400	3.52881300	-0.25868500
H	2.92637200	3.25192500	-1.28443200
H	2.64115900	4.43672000	0.00653300
H	4.26467800	3.77550900	-0.24264100
C	2.97289600	-3.69380300	0.62604300

H	4.02101400	-3.99744600	0.51602100
H	2.83033400	-3.32836100	1.65026900
H	2.34808900	-4.58569700	0.49338300
C	2.75044300	-3.16027500	-1.84614600
H	2.45837600	-2.40998700	-2.59037600
H	3.78804300	-3.45261700	-2.04763700
H	2.11833200	-4.04510800	-1.98827900
C	-1.97016600	-2.29939700	-1.19959300
H	-1.20753500	-2.23193200	-0.41801900
C	-1.42191400	2.82623700	-0.96049700
H	-0.80231900	2.53906900	-0.10447400
C	-1.32428400	-3.01360000	-2.40327500
H	-0.47112700	-2.44659500	-2.79355300
H	-0.96610000	-4.00585200	-2.10275100
H	-2.04600100	-3.14791500	-3.21835500
C	-3.13254600	-3.13122100	-0.62595500
H	-3.91006000	-3.31310200	-1.37752900
H	-2.75973400	-4.10675500	-0.29023700
H	-3.59842600	-2.63295300	0.23221700
C	-0.48215400	3.38892900	-2.04636200
H	0.07285200	4.25027900	-1.65539600
H	0.24210800	2.63742300	-2.38055800
H	-1.05391300	3.72255500	-2.92149000
C	-2.39244900	3.91555100	-0.46866700
H	-1.82294300	4.73991900	-0.02240000
H	-2.98800600	4.33189400	-1.28945900
H	-3.08264600	3.53053200	0.29121800

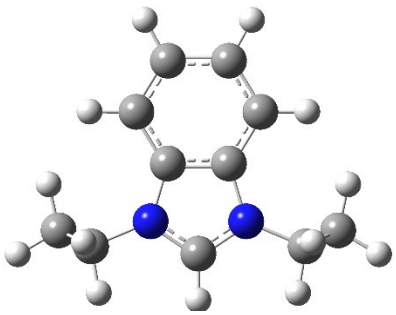
Benzannulated NHC (*bz*NHC)



Singlet:

Electronic energy: -615.654258 Hartree/particle
Zero-point correction= 0.287023 (Hartree/Particle)
Thermal correction to Energy= 0.300711
Thermal correction to Enthalpy= 0.301655
Thermal correction to Gibbs Free Energy= 0.248300
Sum of electronic and zero-point Energies= -615.367235
Sum of electronic and thermal Energies= -615.353548
Sum of electronic and thermal Enthalpies= -615.352603
Sum of electronic and thermal Free Energies= -615.405959

C	0.70519400	0.55647000	-0.00006600
C	-0.70517900	0.55648800	0.00003900
C	-1.42725700	1.75714500	0.00018600
C	-0.70372300	2.95050400	0.00020500
C	0.70380700	2.95048400	0.00009200
C	1.42730700	1.75710400	-0.00006400
H	-2.51115500	1.77164900	0.00023200
H	-1.24004800	3.89594600	0.00030900
H	1.24016000	3.89591000	0.00010600
H	2.51120600	1.77157200	-0.00016100
C	2.46748900	-1.32386200	-0.00006000
H	2.32182300	-2.40720600	-0.00024800
C	-2.46751800	-1.32381300	-0.00011000
H	-2.32186400	-2.40715800	-0.00034400
C	-0.00001900	-1.61844400	-0.00030000
N	1.08578300	-0.79062800	-0.00009400
N	-1.08580100	-0.79060200	-0.00010900
C	3.22396500	-0.94571200	1.27827200
H	4.18421800	-1.47421300	1.29901900
H	3.43166600	0.12797500	1.33663200
H	2.65485100	-1.23821200	2.16854000
C	3.22413700	-0.94521900	-1.27813200
H	3.43191100	0.12849100	-1.33594600
H	4.18435300	-1.47378000	-1.29901500
H	2.65510100	-1.23725500	-2.16860100
C	-3.22417200	-0.94516700	-1.27818700
H	-4.18445300	-1.47361700	-1.29898100
H	-3.43182600	0.12855300	-1.33611300
H	-2.65520800	-1.23736500	-2.16865000
C	-3.22399600	-0.94569400	1.27822400
H	-3.43181800	0.12797900	1.33649700
H	-4.18418600	-1.47430900	1.29905100
H	-2.65481300	-1.23805200	2.16849400



Carbene-H^+:

Electronic energy: -616.147042 Hartree/particle

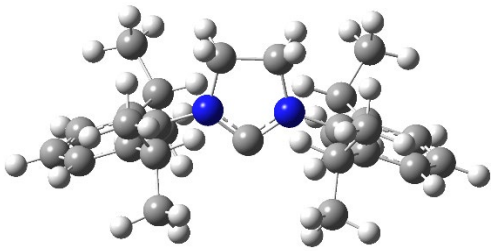
Zero-point correction= 0.301343 (Hartree/Particle)

Thermal correction to Energy= 0.314984

Thermal correction to Enthalpy= 0.315928
Thermal correction to Gibbs Free Energy= 0.262722
Sum of electronic and zero-point Energies= -615.845698
Sum of electronic and thermal Energies= -615.832057
Sum of electronic and thermal Enthalpies= -615.831113
Sum of electronic and thermal Free Energies= -615.884320

C	0.70575200	0.59855900	0.00017200
C	-0.70563200	0.59873000	-0.00016100
C	-1.43278700	1.79593600	-0.00026400
C	-0.70487300	2.98135900	-0.00000100
C	0.70565900	2.98116800	0.00030700
C	1.43324400	1.79554700	0.00040500
H	-2.51624800	1.80436800	-0.00046400
H	-1.23733900	3.92820500	-0.00005700
H	1.23838800	3.92786700	0.00046300
H	2.51671400	1.80364200	0.00054500
C	2.48022400	-1.32429000	-0.00017600
H	2.30280100	-2.40270800	-0.00039500
C	-2.48050100	-1.32386900	-0.00002700
H	-2.30308700	-2.40228300	-0.00028400
N	1.10501400	-0.74323800	0.00014700
N	-1.10519400	-0.74299800	-0.00035500
C	-0.00017000	-1.49236900	-0.00023100
H	-0.00028700	-2.57355900	-0.00035900
C	3.22997700	-0.95363400	1.28069300
H	4.17605500	-1.50553100	1.30394400
H	3.46122400	0.11513800	1.32823100
H	2.65040000	-1.22944000	2.16865300
C	3.22961200	-0.95290900	-1.28106000
H	3.46090200	0.11589200	-1.32793600
H	4.17565500	-1.50484000	-1.30496100
H	2.64975300	-1.22808200	-2.16902600
C	-3.23046500	-0.95275000	-1.28065400
H	-4.17651200	-1.50469800	-1.30399900
H	-3.46179900	0.11602100	-1.32774400
H	-2.65100300	-1.22816400	-2.16881000
C	-3.22969400	-0.95313500	1.28118100
H	-3.46119300	0.11559100	1.32857600
H	-4.17563400	-1.50524600	1.30506100
H	-2.64960700	-1.22857700	2.16891300

Saturated NHC-5 (*s*NHC-5)

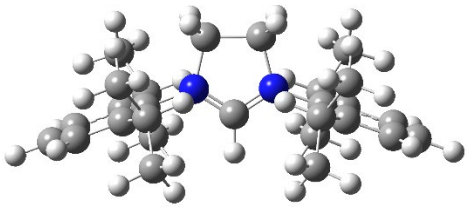


Singlet:

Electronic energy: -1161.112838 Hartree/particle
Zero-point correction= 0.591237 (Hartree/Particle)
Thermal correction to Energy= 0.620573
Thermal correction to Enthalpy= 0.621517
Thermal correction to Gibbs Free Energy= 0.534056
Sum of electronic and zero-point Energies= -1160.521601
Sum of electronic and thermal Energies= -1160.492265
Sum of electronic and thermal Enthalpies= -1160.491321
Sum of electronic and thermal Free Energies= -1160.578782

N	-1.08087800	0.00001900	0.46234700
C	0.00000000	0.00004900	-0.34424100
C	0.76831100	0.00004000	1.91786000
H	1.19350200	-0.88883600	2.39582900
H	1.19368000	0.88875400	2.39596600
N	1.08087800	0.00010900	0.46234700
C	-0.76831200	0.00018100	1.91786000
H	-1.19367700	-0.88850600	2.39602000
H	-1.19350700	0.88908400	2.39577400
C	2.44498300	0.00005100	0.01315600
C	3.10750100	-1.23375400	-0.18935900
C	3.10754000	1.23381600	-0.18946800
C	4.43999100	-1.20720200	-0.62708200
C	4.44002300	1.20718400	-0.62720400
C	5.10217200	-0.00003000	-0.84871500
H	4.96517300	-2.14389200	-0.79707800
H	4.96523200	2.14384200	-0.79729100
H	6.13493800	-0.00006100	-1.19014700
C	-2.44498200	-0.00002300	0.01315400
C	-3.10759000	1.23372500	-0.18942300
C	-3.10745100	-1.23384500	-0.18940800
C	-4.44007900	1.20705400	-0.62714300
C	-4.43993500	-1.20733300	-0.62714600
C	-5.10217200	-0.00017800	-0.84871600
H	-4.96533000	2.14369700	-0.79718200
H	-4.96507600	-2.14403700	-0.79718900
H	-6.13493800	-0.00023900	-1.19014800
C	2.42501300	-2.57719000	0.05141300
H	1.41210000	-2.37882900	0.41231100
C	-2.42490600	-2.57724900	0.05138600

H	-1.41200800	-2.37882000	0.41229700
C	-2.42521200	2.57722600	0.05129400
H	-1.41228600	2.37896400	0.41220800
C	2.42510600	2.57728500	0.05127200
H	1.41219800	2.37895700	0.41220600
C	3.14946000	3.39665700	1.13699700
H	3.22206300	2.83869200	2.07879100
H	4.16633300	3.66844700	0.82727300
H	2.60271100	4.32694700	1.33788100
C	2.29968500	3.39270700	-1.25021500
H	3.28527400	3.66282300	-1.64993700
H	1.76346900	2.83231500	-2.02558100
H	1.74798000	4.32309000	-1.06404800
C	3.14932100	-3.39655500	1.13717900
H	4.16616800	-3.66844100	0.82744700
H	3.22198900	-2.83854300	2.07893800
H	2.60250200	-4.32679000	1.33812500
C	2.29961700	-3.39265600	-1.25004800
H	1.76344400	-2.83228000	-2.02545600
H	3.28521600	-3.66281200	-1.64972200
H	1.74788300	-4.32301800	-1.06386800
C	-2.29943400	-3.39271900	-1.25006600
H	-1.76326600	-2.83232100	-2.02546100
H	-1.74765700	-4.32305300	-1.06386200
H	-3.28500600	-3.66292700	-1.64976800
C	-3.14917600	-3.39663000	1.13716000
H	-3.22182300	-2.83862200	2.07892500
H	-4.16602600	-3.66853000	0.82745800
H	-2.60234000	-4.32685900	1.33809000
C	-3.14959700	3.39658000	1.13701800
H	-4.16646800	3.66835600	0.82727000
H	-3.22221600	2.83860800	2.07880500
H	-2.60286400	4.32687500	1.33791700
C	-2.29987600	3.39264600	-1.25020100
H	-1.76366000	2.83227800	-2.02558400
H	-3.28549400	3.66271000	-1.64988900
H	-1.74821300	4.32305800	-1.06406000



Carbene-H^+:

Electronic energy: -1161.604798 Hartree/particle

Zero-point correction= 0.604661 (Hartree/Particle)

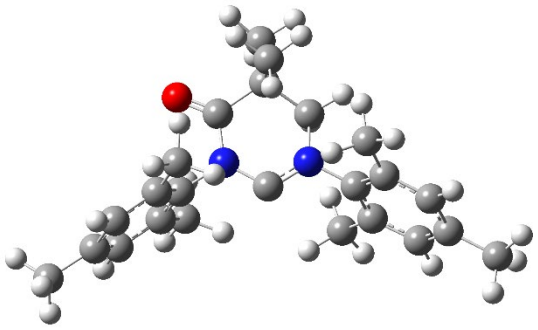
Thermal correction to Energy= 0.634398

Thermal correction to Enthalpy= 0.635343
Thermal correction to Gibbs Free Energy= 0.546484
Sum of electronic and zero-point Energies= -1161.000137
Sum of electronic and thermal Energies= -1160.970400
Sum of electronic and thermal Enthalpies= -1160.969455
Sum of electronic and thermal Free Energies= -1161.058314

N	-1.10663300	0.00002600	0.53528300
C	0.77359700	-0.00033000	1.98485300
H	1.19809600	-0.89104700	2.45407400
H	1.19791600	0.89030300	2.45440100
N	1.10662200	-0.00000900	0.53526600
C	-0.77359300	-0.00045800	1.98486200
H	-1.19793400	-0.89133100	2.45393700
H	-1.19805600	0.89002400	2.45456400
C	-0.00001000	0.00019800	-0.18432800
H	-0.00002100	0.00051700	-1.26795800
C	-2.45700800	0.00010600	0.02807000
C	-3.09808100	1.23898800	-0.19255400
C	-3.09822300	-1.23874500	-0.19245400
C	-4.41499800	1.20907700	-0.67319100
C	-4.41513400	-1.20874000	-0.67304600
C	-5.06710000	0.00020000	-0.91373100
H	-4.93512900	2.14463100	-0.86093000
H	-4.93538800	-2.14424700	-0.86067900
H	-6.08849000	0.00023100	-1.28688500
C	2.45699200	-0.00003700	0.02804500
C	3.09807900	-1.23893500	-0.19253800
C	3.09819500	1.23879600	-0.19252200
C	4.41501000	-1.20904200	-0.67310200
C	4.41511500	1.20877200	-0.67313300
C	5.06710100	-0.00016200	-0.91372000
H	4.93516300	-2.14460000	-0.86075500
H	4.93535200	2.14428000	-0.86081000
H	6.08849900	-0.00021200	-1.28685200
C	-2.41798600	2.58014400	0.06631300
H	-1.41714500	2.38662300	0.46348900
C	-2.41819600	-2.57992800	0.06643400
H	-1.41731100	-2.38645500	0.46351400
C	-2.24738200	3.38519400	-1.23646600
H	-1.70935200	4.31986200	-1.03475900
H	-1.67738500	2.82078500	-1.98454800
H	-3.21838100	3.64451900	-1.67593700
C	-3.17734300	3.40505900	1.12337200
H	-4.18051700	3.67934800	0.77496300
H	-3.28500700	2.85020300	2.06337800
H	-2.63239800	4.33288700	1.33832500

C	-3.17751800	-3.40477600	1.12355700
H	-3.28506800	-2.84991500	2.06357500
H	-4.18074500	-3.67899200	0.77523900
H	-2.63262800	-4.33264600	1.33846900
C	-2.24772800	-3.38502600	-1.23634400
H	-1.67778500	-2.82065100	-1.98449100
H	-1.70969600	-4.31969900	-1.03465300
H	-3.21877700	-3.64433900	-1.67570800
C	2.41826500	2.58001300	0.06647000
H	1.41732500	2.38658800	0.46344100
C	2.41791000	-2.58006500	0.06623700
H	1.41707200	-2.38651600	0.46340800
C	3.17717100	-3.40516100	1.12320500
H	4.18033600	-3.67949400	0.77480000
H	3.28485900	-2.85043700	2.06328800
H	2.63214600	-4.33297200	1.33802200
C	2.24726400	-3.38497100	-1.23664300
H	1.67738500	-2.82041300	-1.98470100
H	3.21826100	-3.64437200	-1.67607200
H	1.70909500	-4.31958500	-1.03505300
C	3.17761300	3.40455400	1.12384200
H	3.28502700	2.84944500	2.06372600
H	4.18089200	3.67871800	0.77563700
H	2.63281400	4.33243400	1.33893300
C	2.24798000	3.38536100	-1.23615800
H	3.21906100	3.64466900	-1.67545200
H	1.67800700	2.82117300	-1.98442900
H	1.71003200	4.32004900	-1.03432400

Monoamidocarbene (MAC)



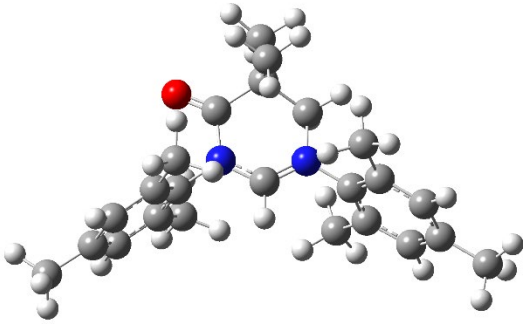
Singlet:

Electronic energy: -1117.251336 Hartree/particle
Zero-point correction= 0.485438 (Hartree/Particle)
Thermal correction to Energy= 0.511860
Thermal correction to Enthalpy= 0.512805
Thermal correction to Gibbs Free Energy= 0.432777
Sum of electronic and zero-point Energies= -1116.765898
Sum of electronic and thermal Energies= -1116.739475
Sum of electronic and thermal Enthalpies= -1116.738531

Sum of electronic and thermal Free Energies= -1116.818558

C	0.07634400	-0.20774000	0.16586700
C	1.24367300	1.73057400	-0.87169400
C	0.04691900	2.63194900	-0.53611900
H	2.17540100	2.23781400	-0.60706900
H	1.26874200	1.52434400	-1.94966500
C	0.17861600	3.24888200	0.87752100
H	1.08340800	3.86667400	0.91911700
H	-0.68296300	3.88927000	1.09615300
H	0.24744300	2.48665700	1.65861600
C	-0.03050700	3.75465500	-1.58192700
H	-0.83899200	4.45301400	-1.34836500
H	0.91336900	4.31292000	-1.59055600
H	-0.20068100	3.35415700	-2.58795100
N	-1.10619800	0.46790600	-0.12716700
C	-1.23675400	1.80473900	-0.54430400
O	-2.33380300	2.27760100	-0.81440000
N	1.19160300	0.43453400	-0.15676700
C	-2.33300900	-0.28817600	0.07269600
C	-2.86516400	-1.02091200	-1.00257400
C	-2.94987000	-0.27941700	1.33454300
C	-4.03637700	-1.75870400	-0.78566300
C	-4.11953700	-1.03479000	1.50448300
C	-4.68031500	-1.77826100	0.45901800
H	-4.45386300	-2.33224300	-1.61149300
H	-4.60178400	-1.03881500	2.48039000
C	2.45794600	-0.25755800	0.00999800
C	3.24392600	0.00211600	1.14783100
C	2.88955900	-1.15294600	-0.98882700
C	4.47587800	-0.65690800	1.26942300
C	4.12950700	-1.78485800	-0.82147700
C	4.93755600	-1.55349300	0.29880300
H	5.08775800	-0.46071800	2.14803700
H	4.47021700	-2.47567800	-1.59075600
C	-2.20246500	-1.02593400	-2.35912600
H	-2.12426400	-0.01447700	-2.77643000
H	-1.18466000	-1.43192300	-2.31039200
H	-2.77532900	-1.63680100	-3.06440400
C	-2.38086600	0.50800000	2.49006800
H	-1.38094500	0.15262200	2.76856400
H	-2.28721000	1.57415300	2.25082100
H	-3.02591400	0.41718400	3.36994700
C	-5.95837100	-2.55944700	0.65693300
H	-6.82633600	-1.99583300	0.28692300
H	-5.93556000	-3.51039100	0.11171200
H	-6.13500100	-2.77494500	1.71651200

C	2.05438100	-1.46002100	-2.20976300
H	1.13168200	-1.98880000	-1.94148900
H	1.75959900	-0.55422800	-2.75128900
H	2.61493800	-2.09664600	-2.90194100
C	2.79357600	0.95701300	2.22618700
H	2.67185000	1.97580700	1.84089800
H	1.82970100	0.65845400	2.65450100
H	3.52793900	0.99048700	3.03742500
C	6.25614200	-2.27173900	0.46509700
H	6.10862900	-3.26938200	0.90195400
H	6.75985200	-2.41238000	-0.49832200
H	6.93082900	-1.72033200	1.12932900



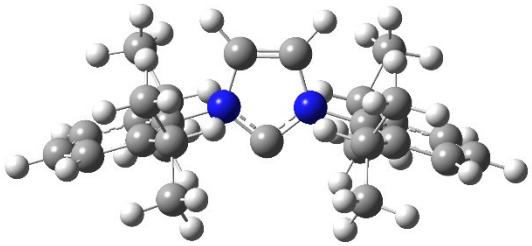
Carbene-H^+:

Electronic energy: -1117.742385 Hartree/particle
Zero-point correction= 0.500122 (Hartree/Particle)
Thermal correction to Energy= 0.526359
Thermal correction to Enthalpy= 0.527303
Thermal correction to Gibbs Free Energy= 0.447914
Sum of electronic and zero-point Energies= -1117.242263
Sum of electronic and thermal Energies= -1117.216026
Sum of electronic and thermal Enthalpies= -1117.215082
Sum of electronic and thermal Free Energies= -1117.294472

C	1.25725500	1.81195600	-0.84542300
C	0.03852500	2.68756300	-0.50124000
H	2.17582300	2.31116400	-0.53233000
H	1.31281300	1.63177500	-1.92517000
C	0.14759800	3.27722800	0.92781600
H	1.04720200	3.90005700	0.98398000
H	-0.72129100	3.90642500	1.14642900
H	0.21632500	2.50367800	1.69759000
C	-0.03401400	3.82842600	-1.52871800
H	-0.84608200	4.51850200	-1.28491100
H	0.90801800	4.38821700	-1.51548200
H	-0.19403600	3.44475600	-2.54230300
N	-1.12702100	0.49785100	-0.14268900
C	-1.24794700	1.86549700	-0.54484700
O	-2.34268100	2.31200900	-0.81656000

N	1.21966600	0.48515500	-0.18745900
C	-2.33102600	-0.29910100	0.06435500
C	-2.84213800	-1.03732700	-1.01626900
C	-2.93365700	-0.29612400	1.33239200
C	-3.99727700	-1.79645000	-0.79212000
C	-4.08646500	-1.07425600	1.50277800
C	-4.63431400	-1.82651500	0.45604100
H	-4.40723100	-2.37786500	-1.61539000
H	-4.56509600	-1.09013300	2.47968400
C	2.46518000	-0.25033700	-0.00708500
C	3.23341300	-0.00602300	1.14432900
C	2.87177700	-1.14801400	-1.01148700
C	4.44688500	-0.69462200	1.27116700
C	4.09486300	-1.80660200	-0.83238800
C	4.89527400	-1.59578500	0.29759700
H	5.05464600	-0.51815900	2.15611700
H	4.42855700	-2.50024500	-1.60131000
C	-2.18163000	-1.02664000	-2.37330500
H	-2.11694900	-0.01252000	-2.78617800
H	-1.15983800	-1.42369400	-2.33062900
H	-2.74998200	-1.64025700	-3.07883700
C	-2.37202900	0.50377700	2.48224800
H	-1.34900100	0.19633500	2.73060900
H	-2.34177100	1.57651300	2.25551400
H	-2.98792300	0.36842500	3.37633900
C	-5.89579200	-2.63081300	0.65877300
H	-6.77689600	-2.06468300	0.32601800
H	-5.87340700	-3.56286700	0.08264000
H	-6.04535600	-2.87965700	1.71495600
C	2.03772400	-1.42238400	-2.24005600
H	1.11318000	-1.95683300	-1.98811200
H	1.75067600	-0.50228000	-2.76110800
H	2.59766000	-2.04601500	-2.94350900
C	2.78717100	0.95398600	2.21906700
H	2.72033000	1.98100700	1.84137400
H	1.79994900	0.68901900	2.61469900
H	3.49722500	0.94815200	3.05146600
C	6.19591700	-2.34207600	0.47159100
H	6.02143800	-3.33117200	0.91745300
H	6.69547400	-2.50360900	-0.49032000
H	6.88181800	-1.80089100	1.13223800
C	0.07405600	-0.08222200	0.07397900
H	0.07055800	-1.08912700	0.47682600

Unsaturated NHC-5 (NHC-5)

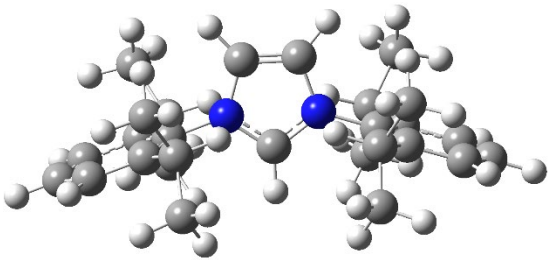


Singlet:

Electronic energy: -1159.917141 Hartree/particle
Zero-point correction= 0.569479 (Hartree/Particle)
Thermal correction to Energy= 0.597839
Thermal correction to Enthalpy= 0.598783
Thermal correction to Gibbs Free Energy= 0.513595
Sum of electronic and zero-point Energies= -1159.347661
Sum of electronic and thermal Energies= -1159.319302
Sum of electronic and thermal Enthalpies= -1159.318358
Sum of electronic and thermal Free Energies= -1159.403546

C	0.00002900	-0.00002000	-0.41824200
N	-1.06752400	-0.00004700	0.44077800
N	1.06755100	0.00004700	0.44081900
C	0.67865600	0.00003800	1.77965000
H	1.39097200	0.00006600	2.59192000
C	-0.67867100	-0.00002000	1.77962400
H	-1.39102200	-0.00008900	2.59186400
C	2.44771500	0.00008000	0.01760800
C	3.10143700	-1.23635000	-0.17398200
C	3.10127500	1.23653600	-0.17438100
C	4.44237200	-1.20789500	-0.58490800
C	4.44220300	1.20812600	-0.58533400
C	5.10745100	0.00012500	-0.79266500
H	4.97172800	-2.14398500	-0.74273900
H	4.97142600	2.14423700	-0.74350100
H	6.14687300	0.00014000	-1.11276200
C	-2.44769600	-0.00007900	0.01759600
C	-3.10141800	1.23635800	-0.17399600
C	-3.10129300	-1.23653100	-0.17427900
C	-4.44238600	1.20789800	-0.58480800
C	-4.44225700	-1.20812100	-0.58511800
C	-5.10749800	-0.00012300	-0.79246600
H	-4.97174400	2.14398600	-0.74265600
H	-4.97150100	-2.14423600	-0.74318600
H	-6.14694500	-0.00013300	-1.11248000
C	2.41259200	2.57832100	0.05954800
H	1.37518800	2.38322700	0.34522000
C	3.07190100	3.34999500	1.21937500
H	3.06597000	2.76209800	2.14556200
H	4.11330600	3.60678100	0.98828100

H	2.52952400	4.28514000	1.40896700
C	2.38283800	3.43705000	-1.21917500
H	3.39408100	3.71220900	-1.54382200
H	1.89354500	2.90701000	-2.04531700
H	1.82682300	4.36527700	-1.03625100
C	2.41288600	-2.57816100	0.06023200
H	1.37548900	-2.38309300	0.34595500
C	2.38311000	-3.43706000	-1.21838300
H	1.82710700	-4.36526900	-1.03532700
H	1.89380600	-2.90713800	-2.04459100
H	3.39435600	-3.71224900	-1.54299900
C	3.07231200	-3.34963600	1.22011500
H	4.11368800	-3.60647900	0.98896400
H	3.06648600	-2.76157200	2.14619600
H	2.52994900	-4.28474300	1.40993600
C	-2.41260000	-2.57832800	0.05954600
H	-1.37522900	-2.38324700	0.34533900
C	-3.07193600	-3.35028200	1.21914800
H	-3.06620500	-2.76252500	2.14543000
H	-4.11327400	-3.60721000	0.98792100
H	-2.52942700	-4.28536600	1.40865700
C	-2.38273800	-3.43679400	-1.21938000
H	-3.39396900	-3.71196900	-1.54405600
H	-1.89351800	-2.90650900	-2.04540300
H	-1.82662300	-4.36500000	-1.03666300
C	-2.41285700	2.57817900	0.06013200
H	-1.37539600	2.38315300	0.34564600
C	-3.07207100	3.34961600	1.22014600
H	-4.11354500	3.60631600	0.98928500
H	-3.06591300	2.76158700	2.14625400
H	-2.52977600	4.28479900	1.40978200
C	-2.38337500	3.43708900	-1.21849900
H	-1.89417400	2.90719900	-2.04478700
H	-3.39471300	3.71217400	-1.54291500
H	-1.82742100	4.36534300	-1.03553400



Carbene-H^+:

Electronic energy: -1160.406968 Hartree/particle

Zero-point correction= 0.582833 (Hartree/Particle)

Thermal correction to Energy= 0.611286

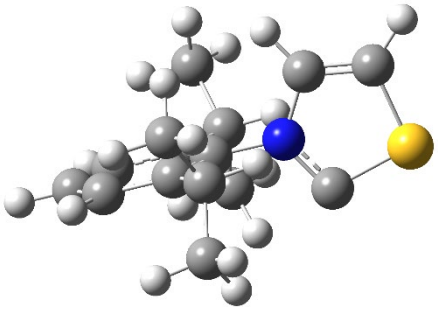
Thermal correction to Enthalpy= 0.612230

Thermal correction to Gibbs Free Energy= 0.526950
Sum of electronic and zero-point Energies= -1159.824134
Sum of electronic and thermal Energies= -1159.795682
Sum of electronic and thermal Enthalpies= -1159.794738
Sum of electronic and thermal Free Energies= -1159.880018

N	1.08794400	0.00005200	0.49971800
N	-1.08795600	0.00005100	0.49971000
C	-0.68096700	0.00014400	1.82625800
H	-1.39465900	0.00019600	2.63605200
C	0.68094600	0.00014900	1.82626300
H	1.39463300	0.00022500	2.63606100
C	-0.00000400	-0.00001800	-0.28185100
H	0.00000100	-0.00009100	-1.36117500
C	2.46357700	0.00001600	0.03434800
C	3.09859900	1.24147800	-0.17067600
C	3.09854400	-1.24148600	-0.17063000
C	4.42837200	1.20950800	-0.61431400
C	4.42829400	-1.20959500	-0.61432400
C	5.08565900	-0.00006300	-0.83629700
H	4.95430800	2.14462600	-0.78576600
H	4.95417100	-2.14474800	-0.78578000
H	6.11696800	-0.00009700	-1.18062300
C	-2.46358900	-0.00000500	0.03433800
C	-3.09854200	-1.24151400	-0.17065100
C	-3.09862200	1.24146000	-0.17067100
C	-4.42830800	-1.20962300	-0.61430900
C	-4.42839400	1.20948000	-0.61429900
C	-5.08568000	-0.00009400	-0.83626500
H	-4.95419000	-2.14477300	-0.78576200
H	-4.95434400	2.14459500	-0.78573200
H	-6.11699400	-0.00013100	-1.18057600
C	2.41218300	2.58168300	0.07625800
H	1.38469000	2.39144000	0.40052100
C	2.41209400	-2.58164600	0.07643900
H	1.38465700	-2.39135300	0.40085900
C	3.10935900	-3.36401300	1.20626600
H	4.14067600	-3.62190100	0.93620800
H	3.13674600	-2.78356300	2.13654600
H	2.56968500	-4.29838200	1.40520300
C	2.33713200	-3.42554200	-1.21028800
H	1.82130700	-2.88583300	-2.01378800
H	3.33656600	-3.69766900	-1.57097100
H	1.78616700	-4.35435000	-1.01741400
C	3.10926600	3.36409500	1.20616700
H	4.14062900	3.62197600	0.93628400
H	2.56957100	4.29848200	1.40496700

H	3.13648900	2.78369900	2.13648700
C	2.33747100	3.42553600	-1.21054200
H	3.33698700	3.69758200	-1.57106300
H	1.82175000	2.88584000	-2.01411100
H	1.78653900	4.35439100	-1.01780200
C	-2.41222700	2.58166000	0.07637100
H	-1.38475100	2.39140400	0.40067900
C	-3.10939400	3.36395900	1.20630600
H	-4.14076100	3.62178700	0.93638900
H	-3.13662400	2.78348500	2.13657800
H	-2.56975500	4.29835800	1.40519400
C	-2.33742800	3.42560200	-1.21034700
H	-1.82164900	2.88594500	-2.01391000
H	-3.33690600	3.69768700	-1.57093300
H	-1.78649200	4.35443100	-1.01749500
C	-2.41203300	-2.58167400	0.07628700
H	-1.38454700	-2.39136400	0.40053400
C	-3.10905200	-3.36410300	1.20621500
H	-3.13624800	-2.78369200	2.13652800
H	-4.14041900	-3.62200800	0.93637800
H	-2.56931500	-4.29846800	1.40499400
C	-2.33727900	-3.42551800	-1.21050100
H	-3.33677800	-3.69758300	-1.57104500
H	-1.82156100	-2.88578400	-2.01405100
H	-1.78631400	-4.35435100	-1.01775700

Thiazolylidene (*thio*NHC)

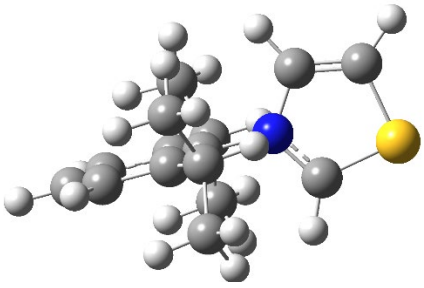


Singlet:

Electronic energy: -1035.869253 Hartree/particle
Zero-point correction= 0.304219 (Hartree/Particle)
Thermal correction to Energy= 0.320371
Thermal correction to Enthalpy= 0.321315
Thermal correction to Gibbs Free Energy= 0.261819
Sum of electronic and zero-point Energies= -1035.565034
Sum of electronic and thermal Energies= -1035.548882
Sum of electronic and thermal Enthalpies= -1035.547938
Sum of electronic and thermal Free Energies= -1035.607434

C	0.00065700	1.73032800	-1.08542600

N	0.00029100	1.00984200	0.05649500
C	0.00077100	3.03177900	1.12698000
H	0.00089900	3.79050600	1.89936100
C	0.00037100	1.68998000	1.28431300
H	0.00009800	1.12203400	2.20591500
S	0.00108600	3.39372600	-0.58510400
C	-0.00014200	-0.44437100	0.01709600
C	-1.23866400	-1.11660900	-0.00095000
C	1.23800200	-1.11730600	-0.00086300
C	-1.20990500	-2.51822300	-0.05202100
C	1.20845500	-2.51890300	-0.05197200
C	-0.00092200	-3.21340100	-0.07807900
H	-2.14533600	-3.07106200	-0.07476000
H	2.14356600	-3.07228100	-0.07469700
H	-0.00122900	-4.30018000	-0.11904200
C	-2.57649500	-0.38177500	0.01493100
H	-2.37997900	0.68811600	0.13038000
C	2.57622400	-0.38316700	0.01493700
H	2.38025500	0.68684400	0.13021400
C	3.32559500	-0.56843400	-1.31877000
H	4.26075700	0.00594200	-1.31123300
H	3.57866600	-1.62205500	-1.49107400
H	2.72101200	-0.22149900	-2.16557100
C	3.45398400	-0.81515100	1.20465500
H	2.93249800	-0.67082600	2.15894600
H	3.74401500	-1.87047600	1.13321100
H	4.37388200	-0.21730600	1.22838300
C	-3.45444300	-0.81352500	1.20459700
H	-3.74491800	-1.86872100	1.13301800
H	-2.93287400	-0.66954300	2.15889400
H	-4.37408000	-0.21528200	1.22840900
C	-3.32598000	-0.56646800	-1.31879200
H	-4.26075800	0.00853000	-1.31122500
H	-2.72116300	-0.21987400	-2.16556600
H	-3.57976400	-1.61990300	-1.49119000



Carbene-H^+:

Electronic energy: -1036.351040 Hartree/particle

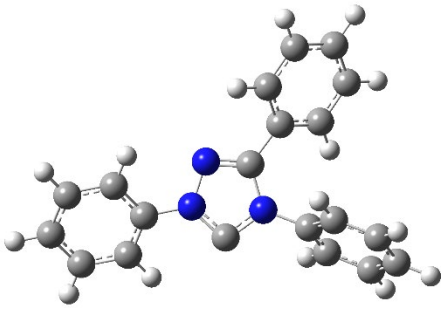
Zero-point correction= 0.317640 (Hartree/Particle)

Thermal correction to Energy= 0.333797

Thermal correction to Enthalpy= 0.334741
Thermal correction to Gibbs Free Energy= 0.275332
Sum of electronic and zero-point Energies= -1036.033400
Sum of electronic and thermal Energies= -1036.017243
Sum of electronic and thermal Enthalpies= -1036.016299
Sum of electronic and thermal Free Energies= -1036.075708

N	0.00031000	0.98288200	0.11087500
C	0.00106600	3.02842900	1.12389600
H	0.00136300	3.80663500	1.87656600
C	0.00067200	1.68570300	1.31070000
H	0.00058400	1.13783800	2.24301900
S	0.00106300	3.41116800	-0.56957200
C	-0.00016500	-0.47679300	0.03579200
C	-1.24436300	-1.13448200	0.00332100
C	1.24363200	-1.13524700	0.00330700
C	-1.21147500	-2.53428900	-0.07263200
C	1.20988400	-2.53503400	-0.07258100
C	-0.00101100	-3.22591600	-0.10985500
H	-2.14597200	-3.08717100	-0.10598000
H	2.14402700	-3.08851300	-0.10589500
H	-0.00134300	-4.31148600	-0.16956300
C	-2.58102100	-0.39870200	0.03162700
H	-2.38984800	0.67135100	0.15901500
C	2.58072200	-0.40024000	0.03157200
H	2.39013500	0.66992600	0.15891000
C	3.33416300	-0.57299300	-1.30144200
H	4.26880100	0.00124600	-1.28244900
H	3.58769700	-1.62472600	-1.48211800
H	2.73447600	-0.21770900	-2.14833400
C	3.45087600	-0.84734600	1.22122700
H	2.92457400	-0.71234400	2.17394300
H	3.73888500	-1.90204400	1.13796700
H	4.37082200	-0.25066400	1.25443900
C	-3.45137500	-0.84542700	1.22128700
H	-3.73987300	-1.89999000	1.13797900
H	-2.92499400	-0.71070900	2.17399700
H	-4.37103900	-0.24831100	1.25452400
C	-3.33461600	-0.57097300	-1.30134900
H	-4.26897100	0.00372300	-1.28225300
H	-2.73480400	-0.21590600	-2.14824600
H	-3.58868400	-1.62256200	-1.48211600
C	0.00047200	1.75902000	-0.96649600
H	0.00023000	1.36829200	-1.97661700

Enders NHC (Ender)

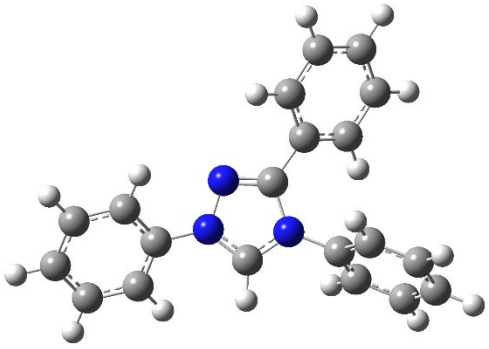


Singlet:

Electronic energy: -935.307949 Hartree/particle
Zero-point correction= 0.300597 (Hartree/Particle)
Thermal correction to Energy= 0.317220
Thermal correction to Enthalpy= 0.318165
Thermal correction to Gibbs Free Energy= 0.256228
Sum of electronic and zero-point Energies= -935.007352
Sum of electronic and thermal Energies= -934.990729
Sum of electronic and thermal Enthalpies= -934.989785
Sum of electronic and thermal Free Energies= -935.051721

C	-0.96340400	-1.29772300	0.05386200
N	-1.01404500	1.00268200	-0.10897300
N	-1.72356300	-0.18330800	-0.02606600
N	0.30070600	-0.76499500	0.00860400
C	0.23885800	0.62446000	-0.08666900
C	1.36817900	1.56796800	-0.16879600
C	1.28564400	2.78960900	0.52297600
C	2.50010500	1.29861700	-0.95716800
C	2.32032200	3.72189900	0.43080500
H	0.41504300	3.00128800	1.13691400
C	3.53166200	2.23574700	-1.04575000
H	2.57056900	0.37090900	-1.51611900
C	3.44688000	3.44707800	-0.35181700
H	2.24747300	4.66054800	0.97400900
H	4.39955700	2.01933700	-1.66325700
H	4.25295200	4.17308500	-0.42187800
C	-3.15173400	-0.12774300	-0.01610400
C	-3.89338100	-1.18347200	-0.55806800
C	-3.79564900	0.98390300	0.53878700
C	-5.28869700	-1.12727100	-0.52893900
H	-3.38557700	-2.03267600	-1.00249700
C	-5.19177600	1.03286800	0.55181500
H	-3.21139700	1.79519200	0.95990100
C	-5.94347100	-0.02122200	0.02294600
H	-5.86253100	-1.94816600	-0.95115900
H	-5.68975400	1.89642900	0.98505400
H	-7.02944800	0.02012200	0.03778100
C	1.48860800	-1.56723100	0.14626100

C	2.29048700	-1.42759400	1.28204400
C	1.81054900	-2.49065000	-0.85134600
C	3.43442600	-2.21959700	1.41377300
H	2.01918500	-0.71356500	2.05427600
C	2.95183000	-3.28435200	-0.70751100
H	1.17742200	-2.58138000	-1.72904400
C	3.76636900	-3.14831000	0.42170400
H	4.06000700	-2.11440000	2.29623800
H	3.20493700	-4.00445900	-1.48117500
H	4.65504100	-3.76483400	0.52916400



Carbene-H^+:

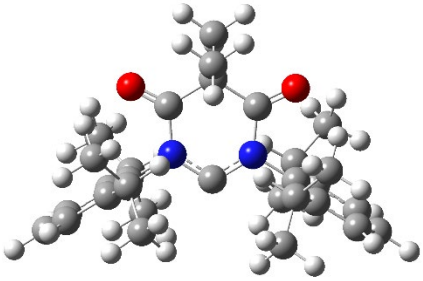
Electronic energy: -935.784074 Hartree/particle
Zero-point correction= 0.314732 (Hartree/Particle)
Thermal correction to Energy= 0.331378
Thermal correction to Enthalpy= 0.332323
Thermal correction to Gibbs Free Energy= 0.270434
Sum of electronic and zero-point Energies= -935.469342
Sum of electronic and thermal Energies= -935.452696
Sum of electronic and thermal Enthalpies= -935.451751
Sum of electronic and thermal Free Energies= -935.513640

N	-0.99886300	1.02695600	-0.12844600
N	-1.72150700	-0.12964500	-0.03284100
N	0.34408900	-0.72837900	0.00325900
C	0.26440400	0.65682200	-0.10306100
C	1.38671500	1.60232600	-0.17235900
C	1.24735200	2.85025200	0.46122500
C	2.56149400	1.30915200	-0.88564600
C	2.27615100	3.78890500	0.38653300
H	0.34213700	3.07546600	1.01718100
C	3.58497300	2.25543100	-0.95583900
H	2.67264200	0.36099000	-1.40108800
C	3.44692400	3.49339200	-0.31999200
H	2.16410300	4.74858200	0.88374200
H	4.48835200	2.02510500	-1.51402800
H	4.24821900	4.22565500	-0.37606000
C	-3.15656100	-0.10241800	-0.02312400

C	-3.86973100	-1.15085800	-0.60954400
C	-3.80034900	0.97957800	0.58156200
C	-5.26509100	-1.11512200	-0.57227500
H	-3.35266500	-1.97072500	-1.09830100
C	-5.19587200	1.00447400	0.59913300
H	-3.22231000	1.77798500	1.03464900
C	-5.92926100	-0.04065800	0.02776800
H	-5.82985400	-1.92413200	-1.02677400
H	-5.70744100	1.84028000	1.06801800
H	-7.01540400	-0.01610400	0.04699800
C	1.51436400	-1.57098400	0.13965500
C	2.26835400	-1.49622200	1.31156100
C	1.84100200	-2.44545400	-0.89728200
C	3.38855000	-2.32066900	1.43958000
H	1.98239400	-0.81314500	2.10565400
C	2.96010000	-3.26912500	-0.75159400
H	1.23746700	-2.47450400	-1.79965600
C	3.73389200	-3.20477300	0.41173600
H	3.98557700	-2.27464300	2.34601200
H	3.22701200	-3.95538800	-1.55031100
H	4.60539000	-3.84503600	0.51849600
C	-0.91965800	-1.18208300	0.04813500
H	-1.21816000	-2.21470600	0.15463000

Diamidocarbene (DAC)

Singlet:



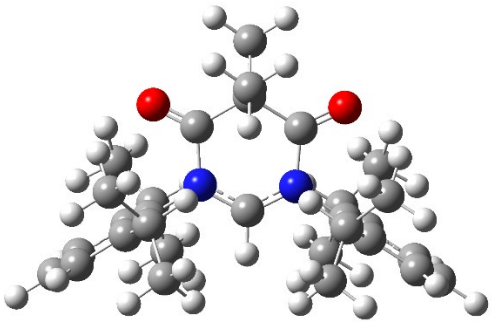
Electronic energy: -1427.111624 Hartree/particle
Zero-point correction= 0.639042 (Hartree/Particle)
Thermal correction to Energy= 0.672859
Thermal correction to Enthalpy= 0.673803
Thermal correction to Gibbs Free Energy= 0.577955
Sum of electronic and zero-point Energies= -1426.472582
Sum of electronic and thermal Energies= -1426.438765
Sum of electronic and thermal Enthalpies= -1426.437821
Sum of electronic and thermal Free Energies= -1426.533669

C	-0.00134200	0.00267600	-0.35768200
C	-0.00682500	-0.17694200	2.58191600
C	-0.09296100	-1.62652900	3.14789500
H	0.78006500	-1.81814800	3.77844400

H	-0.99716300	-1.72359900	3.75571100
H	-0.12216600	-2.37496700	2.34932200
C	0.05670900	0.83464500	3.74708600
H	-0.83895200	0.73878500	4.36539800
H	0.93561500	0.62979900	4.36292200
H	0.11907700	1.86386700	3.37692700
N	-1.15821400	0.03812100	0.36179300
C	-1.27492100	0.05869000	1.77205900
O	-2.35820000	0.21825600	2.30573000
N	1.15637100	-0.05625300	0.35943500
C	1.27801300	-0.09376000	1.76862200
O	2.37426000	-0.09276700	2.29979100
C	2.40411700	-0.05498200	-0.40486600
C	2.92040800	-1.28507000	-0.86211300
C	3.04694800	1.17547800	-0.65408800
C	4.11104200	-1.25408700	-1.60414000
C	4.23557300	1.14794600	-1.39839800
C	4.76440000	-0.05222900	-1.87121200
H	4.53227400	-2.18469700	-1.97519800
H	4.75344900	2.07975900	-1.61027600
H	5.68651100	-0.05058400	-2.44786100
C	-2.40573000	0.11026000	-0.39929400
C	-2.89310100	1.37263600	-0.79577400
C	-3.07809400	-1.09119700	-0.70595700
C	-4.08409800	1.40488600	-1.53683600
C	-4.26501100	-1.00050100	-1.44808300
C	-4.76519800	0.23294500	-1.86208100
H	-4.48397300	2.36194800	-1.86112900
H	-4.80230500	-1.90912600	-1.70615500
H	-5.68663100	0.28108800	-2.43779400
C	2.25402600	-2.62953600	-0.57978700
H	1.33327800	-2.44808200	-0.01888700
C	2.51440100	2.51572200	-0.15232000
H	1.57098000	2.34071100	0.37290100
C	3.48469400	3.17026500	0.85070800
H	3.69393000	2.50732100	1.69793800
H	4.43967300	3.42486900	0.37442500
H	3.05104000	4.09805900	1.24540700
C	2.21304900	3.47844000	-1.31744700
H	1.51231700	3.03581000	-2.03487500
H	1.76683600	4.40481100	-0.93471000
H	3.12712700	3.74888900	-1.86038700
C	3.14985400	-3.53169700	0.29253500
H	4.07005000	-3.81233900	-0.23483300
H	3.43460500	-3.03471000	1.22741700
H	2.61723500	-4.45596300	0.55049300
C	1.86407700	-3.35466100	-1.88302300

H	1.31354200	-4.27566900	-1.65423200
H	1.22719200	-2.72885600	-2.51902900
H	2.75143000	-3.63269200	-2.46514700
C	-2.57334400	-2.46761300	-0.27815100
H	-1.65695800	-2.33759500	0.30451600
C	-2.21879700	-3.33894800	-1.49919700
H	-3.10677000	-3.55252600	-2.10698200
H	-1.47915200	-2.84922500	-2.14298700
H	-1.80027400	-4.29854900	-1.17052300
C	-3.58982000	-3.19524900	0.62356900
H	-3.85219100	-2.59630500	1.50365600
H	-4.51600200	-3.42414400	0.08201000
H	-3.16765200	-4.14502700	0.97578800
C	-2.19774400	2.68652400	-0.44783300
H	-1.28146800	2.45904700	0.10403200
C	-3.07632900	3.56427200	0.46592700
H	-3.99307000	3.88155100	-0.04643200
H	-3.36590800	3.03098400	1.37878400
H	-2.52824300	4.46808600	0.76137000
C	-1.79006800	3.46574000	-1.71401400
H	-1.22804600	4.36680600	-1.43911100
H	-1.15848400	2.86091600	-2.37495300
H	-2.66996800	3.78397200	-2.28686500

Carbene-H^+:



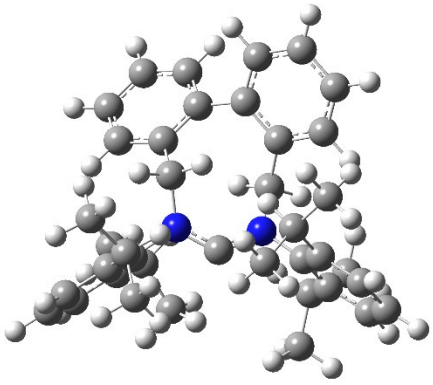
Electronic energy: -1427.590155 Hartree/particle
Zero-point correction= 0.651932 (Hartree/Particle)
Thermal correction to Energy= 0.686043
Thermal correction to Enthalpy= 0.686987
Thermal correction to Gibbs Free Energy= 0.590380
Sum of electronic and zero-point Energies= -1426.938223
Sum of electronic and thermal Energies= -1426.904112
Sum of electronic and thermal Enthalpies= -1426.903168
Sum of electronic and thermal Free Energies= -1426.999775

C	0.00000000	-0.35594400	2.59631200
C	0.00008000	-1.89759600	2.87438400
H	0.89078800	-2.15199100	3.45571400
H	-0.89052400	-2.15205900	3.45585100

H	0.00003000	-2.47602300	1.94530300
C	-0.00005900	0.42349300	3.92465600
H	-0.88750700	0.15986900	4.50406400
H	0.88741700	0.15999700	4.50407400
H	-0.00013800	1.50406200	3.74843400
N	-1.17993100	-0.01794300	0.38747200
C	-1.28021500	-0.06404100	1.82326100
O	-2.36197600	0.06643100	2.34296200
N	1.17994100	-0.01782100	0.38749600
C	1.28018700	-0.06387800	1.82326000
O	2.36189300	0.06689100	2.34301900
C	2.41122300	0.05538100	-0.40816500
C	3.00704400	-1.15440200	-0.81807600
C	2.95188600	1.32535400	-0.69237200
C	4.18816400	-1.05794600	-1.56763200
C	4.13677700	1.35539200	-1.44188600
C	4.74752300	0.18045000	-1.87673000
H	4.67520500	-1.96690200	-1.90896300
H	4.58704100	2.31355800	-1.68510600
H	5.66525400	0.23033000	-2.45756100
C	-2.41121100	0.05528100	-0.40819300
C	-2.95195000	1.32526600	-0.69221400
C	-3.00695700	-1.15447100	-0.81829000
C	-4.13685200	1.35534700	-1.44170900
C	-4.18808800	-1.05797500	-1.56782500
C	-4.74752500	0.18043200	-1.87673100
H	-4.58719400	2.31352000	-1.68474900
H	-4.67508000	-1.96690900	-1.90928200
H	-5.66526100	0.23033800	-2.45755300
C	2.43981900	-2.53245700	-0.48890000
H	1.53536200	-2.40647600	0.11287900
C	2.32590300	2.63715300	-0.22715600
H	1.39767300	2.41612600	0.30902600
C	3.25246900	3.38661700	0.75084000
H	3.51114500	2.76718800	1.61721700
H	4.18459400	3.69183700	0.26007800
H	2.75363900	4.29250600	1.11710300
C	1.95755100	3.53894800	-1.42135200
H	1.29174100	3.02489200	-2.12398100
H	1.44677700	4.44154100	-1.06504500
H	2.85127300	3.85628100	-1.97208900
C	3.43035600	-3.36589000	0.34763400
H	4.34521800	-3.58485700	-0.21609700
H	3.71625800	-2.84628000	1.26968000
H	2.97063500	-4.32230500	0.62594100
C	2.03675800	-3.29181700	-1.76838500
H	1.57226900	-4.25016000	-1.50591200

H	1.31985100	-2.71923500	-2.36834900
H	2.91079400	-3.50299000	-2.39635000
C	-2.43962300	-2.53254100	-0.48936500
H	-1.53504200	-2.40658600	0.11223300
C	-2.03679300	-3.29178000	-1.76898900
H	-2.91093800	-3.50289500	-2.39681500
H	-1.31997100	-2.71916300	-2.36901900
H	-1.57226500	-4.25015100	-1.50667300
C	-3.42995700	-3.36609300	0.34729600
H	-3.71571800	-2.84656200	1.26943000
H	-4.34491000	-3.58507900	-0.21627500
H	-2.97012200	-4.32249700	0.62545100
C	-2.32609500	2.63702800	-0.22671700
H	-1.39798100	2.41595700	0.30964500
C	-3.25288300	3.38637800	0.75115300
H	-4.18491700	3.69162800	0.26023500
H	-3.51172600	2.76686400	1.61742100
H	-2.75414300	4.29223900	1.11761200
C	-1.95747100	3.53897800	-1.42071500
H	-1.44676900	4.44151100	-1.06416100
H	-1.29149900	3.02500500	-2.12325600
H	-2.85106400	3.85639200	-1.97161100
C	0.00000500	0.00613400	-0.22469100
H	0.00001600	0.06644100	-1.30739900

NHC-9 (biphenyl backbone)

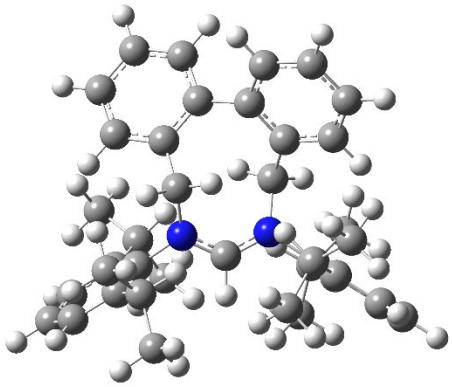


Singlet:

Electronic energy: -1623.157808 Hartree/particle
Zero-point correction= 0.754465 (Hartree/Particle)
Thermal correction to Energy= 0.792004
Thermal correction to Enthalpy= 0.792949
Thermal correction to Gibbs Free Energy= 0.689962
Sum of electronic and zero-point Energies= -1622.403343
Sum of electronic and thermal Energies= -1622.365803
Sum of electronic and thermal Enthalpies= -1622.364859
Sum of electronic and thermal Free Energies= -1622.467846

N	-1.13886600	0.28882400	-0.35224700
C	-1.20082900	-1.07523600	-0.96738600
H	-0.22998200	-1.25280000	-1.43109100
H	-1.92895100	-0.97592700	-1.77394200
C	1.20079800	-1.07524600	0.96728800
H	0.22995100	-1.25284000	1.43097600
H	1.92890600	-0.97593700	1.77385400
N	1.13882300	0.28884200	0.35221600
C	-2.34937200	1.10831300	-0.37216800
C	-3.05316900	1.29824300	0.83965500
C	-4.23367000	2.05497400	0.79380600
H	-4.79317700	2.22651800	1.70860200
C	-4.70429100	2.58861600	-0.40368500
H	-5.62684800	3.16406300	-0.41734000
C	-3.98728100	2.39400400	-1.58236600
H	-4.35618600	2.82801300	-2.50755600
C	-2.79121000	1.66184300	-1.59649600
C	-2.56856700	0.75743000	2.18243300
H	-1.79115600	0.01183900	1.99112400
C	-3.68151900	0.06284000	2.98815700
H	-3.24839600	-0.42570400	3.86991200
H	-4.19601500	-0.70321500	2.39823700
H	-4.43160200	0.77754800	3.34675800
C	-1.93972900	1.88994000	3.01778800
H	-1.54747000	1.49513200	3.96311400
H	-2.68748000	2.65715700	3.25646900
H	-1.11816300	2.37763600	2.48285400
C	-2.02506500	1.53581500	-2.91183700
H	-1.09711800	0.98766400	-2.72602400
C	-2.82720700	0.75669900	-3.97275800
H	-2.22591100	0.63315700	-4.88211200
H	-3.74456500	1.29093800	-4.24884500
H	-3.11255500	-0.24100300	-3.61840900
C	-1.63035500	2.92301000	-3.45769400
H	-1.01920100	2.81099200	-4.36129900
H	-1.05135900	3.49634200	-2.72467300
H	-2.51478200	3.51313600	-3.72531100
C	2.34930400	1.10836500	0.37222200
C	3.05310800	1.29835700	-0.83958500
C	4.23361000	2.05508300	-0.79369000
H	4.79313300	2.22665600	-1.70846900
C	4.70422700	2.58866400	0.40383200
H	5.62677800	3.16412500	0.41751900
C	3.98722000	2.39397200	1.58249800
H	4.35612500	2.82792300	2.50771500
C	2.79115000	1.66180300	1.59658400
C	2.56851300	0.75760300	-2.18238200

H	1.79103100	0.01207400	-1.99112200
C	3.68145700	0.06294700	-2.98807800
H	3.24833800	-0.42560500	-3.86983100
H	4.19592400	-0.70311500	-2.39814000
H	4.43156700	0.77762300	-3.34668400
C	1.93982800	1.89018000	-3.01775600
H	1.54756700	1.49540900	-3.96309700
H	2.68767400	2.65732000	-3.25639600
H	1.11829400	2.37795300	-2.48285400
C	2.02509200	1.53555500	2.91195200
H	1.09710800	0.98748200	2.72607900
C	2.82730000	0.75617600	3.97264000
H	2.22602800	0.63233300	4.88196900
H	3.74462300	1.29042000	4.24884700
H	3.11273400	-0.24140800	3.61802000
C	1.63046000	2.92262400	3.45817200
H	1.01947500	2.81038300	4.36186500
H	1.05131700	3.49610900	2.72539100
H	2.51490600	3.51271900	3.72578300
C	-1.61806800	-2.24466400	-0.09596300
C	-0.71395200	-3.28349000	0.22096600
C	-1.18690000	-4.39471500	0.94475100
H	-0.49426300	-5.19371000	1.19599200
C	-2.51846900	-4.48552300	1.34901700
H	-2.85566100	-5.35264700	1.91143600
C	-3.41351500	-3.46392000	1.01900600
H	-4.45763100	-3.52891000	1.31405100
C	-2.96112100	-2.36224500	0.29316700
H	-3.66323500	-1.58273300	0.01048700
C	1.61806700	-2.24462400	0.09581300
C	0.71397500	-3.28346000	-0.22116200
C	1.18695100	-4.39463700	-0.94500500
H	0.49433800	-5.19363800	-1.19629100
C	2.51852000	-4.48538600	-1.34928000
H	2.85573500	-5.35247800	-1.91173300
C	3.41354100	-3.46377600	-1.01922200
H	4.45765700	-3.52872700	-1.31427400
C	2.96111800	-2.36214300	-0.29333900
H	3.66321000	-1.58261800	-0.01063900
C	-0.00002500	0.87779300	-0.00001600



Carbene-H^+:

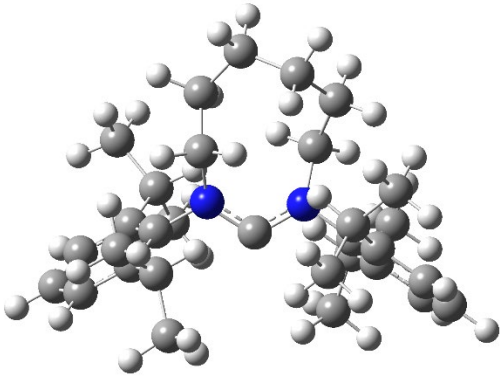
Electronic energy: -1623.667539 Hartree/particle
Zero-point correction= 0.769114 (Hartree/Particle)
Thermal correction to Energy= 0.806430
Thermal correction to Enthalpy= 0.807374
Thermal correction to Gibbs Free Energy= 0.705142
Sum of electronic and zero-point Energies= -1622.898425
Sum of electronic and thermal Energies= -1622.861109
Sum of electronic and thermal Enthalpies= -1622.860164
Sum of electronic and thermal Free Energies= -1622.962397

N	-1.13886600	0.28216300	-0.35224700
C	-1.20082900	-1.08189700	-0.96738600
H	-0.22998200	-1.25946100	-1.43109100
H	-1.92895100	-0.98258800	-1.77394200
C	1.20079800	-1.08190700	0.96728800
H	0.22995100	-1.25950100	1.43097600
H	1.92890600	-0.98259800	1.77385400
N	1.13882300	0.28218100	0.35221600
C	-2.34937200	1.10165200	-0.37216800
C	-3.05316900	1.29158100	0.83965500
C	-4.23367000	2.04831200	0.79380600
H	-4.79317700	2.21985600	1.70860200
C	-4.70429100	2.58195400	-0.40368500
H	-5.62684900	3.15740100	-0.41734000
C	-3.98728100	2.38734200	-1.58236600
H	-4.35618600	2.82135100	-2.50755600
C	-2.79121000	1.65518100	-1.59649600
C	-2.56856700	0.75076800	2.18243300
H	-1.79115600	0.00517800	1.99112400
C	-3.68151900	0.05617800	2.98815700
H	-3.24839600	-0.43236600	3.86991200
H	-4.19601500	-0.70987700	2.39823700
H	-4.43160200	0.77088600	3.34675800
C	-1.93972900	1.88327900	3.01778800
H	-1.54747000	1.48847100	3.96311400
H	-2.68748000	2.65049500	3.25646900

H	-1.11816300	2.37097500	2.48285400
C	-2.02506500	1.52915400	-2.91183700
H	-1.09711800	0.98100300	-2.72602400
C	-2.82720700	0.75003700	-3.97275800
H	-2.22591100	0.62649600	-4.88211200
H	-3.74456500	1.28427600	-4.24884500
H	-3.11255500	-0.24766500	-3.61840900
C	-1.63035500	2.91634900	-3.45769400
H	-1.01920100	2.80433100	-4.36129900
H	-1.05136000	3.48968100	-2.72467300
H	-2.51478300	3.50647400	-3.72531100
C	2.34930400	1.10170400	0.37222200
C	3.05310800	1.29169700	-0.83958500
C	4.23361000	2.04842300	-0.79369000
H	4.79313300	2.21999600	-1.70846900
C	4.70422700	2.58200400	0.40383200
H	5.62677700	3.15746500	0.41751900
C	3.98722000	2.38731200	1.58249800
H	4.35612500	2.82126300	2.50771500
C	2.79115000	1.65514200	1.59658400
C	2.56851300	0.75094200	-2.18238200
H	1.79103100	0.00541300	-1.99112200
C	3.68145700	0.05628700	-2.98807800
H	3.24833800	-0.43226500	-3.86983100
H	4.19592400	-0.70977500	-2.39814000
H	4.43156700	0.77096300	-3.34668400
C	1.93982800	1.88351900	-3.01775600
H	1.54756700	1.48874800	-3.96309700
H	2.68767400	2.65065900	-3.25639600
H	1.11829400	2.37129200	-2.48285400
C	2.02509200	1.52889400	2.91195200
H	1.09710800	0.98082100	2.72607900
C	2.82730000	0.74951500	3.97264000
H	2.22602800	0.62567200	4.88196900
H	3.74462300	1.28376000	4.24884700
H	3.11273400	-0.24806800	3.61802000
C	1.63046000	2.91596300	3.45817200
H	1.01947500	2.80372200	4.36186500
H	1.05131600	3.48944800	2.72539100
H	2.51490500	3.50605800	3.72578300
C	-1.61806800	-2.25132500	-0.09596300
C	-0.71395100	-3.29015100	0.22096600
C	-1.18689900	-4.40137600	0.94475100
H	-0.49426200	-5.20037100	1.19599200
C	-2.51846800	-4.49218500	1.34901700
H	-2.85566000	-5.35930900	1.91143600
C	-3.41351400	-3.47058200	1.01900600

H	-4.45763000	-3.53557200	1.31405100
C	-2.96112000	-2.36890700	0.29316700
H	-3.66323500	-1.58939500	0.01048700
C	1.61806700	-2.25128500	0.09581300
C	0.71397600	-3.29012100	-0.22116200
C	1.18695200	-4.40129800	-0.94500500
H	0.49433900	-5.20029900	-1.19629100
C	2.51852100	-4.49204700	-1.34928000
H	2.85573600	-5.35913900	-1.91173300
C	3.41354200	-3.47043600	-1.01922200
H	4.45765800	-3.53538700	-1.31427400
C	2.96111900	-2.36880300	-0.29333900
H	3.66321000	-1.58927800	-0.01063900
C	-0.00002500	0.87113200	-0.00001600
H	-0.00004500	1.95834500	0.00001400

NHC-9 (saturated backbone)



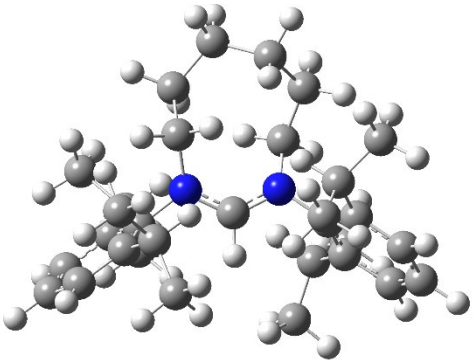
Singlet:

Electronic energy: -1318.305901 Hartree/particle
Zero-point correction= 0.706156 (Hartree/Particle)
Thermal correction to Energy= 0.739485
Thermal correction to Enthalpy= 0.740429
Thermal correction to Gibbs Free Energy= 0.646403
Sum of electronic and zero-point Energies= -1317.599745
Sum of electronic and thermal Energies= -1317.566417
Sum of electronic and thermal Enthalpies= -1317.565473
Sum of electronic and thermal Free Energies= -1317.659498

C	1.85909100	-0.02204100	2.93527600
C	1.09800900	-1.21258300	3.54049100
C	-0.33951300	-0.95854300	4.03943600
C	-1.36576800	-0.43470600	3.00065300
C	-1.20634300	-1.08856400	1.60844600
C	-0.03753800	0.09271200	-0.30305900
C	1.24533700	0.79801800	1.78499700
H	2.85772600	-0.36325200	2.63121000
H	2.02788700	0.71760300	3.73296000

H	1.68427600	-1.55828500	4.40363600
H	1.10651700	-2.05485400	2.83858600
H	-0.70840700	-1.90828500	4.45216800
H	-0.31221000	-0.25384800	4.88242800
H	-2.37451300	-0.63623900	3.38183300
H	-1.30017600	0.65224300	2.92090700
H	-0.28954000	-1.67810600	1.57222100
H	-2.02765100	-1.79022500	1.44650300
H	1.89590200	1.67075700	1.66736600
H	0.26770800	1.18923300	2.05616600
C	-2.40501200	-0.15918100	-0.36048000
C	-3.21098200	0.99576600	-0.23849900
C	-2.80114000	-1.24593000	-1.17918200
C	-4.41922900	1.04590900	-0.95273000
C	-4.01719700	-1.14692300	-1.87026800
C	-4.82351800	-0.01371500	-1.76148500
H	-5.04998500	1.92757400	-0.87138700
H	-4.33744300	-1.96953600	-2.50474400
H	-5.76312200	0.04188600	-2.30674700
C	2.32856000	0.33602400	-0.38992200
C	3.12499400	-0.81798000	-0.57655100
C	2.70429200	1.58253100	-0.95104600
C	4.30201000	-0.70305100	-1.33379000
C	3.89140300	1.64403300	-1.69541500
C	4.68791000	0.51541900	-1.88745500
H	4.92177600	-1.58161600	-1.49284200
H	4.19505400	2.59034300	-2.13614900
H	5.60392400	0.58648400	-2.46982800
N	-1.16279800	-0.23098200	0.38788600
N	1.11711700	0.22899800	0.40711600
C	1.87308600	2.85557800	-0.79662400
H	0.98540000	2.61821100	-0.20497200
C	2.73980800	-2.18405300	-0.01363500
H	1.86815300	-2.04373000	0.62951500
C	2.65073300	3.95798500	-0.05019400
H	2.00493100	4.82956100	0.11696600
H	3.00851300	3.61116900	0.92695100
H	3.52156700	4.29420500	-0.62671000
C	1.38026800	3.38202800	-2.15940400
H	2.21827900	3.66664500	-2.80782100
H	0.78340500	2.63043800	-2.68936500
H	0.75449900	4.27204600	-2.01594900
C	3.85521300	-2.80306200	0.85012600
H	4.16480400	-2.12664800	1.65598200
H	3.50025200	-3.73403800	1.31057400
H	4.74430600	-3.04797800	0.25574100
C	2.33045100	-3.15551300	-1.13843800

H	1.51009800	-2.75021200	-1.74198700
H	3.17188300	-3.36402200	-1.81183200
H	1.99754400	-4.11154000	-0.71354400
C	-2.82098200	2.18490200	0.63570200
H	-1.86660500	1.94841300	1.11230400
C	-2.61639800	3.46376100	-0.19924100
H	-2.27480200	4.28620400	0.44250700
H	-1.86561800	3.31597400	-0.98508800
H	-3.54880800	3.78257300	-0.68202600
C	-3.85100600	2.42856300	1.75524700
H	-4.82727000	2.71945700	1.34715300
H	-3.99755700	1.53173800	2.36922800
H	-3.51260400	3.23758600	2.41563500
C	-1.96328700	-2.51323900	-1.34153900
H	-1.03792700	-2.38542500	-0.77350300
C	-1.56603800	-2.75190300	-2.81173200
H	-2.44605900	-2.92798500	-3.44288500
H	-1.01952600	-1.89624800	-3.22563000
H	-0.92094200	-3.63610300	-2.89069800
C	-2.69026000	-3.75092000	-0.77790900
H	-2.96143300	-3.61630200	0.27612300
H	-3.60993700	-3.96441800	-1.33734400
H	-2.04422200	-4.63547500	-0.84929300



Carbene-H^+:

Electronic energy: -1318.811371 Hartree/particle
Zero-point correction= 0.720410 (Hartree/Particle)
Thermal correction to Energy= 0.753992
Thermal correction to Enthalpy= 0.754936
Thermal correction to Gibbs Free Energy= 0.659916
Sum of electronic and zero-point Energies= -1318.090961
Sum of electronic and thermal Energies= -1318.057380
Sum of electronic and thermal Enthalpies= -1318.056435
Sum of electronic and thermal Free Energies= -1318.151455

C	1.91002400	-0.02184900	2.97677800
C	1.13993400	-1.22569800	3.53758800
C	-0.28314500	-0.97511700	4.07349500

C	-1.34443800	-0.45642600	3.06977300
C	-1.26878300	-1.15203000	1.69255500
C	-0.03320000	0.05624400	-0.10486600
C	1.29136400	0.83382800	1.86413200
H	2.90513700	-0.35317800	2.65568000
H	2.08115800	0.69460300	3.79341500
H	1.73572800	-1.61746100	4.37327900
H	1.12675900	-2.03525900	2.79868100
H	-0.63930200	-1.92593300	4.49339800
H	-0.23717900	-0.26995100	4.91464900
H	-2.33685500	-0.63404600	3.49947400
H	-1.27127300	0.62617200	2.95647600
H	-0.40996700	-1.82273300	1.64395100
H	-2.15669400	-1.76509000	1.53709500
H	-0.05608800	0.19095400	-1.18412400
H	1.95065600	1.69484300	1.72557800
H	0.31963500	1.22998700	2.14938800
C	-2.38512100	-0.18020800	-0.35401000
C	-3.14763200	1.00293600	-0.24527700
C	-2.75978000	-1.24724700	-1.20300100
C	-4.31275200	1.09849200	-1.02213400
C	-3.93390900	-1.09614100	-1.95392800
C	-4.70467400	0.06253800	-1.86677900
H	-4.92083600	1.99656700	-0.95888900
H	-4.24762100	-1.89780200	-2.61686600
H	-5.61253500	0.15668300	-2.45786900
C	2.30618400	0.35559500	-0.39001400
C	3.06028100	-0.81606500	-0.62212200
C	2.64531800	1.60011100	-0.97074400
C	4.18968400	-0.71004600	-1.44865700
C	3.78638100	1.64598100	-1.78392800
C	4.55474900	0.50672200	-2.01975000
H	4.78799800	-1.59484500	-1.64753200
H	4.07244500	2.58717500	-2.24535700
H	5.43505100	0.56739500	-2.65528600
N	-1.17959400	-0.31227700	0.45992300
N	1.13919400	0.27547300	0.48561100
C	1.82378400	2.87406700	-0.78012900
H	0.96918700	2.65002200	-0.13548300
C	2.69946300	-2.17576700	-0.03011300
H	1.81858800	-2.04800500	0.60379700
C	2.64145400	3.98152200	-0.08731500
H	2.00701300	4.85749700	0.09672800
H	3.04092100	3.64444600	0.87692600
H	3.48596700	4.30470600	-0.70823300
C	1.25501100	3.37885900	-2.12147600
H	2.05539200	3.65907900	-2.81710300

H	0.63548600	2.61625000	-2.60845700
H	0.63252300	4.26658800	-1.95504700
C	3.82858800	-2.73693800	0.85572100
H	4.10656100	-2.03636800	1.65138700
H	3.50353800	-3.67264400	1.32768200
H	4.72909100	-2.95613000	0.26889600
C	2.33236000	-3.18987900	-1.13168800
H	1.52161600	-2.82247700	-1.77121400
H	3.19357400	-3.40925600	-1.77509000
H	2.00491200	-4.13433100	-0.67892400
C	-2.77764800	2.15835400	0.68115400
H	-1.84146800	1.90791300	1.18644300
C	-2.54028500	3.46378100	-0.10163200
H	-2.22115200	4.25972400	0.58292000
H	-1.76101200	3.34122000	-0.86332900
H	-3.45362300	3.80359500	-0.60519700
C	-3.84653700	2.36492500	1.77207300
H	-4.80826000	2.66519600	1.33785800
H	-4.01008700	1.45053000	2.35458900
H	-3.53076600	3.15536900	2.46469500
C	-1.95066700	-2.53562200	-1.33718800
H	-1.05031200	-2.44753000	-0.72221700
C	-1.48880900	-2.76724100	-2.78925300
H	-2.34151700	-2.92170500	-3.46139800
H	-0.90979400	-1.91688500	-3.16885200
H	-0.85665700	-3.66185400	-2.84583400
C	-2.74362700	-3.75220300	-0.81919900
H	-3.05899500	-3.61343100	0.22186200
H	-3.64168300	-3.92841100	-1.42397100
H	-2.12389200	-4.65643300	-0.86769500

Chapter 5- Harnessing Empty Orbitals and Adjacent Lone Pairs for concerted reactions: Readily Available Primary Aminoboranes as Powerful Reagents for Aldimine Synthesis

In chapters 2-4, I discussed how carbene structure determines the properties of the frontier orbitals and the techniques used to measure them. I showed that by expanding the ring size of CAAC, the carbene becomes more ambiphilic, leading to promising new reactivity. Then, we saw that a popular method for measuring the carbene empty orbital can be confounded by unusual intramolecular hydrogen bonding to selenium. Afterwards, we discussed how Brønsted basicity can serve as an excellent probe for the strength of a carbene lone-pair.

Until now, all discussion of ambiphiles has centered on carbenes, which belong to the family of 1,1-ambiphiles, where both the empty orbital and lone pair lie on the same atom. The equally interesting 1,2-ambiphiles feature their empty orbitals and lone pairs on adjacent atoms. Since all ambiphiles exhibit both nucleophilic and electrophilic reactivity simultaneously, they are often noted for their ability to form multiple bonds in a single reaction. In 1,1-ambiphiles, the two bonds form on the same atom. 1,2-ambiphiles create bonds on adjacent atoms (Figure 5.1).

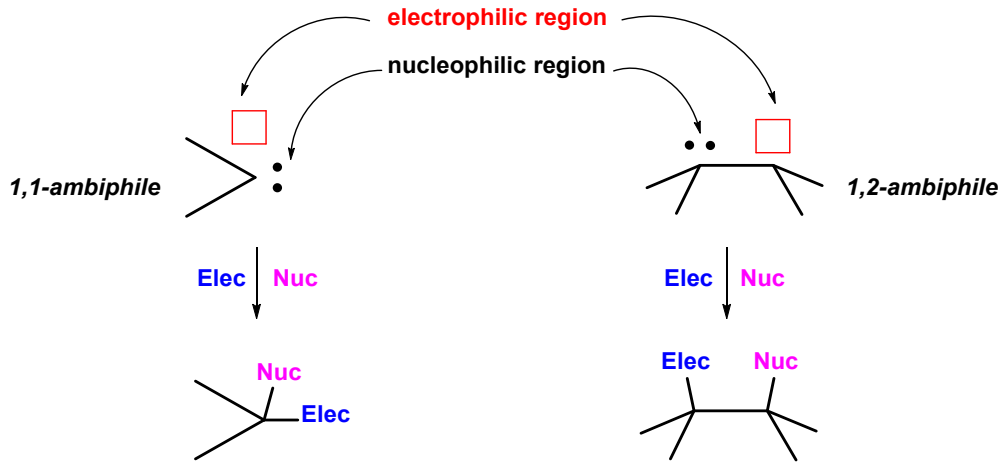


Figure 5.1: Reactivity of 1,1- and 1,2-ambiphiles.

Aminoboranes[203-213] feature a boron-centered lewis-acidic empty orbital directly adjacent to a nucleophilic nitrogen-centered lone-pair (Figure 5.2, left). In this way, aminoboranes are isolobal to phosphorus ylides (Figure 5.2, right), famous 1,2-ambiphiles used in the Wittig reaction.[214-217] For Wittig ylides, the reactivity is owed to the significant population of the charge-separated resonance structure, caused by incomplete backbonding into the P-R antibonding σ*

orbital.[218-219] Similarly, aminoboranes maintain significant separation of the lone-pair and empty orbital, though in this instance to avoid the formation of a zwitterionic double bond. Nevertheless, due to the ambiphilic electronic structure in both, I hypothesized that primary aminoboranes would react in a manner reminiscent of Wittig ylides.

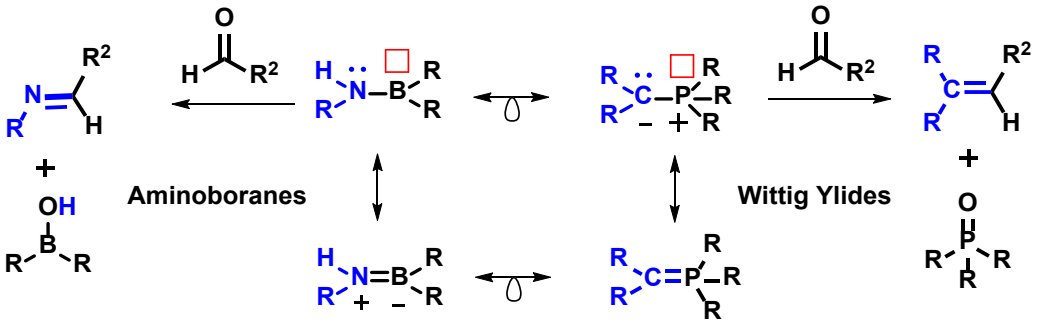


Figure 5.2: Isolobal analogy between primary aminoborane (Left) phosphorus ylide (Right) and how this corresponds to similar reactivity. Lewis-acidic empty orbitals are red squares.

The Wittig reaction (Figure 5.2, right) involves an ylide reacting with a carbonyl compound (i.e. ketone, aldehyde, etc) to form a C-C double bond and phosphine oxide with very high selectivity.[214-216] I imagined the isolobal primary aminoboranes would form N-C double bonds, imines,[220-232] in an analogous fashion (Figure 5.2, left). Furthermore, the development of a new method for imine synthesis with a unique mechanism may give access to products that are hardly accessible with previous methods.[231-232]

To test this hypothesis, we considered the reaction of *p*-tolyl-anilino-pinacolborane with pivaldehyde (Figure 5.3). In a benzene-d_6 solution full conversion to the desired aldimine with concomitant elimination of PinBOH occurred at room temperature within a few minutes.

In an effort to optimize the conditions (Table 5.1), we found that the reaction of *p*-tolyl-anilino-pinacolborane with pivaldehyde proceeds well in various solvents. However, when using bulkier amines, we observed that the reaction was faster at higher concentrations and in less polar solvents.

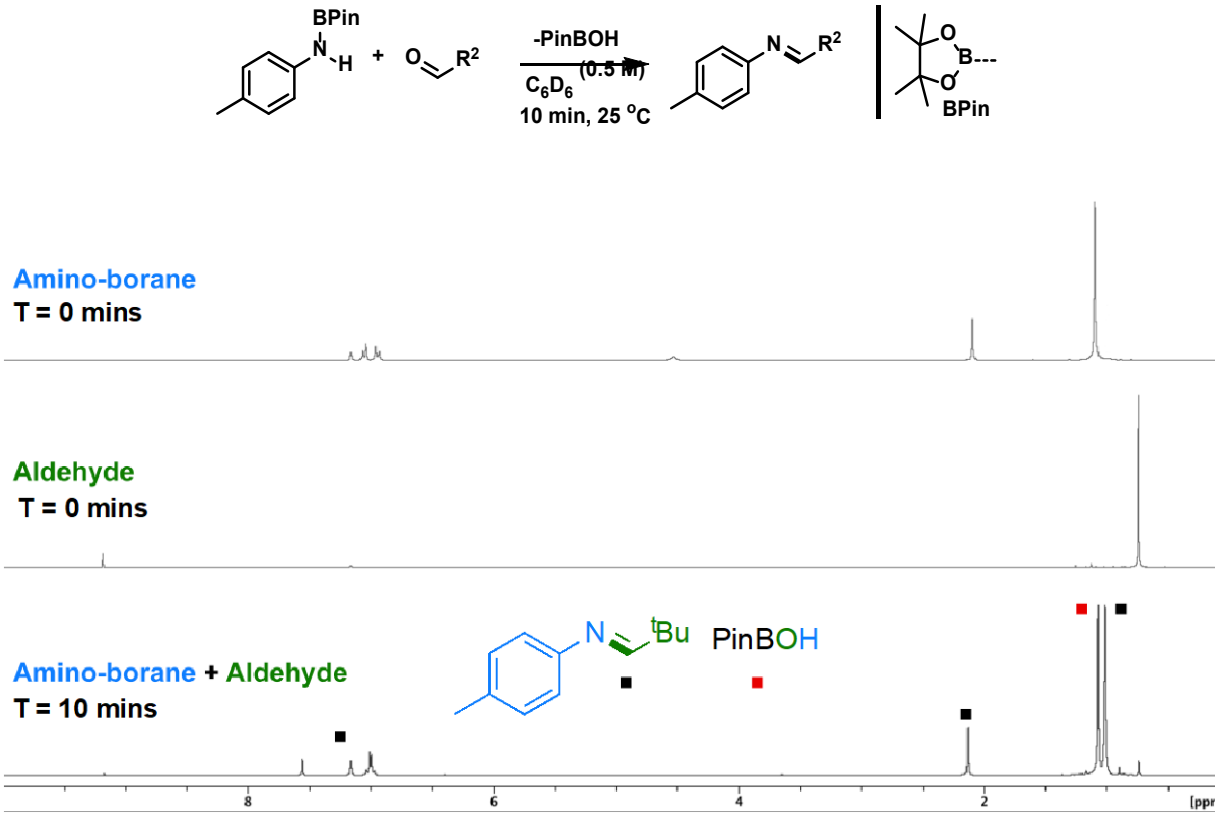
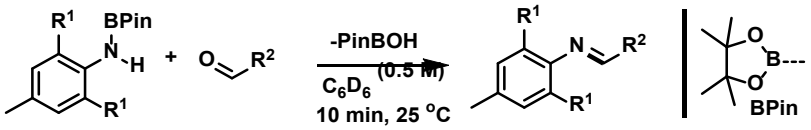


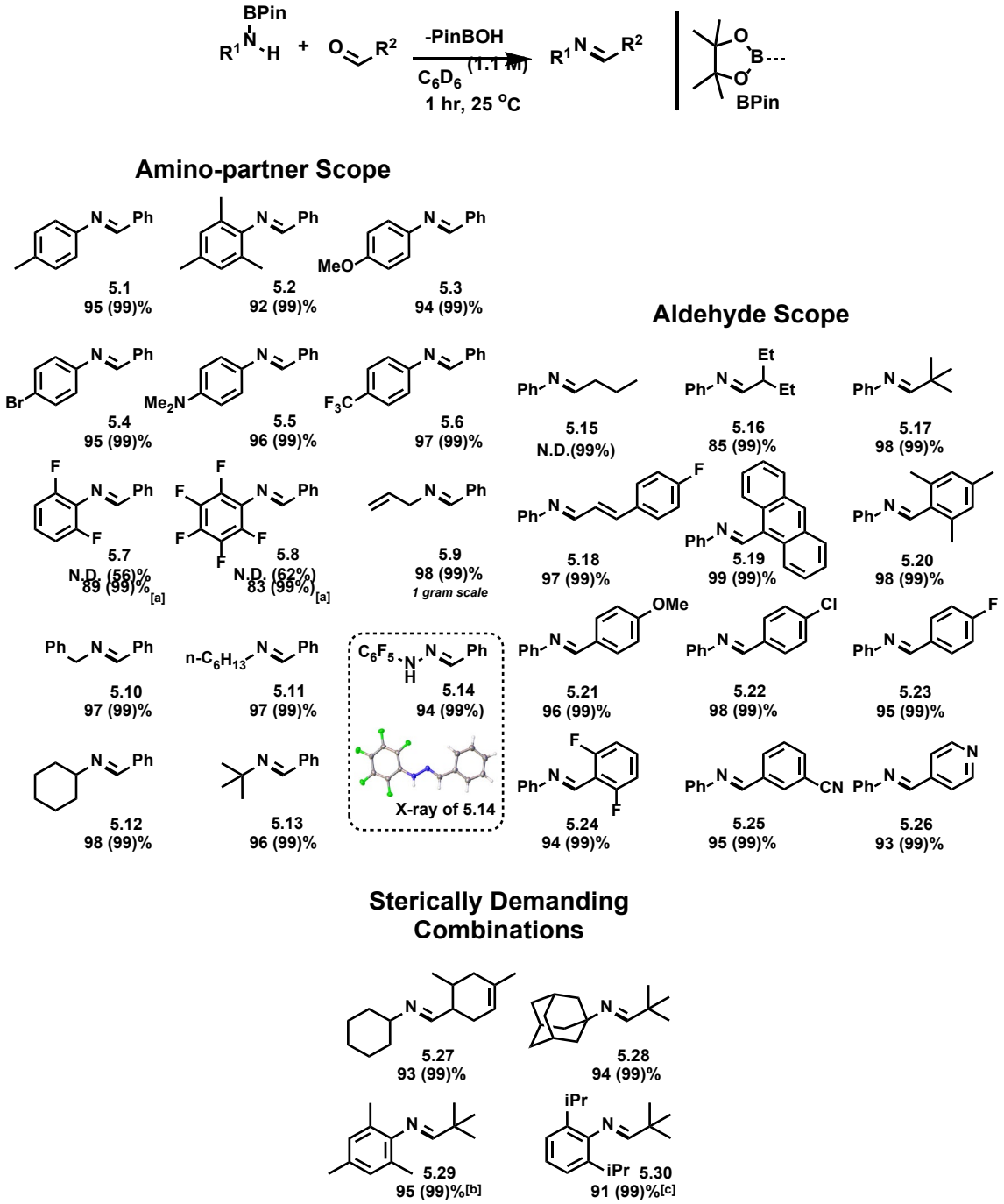
Figure 5.3: ^{1}H NMR monitoring of the reaction

Table 5.1: Optimization of the reaction conditions



R^1	R^2	Solvent	Time	Conc. (M)	Yield[a]
H	^{t}Bu	C_6D_6	10 min	0.5	99
H	^{t}Bu	$CDCl_3$	10 min	0.5	99
H	^{t}Bu	CD_3CN	10 min	0.5	99
Me	$CH(Et)_2$	C_6D_6	4 h	0.5	93
Me	$CH(Et)_2$	$CDCl_3$	4 h	0.5	91
Me	$CH(Et)_2$	CD_3CN	4 h	0.5	89
Me	$CH(Et)_2$	C_6D_6	4 h	0.1	82
Me	$CH(Et)_2$	**C_6D_6**	**1 h**	**1.1**	**99**

[a] Yield determined by ^{1}H NMR



Scheme 5.1. Substrate scope. Isolated yields and NMR yields in parentheses. [a] Reaction performed using 2 equivalents of aminoborane. [b] Reaction time 24 h. [c] Reaction time 48 h.

Using our optimized conditions [1:1 ratio of aminoborane to aldehyde in C_6D_6 (1.1 M) at 25 °C], we examined the substrate scope (Scheme 5.2). With respect to the substituents on nitrogen this methodology is readily applicable to a variety of amines featuring different steric and

electronic properties (**5.1-13**), and even to hydrazines (**5.14**). Although aminoboranes derived from very electron poor anilines (**5.7,8**) exhibit lower conversions this is circumvented by using 2 equivalents of the corresponding aminoborane. With respect to aldehydes, the reaction is widely applicable to both alkyl- and aryl-aldehydes (**5.15-26**). The reaction is applicable to two aliphatic partners (**5.27-28**) and also two bulky substrates (**5.29-30**) with longer reaction times.

We also probed the reactivity of the more electrophilic borane partner, 9-borabicyclononane (9-BBN). As shown by the kinetic plot of the reaction, the 9-BBN aminoborane derived from the electron-poor pentafluoroaniline performs faster than its pinacol counterpart (Figure 5.4). Here we noticed again that increasing the concentration leads to a faster reaction.

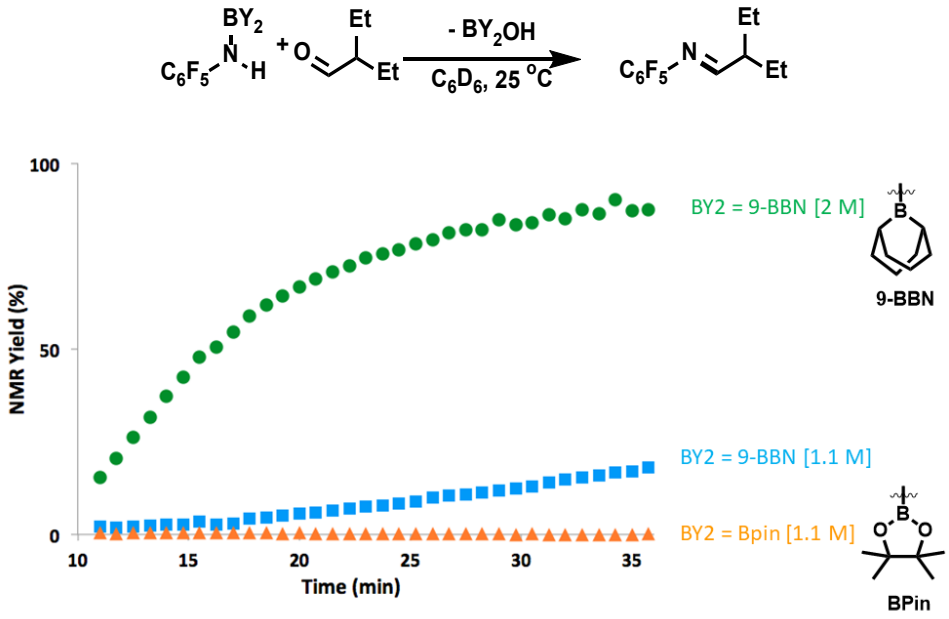
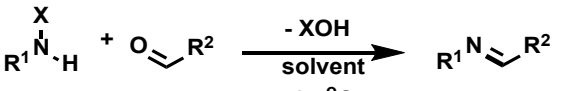


Figure 5.4: Influence of the borane partner and of the concentration on the rate of the reaction.

We next compared the efficiency of this aminoborane methodology with the most effective methods reported in the literature (Table 5.2): 4 Å molecular sieves (Method 1)[233-235] and 4 Å molecular sieves plus a pyrrolidine organocatalyst (Method 2).[236] We found that our method performs equally well with electron rich substrates, but more importantly, it is much more efficient with troublesome bulky and electron-poor substrates.

Table 5.2: Method comparison

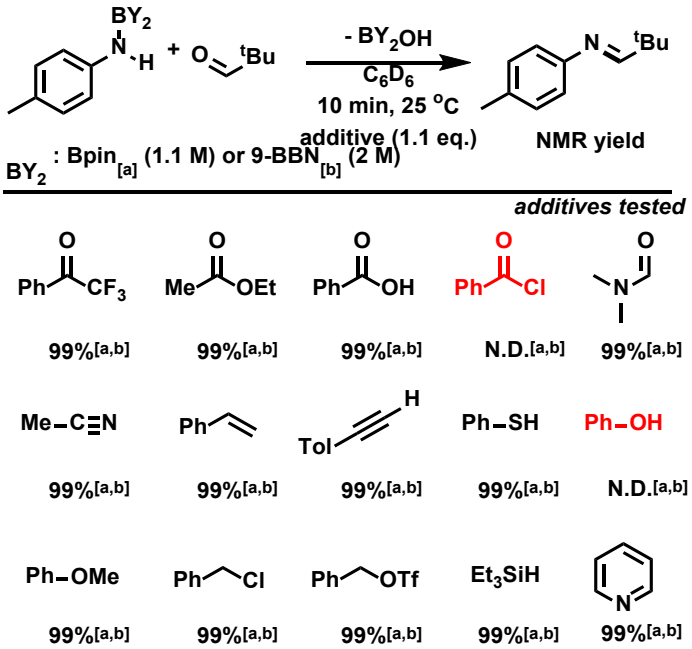


X = H *(Method 1 and 2)*
X = BPin or 9-BBN *(this work)*

R^1	R^2	Time (h)	Conc. (M)	Method 1	Method 2	This work
Cy	^{t}Bu	1	1.1[a]	99	99	99 (Bpin)
Mes	Ph	1	1.1[a]	13	72	99 (Bpin)
Mes	$CH(Et)_2$	1	1.1[a]	46	30	99 (Bpin)
$C_6F_2H_3$	Ph	1	2[a]	4	18	99 (9-BBN)
$C_6F_2H_3$	$CH(Et)_2$	1	2[a]	5	8	99 (9-BBN)
C_6F_5	Ph	12	2[b]	1	69	96 (9-BBN)
C_6F_5	$CH(Et)_2$	3	2[b]	2	24	93 (9-BBN)

[a] in C_6H_6; [b] in cyclohexane

To demonstrate further the broad usefulness of this synthetic route, we examined the functional group tolerance using a modified Glorius robustness screen (Scheme 5.3).[237-238] We found that the reaction is unaffected by various common functional groups such as ketones, esters, ethers, alkenes, alkynes, amides, thiols, silanes, pyridines, alkyl halides and triflates. Unsurprisingly, alcohols and acyl halides, which react with aminoboranes, are not compatible with this reaction. Note that pinacolborane and 9-BBN adducts performed equally well in this screening.



Scheme 5.2: Modified Glorius robustness screen for aldimine formation in the presence of common functional groups.

To gain insight into the reaction mechanism, we performed calculations at the M062X[83] 6-31G**[239] level of theory to compare the reaction of anilino-pinacolborane (methyl groups on pinacol were replaced by hydrogens) with isobutyraldehyde and benzaldehyde in benzene (Figure 5.5).[240-241] We found that the concerted addition of the aminoborane across the carbonyl bond, leading to the hemi-aminal **I**, is exergonic with an energy barrier of 28-29 kcal.mol^{-1} (**TS1**). From **I**, we considered two possible pathways leading to the aldimine. **Path 1** involves a concerted 1,3-proton shift from nitrogen to oxygen with concomitant elimination of PinBOH. We were able to locate a transition state **TS2** showing a barrier of 44 kcal.mol^{-1}, which makes this process highly unlikely at room temperature. **Path 2** involves the dimerization of **I** followed by a double intermolecular proton transfer/elimination, giving two molecules of both PinBOH and aldimine, through a barrier of 26-32 kcal.mol^{-1}. It is worth noting that these data clearly show why the reaction is not reversible. Indeed, reverse addition of PinBOH to the aldimine should occur through

the **Reverse Path 1**, which proceeds through an inaccessible ~40-45 kcal.mol^{-1} reaction barrier.

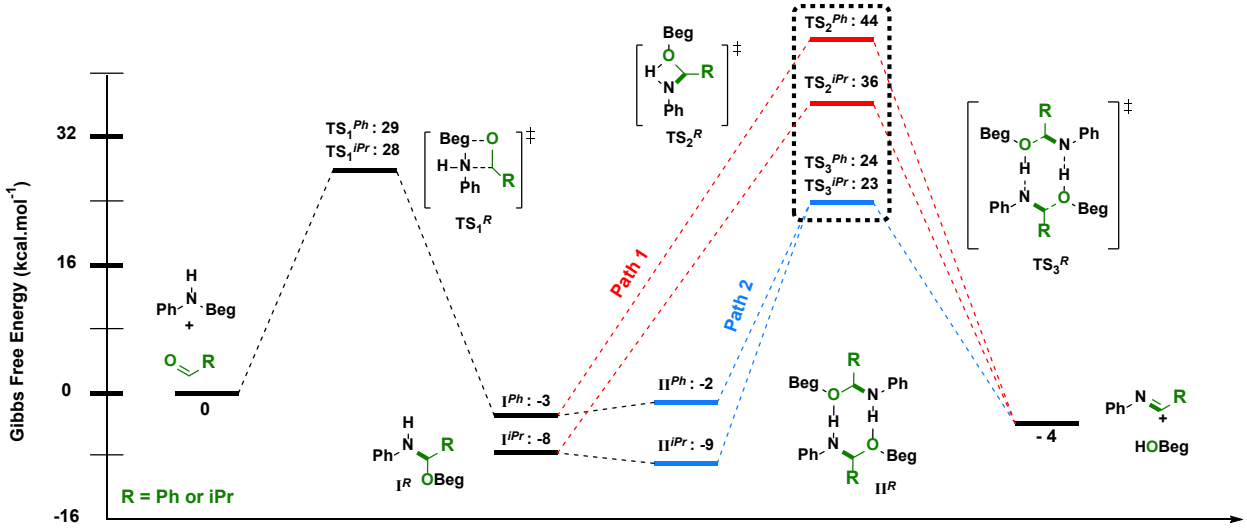
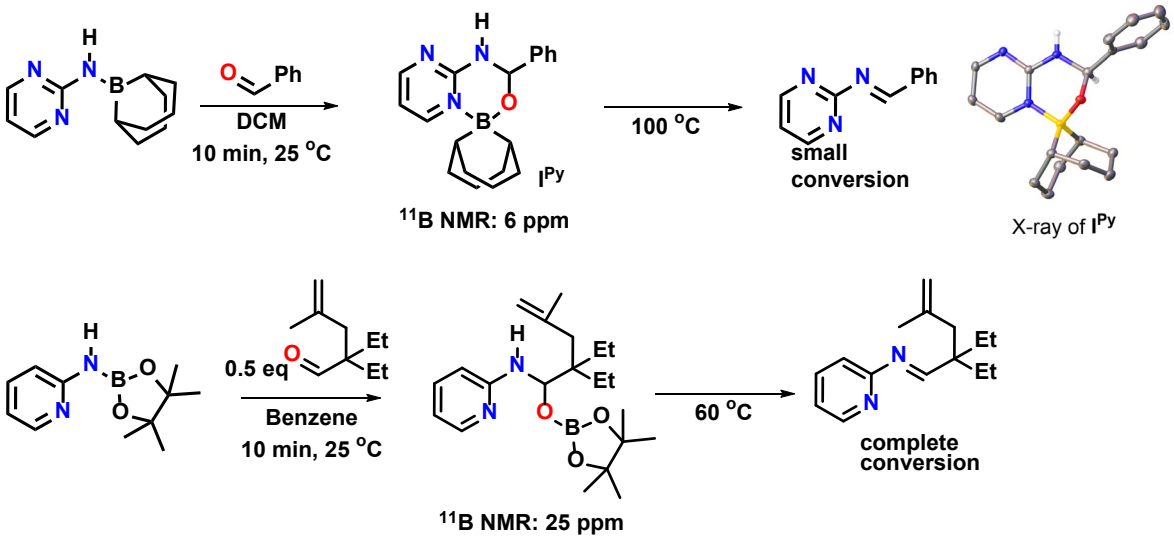


Figure 5.5: Proposed reaction mechanism at the M062X 6-31G** level of theory.[240] Beg = B(OCH$_2$CH$_2$O)

To further support this mechanism, we were able to characterize the pyrimidine-stabilized hemi-aminal **I^{Py}** from the reaction of 2-aminopyrimidine-9-BBN and benzaldehyde (Scheme 5.4). As anticipated, the locked configuration of **I^{Py}** prevented the formation of a dimeric structure of type **II** and thus the efficient formation of the corresponding aldimine even at elevated temperatures (100 °C).

In contrast, the use of a ring-opened analogue should allow rotation around the N-C and O-C bonds to facilitate proton transfer through the dimer structure. To again test this hypothesis, I made the aminoborane with 2-aminopyridine (fewer coordinating groups than the corresponding pyrimidine) and pinacolborane (less electrophilic borane than 9-BBN). Reaction with an aldehyde like that shown in Scheme 5.4 leads to a ring-opened intermediate (confirmed by ^{11}B NMR where a signal at 25 ppm indicates a tricoordinate boron) that completely converts to product aldimine upon mild heating. Keep in mind, most aminoborane/aldehyde combinations result in rapid aldimine product formation, making it somewhat difficult to find substituents that stop at the reaction intermediate.



Scheme 5.3: Isolation of hemi-aminal $\mathbf{I^{Py}}$ and comparison to uncyclized analogue.

In summary, we have shown that primary aminoboranes, which are readily available by spontaneous dehydrocoupling of amines and boranes,[203] are powerful tools for the preparation of aldimines. The overall transformation from amines to aldimines can be conveniently performed by a sequential one-pot reaction. The method is shown to be chemoselective, functional group tolerant, and widely applicable to various amines, aldehydes and boranes. Computational and experimental data support the irreversible formation of the aldimine, which is mechanistically orthogonal to traditional methods.

Acknowledgments

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as well as the Extreme Science and Engineering Discovery Environment (XSEDE),[242] which is supported by National Science Foundation grant number ACI-1548562 for provided computational resources.

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Supporting Information

General Considerations

All reactions were performed under an atmosphere of argon using standard Schlenk or dry box techniques unless otherwise stated. Solvents were dried over Na metal or CaH_2. Reagents of analytical grade were obtained from commercial suppliers and used without further purification. Aminoborane precursors were synthesized according to known literature procedures.[203] ^{1}H, ^{11}B, and ^{13}C NMR spectra were obtained using either a Bruker Avance 300 MHz, Varian INOVA 500 MHz, or JOEL 500 MHz spectrometer. Spectra are referenced to residual solvent peak and chemical shifts, δ, are reported in parts per million (ppm) relative to TMS. NMR multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sept = septet, m = multiplet, br = broad.

Crystallographic data

The single crystal X-ray diffraction studies were carried out on a Bruker D8 diffractometer equipped with a Dectris Eiger R 1M HPAD detector and Cu K_a radiation (I = 1.5478). Crystals of the subject compound were mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using f and v scans. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

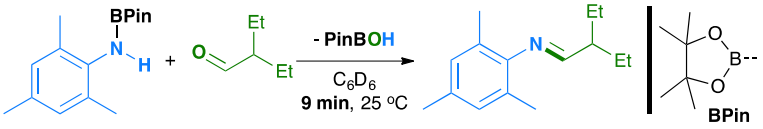
All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table 3.5, 3.6 and 3.7. **NB**: Solutions were finalized using the OLEX2 program[142]

Experimental Methods

1) Optimization of the reaction conditions

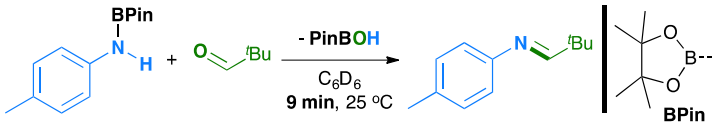
A J-Young NMR tube was charged with the aldehyde (0.25 mmol), the aminoborane (0.25 mmol) and the appropriate amount of solvent. The reaction was monitored by ^{1}H NMR. We observed that increased steric hindrance on the aminoborane partner decreases the reaction rate; however, performing the reaction at higher concentration improves the reactivity and the conversion.

Table 5.3: Reaction optimization with 2-ethylbutyraldehyde



Entry	Solvent	Time	Conc. (M)	NMR Yield **5.1a** (%)
1	C_6D_6	4 h	0.5	93
2	$CDCl_3$	4 h	0.5	91
3	CD_3CN	4 h	0.5	89
4	**C_6D_6**	**1 h**	**1.1**	**99**
5	C_6D_6	4 h	0.1	82

Table 5.4: Reaction optimization with 2-ethylbutyraldehyde



Entry	Solvent	Time	Conc. (M)	NMR Yield **5.1a** (%)
1	C_6D_6	10 min	1.1	99
2	$CDCl_3$	10 min	1.1	99
3	CD_3CN	10 min	1.1	99

2) General Procedures for Aldimine Formation

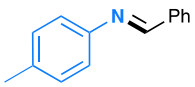
Starting from aminoboranes: Under argon, a Schlenk tube was charged with the aldehyde (1 mmol), the aminoborane (1 mmol) and benzene (NB: the concentration for each substrate was adjusted to 1.1M when using BPin and 2M for 9-BBN). After stirring for 1 h at 25 °C (unless otherwise stated), an aliquot was taken to determine the NMR yield. After evaporation of the combined volatiles the product was isolated by flash chromatography gradient using a Revelerys X-2 system: EtOAc/Hexane with 5% Et_3N (unless otherwise stated). **NB**: NMR spectra were compared with reported data when available.

The same results can be achieved from the amine using a sequential one-pot protocol.

Sequential one-pot protocol starting from the amine: Under argon, a Schlenk tube was charged with the amine (1 mmol), the borane (1 mmol) and acetonitirile (NB: the concentration was adjusted to 3M). The reaction was stirred for 24h at 25 °C (reaction time has been shown to be substrate dependent,[203] and is in most cases much shorter, but we found that after 24h all the amines were converted into the corresponding aminoborane). After this time, the solvent was removed under vacuum, and benzene (NB: the concentration for each substrate was adjusted to 1.1M when using BPin and 2M for 9-BBN) and the aldehyde (1 mmol) were added.

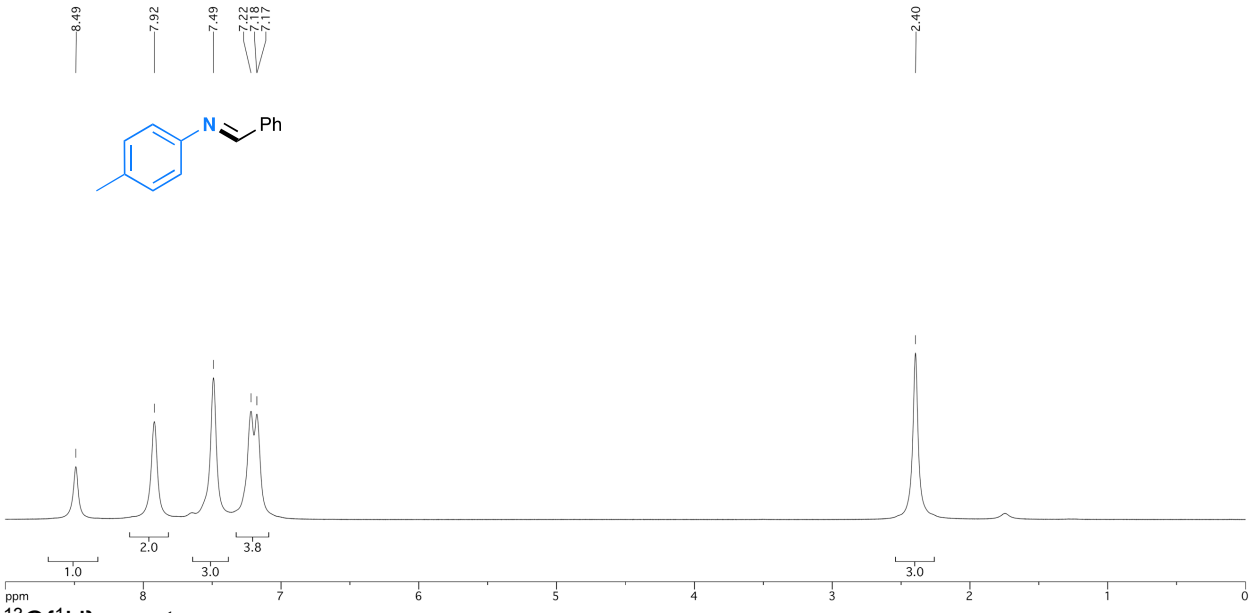
After stirring for 1h at 25 ºC (unless otherwise stated), an aliquot was taken to determine the NMR yield. After evaporation of the combined volatiles the product was isolated by flash chromatography gradient using a Revelerys X-2 system: EtOAc/Hexane with 5% Et_3N (unless otherwise stated).

5.1[243]

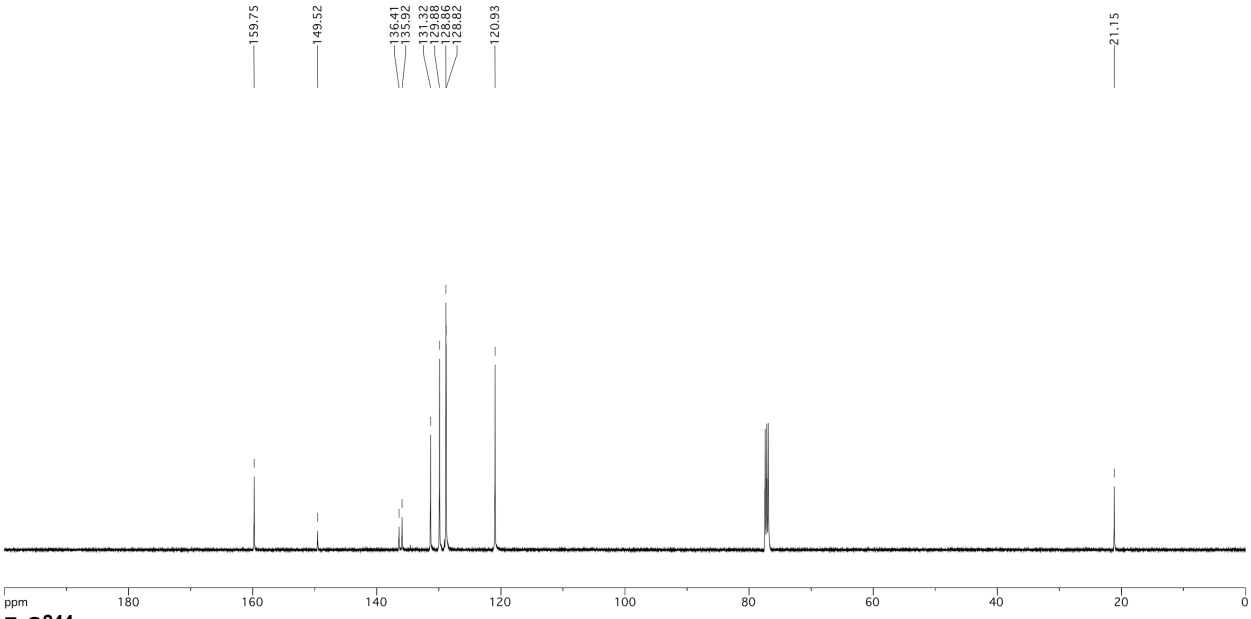


Compound **5.1** was isolated in 95% yield (186 mg). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 8.49 (s, 1H, NCH), 7.92 (brs, 2H), 7.49 (m, 3H), 7.22 (brs, 2H), 7.18 (brs, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$, 293K): δ 159.7 (s, NCH), 149.5, 136.4, 135.9, 131.3, 129.8, 128.9, 128.8, 120.9, 21.1.

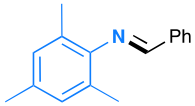
^1H spectrum



$^{13}C\{^1H\}$ spectrum

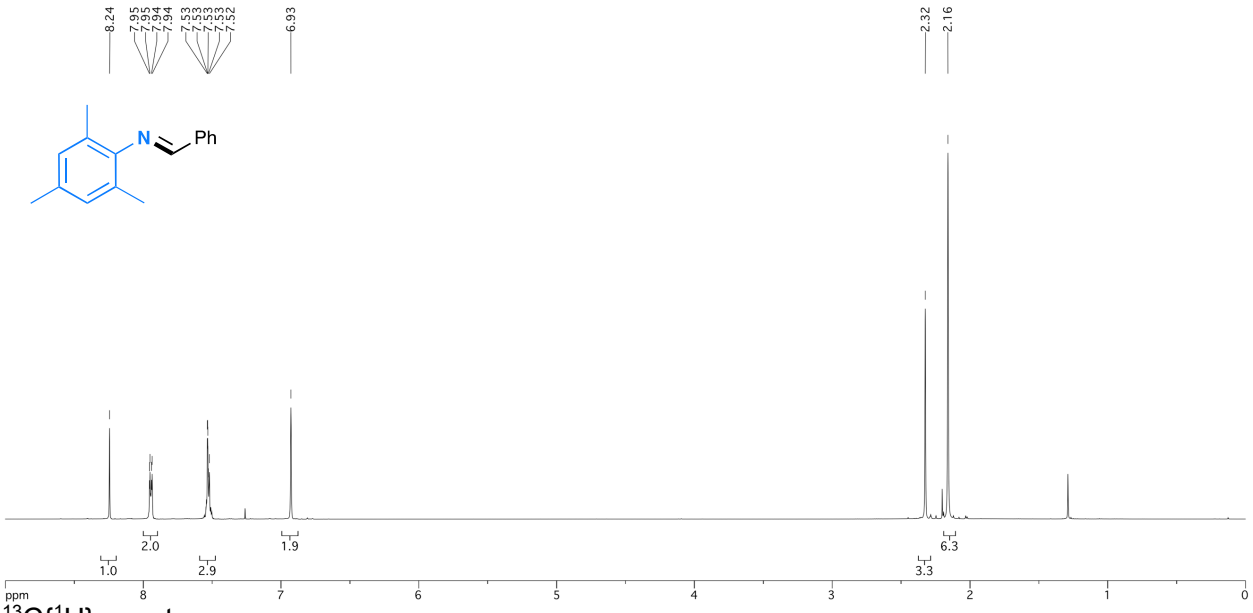


5.2[244]

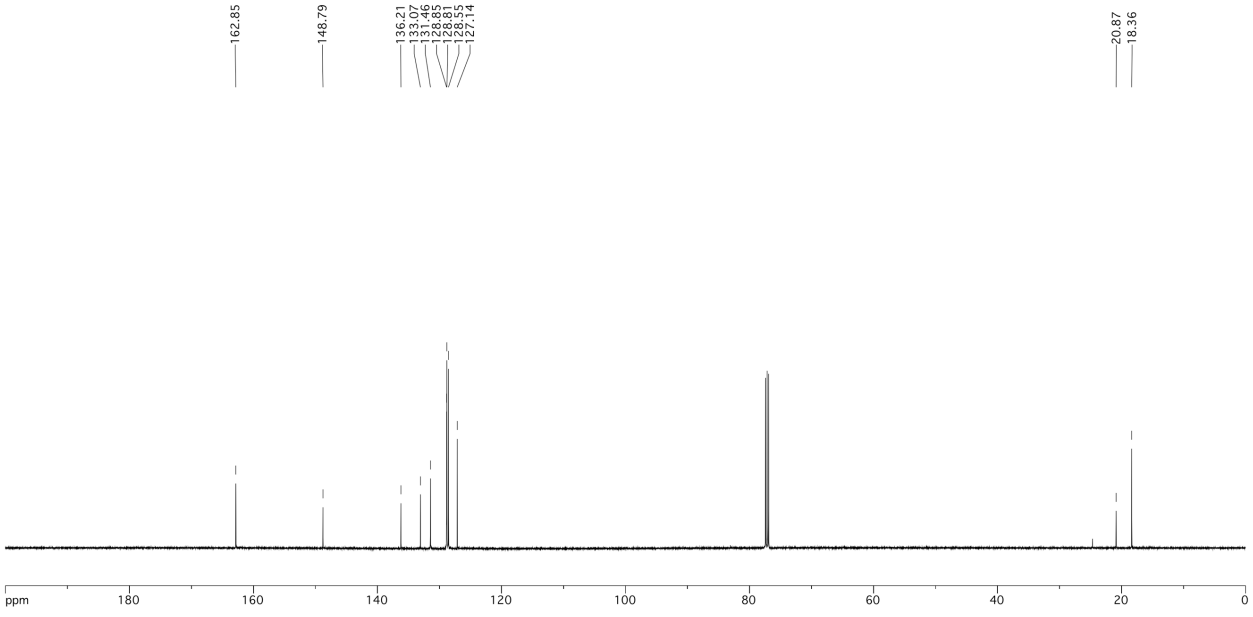


Compound **5.2** was isolated in 92% yield (205 mg). ^{1}H-NMR (500 MHz; C_6H_6): δ 8.24 (s, 1H), 7.95 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.53-7.52 (m, 3H), 6.93 (s, 2H), 2.32 (s, 3H), 2.16 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 162.9, 148.8, 136.2, 133.1, 131.5, 128.8, 128.8, 128.6, 127.1, 20.9, 18.4.

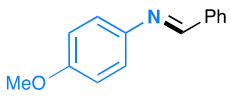
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

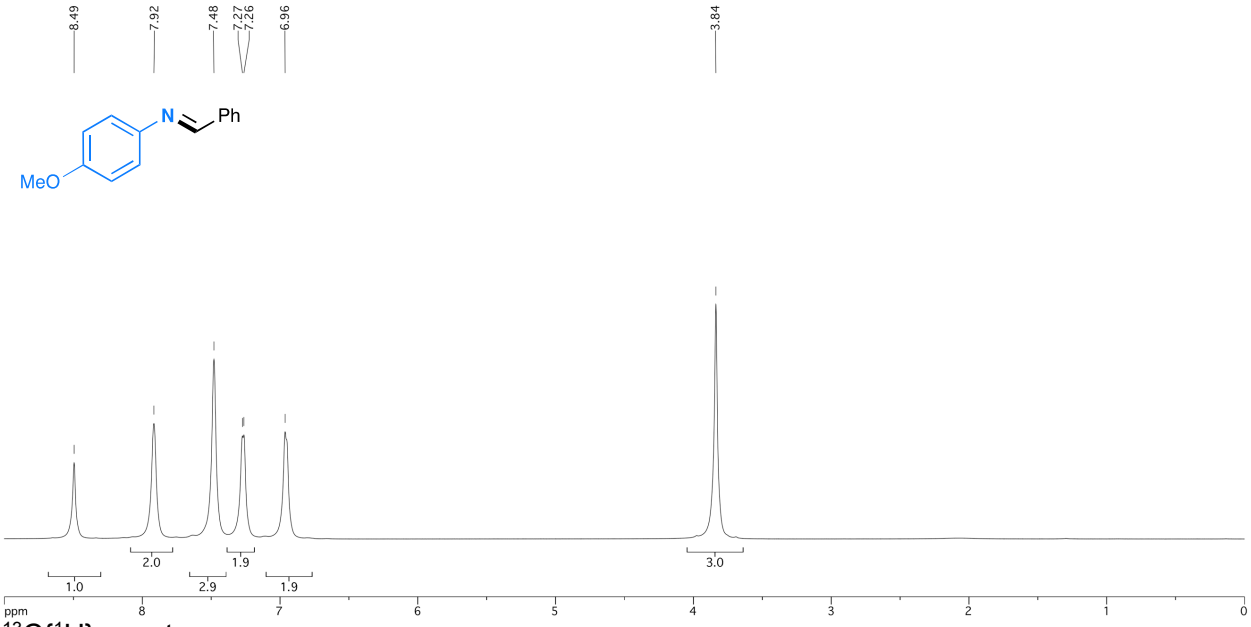


5.3[245]

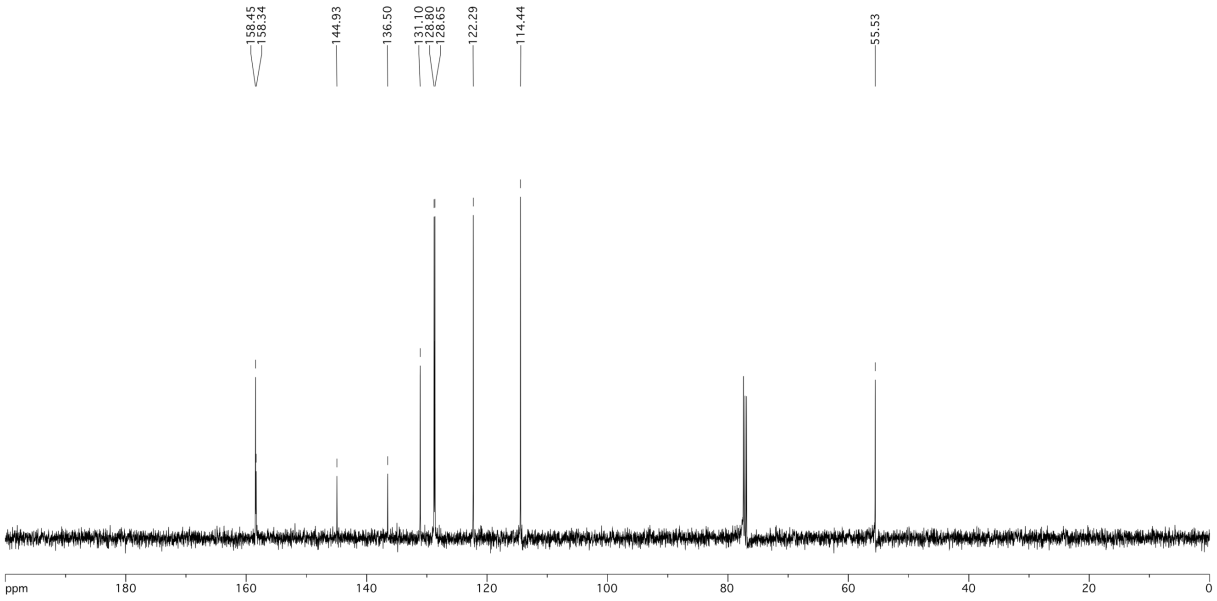


Compound **5.3** was isolated in 94% yield (199 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (s, 1 H), 7.92 (s, 2 H), 7.48 (s, 3 H), 7.27 (d, *J* = 5.1 Hz, 2 H), 6.96 (s, 2 H) 3.84 (s, 3 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 158.45, 158.34, 144.93, 136.50, 131.10, 128.80, 128.6, 122.3, 114.4, 55.5.

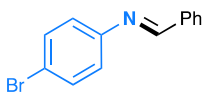
^{1}H spectrum



^{13}C{^{1}H} spectrum

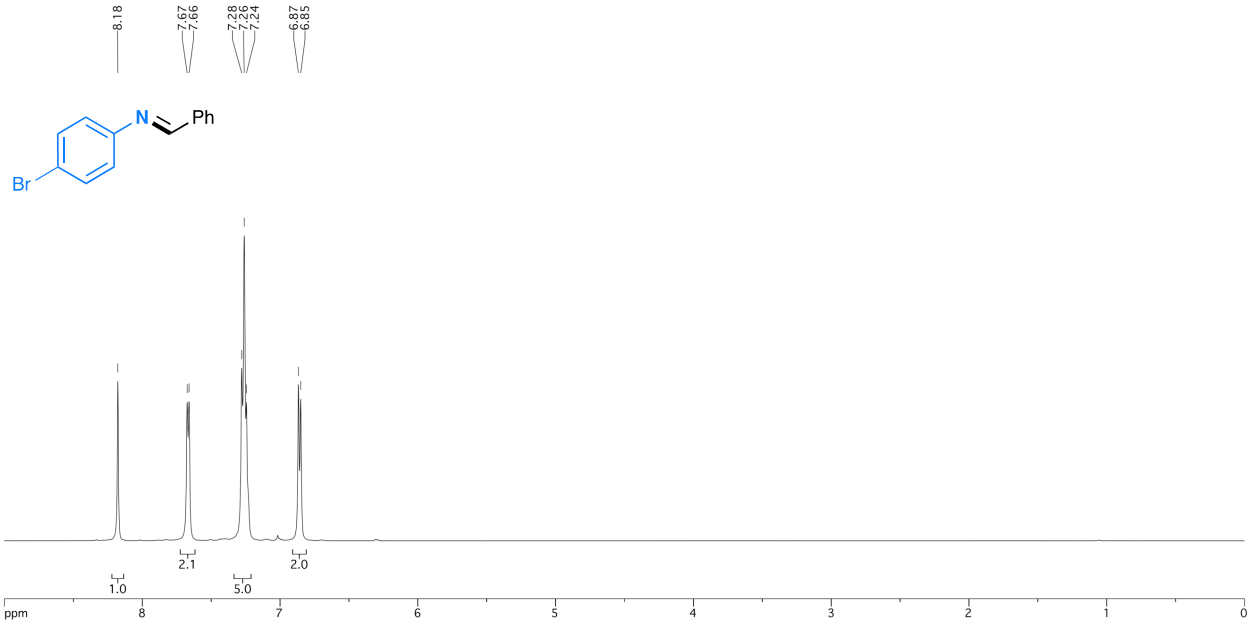


5.4[246]

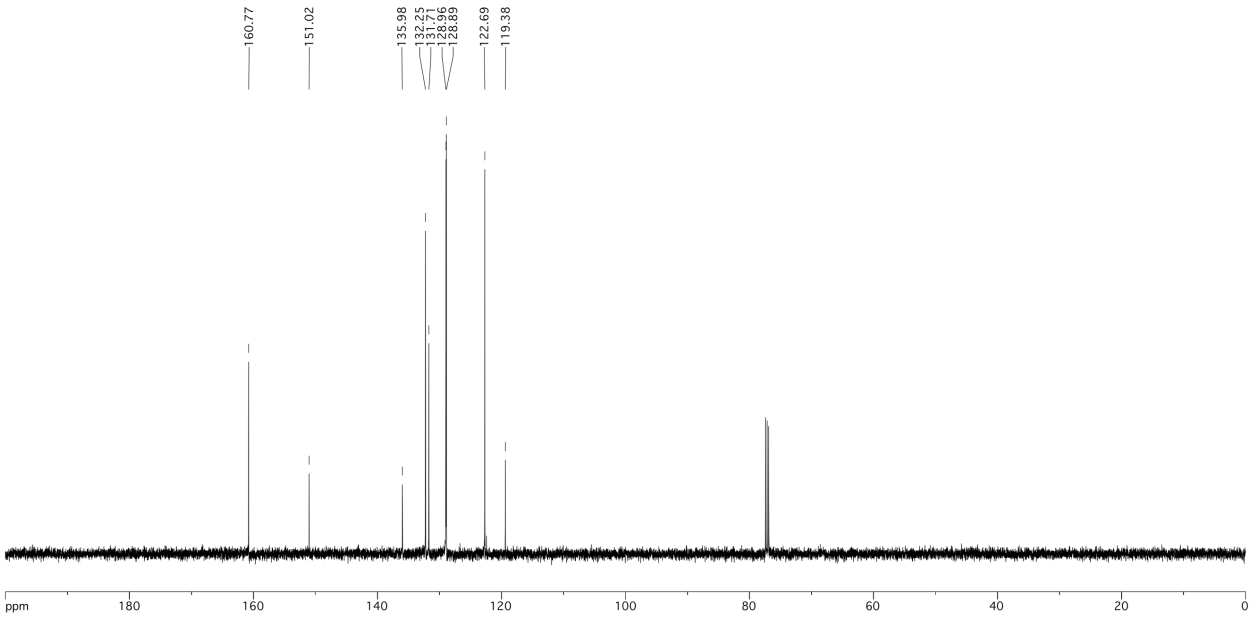


Compound **5.4** was isolated in 95% yield (247 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1 H), 7.67 (d, *J* = 6.7 Hz, 2 H), 7.26 (t, *J* = 8.6 Hz, 5 H) 6.86 (d, *J* = 8.1 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 160.7, 151.0, 135.9, 132.2, 131.7, 128.9, 128.8, 122.6, 119.3.

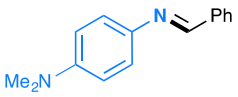
^{1}H spectrum



^{13}C{^{1}H} spectrum

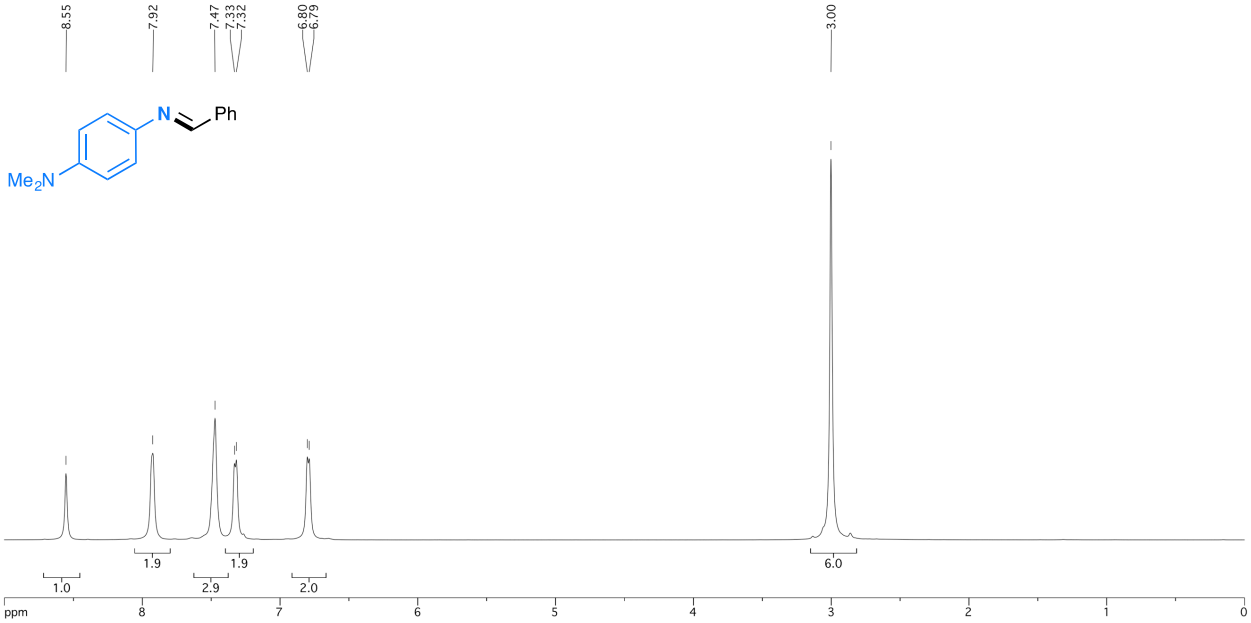


5.5[247]

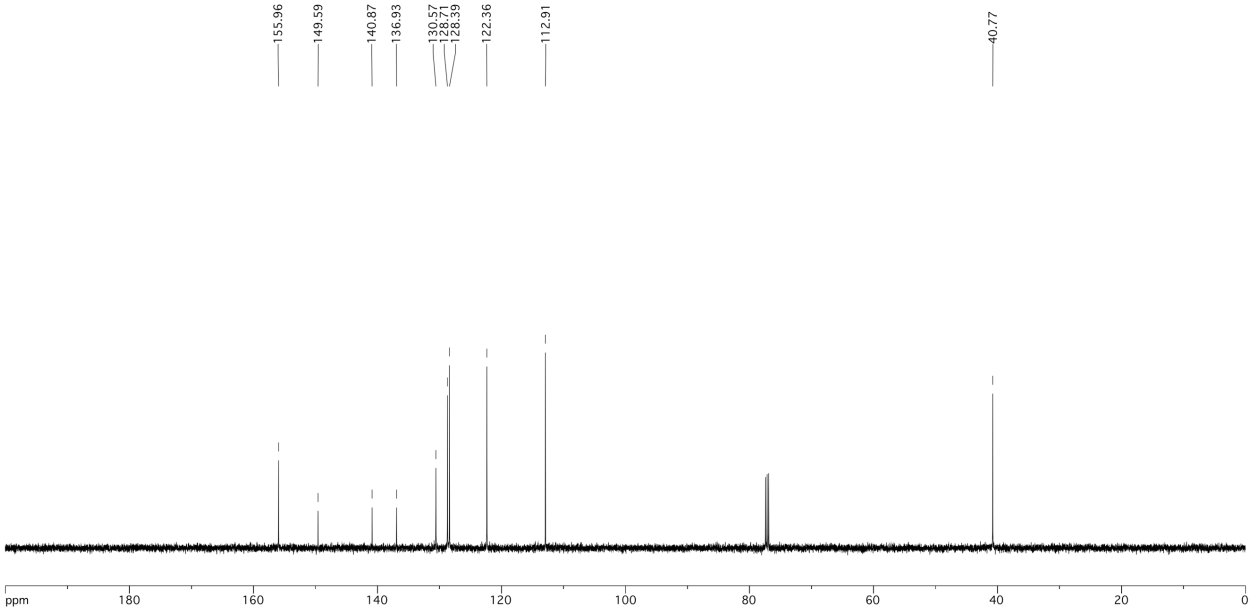


Compound **5.5** was isolated in 96% yield (215 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1 H), 7.92 (s, 2 H), 7.47 (s, 3 H), 7.32 (d, *J* = 6.6 Hz, 2 H), 6.80 (d, *J* = 6.6 Hz, 2 H) 3.00 (s, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 156.0, 149.6, 140.9, 136.9, 130.6, 128.7, 128.4, 122.4, 112.9, 40.8.

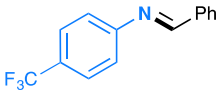
^{1}H spectrum



^{13}C{^{1}H} spectrum

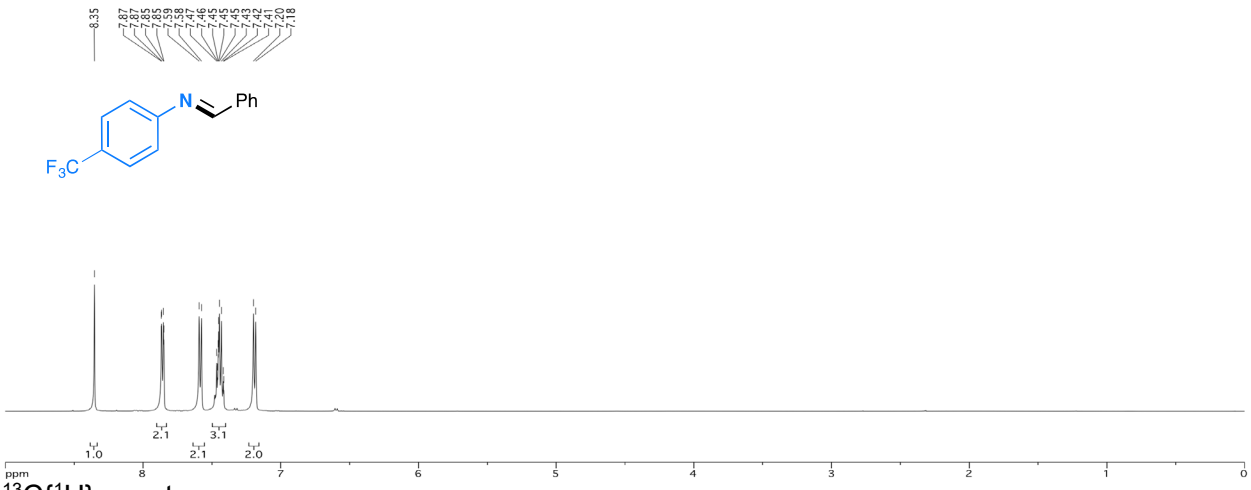


5.6[248]

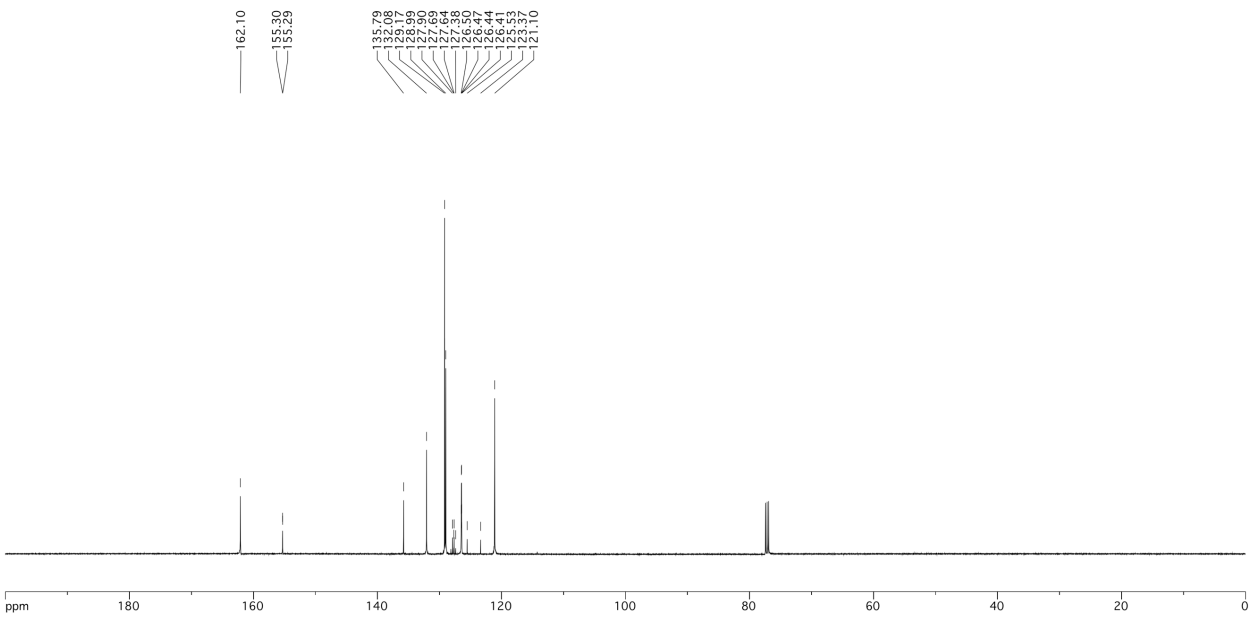


Compound **5.6** was isolated in 97% yield (242 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ , 8.35 (s, 1 H), 7.86 (dd, J = 7.9, 1.5 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.41-7.47 (m, 3 H) 7.19 (d, J = 8.3 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 162.1, 155.3, 135.8, 132.1, 129.17, 127.8 (q, J = 32.6 Hz), 126.4 (q, J = 3.6 Hz), 124.4 (q, J = 272.3 Hz), 121.1.

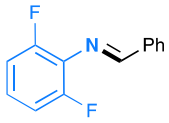
^{1}H spectrum



^{13}C{^{1}H} spectrum

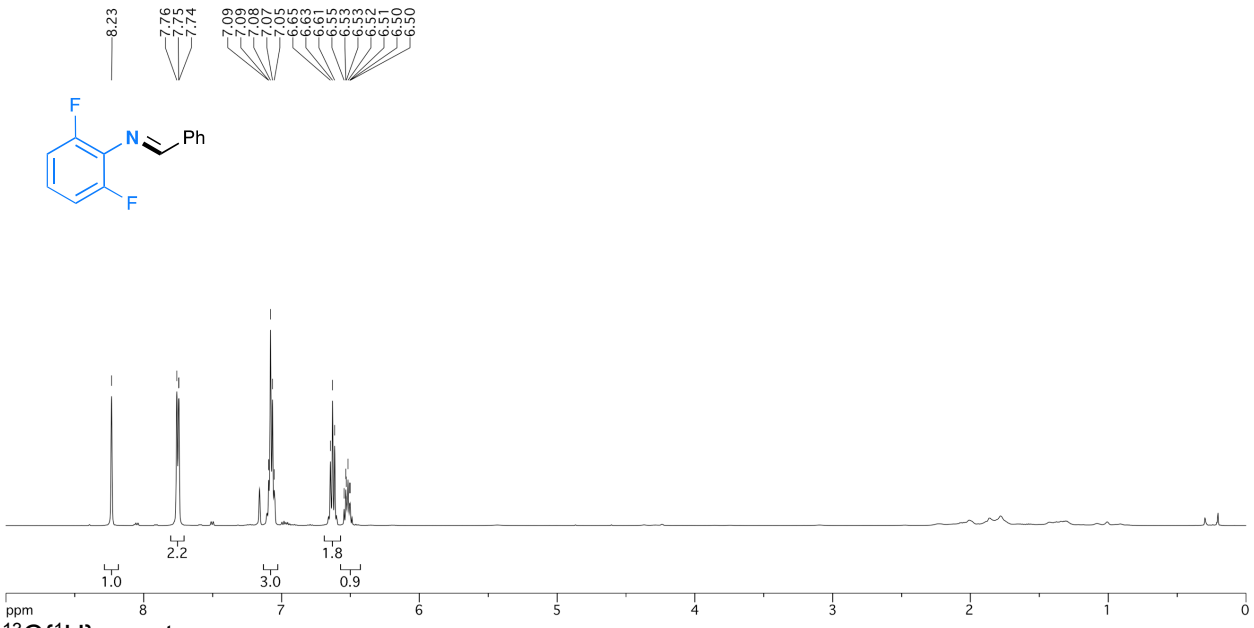


5.7

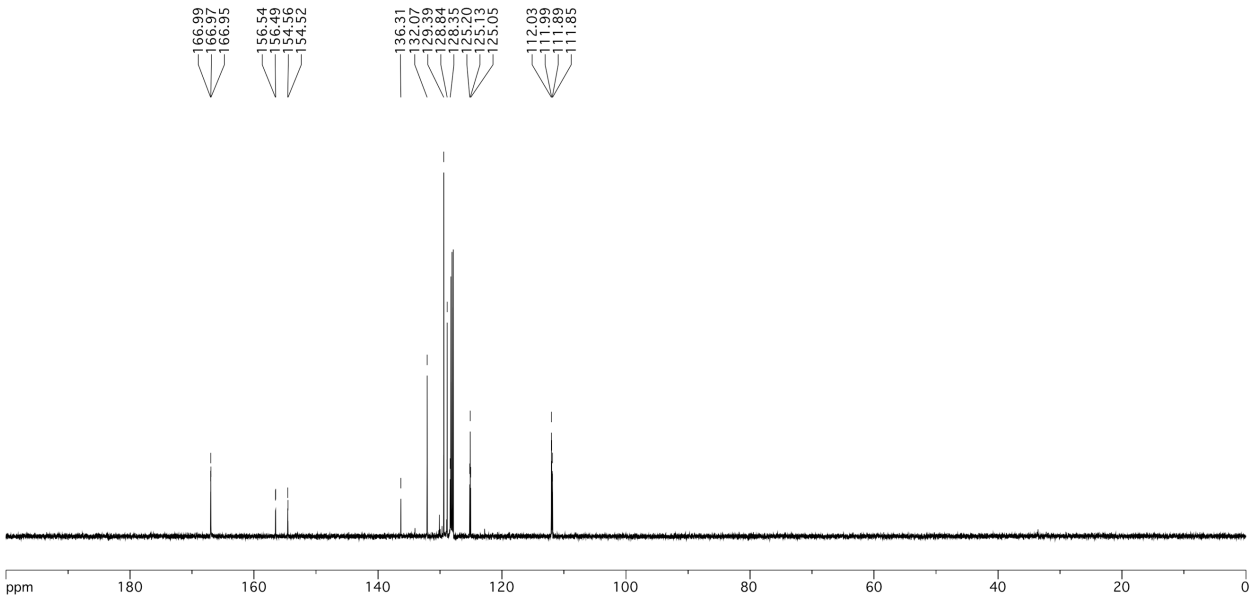


The reaction was performed using 2 mmol of aminoborane and 1 mmol of benzaldehyde. Compound **5.7** proved too reactive to be isolated using the standard procedure, hence it was isolated by removing the volatiles under vacuum in 89% yield (217 mg). ^{1}H NMR (500 MHz, C_6D_6): δ 8.23 (s, 1 H), 7.74-7.76 (m, 2 H), 7.05-7.09 (m, 3 H), 6.63 (t, J = 7.8 Hz, 2 H) 6.50-6.55 (m, 1 H). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): δ 166.97 (t, J = 2.5 Hz), 156.5 (dd, J = 6.5, 249.6 Hz), 136.3, 129.4, 128.8, 128.4, 125.13 (t, J = 8.8 Hz), 111.9 (dd, J = 17.6, 5.1 Hz). ^{19}F{^{1}H} NMR (471 MHz; C_6D_6): δ -124.4.

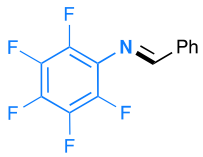
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum



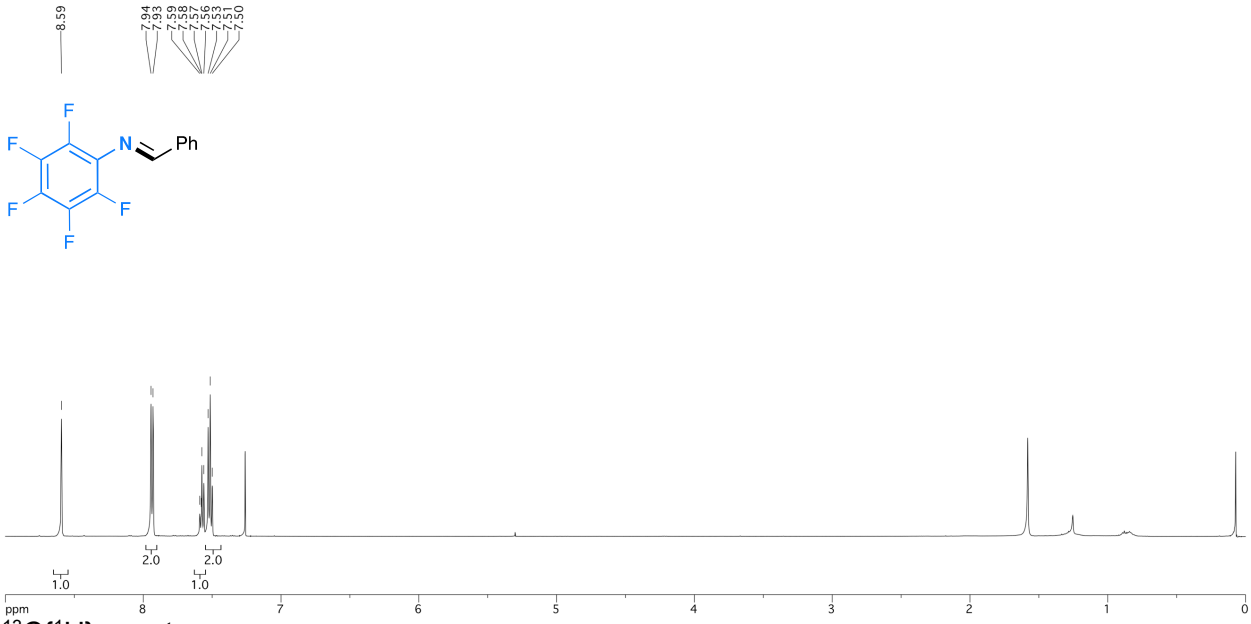
5.8[249]



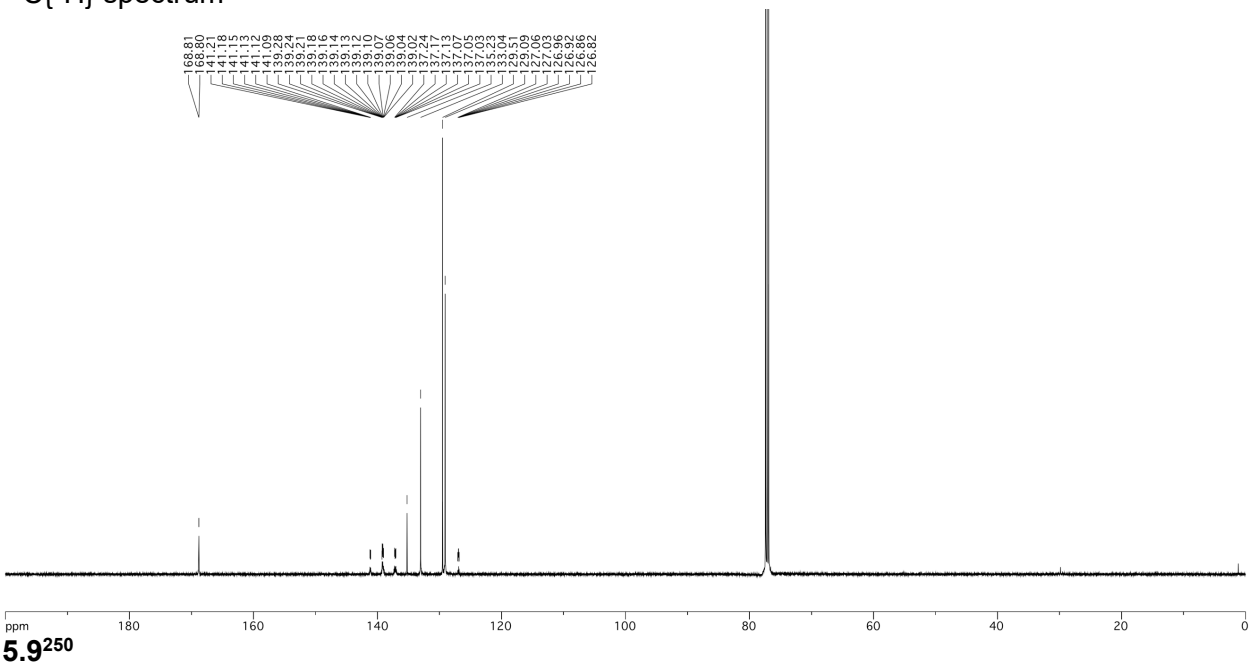
The reaction was performed using 2 mmol of aminoborane and 1 mmol of benzaldehyde. Compound **5.8** proved too reactive to be isolated using the standard procedure, hence it was

isolated by removing the volatiles under vacuum in 83% yield (291 mg). (157 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (s, 1 H), 7.94 (d, J = 7.2 Hz, 2 H), 7.57 (t, J = 7.3 Hz, 1 H) 7.51 (t, J = 7.5 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 168.8, 141.2-141.0 (m), 139.4-138.9 (m), 137.4-136.9 (m), 136.9, 135.2, 133.0, 129.5, 129.1, 127.0 (dt, *J* = 12.7, 4.3 Hz).

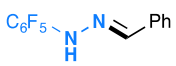
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

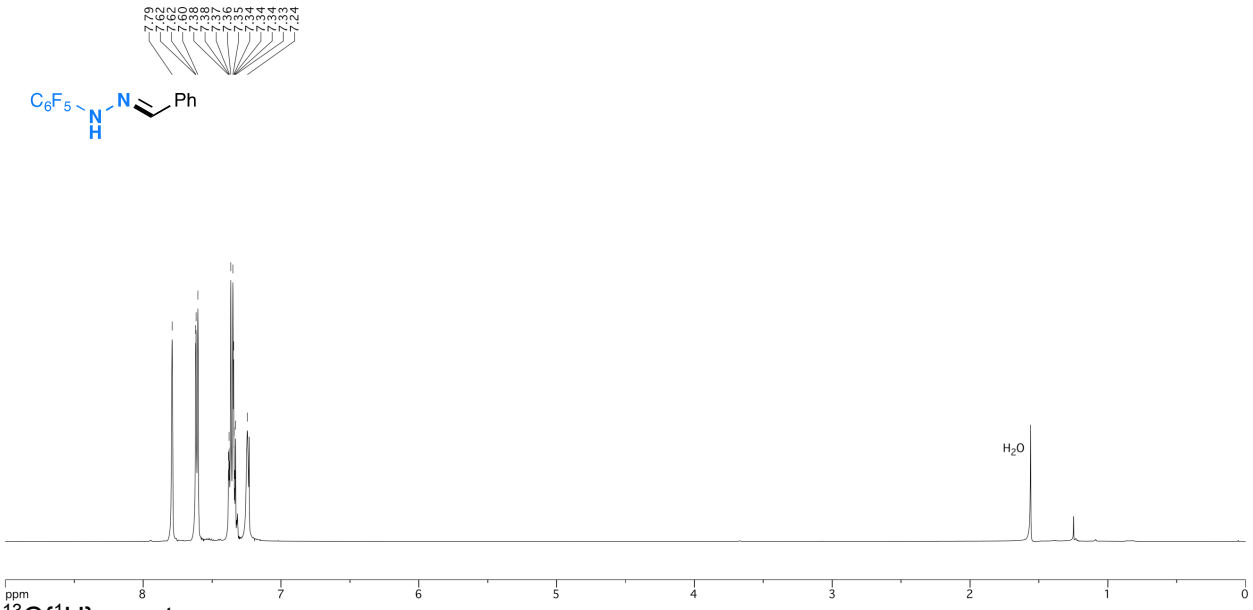


5.9[250]

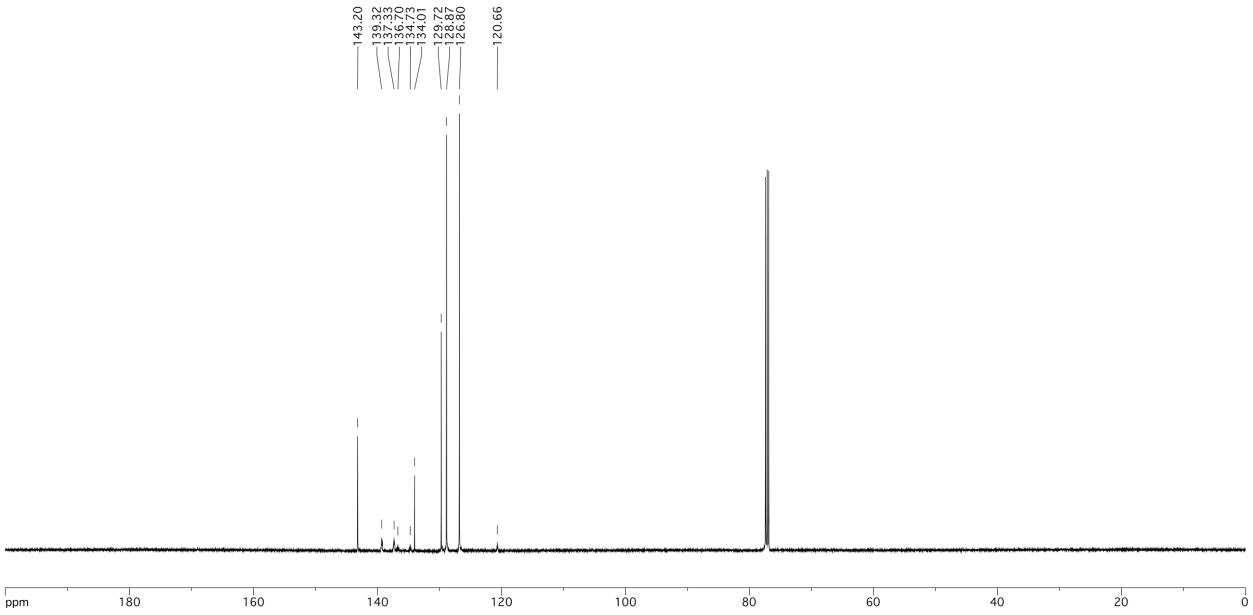


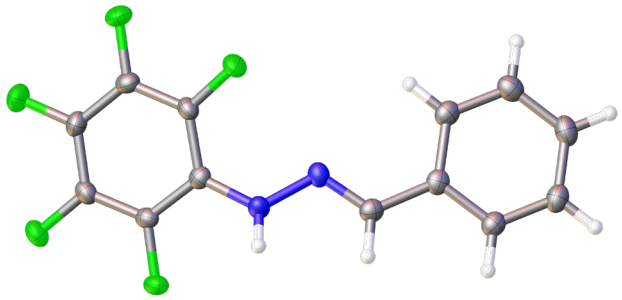
Compound **5.9** was isolated by removing the volatiles under vacuum in 94% yield (269 mg). Crystals suitable for X-ray diffraction study were obtained from layering a $CHCl_3$ solution with pentane. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 1 H), 7.64 (d, J = 6.6 Hz, 2 H), 7.41-7.36 (m, 3 H) 7.27 (s, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 143.2, 139.5-139.2 (m), 137.5-137.2 (m), 136.8-136.6 (m), 134.9-134.6 (m), 134.0, 129.7, 128.9, 126.8, 120.7-120.5 (m).

^1H spectrum



$^{13}C\{^1H\}$ spectrum



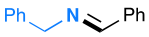


Crystal data and structure refinement for compound_5.9 (CCDC – 1883939)

Identification code	**compound_10**
Empirical formula	$C_{13}H_7F_5N_2$
Formula weight	286.21
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.2044(2)
b/Å	23.8010(8)
c/Å	7.4016(2)
α/°	90
β/°	114.710(2)
γ/°	90
Volume/Å^3	1152.96(6)
Z	4
ρ_{calc}g/cm^3	1.649
μ/mm^{-1}	1.391
F(000)	576.0
Crystal size/mm^3	0.23 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.428 to 136.856

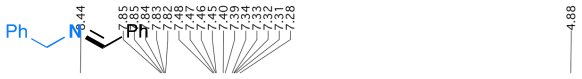
Index ranges	-8 ≤ h ≤ 8, -26 ≤ k ≤ 28, -8 ≤ l ≤ 8
Reflections collected	7081
Independrent reflections	2115 [R_{int} = 0.0321, R_{sigma} = 0.0292]
Data/restraints/parameters	2115/0/181
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1115
Largest diff. peak/hole / e Å^{-3}	0.51/-0.43

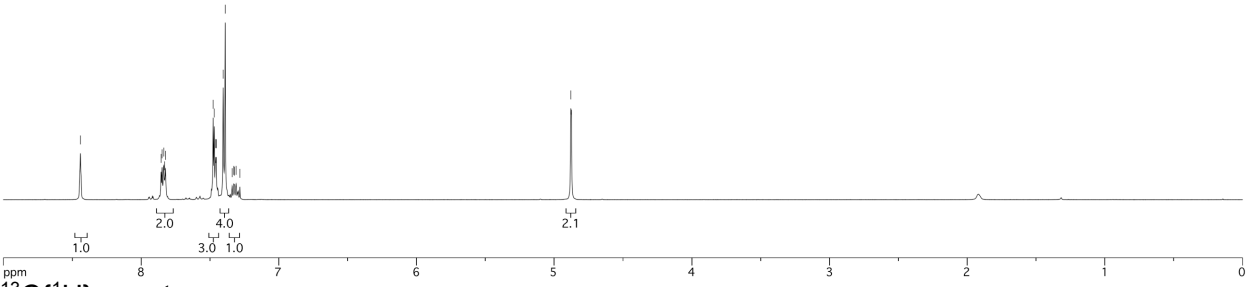
5.10[243]



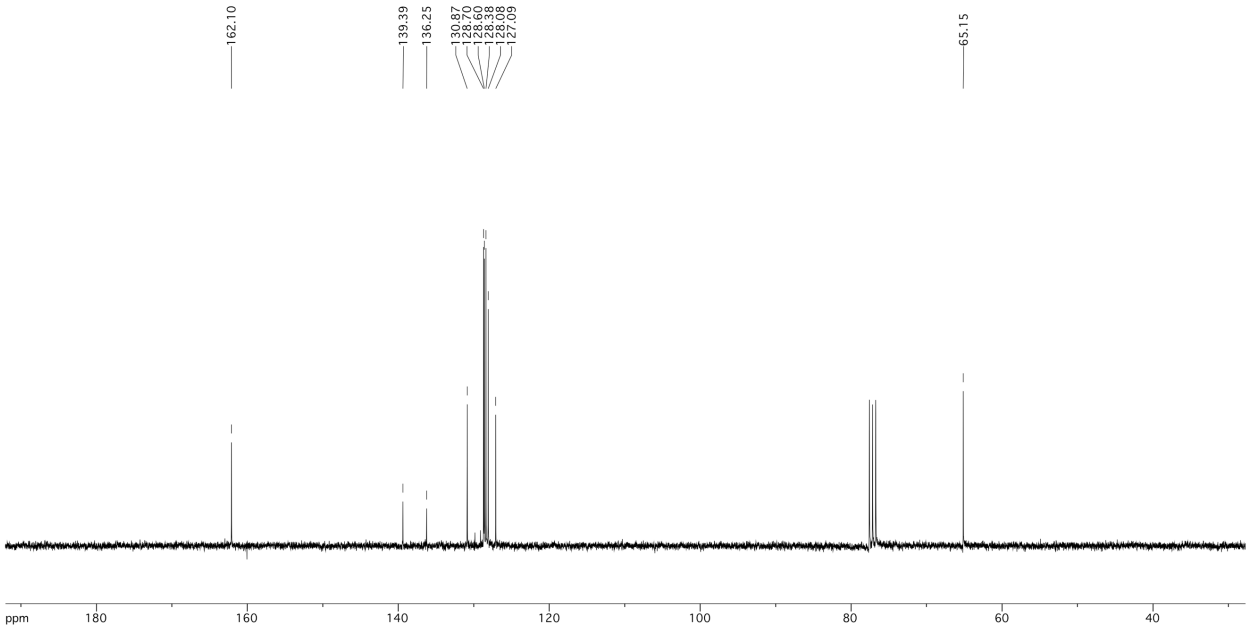
Compound **5.10** was isolated in 97% yield (189 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1 H), 7.82-7.85 (m, 2 H), 7.48-7.46 (m, 3 H), 7.41-7.38 (m, 4 H), 7.34-7.29 (m, 1 H), 4.88 (s, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 162.1, 139.4, 136.2, 130.8, 128.7, 128.6, 128.4, 128.1, 127.1, 65.1.

^{1}H spectrum

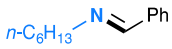




^{13}C{^{1}H} spectrum

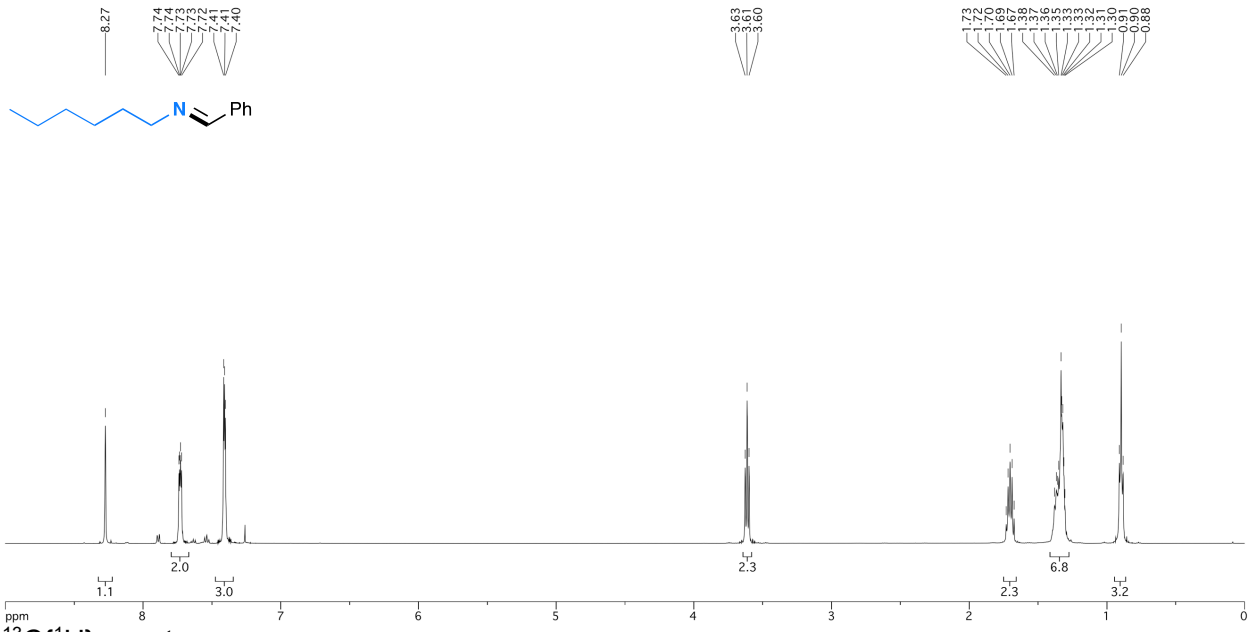


5.11[251]

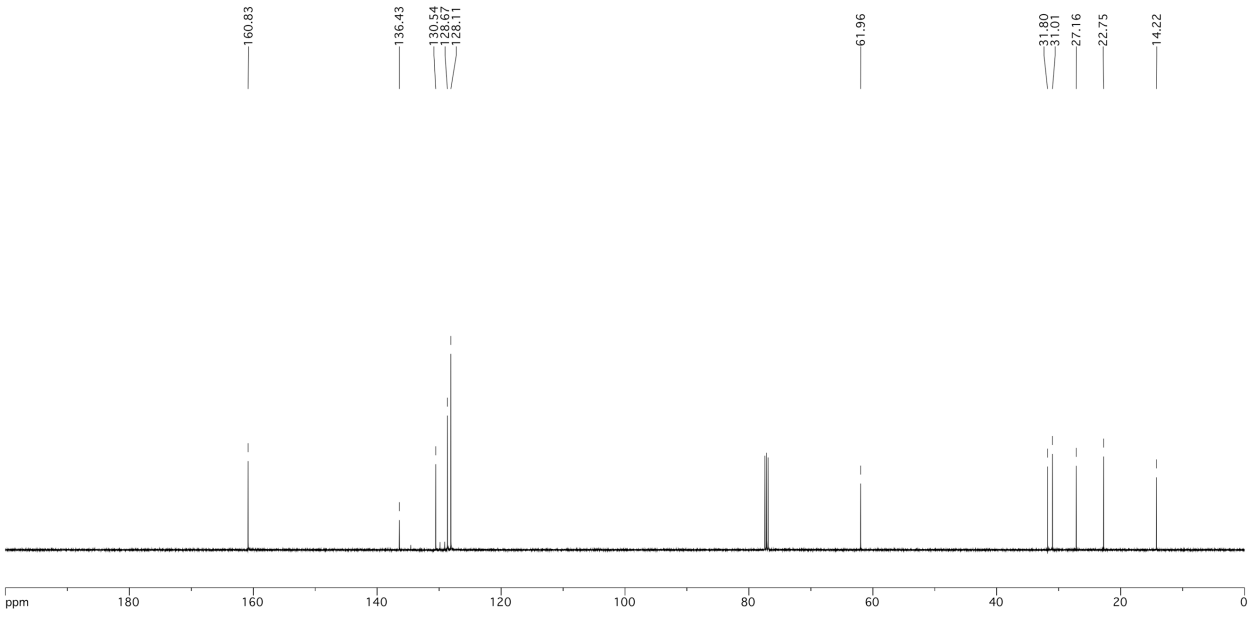


Compound **5.11** was isolated in 97% yield (101 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.74-7.72 (m, 2 H), 7.42-7.40 (m, 3 H), 3.61 (t, *J* = 7.2 Hz, 2 H), 1.70 (quintet, *J* = 7.2 Hz, 2 H), 1.30-1.38 (m, 6 H), 0.90 (br t, *J* = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 160.8, 136.4, 130.5, 128.7, 128.1, 62.0, 31.8, 31.0, 27.2, 22.8, 14.2

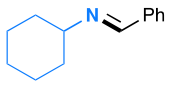
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum



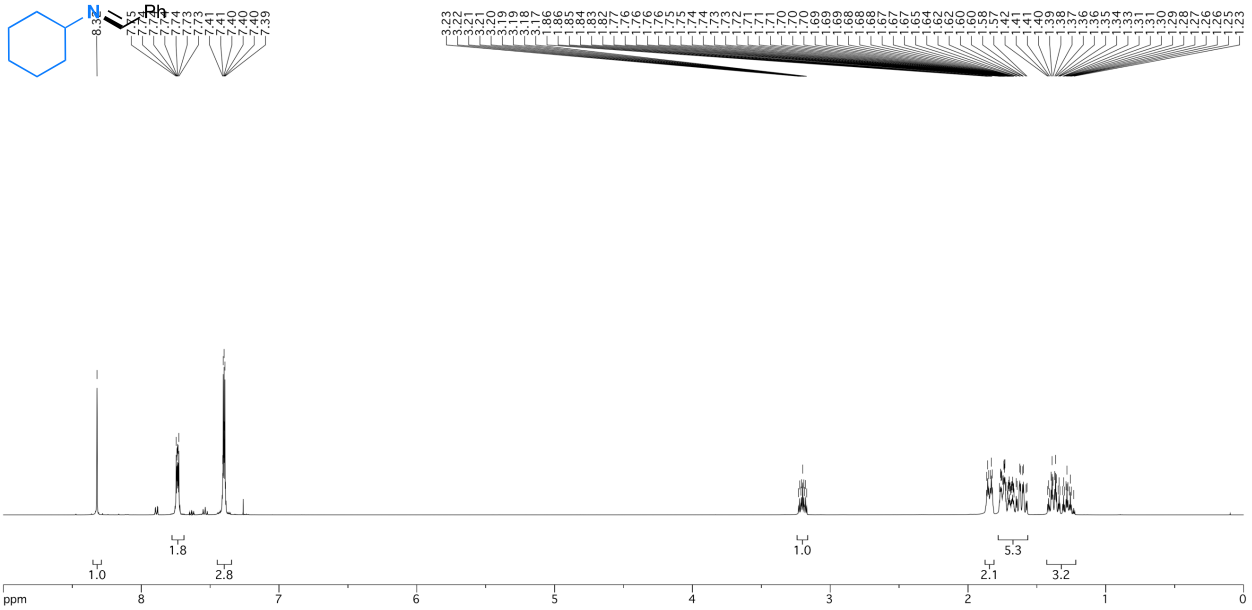
5.12[243]



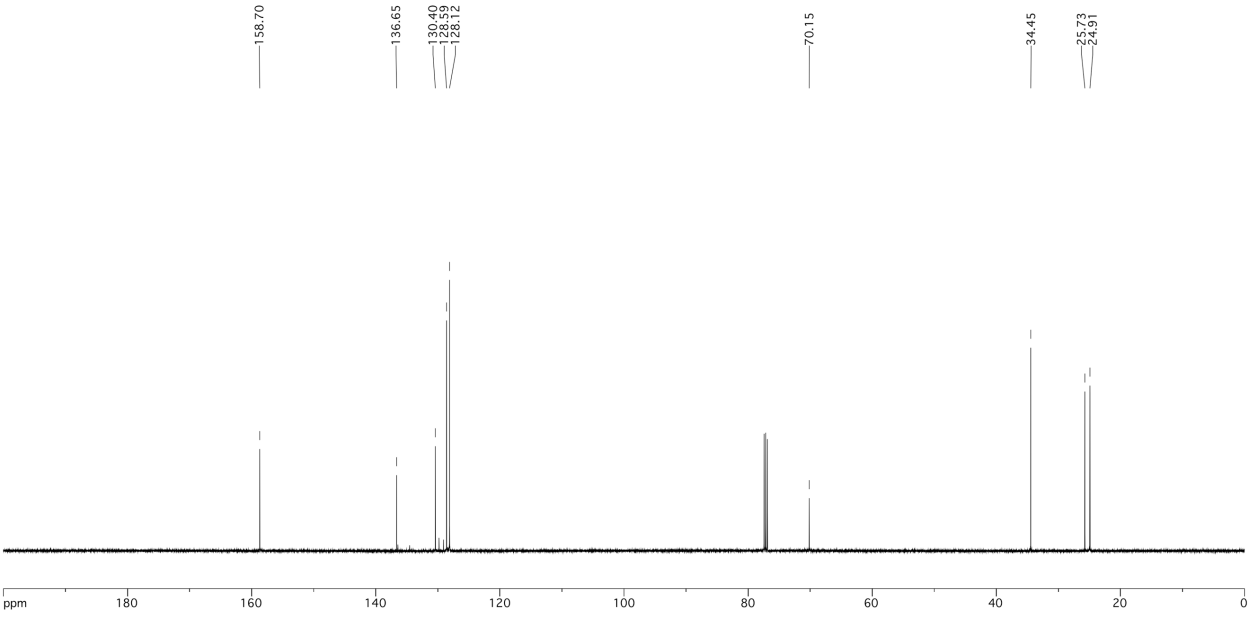
Compound **5.12** was isolated in 98% yield (184 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (s, 1 H), 7.73-7.75 (m, 2 H), 7.38-7.41 (m, 3 H), 3.20 (tt, J = 6.9, 3.7 Hz, 1 H), 1.84 (dt, J = 13.2, 3.5 Hz, 2 H), 1.72-1.77 (m, 2 H), 1.67-1.71 (m, 1 H), 1.61 (qd, J = 11.6, 3.0 Hz, 2 H), 1.33-1.42

(m, 2 H) 1.28 (tt, J = 12.3, 3.4 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 158.7, 136.7, 130.4, 128.6, 128.1, 70.1, 34.4, 25.7, 24.9

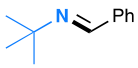
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

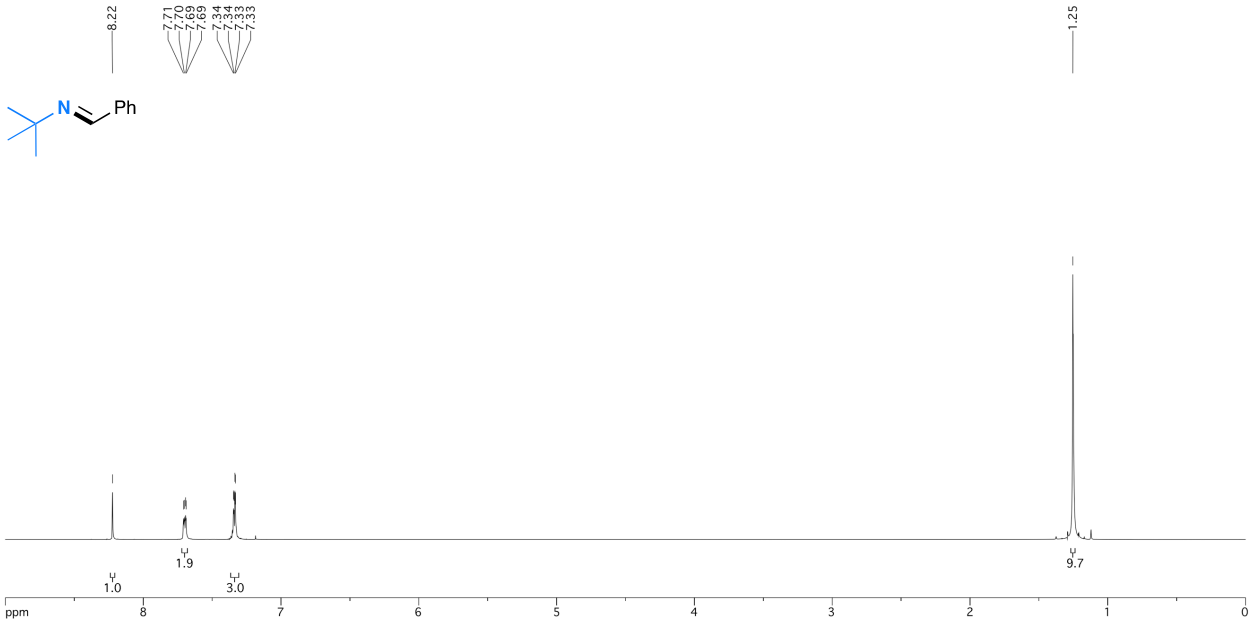


5.13[252]

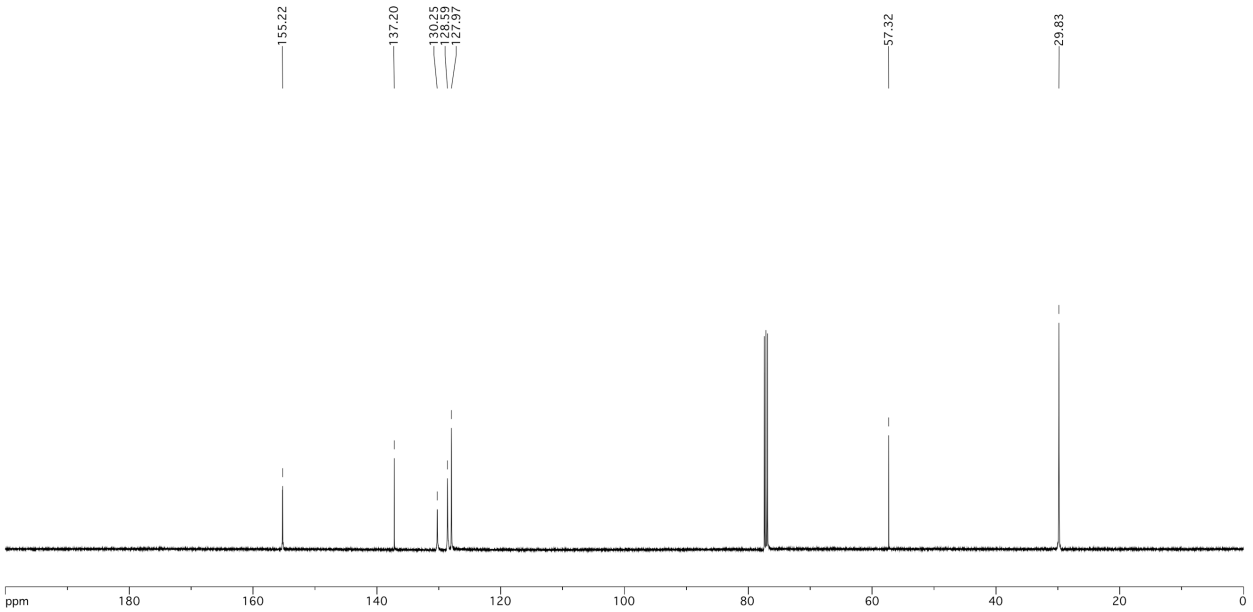


Compound **5.13** was isolated in 96% yield (155 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1 H), 7.75-7.69 (m, 2 H), 7.34-7.33 (m, 3 H), 1.25 (s, 9 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 155.3, 137.2, 130.3, 128.6, 128.0, 57.3, 29.8.

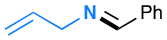
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

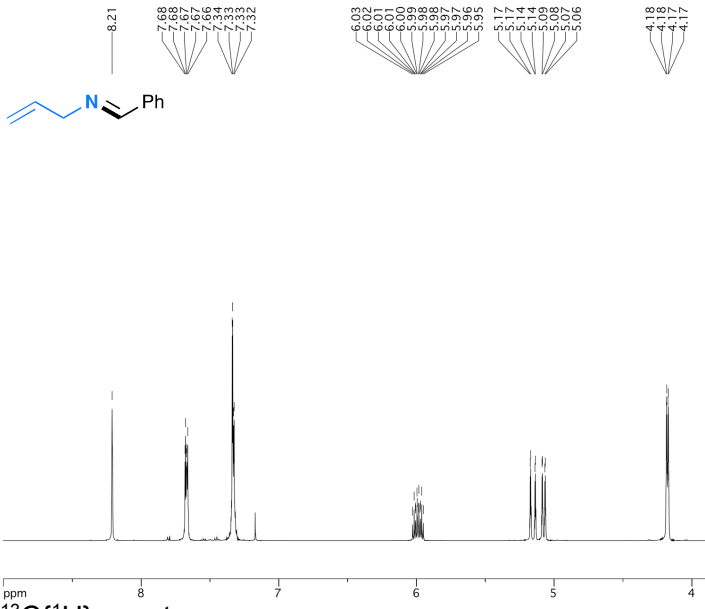


5.14[253]

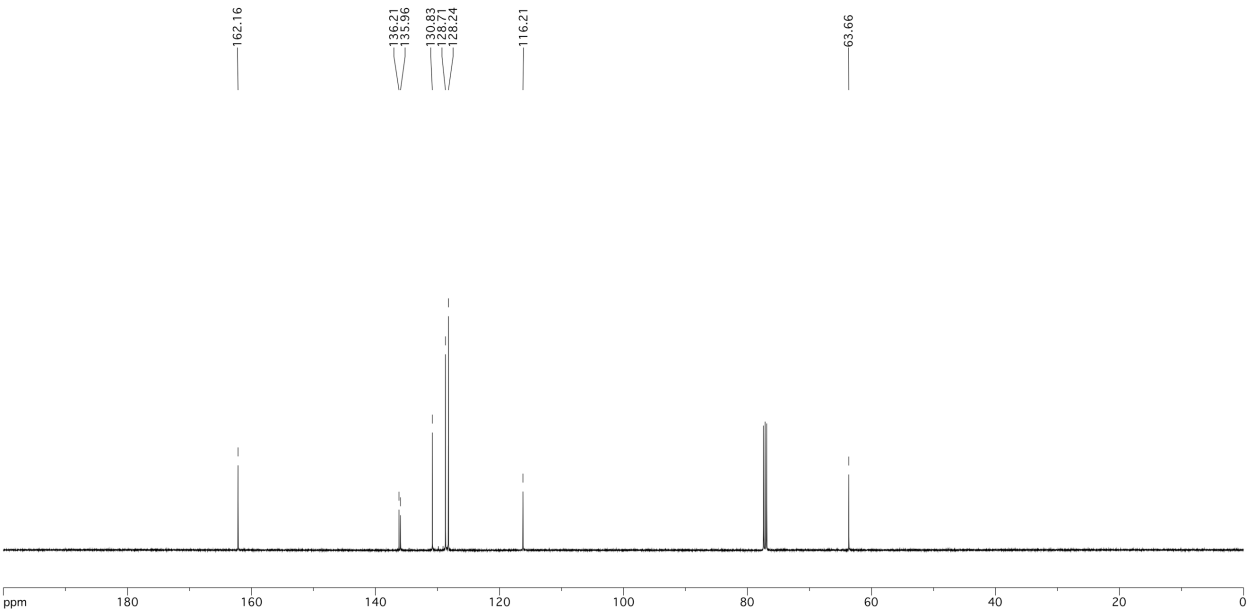


Compound **5.14** was isolated in 98% yield (142 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 7.76 (dt, J = 4.7, 2.4 Hz, 2 H), 7.42 (dd, J = 5.1, 2.0 Hz, 3 H), 6.08 (ddt, J = 17.2, 10.3, 5.7 Hz, 1 H), 5.26-5.15 (m, 2 H) 4.27 (dd, J = 5.7, 1.5 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 162.2, 136.2, 136.0, 130.8, 128.7, 128.2, 116.2, 63.7.

^{1}H spectrum



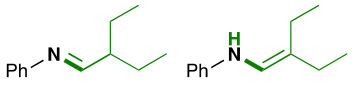
^{13}C{^{1}H} spectrum



5.15

NB: Compound **5.15** was too unstable to be isolated and was characterized from the crude reaction mixture. ^{1}H NMR (500 MHz, CDCl3): δ 7.60 (t, J = 4.8 Hz, 1 H), 7.27 (t, J = 7.8 Hz, 2 H),7.15 (t, J = 6.0 Hz, 2 H), 2.32 (td, J = 7.3, 5.0 Hz, 2 H), 1.57 (q, J = 7.4 Hz, 2 H) 0.95 (t, J = 7.4 Hz, 3 H). 13C{1H} NMR ($CDCl_3$, 126 MHz): δ 166.4, 152.5, 129.2, 125.7, 121.1, 38.3, 19.3, 13.9.

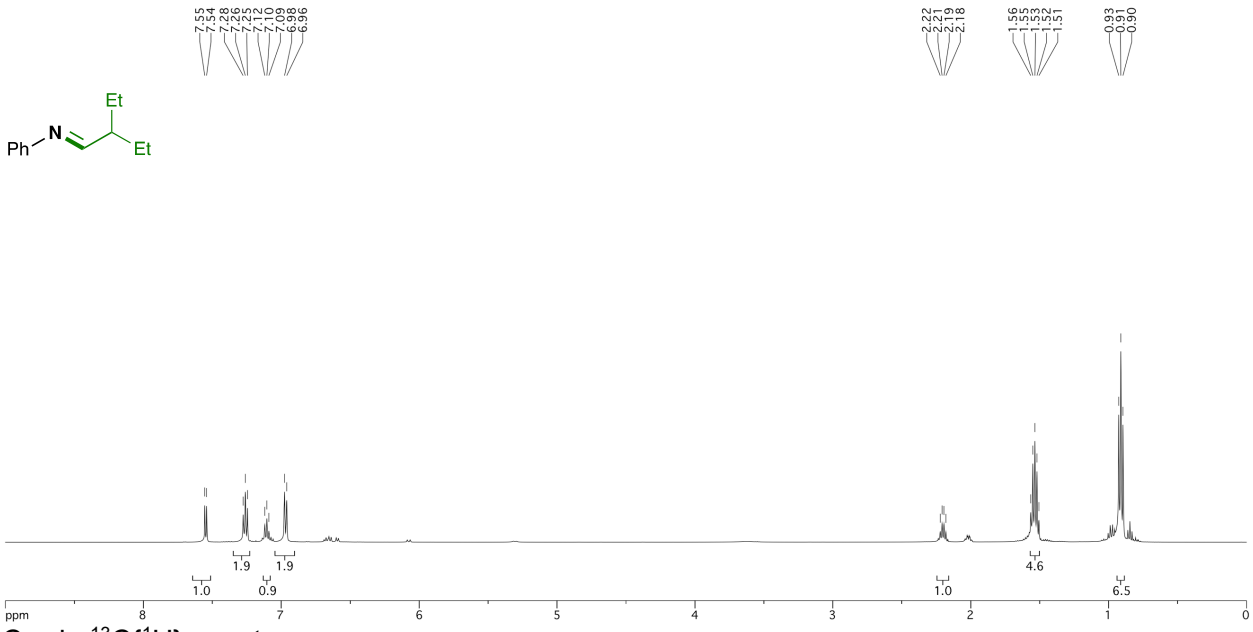
5.16



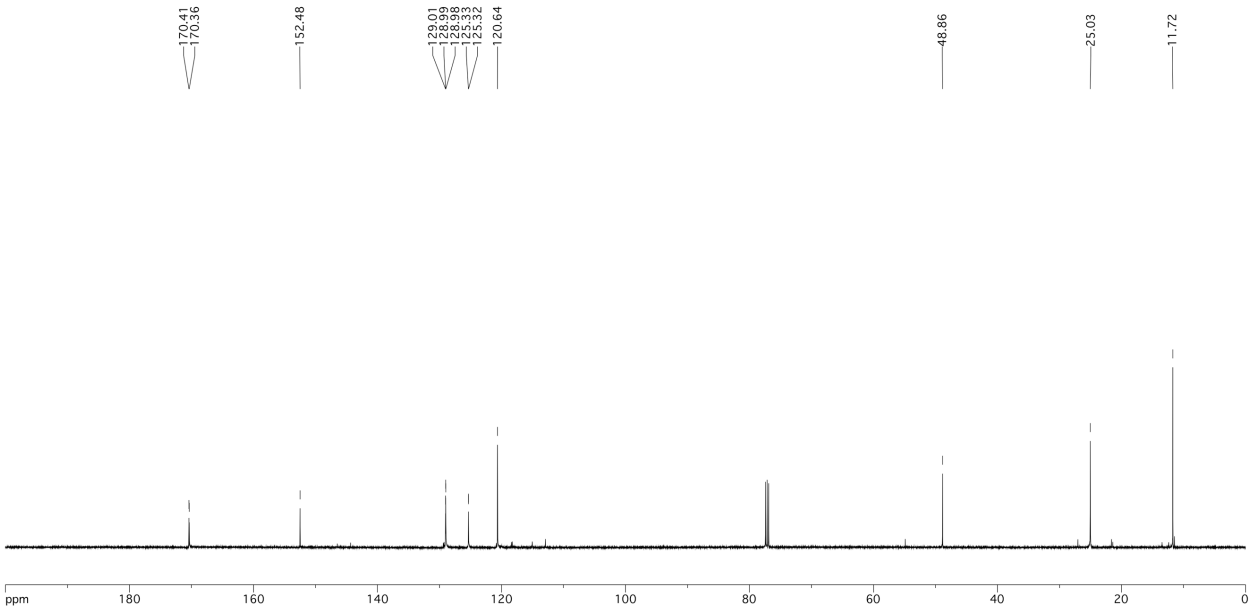
16-enamine

Despite several attempts, we systematically observed the formation of the corresponding **5.16-enamine** during the purification of compound **5.16**. This has been accounted for when determining the isolated yield of **5.16**. Compound **5.16** was obtained in 85% yield(149 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ , 7.55 (d, *J* = 6.7 Hz, 1 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 2.20 (q, *J* = 6.8 Hz, 1 H), 1.53 (quintet, *J* = 7.4 Hz, 5 H) 0.91 (t, *J* = 7.5 Hz, 7 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 170.41, 170.36, 152.5, 129.01, 128.99, 128.98, 125.33, 125.32, 120.6, 48.9, 25.0, 11.7

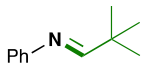
Crude ^{1}H spectrum



Crude $^{13}C\{^{1}H\}$ spectrum

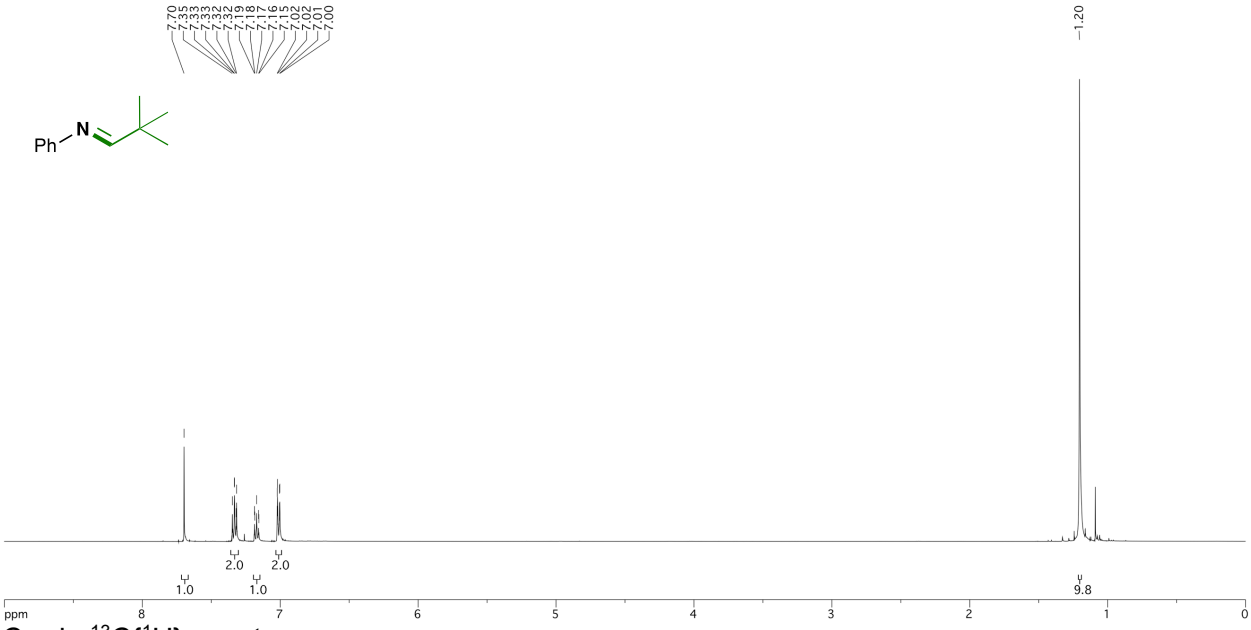


5.17[254]

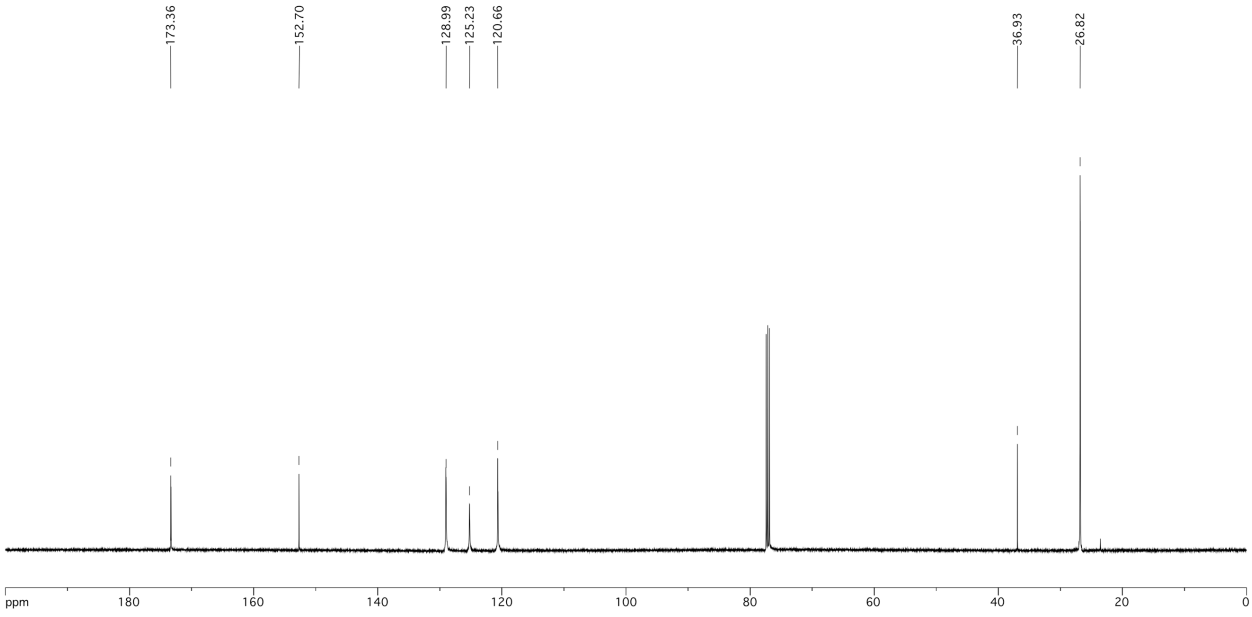


Compound **5.17** was isolated in 98% yield (158 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.32-7.35 (m, 2 H), 7.15-7.19 (m, 1 H), 7.01 (dd, J = 8.4, 1.2 Hz, 2 H) 1.20 (s, 10 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 173.4, 152.7, 129.0, 125.2, 120.7, 36.9, 26.8.

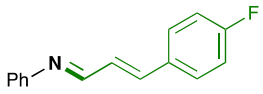
Crude ^{1}H spectrum



Crude $^{13}C\{^{1}H\}$ spectrum



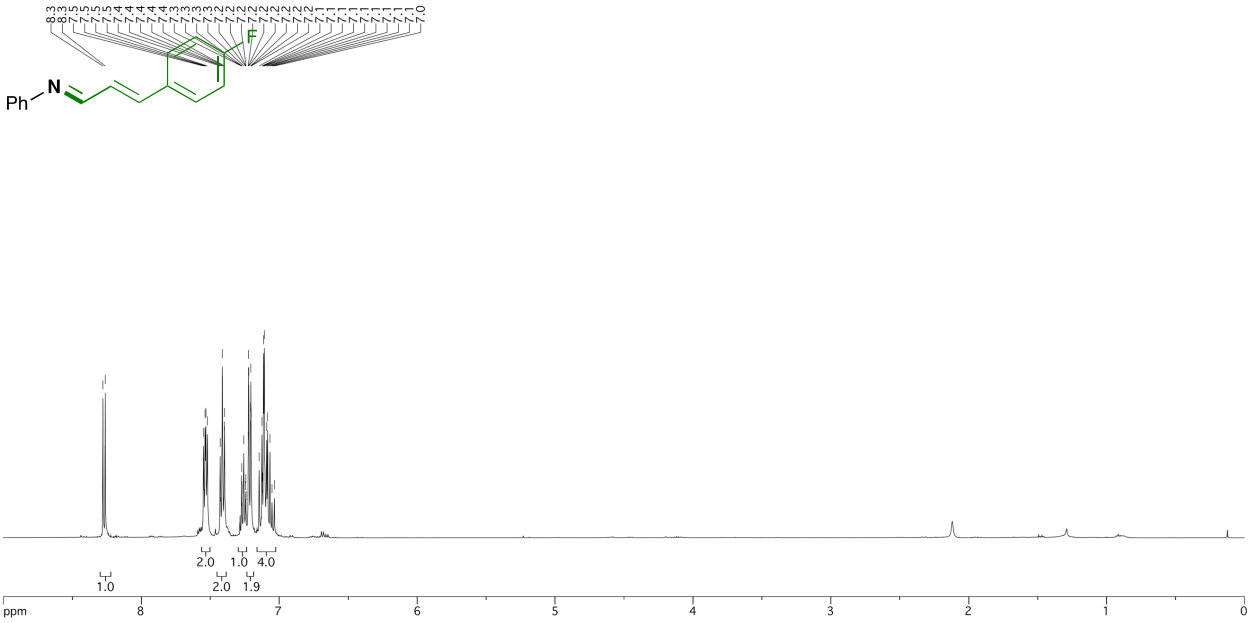
5.18



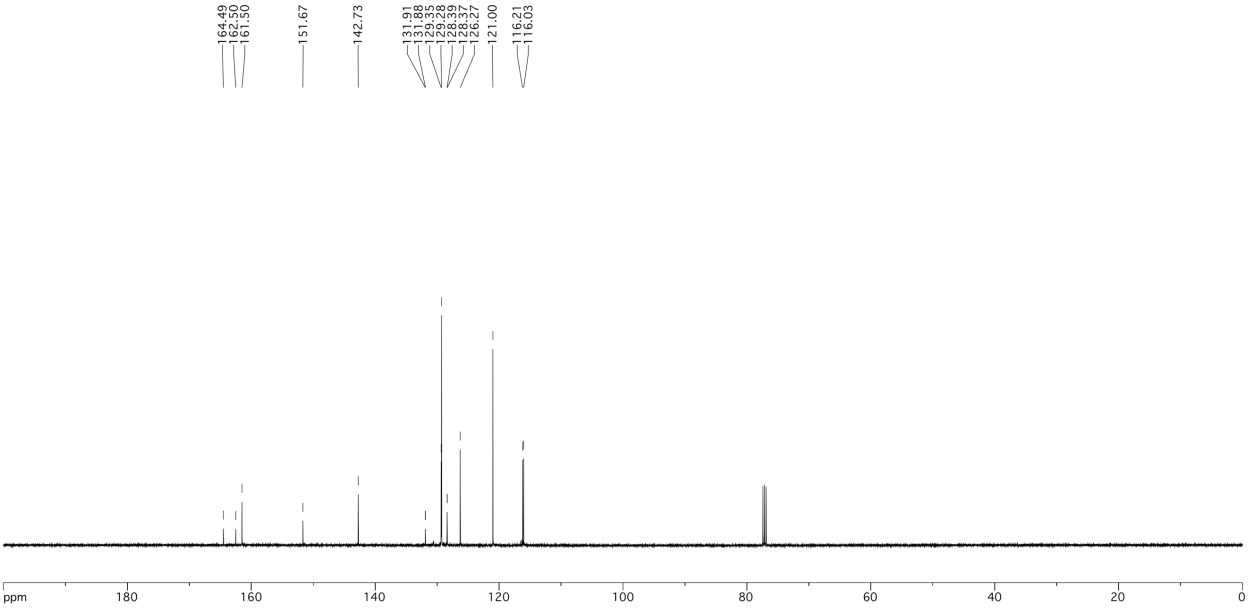
Compound **5.18** was isolated in 97% yield (219 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 8.4 Hz, 1 H), 7.54 (dd, J = 8.6, 5.4 Hz, 2 H), 7.43-7.40 (m, 2 H), 7.27-7.24 (m, 1 H), 7.21

(dt, J = 8.4, 1.1 Hz, 2 H) 7.15-7.04 (m, 4 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): 13-C NMR (126 MHz; acetone): δ 163.5 (d, J = 252 Hz), 161.5, 151.7, 142.7, 131.91, 131.88, 129.35, 129.28, 128.39, 128.37, 126.3, 121.0, 116.1 (d, J = 23 Hz).

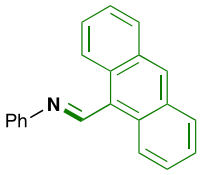
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

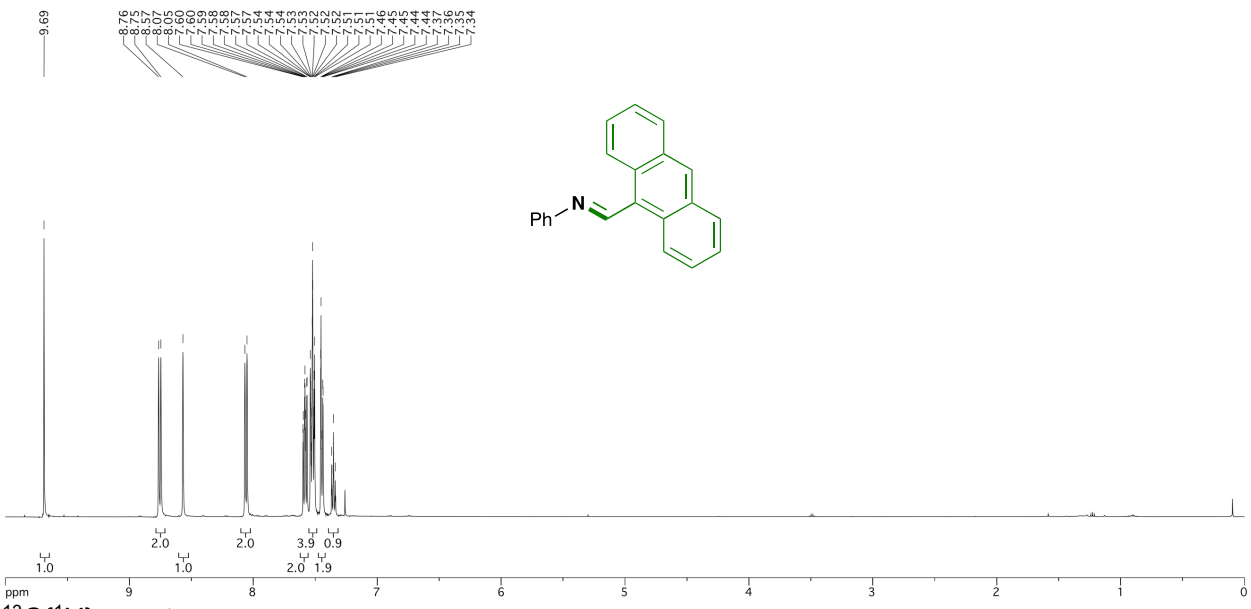


5.19[255]

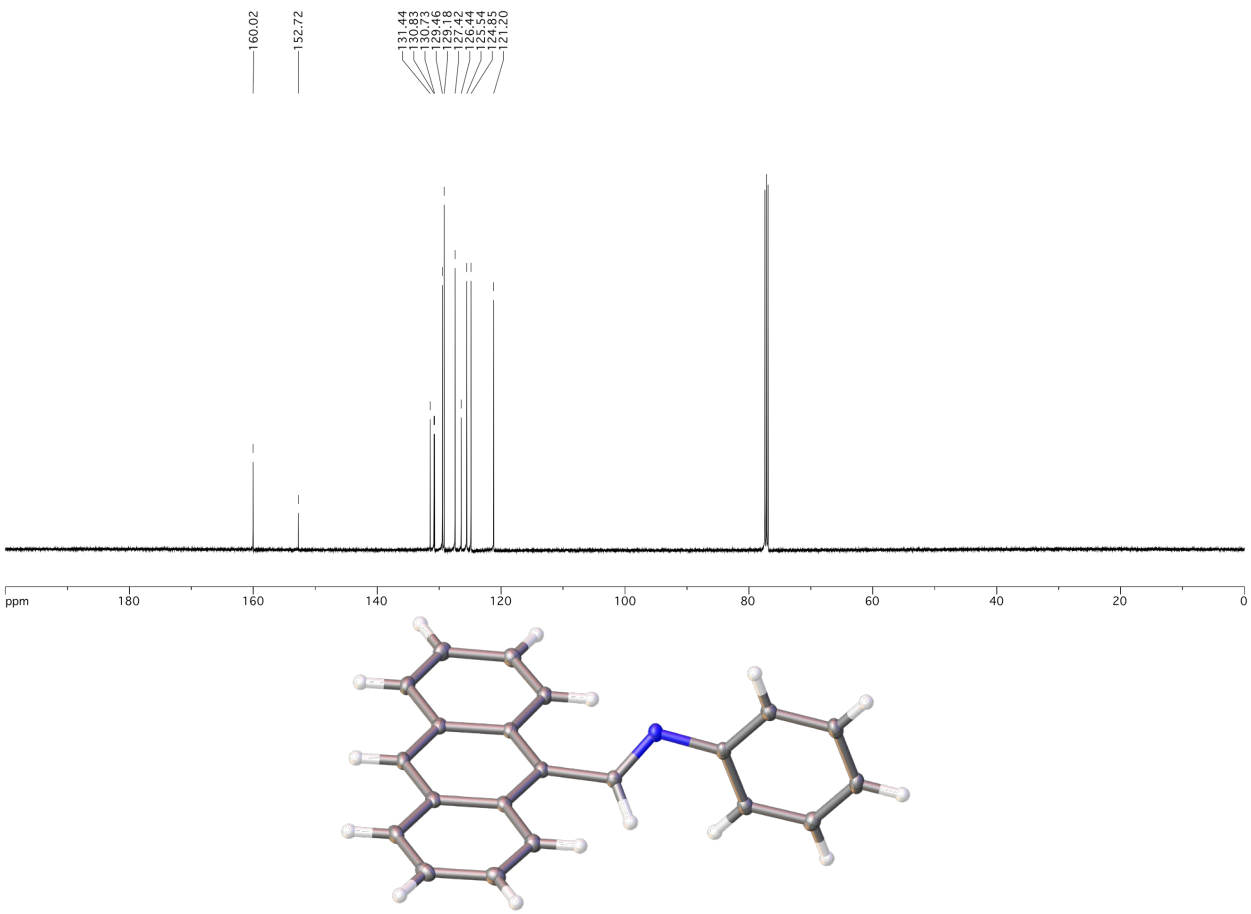


Compound **5.19** was isolated in 99% yield. (279 mg) Crystals suitable for X-ray diffraction study were obtained from layering a $CHCl_3$ solution with pentane. ^1H NMR (500 MHz, $CDCl_3$): δ 9.69 (s, 1 H), 8.75 (d, J = 8.9 Hz, 2 H), 8.57 (s, 1 H), 8.06 (d, J = 8.4 Hz, 2 H), 7.58 (ddd, J = 8.6, 6.8, 1.6 Hz, 2 H), 7.52 (ddt, J = 9.1, 6.0, 1.4 Hz, 4 H), 7.46-7.44 (m, 2 H) 7.37-7.34 (m, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 160.0, 152.7, 131.4, 130.83, 130.73, 129.5, 129.2, 127.4, 126.4, 125.5, 124.9, 121.2.

^1H spectrum



$^{13}C\{^1H\}$ spectrum

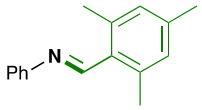


Crystal data and structure refinement for compound_5.19 (CCDC – 1883940)

Identification code	**compound_19**
Empirical formula	$C_{21}H_{15}N$
Formula weight	281.34
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	4.98360(10)
b/Å	11.5286(3)
c/Å	24.9717(5)
α/°	90

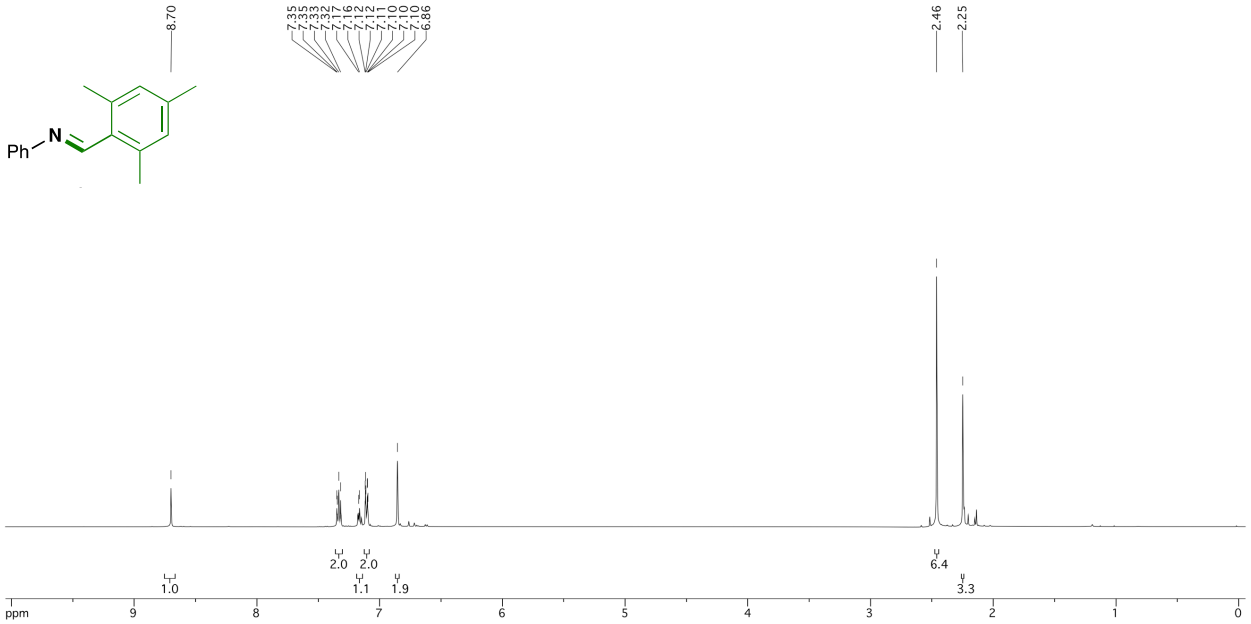
β/°	92.0040(10)
γ/°	90
Volume/Å^3	1433.84(6)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.578
F(000)	592.0
Crystal size/mm^3	0.32 × 0.215 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.084 to 136.686
Index ranges	-4 ≤ h ≤ 6, -13 ≤ k ≤ 10, -29 ≤ l ≤ 30
Reflections collected	12954
Independent reflections	2567 [R_{int} = 0.0205, R_{sigma} = 0.0165]
Data/restraints/parameters	2567/0/199
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0334, wR_2 = 0.0854
Largest diff. peak/hole / e Å^{-3}	0.15/-0.16

5.20[256]

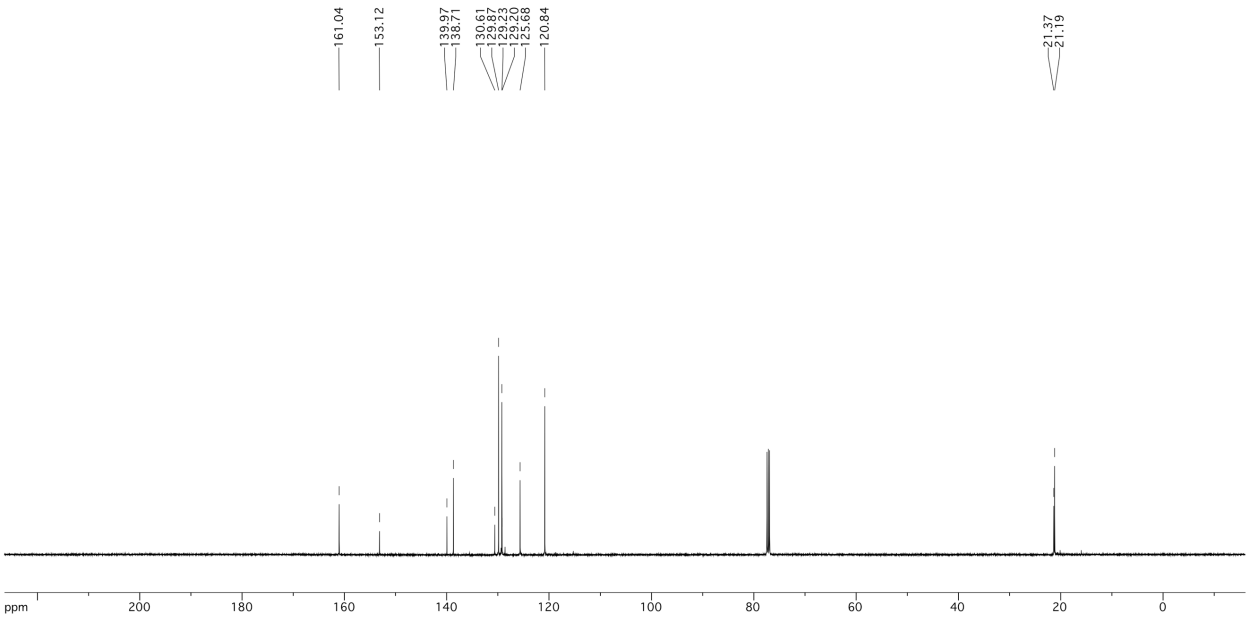


Compound **5.20** was isolated in 98% yield (218 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1 H), 7.35-7.32 (m, 2 H), 7.19-7.15 (m, 1 H), 7.13-7.90 (m, 2 H), 6.86 (s, 2 H), 2.46 (s, 6 H) 2.25 (s, 3 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 161.0, 153.1, 140.0, 138.7, 130.6, 129.9, 129.23, 129.20, 125.7, 120.8, 21.4, 21.2.

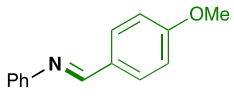
^{1}H spectrum



^{13}C{^{1}H} spectrum



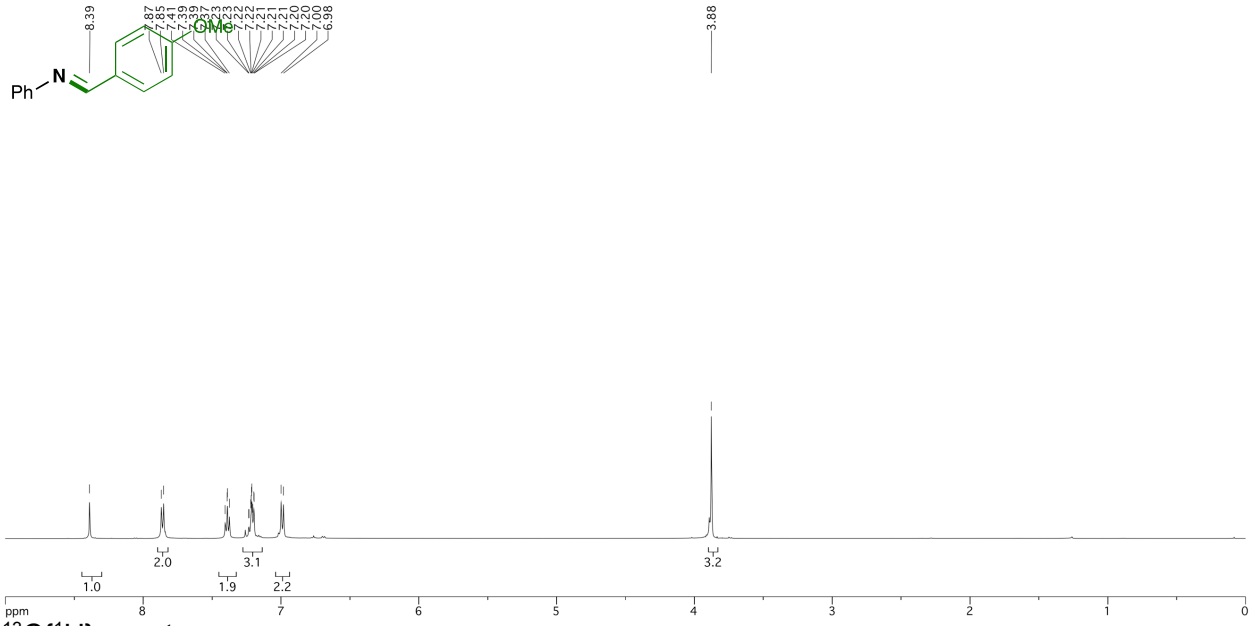
5.21[256]



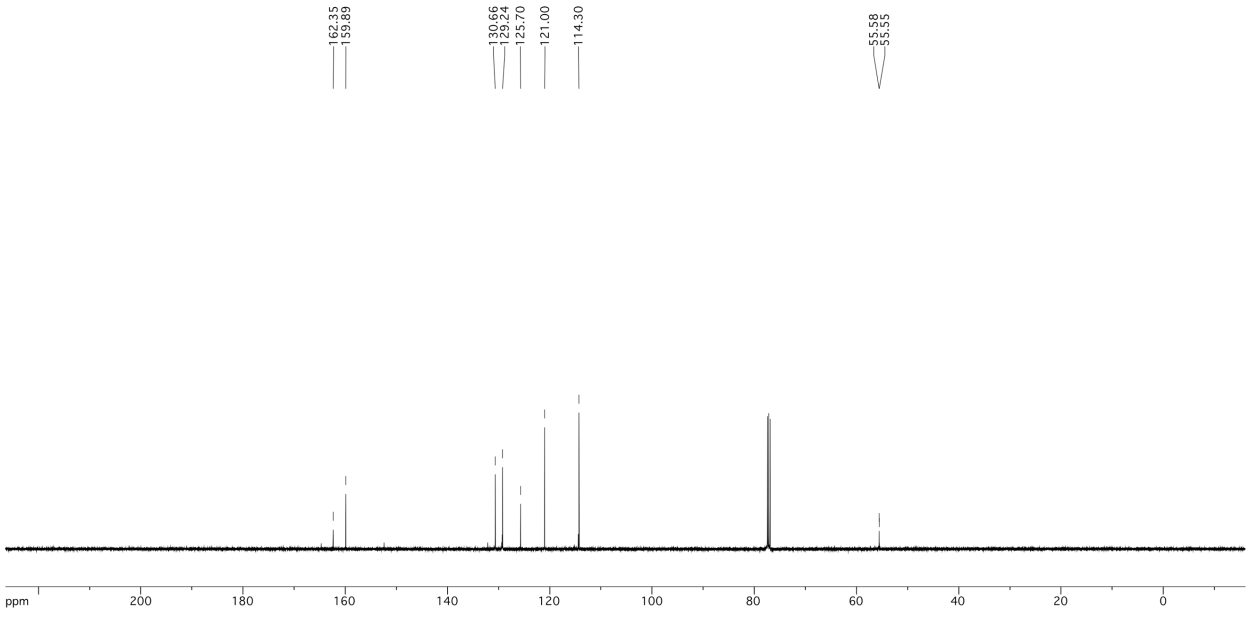
Compound **5.21** was isolated in 96% yield (203 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1 H), 7.86 (d, J = 8.7 Hz, 2 H), 7.39 (dd, J = 8.3, 7.4 Hz, 2 H), 7.23-7.20 (m, 3 H), 6.99 (d, J =

8.8 Hz, 2 H), 3.88 (s, 3 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 162.4, 159.9, 130.7, 129.2, 125.7, 121.0, 114.3, 55.5.

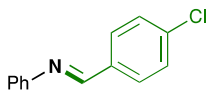
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum

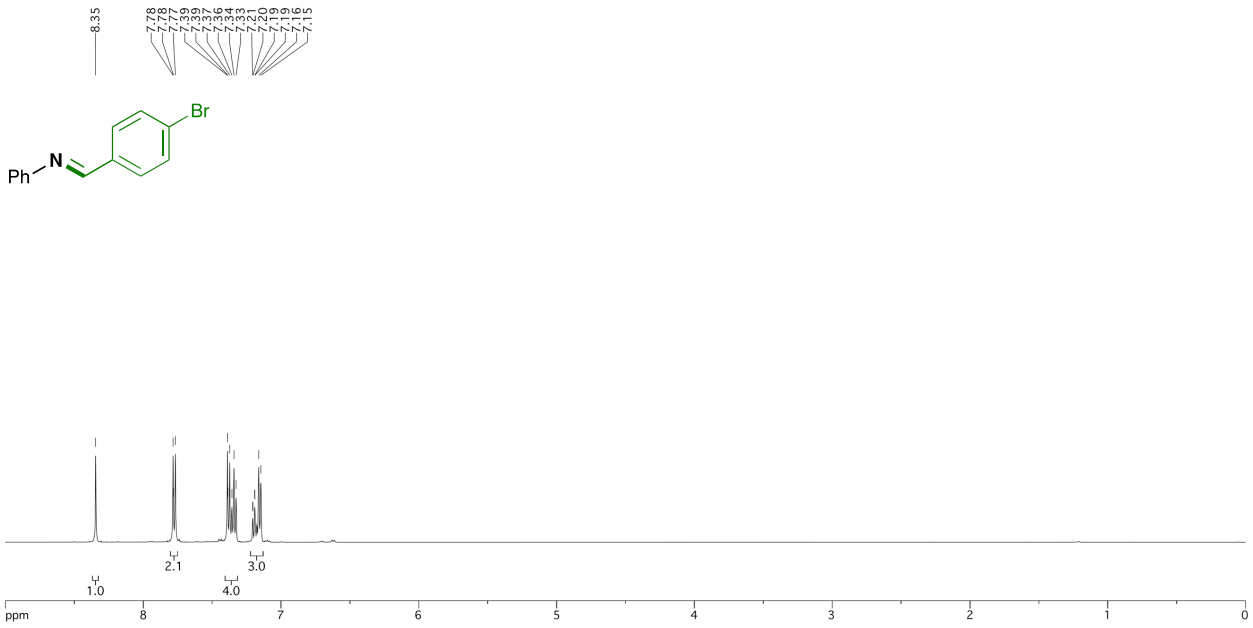


5.22[257]

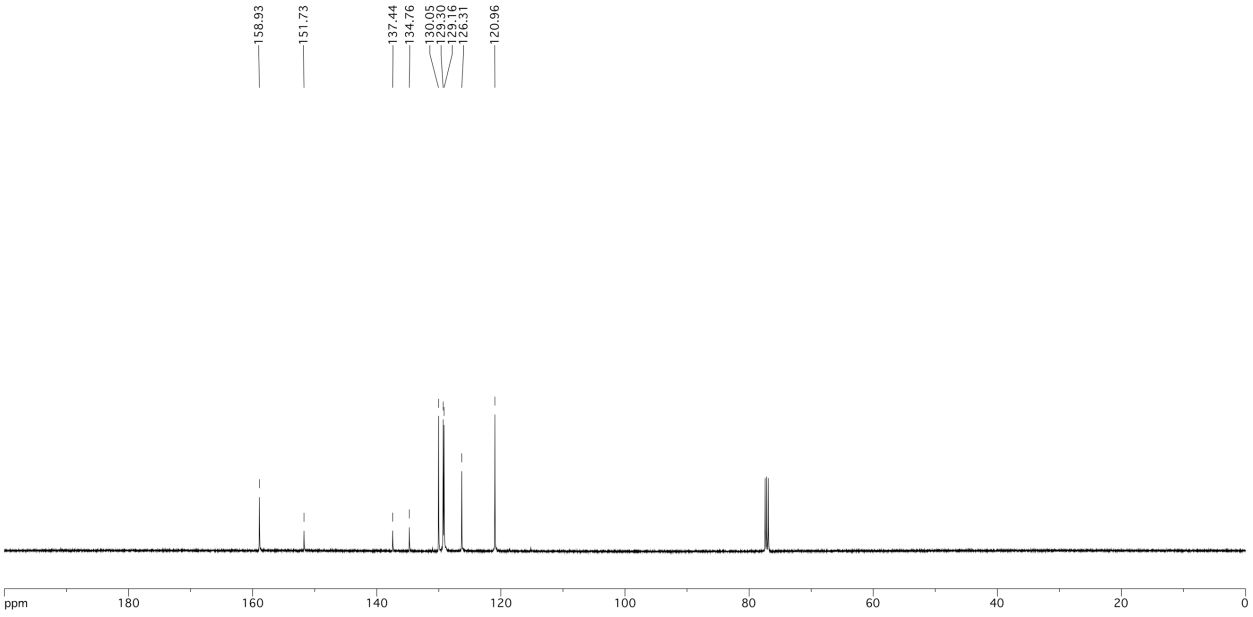


Compound **5.22** was isolated in 98% yield (211 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ , 8.35 (s, 1 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), m, 4 H), 7.34 (t, J = 8.4 Hz, 2 H), 7.21-7.15 (m, 3 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 158.9, 151.7, 137.4, 134.8, 130.1, 129.30, 129.16, 126.3, 121.0.

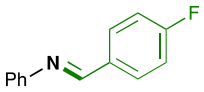
^{1}H spectrum



^{13}C{^{1}H} spectrum

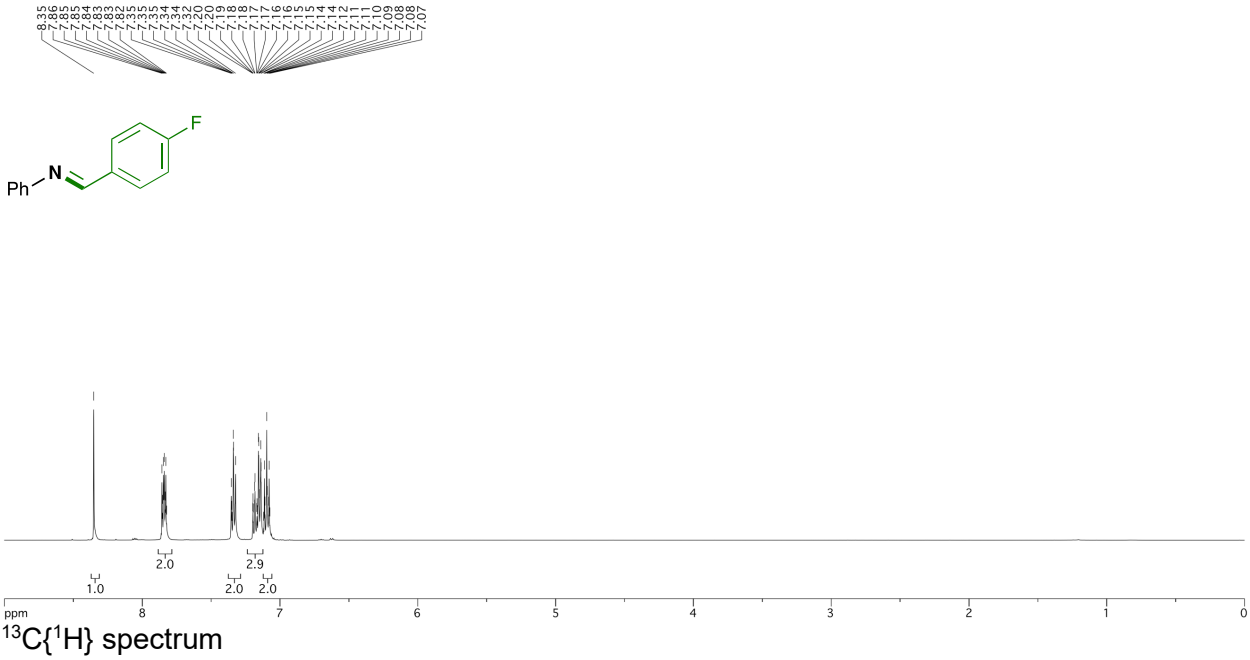


5.23

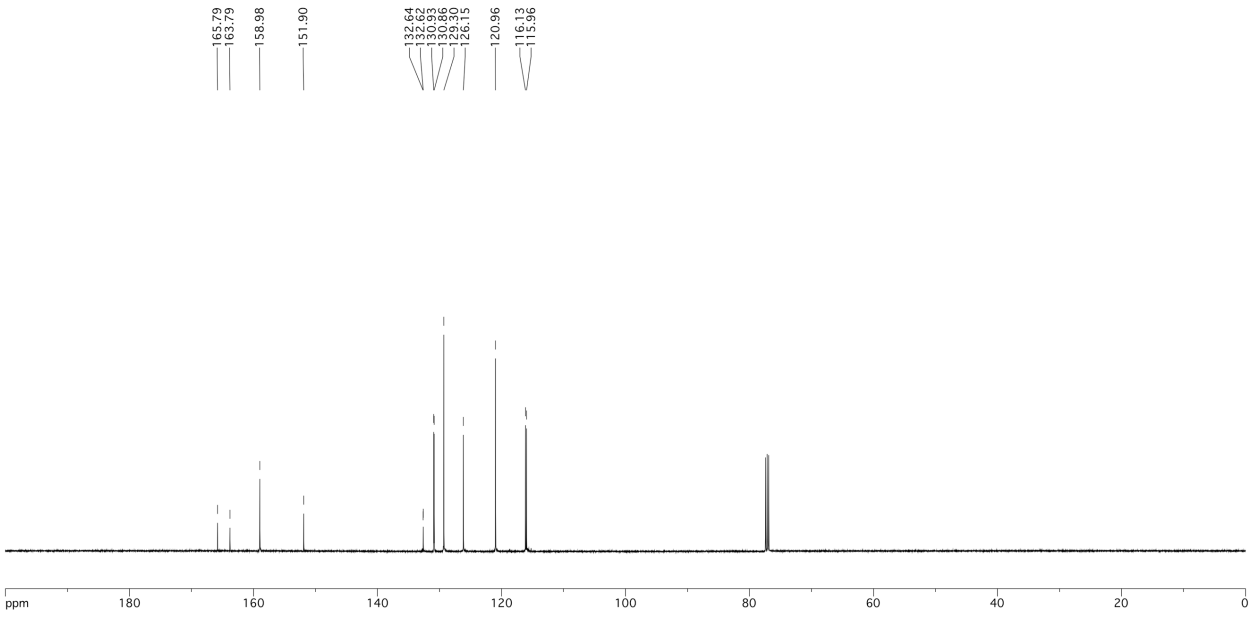


Compound **5.23** was isolated in 95% yield (189 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 7.84 (ddd, J = 8.9, 5.6, 2.8 Hz, 2 H), 7.32-7.35 (m, 2 H), 7.14-7.20 (m, 3 H) 7.07-7.12 (m, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 164.8 (d, J = 252 Hz), 159.0, 151.9, 132.64, 132.62, 130.93, 130.86, 129.3, 126.1, 121.0, 116.0 (d, J = 23 Hz).

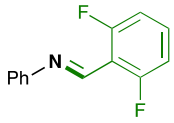
^{1}H spectrum



^{13}C{^{1}H} spectrum

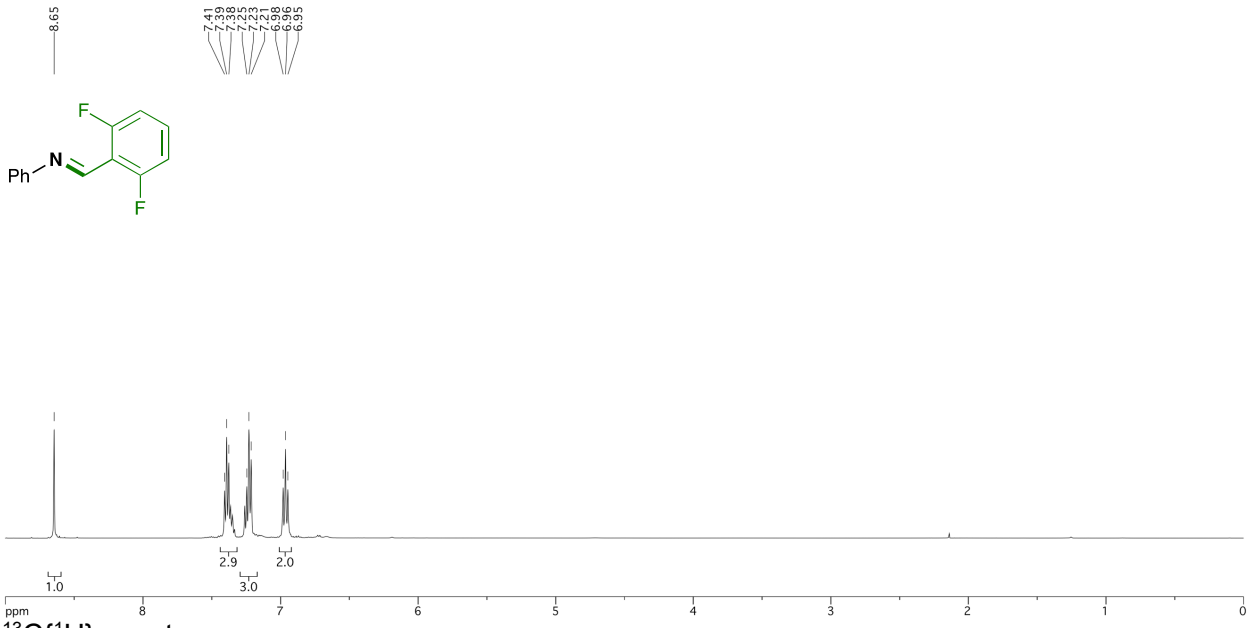


5.24

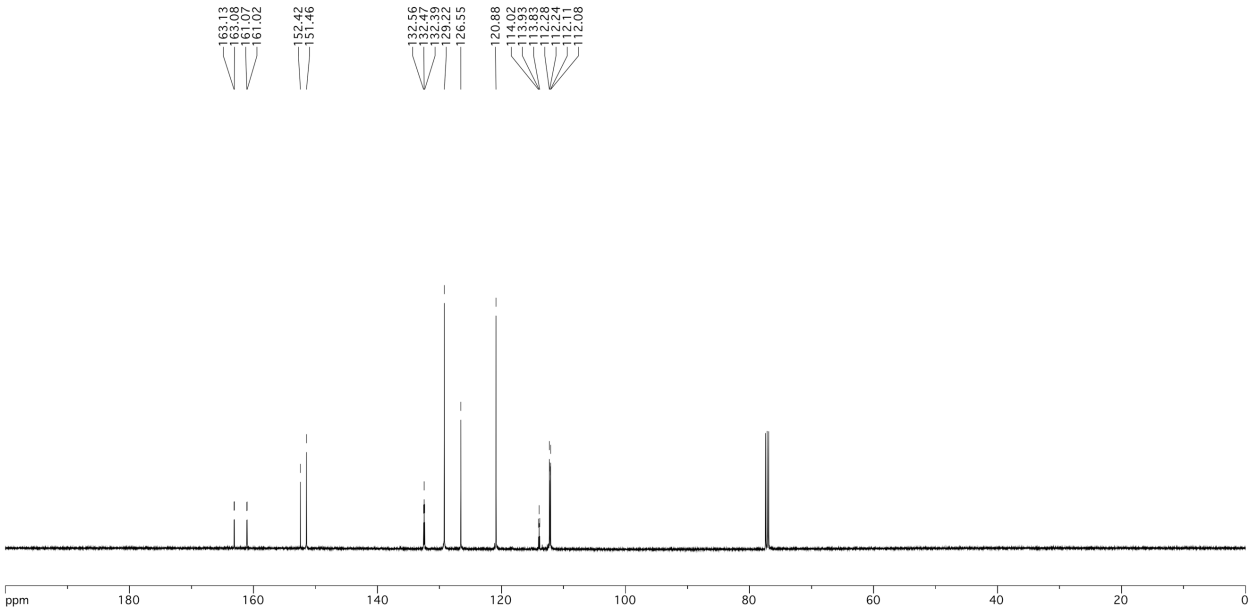


Compound **5.24** was isolated in 94% yield (204 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1 H), 7.39 (t, J = 7.8 Hz, 3 H), 7.23 (t, J = 7.8 Hz, 3 H) 6.96 (t, J = 8.6 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 162.1 (d, J = 259 Hz), 162.0 (d, J = 259 Hz), 152.4, 151.5, 132.5 (t, J = 11 Hz), 129.2, 126.6, 120.9, 113.9 (t, J = 12 Hz), 112.2 (m).

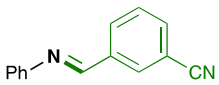
^{1}H spectrum



$^{13}C\{^{1}H\}$ spectrum



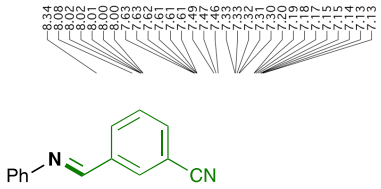
5.25

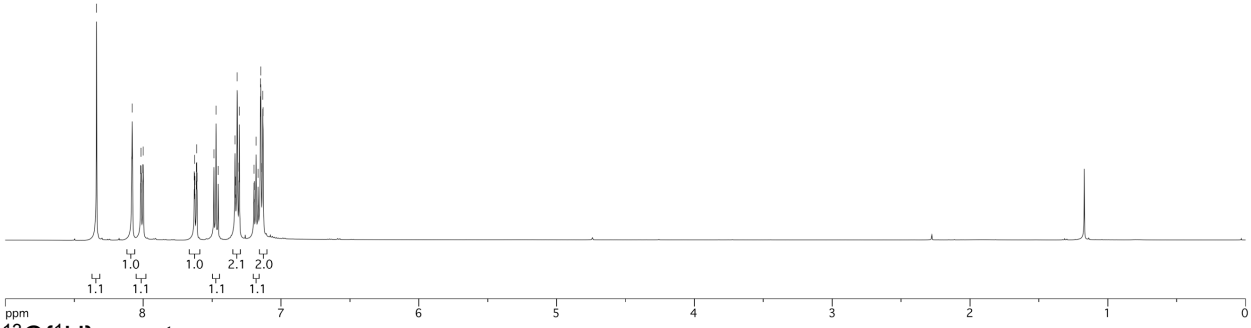


Compound **5.25** was isolated in 95% yield (196 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 8.08 (s, 1 H), 8.00-8.02 (m, 1 H), 7.62 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 1 H),

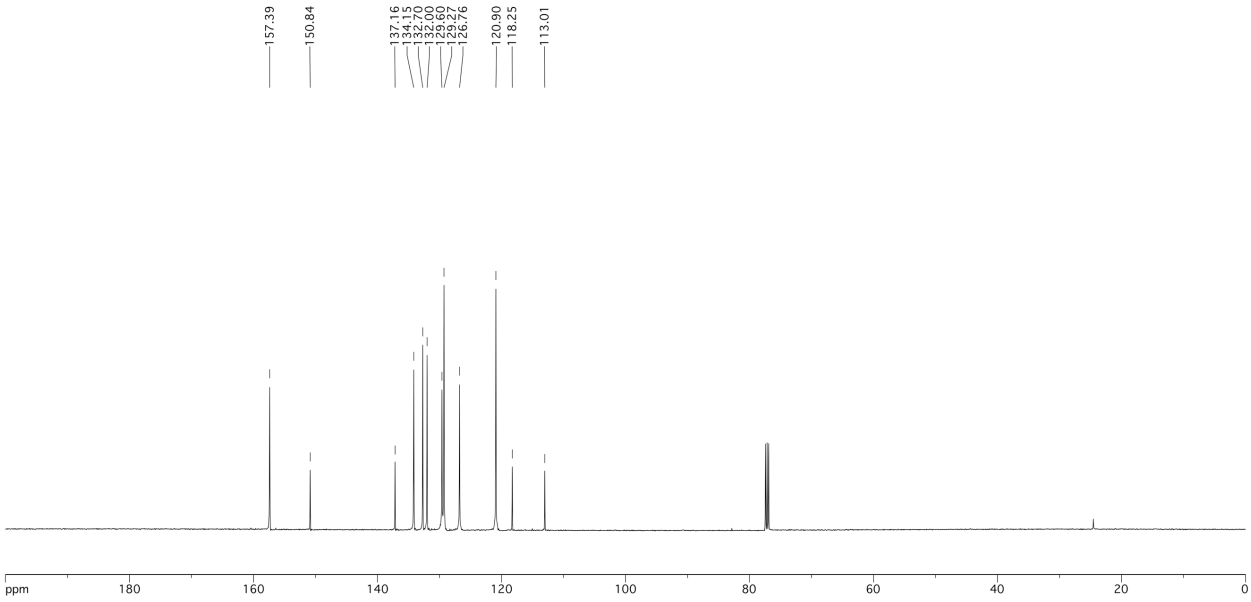
7.30-7.33 (m, 2 H), 7.17-7.20 (m, 1 H) 7.13-7.15 (m, 2 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 157.4, 150.8, 137.2, 134.1, 132.7, 132.0, 129.6, 129.3, 126.8, 120.9, 118.3, 113.0.

^{1}H spectrum

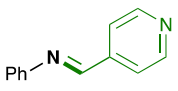




$^{13}C\{^{1}H\}$ spectrum

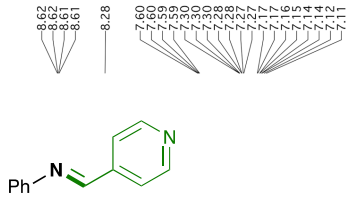


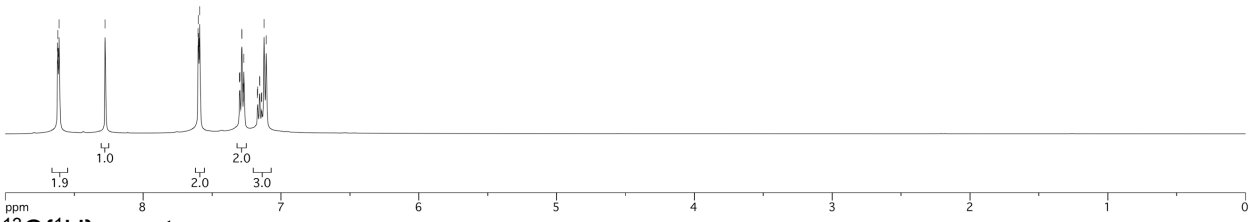
5.26



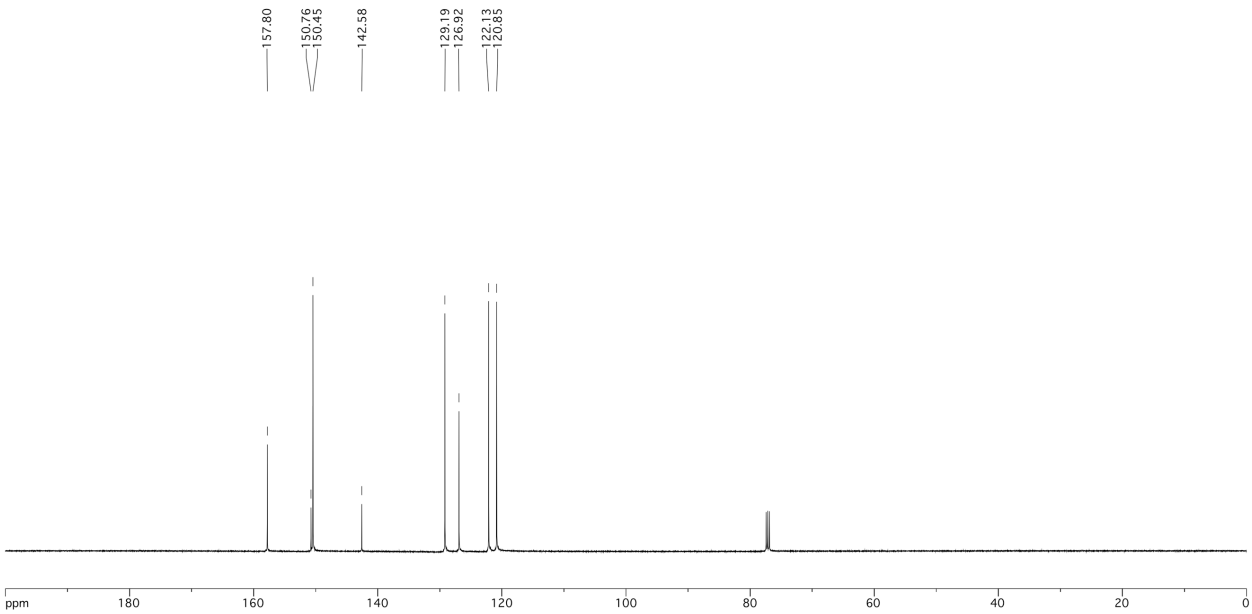
Compound **5.26** was isolated in 96% yield (169 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (dd, *J* = 4.4, 1.6 Hz, 2 H), 8.28 (s, 1 H), 7.60 (dd, *J* = 4.4, 1.6 Hz, 2 H), 7.27-7.30 (m, 2 H) 7.11-7.17 (m, 3 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 157.8, 150.8, 150.4, 142.6, 129.2, 126.9, 122.1, 120.9.

^{1}H spectrum

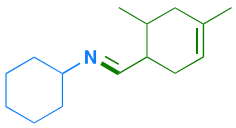




^{13}C{^{1}H} spectrum

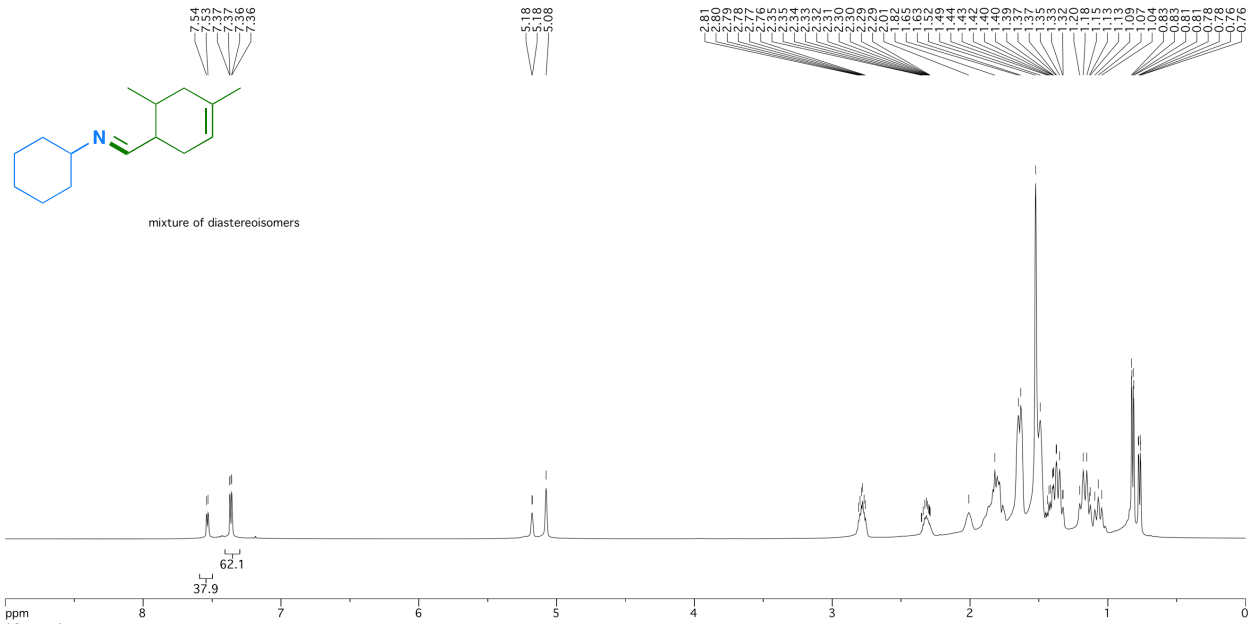


5.27

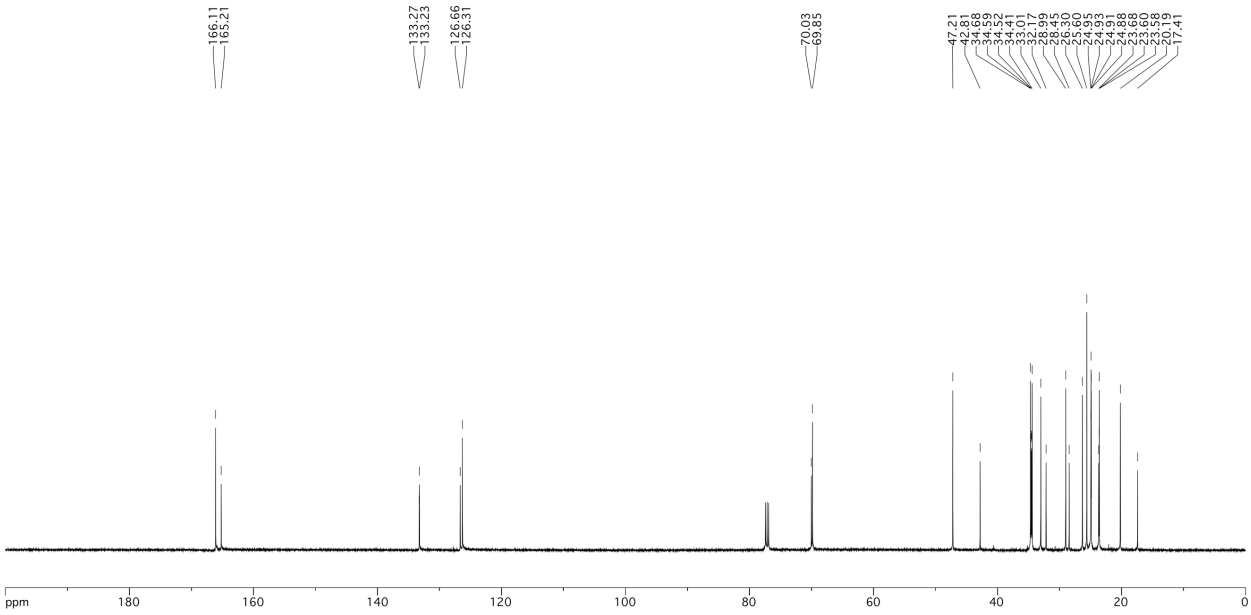


Trivertal is commercially available as a mixture of 2 diastereoisomers, consequently compound **5.27** was obtained in 93% yield (204 mg) as mixture of 2 diastereoisomers in a 68:32 % ratio. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 5.1 Hz, 1 H), 7.36 (dd, J = 6.7, 0.7 Hz, 1 H), 5.18 (s, 1H), 5.08 (s, 1 H), 2.78 (td, J = 10.0, 4.5 Hz, 2 H), 2.29-2.35 (m, 1 H), 2.01 (s, 1 H), 1.82 (s, 6 H), 1.64 (d, J = 8.9 Hz, 6 H), 1.51 (d, J = 16.7 Hz, 10 H), 1.32-1.44 (m, 5 H), 1.13-1.20 (m, 4 H), 1.07 (t, J = 12.5 Hz, 2 H), 0.82 (dd, J = 7.0, 1.4 Hz, 3 H) 0.77 (dd, J = 7.0, 1.4 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 166.1, 165.2, 133.27, 133.23, 126.7, 126.3, 70.03, 69.85, 47.2, 42.8, 34.68, 34.59, 34.52, 34.41, 33.0, 32.2, 29.0, 28.4, 26.3, 25.6, 24.95, 24.93, 24.91, 24.88, 23.68, 23.60, 23.58, 20.2, 17.4

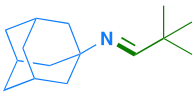
^{1}H spectrum



^{13}C{^{1}H} spectrum

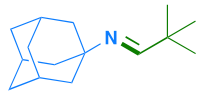


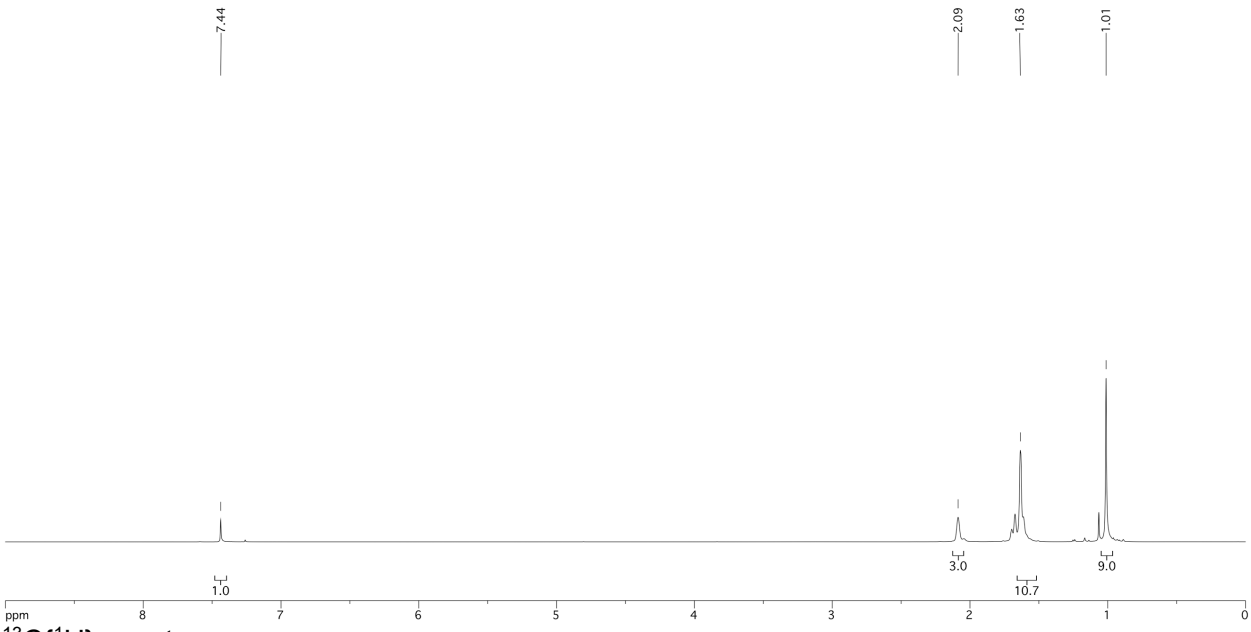
5.28



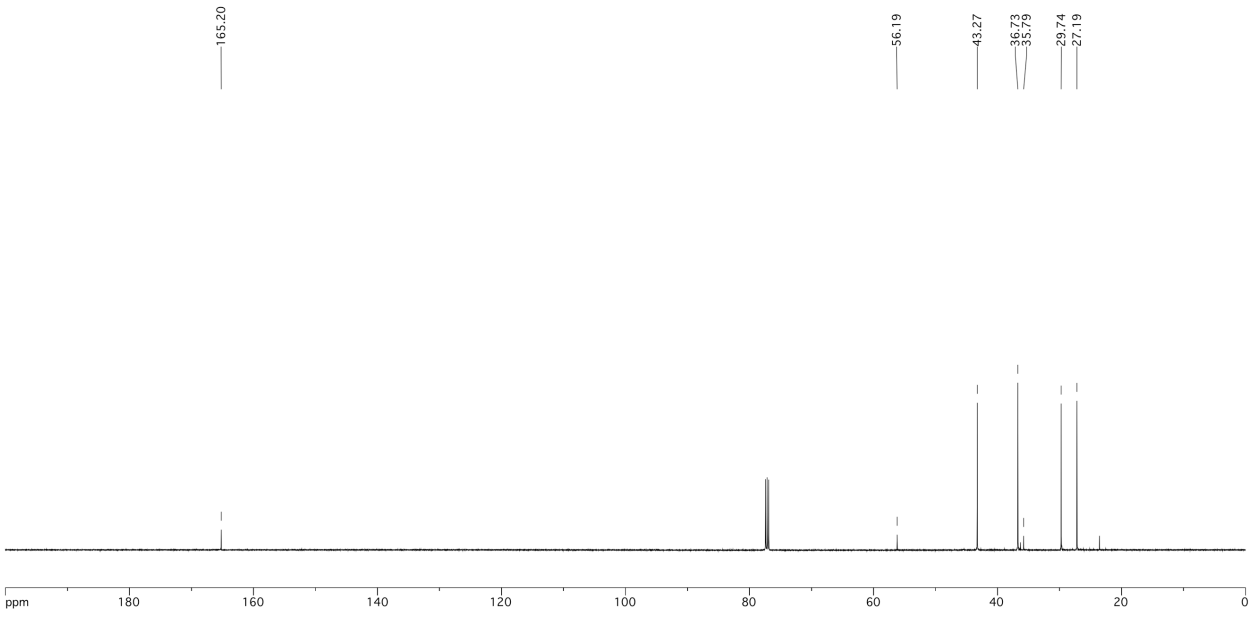
Compound **5.28** was isolated in 94% yield (206 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (s, 1 H), 2.09 (s, 3 H), 1.63 (s, 11 H) 1.01 (s, 9 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 165.2, 56.2, 43.3, 36.7, 35.8, 29.7, 27.2.

^{1}H spectrum

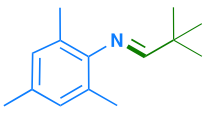




$^{13}C\{^{1}H\}$ spectrum

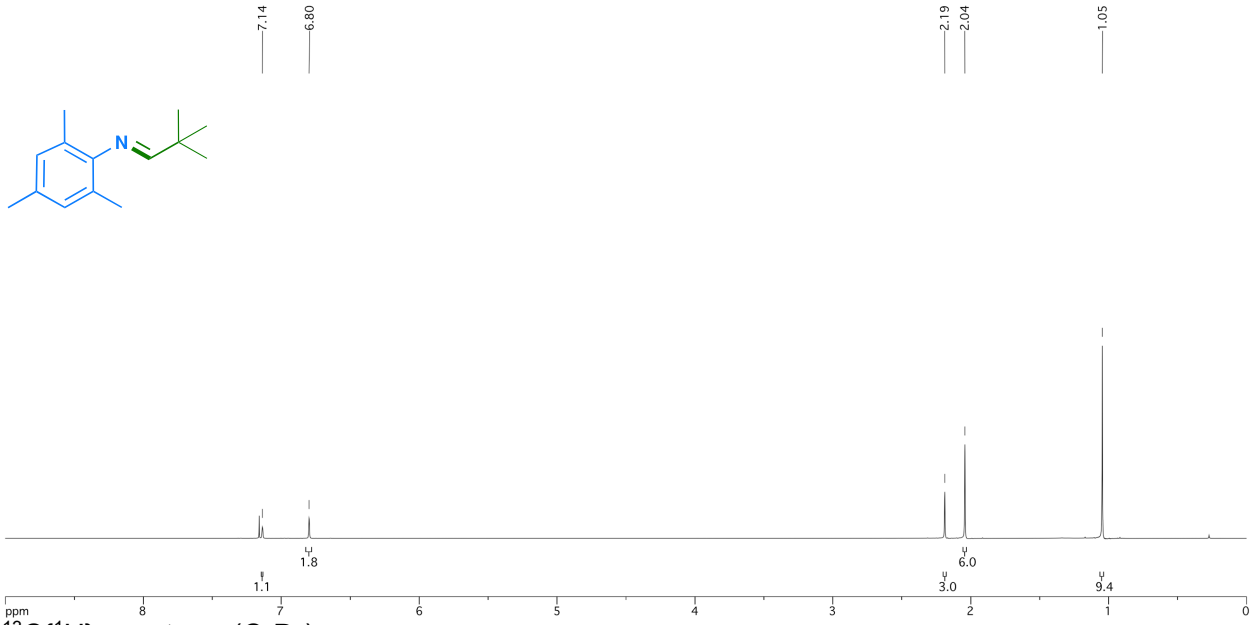


5.29

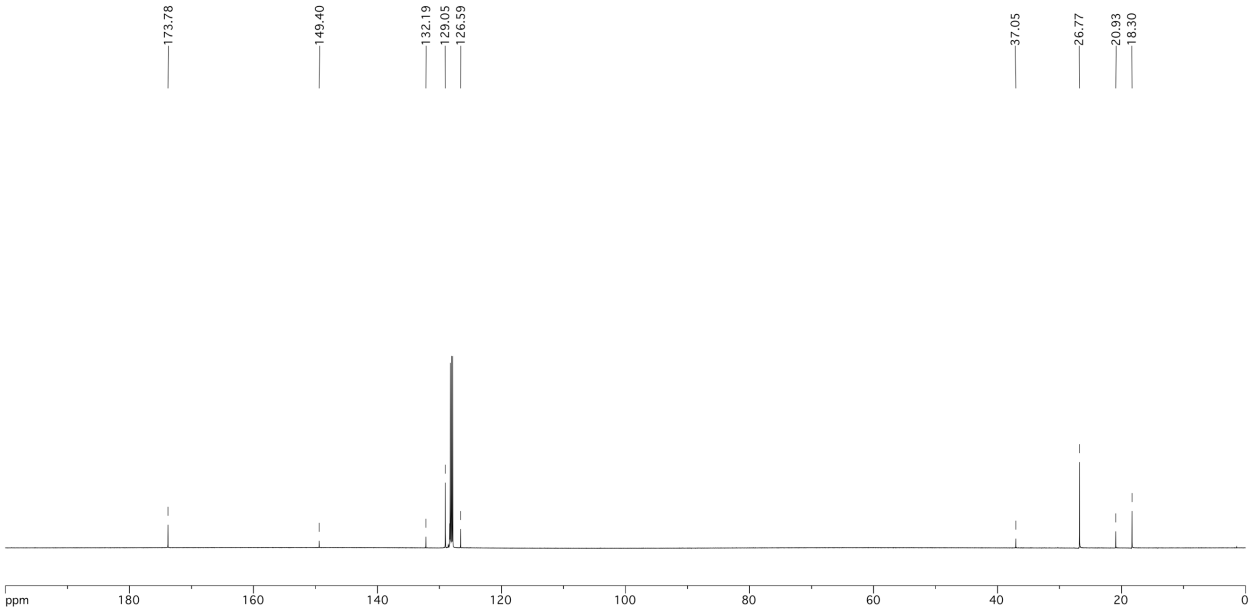


The reaction time is 24h. Compound **5.29** was isolated in 95% yield (193 mg). ^{1}H NMR (500 MHz, C_6D_6): δ , 7.14 (s, 1 H), 6.80 (s, 2 H), 2.19 (s, 3 H), 2.04 (s, 6 H) 1.05 (s, 9 H). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): δ 173.8, 149.4, 132.2, 129.1, 126.6, 37.0, 26.8, 20.9, 18.3.

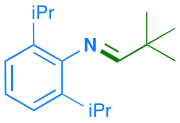
^{1}H spectrum (C_6D_6)



^{13}C{^{1}H} spectrum (C_6D_6)

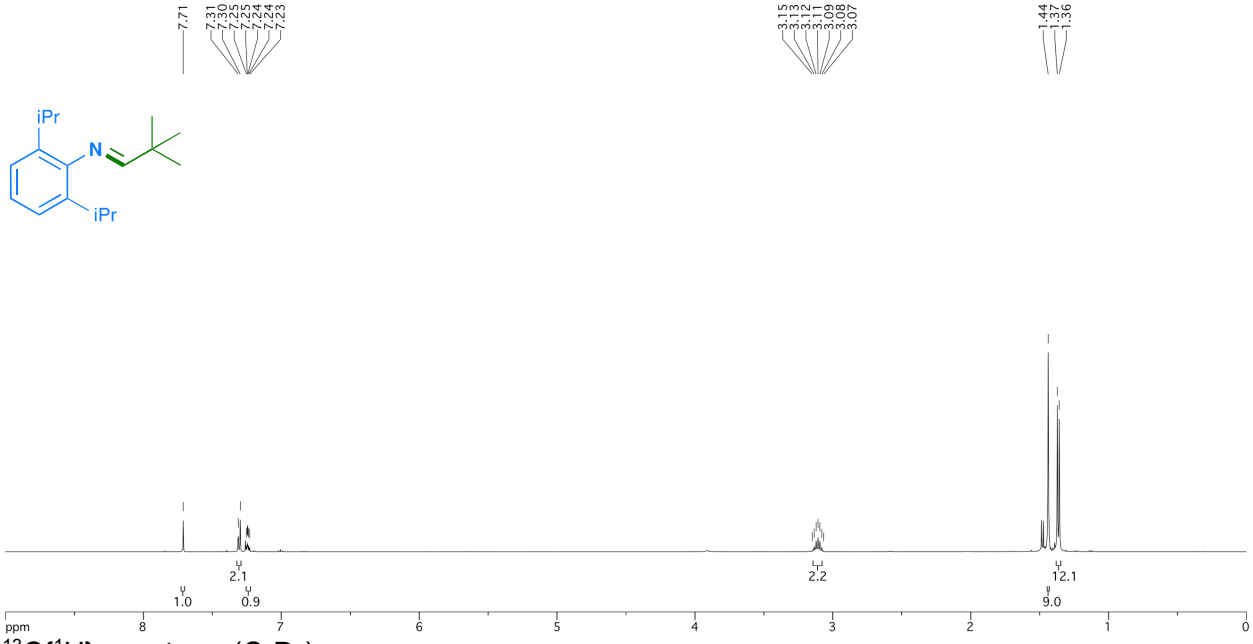


5.30

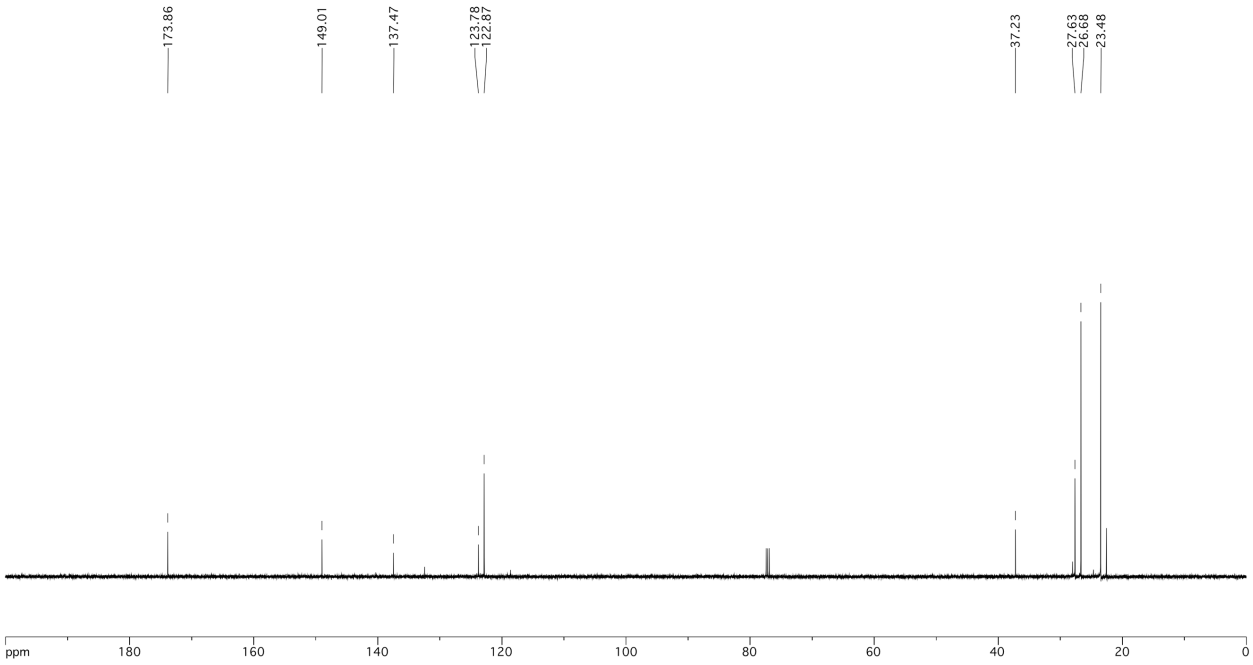


The reaction time is 48h. Compound **5.30** was isolated in 91% yield (223 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 1 H), 7.30 (d, J = 7.1 Hz, 2 H), 7.23-7.25 (m, 1 H), 3.11 (sept, J = 7 Hz, 2 H), 1.44 (s, 9 H) 1.36 (d, J = 7.0 Hz, 12 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 173.9, 149.0, 137.5, 123.8, 122.9, 37.2, 27.6, 26.7, 23.5.

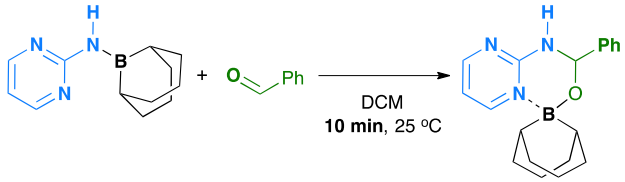
^{1}H spectrum (C_6D_6)



^{13}C{^{1}H} spectrum (C_6D_6)



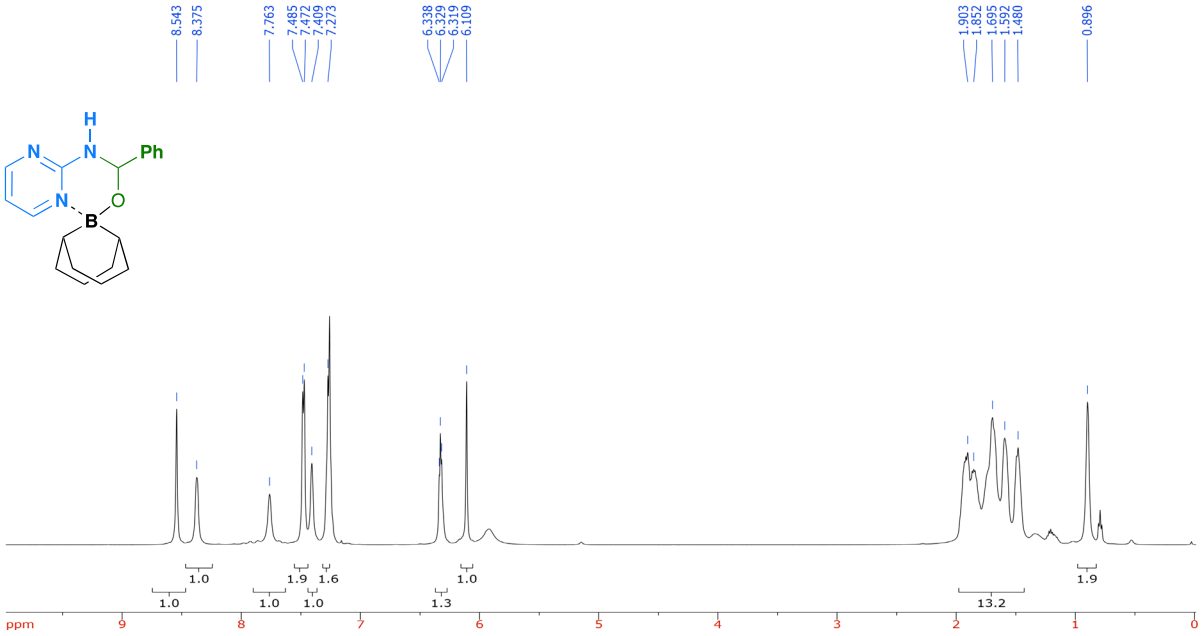
3) Preparation of intermediate I^{Py}.



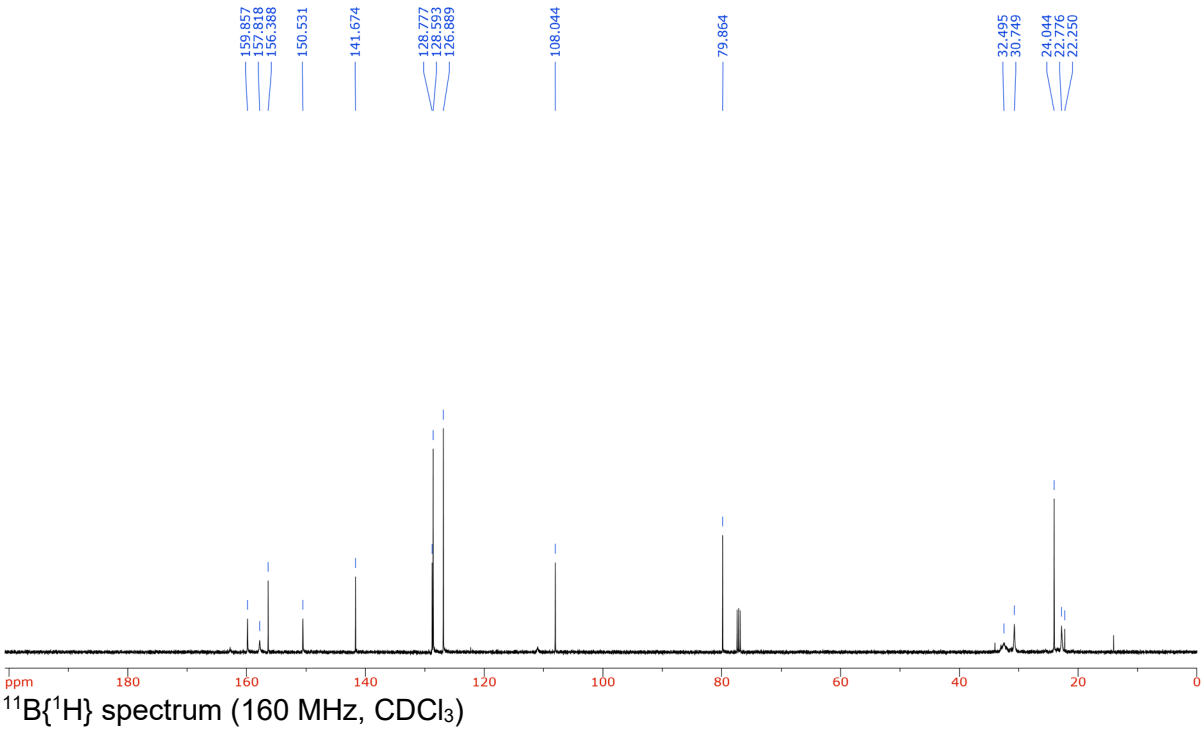
A Schlenk tube under argon was charged with pyrimidine-amino-borabicyclononane (100 mg, 0.46 mmol, 1 eq.) and 0.42 mL anhydrous dichloromethane (1 M solution). After addition of benzaldehyde (47.4 µL, 0.46 mmol, 1 eq.) the reaction mixture was stirred for 10 minutes at 25 °C to afford a light-yellow solution. Evaporation of the volatiles under vacuum, and trituration of the residue with 5 mL of pentane (12 hours) afforded the title compound as a light-yellow powder. Filtration and drying of the residue under vaccum afforded **I^{Py}** in 99% yield (192 mg). Single crystals suitable for X-ray crystallography were grown by vapor diffusion of pentane into a saturated chloroform solution at -40 °C for 48 h M.P. 138.6-141.3 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.54 (s, 1 H), 8.38 (s broad, 1 H), 7.76 (s broad, 1 H), 7.48 (d, J = 7 Hz, 2 H), 7.41 (s broad, 1 H), 7.27 (d, J = 7 Hz, 2 H), 6.33 (t, J = 5 Hz, 1 H), 6.11 (s, 1 H), 1.69 (m, 12 H), 0.90 (s, 2 H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.9, 157.8, 156.4, 150.5, 141.7, 128.8, 128.6, 126.9, 108.0, 79.9, 32.5 (broad), 30.7, 24.0, 22.8, 22.3 ppm. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 5.95 (s broad) ppm.

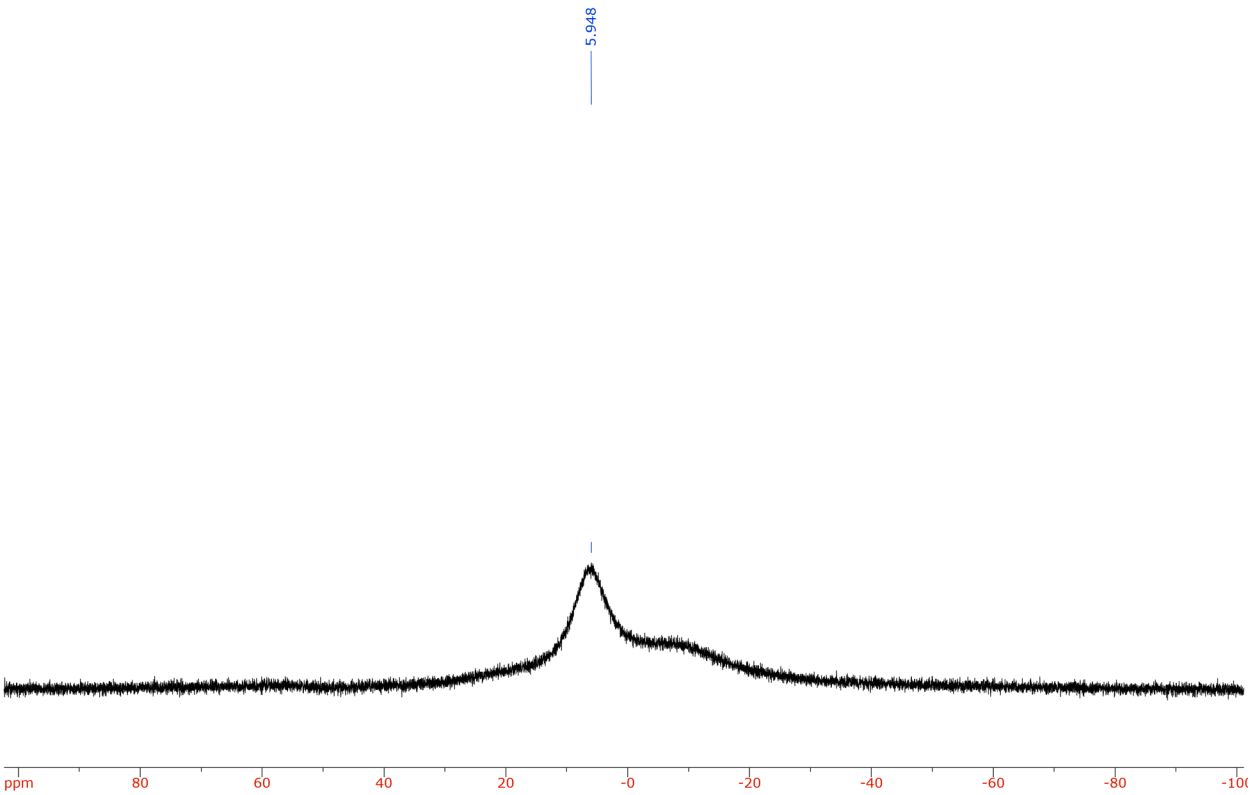
^{1}H spectrum (500 MHz, $CDCl_3$)



^{13}C{^{1}H} spectrum (125 MHz, $CDCl_3$)



^{11}B{^{1}H} spectrum (160 MHz, $CDCl_3$)

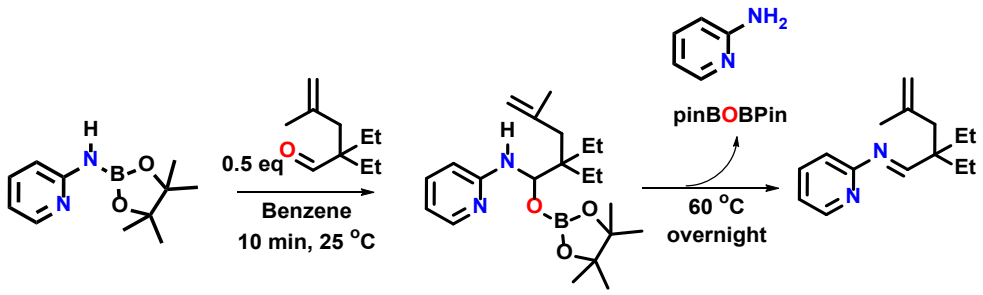


Crystal data and structure refinement for compound_IPy (CCDC – 1883941)

Identification code	compound_IPy
Empirical formula	$C_{19}H_{24}BN_3O$
Formula weight	321.22
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$

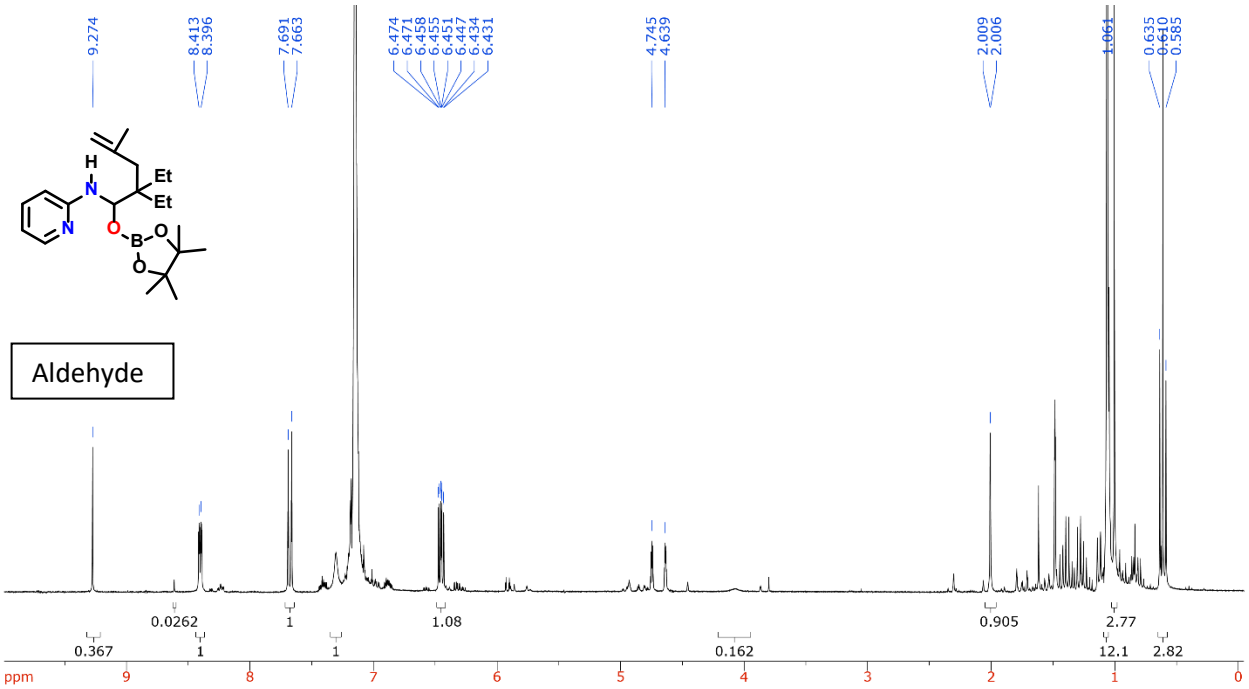
a/Å	11.5481(2)
b/Å	12.6068(3)
c/Å	11.6167(2)
α/°	90
β/°	94.2472(12)
γ/°	90
Volume/Å^3	1686.57(6)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.614
F(000)	688.0
Crystal size/mm^3	0.1 × 0.09 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.37 to 136.444
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 14, -11 ≤ l ≤ 13
Reflections collected	10466
Independent reflections	3066 [R_{int} = 0.0281, R_{sigma} = 0.0271]
Data/restraints/parameters	3066/0/217
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1242
Final R indexes [all data]	R_1 = 0.0603, wR_2 = 0.1304
Largest diff. peak/hole / e Å^{-3}	0.68/-0.30

4) Preparation of ring-opened intermediate

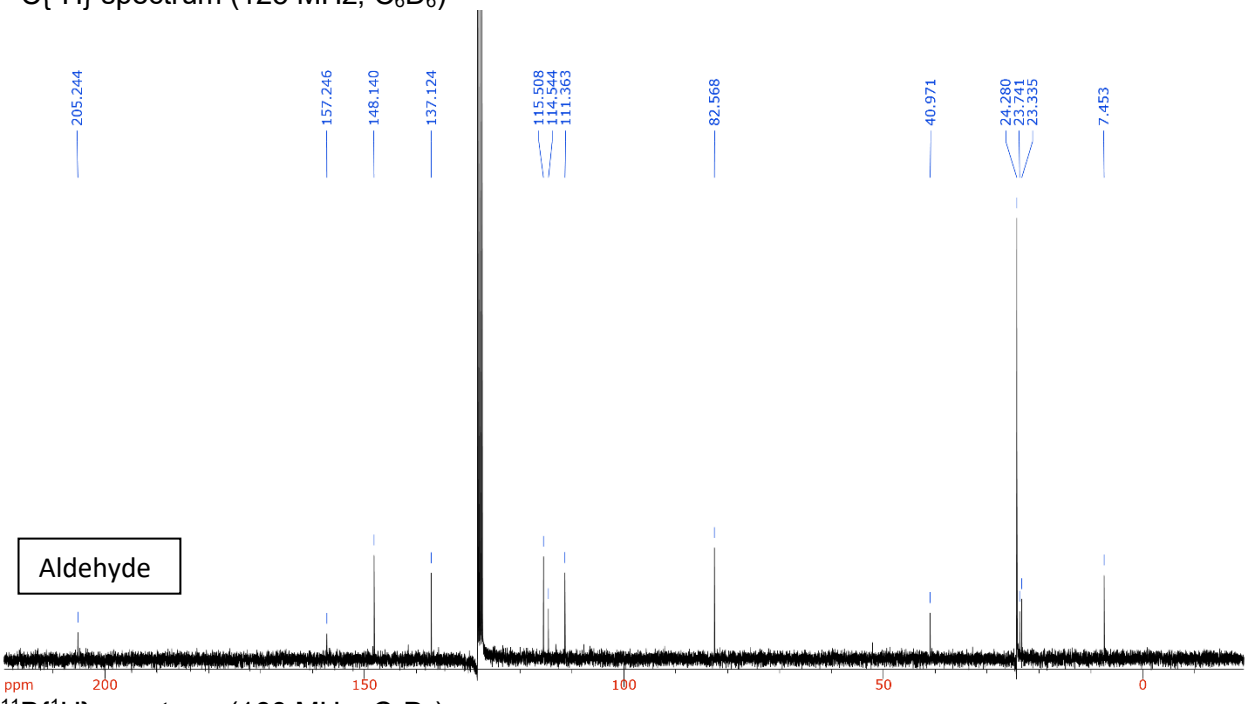


A Schlenk tube under argon was charged with pyridine-amino-pinacolatoborane (772 mg, 3.5 mmol, 1 eq.) and 3 mL anhydrous C_6D_6 (1.2 M solution). After addition of aldehyde (270 mg, 1.75 mmol, 0.5 eq.) the reaction mixture was stirred for 10 minutes at 25 °C to afford a light-yellow solution. Aliquot for NMR was taken from the reaction mixture to see the intermediate product. Schlenk flask was then placed in 60 °C oil bath overnight. Final aldimine product was isolated by removing the volatiles under vacuum at 80 °C in 93% yield based on starting aldehyde. Note, among the volatile compounds are solids that sublime; therefore, heating/pumping overnight is recommended since the lack of liquids does not necessarily ensure purity. Sometimes, the product can still be quite pure at shorter pump times. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.62 (s, 1 H), 8.32 (d, 1 H), 7.11 (m, 2 H), 6.57 (t, 1 H), 4.86 (s, 1 H), 4.81 (s, 1 H), 2.30 (s, 2 H), 1.80-1.50 (m, 7 H), 0.83 (t, 6 H), ppm. ^{13}C NMR (C_6D_6, 125 MHz): δ 175.5, 161.6, 148.8, 142.6, 137.2, 121.0, 119.1, 114.5, 46.1, 43.9, 26.3, 24.5, 7.9 ppm.

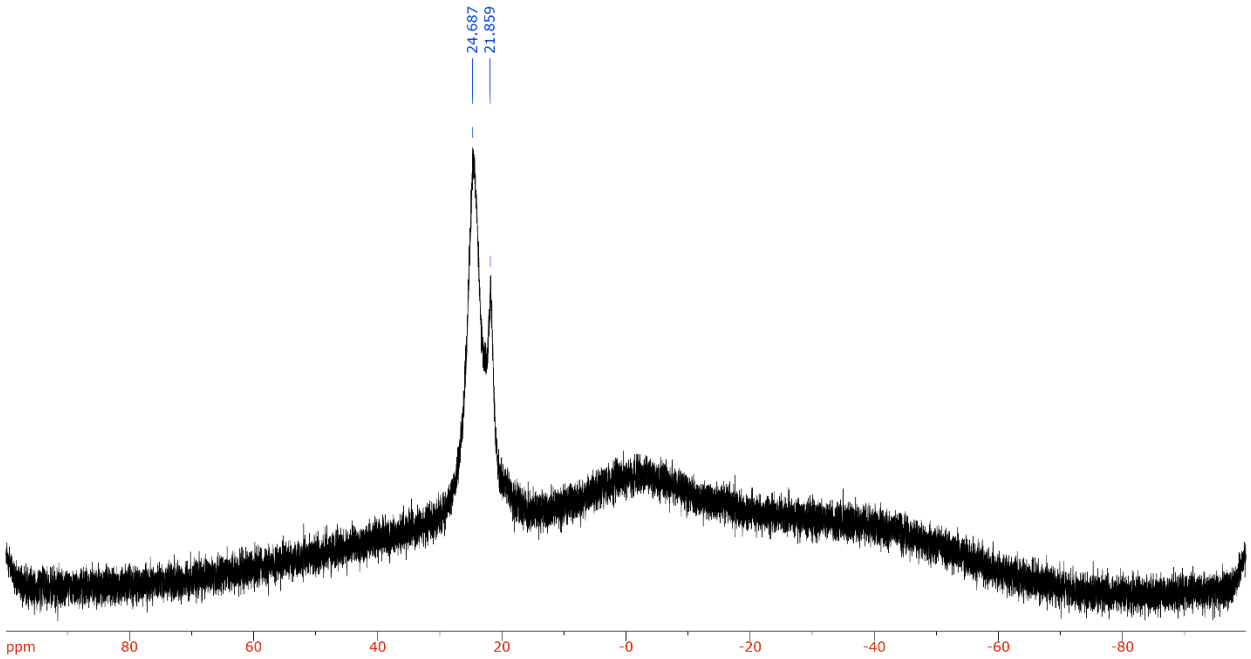
^{1}H spectrum (500 MHz, C_6D_6) (unpurified reaction aliquot)



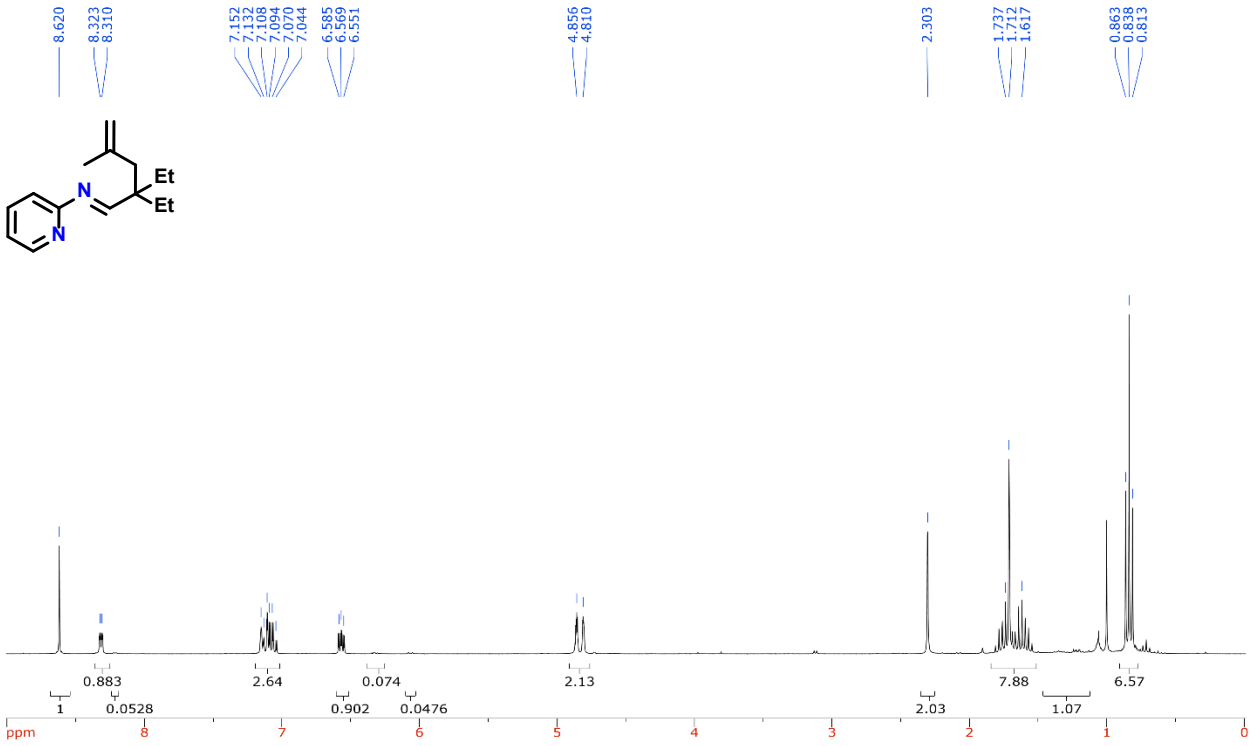
$^{13}C\{^{1}H\}$ spectrum (125 MHz, C_6D_6)



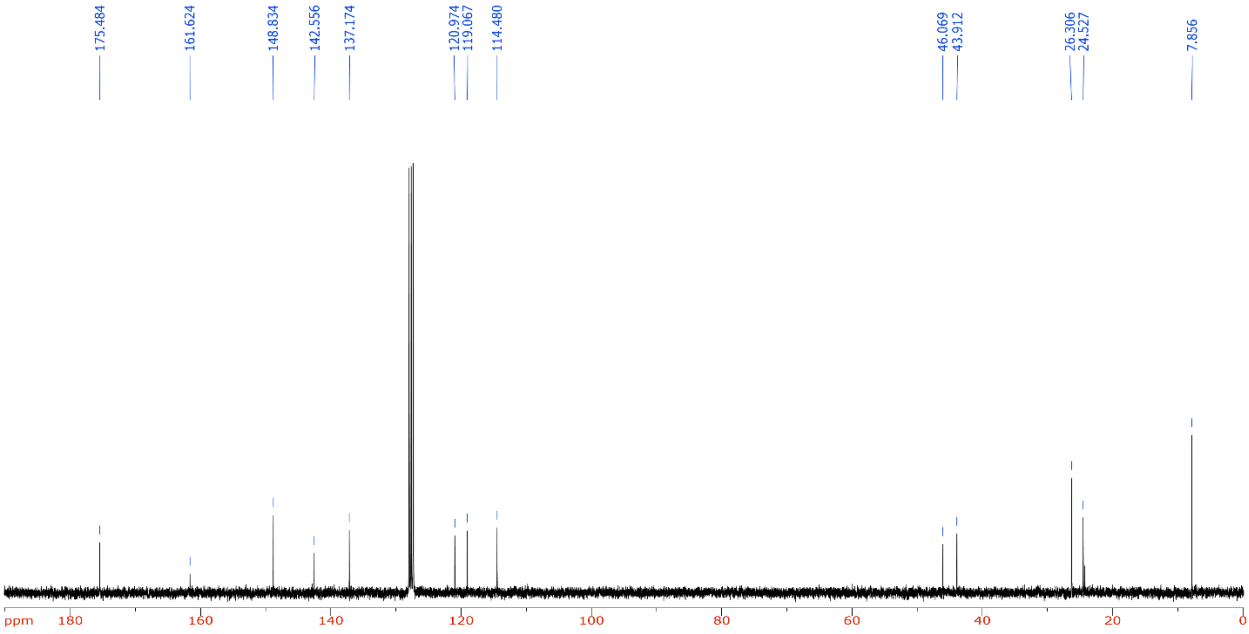
$^{11}B\{^{1}H\}$ spectrum (160 MHz, C_6D_6)



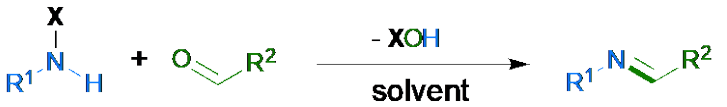
^{1}H spectrum (500 MHz, C_6D_6)



^{13}C{^{1}H} spectrum (125 MHz, C_6D_6)



5) Method comparison



X = H *(Method 1 and 2)*
X = BPin or 9-BBN *(this work)*

NMR yields

R^1	R^2	Time (h)	Conc. (M)	Method 1	Method 2	This work
Cy	^{t}Bu	1	1.1[a]	99	99	99 (Bpin)
Mes	Ph	1	1.1[a]	13	72	99 (Bpin)
Mes	$CH(Et)_2$	1	1.1[a]	46	30	99 (Bpin)
$C_6F_2H_3$	Ph	1	2[a]	4	18	99 (9-BBN)
$C_6F_2H_3$	$CH(Et)_2$	1	2[a]	5	8	99 (9-BBN)
C_6F_5	Ph	12	2[b]	1	69	96 (9-BBN)
C_6F_5	$CH(Et)_2$	3	2[b]	2	24	93 (9-BBN)

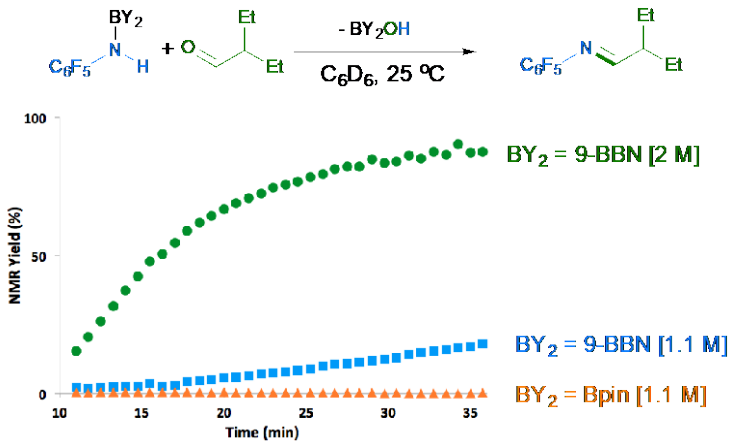
[a] reaction solvent is C_6H_6; [b] reaction solvent is cyclohexane

Method 1: To a Schlenk tube charged with degassed solvent (1 mL) and freshly activated sieves, the amine and the aldehyde (1:1 mol ratio) were added under stirring in amounts corresponding to the desired concentration. After the designated amount of time, an aliquot was removed from the reaction mixture and diluted in C_6D_6 to determine the NMR yield.

Method 2: To a Schlenk tube charged with degassed solvent (1 mL) and freshly activated sieves, the amine and pyrrolidine (1: 0.2 mol ratio) were added under stirring in amounts corresponding to the desired concentration. Then, the aldehyde (1 eq) was added. After the designated amount of time, an aliquot was removed from the reaction mixture and diluted in C_6D_6 to determine the NMR yield.

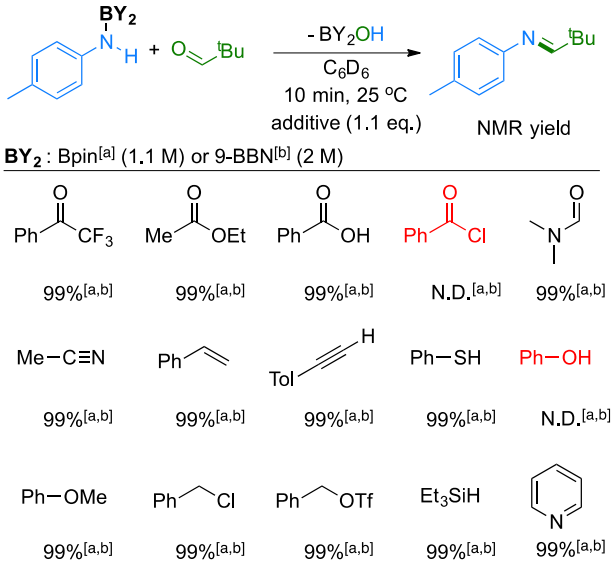
This work: Under argon, a Schlenk tube was charged with the solvent, aminoborane (1 mmol), and aldehyde (1 mmol), while stirring. The concentration for each substrate was adjusted to 1.1M when using BPin and 2M for 9-BBN. After stirring at 25 °C for the designated amount of time, an aliquot of the solution was taken and diluted in C_6D_6 to determine NMR yield.

6) Kinetic experiments



All kinetic experiments were performed in a *J-Young* NMR tube at room temperature on a Bruker 300MHz NMR spectrometer using the multi_zgvd command. Conversions were measured by following the change in characteristic signals for the starting aldehyde and aldimine. For each kinetic run, the *J-Young* tube was charged with the appropriate amount of solvent, aminoborane (1 mmol), and aldehyde (1 mmol) and placed into the NMR spectrometer as fast as possible.

7) Modified Glorius robustness screen



In a J-Young NMR tube under argon, *p*-TolNHBR$_2$ (0.55 mmol, 1 eq.) was dissolved in C_6D_6 (BR$_2$ = pinacol: 1.1 M = 500 µL C_6D_6; BR$_2$ = BBN: 2 M = 275 µL C_6D_6). The functional group additive (0.61 mmol, 1.1 eq.) was added and the mixture was shaken to homogenize. After 10 minutes at room temperature, the ^{1}H NMR spectrum was collected to ensure that the aminoborane does not react with the additive. In cases where no reaction occurred, the tube was reintroduced into the glovebox where pivaldehyde (0.55 mmol, 1 eq.) was added and the resulting mixture shaken and left at room temperature for 10 minutes. At this time, NMR yields were determined by ^{1}H NMR spectroscopy.

DFT Methods and Cartesian Coordinates

All calculations were performed with the Gaussian09[86] program package using density functional theory (DFT). All calculations were performed with the M06-2X functional,[83] employing 6-31g** basis set[239, 258] in a benzene polarized continuum solvent model, PCM.[152, 259] Ground states and transition states were optimized without constraints at the corresponding level of theory and uniquely characterized by occurrence of zero or one imaginary frequency, respectively, as verified by the corresponding frequency calculation. Gibbs free reaction energies and enthalpies were calculated for standard conditions (p = 1 atm, T = 298 K). All output and checkpoint files

used in figures are available for download, free of charge, from UCSD Library Digital Collections.[241]

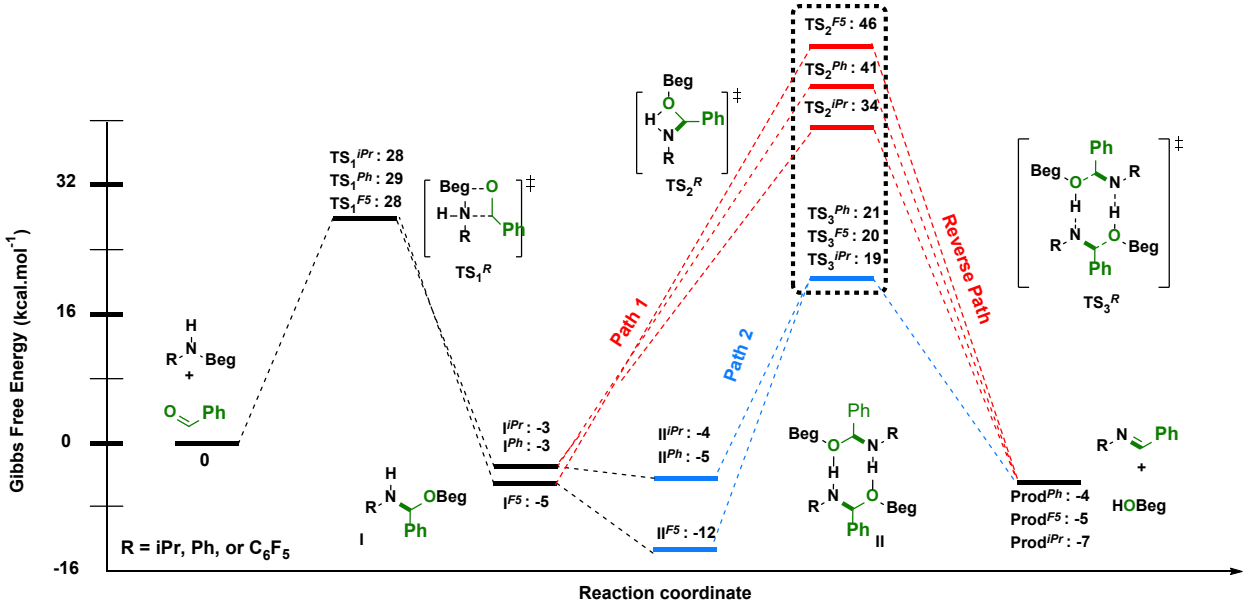


Figure 5.6: Proposed reaction mechanism calculated at M062X 6-31G** level of theory using RNH-Beg (R = iPr, Ph or C_6F_5) and benzaldehyde.

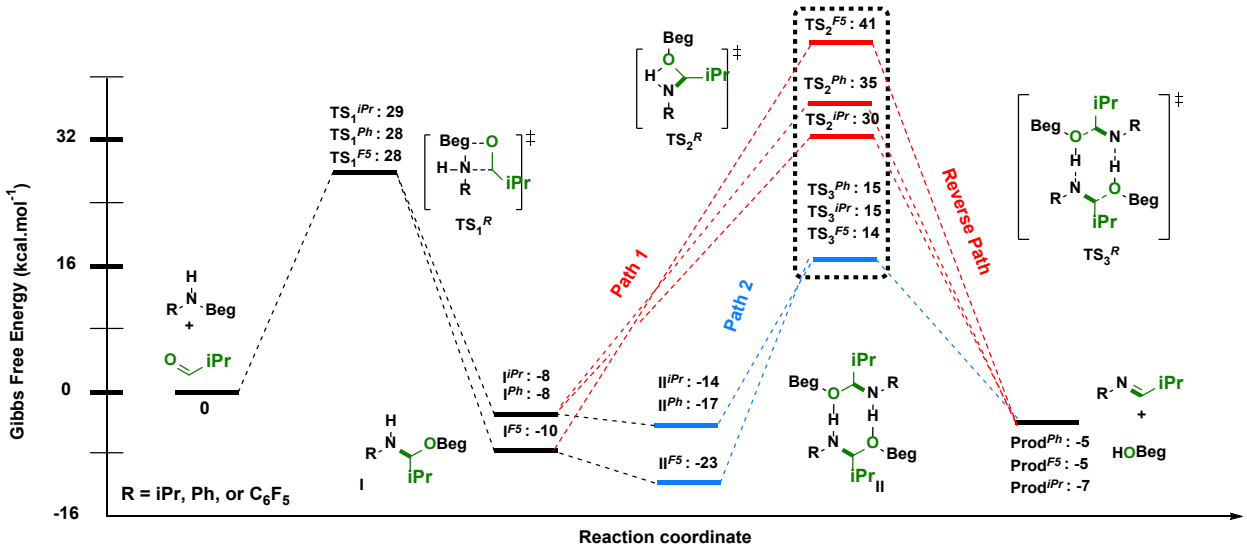


Figure 5.7: Proposed reaction mechanism calculated at M062X 6-31G** level of theory using RNH-Beg (R = iPr, Ph or C_6F_5) and isobutyraldehyde.

Chapter 6- Conclusions

The most elementary lesson of quantum mechanics, in my mind, is that electrons are allowed to take only a few, select shapes and energies. [1-3] My interest is in how such a principle is experienced in daily life, which I think cannot be more readily obvious than in the behavior of molecules. So, throughout this dissertation I have sought to demonstrate how the principles of quantum mechanics can be harnessed for the synthesis, characterization, and application of new, useful ambiphilic molecules. Though it is true that any class of molecule could have been chosen for such an endeavor, I decided to focus on a few unusual ones like carbenes and aminoboranes.

Through the synthesis of CAAC-6 discussed in chapter 2,[75] we showed that molecular orbital interactions can be harnessed to drive the reactivity of singlet carbenes to new heights, without the carbenes breaking down. The new carbenes are powerful σ-donors, strong π-acceptors, and are even capable of alkyl C-H activation if a substituent gets too close.

On the other hand, in chapter 3, we demonstrated how some carbene-selenium adducts will undergo significant distortions to facilitate the overlap of orbitals, even allowing unusual interactions between alkyl hydrogens and selenium atoms, detectable by single crystal X-ray crystallography and NMR.[76, 134] These unexpected H-Se interactions cause major deviations from expected trends in ^{77}Se NMR, casting doubt on the usefulness of one popular method for the measurement of carbene π-acidity.

After such a close look at carbene empty orbital measurements, we trained our sights on techniques for studying carbene lone pairs in chapter 4. Here, we sought a method to accurately scale the power of carbene σ-donation. More established methods, like the Tolman Electronic Parameter (TEP), did not satisfactorily disentangle the carbene lone pair from its nearby acidic empty orbital, and thus often produce conflicting results. Also, a number of newer quantitative methods have thus far struggled to be widely applicable. Wanting to fill this gap in our understanding, we developed a proton exchange method and ranked 16 very different types of carbenes by their σ-donor strength. This study highlighted a number of major errors present in

popular density functional theory (DFT) methods and suggests caution when using DFT in the absence of experimental measurement.

Returning to the broader topic of harnessing the quantization of electrons to make important molecules, in chapter 5, we looked at the frontier orbitals of a class of molecules which just became readily available: primary aminoboranes. Realizing that their electron configuration closely resembles that of phosphorus ylides, an important class of molecules that won Georg Wittig a share of the 1979 Nobel Prize in Chemistry, we sought to use aminoboranes for an analogous transformation. As hypothesized, primary aminoboranes are capable of transforming C-O double bonds into C-N double bonds.[241, 260] Furthermore, the preliminary studies on the reaction mechanism (with DFT and the isolation of intermediates) suggest that the method is orthogonal to conventional C-N bond forming methods. In fact, the formation of aldimines from aminoboranes does not seem to occur under equilibrium conditions, contrasting with popular dehydration methods. Such stark differences may lead to creative uses of this new method to generate products conventionally inaccessible with aldimine condensations.

Thus, by trying my hand at the synthesis, measurement, and use of several types of reactive molecules, I have been privileged with experience in many aspects of chemistry and the quantum phenomena that underlie them. However, the few ambiphilic molecules explored in this dissertation occupy but a small subset of interesting species that must obey the selection rules of quantum mechanics. My hope is that my discussion of how quantum mechanics permeates my interests will inspire the next generation to consider how it impacts theirs.

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