Reactivity Studies of Boron-Nitrogen Containing Reactive Intermediates Using Matrix Isolation and Computational Tools

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॥ तत्परिवर्तनं भव ॥

"Be the change you wish to see in the world."

To my sister Varsha

You are with us.

Acknowledgments

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Table of Contents

Abbreviations and Symbols

Å	Ångström
°C	Grad Celsius
cm^{-1}	Wavenumber
FVP	Flash vacuum pyrolysis
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
IR	Infrared
UV-Vis	Ultraviolet-visible
K	Kelvin
λ	Wavelength
NBO	Natural bond orbital
NLMO	Natural localized molecular orbital
nm	Nanometer
ν	Frequency
TS	Transition state
ZPVE	Zero-point vibration energy
IRC	Intrinsic reaction coordinate
MP2	Second-order Møller-Plesset perturbation theory
SCS	Spin-component scaled
TD	Time dependent
DFT	Density functional theory
CC	Coupled cluster
sccm	Standard cubic centimeters per minute
PES	Potential energy surface
Ar	Argon
Xe	Xenon

Abstract

Cyclic iminoboranes are a class of organic compounds which were studied in this thesis for isolation and reactivity through a combined computational and experimental approach. Matrix isolation experiments generated and isolated these reactive species, with computational methods supporting the experimental findings.

The computational studies on the reactivity of 1,2-azaborinine, a cyclic iminoborane, focusing on (2 + 2) cycloaddition and (2 + 4) cycloaddition, with various organic π-substrates revealed the barrierless formation of Lewis acid-base complexes. The complexes are the central reactive intermediate in any further reaction. The symmetry allowed (2 + 4) cycloaddition of 1,2-azaborinine with organic π-substrate is preferred over symmetry forbidden (2 + 2) cycloaddition reaction.

Dibenzo derivatives of 1,2-azaborinine were investigated for spectroscopic evidence and reactivity insights. Dibenzo[c,e][1,2]azaborinine was generated through gas-phase thermolysis, under matrix isolation conditions, it resulted in the formation of a dinitrogen adduct. Steric hindrance from tert-butyl groups in 2,4,7,9-tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine prevented nitrogen fixation during generation and isolation under cryogenic matrix conditions.

The impact of ring size on cyclic iminoborane reactivity was investigated by isolating and characterizing 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine, a seven-membered cyclic iminoborane. Despite showing no interaction with dinitrogen, it unexpectedly underwent a (2 + 2) cycloaddition reaction with C_2H_4.

Zusammenfassung

Cyclische Iminoborane sind eine Klasse von organischen Verbindungen, deren Isolierung und Reaktivität in dieser Arbeit durch einen kombinierten computerchemischen und experimentellen Ansatz untersucht wurde. Durch Matrixisolierungsexperimente wurden diese reaktiven Spezies erzeugt und isoliert, wobei die experimentellen Ergebnisse durch quantenchemische Berechnungen unterstützt wurden.

Die computerchemischen Untersuchungen zur Reaktivität von 1,2-Azaborinin, einem cyclischen Iminoboran, mit Schwerpunkt auf der (2 + 2) -Cycloaddition und der (2 + 4) -Cycloaddition, mit verschiedenen organischen π-Substraten ergaben die barrierefreie Bildung von Lewis-Säure-Base-Komplexen. Die Komplexe sind das zentrale reaktive Zwischenprodukt in jeder weiteren Reaktion. Die symmetrieerlaubte (2 + 4) -Cycloaddition von 1,2-Azaborinin mit einem organischen π-Substrat wird gegenüber der symmetrieverbotenen (2 + 2)-Cycloaddition bevorzugt.

Dibenzoderivate von 1,2-Azaborinin wurden auf spektroskopischen Nachweis und Reaktivität hin untersucht. Dibenzo[c,e][1,2]azaborinin wurde durch Gasphasenthermolyse erzeugt und führte unter Matrixisolierungsbedingungen zur Bildung eines Stickstoffaddukts. Die sterische Hinderung durch tert-Butylgruppen in 2,4,7,9-Tetra-*tert*-Butyldibenzo[c,e][1,2]azaborinin verhinderte die Stickstofffixierung während der Erzeugung und Isolierung unter kryogenen Matrixbedingungen.

Der Einfluss der Ringgröße auf die Reaktivität zyklischer Iminoborane wurde durch Isolierung und Charakterisierung von 1-(*tert*-Butyldimethylsilyl) -1,3,2-diazaborepin, einem siebengliedrigen zyklischen Iminoboran, untersucht. Obwohl es keine Wechselwirkung mit Stickstoff zeigte, führte es unerwartet eine (2 + 2)-Cycloadditionsreaktion mit C_2H_4 durch.

List of Publications

Publications Included in the Thesis

Publication I

Reactions of 1,2-Azaborinine, a BN-Benzyne, with Organic π Systems.

Divanshu Gupta and Holger F. Bettinger *J. Org. Chem.* **2023,** *88* (13), 8369-8378.

Publication II

Direct Spectroscopic Identification of BN-Arynes and Subtle Steric Effects on Nitrogen Fixation

Divanshu Gupta, Constanze Keck, Christina Tönshoff, Virinder Bhagat, Raphael Strobel, Manuel Eder, Patrick Baylère, Stéphane Labat, Anna Chrostowska, and Holger F. Bettinger, *Chem. Eur. J.* **2023,** e202302444.

Publication III

Strain induced reactivity of cyclic iminoboranes: the (2 + 2) cycloaddition of a 1H-1,3,2-diazaborepine with ethene.

Divanshu Gupta, Ralf Einholz and Holger F. Bettinger, *Chem. Sci.* **2024**, 15, 666-674.

Other Publications

Solution Phase Reactivity of Dibenzo[c,e][1,2]azaborinine: Activation and Insertion into Si-E Single Bonds (E=H, OSi(CH3)3, F, Cl) by a BN-Aryne

Constanze Keck, Jennifer Hahn, Divanshu Gupta and Holger F. Bettinger, *Chem. Eur. J.* **2022,** *28*, e202103614.

Energetics of Formation of Cyclacenes from 2,3-Didehydroacenes and Implications for Astrochemistry

Divanshu Gupta, Alain Omont and Holger F. Bettinger, *Chem. Eur. J.* **2021,** *27*, 4605.

Personal Contributions

Publication I

Reactions of 1,2-Azaborinine, a BN-Benzyne, with Organic π Systems.

Divanshu Gupta and Holger F. Bettinger *J. Org. Chem.* **2023,** *88* (13), 8369-8378.

Divanshu Gupta: Computational data generation using Gaussian 16 and ORCA 5.0.1 quantum chemistry software. Additionally, interpretation of the generated data along with writing the publication was done.

Holger F. Bettinger: Provided the scientific ideas pertinent to the study. Furthermore, offered his suggestions/corrections during the writing process of the publication.

Publication II

Direct Spectroscopic Identification of BN-Arynes and Subtle Steric Effects on Nitrogen Fixation

Divanshu Gupta, Constanze Keck, Christina Tönshoff, Virinder Bhagat, Raphael Strobel, Manuel Eder, Patrick Baylère, Stéphane Labat, Anna Chrostowska, and Holger F. Bettinger, *Chem. Eur. J.* **2023,** e202302444.

Divanshu Gupta: Experimental data generation using matrix isolation setup related to precursor **6**. Additionally, computational data generation using different quantum chemistry software. Also, interpretation of the generated data along with writing the publication was done.

Christina Tönshoff: Did the experimental work on the isolation of azidoborole **2** in different matrices under cryogenic conditions.

Constanze Keck, Raphael Strobel: Synthesized the azide precursors **2●py** and **6.**

Virinder Bhagat: Supported in the generation and analysis of EPR spectroscopy data.

Manuel Eder: Performed matrix isolation experiments of precursor **6** as part of his master's practical.

Patrick Baylère, Stéphane Labat, Anna Chrostowska: Performed and characterized UV-PE spectroscopy measurements of compound **2●py**.

Holger F. Bettinger: Provided the scientific ideas pertinent to the study. Furthermore, offered his suggestions/corrections during the writing process of the publication.

Publication III

Strain induced reactivity of cyclic iminoboranes: the (2 + 2) cycloaddition of a 1H-1,3,2-diazaborepine with ethene.

Divanshu Gupta, Ralf Einholz and Holger F. Bettinger, *Chem. Sci.* **2024**, 15, 666-674.

Divanshu Gupta: Experimental data generation using matrix isolation setup related to precursor **3** and its reaction with CO and C_2H_4. Additionally, computational data generation using different quantum chemistry software. Also, interpretation of the generated data along with writing the publication was done.

Ralf Einholz: Synthesized the azide precursor **3** and characterized it using NMR spectroscopy.

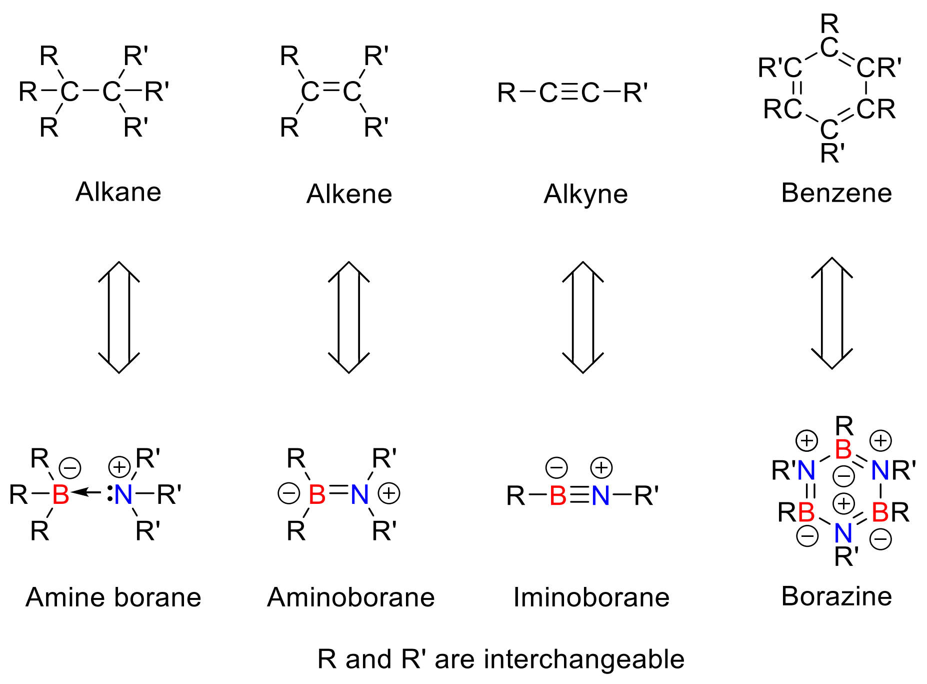
Holger F. Bettinger: Provided the scientific ideas pertinent to the study. Furthermore, offered his suggestions/corrections during the writing process of the publication.

* *The chemical species are numbered as they appear in the respective publications.*

1 Introduction

1.1 Comparative Study of Isostructural CC and BN Compounds

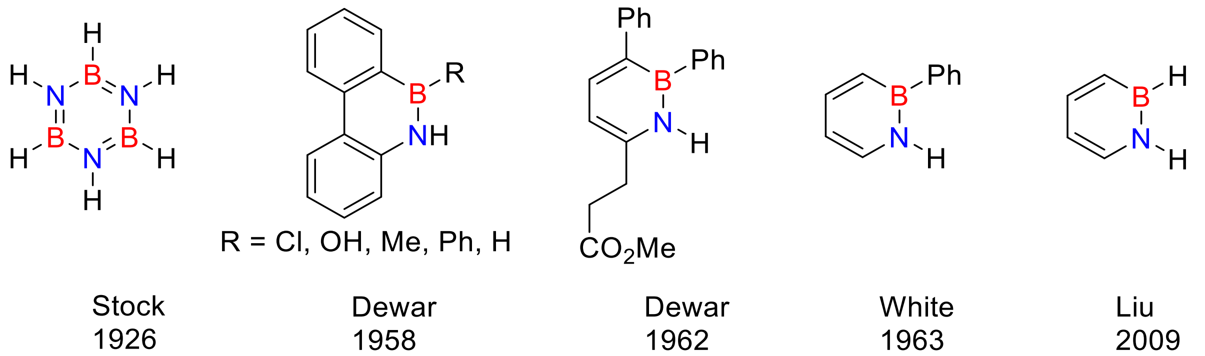
The distinctive behavior of compounds containing boron-nitrogen units that substitute carbon-carbon units, motivated chemists to explore their properties.[1-6] This type of replacement in organic compounds, especially in polycyclic aromatic hydrocarbons (PAH) modifies their HOMO-LUMO gap.[7-10] This has been proven highly beneficial for modifying properties relevant to materials and biomedical applications.[11-13] The key aspect of this chemistry is the boron atom's vacant p orbital, which influences the characteristics of such systems by coordination with the lone pair of donor atoms and the isoelectronic link between B-N and C-C units. The dissimilarity in reactivity between BN and CC compounds arises from the polarity variance in the B-N bond as compared to the C-C bond.[14] The substitution of a C=C unit by an isoelectronic and isosteric B=N unit provides a strategy for the manipulation of the electronic structure of nanographene molecules.[13, 15-18]



Scheme 1. Carbon compounds and their BN analogues.

Four organic BN compound classes resemble isoelectronic carbon analogs as shown in Scheme 1.[19-20] These include amine boranes (R_3B–NR'_3), which mirror alkanes; aminoboranes (R_2B=NR'_2), analogous to alkenes; iminoboranes (RB≡NR'), resembling alkynes; and borazines ($(–RB–NR'–)_3$), akin to benzene.

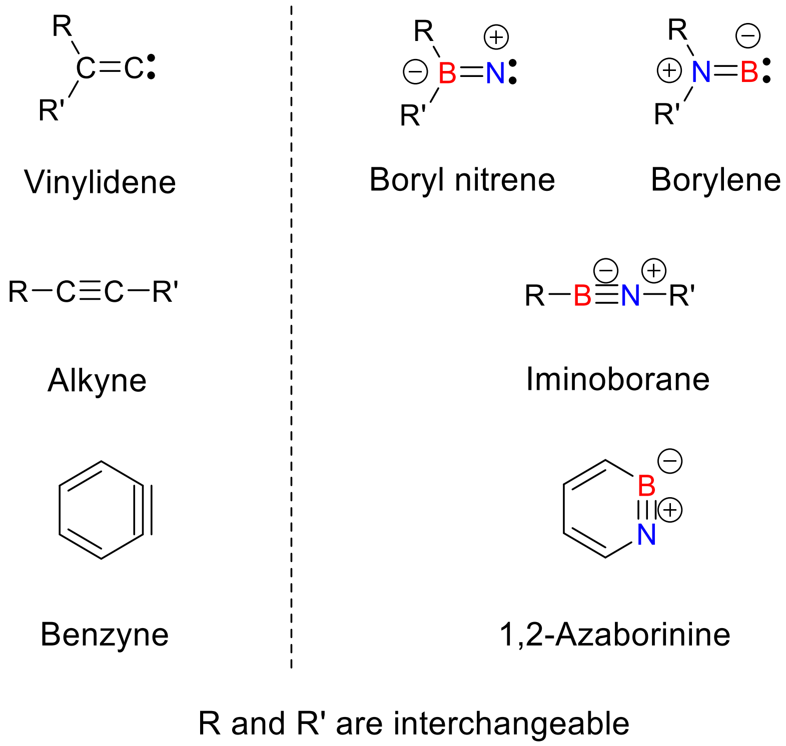
Among these organic BN compounds, iminoboranes (RB≡NR') typically exhibit instability under normal conditions, necessitating the use of bulky substituents for isolation. Amine boranes, aminoboranes, and iminoboranes possess vacant p_z orbitals on boron centers, making them prone to coordination with donor atoms and thus susceptible to interaction with water or oxygen. The synthesis and isolation of boron-nitrogen compounds present significant challenges due to this characteristic. Notably, borazines are the only ones that remain stable in the presence of moisture. Often referred to as "inorganic benzene", borazine was first synthesized by Alfred Stock in 1926.[21] The first heteroaromatic compound with only one BN unit was reported by Dewar in 1958.[22] Subsequently in the 1960s, Dewar and White developed the synthesis of 1,2-dihydro-1,2-azaborine, consisting of only one six-membered ring (Scheme 2).[23-24] The first synthesis for the parent system of 1,2-dihydro-1,2-azaborine was developed by Liu et al.[25] In the last few decades, 1,2-dihydro-1,2-azaborine has gained interest, and major advances were made by several groups, such as Ashe,[26-27] Yamaguchi,[8] Liu,[25, 28-29] Braunschweig[30] and Bettinger.[31-36]



Scheme 2. Various examples of BN substituted heteroaromatics.

1.2 BN Analogs of CC Reactive Intermediates

The modification of the organic system by replacing the CC unit with a BN unit is not only limited to stable compounds, but can be transferred to reactive intermediates as well.[11-13, 17-18] Several reactive intermediates exemplify the isoelectronic and isosteric connection between CC and BN substitution. The formal substitution of the basic carbon-carbon double bond intermediate, vinylidene,[37-38] with a BN bond yields boryl nitrene[39-44] and aminoborylene[45-48] (see Scheme 3), both possessing intriguing reactivity due to the incorporation of boron and nitrogen. The generation of borylnitrene is achievable through the photochemical and thermal decomposition of azidoboranes, involving the elimination of a nitrogen molecule. In 1981, Pieper et al. achieved a significant milestone by successfully trapping a donor-stabilized borylnitrene.[39]

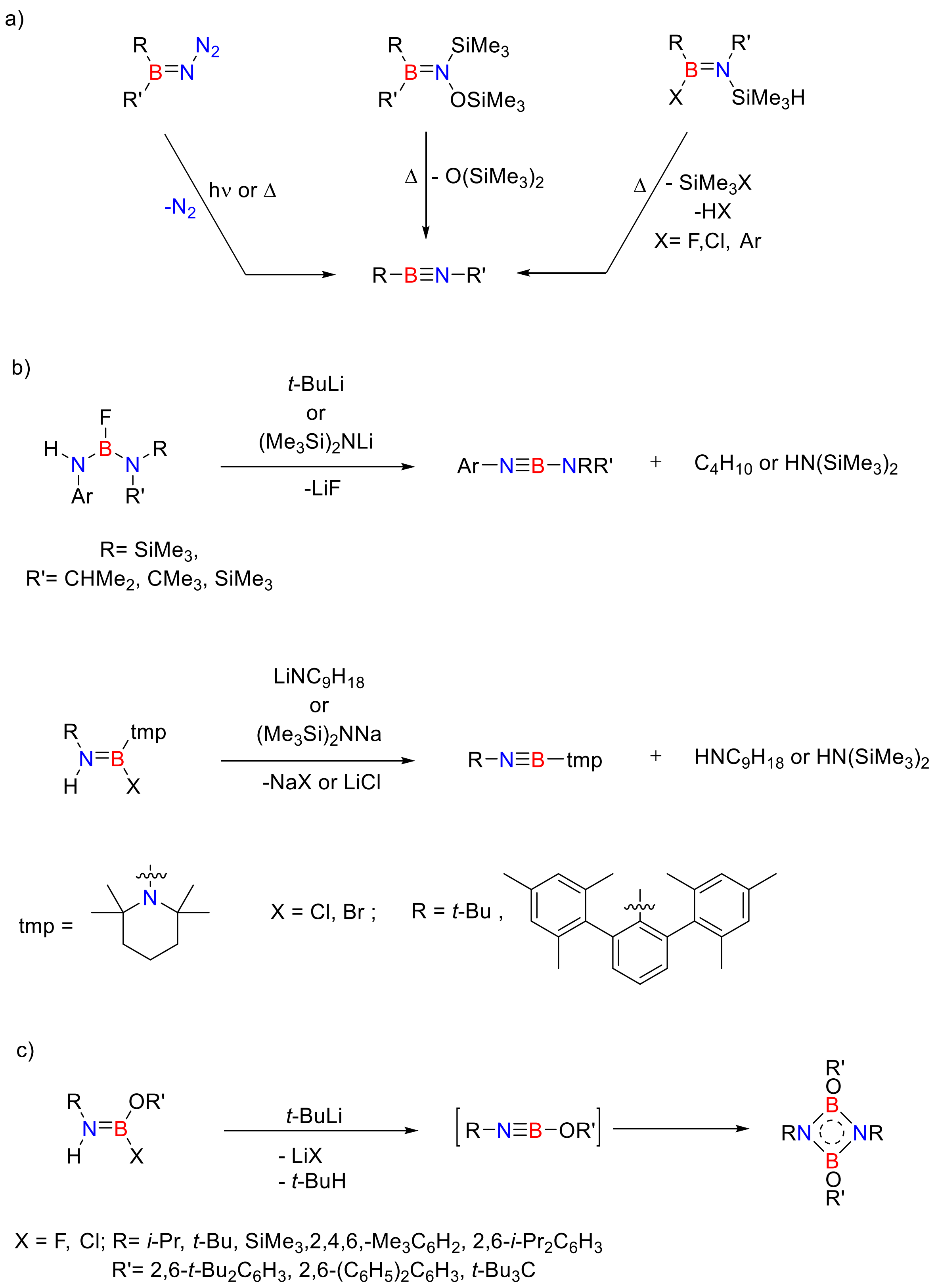


Scheme 3. Reactive intermediates and their BN analogues.

Borylenes, also known as boranediyls or borenes are analogs of carbenes and nitrenes. Borylenes are extremely rare as their unique structure makes them highly reactive.[45] Iminoboranes, double-bonded compounds of boron and nitrogen, and isoelectronic to ethyne are of particular interest as reactive intermediates, albeit their isolation is challenging.[19-20] Comparatively, benzyne, a reactive aromatic carbon species, has its BN analog, 1,2-azaborinine, which was detected and isolated by Bettinger et al. under cryogenic conditions.[33-34] These compounds display the synergy between carbon and boron-nitrogen chemistry by shedding light on their distinct properties and potential synthetic applications.

1.3 Iminoborane

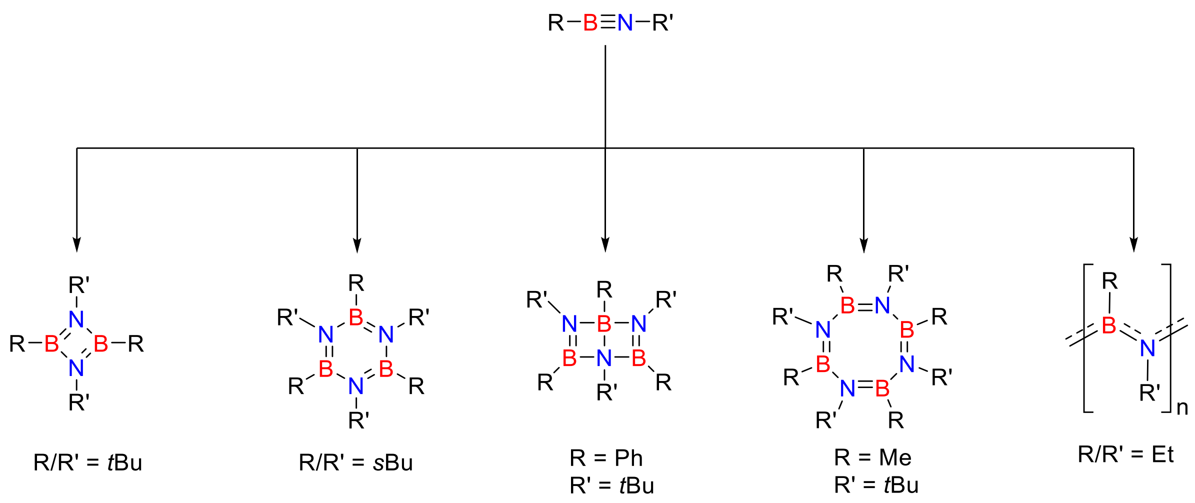
Iminoboranes represent a significant class of BN-containing compounds. Due to their high reactivity, isolating and handling these compounds poses a significant challenge. However, lower temperatures, high dilutions, and sterically demanding substituents are proven to ease the isolation and handling of iminoboranes.[19] The parent iminoborane HBNH was first identified spectroscopically by Lory and Porter in 1973. They observed it through photolysis of amine-borane in an Ar matrix using a hydrogen discharge lamp.[49] Subsequently, Kawashima et al. reported the measurement of the BN stretching mode for HBNH in an NH_3 discharge using diode laser spectroscopy. They also determined the lifetime of HBNH to be a few hundred milliseconds.[50-52] In 1979, Paetzold et al. isolated and characterized the first iminoboranes with two coordinate boron, i.e., F_5C_6-BN-tBu, which can be stored and handled at -30 °C.[53] Numerous more examples followed,[20, 54-55] including $(Me_3Si)_3C$-BN-$SiMe_3$ and $(Me_3Si)_3Si$-BN-$SiMe_3$ from Haase and Klingebiel,[56] which are stable at room temperature. Apart from this, Paetzold et al. have produced and studied iminoboranes to a great extent.[53, 57-66]



Scheme 4. Various approaches to synthesize iminoboranes.

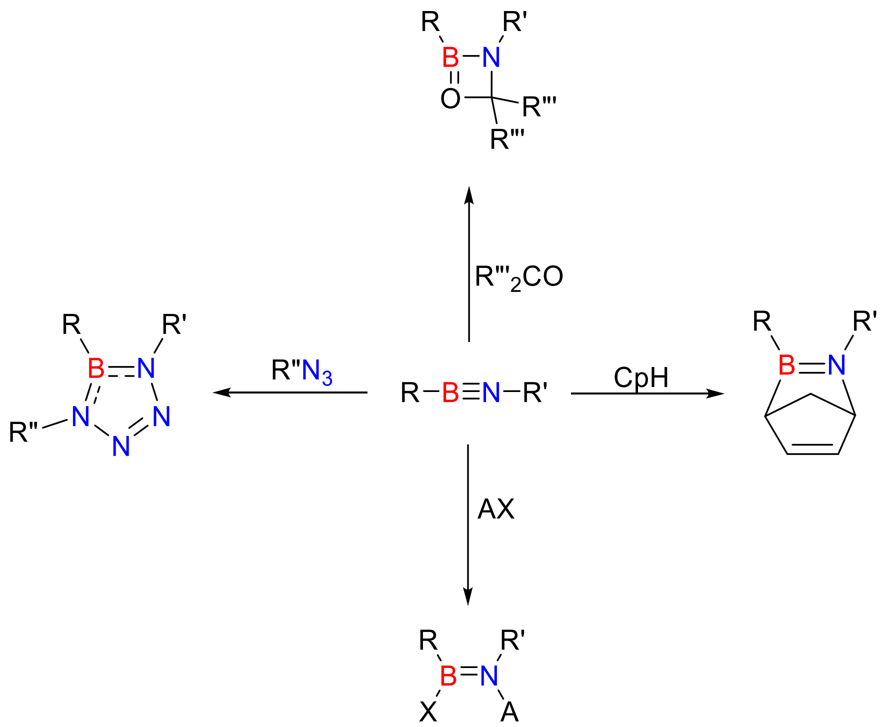
There are several ways in which iminoboranes can be produced. One approach is to eliminate nitrogen photochemically or thermally from azidoboranes followed by a 1,2-shift from the boron atom to the nitrogen atom.[65, 67] Another way is the thermolysis of silyl(silyloxy)aminoboranes which would eliminate hexamethyldisiloxane followed by migration of substituent from boron to nitrogen atom.[65, 68] Iminoboranes can also be produced by thermal elimination of Me_3SiX or HX (X= F, Cl) from $R(X)B{=}N(SiMe_3)R'$ (Scheme 4a).[57-58, 65, 69]

In addition to the mentioned methods, another approach for producing iminoboranes is base-induced dehydrohalogenation reaction. Upon treatment with different bases, the bis-(amino)(halo)boranes are able to produce iminoboranes (see Scheme 4b).[70-73] In 2000, Meller et al. presented the in-situ generation of organyloxyiminoboranes by treating amino(halo)(organyloxy)boranes with t-BuLi.[55] However, the iminoboranes proved to be unstable and formed cyclodimers; their presence was detected by ^{11}B NMR studies (Scheme 4c).[55]



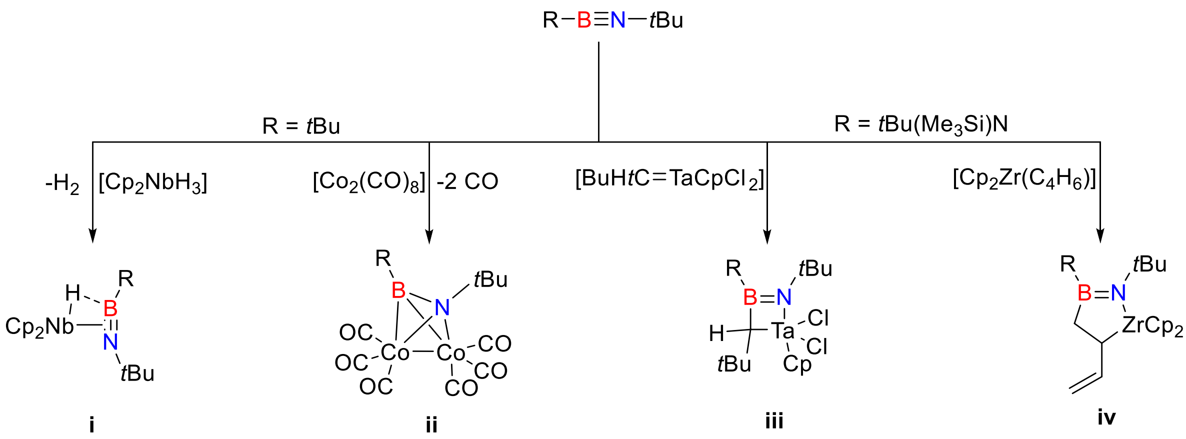
Scheme 5. Self- oligomerization of iminoboranes due to different substituents.

Although iminoboranes are isoelectronic to alkynes, they are not kinetically inert due to dipole moment and prefer to undergo oligomerization in the absence of a trapping agent.[19] Moreover, they tend to form higher oligomers and the extent of oligomerization depends on the size of the substituents (Scheme 5).[74-76] This multifaceted result of the cyclooligomerization with different substituents creates difficulty in comprehending the factors that determine the products of such reactions.[76-80]



Scheme 6. Typical (2 + 2), (2 + 3), and 1,2-addition reaction of iminoboranes.

Other than self-oligomerization, iminoboranes undergo (2 + 2) and (2 + 3) cycloaddition reactions with several polar double bonds (e.g., RR'C=O) and dipolar reagents (Scheme 6).[66, 81-85] Gilbert conducted a series of ab initio computational studies that compared iminoboranes and alkynes concerning their electronic and geometric structures, along with their reactivity in (2 + 2) and (2 + 4) cycloadditions with alkenes and alkynes.[86-88] There are several cases where the BN bond reacts with polar molecules in 1,2-addition reactions (Scheme 6).[58, 65, 68, 73, 84, 89]

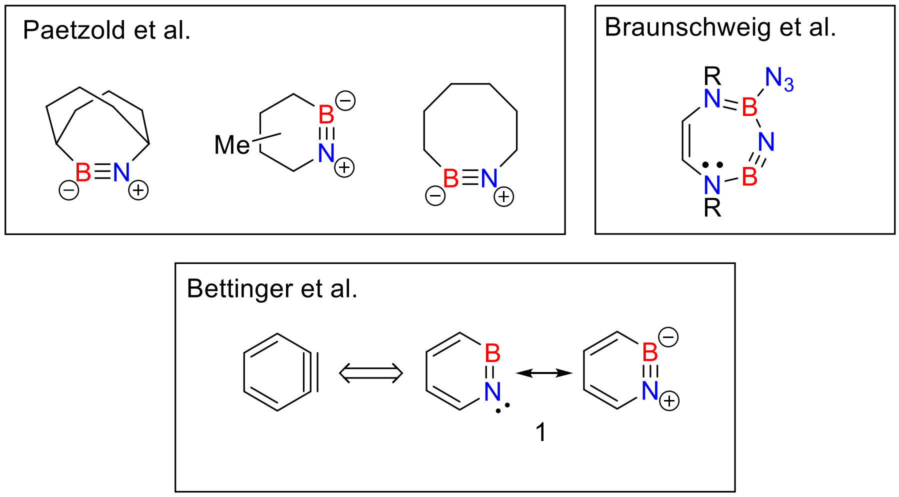


Scheme 7. Examples of transition metal complexes with iminoboranes.

Another form of addition to iminoborane occurs when neutral Lewis acids coordinate to the nitrogen atom.[90] The reaction between iminoborane and metal complexes has also been studied. Similar to alkynes, iminoboranes can coordinate to metal atoms in different ways (Scheme 7). They can undergo side-on coordination (η^1) (**i**),[54, 91-92] bridge two metal atoms (η^2) (**ii**),[93] and undergo cyclodimerization at a metal center (η^4) (**iii** and **iv**).[77, 94-96]

1.3.1 Cyclic Iminoboranes

Cyclic iminoboranes are quite rare, being isosteric with cycloalkynes.[19, 65, 97] Due to ring strain, they are more reactive than linear iminoboranes,[19] however coordination by N-heterocyclic carbenes (NHC) provides a way of stabilization.[14, 29, 98] The existence of cyclic iminoboranes was first inferred by Paetzold et al. in 2004 [65] and by Braunschweig et al. in 2020 (Scheme 8).[97] Bettinger et al. were the first to study unsaturated cyclic iminoboranes. They detected 1,2-azaborinine (**1**), six-membered cyclic iminoborane under cryogenic conditions.[33]

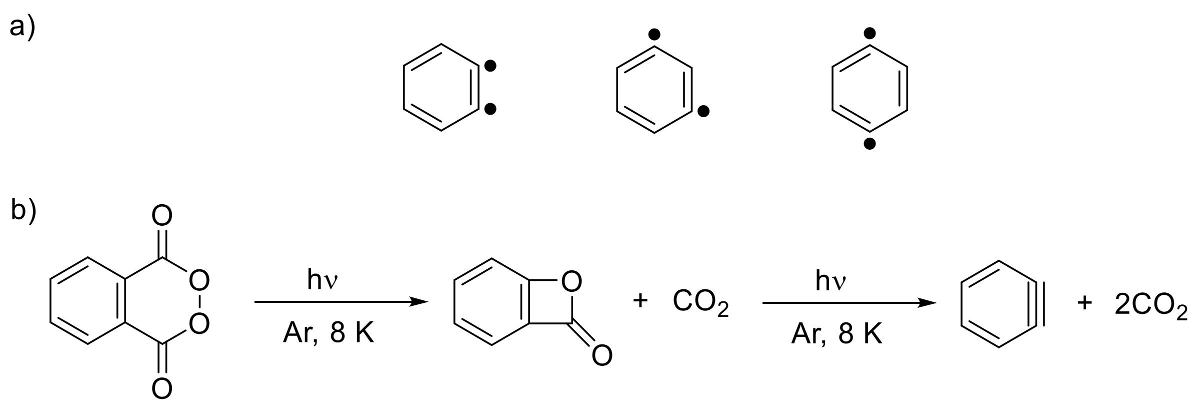


Scheme 8. Illustration of cyclic iminoboranes previously deduced by Paetzold et al,[65] Braunschweig et al.[97] and Bettinger et al. [33]

1.4 1,2-Azaborinine and its Dibenzo Derivatives

1.4.1 Aryne

1,2-Azaborinine (BN-aryne or BN-benzyne) is the isoelectronic BN analogue of *ortho*-benzyne. Arynes were proposed as reactive intermediates approximately 120 years ago and have since been recognized as valuable in organic synthesis.[99-109]

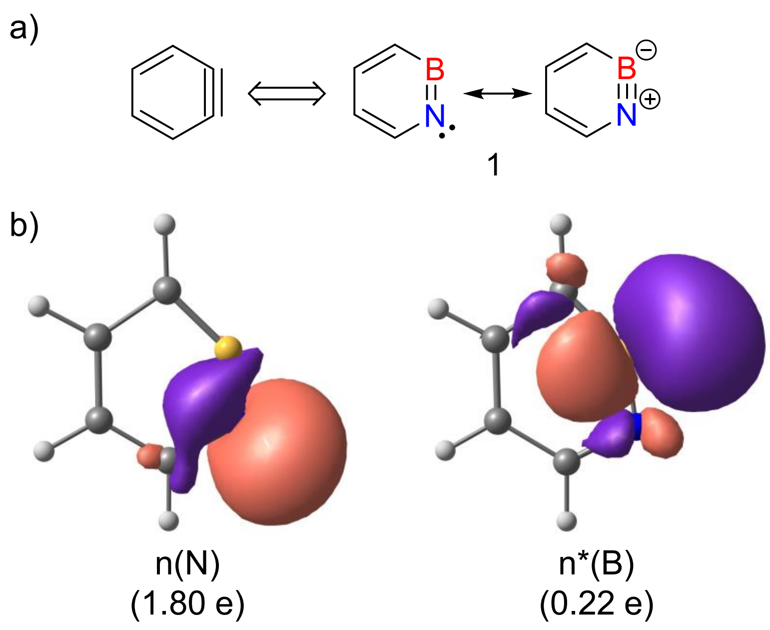


Scheme 9. a) Isomers of *ortho*-benzyne. b) Generation of *ortho*-benzyne at 8 K by Chapman et al. using matrix isolation technique.[110]

The occurrence of arynes was first reported by Stoermer and Kahlert in 1902.[111] Later on, the evidence for their structure was provided by Wittig et al.[112-114] and Robert et al.[115-117] However, the first spectroscopic evidence of *ortho*-benzye was presented in 1973 by Chapman using the matrix isolation technique (Scheme 9).[110] Subsequently, Warmuth was able to produce and isolate *ortho*-benzyne in a molecular container and measure NMR spectra of *ortho*-benzyne in solution.[118-119]

1.4.2 1,2-Azaborinine

A distinct example of cyclic iminoboranes is the aromatic BN-aryne referred to as 1,2-azaborinine **1**, which is analogous to *ortho*-benzyne.[33-34, 36] It has been detected and studied using matrix isolation spectroscopy in the Bettinger research group (Scheme 10). This compound exhibits exceptionally high reactivity towards inert molecules.[33-34, 36]

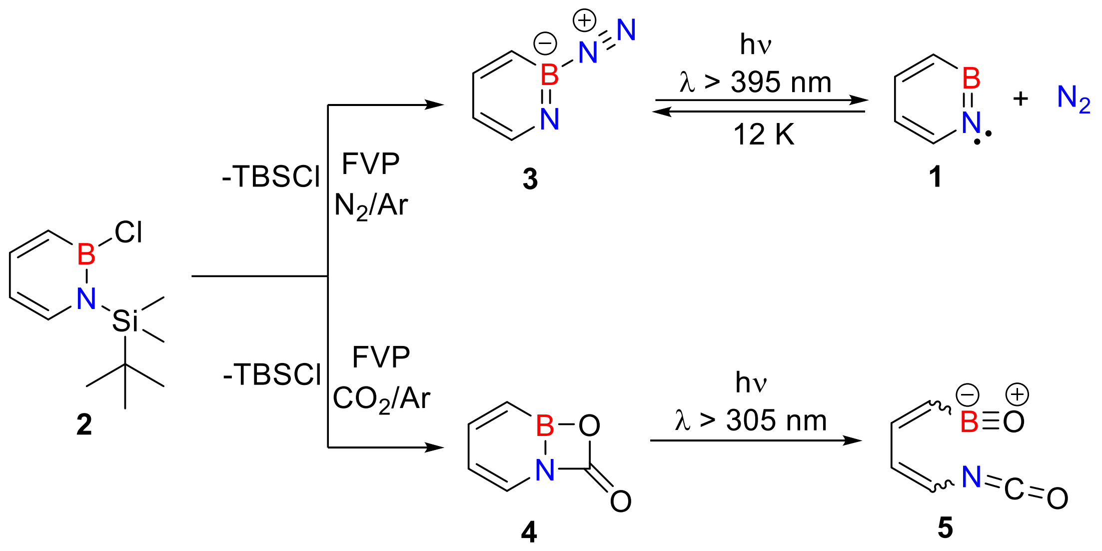


Scheme 10. a) Isoelectronic relationship between *ortho*-benzyne and 1,2-azaborinine demonstrated by its resonance forms. b) Natural bond orbitals (NBOs) and their occupation numbers as computed at the B3LYP/6-311+G(d,p) level of theory.[33]

The high reactivity of **1** is attributed to the polar nature of the BN link that results in a distinct bonding scenario as compared to the strained triple bond in arynes and BN unit in linear iminoboranes.[33-34] In contrast to *ortho*-benzyne, 1,2-azaborinine **1** shows a distorted geometrical structure.[32, 120] The singlet state is preferred over the triplet state with 53.0 kcal/mol at the CCSD(T)/6-311+G(d,p) level of theory.[120]

1,2-Azaborinine (**1**) was first synthesized and isolated by Bettinger et al. in 2015 under argon matrix isolation conditions. It was generated by flash vacuum pyrolysis at temperature ranging from 800 °C to 850 °C of the precursor, 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-chloro-1,2-azaborine **2** (Scheme 11) and subsequent trapping in an argon matrix doped with 30 % nitrogen.[33] 1,2-Azaborinine, generated after the elimination of *tert*-butyldimethylsilyl chloride, spontaneously binds with N_2 to form acid/base adduct **3** in a photochemically reversible reaction (Scheme 11). The band at 2266 cm^{-1} is the most prominent signal observed and is reminiscent of the dinitrogen stretching vibration ν(NN), observed previously by Maier et al. for the borabenzene-dinitrogen adduct.[121] Bettinger et al. also verified the formation of adduct by employing $^{15}N_2$, and observed the isotopic shift of the compound.[33] The adduct was found to be photolabile, as the irradiation with $\lambda > 395$ nm results in the decrease in the signals of **3**, accompanied by the consequent growth of signals assigned to the 1,2-azaborinine **1**. Furthermore, **1** can be transformed to **3,** by carefully annealing the matrix from 4 K to 12 K indicating that the reaction of **1** and nitrogen is barrierless.

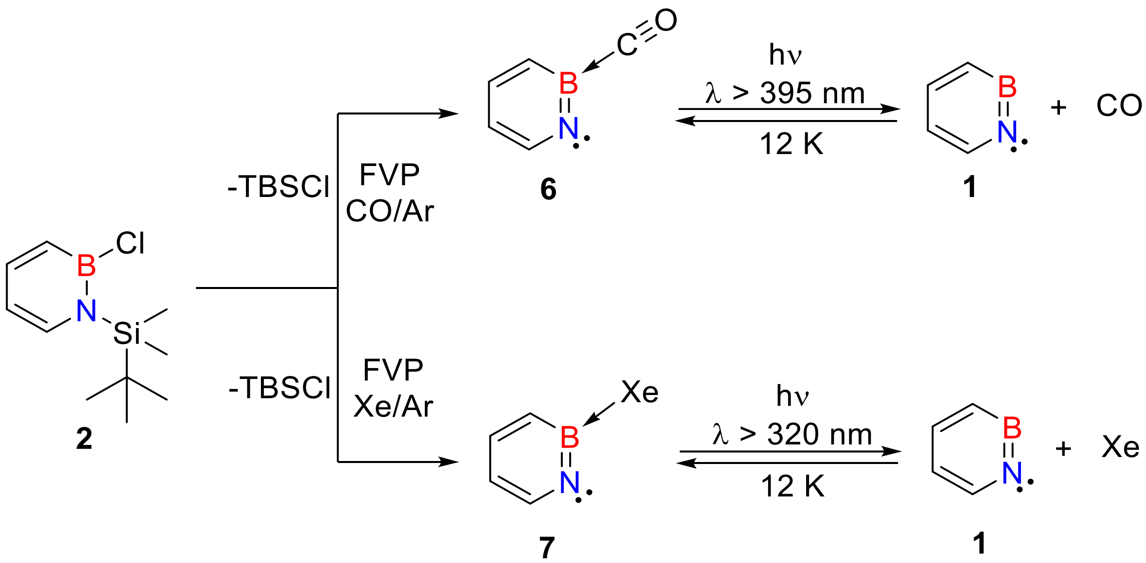
In addition to the reaction of **1** with N_2, Bettinger et al. were able to trap **1** with CO_2 (Scheme 11). After the pyrolysis of the precursor **2**, new signals emerged in the reaction with CO_2, which were assigned to compound **4** through comparison with the computational spectrum. The distinguished peak at 1874/1879 cm^{-1} is associated with the carbonyl stretching vibration ν(CO) of cyclic carbamate. The formation of **4** is confirmed by using isotopically labeled carbon dioxide $C(^{18}O)_2$ and $^{13}CO_2$, respectively. The isotopic shifts observed were in good agreement with computational results. Unlike *ortho*-benzyne, further irradiation of **4** with λ > 305 nm did not lead to the loss of CO_2.[110] Rather, **4** undergoes ring opening via retro [2 + 2] cycloaddition to give compound **5** with isocyanate and BO unit which have characteristic stretching vibrations in the range 2303 - 2236 cm^{-1} and 1900 - 2200 cm^{-1}, respectively (Scheme 11). The occurrence of **5** was also supported by measured and computed isotopic shifts.



Scheme 11. Generation of 1,2-azaborinine **1** by flash vacuum pyrolysis (FVP) of **2** and trapping with N_2 and CO_2.

After the reaction with N_2 and CO_2, Bettinger et al. studied the reactivity of **1** with Lewis bases. CO and Xe were chosen due to differences in the Lewis basicity. CO is a stronger Lewis base compared to N_2 and can undergo cycloaddition reaction while Xe is a very weak Lewis base that reacts only with very strong electrophiles. The FVP of **2** in CO-doped argon matrix results in the formation of Lewis acid-base complex **6** (Scheme 12). The most intense and prominent peak was observed at 2134 cm^{-1}. The formation of **6** was verified by employing isotopologues ^{13}CO and $C^{18}O$ to obtain isotopic shifts of bands in comparison with computations. Further irradiation of **6** with λ > 395 nm resulted in the formation of **1** and CO.

Interestingly, these could react again to form **6** by annealing the matrix to 12 K. The trapping with CO exhibits that the formation of Lewis acid-base complex is favored over [2 + 1] and [2 + 2] cycloaddition reactions. In addition, **1** was trapped with a mixture of argon and xenon (see Scheme 12). The FVP of **2** with a mixture of argon and xenon produces compound **7**, which under irradiation with λ > 320 nm forms **1**. Notably, this reaction is reversible through subsequent annealing of the matrix to 12 K (Scheme 12). The compound formed after FVP of **2** was assigned to the Lewis acid-base complex between **1** and Xe which is verified by comparison with computational spectra. This shows that **1** not only reacts with CO, N_2, and CO_2 but also with the weaker Lewis base Xe, which reveals the super electrophilicity of 1,2-azaborinine **1**.

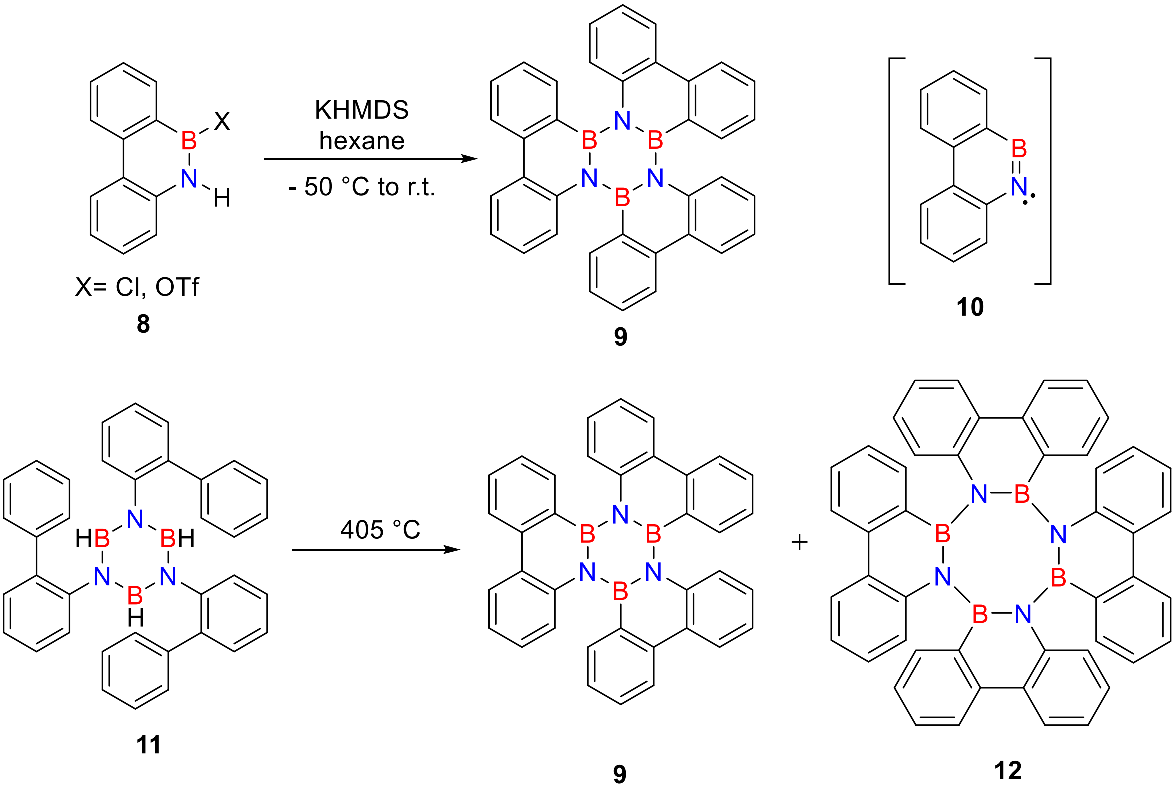


Scheme 12. Generation of 1,2-azaborinine **1** by flash vacuum pyrolysis (FVP) of **2** and trapping with CO and Xe.

1.4.3 Dibenzo Derivative of 1,2-Azaborinine

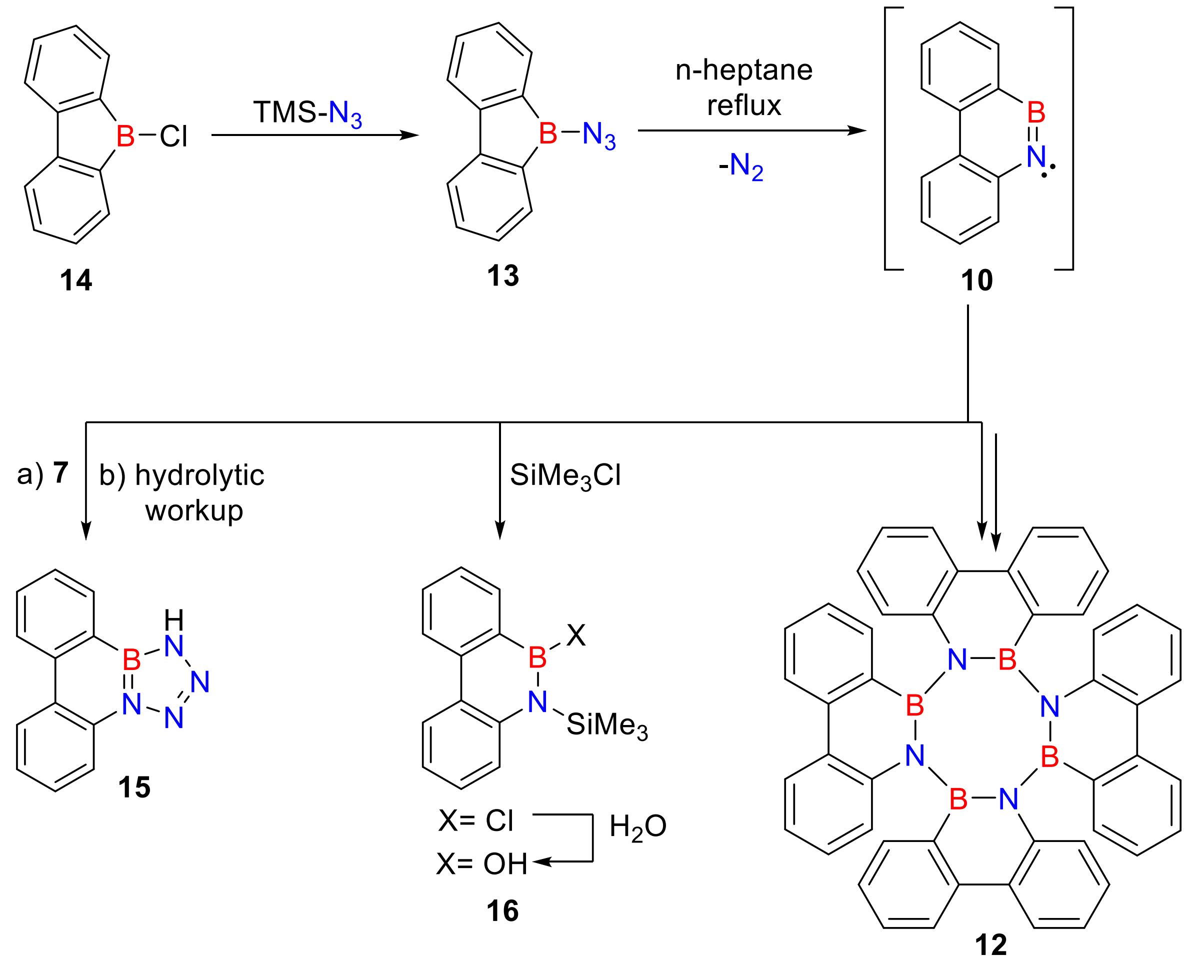
The observation of the formation of 1,2-azaborinines as a reactive intermediate was first done by Bettinger et al., during investigating the trapping reactions of the dibenzo derivative of **1**, dibenzo[c,e][1,2]azaborinine.[32, 122] In 2012, Bettinger et al. examined the reaction of the precursor, 10-chloro-9-aza-10-boraphenanthrene **8**, with a bulky base such as potassium hexamethyldisilazide. This led to cyclotrimerization following HCl elimination, resulting in the borazine analogue of hexabenzotriphenylene **9,** which is a trimer of dibenzo[c,e][1,2]azaborinine **10** (see Scheme 13a). This study marked the first inference of dibenzo[c,e][1,2]azaborinine as an intermediate.[122] Bettinger et al. also reported the formation of compound **12,** which is the tetramer of **10**, in addition to the synthesis of **9** as described by Köster[123] in 1965 by thermal dehydrogenation of **11** (see Scheme 13b).

a)



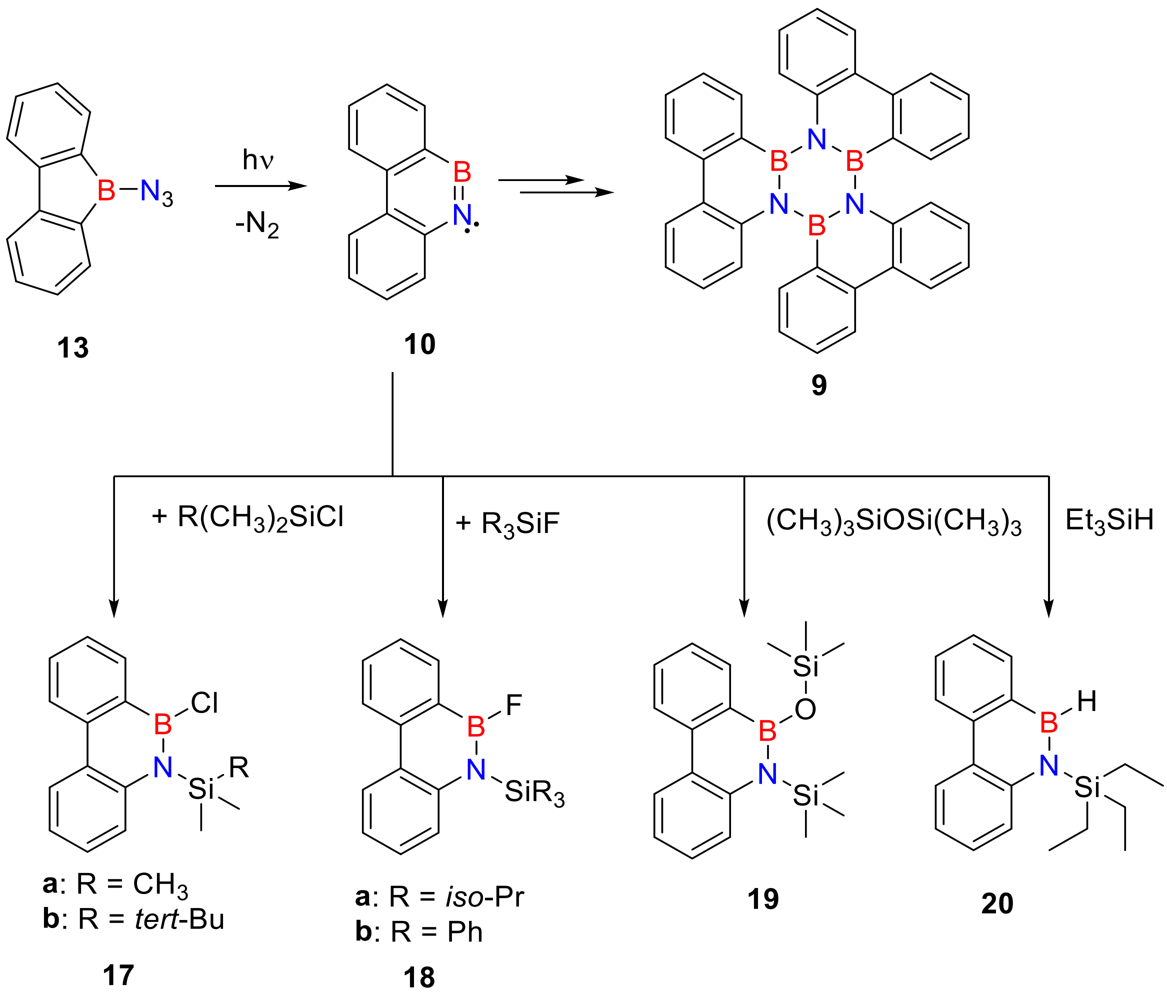
Scheme 13. a) Dehydrohalogenation reaction of 10-Chloro-9-aza-10-boraphenanthrene **8** according to Bettinger et al.[122] b) Thermolysis of N,N',N''-tris-(2-biphenyl)borazine **11** according to Köster et al.[123] and Bettinger et al.[122]

Bettinger et al. reported the thermal decomposition of 9-azido-9-borafluorene **13** [32] by building on the chemistry of the cyclic and acyclic azidoorganylboranes R_2BN_3 reported by Paetzold et al.[19, 65] Bettinger et al. subjected compound **13** to heating in a n-heptane solution, yielding to produce the tetramer **12** in 8 - 10% yield (Scheme 14). The subsequent aqueous workup of the reaction mixture enabled the detection of compounds **15** and **16** by GC-MS analysis. These findings suggest that compounds **15** and **16** can interpreted as interception products of **10** (see Scheme 14).[32]



Scheme 14. Trapping of **12** via thermal decomposition reaction of azidoborole **13** by Bettinger et al.[32]

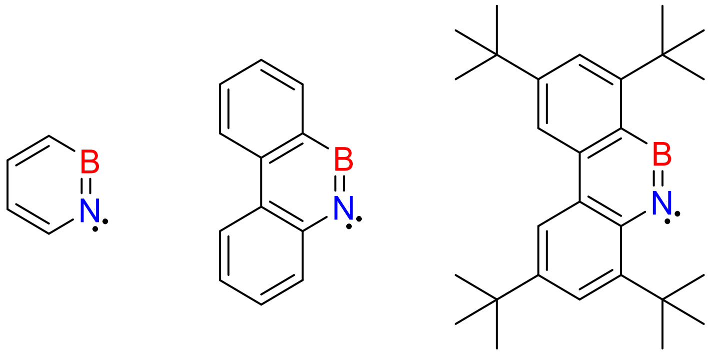
Subsequent to these investigations, Bettinger et al. reported that the dibenzo derivative of **1**, dibenzo[c,e][1,2]azaborinine **10**, was inferred as a reactive intermediate in solution during photolysis of azide **13**.[31-32] Compound **10** is capable of even activating the strong Si−F bond for subsequent insertion reaction.[35] In this context, they demonstrated that the Lewis acidity of boron allows coordinative interaction with Si-E bonds (E = F, Cl, OR, H) followed by subsequent insertion reaction to produce compounds **17-20**, respectively (Scheme 15).[35]



Scheme 15. Self-trapping reactions of dibenzo[c,e][1,2]azaborinine **2** generated by photolysis of 9-azido-9-borafluorene **7.**

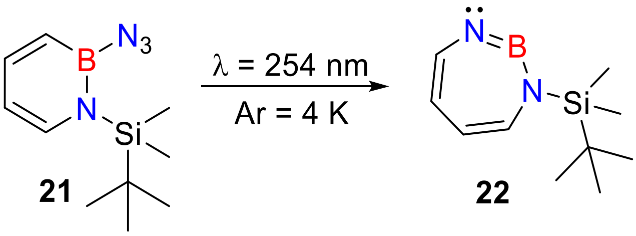
2 Objective

My thesis focuses on investigating the reactivity of 1,2-azaborinine **1**, a cyclic iminoborane, with various organic substrates. The research encompasses both computational and experimental approaches, utilizing matrix isolation spectroscopy.



1 **10** **33**

Additionally, the objective was to obtain direct spectroscopic evidence of **10** and **33**, the dibenzo derivative of 1,2-azaborinine. Subsequently, the introduction of *tert*-butyl groups has been pursued to delve into the effects of steric hindrance.



In addition to 1,2-azaborinine **1**, a novel category of cyclic iminoboranes, specifically 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22**, has been isolated and investigated under matrix isolation conditions.

3 Methodology

3.1 Matrix Setup

The challenges associated with isolating and characterizing reactive intermediates are substantial for chemists, mainly due to the brief lifespan of these highly reactive species. To overcome this hurdle, techniques like matrix isolation spectroscopy have been developed. George C. Pimentel pioneered the matrix isolation technique, which involves trapping reactive species in an abundant inert gas matrix (typically in a 1:1000 ratio) at extremely low temperatures and pressures.[124-126] The elevated concentration of inert gases serves to suppress diffusion and intermolecular interactions, enabling scientists to analyze and characterize these species using various spectroscopic methods such as UV-Vis, IR, and electron paramagnetic resonance spectroscopy. Depending on the chosen spectroscopic method, different window materials, such as CsI for IR and sapphire for UV-Vis, are used.

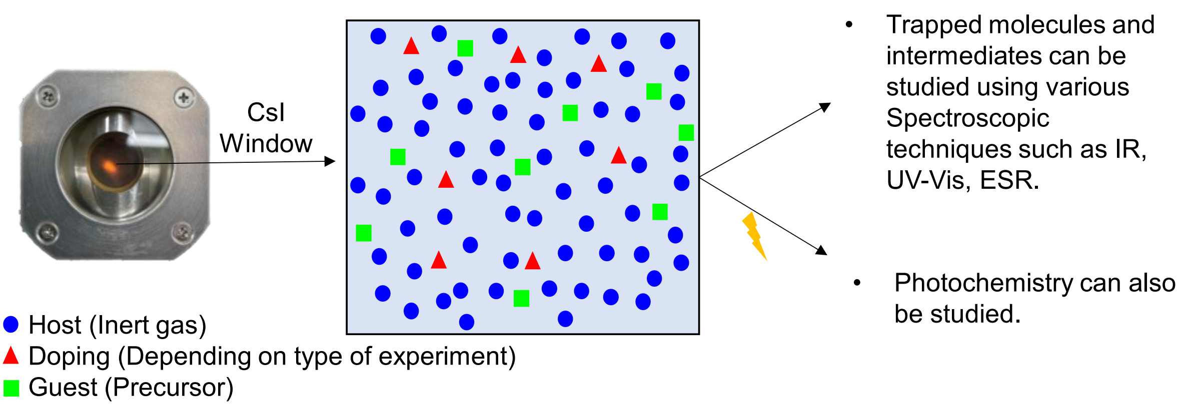


Figure 1. Molecules trapped within inert gases on the cold matrix window.

The selection of precursor molecules is very important, as they must have the ability to sublime onto the matrix window. The matrix isolation technique employs two main methods to generate reactive intermediates from their precursors: photolysis, and flash vacuum pyrolysis (FVP) (Figure 2). In photolysis, the intermediate is generated photochemically using a UV-Vis light source whereas, in the case of flash vacuum pyrolysis, the intermediate is produced by passing the precursor through an oven at a certain temperature and then deposited on the cold spectroscopic window. Apart from the method used for generating the intermediate, the inert gas chosen for the matrix must not react with the intermediate, alongside being transparent for the spectroscopic method. The inert nature of matrix gases contributes to high spectral resolution facilitating easier structural analysis.

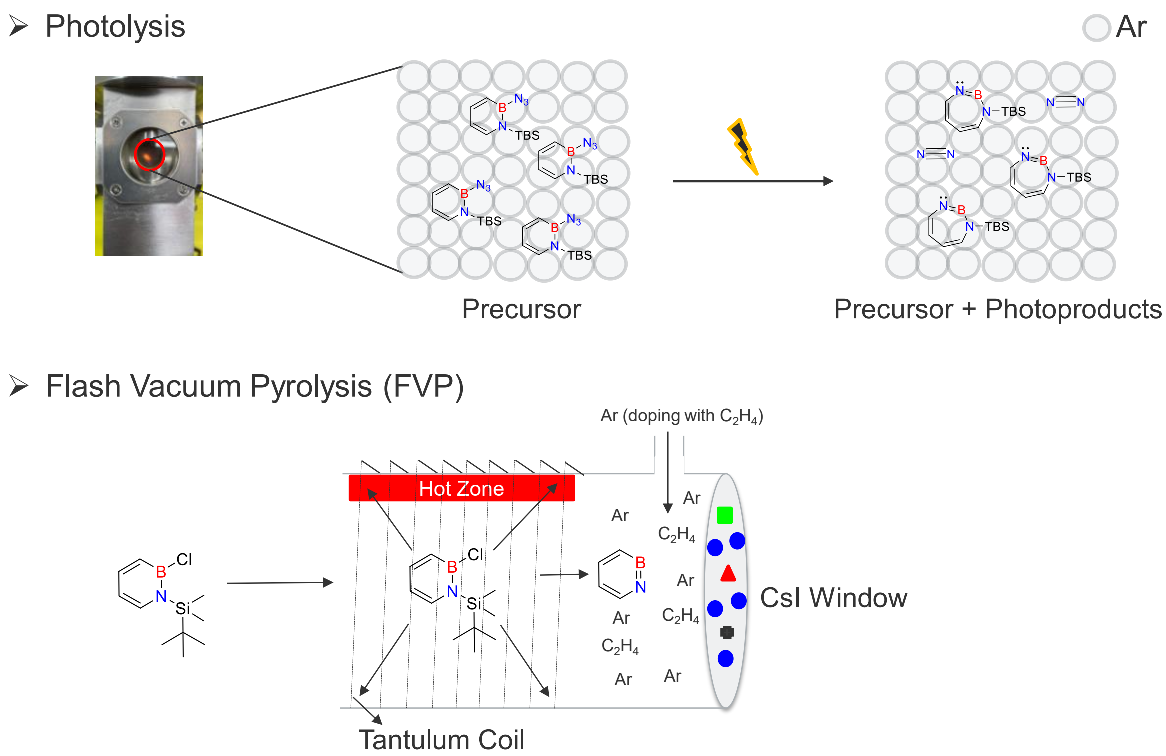


Figure 2. Two different ways to generate reactive intermediates.

Matrix isolation is also used in studying the reactivity of intermediates by doping the host matrix with typically 2-5% of the reactant. The mixture is deposited with the precursor to induce reactivity between molecules present in close vicinity. This reaction is induced either thermally or photochemically. In the thermal reaction, the matrix window is heated slightly to a specific temperature depending on the host gas while in the case of photochemical reaction, the matrix window is irradiated with UV-Vis light which is absorbed by the reacting molecules.

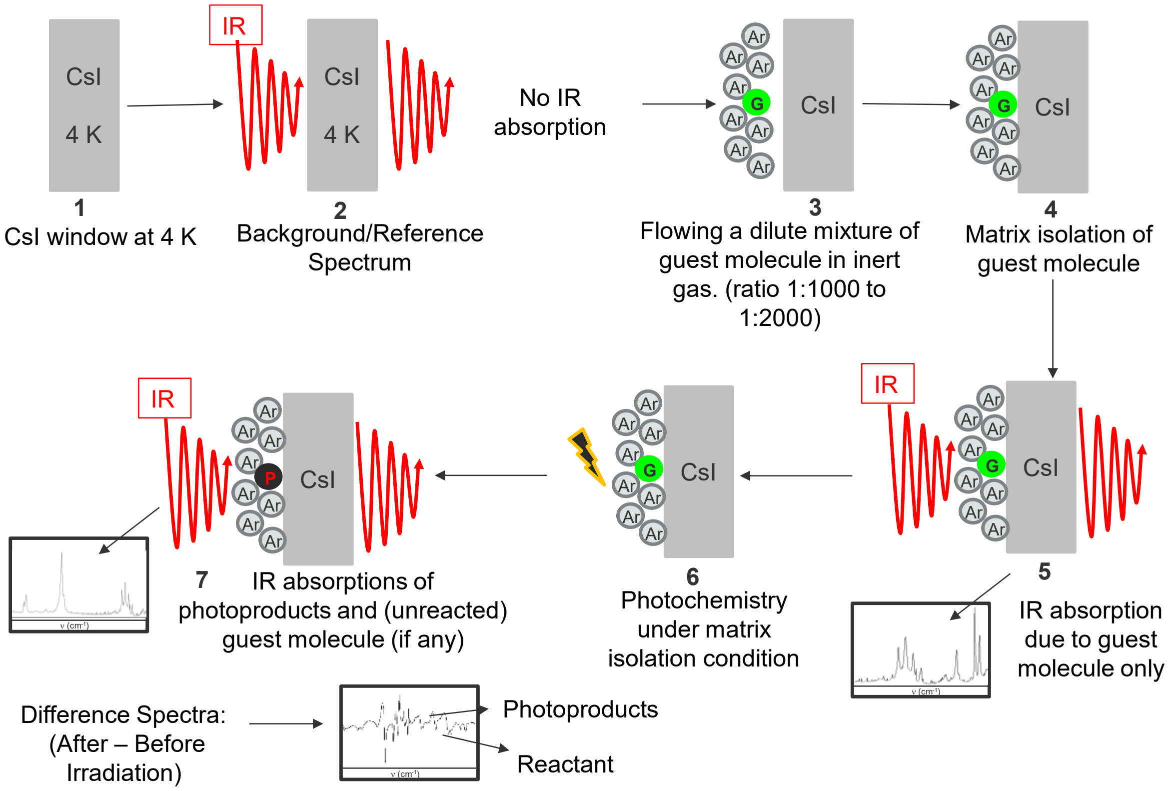


Figure 3. Schematic representation of the matrix isolation experiment setup for IR spectroscopy.

After the generation of the experimental results, the spectra are compared with the computed spectra of potential products for the verification of the product assignments. The assigned product could further be validated by employing different isotopes of the reactant and comparing the isotopic shifts obtained from the experiments with computational data.

In matrix isolation experiments described in this thesis, a Sumitomo SH-1 closed-cycle helium cryostat was used to obtain a temperature as low as 4 K. For IR spectroscopy, a Bruker Vertex 70 FTIR spectrometer with 0.5 cm^{-1} resolution in the range of 400 – 4000 cm^{-1} was utilized. A Perkin Elmer Lambda 1050 spectrometer was used to obtain the absorption spectra. Photochemistry within the matrix was induced by using a low-pressure PenRay mercury lamp (λ = 254 nm) and high-pressure mercury lamps (USHIO, USH-508S) in combination with various dichroic mirrors and Schott cut-off glass filters. The host gases or reactants used for the matrix experiments were as follows: Argon 6.0 (Westfalen AG, 99.9999 %), N_2 6.0 (Messer-Griesheim, 99.9999%) carbon monoxide 3.7 (Westfalen AG), $C^{18}O$ 2.0 (95 % ^{18}O) (Sigma Aldrich) or ^{13}CO 2.3 (99.1 % ^{13}C) (Westfalen AG) and 5 % of C_2H_4 (Sigma-Aldrich, 99.95 %) or C_2D_4 (Sigma-Aldrich, 99 %).

3.2 Computational Details

Computational chemistry serves as a valuable and essential tool in understanding numerous concepts and mechanisms across diverse areas of chemistry, enhancing insights into experimental results. Various quantum chemistry packages including Gaussian 16,[127] ORCA 5.0[128-130], and Q-Chem[131], were employed for computational tools, with graphical user interfaces (GUIs) like GaussView[132] and Chemcraft to visualize the results.

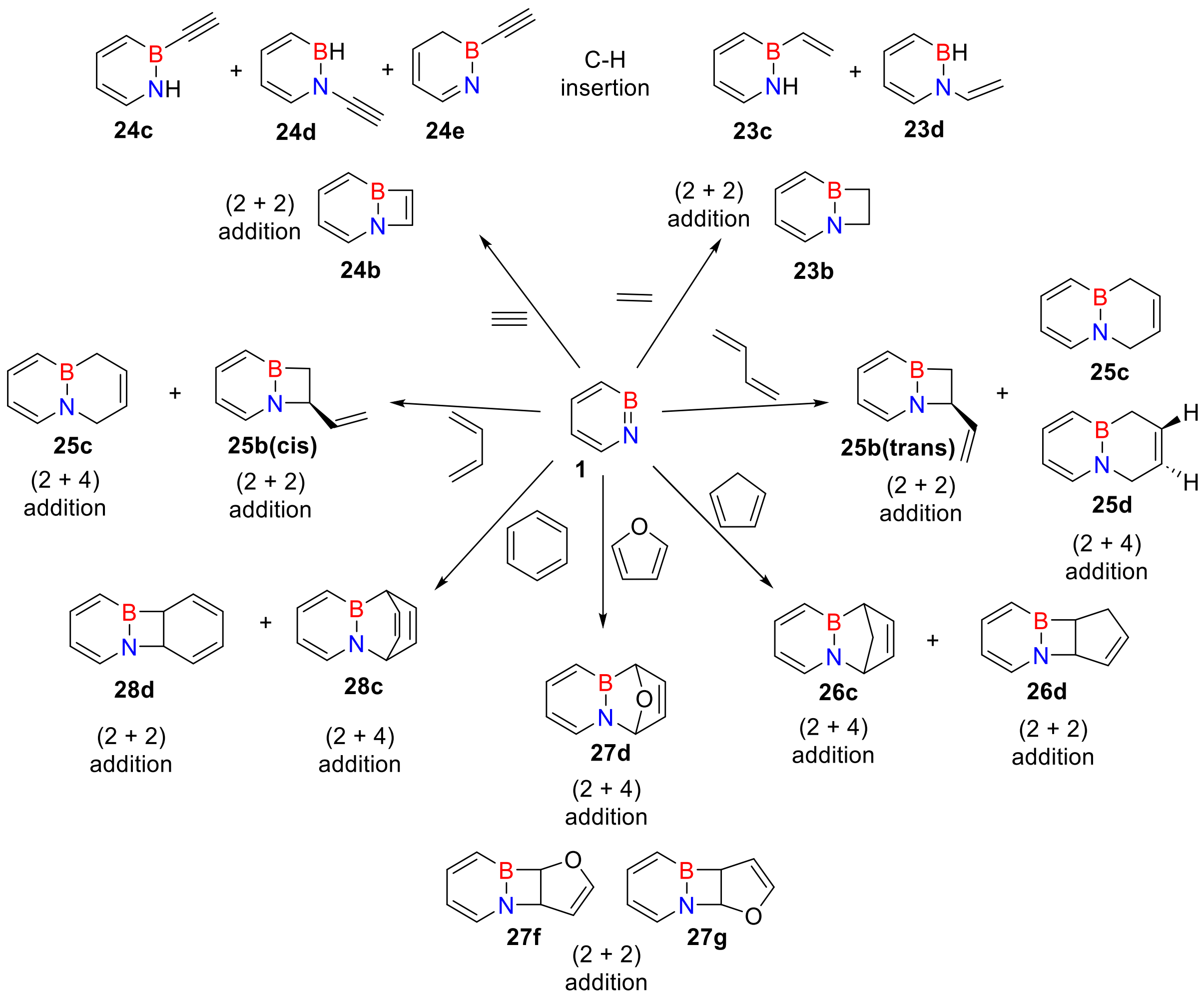
Two distinct methodologies were utilized to compute various molecular properties. The first, known as the *ab-initio* method is a wavefunction based theory where the Schrödinger equation is solved with a molecular Hamiltonian operator to calculate energy. This method depends solely on fundamental physical constants without incorporating any experimental parameters. Complete active space self-consistent field (CASSCF) method and coupled cluster methods are examples of the *ab-initio* methods.[133-139] Another widely used computational method is density functional theory (DFT), which expresses the total energy of the system in terms of electron density.[140-142] When considering electron-electron interaction in DFT, $\rho(r)$ is defined as a collection of electrons within a radius r, with the assumption that each electron interacts with the total electron density in that spatial region. The comprehensive electron-electron interaction energy is effectively described through Coulomb energy, and the external potential can be represented as the product of nuclear position and electron density across space. The kinetic energy term is articulated as a function of electron density using a formula derived by Thomas Fermi. Thus, DFT establishes that each energy component can be expressed in relation to electron density, reinforcing the Hohenberg-Kohn theorem, which posits that the ground state energy can be derived from electron density.

In this thesis, all structures were optimized using various functionals, including the B3LYP[143-144] hybrid exchange-correlation energy functional, along with Grimme's[145] London dispersion correction B3LYP-D3,[143-144] M06-2X[146] global hybrid functional as well as second-order Møller–Plesset perturbation theory[147] (MP2) and its spin-component scaled[148] variant (SCS-MP2). For all geometry optimizations, split-valence triple- ζ basis set 6-311+G(d,p) was used.[149] The nature of the stationary points (minimum or saddle point) was confirmed by harmonic vibrational frequency calculations, to get ZPVE corrected and Gibbs free energies. For the verifications of TS, intrinsic reaction coordinate (IRC)[150-151] paths were computed for each reaction. To improve the energies in section 4.1, coupled cluster theory with single, double, and a perturbative estimate of triple excitations (CCSD(T))[152] was performed. Single point calculations using domain-based local pair natural orbital (DLPNO) coupled cluster theory with single, double, and a perturbative estimate of triple excitation (DLPNO-CCSD(T))[153-156] in conjunction with Dunning's[157] triple-ζ (cc-pVTZ) basis set were performed for all the structures, in sections 4.2 and 4.3. The DLPNO-CCSD(T) computations used the TightPNO cutoff for increased accuracy and the frozen core approximation. Natural bond orbital (NBO) analysis was carried out using the B3LYP-D3/6-311+G(d,p) geometries to understand the nature of bonding.[158-161] Excited state computations were run using time-dependent DFT (TD-DFT) at CAM-B3LYP/6-311+G(d,p) level of theory.[127, 162] Magnetic shielding values were computed by employing the GIAO method.[163-164] Lewis acidity of the compounds was determined through isodesmic reactions computed at the SMD(DCM)[165]/MN15[166]/def2-TZVP[167] level of theory. Additional computational details used for the studies can be found in the published articles.[35, 168-171]

4 Results and Discussion

4.1 Computational Studies on the Reactivity of 1,2-Azaborinine

The reactivity of 1,2-azaborinine, a compound isosteric and isoelectronic to *ortho*-benzyne, was investigated by quantum chemical methods in order to shed light on its interaction with different organic π systems. Various computational methods, including density functional, second-order perturbation, and coupled-cluster theories were employed. We explored the (2 + 2) and (2 + 4) cycloaddition reactions between 1,2-azaborinine and the substrates, ethene, ethyne, 1,3-butadiene, cyclopentadiene, furan, and benzene (Scheme 16).



Scheme 16. The reaction of 1,2-azaborinine with different organic substrates.

These reactions exhibited high exothermicity and were characterized by the formation of complexes between 1,2-azaborinine and the π substrates. These complexes showcased a strong binding interaction between the π bonds of the substrates and the vacant p-orbital of the boron atom, leading to a two-step mechanism in the (2 + 2) and (2 + 4) cycloaddition reactions. All data presented in this section and subsection were calculated at CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) level of theory unless stated otherwise.

4.1.1 Cycloaddition Reaction to Organic π Substrates

The (2 + 2) cycloaddition reaction of 1,2-azaborinine with π bonds of different organic substrates initiate from the formation of Lewis acid-base complexes (discussed in detail below). These reactions are highly exothermic as compared to separated reactants. Even though the (2 + 2) cycloaddition reactions are symmetry forbidden according to Woodward-Hoffmann rules, they exhibit relatively low activation barriers compared to *ortho*-benzyne in (2 + 2) cycloaddition reactions. The smallest barrier was computed for ethyne (10.2 kcal/mol) while the largest barrier was found to be 17.9 kcal/mol for benzene. The transition state for all the (2 + 2) cycloaddition reactions was below the energy of separated reactants, except for benzene, which was 9.0 kcal/mol above the energy of separated reactants. All transition states were asymmetric in nature. The highest exothermicity was found for s-*trans*-1,3-butadiene (-48.1 kcal/mol), while the lowest was for benzene (-15.0 kcal/mol) (see Table 1). In the case of furan, two (2 + 2) cycloaddition products **27f** and **27g**, were observed to form with a barrier of 11.9 kcal/mol and 11.2 kcal/mol, respectively, from the complex.

Table 1. Reaction barriers and energies (in kcal/mol) computed (CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)) for the (2 + 2) cycloaddition of 1,2-azaborinine **1** with various organic π substrates. All energies are ZPVE corrected energies.

Organic π substrates	**Reaction Barrier (kcal/mol)**	**Reaction Energy (kcal/mol)**
ethene (C_2H_4)	14.6	-46.8
ethyne (C_2H_2)	10.2	-40.7
s-*cis*-1,3-butadiene	12.6	-46.1
s-*trans*-1,3-butadiene	13.6	-48.1
cyclopentadiene	13.5	-43.4
furan	11.9, 11.2	-28.6, -34.3
benzene	17.9	-15.0

1,2-Azaborinine could also undergo (2 + 4) cycloaddition reactions, which are symmetry allowed reactions according to Woodward-Hoffmann rules with s-*cis*-1,3-butadiene, s-*trans*-1,3-butadiene, cyclopentadiene, furan, and benzene. The reactions proceed from the Lewis acid-base complexes and the activation barriers for (2 + 4) cycloaddition barriers are relatively lower as compared to the (2 + 2) cycloaddition. All transition states are asymmetric in nature and are below the energy of the separated reactants, except for benzene, where the TS lies 2.1 kcal/mol above the separated reactants. The activation barriers, with respect to the corresponding Lewis acid-base complexes, increase from furan to benzene (see Table 2). The highest exothermicity for the formation of (2 + 4) cycloaddition product was found for s-cis-butadiene (-74.1 kcal/mol) while the lowest exothermicity is for benzene (-26.9 kcal/mol). All these reactions proceed in a concerted way from the complex except for s-*trans*-1,3-butadiene, which undergoes a stepwise reaction. The reaction proceeds initially from the complex **25a(trans)** to form an intermediate **25d** with a barrier of 18.9 kcal/mol, and from **25d**, it further proceeds with a high barrier of 44.8 kcal/mol to yield product **25c**.

Table 2. Reaction barriers and energies (in kcal/mol) computed (CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)) for the (2 + 4) cycloaddition of 1.2-azaborinine **1** with various organic π substrates. All energies are ZPVE corrected energies.

Organic π substrates	**Reaction Barrier (kcal/mol)**	**Reaction Energy (kcal/mol)**
s-*cis*-1,3-butadiene	6.4	-74.1
cyclopentadiene	4.7	-52.4
furan	3.8	-34.0
benzene	11.0	-26.9

4.1.2 CH Insertion Reaction

The CH insertion reactions with ethene (C_2H_4) and ethyne (C_2H_2) in the case of 1,2-azaborinine involved the possibility of CH insertion at the boron or nitrogen center. In the case of C_2H_4, the C-H insertion reaction proceeded in a concerted manner from the complex, yielding a higher exothermic product as compared to the (2 + 2) cycloaddition reaction. However, these reactions had high activation barrier due to direct transfer of a hydrogen atom to the azaborinine ring. The formation of **23d** (N-substituted vinyl-azaborinine) was associated with a barrier of 83.5 kcal/mol, higher than the barrier of 33.9 kcal/mol associated with **23c** (B-substituted vinyl-azaborinine).

In the case of ethyne (C_2H_2), the C-H insertion yielded three products: B-substituted ethynylazaborinine (**24c**), N-substituted ethynylazaborinine (**24d**) and 2-ethynyl-3-dihydro-1,2-azaborinine (**24e**). The formation of **24c** involved direct transfer of a hydrogen atom to the azaborinine ring, resulting in a strained four-membered TS with a barrier of 23.8 kcal/mol, with respect to the complex. There was no direct pathway observed from **24a** to **24d**. However, starting from the complex **24a**, a high energy barrier for the transfer of hydrogen (25.9 kcal/mol) was involved to yield **24e**. In the subsequent step, the reaction faced an even higher energy barrier (59.4 kcal/mol), leading to the generation of **24d**, wherein the ethynyl group transitioned from boron to nitrogen, while simultaneously, the hydrogen atom shifted from carbon to boron.

4.1.3 Lewis Acid-Base Complexes between 1,2-Azaborinine and Organic π Substrates

In addition to the transition states and products, Lewis acid-base complexes corresponding to minima on the potential energy surfaces were found. These complexes were identified in the IRC profiles and their geometries were effectively optimized for the aforementioned reactions. These Lewis acid-base complexes arose from the interaction between the π bonds of organic substrates and the vacant p-orbital of the boron atom.

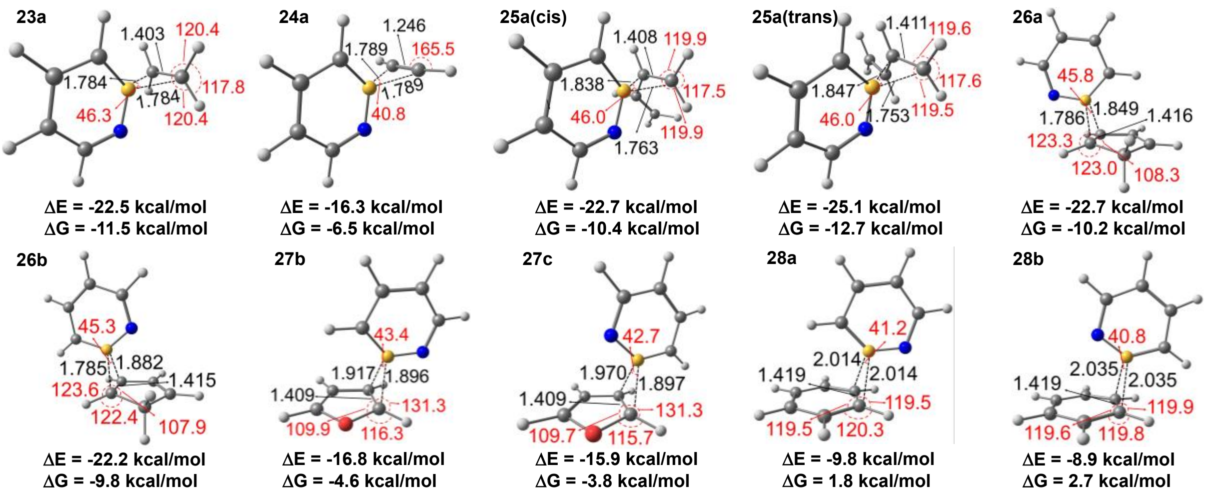


Figure 4. Computed (SCS-MP2/6-311+G(d,p)) geometrical parameters of complexes between **1** and organic p substrates. ΔE and ΔG (298.15 K) correspond to the relative ZPVE-corrected binding energy and free energies, respectively, in relation to the separated reactants. Bond lengths and bond angles are given in [Å] and [°] respectively.

The distinguishing feature of these reactions was the high exothermicity of the complexes formed between **1** and the π substrates. All complexes exhibited carbon–boron distances that fall below the sum of van der Waals radii (3.62 Å) (Figure 4). For instance, in **23a**, these distances were 1.784 Å, and subtle digression from planarity around carbon atoms in C_2H_4 was observed - the H–C–H and H–C–C angles had undergone a slight alteration, resulting in a total bond angle around carbon of 358.3°. Similarly, in **24a**, the angle H–C–C was found to be 165.5°, again signifying subtle variance from linearity around carbon. Upon scrutinizing all complexes, the longest B–C distance was identified as 2.035 Å for **28b**, while the shortest distance was observed for **25a(trans)** (1.753 Å and 1.847 Å), as illustrated in Figure 4. The planarity around the carbon atom showed the largest deviation in **26b**, and the smallest deviation in complexes **28a** and **28b**.

To get a deeper insight into the bonding nature between 1,2-azaborinine and the organic substrates, we performed a natural bond orbital analysis. The analyses revealed a significant stabilization due to the delocalization from π(substrate) → n*(B) (vacant orbital on boron). This effect was evaluated via second-order perturbation theory in the NBO basis for the complexes **23a**, **24a**, **25a-cis**, **25a-trans**, **26a**, **26b**, **27b**, **27c**, **28a**, and **28b** (Table 3)**.**

Table 3. NBO analysis of the R→B (R is π substrate in C_2H_2, C_2H_4, 1,3-butadiene, cyclopentadiene, furan and benzene respectively) interaction for complexes **23a**, **24a**, **25a-cis**, **25a-trans**, **26a**, **26b**, **27b**, **27c**, **28a**, and **28b** formed at the B3LYP-D3/6-311+G(d,p) level of theory.

	ΔE[(a)]	**%R[(b)]**	**%B[(b)]**	**Occ. R[(c)]**	**Occ.B[(c)]**
23a	319.7	77.1	22.4	1.557	0.502
24a	313.7	77.7	21.9	1.574	0.505
25a-cis	290.5	77.1	21.4	1.559	0.490
25a-trans	291.7	76.9	21.3	1.555	0.488
26a	244.6	77.6	19.9	1.572	0.462
26b	244.9	77.9	19.5	1.576	0.475
27b	192.7	79.1	17.8	1.598	0.437
27c	208.1	78.2	18.5	1.586	0.477
28a	65.5	79.1	9.8	1.591	0.319
28b	71.4	79.1	10.5	1.593	0.337

(a) NBO second-order perturbation interaction energy associated with the R→B interaction, in kcal mol^{-1}. (b) Percentage of the donor and acceptor NBO in the corresponding NLMO. (c) Occupancy of the donor and acceptor NBO orbitals.

The corresponding natural localized molecular orbitals (NLMO) exhibited significant contributions from the π(C≡C) and π(C═C) bond orbitals, accompanied by "delocalization tails" ranging from 17.8% to 22.4%, from a slightly hybridized empty orbital at boron (Figure 5 and Table 3). However, in the reaction with benzene, the NLMO exhibits reduced "delocalization tails", of only 9.8% and 10.5% for complexes **28a** and **28b**, respectively. This observation aligns with the lower binding energy obtained for complexes **28a** and **28b**.

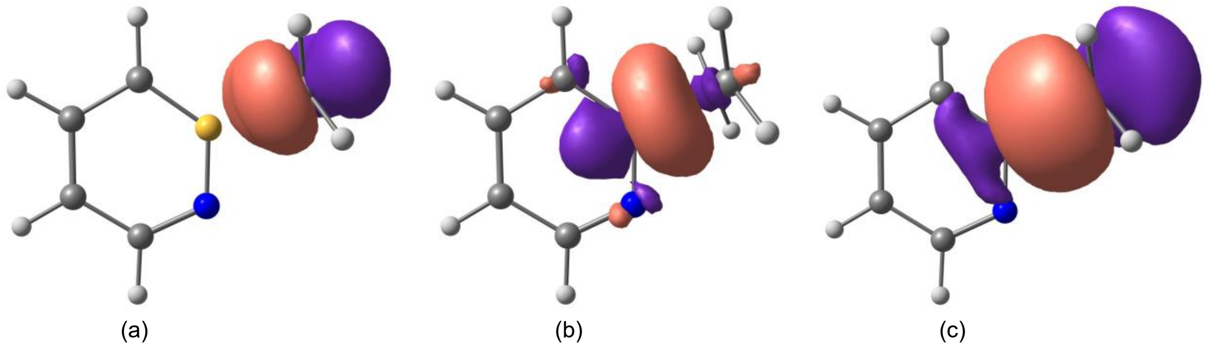


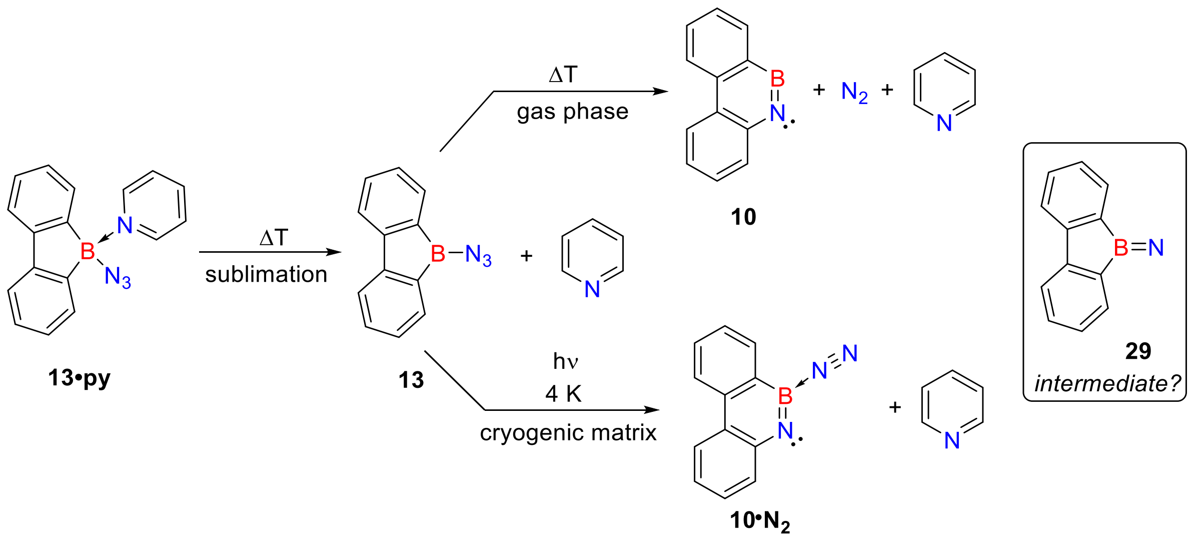
Figure 5. (a) donor NBO, (b) acceptor NBO, and (c) corresponding NLMO associated with the C=C → B interaction for complex **23a** at the B3LYP-D3/6-311+G(d,p) level of theory.

Summing it up, the computational examination of (2 + 2) and (2 + 4) cycloaddition as well as CH insertion reactions of 1,2-azaborinine with various organic π systems reveals strong exothermicity. The boron–nitrogen bonding in 1,2-azaborinine mimics a frustrated Lewis pair, leading to barrierless formation of complexes with organic π systems, acting as key intermediates. (2 + 4) cycloaddition reaction are favored over symmetry-forbidden (2 + 2) cycloaddition reaction. C–H insertion reactions into ethyne and ethene exhibit higher exothermicity but also higher barriers compared to cycloaddition reactions. Though reactions with unsaturated organic substrates are theoretically feasible, in solution phase, cyclooligomerizations may compete due to lack of barriers. However, in noble gas matrix isolation conditions, the formation of strongly bound Lewis acid–base complexes may act as a thermodynamic trap, hindering reaction towards cycloaddition products at low temperatures.

4.2 Dibenzo Derivatives of 1,2-Azaborinine

4.2.1 Dibenzo[c,e][1,2]azaborinine

As detailed in section **1.4.3**, the observations of trapping experiments suggested the involvement of the dibenzo[c,e][1,2]azaborinine **10**. However, direct spectroscopic evidence for it was not reported due to sensitivity of azidoborole **13**, a precursor to **10**. It is monomeric in solution, but in solid state, it oligomerizes to cyclic trimer which decomposes rather quickly.[172] Conversely, the Lewis adduct with pyridine, **13•py**, exhibits substantial stability.[172] This rationale led Dr. Christina Tönshoff to consider **13•py** as a promising precursor for conducting matrix isolation and gas phase studies of **10** as heating of **13•py** under high vacuum conditions leads to the sublimation of **13** and pyridine (Scheme 17).



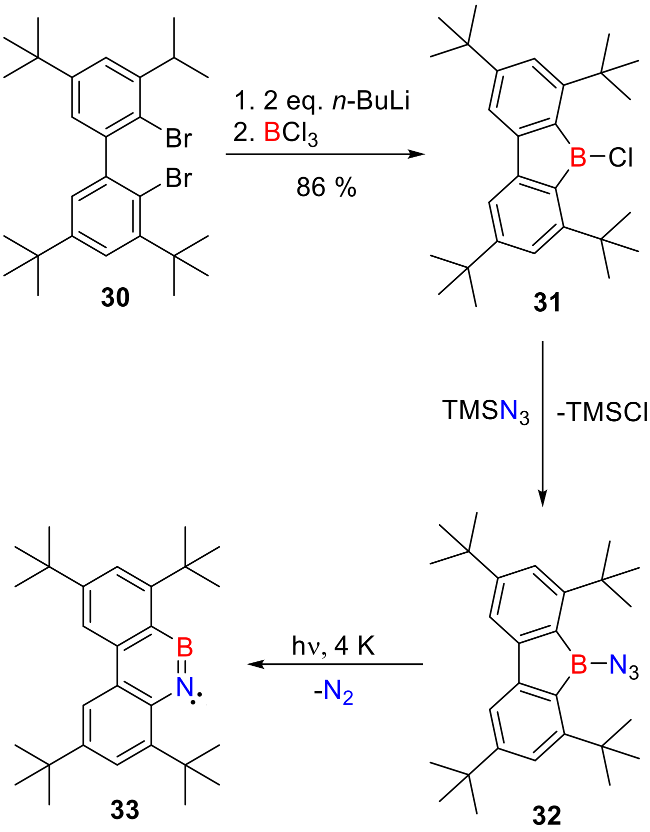
Scheme 17. Generation of dibenzo[c,e][1,2]azaborinine **10** from the precursor **13•py.**

Dr. Tönshoff sublimed the precursor **13•py** at 110-120 °C under cryogenic conditions and froze it in excess argon or nitrogen at 30 K and 28 K, respectively. After successful sublimation, signals corresponding to free pyridine and azide **13** were observed, along with small amounts of HN_3, which was due to hydrolysis of azide.[173-

176] Further irradiation of **13** with λ > 280 nm, revealed a distinctive band at 2259 cm^{-1}, corresponding to the ν(NN) stretching mode, while the peaks corresponding to free pyridine remained unchanged in intensity. This suggests the formation of Lewis acid-base adduct **13•N2** similar to 1,2-azaborinine adduct **3**.[33] However, subsequent irradiation of the N_2 adduct at different wavelengths did not facilitate the removal of the N_2 molecule, contrary to the behavior observed for parent 1,2-azaborinine **1**.[33]

4.2.2 2,4,7,9-Tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine

To investigate the photochemical N_2 extrusion and the impact of steric hindrance on N_2 fixation, we investigated the compound **32** (5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole) (Scheme 18) that was synthesized by Dr. Constanze Keck.[177] The compound **32** was sublimed at 150 °C under cryogenic conditions and trapped with excess argon at 30 K. The IR spectrum recorded after the deposition of **32** revealed presence of photostable contaminations. The most prominent peak was observed at 2155 cm^{-1}, representing the ν(N_3) stretching mode of **32** (Figure 6). The shift of this peak, compared to ν(N_3) stretching of **13,** is 19 cm^{-1} higher, implying a reduction in the electron density donation from the azide group to vacant boron orbital in comparison to **13**.



Scheme 18. Generation of **33** from the precursor **32**.

After the deposition of azide **32**, the matrix window was irradiated with 260 nm < λ < 320 nm at 4 K. This resulted in the decreased intensity of peaks corresponding to **32**, accompanied by emergence of new signals. The prominent feature observed was a broad peak at 1751 cm^{-1}, associated with the ν(BN) stretching mode of the ring (Figure 6), that were assigned to BN-aryne **33** based on the comparison with computational data. However, the presence of *tert*-butyl groups at the 2,4,7,9 positions hindered the formation of the N_2 adduct, impacting the boron center's ability to bind with N_2 by reducing its Lewis acidity. Additionally, no changes were observed when the matrix was annealed to 35 K, implying involvement of an activation barrier on the PES.

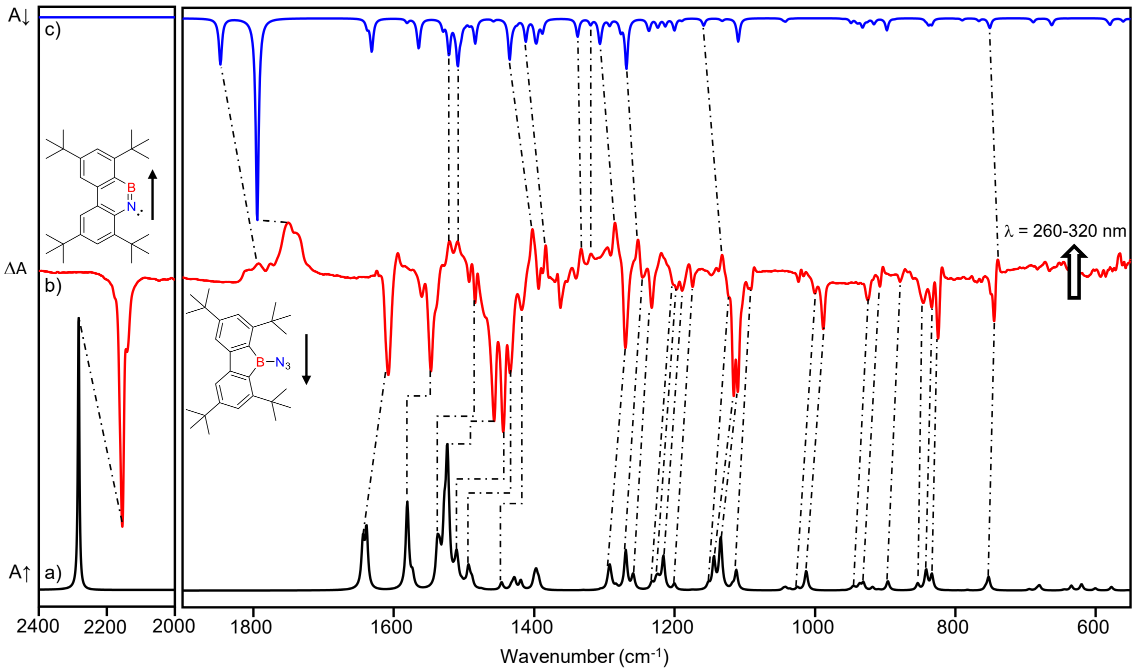
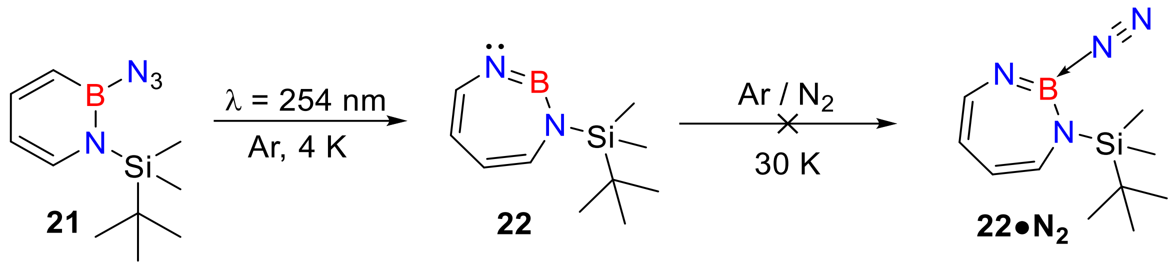


Figure 6. Comparison of experimental (Ar matrix at 10 K) and harmonic computed (B3LYP-D3(BJ)/6-311+G(d,p)) IR spectra **32** and **33**. a) Harmonic IR spectrum of **32**; c) Harmonic IR spectrum of **33**; b) Experimental IR difference spectrum obtained after photolysis of **32** (260 nm < λ < 320 nm) in Ar at 10 K.

All in all, matrix isolation of azaidoborle **13** was successful despite its instability via sublimation of pyridine adduct **13•py**. Under investigation, it undergoes a novel photoinduced isomerization to form the dibenzo[c,e][1,2]azaborinine-N_2 Lewis acid-base adduct **10•N₂**. Introducing *tert*-Bu groups at 2,4,7,9 positions reduce the Lewis acidity of BN-aryne **33**, hindering N_2 fixation and highlighting the potential of kinetically protective groups in attenuating BN-aryne reactivity.

4.3 1H-1,3,2-Diazaborepine

To understand more about the reactivity of cyclic iminoboranes, we successfully isolated, for the first time, the cyclic seven-membered iminoborane **22**, 1-(*tert*-butyldimethylsilyl)-1*H*-1,3,2-diazaborepine in inert matrices under cryogenic conditions. The iminoborane **22** was generated from 2-azido-1-(*tert*-butyldimethylsilyl)-1,2-dihydro-1,2-azaborinine **21** (Scheme 19) that was synthesized by Dr. Ralf Einholz. Azide **21** could be successfully isolated in an argon matrix.



Scheme 19. Photogeneration of 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22** under matrix isolation conditions.

The most prominent peak was found at 2141 cm^{-1} attributing to the ν(N_3) stretching vibration. Upon further irradiation of **21** with λ = 254 nm, iminoborane **22** was formed, as confirmed by comparing the measured IR spectrum to the one computed. The anticipated product, nitrene, was excluded based on comparison with computational data, indicating that after the photochemical extrusion of N_2 from compound **21**, it undergoes ring enlargement isomerization to produce **22**. This is in agreement with the behavior of diorganyl azidoboranes.[19] The most distinguished peak observed after irradiation was at 1751 cm^{-1} belonging to the ν(BN) stretching vibration of **22,** while the peak at 1809 cm^{-1} was attributed to the ν(BN) stretching vibration of ^{10}B isotopologues (see Figure 7). However, even after annealing the matrix up to 35 K, **22** did not form Lewis acid-base adduct with N_2, **22●N$_2$**. This is in contrast to the case of 1,2-azaborinine **1** (Scheme 16) that readily binds N_2 upon slight annealing of the matrix.[33] The observation for **22•N2** can be rationalized by computing the potential energy scan with the B-N_2 distance. This indicates that the formation of the N_2 adduct is energetically unfavorable and involves a barrier.

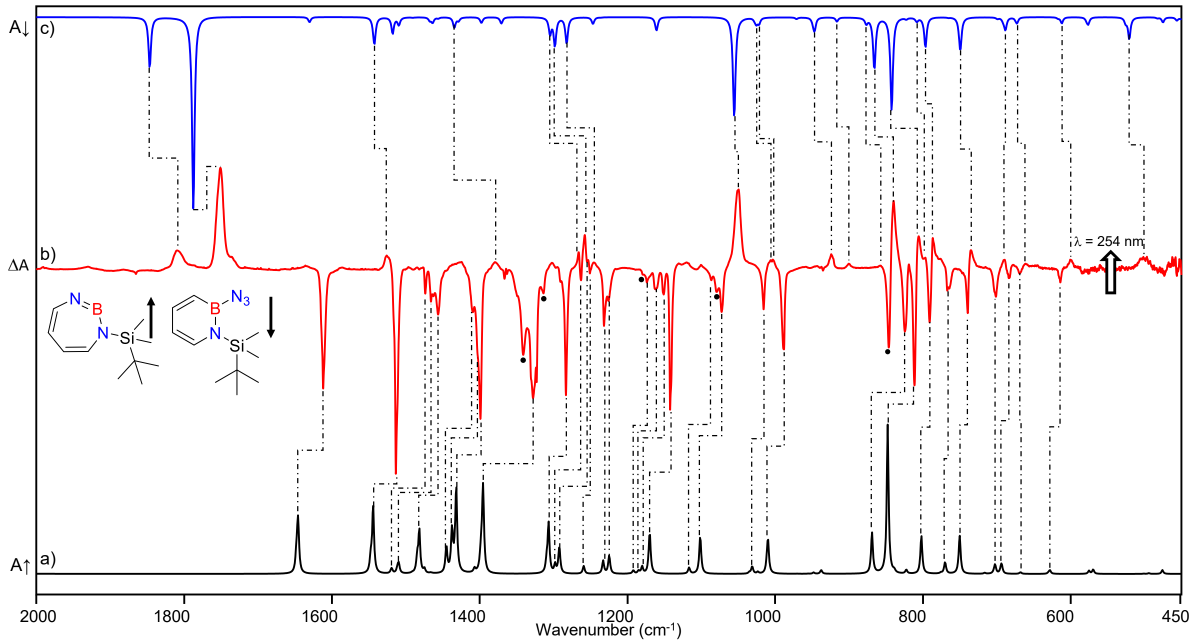


Figure 7. Comparison of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) IR spectra **21** and **22**. a) Harmonic IR spectrum of **21**; b) Experimental difference IR spectrum obtained after photolysis of **21** (λ = 254 nm) at 4 K. c) Harmonic IR spectrum of **22**. (● attributed to the overtones and combination bands based on computed anharmonic vibrational frequency analysis).

The quantum chemical analysis of the structure of **22** shows that the compound is not planar, with a distortion of the heptagon. In the singlet ground state, the compound has an angle of 104.9° at nitrogen and a wide angle of 161.4° at boron, as shown in Figure 8a. This is due to the electronegativity difference between nitrogen and boron center. The natural bond orbital (NBO) analysis reveals occupancies of 1.82 e^- and 0.34 e^- for the nitrogen lone pair orbital (HOMO-1) and vacant boron orbital (LUMO), respectively. These values are slightly higher compared to the NBO occupancies of **1** at the M06-2X/6-311+G(d,p) level of theory (Figure 8b). As per the second-order perturbation assessment of the donor-acceptor interaction, the n(N) → n*(B) interaction was estimated to have an E(2) value of 34.5 kcal/mol. The natural charges obtained on N (-0.91) and B (+1.16) are large, while the Wiberg bond index was only 1.55 between B and N. We also analyzed Lewis acidity of **1** and **22** by employing the method by Ofial et al. from known Lewis basicities LB_B and Lewis acidities LA_B, computed equilibrium constants ($\Delta G_{iso}° = -RT \ln K_B$), and the equation $\log K_B = LA_B + LB_B$.[178] The LA_B value obtained from ΔG_{iso} is $LA_B = 21.5 \pm 2.6$ for **1** and $LA_B = 9.1 \pm 2.6$ for **22**. This indicates that Lewis's acidity of **22** is 12 magnitudes smaller than that of 1,2-azaborinine **1**.

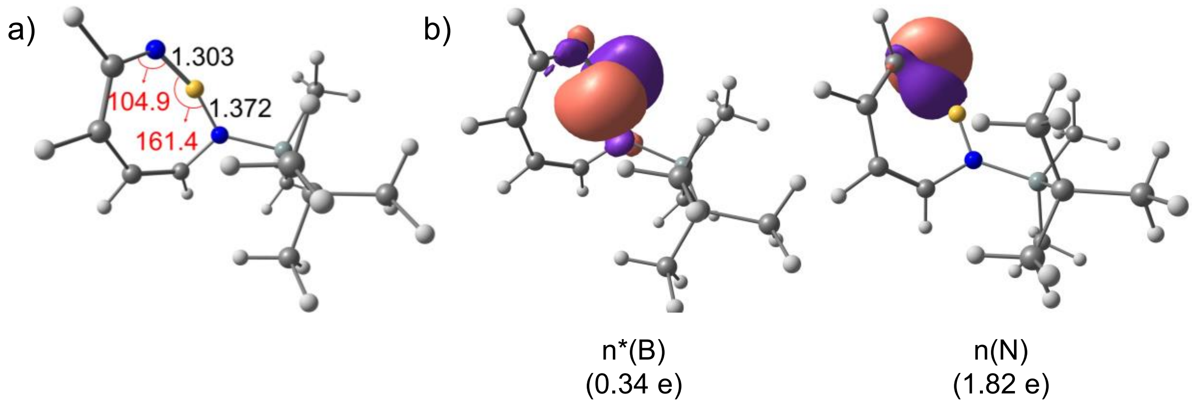
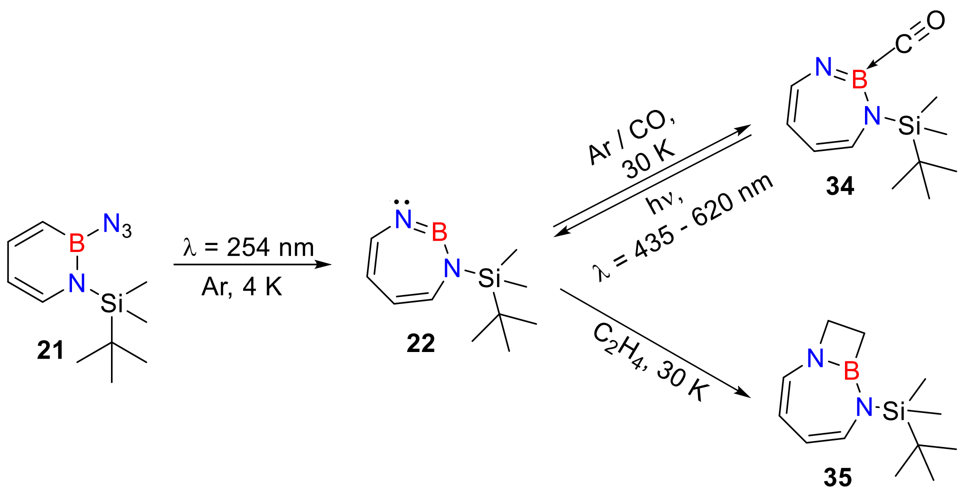


Figure 8. a) Computed (M06-2X/6-311+G(d,p)) optimized geometry of **22**. b) Natural bond orbitals (NBOs) and their occupation numbers. Important bond lengths [Å] and bond angles [°] are given.

Following the successful generation and isolation of 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22**, and considering its non-reactivity with nitrogen, we opted to investigate its reactivity with a stronger Lewis base, CO (Scheme 20). In the reaction with CO, after deposition of precursor **21**, the matrix window was irradiated with λ = 254 nm to generate **22**. After the successful generation of **22**, the matrix was annealed to 30 K, wherein peaks corresponding to **22** decreased in intensity while concomitantly new peaks were observed. The new peaks observed were attributed to Lewis acid-base adduct **34** (Figure 9), supported by computational data. The isotopic shifts of CO stretching were obtained through separate experiments using isotopologues ^{13}CO and $C^{18}O$ and are in good agreement with computationally predicted shifts.



Scheme 20. Photochemical generation of **22** from its precursor **21** and its reaction with CO and C_2H_4.

Subsequent irradiation of the matrix with 435 nm > λ > 620 nm, following the annealing step, led to the regeneration of **22**, implying that the reaction of 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22** with CO was a photochemically reversible reaction (Figure 10). The most intense peak observed for Lewis acid-base adduct **34** was at 2112 cm^{-1}, corresponding to ν(CO) stretching vibration, while for $C^{18}O$ and ^{13}CO isotopologues, the peak was observed at 2065 cm^{-1} and 2064 cm^{-1}, respectively.[169] This observation suggested a notable preference for the formation of Lewis acid-base adduct over (2 + 1) and (2 + 2) cycloaddition reactions, as observed in the reaction of 1,2-azaborinine **1** with CO.[34]

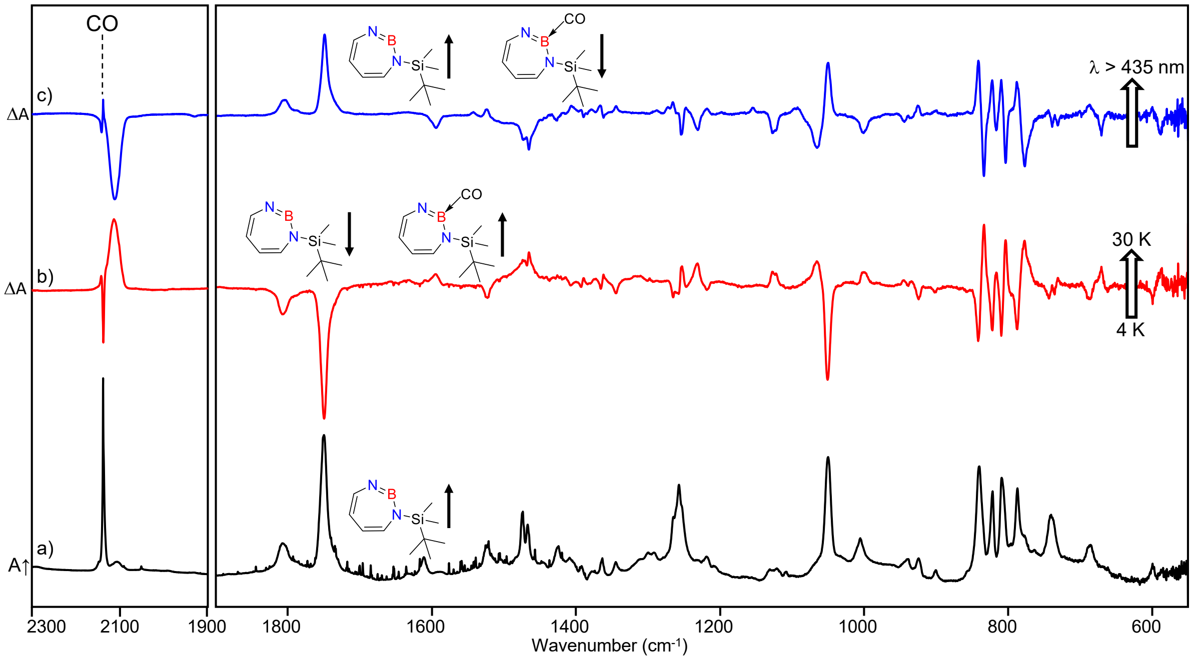


Figure 9. Infrared spectra obtained after irradiation of **3** in CO (2–3%) doped argon matrix. a) After 60 min irradiation with λ = 254 nm at T = 4 K. b) Experimental difference spectrum after annealing for 30 min at 30 K (following the irradiation with λ = 254 nm). c) Experimental difference spectrum obtained after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing at 30 K).

After successfully trapping **22** with CO, we studied the reactivity of **22** with olefin, using ethene for the study of (2 + 2) cycloaddition reaction with **22** (Scheme 20). To examine the reactivity of **22** with ethene (C_2H_4), precursor **21** was irradiated with λ = 254 nm which resulted in the formation of 1,3,2-diazaborepine **22**. However, in addition to **22**, various new peaks were observed, attributed to **35** based on computational analyses. Following this, we annealed the matrix up to 30 K, which resulted in the decrease of the signals corresponding to **22** and increase in the intensity of the signals attributing to **35**. This indicated that the formation of (2 + 2) cycloaddition product **35** from **22** proceeds thermally via a low activation barrier of 1.0 kcal/mol at DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) level of theory. The most intense peaks of **35**, at 1637 cm^{-1}, and 1615 cm^{-1}, were assigned to the π(C=C) stretching vibration of the ring (Figure 10). For further verification of the formation of **35**, C_2D_4 was employed in Ar matrix to observe the isotopic shift of the compound. The experimental isotopic shifts aligned well with the isotopic shifts obtained computationally (as shown in Publication III).

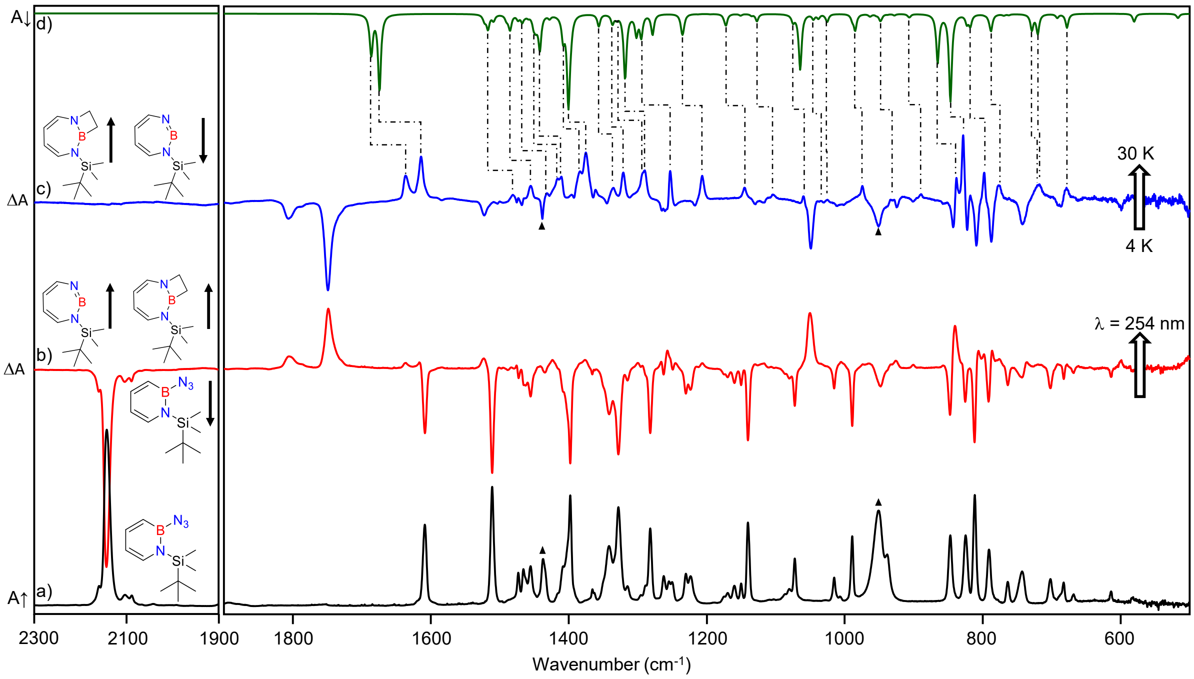


Figure 1. Infrared spectra obtained after a) deposition of **3** in C_2H_4 (5%) doped argon matrix. b) Experimental difference spectrum after 60 min irradiation with λ = 254 nm at T = 4 K. c) Experimental difference spectrum after annealing for 30 min at 30 K (following the irradiation with λ = 254 nm). d) Computed (B3LYP-D3(BJ)/6-311+G(d,p)) harmonic IR spectrum of **35**. (▲ = C_2H_4)

An informative analysis can be obtained from comparing the reaction mechanism involving ethene with 1,2-azaborinine **1** and 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22**. The formation of (2 + 2) cycloaddition product **23b** in the reaction of **1** with C_2H_4 was associated with a barrier of 14.6 kcal/mol at CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) from the Lewis acid-base complex.[168] This is significantly higher than the barrier for the (2 + 2) cycloaddition product **35** (1.0 kcal/mol from Lewis acid-base complex).[168] The observation of (2 + 2) cycloaddition of ethene and less Lewis acidic **22** is both intriguing and unexpected. Despite having high Lewis acidity, **1** forms a stable Lewis acid-base complex with ethene, and the (2 + 2) cycloaddition reaction was unexpected to be observed at 30 K under matrix isolation conditions.

In conclusion, detailed investigations, blending experimental and computational approaches, have unveiled the pronounced reactivity of 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **22** towards CO and C_2H_4. When interacting with CO, **22** forms the Lewis acid–base adduct **34**, with no observed (2 + 1) or (2 + 2) cycloaddition reactions due to formidable energy barriers. On the other hand, when encountering C_2H_4, **22** participates in a (2 + 2) cycloaddition reaction, generating product **35**. This newly discovered (2 + 2) cycloaddition with ethene underlines the potential of **22** to introduce innovative reactivity pathways for constructing BN-containing heterocycles.

5 References

[1] E. R. Abbey, A. N. Lamm, A. W. Baggett, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 12908-12913.

[2] E. R. Abbey, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 11508-11511.

[3] T. Hatakeyama, S. Hashimoto, S. Seki, M. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 18614-18617.

[4] C. A. Jaska, D. J. Emslie, M. J. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *J. Am. Chem. Soc.* **2006**, *128*, 10885-10896.

[5] S. M. Mansell, N. C. Norman, C. A. Russell, *Dalton Trans.* **2010**, *39*, 5084-5086.

[6] X. Y. Wang, H. R. Lin, T. Lei, D. C. Yang, F. D. Zhuang, J. Y. Wang, S. C. Yuan, J. Pei, *Angew. Chem.* **2013**, *125*, 3199-3202.

[7] M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem., Int. Ed.* **2007**, *46*, 4940-4943.

[8] T. Taniguchi, S. Yamaguchi, *Organometallics* **2010**, *29*, 5732-5735.

[9] J. Dosso, J. Tasseroul, F. Fasano, D. Marinelli, N. Biot, A. Fermi, D. Bonifazi, *Angew. Chem.* **2017**, *129*, 4554-4558.

[10] M. Lepeltier, O. Lukoyanova, A. Jacobson, S. Jeeva, D. F. Perepichka, *ChemComm* **2010**, *46*, 7007-7009.

[11] M. J. Bosdet, W. E. Piers, *Can. J. Chem.* **2009**, *87*, 8-29.

[12] Z. Liu, T. B. Marder, *Angew. Chem., Int. Ed.* **2008**, *47*, 242-244.

[13] X.-Y. Wang, J.-Y. Wang, J. Pei, *Chem. Eur. J.* **2015**, *21*, 3528-3539.

[14] P. G. Campbell, A. J. Marwitz, S. Y. Liu, *Angew. Chem., Int. Ed.* **2012**, *51*, 6074-6092.

[15] M. Stępień, E. Gońka, M. Żyła, N. Sprutta, *Chem. Rev.* **2016**, *117*, 3479–3716.

[16] D. Bonifazi, F. Fasano, M. M. Lorenzo-Garcia, D. Marinelli, H. Oubaha, J. Tasseroul, *ChemComm* **2015**, *51*, 15222-15236.

[17] H. Helten, *Chem. Eur. J.* **2016**, *22*, 12972-12982.

[18] M. M. Morgan, W. E. Piers, *Dalton Trans.* **2016**, *45*, 5920-5924.

[19] P. Paetzold, in *Advances in Inorganic Chemistry, Vol. 31*, Elsevier, **1987**, pp. 123-170.

[20] P. Paetzold, *Pure Appl. Chem.* **1991**, *63*, 345-350.

[21] A. Stock, E. Pohland, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2215-2223.

[22] M. J. S. Dewar, V. P. Kubba, R. Pettit, *J. Chem. Soc.* **1958**, 3073-3076.

[23] M. J. Dewar, P. A. Marr, *J. Am. Chem. Soc.* **1962**, *84*, 3782-3782.

[24] D. G. White, *J. Am. Chem. Soc.* **1963**, *85*, 3634-3636.

[25] A. J. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S. Y. Liu, *Angew. Chem., Int. Ed.* **2009**, *48*, 973-977.

[26] A. J. Ashe, Fang, *Org. Lett.* **2000**, *2*, 2089-2091.

[27] A. J. Ashe, X. Fang, X. Fang, J. W. Kampf, *Organometallics* **2001**, *20*, 5413-5418.

[28] E. R. Abbey, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 7250-7252.

[29] Z. X. Giustra, S.-Y. Liu, *J. Am. Chem. Soc.* **2018**, *140*, 1184-1194.

[30] H. Braunschweig, A. Gackstatter, T. Kupfer, T. Scheller, F. Hupp, A. Damme, N. Arnold, W. Ewing, *Chem. Sci.* **2015**, *6*, 3461-3465.

[31] H. F. Bettinger, M. Müller, *J. Phys. Org. Chem.* **2015**, *28*, 97-103.

[32] M. Müller, C. Maichle-Mössmer, H. F. Bettinger, *Angew. Chem., Int. Ed.* **2014**, *53*, 9380-9383.

[33] K. Edel, S. A. Brough, A. N. Lamm, S.-Y. Liu, H. F. Bettinger, *Angew. Chem., Int. Ed.* **2015**, *54*, 7819-7822.

[34] K. Edel, J. S. A. Ishibashi, S.-Y. Liu, H. F. Bettinger, *Angew. Chem., Int. Ed.* **2019**, *58*, 4061-4064.

[35] C. Keck, J. Hahn, D. Gupta, H. F. Bettinger, *Chem. Eur. J.* **2022**, *28*, e202103614.

[36] K. Edel, R. F. Fink, H. F. Bettinger, *J. Comput. Chem.* **2016**, *37*, 110-116.

[37] W. Sander, C. Kötting, *Chem. Eur. J.* **1999**, *5*, 24-28.

[38] J. Breidung, H. Bürger, C. Kötting, R. Kopitzky, W. Sander, M. Senzlober, W. Thiel, H. Willner, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1983-1985.
[39] W. Pieper, D. Schmitz, P. Paetzold, *Chem. Ber.* **1981**, *114*, 3801-3812.
[40] H. F. Bettinger, H. Bornemann, *J. Am. Chem. Soc.* **2006**, *128*, 11128-11134.
[41] H. F. Bettinger, *Inorg. Chem.* **2007**, *46*, 5188-5195.
[42] H. F. Bettinger, M. Filthaus, *Org. Biomol. Chem.* **2010**, *8*, 5477-5482.
[43] V. Bhagat, J. Schumann, H. F. Bettinger, *Chem. Eur. J.* **2020**, *26*, 12654-12663.
[44] V. Bhagat, J. Schumann, H. F. Bettinger, *Angew. Chem., Int. Ed.* **2021**, *60*, 23112-23116.
[45] W. Maringgele, U. Seebold, A. Heine, D. Stalke, M. Noltemeyer, G. M. Sheldrick, A. Meller, *Organometallics* **1991**, *10*, 2097-2098.
[46] A. Meller, U. Seebold, W. Maringgele, M. Noltemeyer, G. M. Sheldrick, *J. Am. Chem. Soc.* **1989**, *111*, 8299-8300.
[47] W. Maringgele, D. Bromm, A. Meller, *Tetrahedron* **1988**, *44*, 1053-1056.
[48] A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1987**, *120*, 1437-1439.
[49] E. R. Lory, R. F. Porter, *J. Am. Chem. Soc.* **1973**, *95*, 1766-1770.
[50] Y. Kawashima, K. Kawaguchi, E. Hirota, *J. Chem. Phys.* **1987**, *87*, 6331-6333.
[51] C. A. Thompson, L. Andrews, J. M. Martin, J. El-Yazal, *J. Phys. Chem.* **1995**, *99*, 13839-13849.
[52] C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1995**, *117*, 10125-10126.
[53] P. Paetzold, A. Richter, T. Thijssen, S. Würtenberg, *Chem. Ber.* **1979**, *112*, 3811-3827.
[54] H. Nöth, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1603-1623.
[55] E. v. Steuber, G. Elter, M. Noltemeyer, H.-G. Schmidt, A. Meller, *Organometallics* **2000**, *19*, 5083-5091.
[56] M. Haase, U. Klingebiel, *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 324-324.
[57] P. I. Paetzold, G. Stohr, H. Maisch, H. Lenz, *Chem. Ber.* **1968**, *101*, 2881-2888.
[58] J. Kiesgen, J. Münster, P. Paetzold, *Chem. Ber.* **1993**, *126*, 1559-1563.
[59] C. Klöfkorn, M. Schmidt, T. Spaniol, T. Wagner, O. Costisor, P. Paetzold, *Chem. Ber.* **1995**, *128*, 1037-1043.
[60] P. Paetzold, *Phosphorus, Sulfur, Silicon Relat. Elem.* **1994**, *93*, 39-50.
[61] P. Paetzold, C. von Plotho, *Chem. Ber.* **1982**, *115*, 2819-2825.
[62] K. Delpy, H.-U. Meier, P. Paetzold, C. v. Plotho, *Z. Naturforsch. B* **1984**, *39*, 1696-1701.
[63] K.-H. v. Bonn, T. v. Bennigsen-Mackiewicz, J. Kiesgen, C. v. Plotho, P. Paetzold, *Z. Naturforsch. B* **1988**, *43*, 61-68.
[64] P. Paetzold, J. Kiesgen, K. Krahé, H.-U. Meier, R. Boese, *Z. Naturforsch. B* **1991**, *46*, 853-860.
[65] J. Münster, P. Paetzold, E. Schröder, H. Schwan, T. von Bennigsen-Mackiewicz, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2641-2651.
[66] B. Kröckert, K.-H. van Bonn, P. Paetzold, *Z. Anorg. Allg. Chem.* **2005**, *631*, 866-868.
[67] H. U. Meier, P. Paetzold, E. Schröder, *Chem. Ber.* **1984**, *117*, 1954-1964.
[68] P. Paetzold, T. von Bennigsen-Mackiewicz, *Chem. Ber.* **1981**, *114*, 298-305.
[69] G. Elter, M. Neuhaus, A. Meller, D. Schmidt-Bäse, *J. Organomet. Chem.* **1990**, *381*, 299-313.
[70] W. Luthin, G. Elter, A. Heine, D. Stalke, G. M. Sheldrick, A. Meller, *Z. Anorg. Allg. Chem.* **1992**, *608*, 147-152.
[71] E. Rivard, W. A. Merrill, J. C. Fettinger, R. Wolf, G. H. Spikes, P. P. Power, *Inorg. Chem.* **2007**, *46*, 2971-2978.
[72] W. Luthin, J. G. Stratmann, G. Elter, A. Meller, A. Heine, H. Gornitzka, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1995-2000.
[73] H. Nöth, S. Weber, *Z. Naturforsch. B* **1983**, *38*, 1460-1465.
[74] P. Paetzold, E. Eleftheriadis, R. Minkwitz, V. Wölfel, R. Gleiter, P. Bischof, G. Friedrich, *Chem. Ber.* **1988**, *121*, 61-66.
[75] H. Viehe, *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 746-752.

[76] P. Paetzold, C. V. Plotho, G. Schmid, R. Boese, B. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter, W. Schüfer, *Chem. Ber.* **1984**, *117*, 1089-1102.

[77] P. Paetzold, K. Delpy, R. Boese, *Z. Naturforsch. B* **1988**, *43*, 839-845.

[78] T. Franz, E. Hanecker, H. Nöth, W. Stöcker, W. Storch, G. Winter, *Chem. Ber.* **1986**, *119*, 900-916.

[79] N. C. Baird, R. K. Datta, *Inorg. Chem.* **1972**, *11*, 17-19.

[80] V. M. Rosas-Garcia, *Comput. Theor. Chem.* **2011**, *967*, 160-164.

[81] P. Paetzold, C. von Plotho, E. Niecke, R. Rüger, *Chem. Ber.* **1983**, *116*, 1678-1681.

[82] P. Paetzold, K. Delpy, R. P. Hughes, W. A. Herrmann, *Chem. Ber.* **1985**, *118*, 1724-1725.

[83] H. Braunschweig, P. Paetzold, R. Boese, *Chem. Ber.* **1993**, *126*, 1571-1577.

[84] P. Paetzold, E. Schröder, G. Schmid, R. Boese, *Chem. Ber.* **1985**, *118*, 3205-3216.

[85] P. Paetzold, R. Truppat, *Chem. Ber.* **1983**, *116*, 1531-1539.

[86] T. M. Gilbert, *Organometallics* **2000**, *19*, 1160-1165.

[87] T. M. Gilbert, *Organometallics* **2003**, *22*, 2298-2304.

[88] T. M. Gilbert, *Organometallics* **2005**, *24*, 6445-6449.

[89] P. Paetzold, C. v. Plotho, H. Schwan, H.-U. Meier, *Z. Naturforsch. B* **1984**, *39*, 610-614.

[90] H. Nöth, S. Weber, *Chem. Ber.* **1985**, *118*, 2554-2556.

[91] E. Bulak, G. E. Herberich, I. Manners, H. Mayer, P. Paetzold, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 958-959.

[92] A. Antiñolo, P. Gómez-Sal, J. M. de Ilarduya, A. Otero, P. Royo, S. M. Carrera, S. G. Blanco, *J. Chem. Soc., Dalton Trans.* **1987**, 975-980.

[93] P. Paetzold, K. Delpy, *Chem. Ber.* **1985**, *118*, 2552-2553.

[94] K. Delpy, D. Schmitz, P. Paetzold, *Chem. Ber.* **1983**, *116*, 2994-2999.

[95] H. Braunschweig, P. Paetzold, R. Boese, *Chem. Ber.* **1990**, *123*, 485-487.

[96] H. Braunschweig, P. Paetzold, R. Boese, *Chem. Ber.* **1993**, *126*, 1571-1577.

[97] T. Thiess, G. Bélanger-Chabot, F. Fantuzzi, M. Michel, M. Ernst, B. Engels, H. Braunschweig, *Angew. Chem., Int. Ed.* **2020**, *59*, 15480-15486.

[98] A. Koner, T. Sergeieva, B. Morgenstern, D. M. Andrada, *Inorg. Chem.* **2021**, *60*, 14202-14211.

[99] H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem., Int. Ed.* **2003**, *42*, 502-528.

[100] J.-A. García-López, M. F. Greaney, *Chem. Soc. Rev.* **2016**, *45*, 6766-6798.

[101] C. M. Gampe, E. M. Carreira, *Angew. Chem., Int. Ed.* **2012**, *51*, 3766-3778.

[102] A. V. Dubrovskiy, N. A. Markina, R. C. Larock, *Org. Biomol. Chem.* **2013**, *11*, 191-218.

[103] D. Pérez, D. Peña, E. Guitián, *Eur. J. Org. Chem.* **2013**, *2013*, 5981-6013.

[104] P. M. Tadross, B. M. Stoltz, *Chem. Rev.* **2012**, *112*, 3550-3577.

[105] H. Yoshida, K. Takaki, *Synlett* **2012**, *23*, 1725-1732.

[106] A. Bhunia, S. R. Yetra, A. T. Biju, *Chem. Soc. Rev.* **2012**, *41*, 3140-3152.

[107] C. Wentrup, *Aust. J. Chem.* **2010**, *63*, 979-986.

[108] R. Sanz, *Org. Prep. Proced. Int.* **2008**, *40*, 215-291.

[109] H. Pellissier, M. Santelli, *Tetrahedron* **2003**, *59*, 701-730.

[110] O. Chapman, K. Mattes, C. McIntosh, J. Pacansky, G. Calder, G. Orr, *J. Am. Chem. Soc.* **1973**, *95*, 6134-6135.

[111] R. v. Stoermer, B. Kahlert, *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 1633-1640.

[112] G. Wittig, *Sci. Nat.* **1942**, *30*, 696-703.

[113] G. Wittig, G. Harborth, *Ber. Dtsch. Chem. Ges.* **1944**, *77*, 306-314.

[114] G. Wittig, L. Pohmer, *Chem. Ber.* **1956**, *89*, 1334-1351.

[115] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, C. W. Vaughan, *J. Am. Chem. Soc.* **1953**, *75*, 3290-3291.

[116] J. D. Roberts, D. A. Semenow, H. E. Simmons Jr, L. Carlsmith, *J. Am. Chem. Soc.* **1956**, *78*, 601-611.

[117] M. Panar, J. D. Roberts, *J. Am. Chem. Soc.* **1960**, *82*, 3629-3632.

[118] R. Warmuth, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1347-1350.

[119] R. Warmuth, *Eur. J. Org. Chem.* **2001**, *2001*, 423-437.

[120] P. J. Fazen, L. A. Burke, *Inorg. Chem.* **2006**, *45*, 2494-2500.

[121] G. Maier, H. P. Reisenauer, J. Henkelmann, C. Kliche, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 295-296.

[122] S. Biswas, M. Müller, C. Tönshoff, K. Eichele, C. Maichle-Mössmer, A. Ruff, B. Speiser, H. F. Bettinger, *Eur. J. Org. Chem.* **2012**, *2012*, 4634-4639.

[123] R. Köster, S. Hattori, Y. Morita, *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 695-695.

[124] E. Whittle, D. A. Dows, G. C. Pimentel, *J. Chem. Phys.* **1954**, *22*, 1943-1943.

[125] I. Dunkin, *Chem. Soc. Rev.* **1980**, *9*, 1-23.

[126] R. N. Perutz, *Annual Reports Section" C"(Physical Chemistry)* **1985**, *82*, 157-191.

[127] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, **2016**.

[128] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73-78.

[129] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, e1327.

[130] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, e1606.

[131] Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock Iii, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio Jr, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, et al., *Mol. Phys.* **2015**, *113*, 184-215.

[132] R. Dennington, T. A. Keith, J. M. Millam, *Semichem Inc Shawnee Mission KS* **2016**.

[133] B. O. Roos, P. R. Taylor, P. E. Sigbahn, *Chem. Phys.* **1980**, *48*, 157-173.

[134] B. O. Roos, *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part 2* **1987**, *69*, 399-445.

[135] P. E. Siegbahn, J. Almlöf, A. Heiberg, B. O. Roos, *J. Chem. Phys.* **1981**, *74*, 2384-2396.

[136] J. Čížek, J. Paldus, *Int. J. Quantum Chem.* **1971**, *5*, 359-379.

[137] R. J. Bartlett, G. D. Purvis, *Int. J. Quantum Chem.* **1978**, *14*, 561-581.

[138] R. J. Bartlett, *J. Phys. Chem.* **1989**, *93*, 1697-1708.

[139] R. J. Bartlett, M. Musiał, *Rev. Mod. Phys.* **2007**, *79*, 291.

[140] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974-12980.

[141] F. Neese, *Coord. Chem. Rev.* **2009**, *253*, 526-563.

[142] C. M. Marian, N. Gilka, *J. Chem. Theory Comput.* **2008**, *4*, 1501-1515.

[143] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
[144] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.
[145] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.
[146] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.
[147] M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.* **1988**, *153*, 503-506.
[148] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095-9102.
[149] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654.
[150] H. P. Hratchian, H. B. Schlegel, *J. Chem. Phys.* **2004**, *120*, 9918-9924.
[151] H. P. Hratchian, H. B. Schlegel, *J. Chem. Theory Comput.* **2005**, *1*, 61-69.
[152] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479-483.
[153] D. G. Liakos, Y. Guo, F. Neese, *J. Phys. Chem. A* **2020**, *124*, 90-100.
[154] C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106.
[155] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.* **2013**, *139*, 134101.
[156] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, *144*, 024109.
[157] T. H. Dunning Jr., *J. Chem. Phys.* **1989**, *90*, 1007-1023.
[158] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899-926.
[159] E. D. Glendening, C. R. Landis, F. Weinhold, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 1-42.
[160] F. Weinhold, *J. Comput. Chem.* **2012**, *33*, 2363-2379.
[161] E. D. Glendening, K. B. J, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, University of Wisconsin, Madison, **2012**.
[162] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51-57.
[163] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260.
[164] R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789-807.
[165] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
[166] H. S. Yu, X. He, S. L. Li, D. G. Truhlar, *Chem. Sci.* **2016**, *7*, 5032-5051.
[167] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
[168] D. Gupta, H. F. Bettinger, *J. Org. Chem.* **2023**, *88*, 8369-8378.
[169] D. Gupta, R. Einholz, H. F. Bettinger, *Chem. Sci.* **2024**.
[170] D. Gupta, C. Keck, C. Tönshoff, V. Bhagat, R. Strobel, M. Eder, P. Baylère, S. Labat, A. Chrostowska, H. F. Bettinger, *Chem. Eur. J.* **2023**, *n/a*, e202302444.
[171] D. Gupta, A. Omont, H. F. Bettinger, *Chem. Eur. J.* **2021**, *27*, 4605-4616.
[172] S. Biswas, I. M. Oppel, H. F. Bettinger, *Inorg. Chem.* **2010**, *49*, 4499-4506.
[173] S. Kudoh, M. Takayanagi, M. Nakata, *J. Photochem. Photobiol. A* **1999**, *123*, 25-30.
[174] D. E. Johnstone, J. R. Sodeau, *J. Phys. Chem.* **1991**, *95*, 165-169.
[175] L. A. Johnson, S. A. Sturgis, I. A. Al-Jihad, B. Liu, J. V. Gilbert, *J. Phys. Chem. A* **1999**, *103*, 686-690.
[176] H.-J. Himmel, M. Junker, H. Schnöckel, *J. Chem. Phys.* **2002**, *117*, 3321-3326.
[177] C. Keck, Dissertation thesis, Eberhard Karls Universität Tübingen **2023**.
[178] R. J. Mayer, N. Hampel, A. R. Ofial, *Chem. Eur. J.* **2021**, *27*, 4070-4080.

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Reactions of 1,2-Azaborinine, a BN-Benzyne, with Organic π Systems

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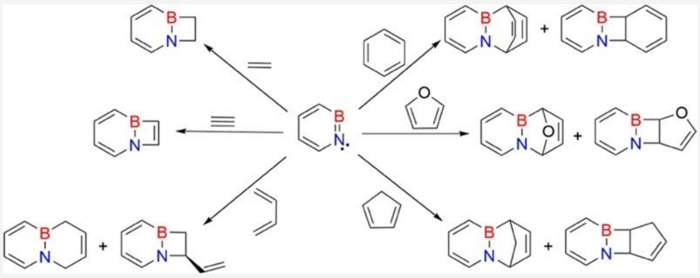
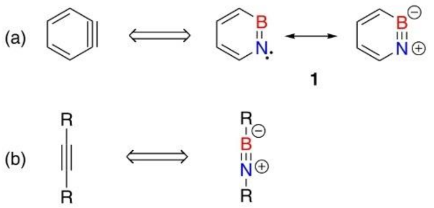


ABSTRACT: Ortho-benzyne and 1,2-azaborinine are related by the formal exchange of the CC triple bond by the isoelectronic BN unit. The (2 + 2) and (2 + 4) cycloaddition reactions of 1,2-azaborinine with the different organic π systems (ethene, ethyne, 1,3-butadiene, 1,3-cyclopentadiene, furan, benzene) were examined computationally using density functional, second-order perturbation, and coupled-cluster methods. All reactions of 1,2-azaborinine with the studied substrates are highly exothermic and involve the formation of Lewis acid−base complexes of 1,2-azaborinine and respective π systems. The interaction between the π bond of the substrates and the empty p orbital of the boron atom in these complexes is remarkably strong, resulting in two-step mechanisms for the (2 + 2) and (2 + 4) cycloaddition reactions. Cycloaddition reactions have lower barriers than CH insertion reactions, and (2 + 4) reactions are favored over (2 + 2) cycloadditions.

■ INTRODUCTION

Arynes are well known as extremely useful reactive intermediates in organic chemistry.[1−11] The formal substitution of the C≡C bond in *ortho*-benzyne by an isoelectronic BN bond results in 1,2-azaborinine **1** that features a formal boron−nitrogen triple bond (see Scheme 1a).[12−14] This type of replacement in organic compounds has been proven very beneficial for modifying the properties relevant for materials and biomedical applications.[15−21] The properties of **1** were initially studied computationally,[12] before its first direct infrared spectroscopic observation was achieved under matrix isolation conditions.[13]

Scheme 1. (a) Resonance Forms of 1,2-Azaborinine (1) and Its Analogy with Ortho-Benzyne; (b) Iminoboranes and Their Analogy with Alkynes



Due to the polar BN link, the already high reactivity of *ortho*-benzyne gets even more boosted. BN-aryne **1** is strongly Lewis acidic as evidenced by bonding to N_2, CO, and Xe as well as by (2 + 2) cycloaddition with CO_2.[13,22] The NBO analysis done previously by Bettinger et al. shows that the N atom has a lone pair of electrons in the molecular plane and the B atom has an empty orbital with high p-character (see Scheme 1a).[13] The dibenzo derivative of **1**, dibenzo[*c*,*e*][1,2]azaborinine, was inferred as a reactive intermediate in benzene solution[14,23] that can even activate the strong Si−F bond for subsequent insertion reaction.[24]

1,2-Azaborinine can also be viewed as a cyclic iminoborane. Iminoboranes are isoelectronic with alkynes (see Scheme 1b),[25−28] but they are not kinetically inert due to a dipole moment and tend to form rings or polymers.[25] Cyclo-oligomerization was indeed also observed for dibenzo[*c*,*e*]-[1,2]azaborinine.[14,24] Paetzold et al. observed the (2 + 2) cycloaddition reaction of iminoborane with iminophosphanes in 1982,[29] and later the (2 + 2) cycloaddition reaction with

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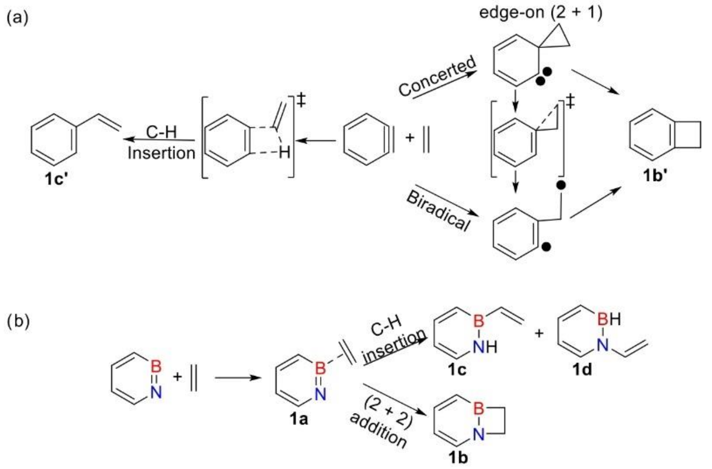
Scheme 2. (a) Reaction of *ortho*-Benzyne and Ethene as Studied by Ozkan and Kinal[58] and Temps et al.;[55] (b) Reaction of 1,2-Azaborinine with Ethene



methylene-titanium[30] and neopentylidenetantalum complexes.[31] Paetzold et al. also reported (2 + 3) cycloaddition reaction of iminoboranes with diazomethane.[32] Gilbert performed a series of ab initio computational studies that compared iminoboranes and alkynes with respect to the electronic and geometric structure, as well as the reactivity in (2 + 2) and (2 + 4) cycloadditions toward alkenes and alkynes.[33−36]

The understanding of the reactivity of 1,2-azaborinine lags far behind that of *ortho*-benzyne. The dibenzo derivative of 1,2-azaborinine is known to undergo dimerization without barrier[23] but can be trapped with large excesses of suitable trapping agents (R_3Si-E, E = F, Cl, OSi$(CH_3)_3$, H) due to low barriers for Si−E insertion reactions.[24] Barriers for reactions with other reagents are not known, but if they are low enough, trapping in solution phase, gas phase, or under matrix isolation conditions might be feasible. We have thus embarked on a theoretical investigation of the reaction of 1,2-azaborinine in (2 + 2) and (2 + 4) cycloaddition reactions with the C≡C bond of ethyne and the C═C bonds in ethene, 1,3-butadiene, cyclopentadiene, furan, as well as benzene.

■ EXPERIMENTAL SECTION

Computational Details. All of the structures were fully optimized using the M06-2X[37] global hybrid functional, the B3LYP[38,39] hybrid exchange−correlation energy functional along with Grimme's[40] London dispersion correction B3LYP-D3,[38,39] as well as second-order Møller−Plesset perturbation theory[41] (MP2) and its spin-component scaled[42] variant (SCS-MP2). The 6-311+G(d,p) (split-valence triple-ζ with diffuse s and p functions for all atoms as well as d polarization functions on nonhydrogen atoms and p polarization functions for hydrogen)[43] basis set was adopted for all geometry optimizations. Apart from that, the polarized continuum model (PCM) solvation model was employed to study the effect of solvation using benzene as a solvent.[44] These data can be found in the SI. Harmonic vibrational frequencies were computed analytically, which confirmed the nature of the stationary points as minima, or first-order saddle points (transition states). Additionally, to reveal which minima are connected to the transition states, intrinsic reaction coordinate (IRC)[45,46] paths were calculated at the different level of theories for each reaction (see the SI). To refine the energies, single-point calculations based on all of the structures were performed using coupled-cluster theory with single, double, and a perturbative estimate of triple excitations (CCSD(T))[47] in conjunction with Dunning's[48] triple-ζ (cc-pVTZ) basis set and the frozen core approximation as implemented in ORCA 5.0.[49] All density functional theory and MP2 calculations were performed with Gaussian 16.[50] SCS-MP2 and CCSD(T) calculations were performed using Orca 5.0.[49] Natural bond orbital analysis was carried with the NBO 6.0 program using the B3LYP-D3/6-311+G(d,p) geometries.[51−54]

For extensive analysis, the structural and energetic data for the molecules were studied at various levels of theory. In general, all models predicted similar structures and energies for the reactants and the products. Unless noted otherwise, the CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) data is discussed in the text, and for the data obtained at other levels, the reader is referred to the Supporting Information (SI).

■ RESULTS AND DISCUSSION

The manuscript is structured as follows: after the discussion of the reaction mechanisms of 1,2-azaborinine with ethene, ethyne, trans-1,3-butadiene, cis-1,3-butadiene, cyclopentadiene, furan, and benzene, a comparative discussion of all van der Waals complexes between 1,2-azaborinine and organic π systems is provided. Finally, the reactivities of 1,2-azaborinine and ortho-benzyne are compared.

Reactions of 1,2-Azaborinine with Ethene. The reaction of *ortho*-benzyne with ethene has already been studied experimentally as well as theoretically,[55−58] and two major products were observed—benzocyclobutane (**1b′**) due to (2 + 2) cycloaddition and styrene (**1c′**) due to C−H insertion (see Scheme 2a). The formation of benzocyclobutane (**1b′**), which is orbital symmetry-forbidden according to the Woodward−Hoffmann rules,[59,60] has been studied theoretically.[55,61] Two possible pathways, i.e., carbene and biradical pathways, were identified. A multistep mechanism was proposed by Ozkan and Kinal[58] indicating passing through a (2 + 1) transition state leading to an edge-on carbene intermediate through a barrier of 20.7 kcal/mol (CAS-MP2/6-31G(d)//CASSCF(6,6)/6-31G(d) level of theory) along with a biradical intermediate, which forms by a lower energy barrier (15.5 kcal/mol at CAS-MP2/6-31G(d)//CASSCF(6,6)/6-31G(d) level of theory).[58] The formation of styrene (**1c′**) as proposed by Temps et al.[55] exhibits a high potential energy barrier (5 kcal/mol more than the carbene pathway) and is going through a concerted H-

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atom transfer pathway. Also, Kinal and Piecuch considered a possible involvement of triplet state species and concluded that all reactions proceed solely on the singlet surfaces.[61]

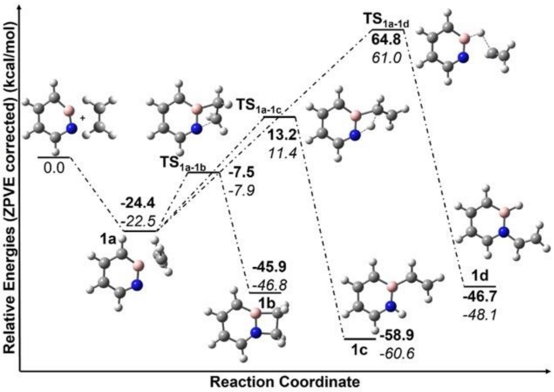


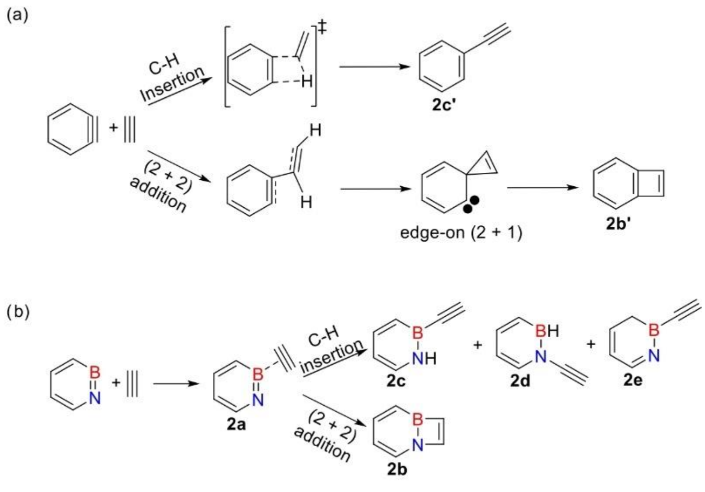
Figure 1. Reaction pathways for the reaction of 1,2-azaborinine with ethene at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated ZPVE-corrected energies in kcal/mol are shown.

Two fundamental reactions were considered for 1,2-azaborinine and ethene which in principle can yield three different products. One of the reactions is (2 + 2) cycloaddition to the C═C bond to give the BN analogue of benzocyclobutane (**1b**). Another reaction considered is C−H insertion to give two BN analogues of styrene, i.e., B-substituted vinyl-azaborinine (**1c**), and N-substituted vinyl-azaborinine (**1d**) (see Scheme 2b). The detailed reaction pathways were explored using ab initio quantum mechanical calculations. Both reactions proceed via a complex (**1a**) between 1,2-azaborinine and ethene that corresponds to a minimum on the potential energy surface (see Figure 1). The complex **1a** is formed due to the interaction between the empty boron orbital with high p-character and the C═C bond (see Figure 7 for geometrical parameters). Its formation is exothermic in nature with respect to the separated reactants by 22.5 kcal/mol at the CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) level of theory. A relaxed scan of the potential energy surface (PES) at the B3LYP/6-311+G(d,p) level of theory confirms that the formation of complex **1a** is barrierless (see SI, Table S15). This observation is very different from that of the reaction between ethene and *ortho*-benzyne. Ozkan and Kinal[58] and later Temps et al.[55] both identified a carbene intermediate and biradical intermediate with high activation barriers on the PES. The formation of the cycloaddition product **1b** is a concerted process from complex **1a** with a barrier of 14.6 kcal/mol. In view of the large binding energy of **1a**, the transition state lies *below* the energy of the free reactants.

The C−H insertion products **1c** and **1d** are also formed via concerted pathways from complex **1a**, but with higher barriers than the (2 + 2) addition product. Here, a hydrogen atom is directly transferred to the 1,2-azaborinine ring. The barrier for the formation of N-substituted vinyl-azaborinine **1d** (83.5 kcal/mol) with respect to **1a** is much higher than that for B-substituted vinyl-azaborinine **1c** (33.9 kcal/mol) (see Figure 1).

Reactions of 1,2-Azaborinine with Ethyne. The reaction of *ortho*-benzyne with ethyne has been studied experimentally as well as theoretically.[55,57] Two major products, benzocyclobutadiene (**2b′**) due to orbital symmetry-forbidden [2 + 2] cycloaddition and phenylethyne (**2c′**) due to C−H insertion (Scheme 3a), were observed.[55,57] Unlike in the case of the alkenes, only one multistep pathway was identified computationally for the cycloaddition reaction.[56] This involves an early-stage addition complex between ethyne and *ortho*-benzyne with a structure that is similar to the structure of the biradical intermediate (barrier of 12 kcal/mol) found for ethene. This easily converts to the edge-on intermediate, and finally, the ring-expansion step takes place over a relatively high barrier (15.1 kcal/mol with respect to reactants).[55] The formation of phenylethyne (**2c′**) displays a higher energy barrier (17.9 kcal/mol) and is going through a concerted H-atom transfer pathway.[55]

Scheme 3. (a) Reaction of *ortho*-Benzyne and Ethyne as Studied Earlier by Temps et al.;[55] (b) Reaction of 1,2-Azaborinine with Ethyne



Two fundamental reactions of 1,2-azaborinine with ethyne, (2 + 2) addition and C−H insertion, were considered in this study. These in principle yield three different products, namely, the BN analogue of benzocyclobutadiene (**2b**) and two BN analogues of phenylethyne, i.e., B-substituted ethynylazaborinine (**2c**) and N-substituted ethynylazaborinine (**2d**) (see Scheme 3b). All reactions proceed from a complex (**2a**) which is formed by the interaction between boron and the C≡C bond (see Figure 7 for geometrical parameters). The formation of **2a** is exothermic in nature with respect to the separated reactants by 16.3 kcal/mol. A relaxed scan of the PES at the B3LYP/6-311+G(d,p) level of theory verifies that the formation of **2a** can proceed without barrier on the potential energy surface (see SI, Table S15).

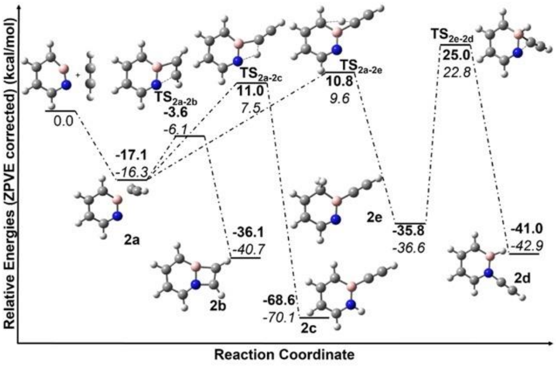


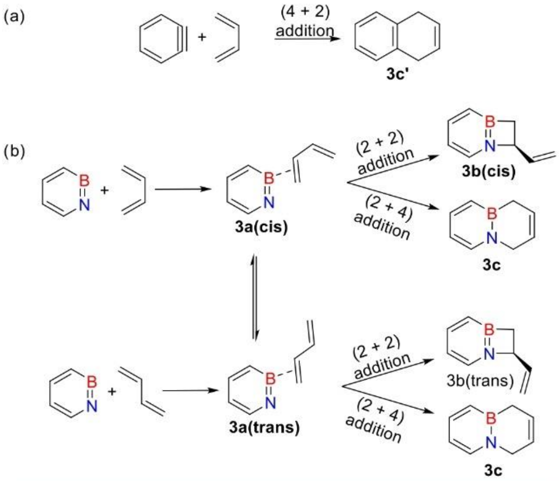
Figure 2. Reaction pathways for the reaction of 1,2-azaborinine with ethyne at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated ZPVE-corrected energies in kcal/mol are shown.

The (2 + 2) cycloaddition product **2b** forms in a concerted process from the complex **2a** with a barrier of 10.2 kcal/mol (see Figure 2). As observed for the reaction with ethene, this is *lower* than the energy of reactants. For the formation of **2c**, a hydrogen atom is directly transferred to the 1,2-azaborinine ring. This C−H insertion involves a strained four-membered transition state and thus has a high activation barrier of 23.8 kcal/mol with respect to **2a**. In contrast, the formation of N-substituted ethynylazaborinine **2d** proceeds stepwise from complex **2a**. It involves a high barrier for hydrogen transfer (25.9 kcal/mol) to give 2-ethynyl-3-dihydro-1,2-azaborinine (**2e**). From **2e**, the reaction needs to proceed over an even higher barrier (59.4 kcal/mol) to give N-substituted ethynylazaborinine **2d**. In this step, the ethynyl group is transferred from B to N, and at the same time, the hydrogen atom shifts from carbon to boron (see Figure 2).

Reactions of 1,2-Azaborinine with 1,3-Butadiene. The reaction of *ortho*-benzyne with s-cis-butadiene has been studied by Peter and Hatch in 1968.[62] They generated benzyne and cis-butadiene by the concurrent thermal decomposition of benzenediazonium-2-carboxylate and 3-sulfolene (2,5-dihydrothiophen-1,1-dioxide), respectively, to give 1,4-dihydronaphthalene (**3c′**) (see Scheme 4a).

We considered the reaction of 1,2-azaborinine with both rotamers of 1,3-butadiene, i.e., s-cis-butadiene and s-trans-butadiene (see Scheme 4b and Figure 3). Both complexes, **3a(cis)** and **3a(trans)**, exist on the potential energy surface. The formation of **3a(cis)** and **3a(trans)** is exothermic in nature with respect to the separated reactants by 22.7 and 25.1 kcal/mol, respectively (see Figure 7 for geometrical parameters). The interconversion barrier between the two complexes **3a(cis)** and **3a(trans)** is 2.9 kcal/mol. In the case of the reaction of 1,2-azaborinine and s-cis-butadiene, (2 + 2) and (2 + 4) addition proceeds from complex **3a(cis)** in single steps each. The formation of (2 + 2) cycloaddition product **3b(cis)** has a higher barrier of 12.6 kcal/mol compared to the formation of (2 + 4) cycloaddition product **3c** with a barrier of 6.4 kcal/mol. In the case of the reaction with s-trans-butadiene, (2 + 2) cycloaddition proceeds via complex **3a(trans)** with a barrier of 13.6 kcal/mol to give the product **3b(trans)**. In the case of (2 + 4) cycloaddition product **3c**, the reaction proceeds in a stepwise manner from the complex **3a(trans)** unlike the case of s-cis-butadiene, in which the barrier is 18.9 kcal/mol to give an intermediate **3d**. From **3d**, the reaction proceeds with a very high barrier of 44.8 kcal/mol to give product **3c** (see Figure 3).

Scheme 4. (a) Reaction of *ortho*-Benzyne and s-cis-1,3-Butadiene Previously Studied by Peter and Hatch;[62] (b) Reaction of 1,2-Azaborinine with s-cis-1,3-Butadiene and s-trans-1,3-Butadiene



Reactions of 1,2-Azaborinine with Cyclopentadiene. The reaction between *ortho*-benzyne and cyclopentadiene was first studied experimentally by Wittig and Knauss,[63] followed by a few more investigations.[64,65] Wittig and Knauss obtained benzonorbornadiene (**4c′**) as product of (2 + 4) cycloaddition. Later on, Comandini and Brezinsky investigated in their theoretical studies pathways for (2 + 2) and (2 + 4) cycloaddition reactions.[66] The (2 + 4) addition reaction has a computed barrier of 2 kcal/mol at the (U)B3LYP/6-311+G(d,p) level of theory.[66] The (2 + 2) reaction proceeds through a diradical intermediate (barrier of 8.4 kcal/mol), which can be characterized by two rings connected through a single C−C bond with the ring planes positioned almost perpendicularly (see Scheme 5a). Rotation about the single bond has a low barrier of around 2 kcal/mol,[66] and the collapse to **4d′** likewise has a negligible barrier.[66]

1,2-Azaborinine can interact through its empty orbital on boron with a double bond of cyclopentadiene to give two complexes, **4a** and **4b** (Scheme 5b, see Figure 4). The complexes are lower in energy than the separated reactants by

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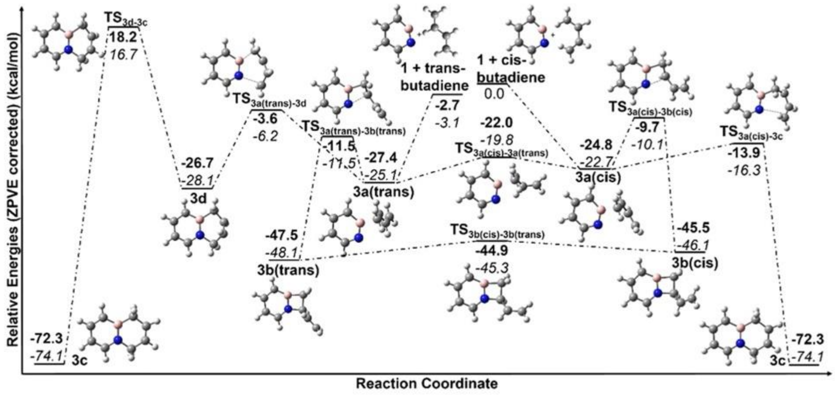
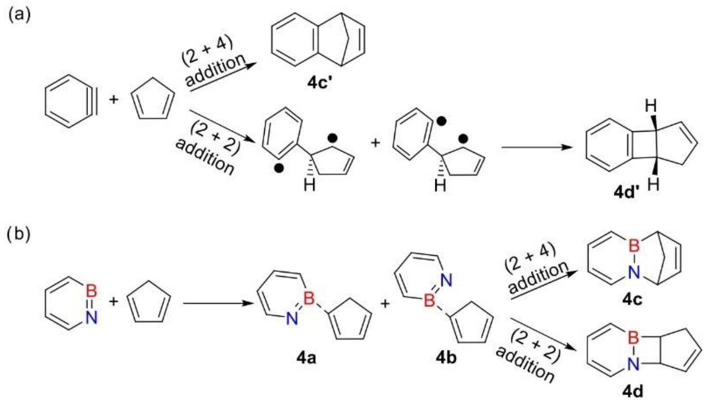


Figure 3. Reaction pathways for the reaction of 1,2-azaborinine with s-cis-1,3-butadiene and s-trans-1,3-butadiene at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated ZPVE-corrected energies in kcal/mol are shown.

Scheme 5. (a) Reaction of *ortho*-Benzyne and Cyclopentadiene Previously Studied by Brezinsky et al.;[66] (b) Reaction of 1,2-Azaborinine with Cyclopentadiene



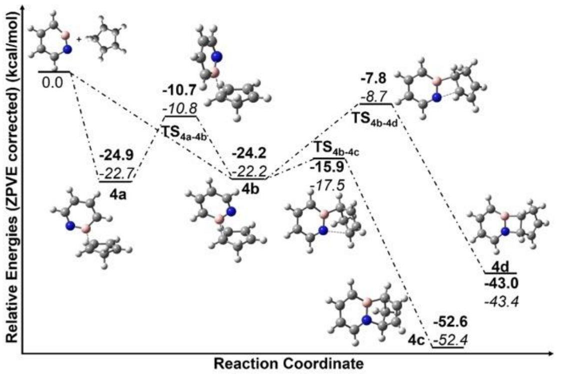


Figure 4. Reaction pathways for the reaction of 1,2-azaborinine with cyclopentadiene at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated ZPVE-corrected energies in kcal/mol are shown.

22.7 and 22.2 kcal/mol, respectively, at the CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) level of theory (see Figure 7 for geometrical parameters). The structures of the complexes have geometrical parameters that are similar to those of the intermediates observed by Comandini and Brezinsky in the (2 + 2) cycloaddition reaction[66] but with the Lewis acid−base interaction between two rings. Structures of **4a** and **4b** differ by the torsional angle between two rings, and their interconversion is associated with a barrier of 11.9 kcal/mol. Further (2 + 4) and (2 + 2) reactions proceed from complex **4b**. The (2 + 2) cycloaddition product **4d** and (2 + 4) cycloaddition product **4c** can form in concerted processes from **4b** with activation energies of 13.5 kcal/mol and 4.7 kcal/mol, respectively (see Figure 4). Neither of the transition states is symmetric. The (2 + 2) product is thermodynamically less stable than the (2 + 4) cycloadduct, and its formation is associated with a higher barrier.

Reactions of 1,2-Azaborinine with Furan. The reaction between *ortho*-benzyne and furan was first studied experimentally by Wittig and Pohmer.[67] They observed (2 + 4) cycloaddition to yield epoxynaphthalene (**5d′**) (Scheme 6a). Kitamura and Yamane observed a trapping reaction of benzyne with furan with their iodine-benzyne precursor to form **5d′**.[68,69] Akai et al. further studied the regioselectivity of substituted benzynes with substituted furans both theoretically and experimentally.[70]

1,2-Azaborinine is expected to form three complexes **5a**−**5c** with furan (Scheme 6b, Figure 5). The Lewis acid−base formation between boron and oxygen atoms in **5a** is exothermic by 20.1 kcal/mol and barrierless with respect to

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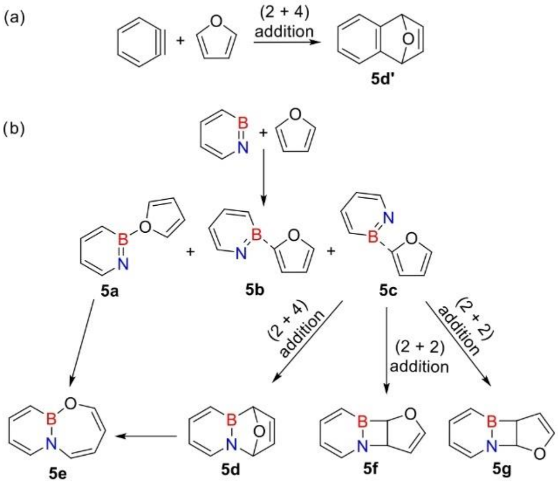
Scheme 6. Schematic Diagram of the Reaction of *ortho*-Benzyne and 1,2-Azaborinine with Furan



the separated reactants as confirmed by a relaxed scan of the PES at the B3LYP/6-311+G(d,p) level of theory (see SI, Table S15). Complexes **5b** and **5c** are slightly higher in energy than **5a** as their formation is exothermic with respect to separated reactants by 16.8 and 15.9 kcal/mol, respectively (see Figure 7 for geometrical parameters). **5b** and **5c** are similar to the corresponding complexes **4a** and **4b** of cyclopentadiene. Interconversion between **5b** and **5c** is associated with a barrier of 9.3 kcal/mol. The two (2 + 2) cycloaddition products **5f** and **5g** can form in a concerted process from **5c** with an activation energy of 11.9 kcal/mol and 11.2 kcal/mol, respectively, through asymmetric transition states $\mathbf{TS_{5c-5f}}$ and $\mathbf{TS_{5c-5g}}$. The (2 + 4) addition reaction proceeds through **5c** to give the Diels–Alder reaction product **5d** with a barrier of 3.8 kcal/mol and an asymmetric transition state $\mathbf{TS_{5c-5d}}$ (see Figure 5). Furthermore, **5d** can isomerize through a ring expansion process to form **5e** with a barrier of 36.4 kcal/mol. This is the most stable reaction product with relative energy of 71.1 kcal/mol with respect to separated reactants. Product **5e** can also directly be formed from **5a** in a concerted process with an activation barrier of 35.1 kcal/mol at the CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) level of theory (see Figure 5).

Reactions of 1,2-Azaborinine with Benzene. The reaction of *ortho*-benzyne with benzene was studied by Miller and Stiles in 1963[71] and later on by Friedman and Lindow in 1967[72] and 1968.[73] Low-temperature pyrolysis of *ortho*-benzyne precursor in benzene and benzene-d_6 indicates the formation of naphthalene-d_4 and ethyne as a major product with benzobicyclo[2.2.2]octatriene **6c′**, biphenyl and benzo-cyclooctatetraene as the minor products (see Scheme 7a). In 1998, Beno et al.[74] studied the initial step of the *ortho*-benzyne and benzene reaction in relation to the interaction between an *ortho*-benzyne molecule located inside a hemicarcerand and the host molecule.[75] Later, Comandini and Brezinsky performed theoretical studies at the (U)CCSD(T)/cc-pVDZ//(U)B3LYP/6-311+G(d,p) level of theory for the formation of naphthalene from the reaction of *ortho*-benzyne with benzene.[76] They suggested that the reaction proceeds through the benzobicyclo[2.2.2]octatriene intermediate (**6c′**) ((2 + 4) cycloaddition with a computed barrier of 6.8 kcal/mol) to finally form naphthalene and ethyne through fragmentation of the intermediate (barrier of 52.1 kcal/mol).[76] Comandini and Brezinsky even considered the reaction on the triplet potential surface to investigate the pathways for minor products. The reaction proceeds through an intermediate (**6a′**) (barrier of 2.9 kcal/mol) to finally form biphenyl (barrier of 42.1 kcal/mol). On the other hand, **6a′** can isomerize to **6b′** (barrier of 2.9 kcal/mol) through torsional motion around the C–C bond between the two rings which can undergo isomerization to form dihydrobiphenylene which has been hypothesized as an intermediate in the formation of benzocyclooctatetraene by Friedman and Lindow.[73]

The reaction of 1,2-azaborinine with benzene has not been studied so far. In the initial step of the reaction of 1,2-azaborinine with benzene, the formation of two Lewis acid–base complexes **6a** and **6b** is expected due to the interaction

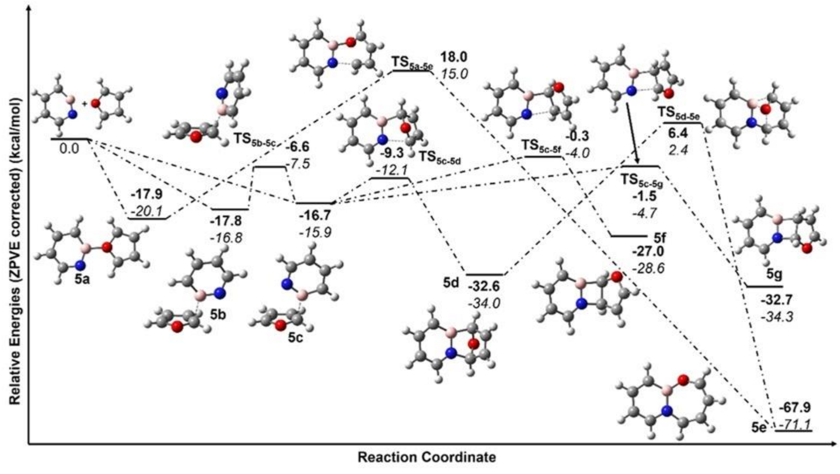


Figure 5. Reaction pathways for the reaction of 1,2-azaborinine with furan at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated ZPVE-corrected energies in kcal/mol are shown.

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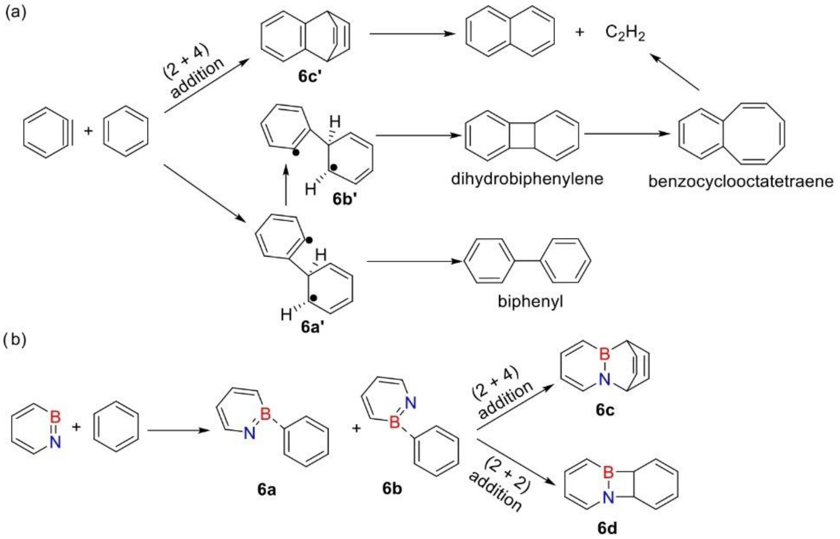
Scheme 7. (a) Reaction of *ortho*-Benzyne and Benzene as Studied by Friedman and Lindow;[73] (b) Reaction of 1,2-Azaborinine with Benzene



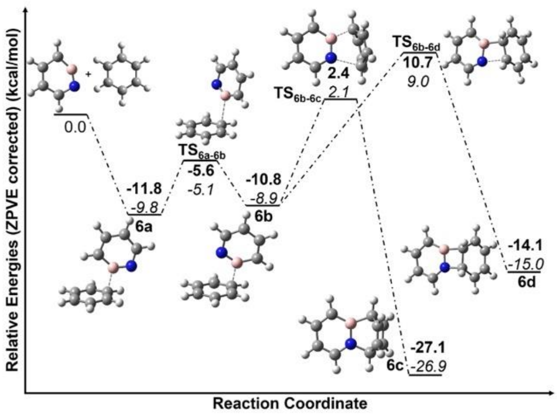


Figure 6. Reaction pathways for the reaction of 1,2-azaborinine with furan at (bold: SCS-MP2/6-311+G(d,p); Italic: CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)). Calculated energies in kcal/mol are shown.

between empty orbital on boron and the π bonds of benzene (Scheme 7b, Figure 6)). The formation of complexes **6a** and **6b** is exothermic with respect to separated reactants by 9.8 and 8.9 kcal/mol, respectively (see Figure 7 for geometrical parameters). The formation of **6a** and **6b** is barrierless with respect to the separated reactants as confirmed by a relaxed scan of the PES at the B3LYP/6-311+G(d,p) level of theory (see SI, Table S15). The interconversion of two complexes **6a** and **6b** has a barrier of 4.7 kcal/mol. The (2 + 4) cycloaddition reaction can proceed through **6b** to give the Diels−Alder reaction product **6c** with an energy barrier of 11.0 kcal/mol. The formation of the (2 + 2) cycloaddition product **6d** has a barrier of 17.9 kcal/mol. Both transition states, $\mathbf{TS_{6b\text{-}6c}}$ and $\mathbf{TS_{6b\text{-}6d}}$, are asymmetric (see Figure 6). The formation of the (2 + 2) cycloproduct is associated with a higher barrier than the (2 + 4) addition product and is thermodynamically less favorable.

Analysis of Complexes between 1 and Organic π Systems. The computations discussed in the preceding sections revealed that the quite exothermic formation of complexes between **1** and the π systems is a distinctive feature of the reactions. This warrants a more detailed discussion of their properties. All complexes have carbon−boron distances that are shorter than the sum of van der Waals radii (3.62 Å) (see Figure 7). In **1a**, these distances are 1.784 Å and the H−C−H and H−C−C angles have changed slightly so that the sum of bond angles around carbon is 358.3°, showing a slight deviation from planarity around carbon atoms in C_2H_4. In **2a**, the angle H−C−C is 165.5° showing the deviation from linearity around carbon. The longest B−C distance was found for **6b** (2.035 Å), while the shortest distance was obtained for **3b(trans)** (1.753 and 1.847 Å) (see Figure 7 for geometric parameters of other complexes). The largest deviation from planarity around carbon in organic substrates is obtained in **4b**, while the smallest deviation is observed in complexes **6a** and **6b** with benzene.

Insight into the nature of the bonding between 1,2-azaborinine and the organic substrates is provided by natural bond orbital analysis.[55] In the complexes **1a**, **2a**, **3a-cis**, **3a-trans**, **4a**, **4b**, **5b**, **5c**, **6a**, and **6b**, strong stabilization due to π(substrate) → n*(B) (empty orbital on boron) delocalization is assessed via second-order perturbation theory analyses in the NBO basis (see Table S13 for E(2) values). The corresponding natural localized molecular orbitals (NLMO) have major contributions from the π(C≡C) and π(C=C) bond orbitals and "delocalization tails" (17.8−22.4%) from a slightly hybridized vacant orbital at boron (Figure 8; Tables S13 and S14). In the case of complex formation with benzene, the NLMO shows "delocalization tails" of only 9.8 and 10.5% from a slightly hybridized vacant orbital at boron (Tables S13 and S14) for complexes **6a** and **6b**, respectively. This is in accordance with the lower binding energy of complexes **6a** and **6b** compared to other complexes.

Comparison of the Reactivity of *ortho*-Benzyne and 1,2-Azaborinine. *Ortho*-benzyne and 1,2-azaborinine are

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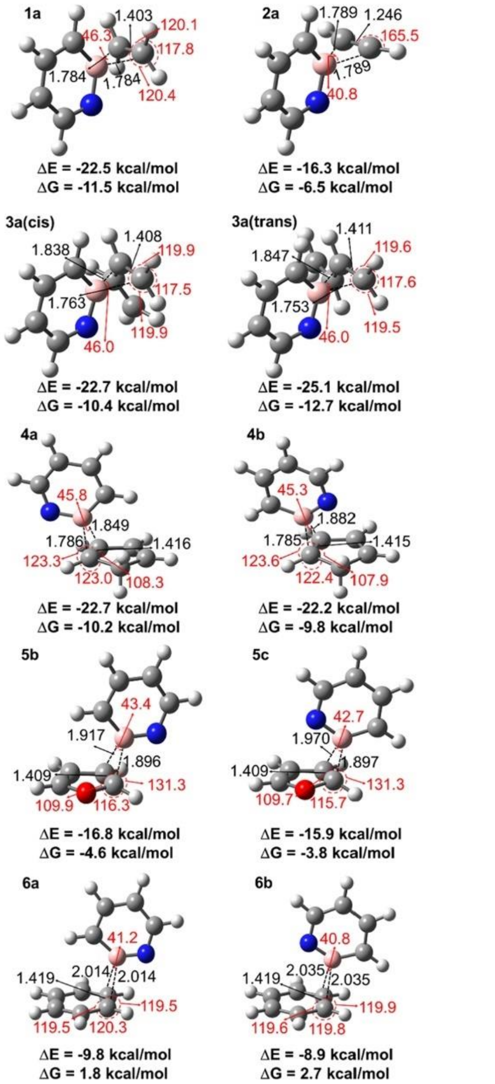

Figure 7. Geometries of complexes between **1** and organic π substrates computed at the SCS-MP2/6-311+G(d,p) level of theory. Important bond lengths [Å] and bond angles [°] are given. ΔE = Relative ZPVE-corrected binding energy with respect to the separated reactants. ΔG = Relative free energies (ΔG at 298.15 K) with respect to the separated reactants.

isoelectronic reactive intermediates, but our computational analysis reveals that the barriers of their reactions toward the set of prototypical organic π systems differ considerably. Due to the polar BN triple bond, 1,2-azaborinine is more reactive than *ortho*-benzyne considering energy barriers with respect to reactants. 1,2-Azaborinine forms a complex with each of the substrates without any barrier on the potential energy surface. According to the NBO analyses, these complexes result from the Lewis acid−base interaction between the boron empty orbital and the π-orbital of the substrates. The interaction energies are remarkably strong and range in energy from −25 to −10 kcal/mol. The complexes are the central intermediates for any reaction ((2 + 2), (2 + 4), and CH insertion), and due to their low energy, the subsequent steps have generally lower barriers than the analogous reactions of *ortho*-benzyne.

■ CONCLUSIONS

The computational study of (2 + 2) and (2 + 4) cycloaddition and CH insertion reactions of 1,2-azaborinine with a set of prototypical organic π systems reveals that all of these reactions are strongly exothermic. The boron−nitrogen bonding in 1,2-azaborinine is reminiscent of a frustrated Lewis pair, and the ensuing strong Lewis acidity of the boron center causes the barrierless formation of complexes with the organic π system. These complexes are the central reactive intermediate in any further reaction of 1,2-azaborinine. Similar complexes do not exist for the analogous reactions of *ortho*-benzyne, highlighting the differences between the two isoelectronic reactive intermediates that arise from the polarity of the BN link.

1,2-Azaborinine can react with the substrates with relatively low activation barriers in (2 + 2) cycloaddition reactions, which are symmetry-forbidden reactions according to the Woodward−Hoffmann rules. The barrier is highest (17.9 kcal/mol) for benzene and lowest for ethyne (10.2 kcal/mol). The symmetry allowed (2 + 4) cycloaddition of 1,2-azaborinine is preferred over possible (2 + 2) cycloadditions. The barriers of the (2 + 4) reactions with respect to the corresponding complexes increase from furan (3.8 kcal/mol), cyclopentadiene (4.7 kcal/mol), s-cis-butadiene (5.4 kcal/mol) to benzene (11.0 kcal/mol).

The C−H insertion reactions of 1,2-azaborinine into the strong CH bonds of ethyne and ethene have higher exothermicity compared to the (2 + 2) symmetry-forbidden cycloaddition, but they are associated with a higher barrier compared to the cycloaddition. There is the possibility of C−H insertion at the boron and nitrogen centers, but the latter regioisomer is generally preferred.

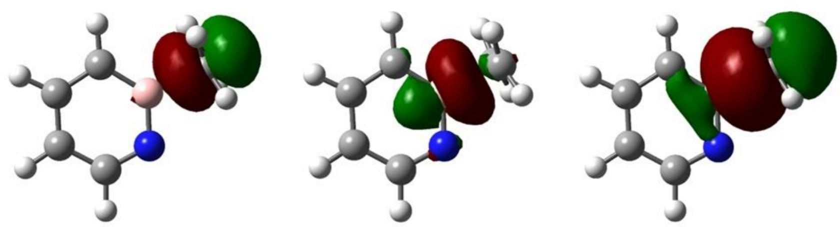

Figure 8. NBO plots for the (a) donor NBO, (b) acceptor NBO, and (c) corresponding NLMO associated with the C═C → B interaction for complexes **1a** at the B3LYP-D3/6-311+G(d,p) level of theory.

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Based on our study, we expect that the reactions of 1,2-azaborinine with unsaturated organic substrates are in principle feasible under appropriate conditions. Under conventional solution phase conditions, however, the reactions need to compete with cyclooligomerizations that can proceed without barriers on the PES.[23] The reaction with benzene has the highest barrier, and indeed trapping with benzene was not observed for dibenzo[*c*,*e*][1,2]azaborinine in benzene solution at room temperature due to self-trapping.[24] Hence, it would be desirable to suppress the rate of cyclooligomerizations, e.g., by introducing kinetically stabilizing sterically demanding groups.

Under noble gas matrix isolation conditions, on the other hand, the facile formation of the relatively strongly bound Lewis acid−base complexes is expected to act as a thermodynamic trap. As the potential energy wells associated with these complexes are quite deep, reactions toward cycloaddition products may not proceed with appreciable rates in typical argon matrix (T < 35 K) experiments.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c00401.

Relative energies and relative free energies of all reactions, details of NBO analyses and images of natural localized molecular orbitals, energy profiles of entrance channels and intrinsic reaction coordinates, and Cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502.
(2) Stoermer, R.; Kahlert, B. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 1633.
(3) Winkler, M.; Wenk, H. H.; Sander, W. *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, M., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; p 741.
(4) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* **2012**, *112*, 3550.
(5) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140.
(6) Gampe, C. M.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3766.
(7) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701.
(8) Roy, T.; Biju, A. T. *ChemComm* **2018**, *54*, 2580.
(9) Wu, D.; Ge, H.; Liu, S. H.; Yin, J. *RSC Adv.* **2013**, *3*, 22727.
(10) Peña, D.; Pérez, D.; Guitián, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 3579.
(11) Werz, D. B.; Biju, A. T. *Angew. Chem., Int. Ed.* **2020**, *59*, 3385.
(12) Fazen, P. J.; Burke, L. A. *Inorg. Chem.* **2006**, *45*, 2494.
(13) Edel, K.; Brough, S. A.; Lamm, A. N.; Liu, S.-Y.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2015**, *54*, 7819.
(14) Müller, M.; Maichle-Mössmer, C.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2014**, *53*, 9380.
(15) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 242.
(16) Giustra, Z. X.; Liu, S.-Y. *J. Am. Chem. Soc.* **2018**, *140*, 1184.
(17) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074.
(18) Helten, H. *Chem.−Eur. J.* **2016**, *22*, 12972.
(19) Wang, X.-Y.; Wang, J.-Y.; Pei, J. *Chem.−Eur. J.* **2015**, *21*, 3528.
(20) Morgan, M. M.; Piers, W. E. *Dalton Trans.* **2016**, *45*, 5920.
(21) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2008**, *86*, 8.
(22) Edel, K.; Ishibashi, J. S. A.; Liu, S.-Y.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2019**, *58*, 4061.
(23) Bettinger, H. F.; Müller, M. *J. Phys. Org. Chem.* **2015**, *28*, 97.
(24) Keck, C.; Hahn, J.; Gupta, D.; Bettinger, H. F. *Chem.−Eur. J.* **2022**, *28*, No. e202103614.
(25) Paetzold, P. In *Advances in Inorganic Chemistry*; Emeléus, H. J.; Sharpe, A. G., Eds.; Academic Press, 1987; Vol. *31*, p 123.
(26) Münster, J.; Paetzold, P.; Schröder, E.; Schwan, H.; von Bennigsen-Mackiewicz, T. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2641.
(27) Thiess, T.; Bélanger-Chabot, G.; Fantuzzi, F.; Michel, M.; Ernst, M.; Engels, B.; Braunschweig, H. *Angew. Chem., Int. Ed.* **2020**, *59*, 15480.
(28) Koner, A.; Sergeieva, T.; Morgenstern, B.; Andrada, D. M. *Inorg. Chem.* **2021**, *60*, 14202.
(29) Paetzold, P.; von Plotho, C.; Niecke, E.; Rüger, R. *Chem. Ber.* **1983**, *116*, 1678.
(30) Paetzold, P.; Delpy, K.; Hughes, R. P.; Herrmann, W. A. *Chem. Ber.* **1985**, *118*, 1724.
(31) Braunschweig, H.; Paetzold, P.; Boese, R. *Chem. Ber.* **1993**, *126*, 1571.
(32) Kröckert, B.; van Bonn, K.-H.; Paetzold, P. *Z. Anorg. Allg. Chem.* **2005**, *631*, 866.
(33) Gilbert, T. M. *Organometallics* **2000**, *19*, 1160.
(34) Gilbert, T. M. *Organometallics* **2003**, *22*, 2298.
(35) Gilbert, T. M. *Organometallics* **2005**, *24*, 6445.
(36) Bissett, K. M.; Gilbert, T. M. *Organometallics* **2004**, *23*, 5048.
(37) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(40) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456.
(41) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.
(42) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.
(43) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(44) Barone, V.; Cossi, M.; et al. *J. Phys. Chem. A* **1998**, *102*, 1995.
(45) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Phys.* **2004**, *120*, 9918.
(46) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Theory Comput.* **2005**, *1*, 61.

(47) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(48) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
(49) Neese, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73.
(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Rev. C.01; Gaussian Inc.:Wallingford, CT, 2016.
(51) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(52) Glendening, E. D.; Landis, C. R.; Weinhold, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 1.
(53) Weinhold, F. *J. Comput. Chem.* **2012**, *33*, 2363.
(54) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. NBO 6.0, 2012.
(55) Friedrichs, G.; Goos, E.; Gripp, J.; Nicken, H.; Schönborn, J.-B.; Vogel, H.; Temps, F. Z. *Phys. Chem.* **2009**, *223*, 387.
(56) Hayes, D. M.; Hoffmann, R. *J. Phys. Chem. A* **1972**, *76*, 656.
(57) Maier, W. F.; Lau, G. C.; McEwen, A. B. *J. Am. Chem. Soc.* **1985**, *107*, 4724.
(58) Ozkan, I.; Kinal, A. *J. Org. Chem.* **2004**, *69*, 5390.
(59) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1969**, *8*, 781.
(60) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17.
(61) Kınal, A.; Piecuch, P. *J. Phys. Chem. A* **2006**, *110*, 367.
(62) Hatch, L. F.; Peter, D. *Chem. Commun.* **1968**, 1499.
(63) Wittig, G.; Knauss, E. *Chem. Ber.* **1958**, *91*, 895.
(64) Mich, T. F.; Nienhouse, E. J.; Farino, T. E.; Tufariello, J. J. *J. Chem. Educ.* **1968**, *45*, 272.
(65) Ford, W. T. *J. Org. Chem.* **1971**, *36*, 3979.
(66) Comandini, A.; Brezinsky, K. *J. Phys. Chem. A* **2012**, *116*, 1183.
(67) Wittig, G.; Pohmer, L. *Angew. Chem.* **1955**, *67*, 348.
(68) Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983.
(69) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674.
(70) Ikawa, T.; Tokiwa, H.; Akai, S. *J. Syn. Org. Chem. JPN* **2012**, *70*, 1123.
(71) Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798.
(72) Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*, 3071.
(73) Friedman, L.; Lindow, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 2329.
(74) Beno, B. R.; Sheu, C.; Houk, K. N.; Warmuth, R.; Cram, D. J. *ChemComm* **1998**, 301.
(75) Warmuth, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 1347.
(76) Comandini, A.; Brezinsky, K. *J. Phys. Chem. A* **2011**, *115*, 5547.

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Supporting Information

Reactions of 1,2-Azaborinine, a BN-Benzyne, with Organic π Systems

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Table S1: The relative ZPVE corrected energies for the reaction of **1** with ethene (C_2H_4) as computed at the different level of theories. (Energies in kcal/mol).

	1 + C_2H_4	**1a**	**TS_{1a-1b}**	**1b**	**TS_{1a-1c}**	**1c**	**TS_{1a-1d}**	**1d**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-18.7 **[-23.1]**	-2.3 **[-8.2]**	-39.4 **[-47.1]**	14.6 **[10.9]**	-55.4 **[-60.6]**	58.9 **[59.9]**	-42.4 **[-48.3]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-21.7 **[-23.1]**	-5.2 **[-8.3]**	-42.1 **[-47.1]**	12.0 **[10.9]**	-58.1 **[-60.5]**	56.3 **[59.9]**	-45.2 **[-48.3]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-29.3 **[-22.4]**	-11.5 **[-7.9]**	-48.2 **[-46.8]**	8.2 **[11.4]**	-59.8 **[-60.6]**	60.4 **[61.4]**	-47.4 **[-48.1]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-24.4 **[-22.5]**	-7.5 **[-7.9]**	-45.9 **[-46.8]**	13.2 **[11.4]**	-58.9 **[-60.6]**	64.8 **[61.0]**	-46.7 **[-48.1]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-23.7 **[-23.0]**	-8.2 **[-8.2]**	-46.4 **[-47.1]**	11.0 **[11.1]**	-59.0 **[-60.7]**	62.0 **[60.6]**	-47.1 **[-48.3]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-24.8 **[-22.5]**	-7.0 **[-7.9]**	-44.1 **[-46.8]**	13.3 **[11.2]**	-58.5 **[-60.6]**	65.4 **[60.8]**	-45.6 **[-48.1]**

Table S2: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with ethene (C_2H_4) as computed at the different level of theories. (Energies in kcal/mol).

	1 + C_2H_4	**1a**	**TS_{1a-1b}**	**1b**	**TS_{1a-1c}**	**1c**	**TS_{1a-1d}**	**1d**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-7.0 **[-11.4]**	9.8 **[3.9]**	-27.2 **[-35.0]**	26.1 **[22.4]**	-44.3 **[-49.5]**	70.1 **[71.1]**	-31.3 **[-37.2]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-10.0 **[-11.4]**	6.8 **[3.8]**	-30.0 **[-35.0]**	23.5 **[22.4]**	-47.0 **[-49.4]**	67.5 **[71.1]**	-33.8 **[-36.9]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-17.5 **[-10.6]**	0.7 **[4.3]**	-36.1 **[-34.7]**	19.8 **[23.0]**	-48.5 **[-49.3]**	71.8 **[72.7]**	-35.8 **[-36.5]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-13.4 **[-11.5]**	3.9 **[3.5]**	-34.6 **[-35.5]**	24.0 **[22.2]**	-48.2 **[-49.9]**	75.6 **[71.8]**	-35.8 **[-37.2]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-11.9 **[-11.3]**	4.0 **[3.9]**	-34.3 **[-34.9]**	22.5 **[22.6]**	-47.8 **[-49.4]**	73.3 **[71.9]**	-35.5 **[-36.8]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-13.8 **[-11.5]**	4.4 **[3.5]**	-33.2 **[-35.5]**	24.1 **[21.9]**	-47.8 **[-49.9]**	76.1 **[71.6]**	-34.7 **[-37.2]**

Table S3: The relative ZPVE corrected energies for the reaction of **1** with ethyne (C_2H_2) as computed at the different level of theories. (Energies in kcal/mol).

	1 + C_2H_2	**2a**	**TS_{2a-2b}**	**2b**	**TS_{2a-2c}**	**2c**	**TS_{2a-2e}**	**2e**	**TS_{2e-2d}**	**2d**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-14.3 **[-16.8]**	-3.0 **[-6.7]**	-35.6 **[-40.9]**	8.7 **[7.3]**	-66.2 **[-70.2]**	10.0 **[9.3]**	-32.9 **[-37.2]**	24.6 **[21.9]**	-39.1 **[-42.9]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-16.5 **[-16.8]**	-5.2 **[-6.7]**	-37.5 **[-40.9]**	7.0 **[7.3]**	-68.0 **[-70.1]**	8.0 **[9.3]**	-34.9 **[-37.2]**	22.2 **[21.9]**	-41.1 **[-42.9]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-21.1 **[-16.1]**	-7.3 **[-5.9]**	-37.6 **[-40.7]**	7.1 **[7.8]**	-69.4 **[-70.0]**	6.4 **[10.0]**	-34.1 **[-36.8]**	23.3 **[22.8]**	-41.2 **[-42.4]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-17.1 **[-16.3]**	-3.6 **[-6.1]**	-36.1 **[-40.7]**	11.0 **[7.5]**	-68.6 **[-70.1]**	10.8 **[9.6]**	-35.8 **[-36.6]**	25.0 **[22.8]**	-41.0 **[-42.9]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-17.7 **[-16.7]**	-6.5 **[-6.5]**	-39.6 **[-40.9]**	8.5 **[6.9]**	-68.3 **[-70.2]**	11.3 **[9.2]**	-34.9 **[-37.3]**	24.5 **[22.0]**	-42.5 **[-42.9]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-17.8 **[-16.3]**	-3.0 **[-6.2]**	-34.0 **[-40.7]**	11.4 **[7.0]**	-68.0 **[-70.1]**	10.9 **[9.7]**	-35.6 **[-36.6]**	25.4 **[22.8]**	-39.0 **[-43.0]**

Table S4: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with ethyne (C_2H_2) as computed at the different level of theories. (Energies in kcal/mol).

	1 + C_2H_2	**2a**	**TS_{2a-2b}**	**2b**	**TS_{2a-2c}**	**2c**	**TS_{2a-2e}**	**2e**	**TS_{2e-2d}**	**2d**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-4.6 **[-7.1]**	7.3 **[3.6]**	-25.3 **[-30.6]**	18.3 **[16.8]**	-56.5 **[-60.5]**	19.5 **[18.9]**	-24.0 **[-28.3]**	34.4 **[31.8]**	-29.2 **[-33.0]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-6.8 **[-7.2]**	5.1 **[3.6]**	-27.2 **[-30.6]**	16.6 **[16.8]**	-58.3 **[-60.5]**	17.5 **[18.8]**	-26.0 **[-28.3]**	32.0 **[31.6]**	-31.3 **[-33.0]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-11.4 **[-6.3]**	3.1 **[4.5]**	-28.1 **[-31.2]**	16.4 **[17.1]**	-59.8 **[-60.4]**	16.2 **[19.7]**	-25.6 **[-28.4]**	33.2 **[32.6]**	-31.5 **[-32.3]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-7.3 **[-6.5]**	6.8 **[4.3]**	-25.9 **[-30.5]**	20.4 **[16.9]**	-58.9 **[-60.4]**	20.6 **[19.4]**	-26.7 **[-27.6]**	34.9 **[32.7]**	-31.3 **[-33.2]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-8.0 **[-7.0]**	3.8 **[3.8]**	-29.3 **[-30.6]**	18.0 **[16.3]**	-58.7 **[-60.6]**	20.9 **[18.8]**	-26.0 **[-28.4]**	34.4 **[31.9]**	-32.6 **[-33.1]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-8.0 **[-6.5]**	7.4 **[4.2]**	-23.8 **[-30.6]**	20.7 **[16.2]**	-58.3 **[-60.4]**	20.6 **[19.4]**	-26.5 **[-27.5]**	35.3 **[32.7]**	-29.2 **[-33.2]**

Table S5: The relative ZPVE corrected energies for the reaction of **1** with 1,3-butadiene as computed at the different level of theories. (Energies in kcal/mol).

	1 + 1,3-cis-butadiene	**1 + 1,3-trans-butadiene**	**3a(cis)**	**$TS_{3a(cis)-3a(trans)}$**	**3a(trans)**	**$TS_{3a(cis)-3b(cis)}$**	**3b(cis)**	**$TS_{3a(trans)-3b(trans)}$**	**$TS_{3b(cis)-3b(trans)}$**	**3b(trans)**	**$TS_{3a(cis)-3c}$**	**$TS_{3a(trans)-3d}$**	**3d**	**TS_{3d-3c}**	**3c**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-3.5 **[-2.9]**	-17.5 **[-22.9]**	-13.9 **[-20.4]**	-20.4 **[-25.4]**	-5.0 **[-9.7]**	-36.6 **[-46.6]**	-6.5 **[-11.1]**	-36.0 **[-45.8]**	-38.6 **[-48.4]**	-13.5 **[-16.6]**	-2.5 **[-6.7]**	-15.9 **[-28.7]**	24.4 **[15.8]**	-64.3 **[-74.9]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-3.3 **[-2.9]**	-21.6 **[-22.9]**	-17.8 **[-20.4]**	-24.3 **[-25.4]**	-8.9 **[-9.8]**	-40.4 **[-46.6]**	-10.2 **[-11.2]**	-39.8 **[-45.8]**	-42.3 **[-48.3]**	-18.0 **[-16.5]**	-7.2 **[-6.6]**	-20.4 **[-28.6]**	20.1 **[15.8]**	-68.1 **[-74.8]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-2.7 **[-3.1]**	-30.2 **[-22.6]**	-27.0 **[-19.7]**	-32.8 **[-24.9]**	-14.2 **[-10.2]**	-48.0 **[-46.1]**	-15.9 **[-11.5]**	-47.3 **[-45.3]**	-50.0 **[-48.1]**	-20.4 **[-15.6]**	-9.5 **[-6.0]**	-30.9 **[-28.0]**	12.9 **[17.0]**	-74.8 **[-73.5]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-2.7 **[-3.1]**	-24.8 **[-22.7]**	-22.0 **[-19.8]**	-27.4 **[-25.1]**	-9.7 **[-10.1]**	-45.5 **[-46.1]**	-11.5 **[-11.5]**	-44.9 **[-45.3]**	-47.5 **[-48.1]**	-13.9 **[-16.3]**	-3.6 **[-6.2]**	-26.7 **[-28.1]**	18.2 **[16.7]**	-72.3 **[-74.1]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-2.8 **[-2.9]**	-22.9 **[-23.1]**	-20.0 **[-20.3]**	-25.5 **[-25.6]**	-9.2 **[-10.5]**	-45.0 **[-46.6]**	-10.4 **[-11.9]**	-44.3 **[-45.8]**	-46.7 **[-48.4]**	-15.7 **[-16.8]**	-6.2 **[-6.7]**	-25.6 **[-28.6]**	15.0 **[15.7]**	-73.7 **[-74.8]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-2.9 **[-3.1]**	-25.4 **[-22.7]**	-22.0 **[-19.8]**	-27.7 **[-25.1]**	-9.2 **[-10.2]**	-42.0 **[-46.1]**	-10.8 **[-11.5]**	-43.4 **[-45.4]**	-46.0 **[-48.1]**	-13.1 **[-16.4]**	-3.0 **[-6.3]**	-25.4 **[-28.1]**	16.2 **[16.4]**	-70.9 **[-74.1]**

Table S6: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with 1,3-butadiene as computed at the different level of theories. (Energies in kcal/mol).

	1 + 1,3-cis-butadiene	**1 + 1,3-trans-butadiene**	**3a(cis)**	**$TS_{3a(cis)-3a(trans)}$**	**3a(trans)**	**$TS_{3a(cis)-3b(cis)}$**	**3b(cis)**	**$TS_{3a(trans)-3b(trans)}$**	**$TS_{3b(cis)-3b(trans)}$**	**3b(trans)**	**$TS_{3a(cis)-3c}$**	**$TS_{3a(trans)-3d}$**	**3d**	**TS_{3d-3c}**	**3c**
B3LYP/6-311+G(d,p)	0.0	-3.3	-5.8	-1.5	-8.5	7.1	-24.2	5.7	-23.0	-26.2	-0.7	10.4	-2.5	37.5	-51.6
[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]	**[0.0]**	**[-2.8]**	**[-11.2]**	**[-8.0]**	**[-13.5]**	**[2.5]**	**[-34.3]**	**[1.1]**	**[-32.8]**	**[-36.0]**	**[-3.8]**	**[6.2]**	**[-15.3]**	**[28.9]**	**[-62.1]**
B3LYP-D3/6-311+G(d,p)	0.0	-3.2	-10.1	-5.4	-12.4	3.3	-28.1	2.0	-26.9	-29.9	-5.3	5.6	-7.0	33.2	-55.4
[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]	**[0.0]**	**[-2.7]**	**[-11.4]**	**[-8.0]**	**[-13.6]**	**[2.3]**	**[-34.3]**	**[1.0]**	**[-32.9]**	**[-36.0]**	**[-3.8]**	**[6.3]**	**[-15.2]**	**[28.9]**	**[-62.1]**
MP2/6-311+G(d,p)	0.0	-2.7	-18.4	-14.5	-20.8	-1.8	-35.7	-3.5	-34.4	-37.8	-7.5	3.3	-17.5	26.1	-62.0
[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]	**[0.0]**	**[-3.1]**	**[-10.8]**	**[-7.2]**	**[-12.9]**	**[2.2]**	**[-33.8]**	**[0.9]**	**[-32.4]**	**[-35.9]**	**[-2.7]**	**[6.7]**	**[-14.7]**	**[30.2]**	**[-60.7]**
SCS-MP2/6-311+G(d,p)	0.0	-2.7	-12.5	-9.3	-15.0	3.0	-32.8	1.3	-31.8	-34.9	-0.9	9.4	-13.3	31.4	-59.4
[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]	**[0.0]**	**[-3.1]**	**[-10.4]**	**[-7.1]**	**[-12.7]**	**[2.6]**	**[-33.5]**	**[1.2]**	**[-32.2]**	**[-35.4]**	**[-3.3]**	**[6.7]**	**[-14.8]**	**[29.9]**	**[-61.2]**
M06-2X/6-311+G(d,p)	0.0	-2.7	-11.2	-7.7	-13.6	3.2	-32.7	2.0	-31.5	-34.5	-2.9	6.6	-12.2	28.1	-61.1
[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]	**[0.0]**	**[-2.9]**	**[-11.3]**	**[-7.9]**	**[-13.7]**	**[1.9]**	**[-34.3]**	**[0.5]**	**[-33.0]**	**[-36.1]**	**[-4.0]**	**[6.1]**	**[-15.2]**	**[28.8]**	**[-62.2]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene)	0.0	-2.8	-13.1	-9.3	-15.3	3.5	-29.3	1.9	-30.3	-33.4	-0.2	10.1	-12.0	29.4	-58.0
[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]	**[0.0]**	**[-3.1]**	**[-10.4]**	**[-7.1]**	**[-12.7]**	**[2.6]**	**[-33.4]**	**[1.3]**	**[-32.3]**	**[-35.4]**	**[-3.4]**	**[6.7]**	**[-14.7]**	**[29.6]**	**[-61.2]**

Table S7: The relative ZPVE corrected energies for the reaction of **1** with cyclopentadiene (CPD) as computed at the different level of theories. (Energies in kcal/mol).

	1 + CPD	4a	TS_{4a-4b}	4b	TS_{4b-4c}	4c	TS_{4b-4d}	4d
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-16.2 **[-23.1]**	-5.2 **[-10.3]**	-16.2 **[-22.5]**	-12.5 **[-17.9]**	-38.5 **[-52.9]**	-4.8 **[-8.7]**	-33.0 **[-43.9]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-20.9 **[-23.1]**	-9.7 **[-10.5]**	-20.9 **[-22.4]**	-17.3 **[-17.8]**	-43.2 **[-52.8]**	-9.0 **[-8.7]**	-37.3 **[-43.8]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-30.3 **[-22.4]**	-13.9 **[-10.7]**	-29.5 **[-21.9]**	-21.8 **[-17.0]**	-55.6 **[-52.3]**	-11.5 **[-8.6]**	-44.6 **[-43.3]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-24.9 **[-22.7]**	-10.7 **[-10.8]**	-24.2 **[-22.2]**	-15.9 **[-17.5]**	-52.6 **[-52.4]**	-7.8 **[-8.7]**	-43.0 **[-43.4]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-23.0 **[-23.3]**	-11.2 **[-11.7]**	-22.5 **[-22.8]**	-15.9 **[-18.2]**	-49.4 **[-52.8]**	-7.0 **[-9.2]**	-41.2 **[-43.9]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-25.3 **[-22.8]**	-12.0 **[-10.5]**	-24.5 **[-22.3]**	-15.5 **[-17.7]**	-51.1 **[-52.4]**	-7.4 **[-9.0]**	-41.3 **[-43.4]**

Table S8: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with cyclopentadiene as computed at the different level of theories. (Energies in kcal/mol).

	1 + CPD	4a	TS_{4a-4b}	4b	TS_{4b-4c}	4c	TS_{4b-4d}	4d
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-3.7 **[-10.6]**	7.1 **[2.1]**	-3.8 **[-10.1]**	0.7 **[-4.7]**	-24.8 **[-39.2]**	7.8 **[3.8]**	-19.9 **[-30.9]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-8.4 **[-10.6]**	2.7 **[1.8]**	-8.5 **[-10.0]**	-4.1 **[-4.7]**	-29.5 **[-39.2]**	3.5 **[3.8]**	-24.3 **[-30.8]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-17.5 **[-9.6]**	1.2 **[2.0]**	-16.8 **[-9.2]**	-8.5 **[-3.7]**	-41.9 **[-38.6]**	1.3 **[4.2]**	-31.6 **[-30.3]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-12.4 **[-10.2]**	1.8 **[1.7]**	-11.7 **[-9.8]**	-2.9 **[-4.5]**	-39.3 **[-39.1]**	4.9 **[4.0]**	-30.1 **[-30.5]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-10.4 **[-10.7]**	1.3 **[1.3]**	-10.0 **[-10.3]**	-2.8 **[-5.0]**	-35.7 **[-39.2]**	5.7 **[3.5]**	-28.2 **[-30.9]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-12.8 **[-10.3]**	0.5 **[2.0]**	-12.1 **[-9.9]**	-2.6 **[-4.8]**	-37.8 **[-39.1]**	5.0 **[3.5]**	-28.5 **[-30.6]**

Table S9: The relative ZPVE corrected energies for the reaction of **1** with furan as computed at the different level of theories. (Energies in kcal/mol).

	1 + Furan	5a	5b	$TS_{5b\text{-}5c}$	5c	$TS_{5c\text{-}5d}$	5d	$TS_{5d\text{-}5e}$	$TS_{5a\text{-}5e}$	5e	$TS_{5c\text{-}5f}$	5f	$TS_{5c\text{-}5g}$	5g
B3LYP/6-311+G(d,p)	0.0	-13.7	-10.5	-3.8	-10.4	-6.1	-21.3	13.5	21.1	-63.8	-0.7	-19.1	2.0	-23.8
[CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p)]	**[0.0]**	**[-20.6]**	**[-17.1]**	**[-8.0]**	**[-15.7]**	**[-12.9]**	**[-34.6]**	**[1.8]**	**[14.7]**	**[-71.4]**	**[-4.6]**	**[-29.2]**	**[-5.1]**	**[-35.0]**
B3LYP-D3/6-311+G(d,p)	0.0	-17.4	-14.9	-7.6	-14.8	-10.3	-25.4	9.2	16.9	-68.1	-4.6	-23.2	-2.0	-28.1
[CCSD(T)/cc-pVTZ//B3LYP-D3/6-311+G(d,p)]	**[0.0]**	**[-20.5]**	**[-17.1]**	**[-8.1]**	**[-15.7]**	**[-13.0]**	**[-34.6]**	**[1.8]**	**[14.8]**	**[-71.4]**	**[-4.6]**	**[-29.2]**	**[-5.1]**	**[-34.9]**
MP2/6-311+G(d,p)	0.0	-19.1	-22.2	-9.5	-21.1	-13.2	-33.3	4.6	14.8	-67.2	-2.4	-27.2	-3.4	-32.9
[CCSD(T)/cc-pVTZ//MP2/6-311+G(d,p)]	**[0.0]**	**[-20.0]**	**[-16.4]**	**[-7.5]**	**[-15.6]**	**[-11.9]**	**[-34.0]**	**[2.6]**	**[15.1]**	**[-70.9]**	**[-4.0]**	**[-28.6]**	**[-4.4]**	**[-34.4]**
SCS-MP2/6-311+G(d,p)	0.0	-17.9	-17.8	-6.6	-16.7	-9.3	-32.6	6.4	18.0	-67.9	-0.3	-27.0	-1.5	-32.7
[CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)]	**[0.0]**	**[-20.1]**	**[-16.8]**	**[-7.5]**	**[-15.9]**	**[-12.1]**	**[-34.0]**	**[2.4]**	**[15.0]**	**[-71.1]**	**[-4.0]**	**[-28.6]**	**[-4.7]**	**[-34.3]**
M06-2X/6-311+G(d,p)	0.0	-19.5	-16.9	-7.1	-16.0	-9.4	-30.1	8.1	17.9	-69.2	-0.4	-25.6	-1.7	-31.5
[CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p)]	**[0.0]**	**[-20.8]**	**[-17.5]**	**[-8.3]**	**[-16.6]**	**[-12.8]**	**[-34.6]**	**[1.9]**	**[14.8]**	**[-71.8]**	**[-4.9]**	**[-29.3]**	**[-5.3]**	**[-35.1]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene)	0.0	-19.2	-18.6	-9.1	-17.8	-9.4	-32.1	6.8	19.3	-66.8	-1.3	-25.8	-2.5	-31.3
[CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) CPCM(benzene)]	**[0.0]**	**[-19.9]**	**[-16.8]**	**[-6.7]**	**[-15.9]**	**[-12.2]**	**[-33.9]**	**[2.4]**	**[14.9]**	**[-71.1]**	**[-4.4]**	**[-28.6]**	**[-5.0]**	**[-34.4]**

Table S10: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with furan as computed at the different level of theories. (Energies in kcal/mol).

	1 + Furan	**5a**	**5b**	**TS$_{5b-5c}$**	**5c**	**TS$_{5c-5d}$**	**5d**	**TS$_{5d-5e}$**	**TS$_{5a-5e}$**	**5e**	**TS$_{5c-5f}$**	**5f**	**TS$_{5c-5g}$**	**5g**
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-2.2 **[-9.0]**	1.5 **[-5.2]**	8.7 **[4.5]**	1.6 **[-3.6]**	7.1 **[0.3]**	-7.9 **[-21.1]**	26.8 **[15.2]**	33.6 **[27.3]**	-51.4 **[-58.9]**	12.0 **[8.1]**	-6.1 **[-16.2]**	14.3 **[7.2]**	-10.8 **[-22.0]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ//B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-5.9 **[-9.0]**	-2.9 **[-5.1]**	5.0 **[4.5]**	-2.7 **[-3.6]**	2.9 **[0.2]**	-11.9 **[-21.1]**	22.5 **[15.2]**	29.4 **[27.4]**	-55.6 **[-58.9]**	8.1 **[8.1]**	-10.2 **[-16.2]**	10.3 **[7.2]**	-15.1 **[-21.9]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ//MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-7.4 **[-8.4]**	-9.7 **[-3.9]**	2.9 **[4.9]**	-8.7 **[-3.1]**	-0.1 **[1.2]**	-19.8 **[-20.5]**	18.0 **[16.0]**	27.6 **[27.9]**	-54.5 **[-58.2]**	10.2 **[8.6]**	-14.3 **[-15.7]**	9.0 **[8.0]**	-19.9 **[-21.4]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-6.0 **[-8.2]**	-5.6 **[-4.6]**	5.5 **[4.6]**	-4.5 **[-3.8]**	3.6 **[0.8]**	-19.5 **[-20.8]**	19.5 **[15.4]**	30.6 **[27.6]**	-55.4 **[-58.6]**	12.3 **[8.6]**	-14.3 **[-15.8]**	10.9 **[7.8]**	-19.9 **[-21.6]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-7.9 **[-9.1]**	-4.7 **[-5.3]**	5.2 **[3.9]**	-3.8 **[-4.5]**	3.8 **[0.4]**	-16.6 **[-21.2]**	21.5 **[15.3]**	30.6 **[27.5]**	-56.6 **[-59.2]**	12.2 **[7.7]**	-12.7 **[-16.3]**	10.7 **[7.0]**	-18.5 **[-22.1]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ//SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-7.3 **[-8.0]**	-6.4 **[-4.6]**	3.4 **[5.9]**	-5.7 **[-3.7]**	3.5 **[0.7]**	-19.0 **[-20.8]**	19.9 **[15.5]**	31.9 **[27.5]**	-54.2 **[-58.6]**	11.4 **[8.3]**	-13.1 **[-15.8]**	10.1 **[7.6]**	-18.5 **[-21.6]**

Table S11: The relative ZPVE corrected energies for the reaction of **1** with benzene as computed at the different level of theories. (Energies in kcal/mol).

	1+benzene	6a	TS_{6a-6b}	6b	TS_{6b-6c}	6c	TS_{6b-6d}	6d
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	-3.5 **[-10.3]**	-1.2 **[-5.2]**	-2.6 **[-9.5]**	10.4 **[0.8]**	-10.3 **[-27.9]**	15.1 **[8.0]**	-3.0 **[-15.9]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	-8.7 **[-10.3]**	-5.3 **[-5.7]**	-7.9 **[-9.5]**	5.0 **[0.8]**	-15.5 **[-27.9]**	10.2 **[7.8]**	-7.8 **[-15.8]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-16.4 **[-9.8]**	-8.5 **[-5.4]**	-15.5 **[-8.9]**	-2.8 **[1.8]**	-28.3 **[-27.4]**	6.7 **[9.5]**	-13.8 **[-15.3]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-11.8 **[-9.8]**	-5.6 **[-5.1]**	-10.8 **[-8.9]**	2.4 **[2.1]**	-27.1 **[-26.9]**	10.7 **[9.0]**	-14.1 **[-15.0]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	-10.2 **[-10.7]**	-5.7 **[-5.9]**	-9.2 **[-9.8]**	4.6 **[1.1]**	-23.0 **[-27.7]**	11.9 **[7.8]**	-11.5 **[-15.8]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-12.7 **[-9.6]**	-5.5 **[-4.7]**	-11.9 **[-8.7]**	3.1 **[2.0]**	-25.9 **[-26.9]**	11.1 **[8.8]**	-12.6 **[-15.0]**

Table S12: The relative free energies (ΔG at 298.15 K) for the reaction of **1** with benzene as computed at the different level of theories. (Energies in kcal/mol).

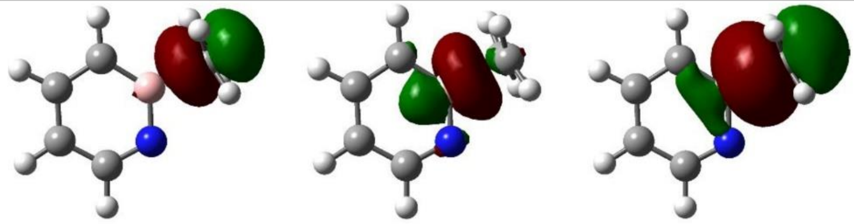
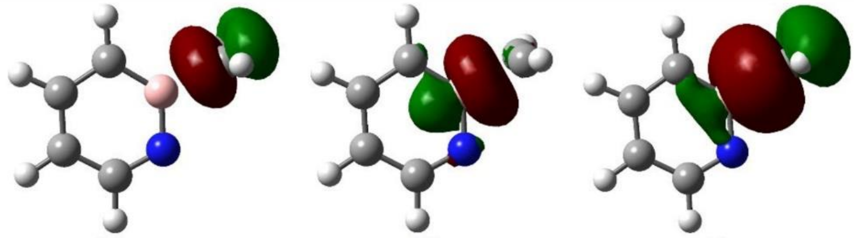
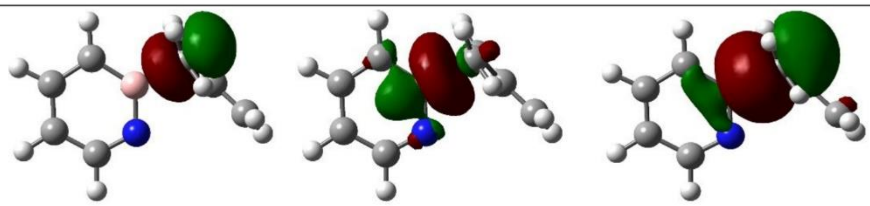
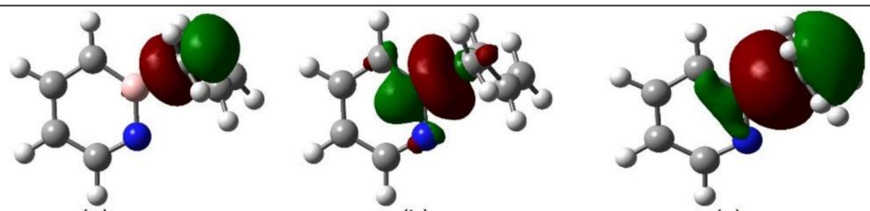
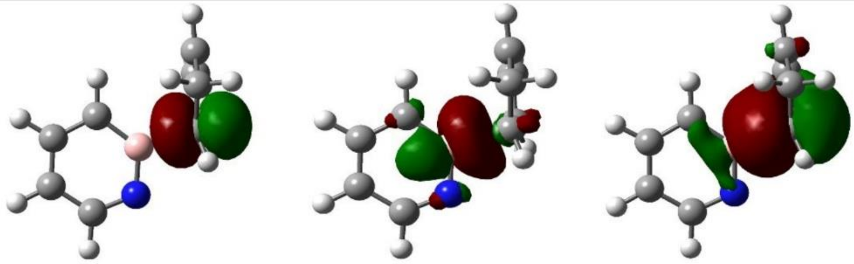
	1+benzene	6a	TS_{6a-6b}	6b	TS_{6b-6c}	6c	TS_{6b-6d}	6d
B3LYP/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP/6-311+G(d,p)]**	0.0 **[0.0]**	7.6 **[0.8]**	9.2 **[5.2]**	8.6 **[1.7]**	23.8 **[14.1]**	3.4 **[-14.1]**	27.8 **[20.7]**	9.9 **[-3.0]**
B3LYP-D3/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// B3LYP-D3/6-311+G(d,p)]**	0.0 **[0.0]**	2.5 **[0.9]**	5.6 **[5.2]**	3.5 **[1.8]**	18.2 **[14.1]**	-1.7 **[-14.1]**	23.0 **[20.6]**	5.1 **[-3.0]**
MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-4.0 **[2.5]**	3.2 **[6.4]**	-3.1 **[3.5]**	10.3 **[14.8]**	-14.5 **[-13.6]**	47.5 **[50.3]**	-1.0 **[-2.5]**
SCS-MP2/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p)]**	0.0 **[0.0]**	-0.2 **[1.8]**	5.7 **[6.2]**	0.7 **[2.7]**	14.8 **[14.5]**	-14.2 **[-14.0]**	23.0 **[21.2]**	-1.8 **[-2.7]**
M06-2X/6-311+G(d,p) **[CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	0.0 **[0.0]**	1.8 **[1.3]**	4.4 **[4.2]**	2.7 **[2.1]**	17.9 **[14.3]**	-9.2 **[-14.0]**	24.6 **[20.5]**	1.3 **[-3.0]**
SCS-MP2/6-311+G(d,p)-CPCM(benzene) **[CCSD(T)/cc-pVTZ// SCS-MP2/6-311+G(d,p) CPCM(benzene)]**	0.0 **[0.0]**	-1.1 **[2.0]**	5.7 **[6.5]**	-0.4 **[2.8]**	15.5 **[14.5]**	-13.0 **[-14.0]**	23.4 **[21.1]**	-0.4 **[-2.7]**

Table S13. NBO analysis of the R→B (R is C=C in C_2H_4, 1,3-butadiene, cyclopentadiene, furan and benzene respectively; and C≡C in C_2H_2) interaction for complexes **1a**, **2a**, **3a-cis**, **3a-trans**, **4a**, **4b**, **5b**, **5c**, **6a** and **6b** formed at the B3LYP-D3/6-311+G(d,p)level of theory.

	ΔE[(a)]	%R[(b)]	%B[(b)]	Occ. R[(c)]	Occ.B[(c)]
1a	319.7	77.1	22.4	1.557	0.502
2a	313.7	77.7	21.9	1.574	0.505
3a-cis	290.5	77.1	21.4	1.559	0.490
3a-trans	291.7	76.9	21.3	1.555	0.488
4a	244.6	77.6	19.9	1.572	0.462
4b	244.9	77.9	19.5	1.576	0.475
5b	192.7	79.1	17.8	1.598	0.437
5c	208.1	78.2	18.5	1.586	0.477
6a	65.5	79.1	9.8	1.591	0.319
6b	71.4	79.1	10.5	1.593	0.337

(a) NBO second order perturbation interaction energy associated with the R→B interaction, in kcal mol^{-1}. (b) Percentage of the donor and acceptor NBO in the corresponding NLMO. (c) Occupancy of the donor and acceptor NBO orbitals.

Table S14. NBO plots for the (a) donor NBO, (b) acceptor NBO and (c) corresponding NLMO associated with the R→B (R is C=C in C_2H_4, 1,3-butadiene, cyclopentadiene, furan and benzene respectively; and C≡C in C_2H_2) interaction for complexes **1a**, **2a**, **3a-cis**, **3a-trans**, **4a**, **4b**, **5b**, **5c**, **6a** and **6b** at the B3LYP-D3/6-311+G(d,p) level of theory.

1a	 (a) (b) (c)
2a	 (a) (b) (c)
3a-cis	 (a) (b) (c)
3a-trans	 (a) (b) (c)
4a	 (a) (b) (c)

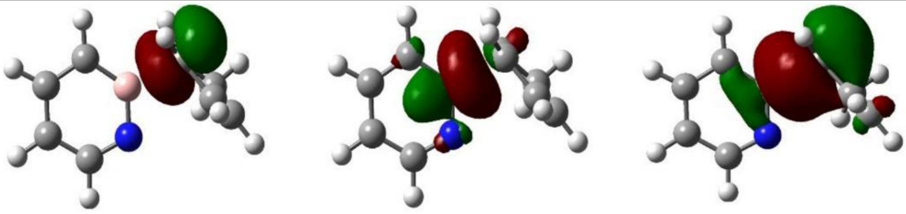
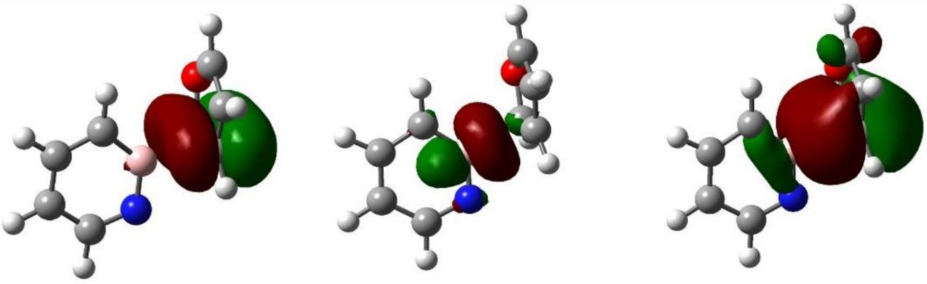
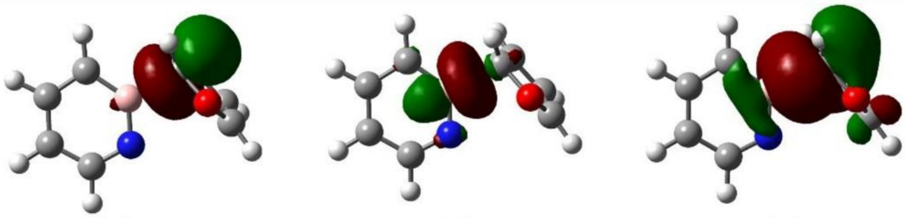
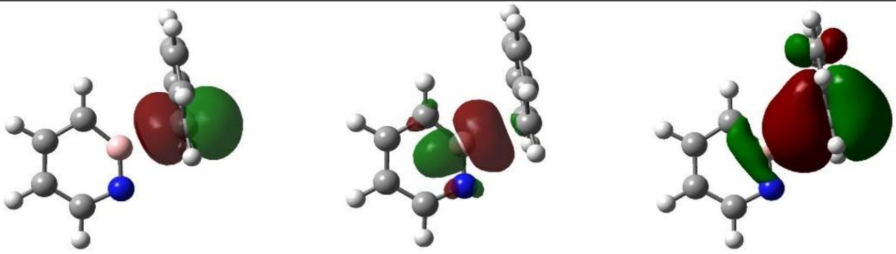
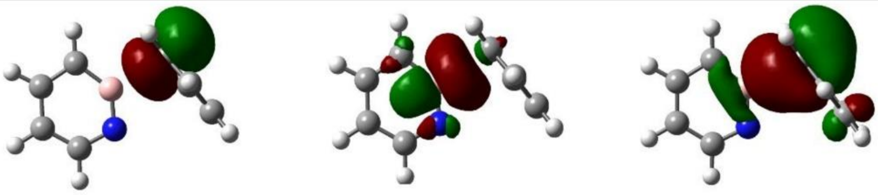
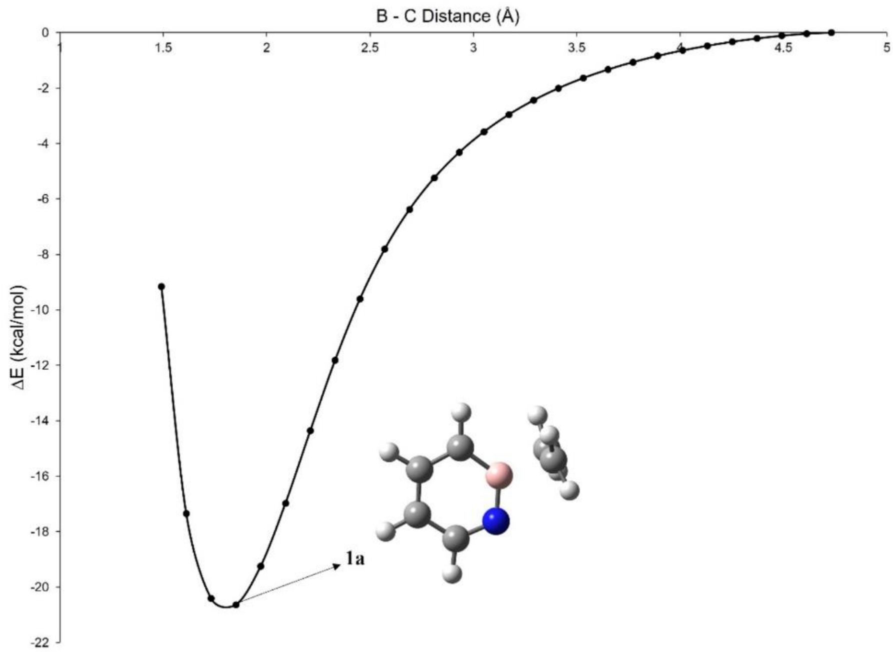
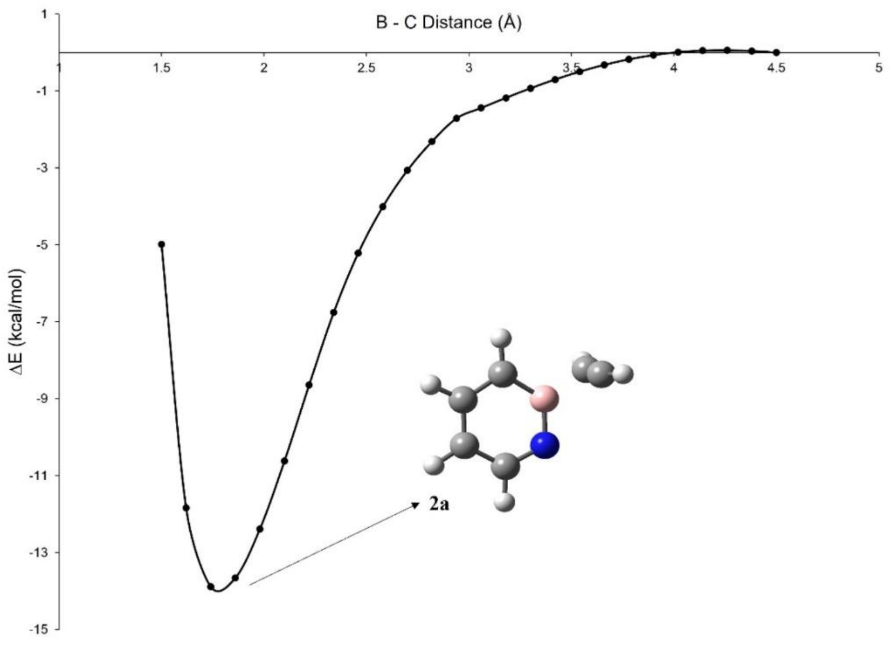
4b	 (a) (b) (c)
5b	 (a) (b) (c)
5c	 (a) (b) (c)
6a	 (a) (b) (c)
6b	 (a) (b) (c)

Table S15. Boron-carbon coordinate Scan for the complexes **1a**, **2a**, **3a(cis)**, **3a(trans)**, **4a**, **4b**, **5a**, **5b**, **6a**, and **6b** and boron-oxygen coordinate scan for the complex **5a** at the B3LYP/6-311+G(d,p) level of theory.

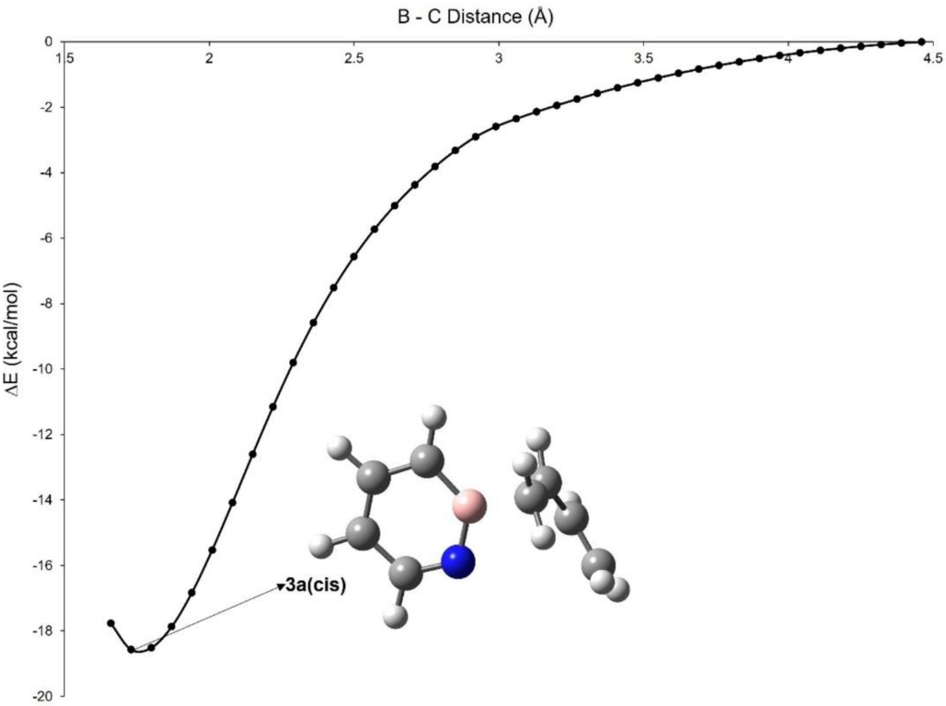
Scan Calculation for the complex **1a**



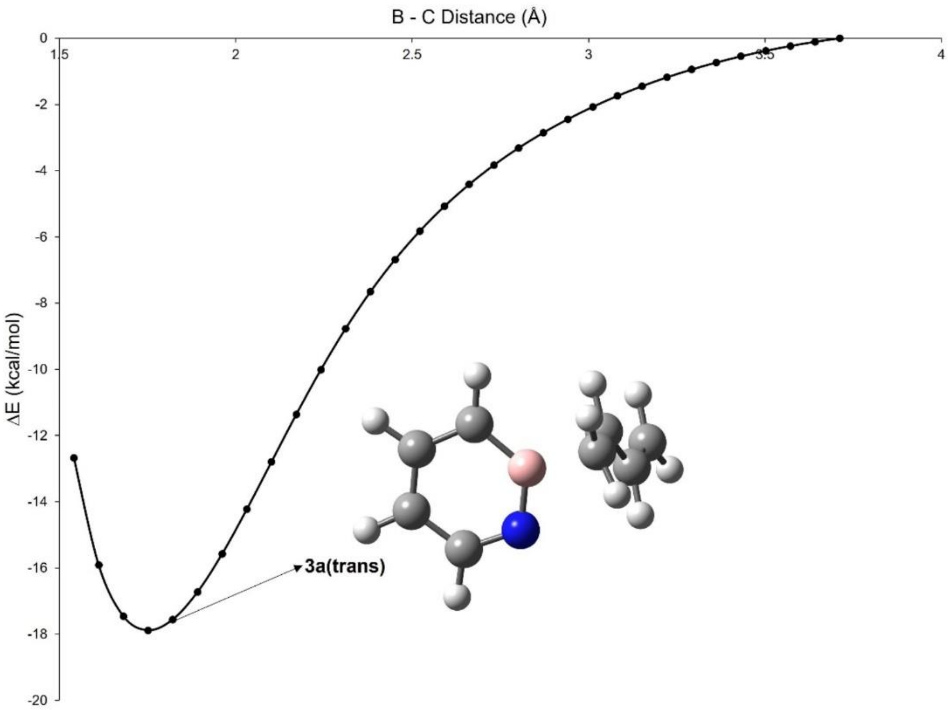
Scan Calculation for the complex **2a**



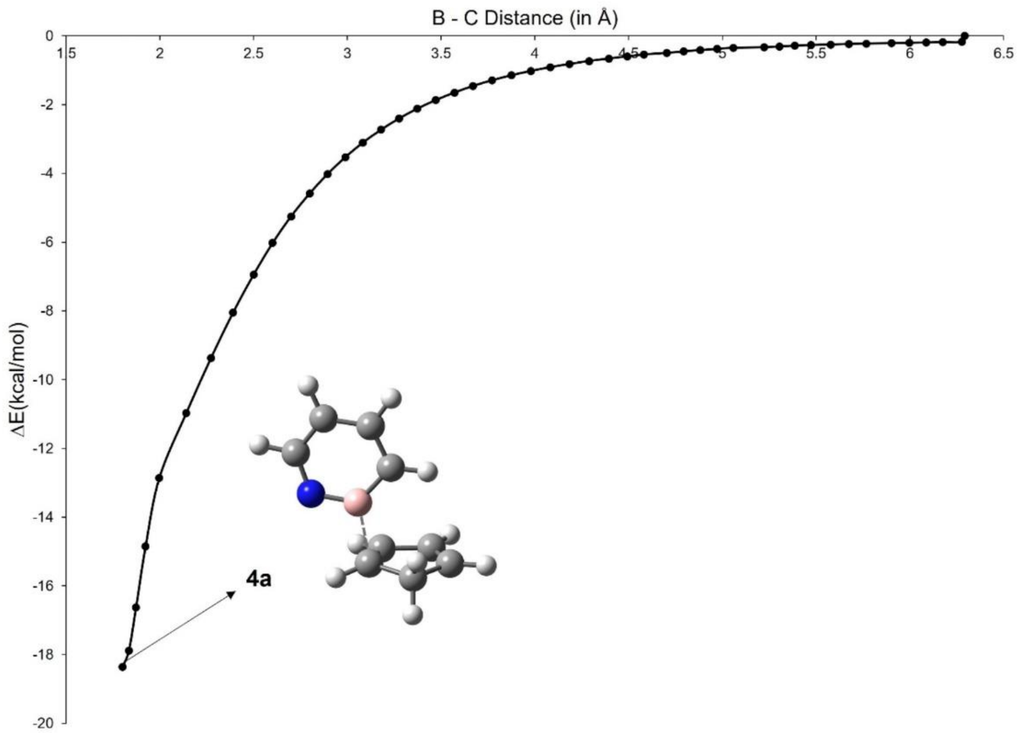
Scan Calculation for the complex **3a(cis)**



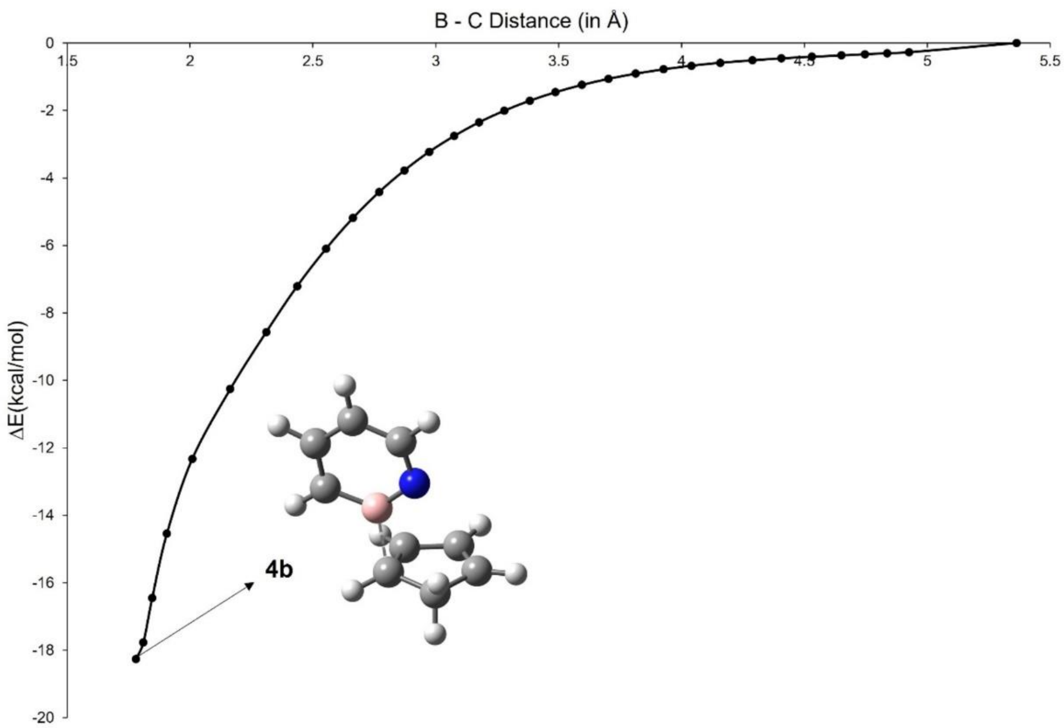
Scan Calculation for the complex **3a(trans)**



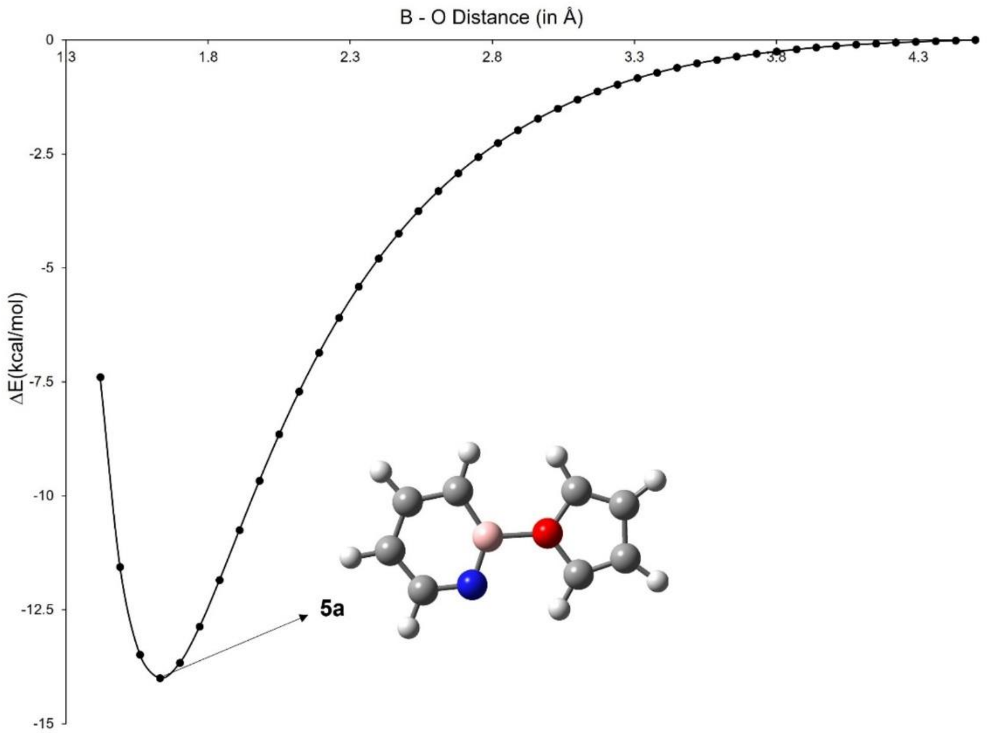
Scan Calculation for the complex **4a**



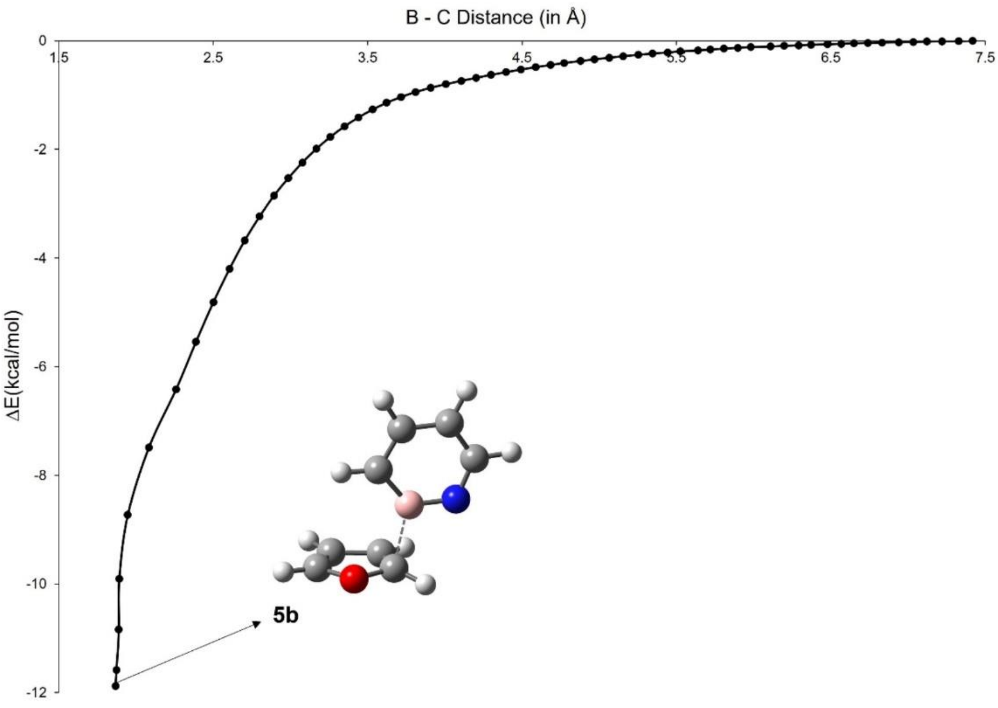
Scan Calculation for the complex **4b**



Scan Calculation for the complex **5a**



Scan Calculation for the complex **5b**



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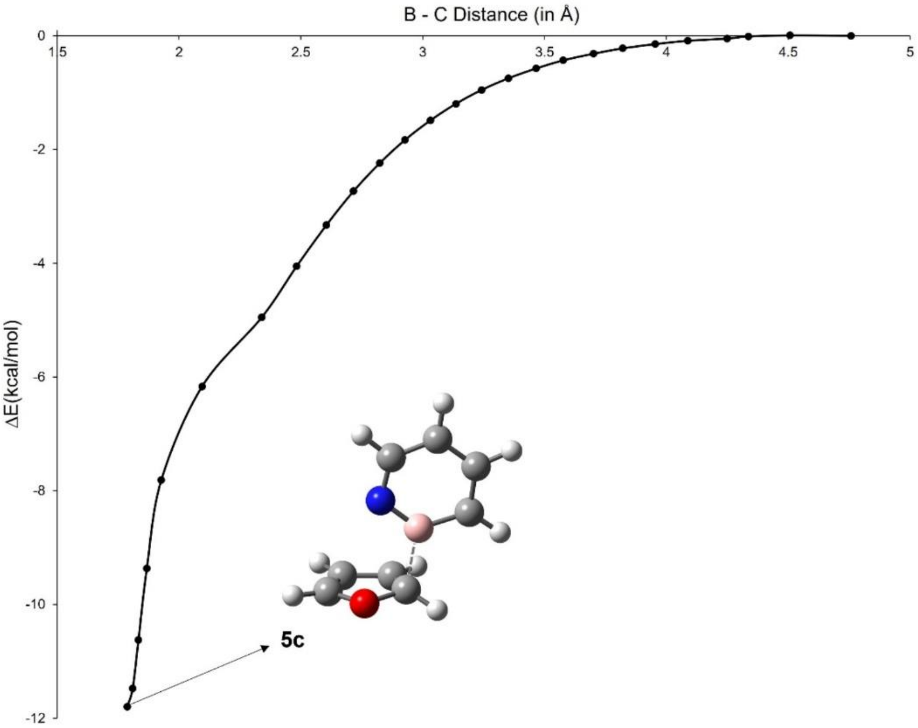
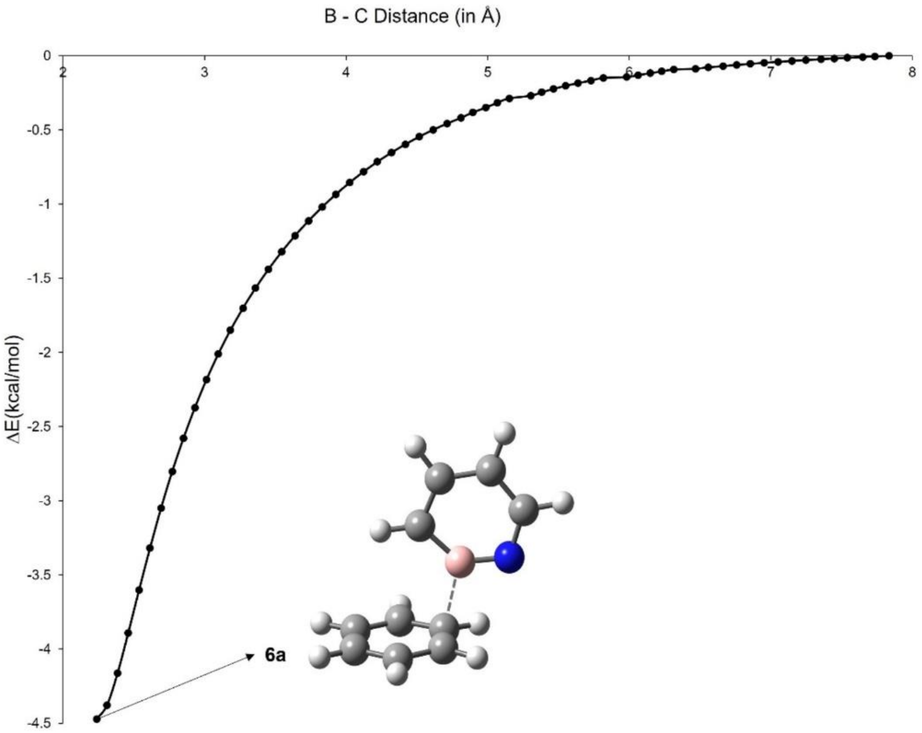
Scan Calculation for the complex **5c**



Scan Calculation for the complex **6a**



Scan Calculation for the complex **6b**

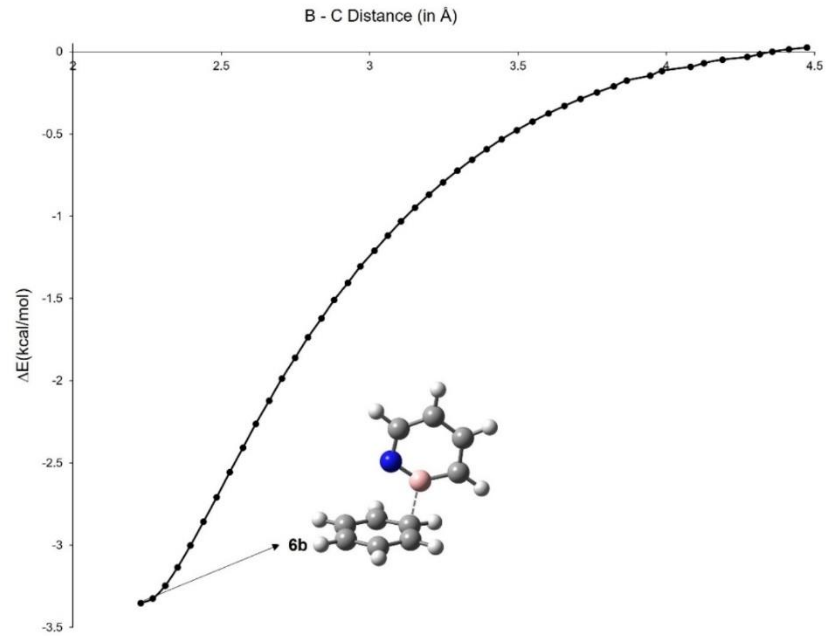
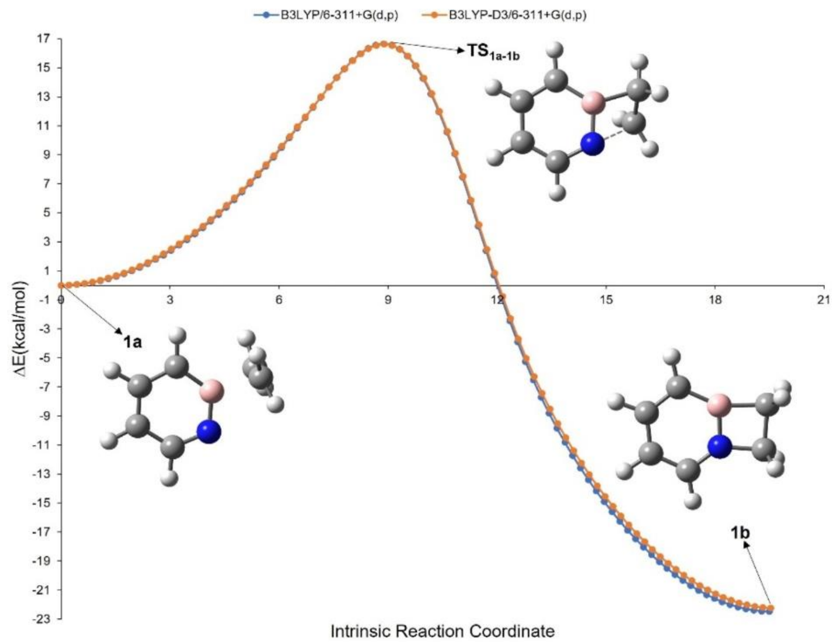
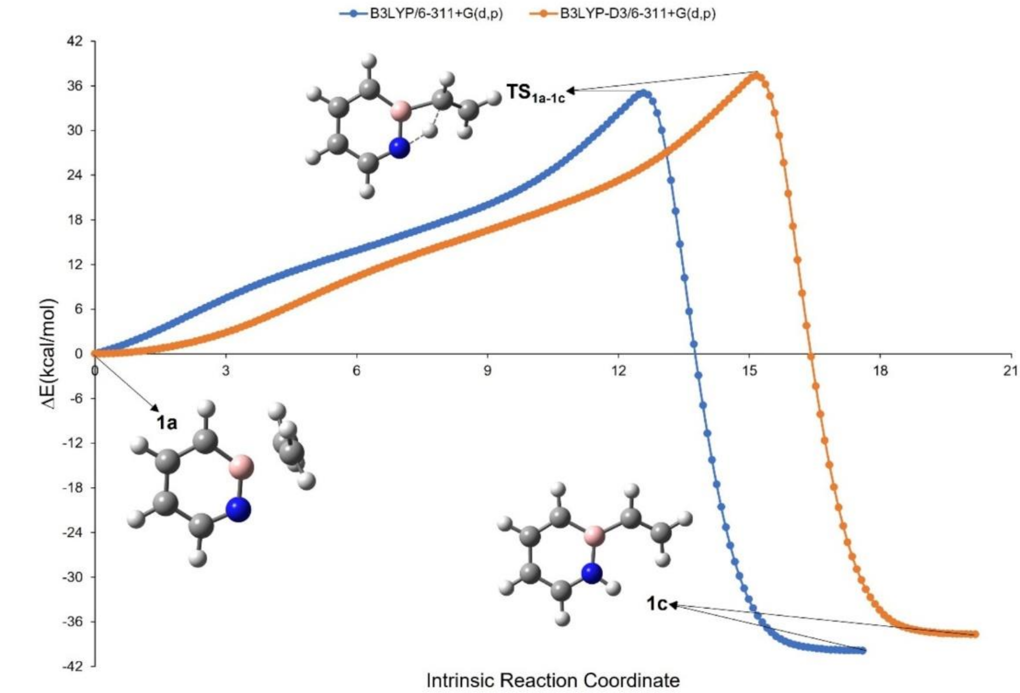


Table S16. Intrinsic reaction Coordinate (IRC) path for the reactions of 1,2-Azaborine with Ethene (C_2H_4), Ethyne (C_2H_2), 1,3-butadiene, cyclopentadiene, furan and benzene respectively at different level of theories.

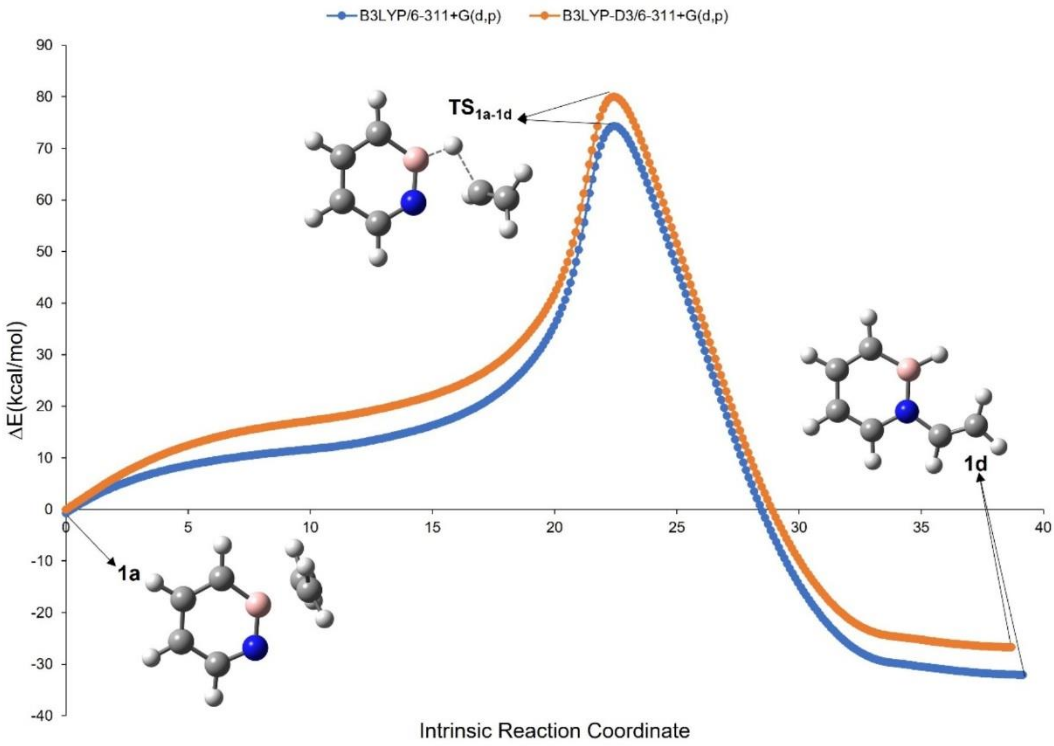
IRC for $\mathbf{TS_{1a\text{-}1b}}$



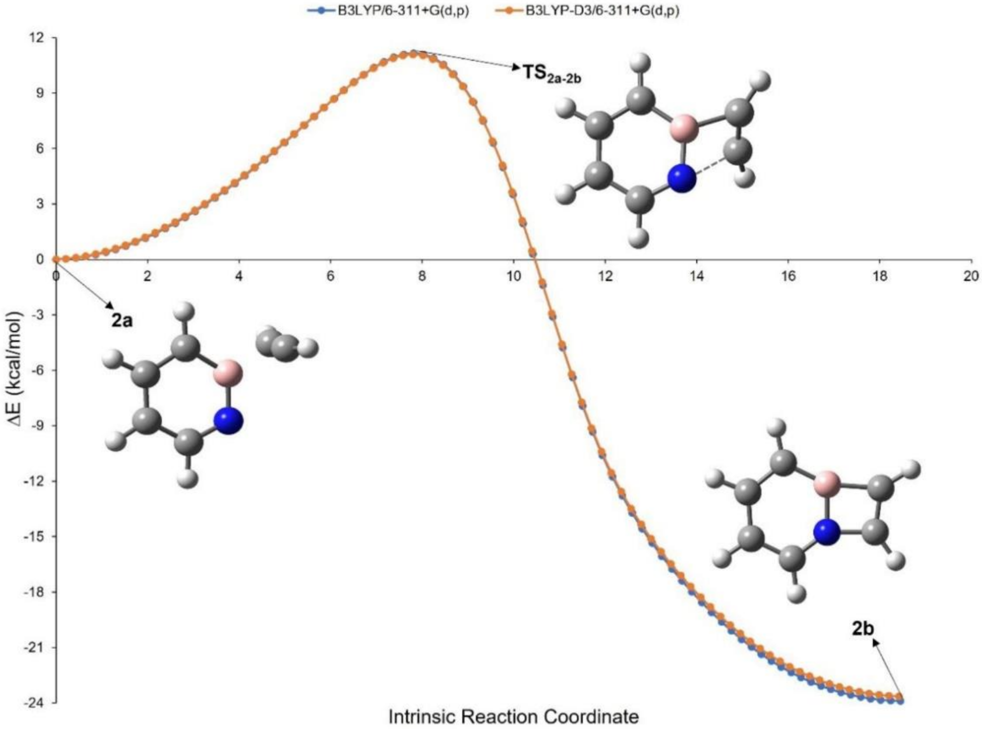
IRC for $\mathbf{TS_{1a\text{-}1c}}$



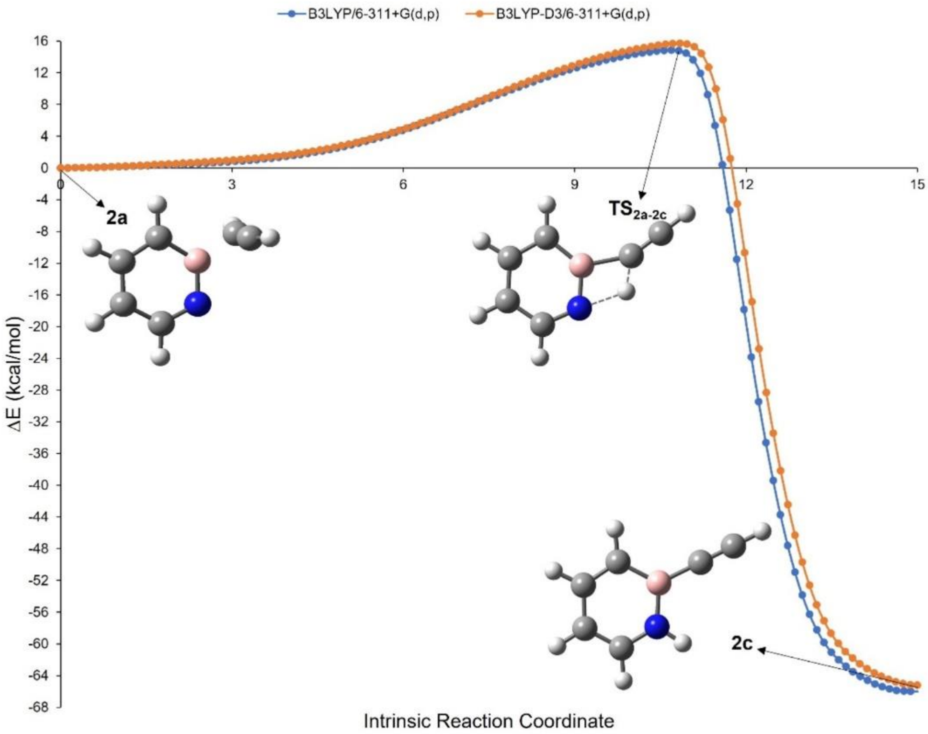
IRC for $\mathbf{TS_{1a\text{-}1d}}$



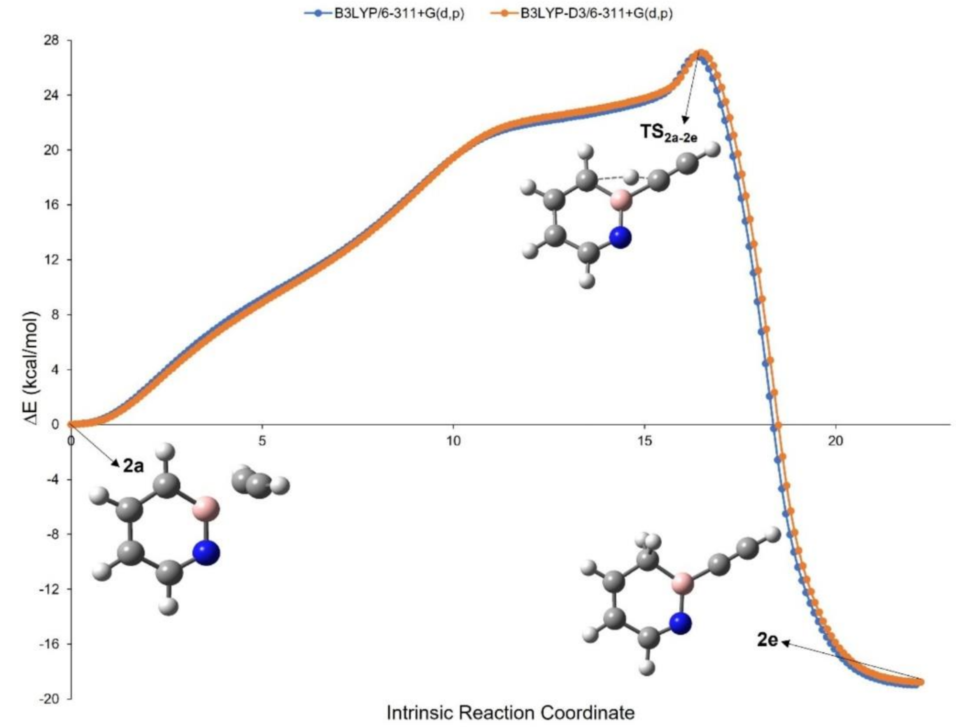
IRC for **TS$_{2a-2b}$**



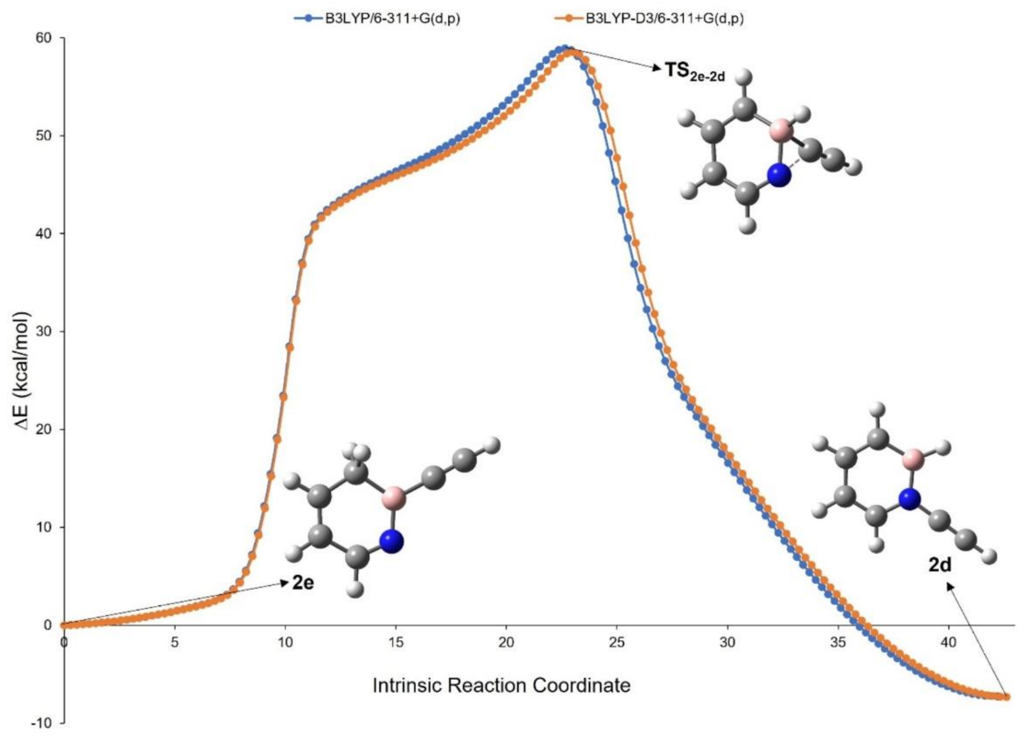
IRC for **TS$_{2a-2c}$**



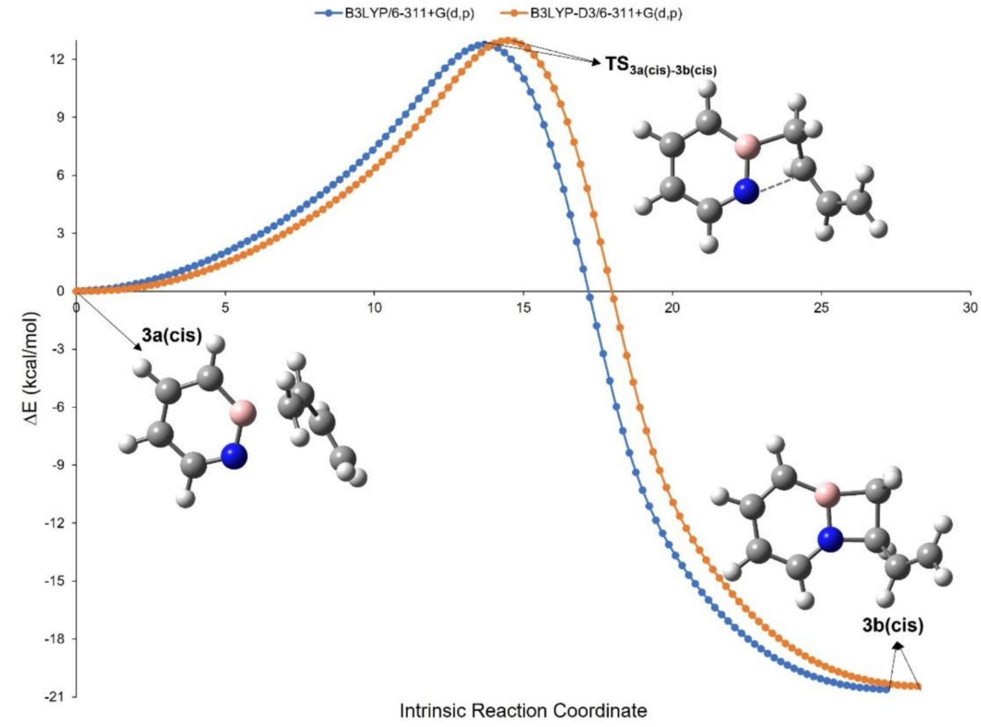
IRC for **TS$_{2a-2e}$**



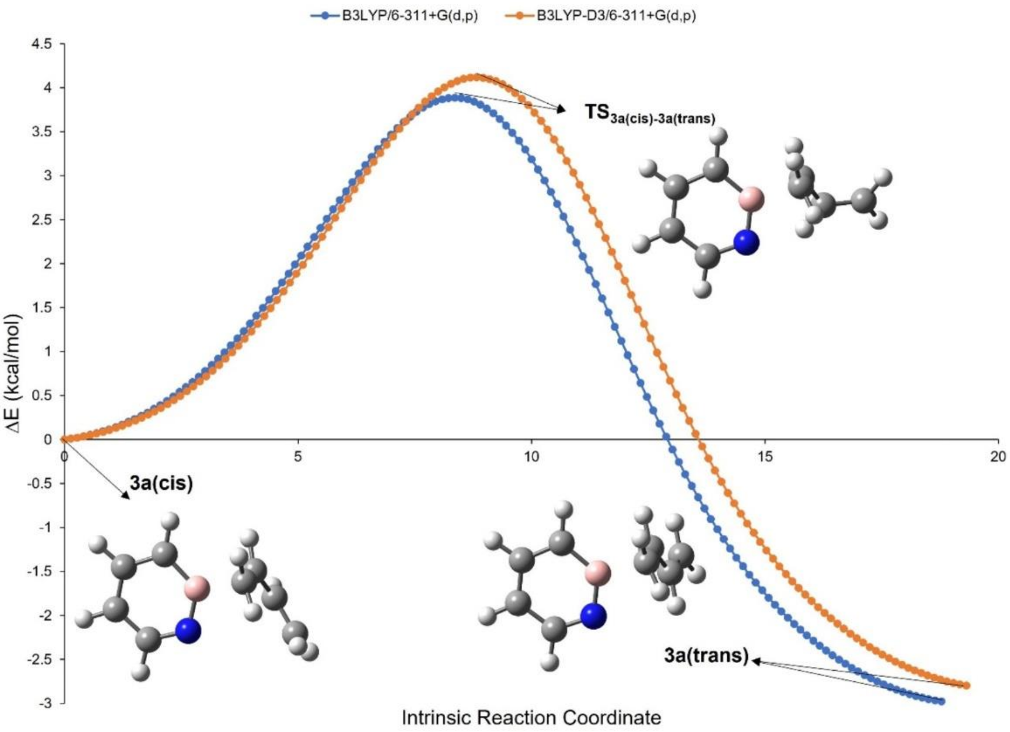
IRC for **TS$_{2e-2d}$**



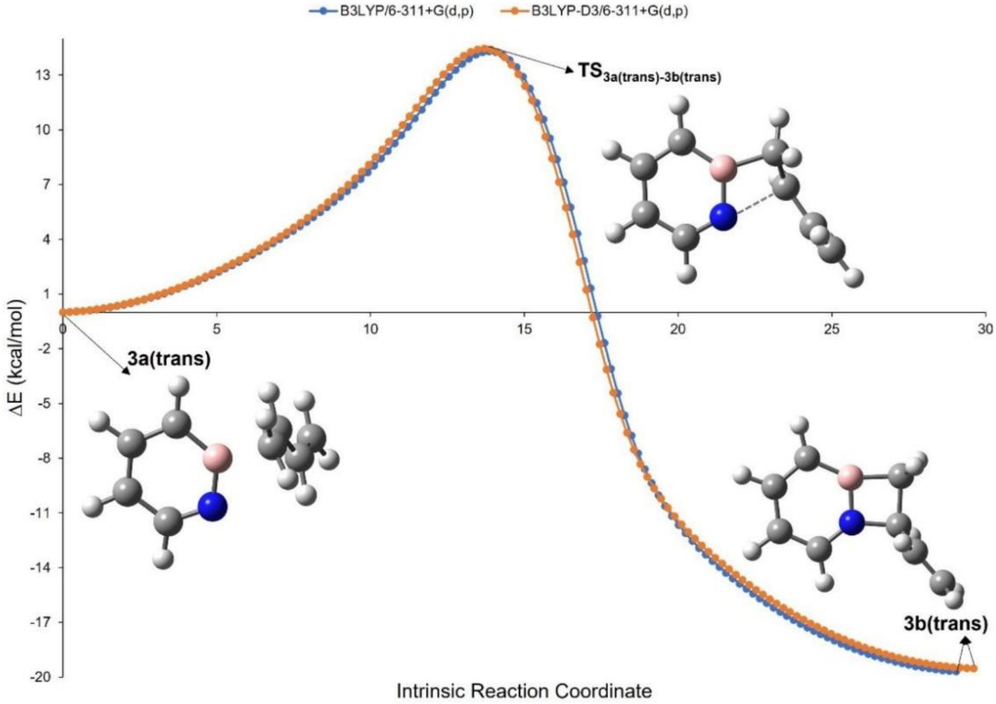
IRC for **TS**$_{\mathbf{3a(cis)-3b(cis)}}$



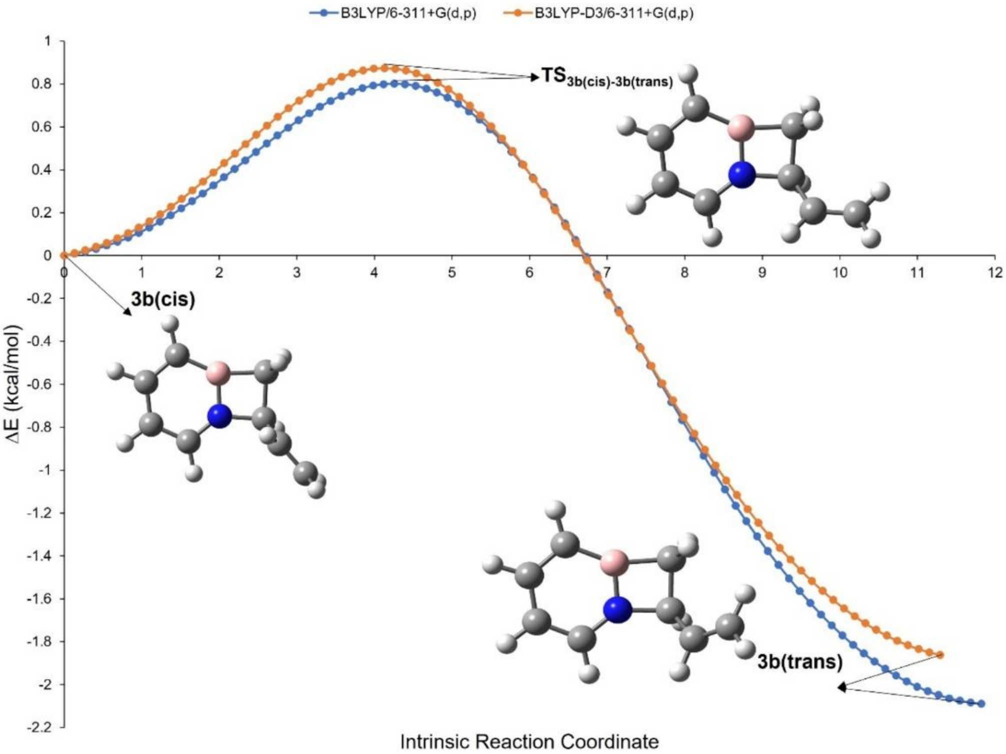
IRC for **TS**$_{\mathbf{3a(cis)-3a(trans)}}$



IRC for **TS$_{3a(trans)-3b(trans)}$**



IRC for **TS$_{3b(cis)-3b(trans)}$**



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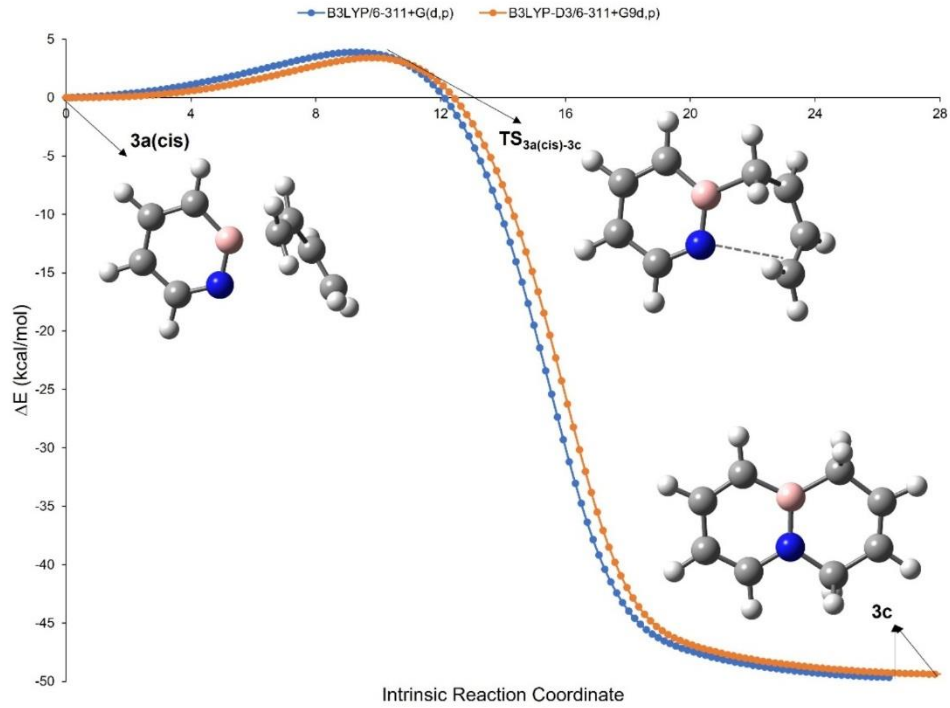
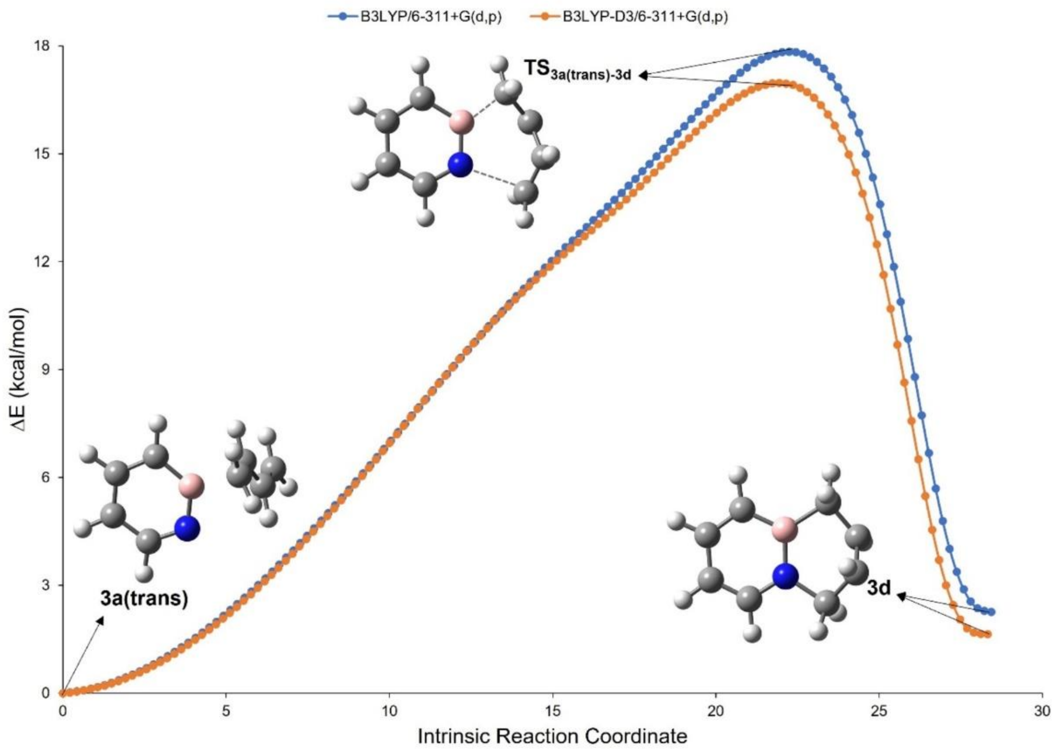
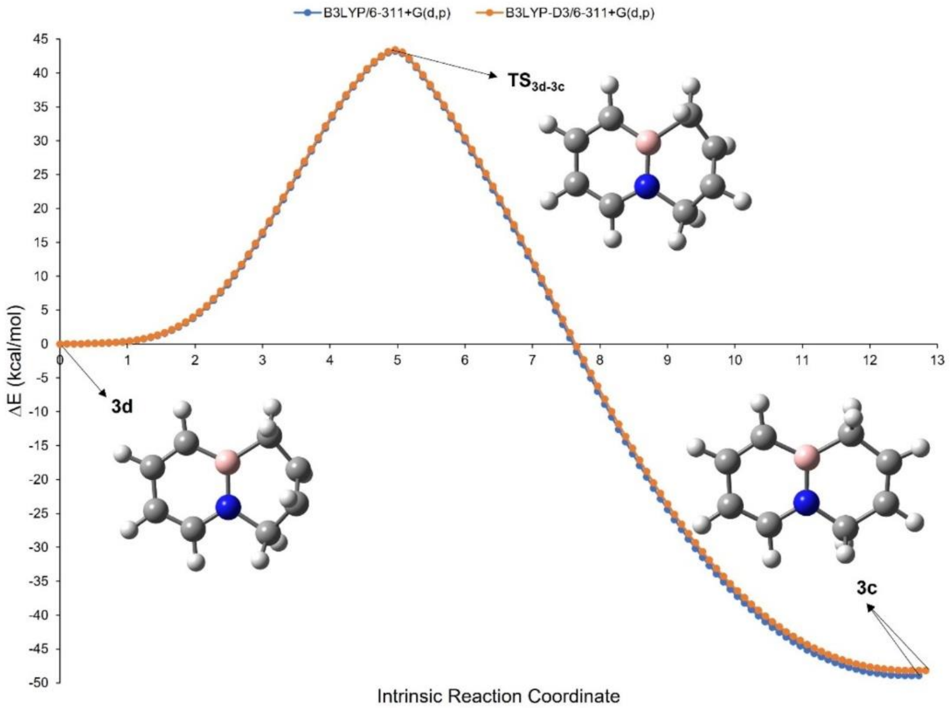
IRC for **TS$_{3a(cis)-3c}$**



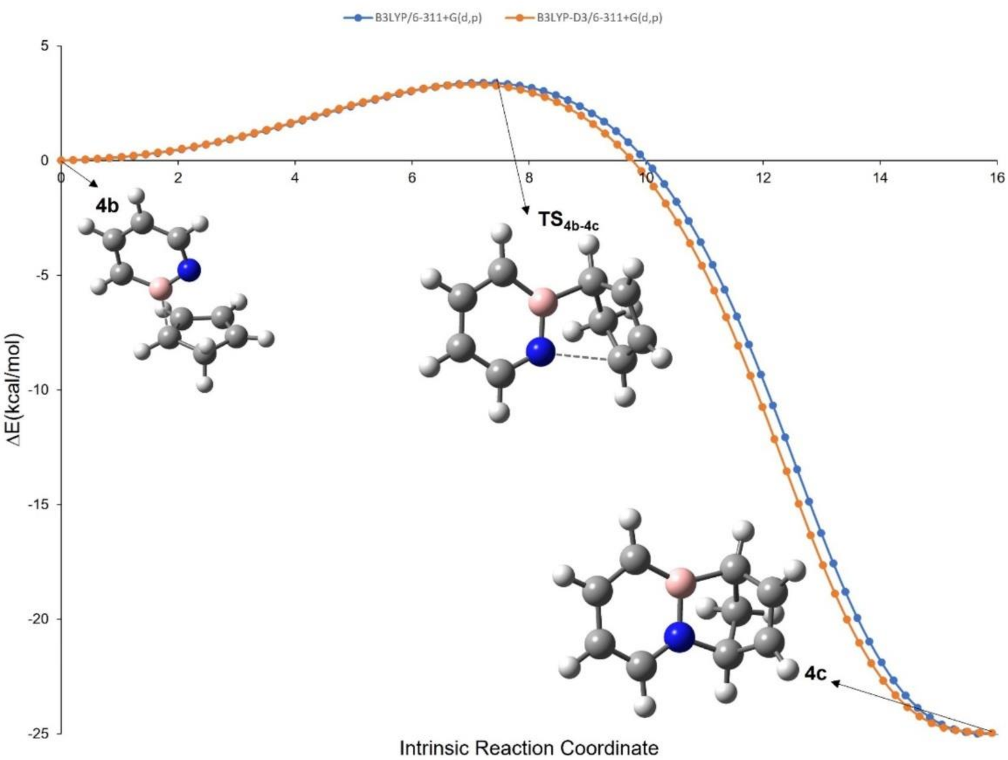
IRC for **TS$_{3a(trans)-3d}$**



IRC for **TS$_{3d\text{-}3c}$**

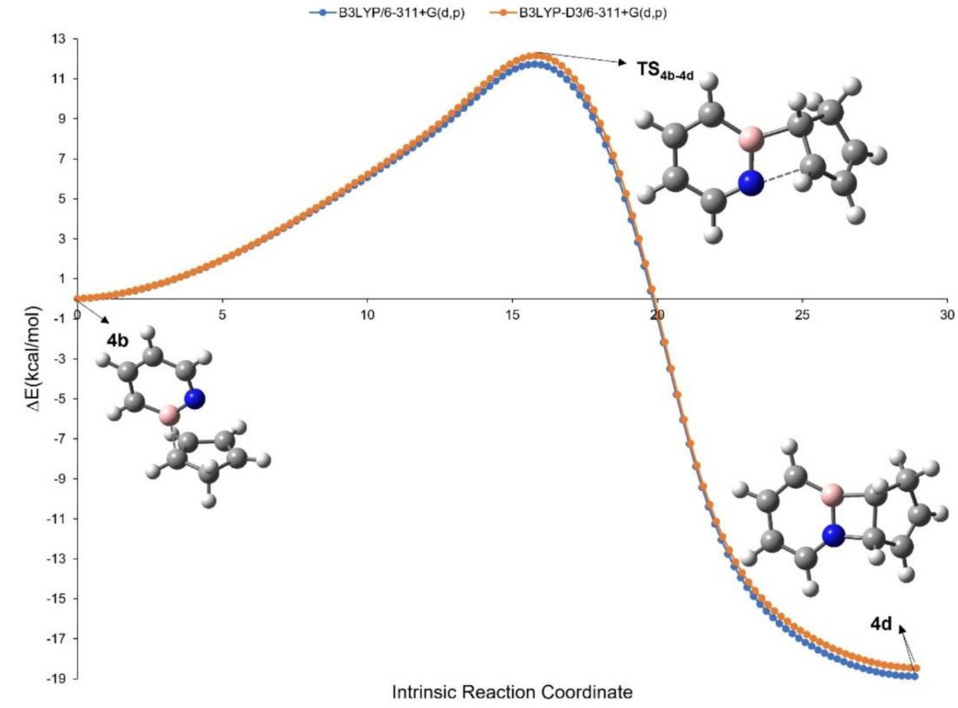


IRC for **TS$_{4b\text{-}4c}$**

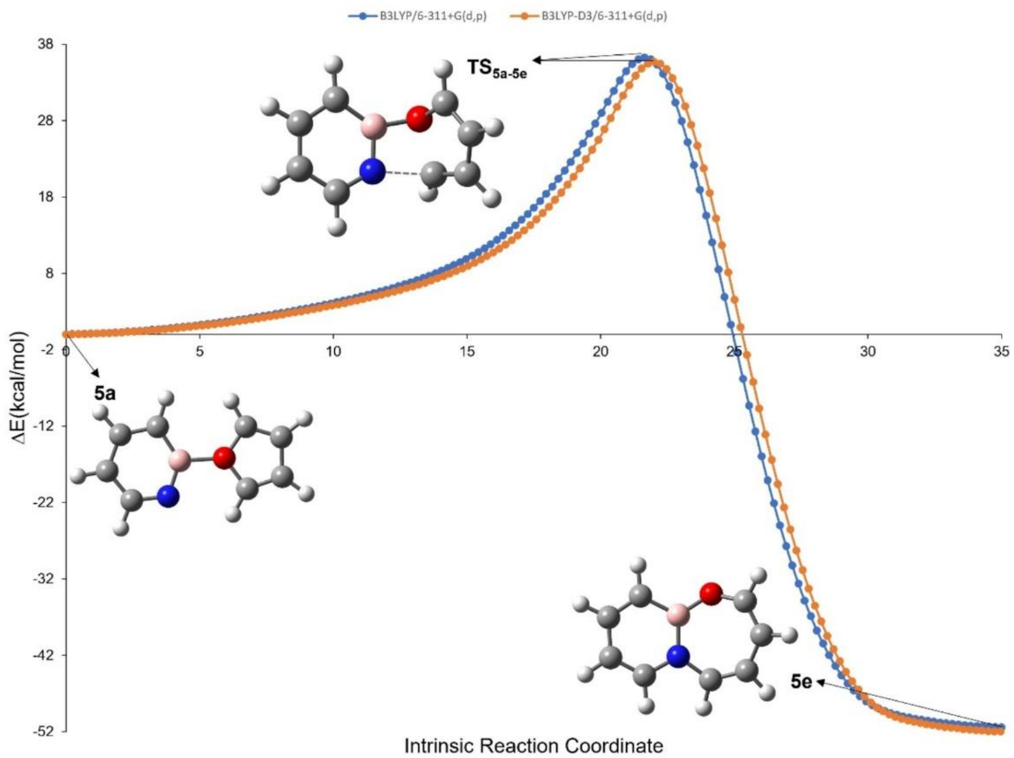


S26

IRC for **TS$_{4b-4d}$**

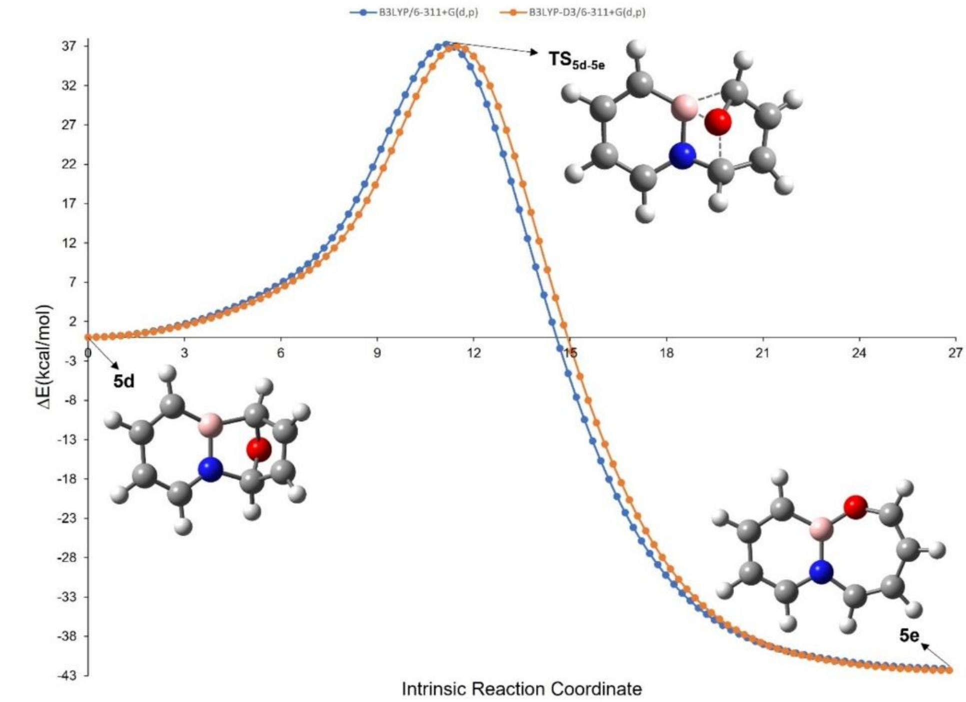


IRC for **TS$_{5a-5e}$**

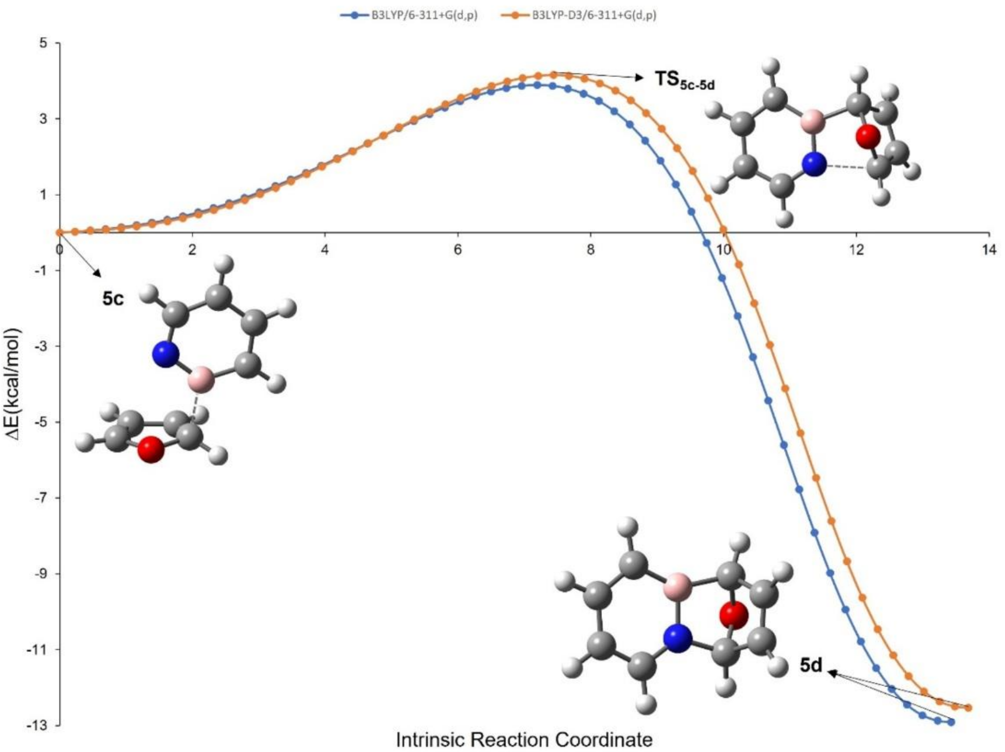


S27

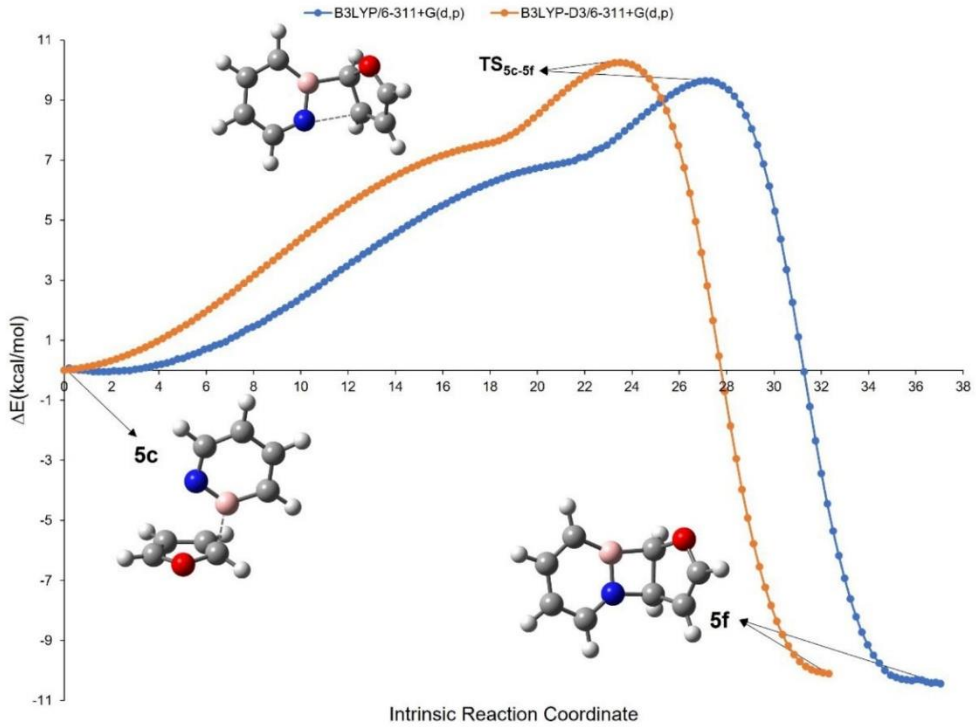
IRC for **$TS_{5d\text{-}5e}$**



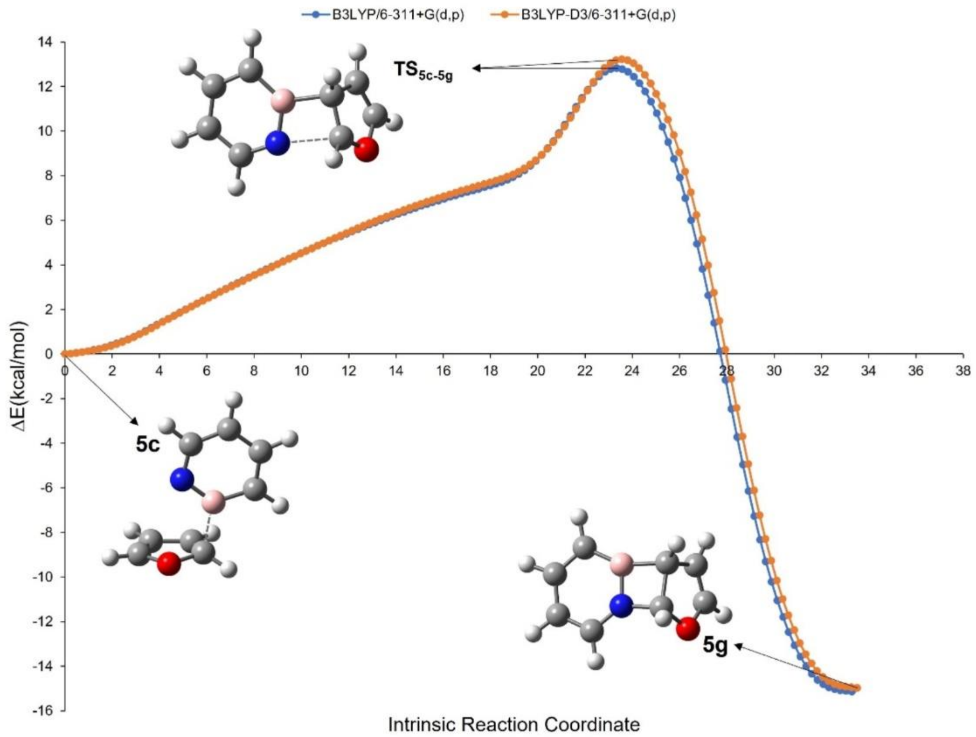
IRC for **$TS_{5c\text{-}5d}$**



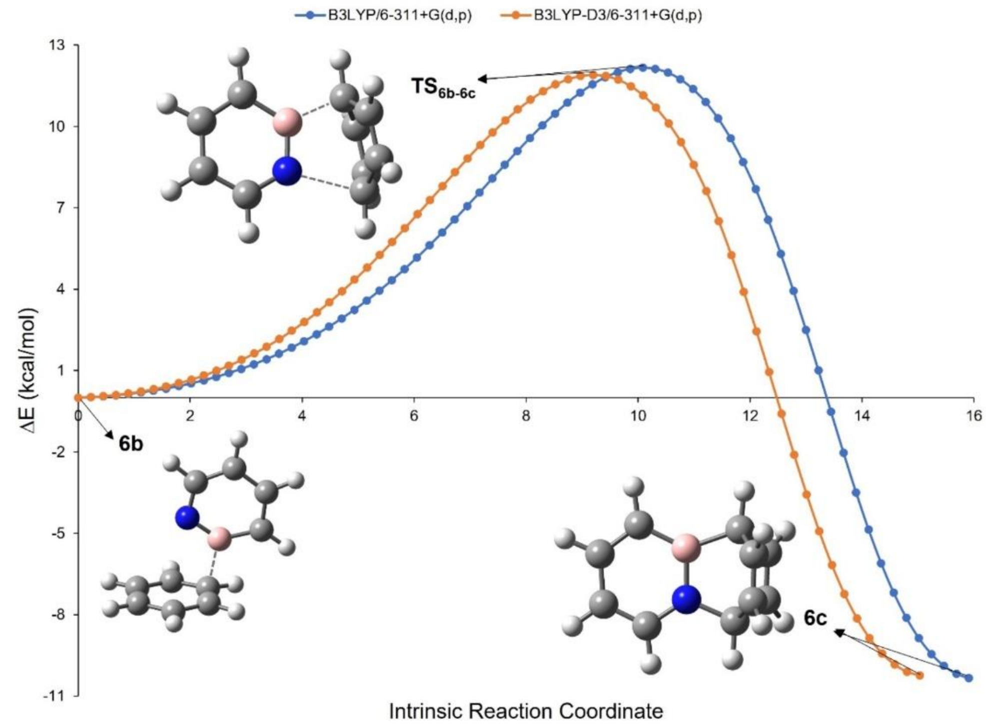
IRC for **TS$_{5c\text{-}5f}$**



IRC for **TS$_{5c\text{-}5g}$**



IRC for **TS$_{6b\text{-}6c}$**



IRC for **TS$_{6b\text{-}6d}$**

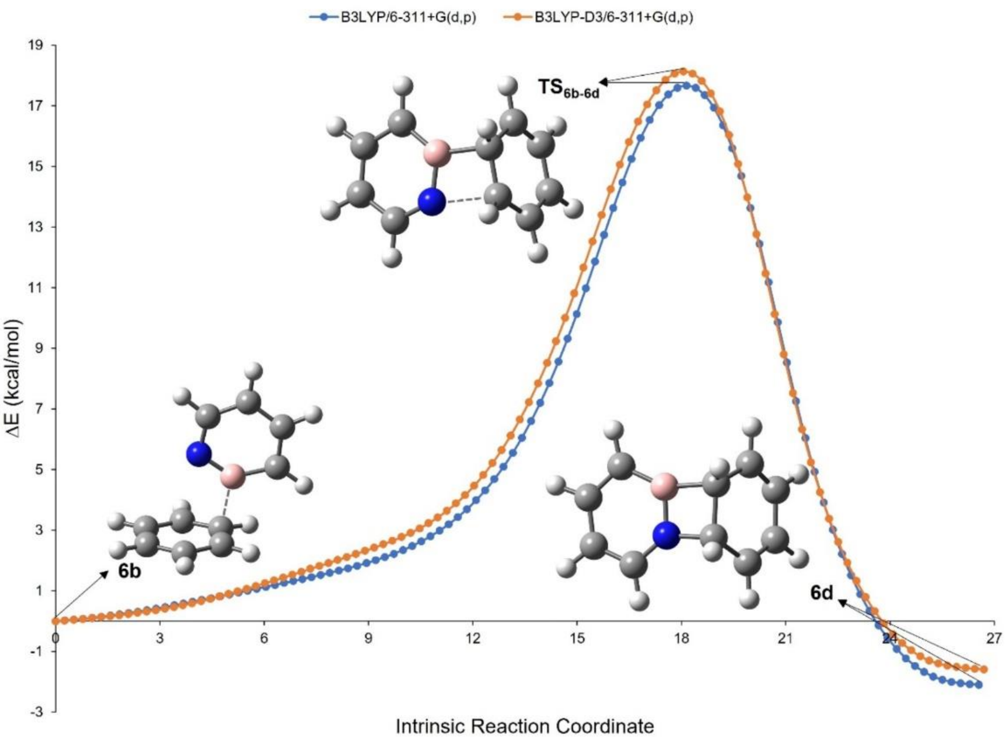
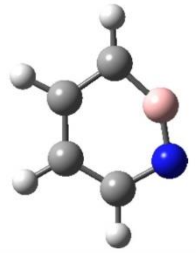
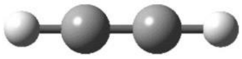
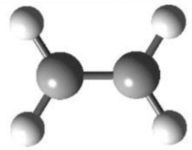


Table S17. Cartesian Coordinates of Stationary Points at different levels of theories.

1,2-Azaborine (1)				**B3LYP/6-311+G(d,p)**			
				N	-1.31781100	-0.76723000	0.00000000
				C	-1.23513500	0.58838300	0.00000000
				C	0.00000000	1.23880900	0.00000000
				C	1.21031400	0.51001000	0.00000000
				C	1.28218200	-0.89661700	0.00000000
				H	0.03056300	2.32157000	0.00000000
				H	-2.16209100	1.15729400	0.00000000
				H	2.14341000	1.06848000	0.00000000
				H	2.22354900	-1.42159000	0.00000000
				B	-0.11098300	-1.27973100	0.00000000
B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
N	-1.31840200	-0.76766600	0.00000000	N	-1.33419500	-0.77743300	0.00000000
C	-1.23562300	0.58843500	0.00000000	C	-1.23886400	0.58877100	0.00000000
C	0.00000000	1.23943100	0.00000000	C	0.00000000	1.23829500	0.00000000
C	1.21090700	0.51048900	0.00000000	C	1.21728800	0.51365900	0.00000000
C	1.28283000	-0.89671800	0.00000000	C	1.29388300	-0.89877300	0.00000000
H	0.03035800	2.32223400	0.00000000	H	0.02810400	2.32380300	0.00000000
H	-2.16261300	1.15736800	0.00000000	H	-2.16675800	1.16015700	0.00000000
H	2.14397700	1.06904400	0.00000000	H	2.15119100	1.07596100	0.00000000
H	2.22472800	-1.42128300	0.00000000	H	2.23955400	-1.42065300	0.00000000
B	-0.11126400	-1.28070500	0.00000000	B	-0.10931300	-1.26979000	0.00000000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	-1.32268300	-0.76818700	0.00000000	N	-1.33956900	-0.78133800	0.00000000
C	-1.22955700	0.58298900	0.00000000	C	-1.23921500	0.58792800	0.00000000
C	0.00000000	1.23637800	0.00000000	C	-0.00179200	1.23836800	0.00000000
C	1.20821900	0.50692200	0.00000000	C	1.22013200	0.51093000	0.00000000
C	1.28356900	-0.89329100	0.00000000	C	1.29309200	-0.89959100	0.00000000
H	0.02886700	2.31790200	0.00000000	H	0.02678200	2.32458100	0.00000000
H	-2.15502600	1.15370900	0.00000000	H	-2.16713200	1.16050400	0.00000000
H	2.14005800	1.06665900	0.00000000	H	2.1537320	1.07494900	0.00000000
H	2.22511000	-1.41638200	0.00000000	H	2.23644800	-1.42727800	0.00000000
B	-0.11072200	-1.26851200	0.00000000	B	-0.11464200	-1.27086600	0.00000000

Ethyne (C_2H_2)				**B3LYP/6-311+G(d,p)**			
				C	0.00000000	0.00000000	0.59977000
				C	0.00000000	0.00000000	-0.59977000
				H	0.00000000	0.00000000	1.66296800
				H	0.00000000	0.00000000	-1.66296800
B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
C	0.00000000	0.00000000	0.59977000	C	0.00000000	0.00000000	0.60807900
C	0.00000000	0.00000000	-0.59977000	C	0.00000000	0.00000000	-0.60807900
H	0.00000000	0.00000000	1.66296800	H	0.00000000	0.00000000	1.67281300
H	0.00000000	0.00000000	-1.66296800	H	0.00000000	0.00000000	-1.67281300
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	0.00000000	0.00000000	0.59851700	C	0.00000000	0.00000000	0.60738400
C	0.00000000	0.00000000	-0.59851700	C	0.0000000	0.00000000	-0.60738400
H	0.00000000	0.00000000	1.66295100	H	0.0000000	0.00000000	1.67326600
H	0.00000000	0.00000000	-1.66295100	H	0.0000000	0.00000000	-1.67326600

Ethene (C_2H_4)



B3LYP/6-311+G(d,p)

C	-0.66442100	0.00000000	0.00000400
C	0.66442100	0.00000000	-0.00000300
H	-1.23518100	-0.92269500	-0.00001100
H	-1.23518100	0.92269500	0.00002200
H	1.23518100	0.92269500	0.00001000
H	1.23518100	-0.92269500	-0.00002400

B3LYP-D3/6-311+G(d,p)

C	-0.66442100	0.00000000	-0.00000400
C	0.66442100	0.00000000	0.00000300
H	-1.23518100	0.92269500	0.00001100
H	-1.23518100	-0.92269500	-0.00002200
H	1.23518100	-0.92269500	-0.00001000
H	1.23518100	0.92269500	0.00002400

MP2/6-311+G(d,p)

C	-0.66957400	0.00000000	-0.00000300
C	0.66957400	0.00000000	0.00000300
H	-1.23586800	0.92598300	0.00001100
H	-1.23586800	-0.92598300	-0.00002300
H	1.23586800	-0.92598300	-0.00001000
H	1.23586800	0.92598300	0.00002300

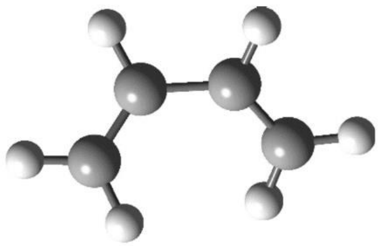
M06-2X/6-311+G(d,p)

C	-0.66288300	0.00000000	-0.00000300
C	0.66288300	0.00000000	0.00000300
H	-1.23099500	0.92337600	0.00001100
H	-1.23099500	-0.92337600	-0.00002300
H	1.23099500	-0.92337600	-0.00001000
H	1.23099500	0.92337600	0.00002300

SCS-MP2/6-311+G(d,p)

C	-0.670107000	0.000000000	-0.000003000
C	0.670107000	0.000000000	0.000003000
H	-1.237136000	0.926929000	0.000011000
H	-1.237136000	-0.926929000	-0.000023000
H	1.237136000	-0.926929000	-0.000010000
H	1.237136000	0.926929000	0.000023000

1,3-cis-butadiene



B3LYP/6-311+G(d,p)

C	-0.270304000	1.523990000	0.489579000
C	-0.270304000	0.682916000	-0.549037000
H	0.176301000	1.256285000	1.441433000
H	-0.704940000	2.513656000	0.411923000
H	-0.680286000	1.026908000	-1.496607000
C	0.270304000	-0.682916000	-0.549037000
C	0.270304000	-1.523990000	0.489579000
H	0.680286000	-1.026908000	-1.496607000
H	0.704940000	-2.513656000	0.411923000
H	-0.176301000	-1.256285000	1.441433000

B3LYP-D3/6-311+G(d,p)

C	0.270963000	1.519728000	-0.490922000
C	0.270963000	0.682772000	0.551216000
H	-0.176669000	1.245599000	-1.440642000
H	0.706228000	2.509607000	-0.419246000
H	0.681450000	1.028176000	1.498122000
C	-0.270963000	-0.682772000	0.551216000
C	-0.270963000	-1.519728000	-0.490922000
H	-0.681450000	-1.028176000	1.498122000
H	-0.706228000	-2.509607000	-0.419246000
H	0.176669000	-1.245599000	-1.440642000

MP2/6-311+G(d,p)

C	0.334729000	1.497314000	-0.493258000
C	0.334729000	0.655446000	0.556885000
H	-0.204204000	1.256054000	-1.405090000
H	0.861296000	2.445169000	-0.453092000
H	0.835399000	0.956293000	1.476417000
C	-0.334729000	-0.655446000	0.556885000
C	-0.334729000	-1.497314000	-0.493258000
H	-0.835399000	-0.956293000	1.476417000
H	-0.861296000	-2.445169000	-0.453092000
H	0.204204000	-1.256054000	-1.405090000

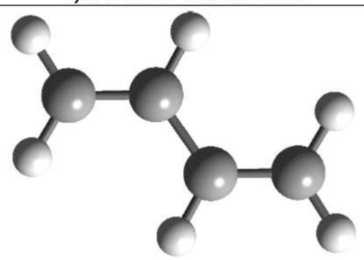
M06-2X/6-311+G(d,p)

C	0.308161000	1.497278000	-0.489949000
C	0.308161000	0.668218000	0.552355000
H	-0.194273000	1.236578000	-1.415448000
H	0.794716000	2.463686000	-0.441573000
H	0.772014000	0.986405000	1.482584000
C	-0.308161000	-0.668218000	0.552355000
C	-0.308161000	-1.497278000	-0.489949000
H	-0.772014000	-0.986405000	1.482584000
H	-0.794716000	-2.463686000	-0.441573000
H	0.194273000	-1.236578000	-1.415448000

SCS-MP2/6-311+G(d,p)

C	0.334653000	1.506843000	-0.491772000
C	0.336373000	0.658365000	0.553173000
H	-0.201924000	1.272693000	-1.408052000
H	0.860576000	2.456192000	-0.445466000
H	0.840800000	0.952673000	1.473978000
C	-0.336373000	-0.658365000	0.553173000
C	-0.334653000	-1.506843000	-0.491772000
H	-0.840800000	-0.952673000	1.473978000
H	-0.860576000	-2.456192000	-0.445466000
H	0.201924000	-1.272693000	-1.408052000

1,3-trans-butadiene



B3LYP/6-311+G(d,p)

C	0.601369000	1.748818000	-0.000094000
C	0.601369000	0.410438000	0.000108000
H	-0.324751000	2.315211000	-0.000192000
H	1.523433000	2.317506000	-0.000172000
H	1.549999000	-0.122798000	0.000280000
C	-0.601369000	-0.410438000	0.000108000
C	-0.601369000	-1.748818000	-0.000094000
H	-1.549999000	0.122798000	0.000280000
H	-1.523433000	-2.317506000	-0.000172000
H	0.324751000	-2.315211000	-0.000192000

B3LYP-D3/6-311+G(d,p)

C	-0.601369000	1.748818000	0.000094000
C	-0.601369000	0.410438000	-0.000108000
H	0.324751000	2.315211000	0.000192000
H	-1.523433000	2.317506000	0.000172000
H	-1.549999000	-0.122798000	-0.000280000
C	0.601369000	-0.410438000	-0.000108000
C	0.601369000	-1.748818000	0.000094000
H	1.549999000	0.122798000	-0.000280000
H	1.523433000	-2.317506000	0.000172000
H	-0.324751000	-2.315211000	0.000192000

MP2/6-311+G(d,p)

C	-0.608203000	1.751007000	0.000014000
C	-0.608203000	0.403899000	-0.000016000
H	0.323167000	2.311157000	0.000032000
H	-1.533801000	2.316737000	0.000018000
H	-1.556222000	-0.133797000	-0.000035000
C	0.608203000	-0.403899000	-0.000016000
C	0.608203000	-1.751007000	0.000014000
H	1.556222000	0.133797000	-0.000035000
H	1.533801000	-2.316737000	0.000018000
H	-0.323167000	-2.311157000	0.000032000

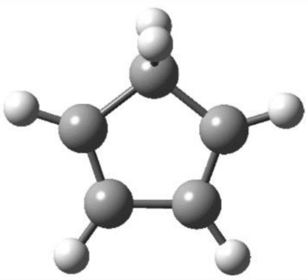
M06-2X/6-311+G(d,p)

C	-0.607560000	1.738350000	0.000005000
C	-0.607560000	0.405277000	-0.000005000
H	0.321764000	2.298734000	0.000011000
H	-1.528976000	2.306919000	0.000006000
H	-1.550678000	-0.136105000	-0.000013000
C	0.607560000	-0.405277000	-0.000005000
C	0.607560000	-1.738350000	0.000005000
H	1.550678000	0.136105000	-0.000013000
H	1.528976000	-2.306919000	0.000006000
H	-0.321764000	-2.298734000	0.000011000

SCS-MP2/6-311+G(d,p)

C	0.603979000	1.755812000	-0.000026000
C	0.609063000	0.408326000	0.000006000
H	-0.328589000	2.316064000	-0.000046000
H	1.528568000	2.325570000	-0.000029000
H	1.559678000	-0.126268000	0.000025000
C	-0.609063000	-0.408326000	0.000006000
C	-0.603979000	-1.755812000	-0.000026000
H	-1.559678000	0.126268000	0.000025000
H	-1.528568000	-2.325570000	-0.000029000
H	0.328589000	-2.316064000	-0.000046000

cyclopentadiene



B3LYP/6-311+G(d,p)

C	-0.009112000	-1.216109000	-0.000002000
C	-1.181428000	-0.272786000	-0.000009000
C	-0.726681000	0.995760000	-0.000008000
C	0.741601000	0.984698000	0.000061000
C	1.177165000	-0.290541000	-0.000047000
H	-0.014207000	-1.877494000	0.877160000
H	-0.014229000	-1.877510000	-0.877150000
H	-2.214959000	-0.591161000	-0.000012000
H	-1.333654000	1.892164000	0.000002000
H	2.205892000	-0.624084000	-0.000075000
H	1.361884000	1.871956000	0.000107000

B3LYP-D3/6-311+G(d,p)

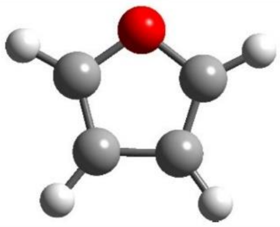
C	0.002082000	-1.215719000	-0.000037000
C	-1.179168000	-0.283722000	0.000001000
C	-0.735900000	0.988770000	0.000042000
C	0.732533000	0.991240000	-0.000040000
C	1.180119000	-0.279745000	0.000044000
H	0.003151000	-1.876356000	0.877537000
H	0.003171000	-1.876287000	-0.877665000
H	-2.209508000	-0.611872000	-0.000002000
H	-1.350978000	1.879626000	0.000066000
H	2.211615000	-0.604255000	0.000067000
H	1.344551000	1.884198000	-0.000063000

MP2/6-311+G(d,p)

C	1.217897000	-0.000232000	0.000022000
C	0.287549000	1.180350000	0.000003000
C	-0.995716000	0.734025000	-0.000022000
C	-0.995995000	-0.733646000	-0.000003000
C	0.287099000	-1.180459000	-0.000005000
H	1.872178000	-0.000355000	-0.882819000
H	1.872144000	-0.000358000	0.882889000
H	0.612065000	2.214697000	0.000009000
H	-1.886050000	1.353798000	-0.000039000
H	0.611221000	-2.214930000	-0.000006000
H	-1.886564000	-1.353080000	-0.000007000

M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	-0.000278000	-1.213961000	-0.000001000	C	1.223071000	-0.000233000	0.000019000
C	-1.176004000	-0.280535000	-0.000007000	C	0.285251000	1.183227000	0.000003000
C	-0.734463000	0.987811000	-0.000012000	C	-0.996547000	0.738232000	-0.000012000
C	0.734923000	0.987466000	0.000068000	C	-0.996828000	-0.737853000	-0.000017000
C	1.175871000	-0.281086000	-0.000052000	C	0.284801000	-1.183336000	0.000008000
H	-0.000435000	-1.870420000	0.878420000	H	1.877038000	-0.000359000	-0.884113000
H	-0.000458000	-1.870437000	-0.878407000	H	1.877013000	-0.000356000	0.884169000
H	-2.206852000	-0.605918000	-0.000011000	H	0.609983000	2.218617000	0.000006000
H	-1.349128000	1.878071000	-0.000008000	H	-1.888288000	1.357599000	-0.000024000
H	2.206580000	-0.606908000	-0.000085000	H	0.609138000	-2.218849000	0.000015000
H	1.349997000	1.877444000	0.000116000	H	-1.888805000	-1.356880000	-0.000032000

furan

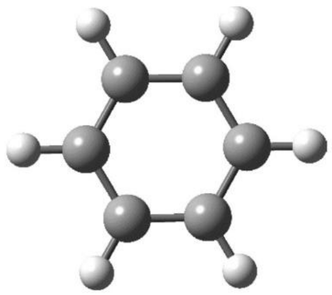


B3LYP/6-311+G(d,p)			
C	1.095132000	-0.346976000	0.000484000
C	0.717722000	0.957851000	-0.000425000
C	-0.717720000	0.957853000	0.000175000
C	-1.095133000	-0.346974000	0.000075000
O	-0.000001000	-1.158589000	-0.000278000
H	2.049628000	-0.845109000	0.000777000
H	1.373079000	1.814201000	-0.000779000
H	-1.373075000	1.814204000	0.000275000
H	-2.049630000	-0.845104000	0.000099000

B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
C	1.095492000	-0.347023000	0.000143000	C	-1.093311000	-0.351901000	0.000013000
C	0.717833000	0.957944000	-0.000268000	C	-0.715993000	0.965414000	0.000085000
C	-0.717831000	0.957945000	-0.000051000	C	0.715993000	0.965414000	0.000246000
C	-1.095493000	-0.347021000	0.000000000	C	1.093311000	-0.351901000	-0.000110000
O	-0.000001000	-1.158868000	0.000169000	O	0.000000000	-1.161611000	-0.000222000
H	2.050777000	-0.844105000	0.000277000	H	-2.048709000	-0.853450000	-0.000016000
H	1.373405000	1.814042000	-0.000495000	H	-1.378437000	1.818817000	0.000152000
H	-1.373403000	1.814044000	-0.000113000	H	1.378436000	1.818817000	0.000469000
H	-2.050778000	-0.844101000	0.000041000	H	2.048709000	-0.853450000	-0.000240000

M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	-1.088691000	-0.347798000	0.000340000	C	1.095099000	-0.350331000	0.000016000
C	-0.717626000	0.955006000	-0.000341000	C	0.720038000	0.964909000	-0.000101000
C	0.717626000	0.955005000	0.000677000	C	-0.720037000	0.964910000	-0.000213000
C	1.088691000	-0.347798000	-0.000386000	C	-1.095099000	-0.350329000	0.000104000
O	0.000000000	-1.151384000	-0.000271000	O	-0.000001000	-1.164579000	0.000218000
H	-2.043108000	-0.845941000	0.000499000	H	2.051787000	-0.851353000	0.000062000
H	-1.375541000	1.808232000	-0.000581000	H	1.381217000	1.820488000	-0.000192000
H	1.375541000	1.808232000	0.001207000	H	-1.381215000	1.820490000	-0.000413000
H	2.043108000	-0.845941000	-0.000695000	H	-2.051788000	-0.851349000	0.000222000

Benzene



B3LYP/6-311+G(d,p)

C	-0.459320000	-1.317222000	-0.000001000
C	-1.370409000	-0.260816000	0.000004000
C	-0.911090000	1.056393000	0.000002000
C	0.459334000	1.317217000	0.000001000
C	1.370406000	0.260830000	-0.000001000
C	0.911079000	-1.056402000	-0.000004000
H	-0.816436000	-2.341257000	-0.000001000
H	-2.435803000	-0.463596000	0.000005000
H	-1.619373000	1.877682000	0.000004000
H	0.816416000	2.341265000	0.000001000
H	2.435807000	0.463575000	-0.000003000
H	1.619389000	-1.877668000	-0.000006000

B3LYP-D3/6-311+G(d,p)

C	-0.475075000	-1.311894000	-0.000001000
C	-1.373672000	-0.244507000	0.000004000
C	-0.898598000	1.067373000	0.000002000
C	0.475089000	1.311889000	0.000001000
C	1.373669000	0.244522000	-0.000001000
C	0.898587000	-1.067382000	-0.000004000
H	-0.844368000	-2.331591000	-0.000001000
H	-2.441398000	-0.434572000	0.000005000
H	-1.597036000	1.897039000	0.000004000
H	0.844348000	2.331598000	0.000001000
H	2.441401000	0.434552000	-0.000003000
H	1.597052000	-1.897026000	-0.000006000

MP2/6-311+G(d,p)

C	0.539364000	1.292194000	0.010599000
C	-0.849391000	1.113200000	-0.010601000
C	-1.388755000	-0.178994000	0.010596000
C	-0.539364000	-1.292194000	-0.010599000
C	0.849391000	-1.113200000	0.010601000
C	1.388755000	0.178994000	-0.010596000
H	0.957986000	2.295117000	-0.000162000
H	-1.508637000	1.977199000	0.000159000
H	-2.466623000	-0.317918000	-0.000168000
H	-0.957986000	-2.295117000	0.000162000
H	1.508637000	-1.977199000	-0.000159000
H	2.466623000	0.317918000	0.000168000

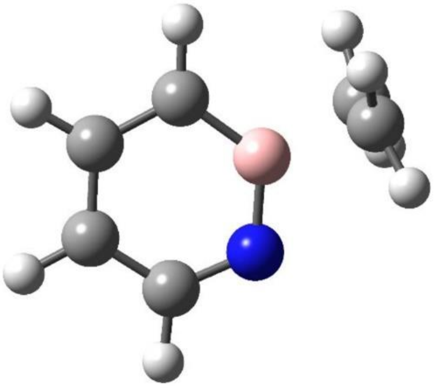
M06-2X/6-311+G(d,p)

C	-0.848389000	1.103159000	0.000001000
C	-1.379570000	-0.183129000	-0.000002000
C	-0.531199000	-1.286282000	-0.000003000
C	0.848392000	-1.103156000	-0.000001000
C	1.379571000	0.183125000	0.000002000
C	0.531196000	1.286284000	0.000003000
H	-1.508962000	1.962196000	0.000001000
H	-2.453802000	-0.325691000	-0.000004000
H	-0.944845000	-2.287884000	-0.000005000
H	1.508957000	-1.962199000	-0.000001000
H	2.453802000	0.325696000	0.000004000
H	0.944850000	2.287882000	0.000005000

SCS-MP2/6-311+G(d,p)

C	0.539948000	1.293592000	0.007138000
C	-0.850310000	1.114405000	-0.007140000
C	-1.390258000	-0.179188000	0.007135000
C	-0.539948000	-1.293592000	-0.007138000
C	0.850310000	-1.114405000	0.007140000
C	1.390258000	0.179188000	-0.007135000
H	0.958924000	2.297363000	-0.000243000
H	-1.510113000	1.979134000	0.000240000
H	-2.469037000	-0.318229000	-0.000249000
H	-0.958924000	-2.297363000	0.000243000
H	1.510113000	-1.979134000	-0.000240000
H	2.469037000	0.318229000	0.000249000

1a



B3LYP/6-311+G(d,p)

C	2.23756700	-0.00633900	-0.69482300
C	2.23692500	-0.00563400	0.69546300
H	2.30442800	-0.93602400	-1.24378700
H	2.39911900	0.90766600	-1.25169600
H	2.39855800	0.90883600	1.25152400
H	2.30375900	-0.93480800	1.24531200
N	-0.04364500	-1.25058100	-0.00023600
C	-1.36544700	-1.25870500	0.00006300
C	-2.15874800	-0.09173600	0.00027400
C	-1.57632600	1.17906700	0.00000900
C	-0.18671500	1.30866500	-0.00049600
H	-3.23951800	-0.19243200	0.00074700
H	-1.87348700	-2.22532600	-0.00017700
H	-2.22340900	2.05246300	0.00012600
H	0.24042300	2.30890500	-0.00102700
B	0.57442000	0.02257600	-0.00046200

B3LYP-D3/6-311+G(d,p)

C	2.23667500	-0.00607900	-0.69526400
C	2.23665000	-0.00603300	0.69534800
H	2.30704900	-0.93522600	-1.24520000
H	2.39202300	0.90952900	-1.25158400
H	2.39197400	0.90961300	1.25161400
H	2.30699900	-0.93514300	1.24535000
N	-0.04716300	-1.25549500	0.00004200
C	-1.36906600	-1.25723300	0.00001900
C	-2.15844500	-0.08654300	-0.00003700
C	-1.57209900	1.18280400	-0.00007000
C	-0.18183800	1.30638500	-0.00004900
H	-3.23954000	-0.18383800	-0.00005300
H	-1.88143800	-2.22152500	0.00004400
H	-2.21623400	2.05837700	-0.00011200
H	0.25366800	2.30283400	-0.00007600
B	0.57287600	0.01680800	0.00000800

MP2/6-311+G(d,p)

C	2.20915400	-0.00211800	-0.70242500
C	2.20915100	-0.00210200	0.70242500
H	2.29204200	-0.93750600	-1.24433500
H	2.37960000	0.91856800	-1.25025400
H	2.37956600	0.91860200	1.25023500
H	2.29201300	-0.93747300	1.24436700
N	-0.02574500	-1.26929800	-0.00000100
C	-1.35769900	-1.26287200	0.00004500
C	-2.15148400	-0.08991800	-0.00000600
C	-1.57027800	1.18832600	-0.00000300
C	-0.17450700	1.31349200	0.00000800
H	-3.23508800	-0.19238000	-0.00006600
H	-1.87252000	-2.22783200	-0.00008100
H	-2.22136700	2.06190200	-0.00001700
H	0.26127000	2.31348600	0.00000900
B	0.58373700	0.01977400	-0.00002300

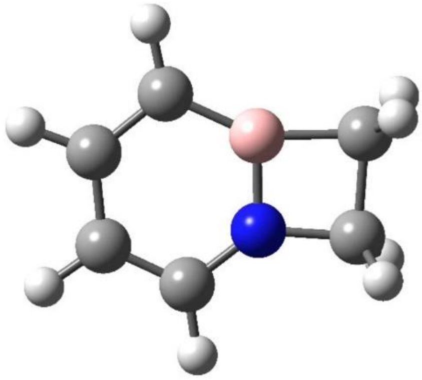
M06-2X/6-311+G(d,p)

C	2.22898800	-0.00603300	-0.69122600
C	2.22896200	-0.00598500	0.69131000
H	2.27642200	-0.93733800	-1.23913200
H	2.37446600	0.91072700	-1.24712900
H	2.37441900	0.91081400	1.24715400
H	2.27637600	-0.93725200	1.23928200
N	-0.03819300	-1.25064300	0.00004200
C	-1.35773600	-1.25617800	0.00001800
C	-2.14947600	-0.09139400	-0.00003700
C	-1.56953600	1.17678100	-0.00007000
C	-0.18152800	1.30850000	-0.00004800
H	-3.22910100	-0.19364500	-0.00005400
H	-1.86540100	-2.22150100	0.00004100
H	-2.21751300	2.04863900	-0.00011200
H	0.24848700	2.30680500	-0.00007400
B	0.56623100	0.02262200	0.00001000

SCS-MP2/6-311+G(d,p)

C	2.221447000	-0.004467000	-0.701724000
C	2.221399000	-0.004138000	0.702065000
H	2.301882000	-0.939511000	-1.245837000
H	2.390493000	0.916569000	-1.250833000
H	2.390394000	0.917157000	1.250755000
H	2.301792000	-0.938925000	1.246626000
N	-0.029444000	-1.271675000	0.000387000
C	-1.360459000	-1.265836000	0.000321000
C	-2.156358000	-0.091112000	-0.000005000
C	-1.574698000	1.187051000	-0.000287000
C	-0.176256000	1.312731000	-0.000245000
H	-3.240651000	-0.194161000	-0.000036000
H	-1.875388000	-2.231522000	0.000523000
H	-2.225216000	2.062034000	-0.000537000
H	0.257899000	2.314245000	-0.000468000
B	0.581068000	0.018151000	0.000110000

1b



B3LYP/6-311+G(d,p)

C	-1.92310700	-0.73974900	0.00069900
C	-2.08054500	0.82384300	-0.00033000
H	-2.30206400	-1.24843200	-0.89044800
H	-2.30007600	-1.24640800	0.89382100
H	-2.58999300	1.21217000	0.88398500
H	-2.58744700	1.21019100	-0.88704800
N	-0.45228900	-0.60106100	-0.00054200
C	0.63334700	-1.39977600	-0.00012600
C	1.86142500	-0.77695800	-0.00015100
C	1.96295100	0.64547500	0.00010900
C	0.87595300	1.50426400	0.00036100
H	2.76085700	-1.37950400	-0.00005700
H	0.50992300	-2.47785600	0.00006200
H	2.97010800	1.05717200	0.00015300
H	1.06866400	2.57241700	0.00075900
B	-0.46882000	0.83301700	-0.00016100

B3LYP-D3/6-311+G(d,p)

C	-1.92194200	-0.74014200	0.00000100
C	-2.08026100	0.82441400	0.00000200
H	-2.29835900	-1.24854100	-0.89245400
H	-2.29835200	-1.24854200	0.89245900
H	-2.58818600	1.21139100	0.88592700
H	-2.58819700	1.21139300	-0.88591600
N	-0.45242300	-0.60001700	-0.00000400
C	0.63180200	-1.39999100	0.00000000
C	1.86061900	-0.77806900	0.00000100
C	1.96302100	0.64488600	0.00000100
C	0.87643800	1.50490000	-0.00000100
H	2.75948700	-1.38143200	0.00000300
H	0.50534200	-2.47758000	0.00000100
H	2.97056200	1.05566800	0.00000300
H	1.06937000	2.57303300	0.00000000
B	-0.46855300	0.83374800	-0.00000300

MP2/6-311+G(d,p)

C	-1.92056700	-0.73948200	0.00043800
C	-2.09010500	0.81878600	-0.00034800
H	-2.28970800	-1.24815500	-0.89576900
H	-2.28881700	-1.24689400	0.89772300
H	-2.59911700	1.19973100	0.88875300
H	-2.59831700	1.19861100	-0.89041500
N	-0.44915700	-0.59856200	-0.00022900
C	0.63389200	-1.40725400	0.00013500
C	1.86592800	-0.77441200	0.00016700
C	1.96803000	0.64696900	0.00006800
C	0.87152700	1.51105300	-0.00014100
H	2.76683000	-1.37972600	0.00036700
H	0.50664500	-2.48736400	0.00027700
H	2.97635000	1.06211400	0.00016600
H	1.07244900	2.58017000	-0.00012400
B	-0.47489100	0.83549700	-0.00025800

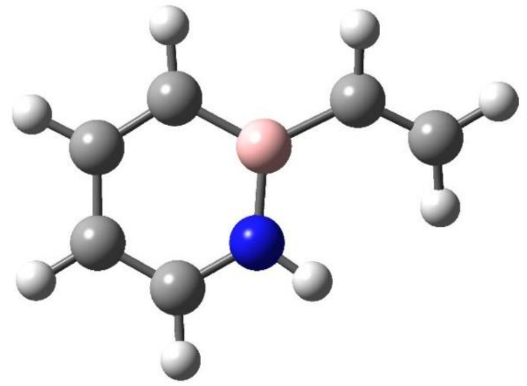
M06-2X/6-311+G(d,p)

C	-1.91463600	-0.73741500	0.00000100
C	-2.07981900	0.81837900	0.00000200
H	-2.28804000	-1.24347100	-0.89279000
H	-2.28803600	-1.24347200	0.89279400
H	-2.58434100	1.20232100	0.88652100
H	-2.58434800	1.20232200	-0.88651300
N	-0.44960500	-0.59861400	-0.00000200
C	0.63362400	-1.39622800	0.00000000
C	1.85734100	-0.77692900	0.00000000
C	1.95461500	0.64648800	0.00000000
C	0.87416300	1.50388400	-0.00000100
H	2.75641700	-1.37821800	0.00000100
H	0.50685900	-2.47347500	0.00000000
H	2.96108100	1.05816600	0.00000100
H	1.06964100	2.57035900	0.00000000
B	-0.47074300	0.82933900	-0.00000200

SCS-MP2/6-311+G(d,p)

C	-1.927951000	-0.738749000	0.000441000
C	-2.092689000	0.825120000	-0.000296000
H	-2.299672000	-1.246557000	-0.896535000
H	-2.298804000	-1.245327000	0.898469000
H	-2.601967000	1.207566000	0.889719000
H	-2.601050000	1.206446000	-0.891343000
N	-0.453500000	-0.596847000	-0.000165000
C	0.634819000	-1.408410000	0.000178000
C	1.865963000	-0.780817000	0.000193000
C	1.971725000	0.648977000	0.000069000
C	0.879727000	1.513408000	-0.000126000
H	2.767521000	-1.386659000	0.000362000
H	0.505271000	-2.488818000	0.000312000
H	2.982449000	1.060618000	0.000149000
H	1.080331000	2.583534000	-0.000125000
B	-0.473286000	0.835321000	-0.000218000

1c



B3LYP/6-311+G(d,p)

C	2.08170200	0.56593400	0.12078800
C	3.04507700	-0.32232100	-0.15609900
H	2.41132600	1.57205600	0.38271100
H	4.10094900	-0.07177500	-0.11268200
H	2.82552300	-1.34469400	-0.45855900
N	0.01399800	-1.02783300	0.09463800
C	-1.31609700	-1.32542900	0.03308600
C	-2.25525200	-0.33614000	-0.05325500
C	-1.85244700	1.02878500	-0.07097000
C	-0.52860300	1.39215700	-0.00807400
H	-3.30279900	-0.60438400	-0.10001500
H	-1.58891400	-2.37408700	0.06174800
H	-2.63318900	1.78339900	-0.13396000
H	-0.28907600	2.45210000	-0.02480500
B	0.53910100	0.31695200	0.07063900
H	0.63641400	-1.82046100	0.17705000

B3LYP-D3/6-311+G(d,p)

C	-2.08044000	0.56741900	-0.12330100
C	-3.03993100	-0.32287300	0.16033500
H	-2.40994200	1.57268300	-0.38855000
H	-4.09727700	-0.07777800	0.11962200
H	-2.81357800	-1.34260000	0.46706800
N	-0.01583300	-1.02856800	-0.09774300
C	1.31443800	-1.32595200	-0.03367700
C	2.25352200	-0.33630700	0.05530800
C	1.85138700	1.02938100	0.07279700
C	0.52753900	1.39279100	0.00738300
H	3.30089200	-0.60494900	0.10408300
H	1.58843100	-2.37435100	-0.06263100
H	2.63261400	1.78334300	0.13766000
H	0.28528500	2.45205300	0.02388100
B	-0.53909200	0.31695800	-0.07340600
H	-0.63922300	-1.81996800	-0.18297300

MP2/6-311+G(d,p)

C	-2.09214200	0.53944800	-0.22326500
C	-3.00566200	-0.31260000	0.29011300
H	-2.47761400	1.44620000	-0.69330500
H	-4.07566500	-0.12902100	0.22617800
H	-2.70690200	-1.21895100	0.81559800
N	-0.02010700	-1.01586300	-0.16763300
C	1.30600000	-1.32885800	-0.05607600
C	2.24754900	-0.33756700	0.09286800
C	1.85131600	1.02843900	0.12295500
C	0.52187900	1.40004600	0.01084200
H	3.29225200	-0.61687600	0.17738200
H	1.57490300	-2.38032000	-0.10189800
H	2.63088100	1.78187300	0.23533900
H	0.29055700	2.46355900	0.04335500
B	-0.54256300	0.32624400	-0.13020900
H	-0.64847900	-1.80009800	-0.30279600

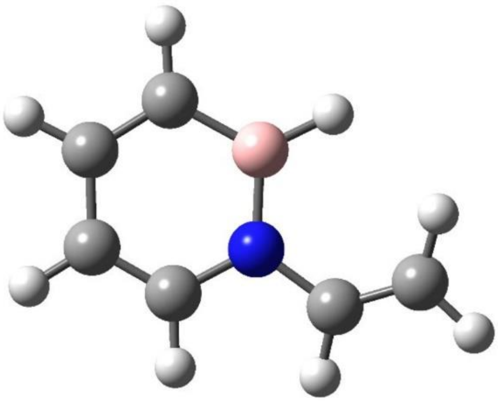
M06-2X/6-311+G(d,p)

C	-2.08378000	0.55707700	-0.17632800
C	-3.00371200	-0.32116900	0.22959700
H	-2.44481200	1.51458300	-0.54959000
H	-4.06847500	-0.11599500	0.18279900
H	-2.72979600	-1.28513200	0.65362800
N	-0.02337200	-1.01647300	-0.13662900
C	1.30158600	-1.32240600	-0.04719700
C	2.24074400	-0.34488000	0.07544600
C	1.84320300	1.02388200	0.10071700
C	0.53011500	1.39736200	0.01083700
H	3.28441400	-0.61955200	0.14381400
H	1.56811400	-2.37185700	-0.08506200
H	2.62705800	1.77130500	0.19248600
H	0.29653000	2.45747100	0.03587600
B	-0.53715000	0.32494800	-0.10476400
H	-0.65260800	-1.79945100	-0.25215300

SCS-MP2/6-311+G(d,p)

C	2.095206000	0.551560000	0.224552000
C	3.024202000	-0.301333000	-0.259523000
H	2.465488000	1.477870000	0.670778000
H	4.091802000	-0.098210000	-0.196420000
H	2.743910000	-1.229389000	-0.758531000
N	0.021994000	-1.019560000	0.190087000
C	-1.311860000	-1.331636000	0.083507000
C	-2.251340000	-0.345487000	-0.080536000
C	-1.852104000	1.028089000	-0.134324000
C	-0.525590000	1.399786000	-0.029999000
H	-3.297747000	-0.623378000	-0.160429000
H	-1.579721000	-2.383353000	0.144662000
H	-2.633398000	1.778914000	-0.259400000
H	-0.291528000	2.463086000	-0.080309000
B	0.542711000	0.321949000	0.131007000
H	0.645687000	-1.804650000	0.337116000

1d



B3LYP/6-311+G(d,p)

C	-1.91263900	-0.47689200	0.06008800
C	-2.93409100	0.36374600	-0.08293700
H	-2.10199900	-1.53517500	0.20942600
H	-3.94269300	-0.02487800	-0.03429000
H	-2.80876600	1.42507500	-0.24378000
N	-0.52494500	-0.15737500	0.03525100
C	0.33701700	-1.23045500	-0.00239100
C	1.69280500	-1.08325900	-0.03505500
C	2.28025000	0.21063500	-0.02890600
C	1.49802400	1.33902700	0.01277100
H	2.31073900	-1.97161200	-0.06504600
H	-0.12180800	-2.21240800	-0.00890000
H	3.36518500	0.27801600	-0.05453400
H	1.98874500	2.30751100	0.02082600
B	-0.00242900	1.19933400	0.05502600
H	-0.77083900	2.10161700	0.11299200

B3LYP-D3/6-311+G(d,p)

C	1.91505400	-0.46669900	-0.11199200
C	2.92334900	0.35968100	0.15343000
H	2.11606700	-1.49688900	-0.38980300
H	3.93916400	-0.00276800	0.06623900
H	2.77699200	1.38893200	0.45031500
N	0.52571900	-0.15545300	-0.06504300
C	-0.33135500	-1.23110700	0.00414800
C	-1.68670500	-1.08615300	0.06381700
C	-2.27797200	0.20660200	0.05253100
C	-1.50046400	1.33662200	-0.02323300
H	-2.30179400	-1.97527500	0.11926700
H	0.12913200	-2.21236100	0.01675100
H	-3.36238100	0.27100000	0.09967300
H	-1.99403200	2.30360200	-0.03727700
B	-0.00022900	1.19968600	-0.09980800
H	0.76652600	2.09982800	-0.20302700

MP2/6-311+G(d,p)

C	1.91841300	-0.42911500	-0.22441100
C	2.88362800	0.33800900	0.29783800
H	2.14907800	-1.34466500	-0.76484400
H	3.92071100	0.06112400	0.14911300
H	2.65873600	1.23770800	0.85803500
N	0.52386500	-0.14004200	-0.12169000
C	-0.30266700	-1.23182100	0.00514800
C	-1.66665400	-1.09936200	0.11381000
C	-2.27292400	0.18485800	0.09557900
C	-1.50606200	1.32976200	-0.03907000
H	-2.26474200	-1.99880300	0.21697400
H	0.18135900	-2.20497100	0.02539900
H	-3.35754300	0.24235800	0.18296300
H	-2.02257700	2.28730800	-0.05890200
B	-0.00390200	1.20900000	-0.17954600
H	0.76502500	2.10125000	-0.35254300

M06-2X/6-311+G(d,p)

C	1.91073700	-0.46029400	-0.13894400
C	2.90168500	0.35747300	0.19032900
H	2.11842500	-1.46808900	-0.48425700
H	3.92273700	0.01688300	0.08692800
H	2.73015100	1.35977800	0.55783500
N	0.52264900	-0.15392700	-0.08013300
C	-0.32709400	-1.22907800	0.00474100
C	-1.67670200	-1.08878600	0.07826400
C	-2.26679000	0.20691300	0.06429300
C	-1.49739400	1.33325700	-0.02860600
H	-2.28998400	-1.97703300	0.14632600
H	0.14077700	-2.20688400	0.01839000
H	-3.35003400	0.27018800	0.12321000
H	-1.99543400	2.29687000	-0.04471500
B	0.00477500	1.19580900	-0.12289400
H	0.77429500	2.08981300	-0.24877400

SCS-MP2/6-311+G(d,p)

C	-1.920057000	-0.456977000	0.226631000
C	-2.900430000	0.305468000	-0.275874000
H	-2.136818000	-1.386507000	0.750270000
H	-3.933569000	0.009087000	-0.128099000
H	-2.695906000	1.221686000	-0.818964000
N	-0.525989000	-0.146118000	0.127224000
C	0.318555000	-1.227597000	-0.037103000
C	1.677650000	-1.077651000	-0.144723000
C	2.273921000	0.219835000	-0.085388000
C	1.497123000	1.348800000	0.087455000
H	2.288108000	-1.965826000	-0.278127000
H	-0.154923000	-2.205494000	-0.086610000
H	3.358597000	0.289689000	-0.173820000
H	2.001565000	2.312893000	0.136853000
B	-0.010615000	1.203972000	0.225541000
H	-0.784655000	2.087646000	0.425275000

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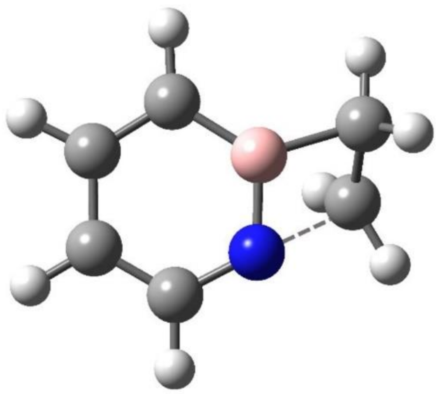

B3LYP/6-311+G(d,p)

C	-1.93082200	-0.53280700	0.67401700
C	-2.21162100	0.51761900	-0.29025800
H	-2.24753600	-1.55238800	0.52458600
H	-1.66323600	-0.26890600	1.69152200
H	-2.50574100	1.47990700	0.12223400
H	-2.78248500	0.21147900	-1.16142400
N	-0.24015800	-0.99328900	-0.41191100
C	1.03779500	-1.33801700	-0.11301900
C	2.03088600	-0.40493800	0.09533800
C	1.73684200	0.98945400	0.13548000
C	0.44910000	1.44609200	-0.00744500
H	3.05425000	-0.73909600	0.23253800
H	1.28118900	-2.39965100	-0.09471000
H	2.56043000	1.67654800	0.31686000
H	0.25655800	2.51090300	0.09515600
B	-0.58907900	0.39396000	-0.36161300

B3LYP-D3/6-311+G(d,p)

C	-1.91734800	-0.53167300	0.68274100
C	-2.21123400	0.51408300	-0.28552300
H	-2.23859300	-1.55202800	0.54558200
H	-1.63430300	-0.26097100	1.69458600
H	-2.50172100	1.47830600	0.12543700
H	-2.79258500	0.20061900	-1.14720600
N	-0.24110000	-0.99568400	-0.42024900
C	1.03700500	-1.33745100	-0.11564200
C	2.02745300	-0.40286100	0.09949900
C	1.73193700	0.99209400	0.13765100
C	0.44477900	1.44685100	-0.01473200
H	3.05013400	-0.73589400	0.24445200
H	1.28157000	-2.39866600	-0.09558800
H	2.55370000	1.67964200	0.32551000
H	0.24743100	2.51076200	0.08716400
B	-0.59069500	0.39235000	-0.37243200

MP2/6-311+G(d,p)

C	-1.77380400	-0.50452100	0.73607800
C	-2.22737000	0.46471300	-0.26871700
H	-2.08352900	-1.54010900	0.70483200
H	-1.43826200	-0.14210200	1.70664300
H	-2.54093700	1.43452500	0.11190400
H	-2.84912700	0.04817800	-1.05551500
N	-0.25684000	-1.02023800	-0.44806600
C	1.03425100	-1.33315400	-0.12090200
C	2.00776800	-0.37579100	0.10944000
C	1.69637300	1.01777200	0.13024600
C	0.39589600	1.44949500	-0.04792800
H	3.03226400	-0.69960700	0.28075700
H	1.30141000	-2.39068400	-0.10014300
H	2.50500800	1.72139900	0.32812200
H	0.18553200	2.51553900	0.03213300
B	-0.62263300	0.37668900	-0.42031300

M06-2X/6-311+G(d,p)

C	-1.79596100	-0.49042600	0.73806400
C	-2.23441100	0.44684100	-0.27910200
H	-2.07746900	-1.53045900	0.70684300
H	-1.47484900	-0.11939300	1.70579900
H	-2.52290400	1.43582000	0.06056000
H	-2.83730900	0.02631200	-1.07459900
N	-0.23283900	-1.02876300	-0.43355400
C	1.06155700	-1.31848000	-0.12339500
C	2.01113300	-0.35892700	0.11446600
C	1.67531500	1.02832700	0.13138700
C	0.38501700	1.43698400	-0.05599300
H	3.03682200	-0.66179900	0.29356700
H	1.34252600	-2.36932100	-0.11114700
H	2.47182800	1.74152700	0.32679100
H	0.15474500	2.49641300	0.01126700
B	-0.61588500	0.34326700	-0.40735300

SCS-MP2/6-311+G(d,p)

C	-1.81732200	-0.47492900	0.68768700
C	-2.22321200	0.51639000	-0.31850600
H	-2.13467100	-1.50723200	0.62676300
H	-1.49547400	-0.13472000	1.67135200
H	-2.52935700	1.48814500	0.06624300
H	-2.83486300	0.12096700	-1.12549000
N	-0.27267500	-1.00930900	-0.50967200
C	1.01619500	-1.35393100	-0.17416000
C	1.99619800	-0.42627100	0.11991600
C	1.70476000	0.97866500	0.19154500
C	0.41987600	1.43669700	-0.00556900
H	3.01158800	-0.77290300	0.30572300
H	1.26612200	-2.41600900	-0.19705000
H	2.51982800	1.65927600	0.44093000
H	0.22286400	2.50364400	0.10444800
B	-0.61348600	0.38839100	-0.43680800

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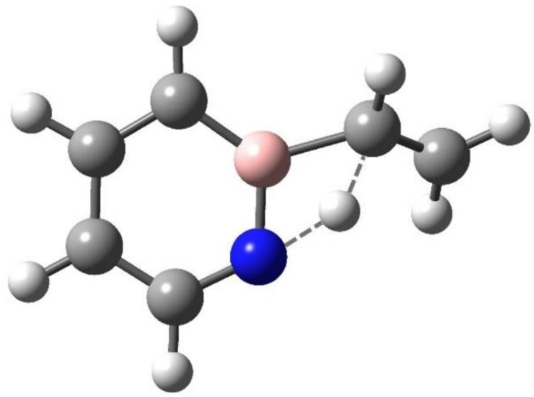	C	-3.02585300	-0.25467900	0.32649500
	C	-2.05759000	0.45569000	-0.29052400
	H	-2.77411500	-1.13352700	0.91198400
	H	-4.07776900	-0.00064900	0.24018900
	H	-1.30962100	-0.55070200	-0.74609800
	H	-2.34446900	1.29073100	-0.92466200
	N	-0.07059400	-1.04831100	-0.09048800
	C	1.23888900	-1.36188400	-0.08852700
	C	2.22537300	-0.40071700	0.06655900
	C	1.89720300	0.97676100	0.13256500
	C	0.59219700	1.42627100	0.03011700
	H	3.26390400	-0.70805500	0.11992000
	H	1.51201900	-2.41077900	-0.19242700
	H	2.71462100	1.68667800	0.23871700
	H	0.39722900	2.49381600	0.04159800
	B	-0.42179100	0.32440200	-0.02318400

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
C	3.02038100	-0.25944700	-0.32080700	C	3.01501700	-0.27422400	-0.31412100
C	2.05514400	0.46445200	0.28545200	C	2.05776300	0.48721200	0.27311900
H	2.76162000	-1.14552000	-0.89250300	H	2.73272300	-1.18075800	-0.84483000
H	4.07349900	-0.00892700	-0.23980700	H	4.07106100	-0.02157300	-0.25816600
H	1.30221000	-0.53819200	0.75864100	H	1.27848400	-0.48493100	0.76817800
H	2.34199400	1.30992600	0.90601700	H	2.34837800	1.35493900	0.86200300
N	0.07546200	-1.04914900	0.08702600	N	0.08887100	-1.05713500	0.08710400
C	-1.23440000	-1.36301000	0.08888200	C	-1.23036300	-1.37025200	0.09435100
C	-2.22306400	-0.40317700	-0.06443400	C	-2.22096600	-0.40614100	-0.06627100
C	-1.89801400	0.97570100	-0.13099300	C	-1.90526200	0.97573400	-0.13603300
C	-0.59332200	1.42641400	-0.03109500	C	-0.59420100	1.43047500	-0.02147000
H	-3.26112400	-0.71263800	-0.11528300	H	-3.25984400	-0.72258700	-0.11693200
H	-1.50615800	-2.41202000	0.19464600	H	-1.50269700	-2.42083700	0.20249500
H	-2.71718200	1.68392300	-0.23470500	H	-2.72762500	1.68306500	-0.24505200
H	-0.39756300	2.49381300	-0.04108600	H	-0.40372900	2.50143000	-0.03262300
B	0.42282300	0.32561600	0.01857300	B	0.42184400	0.32687400	0.01555000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
C	2.98268300	-0.26401300	-0.36058500	C	-3.02958400	-0.26881800	0.31848900
C	2.07114100	0.45826200	0.31053300	C	-2.06916800	0.46796500	-0.29483500
H	2.66919400	-1.13936900	-0.92241900	H	-2.75513000	-1.16181100	0.87685700
H	4.04129400	-0.02408600	-0.35219900	H	-4.08532600	-0.01138300	0.25747500
H	1.32932700	-0.53280600	0.75081800	H	-1.28244100	-0.51604500	-0.75242800
H	2.38301700	1.29414900	0.92763800	H	-2.35584500	1.32244600	-0.90596100
N	0.07760000	-1.04357500	0.12390900	N	-0.08874900	-1.06014700	-0.07254800
C	-1.23025900	-1.35743500	0.08853900	C	1.23738600	-1.37153100	-0.07841800
C	-2.21342000	-0.40201700	-0.08116600	C	2.22414500	-0.40597300	0.06763900
C	-1.88549900	0.97438500	-0.14383900	C	1.90123900	0.98222200	0.12907800
C	-0.58780400	1.42946100	-0.02519700	C	0.59083900	1.43280300	0.01991800
H	-3.24932800	-0.71098900	-0.14945100	H	3.26576600	-0.71653500	0.11460700
H	-1.50198200	-2.40668400	0.18144900	H	1.50958100	-2.42387900	-0.17365400
H	-2.70220700	1.68161200	-0.26601000	H	2.72327600	1.69248200	0.23036800
H	-0.39313700	2.49556900	-0.04372600	H	0.39636400	2.50392400	0.02932300
B	0.41191500	0.32315500	0.05536500	B	-0.42272100	0.31932700	-0.01367600

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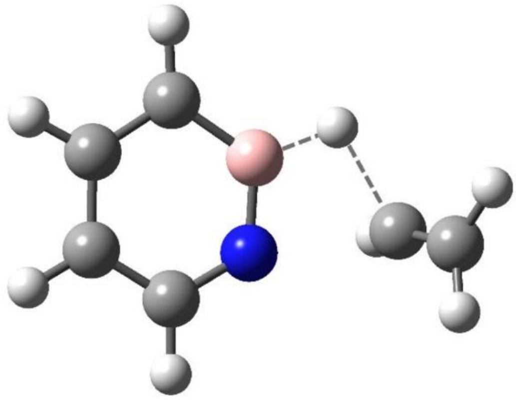


B3LYP/6-311+G(d,p)

C	-2.34666700	0.05946500	0.45178800
C	-3.15673800	-0.01054900	-0.56661200
H	-2.07564700	-0.06485800	1.47338600
H	-1.25622800	1.41523200	0.45825000
H	-3.55767800	0.87717100	-1.04415100
H	-3.34462300	-0.96889700	-1.04380000
N	-0.24611500	-0.56027600	0.30774600
C	0.78963300	-1.37673200	0.08023900
C	2.04353100	-0.84020700	-0.18391700
C	2.22587300	0.56059900	-0.21935700
C	1.19114100	1.46077400	-0.00129900
H	2.88039500	-1.50663300	-0.35907800
H	0.63647600	-2.45332700	0.11199800
H	3.22616900	0.93368400	-0.43099800
H	1.39189000	2.52529200	-0.04728800
B	-0.13171600	0.80883300	0.27248000

B3LYP-D3/6-311+G(d,p)

C	-2.33966000	0.06188100	0.45148800
C	-3.13680900	-0.01069200	-0.57817000
H	-2.09231400	-0.06246600	1.47987000
H	-1.26074800	1.41605200	0.46737400
H	-3.52577400	0.87636200	-1.06640200
H	-3.31465600	-0.97091800	-1.05520700
N	-0.25039200	-0.55966300	0.31897200
C	0.78277000	-1.37713500	0.08458200
C	2.03594200	-0.84172400	-0.18828500
C	2.22018100	0.55925500	-0.22466800
C	1.18808000	1.46146900	0.00071200
H	2.87068200	-1.50916800	-0.36956200
H	0.62802700	-2.45338500	0.11733300
H	3.21953900	0.93069100	-0.44335500
H	1.38935100	2.52580500	-0.04617600
B	-0.13287800	0.80927100	0.28187200

MP2/6-311+G(d,p)

C	-2.16607500	0.10459400	0.43692300
C	-3.00208400	-0.02574300	-0.60435100
H	-2.13093200	0.03822500	1.51026300
H	-1.36293700	1.37908600	0.44278700
H	-3.35973000	0.84189300	-1.14666200
H	-3.11119500	-1.00265700	-1.06562300
N	-0.31262600	-0.50994300	0.36094400
C	0.68003900	-1.38951700	0.10937200
C	1.94397700	-0.88325500	-0.18758600
C	2.18316800	0.51324600	-0.24016500
C	1.18784700	1.47038300	-0.00801500
H	2.75621300	-1.57875200	-0.38140900
H	0.47948800	-2.45869900	0.15640900
H	3.19496100	0.84153700	-0.48008900
H	1.44115500	2.52437800	-0.07501300
B	-0.13597400	0.84926800	0.29513200

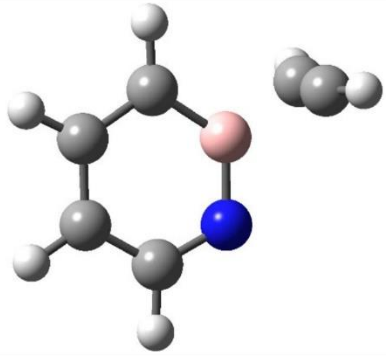
M06-2X/6-311+G(d,p)

C	-2.19685300	0.08870900	0.44446500
C	-3.01445000	-0.01653400	-0.58590300
H	-2.08613400	0.01004300	1.50698200
H	-1.32760800	1.39563700	0.44765800
H	-3.39978300	0.85773300	-1.09242200
H	-3.16628800	-0.99032500	-1.03627800
N	-0.30747200	-0.52393200	0.32572400
C	0.70033800	-1.37465700	0.09584000
C	1.96039300	-0.87228800	-0.17799900
C	2.18214400	0.52365100	-0.22342200
C	1.18524100	1.46180400	-0.00883200
H	2.77869600	-1.55855000	-0.35620800
H	0.51325900	-2.44404400	0.13472500
H	3.19225800	0.86066200	-0.44396000
H	1.42354800	2.51610300	-0.06574500
B	-0.13530500	0.83123000	0.27205700

SCS-MP2/6-311+G(d,p)

C	-2.19441300	0.06622100	0.46534100
C	-3.03548500	-0.03864200	-0.57122800
H	-2.12226300	-0.01673100	1.53445100
H	-1.35601900	1.37066500	0.48519100
H	-3.39937500	0.84384400	-1.08660600
H	-3.15349300	-1.00635400	-1.05123300
N	-0.29774500	-0.53145600	0.36051600
C	0.72267300	-1.37749900	0.08034500
C	1.97232900	-0.84273700	-0.21609100
C	2.18275200	0.56531600	-0.24202400
C	1.16845300	1.49093600	0.01682500
H	2.79827400	-1.51733400	-0.42952700
H	0.54812900	-2.45280300	0.10685000
H	3.18642600	0.91953000	-0.48326800
H	1.39496600	2.55333700	-0.02802700
B	-0.14551300	0.83327800	0.31787300

2a



B3LYP/6-311+G(d,p)

C	-2.32321200	-0.00219000	-0.61638000
C	-2.32327000	-0.00195900	0.61665700
H	-2.61672800	-0.02957300	-1.64473600
H	-2.61644300	-0.02910700	1.64512000
N	-0.02212800	-1.26176400	-0.00008400
C	1.29971000	-1.25378700	-0.00002100
C	2.08154800	-0.07777600	0.00013500
C	1.48730900	1.18662900	0.00002000
C	0.09492500	1.29814000	-0.00020300
H	3.16338900	-0.16834000	0.00040500
H	1.81999700	-2.21418700	0.00019200
H	2.12493700	2.06703700	0.00015000
H	-0.35027600	2.28970800	-0.00035600
B	-0.65440800	0.00449300	-0.00028600

B3LYP-D3/6-311+G(d,p)

C	-2.32312500	-0.00216500	-0.61666800
C	-2.32315400	-0.00199000	0.61670100
H	-2.61593800	-0.02828600	-1.64557800
H	-2.61565600	-0.02795300	1.64569300
N	-0.02028400	-1.26532000	0.00003900
C	1.30163400	-1.25310000	0.00004900
C	2.08160100	-0.07474400	0.00007200
C	1.48542200	1.18912600	-0.00003500
C	0.09267900	1.29714900	-0.00014100
H	3.16362000	-0.16346900	0.00018100
H	1.82439800	-2.21207700	0.00023700
H	2.12144300	2.07068000	-0.00002100
H	-0.35854900	2.28576500	-0.00021200
B	-0.65353400	0.00138500	-0.00008800

MP2/6-311+G(d,p)

C	2.31281200	0.00104500	0.62466600
C	2.31281600	0.00114800	-0.62464000
H	2.58637800	-0.02607600	1.66090900
H	2.58640800	-0.02581300	-1.66088000
N	0.03832100	-1.27702600	-0.00010100
C	-1.29660100	-1.25645600	-0.00010700
C	-2.08052900	-0.07886000	-0.00001800
C	-1.48533600	1.19355300	0.00008600
C	-0.08754000	1.30522400	0.00010300
H	-3.16496500	-0.17127500	-0.00003100
H	-1.81944000	-2.21729700	-0.00018500
H	-2.12733200	2.07411900	0.00015300
H	0.36406600	2.29717300	0.00018400
B	0.65058200	0.00288500	0.00000200

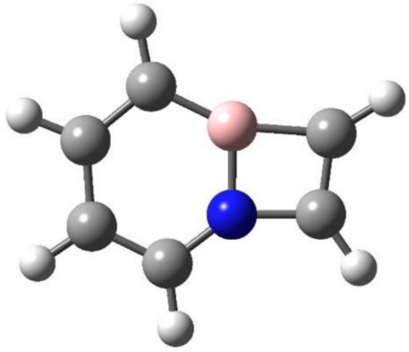
M06-2X/6-311+G(d,p)

C	-2.32931100	-0.00334700	-0.61242700
C	-2.32931700	-0.00324400	0.61240600
H	-2.55493000	-0.02647600	-1.65738400
H	-2.55495000	-0.02627900	1.65736200
N	-0.02681500	-1.25888300	0.00010500
C	1.29503700	-1.25095000	0.00010500
C	2.07622900	-0.08025000	0.00001800
C	1.48376600	1.18244000	-0.00009200
C	0.09365100	1.30014100	-0.00010900
H	3.15676700	-0.17255700	0.00003600
H	1.81118500	-2.21189400	0.00020400
H	2.12300200	2.06089400	-0.00016000
H	-0.35208800	2.29044200	-0.00019100
B	-0.63632200	0.00586100	-0.00000100

SCS-MP2/6-311+G(d,p)

C	2.32434700	0.00048800	0.62320800
C	2.32435300	0.00058800	-0.62318000
H	2.59230300	-0.02658500	1.66120200
H	2.59232600	-0.02632900	-1.66117300
N	0.03457000	-1.27783000	-0.00010200
C	-1.29932800	-1.25793500	-0.00010800
C	-2.08518400	-0.07820600	-0.00001800
C	-1.48962400	1.19403200	0.00008700
C	-0.08904200	1.30607900	0.00010400
H	-3.17028000	-0.17142300	-0.00003200
H	-1.82258300	-2.21928000	-0.00018800
H	-2.13063500	2.07622900	0.00015400
H	0.36091500	2.29957300	0.00018500
B	0.64750200	0.00294200	0.00000300

2b



B3LYP/6-311+G(d,p)

C	1.98546800	-0.61043100	-0.00008600
C	2.16792000	0.71890900	-0.00013000
H	2.60625400	-1.50013500	0.00017400
H	3.08910300	1.27973800	0.00012300
N	0.52141600	-0.60596500	0.00011900
C	-0.54562200	-1.40310800	0.00002100
C	-1.78669800	-0.77911900	-0.00006900
C	-1.87714500	0.63504700	0.00000100
C	-0.78921700	1.51289700	0.00003600
H	-2.68486400	-1.38176100	-0.00016600
H	-0.41885100	-2.48078400	0.00004900
H	-2.88256200	1.05132600	-0.00009900
H	-0.99230700	2.57796600	-0.00000300
B	0.54101600	0.85004700	0.00009000

B3LYP-D3/6-311+G(d,p)

C	1.98565300	-0.61010100	0.00007300
C	2.16775000	0.71956600	-0.00004900
H	2.60597100	-1.50014900	0.00014500
H	3.08934500	1.28010000	-0.00014100
N	0.52180100	-0.60557600	0.00014200
C	-0.54452900	-1.40352800	-0.00004800
C	-1.78624000	-0.78019900	-0.00010400
C	-1.87784400	0.63448900	-0.00008800
C	-0.79029500	1.51347300	0.00002100
H	-2.68379000	-1.38377600	-0.00016700
H	-0.41573200	-2.48080900	-0.00005300
H	-2.88367100	1.04979500	-0.00013700
H	-0.99345300	2.57857800	0.00002800
B	0.54035200	0.85061800	0.00010200

MP2/6-311+G(d,p)

C	1.98755100	-0.61713500	-0.00722900
C	2.17650700	0.72434000	-0.00401700
H	2.59925000	-1.51624400	-0.02088100
H	3.10530400	1.27775500	-0.01749700
N	0.51911300	-0.60147800	0.01888800
C	-0.54551000	-1.40897000	-0.00075600
C	-1.79045000	-0.77813100	-0.00386300
C	-1.88389900	0.63437000	-0.00413400
C	-0.78830300	1.51752400	0.00059100
H	-2.68936200	-1.38449100	-0.01051400
H	-0.41272800	-2.48837600	-0.00537500
H	-2.89110900	1.05298700	-0.00964300
H	-0.99976300	2.58336900	-0.00725400
B	0.54384800	0.85067200	0.01108000

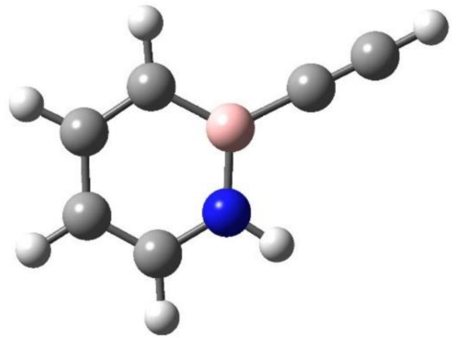
M06-2X/6-311+G(d,p)

C	-1.97733800	-0.60898500	-0.00003600
C	-2.16763900	0.71451900	-0.00004400
H	-2.59304000	-1.50186300	-0.00001100
H	-3.09168700	1.26920200	-0.00003100
N	-0.51716800	-0.60630100	-0.00007300
C	0.55000500	-1.39962600	0.00000800
C	1.78460800	-0.77675000	0.00006300
C	1.86749500	0.63881100	0.00006900
C	0.78549400	1.51240300	0.00002500
H	2.68433500	-1.37511800	0.00010400
H	0.42205900	-2.47668000	0.00001700
H	2.87184300	1.05637000	0.00011700
H	0.98796300	2.57636000	0.00005200
B	-0.54341000	0.84272100	-0.00005100

SCS-MP2/6-311+G(d,p)

C	1.99376600	-0.61869700	-0.00725700
C	2.17973300	0.72355200	-0.00481600
H	2.60747000	-1.51674800	-0.01974800
H	3.10756000	1.28034200	-0.01750200
N	0.52129300	-0.60352300	0.01812500
C	-0.54865400	-1.41047200	-0.00058800
C	-1.79217700	-0.78166700	-0.00416900
C	-1.88524800	0.63824000	-0.00407600
C	-0.79206900	1.52024400	0.00071400
H	-2.69281900	-1.38701700	-0.01067900
H	-0.41661300	-2.49059500	-0.00504000
H	-2.89368900	1.05624200	-0.00968900
H	-1.00245500	2.58729400	-0.00615700
B	0.54435100	0.84899800	0.01027700

2c



B3LYP/6-311+G(d,p)

C	-2.15930800	0.04032900	0.00005700
C	-3.36832800	0.00684700	-0.00008700
H	-4.43162000	-0.01461000	-0.00047600
N	0.10239200	-1.15045300	0.00005900
C	1.46475500	-1.22064400	-0.00003700
C	2.22515200	-0.08476100	-0.00006300
C	1.60090200	1.19375600	-0.00002800
C	0.23351700	1.33449300	0.00004300
H	3.30393900	-0.17188700	-0.00016000
H	1.90748500	-2.20964500	-0.00011400
H	2.24605100	2.06908300	-0.00013300
H	-0.18439800	2.33591000	-0.00005400
B	-0.62921600	0.09127900	0.00024400
H	-0.39225600	-2.03219400	-0.00000600

B3LYP-D3/6-311+G(d,p)

C	2.15845200	0.04020300	-0.00004000
C	3.36741900	0.00679400	-0.00002100
H	4.43086800	-0.01404400	0.00046600
N	-0.10263800	-1.15200100	-0.00002900
C	-1.46546100	-1.22062000	0.00004300
C	-2.22487500	-0.08364100	0.00004100
C	-1.59986900	1.19510100	0.00003000
C	-0.23221000	1.33460100	-0.00000600
H	-3.30372800	-0.17004100	0.00010000
H	-1.91009300	-2.20882400	0.00010000
H	-2.24477500	2.07060400	0.00008900
H	0.18867800	2.33471500	0.00003900
B	0.62890300	0.09010000	-0.00017300
H	0.39226400	-2.03353400	-0.00000200

MP2/6-311+G(d,p)

C	2.16263900	0.04266900	-0.00035300
C	3.39025400	0.00894000	0.00003300
H	4.45633400	-0.01406400	0.00093100
N	-0.09872700	-1.14533900	-0.00009400
C	-1.46244100	-1.22978800	0.00007300
C	-2.23247400	-0.08963000	0.00017900
C	-1.61775900	1.19242200	0.00013100
C	-0.24004200	1.33789100	-0.00003000
H	-3.31258600	-0.18900300	0.00031000
H	-1.89873500	-2.22428500	0.00011600
H	-2.26639700	2.06809200	0.00023000
H	0.16901000	2.34575100	-0.00004700
B	0.62791900	0.09642300	-0.00018400
H	0.40280700	-2.02626600	-0.00016000

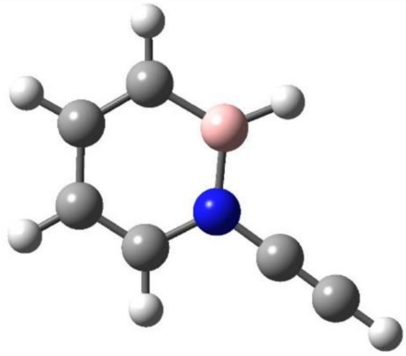
M06-2X/6-311+G(d,p)

C	2.15918800	0.04300100	0.00022100
C	3.36476600	0.00601400	-0.00008400
H	4.42938300	-0.01901800	-0.00017400
N	-0.09866900	-1.14509000	0.00005800
C	-1.45888700	-1.21984400	-0.00003900
C	-2.22186400	-0.09220800	-0.00010800
C	-1.60029500	1.18959700	-0.00008200
C	-0.23954700	1.33703700	0.00001200
H	-3.29929200	-0.18383500	-0.00018600
H	-1.89671500	-2.21051700	-0.00005800
H	-2.24942400	2.06114400	-0.00014300
H	0.17518100	2.33890100	0.00002600
B	0.62187500	0.09408300	0.00010100
H	0.40200800	-2.02304200	0.00010700

SCS-MP2/6-311+G(d,p)

C	2.16914000	0.04182700	-0.000261000
C	3.39441800	0.01069800	0.000113000
H	4.46134100	-0.01027400	0.000791000
N	-0.09671500	-1.14934000	-0.000092000
C	-1.46741000	-1.23074100	0.000069000
C	-2.23559200	-0.09320400	0.000172000
C	-1.61632400	1.19638100	0.000127000
C	-0.24166500	1.34124300	-0.000026000
H	-3.31686900	-0.18982000	0.000293000
H	-1.90367500	-2.22605000	0.000102000
H	-2.26609400	2.07222000	0.000211000
H	0.16892400	2.34957000	-0.000053000
B	0.62801300	0.09252100	-0.000145000
H	0.40231100	-2.03122100	-0.000164000

2d



B3LYP/6-311+G(d,p)

C	1.95564200	0.04095600	-0.00028700
C	3.15603100	0.02316000	-0.00002100
H	4.21795600	0.01213200	0.00306100
N	0.59586400	0.06155500	-0.00004700
C	-0.05989400	-1.16098800	-0.00027200
C	-1.41826500	-1.22984500	0.00002100
C	-2.21315500	-0.04692100	0.00030900
C	-1.63985700	1.19963400	0.00014500
H	-1.88577900	-2.20616500	-0.00003300
H	0.57421200	-2.03763900	-0.00042500
H	-3.29374700	-0.16584700	0.00063200
H	-2.29165400	2.06763000	0.00041500
B	-0.13612100	1.32431700	-0.00038200
H	0.50555900	2.32145000	-0.00078000

B3LYP-D3/6-311+G(d,p)

C	1.95546300	0.04276000	0.00030900
C	3.15574400	0.02164800	0.00035200
H	4.21747200	0.01357700	0.00055900
N	0.59587100	0.06169100	0.00010200
C	-0.05940400	-1.16151800	-0.00000700
C	-1.41806300	-1.23040400	-0.00020100
C	-2.21326600	-0.04710200	-0.00029600
C	-1.64020300	1.19989700	-0.00021100
H	-1.88559700	-2.20671200	-0.00027400
H	0.57436300	-2.03853400	0.00007800
H	-3.29382000	-0.16649400	-0.00043700
H	-2.29195700	2.06793900	-0.00028700
B	-0.13580700	1.32485400	-0.00002300
H	0.50584600	2.32243100	0.00009400

MP2/6-311+G(d,p)

C	1.95514100	0.04570200	0.00024800
C	3.17088100	0.01639100	0.00041300
H	4.23490500	0.00239300	0.00060100
N	0.58698200	0.06833800	0.00008600
C	-0.05324400	-1.15897500	-0.00013400
C	-1.42233300	-1.23399900	-0.00031300
C	-2.22038500	-0.05509000	-0.00028800
C	-1.64370000	1.20195600	-0.00008800
H	-1.88087700	-2.21723700	-0.00047500
H	0.58905300	-2.03379100	-0.00015900
H	-3.30347800	-0.17276100	-0.00043600
H	-2.30583900	2.06495900	-0.00008500
B	-0.13498400	1.33093400	0.00012700
H	0.51412000	2.32748600	0.00028800

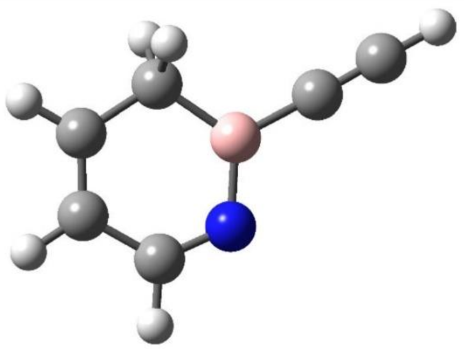
M06-2X/6-311+G(d,p)

C	-1.95157400	0.04615000	-0.00032400
C	-3.14921300	0.02125900	-0.00046600
H	-4.21203400	0.00916600	-0.00032000
N	-0.58978200	0.06535700	-0.00010700
C	0.05752700	-1.15740300	0.00000600
C	1.41000100	-1.23309600	0.00022200
C	2.20677700	-0.04783400	0.00034200
C	1.64240800	1.19560900	0.00024200
H	1.87435200	-2.20980000	0.00030600
H	-0.58346600	-2.02931100	-0.00008700
H	3.28637400	-0.17033900	0.00051800
H	2.29888600	2.05889000	0.00034500
B	0.13539800	1.32349400	-0.00000800
H	-0.50818300	2.31831700	-0.00010800

SCS-MP2/6-311+G(d,p)

C	1.96288600	0.04683200	0.00025100
C	3.17678300	0.01483300	0.00041400
H	4.24166600	-0.00159900	0.00058400
N	0.59048700	0.07148700	0.00008400
C	-0.05444600	-1.16118500	-0.00013100
C	-1.42010800	-1.23750700	-0.00031300
C	-2.22443400	-0.05139600	-0.00029300
C	-1.65036400	1.20314600	-0.00008800
H	-1.88118600	-2.22052100	-0.00047600
H	0.58840000	-2.03628200	-0.00014300
H	-3.30804300	-0.17191800	-0.00044800
H	-2.31242100	2.06751900	-0.00008900
B	-0.13387500	1.33115800	0.00013000
H	0.51089700	2.33173800	0.00030300

2e



B3LYP/6-311+G(d,p)

C	2.14614800	-0.04895800	0.00005900
C	3.35509400	0.00261000	0.00010700
H	0.13233100	1.91788000	0.85824200
H	4.41858100	0.02801600	0.00016700
N	-0.08906800	-1.33057800	0.00009300
C	-1.38167400	-1.28168000	-0.00018600
C	-2.21908600	-0.08279900	0.00023400
C	-1.66136400	1.14155700	0.00005600
C	-0.17861300	1.30110600	-0.00036400
H	-3.29580700	-0.21501000	0.00062900
H	-1.92322500	-2.23464600	-0.00083600
H	-2.29067000	2.02811200	0.00047000
H	0.13226800	1.91891700	-0.85814400
B	0.61739400	-0.06404600	-0.00012400

B3LYP-D3/6-311+G(d,p)

C	2.14466800	-0.05367400	0.00057600
C	3.35329100	0.00435400	-0.00070100
H	0.14155400	1.91217500	0.85936800
H	4.41679800	0.03535900	-0.00047500
N	-0.09317800	-1.33507500	-0.00003400
C	-1.38571200	-1.27949300	-0.00006700
C	-2.21916200	-0.07639800	-0.00001400
C	-1.65692700	1.14596500	-0.00008300
C	-0.17320600	1.29851900	0.00018200
H	-3.29641100	-0.20473600	-0.00013200
H	-1.93157200	-2.22992800	-0.00024900
H	-2.28174600	2.03554500	-0.00034400
H	0.14196400	1.91308900	-0.85816400
B	0.61679000	-0.07032100	0.00017600

MP2/6-311+G(d,p)

C	2.14370200	-0.04633000	-0.00031500
C	3.37053600	0.00736200	0.00013300
H	0.14153800	1.90633800	0.86403800
H	4.43680500	0.03475400	0.00033000
N	-0.08405600	-1.34745700	-0.00024100
C	-1.38566700	-1.28443700	0.00003100
C	-2.22320100	-0.08083400	0.00028400
C	-1.66563900	1.15275200	0.00008400
C	-0.18136000	1.30254200	0.00000800
H	-3.30206100	-0.21213600	0.00042600
H	-1.93152800	-2.23615800	-0.00003000
H	-2.29976500	2.03844500	0.00007100
H	0.14156500	1.90735700	-0.86325800
B	0.61032100	-0.06254600	-0.00025000

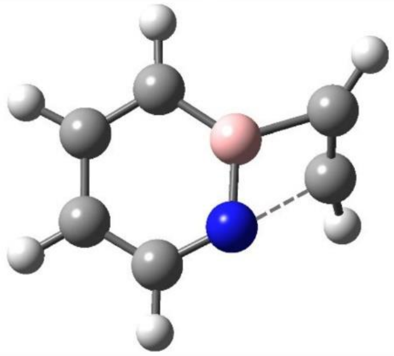
M06-2X/6-311+G(d,p)

C	2.14403400	-0.05143200	-0.00006500
C	3.34928000	0.00453000	-0.00009500
H	0.14493000	1.90460300	0.85997300
H	4.41397400	0.03608600	-0.00013300
N	-0.09520100	-1.33677200	-0.00006600
C	-1.38037200	-1.27928200	-0.00003700
C	-2.21568200	-0.07246200	0.00000100
C	-1.65495200	1.14422700	0.00004600
C	-0.17266700	1.29667200	0.00014700
H	-3.29161500	-0.20215500	-0.00003500
H	-1.92778600	-2.22766200	-0.00007400
H	-2.28025700	2.03277900	0.00003600
H	0.14509500	1.90518100	-0.85918700
B	0.60884300	-0.06898900	-0.00002000

SCS-MP2/6-311+G(d,p)

C	2.15029200	-0.04738200	-0.00034900
C	3.37489000	0.00381300	0.00011400
H	0.14029500	1.91232400	0.86647500
H	4.44198400	0.02911300	0.00034500
N	-0.08485700	-1.34986800	-0.00020900
C	-1.38385100	-1.28909300	0.00003200
C	-2.22631200	-0.07916400	0.00019800
C	-1.67100500	1.15398100	0.00009800
C	-0.18020000	1.30917300	0.00004400
H	-3.30579100	-0.21350500	0.00031900
H	-1.92990300	-2.24132700	0.00008200
H	-2.30626800	2.03978400	0.00014600
H	0.14030400	1.91331500	-0.86565700
B	0.61161100	-0.06151000	-0.00032800

TS_{2a-2b}



B3LYP/6-311+G(d,p)

C	-2.05224600	-0.49675400	0.57042700
C	-2.29445400	0.44403600	-0.24016300
H	-2.10895600	-1.18851700	1.38592800
H	-3.05975600	1.14981600	-0.51172500
N	-0.27741400	-1.03413900	-0.39694900
C	1.01079800	-1.32589700	-0.09332100
C	1.97378900	-0.35558600	0.10307700
C	1.63517200	1.02744300	0.12933000
C	0.32899300	1.43792700	0.01110700
H	3.00882600	-0.65430200	0.23419300
H	1.29313400	-2.37762400	-0.07471400
H	2.43610800	1.74486300	0.29233300
H	0.10004200	2.49537200	0.10802600
B	-0.66796100	0.33646900	-0.30762800

B3LYP-D3/6-311+G(d,p)

C	-2.04790200	-0.49714000	0.57365600
C	-2.29397600	0.44337400	-0.23704700
H	-2.10080400	-1.18687600	1.39168000
H	-3.06099800	1.14963000	-0.50364000
N	-0.27755900	-1.03580200	-0.40165500
C	1.01052000	-1.32588800	-0.09415800
C	1.97239000	-0.35480800	0.10623400
C	1.63367400	1.02888500	0.13063000
C	0.32785300	1.43878200	0.00707700
H	3.00693100	-0.65326900	0.24192400
H	1.29329700	-2.37737800	-0.07431200
H	2.43409500	1.74620400	0.29662700
H	0.09578700	2.49553600	0.10312200
B	-0.66815000	0.33550700	-0.31243600

MP2/6-311+G(d,p)

C	-1.97897800	-0.50452200	0.57714200
C	-2.30649600	0.43533800	-0.22744500
H	-1.99981600	-1.17295600	1.42012400
H	-3.08348800	1.13892400	-0.47337200
N	-0.29242800	-1.04317000	-0.41302300
C	0.99858100	-1.33027600	-0.08665400
C	1.96497600	-0.34869100	0.10082000
C	1.63140900	1.03607800	0.11677400
C	0.31186100	1.44498500	0.01416600
H	3.00109900	-0.65264100	0.23499000
H	1.28430300	-2.38261300	-0.05424200
H	2.43389900	1.75622000	0.27559300
H	0.08385200	2.50485400	0.11471600
B	-0.68019500	0.34258600	-0.31909400

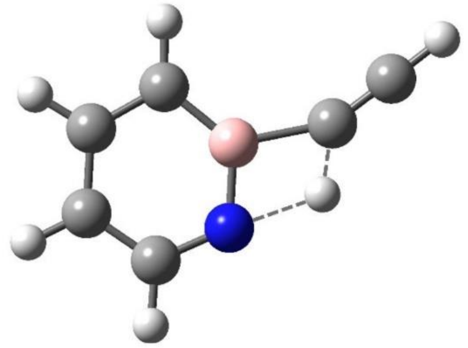
M06-2X/6-311+G(d,p)

C	-2.01307300	-0.48322700	0.58663100
C	-2.31244800	0.41655400	-0.23839000
H	-2.02307400	-1.16336500	1.41464100
H	-3.06147900	1.11296100	-0.56518000
N	-0.26817400	-1.05033000	-0.39308900
C	1.02873400	-1.31428100	-0.09740700
C	1.97087700	-0.33189500	0.10315500
C	1.61024800	1.04492700	0.12429800
C	0.30144400	1.43132400	0.00409800
H	3.00795600	-0.61437700	0.24557300
H	1.32962400	-2.35963400	-0.08164200
H	2.39863300	1.77529500	0.28566100
H	0.05315100	2.48431400	0.09110300
B	-0.66845700	0.30734000	-0.30656900

SCS-MP2/6-311+G(d,p)

C	-1.99634100	-0.48781300	0.60356900
C	-2.31053200	0.43705000	-0.22044400
H	-2.01434400	-1.15014700	1.45128400
H	-3.08447400	1.13534900	-0.49258800
N	-0.29240200	-1.05181600	-0.41711600
C	1.01108400	-1.33369400	-0.10135200
C	1.97026000	-0.35397200	0.10005600
C	1.63064000	1.03848200	0.12242700
C	0.31454400	1.44151600	0.00827900
H	3.00762700	-0.65351700	0.24118100
H	1.30007800	-2.38594300	-0.08327800
H	2.43251900	1.75872100	0.28921000
H	0.07987600	2.50202600	0.09822400
B	-0.67995700	0.32787400	-0.31895600

TS_{2a-2c}



B3LYP/6-311+G(d,p)

C	3.32207100	0.12879500	0.00047900
C	2.14058600	-0.19422900	0.00028800
H	4.34915600	0.41709800	0.00063400
H	1.57090900	-1.23863600	0.00017000
N	-0.08631400	-1.19165000	-0.00009300
C	-1.42270200	-1.25655200	-0.00028000
C	-2.21564900	-0.11058400	-0.00031800
C	-1.63604300	1.17560600	-0.00015300
C	-0.25770900	1.37637800	0.00005200
H	-3.29498800	-0.21316500	-0.00047400
H	-1.89051200	-2.24001700	-0.00040500
H	-2.30494600	2.03375300	-0.00018700
H	0.13659300	2.38569500	0.00018000
B	0.49093300	0.09606600	0.00006600

B3LYP-D3/6-311+G(d,p)

C	-3.31866300	0.13088000	-0.00047500
C	-2.14071600	-0.20325900	-0.00028800
H	-4.34243600	0.43085900	-0.00063700
H	-1.55900000	-1.24278100	-0.00014100
N	0.08947800	-1.19505600	0.00008800
C	1.42631100	-1.25460900	0.00028000
C	2.21497000	-0.10512800	0.00031800
C	1.63083800	1.17965400	0.00015500
C	0.25158700	1.37552300	-0.00005200
H	3.29466600	-0.20386500	0.00047700
H	1.89784900	-2.23617700	0.00040900
H	2.29690700	2.03997400	0.00019400
H	-0.14868600	2.38240200	-0.00017200
B	-0.49032200	0.09132200	-0.00007500

MP2/6-311+G(d,p)

C	-3.32558900	0.13326800	0.00769300
C	-2.16802800	-0.27285100	0.00558500
H	-4.32460400	0.51272100	-0.00708100
H	-1.40277400	-1.21024200	0.11554000
N	0.13717800	-1.23293800	-0.02720600
C	1.48782400	-1.23167500	0.00922700
C	2.21894900	-0.04292500	0.00740700
C	1.58009500	1.22039600	0.00025300
C	0.18746800	1.35960500	0.00202500
H	3.30442000	-0.09314000	0.01667000
H	2.00156300	-2.19310900	0.02884800
H	2.21031100	2.11017200	0.00312700
H	-0.25963700	2.34862200	0.01153600
B	-0.47476800	0.03212500	-0.03426800

M06-2X/6-311+G(d,p)

C	-3.30607500	0.14275500	-0.00047700
C	-2.16795500	-0.27591600	-0.00028900
H	-4.30061800	0.53077000	-0.00064000
H	-1.43805400	-1.24337500	-0.00012300
N	0.12402200	-1.21128200	0.00009100
C	1.46279700	-1.23027900	0.00028300
C	2.21223200	-0.06282300	0.00031700
C	1.58730100	1.20226600	0.00015100
C	0.20881700	1.36196500	-0.00005400
H	3.29319200	-0.12674700	0.00047400
H	1.96034200	-2.19737300	0.00041400
H	2.22780000	2.08087700	0.00018800
H	-0.22372700	2.35367700	-0.00017400
B	-0.47395700	0.05066800	-0.00007100

SCS-MP2/6-311+G(d,p)

C	-3.34091900	0.16297600	-0.00668400
C	-2.18690900	-0.24976600	0.00291000
H	-4.33900300	0.54711500	-0.01767800
H	-1.43077700	-1.21096200	0.06711000
N	0.09627500	-1.23414000	-0.02900200
C	1.45025600	-1.27328500	-0.00585900
C	2.21351300	-0.10679400	-0.00363200
C	1.60620700	1.17818800	-0.00208200
C	0.21932500	1.35726100	0.00143700
H	3.29813400	-0.18523900	0.00123600
H	1.93511600	-2.25029400	0.00458000
H	2.26276900	2.04976900	0.00348000
H	-0.19918200	2.35966400	0.01331000
B	-0.48202000	0.04524700	-0.02904700

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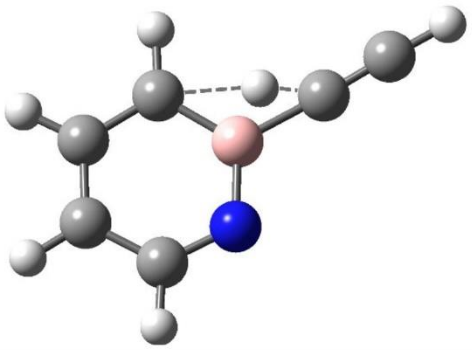


B3LYP/6-311+G(d,p)

C	-1.62921700	0.61732100	0.59028500
C	-2.73029400	1.11121000	0.74431300
H	-3.70360400	1.50427700	0.91620300
H	-0.62411900	1.07505000	-0.41616200
N	-0.03076900	-1.12509100	-0.50093500
C	1.18819200	-1.56612000	-0.66108600
C	2.35467700	-0.92601200	-0.14511100
C	2.27386400	0.25538000	0.57884200
C	1.01670600	0.81096700	0.84515100
H	3.32391200	-1.36649000	-0.35822600
H	1.33531000	-2.47604800	-1.24831900
H	3.18608200	0.72948100	0.92957200
H	0.96387200	1.75382700	1.38258600
B	-0.18682300	0.07102100	0.30113200

B3LYP-D3/6-311+G(d,p)

C	-1.62753000	0.61790900	0.58699400
C	-2.72705800	1.11460400	0.74481100
H	-3.69872500	1.51125500	0.91850700
H	-0.62911300	1.07475500	-0.41231500
N	-0.03093700	-1.12979600	-0.50251700
C	1.18959600	-1.56793600	-0.66137200
C	2.35539600	-0.92511500	-0.14551000
C	2.27275900	0.25615500	0.57907400
C	1.01436900	0.80924600	0.84518300
H	3.32537500	-1.36361500	-0.35931000
H	1.33884300	-2.47782500	-1.24803400
H	3.18419900	0.73182500	0.92973400
H	0.95699600	1.75149800	1.38302600
B	-0.18638100	0.06581300	0.29997500

MP2/6-311+G(d,p)

C	-1.62352600	0.60067700	0.56905200
C	-2.71597500	1.17286100	0.65967300
H	-3.67514000	1.62976300	0.76655100
H	-0.53052900	1.12131800	-0.12129700
N	-0.05139700	-1.22991200	-0.43704100
C	1.20154500	-1.60215700	-0.64661900
C	2.36202400	-0.89515300	-0.20944400
C	2.25240100	0.28260800	0.52633800
C	0.97207600	0.75858600	0.87980300
H	3.34245000	-1.27874200	-0.48419800
H	1.36335700	-2.51518600	-1.22823300
H	3.15532900	0.80868000	0.83280400
H	0.88566000	1.68335100	1.45107300
B	-0.20048500	-0.06792100	0.39978400

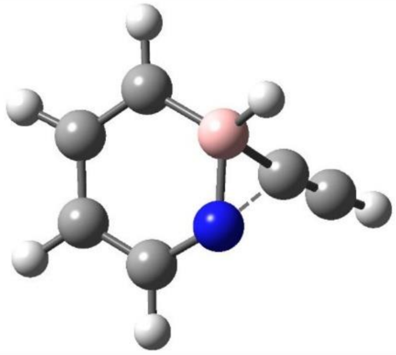
M06-2X/6-311+G(d,p)

C	-1.62225000	0.61461300	0.56932700
C	-2.70583900	1.14807000	0.68520700
H	-3.66776200	1.58921900	0.81055100
H	-0.59931200	1.11994800	-0.19377800
N	-0.03066500	-1.19409200	-0.45677000
C	1.19609100	-1.58938700	-0.64892600
C	2.35860300	-0.90274600	-0.18244300
C	2.25599000	0.26606100	0.54079800
C	0.98130100	0.77151600	0.86062500
H	3.33319300	-1.30544500	-0.43540300
H	1.35492100	-2.49675100	-1.23492200
H	3.15780400	0.77894200	0.86028800
H	0.90570000	1.70176800	1.41551300
B	-0.17998500	-0.03294200	0.36817800

SCS-MP2/6-311+G(d,p)

C	-1.62774600	0.61280500	0.57615100
C	-2.72899200	1.15959100	0.68215100
H	-3.69695600	1.59417600	0.80675700
H	-0.56982500	1.12004600	-0.18932500
N	-0.04908200	-1.21622400	-0.44263500
C	1.19559700	-1.60651500	-0.63465100
C	2.36824000	-0.90851400	-0.18626000
C	2.26895800	0.28042900	0.52663600
C	0.98508900	0.78141600	0.85749700
H	3.34551200	-1.31315100	-0.44511800
H	1.35501100	-2.52592400	-1.20831200
H	3.17557300	0.80185400	0.83242500
H	0.90727700	1.72181500	1.40494200
B	-0.19086500	-0.03303000	0.37798700

TS_{2e-2d}



B3LYP/6-311+G(d,p)

C	-1.59899600	0.22022200	0.10202400
C	-2.53260300	-0.02654500	0.83836100
H	-0.91614900	1.33341000	-1.79643400
H	-3.36245100	-0.20195500	1.47999100
N	-0.40709300	-0.73195300	-0.91753000
C	0.53149600	-1.40279500	-0.20907900
C	1.59509500	-0.77888100	0.41587100
C	1.71864000	0.63642200	0.49462400
C	0.76760300	1.43375500	-0.08237600
H	2.35434800	-1.40019000	0.88261500
H	0.44836800	-2.48752900	-0.17822500
H	2.57372300	1.04840100	1.02334700
H	0.86492400	2.51186900	0.02319200
B	-0.40010500	0.76531800	-0.87366500

B3LYP-D3/6-311+G(d,p)

C	1.59333500	0.22005400	-0.10059100
C	2.51736700	-0.02594200	-0.84913500
H	0.91573900	1.33653000	1.80378100
H	3.33969100	-0.20175800	-1.50034800
N	0.40830400	-0.73162600	0.92507300
C	-0.52818100	-1.40315800	0.21337200
C	-1.58799900	-0.78001400	-0.41913400
C	-1.71171300	0.63557400	-0.49963500
C	-0.76595200	1.43420800	0.08465800
H	-2.34317300	-1.40186800	-0.89167100
H	-0.44292700	-2.48757200	0.18283200
H	-2.56276700	1.04660000	-1.03558400
H	-0.86204100	2.51217300	-0.02231800
B	0.39924100	0.76658800	0.88211700

MP2/6-311+G(d,p)

C	1.52252400	0.16725200	-0.11920000
C	2.43937000	-0.02780200	-0.91605300
H	1.02452400	0.95752100	2.02542600
H	3.22743900	-0.15968200	-1.62284700
N	0.30044300	-0.93269800	0.90533100
C	-0.68437400	-1.39008400	0.12088600
C	-1.63624100	-0.57964000	-0.51961000
C	-1.54188500	0.82450400	-0.50110200
C	-0.54661200	1.43404700	0.25732900
H	-2.42506900	-1.06106400	-1.09571300
H	-0.75352300	-2.47227500	-0.00941600
H	-2.26242100	1.40703600	-1.07255000
H	-0.46957000	2.52155800	0.21497800
B	0.44776500	0.55322700	1.05786100

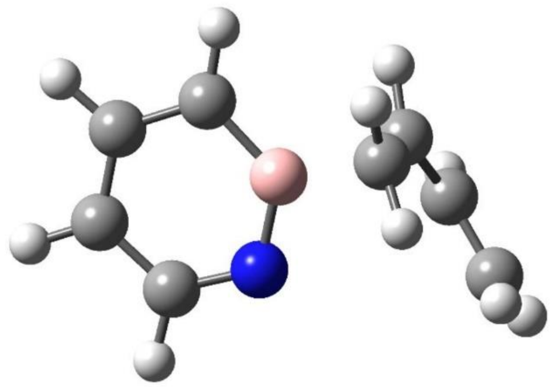
M06-2X/6-311+G(d,p)

C	1.58005000	0.21033300	-0.10312200
C	2.47661500	-0.02698400	-0.87823700
H	0.95485400	1.18135400	1.89930300
H	3.27797600	-0.20275400	-1.55683200
N	0.35275300	-0.81244400	0.92775600
C	-0.59269900	-1.40349200	0.18029600
C	-1.59514300	-0.70085400	-0.46757400
C	-1.64266700	0.71422900	-0.50450600
C	-0.68113400	1.43378300	0.15006400
H	-2.35920200	-1.26674100	-0.99262500
H	-0.57096100	-2.48860800	0.11400600
H	-2.44280100	1.19016500	-1.06234500
H	-0.70845500	2.51786800	0.07157100
B	0.42183800	0.67874700	0.95422000

SCS-MP2/6-311+G(d,p)

C	1.54948300	0.25814700	-0.11500900
C	2.45814400	0.03694200	-0.91165800
H	0.90880000	1.30317100	1.87645300
H	3.25921500	-0.12121100	-1.59941600
N	0.38103200	-0.76702200	1.00243400
C	-0.54540400	-1.41805300	0.27416900
C	-1.58176800	-0.78499200	-0.42217900
C	-1.65901400	0.62562600	-0.54505400
C	-0.72495600	1.41753700	0.10241700
H	-2.32360800	-1.40725500	-0.92269700
H	-0.49255800	-2.50865100	0.26034400
H	-2.46308200	1.05271800	-1.14321700
H	-0.78562200	2.49791200	-0.04102800
B	0.38826200	0.73492000	0.95785900

3a(cis)



B3LYP/6-311+G(d,p)

N	-0.364700000	0.993807000	-0.445349000
C	-1.575658000	1.487479000	-0.255799000
C	-2.682011000	0.719177000	0.164857000
C	-2.555987000	-0.654142000	0.399106000
C	-1.327789000	-1.286338000	0.206320000
H	-3.635463000	1.212654000	0.324150000
H	-1.724473000	2.558125000	-0.413544000
H	-3.428140000	-1.211081000	0.732469000
H	-1.264425000	-2.357966000	0.382741000
B	-0.218668000	-0.397206000	-0.264037000
C	3.159736000	0.959631000	0.129560000
C	2.353487000	0.156978000	0.832104000
H	3.271972000	0.870264000	-0.944561000
H	3.734019000	1.737731000	0.617694000
H	2.290617000	0.278549000	1.909257000
C	1.552482000	-0.930845000	0.273442000
C	1.183101000	-1.094394000	-1.064626000
H	1.338109000	-1.746968000	0.955745000
H	0.908446000	-2.076802000	-1.427004000
H	1.511411000	-0.380397000	-1.809096000

B3LYP-D3/6-311+G(d,p)

N	0.344853000	0.987264000	0.449422000
C	1.552289000	1.487895000	0.257010000
C	2.662814000	0.726271000	-0.168708000
C	2.545778000	-0.648257000	-0.402077000
C	1.322619000	-1.288596000	-0.201971000
H	3.611172000	1.227183000	-0.335022000
H	1.694802000	2.559682000	0.412491000
H	3.420051000	-1.198830000	-0.740429000
H	1.260667000	-2.360771000	-0.374227000
B	0.211588000	-0.405418000	0.273389000
C	-3.076898000	1.012820000	-0.128814000
C	-2.350975000	0.140641000	-0.836793000
H	-3.129833000	0.977699000	0.952741000
H	-3.636904000	1.799417000	-0.619831000
H	-2.335273000	0.217426000	-1.919663000
C	-1.564094000	-0.953765000	-0.275084000
C	-1.187632000	-1.115156000	1.062438000
H	-1.347489000	-1.769998000	-0.956582000
H	-0.909538000	-2.098183000	1.420754000
H	-1.522972000	-0.408497000	1.810850000

MP2/6-311+G(d,p)

N	0.319498000	1.008135000	0.430965000
C	1.547252000	1.493044000	0.264980000
C	2.667856000	0.721667000	-0.134260000
C	2.555532000	-0.656558000	-0.378459000
C	1.315283000	-1.287689000	-0.215511000
H	3.627124000	1.219807000	-0.263034000
H	1.700234000	2.563206000	0.434116000
H	3.440464000	-1.210070000	-0.691315000
H	1.247088000	-2.361224000	-0.399331000
B	0.189052000	-0.394822000	0.220921000
C	-3.193522000	0.882711000	-0.116468000
C	-2.277870000	0.204768000	-0.833647000
H	-3.393256000	0.643772000	0.923478000
H	-3.757417000	1.694671000	-0.564004000
H	-2.117186000	0.456695000	-1.879898000
C	-1.481457000	-0.909753000	-0.301318000
C	-1.170964000	-1.097660000	1.061568000
H	-1.300489000	-1.742834000	-0.978606000
H	-0.901175000	-2.084188000	1.423612000
H	-1.499795000	-0.365857000	1.792309000

M06-2X/6-311+G(d,p)

N	0.347963000	0.991680000	0.435394000
C	1.562826000	1.480716000	0.270750000
C	2.673459000	0.714443000	-0.130673000
C	2.552018000	-0.653686000	-0.377343000
C	1.319928000	-1.284849000	-0.220628000
H	3.631541000	1.206268000	-0.257217000
H	1.711842000	2.547270000	0.445178000
H	3.431534000	-1.208620000	-0.691684000
H	1.252563000	-2.352978000	-0.411932000
B	0.212754000	-0.389762000	0.216588000
C	-3.205953000	0.879383000	-0.119099000
C	-2.280983000	0.230051000	-0.821084000
H	-3.442513000	0.605906000	0.902849000
H	-3.757273000	1.704606000	-0.551897000
H	-2.079869000	0.509224000	-1.849714000
C	-1.508096000	-0.904741000	-0.294874000
C	-1.203564000	-1.102713000	1.042305000
H	-1.307309000	-1.711902000	-0.991982000

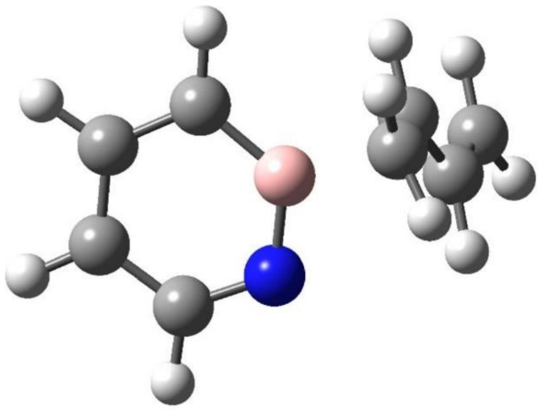
SCS-MP2/6-311+G(d,p)

N	0.338555000	1.012546000	0.437503000
C	1.566296000	1.494246000	0.265440000
C	2.685038000	0.718380000	-0.138663000
C	2.566474000	-0.659466000	-0.382999000
C	1.321999000	-1.287825000	-0.217177000
H	3.646393000	1.213702000	-0.268766000
H	1.723346000	2.564349000	0.435142000
H	3.448374000	-1.217733000	-0.698660000
H	1.250942000	-2.361305000	-0.404238000
B	0.201847000	-0.389646000	0.223120000
C	-3.227800000	0.871002000	-0.125298000
C	-2.285873000	0.215961000	-0.828896000
H	-3.450027000	0.619374000	0.908125000
H	-3.794533000	1.680341000	-0.576675000
H	-2.102698000	0.481813000	-1.868662000
C	-1.486500000	-0.903579000	-0.291975000
C	-1.175891000	-1.094050000	1.068076000
H	-1.310441000	-1.736479000	-0.971532000

H	-0.899483000	-2.077156000	1.399551000
H	-1.498360000	-0.367186000	1.780018000

H	-0.902726000	-2.081023000	1.428570000
H	-1.496522000	-0.362789000	1.803663000

3a(trans)



B3LYP/6-311+G(d,p)

N	-0.541752000	-0.830940000	0.849135000
C	-1.725198000	-1.324916000	0.527962000
C	-2.653320000	-0.667162000	-0.306357000
C	-2.365213000	0.587254000	-0.854469000
C	-1.150761000	1.212559000	-0.571939000
H	-3.595888000	-1.155462000	-0.532065000
H	-1.994636000	-2.308003000	0.920357000
H	-3.101543000	1.057610000	-1.501452000
H	-0.956820000	2.189791000	-1.008337000
B	-0.244807000	0.454844000	0.345848000
C	3.132744000	-0.875532000	-1.041684000
C	2.366025000	-0.524859000	-0.001576000
H	3.222173000	-0.246372000	-1.921580000
H	3.694646000	-1.801480000	-1.040714000
H	2.274209000	-1.175866000	0.860900000
C	1.644691000	0.737517000	0.051068000
C	1.047885000	1.274916000	1.197754000
H	1.701232000	1.358702000	-0.837460000
H	0.821266000	2.332681000	1.233687000
H	1.170536000	0.772110000	2.148925000

B3LYP-D3/6-311+G(d,p)

N	-0.537196000	-0.817533000	0.869467000
C	-1.718158000	-1.316786000	0.547251000
C	-2.642835000	-0.671454000	-0.302060000
C	-2.354760000	0.576704000	-0.865072000
C	-1.143236000	1.207968000	-0.582230000
H	-3.582402000	-1.165518000	-0.527784000
H	-1.988454000	-2.295273000	0.950229000
H	-3.087853000	1.036231000	-1.523400000
H	-0.943145000	2.179218000	-1.028631000
B	-0.243023000	0.462789000	0.350410000
C	3.102549000	-0.905292000	-1.040053000
C	2.351080000	-0.527096000	0.001410000
H	3.193325000	-0.290069000	-1.929795000
H	3.649089000	-1.840391000	-1.030883000
H	2.251239000	-1.163470000	0.873895000
C	1.645909000	0.744433000	0.039926000
C	1.055172000	1.297170000	1.182683000
H	1.698609000	1.352929000	-0.857938000
H	0.827475000	2.355159000	1.205369000
H	1.183275000	0.806083000	2.139483000

MP2/6-311+G(d,p)

N	-0.492022000	-0.833719000	0.868577000
C	-1.685170000	-1.325412000	0.544486000
C	-2.618904000	-0.673261000	-0.299699000
C	-2.342179000	0.582895000	-0.862711000
C	-1.122872000	1.213263000	-0.580893000
H	-3.563176000	-1.169399000	-0.516408000
H	-1.959973000	-2.304901000	0.946963000
H	-3.085507000	1.043956000	-1.512521000
H	-0.924087000	2.190264000	-1.024155000
B	-0.203510000	0.456209000	0.332547000
C	3.069673000	-0.884463000	-1.057705000
C	2.309886000	-0.530490000	-0.001812000
H	3.140495000	-0.249924000	-1.937576000
H	3.630970000	-1.812917000	-1.058379000
H	2.224324000	-1.176151000	0.868328000
C	1.582478000	0.737304000	0.036804000
C	1.034334000	1.299785000	1.211507000
H	1.656000000	1.369291000	-0.847506000
H	0.808932000	2.360517000	1.240506000
H	1.170249000	0.786524000	2.158117000

M06-2X/6-311+G(d,p)

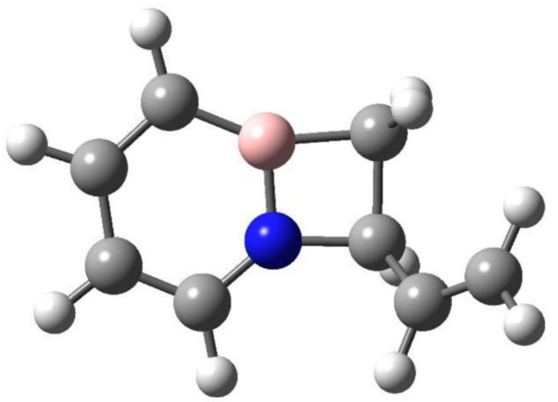
N	-0.507218000	-0.829940000	0.838253000
C	-1.693405000	-1.321468000	0.531916000
C	-2.630174000	-0.665810000	-0.289125000
C	-2.352387000	0.585816000	-0.839850000
C	-1.135883000	1.212506000	-0.576361000
H	-3.576026000	-1.153162000	-0.497545000
H	-1.959228000	-2.300709000	0.932335000
H	-3.099423000	1.055327000	-1.473786000
H	-0.944794000	2.188829000	-1.014224000
B	-0.223649000	0.443126000	0.311875000
C	3.080453000	-0.878650000	-1.042403000
C	2.320495000	-0.534497000	-0.003753000
H	3.177018000	-0.233671000	-1.909590000
H	3.625473000	-1.813843000	-1.055363000

SCS-MP2/6-311+G(d,p)

N	-0.500323000	-0.843429000	0.855811000
C	-1.694438000	-1.330139000	0.529321000
C	-2.628647000	-0.669215000	-0.311177000
C	-2.347457000	0.589616000	-0.866621000
C	-1.123175000	1.215321000	-0.582517000
H	-3.575668000	-1.161090000	-0.529242000
H	-1.971874000	-2.311555000	0.926979000
H	-3.090020000	1.058844000	-1.512766000
H	-0.923122000	2.194823000	-1.021413000
B	-0.206842000	0.447867000	0.324989000
C	3.099809000	-0.879861000	-1.047819000
C	2.332174000	-0.534659000	0.004970000
H	3.176085000	-0.241374000	-1.925577000
H	3.664409000	-1.807564000	-1.050459000

H	2.204326000	-1.187793000	0.853854000	H	2.243765000	-1.185248000	0.871742000
C	1.613305000	0.745431000	0.048653000	C	1.596647000	0.736024000	0.047166000
C	1.066709000	1.287009000	1.203169000	C	1.042620000	1.291357000	1.219687000
H	1.672705000	1.366232000	-0.839929000	H	1.673122000	1.372037000	-0.834170000
H	0.796131000	2.333254000	1.240791000	H	0.810916000	2.351320000	1.252734000
H	1.157918000	0.757467000	2.142819000	H	1.167488000	0.774316000	2.166367000

3b(cis)



B3LYP/6-311+G(d,p)

N	0.157498000	-0.311587000	0.314945000
C	0.968502000	-1.387627000	0.262823000
C	2.278094000	-1.160338000	-0.096058000
C	2.742225000	0.156990000	-0.384170000
C	1.948631000	1.290817000	-0.329748000
H	2.962944000	-1.996624000	-0.156852000
H	0.578582000	-2.372587000	0.497411000
H	3.790913000	0.250054000	-0.658845000
H	2.406343000	2.246926000	-0.563035000
B	0.515026000	1.050164000	0.052256000
C	-3.338856000	-0.222612000	-0.725545000
C	-2.283678000	-0.752059000	-0.112816000
H	-3.532076000	0.844364000	-0.720776000
H	-4.053804000	-0.846104000	-1.250153000
H	-2.142481000	-1.831632000	-0.140827000
C	-1.253453000	0.004302000	0.676826000
C	-0.987569000	1.526153000	0.376695000
H	-1.412254000	-0.184714000	1.746452000
H	-1.150481000	2.178548000	1.236834000
H	-1.568677000	1.908296000	-0.464144000

B3LYP-D3/6-311+G(d,p)

N	0.156834000	-0.305905000	0.321317000
C	0.961856000	-1.385544000	0.268812000
C	2.271631000	-1.163809000	-0.093694000
C	2.739017000	0.152094000	-0.386058000
C	1.949248000	1.289313000	-0.333357000
H	2.953607000	-2.002394000	-0.154565000
H	0.564985000	-2.367001000	0.505723000
H	3.787317000	0.240838000	-0.663643000
H	2.409243000	2.243164000	-0.571389000
B	0.515741000	1.053838000	0.052727000
C	-3.334933000	-0.229797000	-0.723626000
C	-2.272878000	-0.753404000	-0.118442000
H	-3.540063000	0.834884000	-0.702216000
H	-4.042487000	-0.853848000	-1.257517000
H	-2.111313000	-1.829600000	-0.160136000
C	-1.252722000	0.008787000	0.677763000
C	-0.987823000	1.530862000	0.373027000
H	-1.417269000	-0.179306000	1.746688000
H	-1.154581000	2.186691000	1.229712000
H	-1.566354000	1.907704000	-0.472063000

MP2/6-311+G(d,p)

N	0.156055000	-0.307462000	0.318926000
C	0.961961000	-1.391753000	0.270850000
C	2.276357000	-1.155042000	-0.097794000
C	2.737032000	0.161549000	-0.389050000
C	1.934733000	1.303122000	-0.332770000
H	2.963396000	-1.993080000	-0.159549000
H	0.568722000	-2.376735000	0.512248000
H	3.786745000	0.259095000	-0.667861000
H	2.400235000	2.257548000	-0.569138000
B	0.500126000	1.058623000	0.055550000
C	-3.311852000	-0.224157000	-0.740440000
C	-2.254259000	-0.765702000	-0.117845000
H	-3.506779000	0.842992000	-0.708863000
H	-4.010963000	-0.845409000	-1.290992000
H	-2.102627000	-1.845076000	-0.161892000
C	-1.250320000	0.000731000	0.690514000
C	-1.011605000	1.520647000	0.382790000
H	-1.400483000	-0.191511000	1.762000000
H	-1.184653000	2.174387000	1.241903000
H	-1.598890000	1.880540000	-0.465611000

M06-2X/6-311+G(d,p)

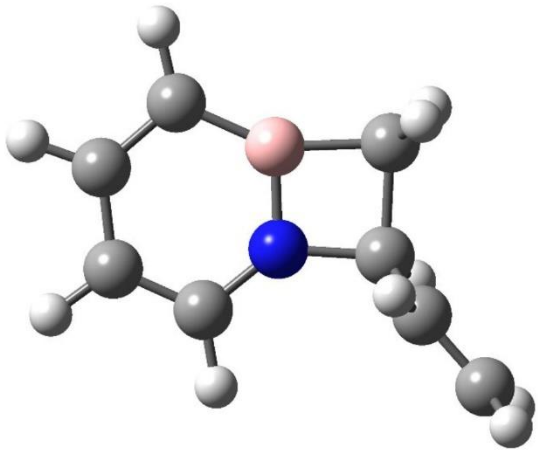
N	0.157938000	-0.306855000	0.324944000
C	0.965689000	-1.382231000	0.269812000
C	2.268218000	-1.156901000	-0.094071000
C	2.726217000	0.163273000	-0.385902000
C	1.938319000	1.293699000	-0.332589000
H	2.954439000	-1.990555000	-0.156921000
H	0.571800000	-2.364451000	0.508563000
H	3.773150000	0.255896000	-0.664934000
H	2.396857000	2.246668000	-0.571635000
B	0.505022000	1.049811000	0.056188000

SCS-MP2/6-311+G(d,p)

N	0.153966000	-0.305789000	0.317224000
C	0.962846000	-1.395686000	0.270942000
C	2.275429000	-1.166543000	-0.096398000
C	2.744691000	0.155267000	-0.392598000
C	1.948881000	1.297280000	-0.339203000
H	2.961166000	-2.006905000	-0.156336000
H	0.565827000	-2.379362000	0.513577000
H	3.795954000	0.245777000	-0.671291000
H	2.415480000	2.251724000	-0.577522000
B	0.507432000	1.055392000	0.052631000

C	-3.319016000	-0.224985000	-0.717554000	C	-3.330559000	-0.215364000	-0.731994000
C	-2.254475000	-0.757922000	-0.131854000	C	-2.269673000	-0.757244000	-0.113887000
H	-3.527399000	0.837626000	-0.661878000	H	-3.526180000	0.852770000	-0.705471000
H	-4.023222000	-0.839067000	-1.265594000	H	-4.035014000	-0.838071000	-1.276420000
H	-2.084230000	-1.830734000	-0.202351000	H	-2.122404000	-1.838196000	-0.155417000
C	-1.245641000	0.001238000	0.679176000	C	-1.253663000	0.006876000	0.692379000
C	-1.000858000	1.517353000	0.373991000	C	-1.003713000	1.530295000	0.383260000
H	-1.414368000	-0.190394000	1.745050000	H	-1.404642000	-0.183926000	1.764765000
H	-1.171914000	2.174322000	1.226303000	H	-1.169331000	2.183728000	1.245750000
H	-1.576505000	1.878477000	-0.478214000	H	-1.591063000	1.898707000	-0.462716000

3b(trans)



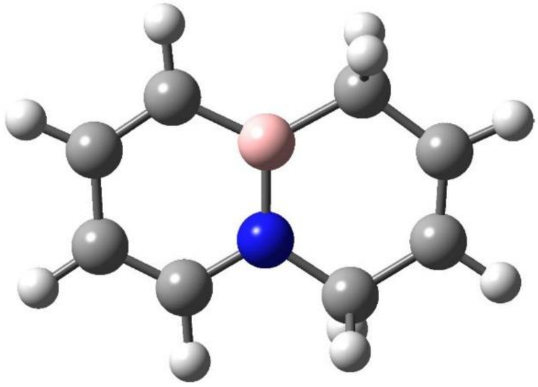
B3LYP/6-311+G(d,p)			
N	-0.101474000	-0.195985000	-0.240043000
C	-0.723872000	-1.392750000	-0.254247000
C	-2.080754000	-1.385640000	-0.023346000
C	-2.778862000	-0.164912000	0.217158000
C	-2.179897000	1.083778000	0.241048000
H	-2.623046000	-2.322705000	-0.023909000
H	-0.150652000	-2.295152000	-0.438529000
H	-3.849785000	-0.247955000	0.390808000
H	-2.807538000	1.947957000	0.434306000
B	-0.697380000	1.085635000	-0.008233000
C	3.459882000	-0.730989000	0.168319000
C	2.290012000	-0.202882000	0.522311000
H	3.748583000	-0.825125000	-0.874328000
H	4.173477000	-1.079508000	0.906288000
H	2.024642000	-0.123168000	1.575247000
C	1.276090000	0.329956000	-0.440024000
C	0.737377000	1.794962000	-0.175799000
H	1.612377000	0.177366000	-1.470497000
H	0.891818000	2.467395000	-1.022287000
H	1.177488000	2.255478000	0.711853000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
N	-0.099644000	-0.189738000	-0.251798000	N	-0.096866000	-0.179602000	-0.264420000
C	-0.714098000	-1.389834000	-0.263691000	C	-0.694585000	-1.392315000	-0.275680000
C	-2.069821000	-1.390228000	-0.024707000	C	-2.057248000	-1.396200000	-0.027984000
C	-2.772081000	-0.172739000	0.223597000	C	-2.766262000	-0.186407000	0.229255000
C	-2.178995000	1.079327000	0.248398000	C	-2.176181000	1.078913000	0.256141000
H	-2.607547000	-2.329887000	-0.023969000	H	-2.588673000	-2.342661000	-0.027327000
H	-0.133754000	-2.286744000	-0.451552000	H	-0.105530000	-2.285630000	-0.470694000
H	-3.841438000	-0.261620000	0.403892000	H	-3.836530000	-0.280658000	0.415998000
H	-2.809152000	1.939834000	0.449768000	H	-2.820222000	1.929802000	0.467590000
B	-0.698030000	1.088471000	-0.010375000	B	-0.693510000	1.098827000	-0.011826000
C	3.445822000	-0.740327000	0.180854000	C	3.417874000	-0.765789000	0.189869000
C	2.278819000	-0.199404000	0.523665000	C	2.254636000	-0.191257000	0.535226000
H	3.740807000	-0.839539000	-0.859658000	H	3.702189000	-0.869911000	-0.854122000
H	4.150046000	-1.094650000	0.925105000	H	4.111952000	-1.134974000	0.938213000
H	2.001011000	-0.113249000	1.572827000	H	1.976100000	-0.093458000	1.585389000
C	1.275685000	0.337352000	-0.447012000	C	1.275690000	0.354875000	-0.450356000
C	0.735716000	1.800994000	-0.177198000	C	0.744855000	1.813311000	-0.180885000
H	1.616363000	0.186428000	-1.476470000	H	1.626159000	0.199448000	-1.478473000
H	0.888620000	2.476827000	-1.021240000	H	0.894221000	2.486421000	-1.029884000
H	1.176416000	2.257572000	0.712332000	H	1.193278000	2.263915000	0.709861000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
N	-0.097934000	-0.184191000	-0.264948000	N	-0.096432000	-0.180300000	-0.250632000
C	-0.707047000	-1.385114000	-0.273602000	C	-0.705251000	-1.394518000	-0.263386000
C	-2.055272000	-1.390663000	-0.026487000	C	-2.065899000	-1.394120000	-0.023296000
C	-2.755650000	-0.172734000	0.229905000	C	-2.777415000	-0.173930000	0.225690000
C	-2.171306000	1.076126000	0.256738000	C	-2.185284000	1.086668000	0.249164000
H	-2.591891000	-2.329781000	-0.023617000	H	-2.602442000	-2.338691000	-0.021758000

H	-0.122524000	-2.278210000	-0.467127000	H	-0.118871000	-2.291184000	-0.453256000
H	-3.822888000	-0.265296000	0.416988000	H	-3.849794000	-0.266443000	0.406025000
H	-2.804641000	1.930725000	0.466818000	H	-2.826329000	1.943484000	0.450149000
B	-0.690320000	1.088130000	-0.012796000	B	-0.694002000	1.097766000	-0.011164000
C	3.417803000	-0.748211000	0.192487000	C	3.439906000	-0.756450000	0.174839000
C	2.256906000	-0.198774000	0.529554000	C	2.274500000	-0.191201000	0.530441000
H	3.712406000	-0.845522000	-0.847722000	H	3.718719000	-0.860286000	-0.871746000
H	4.113517000	-1.110142000	0.939855000	H	4.143846000	-1.120364000	0.918223000
H	1.969886000	-0.109525000	1.575928000	H	2.005712000	-0.095772000	1.584015000
C	1.269797000	0.343276000	-0.453450000	C	1.278870000	0.350369000	-0.450044000
C	0.742397000	1.799945000	-0.180598000	C	0.747155000	1.814558000	-0.184842000
H	1.622724000	0.190071000	-1.477291000	H	1.619904000	0.191456000	-1.481387000
H	0.889278000	2.475914000	-1.022960000	H	0.896443000	2.485948000	-1.036713000
H	1.185499000	2.247350000	0.710461000	H	1.195150000	2.268765000	0.705775000

3c



B3LYP/6-311+G(d,p)

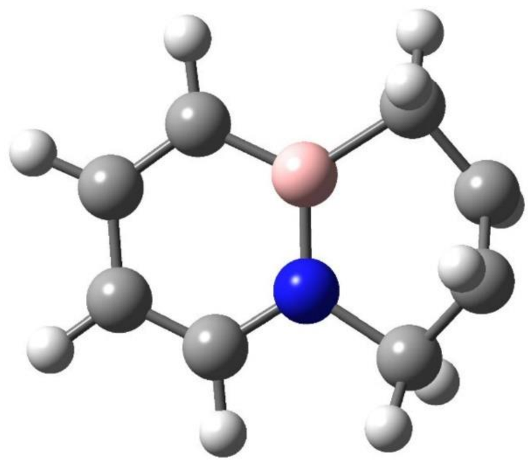
N	0.015801000	-0.653940000	-0.046671000
C	-1.080237000	-1.475891000	-0.063253000
C	-2.356177000	-0.999722000	0.028233000
C	-2.591177000	0.398501000	0.146265000
C	-1.548217000	1.288239000	0.170479000
H	-3.180237000	-1.701589000	0.009206000
H	-0.882927000	-2.539172000	-0.153958000
H	-3.621933000	0.738212000	0.216508000
H	-1.779716000	2.346643000	0.262093000
B	-0.121556000	0.779546000	0.070245000
C	1.319664000	-1.338409000	-0.155788000
C	2.507173000	-0.422692000	-0.137909000
H	1.405215000	-2.061333000	0.666704000
H	1.328746000	-1.927953000	-1.082456000
H	3.465486000	-0.928452000	-0.219718000
C	2.459043000	0.904532000	-0.032866000
C	1.179869000	1.681710000	0.084271000
H	3.397130000	1.455503000	-0.031867000
H	1.125561000	2.426075000	-0.723914000
H	1.201218000	2.290690000	1.000159000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
N	0.015850000	-0.655979000	-0.046785000	N	0.020582000	-0.653395000	0.044978000
C	-1.080928000	-1.477055000	-0.063120000	C	-1.060573000	-1.479753000	-0.100264000
C	-2.356438000	-0.998976000	0.028442000	C	-2.346503000	-0.989763000	-0.139389000
C	-2.590381000	0.399993000	0.146286000	C	-2.586883000	0.405061000	-0.029153000
C	-1.546230000	1.288611000	0.170226000	C	-1.538240000	1.297471000	0.118451000
H	-3.181288000	-1.699906000	0.009668000	H	-3.164491000	-1.691421000	-0.265659000
H	-0.885393000	-2.540721000	-0.153640000	H	-0.853108000	-2.544191000	-0.186716000
H	-3.620955000	0.740282000	0.216462000	H	-3.618521000	0.754375000	-0.069156000
H	-1.773907000	2.347784000	0.261557000	H	-1.781867000	2.356646000	0.193684000
B	-0.121303000	0.777091000	0.069937000	B	-0.115287000	0.777401000	0.171408000
C	1.320654000	-1.338649000	-0.155973000	C	1.343683000	-1.302654000	0.127470000
C	2.507980000	-0.421904000	-0.137888000	C	2.441660000	-0.418155000	-0.398525000
H	1.407359000	-2.060855000	0.666979000	H	1.534689000	-1.568689000	1.177136000
H	1.330837000	-1.927061000	-1.083319000	H	1.306047000	-2.235611000	-0.444593000
H	3.466019000	-0.928088000	-0.219656000	H	3.304563000	-0.911725000	-0.839598000
C	2.458837000	0.905235000	-0.032834000	C	2.389997000	0.922013000	-0.303457000
C	1.178257000	1.680320000	0.084249000	C	1.219875000	1.624903000	0.332335000
H	3.395617000	1.458281000	-0.031605000	H	3.218412000	1.508903000	-0.698080000
H	1.121334000	2.424061000	-0.724080000	H	1.095786000	2.629475000	-0.087974000
H	1.196808000	2.288033000	1.000858000	H	1.432908000	1.779604000	1.402867000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
N	-0.070854000	-0.642927000	0.000000000	N	0.020856000	-0.653134000	0.005636000
C	-1.247307000	-1.340292000	0.000000000	C	-1.074983000	-1.481689000	-0.091735000

C	-2.462289000	-0.730246000	0.000000000	C	-2.359221000	-0.998029000	-0.078237000
C	-2.544651000	0.692542000	0.000000000	C	-2.600683000	0.406235000	0.035837000
C	-1.417536000	1.462691000	0.000000000	C	-1.550726000	1.296689000	0.134606000
H	-3.355743000	-1.339782000	0.000000000	H	-3.182204000	-1.701320000	-0.164909000
H	-1.160052000	-2.422338000	0.000000000	H	-0.869606000	-2.546971000	-0.180845000
H	-3.533459000	1.143613000	0.000000000	H	-3.635339000	0.751355000	0.038136000
H	-1.533913000	2.542910000	0.000000000	H	-1.789344000	2.357751000	0.215889000
B	-0.052739000	0.794786000	0.000000000	B	-0.116237000	0.776634000	0.131470000
C	1.143367000	-1.471282000	0.000000000	C	1.332796000	-1.333055000	0.027735000
C	2.423146000	-0.691920000	0.000000000	C	2.484069000	-0.418546000	-0.306179000
H	1.118411000	-2.126528000	0.878929000	H	1.482674000	-1.777946000	1.023083000
H	1.118411000	-2.126528000	-0.878929000	H	1.302701000	-2.158800000	-0.694383000
H	3.321223000	-1.302264000	0.000000000	H	3.404148000	-0.913818000	-0.614011000
C	2.519977000	0.633716000	0.000000000	C	2.436053000	0.920999000	-0.209223000
C	1.334627000	1.552910000	0.000000000	C	1.201921000	1.661667000	0.243802000
H	3.513431000	1.074900000	0.000000000	H	3.330138000	1.491588000	-0.463007000
H	1.389279000	2.224254000	-0.866603000	H	1.084232000	2.588768000	-0.334655000
H	1.389279000	2.224254000	0.866603000	H	1.341486000	1.992120000	1.286754000

3d



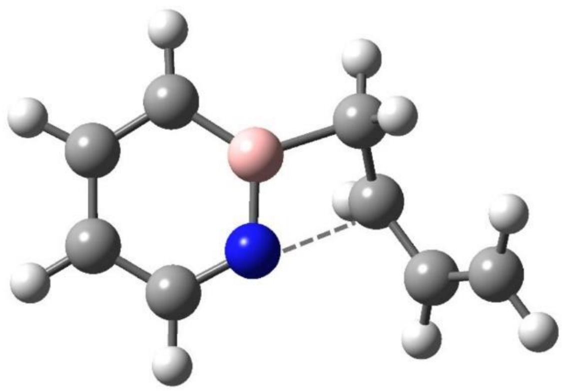
B3LYP/6-311+G(d,p)

N	-0.005534000	-0.664025000	-0.020294000
C	-1.183567000	-1.351286000	-0.002538000
C	-2.405246000	-0.732496000	0.015081000
C	-2.487692000	0.682678000	0.009174000
C	-1.353505000	1.460040000	-0.007225000
H	-3.300843000	-1.340823000	0.024885000
H	-1.108736000	-2.433849000	-0.014339000
H	-3.475313000	1.137867000	0.017976000
H	-1.470917000	2.540307000	-0.010319000
B	0.005824000	0.801073000	0.010511000
C	1.281932000	-1.527717000	-0.101473000
C	2.331761000	-0.588829000	0.386621000
H	1.407937000	-1.826813000	-1.145398000
H	1.120310000	-2.413951000	0.516032000
H	2.303577000	-0.426506000	1.465701000
C	2.263190000	0.520747000	-0.393805000
C	1.433700000	1.637766000	0.101841000
H	2.212109000	0.362986000	-1.474720000
H	1.430656000	2.555493000	-0.491987000
H	1.607400000	1.882683000	1.155611000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
N	0.005278000	-0.666233000	0.018370000	N	-0.001834000	-0.658957000	0.024468000
C	1.183969000	-1.352185000	0.003294000	C	1.178536000	-1.352036000	-0.007419000
C	2.405130000	-0.731694000	-0.013358000	C	2.406050000	-0.725726000	-0.023827000
C	2.486551000	0.684005000	-0.009124000	C	2.490350000	0.688105000	-0.006812000
C	1.351257000	1.460047000	0.005863000	C	1.342228000	1.463418000	0.022952000
H	3.301374000	-1.339107000	-0.020751000	H	3.299998000	-1.340911000	-0.043738000
H	1.111355000	-2.434860000	0.017316000	H	1.101242000	-2.437154000	0.003057000
H	3.473933000	1.139734000	-0.017668000	H	3.477527000	1.149574000	-0.014609000
H	1.464580000	2.540666000	0.008034000	H	1.462151000	2.546045000	0.032705000
B	-0.005959000	0.798713000	-0.011630000	B	-0.021884000	0.807079000	-0.007243000
C	-1.282504000	-1.529496000	0.099195000	C	-1.267427000	-1.533217000	0.115899000
C	-2.332449000	-0.587409000	-0.384359000	C	-2.306604000	-0.600133000	-0.397546000
H	-1.402716000	-1.834166000	1.142422000	H	-1.406175000	-1.802928000	1.168049000
H	-1.125621000	-2.412698000	-0.523974000	H	-1.089907000	-2.429737000	-0.485886000
H	-2.301533000	-0.424208000	-1.463403000	H	-2.264900000	-0.429764000	-1.476151000
C	-2.262399000	0.522784000	0.395735000	C	-2.263697000	0.515173000	0.397817000
C	-1.431266000	1.638505000	-0.101612000	C	-1.444641000	1.637847000	-0.115656000
H	-2.212090000	0.367563000	1.477339000	H	-2.186736000	0.340619000	1.476792000
H	-1.423294000	2.556124000	0.492273000	H	-1.450852000	2.564266000	0.467306000

H	-1.602884000	1.883680000	-1.155836000	H	-1.628857000	1.856715000	-1.175038000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	0.000597000	-0.660675000	0.019072000	N	-0.007758000	-0.658163000	0.022743000
C	1.177547000	-1.345957000	0.005728000	C	1.178030000	-1.356853000	-0.001056000
C	2.396215000	-0.732943000	-0.011803000	C	2.405472000	-0.738502000	-0.017144000
C	2.477470000	0.684069000	-0.011325000	C	2.497057000	0.684009000	-0.010110000
C	1.348738000	1.459050000	0.002173000	C	1.355864000	1.463261000	0.010470000
H	3.289830000	-1.342300000	-0.018727000	H	3.298955000	-1.356016000	-0.031029000
H	1.098973000	-2.428464000	0.019924000	H	1.096609000	-2.442152000	0.010966000
H	3.464957000	1.137953000	-0.021672000	H	3.488313000	1.138708000	-0.018877000
H	1.465687000	2.538618000	0.001565000	H	1.479523000	2.546511000	0.013588000
B	-0.010829000	0.798005000	-0.011333000	B	-0.018057000	0.808594000	-0.011455000
C	-1.269730000	-1.524095000	0.096436000	C	-1.272789000	-1.532026000	0.107527000
C	-2.320390000	-0.585286000	-0.390604000	C	-2.315038000	-0.586895000	-0.398535000
H	-1.399701000	-1.823978000	1.138995000	H	-1.415209000	-1.817686000	1.155774000
H	-1.104776000	-2.406322000	-0.524297000	H	-1.102524000	-2.422360000	-0.506823000
H	-2.289092000	-0.414064000	-1.466832000	H	-2.272088000	-0.412148000	-1.477256000
C	-2.250179000	0.510116000	0.398167000	C	-2.278948000	0.522640000	0.402936000
C	-1.434799000	1.636499000	-0.094913000	C	-1.440455000	1.645901000	-0.104226000
H	-2.186030000	0.340142000	1.476077000	H	-2.200023000	0.342511000	1.481377000
H	-1.428186000	2.548954000	0.503025000	H	-1.444806000	2.567338000	0.489006000
H	-1.610926000	1.875460000	-1.148059000	H	-1.631417000	1.883093000	-1.159750000

TS$_{3a(cis)\text{-}3b(cis)}$



B3LYP/6-311+G(d,p)

N	-0.300815000	0.704612000	0.067409000
C	-1.431446000	1.262354000	0.528212000
C	-2.671221000	0.650180000	0.406403000
C	-2.784730000	-0.662872000	-0.118811000
C	-1.670356000	-1.379929000	-0.506998000
H	-3.563144000	1.188745000	0.709349000
H	-1.367218000	2.257107000	0.970983000
H	-3.778685000	-1.101660000	-0.178989000
H	-1.800993000	-2.405792000	-0.841966000
B	-0.364937000	-0.622068000	-0.460043000
C	3.339381000	0.929063000	-0.282523000
C	2.425578000	0.607150000	0.644105000
H	3.425760000	0.389627000	-1.218104000
H	4.035725000	1.742730000	-0.119723000
H	2.379744000	1.163258000	1.574342000
C	1.520451000	-0.516696000	0.525493000
C	1.157580000	-1.214000000	-0.684387000
H	1.197812000	-0.959396000	1.463199000
H	1.113226000	-2.298762000	-0.583053000
H	1.664353000	-0.895396000	-1.591467000

B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
N	-0.292858000	0.709378000	0.037609000	N	-0.246200000	0.774721000	-0.288779000
C	-1.417641000	1.265493000	0.515843000	C	-1.319809000	1.317973000	0.352051000
C	-2.657612000	0.650141000	0.415096000	C	-2.520833000	0.642747000	0.513167000
C	-2.777260000	-0.665555000	-0.105318000	C	-2.672586000	-0.716053000	0.103818000
C	-1.667708000	-1.381130000	-0.508504000	C	-1.605175000	-1.415393000	-0.430611000
H	-3.545809000	1.186895000	0.731964000	H	-3.363155000	1.165997000	0.961260000
H	-1.347485000	2.260611000	0.956530000	H	-1.229593000	2.349513000	0.698053000
H	-3.771331000	-1.106140000	-0.147534000	H	-3.639835000	-1.193826000	0.261076000
H	-1.798405000	-2.409018000	-0.836905000	H	-1.744056000	-2.467803000	-0.676619000
B	-0.362772000	-0.620361000	-0.483263000	B	-0.339936000	-0.606878000	-0.690132000
C	3.333570000	0.927540000	-0.269375000	C	3.313489000	0.841096000	-0.065848000
C	2.407845000	0.609098000	0.646101000	C	2.173957000	0.654998000	0.626616000
H	3.433737000	0.382256000	-1.200256000	H	3.584302000	0.200229000	-0.898552000
H	4.025453000	1.744169000	-0.102393000	H	3.994133000	1.644551000	0.195363000
H	2.343888000	1.171248000	1.571637000	H	1.928656000	1.299195000	1.467871000

C	1.503300000	-0.515323000	0.518852000
C	1.156838000	-1.215926000	-0.697025000
H	1.172402000	-0.959057000	1.453607000
H	1.113272000	-2.300622000	-0.596086000
H	1.674641000	-0.895441000	-1.597149000

C	1.254285000	-0.458305000	0.363997000
C	1.159781000	-1.184171000	-0.902085000
H	0.875595000	-0.966279000	1.253743000
H	1.170475000	-2.270634000	-0.826291000
H	1.752568000	-0.773423000	-1.714664000

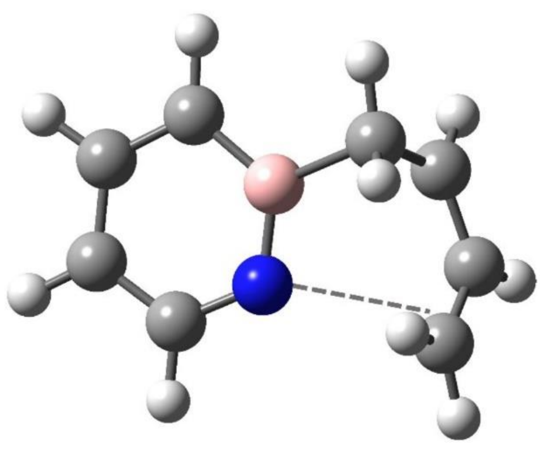
M06-2X/6-311+G(d,p)

N	-0.264516000	0.782592000	-0.246537000
C	-1.353735000	1.317578000	0.359236000
C	-2.540340000	0.641207000	0.507486000
C	-2.668397000	-0.717273000	0.094168000
C	-1.601746000	-1.398820000	-0.426696000
H	-3.392278000	1.150732000	0.943456000
H	-1.277009000	2.348711000	0.699898000
H	-3.631711000	-1.201389000	0.233723000
H	-1.724747000	-2.446379000	-0.686079000
B	-0.341143000	-0.578524000	-0.647876000
C	3.326103000	0.825374000	-0.071769000
C	2.200337000	0.653370000	0.616106000
H	3.600253000	0.168159000	-0.888594000
H	4.010128000	1.628407000	0.172113000
H	1.944324000	1.309406000	1.440265000
C	1.285731000	-0.468671000	0.369065000
C	1.163929000	-1.175679000	-0.885761000
H	0.923840000	-0.972578000	1.262701000
H	1.133696000	-2.259286000	-0.827897000
H	1.733346000	-0.768685000	-1.713578000

SCS-MP2/6-311+G(d,p)

N	-0.251430000	0.787142000	-0.299305000
C	-1.337185000	1.332964000	0.334702000
C	-2.529957000	0.654214000	0.510407000
C	-2.676177000	-0.717581000	0.113796000
C	-1.610791000	-1.411188000	-0.423551000
H	-3.374343000	1.174864000	0.959574000
H	-1.251606000	2.370386000	0.665182000
H	-3.640154000	-1.199577000	0.283436000
H	-1.744717000	-2.465876000	-0.666975000
B	-0.343414000	-0.593356000	-0.688527000
C	3.326826000	0.837438000	-0.052519000
C	2.187588000	0.639242000	0.637675000
H	3.602133000	0.210268000	-0.895316000
H	4.006464000	1.639472000	0.220210000
H	1.940707000	1.272120000	1.487734000
C	1.267487000	-0.477100000	0.363064000
C	1.156348000	-1.182943000	-0.914159000
H	0.890749000	-0.994227000	1.248497000
H	1.160879000	-2.271494000	-0.853687000
H	1.746658000	-0.766514000	-1.726807000

$TS_{3a(cis)-3c}$



B3LYP/6-311+G(d,p)

N	-0.222388000	-0.823494000	0.177311000
C	-1.378171000	-1.471829000	0.089029000
C	-2.592336000	-0.806563000	-0.115804000
C	-2.618777000	0.595666000	-0.209204000
C	-1.459429000	1.353807000	-0.086658000
H	-3.498628000	-1.385249000	-0.256559000
H	-1.366711000	-2.562328000	0.116631000
H	-3.576502000	1.082238000	-0.382127000
H	-1.539243000	2.437568000	-0.108604000
B	-0.208086000	0.567310000	0.183690000
C	2.381717000	-1.313029000	0.278825000
C	2.544153000	-0.308703000	-0.624872000
H	2.030623000	-1.143780000	1.285055000
H	2.667774000	-2.329532000	0.035236000
H	2.963161000	-0.531996000	-1.599872000
C	1.974986000	0.971791000	-0.431913000
C	1.220012000	1.370796000	0.699952000
H	2.000844000	1.653903000	-1.277958000
H	1.006652000	2.432473000	0.775176000
H	1.476243000	0.922997000	1.657261000

B3LYP-D3/6-311+G(d,p)

N	0.219756000	0.824929000	0.183141000
C	1.375683000	1.471762000	0.092565000
C	2.588927000	0.804752000	-0.117055000
C	2.613760000	-0.597796000	-0.212578000
C	1.453442000	-1.354558000	-0.087124000
H	3.495319000	1.382650000	-0.260398000
H	1.364959000	2.562130000	0.121479000
H	3.570473000	-1.084822000	-0.389648000
H	1.528332000	-2.438552000	-0.109986000
B	0.205149000	-0.566048000	0.187665000
C	-2.373147000	1.315258000	0.275275000

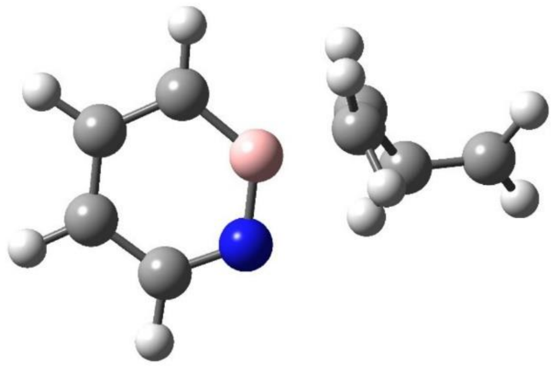
MP2/6-311+G(d,p)

N	0.150124000	0.830544000	0.139125000
C	1.327249000	1.465506000	0.116591000
C	2.536639000	0.779316000	-0.080400000
C	2.555985000	-0.624415000	-0.200807000
C	1.374714000	-1.368233000	-0.112654000
H	3.453302000	1.352698000	-0.198218000
H	1.328901000	2.557183000	0.156622000
H	3.513805000	-1.118859000	-0.364067000
H	1.444513000	-2.455733000	-0.133540000
B	0.124140000	-0.572486000	0.141510000
C	-2.193577000	1.328269000	0.280573000

C	-2.536964000	0.309928000	-0.628054000	C	-2.413908000	0.347255000	-0.653281000
H	-2.031556000	1.146586000	1.285059000	H	-1.995843000	1.103374000	1.321802000
H	-2.647793000	2.333601000	0.026955000	H	-2.387642000	2.370297000	0.041691000
H	-2.946366000	0.535557000	-1.606583000	H	-2.732291000	0.621571000	-1.654688000
C	-1.971221000	-0.971869000	-0.432618000	C	-1.903432000	-0.958854000	-0.446816000
C	-1.220929000	-1.372509000	0.702327000	C	-1.255745000	-1.371560000	0.748315000
H	-1.990970000	-1.652593000	-1.279924000	H	-1.899527000	-1.651841000	-1.287601000
H	-1.004658000	-2.433656000	0.777035000	H	-1.038006000	-2.431217000	0.846057000
H	-1.479080000	-0.924976000	1.659269000	H	-1.526329000	-0.882552000	1.681393000

M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	0.188673000	0.814551000	0.165572000	N	0.160743000	0.822009000	0.140193000
C	1.348705000	1.457782000	0.081605000	C	1.339193000	1.464566000	0.096511000
C	2.558814000	0.794476000	-0.111874000	C	2.552444000	0.786728000	-0.085937000
C	2.585395000	-0.607501000	-0.195792000	C	2.580283000	-0.623806000	-0.179671000
C	1.430418000	-1.366301000	-0.077294000	C	1.405775000	-1.375812000	-0.083079000
H	3.467445000	1.370880000	-0.236543000	H	3.467994000	1.363245000	-0.203265000
H	1.338236000	2.546954000	0.117552000	H	1.332787000	2.557225000	0.126845000
H	3.544914000	-1.093355000	-0.356092000	H	3.543210000	-1.114727000	-0.330034000
H	1.509293000	-2.448886000	-0.100742000	H	1.481865000	-2.463711000	-0.098095000
B	0.187565000	-0.569556000	0.162476000	B	0.151180000	-0.576770000	0.155037000
C	-2.250797000	1.317918000	0.306578000	C	-2.206248000	1.333756000	0.286179000
C	-2.494648000	0.355136000	-0.619586000	C	-2.447822000	0.357120000	-0.647377000
H	-1.953039000	1.092286000	1.319592000	H	-1.989002000	1.107444000	1.323109000
H	-2.451386000	2.360375000	0.089188000	H	-2.387113000	2.379535000	0.049954000
H	-2.873463000	0.627259000	-1.596658000	H	-2.779591000	0.635459000	-1.644039000
C	-1.972263000	-0.947810000	-0.445024000	C	-1.946361000	-0.955584000	-0.450065000
C	-1.261439000	-1.389796000	0.681700000	C	-1.266771000	-1.381988000	0.720685000
H	-1.999663000	-1.612352000	-1.305100000	H	-1.953994000	-1.637337000	-1.301343000
H	-1.031783000	-2.447496000	0.731995000	H	-1.054024000	-2.445625000	0.797287000
H	-1.474198000	-0.933184000	1.643541000	H	-1.521476000	-0.911464000	1.668712000

$TS_{3a(cis)-3a(trans)}$

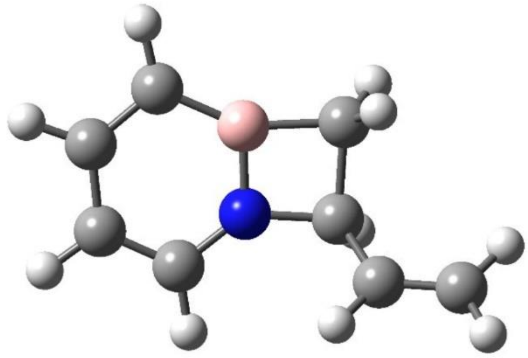


B3LYP/6-311+G(d,p)			
N	-0.559694000	1.062175000	-0.409884000
C	-1.793296000	1.454422000	-0.137201000
C	-2.812902000	0.586806000	0.305000000
C	-2.569636000	-0.778852000	0.482460000
C	-1.304616000	-1.303898000	0.215751000
H	-3.795707000	0.995474000	0.517147000
H	-2.033133000	2.513472000	-0.253418000
H	-3.379773000	-1.414629000	0.830499000
H	-1.147335000	-2.370938000	0.356898000
B	-0.291150000	-0.313155000	-0.257387000
C	3.622095000	0.540606000	0.436409000
C	2.292202000	0.520037000	0.494678000
H	4.198359000	-0.296397000	0.054645000
H	4.180071000	1.406344000	0.774652000
H	1.742174000	1.376012000	0.866973000
C	1.499945000	-0.672015000	0.071486000
C	1.089756000	-0.902706000	-1.238996000
H	1.476437000	-1.505334000	0.767960000
H	0.830512000	-1.899572000	-1.571908000
H	1.281757000	-0.159595000	-2.002336000

B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
N	-0.558738000	1.066559000	-0.413954000	N	-0.527792000	1.080174000	-0.417321000
C	-1.792171000	1.456059000	-0.136695000	C	-1.775142000	1.455840000	-0.143539000
C	-2.809848000	0.586421000	0.308732000	C	-2.794865000	0.579882000	0.305035000
C	-2.565530000	-0.779605000	0.484431000	C	-2.550661000	-0.789891000	0.492000000
C	-1.300617000	-1.302501000	0.212447000	C	-1.275872000	-1.307245000	0.224665000
H	-3.791989000	0.994490000	0.525135000	H	-3.781758000	0.989060000	0.513167000
H	-2.033970000	2.514820000	-0.250846000	H	-2.028580000	2.512971000	-0.266137000

H	-3.373969000	-1.416026000	0.835205000	H	-3.362146000	-1.426314000	0.843540000
H	-1.136472000	-2.368647000	0.351133000	H	-1.104873000	-2.375194000	0.368775000
B	-0.291180000	-0.309268000	-0.262559000	B	-0.261214000	-0.308599000	-0.248945000
C	3.616317000	0.537785000	0.440338000	C	3.598802000	0.522282000	0.446195000
C	2.286354000	0.521179000	0.492384000	C	2.256505000	0.535561000	0.493866000
H	4.190428000	-0.305016000	0.067780000	H	4.148704000	-0.343804000	0.087380000
H	4.176047000	1.404566000	0.773194000	H	4.172489000	1.385391000	0.769215000
H	1.732816000	1.380284000	0.851974000	H	1.720270000	1.413678000	0.839821000
C	1.497325000	-0.673474000	0.071449000	C	1.463387000	-0.660911000	0.082018000
C	1.091696000	-0.904025000	-1.240474000	C	1.067165000	-0.888744000	-1.251843000
H	1.471433000	-1.504923000	0.770034000	H	1.468617000	-1.514936000	0.758376000
H	0.829568000	-1.900040000	-1.573986000	H	0.826068000	-1.891248000	-1.591162000
H	1.288566000	-0.160381000	-2.002295000	H	1.266964000	-0.129696000	-2.001678000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	-0.537176000	1.059953000	-0.395402000	N	-0.538032000	1.082140000	-0.420544000
C	-1.769707000	1.450533000	-0.124838000	C	-1.785099000	1.457614000	-0.146458000
C	-2.790984000	0.584929000	0.307621000	C	-2.805326000	0.580441000	0.305367000
C	-2.553594000	-0.779383000	0.477919000	C	-2.558682000	-0.788905000	0.495112000
C	-1.291253000	-1.307916000	0.214206000	C	-1.281179000	-1.306977000	0.228165000
H	-3.772581000	0.995567000	0.516257000	H	-3.793473000	0.989062000	0.512509000
H	-2.006469000	2.509314000	-0.237081000	H	-2.039288000	2.514868000	-0.271796000
H	-3.367510000	-1.413203000	0.818476000	H	-3.369217000	-1.426962000	0.848390000
H	-1.133868000	-2.375054000	0.349081000	H	-1.110880000	-2.375239000	0.375953000
B	-0.284764000	-0.312678000	-0.242337000	B	-0.269601000	-0.306307000	-0.248136000
C	3.595980000	0.539916000	0.441234000	C	3.611139000	0.522912000	0.449724000
C	2.268913000	0.529508000	0.479311000	C	2.268335000	0.534818000	0.495215000
H	4.165809000	-0.315844000	0.093942000	H	4.165031000	-0.340850000	0.088048000
H	4.153982000	1.412313000	0.759061000	H	4.184812000	1.385613000	0.777366000
H	1.706644000	1.393787000	0.810931000	H	1.730218000	1.410364000	0.845977000
C	1.495163000	-0.678344000	0.067257000	C	1.472547000	-0.664254000	0.075560000
C	1.096537000	-0.905550000	-1.237987000	C	1.074170000	-0.889595000	-1.255869000
H	1.469268000	-1.507343000	0.768195000	H	1.474836000	-1.518164000	0.752528000
H	0.810556000	-1.894483000	-1.571080000	H	0.827380000	-1.891282000	-1.595364000
H	1.271119000	-0.147765000	-1.991338000	H	1.268371000	-0.131043000	-2.008319000

TS$_{3b(cis)-3b(trans)}$



B3LYP/6-311+G(d,p)			
N	0.172105000	-0.343234000	0.353547000
C	1.009846000	-1.398625000	0.286560000
C	2.300919000	-1.140467000	-0.114885000
C	2.720262000	0.185933000	-0.430589000
C	1.899017000	1.299014000	-0.362821000
H	3.006303000	-1.958456000	-0.188230000
H	0.651572000	-2.390005000	0.544047000
H	3.757034000	0.303549000	-0.738998000
H	2.323599000	2.263969000	-0.620895000
B	0.484718000	1.025087000	0.067295000
C	-3.571939000	-0.581710000	-0.021648000
C	-2.265354000	-0.832286000	-0.050612000
H	-3.991487000	0.210146000	0.591848000
H	-4.269841000	-1.158443000	-0.617152000
H	-1.887049000	-1.630018000	-0.686108000
C	-1.232150000	-0.077887000	0.746940000
C	-1.018712000	1.461283000	0.438464000
H	-1.373541000	-0.265392000	1.817618000
H	-1.167186000	2.103818000	1.309057000
H	-1.655865000	1.818195000	-0.372413000

B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
N	0.172513000	-0.337839000	0.363501000	N	0.172410000	-0.334093000	0.370767000
C	1.004378000	-1.396781000	0.293777000	C	0.997524000	-1.403607000	0.307171000
C	2.295204000	-1.143475000	-0.112305000	C	2.292878000	-1.146060000	-0.110877000

C	2.717108000	0.181871000	-0.431712000	C	2.714616000	0.175016000	-0.440195000
C	1.899151000	1.298070000	-0.364547000	C	1.891149000	1.300778000	-0.374110000
H	2.997771000	-1.963708000	-0.187214000	H	2.995293000	-1.970346000	-0.183619000
H	0.639562000	-2.385277000	0.552464000	H	0.630493000	-2.391386000	0.577301000
H	3.753172000	0.295631000	-0.743933000	H	3.751262000	0.289137000	-0.758777000
H	2.325147000	2.261052000	-0.627671000	H	2.326881000	2.259597000	-0.646560000
B	0.485444000	1.028641000	0.070736000	B	0.476237000	1.033983000	0.069761000
C	-3.564600000	-0.591092000	-0.016535000	C	-3.555279000	-0.586901000	-0.023630000
C	-2.256135000	-0.827703000	-0.059892000	C	-2.235085000	-0.822093000	-0.070407000
H	-3.983862000	0.181907000	0.621028000	H	-3.970594000	0.174304000	0.632296000
H	-4.262600000	-1.157112000	-0.622135000	H	-4.247713000	-1.146218000	-0.643868000
H	-1.867484000	-1.602088000	-0.717589000	H	-1.842414000	-1.585100000	-0.742221000
C	-1.231623000	-0.074565000	0.748890000	C	-1.229845000	-0.069036000	0.758943000
C	-1.019617000	1.464703000	0.437193000	C	-1.033207000	1.465355000	0.445885000
H	-1.382032000	-0.262767000	1.818137000	H	-1.379256000	-0.262120000	1.829287000
H	-1.172871000	2.109217000	1.305487000	H	-1.181849000	2.106625000	1.319626000
H	-1.656374000	1.815786000	-0.376655000	H	-1.681249000	1.806636000	-0.365748000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	0.171847000	-0.334789000	0.370981000	N	0.173271000	-0.334749000	0.343204000
C	1.000316000	-1.394318000	0.301541000	C	1.012577000	-1.401229000	0.271563000
C	2.284965000	-1.145697000	-0.106861000	C	2.302359000	-1.135988000	-0.146899000
C	2.703817000	0.180430000	-0.430900000	C	2.721560000	0.198567000	-0.464473000
C	1.893571000	1.294236000	-0.367580000	C	1.895887000	1.316965000	-0.384378000
H	2.987455000	-1.964694000	-0.181512000	H	3.010404000	-1.955915000	-0.229978000
H	0.632333000	-2.380518000	0.564618000	H	0.652235000	-2.393715000	0.535777000
H	3.738757000	0.291505000	-0.745657000	H	3.759784000	0.318320000	-0.779310000
H	2.322873000	2.252918000	-0.636218000	H	2.326779000	2.283624000	-0.640956000
B	0.479094000	1.025598000	0.072404000	B	0.475611000	1.033953000	0.056730000
C	-3.547928000	-0.593306000	-0.010955000	C	-3.572309000	-0.601819000	0.026536000
C	-2.241583000	-0.818690000	-0.073714000	C	-2.253140000	-0.843236000	-0.033163000
H	-3.959531000	0.160090000	0.654265000	H	-3.978918000	0.184557000	0.659159000
H	-4.247588000	-1.146684000	-0.624744000	H	-4.275780000	-1.178454000	-0.566750000
H	-1.848778000	-1.570166000	-0.754704000	H	-1.874985000	-1.628933000	-0.688207000
C	-1.227396000	-0.069795000	0.749169000	C	-1.224458000	-0.075639000	0.763329000
C	-1.025852000	1.460382000	0.435884000	C	-1.036541000	1.463040000	0.443375000
H	-1.387238000	-0.260255000	1.815173000	H	-1.346304000	-0.261646000	1.839244000
H	-1.176862000	2.105454000	1.301662000	H	-1.186195000	2.109039000	1.314805000
H	-1.660020000	1.802769000	-0.381828000	H	-1.689585000	1.797727000	-0.368583000

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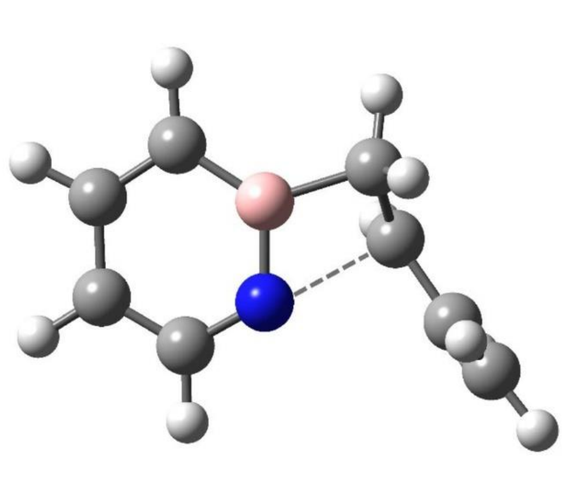

B3LYP/6-311+G(d,p)			
N	-1.146468000	-0.384770000	1.261415000
C	-2.100774000	-1.088591000	0.630808000
C	-2.681080000	-0.657507000	-0.552838000
C	-2.204821000	0.503965000	-1.217146000
C	-1.140711000	1.230375000	-0.722585000
H	-3.515324000	-1.211988000	-0.969963000
H	-2.456993000	-2.005276000	1.102214000
H	-2.687114000	0.786953000	-2.150645000
H	-0.769117000	2.071000000	-1.303020000
B	-0.620646000	0.783529000	0.624475000
C	1.741811000	-2.122165000	2.839162000
C	1.099629000	-0.947383000	2.757260000
H	2.191412000	-2.584570000	1.966477000
H	1.835724000	-2.651624000	3.779592000
H	0.647393000	-0.499151000	3.635302000
C	1.036163000	-0.187147000	1.531389000
C	0.730028000	1.230766000	1.427953000
H	1.457627000	-0.669444000	0.653343000
H	1.395768000	1.779944000	0.761231000
H	0.584931000	1.734772000	2.381540000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
N	-1.150833000	-0.359959000	1.288444000	N	-1.206303000	-0.152020000	1.512433000
C	-2.089934000	-1.081786000	0.654115000	C	-2.059348000	-0.995439000	0.867561000
C	-2.659079000	-0.671545000	-0.542045000	C	-2.493830000	-0.771200000	-0.430684000
C	-2.186317000	0.487367000	-1.215984000	C	-1.988717000	0.312980000	-1.210570000
C	-1.135859000	1.230131000	-0.717695000	C	-1.013797000	1.154226000	-0.704674000
H	-3.481090000	-1.240693000	-0.963731000	H	-3.237311000	-1.439884000	-0.859925000
H	-2.440627000	-1.996888000	1.132328000	H	-2.441567000	-1.851149000	1.427294000
H	-2.659461000	0.752312000	-2.159387000	H	-2.364202000	0.430428000	-2.227319000
H	-0.762251000	2.066100000	-1.303392000	H	-0.610779000	1.931053000	-1.353886000
B	-0.626931000	0.804539000	0.641325000	B	-0.639966000	0.940727000	0.757622000
C	1.716484000	-2.129686000	2.813214000	C	1.544551000	-2.162620000	2.536712000
C	1.091423000	-0.945265000	2.743896000	C	0.975087000	-0.943652000	2.628610000
H	2.151627000	-2.593203000	1.933611000	H	1.870553000	-2.558059000	1.578248000
H	1.809479000	-2.666711000	3.749472000	H	1.689389000	-2.783185000	3.414891000
H	0.649594000	-0.494997000	3.626133000	H	0.638200000	-0.547695000	3.582825000
C	1.022335000	-0.177202000	1.522252000	C	0.829140000	-0.073797000	1.463738000
C	0.728476000	1.247015000	1.434429000	C	0.704251000	1.392100000	1.521902000
H	1.432152000	-0.655732000	0.636128000	H	1.195024000	-0.499344000	0.525740000
H	1.392881000	1.797373000	0.767571000	H	1.389535000	1.938470000	0.874694000
H	0.595367000	1.740516000	2.395279000	H	0.617529000	1.789748000	2.530754000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	-1.218419000	-0.196141000	1.483296000	N	-1.227895000	-0.150636000	1.520210000
C	-2.101371000	-0.993857000	0.833565000	C	-2.097734000	-0.984288000	0.868987000
C	-2.529449000	-0.748367000	-0.448362000	C	-2.514411000	-0.767695000	-0.432495000
C	-1.999609000	0.336928000	-1.207406000	C	-1.985213000	0.309913000	-1.220559000
C	-1.021387000	1.144870000	-0.694486000	C	-1.010775000	1.143123000	-0.709755000
H	-3.283566000	-1.390756000	-0.889096000	H	-3.260766000	-1.431249000	-0.866735000
H	-2.505145000	-1.841573000	1.383989000	H	-2.500510000	-1.826883000	1.434809000
H	-2.377063000	0.481253000	-2.216597000	H	-2.350576000	0.423079000	-2.242327000
H	-0.608883000	1.930355000	-1.321143000	H	-0.596864000	1.917832000	-1.356339000
B	-0.642066000	0.882929000	0.755568000	B	-0.646695000	0.926786000	0.762728000
C	1.601500000	-2.133397000	2.577872000	C	1.575953000	-2.161568000	2.537323000
C	0.986708000	-0.953054000	2.636371000	C	0.988050000	-0.951087000	2.628140000
H	1.982024000	-2.524706000	1.640243000	H	1.919738000	-2.551430000	1.581655000
H	1.741269000	-2.740665000	3.463291000	H	1.719806000	-2.784345000	3.415465000
H	0.593840000	-0.559607000	3.566651000	H	0.634650000	-0.564352000	3.580619000
C	0.856602000	-0.093337000	1.460832000	C	0.845955000	-0.073146000	1.462695000
C	0.713416000	1.354549000	1.515351000	C	0.699641000	1.391478000	1.527381000
H	1.229298000	-0.524009000	0.533880000	H	1.218935000	-0.490649000	0.524026000
H	1.358388000	1.916143000	0.846329000	H	1.378133000	1.950649000	0.882157000
H	0.621351000	1.764130000	2.515815000	H	0.608017000	1.786158000	2.537981000

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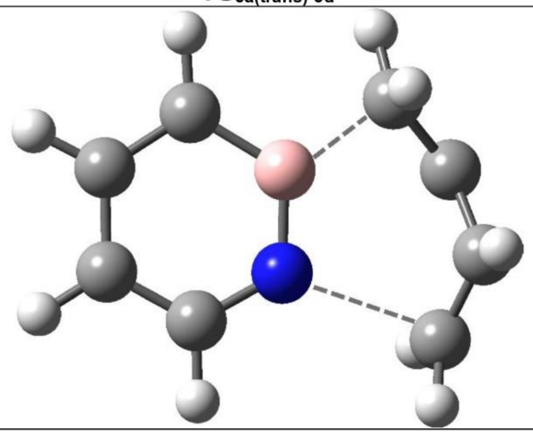
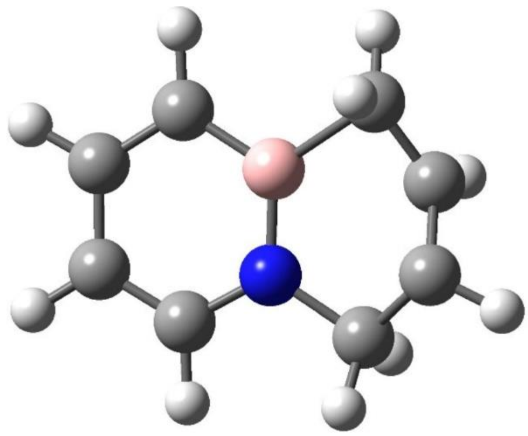


B3LYP/6-311+G(d,p)			
N	-0.432362000	-0.919281000	0.226510000
C	-1.649458000	-1.434769000	0.015617000
C	-2.755709000	-0.647119000	-0.273985000
C	-2.608688000	0.751651000	-0.361863000
C	-1.384035000	1.367883000	-0.160519000
H	-3.715810000	-1.116658000	-0.454894000
H	-1.756162000	-2.519316000	0.052263000
H	-3.487030000	1.348257000	-0.599986000
H	-1.324799000	2.451107000	-0.227618000
B	-0.235239000	0.462893000	0.195561000
C	1.605284000	-2.067281000	0.528700000
C	2.162887000	-0.951753000	1.097343000
H	1.617663000	-2.217141000	-0.543323000
H	1.273654000	-2.905894000	1.128948000
H	2.082135000	-0.815592000	2.171941000
C	2.089252000	0.177666000	0.270387000

				C	1.265090000	1.269753000	0.631407000
				H	2.318710000	0.049638000	-0.786506000
				H	1.314582000	2.168915000	0.021675000
				H	1.177762000	1.478709000	1.697980000
B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
N	-0.435751000	-0.922696000	0.231853000	N	-0.421372000	-0.968718000	0.257215000
C	-1.653043000	-1.435559000	0.019999000	C	-1.664216000	-1.452201000	0.056192000
C	-2.757280000	-0.645220000	-0.274075000	C	-2.751377000	-0.636619000	-0.258953000
C	-2.606782000	0.753391000	-0.365415000	C	-2.575088000	0.756083000	-0.391132000
C	-1.380483000	1.367310000	-0.163463000	C	-1.321231000	1.344607000	-0.211866000
H	-3.718236000	-1.112623000	-0.456078000	H	-3.724754000	-1.089821000	-0.428125000
H	-1.761338000	-2.519810000	0.059109000	H	-1.800491000	-2.534918000	0.110976000
H	-3.483393000	1.351165000	-0.606894000	H	-3.437750000	1.369506000	-0.653228000
H	-1.315243000	2.449971000	-0.232391000	H	-1.235189000	2.425875000	-0.314499000
B	-0.237395000	0.458259000	0.196998000	B	-0.215243000	0.411340000	0.193595000
C	1.612865000	-2.070255000	0.527887000	C	1.606194000	-2.066153000	0.509665000
C	2.166792000	-0.951546000	1.092704000	C	2.146617000	-0.939570000	1.076060000
H	1.615865000	-2.221592000	-0.544259000	H	1.598752000	-2.190958000	-0.568938000
H	1.281464000	-2.906239000	1.131585000	H	1.335984000	-2.931743000	1.107873000
H	2.086766000	-0.815117000	2.167372000	H	2.106469000	-0.813170000	2.155445000
C	2.087282000	0.180746000	0.267653000	C	2.026263000	0.203648000	0.255260000
C	1.262634000	1.269247000	0.635695000	C	1.260765000	1.296641000	0.690679000
H	2.315751000	0.059405000	-0.790418000	H	2.218151000	0.098714000	-0.814301000
H	1.304921000	2.170527000	0.028628000	H	1.241317000	2.204011000	0.091794000
H	1.172332000	1.472303000	1.703146000	H	1.163926000	1.445114000	1.765926000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
N	-0.422153000	-0.943688000	0.227438000	N	-0.408737000	-0.958183000	0.233191000
C	-1.644647000	-1.439240000	0.010070000	C	-1.651344000	-1.453885000	0.028539000
C	-2.742554000	-0.644797000	-0.277103000	C	-2.749866000	-0.649870000	-0.265145000
C	-2.585889000	0.751840000	-0.359372000	C	-2.592307000	0.753818000	-0.369491000
C	-1.360492000	1.358684000	-0.156848000	C	-1.348506000	1.355937000	-0.184083000
H	-3.706028000	-1.105610000	-0.455810000	H	-3.720041000	-1.111832000	-0.434048000
H	-1.763122000	-2.522234000	0.046044000	H	-1.773503000	-2.539494000	0.071809000
H	-3.460081000	1.354452000	-0.594271000	H	-3.467255000	1.359643000	-0.611709000
H	-1.292304000	2.440266000	-0.223631000	H	-1.277117000	2.440930000	-0.266821000
B	-0.234177000	0.431705000	0.191610000	B	-0.220859000	0.425981000	0.188877000
C	1.601498000	-2.053795000	0.533753000	C	1.592692000	-2.058370000	0.517355000
C	2.157173000	-0.946181000	1.102101000	C	2.152676000	-0.942920000	1.096102000
H	1.604184000	-2.190804000	-0.540702000	H	1.618814000	-2.195131000	-0.560008000
H	1.275004000	-2.898098000	1.129141000	H	1.281408000	-2.913222000	1.112156000
H	2.092411000	-0.806149000	2.175890000	H	2.077719000	-0.809028000	2.173418000
C	2.049301000	0.177797000	0.264103000	C	2.054703000	0.193173000	0.263387000
C	1.276021000	1.280686000	0.638647000	C	1.274121000	1.295662000	0.661458000
H	2.267370000	0.046585000	-0.794765000	H	2.260946000	0.070190000	-0.802219000
H	1.281591000	2.165027000	0.010023000	H	1.281037000	2.192405000	0.044139000
H	1.164620000	1.475223000	1.703320000	H	1.173149000	1.475863000	1.732730000

$TS_{3d\text{-}3c}$	**B3LYP/6-311+G(d,p)**



N	0.010747000	-0.711256000	-0.016375000
C	1.186132000	-1.393849000	-0.024665000
C	2.402081000	-0.756143000	-0.031567000
C	2.469207000	0.655549000	0.016527000
C	1.328887000	1.431367000	0.058620000
H	3.305814000	-1.351140000	-0.057512000
H	1.112941000	-2.475396000	-0.021801000
H	3.451220000	1.121491000	0.027678000
H	1.431385000	2.510392000	0.102228000
B	0.012786000	0.718889000	-0.013865000
C	-1.275895000	-1.482570000	0.101887000
C	-2.350115000	-0.561560000	-0.457495000
H	-1.340750000	-1.760231000	1.178805000
H	-1.205956000	-2.403915000	-0.481064000
H	-3.345937000	-1.003914000	-0.372734000
C	-2.132726000	0.619334000	0.344930000
C	-1.417147000	1.698768000	-0.179639000
H	-2.203984000	0.625023000	1.462341000
H	-1.253694000	2.589626000	0.428496000
H	-1.482786000	1.835154000	-1.258920000

B3LYP-D3/6-311+G(d,p)

N	0.010236000	-0.714933000	-0.019964000
C	1.186568000	-1.395506000	-0.025683000
C	2.401495000	-0.755058000	-0.030387000
C	2.466573000	0.657118000	0.018388000
C	1.324548000	1.430843000	0.059573000
H	3.306302000	-1.348480000	-0.054576000
H	1.115920000	-2.477189000	-0.021954000
H	3.447979000	1.124245000	0.031411000
H	1.421627000	2.510204000	0.104429000
B	0.011729000	0.714587000	-0.015594000
C	-1.276900000	-1.485200000	0.099516000
C	-2.350732000	-0.560282000	-0.454085000
H	-1.336613000	-1.765464000	1.176282000
H	-1.211419000	-2.404916000	-0.486553000
H	-3.347480000	-0.999186000	-0.365955000
C	-2.129266000	0.621913000	0.347187000
C	-1.416222000	1.700206000	-0.182225000
H	-2.196238000	0.628443000	1.465170000
H	-1.245561000	2.591802000	0.423042000
H	-1.480337000	1.832472000	-1.262147000

MP2/6-311+G(d,p)

N	-0.002629000	-0.769741000	-0.054186000
C	1.185129000	-1.426665000	-0.068374000
C	2.389638000	-0.743358000	-0.040093000
C	2.417532000	0.661793000	0.074673000
C	1.240756000	1.404936000	0.151595000
H	3.310926000	-1.315051000	-0.081647000
H	1.135983000	-2.512298000	-0.092357000
H	3.385495000	1.159103000	0.120592000
H	1.319263000	2.484611000	0.251371000
B	-0.047174000	0.655677000	0.013652000
C	-1.278945000	-1.536894000	0.075057000
C	-2.324329000	-0.551786000	-0.403169000
H	-1.310049000	-1.838734000	1.146410000
H	-1.217788000	-2.442526000	-0.537776000
H	-3.339434000	-0.903976000	-0.177097000
C	-2.001300000	0.657604000	0.359283000
C	-1.442044000	1.753031000	-0.287226000
H	-2.010324000	0.728520000	1.474199000
H	-1.193065000	2.666287000	0.253991000
H	-1.515430000	1.775085000	-1.373024000

M06-2X/6-311+G(d,p)

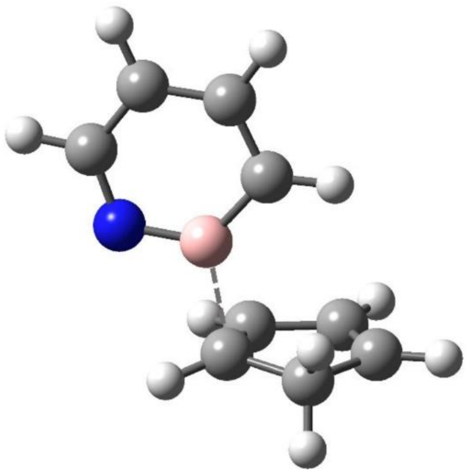
N	0.002472000	-0.735746000	-0.027050000
C	1.181591000	-1.401821000	-0.024580000
C	2.386872000	-0.752057000	-0.016910000
C	2.432248000	0.659879000	0.034788000
C	1.286450000	1.420282000	0.070852000
H	3.297718000	-1.334571000	-0.034489000
H	1.116220000	-2.484233000	-0.025133000
H	3.407413000	1.138154000	0.055020000
H	1.375981000	2.499595000	0.117365000
B	-0.015068000	0.686354000	-0.013155000
C	-1.276188000	-1.505646000	0.077342000
C	-2.334092000	-0.555190000	-0.451170000
H	-1.338689000	-1.799035000	1.146787000
H	-1.199748000	-2.414289000	-0.523294000
H	-3.340653000	-0.947803000	-0.283287000
C	-2.059204000	0.628624000	0.350991000
C	-1.432423000	1.729175000	-0.208340000
H	-2.080579000	0.631137000	1.465116000
H	-1.216228000	2.615029000	0.385271000

SCS-MP2/6-311+G(d,p)

N	-0.002732000	-0.763135000	-0.036248000
C	1.189940000	-1.425792000	-0.039419000
C	2.395469000	-0.751407000	-0.023099000
C	2.430592000	0.664334000	0.052652000
C	1.261274000	1.414383000	0.108662000
H	3.315426000	-1.327550000	-0.050915000
H	1.136871000	-2.511902000	-0.051285000
H	3.402829000	1.156499000	0.081197000
H	1.343242000	2.497223000	0.176320000
B	-0.035291000	0.662094000	0.001516000
C	-1.283900000	-1.535424000	0.075305000
C	-2.328793000	-0.552783000	-0.428088000
H	-1.335640000	-1.839786000	1.145329000
H	-1.212077000	-2.439730000	-0.539285000
H	-3.349640000	-0.909790000	-0.233392000
C	-2.022473000	0.649405000	0.360517000
C	-1.450972000	1.758396000	-0.251353000
H	-2.019777000	0.683651000	1.477045000
H	-1.211670000	2.658440000	0.317247000

H	-1.491884000	1.827780000	-1.290252000	H	-1.520469000	1.818489000	-1.336831000s

4a



B3LYP/6-311+G(d,p)

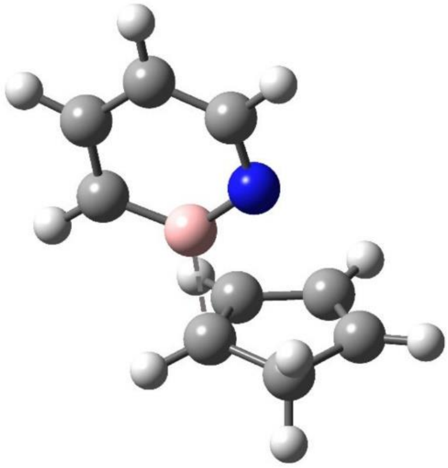
C	-2.210309000	0.068929000	-1.174275000
C	-1.227623000	-0.943273000	-0.613871000
C	-1.306311000	-0.884231000	0.786494000
C	-2.187890000	0.221430000	1.165035000
C	-2.703879000	0.783318000	0.055559000
H	-3.034346000	-0.471685000	-1.663759000
H	-1.793071000	0.740324000	-1.928874000
H	-0.932622000	-1.829536000	-1.156505000
H	-0.930556000	-1.636711000	1.464306000
H	-3.363299000	1.641068000	0.025465000
H	-2.362722000	0.532890000	2.185813000
N	1.312749000	-1.312357000	0.033483000
C	2.578581000	-0.921813000	0.013164000
C	2.982126000	0.425909000	-0.033220000
C	2.033547000	1.455695000	-0.036804000
C	0.669718000	1.164566000	-0.002962000
H	4.041505000	0.660890000	-0.041335000
H	3.352349000	-1.692046000	0.043811000
H	2.382240000	2.485744000	-0.043559000
H	-0.032060000	1.992026000	0.038480000
B	0.343114000	-0.291930000	-0.022589000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
C	-2.194125000	0.082875000	-1.175871000	C	-2.159758000	0.066381000	-1.188268000
C	-1.228625000	-0.947773000	-0.619138000	C	-1.200638000	-0.964641000	-0.630489000
C	-1.315804000	-0.900881000	0.780844000	C	-1.265847000	-0.904574000	0.788083000
C	-2.184495000	0.212586000	1.164849000	C	-2.128036000	0.223017000	1.160054000
C	-2.685065000	0.792634000	0.057766000	C	-2.616341000	0.812241000	0.038423000
H	-3.022149000	-0.439877000	-1.676893000	H	-3.005809000	-0.472641000	-1.644563000
H	-1.757351000	0.756321000	-1.916976000	H	-1.730637000	0.710668000	-1.961934000
H	-0.940335000	-1.831576000	-1.169473000	H	-0.913373000	-1.859952000	-1.169584000
H	-0.946280000	-1.660172000	1.454690000	H	-0.946545000	-1.697701000	1.454814000
H	-3.329255000	1.661721000	0.031280000	H	-3.243606000	1.697628000	0.009710000
H	-2.357464000	0.518615000	2.187368000	H	-2.293453000	0.550492000	2.180830000
N	1.319108000	-1.317998000	0.029502000	N	1.292639000	-1.334771000	0.058701000
C	2.581697000	-0.914555000	0.010953000	C	2.553859000	-0.907215000	0.001155000
C	2.973153000	0.437327000	-0.030404000	C	2.929244000	0.454743000	-0.066948000
C	2.015836000	1.460164000	-0.029590000	C	1.963858000	1.475512000	-0.045153000
C	0.655262000	1.156036000	0.004025000	C	0.602733000	1.154614000	0.041586000
H	4.030531000	0.681232000	-0.037317000	H	3.986962000	0.706973000	-0.113222000
H	3.362538000	-1.677568000	0.039013000	H	3.348111000	-1.659330000	0.010543000
H	2.356142000	2.493025000	-0.031816000	H	2.298167000	2.512773000	-0.066122000
H	-0.059337000	1.971898000	0.051068000	H	-0.117276000	1.968564000	0.115121000
B	0.344440000	-0.303622000	-0.023612000	B	0.298909000	-0.314910000	0.036568000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
C	-2.178393000	0.079544000	-1.175491000	C	-2.180402000	0.064437000	-1.188895000
C	-1.242492000	-0.967006000	-0.620174000	C	-1.213378000	-0.966542000	-0.629337000
C	-1.291489000	-0.906442000	0.769138000	C	-1.266408000	-0.903909000	0.784271000
C	-2.151742000	0.220012000	1.159192000	C	-2.139553000	0.223947000	1.164532000
C	-2.648003000	0.800382000	0.057411000	C	-2.644104000	0.802730000	0.047433000
H	-3.018299000	-0.429070000	-1.667814000	H	-3.021626000	-0.474398000	-1.654629000
H	-1.724427000	0.737760000	-1.918775000	H	-1.747522000	0.718492000	-1.953263000
H	-0.901856000	-1.824944000	-1.180141000	H	-0.918856000	-1.856180000	-1.174544000
H	-0.918300000	-1.667599000	1.439083000	H	-0.938650000	-1.692266000	1.452943000
H	-3.282705000	1.675990000	0.031776000	H	-3.283431000	1.680463000	0.020480000
H	-2.312400000	0.529639000	2.182053000	H	-2.298771000	0.548346000	2.187861000
N	1.301411000	-1.315104000	0.044112000	N	1.300407000	-1.331493000	0.052462000
C	2.561176000	-0.910406000	0.005527000	C	2.563901000	-0.909280000	0.004972000

C	2.949713000	0.437361000	-0.046354000	C	2.946282000	0.452882000	-0.055754000
C	1.993542000	1.456450000	-0.039308000	C	1.983483000	1.477079000	-0.044005000
C	0.634238000	1.157499000	0.016031000	C	0.617772000	1.161005000	0.025954000
H	4.005536000	0.681511000	-0.074542000	H	4.006065000	0.701133000	-0.092077000
H	3.341058000	-1.672919000	0.018543000	H	3.355086000	-1.665471000	0.017485000
H	2.334196000	2.488313000	-0.057796000	H	2.320439000	2.514305000	-0.064688000
H	-0.076349000	1.976607000	0.062177000	H	-0.098705000	1.980196000	0.081527000
B	0.336874000	-0.298785000	0.020162000	B	0.311135000	-0.307605000	0.026576000

4b



B3LYP/6-311+G(d,p)

C	2.148129000	-0.193097000	-1.156053000
C	2.618039000	-0.832236000	0.118428000
C	2.183626000	-0.137026000	1.189609000
C	1.375626000	0.978763000	0.733123000
C	1.238393000	0.922554000	-0.666110000
H	1.665686000	-0.905672000	-1.827436000
H	2.995159000	0.246057000	-1.703890000
H	3.196624000	-1.746094000	0.148913000
H	2.353707000	-0.380895000	2.228802000
H	1.038540000	1.795500000	-1.273528000
H	1.032809000	1.786044000	1.365023000
N	-0.526310000	-1.033773000	-0.021610000
C	-1.777088000	-1.471116000	0.009374000
C	-2.900831000	-0.624669000	0.040415000
C	-2.744649000	0.767437000	0.026215000
C	-1.472837000	1.336317000	-0.032927000
H	-3.891933000	-1.062200000	0.100979000
H	-1.942430000	-2.550552000	0.040658000
H	-3.633728000	1.392644000	0.064328000
H	-1.391213000	2.420819000	-0.060458000
B	-0.349901000	0.351840000	-0.100913000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
C	2.138718000	-0.199608000	-1.156246000	C	-2.126955000	0.202092000	-1.158466000
C	2.605286000	-0.838736000	0.119445000	C	-2.559690000	0.833717000	0.135961000
C	2.183234000	-0.133331000	1.189186000	C	-2.107108000	0.114717000	1.194032000
C	1.384237000	0.987182000	0.730536000	C	-1.289598000	-0.996514000	0.708471000
C	1.238999000	0.924961000	-0.667649000	C	-1.220293000	-0.926121000	-0.709441000
H	1.645353000	-0.910716000	-1.820785000	H	-1.650174000	0.913664000	-1.838551000
H	2.988406000	0.229887000	-1.706860000	H	-2.988060000	-0.242811000	-1.682308000
H	3.171419000	-1.760025000	0.151618000	H	-3.126496000	1.756984000	0.194297000
H	2.351843000	-0.375544000	2.228822000	H	-2.247299000	0.354775000	2.241773000
H	1.039759000	1.796114000	-1.277740000	H	-1.003714000	-1.783285000	-1.337772000
H	1.042178000	1.796628000	1.360334000	H	-1.002878000	-1.857474000	1.302768000
N	-0.521321000	-1.033722000	-0.020743000	N	0.461233000	1.049461000	0.023901000
C	-1.772187000	-1.471071000	0.012382000	C	1.721594000	1.480245000	0.002527000
C	-2.897071000	-0.624795000	0.043761000	C	2.856307000	0.633460000	0.002419000
C	-2.742730000	0.767873000	0.027204000	C	2.718258000	-0.763939000	0.004499000
C	-1.471088000	1.337508000	-0.035458000	C	1.438059000	-1.334452000	-0.006769000
H	-3.887493000	-1.063406000	0.107353000	H	3.847145000	1.083484000	0.018097000
H	-1.937067000	-2.550411000	0.046586000	H	1.891099000	2.561385000	0.011074000
H	-3.632476000	1.392035000	0.066588000	H	3.615611000	-1.382411000	0.013674000
H	-1.384988000	2.421388000	-0.065115000	H	1.352625000	-2.422378000	-0.023812000
B	-0.350415000	0.352042000	-0.104916000	B	0.300013000	-0.357477000	-0.021191000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
C	2.136667000	-0.243995000	-1.139781000	C	-2.180402000	0.064437000	-1.188895000
C	2.579380000	-0.829563000	0.168464000	C	-1.213378000	-0.966542000	-0.629337000
C	2.133598000	-0.091807000	1.195488000	C	-1.266408000	-0.903909000	0.784271000
C	1.332745000	1.014649000	0.671665000	C	-2.139553000	0.223947000	1.164532000
C	1.266265000	0.914859000	-0.714632000	C	-2.644104000	0.802730000	0.047433000
H	1.624071000	-0.973430000	-1.768579000	H	-3.021626000	-0.474398000	-1.654629000

H	2.993927000	0.144357000	-1.705331000	H	-1.747522000	0.718492000	-1.953263000
H	3.147473000	-1.746381000	0.246263000	H	-0.918856000	-1.856180000	-1.174544000
H	2.274710000	-0.291395000	2.247505000	H	-0.938650000	-1.692266000	1.452943000
H	1.000005000	1.726488000	-1.376355000	H	-3.283431000	1.680463000	0.020480000
H	0.991958000	1.856828000	1.257453000	H	-2.298771000	0.548346000	2.187861000
N	-0.496847000	-1.032480000	-0.003106000	N	1.300407000	-1.331493000	0.052462000
C	-1.746370000	-1.468845000	0.014413000	C	2.563901000	-0.909280000	0.004972000
C	-2.871583000	-0.629075000	0.031523000	C	2.946282000	0.452882000	-0.055754000
C	-2.723169000	0.760364000	0.016020000	C	1.983483000	1.477079000	-0.044005000
C	-1.455479000	1.335717000	-0.026428000	C	0.617772000	1.161005000	0.025954000
H	-3.860203000	-1.071931000	0.069782000	H	4.006065000	0.701133000	-0.092077000
H	-1.908369000	-2.547664000	0.033730000	H	3.355086000	-1.665471000	0.017485000
H	-3.615671000	1.380111000	0.037031000	H	2.320439000	2.514305000	-0.064688000
H	-1.373929000	2.419496000	-0.049568000	H	-0.098705000	1.980196000	0.081527000
B	-0.341673000	0.351412000	-0.054115000	B	0.311135000	-0.307605000	0.026576000

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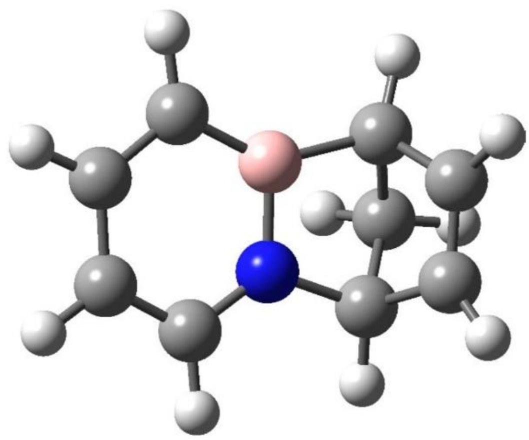
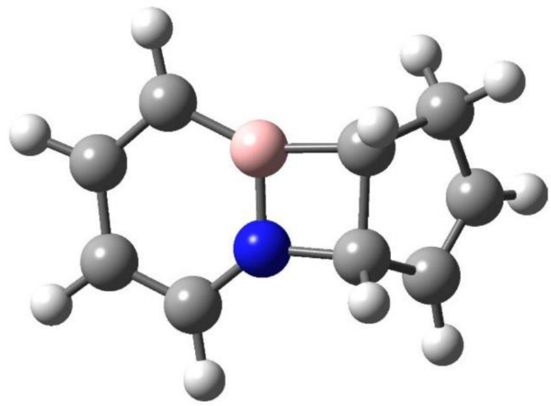


B3LYP/6-311+G(d,p)			
C	-1.739324000	-0.000438000	1.250511000
C	-1.201733000	-1.087514000	0.294464000
C	-1.927600000	-0.689042000	-0.995353000
C	-1.999519000	0.647400000	-0.993438000
C	-1.365339000	1.183074000	0.289680000
H	-1.211366000	0.013342000	2.207375000
H	-2.816806000	-0.082884000	1.412477000
H	-1.257674000	-2.130247000	0.604420000
H	-2.210567000	-1.373027000	-1.783719000
H	-1.678973000	2.180629000	0.591208000
H	-2.368621000	1.274285000	-1.795539000
N	0.216728000	-0.612894000	0.159800000
C	1.322280000	-1.370381000	0.017388000
C	2.547130000	-0.759789000	-0.132299000
C	2.646293000	0.656584000	-0.142748000
C	1.548901000	1.489810000	-0.014649000
H	3.433324000	-1.372244000	-0.237305000
H	1.208519000	-2.449799000	0.034744000
H	3.640652000	1.082389000	-0.259542000
H	1.716314000	2.562415000	-0.033940000
B	0.208315000	0.833434000	0.139977000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
C	-1.742061000	-0.001368000	1.249621000	C	-1.744910000	0.001793000	1.240681000
C	-1.201631000	-1.087594000	0.294072000	C	-1.196615000	-1.084022000	0.297293000
C	-1.922180000	-0.688561000	-0.998832000	C	-1.911395000	-0.703672000	-0.995307000
C	-1.993871000	0.648049000	-0.996389000	C	-1.990323000	0.647173000	-0.998342000
C	-1.365470000	1.182954000	0.290196000	C	-1.373528000	1.183861000	0.286612000
H	-1.216277000	0.011054000	2.207833000	H	-1.217377000	0.020354000	2.200254000
H	-2.819872000	-0.083979000	1.410312000	H	-2.826891000	-0.088205000	1.387022000
H	-1.257978000	-2.130334000	0.603462000	H	-1.242285000	-2.127313000	0.617232000
H	-2.198081000	-1.372253000	-1.789525000	H	-2.175621000	-1.390340000	-1.791649000
H	-1.680017000	2.180230000	0.591304000	H	-1.699941000	2.180115000	0.587456000
H	-2.355810000	1.276021000	-1.800424000	H	-2.349240000	1.268933000	-1.812851000
N	0.216141000	-0.612832000	0.163143000	N	0.213058000	-0.602261000	0.170637000
C	1.320189000	-1.370760000	0.018580000	C	1.312380000	-1.374690000	0.022415000
C	2.545154000	-0.760166000	-0.132387000	C	2.544908000	-0.761503000	-0.131770000
C	2.644402000	0.656742000	-0.142451000	C	2.650955000	0.652651000	-0.144215000
C	1.547100000	1.490481000	-0.012773000	C	1.546004000	1.494074000	-0.012846000
H	3.431048000	-1.372719000	-0.239167000	H	3.428263000	-1.382265000	-0.239621000
H	1.203898000	-2.449782000	0.034698000	H	1.187323000	-2.455618000	0.043280000
H	3.638800000	1.082076000	-0.260562000	H	3.647361000	1.079027000	-0.264137000
H	1.713063000	2.563237000	-0.032528000	H	1.724114000	2.567375000	-0.035884000
B	0.207690000	0.833522000	0.142955000	B	0.201607000	0.841952000	0.145463000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
C	-1.737436000	0.000135000	1.244800000	C	-1.750107000	0.001821000	1.243006000
C	-1.193446000	-1.083149000	0.295914000	C	-1.197773000	-1.086331000	0.297261000
C	-1.913738000	-0.690448000	-0.995678000	C	-1.915885000	-0.702681000	-1.000005000
C	-1.989331000	0.642252000	-0.993963000	C	-1.997091000	0.647071000	-1.002861000
C	-1.367138000	1.180209000	0.290154000	C	-1.373132000	1.185795000	0.286983000
H	-1.208357000	0.015210000	2.199634000	H	-1.225184000	0.020048000	2.205232000
H	-2.814392000	-0.086502000	1.398319000	H	-2.832971000	-0.087358000	1.389608000
H	-1.244771000	-2.124723000	0.608311000	H	-1.247359000	-2.130557000	0.616154000
H	-2.191353000	-1.374729000	-1.784815000	H	-2.187135000	-1.391026000	-1.793793000
H	-1.685494000	2.175174000	0.589022000	H	-1.700311000	2.183000000	0.587978000
H	-2.355594000	1.266638000	-1.798545000	H	-2.362816000	1.269888000	-1.814544000
N	0.214143000	-0.606988000	0.163643000	N	0.214191000	-0.604569000	0.172562000
C	1.315130000	-1.365694000	0.019679000	C	1.320277000	-1.376643000	0.022857000
C	2.537596000	-0.762557000	-0.131348000	C	2.550500000	-0.765567000	-0.130541000
C	2.636093000	0.654769000	-0.142549000	C	2.656374000	0.657012000	-0.143647000
C	1.547181000	1.489602000	-0.015491000	C	1.554321000	1.496909000	-0.013542000
H	3.421737000	-1.375922000	-0.236772000	H	3.435972000	-1.384847000	-0.238133000
H	1.193571000	-2.444210000	0.037737000	H	1.196424000	-2.458269000	0.042615000
H	3.630967000	1.077578000	-0.260207000	H	3.654141000	1.082424000	-0.263699000
H	1.719019000	2.560274000	-0.037006000	H	1.731027000	2.571409000	-0.037760000
B	0.205239000	0.833883000	0.141945000	B	0.204382000	0.839891000	0.145993000

4d



B3LYP/6-311+G(d,p)			
C	-1.659367000	1.528147000	-0.089561000
C	-2.724769000	0.687133000	-0.370137000
C	-2.663553000	-0.734817000	-0.297092000
C	-1.500310000	-1.376163000	0.068811000
H	-3.680804000	1.114803000	-0.665195000
H	-1.818397000	2.598685000	-0.173440000
H	-3.541967000	-1.323085000	-0.530629000
H	-1.410900000	-2.455375000	0.137898000
C	0.985084000	-0.751382000	0.762887000
C	1.157971000	0.822279000	0.780442000
H	1.078568000	-1.289386000	1.711870000
H	1.364877000	1.228937000	1.771699000
C	1.924640000	-1.221231000	-0.314020000
C	2.287772000	1.134000000	-0.234249000
C	2.610820000	-0.208564000	-0.847429000
H	2.012433000	-2.259870000	-0.612548000
H	3.333834000	-0.317840000	-1.649581000
H	3.174625000	1.558887000	0.251109000
H	1.985649000	1.856447000	-1.001465000
N	-0.438962000	-0.595850000	0.349400000
B	-0.386980000	0.836466000	0.311313000

B3LYP-D3/6-311+G(d,p)				MP2/6-311+G(d,p)			
C	-1.655439000	1.528592000	-0.084660000	C	-1.636017000	1.539259000	-0.087693000
C	-2.716637000	0.684680000	-0.374895000	C	-2.708230000	0.692468000	-0.381604000
C	-2.652788000	-0.737755000	-0.304166000	C	-2.650026000	-0.728068000	-0.302229000
C	-1.490435000	-1.376907000	0.069571000	C	-1.487970000	-1.380799000	0.079671000
H	-3.671205000	1.110214000	-0.677765000	H	-3.661321000	1.124085000	-0.689279000
H	-1.815526000	2.598815000	-0.170147000	H	-1.801536000	2.610588000	-0.180862000
H	-3.527537000	-1.327847000	-0.546547000	H	-3.527812000	-1.318177000	-0.546235000
H	-1.395029000	-2.455650000	0.135263000	H	-1.395070000	-2.462086000	0.152963000
C	0.987786000	-0.749734000	0.771246000	C	0.987743000	-0.749935000	0.780222000
C	1.160779000	0.823872000	0.787439000	C	1.179043000	0.817263000	0.798447000
H	1.084848000	-1.288186000	1.719365000	H	1.085254000	-1.289280000	1.729948000
H	1.380802000	1.231819000	1.775005000	H	1.406829000	1.216265000	1.790495000
C	1.916758000	-1.221819000	-0.313445000	C	1.882269000	-1.231012000	-0.323813000
C	2.274225000	1.134275000	-0.245764000	C	2.282341000	1.124988000	-0.240690000

C	2.591571000	-0.209038000	-0.859994000	C	2.556388000	-0.211615000	-0.890031000
H	1.999229000	-2.261122000	-0.610326000	H	1.940346000	-2.269465000	-0.638852000
H	3.301960000	-0.317428000	-1.673261000	H	3.237452000	-0.326293000	-1.730583000
H	3.167863000	1.563278000	0.222860000	H	3.193930000	1.513615000	0.230962000
H	1.955507000	1.851794000	-1.010750000	H	1.967118000	1.868736000	-0.983299000
N	-0.435479000	-0.593614000	0.362331000	N	-0.433857000	-0.589004000	0.373000000
B	-0.385497000	0.838524000	0.325598000	B	-0.368287000	0.843951000	0.332013000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	-1.642123000	1.530441000	-0.089623000	C	-1.647572000	1.543064000	-0.087160000
C	-2.698144000	0.690151000	-0.378237000	C	-2.717760000	0.698121000	-0.377300000
C	-2.643077000	-0.733028000	-0.302997000	C	-2.658302000	-0.731114000	-0.299550000
C	-1.488928000	-1.371182000	0.076109000	C	-1.496848000	-1.380746000	0.077282000
H	-3.649817000	1.116876000	-0.686246000	H	-3.673380000	1.128562000	-0.681892000
H	-1.801712000	2.599052000	-0.181376000	H	-1.811772000	2.615689000	-0.178423000
H	-3.518938000	-1.318855000	-0.547152000	H	-3.538193000	-1.320362000	-0.541792000
H	-1.395106000	-2.449597000	0.146098000	H	-1.403636000	-2.462627000	0.149227000
C	0.982736000	-0.748094000	0.773590000	C	0.988850000	-0.753049000	0.777064000
C	1.167793000	0.815677000	0.793907000	C	1.179093000	0.818114000	0.795237000
H	1.087231000	-1.289821000	1.717380000	H	1.088356000	-1.291871000	1.727654000
H	1.385087000	1.219400000	1.782042000	H	1.405712000	1.218761000	1.788233000
C	1.893380000	-1.220834000	-0.325582000	C	1.892918000	-1.234769000	-0.326547000
C	2.271842000	1.127099000	-0.239559000	C	2.289358000	1.127072000	-0.242969000
C	2.566770000	-0.211468000	-0.872348000	C	2.571650000	-0.216090000	-0.887967000
H	1.962858000	-2.257835000	-0.632048000	H	1.954069000	-2.274717000	-0.639162000
H	3.263026000	-0.319880000	-1.696916000	H	3.261850000	-0.330286000	-1.722180000
H	3.173756000	1.534393000	0.227950000	H	3.197736000	1.520465000	0.233318000
H	1.954492000	1.855252000	-0.992469000	H	1.974939000	1.867741000	-0.990443000
N	-0.434760000	-0.590841000	0.372082000	N	-0.435118000	-0.588794000	0.370562000
B	-0.375809000	0.834866000	0.329320000	B	-0.373363000	0.842322000	0.329359000

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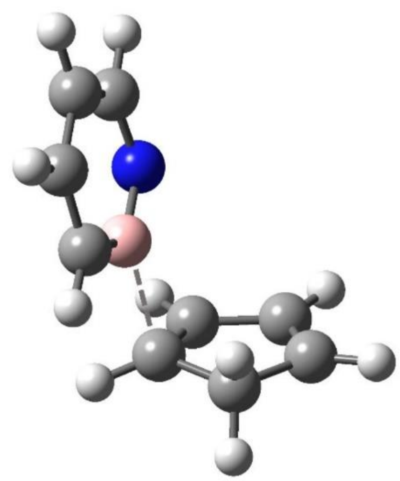

B3LYP/6-311+G(d,p)			
C	-2.026410000	1.225975000	0.258577000
C	-1.326660000	0.505058000	-0.880281000
C	-1.758036000	-0.805646000	-0.853379000
C	-2.560709000	-1.053157000	0.318287000
C	-2.735662000	0.120010000	0.972433000
H	-2.741036000	1.965858000	-0.128371000
H	-1.348560000	1.772192000	0.923182000
H	-1.027614000	1.008478000	-1.792106000
H	-1.483497000	-1.562960000	-1.575114000
H	-3.268818000	0.253519000	1.905098000
H	-2.934384000	-2.022527000	0.615843000
N	0.916225000	-1.197759000	-0.126536000
C	2.201613000	-1.315901000	0.244000000
C	3.072357000	-0.235924000	0.388369000
C	2.622812000	1.071950000	0.134473000
C	1.311228000	1.334224000	-0.259809000
H	4.098675000	-0.411056000	0.691638000
H	2.575613000	-2.322619000	0.439266000
H	3.326838000	1.894499000	0.247280000
H	1.007487000	2.357707000	-0.455071000
B	0.503622000	0.090738000	-0.357282000

B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
C	-2.014874000	1.234528000	0.251252000	C	-2.044340000	1.303871000	0.207558000
C	-1.342462000	0.525210000	-0.909888000	C	-1.415236000	0.649051000	-0.996846000
C	-1.749335000	-0.790638000	-0.873652000	C	-1.615048000	-0.708919000	-0.906281000
C	-2.512018000	-1.052035000	0.324169000	C	-2.252779000	-1.027183000	0.369929000
C	-2.684893000	0.116147000	0.985331000	C	-2.515312000	0.134418000	1.023774000
H	-2.750865000	1.964311000	-0.112912000	H	-2.889354000	1.927159000	-0.120061000
H	-1.320279000	1.786718000	0.892921000	H	-1.353074000	1.949114000	0.762218000

H	-1.047971000	1.036012000	-1.818220000	H	-1.115317000	1.177479000	-1.894445000
H	-1.482210000	-1.543136000	-1.602805000	H	-1.345341000	-1.438147000	-1.660800000
H	-3.189152000	0.240643000	1.934811000	H	-2.954132000	0.226200000	2.011200000
H	-2.856993000	-2.028594000	0.632062000	H	-2.440941000	-2.032957000	0.723936000
N	0.895261000	-1.210541000	-0.135677000	N	0.814070000	-1.308581000	-0.171249000
C	2.175718000	-1.324047000	0.254562000	C	2.090411000	-1.395505000	0.266811000
C	3.042294000	-0.241266000	0.408959000	C	2.932727000	-0.294804000	0.461342000
C	2.595144000	1.065952000	0.144483000	C	2.482140000	1.009774000	0.186411000
C	1.289241000	1.324303000	-0.270977000	C	1.179895000	1.250466000	-0.277892000
H	4.063802000	-0.413802000	0.729394000	H	3.945551000	-0.457826000	0.820439000
H	2.548586000	-2.329127000	0.459249000	H	2.473718000	-2.397031000	0.476937000
H	3.295788000	1.889848000	0.267378000	H	3.168041000	1.844755000	0.335120000
H	0.980470000	2.344764000	-0.472695000	H	0.874289000	2.271631000	-0.492400000
B	0.489832000	0.077410000	-0.377249000	B	0.405116000	-0.010306000	-0.415205000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	-2.058794000	1.283995000	0.232429000	C	-2.069312000	1.308687000	0.208199000
C	-1.417846000	0.638501000	-0.969933000	C	-1.426964000	0.647348000	-0.993640000
C	-1.635763000	-0.704514000	-0.905488000	C	-1.623373000	-0.708637000	-0.903731000
C	-2.313781000	-1.034861000	0.347178000	C	-2.279776000	-1.028145000	0.372078000
C	-2.571746000	0.106187000	1.006180000	C	-2.552130000	0.132175000	1.020055000
H	-2.876058000	1.943673000	-0.082798000	H	-2.908725000	1.936987000	-0.125495000
H	-1.361690000	1.890835000	0.818541000	H	-1.378815000	1.948051000	0.771726000
H	-1.086832000	1.180459000	-1.844639000	H	-1.115274000	1.176851000	-1.887455000
H	-1.344743000	-1.429386000	-1.652623000	H	-1.346253000	-1.439887000	-1.654275000
H	-3.041156000	0.189580000	1.976870000	H	-3.007127000	0.225384000	2.000954000
H	-2.530875000	-2.041407000	0.671885000	H	-2.472082000	-2.035326000	0.722227000
N	0.830381000	-1.271167000	-0.112671000	N	0.830442000	-1.309062000	-0.158585000
C	2.101553000	-1.369824000	0.297989000	C	2.113559000	-1.396817000	0.267916000
C	2.962998000	-0.286151000	0.441275000	C	2.960689000	-0.298188000	0.450675000
C	2.519012000	1.010856000	0.139916000	C	2.506997000	1.010802000	0.178236000
C	1.224406000	1.261311000	-0.301823000	C	1.201344000	1.254330000	-0.272526000
H	3.977838000	-0.450696000	0.781561000	H	3.978080000	-0.461660000	0.798915000
H	2.471144000	-2.368553000	0.530471000	H	2.496468000	-2.399314000	0.477325000
H	3.217073000	1.836804000	0.254697000	H	3.197064000	1.844649000	0.319763000
H	0.923572000	2.276923000	-0.531795000	H	0.892344000	2.275993000	-0.482844000
B	0.436390000	0.010094000	-0.386725000	B	0.427929000	-0.011563000	-0.399020000

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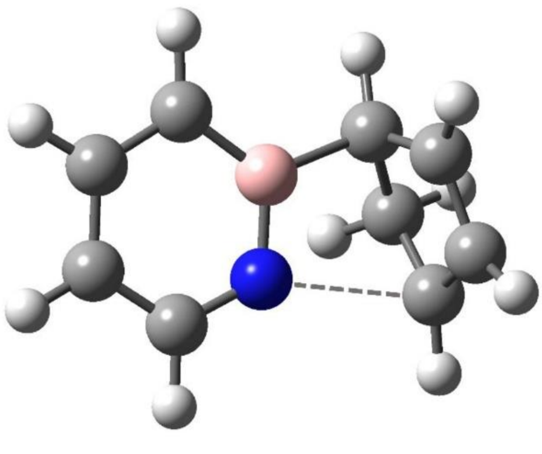

B3LYP/6-311+G(d,p)			
C	1.850722000	-0.035728000	-1.253167000
C	2.087481000	-1.057114000	-0.189196000
C	2.254326000	-0.425329000	1.032356000
C	1.789957000	0.887124000	0.900689000
C	1.252657000	1.110546000	-0.416233000
H	1.241015000	-0.381389000	-2.084243000
H	2.828617000	0.284448000	-1.648016000
H	2.257410000	-2.107309000	-0.383880000
H	2.531667000	-0.904195000	1.960562000
H	1.246392000	2.121249000	-0.815184000
H	1.734776000	1.608541000	1.707441000
N	-0.405968000	-0.830245000	0.014982000
C	-1.588199000	-1.440123000	0.036697000
C	-2.783073000	-0.716840000	0.068452000
C	-2.754844000	0.690768000	0.049128000
C	-1.560667000	1.402814000	-0.011473000
H	-3.725197000	-1.247741000	0.148286000
H	-1.616157000	-2.529682000	0.077570000
H	-3.705100000	1.220460000	0.080084000
H	-1.602749000	2.487374000	-0.068433000
B	-0.328528000	0.553816000	-0.076893000

B3LYP-D3/6-311+G(d,p)	MP2/6-311+G(d,p)

C	1.849812000	-0.036063000	-1.254105000	C	1.828811000	-0.059736000	-1.268526000
C	2.083865000	-1.057056000	-0.188388000	C	1.999581000	-1.069134000	-0.173552000
C	2.253109000	-0.423286000	1.032271000	C	2.181990000	-0.407190000	1.032497000
C	1.788340000	0.889195000	0.899415000	C	1.731984000	0.920085000	0.862067000
C	1.251800000	1.111441000	-0.418082000	C	1.268585000	1.121804000	-0.477831000
H	1.239320000	-0.382147000	-2.084444000	H	1.213646000	-0.394658000	-2.103657000
H	2.828296000	0.283086000	-1.647566000	H	2.827016000	0.226817000	-1.642193000
H	2.246587000	-2.108271000	-0.381418000	H	2.168335000	-2.127251000	-0.344439000
H	2.525961000	-0.902185000	1.961598000	H	2.413768000	-0.871153000	1.983586000
H	1.242830000	2.121609000	-0.817962000	H	1.226863000	2.121839000	-0.902754000
H	1.728739000	1.610475000	1.705639000	H	1.664188000	1.666258000	1.649439000
N	-0.402599000	-0.832052000	0.014847000	N	-0.334323000	-0.831800000	0.062100000
C	-1.584516000	-1.441357000	0.034930000	C	-1.524709000	-1.448145000	0.000545000
C	-2.779697000	-0.717194000	0.067545000	C	-2.722513000	-0.721725000	0.040246000
C	-2.751599000	0.690910000	0.050783000	C	-2.710316000	0.689384000	0.083502000
C	-1.556928000	1.402922000	-0.008658000	C	-1.509670000	1.409230000	0.078854000
H	-3.721915000	-1.248064000	0.146509000	H	-3.665583000	-1.261784000	0.079756000
H	-1.612239000	-2.530885000	0.074003000	H	-1.550149000	-2.540279000	-0.000145000
H	-3.702037000	1.220180000	0.082667000	H	-3.667136000	1.211638000	0.117140000
H	-1.595754000	2.487550000	-0.064323000	H	-1.556988000	2.497318000	0.052847000
B	-0.326838000	0.552635000	-0.075733000	B	-0.278844000	0.559927000	0.000047000

M06-2X/6-311+G(d,p)				SCS-MP2/6-311+G(d,p)			
C	1.841783000	-0.037144000	-1.253922000	C	1.840361000	-0.052763000	-1.270834000
C	2.040591000	-1.054668000	-0.182168000	C	2.023415000	-1.068370000	-0.178956000
C	2.218852000	-0.423037000	1.033549000	C	2.204957000	-0.415177000	1.032697000
C	1.769912000	0.893956000	0.885185000	C	1.757475000	0.913809000	0.867763000
C	1.275486000	1.123225000	-0.432210000	C	1.273583000	1.123279000	-0.464743000
H	1.227982000	-0.373281000	-2.084458000	H	1.221840000	-0.390504000	-2.102892000
H	2.833602000	0.253843000	-1.630605000	H	2.836136000	0.237215000	-1.649790000
H	2.186958000	-2.109271000	-0.372377000	H	2.182450000	-2.127587000	-0.355424000
H	2.466658000	-0.901667000	1.968872000	H	2.441523000	-0.884330000	1.980696000
H	1.245492000	2.131323000	-0.831277000	H	1.241476000	2.128326000	-0.881640000
H	1.705278000	1.620248000	1.687181000	H	1.692451000	1.653953000	1.662233000
N	-0.372975000	-0.827423000	-0.007238000	N	-0.347572000	-0.832400000	0.040668000
C	-1.554197000	-1.436017000	0.026476000	C	-1.544401000	-1.446922000	0.016936000
C	-2.749300000	-0.721888000	0.077176000	C	-2.742319000	-0.723864000	0.061447000
C	-2.728620000	0.684069000	0.064789000	C	-2.728891000	0.692268000	0.079990000
C	-1.543584000	1.404411000	-0.005563000	C	-1.530082000	1.412912000	0.047905000
H	-3.687396000	-1.257733000	0.154673000	H	-3.685800000	-1.263330000	0.116445000
H	-1.578216000	-2.525303000	0.051287000	H	-1.569138000	-2.539806000	0.027190000
H	-3.681418000	1.206799000	0.108989000	H	-3.686479000	1.215012000	0.117565000
H	-1.591499000	2.487967000	-0.049272000	H	-1.577866000	2.501697000	0.014442000
B	-0.320851000	0.553036000	-0.079559000	B	-0.298585000	0.558031000	-0.032171000

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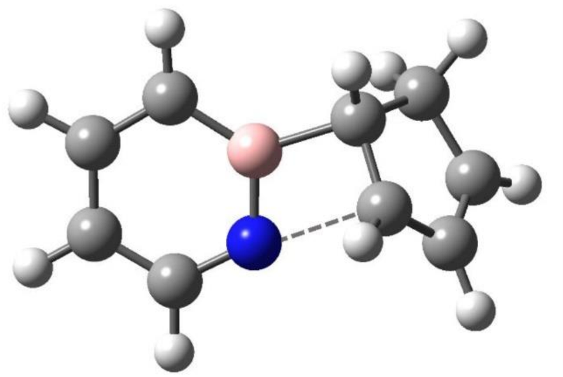

B3LYP/6-311+G(d,p)			
C	-1.639820000	1.356388000	0.345889000
C	-2.844080000	0.756905000	0.008233000
C	-2.916121000	-0.608243000	-0.348954000
C	-1.765615000	-1.391528000	-0.381217000
H	-3.771069000	1.327133000	0.032179000
H	-1.648328000	2.396924000	0.661307000
H	-3.871388000	-1.053031000	-0.607133000
H	-1.851598000	-2.450693000	-0.630785000
C	1.462593000	-0.498307000	0.980831000
C	1.149713000	0.855413000	0.581107000
H	1.112064000	-0.964605000	1.891132000
H	1.100500000	1.592038000	1.385785000
C	2.403431000	-1.090016000	0.083178000
C	2.119790000	1.163082000	-0.572627000
C	2.806703000	-0.146281000	-0.802466000

				H	2.725825000	-2.120975000	0.118078000
				H	3.528317000	-0.307739000	-1.595201000
				H	2.849767000	1.941280000	-0.308816000
				H	1.620257000	1.512778000	-1.482508000
				N	-0.542063000	-0.899707000	-0.152881000
				B	-0.431576000	0.477129000	0.206327000
B3LYP-D3/6-311+G(d,p)				**MP2/6-311+G(d,p)**			
C	-1.637417000	1.359065000	0.347257000	C	-1.652041000	1.323520000	0.464618000
C	-2.839229000	0.756018000	0.007195000	C	-2.825916000	0.615024000	0.269922000
C	-2.906007000	-0.609818000	-0.351708000	C	-2.797483000	-0.716137000	-0.240725000
C	-1.752920000	-1.389923000	-0.383768000	C	-1.603744000	-1.330411000	-0.591098000
H	-3.768560000	1.322439000	0.030556000	H	-3.793770000	1.042225000	0.534407000
H	-1.646969000	2.398665000	0.665316000	H	-1.711110000	2.315996000	0.911045000
H	-3.859621000	-1.057334000	-0.611334000	H	-3.728453000	-1.266915000	-0.358831000
H	-1.834866000	-2.449279000	-0.633296000	H	-1.612064000	-2.363033000	-0.946002000
C	1.456763000	-0.496900000	0.984907000	C	1.082437000	-0.345219000	0.816468000
C	1.149447000	0.859861000	0.586722000	C	1.135547000	1.057874000	0.386515000
H	1.108778000	-0.961725000	1.897086000	H	0.631659000	-0.680830000	1.747015000
H	1.103783000	1.596635000	1.391061000	H	1.082427000	1.811646000	1.173484000
C	2.393238000	-1.091369000	0.083836000	C	2.111669000	-1.099286000	0.113062000
C	2.115229000	1.162555000	-0.571770000	C	2.299173000	1.151250000	-0.608346000
C	2.794787000	-0.150273000	-0.804686000	C	2.823962000	-0.258458000	-0.674927000
H	2.709190000	-2.124276000	0.116324000	H	2.248303000	-2.170587000	0.207092000
H	3.509704000	-0.315315000	-1.602464000	H	3.647692000	-0.560103000	-1.315933000
H	2.850221000	1.937256000	-0.312815000	H	3.070841000	1.851433000	-0.260720000
H	1.610123000	1.511813000	-1.478530000	H	1.976360000	1.493184000	-1.599041000
N	-0.531194000	-0.893477000	-0.155623000	N	-0.405878000	-0.681106000	-0.573932000
B	-0.427178000	0.483325000	0.207193000	B	-0.382308000	0.657881000	-0.042615000
M06-2X/6-311+G(d,p)				**SCS-MP2/6-311+G(d,p)**			
C	-1.651056000	1.316499000	0.456936000	C	-1.657978000	1.320363000	0.469438000
C	-2.818859000	0.628365000	0.248349000	C	-2.833591000	0.621803000	0.268353000
C	-2.810477000	-0.701516000	-0.259013000	C	-2.810826000	-0.712793000	-0.254612000
C	-1.627407000	-1.324044000	-0.584674000	C	-1.621472000	-1.328903000	-0.603941000
H	-3.781419000	1.071968000	0.491730000	H	-3.801084000	1.052400000	0.532007000
H	-1.698486000	2.310951000	0.891393000	H	-1.711334000	2.314122000	0.916223000
H	-3.746414000	-1.232289000	-0.391143000	H	-3.746105000	-1.256138000	-0.380315000
H	-1.644650000	-2.352528000	-0.942277000	H	-1.633999000	-2.358040000	-0.970319000
C	1.132908000	-0.355657000	0.844904000	C	1.112338000	-0.345234000	0.842885000
C	1.139990000	1.033814000	0.414441000	C	1.138147000	1.052445000	0.396282000
H	0.685349000	-0.708290000	1.765424000	H	0.664369000	-0.682344000	1.774273000
H	1.070568000	1.794788000	1.187557000	H	1.085674000	1.814614000	1.176418000
C	2.154893000	-1.093541000	0.118298000	C	2.134906000	-1.100660000	0.124927000
C	2.275127000	1.148617000	-0.605644000	C	2.293847000	1.151865000	-0.614576000
C	2.818412000	-0.249188000	-0.682798000	C	2.829125000	-0.259805000	-0.678747000
H	2.310475000	-2.158234000	0.214802000	H	2.280996000	-2.170596000	0.226255000
H	3.628665000	-0.531077000	-1.344157000	H	3.646919000	-0.558773000	-1.329870000
H	3.045665000	1.857326000	-0.283598000	H	3.065091000	1.858846000	-0.277019000
H	1.929492000	1.481169000	-1.588877000	H	1.958094000	1.485434000	-1.604575000
N	-0.424962000	-0.706029000	-0.529883000	N	-0.410137000	-0.691205000	-0.569693000
B	-0.390511000	0.616841000	-0.010310000	B	-0.385677000	0.640544000	-0.031934000

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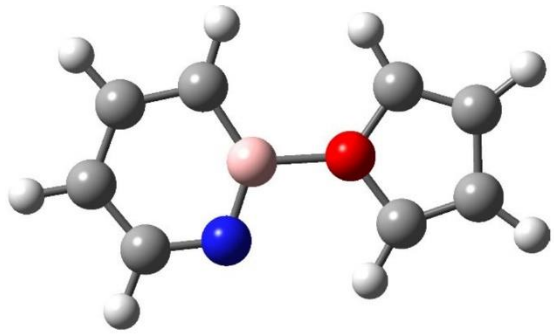

B3LYP/6-311+G(d,p)			
N	1.073426000	-1.207674000	-0.000146000
C	2.413391000	-1.272002000	-0.000206000
C	3.240039000	-0.147573000	-0.000043000
C	2.680554000	1.142797000	0.000103000
C	1.299703000	1.348169000	0.000111000
H	4.316675000	-0.274654000	-0.000049000
H	2.869987000	-2.262714000	-0.000297000
H	3.353586000	1.997194000	0.000191000
H	0.925978000	2.367028000	0.000201000
B	0.569104000	0.065826000	0.000026000
C	-3.193125000	0.671114000	0.000347000
C	-1.930799000	1.140108000	-0.000143000
C	-1.822007000	-1.118983000	0.000361000
H	-4.084952000	1.276903000	0.000576000
H	-1.464901000	2.107861000	-0.000260000
H	-1.229276000	-2.017176000	0.000646000
O	-1.060760000	0.052892000	0.000010000
C	-3.122383000	-0.769621000	-0.000430000
H	-3.952755000	-1.457035000	-0.000799000

B3LYP-D3/6-311+G(d,p)			
N	1.077288000	-1.212733000	-0.000082000
C	2.417526000	-1.270359000	-0.000093000
C	3.239607000	-0.141782000	-0.000021000
C	2.674977000	1.146762000	0.000066000
C	1.293135000	1.345877000	0.000085000
H	4.316774000	-0.264271000	-0.000032000
H	2.878662000	-2.258894000	-0.000158000
H	3.344746000	2.003696000	0.000120000
H	0.912414000	2.361995000	0.000154000
B	0.568970000	0.059324000	0.000005000
C	-3.188294000	0.676589000	0.000032000
C	-1.923251000	1.138599000	0.000081000
C	-1.826657000	-1.121303000	-0.000075000
H	-4.076712000	1.287178000	0.000058000
H	-1.452386000	2.104038000	0.000142000
H	-1.241994000	-2.024910000	-0.000142000
O	-1.059822000	0.046832000	0.000008000
C	-3.125299000	-0.764907000	-0.000013000
H	-3.959256000	-1.447829000	-0.000033000

MP2/6-311+G(d,p)			
N	-1.079216000	-1.224652000	-0.140655000
C	-2.427306000	-1.259548000	-0.066448000
C	-3.229098000	-0.119995000	0.065560000
C	-2.648772000	1.161628000	0.141036000
C	-1.258344000	1.343336000	0.087292000
H	-4.308789000	-0.232312000	0.113762000
H	-2.906487000	-2.240222000	-0.115628000
H	-3.305224000	2.024781000	0.253290000
H	-0.864347000	2.353406000	0.167572000
B	-0.560447000	0.048236000	-0.066480000
C	3.174445000	0.680438000	0.027383000
C	1.906752000	1.116169000	-0.201056000
C	1.808720000	-1.119998000	0.090967000
H	4.053922000	1.307113000	0.051931000
H	1.436409000	2.063948000	-0.404355000
H	1.224085000	-2.025480000	0.139624000
O	1.059432000	0.020350000	-0.181987000
C	3.110151000	-0.746310000	0.213824000
H	3.932434000	-1.416973000	0.415340000

M06-2X/6-311+G(d,p)			
N	1.061730000	-1.212326000	-0.000085000
C	2.397947000	-1.266689000	-0.000091000
C	3.220504000	-0.143133000	-0.000022000
C	2.656216000	1.142926000	0.000066000
C	1.279915000	1.346117000	0.000087000
H	4.296151000	-0.267174000	-0.000034000
H	2.858964000	-2.254376000	-0.000157000
H	3.326929000	1.998374000	0.000122000
H	0.906552000	2.364141000	0.000162000
B	0.555030000	0.059998000	-0.000001000
C	-3.166353000	0.678084000	0.000052000
C	-1.902822000	1.132590000	0.000068000
C	-1.807619000	-1.115398000	-0.000057000
H	-4.052131000	1.291306000	0.000089000
H	-1.426076000	2.096195000	0.000116000
H	-1.219239000	-2.017646000	-0.000116000
O	-1.050566000	0.045661000	0.000007000
C	-3.104083000	-0.764662000	-0.000030000
H	-3.936114000	-1.448824000	-0.000066000

SCS-MP2/6-311+G(d,p)			
N	1.073557000	-1.231306000	0.142517000
C	2.424039000	-1.271994000	0.077496000
C	3.235273000	-0.137736000	-0.040097000
C	2.660660000	1.151345000	-0.107622000
C	1.271926000	1.341310000	-0.060237000
H	4.315467000	-0.255860000	-0.082193000
H	2.896661000	-2.256921000	0.122017000
H	3.324167000	2.011901000	-0.206662000
H	0.884457000	2.355710000	-0.130363000
B	0.561873000	0.045378000	0.075927000
C	-3.178790000	0.689672000	-0.045098000
C	-1.910925000	1.128630000	0.158443000
C	-1.821126000	-1.123082000	-0.041060000
H	-4.057777000	1.317164000	-0.092405000
H	-1.439456000	2.084676000	0.318030000
H	-1.242505000	-2.033765000	-0.057869000
O	-1.060856000	0.028005000	0.180189000
C	-3.119594000	-0.752039000	-0.173287000
H	-3.946632000	-1.427138000	-0.342247000

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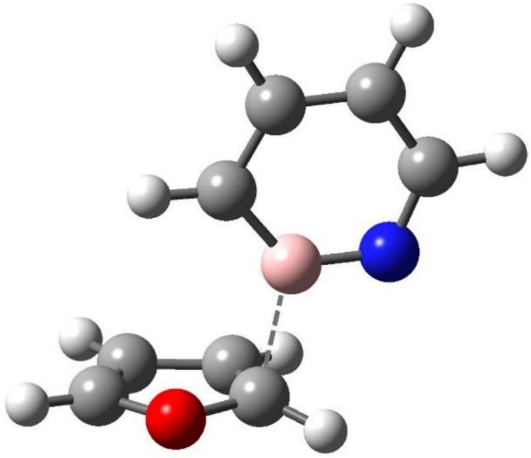

B3LYP/6-311+G(d,p)			
N	-1.268023000	-1.303893000	-0.005987000
C	-2.556628000	-0.959309000	0.002180000
C	-3.003435000	0.368482000	0.013483000
C	-2.085416000	1.431398000	0.030315000
C	-0.710562000	1.199187000	0.032569000
H	-4.069047000	0.570518000	0.026110000
H	-3.296900000	-1.761155000	0.007378000
H	-2.470529000	2.448196000	0.056303000
H	-0.038180000	2.049960000	0.068377000
B	-0.370623000	-0.244518000	-0.027944000
C	1.280177000	-0.842460000	-0.662539000
C	1.400662000	-0.910266000	0.731143000
C	2.294995000	0.145894000	1.107383000
H	1.006705000	-1.594215000	-1.383074000
H	0.994690000	-1.686787000	1.357092000
H	2.583605000	0.427987000	2.106496000
C	2.677283000	0.744238000	-0.048342000
O	2.115445000	0.155225000	-1.130023000
H	3.312915000	1.590548000	-0.254017000

B3LYP-D3/6-311+G(d,p)			
N	-1.276454000	-1.310686000	-0.005922000
C	-2.561445000	-0.951220000	0.003023000
C	-2.994543000	0.381860000	0.014103000
C	-2.066081000	1.436694000	0.030332000
C	-0.694042000	1.189435000	0.032269000
H	-4.058139000	0.594305000	0.027802000
H	-3.310522000	-1.744803000	0.009380000
H	-2.441348000	2.457166000	0.056949000
H	-0.007151000	2.028342000	0.069368000
B	-0.372511000	-0.257935000	-0.029797000
C	1.281960000	-0.852552000	-0.660607000
C	1.407719000	-0.918862000	0.733048000
C	2.287073000	0.150505000	1.106511000
H	1.014642000	-1.608905000	-1.379173000
H	1.008261000	-1.697369000	1.361092000
H	2.570318000	0.439846000	2.104906000
C	2.658063000	0.754058000	-0.050892000
O	2.103813000	0.155622000	-1.131271000
H	3.278944000	1.611411000	-0.256438000

MP2/6-311+G(d,p)			
N	-1.240966000	-1.324364000	0.058930000
C	-2.525700000	-0.945190000	-0.008355000
C	-2.947062000	0.396788000	-0.054852000
C	-2.014559000	1.450958000	-0.015009000
C	-0.641022000	1.189516000	0.074517000
H	-4.011342000	0.614393000	-0.110472000
H	-3.285170000	-1.731314000	-0.028416000
H	-2.384900000	2.476117000	-0.034344000
H	0.046269000	2.031333000	0.137788000
B	-0.316558000	-0.266162000	0.081659000
C	1.265505000	-0.900227000	-0.643557000
C	1.331793000	-0.876481000	0.771480000
C	2.211090000	0.219341000	1.089981000
H	0.972842000	-1.685367000	-1.323786000
H	0.998057000	-1.671525000	1.422736000
H	2.473243000	0.581704000	2.073493000
C	2.596083000	0.759418000	-0.102625000
O	2.074152000	0.076323000	-1.158664000
H	3.210565000	1.610699000	-0.357977000

M06-2X/6-311+G(d,p)			
N	-1.256890000	-1.308173000	0.056032000
C	-2.538338000	-0.947226000	-0.004137000
C	-2.969286000	0.380855000	-0.046099000
C	-2.042008000	1.432688000	-0.015835000
C	-0.673388000	1.192655000	0.057896000
H	-4.030586000	0.593153000	-0.095496000
H	-3.285730000	-1.740582000	-0.023058000
H	-2.417905000	2.452336000	-0.039721000
H	0.007947000	2.034890000	0.101977000
B	-0.363866000	-0.253778000	0.078767000
C	1.322559000	-0.902056000	-0.644967000
C	1.364114000	-0.885526000	0.743327000
C	2.228343000	0.216937000	1.088653000
H	0.963208000	-1.636199000	-1.345210000
H	0.980188000	-1.656069000	1.390965000
H	2.477715000	0.560563000	2.078236000
C	2.617979000	0.761841000	-0.081561000
O	2.104036000	0.087848000	-1.139067000
H	3.230589000	1.614217000	-0.324878000

SCS-MP2/6-311+G(d,p)			
N	-1.244351000	-1.328545000	0.031526000
C	-2.534892000	-0.955165000	-0.008034000
C	-2.965102000	0.384383000	-0.005838000
C	-2.034836000	1.443491000	0.052004000
C	-0.657114000	1.189946000	0.111703000
H	-4.031683000	0.598379000	-0.041275000
H	-3.288807000	-1.746725000	-0.045280000
H	-2.410800000	2.467670000	0.065058000
H	0.026494000	2.034699000	0.181409000
B	-0.333037000	-0.265793000	0.078913000
C	1.290495000	-0.885897000	-0.679843000
C	1.352999000	-0.908157000	0.727494000
C	2.235976000	0.181981000	1.086849000
H	0.972532000	-1.633914000	-1.390220000
H	1.011995000	-1.720016000	1.354233000
H	2.497811000	0.508339000	2.083621000
C	2.618968000	0.759856000	-0.085660000
O	2.088460000	0.113269000	-1.166765000
H	3.233449000	1.619110000	-0.315212000

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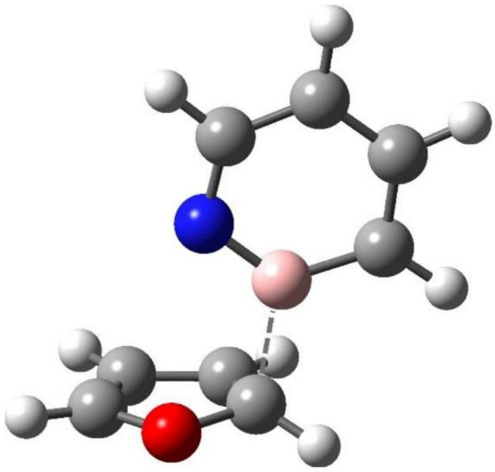

B3LYP/6-311+G(d,p)

N	0.536444000	-1.010259000	-0.018245000
C	1.788633000	-1.461171000	0.030988000
C	2.909443000	-0.619804000	0.062200000
C	2.750244000	0.774765000	0.031551000
C	1.484989000	1.357832000	-0.040134000
H	3.900257000	-1.054953000	0.135571000
H	1.942768000	-2.541016000	0.077866000
H	3.640788000	1.398738000	0.066018000
H	1.410473000	2.441300000	-0.087378000
B	0.381635000	0.359867000	-0.116684000
C	-2.333466000	-0.287247000	1.058933000
C	-2.530994000	-0.817019000	-0.191402000
H	-2.651685000	-0.717517000	1.993905000
H	-3.032245000	-1.716506000	-0.513824000
C	-1.258025000	0.944620000	-0.519795000
H	-1.155273000	1.836634000	-1.121006000
O	-1.996982000	-0.067399000	-1.151533000
C	-1.563741000	0.873390000	0.861485000
H	-1.225001000	1.572793000	1.609289000

B3LYP-D3/6-311+G(d,p)

N	0.531005000	-1.011565000	-0.022018000
C	1.783422000	-1.461729000	0.029302000
C	2.904989000	-0.620041000	0.063327000
C	2.747335000	0.775100000	0.033088000
C	1.482053000	1.358407000	-0.041169000
H	3.895288000	-1.055973000	0.139015000
H	1.937789000	-2.541471000	0.076008000
H	3.638427000	1.398081000	0.070333000
H	1.403341000	2.441449000	-0.087744000
B	0.380979000	0.359309000	-0.120421000
C	-2.324106000	-0.286234000	1.062191000
C	-2.523658000	-0.819902000	-0.186611000
H	-2.634257000	-0.717891000	1.999077000
H	-3.019405000	-1.724263000	-0.503941000
C	-1.259071000	0.946735000	-0.522617000
H	-1.156265000	1.838156000	-1.124926000
O	-1.997093000	-0.068979000	-1.150516000
C	-1.559618000	0.877557000	0.860375000
H	-1.218177000	1.578799000	1.605224000

MP2/6-311+G(d,p)

N	0.483445000	-1.053622000	0.055101000
C	1.756136000	-1.468687000	0.015386000
C	2.869080000	-0.603856000	-0.007102000
C	2.699188000	0.791799000	-0.004002000
C	1.412204000	1.350251000	0.014229000
H	3.869265000	-1.031148000	-0.017098000
H	1.937430000	-2.547302000	0.017502000
H	3.584086000	1.428282000	-0.018324000
H	1.313285000	2.436082000	-0.000307000
B	0.322596000	0.334188000	0.030810000
C	-2.182944000	-0.177063000	1.112343000
C	-2.509875000	-0.816923000	-0.049324000
H	-2.410796000	-0.510482000	2.113817000
H	-3.042031000	-1.733931000	-0.254270000
C	-1.295503000	0.891830000	-0.681395000
H	-1.077648000	1.661171000	-1.407320000
O	-2.040608000	-0.156864000	-1.139502000
C	-1.376133000	0.945152000	0.732171000
H	-1.078732000	1.781633000	1.348422000

M06-2X/6-311+G(d,p)

N	0.514411000	-1.035423000	0.031803000
C	1.775431000	-1.457597000	0.020608000
C	2.883396000	-0.602183000	0.013813000
C	2.707863000	0.787107000	0.007124000
C	1.435080000	1.354384000	0.002765000
H	3.880580000	-1.025673000	0.019853000
H	1.948902000	-2.534204000	0.027026000
H	3.591002000	1.420781000	0.003684000
H	1.339085000	2.435883000	-0.012780000
B	0.366555000	0.331539000	0.007504000
C	-2.200006000	-0.154015000	1.116168000
C	-2.516777000	-0.827495000	-0.011559000
H	-2.419736000	-0.446623000	2.128294000
H	-3.037424000	-1.754401000	-0.184652000
C	-1.349770000	0.877886000	-0.697217000
H	-1.075545000	1.591243000	-1.455960000
O	-2.058292000	-0.199104000	-1.113577000
C	-1.420829000	0.971138000	0.687892000
H	-1.080504000	1.800738000	1.285446000

SCS-MP2/6-311+G(d,p)

N	0.489826000	-1.064864000	0.004587000
C	1.767477000	-1.474353000	-0.023767000
C	2.877260000	-0.607866000	0.034546000
C	2.700323000	0.787166000	0.115965000
C	1.411241000	1.343174000	0.134922000
H	3.880064000	-1.030705000	0.023071000
H	1.951513000	-2.551406000	-0.082829000
H	3.583486000	1.426028000	0.162058000
H	1.308241000	2.428016000	0.185936000
B	0.331295000	0.318373000	0.063693000
C	-2.233497000	-0.250184000	1.061278000
C	-2.538906000	-0.823804000	-0.137339000
H	-2.478009000	-0.633841000	2.041240000
H	-3.067913000	-1.727415000	-0.403504000
C	-1.318179000	0.921502000	-0.653036000
H	-1.061771000	1.717502000	-1.336809000
O	-2.043773000	-0.105737000	-1.184423000
C	-1.420453000	0.898468000	0.752110000
H	-1.125248000	1.695492000	1.420276000

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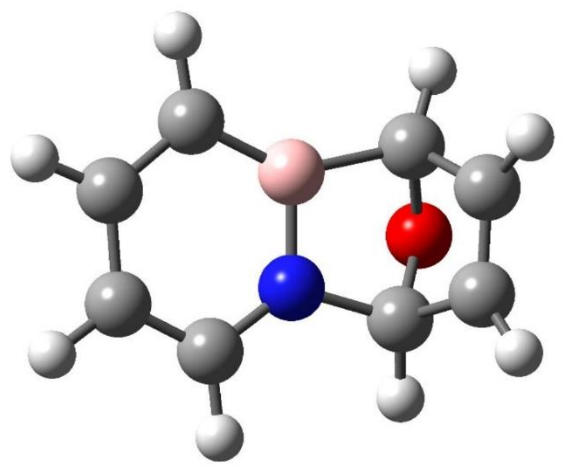

B3LYP/6-311+G(d,p)			
C	1.380001000	1.129152000	-0.340529000
C	2.029276000	0.650497000	0.956923000
C	1.950743000	-0.681684000	0.955938000
C	1.219385000	-1.027478000	-0.349018000
O	1.682628000	-0.020266000	-1.220284000
H	1.762476000	2.045457000	-0.780134000
H	2.393700000	1.298022000	1.742487000
H	2.239673000	-1.387443000	1.721129000
H	1.325579000	-2.024045000	-0.771960000
N	-0.214997000	-0.607646000	-0.171325000
B	-0.211508000	0.834721000	-0.166847000
C	-1.310355000	-1.372526000	-0.010037000
C	-1.543375000	1.493637000	0.015868000
C	-2.534435000	-0.762726000	0.157485000
H	-1.194046000	-2.451753000	-0.029977000
C	-2.635052000	0.653548000	0.164914000
H	-1.715179000	2.565126000	0.036606000
H	-3.419220000	-1.375074000	0.273562000
H	-3.628622000	1.077241000	0.294814000

B3LYP-D3/6-311+G(d,p)			
C	1.380395000	1.128663000	-0.340659000
C	2.018568000	0.650903000	0.963673000
C	1.940068000	-0.681083000	0.963001000
C	1.219916000	-1.027254000	-0.348892000
O	1.690627000	-0.021126000	-1.217933000
H	1.766535000	2.045788000	-0.775823000
H	2.372173000	1.299667000	1.752612000
H	2.218324000	-1.386950000	1.731517000
H	1.326496000	-2.025090000	-0.768778000
N	-0.214486000	-0.607023000	-0.180843000
B	-0.211185000	0.834661000	-0.175168000
C	-1.307405000	-1.373113000	-0.012872000
C	-1.541095000	1.494273000	0.011899000
C	-2.530686000	-0.763098000	0.158815000
H	-1.187516000	-2.451622000	-0.031354000
C	-2.631743000	0.653501000	0.165610000
H	-1.711955000	2.565731000	0.034375000
H	-3.414797000	-1.375414000	0.279086000
H	-3.625051000	1.076007000	0.300122000

MP2/6-311+G(d,p)			
C	1.389894000	1.125142000	-0.340787000
C	2.007987000	0.652282000	0.970383000
C	1.919836000	-0.693341000	0.968153000
C	1.217370000	-1.021839000	-0.349104000
O	1.702060000	-0.021122000	-1.211536000
H	1.788900000	2.039013000	-0.775886000
H	2.353391000	1.298309000	1.769148000
H	2.181025000	-1.402069000	1.743968000
H	1.316611000	-2.018838000	-0.778426000
N	-0.211210000	-0.596802000	-0.188623000
B	-0.204305000	0.842175000	-0.179010000
C	-1.299146000	-1.376934000	-0.018101000
C	-1.539041000	1.498140000	0.010534000
C	-2.529671000	-0.764094000	0.156324000
H	-1.172107000	-2.457430000	-0.042806000
C	-2.637066000	0.650120000	0.165505000
H	-1.721410000	2.570164000	0.035674000
H	-3.411502000	-1.384221000	0.277542000
H	-3.632369000	1.073932000	0.301042000

M06-2X/6-311+G(d,p)			
C	1.384745000	1.119272000	-0.348506000
C	2.007673000	0.647879000	0.964343000
C	1.923252000	-0.679850000	0.968122000
C	1.214158000	-1.021776000	-0.348731000
O	1.691898000	-0.022153000	-1.204655000
H	1.777515000	2.032739000	-0.781938000
H	2.360372000	1.297468000	1.752597000
H	2.194764000	-1.385188000	1.739003000
H	1.319385000	-2.018728000	-0.769245000
N	-0.212409000	-0.600647000	-0.188052000
B	-0.209156000	0.835519000	-0.179775000
C	-1.301895000	-1.367982000	-0.017899000
C	-1.540817000	1.493808000	0.012844000
C	-2.521620000	-0.765323000	0.157638000
H	-1.177455000	-2.446014000	-0.038138000
C	-2.622235000	0.651898000	0.166801000
H	-1.717461000	2.563163000	0.037773000
H	-3.403596000	-1.378434000	0.280026000
H	-3.615624000	1.071590000	0.304738000

SCS-MP2/6-311+G(d,p)			
C	1.389287000	1.128688000	-0.346410000
C	2.024200000	0.656404000	0.965124000
C	1.933830000	-0.688401000	0.966338000
C	1.217574000	-1.023170000	-0.348880000
O	1.701137000	-0.021300000	-1.217538000
H	1.786250000	2.042122000	-0.786606000
H	2.381831000	1.305301000	1.757261000
H	2.205085000	-1.397596000	1.739570000
H	1.320234000	-2.021583000	-0.775752000
N	-0.210462000	-0.598744000	-0.185264000
B	-0.206319000	0.840479000	-0.178634000
C	-1.305077000	-1.378922000	-0.012256000
C	-1.546314000	1.501407000	0.012031000
C	-2.532933000	-0.767669000	0.161169000
H	-1.178573000	-2.460022000	-0.033775000
C	-2.641038000	0.654870000	0.168475000
H	-1.726821000	2.574764000	0.035089000
H	-3.416749000	-1.386146000	0.284107000
H	-3.637958000	1.076939000	0.304340000

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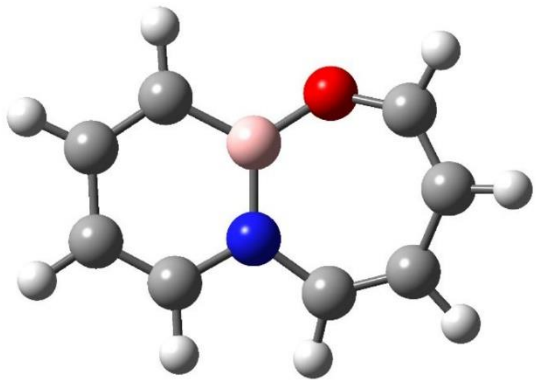

B3LYP/6-311+G(d,p)

N	0.271476000	0.704651000	-0.079395000
C	1.476971000	1.357909000	0.092875000
C	2.670012000	0.710259000	0.188768000
C	2.728314000	-0.711346000	0.102878000
C	1.590538000	-1.452353000	-0.063405000
H	3.570267000	1.295264000	0.324645000
H	1.419271000	2.438450000	0.147584000
H	3.702668000	-1.188399000	0.171738000
H	1.665897000	-2.533158000	-0.129439000
B	0.253127000	-0.752414000	-0.157967000
C	-2.715359000	-0.048620000	0.336345000
C	-2.134112000	-1.245077000	0.190253000
C	-0.862585000	1.551120000	-0.246007000
H	-3.713539000	-0.044374000	0.759387000
H	-2.642583000	-2.157811000	0.483447000
H	-0.603920000	2.563071000	-0.534982000
O	-0.916291000	-1.494446000	-0.364288000
C	-2.150055000	1.233044000	-0.059730000
H	-2.856051000	2.042426000	-0.214340000

B3LYP-D3/6-311+G(d,p)

N	0.267542000	0.706045000	-0.091113000
C	1.469514000	1.360879000	0.098363000
C	2.661824000	0.712847000	0.205696000
C	2.723272000	-0.708658000	0.115031000
C	1.588433000	-1.450915000	-0.067646000
H	3.559966000	1.297822000	0.355202000
H	1.411694000	2.441231000	0.158533000
H	3.697642000	-1.184124000	0.193941000
H	1.663862000	-2.531384000	-0.137011000
B	0.252846000	-0.750616000	-0.176345000
C	-2.698134000	-0.054652000	0.372062000
C	-2.114012000	-1.247801000	0.208255000
C	-0.869453000	1.545567000	-0.268773000
H	-3.677468000	-0.051134000	0.837201000
H	-2.598979000	-2.164078000	0.529989000
H	-0.618787000	2.552078000	-0.583493000
O	-0.919668000	-1.482651000	-0.403548000
C	-2.153004000	1.224029000	-0.060261000
H	-2.868254000	2.023784000	-0.222826000

MP2/6-311+G(d,p)

N	0.244138000	0.707886000	-0.161828000
C	1.424340000	1.378876000	0.089741000
C	2.616343000	0.723281000	0.265064000
C	2.682997000	-0.697419000	0.192743000
C	1.551664000	-1.447541000	-0.058080000
H	3.504029000	1.314985000	0.461949000
H	1.352922000	2.461837000	0.145917000
H	3.651358000	-1.175963000	0.334613000
H	1.644128000	-2.529836000	-0.116678000
B	0.229081000	-0.742477000	-0.267141000
C	-2.569871000	-0.091348000	0.564641000
C	-1.970103000	-1.267150000	0.278345000
C	-0.901309000	1.521443000	-0.358043000
H	-3.415921000	-0.111800000	1.245860000
H	-2.301612000	-2.205155000	0.720069000
H	-0.688344000	2.509425000	-0.758532000
O	-0.960918000	-1.402812000	-0.638490000
C	-2.165211000	1.176336000	-0.021451000
H	-2.926683000	1.937325000	-0.174529000

M06-2X/6-311+G(d,p)

N	0.257029000	0.701393000	-0.112401000
C	1.446526000	1.361979000	0.106258000
C	2.634292000	0.722074000	0.238353000
C	2.701085000	-0.701352000	0.140613000
C	1.581245000	-1.445917000	-0.075938000
H	3.525712000	1.308908000	0.411844000
H	1.377099000	2.441607000	0.169753000
H	3.674917000	-1.172282000	0.241323000
H	1.666965000	-2.524583000	-0.151384000
B	0.245639000	-0.746004000	-0.214783000
C	-2.645366000	-0.069266000	0.450743000
C	-2.059640000	-1.249288000	0.243920000
C	-0.880447000	1.528380000	-0.311029000
H	-3.572471000	-0.067153000	1.010758000
H	-2.486463000	-2.171289000	0.625005000
H	-0.639512000	2.520834000	-0.674455000
O	-0.931070000	-1.449363000	-0.488356000
C	-2.151003000	1.203241000	-0.062990000
H	-2.885246000	1.980021000	-0.244850000

SCS-MP2/6-311+G(d,p)

N	0.247801000	0.708849000	-0.142193000
C	1.441474000	1.362872000	0.129707000
C	2.627004000	0.697052000	0.282550000
C	2.685172000	-0.729921000	0.155614000
C	1.550434000	-1.460907000	-0.114585000
H	3.521011000	1.273826000	0.498928000
H	1.379185000	2.444793000	0.217215000
H	3.652885000	-1.217672000	0.275332000
H	1.631786000	-2.542362000	-0.211183000
B	0.221188000	-0.737667000	-0.278447000
C	-2.630604000	-0.041538000	0.457735000
C	-2.046290000	-1.230469000	0.207746000
C	-0.879776000	1.552064000	-0.363630000
H	-3.519943000	-0.043346000	1.083257000
H	-2.437542000	-2.159967000	0.617829000
H	-0.630990000	2.536834000	-0.752840000
O	-0.966924000	-1.409205000	-0.621579000
C	-2.162771000	1.230969000	-0.093338000
H	-2.904264000	2.004063000	-0.284863000

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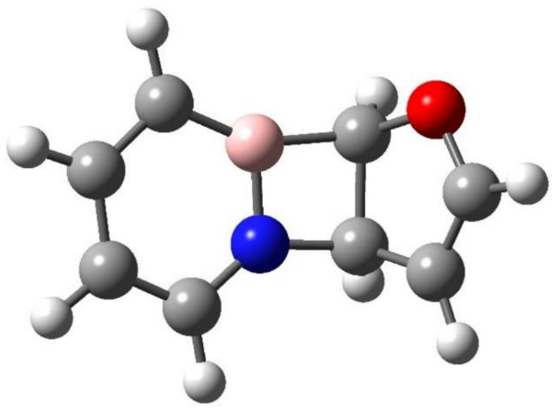


B3LYP/6-311+G(d,p)			
N	-0.40846300	-0.60640500	-0.34167700
C	-1.46706500	-1.38932900	-0.05694600
C	-2.63644900	-0.74982500	0.29342500
C	-2.70902300	0.67130200	0.35219900
C	-1.64688400	1.51716600	0.07074600
H	-3.51227600	-1.34158700	0.52788800
H	-1.36973100	-2.46839100	-0.10965600
H	-3.66931000	1.09519000	0.63771600
H	-1.80813900	2.58732500	0.14652500
B	-0.37543500	0.82630100	-0.31627000
C	1.98354800	-1.15200000	0.35038800
C	2.54489700	-0.03308900	0.82705500
H	2.19517000	-2.15401600	0.69106100
H	3.26903400	0.07840100	1.62337800
C	1.17510200	0.80015800	-0.77733200
H	1.50517400	1.24213700	-1.71666900
O	2.17304000	1.13027600	0.24007400
C	1.02496200	-0.77097600	-0.73846500
H	1.12764500	-1.32838000	-1.67416500

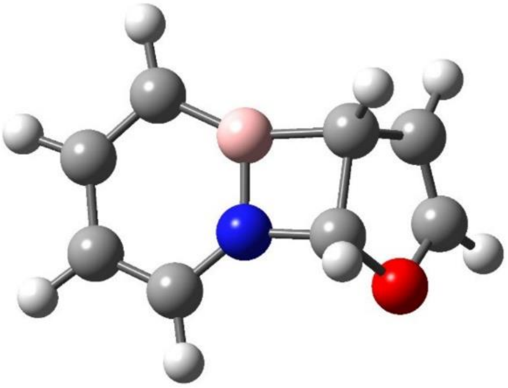
B3LYP-D3/6-311+G(d,p)			
N	-0.40592700	0.60311400	0.35021600
C	-1.45906100	1.38989500	0.05825500
C	-2.62886700	0.75368200	-0.29735600
C	-2.70515700	-0.66787600	-0.35526100
C	-1.64685700	-1.51741400	-0.06832700
H	-3.50155700	1.34781800	-0.53735600
H	-1.35501600	2.46822300	0.10922500
H	-3.66524500	-1.08876100	-0.64586400
H	-1.81009500	-2.58711900	-0.14579300
B	-0.37586600	-0.82935800	0.32464500
C	1.97793000	1.15335300	-0.34811300
C	2.53337700	0.03563700	-0.83447100
H	2.18342100	2.15635500	-0.68889700
H	3.24926200	-0.07174900	-1.63898100
C	1.17699200	-0.80381400	0.77923500
H	1.51580000	-1.24693500	1.71493300
O	2.16631500	-1.13035300	-0.24924700
C	1.02559800	0.76778800	0.74447400
H	1.13000100	1.32247400	1.68135500

MP2/6-311+G(d,p)			
N	-0.40134200	0.59953500	0.36282400
C	-1.44901100	1.39720500	0.06055600
C	-2.62065000	0.75006000	-0.30168000
C	-2.69751400	-0.66997900	-0.35991500
C	-1.63302600	-1.52514600	-0.06135700
H	-3.49290700	1.34653100	-0.55008900
H	-1.34244200	2.47812700	0.11025100
H	-3.65677400	-1.09432200	-0.65730700
H	-1.80525300	-2.59578700	-0.14187700
B	-0.36266000	-0.83471000	0.34344600
C	1.95347400	1.16256800	-0.35044400
C	2.49900100	0.03506000	-0.85693400
H	2.15081100	2.16562600	-0.70384500
H	3.19028600	-0.07129900	-1.68568000
C	1.19357100	-0.80004600	0.78729700
H	1.55727100	-1.23255200	1.72073800
O	2.15578800	-1.13041200	-0.25969000
C	1.02801600	0.76765800	0.75464200
H	1.13223500	1.31950800	1.69534900

M06-2X/6-311+G(d,p)			
N	-0.40507700	0.59963600	0.35698000
C	-1.45868600	1.38393300	0.06641200
C	-2.62113400	0.74918100	-0.29250600
C	-2.68864900	-0.67316600	-0.35731400
C	-1.63468200	-1.51927700	-0.07628600
H	-3.49562200	1.33950600	-0.53086700
H	-1.35622100	2.46193700	0.12349300
H	-3.64673800	-1.09492400	-0.65106100
H	-1.79753200	-2.58740300	-0.16092400
B	-0.36591000	-0.82662200	0.32326000
C	1.95448300	1.15168000	-0.36535000
C	2.51391200	0.03587900	-0.83951200
H	2.14739100	2.15079200	-0.72254700
H	3.22277500	-0.07709100	-1.64876900
C	1.18580800	-0.79616600	0.78001100
H	1.51518600	-1.22990300	1.72200000
O	2.16533500	-1.11911800	-0.23297400
C	1.01915200	0.76768700	0.74188000
H	1.13194500	1.32718800	1.67328900

SCS-MP2/6-311+G(d,p)			
N	-0.401937000	-0.598843000	-0.356733000
C	-1.456948000	-1.398710000	-0.056910000
C	-2.626912000	-0.755471000	0.304023000
C	-2.705902000	0.673026000	0.364133000
C	-1.644570000	1.527579000	0.069153000
H	-3.500862000	-1.351835000	0.550479000
H	-1.349722000	-2.479887000	-0.109391000
H	-3.667814000	1.094259000	0.660431000
H	-1.815866000	2.599311000	0.148841000
B	-0.367740000	0.833106000	-0.334982000
C	1.967141000	-1.158868000	0.344776000
C	2.522950000	-0.031236000	0.836426000
H	2.165110000	-2.161803000	0.701155000
H	3.228438000	0.079244000	1.653232000
C	1.189914000	0.802907000	-0.793248000
H	1.535966000	1.234718000	-1.734833000
O	2.169239000	1.136392000	0.237900000
C	1.026210000	-0.768079000	-0.757261000
H	1.129102000	-1.321553000	-1.697917000

5g



B3LYP/6-311+G(d,p)

C	-1.729531000	1.492558000	-0.024408000
C	-2.721385000	0.579321000	-0.335885000
C	-2.546402000	-0.838643000	-0.320893000
C	-1.341399000	-1.402040000	0.022835000
H	-3.709437000	0.938913000	-0.615283000
H	-1.972419000	2.549048000	-0.069614000
H	-3.376940000	-1.482336000	-0.581236000
H	-1.161075000	-2.470760000	0.050118000
C	2.110136000	1.110526000	-0.420378000
C	2.473746000	-0.089429000	-0.869980000
H	2.425189000	2.051267000	-0.846590000
H	3.110502000	-0.368527000	-1.696141000
C	1.050116000	-0.616606000	0.796393000
H	1.172380000	-1.151997000	1.738875000
O	1.960060000	-1.161763000	-0.156639000
C	1.164052000	0.956350000	0.745583000
H	1.488771000	1.462364000	1.657435000
B	-0.403039000	0.887429000	0.339510000
N	-0.342608000	-0.546178000	0.336913000

B3LYP-D3/6-311+G(d,p)

C	-1.726442000	1.492006000	-0.021243000
C	-2.714025000	0.576067000	-0.340176000
C	-2.535997000	-0.842142000	-0.325682000
C	-1.331718000	-1.402886000	0.025822000
H	-3.700732000	0.933351000	-0.627208000
H	-1.970400000	2.548107000	-0.069550000
H	-3.362858000	-1.487462000	-0.593483000
H	-1.145000000	-2.470364000	0.051225000
C	2.095092000	1.111045000	-0.429914000
C	2.454238000	-0.089404000	-0.882386000
H	2.398725000	2.051344000	-0.864765000
H	3.077207000	-0.367282000	-1.719558000
C	1.053527000	-0.614867000	0.802535000
H	1.181559000	-1.149536000	1.744590000
O	1.954801000	-1.161465000	-0.158327000
C	1.166485000	0.958880000	0.750336000
H	1.502924000	1.466574000	1.656708000
B	-0.401647000	0.888920000	0.351723000
N	-0.339794000	-0.544257000	0.350613000

MP2/6-311+G(d,p)

C	-1.735663000	1.487409000	-0.007949000
C	-2.714781000	0.550977000	-0.339086000
C	-2.513274000	-0.862610000	-0.331157000
C	-1.297248000	-1.415593000	0.025823000
H	-3.707250000	0.897370000	-0.629009000
H	-2.005651000	2.539762000	-0.054426000
H	-3.329483000	-1.522567000	-0.607067000
H	-1.091799000	-2.482571000	0.049431000
C	2.050202000	1.112270000	-0.479138000
C	2.410811000	-0.110740000	-0.904686000
H	2.323326000	2.038280000	-0.968327000
H	3.003011000	-0.412073000	-1.758937000
C	1.067063000	-0.580891000	0.821001000
H	1.188488000	-1.086434000	1.781503000
O	1.962943000	-1.158147000	-0.117606000
C	1.173660000	0.987047000	0.740963000
H	1.543974000	1.512643000	1.625388000
B	-0.399706000	0.900603000	0.365655000
N	-0.324892000	-0.532780000	0.359914000

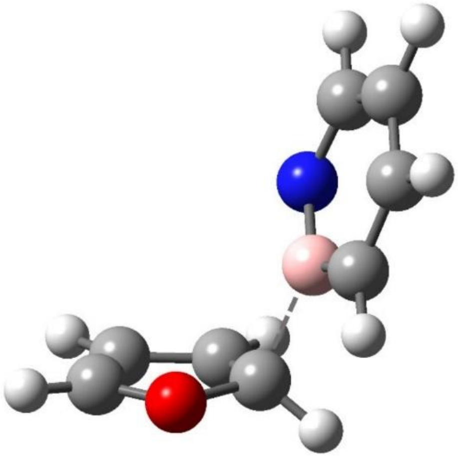
M06-2X/6-311+G(d,p)

C	-1.727088000	1.487227000	-0.015434000
C	-2.702200000	0.568508000	-0.335843000
C	-2.519330000	-0.850044000	-0.327232000
C	-1.317191000	-1.401547000	0.023176000
H	-3.690493000	0.920307000	-0.621944000
H	-1.980520000	2.540080000	-0.060425000
H	-3.342307000	-1.497268000	-0.598446000
H	-1.122773000	-2.467601000	0.046980000
C	2.072739000	1.104991000	-0.451712000
C	2.426758000	-0.098511000	-0.889266000
H	2.366447000	2.037913000	-0.907365000
H	3.036437000	-0.387242000	-1.732033000
C	1.057188000	-0.600326000	0.807939000
H	1.178678000	-1.122513000	1.756538000
O	1.948657000	-1.152719000	-0.138573000
C	1.168656000	0.965166000	0.746879000
H	1.517950000	1.480957000	1.640901000
B	-0.397783000	0.887519000	0.355158000
N	-0.331565000	-0.539037000	0.351077000

SCS-MP2/6-311+G(d,p)

C	-1.732269000	1.505076000	-0.002378000
C	-2.718488000	0.584070000	-0.341364000
C	-2.530409000	-0.840184000	-0.346213000
C	-1.322497000	-1.406580000	0.004029000
H	-3.709116000	0.941342000	-0.627554000
H	-1.990074000	2.561905000	-0.036354000
H	-3.355684000	-1.487649000	-0.628066000
H	-1.127619000	-2.476168000	0.018032000
C	2.088996000	1.105944000	-0.430798000
C	2.445843000	-0.112188000	-0.871632000
H	2.386211000	2.039309000	-0.893253000
H	3.059722000	-0.403112000	-1.715019000
C	1.055539000	-0.606128000	0.819265000
H	1.164050000	-1.129657000	1.772430000
O	1.961465000	-1.173561000	-0.120376000
C	1.175482000	0.965832000	0.766679000
H	1.529941000	1.470538000	1.670808000
B	-0.397319000	0.896198000	0.367495000
N	-0.333057000	-0.535491000	0.344884000

$TS_{5b\text{-}5c}$



B3LYP/6-311+G(d,p)

N	-1.049385000	-0.731670000	0.718673000
C	-2.348140000	-0.480420000	0.942042000
C	-3.088300000	0.479706000	0.251331000
C	-2.480270000	1.252537000	-0.753644000
C	-1.137686000	1.086029000	-1.086834000
H	-4.136369000	0.622757000	0.491659000
H	-2.847576000	-1.070818000	1.713168000
H	-3.084160000	1.991124000	-1.277936000
H	-0.705881000	1.701738000	-1.870602000
B	-0.464447000	0.040571000	-0.267941000
C	1.283027000	-0.235288000	-0.636031000
C	1.730526000	-1.270020000	0.217606000
C	2.570650000	-0.719553000	1.178271000
H	1.240769000	-0.320200000	-1.717093000
H	1.368406000	-2.285563000	0.175467000
H	3.014971000	-1.204199000	2.032300000
C	2.694303000	0.617948000	0.836290000
O	2.010376000	0.928901000	-0.239109000
H	3.226317000	1.425452000	1.319284000

B3LYP-D3/6-311+G(d,p)

N	-1.035823000	-0.742917000	0.717531000
C	-2.331679000	-0.482337000	0.949089000
C	-3.070845000	0.482737000	0.262910000
C	-2.465725000	1.252295000	-0.747070000
C	-1.126543000	1.076744000	-1.089599000
H	-4.116083000	0.632602000	0.511271000
H	-2.829607000	-1.068738000	1.724080000
H	-3.068794000	1.995215000	-1.266107000
H	-0.691558000	1.688194000	-1.874718000
B	-0.457312000	0.026222000	-0.275006000
C	1.290975000	-0.238639000	-0.658231000
C	1.726033000	-1.270328000	0.203312000
C	2.542315000	-0.712685000	1.181396000
H	1.247421000	-0.320810000	-1.738956000
H	1.363774000	-2.285354000	0.157998000
H	2.967874000	-1.192877000	2.047275000
C	2.666698000	0.624309000	0.839588000
O	2.003336000	0.929913000	-0.251600000
H	3.182674000	1.435486000	1.333737000

MP2/6-311+G(d,p)

N	-0.990018000	-0.830162000	0.733293000
C	-2.278146000	-0.506457000	0.996769000
C	-2.989460000	0.495650000	0.326017000
C	-2.384167000	1.245116000	-0.701437000
C	-1.053567000	1.015712000	-1.084791000
H	-4.021947000	0.689416000	0.605116000
H	-2.781792000	-1.074743000	1.782630000
H	-2.969677000	2.016321000	-1.203606000
H	-0.611266000	1.612803000	-1.878199000
B	-0.444169000	-0.062986000	-0.270024000
C	1.431713000	-0.245342000	-0.796807000
C	1.696418000	-1.259647000	0.123100000
C	2.368012000	-0.661018000	1.207948000
H	1.266407000	-0.294611000	-1.864427000
H	1.335741000	-2.275634000	0.048041000
H	2.661487000	-1.118538000	2.140922000
C	2.552342000	0.659124000	0.849076000
O	2.027751000	0.920167000	-0.355779000
H	2.981469000	1.503858000	1.369058000

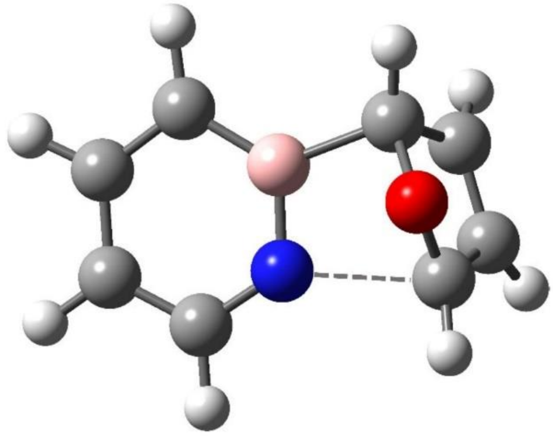
M06-2X/6-311+G(d,p)

N	-0.983727000	-0.767011000	0.735252000
C	-2.268550000	-0.483025000	0.989186000
C	-3.005915000	0.480489000	0.307308000
C	-2.411627000	1.226531000	-0.723768000
C	-1.086800000	1.033193000	-1.096364000
H	-4.041874000	0.648668000	0.575177000
H	-2.756296000	-1.051520000	1.781465000
H	-3.014960000	1.971369000	-1.237711000
H	-0.659230000	1.629599000	-1.894403000
B	-0.439220000	-0.013690000	-0.271512000
C	1.395119000	-0.226789000	-0.756726000
C	1.687731000	-1.248734000	0.137757000
C	2.407388000	-0.683636000	1.202326000
H	1.252616000	-0.272052000	-1.826441000
H	1.314298000	-2.257834000	0.063889000
H	2.722739000	-1.159278000	2.115190000
C	2.587361000	0.631567000	0.857354000
O	2.040154000	0.919578000	-0.309145000
H	3.057924000	1.451605000	1.378065000

SCS-MP2/6-311+G(d,p)

N	-0.995023000	-0.817887000	0.757055000
C	-2.289116000	-0.497531000	1.012860000
C	-3.004589000	0.490386000	0.327160000
C	-2.397373000	1.232600000	-0.711126000
C	-1.065246000	1.008436000	-1.089249000
H	-4.040040000	0.682503000	0.599323000
H	-2.790381000	-1.058844000	1.805901000
H	-2.987333000	1.994196000	-1.224304000
H	-0.622227000	1.598341000	-1.888114000
B	-0.459692000	-0.058688000	-0.252106000
C	1.467444000	-0.230977000	-0.809607000
C	1.695772000	-1.250485000	0.107985000
C	2.367935000	-0.663774000	1.210919000
H	1.278689000	-0.265599000	-1.873774000
H	1.329587000	-2.264028000	0.020013000
H	2.641238000	-1.132355000	2.145331000
C	2.577551000	0.650319000	0.859593000
O	2.071196000	0.926743000	-0.356647000
H	3.018738000	1.485678000	1.385688000

$TS_{5c\text{-}5d}$



B3LYP/6-311+G(d,p)

N	0.349320000	-0.743388000	-0.010016000
C	1.497197000	-1.409338000	0.104601000
C	2.720453000	-0.740825000	0.077763000
C	2.754424000	0.658182000	-0.082710000
C	1.597039000	1.420460000	-0.220857000
H	3.638641000	-1.305720000	0.190391000
H	1.468093000	-2.491127000	0.232632000
H	3.728563000	1.143040000	-0.099419000
H	1.694306000	2.493685000	-0.358742000
B	0.327698000	0.636794000	-0.191654000
C	-2.179913000	-0.386662000	1.063869000
C	-1.905065000	-0.938449000	-0.223699000
H	-2.459074000	-0.947702000	1.941469000
H	-2.065021000	-1.943042000	-0.585870000
C	-1.285058000	1.147284000	-0.371593000
H	-1.457283000	2.076899000	-0.903810000
O	-1.786575000	0.014075000	-1.127520000
C	-1.837031000	0.927200000	0.967818000
H	-1.802451000	1.655682000	1.765151000

B3LYP-D3/6-311+G(d,p)

N	0.346248000	-0.744840000	-0.018852000
C	1.493046000	-1.410553000	0.100585000
C	2.716526000	-0.740852000	0.080829000
C	2.750795000	0.658881000	-0.077487000
C	1.593507000	1.421146000	-0.220658000
H	3.634399000	-1.305396000	0.197653000
H	1.462781000	-2.492360000	0.227173000
H	3.724978000	1.143785000	-0.087906000
H	1.688982000	2.494753000	-0.356164000
B	0.325521000	0.636102000	-0.198639000
C	-2.173893000	-0.385588000	1.065381000
C	-1.903655000	-0.939118000	-0.223705000
H	-2.443837000	-0.946978000	1.945434000
H	-2.060693000	-1.945349000	-0.582496000
C	-1.286414000	1.147449000	-0.376547000
H	-1.459596000	2.077993000	-0.907143000
O	-1.792940000	0.013267000	-1.129769000
C	-1.830817000	0.928203000	0.966753000
H	-1.786675000	1.656503000	1.763362000

MP2/6-311+G(d,p)

N	0.328998000	-0.758407000	0.021819000
C	1.494156000	-1.421969000	0.103778000
C	2.712655000	-0.736000000	0.075708000
C	2.742067000	0.667835000	-0.067195000
C	1.569210000	1.426456000	-0.185185000
H	3.637988000	-1.297259000	0.175976000
H	1.475186000	-2.507566000	0.219667000
H	3.715158000	1.160217000	-0.087395000
H	1.660345000	2.503186000	-0.319164000
B	0.316116000	0.617852000	-0.154987000
C	-2.154980000	-0.387150000	1.060006000
C	-1.929681000	-0.937276000	-0.228489000
H	-2.401278000	-0.945356000	1.951972000
H	-2.108422000	-1.939090000	-0.596648000
C	-1.313306000	1.136693000	-0.403478000
H	-1.436165000	2.064648000	-0.953509000
O	-1.790255000	0.011624000	-1.136952000
C	-1.801868000	0.938988000	0.948405000
H	-1.717660000	1.669622000	1.743476000

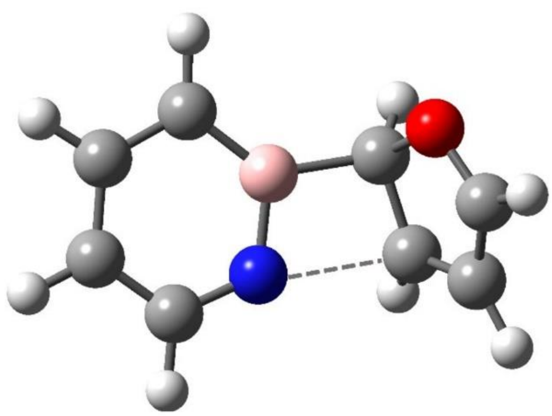
M06-2X/6-311+G(d,p)

N	0.340481000	-0.760614000	-0.021624000
C	1.496103000	-1.408436000	0.094066000
C	2.712879000	-0.733742000	0.083066000
C	2.738234000	0.664754000	-0.064998000
C	1.581088000	1.420446000	-0.205789000
H	3.633388000	-1.292521000	0.196432000
H	1.478636000	-2.491325000	0.210972000
H	3.708926000	1.155360000	-0.069655000
H	1.670923000	2.494154000	-0.333392000
B	0.331157000	0.613535000	-0.190564000
C	-2.167771000	-0.380696000	1.066473000
C	-1.933671000	-0.931129000	-0.222015000
H	-2.424642000	-0.937415000	1.952241000
H	-2.096317000	-1.935544000	-0.583601000
C	-1.303080000	1.132697000	-0.392945000
H	-1.443051000	2.062440000	-0.930839000
O	-1.793222000	0.009995000	-1.119877000
C	-1.803384000	0.926722000	0.954254000
H	-1.728414000	1.658366000	1.745599000

SCS-MP2/6-311+G(d,p)

N	0.338932000	-0.775338000	0.006203000
C	1.514908000	-1.422444000	0.108901000
C	2.731407000	-0.733622000	0.087149000
C	2.754836000	0.673393000	-0.066968000
C	1.579348000	1.422662000	-0.202035000
H	3.659548000	-1.289912000	0.198136000
H	1.504108000	-2.508497000	0.231085000
H	3.726379000	1.171250000	-0.080782000
H	1.663549000	2.500586000	-0.340467000
B	0.326565000	0.604269000	-0.177688000
C	-2.178473000	-0.382642000	1.061882000
C	-1.970437000	-0.928784000	-0.236890000
H	-2.438517000	-0.944601000	1.948363000
H	-2.155639000	-1.930573000	-0.603967000
C	-1.299364000	1.135360000	-0.397061000
H	-1.437587000	2.065449000	-0.942020000
O	-1.803433000	0.012996000	-1.137105000
C	-1.805512000	0.935629000	0.955929000
H	-1.712354000	1.661867000	1.755140000

$TS_{5c\text{-}5f}$



B3LYP/6-311+G(d,p)

N	-0.60036800	-0.89390300	-0.40828600
C	-1.78602600	-1.44279400	-0.12654000
C	-2.88217300	-0.67364300	0.25546500
C	-2.77029300	0.72875600	0.35993600
C	-1.58041800	1.39811400	0.09450500
H	-3.82724700	-1.16274600	0.46520600
H	-1.88786700	-2.52549400	-0.20934200
H	-3.65578000	1.28572700	0.66071300
H	-1.56127200	2.47921200	0.20292000
B	-0.44216000	0.52231100	-0.30911400
C	2.48318900	-1.00994100	-0.03566300
C	2.63633900	0.06047500	0.82183300
H	2.97872800	-1.96357400	0.04925000
H	3.25632800	0.14308200	1.70633800
C	1.12428900	0.77308000	-0.68379000
H	1.35915800	1.53331100	-1.43211100
O	1.92845200	1.11734700	0.51565400
C	1.54686200	-0.61070400	-0.99217800
H	1.32611500	-1.11357100	-1.91825600

B3LYP-D3/6-311+G(d,p)

N	-0.59954000	-0.89809300	-0.42124700
C	-1.78360900	-1.44433900	-0.12906700
C	-2.87618900	-0.67378100	0.26280100
C	-2.76242100	0.72890700	0.36693700
C	-1.57358700	1.39673700	0.09148900
H	-3.81989800	-1.16216700	0.48034300
H	-1.88757300	-2.52688000	-0.21113800
H	-3.64469000	1.28638000	0.67614000
H	-1.54903800	2.47754100	0.20099300
B	-0.44196400	0.51792000	-0.32271400
C	2.47765000	-1.00759300	-0.03446800
C	2.61901300	0.06142700	0.82785900
H	2.97021700	-1.96208800	0.05640600
H	3.22563400	0.14022400	1.72204800
C	1.12477200	0.77421200	-0.69462600
H	1.36040100	1.53694400	-1.43998100
O	1.91549200	1.11879400	0.51397400
C	1.55332000	-0.60753700	-1.00125500
H	1.33786400	-1.11155900	-1.92795300

MP2/6-311+G(d,p)

N	-0.58654800	-0.90389600	-0.54124900
C	-1.76535300	-1.45393300	-0.18035900
C	-2.82798100	-0.68152300	0.29262000
C	-2.70746100	0.72038500	0.42751900
C	-1.52234300	1.39113900	0.10760100
H	-3.76319700	-1.17324600	0.55024600
H	-1.88269300	-2.53559900	-0.27982400
H	-3.57032200	1.27389400	0.80071100
H	-1.48659800	2.47006800	0.25214900
B	-0.42667600	0.51075700	-0.40320600
C	2.40896200	-1.00597200	0.00364400
C	2.51529400	0.09096100	0.85077700
H	2.87248600	-1.96944200	0.15665800
H	3.05158100	0.18292400	1.78984100
C	1.14633500	0.78299600	-0.76986100
H	1.40078200	1.53117200	-1.52374800
O	1.86029500	1.15122800	0.46073800
C	1.54829300	-0.61018200	-1.02202400
H	1.38100000	-1.12668200	-1.95569200

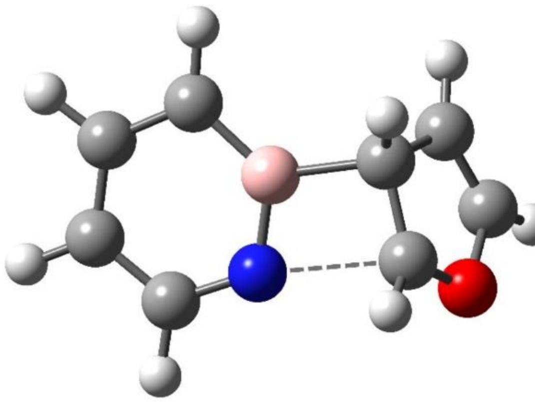
M06-2X/6-311+G(d,p)

N	-0.57831800	-0.89451400	-0.45154400
C	-1.75814600	-1.44101700	-0.14676000
C	-2.84332800	-0.68001000	0.26643000
C	-2.72961200	0.71999700	0.38429000
C	-1.55153600	1.39414700	0.10257000
H	-3.78197400	-1.17129700	0.49302500
H	-1.86228200	-2.52210100	-0.23555400
H	-3.60867600	1.27117800	0.71114900
H	-1.52992400	2.47250300	0.22285800
B	-0.43194800	0.51418400	-0.33760800
C	2.42859000	-1.01293900	-0.01286700
C	2.57221000	0.06783300	0.82866200
H	2.89315900	-1.97707100	0.10641600
H	3.15543400	0.15441100	1.73718200
C	1.14314400	0.78921900	-0.71628400
H	1.36151700	1.53868600	-1.47675900
O	1.90837000	1.12912700	0.47410700
C	1.53371900	-0.60039600	-1.00259000
H	1.32545700	-1.10689300	-1.93018100

SCS-MP2/6-311+G(d,p)

N	-0.582614000	-0.903585000	-0.491659000
C	-1.772715000	-1.452500000	-0.155985000
C	-2.849443000	-0.681199000	0.282542000
C	-2.735661000	0.727808000	0.403152000
C	-1.548263000	1.399292000	0.099913000
H	-3.789306000	-1.173100000	0.525912000
H	-1.883177000	-2.536436000	-0.246003000
H	-3.610331000	1.282204000	0.749399000
H	-1.520681000	2.481845000	0.225744000
B	-0.433102000	0.512144000	-0.370465000
C	2.437458000	-1.012547000	-0.013783000
C	2.556898000	0.076564000	0.842289000
H	2.909669000	-1.975773000	0.117552000
H	3.123556000	0.161746000	1.764959000
C	1.141967000	0.785272000	-0.738750000
H	1.395967000	1.536290000	-1.491632000
O	1.886557000	1.138849000	0.484210000
C	1.550994000	-0.608536000	-1.016509000
H	1.368084000	-1.113292000	-1.954343000

$TS_{5c\text{-}5g}$



B3LYP/6-311+G(d,p)

C	-1.444059000	2.147696000	0.061298000
C	-2.662241000	1.582337000	-0.304683000
C	-2.831242000	0.188858000	-0.439585000
C	-1.765937000	-0.677184000	-0.206716000
H	-3.524185000	2.219853000	-0.493365000
H	-1.380330000	3.227975000	0.158293000
H	-3.795678000	-0.217158000	-0.724433000
H	-1.918360000	-1.752720000	-0.305385000
C	2.120410000	1.672019000	-0.467367000
C	2.740755000	0.539391000	-0.797704000
H	2.171608000	2.605113000	-1.005523000
H	3.388065000	0.222655000	-1.596080000
C	1.570641000	0.014022000	0.989234000
H	1.301515000	-0.607851000	1.826904000
O	2.426116000	-0.478482000	0.137515000
C	1.263464000	1.400014000	0.714933000
H	1.275439000	2.094807000	1.555504000
B	-0.356439000	1.151602000	0.269622000
N	-0.545517000	-0.244820000	0.136376000

B3LYP-D3/6-311+G(d,p)

C	-1.431059000	2.148363000	0.061264000
C	-2.645990000	1.584141000	-0.318104000
C	-2.815561000	0.189988000	-0.450950000
C	-1.754677000	-0.678055000	-0.201979000
H	-3.504353000	2.222290000	-0.520452000
H	-1.362929000	3.228619000	0.154428000
H	-3.777145000	-0.215136000	-0.746531000
H	-1.907827000	-1.753487000	-0.299615000
C	2.097433000	1.673418000	-0.462798000
C	2.707016000	0.539492000	-0.809863000
H	2.133390000	2.606739000	-1.001204000
H	3.332411000	0.223206000	-1.625819000
C	1.573796000	0.012194000	1.000581000
H	1.318420000	-0.610491000	1.842234000
O	2.411356000	-0.479411000	0.130653000
C	1.266045000	1.400029000	0.736455000
H	1.282812000	2.094492000	1.576361000
B	-0.350831000	1.149028000	0.287866000
N	-0.538283000	-0.247293000	0.156310000

MP2/6-311+G(d,p)

C	-1.306591000	2.139754000	-0.067498000
C	-2.508408000	1.570227000	-0.497712000
C	-2.716688000	0.170937000	-0.486564000
C	-1.734308000	-0.699831000	-0.015860000
H	-3.313336000	2.204129000	-0.872481000
H	-1.196050000	3.221501000	-0.128052000
H	-3.659773000	-0.239050000	-0.839640000
H	-1.917075000	-1.776445000	-0.015233000
C	1.967160000	1.761567000	-0.346060000
C	2.457063000	0.640330000	-0.913200000
H	1.972698000	2.749089000	-0.785268000
H	2.930279000	0.405939000	-1.853301000
C	1.549318000	-0.055983000	0.959748000
H	1.443945000	-0.756082000	1.774310000
O	2.250994000	-0.462659000	-0.070760000
C	1.296993000	1.367248000	0.914495000
H	1.390461000	1.957091000	1.824576000
B	-0.314539000	1.144587000	0.444959000
N	-0.558119000	-0.254224000	0.482376000

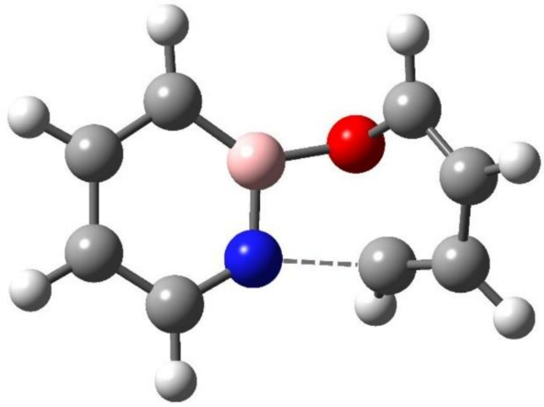
M06-2X/6-311+G(d,p)

C	-1.413518000	2.156266000	0.043643000
C	-2.611292000	1.576510000	-0.346162000
C	-2.774079000	0.180543000	-0.456919000
C	-1.719349000	-0.674512000	-0.169980000
H	-3.468394000	2.204740000	-0.578946000
H	-1.354719000	3.237682000	0.111026000
H	-3.727208000	-0.233096000	-0.763054000
H	-1.863478000	-1.751223000	-0.252283000
C	2.079160000	1.686061000	-0.438994000
C	2.628909000	0.540355000	-0.833386000
H	2.135611000	2.630089000	-0.956284000
H	3.219171000	0.229480000	-1.676969000
C	1.532927000	0.002235000	0.981067000
H	1.300326000	-0.630223000	1.822593000
O	2.331256000	-0.483872000	0.081065000
C	1.276085000	1.408662000	0.775500000
H	1.317537000	2.074261000	1.634414000
B	-0.337499000	1.164418000	0.318919000
N	-0.517418000	-0.230251000	0.213589000

SCS-MP2/6-311+G(d,p)

C	-1.447392000	2.166959000	0.089728000
C	-2.656874000	1.584551000	-0.299499000
C	-2.796775000	0.181510000	-0.457426000
C	-1.721659000	-0.675806000	-0.224462000
H	-3.532250000	2.209230000	-0.489034000
H	-1.404973000	3.250185000	0.203349000
H	-3.755314000	-0.237972000	-0.755998000
H	-1.854870000	-1.754891000	-0.336287000
C	2.113180000	1.671539000	-0.469096000
C	2.680804000	0.503021000	-0.816625000
H	2.183018000	2.599079000	-1.021278000
H	3.292778000	0.160680000	-1.636541000
C	1.530622000	0.021470000	0.988444000
H	1.278631000	-0.580061000	1.850403000
O	2.360414000	-0.501908000	0.130275000
C	1.273838000	1.426908000	0.735361000
H	1.327788000	2.107581000	1.587880000
B	-0.338560000	1.178559000	0.291692000
N	-0.498378000	-0.222510000	0.137954000

$TS_{5a\text{-}5e}$



B3LYP/6-311+G(d,p)

N	0.479879000	-0.837715000	0.188883000
C	1.621938000	-1.425174000	-0.192357000
C	2.756187000	-0.650768000	-0.393084000
C	2.712427000	0.750758000	-0.197672000
C	1.564175000	1.431913000	0.192187000
H	3.680631000	-1.127733000	-0.696442000
H	1.639166000	-2.503584000	-0.334254000
H	3.631951000	1.306451000	-0.367266000
H	1.608539000	2.508129000	0.317011000
B	0.395879000	0.536211000	0.381683000
C	-2.612262000	0.314466000	-0.845979000
C	-1.847777000	1.244898000	-0.260224000
C	-1.415601000	-1.026961000	0.648948000
H	-3.340649000	0.537311000	-1.612245000
H	-1.836499000	2.319403000	-0.340415000
H	-1.241856000	-1.642679000	1.514267000
O	-1.033377000	0.697330000	0.758233000
C	-2.451195000	-0.975841000	-0.204879000
H	-3.180165000	-1.772732000	-0.258757000

B3LYP-D3/6-311+G(d,p)

N	0.479423000	-0.845512000	0.201147000
C	1.619527000	-1.427531000	-0.192970000
C	2.750927000	-0.649702000	-0.401292000
C	2.705739000	0.751589000	-0.201669000
C	1.558535000	1.428137000	0.199955000
H	3.673609000	-1.124080000	-0.714048000
H	1.637672000	-2.505332000	-0.339081000
H	3.622131000	1.310096000	-0.378886000
H	1.597840000	2.504510000	0.325409000
B	0.394772000	0.527959000	0.397371000
C	-2.591574000	0.325374000	-0.859483000
C	-1.827231000	1.247842000	-0.261001000
C	-1.432915000	-1.034285000	0.650114000
H	-3.303313000	0.555504000	-1.638927000
H	-1.799984000	2.321648000	-0.350134000
H	-1.263815000	-1.653399000	1.513174000
O	-1.033341000	0.697775000	0.769879000
C	-2.455476000	-0.967456000	-0.215405000
H	-3.192420000	-1.756160000	-0.280919000

MP2/6-311+G(d,p)

N	-0.433712000	-0.826774000	-0.300487000
C	-1.540595000	-1.446948000	0.158856000
C	-2.666255000	-0.675331000	0.434412000
C	-2.653842000	0.731560000	0.251818000
C	-1.533460000	1.439163000	-0.199520000
H	-3.569431000	-1.166155000	0.785813000
H	-1.531587000	-2.529187000	0.284724000
H	-3.569709000	1.274706000	0.485382000
H	-1.603657000	2.518989000	-0.297090000
B	-0.367881000	0.554129000	-0.456318000
C	2.452229000	0.295810000	0.954697000
C	1.755112000	1.245685000	0.286733000
C	1.382237000	-0.965279000	-0.679857000
H	3.084374000	0.514581000	1.806602000
H	1.762177000	2.324399000	0.330195000
H	1.321012000	-1.558666000	-1.583780000
O	1.074481000	0.689399000	-0.836223000
C	2.359605000	-0.972141000	0.272315000
H	3.056168000	-1.792207000	0.386212000

M06-2X/6-311+G(d,p)

N	-0.420828000	-0.789520000	-0.262569000
C	-1.520538000	-1.431467000	0.151899000
C	-2.657955000	-0.692316000	0.408488000
C	-2.656975000	0.717095000	0.243741000
C	-1.555663000	1.451327000	-0.164987000
H	-3.559229000	-1.195813000	0.732886000
H	-1.492230000	-2.510899000	0.268389000
H	-3.586093000	1.236625000	0.463670000
H	-1.641335000	2.527033000	-0.250937000
B	-0.376596000	0.588805000	-0.411810000
C	2.511074000	0.241810000	0.899220000
C	1.831578000	1.228808000	0.300347000
C	1.299457000	-0.899504000	-0.689104000
H	3.200927000	0.413887000	1.712826000
H	1.856720000	2.302122000	0.351126000
H	1.223679000	-1.439676000	-1.622840000
O	1.063727000	0.689724000	-0.792280000
C	2.308515000	-1.015366000	0.231704000
H	2.959544000	-1.870777000	0.292307000

SCS-MP2/6-311+G(d,p)

N	0.440952000	-0.828438000	0.260086000
C	1.563655000	-1.433856000	-0.193113000
C	2.690186000	-0.656241000	-0.436633000
C	2.669490000	0.753141000	-0.225469000
C	1.542554000	1.446250000	0.225169000
H	3.600449000	-1.135798000	-0.787681000
H	1.559467000	-2.513328000	-0.345205000
H	3.588338000	1.302861000	-0.435112000
H	1.606233000	2.524539000	0.350949000
B	0.375048000	0.546371000	0.453379000
C	-2.512564000	0.299899000	-0.901140000
C	-1.798446000	1.242560000	-0.246797000
C	-1.379098000	-0.990854000	0.676437000
H	-3.176620000	0.525481000	-1.727641000
H	-1.793490000	2.321852000	-0.294641000
H	-1.285106000	-1.591249000	1.572995000
O	-1.064292000	0.679495000	0.840346000
C	-2.386762000	-0.987442000	-0.240481000
H	-3.099888000	-1.798266000	-0.322215000

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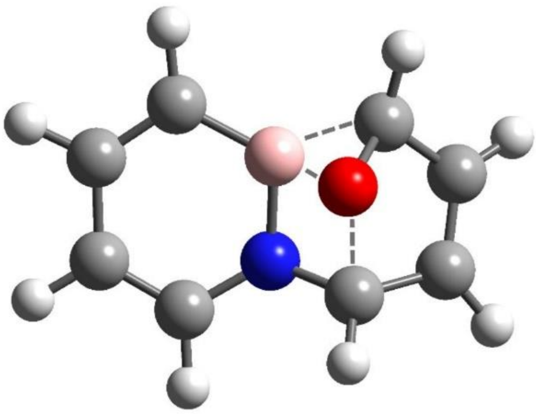


B3LYP/6-311+G(d,p)

C	-1.438222000	1.233142000	-0.053796000
C	-2.395599000	0.352897000	-0.730128000
C	-2.239776000	-0.924656000	-0.344499000
C	-1.019663000	-1.114965000	0.452538000
O	-1.004123000	0.587027000	1.204696000
H	-1.733150000	2.265920000	0.107761000
H	-3.126358000	0.714518000	-1.442488000
H	-2.865062000	-1.765926000	-0.610604000
H	-0.970234000	-1.918473000	1.186141000
N	0.179583000	-0.747724000	-0.159248000
B	0.093269000	0.750852000	-0.058580000
C	1.374882000	-1.416847000	-0.058838000
C	1.446826000	1.474997000	-0.126647000
C	2.547482000	-0.732849000	-0.126977000
H	1.333057000	-2.496870000	0.035614000
C	2.573172000	0.710984000	-0.182207000
H	1.550423000	2.555444000	-0.152901000
H	3.477733000	-1.286476000	-0.121109000
H	3.552095000	1.179814000	-0.252660000

B3LYP-D3/6-311+G(d,p)

C	-1.436621000	1.232999000	-0.053700000
C	-2.398832000	0.353787000	-0.726421000
C	-2.241418000	-0.924509000	-0.344218000
C	-1.017175000	-1.115187000	0.447832000
O	-0.995737000	0.585020000	1.203044000
H	-1.729084000	2.266647000	0.108379000
H	-3.132393000	0.717296000	-1.434636000
H	-2.866358000	-1.766021000	-0.609407000
H	-0.964867000	-1.916094000	1.183607000
N	0.178718000	-0.750656000	-0.170962000
B	0.093129000	0.748780000	-0.065621000
C	1.374592000	-1.417735000	-0.061124000
C	1.445486000	1.474932000	-0.130967000
C	2.546935000	-0.732833000	-0.122607000
H	1.332022000	-2.497458000	0.035831000
C	2.572570000	0.711742000	-0.179969000
H	1.545935000	2.555576000	-0.157196000
H	3.477509000	-1.285840000	-0.109907000
H	3.551923000	1.180363000	-0.245888000

MP2/6-311+G(d,p)

C	-1.449618000	1.241623000	-0.055816000
C	-2.395225000	0.363166000	-0.734751000
C	-2.234880000	-0.924053000	-0.337750000
C	-1.012428000	-1.117992000	0.443023000
O	-0.976167000	0.593979000	1.198413000
H	-1.743614000	2.273088000	0.121510000
H	-3.126014000	0.721573000	-1.452556000
H	-2.873557000	-1.762056000	-0.592717000
H	-0.953313000	-1.946230000	1.155067000
N	0.176748000	-0.749839000	-0.175275000
B	0.087449000	0.743687000	-0.044893000
C	1.370973000	-1.422758000	-0.051471000
C	1.436507000	1.477075000	-0.127715000
C	2.550591000	-0.731304000	-0.118643000
H	1.325133000	-2.504957000	0.049273000
C	2.575936000	0.711266000	-0.186707000
H	1.544023000	2.559464000	-0.159473000
H	3.479952000	-1.291256000	-0.097850000
H	3.553842000	1.186335000	-0.265599000

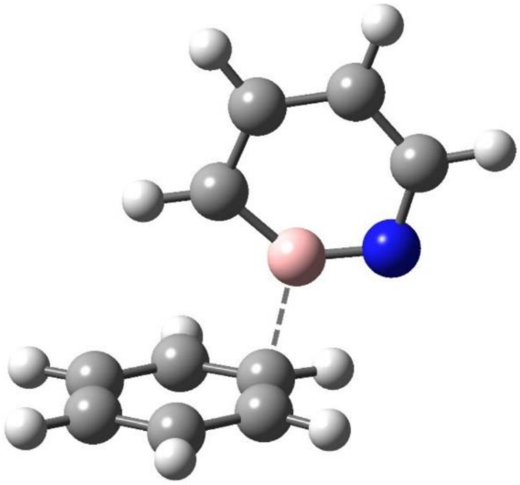
M06-2X/6-311+G(d,p)

C	-1.449960000	1.242868000	-0.072267000
C	-2.404100000	0.350864000	-0.724862000
C	-2.240666000	-0.919232000	-0.330864000
C	-1.001580000	-1.099169000	0.437374000
O	-0.952639000	0.595868000	1.139576000
H	-1.749179000	2.269503000	0.106253000
H	-3.148860000	0.703991000	-1.425830000
H	-2.866492000	-1.765187000	-0.575685000
H	-0.939951000	-1.885604000	1.189553000
N	0.176908000	-0.758394000	-0.211148000
B	0.087717000	0.736248000	-0.049651000
C	1.376460000	-1.422307000	-0.076997000
C	1.444800000	1.468442000	-0.113394000
C	2.541726000	-0.740341000	-0.115258000
H	1.333166000	-2.502940000	0.009058000
C	2.565279000	0.710359000	-0.167501000
H	1.547320000	2.548334000	-0.133822000
H	3.472329000	-1.291236000	-0.088380000
H	3.544056000	1.178742000	-0.230085000

SCS-MP2/6-311+G(d,p)

C	-1.441243000	1.247481000	-0.065605000
C	-2.430531000	0.368412000	-0.705269000
C	-2.253963000	-0.919820000	-0.334975000
C	-0.996054000	-1.134962000	0.400728000
O	-0.936795000	0.599970000	1.178104000
H	-1.725447000	2.282063000	0.116144000
H	-3.199824000	0.735578000	-1.378342000
H	-2.898368000	-1.758135000	-0.578695000
H	-0.930162000	-1.960838000	1.115514000
N	0.171733000	-0.768755000	-0.241911000
B	0.081925000	0.737807000	-0.080091000
C	1.381458000	-1.427388000	-0.055466000
C	1.442350000	1.476485000	-0.154228000
C	2.555007000	-0.733315000	-0.079863000
H	1.340568000	-2.510215000	0.047880000
C	2.583051000	0.720286000	-0.170608000
H	1.542100000	2.560244000	-0.203092000
H	3.486792000	-1.287952000	-0.013381000
H	3.563737000	1.193863000	-0.230773000

6a



B3LYP/6-311+G(d,p)

N	-1.646321000	-1.268730000	0.000220000
C	-2.926729000	-0.851788000	0.000217000
C	-3.285249000	0.496387000	-0.000021000
C	-2.297078000	1.502172000	-0.000145000
C	-0.932765000	1.205169000	-0.000100000
H	-4.334524000	0.769046000	-0.000104000
H	-3.706503000	-1.613494000	0.000245000
H	-2.619993000	2.541029000	-0.000310000
H	-0.201563000	2.002607000	-0.000214000
B	-0.754290000	-0.252929000	0.000070000
C	1.189996000	-1.111454000	-0.702872000
C	1.978598000	-0.175669000	-1.401126000
C	2.734757000	0.748098000	-0.703489000
C	2.734782000	0.748253000	0.703203000
C	1.978646000	-0.175363000	1.401067000
C	1.190019000	-1.111300000	0.703043000
H	0.658946000	-1.885559000	-1.240266000
H	1.987062000	-0.186729000	-2.484493000
H	3.338109000	1.471520000	-1.240138000
H	3.338151000	1.471792000	1.239673000
H	1.987147000	-0.186188000	2.484436000
H	0.658997000	-1.885295000	1.240624000

B3LYP-D3/6-311+G(d,p)

N	-1.647873000	-1.278526000	-0.000043000
C	-2.922133000	-0.837773000	-0.000008000
C	-3.256606000	0.516901000	0.000039000
C	-2.251111000	1.507359000	0.000058000
C	-0.892257000	1.186718000	0.000032000
H	-4.301037000	0.807524000	0.000058000
H	-3.715071000	-1.585523000	-0.000029000
H	-2.556863000	2.551345000	0.000091000
H	-0.141796000	1.965711000	0.000043000
B	-0.745530000	-0.273891000	-0.000014000
C	1.210409000	-1.143943000	-0.703226000
C	1.959250000	-0.176980000	-1.401571000
C	2.672294000	0.780497000	-0.702982000
C	2.672268000	0.780334000	0.703209000
C	1.959200000	-0.177306000	1.401548000
C	1.210385000	-1.144109000	0.702950000
H	0.700222000	-1.932366000	-1.240618000
H	1.964101000	-0.184821000	-2.484801000
H	3.239433000	1.532711000	-1.239352000
H	3.239387000	1.532426000	1.239774000
H	1.964011000	-0.185401000	2.484776000
H	0.700186000	-1.932662000	1.240139000

MP2/6-311+G(d,p)

N	1.573614000	-1.285482000	-0.000186000
C	2.830851000	-0.799828000	-0.000169000
C	3.138755000	0.568529000	0.000006000
C	2.116661000	1.540156000	0.000136000
C	0.766609000	1.168692000	0.000113000
H	4.181751000	0.876279000	0.000046000
H	3.649225000	-1.524143000	-0.000231000
H	2.397980000	2.593626000	0.000264000
H	0.007765000	1.948069000	0.000220000
B	0.583341000	-0.306110000	-0.000047000
C	-1.038736000	-1.121499000	0.713400000
C	-1.856281000	-0.190963000	1.410726000
C	-2.602768000	0.741387000	0.708801000
C	-2.602796000	0.741549000	-0.708521000
C	-1.856338000	-0.190641000	-1.410690000
C	-1.038764000	-1.121335000	-0.713608000
H	-0.563642000	-1.939860000	1.243119000
H	-1.877243000	-0.212019000	2.496785000
H	-3.214953000	1.460713000	1.246537000
H	-3.215003000	1.460998000	-1.246068000
H	-1.877345000	-0.211450000	-2.496753000
H	-0.563691000	-1.939575000	-1.243534000

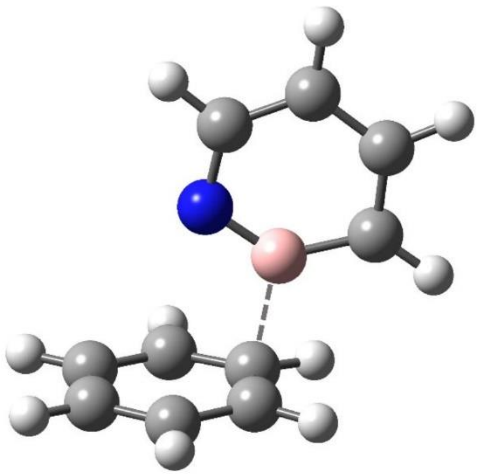
M06-2X/6-311+G(d,p)

N	1.592049000	-1.273861000	-0.000171000
C	2.851355000	-0.816276000	-0.000137000
C	3.180309000	0.536505000	-0.000001000
C	2.169891000	1.515972000	0.000136000
C	0.821707000	1.180677000	0.000129000
H	4.222553000	0.831218000	-0.000001000
H	3.652825000	-1.554522000	-0.000257000
H	2.467430000	2.561647000	0.000245000
H	0.071591000	1.962032000	0.000236000
B	0.650958000	-0.284372000	-0.000040000
C	-1.111540000	-1.129454000	0.702054000
C	-1.891528000	-0.181140000	1.400542000
C	-2.624327000	0.750865000	0.705116000
C	-2.624350000	0.751028000	-0.704856000
C	-1.891574000	-0.180817000	-1.400520000
C	-1.111563000	-1.129293000	-0.702276000
H	-0.597285000	-1.916556000	1.236849000
H	-1.899647000	-0.194188000	2.483198000
H	-3.214893000	1.485231000	1.239793000
H	-3.214934000	1.485516000	-1.239345000
H	-1.899728000	-0.193616000	-2.483179000
H	-0.597325000	-1.916270000	-1.237269000

SCS-MP2/6-311+G(d,p)

N	1.591452000	-1.280802000	-0.000175000
C	2.853997000	-0.795179000	-0.000145000
C	3.164626000	0.570898000	0.000008000
C	2.140065000	1.546555000	0.000139000
C	0.788057000	1.181750000	0.000123000
H	4.208334000	0.878569000	0.000024000
H	3.669829000	-1.523061000	-0.000242000
H	2.424514000	2.600151000	0.000256000
H	0.029227000	1.961062000	0.000227000
B	0.618417000	-0.295696000	-0.000043000
C	-1.069178000	-1.136230000	0.709212000
C	-1.876978000	-0.195322000	1.411927000
C	-2.625230000	0.734542000	0.710891000
C	-2.625257000	0.734705000	-0.710614000
C	-1.877033000	-0.194997000	-1.411893000
C	-1.069206000	-1.136067000	-0.709426000
H	-0.580817000	-1.944409000	1.243533000
H	-1.888715000	-0.212212000	2.498769000
H	-3.233693000	1.459154000	1.247292000
H	-3.233742000	1.459441000	-1.246824000
H	-1.888812000	-0.211637000	-2.498739000
H	-0.580866000	-1.944123000	-1.243952000

6b



B3LYP/6-311+G(d,p)

N	0.774428000	-1.037805000	-0.000218000
C	2.022810000	-1.526989000	-0.000387000
C	3.161266000	-0.713348000	-0.000099000
C	3.036722000	0.687179000	0.000061000
C	1.789011000	1.320082000	0.000100000
H	4.144032000	-1.171169000	-0.000021000
H	2.144403000	-2.610990000	-0.000337000
H	3.944171000	1.287096000	0.000227000
H	1.732697000	2.402419000	0.000268000
B	0.717385000	0.311471000	0.000007000
C	-1.221565000	1.155571000	-0.703345000
C	-1.941112000	0.167821000	-1.401867000
C	-2.614245000	-0.815374000	-0.702953000
C	-2.614203000	-0.815569000	0.702879000
C	-1.941021000	0.167427000	1.402024000
C	-1.221519000	1.155373000	0.703732000
H	-0.757684000	1.968754000	-1.246521000
H	-1.947323000	0.175727000	-2.485066000
H	-3.150199000	-1.590340000	-1.238632000
H	-3.150120000	-1.590686000	1.238375000
H	-1.947158000	0.175026000	2.485226000
H	-0.757599000	1.968401000	1.247107000

B3LYP-D3/6-311+G(d,p)

N	0.748972000	-1.029919000	-0.000153000
C	1.995178000	-1.525835000	-0.000249000
C	3.138962000	-0.718026000	-0.000148000
C	3.023655000	0.683872000	0.000045000
C	1.779108000	1.324186000	0.000152000
H	4.118855000	-1.181928000	-0.000222000
H	2.110723000	-2.610381000	-0.000390000
H	3.934889000	1.277919000	0.000116000
H	1.723751000	2.406373000	0.000303000
B	0.705294000	0.319278000	0.000035000
C	-1.234813000	1.175061000	-0.703627000
C	-1.925779000	0.167808000	-1.402512000
C	-2.565044000	-0.837580000	-0.702848000
C	-2.565022000	-0.837768000	0.702710000
C	-1.925733000	0.167434000	1.402621000
C	-1.234789000	1.174873000	0.703982000
H	-0.785318000	1.997231000	-1.245819000
H	-1.928389000	0.173520000	-2.485558000
H	-3.072292000	-1.631634000	-1.238271000
H	-3.072252000	-1.631964000	1.237937000
H	-1.928307000	0.172856000	2.485668000
H	-0.785278000	1.996899000	1.246378000

MP2/6-311+G(d,p)

N	0.619456000	-1.028228000	-0.000168000
C	1.859441000	-1.540515000	-0.000276000
C	3.034120000	-0.763194000	-0.000138000
C	2.967132000	0.640349000	0.000050000
C	1.725361000	1.298309000	0.000139000
H	3.999457000	-1.263834000	-0.000170000
H	1.955393000	-2.630056000	-0.000360000
H	3.896117000	1.211201000	0.000140000
H	1.705255000	2.387674000	0.000290000
B	0.576929000	0.356750000	0.000035000
C	-1.077484000	1.160033000	-0.713042000
C	-1.838952000	0.188325000	-1.411346000
C	-2.512046000	-0.796962000	-0.707489000
C	-2.512027000	-0.797153000	0.707360000
C	-1.838911000	0.187942000	1.411463000
C	-1.077464000	1.159839000	0.713400000
H	-0.655588000	2.003194000	-1.250062000
H	-1.856087000	0.204365000	-2.497308000
H	-3.064441000	-1.563369000	-1.244388000
H	-3.064406000	-1.563706000	1.244067000
H	-1.856010000	0.203684000	2.497430000
H	-0.655550000	2.002853000	1.250636000

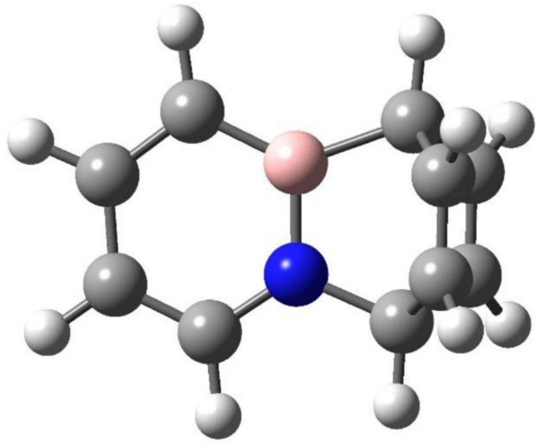
M06-2X/6-311+G(d,p)

N	0.679689000	-1.025109000	-0.000140000
C	1.915121000	-1.525925000	-0.000230000
C	3.072121000	-0.740387000	-0.000150000
C	2.977701000	0.658023000	0.000039000
C	1.744512000	1.308318000	0.000150000
H	4.042315000	-1.221851000	-0.000236000
H	2.019512000	-2.611288000	-0.000377000
H	3.896863000	1.238562000	0.000098000
H	1.709504000	2.392258000	0.000296000
B	0.636135000	0.335655000	0.000040000
C	-1.152497000	1.165955000	-0.702394000
C	-1.870638000	0.174412000	-1.401075000
C	-2.527209000	-0.811243000	-0.703887000
C	-2.527193000	-0.811432000	0.703737000
C	-1.870607000	0.174034000	1.401176000
C	-1.152481000	1.165766000	0.702747000
H	-0.697654000	1.985111000	-1.244017000
H	-1.876769000	0.184586000	-2.483544000
H	-3.055467000	-1.591686000	-1.237862000
H	-3.055440000	-1.592019000	1.237514000
H	-1.876715000	0.183917000	2.483648000
H	-0.697624000	1.984774000	1.244582000

SCS-MP2/6-311+G(d,p)

N	0.642192000	-1.032780000	-0.000143000
C	1.886565000	-1.545381000	-0.000231000
C	3.059733000	-0.767951000	-0.000138000
C	2.989809000	0.639421000	0.000053000
C	1.749657000	1.301366000	0.000157000
H	4.026813000	-1.266689000	-0.000215000
H	1.981202000	-2.635470000	-0.000375000
H	3.919643000	1.210625000	0.000119000
H	1.728150000	2.390780000	0.000304000
B	0.611961000	0.346668000	0.000044000
C	-1.108166000	1.169727000	-0.709272000
C	-1.860105000	0.188989000	-1.412704000
C	-2.536630000	-0.792901000	-0.709610000
C	-2.536611000	-0.793092000	0.709475000
C	-1.860067000	0.188608000	1.412816000
C	-1.108146000	1.169536000	0.709628000
H	-0.672504000	2.004685000	-1.249702000
H	-1.868943000	0.201930000	-2.499408000
H	-3.086773000	-1.562919000	-1.245210000
H	-3.086740000	-1.563255000	1.244882000
H	-1.868876000	0.201256000	2.499524000
H	-0.672470000	2.004348000	1.250271000

6c



B3LYP/6-311+G(d,p)

N	0.341796000	-0.627492000	0.000000000
C	1.477534000	-1.359562000	-0.000012000
C	2.706386000	-0.742421000	-0.000036000
C	2.794372000	0.673565000	-0.000050000
C	1.675690000	1.484022000	-0.000040000
H	3.601188000	-1.351190000	-0.000045000
H	1.376846000	-2.440290000	0.000001000
H	3.789293000	1.113472000	-0.000071000
H	1.820188000	2.560305000	-0.000054000
B	0.331988000	0.813445000	-0.000012000
C	-1.787645000	0.652613000	-1.233357000
C	-1.735990000	-0.679894000	-1.230011000
C	-1.030140000	-1.244985000	0.000032000
C	-1.735946000	-0.679863000	1.230086000
C	-1.787612000	0.652643000	1.233395000
C	-1.205867000	1.332412000	0.000003000
H	-2.179975000	1.243179000	-2.052516000
H	-2.110919000	-1.328235000	-2.010755000
H	-0.947641000	-2.330708000	0.000044000
H	-2.110847000	-1.328185000	2.010859000
H	-2.179920000	1.243230000	2.052549000
H	-1.335405000	2.412466000	-0.000009000

B3LYP-D3/6-311+G(d,p)

N	0.341427000	-0.629188000	0.000003000
C	1.477105000	-1.360461000	-0.000003000
C	2.706100000	-0.742431000	-0.000031000
C	2.793301000	0.674169000	-0.000053000
C	1.673814000	1.484399000	-0.000047000
H	3.601408000	-1.350619000	-0.000037000
H	1.377115000	-2.441272000	0.000013000
H	3.788207000	1.114379000	-0.000074000
H	1.815653000	2.560994000	-0.000063000
B	0.331387000	0.812360000	-0.000018000
C	-1.785779000	0.653309000	-1.234595000
C	-1.736049000	-0.679613000	-1.230854000
C	-1.031167000	-1.245398000	0.000029000
C	-1.736014000	-0.679586000	1.230921000
C	-1.785732000	0.653336000	1.234640000
C	-1.205341000	1.332893000	0.000004000
H	-2.174395000	1.244743000	-2.054551000
H	-2.109141000	-1.328045000	-2.012119000
H	-0.951998000	-2.331389000	0.000040000
H	-2.109083000	-1.328002000	2.012211000
H	-2.174317000	1.244788000	2.054598000
H	-1.331800000	2.413241000	-0.000005000

MP2/6-311+G(d,p)

N	0.337833000	-0.618177000	0.000003000
C	1.469998000	-1.363101000	-0.000005000
C	2.706375000	-0.741279000	-0.000033000
C	2.799403000	0.672320000	-0.000053000
C	1.670051000	1.487651000	-0.000046000
H	3.599140000	-1.357820000	-0.000038000
H	1.359287000	-2.445640000	0.000011000
H	3.795705000	1.114944000	-0.000074000
H	1.821835000	2.565489000	-0.000062000
B	0.323804000	0.819285000	-0.000017000
C	-1.786302000	0.656268000	-1.229905000
C	-1.729311000	-0.690744000	-1.225311000
C	-1.022155000	-1.244713000	0.000030000
C	-1.729274000	-0.690717000	1.225380000
C	-1.786259000	0.656295000	1.229948000
C	-1.213280000	1.335374000	0.000004000
H	-2.177793000	1.241274000	-2.057123000
H	-2.102222000	-1.338794000	-2.010974000
H	-0.926420000	-2.332364000	0.000041000
H	-2.102162000	-1.338749000	2.011068000
H	-2.177723000	1.241319000	2.057166000
H	-1.348973000	2.417030000	-0.000005000

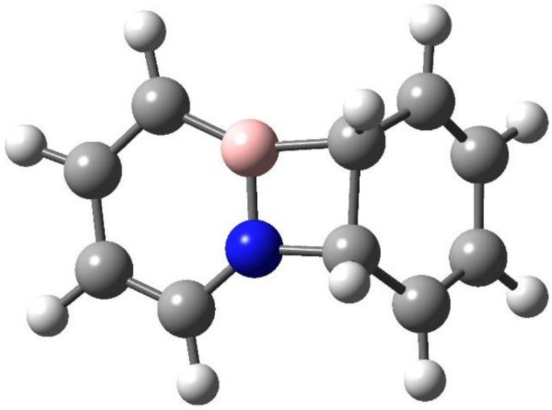
M06-2X/6-311+G(d,p)

N	0.338944000	-0.622702000	0.000004000
C	1.471470000	-1.354884000	-0.000002000
C	2.697786000	-0.744595000	-0.000031000
C	2.785246000	0.672445000	-0.000054000
C	1.674241000	1.483455000	-0.000049000
H	3.590409000	-1.354591000	-0.000036000
H	1.364985000	-2.435013000	0.000014000
H	3.780589000	1.109816000	-0.000076000
H	1.821872000	2.558217000	-0.000065000
B	0.329626000	0.812659000	-0.000018000
C	-1.783116000	0.649406000	-1.229431000
C	-1.729655000	-0.679667000	-1.226890000
C	-1.021138000	-1.241026000	0.000029000
C	-1.729623000	-0.679641000	1.226956000
C	-1.783069000	0.649432000	1.229477000
C	-1.204919000	1.330569000	0.000005000
H	-2.179806000	1.237754000	-2.047230000
H	-2.106664000	-1.327260000	-2.006282000
H	-0.933312000	-2.325749000	0.000039000
H	-2.106611000	-1.327217000	2.006371000
H	-2.179729000	1.237798000	2.047278000
H	-1.335801000	2.408895000	-0.000004000

SCS-MP2/6-311+G(d,p)

N	0.340119000	-0.620325000	0.000002000
C	1.478864000	-1.365166000	-0.000007000
C	2.713210000	-0.746245000	-0.000034000
C	2.806699000	0.675764000	-0.000052000
C	1.680985000	1.490392000	-0.000044000
H	3.607795000	-1.361612000	-0.000041000
H	1.369520000	-2.448392000	0.000007000
H	3.804644000	1.116935000	-0.000073000
H	1.833041000	2.569170000	-0.000059000
B	0.328039000	0.818665000	-0.000015000
C	-1.795691000	0.656458000	-1.233500000
C	-1.733808000	-0.689489000	-1.230149000
C	-1.022666000	-1.245865000	0.000031000
C	-1.733769000	-0.689460000	1.230220000
C	-1.795652000	0.656487000	1.233541000
C	-1.210247000	1.336848000	0.000004000
H	-2.197328000	1.241991000	-2.056579000
H	-2.108205000	-1.339036000	-2.015267000
H	-0.930252000	-2.334567000	0.000042000
H	-2.108142000	-1.338989000	2.015365000
H	-2.197263000	1.242039000	2.056620000
H	-1.348337000	2.419548000	-0.000007000

6d



B3LYP/6-311+G(d,p)

N	-0.64258100	-0.58137200	0.37856400
C	-1.65383100	-1.39078600	0.00421900
C	-2.80823800	-0.78219700	-0.43550000
C	-2.91666200	0.63799000	-0.48746900
C	-1.90711300	1.50973700	-0.11233100
H	-3.64440100	-1.39601400	-0.74563900
H	-1.53080300	-2.46710700	0.05675500
H	-3.86206200	1.03798700	-0.84778600
H	-2.09435200	2.57559400	-0.19235300
B	-0.64953100	0.84911400	0.37008400
C	0.87154200	0.87556000	0.94148700
C	0.74068600	-0.70542700	0.92715800
C	1.71234800	-1.44173100	0.05043800
C	2.56261900	-0.78575000	-0.75446600
C	2.64587300	0.67215000	-0.79608900
C	1.89637100	1.43707900	0.01483400
H	0.98101600	1.29265200	1.94759000
H	0.70354100	-1.14680500	1.92902800
H	1.71962000	-2.52653300	0.09601300
H	3.24684700	-1.35054100	-1.38040200
H	3.35797000	1.12731800	-1.47535800
H	2.00678100	2.51772700	-0.00189900

B3LYP-D3/6-311+G(d,p)

N	-0.63335600	-0.58093500	0.39642100
C	-1.63271600	-1.39401500	0.00119300
C	-2.78469800	-0.78860100	-0.44989900
C	-2.89940300	0.63201000	-0.49483600
C	-1.89901000	1.50720600	-0.10207300
H	-3.61330600	-1.40462100	-0.77546400
H	-1.50027000	-2.46933300	0.04700500
H	-3.84164300	1.02905900	-0.86653400
H	-2.08851600	2.57270200	-0.18118400
B	-0.64568000	0.84900500	0.39356000
C	0.87583100	0.87782700	0.95981200
C	0.74763500	-0.70403900	0.94431700
C	1.71189400	-1.43992200	0.05964100
C	2.53517800	-0.78178800	-0.77106200
C	2.60339200	0.67649800	-0.82430300
C	1.87329800	1.44051500	0.00532900
H	1.00247300	1.29885700	1.96176700
H	0.71306000	-1.14659800	1.94546300
H	1.72760100	-2.52398700	0.11411700
H	3.20990700	-1.34391800	-1.40958400
H	3.29098300	1.13338900	-1.52725400
H	1.97319000	2.52182400	-0.01979300

MP2/6-311+G(d,p)

N	-0.59277400	-0.57763200	0.40292500
C	-1.55622700	-1.42153300	-0.03030500
C	-2.72317200	-0.82887300	-0.48546700
C	-2.88408900	0.58655800	-0.49050400
C	-1.91096800	1.48805000	-0.05292800
H	-3.52794200	-1.46326100	-0.84342000
H	-1.38816400	-2.49557000	-0.01111200
H	-3.83443300	0.96741800	-0.86581500
H	-2.14406900	2.54908300	-0.10621000
B	-0.64240100	0.85279200	0.44459900
C	0.88656600	0.90484300	0.99636200
C	0.77218300	-0.67206100	0.99086900
C	1.74998500	-1.41715100	0.13846500
C	2.49052400	-0.76785900	-0.79216200
C	2.47456700	0.68436300	-0.92605700
C	1.78999300	1.46134600	-0.05023200
H	1.06798700	1.34890600	1.98095000
H	0.70860200	-1.09285600	2.00138300
H	1.84296600	-2.49375400	0.26699200
H	3.16580100	-1.33737500	-1.42748000
H	3.07904800	1.14460000	-1.70282900
H	1.85545500	2.54618200	-0.12418900

M06-2X/6-311+G(d,p)

N	-0.62680400	-0.57485800	0.40617600
C	-1.61614700	-1.39233000	0.00067400
C	-2.76326000	-0.79531600	-0.45602000
C	-2.88147100	0.62579900	-0.49710600
C	-1.89508000	1.50450100	-0.09960500
H	-3.58618200	-1.41259600	-0.79010700
H	-1.47578200	-2.46667700	0.04587100
H	-3.82309700	1.01771400	-0.87402300
H	-2.09366600	2.56713100	-0.17953400
B	-0.64028300	0.84932800	0.40298200
C	0.88030400	0.88003000	0.96723100
C	0.74575000	-0.69011100	0.95502500
C	1.70162400	-1.43404900	0.06916400
C	2.51130600	-0.78786500	-0.77585100
C	2.57630400	0.67325200	-0.84170100
C	1.86201800	1.43639000	-0.00557600
H	1.01698900	1.30589300	1.96324700
H	0.71310100	-1.12745600	1.95693900
H	1.71870500	-2.51716800	0.13392600
H	3.17782900	-1.35579500	-1.41637600
H	3.25106600	1.12737300	-1.55722800
H	1.96199100	2.51714100	-0.03827700

SCS-MP2/6-311+G(d,p)

N	-0.607053000	-0.578679000	0.392564000
C	-1.589360000	-1.429390000	-0.001886000
C	-2.761354000	-0.845681000	-0.445886000
C	-2.918778000	0.578201000	-0.479432000
C	-1.937262000	1.483260000	-0.080217000
H	-3.576951000	-1.483651000	-0.774339000
H	-1.424904000	-2.503945000	0.039412000
H	-3.876982000	0.952127000	-0.844135000
H	-2.166830000	2.545232000	-0.148072000
B	-0.654993000	0.850824000	0.407355000
C	0.875762000	0.912320000	0.960594000
C	0.768645000	-0.668868000	0.961007000
C	1.743671000	-1.414280000	0.093002000
C	2.534057000	-0.761026000	-0.789246000
C	2.556559000	0.703601000	-0.888556000
C	1.834591000	1.475953000	-0.043434000
H	1.034073000	1.345440000	1.955628000
H	0.727371000	-1.092100000	1.973015000
H	1.791913000	-2.498828000	0.182851000
H	3.212044000	-1.329875000	-1.423629000
H	3.207400000	1.163744000	-1.628477000
H	1.907820000	2.561838000	-0.104285000

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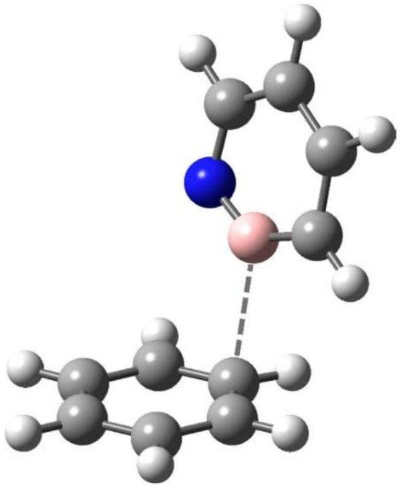


B3LYP/6-311+G(d,p)

N	-1.327078000	0.177434000	1.337908000
C	-2.594167000	0.622603000	1.509431000
C	-3.450291000	0.847307000	0.430669000
C	-3.022371000	0.616628000	-0.894296000
C	-1.736921000	0.156179000	-1.219616000
H	-4.456922000	1.203551000	0.614833000
H	-2.936887000	0.803308000	2.526881000
H	-3.726315000	0.807865000	-1.701190000
H	-1.440766000	-0.007715000	-2.244236000
B	-1.055427000	0.007066000	0.056032000
C	1.749017000	-0.426195000	-1.331298000
C	2.663971000	0.591157000	-1.065414000
C	3.148303000	0.768277000	0.229994000
C	2.717352000	-0.066852000	1.261389000
C	1.803277000	-1.083314000	0.998679000
C	1.314440000	-1.264991000	-0.298956000
H	1.377725000	-0.571879000	-2.339340000
H	2.998182000	1.242690000	-1.864712000
H	3.858222000	1.561180000	0.437574000
H	3.089319000	0.079185000	2.268880000
H	1.456598000	-1.724015000	1.800339000
H	0.640933000	-2.087892000	-0.514029000

B3LYP-D3/6-311+G(d,p)

N	-1.240958000	0.042155000	1.344786000
C	-2.491597000	0.532409000	1.511173000
C	-3.315187000	0.856039000	0.431530000
C	-2.869495000	0.681494000	-0.896185000
C	-1.597447000	0.183434000	-1.213683000
H	-4.309087000	1.245579000	0.618227000
H	-2.850462000	0.670736000	2.529923000
H	-3.545719000	0.948489000	-1.705182000
H	-1.282485000	0.062846000	-2.239405000
B	-0.932812000	-0.074158000	0.058603000
C	1.661982000	-0.475564000	-1.332590000
C	2.533011000	0.583704000	-1.088918000
C	2.997809000	0.815501000	0.205433000
C	2.590637000	-0.005560000	1.257787000
C	1.720356000	-1.064136000	1.017670000
C	1.246084000	-1.300145000	-0.278563000
H	1.297665000	-0.660345000	-2.336314000
H	2.846110000	1.226920000	-1.903059000
H	3.671676000	1.643218000	0.396340000
H	2.943670000	0.186358000	2.264130000
H	1.380815000	-1.687193000	1.835308000
H	0.615630000	-2.160203000	-0.477489000

MP2/6-311+G(d,p)

N	-1.104411000	-0.111603000	1.341027000
C	-2.335606000	0.441500000	1.495388000
C	-3.134062000	0.862614000	0.426153000
C	-2.691121000	0.727903000	-0.906231000
C	-1.438557000	0.172680000	-1.222150000
H	-4.108631000	1.296989000	0.631919000
H	-2.707106000	0.550104000	2.516459000
H	-3.344717000	1.067071000	-1.710619000
H	-1.131015000	0.081605000	-2.257379000
B	-0.757920000	-0.191595000	0.032368000
C	1.535211000	-0.493739000	-1.328107000
C	2.370631000	0.603407000	-1.097940000
C	2.833270000	0.867859000	0.196442000
C	2.433643000	0.058019000	1.268251000
C	1.599811000	-1.038782000	1.044735000
C	1.116427000	-1.304654000	-0.252394000
H	1.181768000	-0.708396000	-2.332621000
H	2.673625000	1.236918000	-1.926668000
H	3.479791000	1.722962000	0.375736000
H	2.780560000	0.275746000	2.274114000
H	1.261909000	-1.647976000	1.876549000
H	0.556695000	-2.217054000	-0.445510000

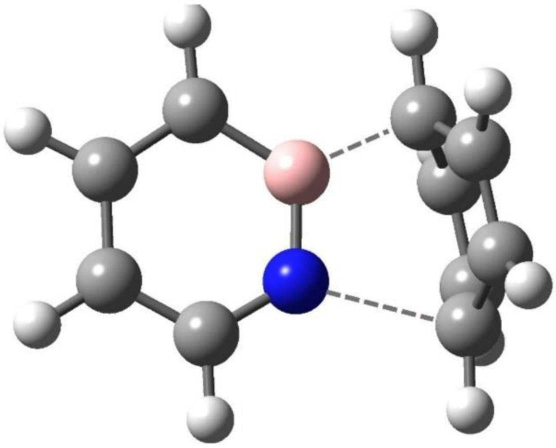
M06-2X/6-311+G(d,p)

N	-1.159470000	0.117556000	1.361602000
C	-2.393747000	0.643313000	1.519742000
C	-3.239030000	0.919224000	0.448691000
C	-2.833881000	0.655682000	-0.875520000
C	-1.587367000	0.114158000	-1.200680000
H	-4.218382000	1.339247000	0.638183000
H	-2.724203000	0.849904000	2.535700000
H	-3.528057000	0.888700000	-1.678944000
H	-1.301389000	-0.075037000	-2.223423000
B	-0.914689000	-0.068427000	0.074029000
C	1.697578000	-0.502302000	-1.367000000
C	2.457653000	0.621279000	-1.061795000
C	2.844079000	0.859749000	0.254429000
C	2.469189000	-0.019547000	1.265184000
C	1.710473000	-1.144835000	0.961994000
C	1.320500000	-1.388322000	-0.354744000
H	1.394210000	-0.691147000	-2.390243000
H	2.744661000	1.311054000	-1.846163000
H	3.430887000	1.738758000	0.493491000
H	2.756766000	0.176817000	2.290617000
H	1.396976000	-1.817299000	1.750703000
H	0.747436000	-2.276948000	-0.596331000

SCS-MP2/6-311+G(d,p)

N	1.362090000	-0.549858000	1.109553000
C	2.614737000	-0.021299000	1.273860000
C	3.266473000	0.732739000	0.291146000
C	2.654048000	1.014135000	-0.958266000
C	1.370278000	0.544245000	-1.286946000
H	4.261137000	1.119409000	0.498392000
H	3.109796000	-0.209309000	2.228517000
H	3.203463000	1.616070000	-1.683833000
H	0.912781000	0.765091000	-2.243782000
B	0.899235000	-0.206776000	-0.108306000
C	-1.318721000	-1.656617000	0.115831000
C	-1.899646000	-1.105220000	1.285403000
C	-2.551270000	0.126700000	1.233850000
C	-2.630292000	0.837213000	0.029577000
C	-2.055911000	0.319954000	-1.131251000
C	-1.395113000	-0.942715000	-1.103683000
H	-0.808440000	-2.613585000	0.155448000
H	-1.811733000	-1.643817000	2.225132000
H	-2.989090000	0.544566000	2.137376000
H	-3.129392000	1.803040000	0.002664000
H	-2.104773000	0.883283000	-2.060321000
H	-0.959656000	-1.357246000	-2.010358000

$TS_{6b\text{-}6c}$



B3LYP/6-311+G(d,p)

N	-0.473278000	-0.748144000	-0.000090000
C	-1.611477000	-1.439330000	-0.000183000
C	-2.842771000	-0.786444000	-0.000121000
C	-2.887108000	0.621411000	0.000042000
C	-1.735322000	1.403707000	0.000145000
H	-3.756093000	-1.369724000	-0.000198000
H	-1.566199000	-2.527851000	-0.000308000
H	-3.865028000	1.098822000	0.000086000
H	-1.837486000	2.485058000	0.000269000
B	-0.455373000	0.634446000	0.000070000
C	1.666760000	0.765127000	-1.230253000
C	1.944641000	-0.564807000	-1.228929000
C	1.716868000	-1.263029000	-0.000127000
C	1.944618000	-0.565089000	1.228839000
C	1.666736000	0.764845000	1.230462000
C	1.155831000	1.364032000	0.000168000
H	1.675557000	1.349712000	-2.142990000
H	2.180058000	-1.110324000	-2.133842000
H	1.741567000	-2.346582000	-0.000252000
H	2.180016000	-1.110813000	2.133631000
H	1.675515000	1.349221000	2.143334000
H	1.049257000	2.444716000	0.000291000

B3LYP-D3/6-311+G(d,p)

N	-0.471410000	-0.749161000	-0.000090000
C	-1.608883000	-1.440159000	-0.000183000
C	-2.840450000	-0.786284000	-0.000120000
C	-2.884496000	0.622138000	0.000042000
C	-1.732128000	1.404374000	0.000145000
H	-3.754018000	-1.369195000	-0.000197000
H	-1.562338000	-2.528516000	-0.000308000
H	-3.862533000	1.099302000	0.000087000
H	-1.831062000	2.485942000	0.000269000
B	-0.453962000	0.633978000	0.000069000
C	1.664839000	0.765307000	-1.230865000
C	1.943518000	-0.564751000	-1.229591000
C	1.713800000	-1.262925000	-0.000127000
C	1.943493000	-0.565033000	1.229501000
C	1.664815000	0.765025000	1.231075000
C	1.154445000	1.364418000	0.000168000
H	1.668858000	1.349233000	-2.143699000
H	2.175081000	-1.110967000	-2.134849000
H	1.732898000	-2.346368000	-0.000252000
H	2.175038000	-1.111457000	2.134638000
H	1.668815000	1.348741000	2.144042000
H	1.045235000	2.444861000	0.000291000

MP2/6-311+G(d,p)

N	-0.462320000	-0.769370000	-0.000091000
C	-1.619965000	-1.451722000	-0.000180000
C	-2.841944000	-0.772976000	-0.000119000
C	-2.873061000	0.638503000	0.000038000
C	-1.702283000	1.409990000	0.000139000
H	-3.766118000	-1.344687000	-0.000194000
H	-1.587898000	-2.543004000	-0.000303000
H	-3.846942000	1.129794000	0.000081000
H	-1.792689000	2.494941000	0.000259000
B	-0.445765000	0.605996000	0.000066000
C	1.644726000	0.775179000	-1.231373000
C	1.925578000	-0.571274000	-1.225186000
C	1.727984000	-1.271535000	-0.000130000
C	1.925555000	-0.571557000	1.225092000
C	1.644707000	0.774895000	1.231591000
C	1.190685000s	1.382196000	0.000175000
H	1.616020000	1.347631000	-2.154863000
H	2.136907000	-1.113092000	-2.141685000
H	1.790119000	-2.357658000	-0.000254000
H	2.136869000	-1.113589000	2.141468000
H	1.615989000	1.347132000	2.155214000
H	1.030903000	2.457943000	0.000297000

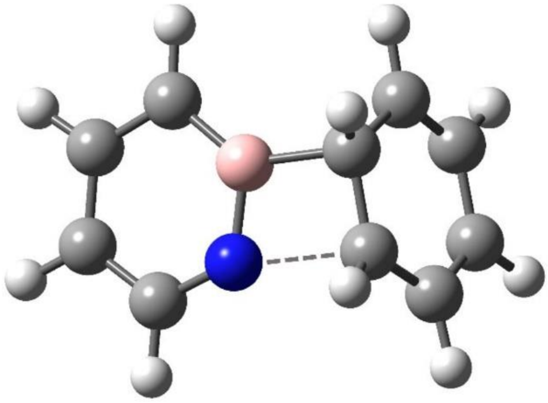
M06-2X/6-311+G(d,p)

N	-0.465704000	-0.765017000	-0.000092000
C	-1.611395000	-1.438828000	-0.000184000
C	-2.836767000	-0.780311000	-0.000120000
C	-2.872024000	0.625782000	0.000045000
C	-1.720125000	1.402312000	0.000148000
H	-3.753016000	-1.356885000	-0.000198000
H	-1.576808000	-2.527474000	-0.000311000
H	-3.846923000	1.107911000	0.000091000
H	-1.814503000	2.483022000	0.000274000
B	-0.460745000	0.609702000	0.000067000
C	1.645780000	0.766583000	-1.226289000
C	1.938715000	-0.560285000	-1.226562000
C	1.732518000	-1.256162000	-0.000126000
C	1.938690000	-0.560565000	1.226473000
C	1.645755000	0.766304000	1.226497000
C	1.171575000	1.370667000	0.000168000
H	1.628083000	1.344847000	-2.142552000
H	2.156691000	-1.103392000	-2.136211000
H	1.765722000	-2.339629000	-0.000248000
H	2.156647000	-1.103879000	2.136003000
H	1.628038000	1.344357000	2.142891000
H	1.023397000	2.444749000	0.000289000

SCS-MP2/6-311+G(d,p)

N	-0.467755000	-0.773676000	-0.001678000
C	-1.632498000	-1.449526000	-0.000833000
C	-2.854860000	-0.773077000	0.000642000
C	-2.885413000	0.643075000	0.001423000
C	-1.715272000	1.412775000	0.000485000
H	-3.780167000	-1.344592000	0.001457000
H	-1.603304000	-2.541716000	-0.000892000
H	-3.860299000	1.134493000	0.002997000
H	-1.804115000	2.498836000	0.001360000
B	-0.455383000	0.604634000	-0.001537000
C	1.652544000	0.772772000	-1.233978000
C	1.941343000	-0.570766000	-1.229775000
C	1.750244000	-1.271538000	-0.000073000
C	1.940166000	-0.570394000	1.229621000
C	1.651099000	0.773096000	1.233227000
C	1.183226000	1.377369000	-0.000740000
H	1.622665000	1.346246000	-2.157744000
H	2.152779000	-1.114407000	-2.145931000
H	1.808396000	-2.358296000	0.000110000
H	2.150696000	-1.113795000	2.146125000
H	1.620219000	1.346815000	2.156806000
H	1.032748000	2.455409000	-0.001033000

$TS_{6b\text{-}6d}$



B3LYP/6-311+G(d,p)

N	0.92107700	-0.59678000	-0.33411900
C	2.11698600	-1.03785600	0.07225000
C	3.08687500	-0.16237800	0.54943700
C	2.82332300	1.22253100	0.63731000
C	1.60076500	1.77560400	0.27344700
H	4.05737600	-0.55067300	0.83763100
H	2.32929700	-2.10407700	-0.00136700
H	3.61741100	1.86241300	1.01731900
H	1.46205100	2.84579600	0.39712500
B	0.60838500	0.79103800	-0.24824400
C	-0.98526100	0.83810900	-0.76621900
C	-1.07909400	-0.63171900	-0.92573500
C	-1.87448700	-1.38600700	-0.02925800
C	-2.47628700	-0.76897700	1.03997200
C	-2.36782600	0.63365200	1.27195500
C	-1.70120200	1.41124300	0.37244300
H	-1.04732700	1.41536600	-1.69110700
H	-0.81171900	-1.06396400	-1.87865600
H	-2.00168000	-2.44919900	-0.19375200
H	-3.07431300	-1.36316700	1.72386500
H	-2.84537600	1.07202600	2.13945900
H	-1.65106800	2.48628800	0.50882800

B3LYP-D3/6-311+G(d,p)

N	0.91348200	-0.59075800	-0.38023500
C	2.09491300	-1.03822700	0.05890300
C	3.05100300	-0.16746900	0.57271100
C	2.78562500	1.21742500	0.66873000
C	1.57281300	1.77431200	0.27954300
H	4.01365800	-0.55903000	0.88206800
H	2.30792100	-2.10377000	-0.01966700
H	3.56901500	1.85181200	1.07885200
H	1.42503700	2.84148000	0.41727300
B	0.59633900	0.79575300	-0.28300900
C	-0.99230200	0.83881800	-0.80283300
C	-1.08253700	-0.63502200	-0.94843700
C	-1.85550600	-1.38495700	-0.02775100
C	-2.42550900	-0.76355200	1.05607800
C	-2.31190600	0.64031500	1.27807700
C	-1.67665100	1.41552500	0.35387000
H	-1.07389800	1.41121100	-1.72848000
H	-0.83870800	-1.07263000	-1.90550100
H	-1.98320500	-2.44943500	-0.18264800
H	-3.00045300	-1.35522800	1.76150000
H	-2.76018500	1.08184800	2.15942000
H	-1.62104200	2.49084500	0.48412100

MP2/6-311+G(d,p)

N	0.86888400	-0.57005400	-0.60387300
C	1.98599300	-1.04717800	-0.00786700
C	2.84960200	-0.19965200	0.68490300
C	2.56961700	1.18088700	0.83597000
C	1.39160300	1.75104300	0.34939200
H	3.77628500	-0.60773200	1.08194800
H	2.23197300	-2.10232700	-0.13872600
H	3.29315200	1.79100900	1.37753500
H	1.20816500	2.80457200	0.55322200
B	0.50137000	0.80089800	-0.39546100
C	-1.07884800	0.83043700	-0.99848300
C	-1.09380100	-0.64160500	-1.05245200
C	-1.74492100	-1.36158600	-0.02067200
C	-2.14507200	-0.72020900	1.14247700
C	-1.99059900	0.67619100	1.30000000
C	-1.53776100	1.43896900	0.23714100
H	-1.17581500	1.39077300	-1.92632400
H	-0.95792700	-1.11924300	-2.01681000
H	-1.88421400	-2.43387600	-0.12820500
H	-2.59173200	-1.30213900	1.94564300
H	-2.27200700	1.15751900	2.23158700
H	-1.49604100	2.52257100	0.32164100

M06-2X/6-311+G(d,p)

N	0.90569200	-0.60914200	-0.44897200
C	2.08612200	-1.04254500	0.00814300
C	3.00872400	-0.17801900	0.57639700
C	2.71224200	1.19483100	0.72192900
C	1.50053200	1.74207600	0.33434800
H	3.97017200	-0.56171200	0.89517100
H	2.32404100	-2.09917200	-0.10184500
H	3.47373800	1.82727100	1.17245500
H	1.32785200	2.79891100	0.50839000
B	0.57173000	0.75689900	-0.28997500
C	-1.02789900	0.83218700	-0.85582300
C	-1.08593900	-0.62741400	-0.96690700
C	-1.81547700	-1.36866200	-0.00345800
C	-2.34858000	-0.73350600	1.08551000
C	-2.24358200	0.67264900	1.27434300
C	-1.66005600	1.43002100	0.30439100
H	-1.04072300	1.40343000	-1.78087400
H	-0.86093000	-1.08390000	-1.91973500
H	-1.93231900	-2.43685600	-0.13291400
H	-2.88617600	-1.31780400	1.82500100
H	-2.65987800	1.13085500	2.16146600
H	-1.61137900	2.50886900	0.40554200

SCS-MP2/6-311+G(d,p)

N	0.909680000	-0.601718000	-0.578019000
C	2.067161000	-1.056278000	-0.035643000
C	2.945157000	-0.202423000	0.627013000
C	2.639275000	1.174728000	0.807448000
C	1.436170000	1.727856000	0.368818000
H	3.892597000	-0.596542000	0.989458000
H	2.321456000	-2.109340000	-0.174409000
H	3.371603000	1.793728000	1.329011000
H	1.242753000	2.778782000	0.581769000
B	0.544672000	0.761948000	-0.361427000
C	-1.051402000	0.835872000	-0.941004000
C	-1.105573000	-0.631832000	-1.014858000
C	-1.772311000	-1.360753000	0.009064000
C	-2.248605000	-0.710059000	1.131647000
C	-2.132019000	0.702987000	1.284156000
C	-1.619346000	1.456271000	0.252717000
H	-1.113021000	1.388894000	-1.878377000
H	-0.939549000	-1.110218000	-1.973660000
H	-1.887072000	-2.436684000	-0.094057000
H	-2.731015000	-1.289341000	1.917157000
H	-2.491563000	1.182978000	2.189950000
H	-1.571140000	2.540411000	0.335830000

Table S18. Cartesian Coordinates of Stationary Points at SCS-MP2/6-311+G(d,p) level of theory with CPCM solvation model and benzene as a solvent.

1,2-Azaborine (1)			
N	-1.343225000	-0.784710000	0.000000000
C	-1.239090000	0.588991000	0.000000000
C	-0.002385000	1.238260000	0.000000000
C	1.221494000	0.510996000	0.000000000
C	1.294047000	-0.898889000	0.000000000
H	0.025154000	2.324554000	0.000000000
H	-2.166357000	1.162156000	0.000000000
H	2.155047000	1.075126000	0.000000000
H	2.236792000	-1.428218000	0.000000000
B	-0.113640000	-1.270078000	0.000000000

furan			
C	1.097221000	-0.350204000	0.000023000
C	0.720602000	0.964732000	-0.000109000
C	-0.720601000	0.964733000	-0.000205000
C	-1.097221000	-0.350203000	0.000099000
O	-0.000001000	-1.164668000	0.000213000
H	2.054462000	-0.851023000	0.000076000
H	1.382523000	1.820253000	-0.000210000
H	-1.382521000	1.820255000	-0.000395000
H	-2.054463000	-0.851020000	0.000212000

Ethene (C_2H_4)			
C	-0.670583000	0.000000000	-0.000003000
C	0.670583000	0.000000000	0.000004000
H	-1.237577000	0.927376000	0.000011000
H	-1.237577000	-0.927376000	-0.000023000
H	1.237577000	-0.927376000	-0.000010000
H	1.237577000	0.927376000	0.000023000

Ethyne (C_2H_2)			
C	0.000000000	0.000000000	0.607877000
C	0.000000000	0.000000000	-0.607877000
H	0.000000000	0.000000000	1.675331000
H	0.000000000	0.000000000	-1.675331000

s-1,3-trans-butadiene			
C	0.603972000	1.756255000	-0.000018000
C	0.609654000	0.408075000	-0.000008000
H	-0.329542000	2.315561000	-0.000024000
H	1.529063000	2.325862000	-0.000019000
H	1.560147000	-0.127303000	-0.000001000
C	-0.609654000	-0.408075000	-0.000008000
C	-0.603972000	-1.756255000	-0.000018000
H	-1.560147000	0.127303000	-0.000001000
H	-1.529063000	-2.325862000	-0.000019000
H	0.329542000	-2.315561000	-0.000024000

s-1,3-cis-butadiene			
C	0.339890000	1.503975000	-0.494235000
C	0.332447000	0.660783000	0.556140000
H	-0.180169000	1.261210000	-1.418157000
H	0.859278000	2.457075000	-0.444511000
H	0.821742000	0.962966000	1.482626000
C	-0.332447000	-0.660783000	0.556140000
C	-0.339890000	-1.503975000	-0.494235000
H	-0.821742000	-0.962966000	1.482626000
H	-0.859278000	-2.457075000	-0.444511000
H	0.180169000	-1.261210000	-1.418157000

cyclopentadiene			
C	1.223298000	-0.000233000	0.000019000
C	0.285583000	1.183170000	0.000003000
C	-0.997418000	0.738569000	-0.000013000
C	-0.997699000	-0.738189000	-0.000015000
C	0.285133000	-1.183279000	0.000007000
H	1.877706000	-0.000359000	-0.883827000
H	1.877680000	-0.000356000	0.883884000
H	0.611394000	2.218620000	0.000007000
H	-1.889941000	1.357383000	-0.000026000
H	0.610549000	-2.218853000	0.000013000
H	-1.890457000	-1.356663000	-0.000029000

benzene			
C	0.540236000	1.294290000	0.007069000
C	-0.850737000	1.114990000	-0.007054000
C	-1.390963000	-0.179270000	0.007046000
C	-0.540236000	-1.294290000	-0.007069000
C	0.850737000	-1.114990000	0.007054000
C	1.390963000	0.179270000	-0.007046000
H	0.959244000	2.298179000	-0.000096000
H	-1.510650000	1.979795000	0.000083000
H	-2.469874000	-0.318305000	-0.000092000
H	-0.959244000	-2.298179000	0.000096000
H	1.510650000	-1.979795000	-0.000083000
H	2.469874000	0.318305000	0.000092000

	1a				1b		
C	2.229529000	-0.002039000	-0.700415000	C	-1.928937000	-0.738971000	0.000369000
C	2.229466000	-0.001698000	0.700759000	C	-2.093487000	0.825106000	-0.000273000
H	2.319943000	-0.935360000	-1.246639000	H	-2.298899000	-1.246434000	-0.896925000
H	2.383194000	0.921995000	-1.249318000	H	-2.298287000	-1.245427000	0.898482000
H	2.383081000	0.922602000	1.249226000	H	-2.602418000	1.207070000	0.890447000
H	2.319832000	-0.934753000	1.247445000	H	-2.601783000	1.206142000	-0.891772000
N	-0.036969000	-1.276719000	0.000374000	N	-0.453202000	-0.596766000	-0.000066000
C	-1.371412000	-1.266497000	0.000311000	C	0.634292000	-1.408674000	0.000267000
C	-2.162775000	-0.090186000	-0.000003000	C	1.866834000	-0.780958000	0.000240000
C	-1.575510000	1.186035000	-0.000280000	C	1.972786000	0.648957000	0.000034000
C	-0.175958000	1.305221000	-0.000247000	C	0.879399000	1.514017000	-0.000190000
H	-3.247158000	-0.190674000	-0.000027000	H	2.768583000	-1.386819000	0.000429000
H	-1.890022000	-2.229935000	0.000517000	H	0.503403000	-2.488948000	0.000464000
H	-2.221913000	2.064155000	-0.000517000	H	2.983763000	1.060525000	0.000070000
H	0.264468000	2.303793000	-0.000465000	H	1.080944000	2.584425000	-0.000272000
B	0.580108000	0.010651000	0.000095000	B	-0.474105000	0.835562000	-0.000219000
	1c				**1d**		
C	2.094579000	0.561753000	0.196127000	C	-1.921742000	-0.457835000	0.229111000
C	3.033761000	-0.312106000	-0.230231000	C	-2.899375000	0.305971000	-0.277906000
H	2.456205000	1.517110000	0.585546000	H	-2.137650000	-1.388127000	0.751225000
H	4.099239000	-0.094275000	-0.174227000	H	-3.933303000	0.009581000	-0.133491000
H	2.764795000	-1.274814000	-0.665702000	H	-2.692746000	1.220769000	-0.823487000
N	0.021916000	-1.021480000	0.164409000	N	-0.525900000	-0.145627000	0.129792000
C	-1.312349000	-1.331468000	0.067490000	C	0.317544000	-1.227939000	-0.035541000
C	-2.255367000	-0.342961000	-0.073780000	C	1.677398000	-1.077181000	-0.145972000
C	-1.857128000	1.030936000	-0.115372000	C	2.274037000	0.220129000	-0.088007000
C	-0.527652000	1.400797000	-0.022582000	C	1.496857000	1.349918000	0.087879000
H	-3.302739000	-0.620156000	-0.145595000	H	2.287951000	-1.965325000	-0.280171000
H	-1.577888000	-2.384317000	0.117682000	H	-0.156176000	-2.205802000	-0.081326000
H	-2.639590000	1.783717000	-0.221668000	H	3.358580000	0.289994000	-0.178913000
H	-0.294470000	2.465161000	-0.062279000	H	2.002113000	2.313989000	0.136855000
B	0.541921000	0.320702000	0.115160000	B	-0.010340000	1.203388000	0.228597000
H	0.642479000	-1.814340000	0.287261000	H	-0.784691000	2.087003000	0.431894000
	TS$_{1a-1b}$				**TS$_{1a-1c}$**		
C	-1.823357000	-0.483830000	0.682562000	C	-3.029055000	-0.231735000	0.345939000
C	-2.223762000	0.517844000	-0.314892000	C	-2.069533000	0.445277000	-0.333206000
H	-2.150193000	-1.512922000	0.614732000	H	-2.761871000	-1.081158000	0.972421000
H	-1.498986000	-0.153591000	1.668724000	H	-4.083470000	0.029351000	0.274523000
H	-2.518882000	1.489541000	0.079184000	H	-1.307135000	-0.576695000	-0.736157000
H	-2.842552000	0.134586000	-1.122655000	H	-2.357413000	1.250488000	-1.007273000
N	-0.271020000	-1.008371000	-0.508197000	N	-0.074710000	-1.063973000	-0.121813000
C	1.019664000	-1.353418000	-0.168354000	C	1.254750000	-1.371384000	-0.114049000
C	1.998766000	-0.424798000	0.123151000	C	2.231572000	-0.402127000	0.064951000
C	1.707449000	0.981377000	0.185927000	C	1.895692000	0.982373000	0.154353000
C	0.421654000	1.438348000	-0.010722000	C	0.582504000	1.427498000	0.043656000
H	3.013921000	-0.770020000	0.312264000	H	3.274894000	-0.705597000	0.118796000
H	1.269324000	-2.415668000	-0.185233000	H	1.534894000	-2.419924000	-0.226544000
H	2.523658000	1.662874000	0.429359000	H	2.711704000	1.695636000	0.281846000
H	0.224484000	2.505707000	0.095874000	H	0.380159000	2.496717000	0.076243000
B	-0.613797000	0.389211000	-0.434374000	B	-0.423349000	0.310300000	-0.041453000
	TS$_{1a-1d}$				**2a**		
C	-2.208812000	0.062833000	0.468018000	C	2.342369000	-0.001276000	0.621704000
C	-3.035120000	-0.036647000	-0.577971000	C	2.342377000	-0.001177000	-0.621676000
H	-2.138416000	-0.013334000	1.537799000	H	2.575860000	-0.019982000	1.669072000
H	-1.346546000	1.374372000	0.498143000	H	2.575880000	-0.019724000	-1.669044000
H	-3.387719000	0.848981000	-1.097326000	N	0.034944000	-1.277463000	-0.000101000
H	-3.153228000	-1.005361000	-1.057954000	C	-1.304371000	-1.257778000	-0.000108000
N	-0.295389000	-0.536816000	0.374856000	C	-2.086814000	-0.079839000	-0.000019000
C	0.726920000	-1.378625000	0.086269000	C	-1.487945000	1.192776000	0.000086000
C	1.974973000	-0.843119000	-0.220021000	C	-0.087589000	1.304053000	0.000104000

C	2.182209000	0.565461000	-0.247872000	H	-3.171803000	-0.171859000	-0.000033000
C	1.166285000	1.488313000	0.019841000	H	-1.826459000	-2.219267000	-0.000188000
H	2.800514000	-1.516060000	-0.440940000	H	-2.127981000	2.075816000	0.000153000
H	0.556393000	-2.454867000	0.114594000	H	0.363709000	2.296755000	0.000186000
H	3.183272000	0.921978000	-0.497445000	B	0.647462000	0.001309000	0.000004000
H	1.391948000	2.551165000	-0.029755000				
B	-0.147587000	0.831296000	0.329151000				
		2b				**2c**	
C	1.994622000	-0.619627000	-0.007125000	C	2.169865000	0.041496000	-0.000201000
C	2.179568000	0.723485000	-0.004735000	C	3.396216000	0.016630000	0.000146000
H	2.606974000	-1.518502000	-0.019511000	H	4.464767000	0.000237000	0.000669000
H	3.107499000	1.280959000	-0.017395000	N	-0.098728000	-1.153295000	-0.000068000
N	0.520942000	-0.603519000	0.017758000	C	-1.468809000	-1.231528000	0.000062000
C	-0.547730000	-1.411036000	-0.000602000	C	-2.235938000	-0.091313000	0.000153000
C	-1.792608000	-0.781406000	-0.004029000	C	-1.615405000	1.196824000	0.000119000
C	-1.886435000	0.638467000	-0.004007000	C	-0.238837000	1.338835000	-0.000007000
C	-0.791845000	1.521220000	0.000623000	H	-3.317622000	-0.185235000	0.000251000
H	-2.693531000	-1.386753000	-0.010549000	H	-1.904577000	-2.226912000	0.000084000
H	-0.414168000	-2.490904000	-0.005294000	H	-2.264148000	2.073563000	0.000190000
H	-2.895276000	1.055968000	-0.009502000	H	0.173201000	2.347035000	-0.000027000
H	-1.002241000	2.588675000	-0.006222000	B	0.625592000	0.087358000	-0.000101000
B	0.544679000	0.849166000	0.009985000	H	0.394226000	-2.039885000	-0.000133000
		2d				**2e**	
C	1.963025000	0.046856000	0.000253000	C	2.151903000	-0.045593000	-0.000460000
C	3.177638000	0.016942000	0.000416000	C	3.377612000	-0.003529000	0.000221000
H	4.244196000	0.001998000	0.000583000	H	0.133666000	1.917357000	0.867142000
N	0.590241000	0.070271000	0.000083000	H	4.446327000	0.015845000	0.000672000
C	-0.054781000	-1.163259000	-0.000131000	N	-0.080761000	-1.344204000	-0.000345000
C	-1.421153000	-1.237867000	-0.000313000	C	-1.382648000	-1.287679000	0.000020000
C	-2.224866000	-0.051175000	-0.000293000	C	-2.225715000	-0.081461000	0.000188000
C	-1.649778000	1.204010000	-0.000089000	C	-1.671875000	1.153019000	0.000153000
H	-1.883345000	-2.220445000	-0.000477000	C	-0.182371000	1.312712000	-0.000039000
H	0.587226000	-2.039051000	-0.000143000	H	-3.304228000	-0.221164000	0.000412000
H	-3.308503000	-0.171494000	-0.000447000	H	-1.926964000	-2.239924000	0.000233000
H	-2.311384000	2.069057000	-0.000087000	H	-2.307441000	2.038473000	0.000378000
B	-0.133956000	1.329647000	0.000125000	H	0.133458000	1.918431000	-0.866514000
H	0.511681000	2.330815000	0.000305000	B	0.610227000	-0.052628000	-0.000750000
		$\mathbf{TS_{2a\text{-}2b}}$				$\mathbf{TS_{2a\text{-}2c}}$	
C	-1.994181000	-0.497871000	0.597214000	C	-3.339715000	0.156281000	0.000442000
C	-2.309405000	0.437232000	-0.215897000	C	-2.176366000	-0.230703000	0.008695000
H	-2.005134000	-1.162679000	1.444449000	H	-4.350330000	0.512182000	-0.008770000
H	-3.084370000	1.144086000	-0.466364000	H	-1.433361000	-1.215210000	-0.010049000
N	-0.295532000	-1.047445000	-0.425698000	N	0.089294000	-1.223897000	0.017831000
C	1.008735000	-1.333095000	-0.099524000	C	1.444786000	-1.271580000	0.003933000
C	1.967365000	-0.355714000	0.107254000	C	2.213954000	-0.109229000	-0.002964000
C	1.630773000	1.038981000	0.120413000	C	1.612182000	1.179369000	-0.003732000
C	0.316419000	1.445061000	-0.003626000	C	0.226018000	1.363001000	0.000866000
H	3.002431000	-0.657415000	0.259420000	H	3.298224000	-0.193708000	-0.009496000
H	1.295690000	-2.385688000	-0.077392000	H	1.925335000	-2.250873000	0.000699000
H	2.433431000	1.758114000	0.288353000	H	2.273131000	2.047721000	-0.010194000
H	0.084508000	2.506738000	0.080175000	H	-0.186372000	2.368551000	-0.003341000
B	-0.682152000	0.333812000	-0.328281000	B	-0.493996000	0.057834000	0.016159000
		$\mathbf{TS_{2a\text{-}2e}}$				$\mathbf{TS_{2e\text{-}2d}}$	
C	-1.627531000	0.606208000	0.594438000	C	1.559838000	0.253494000	-0.091455000
C	-2.729284000	1.152532000	0.701606000	C	2.447199000	-0.004899000	-0.903720000
H	-3.704018000	1.580570000	0.808554000	H	0.896102000	1.336497000	1.871458000
H	-0.588105000	1.093075000	-0.214595000	H	3.230103000	-0.167835000	-1.613612000
N	-0.049253000	-1.254808000	-0.363053000	N	0.397824000	-0.740071000	1.001924000
C	1.197315000	-1.641859000	-0.566340000	C	-0.520840000	-1.408239000	0.270641000
C	2.369898000	-0.909406000	-0.181313000	C	-1.561568000	-0.789971000	-0.428150000
C	2.272016000	0.313528000	0.472949000	C	-1.661345000	0.621800000	-0.548270000

C	0.990232000	0.817740000	0.808241000	C	-0.743155000	1.429864000	0.100464000
H	3.345260000	-1.317744000	-0.440541000	H	-2.293793000	-1.423000000	-0.928293000
H	1.355280000	-2.586986000	-1.095912000	H	-0.452546000	-2.497350000	0.260818000
H	3.178788000	0.859420000	0.731657000	H	-2.475744000	1.036054000	-1.141037000
H	0.914863000	1.786630000	1.303584000	H	-0.833065000	2.509853000	-0.028460000
B	-0.187671000	-0.030126000	0.398969000	B	0.379914000	0.763592000	0.951109000
		3a(cis)				**3a(trans)**	
N	0.353497000	1.023801000	0.433988000	N	-0.512819000	-0.851359000	0.858435000
C	1.588378000	1.497930000	0.262144000	C	-1.711848000	-1.332704000	0.526492000
C	2.700696000	0.714121000	-0.137774000	C	-2.638022000	-0.667514000	-0.316650000
C	2.571744000	-0.663950000	-0.379719000	C	-2.346423000	0.590296000	-0.870656000
C	1.321427000	-1.281759000	-0.215421000	C	-1.118736000	1.208132000	-0.581093000
H	3.665522000	1.202773000	-0.266011000	H	-3.586883000	-1.154347000	-0.537253000
H	1.752900000	2.566814000	0.430418000	H	-1.996714000	-2.311950000	0.923618000
H	3.449875000	-1.229865000	-0.692470000	H	-3.083033000	1.064907000	-1.519820000
H	1.239822000	-2.354497000	-0.400921000	H	-0.908715000	2.185932000	-1.018494000
B	0.204903000	-0.377903000	0.220102000	B	-0.208460000	0.437350000	0.328344000
C	-3.250324000	0.857281000	-0.123488000	C	3.095297000	-0.878688000	-1.054007000
C	-2.293937000	0.221036000	-0.826827000	C	2.350795000	-0.526759000	0.013969000
H	-3.475306000	0.592510000	0.906492000	H	3.135861000	-0.253100000	-1.943550000
H	-3.827590000	1.659786000	-0.574611000	H	3.676087000	-1.796759000	-1.054181000
H	-2.110799000	0.493078000	-1.865159000	H	2.304707000	-1.160151000	0.897022000
C	-1.488487000	-0.896453000	-0.292072000	C	1.602073000	0.737031000	0.052838000
C	-1.180117000	-1.087744000	1.065885000	C	1.049041000	1.289482000	1.223379000
H	-1.304890000	-1.725257000	-0.974636000	H	1.664503000	1.367040000	-0.833811000
H	-0.894136000	-2.072655000	1.422294000	H	0.799297000	2.345540000	1.252315000
H	-1.506925000	-0.361226000	1.803883000	H	1.179461000	0.775013000	2.171108000
		3b(cis)				**3b(trans)**	
N	0.153966000	-0.305789000	0.317224000	N	-0.096631000	-0.180902000	-0.251760000
C	0.962846000	-1.395686000	0.270942000	C	-0.705283000	-1.394861000	-0.265047000
C	2.275429000	-1.166543000	-0.096398000	C	-2.066947000	-1.395039000	-0.023739000
C	2.744691000	0.155267000	-0.392598000	C	-2.778114000	-0.174657000	0.226562000
C	1.948881000	1.297280000	-0.339203000	C	-2.184812000	1.086908000	0.249777000
H	2.961166000	-2.006905000	-0.156336000	H	-2.604003000	-2.339476000	-0.022900000
H	0.565827000	-2.379362000	0.513577000	H	-0.119146000	-2.291232000	-0.457965000
H	3.795954000	0.245777000	-0.671291000	H	-3.850566000	-0.267069000	0.407713000
H	2.415480000	2.251724000	-0.577522000	H	-2.826295000	1.943760000	0.451600000
B	0.507432000	1.055392000	0.052631000	B	-0.693126000	1.097792000	-0.011208000
C	-3.330559000	-0.215364000	-0.731994000	C	3.439937000	-0.756855000	0.175441000
C	-2.269673000	-0.757244000	-0.113887000	C	2.274942000	-0.189637000	0.531754000
H	-3.526180000	0.852770000	-0.705471000	H	3.716028000	-0.864351000	-0.871794000
H	-4.035014000	-0.838071000	-1.276420000	H	4.144614000	-1.119280000	0.919425000
H	-2.122404000	-1.838196000	-0.155417000	H	2.007873000	-0.089478000	1.585704000
C	-1.253663000	0.006876000	0.692379000	C	1.279834000	0.350490000	-0.450458000
C	-1.003713000	1.530295000	0.383260000	C	0.747742000	1.814570000	-0.184690000
H	-1.404642000	-0.183926000	1.764765000	H	1.620841000	0.191055000	-1.481181000
H	-1.169331000	2.183728000	1.245750000	H	0.896490000	2.485143000	-1.037618000
H	-1.591063000	1.898707000	-0.462716000	H	1.195107000	2.268873000	0.706482000
		3c				**3d**	
N	0.020844000	-0.652961000	0.006606000	N	-0.008681000	-0.658529000	0.023364000
C	-1.074475000	-1.482008000	-0.091956000	C	1.176922000	-1.357643000	-0.002143000
C	-2.359790000	-0.998106000	-0.079674000	C	2.405120000	-0.738609000	-0.018438000
C	-2.601667000	0.406448000	0.034558000	C	2.496635000	0.684222000	-0.009799000
C	-1.550724000	1.297440000	0.134892000	C	1.354364000	1.463871000	0.012116000
H	-3.182742000	-1.701611000	-0.167002000	H	3.298783000	-1.356104000	-0.033218000
H	-0.868216000	-2.547005000	-0.181464000	H	1.095215000	-2.442893000	0.008621000
H	-3.636544000	0.751592000	0.035937000	H	3.488085000	1.138984000	-0.018512000
H	-1.789833000	2.358740000	0.216109000	H	1.477712000	2.547449000	0.016042000
B	-0.115673000	0.776870000	0.133161000	B	-0.019500000	0.808584000	-0.010219000
C	1.333768000	-1.334331000	0.029301000	C	-1.273309000	-1.534707000	0.109285000
C	2.483462000	-0.419075000	-0.308449000	C	-2.312998000	-0.586171000	-0.399117000

H	1.484349000	-1.775014000	1.025777000	H	-1.414831000	-1.818039000	1.157924000
H	1.302613000	-2.161962000	-0.689542000	H	-1.102494000	-2.424527000	-0.504648000
H	3.402860000	-0.915096000	-0.617628000	H	-2.268296000	-0.410554000	-1.477815000
C	2.435773000	0.921375000	-0.211633000	C	-2.277732000	0.523099000	0.403056000
C	1.202320000	1.661990000	0.245469000	C	-1.441043000	1.647226000	-0.105398000
H	3.329154000	1.492851000	-0.467060000	H	-2.198384000	0.342812000	1.481430000
H	1.083898000	2.590499000	-0.330837000	H	-1.444607000	2.568967000	0.487518000
H	1.343355000	1.989862000	1.289201000	H	-1.630250000	1.882326000	-1.161925000
$TS_{3a(cis)-3b(cis)}$				**$TS_{3a(cis)-3c}$**			
N	-0.253953000	0.782967000	-0.295739000	N	0.166317000	0.817622000	0.143349000
C	-1.344365000	1.329740000	0.336060000	C	1.346626000	1.464379000	0.081382000
C	-2.537330000	0.651276000	0.506119000	C	2.561641000	0.791696000	-0.095079000
C	-2.683121000	-0.719804000	0.103799000	C	2.593898000	-0.621636000	-0.167396000
C	-1.614489000	-1.413286000	-0.428368000	C	1.422135000	-1.376848000	-0.055121000
H	-3.382737000	1.170849000	0.954475000	H	3.475827000	1.369952000	-0.214684000
H	-1.259740000	2.366022000	0.670242000	H	1.336548000	2.557429000	0.105954000
H	-3.648790000	-1.200748000	0.267000000	H	3.558507000	-1.111295000	-0.313670000
H	-1.747023000	-2.467670000	-0.674278000	H	1.500805000	-2.464697000	-0.063970000
B	-0.343153000	-0.598792000	-0.683309000	B	0.163498000	-0.579662000	0.167014000
C	3.328292000	0.846141000	-0.071521000	C	-2.206447000	1.332983000	0.291256000
C	2.200656000	0.644663000	0.638320000	C	-2.464150000	0.362678000	-0.645072000
H	3.587171000	0.226052000	-0.925099000	H	-1.987168000	1.098412000	1.326053000
H	4.015256000	1.643141000	0.198956000	H	-2.379158000	2.381631000	0.060147000
H	1.971477000	1.268690000	1.500025000	H	-2.806128000	0.645148000	-1.637087000
C	1.273740000	-0.467827000	0.372140000	C	-1.971669000	-0.953746000	-0.453941000
C	1.158833000	-1.187781000	-0.896459000	C	-1.275298000	-1.388040000	0.700885000
H	0.892113000	-0.971850000	1.262854000	H	-1.994100000	-1.631320000	-1.308799000
H	1.158269000	-2.275501000	-0.818164000	H	-1.065114000	-2.453157000	0.764662000
H	1.754958000	-0.788026000	-1.713623000	H	-1.513499000	-0.921264000	1.655724000
$TS_{3a(cis)-3a(trans)}$				**$TS_{3b(cis)-3b(trans)}$**			
N	-0.553961000	1.089176000	-0.433723000	N	0.315394000	-0.357289000	0.418097000
C	-1.804436000	1.458077000	-0.153001000	C	1.100381000	-1.462253000	0.335871000
C	-2.814420000	0.576884000	0.311219000	C	2.446134000	-1.237977000	0.108855000
C	-2.555841000	-0.789761000	0.506429000	C	2.964882000	0.092603000	-0.020418000
C	-1.275582000	-1.299675000	0.232917000	C	2.189582000	1.247810000	0.070032000
H	-3.803804000	0.980110000	0.522261000	H	3.118610000	-2.087473000	0.028781000
H	-2.068519000	2.512021000	-0.283706000	H	0.657886000	-2.450398000	0.445722000
H	-3.359045000	-1.432233000	0.868519000	H	4.038212000	0.179788000	-0.198556000
H	-1.095163000	-2.365419000	0.384897000	H	2.696488000	2.205384000	-0.042100000
B	-0.271893000	-0.297348000	-0.254371000	B	0.713077000	1.014421000	0.312954000
C	3.620888000	0.506564000	0.470296000	C	-3.364940000	-0.390858000	-0.401997000
C	2.277143000	0.537535000	0.482713000	C	-2.054929000	-0.680223000	-0.337578000
H	4.170770000	-0.370500000	0.134972000	H	-3.824065000	0.318085000	0.284823000
H	4.197810000	1.366629000	0.800132000	H	-4.006535000	-0.853700000	-1.146643000
H	1.744925000	1.424393000	0.814352000	H	-1.619943000	-1.392617000	-1.039773000
C	1.476017000	-0.657616000	0.060636000	C	-1.115431000	-0.061192000	0.670804000
C	1.073305000	-0.880993000	-1.268179000	C	-0.817467000	1.488247000	0.542577000
H	1.478757000	-1.513459000	0.735200000	H	-1.394641000	-0.346956000	1.693569000
H	0.822775000	-1.882517000	-1.605598000	H	-1.058789000	2.051353000	1.450367000
H	1.266336000	-0.123612000	-2.022536000	H	-1.335101000	1.940421000	-0.309531000
$TS_{3a(trans)-3b(trans)}$				**$TS_{3a(trans)-3d}$**			
N	-1.234058000	-0.148790000	1.521148000	N	-0.404447000	-0.946722000	0.225927000
C	-2.101320000	-0.985369000	0.862660000	C	-1.645363000	-1.449366000	0.017470000
C	-2.510311000	-0.770934000	-0.440658000	C	-2.750412000	-0.651703000	-0.268798000
C	-1.983555000	0.312327000	-1.224530000	C	-2.602141000	0.755467000	-0.360338000
C	-1.017656000	1.150518000	-0.705504000	C	-1.361493000	1.363004000	-0.168914000
H	-3.248707000	-1.439594000	-0.880490000	H	-3.718037000	-1.119199000	-0.438460000
H	-2.505388000	-1.829473000	1.425446000	H	-1.759794000	-2.536246000	0.055750000
H	-2.344069000	0.423800000	-2.248226000	H	-3.482139000	1.357162000	-0.595736000
H	-0.603042000	1.929119000	-1.347180000	H	-1.297077000	2.449288000	-0.244354000
B	-0.652343000	0.931016000	0.766665000	B	-0.219074000	0.442101000	0.189735000

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C	1.573977000	-2.162352000	2.540183000
C	0.996147000	-0.946806000	2.636902000
H	1.891943000	-2.559216000	1.578276000
H	1.736726000	-2.778101000	3.420411000
H	0.673128000	-0.548715000	3.596003000
C	0.837553000	-0.077158000	1.466991000
C	0.698365000	1.388705000	1.527148000
H	1.197004000	-0.502451000	0.526642000
H	1.376362000	1.941105000	0.875376000
H	0.616684000	1.784060000	2.538703000

C	1.569946000	-2.049659000	0.519179000
C	2.143924000	-0.942899000	1.108467000
H	1.624112000	-2.190969000	-0.556848000
H	1.233189000	-2.898299000	1.109327000
H	2.047737000	-0.802438000	2.183426000
C	2.060836000	0.183491000	0.265729000
C	1.277150000	1.294894000	0.643574000
H	2.273851000	0.046320000	-0.797085000
H	1.301243000	2.184836000	0.016109000
H	1.178753000	1.490410000	1.713129000

$TS_{3d\text{-}3c}$

N	-0.006337000	-0.771568000	-0.033189000
C	1.188800000	-1.433212000	-0.030824000
C	2.391702000	-0.753754000	-0.021898000
C	2.423087000	0.663322000	0.043509000
C	1.252325000	1.412527000	0.099162000
H	3.313804000	-1.326807000	-0.046961000
H	1.138224000	-2.519530000	-0.035038000
H	3.394434000	1.157614000	0.067717000
H	1.331539000	2.495774000	0.162506000
B	-0.042559000	0.657567000	-0.002144000
C	-1.290180000	-1.544389000	0.094052000
C	-2.312199000	-0.555050000	-0.438072000
H	-1.353997000	-1.813792000	1.170637000
H	-1.216919000	-2.465011000	-0.494540000
H	-3.353721000	-0.881030000	-0.332690000
C	-2.000239000	0.643384000	0.354751000
C	-1.461614000	1.777563000	-0.240571000
H	-1.934620000	0.628524000	1.466343000
H	-1.221716000	2.664555000	0.347014000
H	-1.537607000	1.868929000	-1.323887000

4a

C	-2.180273000	0.069756000	-1.185240000
C	-1.227452000	-0.973326000	-0.627469000
C	-1.280960000	-0.912140000	0.782153000
C	-2.143148000	0.221934000	1.167712000
C	-2.642000000	0.807210000	0.050580000
H	-3.023167000	-0.463957000	-1.654032000
H	-1.743503000	0.721884000	-1.948946000
H	-0.932809000	-1.859043000	-1.179087000
H	-0.952930000	-1.698086000	1.454015000
H	-3.275112000	1.689476000	0.023226000
H	-2.300950000	0.540784000	2.193017000
N	1.309795000	-1.332556000	0.053771000
C	2.576475000	-0.903981000	0.008535000
C	2.953027000	0.456716000	-0.053323000
C	1.983857000	1.476601000	-0.047850000
C	0.619334000	1.153984000	0.018238000
H	4.011813000	0.708696000	-0.087463000
H	3.369790000	-1.657555000	0.023763000
H	2.315031000	2.515730000	-0.072258000
H	-0.100960000	1.970237000	0.064349000
B	0.317304000	-0.314493000	0.025611000

4b

C	-2.154770000	0.196491000	-1.160541000
C	-2.606464000	0.823045000	0.136263000
C	-2.134605000	0.121908000	1.196473000
C	-1.302374000	-0.988436000	0.707515000
C	-1.240094000	-0.925282000	-0.700812000
H	-1.682136000	0.912534000	-1.840190000
H	-3.005519000	-0.259409000	-1.692553000
H	-3.202590000	1.729379000	0.188014000
H	-2.280902000	0.353696000	2.246092000
H	-0.991759000	-1.772247000	-1.331824000
H	-0.992912000	-1.835967000	1.310517000
N	0.495546000	1.064363000	0.022833000
C	1.765973000	1.484482000	0.010285000
C	2.891646000	0.628787000	0.004855000
C	2.737101000	-0.769409000	-0.001309000
C	1.449411000	-1.327987000	-0.013272000
H	3.887135000	1.069831000	0.018757000
H	1.944157000	2.564523000	0.024519000
H	3.627697000	-1.399327000	0.002862000
H	1.351872000	-2.415277000	-0.030905000
B	0.323265000	-0.338577000	-0.022393000

4c

C	-1.750016000	0.001331000	1.243443000
C	-1.198620000	-1.087562000	0.297942000
C	-1.913969000	-0.702495000	-1.000656000
C	-1.995668000	0.648006000	-1.003494000
C	-1.373568000	1.186394000	0.287796000
H	-1.225340000	0.018899000	2.205883000
H	-2.832803000	-0.087741000	1.390894000
H	-1.246943000	-2.131815000	0.615035000
H	-2.185525000	-1.392202000	-1.793648000
H	-1.701409000	2.183751000	0.587883000
H	-2.361288000	1.272249000	-1.814649000
N	0.214058000	-0.604577000	0.172148000
C	1.319310000	-1.377357000	0.023509000
C	2.550588000	-0.765573000	-0.130518000
C	2.656778000	0.657085000	-0.144514000
C	1.553436000	1.497594000	-0.014076000
H	3.436460000	-1.384665000	-0.237991000
H	1.194047000	-2.458731000	0.044088000
H	3.654880000	1.081997000	-0.265267000
H	1.730326000	2.572439000	-0.038715000
B	0.203112000	0.840394000	0.146631000

4d

C	-1.647553000	1.543580000	-0.086935000
C	-2.718787000	0.697956000	-0.377768000
C	-2.658957000	-0.731518000	-0.299691000
C	-1.496591000	-1.381680000	0.077608000
H	-3.674789000	1.127902000	-0.682492000
H	-1.811958000	2.616564000	-0.178238000

$TS_{4a\text{-}4b}$

C	-2.044220000	1.276572000	0.235950000
C	-1.393231000	0.605661000	-0.958470000
C	-1.629263000	-0.748293000	-0.871993000
C	-2.286564000	-1.058866000	0.401192000
C	-2.538941000	0.108094000	1.049029000
H	-2.883769000	1.894561000	-0.116943000

H	-3.539220000	-1.320616000	-0.541731000	H	-1.370524000	1.929417000	0.803266000
H	-1.402204000	-2.463375000	0.150498000	H	-1.121867000	1.126731000	-1.870932000
C	0.989324000	-0.752855000	0.777637000	H	-1.376151000	-1.481481000	-1.629890000
C	1.179474000	0.818603000	0.795426000	H	-2.994161000	0.208965000	2.029512000
H	1.087465000	-1.292506000	1.727268000	H	-2.502765000	-2.062730000	0.748020000
H	1.406264000	1.218741000	1.788692000	N	0.852434000	-1.289536000	-0.175784000
C	1.892086000	-1.234891000	-0.327070000	C	2.144527000	-1.360769000	0.230794000
C	2.290022000	1.127645000	-0.242970000	C	2.982507000	-0.255726000	0.409398000
C	2.571412000	-0.215666000	-0.888839000	C	2.506057000	1.049658000	0.153424000
H	1.952165000	-2.275495000	-0.638365000	C	1.190451000	1.271089000	-0.272826000
H	3.262697000	-0.329356000	-1.722544000	H	4.007088000	-0.410804000	0.740668000
H	3.198499000	1.519839000	0.233989000	H	2.545042000	-2.359481000	0.427175000
H	1.977062000	1.868829000	-0.990734000	H	3.185534000	1.893232000	0.290115000
N	-0.435203000	-0.588870000	0.369625000	H	0.861731000	2.290347000	-0.468555000
B	-0.372621000	0.842654000	0.329186000	B	0.403926000	0.005964000	-0.406507000
		TS_{4b-4c}				**TS_{4b-4d}**	
C	1.837117000	-0.042239000	-1.264654000	C	-1.663082000	1.337212000	0.433037000
C	2.021876000	-1.066501000	-0.186567000	C	-2.848837000	0.656769000	0.212673000
C	2.219004000	-0.424519000	1.032193000	C	-2.842418000	-0.695249000	-0.260109000
C	1.785139000	0.906461000	0.879894000	C	-1.655015000	-1.349655000	-0.544406000
C	1.274099000	1.128585000	-0.442107000	H	-3.814311000	1.119730000	0.425298000
H	1.224670000	-0.372009000	-2.104028000	H	-1.709733000	2.346270000	0.845180000
H	2.835393000	0.250737000	-1.634088000	H	-3.785548000	-1.221544000	-0.398227000
H	2.171539000	-2.125674000	-0.373207000	H	-1.679671000	-2.392201000	-0.871241000
H	2.476157000	-0.900488000	1.971543000	C	1.176239000	-0.388906000	0.857190000
H	1.255937000	2.139434000	-0.847086000	C	1.140927000	1.010134000	0.431530000
H	1.742912000	1.642494000	1.680272000	H	0.746956000	-0.758576000	1.784633000
N	-0.356087000	-0.830062000	0.018250000	H	1.086097000	1.755779000	1.228243000
C	-1.555118000	-1.446366000	0.033661000	C	2.190708000	-1.107223000	0.098620000
C	-2.755439000	-0.728576000	0.080798000	C	2.272062000	1.163958000	-0.599973000
C	-2.744025000	0.688559000	0.068661000	C	2.836468000	-0.231860000	-0.711758000
C	-1.546126000	1.410339000	0.005242000	H	2.371605000	-2.173381000	0.182593000
H	-3.696889000	-1.269937000	0.151225000	H	3.646333000	-0.494179000	-1.388509000
H	-1.577449000	-2.539524000	0.057111000	H	3.037407000	1.873277000	-0.254144000
H	-3.702323000	1.210697000	0.108529000	H	1.916280000	1.521641000	-1.574495000
H	-1.597098000	2.498823000	-0.040612000	N	-0.431975000	-0.735409000	-0.489310000
B	-0.308755000	0.561215000	-0.065500000	B	-0.393189000	0.611358000	0.004635000
		5a				**5b**	
N	1.092075000	-1.242364000	0.214341000	N	-1.258495000	-1.334833000	0.036205000
C	2.445360000	-1.262430000	0.150344000	C	-2.550318000	-0.949243000	0.001281000
C	3.239949000	-0.124705000	-0.025244000	C	-2.971298000	0.390636000	-0.001413000
C	2.643760000	1.150928000	-0.159447000	C	-2.030858000	1.443418000	0.045384000
C	1.252750000	1.315969000	-0.121546000	C	-0.655638000	1.178274000	0.098867000
H	4.321946000	-0.229328000	-0.061130000	H	-4.036580000	0.611257000	-0.032276000
H	2.934670000	-2.235739000	0.246147000	H	-3.310011000	-1.735595000	-0.027874000
H	3.292680000	2.016300000	-0.304294000	H	-2.397627000	2.471092000	0.053761000
H	0.843685000	2.316739000	-0.245556000	H	0.034839000	2.018194000	0.157775000
B	0.549016000	0.021319000	0.082417000	B	-0.338257000	-0.280106000	0.074762000
C	-3.163949000	0.703338000	0.003899000	C	1.309425000	-0.892045000	-0.682704000
C	-1.892705000	1.116163000	0.231465000	C	1.369574000	-0.919384000	0.721901000
C	-1.831067000	-1.125055000	-0.115106000	C	2.233070000	0.181534000	1.091270000
H	-4.036613000	1.341821000	0.001892000	H	0.996897000	-1.634491000	-1.402119000
H	-1.410813000	2.054082000	0.456966000	H	1.034354000	-1.734406000	1.348305000
H	-1.275514000	-2.046396000	-0.188984000	H	2.490959000	0.501356000	2.091382000
O	-1.051831000	0.002096000	0.177644000	C	2.610141000	0.773633000	-0.076418000
C	-3.123270000	-0.728403000	-0.218840000	O	2.085390000	0.125271000	-1.161508000
H	-3.959710000	-1.380384000	-0.429490000	H	3.212991000	1.642349000	-0.301897000
		5c				**5d**	
N	0.508248000	-1.076772000	-0.008058000	C	1.388783000	1.131325000	-0.345457000
C	1.793958000	-1.477167000	-0.031453000	C	2.024501000	0.656833000	0.964461000
C	2.895913000	-0.605079000	0.034633000	C	1.933670000	-0.688633000	0.965644000

C	2.706295000	0.790225000	0.120644000	C	1.216384000	-1.026858000	-0.347414000
C	1.413170000	1.334542000	0.136796000	O	1.700238000	-0.021376000	-1.219158000
H	3.901525000	-1.021122000	0.024339000	H	1.784578000	2.045924000	-0.784182000
H	1.985538000	-2.552625000	-0.094346000	H	2.383697000	1.307005000	1.755195000
H	3.583879000	1.436697000	0.172143000	H	2.205930000	-1.399257000	1.737509000
H	1.297744000	2.417586000	0.192571000	H	1.316859000	-2.025880000	-0.771702000
B	0.337200000	0.304679000	0.058497000	N	-0.210346000	-0.598467000	-0.185295000
C	-2.247418000	-0.243964000	1.064502000	B	-0.205403000	0.841319000	-0.176712000
C	-2.566079000	-0.816498000	-0.131856000	C	-1.304371000	-1.380030000	-0.012762000
H	-2.503894000	-0.614404000	2.046957000	C	-1.545597000	1.502444000	0.012263000
H	-3.115442000	-1.708999000	-0.396459000	C	-2.532973000	-0.767882000	0.160122000
C	-1.325544000	0.916668000	-0.653562000	H	-1.175530000	-2.460678000	-0.033637000
H	-1.054922000	1.705567000	-1.340894000	C	-2.641360000	0.654972000	0.167585000
O	-2.056059000	-0.108883000	-1.181303000	H	-1.726233000	2.576023000	0.035931000
C	-1.424812000	0.895539000	0.749139000	H	-3.417038000	-1.386264000	0.283195000
H	-1.116321000	1.689556000	1.415686000	H	-3.638604000	1.076901000	0.302802000
		5e				**5f**	
N	0.246978000	0.712607000	-0.158526000	N	-0.401968000	-0.598316000	-0.357582000
C	1.440498000	1.365328000	0.118864000	C	-1.455766000	-1.399312000	-0.057164000
C	2.622118000	0.694229000	0.284918000	C	-2.626352000	-0.756073000	0.305979000
C	2.675516000	-0.733718000	0.169443000	C	-2.705848000	0.672600000	0.365896000
C	1.539778000	-1.462638000	-0.108305000	C	-1.644580000	1.528371000	0.067625000
H	3.517181000	1.268620000	0.503945000	H	-3.500113000	-1.352486000	0.553460000
H	1.380985000	2.447965000	0.198171000	H	-1.347185000	-2.480294000	-0.111366000
H	3.639853000	-1.224622000	0.303123000	H	-3.667647000	1.093578000	0.663512000
H	1.620111000	-2.545275000	-0.195724000	H	-1.817497000	2.600330000	0.146074000
B	0.217945000	-0.732630000	-0.294020000	B	-0.368278000	0.833872000	-0.338182000
C	-2.618898000	-0.045254000	0.464392000	C	1.965031000	-1.157937000	0.345715000
C	-2.036056000	-1.231749000	0.198762000	C	2.523464000	-0.033040000	0.839817000
C	-0.882312000	1.556345000	-0.371775000	H	2.160380000	-2.162222000	0.700851000
H	-3.495569000	-0.050251000	1.107916000	H	3.229101000	0.076166000	1.656943000
H	-2.408975000	-2.166488000	0.613557000	C	1.189556000	0.803529000	-0.796317000
H	-0.636331000	2.545128000	-0.752091000	H	1.537004000	1.234463000	-1.737527000
O	-0.973449000	-1.392535000	-0.663155000	O	2.169471000	1.137862000	0.238719000
C	-2.162621000	1.229952000	-0.090475000	C	1.026908000	-0.766403000	-0.758874000
H	-2.907915000	2.003253000	-0.265764000	H	1.130116000	-1.320432000	-1.698304000
		5g				**TS_{5b-5c}**	
C	-1.730556000	1.505295000	-0.004260000	N	-1.032135000	-0.780876000	0.681905000
C	-2.718120000	0.584310000	-0.344045000	C	-2.334644000	-0.498258000	0.924029000
C	-2.531498000	-0.840661000	-0.346117000	C	-3.072205000	0.494714000	0.269456000
C	-1.323952000	-1.408324000	0.006645000	C	-2.469096000	1.288833000	-0.732768000
H	-3.708253000	0.942209000	-0.631548000	C	-1.127755000	1.097438000	-1.082413000
H	-1.987659000	2.562590000	-0.038868000	H	-4.116699000	0.645557000	0.536163000
H	-3.357981000	-1.487664000	-0.625973000	H	-2.839572000	-1.097825000	1.688878000
H	-1.131897000	-2.478457000	0.027241000	H	-3.071897000	2.052564000	-1.229161000
C	2.088583000	1.107398000	-0.430153000	H	-0.697338000	1.727996000	-1.862131000
C	2.447383000	-0.109103000	-0.875125000	B	-0.428180000	0.013072000	-0.313044000
H	2.385538000	2.042804000	-0.889701000	C	1.239673000	-0.265721000	-0.646679000
H	3.061753000	-0.398152000	-1.719258000	C	1.726200000	-1.291159000	0.233054000
C	1.055179000	-0.607367000	0.820827000	C	2.545849000	-0.713347000	1.185084000
H	1.163489000	-1.132228000	1.772555000	H	1.322109000	-0.382322000	-1.728611000
O	1.962062000	-1.173151000	-0.123698000	H	1.405026000	-2.324508000	0.184898000
C	1.176058000	0.963807000	0.767863000	H	3.019586000	-1.171135000	2.042207000
H	1.530065000	1.468000000	1.672254000	C	2.631893000	0.640762000	0.820464000
B	-0.396312000	0.895115000	0.367595000	O	1.947075000	0.928994000	-0.246127000
N	-0.333164000	-0.536926000	0.344380000	H	3.149239000	1.464255000	1.301698000
		TS_{5c-5d}				**TS_{5c-5f}**	
N	0.332099000	-0.762992000	-0.007084000	N	-0.561345000	-0.865037000	-0.448375000
C	1.503019000	-1.419216000	0.109432000	C	-1.744900000	-1.443052000	-0.132816000
C	2.725691000	-0.741186000	0.088882000	C	-2.844266000	-0.687498000	0.274866000
C	2.759812000	0.665923000	-0.074723000	C	-2.759119000	0.726960000	0.376421000

C	1.589500000	1.422379000	-0.218603000	C	-1.580996000	1.420212000	0.084282000
H	3.649214000	-1.304733000	0.203347000	H	-3.778741000	-1.194019000	0.509219000
H	1.482181000	-2.504935000	0.234576000	H	-1.828291000	-2.530165000	-0.211086000
H	3.735666000	1.155892000	-0.088455000	H	-3.652029000	1.267347000	0.697917000
H	1.683803000	2.499789000	-0.356859000	H	-1.583416000	2.505384000	0.191985000
B	0.321690000	0.622767000	-0.189296000	B	-0.428849000	0.556729000	-0.349296000
C	-2.171494000	-0.385899000	1.066535000	C	2.417932000	-1.033751000	-0.019406000
C	-1.931607000	-0.932233000	-0.233817000	C	2.575891000	0.043400000	0.839374000
H	-2.447046000	-0.951917000	1.946232000	H	2.890924000	-2.000109000	0.085605000
H	-2.107301000	-1.936591000	-0.600157000	H	3.177630000	0.114924000	1.740750000
C	-1.293889000	1.146159000	-0.384512000	C	1.139697000	0.800951000	-0.708878000
H	-1.456267000	2.076044000	-0.924199000	H	1.431638000	1.535620000	-1.464843000
O	-1.791928000	0.015129000	-1.132873000	O	1.905637000	1.122938000	0.512370000
C	-1.822367000	0.935808000	0.965398000	C	1.507107000	-0.611656000	-0.999666000
H	-1.762512000	1.666861000	1.763980000	H	1.338478000	-1.087296000	-1.956255000
	TS$_{5c\text{-}5g}$				**TS$_{5a\text{-}5e}$**		
C	-1.462211000	2.177655000	0.081324000	N	0.440608000	-0.826342000	0.239948000
C	-2.669157000	1.587050000	-0.303255000	C	1.569411000	-1.433890000	-0.196930000
C	-2.802525000	0.180827000	-0.453129000	C	2.699753000	-0.657137000	-0.429265000
C	-1.721229000	-0.667539000	-0.215781000	C	2.676984000	0.753164000	-0.219601000
H	-3.548339000	2.205658000	-0.496498000	C	1.544883000	1.446718000	0.219573000
H	-1.427836000	3.262641000	0.184476000	H	3.614134000	-1.137116000	-0.769447000
H	-3.758755000	-0.246559000	-0.748463000	H	1.566208000	-2.513747000	-0.347438000
H	-1.846899000	-1.748220000	-0.323195000	H	3.598668000	1.302270000	-0.419004000
C	2.111273000	1.667517000	-0.470835000	H	1.607890000	2.525049000	0.347251000
C	2.684875000	0.504537000	-0.820520000	B	0.372670000	0.548559000	0.437681000
H	2.189441000	2.599545000	-1.015249000	C	-2.524427000	0.301065000	-0.897137000
H	3.312780000	0.168225000	-1.631478000	C	-1.803774000	1.244886000	-0.251233000
C	1.512631000	0.000315000	0.970439000	C	-1.383333000	-0.998458000	0.674703000
H	1.277349000	-0.598041000	1.840187000	H	-3.197467000	0.527005000	-1.716618000
O	2.356283000	-0.511526000	0.121088000	H	-1.793748000	2.324382000	-0.307303000
C	1.257770000	1.420086000	0.730359000	H	-1.273803000	-1.602851000	1.566636000
H	1.371128000	2.076286000	1.598431000	O	-1.060705000	0.684974000	0.832314000
B	-0.336497000	1.205774000	0.299048000	C	-2.400055000	-0.985104000	-0.230555000
N	-0.501909000	-0.200419000	0.146863000	H	-3.113793000	-1.796450000	-0.310342000
	TS$_{5d\text{-}5e}$				**6a**		
C	-1.437220000	1.248003000	-0.069556000	N	1.600771000	-1.285177000	-0.000180000
C	-2.435408000	0.369726000	-0.700985000	C	2.861958000	-0.787290000	-0.000149000
C	-2.255506000	-0.919450000	-0.336299000	C	3.163758000	0.579251000	0.000005000
C	-0.993534000	-1.139432000	0.392382000	C	2.129401000	1.546743000	0.000145000
O	-0.932612000	0.595053000	1.178778000	C	0.781930000	1.168649000	0.000131000
H	-1.716640000	2.283524000	0.113415000	H	4.205387000	0.893900000	0.000018000
H	-3.213050000	0.740227000	-1.362776000	H	3.683741000	-1.508667000	-0.000253000
H	-2.900613000	-1.758838000	-0.575691000	H	2.404024000	2.603080000	0.000264000
H	-0.924546000	-1.962559000	1.108880000	H	0.017463000	1.942681000	0.000241000
N	0.171099000	-0.770868000	-0.256227000	B	0.612711000	-0.311547000	-0.000042000
B	0.079807000	0.736105000	-0.087940000	C	-1.077690000	-1.145007000	0.709201000
C	1.382466000	-1.427609000	-0.055714000	C	-1.872475000	-0.194398000	1.413080000
C	1.441481000	1.476675000	-0.157863000	C	-2.611730000	0.743227000	0.710687000
C	2.555611000	-0.732808000	-0.076279000	C	-2.611757000	0.743388000	-0.710415000
H	1.339376000	-2.509342000	0.056521000	C	-1.872527000	-0.194079000	-1.413048000
C	2.583662000	0.721948000	-0.170141000	C	-1.077716000	-1.144847000	-0.709412000
H	1.539579000	2.560982000	-0.206598000	H	-0.601224000	-1.959260000	1.245635000
H	3.487685000	-1.286048000	-0.000397000	H	-1.885086000	-0.211683000	2.499943000
H	3.564695000	1.195521000	-0.227440000	H	-3.212727000	1.473971000	1.247189000
				H	-3.212773000	1.474253000	-1.246730000
				H	-1.885179000	-0.211118000	-2.499914000
				H	-0.601269000	-1.958978000	-1.246048000
	6b				**6c**		
N	0.672775000	-1.055103000	-0.000150000	N	0.339924000	-0.620375000	0.000002000
C	1.928719000	-1.549450000	-0.000231000	C	1.478248000	-1.365996000	-0.000007000

C	3.090055000	-0.757929000	-0.000136000	C	2.713427000	-0.746243000	-0.000034000
C	2.998943000	0.650249000	0.000058000	C	2.807262000	0.676111000	-0.000052000
C	1.749398000	1.291076000	0.000158000	C	1.680349000	1.491223000	-0.000044000
H	4.063620000	-1.243909000	-0.000212000	H	3.608343000	-1.361483000	-0.000041000
H	2.039033000	-2.638035000	-0.000382000	H	1.367726000	-2.449034000	0.000007000
H	3.920097000	1.235674000	0.000129000	H	3.805576000	1.116915000	-0.000073000
H	1.709416000	2.379940000	0.000307000	H	1.832183000	2.570350000	-0.000059000
B	0.616522000	0.326486000	0.000039000	B	0.326808000	0.819305000	-0.000015000
C	-1.100592000	1.152136000	-0.709278000	C	-1.794913000	0.656940000	-1.234001000
C	-1.869560000	0.184687000	-1.413370000	C	-1.733413000	-0.689973000	-1.230182000
C	-2.575643000	-0.777618000	-0.709880000	C	-1.022981000	-1.247851000	0.000031000
C	-2.575623000	-0.777809000	0.709753000	C	-1.733374000	-0.689945000	1.230253000
C	-1.869518000	0.184307000	1.413480000	C	-1.794874000	0.656968000	1.234042000
C	-1.100571000	1.151945000	0.709625000	C	-1.210381000	1.337890000	0.000004000
H	-0.653348000	1.981166000	-1.249781000	H	-2.196180000	1.243590000	-2.056958000
H	-1.880458000	0.199592000	-2.500178000	H	-2.108220000	-1.340708000	-2.014591000
H	-3.149954000	-1.529661000	-1.245960000	H	-0.930504000	-2.335938000	0.000042000
H	-3.149918000	-1.529995000	1.245647000	H	-2.108156000	-1.340661000	2.014689000
H	-1.880385000	0.198921000	2.500292000	H	-2.196115000	1.243638000	2.056998000
H	-0.653312000	1.980831000	1.250337000	H	-1.349177000	2.420429000	-0.000007000
		6d				**$TS_{6a\text{-}6b}$**	
N	-0.606821000	-0.578985000	0.392292000	N	1.150008000	-0.566183000	1.347888000
C	-1.589624000	-1.430531000	0.000013000	C	2.418268000	-1.057846000	1.198929000
C	-2.762000000	-0.846499000	-0.445247000	C	3.239313000	-0.764432000	0.109741000
C	-2.918782000	0.577930000	-0.480946000	C	2.793773000	0.080409000	-0.936139000
C	-1.935994000	1.483612000	-0.082185000	C	1.518167000	0.669554000	-0.933694000
H	-3.578267000	-1.484638000	-0.772168000	H	4.235803000	-1.197252000	0.065091000
H	-1.425702000	-2.505062000	0.045089000	H	2.790206000	-1.712155000	1.990006000
H	-3.876975000	0.951970000	-0.846009000	H	3.468328000	0.271643000	-1.772381000
H	-2.165771000	2.545814000	-0.151049000	H	1.189851000	1.297384000	-1.745286000
B	-0.653760000	0.850774000	0.407190000	B	0.826867000	0.220868000	0.295095000
C	0.876369000	0.912075000	0.961577000	C	-1.255993000	1.450805000	-0.074059000
C	0.769269000	-0.669289000	0.961776000	C	-1.806681000	0.828155000	-1.240009000
C	1.742716000	-1.414641000	0.091378000	C	-2.507999000	-0.371243000	-1.117932000
C	2.534436000	-0.760807000	-0.790399000	C	-2.683875000	-0.968590000	0.143880000
C	2.557591000	0.705069000	-0.888311000	C	-2.141152000	-0.379647000	1.284626000
C	1.834690000	1.477341000	-0.042538000	C	-1.432844000	0.835820000	1.191801000
H	1.032951000	1.345420000	1.956670000	H	-0.727080000	2.401570000	-0.153652000
H	0.727277000	-1.093817000	1.972453000	H	-1.656923000	1.280347000	-2.217871000
H	1.788050000	-2.499452000	0.179550000	H	-2.920188000	-0.849787000	-2.003338000
H	3.212253000	-1.329060000	-1.425724000	H	-3.228107000	-1.906730000	0.225369000
H	3.209428000	1.165445000	-1.627622000	H	-2.253213000	-0.857933000	2.254179000
H	1.908108000	2.563546000	-0.101956000	H	-1.016532000	1.295245000	2.087756000
		$TS_{6b\text{-}6c}$				**$TS_{6b\text{-}6d}$**	
N	-0.462579000	-0.771000000	-0.001143000	N	0.905386000	-0.594568000	-0.567486000
C	-1.626932000	-1.448740000	-0.000235000	C	2.059768000	-1.057391000	-0.020574000
C	-2.852594000	-0.776790000	0.000204000	C	2.948541000	-0.204607000	0.628614000
C	-2.886636000	0.640222000	0.000043000	C	2.656658000	1.179591000	0.788963000
C	-1.716549000	1.411171000	-0.000531000	C	1.458222000	1.739289000	0.344252000
H	-3.776151000	-1.351493000	0.000544000	H	3.890649000	-0.604478000	0.998862000
H	-1.594976000	-2.541096000	-0.000237000	H	2.299933000	-2.116060000	-0.141953000
H	-3.863004000	1.129249000	0.000433000	H	3.396795000	1.798055000	1.300563000
H	-1.807400000	2.497406000	-0.000360000	H	1.276821000	2.795486000	0.542710000
B	-0.448577000	0.611842000	-0.000768000	B	0.547430000	0.775283000	-0.369149000
C	1.651174000	0.774447000	-1.233836000	C	-1.043485000	0.843626000	-0.925354000
C	1.937361000	-0.569306000	-1.230889000	C	-1.094759000	-0.627148000	-1.010120000
C	1.736212000	-1.270591000	-0.000904000	C	-1.767578000	-1.366760000	0.005813000
C	1.937052000	-0.571062000	1.230287000	C	-2.253759000	-0.723478000	1.126636000
C	1.651535000	0.772757000	1.235271000	C	-2.144866000	0.692859000	1.290190000
C	1.176375000	1.377734000	0.001211000	C	-1.629101000	1.455253000	0.269582000
H	1.628773000	1.351736000	-2.155695000	H	-1.125524000	1.397166000	-1.861745000

H	2.155410000	-1.113897000	-2.145123000	H	-0.936252000	-1.095909000	-1.975231000
H	1.788311000	-2.357737000	-0.001666000	H	-1.883651000	-2.441500000	-0.107909000
H	2.155374000	-1.117116000	2.143591000	H	-2.745661000	-1.307701000	1.902684000
H	1.629888000	1.348843000	2.157895000	H	-2.519561000	1.162810000	2.195302000
H	1.034995000	2.457159000	0.001947000	H	-1.588095000	2.539450000	0.357939000

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Direct Spectroscopic Identification of BN-Arynes and Subtle Steric Effects on Nitrogen Fixation**

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1,2-Azaborinines are the BN analogues of arynes through exchange of the formal CC triple bond by an isoelectronic BN bond. The BN-arynes are an underexplored class of reactive intermediates. Dibenzo[c,e][1,2]azaborinine (10,9-BN-phenanthryne) **1** was inferred as reactive intermediate by trapping reactions. Here it is shown that **1** can be generated in the gas phase by thermolysis from the pyridine adduct of 9-azido-9-borafluorene by cleavage of the dative bond with pyridine and dinitrogen extrusion. The ionization potential of **1** is 8.2 eV with ionization resulting from the π HOMO. Under cryogenic matrix isolation conditions, 9-azido-9-borafluorene photolysis results in isomerization to the dinitrogen adduct of **1** without involvement of a triplet borylnitrene intermediate. Photochemical nitrogen extrusion from **1**$\cdot N_2$ is not possible and nitrogen fixation is irreversible under cryogenic conditions. In contrast, 2,4,7,9-tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine can be photogenerated from the corresponding azidoborole precursor under cryogenic matrix isolation conditions, and nitrogen fixation is precluded due to steric hindrance. The BN stretching vibration at about 1750 cm^{-1} is much weaker than in typical linear diaryl iminoboranes.

Introduction

1,2-Dihydro-1,2-azaborinine, a heterocyclic system that is isosteric and isoelectronic to benzene, has received significant attention during the last decade due to potential applications in materials science, medicinal chemistry, and catalysis.[1–5] For convenience, this BN analogue of benzene is often called "1,2-azaborine" (Chemical Abstract Service nomenclature) or "1,2-azaborinine" (IUPAC nomenclature) in the literature. The "real" 1,2-azaborinine is isoelectronic with *ortho*-benzyne (1,2-didehydrobenzene) (see Scheme 1a).

Following an earlier computational investigation of its structure and singlet-triplet energy gap,[6] it was observed for the first time in 2015 by matrix isolation.[7,8] 1,2-Azaborinine is a superelectrophilic singlet ground state species that reacts with N_2, CO, CO_2, and Xe at cryogenic temperatures.[7,8]

In solution, the derivative dibenzo[c,e][1,2]azaborinine **1** can be generated thermally or photochemically from 9-azido-9-borafluorene **2** (see Scheme 1b).[9,10] As a highly strained cyclic iminoborane,[11–13] it undergoes cyclooligomerization.[9,10] According to computations, the initial dimerization can proceed without barrier on the potential energy surface.[14] In the presence of triorganosilanes R_3Si–E (E=F, Cl, $OSiR_3$, H), dibenzo[c,e][1,2]azaborinine can be trapped by insertion into the Si–E bond.[10]

Although the reported (self)trapping experiments clearly support the involvement of the free dibenzo[c,e][1,2]azaborinine **1** in these reactions, its direct spectroscopic identification has not been reported yet. A major problem is that **2**, the only known precursor to **1**, is a rather sensitive compound. It is monomeric only in solution, while in the solid state it is a cyclic trimer, which quickly decomposes.[15]

On the other hand, the Lewis adduct with pyridine, **2·py**, enjoys significant stability.[15] We reasoned that **2·py** could be a good precursor for matrix isolation and gas phase studies of **1** as heating of **2·py** under high vacuum conditions results in sublimation of **2** and pyridine (see Scheme 2a). As reported here, this allowed us for the first time to perform matrix isolation and gas phase flash pyrolysis studies of **2** and gain experimental spectroscopic signatures of the target compound dibenzo[c,e][1,2]azaborinine **1**. Gas phase UV-photoelectron spectroscopy (UV-PES) was employed to probe the energy levels of the BN-aryne derivative and to reveal the impact of the heteroatom substitution on the electronic structure in comparison with the isosteric phenanthryne. Under matrix isolation conditions, irreversible fixation of N_2 was observed (**1·N₂**), while

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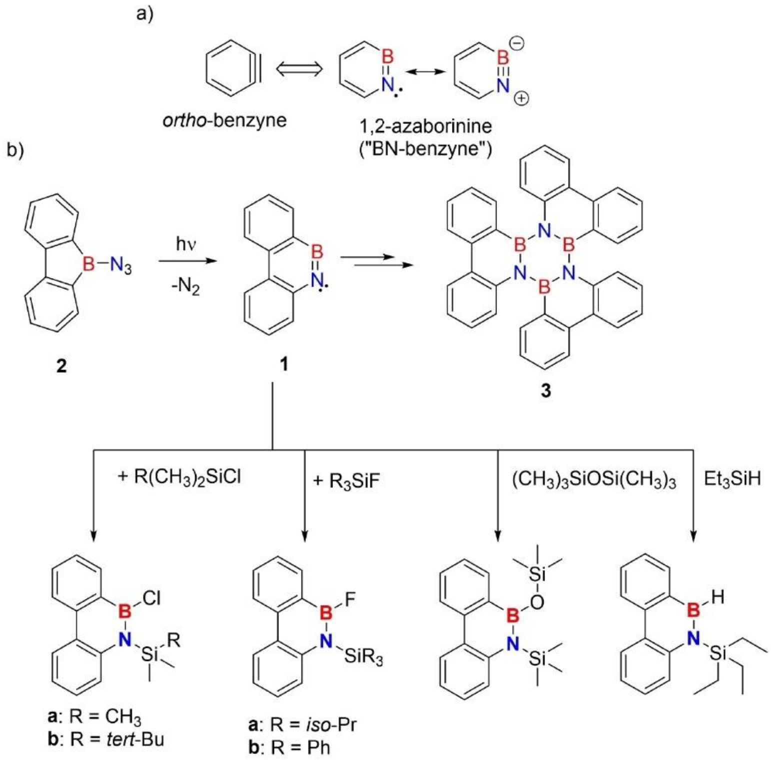

Scheme 1. a) Resonance forms of 1,2-azaborinine (**2**) and its analogy with *ortho*-benzyne. b) Generation of dibenzo[c,e][1,2]azaborinine **1** by photolysis of 9-azido-9-borafluorene **2** and its (self)trapping reactions.

its sterically congested derivative **5** that carries four *tert*-Bu groups is unable to bind N_2 (Scheme 2b).

Results and Discussion

Matrix isolation of 5-azido-5H-dibenzo[b,d]borole 2. The solid pyridine coordination complex of **2** with pyridine (**2·py**), was sublimed at 105–115 °C under the high vacuum conditions of the matrix isolation apparatus and the gas phase species were trapped in a large excess of argon or nitrogen gas at 30 K or 28 K, respectively. The data discussed in the manuscript were obtained in Ar, while the N_2 matrix results are available in the Supporting Information. According to IR spectroscopy, free pyridine is frozen in the matrices under these conditions based on comparison with previously reported IR data of matrix isolated pyridine (Figures 1 and 2).[16,17] In addition, also small amounts of HN_3 are trapped due to inevitable hydrolysis of the azide.[18,19] More importantly, signals were observed that we assign to azide **2** based on comparison with computed data and experimental data reported previously (Figure 1).[15]

In particular, the azide stretching mode is observed at 2136 cm^{-1} (Figure 1, bottom), in very good agreement with its value in dichloromethane solution, 2136 cm^{-1}.[15] This shows that the matrix isolated azide is indeed **2** and not its pyridine adduct **2·py** as the latter has its azide stretching frequency at 2176 cm^{-1}.[15] Besides the characteristic azide stretching mode, the spectrum of **2** shows a strongly structured band around 1381 cm^{-1} that is associated mainly with a stretching vibration of the B–N bond, according to computed anharmonic vibrational frequencies (B3LYP-D3(BJ)/6-311+G(d,p)).

Photolysis of the matrix with the output of a high pressure mercury lamp (λ > 280 nm) results in decrease of the signals of **2** and concomitant growth of a new set of signals (see Figure 1, center), among them a most characteristic band at 2259 cm^{-1} corresponding to a N–N stretching vibration. On the other hand, the signals of pyridine do not change in intensity (see difference spectrum Figure 1, top). This excludes **2·py** as photoactive precursor as well as pyridine adducts in product formation. The strong band at 2259 cm^{-1} is reminiscent of the band observed for the 1,2-azaborinine-N_2 adduct at 2266 cm^{-1},[7] which suggests the formation of the N_2 adduct of **1** (**1·N₂**). The closely related borabenzene-N_2 adduct has its strong N_2 stretching vibration at 2198 cm^{-1}.[20] The adduct **1·N₂** has no strong absorption bands in the 800–2000 cm^{-1} range and a set of weak bands around 750 cm^{-1} in agreement with anharmonic computations (Figure 2).

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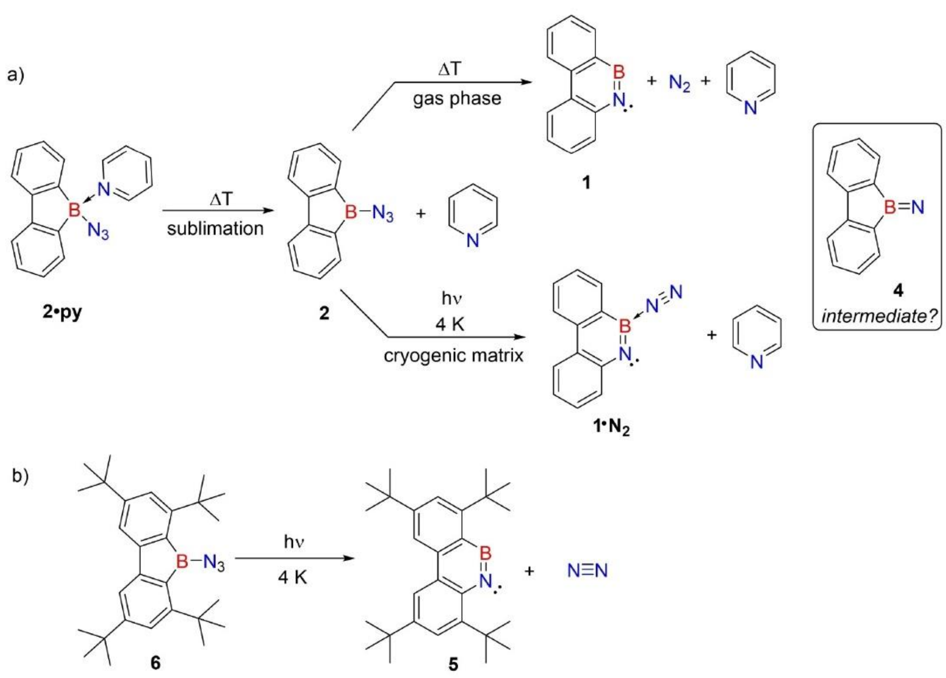

Scheme 2. a) Generation of dibenzo[c,e][1,2]azaborinine **1** from the precursor **2·py**. b) Generation of BN-aryne **5** from precursor **6**.

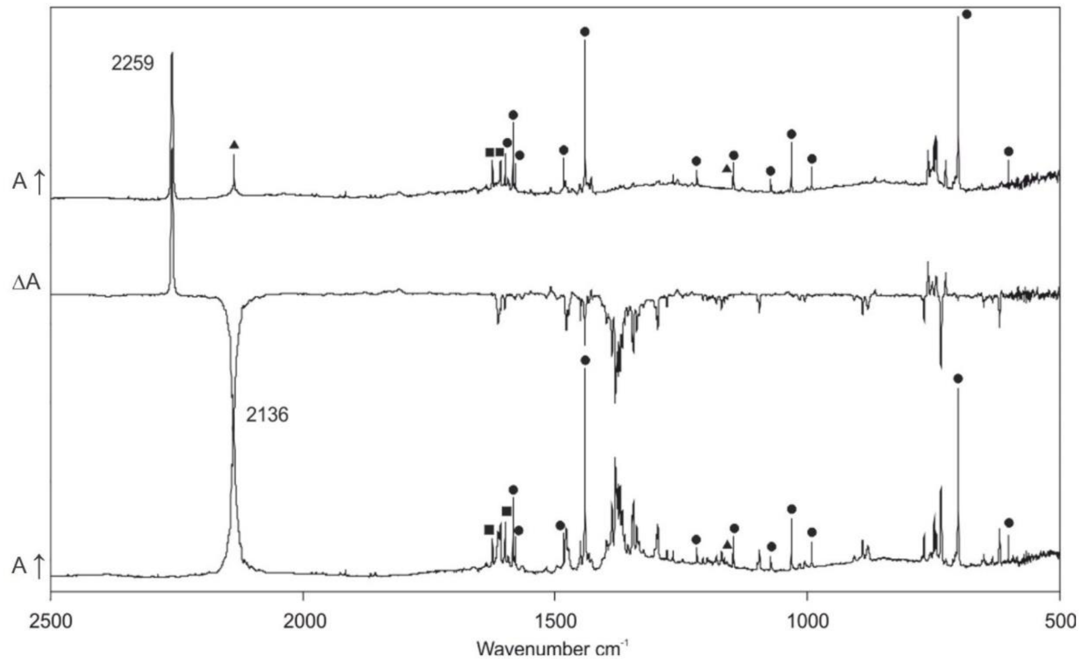

Figure 1. Photochemistry of **2** in an Ar matrix at 10 K. Bottom: IR spectrum obtained after sublimation of **2·py** (105–115 °C); top: IR spectrum obtained after subsequent photolysis (λ > 280 nm, 10 min); center: difference spectrum between the two spectra where peaks pointing upwards increase and peaks pointing downwards decrease upon irradiation. (● denotes peaks of pyridine, ▲denotes peaks of HN_3, ■ denotes H_2O).

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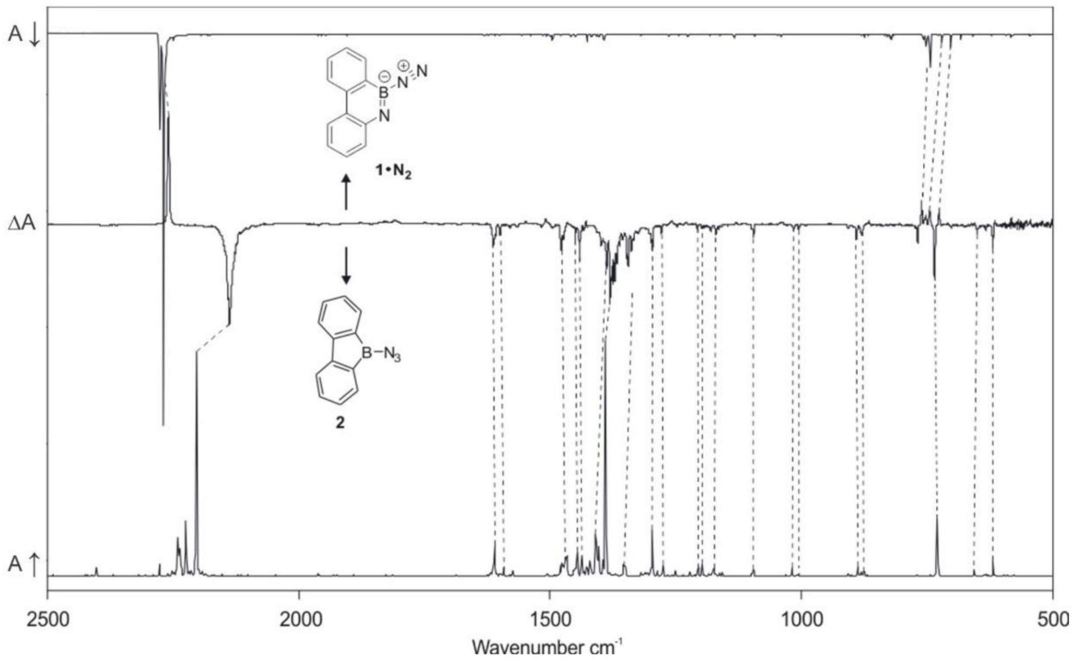

Figure 2. Comparison of experimental (Ar matrix at 10 K) and anharmonic computed (for ^{11}B and ^{10}B isotopologues (81:19) at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory) IR spectra of **2** and **1·N$_2$**. Bottom: anharmonic IR spectrum of **2**; top: anharmonic IR spectrum of **1·N$_2$**; center: experimental IR difference spectrum obtained after photolysis of **2** ($\lambda > 280$ nm, 10 min) at 10 K where peaks pointing upwards increase and peaks pointing downwards decrease upon irradiation.

Note that we have no spectroscopic evidence for the formation of the expected boryl nitrene **4** by IR spectroscopy. The parent nitreno borole **4'**, i.e. without dibenzo annulation, was computed to have a triplet ground state.[21] As triplet species should be detectable even in low concentration by ESR spectroscopy, we investigated the photolysis of **2** in methyl cyclohexane solid solution at 4 K. No triplet signal was observed, indicating that the triplet boryl nitrene does not form in detectable amounts from **2**. This observation is in agreement with CASPT2 computations for the parent nitreno borole **4'** that show that the lowest energy singlet state $^1A_1$ is a first-order saddle point rather than a minimum, while the triplet state ($^3A_2$) is a minimum lower in energy than the $^1A_1$ state.[21] The nature of the stationary points on the singlet and triplet surface and their energetic order is similar to that parent boryl nitrene H_2BN.[22–24] The concerted N_2 extrusion and rearrangement under thermal conditions is well established for diorganyl azidoboranes R_2BN_3.[11] The lack of triplet nitrene formation during photolysis of **2** suggests that this reaction proceeds on the singlet potential energy surface (PES) by concerted extrusion of N_2 and rearrangement to **1**, similar to the formation of **1** from **2** on the ground state PES.[9]

The high Lewis acidity of the boron center of **1** results in trapping of the extruded N_2 molecule that cannot diffuse away in the solid matrix. The photolysis of **2** thus triggers an unprecedented isomerization of a boryl azide to the 1,2-azaborinine-N_2 coordination complex **1·N$_2$**. This reaction is exothermic by -25.7 kcal mol^{-1} according to computations (DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/6-311+G(d,p)) (see Figure 3).[9]

Unfortunately, further irradiation of complex **1·N$_2$** at various wavelengths does not allow extrusion of the N_2 molecule. This contrasts the observations that we made previously for 1,2-azaborinine-N_2 where photoextrusion at 4 K and N_2 capture at slightly higher temperatures was established.[7] It is, however, similar to the observation made by Maier et al. for the borabenzene-N_2 adduct.[20] The N_2 binding energy (DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/6-311+G(d,p)) of **1** is slightly lower than that of 1,2-azaborinine (-5.0 kcal/mol for **1** compared to -5.9 kcal/mol for the parent 1,2-azaborinine (Δ(E+ZPVE)). This suggests that the different behavior of **1·N$_2$** during photolysis is not due to thermodynamics. Most likely, the larger π system in **1·N$_2$** opens photophysical deactivation channels.

Gas phase thermolysis of 5-azido-5H-dibenzo[b,d]borole 2 and UV-PES data of BN-phenanthryne 1. The Lewis acidic **1** cannot bind the N_2 molecule at higher temperatures as observed previously during solution phase thermolysis,[9] and rationalized by the computed binding free energy $\Delta G°$(298.15 K) (Figure 3). It is thus reasonable to conclude that the observation of free **1** should be achievable by gas phase thermolysis of **2**. We therefore employed flash vacuum thermolysis (FVT) with UV-photoelectron spectroscopy (UV-PES) as a detection method as it provides insight into the energies of

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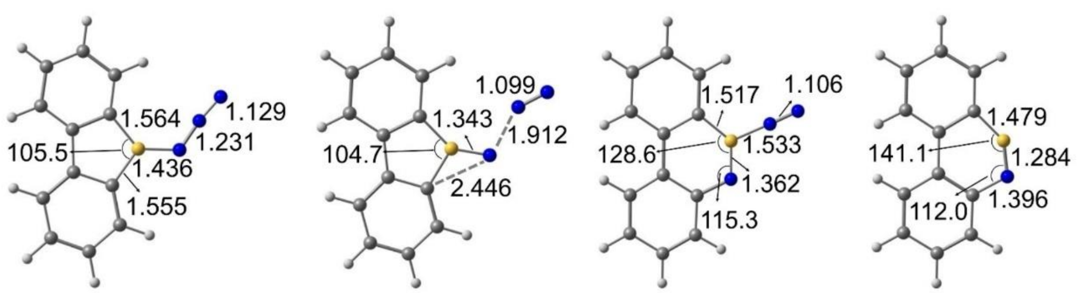

2	**TS2_1•N$_2$**	**1•N$_2$**	**1**
0.0	33.0	-25.7	-20.7 (**1**+N$_2$)
0.0	31.9	-25.4	-29.9

Figure 3. Structures calculated at DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/6-311+G(d,p) level of theory and their corresponding zero-point vibrational corrected energies (black values) and Gibbs free energies ΔG°(298.15 K) (blue values) in kcal/mol. Nitrogen: blue, boron: yellow.

the occupied molecular orbitals of **1**. This technique is particularly well suited for the experimental determination of gas phase vertical ionization energies (IE). The pyridine adduct of 9-azido-9-borafluorene **2·py** was subjected to FVT conditions at 155 °C, and the UV-PE spectrum obtained is presented in Figure 4. Combination with TD-DFT estimated IEs as described in the literature[25–27] (Table 1) makes it possible to attribute the UV-PE bands and to know not only the energy level of high energy molecular orbitals (low values of ionization energy since according to Koopmans' approximation IE = $-\varepsilon_i$, where ε means calculated energy of *i* MO), but also their nature (σ, π, lone pair, etc.). Based on this data and the clearly visible N_2 band (15.6 eV), the obtained spectrum can be reasonably associated with the expected **1**.

Thus, the lowest first ionization energy (IE_1) of 8.2 eV is attributed to the highest occupied molecular orbital (HOMO), which corresponds to the antibonding interaction of the B═N bond and π system of aromatic rings. The second band at 8.5 eV (IE_2) and the third one at 9.8 eV (IE_3) are related to the nitrogen contribution in the delocalized π-system, while the fourth band at 10.0 eV (IE_4) relates to the nitrogen lone pair in the σ-plane. Two next bands at 10.2 eV (IE_5) and 10.8 eV (IE_6) are attributed to a π-type antibonding orbitals extending over the entire heterocycle.

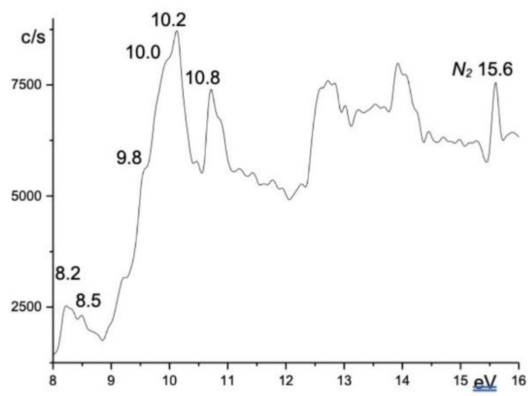

Figure 4. FVT-UV-PE spectrum of dibenzo[c,e][1,2]azaborinine **1** generated from pyridine adduct of 9-azido-9-borafluorene (**2·py**) at 155 °C. Ionization energy in eV with the estimated error ±0.05 eV.

The comparison between the four lowest experimental ionization energies of **1** (Table 1) and that calculated at CAM-B3LYP ΔSCF+TD-DFT for the PAH parent molecule, 9,10-phenanthryne (Table S2 in Supporting Information), is presented in Figure 5. 9,10-Phenanthryne is known as reactive intermediate since the 1960s and was detected by pyrolysis/mass spectrometry,[28–31] but experimental ionization energies are not available.

The replacement of the CC by the BN bond follows the general stabilization of all molecular orbitals vs that of the all-carbon analogue. For the HOMO, this effect is very slight (0.057 eV), but for the HOMO-2, which is the π-bond in the molecular plane, the stabilization of 0.619 eV is much more important.

Tert-butyl dibenzo derivative of BN-phenanthryne. We synthesized a sterically encumbered system **6** to investigate the photochemical N_2 extrusion and the impact of the *tert*-butyl groups on N_2 fixation by BN-aryne **5** (2,4,7,9-tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine) (Scheme 2b).

The synthesis of **6** started from the known 2,2′-dibromobiphenyl derivative **7** that was lithiated as described previously (Scheme 3).[32] Treatment of the dilithio intermediate with boron trichloride resulted in formation of the chloroborole **8**. Its ^{11}B chemical shift of 64 ppm in CD_2Cl_2 is essentially identical to that of the unsubstituted 9-chloro-9-borafluorene.[15] Reaction of **8** with trimethylsilyl azide in dichloromethane at room temperature overnight resulted in almost quantitative formation of azide **6**.

Compound **6** (5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole) was sublimed at 150 °C with a large excess of argon onto the CsI window kept at 30 K. The infrared spectrum obtained after the deposition of **6** in argon shows some contaminations that were largely photostable (see Figure S9). The most distinguished peak at 2155 cm^{-1} corresponds to the ν(N_3) stretching vibration of **6** (see Figure 6 and Table S3). This value is

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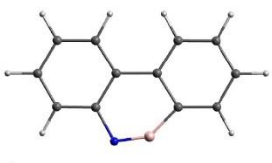
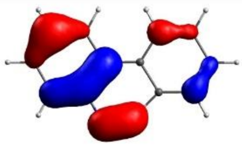
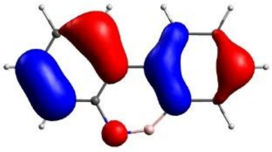
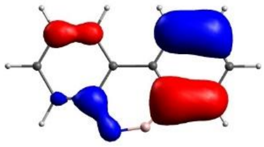
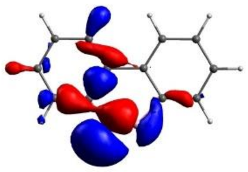
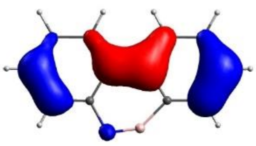
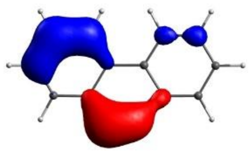
Table 1. Comparison of DFT and experimental ionization energies (eV) for **1**.

Nature of MO	CAM-B3LYP $-\varepsilon^{KS}$	CAM-B3LYP ΔSCF + TD-DFT	Corrected $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.539$	Corrected $-\varepsilon^{KS} + x_{exp}$ $x_{exp} = 0.851$	Exp.
 C_s					
 HOMO a″	7.313	7.864	7.864	8.2	**8.2**
 a″	7.692	8.358	8.243	8.579	**8.5**
 a″	9.076	9.526	9.627	9.963	**9.8**
	9.4544	10.218	10.005	10.341	**10.0**
 a″	9.821	10.373	10.372	10.708	**10.2**
 a″	10.537	10.817	11.081	11.424	**10.8**

shifted by 19 cm^{-1} to higher energy compared to the value in **2**. This indicates that the donation of electron density from the azido group into the boron vacant π orbital in **6** is reduced compared to **2**.

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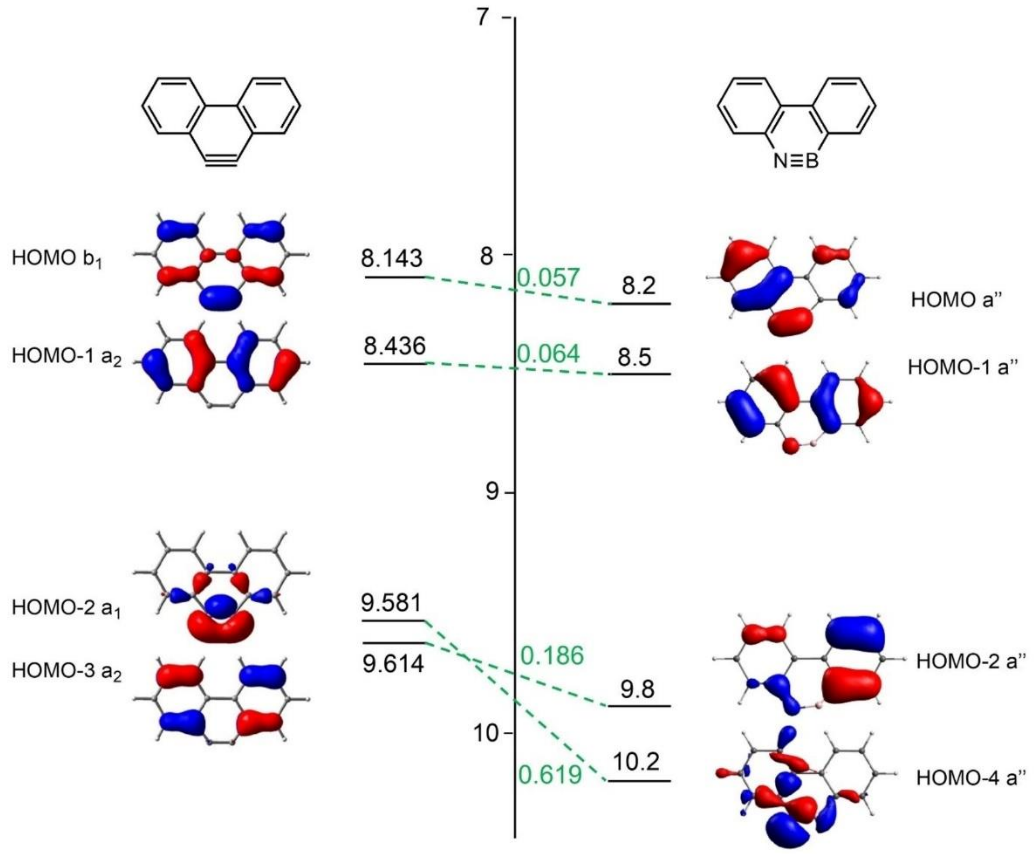
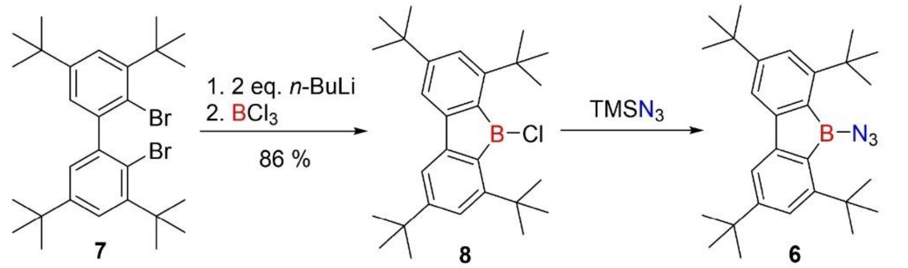


Figure 5. Comparison between the four lowest experimental ionization energies (in eV) of 10,9-BN-phenanthryne **1** (right) and CAM-B3LYP ΔSCF + TD-DFT calculated values for 9,10-phenanthryne (left); all values are in eV.



Scheme 3. Synthesis of **6**.

After successful deposition of **6**, the matrix was irradiated at 4 K with 260 nm < λ < 320 nm. The signals attributed to **6** decreased in intensity while new signals were observed, especially a rather broad one with a maximum at 1751 cm^{-1}. These new peaks can be attributed to the BN-aryne **5** based on comparison with the harmonic vibrational spectrum computed at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory (Figure 6). The very intense band at 1751 cm^{-1} is associated with ν(^{11}BN) stretching of the azaborinine ring, while its maximum for the ^{10}B isotopologue is at 1793 cm^{-1}.

Typically, linear diorganyl iminoboranes have their ν(^{11}BN) stretching vibrations slightly above 2000 cm^{-1}.[33] In parent iminoborane HBNH, on the other hand, the ν(^{11}BN) stretching vibration was assigned to a band at 1786–1789 cm^{-1} in argon matrix[34–36] and 1786 cm^{-1} in the gas phase.[37] The ν(^{11}BN) stretching vibration of the parent 1,2-azaborinine is at

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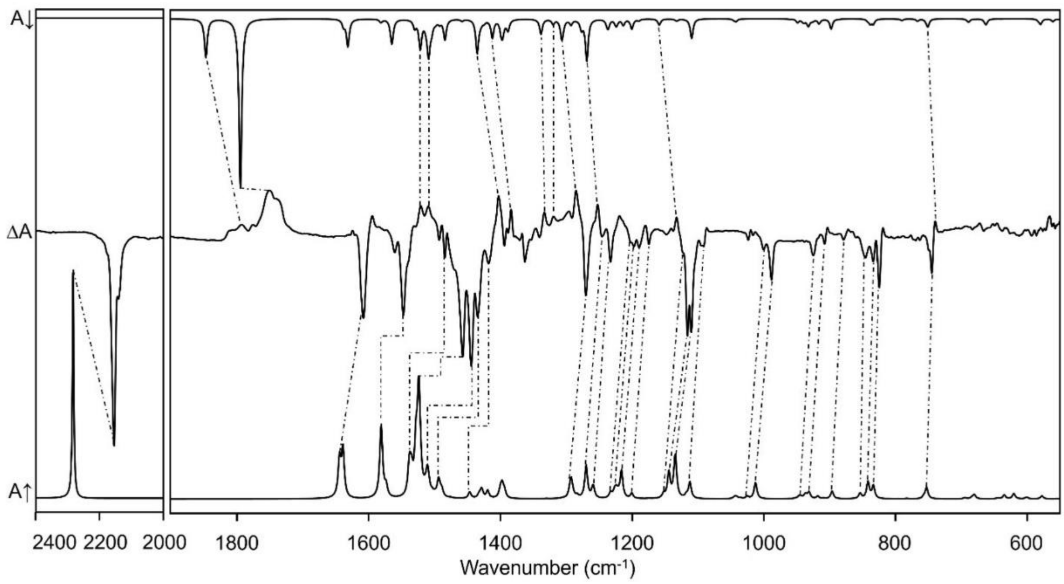

Figure 6. Comparison of experimental (Ar matrix at 10 K) and harmonic computed (for ^{11}B and ^{10}B isotopologues (81 : 19) at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory) IR spectra of **6** and **5**. Bottom: harmonic IR spectrum of **6**; top: harmonic IR spectrum of **5**; center: experimental IR difference spectrum obtained after photolysis of **6** (260 nm < λ < 320 nm) in Ar at 10 K where peaks pointing upwards increase and peaks pointing downwards decrease upon irradiation.

1637/1634 cm^{-1}.[7] The quite large shift of almost 100 cm^{-1} due to dibenzo annulation (and four *tert*-Bu groups, that are expected to have less impact) indicates that the BN bond acquires more iminoborane character (Figure 7). This is reminiscent of the increased double bond character of the 9,10-bond in phenanthrene compared to benzene.

Obviously, the presence of the *tert*-butyl groups has a pronounced impact on the ability of the boron center to bind dinitrogen: while photolysis of **2** results in isomerization to the adduct **1**·N_2, photolysis of **6** gives the expected uncoordinated BN-aryne **5**. Annealing of the matrix up to 35 K did not lead to any further changes in the IR spectrum, indicating that the

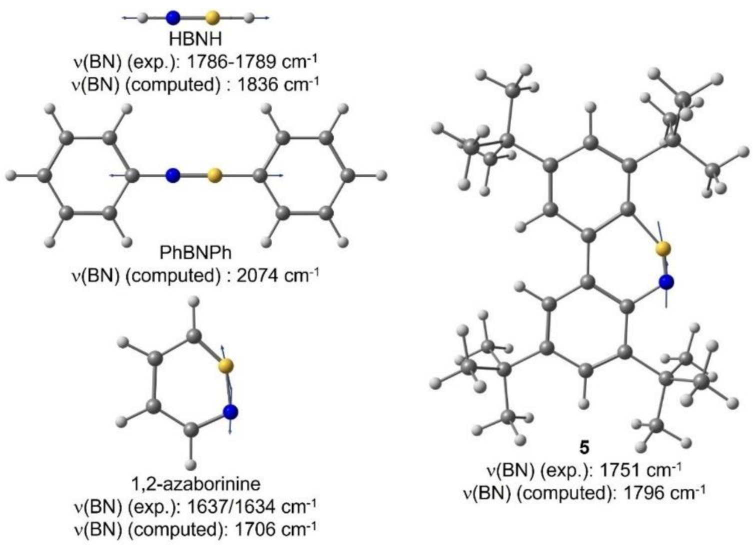

Figure 7. Experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) BN vibration stretching energies and displacement vectors of different iminoboranes: HBNH, PhBNPh, 1,2-azaborinine, and **5**.

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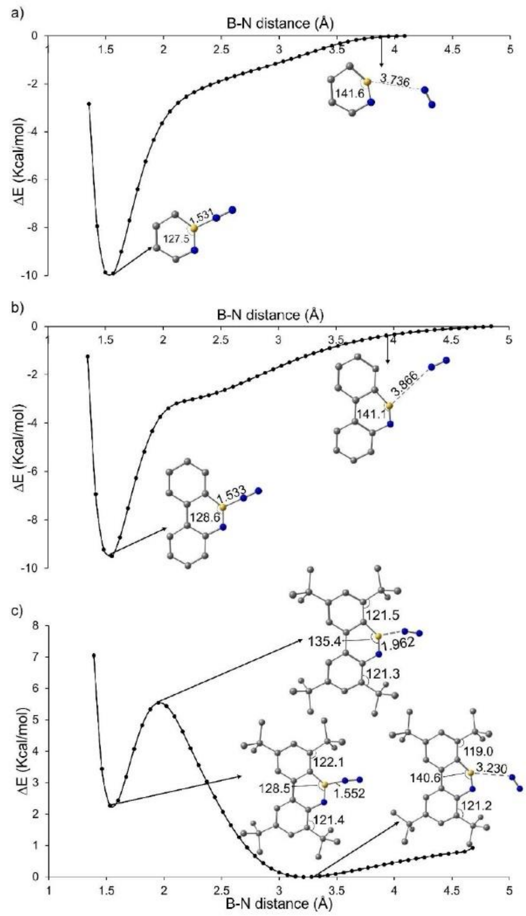

Figure 8. Plot of the relative energy ΔE (in kcal mol^{-1}) as a function of the B-N_2 distance for a) 1,2-azaborinine, b) 10,9-BN-phenanthryne **1**, and c) 2,4,7,9-tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine **5**, respectively, at the B3LYP-D3(BJ)/6-311 + G(d,p) level of theory. Hydrogen atoms omitted for clarity, all bond lengths in Å and angles in degree.

formation of adduct **5**·N_2 is prevented by a barrier on the potential energy surface. This is confirmed by a scan of the potential energy surface varying the B-N_2 distances at the B3LYP-D3(BJ)/6-311 + G(d,p) level of theory (Figure 8).

The emergence of an energy barrier of 5.5 kcal mol^{-1} in the case of **5** can be explained by the deformation of the CCC angle of a *tert*-butyl group (Figure 8). During N_2 adduct formation, the angle increases from 119.0° to 122.1°. The steric hindrance due to the *tert*-butyl groups also explains that formation of the Lewis acid-base adduct **5**·N_2 is endothermic compared to the van der Waals minimum between **5** and N_2 which has a nitrogen-boron distance of 3.230 Å.

Conclusions

The combined experimental and computational investigation of the synthesis, photogeneration, matrix isolation, and UV-PES of BN-arynes of the dibenzo[c,e][1,2]azaborinine type (BN-phenanthrynes) reveals a number of quite interesting results:

1. The 9-azido-9-borafluorene **2** can be investigated by matrix isolation despite its pronounced instability by using its pyridine adduct **2·py** as precursor for sublimation.
2. The azide **2** undergoes an unprecedented photoinduced isomerization to the dibenzo[c,e][1,2]azaborinine-N_2 Lewis acid-base adduct **1**·N_2. This novel structural isomer of a boryl azide results from the pronounced Lewis acidity of the boron center of the 1,2-azaborinine derivative **1** and the close proximity of the photoextructed N_2 within the matrix cage.
3. In contrast to parent 1,2-azaborinine-N_2-adduct, **1**·N_2 cannot be photoconverted to free **1**. As this is not due to an increased boron-N_2 interaction energy, a photophysical effect is more likely.
4. The triplet boryl nitrene **4** cannot be detected by ESR spectroscopy, suggesting that the ring enlargement from **2** to **1**·N_2 does most likely not proceed through the free boryl nitrene **4**, but by a concerted mechanism.
5. Gas phase flash vacuum thermolysis of **2·py** generates **1**, N_2, and pyridine as gas phase species as evidenced by UV-PES. The first ionization potential of **1** is 8.2 eV and is associated with ionization from the π HOMO.
6. The introduction of *tert*-Bu groups at positions 2,4,7,9 reduces the Lewis acidity of the boron center of the BN-aryne **5** sufficiently to preclude N_2 fixation due to steric hindrance as revealed by computations. This suggests that the high reactivity of BN-arynes is attenuated by kinetically protecting groups, which may open the way to a further investigations of BN-aryne reactivity.

Acknowledgements

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Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] Z. X. Giustra, S.-Y. Liu, *J. Am. Chem. Soc.* **2018**, *140*, 1184–1194.
[2] G. Belanger-Chabot, H. Braunschweig, D. K. Roy, *Eur. J. Inorg. Chem.* **2017**, 4353–4368.
[3] P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074–6092.
[4] M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.* **2009**, *87*, 8–29.
[5] Z. Liu, T. B. Marder, *Angew. Chem. Int. Ed.* **2008**, *47*, 242–244.
[6] P. J. Fazen, L. A. Burke, *Inorg. Chem.* **2006**, *45*, 2494–2500.
[7] K. Edel, S. A. Brough, A. N. Lamm, S.-Y. Liu, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2015**, *54*, 7819–7822.
[8] K. Edel, J. S. A. Ishibashi, S.-Y. Liu, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2019**, *58*, 4061–4064.
[9] M. Müller, C. Maichle-Mössmer, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2014**, *53*, 9380–9383.
[10] C. Keck, J. Hahn, D. Gupta, H. F. Bettinger, *Chem. Eur. J.* **2022**, *28*, e202103614.
[11] P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123–170.
[12] J. Münster, P. Paetzold, E. Schröder, H. Schwan, T. von Bennigsen-Mackiewicz, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2641–2651.
[13] T. Thiess, G. Bélanger-Chabot, F. Fantuzzi, M. Michel, M. Ernst, B. Engels, H. Braunschweig, *Angew. Chem. Int. Ed.* **2020**, *59*, 15480–15486.
[14] H. F. Bettinger, M. Müller, *J. Phys. Org. Chem.* **2015**, *28*, 97–103.
[15] S. Biswas, I. M. Oppel, H. F. Bettinger, *Inorg. Chem.* **2010**, *49*, 4499–4506.
[16] S. Kudoh, M. Takayanagi, M. Nakata, *J. Photochem. Photobiol., A* **1999**, *123*, 25–30.
[17] D. E. Johnstone, J. R. Sodeau, *J. Phys. Chem.* **1991**, *95*, 165–169.
[18] L. A. Johnson, S. A. Sturgis, I. A. Al-Jihad, B. Liu, J. V. Gilbert, *J. Phys. Chem. A* **1999**, *103*, 686–690.
[19] H.-J. Himmel, M. Junker, H. Schnöckel, *J. Chem. Phys.* **2002**, *117*, 3321–3326.
[20] G. Maier, H. P. Reisenauer, J. Henkelmann, C. Kliche, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 295–296.
[21] K. Edel, R. F. Fink, H. F. Bettinger, *J. Comput. Chem.* **2016**, *37*, 110–116.
[22] M. T. Nguyen, *J. Chem. Soc., Chem. Commun.* **1987**, 342–344.
[23] M. L. McKee, *J. Phys. Chem.* **1994**, *98*, 13243–13248.
[24] H. F. Bettinger, H. Bornemann *J. Am. Chem. Soc.* **2006**, *128*, 11128–11134.
[25] V. Lemierre, A. Chrostowska, A. Dargelos, H. Chermette, *J. Phys. Chem. A* **2005**, *109*, 8348–8355.
[26] A. Mazière, A. Chrostowska, C. Darrigan, A. Dargelos, A. Graciaa, H. Chermette, *J. Chem. Phys.* **2017**, *147*, 164306.
[27] R. Stowasser, R. Hoffmann, *J. Am. Chem. Soc.* **1999**, *121*, 3414–3420.
[28] G. Wittig, W. Uhlenbrock, P. Weinhold, *Chem. Ber.* **1962**, *95*, 1692–1702.
[29] H. F. Grützmacher, J. Lohmann, *Justus Liebigs Ann. Chem.* **1969**, *726*, 47–56.
[30] H.-F. Grützmacher, U. Straetmans, *Tetrahedron* **1980**, *36*, 807–813.
[31] R. Huisgen, W. Mack, L. Möbius, *Tetrahedron* **1960**, *9*, 29–39.
[32] M. M. Gragert, A. K. Tomov, S. Bettonville, G. Pannier, A. J. P. White, G. J. P. Britovsek, *Eur. J. Inorg. Chem.* **2020**, *2020*, 4088–4092.
[33] J. Kiesgen, J. Muenster, P. Paetzold, *Chem. Ber.* **1993**, *126*, 1559–1563.
[34] E. R. Lory, R. F. Porter, *J. Am. Chem. Soc.* **1973**, *95*, 1766–1770.
[35] C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1995**, *117*, 10125–10126.
[36] C. A. Thompson, L. Andrews, J. M. L. Martin, J. El-Yazal, *J. Phys. Chem.* **1995**, *99*, 13839–13849.
[37] Y. Kawashima, K. Kawaguchi, E. Hirota, *J. Chem. Phys.* **1987**, *87*, 6331–6333.

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Supporting Information

Direct Spectroscopic Identification of BN-Arynes and Subtle Steric Effects on Nitrogen Fixation

Divanshu Gupta, Constanze Keck, Christina Tönshoff, Virinder Bhagat, Raphael Strobel, Manuel Eder, Patrick Baylère, Stéphane Labat, Anna Chrostowska,* and Holger F. Bettinger*

I. Experimental Details

General Synthetic Procedures. All experiments were performed under anhydrous conditions using argon as protective gas. All NMR spectra were referenced to residual solvent signals (^{1}H, ^{13}C) and externally (^{11}B: BF_3•OEt_2). All commercially available compounds and dry solvents were purchased. NMR spectra were recorded on Bruker AVIII HDX+600 spectrometers. For EI-MS measurements an MSD 5977 Agilent MSD spectrometer was used. Compound **2•py**,[1] 9-chloro-9-borafluorene,[1] and 2,2'-dibromo-3,3',5,5'-tetra-*tert*-butylbiphenyl[2] were synthesized as reported previously

Matrix Isolation Experiments.

The precursors were sublimed from a glass flask at room temperature and condensed onto a cold CsI window (for IR) with a large excess of argon 6.0 (Westfalen AG, 99.9999 %) and dinitrogen 6.0 (Westfalen AG, 99.9999 %) or mixtures of these gases were dosed to 2.0 sccm by a mass flow controller (MKS mass flow PR400B). The deposition temperature was 30 K or 28 K for argon or nitrogen respectively. A Sumitomo SH-1 closed-cycle helium cryostat was used to obtain the temperature as low as 4 K.[3] An oven (BÜCHI GKR-51) was used for the sublimation of the compounds **2•py** and **6**. The infrared spectra in the range 400-4000 cm^{-1} were measured using a Bruker Vertex 70 FTIR spectrometer with a standard resolution of 0.5 cm^{-1}. For inducing photochemistry in the deposited matrix, an Osram HBO-500-W/2 high pressure mercury lamp in an Oriel housing with quartz optics, dichroic mirror (280 – 400 nm) and (260 - 320 nm) and a Schott cutoff filter (305 nm) was used. Photolysis were performed at 4 K.

Computational Methods. The structures of stationary points were optimized using the B3LYP[4, 5] functional as implemented[6] in Gaussian 16[7] along with Grimme's[8] London dispersion correction with Becke-Johnson damping B3LYP-D3(BJ)[9, 10] in conjunction with the 6-311+G(d,p) basis set.[11] Harmonic vibrational frequencies were computed to identify minima and transition states and to obtain Gibbs energies using the standard approximations. Single point computations based on the B3LYP-D3(BJ)/6-311+G(d,p) geometries were performed using domain based local pair natural orbital (DLPNO) coupled cluster theory with single, double, and a perturbative estimate of triple excitation (DLPNO-CCSD(T))[12-15] as implemented in ORCA 5.0[16, 17] in conjunction with Dunning's[18, 19] correlation consistent triple-ζ basis set. For the interpretation of UV-PES data, compound **1** and phenanthryne was optimized at the CAM-B3LYP/6-311G(d,p) level of theory and the same geometry was considered to calculate the single point energy of their respective cations for the calculation of vertical ionization energies (IE_n) as described in the literature before.[20, 21] The CAM-B3LYP/6-311G(d,p) geometries of **1** were also employed for computation of the lowest energy singlet and triplet electronically excited states using time-dependent DFT (TD-CAMB3LYP/6-311G(d,p)).[22]

II. Syntheses

Synthesis of 5-chloro-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole (8)

2,2'-Dibromo-3,3',5,5'-tetra-*tert*-butylbiphenyl (200 mg, 373 mmol) was dissolved in diethyl ether (5 mL) and cooled to 0 °C. n-Butyllithium (2.5 M in hexane, 0.29 mL, 746 mmol) was added. After stirring at 0 °C for 15 minutes, the solution was stirred at room temperature. The solution turned yellow. After 3 hours of stirring, the solvent was removed and the residue was suspended in pentane (5 mL). The suspension was cooled to 0 °C and boron trichloride (1 M in hexane, 0.37 mL, 0.37 mmol) was added. The suspension turned yellow immediately and was stirred for 15 minutes at 0 °C and for an additional 5 minutes at room temperature. The solvent was removed and the product was extracted with pentane. The product remained as a bright yellow crystalline compound (136 mg, 86 %).

^{1}H NMR: 700 MHz, CD_2Cl_2: 1.34 (s, 18H), 1.50 (s, 18H), 7.24 (d, 2H), 7.29 (d, 2H).

$^{11}B\{^1H\}$ NMR: 128 MHz, CD_2Cl_2: 63.7.

$^{13}C\{^1H\}$ NMR: 176 MHz, CD_2Cl_2: 31.1, 32.3, 35.7, 36.8, 114.5, 123.8, 152.6, 158.1, 158.8

HRMS m/z: calc. 422.291 Da, found 422.286 Da.

Synthesis of 5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole (6)

5-Chloro-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole (20 mg, 0.047 mmol) was dissolved in dichloromethane (1 mL). Trimethylsilyl azide (6.2 μL, 0.047 mmol) was added, the solution was shaken and left standing overnight. The next morning, the solution was dried and the remaining solid was directly used for experiments.

^1H NMR: 400 MHz, CD_2Cl_2: 1.36 (s, 18H), 1.47 (s, 18H), 7.24 (d, 2H), 7.35-7.36 (d, 2H).

$^{11}B\{^1H\}$ NMR: 128 MHz, CD_2Cl_2: 50.6.

$^{13}C\{^1H\}$ NMR: 176 MHz, CD_2Cl_2: 31.2, 32.0, 35.6, 36.7, 114.5, 123.4, 151.9, 156.6, 157.6

HRMS m/z: calc. 429.331 Da, found 429.328 Da.

III. NMR Spectra

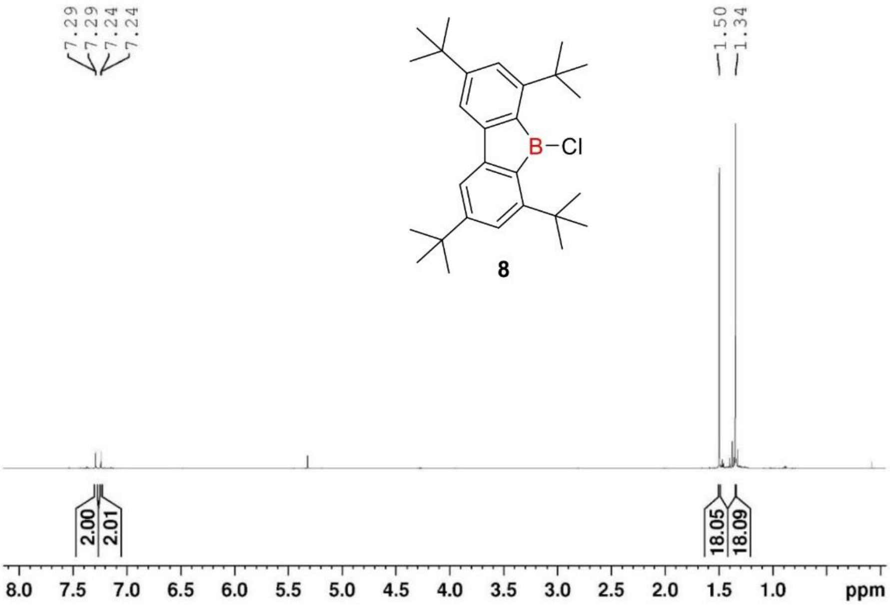

Figure S1. ^{1}H NMR spectrum (700 MHz) of 5-chloro-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **8** in CD_2Cl_2.

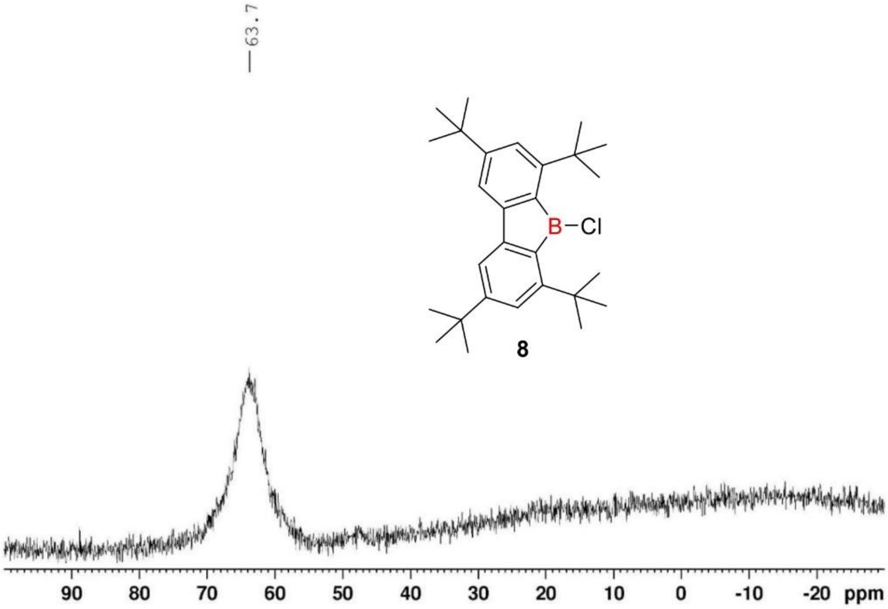

Figure S2. $^{11}B\{^{13}C\}$ NMR spectrum (128 MHz) of 5-chloro-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **8** in CD_2Cl_2.

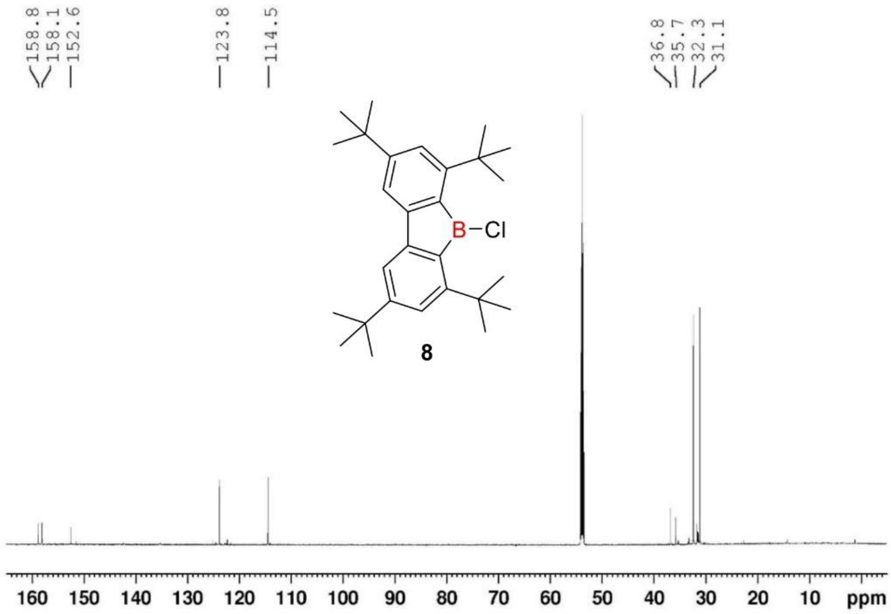

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz) of 5-chloro-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **8** in CD_2Cl_2.

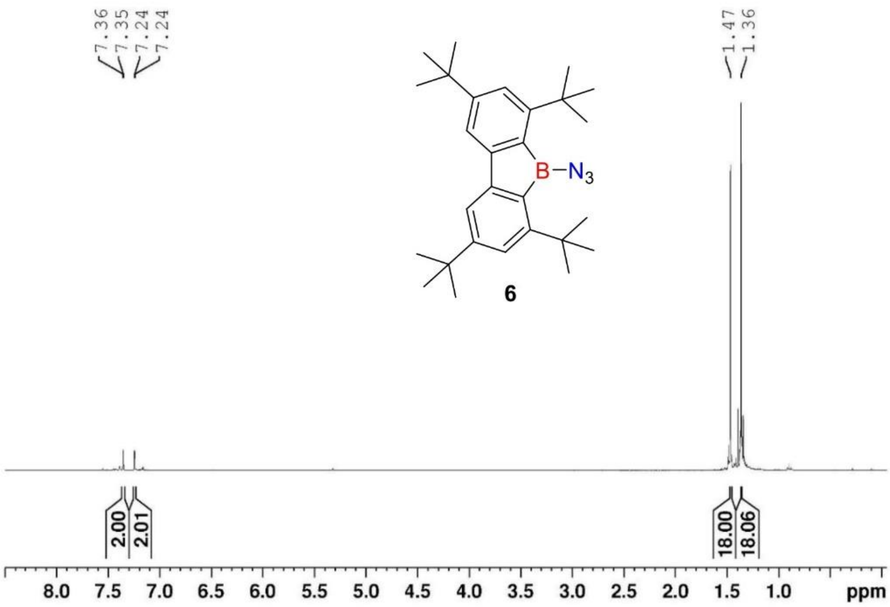

Figure S4. ^{1}H NMR spectrum (400 MHz) of 5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **6** in CD_2Cl_2.

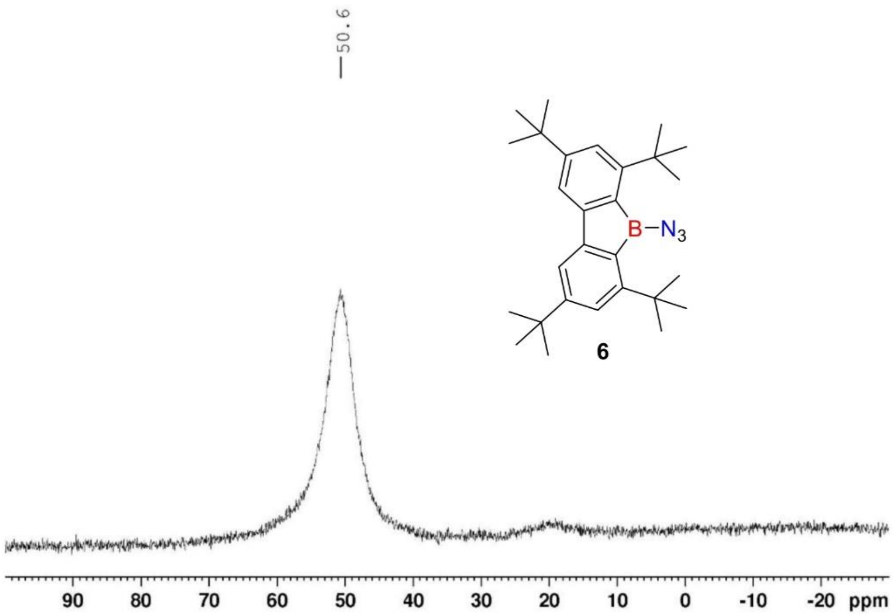

Figure S5. $^{11}B\{^{13}C\}$ NMR spectrum (128 MHz) of 5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **6** in CD_2Cl_2.

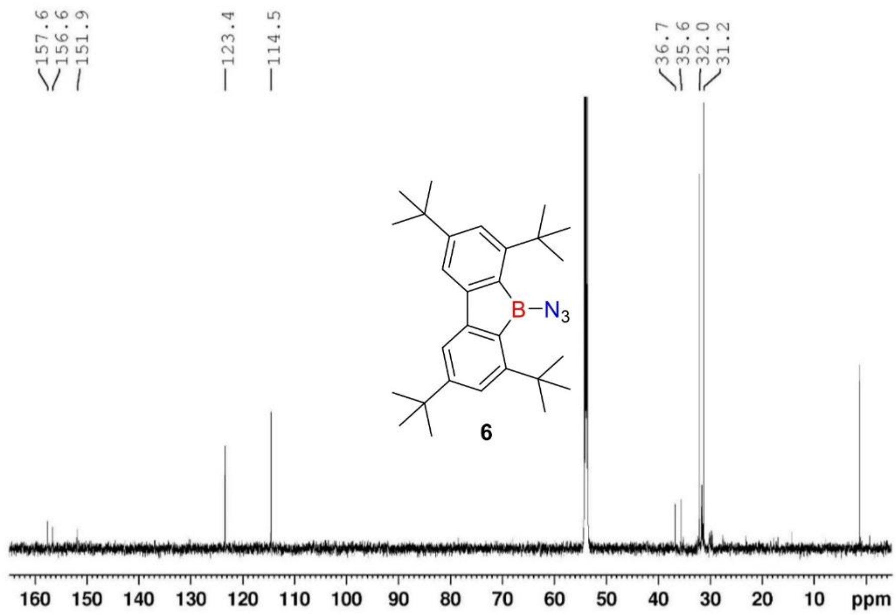

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz) of 5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **6** in CD_2Cl_2.

–S6–

IV. Matrix Isolation Data

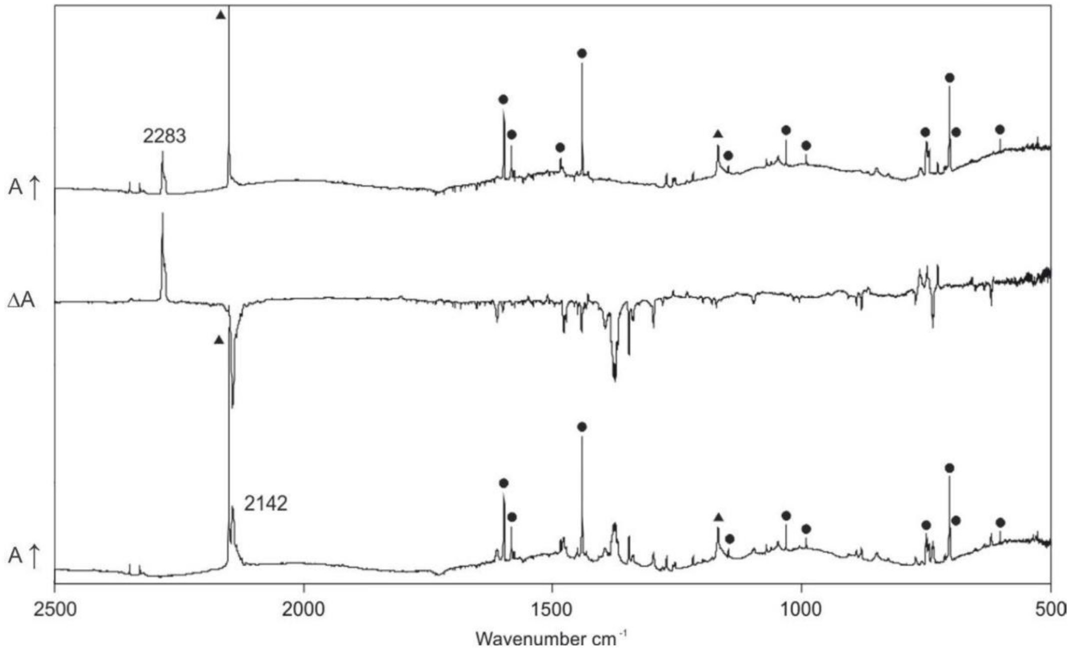

Figure S7. Photochemistry of **2** in an N_2 matrix at 10 K. Bottom: IR spectrum obtained after sublimation of **2·py** (105-115 °C). Top: IR spectrum obtained after subsequent photolysis (λ>280 nm, 10 min). Center: Difference spectrum of top and bottom, peaks pointing upwards increase upon irradiation, peaks pointing downwards decrease. (● denotes peaks of pyridine, ▲ denotes peaks of HN_3, ■ denotes H_2O)

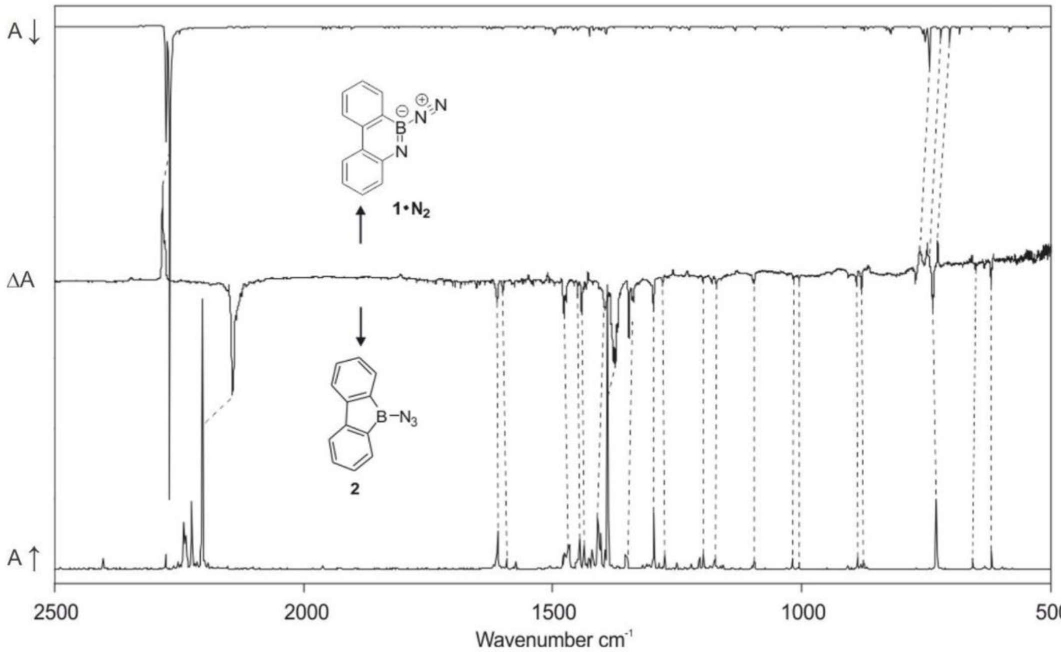

Figure S8. Photochemistry of **2** in an N_2 matrix at 10 K. Bottom: anharmonic IR spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **2** computed at B3LYP-D3(BJ)/6-311+G(d,p) level of theory. Center: IR difference spectrum obtained after photolysis of **2** (λ > 280 nm, 10 min) in N_2 at 10 K. Top: anharmonic IR spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **1•N$_2$** computed at B3LYP-D3(BJ)/6-311+G(d,p) level of theory.

The deposition of 5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole **6** was performed at 150 °C. Besides azide **6**, trimethylsilyl chloride and trimethylsilyl azide left over from the synthesis were deposited (see Figure S9). In addition, inevitable traces of H_2O and hydrazoic acid from hydrolysis of **6** were isolated. Four additional bands in the spectrum are tentatively assigned to 2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borol-5-ol based on the expected product of hydrolysis of **6** and the computed vibrational spectrum of the hydroxyl borole.

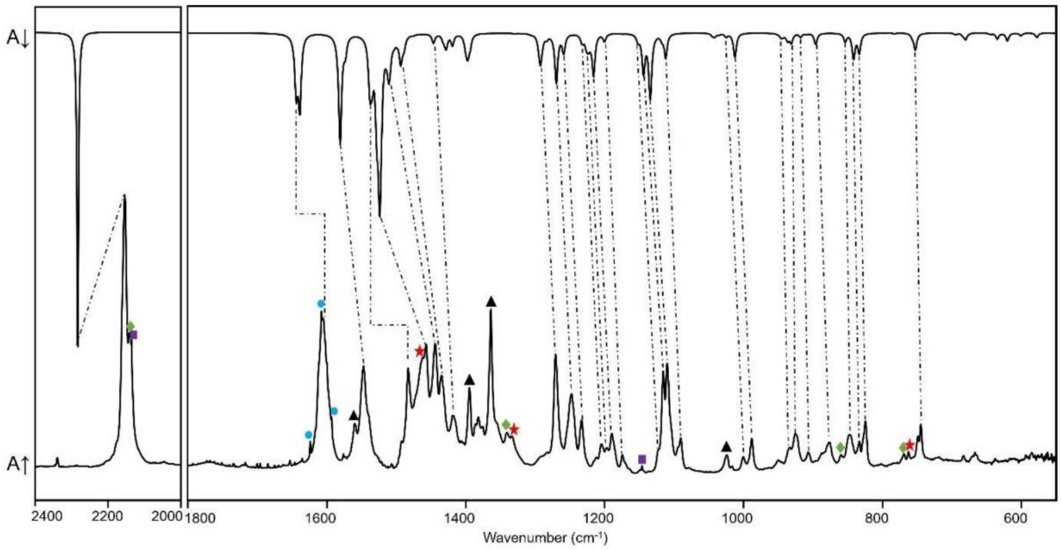

Figure S9. Top: harmonic IR spectrum of **6** computed at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory. Bottom: IR spectrum obtained after deposition of **6** in argon at 28 K. The spectrum also shows: trimethylsilyl chloride (★), trimethylsilyl azide (◆), hydrazoic acid (■), H_2O (●), and tentatively 2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borol-5-ol (▲).

–S9–

Table S1. Experimental and calculated harmonic and anharmonic vibrational frequencies (fundamentals, in cm^{-1}) of azidoborafluorene **2.**

Vibrational Mode No.	Experimental		Computational (B3LYP-D3(BJ)/6-311+G(d,p))				Assignments
	Ar matrix, 10K [a]	N_2 matrix, 10K [b]	Harmonic		Anharmonic		
	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	I[c]	ν (cm^{-1})	I[c]	
1			3190	2	3057	6	ν (C-H)
2			3189	5	3056	6	ν (C-H)
3			3179	4	3068	8	ν (C-H)
9	2136	2142	2263 (^{11}B)	100[d]	2204	95	ν (N-N)
			2264 (^{10}B)	100[f]			
10	1613	1611	1649	12	1611	11	ν (C-B, C-C)
11	1599	1600	1631	4	1593	4	ν (C-B, C-C)
12	1566 or 1579		1616	1	1575	2	ν (C-C), δ (B-C)
14	1478	1477	1503	14	1468	8	ν (B-N, C-C), δ (C-H)
16	1450	1450	1478	4	1451	8	ν (B-C, C-C), δ (C-H)
17	1441	1442	1467	6	1439	12	ν (C-C),δ (B-C) δ (C-H)
18	1381 (^{11}B)	1374 and 1378	1430 (^{11}B)	87	1391	100[e]	ν (B-N, N-N), δ (C-H)
	1398 (^{10}B)	1394	1447 (^{10}B)		1406 (^{10}B)	100[g]	
19	1345 or 1348	1347	1382	5	1351	6	ν (C-C), δ (B-C) δ (C-H)
20	1299		1323	4	1298	26	δ (C-C) δ (C-H)
21	1297	1297	1318	6	1285	0.2	ν (C-C), δ (B-C) δ (C-H)
23	1198 or 1207	1199	1247	6	1223	2	ν (C-C, B-N, N-N) δ (C-B), δ (C-H)
24	1181	1198	1227	5	1208	2	ν (C-C, B-N, N-N) δ (C-B), δ (C-H)
25	1170	1172	1196	5	1177	3	ν (B-C), δ (C-C), δ (C-H)
29	1095	1095	1115	3	1096	6	δ (B-C), δ (C-C), δ (C-H)
32	1005or 1015.0	1005 or 1016	1035	3	1020	3	δ (B-N, N-N), δ (C-C), δ (C-H)

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34	880 or 891 (^{11}B)	880 or 890 (^{11}B)	900 (^{11}B)	8	889	7	δ (B-N, N-N), δ (C-C), δ (C-H)
	907 (^{10}B)	907 (^{10}B)	919 (^{10}B)				
53	769	772	786	3	773	0.5	γ (C-B, B-N), γ (C-C), γ (C-H)
54			750	7	731	22	γ (C-C, C-H)
55	736	737	749	6	730	5	γ (C-C, C-H)
37	651	651	665	2	658	3	δ (N-N, N-B), δ (C-C)
56	619 (^{11}B)	619	634 (^{11}B)	4	621	7	δ (N-B, B-C), δ (C-C)
	633 (^{10}B)	633	648 (^{10}B)				

[a] The bands at 602, 701, 747, 991, 1032, 1073, 1148, 1219, 1441, 1483, 1579, and 1583 cm^{-1} are assigned to pyridine[A], the bands at 1146 and at 2137 cm^{-1} (the later one coinciding with the azide band of the azidoborafluorene) are assigned to HN_3[B]

[b] The bands at 602, 703, 744, 991, 1032, 1148, 1218, 1441, 1484, 1578 and 1582 are assigned to pyridine, the bands at 1168 and at 2149 cm^{-1} are assigned to HN_3

[c] Intensity relative to the strongest band [d] Computed absolute intensity: 762 km mol^{-1}

[e] Computed absolute intensity 397 km mol^{-1} [f] Computed absolute intensity:753 km mol^{-1}

[g] Computed absolute intensity: 152 km mol^{-1}.

Table S2. Experimental and calculated harmonic and anharmonic vibrational frequencies (fundamentals, in cm^{-1}) of azidoborafluorene **1·N_2**

Vibrational Mode No.	Experimental		Computational (B3LYP-D3(BJ)/6-311+G(d,p))				Assignments
	Ar matrix, 10K [a]	N_2 matrix, 10K[b]	Harmonic		Anharmonic		
	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	I[a]	ν (cm^{-1})	I[a]	
1			3208	3	3086	10	ν (C-H)
2			3196	2	3085	5	ν (C-H)
4			3185	2	3063	1	ν (C-H)
5			3178	2	3050	0.4	ν (C-H)
9	2259	2283, 2278 (shoulder)	2306	100[b]	2277	100[c]	ν (N-N)
			2306 (^{10}B)	100[d]	2277 (^{10}B)	100[e]	
14			1529	3	1500	1	ν(N_{ring}-B, B-C, C-C), δ(C-H, C-C)
			1545 (^{10}B)	5	1515 (^{10}B)	4	
16			1477	2	1440	4	δ(C-H, C-C), ν(C-C)
17			1454	3	1427	9	ν(N_{ring}-B, C-C), δ(C-H, C-C)
18			1425	4	1396	4	ν(N_{ring}-B, B-C), δ(C-H, C-C)
23			1271	1	1249	1	δ(,N-B-C, C-H, C-C), ν(N-C)
33			897	2	876	4	δ(B-N-C, N-B-N,C-C)
34			842	3	822	7	δ(C-B-N, C-C), ν (B-N)
53	761	763	778	4	753	22	γ(C-H, C-C)
54			758	4	745	38	γ(C-H, C-C)
55			742	5	704	14	γ(C-H, C-C)
35	745	749	740	3	723	18	δ(N-B-C, C-C)
		753					
36	727	727	698	1	685	8	δ(N-B-C, C-C)

[a] Intensity relative to the strongest band [b] Computed absolute intensity: 980 km mol^{-1} [c] Computed absolute intensity 163 km mol^{-1} [d] Computed absolute intensity: 976 km mol^{-1} [e] Computed absolute intensity: 621 km mol^{-1}

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Table S3. Absolute energies, zero-point corrected energies, enthalpies and free energies computed at B3LYP-D3(BJ)/6-311+G(d,p) level of theory at 298.15 K and at 373.15 K (values for 373.15 K in italics)

	E (a.u.)	ΔE (kcal/mol)	E+ZPVE (a.u.)	Δ(E+ZPVE) (kcal/mol)	H (a.u.)	ΔH (kcal/mol)	G (a.u.)	ΔG (kcal/mol)
2·py	-899.8203	0.0	-899.5513 *-899.5515*	0.0 *0.0*	-899.5332 *-899.5241*	0.0 *0.0*	-899.5990 *-899.6169*	0.0 *0.0*
2+py	-899.7864	21.28	-899.5201 *-899.5201*	19.57 *19.60*	-899.5021 *-899.4931*	19.52 *19.43*	-899.5855 *-899.6075*	8.45 *5.86*

Table S4. Absolute energies, zero-point corrected energies, enthalpies and free energies computed at B3LYP-D3(BJ)/6-311+G(d,p) and DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/6-311+G(d,p) (bold) level of theory at 298.15 K

	E (a.u.)	ΔE (kcal/mol)	E+ZPVE (a.u.)	Δ(E+ZPVE) (kcal/mol)	H (a.u.)	ΔH (kcal/mol)	G (a.u.)	ΔG (kcal/mol)
2	-651.4180 **-650.0022**	0.0 **0.0**	-651.2402 **-649.8244**	0.0 **0.0**	-651.2274 **-649.8116**	0.0 **0.0**	-651.2789 **-649.8631**	0.0 **0.0**
TS 2_1•N_2	-651.3585 **-649.9449**	37.31 **35.94**	-651.1854 **-649.7718**	34.34 **32.97**	-651.1718 **-649.7582**	34.90 **33.54**	-651.2258 **-649.8122**	33.30 **31.94**
1•N_2	-651.4560 **-650.0425**	-23.86 **-25.32**	-651.2788 **-649.8653**	-24.21 **-25.66**	-651.2660 **-649.8526**	-24.24 **-25.69**	-651.3170 **-649.9036**	-23.94 **-25.39**
1+N_2	-651.4395 **-650.0311**	-13.49 **-18.11**	-651.2657 **-649.8573**	-16.03 **-20.65**	-651.2519 **-649.8435**	-15.38 **-19.98**	-651.3192 **-649.9108**	-25.30 **-29.92**

Table S5. Zero-point corrected energies, enthalpies and free energies computed at B3LYP-D3(BJ)/6-311+G(d,p)) and DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/6-311+G(d,p) (bold) level of theory at 298.15 K.

	E (a.u.)	ΔE (kcal/mol)	E+ZPVE (a.u.)	Δ(E+ZPVE) (kcal/mol)	H (a.u.)	ΔH (kcal/mol)	G (a.u.)	ΔG (kcal/mol)
1 •N_2			-651.2788 **-649.8653**	0.0 **0.0**	-651.2660 **-649.8526**	0.0 **0.0**	-651.3170 **-649.9036**	0.0 **0.0**
1 +N_2			-651.2657 **-649.8573**	8.18 **5.01**	-651.2519 **-649.8435**	8.86 **5.71**	-651.3192 **-649.9108**	-1.36 **-4.53**
1,2-Azaborinine•N2			-343.9761 **-343.2528**	0.0 0.0	-343.9687 **-343.2454**	0.0 **0.0**	-344.0069 **-343.2836**	0.0 **0.0**
1,2-Azaborinine+N2			-343.9611 **-343.2435**	9.42 **5.86**	-343.9524 **-343.2347**	10.23 **6.67**	-344.0069 **-343.2893**	0.00 **3.57**

Table S6. Infrared spectroscopic data of experimental and computed (harmonic B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **6** (5-azido-2,4,6,8-tetra-*tert*-butyl-5H-dibenzo[b,d]borole), and relative intensity in argon matrix.

Vibrational Mode No. [a]	Experimental		Computational		Tentative Assignment
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
204	3015	0.03	3150	0.05	ν(asym. CH str.) (tert-butyl)
195	2974	0.76	3094	0.12	ν (asym. CH str.) (tert-butyl)
191	2962	0.43	3091	0.08	ν (asym. CH str.) (tert-butyl)
184	2944	0.07	3080	0.01	ν (asym. CH str.) (tert-butyl)
179	2911	0.17	3030	0.05	ν (sym. CH str.) (tert-butyl)
173	2876	0.16	3023	0.04	ν (sym. CH str.) (tert-butyl)
170	2155	1	2284	1	ν (N3 asym. str.)
169/168	1605/ 1600	0.24	1645/ 1640	0.12	ν (sym. ring str.)
167	1547	0.25	1582	0.19	ν (ring str.)
164	1483	0.25	1539	0.09	ν (CH scissor) (tert-butyl)
163	1462	0.02	1525	0.29	ν (BN str.) + ν (CH rock) (tert-butyl)
158	1444	0.23	1512	0.05	ν (CH bend) (ring) + ν (CH scissor) (tert-butyl)
149	1435	0.2	1495	0.04	ν (CH scissor) (tert-butyl)
138	1418	0.11	1448	0.02	ν (sym. ring str.)
131			1400	0.01	ν (out of plane CH wag.) (tert-butyl)
129			1398	0.01	ν (CH wag.) (tert-butyl)
126			1395	0.01	ν (CH wag.) (tert-butyl)
121	1271	0.43	1294	0.05	ν (ring str.) + ν (CH bend)
118	1248	0.24	1271	0.08	ν (sym. CH bend) (ring) + ν (CH twist) (tert-butyl)
117	1233	0.18	1260	0.03	ν (CH bend) (ring) + ν (CH twist) (tert-butyl)
116	1205	0.05	1234	0.01	ν (CH twist) (tert-butyl)
114[^{10}B]	1197	0.02	1228	0.02	ν (ring breathing) + ν (CH twist) (tert-butyl)
108	1190	0.13	1217	0.08	ν (BN str.) + ν (ring str.)
107	1174	0.06	1202	0.01	ν (CC str.) (tert-butyl) + ν (CH bend) + □(ring breathing)
105[^{10}B]	1123	0.07	1153	0.01	ν (BN str.) + ν (ring breathing)
105	1116	0.27	1146	0.08	ν (BN str.) + ν (ring breathing)
104	1110	0.36	1135	0.11	ν (BC str.) + ν (ring breathing) + ν (CH bend) + ν (CH wag.) (tert-butyl)
103[^{10}B]	1094	0.03	1119	0.01	ν (BC str.) + ν (ring breathing) + ν (CH bend)
103	1091	0.09	1113	0.05	ν (BC str.) + ν (ring breathing) + ν (CH bend)
94[^{10}B]	1001	0.05	1026	0.01	ν (BN str.) + ν (ring breathing)
94	988	0.12	1014	0.05	ν (BN str.) + ν (ring breathing)
88	934	0.05	947	0.01	ν (CH wag.) (tert-butyl)
82	926	0.10	933	0.01	ν (CH wag.) (tert-butyl)

79	908	0.04	919	0.01	ν (ring breathing) + ν (CH wag.) (tert-butyl)
75	876	0.08	898	0.02	ν (ring deformation)
74 [^{10}B]	846	0.08	855	0.02	ν (sym. CH bend) (C6 ring) + ν (CH rock) (tert-butyl)
74	833	0.05	843	0.05	ν (sym. CH bend) (C6 ring) + ν (CH rock) (tert-butyl)
73	825	0.16	835	0.04	ν (CH rock) (tert-butyl)
68	745	0.13	754	0.03	ν (ring breathing) + ν (CH str.) (tert-butyl)
67			696	0.001	ν (ring str.) + ν (CH str.) (tert-butyl)
65			682	0.01	ν (ring breathing.) + ν (CH wag.) (tert-butyl)

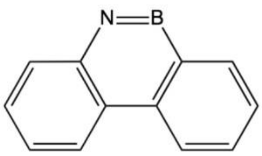
[a] the numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band.

Table S7. Infrared spectroscopic data of experimental and computed (harmonic B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **5** (2,4,7,9-tetra-*tert*-butyldibenzo[c,e][1,2]azaborinine), and relative intensity in argon matrix.

Vibrational Mode No. [a]	Experimental		Computational		Tentative Assignment
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
164[^{10}B]	1793	0.17	1848	0.24	ν (BN str.)
164	1751	1	1796	1	ν (BN str.)
162			1633	0.14	ν (CC ring str.) + ν (CH bend)
160			1566	0.13	ν (CC ring str.) + ν (CH bend)
156	1522	0.07	1524	0.08	ν (CH scissor) (tert-butyl)
152	1507	0.09	1510	0.12	ν (CH scissor) (tert-butyl)
139			1486	0.10	ν (CH scissor) (tert-butyl)
133	1403	0.18	1436	0.16	ν (asym. CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
128	1383	0.08	1413	0.09	ν (sym. CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
124			1398	0.03	ν (CH wag) (tert-butyl)
120			1389	0.03	ν (CH wag) (tert-butyl)
119	1333	0.06	1339	0.07	ν (CC str.) (C6 + tert-butyl)
118	1321	0.03	1321	0.02	ν (CC ring str.) + ν (CH bend) (C6 ring)
117	1285	0.09	1308	0.08	ν (CH bend) (C6-ring)
115			1294	0.02	ν (CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
114			1278	0.04	ν (sym. CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
113	1252	-	1270	0.20	ν (CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
110			1237	0.04	ν (asym. CH bend) (C6-ring) + ν (CH wag) (tert-butyl)
104			1224	0.01	ν (CH twist) (tert-butyl)
103			1215	0.03	ν (CC ring str.) + ν (CH bend) (C6-ring) + ν (CH wag) (tert-butyl)

102			1201	0.05	ν (ring str.) + ν (CH twist) (tert-butyl)
100	1132	0.04	1160	0.03	ν (ring breathing) + ν (CH bend) (C6-ring)
98			1111	0.10	ν (ring str.) + ν (CH twist) (tert-butyl)
85			950	0.02	ν (CH wag) (tert-butyl)
83			941	0.01	ν (CH twist) (tert-butyl)
80			934	0.03	ν (CH wag) (tert-butyl)
79			933	0.01	ν (CH twist) (tert-butyl)
75			918	0.02	ν (ring breathing) + ν (CH twist) (tert-butyl)
72			899	0.05	ν (out of plane CH bend) (C6-ring)
70			840	0.03	ν (CBNC str.) + ν (ring breathing)
69			835	0.02	ν (CH out of plane wag) (tert-butyl)
64	740	0.03	752	0.04	ν (CC ring str.) + ν (sym. CH str.) (tert-butyl)
[a] the numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band.					

Table S8. Computational results and cartesian coordinates for the UV-PES data of **1** for neutral and cation ground state at CAM-B3LYP/6-311+G(d,p) level of theory.



SCF Energy: -541.5025393720000 au
Dipole moment (Debye):
x : 1.2562
y : 1.2284
z : 0.0000
Norm= 1.7570

HOMO = -7.313 eV
LUMO = -0.393 eV
Gap (HOMO-LUMO) = 6.920 eV

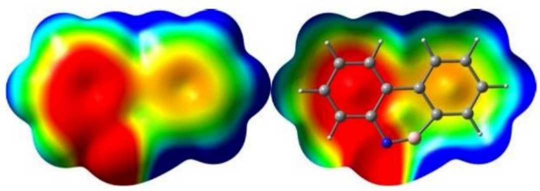
CAM-B3LYP/6-311+G(d,p)			
C	-1.53412	3.081534	0
C	-2.15696	1.86223	0
C	-1.41464	0.664176	0
C	0.000000	0.709658	0
C	0.610611	1.982543	0
C	-0.13314	3.135411	0
C	-2.08279	-0.598894	0
C	0.745997	-0.53539	0
C	0.030552	-1.764254	0
C	-1.39638	-1.761747	0
C	2.96104	-1.696152	0
C	2.175231	-0.556329	0
H	-3.16723	-0.604518	0
H	-2.1144	3.995986	0
H	-3.23949	1.799094	0
H	1.688407	2.068952	0
H	0.368935	4.095598	0
H	-1.89357	-2.72295	0
H	4.037132	-1.648034	0
H	2.694289	0.394764	0
B	1.977824	-2.762655	0
N	0.70061	-2.957476	0

MOs and their respective energies			
MO	No.	au	eV
LUMO+4	(51)	0.07259	1.9753
LUMO+3	(50)	0.0466	1.2681
LUMO+2	(49)	-0.00149	-0.0405
LUMO+1	(48)	-0.00693	-0.1886
LUMO	(47)	-0.00732	-0.1992

HOMO	(46)	-0.27008	-7.3493
HOMO-1	(45)	-0.28802	-7.8374
HOMO-2	(44)	-0.33299	-9.0611
HOMO-3	(43)	-0.34849	-9.4829
HOMO-4	(42)	-0.35513	-9.6636
HOMO-5	(41)	-0.39398	-10.7207
HOMO-6	(40)	-0.41003	-11.1575
HOMO-7	(39)	-0.42107	-11.4579
HOMO-8	(38)	-0.42721	-11.625
HOMO-9	(37)	-0.44433	-12.0908
HOMO-10	(36)	-0.44586	-12.1325
HOMO-11	(35)	-0.48792	-13.277
HOMO-12	(34)	-0.49229	-13.3959
HOMO-13	(33)	-0.49536	-13.4794
HOMO-14	(32)	-0.50748	-13.8092
HOMO-15	(31)	-0.51564	-14.0313

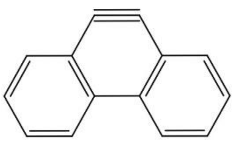
Gap (au ; eV ; nm) 0.26276 ; 7.1501 ; 173.40

Electrostatic potential map (from –12.55 (red) to +12.55 (blue) kcal/mol) plotted on the 0.001 electron.bohr^{-3} isodensity surface.



Cation, ground state, CAM-B3LYP/6-311G(d,p)
SCF Energy of cation: -541.2135571049 au
First IE Delta-SCF: 7.864 eV

Table S9. Computational results and cartesian coordinates for the UV-PES data of **phenanthryne** for neutral and cation ground state at CAM-B3LYP/6-311+G(d,p) level of theory.

	CAM-B3LYP/6-311+G(d,p)			
 SCF Energy: -538.010433489 au Dipole moment (Debye): X = -0.23231;	C	-0.73738	-0.27336	0.000008
	C	-1.48669	0.950155	-3.5E-05
	C	-2.88369	0.946466	-2.5E-05
	C	-3.56922	-0.24593	0.00003
	C	-2.86372	-1.45106	0.000075
	C	-1.48631	-1.46163	0.000065
	C	0.737415	-0.2733	0.000002
	C	1.486664	0.950101	-5.6E-05

–S17–

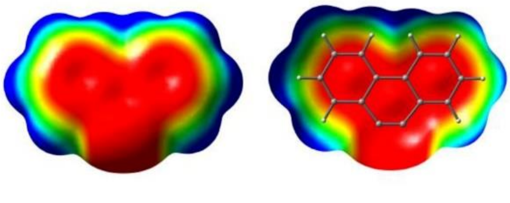
y =-1.3960; z = 0.000 Norm = 1.917 HOMO =-7.5686 eV; LUMO =-0.63485 eV Gap(HOMO-LUMO) = 6.934 eV	H	-3.40936	1.892526	-6.3E-05
	H	-4.65227	-0.25098	0.000039
	H	-3.40314	-2.39039	0.000116
	H	-0.98118	-2.41793	0.000097
	C	3.569308	-0.2457	0.000004
	C	1.486515	-1.4616	0.000072
	C	2.863867	-1.45092	0.000073
	H	4.65236	-0.25069	0.000005
	H	0.981367	-2.4179	0.00013
	H	3.403437	-2.39017	0.000128
	C	2.883689	0.946641	-5.9E-05
	H	3.40928	1.892728	-0.00011
	C	-0.60806	2.063066	-9.6E-05
	C	0.607524	2.062525	-0.00012

MOs and their respective energies			
MO	No.	au	eV
LUMO+4	(51)	0.07031	1.91325
LUMO+3	(50)	0.03804	1.03513
LUMO+2	(49)	0.00086	0.02340
LUMO+1	(48)	-0.00847	-0.23048
LUMO	(47)	-0.02333	-0.63485
HOMO	(46)	-0.27814	-7.56863
HOMO-1	(45)	-0.28889	-7.86135
HOMO-2	(44)	-0.33010	-9.00696
HOMO-3	(43)	-0.33220	-9.03969
HOMO-4	(42)	-0.35586	-9.68352
HOMO-5	(41)	-0.39768	-10.82151
HOMO-6	(40)	-0.41234	-11.22043
HOMO-7	(39)	-0.42649	-11.60548
HOMO-8	(38)	-0.43560	-11.85337
HOMO-9	(37)	-0.44400	-12.08195
HOMO-10	(36)	-0.44895	-12.21665
HOMO-11	(35)	-0.49037	-13.34375
HOMO-12	(34)	-0.50128	-13.64063
HOMO-13	(33)	-0.50188	-13.65696
HOMO-14	(32)	-0.51225	-13.93914
HOMO-15	(31)	-0.51437	-13.99683

Gap (au ; eV ; nm): 0,25482; 6.934; 168,16

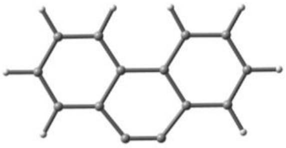
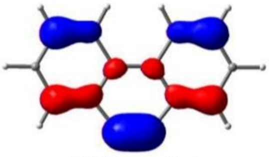
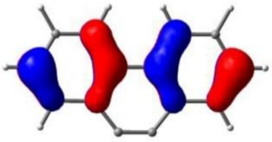
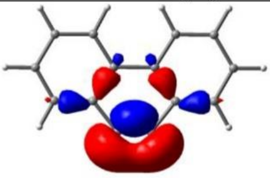
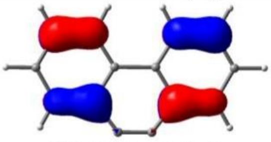
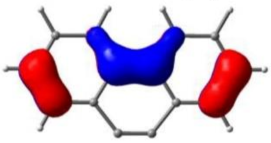
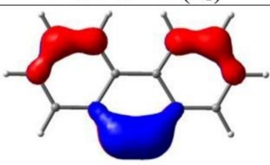
Electrostatic potential map (from –12.55 (red) to +12.55 (blue) kcal/mol) plotted on the 0.001 electron.bohr^{-3} isodensity surface.

–S18–



Cation, ground state, CAM-B3LYP/6-311G(d,p)
SCF Energy of cation: -537.7111880000 au
First IE Delta-SCF: 8.1430 eV

Table S10. Calculated CAM-B3LYP ionization energies for phenanthryne (eV).

Nature of MO 	**CAM-B3LYP** $-\varepsilon^{KS}$	**CAM-B3LYP ΔSCF+TD-DFT**	**Corrected** $-\varepsilon^{KS}+x_{\Delta SCF}$ **x = 0.574**
 HOMO (b_1)	7.569	8.143	8.143
 HOMO - 1 (a_2)	7.861	8.544	8.436
 HOMO - 2 (a_1)	9.007	9.495	9.581
 HOMO - 3 (a_2)	9.040	9.556	9.614
 HOMO - 4 (b_1)	9.684	9.696	10.258
 HOMO - 5 (b_1)	10.822	10.266	11.396

V. Coordinates

Cartesian coordinates of stationary points at B3LYP-D3(BJ)/6-311+G(d,p) level of theory.

1	C	-1.024540000	3.399001000	0.000000000
	C	-1.898035000	2.328040000	0.000000000
	C	-1.416447000	1.008815000	0.000000000
	C	0.000000000	0.759629000	0.000000000
	C	0.851566000	1.882343000	0.000000000
	C	0.358320000	3.174593000	0.000000000
	C	0.532270000	-0.616062000	0.000000000
	C	-0.341020000	-1.769687000	0.000000000
	C	0.173714000	-3.073498000	0.000000000
	H	-0.509210000	-3.914354000	0.000000000
	C	1.538547000	-3.285494000	0.000000000
	C	2.405154000	-2.183610000	0.000000000
	C	1.916300000	-0.890226000	0.000000000
	H	-1.410493000	4.411886000	0.000000000
	H	-2.971093000	2.472078000	0.000000000
	H	1.924556000	1.744288000	0.000000000
	H	1.045551000	4.012062000	0.000000000
	H	1.937034000	-4.292661000	0.000000000
	H	3.477052000	-2.344265000	0.000000000
	H	2.624301000	-0.072813000	0.000000000
	N	-2.310724000	-0.063598000	0.000000000
	B	-1.703521000	-1.194821000	0.000000000
1·N2	C	3.503638000	-1.474528000	0.000000000
	C	2.253732000	-2.049966000	0.000000000
	C	1.074294000	-1.261905000	0.000000000
	C	1.195722000	0.172515000	0.000000000
	C	2.494219000	0.721801000	0.000000000
	C	3.623446000	-0.074055000	0.000000000
	C	0.000000000	1.013935000	0.000000000
	C	-1.288509000	0.404424000	0.000000000
	C	-2.443412000	1.209957000	0.000000000
	H	-3.424001000	0.743292000	0.000000000
	C	-2.352292000	2.587751000	0.000000000
	C	-1.085590000	3.193184000	0.000000000
	C	0.062585000	2.425721000	0.000000000
	H	4.392036000	-2.095513000	0.000000000
	H	2.122750000	-3.125113000	0.000000000
	H	2.624008000	1.795757000	0.000000000
	H	4.604604000	0.386264000	0.000000000
	H	-3.247179000	3.198927000	0.000000000
	H	-1.006135000	4.274305000	0.000000000
	H	1.019682000	2.929348000	0.000000000
	N	-0.125492000	-1.914331000	0.000000000
	B	-1.224779000	-1.110871000	0.000000000
	N	-2.541694000	-1.895684000	0.000000000
	N	-3.502652000	-2.442258000	0.000000000
2	C	-1.866387000	-2.145559000	0.000000000
	C	-0.955903000	-1.09933000	0.000000000
	C	0.438808000	-1.352183000	0.000000000
	C	0.900525000	-2.663696000	0.000000000
	C	-0.015378000	-3.721975000	0.000000000
	C	-1.384018000	-3.460771000	0.000000000
	C	-1.218812000	0.363631000	0.000000000
	C	0.000000000	1.092136000	0.000000000
	C	-0.036693000	2.483492000	0.000000000
	C	-1.268026000	3.149978000	0.000000000
	C	-2.455067000	2.422539000	0.000000000
	C	-2.439240000	1.021952000	0.000000000
	B	1.149176000	0.031100000	0.000000000
	N	2.574170000	0.207511000	0.000000000
	H	1.966150000	-2.866628000	0.000000000
	H	-1.298888000	4.233158000	0.000000000

	H	0.878941000	3.064609000	0.000000000
	H	-3.372760000	0.470499000	0.000000000
	H	-3.404531000	2.945941000	0.000000000
	H	0.336787000	-4.746922000	0.000000000
	H	-2.086703000	-4.286475000	0.000000000
	H	-2.934845000	-1.961157000	0.000000000
	N	3.115151000	1.313747000	0.000000000
	N	3.735124000	2.257342000	0.000000000
2·Py	N	-0.607126000	-0.000091000	2.208166000
	N	0.301124000	-0.000011000	3.016568000
	N	1.094265000	-0.000029000	3.831486000
	N	-1.762778000	-0.000101000	0.002342000
	C	0.401481000	-2.615357000	0.251621000
	H	-0.431853000	-3.018873000	0.819862000
	C	1.314139000	-3.489107000	-0.349552000
	H	1.187346000	-4.561586000	-0.250934000
	C	2.394491000	-2.983356000	-1.072964000
	H	3.099725000	-3.665552000	-1.534550000
	C	2.578963000	-1.605360000	-1.201119000
	H	3.426398000	-1.222012000	-1.759410000
	C	1.667720000	-0.739853000	-0.598588000
	C	1.667634000	0.740019000	-0.598571000
	C	2.578770000	1.605645000	-1.201093000
	H	3.426248000	1.222407000	-1.759396000
	C	2.394138000	2.983617000	-1.072911000
	H	3.099288000	3.665905000	-1.534490000
	C	1.313732000	3.489228000	-0.349482000
	H	1.186814000	4.561691000	-0.250844000
	C	0.401180000	2.615360000	0.251680000
	H	-0.432198000	3.018768000	0.819935000
	C	0.566505000	1.240513000	0.131742000
	C	0.566645000	-1.240489000	0.131709000
	B	-0.296911000	-0.000048000	0.702513000
	C	-2.901038000	-0.000098000	0.713671000
	H	-2.769762000	-0.000092000	1.786668000
	C	-4.142885000	-0.000108000	0.092362000
	H	-5.038849000	-0.000103000	0.698747000
	C	-4.206063000	-0.000125000	-1.295052000
	H	-5.162280000	-0.000131000	-1.804014000
	C	-3.016635000	-0.000130000	-2.023133000
	H	-3.016579000	-0.000148000	-3.104812000
	C	-1.813812000	-0.000118000	-1.343774000
	H	-0.857937000	-0.000118000	-1.848537000
TS2_1·N_2	C	-2.753990000	0.801793000	0.000038000
	C	-1.415045000	0.422274000	-0.000004000
	C	-1.074506000	-0.954389000	-0.000047000
	C	-2.066422000	-1.923900000	-0.000078000
	C	-3.408781000	-1.530981000	-0.000055000
	C	-3.747221000	-0.179201000	0.000009000
	C	-0.219229000	1.288133000	0.000022000
	C	0.964826000	0.514461000	0.000044000
	C	2.206477000	1.134013000	0.000006000
	C	2.277255000	2.531034000	-0.000024000
	C	1.107998000	3.290869000	-0.000036000
	C	-0.147310000	2.676830000	-0.000018000
	B	0.540123000	-0.985405000	0.000035000
	N	1.002497000	-2.246061000	0.000141000
	H	-1.810298000	-2.975901000	-0.000116000
	H	3.241748000	3.025054000	-0.000054000
	H	3.118863000	0.547487000	-0.000007000
	H	-1.046850000	3.281892000	-0.000039000
	H	1.173347000	4.372963000	-0.000069000
	H	-4.189107000	-2.283066000	-0.000075000
	H	-4.790531000	0.114624000	0.000041000
	H	-3.026624000	1.851395000	0.000089000
	N	2.914392000	-2.253184000	0.000301000
	N	3.838043000	-2.848333000	-0.000312000

1,2-azaborinine	N	-1.31475400	-0.76594900	0.00000000
	C	-1.23525000	0.59055000	0.00000000
	C	0.00000000	1.23994400	0.00000000
	C	1.20987300	0.51116400	0.00000000
	C	1.28011400	-0.89604600	0.00000000
	H	0.03101900	2.32227300	0.00000000
	H	-2.16260500	1.15789500	0.00000000
	H	2.14320200	1.06840700	0.00000000
	H	2.22279900	-1.41819600	0.00000000
	B	-0.11191300	-1.28848200	0.00000000
1,2-azaborinine·N$_2$	N	-1.26469200	-0.06268700	0.00000000
	C	-1.24528000	-1.39130000	0.00000000
	C	-0.06896900	-2.16127300	0.00000000
	C	1.19220000	-1.55250900	0.00000000
	C	1.31425100	-0.16331900	0.00000000
	H	-0.14760600	-3.24262100	0.00000000
	H	-2.20471100	-1.90970300	0.00000000
	H	2.07661400	-2.18330400	0.00000000
	H	2.30050500	0.28758100	0.00000000
	B	0.00000000	0.52504400	0.00000000
	N	-0.02360500	2.05260500	0.00000000
	N	-0.02284800	3.15768700	0.00000000
Pyridine	C	0.000000000	0.000000000	-1.382574000
	C	0.000000000	1.195982000	-0.671427000
	C	0.000000000	1.141205000	0.720804000
	N	0.000000000	0.000000000	1.416742000
	C	0.000000000	-1.141205000	0.720804000
	C	0.000000000	-1.195982000	-0.671427000
	H	0.000000000	0.000000000	-2.466467000
	H	0.000000000	2.152628000	-1.179470000
	H	0.000000000	2.056412000	1.305566000
	H	0.000000000	-2.056412000	1.305566000
	H	0.000000000	-2.152628000	-1.179470000
N$_2$	N	0.000000000	0.000000000	0.547783000
	N	0.000000000	0.000000000	-0.547783000
6	C	3.11923900	-1.36765900	0.00000000
	C	2.39487600	-2.56406000	0.00000000
	C	0.99508100	-2.63804200	0.00000000
	C	0.27536700	-1.41579300	0.00000000
	C	1.01419300	-0.21114200	0.00000000
	C	2.40023300	-0.17214100	0.00000000
	C	0.56896100	2.29284200	0.00000000
	C	0.12900300	0.97698600	0.00000000
	C	-1.24209700	0.62454500	0.00000000
	C	-2.18885900	1.67771500	0.00000000
	C	-1.71563700	2.99483300	0.00000000
	C	-0.35908500	3.33429200	0.00000000
	C	4.65173500	-1.41345700	0.00000000
	C	5.13981500	-2.15946800	1.26040500
	C	5.13981500	-2.15946800	-1.26040500
	C	5.27642000	-0.00944700	0.00000000
	C	0.05097000	4.81130000	0.00000000
	C	-0.51763700	5.49776500	1.26047400
	C	1.57693500	4.99244200	0.00000000
	C	-0.51763700	5.49776500	-1.26047400
	C	-3.70225300	1.42816700	0.00000000
	C	-4.08105800	0.67249700	1.29446300
	C	-4.54016000	2.72188300	0.00000000
	C	-4.08105800	0.67249700	-1.29446300
	C	0.33223600	-4.03001200	0.00000000
	C	-0.51763700	-4.20380300	-1.27724800
	C	1.35750000	-5.18197100	0.00000000
	C	-0.51763700	-4.20380300	1.27724800
	B	-1.23681200	-0.96067100	0.00000000
	H	2.95888100	-3.48290300	0.00000000
	H	2.91305200	0.77905600	0.00000000
	H	1.62909700	2.50201800	0.00000000

	H	-2.43390800	3.79971000	0.00000000
	H	6.23309100	-2.19646700	1.27798200
	H	4.79932100	-1.65168000	2.16649200
	H	4.76818500	-3.18550500	1.29130700
	H	6.23309100	-2.19646700	-1.27798200
	H	4.79932100	-1.65168000	-2.16649200
	H	4.76818500	-3.18550500	-1.29130700
	H	4.98830600	0.56145700	0.88649300
	H	6.36605200	-0.09396900	0.00000000
	H	4.98830600	0.56145700	-0.88649300
	H	-0.22976800	6.55304200	1.27821600
	H	-1.60774600	5.44626400	1.29116900
	H	-0.13327800	5.02230400	2.16652800
	H	1.81856900	6.05828100	0.00000000
	H	2.03707600	4.54835800	-0.88644900
	H	2.03707600	4.54835800	0.88644900
	H	-1.60774600	5.44626400	-1.29116900
	H	-0.22976800	6.55304200	-1.27821600
	H	-0.13327800	5.02230400	-2.16652800
	H	-5.11605800	0.32449800	1.25610600
	H	-3.43504800	-0.17834400	1.49611200
	H	-3.97890500	1.34817800	2.14766600
	H	-5.60050400	2.45583100	0.00000000
	H	-4.35447500	3.33140000	-0.88752900
	H	-4.35447500	3.33140000	0.88752900
	H	-3.43504800	-0.17834400	-1.49611200
	H	-5.11605800	0.32449800	-1.25610600
	H	-3.97890500	1.34817800	-2.14766600
	H	-1.00717000	-5.18254100	-1.27063200
	H	-1.28627600	-3.44137200	-1.36638100
	H	0.12197000	-4.15114200	-2.16270800
	H	0.81741500	-6.13199700	0.00000000
	H	1.99480200	-5.16767200	0.88774300
	H	1.99480200	-5.16767200	-0.88774300
	H	-1.28627600	-3.44137200	1.36638100
	H	-1.00717000	-5.18254100	1.27063200
	H	0.12197000	-4.15114200	2.16270800
	N	-3.48849200	-2.03180300	0.00000000
	N	-2.27917300	-1.94302200	0.00000000
	N	-4.59267600	-2.28743400	0.00000000
5	C	0.09322900	3.52708700	0.00000000
	C	-1.14361100	2.88898400	0.00000000
	C	-1.15925000	1.47151100	0.00000000
	C	0.07671000	0.73234200	0.00000000
	C	1.27831000	1.45659800	0.00000000
	C	1.31598600	2.84176100	0.00000000
	C	0.09659500	-0.75055800	0.00000000
	C	-1.12424100	-1.52116800	0.00000000
	C	-1.12161700	-2.92045400	0.00000000
	C	0.10222200	-3.57899300	0.00000000
	C	1.31765400	-2.87938700	0.00000000
	C	1.29042900	-1.48772500	0.00000000
	H	0.11157400	4.60410100	0.00000000
	H	2.21507600	0.91787200	0.00000000
	H	0.11433800	-4.65897800	0.00000000
	H	2.23234900	-0.95944800	0.00000000
	N	-2.36492000	0.75901000	0.00000000
	B	-2.20074300	-0.51501900	0.00000000
	C	-2.43190700	-3.72084100	0.00000000
	C	-2.48684000	-4.60780300	1.26162300
	H	-3.41562200	-5.18537900	1.28104400
	H	-1.65292200	-5.31170500	1.29173600
	H	-2.44299700	-3.99673400	2.16677600
	C	-3.66724100	-2.80840600	0.00000000
	H	-3.70849000	-2.17758300	0.89552300
	H	-3.70849000	-2.17758300	-0.89552300
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	C	-2.48684000	-4.60780300	-1.26162300

	H	-2.44299700	-3.99673400	-2.16677600
	H	-1.65292200	-5.31170500	-1.29173600
	H	-3.41562200	-5.18537900	-1.28104400
	C	2.67490500	-3.59906100	0.00000000
	C	3.46732000	-3.19198500	-1.26065300
	H	3.65115100	-2.11628700	-1.29346900
	H	4.43642300	-3.69909800	-1.27819500
	H	2.92074500	-3.46573200	-2.16678600
	C	3.46732000	-3.19198500	1.26065300
	H	4.43642300	-3.69909800	1.27819500
	H	3.65115100	-2.11628700	1.29346900
	H	2.92074500	-3.46573200	2.16678600
	C	2.52843400	-5.12895300	0.00000000
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	H	1.99855300	-5.48619300	-0.88683100
	H	3.51949000	-5.58930700	0.00000000
	C	2.67032300	3.56636300	0.00000000
	C	3.46732000	3.16488700	-1.25938500
	H	4.43636500	3.67312500	-1.27660300
	H	3.65242100	2.08896700	-1.29296800
	H	2.92021100	3.43772300	-2.16549300
	C	3.46732000	3.16488700	1.25938500
	H	4.43636500	3.67312500	1.27660300
	H	2.92021100	3.43772300	2.16549300
	H	3.65242100	2.08896700	1.29296800
	C	2.51609800	5.09559300	0.00000000
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	H	1.98244600	5.44896200	0.88604100
	H	3.50440500	5.56266400	0.00000000
	C	-2.44984900	3.70480600	0.00000000
	C	-3.27389300	3.38410400	1.26669700
	H	-4.19071900	3.98210100	1.27395800
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	H	-3.54565000	2.33136300	-1.30670300
	H	-4.19071900	3.98210100	-1.27395800
	H	-2.70169000	3.63063700	-2.16585100
	C	-2.18370800	5.22111500	0.00000000
	H	-1.63108100	5.54138900	0.88737600
	H	-1.63108100	5.54138900	-0.88737600
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5•N$_2$	C	3.60107600	0.18093400	0.00009000
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	C	1.48390800	-0.98832700	0.00004300
	C	0.79792200	0.27110000	0.00001800
	C	1.56942100	1.44499500	0.00003500
	C	2.95352400	1.42894600	0.00007100
	C	-0.67576800	0.32508700	-0.00002100
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	C	3.35336600	3.56564400	1.25998200
	H	3.60482600	3.00852100	2.16612200
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H	5.54257400	-1.59002800	0.88742300
H	5.69182500	-3.10667200	0.00017500

VI. References

[1] S. Biswas, I. M. Oppel, H. F. Bettinger, Synthesis and structural characterization of 9-azido-9-borafluorene: monomer and cyclotrimer of a borole azide, *Inorg. Chem.* **2010**, *49*, 4499.
[2] M. M. Gragert, A. K. Tomov, S. Bettonville, G. Pannier, A. J. P. White, G. J. P. Britovsek, Biaryl Group 4 Metal Complexes as Non-Metallocene Catalysts for Polyethylene with Long Chain Branching, *Eur. J. Inorg. Chem.* **2020**, *2020*, 4088.
[3] I. R. Dunkin, *Matrix-isolation techniques: a practical approach*, Oxford University Press, **1998**.
[4] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* **1993**, *98*, 5648.
[5] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **1988**, *37*, 785.
[6] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *J. Phys. Chem.* **1994**, *98*, 11623.
[7] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[8] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* **2011**, *32*, 1456.
[9] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **1993**, *98*, 5648.
[10] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* . **1988**, *37*, 785.
[11] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* **1980**, *72*, 650.
[12] D. G. Liakos, Y. Guo, F. Neese, Comprehensive Benchmark Results for the Domain Based Local Pair Natural Orbital Coupled Cluster Method (DLPNO-CCSD(T)) for Closed- and Open-Shell Systems, *J. Phys. Chem. A* **2020**, *124*, 90.
[13] C. Riplinger, F. Neese, An efficient and near linear scaling pair natural orbital based local coupled cluster method, *J. Chem. Phys.* **2013**, *138*, 034106.
[14] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals, *J. Chem. Phys.* **2013**, *139*, 134101.
[15] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, Sparse maps—A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory, *J. Chem. Phys.* **2016**, *144*, 024109.
[16] F. Neese, The ORCA program system, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73.

[17] F. Neese, Software update: the ORCA program system, version 4.0, *WIREs Computational Molecular Science* **2018**, *8*, e1327.
[18] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **1989**, *90*, 1007.
[19] F. Weigend, A. Köhn, C. Hättig, Efficient use of the correlation consistent basis sets in resolution of the identiy MP2 calculations, *J. Chem. Phys.* **2002**, *116*, 3175.
[20] V. Lemierre, A. Chrostowska, A. Dargelos, H. Chermette, Calculation of Ionization Potentials of Small Molecules: A Comparative Study of Different Methods, *J. Phys. Chem. A* **2005**, *109*, 8348.
[21] A. Mazière, A. Chrostowska, C. Darrigan, A. Dargelos, A. Graciaa, H. Chermette, Electronic structure of BN-aromatics: Choice of reliable computational tools, *J. Chem. Phys.* **2017**, *147*, 164306.
[22] R. E. Stratmann, G. E. Scuseria, M. J. Frisch, An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules, *J. Chem. Phys.* **1998**, *109*, 8218.

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Strain induced reactivity of cyclic iminoboranes: the (2 + 2) cycloaddition of a 1*H*-1,3,2-diazaborepine with ethene†

Divanshu Gupta, Ralf Einholz and Holger F. Bettinger *

Iminoboranes have gathered immense attention due to their reactivity and potential applications as isoelectronic and isosteric alkynes. While cyclic alkynes are well investigated and useful reagents, cyclic iminoboranes are underexplored and their existence was inferred only *via* trapping experiments. We report the first direct spectroscopic evidence of a cyclic seven-membered iminoborane, 1-(*tert*-butyldimethylsilyl)-1*H*-1,3,2-diazaborepine **2**, under cryogenic matrix isolation conditions. The amino-iminoborane **2** was photochemically generated in solid argon at 4 K from 2-azido-1-(*tert*-butyldimethylsilyl)-1,2-dihydro-1,2-azaborinine (**3**) and was characterized using FT-IR, UV-vis spectroscopy, and computational chemistry. The characteristic BN stretching vibration (1751 cm^{-1}) is shifted by about 240 cm^{-1} compared to linear amino-iminoboranes indicating a significant weakening of the bond. The Lewis acidity value determined computationally ($LA_B = 9.1 \pm 2.6$) is similar to that of boron trichloride, and twelve orders of magnitude lower than that of 1,2-azaborinine (BN-aryne, $LA_B = 21.5 \pm 2.6$), a six-membered cyclic iminoborane. In contrast to the latter, the reduced ring strain of **2** precludes nitrogen fixation, but it unexpectedly allows facile (2 + 2) cycloaddition reaction with C_2H_4 under matrix isolation conditions at 30 K.

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Introduction

Iminoboranes are an important class of BN containing compounds.[1–3] The BN/CC isosterism relates iminoboranes and alkynes (Scheme 1a).[4] In contrast to the latter, iminoboranes are kinetically unstable towards cyclooligomerization or polymerization and thus special conditions or steric protection are required for their synthesis and isolation.[1,2,5–12] The first iminoborane stable at room temperature, F_5C_6-BN-*t*Bu, was reported by Paetzold *et al.*,[11] and followed by numerous examples.[2,9,13–15] Since then, iminoboranes have attracted tremendous attention.[16–23] Various iminoboranes have been investigated over the past decades to understand their reactivity[24–27] including the formation of BN-doped polycyclic aromatic hydrocarbons (PAHs),[28–32] formation of N-heterocyclic carbene coordinated iminoboranes,[25,33–36] synthesis of BN containing heterocycles,[37–44] (2 + 2) and (2 + 3) cycloaddition reactions with a number of polar double bonds (*e.g.*, RR′C=O) and dipolar reagents,[45–50] formation of iminoboryl carboranes,[19,51] and use of frustrated Lewis pairs to stabilize iminoboranes.[19,52–57] A series of *ab initio* computational studies performed by Gilbert compared iminoboranes and alkynes with respect to the electronic and geometric structure, as well as the reactivity in (2 + 2) and (2 + 4) cycloadditions towards alkenes and alkynes.[58–60]

Studies on cyclic iminoboranes are quite rare.[42,61] Due to ring strain, they are more reactive than linear iminoboranes,[1] but coordination by N-heterocyclic carbenes (NHC) provides a way of stabilization.[36,62,63] A special case of cyclic iminoboranes is the aromatic BN-aryne, 1,2-azaborinine **1**, the BN analogue of *ortho*-benzyne (Scheme 1b).[64–66] This was detected by matrix isolation methods by our group and shows remarkably high reactivity towards inert molecules.[64–66] The polarity of the strained BN link of **1** results in a bonding situation that differs from that of the strained triple bond in arynes and from that of the BN unit in linear iminoboranes.[64,66,67] The dibenzo derivative of **1**, dibenzo [*c*,*e*][1,2]azaborinine, was inferred as reactive intermediate in solution,[68–70] and can even activate the strong Si–F bond for subsequent insertion reaction.[70]

As iminoborane units in larger than six-membered rings have never been observed directly, but only inferred from trapping experiments (Scheme 1c),[42,61] we studied the seven membered 1-(*tert*-butyldimethylsilyl)-1*H*-1,3,2-diazaborepine **2** to elucidate the impact of ring size on the reactivity of cyclic iminoboranes. The matrix isolation technique is ideally suited to study such highly reactive intermediates directly, and furthermore probe their reactivity towards interesting compounds. We generated target compound **2** in solid argon by the photolysis of 2-azido-1-(*tert*-butyldimethylsilyl)-1,2-dihydro-1,2-azaborinine (**3**) under cryogenic matrix conditions (see Scheme 2). On one hand, ring strain

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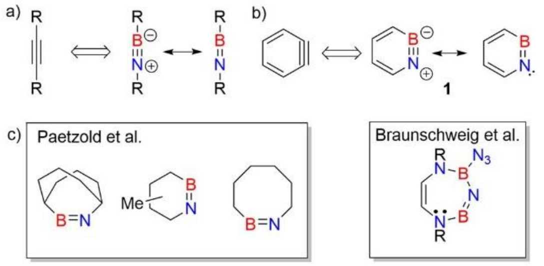


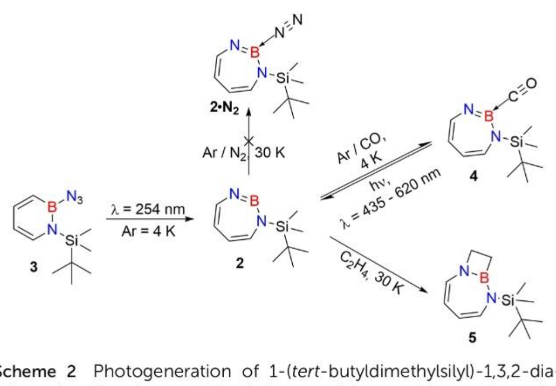
Scheme 1 (a) Iminoboranes and their analogy with alkynes. (b) Resonance forms of 1,2-azaborinine (**1**) and its analogy with *ortho*-benzyne. (c) Representative examples of cyclic iminoboranes previously inferred as reactive intermediates by Paetzold *et al.*[61] and Braunschweig *et al.*[42]

will be reduced in this seven-membered ring iminoborane compared to **1** and this is expected to reduce its reactivity, while on the other hand, the eight π-electron count may induce some degree of antiaromaticity that will potentially destabilize **2**. Seven-membered cyclic iminoboranes were never directly observed, but recently inferred as reactive intermediate in the formation of diazadiboretidines by Braunschweig and co-workers.[42] We provide here for the first time direct spectroscopic evidence for a cyclic seven-ring iminoborane and reveal its unexpectedly facile (2 + 2) cycloaddition reaction (Scheme 2).

Results and discussion

Generation and characterization of cyclic iminoborane 2

Matrix-isolation infrared spectroscopic studies of **3** were performed in solid Ar at 4 K. The most distinguished peak at 2141 cm^{-1} corresponds to the azide stretching vibration (Fig. 1, S9, S10 and Table S13 in ESI†). Irradiation of matrix isolated precursor **3** with $\lambda = 254$ nm until it was completely bleached, as shown in the difference spectrum (Fig. 1d), resulted in a new set of IR bands. This set is assigned to **2** based on comparison with computational data obtained at



Scheme 2 Photogeneration of 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **2** under matrix isolation conditions and its reaction with CO and C_2H_4.

the B3LYP-D3(BJ)/6-311+G(d,p) level of theory (Fig. 1e). The formation of the structural isomer 1*H*-1,2,3-diazaborepine or the triplet boryl nitrene, the expected primary product of N_2 extrusion from **3**, can be excluded based on the computations (see Fig. S15†). Among the new bands formed during photolysis of **3**, the most intense peak, 1751 cm^{-1} corresponds to the BN stretching vibration of **2** (Table S15†) by comparison with the computations (Fig. 1e). The band at 1809 cm^{-1} corresponds to the BN stretching vibration of the ^{10}B isotopologue, and the isotopic shift of 58 cm^{-1} is in good agreement with computations (60 cm^{-1}). The formation of the 1*H*-1,3,2-diazaborepine isomer is in agreement with the known behavior of azidoboranes: thermolysis or photolysis of diorganyl azidoboranes results in iminoboranes without trappable borylnitrenes,[1] while only in the case of donor substitution (X = NR_2, OR) the borylnitrenes X_2BN could be trapped or directly observed.[71–77] The photolysis of azide **3** is thus expected to result in ring enlargement by shift of the carbon rather than the nitrogen center to give the cyclic iminoborane **2**.

For linear amino-iminoboranes, the BN stretching mode was reported around 1990 cm^{-1} and 2030 cm^{-1} for the ^{11}B and ^{10}B isotopologues, respectively.[78,79] The large shift of the BN stretching frequency of **2** from linear diorganyl substituted amino-iminoboranes of around 240 cm^{-1} is due to the cyclic nature of **2** which results in considerable weakening of the BN bond. Note that the BN stretching for **1** at 1637/1634 cm^{-1} indicates an even weaker BN bond in the six-membered ring.[64]

UV/vis spectroscopy (Fig. 2) of the azide **3** in Ar at 8 K shows a strong feature around 290 nm with fine structure and maxima at 296 nm, 288 nm, and 244 nm that is typical for 1,2-dihydro-1,2-azaborinines.[80,81] Irradiation with $\lambda = 254$ nm results in quick decrease of the azide absorption band with an isosbestic point at 313 nm. The photoproduct **2** only has a relatively weaker and broad absorption maximum centered at 305 nm. The measured spectra of **3** and **2** are in good agreement with TD-CAM-B3LYP/6-311+G(d,p) computations (Fig. S8†).

The most remarkable feature of the computed geometry (M06-2X/6-311+G(d,p)) of **2** is the distortion of the heptagon with a small angle of 104.9° at dicoordinated nitrogen and a large angle of 161.4° at boron in the singlet ground state (Fig. 3a). Similarly to the case of 1,2-azaborinine,[64] this feature can be rationalized by the difference in electronegativity: the more electronegative N atom prefers to have a σ-type lone pair (HOMO-1), while the more electropositive B atom prefers an empty σ-type orbital (LUMO) which has a strong p character (Fig. 3b). The natural bond orbital (NBO) analysis at the M06-2X/6-311+G(d,p) level of theory arrives at occupancies of 1.82e^- and 0.34e^- for the lone pair and empty orbitals, respectively. There is a pronounced n(N) → n*(B) interaction [$E(2) = 34.5$ kcal mol^{-1}] according to the second-order perturbation estimate of the donor–acceptor interaction in the NBO basis that is smaller than that in **1** (39.7 kcal mol^{-1}). The natural charges obtained from the NBO analysis on N and B are large (−0.91 on N and +1.16 on B) while the Wiberg bond index between B and N is only 1.55. Compared to 1,2-azaborinine **1** the Wiberg bond index is larger (1.43 in **1**) and the polarity of the BN bond

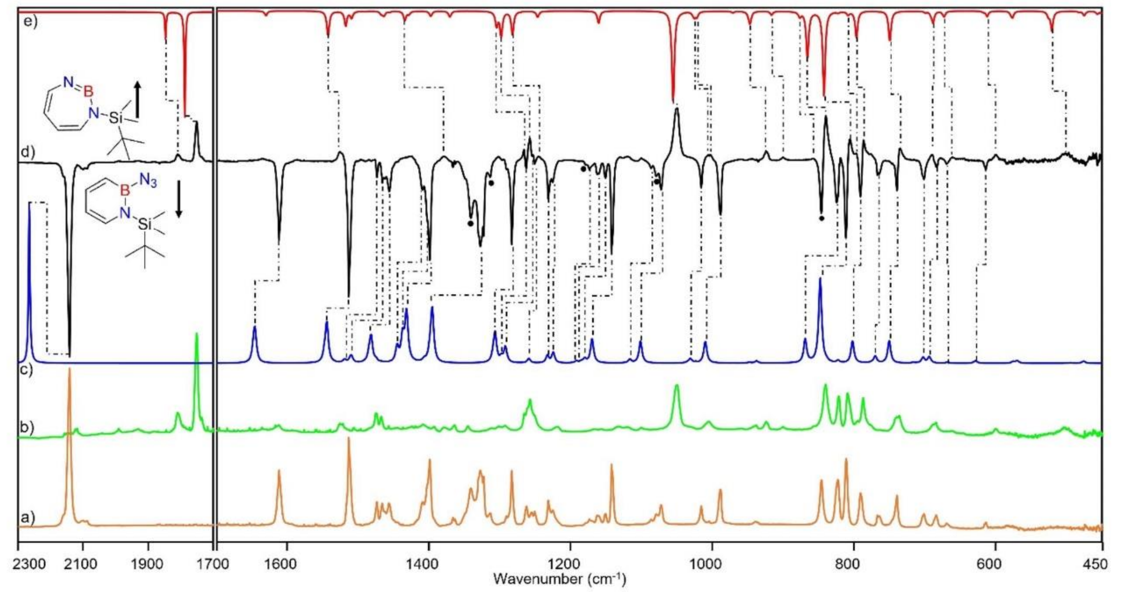


Fig. 1 (a) IR spectrum obtained after deposition of **3** in Ar matrix at 28 K. (b) IR spectrum obtained after irradiation of Ar matrix with $\lambda = 254$ nm (following the deposition of **3**). (c) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of **3** calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory. (d) Difference spectrum obtained after irradiation of Ar matrix with $\lambda = 254$ nm (following the deposition of **3**). (e) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of **2** calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory (● corresponds to the overtones and combination bands according to computed anharmonic vibrational frequency analysis).

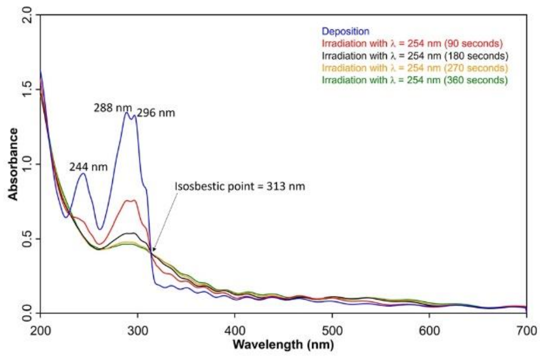


Fig. 2 UV-vis spectra of **3** (blue: after deposition at 28 K, $\lambda_{max} = 288$ nm) and subsequent formation **2** ($\lambda_{max} = 308$ nm) after various irradiation ($\lambda = 254$ nm) steps under matrix isolation conditions.

(natural charges in **1**: −0.81 on N and +1.00 on B; NBO occupancies of 1.82e$^-$ and 0.21e$^-$ for the lone pair and empty orbitals) is slightly increased in **2**.

We compared the aromatic character of **2** with that of **1**, benzene, and benzyne using nuclear independent chemical shift (NICS) calculations,[82–84] placing the dummy atom 1 Å above the center of the ring to get the NICS$(1)_{zz}$ value. 1,2-Azaborinine **1** has a NICS$(1)_{zz}$ value of −25.2 which is lower than that of benzene (−29.3) and benzyne (−33.5), but still suggests aromatic character that is slightly larger than that of 1,2-dihydro-1,2-azaborine (NICS$(1)_{zz}$ = −21.1) (Scheme 3).[85] The NICS$(1)_{zz}$ value of −1.1 and −3.1 computed for **2** is significantly lower suggesting that the antiaromaticity expected on the basis of the formal electron count is not relevant (see Fig. S17†). The two slightly differing values for **2** are due to the non-planar ring. The NICS$(1)_{zz}$ value of antiaromatic D_{2h} cyclobutadiene is +10.9 computed at the same level of theory.

We compared the strain of the two cyclic iminoboranes **1** and **2** by considering homodesmotic reactions (Scheme 3). As expected, the strain energy of the seven-membered ring iminoborane **2** is lower than that of **1** by approximately 6.3 kcal mol^{-1} at the M06-2X/6-311+G(d,p) level of theory. We also computed the Lewis acidities (LA_B) of **1** and **2** using the method of Ofial *et al.* from known Lewis basicities LB_B and Lewis acidities LA_B, computed equilibrium constants (Scheme 4, $\Delta G^\circ_{iso} = -RT \ln K_B$), and the equation $\log K_B = LA_B + LB_B$.[86] Ofial

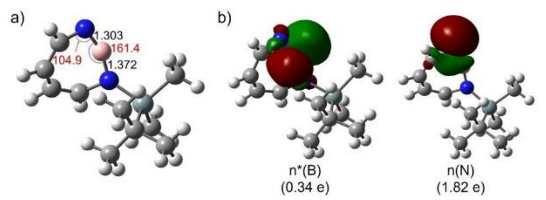
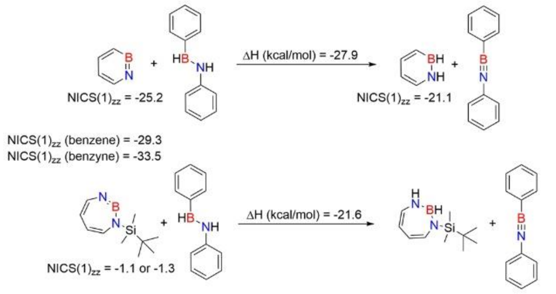
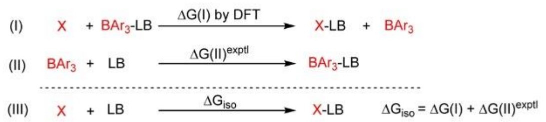


Fig. 3 (a) Geometrical parameters of **2**. (b) Natural bond orbitals (NBOs) and their occupation numbers of **2**. Important bond lengths [Å] and bond angles [°] are given. All computations at the M06-2X/6-311+G(d,p) level of theory.



Scheme 3 NICS(1)$_{zz}$ values and homodesmotic reactions for the calculation of strain energy.



Scheme 4 Combining the isodesmic reaction [eqn (I)] with an experimental reference reaction [eqn (II)] allows one to determine the Lewis acidities of X (X= **1** or **2**) from ΔG_{iso} [eqn (III)]. The Lewis bases pyridine, acetonitrile, and benzaldehyde and the Lewis acids BAr_3 (Ar = C_6H_5, 4-ClC_6H_4, 3,4,5-$F_3C_6H_2$) were chosen as references. The borane Lewis acidity scale is defined so that LA_B(triphenylborane) = 0 following Ofial *et al.*[86]

et al.[86] obtained the LA_B parameters from ΔG_{iso} to give $LA_B = 8.4 \pm 2.0$ for BF_3, $LA_B = 9.3 \pm 1.8$ for BCl_3, and $LA_B = 10.1 \pm 1.3$ for BBr_3. The qualitative ordering obtained by Ofial *et al.*[86] of Lewis acidities LA_B with $BF_3 < BCl_3 < BBr_3$ is in accordance with Lewis acidity rankings based on spectroscopic data.[87–89] The individual LA_B parameters obtained from ΔG_{iso} for three different reference bases were averaged to give $LA_B = 21.5 \pm 2.6$ for **1** and $LA_B = 9.1 \pm 2.6$ for **2** (see the ESI† for further details). While the Lewis acidity of **2** is thus similar to that of BCl_3, that of **1** is 12 orders of magnitudes larger.

Interaction of 2 with N_2

A hallmark of the superelectrophilic 1,2-azaborinine **1** is its ability to bind nitrogen to give adduct **1**·N_2 under cryogenic conditions.[64] In order to study the Lewis acidity of the photogenerated 1*H*-1,3,2-diazaborepine **2** experimentally, the matrix was annealed up to 35 K. This did not lead to any further spectral changes, indicating that **2** cannot bind the photochemically extruded N_2 that is lying in its vicinity. The potential energy paths computed with the B–N_2 distance as parameter (B3LYP-D3(BJ)/6-311+G(d,p)) reveal that formation of the dative complex **2**·N_2 is energetically unfavorable and involves a barrier (Fig. 4a). In contrast, formation of **1**·N_2 is without barrier and exothermic (Fig. 4b).

Interaction of 2 with CO

The stronger Lewis base CO can undergo formation of adduct **4** as revealed in experiments using mixtures of Ar and CO (1–2% in Ar) (Scheme 2 and Fig. 5). In separate experiments, the isotopologues ^{13}CO and $C^{18}O$ (Fig. S11–S13†) were employed in order to obtain isotopic shifts of vibrational bands for comparison with computations.

Irradiation of matrix-isolated precursor **3** with $\lambda = 254$ nm forms **2** in the presence of CO. Annealing the matrix to 30 K allows the formation of distinct bands which decrease upon subsequent irradiation with 435 nm > λ > 620 nm, while the bands corresponding to **2** collectively form again (see Fig. 5). We assign the bands formed after annealing of the matrix to 30 K to the Lewis acid–base adduct **4** based on comparison with the vibrational spectrum computed at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory (see Fig. 6). The formation of the (2 + 1) product **4_(2 + 1)** can be excluded based on the computations (see Fig. S16†).

The most intense peak at 2112 cm^{-1} is due to the CO stretching vibration of the Lewis acid–base adduct **4** (Table S16†). It is observable at 2065 cm^{-1} and 2064 cm^{-1} for the $C^{18}O$ and ^{13}CO isotopologues, respectively (Tables S17 and S18†). These isotopic shifts of 47 cm^{-1} ($^{12}C^{18}O$ *vs.* $^{12}C^{16}O$) and 48 cm^{-1} ($^{13}C^{16}O$ *vs.*

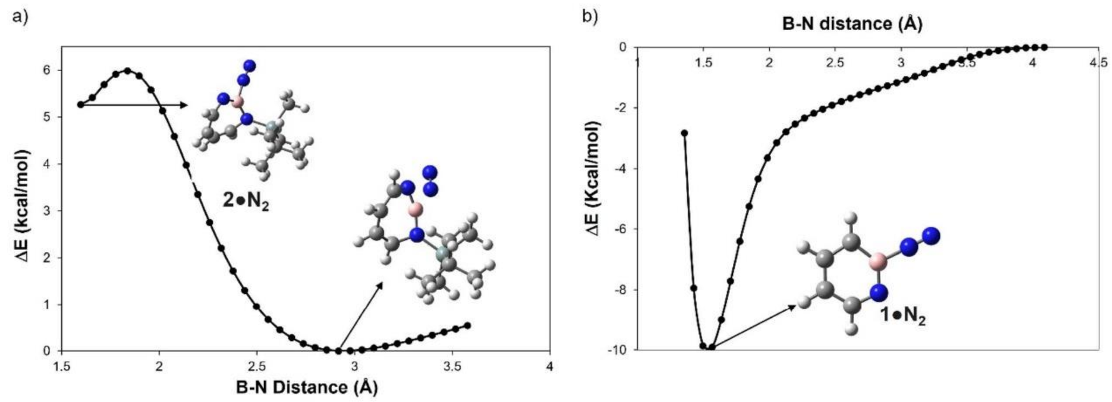


Fig. 4 Plot for the relative energy in kcal mol^{-1} as a function of the boron N_2 distance in Å for (a) **2** and (b) **1** computed at B3LYP-D3(BJ)/6-311+G(d,p) level of theory.

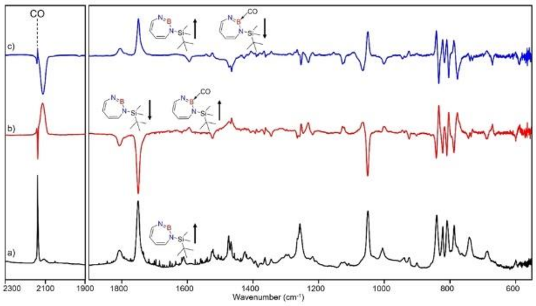


Fig. 5 Infrared spectra obtained after irradiation of **3** in CO (2–3%) doped argon matrix. (a) After 60 min irradiation with $\lambda = 254$ nm at $T = 4$ K. (b) Difference spectrum after annealing for 30 min at 30 K (following the irradiation with $\lambda = 254$ nm). (c) Difference spectrum after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing at 30 K).

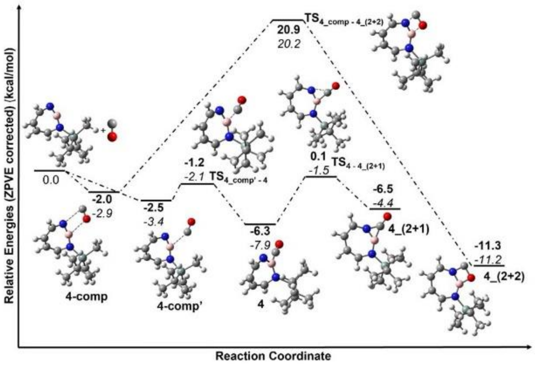


Fig. 7 Reaction pathways for the reaction of **2** with CO at (bold: M06-2X/6-311+G(d,p); italics: DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p)). Calculated ZPVE corrected energies in kcal mol^{-1} are shown.

$^{12}C^{16}O$) are in very good agreement with those computed for **4** (47 cm^{-1} and 50 cm^{-1}, respectively, see Table S19†).

The trapping of **2** with CO demonstrates that Lewis acid–base interaction is significantly preferred over (2 + 1) or (2 + 2) cycloaddition reactions, similar to the reaction of 1,2-azaborinine with CO.[66] The formation of **4** has a barrier of 1.3 kcal mol^{-1} from the complex **4_comp′** at the DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) level of theory (Fig. 7). The formation of the (2 + 1) product **4_(2 + 1)** from **4** is energetically uphill and cannot proceed thermally as its barrier of 6.4 kcal mol^{-1} (Fig. 7) is too high for this reaction to be observable at 30 K under matrix isolation conditions. The formation of the (2 + 2) cycloaddition product *via* complex **4_comp**, the most stable product (−11.2 kcal mol^{-1} with respect to **2** + CO), is more favourable than **4** or **4_(2+1)** by 3.3 kcal mol^{-1} and 6.8 kcal mol^{-1}, respectively. But as it involves a barrier of 23.1 kcal mol^{-1} at the DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) level of theory, the reaction to **4_(2+2)** cannot proceed under our experimental conditions. The trapping of **2** with CO demonstrates that Lewis acid–

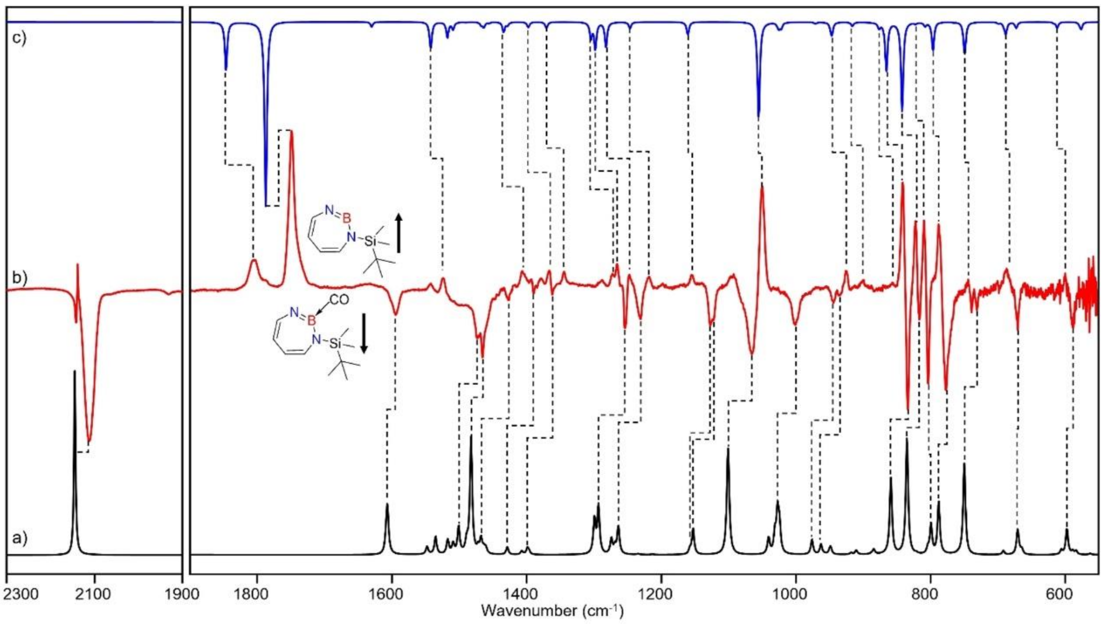


Fig. 6 (a) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of **4** calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory. (b) Difference IR spectrum after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing step). (c) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of **2** calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory.

base interaction is significantly preferred over (2 + 1) or (2 + 2) cycloaddition reactions.

Reaction of 2 with ethene

After the successful generation of 2 and its trapping with CO, we used ethene as the simplest olefin for studying of the reactivity of 2 in (2 + 2) cycloaddition reactions. To examine the trapping of 2 with ethene, matrix-isolated precursor 3 was irradiated in the presence of 5% C_2H_4 in Ar with $\lambda = 254$ nm, which again resulted in 1*H*-1,3,2-diazaborepine 2. But apart from 2, new signals were also observed (Fig. 8) that we assigned with the help of the computed spectrum to 5, the (2 + 2) cycloaddition product between 2 and C_2H_4 (Scheme 2 and Fig. 9). Subsequently, the matrix was annealed to 30 K and it was observed that the set of signals corresponding to 2 were diminished (Fig. 8c), while the set of signals assigned to 5 increased in intensity (Fig. 8c). This shows that the formation of 5 from 2 and ethene can proceed thermally with a very low activation barrier.

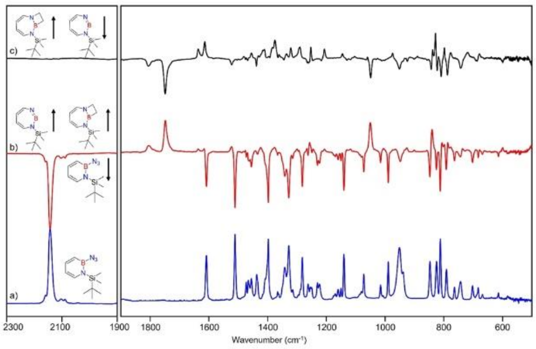


Fig. 8 Infrared spectra obtained after (a) deposition of 3 in C_2H_4 (5%) doped argon matrix. (b) Difference spectrum after 60 min irradiation with $\lambda = 254$ nm at $T = 4$ K. (c) Difference spectrum after annealing for 30 min at 30 K (following the irradiation with $\lambda = 254$ nm).

The prominent and characteristic signals of 5, 1637 cm^{-1} and 1615 cm^{-1}, are attributed to the C=C stretching vibration of the diazaborepine ring (Tables S20 and S21†). The same C=C stretching vibrations at 1637 cm^{-1} and 1615 cm^{-1} were also observed for the C_2D_4 isotope as the stretching mode does not involve any vibration of the ethene unit (Fig. S14†). The other most intense peaks were observed at 828 cm^{-1} and 1376 cm^{-1}, which we assigned to a vibration including ring stretching and CH wagging of C_2H_4 and BN stretching and CH wagging, respectively. In case of C_2D_4, the most intense peak was observed at 1372 cm^{-1} attributed to BN stretching and CH wagging while a peak at 813 cm^{-1} corresponding to CH wagging of C_2D_4 was not so intense in case of reaction with C_2D_4. The experimentally observed isotopic shifts are in good agreement

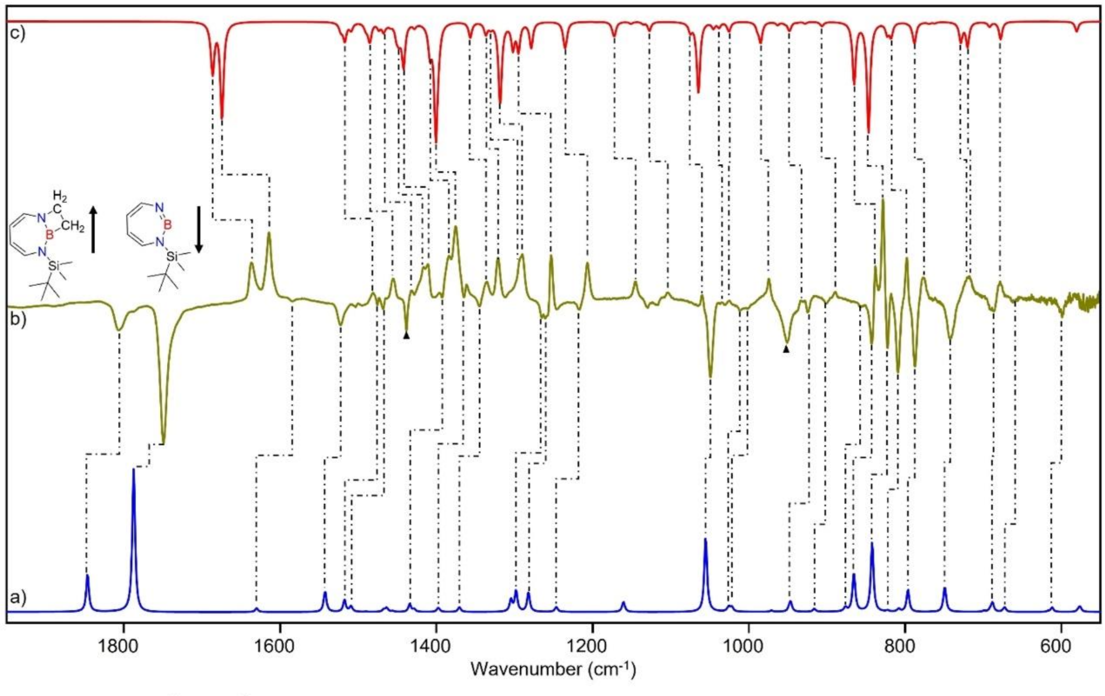


Fig. 9 (a) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of 2 calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory. (b) Difference IR spectrum after annealing to 30 K for 60 min (following the irradiation step). (c) Spectrum for ^{11}B and ^{10}B isotopologues (81 : 19) of 5 calculated at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory. (▲ corresponds to the peaks of C_2H_4)

with the isotopic shift computed at the B3LYP-D3(BJ)/6-311+G(d,p) level of theory (see Table S22 in ESI†).

According to computations at the DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) level of theory, **2** can interact with ethene to give two complexes, **5_comp′** and **5_comp**, that are lower in energy than the separated reactants by 4.6 and 6.7 kcal mol^{-1}, respectively (see Fig. 10). The interconversion between complexes **5_comp′** and **5_comp** is associated with a barrier of 1.2 kcal mol^{-1}. The formation of the (2 + 2) cycloaddition product **5** from complex **5_comp** can proceed thermally as its barrier of 1.0 kcal mol^{-1} (Fig. 10) is small enough for this reaction to be observable at 30 K under matrix isolation conditions. Formation of the C–H insertion product **6** *via* a concerted pathway from complex **5_comp′** involves a barrier of 23.0 kcal mol^{-1}. This is significantly higher than the barrier of (2 + 2) addition product formation (Fig. 10) and explains the preferred formation of **5** in the experiment.

Complex **5_comp** has carbon-boron distances (1.771 Å and 1.887 Å) that are shorter than the sum of van-der-Waals radii (3.62 Å) (see Fig. 10) indicative of a Lewis acid–base interaction.[90,91] The H–C–H and H–C–C angles have changed so that the sum of bond angles around carbon is 357.1 and 359.6°, showing a slight deviation from planarity around carbon atoms in C_2H_4. The complex **5_comp** is formed due to the interaction between the empty boron orbital with high p-character and the C═C π-bond. Further insight into the nature of bonding in **5_comp** is provided by natural bond orbital analysis.[92–95] The second-order perturbation theory analysis in the NBO basis gives an $E(2)$ value of 314.8 kcal mol^{-1}, implying strong stabilization due to $\pi(C_2H_4) \rightarrow n^*(B)$(empty orbital on boron) delocalization. The corresponding natural localized molecular orbitals (NLMO) have major contributions from the π(C═C) bond orbitals and "delocalization tails" of 20.6% from a slightly hybridized vacant orbital at boron (Tables S11 and S12†).

The comparison of the reaction mechanism for the reaction of ethene with 1,2-azaborinine **1** and 1-(*tert*-butyldimethylsilyl)-1,3,2-diazaborepine **2** is instructive. The former interacts with ethene to give a Lewis acid–base complex whose formation is thermodynamically highly exothermic (−23.7 kcal mol^{-1} at CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p)).[67] This complex is so low in energy that the formation of the (2 + 2) cycloaddition product has a barrier of 14.6 kcal mol^{-1} at CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p).[67] This is significantly higher than the barrier for the (2 + 2) cycloaddition product **5** (1.0 kcal mol^{-1} from **5_comp**).[67] It is highly interesting and unexpected that the much less Lewis acidic **2** is undergoing unprecedented (2 + 2) cycloaddition with ethene while the highly Lewis acidic **1** is expected to be trapped in the Lewis acid–base complex with ethene as this reaction should not be observable at 30 K under matrix isolation conditions. Preliminary experiments of **1** + C_2H_4 indicate that thermally initiated (2 + 2) cycloaddition is not occurring under similar matrix isolation conditions.

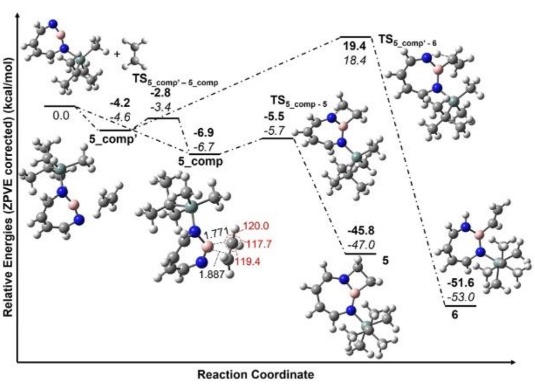


Fig. 10 Pathways for the reaction of **2** with C_2H_4 at M06-2X/6-311+G(d,p) (bold) and DLPNO-CCSD(T)/cc-pVTZ//M06-2X/6-311+G(d,p) (italics). Calculated ZPVE corrected energies in kcal mol^{-1} are shown. Geometrical parameters of complex **5_comp** computed at the M06-2X/6-311+G(d,p) level of theory. Important bond lengths [Å] and bond angles [°] are given.

Conclusions

We here for the first time reveal the generation, spectroscopic detection by matrix isolation, and reactivity studies of a seven-membered cyclic iminoborane of the 1*H*-1,3,2-diazaborepine type. The precursor 2-azido-1-(*tert*-butyldimethylsilyl)-1,2-dihydro-1,2-azaborinine (**3**) undergoes a photoinduced N_2 extrusion and rearrangement to the 1-(*tert*-butyldimethylsilyl)-1*H*-1,3,2-diazaborepine **2** without detectable intermediates. Detailed combined experimental and computational investigations reveal that **2** shows high reactivity towards carbon monoxide and ethene even at the very low temperature. With CO, **2** reacts to form Lewis acid–base adduct **4** while the alternative (2 + 1) or (2 + 2) cycloaddition reactions were not observed due to high energy barriers. With C_2H_4, **2** undergoes (2 + 2) cycloaddition reaction to from product **5**. The (2 + 2) cycloaddition with ethene discovered here shows that the **2** has the potential to provide novel modes of reactivity for the construction of BN-containing heterocycles.

Data availability

The data underlying this study are available in the published article and its ESI.†

Author contributions

D. G. investigation and writing of original draft, R. E. investigation and review & editing of the manuscript, H. F. B. conceptualization, supervision, providing resources, acquiring funding, and review & editing of manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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Eberle foundation. The computations were performed on BwForCluster JUSTUS2 cluster. The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no. INST 40/575-1 FUGG (JUSTUS 2 cluster) for computation facilities.

References

1 P. Paetzold, in *Advances in Inorganic Chemistry*, Elsevier, 1987, vol. 31, pp. 123–170.
2 H. Nöth, *Angew Chem. Int. Ed. Engl.*, 1988, **27**, 1603–1623.
3 Y. Fan, J. Cui and L. Kong, *Eur. J. Org Chem.*, 2022, **2022**, e202201086.
4 Z. Liu and T. B. Marder, *Angew. Chem., Int. Ed.*, 2008, **47**, 242–244.
5 E. R. Lory and R. F. Porter, *J. Am. Chem. Soc.*, 1973, **95**, 1766–1770.
6 C. A. Thompson and L. Andrews, *J. Am. Chem. Soc.*, 1995, **117**, 10125–10126.
7 F. Zhang, P. Maksyutenko, R. I. Kaiser, A. M. Mebel, A. Gregušová, S. A. Perera and R. J. Bartlett, *J. Phys. Chem. A*, 2010, **114**, 12148–12154.
8 N. C. Baird and R. K. Datta, *Inorg. Chem.*, 1972, **11**, 17–19.
9 P. Paetzold, C. V. Plotho, G. Schmid, R. Boese, B. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter and W. Schüfer, *Chem. Ber.*, 1984, **117**, 1089–1102.
10 V. M. Rosas-Garcia, *J. Theor. Comput. Chem.*, 2011, **967**, 160–164.
11 P. Paetzold, A. Richter, T. Thijssen and S. Würtenberg, *Chem. Ber.*, 1979, **112**, 3811–3827.
12 P. Paetzold and C. von Plotho, *Chem. Ber.*, 1982, **115**, 2819–2825.
13 P. Paetzold, *Pure Appl. Chem.*, 1991, **63**, 345–350.
14 E. v. Steuber, G. Elter, M. Noltemeyer, H.-G. Schmidt and A. Meller, *Organometallics*, 2000, **19**, 5083–5091.
15 M. Haase and U. Klingebiel, *Angew Chem. Int. Ed. Engl.*, 1985, **24**, 324.
16 R. Guo, T. Li, R. Wei, X. Zhang, Q. Li, L. L. Liu, C.-H. Tung and L. Kong, *J. Am. Chem. Soc.*, 2021, **143**, 13483–13488.
17 R. Guo, X. Zhang, T. Li, Q. Li, D. A. Ruiz, L. L. Liu, C.-H. Tung and L. Kong, *Chem. Sci.*, 2022, **13**, 2303–2309.
18 D. Schleier, D. Schaffner, M. Gerlach, P. Hemberger and I. Fischer, *Phys. Chem. Chem. Phys.*, 2022, **24**, 20–24.
19 J. Wang, P. Jia, W. Sun, Y. Wei, Z. Lin and Q. Ye, *Inorg. Chem.*, 2022, **61**, 8879–8886.
20 B. Wrackmeyer, *Z. Anorg. Allg. Chem.*, 2015, **641**, 2525–2529.
21 M. Bao, Y. Dai, C. Liu and Y. Su, *Inorg. Chem.*, 2022, **61**, 11137–11142.
22 D. Raiser, H. Schubert, H. F. Bettinger and L. Wesemann, *Chem. – Eur. J.*, 2021, **27**, 1981–1983.
23 L. Winner, W. C. Ewing, K. Geetharani, T. Dellermann, B. Jouppi, T. Kupfer, M. Schaefer and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2018, **57**, 12275–12279.
24 H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, B. Pfaffinger, K. Radacki and J. Wolf, *Angew. Chem., Int. Ed.*, 2012, **51**, 10034.
25 H. Braunschweig, W. C. Ewing, K. Geetharani and M. Schaefer, *Angew. Chem., Int. Ed.*, 2015, **54**, 1662–1665.
26 M. Schaefer, N. A. Beattie, K. Geetharani, J. Schaefer, W. C. Ewing, M. Krahfuss, C. Hoerl, R. D. Dewhurst, S. A. Macgregor, C. Lambert and H. Braunschweig, *J. Am. Chem. Soc.*, 2016, **138**, 8212–8220.
27 M. Schaefer, J. Schaefer, R. D. Dewhurst, W. C. Ewing, M. Krahfuss, M. W. Kuntze-Fechner, M. Wehner, C. Lambert and H. Braunschweig, *Chem. – Eur. J.*, 2016, **22**, 8603–8609.
28 O. Ayhan, T. Eckert, F. A. Plamper and H. Helten, *Angew. Chem., Int. Ed.*, 2016, **55**, 13321–13325.
29 T. Lorenz, M. Crumbach, T. Eckert, A. Lik and H. Helten, *Angew. Chem., Int. Ed.*, 2017, **56**, 2780–2784.
30 O. Ayhan, N. A. Riensch, C. Glasmacher and H. Helten, *Chem. – Eur. J.*, 2018, **24**, 5883–5894.
31 T. Beweries and H. Helten, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley Online Library, 2020, pp. 1–25.
32 L. Winner, A. Hermann, G. Belanger-Chabot, O. F. Gonzalez-Belman, J. O. C. Jimenez-Halla, H. Kelch and H. Braunschweig, *Chem. Commun.*, 2018, **54**, 8210–8213.
33 D. Franz and S. Inoue, *Chem. – Asian J.*, 2014, **9**, 2083–2087.
34 H. Braunschweig, R. D. Dewhurst, W. C. Ewing, M. W. Kuntze-Fechner and M. Schaefer, *Chem. – Eur. J.*, 2017, **23**, 5953–5956.
35 P. Cui, R. Guo, L. Kong and C. Cui, *Inorg. Chem.*, 2020, **59**, 5261–5265.
36 A. Koner, T. Sergeieva, B. Morgenstern and D. M. Andrada, *Inorg. Chem.*, 2021, **60**, 14202–14211.
37 D. Prieschl, G. Belanger-Chabot, X. Guo, M. Dietz, M. Mueller, I. Krummenacher, Z. Lin and H. Braunschweig, *J. Am. Chem. Soc.*, 2020, **142**, 1065–1076.
38 M. Noguchi, K. Suzuki, J. Kobayashi, T. Yurino, H. Tsurugi, K. Mashima and M. Yamashita, *Organometallics*, 2018, **37**, 1833–1836.
39 M. W. Lui, N. R. Paisley, R. McDonald, M. J. Ferguson and E. Rivard, *Chem. – Eur. J.*, 2016, **22**, 2134–2145.
40 L. Xie, J. Zhang and C. Cui, *Chem. – Eur. J.*, 2014, **20**, 9500–9503.
41 L. Xie, J. Zhang, H. Hu and C. Cui, *Organometallics*, 2013, **32**, 6875–6878.
42 T. Thiess, G. Belanger-Chabot, F. Fantuzzi, M. Michel, M. Ernst, B. Engels and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2020, **59**, 15480–15486.
43 A. Matler, M. Arrowsmith, F. Schorr, A. Hermann, A. Hofmann, C. Lenczyk and H. Braunschweig, *Eur. J. Inorg. Chem.*, 2021, **2021**, 4619–4631.
44 T.-T. Liu, J. Chen, B.-T. Guan, Z. Lin and Z.-J. Shi, *Chem. – Eur. J.*, 2023, **29**, e202203676.
45 P. Paetzold, C. von Plotho, E. Niecke and R. Rüger, *Chem. Ber.*, 1983, **116**, 1678–1681.
46 P. Paetzold, K. Delpy, R. P. Hughes and W. A. Herrmann, *Chem. Ber.*, 1985, **118**, 1724–1725.
47 H. Braunschweig, P. Paetzold and R. Boese, *Chem. Ber.*, 1993, **126**, 1571–1577.
48 B. Kröckert, K.-H. van Bonn and P. Paetzold, *Z. Anorg. Allg. Chem.*, 2005, **631**, 866–868.

49 M. Nutz, B. Borthakur, R. D. Dewhurst, A. Deissenberger, T. Dellermann, M. Schaefer, I. Krummenacher, A. K. Phukan and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2017, **56**, 7975–7979.
50 L. Winner, G. Belanger-Chabot, M. A. Celik, M. Schaefer and H. Braunschweig, *Chem. Commun.*, 2018, **54**, 9349–9351.
51 H. Zhang, J. Wang, W. Yang, L. Xiang, W. Sun, W. Ming, Y. Li, Z. Lin and Q. Ye, *J. Am. Chem. Soc.*, 2020, **142**, 17243–17249.
52 B. L. Frenette, A. A. Omana, M. J. Ferguson, Y. Zhou and E. Rivard, *Chem. Commun.*, 2021, **57**, 10895–10898.
53 A. Wong, J. Chu, G. Wu, J. Telser, R. Dobrovetsky and G. Menard, *Inorg. Chem.*, 2020, **59**, 10343–10352.
54 M. Mehta and J. M. Goicoechea, *Chem. Commun.*, 2019, **55**, 6918–6921.
55 A. A. Omana, R. Watt, Y. Zhou, M. J. Ferguson and E. Rivard, *Inorg. Chem.*, 2022, **61**, 16430–16440.
56 A. K. Swarnakar, C. Hering-Junghans, K. Nagata, M. J. Ferguson, R. McDonald, N. Tokitoh and E. Rivard, *Angew. Chem., Int. Ed.*, 2015, **54**, 10666–10669.
57 A. K. Swarnakar, C. Hering-Junghans, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Sci.*, 2017, **8**, 2337–2343.
58 T. M. Gilbert, *Organometallics*, 2000, **19**, 1160–1165.
59 T. M. Gilbert, *Organometallics*, 2003, **22**, 2298–2304.
60 T. M. Gilbert, *Organometallics*, 2005, **24**, 6445–6449.
61 J. Münster, P. Paetzold, E. Schröder, H. Schwan and T. von Bennigsen-Mackiewicz, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2641–2651.
62 Z. X. Giustra and S.-Y. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 1184–1194.
63 P. G. Campbell, A. J. V. Marwitz and S.-Y. Liu, *Angew. Chem., Int. Ed.*, 2012, **51**, 6074–6092.
64 K. Edel, S. A. Brough, A. N. Lamm, S.-Y. Liu and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2015, **54**, 7819–7822.
65 K. Edel, R. F. Fink and H. F. Bettinger, *J. Comput. Chem.*, 2016, **37**, 110–116.
66 K. Edel, J. S. A. Ishibashi, S.-Y. Liu and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2019, **58**, 4061–4064.
67 D. Gupta and H. F. Bettinger, *J. Org. Chem.*, 2023, **88**, 8369–8378.
68 M. Müller, C. Maichle-Mössmer and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2014, **53**, 9380–9383.
69 H. F. Bettinger and M. Müller, *J. Phys. Org. Chem.*, 2015, **28**, 97–103.
70 C. Keck, J. Hahn, D. Gupta and H. F. Bettinger, *Chem. – Eur. J.*, 2022, **28**, e202103614.
71 W. Pieper, D. Schmitz and P. Paetzold, *Chem. Ber.*, 1981, **114**, 3801–3812.
72 H. F. Bettinger and H. Bornemann, *J. Am. Chem. Soc.*, 2006, **128**, 11128–11134.
73 H. F. Bettinger, M. Filthaus, H. Bornemann and I. M. Oppel, *Angew. Chem., Int. Ed.*, 2008, **47**, 4744–4747.
74 H. F. Bettinger and M. Filthaus, *Org. Biomol. Chem.*, 2010, **8**, 5477–5482.
75 M. Filthaus, L. Schwertmann, P. Neuhaus, R. d. W. Seidel, I. M. Oppel and H. F. Bettinger, *Organometallics*, 2012, **31**, 3894–3903.
76 M. Müller, C. Maichle-Mössmer and H. F. Bettinger, *Chem. Commun.*, 2013, **49**, 11773–11775.
77 H. F. Bettinger, M. Filthaus and P. Neuhaus, *Chem. Commun.*, 2009, 2186–2188.
78 K.-H. v. Bonn, T. v. Bennigsen-Mackiewicz, J. Kiesgen, C. v. Plotho and P. Paetzold, *Z. Naturforsch., B*, 1988, **43**, 61–68.
79 H. Noeth and S. Weber, *Z. Naturforsch. B*, 1983, **38**, 1460–1465.
80 A. Chrostowska, S. Xu, A. N. Lamm, A. Mazière, C. D. Weber, A. Dargelos, P. Baylère, A. Graciaa and S.-Y. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 10279–10285.
81 K. Edel, X. Yang, J. S. A. Ishibashi, A. N. Lamm, C. Maichle-Mössmer, Z. X. Giustra, S.-Y. Liu and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2018, **57**, 5296–5300.
82 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.
83 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
84 R. Gershoni-Poranne and A. Stanger, *Chem. Soc. Rev.*, 2015, **44**, 6597–6615.
85 A. G. Papadopoulos, N. D. Charistos, K. Kyriakidou and M. P. Sigalas, *J. Phys. Chem. A*, 2015, **119**, 10091–10100.
86 R. J. Mayer, N. Hampel and A. R. Ofial, *Chem. – Eur. J.*, 2021, **27**, 4070–4080.
87 I. B. Sivaev and V. I. Bregadze, *Coord. Chem. Rev.*, 2014, **270–271**, 75–88.
88 S. Döring, G. Erker, R. Fröhlich, O. Meyer and K. Bergander, *Organometallics*, 1998, **17**, 2183–2187.
89 A. Massey and A. Park, *J. Organomet. Chem.*, 1966, **5**, 218–225.
90 A. v. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
91 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. A*, 2009, **113**, 5806–5812.
92 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
93 E. Glendening, C. Landis and F. Weinhold, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 1–42.
94 F. Weinhold, *J. Comput. Chem.*, 2012, **33**, 2363–2379.
95 E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429–1437.

Electronic Supporting Information

Strain induced reactivity of cyclic iminoboranes: The (2 + 2) cycloaddition of a 1-*H*-1,3,2-diazaborepine with ethene

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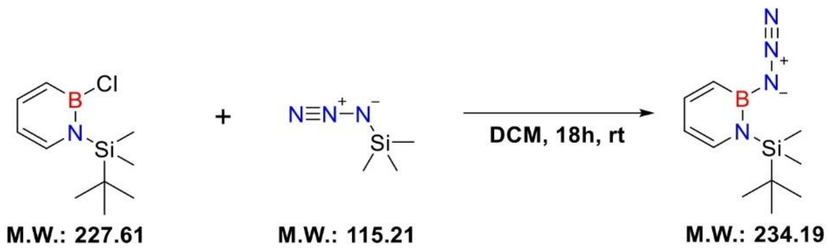
Contents

Experimental and Computational Details

General Procedure. All experiments were performed under anhydrous conditions using argon as protective gas. All commercially available compounds and dry solvents were purchased. ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane, ^{11}B NMR spectra were referenced externally to BF_3•OEt_2. ^{1}H and ^{13}C spectra were calibrated to residual solvent signals. NMR spectra were recorded on a Bruker Avance III+ 400 spectrometer. MSD 5977 (Agilent) with DIP (SIM) was used for recording EI-MS. 1-(*Tert*-butyldimethylsilyl)-2-chloro-1,2-dihydro-1,2-azaborine and azidotrimethylsilane were purchased from abcr (Article ID AB541736 (now discontinued)) and AlfaAesar (Stock No. L00173), respectively.

Synthesis



The reaction was conducted in a glove box under argon atmosphere. In a J-Young-NMR tube a solution of 45,4mg (0,2 mmol) 1-(*tert*-butyldimethylsilyl)-2-chloro-1,2-dihydro-1,2-azaborine in 0.5 mL deuterated dichloromethane was prepared. To this a solution of 23 mg (0.2 mmol) azidotrimethylsilane in 0.5 mL deuterated dichloromethane was added slowly by syringe. The progress of the reaction was monitored by NMR spectroscopy. After 18 h at room temperature all volatiles were removed under vacuum. 1-(*tert*-

butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborine remained and was used in all experiments without additional purification.

^{1}H-NMR: 400 MHz, CD_2Cl_2: 7.61 (1H, m), 7.15 (1H, m), 6.62 (1H, m), 6.19 (1H, m), 0.92 (9H, s), 0.47 (6H, s).

^{11}B{^{1}H}-NMR: 128 MHz, CD_2Cl_2: 31.9.

^{13}C{^{1}H}-NMR: 101 MHz, CD_2Cl_2: 146.3, 138.6, 121.5 (determined by 2D-NMR), 110.6, 26.6, 19.0, -2.8.

EI-MS: m/z (Int.%): 234.2 (25) M+, 177.1 (26) [M-C(CH_3)$_3$]+, 149.1 (100) [M-HC(CH_3)$_3$-N_2]+;

HRMS m/z: With our available equipment, high resolution mass spectrometry cannot be performed for air and moisture sensitive compounds.

Matrix Isolation Experimental Details

The precursor 1-(*tert*-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborine **3** was sublimed from a glass flask at room temperature, and all gaseous materials leaving the flask were condensed onto a cold CsI window (for IR) or sapphire window (for UV-Vis) with a large excess of Argon 6.0 (Westfalen AG, 99.9999 %), or doped with 1-2 % of carbon monoxide 3.7 (Westfalen AG), $C^{18}O$ 2.0 (95 % ^{18}O) (Sigma Aldrich) or ^{13}CO 2.3 (99.1 % ^{13}C) (Westfalen AG) and 5 % of C_2H_4 (Sigma-Aldrich, 99.95 %) or C_2D_4 (Sigma-Aldrich, 99 %). The mixtures of these gases were dosed to 2.0 sccm by a mass flow controller (MKS mass flow PR400B). A Sumitomo SH-1 closed-cycle helium cryostat was used to obtain the temperature as low as 4 - 7 K.[1] The infrared spectra in the range 400-4000 cm^{-1} were obtained using a Bruker Vertex 70 FTIR spectrometer with a standard resolution of 0.5 cm^{-1}, while electronic absorption spectra were measured using a Perkin Elmer Lambda 1050 spectrometer. For inducing photochemistry in the deposited matrix, a low-pressure mercury lamp (λ = 254 nm, PenRay) and high-pressure mercury lamps (USHIO, USH-508S) were used. The combination of dichroic mirrors of required wavelength (420 - 630 nm) range along with a Schott cutoff filter (GG-435) was employed to obtain 435 nm > λ > 630 nm.

Computational Details

All the structures were fully optimized using the M06-2X[2] global hybrid functional as well as B3LYP[3, 4] hybrid exchange–correlation energy functional along with Grimme's[5] London dispersion correction with Becke-Johnson damping B3LYP-D3(BJ).[3, 4] The 6-311+G(d,p) (split-valence triple-ζ with diffuse s and p functions for all atoms as well as d polarization functions on non-hydrogen atoms and p polarization functions for hydrogen)[6] basis set was adopted for all geometry optimizations. Harmonic vibrational frequencies were computed analytically which confirmed the nature of the stationary points as minima or first order saddle points (transition states) as well as to reproduce the simulated spectra of species **2-5** (including various isotopes). For identifying the combination bands and overtones, which were seen in addition to the fundamental bands in the experimental spectrum, anharmonic calculations were performed at B3LYP-D3(BJ)/6-311+G(d,p) level of theory using second-order vibrational perturbative approach.[7-9] Additionally, to reveal which minima are connected to the transition states, intrinsic reaction coordinate (IRC)[10,

[11] paths were calculated at the different level of theories for each reaction (see SI). To refine the energies, single point calculations based on all the structures were performed using domain based local pair natural orbital (DLPNO) coupled cluster theory with single, double, and a perturbative estimate of triple excitation (DLPNO-CCSD(T))[12-14] in conjunction with Dunning's[15, 16] triple-ζ (cc-pVTZ) basis set as implemented in ORCA 5.0.[17] The DLPNO-CCSD(T) computations used TightPNO cutoff for increased accuracy and the frozen core approximation. All density functional theory calculations were performed with Gaussian 16.[18] The excitation spectra were calculated using time-dependent DFT (TD-DFT) with Gaussian 16 at CAM-B3LYP/6-311+G(d,p) level of theory.[18, 19] Natural bond orbital analysis was carried with the NBO 6.0 program using the M06-2X/6-311+G(d,p) geometries.[20-23] Magnetic shielding values were computed by employing the GIAO method[24, 25] at B3LYP/6-311+G(d,p)//M06-2X/6-311+G(d,p) level of theory. To determine the Lewis acidity of the compounds, isodesmic reactions were computed at SMD(DCM)[26]/MN15[27]/def2-TZVP[28] level of theory.

Spectra

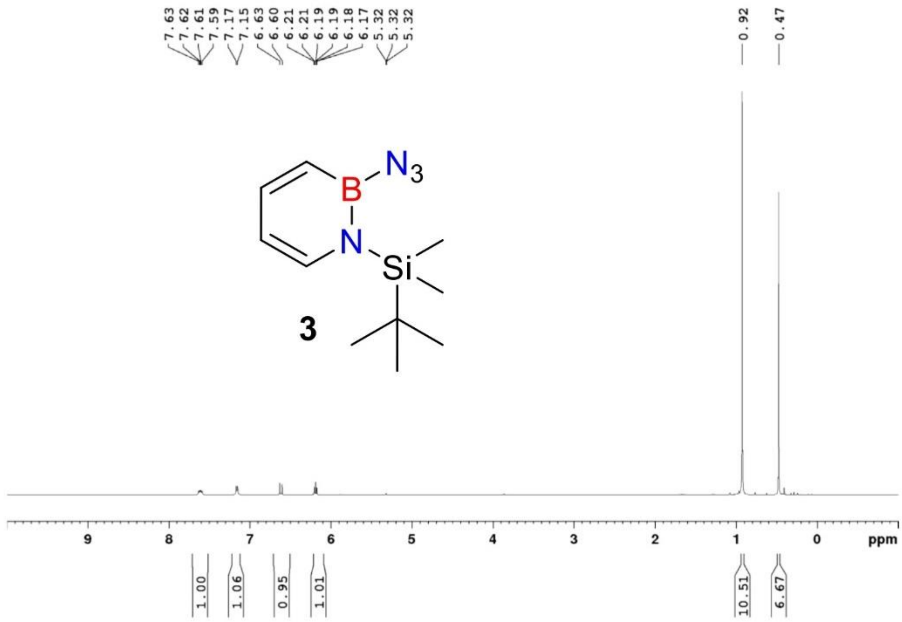


Figure S1. ^{1}H-NMR spectrum (400 MHz) of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

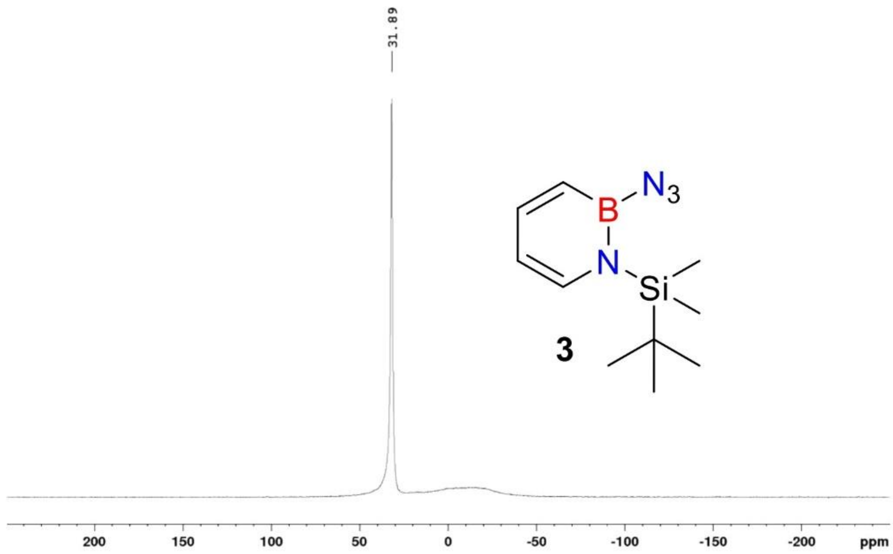


Figure S2. ^{11}B{^{13}C} -NMR spectrum (128 MHz) of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

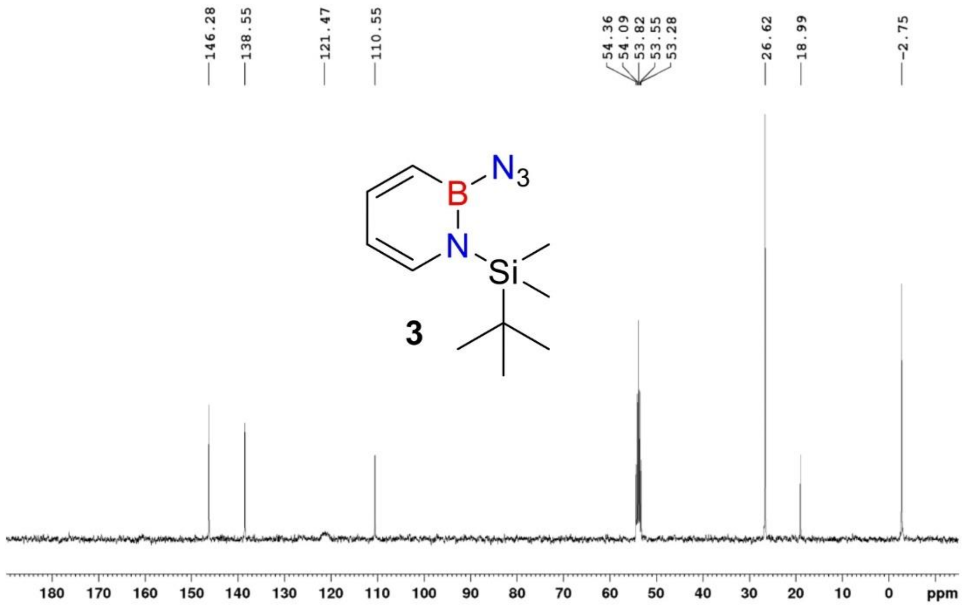


Figure S3. $^{13}C\{^{1}H\}$ -NMR spectrum (101 MHz) of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

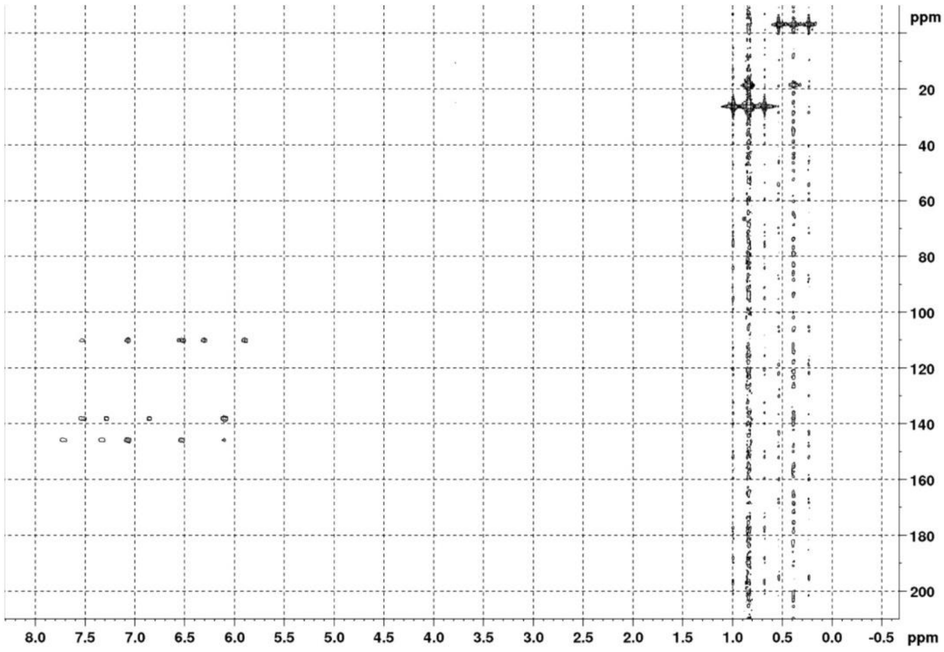


Figure S4. HMBC - NMR spectrum of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

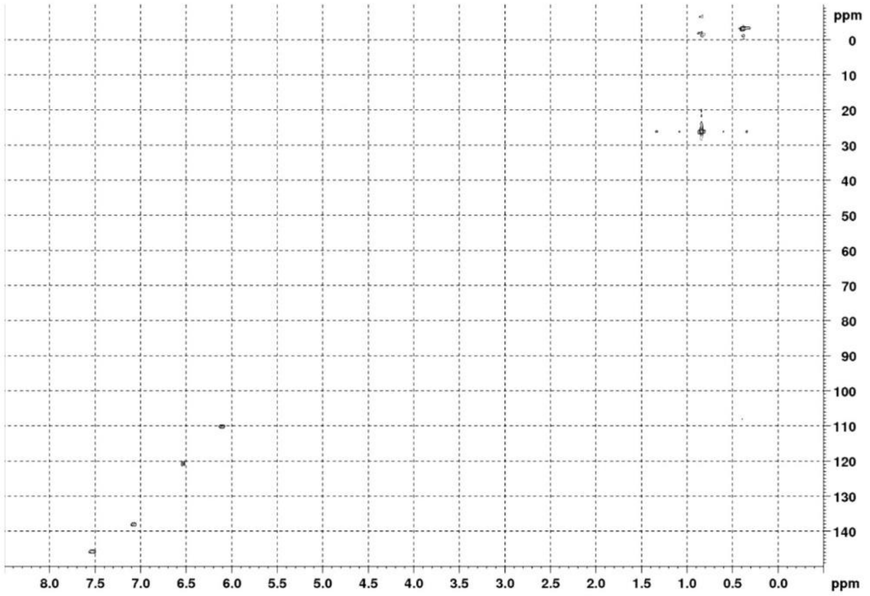


Figure S5. HSQC - NMR spectrum of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

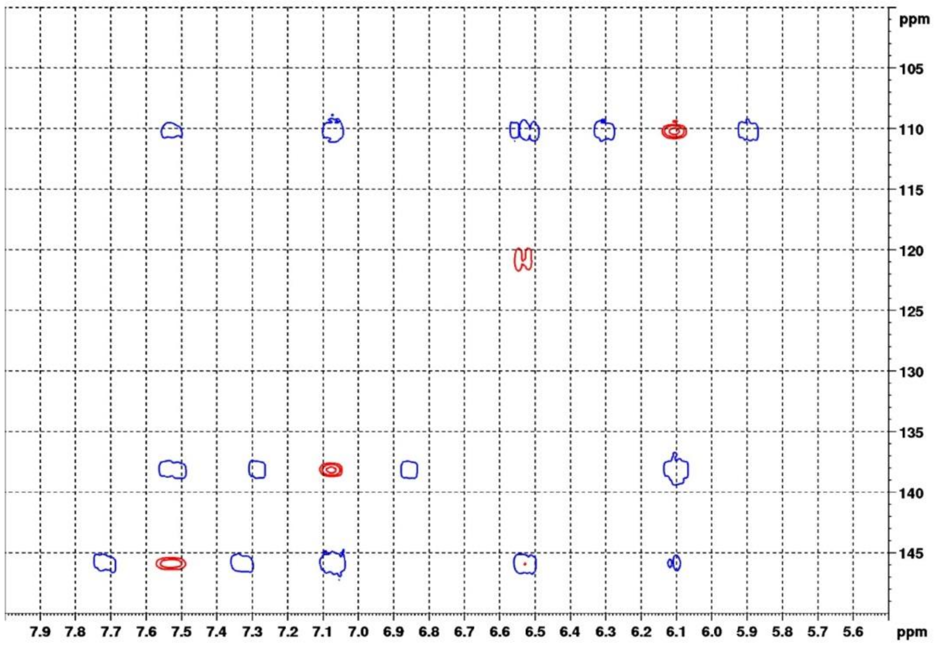


Figure S6. Overlapped HMBC-NMR and HSQC-NMR spectrum of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3** in CD_2Cl_2.

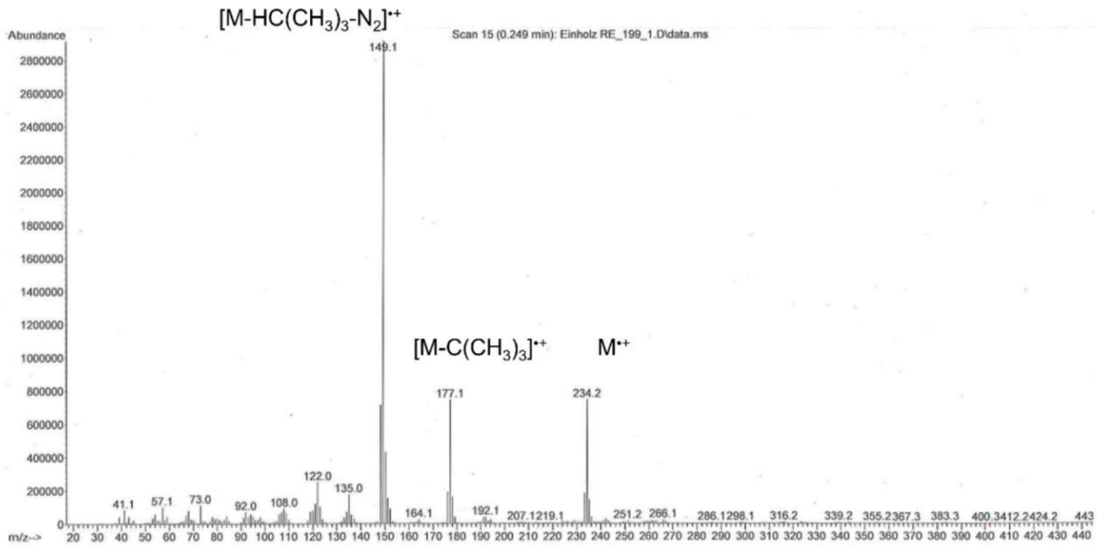


Figure S7. EI-MS spectrum of 1-(tert-butyldimethylsilyl)-2-azido-1,2-dihydro-1,2-azaborinine **3**.

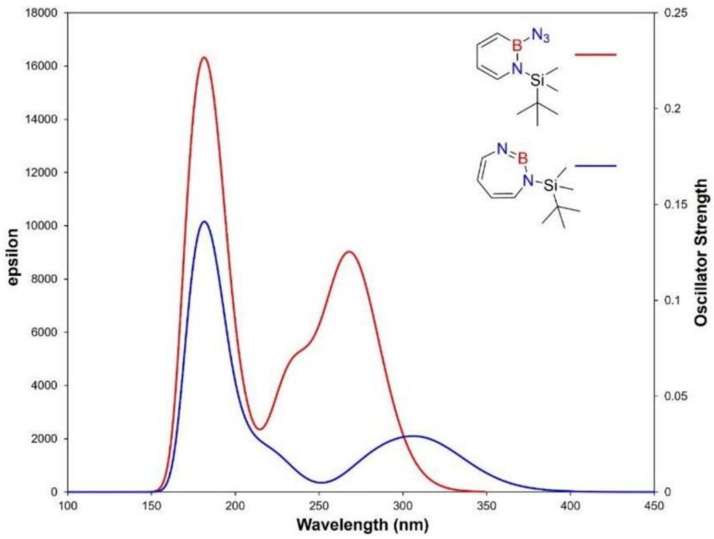


Figure S8. UV-Vis spectra of **3** (red) and **2** (blue) computed at TD-CAM-B3LYP/6-311+G(d,p) level of theory (half-width= 0.333 eV, first computed transition energy for **3** = 4.6 eV at λ_{max} = 269 nm, oscillator strength = 0.2157; first computed transition energy for **2** = 3.9 eV at λ_{max} = 317 nm, oscillator strength = 0.0403).

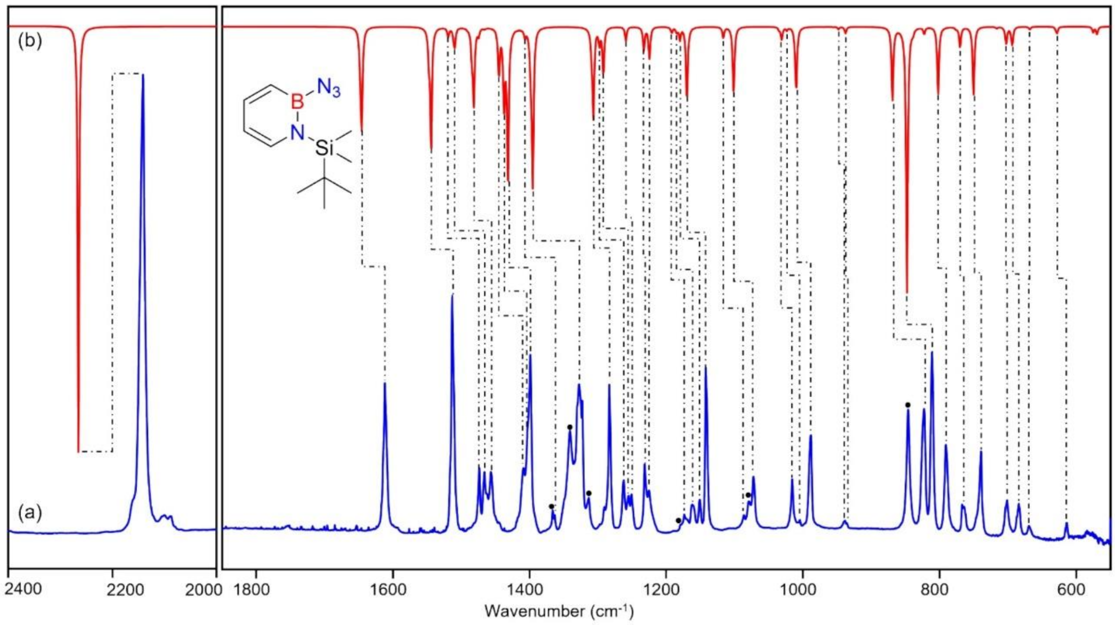


Figure S9. a) IR spectrum obtained after deposition of **3** in Ar matrix at 28 K. b) Spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **3** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory. (● corresponds to the overtones and combination bands (Table S9)).

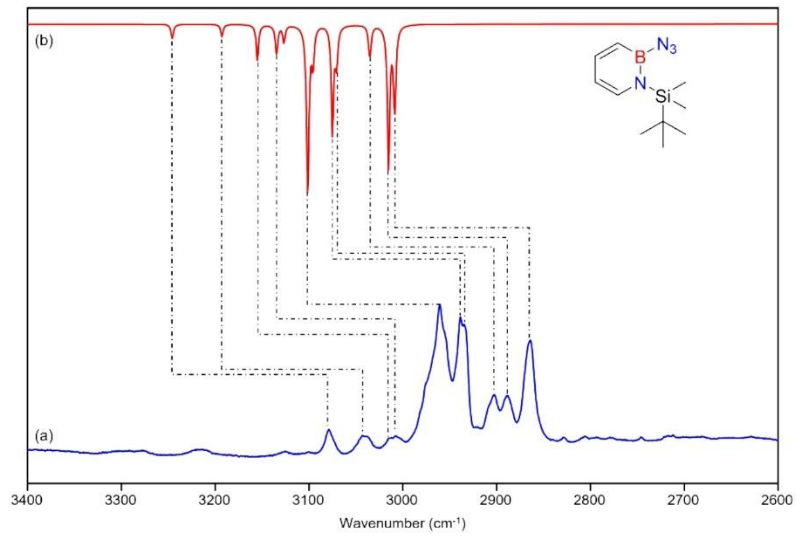


Figure S10. a) IR spectrum obtained after deposition of **3** in Ar matrix at 28 K. b) Spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **3** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory.

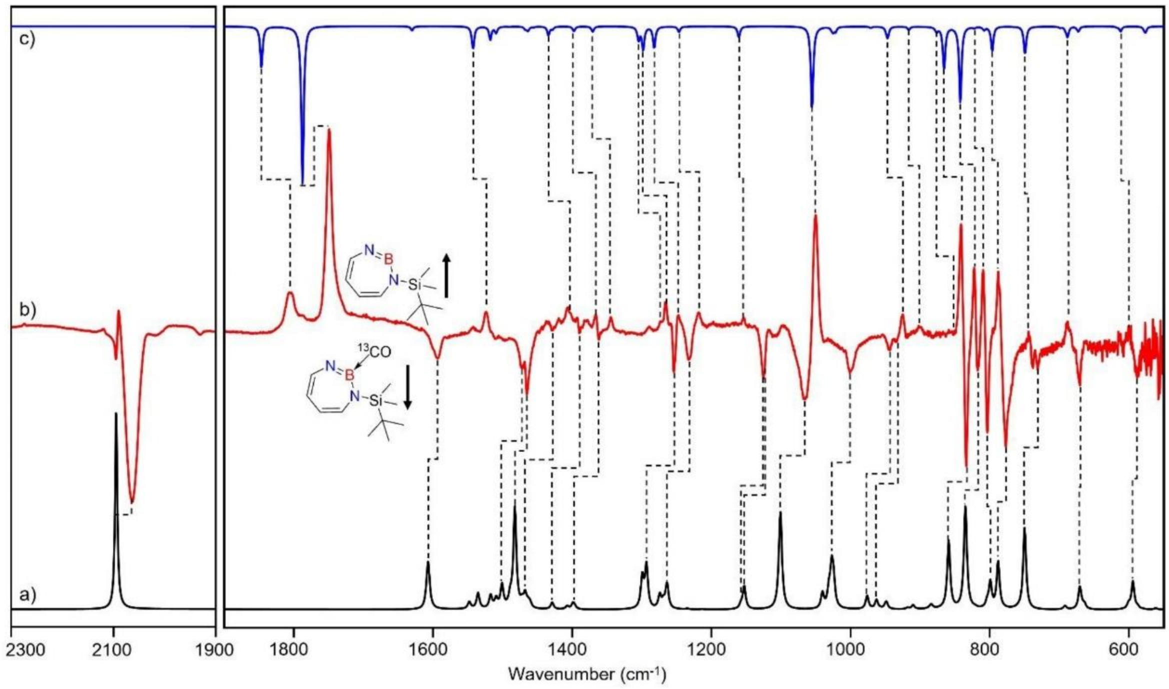


Figure S11. a) Spectrum for ^{11}B and ^{10}B (81:19) and ^{13}CO isotopologues of **4** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory. b) Difference IR spectrum after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing step). c) Spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **2** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory.

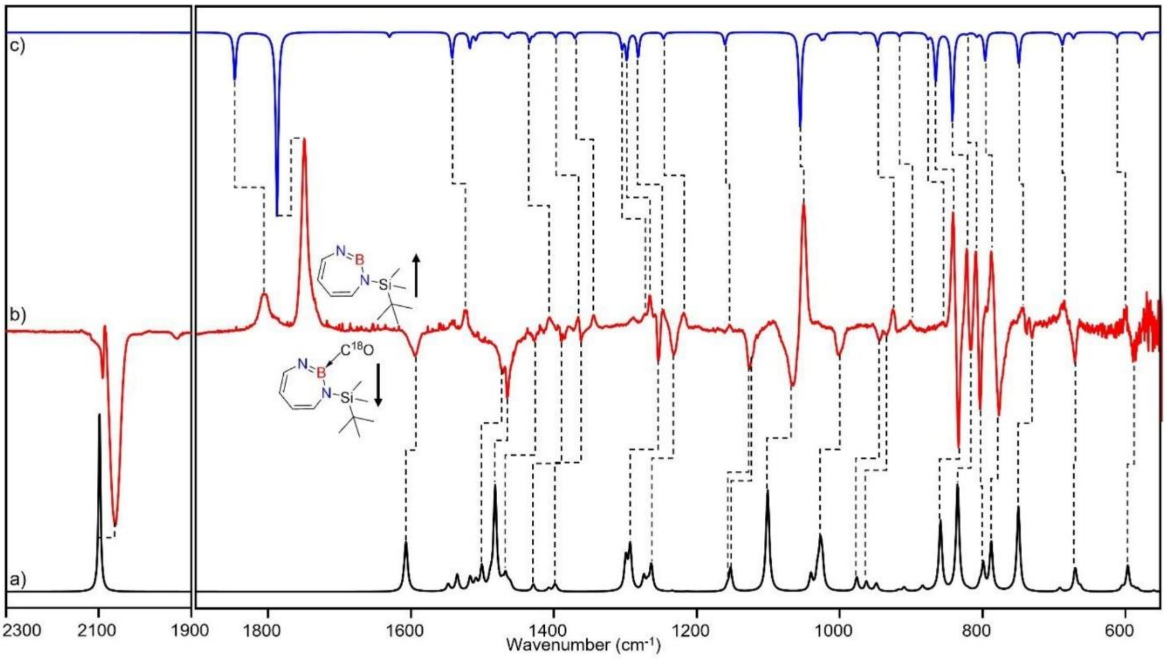


Figure S12. a) Spectrum for ^{11}B and ^{10}B (81:19) and $C^{18}O$ isotopologues of **4** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory. b) Difference IR spectrum after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing step). c) Spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **2** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory.

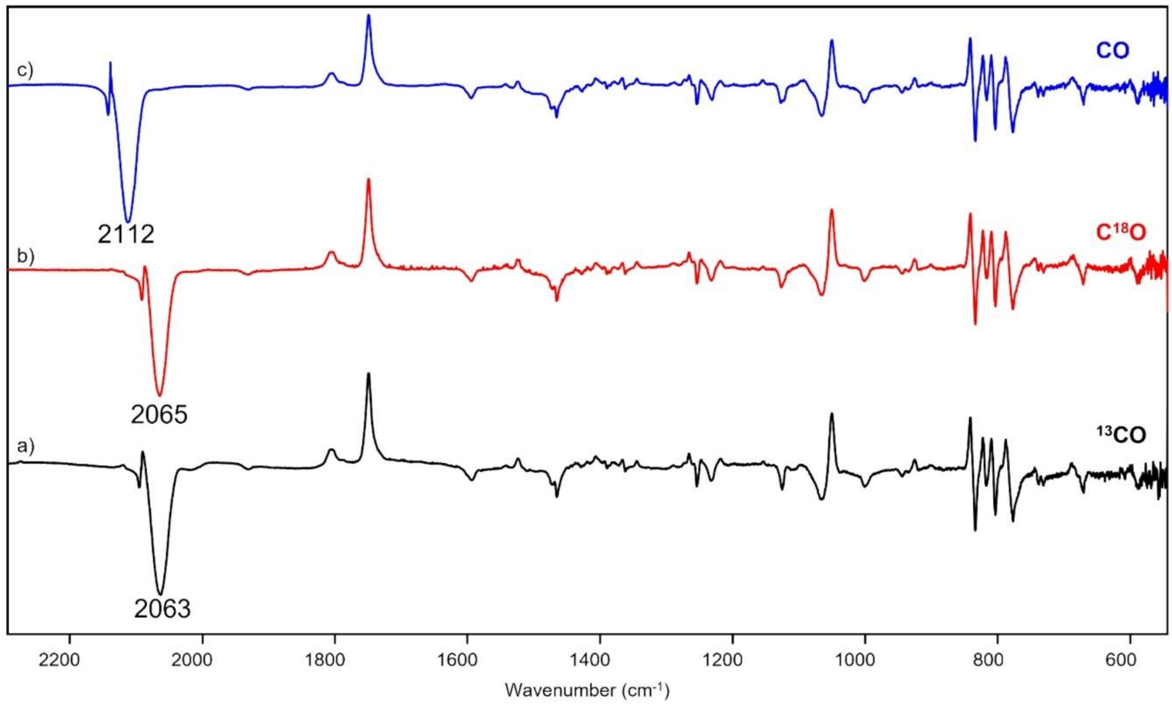


Figure S13. Difference IR spectrum after irradiation with 435 nm > λ > 620 nm for 30 min (following the annealing step) with a) $^{13}C^{16}O$ isotope, b) $^{12}C^{18}O$ isotope and c) $^{12}C^{16}O$ isotopes of **4** in Ar matrix.

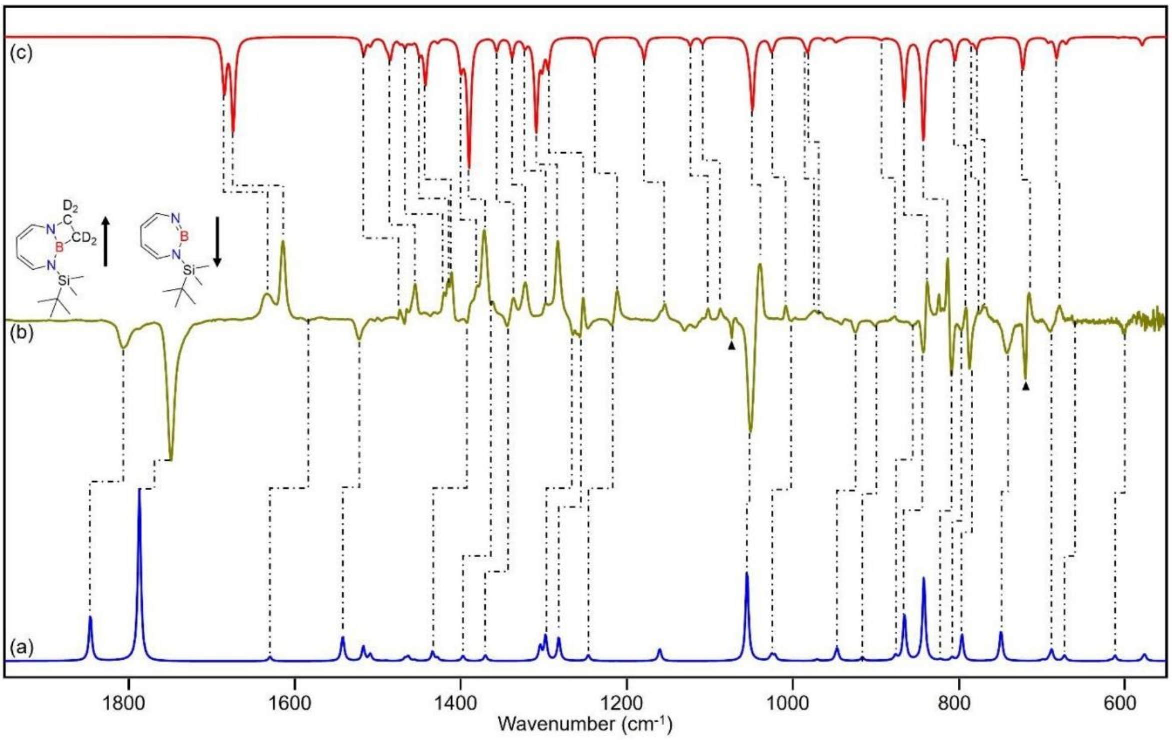


Figure S14. a) Spectrum for ^{11}B and ^{10}B isotopologues (81:19) of **2** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory. b) Difference IR spectrum after annealing to 30 K for 60 min (following the irradiation step). c) Spectrum for ^{11}B and ^{10}B (81:19) and C_2D_4 isotopologues of **5** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory. (▲ corresponds to the peaks of C_2D_4)

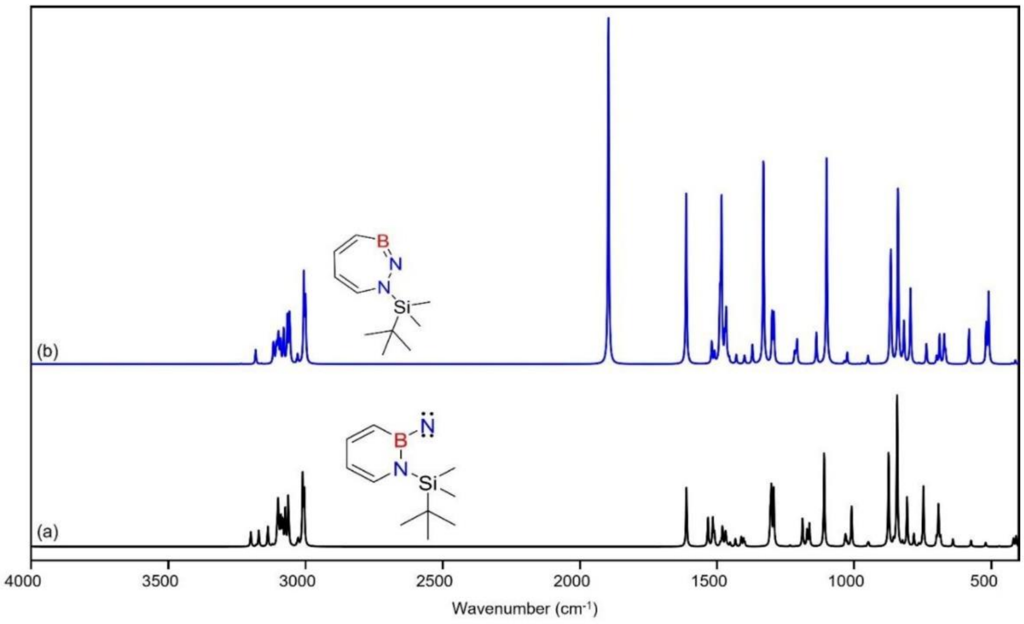


Figure S15. Spectrum for a) triplet boryl nitrene and b) 1*H*-1,2,3-diazaborepine calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory.

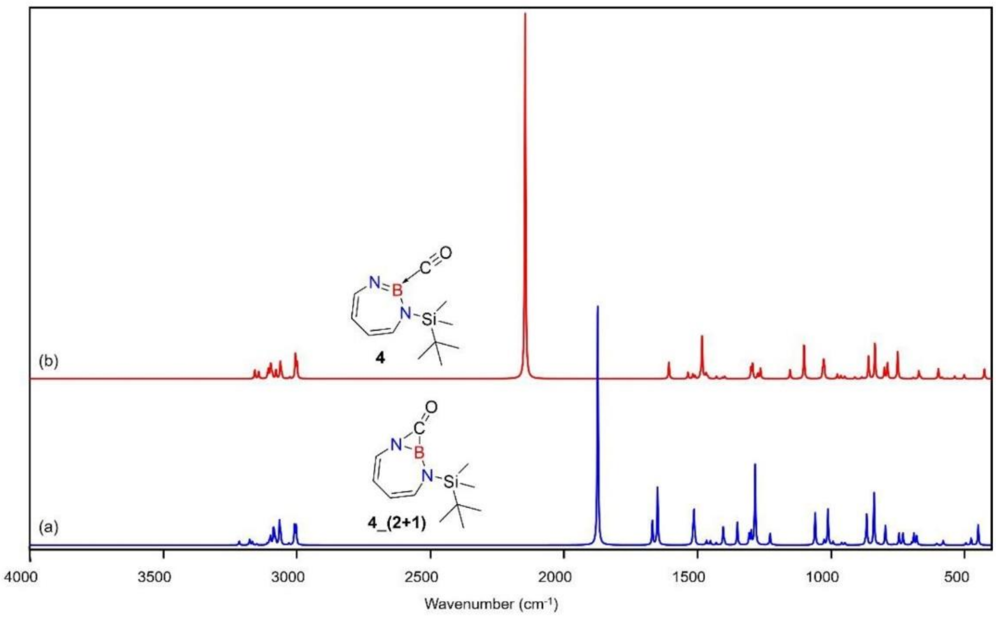


Figure S16. Spectrum for a) **4_(2 + 1)** and b) **4** calculated at the B3LYP-D3(BJ)/6–311+G(d,p) level of theory.

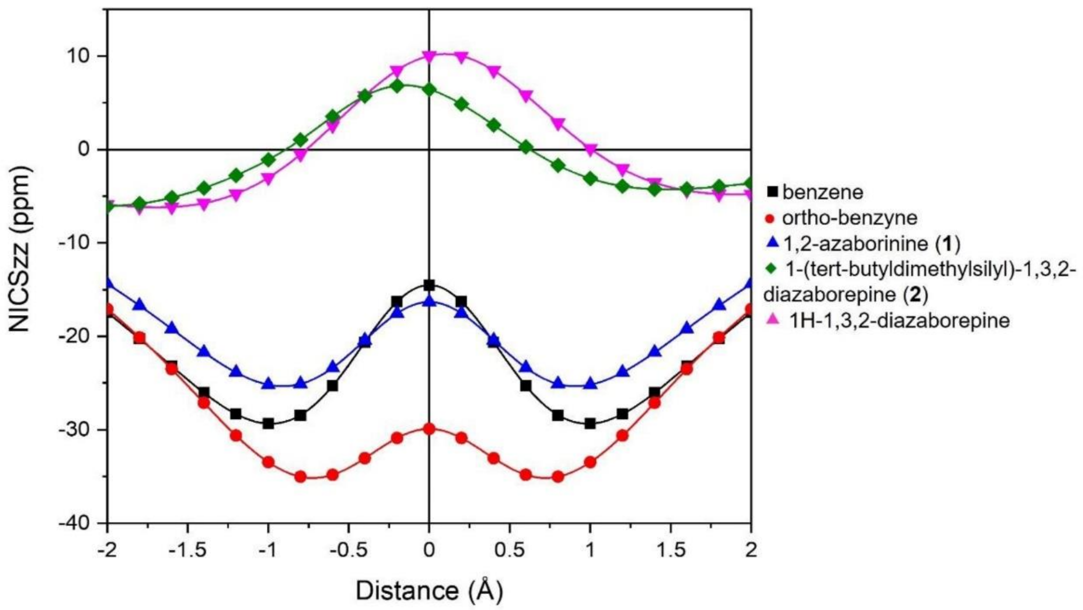


Figure S17. Plot of $NICS_{zz}$ value calculated along a line perpendicular to the molecular plane, starting at the ring center, at B3LYP/6-311+G(d,p)//M06-2X/6-311+G(d,p) level of theory.

Table S1. The relative ZPVE corrected energies in kcal/mol for the reaction of **2** with CO as computed at the different level of theories.

	2 + CO	4_comp	4_comp'	$TS_{4comp'-4}$	4	$TS_{4-4\_(2+1)}$	4_(2+1)	$TS_{4\_comp-4\_(2+2)}$	4_(2+2)
B3LYP-D3(BJ)/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// B3LYP-D3(BJ)/6-311+G(d,p)]**	*0.0* **[0.0]**	*-2.0* **[-2.9]**	*-2.7* **[-3.2]**	*-2.4* **[-2.1]**	*-12.8* **[-7.0]**	*-4.6* **[-1.4]**	*-8.4* **[-4.6]**	*19.6* **[20.0]**	*-10.2* **[-11.1]**
M06-2X/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	*0.0* **[0.0]**	*-2.0* **[-2.9]**	*-2.5* **[-3.4]**	*-1.2* **[-2.1]**	*-6.3* **[-7.9]**	*0.1* **[-1.5]**	*-6.5* **[-4.4]**	*20.9* **[20.2]**	*-11.3* **[-11.2]**

Table S2. The relative free energies (ΔG at 298 K in kcal/mol) for the reaction of **2** with CO as computed at the different level of theories.

	2+ CO	4_comp	4_comp'	$TS_{4comp'-4}$	4	$TS_{4-4\_(2+1)}$	4_(2+1)	$TS_{4\_comp-4\_(2+2)}$	4_(2+2)
B3LYP-D3(BJ)/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// B3LYP-D3(BJ)/6-311+G(d,p)]**	*0.0* **[0.0]**	*-2.0* **[-2.9]**	*-2.7* **[-3.2]**	*-2.4* **[-2.1]**	*-12.8* **[-7.0]**	*-4.6* **[-1.4]**	*-8.4* **[-4.6]**	*19.6* **[20.0]**	*-10.2* **[-11.1]**
M06-2X/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	*0.0* **[0.0]**	*-2.0* **[-2.9]**	*-2.5* **[-3.4]**	*-1.2* **[-2.1]**	*-6.3* **[-7.9]**	*0.1* **[-1.5]**	*-6.5* **[-4.4]**	*20.9* **[20.2]**	*-11.3* **[-11.2]**

Table S3. The relative ZPVE corrected energies in kcal/mol for the reaction of **2** with ethene (C_2H_4) as computed at the different level of theories.

	2+ C_2H_4	**5_comp'**	**$TS_{comp\_5'-comp\_5}$**	**5_comp**	**TS_{comp_5-5}**	**5**	**$TS_{comp\_5'-6}$**	**6**
B3LYP-D3(BJ)/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// B3LYP-D3(BJ)/6-311+G(d,p)]**	*0.0* **[0.0]**	*-3.8* **[-4.3]**	*-3.3* **[-3.3]**	*-7.8* **[-6.6]**	*-5.9* **[-5.7]**	*-41.6* **[-46.9]**	*15.8* **[18.6]**	*-49.6* **[53.1]**
M06-2X/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	*0.0* **[0.0]**	*-4.2* **[-4.6]**	*-2.8* **[-3.4]**	*-6.9* **[-6.7]**	*-5.5* **[-5.7]**	*-45.8* **[-47.0]**	*19.4* **[18.4]**	*-51.6* **[-57.1]**

Table S4. The relative free energies (ΔG at 298 K in kcal/mol) for the reaction of **2** with ethene (C_2H_4) as computed at the different level of theories.

	2 + C_2H_4	**5_comp'**	**$TS_{comp\_5'-comp\_5}$**	**5_comp**	**TS_{comp_5-5}**	**5**	**$TS_{comp\_5'-6}$**	**6**
B3LYP-D3(BJ)/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// B3LYP-D3(BJ)/6-311+G(d,p)]**	*0.0* **[0.0]**	*4.0* **[3.6]**	*6.6* **[6.7]**	*3.5* **[4.7]**	*5.5* **[5.7]**	*-30.1* **[-35.4]**	*26.7* **[29.5]**	*-38.0* **[-41.5]**
M06-2X/6-311+G(d,p) **[DLPNO-CCSD(T)/cc-pVTZ// M06-2X/6-311+G(d,p)]**	*0.0* **[0.0]**	*7.2* **[6.6]**	*4.7* **[4.9]**	*4.7* **[4.9]**	*6.6* **[6.4]**	*-34.9* **[-36.1]**	*30.4* **[29.5]**	*-39.9* **[-41.2]**

Isodesmic Reactions as Tool to Calculate Equilibrium Constants for determining Lewis Acidity

We determined the Lewis acidity of **1** and **2** using the computational protocol used by Ofial et al. by determining the Lewis acidity from equilibrium constants of Lewis acid-base adduct formation.[29] We used the following equations (Figure S17) for the computation of Gibbs energies of association of boranes and Lewis bases at the SMD(DCM)/MN15/def2-TZVP level of theory following Ofial et al.[29] ΔG^{exptl} values are taken from the paper by Ofial et al.[29]

$$\text{(I)}\quad X + BAr_3\text{-}LB \xrightarrow{\Delta G(I)\text{ by DFT}} X\text{-}LB + BAr_3$$

$$\text{(II)}\quad BAr_3 + LB \xrightarrow{\Delta G(II)^{exptl}} BAr_3\text{-}LB$$

$$\text{(III)}\quad X + LB \xrightarrow{\Delta G_{iso}} X\text{-}LB \qquad \Delta G_{iso} = \Delta G(I) + \Delta G(II)^{exptl}$$

Figure S17. Combining the isodesmic reaction [Eq. (I)] with an experimental reference reaction [Eq.(II)] allows one to determine the Lewis acidities of X from ΔG_{iso} [Eq.(III)].

To assess the Lewis acidity LA_B of 1,2-azaborinine **1** and 1,3,2-diazaborepine **2**, triaryl boranes (BAr_3) (Ar= C_6H_5 (**7a**), 4-Cl-C_6H_4 (**7b**), 3,4,5-F_3-C_6H_2 (**7c**)) were chosen as reference Lewis acids. We used three structurally diverse Lewis bases (pyridine (**8a**), acetonitrile (**8b**), and benzaldehyde (**8c**)) as reference to estimate the LA_B values. Based on the experimental ΔG for the formation of Lewis adducts of **7a•8a**, **7b•8b**, and **7c•8c**, we estimate LA_B values of azaborinine **1** or 1,3,2-diazaborepine **2**. As outlined in Figure S17, the Gibbs reaction energies, ΔG(I), for isodesmic Lewis base transfer reactions between the Lewis adduct Ar_3B–LB and X (**1** or **2**) were computed by using the

SMD(DCM)/MN15/def2-TZVP method. To determine LA_B of **1** and **2**, experimentally determined Gibbs energy, ΔG^{exptl} (Figure S17), for the formation of a Lewis adduct of Ar_3B and the investigated Lewis base was added to $\Delta G(I)$ to give ΔG_{iso} (Figure S17). The Gibbs energy, ΔG_{iso}, in Equation III (Figure S17) now describes the thermodynamics of Lewis adduct formation between X (X = **1** or **2**) and a Lewis base, which can be used to estimate the Lewis acidity, LA_B, of **1** or **2** if LB_B of the Lewis base is known according to the following equation:

$$\log K_B = LA_B + LB_B$$

Table S5. Energies of the reaction of equation (I), (II), and (III) with pyridine (**8a**) and BAr_3 (**7a**) as reference Lewis base and acid, respectively, at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species (X)	ΔG(I) (kJ/mol)	$\Delta G(II)_{exptl}$[a] (kJ/mol)	ΔG_{iso} (kJ/mol)	K_B (M^{-1})[b]	LA_B[b]
1	-139.8	-34.5	-174.3	$1.2 * 10^{31}$	25.0
2	-71.6	-34.5	-106.1	$8.3 * 10^{18}$	12.8
[a] Experimental K_B for the reaction of 7a with 8a (see SI of ref. [29]) converted to ΔG with $\Delta G = -RT \ln K_B$. [b] At 20 °C.					

Table S6. Energies of the reaction of equation (I), (II), and (III) with acetonitrile (**8b**) and BAr_3 (**7b**) as reference Lewis base and acid, respectively, at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species (X)	ΔG(I) (kJ/mol)	$\Delta G(II)_{exptl}$[a] (kJ/mol)	ΔG_{iso} (kJ/mol)	K_B (M^{-1})[b]	LA_B[b]
1	-109.9	-3.9	-113.8	$1.9 * 10^{20}$	20.8
2	-36.2	-3.9	-40.1	$1.4 * 10^{7}$	7.6

[a] Experimental K_B for the reaction of **7b** with **8b** (see SI of ref. [29]) converted to ΔG with $\Delta G = -RT \ln K_B$. [b] At 20 °C.

Table S7. Energies of the reaction of equation (I), (II) and (III) with benzaldehyde (**8c**) and BAr_3 (**7c**) as reference Lewis base and acid, respectively, at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species (X)	ΔG(I) (kJ/mol)	$\Delta G(II)_{exptl}$[a] (kJ/mol)	ΔG_{iso} (kJ/mol)	K_B (M^{-1})[b]	LA_B[b]
1	-81.7	-13.2	-94.9	$8.4 * 10^{16}$	18.7
2	-15.8	-13.2	-29.0	$1.5 * 10^{5}$	6.9

[a] Experimental K_B for the reaction of **7c** with **8c** (see SI of ref. [29]) converted to ΔG with $\Delta G = -RT \ln K_B$. [b] At 20 °C.

Table S8. LA_B from the three reference reactions and averaged LA_B.

Lewis Acid	LA_B from 8a	LA_B from 8b	LA_B from 8c	LA_B Average
1	25.0	20.8	18.7	21.5 ± 2.6
2	12.8	7.6	6.9	9.1 ± 2.6

CASSCF Calculation to Understand the Ring Enlargement Process.

Complete active space self-consistent field (CASSCF) theory in combination with def2-SV(P)[28] basis set was used to compute the energies of nitrene electronic states. We considered a model system without the TBS group to interpret compound **2**. The active space consisted of 8 orbitals and 8 electrons (Figure S18). We also computed single point energies with fully internally contracted N-electron valence state perturbation theory (FIC-NEVPT2)[30] to include the effects of dynamic correlation. This results in singlet A'' state as the lowest singlet state which is energetically very close to the A' singlet state (Table S9).

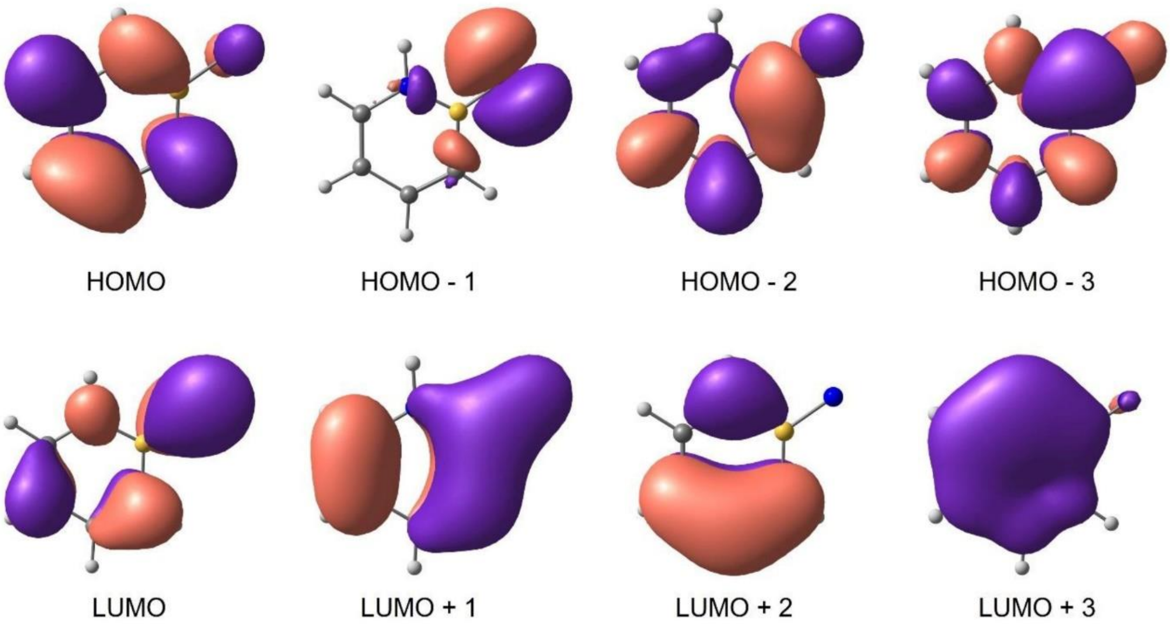


Figure S18. Active space orbitals used for the calculation of transition energies at CASSCF(8,8)/def2-SV(P) level of theory.

Table S9. Transition energies obtained with FIC-NEVPT2/def2-SV(P)//CASSCF(8,8)/def2-SV(P) (bold) and CASSCF(8,8)/def2-SV(P) (italics) level of theory.

State	Root	Multiplicity	IRREP	ΔE (kcal/mol)
0	0	3	A"	**0.0** / *0.0*
1	0	1	A"	**33.60** / *37.38*
2	0	1	A'	**34.89** / *37.54*
3	0	3	A'	**120.35** / *119.52*

We also scanned the potential energy surface by fixing the C-B-N angle in the ^{1}A' state to determine the barrier for the ring enlargement reaction (Figure 20). For this we considered an active space consisting of 10 orbitals and 10 electrons (Figure 19).

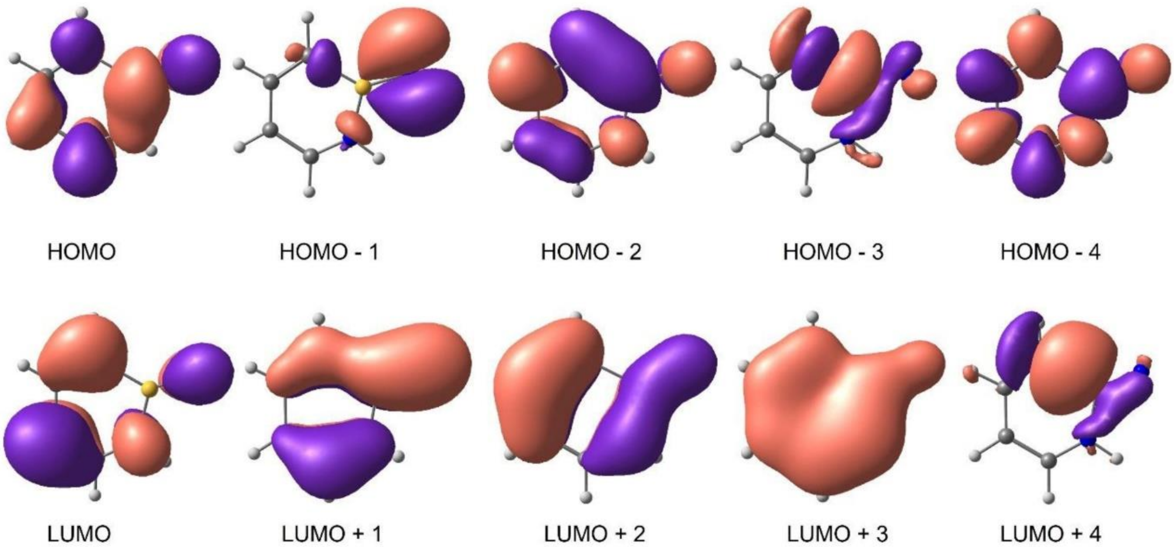


Figure S19. Active space orbitals used for the scan calculation of angle CBN at CASSCF(10,10)/def2-SV(P) level of theory.

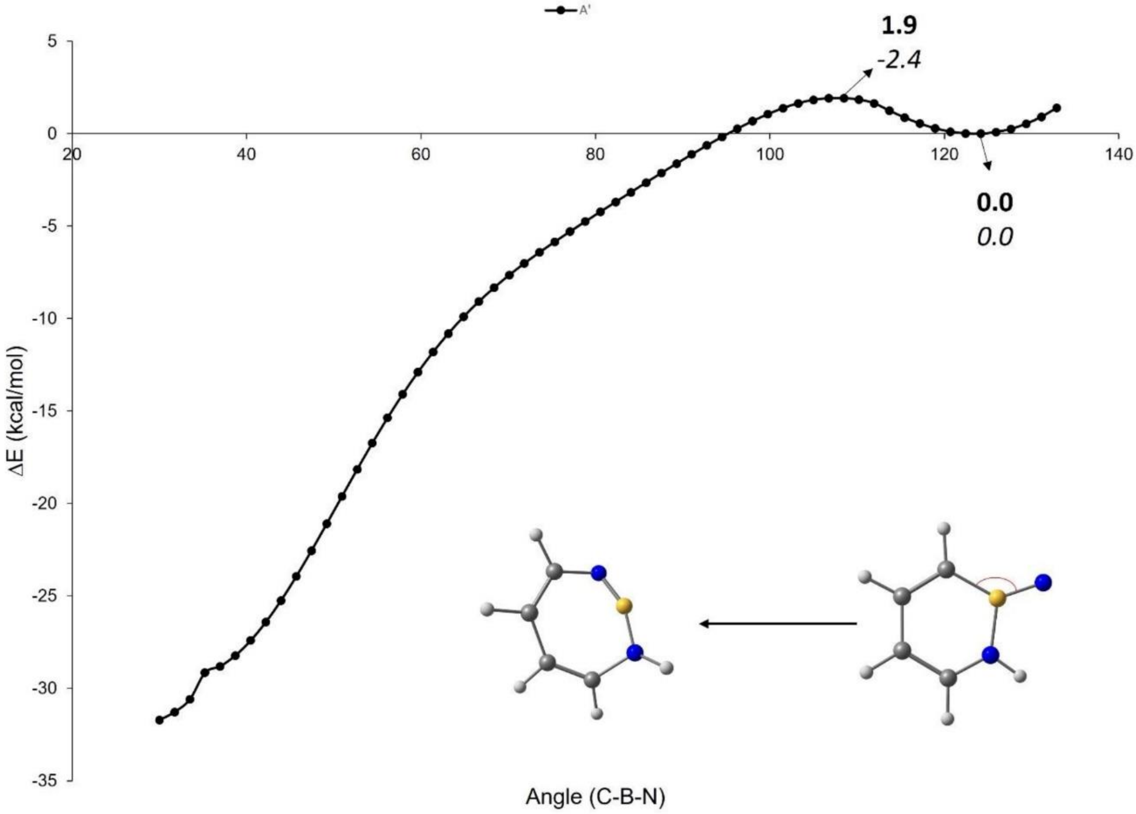
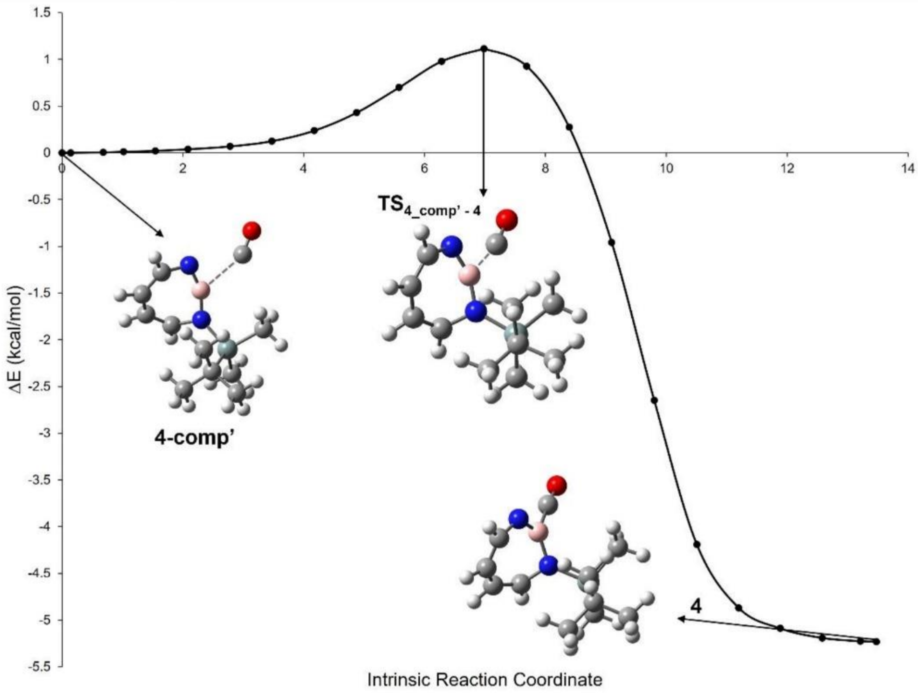


Figure S20. Scan calculation of angle CBN at CASSCF(10,10)/def2-SV(P) (bold) and single point at maximum and minimum at FIC-NEVPT2/def2-SV(P)//CASSCF(10,10)/def2-SV(P) (italics) level of theory.

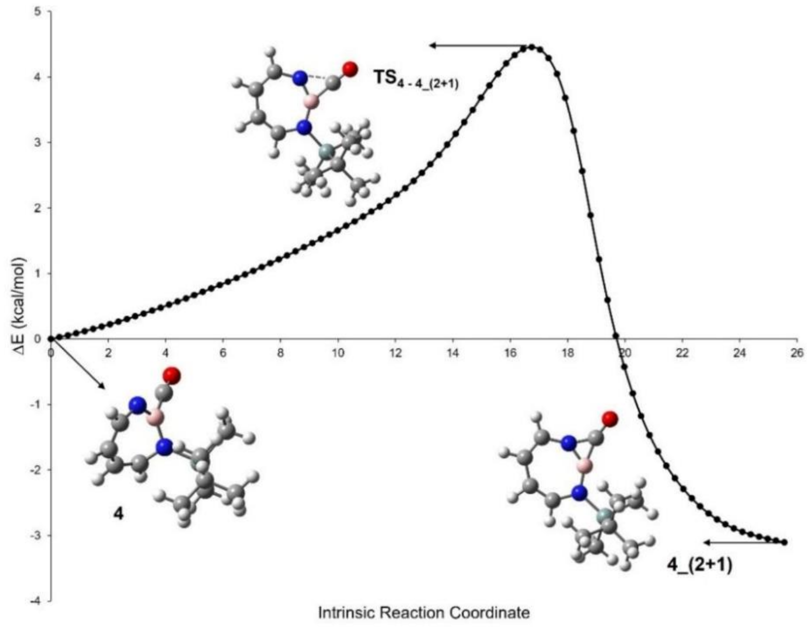
The barrier is very small (1.9 kcal/mol) at the CASSCF level of theory, and it disappears entirely at NEVPT2//CASSCF. This implies that the singlet nitrene is not an observable species and N_2 extrusion and ring enlargement are concerted.

Table S10. Intrinsic reaction coordinate (IRC) path for the reactions of **2** with CO and C_2H_4 respectively at M06-2X/6-311+G(d,p) level of theory.

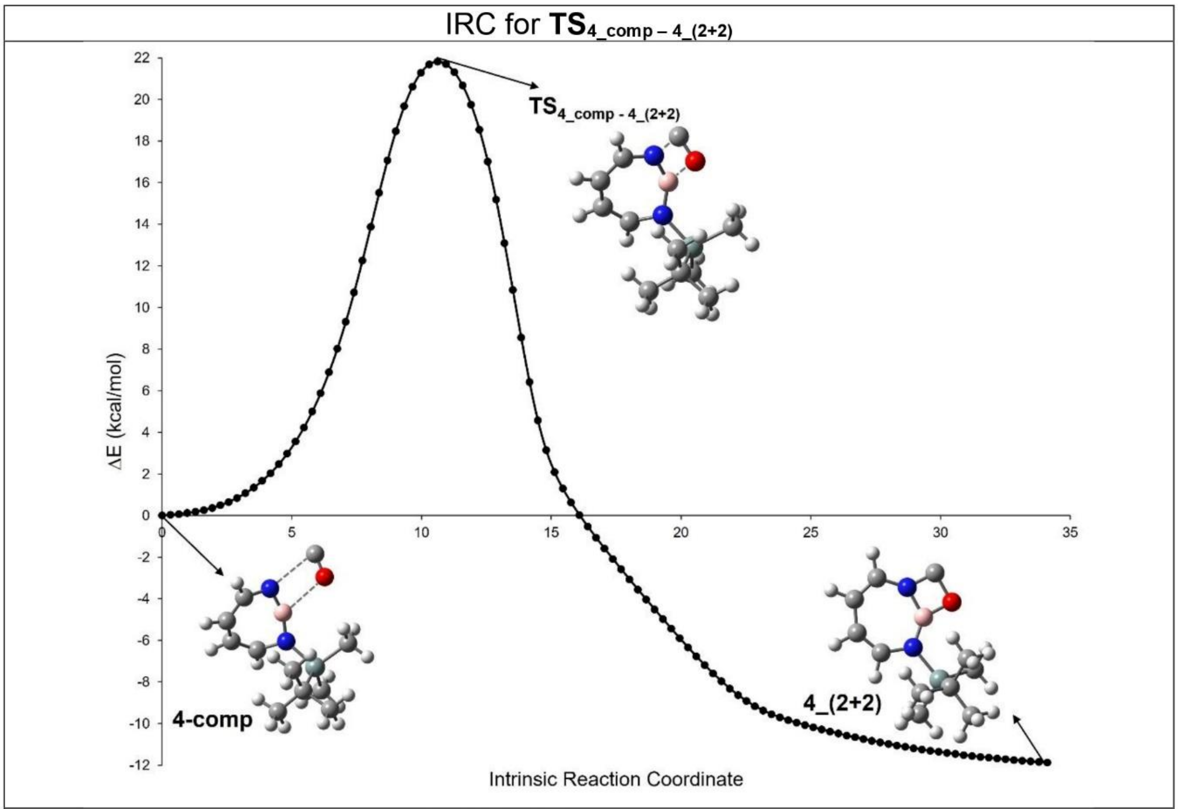
IRC for **$TS_{4\_comp' - 4}$**

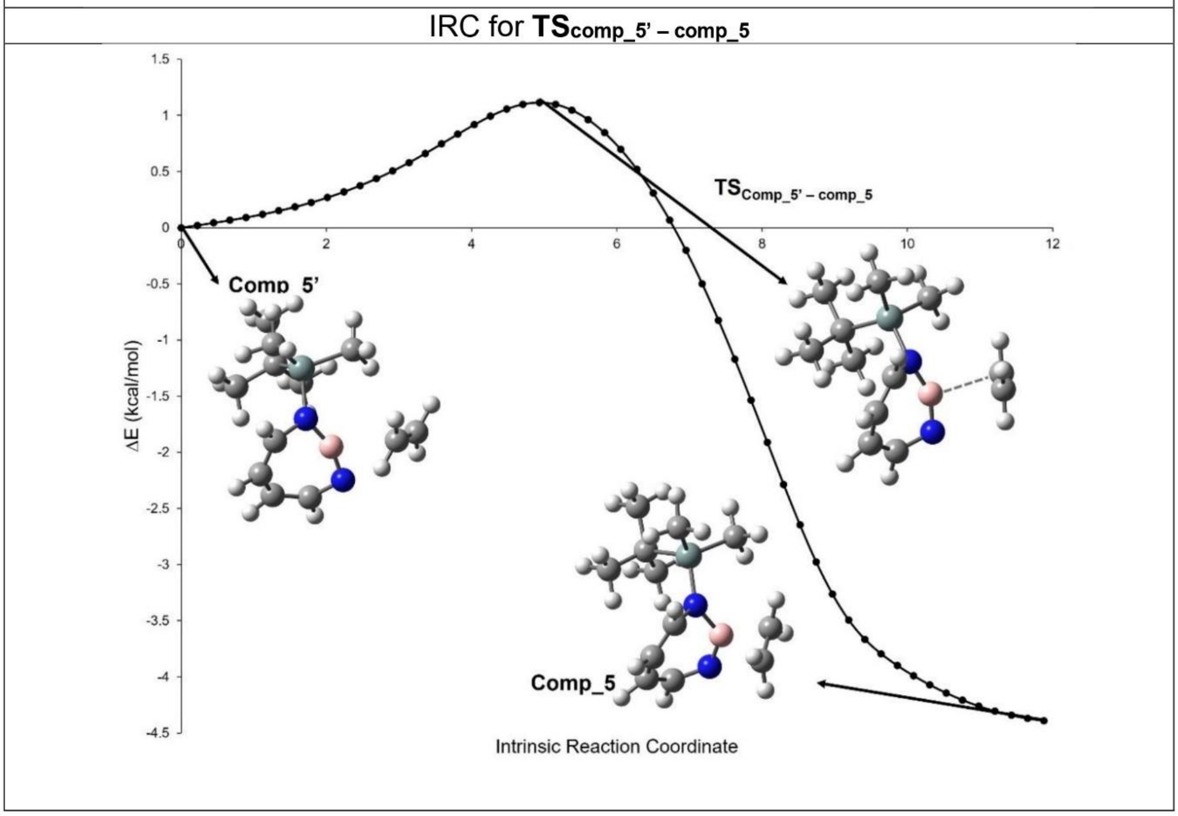


IRC for **$TS_{4 - 4\_(2+1)}$**



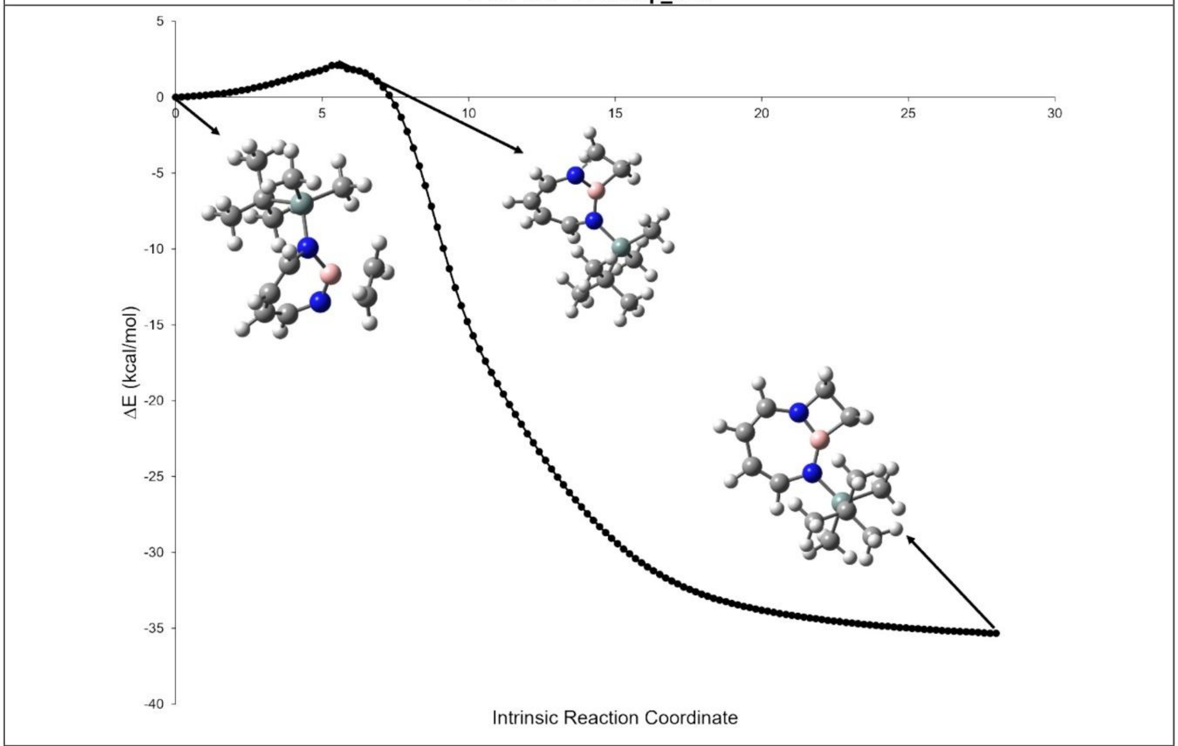
S26


IRC for TS4_comp – 4_(2+2)
TS4_comp - 4_(2+2)
ΔE (kcal/mol)
4-comp
4_(2+2)
Intrinsic Reaction Coordinate


IRC for TScomp_5' – comp_5
TSComp_5' – comp_5
Comp_5'
ΔE (kcal/mol)
Comp_5
Intrinsic Reaction Coordinate

S27

IRC for **TS$_{comp_5 - 5}$**



IRC for **TS$_{comp_5' – 6}$**

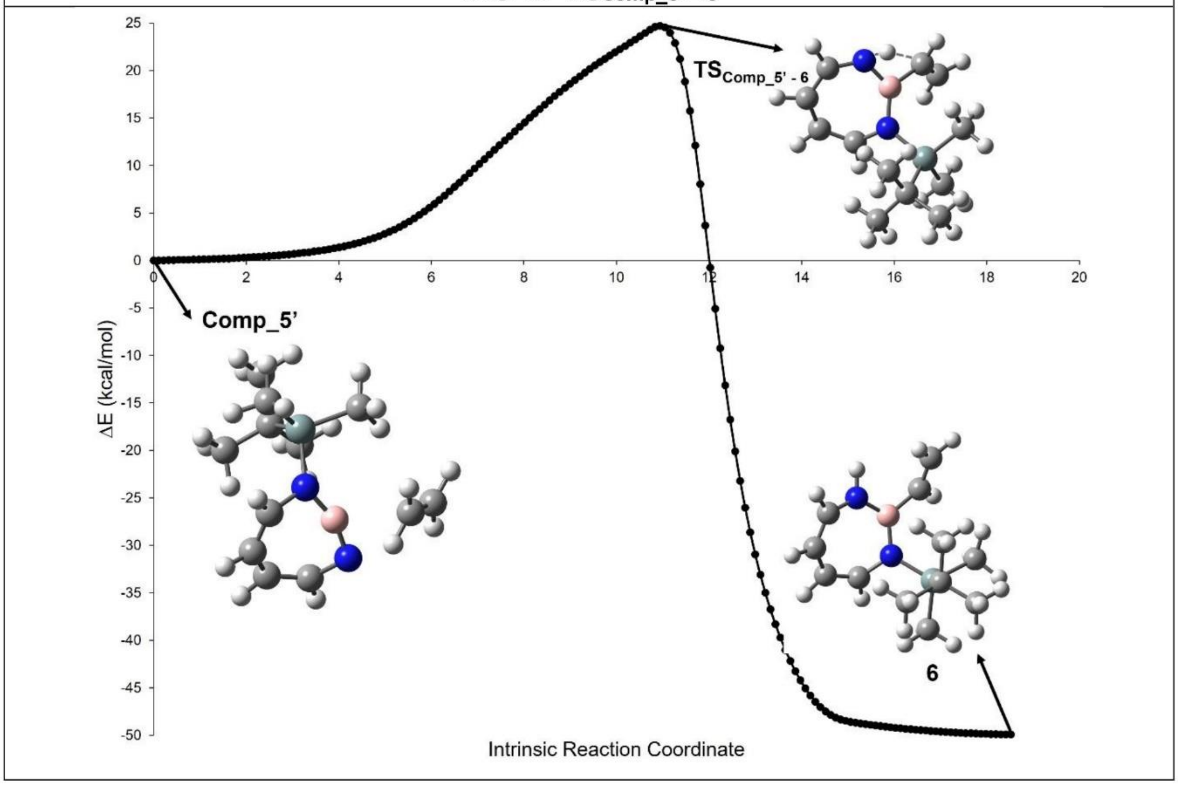


Table S11. NBO analysis of the C=C→B interaction for complex **5_comp** formed at the M06-2X/6-311+G(d,p) level of theory.

	ΔE[(a)]	%(C=C)[(b)]	%B[(b)]	Occ. (C=C)[(c)]	Occ.B[(c)]
5_comp	314.8	78.4	20.6	1.589	0.497

(a) NBO second order perturbation interaction energy associated with the R→B interaction, in kcal mol^{-1}. (b) Percentage of the donor and acceptor NBO in the corresponding NLMO. (c) Occupancy of the donor and acceptor NBO orbitals.

Table S12. NBO plots for the (a) donor NBO, (b) acceptor NBO and (c) corresponding NLMO associated with the C=C→B interaction for complex **5_comp** at the M06-2X/6-311+G(d,p) level of theory.

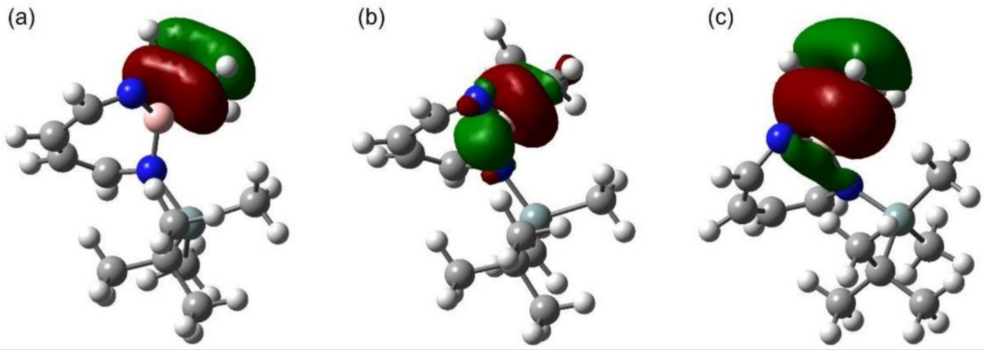


Table S13. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **3** in argon matrix.

Vibrational Mode[a]	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
99	3079	0.012	3246	0.007	CH str. (ring)
98	3043	0.008	3193	0.006	CH str. (ring)
97	3007	0.006	3155	0.017	CH str. (ring)
96			3135	0.016	CH str. (ring)
91	2961	0.070	3102	0.072	CH str. (tert-butyl grp)
89			3096	0.021	CH asym. str. (tert-butyl grp)
88	2939	0.028	3076	0.053	CH sym. str. (tert-butyl grp)
87	2935	0.050	3071	0.015	CH sym. str. (tert-butyl grp)
85	2903	0.016	3036	0.011	CH str. (methyl grp)
83	2888	0.012	3016	0.07	CH sym. str. (tert-butyl grp)
82	2864	0.054	3010	0.023	CH sym. str. (tert-butyl grp)
80	2141	1.000	2266	1.000[c]	N3 str.
79	1612	0.262	1647	0.117	ring str.
78	1513	0.431	1545	0.129	ring str.
77	1474	0.093	1520	0.009	CH scissor (tert-butyl grp)
75	1466	0.063	1511	0.016	CH scissor (tert-butyl grp)
71	1457	0.070	1483	0.083	ring breathing
66 [^{10}B]	1409	0.062	1447 [^{10}B]	0.055	CH bend (ring), BN str.
66	1402	0.102	1438	0.091	CH bend (ring), BN str.
65	1399	0.209	1433	0.166	CH wag (tert-butyl grp), CH bend (ring)
64	1363	0.020	1408	0.006	CH wag (tert-butyl grp)
62	1327	0.054	1396	0.176	CH bend (ring), N3 str.
61 [^{10}B]	1291	0.016	1310 [^{10}B]	0.021	CH bend (ring)
61	1283	0.206	1308	0.097	CH bend (ring)
60	1262	0.053	1299	0.013	CH wag (methyl grp)
59	1255	0.022	1293	0.046	CH wag (methyl grp)
58 [^{10}B]	1251	0.054	1260 [^{10}B]	0.016	CH wag (tert-butyl grp), BN str.
58	1232	0.086	1234	0.006	CH wag (tert-butyl grp), BN str.
57	1225	0.039	1226	0.039	CH wag (tert-butyl grp), ring str.

54 [10B]	1174	0.016	1193 [10B]	0.007	CH bend (ring)
54	1162	0.034	1186	0.006	CH bend (ring)
53 [10B]	1151	0.043	1181 [10B]	0.014	ring str., BN str
53	1142	0.257	1171	0.088	ring str., BN str
52 [10B]	1086	0.016	1118 [10B]	0.013	ring deformation, BN str
52	1072	0.074	1103	0.081	ring deformation, BN str
50	1016	0.068	1032	0.013	CH bend (ring)
49	1004	0.007	1025	0.003	CH wag (tert-butyl grp)
47	988	0.161	1011	0.065	ring str.
44	938	0.012	949	0.002	CH twist (tert-butyl grp)
43	935	0.004	939	0.006	CH wag (tert-butyl grp)
42	823	0.168	870	0.065	CH rock (methyl grp)
41	811	0.318	849	0.231	CH wag (methyl grp)
38	791	0.145	804	0.061	CH twist (methyl grp)
36	764	0.034	771	0.02	ring str., N3 bend
35	739	0.135	752	0.061	CH wag (ring)
34	701	0.060	706	0.001	CH wag (methyl grp)
32	684	0.054	695	0.019	ring breathing, N3 bend
31	669	0.017	669	0.003	ring breathing, N3 bend, CH wag(methyl grp)
30	614	0.028	630	0.008	ring deformation

[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 880.3 km mol^{-1}.

Table S14. Combination and overtone bands for **3** observed in experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) spectra.

Computational		**Experimental**
Combination/overtone	**ν (cm-1)**	**ν (cm-1)**
ν30 + ν36	1379	1366
2ν32	1371	1341
ν31 + ν32	1344	1313
ν4 + ν57	1268	1255
2ν29	1176	1179
ν23 + ν32	1095	1079
ν15+ ν30	862	846

Table S15. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **2** in argon matrix.

Vibrational Mode	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
74 [^{10}B]	1809	0.161	1848 [^{10}B]	0.248	BN str.
74	1751	1.000	1788	1.000[c]	BN str.
73[e]	1587	0.014	1631	0.022	C=C str. (ring)
72	1526	0.123	1544	0.116	C=C str. (ring)
71[e]	1476	-	1518	0.016	CH scissor (tert-butyl grp)
69[e]	1468	-	1519	0.065	CH scissor (tert-butyl grp)
61[d]	1393	0.123	1436	0.043	CH bend (ring)
60	1378	0.018	1430	0.014	CH wag (tert-butyl grp)
59[d]	1365	0.006	1399	0.011	CH str.(tert-butyl grp)
58[d]	1364	0.008	1398	0.013	CH scissor (tert-butyl grp)
57[d]	1345	0.008	1372	0.029	CH bend (ring)
56	1293	0.006	1306	0.070	CH wag (methyl grp)
55	1265	0.017	1299	0.121	CH wag (methyl grp)
54	1257	0.132	1283	0.108	CH bend (ring)
53	1219	0.031	1248	0.029	CH bend (ring)
49	1155	0.006	1162	0.060	ring str.
48	1050	0.567	1057	0.417	ring str.
46	1008	0.009	1027	0.025	CH twist (tert-butyl grp, methyl grp)
45	1005	0.009	1023	0.023	ring breathing
40	924	0.013	948	0.055	CH wag (ring), CH twist (tert-butyl grp)
39	900	0.005	918	0.017	CH bend (ring)
38	857	0.005	878	0.025	ring deformation
37	840	0.385	867	0.226	CH twist (methyl grp)
36	809	0.232	844	0.376	CH rock (methyl grp)
34	796	0.056	810	0.016	CH wag (ring)
33	787	0.005	798	0.123	CH wag (methyl grp)
31	736	0.101	751	0.144	CH wag (ring)
30	688	0.120	701	0.006	CH twist (methyl grp)

29	684	0.010	690	0.064	CH wag (ring), CH wag (methyl grp)
28	662	0.011	674	0.026	ring str., CH wag (methyl grp)
27	600	0.031	614	0.030	ring breathing, CH twist (tert-butyl grp, methyl grp)
25	504	0.077	522	0.110	ring str., CH str. (tert-butyl grp)

[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 352.9 km mol^{-1}. [d] these peaks are observed in the irradiation spectrum see Figure1 but are not visible in the difference spectrum as their intensity is low. [e] these peaks are only observed in the experiment with C_2H_4 but not observed in with CO and Ar due to the overlapping of peaks of **3** and **4** in the same region.

Table S16. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **4** in argon matrix.

Vibrational Mode	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
80	2112	1.000	2146	1.000[c]	CO str.
79	1595	0.029	1608	0.045	C=C str. (ring)
74 [^{10}B]	1474	0.030	1502 [^{10}B]	0.025	BN str., C=C str. (ring)
71	1467	0.074	1484	0.113	BN str., C=C str. (ring)
69	1426	0.014	1469	0.013	CH Scissor (methyl grp)
65	1391	0.003	1430	0.006	CH wag (tert-butyl grp)
63	1363	0.002	1400	0.005	CH wag (tert-butyl grp)
60	1254	0.028	1294	0.039	CH wag (methyl grp)
58	1232	0.068	1265	0.028	CH bend (ring)
54 [^{10}B]	1128	0.006	1159 [^{10}B]	0.005	ring str.
54	1122	0.014	1154	0.024	ring str.
53	1063	0.068	1102	0.093	ring str.
51	1005	0.018	1029	0.041	ring str. ,CH wag (tert-butyl grp)
52 [^{10}B]			1042 [^{10}B]	0.017	ring str. ,CH wag (tert-butyl grp)
49	945	0.007	977	0.012	CH twist (ring)
48	934	-	964	0.008	CH twist (ring)
41	835	0.034	860	0.060	CH twist (methyl grp)
40	822	-	836	0.097	CH wag (ring), CH twist (methyl grp)

38	805	0.026	801	0.028	CH wag (ring)
37	778	0.016	790	0.042	CH wag (methyl grp))
35	733	0.025	751	0.073	CH wag (ring)
33	671	0.015	672	0.021	CH wag (methyl grp)
31	588	0.014	599	0.027	ring str., CH twist (methyl grp, tert-butyl grp)
[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 1064.2 km mol^{-1}.					

Table S17. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **4** ($C^{18}O$) in argon matrix.

Vibrational Mode	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
80	2065	1.000	2099	1.000[c]	CO str.
79	1595	0.047	1608	0.046	C=C str. (ring)
74 [^{10}B]	1474	0.045	1502 [^{10}B]	0.027	BN str., C=C str. (ring)
71	1467	0.112	1483	0.120	BN str., C=C str. (ring)
69	1424	0.011	1469	0.014	CH Scissor (methyl grp)
65	1391	0.002	1430	0.006	CH wag (tert-butyl grp)
63	1363	0.003	1400	0.005	CH wag (tert-butyl grp)
60	1254	0.031	1294	0.041	CH wag (methyl grp)
58	1233	0.053	1265	0.029	CH bend (ring)
54 [^{10}B]	1126	0.008	1159 [^{10}B]	0.005	ring str.
54	1121	0.014	1154	0.025	ring str.
53	1063	0.074	1102	0.097	ring str.
51	1005	0.024	1029	0.043	ring str. ,CH wag (tert-butyl grp)
52 [^{10}B]			1042 [^{10}B]	0.018	ring str. ,CH wag (tert-butyl grp)
49	945	0.006	977	0.012	CH twist (ring)
48	938	0.005	964	0.008	CH twist (ring)
41	835	0.047	860	0.063	CH twist (methyl grp)
40	821	-	836	0.100	CH wag (ring), CH twist (methyl grp)
38	805	0.036	801	0.029	CH wag (ring)
37	778	0.030	790	0.044	CH wag (methyl grp))

35	732	0.025	751	0.076	CH wag (ring)
33	671	0.023	672	0.022	CH wag (methyl grp)
31	590	0.011	598	0.029	ring str., CH twist (methyl grp, tert-butyl grp)
[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 1024.2 km mol^{-1}					

Table S18. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **4** (^{13}CO) in argon matrix.

Vibrational Mode	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
80	2064	1.000	2096	1.000[c]	CO str.
79	1595	0.046	1608	0.047	C=C str. (ring)
74 [^{10}B]	1474	0.052	1502 [^{10}B]	0.027	BN str., C=C str. (ring)
71	1467	0.128	1483	0.121	BN str., C=C str. (ring)
69	1425	0.012	1469	0.014	CH Scissor (methyl grp)
65	1392	0.004	1430	0.006	CH wag (tert-butyl grp)
63	1363	0.006	1400	0.005	CH wag (tert-butyl grp)
60	1255	0.044	1294	0.041	CH wag (methyl grp)
58	1231	0.057	1265	0.030	CH bend (ring)
54 [^{10}B]	1128	0.012	1159 [^{10}B]	0.005	ring str.
54	1125	0.019	1154	0.026	ring str.
53	1063	0.017	1102	0.099	ring str.
51	1004	0.036	1029	0.044	ring str. ,CH wag (tert-butyl grp)
52 [^{10}B]			1042 [^{10}B]	0.018	ring str. ,CH wag (tert-butyl grp)
49	944	0.007	977	0.013	CH twist (ring)
48	939	0.004	964	0.008	CH twist (ring)
41	837	0.057	860	0.064	CH twist (methyl grp)
40	822	-	836	0.102	CH wag (ring), CH twist (methyl grp)
38	805	0.046	801	0.030	CH wag (ring)
37	777	0.033	790	0.045	CH wag (methyl grp))
35	733	0.044	751	0.078	CH wag (ring)
33	671	0.026	672	0.023	CH wag (methyl grp)

31	590	0.010	596	0.032	ring str., CH twist (methyl grp, tert-butyl grp)
[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 1004.0 km mol^{-1}					

Table S19. Isotopic shifts observed in experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **4** in argon matrix.

Experimental	**Computational**	**Experimental**	**Computational**	**Experimental**	**Computational**
ν (cm^{-1}) (CO)	**ν (cm^{-1}) (CO)**	**ν (cm^{-1}) (C^{18}O)**	**ν (cm^{-1}) (C^{18}O)**	**ν (cm^{-1}) (^{13}CO)**	**ν (cm^{-1}) (^{13}CO)**
2112	2146	2065	2099	2064	2096
Isotopic Difference					

Table S20. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **5** in argon matrix.

Vibrational Mode	**Experimental**		**Computational**		**Assignments**
	ν (cm^{-1})	**I[b]**	**ν (cm^{-1})**	**I[b]**	
88	1637	0.402	1687	0.522	C=C str. (ring)
87	1615	0.982	1675	0.878	C=C str. (ring)
85	1481	0.049	1518	0.178	CH scissor (ter-butyl grp)
79	1457	0.144	1486	0.191	CH rock (ring), CH scissor (tert-butyl grp)
77	1433	0.022	1469	0.081	CH scissor (methyl grp)
74	1417	0.336	1449	0.139	CH scissor (C_2H_4)
73	1411	0.445	1443	0.492	CH rock (ring)
71 [^{10}B]	1383	0.441	1410	0.338	BN str., CH wag (C_2H_4), CH bend (ring)
71	1376	0.985	1402	1.267	BN str., CH wag (C_2H_4), CH bend (ring)
68 [^{10}B]	1337	0.151	1358	0.179	BN str., CH bend (ring)
68	1321	0.331	1338	0.137	BN str., CH bend (ring)
67 [^{10}B]	1297	0.041	1332	0.054	BN str., CH wag (C_2H_4), CH bend (ring)
67	1290	0.363	1320	0.985	BN str., CH wag (C_2H_4), CH bend (ring)
65	1254	0.333	1296	0.269	CH wag (methyl grp)

63	1207	0.297	1237	0.192	CH wag (C_2H_4), CH bend (ring), CH twist (tert-butyl grp)
58	1145	0.115	1173	0.143	CH wag (C_2H_4), CH bend (ring)
56	1105	0.066	1129	0.105	BN str., NC str., CH wag (C_2H_4)
55 [^{10}B]	1059	0.041	1076	0.107	Ring breathing, CH wag (C_2H_4)
54	1035	0.010	1040	0.063	Ring str., CH wag (C_2H_4)
52	1026	0.023	1027	0.087	CH twist (tert-butyl grp)
51	974	0.069	986	0.23	Ring str., CC str. (C_2H_4)
47	930	0.016	950	0.037	CH twist (C_2H_4), CH twist (tert-butyl grp), CH wag (ring)
43	890	0.038	908	0.045	Ring breathing, CH wag (C_2H_4), CC str. (C_2H_4)
42	839	0.578	867	0.555	CH twist (methyl grp)
41	828	1	848	1[c]	Ring str., CH twist (methyl grp), CH wag (C_2H_4)
39	798	0.469	819	0.14	Ring str., CH twist (methyl grp), CH wag (tert-butyl grp), CH wag (C_2H_4)
37	777	0.044	790	0.196	CH twist (methyl grp), CH wag (C_2H_4)
34	720	0.073	730	0.188	CH wag (ring), CH wag (C_2H_4)
33	718	0.073	722	0.223	Ring str., CH wag (ring), CH wag (C_2H_4)
31	679	0.060	679	0.160	CH str. (methyl grp)

[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 1064.2 km mol^{-1}.

Table S21. Infrared spectroscopic data of experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **5** (C_2D_4) in argon matrix.

Vibrational Mode	Experimental		Computational		Assignments
	ν (cm^{-1})	I[b]	ν (cm^{-1})	I[b]	
88	1636	0.308	1686	0.369	C=C str. (ring)
87	1615	0.930	1675	0.588	C=C str. (ring)
86	1474	0.092	1518	0.122	CH scissor (tert-butyl grp)
80	1455	0.135	1486	0.149	CH rock (ring), CH scissor (tert-butyl grp)
78	1421	0.040	1469	0.055	CH scissor (methyl grp)

75 [^{10}B]	1416	0.148	1451	0.111	CH rock (ring)
75	1411	0.190	1443	0.372	CH rock (ring)
73 [^{10}B]	1380	0.127	1401	0.228	BN str., CH bend (ring), CH wag (C_2H_4)
71	1372	1	1391	1[c]	BN str., CH bend (ring), CH wag (C_2H_4)
70 [^{10}B]	1337	0.102	1358	0.112	BN str., CH bend (ring)
70	1322	0.321	1340	0.152	BN str., CH bend (ring)
69 [^{10}B]	1298	0.098	1324	0.074	BN str., CH bend (ring)
69	1283	0.765	1311	0.709	BN str., CH bend (ring)
67	1253	0.134	1296	0.189	CH wag (methyl grp)
66	1212	0.120	1241	0.148	CH bend (ring), CH twist (tert-butyl grp)
62	1155	0.088	1181	0.171	BN str., CH wag (C_2H_4), CH bend (ring)
61	1102	0.062	1125	0.068	CH wag (C_2H_4), CH bend (ring)
60	1088	0.058	1110	0.046	BN str., NC str., CH wag (C_2H_4)
58	1041	0.325	1050	0.488	Ring breathing, CH wag (C_2H_4)
56	1008	0.014	1027	0.08	CH twist (tert-butyl grp)
54 [^{10}B]	975	0.008	987	0.038	Ring str., CC str. (C_2H_4)
54	966	0.011	983	0.112	Ring str., CC str. (C_2H_4)
46	878	0.010	895	0.017	Ring breathing, CH wag (C_2H_4), CC str. (C_2H_4)
45	840	0.330	867	0.401	CH twist (methyl grp)
43	813	0.384	844	0.709	Ring str., CH twist (methyl grp), CH wag (C_2H_4)
41	790	0.154	806	0.157	Ring str., CH twist (methyl grp), CH wag (tert-butyl grp), CH wag (C_2H_4)
38 [^{10}B]	778	0.013	782	0.024	CH twist (methyl grp), CH wag (C_2H_4)
38	767	0.099	780	0.081	CH twist (methyl grp), CH wag (C_2H_4)
35	716	-	725	0.222	CH wag (ring), CH wag (C_2H_4)
33	680	0.030	684	0.133	Ring str., CH wag (ring), CH wag (C_2H_4)

[a] The numbering of the vibrational modes is according to calculated spectrum. [b] Intensity relative to the strongest band. [c] Computed absolute intensity: 1024.2 km mol^{-1}

Table S22. Isotopic shifts observed in experimental and computed (B3LYP-D3(BJ)/6-311+G(d,p)) vibrational frequencies of **5** in argon matrix.

Experimental		**Computational**		**Isotopic Difference**	
ν (cm^{-1}) (C_2H_4)	**ν (cm^{-1}) (C_2D_4)**	**ν (cm^{-1}) (C_2H_4)**	**ν (cm^{-1}) (C_2D_4)**	**Experimental**	**Computational**
718	680	(ν33) 721	(ν33) 684	38	37
777	767	(ν37) 790	(ν38) 780	10	10
798	790	(ν39) 819	(ν41) 806	8	13
828	813	(ν41) 848	(ν43) 844	15	4
890	878	(ν43) 908	(ν46) 895	12	13
974	966	(ν51) 986	(ν54) 984	8	2
-	1041	(ν55) 1065	(ν58) 1050	-	-
1059	-	(ν55) 1076 [^{10}B]	(ν58) 1051 [^{10}B]	-	-
1145	1102	(ν58) 1173	(ν61) 1125	43	48
1290	1283	(ν67) 1320	(ν69) 1311	7	9
1376	1372	(ν71) 1401	(ν71) 1391	4	10

Table S23. Cartesian coordinates of stationary points at different level of theories.

CO							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	0.00000000	0.00000000	-0.64435700	C	0.00000000	0.00000000	-0.64123200
O	0.00000000	0.00000000	0.48326800	O	0.00000000	0.00000000	0.48092400

C_2H_4							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	0.00000000	0.00000000	0.66432900	C	0.00000000	0.00000000	0.66289000
C	0.00000000	0.00000000	-0.66432900	C	0.00000000	0.00000000	-0.66289000
H	0.00000000	0.92290900	-1.23478300	H	0.00000000	0.92339000	-1.23097700
H	0.00000000	-0.92290900	-1.23478300	H	0.00000000	-0.92339000	-1.23097700
H	0.00000000	-0.92290900	1.23478300	H	0.00000000	-0.92339000	1.23097700
H	0.00000000	0.92290900	1.23478300	H	0.00000000	0.92339000	1.23097700

2							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	-3.23970600	0.32027300	-0.94728100	C	-3.25472900	0.16390800	-0.94876400
C	-1.32800700	-0.30197100	1.51853300	C	-1.28348600	0.00504600	1.52767600
C	-3.04451500	1.03071500	0.20190200	C	-3.02134300	1.07870000	0.02942000
C	-2.35401000	0.56706800	1.40211500	C	-2.30797600	0.84334300	1.28639200
H	-3.84158400	0.76068500	-1.73988100	H	-3.85512200	0.46248300	-1.80556500
H	-0.97669100	-0.63346000	2.48949100	H	-0.89209500	-0.13317400	2.53073600
H	-3.55573000	1.98396600	0.28427900	H	-3.49540100	2.04779900	-0.07716400
H	-2.73484800	0.95588200	2.34328900	H	-2.66028000	1.40583900	2.14642300
N	-2.78462400	-0.98558200	-1.17069300	N	-2.84953600	-1.17901400	-0.92466000
N	-0.65047900	-0.88964700	0.37197300	N	-0.65802400	-0.79597400	0.49600300
B	-1.64712500	-1.11857000	-0.54373800	B	-1.69541800	-1.17045200	-0.32022200
C	1.58877700	1.01743700	-0.27573300	C	1.61387800	0.95567400	-0.36974400
C	1.94909700	-1.41546800	1.65870600	C	1.95997500	-1.30522500	1.73641900
H	1.67437500	-2.45641500	1.84910500	H	1.70106900	-2.33371300	1.99823700
H	3.03726500	-1.36839100	1.56093000	H	3.04546300	-1.24988100	1.61730900
H	1.67255800	-0.82641200	2.53648700	H	1.68957100	-0.66180600	2.57736100
C	1.43584400	-1.91179500	-1.36136100	C	1.31937500	-2.02872900	-1.21175000
H	1.13363400	-2.93811100	-1.13621400	H	0.92304100	-3.00565900	-0.92375800
H	0.88687500	-1.58710400	-2.24978400	H	0.81063900	-1.71488200	-2.12762300
H	2.49873400	-1.92585600	-1.61587500	H	2.37895300	-2.15566100	-1.44646800
C	3.06182100	1.06500700	-0.72744400	C	2.99826500	0.87559400	-1.03343600
H	3.22628500	0.49838900	-1.64819700	H	2.97434100	0.27981900	-1.95020200
H	3.35952600	2.10179600	-0.92391100	H	3.34033500	1.88161600	-1.30193800
H	3.73952700	0.67258100	0.03728700	H	3.75104500	0.44298000	-0.36591800
C	0.68942000	1.56103800	-1.40159600	C	0.59573700	1.51108100	-1.37605300
H	0.78018000	0.97182500	-2.31902100	H	0.48625900	0.85932600	-2.24916600
H	-0.36358800	1.57245900	-1.10929100	H	-0.39212200	1.63514800	-0.92326200
H	0.97671500	2.59059800	-1.64617400	H	0.92644700	2.49135600	-1.73855700
C	1.41670500	1.89546600	0.97845700	C	1.69266500	1.89447500	0.84373600
H	1.68563000	2.93312300	0.74654300	H	1.97703500	2.90119100	0.51577900
H	0.38478600	1.89306000	1.33657000	H	0.73032200	1.97458900	1.35741600
H	2.06237200	1.56655900	1.79779900	H	2.44186500	1.55957200	1.56712100
Si	1.11305600	-0.78659500	0.10275100	Si	1.09103400	-0.78378400	0.16411200

3							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	1.68701500	2.80708300	-0.28495200	C	1.66622800	2.79807500	-0.26797000
C	0.54357600	2.17273600	0.10585100	C	0.52822400	2.16082800	0.11932000
C	2.91807800	0.71402300	-0.33578700	C	2.90597500	0.70825000	-0.32504100
C	2.88436800	2.07181400	-0.50659300	C	2.86662100	2.06158000	-0.49016500
H	1.66671400	3.88066000	-0.42004900	H	1.64465200	3.87131500	-0.39997100
H	-0.35727700	2.74797600	0.27291000	H	-0.37635400	2.73348600	0.28838400
H	3.85151700	0.18862600	-0.51528400	H	3.84286600	0.18898900	-0.50563700
H	3.77166800	2.61868500	-0.81492600	H	3.75268500	2.61177600	-0.79528500
B	1.64646600	0.01916500	0.09147800	B	1.63020400	0.01017400	0.09971100
N	0.45739300	0.81364200	0.31018700	N	0.44512500	0.80234900	0.31932400
Si	-1.16579100	0.11757300	0.74469500	Si	-1.16759400	0.09544200	0.74400000
C	-0.98906900	-1.25577200	2.00573300	C	-0.99118300	-1.31410200	1.95942200
H	-1.96732200	-1.46410700	2.44961500	H	-1.93798100	-1.44943500	2.48992600
H	-0.59576000	-2.17318000	1.57123000	H	-0.72227900	-2.24991500	1.47056700
H	-0.31445700	-0.95248500	2.81072400	H	-0.21693700	-1.09304300	2.69772800
C	-2.15958400	1.50051900	1.54961300	C	-2.15538000	1.45533600	1.58565200
H	-2.46228100	2.29147700	0.86049400	H	-2.47597100	2.25743100	0.91835700
H	-3.07221500	1.07393100	1.97518000	H	-3.05588400	1.01401800	2.02135800
H	-1.60072900	1.95881800	2.37039900	H	-1.58253500	1.90063500	2.40377000
C	-2.01844500	-0.45352000	-0.86158100	C	-2.01321400	-0.43505900	-0.86589400
C	-1.23795500	-1.59354700	-1.53901600	C	-1.18106300	-1.49126300	-1.60591600
H	-1.12354100	-2.45955500	-0.88280000	H	-0.99225700	-2.37333600	-0.98849800
H	-1.77207300	-1.92366900	-2.43822600	H	-1.71640400	-1.81644500	-2.50578700
H	-0.23875700	-1.27566600	-1.84328000	H	-0.21271400	-1.09175000	-1.91868500
C	-2.12516300	0.72944400	-1.84195400	C	-2.19980600	0.78113600	-1.78469900
H	-2.62001200	0.40701700	-2.76569400	H	-2.67581500	0.47014600	-2.72187200
H	-2.71343500	1.55412600	-1.42942000	H	-2.83968700	1.54352400	-1.33111000
H	-1.14045500	1.11846000	-2.11474000	H	-1.24144200	1.24406400	-2.03997400
C	-3.43366500	-0.95309200	-0.50664900	C	-3.38743800	-1.02764700	-0.51453200
H	-3.95205500	-1.28456700	-1.41404200	H	-3.90676900	-1.33420800	-1.42972700
H	-3.40444400	-1.80329200	0.18117100	H	-3.29515400	-1.91192600	0.12340300
H	-4.04424400	-0.16868500	-0.05019600	H	-4.02674300	-0.30204300	-0.00213300
N	1.51590000	-1.43072400	0.29162000	N	1.49515000	-1.44282600	0.29724100
N	3.25425900	-2.97921200	-0.04659200	N	3.30631700	-2.88452300	-0.07378800
N	2.45287300	-2.19149900	0.10275800	N	2.46715500	-2.15830500	0.09287600

4_comp							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	-2.34416700	2.03077200	-0.94334700	C	-2.39978700	1.95309200	-0.93564700
C	-0.64739600	1.02342100	1.55313500	C	-0.61653500	1.02656100	1.51424700
C	-1.68404300	2.75318100	0.00764000	C	-1.71365000	2.70311400	-0.03372700
C	-1.14260200	2.24558200	1.26563300	C	-1.13510100	2.23460100	1.22744100
H	-2.75831700	2.55187700	-1.80430400	H	-2.82393400	2.44841300	-1.80651600
H	-0.36273900	0.75400700	2.56438900	H	-0.28074100	0.78062300	2.51694300
H	-1.65884300	3.83003900	-0.12142200	H	-1.67195500	3.77197000	-0.21035000
H	-1.15899100	2.94239600	2.09988500	H	-1.13393500	2.94849200	2.04614800
N	-2.60533000	0.65480700	-0.87037200	N	-2.68371300	0.58300400	-0.81391500
N	-0.49926100	-0.02691300	0.55913400	N	-0.50156600	-0.03355700	0.53775500
B	-1.59366400	0.09849300	-0.25831700	B	-1.63134400	0.07733600	-0.23143000
C	2.30718400	0.28883100	-0.47409300	C	2.31263300	0.31792100	-0.41290100
C	1.58730100	-1.62781500	1.89354200	C	1.54102300	-1.74820800	1.78119800
H	0.84224400	-2.32673100	2.28296700	H	0.80850500	-2.50045800	2.08285500
H	2.52885400	-2.17160700	1.77655700	H	2.50588200	-2.24680700	1.65485000
H	1.74804600	-0.85087300	2.64493800	H	1.64726500	-1.03042400	2.59842800
C	0.55214300	-2.25566700	-0.96354200	C	0.54167600	-2.14715300	-1.12813400
H	-0.22123200	-2.90462000	-0.54517600	H	-0.28573100	-2.77795800	-0.79410700
H	0.16857300	-1.83705400	-1.89826000	H	0.23508100	-1.64984700	-2.05277700
H	1.41638500	-2.87808500	-1.20934500	H	1.38623800	-2.79902200	-1.36434000
C	3.53419800	-0.51393700	-0.94918800	C	3.45686600	-0.46149600	-1.08116500
H	3.27773100	-1.22228900	-1.74186400	H	3.11658600	-0.99727100	-1.97176900
H	4.29415700	0.16640800	-1.35143100	H	4.24598100	0.23181000	-1.39402700
H	4.00028700	-1.07411100	-0.13243500	H	3.91276000	-1.18822000	-0.40040100
C	1.68813100	1.03629100	-1.66992800	C	1.67870700	1.27282100	-1.43478000
H	1.36154100	0.34979700	-2.45677700	H	1.23985200	0.73310300	-2.28036800
H	0.82773000	1.63961400	-1.36946400	H	0.89256200	1.88407100	-0.98218100
H	2.42891000	1.71192100	-2.11391400	H	2.44230600	1.94826600	-1.83779600
C	2.75323900	1.31252300	0.58728700	C	2.87861000	1.13215000	0.76030300
H	3.48649900	2.00356300	0.15408600	H	3.61776100	1.85212200	0.38985200
H	1.91401200	1.90829700	0.95359100	H	2.09700300	1.69820400	1.27514400
H	3.22829600	0.82886300	1.44564200	H	3.37966900	0.49262300	1.49287500
Si	1.02267400	-0.91203400	0.25517100	Si	1.00810000	-0.91225800	0.19485400
C	-4.16904200	-2.25609300	-0.18014400	C	-4.07677000	-2.24604100	-0.09845900
O	-3.07372500	-2.47039800	-0.00522100	O	-2.97461600	-2.41063100	0.05620000

4_comp'							
B3LYP-D3(BJ)/6-311+G(d,p)				M06-2X/6-311+G(d,p)			
C	2.65479200	-1.46222200	-1.05956800	C	2.45673000	-1.73921500	-0.84256900
C	0.90509000	-0.91266300	1.53692600	C	0.91506400	-0.71371300	1.72385700
C	2.17342300	-2.34237200	-0.13504600	C	2.00267300	-2.43866900	0.23122900
C	1.59904700	-2.00840800	1.16505100	C	1.55426100	-1.87643700	1.50656000
H	3.12988300	-1.85372000	-1.95692100	H	2.82519800	-2.29366600	-1.70319400
H	0.61788300	-0.75364100	2.57079000	H	0.69132300	-0.36880100	2.72822800
H	2.34241700	-3.39714100	-0.32472200	H	2.08285000	-3.51900700	0.18589900
H	1.77445900	-2.73230900	1.95702000	H	1.77197300	-2.46498800	2.39315900
N	2.66049600	-0.07035500	-0.91770100	N	2.56862800	-0.34382700	-0.92380500
N	0.52958500	0.14395500	0.61223400	N	0.51853400	0.17672800	0.65333100
B	1.60784600	0.29026000	-0.22841000	B	1.55909400	0.12634300	-0.24109900
C	-2.17129700	-0.65659500	-0.44702400	C	-2.10446200	-0.59468500	-0.55688400
C	-1.81960400	1.15016200	2.08256100	C	-1.88049400	1.03543000	2.09200900
H	-1.22576000	1.94728700	2.53787100	H	-1.24768800	1.71613400	2.66725200
H	-2.85317800	1.50032800	2.01187700	H	-2.86975000	1.49203900	2.00695700
H	-1.80918800	0.29201600	2.75895200	H	-1.98957000	0.10894100	2.66093300
C	-0.99951800	2.22999700	-0.70574600	C	-1.00071200	2.30816000	-0.60058400
H	-0.39425600	2.99928900	-0.22015200	H	-0.52465800	3.09362200	-0.00906600
H	-0.53349800	1.99317000	-1.66629000	H	-0.39265500	2.14972400	-1.49599300
H	-1.98441400	2.65709200	-0.91120600	H	-1.97980200	2.67076500	-0.92365900
C	-3.55186400	-0.09160500	-0.83451100	C	-3.58207500	-0.18917100	-0.66382900
H	-3.47172400	0.72398900	-1.55860600	H	-3.70910800	0.77392900	-1.16820300
H	-4.16284800	-0.87774800	-1.29383900	H	-4.13337700	-0.93743300	-1.24488000
H	-4.10276100	0.28059500	0.03503200	H	-4.05620000	-0.12386300	0.32006500
C	-1.44158300	-1.14220400	-1.71335700	C	-1.50612500	-0.73466600	-1.96469600
H	-1.28755900	-0.33259500	-2.43305400	H	-1.60356300	0.18837400	-2.54353000
H	-0.46629900	-1.57517700	-1.47728600	H	-0.44581900	-1.00832400	-1.92825800
H	-2.03556700	-1.91542000	-2.21516600	H	-2.02811500	-1.52605400	-2.51491400
C	-2.36345700	-1.84579100	0.51336900	C	-1.99482200	-1.94540600	0.16559800
H	-2.94624300	-2.63322800	0.02014800	H	-2.57733700	-2.70146900	-0.37405400
H	-1.40817800	-2.28081800	0.81553400	H	-0.95850600	-2.29110400	0.21124100
H	-2.90672600	-1.55571300	1.41734400	H	-2.38503000	-1.89850500	1.18703100
Si	-1.14584300	0.71388200	0.38749700	Si	-1.15175100	0.73310200	0.39604700
C	2.70398700	2.77504100	-0.13645200	C	2.73568200	2.63614800	-0.64054600
O	3.54221100	3.45270100	-0.46571300	O	3.59936100	3.20960600	-1.06819400

4							
B3LYP-D3(BJ)/6-311+G(d,p)				M06-2X/6-311+G(d,p)			
C	2.42502200	-1.71401100	-0.99516600	C	2.42027100	-1.65526500	-1.00224500
C	1.01210400	-0.66239000	1.60510100	C	0.97431200	-0.77341200	1.63890700
C	2.08916100	-2.40257800	0.15098800	C	2.04047200	-2.41153800	0.06569100
C	1.66288000	-1.84003100	1.40163900	C	1.61677500	-1.92686300	1.36754400
H	2.81869900	-2.29166700	-1.83046000	H	2.80245800	-2.17212900	-1.88007700
H	0.77570300	-0.36356600	2.62493800	H	0.73934800	-0.52215500	2.67178000
H	2.30141000	-3.46777000	0.15245900	H	2.18444300	-3.48390900	-0.02194100
H	1.86472300	-2.42806700	2.29248200	H	1.83061400	-2.56741900	2.21788400
N	2.49316400	-0.36771300	-1.10078800	N	2.51287000	-0.28716300	-1.02110400
N	0.58928000	0.19945200	0.57190400	N	0.57331500	0.17019700	0.65428200
B	1.74116000	0.44225300	-0.30611800	B	1.70117800	0.43747400	-0.22314400
C	-2.08821300	-0.58410500	-0.54476900	C	-2.03581800	-0.52056200	-0.64957700
C	-1.79574600	1.10223100	2.06007600	C	-1.87384800	0.82933200	2.14421300
H	-1.19562500	1.84721100	2.59038600	H	-1.28283800	1.47914700	2.79505300
H	-2.81255600	1.49475500	1.97280100	H	-2.87865500	1.25329500	2.07221700
H	-1.84276700	0.20403800	2.68096000	H	-1.95971900	-0.14611800	2.62952300
C	-0.98593400	2.32400300	-0.66306300	C	-0.99612900	2.38448300	-0.37990300
H	-0.47270900	3.12403100	-0.12207500	H	-0.51454500	3.11815000	0.27296700
H	-0.46629200	2.16759000	-1.61232100	H	-0.44296000	2.34697700	-1.32320200
H	-1.99206500	2.68178600	-0.89823600	H	-1.99691900	2.75939500	-0.60995600
C	-3.54260400	-0.10991800	-0.72104400	C	-3.51278500	-0.11426700	-0.74691700
H	-3.60579300	0.80925500	-1.31120000	H	-3.63582800	0.89044500	-1.16358800
H	-4.12772700	-0.87457100	-1.24652300	H	-4.05031600	-0.80812400	-1.40410600
H	-4.03315300	0.07137400	0.23994800	H	-4.00539800	-0.14037600	0.22973600
C	-1.46371300	-0.84916500	-1.92700000	C	-1.40948200	-0.52825200	-2.05169800
H	-1.48580500	0.04119400	-2.56227300	H	-1.50893100	0.44224700	-2.54727400
H	-0.42565000	-1.17998400	-1.84176500	H	-0.34662900	-0.78958200	-2.01367800
H	-2.02174500	-1.63640500	-2.44852500	H	-1.91069500	-1.27199000	-2.68247600
C	-2.07287100	-1.89087800	0.27025400	C	-1.93092700	-1.93223300	-0.05375000
H	-2.65379000	-2.66363700	-0.24834600	H	-2.48594100	-2.64230300	-0.67867900
H	-1.05756200	-2.27103800	0.40193200	H	-0.89102900	-2.26728600	-0.00714300
H	-2.51763400	-1.75982900	1.26132300	H	-2.35315500	-1.98377900	0.95479000
Si	-1.06914100	0.74944900	0.36197600	Si	-1.08610300	0.69928800	0.44754800
C	2.36473600	1.86965700	-0.27597900	C	2.32472300	1.92778100	-0.25113600
O	2.75080900	2.93908700	-0.26207600	O	2.76219600	2.95895700	-0.32260100

4_(2+1)							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	3.66899500	-0.43420100	-0.42701600	C	3.67512500	-0.48656700	-0.41110700
C	0.79603100	-1.75371500	0.33086200	C	0.76454400	-1.72839900	0.33285900
C	3.29689800	-1.72317000	-0.39062200	C	3.28050100	-1.76176500	-0.34919800
C	1.98871600	-2.28664000	-0.01891700	C	1.94786100	-2.28875800	0.01105700
H	4.65685100	-0.09905800	-0.71085300	H	4.67339100	-0.17276000	-0.68154500
H	0.00967900	-2.46813900	0.54836900	H	-0.04026700	-2.42590500	0.54859900
H	4.04909900	-2.45559100	-0.66303500	H	4.02226100	-2.51583400	-0.58660900
H	1.97519700	-3.37118700	-0.02795500	H	1.91036200	-3.37218800	0.01920200
N	2.71692500	0.53679900	-0.07830400	N	2.72871500	0.50789900	-0.10830300
N	0.37283100	-0.40458800	0.47719700	N	0.36368800	-0.37144300	0.45306400
B	1.36123400	0.57723600	0.26799200	B	1.37414800	0.58364400	0.22862400
C	-2.24954400	0.06225600	-0.90347100	C	-2.27787300	0.03908200	-0.88304500
C	-2.07672300	-1.26981200	1.91653100	C	-2.05241700	-1.17761800	1.96258200
H	-1.45336300	-1.39692400	2.80585200	H	-1.37021000	-1.34370500	2.80015400
H	-3.06747400	-0.94772400	2.24923200	H	-2.99305100	-0.79682000	2.36945700
H	-2.19477600	-2.24730500	1.44316400	H	-2.26603300	-2.14435900	1.50027100
C	-1.32780600	1.70628500	1.58966700	C	-1.30468800	1.78415600	1.50135000
H	-0.83318800	1.65690700	2.56362700	H	-0.82974600	1.77033000	2.48558300
H	-0.80582800	2.45513500	0.99009000	H	-0.75381400	2.49025300	0.87533500
H	-2.35002500	2.05899600	1.75285100	H	-2.32118000	2.16711300	1.62600700
C	-3.73938600	0.37910500	-0.67261400	C	-3.78180600	0.20081100	-0.61617200
H	-3.88080300	1.34899300	-0.18673100	H	-4.00578500	1.13398400	-0.08983000
H	-4.27094300	0.41431600	-1.63099900	H	-4.33151700	0.22037000	-1.56424400
H	-4.22770700	-0.38187000	-0.05669000	H	-4.17895200	-0.62783400	-0.02230600
C	-1.62760600	1.14894200	-1.79975300	C	-1.78843100	1.19036600	-1.77309000
H	-1.71647800	2.14515500	-1.35858600	H	-2.00039600	2.16623700	-1.32765600
H	-0.56723900	0.95988000	-1.99059000	H	-0.71090700	1.13045100	-1.95853700
H	-2.13491000	1.17275500	-2.77148300	H	-2.29106900	1.15355600	-2.74643500
C	-2.12139200	-1.30203100	-1.60639800	C	-2.02984000	-1.29365900	-1.60470400
H	-2.64298800	-1.27856100	-2.57069000	H	-2.59216800	-1.31931600	-2.54535900
H	-1.07771400	-1.56011500	-1.80523500	H	-0.97203300	-1.43069900	-1.84755200
H	-2.56496600	-2.11037900	-1.01746400	H	-2.35671300	-2.15114500	-1.00747000
Si	-1.33960900	0.02235900	0.76915800	Si	-1.33655000	0.06953100	0.75959600
C	2.19234900	1.84194900	0.03619800	C	2.25509800	1.82140500	-0.00251900
O	2.57680500	2.97077800	-0.09876500	O	2.68419000	2.92838900	-0.13074000

4_(2+2)							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	3.72828000	-0.10805200	-0.43733500	C	3.72550000	-0.12156500	-0.43849200
C	0.96980300	-1.59833100	0.35444600	C	0.96287200	-1.58496300	0.37861100
C	3.45644600	-1.42429600	-0.33688600	C	3.45066300	-1.42948500	-0.33258300
C	2.20094800	-2.06190000	0.03230600	C	2.18698100	-2.05532500	0.05977200
H	4.69876300	0.27429000	-0.72881900	H	4.68904700	0.26353500	-0.74871300
H	0.22711600	-2.35130600	0.58437900	H	0.21856600	-2.33542600	0.62254700
H	4.27135200	-2.10298600	-0.55905800	H	4.25458600	-2.11645000	-0.56637500
H	2.25629100	-3.14516100	0.05432700	H	2.23766500	-3.13773600	0.09963100
N	2.75213500	0.82832000	-0.16810000	N	2.75136800	0.81610700	-0.14833600
N	0.46592500	-0.27649000	0.45394900	N	0.45762600	-0.26273600	0.45996400
B	1.33194900	0.78713200	0.21442500	B	1.33352200	0.79210600	0.22105100
C	-2.19255400	-0.05019300	-0.91785400	C	-2.18598500	-0.07195900	-0.91249400
C	-1.88711800	-1.40192000	1.88411000	C	-1.88941200	-1.35352300	1.90245600
H	-1.22883300	-1.50692700	2.75080600	H	-1.19430000	-1.49282900	2.73437800
H	-2.88728300	-1.16313300	2.25693900	H	-2.85779300	-1.07012900	2.32381300
H	-1.94910800	-2.37084900	1.38410700	H	-2.02113500	-2.31528200	1.40145500
C	-1.48432200	1.63228500	1.62896500	C	-1.47881900	1.67562500	1.57041700
H	-0.98365000	1.61332700	2.60073400	H	-0.98758900	1.68245400	2.54660000
H	-1.05799600	2.45399400	1.05257200	H	-1.04203600	2.47626100	0.97156200
H	-2.54349200	1.84212800	1.80395200	H	-2.53803900	1.89770100	1.72800100
C	-3.70897100	0.09544300	-0.68287300	C	-3.70409100	-0.07009400	-0.67514400
H	-3.95716000	1.03837200	-0.18712400	H	-4.03223500	0.82374000	-0.13554200
H	-4.24033000	0.08184800	-1.64167800	H	-4.23262700	-0.08477400	-1.63510700
H	-4.10986400	-0.72213900	-0.07635700	H	-4.02721600	-0.94831600	-0.10807300
C	-1.69764500	1.11344400	-1.79620800	C	-1.79824000	1.14806800	-1.76012800
H	-1.88606200	2.08578700	-1.33437500	H	-2.11085700	2.08453800	-1.29046700
H	-0.62549200	1.04480500	-1.99827600	H	-0.71801200	1.20302300	-1.92704800
H	-2.21505400	1.09934100	-2.76268600	H	-2.28136100	1.08986400	-2.74218900
C	-1.91478200	-1.38142800	-1.64048000	C	-1.78995300	-1.35327200	-1.66051300
H	-2.43449600	-1.39875300	-2.60572200	H	-2.32522500	-1.40731500	-2.61551000
H	-0.84907800	-1.52174600	-1.83927300	H	-0.71856800	-1.37948000	-1.87914000
H	-2.26883600	-2.24258400	-1.06605300	H	-2.04384700	-2.25498800	-1.09388600
Si	-1.30050300	-0.01408000	0.76244600	Si	-1.29920000	0.00707700	0.75613900
O	1.25519900	2.17787200	0.17730200	O	1.26192800	2.17936100	0.15599000
C	2.65699600	2.17950800	-0.23054700	C	2.63611600	2.15874600	-0.26631200

TS4_comp - 4_(2+2)							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	3.02606500	-1.15947000	-0.88604200	C	2.90395400	-1.24595600	-0.89427000
C	0.85095300	-0.88258700	1.40622500	C	0.81930000	-0.81932400	1.45366500
C	2.60496600	-2.08129500	0.01770200	C	2.44597100	-2.13090600	0.01989300
C	1.75603200	-1.85626200	1.17469800	C	1.65892000	-1.84195200	1.21453700
H	3.71698100	-1.46901500	-1.66564600	H	3.54039300	-1.60887000	-1.69631300
H	0.34418800	-0.85702300	2.36636700	H	0.34173700	-0.74251000	2.42746600
H	2.99754300	-3.08768900	-0.09047600	H	2.75667900	-3.16357200	-0.10015900
H	1.86697400	-2.57455900	1.98168300	H	1.76716700	-2.54950500	2.03070500
N	2.69645800	0.18355300	-0.87093000	N	2.68673100	0.12575700	-0.87338400
N	0.48674500	0.16622100	0.51080100	N	0.49293600	0.22548700	0.54065600
B	1.59490000	0.63894800	-0.21383900	B	1.61207600	0.61590800	-0.21627800
C	-2.18950000	-0.66476100	-0.53559100	C	-2.14881700	-0.67227800	-0.49513100
C	-1.89024100	1.09572500	2.03153100	C	-1.91440400	1.26125800	1.92830000
H	-1.30306700	1.88098900	2.51533400	H	-1.38445000	2.12372400	2.33933700
H	-2.92296400	1.44804600	1.95691400	H	-2.96667100	1.53575000	1.81260100
H	-1.89000000	0.22142900	2.68679100	H	-1.86719500	0.45229500	2.66127100
C	-1.12231500	2.26333200	-0.72631100	C	-1.05392200	2.21631200	-0.88663500
H	-0.54635100	3.05014200	-0.23418800	H	-0.44014400	3.01274500	-0.45975400
H	-0.66687700	2.07476200	-1.70237500	H	-0.61611800	1.93092100	-1.84785900
H	-2.13043700	2.64740900	-0.90279900	H	-2.04626500	2.62846400	-1.08531700
C	-3.60174300	-0.14701100	-0.86999900	C	-3.44160900	-0.12669900	-1.12149000
H	-3.57405000	0.70357100	-1.55679000	H	-3.23281500	0.56349000	-1.94363000
H	-4.18706800	-0.93828500	-1.35336900	H	-4.03781200	-0.95252500	-1.52647100
H	-4.14921000	0.15980500	0.02663000	H	-4.06495600	0.39656100	-0.38854500
C	-1.46873600	-1.06866100	-1.83513900	C	-1.29112000	-1.33395500	-1.58384600
H	-1.38051600	-0.22916300	-2.53112900	H	-0.98452100	-0.61810600	-2.35363900
H	-0.46340100	-1.44869900	-1.63663000	H	-0.38586900	-1.78281800	-1.16452000
H	-2.02996000	-1.85934100	-2.34726700	H	-1.86355300	-2.12576000	-2.08107400
C	-2.30826300	-1.89841800	0.37934400	C	-2.51009300	-1.71970500	0.56903500
H	-2.87947000	-2.68565100	-0.12760700	H	-3.04778100	-2.55353000	0.10234500
H	-1.32918500	-2.31277600	0.63121900	H	-1.61881100	-2.13250900	1.05079700
H	-2.83035000	-1.66632000	1.31211500	H	-3.15843500	-1.30237800	1.34509200
Si	-1.19808200	0.71427400	0.32847400	Si	-1.17769100	0.75919400	0.28146400
C	3.24115000	1.96719700	-0.13054900	C	3.27270200	1.88847400	-0.05191300
O	2.06040400	2.23658200	-0.06156700	O	2.12921900	2.23369300	-0.07065200

TS4_comp' - 4							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	2.58305100	-1.58367600	-0.99747900	C	2.42246900	-1.78333600	-0.85645300
C	0.93978700	-0.83673600	1.60793900	C	0.96070100	-0.68714500	1.71516200
C	2.10754700	-2.39787100	-0.01200600	C	1.97195400	-2.46031900	0.23178500
C	1.58609800	-1.97478300	1.28233300	C	1.55907500	-1.87150100	1.50516500
H	3.02569300	-2.04003600	-1.88072700	H	2.77906000	-2.35874900	-1.70832500
H	0.68910800	-0.61408900	2.63994300	H	0.76399400	-0.33013600	2.72170400
H	2.24608700	-3.46569700	-0.14589600	H	2.03743700	-3.54239800	0.20200300
H	1.76400100	-2.65757000	2.10957500	H	1.77358000	-2.45466000	2.39634800
N	2.63145000	-0.19332700	-0.93818500	N	2.55523100	-0.40100100	-0.96270800
N	0.56663000	0.17779900	0.64019200	N	0.57185300	0.20696600	0.64852900
B	1.64285800	0.29541100	-0.22331900	B	1.62437100	0.20152700	-0.25816200
C	-2.11229100	-0.61672600	-0.48868900	C	-2.05792300	-0.57123800	-0.56177700
C	-1.81524300	1.09226700	2.11274200	C	-1.83329300	1.03264200	2.10020700
H	-1.22913700	1.86639700	2.61561900	H	-1.21387800	1.72519000	2.67601600
H	-2.84596600	1.44942000	2.03650300	H	-2.83197500	1.46860100	2.01672300
H	-1.82095600	0.20488100	2.75015400	H	-1.92201400	0.10387300	2.66890300
C	-0.99469600	2.29273900	-0.61978200	C	-0.98696400	2.33860400	-0.57558900
H	-0.44137800	3.07091300	-0.08791400	H	-0.47914400	3.11496800	0.00256500
H	-0.49501000	2.11492300	-1.57599500	H	-0.44122300	2.19925300	-1.51317300
H	-1.99170000	2.68456300	-0.83721700	H	-1.98289400	2.71055000	-0.82966700
C	-3.51309100	-0.07118600	-0.82737800	C	-3.52958100	-0.15065500	-0.68827900
H	-3.46635000	0.78720900	-1.50349100	H	-3.64061300	0.80916200	-1.20248900
H	-4.10686700	-0.84686400	-1.32559100	H	-4.08263700	-0.89799000	-1.26905600
H	-4.06341800	0.23302200	0.06845900	H	-4.01434300	-0.07185000	0.28948200
C	-1.38700200	-1.01072300	-1.78886700	C	-1.44369500	-0.72160800	-1.96164700
H	-1.26701900	-0.15929400	-2.46550200	H	-1.52520300	0.20066200	-2.54449500
H	-0.39705300	-1.42770900	-1.58799700	H	-0.38711000	-1.00596400	-1.91010900
H	-1.96506400	-1.77333500	-2.32447200	H	-1.96785800	-1.50848700	-2.51645300
C	-2.25706500	-1.86309200	0.40518200	C	-1.97238300	-1.92195600	0.16413800
H	-2.82558100	-2.63763100	-0.12395200	H	-2.55193900	-2.67386500	-0.38461800
H	-1.28581900	-2.28637100	0.66980600	H	-0.93983000	-2.27560200	0.22749700
H	-2.79433500	-1.63991100	1.33153700	H	-2.37997600	-1.86990500	1.17848200
Si	-1.10978000	0.72909200	0.41249600	Si	-1.09798600	0.74402200	0.40338400
C	2.48521600	2.48123700	-0.37708600	C	2.42048900	2.27682100	-0.63049600
O	3.07704800	3.32679800	-0.82949200	O	3.00200400	3.13556800	-1.05315700

TS4 – 4_(2+1)							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	3.66975800	-0.32113300	-0.26074600	C	3.68290400	-0.31374600	-0.04103800
C	0.81104800	-1.74568900	0.24963100	C	0.80192400	-1.74719000	0.19487900
C	3.35233400	-1.62915800	-0.20999700	C	3.37392900	-1.61777600	0.02832000
C	2.03618600	-2.25063300	-0.00812600	C	2.04114100	-2.24728300	0.04439500
H	4.69067200	0.00003200	-0.43044200	H	4.71700500	0.00846700	-0.07410100
H	0.00896800	-2.46936700	0.34396300	H	-0.01557600	-2.46235800	0.16103100
H	4.17025200	-2.32994200	-0.34744000	H	4.20722500	-2.31278700	0.04744900
H	2.04814600	-3.33279900	-0.07990100	H	2.06065200	-3.32354700	-0.08567500
N	2.70767600	0.68305500	-0.11403600	N	2.71145700	0.69523400	-0.09653700
N	0.38278500	-0.40468900	0.42351800	N	0.37882400	-0.40742000	0.39003700
B	1.36421800	0.59372100	0.14670400	B	1.36532700	0.57739100	0.08011100
C	-2.28435500	0.07313400	-0.88755000	C	-2.28833100	0.07389500	-0.89923200
C	-2.02078500	-1.33691600	1.88749200	C	-2.00598000	-1.33536300	1.85954900
H	-1.39405400	-1.45169100	2.77606500	H	-1.34432800	-1.48122400	2.71714100
H	-3.02286300	-1.05246300	2.22065600	H	-2.98460200	-1.03042500	2.23955100
H	-2.10256800	-2.31352500	1.40524900	H	-2.13195700	-2.30071400	1.36449600
C	-1.33704000	1.65046100	1.63039100	C	-1.31587800	1.64961500	1.59246600
H	-0.70249100	1.62420100	2.52062900	H	-0.66681700	1.62216200	2.47170000
H	-0.99266900	2.47017200	0.99645200	H	-0.97962300	2.46723900	0.95044400
H	-2.35276800	1.89185000	1.95586500	H	-2.32474200	1.89588400	1.93406400
C	-3.75053300	0.45513700	-0.61067100	C	-3.75488500	0.42052200	-0.60383800
H	-3.83332800	1.43492700	-0.13135300	H	-3.85132600	1.39061600	-0.10691200
H	-4.31348900	0.50275500	-1.55056200	H	-4.32526500	0.47252000	-1.53853700
H	-4.24902900	-0.27786000	0.03068000	H	-4.23058800	-0.33503000	0.02889900
C	-1.64453300	1.13072300	-1.80593500	C	-1.68052600	1.15218200	-1.80799900
H	-1.65841200	2.12832100	-1.35836300	H	-1.70639700	2.14378200	-1.34640200
H	-0.60709000	0.88164800	-2.04679300	H	-0.64232500	0.92002300	-2.06642700
H	-2.19298100	1.19006300	-2.75356500	H	-2.24280900	1.21323400	-2.74704500
C	-2.23698500	-1.29411500	-1.59484200	C	-2.21923300	-1.27742900	-1.62575300
H	-2.77886100	-1.24515300	-2.54704200	H	-2.78058500	-1.22645800	-2.56612800
H	-1.21104900	-1.59959500	-1.81831400	H	-1.18841700	-1.54866200	-1.87347700
H	-2.70362400	-2.08145400	-0.99574700	H	-2.65416300	-2.08568300	-1.02995300
Si	-1.32077100	-0.01077600	0.75562100	Si	-1.31438700	-0.01275100	0.72616600
C	1.61839700	2.06004400	-0.13717300	C	1.53736600	2.04195400	-0.35264800
O	1.78118600	3.19219900	-0.33697800	O	1.70233500	3.13660800	-0.65165400

5_Comp'							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	-2.23111000	2.10853400	-0.97404600	C	2.17437800	-2.04386100	-1.01458100
C	-0.69868200	1.00435900	1.57458900	C	0.76285400	-1.02676200	1.62404900
C	-1.59827200	2.79589000	0.02068300	C	1.61048600	-2.75982000	-0.00568500
C	-1.14030200	2.24766900	1.29279900	C	1.23204000	-2.24751100	1.31206600
H	-2.59367200	2.66065400	-1.83928000	H	2.47218500	-2.57166500	-1.91845500
H	-0.47839800	0.70402800	2.59344100	H	0.57699000	-0.73790000	2.65366600
H	-1.54184300	3.87431400	-0.08360700	H	1.53648500	-3.83281300	-0.14296200
H	-1.18250700	2.92528500	2.14214400	H	1.35257400	-2.93204300	2.14685900
N	-2.53432100	0.74535600	-0.94468400	N	2.48814100	-0.67936500	-0.97523700
N	-0.52314900	-0.02628500	0.56449400	N	0.50930800	-0.00486900	0.63153200
B	-1.60122100	0.10487400	-0.28451000	B	1.55076200	-0.11496900	-0.25983200
C	2.27060000	0.31602400	-0.50480700	C	-2.18563800	-0.28333100	-0.62935700
C	1.61814000	-1.47263000	1.97670200	C	-1.75401200	1.05394500	2.15358300
H	0.88973600	-2.15531300	2.42278200	H	-1.03493200	1.58166700	2.78551700
H	2.56596800	-2.00975700	1.88209400	H	-2.66618000	1.65460300	2.11397100
H	1.77712900	-0.64540600	2.67254800	H	-2.00081600	0.10571100	2.63722200
C	0.62018400	-2.31522700	-0.83056500	C	-0.68953200	2.42941300	-0.41522500
H	-0.07743800	-3.00188600	-0.34624000	H	-0.09534600	3.07575600	0.23518400
H	0.16417800	-1.98139100	-1.76647300	H	-0.11894100	2.27098800	-1.33479700
H	1.52553700	-2.87397300	-1.08135900	H	-1.60936000	2.95826700	-0.67795400
C	3.53784300	-0.46658600	-0.90036800	C	-3.59283000	0.32963800	-0.68385200
H	3.32504600	-1.24412800	-1.63934100	H	-3.58402300	1.34468300	-1.09349300
H	4.27467300	0.21334000	-1.34440400	H	-4.23991000	-0.27702700	-1.32788600
H	4.01409000	-0.94151500	-0.03683800	H	-4.05692000	0.36577300	0.30631900
C	1.64061500	0.94223700	-1.76295000	C	-1.60749000	-0.37255800	-2.04957700
H	1.35332600	0.18437100	-2.49798300	H	-1.57823200	0.60460800	-2.54028800
H	0.75351800	1.53214400	-1.51916100	H	-0.59356100	-0.78789300	-2.04785100
H	2.36039500	1.61157100	-2.24926500	H	-2.22935000	-1.03285100	-2.66510300
C	2.65543000	1.43763000	0.47857000	C	-2.26504000	-1.69771700	-0.03635300
H	3.36628500	2.12382400	0.00221100	H	-2.94515900	-2.31293700	-0.63733900
H	1.78570000	2.02184800	0.78657600	H	-1.28617800	-2.18491600	-0.03410700
H	3.13615600	1.04311100	1.37846800	H	-2.64694500	-1.69307000	0.98931800
Si	1.02186900	-0.87548600	0.30100400	Si	-1.06066100	0.80522300	0.43360200
C	-3.10692900	-2.44551000	-0.76475200	C	2.92607300	2.53340700	-0.84634500
C	-3.18870300	-2.17231300	0.53554200	C	3.16628500	2.24331200	0.42805300
H	-2.71913000	-2.80254300	1.28367700	H	2.85474300	2.90222400	1.23177500
H	-2.57128300	-3.31519800	-1.13064800	H	2.41255700	3.44554700	-1.13201600
H	-3.73261200	-1.30586000	0.89540800	H	3.69112900	1.33449300	0.70483900
H	-3.56552400	-1.79904300	-1.50330800	H	3.23703800	1.86121800	-1.63840400

5_Comp							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	2.26659100	-1.67011000	-0.98550000	C	2.21834200	-1.68690600	-0.98909700
C	1.04626900	-0.38063400	1.57999900	C	1.04321400	-0.42527600	1.60506300
C	2.07372000	-2.23718700	0.26613900	C	1.96010100	-2.28400200	0.21960800
C	1.74376400	-1.55547300	1.47037400	C	1.67139000	-1.61948900	1.46174500
H	2.59008900	-2.33897700	-1.78378300	H	2.50718500	-2.33616800	-1.81452500
H	0.82141200	-0.00759000	2.57976300	H	0.87192600	-0.03796500	2.61013100
H	2.33988900	-3.28609400	0.36194100	H	2.12014300	-3.35668800	0.27169900
H	2.00804300	-2.04198300	2.40478200	H	1.93957800	-2.13930800	2.37648800
N	2.32943800	-0.35577500	-1.23609800	N	2.36760700	-0.35498800	-1.18851200
N	0.54914600	0.33718000	0.49694100	N	0.56868200	0.34752800	0.52997600
B	1.66831800	0.57705400	-0.45887800	B	1.68630400	0.54580800	-0.41757600
C	-2.10863200	-0.67441200	-0.47125900	C	-2.08147400	-0.63808800	-0.50233200
C	-1.82874700	1.12844500	2.05065600	C	-1.82178500	1.05738800	2.07665500
H	-1.24304000	1.90983900	2.54383100	H	-1.22440200	1.80030100	2.61224300
H	-2.86221900	1.47976900	1.98650000	H	-2.84556200	1.43536800	2.01464300
H	-1.82138000	0.24520400	2.69420000	H	-1.84163300	0.14416600	2.67680600
C	-1.28086600	2.29679400	-0.75285900	C	-1.25532100	2.31926300	-0.68122700
H	-0.89849600	3.18519500	-0.24363100	H	-0.92040100	3.20116500	-0.12905300
H	-0.73083700	2.18010900	-1.68955400	H	-0.66718300	2.24447700	-1.59981900
H	-2.32741400	2.48846600	-1.00530600	H	-2.29538300	2.49154500	-0.97076400
C	-3.61316700	-0.34916900	-0.51329500	C	-3.58546200	-0.32969100	-0.50560400
H	-3.82253600	0.55886000	-1.08687800	H	-3.81330900	0.61298100	-1.01281400
H	-4.16314300	-1.16910900	-0.99147600	H	-4.12901700	-1.12275600	-1.03301400
H	-4.03067400	-0.21842500	0.48940900	H	-3.98930500	-0.27551100	0.50986300
C	-1.59218600	-0.89273800	-1.90527000	C	-1.58101100	-0.77023800	-1.94792500
H	-1.76940300	-0.01899400	-2.53930100	H	-1.78934600	0.13086800	-2.53294200
H	-0.52109800	-1.10924000	-1.91808900	H	-0.50309600	-0.95981100	-1.98120200
H	-2.10852800	-1.74300400	-2.36782200	H	-2.08185200	-1.60952100	-2.44535400
C	-1.88993200	-1.96374600	0.34113900	C	-1.84035900	-1.96509000	0.23076400
H	-2.44889300	-2.79239400	-0.11149600	H	-2.40988900	-2.76754900	-0.25402700
H	-0.83612300	-2.24742100	0.36654900	H	-0.78371900	-2.24278500	0.21048200
H	-2.23931400	-1.86154500	1.37321800	H	-2.16263600	-1.91991700	1.27602200
Si	-1.14748800	0.76700000	0.33295100	Si	-1.12488400	0.75852800	0.35814500
C	2.12146100	2.20496700	-0.66486400	C	2.13784200	2.23594500	-0.69488300
C	3.17736000	1.61952100	0.06644700	C	3.13379900	1.65090100	0.07573700
H	3.17093200	1.62453500	1.14921600	H	3.07641400	1.67115700	1.15831100
H	1.42993100	2.86073400	-0.15479400	H	1.37337700	2.83769400	-0.22447900
H	4.06640400	1.25088500	-0.42017400	H	4.04128700	1.27094000	-0.36722900
H	2.27575100	2.40051500	-1.72018600	H	2.29400000	2.36281200	-1.75888700

5							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	-3.54119700	-0.46036000	0.51033300	C	-3.52184400	-0.45950700	0.52331400
C	-0.80384300	-1.68304800	-0.57736900	C	-0.80419000	-1.67949200	-0.60305400
C	-3.19302200	-1.75164200	0.38698600	C	-3.17232400	-1.74668900	0.41205300
C	-1.95134100	-2.27374400	-0.19091300	C	-1.94617200	-2.26831600	-0.21016000
H	-4.49876700	-0.17618400	0.93395900	H	-4.46371300	-0.16973100	0.97801200
H	-0.05112900	-2.34447100	-0.99005000	H	-0.06257800	-2.33762300	-1.04573000
H	-3.90972500	-2.49151600	0.72207600	H	-3.86962800	-2.48553300	0.78621500
H	-1.95345500	-3.34774700	-0.34877100	H	-1.96197600	-3.33751500	-0.39381400
N	-2.71708000	0.58289000	0.11860100	N	-2.71689800	0.57963400	0.08198600
N	-0.39276900	-0.31636000	-0.55263000	N	-0.38561000	-0.31919900	-0.55292700
B	-1.35166900	0.70060200	-0.27709900	B	-1.34758400	0.69795600	-0.28801200
C	2.18490000	-0.04746500	0.96134500	C	2.17175400	-0.05081500	0.96112700
C	2.09842900	-1.20576500	-1.92703100	C	2.10496700	-1.19313200	-1.91970900
H	1.51770100	-1.26917200	-2.85165200	H	1.49808300	-1.29324700	-2.82364300
H	3.11047900	-0.88781300	-2.19358300	H	3.09487800	-0.84191700	-2.22343800
H	2.17305200	-2.21036300	-1.50551300	H	2.22964100	-2.18653400	-1.48350900
C	1.54571400	1.75887400	-1.49790200	C	1.53417700	1.76506200	-1.47735600
H	0.96603800	1.84942700	-2.42013800	H	0.94852200	1.85631300	-2.39567000
H	1.23883200	2.56204300	-0.82736300	H	1.22408900	2.56181800	-0.79986400
H	2.59837000	1.91718400	-1.75019800	H	2.58420600	1.93118700	-1.73435200
C	3.68746800	0.25761000	0.81858300	C	3.68119900	0.19007500	0.81929100
H	3.86387800	1.26261700	0.42392800	H	3.89744800	1.17895200	0.40306600
H	4.18165200	0.19854000	1.79608400	H	4.16716400	0.13305100	1.80051300
H	4.18698700	-0.45671200	0.15740900	H	4.15166600	-0.55981800	0.17603700
C	1.54537100	0.97617900	1.91681500	C	1.57085700	1.00800400	1.89635900
H	1.66225700	2.00200100	1.55580200	H	1.73915300	2.02345200	1.52506100
H	0.47759200	0.78491900	2.05449200	H	0.49310800	0.86412700	2.02379900
H	2.01978500	0.91985900	2.90411500	H	2.03227200	0.93900200	2.88861500
C	2.00243500	-1.45843100	1.55136300	C	1.92788000	-1.44075700	1.56739500
H	2.46607100	-1.51506100	2.54398900	H	2.39169900	-1.50406700	2.55908000
H	0.94634000	-1.71737400	1.66364200	H	0.85974100	-1.64696800	1.68426200
H	2.47281200	-2.22496100	0.92877300	H	2.36144900	-2.23574100	0.95306800
Si	1.33836100	0.04956500	-0.74711300	Si	1.33830600	0.05242300	-0.74035500
C	-1.44126800	2.29503200	-0.21562100	C	-1.42684400	2.29251900	-0.20926900
H	-1.35697700	2.83726600	-1.15871800	H	-1.33579500	2.84393400	-1.14545400
C	-2.91293600	2.03559400	0.24216800	C	-2.89728500	2.02816500	0.23582400
H	-3.68336900	2.43178600	-0.42833200	H	-3.66214800	2.44400200	-0.42625700
H	-3.13211100	2.35401500	1.26780400	H	-3.11183900	2.32213200	1.26820000
H	-0.83033600	2.80208900	0.53297400	H	-0.81932000	2.78327600	0.55252800

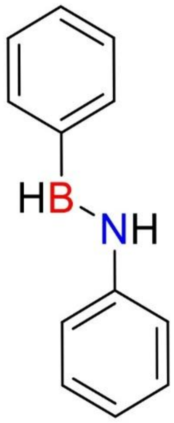
6							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	3.03108100	-0.64497100	-0.93258700	C	-3.02845000	-0.56386200	0.92153100
C	1.03655500	-1.41145900	1.29453400	C	-1.05010100	-1.43357900	-1.27261800
C	2.70890300	-1.87640900	-0.51100100	C	-2.71054600	-1.81089200	0.55849500
C	1.96082900	-2.17889500	0.70091800	C	-1.98307500	-2.16633200	-0.65760800
H	3.66345100	-0.52394400	-1.80657000	H	-3.64486200	-0.40183700	1.80028100
H	0.59927000	-1.76986700	2.22163200	H	-0.61991900	-1.82138700	-2.19227600
H	3.09975300	-2.71205300	-1.08075000	H	-3.08653200	-2.61841200	1.17572200
H	2.19498700	-3.11756400	1.19470400	H	-2.24118500	-3.11205700	-1.12352000
N	2.64269300	0.55608600	-0.32683500	N	-2.64687200	0.60602900	0.25441400
N	0.52927400	-0.15061000	0.85911600	N	-0.52722700	-0.16969300	-0.87017000
B	1.45035700	0.86576000	0.39614800	B	-1.42867000	0.87458600	-0.44103800
C	-1.72392400	-0.28440000	-1.09996300	C	1.68982600	-0.27096600	1.10607000
C	-2.02020300	-1.32636700	1.81515100	C	1.99873900	-1.41475100	-1.75808400
H	-1.73738300	-1.19310500	2.86348300	H	1.74731900	-1.29495200	-2.81565400
H	-3.10954100	-1.24677700	1.75856500	H	3.08814800	-1.37242300	-1.67462300
H	-1.74333200	-2.33921900	1.51636900	H	1.67579000	-2.40902700	-1.44311500
C	-1.87041500	1.66889000	1.31219400	C	1.90452900	1.59504000	-1.35164000
H	-1.51716400	1.89014000	2.32272600	H	1.52251600	1.82065600	-2.35018600
H	-1.57249000	2.49087300	0.66100600	H	1.66618500	2.43436500	-0.69646800
H	-2.96402500	1.64080100	1.34293700	H	2.99378100	1.51923300	-1.42332600
C	-3.25009400	-0.15991200	-1.26330100	C	3.20023500	-0.07702100	1.30153900
H	-3.60981100	0.83752900	-0.99411500	H	3.51524900	0.93789900	1.04092700
H	-3.53487900	-0.33936100	-2.30742600	H	3.46893300	-0.24604700	2.35114700
H	-3.78759700	-0.88947100	-0.65016800	H	3.78365200	-0.77976800	0.69833800
C	-1.03280300	0.76088700	-1.99436100	C	0.93455000	0.75430100	1.96472100
H	-1.30206700	1.78408000	-1.71843700	H	1.14555400	1.78441000	1.66131000
H	0.05578200	0.67455300	-1.94562700	H	-0.14816500	0.59902200	1.91200000
H	-1.32606000	0.61221300	-3.04105200	H	1.23001000	0.64926200	3.01572500
C	-1.27333300	-1.68942400	-1.54110300	C	1.28750400	-1.68256900	1.55790400
H	-1.52270200	-1.85046500	-2.59743100	H	1.49544600	-1.80777600	2.62752500
H	-0.19408400	-1.81894600	-1.42949100	H	0.21895300	-1.86227500	1.40091400
H	-1.76923000	-2.47569400	-0.96491200	H	1.84665500	-2.45463800	1.02129700
Si	-1.23898300	-0.00367200	0.72725200	Si	1.23656900	-0.04404000	-0.72520500
C	1.17764300	2.39279800	0.64160100	C	-1.09870800	2.39714100	-0.68053600
C	1.41635200	3.35834300	-0.25198800	C	-1.30366200	3.34383700	0.23742200
H	1.79674200	3.13539300	-1.24597400	H	-1.69308500	3.10155400	1.22389700
H	1.21895400	4.40634200	-0.04643300	H	-1.07043300	4.38924000	0.05996500
H	0.75498600	2.69324700	1.59820200	H	-0.66781700	2.70345300	-1.63182900
H	3.23309900	1.34108800	-0.56004800	H	-3.22115600	1.40870400	0.46714100

TS5_comp' - 5_comp							
B3LYP-D3(BJ)/6-311+G(d,p)				M06-2X/6-311+G(d,p)			
C	2.15196600	-1.95927600	-0.98840600	C	2.106024000	-1.945334000	-0.990886000
C	0.91351300	-0.73627200	1.64307700	C	0.941006000	-0.680868000	1.639829000
C	1.67027600	-2.60286900	0.11761700	C	1.642335000	-2.568340000	0.128584000
C	1.35979900	-1.98654900	1.39693200	C	1.384333000	-1.931728000	1.413925000
H	2.43353300	-2.56023000	-1.85178200	H	2.345588000	-2.561846000	-1.855645000
H	0.81583400	-0.36751200	2.65896400	H	0.859149000	-0.288955000	2.649582000
H	1.65215900	-3.68739400	0.08786900	H	1.589760000	-3.651274000	0.105551000
H	1.53125000	-2.60117600	2.27758300	H	1.586236000	-2.528563000	2.299328000
N	2.42198900	-0.60251800	-1.07506200	N	2.413222000	-0.598665000	-1.101710000
N	0.56588100	0.20402700	0.59228100	N	0.572050000	0.226970000	0.577346000
B	1.60018900	0.11618300	-0.33456300	B	1.607005000	0.122400000	-0.348718000
C	-2.13944100	-0.42616600	-0.59961700	C	-2.137060000	-0.451107000	-0.550450000
C	-1.78232800	1.04223600	2.13663300	C	-1.748497000	1.120304000	2.109276000
H	-1.14997000	1.71981200	2.71735900	H	-1.089922000	1.796487000	2.660829000
H	-2.78496200	1.47636600	2.09611500	H	-2.738765000	1.580678000	2.066423000
H	-1.85129000	0.09638300	2.67872000	H	-1.835910000	0.192577000	2.679799000
C	-0.99385900	2.45885800	-0.49016000	C	-0.986001000	2.414955000	-0.593196000
H	-0.47505000	3.20236500	0.12010700	H	-0.526512000	3.208572000	0.000849000
H	-0.46859700	2.37433500	-1.44458200	H	-0.402010000	2.289827000	-1.509249000
H	-1.99668300	2.84167600	-0.69779600	H	-1.984601000	2.752698000	-0.881926000
C	-3.57565800	0.11325700	-0.74360300	C	-3.586337000	0.049418000	-0.645773000
H	-3.60522200	1.07221600	-1.26922900	H	-3.659637000	1.006427000	-1.171124000
H	-4.18437600	-0.59293200	-1.32101800	H	-4.193231000	-0.674839000	-1.201574000
H	-4.06328500	0.24395500	0.22711000	H	-4.041362000	0.166602000	0.342454000
C	-1.51924500	-0.60621100	-1.99790600	C	-1.564807000	-0.637628000	-1.963551000
H	-1.49589700	0.33225000	-2.55963400	H	-1.601375000	0.289490000	-2.543687000
H	-0.49969500	-0.99531400	-1.94142400	H	-0.527163000	-0.986004000	-1.934395000
H	-2.11157400	-1.32122000	-2.58156600	H	-2.149157000	-1.389284000	-2.507185000
C	-2.17966300	-1.79178100	0.11090900	C	-2.116935000	-1.802488000	0.178193000
H	-2.79344600	-2.49376900	-0.46688600	H	-2.751781000	-2.519423000	-0.356257000
H	-1.18241100	-2.22422500	0.20848000	H	-1.106934000	-2.217060000	0.221205000
H	-2.61947400	-1.72008500	1.11001400	H	-2.500574000	-1.722688000	1.200025000
Si	-1.09538900	0.81145100	0.40536100	Si	-1.086251000	0.818535000	0.383804000
C	2.60627100	2.45112200	-0.74468200	C	2.578825000	2.400429000	-0.771449000
C	3.36637500	1.95136300	0.23478200	C	3.343418000	1.894850000	0.199232000
H	3.18520900	2.20023700	1.27501500	H	3.169249000	2.142760000	1.241195000
H	1.79720600	3.14075400	-0.53815600	H	1.775245000	3.093790000	-0.552790000
H	4.18380100	1.27385200	0.02456600	H	4.157744000	1.216735000	-0.022881000
H	2.79707700	2.20817200	-1.78321200	H	2.763733000	2.158890000	-1.812059000

$TS_{5\_comp\ -\ 5}$							
B3LYP-D3(BJ)/6-311+G(d,p)				**M06-2X/6-311+G(d,p)**			
C	2.75890600	-1.40817000	-0.99995200	C	2.50012900	-1.48063500	-0.97417300
C	0.81735600	-0.77861600	1.35786400	C	0.97285000	-0.50420600	1.56035800
C	2.42323700	-2.20133700	0.06541400	C	2.30944800	-2.12432500	0.21161200
C	1.69949700	-1.81054200	1.23831800	C	1.81433600	-1.56043000	1.44217600
H	3.34335500	-1.86209300	-1.79934400	H	2.93266700	-2.05030800	-1.79409700
H	0.30558800	-0.66542400	2.31284300	H	0.62043600	-0.23948400	2.55773600
H	2.80280000	-3.21963000	0.05364900	H	2.63680900	-3.15894900	0.25844200
H	1.80236900	-2.44385200	2.11370600	H	2.07127900	-2.07569500	2.36148700
N	2.59752100	-0.05696900	-1.07650300	N	2.39797800	-0.13039800	-1.18405500
N	0.47327800	0.13563100	0.36786800	N	0.49114000	0.27507800	0.50900400
B	1.63060600	0.66658100	-0.38942600	B	1.54339200	0.67727100	-0.45788300
C	-2.30163200	-0.65844000	-0.38995500	C	-2.10781200	-0.67969700	-0.55865900
C	-1.76765900	1.38812000	1.90264100	C	-1.91510900	0.86060900	2.12517400
H	-1.10994500	2.18364400	2.26460000	H	-1.31422400	1.54702000	2.72801000
H	-2.77806500	1.80009900	1.82768100	H	-2.93062700	1.26288700	2.07857600
H	-1.79108800	0.60220800	2.66169100	H	-1.96408600	-0.09733100	2.64881900
C	-1.14698900	2.15903800	-1.01889800	C	-1.36599200	2.32039100	-0.53480200
H	-0.62040900	3.03323200	-0.63054800	H	-1.01745800	3.15985900	0.07175700
H	-0.66142900	1.86215000	-1.95181400	H	-0.79068300	2.31237100	-1.46397300
H	-2.16796500	2.46802000	-1.25850600	H	-2.41168500	2.50973500	-0.79275200
C	-3.73230700	-0.13141100	-0.60994400	C	-3.62739400	-0.47620900	-0.49074400
H	-3.76659800	0.66294300	-1.36088300	H	-3.93125500	0.49262000	-0.90014800
H	-4.38150100	-0.94168000	-0.96343900	H	-4.13815200	-1.25156800	-1.07411600
H	-4.17187800	0.25759400	0.31360700	H	-3.99744900	-0.54117100	0.53689000
C	-1.74132700	-1.19679900	-1.71946400	C	-1.64862300	-0.65614600	-2.02373900
H	-1.73181500	-0.42784000	-2.49766700	H	-1.93710100	0.27284800	-2.52470400
H	-0.72020100	-1.56820600	-1.60168900	H	-0.56171500	-0.76673200	-2.10392900
H	-2.36184100	-2.02440900	-2.08446100	H	-2.10635300	-1.48560500	-2.57591100
C	-2.34397800	-1.80521800	0.63718300	C	-1.74465000	-2.04108700	0.05190400
H	-3.00057900	-2.60651000	0.27602200	H	-2.27548000	-2.84148400	-0.47769500
H	-1.35526300	-2.23964100	0.80109600	H	-0.67160800	-2.23783100	-0.02661900
H	-2.73576000	-1.47467600	1.60387600	H	-2.02553600	-2.10503000	1.10829000
Si	-1.17769100	0.75555400	0.22932900	Si	-1.21108400	0.69608100	0.39167200
C	2.10967600	2.22436700	-0.16604000	C	2.00919000	2.27407900	-0.49883300
C	3.32107200	1.53787800	0.23557900	C	3.14407300	1.54739100	-0.01527200
H	3.42928700	1.18282600	1.25422400	H	3.23998200	1.33489700	1.04488600
H	1.54623700	2.71331400	0.62238400	H	1.43108900	2.84765900	0.21386300
H	4.20373400	1.51884300	-0.38153200	H	4.02374300	1.39477700	-0.61857100
H	2.18491100	2.81457000	-1.07501100	H	2.08912100	2.69385300	-1.49488200

TS5_comp' - 6							
B3LYP-D3(BJ)/6-311+G(d,p)				M06-2X/6-311+G(d,p)			
C	2.76049900	-1.80321500	-1.11864400	C	2.65874300	-1.72833900	-1.30560300
C	0.82363700	-1.01930500	1.22114900	C	0.86113000	-1.03121400	1.15505300
C	2.32915600	-2.56858700	-0.06750800	C	2.19096000	-2.55180700	-0.33053000
C	1.59833600	-2.12882600	1.08744700	C	1.56359200	-2.15889500	0.91364900
H	3.34839300	-2.29648500	-1.89114500	H	3.17383200	-2.18338000	-2.14880600
H	0.34248500	-0.85646700	2.18400300	H	0.45839500	-0.87621200	2.15625500
H	2.63312900	-3.61156000	-0.07038200	H	2.38925300	-3.61224700	-0.45190800
H	1.63775200	-2.77478400	1.95898800	H	1.64831800	-2.85333600	1.74343700
N	2.64556400	-0.45029600	-1.23062300	N	2.67556300	-0.35360800	-1.27235900
N	0.55863400	-0.06029600	0.23981500	N	0.58689800	-0.01987600	0.21721400
B	1.73077900	0.33596600	-0.54191400	B	1.75827100	0.37348400	-0.55007200
C	-2.35612400	-0.56029800	-0.18999000	C	-2.31248300	-0.57464700	-0.13626800
C	-1.35278000	1.64232000	1.78586900	C	-1.32709900	1.68007000	1.75290500
H	-0.60492400	2.42222500	1.95368400	H	-0.66904100	2.54847300	1.84293000
H	-2.33619900	2.12088300	1.77582000	H	-2.35933300	2.03928200	1.79365100
H	-1.32681200	0.96289700	2.64173000	H	-1.16666000	1.04241700	2.62637500
C	-0.91916800	1.98770100	-1.24993300	C	-0.93151200	1.95723800	-1.29173600
H	-0.24099200	2.80899800	-1.01170400	H	-0.18156300	2.73443300	-1.13011900
H	-0.57087900	1.51979900	-2.17459500	H	-0.69341200	1.44563000	-2.22855500
H	-1.90655900	2.41457500	-1.44415900	H	-1.89933500	2.44992800	-1.41434200
C	-3.70371300	0.14167000	-0.44762200	C	-3.61184900	0.09518600	-0.61096900
H	-3.66360300	0.80089000	-1.31889100	H	-3.48394000	0.58716200	-1.57899100
H	-4.48424800	-0.60452600	-0.63897400	H	-4.39944800	-0.65868800	-0.72558900
H	-4.02755500	0.73668800	0.41199600	H	-3.97592900	0.84104700	0.10378200
C	-1.95130500	-1.36796000	-1.43710100	C	-1.82084100	-1.55309800	-1.21297300
H	-1.86175400	-0.73087700	-2.32199000	H	-1.59782000	-1.04052700	-2.15402100
H	-0.99445500	-1.87553500	-1.29270500	H	-0.91393600	-2.07572200	-0.89629900
H	-2.70918200	-2.12975200	-1.65716800	H	-2.59470700	-2.30213300	-1.41958900
C	-2.52052200	-1.52214100	1.00160900	C	-2.60317000	-1.35031400	1.15748000
H	-3.31818700	-2.24486000	0.78976500	H	-3.37762600	-2.10415900	0.97154400
H	-1.60802500	-2.09054200	1.19379100	H	-1.71764100	-1.87675900	1.52355800
H	-2.79496400	-0.99422300	1.91979700	H	-2.96765900	-0.69330000	1.95302900
Si	-1.01426100	0.75347000	0.16107400	Si	-0.98991000	0.75981900	0.14822500
C	2.35762800	1.86162000	-0.46435900	C	2.40790400	1.94027300	-0.33733800
C	2.35185100	2.66908700	0.63261900	C	2.28015400	2.62647100	0.81234600
H	2.58258800	3.72646900	0.57042000	H	2.44349900	3.69744900	0.86616100
H	2.60425700	2.31689000	-1.42204100	H	2.72124200	2.45823800	-1.23974800
H	2.11659100	2.27919900	1.61806300	H	1.99026700	2.12404500	1.73143300
H	3.15511300	0.82104500	-0.43584600	H	3.09707600	0.82947400	-0.31286700

M06-2X/6-311+G(d,p)



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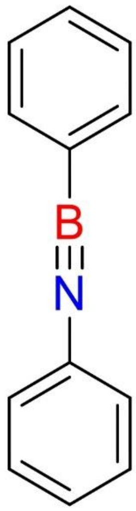
C	-2.44033800	1.04962700	-0.00001100
C	-2.96194300	-1.28863200	0.00001000
C	-3.79412400	1.35767900	-0.00001000
H	-1.72946300	1.87101800	-0.00002100
C	-4.32145000	-0.99218600	0.00001100
H	-2.64197600	-2.32551000	0.00001700
C	-4.73899400	0.33368200	0.00000100
H	-4.11656700	2.39234200	-0.00001800
H	-5.05273100	-1.79200300	0.00002000
H	-5.79639900	0.57170300	0.00000200
C	1.93988500	0.12116300	0.00000000
C	2.55014100	-1.13570100	-0.00001100
C	2.74529800	1.26281800	0.00001000
C	3.93515300	-1.23502000	-0.00000900
H	1.94410900	-2.03100900	-0.00002000
C	4.12992100	1.15426800	0.00001100
H	2.27920100	2.24319400	0.00001800
C	4.73594300	-0.09663900	0.00000200
H	4.39240700	-2.21757000	-0.00001700
H	4.73449900	2.05350700	0.00002000
H	5.81509000	-0.18442700	0.00000300
H	0.26678500	1.25187600	0.00000100
H	-0.19696400	-1.84400000	0.00000000



B	-0.56639100	0.00007400	0.00008500
N	0.67820300	0.00005700	0.00005800
C	-2.09100800	0.00003100	0.00003400
C	-2.80493400	1.20636000	-0.00013500
C	-2.80486700	-1.20633700	0.00016300
C	-4.19411400	1.20551800	-0.00017700
H	-2.26898400	2.14858100	-0.00023700
C	-4.19404700	-1.20557100	0.00012200
H	-2.26886500	-2.14852800	0.00029800
C	-4.88933100	-0.00004600	-0.00004800
H	-4.73474600	2.14436700	-0.00031000
H	-4.73462700	-2.14445000	0.00022400
H	-5.97299200	-0.00007600	-0.00008000
C	2.04880800	0.00002500	0.00002300
C	2.75798500	1.20739000	0.00015600
C	2.75792800	-1.20737400	-0.00014300
C	4.14617800	1.20187600	0.00012200
H	2.20321800	2.13758200	0.00028700
C	4.14612200	-1.20192500	-0.00017600
H	2.20311700	-2.13753900	-0.00024700
C	4.84824900	-0.00004100	-0.00004400
H	4.68271200	2.14347300	0.00022800
H	4.68261100	-2.14354800	-0.00030700
H	5.93126400	-0.00006700	-0.00007000

M06-2X/6-311+G(d,p)				
	N	-1.26767000	0.50424300	-0.00008100
	B	-0.20647400	1.46774800	0.00000400
	C	1.18600600	0.87380800	-0.00001300
	C	1.32335100	-0.48849500	0.00003300
	C	0.19641700	-1.36003200	0.00009900
	C	-1.06300200	-0.84412100	-0.00004700
	H	-2.23217500	0.80327800	-0.00013100
	H	-0.50008600	2.62001400	-0.00009000
	H	2.08731500	1.47759800	0.00004400
	H	2.30950600	-0.94569500	0.00014600
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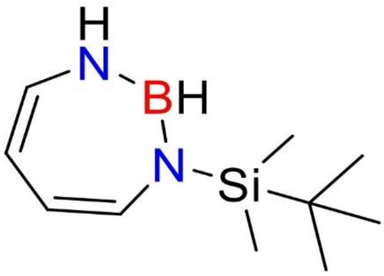	C	3.82324200	-0.64094700	-0.12100700
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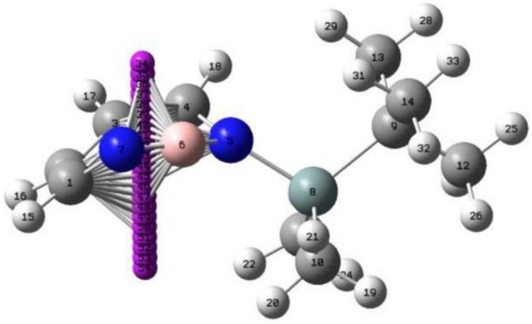
	C	2.60228000	1.52499600	-0.39142100
	C	1.31067000	1.20904200	-0.25074300
	N	0.72866700	-0.01161500	0.18286700
	B	1.35591000	-1.28485300	-0.00688600
	N	2.73464200	-1.51082700	-0.28465700
	Si	-0.96061000	0.05787300	0.73782100
	C	-2.14982200	-0.08754000	-0.73745100
	C	-1.26237300	-1.31827300	1.97403300
	C	-1.20434100	1.70879100	1.60011500
	C	-3.58535300	0.16245600	-0.25078800
	C	-1.79158600	0.95061100	-1.81069600
	C	-2.06243900	-1.48792400	-1.35981600
	H	4.77324100	-1.13978300	0.03839400
	H	4.71939000	1.21115400	0.01547800
	H	2.79959600	2.53258200	-0.74091200
	H	0.58707800	1.98022800	-0.50065800
	H	0.68141600	-2.26609700	0.07558000
	H	3.00372800	-2.47523100	-0.39765200
	H	-2.25375700	-1.20528400	2.42175200
	H	-0.52590600	-1.26779400	2.78029100
	H	-1.20402800	-2.31178800	1.52766500
	H	-0.36346600	1.91477200	2.26764600
	H	-1.29367200	2.54870400	0.90729500
	H	-2.11476700	1.68233100	2.20471600
	H	-4.28784400	0.06767200	-1.08727200
	H	-3.88762600	-0.55991500	0.51386000
	H	-3.70286700	1.16735900	0.16570900
	H	-2.49250900	0.87731800	-2.65083100
	H	-0.78388100	0.78916600	-2.20454400
	H	-1.84972100	1.97427200	-1.42722600
	H	-2.33756600	-2.26939800	-0.64570100
	H	-2.74858300	-1.56216700	-2.21201900
	H	-1.05486900	-1.70314700	-1.72692000

B3LYP/6-311+G(d,p)//M06-2X/6-311+G(d,p)



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C	-3.59466600	-0.54809400	0.30490100
C	-2.61777600	-1.52129500	-0.18345200
C	-1.33113300	-1.32225100	-0.52183400
N	-0.66994400	-0.04092300	-0.36124900
B	-1.62792400	0.87480800	-0.71138300
N	-2.78945500	1.43183200	-0.90955400
Si	0.79452400	0.18091900	0.62800300
C	2.31157500	-0.07684300	-0.47179400
C	0.69860000	1.93406300	1.27093400
C	0.71357100	-1.08700100	1.99908100
C	3.56619800	-0.17913500	0.40837400
C	2.15282400	-1.36949200	-1.28533400
C	2.45679600	1.10770200	-1.43725200
H	-4.49038400	1.35943900	0.34553400
H	-4.40798800	-0.94447400	0.90180400
H	-2.98074100	-2.53703400	-0.31311400
H	-0.73042900	-2.11628000	-0.95309100
H	1.61857400	2.21077200	1.79265300
H	-0.13234800	2.04145900	1.97248800
H	0.54927600	2.65334800	0.46110000
H	-0.25956600	-1.04001200	2.49445600
H	0.84602400	-2.10436800	1.62249100
H	1.48896600	-0.90131600	2.74654600
H	4.45838600	-0.28073300	-0.22001200
H	3.70430200	0.71164700	1.02971800
H	3.52634300	-1.05014000	1.06886900
H	3.05072300	-1.54481300	-1.88909200
H	1.30219900	-1.30591600	-1.96996500
H	2.01518300	-2.24556500	-0.64329900
H	1.56016300	1.24013000	-2.05122700
H	2.64517300	2.04356800	-0.90379400
H	3.29969800	0.93800600	-2.11698700
Bq	-2.26360500	0.06884900	-2.00000000
Bq	-2.26360500	0.06884900	-1.80000000
Bq	-2.26360500	0.06884900	-1.60000000
Bq	-2.26360500	0.06884900	-1.40000000
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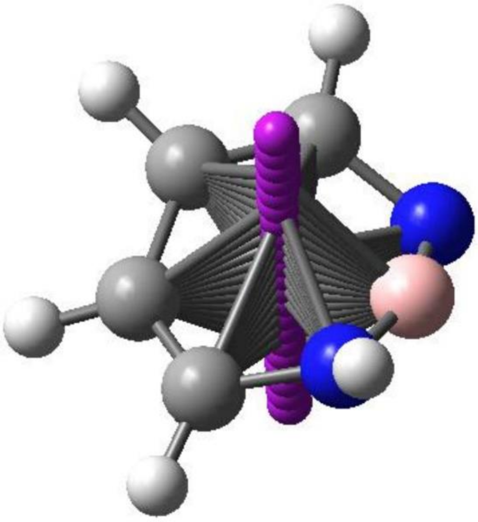
B3LYP/6-311+G(d,p)//M06-2X/6-311+G(d,p)



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C	-0.57926500	1.30529900	-0.17110300
C	-1.54459900	0.37103200	-0.15651700
N	-1.29772900	-0.97486700	0.28693400
B	-0.00880400	-1.30738800	-0.03892000
N	1.22445900	-1.15253600	-0.41624900
H	2.65794700	0.16371200	0.42265100
H	1.30068500	2.10053200	0.56092600
H	-0.88530400	2.28267500	-0.53257500
H	-2.54063000	0.57277800	-0.53334900
H	-1.87095100	-1.36808600	1.01700200
Bq	0.00000000	0.00000000	-2.00000000
Bq	0.00000000	0.00000000	-1.80000000
Bq	0.00000000	0.00000000	-1.60000000
Bq	0.00000000	0.00000000	-1.40000000
Bq	0.00000000	0.00000000	-1.20000000
Bq	0.00000000	0.00000000	-1.00000000
Bq	0.00000000	0.00000000	-0.80000000
Bq	0.00000000	0.00000000	-0.60000000
Bq	0.00000000	0.00000000	-0.40000000
Bq	0.00000000	0.00000000	-0.20000000
Bq	0.00000000	0.00000000	0.00000000
Bq	0.00000000	0.00000000	0.20000000
Bq	0.00000000	0.00000000	0.40000000
Bq	0.00000000	0.00000000	0.60000000
Bq	0.00000000	0.00000000	0.80000000
Bq	0.00000000	0.00000000	1.00000000
Bq	0.00000000	0.00000000	1.20000000
Bq	0.00000000	0.00000000	1.40000000
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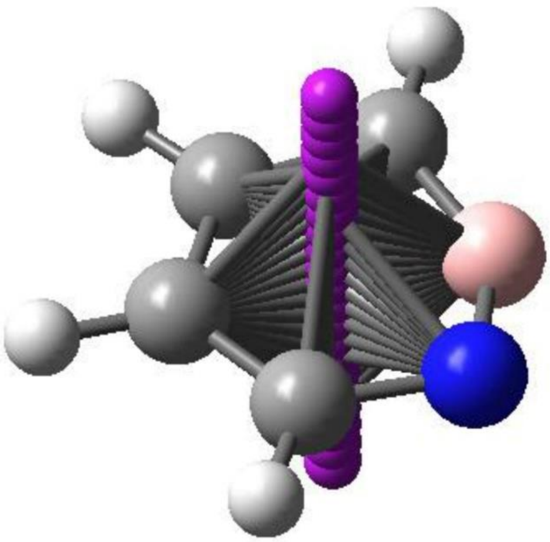

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C	1.20821900	0.50692200	0.00000000
C	1.28356900	-0.89329100	0.00000000
H	0.02886700	2.31790200	0.00000000
H	-2.15502600	1.15370900	0.00000000
H	2.14005800	1.06665900	0.00000000
H	2.22511000	-1.41638200	0.00000000
B	-0.11072200	-1.26851200	0.00000000
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Bq	0.00000000	0.00000000	-1.80000000
Bq	0.00000000	0.00000000	-1.60000000
Bq	0.00000000	0.00000000	-1.40000000
Bq	0.00000000	0.00000000	-1.20000000
Bq	0.00000000	0.00000000	-1.00000000
Bq	0.00000000	0.00000000	-0.80000000
Bq	0.00000000	0.00000000	-0.60000000
Bq	0.00000000	0.00000000	-0.40000000
Bq	0.00000000	0.00000000	-0.20000000
Bq	0.00000000	0.00000000	0.00000000
Bq	0.00000000	0.00000000	0.20000000
Bq	0.00000000	0.00000000	0.40000000
Bq	0.00000000	0.00000000	0.60000000
Bq	0.00000000	0.00000000	0.80000000
Bq	0.00000000	0.00000000	1.00000000
Bq	0.00000000	0.00000000	1.20000000
Bq	0.00000000	0.00000000	1.40000000

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	Bq	0.00000000	0.00000000	1.80000000
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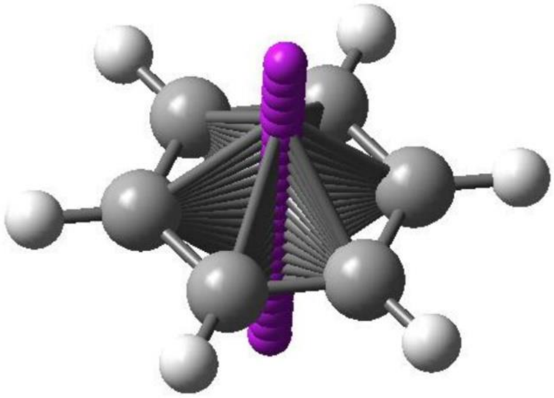	C	0.38290700	1.33759100	-0.00000100
	C	1.34986100	0.33715000	0.00002000
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	C	-0.38296500	-1.33757400	0.00000300
	C	-1.34984600	-0.33720700	0.00001600
	C	-0.96692800	1.00041900	-0.00001600
	H	0.68118600	2.37929800	-0.00000100
	H	2.40113100	0.59977000	0.00001000
	H	1.71990000	-1.77963500	-0.00001800
	H	-0.68110900	-2.37932000	-0.00000700
	H	-2.40115000	-0.59969700	0.00001500
	H	-1.71995600	1.77958100	-0.00002500
	Bq	0.00000000	0.00000000	-2.00000000
	Bq	0.00000000	0.00000000	-1.80000000
	Bq	0.00000000	0.00000000	-1.60000000
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	Bq	0.00000000	0.00000000	-0.80000000
	Bq	0.00000000	0.00000000	-0.60000000
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	Bq	0.00000000	0.00000000	-0.20000000
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	Bq	0.00000000	0.00000000	0.20000000
	Bq	0.00000000	0.00000000	0.40000000
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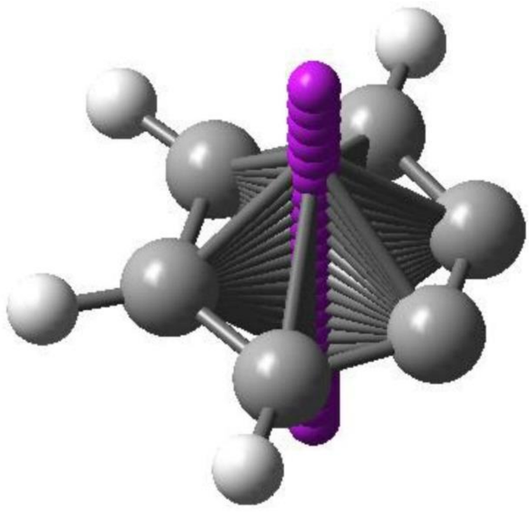	C	0.70192500	1.05194300	0.00001300
	C	-0.70191300	1.05194900	0.00001100
	C	-1.45877600	-0.13281000	0.00002600
	C	-0.61973600	-1.23033400	-0.00004200
	C	0.61972000	-1.23033300	-0.00004000
	C	1.45877700	-0.13282500	0.00003000
	H	1.22521800	2.00186800	-0.00000100
	H	-1.22519600	2.00188000	-0.00000500
	H	-2.54012000	-0.13462800	0.00000400
	H	2.54012000	-0.13465600	0.00001200
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SMD(DCM)/MN15/def2-TZVP				
7a	B	0.00062300	-0.00111800	0.00069500
	C	-0.42197300	-1.50492700	0.00104300
	C	-1.59280800	-1.93377900	0.64777200
	C	0.35295200	-2.48188300	-0.64553800
	C	-1.96435700	-3.27193500	0.66403600
	H	-2.21236400	-1.20461800	1.15908200
	C	-0.02848300	-3.81728500	-0.66144900
	H	1.26181600	-2.18339800	-1.15724900
	C	-1.18532200	-4.21525600	0.00132600
	H	-2.86239700	-3.57998900	1.18589600
	H	0.57677300	-4.54901500	-1.18292400
	H	-1.47909800	-5.25811600	0.00141200
	C	1.51398500	0.38600800	-0.00020500
	C	2.47295100	-0.41247000	0.64466000
	C	1.96983100	1.54723300	-0.64582700
	C	3.81697000	-0.06258500	0.65998700
	H	2.15357000	-1.31470700	1.15546500
	C	3.31631700	1.88730900	-0.66256900
	H	1.25514200	2.18433000	-1.15598900
	C	4.24153200	1.08547700	-0.00156100
	H	4.53464800	-0.68557200	1.18010500
	H	3.64500400	2.77854800	-1.18348500
	H	5.29106100	1.35450200	-0.00209100
	C	-1.09084900	1.11644400	0.00073000
	C	-0.87894600	2.34402100	0.64966200
	C	-2.32275400	0.93388600	-0.64894100
	C	-1.85262200	3.33433400	0.66489000
	H	0.06102800	2.51590500	1.16336500
	C	-3.28874900	1.93169200	-0.66637100
	H	-2.51715500	-0.00210300	-1.16191900
	C	-3.05722100	3.13170000	-0.00131200
	H	-1.67208900	4.26561300	1.18819100
	H	-4.22367000	1.77351500	-1.19041000
	H	-3.81382800	3.90729100	-0.00223100
7b	B	0.00017900	-0.00340600	0.00055100
	C	1.35704600	-0.77517000	0.00054000
	C	2.49334100	-0.25311000	0.63907400
	C	1.49239500	-2.01831000	-0.63800000
	C	3.70089600	-0.93544200	0.65829700
	H	2.42753700	0.70226400	1.14779400
	C	2.69813800	-2.70397500	-0.65748000
	H	0.63890000	-2.45279500	-1.14657700
	C	3.78972800	-2.15413500	0.00015000
	H	4.56511500	-0.53046100	1.16879000
	H	2.79417200	-3.65332700	-1.16841300
	C	-0.00845600	1.55758700	0.00114900
	C	1.00120500	2.29438200	-0.63834100
	C	-1.02640800	2.28254300	0.64104300
	C	0.99507500	3.68141500	-0.65753200
	H	1.80247500	1.77073100	-1.14786000
	C	-1.03613300	3.66954300	0.66083900
	H	-1.82172900	1.74956300	1.15023400
	C	-0.02442000	4.35391600	0.00177700

	H	1.77013700	4.23744800	-1.16900500
	H	-1.81744000	4.21653100	1.17254300
	C	-1.34815000	-0.78998000	-0.00002800
	C	-1.46986800	-2.03490900	0.63776500
	C	-2.49004900	-0.28012800	-0.63841800
	C	-2.66792200	-2.73394500	0.65657100
	H	-0.61169100	-2.46016600	1.14625300
	C	-3.68996700	-0.97577500	-0.65823100
	H	-2.43483800	0.67620200	-1.14659200
	C	-3.76541000	-2.19585000	-0.00096400
	H	-2.75341000	-3.68460800	1.16694000
	H	-4.55855200	-0.58002200	-1.16854200
	Cl	-0.03436900	6.08363300	0.00207700
	Cl	5.29492300	-3.00624700	-0.00072000
	Cl	-5.26103500	-3.06469700	-0.00121900
7c	B	0.00034500	0.00000800	-0.00067900
	C	1.12321600	1.08427500	-0.00037300
	C	2.34397600	0.85219200	-0.65115300
	C	0.93247800	2.31188300	0.65101500
	C	3.32152500	1.82390000	-0.65792200
	H	2.53806200	-0.07769900	-1.17224600
	C	1.93643600	3.25624500	0.65819400
	H	0.00956100	2.53651800	1.17223700
	C	3.13524400	3.02975000	0.00004600
	C	0.37762500	-1.51472200	-0.00070800
	C	1.53540300	-1.96472200	0.65105200
	C	-0.43401900	-2.45501300	-0.65245600
	C	1.84997100	-3.30665000	0.65803400
	H	2.19214600	-1.27884200	1.17270700
	C	-0.08268200	-3.78783600	-0.65914300
	H	-1.33537200	-2.15697400	-1.17457700
	C	1.05367600	-4.23087000	-0.00025800
	C	-1.50016800	0.43054000	-0.00042600
	C	-1.90954200	1.60293600	-0.65297200
	C	-2.46805100	-0.34694300	0.65267100
	C	-3.23963900	1.96428300	-0.65962000
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	C	-3.78766700	0.05118900	0.66005300
	H	-2.20158700	-1.25784200	1.17533500
	C	-4.19084900	1.20162400	0.00008300
	F	4.08876000	3.95213900	-0.00015900
	F	4.48077500	1.63040400	-1.29091600
	F	1.78184100	4.42124000	1.29136700
	F	2.93570600	-3.75634400	1.29114600
	F	1.37408900	-5.51831600	-0.00000900
	F	-0.83043900	-4.69427700	-1.29259000
	F	-3.65148900	3.06450600	-1.29346600
	F	-5.46613500	1.56739200	0.00044100
	F	-4.71935500	-0.66320700	1.29535500
Pyridine (8a)	C	-1.14259200	-0.71900000	-0.00021700
	C	-1.19399900	0.66871400	-0.00012500
	C	0.00014600	1.37642500	0.00010500
	C	1.19414300	0.66848300	0.00021300
	C	1.14243600	-0.71922400	0.00011800
	N	-0.00014600	-1.40906000	-0.00009000
	H	0.00020700	2.45938000	0.00016300
	H	-2.05840200	-1.30060300	-0.00037600
	H	-2.14917800	1.17688400	-0.00024500
	H	2.14946300	1.17638600	0.00034800
	H	2.05812500	-1.30101500	0.00017900
Acetonitrile (8b)	N	0.00000000	0.00000000	1.42906400
	C	0.00000000	0.00000000	0.27783500

	C	0.00000000	0.00000000	-1.17399100
	H	0.00000000	1.02496800	-1.54217100
	H	0.88764800	-0.51248400	-1.54217100
	H	-0.88764800	-0.51248400	-1.54217100
Benzaldehyde (8c)	C	-1.72052400	1.06346800	0.00000500
	C	-2.20659100	-0.23918400	-0.00000300
	C	-1.32860000	-1.32323200	-0.00000600
	C	0.03871500	-1.10445400	-0.00001100
	C	0.52993400	0.20257400	0.00000100
	C	-0.34921400	1.28360000	0.00001800
	H	-2.40735500	1.90032600	0.00001200
	H	-3.27547200	-0.41453600	-0.00000400
	H	-1.71764700	-2.33366700	-0.00000600
	H	0.73988900	-1.93043900	-0.00002000
	H	0.05020300	2.29239800	0.00003300
	C	1.98020100	0.46630400	-0.00000800
	H	2.25651900	1.53659400	-0.00021900
	O	2.83629200	-0.39314200	0.00002700
7a●8a	B	-0.02041000	0.01958400	-0.06134200
	C	-1.03716900	-1.15792300	-0.52390600
	C	-1.37740100	-2.28825700	0.22565500
	C	-1.72900800	-0.98291600	-1.73367300
	C	-2.33332400	-3.20620700	-0.21033500
	H	-0.90373800	-2.46835800	1.18645700
	C	-2.67834900	-1.89021700	-2.18370500
	H	-1.52043100	-0.09907300	-2.33177400
	C	-2.98386500	-3.01562100	-1.42110400
	H	-2.56982300	-4.06852600	0.40284900
	H	-3.18669000	-1.71897700	-3.12581500
	H	-3.72552900	-3.72674200	-1.76485700
	C	1.21240400	0.29677800	-1.08645600
	C	1.41187400	-0.37396900	-2.29609200
	C	2.19268600	1.23362500	-0.72198200
	C	2.51556100	-0.11619000	-3.10927100
	H	0.69658400	-1.12443300	-2.61591400
	C	3.29764600	1.50109300	-1.51960500
	H	2.08307600	1.76922900	0.21925700
	C	3.46171500	0.82487800	-2.72637200
	H	2.63576800	-0.65698800	-4.04121500
	H	4.03146400	2.23382200	-1.20348400
	H	4.32034700	1.02770000	-3.35544800
	C	-0.92495500	1.33770700	0.23995500
	C	-2.01265000	1.24245000	1.12432400
	C	-0.75653100	2.56440500	-0.40831700
	C	-2.86451900	2.31009500	1.37125200
	H	-2.19636600	0.29646800	1.62986200
	C	-1.61268800	3.64275900	-0.18170200
	H	0.05483600	2.68643500	-1.11806000
	C	-2.66601000	3.52270900	0.71378000
	H	-3.68965600	2.19746800	2.06530400
	H	-1.45365900	4.57637000	-0.70939800
	H	-3.33201200	4.35834100	0.89345800
	N	0.73760100	-0.46062900	1.30654900
	C	1.48532500	-1.57574500	1.21847400
	C	0.72301000	0.22521300	2.45586400
	C	2.22072800	-2.05085800	2.28279800
	H	1.47733000	-2.07227700	0.25658000
	C	1.44187100	-0.19011800	3.56403300
	H	0.12762500	1.12655200	2.47174600
	C	2.19917000	-1.34715400	3.48166700
	H	2.80356500	-2.95342700	2.16632900
	H	1.40290800	0.39754000	4.47017300

	H	2.77010700	-1.69386000	4.33313400
7b•8b	B	0.00412200	-0.00152100	0.63993700
	C	-0.43472200	1.49544100	0.20968700
	C	-1.54010600	2.11451800	0.80747600
	C	0.20894600	2.19925900	-0.81062100
	C	-1.98339600	3.37231700	0.42178900
	H	-2.08039000	1.59619600	1.59515200
	C	-0.21902000	3.45861900	-1.22339600
	H	1.06926400	1.75976300	-1.30495400
	C	-1.31192800	4.03372500	-0.59749800
	H	-2.83849600	3.83586600	0.89792700
	H	0.29138200	3.98747100	-2.01868400
	C	-1.07709400	-1.12450200	0.20347100
	C	-2.03280500	-0.89832000	-0.78944500
	C	-1.04201700	-2.40564300	0.76955700
	C	-2.91532400	-1.89216000	-1.20586700
	H	-2.09769200	0.07776800	-1.25914100
	C	-1.91423400	-3.41264900	0.37923000
	H	-0.30415400	-2.63070000	1.53498000
	C	-2.84761700	-3.14087400	-0.61188600
	H	-3.64796200	-1.69826200	-1.97930100
	H	-1.87265900	-4.39626600	0.83030900
	C	1.51381300	-0.37059100	0.18650700
	C	2.61110500	0.28303800	0.76235100
	C	1.78735100	-1.28870600	-0.82980600
	C	3.91644500	0.03530200	0.35993300
	H	2.44407400	1.01702900	1.54610900
	C	3.08613700	-1.55093900	-1.25900500
	H	0.97002300	-1.81867500	-1.30802800
	C	4.13928500	-0.88613900	-0.65420900
	H	4.75173600	0.54856100	0.81995800
	H	3.27796800	-2.26477600	-2.05039700
	Cl	-3.94540400	-4.38818000	-1.11306600
	Cl	-1.85368700	5.60602100	-1.09393900
	Cl	5.76450900	-1.20733600	-1.17126300
	N	0.01821300	-0.01078000	2.23137100
	C	0.03464700	-0.02671200	3.37543500
	C	0.05947200	-0.05249700	4.81736900
	H	0.06151300	0.96905900	5.19550100
	H	-0.82271400	-0.57766200	5.18195000
	H	0.95871300	-0.56978300	5.15030700
7c•8c	B	0.17808900	-0.00357100	-0.04442300
	C	0.41378300	-1.25011200	0.95892400
	C	-0.56573800	-2.19726000	1.26284400
	C	1.65249300	-1.35743100	1.60355500
	C	-0.30920600	-3.20571300	2.17491900
	H	-1.54789500	-2.19177700	0.80322500
	C	1.88613900	-2.36508700	2.51481800
	H	2.45202800	-0.65142100	1.40392800
	C	0.91224000	-3.30573800	2.81310400
	C	-0.15218900	1.38027800	0.72489300
	C	-0.21032300	1.48396600	2.11515900
	C	-0.41540100	2.52941100	-0.03443000
	C	-0.51296600	2.69301400	2.71666100
	H	-0.02096700	0.63014700	2.75600900
	C	-0.72462100	3.72249900	0.58245100
	H	-0.37597400	2.50670600	-1.11904200
	C	-0.77554000	3.82297600	1.96512700
	C	1.38786000	0.13051800	-1.10610200
	C	1.47608800	-0.75140800	-2.18951100
	C	2.41222500	1.06424200	-0.93276800
	C	2.54413600	-0.68675500	-3.05969400

	H	0.71711100	-1.50527200	-2.36684700
	C	3.47960300	1.10595600	-1.81019400
	H	2.39756200	1.77458700	-0.11322300
	C	3.56055200	0.23851900	-2.88432700
	F	1.15118600	-4.28299500	3.68708600
	F	-1.24504000	-4.11839200	2.46161800
	F	3.06559300	-2.46968100	3.13689900
	F	-0.56606300	2.79944100	4.04906400
	F	-1.06961600	4.98190200	2.55159100
	F	-0.97986300	4.82363900	-0.13258900
	F	2.63264500	-1.52119500	-4.10316400
	F	4.58827600	0.29235800	-3.73180200
	F	4.46544100	1.99676700	-1.64763900
	O	-1.07217300	-0.37885600	-0.92876600
	C	-2.25703900	-0.13421700	-0.62506400
	H	-2.46799200	0.41025100	0.30036800
	C	-3.36204600	-0.54338300	-1.44251900
	C	-4.65147400	-0.22293200	-0.99975700
	C	-3.16729000	-1.23960300	-2.64520100
	C	-5.74788700	-0.59955500	-1.75703000
	H	-4.77327500	0.31665900	-0.06748300
	C	-4.26565600	-1.61053100	-3.39392000
	H	-2.16163000	-1.47432000	-2.97115400
	C	-5.55071000	-1.29051300	-2.94849900
	H	-6.74940300	-0.35888200	-1.42653000
	H	-4.13456900	-2.14710200	-4.32423300
	H	-6.40736900	-1.58504200	-3.54201400
1	N	-1.32421600	-0.76236700	0.00000000
	C	-1.23140100	0.59267800	0.00000000
	C	0.00000000	1.23287200	0.00000000
	C	1.20756300	0.49979400	0.00000000
	C	1.28494700	-0.89731200	0.00000000
	H	0.03736000	2.31418300	0.00000000
	H	-2.15194700	1.16921700	0.00000000
	H	2.13787200	1.06095500	0.00000000
	H	2.22640100	-1.42114700	0.00000000
	B	-0.10936500	-1.27096800	0.00000000
1●pyridine	N	-1.39861400	-1.20960700	0.19692700
	C	-2.73173300	-1.23308100	0.20175400
	C	-3.53521400	-0.11143300	0.02045900
	C	-2.94054400	1.14195500	-0.18859900
	C	-1.56215400	1.29412100	-0.21020000
	H	-4.61376000	-0.21442800	0.03682300
	H	-3.22140700	-2.19608700	0.35855000
	H	-3.58904500	2.00135900	-0.34044400
	H	-1.16906800	2.29048700	-0.39447900
	B	-0.78399900	0.03501100	0.00080900
	N	0.77564800	0.02300100	0.00361700
	C	1.42702200	-1.13762100	-0.19196400
	C	1.47261400	1.15682800	0.19797200
	C	2.80477400	-1.19593500	-0.20257300
	H	0.79278200	-2.00128600	-0.33328400
	C	2.85105100	1.16438200	0.19829400
	H	0.89107200	2.05230700	0.36258600
	C	3.53164900	-0.02929900	-0.00582700
	H	3.29474400	-2.14524100	-0.36551400
	H	3.37702400	2.09400700	0.36177100
	H	4.61362300	-0.04942400	-0.00975200
1●acetonitrile	N	-0.71706000	-1.25219300	-0.00006000
	C	-2.05112500	-1.23967700	-0.00008300
	C	-2.82666800	-0.08245800	-0.00011000
	C	-2.21091400	1.17742400	-0.00010800

	C	-0.82897800	1.29863700	-0.00008200
	H	-3.90714500	-0.16495500	-0.00012900
	H	-2.56578600	-2.20181500	-0.00008700
	H	-2.84268000	2.06195200	-0.00012300
	H	-0.38850000	2.29132200	-0.00007600
	B	-0.09487200	0.00260000	-0.00006500
	N	1.43203600	-0.00925100	0.00001100
	C	2.57686500	-0.00792200	0.00011300
	C	4.01624300	-0.00518600	0.00028500
	H	4.37377400	0.50989000	-0.89118300
	H	4.37355200	0.51001000	0.89177300
	H	4.37377600	-1.03420000	0.00039800
1●benzaldehyde	N	-1.67715400	0.03767400	1.21422700
	C	-2.64621000	-0.88087300	1.25305600
	C	-3.53010300	-1.13304200	0.20800200
	C	-3.44447000	-0.38279300	-0.97674900
	C	-2.49007000	0.61045900	-1.13646700
	H	-4.28612800	-1.90121600	0.31892000
	H	-2.74719900	-1.47043200	2.16589500
	H	-4.15342400	-0.59550200	-1.77325400
	H	-2.46243600	1.16921200	-2.06718800
	B	-1.58625000	0.77774300	0.03482500
	O	-0.52074500	1.83361200	0.01560900
	C	0.72501000	1.76520900	0.10709700
	C	1.57823800	0.61726800	0.00344100
	H	1.22462600	2.72278100	0.26111600
	C	1.15290100	-0.67855900	-0.34061500
	C	2.94146300	0.87373700	0.22658500
	C	2.08646500	-1.68982300	-0.44499600
	H	0.10801100	-0.88513500	-0.52682100
	C	3.86711200	-0.14994000	0.13643700
	H	3.25430200	1.88244400	0.47013700
	C	3.43588300	-1.42907100	-0.19853000
	H	1.77038800	-2.68878400	-0.71427200
	H	4.91566200	0.04413700	0.31798200
	H	4.15616800	-2.23425200	-0.27467700
2	C	-3.30564700	0.08819100	-0.94675300
	C	-1.27276500	0.19137300	1.49194700
	C	-3.06131700	1.08384800	-0.05817300
	C	-2.32923000	0.97310000	1.20362500
	H	-3.90545100	0.30773600	-1.82662100
	H	-0.83690800	0.16952200	2.48539800
	H	-3.52514500	2.04410800	-0.25589700
	H	-2.67686000	1.60830200	2.01253900
	N	-2.89196300	-1.24944700	-0.78912200
	N	-0.66230900	-0.67626800	0.51791700
	B	-1.71330600	-1.14543700	-0.22206100
	C	1.67152600	0.89415800	-0.41011900
	C	1.90900500	-1.23706100	1.79314000
	H	1.64435000	-2.25287700	2.09654500
	H	2.99662400	-1.18864200	1.68577900
	H	1.62735200	-0.55659100	2.60139900
	C	1.22767900	-2.07450000	-1.10538900
	H	0.74279800	-3.00352400	-0.79312300
	H	0.76576700	-1.74803300	-2.04237300
	H	2.27670200	-2.30089000	-1.31219500
	C	3.02498000	0.70120900	-1.09967800
	H	2.93518200	0.08421500	-1.99815300
	H	3.42937700	1.67459000	-1.40196700
	H	3.75924800	0.23061100	-0.43693900
	C	0.66691400	1.46007800	-1.41431400
	H	0.46843000	0.76027500	-2.23337700

	H	-0.28827300	1.69657200	-0.93534400
	H	1.05992900	2.38379400	-1.85574700
	C	1.83909100	1.87627800	0.75026500
	H	2.15022800	2.85500900	0.36521700
	H	0.90541100	2.02053100	1.30308100
	H	2.60323200	1.53903600	1.45643800
	Si	1.07807400	-0.77547100	0.20476900
2●pyridine	C	0.15148100	3.06980900	-0.78180400
	C	0.63179200	1.26093800	1.66342300
	C	1.01098000	3.27543900	0.25868900
	C	0.98548700	2.55086200	1.51406900
	H	0.24976600	3.74842100	-1.63151300
	H	0.60525700	0.81659100	2.65873800
	H	1.68190600	4.12615400	0.18873000
	H	1.27700400	3.08732200	2.41335400
	N	-0.89346300	2.19573000	-0.83027500
	N	0.27294000	0.41045500	0.57877800
	B	-0.85063200	1.01829600	-0.14546200
	C	2.73570000	-0.78558400	-0.62447100
	C	1.40980300	-1.96253900	1.86617400
	H	0.49225500	-2.02895400	2.45960100
	H	1.76368900	-2.98184800	1.68769600
	H	2.16416300	-1.45240400	2.47251800
	C	0.00407500	-2.08820900	-0.86681800
	H	-0.82891400	-2.55347300	-0.33315700
	H	-0.40942500	-1.47615600	-1.67518300
	H	0.58598000	-2.89039700	-1.33080600
	C	3.53775900	-2.08575200	-0.68320900
	H	2.97619800	-2.89633200	-1.15923500
	H	4.45543200	-1.93425700	-1.26566000
	H	3.83317700	-2.42060100	0.31570700
	C	2.45482800	-0.29305400	-2.04458600
	H	1.95761800	-1.05854000	-2.64794900
	H	1.82085400	0.60171800	-2.03785500
	H	3.39435000	-0.03153100	-2.54772100
	C	3.55584700	0.27407800	0.11078600
	H	4.53876700	0.38230100	-0.36596600
	H	3.05951200	1.24776100	0.08065300
	H	3.72471100	0.01005200	1.16033600
	Si	1.09604300	-1.07718000	0.25662700
	N	-2.19851100	0.21327300	-0.09373300
	C	-3.12162800	0.41197500	-1.05269300
	C	-2.44474200	-0.64778400	0.90845800
	C	-4.32456700	-0.26069200	-1.03864900
	H	-2.84528600	1.12805000	-1.81346300
	C	-3.63518300	-1.34026300	0.98632700
	H	-1.65624700	-0.75505500	1.64149500
	C	-4.58955800	-1.14993400	-0.00398800
	H	-5.04002300	-0.08601100	-1.82930500
	H	-3.80360100	-2.01771600	1.81104900
	H	-5.52780000	-1.68800500	0.02883000
2●acetonitrile	C	-0.84950000	2.89186200	-1.01292400
	C	-0.10353500	1.35997700	1.56274600
	C	-0.06514400	3.31262900	0.01872500
	C	0.01562900	2.67819200	1.32116700
	H	-0.85845100	3.51748700	-1.90674100
	H	-0.06018200	0.99263600	2.58729900
	H	0.44930400	4.26093900	-0.10275600
	H	0.19200100	3.31813000	2.18154600
	N	-1.72021000	1.83719700	-1.01141700
	N	-0.29023100	0.37905400	0.54830500
	B	-1.46210400	0.74010500	-0.25377100

	C	2.29683200	-0.56041500	-0.57875700
	C	1.24466900	-1.57434100	2.10638600
	H	0.36754700	-1.70844800	2.74590800
	H	1.76344200	-2.53554200	2.04776400
	H	1.91636600	-0.86683700	2.60086400
	C	-0.17953800	-2.32899700	-0.50617300
	H	-0.96932700	-2.76460300	0.11212100
	H	-0.63533300	-1.94504500	-1.42379300
	H	0.50169900	-3.13626000	-0.79165400
	C	3.30345400	-1.70936200	-0.52755900
	H	2.87557000	-2.64799800	-0.89459700
	H	4.17304600	-1.47604500	-1.15506300
	H	3.66781600	-1.87895000	0.49018700
	C	1.89986500	-0.29073600	-2.03035700
	H	1.51768500	-1.19190600	-2.51942300
	H	1.12867600	0.48631900	-2.09560600
	H	2.76935400	0.05516500	-2.60346900
	C	2.94298300	0.69929000	-0.00257300
	H	3.86831100	0.92784100	-0.54701600
	H	2.27774700	1.56264900	-0.09454100
	H	3.20232100	0.58144600	1.05491300
	Si	0.75171900	-0.99802100	0.40594700
	N	-2.61716200	-0.28874100	-0.19558800
	C	-3.45432500	-1.06828600	-0.14669600
	C	-4.49995600	-2.05493500	-0.08473600
	H	-4.87307900	-2.11482000	0.93749100
	H	-5.30722300	-1.76454800	-0.75608100
	H	-4.09622900	-3.02167500	-0.38635200
2●benzaldehyde	C	0.99432400	3.18859000	-0.95702600
	C	0.23851900	1.28172700	1.36337400
	C	1.19996600	3.37036400	0.37360500
	C	0.58397200	2.57615500	1.42714400
	H	1.46440000	3.91719900	-1.62103200
	H	-0.26913000	0.82714800	2.21193100
	H	1.77570100	4.23838900	0.67882000
	H	0.36286400	3.08146400	2.36399200
	N	0.22074400	2.24180100	-1.57567700
	N	0.45085600	0.41712600	0.24567400
	B	0.02579700	1.02233300	-1.01335700
	C	3.08581000	-0.89608800	-0.07858900
	C	1.24023500	-1.50462400	2.29386700
	H	0.21370300	-1.68404700	2.62647200
	H	1.81297600	-2.41805100	2.48198400
	H	1.66247200	-0.71166000	2.91563500
	C	0.51605600	-2.48315800	-0.47828300
	H	-0.55062200	-2.57629600	-0.24902200
	H	0.63276100	-2.38291400	-1.56059200
	H	0.98994900	-3.42450300	-0.18343400
	C	3.78698900	-2.25434500	-0.09647200
	H	3.35220800	-2.92138700	-0.84681900
	H	4.84825600	-2.12574200	-0.34376700
	H	3.73343800	-2.75726800	0.87488600
	C	3.12072000	-0.29327400	-1.48374500
	H	2.52862300	-0.87546100	-2.19910900
	H	2.74312700	0.73377900	-1.48603400
	H	4.15300600	-0.26751600	-1.85511000
	C	3.81603600	0.04548500	0.87953300
	H	4.83114000	0.24441400	0.51328900
	H	3.29860600	1.00836400	0.96423900
	H	3.90293200	-0.38494900	1.88157900
	Si	1.29951600	-1.08952100	0.48256100
	O	-0.72037600	0.03896600	-1.89578100

	C	-1.77286400	-0.62068300	-1.74921100
	C	-2.78891000	-0.42905700	-0.75935800
	H	-1.92185400	-1.42883800	-2.46674000
	C	-2.84346000	0.69041300	0.08668500
	C	-3.76321600	-1.43620700	-0.67060200
	C	-3.85205400	0.77910900	1.02521900
	H	-2.12260700	1.49331200	-0.01049800
	C	-4.76077400	-1.34644900	0.28315000
	H	-3.71376800	-2.28024900	-1.34931100
	C	-4.79933800	-0.24118800	1.12886100
	H	-3.90940500	1.64079000	1.67694400
	H	-5.50829100	-2.12378900	0.36739700
	H	-5.58297000	-0.16539300	1.87259200

References

1. I. R. Dunkin, *Matrix-isolation techniques: a practical approach*, Oxford University Press, 1998.
2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
4. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* . 1988, **37**, 785.
5. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
6. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
7. J. Bloino and V. Barone, *J. Chem. Phys.*, 2012, **136**.
8. V. Barone, M. Biczysko and J. Bloino, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1759-1787.
9. V. Barone, *J. Chem. Phys.*, 2004, **122**.
10. H. P. Hratchian and H. B. Schlegel, *J. Chem. Phys.*, 2004, **120**, 9918-9924.
11. H. Hratchian and H. Schlegel, *J. Chem. Theory Comput.*, 2005, **1**, 61-69.
12. C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.
13. C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
14. D. G. Liakos, Y. Guo and F. Neese, *J. Phys. Chem. A*, 2019, **124**, 90-100.
15. D. E. Woon and T. H. Dunning Jr, *J. Chem. Phys.*, 1993, **98**, 1358-1371.
16. T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
17. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73-78.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
19. T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51-57.
20. E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429-1437.
21. F. Weinhold, *J. Comput. Chem.*, 2012, **33**, 2363-2379.
22. E. Glendening, C. Landis and F. Weinhold, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 1-42.
23. A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926.

24. K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260.
25. R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789-807.
26. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B*, 2009, **113**, 6378-6396.
27. H. S. Yu, X. He, S. L. Li and D. G. Truhlar, *Chem. Sci.*, 2016, **7**, 5032-5051.
28. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
29. R. J. Mayer, N. Hampel and A. R. Ofial, *Chem. Eur. J.*, 2021, **27**, 4070-4080.
30. C. Angeli, R. Cimiraglia and J.-P. Malrieu, *J. Chem. Phys.*, 2002, **117**, 9138-9153.