博士論文

Study on Isolable π-Electron Species Containing an Inverted Si=Si Bond and an Unsupported Si-Si π-Bond

（反転 Si=Si 結合および Si-Si π 単結合を持つ単離可能 π 電子化学種の研究）

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Study on Isolable π-Electron Species Containing an Inverted Si=Si Bond and an Unsupported Si-Si π-Bond

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Preface

The studies described in this doctoral dissertation have been carried out under the direction of Professor Takeaki Iwamoto at the Department of Chemistry, Graduate School of Science, Tohoku University during 2016 to 2021.

This doctoral dissertation is concerned with the chemistry of silicon π-electron species having unique structure, electronic properties and reactivity. The author convinces that the present studies have contributes not only to the progress of the field in silicon chemistry but also to more in general of the field in organic chemistry and organometallic chemistry.

The author especially wishes to express great thanks to Professor Takeaki Iwamoto for his continuing guidance and valuable discussions throughout the course of studies. It is a great pleasure to thanks Professor Shintaro Ishida for his helpful discussions and encouragement. The author is grateful to Ms. Masako Sasaki and Ms. Mika Ando for their establishment of the comfortable environment in research. The author should like to express appreciation to Dr. Shigeru Sasaki, Naohiko Akasaka, Tomohiro Iimura, Tomoyuki Kosai, Yuki Yokouchi, Siwat Chinaroj, Ryo Kobayashi, Shunya Honda, Messrs. Yushi Kato, Yuko Suzuki, Tomofumi Tamura, Ryo Yamaguchi, Yasunori Miura, Hitomi Ichikawa, Shohei Sugawara, Makoto Tamura, Takuro Karakida, Kaho Tanaka, Kentaro Fujieda, Yuichiro Matsumoto, Maiko Mori, Shunya Abe, Kaho Ishikawa, Taichi Koike, Takehiro Sato, Hiroshi Nakagawa, Takuya Nomura, Takuro Hatakeyama, Daichi Yanagisawa, Kenya Uchida, Hiroki Kawauchi, Shohei Kawakami, Atsuhiro Sato, Kotone Kubota, Mayu Nozawa, Sei Yokoyama, Kouta Asami, Yuya Ushijima, Kazuma Oshima, Yoshiki Ota, Hayato Sasaki, Kento Masuda, Kazuto Mizoguchi, Raiki Osawa, Kawai Kentaro, Masaki Kuribayashi, Kengo Sakamoto, Ryoya Chino, Takuro Shiojima, Kazutoshi Fujita, Yukihiro Morino, Yusuke Yoshida, Keitaro Watanabe, Shohei Wada, Tomoki Ishikawa, Yasuhiro Katayama, Naoki Sakurada, Ryotaro Hayasaka, Kosuke Machida, Kento Miwa for their valuable discussions to all of the members of Professor Iwamoto's group at Tohoku University for the establishment of the comfortable environment in research.

Finally, the author would also like to express his deep appreciation to his family members, Mr. Shigemi Nukazawa, Ms. Hiroko Nukazawa, Ms. Mami Nukazawa, Ms. Mina Nukazawa for their kind encouragement and support.

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Contents

(Compounds are independently numbered in each chapter.)

List of Abbreviations

Bu: *n*-Butyl

t-Bu: *tert*-Butyl

Cp*: Pentamethylcyclopentadienyl (C_5Me_5)

DME: 1,2-Dimethoxy ethane

Dep: 2,6-Diethylphenyl

DMAP: 4-(Dimethylamino)pyridine

Et: Ethyl

Et_2O: Diethylether

$Et_3N{\cdot}HBr$: Triethylamine hydrobromide

eV: Electron volt

Hex: Hexyl

HOMO: Highest occupied molecular orbital

i-Pr: Isopropyl

LUMO: Lowest unoccupied molecular orbital

Me: Methyl

Mes*: 2,4,6-Tri(*tert*-butyl)phenyl

NHC: *N*-Heterocyclic carbene

Ph: Phenyl

THF: Tetrahydrofuran

Tip: 2,4,6-Triisopropylphenyl

TD-DFT: Time-dependent density functional theory

UV: Ultraviolet

VT: Variable-Temperature

vis: Visible

WBI: Wiberg bond indices

XRD: X-ray diffraction

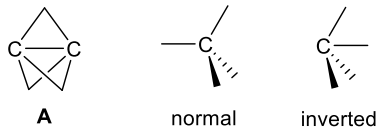
Chapter 1

General Introduction

1-1. Introduction

Molecules that exhibit nonclassical geometries and chemical bonds have fascinated experimental and theoretical chemists,[1] since the exploration of such molecules usually leads to a deeper understanding of their molecular structures and chemical bonds as well as to the discovery of unexpected reactivity. A representative example of such an intriguing organic molecule is [1.1.1]propellane **A** (Chart 1-1).[2] This compound has a nonclassical single bond between bridgehead carbon atoms that adopt an inverted (or a hemispheroidal) geometry; the direction of the bridgehead single bond is diametrically opposite to that expected for typical C–C bonds in a normal tetrahedral geometry (Chart 1-1).[3] The theoretical and experimental investigation for the nature of the inverted single bond in **A** revealed that the single bond exhibits diradical or ionic characters. Currently, the high reactivity of **A** has been utilized for the bond-forming reactions.[4]

Chart 1-1. [1.1.1]Propellane **A** and Schematic Representation of Normal/Inverted Single Bonds



Such nonclassical bonds with an inverted geometry should also be possible for multiple bonds. Bicyclo[1.1.0]but-1(3)-ene **B** represents one extreme example of compounds with an inverted double bond, whereby the direction of the double bond is formally oriented in the diametrically opposite direction to that expected for a normal C=C double bond geometry (Chart 1-2).[5,6] Theoretical study suggested that compound **B** exhibits the several resonance structures (Chart 1-3),[5] implying the high reactivity of the inverted double bond. Although **B** and its derivatives have been proposed as reactive intermediates,[6] they have not yet been isolated and their molecular structures and reactivity have not been investigated experimentally.

Chart 1-2. Bicyclo[1.1.0]but-1(3)-ene **B** and Schematic Representation of Normal/Inverted Double Bonds

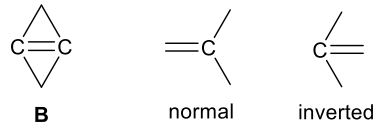
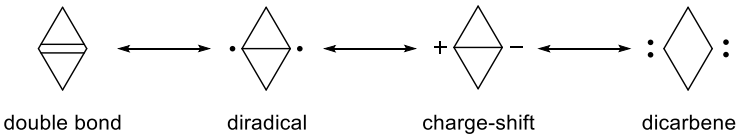
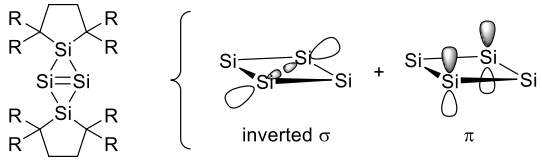


Chart 1-3. Resonance Structures of Bicyclo[1.1.0]but-1(3)-ene **B**



Recently, our group synthesized tetrasilabicyclo[1.1.0]but-1(3)-ene **1**, the first isolable silicon analogue of bicyclo[1.1.0]but-1(3)-ene (Chart 1-4).[7] Single-crystal X-ray diffraction (XRD) analysis of **1** revealed that the central Si_4 bicyclic skeleton is planar, and DFT calculation suggested that the bridgehead Si=Si bond comprises a π-bond and an inverted σ-bond as found between bridgehead atoms in pentasila[1.1.1]propellane (Chart 1-4).[8] In spite of the highly-distorted Si=Si bond in **1**, it exhibits very low reactivity toward small molecules such as H_2O, methanol, cyclohexa-1,4-diene, Bu_3SnH, Ph_3P, or BPh_3 probably due to severe steric demand of the Si(*i*-Pr)Me_2 groups. In this thesis, the author synthesized new tetrasilabicyclo[1.1.0]but-1(3)-ene **2** that has less bulky $SiMe_3$ groups to examine the reactivity of the inverted Si=Si bond (Chart 1-4). Through the investigation of the reactivity of **2** for various reagents, the author found that **2** could be the useful precursor for the synthesis of unconventional π-electron compounds of silicon.

Chart 1-4. Tetrasilabicyclo[1.1.0]but-1(3)-enes **1** and **2**



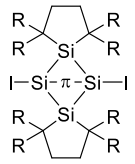
1 (R = Si(*i*-Pr)Me_2)
2 (R = $SiMe_3$)

In chapter 2, the author described the synthesis and isolation of tetrasilabicyclo[1.1.0]but-1(3)-ene **2**. Single-crystal XRD analysis and spectroscopic analysis indicated that the structural and electronic characteristics of **2** are virtually identical to those of **1**. The reactions of **2** with carbon tetrachloride and methanol were also described.

In chapter 3, the author described the synthesis and properties of 1,3-diiodotetrasilabicyclo[1.1.0]butane **3** via 1,2-diiodination of **2** (Chart 1-5). Single-crystal

XRD analysis and theoretical study suggested that **3** exhibits the π-type single bond (the unsupported π-bond) between the bridgehead silicon atoms.

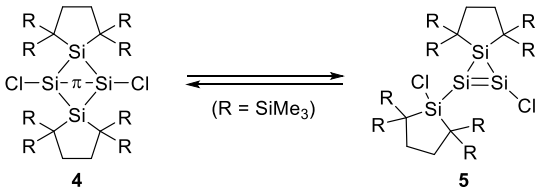
Chart 1-5. 1,3-Diiodotetrasilabicyclo[1.1.0]butane **3**



3

In chapter 4, the author described the synthesis of 1,3-dichlorotetrasilabicyclo[1.1.0]butane **4** with the π-type bridgehead Si–Si bond via 1,2-dichlorination of **2**. The interconversion between **4** and its isomer, 1-chloro-2-(chlorosilyl)cyclotrisilene **5** is also described (Scheme 1-1).

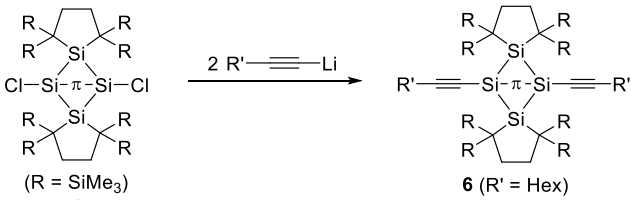
Scheme 1-1. Interconversion between **4** and **5**



4 **5**

In chapter 5, the author described the reactions of **4** with a lithium acetylide to provide bicyclo[1.1.0]tetrasilanes **6** and **7** with alkynyl groups on the bridgehead silicon atoms (Scheme 1-2). π-Conjugation between the unsupported Si–Si π-bond of the bicyclo[1.1.0]tetrasilane unit and the alkynyl groups were examined in detail.

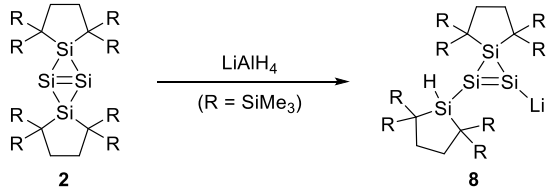
Scheme 1-2. Reactions of **4** with a lithium acetylide



4

In chapter 6, the author described the reactions of **2** with nucleophilic reagents. The reaction of **2** with lithium aluminum hydride ($LiAlH_4$) unexpectedly provided the first isolable cyclotrisilenide **8** (Scheme 1-3).

Scheme 1-3. Reaction of **2** with $LiAlH_4$



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Chapter 2

Synthesis and Reactivity of a New Tetrasilabicyclo[1.1.0]but-1(3)-ene

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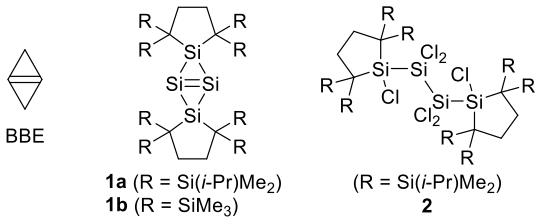
2-1. Introduction

Molecules that exhibit a distorted structure have attracted experimental and theoretical chemists.[1] Among such molecules, bicyclo[1.1.0]but-1(3)-ene (BBE) (Chart 2-1) is an intriguing molecule as it has an extremely-strained bridgehead C=C double bond in the bicyclic framework, whereby the orientation of the double bond is diametrically opposite to that of typical double bonds in acyclic alkenes.[2] Although BBE and its derivatives have been proposed as reactive intermediates[3] and theoretically examined,[4] their molecular structures have not been proved experimentally. Recently, we reported synthesis and X-ray diffraction analysis of tetrasilabicyclo[1.1.0]but-1(3)-ene **1a**, the first isolable silicon analogue of BBE (Chart 2-1).[5] While the Si=Si distance in **1a** [2.4716(12) Å] is rather long compared to those of typical Si=Si bonds (2.118–2.312 Å),[6] DFT calculation suggested that the bridgehead bond comprises a σ-bond as found between bridgehead atoms in pentasila[1.1.1]propellane[7] and a π-bond. In spite of the highly-distorted Si=Si bond in **1a**, it exhibits very low reactivity toward small molecules probably due to severe steric demand of the Si(*i*-Pr)Me_2 groups; **1a** does not react with H_2O, methanol, cyclohexa-1,4-diene, Bu_3SnH, Ph_3P, or BPh_3. **1a** only reacted with CCl_4 to provide hexachlorinated product **2**, although the mechanism for the reaction remains unclear. To examine further reactivity of tetrasilabicyclo[1.1.0]but-1(3)-ene, the author designed a new derivative that contains less bulky $SiMe_3$ substituents (**1b**). In this chapter, the author reports the synthesis, molecular structure and reactivity of **1b**. While the structural and spectroscopic characteristics of **1b** resemble those of **1a**, **1b** reacts with CCl_4 or methanol and the products of the reaction with CCl_4 substantially depend on the reaction conditions.

Chart 2-1. Structures of Bicyclo[1.1.0]but-1(3)-ene (BBE), Tetrasilabicyclo[1.1.0]but-1(3)-ene **1a** (R = Si(*i*-Pr)Me_2) and **1b** (R = $SiMe_3$) as well as Hexachlorinated Product **2**

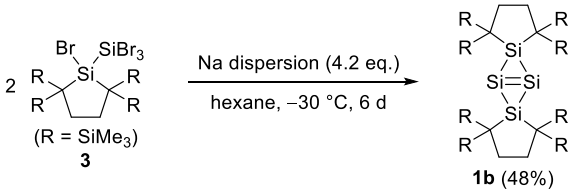


2-2. Results and Discussion

2-2-1. Synthesis of Tetrasilabicyclo[1.1.0]but-1(3)-ene 1b

Orange crystals of **1b** were obtained in 48% yield by the reductive debromination of tetrabromodisilane **3** with finely dispersed sodium in hexane at −30 °C (Scheme 2-1)[8] and characterized by a combination of multinuclear NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and single-crystal X-ray diffraction (XRD) analysis. Compound **1b** was air- and moisture sensitive but thermally stable.

Scheme 2-1. Synthesis of **1b**



2-2-2. Molecular Structure of 1b

The molecular structure of **1b** determined by XRD analysis is displayed in Figure 2-1. The molecule has a crystallographic inversion centre between Si1 and Si1* atoms and the central Si_4 bicyclic skeleton is planar with the dihedral angle of Si2–Si1–Si1*–Si2* of 180°, accordingly. The Si1–Si1* distance in **1b** [2.4873(10) Å] is substantially longer than the reported range of Si=Si double bonds with three-coordinate unsaturated silicon atoms (2.118–2.312 Å)[6] and very similar to that of **1a** [2.4716(12) Å].[5] The distances of the peripheral Si–Si bond forming the four-membered ring of **1b** [Si1–Si2: 2.2928(7) Å, and Si1–Si2*: 2.3004(7) Å] are also comparable to those of **1a** [2.2959(8) Å and 2.3098(8) Å].

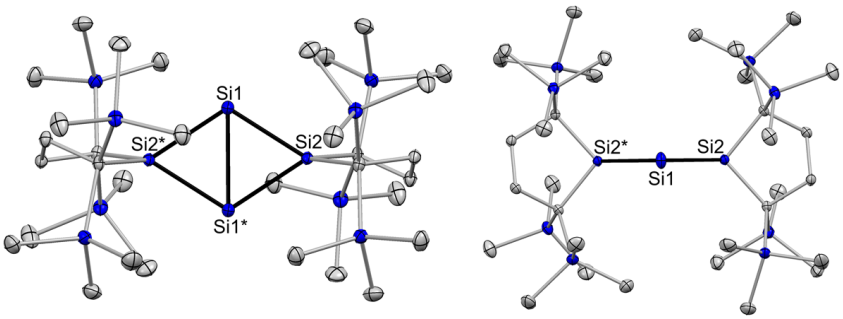


Figure 2-1. ORTEPs of **1b** (left: top view, right: side view; atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–Si1* 2.4873(10), Si1–Si2 2.2928(7), Si1–Si2* 2.3004(7), Si2–Si1–Si2* 114.43(2), Si1–Si2–Si1* 65.57(2), Si2–Si1–Si1*–Si2* 180.

2-2-3. NMR Spectra and UV-vis Absorption Spectrum of 1b

The ^{1}H NMR spectrum of **1b** in a C_6D_6 solution shows one singlet signal (0.32 ppm) due to eight equivalent $SiMe_3$ groups and one singlet signal (2.21 ppm) due to eight methylene protons in the five-membered rings, suggesting a facile ring flipping of the terminal silacyclopentane rings on the NMR time scale. In the ^{29}Si NMR spectrum, Si1 (Si1*) and Si2 (Si2*) nuclei resonate at 216.6 and 94.6 ppm (Figure 2-2a), respectively. These values are virtually the same as those of **1a** (217.0 and 94.5 ppm).[5] The UV-vis absorption spectrum of **1b** in hexane (Figure 2-2b) exhibits a weak and broad band around 400 nm (ε 1800) and two broad and intense bands at 342 and 326 nm (ε 14000 and 12000), which resembles that of **1a**. These results indicate that the structural and electronic characteristics of **1b** are virtually identical to those of **1a**.

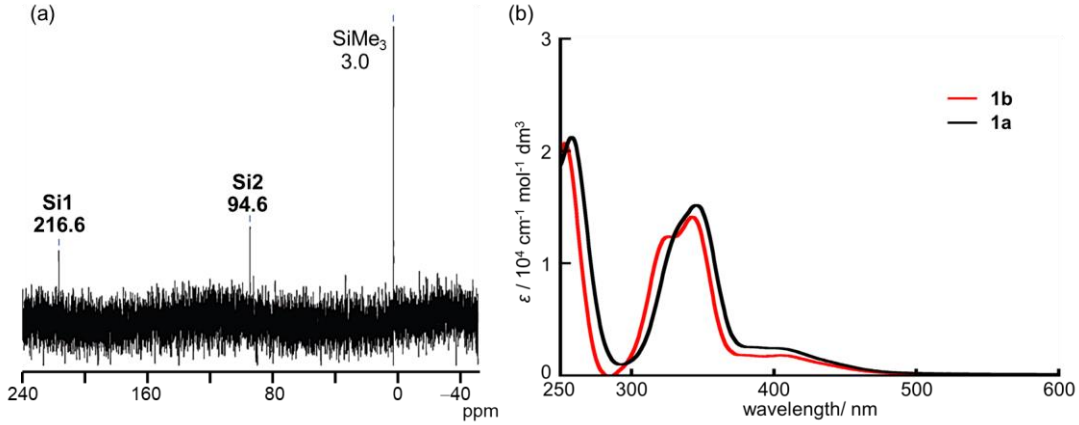


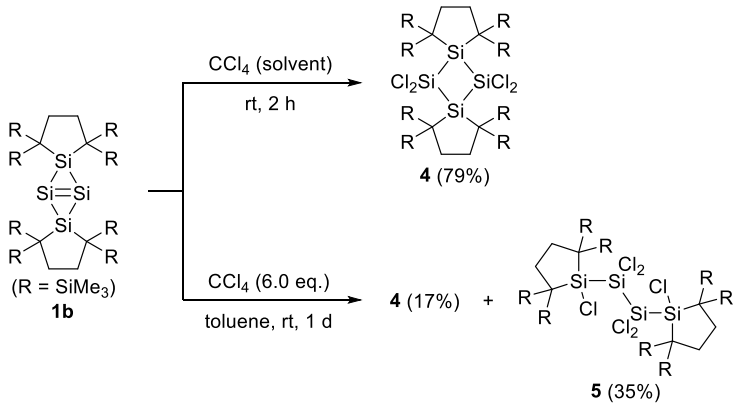
Figure 2-2. (a) ^{29}Si NMR spectrum of **1b** in C_6D_6 at room temperature. (b) UV-vis absorption spectra of **1b** (red) and **1a** (black) in hexane at room temperature.

2-2-4. Reaction of 1b with Carbon Tetrachloride

The reaction of **1b** with an excess amount of carbon tetrachloride as a solvent proceeded at room temperature to provide 1,1,3,3-tetrachlorocyclotetrasilane **4** in 79% yield (Scheme 2-2, Figure 2-3a). Interestingly, the reaction of **1b** with six equivalents of carbon tetrachloride in toluene afforded hexachlorotetrasilane **5** (35%) together with **4** (17%) (Scheme 2-2). Formation of an acyclic hexachlorotetrasilane (**2**) was also found in the reaction of **1a** with carbon tetrachloride as shown in Chart 2-1. The formation of hexachloroethane (CCl_3–CCl_3) was confirmed by ^{13}C NMR spectrum measured during the reaction of **1b** with excess carbon

tetrachloride in C_6D_6 (Figure 2-27), which suggests chlorine abstraction from carbon tetrachloride to form trichloromethyl radical during the reaction similar to the reaction of tetrasilyldisilene with carbon tetrachloride providing a 1,2-dichlorinated product.[9] As **4** does not react with two equivalents of carbon tetrachloride in toluene, **4** is not an intermediate for the formation of **5**.

Scheme 2-2. Reaction of **1b** with CCl_4



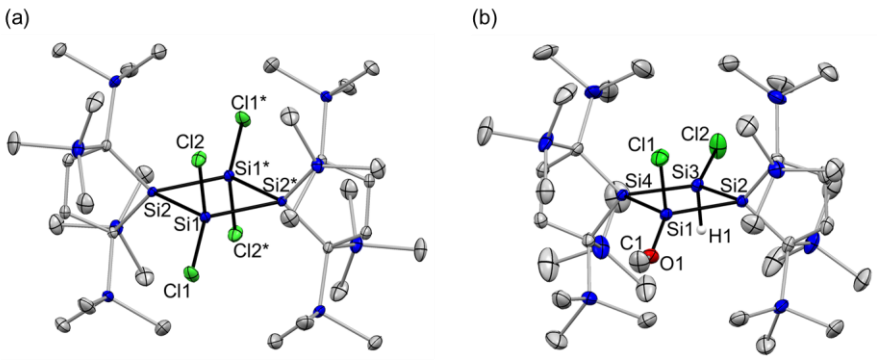


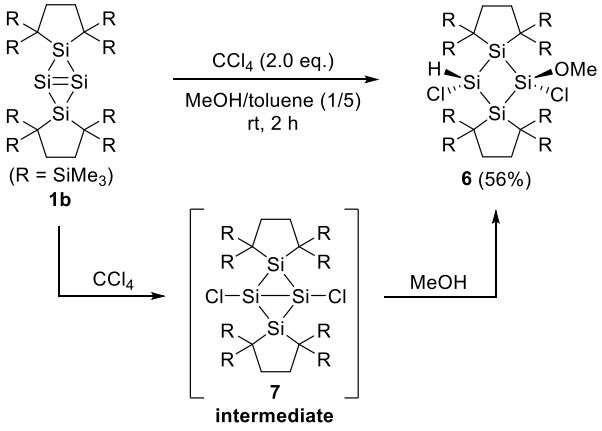
Figure 2-3. ORTEPs of (a) **4** and (b) **6** with thermal ellipsoids at 50% probability; hydrogen atoms have been omitted for clarity.

2-2-5. Trapping Reaction of the Intermediate in Reaction of 1b with CCl_4

Although the reaction of **1b** with two equivalents of carbon tetrachloride in toluene at room temperature afforded a complex mixture that does not exhibit NMR signals of **4** and **5**,[10] a similar reaction of **1b** in the presence of methanol (toluene/methanol=5/1) afforded *cis*-1,3-dichloro-1-methoxycyclotetrasilane **6** in 56% yield (Scheme 2-3, Figure 2-3). As **1b** does not react with methanol in toluene in the absence of carbon tetrachloride at room temperature, these results indicate that **6** is a product resulting from the reaction of an

intermediate with methanol after the reaction with carbon tetrachloride. As *syn*-addition of H_2O toward the bridgehead Si–Si bond of bicyclo[1.1.0]tetrasilane was reported by Masamune et al.,[11] the intermediate is likely to be 1,3-dichlorobicyclo[1.1.0]tetrasilane **7** (Scheme 2-3) resulting from the 1,2-addition of chlorine atoms across the Si=Si double bond of **1b**.

Scheme 2-3. Reaction of **1b** with CCl_4 in the presence of MeOH



2-2-6. Monitoring Reaction of 1b with CCl_4 by ^{1}H NMR Spectroscopy

The reaction of **1b** with excess carbon tetrachloride in toluene-d_8 monitored by ^{1}H NMR spectroscopy at lower temperatures provided further insight into the reaction with carbon tetrachloride. The ^{1}H NMR spectrum just after the addition of excess carbon tetrachloride to a toluene-d_8 solution of **1b** at −30 °C (Figure 2-4) exhibited mainly two singlet signals at 0.36 and 1.78 ppm with the ratio of 9 : 1 together with signals of a trace amount of **4** and no signals due to **1b** were observed. At −30 °C, the observed signals of the intermediate gradually decreased, while signals of **4** gradually increased but signals assignable to **5** were not observed (Figure 2-4).[12] This result indicates that **1b** reacted immediately with carbon tetrachloride at −30 °C to provide an intermediate. Although the intermediate has not been able to be fully identified on account of its low solubility, the ^{1}H NMR signals are consistent with the structure of **7** which contains thirty-six protons of $SiMe_3$ moiety and four protons of CH_2 moiety in the silacyclopentane rings. After the mixture was warmed up above 10 °C, the ^{1}H signals of **5** appeared and increased (Figure 2-4). These results suggest that the activation barrier of the rate controlling step to afford **5** from the intermediate is higher than those to provide **4**.

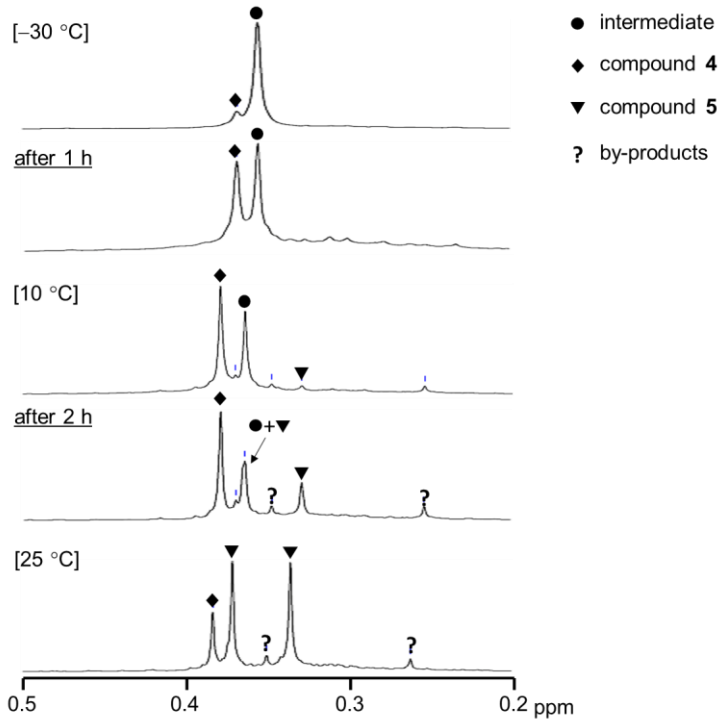
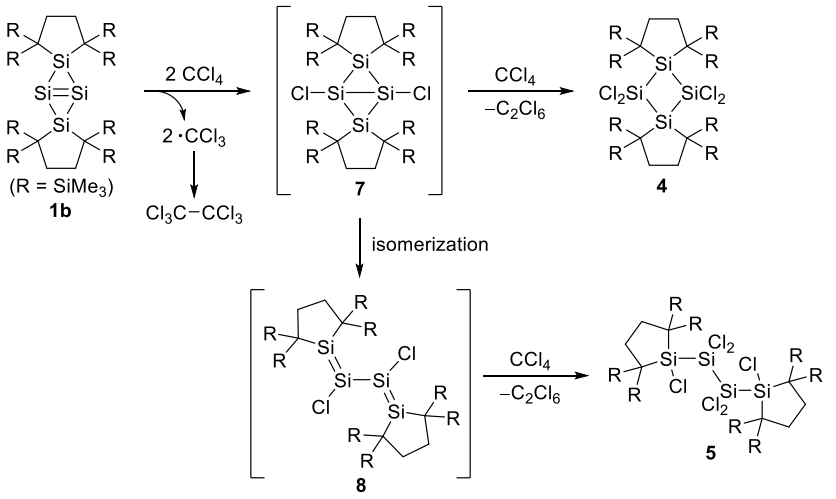


Figure 2-4. ^{1}H NMR spectra ($SiMe_3$ region) of the reaction mixture of the reaction of **1b** with excess carbon tetrachloride in toluene-d_8 at –30 °C, 10 °C, and 25 °C.

2-2-7. Possible Mechanism for Reaction of 1b with CCl_4

Scheme 2-4 exhibits a possible mechanism for the reaction of **1b** with carbon tetrachloride. Compound **1b** reacts with carbon tetrachloride to afford 1,3-dichlorobicyclo[1.1.0]tetrasilane **7**. In the presence of a large excess amount (>ca. 500 eq.) of carbon tetrachloride, **7** reacts with an extra amount of carbon tetrachloride to provide **4**. When six equivalents of carbon tetrachloride are used, isomerisation of **7** to a tetrasiladiene **8** may compete with the chlorination of **7**, and **8** should undergo further chlorination reactions at the Si=Si double bonds to furnish **5**.[13] These processes are consistent with the mechanism proposed previously for the reaction of **1a** with carbon tetrachloride[5] and the results of the ^{1}H NMR spectra observed during the reaction in toluene-d_8 at low temperatures. In the case of the reaction of **1b** with two equivalents of carbon tetrachloride, the isomerisation of **7** to **8** and the subsequent decomposition of **8** may occur. The generation of **7** even in this condition is supported by the formation of **6** that should result from *syn*-addition of methanol to the bridgehead Si–Si bond of **7**.[14]

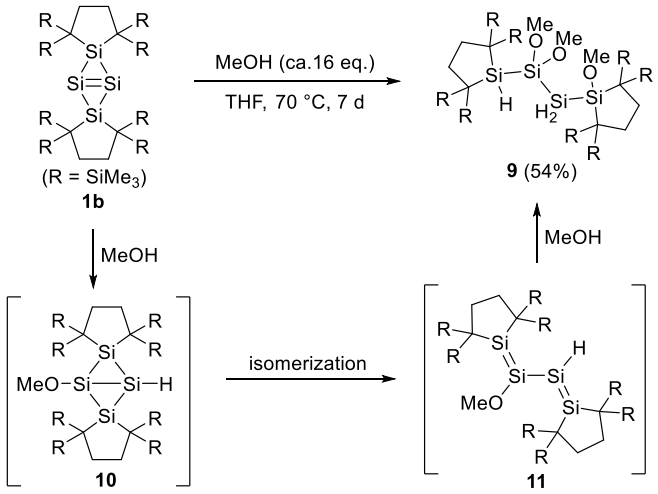
Scheme 2-4. Possible Mechanism for Reaction of **1b** and CCl_4



2-2-8. Reaction of 1b with Methanol

The existence of an intermediate similar to **8** was suggested in the reaction of **1b** with methanol. The reaction of **1b** with methanol in THF proceeded at 70 °C to provide 1,3,3-trimethoxytetrasilane **9** as a sole product, which was isolated in 54% yield (Scheme 2-5), while this reaction did not proceed at room temperature. Compound **9** was characterised by a combination of multinuclear NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and single-crystal XRD analysis (Figure 2-5). Although the mechanism for the regioselective addition of methanol to **1b** providing **9** remains unclear, one possible mechanism can involve the addition of methanol to the Si=Si double bond in **1b** affording 1-methoxybicyclo[1.1.0]tetrasilane **10** followed by valence isomerisation to a 2-methoxytetrasiladiene **11** similar to isomerisation of **7** to **8**,[14] and the subsequent addition of methanol to the Si=Si double bond in the 2-methoxytetrasiladiene to furnish **9** (Scheme 2-5). The selective formation of **9** suggests that the Si=Si double bonds in intermediate **11** are significantly polarised as found in the unsymmetrically-substituted disilenes,[15a] or suggested for possible intermediates in the double alcohol addition to an Si–Si triple bond in a disilyne[15b] or cumulative Si=Si double bonds in a trisilaallene.[15c]

Scheme 2-5. Reaction of **1b** with Methanol and the Possible Mechanism



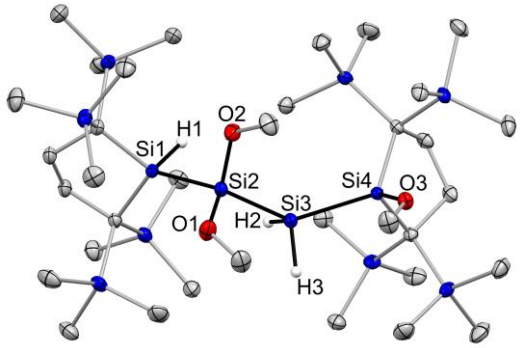


Figure 2-5. ORTEP of **9** with thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity.

2-3. Summary

Tetrasilabicyclo[1.1.0]but-1(3)-ene **1b** was newly synthesized as orange crystals by the reductive debromination of the corresponding tetrabromodisilane **3** with finely dispersed sodium in hexane. The structural and spectroscopic characteristics of **1b** closely resemble those of **1a**. The reaction of **1b** with carbon tetrachloride providing tetrachlorocyclotetrasilane **4** and hexachlorotetrasilane **5** suggests the generation of 1,3-dichlorobicyclo[1.1.0]tetrasilane **7** and tetrasiladiene **8**, the latter of which was supported by the reaction of **1b** with methanol.

2-4. Experimental Section

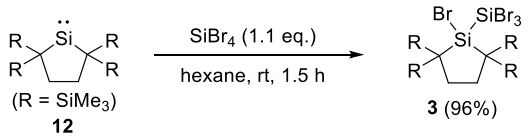
General Procedures

All reactions involving air-sensitive compounds were performed under argon or nitrogen atmosphere using a high vacuum line and standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. Reactions at lower temperatures were performed using an EYELA PSL-1400 cryobath. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C shifts of the solvents: C_6D_6 (^{1}H: δ 7.16 and ^{13}C: δ 128.0).[16] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). The sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4 T spectrometer. UV-vis spectra were recorded on a JASCO V-770 spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer. Recycling preparative gel permeation chromatography (GPC) using dry toluene as an eluent was performed at 5.0 mL min^{-1} rate using a Japan Analytical Industry Co., LC-9201 equipped with a JAIGEL-H column (Japan Analytical Industry Co., φ 20 mm × 600 nm) which was connected to the glove box.

Materials

Dry and degassed hexane, THF and toluene were prepared using a VAC 103991 solvent purifier. C_6D_6 was dried by molecular sieves 4Å after degassing through five freeze–pump–thaw cycles. Carbon tetrachloride was dried by calcium hydride after degassing through three freeze–pump–thaw cycles. Methanol was dried by molecular sieves 3Å after degassing through three freeze–pump–thaw cycles. 2,2,5,5-Tetrakis(trimethylsilyl)-1-silacyclopentane-1,1-diyl **12**[17] was prepared according to published procedure. Silicon tetrabromide and finely dispersed sodium (Strem) were commercially available and used without further purification.

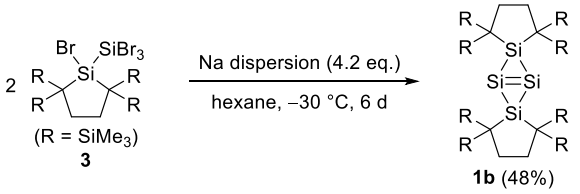
Synthesis of Tetrabromodisilane 3



To a Schlenk tube (100 mL) equipped with a magnetic stir bar, a solution of **12** (2.01 g, 5.39 mmol) in hexane (18.0 mL) was placed. To the solution, silicon tetrabromide (0.74 mL, 5.96 mmol) was added and the mixture was stirred for 1.5 hours at room temperature. The colour of the solution turned immediately from orange to colourless. After the volatiles were removed in vacuo at room temperature, **3** was obtained as a white powder (3.74 g, 5.19 mmol) in 96% yield.

3: A white powder; mp 151-152 °C; δ_H (500 MHz, C_6D_6, 298 K) 0.339 (18H, s, SiC*H*$_3$), 0.341 (18H, s, SiC*H*$_3$), 1.86-1.96 (4H, m, C*H*$_2$); δ_C (125 MHz, C_6D_6, 297 K) 4.8 (Si*C*H$_3$), 5.2 (Si*C*H$_3$), 17.3 (*C*), 34.0 (*C*H$_2$); δ_{Si} (99 MHz, C_6D_6, 296 K) −20.6 (Si-*Si*Br$_3$), 4.1 (*Si*Me$_3$), 7.8 (*Si*Me$_3$), 30.4 (*Si*-SiBr$_3$); HRMS (APCI) found, 700.82391. Calcd for $C_{15}H_{37}Br_4Si_6$ [(M−Me)$^+$], 700.82389; Found: C, 27.02; H, 5.78. Calcd for $C_{16}H_{40}Br_4Si_6$: C, 26.67; H, 5.60%.

Synthesis of Tetrasilabicyclo[1.1.0]but-1(3)-ene 1b[8]



To a Schlenk tube (30 mL) equipped with a magnetic stir bar and four nichrome wires (φ = 1.0 mm, l = 2.0 cm, Figure 2-6), **3** (500 mg, 0.695 mmol) and finely dispersed sodium (66.7 mg, 2.90 mmol) were placed. To the Schlenk tube, hexane (5.0 mL) was added and then the mixture was stirred for 6 days at −30 °C. After the solvent was distilled off at room temperature, the crude materials were extracted with hot toluene (ca. 150 mL). The filtrate was concentrated in vacuo, and the residue was washed with hexane to provide an orange powder of **1b** (134 mg, 167 μmol) in 48% yield.

1b: An orange powder; mp 275-276 °C; δ_H (500 MHz, C_6D_6, 300 K) 0.32 (72H, s, SiC*H*$_3$), 2.21 (8H, s, C*H*$_2$); δ_C (125 MHz, C_6D_6, 333 K) 4.4 (Si*C*H$_3$), 19.5 (*C*), 34.6 (*C*H$_2$); δ_{Si} (99 MHz, C_6D_6, 333 K) 3.0 (*Si*Me$_3$), 94.5 (*Si*), 216.6 (*Si*=*Si*); λ_{max}(hexane)/nm 405sh (ε/dm^3 mol^{-1} cm^{-1} 1.8 × 10^3), 342 (1.4 × 10^4), 326sh (1.2 × 10^4); HRMS (APCI) found, 800.34856. Calcd for $C_{32}H_{80}Si_{12}$ [M$^+$], 800.34857; Found: C, 47.68; H, 10.10. Calcd for $C_{32}H_{80}Si_{12}$: C, 47.92; H, 10.05%.

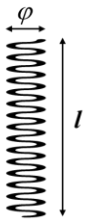
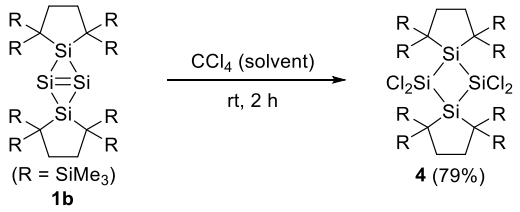


Figure 2-6. Nichrome wire (φ: diameter, *l*: length).

Reaction of 1b with Carbon Tetrachloride

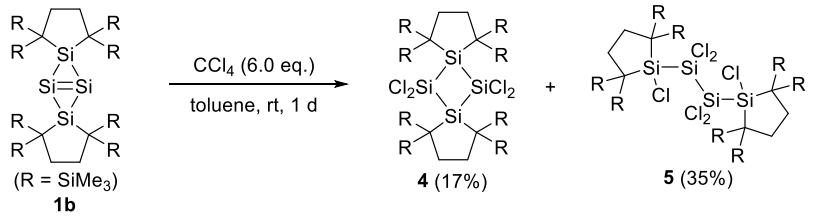


To a Schlenk tube (10 mL) equipped with a magnetic stir bar, **1b** (49.8 mg, 62.1 μmol) was placed. To the Schlenk tube, dry and degassed carbon tetrachloride (2 mL) was transferred and then the mixture was stirred at room temperature for 2 hours. The colour of the resulting suspension turned gradually from orange to yellow. After the volatiles were removed in vacuo, the crude material was washed with hexane to furnish a pale yellow powder of **4** (46.4 mg, 49.2 μmol) in 79% yield.

4: A pale yellow powder; mp 170-173 °C (decomp.); δ_H (500 MHz, C_6D_6, 333 K) 0.43 (72H, s, SiC*H*$_3$), 2.09 (8H, s, C*H*$_2$); δ_C (CP MAS, 294 K) 5.7 (Si*C*H$_3$), 7.3 (Si*C*H$_3$), 18.8 (*C*), 37.5 (*C*H$_2$); δ_{Si} (CP MAS, 294 K) 6.4 (*Si*Me$_3$), 8.8 (*Si*Me$_3$), 28.1 (ring *Si*), 31.6 (ring *Si*); HRMS (APCI) found, 940.22440. Calcd for $C_{32}H_{80}Cl_4Si_{12}$ [M$^+$], 940.22398; Found: C, 40.76; H, 8.36. Calcd for $C_{32}H_{80}Cl_4Si_{12}$: C, 40.72; H, 8.54%.

We tried to measure the ^{13}C and ^{29}Si NMR spectra of **4**, but **4** is less soluble in organic solvent and measurement of these spectra was unsuccessful.

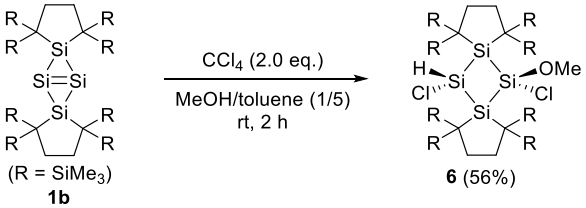
Reaction of 1b with Carbon Tetrachloride in Toluene



To a Schlenk tube (100 mL) equipped with a magnetic stir bar, **1b** (50.3 mg, 62.7 μmol) and toluene (4.0 mL) were placed. To the Schlenk tube, a toluene solution of carbon tetrachloride (381 μmol, (1.0 mL, 0.381 M)) was added and then the mixture was stirred at room temperature for 1 day. The colour of the resulting suspension turned gradually from orange to pale yellow. After the volatiles were removed in vacuo, the crude material was washed with hexane to give a pale yellow powder of **4** (10.0 mg, 10.6 μmol) in 17% yield. The filtrate was purified by recrystallisation from hot DME to give colourless crystals of **5** (22.1 mg, 21.8 μmol) in 35% yield.

5: Colourless crystals; mp. 234-236 °C (from hexane, decomp.); δ_H (500 MHz, C_6D_6, 298 K) 0.38 (36H, s, SiC*H*$_3$), 0.41 (36H, s, SiC*H*$_3$), 1.90-2.08 (8H, m, C*H*$_2$); δ_C (125 MHz, C_6D_6, 298 K) 4.9 (Si*C*H$_3$), 5.3 (Si*C*H$_3$), 19.6 (*C*), 34.6 (*C*H$_2$); δ_{Si} (99 MHz, C_6D_6, 297 K) 3.2 (*Si*Cl$_2$), 3.5 (*Si*Me$_3$), 6.8 (*Si*Me$_3$), 39.7 (*Si*Cl); HRMS (APCI) found, 995.13872. Calcd for $C_{31}H_{77}Cl_6Si_{12}$ [(M−Me)$^+$], 995.13821; Found: C, 38.20; H, 8.07. Calcd for $C_{32}H_{80}Cl_6Si_{12}$: C, 37.88; H, 7.95%.

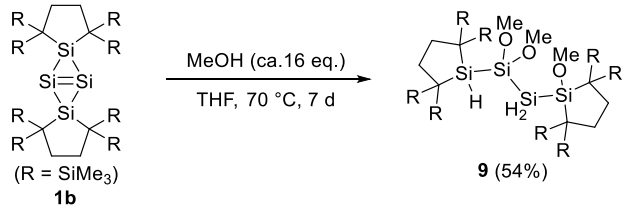
Reaction of 1b with Carbon Tetrachloride in the presence of Methanol



To a Schlenk tube (20 mL) equipped with a magnetic stir bar, **1b** (30.1 mg, 37.5 μmol), toluene (2.8 mL) and methanol (0.6 mL) were placed. To the Schlenk tube, a toluene solution of carbon tetrachloride (76.2 μmol, (0.2 mL, 0.381 M)) was added and then the mixture was stirred at room temperature for 2 hours. The colour of the resulting suspension turned gradually from orange to pale yellow. After the volatiles were removed in vacuo, the crude material was purified by recrystallisation from hot hexane to provide yellow crystals of **6** (18.9 mg, 20.9 μmol) in 56% yield.

6: Yellow crystals; mp 163-165 °C (from hexane, decomp.); δ_H (500 MHz, C_6D_6, 295 K) 0.33 (18H, s, SiCH_3), 0.42 (18H, s, SiCH_3), 0.44 (18H, s, SiCH_3), 0.46 (18H, s, SiCH_3), 1.75-1.90 (4H, m. CH_2), 2.03-2.20 (4H, m, CH_2), 3.55 (3H, s, OCH_3), 5.73 (1H, s, Si*H*); δ_C (125 MHz, C_6D_6, 297 K) 4.6 (Si*C*H$_3$), 5.0 (Si*C*H$_3$), 5.5 (Si*C*H$_3$), 6.0 (Si*C*H$_3$), 15.4 (*C*), 16.2 (*C*), 36.5 (*C*H$_2$), 36.6 (*C*H$_2$), 53.8 (O*C*H$_3$); δ_{Si} (99 MHz, C_6D_6, 296 K) −16.5 (*Si*HCl), 4.9 (*Si*Me$_3$), 5.2 (*Si*Me$_3$), 5.8 (*Si*Me$_3$), 6.0 (*Si*Me$_3$), 11.8 (*Si*(OMe)Cl), 22.9 (*Si*); HRMS (APCI) found, 901.30481. Calcd for $C_{33}H_{83}Cl_2OSi_{12}$ [(M−H)$^+$], 901.30467; Found: C, 43.70; H, 9.35. Calcd for $C_{33}H_{84}Cl_2OSi_{12}$: C, 43.80; H, 9.36%.

Reaction of 1b with Methanol



To a stock bottle (10 mL) equipped with a magnetic stir bar, **1b** (50.3 mg, 62.7 μmol) was placed. To the bottle, dry and degassed THF (5.0 ml) and methanol (ca.32 mg, 1.0 mmol) were added, and then the mixture was stirred at 70 °C for 7 days. The colour of the resulting suspension turned to pale yellow from orange. After the volatiles were removed in vacuo, the crude was purified by GPC (eluent: toluene) to provide a white solid of **9** (30.1 mg, 33.5 μmol) in 54% yield.

9: A white solid; mp 150-152 °C (decomp.); δ_H (500 MHz, C_6D_6, 298 K) 0.31 (18H, s, SiC*H*$_3$), 0.32 (18H, s, SiC*H*$_3$), 0.35 (36H, s, SiC*H*$_3$), 1.86-2.16 (8H, m, C*H*$_2$), 3.56 (3H, s, OC*H*$_3$), 3.59 (6H, s, OC*H*$_3$), 3.62 (2H, s, Si*H*), 4.46 (1H, s, Si*H*); δ_C (125 MHz, C_6D_6, 298 K) 2.9 (Si*C*H$_3$), 3.7 (Si*C*H$_3$), 4.1 (Si*C*H$_3$), 4.8 (Si*C*H$_3$), 7.7 (*C*), 18.8 (*C*), 34.3 (*C*H$_2$), 34.9 (*C*H$_2$), 53.4 (O*C*H$_3$), 54.0 (O*C*H$_3$); δ_{Si} (99 MHz, C_6D_6, 298 K) −110.6 (*Si*H$_2$), −18.7 (*Si*H), 1.5 (*Si*Me$_3$), 3.3 (*Si*Me$_3$), 3.7 (*Si*Me$_3$), 4.9 (*Si*Me$_3$), 9.0 (*Si*(OMe)$_2$), 41.7 (*Si*OMe); HRMS (APCI) found, 895.41979. Calcd for $C_{35}H_{91}O_3Si_{12}$ [(M−H)$^+$], 895.41939; Found: C, 46.97; H, 10.31. Calcd for $C_{35}H_{92}O_3Si_{12}$: C, 46.81; H, 10.33%.

NMR Spectra

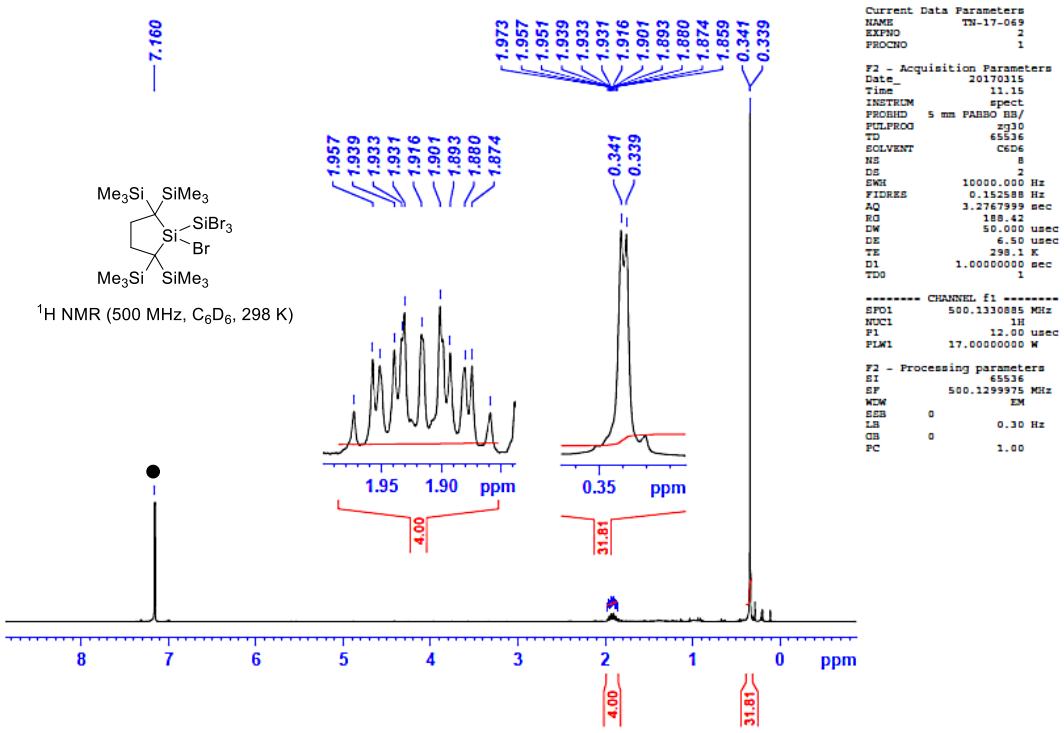


Figure 2-7. ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K (● = C_6HD_5).

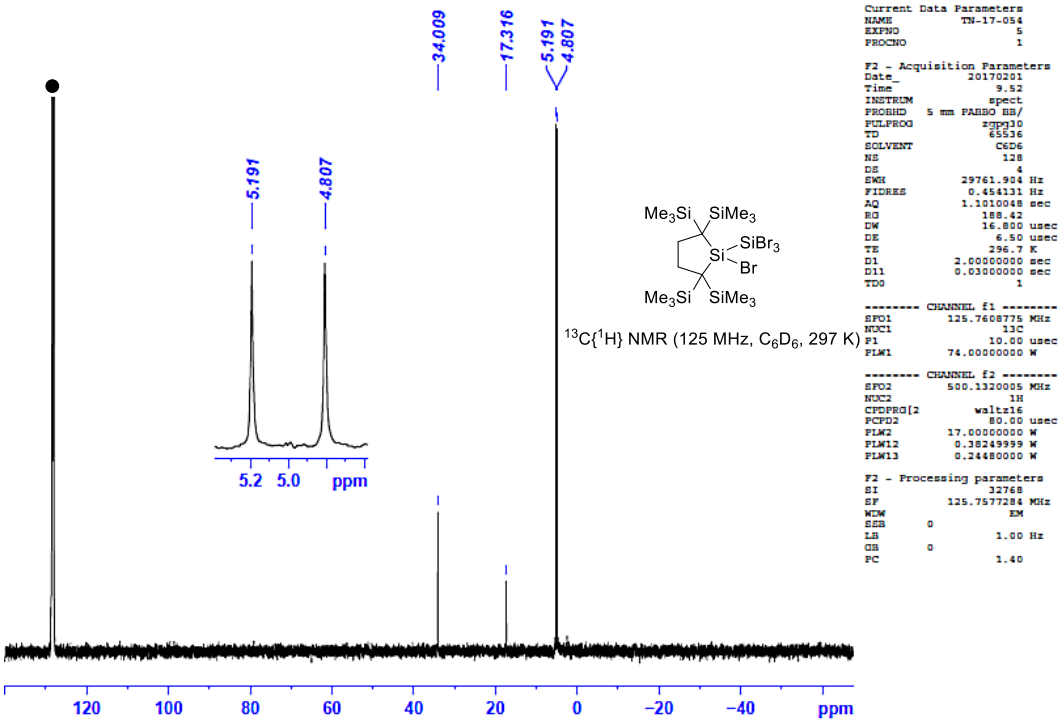


Figure 2-8. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 in 297 K (● = C_6D_6).

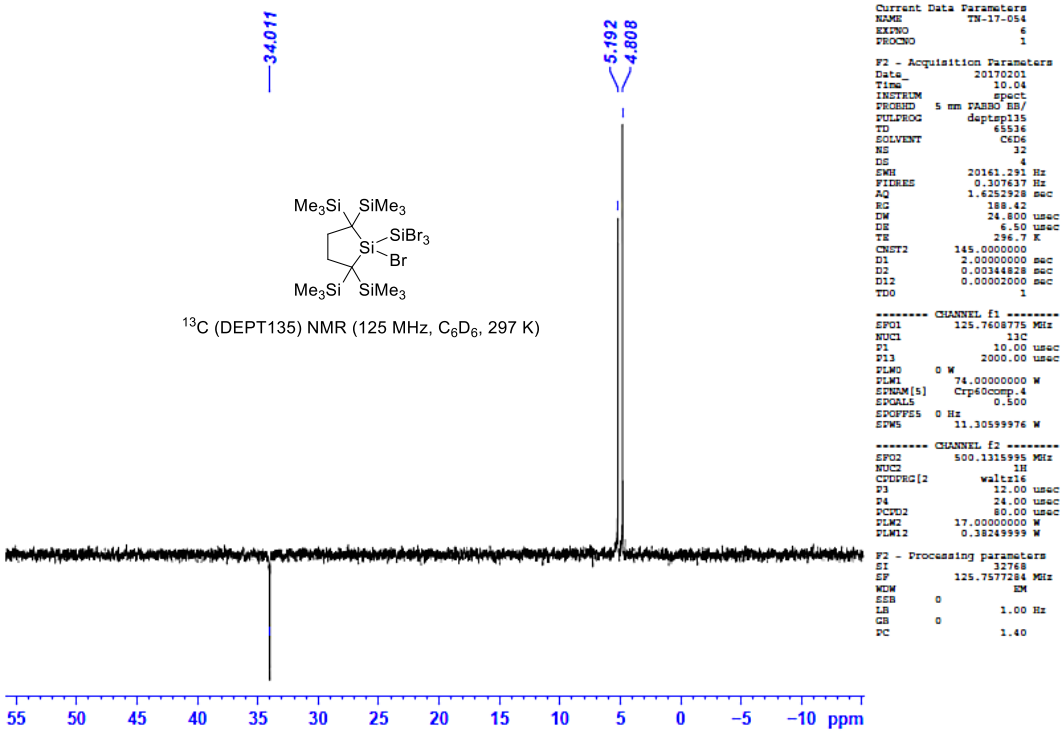


Figure 2-9. ^{13}C (DEPT135) NMR spectrum of **3** in C_6D_6 at 297 K.

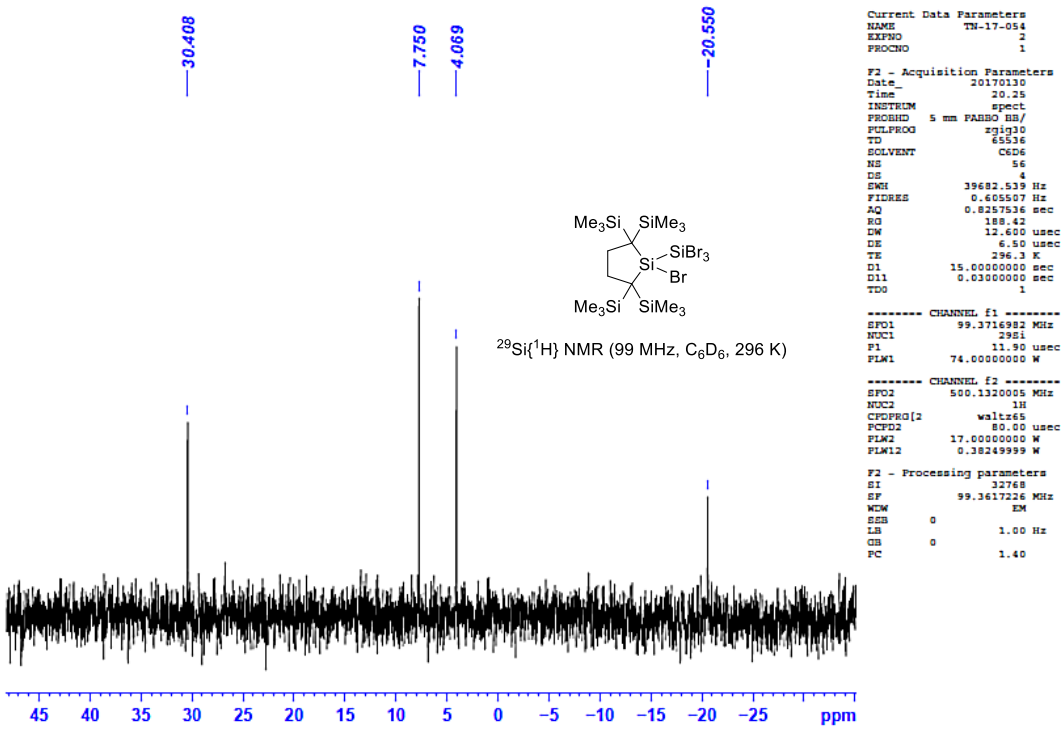


Figure 2-10. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 296 K.

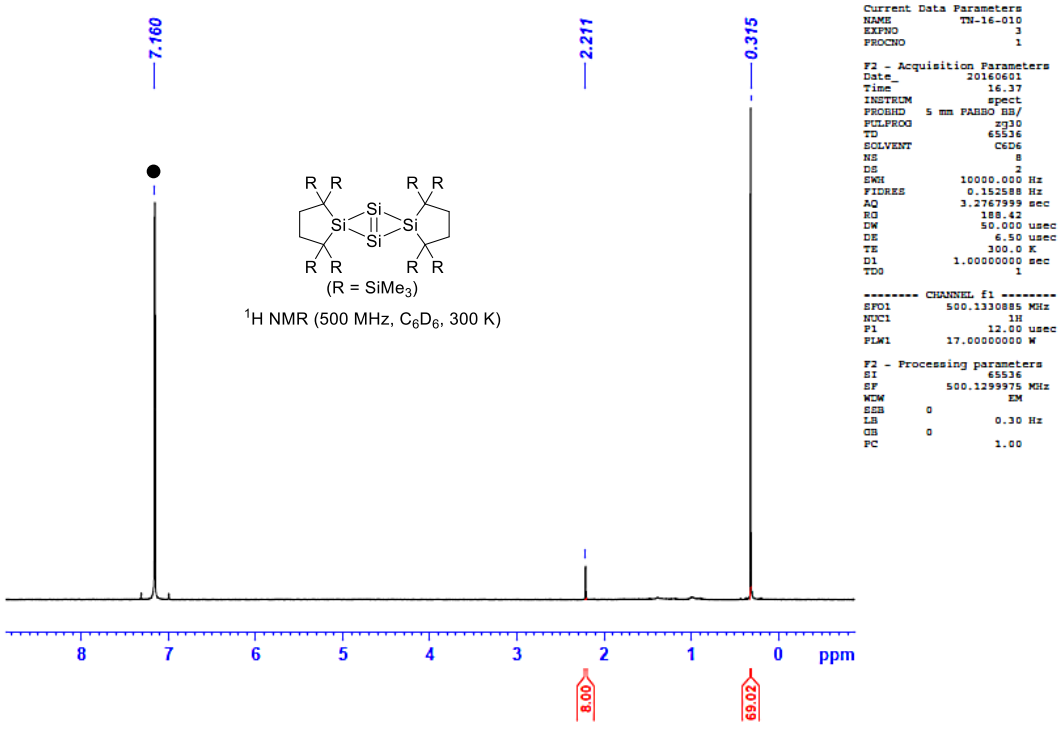


Figure 2-11. ^{1}H NMR spectrum of **1b** in C_6D_6 at 300 K (● = C_6HD_5).

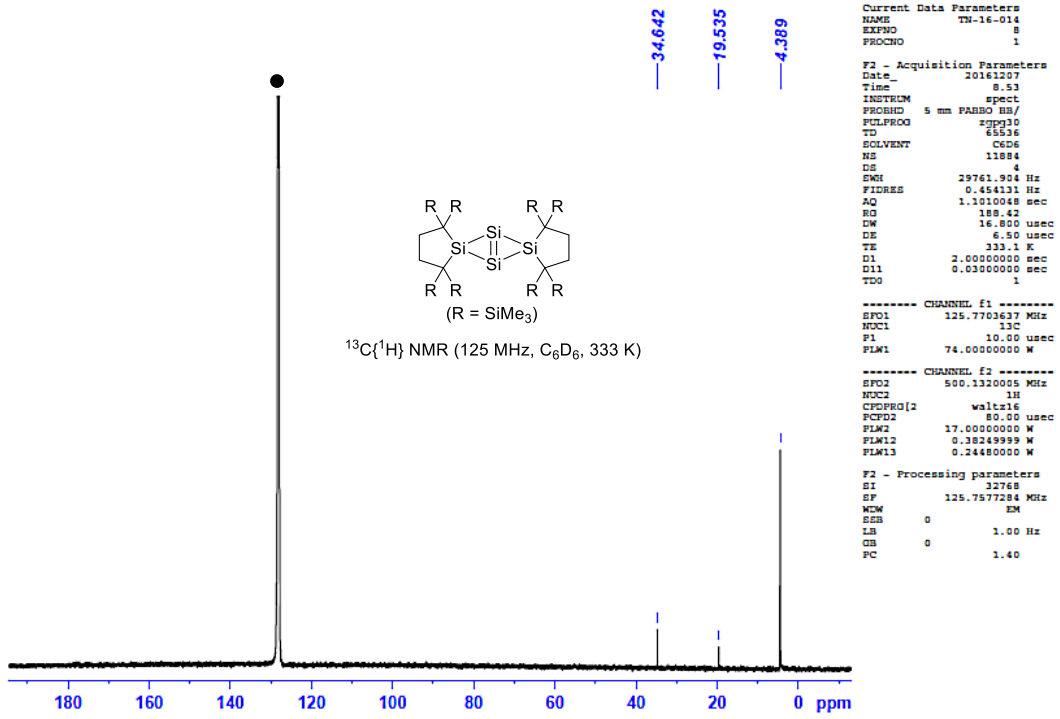


Figure 2-12. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 333 K (● = C_6D_6).

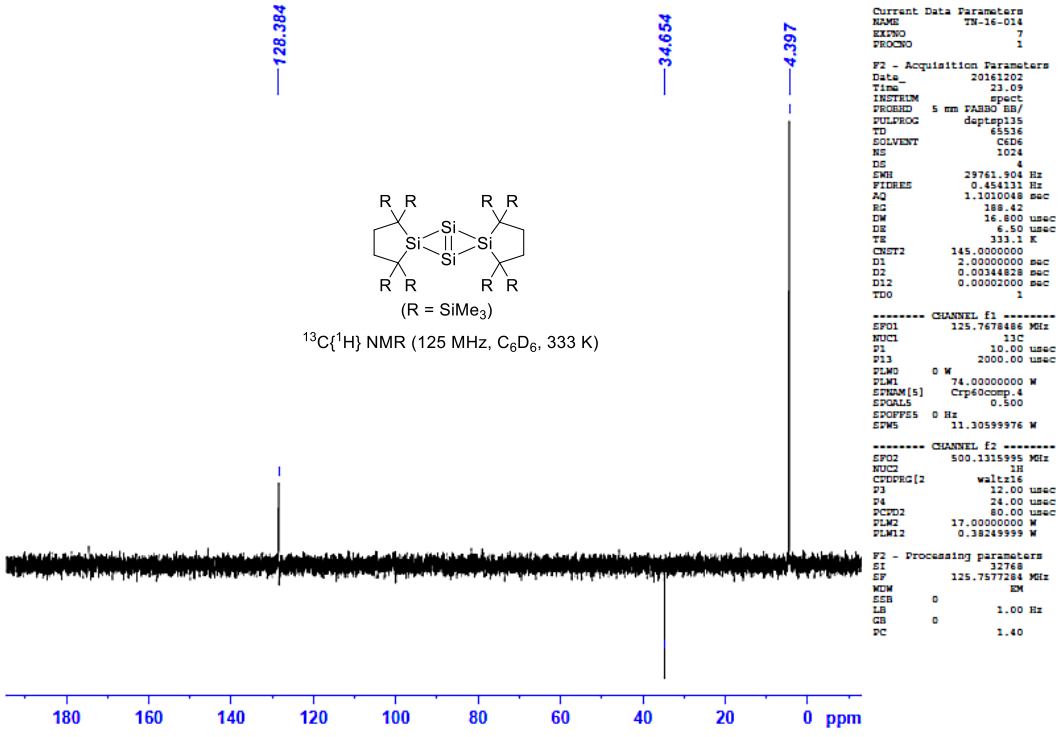


Figure 2-13. ^{13}C (DEPT135) NMR spectrum of **1b** in C_6D_6 at 333 K.

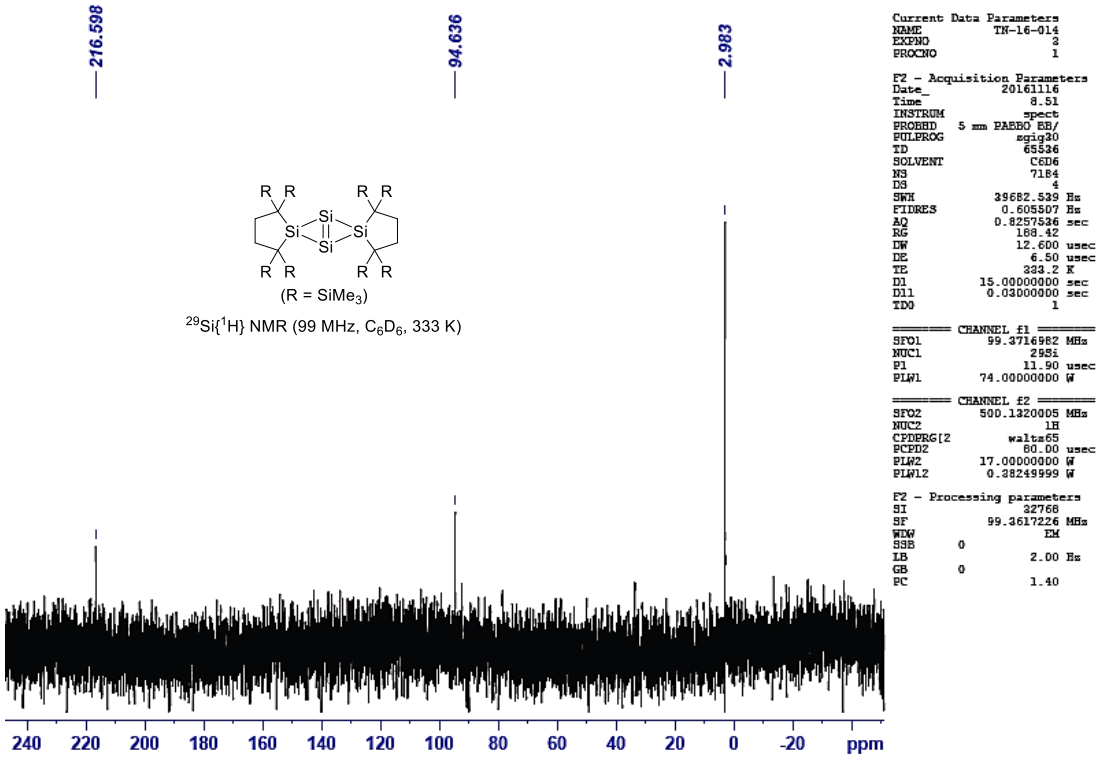


Figure 2-14. $^{29}Si\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 333 K.

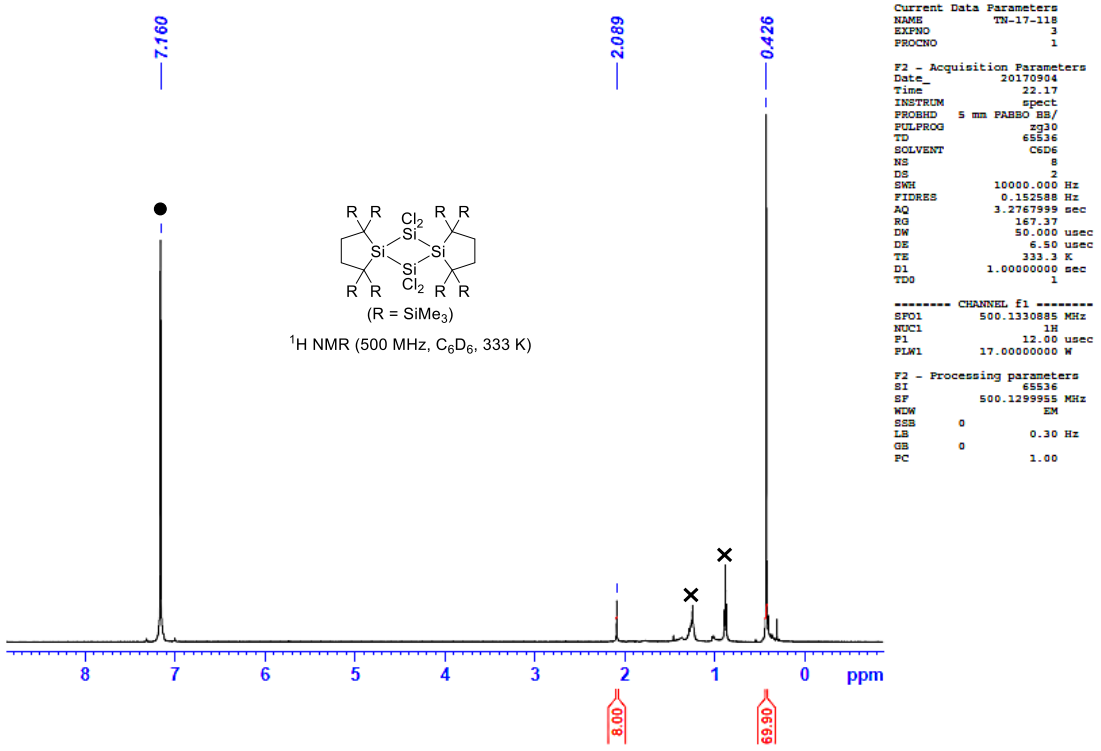


Figure 2-15. ^{1}H NMR spectrum of **4** in C_6D_6 at 333 K (● = C_6HD_5, × = hexane).

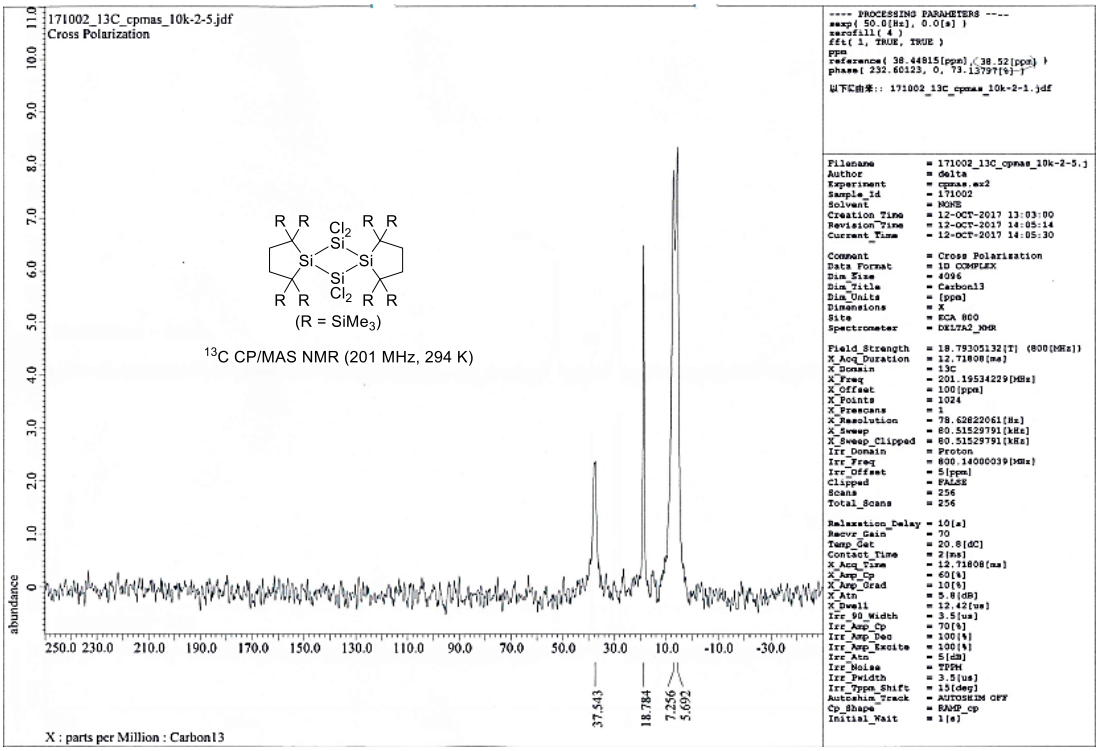


Figure 2-16. $^{13}C\{^{1}H\}$ CP/MAS spectrum of **4** at 294 K.

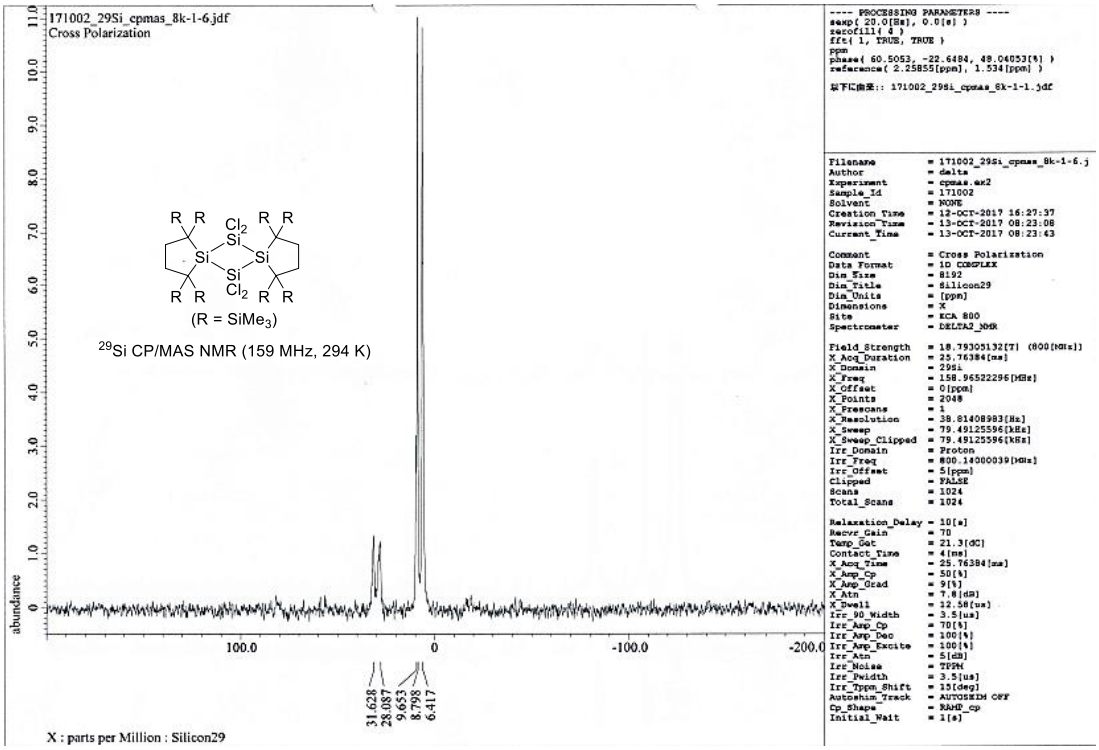


Figure 2-17. $^{29}Si\{^{1}H\}$ CP/MAS spectrum of **4** at 294 K.

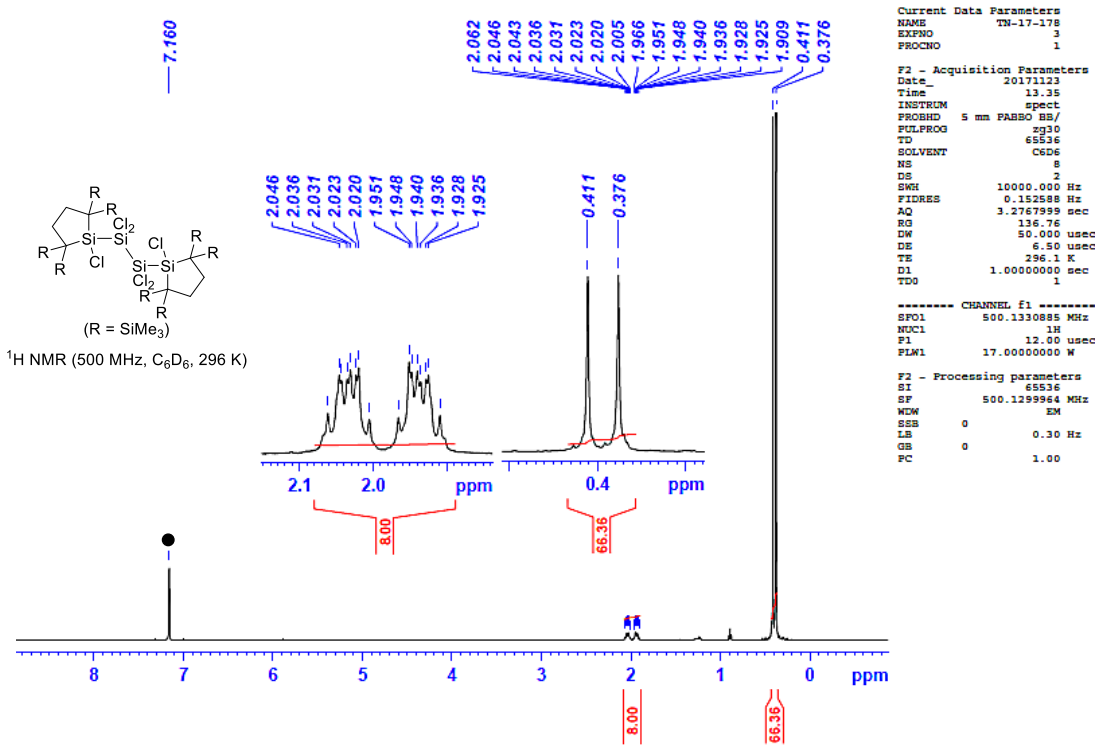


Figure 2-18. ^{1}H NMR spectrum of **5** in C_6D_6 at 296 K (● = C_6HD_5).

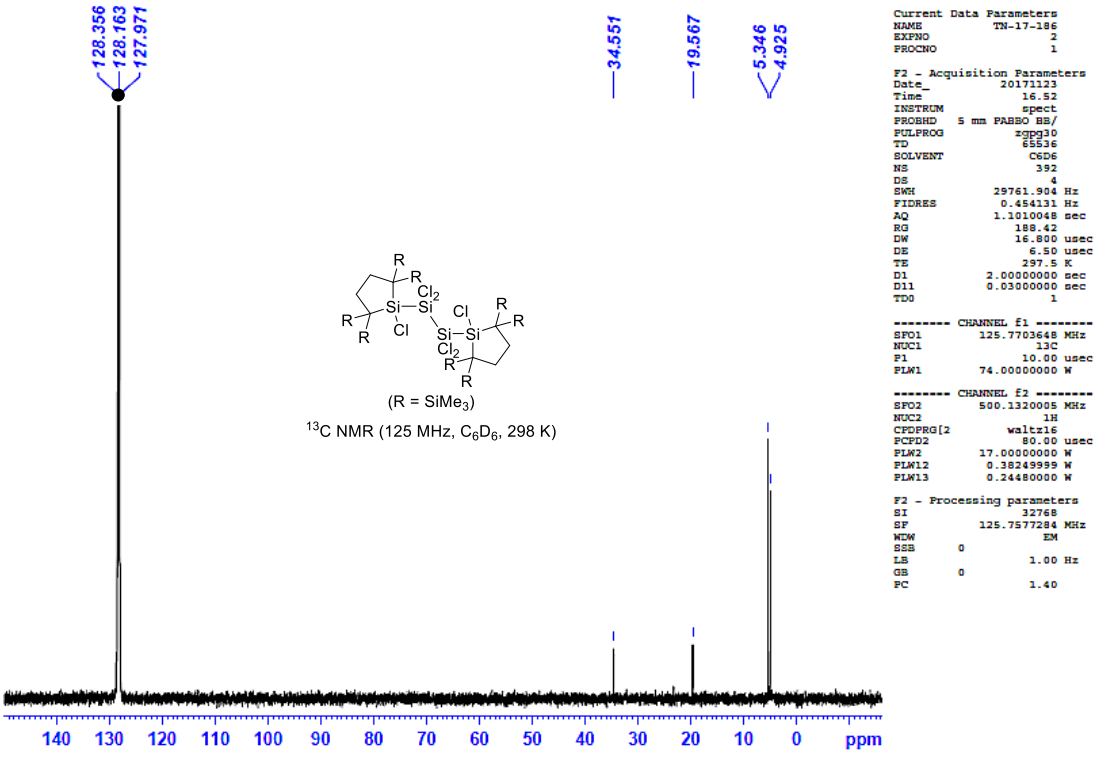


Figure 2-19. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 298 K (● = C_6D_6).

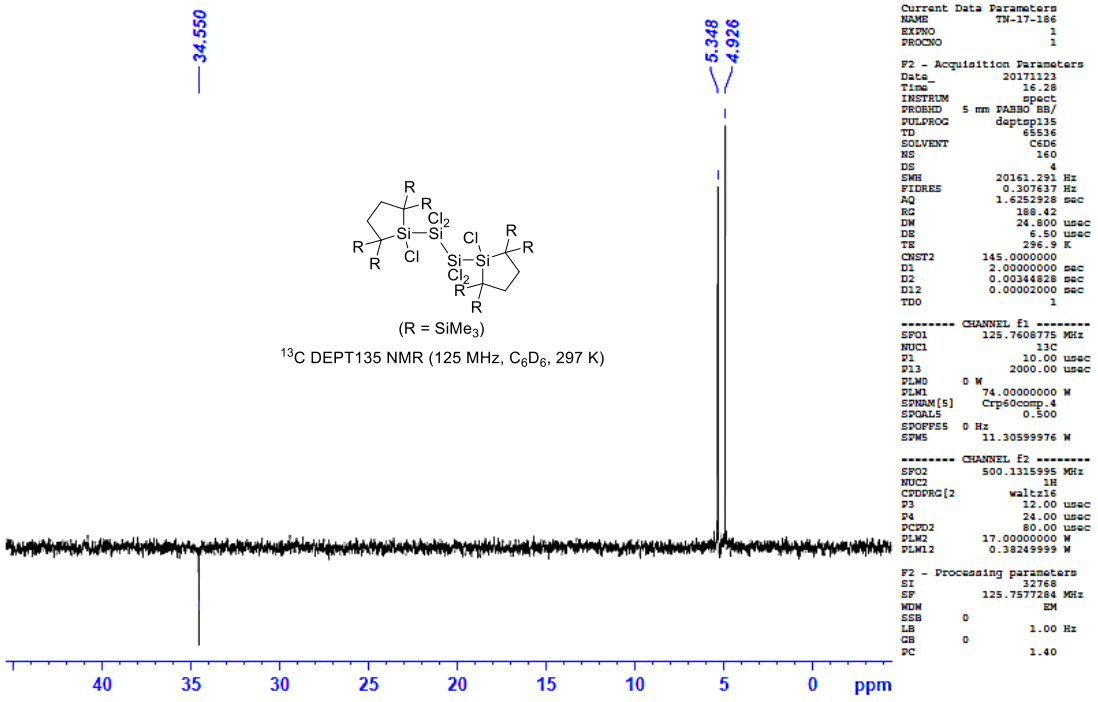


Figure 2-20. ^{13}C (DEPT135) NMR spectrum of **5** in C_6D_6 at 297 K.

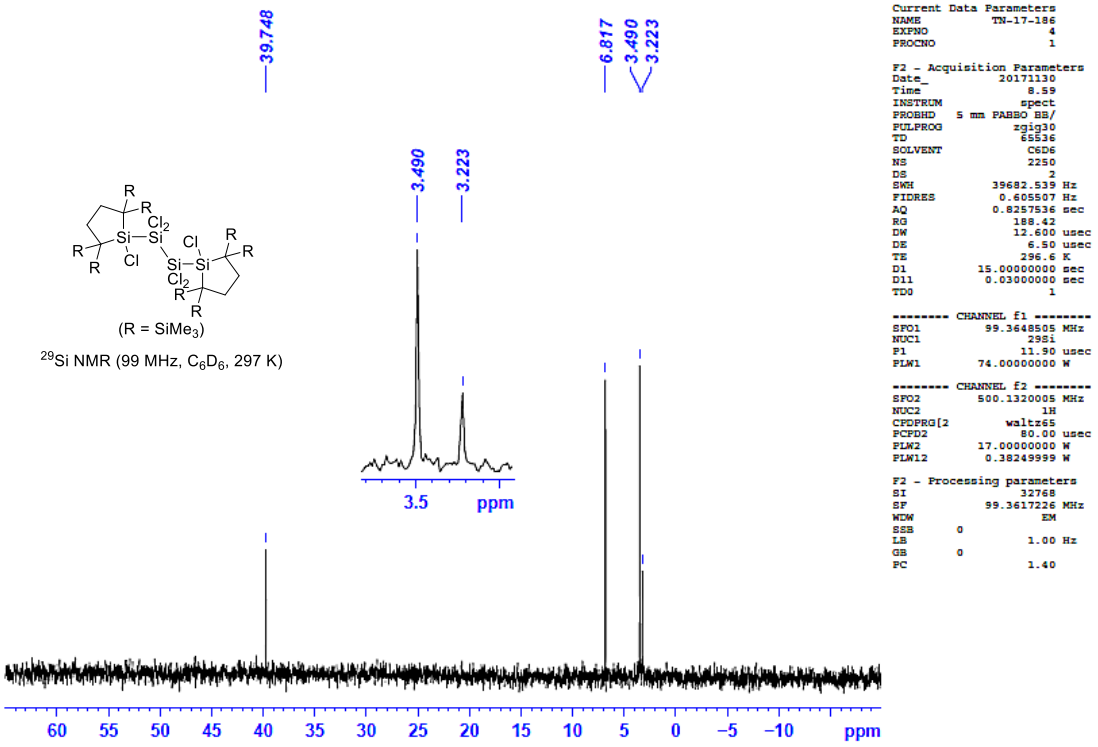


Figure 2-21. $^{29}Si\{^1H\}$ NMR spectrum of **5** in C_6D_6 at 297 K.

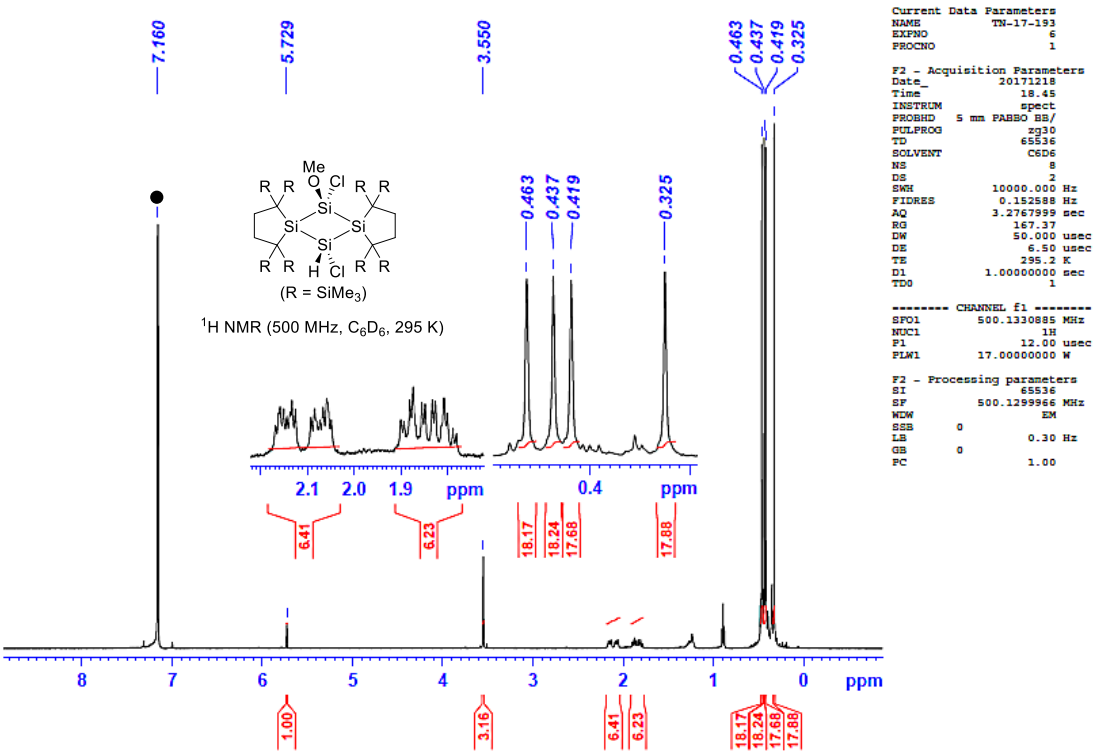


Figure 2-22. ^{1}H NMR spectrum of **6** in C_6D_6 at 295 K (● = C_6HD_5).

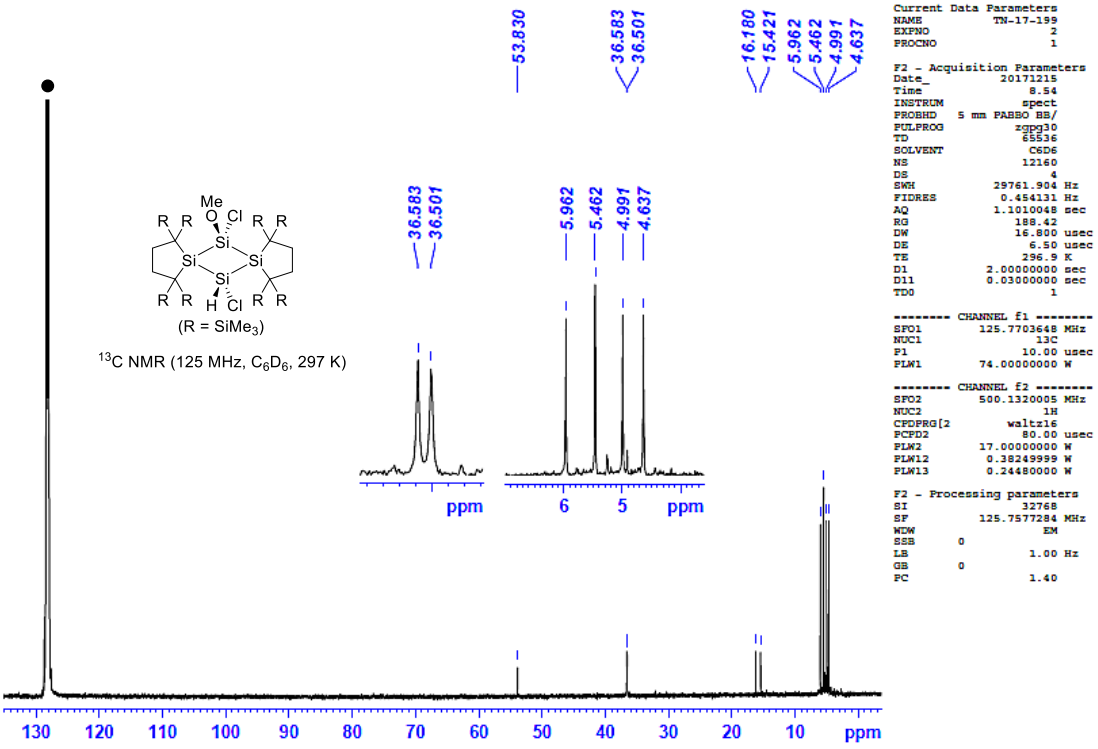


Figure 2-23. ^{13}C{^{1}H} NMR spectrum of **6** in C_6D_6 at 297 K (● = C_6D_6).

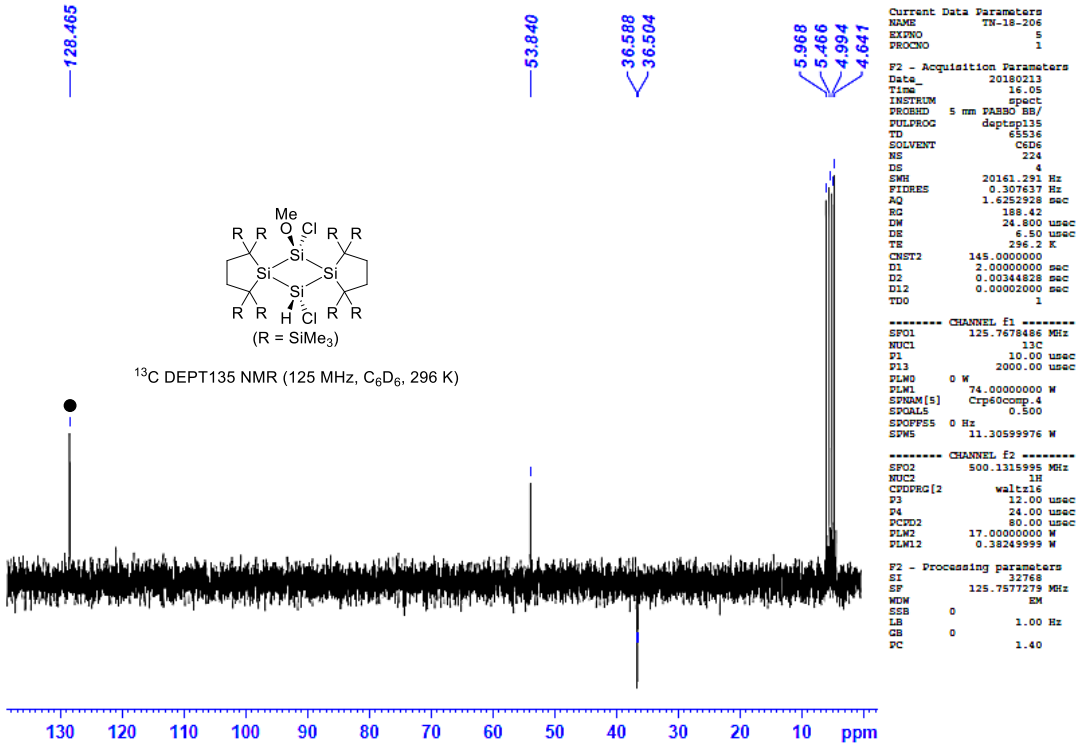


Figure 2-24. ^{13}C (DEPT135) NMR spectrum of **6** in C_6D_6 at 296 K (● = C_6D_6).

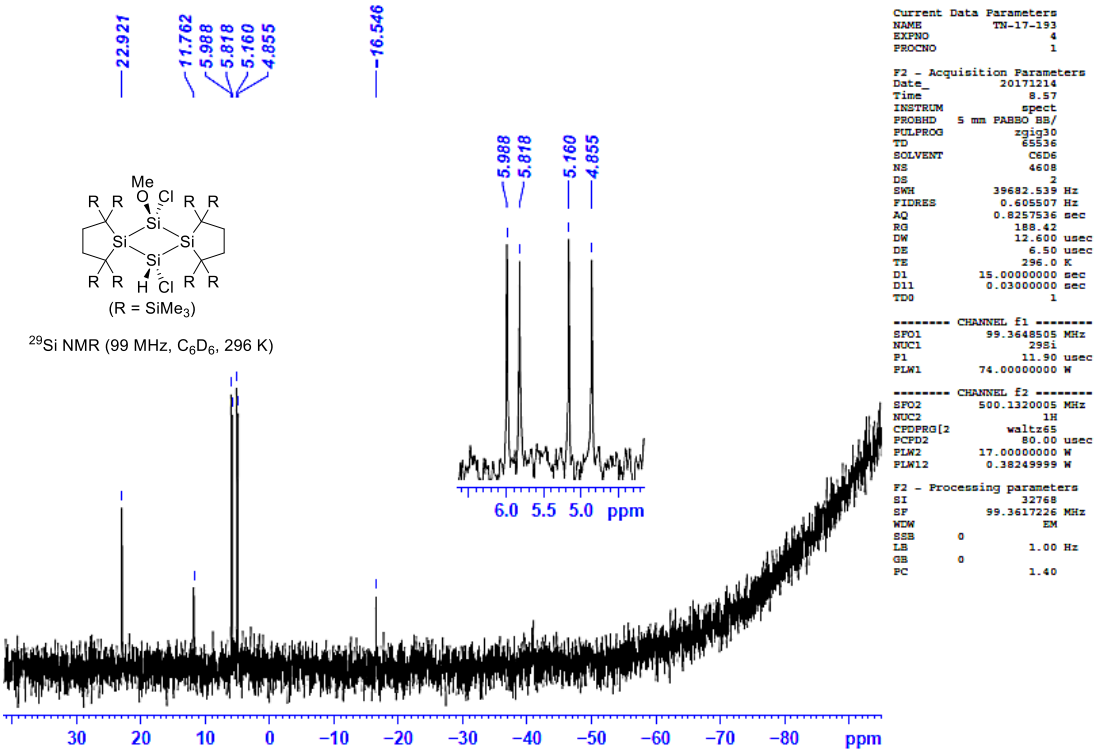


Figure 2-25. $^{29}Si\{^1H\}$ NMR spectrum of **6** in C_6D_6 at 296 K.

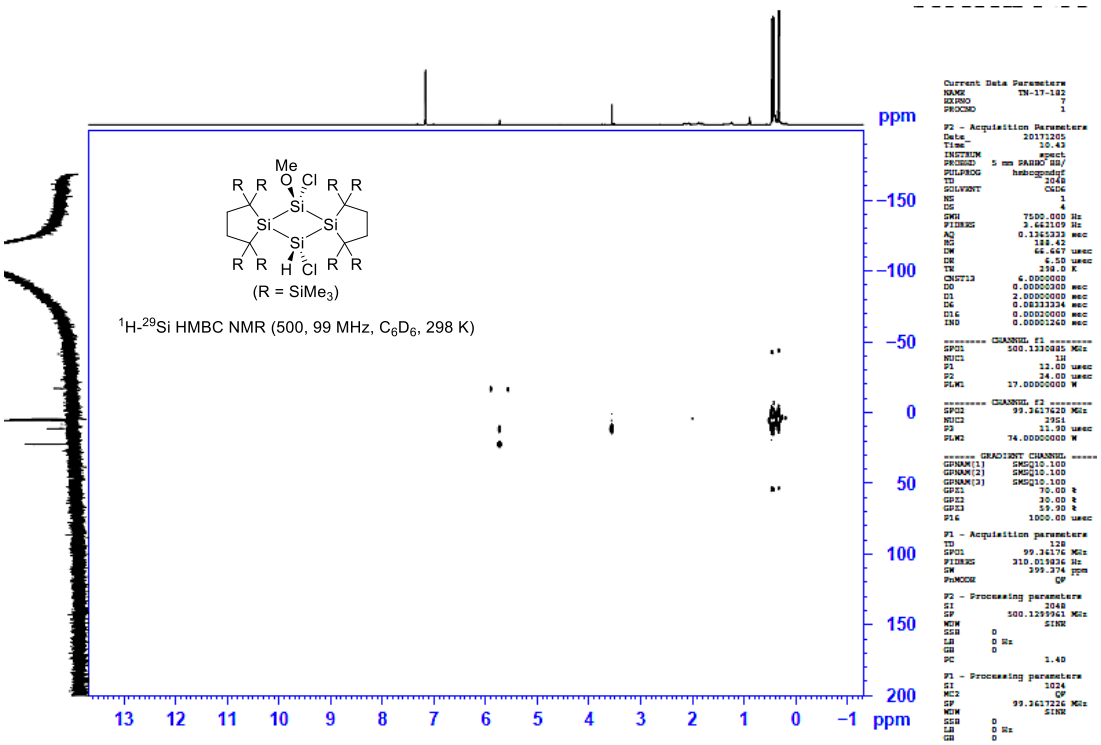


Figure 2-26. ^{1}H-^{29}Si HMBC NMR spectrum of **6** in C_6D_6 at 298 K.

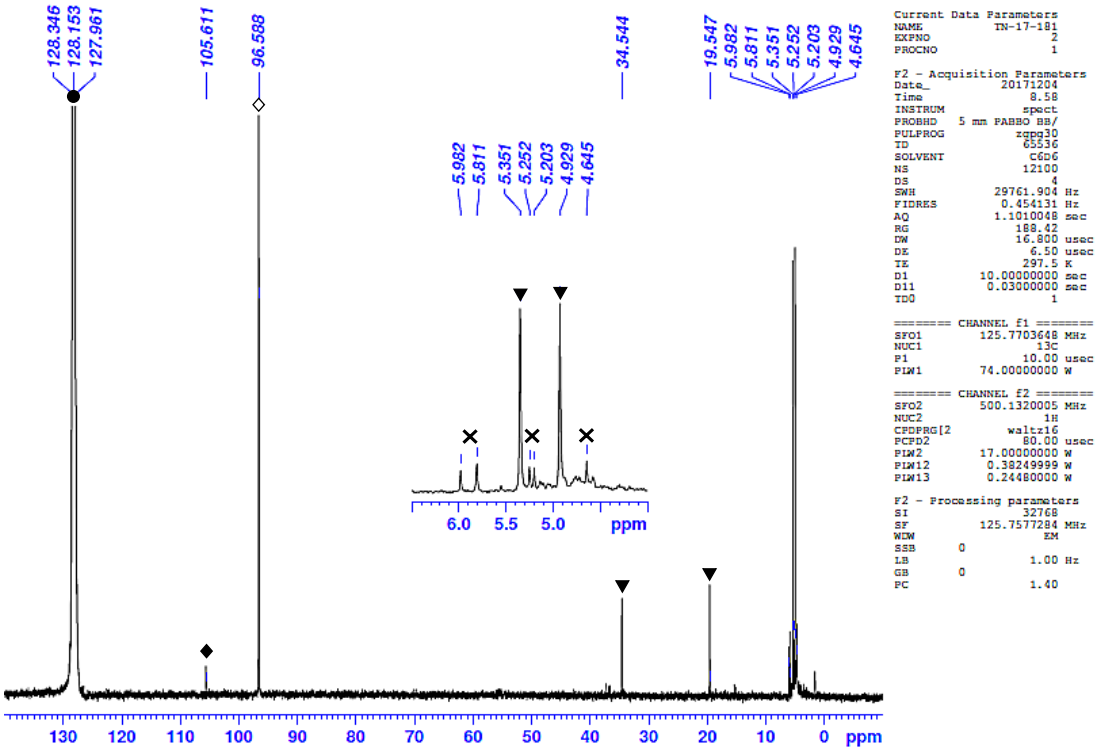


Figure 2-27. ^{13}C NMR spectrum of the reaction mixture of **1b** with CCl_4 in C_6D_6 at 298 K (● = C_6D_6, ▼ = **5**, ◊ = Carbon Tetrachloride, ♦ = Hexachloroethane, × = by products).

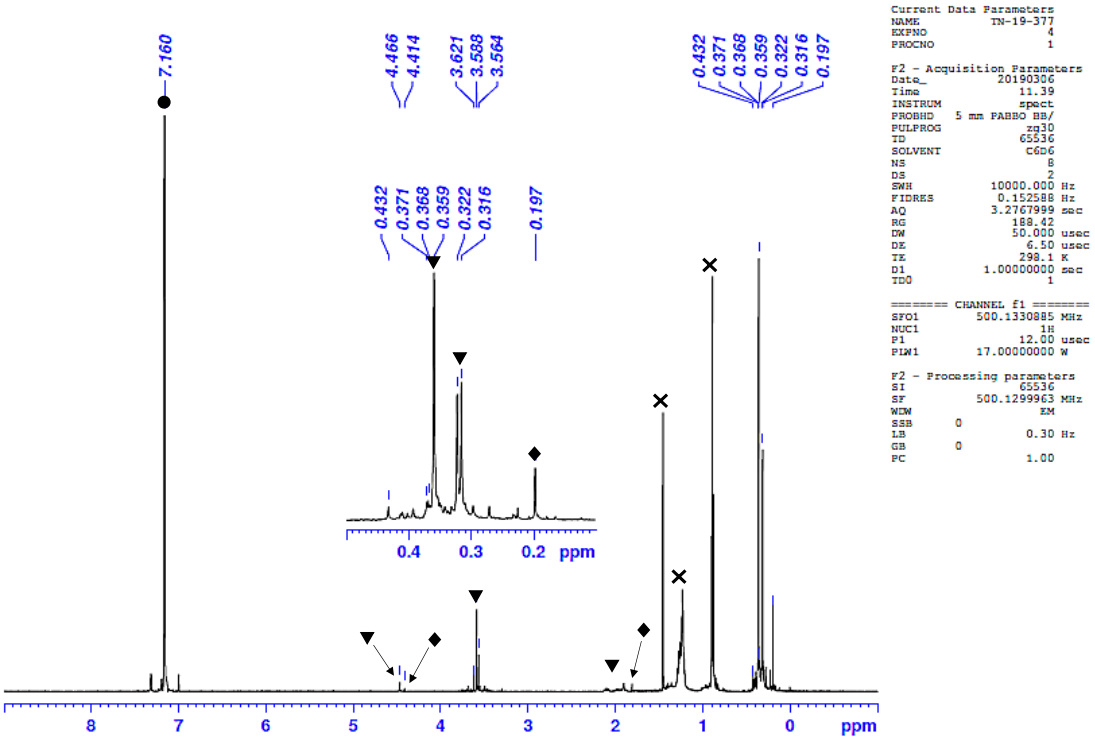


Figure 2-28. ^{1}H NMR spectrum of the reaction mixture of **1b** with MeOH in C_6D_6 at 298 K (● = C_6HD_5, ▼ = **9**, ♦ = Dihydrosilane[18], × = impurity).

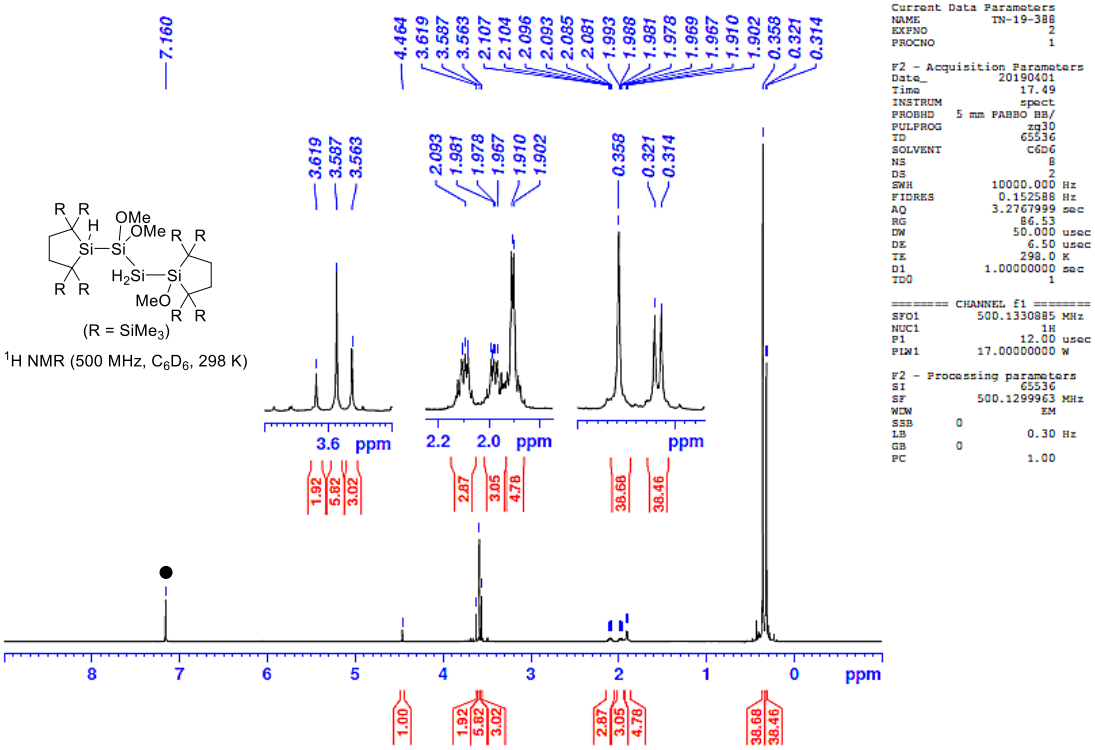


Figure 2-29. ^{1}H NMR spectrum of **9** in C_6D_6 at 298 K (● = C_6HD_5).

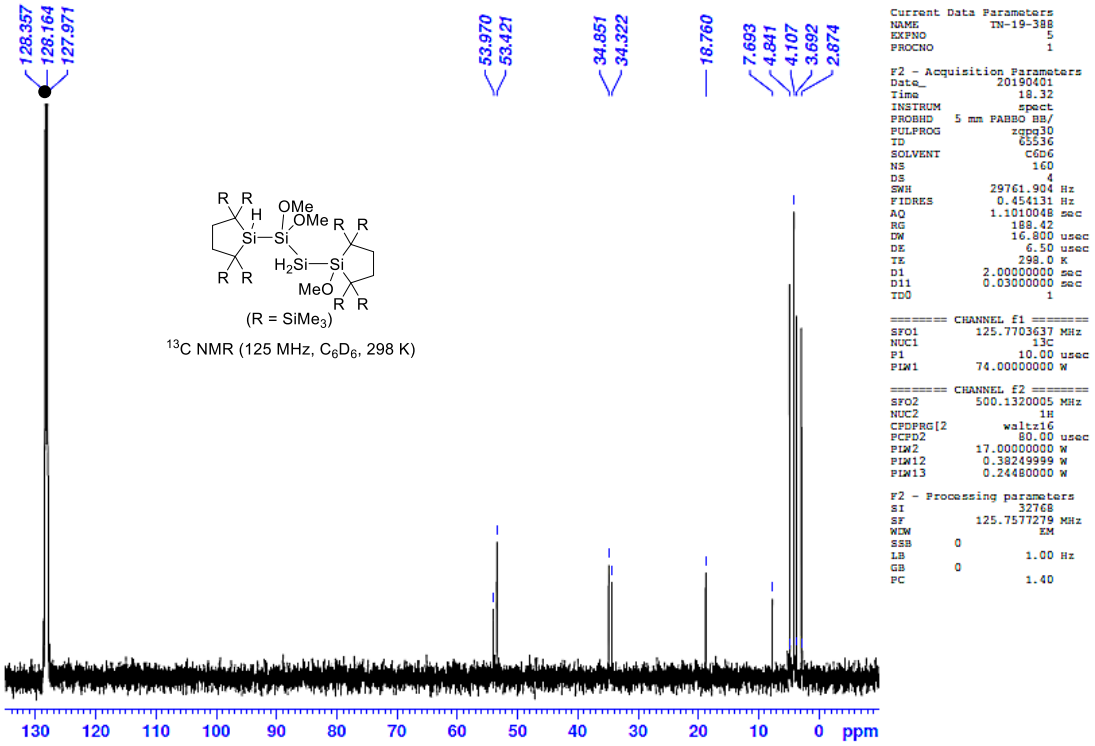


Figure 2-30. $^{13}C\{^{1}H\}$ spectrum of **9** in C_6D_6 at 298 K (● = C_6D_6).

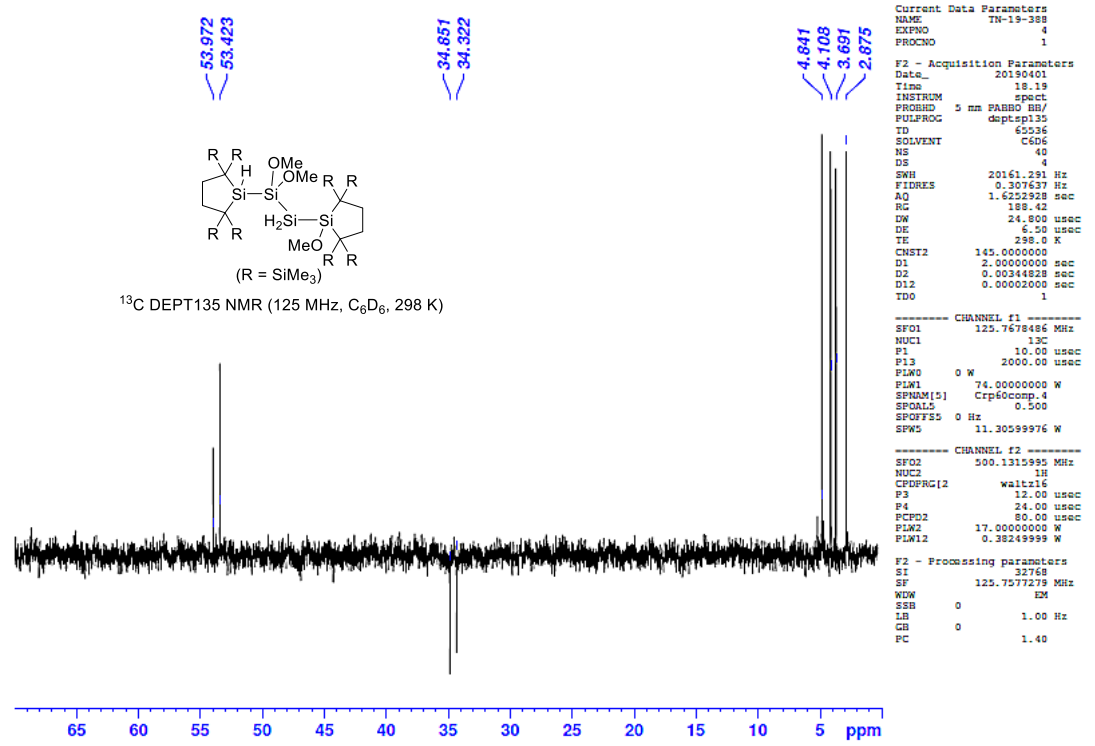


Figure 2-31. ^{13}C (DEPT135) NMR spectrum of **9** in C_6D_6 at 298 K.

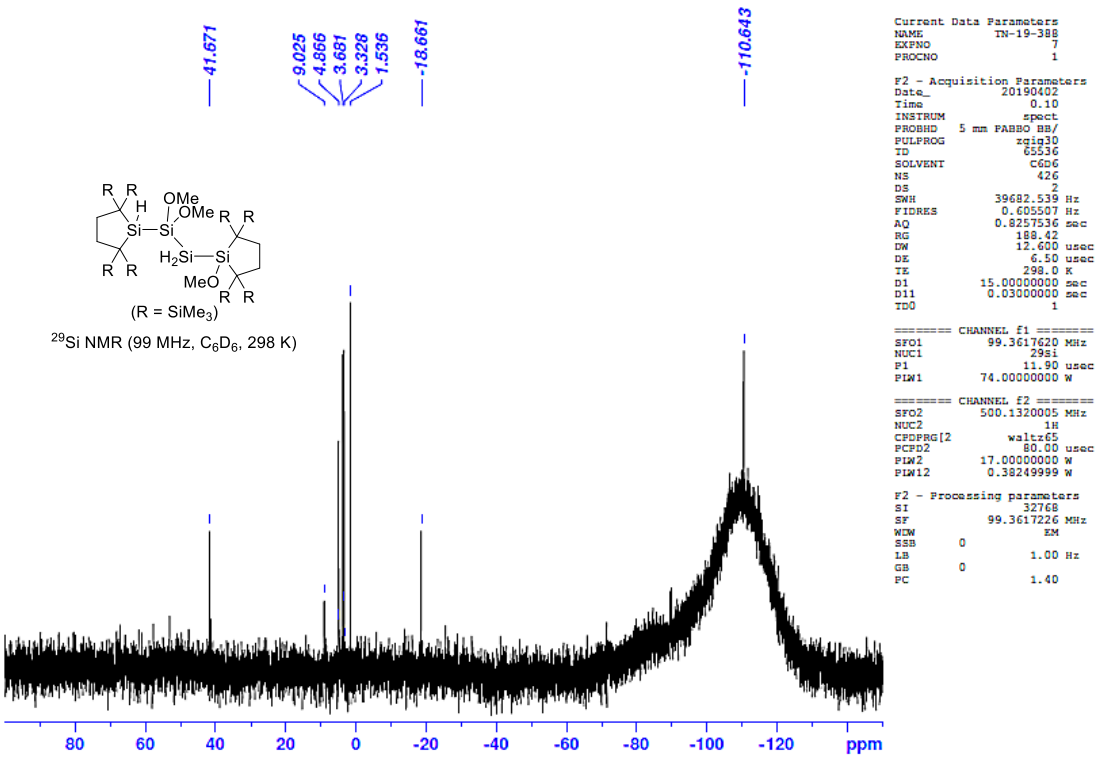


Figure 2-32. $^{29}Si\{^{1}H\}$ spectrum of **9** in C_6D_6 at 298 K.

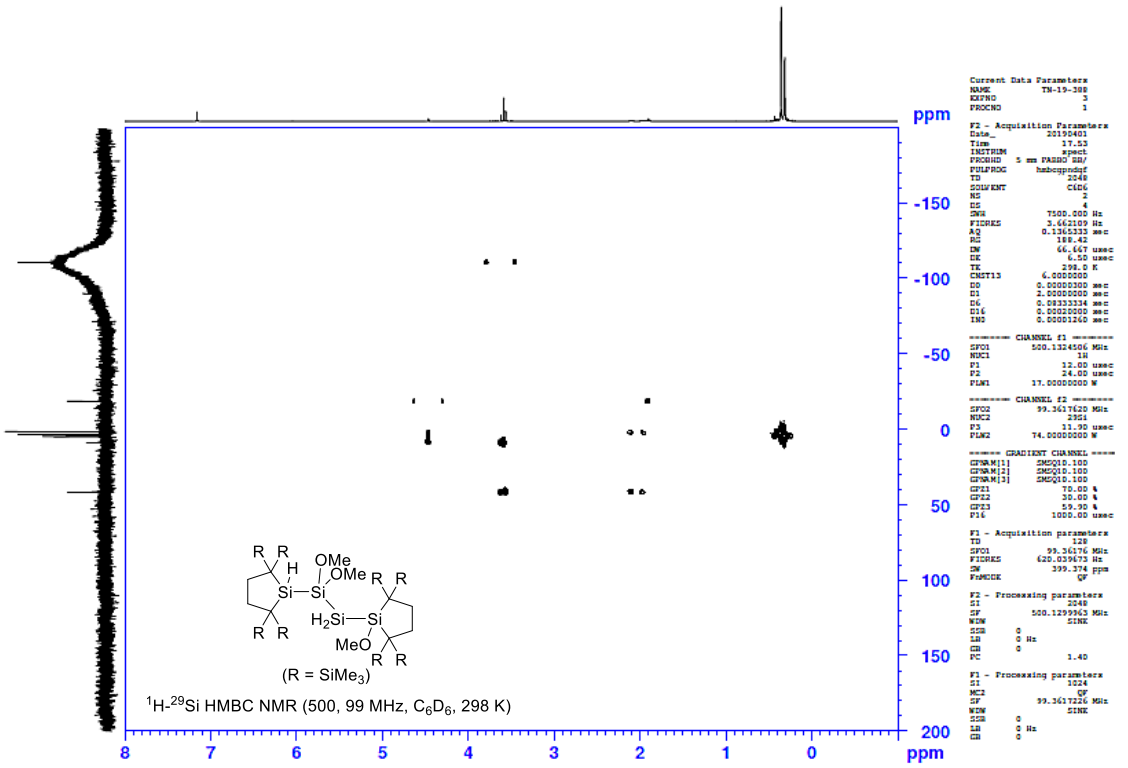


Figure 2-33. ^{1}H-^{29}Si HMBC NMR spectrum of **9** in C_6D_6 at 298 K.

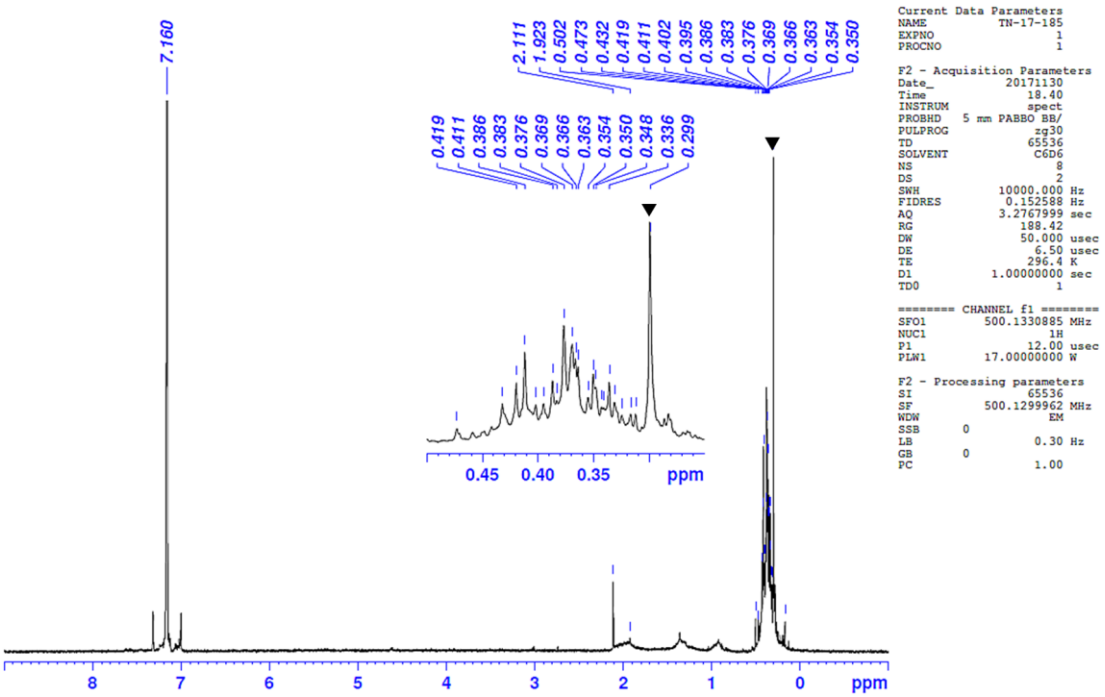


Figure 2-34. ^{1}H NMR spectrum for the reaction mixture of **1b** with 2 equivalents of CCl_4 recorded in C_6D_6 at 296 K (▼ = silicon grease).

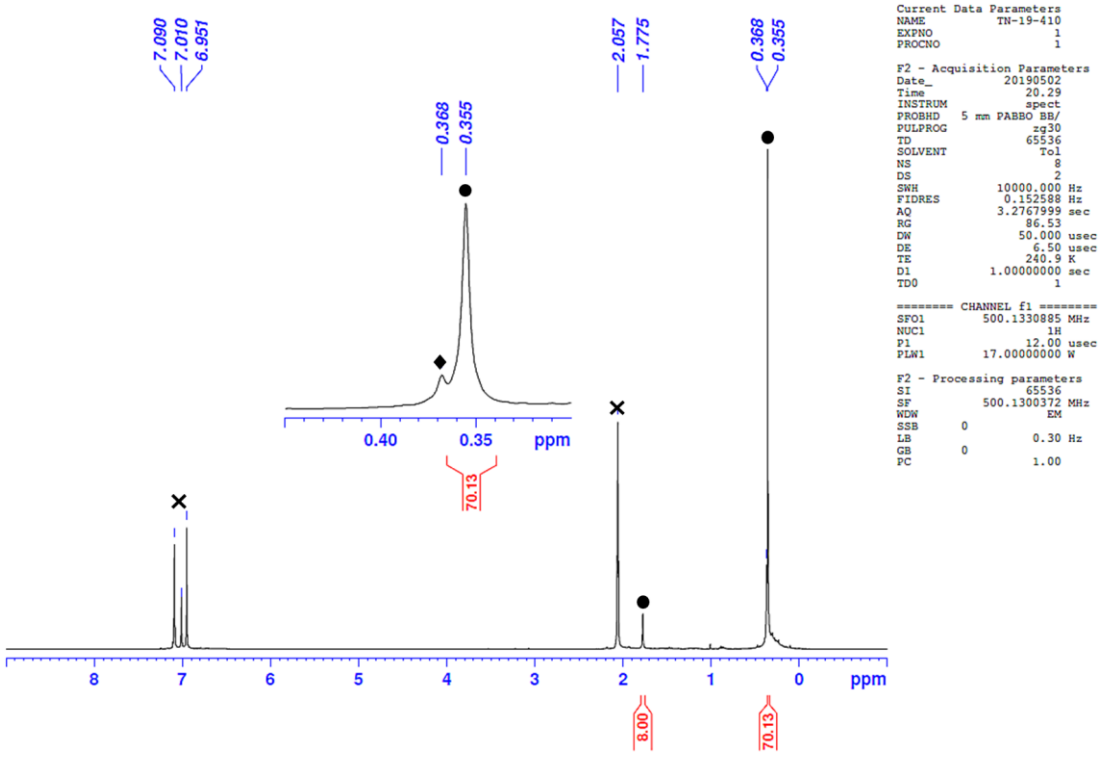


Figure 2-35. ^{1}H NMR spectrum of the mixture after addition of excess carbon tetrachloride to a toluene-d_8 solution of **1b** at 241 K (● = intermediate, ♦ = **4**, × = C_7D_7H).

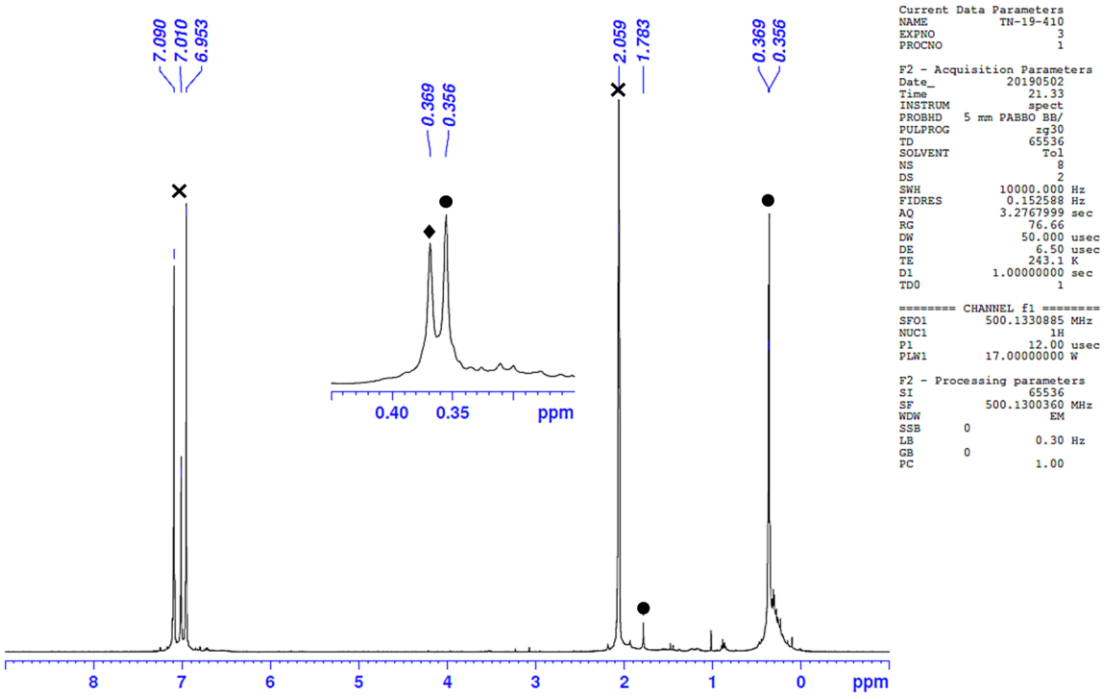


Figure 2-36. ^{1}H NMR spectrum of the reaction mixture after the reaction of **1b** with excess carbon tetrachloride for 1 hour in toluene-d_8 at 243 K (● = intermediate, ♦ = **4**, × = C_7D_7H).

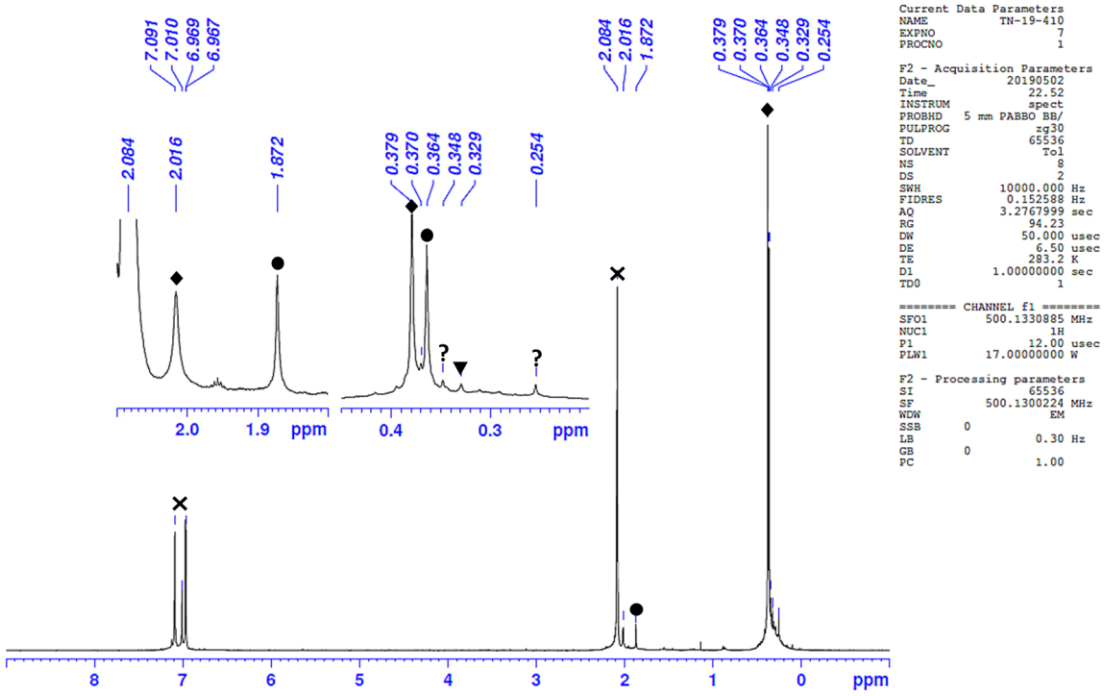


Figure 2-37. ^{1}H NMR spectrum of the reaction mixture of the reaction of **1b** with excess carbon tetrachloride in toluene-d_8 at 283 K (● = intermediate, ♦ = **4**, ▼ = **5**, × = C_7D_7H).

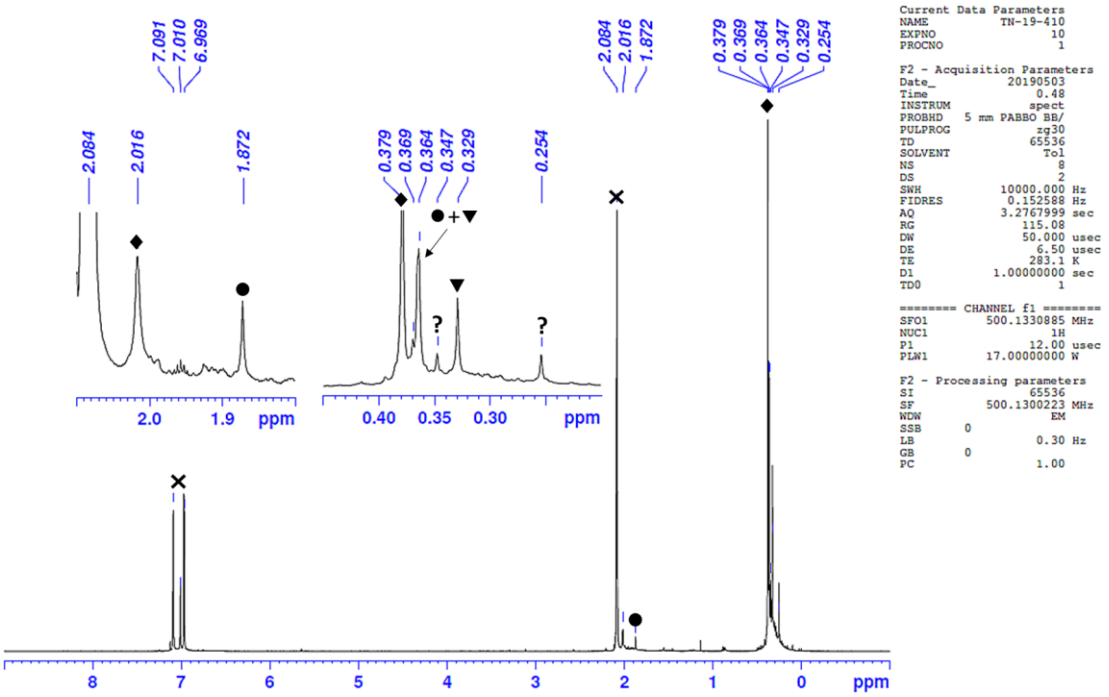


Figure 2-38. ^{1}H NMR spectrum of the reaction mixture of the reaction of **1b** with excess carbon tetrachloride in toluene-d_8 for additional 2 hours at 283 K (● = intermediate, ♦ = **4**, ▼ = **5**, × = C_7D_7H).

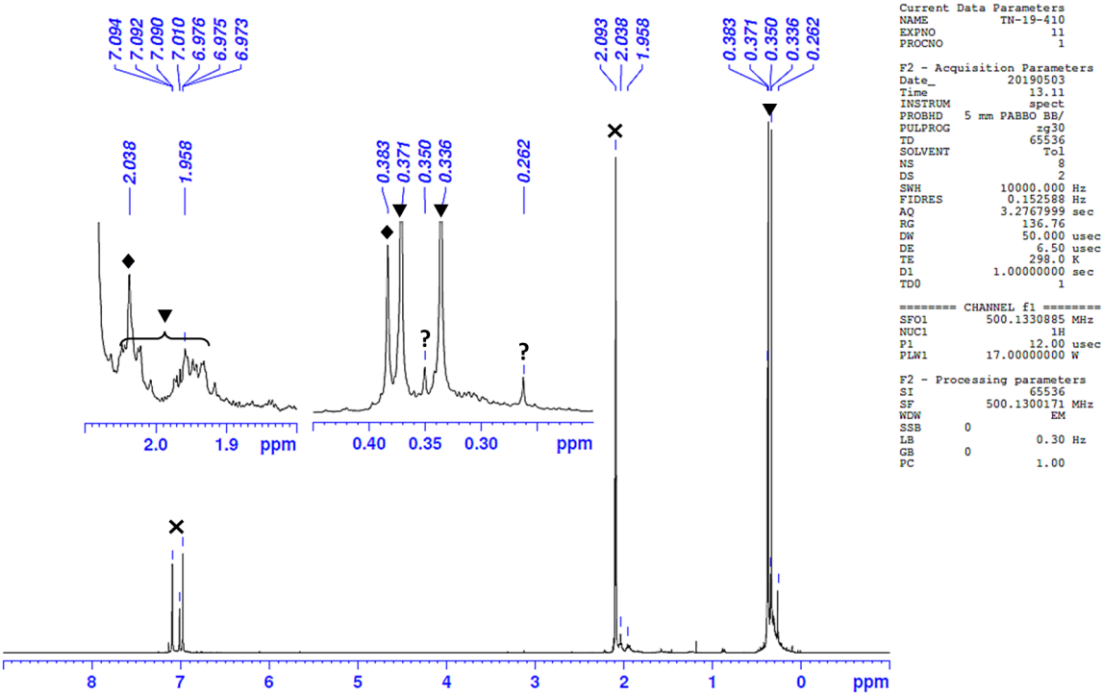


Figure 2-39. ^{1}H NMR spectrum of the reaction mixture of the reaction of **1b** with excess carbon tetrachloride in toluene-d_8 for additional several hours at 298 K (♦ = **4**, ▼ = **5**, × = C_7D_7H).

X-ray Diffraction Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallisation in an inert atmosphere using the following conditions; from toluene at room temperature for **1b**, from toluene at room temperature for **4**, from hexane at −35 °C for **5**, from hexane at room temperature for **6**, and from hexane at −35 °C for **9**. For data collection, the single crystals coated by Apiezon grease were mounted on the glass fibre and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer using a graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[19] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2014).[20] Molecular structure was analysed by Yadokari-XG software.[21]

Crystal data of **1b** (100 K) [CCDC-1908502]: $C_{32}H_{80}Si_{12}$; Fw 802.04; triclinic; *P*-1, a = 9.2308(5) Å, b = 11.5172(6) Å, c = 13.2387(6) Å, α = 64.9580(10)°, β = 75.3080(10)°, γ = 66.7880(10)°, V = 1165.54(10) Å^3, Z = 1, D_{calc} = 1.143 Mg/m^3, $R1$ = 0.0333 ($I > 2\sigma(I)$), $wR2$ = 0.0841 (all data), GOF = 0.997.

Crystal data of **4** (100 K) [CCDC-1908503]: $C_{32}H_{80}Cl_4Si_{12}$; Fw 943.84; triclinic; *P*-1, a = 10.6683(5) Å, b = 10.7582(5) Å, c = 12.9529(6) Å, α = 69.0200(10)°, β = 84.5210(10)°, γ = 65.6520(10)°, V = 1262.24(10) Å^3, Z = 1, D_{calc} = 1.242 Mg/m^3, $R1$ = 0.0318 ($I > 2\sigma(I)$), $wR2$ = 0.0816 (all data), GOF = 1.049.

Crystal data of **5** (100 K) [CCDC-1908504]: $C_{32}H_{80}Cl_6Si_{12}$; Fw 1014.74; triclinic, *P*-1, a = 11.7581(5) Å, b = 20.4191(9) Å, c = 23.6336(10) Å, α = 99.4190(10)°, β = 104.2580(10)°, γ = 94.1290(10)°, V = 5387.7(4) Å^3, Z = 4, D_{calc} = 1.251 Mg/m^3, $R1$ = 0.0330 ($I > 2\sigma(I)$), $wR2$ = 0.0913, GOF = 1.023.

Crystal data of **6** (100 K) [CCDC-1908505]: $C_{36}H_{91}Cl_2OSi_{12}$; Fw 948.06; monoclinic; $P2_1/c$, a = 18.4326(8) Å, b = 12.7398(6) Å, c = 23.2524(10) Å, β = 93.1569(12)°, V = 5452.0(4) Å^3, Z = 4, D_{calc} = 1.155 Mg/m^3, $R1$ = 0.0428 ($I > 2\sigma(I)$), $wR2$ = 0.1130 (all data), GOF = 1.060.

Crystal data of **9** (100 K) [CCDC-1908569]: $C_{35}H_{92}O_3Si_{12}$; Fw 898.14; triclinic, P-1, a = 11.3627(5) Å, b = 16.4034(8) Å, c = 17.0141(8) Å, α = 112.0530(10)°, β = 94.2250(10)°, γ = 109.5290 (10)°, V = 2697.1(2) Å^3, Z = 2, D_{calc} = 1.106 Mg/m^3, $R1$ = 0.0270 ($I > 2\sigma(I)$), $wR2$ = 0.0769, GOF = 1.033.

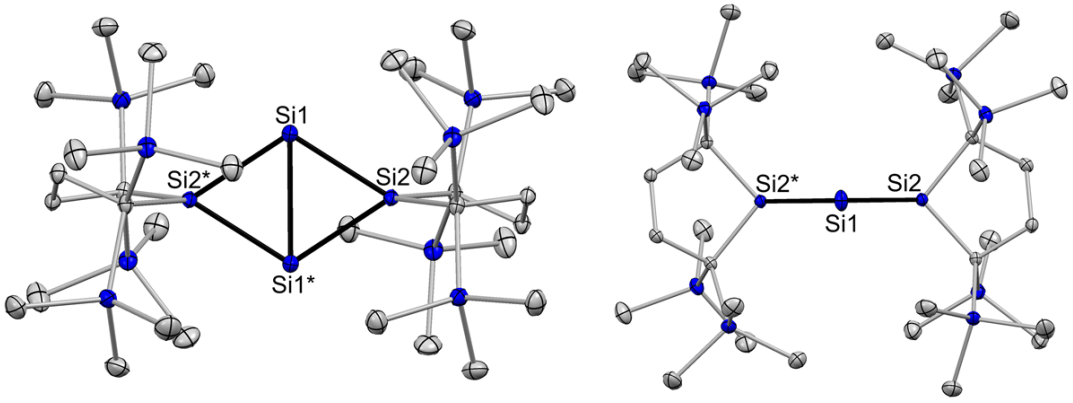


Figure 2-40. ORTEPs of **1b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

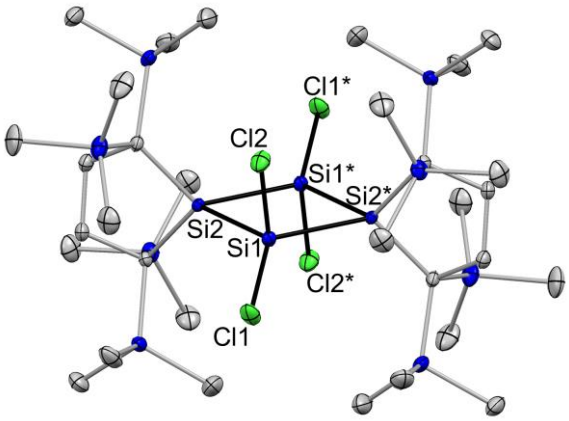


Figure 2-41. ORTEP of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

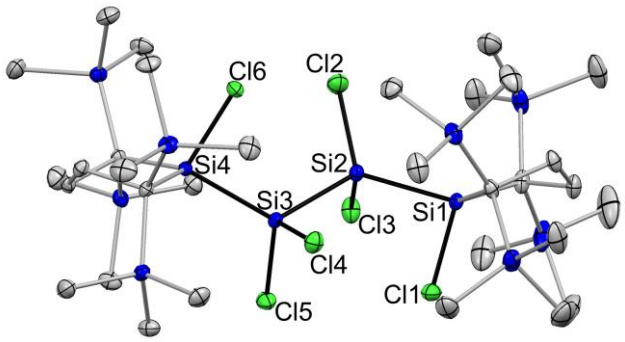


Figure 2-42. ORTEP of **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

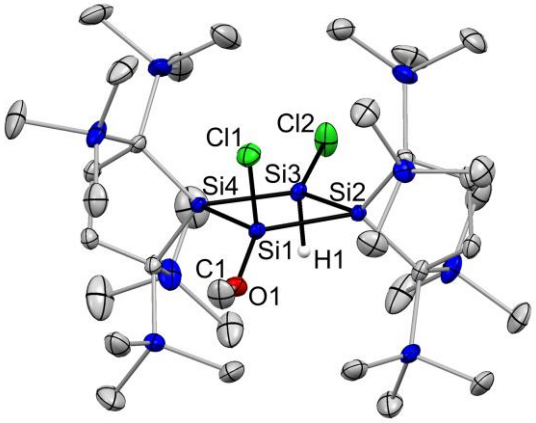


Figure 2-43. ORTEP of **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

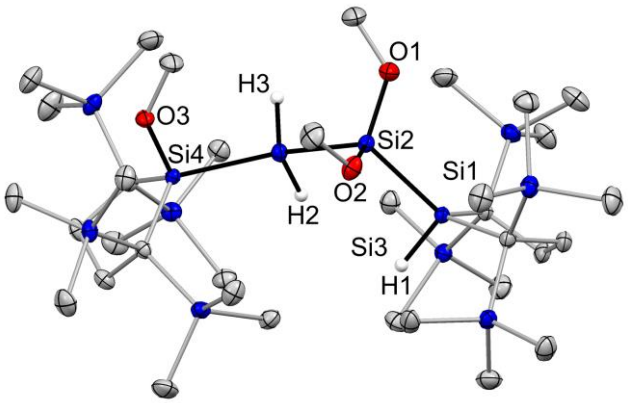


Figure 2-44. ORTEP of **9**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

UV-vis Absorption Spectrum

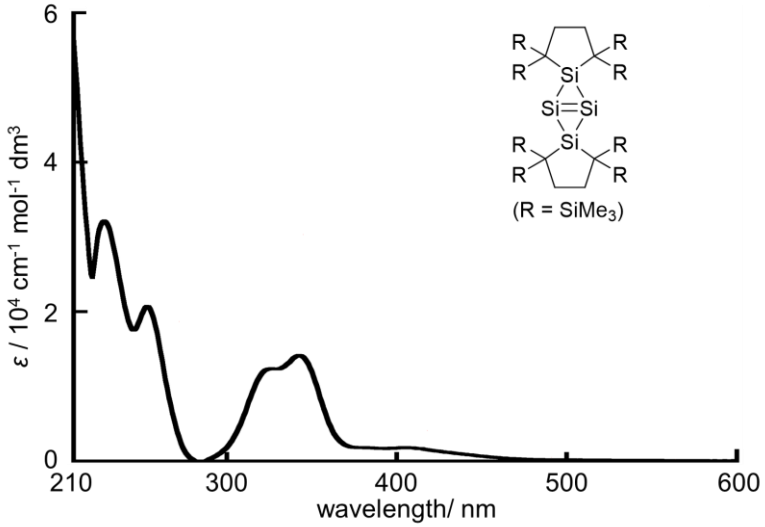
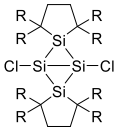


Figure 2-45. UV-vis absorption spectrum of **1b** in hexane at room temperature.

Computational Study

All theoretical calculations were performed using a Gaussian 09[22] program. Geometry optimization was carried out at the B3LYP-D3/6-31G(d) level of theory. For bicyclo[1.1.0]tetrasilanes **7** and **10**, two conformers, which differ primarily in the geometry around the bridgehead silicon atoms, were located. Although the free energy differences between the two conformers are rather small (13.2 and 27.7 kJ mol^{-1} for **7** and **10**, respectively), the energies of more stable conformers were used to estimate the free energy differences for the isomerization of bicyclo[1.1.0]tetrasilanes to the corresponding tetrasila-1,3-dienes. The atomic coordinates and energies of the optimized structures are summarized in Tables 2-1 to 2-6.

Table 2-1. Atomic Coordinates of **7** (SB) at the B3LYP-D3/6-31G(d) Level of Theory



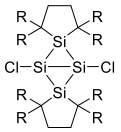
7

Atom	X	Y	Z
Si	0.0442091195	1.2271276015	0.0491167086
Si	0.0508583763	-1.2270579803	0.04370215
Si	-1.6088816335	-0.0195568032	1.1266099575
Si	1.0537451361	0.0192361516	-1.6559799213
C	3.0093720023	-0.0158627755	-1.7611526686
C	3.1770519156	-0.3140229673	-3.2935595434
C	2.087705982	0.3947752555	-4.1174459936
C	0.6514623208	0.069634806	-3.549474391
C	-3.5182222973	-0.0713226813	0.8081068778
C	-4.0222051534	-0.3959518137	2.2681514496
C	-3.151618612	0.3139990045	3.3197662425
C	-1.6278830788	0.0166945932	3.0849561954
Cl	0.5859271666	3.196743634	0.5682382301
Cl	0.5945458605	-3.1960146584	0.5632946537
Si	3.913697695	1.6375149344	-1.3180368718
C	5.6318197073	1.7172909625	-2.131898094
C	4.1215500069	1.8338629123	0.5536553805
C	3.1245867017	3.2262954218	-1.9701145259
Si	3.837136969	-1.4566534962	-0.7749530485
C	3.3307561733	-3.1261063119	-1.5199045281
C	3.4961076467	-1.4091405361	1.093925997
C	5.7301260718	-1.4763714189	-0.9397243442
Si	-0.4655442576	1.5318362141	-4.1157644513
C	-2.2895675619	1.3623803617	-3.654478951
C	-0.2458196289	1.7455934495	-5.9922644197
C	0.0044825313	3.224505106	-3.4091609333
Si	0.0031076582	-1.6215907633	-4.2848194192
C	-0.3519067827	-3.0039920529	-3.0374347967
C	1.2562201728	-2.3177261125	-5.532483813
C	-1.6255578594	-1.5387609508	-5.2666321513
Si	-0.6071560408	1.4586256454	3.8676622191
C	1.2449071753	1.412111703	3.4446490288
C	-0.6884193697	1.4793630945	5.7660592438
C	-1.3748158531	3.1272907861	3.3936462611

Si	-1.1443396806	-1.6358589414	3.9698568519
C	-1.8295286353	-3.2255094324	3.2111367797
C	-1.8817863124	-1.715125383	5.7221645944
C	0.7348089215	-1.8309250552	4.0952683006
Si	-4.2824350551	1.6190828856	0.1918124121
C	-3.0527024433	3.0019739706	-0.218571302
C	-5.4741464587	2.315209176	1.4982554859
C	-5.3349752068	1.534753834	-1.3919876782
Si	-4.1322795306	-1.534530369	-0.2820258399
C	-3.4046068979	-3.2265010577	0.1573864653
C	-3.7519441911	-1.3659077118	-2.124707884
C	-5.9971479935	-1.7492476577	0.0202819213
H	3.0969616603	-1.390515042	-3.4817257276
H	4.1694332849	-0.0201626401	-3.6560250481
H	2.2745330968	1.4752166064	-4.0728125841
H	2.1776531875	0.1202579274	-5.1732723692
H	-3.9687063579	-1.4762537696	2.4534471016
H	-5.0732221425	-0.1220227773	2.4043347943
H	-3.3438278735	1.3903257083	3.2474326862
H	-3.469852015	0.0204961738	4.3273084674
H	5.5477295988	1.7893571388	-3.2229153668
H	6.1094214982	2.6453280433	-1.7910481785
H	6.3081726902	0.8934959435	-1.9004617372
H	3.1901026694	1.6712718957	1.1034789819
H	4.4492044612	2.8589718723	0.7654074375
H	4.8765182549	1.1541337603	0.9616536852
H	3.7286398783	4.0624702497	-1.5939715083
H	3.1567880028	3.272950239	-3.0639967481
H	2.1009242663	3.394082486	-1.6424313249
H	3.9012873912	-3.3324859854	-2.4331072942
H	3.5576705022	-3.9226311652	-0.8015738623
H	2.2699240266	-3.2024286782	-1.7586557954
H	4.3652639562	-1.0116752897	1.6283327209
H	3.3020064742	-2.4190240925	1.4682561914
H	2.6381377733	-0.7883919925	1.3638669908
H	6.0837478568	-2.429056647	-0.5235951044
H	6.0668695127	-1.4299666059	-1.9813289887
H	6.2222947619	-0.6741740106	-0.3809464201
H	-2.3893202935	1.1051918561	-2.5965719543
H	-2.7701831719	2.3380696185	-3.7970121412
H	-2.8472757687	0.625535457	-4.2336666313
H	0.7509131873	2.1497586935	-6.2063899858
H	-0.9789689602	2.4677320939	-6.3724515857
H	-0.3560328337	0.822924739	-6.569321723
H	-0.0641704265	3.2888877833	-2.3194829577
H	0.9986077065	3.5630976793	-3.7077830261
H	-0.7184198211	3.9417034099	-3.8202728288
H	0.5131097085	-3.3303414946	-2.4574708819
H	-1.1485309513	-2.7458744738	-2.3331819499
H	-0.7034124214	-3.8706252652	-3.6129330201
H	1.376097292	-1.6633280912	-6.4038649119
H	0.8690189771	-3.2771736939	-5.8973753988
H	2.2491888745	-2.5032356636	-5.1118058867
H	-2.5009204167	-1.4773289492	-4.6147957853
H	-1.6912640901	-0.7366910992	-6.0054575696
H	-1.6977709034	-2.4897232095	-5.8107606168
H	1.4771299346	0.7913329618	2.575733312
H	1.6097267779	2.422167258	3.2340324112
H	1.8173388159	1.0151464398	4.2894795437
H	-1.7141657816	1.4325174413	6.1483428505
H	-0.2577322826	2.4325024478	6.1005021568
H	-0.1080213408	0.6777832059	6.2335984938
H	-1.6600192766	3.2028765765	2.3442986024
H	-2.2621929918	3.3333734688	4.0036699093
H	-0.6477525417	3.9244180484	3.5883561887
H	-1.5471538972	-3.3937250424	2.1741327155
H	-1.4266239496	-4.0610918555	3.7985236035
H	-2.9209011326	-3.2727931602	3.291523935
H	-1.6216393339	-0.8906470894	6.3871528251
H	-1.519410518	-2.6425173846	6.1849435594
H	-2.9753766385	-1.7882485447	5.6861272985
H	0.9614467122	-2.8557394135	4.4137579498
H	1.2430362	-1.6684204829	3.1404735713
H	1.17515348	-1.1505714647	4.8312634037
H	-3.6436137147	3.8680600464	-0.5449520368
H	-2.4354447921	3.3291910153	0.6199029374
H	-2.3840168661	2.743745272	-1.0452418024
H	-5.8563026704	3.2742294015	1.1269770832
H	-5.0103103374	2.5015087597	2.4716606851
H	-6.3390129146	1.6603657986	1.6566855755
H	-4.722306303	1.4730396734	-2.2951762199
H	-6.0756049494	0.7323177075	-1.4245758469
H	-5.8821970317	2.4854320533	-1.4407513249
H	-3.6589750275	-3.5647012688	1.1638780671
H	-3.8466758966	-3.9443650971	-0.5463322623
H	-2.3189666851	-3.2902572533	0.0408796902
H	-4.3556303038	-0.629766147	-2.6567751158
H	-3.9148853767	-2.3419796718	-2.5980057266
H	-2.6996313925	-1.1081160086	-2.2711462997
H	-6.4088338363	-2.4720437584	-0.6949902656
H	-6.1669239333	-2.1529267431	1.0257142282
H	-6.5790466741	-0.8269725819	-0.0649440569

E+ZPVE = -5661.395411 au, Free E (298.15 K) = -5661.498712 au.
Job name: TN_Cl_ba

Table 2-2. Atomic Coordinates of **7** (metastable conformer, LB) at the B3LYP-D3/6-31G(d) Level of Theory



(R = $SiMe_3$)

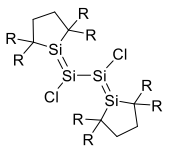
7

Atom	X	Y	Z
Si	-0.2696530305	1.436001817	-0.2998776909
Si	-0.3118095275	-1.4364240065	-0.2546581865
Si	-1.6661382226	0.020925348	1.1273509816
Si	1.0523636588	-0.0213711319	-1.7127968379
C	3.0119650913	0.0515416019	-1.7246882445
C	3.2584043375	-0.4414279673	-3.2005197384
C	2.2292322687	0.1999309108	-4.1333075305
C	0.7742780035	-0.1517572841	-3.6388709089
C	-3.6025908195	0.1504190872	0.9337929516
C	-4.0327283962	-0.2008061503	2.4091430797
C	-3.056042593	0.441343547	3.3962517739
C	-1.5922121652	-0.051145208	3.0856280976
Cl	1.2147563899	2.2957038412	0.9834526293
Cl	1.0355803306	-2.2950278315	1.1725105129
Si	3.8138769433	1.8429616466	-1.5704103194
C	5.2242688882	1.9990666595	-2.8405009556
C	4.6123003242	2.224876789	0.1073013367
C	2.7183172572	3.3302095156	-1.9948129128
Si	4.0408951365	-1.1290547532	-0.5856001695
C	3.6547181404	-2.9554009398	-0.9141580874
C	3.9191853604	-0.7317530078	1.2614619251
C	5.879698078	-1.0205233196	-1.0723170712
Si	-0.396787599	1.1236710012	-4.4835674847
C	-2.1772914433	1.067216313	-3.8796716183
C	-0.3799529979	0.8702891171	-6.3659891976
C	0.135534324	2.9210078242	-4.230913437
Si	0.359083994	-1.9513215678	-4.2802096319
C	0.9327900734	-3.4053521762	-3.2093427855
C	1.2342266356	-2.2563691158	-5.9409553615
C	-1.4850938874	-2.2631382375	-4.5719614875
Si	-0.4096456674	1.1303265389	4.0632394831
C	1.4304718131	0.7337343949	3.8608378556
C	-0.8152926982	1.022286449	5.9216383661
C	-0.7555951025	2.9563977322	3.6912107167
Si	-1.4022126235	-1.842101587	3.8808382968
C	-1.8736434099	-3.3300980187	2.8057198141
C	-2.6091403112	-1.9979184164	5.3456771384
C	0.309041922	-2.2229531395	4.6051702501
Si	-4.2622819192	1.9495051883	0.546204674
C	-3.1680618051	3.404304406	1.0718779244
C	-5.8833284635	2.2542126974	1.4929623421
C	-4.6345172441	2.2603021885	-1.2835959054
Si	-4.4971810897	-1.1258960208	-0.1986108775
C	-4.2208052042	-2.9228775237	0.3230201876
C	-3.9716980224	-1.0701020089	-2.0038341652
C	-6.3771645281	-0.873213001	-0.0996273938
H	3.1595649046	-1.5322601196	-3.2651054191
H	4.274062589	-0.2152202852	-3.5370833393
H	2.3877232205	1.2858667329	-4.1255694057
H	2.3901490869	-0.1185281168	-5.1682127072
H	-4.017642255	-1.2866709338	2.567595064
H	-5.0597293706	0.1173263293	2.6150646692
H	-3.1253434358	1.5321060013	3.2999126965
H	-3.3477140733	0.2154067354	4.4257609048
H	4.8557424305	2.0043819865	-3.8727656697
H	5.7116002737	2.9672202874	-2.6669858343
H	5.991907466	1.2247248837	-2.7566115558
H	3.9377681069	2.103022051	0.955445807
H	4.9185058311	3.2782924798	0.075079542
H	5.5106538084	1.6306968905	0.2959777021
H	3.2301241962	4.2243348937	-1.6166059432
H	2.6139979995	3.4501865018	-3.0759573436
H	1.7221723955	3.3228135263	-1.5523402987
H	4.0621998243	-3.2752122606	-1.8803291202
H	4.1584858256	-3.5478666053	-0.1397331275
H	2.5965487408	-3.212916602	-0.8800119429
H	4.8170387065	-0.2111508507	1.6088213308
H	3.8141754874	-1.6541953586	1.8409634986
H	3.0587976819	-0.1011729491	1.4912123719
H	6.4158300955	-1.7977389796	-0.5119325767
H	6.0366017858	-1.2252953199	-2.1375504633
H	6.3555064347	-0.0644343499	-0.8380283198
H	-2.208651959	1.0888597423	-2.7870160318
H	-2.700014427	4 1.9624841481	-4.2380692389
H	-2.7367334124	0.1935840375	-4.2156973069
H	0.6373696712	0.9212921221	-6.7709641548

H	-0.9575757799	1.6779388235	-6.8331270567
H	-0.8226303887	-0.0778839477	-6.685718046
H	0.1407152753	3.2166165514	-3.1787649251
H	1.1137981142	3.1563636672	-4.6601118109
H	-0.6033592341	3.5487056821	-4.7456770153
H	2.018150155	-3.4487927771	-3.0954689452
H	0.4854289434	-3.4283778097	-2.2115938303
H	0.62277994	-4.3221652456	-3.7280585571
H	1.0431060943	-1.490121621	-6.6971201124
H	0.8708086356	-3.2124597025	-6.3387938966
H	2.3195988491	-2.3499949489	-5.820048721
H	-2.0786549825	-2.1795409891	-3.6590291905
H	-1.9269850404	-1.6062946288	-5.3265870674
H	-1.5856598405	-3.2942774599	-4.933807314
H	1.6225591775	0.1028804472	2.99146164
H	2.0044206026	1.6563664901	3.7301510076
H	1.817069264	0.2136430614	4.7428131336
H	-1.8727264526	1.2266081714	6.1249987524
H	-0.2323383188	1.7999873087	6.4324010671
H	-0.5599056916	0.0664975491	6.3870783415
H	-0.7679103757	3.2135556024	2.6324772005
H	-1.7031449585	3.2759354913	4.1404889324
H	0.0398624328	3.5493857105	4.1604061658
H	-1.4752052503	-3.3231253768	1.7911554271
H	-1.4730650865	-4.2238000896	3.3009785361
H	-2.958273026	-3.4505081227	2.7488951164
H	-2.4919391241	-1.2231218113	6.1084815845
H	-2.4140291538	-2.9657390713	5.8254404153
H	-3.6565782968	-2.0038023799	5.0228021534
H	0.2906693484	-3.2762024218	4.913090725
H	1.1267696147	-2.1011776657	3.8940608655
H	0.5366769604	-1.6281992006	5.4940658612
H	-3.7003141337	4.3207215576	0.7844629799
H	-3.0068451314	3.4482914275	2.1511910824
H	-2.1908499351	3.4276169689	0.5812877905
H	-6.2971355394	3.2099537258	1.1468696269
H	-5.7151323649	2.3483960445	2.5719697523
H	-6.646755204	1.4875262731	1.3354264682
H	-3.7483830863	2.1768188884	-1.9164786672
H	-5.4074621335	1.60293162	-1.6917538095
H	-5.0008676784	3.2912436379	-1.3687044859
H	-4.6067126692	-3.1579087228	1.3192345755
H	-4.7671509336	-3.5511287641	-0.3923522346
H	-3.169324379	-3.218099943	0.2823109513
H	-4.3321903443	-0.1968891891	-2.5485013678
H	-4.352230053	-1.9657709323	-2.5099650758
H	-2.8814430159	-1.0913634476	-2.0828974122
H	-6.8687751016	-1.6813131988	-0.6559151116
H	-6.7372565206	-0.9238953238	0.9344501686
H	-6.716322011	0.074631272	-0.5283317937

E+ZPVE = -5661.393862 au, Free E (298.15 K) = -5661.493676 au.
Job name: TN_Cl_aa

Table 2-3. Atomic Coordinates of **8** at the B3LYP-D3/6-31G(d) Level of Theory



(R = $SiMe_3$)
8

Atom	X	Y	Z
C	-4.5405149746	4.2420452629	-0.7250266577
C	-5.4190596154	2.9881276411	-0.5718044227
C	-4.6365349241	1.7005246138	-1.0432922495
Si	-2.8846065482	2.1315357174	-0.3731812343
C	-3.1250436523	4.0208083616	-0.0628848244
Si	-0.9784469566	1.1449926683	-1.1893607301
Si	0.7168056381	0.4108976025	0.3585049018
Si	2.6395572585	0.239168781	-0.9751795393
C	4.1905622382	1.3109155028	-1.0384180744
C	5.225412727	0.3678178468	-1.7713936628
C	4.5242326664	-0.7398534314	-2.5890150293
C	3.294669479	-1.33061399	-1.8071844816
Cl	-1.634818327	-0.7003452661	-2.0871381643
Cl	1.1009563361	2.2903390121	1.3958212645
Si	-1.8588270303	5.2230910443	-0.9137573944
Si	-3.2065177323	4.4674012904	1.8283563886
C	-0.2936904698	5.5052746248	0.1091422479
C	-2.7226525474	6.8846413042	-1.2397563117
Si	2.0346260951	-2.0617971281	-3.0789106389
C	-1.2615160991	4.7028780654	-2.6336861645
C	-3.2155898988	6.3459983977	2.1283584372
C	-1.7961716262	3.6937883329	2.8125354202
C	-4.8228239815	3.9385504584	2.6692389837
Si	3.873664221	-2.701393048	-0.5596621927
Si	-5.37744649	0.1785637587	-0.1131458015
Si	-4.8532979363	1.4784838502	-2.9658143796
C	-7.1980106812	-0.0221421339	-0.6178501613
Si	4.8875960235	1.8496373309	0.7005194745
C	-5.4051777925	0.4450612779	1.7664975838
C	-4.4526804404	-1.4510761414	-0.3355508519
Si	3.8813266971	2.8654638409	-2.1518344717
C	-4.9074015891	-0.3097387365	-3.5884870385
C	-3.5451510465	2.3578913812	-4.0085116248
C	-6.5154743036	2.2447532644	-3.4834925344
C	1.2406306376	-0.666986015	-4.0883628513
C	0.725544797	-3.1247723105	-2.226901879
C	2.9477396401	-3.098935474	-4.3802538295
C	4.1219347519	-4.3747834803	-1.4214438344
C	2.6659226364	-2.9395315681	0.8719783747
C	5.605507529	-2.3615705596	0.144513137
C	6.7826156576	1.7906943599	0.5935027431
C	4.3330778322	0.6967852747	2.0995964888
C	4.4425942237	3.5960647589	1.2780995758
C	5.480004326	3.8823549614	-2.2534056506
C	2.4322312992	3.92464763	-1.5786014142
C	3.4950485899	2.3580947306	-3.9365572711
H	-5.05067675	5.116716856	-0.2983553052
H	-4.4299007767	4.4537397706	-1.7984595566
H	-6.3591714631	3.1178420977	-1.11638148
H	-5.69857719	2.8900765896	0.4808786842
H	5.8926650657	0.9398637905	-2.428936124
H	5.8787271355	-0.1099023082	-1.0411210237
H	5.2492791572	-1.5231432721	-2.8480213565
H	4.1880808593	-0.3196210646	-3.5447705404
H	0.2214898042	4.5639226808	0.3155085729
H	0.390603016	6.12980915	-0.4779858144
H	-0.4678018305	6.0088680536	1.0635747543
H	-3.5611299973	6.759825355	-1.9346630752
H	-2.0033718966	7.5599222546	-1.7206280379
H	-3.1004187116	7.3854207879	-0.3460070686
H	-0.8083871836	3.7086058785	-2.6633963331
H	-2.0617950426	4.7325817361	-3.3779293479
H	-0.4997640845	5.4310098767	-2.942417672
H	-4.0806283622	6.8203938255	1.6501948608
H	-3.319095501	6.502153425	3.2098327591
H	-2.3170110267	6.8755612132	1.8034325179
H	-1.7538724032	2.6068880001	2.6811567036
H	-1.9519567611	3.895183949	3.8800619225
H	-0.8162317189	4.0874667179	2.5347077402
H	-5.713487736	4.32591494	2.1622093151
H	-4.9283071018	2.8583311324	2.777750367
H	-4.8146068353	4.3677482437	3.6797290366
H	-7.329720556	-0.3167519657	-1.663613137
H	-7.6714251618	-0.7902413427	0.0062856728
H	-7.7494396117	0.9132601	-0.4635418114
H	-4.4160379957	0.6871753579	2.1725763634
H	-5.7254668156	-0.4948175614	2.2339508233
H	-6.1094142214	1.2203429905	2.0828020973
H	-4.3649960124	-1.7891807114	-1.3683899384
H	-3.4395715406	-1.3802362253	0.0731796231
H	-4.9891695928	-2.2228114591	0.2322589341
H	-5.7099655147	-0.9083506307	-3.147674909
H	-5.0928322595	-0.259923645	-4.6694480608
H	-3.9612646556	-0.8325601107	-3.4375908111
H	-3.6207519358	3.4448192879	-3.9078086846
H	-3.7159489186	2.1123281955	-5.0644705278
H	-2.5209480595	2.0665934455	-3.7575376854
H	-7.3632041463	1.8416852743	-2.9188369806
H	-6.5275623643	3.3359612819	-3.3815372932
H	-6.6847061854	2.0148457336	-4.5430496673
H	1.9681949306	-0.2400184346	-4.7880525987
H	0.414074348	-1.0769340603	-4.6806782187
H	0.8223357456	0.1475211326	-3.4893089076
H	1.1349394226	-4.0798186603	-1.8813269273
H	-0.0856348023	-3.3434608251	-2.9306272235
H	0.2710612677	-2.6186834266	-1.3711869712
H	2.2680088568	-3.2781435225	-5.2231290294
H	3.8193458342	-2.5645871382	-4.776384551
H	3.2856714585	-4.0720106457	-4.0159378468
H	4.817865445	-4.2953448882	-2.2639591596
H	4.5699730166	-5.0602950729	-0.6908689904
H	3.2008849797	-4.8374298133	-1.7846851798
H	2.6182162393	-2.0670121004	1.5315245671
H	2.9889247367	-3.7989420453	1.4732653865
H	1.6471354508	-3.1388283408	0.5246515245
H	6.3589585465	-2.3394293207	-0.6516491481
H	5.7039848358	-1.4441967347	0.7281122169
H	5.8627345429	-3.198586331	0.8064993719
H	7.1578153689	2.3247228511	-0.2863666449
H	7.2015712819	2.2770242264	1.483090678
H	7.1787990158	0.7700191825	0.5613804443
H	3.3023590409	0.9130731804	2.3962106786
H	4.9715291301	0.8730887193	2.9749949779
H	4.3998443384	-0.3674206571	1.8586221181
H	4.8239736762	4.3924556257	0.6326857882
H	3.3665359364	3.7326247196	1.4000503092
H	4.9036971946	3.7279379124	2.2659069431
H	6.3044348769	3.2826884888	-2.6570079245

H	5.3266333108	4.7264052893	-2.9374287274
H	5.8043046705	4.2889091287	-1.2917784049
H	1.5166818335	3.3291747905	-1.4945117192
H	2.2456113495	4.7059605111	-2.3261588922
H	2.5967369397	4.4111158652	-0.6160944951
H	3.4144685282	3.2680197205	-4.5448595891
H	4.2780850639	1.7359674764	-4.3833096152
H	2.5427762939	1.8260756274	-4.0218610105

E+ZPVE = -5661.372998 au, Free E (298.15 K) = -5661.479784 au.
Job name: TN_Cl_diene

Table 2-4. Atomic Coordinates of **10** (LB) at the B3LYP-D3/6-31G(d) Level of Theory

10

Atom	X	Y	Z
C	-4.730330135	-0.6014987919	1.261088912
C	-4.215784983	-2.0375297153	1.1017698487
C	-3.0840653513	-2.1036857255	0.0132183441
Si	-2.1487140396	-0.4435989267	0.4040253045
C	-3.5446193171	0.4240094289	1.4582380245
Si	-0.8944798007	0.5702467525	-1.3220699699
Si	0.1684797111	-0.3865898366	1.187255311
Si	1.2425087744	1.0621021745	-0.3985198822
C	1.8251180488	2.8816400258	-0.0148465111
C	3.3221555769	2.8072178742	-0.5128470077
C	3.4707271851	1.8414802495	-1.6966218444
C	2.8206279684	0.4529730132	-1.3558448639
Si	-3.0785792888	0.5131433908	3.331462481
Si	-4.2530830413	2.1626694002	0.9468832406
C	-4.5587345073	1.0993526704	4.374340956
C	-1.609904814	1.676195639	3.643840785
C	-2.6242290282	-1.1505417695	4.1178719967
C	-3.5468537196	3.6405764633	1.9071138991
C	-6.1186546591	2.1836616961	1.3218641818
C	-4.1170907165	2.6390576681	-0.8822497922
C	-0.5888879929	-4.0609301918	-0.7015998933
C	-3.3377851686	-5.2362073709	-0.1253857465
C	-1.7428052898	-4.0420524845	2.1048424934
C	-4.4187937125	-0.4129649802	-2.4357596186
C	-5.5386338801	-3.0596080161	-1.7232205683
Si	-2.1751294624	-3.7850701282	0.2760154329
Si	4.0684526812	-0.5833378119	-0.2896009876
C	-2.7829672447	-2.854398552	-3.0896520555
O	0.9623249042	-1.8812585332	1.005151954
Si	-3.8964921186	-2.1009422533	-1.75422204
Si	2.5128674962	-0.4675554868	-3.0208490645
C	1.4351995475	-2.679623937	2.0843722328
C	1.6245351181	-2.1294473555	-2.8246331538
C	4.1752487717	-0.7788463911	-3.8926654951
C	1.5335749067	0.5683909023	-4.273276655
Si	0.8722870599	4.1888957253	-1.075025199
C	4.0343419745	-0.2125816605	1.5681021731
C	5.8512528562	-0.1506303931	-0.7906766946
Si	1.8810561292	3.5301805268	1.8174575661
C	3.8805866354	-2.4566567025	-0.4895569926
C	0.9413141134	3.8977134288	-2.9454190468
C	1.6402097209	5.9171563412	-0.8664095262
C	-0.96357067	4.2759684514	-0.6103405241
C	2.0936592966	2.2303976201	3.1806318025
C	0.3801317914	4.558146644	2.3512102979
C	3.3865049423	4.6765980596	2.0049893065
H	-5.3083200551	-0.349777407	0.3633900372
H	-5.4442633817	-0.5492298093	2.0929204192
H	-5.0510264228	-2.7064337794	0.8617314465
H	-3.8284751447	-2.3760167499	2.0667642884
H	-0.5932102165	-0.6733404699	-2.1100342108
H	3.9766311078	2.4556634078	0.2952975758
H	3.7017187344	3.8004056286	-0.78471077
H	2.9829792046	2.2802591921	-2.5718884498
H	4.5286035794	1.7408838154	-1.9641404561
H	-5.4292292378	0.4435017434	4.2554991561
H	-4.2674956327	1.0594277511	5.4318529227
H	-4.8797675438	2.1221042698	4.159718343
H	-1.0885670161	1.9385133136	2.720484711
H	-0.8747912356	1.1912316147	4.2951891011
H	-1.9208603819	2.6099346064	4.1234132303
H	-3.4422889781	-1.8780470364	4.1005272604
H	-1.7487922194	-1.6098437351	3.6542318301
H	-2.3778429085	-0.9608050617	5.1708008437
H	-2.4714106651	3.7738468505	1.7874293582
H	-4.027453425	4.5389843952	1.4993294965
H	-3.76453898	3.6129947679	2.9781949227
H	-6.6832441898	1.5139208006	0.6640895771
H	-6.4916037279	3.201035873	1.1478082336
H	-6.3563242286	1.9160818115	2.3555352054
H	-3.157382828	2.3847667142	-1.3366926
H	-4.9075148137	2.182801531	-1.4831710714
H	-4.2385670403	3.7274177478	-0.9482678162
H	0.1812810907	-3.3593965278	-0.3782885166
H	-0.2341111185	-5.0778851561	-0.4875300193
H	-0.7045292837	-3.9716758558	-1.782647474
H	-4.2937932776	-5.166244336	0.4058457403
H	-2.8474315664	-6.1612443428	0.2041244102
H	-3.5495378383	-5.3427522522	-1.1939779744
H	-1.1741754791	-3.2116171609	2.5253381675
H	-2.6291037301	-4.19230982	2.7298985498
H	-1.1242082376	-4.9441370714	2.191128175
H	-3.5995933601	0.3011210639	-2.5507876082
H	-4.8542040548	-0.5826443825	-3.4293588874
H	-5.1912403108	0.0561481861	-1.819282867
H	-5.4712253488	-4.0743766891	-1.3248079542
H	-5.9079132456	-3.1299218169	-2.7544010997
H	-6.299271572	-2.5194860254	-1.1468186292
H	-3.2611335757	-2.6888934255	-4.0632126572
H	-1.7985592788	-2.3763452101	-3.1180000992
H	-2.6354710387	-3.9324367497	-2.9733853904
H	1.165581975	-3.7231760014	1.8934773842
H	2.5256269739	-2.6015438334	2.1534037669
H	1.0031459497	-2.3805849749	3.0497064976
H	1.1796309258	-2.2353276984	-1.8355629027
H	0.8159326974	-2.2158612123	-3.5596654512
H	2.3077754275	-2.9713307471	-2.9760116483
H	4.7621797981	0.1407304523	-4.0009436114
H	3.9737058022	-1.1594375676	-4.902068223
H	4.7990232304	-1.5197409172	-3.3824784169
H	0.5093974843	0.781740625	-3.9535933212
H	2.0185357444	1.5172110392	-4.522997047
H	1.4694364557	-0.0185815779	-5.1990233631
H	3.0407091469	-0.2713972047	2.0160447429
H	4.6791089435	-0.9368180992	2.0823204142
H	4.4376765389	0.7842901388	1.7735193389
H	6.0418968795	-0.2431789317	-1.8634663251
H	6.5311135322	-0.8381529946	-0.2714282827
H	6.1240467838	0.8665161324	-0.4855598276
H	4.5324451385	-2.9462703189	0.2452368031
H	2.8564999598	-2.7886515575	-0.3111213153
H	4.185946999	-2.8063046153	-1.4806485142
H	0.5296680951	2.930453849	-3.2406834271
H	0.3265362506	4.6748999287	-3.4184762134
H	1.9511483081	3.9871032944	-3.3596369483
H	1.536443752	6.3366251997	0.1383134349
H	1.1340570253	6.5996906924	-1.5612492579
H	2.7055503517	5.9272826588	-1.125145799
H	-1.5770635527	4.3271391152	-1.5159324143
H	-1.2904841042	3.3922304723	-0.0582854477
H	-1.1922983822	5.153616991	0.0012846279
H	3.0909141175	1.7851952151	3.1854103834
H	1.9577218875	2.7450436926	4.1407395946
H	1.3599758639	1.4217672749	3.130597481
H	0.5144865884	4.8010060267	3.412699454
H	-0.5650192535	4.0219444163	2.2624172195
H	0.2843882132	5.5017969129	1.8079801832
H	4.3328049617	4.1294258271	1.9334281352
H	3.4103392394	5.4838364631	1.2674517573
H	3.350616805	5.1365644882	3.0006374069

E+ZPVE = -4856.623293 au, Free E (298.15 K) = -4856.722926 au.
Job name: TN13_Si4BBA_OMe

Table 2-5. Atomic Coordinates of **10** (metastable conformer, SB) at the B3LYP-D3/6-31G(d) Level of Theory

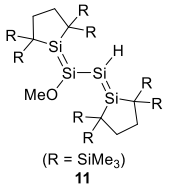
(R = $SiMe_3$)

10

Atom	X	Y	Z
C	-4.4974264645	0.956148829	-0.0021058323
C	-4.5185020754	-0.4938352232	0.5130263562
C	-3.3129963058	-1.3110665428	-0.0702062652
Si	-1.9194650357	0.0598929971	-0.0440889026
C	-3.0743295986	1.6142995364	0.1688101012
Si	-0.0822693689	-0.2958755307	-1.3779633249
Si	-0.0002847047	-0.3528456311	1.1956032341
Si	1.8671246108	-0.0214263062	-0.1585846
C	3.0529309113	1.5288179923	-0.1926414457
C	4.4675995955	0.8390669208	-0.147107913
C	4.4457698755	-0.5261692228	-0.8544703268
C	3.2464802356	-1.40155589	-0.3427555495
Si	-2.9000644256	2.3490461234	1.9459138642
Si	-2.9535853393	3.0638790412	-1.1093452192
C	-4.220764755	3.685461767	2.2414815712
C	-1.1806245986	3.0913972335	2.250569107
C	-3.139570597	1.1060712533	3.3554492462
C	-1.9271969	4.5627329231	-0.5568422656
C	-4.6996885281	3.7560135196	-1.4074510124
C	-2.2788222634	2.6123396916	-2.8241475099
C	-1.4350887331	-3.7942332736	0.7833604623
C	-4.4507103498	-4.1411084065	0.7796509891
C	-3.1781883831	-2.4504745513	2.8880675744
C	-3.5279306213	-0.5762126009	-3.2269214358
C	-5.5652645118	-2.3605872483	-2.0087500364
Si	-3.0647992313	-2.8649751739	1.0430757332
Si	3.7445708558	-2.2060060258	1.3367358863
C	-2.6706258177	-3.3448792324	-2.4512072282
O	-0.1800913455	-0.9715107606	2.7312220142
Si	-3.7303988549	-1.8829746708	-1.8708640685
Si	2.9376864237	-2.7746119594	-1.6617509079
C	0.2512315707	-2.0472539647	3.5476916437
C	1.371947109	-3.8123282882	-1.4367929568
C	4.4055771907	-3.9834580884	-1.7260798711
C	2.824777247	-2.0868199567	-3.4263237379
Si	2.8825605471	2.506388118	-1.8496261756
C	3.6148183921	-1.0552301898	2.838851526
C	5.5762883204	-2.7092921803	1.3437983288
Si	2.9750555918	2.8058994297	1.2648900119
C	2.7221130392	-3.7583304036	1.7200073733
C	3.1478511257	1.4684020269	-3.4131158306
C	4.2220353277	3.8519518196	-1.9722729612
C	1.1745002467	3.3048441279	-2.051314147
C	2.3288929383	2.1704327468	2.935103953
C	1.9669153035	4.3742680765	0.9132717481
C	4.7416211031	3.4124864166	1.6206042081
H	-4.7880434023	0.9420447988	-1.0596427748
H	-5.2748849232	1.5413900069	0.5057107868
H	-5.4830015751	-0.957090675	0.2698794986
H	-4.465009328	-0.4712613351	1.6046837654
H	-0.1397049436	-0.878668617	-2.7528095647
H	4.785424366	0.6815861983	0.890385401
H	5.2430602316	1.4759415779	-0.5918915378
H	4.3565548051	-0.356658094	-1.9305252067
H	5.4083276348	-1.0323025481	-0.7116013376
H	-5.2362611856	3.2908442335	2.1182731766
H	-4.1348413366	4.0411910028	3.2761164865
H	-4.118733787	4.5542371032	1.5845580539
H	-0.435266603	2.6774527686	1.5667246174
H	-0.8506050979	2.8541627448	3.2684095315
H	-1.1652696175	4.1790307853	2.1399943851
H	-4.108286935	0.5979501438	3.3547607504
H	-2.3496207654	0.3504021793	3.3653933414
H	-3.0648292056	1.6680808286	4.2961106727
H	-0.8869194768	4.3246871062	-0.3321303946
H	-1.9215580046	5.269321083	-1.3966812115
H	-2.3484836884	5.0867227922	0.3059651589
H	-5.3549462193	3.0406667206	-1.9160740971
H	-4.6204262489	4.6418691125	-2.0502967849
H	-5.1952557568	4.0625994618	-0.4804934303
H	-1.4031386365	1.9591303021	-2.7895492814
H	-3.0326580113	2.1354014871	-3.4546445845
H	-1.9737910502	3.5428187538	-3.3189040464
H	-0.5586669199	-3.1498287083	0.8899560932
H	-1.3640350023	-4.5857191648	1.5409425824
H	-1.3664126221	-4.2694920186	-0.197240212
H	-5.4419359493	-3.7037779983	0.9457314461
H	-4.3216385981	-4.9432009445	1.5178991455
H	-4.4472341005	-4.6046323587	-0.2116540335
H	-2.4472054181	-1.7031390803	3.1966305205
H	-4.1733389987	-2.0975529296	3.1784406439
H	-2.9819519851	-3.3702206912	3.4541698179
H	-2.5023295686	-0.2213771487	-3.3500209352
H	-3.8327068326	-1.0390067613	-4.1748435089
H	-4.1732673973	0.292947955	-3.0688867696
H	-5.9048110005	-3.083424991	-1.2635799757
H	-5.7363964872	-2.7974841805	-3.0008462521
H	-6.2059993227	-1.4738167305	-1.9335756329
H	-2.8806592786	-3.5169248257	-3.5144148378
H	-1.5995700088	-3.1382927821	-2.3599222449
H	-2.8811968796	-4.2782350851	-1.9203362083
H	-0.2052821286	-2.9855926341	3.2157325751
H	1.3369725132	-2.157100441	3.5414715142
H	-0.0806074446	-1.8390701613	4.5696414502
H	0.4836375211	-3.1844641959	-1.3395633776
H	1.24446304	-4.4290067111	-2.3358705008
H	1.3998684483	-4.4833089054	-0.5757195831
H	5.3622318354	-3.4640893782	-1.8549944127
H	4.271579124	-4.6420901899	-2.593456598
H	4.4848495845	-4.6223618756	-0.8404347103
H	1.9401380584	-1.4641848262	-3.583369785
H	3.7041656047	-1.5143618146	-3.7359157221
H	2.7400955509	-2.9467764632	-4.1033574483
H	2.6469221087	-0.564926787	2.9511273943
H	3.8007050553	-1.6415711543	3.748276276
H	4.3788098747	-0.2716852309	2.800751324
H	5.8708079791	-3.3383328298	0.5005841759
H	5.7797111744	-3.2690499569	2.2657531084
H	6.2287476166	-1.8282348849	1.3511367753
H	2.888760246	-4.0550393158	2.7629301029
H	1.6473750298	-3.610964355	1.582801401
H	3.0223684336	-4.6006946124	1.0882396843
H	2.4382907384	0.6427433488	-3.5020146116
H	2.9879193395	2.1313209474	-4.2737355348
H	4.1601595224	1.0610061208	-3.5020373032
H	4.1351108009	4.6396699808	-1.2184801984
H	4.1429932183	4.3288614908	-2.9577066891
H	5.2314454006	3.430116523	-1.8990619393
H	0.8223475584	3.1765156515	-3.0809398897
H	0.4297656408	2.8439097373	-1.398843226
H	1.1913815377	4.3770995567	-1.8369227597
H	3.081639987	1.5839610187	3.467694884
H	2.1042103031	3.0504358612	3.5510753266
H	1.4132554194	1.5758731087	2.8782889154
H	1.9678447199	4.9711336879	1.8340761687
H	0.9253544609	4.1742521867	0.661039713
H	2.3931526635	4.9950722165	0.1207147089
H	5.3718518074	2.6273903612	2.0526478935
H	5.2458776451	3.7891936646	0.7251605853
H	4.6958240503	4.2330307155	2.347662172

E+ZPVE = -4856.612432 au, Free E (298.15 K) = -4856.712362 au.
Job name: TN22

Table 2-6. Atomic Coordinates of **11** at the B3LYP-D3/6-31G(d) Level of Theory



(R = $SiMe_3$)

11

Atom	X	Y	Z
C	-3.4227080783	1.6427884371	3.0712952186
C	-4.1144936155	0.3057517859	2.7193195517
C	-3.9469225979	-0.0414318128	1.1942619971
Si	-2.1644229123	0.5934871686	0.9165041642
C	-1.9952939047	1.7868495182	2.4007163984
Si	-1.0898307922	0.7453948305	-1.0287500043
Si	1.2216707637	0.9643954697	-0.9089158184
Si	2.613854173	-0.6042995492	-1.6112271278
C	4.4008306542	-0.2828197032	-2.1846182941
C	5.0736793333	-1.6736629704	-1.8849576
C	4.0608524817	-2.8366282095	-2.0156538491
C	2.6749973714	-2.4851559319	-1.3503796442
O	-1.6480580504	-0.4837312146	-2.0688321441
Si	-1.7257600586	3.6294808939	1.8800507603
Si	-0.6568286446	1.2377296724	3.6759082026
C	-1.7400238733	-0.2508025178	-3.4690722386
C	0.0983455575	4.1191107961	1.7438833195
C	-2.5524593454	4.7585341688	3.1655514717
C	-2.4786552878	4.0987579254	0.2028834253
C	-0.6894327791	2.3893167131	5.1873087991
C	1.1205141323	1.2250423376	3.0275271461
C	-1.0134505045	-0.5089227633	4.318335801
C	-5.5110878764	-2.6740291044	1.9030619152
Si	-4.0209381244	-1.9565051846	0.9665905343
C	-2.5271414396	-2.8196625342	1.7525446898

C	-4.0722981536	-2.4612533159	-0.8538483311	H	-1.5735016672	-2.5063954328	1.3212261864
C	-4.7476007721	1.1296406205	-1.6473000793	H	-2.6275049644	-3.8995568577	1.5825809906
C	-5.9066014106	2.4569508895	0.899853595	H	-2.4838402801	-2.6626447484	2.8352404042
C	-6.9160762664	-0.1846514221	0.046561431	H	-4.9892429314	-2.1433226432	-1.3606532981
Si	-5.3063179053	0.8245707026	0.1319518195	H	-3.2206962949	-2.0366507977	-1.3941875114
C	0.8675093534	-2.6200355325	-3.9728920422	H	-4.0130656629	-3.5543705735	-0.9272369071
C	-0.3615539392	-3.4404709634	-1.3079455984	H	-4.3132325674	0.2248094515	-2.0831720634
Si	1.2531302072	-3.4022276828	-2.2849795039	H	-5.6082500361	1.4268998165	-2.2591541076
Si	5.2998210324	1.0916361147	-1.1650028558	H	-3.9937741449	1.9207101053	-1.7108341307
C	1.7926253269	-5.1755872754	-2.697116757	H	-6.3187904392	2.2907041017	1.9022316358
C	2.4387335673	-4.8902300369	0.6917891313	H	-6.7235118746	2.8413855269	0.2755982746
Si	2.6547819976	-3.0118523124	0.5040560092	H	-5.1532317332	3.2440699255	0.9718850657
C	1.2910216673	-2.1313170811	1.4765059022	H	-7.6585113387	0.4174820427	-0.4927928617
C	4.3042445708	-2.6584354496	1.3632028458	H	-6.8176224091	-1.1363182829	-0.4831355647
C	7.1793828009	0.8706642099	-1.3242451725	H	-7.3240462799	-0.3916017062	1.0421191197
C	4.9748745393	0.9846637776	0.700949083	H	1.5665308135	-2.9598234475	-4.7441078552
C	4.8204376044	2.8424861539	-1.7015467968	H	-0.1351311391	-2.9395239688	-4.2829838635
Si	4.4472473593	0.1480123251	-4.0680677483	H	0.8722132982	-1.5257647554	-3.9608274983
C	6.1216542246	0.8617484092	-4.6113270688	H	-0.2694847645	-3.8829380991	-0.3123878727
C	3.084981084	1.369832559	-4.5492717912	H	-1.0935326583	-4.0367169753	-1.8678381948
C	4.251125705	-1.3957153144	-5.1498409813	H	-0.7812020268	-2.4359090685	-1.2079231604
H	-3.3605155636	1.7439756236	4.1624934751	H	1.0531282567	-5.6151109819	-3.378875386
H	-4.0725185966	2.4573487284	2.7435543192	H	2.7597408885	-5.1927961553	-3.2129703565
H	-5.1731674069	0.3550643743	3.0080942978	H	1.8661568443	-5.8283037715	-1.8238724123
H	-3.677228643	-0.4899606096	3.3355708009	H	3.1862933222	-5.4504718061	0.1187263194
H	1.6498570138	2.2010754768	-1.6385613358	H	2.5837322752	-5.14104302	1.7505066031
H	5.9322315755	-1.8580030537	-2.5450241287	H	1.4480139579	-5.2518520997	0.4015668635
H	5.4755780935	-1.6774938694	-0.8651968063	H	1.7235472565	-1.3377353258	2.0913414336
H	4.4899648653	-3.750092375	-1.5821695678	H	0.7758086695	-2.8308042421	2.145213117
H	3.9202043415	-3.0541827402	-3.079924778	H	0.5370761208	-1.6645213618	0.8364056365
H	-1.9490251462	-1.2091459012	-3.9541988588	H	5.1495151992	-3.1596511934	0.878220243
H	-2.551748945	0.4512308382	-3.7046858027	H	4.5223416198	-1.5902842637	1.4227841599
H	-0.8015858978	0.1485359283	-3.878817028	H	4.2442999881	-3.0399795206	2.3906637145
H	0.667395637	3.4223674655	1.1177955292	H	7.5738213874	1.1324412714	-2.3087430191
H	0.1511193513	5.107610764	1.2704519601	H	7.6738547382	1.5134928274	-0.5849072661
H	0.5997337627	4.1903647915	2.7142942687	H	7.476304425	-0.162051322	-1.1064145651
H	-3.6456119138	4.7204898361	3.0948796768	H	3.9175961676	0.8806573547	0.9635793214
H	-2.2504579791	5.7962892341	2.9762692259	H	5.3398605607	1.9123843339	1.1605996175
H	-2.2762271009	4.511873444	4.1948237165	H	5.533184849	0.1614442503	1.158671911
H	-1.8133811855	3.8168191937	-0.6186830942	H	5.0290692808	3.0500696174	-2.7551989507
H	-3.4489325526	3.6398109456	0.0001853125	H	3.7582803185	3.0378086411	-1.5227284105
H	-2.6113885266	5.1886533247	0.1777118265	H	5.3943502617	3.5610470949	-1.1030006071
H	-1.6870109069	2.4872539765	5.6303091044	H	6.9467896221	0.1816063371	-4.3713334084
H	-0.0267995995	1.9781648333	5.9594443196	H	6.1020892852	0.9779403529	-5.7026253832
H	-0.3274139156	3.3952951571	4.9483950218	H	6.3534539718	1.8401638014	-4.1809068474
H	1.1903223184	0.9180220647	1.9793255965	H	2.0993079058	0.8924278872	-4.5351835855
H	1.7034970927	0.5126536045	3.6247362516	H	3.267226315	1.7381140161	-5.5668033893
H	1.6042354154	2.2013783027	3.1177881459	H	3.0338200116	2.2332689229	-3.8794715665
H	-0.2863442796	-0.7548846339	5.1026113279	H	4.3498674021	-1.0967433031	-6.201161383
H	-2.0136784014	-0.6083235178	4.7533459704	H	5.0275911625	-2.1428018035	-4.9493716762
H	-0.9066430268	-1.2552977262	3.5254848918	H	3.2765950101	-1.8743800498	-5.0354561133
H	-6.4697048488	-2.5112346714	1.4044694549				
H	-5.3722303097	-3.7573586276	2.0098688505				
H	-5.5820718688	-2.25577788	2.9143348895				

E+ZPVE = -4856.598911 au, Free E (298.15 K) = -4856.705569 au.
Job name: TN14_diene_OMe

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Chapter 3

Synthesis of 1,3-Diiodotetrasilabicyclo[1.1.0]butane with π-Type Single-Bonding Character

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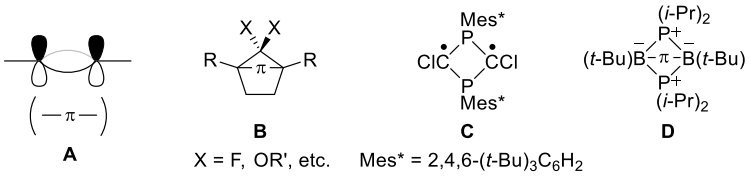
3-1. Introduction

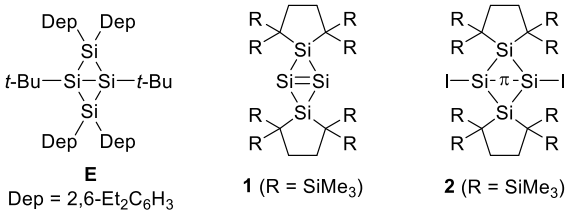
π-Bonding interactions are crucial for controlling the structure, reactivity, and electronic properties of organic/inorganic π-electron systems. In organic compounds and compounds of main-group elements, these interactions are typically found in multiple bonds with an underlying σ-bond framework. Although compounds that contain a π-bond without a σ-bond framework (π-single bonding; Chart 3-1, **A**)[1] are generally unstable and tend to isomerize into the singly σ-bonded structures, meticulous molecular design can increase the lifetime of such compounds. For instance, singlet cycloalkane-1,3-diyl derivatives such as **B** (Chart 3-1), which exhibit π-type single bonding between the bridgehead carbon atoms, have been generated as persistent compounds.[1,2] Abe et al. found that such structures can be thermodynamically stabilized by the introduction of electronegative substituents X at the bridge positions[1,2b,c] and electron-donating groups as the bridgehead substituents R.[2d] Abe et al. also found that the lifetime of such species can be increased up to ~20 μs at room temperature by kinetic stabilization with substituents that lengthen the bridgehead bond distance[3a,b] or increase the planarity.[3c,d] Noticeably, these species have small π–π* gaps,[2] which is reflected in their bathochromically shifted π → π* absorption bands ($\lambda \approx 600$ nm) compared with those of typical monoalkenes ($\lambda < 300$ nm). Moreover, various isolable diradicaloids have been reported since the first isolation of **C** (Chart 3-1),[4,5] reported by Niecke and co-workers.[4a] While these diradicaloids have planar ring structures, most of these species do not exhibit bonding character between the bridgehead atoms. Among these, an important example is the isolable 1,3-dibora-2,4-diphosphacyclobutane-1,3-diyl **D**, reported by Bertrand and co-workers, which contains a planar four-membered P_2B_2 ring with through-space π-type single-bond character between the bridgehead boron atoms (Chart 3-1).[5] The planar structure of **D** was attributed to the presence of the bulky groups on the ring.[5d,e] Compound **D** exhibits ionic and radical reactivity in various reactions.[6] Although compounds that contain π-type single bonding exhibit intriguing photophysical properties and reactivity, isolable examples of these compounds remain scarce.[7,8]

Chart 3-1. Schematic Illustration of π-Bonding without a σ-Bond Framework (**A**) and Structures of Compounds **B**–**D**



We recently reported tetrasilabicyclo[1.1.0]but-1(3)-ene **1** (Chart 3-2), which contains a highly strained bridgehead Si=Si bond. We found that the reaction of **1** with carbon tetrachloride and methanol resulted in the addition of multiple Cl atoms or methanol moieties to the silicon framework.[9] In this chapter, the author reports that the 1,2-diiodination of **1** provides 1,3-diiodotetrasilabicyclo[1.1.0]butane **2** (Chart 3-2), which exhibits a planar structure with π-type single bonding between the bridgehead silicon atoms. Such a planar structure has been proposed as a possible intermediate or transition state for the ring inversion of bent tetrasilabicyclo[1.1.0]butanes such as **E**, the first tetrasilabicyclo[1.1.0]butane reported by Masamune et al.,[10a] which have been examined theoretically.[11] DFT calculations indicated that the high planarity of **2** should most likely be attributed to the bulky substituents at the bridge positions.

Chart 3-2. Structures of Compounds **E**, **1**, and **2**

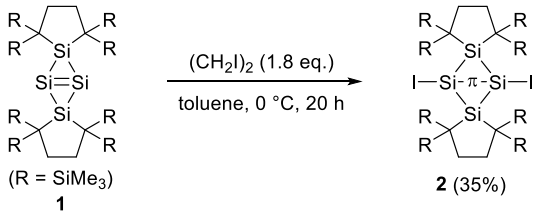


3-2. Results and Discussion

3-2-1. Synthesis of 1,3-Diiodotetrasilabicyclo[1.1.0]butane 2

The reaction of **1** with 1,2-diiodoethane (1.8 equiv) at 0 °C delivered air-sensitive reddish-orange crystals of **2** in 35% yield after recrystallization from toluene (Scheme 3-1). The molecular structure of **2** was determined using a combination of multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and single crystal X-ray diffraction (XRD) analysis.[12]

Scheme 3-1. Synthesis of **2**



3-2-2. Molecular Structures of 2

Compound **2** provided two different types of single crystals (Figure 3-1). The red crystalline blocks that were obtained from recrystallization from benzene at room temperature, $\mathbf{2_p}$, contain a planar Si_4 ring (dihedral angle of the bicyclic ring, φ, equal to 180°) on a crystallographic inversion center (Figure 3-1a and Table 3-1). The geometry around the bridgehead atoms is planar [sum of the angles of the bridgehead Si1 atom excluding the central bridgehead bond, ΣSi, equal to 360.00(3)°], and the Si−I moieties are very slightly bent in a *trans* configuration [Si1*−Si1−I1 angle, θ, equal to 178.49(4)°] with respect to the Si_4 ring plane. Noticeably, the distance between the bridgehead silicon atoms [d = 2.5822(11) Å] is much longer than those in previously reported tetrasilabicyclo[1.1.0]butanes (2.35−2.47 Å)[10] and **1** [2.4873(10) Å][9b] but still shorter than the longest hitherto-reported Si−Si single bond [2.697 Å for $(t\text{-Bu})_3\text{Si}-\text{Si}(t\text{-Bu})_3$][13] and the corresponding transannular Si···Si distance in a 1,1,3,3-tetrachlorocyclotetrasilane without a bridgehead bond, obtained from the tetrachlorination of **1** [2.9182(9) Å].[9b] The two silacyclopentane moieties at the bridge positions adopt a half-chair conformation and exhibit an eclipsed conformation as viewed along the Si2−Si2* axis (Figure 3-1a). On the other hand, the orange plates that were obtained upon recrystallization from hexane at −35 °C, $\mathbf{2_c}$, adopt a slightly *cis*-bent Si_4 framework [φ = 161.57(4)°, θ = 168.55°] (Figure 3-1b and Table 3-1). The bridgehead Si atoms adopt an almost planar geometry (ΣSi = 359.9°). The distance between the bridgehead Si atoms [d = 2.5251(10) Å] is slightly shorter than that in $\mathbf{2_p}$ [2.5822(11) Å]. The two silacyclopentane moieties exhibit a staggered conformation as viewed along the Si3−Si4 axis (Figure 3-1b). As mentioned above, both $\mathbf{2_p}$ and $\mathbf{2_c}$ exhibit highly planar silicon rings (φ > 160°) and a planar geometry around the bridgehead silicon atoms (ΣSi > 359.9°, θ > 169°) as well as

substantially elongated bridgehead distances (d = 2.53−2.58 Å). These properties contrast sharply with the structural characteristics reported for highly bent tetrasilabicyclo[1.1.0]butanes, which exhibit short bridgehead Si−Si distances (φ = 121.0−129.3°, θ = 146.3−151.7°, d = 2.35−2.47 Å).

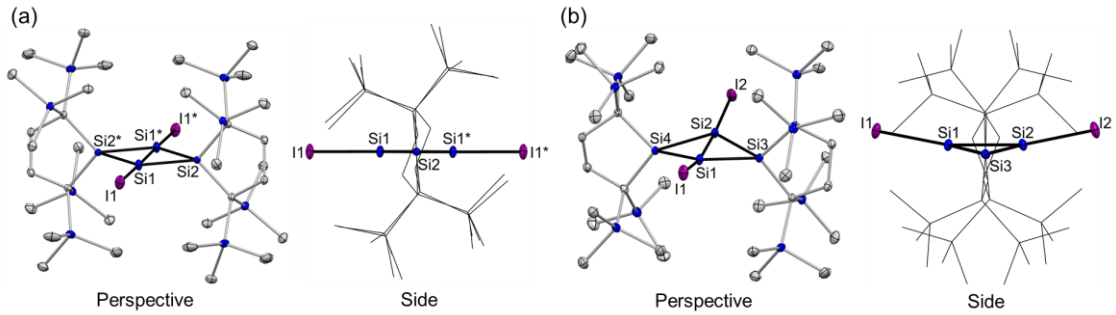
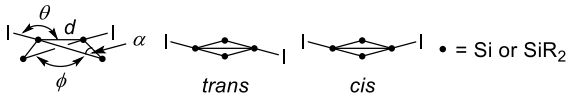


Figure 3-1. (a) ORTEPs of (a) $\mathbf{2_p}$ and (b) $\mathbf{2_c}$ with thermal ellipsoids at 50% probability; hydrogen atoms have been omitted for clarity.

Table 3-1. Selected Structural Parameters of **2** and **2'**



compound	d/Å	θ/deg	φ/deg	α/deg	$\Delta G^{a,b}$
XRD					
$\mathbf{2_p}$	2.5822(11)	178.49(4) (*trans*)	180.00	66.98(3)	-
$\mathbf{2_c}$	2.5251(10)	168.55(4) 168.56(4) (*cis*)	161.57(4)	65.34(3) 65.28(3)	-
DFT[a]					
$\mathbf{2'_c}$	2.501	168.77 (*cis*)	159.59	64.48	0.0
$\mathbf{2'_p}$	2.609	178.54 (*trans*)	180.00	67.80	15.7
$\mathbf{2'_I}$	2.847	121.54 129.16 (*cis*)	176.55	71.85 71.87	28.1

[a]Calculated at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory. [b]At 298.15 K, in kJ mol^{-1}.

3-2-3. NMR Spectra of 2

The NMR spectra of **2** indicate that **2** adopts a highly symmetric structure in solution. The ^{1}H NMR spectrum of **2** in benzene-d_6 at room temperature shows one singlet at 0.47 ppm for the eight equivalent $SiMe_3$ groups and another singlet for the eight methylene protons of the five-membered rings at 1.98 ppm. In the ^{29}Si NMR spectrum of **2**, signals were observed at 4.0 (bridge Si), 5.0 ($SiMe_3$), and 103.8 ppm (bridgehead Si) (Figure 3-2). These results suggest that **2** adopts an almost planar structure similar to $\mathbf{2_p}$ or a slightly *cis*-bent structure similar to that of $\mathbf{2_c}$ in which

the Si_4 ring undergoes facile ring flipping on the NMR time scale. Notably, the ^{29}Si NMR resonance of the bridgehead Si nuclei appears much further downfield (103.8 ppm) than those of reported tetrasilabicyclo[1.1.0]butanes (−145.1 to 14.8 ppm)[10] and close to that of a structurally similar trisilacyclopropene (142.9 ppm).[14]

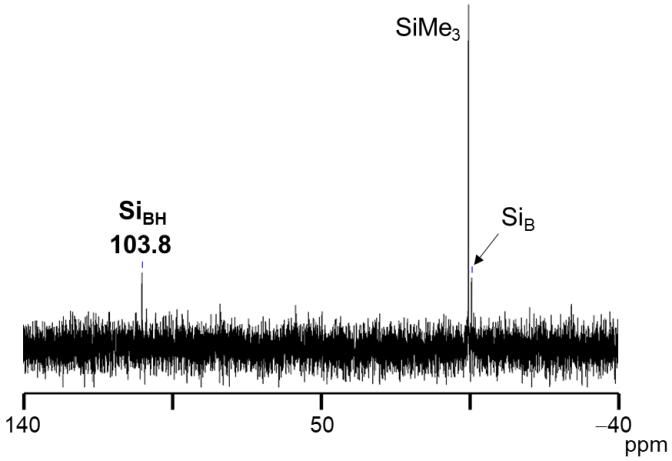


Figure 3-2. ^{29}Si NMR spectrum of **2** in benzene-d_6 at room temperature (Si_{BH}: bridgehead Si, Si_B: bridge Si).

3-2-4. Theoretical Study

The molecular structure of **2** was further examined using theoretical calculations. The two structures of **2** observed in the solid state ($\mathbf{2_p}$ and $\mathbf{2_c}$) were located as local minima ($\mathbf{2'_p}$ and $\mathbf{2'_c}$) at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory, and the structural characteristics of $\mathbf{2'_p}$ and $\mathbf{2'_c}$ are in good agreement with those obtained from the XRD analysis (Table 3-1). Our calculations suggest that at 298.15 K, $\mathbf{2'_c}$ is more stable than $\mathbf{2'_p}$ in terms of free energy by 15.7 kJ mol^{-1}. The chemical shift of the ^{29}Si NMR resonance of the bridgehead silicon nuclei of $\mathbf{2'_c}$, calculated at the M06L/6-311+G(2df,p) [H,C,Si], SDD [I] level of theory (99.8 ppm), is closer to the observed value (103.8 ppm) than that calculated for $\mathbf{2'_p}$ (152.3 ppm).[15] These results imply that **2** predominantly adopts a structure similar to $\mathbf{2'_c}$ in solution, which is consistent with the features of the UV-vis spectrum (*vide infra*).

The frontier Kohn−Sham orbitals of $\mathbf{2'_p}$ and $\mathbf{2'_c}$ provide further insight into the characteristics of the bridgehead Si−Si bond. The HOMO and LUMO orbitals of $\mathbf{2'_p}$ represent an in-phase and out-of-phase combination of the bridgehead Si 3p orbitals (π- and π*-orbitals) (Figure 3-3a). Conversely, $\mathbf{2'_c}$ exhibits similar but slightly *cis*-oriented π- and π*-type orbitals,[16]

which could be considered as extremely distorted σ- and σ*- (banana-type) orbitals (Figure 3-3b). Natural bond orbital analysis[17] indicated that the bridgehead bond is formed by interactions between almost pure p orbitals of Si (**2′**$_{\mathbf{p}}$, 99.9%; **2′**$_{\mathbf{c}}$, 95.2%). The angles of deviation between the axis through the two bridgehead silicon atoms and the direction of the natural hybrid orbital that forms the bridgehead natural bond (**2′**$_{\mathbf{p}}$, 82.1°; **2′**$_{\mathbf{c}}$, 61.9°) are substantially higher than those of the peripheral banana-type σ(Si−Si) bond (13.6−18.6°), suggesting that both **2′**$_{\mathbf{p}}$ and **2′**$_{\mathbf{c}}$ involve formally π-type bonding interactions between the bridgehead silicon atoms with very slight *trans* or *cis* deformation.[18] The Wiberg bond indices between the bridgehead silicon atoms of **2′**$_{\mathbf{c}}$ (0.77) and **2′**$_{\mathbf{p}}$ (0.70) are not substantially lower than those of the peripheral Si−Si bonds (0.95−0.98). The significantly larger singlet−triplet gap (**2′**$_{\mathbf{p}}$, 107.2 kJ mol^{-1}; **2′**$_{\mathbf{c}}$, 149.8 kJ mol^{-1}) also provides evidence for the presence of considerable bonding interactions between the bridgehead silicon atoms in **2′**$_{\mathbf{p}}$ and **2′**$_{\mathbf{c}}$.

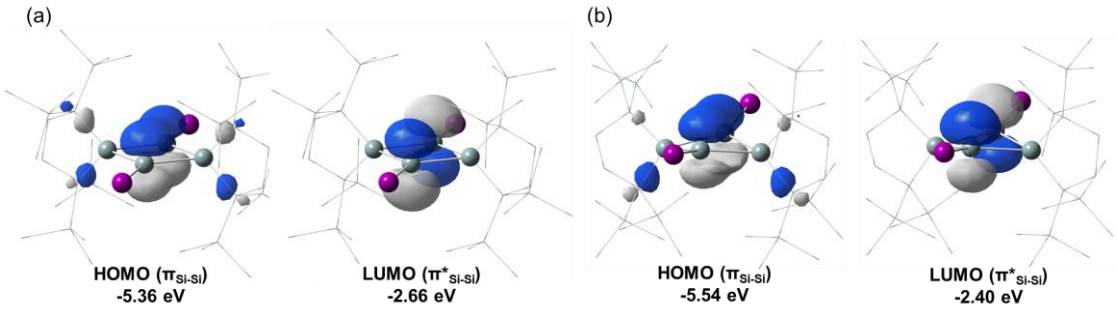


Figure 3-3. Frontier orbitals of (a) **2′**$_{\mathbf{p}}$ and (b) **2′**$_{\mathbf{c}}$ calculated at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory (isosurface level: 0.05 e·au^{-3}); hydrogen atoms have been omitted for clarity.

3-2-5. UV-vis Absorption Spectrum of 2

The UV-vis absorption spectrum of **2** provided further insight into its structure in solution. In hexane, **2** exhibits an intense absorption band at 435 nm (ε = 2400 M^{-1} cm^{-1}) with a tail extending up to 600 nm (Figure 3-4). The observed absorption spectrum of **2** was in better agreement with the band positions and corresponding oscillator strengths of **2′**$_{\mathbf{c}}$ (Figure 3-4, red bars) than those of **2′**$_{\mathbf{p}}$ (Figure 3-15) calculated at the TD-B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory. The absorption band at 435 nm was assigned to the HOMO(π)→LUMO(π*) transition (λ_{calcd} = 446 nm). Thus, it is reasonable to conclude that **2**$_{\mathbf{c}}$ is the dominant structure in

solution, which is consistent with the calculated relative stabilities of $\mathbf{2'_p}$ and $\mathbf{2'_c}$.[19] It is noteworthy that the band of **2** is bathochromically shifted compared to the $\pi \rightarrow \pi^*$ transition of a structurally similar trisilacyclopropene that exhibits a planar Si=Si double bond in the three-membered ring (391 nm).[14]

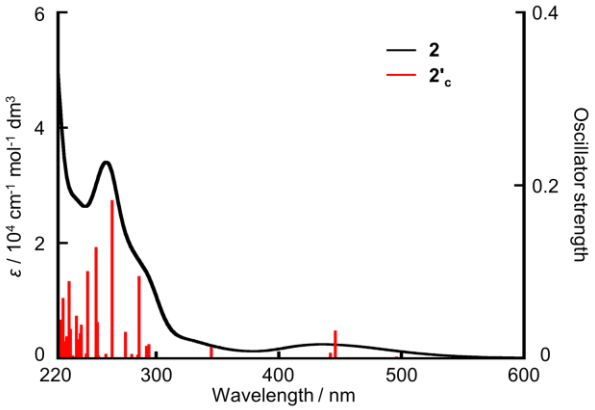


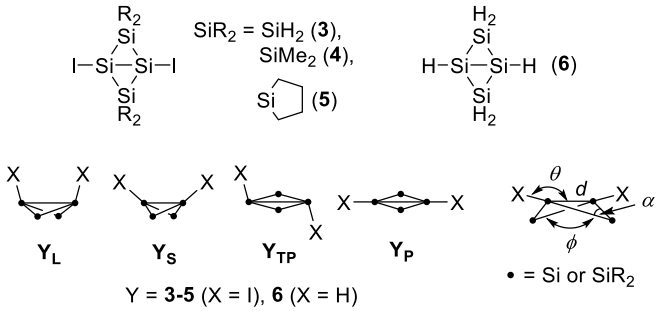
Figure 3-4. UV-vis spectrum of **2** in hexane at room temperature (black) and calculated band positions (red bars).

3-2-6. The Effects of the Substituents for the Planar Structure of 2

The reason that **2** adopts a planar structure merits further discussion. Similar to previously reported theoretical studies,[11] three different structures of 1,3-diiodotetrasilabicyclo[1.1.0]butane ($\mathbf{3_L}$, $\mathbf{3_S}$, and $\mathbf{3_{TP}}$) were located as local minima at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory (Table 3-2). These correspond to (i) a bent structure (φ = 152.4°) with an acute Si−Si−I bond angle (θ = 103.2°) and an extremely long Si−Si bridgehead distance (d = 3.063 Å) ($\mathbf{3_L}$); (ii) a highly bent structure (φ = 124.5°) with a wide Si−Si−I bond angle (θ = 150.8°) and a typical Si−Si single bond distance (d = 2.357 Å) ($\mathbf{3_S}$); and (iii) a planar structure (φ = 180.0°) with an acute Si−Si−I bond angle (θ = 100.9°) in a *trans* arrangement and a long Si−Si distance (d = 3.073 Å) ($\mathbf{3_{TB}}$). A planar structure ($\mathbf{3_P}$) similar to $\mathbf{2_p}$ and $\mathbf{2_c}$ was located as a saddle point with two imaginary vibrational frequencies. $\mathbf{3_L}$ is the most stable isomer and is more than 90 kJ mol^{-1} lower in energy than $\mathbf{3_P}$, which in turn is similar to the parent system (**6**, Table 3-2),[11] implying that the electronic effects of the iodine atoms are not crucial for the observed planar structure of **2**. The relative energies of the isomers remain essentially unchanged with increasing steric demand at the bridge SiR_2 moieties (SiH_2 (**3**) < $SiMe_2$ (**4**) < $Si(CH_2)_4$ (**5**); Table 3-2).[20] However, in the case of **2′**, which contains very bulky SiR_2 groups, the planar and almost planar structures $\mathbf{2'_p}$ and $\mathbf{2'_c}$

were located as local minima,[21] while structures corresponding to $\mathbf{3_S}$ and $\mathbf{3_{TB}}$ were not located, which is probably due to the severe steric demand. Structure $\mathbf{2'_I}$, which corresponds to $\mathbf{3_L}$ (Table 3-1), was located as another local minimum, but its free energy was 28.1 kJ mol^{-1} higher than that of $\mathbf{2'_C}$. These results indicate that the presence of sterically highly demanding substituents at the bridge positions is most likely responsible for the observed planar structures. The prediction of such steric effects is unprecedented for tetrasilabicyclo[1.1.0]butanes.[22]

Table 3-2. Selected Structural Parameters and the Relative Energies of Isomers of **3-6**



Compound[a,b]	distance/Å		angle/deg		ΔG^{d}
	d (Si-Si)	θ (X-Si-Si)	φ (Si_4 ring)	α (Si-Si-Si)	
$\mathbf{3_L}$ (C_{2v})	3.0625	103.24	152.42	80.82	0.0
$\mathbf{3_S}$ (C_{2v})	2.3569	150.79	124.53	61.17	43.3
$\mathbf{3_{TP}}$ (C_{2h})	3.0734	100.93	180.00	80.34	25.0
$\mathbf{3_P}$ (D_{2h})[c]	2.6691	180.00	180.00	71.26	91.1
$\mathbf{4_L}$ (C_{2v})	2.9944	104.11	157.85	78.58	0.0
$\mathbf{4_{TP}}$ (C_{2h})	3.0428	102.98	180.00	78.84	27.6
$\mathbf{4_P}$ (D_{2h})[c]	2.6449	180.00	180.00	70.14	96.0
$\mathbf{5_L}$ (C_s)	3.0057	104.27	160.56	79.04	0.0
$\mathbf{5_{TP}}$ (C_{2h})	3.0131	99.48	180.00	78.33	16.0
$\mathbf{5_P}$ (C_i)[c]	2.6583	179.91	180.00	70.71	84.8
$\mathbf{6_L}$ (C_{2v})	2.8796	92.34	141.99	76.02	0.0
$\mathbf{6_{TP}}$ (C_{2h})	2.9474	89.78	180.00	77.48	45.1
$\mathbf{6_P}$ (D_{2h})[c]	2.8160	180.00	180.00	75.47	102.8

[a]Calculated at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory. [b]$\mathbf{4_s}$, $\mathbf{5_s}$, and $\mathbf{6_s}$ were not found. [c]Saddle point with two imaginary vibrational frequencies. [d]At 298.15 K, in kJ mol^{-1}.

3-3. Conclusion

In conclusion, the author has synthesized a planar silicon analogue of bicyclo[1.1.0]butane that exhibits π-type single bonding between the bridgehead Si atoms.[23] 1,3-Diiodotetrasilabicyclo[1.1.0]butane **2** was obtained by 1,2-diiodination of the corresponding

bridgehead disilene **1**. The formal formation of a π-bonding species after a 1,2-addition is interesting, as 1,2-additions of double bonds usually afford singly σ-bonded compounds. While planar silicon rings with slight *trans* or *cis* deformation (**2$_p$** and **2$_c$**) were observed in the XRD analysis, the NMR analysis and DFT calculations suggest that **2$_c$** is the dominant structure in solution. The distinct absorption band of **2** in the visible region indicates that this silicon species with π-single bonding should represent an intriguing silicon-based chromophore.

3-4. Experimental Section

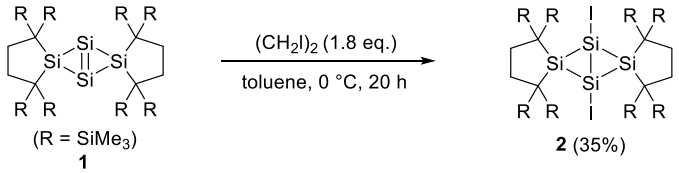
General Procedures

All reactions involving air-sensitive compounds were performed under argon or nitrogen atmosphere using a high-vacuum line and a standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. The reactions at lower temperatures were performed using an EYELA PSL-1400 cryobath. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C shifts of the solvents: C_6D_6 (^{1}H: δ 7.16 and ^{13}C: δ 128.0).[24] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). The sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra was recorded on a Bruker Daltonics SolariX 9.4T spectrometer. UV-vis spectra were recorded on a JASCO V-770 and V-660 spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer.

Materials

Dry and degassed hexane, benzene, and toluene were prepared using a VAC 103991 solvent purifier. Benzene-d_6 was degassed through five freeze-pump-thaw cycles and then dried over molecular sieves 4Å. 3-Methylpentane was dried in a tube covered with potassium mirror and then distilled under reduced pressure prior to use. 1,2-Diiodoethane was purified by recrystallization from hexane. Tetrasilabicyclo[1.1.0]but-1(3)-ene **1** was prepared according to published procedure.[9b]

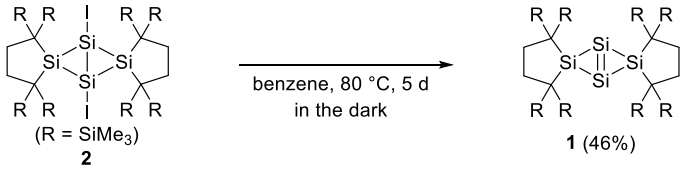
Synthesis of 1,3-Diiodobicyclo[1.1.0]tetrasilane 2 [TN470,504]



To a Schlenk tube (30 mL) equipped with a magnetic stir bar, **1** (30.3 mg, 37.8 μmol) and 1,2-diiodoethane (19.6 mg, 69.5 μmol) were placed. To the mixture, dry and degassed toluene (3.0 mL, cooled to −35 °C) was added, and then the mixture was stirred at 0 °C for 20 hours. The original orange suspension turned to a red solution. After the volatiles were removed in vacuo at room temperature, recrystallization from hot toluene provided red crystals of **2** (13.9 mg, 13.2 μmol) in 35% yield.

2: red crystals; mp 125-127 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 300 K) 0.47 (s, 72H, SiCH_3), 1.98 (s, 8H, CH_2); ^{13}C NMR (126 MHz, C_6D_6, 302 K) 6.0 (SiCH$_3$), 16.0 (*C*), 34.4 (*C*H$_2$); ^{29}Si NMR (99 MHz, C_6D_6, 301 K) 4.0 (*Si*), 5.0 (*Si*Me$_3$), 103.8 (*Si*-I); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 435 (2.4×10^3), 292 (sh, 1.5×10^4), 259 (3.4×10^4); HRMS (APCI_positive) Calcd for $C_{32}H_{81}I_2Si_{12}$ [$(M+H)^+$], 1055.16520; Found, 1055.16533; Anal. Calcd for $C_{32}H_{80}I_2Si_{12}$: C, 36.40; H, 7.64%. Found: C, 36.62; H, 7.74%.

Thermolysis of 2 [TN581]



To a stock bottle (10 mL) equipped with a magnetic stir bar, **2** (30.5 mg, 28.9 μmol) and then dry and degassed benzene (3.0 mL) were added. The mixture was stirred at 80 °C for 5 days in the dark. The resulting solution turned from red to orange. After the volatiles were removed in vacuo at room temperature, the crude was washed with hexane to provide an orange solid of **1** (10.7 mg, 13.3 μmol) in 46% yield.

NMR spectra

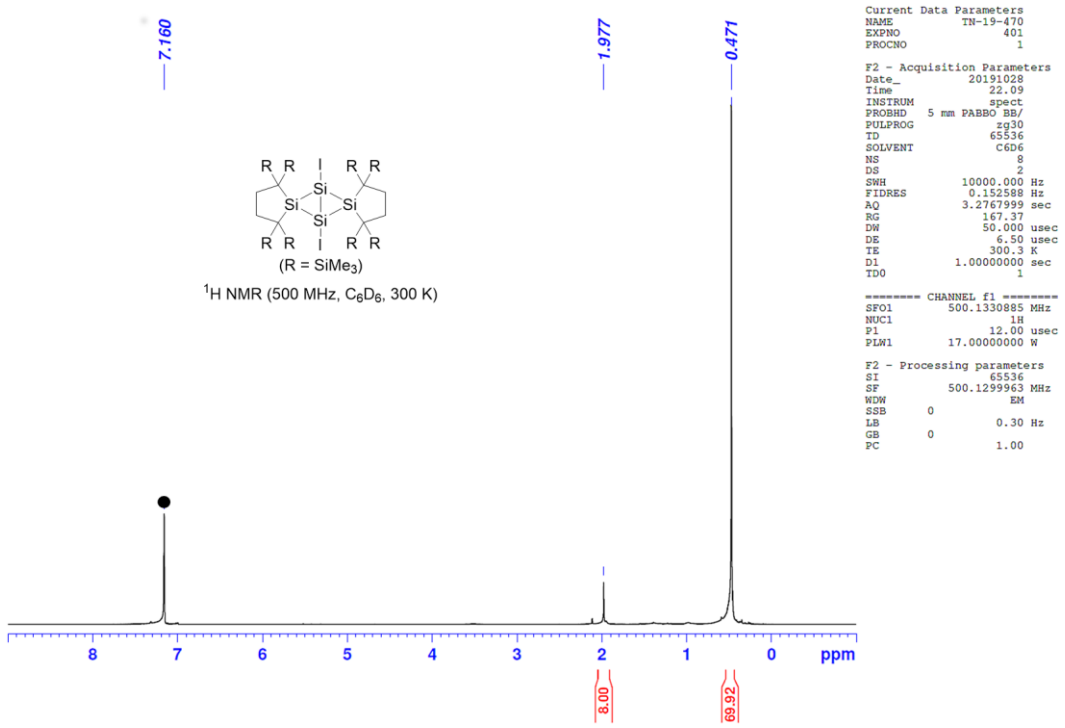


Figure 3-5. ^{1}H NMR spectrum of **2** in C_6D_6 at 300 K (● = C_6HD_5).

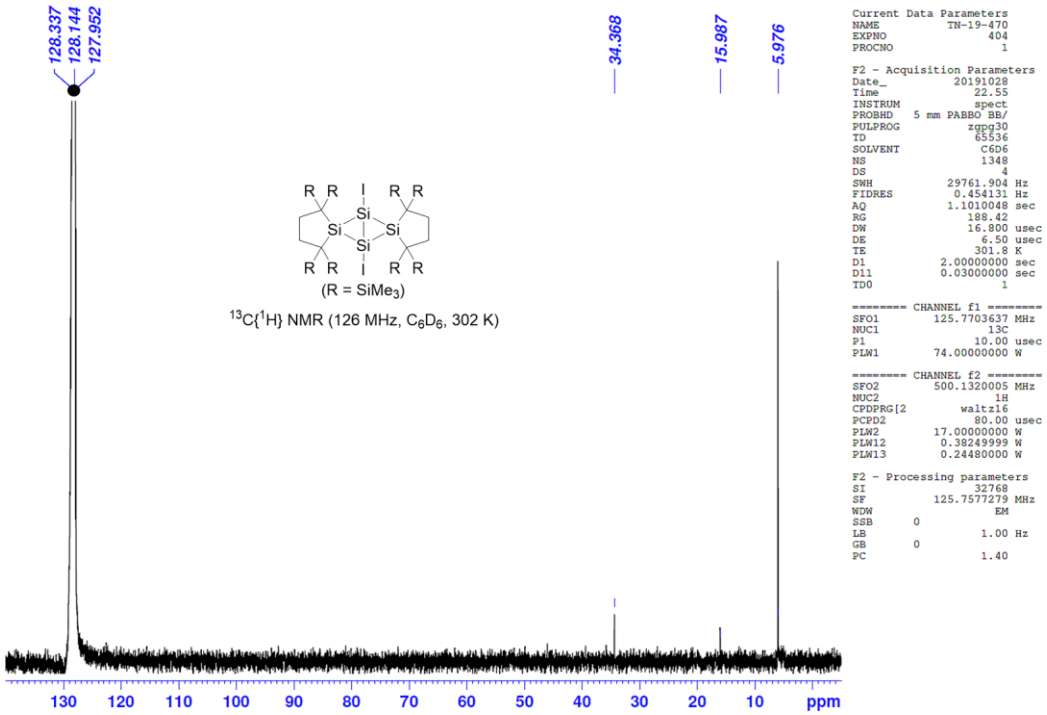


Figure 3-6. ^{13}C{^{1}H} NMR spectrum of **2** in C_6D_6 in 302 K (● = C_6D_6).

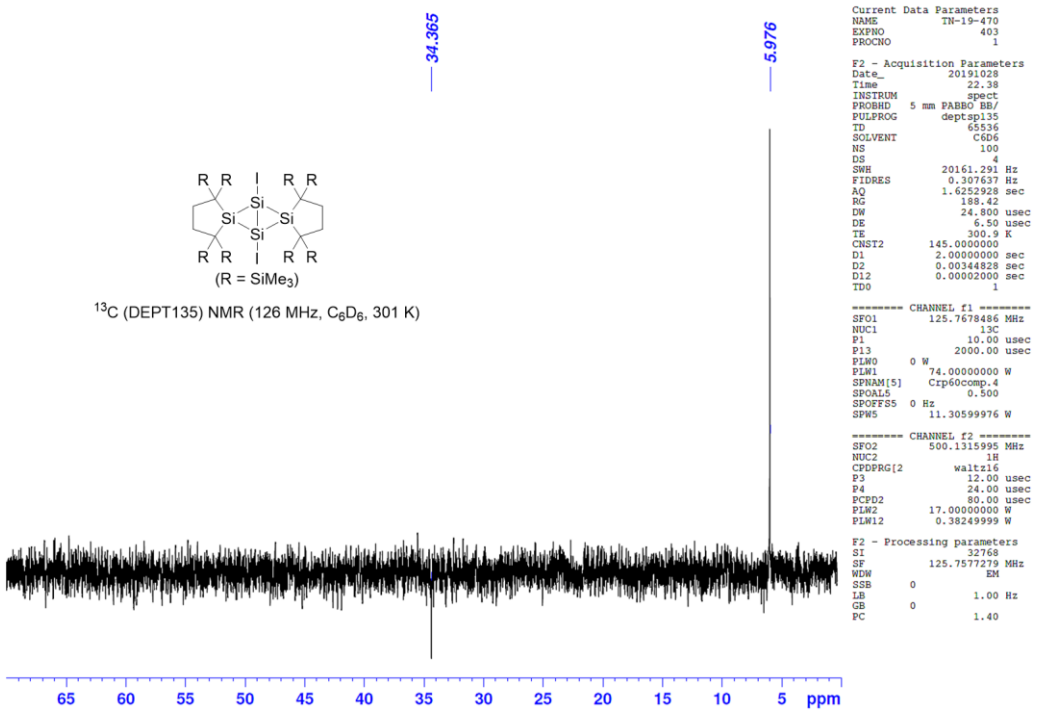


Figure 3-7. ^{13}C (DEPT135) NMR spectrum of **2** in C_6D_6 at 301 K.

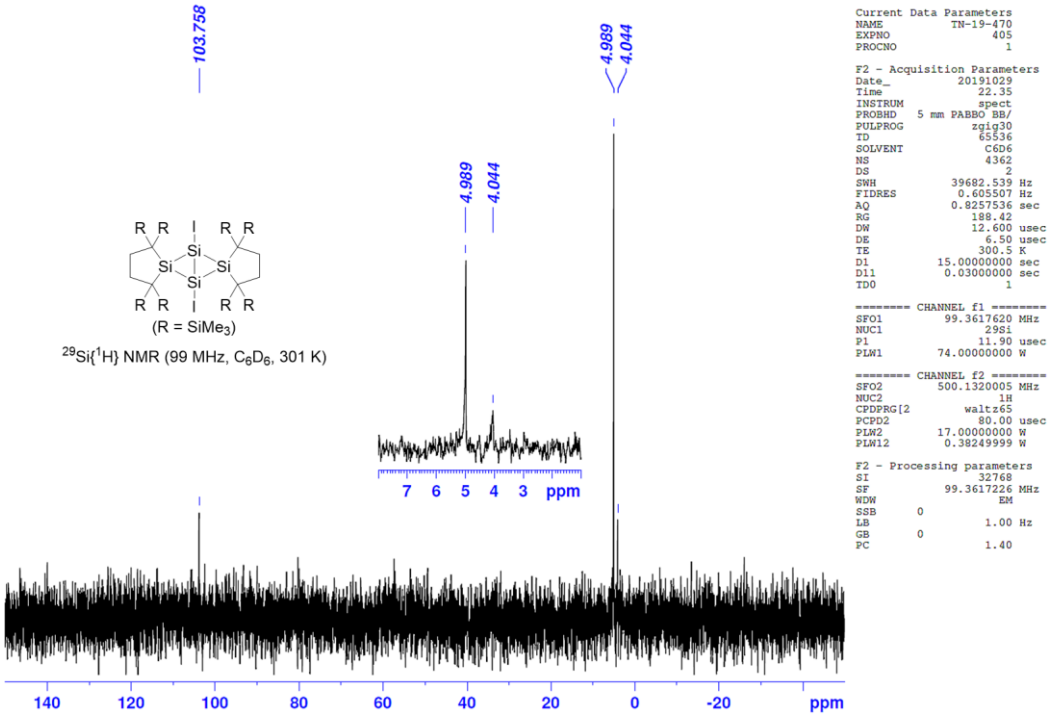


Figure 3-8. $^{29}Si\{^1H\}$ NMR spectrum of **2** in C_6D_6 at 301 K.

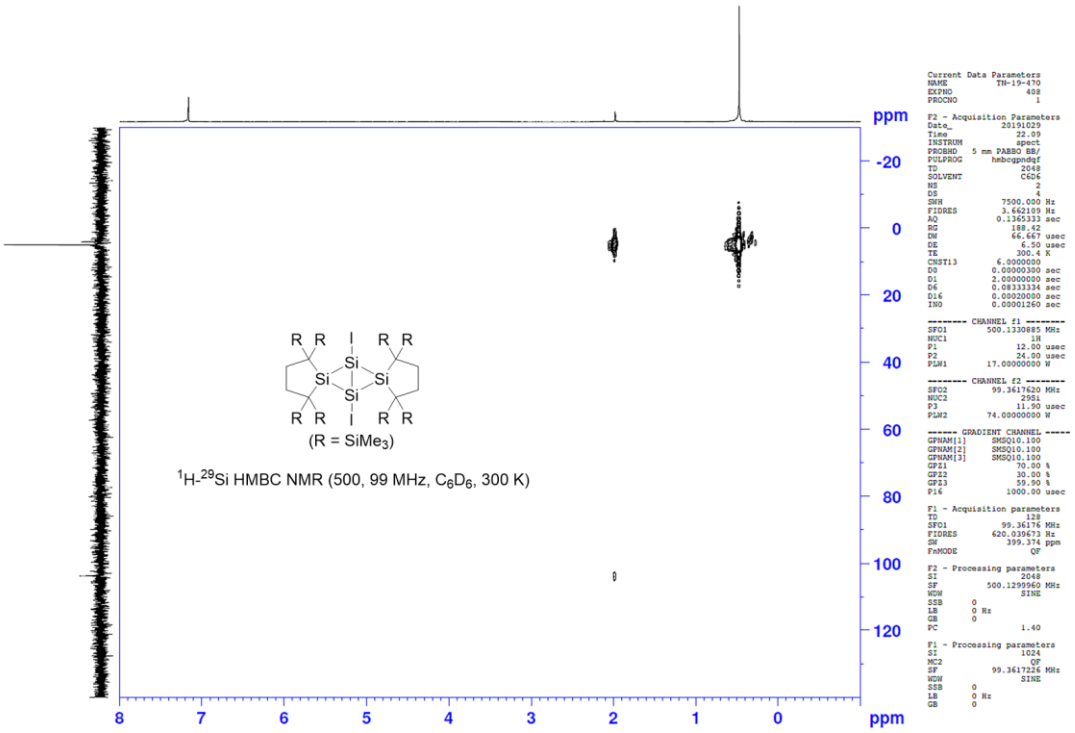


Figure 3-9. ^{1}H-^{29}Si HMBC NMR spectrum of **2** in C_6D_6 at 300 K.

X-ray Diffraction Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere using the following conditions; from benzene at room temperature for $\mathbf{2_p}$, from hexane at −35 °C for $\mathbf{2_c}$. For data collection, the single crystals coated by Apiezon grease were mounted on the glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer using a graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[25] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2014/7).[26] Molecular structure was analysed by Yadokari-XG software.[27]

Crystal data of $\mathbf{2_p}$ (100 K) [CCDC-1992431]: $C_{32}H_{80}Si_{12}I_2$; Fw 1055.82; monoclinic; $P2_1/n$, a = 11.0227(3) Å, b = 18.3233(5) Å, c = 12.8616(3) Å, β = 107.8710(10)˚, V = 2472.35(11) Å^3, Z = 2, D_{calc} = 1.418 Mg/m^3, $R1$ = 0.0235 ($I > 2\sigma(I)$), $wR2$ = 0.0523 (all data), GOF = 1.026.

Crystal data of $\mathbf{2_c}$ (100 K) [CCDC-1992432]: $C_{32}H_{80}Si_{12}I_2$; Fw 1055.82; triclinic; P-1, a = 11.6852(3) Å, b = 14.2348(4) Å, c = 17.0541(5) Å, α = 68.0820(10)˚, β = 78.1770(10)˚, γ = 76.5200(10)˚, V = 2537.24(12) Å^3, Z = 2, D_{calc} = 1.382 Mg/m^3, $R1$ = 0.0313 ($I > 2\sigma(I)$), $wR2$ = 0.0687 (all data), GOF = 1.013.

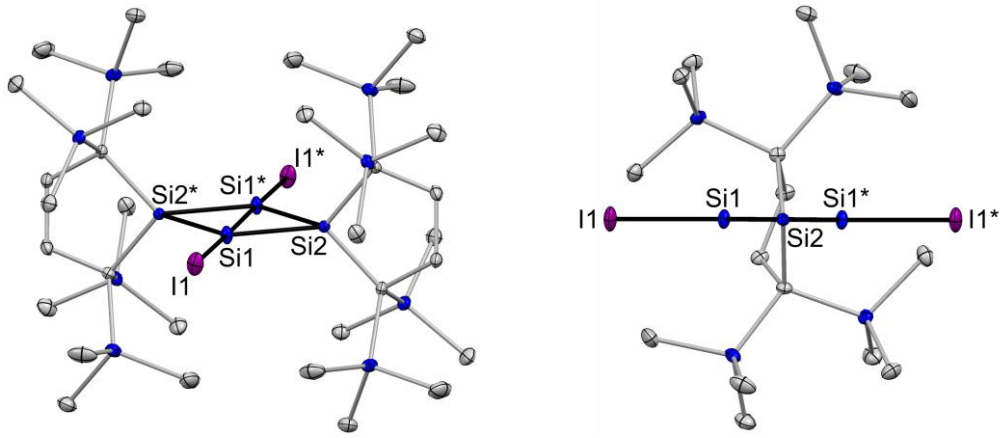


Figure 3-10. ORTEPs of $\mathbf{2_p}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

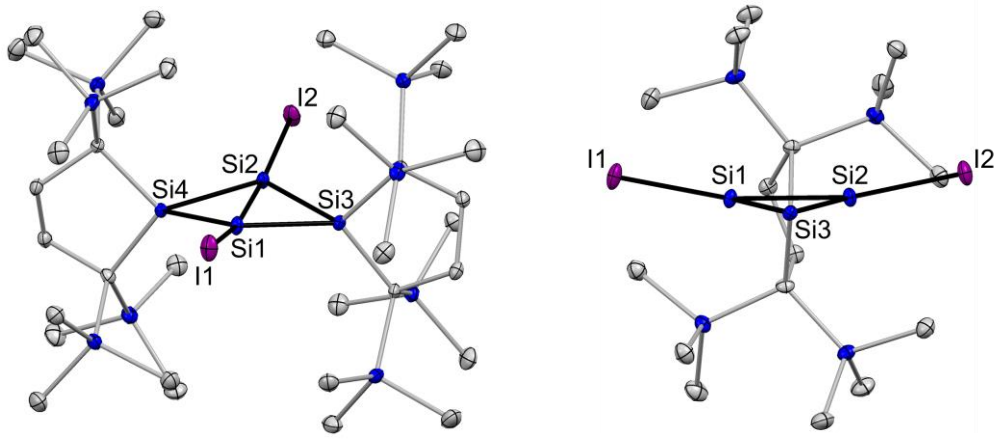


Figure 3-11. ORTEPs of $\mathbf{2_c}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

UV-vis Absorption Spectra

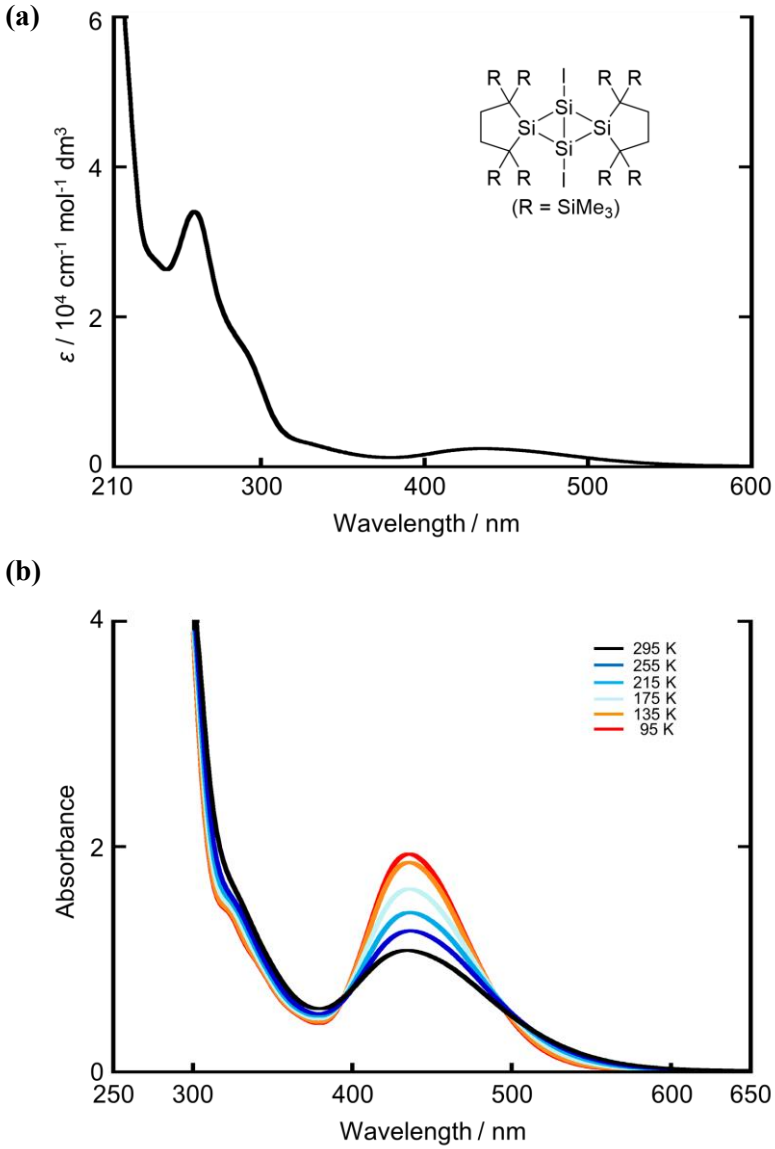


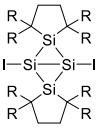
Figure 3-12. (a) UV-vis absorption spectrum of **2** in hexane at room temperature and (b) Temperature-dependent UV-vis absorption spectra of **2** in 3-methylpentane at 295 K to 95 K.

Computational Study

All theoretical calculations were performed using a Gaussian 09[28] program or GRRM14 program.[29] Geometry optimization was carried out at the B3LYP-D3/B1 (B1: SDD[I], 6-311G(d) [others]) level of theory. The atomic coordinates and energies of optimized structures are summarized in Tables 3-3 to 3-18. Isotropic chemical shielding tensors were calculated at the GIAO/M06L/B2 and B3 (B2: 6-311G(d) [I], 6-311+G(2df,p) [others]; B3: SDD [I], 6-

311+G(2df,p) [others]) level of theory (Table 3-19). Absolute isotropic shielding tensors of ^{29}Si nucleus in tetramethylsilane were calculated to be 361.4 (GIAO/M06L/B2 and B3). Natural bond orbital (NBO)[30] calculations of **2′$_c$** and **2′$_p$** were performed at the B3LYP-D3/B1 level of theory (Tables 3-20 and 3-21). Excitation energies and oscillator strengths of **2′$_c$**, **2′$_p$**, and **2′$_I$** were calculated at the B3LYP/B1 level of theory (Tables 3-22 to 3-24).

Table 3-3. Atomic Coordinates of **2′$_c$** at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory



(R = $SiMe_3$)
2′$_c$

Atom	X	Y	Z
Si	11.844852084991	9.553027254733	12.512055885122
Si	11.981065972061	5.949830017868	11.016803044828
Si	12.253694645279	7.278997011780	12.925642274061
Si	12.274417055003	8.244249683971	10.618051212204
Si	8.846203940731	10.838304654481	11.748065610370
Si	9.672403319674	5.617980648655	8.814244195547
Si	14.031153179728	3.661534410087	12.048288352971
Si	14.948728643098	5.386039042447	9.581136489834
Si	13.800467182515	11.957635449648	11.565195120368
Si	9.032446899775	4.491863290848	11.655151238797
Si	9.429945942391	9.747719525092	14.614824529841
Si	14.711590479723	10.286230290920	14.070980108441
I	12.716627808241	6.409784154853	15.259318479346
I	12.784220269777	9.141707646518	8.304925054210
C	15.615394845704	8.803249881240	13.342481132148
H	16.407780716486	8.499607387954	14.034325429414
H	16.084912638623	9.034500503923	12.386106397905
H	14.974260898154	7.937196245534	13.183735850232
C	14.263991298989	9.924432146766	15.870720119206
H	13.457995098014	9.211254649472	16.014966079238
H	14.007584139399	10.839035630381	16.412540928970
H	15.150037858293	9.502442647901	16.356627427553
C	16.032789832577	11.634180818185	14.270090158548
H	16.809367957248	11.222043093975	14.923934035734
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H	16.524774770838	11.945397709739	13.347787535267
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H	13.474454851044	14.273624501073	12.467296970273
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H	11.938781855410	11.527669104219	9.893621462905
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H	11.465619991198	9.222090106678	16.022196191450
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H	7.555348328035	10.316953667119	16.105645078696
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H	7.789147291880	8.580489144882	11.439790241988
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H	16.341736345316	4.572883764236	12.484031291681
H	15.539191221386	4.065202437576	13.967894803639
C	14.690771221097	1.974230234402	11.488411017595
H	15.122657027708	1.477147963028	12.364192801375
H	15.457522693126	1.995688245532	10.716725894243
H	13.878371469647	1.331642734494	11.136071491002
C	15.733453312018	6.918048852102	10.345307362761
H	16.535381655298	7.267985052911	9.687144578026
H	16.174817328437	6.713247279235	11.320925403502
H	15.037041968962	7.745264516009	10.475795637327
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H	14.377405826412	4.796202285672	7.212633041181
H	15.437036986139	6.196736662146	7.315067829794
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C	12.619229931659	3.761263953778	9.565998120779
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C	8.365519870522	2.762752483067	11.258219502072
H	9.089383490808	1.979208791524	11.497271910445
H	8.069781665631	2.631349554730	10.216633602243
H	7.480436828142	2.577899419352	11.876150514339
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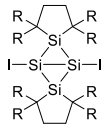
H	9.457148493463	8.058796984920	8.348538786768
H	9.300387771174	7.768391449042	10.071075073880
H	7.945231630554	7.436080913257	9.005467509711
C	10.838524463205	5.663393413531	7.331299448250
H	11.146588944656	4.668523239024	7.000483878214
H	11.731736274086	6.262515772633	7.493383730083
H	10.296393995871	6.124632634531	6.498432141272
C	8.253893455430	4.521739381026	8.193227066509
H	7.898557788770	4.942807565363	7.246346567136
H	7.393284166099	4.452960168878	8.858891034504
H	8.590322486827	3.503585674008	7.977642597893

E+ZPVE = -4764.385798 au, Free E (298.15 K) = -4764.492166 au.
Job name: TN87a_bent

Table 3-4. Atomic Coordinates of **2′$_p$** at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory



(R = $SiMe_3$)
2′$_p$

Atom	X	Y	Z
I	0.458661316324	6.885349461895	5.921936860855
Si	2.496481950878	8.377627113979	6.071742644396
Si	4.093683750162	8.516905463403	4.375803439341
C	5.407673637631	7.190003065321	3.828141509524
C	5.178541772882	7.189535874321	2.265157642694
H	6.083931584610	6.887957776892	1.730308249910
H	4.425531855358	6.452638078844	1.986401016451
C	4.718263254290	8.569888056704	1.759808963219
H	4.460920795081	8.503666212315	0.698537117856
H	5.554696206387	9.266546195012	1.815586054789
C	3.516102907052	9.091563640065	2.617740298804
Si	3.332814553743	10.993738648434	2.398388548012
C	4.984878832885	11.888306918751	2.584779877052
H	4.811201166170	12.955061422583	2.407191511588
H	5.731828296535	11.562482290934	1.857060641014
H	5.426136050615	11.804510741741	3.576786512274
C	2.745606720318	11.456141549012	0.657939117018
H	1.705849602294	11.185792758252	0.462498856644
H	3.363492845755	11.010545151982	-0.126461089756
H	2.820480411114	12.543282020473	0.548395331445
C	2.117116767352	11.777553627915	3.611247681895
H	2.228025133421	11.383194653754	4.620886900883
H	1.077605335792	11.633246787177	3.314704292064
H	2.297006833635	12.855601902342	3.659241292590
Si	1.912980653624	8.197888933657	1.994186550325
C	1.854125341588	8.154857898532	0.099976416772
H	0.899646772661	7.703221499964	-0.193200972233
H	2.640295722322	7.518200148060	-0.315676068228
H	1.918078060160	9.125874666403	-0.388892014731
C	0.334346001222	9.042788088291	2.593639490898
H	-0.514056150739	8.373630241049	2.421188587181
H	0.133823569247	9.967354273940	2.046802457662
H	0.341298998782	9.279255580198	3.657300142579
C	1.829441834347	6.363500107391	2.453078542124
H	2.229342481485	6.133113309895	3.435187293180
H	2.364723159245	5.751853043471	1.721820711339
H	0.787080332667	6.032332539001	2.454268205984
Si	7.248216761293	7.733086002336	4.092841622641
C	8.410575619179	6.506474081549	3.222484362074
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H	8.264483785918	5.457256602251	3.478912525405
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C	7.684513093247	9.366266095682	3.245760949104
H	7.027383380124	10.198444568117	3.485407981142
H	7.715578944449	9.257201443627	2.158339319133
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C	7.732402729399	7.843121311916	5.920180310805
H	8.317055316670	8.745936978746	6.103464132527
H	8.338817372607	6.987790395341	6.222571197622
H	6.870369727690	7.877482512119	6.587824182712
Si	5.250347412497	5.370657920370	4.516519112098
C	6.570257103903	4.847049698711	5.774659329069
H	6.522754341778	5.416921887460	6.702051757565
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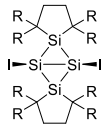
C	5.410822410436	4.177271367033	3.054411142206
H	5.523762934698	3.158065344779	3.437497669998
H	6.278891655865	4.389736759454	2.425858692856
H	4.527105839530	4.182472575616	2.411128607187
C	3.660874855062	4.903555862580	5.422096100091
H	3.783360856617	3.865644968562	5.751577214836
H	2.754946180848	4.936617802398	4.821355472881
H	3.488183388581	5.496305705550	6.320730702797
I	6.617139349965	11.437949110192	6.319078732427
Si	4.579318715411	9.945671458108	6.169272948886
Si	2.982116916127	9.806393108684	7.865212153941
C	1.668127028658	11.133295506766	8.412874083758
C	1.897258893407	11.133762697766	9.975857950587
H	0.991869081679	11.435340795195	10.510707343372
H	2.650268810931	11.870660493243	10.254614576831
C	2.357537411999	9.753410515383	10.481206630063
H	2.614879871208	9.819632359772	11.542478475426
H	1.521104459902	9.056752377075	10.425429538493
C	3.559697759238	9.231734932022	9.623275294478
Si	3.742986112546	7.329559923653	9.842627045269
C	2.090921833404	6.434991653336	9.656235716230
H	2.264599500119	5.368237149504	9.833824081694
H	1.343972369754	6.760816281153	10.383954952268
H	1.649664615674	6.518787830346	8.664229081008
C	4.330193945972	6.867157023075	11.583076476264
H	5.369951063995	7.137505813835	11.778516736638
H	3.712307820534	7.312753420105	12.367476683038
H	4.255320255175	5.780016551614	11.692620261837
C	4.958683898937	6.545744944172	8.629767911387
H	4.847775532869	6.940103918333	7.620128692399
H	5.998195330497	6.690051784910	8.926311301218
H	4.778793832654	5.467696669745	8.581774300692
Si	5.162820012665	10.125409638430	10.246829042957
C	5.221675324702	10.168440673555	12.141039176510
H	6.176153893628	10.620077072123	12.434216565515
H	4.435504943968	10.805098424027	12.556691661510
H	5.157722606129	9.197423905684	12.629907608013
C	6.741454665067	9.280510483796	9.647376102384
H	7.589856817028	9.949668331038	9.819827006101
H	6.941977097042	8.355944298147	10.194213135620
H	6.734501667508	9.044042991889	8.583715450703
C	5.246358831942	11.959798464696	9.787937051158
H	4.846458184804	12.190185262192	8.805828300102
H	4.711077507045	12.571445528616	10.519194881943
H	6.288720333623	12.290966033086	9.786747387298
Si	-0.172416095004	10.590212569751	8.148173970641
C	-1.334774952890	11.816824490538	9.018531231208
H	-1.266016034803	11.731521139874	10.106582354952
H	-1.188683119629	12.866041969836	8.762103067877
H	-2.364841737141	11.558336879085	8.748984531312
C	-0.608712426958	8.957032476405	8.995254644178
H	0.048417286165	8.124854003970	8.755607612140
H	-0.639778278159	9.066097128460	10.082676274149
H	-1.614803572284	8.666961486767	8.673973076011
C	-0.656602063110	10.480177260171	6.320835282477
H	-1.241254650381	9.577361593341	6.137551460755
H	-1.263016706318	11.335508176746	6.018444395660
H	0.205430938600	10.445816059968	5.653191410569
Si	1.825453253792	12.952640651718	7.724496481184
C	0.505543562386	13.476248873376	6.466356264213
H	0.553046324511	12.906376684627	5.538963835717
H	-0.522847572595	13.453020561716	6.824465549125
H	0.729375115698	14.517590205061	6.209930664067
C	1.664978255853	14.146027205054	9.186604451076
H	1.552037731591	15.165233227308	8.803517923284
H	0.796909010424	13.933561812633	9.815156900426
H	2.548694826759	14.140825996471	9.829886986095
C	3.414925811227	13.419742709507	6.818919493191
H	3.292439809672	14.457653603525	6.489438378446
H	4.320854485441	13.386680769689	7.419660120401
H	3.587617277708	12.826992866537	5.920284890485

E+ZPVE = -4764.381407 au, Free E (298.15 K) = -4764.486143 au.
Job name: TN87a_planar

Table 3-5. Atomic Coordinates of **2′$_I$** at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory



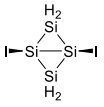
(R = $SiMe_3$)
2′$_I$

Atom	X	Y	Z
I	-0.149133220871	-0.998135872420	3.398857620056
Si	-0.048844482464	0.549274853588	1.365383931219
Si	-1.963994614462	0.298603081309	-0.123469691083
C	-3.474876888607	-0.952061032929	-0.131205415092
C	-4.648245355727	0.077873904832	0.058153924245
H	-5.614849716152	-0.362101794853	-0.191570398218
H	-4.727948999512	0.383135111186	1.105573614158
C	-4.375537074323	1.319557440338	-0.792388499091
H	-5.188758708784	2.041025480357	-0.699854190543
H	-4.358378636393	1.028595990286	-1.847670882923
C	-2.995730038939	1.937884997732	-0.362352977909
Si	-2.454507059207	3.142894102089	-1.754224562604
C	-2.333089070802	2.338078043404	-3.457233608700
H	-2.032986164167	3.117479395846	-4.166055938352
H	-3.278702286163	1.928641212040	-3.815282463033
H	-1.582691992597	1.548839655169	-3.512558696231
C	-3.751686240486	4.508752596817	-1.957239695617
H	-3.837249732677	5.169250682964	-1.092462402729
H	-4.745158798332	4.098823084187	-2.160778194693
H	-3.480846228485	5.133008013703	-2.815140461962
C	-0.780379438101	3.934992755440	-1.427564827334
H	-0.084014222298	3.218597201572	-0.990570362915
H	-0.833639301279	4.791222869064	-0.757512760092
H	-0.339523885261	4.278279411612	-2.366057770747
Si	-3.319039390796	2.955574752840	1.281305969688
C	-5.111707122329	3.575452810310	1.284141318492

H	-5.235971229799	4.243048357194	2.143235874540
H	-5.836211478600	2.765402315749	1.404650454087
H	-5.387442321735	4.141277561859	0.392123154199
C	-2.247229287412	4.495520287616	1.503306698659
H	-2.524852270682	4.933387627091	2.468068843547
H	-2.410640256770	5.264722691695	0.747107798609
H	-1.180749929083	4.282016637520	1.547736978746
C	-3.153061837205	2.025596178353	2.915109319173
H	-2.176472253865	1.572605885792	3.087865646328
H	-3.908922837053	1.252038062851	3.042537259723
H	-3.309615203170	2.755817200578	3.716697262924
Si	-3.829037504479	-1.870603672317	-1.836821095290
C	-5.698769625270	-1.874628849108	-2.166829452596
H	-6.098961376378	-0.877593257449	-2.369026674570
H	-6.292137533526	-2.324153745319	-1.369058891496
H	-5.865824095596	-2.472595146392	-3.069701420873
C	-3.145687458011	-1.035552610744	-3.392018704690
H	-2.145558616113	-0.618520917954	-3.311270103467
H	-3.811460260981	-0.237286237120	-3.725605605528
H	-3.112682862090	-1.781037855134	-4.192586573725
C	-3.337179354283	-3.702888763076	-1.875113581296
H	-3.097185496592	-3.968760744527	-2.908686178285
H	-4.171105798092	-4.336255824651	-1.564315253149
H	-2.472680377903	-3.969714321687	-1.274728412127
Si	-3.627597288928	-2.261784800966	1.278987329517
C	-2.177606103610	-3.470371766439	1.330509555657
H	-1.341892465705	-3.155256915910	0.706174183682
H	-2.483294906447	-4.461629540431	0.986422966337
H	-1.794816849386	-3.575251566389	2.347037303633
C	-5.235541130704	-3.251499440733	1.077826289791
H	-5.344716903842	-3.887371140407	1.963335884839
H	-5.274850062639	-3.906332885294	0.208007421214
H	-6.112468075920	-2.598378176875	1.049560287146
C	-3.888455514503	-1.473605359714	2.975021962667
H	-4.868104012536	-0.992186143794	3.046392660201
H	-3.129113653136	-0.758277411177	3.275321007301
H	-3.876974214081	-2.278820156652	3.717670575961
I	0.090699589502	-2.538917305070	-2.182612669774
Si	0.039027345166	-0.119770740730	-1.400392268815
Si	1.959322883068	0.225571000694	-0.023540864685
C	3.113947707729	1.803098648498	-0.097010612157
C	4.535608895854	1.114962870001	-0.098214410731
H	5.300031430660	1.783701060966	0.307289039315
H	4.859519141682	0.896943038499	-1.115901434337
C	4.508090537407	-0.195613184980	0.684472523112
H	5.482695712102	-0.686602680879	0.630142199249
H	4.347874735255	0.020095619817	1.739644861406
C	3.360800315901	-1.120064833723	0.140406685851
Si	3.190603588560	-2.555572778353	1.418248638416
C	3.426742357046	-1.904186257704	3.180140546957
H	3.061395203550	-2.654468985737	3.888085114090
H	4.490580821414	-1.754074874348	3.388457399802
H	2.907850004546	-0.977143002092	3.408495196282
C	4.634953705604	-3.776351387184	1.259587496150
H	4.647542612474	-4.365480818984	0.343044715088
H	5.602206594324	-3.274991464463	1.355331038259
H	4.564015364737	-4.481986516660	2.094900884330
C	1.585451368061	-3.525415994277	1.254427816056
H	0.740889167041	-2.888612720375	1.003542628550
H	1.645879228202	-4.299087414070	0.486659400483
H	1.343709497698	-4.016041690681	2.201277737195
Si	3.990420275136	-1.844195822810	-1.571831957921
C	5.888568188503	-1.867274158232	-1.573382523358
H	6.207665830154	-2.327805281630	-2.514666570012
H	6.346462102196	-0.876270786318	-1.531581630291
H	6.309040094797	-2.469495472832	-0.765135675225
C	3.495033885353	-3.636632838452	-1.962940561344
H	3.086096913544	-3.685562624895	-2.974828794643
H	4.381805196364	-4.276253527479	-1.935186246730
H	2.749954562865	-4.073277573637	-1.302873228206
C	3.544705719655	-0.809514228928	-3.089108364978
H	2.473826472077	-0.693583304775	-3.252777007990
H	3.997614247496	0.182386100950	-3.065913638579
H	3.947392926952	-1.323423581254	-3.968665205612
Si	3.039668398395	2.856459347905	1.531675151188
C	4.571812464669	3.980308957096	1.599323490499
H	5.430855358524	3.448633648867	2.018305325081
H	4.881120950996	4.391080400170	0.636892999438
H	4.368843730652	4.826556319736	2.263788294296
C	3.134039029215	1.878397206735	3.148911131626
H	2.316130278699	1.170547071751	3.290349659097
H	4.075373041490	1.344552853062	3.290531007073
H	3.059290134651	2.608317600668	3.963346556729
C	1.471859677805	3.904203990421	1.666728033203
H	1.030364801553	3.784109682938	2.659468510031
H	1.675296413443	4.966886021621	1.518002110649
H	0.714510176980	3.612527141102	0.943528301171
Si	3.060146163964	3.004092836854	-1.640062152763
C	2.579856688722	4.798640245730	-1.259772082176
H	1.568675767688	4.931382228364	-0.885425788439
H	3.262155042119	5.292297117229	-0.566035481992
H	2.643840415482	5.343072604661	-2.208340178293
C	4.809888309102	3.166943720606	-2.358583259754
H	4.795742644999	3.967035158497	-3.105786026771
H	5.554948779319	3.439297940945	-1.606687054079
H	5.166699192619	2.266643241779	-2.864499427091
C	1.971125355092	2.474499328912	-3.091941999578
H	1.968006452898	3.296562068544	-3.816408815029
H	2.355124582958	1.593977235472	-3.605551322321
H	0.934153040626	2.272223239937	-2.830526586375

E+ZPVE = -4764.376320 au, Free E (298.15 K) = -4764.481479 au.
Job name: TN85aa

Table 3-6. Atomic Coordinates of $\mathbf{3_L}$ at the B3LYP-D3/6-311G(d) [H,Si], SDD [I] Level of Theory

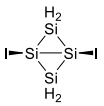


$\mathbf{3_L}$

Atom	X	Y	Z
Si	1.531248777162	0.000000000000	0.699942234149
Si	0.000000000000	1.746617726618	1.128687953632
I	2.111682964067	0.000000000000	-1.766481603830
Si	-1.531248777162	0.000000000000	0.699942234149
Si	0.000000000000	-1.746617726618	1.128687953632
I	-2.111682964067	0.000000000000	-1.766481603830
H	0.000000000000	2.945532103941	0.258447423913
H	0.000000000000	2.128533507174	2.563274752148
H	0.000000000000	-2.945532103941	0.258447423913
H	0.000000000000	-2.128533507174	2.563274752148

E+ZPVE = -1183.320927 au, Free E (298.15 K) = -1183.360091 au.
Job name: ti554MIN24G1LB

Table 3-7. Atomic Coordinates of $\mathbf{3_S}$ at the B3LYP-D3/6-311G(d) [H,Si], SDD [I] Level of Theory

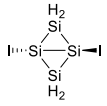


$\mathbf{3_S}$

Atom	X	Y	Z
Si	1.178453126457	0.000000000000	0.063671315245
Si	0.000000000000	1.764641646345	0.991581621944
I	3.348868093697	0.000000000000	-1.149582576812
Si	-1.178453126457	0.000000000000	0.063671315245
Si	0.000000000000	-1.764641646345	0.991581621944
I	-3.348868093697	0.000000000000	-1.149582576812
H	0.000000000000	2.956163056891	0.111670030044
H	0.000000000000	2.162182725687	2.423589469576
H	0.000000000000	-2.956163056891	0.111670030044
H	0.000000000000	-2.162182725687	2.423589469576

E+ZPVE = -1183.303701 au, Free E (298.15 K) = -1183.343596 au.
Job name: ti554MIN24G1SB

Table 3-8. Atomic Coordinates of $\mathbf{3_{TP}}$ at the B3LYP-D3/6-311G(d) [H,Si], SDD [I] Level of Theory

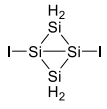


$\mathbf{3_{TP}}$

Atom	X	Y	Z
Si	-1.180735705629	0.983516528972	0.000000000000
Si	0.000000000000	0.000000000000	1.820290726303
I	0.074366626853	3.261015647536	0.000000000000
Si	1.180735705629	-0.983516528972	0.000000000000
Si	0.000000000000	0.000000000000	-1.820290726303
I	-0.074366626853	-3.261015647536	0.000000000000
H	-0.666586418481	-1.023395540652	2.656297120409
H	0.666586418481	1.023395540652	2.656297120409
H	-0.666586418481	-1.023395540652	-2.656297120409
H	0.666586418481	1.023395540652	-2.656297120409

E+ZPVE = -1183.310452 au, Free E (298.15 K) = -1183.350584 au.
Job name: ti554MIN24G1TP

Table 3-9. Atomic Coordinates of $\mathbf{3_P}$ at the B3LYP-D3/6-311G(d) [H,Si], SDD [I] Level of Theory

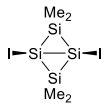


$\mathbf{3_P}$

Atom	X	Y	Z
Si	0.2854111920708	-0.969712882368	-0.871351342250
Si	-0.431831060038	1.138598150242	-1.408572935572
I	0.818201044808	-2.779837371744	-2.497869892263
Si	-0.285435800525	0.969713793529	0.871353915456
Si	0.431807180221	-1.138597239082	1.408575508779
I	-0.818224924625	2.779838282905	2.497872465469
H	-1.777069866868	1.291547520878	-2.019439628122
H	0.510977675031	2.046754994248	-2.110414733423
H	-0.511001554848	-2.046754083087	2.110417306629
H	1.777045987051	-1.291546609717	2.019442201329

E+ZPVE = -1183.288909 au, Free E (298.15 K) = -1183.325406 au.
Job name: ti554MIN24G1SAD

Table 3-10. Atomic Coordinates of $\mathbf{4_L}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory

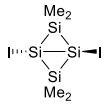


$\mathbf{4_L}$

Atom	X	Y	Z
Si	-1.497210957574	0.000000000000	0.373990115235
Si	0.000000000000	1.795867712087	0.725521802508
I	-2.119761092547	0.000000000000	-2.102196679705
Si	1.497210957575	0.000000000000	0.373990115235
Si	0.000000000000	-1.795867712087	0.725521802508
I	2.119761092546	0.000000000000	-2.102196679705
C	0.000000000000	2.414284981742	2.508447377151
H	0.884511593288	3.028315874908	2.700566147136
H	-0.884511593288	3.028315874908	2.700566147136
H	0.000000000000	1.591994366244	3.227847242182
C	0.000000000000	3.194623702429	-0.526849862742
H	-0.884395576188	3.825853928626	-0.402003917461
H	0.884395576188	3.825853928626	-0.402003917461
H	0.000000000000	2.802770766062	-1.545091066952
C	0.000000000000	-2.414284981742	2.508447377151
H	-0.884511593288	-3.028315874908	2.700566147136
H	0.884511593288	-3.028315874908	2.700566147136
H	0.000000000000	-1.591994366244	3.227847242182
C	0.000000000000	-3.194623702429	-0.526849862742
H	0.884395576188	-3.825853928626	-0.402003917461
H	-0.884395576188	-3.825853928626	-0.402003917461
H	0.000000000000	-2.802770766062	-1.545091066952

E+ZPVE = -1340.568198 au, Free E (298.15 K) = -1340.617029 au.
Job name: ti554MIN24G2LB

Table 3-11. Atomic Coordinates of $\mathbf{4_{TP}}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory

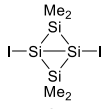


$\mathbf{4_{TP}}$

Atom	X	Y	Z
Si	1.520636320627	-0.047970553497	-0.000000000127
Si	-0.000004207451	-0.000002582559	1.850840575881
I	2.028134011796	-2.617872149388	-0.000000000679
Si	-1.520644736367	0.047965389008	0.000000000578
Si	-0.000004208290	-0.000002581930	-1.850840575430
I	-2.028142427537	2.617866984898	0.000000001130
C	-0.001492690317	1.538779128230	2.932990252203
H	-0.980002458259	1.678729861534	3.400680189241
H	0.739369247801	1.421061859079	3.729765308604
H	0.228130742052	2.443538654177	2.371138281265
C	0.001484275906	-1.538784293716	2.932990251679
H	0.979994044060	-1.678735027179	3.400680188226
H	-0.739377661851	-1.421067024836	3.729765308456
H	-0.228139156718	-2.443543819472	2.371138280538
C	-0.001492691647	1.538779129227	-2.932990251228
H	0.739369246110	1.421061860347	-3.729765308005
H	-0.980002459800	1.678729862690	-3.400680187775
H	0.228130740977	2.443538654983	-2.371138280087
C	0.001484274576	-1.538784292719	-2.932990251752
H	-0.739377663542	-1.421067023569	-3.729765308153
H	0.979994042518	-1.678735026023	-3.400680188790
H	-0.228139157793	-2.443543818666	-2.371138280814

E+ZPVE = -1340.557669 au, Free E (298.15 K) = -1340.606512 au.
Job name: ti554MIN24G2TP

Table 3-12. Atomic Coordinates of $\mathbf{4_P}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory



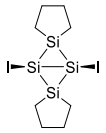
$\mathbf{4_P}$

Atom	X	Y	Z
Si	1.322469409544	0.000000000000	0.000000000000
Si	0.000000000000	1.883643754939	0.000000000000
I	3.835635746357	0.000000000000	0.000000000000
Si	-1.322469409544	0.000000000000	0.000000000000
Si	0.000000000000	-1.883643754939	0.000000000000
I	-3.835635746357	0.000000000000	0.000000000000

C	0.000000000000	2.988241125774	-1.530843037140
H	-0.882238272526	3.636395555049	-1.535369487410
H	0.882238272526	3.636395555049	-1.535369487410
H	0.000000000000	2.403215294490	-2.451487466808
C	0.000000000000	2.988241125774	1.530843037140
H	0.882238272526	3.636395555049	1.535369487410
H	-0.882238272526	3.636395555049	1.535369487410
H	0.000000000000	2.403215294490	2.451487466808
C	0.000000000000	-2.988241125774	-1.530843037140
H	0.882238272526	-3.636395555049	-1.535369487410
H	-0.882238272526	-3.636395555049	-1.535369487410
H	0.000000000000	-2.403215294490	-2.451487466808
C	0.000000000000	-2.988241125774	1.530843037140
H	-0.882238272526	-3.636395555049	1.535369487410
H	0.000000000000	-2.403215294490	2.451487466808

E+ZPVE = -1340.533937 au, Free E (298.15 K) = -1340.580461 au.
Job name: ti554MIN24G2SAD

Table 3-13. Atomic Coordinates of $\mathbf{5_L}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory

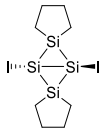


$\mathbf{5_L}$

Atom	X	Y	Z
Si	-1.445806216284	0.977748329690	0.000000000000
Si	-1.117391707324	-0.519305291345	1.795551985524
I	0.559502020743	2.564691150563	0.000000000000
C	-2.627663132550	-1.175133783332	2.752421062230
C	-2.396455264703	-0.593793751630	4.169732345273
H	-2.732692319873	0.449738175924	4.195853595935
H	-2.982720184640	-1.131709321675	4.921277034889
C	-0.888935449834	-0.647401609529	4.492684623584
H	-0.589522614210	-1.693498044139	4.627379030128
H	-0.670318247685	-0.134613660981	5.434209603864
C	-0.095113166862	-0.031598907144	3.315361808768
Si	-0.225623569776	-1.769162616646	0.000000000000
Si	-1.117391707324	-0.519305291345	-1.795551985524
I	2.296274176710	-1.339115999913	0.000000000000
C	-0.095113166862	-0.031598907144	-3.315361808768
C	-0.888935449834	-0.647401609529	-4.492684623584
H	-0.589522614210	-1.693498044139	-4.627379030128
H	-0.670318247685	-0.134613660981	-5.434209603864
C	-2.396455264703	-0.593793751630	-4.169732345273
H	-2.732692319873	0.449738175924	-4.195853595935
H	-2.982720184640	-1.131709321675	-4.921277034889
C	-2.627663132550	-1.175133783332	-2.752421062230
H	-3.592719093974	-0.890336044319	2.329380545359
H	-2.593646801357	-2.269373892529	2.779460308346
H	-0.064801421152	1.060727443579	3.385457934177
H	0.940846008879	-0.370933742621	3.262930624018
H	0.940846008879	-0.370933742621	-3.262930624018
H	-0.064801421152	1.060727443579	-3.385457934177
H	-2.593646801357	-2.269373892529	-2.779460308346
H	-3.592719093974	-0.890336044319	-2.329380545359

E+ZPVE = -1495.350671 au, Free E (298.15 K) = -1495.402237 au.
Job name: ti554MIN24G3LB

Table 3-14. Atomic Coordinates of $\mathbf{5_{TP}}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory

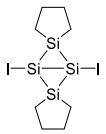


$\mathbf{5_{TP}}$

Atom	X	Y	Z
Si	-1.413420437365	0.521412835850	0.000000000000
Si	0.000000000000	0.000000000000	-1.849455843720
I	-2.717963099908	-1.763345214185	0.000000000000
C	0.622233655252	1.268547620036	-3.115564646693
C	0.000425513781	0.771118199234	-4.441843641021
H	-1.032638284601	1.130060246929	-4.522568462243
H	0.539555028814	1.167737091175	-5.307517771334
C	-0.000425513781	-0.771118199234	-4.441843641021
H	1.032638284601	-1.130060246929	-4.522568462243
H	-0.539555028814	-1.167737091175	-5.307517771334
C	-0.622233655252	-1.268547620036	-3.115564646693
Si	1.413420437365	-0.521412835850	0.000000000000
Si	0.000000000000	0.000000000000	1.849455843720
I	2.717963099908	1.763345214185	0.000000000000
C	-0.622233655252	-1.268547620036	3.115564646693
C	-0.000425513781	-0.771118199234	4.441843641021
H	1.032638284601	-1.130060246929	4.522568462243
H	-0.539555028814	-1.167737091175	5.307517771334
C	0.000425513781	0.771118199234	4.441843641021
H	-1.032638284601	1.130060246929	4.522568462243
H	0.539555028814	1.167737091175	5.307517771334
C	0.622233655252	1.268547620036	3.115564646693
H	0.363268284059	2.299362021415	-2.870030200232
H	1.715271051257	1.222370183321	-3.154263383595
H	-1.715271051257	-1.222370183321	-3.154263383595
H	-0.363268284059	-2.299362021415	-2.870030200232
H	-0.363268284059	-2.299362021415	2.870030200232
H	-1.715271051257	-1.222370183321	3.154263383595
H	1.715271051257	1.222370183321	3.154263383595
H	0.363268284059	2.299362021415	2.870030200232

E+ZPVE = -1495.345616 au, Free E (298.15 K) = -1495.396126 au.
Job name: ti554MIN24G3TP

Table 3-15. Atomic Coordinates of $\mathbf{5_P}$ at the B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] Level of Theory

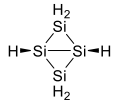


$\mathbf{5_P}$

Atom	X	Y	Z
Si	0.179454959277	-0.951614457666	-0.910435447533
Si	-0.432564054140	1.216804171297	-1.357248808526
I	0.514892582832	-2.750810680476	-2.629267493655
C	-2.091043581166	1.698270014383	-2.164006529821
C	-1.664487208374	2.499207508662	-3.414553638574
H	-1.426151171008	1.805215384575	-4.229735264008
H	-2.470571470380	3.144193117650	-3.777512655911
C	-0.404344493231	3.325349150629	-3.073860933504
H	-0.681179770140	4.127651746428	-2.379149383949
H	0.000744815317	3.810186699109	-3.967365100239
C	0.635052000195	2.399137000802	-2.403756717830
Si	-0.179454959277	0.951614457666	0.910435447533
Si	0.432564054140	-1.216804171297	1.357248808526
I	-0.514892582832	2.750810680476	2.629267493655
C	2.091043581166	-1.698270014383	2.164006529821
C	1.664487208374	-2.499207508662	3.414553638574
H	1.426151171008	-1.805215384575	4.229735264008
H	2.470571470380	-3.144193117650	3.777512655911
C	0.404344493231	-3.325349150629	3.073860933504
H	0.681179770140	-4.127651746428	2.379149383949
H	-0.000744815317	-3.810186699109	3.967365100239
C	-0.635052000195	-2.399137000802	2.403756717830
H	-2.723985209900	0.839870475743	-2.397308829904
H	-2.655968319155	2.333340448672	-1.472110203817
H	1.179304883722	1.819247066465	-3.157874103984
H	1.381114824448	2.940479131558	-1.818737824138
H	2.723985209900	-0.839870475743	2.397308829904
H	2.655968319155	-2.333340448672	1.472110203817
H	-1.179304883722	-1.819247066465	3.157874103984
H	-1.381114824448	-2.940479131558	1.818737824138

E+ZPVE = -1495.320608 au, Free E (298.15 K) = -1495.369943 au.
Job name: ti554MIN24G3SAD

Table 3-16. Atomic Coordinates of $\mathbf{6_L}$ at the B3LYP-D3/6-311G(d) Level of Theory

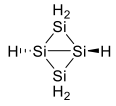


$\mathbf{6_L}$

Atom	X	Y	Z
Si	-1.439767966756	0.435207437142	0.000225108213
Si	0.000228096595	1.034701389212	1.742127972419
H	-1.501123470425	-1.063035755931	-0.000140653645
Si	1.439837033175	0.435136883286	-0.000070570317
Si	-0.000129599978	1.035566528514	-1.741675458315
H	1.501119042772	-1.063109314556	-0.000448924625
H	0.000335645888	0.222258629545	2.983410017394
H	0.000296586173	2.481055606350	2.064021706503
H	-0.000276987269	0.223740368711	-2.983360856883
H	-0.000127136975	2.482080440179	-2.062850808430

E+ZPVE = -1161.579368 au, Free E (298.15 K) = -1161.609617 au.
Job name: ti554MIN23G5L

Table 3-17. Atomic Coordinates of $\mathbf{6_{TP}}$ at the B3LYP-D3/6-311G(d) Level of Theory

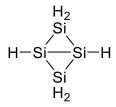


$\mathbf{6_{TP}}$

Atom	X	Y	Z
Si	-1.128758438050	0.947499098181	0.000000000000
Si	0.000000000000	0.000000000000	1.836836798354
H	-0.147343070151	2.107492947122	0.000000000000
Si	1.128758438050	-0.947499098181	0.000000000000
Si	0.000000000000	0.000000000000	-1.836836798354
H	0.147343070151	-2.107492947122	0.000000000000
H	-0.605980736278	-1.051219592740	2.688324629783
H	0.605980736278	1.051219592740	2.688324629783
H	-0.605980736278	-1.051219592740	-2.688324629783
H	0.605980736278	1.051219592740	-2.688324629783

E+ZPVE = -1161.561993 au, Free E (298.15 K) = -1161.592445 au.
Job name: ti554MIN23G5PT

Table 3-18. Atomic Coordinates of $\mathbf{6_P}$ at the B3LYP-D3/6-311G(d) Level of Theory



$\mathbf{6_P}$

Atom	X	Y	Z
Si	1.407981345557	0.000000000000	0.000000000000
Si	0.000000000000	1.819499831760	0.000000000000
H	2.901895517455	0.000000000000	0.000000000000
Si	-1.407981345557	0.000000000000	0.000000000000
Si	0.000000000000	-1.819499831760	0.000000000000
H	-2.901895517455	0.000000000000	0.000000000000
H	0.000000000000	2.710612256493	-1.193741394528
H	0.000000000000	2.710612256493	1.193741394528
H	0.000000000000	-2.710612256493	-1.193741394528
H	0.000000000000	-2.710612256493	1.193741394528

E+ZPVE = -1161.541984 au, Free E (298.15 K) = -1161.570454 au.
Job name: ti554MIN23G5SAD

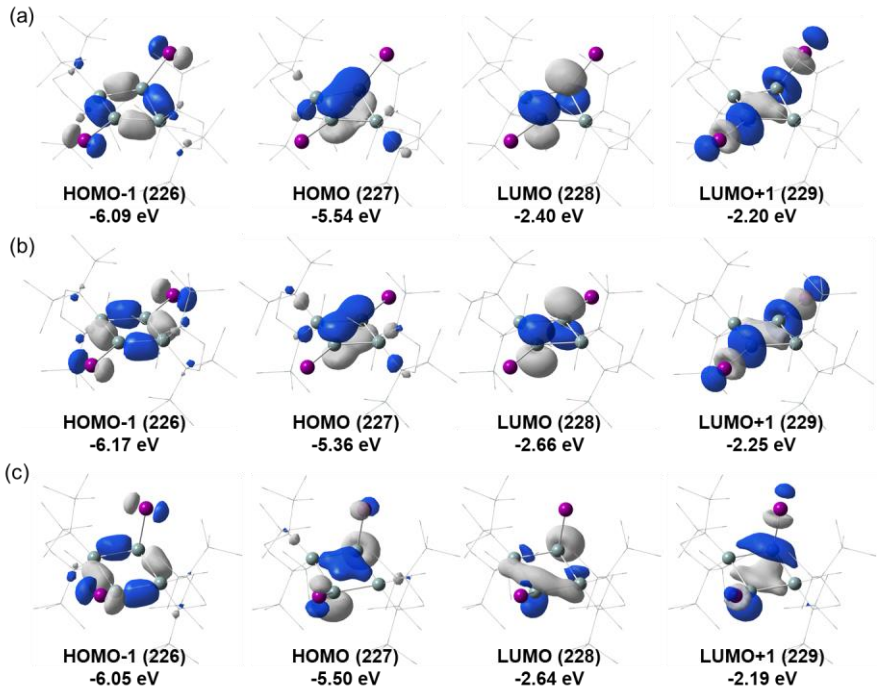


Figure 3-13. Frontier Kohn-Sham orbitals of (a) **2′$_c$**, (b) **2′$_p$** and (c) **2′$_I$** at the TD-B3LYP-D3/6-311G(d) [H,C,Si], SDD [I]//B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory. [td_b_TN81b_bent, td_a_TN81b_planar, td_a_TN85a]

Table 3-19. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of Iodosilanes

Compound	^{29}Si chemical shift			Note
	observed	calculated[a,c]	calculated[b,c]	
H_3SiI	−83.3[d]	−43.2 (404.6)	−35.2 (396.6)	TN86a_H
Me_3SiI	8.9[d]	39.0 (322.4)	46.3 (315.1)	TN86a_Me
$(Me_3Si)_3SiI$	−54.1[e]	−35.9 (397.3)	−19.7 (381.1)	TN86a_TMS_GRRM
$Tip_2Si{=}SiTipI$[f]	51.7[g]	80.3 (281.1)	94.1 (267.3)	TN83a
2 (bridge)	4.0	-	-	
2 (bridgehead)	103.8	-	-	
2′$_c$ (bridge)	-	−2.8 (364.2)	−2.9 (364.3)	TN81b_bent
2′$_c$ (bridgehead)	-	129.3 (232.1)	139.1 (222.3)	TN81b_bent
2′$_p$ (bridge)	-	5.7 (355.7)	5.2 (356.2)	TN81b_planar
2′$_p$ (bridgehead)	-	182.6 (178.7)	191.0 (170.4)	TN81b_planar
2′$_I$ (bridge)	-	119.9 (241.5)	119.8 (241.6)	TN85a
		118.6 (242.8)	118.3 (243.1)	
2′$_I$ (bridgehead)	-	12.1 (349.3)	23.6 (337.8)	TN85a
		−6.3 (367.7)	6.4 (355.0)	

[a]GIAO/M06L/6-311G(d) [I], 6-311+G(2df,p) [others] level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [b]GIAO/M06L/SDD [I], 6-311+G(2df,p) [others] level of theory. [c]The absolute chemical shift is shown in the parentheses. [d]Reference 31. [e]Reference 32. [f]Tip = 2,4,6-triisopropylphenyl. [g]Reference 33.

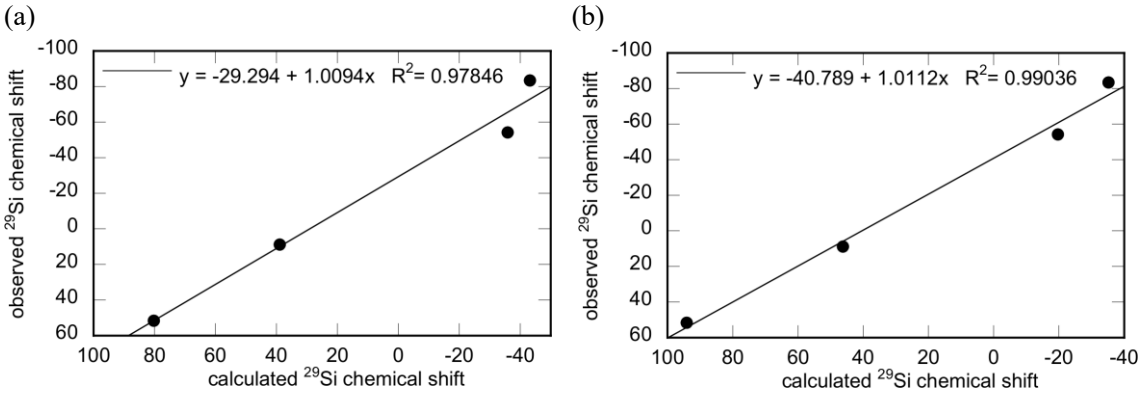
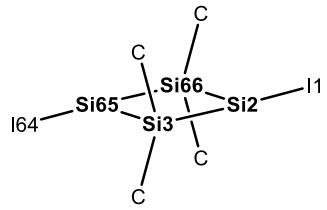


Figure 3-14. A plot of observed ^{29}Si chemical shift (δ_{obs}) vs calculated ^{29}Si chemical shift (δ_{calc}) at (a) the M06L/6-311G(d) [I], 6-311+G(2df,p) [others] level of theory ($\delta_{obs} = 1.009\delta_{clac} - 29.3$, $R^2 = 0.978$) and (b) the M06L/SDD [I], 6-311+G(2df,p) [others] level of theory ($\delta_{obs} = 1.011\delta_{clac} - 40.8$, $R^2 = 0.990$).

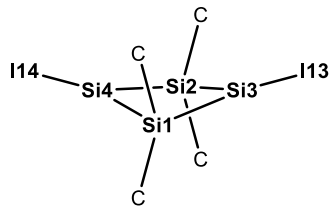
Table 3-20. Natural Bond Orbital (NBO) Analysis for **2′$_p$**



NBO	NBO[a] analysis				
	occ.,[a]	population	hybrids	NHO[a] bond bending	WBI[a]
Si2-Si65	1.633	50.00% (Si2)	s 0.72%, p 98.96%, d 0.32% ($sp^{99.99}d^{0.45}$) (Si2)	82.1 (Si2)	0.6990
		50.00% (Si65)	s 0.72%, p 98.96%, d 0.32% ($sp^{99.99}d^{0.45}$) (Si65)	82.1 (Si65)	
Si2-Si3	1.883	55.48% (Si2)	s 41.20%, p 58.52%, d 0.28% ($sp^{1.42}d^{0.01}$) (Si2)	13.9 (Si2)	0.9777
		44.52% (Si3)	s 21.14%, p 78.22%, d 0.64% ($sp^{3.70}d^{0.03}$) (Si3)	13.6 (Si3)	
Si2-Si66	1.884	56.18% (Si2)	s 42.23%, p 57.51%, d 0.26% ($sp^{1.36}d^{0.01}$) (Si2)	14.4 (Si2)	0.9707
		43.82% (Si66)	s 20.11%, p 79.25%, d 0.63% ($sp^{3.94}d^{0.03}$) (Si66)	14.2 (Si66)	
Si2-I1	1.966	34.27% (Si1)	s 15.69%, p 83.56%, d 0.74% ($sp^{5.32}d^{0.05}$) (Si2)	2.7 (Si2)	0.9181
		65.73% (I1)	s 17.38%, p 82.62% ($sp^{4.72}$) (I1)		

[a]NBO: natural bond orbital. NHO: natural hybrid orbital. NPA: natural atomic orbital. occ.: occupancy. WBI: Wiberg bond index. JOB number: TN87a_planarNBO

Table 3-21. Natural Bond Orbital (NBO) Analysis for **2′$_c$**



NBO	NBO[a] analysis				
	occ.,[a]	population	hybrids	NHO[a] bond bending	WBI[a]
Si3-Si4	1.689	50.00% (Si3)	s 4.38%, p 95.25%, d 0.37% ($sp^{21.73}d^{0.08}$) (Si3)	62.0 (Si3)	0.7693
		50.00% (Si4)	s 4.38%, p 95.25%, d 0.37% ($sp^{21.73}d^{0.08}$) (Si4)	62.0 (Si4)	

Si3-Si1	1.874	56.39% (Si3)	s 39.92%, p 59.80%, d 0.29% ($sp^{1.50}d^{0.01}$) (Si3)	16.9 (Si3)	0.9467
		43.61% (Si1)	s 20.17%, p 79.22%, d 0.61% ($sp^{3.93}d^{0.03}$) (Si1)	15.3 (Si1)	
Si3-Si2	1.885	56.06% (Si3)	s 39.70%, p 60.02%, d 0.28% ($sp^{1.51}d^{0.01}$) (Si3)	18.8 (Si3)	0.9595
		43.94% (Si2)	s 20.63%, p 78.79%, d 0.59% ($sp^{3.82}d^{0.03}$) (Si2)	16.6 (Si2)	
Si3-I13	1.969	34.83% (Si3)	s 15.86%, p 83.47%, d 0.68% ($sp^{5.26}d^{0.04}$) (Si3)	2.0 (Si3)	0.9044
		65.17% (I13)	s 16.95%, p 83.05% ($sp^{4.90}$) (I13)	1.2 (I13)	

[a]NBO: natural bond orbital. NHO: natural hybrid orbital. NPA: natural atomic orbital. occ.: occupancy. WBI: Wiberg bond index. JOB number: TN87a_bentNBO

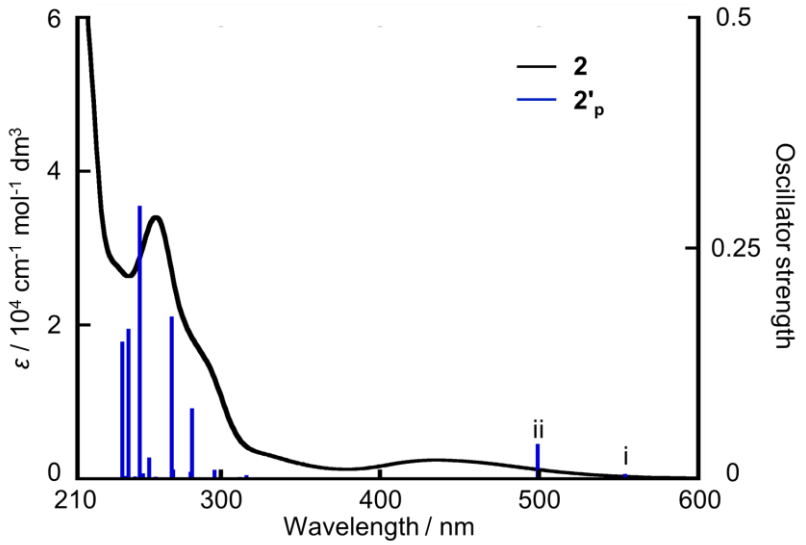


Figure 3-15. Experimental UV-vis absorption spectrum of **2** in hexane (black) and calculated band positions of **2′$_p$** at the TD-B3LYP-D3/6-311G(d) [H,C,Si], SDD [I]//B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory (blue). i: π(Si-Si) → σ*(I-Si), ii: a mixture of π(Si-Si) → π*(Si-Si) and π(Si-Si) → σ*(I-Si) transitions. [td_a_TN81b_planar]

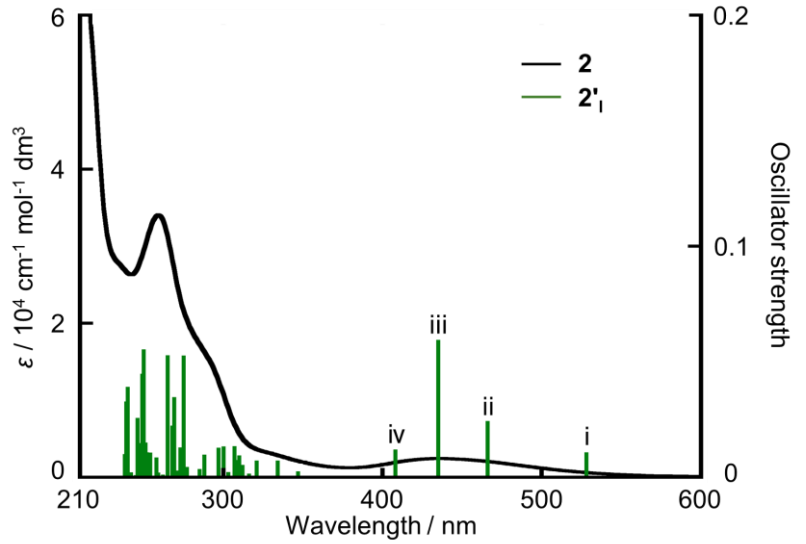


Figure 3-16. Experimental UV-vis absorption spectrum of **2** in hexane (black) and calculated band positions of **2′$_I$** at the TD-B3LYP-D3/6-311G(d) [H,C,Si], SDD [I]//B3LYP-D3/6-311G(d) [H,C,Si], SDD [I] level of theory (green). i: σ(Si-Si) → σ*(Si-Si), ii: σ(peripheral Si_4 ring) →

σ*(Si-Si), iii: a mixture of σ(Si-Si) → σ*(Si-Si) and σ(Si-Si) → σ*(I-Si), iv: σ(peripheral Si_4 ring) → σ*(I-Si) transitions. [td_a_TN85a]

Table 3-22. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **2′$_c$** (The 227th orbital is highest occupied orbital shown in Figure 3-13) [td_b_TN81b_bent]

Excited State 1: Singlet-A 2.4989 eV 496.15 nm f=0.0021 <S**2>=0.000
227 -> 229 0.70371

Excited State 2: Singlet-B 2.7813 eV 445.78 nm f=0.0324 <S**2>=0.000
225 -> 229 -0.11590
226 -> 228 -0.22127
227 -> 228 0.65426

Excited State 3: Singlet-B 2.8057 eV 441.90 nm f=0.0064 <S**2>=0.000
226 -> 228 0.66903
227 -> 228 0.21504

Excited State 4: Singlet-A 3.0712 eV 403.70 nm f=0.0001 <S**2>=0.000
226 -> 229 0.70427

Excited State 5: Singlet-B 3.5864 eV 345.71 nm f=0.0014 <S**2>=0.000
227 -> 230 0.70132

Excited State 6: Singlet-A 3.5907 eV 345.29 nm f=0.0129 <S**2>=0.000
225 -> 228 0.18836
227 -> 231 0.67441

Excited State 7: Singlet-A 3.9556 eV 313.44 nm f=0.0003 <S**2>=0.000
222 -> 228 -0.11422
224 -> 228 -0.10557
225 -> 228 0.65860
227 -> 231 -0.17828

Excited State 8: Singlet-A 4.0595 eV 305.42 nm f=0.0002 <S**2>=0.000
222 -> 228 0.37953
224 -> 228 0.56522
225 -> 228 0.13496

Excited State 9: Singlet-B 4.1888 eV 295.99 nm f=0.0015 <S**2>=0.000
219 -> 228 -0.10544
221 -> 228 0.40139
223 -> 228 0.53068
225 -> 229 0.17240

Excited State 10: Singlet-B 4.2145 eV 294.18 nm f=0.0164 <S**2>=0.000
219 -> 228 0.12845
221 -> 228 0.42234
222 -> 229 -0.14515
223 -> 228 -0.35395
224 -> 229 -0.21799
225 -> 229 0.28659
226 -> 230 0.12822

Excited State 11: Singlet-A 4.2276 eV 293.27 nm f=0.0011 <S**2>=0.000
220 -> 228 0.10947
222 -> 228 0.52162
224 -> 228 -0.39001
226 -> 231 0.23724

Excited State 12: Singlet-A 4.2353 eV 292.74 nm f=0.0001 <S**2>=0.000
220 -> 228 0.29099
222 -> 228 -0.25529
226 -> 231 0.57583

Excited State 13: Singlet-B 4.2357 eV 292.71 nm f=0.0146 <S**2>=0.000
219 -> 228 -0.12059
221 -> 228 0.26258
222 -> 229 0.30175
223 -> 228 -0.28274
224 -> 229 0.40823
226 -> 230 -0.23257

Excited State 14: Singlet-A 4.3097 eV 287.69 nm f=0.0002 <S**2>=0.000
220 -> 228 0.61492
226 -> 231 -0.30836

Excited State 15: Singlet-B 4.3400 eV 285.68 nm f=0.0951 <S**2>=0.000
219 -> 228 -0.28092
224 -> 229 0.17377
226 -> 230 0.57994
227 -> 232 0.17340

Excited State 16: Singlet-B 4.3535 eV 284.79 nm f=0.0043 <S**2>=0.000
219 -> 228 0.59193
222 -> 229 0.17330
224 -> 229 0.24108
226 -> 230 0.19093

Excited State 17: Singlet-A 4.3782 eV 283.19 nm f=0.0010 <S**2>=0.000
216 -> 229 0.10740
218 -> 228 -0.28424
221 -> 229 0.57863
223 -> 229 0.24297

Excited State 18: Singlet-B 4.4357 eV 279.52 nm f=0.0051 <S**2>=0.000
218 -> 229 -0.19894
221 -> 228 -0.14189
222 -> 229 0.54043
224 -> 229 -0.28976
225 -> 229 0.20926

Excited State 19: Singlet-A 4.4457 eV 278.88 nm f=0.0000 <S**2>=0.000
218 -> 228 0.12571
219 -> 229 -0.13470
221 -> 229 -0.20441
223 -> 229 0.64659

Excited State 20: Singlet-A 4.4940 eV 275.89 nm f=0.0008 <S**2>=0.000
218 -> 228 0.60815
221 -> 229 0.31397

Excited State 21: Singlet-B 4.5130 eV 274.73 nm f=0.0307 <S**2>=0.000
218 -> 229 -0.22600
220 -> 229 0.54368
224 -> 229 -0.18555
225 -> 229 -0.30052

Excited State 22: Singlet-B 4.5351 eV 273.39 nm f=0.0005 <S**2>=0.000
218 -> 229 0.61143
220 -> 229 0.16757
222 -> 229 0.20756
224 -> 229 -0.16157

Excited State 23: Singlet-A 4.5576 eV 272.04 nm f=0.0008 <S**2>=0.000
218 -> 228 0.10376
219 -> 229 0.66349
223 -> 229 0.13151

Excited State 24: Singlet-A 4.6544 eV 266.38 nm f=0.0000 <S**2>=0.000
217 -> 228 0.68395

Excited State 25: Singlet-B 4.6892 eV 264.40 nm f=0.1829 <S**2>=0.000
215 -> 229 -0.18709
216 -> 228 0.11051
217 -> 229 -0.11552
220 -> 229 0.38947
221 -> 228 -0.19121
224 -> 229 0.18845
225 -> 229 0.39397

Excited State 26: Singlet-A 4.7726 eV 259.79 nm f=0.0004 <S**2>=0.000
215 -> 228 0.67988

Excited State 27: Singlet-B 4.7864 eV 259.04 nm f=0.0053 <S**2>=0.000
212 -> 228 0.15993
216 -> 228 0.65747

Excited State 28: Singlet-A 4.8959 eV 253.24 nm f=0.0029 <S**2>=0.000
213 -> 228 0.13790
214 -> 228 -0.24234
216 -> 229 0.61720

Excited State 29: Singlet-B 4.9053 eV 252.76 nm f=0.0009 <S**2>=0.000
212 -> 228 0.64887
216 -> 228 -0.15351

Excited State 30: Singlet-A 4.9121 eV 252.41 nm f=0.0009 <S**2>=0.000
213 -> 228 -0.28539
214 -> 228 0.56694

216 -> 229 0.27277

Excited State 31: Singlet-B 4.9198 eV 252.01 nm f=0.0420 <S**2>=0.000
215 -> 229 -0.20011
217 -> 229 0.56529
227 -> 232 -0.32413

Excited State 32: Singlet-B 4.9451 eV 250.72 nm f=0.1287 <S**2>=0.000
215 -> 229 -0.19129
217 -> 229 0.29893
226 -> 230 -0.14087
227 -> 232 0.53831
227 -> 237 -0.10899

Excited State 33: Singlet-A 5.0063 eV 247.65 nm f=0.0000 <S**2>=0.000
213 -> 228 0.61995
214 -> 228 0.31654

Excited State 34: Singlet-B 5.0657 eV 244.75 nm f=0.0010 <S**2>=0.000
209 -> 228 0.34965
211 -> 228 0.57881
212 -> 228 -0.14569

Excited State 35: Singlet-B 5.0913 eV 243.52 nm f=0.1010 <S**2>=0.000
213 -> 229 0.19354
214 -> 229 -0.27101
215 -> 229 0.52678
217 -> 229 0.19255
225 -> 229 0.11342
226 -> 232 0.11913

Excited State 36: Singlet-B 5.1005 eV 243.08 nm f=0.0056 <S**2>=0.000
205 -> 228 -0.12129
206 -> 228 -0.12400
209 -> 228 0.58235
211 -> 228 -0.33573
215 -> 229 0.10387

Excited State 37: Singlet-A 5.1123 eV 242.52 nm f=0.0015 <S**2>=0.000
210 -> 228 0.67575
212 -> 229 -0.14476

Excited State 38: Singlet-A 5.1184 eV 242.23 nm f=0.0008 <S**2>=0.000
210 -> 228 0.14838
211 -> 229 0.11968
212 -> 229 0.64243
219 -> 229 -0.11470

Excited State 39: Singlet-B 5.1837 eV 239.18 nm f=0.0390 <S**2>=0.000
204 -> 228 0.17257
205 -> 228 0.35458
206 -> 228 0.38446
209 -> 228 0.11133
211 -> 228 -0.17731
214 -> 229 -0.32450
215 -> 229 -0.15283

Excited State 40: Singlet-A 5.1903 eV 238.87 nm f=0.0001 <S**2>=0.000
208 -> 228 0.68489

Excited State 41: Singlet-B 5.1937 eV 238.72 nm f=0.0292 <S**2>=0.000
205 -> 228 0.26196
206 -> 228 0.12403
207 -> 228 0.43898
214 -> 229 0.38334
215 -> 229 0.10662
225 -> 231 0.14720
226 -> 232 0.11921

Excited State 42: Singlet-B 5.2141 eV 237.79 nm f=0.0136 <S**2>=0.000
204 -> 228 -0.11542
206 -> 228 -0.24578
207 -> 228 0.50180
214 -> 229 -0.37561

Excited State 43: Singlet-B 5.2486 eV 236.23 nm f=0.0221 <S**2>=0.000
207 -> 228 0.13309
213 -> 229 0.58166
214 -> 229 0.12294
225 -> 231 -0.26984
226 -> 232 -0.12330

Excited State 44: Singlet-B 5.2621 eV 235.62 nm f=0.0494 <S**2>=0.000
206 -> 228 -0.11178
213 -> 229 0.25963
225 -> 231 0.59179
226 -> 232 -0.15267

Excited State 45: Singlet-B 5.2782 eV 234.90 nm f=0.0010 <S**2>=0.000
204 -> 228 -0.19314
205 -> 228 -0.44017
206 -> 228 0.48341
207 -> 228 0.14072

Excited State 46: Singlet-A 5.2938 eV 234.21 nm f=0.0003 <S**2>=0.000
209 -> 229 -0.14873
211 -> 229 -0.35482
212 -> 229 0.13191
224 -> 230 -0.10317
225 -> 230 0.53410

Excited State 47: Singlet-B 5.3053 eV 233.70 nm f=0.0001 <S**2>=0.000
204 -> 228 0.60536
205 -> 228 -0.24966
210 -> 229 -0.10542
226 -> 232 -0.17418

Excited State 48: Singlet-A 5.3053 eV 233.70 nm f=0.0000 <S**2>=0.000
209 -> 229 0.32103
211 -> 229 0.45137
212 -> 229 -0.11359
225 -> 230 0.40055

Excited State 49: Singlet-A 5.3276 eV 232.72 nm f=0.0002 <S**2>=0.000
203 -> 228 0.17271
209 -> 229 0.57448
211 -> 229 -0.33426

Excited State 50: Singlet-B 5.3425 eV 232.07 nm f=0.0035 <S**2>=0.000
204 -> 228 0.10035
210 -> 229 0.67721

Excited State 51: Singlet-A 5.3477 eV 231.85 nm f=0.0008 <S**2>=0.000
202 -> 228 -0.19208
203 -> 228 0.63951
209 -> 229 -0.14927
211 -> 229 0.10859

Excited State 52: Singlet-B 5.3816 eV 230.38 nm f=0.0340 <S**2>=0.000
222 -> 231 0.11222
224 -> 231 0.23462
227 -> 234 -0.24394
227 -> 235 0.44316
227 -> 237 0.36369

Excited State 53: Singlet-A 5.4130 eV 229.05 nm f=0.0004 <S**2>=0.000
205 -> 229 0.20227
206 -> 229 0.12494
207 -> 229 0.25566
223 -> 231 0.31968
224 -> 230 0.39441
227 -> 233 -0.18938
227 -> 236 -0.22230

Excited State 54: Singlet-B 5.4154 eV 228.95 nm f=0.0893 <S**2>=0.000
204 -> 228 0.11220
213 -> 229 0.10665
221 -> 230 -0.22761
222 -> 231 -0.28480
224 -> 231 0.28361
226 -> 232 0.39066
227 -> 234 0.12038

Excited State 55: Singlet-A 5.4212 eV 228.70 nm f=0.0034 <S**2>=0.000
202 -> 228 0.38708
203 -> 228 0.15538
205 -> 229 0.26327
206 -> 229 0.15591
207 -> 229 0.26258
227 -> 233 0.29728
227 -> 236 0.21658

Excited State 56: Singlet-B 5.4285 eV 228.39 nm f=0.0022 <S**2>=0.000
208 -> 229 0.67415
223 -> 230 -0.13781

Excited State 57: Singlet-A 5.4289 eV 228.38 nm f=0.0016 <S**2>=0.000
202 -> 228 0.15363
205 -> 229 -0.18590
206 -> 229 -0.10025
207 -> 229 -0.26089
223 -> 231 0.56260
227 -> 233 0.13389

Excited State 58: Singlet-A 5.4324 eV 228.23 nm f=0.0019 <S**2>=0.000
202 -> 228 0.50748
203 -> 228 0.14112
205 -> 229 -0.17260
206 -> 229 -0.19452
223 -> 231 -0.13457
227 -> 233 -0.26848
227 -> 236 -0.20004

Excited State 59: Singlet-A 5.4471 eV 227.61 nm f=0.0003 <S**2>=0.000
202 -> 228 -0.11991
204 -> 229 -0.10649
205 -> 229 -0.19837
206 -> 229 -0.37547
207 -> 229 0.49726
224 -> 230 -0.12789

Excited State 60: Singlet-B 5.4487 eV 227.55 nm f=0.0189 <S**2>=0.000
222 -> 231 -0.16085
223 -> 230 0.35276
224 -> 231 0.46467
226 -> 232 -0.24795
227 -> 235 -0.15879

Excited State 61: Singlet-A 5.4549 eV 227.29 nm f=0.0255 <S**2>=0.000
205 -> 229 -0.16109
206 -> 229 -0.12934
221 -> 231 0.13759
222 -> 230 0.10616
223 -> 231 -0.17194
224 -> 230 0.48749
225 -> 230 0.13768
227 -> 233 0.30786
227 -> 236 0.13609

Excited State 62: Singlet-B 5.4581 eV 227.15 nm f=0.0196 <S**2>=0.000
220 -> 231 0.11318
221 -> 230 -0.17133
223 -> 230 0.55938
224 -> 231 -0.24697
226 -> 232 0.18767

Excited State 63: Singlet-A 5.4809 eV 226.21 nm f=0.0164 <S**2>=0.000
220 -> 230 0.12128
222 -> 230 0.65221
224 -> 230 -0.16213

Excited State 64: Singlet-B 5.4964 eV 225.57 nm f=0.0001 <S**2>=0.000
201 -> 228 0.66115
222 -> 231 -0.14595

Excited State 65: Singlet-A 5.5040 eV 225.26 nm f=0.0001 <S**2>=0.000
205 -> 229 -0.47384
206 -> 229 0.48312
207 -> 229 0.17069

Excited State 66: Singlet-B 5.5085 eV 225.08 nm f=0.0698 <S**2>=0.000
201 -> 228 0.18802
219 -> 230 -0.20414
221 -> 230 0.13491
222 -> 231 0.50854
224 -> 231 0.19113
226 -> 232 0.13092
227 -> 234 0.17758

Excited State 67: Singlet-A 5.5211 eV 224.56 nm f=0.0030 <S**2>=0.000
220 -> 230 0.25518
227 -> 233 -0.34970
227 -> 236 0.48021
227 -> 238 0.11257
227 -> 239 0.15310

Excited State 68: Singlet-B 5.5385 eV 223.86 nm f=0.0247 <S**2>=0.000
218 -> 231 -0.15922
219 -> 230 0.10454
221 -> 230 0.57624
222 -> 231 -0.19598
226 -> 232 0.14887
227 -> 234 0.13201

Excited State 69: Singlet-A 5.5458 eV 223.57 nm f=0.0008 <S**2>=0.000
204 -> 229 0.67934

Excited State 70: Singlet-A 5.5492 eV 223.43 nm f=0.0029 <S**2>=0.000
200 -> 228 0.10619
220 -> 230 0.57385
221 -> 231 -0.17259
222 -> 230 -0.12942
227 -> 233 0.20225
227 -> 236 -0.18756

Excited State 71: Singlet-A 5.5661 eV 222.75 nm f=0.0447 <S**2>=0.000
218 -> 230 -0.23019
220 -> 230 0.14755
221 -> 231 0.61398
224 -> 230 -0.11628
227 -> 236 -0.12279

Excited State 72: Singlet-B 5.5669 eV 222.72 nm f=0.0076 <S**2>=0.000
202 -> 229 -0.11346
203 -> 229 0.22884
226 -> 232 -0.18684
227 -> 234 0.53843
227 -> 235 0.28881

Table 3-23. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **2′p** (The 227th orbital is highest occupied orbital shown in Figure 3-13) [td_a_TN81b_planar]

Excited State 1: Singlet-AU 2.2364 eV 554.39 nm f=0.0054 <S**2>=0.000
227 -> 228 -0.39735
227 -> 229 0.58096

Excited State 2: Singlet-AU 2.4845 eV 499.02 nm f=0.0378 <S**2>=0.000
227 -> 228 0.57396
227 -> 229 0.39673

Excited State 3: Singlet-AG 2.6239 eV 472.52 nm f=0.0000 <S**2>=0.000
226 -> 228 0.70477

Excited State 4: Singlet-AG 3.1095 eV 398.72 nm f=0.0000 <S**2>=0.000
226 -> 229 0.70449

Excited State 5: Singlet-AG 3.3945 eV 365.25 nm f=0.0000 <S**2>=0.000
227 -> 230 0.70446

Excited State 6: Singlet-AU 3.5280 eV 351.43 nm f=0.0114 <S**2>=0.000
225 -> 228 0.24676
227 -> 231 0.64635

Excited State 7: Singlet-AU 3.7611 eV 329.65 nm f=0.0002 <S**2>=0.000
221 -> 228 0.19326
222 -> 228 0.23735
223 -> 228 0.57315
225 -> 228 -0.26948

Excited State 8: Singlet-AU 3.8492 eV 322.10 nm f=0.0011 <S**2>=0.000
221 -> 228 0.10491
223 -> 228 0.25899
225 -> 228 0.57842
227 -> 231 -0.26791

Excited State 9: Singlet-AG 3.9080 eV 317.26 nm f=0.0000 <S**2>=0.000
224 -> 228 0.70129

Excited State 10: Singlet-AU 3.9194 eV 316.33 nm f=0.0039 <S**2>=0.000
221 -> 228 0.14793
222 -> 228 0.61511
223 -> 228 -0.23853
225 -> 228 0.13270
225 -> 229 -0.13134

Excited State 11: Singlet-AU 3.9684 eV 312.43 nm f=0.0020 <S**2>=0.000
221 -> 228 0.64422
222 -> 228 -0.22306
223 -> 228 -0.14812

Excited State 12: Singlet-AG 4.0267 eV 307.90 nm f=0.0000 <S**2>=0.000
218 -> 228 0.19663
219 -> 228 0.58839
220 -> 228 -0.32020

Excited State 13: Singlet-AG 4.0617 eV 305.25 nm f=0.0000 <S**2>=0.000

219 -> 228 0.31438
220 -> 228 0.62178

Excited State 14: Singlet-AU 4.1869 eV 296.12 nm f=0.0098 <S**2>=0.000
221 -> 229 0.14680
222 -> 229 0.18189
223 -> 229 0.61034
225 -> 229 -0.21669
226 -> 230 -0.11624

Excited State 15: Singlet-AG 4.2184 eV 293.91 nm f=0.0000 <S**2>=0.000
218 -> 228 0.64939
219 -> 228 -0.20829
224 -> 229 -0.11749

Excited State 16: Singlet-AU 4.2927 eV 288.82 nm f=0.0016 <S**2>=0.000
216 -> 228 -0.13617
217 -> 228 0.26833
221 -> 229 0.38159
222 -> 229 0.44513
223 -> 229 -0.20332

Excited State 17: Singlet-AU 4.2946 eV 288.70 nm f=0.0007 <S**2>=0.000
216 -> 228 -0.14547
217 -> 228 0.60811
221 -> 229 -0.16538
222 -> 229 -0.21534
223 -> 229 0.10088

Excited State 18: Singlet-AG 4.3068 eV 287.88 nm f=0.0000 <S**2>=0.000
218 -> 228 0.12800
218 -> 229 0.16555
219 -> 229 -0.19356
224 -> 229 0.63828

Excited State 19: Singlet-AU 4.3895 eV 282.46 nm f=0.0763 <S**2>=0.000
222 -> 229 0.18396
223 -> 229 0.10712
226 -> 230 0.61958
227 -> 232 -0.23451

Excited State 20: Singlet-AU 4.4123 eV 280.99 nm f=0.0076 <S**2>=0.000
221 -> 229 0.50902
222 -> 229 -0.40141
225 -> 229 -0.22346
226 -> 230 0.14350

Excited State 21: Singlet-AG 4.4379 eV 279.38 nm f=0.0000 <S**2>=0.000
218 -> 229 0.14655
219 -> 229 0.48022
220 -> 229 -0.18411
224 -> 229 0.14420
226 -> 231 -0.41795

Excited State 22: Singlet-AU 4.4525 eV 278.46 nm f=0.0016 <S**2>=0.000
215 -> 228 0.24865
216 -> 228 0.61184
217 -> 228 0.17407

Excited State 23: Singlet-AG 4.4829 eV 276.57 nm f=0.0000 <S**2>=0.000
218 -> 229 -0.20931
219 -> 229 0.36995
220 -> 229 -0.20973
224 -> 229 0.15359
226 -> 231 0.48712

Excited State 24: Singlet-AG 4.5083 eV 275.01 nm f=0.0000 <S**2>=0.000
218 -> 229 0.57506
220 -> 229 -0.27780
224 -> 229 -0.17779
226 -> 231 0.21028

Excited State 25: Singlet-AG 4.5325 eV 273.54 nm f=0.0000 <S**2>=0.000
218 -> 229 0.23926
219 -> 229 0.27547
220 -> 229 0.58004
226 -> 231 0.13319

Excited State 26: Singlet-AU 4.5994 eV 269.56 nm f=0.0100 <S**2>=0.000
215 -> 228 0.63893
216 -> 228 -0.22074

Excited State 27: Singlet-AU 4.6094 eV 268.98 nm f=0.1759 <S**2>=0.000
215 -> 229 0.15035
216 -> 228 0.13014
216 -> 229 0.22308
221 -> 229 0.15581
222 -> 229 -0.13081
223 -> 229 0.19256
225 -> 229 0.52790

Excited State 28: Singlet-AG 4.6097 eV 268.96 nm f=0.0000 <S**2>=0.000
210 -> 228 0.12771
212 -> 228 0.18620
214 -> 228 0.64410
226 -> 231 -0.10323

Excited State 29: Singlet-AU 4.7146 eV 262.98 nm f=0.0004 <S**2>=0.000
206 -> 228 0.11616
213 -> 228 0.68377

Excited State 30: Singlet-AG 4.7559 eV 260.69 nm f=0.0000 <S**2>=0.000
207 -> 228 0.11137
209 -> 228 -0.13347
210 -> 228 0.45626
212 -> 228 0.43112
214 -> 228 -0.24120

Excited State 31: Singlet-AU 4.7886 eV 258.91 nm f=0.0022 <S**2>=0.000
217 -> 229 0.69205

Excited State 32: Singlet-AU 4.8281 eV 256.80 nm f=0.0004 <S**2>=0.000
206 -> 228 0.17609
211 -> 228 0.67968

Excited State 33: Singlet-AG 4.8290 eV 256.75 nm f=0.0000 <S**2>=0.000
209 -> 228 0.57650
210 -> 228 -0.16168
212 -> 228 0.35232

Excited State 34: Singlet-AU 4.8689 eV 254.65 nm f=0.0232 <S**2>=0.000
215 -> 229 -0.37209
216 -> 229 0.55527

Excited State 35: Singlet-AG 4.8756 eV 254.30 nm f=0.0000 <S**2>=0.000
207 -> 228 0.11844
209 -> 228 0.36455
210 -> 228 0.45222
212 -> 228 -0.36846

Excited State 36: Singlet-AU 4.9322 eV 251.38 nm f=0.0059 <S**2>=0.000
206 -> 228 0.23044
208 -> 228 0.65415
213 -> 228 -0.11370

Excited State 37: Singlet-AG 4.9333 eV 251.32 nm f=0.0000 <S**2>=0.000
205 -> 228 -0.20390
207 -> 228 0.64962
210 -> 228 -0.15093

Excited State 38: Singlet-AG 4.9363 eV 251.17 nm f=0.0000 <S**2>=0.000
227 -> 233 0.68874
227 -> 236 0.12077

Excited State 39: Singlet-AU 4.9625 eV 249.84 nm f=0.0031 <S**2>=0.000
206 -> 228 0.61936
208 -> 228 -0.24343
211 -> 228 -0.17504

Excited State 40: Singlet-AU 4.9650 eV 249.72 nm f=0.2959 <S**2>=0.000
217 -> 231 -0.12287
226 -> 230 0.22709
227 -> 232 0.61794

Excited State 41: Singlet-AG 4.9758 eV 249.17 nm f=0.0000 <S**2>=0.000
204 -> 228 0.26000
205 -> 228 0.61314
207 -> 228 0.18264

Excited State 42: Singlet-AG 5.0384 eV 246.08 nm f=0.0000 <S**2>=0.000
204 -> 228 0.64550
205 -> 228 -0.24513

Excited State 43: Singlet-AU 5.0408 eV 245.96 nm f=0.0024 <S**2>=0.000
203 -> 228 0.69427

Excited State 44: Singlet-AG 5.0582 eV 245.12 nm f=0.0000 <S**2>=0.000
210 -> 229 0.15717
212 -> 229 0.20832
214 -> 229 0.62858

Excited State 45: Singlet-AU 5.1219 eV 242.07 nm f=0.1624 <S**2>=0.000
202 -> 228 0.27920
213 -> 229 -0.19054

215 -> 229 0.49957
216 -> 229 0.26890
225 -> 229 -0.11453
226 -> 233 0.11057

Excited State 46: Singlet-AU 5.1750 eV 239.58 nm f=0.0031 <S**2>=0.000
202 -> 228 0.47325
213 -> 229 0.50423

Excited State 47: Singlet-AG 5.1917 eV 238.81 nm f=0.0000 <S**2>=0.000
201 -> 228 0.67578
210 -> 229 0.10164

Excited State 48: Singlet-AU 5.2189 eV 237.57 nm f=0.1486 <S**2>=0.000
202 -> 228 0.41692
211 -> 229 0.16149
213 -> 229 -0.40573
215 -> 229 -0.18775
216 -> 229 -0.18753
225 -> 229 0.10330
226 -> 233 -0.11684

Table 3-24. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **2′$_1$** (The 227th orbital is highest occupied orbital shown in Figure 3-13) [td_a_TN85a]

Excited State 1: Singlet-A 2.3474 eV 528.18 nm f=0.0108 <S**2>=0.000
227 -> 228 0.58145
227 -> 229 -0.39803
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4765.34702507
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.6587 eV 466.33 nm f=0.0243 <S**2>=0.000
226 -> 228 0.69611

Excited State 3: Singlet-A 2.8477 eV 435.38 nm f=0.0595 <S**2>=0.000
227 -> 228 0.38512
227 -> 229 0.57388

Excited State 4: Singlet-A 3.0372 eV 408.21 nm f=0.0120 <S**2>=0.000
226 -> 229 0.69583

Excited State 5: Singlet-A 3.5703 eV 347.27 nm f=0.0026 <S**2>=0.000
225 -> 228 0.70346

Excited State 6: Singlet-A 3.7151 eV 333.73 nm f=0.0072 <S**2>=0.000
227 -> 230 0.69686

Excited State 7: Singlet-A 3.8635 eV 320.91 nm f=0.0073 <S**2>=0.000
224 -> 228 0.40348
227 -> 231 0.56338

Excited State 8: Singlet-A 3.9288 eV 315.58 nm f=0.0016 <S**2>=0.000
222 -> 228 -0.14040
223 -> 228 -0.11314
224 -> 228 0.53966
227 -> 231 -0.38933

Excited State 9: Singlet-A 3.9777 eV 311.70 nm f=0.0054 <S**2>=0.000
219 -> 228 -0.12429
221 -> 228 0.31773
222 -> 228 0.21357
223 -> 228 0.54711

Excited State 10: Singlet-A 3.9945 eV 310.39 nm f=0.0095 <S**2>=0.000
219 -> 228 0.17061
220 -> 228 -0.14987
221 -> 228 0.18871
222 -> 228 0.55514
223 -> 228 -0.29132

Excited State 11: Singlet-A 4.0139 eV 308.89 nm f=0.0075 <S**2>=0.000
225 -> 229 0.69591

Excited State 12: Singlet-A 4.0399 eV 306.90 nm f=0.0135 <S**2>=0.000
220 -> 228 0.10877
221 -> 228 0.57306
222 -> 228 -0.27389
223 -> 228 -0.23692
224 -> 228 -0.10570

Excited State 13: Singlet-A 4.0869 eV 303.37 nm f=0.0022 <S**2>=0.000
218 -> 228 0.12355
219 -> 228 -0.38470
220 -> 228 0.49442
222 -> 228 0.20208
223 -> 228 -0.18131

Excited State 14: Singlet-A 4.1300 eV 300.21 nm f=0.0134 <S**2>=0.000
218 -> 228 0.26589
219 -> 228 0.51357
220 -> 228 0.36871

Excited State 15: Singlet-A 4.1719 eV 297.19 nm f=0.0128 <S**2>=0.000
218 -> 228 0.60343
219 -> 228 -0.12500
220 -> 228 -0.21981
221 -> 229 -0.11285
224 -> 229 -0.18141

Excited State 16: Singlet-A 4.3036 eV 288.09 nm f=0.0098 <S**2>=0.000
216 -> 228 -0.17359
217 -> 228 -0.20814
226 -> 230 0.62682

Excited State 17: Singlet-A 4.3138 eV 287.41 nm f=0.0008 <S**2>=0.000
217 -> 228 0.14729
218 -> 228 0.14375
224 -> 229 0.63623

Excited State 18: Singlet-A 4.3428 eV 285.49 nm f=0.0036 <S**2>=0.000
216 -> 228 0.39538
217 -> 228 0.48763
226 -> 230 0.27350

Excited State 19: Singlet-A 4.4046 eV 281.49 nm f=0.0031 <S**2>=0.000
219 -> 229 -0.18365
221 -> 229 0.35096
222 -> 229 0.18471
223 -> 229 0.51491

Excited State 20: Singlet-A 4.4245 eV 280.22 nm f=0.0032 <S**2>=0.000
219 -> 229 0.13286
220 -> 229 -0.26661
221 -> 229 0.19589
222 -> 229 0.52471
223 -> 229 -0.25572

Excited State 21: Singlet-A 4.4689 eV 277.44 nm f=0.0044 <S**2>=0.000
216 -> 228 0.52140
217 -> 228 -0.40457
221 -> 229 -0.12833
224 -> 229 0.11914

Excited State 22: Singlet-A 4.4927 eV 275.97 nm f=0.0031 <S**2>=0.000
219 -> 229 -0.23013
220 -> 229 0.11336
221 -> 229 0.45750
222 -> 229 -0.24294
223 -> 229 -0.36099

Excited State 23: Singlet-A 4.5157 eV 274.56 nm f=0.0527 <S**2>=0.000
215 -> 228 0.14087
219 -> 229 -0.14629
220 -> 229 0.13300
221 -> 229 -0.16551
222 -> 229 0.18780
223 -> 229 -0.10987
226 -> 231 0.56667

Excited State 24: Singlet-A 4.5351 eV 273.39 nm f=0.0129 <S**2>=0.000
215 -> 228 -0.19618
219 -> 229 -0.21401
220 -> 229 0.47643
221 -> 229 -0.13171
222 -> 229 0.28356
223 -> 229 -0.10603
226 -> 231 -0.23395

Excited State 25: Singlet-A 4.5765 eV 270.92 nm f=0.0029 <S**2>=0.000
215 -> 228 0.62973
220 -> 229 0.18407
226 -> 231 -0.18035

Excited State 26: Singlet-A 4.6047 eV 269.26 nm f=0.0347 <S**2>=0.000
214 -> 228 -0.30133
219 -> 229 0.49134
220 -> 229 0.26916
221 -> 229 0.10586
226 -> 231 0.16818
227 -> 232 -0.10478

Excited State 27: Singlet-A 4.6326 eV 267.64 nm f=0.0224 <S**2>=0.000
214 -> 228 0.52895
218 -> 229 0.35243
219 -> 229 0.19980
220 -> 229 0.16092

Excited State 28: Singlet-A 4.6804 eV 264.90 nm f=0.0528 <S**2>=0.000
214 -> 228 -0.26096
218 -> 229 0.53280
219 -> 229 -0.10579
221 -> 229 -0.12509
227 -> 233 0.21263

Excited State 29: Singlet-A 4.7268 eV 262.30 nm f=0.0012 <S**2>=0.000
210 -> 228 -0.10403
213 -> 228 0.67255

Excited State 30: Singlet-A 4.7898 eV 258.85 nm f=0.0020 <S**2>=0.000
211 -> 228 -0.10851
212 -> 228 0.66493

Excited State 31: Singlet-A 4.8019 eV 258.20 nm f=0.0004 <S**2>=0.000
211 -> 228 0.66125
212 -> 228 0.13108

Excited State 32: Singlet-A 4.8114 eV 257.69 nm f=0.0086 <S**2>=0.000
216 -> 229 0.33268
217 -> 229 0.59110

Excited State 33: Singlet-A 4.8781 eV 254.17 nm f=0.0005 <S**2>=0.000
209 -> 228 -0.27450
210 -> 228 -0.27224
216 -> 229 0.47626
217 -> 229 -0.28281
227 -> 233 -0.11484

Excited State 34: Singlet-A 4.8847 eV 253.82 nm f=0.0011 <S**2>=0.000
209 -> 228 0.37042
210 -> 228 0.38280
216 -> 229 0.35869
217 -> 229 -0.19454

Excited State 35: Singlet-A 4.8915 eV 253.47 nm f=0.0107 <S**2>=0.000
207 -> 228 -0.17714
208 -> 228 0.17490
209 -> 228 0.46601
210 -> 228 -0.42499

Excited State 36: Singlet-A 4.9265 eV 251.67 nm f=0.0108 <S**2>=0.000
207 -> 228 0.12278
208 -> 228 -0.34435
210 -> 228 -0.26318
214 -> 229 0.13049
215 -> 229 -0.11207
227 -> 232 0.19504
227 -> 233 0.42616

Excited State 37: Singlet-A 4.9399 eV 250.99 nm f=0.0150 <S**2>=0.000
206 -> 228 -0.17705
208 -> 228 0.54614
214 -> 229 0.12904
215 -> 229 -0.13103
227 -> 233 0.30193

Excited State 38: Singlet-A 4.9686 eV 249.54 nm f=0.0554 <S**2>=0.000
204 -> 228 0.13220
205 -> 228 0.26577
206 -> 228 0.24546
207 -> 228 0.37344
209 -> 228 0.10059
215 -> 229 -0.17426
227 -> 232 -0.33670

Excited State 39: Singlet-A 4.9717 eV 249.38 nm f=0.0448 <S**2>=0.000
206 -> 228 0.14626
207 -> 228 0.35341
208 -> 228 0.13745
209 -> 228 0.16185
215 -> 229 0.21257
227 -> 232 0.39562
227 -> 233 -0.17693

Excited State 40: Singlet-A 4.9871 eV 248.61 nm f=0.0123 <S**2>=0.000
204 -> 228 0.12132
206 -> 228 0.58022
207 -> 228 -0.28904
227 -> 233 0.14057

Excited State 41: Singlet-A 5.0290 eV 246.54 nm f=0.0148 <S**2>=0.000
205 -> 228 0.36354
207 -> 228 -0.17710
214 -> 229 0.25236
215 -> 229 0.45969
227 -> 232 -0.10540

Excited State 42: Singlet-A 5.0331 eV 246.34 nm f=0.0257 <S**2>=0.000
204 -> 228 0.19232
205 -> 228 0.45445
207 -> 228 -0.24830
214 -> 229 -0.12690
215 -> 229 -0.28701
227 -> 232 0.17458
227 -> 233 -0.13422

Excited State 43: Singlet-A 5.0578 eV 245.14 nm f=0.0009 <S**2>=0.000
204 -> 228 0.62592
205 -> 228 -0.21443
206 -> 228 -0.14517
214 -> 229 0.14557

Excited State 44: Singlet-A 5.0838 eV 243.88 nm f=0.0004 <S**2>=0.000
227 -> 232 0.12307
227 -> 234 0.63973
227 -> 235 0.13976
227 -> 236 0.17969

Excited State 45: Singlet-A 5.1275 eV 241.80 nm f=0.0021 <S**2>=0.000
203 -> 228 0.67480

Excited State 46: Singlet-A 5.1634 eV 240.12 nm f=0.0391 <S**2>=0.000
201 -> 228 0.11393
203 -> 228 -0.13327
211 -> 229 -0.10656
212 -> 229 0.14850
213 -> 229 0.39739
214 -> 229 -0.37528
215 -> 229 0.24102
227 -> 233 0.12527

Excited State 47: Singlet-A 5.1840 eV 239.17 nm f=0.0328 <S**2>=0.000
201 -> 228 -0.14655
210 -> 229 -0.10022
213 -> 229 0.52232
214 -> 229 0.37146
227 -> 233 -0.11323

Excited State 48: Singlet-A 5.2160 eV 237.70 nm f=0.0101 <S**2>=0.000
202 -> 228 0.66930
225 -> 230 -0.10610

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(16) According to the IUPAC definition, a π-bond contains a nodal plane that includes the internuclear bond axis. See: IUPAC. σ, π (Sigma, Pi). In *Compendium of Chemical Terminology* (*the "Gold Book"*), 2nd ed. [Online]; McNaught, A. D., Wilkinson, A., Eds.; Blackwell, 1997. DOI: 10.1351/goldbook

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(18) The deformation of the bicyclic ring relative to the planar structure in the parent tetrasilabicyclo[1.1.0]butane has been qualitatively explained by a second-order Jahn−Teller distortion. For details, see ref 11k.

(19) We did not observe a significant change in the UV-vis spectrum at lower temperatures (Figure 3-12).

(20) A structure similar to **3**$_S$ was not located for **4** or **5** as a local minimum.[11]

(21) Although the origin of the difference between the relative stabilities of **2′**$_p$ and **2′**$_c$ remains unclear at this point, it may originate from a balance among the bonding interactions between the bridgehead Si atoms [d = 2.501 Å (**2′**$_c$), 2.609 Å (**2′**$_p$)], the strain originating from the Si(bridgehead)−Si(bridge)−Si(bridgehead) angle [α = 64.5°

(**2′**$_c$), 68.0° (**2′**$_p$)], and the arrangement of the bulky silacyclopentane rings at the bridge positions.

(22) In previously reported theoretical studies, the introduction of bulky substituents at the bridgehead position resulted in destabilization of structures similar to **3**$_L$ and **3**$_{TP}$ with acute bond angles ($\theta \approx 100°$) and the stabilization of structures similar to **3**$_S$;[11f,g,i] these predictions are consistent with the reported structures of such species with bulky bridgehead groups.[10]

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Chapter 4

Synthesis and Isomerization of a Planar 1,3-Dichlorotetrasilabicyclo[1.1.0]butane

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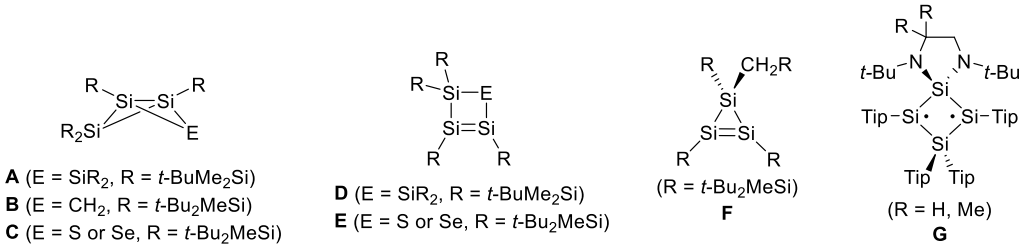
4-1. Introduction

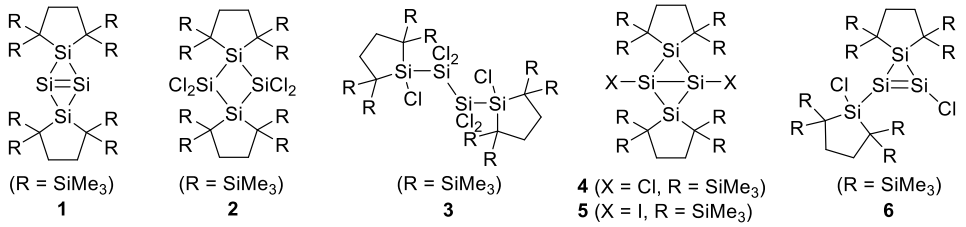
Bicyclo[1.1.0]butane is a highly strained compound and the interconversion between it and its C_4R_6 skeletal isomers such as cyclobutene and 1,3-butadiene, etc. has attracted experimental and theoretical chemists.[1,2] Its heavy element analogues, in which the carbon atoms in the bicyclo[1.1.0]butane framework are partially or fully replaced with heavy element atoms, have also been extensively studied, as they often exhibit structures and properties that are not found in all-carbon bicyclo[1.1.0]butanes.[3,4] Silabicyclo[1.1.0]butanes are among such heavy element analogues of bicyclo[1.1.0]butane. After the pioneering works on 2,4-disilabicyclo[1.1.0]butane by Fritz[5l] and tetrasilabicyclo[1.1.0]butane by Masamune,[5a] various silabicyclo[1.1.0]butane derivatives have been synthesized and some of these compounds exhibited the conversion to skeletal isomers.[5,6] For example, bicyclo[1.1.0]tetrasilane **A** thermally isomerises to the corresponding cyclotetrasilene **D**, which reverts to **A** upon irradiation (Chart 4-1).[5d,e,6b] 1,2,3-Trisilabicyclo[1.1.0]butane **B** undergoes thermal isomerization to 3-alkylcyclotrisilene **F**, while trisilabicyclo[1.1.0]butane **C** containing a chalcogen atom (S, Se) was photochemically transformed into the corresponding cyclobutene **E** (Chart 4-1).[5j,k] Very recently, Scheschkewitz reported cyclotetrasilane-1,3-diyl **G** converts into the corresponding cyclotetrasilene.[7] As aforementioned, silabicyclobutanes often exhibit interconversion modes which are not observed in all-carbon bicyclo[1.1.0]butanes. Theoretical studies on silabicyclo[1.1.0]butanes have revealed that the relative stabilities among the skeletal isomers and bond stretch isomers are substantially different from those of all-carbon C_4R_6 isomers and are remarkably dependent on the steric demand of the substituents on the bicyclobutane framework,[8] which should be responsible for the interconversion modes of silabicyclo[1.1.0]butane.

Chart 4-1. Structures of Compounds **A**−**G** (Tip = 2,4,6-triisopropylphenyl)



Previously, we reported the reaction of bicyclo[1.1.0]tetrasil-1(3)-ene **1** with carbon tetrachloride providing tetra- and hexa-chlorinated tetrasilanes **2** and **3**, suggesting the existence of 1,3-dichlorobicyclo[1.1.0]tetrasilane **4** and its isomer as intermediates in this reaction (Chart 4-2).[9] The formation of **4** was also supported by the formation of a methanol adduct of **4** in the reaction of **1** with carbon tetrachloride in the presence of methanol and the observation of ^{1}H NMR signals that are consistent with the structure of **4** at low temperature. Our recent results on the 1,2-iodination of **1** providing 1,3-diiodobicyclo[1.1.0]tetrasilane **5**[10] encouraged us to isolate **4** by carefully conducting the reaction of **1** with carbon tetrachloride at lower temperatures. In this chapter, the author reports the synthesis and isolation of 1,3-dichlorobicyclo[1.1.0]tetrasilane **4** by the 1,2-dichlorination of **1** and the interconversion between **4** and its isomer, 1-chloro-2-(chlorosilyl)cyclotrisilene **6** (Chart 4-2).

Chart 4-2. Structures of Compounds **1**−**6**



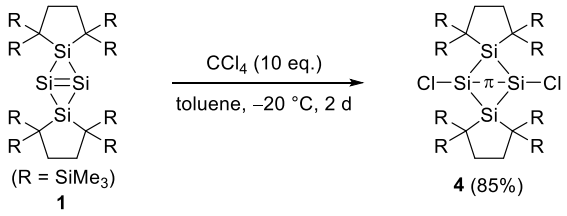
4-2. Results and Discussion

4-2-1. Synthesis of 1,3-Dichlorotetrasilabicyclo[1.1.0]butane 4

A mixture of **1** and carbon tetrachloride was stirred at −20 °C for two days (Scheme 4-1). After the volatiles were removed under reduced pressure at 0 °C, pure **4** was obtained as an orange solid in 85% yield. The molecular structure of **4** was determined using a combination of

multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray diffraction (XRD) analysis.[11]

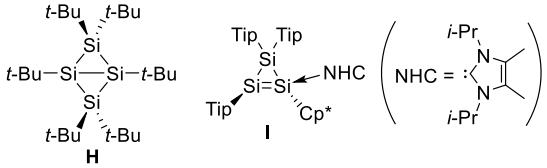
Scheme 4-1. Synthesis of **4**



4-2-2. Molecular Structure of 4

Recrystallization from toluene at −35 °C provided single crystals of **4** suitable for XRD analysis (Figure 4-1). While 1,3-diiodo derivative **5** provides two types of single crystals that exhibit different structures, *cis*-bent (**5**$_c$) and planar structures (**5**$_p$) in the solid state, **4** forms only single crystals, the structural characteristics of which are very similar to those of **5**$_p$. The molecule has a crystallographic inversion centre between the Si1 and Si1* atoms and the central Si_4 bicyclic skeleton is planar [dihedral angle Si2–Si1–Si1*–Si2*, 180°]. The geometry around the bridgehead silicon atoms is almost planar [the angle sum of the bridgehead Si1 atom excluding the central bridgehead bond is 359.97°] and the Si–Cl moieties are very slightly bent in a *trans* configuration [the Si1*–Si1–Cl1 angle is 178.27(11)°] with respect to the Si_4 ring plane. The Si1–Si1* distance in **4** [2.581(2) Å] is very similar to that in **5**$_p$ [2.5822(11) Å][10] but much longer than those of the previously reported bicyclo[1.1.0]tetrasilanes with bent structures (2.35–2.47 Å)[5] and much shorter than those of cyclotetrasilane-1,3-diyls **G** [2.871(1) Å] (Chart 4-1) and bicyclo[1.1.0]tetrasilane **H** [2.853(1) Å] (Chart 4-3) containing a planar Si_4 ring reported very recently by Scheschkewitz and Kyushin, respectively.[7,12]

Chart 4-3. Related Compounds **H** and **I** (Tip = 2,4,6-triisopropylphenyl and Cp* = C_5Me_5)



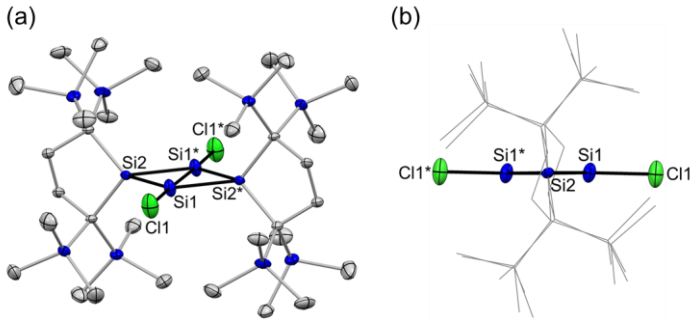


Figure 4-1. ORTEPs of **4** (a: perspective view; b: side view) with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si1* 2.581(2), Si1–Cl1 2.0690(18), Si1–Si2 2.3249(17), Si1–Si2* 2.3361(17), Si2–Si1–Si2* 112.74(6), Si1–Si2–Si1* 67.26(6), Si1*–Si1–Cl1 178.27(11), Si2–Si1–Si1*–Si2* 180.0.

4-2-3. NMR Spectra of 4

The NMR spectra of **4** indicate that **4** adopts a highly symmetrical structure in solution. The ^{1}H NMR spectrum of **4** in C_6D_6 solution at room temperature shows two singlet signals at 0.42 and 1.93 ppm due to the eight equivalent $SiMe_3$ groups and the eight methylene protons of the five-membered rings, respectively. Compound **4** exhibits three ^{29}Si resonances at −7.9 (bridge Si), 4.6 ($SiMe_3$), and 126.4 ppm (bridgehead Si).[13] The chemical shift of the bridgehead Si nuclei (126.4 ppm) is similar to that of **5** (103.8 ppm)[10] but far downfield shifted compared with those of the reported bent bicyclo[1.1.0]tetrasilanes (−145.1 to 14.8 ppm) (Figure 4-2).[5] Similar downfield-shifted ^{29}Si resonances were observed for the bridgehead silicon nuclei of **G** (198.24 ppm)[7] and **H** (117.4 ppm)[12] that have planar ring structures (Figure 4-2).

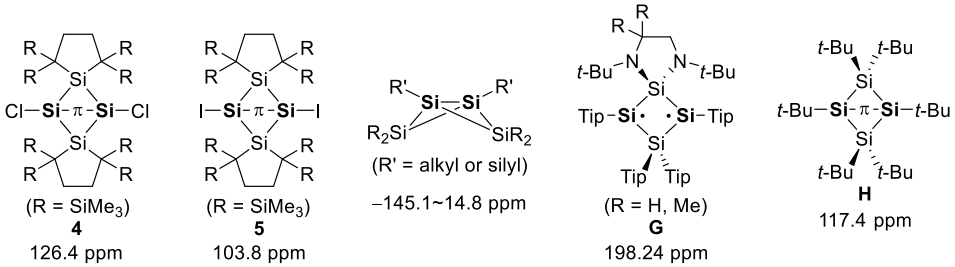


Figure 4-2. ^{29}Si NMR Chemical shifts of the bridgehead silicon atoms in **4** and the related compounds.

4-2-4. Theoretical Study

The structure of **4** was further examined by DFT calculations. The planar structure of **4** observed in the solid state is in good agreement with the optimized structure of **4** ($\mathbf{4_{opt}}$)

calculated at the B3LYP-D3/6-311G(d) level of theory (Table 4-1). The frontier orbitals of **4**$_{opt}$ (Figure 4-3a), which are π and π*-type orbitals on the bridgehead silicon atoms, are similar to those of **5** (**5**$_p$) indicating that compound **4** is another example of a molecule with a π-type single bonding.[7,10,12] It should be noted that two slightly-bent 1,3-dichlorobicyclotetrasilanes with highly pyramidalized bridgehead silicon atoms (**4′**$_{opt}$) and almost planar bridgehead silicon atoms (**4″**$_{opt}$) were located as local minima and higher in free energy (298.15 K) by 1.6 and 5.3 kJ mol^{-1} than **4**$_{opt}$ (Figure 4-3b, Table 4-1). Although the small relative energies suggest that these two structures could also exist in solution, the observed ^{29}Si resonances of bridge and bridgehead Si nuclei (−7.9 and 126.4) are close to those of **4**$_{opt}$ (−17.1 and 150.2) calculated at the GIAO/M06L/6-311+G(2df,p) level of theory but substantially far from those of **4′**$_{opt}$ (138.3, −43.5) and **4″**$_{opt}$ (−25.1, 86.5) implying that **4** predominantly adopts a planar structure similar to that of **4**$_{opt}$ in solution.

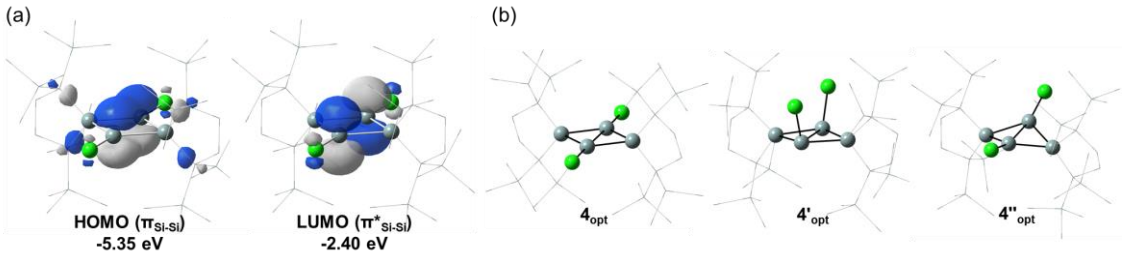
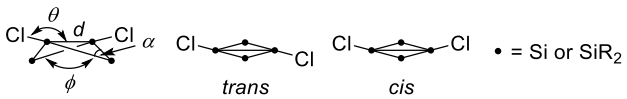


Figure 4-3. (a) Frontier orbitals of **4**$_{opt}$ calculated at the B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·a.u.$^{-3}$); hydrogen atoms are omitted for clarity. (b) Structures of **4**$_{opt}$, **4′**$_{opt}$, and **4″**$_{opt}$ optimized at the B3LYP-D3/6-311G(d) level of theory.

Table 4-1. Selected Structural Parameters of **4, 4**$_{opt}$, **4′**$_{opt}$ and **4″**$_{opt}$



compound	*d*/Å	*θ*/deg	*φ*/deg	*α*/deg	Δ*G*[a,b]
XRD					
4	2.581(2)	178.27(11) (*trans*)	180.00	67.26(6)	-
DFT[a]					
4$_{opt}$	2.583	178.57 (*trans*)	180.00	67.49	0.0
4′$_{opt}$	2.893	109.187	–174.45	73.12	1.6
		118.79 (*cis*)		73.23	
4″$_{opt}$	2.443	160.68 (*cis*)	–149.60	63.15	5.3

[a]Calculated at the B3LYP-D3/6-311G(d) level of theory. [b]At 298.15 K, in kJ mol^{-1}.

4-2-5. Interconversion between Tetrasilabicyclo[1.1.0]butane 4 and Cyclotrisilene 6

The author found an unexpected spectral change in the ^{1}H NMR spectrum of **4**. Immediately after the crystals of **4** were dissolved in C_6D_6 solution at room temperature, the ^{1}H NMR spectrum of the resulting solution showed only two singlet signals at 0.42 and 1.93 ppm (Figure 4-4a). After a few minutes, a set of new signals appeared at 0.37, 0.43, and 0.50 ppm in the ratio of 1:2:1 in the region for $SiMe_3$ protons with a decrease in the intensity of the signals of **4** (Figure 4-4b). After one day, no further decrease of the intensity of the original signals of **4** and an increase in the intensity of new signals were observed at room temperature. This observed behavior suggests that **4** equilibrates with a new species in solution at room temperature. The new species can be identified as chloro(chlorosilyl)-substituted cyclotrisilene **6** (Scheme 4-2) by NMR spectroscopy and the product analysis of the reaction with 4-(dimethylamino)pyridine (DMAP) (*vide infra*).

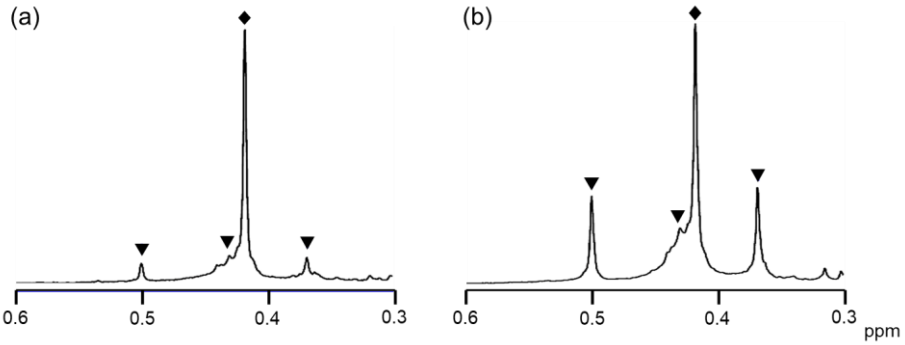
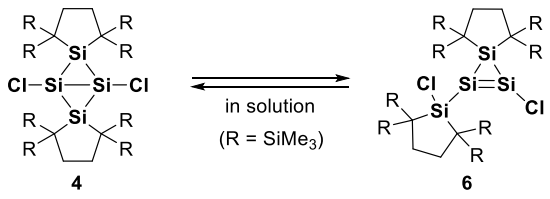


Figure 4-4. ^{1}H NMR spectra ($SiMe_3$ region, a: 5 min, b: 1 day) of **4** in C_6D_6 at room temperature (♦ = **4**, ▼ = **6**).

Scheme 4-2. Interconversion between **4** and **6**



4-2-6. Trapping Cyclotrisilene 6 with 4-(Dimethylamino)pyridine (DMAP)

As soon as DMAP was added to the equilibrium mixture of **4** and **6** in C_6D_6 solution, the ^{1}H NMR spectrum showed that the signals of **6** disappeared and new signals assignable to

cyclotrisilene-DMAP adduct **7** appeared, while the signals of **4** remained unchanged (Figure 4-5), suggesting that **7** was a product resulting from the reaction of **6** with DMAP. DMAP-adduct **7** could be alternatively obtained as dark red crystals in 64% yield by the reaction of **4** with DMAP in toluene at room temperature for one day (Scheme 4-3). Compound **7** was characterized by a combination of multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and XRD analysis. As Scheschkewitz reported that an *N*-heterocyclic carbene (NHC) can coordinate a double-bond silicon atom of a cyclotrisilene providing complex **I** (Chart 4-3) similar to **7**,[14] it is reasonable to consider that cyclotrisilene **6** was generated from **4** in solution (Scheme 4-2).

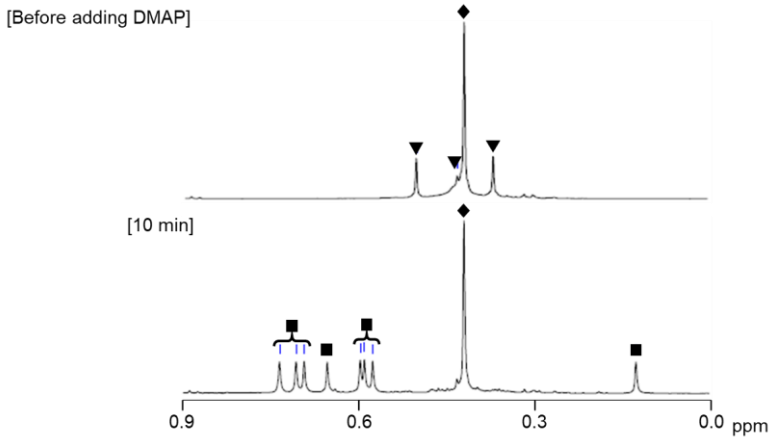
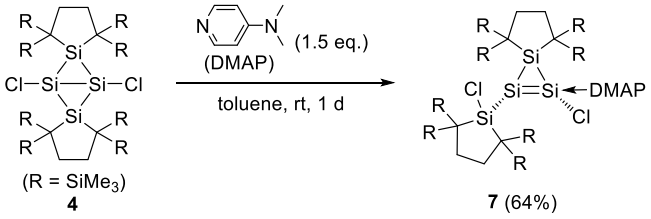


Figure 4-5. ^{1}H NMR spectra ($SiMe_3$ region) of the reaction mixture of **4**+**6** with DMAP in C_6D_6 at room temperature (♦ = **4**, ▼ = **6**, ■ = **7**).

Scheme 4-3. Synthesis of **7**



4-2-7. Molecular Structure of 7

The molecular structure of **7** determined by XRD analysis reveals that DMAP coordinates to the chlorinated double bond silicon atom (Si1) (Figure 4-6). The DMAP and the chlorosilyl groups are arranged in a *trans* fashion with respect to the cyclotrisilene ring plane.

The Si1–Si2 distance [2.2145(7) Å] is significantly longer than those of the reported base-free cyclotrisilenes (2.118–2.186 Å).[15] The elongation of the Si=Si bond upon the coordination of a Lewis base was found in cyclotrisilene-NHC adduct **I** [2.2700(5) Å][14a] and related base-coordinated disilenes.[16] The geometry around the Si2 atom is highly pyramidalized [the angle sum: 333.19°]. In the ^{29}Si NMR spectrum of **7**, the Si1 and Si2 nuclei resonate at 6.1 and −114.2 ppm, respectively, indicating the highly polarized Si=Si double bond similar to the reported base-coordinated disilenes.[16]

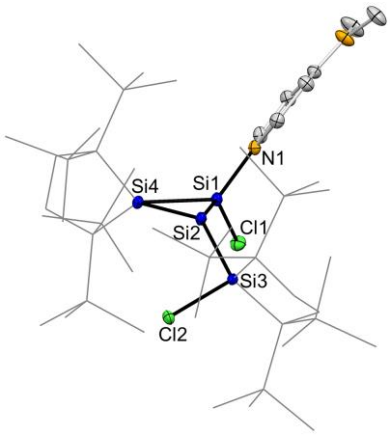
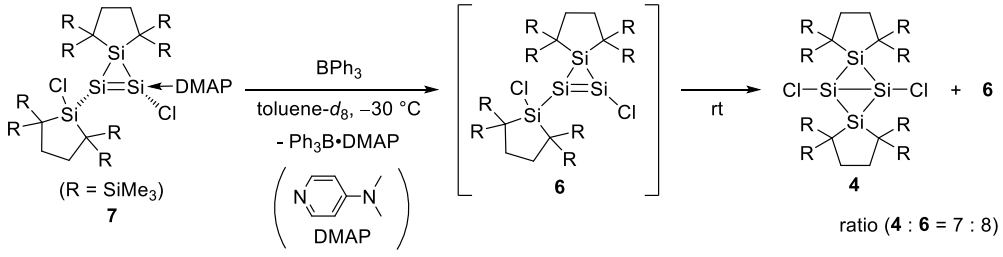


Figure 4-6. ORTEP of **7** with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.2145(7), Si1–N1 1.8789(15), Si1–Si4 2.2986(7), Si1–Cl1 2.1107 (6), Si2–Si3 2.3791(7), Si2–Si4 2.3893(7), Si3–Cl2 2.1317(6), Si2–Si1–Si4 63.90(2), Si1–Si2–Si4 59.76(2), Si1–Si4–Si2 56.34(2).

4-2-8. Elimination Reaction of DMAP from 7

The elimination of DMAP from **7** provided further information on the equilibrium between **4** and **6**. When **7** was treated with BPh_3 in toluene-d_8 solution at −30 °C, the ^{1}H NMR spectrum of the reaction mixture showed four singlet signals at 0.35, 0.38, 0.45, and 0.48 ppm in the region for $SiMe_3$ protons, which correspond with those of **6** in the equilibrium mixture of **4** and **6** (Scheme 4-4 and Figure 4-7a,b). The seven ^{29}Si NMR resonances observed at 2.9, 3.3, 6.1, 32.9, 48.7, 78.2, and 104.1 ppm[13] are comparable to the theoretical ^{29}Si chemical shifts of $\mathbf{6}_{opt}$ calculated at the M06L/6-311+G(2df,p) level of theory (Table 4-20). Upon warming to room temperature, the signals of **4** gradually appeared and the ratio of **4** : **6** reached 7 : 8 after one day (Scheme 4-4 and Figure 4-7c). These results are consistent with the notion that cyclotrisilene **6** equilibrates with bicyclo[1.1.0]tetrasilane **4** in solution.

Scheme 4-4. Reaction of **7** with BPh_3



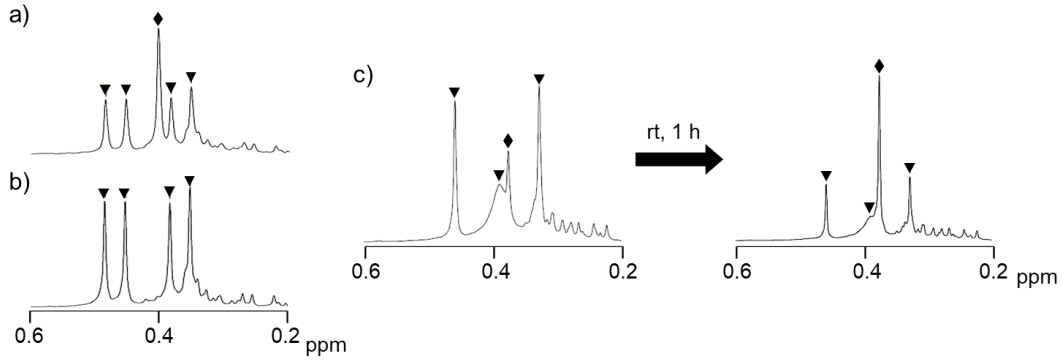
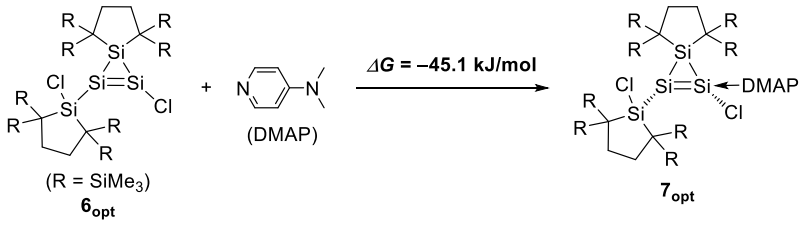


Figure 4-7. ^{1}H NMR spectra ($SiMe_3$ region) of a) the equilibrium mixture of **4**+**6** and b) the reaction mixture of **7** with BPh_3 in toluene-d_8 at −30 °C. c) ^{1}H NMR spectra ($SiMe_3$ region) of the reaction mixture of **7** with BPh_3 (left: just after warming up, right: after 1 hour) in toluene-d_8 at room temperature (♦ = **4**, ▼ = **6**).

4-2-9. Theoretical Calculations for 6 and 7

The theoretical calculations provided further insight into the behavior of **4** in solution. In addition to **4**, **6** and **7** were located as local minima ($\mathbf{6}_{opt}$ and $\mathbf{7}_{opt}$) at the B3LYP-D3/6-311G(d) level of theory, and the structural parameters of $\mathbf{7}_{opt}$ are in good agreement with those obtained from the XRD analysis. Cyclotrisilene $\mathbf{6}_{opt}$ is lower only by 6.9 kJ mol^{-1} in free energy (298.15 K) than $\mathbf{4}_{opt}$, which is consistent with the fact that **6** is a dominant species in the equilibrium mixture.[17] The formation of DMAP-adduct $\mathbf{7}_{opt}$ from $\mathbf{6}_{opt}$ and DMAP was found to be exergonic (−45.1 kJ mol^{-1}), which is also consistent with the observed facile formation of **7** (Scheme 4-5). These experimental and theoretical results corroborate that the compound which equilibrates with **4** in solution is cyclotrisilene **6**.

Scheme 4-5. Formation of DMAP-adduct $\mathbf{7_{opt}}$



4-2-10. Possible Isomerization Mechanism

A possible isomerisation route between **4** and **6** examined by the DFT calculation at the B3LYP-D3/B1 level of theory (B1: 6-311G(d) [Si_4Cl_2 core], 6-31G(d) [C atoms in silacyclopentane rings], 3-21G* [other atoms]) is shown in Figure 4-8. After the isomerization of $\mathbf{4_{opt}}$ to *cis*-bent bicyclotetrasilane $\mathbf{4'_{opt}}$ that has a long bridgehead Si–Si distance [2.888 Å] and highly-pyramidalized bridgehead silicon atoms, which should be regarded as a long bond isomer of bicyclo[1.1.0]tetrasilane,[8,18,19] the ring-opening reaction of $\mathbf{4'_{opt}}$ provides tetrasila-1,3-diene $\mathbf{8_{opt}}$.[20,21] Finally, the 1,2-chlorine migration accompanied by the ring closure, which can be rationalized by a simultaneous disilene–silylsilylene isomerisation via 1,2-chlorine migration and disilenylsilylene–cyclotrisilene isomerisation,[14,22] afforded $\mathbf{6_{opt}}$. The calculated activation barrier of the rate-controlling step (isomerisation of $\mathbf{8_{opt}}$ to $\mathbf{6_{opt}}$) [61.5 kJ mol^{-1}] is consistent with the fact that the isomerisation occurs at room temperature.[23]

The observed isomerisation mode between **4** and **6** is different from the isomerisation of **G** containing a similar planar silicon ring to the corresponding cyclotetrasilene derivative.[7] As for **4**, the bulky dialkylsilylene [2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl] moiety located at the bridge positions, which cannot dimerize due to its steric demand,[24] should prohibit such isomerisation to the corresponding cyclotetrasilene derivative in which two silylene moieties need to connect.

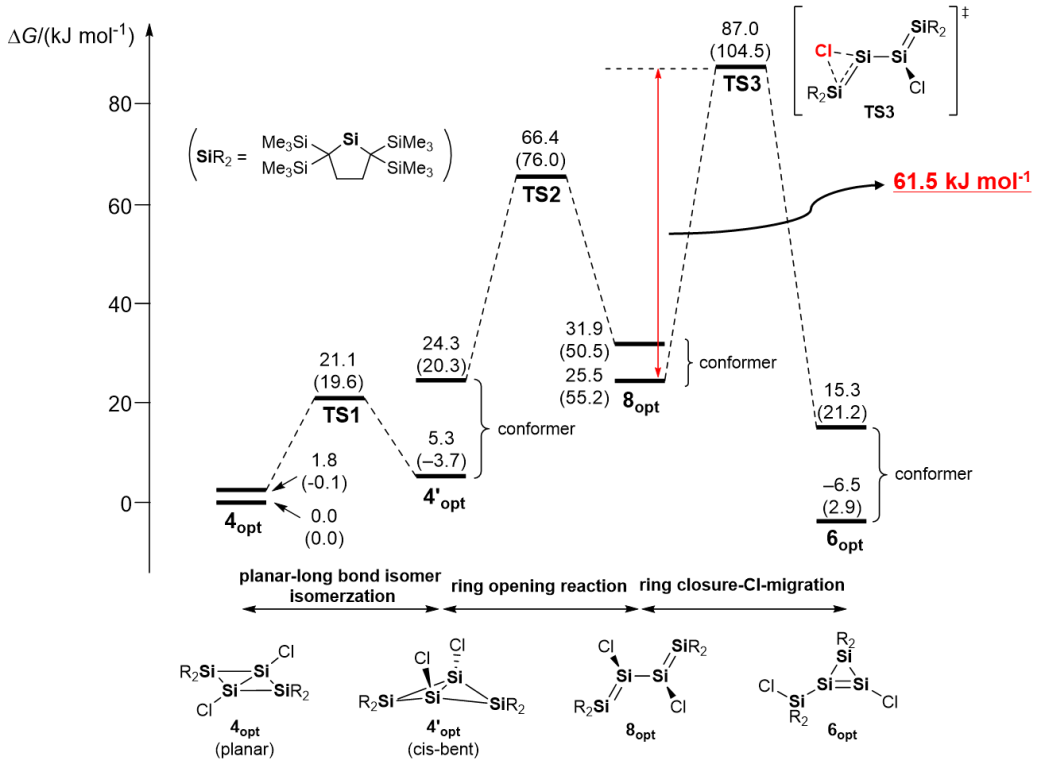
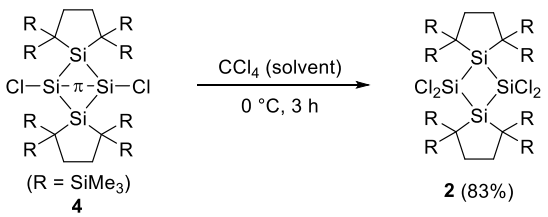


Figure 4-8. A possible isomerization route between $\mathbf{4}_{opt}$ and $\mathbf{6}_{opt}$ calculated at the B3LYP-D3/6-311G(d) [Si_4Cl_2 core], 6-31G(d) [C atoms in silacyclopentane rings], 3-21G* [other atoms] level of theory. The values in brackets and parentheses are relative Gibbs free energies (298.15 K) and relative energies including zero-point vibrational energy correction in kJ mol^{-1}, respectively.

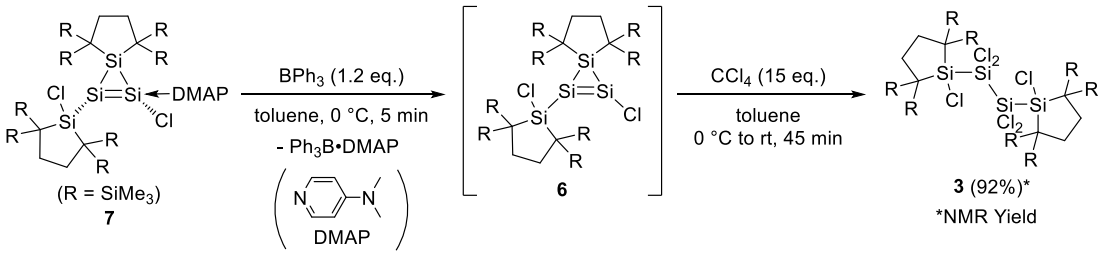
4-2-11. Reaction of 4 and 6 with CCl_4

Finally, we examined the reaction of **4** and **6** with carbon tetrachloride. As expected, **4** was treated with carbon tetrachloride at 0 °C to provide **2** as a major product in 83% yield (Scheme 4-6). Conversely, when carbon tetrachloride was added to **6**, which was generated in situ from **7** and BPh_3 in toluene at 0 °C, acyclic tetrasilane **3** was obtained as a major product (NMR yield: 92%) and cyclic tetrasilane **2** was not observed (Scheme 4-7). These results indicated that **6** was a key intermediate for the generation of **3**.[25]

Scheme 4-6. Reaction of **4** with CCl_4



Scheme 4-7. Reaction of **6** with CCl_4



4-3. Conclusion

In conclusion, 1,3-dichlorobicyclo[1.1.0]tetrasilane **4** was synthesized by 1,2-dichlorination of the corresponding bridgehead disilene **1** at low temperature. The molecular structure and ^{29}Si NMR suggest that **4** exhibits a π-type single bonding between the bridgehead silicon atoms. Compound **4** equilibrates with cyclotrisilene **6** in solution at room temperature, which is an unprecedented interconversion mode among Si_4R_6 isomers.

4-4. Experimental Section

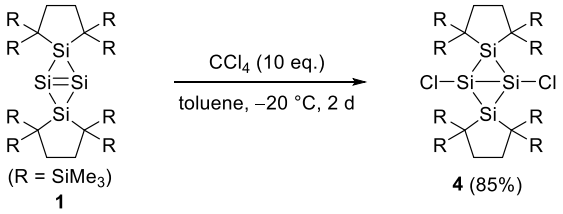
General Procedures

All reactions involving air-sensitive compounds were performed under an argon or nitrogen atmosphere using a high-vacuum line and standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. The reactions at lower temperatures were performed using an EYELA PSL-1400 cryobath. The NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C shifts of the solvents: C_6D_6 (^{1}H: δ 7.16 and ^{13}C: δ 128.0), THF-d_8 (^{1}H: δ 3.58 and ^{13}C: δ 67.2), and toluene-d_8 (^{1}H: δ 2.08).[26] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). The sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4 T spectrometer. UV-vis spectra were recorded on a JASCO V-770 spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer.

Materials

Dry and degassed hexane, benzene, and toluene were prepared using a VAC 103991 solvent purifier. C_6D_6 was degassed through five freeze–pump–thaw cycles and then dried over molecular sieves 4Å. THF-d_8 and toluene-d_8 were dried in a tube covered with a potassium mirror and then distilled under reduced pressure prior to use. Carbon tetrachloride was dried over calcium hydride and degassed through three freeze–pump–thaw cycles. 4-(Dimethylamino)pyridine (DMAP), triphenylborane, and ferrocene were commercially available and used without further purification. Bicyclo[1.1.0]tetrasil-1(3)-ene **1** was prepared according to the published procedure.[9b]

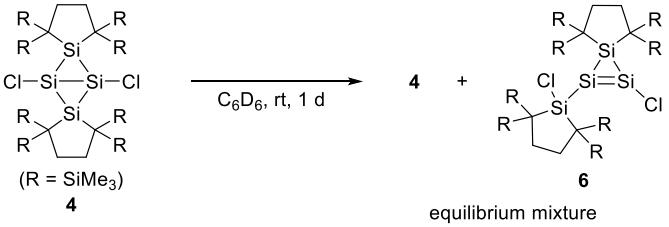
Synthesis of 1,3-Dichlorobicyclo[1.1.0]tetrasilane 4 [TN420,438]



To a Schlenk tube (10 mL) equipped with a magnetic stir bar, **1** (30.4 mg, 37.9 μmol) and toluene (3.0 mL) were added. After the mixture was cooled to −20 °C, carbon tetrachloride (59 mg, 384 μmol) was added to the Schlenk tube. Then the mixture was stirred at −20 °C for **2** days. The resulting suspension turned from orange to deep orange. After the volatiles were removed in vacuo at 0 °C, the crude was washed with hexane to provide an orange solid of **4** (28.2 mg, 32.3 μmol) in 85% yield.

4: an orange solid; mp 161–162 °C (decomp.); δ_H (500 MHz, C_6D_6, 298 K) 0.42 (72H, s, SiCH_3), 1.93 (8H, s, CH_2); δ_C (126 MHz, C_6D_6, 333 K) 5.0 (SiCH$_3$), 15.9 (C), 34.5 (CH$_2$); δ_{Si} (99 MHz, C_6D_6, 333 K) −7.9 (*Si*), 4.6 (*Si*Me$_3$), 126.4 (*Si*–Cl); HRMS (APCI_positive) found, 870.28636. Calcd for $C_{32}H_{80}Cl_2Si_{12}$ [M^+], 870.28628; found: C, 44.10; H, 9.13. Calcd for $C_{32}H_{80}Cl_2Si_{12}$: C, 44.03; H, 9.24%.

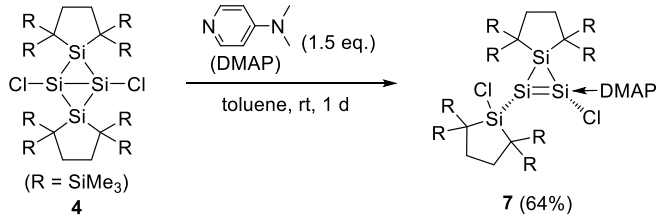
Thermal Isomerisation of 4 to (Chloro)(chlorosilyl)cyclotrisilene 6 [TN631]



To a J. Young NMR tube, **4** was added. To the NMR tube, C_6D_6 was added and immediately the ^{1}H NMR spectrum of the mixture was recorded at room temperature. Then, the mixture was left for one day at room temperature and the NMR spectra of the mixture were recorded again. See Figures 4-9 and 4-10 for details. The NMR data of **6** were obtained by subtracting the signals of **4** from the spectrum of the equilibrium mixture.

6: δ_H (500 MHz, C_6D_6, 302 K) 0.37 (18H, s, SiC*H*$_3$), 0.43 (36H, brs, SiC*H*$_3$), 0.50 (18H, s, SiC*H*$_3$), 1.86–2.05 (8H, m, C*H*$_2$); δ_C (126 MHz, C_6D_6, 333 K) 4.1 (Si*C*H$_3$), 5.0 (Si*C*H$_3$), 5.5 (Si*C*H$_3$), 20.7 (*C*), 21.4 (*C*), 33.9 (*C*H$_2$), 34.4 (*C*H$_2$); δ_{Si} (99 MHz, C_6D_6, 333 K) 2.9 (*Si*Me$_3$), 3.3 (*Si*Me$_3$), 6.1 (*Si*Me$_3$), 32.9 (*Si*), 48.7 (*Si*=Si–Cl), 78.2 (*Si*), 104.1 (Si=*Si*–Cl).

Reaction of 4 with 4-(Dimethylamino)pyridine (DMAP) [TN590,680]

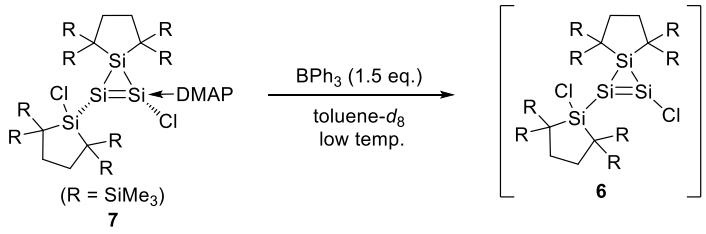


To a Schlenk tube (30 mL) equipped with a magnetic stir bar, **4** (60.6 mg, 69.4 μmol) and DMAP (12.3 mg, 101 μmol) were added. To the mixture, toluene (5.0 mL) was added and then the mixture was stirred at room temperature for one day. The resulting suspension turned from orange to dark red. After the volatiles were removed in vacuo at room temperature, recrystallization from hot benzene provided dark red crystals of **7**·(benzene)$_2$ (51.3 mg, 44.6 μmol) in 64% yield.

7·(benzene)$_2$: red crystals; mp 80–81 °C (decomp.); δ_H (500 MHz, THF-d_8, 296 K) −0.11 (9H, s, SiC*H*$_3$), 0.278 (9H, s, SiC*H*$_3$), 0.284 (9H, s, SiC*H*$_3$), 0.29 (9H, s, SiC*H*$_3$), 0.31 (9H, s, SiC*H*$_3$),

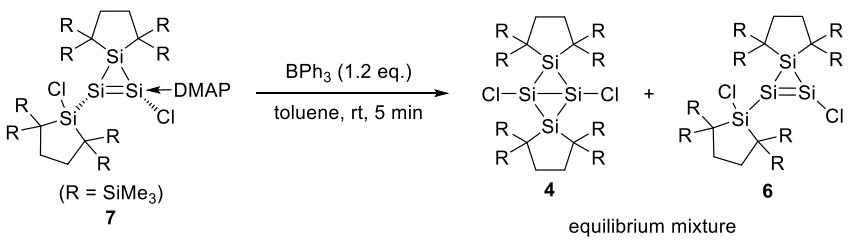
0.32 (9H, s, SiCH_3), 0.35 (9H, s, SiCH_3), 0.42 (9H, s, SiCH_3), 1.61–1.70 (1H, m, CH_2), 1.85–2.20 (7H, m, CH_2), 3.21 (6H, s, N(CH_3)$_2$ of DMAP), 6.91 (2H, d, J = 7.6 Hz, *m*-C*H* of DMAP), 7.30 (12H, s, benzene), 8.79 (2H, d, J = 7.6 Hz, *o*-C*H* of DMAP); δ_C (126 MHz, THF-d_8, 301 K) 4.1 (Si*C*H$_3$), 4.6 (Si*C*H$_3$), 5.4 (Si*C*H$_3$), 5.48 (Si*C*H$_3$), 5.52 (Si*C*H$_3$), 5.54 (Si*C*H$_3$), 5.55 (Si*C*H$_3$), 5.7 (Si*C*H$_3$), 16.1 (*C*), 18.5 (*C*), 20.2 (*C*), 21.0 (*C*), 34.5 (*C*H$_2$), 35.3 (*C*H$_2$), 35.5 (*C*H$_2$), 35.9 (*C*H$_2$), 39.6 (N*C*H$_3$), 107.1 (*m*-*C*H, DMAP), 128.9 (benzene), 146.7 (*o*-*C*H, DMAP), 157.2 (*p*-*C*, DMAP); δ_{Si} (99 MHz, THF-d_8, 301 K) −114.2 (*Si*=Si←DMAP), 1.3 (*Si*Me$_3$), 1.7 (*Si*Me$_3$), 1.9 (*Si*Me$_3$), 3.1 (*Si*Me$_3$), 3.3 (*Si*Me$_3$), 3.8 (*Si*Me$_3$), 4.5 (*Si*Me$_3$), 5.0 (*Si*Me$_3$), 6.0 (*Si*), 6.1 (Si=*Si*←DMAP), 42.4 (*Si*); λ_{max}(hexane)/nm 519 (ε/dm^3 mol^{-1} cm^{-1}, 1.1 × 10^3), 362 (5.4 × 10^3), 315sh (7.6 × 10^3); HRMS (APCI_solid) found, 993.37924. Calcd for $C_{39}H_{90}Cl_2N_2Si_{12}$ [M$^+$], 993.37850; found: C, 52.98; H, 8.91; N, 2.50. Calcd for $C_{39}H_{90}Cl_2N_2Si_{12}$ + 2C_6H_6: C, 53.21; H, 8.93; N, 2.43%.

Reaction of 7 and BPh_3 at Low Temperature [TN675,721]



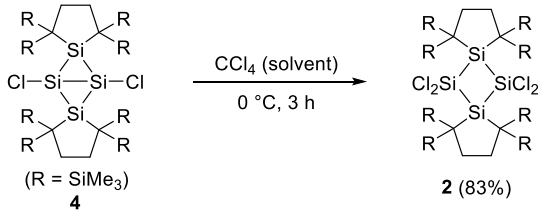
In a sealed NMR tube, **7** (10.3 mg, 9.0 μmol), triphenylborane (3.3 mg, 13.6 μmol) and toluene-d_8 (ca. 0.5 mL) were mixed at −30 °C and then the ^{1}H NMR spectrum of the mixture was recorded at the same temperature. Then, the ^{1}H NMR spectra of the mixture were recorded at −20, −10, 0 °C, and finally room temperature. See Figure 4-25 for details.

Reaction of 7 and BPh_3 at Room Temperature [TN699]



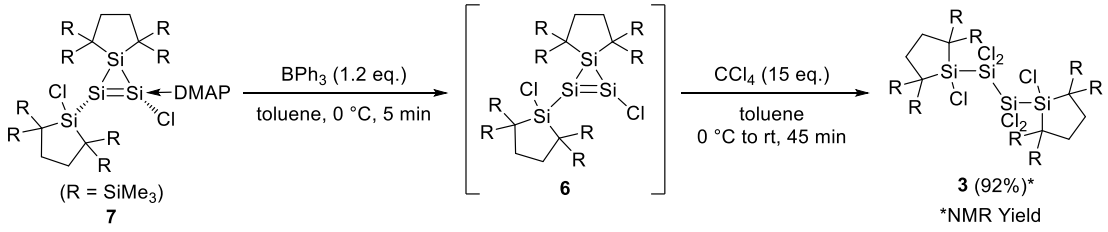
To a Schlenk tube (30 mL) equipped with a magnetic stir bar, compound **7** (24.9 mg, 21.6 μmol) and toluene (10.0 mL) were added. To the mixture triphenylborane (6.2 mg, 25.6 μmol) was added at room temperature and then the mixture was stirred for 5 min. The resulting solution turned to orange from dark red and the equilibrium mixture of **4** and **6** was obtained in 86% yield. The yield was determined by ^{1}H HMR integral using ferrocene as an internal standard. See Figure 4-26.

Reaction of 4 with CCl_4 [TN704]



To a Schlenk tube (10 mL) equipped with a magnetic stir bar, **4** (30.0 mg, 34.4 μmol) was added. To the Schlenk tube, carbon tetrachloride (2.0 mL, cooled to 0 °C) was added and then the mixture was stirred for 3 hours at 0 °C. The resulting suspension turned from orange to yellow. After the volatiles were removed in vacuo at 0 °C, the residue was washed with hexane to provide a pale yellow solid of **2** (26.8 mg, 28.4 μmol) in 83% yield. The formation of **2** (ref. 9b) was confirmed by comparison with the ^{1}H NMR spectrum of the authentic sample reported in the literature.

Reaction of 7 with CCl_4 in the Presence of BPh_3 (Reaction of 6 with CCl_4) [TN667]



To a Schlenk tube (30 mL) equipped with a magnetic stir bar, **7** (30.4 mg, 26.4 μmol) and toluene (5.0 mL) were added. To the mixture, a toluene solution of triphenylborane (0.20 mL, 7.8 mg, 32.2 μmol) was added at 0 °C, and then the mixture was stirred for 5 min. The

resulting solution turned from dark red to deep orange. Then, carbon tetrachloride (ca. 61 mg, 397 μmol) was added at 0 °C, and the mixture was further stirred at room temperature for 45 min. The volatiles were removed in vacuo at room temperature to provide **3** in 92% yield. The yield was determined by ^{1}H HMR integral using ferrocene as an internal standard. See Figure 4-23. The formation of **3** (ref. 9b) was confirmed by comparison with the ^{1}H NMR spectrum of the authentic sample reported in the literature.

NMR spectra

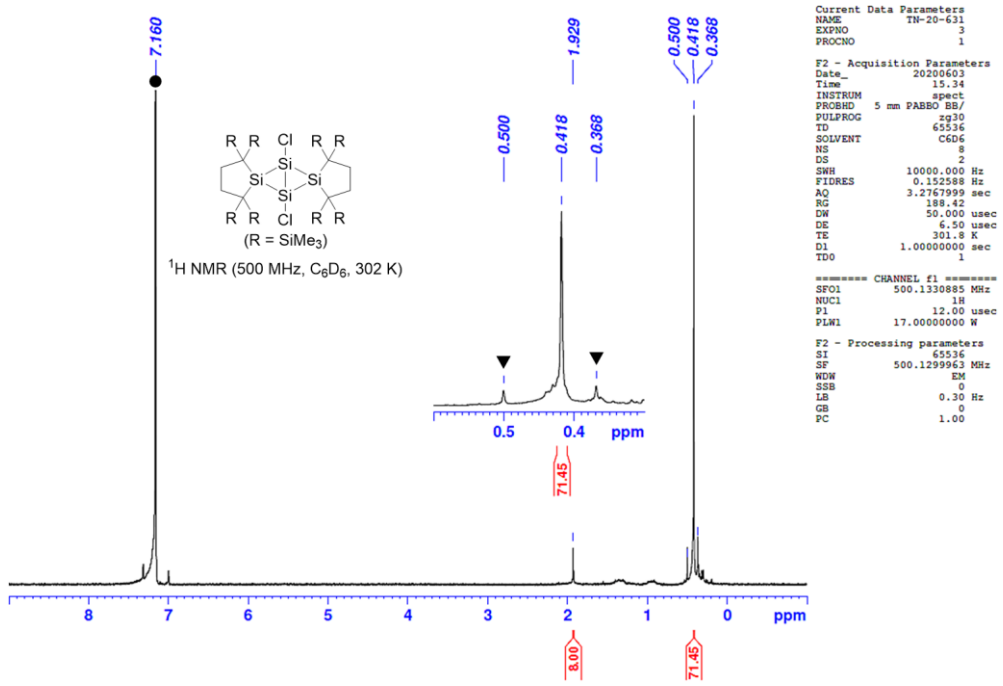


Figure 4-9. ^{1}H NMR spectrum of **4** in C_6D_6 at 302 K (● = C_6HD_5, ▼ = **6**).

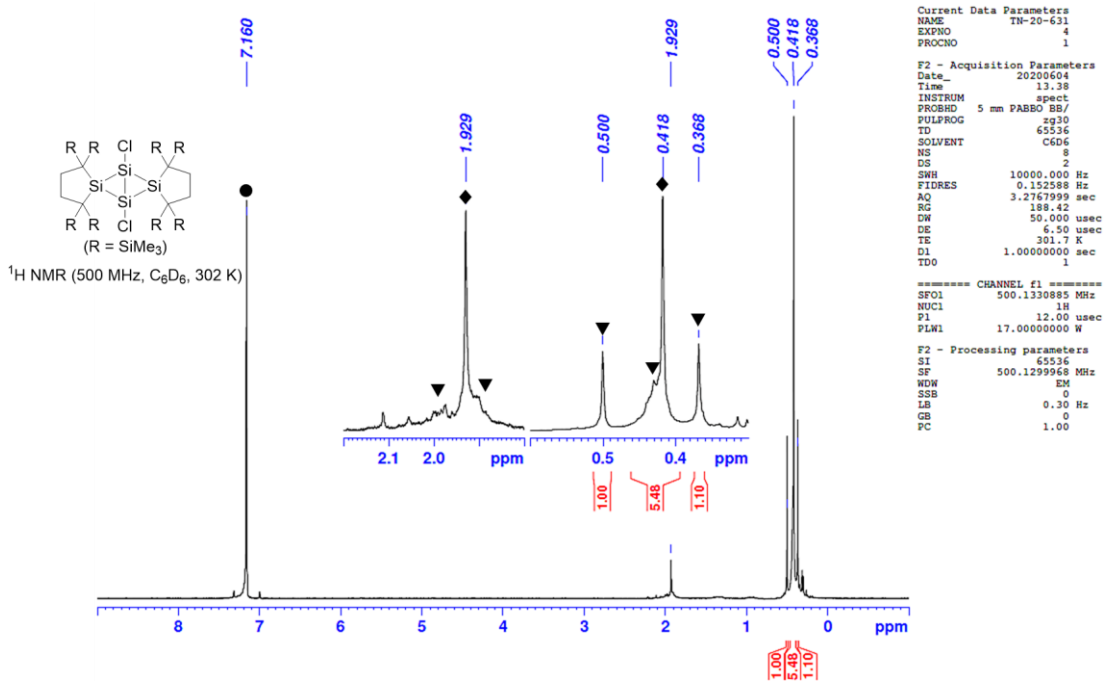


Figure 4-10. ^{1}H NMR spectrum of **4** in C_6D_6 at 302 K after 1 day (● = C_6HD_5, ♦ = **4**, ▼ = **6**).

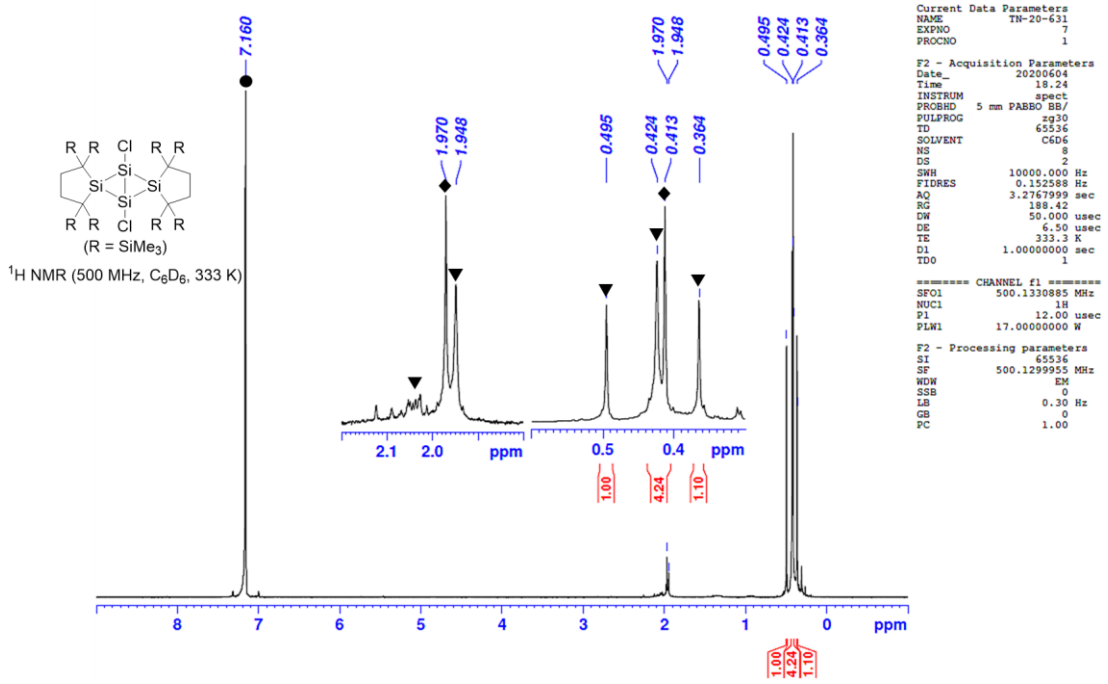


Figure 4-11. ^{1}H NMR spectrum of **4** in C_6D_6 at 333 K (● = C_6HD_5, ♦ = **4**, ▼ = **6**).

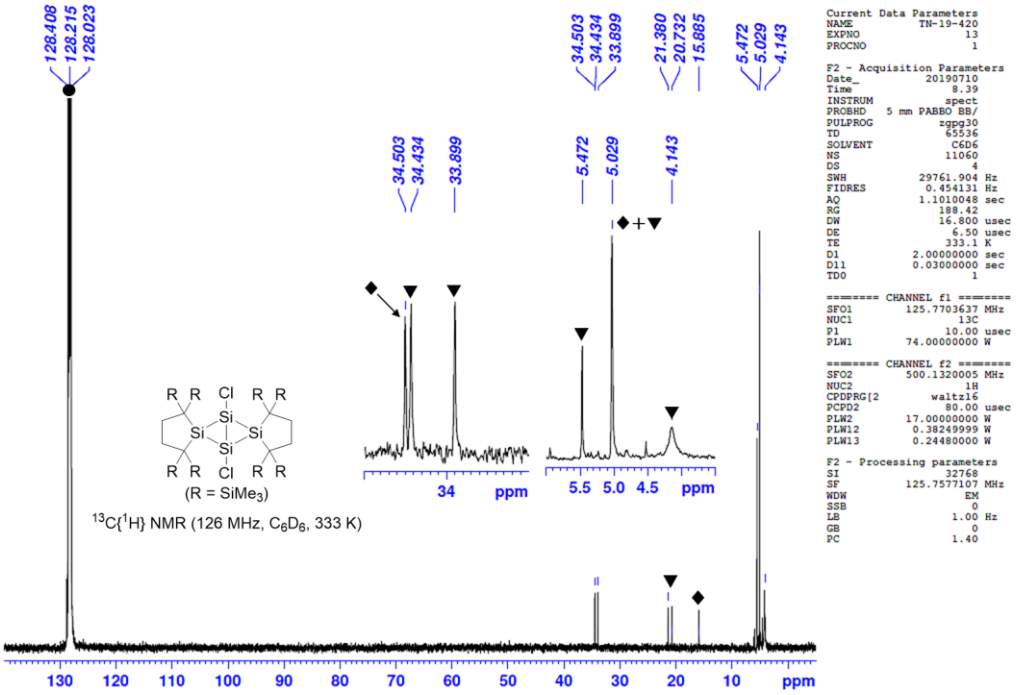


Figure 4-12. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 in 333 K (● = C_6D_6, ♦ = **4**, ▼ = **6**).

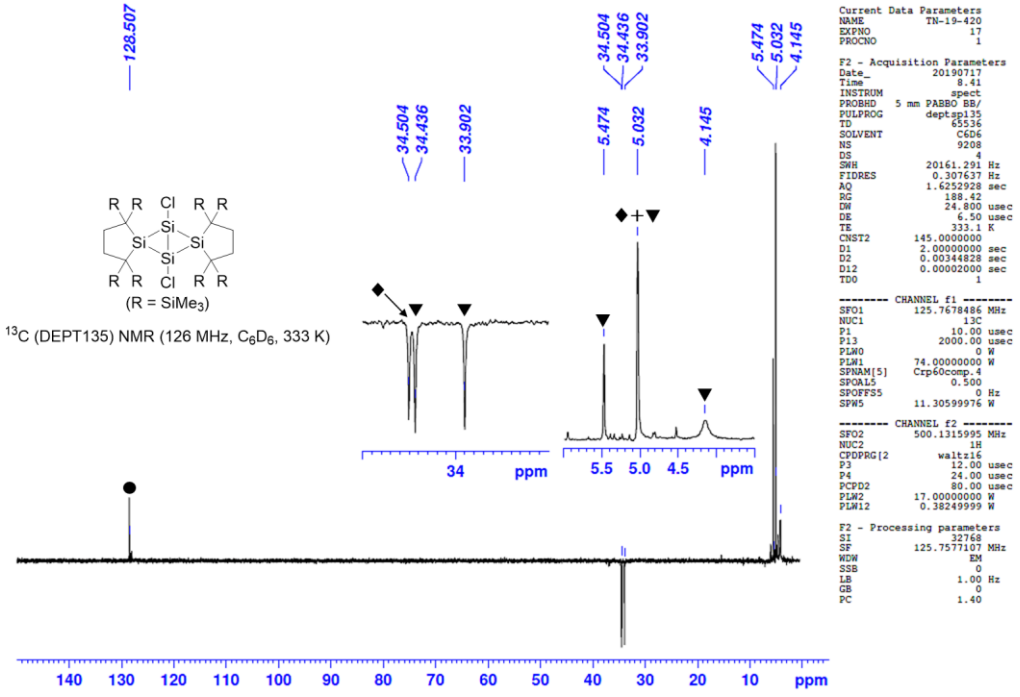


Figure 4-13. ^{13}C (DEPT135) NMR spectrum of **4** in C_6D_6 at 333 K (● = C_6D_6, ♦ = **4**, ▼ = **6**).

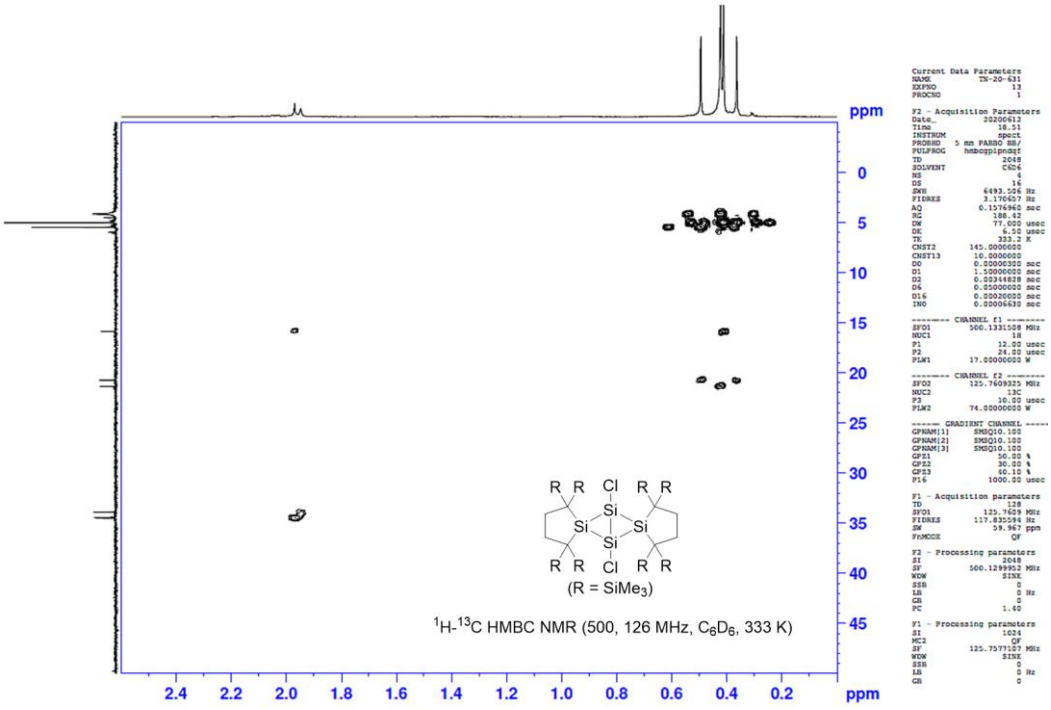


Figure 4-14. ^{1}H-^{13}C HMBC NMR spectrum of **4** in C_6D_6 at 333 K.

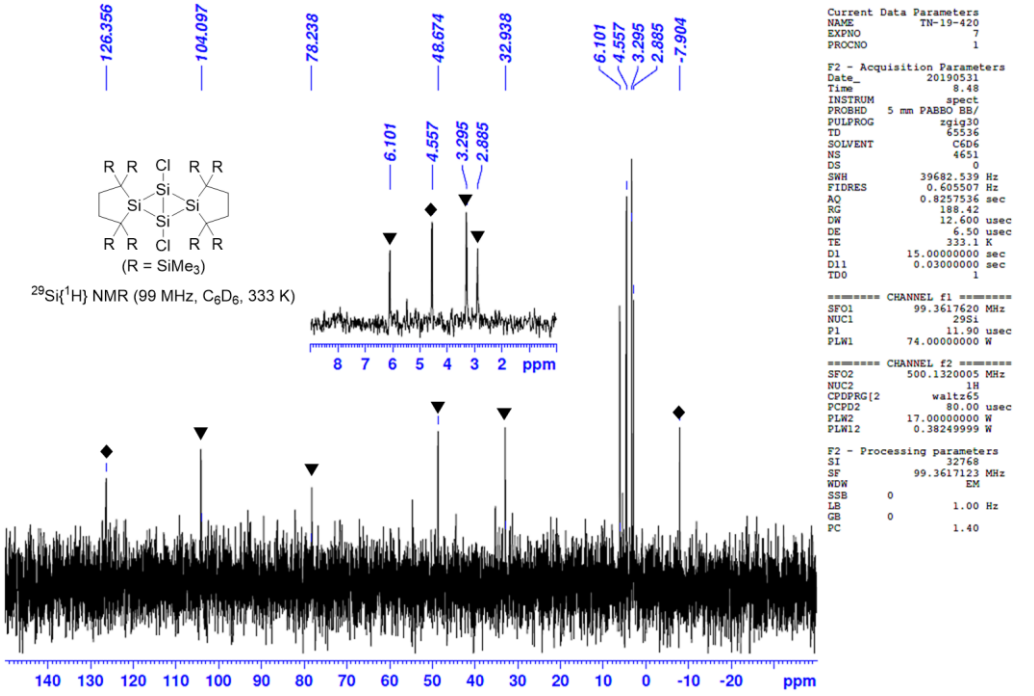


Figure 4-15. $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 333 K. (♦ = **4**, ▼ = **6**).

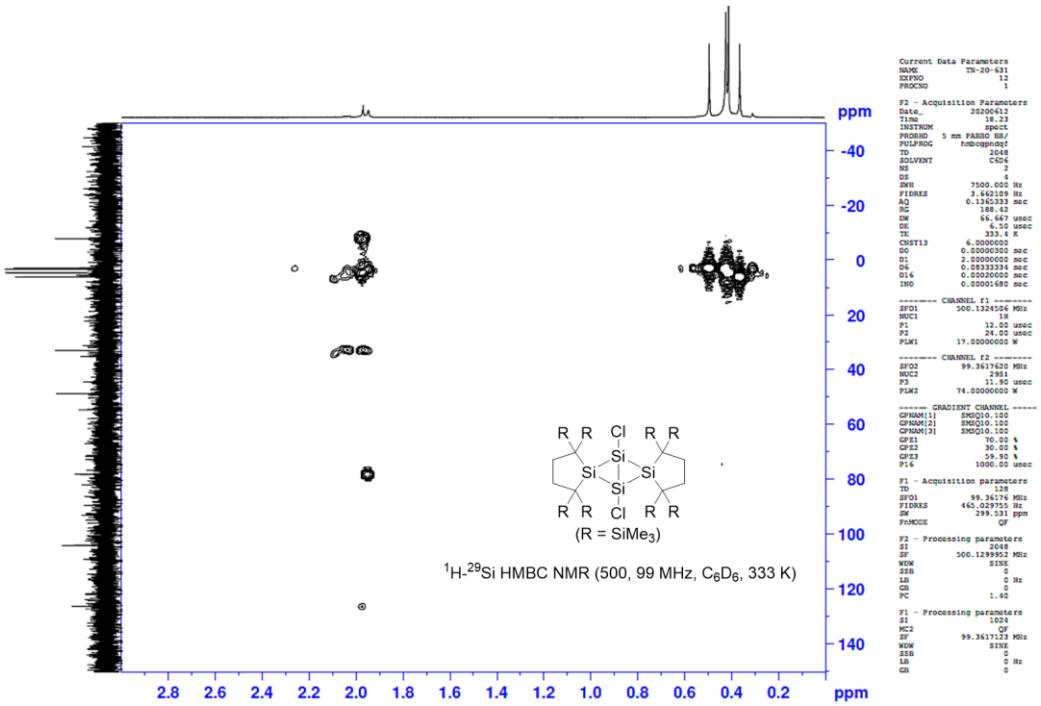


Figure 4-16. ^{1}H-^{29}Si HMBC NMR spectrum of **4** in C_6D_6 at 333 K.

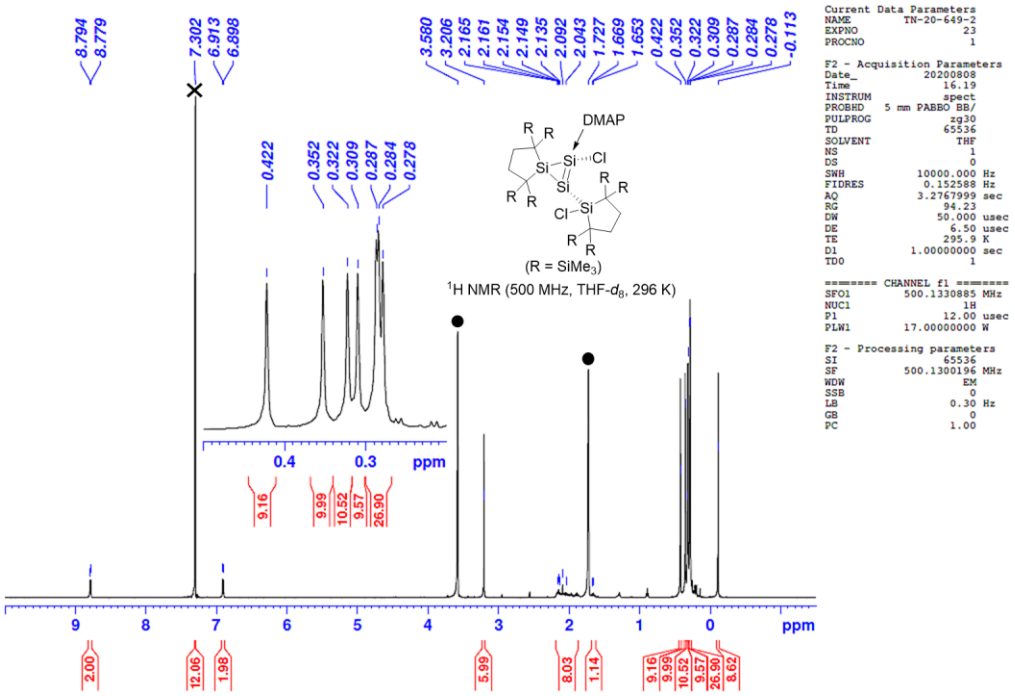


Figure 4-17. ^{1}H NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 296 K (● = THF-d_8, × = benzene).

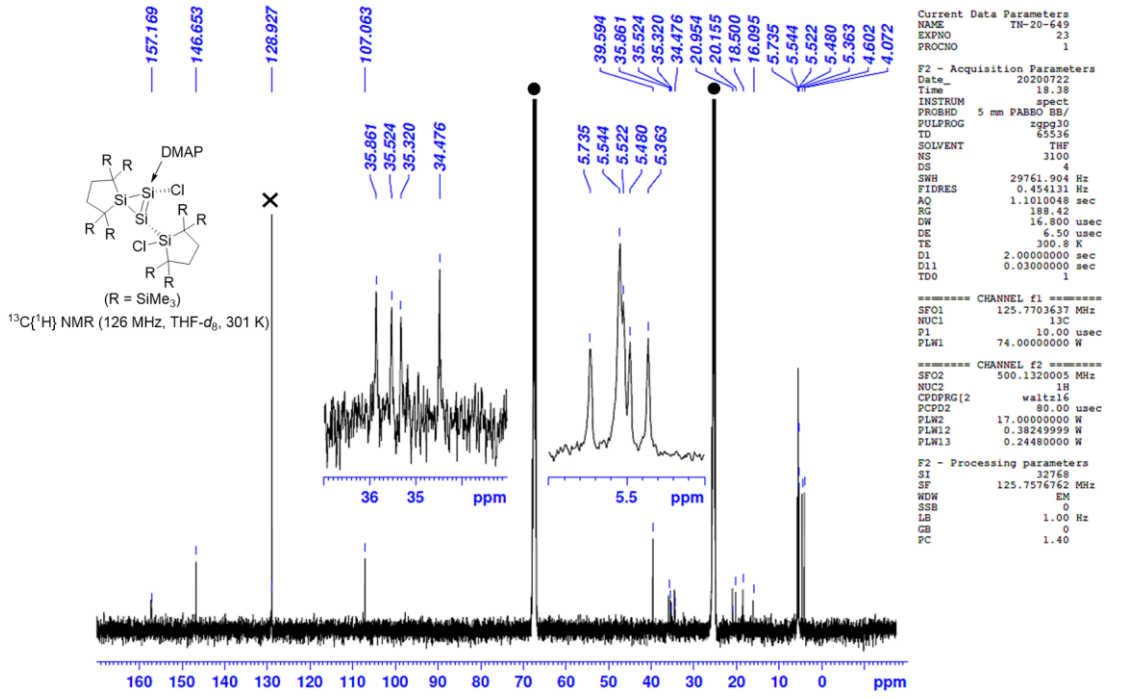


Figure 4-18. $^{13}C\{^{1}H\}$ NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 in 301 K (● = THF-d_8, × = benzene).

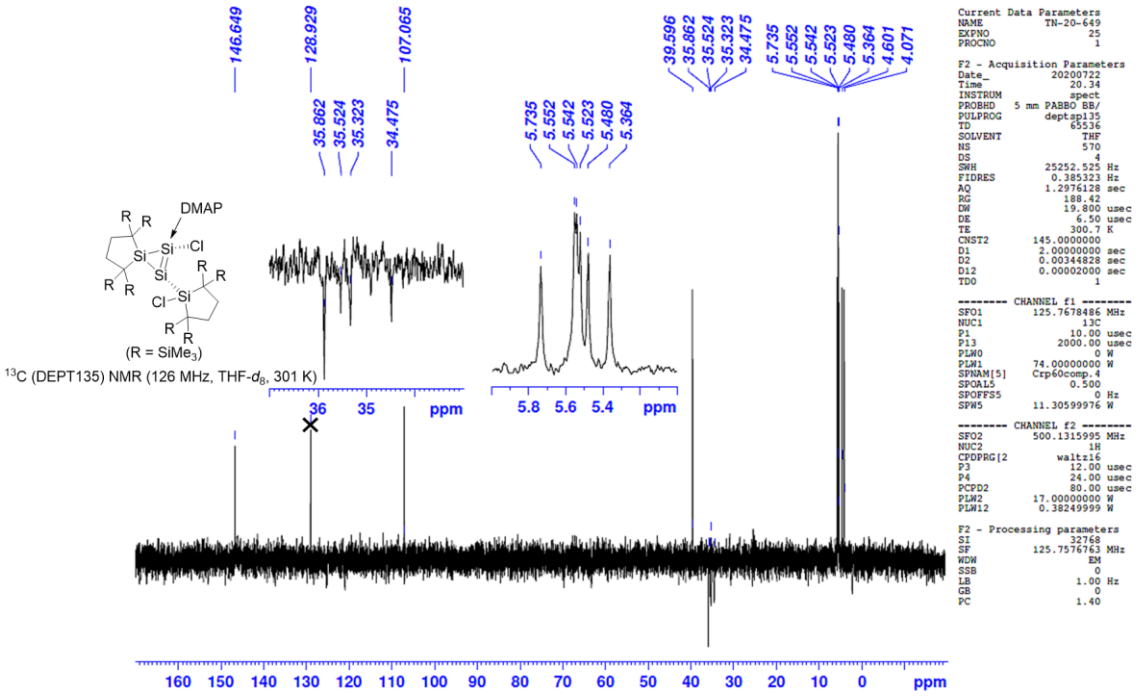


Figure 4-19. ^{13}C (DEPT135) NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K (× = benzene).

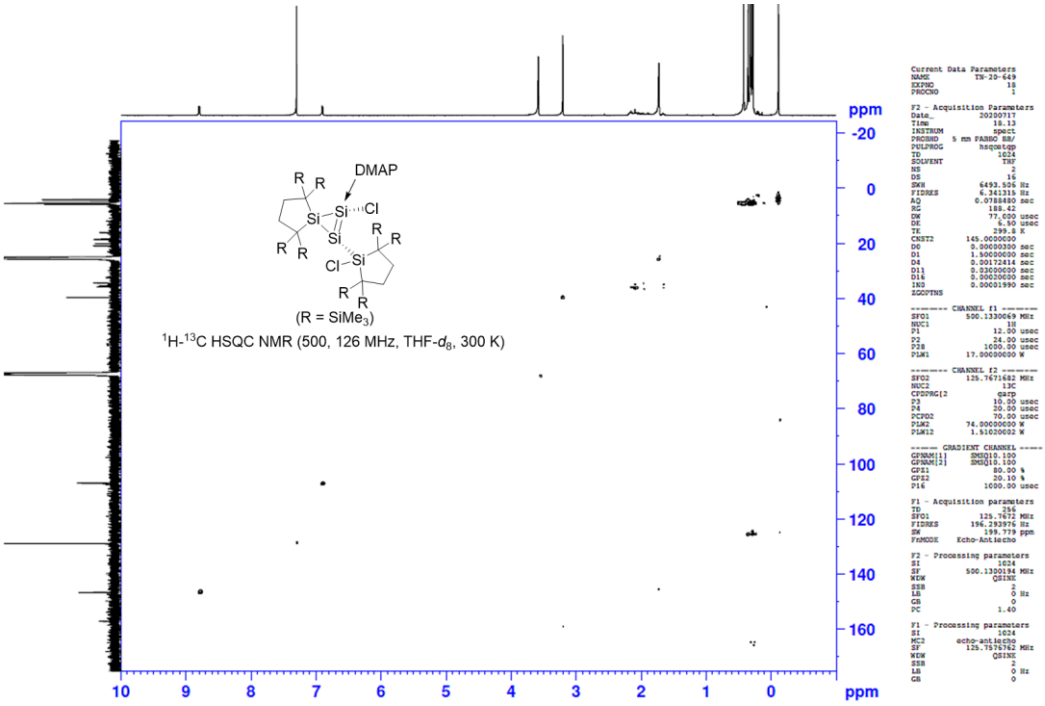


Figure 4-20. ^{1}H-^{13}C HSQC NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 300 K.

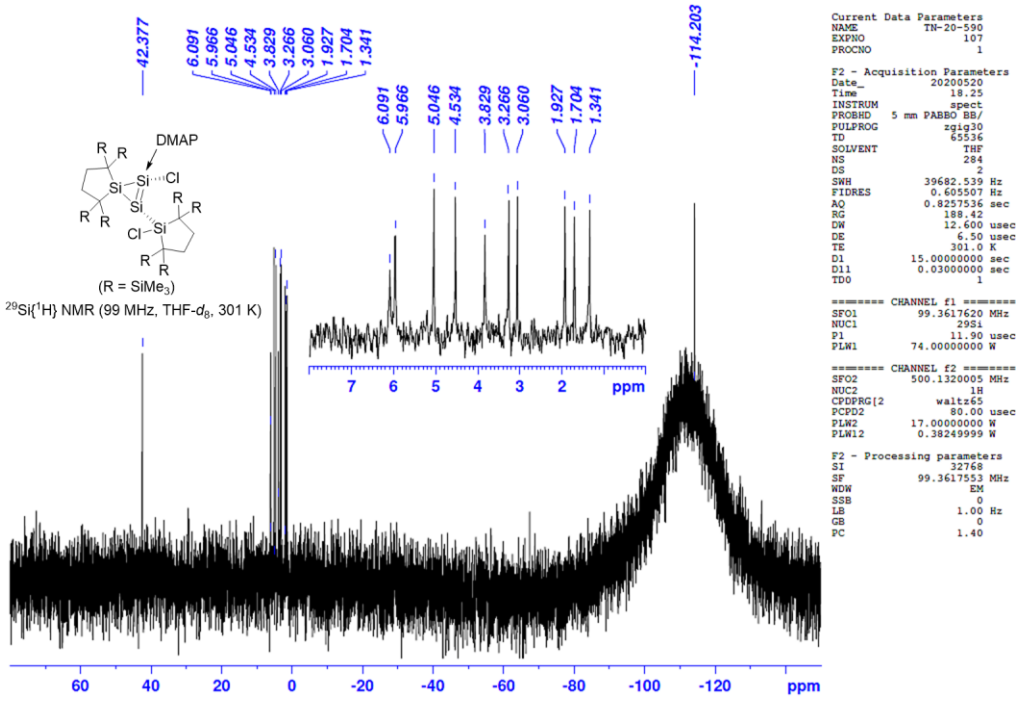


Figure 4-21. ^{29}Si{^{1}H} NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K.

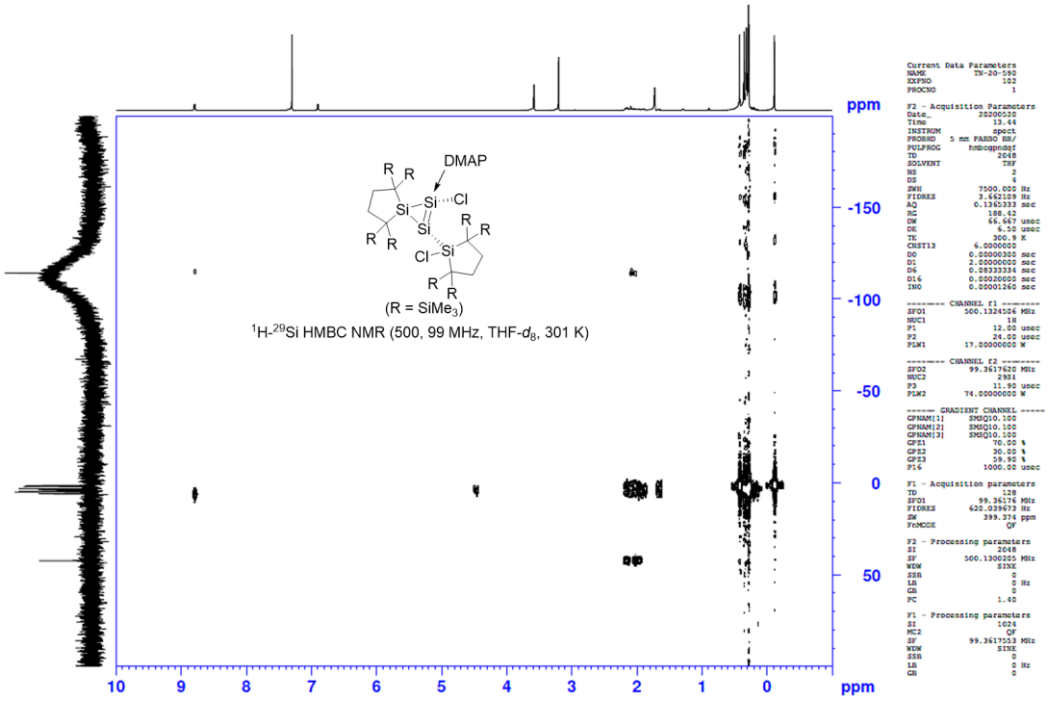


Figure 4-22. ^{1}H-^{29}Si HMBC NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K.

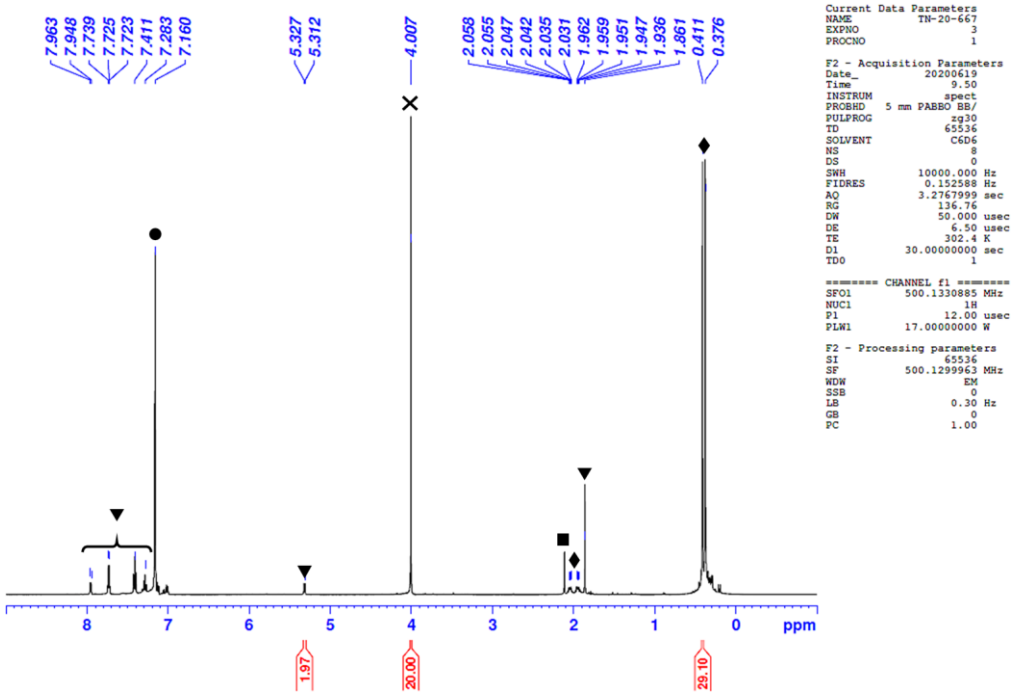


Figure 4-23. ^{1}H NMR spectrum of the reaction mixture of **7** with CCl_4 in the presence of BPh_3 in C_6D_6 at 302 K (● = C_6HD_5, ▼ = BPh_3•DMAP, ♦ = **3**, × = ferrocene, ■ = toluene).

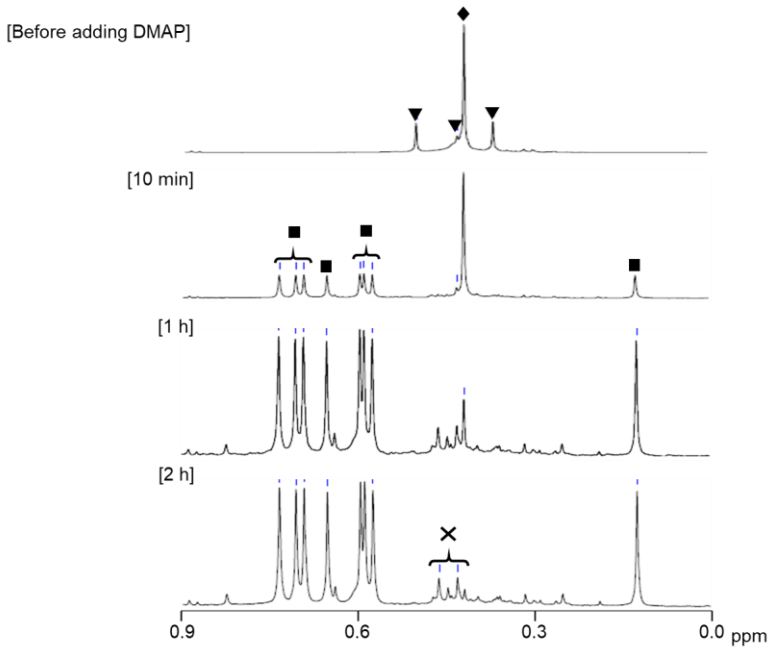


Figure 4-24. ^{1}H NMR spectra ($SiMe_3$ region) of the reaction mixture of **4**+**6** with DMAP in C_6D_6 at room temperature (♦ = **4**, ▼ = **6**, ■ = **7**, × = by products). [TN579]

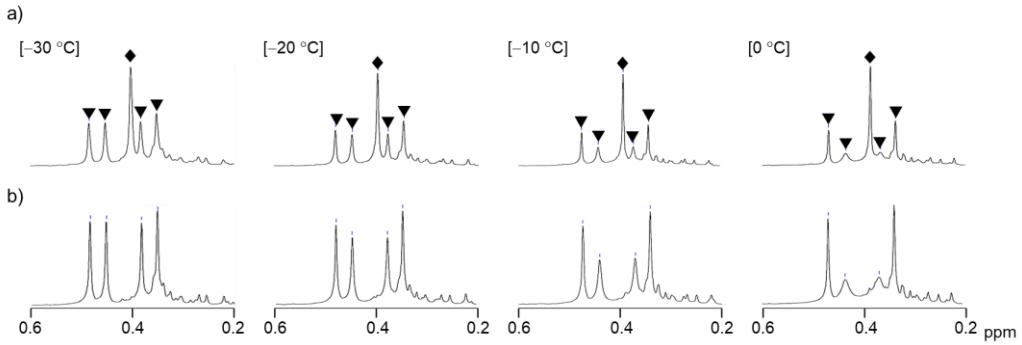


Figure 4-25. ^{1}H NMR spectra ($SiMe_3$ region) of a) the equilibrium mixture of **4**+**6** and b) the reaction mixture of **7** with BPh_3 in toluene-d_8 at variable temperature (♦ = **4**, ▼ = **6**).

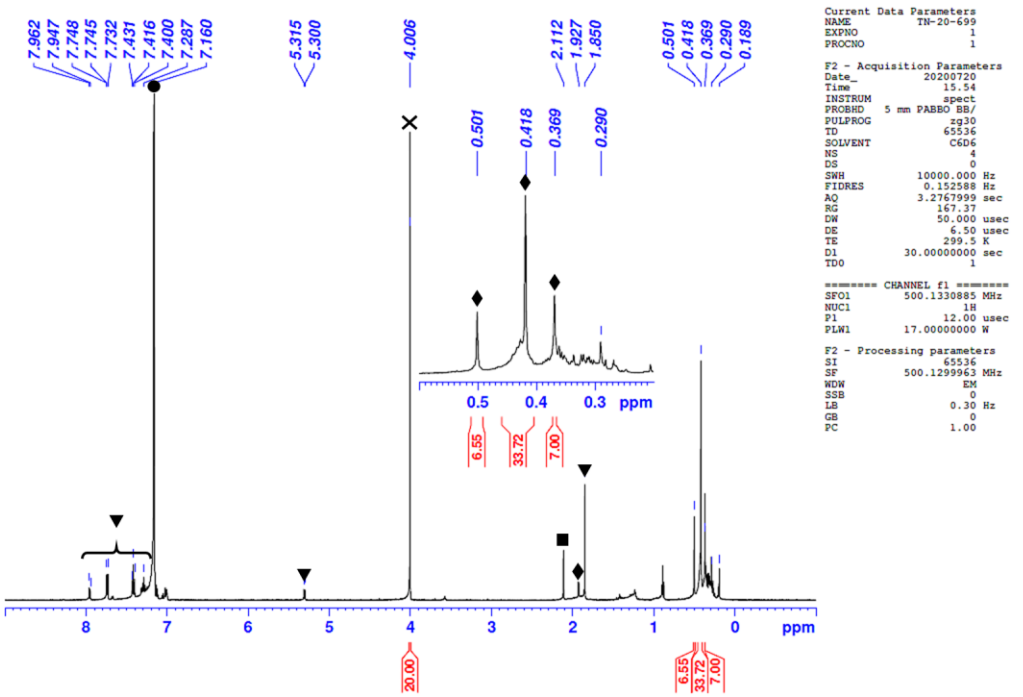


Figure 4-26. ^{1}H NMR spectrum of the reaction mixture of **7** with BPh_3 in C_6D_6 at 300 K (● = C_6HD_5, ▼ = BPh_3•DMAP, ♦ = **4**+**6**, × = ferrocene, ■ = toluene).

X-ray Diffraction Analysis

Single crystals suitable for the X-ray diffraction study were obtained by recrystallization in an inert atmosphere under the following conditions; from toluene at −35 °C for **4** and from benzene at room temperature for **7**. For data collection, the single crystals coated with Apiezon grease were mounted on the glass fibre and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected using a Bruker AXS APEX II CCD diffractometer using a graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[27] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2014/7).[28] The molecular structure was analysed by using the Yadokari-XG software.[29]

Crystal data of **4** (100 K) [CCDC-2032837]: $C_{32}H_{80}Si_{12}Cl_2$; Fw 872.91; monoclinic; space group $P2_1/n$, a = 11.4596(9) Å, b = 17.1621(13) Å, c = 13.4942(10) Å, β = 112.624(2)°, V = 2449.7(3) Å^3, Z = 2, D_{calc} = 1.183 Mg m^{-3}, $R1$ = 0.0661 ($I > 2\sigma(I)$), wR_2 = 0.1657 (all data), GOF = 1.079.

Crystal data of **7** (100 K) [CCDC-2032838]: $C_{39}H_{90}Si_{12}Cl_2N_2$; Fw 995.08; triclinic; space group *P*-1, a = 13.5086(3) Å, b = 15.0599(4) Å, c = 16.6833(4) Å, α = 89.3640(10)°, β = 85.2090(10)°, γ = 76.7430(10)°, V = 3291.92(14) Å^3, Z = 2, D_{calc} = 1.162 Mg m^{-3}, $R1$ = 0.0356 ($I > 2\sigma(I)$), $wR2$ = 0.0887 (all data), GOF = 1.015.

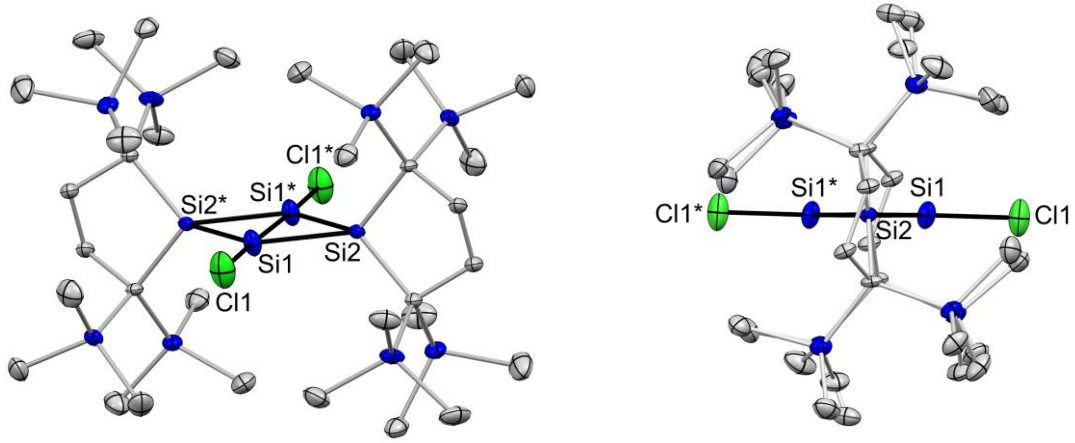


Figure 4-27. ORTEPs of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

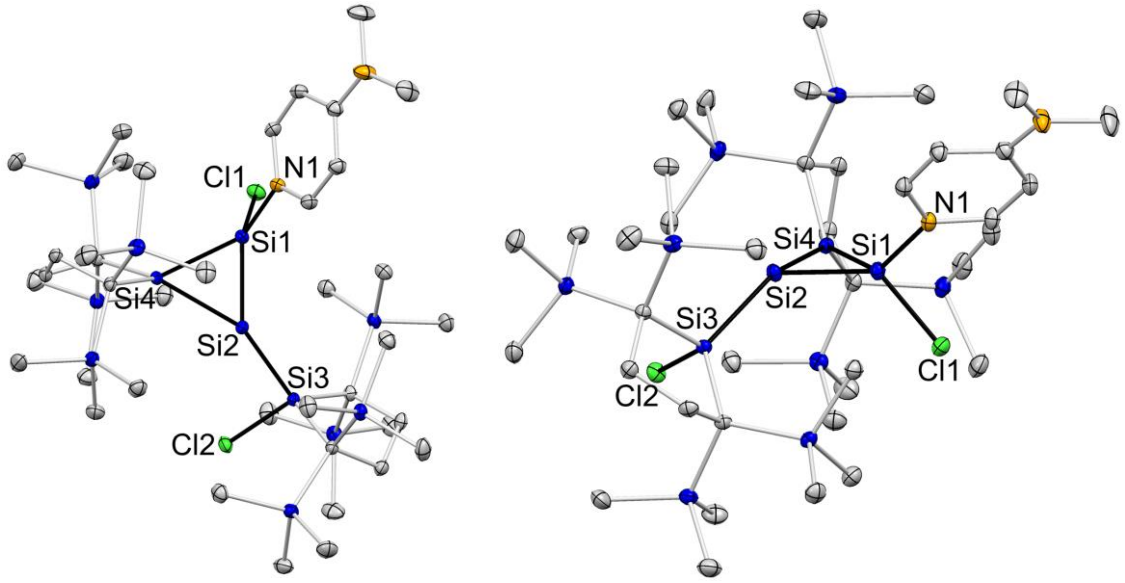


Figure 4-28. ORTEPs of **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

UV-vis Absorption Spectrum

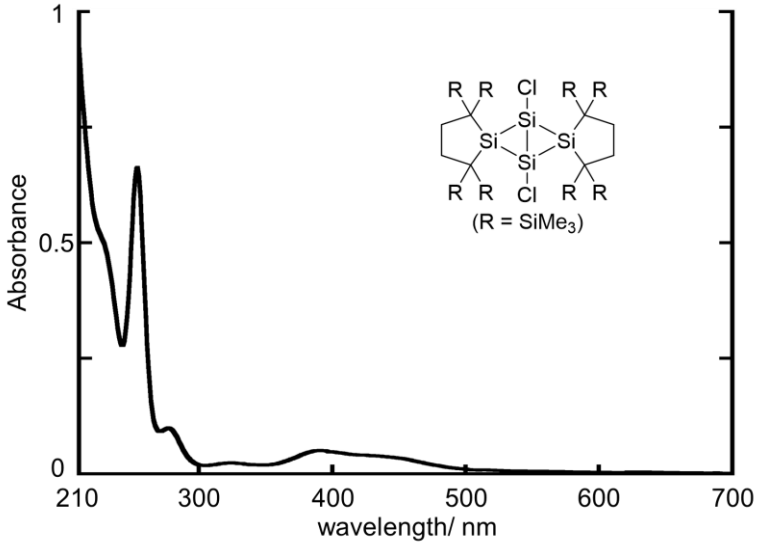


Figure 4-29. UV-vis absorption spectrum of the equilibrium mixture of **4** and **6** in hexane at room temperature.

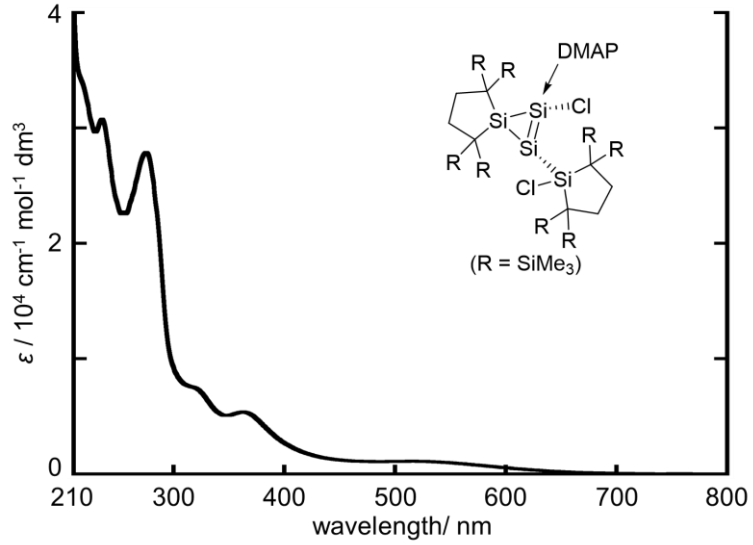


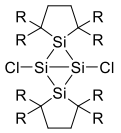
Figure 4-30. UV-vis absorption spectrum of **7**·(benzene)$_2$ dissolved in hexane at room temperature.

Computational Study

All theoretical calculations were performed using the Gaussian 09[30] program or GRRM14[31] program. Geometry optimization and frequency analyses were carried out at the B3LYP-D3/6-311G(d) level of theory. The atomic coordinates and energies of all equilibrium

and transition structures are summarized in Tables 4-2 to 4-18. Frontier Kohn-Sham orbitals and their energy levels of $\mathbf{4}_{\mathbf{opt}}$ were shown in Figure 4-31. Isotropic chemical shielding tensors were calculated at the GIAO/M06L/6-311+G(2df,p) level of theory (Tables 4-19 and 4-20). Absolute isotropic shielding tensors of the ^{29}Si nucleus in tetramethylsilane were calculated to be 361.4. Excitation energies and oscillator strengths of $\mathbf{4}_{\mathbf{opt}}$ and $\mathbf{6}_{\mathbf{opt}}$ were calculated at the B3LYP-D3/6-311G(d) level of theory (Tables 4-21 and 4-22). A possible reaction route between $\mathbf{4}_{\mathbf{opt}}$ and $\mathbf{6}_{\mathbf{opt}}$ calculated at the B3LYP-D3/B1 (basis B1: 6-311G(d) [core Si_4Cl_2], 6-31G(d) [carbon atoms in silacyclopentane rings], 3-21G* [others]) were shown in Figure 4-33. As for the isomerisation of **4** to **6**, the molecular geometries for the transition states were initially estimated by using the Reaction Plus software package,[32] based on the nudged elastic band (NEB) method[33] and subsequently optimized and confirmed by IRC calculations[34] at the B3LYP-D3/B1 level of theory (B1: 6-311G(d) [Si_4Cl_2 core], 6-31G(d) [C atoms in silacyclopentane rings], and 3-21G* [other atoms]) using the GRRM14 software package. The natural atomic orbital charges of $\mathbf{8}_{\mathbf{opt}}$ were calculated using the NBO 7.0 program.[35]

Table 4-2. Atomic Coordinates of $\mathbf{4}_{\mathbf{opt}}$ at the B3LYP-D3/6-311G(d) Level of Theory



(R = $SiMe_3$)

$\mathbf{4}_{\mathbf{opt}}$

Atom	X	Y	Z
Si	3.426576512558	7.649231326746	5.382876149481
Si	2.670897947823	9.750379906139	4.759720262665
Si	-0.172950389434	8.841661428408	3.294906639985
Si	-0.120556321694	11.352125968377	5.170816294436
Si	4.567127466580	9.962696174208	2.143886624513
Si	5.183443062327	11.815517338871	4.635731267228
Cl	3.946132147209	6.115244931738	4.031612579994
C	-0.719805232579	10.408529129037	6.700580716008
H	-0.207060136301	9.455966718530	6.838277865706
H	-1.788010165124	10.189770386584	6.641503670504
H	-0.547695666813	11.000363260100	7.601855739759
C	0.744234914891	12.926820378730	5.759144309345
H	0.909533881137	13.634642377354	4.942798733464
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H	-1.314530916336	12.795804761161	3.495531016284
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C	2.751076658847	11.909397679427	3.157541714619
H	2.561477392233	12.667205464900	3.918248842096
H	3.110679189379	12.454635159167	2.280220364728
C	3.808663177770	10.875397517517	3.675341736931
C	4.470173436127	13.022507291603	5.903479515832
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H	5.309394816154	13.562265542047	6.355439252356
C	6.225486720326	12.892903111339	3.478090923984
H	5.615112261950	13.593062959674	2.900700520259
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H	5.455155328293	10.724786875721	-0.033504845141
C	6.364854010166	10.683849637464	5.572704948949
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H	6.486891779970	8.494491235146	1.669365789719
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Si	3.597727425359	7.411719720588	7.696092344986
Si	6.441575762617	8.320438198319	9.160905967666
Si	6.389181694877	5.809973658349	7.284996313214
Si	1.701497906603	7.199403452519	10.311925983138
Si	1.085182310855	5.346582287856	7.820081340423
Cl	2.322493225973	11.046854694989	8.424200027657
C	6.988430605761	6.753570497690	5.755231891643
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H	6.816321039996	6.161736366626	4.853956867892
C	5.524390458292	4.235279247996	6.696668298306
H	5.359091492045	3.527457249373	7.513013874187

H	4.576403845511	4.401993151544	6.190032009721
H	6.185361098013	3.741459537452	5.975829518745
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C	5.639626870515	10.018845564521	9.345098252347
H	5.423207956620	10.488587664363	8.384047214646
H	4.728280011120	10.033115614121	9.937565759755
H	6.363556124208	10.666250424875	9.852726761996
C	5.310164312666	6.901811203821	8.460751575523
C	4.841817486146	5.960234117189	9.637204457836
H	4.699843120165	6.527317717028	10.557917986599
H	5.604906946348	5.214175133175	9.879287380197
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H	3.157946183803	4.707464667559	10.175592242922
C	2.459962195412	6.286702109210	8.780470870720
C	1.798451937055	4.139592335124	6.552333091819
H	2.336820578917	4.620772572241	5.735741536611
H	2.458636618737	3.388440531267	6.991426047786
H	0.959230557028	3.599834084680	6.100373355294
C	0.043138652857	4.269196515388	8.977721683667
H	0.653513111232	3.569036667053	9.555112087391
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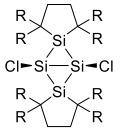
C	1.433689779214	5.961263531911	11.722326992425
H	0.939585394628	5.034547806944	11.431489891001
H	2.380521386678	5.696985100040	12.202837783386
H	0.813470044889	6.437312751006	12.489317452792
C	-0.096228636984	6.478249989263	6.883107658702
H	-0.663123587514	5.886883740119	6.157823219518
H	-0.815455924030	6.981327258139	7.529472533568
H	0.440783923235	7.246749233314	6.327689367201
C	0.059898985277	8.049492570049	9.926702418544
H	0.122763201659	8.715945291461	9.064279129794
H	-0.760423655449	7.350145556926	9.752927230716
H	-0.218266406788	8.667608391581	10.786446817931
C	2.772959925643	8.541240804593	11.103225297814
H	2.296740284427	8.811692657216	12.052366103578
H	3.790011608308	8.225759278391	11.339225412264
H	2.824078887831	9.451685338732	10.510033979435

E+ZPVE = -5662.014735 au, Free E (298.15 K) = -5662.116181 au.
Job name: TN74a

Table 4-3. Atomic Coordinates of **4′$_{opt}$** at the B3LYP-D3/6-311G(d) Level of Theory



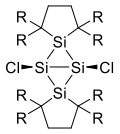
4′$_{opt}$

Atom	X	Y	Z
Si	0.046239129909	0.151398733955	1.514217209731
Si	1.955402830042	0.080222334694	-0.001523639086
Si	3.507733001013	-2.635645534416	1.230781821464
Si	3.713603330998	-2.043977059779	-1.848834757402
Si	3.330206507247	2.565733646504	1.632287123845
Si	2.519953064257	3.009825784856	-1.390597483859
Cl	0.150403651360	-1.663172365443	2.643856887386
C	3.174624099686	-3.850618794151	-2.004145630830
H	2.134025320879	-4.030202030832	-1.746282253760
H	3.791240747980	-4.534282123613	-1.419102147673
H	3.300601665762	-4.127470301487	-3.056404379353
C	3.008227277144	-1.146719235429	-3.354739423641
H	3.491231332951	-0.185200670994	-3.524744420947
H	1.931080108539	-0.988888477701	-3.346746799776
H	3.229009738616	-1.771894201561	-4.226839040563
C	5.578902786171	-2.049610780433	-2.204566223108
H	5.736253521569	-2.607181965082	-3.134031318828
H	6.179262477630	-2.534008125905	-1.432665008296
H	5.982008805600	-1.045853310050	-2.365032058007
C	5.169467379338	-3.536473110610	1.037316920690
H	6.016823840045	-2.849516878695	1.118951757719
H	5.284624688875	-4.098570153202	0.110126348147
H	5.262412919225	-4.253245535382	1.860546101269
C	2.116408872827	-3.903728674149	1.096934932800
H	1.738680528510	-4.154769273762	2.090421036041
H	2.462135221805	-4.826375886211	0.626186626407
H	1.269928373428	-3.537580933557	0.519670057341
C	3.612515994777	-1.994824826874	3.004556229105
H	2.794935015534	-1.345908679882	3.307199289753
H	4.558267658650	-1.482611082330	3.200468765559
H	3.586695780839	-2.869033237389	3.664504127897
C	3.407947068622	-1.221780938203	-0.085420453456
C	4.620260397044	-0.253877591627	0.185100087160
H	4.714347278342	-0.047839274688	1.255912274888
H	5.568859570756	-0.703512081230	-0.110053969180
C	4.397657520540	1.069931398647	-0.550600682953
H	4.391040247462	0.873405663573	-1.627896199770
H	5.231427739537	1.754123487338	-0.380903435878
C	3.028816238076	1.694538004436	-0.092001840909
C	2.485150161562	2.345943763398	-3.157146691374
H	1.800453823921	1.508662038614	-3.294432013012
H	3.469561435409	2.044010616088	-3.521511375061
H	2.141599038263	3.156424796856	-3.808992021350
C	3.781010563708	4.422276685333	-1.430928427170
H	4.792888218557	4.054788829638	-1.625231754991
H	3.814107391341	5.014584924244	-0.514727894306
H	3.525899532826	5.104487921538	-2.248594997926
C	5.110644249796	3.214227869189	1.695101060503
H	5.386824236774	3.839293258489	0.844059152811
H	5.843922292339	2.406232843661	1.768832205708
H	5.220309703681	3.825383287757	2.597069753602
C	0.812144412728	3.726643643984	-1.059979695324
H	0.417903740225	4.181922503707	-1.971591271855
H	0.808304937255	4.490142982256	-0.283987821610
H	0.104763179139	2.951816895983	-0.760171116049
C	2.206313186596	4.044199450556	1.977988674714
H	1.148567651896	3.783900884362	1.993732878126
H	2.341286541754	4.881259449975	1.291537419488
H	2.458737455917	4.408662166163	2.979427670003
C	3.173235384924	1.491617991124	3.177138516699
H	3.339232687232	2.145041578822	4.040798720457
H	3.919992803724	0.701197602808	3.230252764759
H	2.190892438513	1.035478531607	3.307452712997
Si	-0.015432009605	-0.258433332272	-1.348812380223
Si	-1.934286688467	-0.011529513771	0.064474333069
Si	-3.049125707586	2.781294500330	-1.507359245704
Si	-3.128140595572	2.534571891475	1.658625373924
Si	-3.769159107082	-2.180476624250	-1.557369055702
Si	-3.153415980303	-2.832377852027	1.469982639878
Cl	0.008034243465	-2.367407054145	-1.761085423038
C	-1.579198357132	3.596016748884	1.876980812427
H	-0.767377861610	3.277563539028	1.226605335224
H	-1.765067548621	4.652529036049	1.675635687407
H	-1.217447314220	3.511636819367	2.905129957878
C	-3.243219871154	1.507864099666	3.243760058882
H	-4.149834898490	0.907340483872	3.331179762389
H	-2.386032616578	0.850627672635	3.395378660655
H	-3.249456197171	2.216951870307	4.079673435910
C	-4.681607328394	3.626792605725	1.707529746254
H	-4.535709731210	4.429483496316	2.437842179496
H	-4.939053734587	4.096197773234	0.756667477378
H	-5.554290042279	3.055289883615	2.036455093679
C	-4.787010493077	2.939527945172	-2.254719254098
H	-5.108529037182	2.050882767215	-2.803842638690
H	-5.556143734776	3.164074077922	-1.511619979925
H	-4.774302436624	3.768499330076	-2.969718716116
C	-2.585024586905	4.565976804132	-1.069890632049
H	-2.622028984629	5.134959609998	-2.005379698565
H	-3.285815982037	5.041977345725	-0.382143311621
H	-1.584058378739	4.685596401736	-0.664074106691
C	-1.933901167110	2.314217846783	-2.959843797746
H	-0.872861779222	2.278649849362	-2.719320515174
H	-2.196457286064	1.362007319043	-3.418853405405
H	-2.066252356021	3.089567516613	-3.723375654516
C	-3.120164715467	1.533706183640	-0.001836155430
C	-4.517244801355	0.800747133484	-0.094221098081
H	-4.774068488398	0.591511137923	-1.134079314451
H	-5.324482258054	1.437620207758	0.278444577869
C	-4.496211188540	-0.526716098414	0.658354910822
H	-4.414875897215	-0.333983051003	1.728381392740
H	-5.448514322284	-1.043338267861	0.522977641641
C	-3.286970637007	-1.405592361400	0.173987017687
C	-3.150713192593	-2.156393731440	3.237725563364
H	-2.469535846102	-1.327518662054	3.410088245684
H	-4.152878892981	-1.842076019378	3.542543887807
H	-2.847078747567	-2.961314552692	3.914923742810
C	-4.753900735600	-3.856418804206	1.432895394647
H	-5.642202606622	-3.242107895361	1.604360030573
H	-4.912293551020	-4.426457381223	0.516597690392
H	-4.706225748189	-4.579607348826	2.254704484619
C	-5.659126602310	-2.293625843590	-1.683844562988
H	-6.118662247554	-2.855536573348	-0.868727008887
H	-6.145215658942	-1.315612460351	-1.733318334340
H	-5.901978278800	-2.817790750834	-2.614304794563
C	-1.716108635774	-4.018394027653	1.182124992255
H	-1.279859015535	-4.324433158318	2.135881474710
H	-2.048810276670	-4.918969971589	0.661286703275
H	-0.915947989586	-3.574862328337	0.594502359359
C	-3.135443067621	-3.935760625912	-1.856940945356
H	-2.070152293509	-4.058110438796	-1.677617915036

H	-3.666406481321	-4.682692135809	-1.264336719210
H	-3.317371196907	-4.173506054547	-2.910562170391
C	-3.274371939222	-1.157633317045	-3.067862749163
H	-3.675543031412	-1.660993932184	-3.954099119083
H	-3.703743691017	-0.154431009239	-3.051641445367
H	-2.197588195512	-1.068876009769	-3.212792396861

E+ZPVE = -5662.015099 au, Free E (298.15 K) = -5662.115585 au.
Job name: TN77_120

Table 4-4. Atomic Coordinates of **4″$_{opt}$** at the B3LYP-D3/6-311G(d) Level of Theory

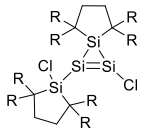


(R = $SiMe_3$)
4″$_{opt}$

Atom	X	Y	Z
Si	0.014068944318	-0.535434852494	-1.221652352238
Si	-0.014014166300	-0.535545780029	1.221567004735
Si	-1.917875946116	-0.014506260642	-0.032858896267
Si	1.917823544590	-0.014114763148	0.032819642230
C	2.970274432568	1.606633314460	0.097194001488
C	4.371476614058	0.999804656319	0.496447407864
C	4.610117586361	-0.372661770747	-0.151444447356
C	3.368683164514	-1.323018845375	0.009104789978
C	-3.368466361742	-1.323710773693	-0.009259817590
C	-4.610096194836	-0.373623220361	0.151373457995
C	-4.371737478339	0.998949548294	-0.496397010739
C	-2.970660115899	1.606031035328	-0.097089924879
Cl	0.035476111291	-1.232247505078	-3.209311456760
Cl	-0.035278016671	-1.232538607296	3.209164474746
Si	3.075062531116	2.536866760213	-1.615129452455
C	4.745531229425	2.234127320840	-2.455784450884
C	2.905763077138	4.426714631607	-1.521832603152
C	1.753248986757	2.076859025414	-2.886579338197
Si	2.585894294924	2.822132577859	1.546967469191
C	2.304373475012	1.978413358461	3.214245181425
C	1.085519224474	3.941848657273	1.329622016600
C	4.130450653154	3.887962214109	1.832751867880
Si	3.358642949659	-2.487470877920	-1.526051089495
C	1.878961987542	-3.668267735095	-1.561221677790
C	4.921410529923	-3.557312992665	-1.607163180687
C	3.455951299964	-1.466113964021	-3.118258349256
Si	3.554995859541	-2.362124298046	1.625168564460
C	3.575294485736	-1.313890875258	3.192842569260
C	5.221857912171	-3.267939384075	1.694547733484
C	2.216697341350	-3.684515089862	1.786914935549
Si	-2.586529964464	2.821737534111	-1.546755883908
C	-1.086385191048	3.941742912317	-1.329311390139
C	-4.131305478282	3.887274783800	-1.832446032892
C	-2.304835656563	1.978223685099	-3.214108206112
Si	-3.075639497234	2.536091469369	1.615315791837
C	-1.753731369629	2.076243126488	2.886725001257
C	-4.746045894839	2.232934161117	2.455943997324
C	-2.906728690971	4.425982360723	1.522186083756
Si	-3.554565377649	-2.362711589465	-1.625415486577
C	-3.575079584696	-1.314343721251	-3.192996779016
C	-5.221241116674	-3.268863303577	-1.694874781336
C	-2.215994942311	-3.684812824888	-1.787278797925
Si	-3.358186665999	-2.488296482450	1.525793071110
C	-3.455705039693	-1.467100421199	3.118090653198
C	-1.878262906432	-3.668792127232	1.560859242318
C	-4.920734201673	-3.558467123897	1.606810530274
H	4.422743542737	0.872502830776	1.582031271004
H	5.191574532515	1.676260923613	0.243634733305
H	4.835484537341	-0.214723533206	-1.207875075932
H	5.514198596204	-0.818490184108	0.274023020464
H	-4.835495611113	-0.215824764402	1.207818048546
H	-5.514085505744	-0.819599916324	-0.274133445723
H	-4.422978236450	0.871733192714	-1.581992128752
H	-5.191974488980	1.675214788297	-0.243524518415
H	4.887461269216	1.200156523622	-2.773788614657
H	4.784777163651	2.852688175944	-3.358298254698
H	5.601388476493	2.516713247502	-1.837393526864
H	1.865062683358	4.736433911829	-1.412261449261
H	3.249426613059	4.818650584184	-2.485248426513
H	3.489492088788	4.924532330051	-0.747892141755
H	1.836155192496	2.790158140133	-3.714105491187
H	1.862400157960	1.082737686195	-3.317147691182
H	0.736139575062	2.160827557379	-2.505160988031
H	3.176521371890	1.432265531106	3.572995071180
H	2.108450940518	2.773657605859	3.942085023863
H	1.448134316480	1.304270161776	3.250202867084
H	1.220170913910	4.739643851520	0.601853887175
H	0.871734605497	4.409900183704	2.295835250726
H	0.195608315762	3.382648395308	1.047417968991
H	3.873984044655	4.757045584142	2.447247876390
H	4.891867809199	3.323170026269	2.377968708598
H	4.597144502208	4.260294474050	0.919517663293
H	1.506757856311	-3.791887594851	-2.580437177354
H	2.165647386093	-4.655780072395	-1.191199151236
H	1.041767684076	-3.329755030128	-0.950071698748
H	5.826480806105	-3.007067899699	-1.336587097466
H	5.047605344131	-3.901221800133	-2.639544475776
H	4.870971567333	-4.446659747089	-0.977374096736
H	2.874185971090	-0.548038820538	-3.101934492047
H	4.492508339235	-1.201988919747	-3.346602589685
H	3.082584407243	-2.061986753536	-3.955830832539
H	4.445956461111	-0.653033750650	3.228285916689
H	2.681620872672	-0.715837551383	3.343641050221
H	3.654202855490	-1.990155837748	4.050720984132
H	5.256865462590	-4.167630020640	1.080821220688
H	5.388618932966	-3.578788183237	2.731467195216
H	6.073977505560	-2.644338687912	1.412173507229
H	1.215845403124	-3.335499370856	1.535992023569
H	2.429480820438	-4.549456408646	1.154703979436
H	2.179864618478	-4.036342970515	2.822376157090
H	-0.196359300215	3.382700714391	-1.047156791558
H	-0.872696839201	4.409923843881	-2.295483223775
H	-1.221200935942	4.739446031470	-0.601472707283
H	-4.892606474844	3.322374245572	-2.377712828973
H	-3.875017605982	4.756465220290	-2.446865174393
H	-4.598075878518	4.259430292792	-0.919178906824
H	-1.448457880317	1.304259769229	-3.250125505487
H	-3.176871224096	1.431928244090	-3.572906404048
H	-2.109076673157	2.773572574241	-3.941877712028
H	-0.736639250864	2.160454555660	2.505314088062
H	-1.836784254570	2.789451986919	3.714314234873
H	-1.862678095621	1.082061285734	3.317205430858
H	-5.601961242642	2.515398766311	1.837578060013
H	-4.785419025782	2.851407110997	3.358512503157
H	-4.887763294792	1.198906077704	2.773856713544
H	-3.250472811678	4.817762424695	2.485636563282
H	-1.866092013320	4.735925341597	1.412642331522
H	-3.490560072491	4.923748451809	0.748289647384
H	-3.653848888098	-1.990549022839	-4.050935000544
H	-4.445877445876	-0.653662528395	-3.228381687610
H	-2.681528980324	-0.716093293528	-3.343742359054
H	-5.387938217962	-3.579654683206	-2.731821732189
H	-6.073488931663	-2.645462833014	-1.412445412302
H	-5.256063641262	-4.168615395182	-1.081227840456
H	-1.215214797323	-3.335613483284	-1.536325010658
H	-2.428600537766	-4.549853793608	-1.155144342165
H	-2.179089876961	-4.036541545320	-2.822771130957
H	-4.492316371736	-1.203208744250	3.346458242691
H	-3.082215607251	-2.062970489089	3.955610437242
H	-2.874128523515	-0.548904218197	3.101847996479
H	-2.164745222426	-4.656330671024	1.190749378400
H	-1.506033351635	-3.792425580936	2.580063808263
H	-1.041138240660	-3.330053212996	0.949739211553
H	-5.046858279693	-3.902493178891	2.639161404670
H	-5.825917617937	-3.008384240622	1.336283103898
H	-4.870112353565	-4.447747784432	0.976942794866

E+ZPVE = -5662.009600 au, Free E (298.15 K) = -5662.114172 au.
Job name: TN84a

Table 4-5. Atomic Coordinates of $\mathbf{6_{opt}}$ at the B3LYP-D3/6-311G(d) Level of Theory

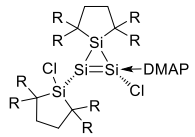


(R = $SiMe_3$)
$\mathbf{6_{opt}}$

Atom	X	Y	Z
Si	1.363988011651	-0.283086132932	2.165756268604
Cl	1.573506886984	-0.936467386215	4.149445204140
Si	-0.006327710814	0.053109499715	0.575559806585
Si	-2.278026608889	0.114055292979	-0.196690224673
Si	2.367531314892	-0.112741788327	0.106832520116
Cl	-1.774409026782	-0.083289790065	-2.278400234616
Si	-4.448760138142	-2.049084914801	-1.258046275841
C	-3.234212967586	-3.084177325880	-2.275028764133
H	-3.664310826705	-4.068587479274	-2.484162602220
H	-2.275674593459	-3.245765652854	-1.787252390893
H	-3.029531278001	-2.597511194711	-3.230584119567
C	-5.858595063666	-3.186339629140	-0.690529319362
H	-6.632618551054	-2.651261365936	-0.133829536752
H	-5.549016743150	-4.044254623198	-0.092868119903
H	-6.336646810410	-3.579191932854	-1.594675522423
C	-5.321516203117	-0.870225307094	-2.447535967066
H	-4.664580400932	-0.114424565830	-2.872243548173
H	-6.182451290170	-0.369644824650	-1.997095579678
H	-5.704702866977	-1.471291538472	-3.279821726866
C	-2.674264411986	-4.186474802190	0.827057308663
H	-1.704287804778	-4.083008661038	0.337387960233
H	-3.359322497244	-4.641043863487	0.111254510829
H	-2.541896801989	-4.899080996142	1.648279982025
C	-1.931914174874	-2.178462809767	2.878759545983
H	-1.968294337865	-2.993097117865	3.610703839849
H	-2.078891465802	-1.251605168795	3.430157328853
H	-0.925290477108	-2.168581578933	2.462847157185
Si	-3.249410725293	-2.552573237787	1.584983615850
C	-4.820528952287	-2.863100254672	2.599266694957
H	-4.667225284477	-3.755851723796	3.214563376408
H	-5.722360606146	-3.023995925782	2.009668503556
H	-5.019050216450	-2.036143661786	3.287010591664
C	-3.635079223549	-1.164168447517	0.278075040554
C	-4.713141052217	-0.194081361213	0.910084719831
H	-5.715995539852	-0.628238596732	0.846933109505
H	-4.525531414626	-0.059287067486	1.979287704288
C	-4.696226525022	1.187788798577	0.234342889672
H	-5.350709514697	1.874337354289	0.779210692403
H	-5.127744149359	1.095970291370	-0.762262199097
C	-3.229354677482	1.739328955533	0.134817804397
Si	-2.749041582746	2.594996187123	1.807433213841
C	-2.345366077713	1.430781155445	3.240766389946
H	-1.456438057920	0.821205389077	3.082702659121
H	-3.175424332251	0.770231729096	3.499626399991
H	-2.146937752200	2.050769999509	4.121978494142
C	-4.220947576735	3.591626362680	2.460736584125
H	-3.870048091383	4.250154447839	3.262321812629
H	-4.973949590592	2.932427997509	2.903037059143
H	-4.720305209864	4.215658981444	1.720720369199
C	-1.235805159304	3.709509249454	1.621135992223
H	-1.001691853548	4.152668069683	2.594398430691
H	-1.355736431036	4.526873311492	0.908939106521
H	-0.358945478742	3.134089630896	1.318239970432
Si	-3.090508740368	3.052541112217	-1.277747716473
C	-3.868445012011	4.711361907549	-0.788920142064
H	-3.394452118812	5.214575392204	0.055012633667
H	-4.934608320246	4.612144814318	-0.565521975671
H	-3.786689976986	5.382032133564	-1.651260182366
C	-1.284291494630	3.340923909192	-1.753834405983
H	-1.096116569183	2.994955651404	-2.771893305558
H	-0.588279633437	2.807659272204	-1.107426901372
H	-1.019364148477	4.400048794535	-1.704490450877
C	-4.044713182858	2.576064765261	-2.837449547455
H	-3.989730942037	3.427056429590	-3.525578460443
H	-5.105122689877	2.380677538406	-2.661402984327
H	-3.617221972004	1.716614523166	-3.352081197973
C	1.472117697722	-1.762569427416	-3.496930039818
H	0.900322410858	-2.494480875657	-4.078194761940
H	2.286618999482	-1.415804617794	-4.137747527325
H	0.804166277452	-0.926309719517	-3.300373649558
C	0.481342582481	-3.181545718363	-1.032691810774
H	-0.309233856700	-2.447630698858	-1.197183564043
H	0.596054386140	-3.306414762785	0.041838050322
H	0.131227106106	-4.132000510691	-1.448009849328
Si	2.053417007677	-2.636289165933	-1.929198725929
C	2.930707196770	-4.183668641089	-2.588376670196
H	3.235328371150	-4.901883355796	-1.825541455465
H	3.815025656302	-3.928563558675	-3.179618744538
H	2.237463604203	-4.700592466293	-3.260606315889
Si	4.110962001920	-2.770721643421	0.415051448686
C	5.580589645675	-3.592754499265	-0.454551094805
H	6.416482653456	-2.892517932223	-0.546525888899
H	5.367604778169	-3.985826569582	-1.447778693507
H	5.934829475489	-4.426451850327	0.160852650385
C	2.953074504458	-4.087584011829	1.125518304187
H	3.537325207669	-4.716231940205	1.805498711795
H	2.486735094666	-4.746525465580	0.392374005394
H	2.156280441013	-3.634517245053	1.722586804683
C	4.894578379641	-2.000658185550	1.950250059398
H	4.180915441627	-1.555297045670	2.643386753971
H	5.657086492847	-1.256672121174	1.722841347993
H	5.393922826543	-2.812234942640	2.491522456807
C	3.214941567299	-1.568149855009	-0.821013309750
C	4.276462399229	-0.799448743466	-1.686631456778
H	5.113974495467	-1.440962548256	-1.976287070386
H	3.825121922540	-0.460404131947	-2.624695531211
C	4.793654198627	0.435207823451	-0.922442202387
H	5.457420174863	1.023512767444	-1.561038762132
H	5.416003880778	0.089158263764	-0.090941397262
C	3.588850326551	1.290629496624	-0.379716351906
C	1.684404623989	1.666294403199	-2.953030214248
H	0.817468194085	1.224561469072	-2.462276299533
H	2.145534499993	0.902006969149	-3.578350785335
H	1.305204075608	2.443520640528	-3.624460123017
C	2.111266058777	4.027866583149	-1.117503740940
H	1.619534005905	4.529093686847	-1.956595161723
H	2.826242905742	4.734059149214	-0.691688864818
H	1.345574616316	3.837477408786	-0.366050816370
C	5.095520763219	1.400385034181	2.431523987133
H	5.420873085165	2.120304049570	3.190463823180
H	5.993579031968	0.895378475808	2.070903159213
H	4.472440374856	0.663158803412	2.938198726586
C	4.366575210689	2.994452471112	-2.888297478350
H	4.010796799902	3.769171222578	-3.575814285819
H	4.738855059314	2.170441552887	-3.503954280833
H	5.214082678485	3.409061140234	-2.339427325856
C	5.463032699696	3.637173563799	0.489832495771
H	5.887311971664	4.161897868590	1.352249704766
H	5.057299669061	4.396054469018	-0.181661654547
H	6.292971428967	3.146571885526	-0.027766013748
Si	4.182202360548	2.378620996921	1.098314998564
C	2.792698343951	3.296627971372	2.000449200956
H	1.832467650226	2.784983496178	1.926018414593
H	2.653345886681	4.315877013537	1.637301025205
H	3.038746661854	3.359683331315	3.064976425555
Si	2.928719379561	2.456182882698	-1.778681126178

E+ZPVE = -5662.013986 au, Free E (298.15 K) = -5662.118815 au.
Job name: TN82b

Table 4-6. Atomic Coordinates of $\mathbf{7_{opt}}$ at the B3LYP-D3/6-311G(d) Level of Theory



(R = $SiMe_3$)
$\mathbf{7_{opt}}$

Atom	X	Y	Z
Si	6.884435984688	6.344769881054	3.454344172786
Cl	6.706112004557	6.934556092182	1.396937961969
Si	7.631356757162	4.517174505236	4.458935524748
Si	9.162419709486	2.856001411234	3.679864470090
Si	5.273017905998	4.980033182641	4.411083166936
Cl	7.794668865151	1.183633995159	3.691607255698
Si	9.890512472773	1.265654445062	0.915523397829
C	8.130225064325	1.032295531044	0.277471860815
H	8.168253112981	0.281385841564	-0.520107389446
H	7.693016216392	1.933605314234	-0.147382442783
H	7.450433038306	0.666141902614	1.044926048508
C	10.980592801130	1.324602108766	-0.638711265613
H	12.027628431238	1.561204212052	-0.435978817858
H	10.617482665475	2.023739474872	-1.394596603726
H	10.956736214059	0.326289827999	-1.088978762229
C	10.402280759389	-0.358541784158	1.737174024822
H	9.887353009700	-0.554427687713	2.675155062893
H	11.479797437108	-0.420426174711	1.912556314327
H	10.145608844866	-1.171146487253	1.048449570959
C	8.679099287887	4.449106974468	-0.259201526411
H	7.728427400107	4.316061087253	0.257052375843
H	8.745892485995	3.698812883153	-1.050070691732
H	8.643541827887	5.431003327168	-0.740247159046

C	10.197159610452	6.056640845936	1.828802124131
H	9.955753060340	6.835336759090	1.098719916519
H	11.187141644674	6.278072325944	2.229578598408
H	9.471532216972	6.141036241659	2.633745539779
Si	10.155497976783	4.402996361793	0.911286987843
C	11.737576757432	4.526166567820	-0.135041671196
H	11.798956112896	5.547255635864	-0.527377943749
H	11.774904235099	3.850224803826	-0.987675585234
H	12.641101535194	4.361118565874	0.458773669795
C	10.204471473019	2.828677127782	2.036434197784
C	11.669675973864	2.715933938953	2.615237614290
H	12.349573666299	2.256844836489	1.888940885455
H	12.081378508243	3.714316906090	2.803472465460
C	11.699252819607	1.920036837838	3.930746518729
H	12.701070472881	1.966870943427	4.369733021276
H	11.528492850915	0.868603926596	3.701581882972
C	10.596360963003	2.436912563065	4.918237491417
Si	11.279131520466	3.947751429738	5.905309998766
C	11.378503003566	5.584319810811	4.963361260105
H	10.436142586746	5.891232513506	4.518413989524
H	12.127927114605	5.562654769942	4.170043542805
H	11.682433386753	6.365564470788	5.669961792245
C	13.092918928759	3.665764184952	6.388287880855
H	13.386592769637	4.435927879373	7.110081780573
H	13.747430527608	3.783857132716	5.519228412943
H	13.312060670521	2.698388420319	6.836941482508
C	10.258215383234	4.350624966787	7.445953773027
H	10.744177810052	5.170641452542	7.986212424735
H	10.132255740458	3.526537730879	8.148747537867
H	9.261008683896	4.692738850985	7.158734971998
Si	10.171776081854	1.060017247408	6.211493938789
C	11.505126823213	0.884630675304	7.555624436804
H	11.651203564912	1.761681034440	8.187972336202
H	12.476227863898	0.604563506970	7.137472596124
H	11.194827282649	0.063749215348	8.211739491147
C	8.525415885974	1.400418123933	7.075719653938
H	7.762333267422	0.702630313601	6.728575064199
H	8.146530730385	2.404308639918	6.885732334594
H	8.617219983886	1.287283236946	8.160147857907
C	10.126353070772	-0.682082502894	5.476242281694
H	9.978255323754	-1.382620391166	6.305901941500
H	11.060430139312	-0.967186075048	4.985436213170
H	9.309268846968	-0.832595978018	4.773199611294
C	4.149685699349	1.303621887891	3.272634801334
H	4.240368990880	0.496548434205	2.536967044597
H	3.309811935688	1.046317187852	3.923418743526
H	5.061430470789	1.297490577761	3.862847961769
C	5.334374404730	3.098724271046	1.141733381827
H	6.264763423401	2.984432296442	1.701291431629
H	5.367013110161	4.062816137740	0.636118050794
H	5.318016061783	2.317537992474	0.376651270454
Si	3.876224778153	2.904794506131	2.314579047435
C	2.273830395963	2.525937899644	1.362093577593
H	1.944392356517	3.287195067350	0.654885926762
H	1.449117103788	2.345661254355	2.059436058422
H	2.417319042178	1.598442131671	0.797328445169
Si	2.877198264464	5.858073093427	2.320433341270
C	0.985649258586	5.709301555131	2.389826381940
H	0.584182732383	5.985798371310	3.369095313887
H	0.616562311023	4.710736664479	2.148134428000
H	0.553976658654	6.402436900953	1.660077434300
C	3.347856277531	5.839531452606	0.485130997580
H	2.736274815267	6.606150085868	-0.004082078354
H	3.160912111212	4.900302230651	-0.034423496581
H	4.389524269409	6.111912761113	0.321640240111
C	3.214684450091	7.643896070053	2.846089565961
H	4.277833858283	7.881577911200	2.869872087046
H	2.788067247523	7.893055756789	3.816862288922
H	2.750115390133	8.303909261428	2.105382515197
C	3.667000626435	4.461493890399	3.418255940558
C	2.689613895225	4.154741474763	4.609711351305
H	1.643600651246	4.147294758569	4.293938631506
H	2.880920836846	3.153537391548	5.008008062408
C	2.903804667158	5.174083140841	5.740333575567
H	2.249224234055	4.949529854861	6.587145048045
H	2.592112212062	6.161347846332	5.380057508346
C	4.418439547971	5.188135545108	6.151801981038
C	5.084224293345	2.042458403743	6.515806095343
H	5.884482381781	2.063023186830	5.777518462907
H	4.191197761821	1.642635722164	6.035711155055
H	5.381262904357	1.327113456775	7.289298959079
C	6.224007640778	3.988606178462	8.515081011688
H	6.429077417633	3.047832636960	9.035320894185
H	6.026974994585	4.744710931228	9.277829321932
H	7.135917091294	4.271109689551	7.989767135652
C	4.326839738472	8.363227289242	6.083910398144
H	4.638388689310	9.242605072249	6.658517651839
H	3.249324615349	8.448996771695	5.928206469677
H	4.811147148009	8.418713795655	5.109745169477
C	3.239408345351	3.396084643961	8.437525737855
H	3.500922497653	2.664459512586	9.209628795518
H	2.409143914582	2.970678758291	7.866140499888
H	2.869637049704	4.288928585823	8.945121830774
C	3.799755836647	6.949183002591	8.664316477733
H	3.923465567383	7.948672478607	9.095278112670
H	4.103174425143	6.228736813482	9.427029208326
H	2.730794722705	6.806083472980	8.480537916159
Si	4.814736515011	6.820459191961	7.066121981174
C	6.642193559291	7.043662369994	7.521215951046
H	7.291628242479	6.404605678859	6.921651678847
H	6.831869283150	6.811899147056	8.570860439883
H	6.943065079513	8.081762466002	7.354296422039
N	7.547303125255	8.063234931981	4.063570394935
C	7.034178886483	9.247988483720	3.650935884018
H	6.264035344796	9.197523901056	2.893629371341
C	8.526213477093	8.097931277436	4.995038412186
H	8.895900475505	7.133481037935	5.315257866006
C	9.018696486764	9.263448335631	5.524238053647
H	9.804784545552	9.188675070777	6.261370511560
C	7.454827228922	10.456513705905	4.143451975229
H	6.981357642050	11.350020000665	3.763167055700
C	8.485664226007	10.513398343423	5.118943428474
C	8.338689692435	12.949731421388	5.196881211596
H	8.481189720816	13.109470286791	4.123537506984
H	8.817768858467	13.771052510005	5.724074410188
H	7.267139659394	12.987230851416	5.416596483284
N	8.928602604797	11.687673872804	5.631802879216
C	9.991038711295	11.695761645627	6.632684575275
H	9.694777353097	11.151522826637	7.534949826820
H	10.210295195893	12.722201740964	6.916154724474
H	10.910904909203	11.249799397485	6.242208065243
Si	4.763130886256	3.701649727574	7.347953859199

E+ZPVE = -6044.246139 au, Free E (298.15 K) = -6044.360196 au.
Job name: TN89aa

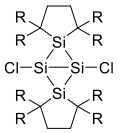
Table 4-7. Atomic Coordinates of DMAP at the B3LYP-D3/6-311G(d) Level of Theory

DMAP

Atom	X	Y	Z
C	0.116393688261	1.954810875699	1.127461148265
C	0.041833835269	0.570732503475	1.195476961091
C	-0.048338599381	-0.179654153087	0.001988222332
C	-0.038985701887	0.571413273443	-1.194438464087
C	0.040025362950	1.955454151622	-1.130827442299
N	0.116404034527	2.670142884855	-0.002771095535
N	-0.141650999718	-1.551293154611	0.004753045848
C	-0.008717173305	-2.280702150348	1.254515091337
C	-0.093464507734	-2.279988295231	-1.251549270332
H	0.183637279640	2.527194958881	2.050508490901
H	0.056020927755	0.094617360403	2.166970934300
H	-0.090470957294	0.095851310502	-2.164942215195
H	0.044768459794	2.528364697354	-2.055982913358
H	0.969361286594	-2.122774910516	1.727855781557
H	-0.783529087147	-1.987368393162	1.969776642583
H	-0.124964357548	-3.346427669618	1.065236073071
H	0.850405258333	-2.121772904140	-1.789794242945
H	-0.196679591288	-3.345823588241	-1.055455895310
H	-0.914821275771	-1.986262475186	-1.912666116180

E+ZPVE = -382.190399 au, Free E (298.15 K) = -382.224206 au.
Job name: DMAPaaa

Table 4-8. Atomic Coordinates of $\mathbf{4_{opt}}$ at the B3LYP-D3/B1 Level of Theory



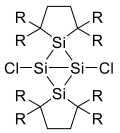
(R = $SiMe_3$)

$\mathbf{4_{opt}}$

Atom	X	Y	Z
Si	0.309507000000	-0.922790000000	-0.844861000000
Si	-0.465330000000	1.166035000000	-1.464725000000
Si	-0.309507000000	0.922790000000	0.844861000000
Si	0.465330000000	-1.166035000000	1.464725000000
Cl	0.864324000000	-2.445754000000	-2.199901000000
Cl	-0.864324000000	2.445754000000	2.199901000000
C	-2.166200000000	1.673007000000	-2.226262000000
C	-1.704053000000	2.647278000000	-3.381926000000
C	-0.375925000000	3.343461000000	-3.024947000000
C	0.670948000000	2.285497000000	-2.532226000000
C	2.166200000000	-1.673007000000	2.226262000000
C	1.704053000000	-2.647278000000	3.381926000000
C	0.375925000000	-3.343461000000	3.024947000000
C	-0.670948000000	-2.285497000000	2.532226000000
H	-1.561533000000	2.105690000000	-4.323886000000
H	-2.472547000000	3.404505000000	-3.595957000000
H	-0.563377000000	4.086033000000	-2.241509000000
H	-0.008597000000	3.906672000000	-3.894388000000
H	1.561533000000	-2.105690000000	4.323886000000
H	2.472547000000	-3.404505000000	3.595957000000
H	0.563377000000	-4.086033000000	2.241509000000
H	0.008597000000	-3.906672000000	3.894388000000
Si	-3.266039000000	0.254583000000	-2.926644000000
Si	-3.248808000000	2.740004000000	-1.059934000000
Si	1.384593000000	1.380472000000	-4.066754000000
Si	2.058456000000	3.177976000000	-1.580908000000
Si	3.266039000000	-0.254583000000	2.926644000000
Si	3.248808000000	-2.740004000000	1.059934000000
Si	-1.384593000000	-1.380472000000	4.066754000000
Si	-2.058456000000	-3.177976000000	1.580908000000
C	-3.867558000000	1.803481000000	0.466928000000
H	-3.315665000000	0.874878000000	0.646654000000
H	-4.927081000000	1.542555000000	0.364776000000
H	-3.748880000000	2.432961000000	1.356995000000
C	-2.396901000000	4.320394000000	-0.462249000000
H	-2.249358000000	5.032827000000	-1.283926000000
H	-1.437215000000	4.151307000000	0.031547000000
H	-3.062153000000	4.797736000000	0.272126000000
C	-4.744334000000	3.406656000000	-2.028414000000
H	-5.510187000000	3.737214000000	-1.312290000000
H	-5.205255000000	2.676459000000	-2.700742000000
H	-4.458249000000	4.281710000000	-2.626977000000
C	-3.821827000000	0.732906000000	-4.675444000000
H	-3.004643000000	0.676965000000	-5.405556000000
H	-4.241242000000	1.746082000000	-4.714280000000
H	-4.602643000000	0.030725000000	-4.998801000000
C	-4.860644000000	-0.104098000000	-1.964085000000
H	-5.374452000000	-0.906904000000	-2.513436000000
H	-5.551978000000	0.740029000000	-1.889532000000
H	-4.661885000000	-0.476062000000	-0.955447000000
C	-2.471979000000	-1.455339000000	-3.053739000000
H	-2.300282000000	-1.906008000000	-2.069689000000
H	-1.531590000000	-1.476733000000	-3.605958000000
H	-3.185478000000	-2.102765000000	-3.585052000000
C	1.369372000000	4.371414000000	-0.285718000000
H	0.815788000000	3.866800000000	0.512323000000
H	0.716772000000	5.139299000000	-0.718213000000
H	2.220710000000	4.886092000000	0.182505000000
C	3.102289000000	4.251308000000	-2.741956000000
H	2.483562000000	4.964834000000	-3.302294000000
H	3.677799000000	3.658834000000	-3.463000000000
H	3.814964000000	4.830505000000	-2.138289000000
C	1.643434000000	2.622535000000	-5.476577000000
H	2.161131000000	3.539105000000	-5.179120000000
H	0.682657000000	2.902411000000	-5.929797000000
H	2.242268000000	2.132336000000	-6.257450000000
C	3.246557000000	2.031595000000	-0.667539000000
H	3.837256000000	2.631179000000	0.038828000000
H	3.940905000000	1.514074000000	-1.336362000000
H	2.708121000000	1.274381000000	-0.090004000000
C	3.030002000000	0.519960000000	-3.718063000000
H	2.963934000000	-0.169641000000	-2.868385000000
H	3.846874000000	1.225111000000	-3.526706000000
H	3.298426000000	-0.075044000000	-4.602250000000
C	0.287912000000	0.049599000000	-4.849686000000
H	0.672864000000	-0.128295000000	-5.864644000000
H	-0.765206000000	0.329937000000	-4.942632000000
H	0.343678000000	-0.898543000000	-4.309349000000
C	3.867558000000	-1.803481000000	-0.466928000000
H	3.315665000000	-0.874878000000	-0.646654000000
H	4.927081000000	-1.542555000000	-0.364776000000
H	3.748880000000	-2.432961000000	-1.356995000000
C	2.396901000000	-4.320394000000	0.462249000000
H	2.249358000000	-5.032827000000	1.283926000000
H	1.437215000000	-4.151307000000	-0.031547000000
H	3.062153000000	-4.797736000000	-0.272126000000
C	4.744334000000	-3.406656000000	2.028414000000
H	5.510187000000	-3.737214000000	1.312290000000
H	5.205255000000	-2.676459000000	2.700742000000
H	4.458249000000	-4.281710000000	2.626977000000
C	3.821827000000	-0.732906000000	4.675444000000
H	3.004643000000	-0.676965000000	5.405556000000
H	4.241242000000	-1.746082000000	4.714280000000
H	4.602643000000	-0.030725000000	4.998801000000
C	4.860644000000	0.104098000000	1.964085000000
H	5.374452000000	0.906904000000	2.513436000000
H	5.551978000000	-0.740029000000	1.889532000000
H	4.661885000000	0.476062000000	0.955447000000
C	2.471979000000	1.455339000000	3.053739000000
H	2.300282000000	1.906008000000	2.069689000000
H	1.531590000000	1.476733000000	3.605958000000
H	3.185478000000	2.102765000000	3.585052000000
C	-1.369372000000	-4.371414000000	0.285718000000
H	-0.815788000000	-3.866800000000	-0.512323000000
H	-0.716772000000	-5.139299000000	0.718213000000
H	-2.220710000000	-4.886092000000	-0.182505000000
C	-3.102289000000	-4.251308000000	2.741956000000
H	-2.483562000000	-4.964834000000	3.302294000000
H	-3.677799000000	-3.658834000000	3.463000000000
H	-3.814964000000	-4.830505000000	2.138289000000
C	-1.643434000000	-2.622535000000	5.476577000000
H	-2.161131000000	-3.539105000000	5.179120000000
H	-0.682657000000	-2.902411000000	5.929797000000
H	-2.242268000000	-2.132336000000	6.257450000000
C	-3.246557000000	-2.031595000000	0.667539000000
H	-3.837256000000	-2.631179000000	-0.038828000000
H	-3.940905000000	-1.514074000000	1.336362000000
H	-2.708121000000	-1.274381000000	0.090004000000
C	-3.030002000000	-0.519960000000	3.718063000000
H	-2.963934000000	0.169641000000	2.868385000000
H	-3.846874000000	-1.225111000000	3.526706000000
H	-3.298426000000	0.075044000000	4.602250000000
C	-0.287912000000	-0.049599000000	4.849686000000
H	-0.672864000000	0.128295000000	5.864644000000
H	0.765206000000	-0.329937000000	4.942632000000
H	-0.343678000000	0.898543000000	4.309349000000

E+ZPVE = -5644.583879 au, Free E (298.15 K) = -5644.684820 au.
Job name: ti554MIN23G7P

Table 4-9. Atomic Coordinates of $\mathbf{4_{opt}}$ at the B3LYP-D3/B1 Level of Theory



(R = $SiMe_3$)

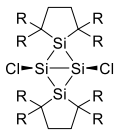
$\mathbf{4_{opt}}$

Atom	X	Y	Z
Si	0.309507000000	-0.922790000000	-0.844861000000
Si	0.060605106253	-0.226272450438	-1.271521968820
Si	1.922767780268	-0.135180659832	0.096875066904
Si	-0.061624137758	0.187596694995	1.269340980156
Si	-1.923788105853	0.096491896040	-0.099054577849
Cl	0.117029466221	-0.603003087350	-3.349590830166
Cl	-0.118046308884	0.564306481352	3.347415944995
C	3.296044487874	1.217288275296	0.216298075340
C	4.599743372442	0.324514805700	0.248816459308
C	4.315816385349	-1.051411955962	0.882868478766
C	3.040221988109	-1.690364670369	0.232559405738
C	-3.297063914391	-1.255978595233	-0.218468907822
C	-4.600763083099	-0.363205432464	-0.250985620337
C	-4.316841411447	1.012718906315	-0.885045417208
C	-3.041242831900	1.651674734201	-0.234748108633
H	4.991547620819	0.158567801101	-0.761046396923
H	5.411985783763	0.824342506982	0.796820263024
H	4.168420814521	-0.922796704435	1.960844066228
H	5.197745270728	-1.698007122134	0.772752084463
H	-4.992560885765	-0.197252883152	0.758878821116
H	-5.413008686921	-0.863036725816	-0.798981284085
H	-4.169455073585	0.884100421063	-1.963021816818
H	-5.198770132697	1.659313432701	-0.774922848556
Si	3.383702920072	2.501928472810	-1.217004637048

Si	3.291056196368	2.178444210046	1.873767543952
Si	3.529104187880	-2.412678749415	-1.476685044478
Si	2.382086595229	-3.067430764648	1.371776418328
Si	-3.384722507150	-2.540611977144	1.214840217533
Si	-3.292076158838	-2.217139656437	-1.875935045315
Si	-3.530117578796	2.374003383213	1.474491002630
Si	-2.383112332830	3.028735217761	-1.373975611179
C	1.764292700265	3.276474055985	2.107365741212
H	0.949878410270	3.021576996838	1.421055840859
H	2.011614855896	4.332106083112	1.947463561503
H	1.381187231446	3.159927955621	3.128243573660
C	3.444007609263	1.070824252581	3.400360121160
H	4.434541240040	0.601976633338	3.459495307121
H	2.682433746036	0.290356211002	3.464340543073
H	3.329505072859	1.711870056923	4.286770925969
C	4.854772459869	3.256964273411	1.977337033110
H	4.701915536164	4.028559156646	2.745391018040
H	5.115214766850	3.760861931342	1.041440998856
H	5.719161989591	2.654899480746	2.287439477440
C	5.176218627442	2.598047363019	-1.828249682730
H	5.475915455253	1.705494601182	-2.391734990647
H	5.887929514038	2.732304320353	-1.003984670634
H	5.271091503497	3.461328865861	-2.501310547565
C	2.903836950700	4.279143900144	-0.760384098917
H	3.043865977001	4.877227037491	-1.673044298137
H	3.513102585174	4.731062468772	0.027410478007
H	1.852283386459	4.364466489342	-0.473846412501
C	2.307008310634	2.161171101886	-2.731653483011
H	1.238678015160	2.272007985697	-2.514345822594
H	2.461809413470	1.180061335302	-3.182726736492
H	2.563320814465	2.919509833852	-3.486423184516
C	2.229850879902	-2.486180908449	3.165033710431
H	1.487889223095	-1.692667823630	3.298140540761
H	3.181302136149	-2.134430046151	3.581651086415
H	1.901467950549	-3.344503574031	3.768659567941
C	3.574479011070	-4.538921143117	1.426017829215
H	4.586093552816	-4.231406637122	1.722684353409
H	3.644949167793	-5.063218915579	0.465724667212
H	3.211539830502	-5.256773766264	2.174872905604
C	5.239865920298	-3.223286662744	-1.360492684886
H	5.363933742482	-3.890575290105	-0.502640928868
H	6.029367673932	-2.460496798248	-1.319158244725
H	5.401946298530	-3.811749738706	-2.274853160608
C	0.687999917074	-3.742887294630	0.887240591391
H	0.288494846936	-4.323132594332	1.730486541832
H	0.723113621195	-4.397755272572	0.011313864715
H	-0.019669051415	-2.935867952195	0.675654398539
C	2.299734405264	-3.697852130217	-2.114370498824
H	1.274796183995	-3.310027687152	-2.145659120383
H	2.301192713456	-4.619205258075	-1.520844081606
H	2.582244738300	-3.959465833349	-3.143737601193
C	3.726437846152	-1.172221751934	-2.893902405924
H	4.295466234400	-1.678560249865	-3.687507708295
H	4.274532646644	-0.264472391722	-2.625309597064
H	2.764215330247	-0.878361634166	-3.319981093273
C	-1.765309242013	-3.315164587260	-2.109530798857
H	-0.950882471528	-3.060233163098	-1.423250200763
H	-2.012614533921	-4.370793480202	-1.949587148190
H	-1.382229453119	-3.198648895266	-3.130421255017
C	-3.445028561832	-1.109524567529	-3.402530822151
H	-4.435561841250	-0.640676445103	-3.461667029635
H	-2.683454395300	-0.329057374907	-3.466514254307
H	-3.330526979576	-1.750573236644	-4.288939600074
C	-4.855789673203	-3.295662584257	-1.979502832323
H	-4.702938859985	-4.067244475247	-2.747574123756
H	-5.116217604492	-3.799577622303	-1.043610827760
H	-5.720186753394	-2.693594460416	-2.289584842874
C	-5.177237288127	-2.636729370728	1.826085878000
H	-5.476941404790	-1.744165080080	2.389547729963
H	-5.888945785823	-2.771013889382	1.001825182686
H	-5.272103187352	-3.499993447967	2.499169943921
C	-2.904855775508	-4.317829482699	0.758230820294
H	-3.044880539582	-4.915907034383	1.670895328038
H	-3.514123283675	-4.769753163504	-0.029558592437
H	-1.853303251232	-4.403153011067	0.471689001332
C	-2.308033495669	-2.199844574676	2.729490672484
H	-1.239702399785	-2.310679333041	2.512191466477
H	-2.462839063225	-1.218733559076	3.180558463547
H	-2.564347878737	-2.958179525029	3.484261919354
C	-2.230876498436	2.447472765652	-3.167228830517
H	-1.488905671241	1.653968306072	-3.300333257483
H	-3.182324927016	2.095707258442	-3.583840067555
H	-1.902507054227	3.305795358805	-3.770861983696
C	-3.575509169559	4.500221701634	-1.428230865796
H	-4.587118445290	4.192705229660	-1.724915590475
H	-3.645996170208	5.024516956937	-0.467937021893
H	-3.212559618013	5.218077518193	-2.177078738689
C	-5.240882382220	3.184604617785	1.358294589348
H	-5.364993453822	3.851800374379	0.500367410058
H	-6.030384643310	2.421798386177	1.317084167755
H	-5.402919525018	3.773173725351	2.272604499103
C	-0.689028031486	3.704202202420	-0.889439987991
H	-0.289464908290	4.284337348584	-1.732733665123
H	-0.724171079630	4.359174786241	-0.013593302988
H	0.018610065782	2.897190435921	-0.677722825106
C	-2.300741257642	3.659181285777	2.112153714354
H	-1.275802124611	3.271358387964	2.143426600690
H	-2.302209468717	4.580532113688	1.518623900699
H	-2.583235037631	3.920798206251	3.141524384730
C	-3.727447167321	1.133562421245	2.891722335094
H	-4.296462938527	1.639914711609	3.685328296363
H	-4.275555390715	0.225816941857	2.623141808050
H	-2.765223945716	0.839695003843	3.317795165224

E+ZPVE = -5644.583591 au, Free E (298.15 K) = -5644.684142 au.
Job name: ti554MIN23G7TS5BE

Table 4-10. Atomic Coordinates of **TS1** at the B3LYP-D3/B1 Level of Theory



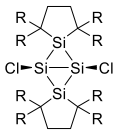
(R = $SiMe_3$)
TS1

Atom	X	Y	Z
Si	0.073073679321	0.066959696897	-1.342013729197
Si	1.931155947859	-0.119925401075	0.091326388955
Si	-0.045430155435	0.138929597818	1.390800454291
Si	-1.925332555670	0.107225727794	-0.026930608746
Cl	0.118850550783	-0.944497372710	-3.202635763435
Cl	-0.149725563224	-0.927636496520	3.217571141316
C	3.249976882444	1.29355421710	0.217155144565
C	4.592713531605	0.45850533743	0.207655444072
C	4.388546344906	-0.938384265707	0.811947363093
C	3.129180597478	-1.626866957330	0.178112194587
C	-3.378361851448	-1.185569582623	-0.089894053627
C	-4.625039003368	-0.221406701564	-0.159328891352
C	-4.281845025488	1.103961670887	-0.854286253151
C	-2.964308342402	1.717572445318	-0.255691794166
H	4.965247267288	0.330182249226	-0.814596376311
H	5.393842353194	0.985918901396	0.745601766336
H	4.258886161414	-0.842694018944	1.895926473535
H	5.296645836090	-1.541725383766	0.667496106676
H	-4.979502403508	0.010041791396	0.858801545717
H	-5.472609289982	-0.704554020048	-0.668987699325
H	-4.157969140935	0.910277017304	-1.926587910665
H	-5.128168620011	1.798545468037	-0.768125671137
Si	3.340841940288	2.617613317380	-1.188574130852
Si	3.181088564978	2.214374833736	1.894842619082
Si	3.594375158027	-2.308652661050	-1.556793916794
Si	2.621306412689	-3.082166465422	1.306338906923
Si	-3.763942523047	-2.404499540083	1.352562331179
Si	-3.268211637838	-2.235030337718	-1.697597955484
Si	-3.356587077910	2.635027058689	1.387114615748
Si	-2.339683192614	2.995870848233	-1.530028006787
C	1.644648678079	3.309194143817	2.086399937732
H	0.915294226669	3.148818784305	1.288315134634
H	1.912885242879	4.372617971276	2.085397117005
H	1.145029166301	3.081334296496	3.037247366210
C	3.210000090582	1.098358373940	3.422102981611
H	4.116376880008	0.485980527307	3.490737378733
H	2.340596477322	0.437486926024	3.492837827077
H	3.189766383586	1.757028371233	4.303274875918
C	4.747130010800	3.275795470872	2.085059360795
H	4.561257276814	4.061375144639	2.830881528279
H	5.066874423523	3.760459680776	1.156840142606
H	5.583840663956	2.666728483276	2.452481665231
C	5.143704922657	2.767298421216	-1.763200749958
H	5.470965678721	1.900455391029	-2.350836847350
H	5.843076929264	2.893549344547	-0.927533654228
H	5.225647603200	3.653069496482	-2.408326394650
C	2.851188273254	4.382468959201	-0.693822125392
H	3.041416793465	5.009391599882	-1.577533834119
H	3.436170517541	4.794672670299	0.134014812287
H	1.791492410512	4.480581578962	-0.447572227314
C	2.329746475829	2.290651181783	-2.752076236070
H	1.251611980713	2.325011832715	-2.565716420145
H	2.561131514969	1.338663148275	-3.234009997201
H	2.567410755549	3.093968248379	-3.465298482186
C	2.859557773414	-2.644027622621	3.131088898763
H	2.501325956357	-1.650906535806	3.405455193014
H	3.920607804466	-2.716031261930	3.405934019482
H	2.306899310432	-3.372719348153	3.740071727643
C	3.734750982458	-4.604759232755	1.101507367626
H	4.778322292472	-4.370686777576	1.349641610671
H	3.711539209385	-5.055993544424	0.104796325250
H	3.389846044246	-5.361184350276	1.821528840345
C	5.340447360903	-3.048584763975	-1.505749229137
H	5.525199959434	-3.722657956616	-0.665254632141
H	6.094879328663	-2.250351365977	-1.479600206463
H	5.496945501554	-3.614715964504	-2.435159238013
C	0.854760571472	-3.661131373794	1.007042539702

H	0.557121213333	-4.339136961641	1.818195573335
H	0.750381333282	-4.197167560794	0.057960897908
H	0.148295049806	-2.825743449595	1.000076179993
C	2.379596570399	-3.627128170293	-2.155350868455
H	1.343363108352	-3.273283608246	-2.131526665746
H	2.437773423702	-4.555756585964	-1.577631796181
H	2.616984265125	-3.865133809141	-3.201668880199
C	3.727074300688	-1.042075462329	-2.957263204048
H	4.212752444603	-1.550637382435	-3.803254405988
H	4.340644359206	-0.171920989412	-2.702011100364
H	2.754247180463	-0.689698581817	-3.305004461473
C	-1.714545297903	-3.314732048969	-1.749937064128
H	-0.876888489868	-2.897877286060	-1.183452149406
H	-1.922144709900	-4.311082330879	-1.345919380197
H	-1.384491566928	-3.427209111927	-2.789553312681
C	-3.373023337345	-1.182796224574	-3.264219322846
H	-4.382578286588	-0.768673681440	-3.389729939143
H	-2.652665098081	-0.365078129583	-3.307149046204
H	-3.173671252642	-1.838094279968	-4.123930785579
C	-4.727234172740	-3.427808361216	-1.906185306583
H	-4.639959085008	-3.867136508403	-2.910626406716
H	-4.724717035646	-4.248260994333	-1.181248789668
H	-5.698305382987	-2.919626356293	-1.852416575080
C	-5.608566822844	-2.858910642475	1.304781382390
H	-6.236986966546	-1.974996999055	1.474622392369
H	-5.945360599711	-3.345352909148	0.387151765849
H	-5.789720329922	-3.551223492995	2.140067485705
C	-2.795742259072	-4.024447361875	1.287357567367
H	-2.982753189183	-4.562840174986	2.226739781116
H	-3.119196022694	-4.670983268353	0.464311965321
H	-1.717081004553	-3.875217429246	1.197110989117
C	-3.614514868567	-1.753517530824	3.119311508307
H	-2.695679010856	-1.220406948395	3.355378874528
H	-4.466263416278	-1.112946874757	3.375030146686
H	-3.666633542112	-2.635147358293	3.775180473495
C	-2.195607931490	2.303431409819	-3.286969115092
H	-1.435707057445	1.522734738508	-3.396193430793
H	-3.144447783366	1.911346675951	-3.671299713796
H	-1.897874359699	3.139800888812	-3.936289489669
C	-3.610079692867	4.394583539664	-1.694652343907
H	-4.606101997457	4.007225810063	-1.947450142432
H	-3.701943130522	4.999833193023	-0.785794140156
H	-3.295175044401	5.059786499391	-2.510856370327
C	-5.124276900218	3.318711729008	1.337023869951
H	-5.331775837258	3.936121620379	0.456644544449
H	-5.865430829080	2.508695602493	1.370322707379
H	-5.277879297336	3.941060853117	2.229949303556
C	-0.673562683086	3.789771897565	-1.126267560722
H	-0.173151219795	4.067792933652	-2.062727338697
H	-0.780807985652	4.694319837593	-0.519758144741
H	-0.013151324746	3.099113951040	-0.594464822959
C	-2.195695912146	4.082838856511	1.751223746949
H	-1.142793658445	3.781402394106	1.758816728992
H	-2.307712921493	4.919156803385	1.053318959176
H	-2.441468430006	4.452022430679	2.756994968022
C	-3.313230710648	1.590431219220	2.954655177954
H	-3.506016250095	2.259671731423	3.805640806616
H	-4.095089995772	0.827342210276	2.952893901829
H	-2.354837864882	1.094168117621	3.137369264316

E+ZPVE = -5644.576842 au, Free E (298.15 K) = -5644.676794 au.
Job name: ti554MIN23G7TS5

Table 4-11. Atomic Coordinates of **4′$_{opt}$** at the B3LYP-D3/B1 Level of Theory



(R = $SiMe_3$)

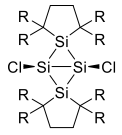
4′$_{opt}$

Atom	X	Y	Z
Si	0.038698843253	-0.315426269476	-1.289381607063
Si	1.903650076819	-0.132322796812	0.184134679396
Si	-0.113165857852	0.085348454332	1.567527854094
Si	-1.955461394984	0.104452364226	-0.015936756022
Cl	-0.040422250606	-2.413822099639	-1.741434166782
Cl	-0.343540957983	-1.711713700748	2.708161308576
C	3.134816149292	1.368005520603	0.132565796793
C	4.514898153602	0.587685012210	0.152524578810
C	4.396970837357	-0.727667763104	0.920722111314
C	3.190308585667	-1.562909904082	0.356974346789
C	-3.457766538495	-1.112767940544	-0.189083144175
C	-4.634653656230	-0.091021230927	0.045137947285
C	-4.306027297299	1.222770365988	-0.672873465653
C	-2.935030831162	1.762720369748	-0.120433730456
H	4.835962821748	0.346284314377	-0.866766171041
H	5.317727380128	1.209281257386	0.574444079802
H	4.247857879987	-0.519559164970	1.985865713097
H	5.340726334633	-1.283451684999	0.849694880329
H	-4.759119010834	0.118484552560	1.117844021716
H	-5.594772764939	-0.495382957581	-0.294662937134
H	-4.243357903199	1.024449303872	-1.753608738370
H	-5.111641439262	1.956529214154	-0.545768280814
Si	3.172159044839	2.547580214362	-1.409340321713
Si	3.134513662463	2.419449039504	1.740235715260
Si	3.733479544021	-2.320763087610	-1.339796940184
Si	2.941429420019	-2.982210209829	1.615514866494
Si	-3.675489868827	-2.539447727038	1.069886758762
Si	-3.716010796990	-1.868020203425	-1.968229121168
Si	-3.289522885433	2.588838790482	1.595941798832
Si	-2.280730132796	3.077464087407	-1.323834342148
C	1.625281916094	3.525364114542	1.960043863306
H	0.707822838639	2.927786834315	1.931531222631
H	1.536838375038	4.326913336566	1.224940246727
H	1.685960141528	3.980148425145	2.959103486982
C	3.193751277787	1.424925960858	3.351310717051
H	4.119403716229	0.852289127024	3.477590779158
H	2.347163957440	0.739021317740	3.461491854642
H	3.138718931909	2.148285737253	4.178343413517
C	4.714625203293	3.481811113551	1.768627794188
H	4.501592309066	4.449445260096	2.243282001751
H	5.121359834653	3.680443271310	0.770940756783
H	5.497095780696	2.987394977954	2.359316218960
C	4.913096918494	2.514373873250	-2.169119544618
H	5.154289322395	1.564720897873	-2.662202205252
H	5.697486930256	2.721958536370	-1.430312877362
H	4.956389527080	3.302299274257	-2.933917447191
C	2.890045402686	4.391550960521	-1.056255300839
H	3.124597543891	4.917785367908	-1.993270940368
H	3.534875041528	4.806008286320	-0.275658440577
H	1.852944493366	4.621072362334	-0.804545033363
C	2.004281979562	2.166871703162	-2.848497448737
H	0.945569376125	2.221840074833	-2.583484947406
H	2.184986521337	1.187917505992	-3.300196691240
H	2.195717057792	2.931604146673	-3.616633973275
C	2.888767368097	-2.307788525873	3.385268717491
H	2.305542766579	-1.391202209354	3.492704871756
H	3.904831448721	-2.116487681380	3.755685369014
H	2.429596077035	-3.063227586055	4.037140590776
C	4.501162844478	-4.067921072782	1.637921581001
H	5.400125884206	-3.477090153262	1.857852596183
H	4.674600645162	-4.622538799373	0.710374472056
H	4.385052266287	-4.801505878441	2.448965943433
C	5.624122511357	-2.489133595699	-1.378921595753
H	6.015878413119	-3.082407340632	-0.545171445913
H	6.137169566602	-1.519189451737	-1.383424629772
H	5.889495074369	-3.007795951758	-2.311266079354
C	1.475186613035	-4.110597153585	1.252739456194
H	1.019248784704	-4.441369822833	2.194233435651
H	1.793578319773	-4.997066609375	0.691876362180
H	0.697570040082	-3.606589266431	0.675250968129
C	3.074595446805	-4.055824401239	-1.698242107472
H	1.989428325566	-4.131063918462	-1.606813589118
H	3.529755031397	-4.816036893019	-1.054710704434
H	3.340999297131	-4.296400880171	-2.737659762316
C	3.331049039966	-1.265958776599	-2.857832000559
H	3.821758095288	-1.729512612233	-3.725735749324
H	3.711629924755	-0.243497294409	-2.770267803280
H	2.258074390663	-1.218035631885	-3.070225074614
C	-3.269767072263	-3.697964670788	-2.150379757501
H	-2.240086727524	-3.925833554758	-1.869983998025
H	-3.936298232734	-4.355476432057	-1.583491194683
H	-3.388267368282	-3.943671778677	-3.215695811866
C	-2.895774182477	-0.977292765110	-3.422089514700
H	-3.323893154446	0.016018903646	-3.585657223260
H	-1.810538046516	-0.874740597400	-3.343263203482
H	-3.103975206076	-1.578987948241	-4.318851970955
C	-5.559473495305	-1.772204802068	-2.417794277644
H	-5.687084859225	-2.299241233896	-3.374291859208
H	-6.215235702908	-2.251899921574	-1.683044419104
H	-5.898597434946	-0.738637436202	-2.564565163578
C	-5.356352699164	-3.372481940252	0.765362980514
H	-6.175682476632	-2.643834539122	0.832114248917
H	-5.438185461011	-3.888596984213	-0.195765413806
H	-5.513119072188	-4.115799862615	1.560066488387
C	-2.320327854318	-3.849886698306	0.981427130006
H	-2.030626563746	-4.150674854353	1.995501005698
H	-2.661089309536	-4.739009420434	0.438858739509
H	-1.420743177680	-3.476206424408	0.485999719506
C	-3.853603780167	-1.943855650756	2.853880406570
H	-3.007629034082	-1.358256403505	3.217148995924
H	-4.775526801707	-1.366417544003	2.999649285758
H	-3.928850558756	-2.842217986940	3.484114189505
C	-2.170394449266	2.469797149464	-3.108933869251
H	-1.515338352527	1.600461274405	-3.223495314808
H	-3.152175302700	2.217896983528	-3.527628453891
H	-1.753698029352	3.287152670099	-3.715036247984
C	-3.471351692593	4.550357098107	-1.390061344147
H	-4.480176728645	4.225290114161	-1.679046812321
H	-3.550054813545	5.088431963502	-0.439280558242
H	-3.120987091079	5.259857840405	-2.152511695839
C	-5.050396746578	3.293890299587	1.596064991623

H	-5.252098303836	3.961984672716	0.751180294229
H	-5.808510274438	2.499886086408	1.596958032640
H	-5.179850238645	3.873290561596	2.521177190304
C	-0.564517890554	3.710012210506	-0.872061259254
H	-0.111111410265	4.155805174949	-1.766012079410
H	-0.585422872955	4.469368363051	-0.086529357960
H	0.098907049782	2.905408945607	-0.534644731433
C	-2.150939094758	4.034342874996	2.028990274537
H	-1.100227123439	3.739251006726	2.090927673273
H	-2.230927262654	4.879729766692	1.338048506146
H	-2.453745380906	4.387627512593	3.024938597856
C	-3.237414322108	1.479565510514	3.125292371461
H	-3.372872338221	2.131185818952	4.000946501045
H	-4.043382579701	0.741104252955	3.137337664767
H	-2.288132761179	0.949071825003	3.252958802942

E+ZPVE = -5644.583830 au, Free E (298.15 K) = -5644.682819 au.
Job name: ti554MIN23G7TS5FE

Table 4-12. Atomic Coordinates of **4′$_{opt}$** at the B3LYP-D3/B1 Level of Theory

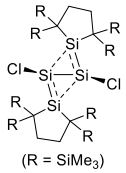


(R = $SiMe_3$)
4′$_{opt}$

Atom	X	Y	Z
Si	0.066039126044	-0.206971220883	-1.457335049444
Si	1.936856512735	0.003343294643	0.019665316568
Si	-0.057947937143	-0.182518855041	1.416796120817
Si	-1.949344533096	-0.129637745893	-0.073858718652
Cl	0.322755645976	-2.112441672553	-2.392556805223
Cl	-0.098587153387	-2.208833818158	2.126461584975
C	2.990992917740	1.620415468076	0.227473416279
C	4.450898551220	1.012256961601	0.184935837009
C	4.469340927564	-0.407985407606	0.749264794722
C	3.383173337636	-1.279755763477	0.019351092003
C	-3.337277654070	-1.472061670412	0.026791772726
C	-4.616079663630	-0.649634098716	-0.420813454514
C	-4.268442248085	0.653117714563	-1.150096879624
C	-3.069682280754	1.403855458421	-0.462278579345
Si	2.911539449530	3.028119476742	-1.101327513318
Si	2.802094221615	2.417721683865	1.960862393738
Si	4.051329030169	-1.701099028978	-1.748233054129
Si	3.279362604877	-2.899271008601	1.031552594142
C	1.139475641956	3.294865076185	2.163056207939
H	0.454081746580	3.064053057413	1.342898143013
H	1.263716650085	4.383646745204	2.199272457525
H	0.653041698974	2.969047821729	3.089937434308
C	2.959134530926	1.239243670005	3.434489873990
H	3.953842018453	0.786810679114	3.520645461261
H	2.214055297869	0.437451993116	3.426196643800
H	2.789453251160	1.836971860781	4.342671610723
C	4.226189085103	3.653404266409	2.221467136044
H	3.903531788906	4.442252020463	2.915188649465
H	4.563233448194	4.135236761520	1.297629700948
H	5.091242699791	3.150899610024	2.674115622599
C	4.671764497529	3.394143924125	-1.710895351066
H	5.080917821651	2.590868573139	-2.336366282916
H	5.375757786183	3.575717048504	-0.889395251167
H	4.631930284845	4.303537824246	-2.326545952753
C	2.281979805759	4.712525163885	-0.490818753361
H	2.398893926420	5.402336957485	-1.339815931725
H	2.852335827309	5.124325127993	0.347301450042
H	1.224771568503	4.710382597413	-0.217164689457
C	1.901538240235	2.704384385144	-2.664224076284
H	0.835366103851	2.596834038261	-2.461111815086
H	2.228438208733	1.824295351828	-3.222039487534
H	2.029269671211	3.583626436377	-3.313356710054
H	4.822716958786	0.965765158521	-0.845218244945
H	5.162898700540	1.651690376816	0.726338706304
H	4.268237765303	-0.376516185254	1.826588421612
H	5.472779481294	-0.839331500185	0.640135108351
C	3.118742162189	-2.519261802825	2.881693810837
H	2.462066632227	-1.675774038262	3.104754691578
H	4.106473070832	-2.311772648435	3.315009930073
H	2.703766454784	-3.398303762440	3.392687210732
C	4.954625396424	-3.793511371052	0.946536951607
H	5.775299513066	-3.147859828080	1.285810749256
H	5.208283471362	-4.177125115762	-0.046675626237
H	4.907473176603	-4.651097508534	1.633539977858
C	5.949397479588	-1.659053332846	-1.734670064950
H	6.387289077528	-2.331118020851	-0.988491970632
H	6.349295583894	-0.650892148015	-1.568079181192
H	6.292621852894	-1.990912687844	-2.725081056158
C	1.971012157384	-4.120541036452	0.432089003312
H	1.502480600388	-4.617066068954	1.290760341768
H	2.423769960909	-4.888494382619	-0.206107938858
H	1.176892556182	-3.633258532958	-0.138921405538
C	3.597193480228	-3.419032145840	-2.393708629899
H	2.527283446297	-3.630176523624	-2.344191156809
H	4.131825896934	-4.216327719687	-1.866568269460
H	3.897846546537	-3.458742262001	-3.450645288159
C	3.576637020959	-0.469577284288	-3.101916930526
H	4.090275028798	-0.773485773542	-4.025296940283
H	3.899324419914	0.549445448509	-2.864357560916
H	2.502247515757	-0.454959361663	-3.309943690326
Si	-3.727312828674	-2.197367553484	1.778946276004
Si	-3.191927530275	-2.911600357610	-1.221591229148
Si	-3.689625056779	2.369840743139	1.087011011263
Si	-2.448994077750	2.613145861235	-1.805582321937
C	-1.765734283445	-4.099957067692	-0.881851209533
H	-0.968742565272	-3.647345847653	-0.285928002126
H	-2.131850737689	-4.980409376311	-0.341160137278
H	-1.321992096077	-4.435464939203	-1.826456846100
C	-3.142451544094	-2.216385434867	-2.982576270471
H	-4.106720234226	-1.759806308903	-3.245071944831
H	-2.355622463466	-1.470650635476	-3.131484888960
H	-2.955862128130	-3.034573131668	-3.691470615847
C	-4.766444933155	-3.973248103046	-1.183603774543
H	-4.669944905527	-4.741139736771	-1.964891669434
H	-4.906066313597	-4.488710243920	-0.227101949995
H	-5.677346131216	-3.399890955216	-1.397145376555
C	-5.613752616944	-2.379789548422	1.942943017696
H	-6.122275293595	-1.430903912249	2.151496311951
H	-6.073978083953	-2.824759283292	1.053464399868
H	-5.806972103301	-3.050805814385	2.792260191771
C	-3.091230662626	-3.946255259728	2.117959163973
H	-3.277870667726	-4.150029700486	3.182726601939
H	-3.636119137400	-4.699474783022	1.537664571316
H	-2.022935827437	-4.073279913219	1.936331550934
C	-3.185828069232	-1.116543188831	3.243327520592
H	-3.093760373936	-0.052725696195	3.008639756087
H	-3.939282593782	-1.212655860366	4.038471744058
H	-2.226170757566	-1.457288704760	3.643454360300
H	-5.228235638142	-0.396980554012	0.444751846560
H	-5.267913600911	-1.253665295332	-1.067185238538
H	-4.017582585270	0.416664215543	-2.195537422604
H	-5.161748438744	1.296113499745	-1.194085258314
C	-1.829621289682	1.760074711986	-3.390447165748
H	-2.272365520891	0.766340802962	-3.531309271035
H	-2.135159595480	2.378599236370	-4.246465173469
H	-0.743698534346	1.643228330052	-3.432535154403
C	-3.878235264147	3.639036299456	-2.515993512189
H	-4.597804464497	2.976061152011	-3.016486399555
H	-4.422818769190	4.261328388420	-1.805804595389
H	-3.456141958821	4.298029696053	-3.288694031106
C	-4.366730140475	4.105918112113	0.719076487103
H	-3.655226047643	4.782543787652	0.236108668600
H	-5.281339146221	4.072415586235	0.115166828160
H	-4.632940140586	4.541432897278	1.693153601272
C	-1.134847806907	3.751376004286	-1.078176373857
H	-0.693186062369	4.398429483965	-1.845793319221
H	-1.544662682101	4.389888196927	-0.286619271460
H	-0.324446464205	3.161984377622	-0.635532433429
C	-2.358334895414	2.677867105615	2.384007765276
H	-1.852064114451	1.774782855726	2.737836931515
H	-1.589686068933	3.358318409817	2.003089663095
H	-2.833599866821	3.164385857496	3.247722704991
C	-5.191710261761	1.585052317515	1.938337617533
H	-5.459146484192	2.240174521881	2.780007634163
H	-6.055771641062	1.555750951133	1.260967371908
H	-5.030860656723	0.583120290281	2.338256611875

E+ZPVE = -5644.575026 au, Free E (298.15 K) = -5644.675560 au.
Job name: ti554MIN23G7TS4FE

Table 4-13. Atomic Coordinates of **TS2** at the B3LYP-D3/B1 Level of Theory

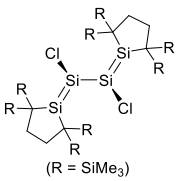


TS2

Atom	X	Y	Z
Si	0.363575170225	0.048408049913	-1.371221427991
Si	2.329714702856	-0.033365290376	-0.220664646878
Si	-0.263529717942	-0.003512410765	1.045943970579
Si	-2.340990233311	-0.152941125901	0.127279039186
Cl	0.264290073848	-1.782303748350	-2.559782096297
Cl	-0.036845482388	-1.888633816927	2.130508119988
C	3.265821683322	1.561261438255	0.263320476752
C	4.747112870111	0.995317131160	0.314844417195
C	4.772838742463	-0.464741061025	0.785971264126
C	3.719145771994	-1.300284663578	-0.022736540087
C	-3.659103578087	-1.495619767447	0.180675549439
C	-4.954920189852	-0.732853272817	-0.301714231684
C	-4.621097664304	0.542801068973	-1.102392096321
C	-3.389342267695	1.309247366503	-0.493395246123
Si	3.205360705981	3.041199645183	-0.995031062771
Si	2.837021167025	2.232799729148	2.013433918659
Si	4.392745049884	-1.685493457892	-1.793916352644
Si	3.416122135504	-2.951395498133	0.890144477415
C	1.181855170720	3.149559732302	2.107708506740
H	0.583569992089	3.041983018371	1.199605517217
H	1.335700884951	4.219735514633	2.290944528553
H	0.586499672559	2.736264217225	2.930545728710
C	2.771813925555	0.919264663874	3.371662944559
H	3.716827952587	0.384551299760	3.515317308643
H	1.980794943873	0.180110964353	3.201236570569
H	2.536226476013	1.435496154028	4.314282357603
C	4.227320715375	3.422399555624	2.528261211202
H	3.859718642676	4.088558771553	3.321045634072
H	4.582995226014	4.047047323399	1.700235429504
H	5.088539003052	2.874089833528	2.932110968683
C	4.990406155954	3.499083626395	-1.446136789437
H	5.478818606434	2.742568882921	-2.073148659945
H	5.617457263267	3.661590131735	-0.560370383777
H	4.965992935436	4.436445980326	-2.018798434779
C	2.439456398984	4.653161018651	-0.353044178051
H	2.664156679440	5.415431347574	-1.113516090699
H	2.838754667544	5.009546252065	0.600992781984
H	1.349859548287	4.587368365725	-0.269564308460
C	2.291996697388	2.785546278547	-2.629708511680
H	1.216227242484	2.653667196902	-2.478441970882
H	2.650886962081	1.942006592749	-3.223071290090
H	2.442271288612	3.702808689210	-3.219150793344
H	5.200571198959	1.027694426348	-0.684201297362
H	5.390972941151	1.617858228548	0.951018995994
H	4.538577171331	-0.505756902176	1.856033896534
H	5.787398510177	-0.873572742563	0.679771800936
C	3.267612013160	-2.680321235644	2.755086681538
H	2.546521733531	-1.910831541044	3.034545294440
H	4.241262996433	-2.427572180711	3.195820107813
H	2.933715536659	-3.624004222682	3.209569264481
C	4.972853181033	-4.030655032161	0.754248281262
H	5.851409499366	-3.498005620732	1.143807511882
H	5.201996161118	-4.367830576056	-0.261718715137
H	4.827354095210	-4.923227859902	1.379506494022
C	6.279588173034	-1.815834986882	-1.719090138393
H	6.628199980808	-2.536216366257	-0.971204426214
H	6.744565474684	-0.844402903553	-1.505516950094
H	6.640707980244	-2.147199902060	-2.702855918090
C	1.939003088877	-3.910659544575	0.215496979438
H	1.386458110536	-4.374549505902	1.041474592661
H	2.258107398950	-4.699305735642	-0.475805589405
H	1.238381747634	-3.262673939380	-0.319223533824
C	3.697408061414	-3.267714670810	-2.547647143064
H	2.602957731840	-3.252194088268	-2.569201865618
H	4.020901683596	-4.178602482442	-2.034895661302
H	4.048923887060	-3.322657012183	-3.587921702507
C	4.031179489963	-0.340068174185	-3.074586638124
H	4.580492086706	-0.596304438097	-3.992209289446
H	4.357979818991	0.657835630467	-2.763438935754
H	2.965803605605	-0.295485793872	-3.331243444128
Si	-3.925584808388	-2.193667506673	1.958226971079
Si	-3.339741400457	-2.925598038445	-1.050871334079
Si	-3.943231960366	2.411152359065	0.993006734194
Si	-2.671943780882	2.399932979547	-1.894482022644
C	-1.739877523982	-3.862474382968	-0.719055190188
H	-0.999616824882	-3.249595540928	-0.196511493279
H	-1.921478440446	-4.757180856000	-0.113213259974
H	-1.289628698996	-4.170883145632	-1.670127385052
C	-3.351525718467	-2.259711045828	-2.818802002994
H	-4.323148954920	-1.821460725587	-3.082189501391
H	-2.571004771688	-1.512922794831	-2.995387867544
H	-3.163163280548	-3.092832595344	-3.510388995085
C	-4.787942002828	-4.146744053379	-0.962661959910
H	-4.625496904696	-4.937263628463	-1.708997801104
H	-4.880003052526	-4.625699020425	0.018553248584
H	-5.747229758170	-3.665739794455	-1.195331442380
C	-5.784855600504	-2.478531695793	2.197286784324
H	-6.341204770577	-1.543388761240	2.338244179048
H	-6.230103295144	-3.016000759945	1.351167637006
H	-5.928645658730	-3.089223465096	3.099593070521
C	-3.084972886572	-3.846675362161	2.304871412837
H	-3.254229384954	-4.082811159008	3.365540939782
H	-3.495301354143	-4.669746943369	1.710113295540
H	-2.004621866137	-3.802669273943	2.143148294482
C	-3.355493929199	-1.025348791439	3.335246005834
H	-3.635134794464	0.020688029741	3.181842397171
H	-3.819017136332	-1.355181404621	4.276669659608
H	-2.269249893552	-1.073977149497	3.464803555225
H	-5.571079479110	-0.451258398105	0.555018827976
H	-5.592420896978	-1.384996473573	-0.916123829790
H	-4.405241051228	0.262310386847	-2.142831620836
H	-5.511086604505	1.189918398910	-1.141234250681
C	-2.163488386542	1.369654473880	-3.399594918028
H	-1.526154487190	0.508567735234	-3.189284250069
H	-3.055842529243	1.015270125820	-3.933464640549
H	-1.608394694207	2.024490725412	-4.086969554614
C	-4.016616757072	3.511739751363	-2.649836984462
H	-5.008552535410	3.042086435123	-2.615831410117
H	-4.089152486830	4.493414351567	-2.173619323982
H	-3.766537960724	3.668749732614	-3.708484514755
C	-4.546581591644	4.129481434491	0.470945115046
H	-3.760709569581	4.760736742730	0.044368100645
H	-5.376873748323	4.081973073285	-0.242657060778
H	-4.915640779500	4.624120875039	1.380947568069
C	-1.276921330354	3.505680791636	-1.261575412550
H	-0.816780234548	4.048299972952	-2.098206928553
H	-1.649309111269	4.245758738213	-0.541916221308
H	-0.492084484136	2.919461162348	-0.773089601437
C	-2.565707425917	2.716622483633	2.241931206950
H	-2.293729821949	1.824886147494	2.816224510017
H	-1.652959621948	3.079704169212	1.756854535309
H	-2.902590853059	3.488686606535	2.948397908080
C	-5.462089177263	1.719283121320	1.892492118157
H	-5.709420526028	2.417713472030	2.704766423464
H	-6.329504662925	1.678909429459	1.220118475652
H	-5.325755089043	0.730719506294	2.336442541554

E+ZPVE = -5644.556871 au, Free E (298.15 K) = -5644.659517 au.
Job name: ti554MIN23G7TS4

Table 4-14. Atomic Coordinates of $\mathbf{8_{opt}}$ at the B3LYP-D3/B1 Level of Theory



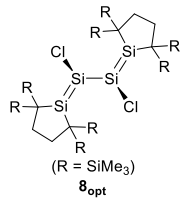
8_{opt}

Atom	X	Y	Z
Si	0.747605569030	0.174511170862	-1.406271908927
Si	2.661806754217	0.018185318626	-0.157965588511
Si	-0.490638029709	0.098421333948	0.617593878522
Si	-2.625480948637	-0.146114252657	-0.135526127968
Cl	0.631984306294	-1.737170499299	-2.471797747583
Cl	-0.159149589610	-1.829363541002	1.635201518146
C	3.465784987845	1.511542571868	0.684966367609
C	4.985378918210	1.112881674079	0.515069748226
C	5.148117781695	-0.406730998705	0.702400013305
C	4.117426691441	-1.167730688629	-0.218443103649
C	-3.941960849973	-1.387693225366	0.346530923197
C	-5.271037009172	-0.677463287640	-0.128515977378
C	-5.007858915319	0.390498071770	-1.213109038991
C	-3.687684389325	1.198856293755	-0.924875242180
Si	3.130721227463	3.210350647769	-0.137389646036
Si	3.036274452228	1.684072260779	2.565261238260
Si	4.804919962918	-1.315767117012	-2.028386450222
Si	3.824277686484	-2.948361172435	0.446099075923
C	1.605306441403	2.867613279560	2.914194680290
H	1.796530687715	3.906231364150	2.627533377366
H	1.435155159893	2.845762940039	4.000413523745
H	0.678810486404	2.538337648025	2.429031734855

C	2.566313646430	0.094584024966	3.457138445773
H	3.398110034779	-0.612331062686	3.515362293000
H	1.704662717968	-0.420395686738	3.020977898327
H	2.294310254130	0.368349010802	4.487313246073
C	4.566385078119	2.318227797495	3.486035824973
H	4.266580899492	2.565718180728	4.514246681986
H	5.011132587267	3.213685032792	3.039796300412
H	5.341475987802	1.542710992099	3.548778064942
C	3.730318111948	3.302224370315	-1.924862697102
H	3.164447842345	2.635727256503	-2.584033721502
H	4.799463399289	3.088106874189	-2.041073777099
H	3.562920541846	4.333636382583	-2.268107673127
C	4.117625215816	4.549581284947	0.770506985204
H	4.018493454782	5.493579434520	0.216710200342
H	5.186391237990	4.299051204751	0.810446028565
H	3.771361639356	4.722996734892	1.795177676098
C	1.304320305361	3.705568530205	-0.172973406974
H	0.639010530741	2.872207651346	0.074775955273
H	1.042151608798	4.047645763705	-1.181625411474
H	1.093465735296	4.518400070862	0.531615882716
H	5.334619820144	1.376122310603	-0.496297688127
H	5.630653360941	1.662007289463	1.213112107189
H	4.958175399829	-0.647995153791	1.759040120136
H	6.182607212169	-0.713266399576	0.501788119263
C	3.487155616779	-3.005467742447	2.302250919936
H	2.517313638346	-2.568455376223	2.557790969336
H	4.265415103364	-2.530438482374	2.911016566689
H	3.454969419452	-4.068357549883	2.583657776804
C	5.438936853781	-3.924835342776	0.242206785308
H	6.262238728878	-3.416403830572	0.763652685243
H	5.744040346775	-4.081055053747	-0.797307620656
H	5.312968790582	-4.911503446316	0.709119354533
C	6.696035840420	-1.351701391411	-1.945648527720
H	7.078852631187	-2.131401818406	-1.277567732729
H	7.107651394005	-0.386612874469	-1.622311102006
H	7.079480512180	-1.553453758539	-2.955623501834
C	2.376132744842	-3.863575037167	-0.329428223122
H	2.337205881253	-4.866639492888	0.120789815567
H	2.427640963543	-3.976387675415	-1.413131812237
H	1.431956631925	-3.360467353529	-0.092232751075
C	4.225068213141	-2.837489129277	-2.981863514487
H	3.145668024694	-2.795081073419	-3.164016915456
H	4.462470292166	-3.796420317384	-2.513363785786
H	4.728319009966	-2.805610215473	-3.959239239072
C	4.372687837945	0.121256424374	-3.173984121299
H	4.767336485947	-0.122597434131	-4.170980429887
H	4.829656586798	1.062786072330	-2.858916258173
H	3.292009312243	0.276755260474	-3.279097140725
Si	-4.004225891297	-1.739884698806	2.242528559098
Si	-3.750983580925	-3.019840459185	-0.642246326990
Si	-4.032781099306	2.649831791310	0.282722877383
Si	-3.029910656504	1.850516584097	-2.602242868907
C	-2.079865655640	-3.858789401416	-0.447093062544
H	-1.266482867886	-3.211219059609	-0.798374967018
H	-1.849287637537	-4.150850829169	0.580057514893
H	-2.073537651315	-4.763026107078	-1.073004472757
C	-3.966862733706	-2.714018620746	-2.495137313274
H	-4.917097231371	-2.224165903285	-2.741543889238
H	-3.146553685247	-2.115381610550	-2.906565577363
H	-3.951704374618	-3.686231429933	-3.007968391483
C	-5.162520587970	-4.189509429570	-0.158501415468
H	-5.056639062843	-5.127886642125	-0.720390658069
H	-5.181164526748	-4.434545616754	0.908402365032
H	-6.137861720270	-3.757302982262	-0.420761432172
C	-5.828796533320	-1.831721496547	2.748396128774
H	-6.317704372093	-0.849674368840	2.756034628977
H	-6.401374632592	-2.492769645053	2.085465917189
H	-5.888074366493	-2.240636407988	3.766522266231
C	-3.216999832117	-3.359513955476	2.811310185154
H	-3.396792643889	-3.441961919032	3.893317717061
H	-3.636959724420	-4.251278635944	2.335498239663
H	-2.135057009655	-3.356745867175	2.654431989460
C	-3.177603438699	-0.392518930001	3.286324990297
H	-3.410228880131	0.630442127526	2.972729476086
H	-3.513407887280	-0.504841460962	4.327603779439
H	-2.088073134438	-0.510399185731	3.272150286267
H	-5.762483067182	-0.191340731218	0.717772136022
H	-5.998784770721	-1.409181320520	-0.509490288151
H	-4.931625637310	-0.103377040283	-2.192441280568
H	-5.876759527503	1.063096242176	-1.284054021860
C	-2.398963879512	0.442519765728	-3.690354662479
H	-1.626850965298	-0.181210270516	-3.227381182194
H	-3.221515689499	-0.211093159311	-4.006923183051
H	-1.960106977202	0.879486124011	-4.598882955905
C	-4.448119545289	2.601468253671	-3.611403604481
H	-5.338132376383	1.958653703495	-3.602344131564
H	-4.744344236625	3.599489778270	-3.275726104309
H	-4.113685713869	2.682556283073	-4.655601620560
C	-4.774131810842	4.143857498481	-0.614970899663
H	-4.082217468612	4.621416681974	-1.316299413778
H	-5.685635733591	3.873617746926	-1.162728261871
H	-5.050736804425	4.887998145916	0.145295362579
C	-1.667455552608	3.138172903550	-2.407598777993
H	-1.395301392048	3.517852926895	-3.402591354576
H	-1.964935018438	3.992882232937	-1.789617696627
H	-0.767020558139	2.694562935441	-1.969199999004
C	-2.488302526598	3.239833418853	1.190597667678
H	-2.164668314389	2.532246083554	1.962567694790
H	-1.638671390398	3.394556686082	0.515251813741
H	-2.710647518986	4.199762691784	1.678243942205
C	-5.361941774541	2.221105681218	1.563562957174
H	-5.479380087202	3.086346539001	2.231558316033
H	-6.331797416519	2.046130114236	1.078938038541
H	-5.127611082706	1.352432995991	2.184358074108

E+ZPVE = -5644.567149 au, Free E (298.15 K) = -5644.672662 au.
Job name: ti554MIN23G7TS4BE

Table 4-15. Atomic Coordinates of $\mathbf{8_{opt}}$ at the B3LYP-D3/B1 Level of Theory



(R = $SiMe_3$)

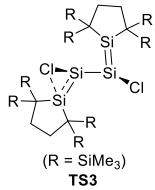
8_{opt}

Atom	X	Y	Z
Si	0.740025338688	0.035320177600	-0.902322157295
Si	2.740361519737	-0.138755898985	0.171961666672
Si	-0.738123003246	0.024004143706	0.925542985316
Si	-2.730325636750	-0.002940537628	-0.184557389706
Cl	0.562689637179	-1.796779817609	-2.074723267584
Cl	-0.619377379460	-1.940568758460	1.889538920404
C	3.643607087335	1.311040231977	1.001857475110
C	5.126648415088	0.984142644153	0.580592357238
C	5.354502289921	-0.540837890205	0.574402678844
C	4.190993024748	-1.271820303396	-0.203466121978
C	-4.206932516186	-1.136588201173	-0.007607608595
C	-5.373765613608	-0.293320138869	-0.658048539390
C	-4.842718925360	0.818484882132	-1.592060568858
C	-3.536370802586	1.486743307655	-1.019659153393
Si	3.121174822228	3.013525742853	0.289585048366
Si	3.457463829507	1.336894006417	2.923388755602
Si	4.627963649503	-1.450933165609	-2.073167721646
Si	3.888613355616	-2.993362430669	0.585143542271
C	1.770886811948	0.715461656563	3.480610193571
H	0.953407318404	1.291011257435	3.028256260273
H	1.693067088162	0.818913736683	4.572189330376
H	1.594342739758	-0.339221337582	3.234323264841
C	4.797068790265	0.335048426590	3.811010771743
H	5.807080112774	0.596637168253	3.470201609730
H	4.667928906066	-0.745368075879	3.723597920268
H	4.735948220252	0.589885867752	4.878682309864
C	3.693345283370	3.053557051266	3.695032060426
H	3.560272597163	2.929661399621	4.779451537357
H	2.982880103211	3.812965347398	3.357924232252
H	4.709560945030	3.431667025203	3.529244550622
C	4.421415350572	4.326699475874	0.716155282916
H	5.437459434672	3.923551110634	0.604451700971
H	4.326941049606	4.733787329401	1.725917668078
H	4.319021058874	5.157485464265	0.004357597562
C	1.411102780064	3.514748761926	0.917530179446
H	1.044760817429	4.373145743391	0.338654954622
H	1.402866327905	3.788757981217	1.977945721152
H	0.690115494560	2.698017826741	0.786523781085
C	3.075438510552	3.065635194929	-1.599180324963
H	2.397064403917	2.333787487040	-2.045524464914
H	4.073832008683	2.926441510694	-2.032498495273
H	2.730414588437	4.069179865307	-1.888572882153
H	5.328052394797	1.373439117424	-0.431865982553
H	5.852821175223	1.475721444184	1.245691705384
H	5.385417290400	-0.889127100300	1.613733539422
H	6.338944012066	-0.774779485783	0.152279015340
C	3.651284732310	-2.856564639016	2.459720876139
H	2.912998760856	-2.096142973968	2.744159573483
H	4.586170978829	-2.651806801105	2.993951497985
H	3.269355606840	-3.822737522785	2.817969763085
C	5.444312067264	-4.042584306719	0.329802058732
H	6.327532189866	-3.523827188697	0.728146101345
H	5.636417690932	-4.270965251295	-0.724712357919
H	5.343017964537	-4.993549410443	0.870334555608
C	6.513630019083	-1.541840666054	-2.240055680335
H	6.950475691248	-2.319864981738	-1.601571174111
H	7.002162895480	-0.587308346623	-2.005616164662
H	6.754216370082	-1.789521939620	-3.283356786943
C	2.348965526670	-3.893412175923	-0.010858441304
H	1.442753045847	-3.354311301753	0.293641444161
H	2.326743279894	-4.877274484226	0.480916323977
H	2.294686582121	-4.048066397637	-1.089501922632
C	3.949978668457	-2.998625156833	-2.913863591966
H	2.857730826860	-2.982510188889	-2.971312765322

H	4.260996010669	-3.933696650110	-2.436314871439
H	4.339499961353	-3.002365148543	-3.942256473712
C	4.061598063501	0.005830819228	-3.129420002575
H	4.382558010305	-0.166851253863	-4.166467390474
H	4.497323398720	0.954170891334	-2.797545537242
H	2.970322057959	0.114275568066	-3.131708889122
Si	-4.607602158818	-1.570830772440	1.827615252847
Si	-3.966588532637	-2.729154912816	-1.048716442620
Si	-3.983504809807	2.873049896729	0.231645288321
Si	-2.547820103316	2.201844402037	-2.497478706085
C	-2.438928749763	-3.730965163308	-0.606734810793
H	-1.526926862832	-3.128569427796	-0.691441811035
H	-2.463690811156	-4.156255392152	0.399236071559
H	-2.352353338036	-4.557295204139	-1.327345450910
C	-3.798001929205	-2.298792769718	-2.881901685920
H	-4.636572011648	-1.702262713092	-3.262106934493
H	-2.864473661564	-1.761042203604	-3.085486871165
H	-3.767855419495	-3.234886255949	-3.457269483369
C	-5.531667362604	-3.787901834296	-0.900007247791
H	-5.402467987535	-4.704405359325	-1.492222747415
H	-5.756290650474	-4.080965607990	0.131296817181
H	-6.408456504492	-3.258872049600	-1.297472048650
C	-6.491403286831	-1.538653646703	2.030388006836
H	-6.903108315782	-0.521888091076	2.016444840922
H	-6.993368446445	-2.120538181195	1.246895288442
H	-6.746023081871	-1.987334695739	3.000500624225
C	-4.030432095407	-3.269955599442	2.411917473708
H	-4.371287962451	-3.387274124571	3.451014039218
H	-4.436656284748	-4.104378493422	1.831362838243
H	-2.938654389324	-3.341034438948	2.411824598425
C	-3.860438979749	-0.353928724544	3.071984742135
H	-3.957295408804	0.699667112186	2.792075597469
H	-4.369011181903	-0.488825760827	4.037808958421
H	-2.795773643545	-0.567304551726	3.224550318466
H	-5.983094579393	0.173062082671	0.119883320400
H	-6.063459178849	-0.938574169640	-1.222067996415
H	-4.633363589677	0.386185531092	-2.581166005391
H	-5.632669616449	1.568130728592	-1.754964293924
C	-1.882429988803	0.828221874497	-3.608667681385
H	-1.236589895276	0.104173750792	-3.102474222339
H	-2.700976969760	0.277495166434	-4.089526015067
H	-1.286180997114	1.291994321013	-4.407771022747
C	-3.698473852662	3.180696854013	-3.643968940901
H	-4.656844136405	2.666075457762	-3.792911475653
H	-3.907347192252	4.195395643219	-3.293059720195
H	-3.212064544080	3.257272175216	-4.626851116440
C	-4.427425815051	4.492272469332	-0.645435908963
H	-3.579252610338	4.958602149384	-1.157291671012
H	-5.233623874875	4.350669873704	-1.375768440596
H	-4.788352868893	5.196050153249	0.117957617441
C	-1.128077723984	3.320896212244	-1.956023222720
H	-0.638371975569	3.731826529348	-2.850083535977
H	-1.461432944837	4.161628191049	-1.336573613672
H	-0.368338159968	2.762107139143	-1.398361803633
C	-2.591939923324	3.258938943162	1.444211882417
H	-2.460067166904	2.471709002991	2.194734424903
H	-1.625579529150	3.392271023434	0.944003291748
H	-2.832938599083	4.194909921660	1.968437702537
C	-5.556396608568	2.481472759184	1.213291858658
H	-5.727042172013	3.307035247877	1.918973196907
H	-6.429991530840	2.430695307488	0.549727303973
H	-5.510948088177	1.555316069440	1.791543020792

E+ZPVE = -5644.566785 au, Free E (298.15 K) = -5644.675110 au.
Job name: ti554MIN23G7TS3BE

Table 4-16. Atomic Coordinates of **TS3** at the B3LYP-D3/B1 Level of Theory



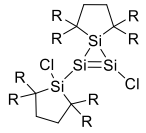
TS3

Atom	X	Y	Z
Si	0.384384411020	0.647764332214	0.070335354923
Si	2.602680679658	0.026803498478	0.137722795273
Si	-0.994460434325	-0.100783556549	1.748160409454
Si	-2.667261633966	0.052594143475	0.187692158751
Cl	0.961126107550	-0.771568859825	-1.816315860655
Cl	-0.943278554073	-2.120591432888	2.550363409084
C	3.846313101285	1.433523519207	0.187416021287
C	5.218031192936	0.676911361477	0.094634845774
C	5.070430338406	-0.739592476346	0.695927995864
C	3.778605753849	-1.452018820753	0.136490545030
C	-3.834297585544	-1.248570326754	-0.486689364981
C	-4.966326497547	-0.394123570305	-1.176727585534
C	-4.490171436735	1.033171100390	-1.523189844847
C	-3.550512731885	1.621943797433	-0.407470327275
Si	3.622199072431	2.757158903513	-1.196348587575
Si	3.758069979738	2.350470575786	1.884007297880
Si	4.219837981309	-2.271820977138	-1.550795687413
Si	3.156673409465	-2.765075268283	1.383958334000
C	2.007310020969	2.789456396627	2.434513722708
H	1.422919053552	3.329327283730	1.684638403294
H	2.078262233127	3.423785136966	3.330104493053
H	1.439610402010	1.892377380004	2.717567682305
C	4.501232881756	1.352708832417	3.309133064723
H	5.543893222861	1.064344630333	3.126460081193
H	3.924851683211	0.455452217560	3.551522137652
H	4.490303492537	2.001077820448	4.197335400374
C	4.833925050473	3.909868455209	1.861757053792
H	4.818701435078	4.338814174461	2.873692552988
H	4.505445070761	4.683022028653	1.161767684153
H	5.877168558101	3.658421595092	1.627905813890
C	5.315350348705	3.522366019405	-1.559926263914
H	6.017234876188	2.760430134623	-1.924662891908
H	5.770002141441	4.015863033406	-0.695661408872
H	5.198823412992	4.270183220938	-2.356897271426
C	2.376524691014	4.106983859399	-0.747103484612
H	2.337974635911	4.812501443019	-1.589523346651
H	2.602610944032	4.677073974359	0.158368581458
H	1.377517720696	3.667312046061	-0.637677152337
C	2.995457605503	2.122990549044	-2.859783885212
H	2.059268162873	1.560257189440	-2.786318906152
H	3.728108457373	1.504778392934	-3.384876426414
H	2.802133044008	3.009187778605	-3.482591520008
H	5.540488246676	0.586159855762	-0.952592822165
H	6.023332335814	1.224054881896	0.609038280667
H	5.011147590812	-0.652475240259	1.788108365856
H	5.971506276701	-1.332156111610	0.494885527620
C	2.785249082569	-1.964768717549	3.057971586331
H	2.061751681788	-1.142021653963	2.986951151199
H	3.689097422368	-1.600158733580	3.560014403693
H	2.327508576058	-2.726582863516	3.703857801278
C	4.514784575464	-4.046396247394	1.692928500543
H	5.475058819564	-3.576536639431	1.943744527142
H	4.667896707242	-4.693810756501	0.820557579926
H	4.221624040828	-4.685134209832	2.537568369465
C	5.964441876380	-3.009319275858	-1.423218898019
H	6.125499302137	-3.605318300328	-0.518771761391
H	6.738611400920	-2.231711706962	-1.465730966111
H	6.114374312772	-3.667394499017	-2.291131673270
C	1.602223295991	-3.656759875940	0.818980261283
H	0.941669026813	-2.997040325034	0.249586668637
H	1.042202870565	-3.991973887622	1.699554636484
H	1.825509033681	-4.530003177118	0.198886366683
C	3.078009779587	-3.680550346913	-2.070456869135
H	2.020349980333	-3.404697620332	-2.024368246588
H	3.232787110002	-4.582188113335	-1.466514734159
H	3.319494461587	-3.931253805659	-3.113336146084
C	4.318892758598	-1.095886257346	-3.023127635469
H	4.720508742200	-1.665376282469	-3.874091359815
H	4.993473784772	-0.250356627911	-2.845846076179
H	3.337807145213	-0.706963004347	-3.308501618112
Si	-4.579823251152	-2.374118917044	0.885501505841
Si	-2.981842801300	-2.311489500580	-1.834791053849
Si	-4.595214070297	2.379650544721	1.024745266365
Si	-2.481605103064	2.988431497783	-1.230456298442
C	-1.473737322724	-3.241417325765	-1.196345794928
H	-1.036280632275	-2.748428335375	-0.322816844325
H	-1.716154925508	-4.271061253748	-0.912131302561
H	-0.697956552907	-3.263930263571	-1.971805692677
C	-2.454017577057	-1.229629020803	-3.289616578584
H	-3.296833171952	-0.688891982621	-3.738410443933
H	-1.680290464220	-0.506120424850	-3.011054115816
H	-2.022967825732	-1.878472296733	-4.065268826629
C	-4.241471013881	-3.543621047744	-2.532584003468
H	-3.763771070920	-4.119990053476	-3.337334455555
H	-4.603459649966	-4.253028040828	-1.779957820267
H	-5.113691226024	-3.034626114783	-2.963923605429
C	-6.381264144974	-2.734782344623	0.421631261976
H	-7.034513577585	-1.865402821126	0.568325463761
H	-6.477909742845	-3.061697752962	-0.621054035063
H	-6.753938986571	-3.542961405601	1.066248187703
C	-3.723779743288	-4.041759504929	1.097624343240
H	-4.201953289090	-4.550287029827	1.947391564753
H	-3.820516212344	-4.692011113543	0.221633110731
H	-2.661615092030	-3.930894800163	1.335031705072
C	-4.578219626583	-1.576476632537	2.603775574931
H	-4.829382814274	-0.511713755998	2.608634575337
H	-5.322820528644	-2.093045506520	3.227000414674
H	-3.601705156457	-1.697398472091	3.085082925582
H	-5.836543269081	-0.316930076267	-0.519989764973
H	-5.333907508640	-0.884775595096	-2.090117205269
H	-3.954309716114	1.010203459057	-2.482422486134
H	-5.367075158757	1.679184011023	-1.684312965805
C	-1.371528073320	2.298166307782	-2.597090582785
H	-0.711623204626	1.485258052926	-2.287758222921
H	-1.970972108327	1.955452562382	-3.450962046876
H	-0.730768056233	3.118551284832	-2.953049082837

C	-3.589102035333	4.192905650842	-2.198310845280
H	-4.451292157618	3.687141224389	-2.652414345667
H	-3.961789265199	5.024934942493	-1.594384968947
H	-2.989676129851	4.614082417672	-3.017843433075
C	-5.144420965618	4.159140220489	0.677795756070
H	-4.320464440542	4.878513782131	0.645103463598
H	-5.709392087934	4.239083722913	-0.258362647274
H	-5.814643583330	4.452851893574	1.498430943271
C	-1.489553735055	3.977916779023	0.035756244314
H	-0.864916597125	4.715078668147	-0.487444065498
H	-2.139144864497	4.520863555549	0.732858141814
H	-0.823061988288	3.332036776009	0.617453206038
C	-3.663898846843	2.411881482747	2.663968451891
H	-3.583896840893	1.422502230068	3.127720466910
H	-2.643011386890	2.795389819339	2.544053724365
H	-4.197724617872	3.073333034277	3.361059353531
C	-6.257873296873	1.498486568727	1.259337625658
H	-6.777748347969	1.988043154760	2.095316967228
H	-6.887871243400	1.617299226503	0.367494430215
H	-6.189401436285	0.433110525347	1.490459616566

E+ZPVE = -5644.546980 au, Free E (298.15 K) = -5644.651691 au.
Job name: ti554MIN23G7TS3

Table 4-17. Atomic Coordinates of $\mathbf{6_{opt}}$ at the B3LYP-D3/B1 Level of Theory

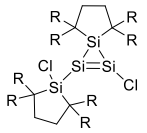


$\mathbf{6_{opt}}$

Atom	X	Y	Z
Si	0.095103808037	0.091367807220	0.637997840006
Si	2.240957107262	-0.097149610688	-0.413153795526
Si	-1.177327917527	-0.149757358042	2.313319619806
Si	-2.313139414817	0.130111615549	0.331541167171
Cl	1.382237806308	-0.345639978453	-2.352573177611
Cl	-1.238343771105	-0.662483170475	4.357710977191
C	3.495901862781	1.340607697054	-0.286637699891
C	4.834113433982	0.534679628778	-0.037391362127
C	4.559527518451	-0.771291374017	0.726855767686
C	3.375187207062	-1.563503117973	0.054860366876
C	-3.319661144255	-1.172891920957	-0.640050573806
C	-4.536700819353	-0.335002414546	-1.197227440699
C	-4.198040010625	1.164591730726	-1.316871398244
C	-3.402541904213	1.657818620306	-0.061442210770
Si	3.771588147184	2.531924587250	-1.783759199431
Si	3.194484792027	2.450276422135	1.253738331338
Si	4.087177695231	-2.533495172735	-1.454658754598
Si	2.704059870678	-2.807696508897	1.358603844145
C	1.562150926900	3.397482598721	1.180499172591
H	0.916247432347	3.097549484504	0.351240218647
H	1.735887697195	4.476865518218	1.090357783728
H	1.001840654286	3.220103479576	2.105784690115
C	3.173178040915	1.512238250210	2.894876374995
H	4.133988588291	1.046331346976	3.143848632830
H	2.394431002234	0.745172996812	2.937357394487
H	2.948955182214	2.246892716175	3.682164340512
C	4.600503423927	3.705238212315	1.462503483126
H	4.411795445261	4.260560026318	2.392406639441
H	4.666839258908	4.430946422416	0.645621205150
H	5.579162184760	3.218770568321	1.565929092040
C	5.617557269784	2.964252257006	-1.830805725885
H	6.212624842835	2.119255903318	-2.201296420385
H	6.024086273028	3.265433589432	-0.860316843888
H	5.758915613907	3.798557075557	-2.532153392484
C	2.803126789957	4.155459463931	-1.680180672940
H	3.046215660277	4.725340872900	-2.588520543757
H	3.045231953818	4.782560102509	-0.817640391977
H	1.721886829696	3.979629623322	-1.683079573069
C	3.370495719239	1.922339935374	-3.526251231873
H	2.292911623862	1.941373355551	-3.719212601309
H	3.736891929141	0.920690447546	-3.756521461646
H	3.853156142946	2.629418201978	-4.217833032601
H	5.317402192745	0.282279056261	-0.990480552452
H	5.567254081637	1.142482786615	0.512280011884
H	4.313724162807	-0.525795658395	1.765511544865
H	5.473901254917	-1.378833980602	0.770894619182
C	2.425419054775	-1.999951147845	3.045664230322
H	1.633498998306	-1.244786594415	3.027255121816
H	3.326778751549	-1.547196642729	3.474136904757
H	2.093057551145	-2.792152311780	3.731910195849
C	3.966768964096	-4.178584816619	1.700052685716
H	4.944989901714	-3.777306686788	1.994348363948
H	4.112447824123	-4.855235430260	0.850351138999
H	3.586511808915	-4.774741160216	2.541527283204
C	5.793161433368	-3.243559475890	-1.021042505445
H	5.859910068635	-3.749198674218	-0.055506297738
H	6.553981688573	-2.451299343532	-1.049245138615
H	6.055336490181	-3.970874966884	-1.803086215719
C	1.080044498625	-3.670473358492	0.946443270321
H	0.237401552164	-2.976261067391	1.026750522937
H	0.930962939492	-4.458129265092	1.699736917875
H	1.048400164715	-4.135947598513	-0.040901092475
C	2.941470970524	-3.932643632404	-1.993496286833
H	1.930141789259	-3.558636017020	-2.194002589037
H	2.869923878352	-4.737358760124	-1.252987410073
H	3.331800877993	-4.364558927695	-2.925354586337
C	4.476292660668	-1.549591070664	-3.026726754437
H	5.140271504002	-2.179491726963	-3.637157627523
H	5.006819665728	-0.611320666447	-2.832078501652
H	3.584398536353	-1.323404842871	-3.615994206934
Si	-3.969867290902	-2.559689367934	0.505931551687
Si	-2.451994606453	-1.909888689556	-2.170716210941
Si	-4.630258109944	2.093513305684	1.343813806863
Si	-2.393712523569	3.195516567827	-0.554303980450
C	-0.860417912513	-2.862270429673	-1.843068370015
H	-0.220343253383	-2.362739611128	-1.114305359073
H	-1.049857901644	-3.879866041282	-1.489289170304
H	-0.295235359780	-2.921348526335	-2.782922861964
C	-2.062361491512	-0.556457219640	-3.432163170648
H	-2.970097166589	-0.075172502581	-3.817489453106
H	-1.403841688852	0.214537765603	-3.018665929043
H	-1.537557637494	-1.012274944211	-4.283439953012
C	-3.614743951052	-3.124880563105	-3.049153178553
H	-3.135719339432	-3.450145208574	-3.983545822925
H	-3.810065825644	-4.019527233958	-2.445303322756
H	-4.581163067003	-2.675356035805	-3.310818321406
C	-5.681116493437	-3.112683897579	-0.091561903321
H	-6.449012997438	-2.360896850751	0.133018041027
H	-5.709410154081	-3.315053192634	-1.167857653594
H	-5.958217421142	-4.036054441072	0.436244832318
C	-2.856545094447	-4.084835389413	0.567831023687
H	-3.239295124444	-4.754090181163	1.351399648103
H	-2.842665505872	-4.644534578306	-0.374159385667
H	-1.822810588354	-3.826587267167	0.825686919770
C	-4.190349026468	-2.064390574142	2.326230850279
H	-4.454097917020	-1.016034559709	2.492118949791
H	-4.995930032617	-2.680072356389	2.752706458147
H	-3.280951073576	-2.272110998593	2.902749633140
H	-5.405864454671	-0.439340533841	-0.542264627835
H	-4.867996875554	-0.712046305653	-2.176359720675
H	-3.605182140189	1.328198286999	-2.228560973385
H	-5.126790674043	1.740387013095	-1.458881521678
C	-0.985203631662	2.781877467916	-1.754413162548
H	-0.264607605229	2.046337175851	-1.385831896326
H	-1.384341805256	2.404475718869	-2.704733322185
H	-0.438367122604	3.709482090263	-1.974564596676
C	-3.439404980757	4.402915356500	-1.577133699516
H	-3.983620604573	3.877652578768	-2.373696656991
H	-4.164165706561	4.970071604602	-0.986657106123
H	-2.762682450163	5.121160433360	-2.061835461433
C	-5.399975158165	3.810672004059	1.102761150967
H	-4.688747775338	4.635732506278	1.210773160764
H	-5.883562950783	3.901041274612	0.121862290316
H	-6.178096642809	3.935037119339	1.869260661228
C	-1.724317435939	4.083685267294	0.969440274666
H	-1.003685883662	4.858290261755	0.678296880249
H	-2.527123064178	4.563566612211	1.541343773484
H	-1.208347786274	3.381469191712	1.632595013694
C	-3.866887940637	2.069458678305	3.071517049562
H	-3.752443619002	1.051339154563	3.462125911224
H	-2.884847184073	2.554742472419	3.107171323733
H	-4.534671353770	2.611791617027	3.756150435347
C	-6.173127883748	0.988914373277	1.382585134968
H	-6.794831025421	1.326100076942	2.224702779877
H	-6.767694777068	1.112171089657	0.467538998166
H	-5.975144458336	-0.076533532268	1.523893650291

E+ZPVE = -5644.575898 au, Free E (298.15 K) = -5644.678990 au.
Job name: ti554MIN23G7TS3FE

Table 4-18. Atomic Coordinates of $\mathbf{6_{opt}}$ at the B3LYP-D3/6-311G(d) Level of Theory



(R = $SiMe_3$)

$\mathbf{6_{opt}}$

Atom	X	Y	Z
Si	0.047599087795	-0.138121332271	0.400016434439
Si	2.254141193153	-0.344525737056	-0.506987537492
Si	-1.142993267462	-0.108401358883	2.149347267639
Si	-2.351049019416	0.231065809299	0.229038687067
Cl	1.716678489971	0.253911150168	-2.504756759664
Cl	-1.167706512551	-0.572906981582	4.204229557980
C	3.543441782834	0.819254516419	0.276176994253
C	4.851690062431	-0.009693902324	0.014938028638
C	4.573888316304	-1.509836131400	0.212876801635
C	3.282104225455	-1.960318006632	-0.586271440017
C	-3.480719997959	-1.010847667555	-0.668662755528
C	-4.698311254755	-0.122801054729	-1.122588766783
C	-4.284677218115	1.354760517940	-1.304061957700
C	-3.351040335502	1.822643318416	-0.133706311062
Si	3.688951441538	2.547575419038	-0.531659405220
Si	3.328961512843	1.039177182883	2.176718924743
Si	3.879903542007	-2.433026743326	-2.360236793880
Si	2.586097247127	-3.575280929038	0.208490965423
C	2.183015299869	2.475479057406	2.617051389631
H	1.216646936005	2.396640370737	2.107932675115
H	2.612841398712	3.455116328004	2.382002508841
H	1.989801394425	2.441267413470	3.698536718298
C	2.670555125872	-0.469989935812	3.108364629379
H	3.309961784052	-1.352621667074	2.990317921616
H	1.651582927197	-0.746028113048	2.827994869472
H	2.651833186542	-0.214322611056	4.177737748142
C	5.017400200550	1.335257610992	2.985025864073
H	4.845019122725	1.669905571930	4.017990771555
H	5.630899243180	2.089886444888	2.484678340710
H	5.593863309678	0.401740462480	3.036906944894
C	4.425740240179	2.483020427216	-2.272996438591
H	3.771020663763	1.984832649764	-2.993239700669
H	5.407607524532	1.994458950248	-2.299665860350
H	4.567410830243	3.521420423494	-2.606635263651
C	4.898624604097	3.659347415495	0.415025519500
H	4.976605385763	4.611739499730	-0.128657146683
H	5.903933424792	3.218571321000	0.450566049266
H	4.587225605783	3.884131541825	1.440321936946
C	2.021791908977	3.431295766237	-0.618065102899
H	1.887059849511	4.120688695481	0.222628761916
H	1.178241415588	2.734800355706	-0.612536311090
H	1.959818640429	4.009440272742	-1.549719978992
H	5.203729254151	0.154787895486	-1.008638880984
H	5.672055437137	0.309238445480	0.672887647836
H	4.455366748878	-1.700783475061	1.287287836479
H	5.450697189788	-2.098039891458	-0.094044417444
C	1.243640154670	-3.403502705192	1.526808345522
H	0.301117406717	-3.024144947922	1.119984163754
H	1.523002297513	-2.775047091793	2.375331957340
H	1.055306524809	-4.417347132613	1.910783855601
C	4.016156230674	-4.466131457895	1.076573974128
H	4.320839377829	-3.937910909220	1.989397686084
H	4.900956356711	-4.587305339783	0.443066722447
H	3.672834163409	-5.466691886500	1.374286475793
C	5.039539792264	-3.935062705902	-2.262813313579
H	4.569039498506	-4.852512584642	-1.897756480594
H	5.917122150497	-3.730926769219	-1.635458076517
H	5.406918794842	-4.126355689522	-3.281503348112
C	1.811198922320	-4.794519700121	-1.016278313468
H	0.885823435623	-4.397665854345	-1.444569709816
H	1.547410846680	-5.693717929751	-0.440688884278
H	2.459338201956	-5.103622066396	-1.840415829904
C	2.476063744263	-2.829646316269	-3.564876084196
H	1.495973327870	-2.859568288635	-3.084659803883
H	2.649103055595	-3.803183877809	-4.042643907095
H	2.437162541581	-2.060640812247	-4.345256093791
C	4.972833017259	-1.128713122106	-3.187480336950
H	5.182623836947	-1.485655961811	-4.206788939152
H	5.937830275701	-1.009014891731	-2.678967981265
H	4.491706400994	-0.150975515350	-3.270380744978
Si	-4.086066438456	-2.375183275450	0.523515127493
Si	-2.701830362883	-1.780834730785	-2.223741196782
Si	-4.410505121942	2.404405065007	1.354382983289
Si	-2.246963916237	3.243825962581	-0.758054629752
C	-1.011924786360	-2.573938774447	-1.937872582907
H	-0.216267505723	-1.847442866005	-2.139127298618
H	-0.873980641638	-2.965835813513	-0.927558550452
H	-0.884360242611	-3.403907975823	-2.647460011746
C	-2.457810021516	-0.517091366088	-3.606007722998
H	-3.397722587194	-0.046407003000	-3.920737316171
H	-1.750586624649	0.269400655724	-3.323234767251
H	-2.038105939893	-1.039157521105	-4.477794047857
C	-3.842363521768	-3.108026149493	-2.950984376829
H	-3.422750490517	-3.436667691847	-3.912185446943
H	-3.936041119718	-3.989240021009	-2.305668023543
H	-4.851100059341	-2.720297293726	-3.144314696963
C	-5.790424790804	-2.992277669935	-0.026962041632
H	-6.549192371434	-2.205344819335	0.076727024150
H	-5.811375615523	-3.347873674434	-1.061799297740
H	-6.089017468581	-3.825448420858	0.624954705081
C	-2.912020370831	-3.853069328973	0.633906485215
H	-3.337612657555	-4.579400703758	1.340659284917
H	-2.754154887870	-4.364957470334	-0.321927132061
H	-1.932838318209	-3.549259324128	1.025908272011
C	-4.318229370725	-1.793496519269	2.316819128964
H	-4.539273654046	-0.727465172330	2.423294503496
H	-5.155618876346	-2.350739410834	2.760819851515
H	-3.426583976325	-2.005762600315	2.918706672768
H	-5.501865162447	-0.167472820220	-0.379014381656
H	-5.144133913944	-0.499836693736	-2.056552542806
H	-3.767361625841	1.463869196031	-2.267887444196
H	-5.187217490986	1.982231274807	-1.376936973704
C	-1.125575556070	2.676862837322	-2.169944810668
H	-0.531516805061	1.784328790936	-1.960215783386
H	-1.722174745584	2.485016916775	-3.071404242139
H	-0.424024453389	3.487758655603	-2.407741308347
C	-3.270347631863	4.614319861540	-1.583181819327
H	-4.144107673170	4.202067413018	-2.106048605514
H	-3.623265489889	5.377458644477	-0.883692577524
H	-2.640826266242	5.109565615161	-2.335670780172
C	-4.958447449614	4.211854843541	1.187372134979
H	-4.131800985776	4.925734717292	1.268873946824
H	-5.481813776197	4.400545561487	0.242417759469
H	-5.661453356456	4.418512358371	2.006918873569
C	-1.229463094666	3.973821276100	0.654424841602
H	-0.546345258884	4.741995155876	0.270716255950
H	-1.868170290359	4.435328196341	1.417708475929
H	-0.624474685672	3.201827044280	1.143945345980
C	-3.539184196407	2.279917121193	3.025751262835
H	-3.527200452382	1.257229234887	3.420214051032
H	-2.503245387729	2.638546445607	2.987763687889
H	-4.083113279751	2.905034231379	3.748341318113
C	-6.069805246202	1.495218835471	1.493141595019
H	-6.618169674421	1.939423340913	2.336303759829
H	-6.680112982575	1.641903160467	0.592133462042
H	-5.988859153076	0.421244139668	1.681544309847

E+ZPVE = -5644.583660 au, Free E (298.15 K) = -5644.687300 au.
Job name: ti554MIN23G7CR6

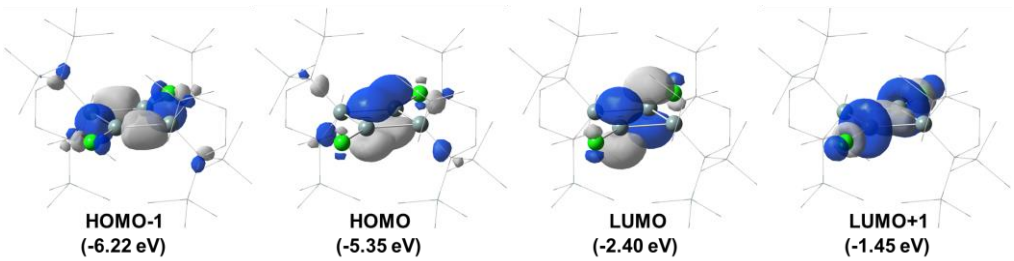


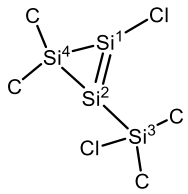
Figure 4-31. Frontier Kohn-Sham orbitals of $\mathbf{4_{opt}}$ at the B3LYP-D3/6-311G(d) level of theory.

Table 4-19. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of **4**, **4**$_{opt}$, **4′**$_{opt}$ and **4′′**$_{opt}$

Compound	$SiMe_3$	Si (bridge)	Si (bridgehead)	note
4[a]	4.6	−7.9	126.4	TN420_7
4$_{opt}$[b,c]	5.0 (356.4)[d]	−17.1 (378.5)	150.2 (211.2)	nmr2_TN74a
4′$_{opt}$[b,c]	5.3 (356.1)[d]	139.5 (221.9)	−37.1 (398.3)	nmr2_TN77_12
		137.1 (224.3)	−49.9 (411.3)	0
4′′$_{opt}$[b,c]	4.8 (356.6)[d]	−25.1 (386.5)	86.5 (274.8)	nmr_TN84a

[a]Experimental ^{29}Si Chemical Shifts of **4** in benzene-d_6 at 333 K. [b]GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [c]The absolute chemical shift is shown in the parentheses. [d]Average values.

Table 4-20. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of **6**$_{opt}$



	$SiMe_3$	Si^2=**Si^1**-Cl	**Si^2**=Si^1-Cl	Si^4 (Si_3 ring)	Si^3 (chlorosilyl)	Note
Experimental[a]	2.9, 3.3, 6.1	104.1	48.7	78.2	32.9	TN420_7
Theoretical[b,c]	4.2 (357.2)[d]	97.0 (264.4)	49.4 (311.9)	75.4 (286.0)	38.1 (323.3)	nmr2_TN82a

[a]Experimental ^{29}Si Chemical Shifts of **6** in benzene-d_6 at 333 K. [b]GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [c]The absolute chemical shift is shown in the parentheses. [d]Average values.

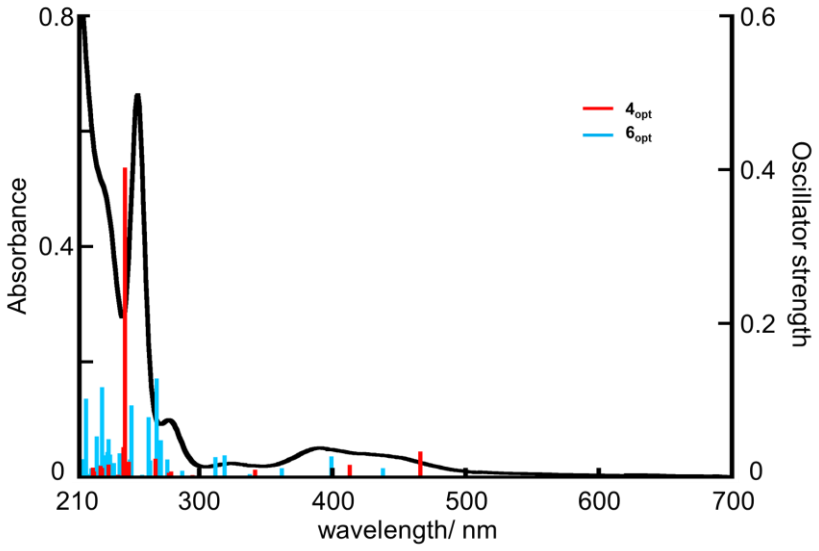


Figure 4-32. Experimental UV-vis absorption spectrum of the equilibrium mixture of **4** and **6** in hexane (black) and calculated band positions of **4**$_{opt}$ and **6**$_{opt}$ at the TD-B3LYP-D3/6-311G(d) level of theory (red and light blue).

Table 4-21. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{4}_{\mathbf{opt}}$ (The 237th orbital is highest occupied orbital shown in Figure 4-31)

Excited State 1: Singlet-AU 2.6596 eV 466.17 nm f=0.0332
<S**2>=0.000
237 -> 238 0.67896
237 -> 239 -0.17174
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5662.97431013
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-AG 2.8801 eV 430.48 nm f=0.0000
<S**2>=0.000
236 -> 238 0.70504

Excited State 3: Singlet-AU 3.0056 eV 412.51 nm f=0.0162
<S**2>=0.000
237 -> 238 0.16949
237 -> 239 0.67597

Excited State 4: Singlet-AU 3.6254 eV 341.99 nm f=0.0096
<S**2>=0.000
237 -> 240 0.68769

Excited State 5: Singlet-AG 3.7152 eV 333.72 nm f=0.0000
<S**2>=0.000
237 -> 241 0.70481

Excited State 6: Singlet-AG 3.8746 eV 319.99 nm f=0.0000
<S**2>=0.000
236 -> 239 0.69880

Excited State 7: Singlet-AG 4.1861 eV 296.18 nm f=0.0000
<S**2>=0.000
233 -> 238 -0.11200
235 -> 238 0.69584

Excited State 8: Singlet-AU 4.1991 eV 295.26 nm f=0.0026
<S**2>=0.000
234 -> 238 0.70535

Excited State 9: Singlet-AG 4.2735 eV 290.12 nm f=0.0000
<S**2>=0.000
233 -> 238 0.68739
235 -> 238 0.11840
236 -> 240 -0.10203

Excited State 10: Singlet-AU 4.3196 eV 287.03 nm f=0.0013
<S**2>=0.000
230 -> 238 -0.35899
231 -> 238 0.19538
232 -> 238 0.56102

Excited State 11: Singlet-AU 4.4516 eV 278.52 nm f=0.0074
<S**2>=0.000
230 -> 238 -0.30886
231 -> 238 0.49899
232 -> 238 -0.37371

Excited State 12: Singlet-AU 4.4717 eV 277.27 nm f=0.0059
<S**2>=0.000
230 -> 238 0.50949
231 -> 238 0.44481
232 -> 238 0.17234

Excited State 13: Singlet-AG 4.5559 eV 272.14 nm f=0.0000
<S**2>=0.000
229 -> 238 0.10870
233 -> 238 0.10925
236 -> 240 0.67874

Excited State 14: Singlet-AU 4.6516 eV 266.54 nm f=0.0240
<S**2>=0.000
236 -> 241 0.55902
237 -> 242 -0.42495

Excited State 15: Singlet-AG 4.6548 eV 266.36 nm f=0.0000
<S**2>=0.000
229 -> 238 0.69462
236 -> 240 -0.11101

Excited State 16: Singlet-AU 4.9319 eV 251.39 nm f=0.0005
<S**2>=0.000
228 -> 238 0.68938

Excited State 17: Singlet-AG 4.9464 eV 250.65 nm f=0.0000
<S**2>=0.000
226 -> 238 -0.10228
227 -> 238 0.68694

Excited State 18: Singlet-AU 5.0255 eV 246.71 nm f=0.0202
<S**2>=0.000
223 -> 238 0.40022
225 -> 238 0.52671
237 -> 242 0.11984

Excited State 19: Singlet-AG 5.0351 eV 246.24 nm f=0.0000
<S**2>=0.000
224 -> 238 -0.18600
226 -> 238 0.66703

Excited State 20: Singlet-AU 5.0715 eV 244.47 nm f=0.4028
<S**2>=0.000
225 -> 238 -0.25689
230 -> 240 -0.16019
236 -> 241 0.36213
237 -> 242 0.48343

Excited State 21: Singlet-AU 5.0853 eV 243.81 nm f=0.0392
<S**2>=0.000
219 -> 238 0.15226
223 -> 238 0.50704
225 -> 238 -0.37875
236 -> 241 -0.11926
237 -> 242 -0.16915

Excited State 22: Singlet-AG 5.1078 eV 242.74 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.10510
221 -> 238 -0.11859
224 -> 238 0.66031
226 -> 238 0.16395

Excited State 23: Singlet-AG 5.1488 eV 240.80 nm f=0.0000
<S**2>=0.000
235 -> 239 0.69109

Excited State 24: Singlet-AU 5.1605 eV 240.26 nm f=0.0005
<S**2>=0.000
219 -> 238 -0.10107
234 -> 239 0.69475

Excited State 25: Singlet-AG 5.1750 eV 239.58 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.19745
220 -> 238 -0.16010
221 -> 238 0.64258
226 -> 238 0.12372

Excited State 26: Singlet-AU 5.1898 eV 238.90 nm f=0.0031
<S**2>=0.000
219 -> 238 0.56210
222 -> 238 -0.37669

Excited State 27: Singlet-AU 5.1938 eV 238.72 nm f=0.0022
<S**2>=0.000
219 -> 238 0.33384
222 -> 238 0.56757
223 -> 238 -0.20751

Excited State 28: Singlet-AG 5.2111 eV 237.93 nm f=0.0000
<S**2>=0.000
218 -> 238 0.35523
220 -> 238 0.52265
221 -> 238 0.23219
233 -> 239 0.10324

Excited State 29: Singlet-AG 5.2177 eV 237.62 nm f=0.0000
<S**2>=0.000
220 -> 238 -0.12864
233 -> 239 0.42332
235 -> 239 0.13669
237 -> 244 -0.39387
237 -> 245 -0.29668
237 -> 246 -0.16483

Excited State 30: Singlet-AU 5.2547 eV 235.95 nm f=0.0003
<S**2>=0.000
216 -> 238 0.50300
217 -> 238 -0.45883

Excited State 31: Singlet-AG 5.2555 eV 235.91 nm f=0.0000
<S**2>=0.000
218 -> 238 0.48456
220 -> 238 -0.35848
233 -> 239 0.26227
237 -> 244 0.17618
237 -> 245 0.12631

Excited State 32: Singlet-AG 5.2592 eV 235.75 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.27171
220 -> 238 0.20680
233 -> 239 0.47753
237 -> 244 0.29746
237 -> 245 0.20868
237 -> 246 0.11740

Excited State 33: Singlet-AU 5.3132 eV 233.35 nm f=0.0009
<S**2>=0.000
216 -> 238 0.45422
217 -> 238 0.51970

Excited State 34: Singlet-AU 5.3368 eV 232.32 nm f=0.0165
<S**2>=0.000
230 -> 239 -0.28837
232 -> 239 0.62008

Excited State 35: Singlet-AU 5.3509 eV 231.71 nm f=0.0007
<S**2>=0.000
230 -> 239 -0.13789
231 -> 239 0.67966

Excited State 36: Singlet-AU 5.4520 eV 227.41 nm f=0.0120
<S**2>=0.000
230 -> 239 0.30533
232 -> 239 0.13337
237 -> 243 0.60911

Excited State 37: Singlet-AG 5.4572 eV 227.19 nm f=0.0000
<S**2>=0.000
215 -> 238 0.69902

Excited State 38: Singlet-AU 5.4674 eV 226.77 nm f=0.0147
<S**2>=0.000
230 -> 239 0.53689
231 -> 239 0.15871
232 -> 239 0.24274
237 -> 243 -0.32682

Excited State 39: Singlet-AU 5.5349 eV 224.00 nm f=0.0018
<S**2>=0.000
214 -> 238 0.63465
219 -> 238 -0.10541
237 -> 247 -0.22362

Excited State 40: Singlet-AG 5.5714 eV 222.54 nm f=0.0000
<S**2>=0.000
237 -> 244 -0.44605
237 -> 245 0.46699
237 -> 246 0.22863
237 -> 251 -0.11452

Excited State 41: Singlet-AG 5.5938 eV 221.65 nm f=0.0000
<S**2>=0.000
229 -> 239 -0.20244
235 -> 240 0.40339
236 -> 242 0.52537

Excited State 42: Singlet-AU 5.6071 eV 221.12 nm f=0.0073
<S**2>=0.000
214 -> 238 0.20388
234 -> 240 0.39718
237 -> 247 0.49449
237 -> 250 0.12358

Excited State 43: Singlet-AG 5.6117 eV 220.94 nm f=0.0000
<S**2>=0.000
229 -> 239 0.66507
235 -> 240 0.16996
236 -> 242 0.12094

Excited State 44: Singlet-AU 5.6269 eV 220.34 nm f=0.0124
<S**2>=0.000
214 -> 238 -0.11933
234 -> 240 0.57325
237 -> 247 -0.36564

Excited State 45: Singlet-AG 5.6392 eV 219.86 nm f=0.0000
<S**2>=0.000
235 -> 240 0.54533
236 -> 242 -0.43265

Excited State 46: Singlet-AG 5.6920 eV 217.82 nm f=0.0000
<S**2>=0.000
213 -> 238 0.69754

Excited State 47: Singlet-AU 5.7024 eV 217.43 nm f=0.0012
<S**2>=0.000
212 -> 238 0.69660

Excited State 48: Singlet-AG 5.7406 eV 215.98 nm f=0.0000
<S**2>=0.000
233 -> 240 -0.45825
234 -> 241 0.52326

Table 4-22. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{6}_{\mathbf{opt}}$ (The 237th orbital is highest occupied orbital)

Excited State 1: Singlet-A 2.8294 eV 438.21 nm f=0.0119
<S**2>=0.000
235 -> 238 -0.10313
237 -> 238 0.55576
237 -> 239 0.41018
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5662.96653789
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1085 eV 398.86 nm f=0.0270
<S**2>=0.000
235 -> 239 0.10704
236 -> 238 -0.11310
237 -> 238 -0.37316
237 -> 239 0.55405

Excited State 3: Singlet-A 3.4281 eV 361.67 nm f=0.0118
<S**2>=0.000
235 -> 238 -0.12710
236 -> 238 0.66975
237 -> 240 0.11911

Excited State 4: Singlet-A 3.6728 eV 337.57 nm f=0.0041
<S**2>=0.000
236 -> 238 -0.11450
236 -> 239 -0.21754
237 -> 240 0.64817

Excited State 5: Singlet-A 3.8813 eV 319.44 nm f=0.0282
<S**2>=0.000
235 -> 238 -0.47416
236 -> 238 -0.10104
236 -> 239 0.49811

Excited State 6: Singlet-A 3.9716 eV 312.17 nm f=0.0262
<S**2>=0.000
235 -> 238 0.44981
235 -> 239 -0.25459
236 -> 239 0.39936
237 -> 238 0.11617
237 -> 240 0.17884

Excited State 7: Singlet-A 4.3211 eV 286.92 nm f=0.0086
<S**2>=0.000
235 -> 239 0.13699
237 -> 241 0.68537

Excited State 8: Singlet-A 4.4902 eV 276.12 nm f=0.0230
<S**2>=0.000
232 -> 238 -0.11710
235 -> 239 -0.43612
236 -> 240 0.48258
237 -> 241 0.10130

Excited State 9: Singlet-A 4.5790 eV 270.77 nm f=0.0479
<S**2>=0.000

232 -> 238 0.12873
234 -> 238 0.59681
235 -> 239 0.13107
236 -> 240 0.28444

Excited State 10: Singlet-A 4.6190 eV 268.42 nm f=0.1284
<S**2>=0.000
231 -> 238 -0.15323
232 -> 238 -0.29016
234 -> 238 0.36315
235 -> 239 -0.27410
235 -> 240 0.15939
236 -> 240 -0.32784
236 -> 241 -0.11324

Excited State 11: Singlet-A 4.7169 eV 262.85 nm f=0.0219
<S**2>=0.000
232 -> 238 0.16718
233 -> 238 0.65947
235 -> 239 -0.10812

Excited State 12: Singlet-A 4.7404 eV 261.55 nm f=0.0779
<S**2>=0.000
232 -> 238 0.58426
233 -> 238 -0.22881
235 -> 239 -0.20115
236 -> 240 -0.11054
236 -> 241 -0.13784

Excited State 13: Singlet-A 4.8290 eV 256.75 nm f=0.0029
<S**2>=0.000
231 -> 238 0.66840
235 -> 239 -0.11868
236 -> 241 -0.12109

Excited State 14: Singlet-A 4.9788 eV 249.02 nm f=0.0933
<S**2>=0.000
229 -> 238 0.11948
230 -> 238 -0.31436
234 -> 239 -0.14263
235 -> 240 0.55196
236 -> 240 0.11793
237 -> 243 0.10112

Excited State 15: Singlet-A 4.9925 eV 248.34 nm f=0.0229
<S**2>=0.000
230 -> 238 0.58306
234 -> 239 0.14760
235 -> 240 0.31559

Excited State 16: Singlet-A 4.9980 eV 248.07 nm f=0.0014
<S**2>=0.000
230 -> 238 -0.19593
234 -> 239 0.67251

Excited State 17: Singlet-A 5.0894 eV 243.61 nm f=0.0030
<S**2>=0.000
229 -> 238 0.11075
233 -> 239 0.68518

Excited State 18: Singlet-A 5.1050 eV 242.87 nm f=0.0006
<S**2>=0.000
229 -> 238 0.59390
230 -> 238 0.11099
232 -> 239 -0.32523

Excited State 19: Singlet-A 5.1132 eV 242.48 nm f=0.0027
<S**2>=0.000
229 -> 238 0.31238
232 -> 239 0.61292

Excited State 20: Singlet-A 5.1707 eV 239.78 nm f=0.0312
<S**2>=0.000
231 -> 239 0.67103
236 -> 241 0.15682

Excited State 21: Singlet-A 5.2568 eV 235.85 nm f=0.0182
<S**2>=0.000
236 -> 241 -0.17062
237 -> 242 0.42620
237 -> 243 0.40154
237 -> 244 -0.14640
237 -> 245 0.18943
237 -> 246 -0.16629

Excited State 22: Singlet-A 5.3215 eV 232.99 nm f=0.0294
<S**2>=0.000
224 -> 238 0.11823
226 -> 238 -0.19520
227 -> 238 0.20345
228 -> 238 0.54467
236 -> 241 -0.25899

Excited State 23: Singlet-A 5.3579 eV 231.40 nm f=0.0493
<S**2>=0.000
222 -> 238 -0.13098
226 -> 238 0.17550
227 -> 238 -0.33953
228 -> 238 0.39113
230 -> 239 0.16730
236 -> 241 0.30798

Excited State 24: Singlet-A 5.3723 eV 230.78 nm f=0.0327
<S**2>=0.000
225 -> 238 0.24705
227 -> 238 0.43905
230 -> 239 0.34197
236 -> 241 0.20959
237 -> 242 0.15964

Excited State 25: Singlet-A 5.3798 eV 230.46 nm f=0.0175
<S**2>=0.000
225 -> 238 -0.24750
226 -> 238 -0.10062
227 -> 238 -0.18094
229 -> 239 -0.11187
230 -> 239 0.52751
236 -> 241 -0.21771

Excited State 26: Singlet-A 5.4182 eV 228.83 nm f=0.0225
<S**2>=0.000
225 -> 238 0.44183
226 -> 238 0.15461
227 -> 238 -0.10278
230 -> 239 0.17462
236 -> 241 -0.15071
237 -> 242 -0.29685
237 -> 243 0.20069
237 -> 245 -0.13121

Excited State 27: Singlet-A 5.4355 eV 228.10 nm f=0.0282
<S**2>=0.000
225 -> 238 -0.33763
226 -> 238 0.43156
227 -> 238 0.28293
230 -> 239 0.10945
237 -> 242 -0.15740
237 -> 243 0.18101
237 -> 244 -0.10193

Excited State 28: Singlet-A 5.4482 eV 227.57 nm f=0.1172
<S**2>=0.000
225 -> 238 0.12299
226 -> 238 0.40380
229 -> 239 -0.21172
236 -> 241 -0.17410
237 -> 242 0.20221
237 -> 243 -0.30213
237 -> 244 0.19641

Excited State 29: Singlet-A 5.4948 eV 225.64 nm f=0.0120
<S**2>=0.000
223 -> 238 0.26757
229 -> 239 0.57807
234 -> 240 0.18565
237 -> 243 -0.10711

Excited State 30: Singlet-A 5.5149 eV 224.82 nm f=0.0159
<S**2>=0.000
222 -> 238 -0.18300
223 -> 238 0.44787
224 -> 238 0.38222
226 -> 238 -0.11551
228 -> 238 -0.11574
229 -> 239 -0.15239
234 -> 240 -0.17387

Excited State 31: Singlet-A 5.5304 eV 224.19 nm f=0.0152
<S**2>=0.000
222 -> 238 -0.10745
223 -> 238 -0.36817
224 -> 238 0.51736
225 -> 238 -0.10285
229 -> 239 0.10611

234 -> 240 0.13521

Excited State 32: Singlet-A 5.5370 eV 223.92 nm f=0.0529
<S**2>=0.000
223 -> 238 0.13264
229 -> 239 -0.21542
234 -> 240 0.62294

Excited State 33: Singlet-A 5.5728 eV 222.48 nm f=0.0008
<S**2>=0.000
220 -> 238 -0.24675
221 -> 238 0.50277
222 -> 238 -0.34434
224 -> 238 -0.13720

Excited State 34: Singlet-A 5.5845 eV 222.02 nm f=0.0096
<S**2>=0.000
232 -> 240 -0.12341
235 -> 241 -0.11700
237 -> 243 0.31238
237 -> 244 0.44435
237 -> 246 0.29082
237 -> 248 0.17765

Excited State 35: Singlet-A 5.5998 eV 221.41 nm f=0.0016
<S**2>=0.000
220 -> 238 -0.19042
221 -> 238 0.29492
222 -> 238 0.53253
223 -> 238 0.15381
224 -> 238 0.16191

Excited State 36: Singlet-A 5.6259 eV 220.38 nm f=0.0035
<S**2>=0.000
219 -> 238 0.22338
220 -> 238 0.25045
231 -> 240 0.15327
232 -> 240 0.50023
233 -> 240 0.12924
237 -> 244 0.13905

Excited State 37: Singlet-A 5.6441 eV 219.67 nm f=0.0082
<S**2>=0.000
219 -> 238 0.61858
232 -> 240 -0.24289

Excited State 38: Singlet-A 5.6499 eV 219.45 nm f=0.0113
<S**2>=0.000
218 -> 238 -0.31698
219 -> 238 -0.13618
220 -> 238 0.46518
221 -> 238 0.27141
232 -> 240 -0.21428

Excited State 39: Singlet-A 5.6580 eV 219.13 nm f=0.0023
<S**2>=0.000
219 -> 238 -0.12110
235 -> 241 -0.21434
237 -> 242 -0.27924
237 -> 244 0.11091
237 -> 245 0.38376
237 -> 246 -0.33587
237 -> 247 0.11529
237 -> 248 0.11496
237 -> 250 0.11578

Excited State 40: Singlet-A 5.7148 eV 216.95 nm f=0.0042
<S**2>=0.000
215 -> 238 0.14424
216 -> 238 0.23376
218 -> 238 0.52346
219 -> 238 -0.12278
220 -> 238 0.23051
233 -> 240 -0.12144
237 -> 244 0.10391
237 -> 246 -0.12245

Excited State 41: Singlet-A 5.7232 eV 216.63 nm f=0.0030
<S**2>=0.000
217 -> 238 0.13852
232 -> 240 -0.19315
233 -> 240 0.61481
237 -> 246 -0.10804

Excited State 42: Singlet-A 5.7277 eV 216.46 nm f=0.0025
<S**2>=0.000
217 -> 238 -0.28535
218 -> 238 0.20137
220 -> 238 0.14849
233 -> 240 0.22360
237 -> 244 -0.26014
237 -> 245 0.26557
237 -> 246 0.32409

Excited State 43: Singlet-A 5.7377 eV 216.09 nm f=0.0006
<S**2>=0.000
215 -> 238 0.22025
217 -> 238 0.53744
237 -> 244 -0.11694
237 -> 245 0.22823
237 -> 246 0.21316

Excited State 44: Singlet-A 5.7490 eV 215.66 nm f=0.1020
<S**2>=0.000
225 -> 239 -0.13323
226 -> 239 -0.13273
228 -> 239 0.19045
235 -> 241 0.47476
237 -> 244 0.18679
237 -> 245 0.25687
237 -> 248 -0.13173

Excited State 45: Singlet-A 5.7659 eV 215.03 nm f=0.0003
<S**2>=0.000
215 -> 238 0.10807
216 -> 238 0.56521
217 -> 238 -0.15022
218 -> 238 -0.18423
220 -> 238 -0.10008
221 -> 238 -0.17573
228 -> 239 0.21036

Excited State 46: Singlet-A 5.7766 eV 214.63 nm f=0.0126
<S**2>=0.000
216 -> 238 -0.14718
218 -> 238 0.10519
228 -> 239 0.61731
231 -> 240 -0.11223
235 -> 241 -0.11925

Excited State 47: Singlet-A 5.7791 eV 214.54 nm f=0.0131
<S**2>=0.000
226 -> 239 -0.21446
227 -> 239 0.63865
235 -> 241 -0.11092

Excited State 48: Singlet-A 5.8101 eV 213.39 nm f=0.0236
<S**2>=0.000
215 -> 238 -0.13203
231 -> 240 0.61093
232 -> 240 -0.19066
237 -> 245 -0.10795

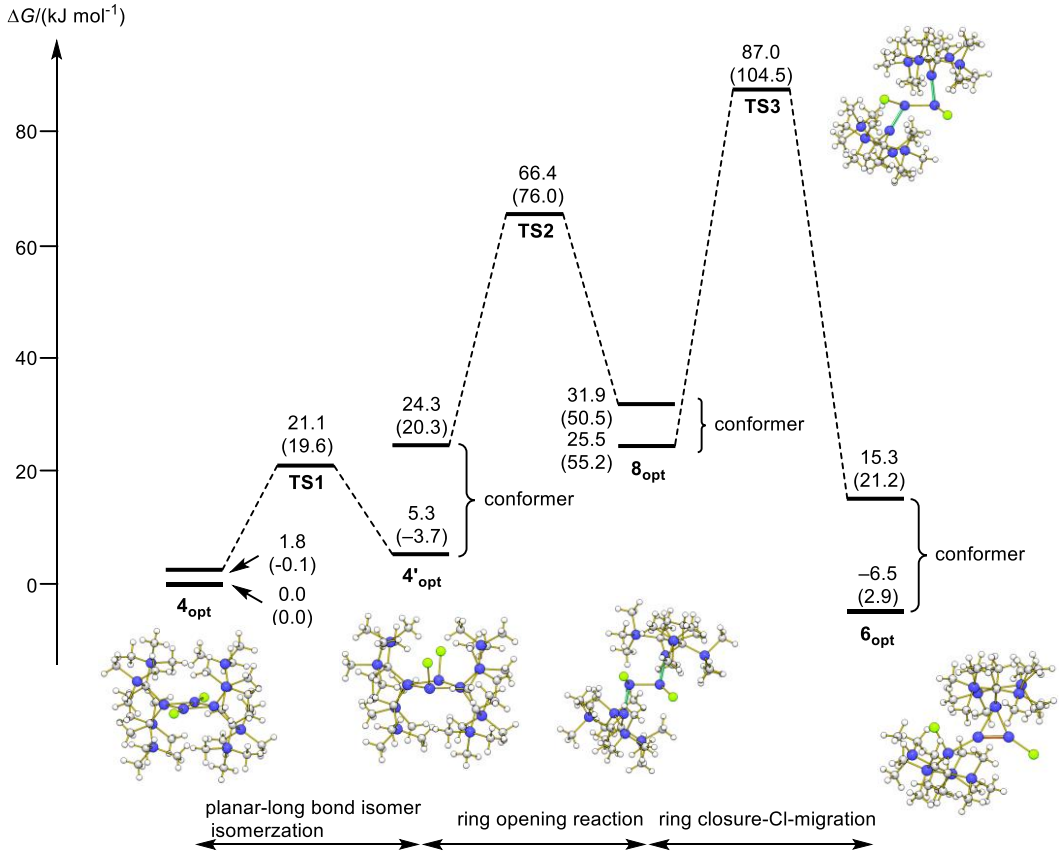


Figure 4-33. A possible reaction route between $\mathbf{4}_{opt}$ and $\mathbf{6}_{opt}$ calculated at the B3LYP-D3/B1 level of theory (basis B1: 6-311G(d) [core Si_4Cl_2], 6-31G(d) [carbon atoms in silacyclopentane rings], 3-21G* [others]).

Preliminary estimation of the thermodynamic parameters for the equilibrium between 4 and 6

In the ^{1}H NMR spectrum of a mixture of bicyclo[1.1.0]tetrasilane **4** and cyclotrisilene **6**, the signals due to four $SiMe_3$ groups (36 H) of **6** were substantially broadened and overlapped with that due to eight $SiMe_3$ groups (72H) of **4** (Figure 4-34). Assuming that only signals of **4** and **6** were overlapped in this region, the equilibrium constants K_{eq} (= [**6**]:[**4**]) were determined by using the integral ratio of the $SiMe_3$ signals of ^{1}H NMR spectra in C_6D_6 (Table 4-23). A plot of lnK_{eq} at various reciprocal temperatures are shown in Figure 4-35. The thermodynamic parameters for the isomerisation of **4** to **6** are calculated to be ΔH = +14.6 ± 2.9 kJ mol^{-1} and ΔS = +49 ± 9 J K^{-1} mol^{-1}.

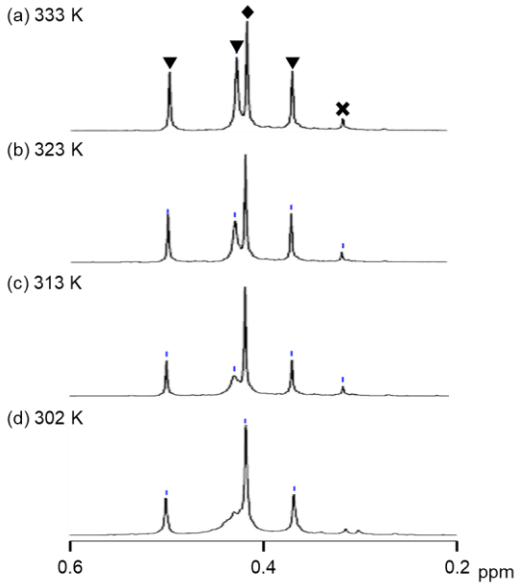


Figure 4-34. ^{1}H NMR spectra ($SiMe_3$ region) of a mixture of **4** and **6** in benzene-d_6 at (a) 333 K, (b) 323 K, (c) 313 K, and (d) 302 K (♦ = **4**, ▼ = **6**, × = **1**).

Table 4-23. The Equilibrium Constants K_{eq} (= [**6**]:[**4**]) in Benzene-d_6 at Various Temperatures

Temperature/K	Integral ratio ($SiMe_3$)		K_{eq} (=[**6**]:[**4**])[a]
	bicyclotetrasilane **4**	cyclotrisilene **6**	
333	2.11	4.00	1.90
323	2.36	4.00	1.69
313	3.24	4.00	1.23
302	3.48	4.00	1.15

[a]Equilibrium constants (K_{eq}) were calculated using the integral ratio of $SiMe_3$ proton signals in the ^{1}H NMR spectrum.

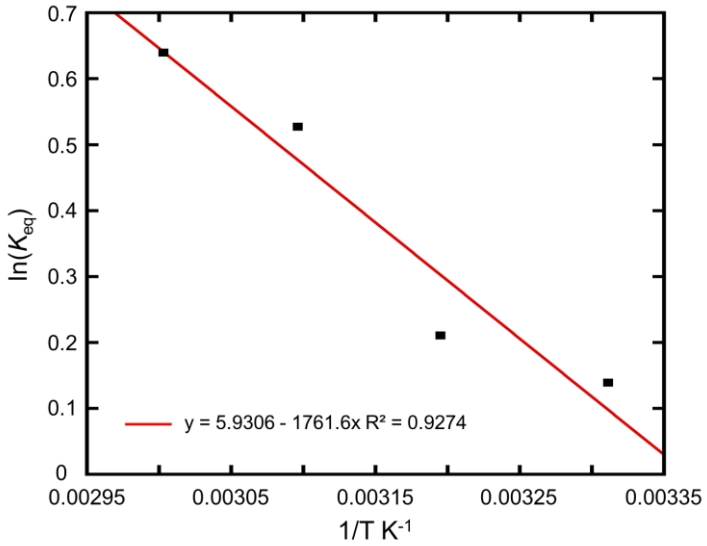


Figure 4-35. A plot of ln(K_{eq}) vs 1/T.

4-5. Reference

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(17) In the ^{1}H NMR spectrum of a mixture of **4** and **6**, the signals due to four $SiMe_3$ groups (36 H) of **6** were substantially broadened and overlapped with that due to eight $SiMe_3$ groups (72H) of **4** (Figure 4-34). Assuming that only the signals of **4** and **6** were overlapped in this region, the equilibrium constants K_{eq} (= [**6**]/[**4**]) at 302–333 K were roughly estimated using the integral ratios (Table 4-23). From the K_{eq}, the thermodynamic parameters for the isomerization of **4** to **6** are calculated to be ΔH = +14.6 ± 2.9 kJ mol^{-1} and ΔS = +49 ± 9 J K^{-1} mol^{-1} (Figure 4-35) which are consistent with the calculated relative energy and free energy.

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Chapter 5

Synthesis of π-Conjugated Species with an Unsupported Si-Si π-Bond via Direct π-Extension

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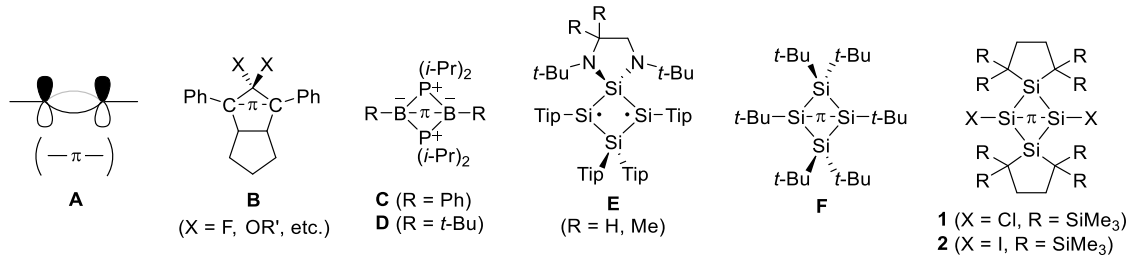
5-1. Introduction

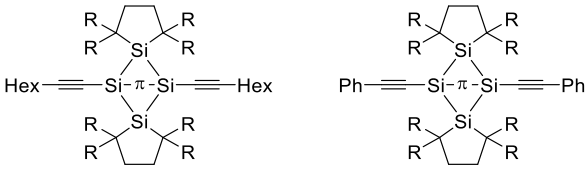
Interactions between π-orbitals, in particular π-conjugation, play a crucial role in the tuning of the structural, electronic, and photochemical properties of organic and inorganic compounds. Generally, π-bonds are found in multiple bonds that have an underlying σ-bond framework in π-electron systems such as aromatic compounds and polyenes. However, compounds that contain π-bonding modes without an underlying strong σ-bond framework (‘‘unsupported’’ π-bonds; Chart 5-1**A**)[1] have been synthesized using meticulous molecular-design processes as unconventional π-electron systems (Chart 5-1**B**–**F** and **1**–**2**).[2–6] For example, Abe and co-workers have reported representative examples of persistent singlet cycloalkane-1,3-diyl derivatives that contain an unsupported π-bond (**B**),[2] which exhibit a substantially red-shifted absorption band arising from a HOMO(π) - LUMO(π*) transition (~600 nm) compared to those of the corresponding monoalkenes such as 1,2-diphenylethene (~300 nm). Bertrand and co-workers have reported that isolable 1,3-diphenyl-1,3-dibora-2,4-diphosphacyclobutane-1,3-diyl **C** has a π-type B–B bonding interaction (Chart 5-1);[3] the longest-wavelength absorption band of **C**, which appears in the visible region, is bathochromically shifted relative to that of 1,3-dialkyl derivative **D**. These results indicate that a compound with an unsupported π-bond may act as a nonclassical π-unit with a substantially narrow π-π* gap. However, such compounds remain quite rare. They require designed bulky substituents to stabilize unsupported π-bonds and the reactive unsupported π-bond was formed at the last stage in the preparation process, which prevents the facile extension of π-units.

Chart 5-1. Schematic Illustration of Unsupported π-Bond (**A**) and the Structures of Related Compounds **B**–**F** and **1**–**2**



Recently, we have synthesized 1,3-dihalobicyclo[1.1.0]tetrasilanes **1** and **2** (Chart 5-1),[4] which have a planar Si_4 framework with a longer bridgehead Si–Si distance (2.58 Å) compared to a typical Si–Si single bond distance (2.36 Å)[7] and bridgehead Si–Si distances in highly bent bicyclo[1.1.0]tetrasilanes (2.35–2.47 Å).[8] Compounds **1** and **2** contain an unsupported π-bond between the bridgehead silicon atoms. Compound **2** shows a distinct absorption band that arises from a π(Si–Si) → π*(Si–Si) transition at λ_{max} = 435 nm, which is substantially red-shifted compared to that of a structurally similar trisilacyclopropene that exhibits a planar Si=Si double bond in the three-membered ring (λ_{max} = 391 nm).[9] Similar structural characteristics with a planar Si_4 framework were found in related compounds **E**[5] and **F**,[6] which were reported independently by Scheschkewitz et al. and Kyushin et al (Chart 5-1). These findings suggest that a compound with an unsupported Si–Si π-bond can serve as a nonclassical π-unit with a narrow π–π* gap similar to **B–D**. However, electronic communication between an unsupported Si–Si π-bond and other π-electron systems has yet to be reported. In this context, **1** and **2** that contain good leaving groups on the bridgehead silicon atoms are expected to be useful precursors for the synthesis of π-conjugated systems with unsupported Si–Si π-bonds.[10] In this chapter, the author reports the reactions of **1** with a lithium acetylide to provide **3** and **4**, *i.e.*, bicyclo[1.1.0]tetrasilanes with alkynyl groups on the bridgehead silicon atoms (Chart 5-2). Single-crystal X-ray diffraction (XRD) analyses, UV-vis absorption spectra, and theoretical calculations indicated that π-conjugation occurs in these compounds between the unsupported Si–Si π-bond of the bicyclo[1.1.0]tetrasilane unit and the alkynyl (and aryl) groups.

Chart 5-2. Structures of Compounds **3** and **4**



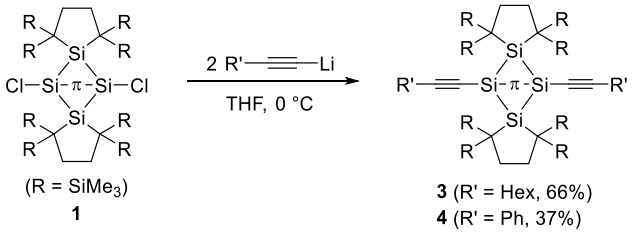
3 (R = $SiMe_3$) **4** (R = $SiMe_3$)

5-2. Results and Discussion

5-2-1. Synthesis of 1,3-Dialkynyltetrasilabicyclo[1.1.0]butanes 3 and 4

Reddish purple crystals of **3** were obtained in 66% yield following the reaction of **1** with 1-octynyllithium in THF at 0 °C (Scheme 5-1). Similarly, the treatment of **1** with lithium phenylacetylide afforded **4** as a blue solid in 37% yield (Scheme 5-1). The molecular structures of **3** and **4** were determined using a combination of multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal XRD analysis. While **3** was stable at room temperature, **4** slowly decomposed to a complex product mixture in solution at room temperature.

Scheme 5-1. Synthesis of **3** and **4**



5-2-2. Molecular Structures of 3 and 4

The molecular structures of **3** and **4**, as determined by single-crystal XRD analysis, are shown in Figure 5-1.[11] Molecules of **3** and **4** reside on a crystallographic inversion centre and the central Si_4 skeleton is planar (Si2–Si1–Si1*–Si2* angle: 180°). The geometry around the bridgehead silicon atoms is almost planar [sums of the angles at the Si1 atom excluding the bridgehead bond: 360.00° (**3**) and 359.94° (**4**)]. The ethynyl moieties are very slightly bent in a *trans* configuration relative to the plane of the Si_4 ring [Si1*–Si1–C1 angles: 178.59(5)° (**3**) and 177.59(9)° (**4**)]. Noticeably, the distances between the bridgehead silicon atoms [Si1–Si1*: 2.7112(7) Å (**3**) and 2.6992(11) Å (**4**)] are longer than those of **1** [2.581(2) Å] and **2** [2.5822(11) Å],[4] even though they are still shorter than those of **E** [2.871(1) Å] and **F** [2.853(1) Å].[5,6] Nevertheless, the length of the C1–C2 bonds [1.200(2) Å (**3**) and 1.208(3) Å (**4**)] are comparable to that of the C≡C bond in bis(trimethylsilyl)acetylene [1.208(3) Å].[12] The Si1–C1

distances [1.8207(15) Å (**3**) and 1.816(2) Å (**4**)] are almost identical to those of the 1,2-dialkynyldisilenes [1.811(4) and 1.8029(19) Å] reported by Tokitoh.[13] The dihedral angle between the plane of the Si_4 ring and the plane of the phenyl ring in **4** (23.0°) is suitable for effective interactions between the bridgehead Si–Si π-bond in the Si_4 skeleton and the π-system on the phenyl rings via the acetylene moieties.

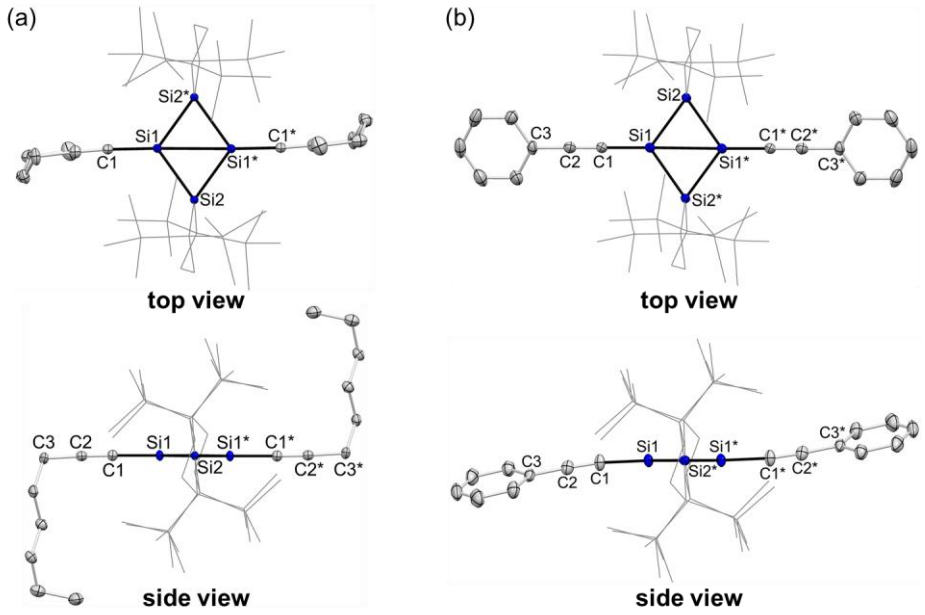


Figure 5-1. ORTEP diagrams of (a) **3** and (b) **4** with thermal ellipsoids at 50% probability; all hydrogen atoms are omitted for clarity.

5-2-3. UV-vis Absorption Spectra of 3 and 4 in the Solid State

The UV-vis spectra of **3** and **4** in the crystalline state demonstrate that substantial interactions occur between the Si_4 framework with an unsupported Si–Si π-bond and the alkynyl groups at the bridgehead silicon atoms. Both **3** and **4** exhibit a distinct absorption band in the visible region (Figure 5-2). The longest-wavelength absorption band maxima of **3** (λ_{max} = 552 nm) and **4** (λ_{max} = 602 nm) (Figure 5-2), which arise from the π → π* transition of the bridgehead Si–Si π-bond (*vide infra*), are red-shifted by more than 100 nm compared to that of **2** (435 nm).[4b] Notably, the maximum of **4** (602 nm) is by 50 nm red-shifted compared to that of **3** (552 nm), even though **3** and **4** exhibit similar bridgehead Si–Si distances. This indicates that the phenyl moieties in **4** interact with the π-orbital of the bridgehead Si–Si bond. A similar

red-shift of the π → π* transition band upon π-extension has been observed for 1,2-dialkynyldisilenes [λ_{max} = 437 (trimethylsilylethynyl), 469 nm (phenylethynyl)].[13]

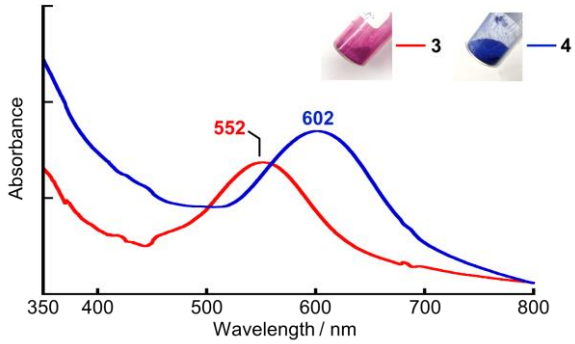


Figure 5-2. UV-vis absorption spectra of **3** (red) and **4** (blue) in a KBr matrix at room temperature.

5-2-4. Theoretical Study

Theoretical calculations for the structures of **3** and **4** in the crystalline state (**3**$_{cry}$ and **4**$_{cry}$) provided further insight into their electronic properties.[14] The frontier Kohn–Sham orbitals of **3**$_{cry}$ and **4**$_{cry}$ show HOMOs and LUMOs that arise from an in-phase and out-of-phase combination of the bridgehead Si 3p orbitals (π- and π*-orbitals) (Figure 5-3). Importantly, they include the π-(π*-) orbitals of the C≡C bonds from the ethynyl moieties, which corroborates the presence of conjugation between the bridgehead Si–Si π-bond and the C≡C bonds of the ethynyl moieties. Notably, the LUMO of **4**$_{cry}$ involves a contribution from the π*-orbitals of the phenyl moieties and its energy level (−2.11 eV) is significantly lower than that of **3**$_{cry}$ (−1.88 eV). However, the HOMO energy levels are almost identical (**3**$_{cry}$: −5.80 eV; **4**$_{cry}$: −5.82 eV), which is consistent with the fact that the absorption band of **4** is red-shifted relative to that of **3**. The Wiberg bond indices (WBI)[14] between the bridgehead silicon atoms of **3**$_{cry}$ (0.63) and **4**$_{cry}$ (0.63) are slightly smaller than that of **2** (0.70), which supports the presence of a bonding interaction between the bridgehead silicon atoms. Time-dependent density functional theory (TD-DFT) calculations indicated that the observed absorption spectra of **3** and **4** in the solid state are in good agreement with the band positions and oscillator strengths of **3**$_{cry}$ and **4**$_{cry}$ (Figures 5-34 and 5-35).

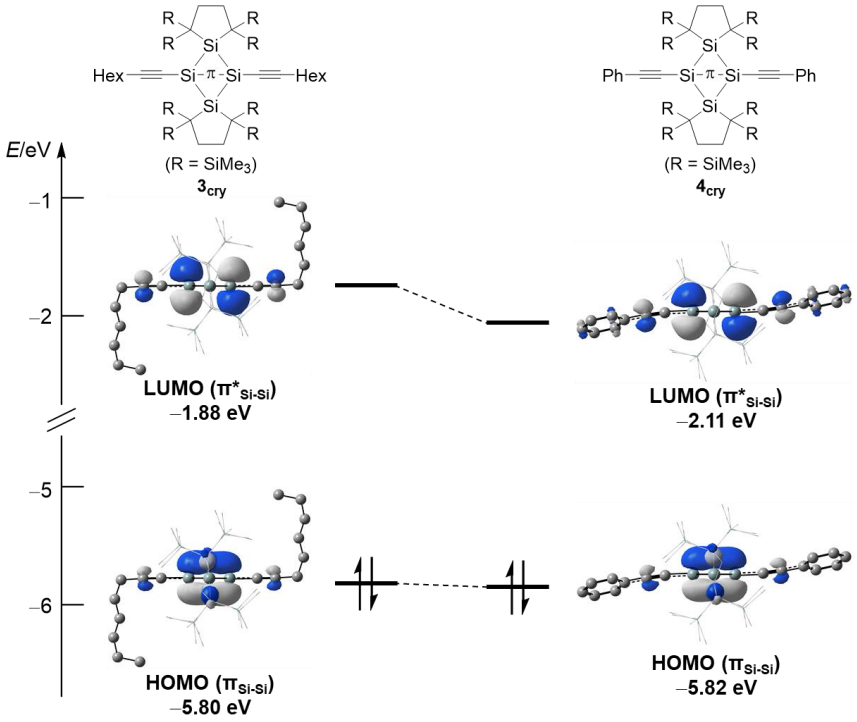


Figure 5-3. Frontier Kohn–Sham orbitals and their energy levels for $\mathbf{3}_{\mathbf{cry}}$ and $\mathbf{4}_{\mathbf{cry}}$ calculated at the M06-2X/6-311G(d) level of theory (isosurface level: 0.04 e·au^{-3}); all hydrogen atoms are omitted for clarity.

5-2-5. UV-vis Absorption Spectra of 3 and 4 in Solution

Interestingly, the colors of **3** and **4** observed in solution differ from those observed in the solid state. In organic solvents, the reddish-purple crystals of **3** provide a red solution at room temperature. In hexane, the UV-vis absorption spectrum of **3** shows a longest-wavelength absorption band (λ_{max} = 518 nm) that is by 34 nm blue-shifted compared to that of **3** in the solid state (Figure 5-4). Similarly, a hexane solution of **4** is purple (λ_{max} = 560 nm), which is blue-shifted relative to that of the blue solid (Figure 5-4). These results suggest that the structures and electronic properties of **3** and **4** in solution are different from those in the solid state.

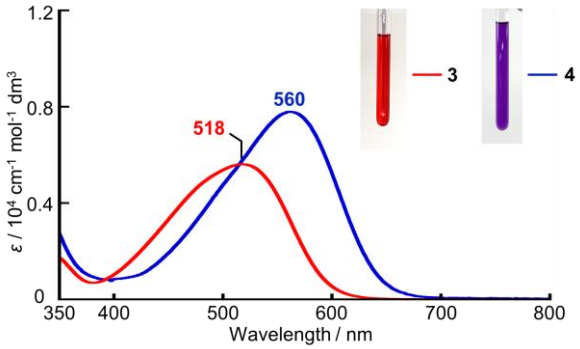


Figure 5-4. UV-vis absorption spectra of **3** (red) and **4** (blue) in hexane at room temperature.

5-2-6. NMR Spectra of 3 and 4

The NMR spectra of **3** and **4** provided information on their structures in solution. The ^{1}H NMR spectra of **3** and **4** in C_6D_6 at room temperature show a singlet signal due to the eight magnetically equivalent $SiMe_3$ groups [**3**: 0.53 ppm; **4**: 0.54 ppm] and another singlet signal due to the eight methylene protons of the five-membered rings [**3**: 2.05 ppm; **4**: 2.05 ppm]. In the ^{29}Si NMR spectra, only three signals [**3**: –8.0 ppm (bridge Si), 4.7 ppm ($SiMe_3$), and 83.3 ppm (bridgehead Si); **4**: –6.1 ppm (bridge Si), 4.9 ppm ($SiMe_3$), and 91.5 ppm (bridgehead Si)] were observed (Figure 5-5). These results indicate that **3** and **4** adopt highly symmetric structures in solution. Notably, the chemical shifts for the bridgehead ^{29}Si nuclei of **3** (83.3 ppm) and **4** (91.5 ppm) are close to those of **1** (126.4 ppm) and **2** (103.8 ppm), *i.e.*, molecules that also possess planar Si_4 rings,[4] but downfield-shifted compared with those of the reported bicyclo[1.1.0]tetrasilanes with highly bent Si_4 rings (–145.1 to 14.8 ppm).[8] This implies that the Si_4 skeletons of **3** and **4** are highly planar in solution.

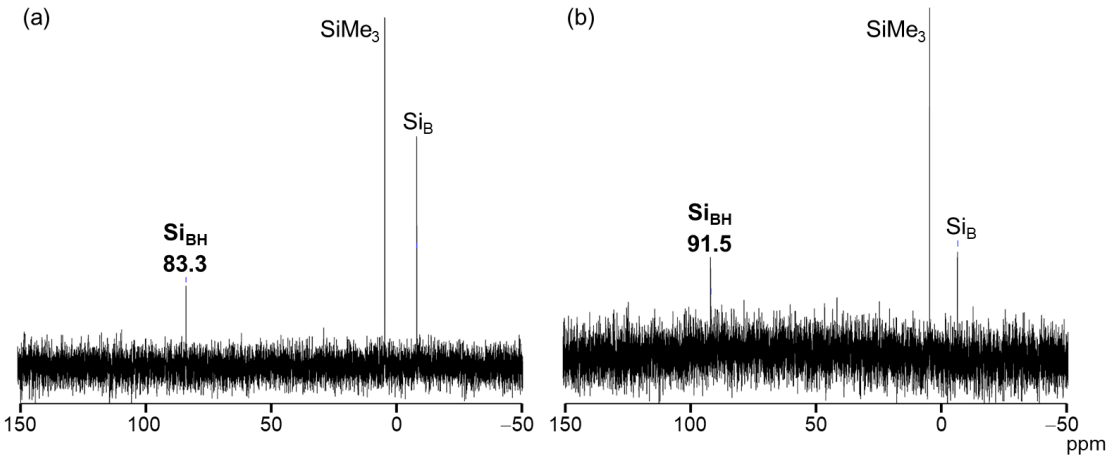


Figure 5-5. ^{29}Si NMR spectra of (a) **3** and (b) **4** in benzene-d_6 at room temperature (Si_{BH}: bridgehead Si, Si_B: bridge Si).

5-2-7. Variable-Temperature (VT) UV-vis Absorption and NMR Spectra of 3 and 4

The variable-temperature (VT) UV-vis absorption and NMR spectra of **3** and **4** provided further insight into their behavior in solution. With decreasing temperature, the absorption band of **3** at 518 nm (293 K) decreased and an absorption band at ~480 nm increased with an isosbestic point at 512 nm (Figure 5-6). At 93 K, an absorption band at 478 nm and a shoulder peak at 561 nm were observed. These spectral changes were observed to be reversible. A similar temperature-dependent effect was observed in the UV-vis spectrum of **4** (Figure 5-31). Additionally, while the features of the ^{1}H NMR spectrum of **3** did not change substantially at lower temperatures (Figure 5-22), the ^{29}Si resonance attributed to the bridgehead silicon nuclei of **3** exhibited a significant upfield-shift upon decreasing the temperature (60 °C: 87.6 ppm; –40 °C: 73.2 ppm) (Figure 5-7 and Table 5-2).[15] These results clearly indicate that the two different structures of **3** and **4** are in equilibrium in solution.

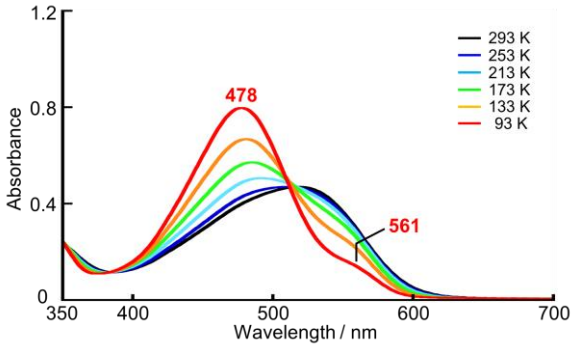


Figure 5-6. VT UV-vis absorption spectra of **3** in 3-methylpentane recorded at 40 K intervals (93–293 K).

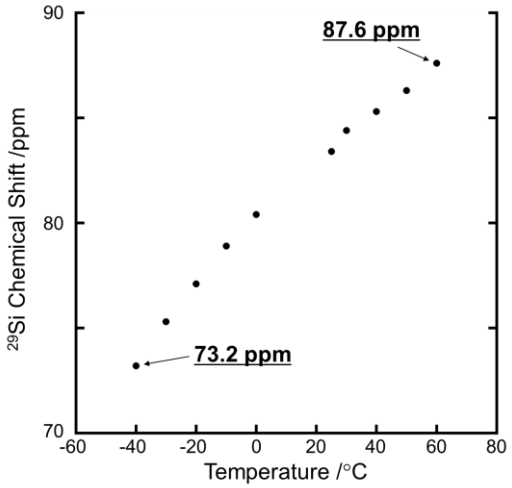
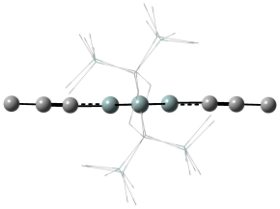
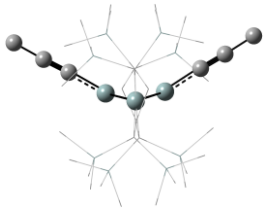


Figure 5-7. A plot of observed ^{29}Si chemical shift of the bridgehead silicon atoms in **3** vs measurement temperature.

5-2-8. Theoretical Calculations for the Behavior of 3 and 4 in Solution

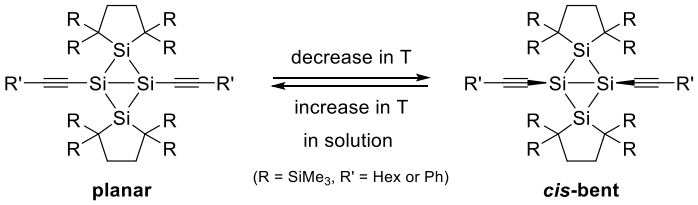
To understand the behavior of **3** and **4** in solution, DFT calculations were conducted using a simplified model (**5**) in which the Hex or Ph groups were replaced by methyl groups. A planar structure ($\mathbf{5_p}$) similar to those observed in the crystalline states of **3** and **4** was located as a local minimum at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) level of theory (Table 5-1). We also found another local minimum of **5** that contains a *cis*-bent Si_4 framework ($\mathbf{5_c}$) similar to that found in **2** (Table 5-1).[4b] Calculating the Gibbs energy values revealed that $\mathbf{5_c}$ is slightly more stable than $\mathbf{5_p}$ (3.5 kJ mol^{-1} at 298.15 K). The bent angle of the silicon framework of $\mathbf{5_c}$ is 158.6° and the distance between the bridgehead silicon atoms of $\mathbf{5_c}$ (2.545 Å) is shorter than that of $\mathbf{5_p}$ (2.680 Å). The longest-wavelength absorption band position of $\mathbf{5_c}$ (430 nm) was blue-shifted compared with that of $\mathbf{5_p}$ (562 nm). The ^{29}Si NMR resonance due to the bridgehead silicon nuclei of $\mathbf{5_c}$ (–25.7 ppm) calculated at the M06L/6-311+G(2df,p) level of theory was upfield-shifted compared to that of $\mathbf{5_p}$ (133.7 ppm). These calculations, in conjunction with the observed hypsochromic shift of the absorption band and the upfield-shift of ^{29}Si resonance at lower temperatures, imply that the dominant structures of **3** and **4** in solution are the *cis*-bent structures similar to $\mathbf{5_c}$ at lower temperature, while at higher temperature they are planar structures similar to $\mathbf{5_p}$ (Scheme 5-2).[16] A similar equilibrium between a planar and *cis*-bent structures in solution was also observed for compound **C**.[3g]

Table 5-1. Selected Structural Parameters and Properties of Compounds $\mathbf{5_p}$ and $\mathbf{5_c}$

 $\mathbf{5_p}$	Optimized Structure[a]	 $\mathbf{5_c}$
2.680	Bridgehead Si-Si /Å	2.545
178.37	Si-Si-C /deg	148.87
180.00	dihedral angle (Si_4 ring) /deg	158.58
0.0	ΔG /kJ mol^{-1}	−3.5
562	λ_{max}(calcd)[b] /nm	430
133.7	$Si_{bridgehead}$(calcd)[c] /ppm	−25.7

[a]optimized at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) level of theory. [b]calculated at the TD-M06-2X/6-311G(d) level of theory. [c]calculated at the GIAO/M06L/6-311+G(2df,p) level of theory.

Scheme 5-2. Possible Behavior of **3** and **4** in Solution



5-3. Conclusion

In conclusion, two bicyclo[1.1.0]tetrasilanes that contain different ethynyl groups (**3** and **4**) were synthesized via direct π-extension of **1**. In the crystalline state, they both possess planar Si_4 bicyclic structures. UV-vis absorption spectra and DFT calculations indicated the presence of effective π-conjugation between an unsupported bridgehead Si–Si π-bond and the two alkynyl units. In solution, a potential equilibrium between a planar structure and a *cis*-bent structure was observed, which may represent the flexible nature of the unsupported π-bond. A compound with an unsupported Si–Si π-bond should be able to serve as a nonclassical π-unit.

5-4. Experimental Section

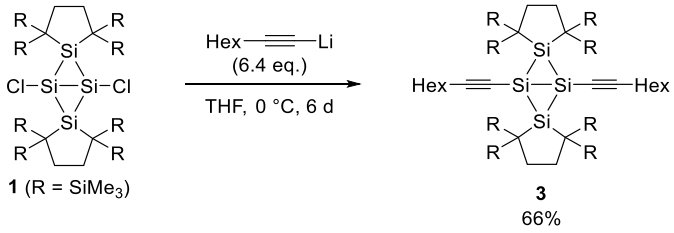
General Procedures

All reactions involving air-sensitive compounds were performed under an argon or nitrogen atmosphere using a high-vacuum line and a standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. Reactions at lower temperatures were performed using an EYELA PSL-1400 cryobath. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C shifts of the solvents: C_6D_6 (^{1}H: δ 7.16 and ^{13}C: δ 128.0), toluene-d_8 (^{1}H: δ 2.08).[17] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). The sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4T spectrometer and JEOL JMS-T100GCV spectrometer. UV-vis spectra were recorded on JASCO V-770 and V-660 spectrometers. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer.

Materials

Dry and degassed hexane, and THF were prepared using a VAC 103991 solvent purifier. Benzene-d_6 was dried by molecular sieves 4Å after degassing through three freeze-pump-thaw cycles. Toluene-d_8 and 3-methylpentane were dried in a tube covered with potassium mirror and then distilled under reduced pressure prior to use. Hexamethyldisiloxane was dried by lithium aluminum hydride after degassing through three freeze-pump-thaw cycles. 1,3-Dichlorobicyclo[1.1.0]tetrasilane **1** was prepared according to the published procedure.[4c] 1-Octynyllithium and lithium phenylacetylide were prepared by the reactions of the corresponding alkyne with butyl lithium in THF. 1-Octyne, phenylacetylene and butyl lithium were commercially available and used without further purification.

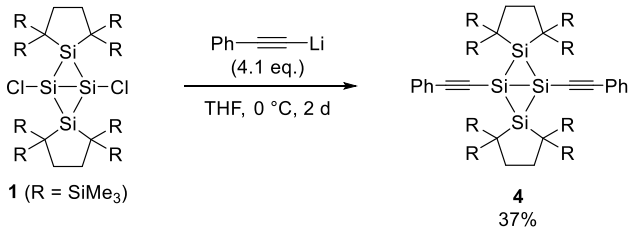
Synthesis of 1,3-Dioctynylbicyclo[1.1.0]tetrasilane 3 [TN864,865]



To a Schlenk tube (30 mL) equipped with a magnetic stir bar, 1,3-dichlorobicyclotetrasilane **1** (30.1 mg, 34.5 μmol) and 1-octynyllithium (25.5 mg, 220 μmol) were charged. To the Schlenk tube, dry and degassed THF (3.0 mL, cooled down to −27 °C) was added and the mixture was stirred at 0 °C for 6 days. The color of the resulting solution turned from orange to dark red. After the volatiles were removed in vacuo at 0 °C, the crude was extracted with hexane and the filtrate was concentrated in vacuo. Recrystallization from hexamethyldisiloxane provided reddish purple crystals of **3** (23.4 mg, 22.9 μmol) in 66% yield.

3: reddish purple crystals; mp 174-176 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 296 K) 0.53 (s, 72H, SiC*H*$_3$), 0.91 (t, *J* = 7.0 Hz, 6H, C*H*$_3$ (octynyl)), 1.16-1.24 (m, 4H, C*H*$_2$ (octynyl)), 1.26-1.38 (m, 8H, C*H*$_2$ (octynyl)), 1.50 (tt, *J* = 7.5 Hz, *J* = 7.0 Hz, 4H, C*H*$_2$ (octynyl)), 2.05 (s, 8H, C*H*$_2$ (silacyclopentane ring)), 2.30 (t, *J* = 7.0 Hz, 4H, C*H*$_2$ (octynyl)); ^{13}C NMR (126 MHz, C_6D_6, 297 K) 5.3 (Si*C*H$_3$), 13.8 (*C*), 14.5 (*C*H$_3$ (octynyl)), 21.6 (*C*H$_2$ (octynyl)), 23.2 (*C*H$_2$ (octynyl)), 28.6 (*C*H$_2$ (octynyl)), 29.2 (*C*H$_2$ (octynyl)), 31.9 (*C*H$_2$ (octynyl)), 34.9 (*C*H$_2$ (silacyclopentane ring)), 88.5 (Si*C*≡), 130.3 (Hex*C*≡); ^{29}Si NMR (99 MHz, C_6D_6, 296 K) −8.0 (*Si*), 4.7 (*Si*Me$_3$), 83.3 (*Si*C≡); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 518 (5.6×10^3), 475 (sh, 4.6×10^3), 340 (1.9×10^3), 248 (4.1×10^4), 212 (4.3×10^4); UV-vis (KBr matrix, 293 K) λ_{max}/nm 552, 340, 249; HRMS (FD) Calcd for $C_{48}H_{106}Si_{12}$ [M^+], 1018.55257; Found, 1018.55232; Anal. Calcd for $C_{48}H_{106}Si_{12}$: C, 56.50; H, 10.47%. Found: C, 56.22; H, 10.78%.

Synthesis of 1,3-Diphenylethynylbicyclo[1.1.0]tetrasilane 4 [TN575,577]



1 (R = $SiMe_3$)

4
37%

To a Schlenk tube (30 mL) equipped with a magnetic stir bar, 1,3-dichlorobicyclotetrasilane **1** (30.0 mg, 34.4 μmol) and lithium phenylacetylide (17.9 mg, 142 μmol) were charged. To the Schlenk tube, dry and degassed THF (5.0 mL, cooled down to –27 °C) was added and the mixture was stirred at 0 °C for 2 days. The color of the resulting suspension turned from orange to purple. After the volatiles were removed in vacuo at 0 °C, the crude was extracted with hexane and the filtrate was concentrated in vacuo. The residue was washed with hexane to provide a blue solid of **4** (12.9 mg, 12.8 μmol) in 37% yield.

4: a blue solid; mp 63-65 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 295 K) 0.54 (s, 72H, SiCH_3), 2.05 (s, 8H, CH_2), 6.94-6.99 (m, 2H, aryl), 7.01-7.05 (m, 4H, aryl), 7.64-7.68 (m, 4H, aryl); ^{13}C NMR (126 MHz, C_6D_6, 296 K) 5.2 (Si*C*H_3), 14.1 (*C*), 34.9 (*C*H_2), 98.6 (Si*C*≡), 123.8 (aryl), 127.2 (Ph*C*≡), 128.9 (aryl), 129.5 (aryl), 131.7 (aryl); ^{29}Si NMR (99 MHz, C_6D_6, 294 K) −6.1 (*Si*), 4.9 (*Si*Me_3), 91.5 (*Si*C≡); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 560 (7.8×10^3), 503 (sh, 4.9×10^3), 312 (2.4×10^4), 298 (sh, 2.2×10^4), 277 (2.2×10^4), 247 (3.8×10^4); UV-vis (KBr matrix, 293 K) λ_{max}/nm 602, 317, 247, 214; HRMS (APCI_positive) Calcd for $C_{48}H_{90}Si_{12}$ [M^+], 1002.42682; Found, 1002.42718; Anal. Calcd for $C_{48}H_{90}Si_{12}$: C, 57.41; H, 9.03%. Found: C, 57.60; H, 9.22%.

NMR Spectra

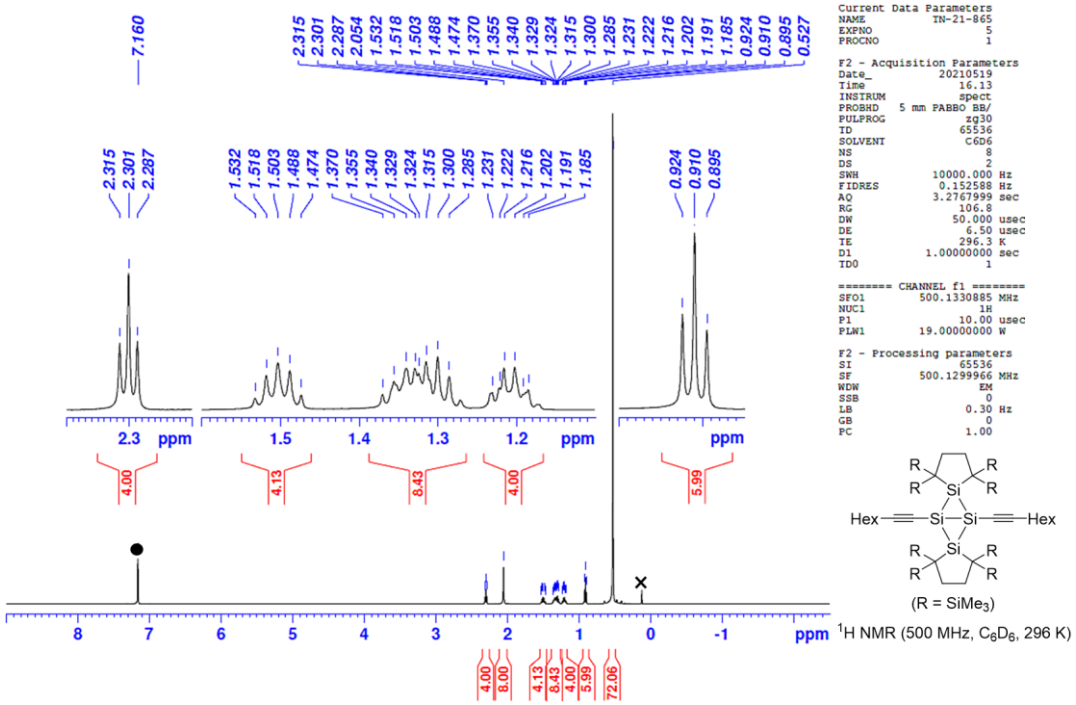


Figure 5-8. ^{1}H NMR spectrum of **3** in C_6D_6 at 296 K (● = C_6HD_5, × = hexamethyldisiloxane).

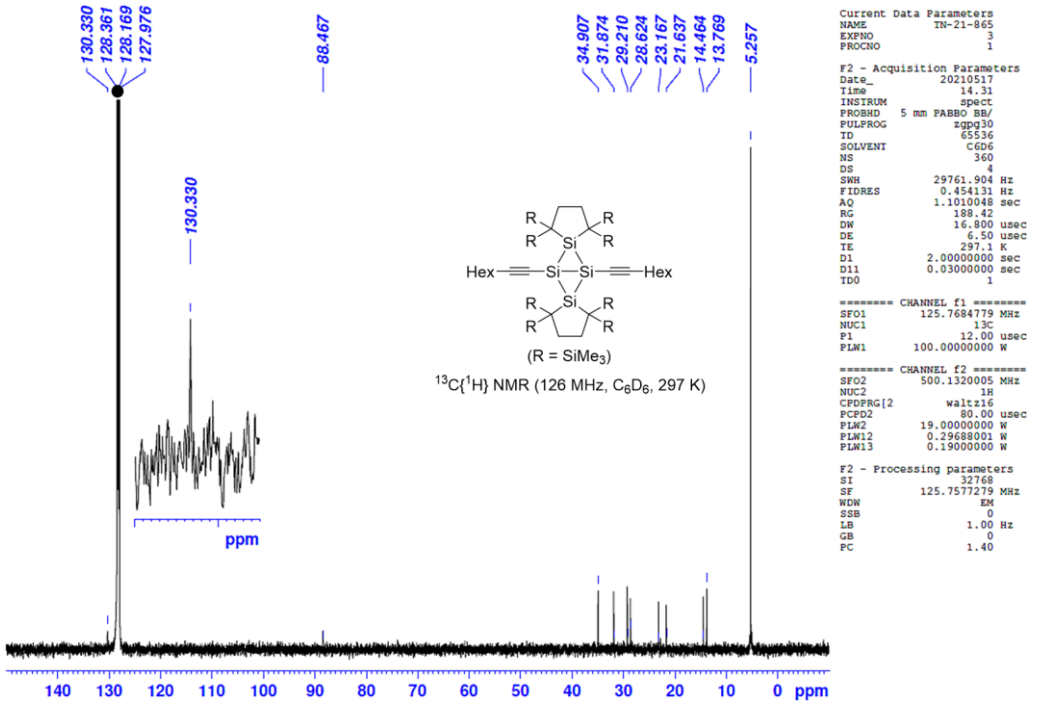


Figure 5-9. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 in 297 K (● = C_6D_6).

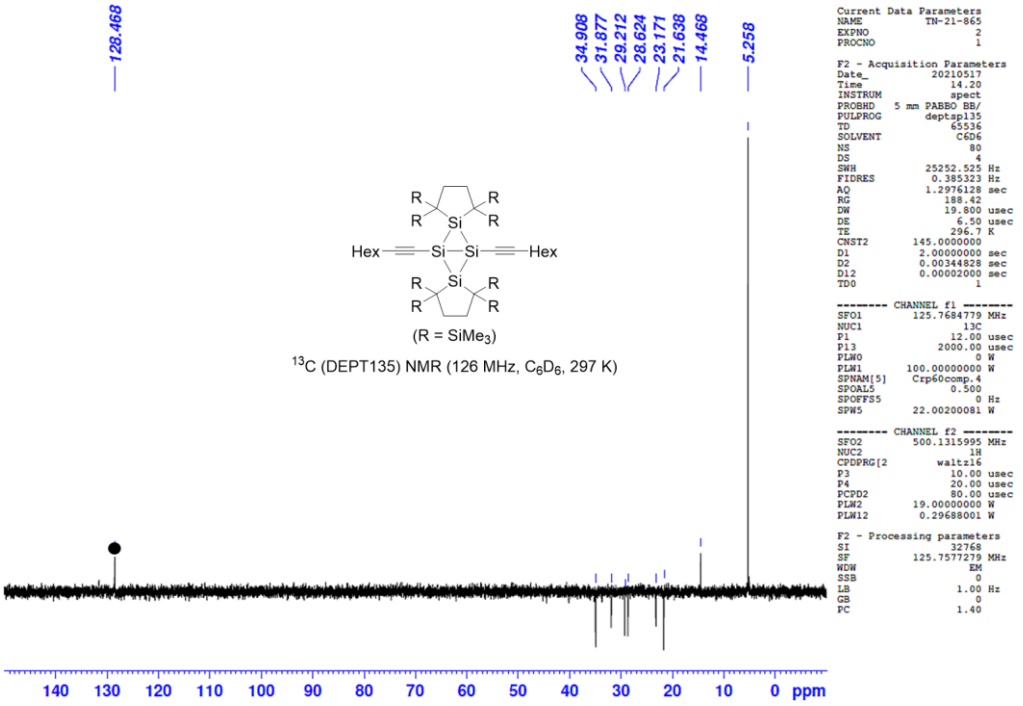


Figure 5-10. ^{13}C (DEPT135) NMR spectrum of **3** in C_6D_6 at 297 K (● = C_6D_6).

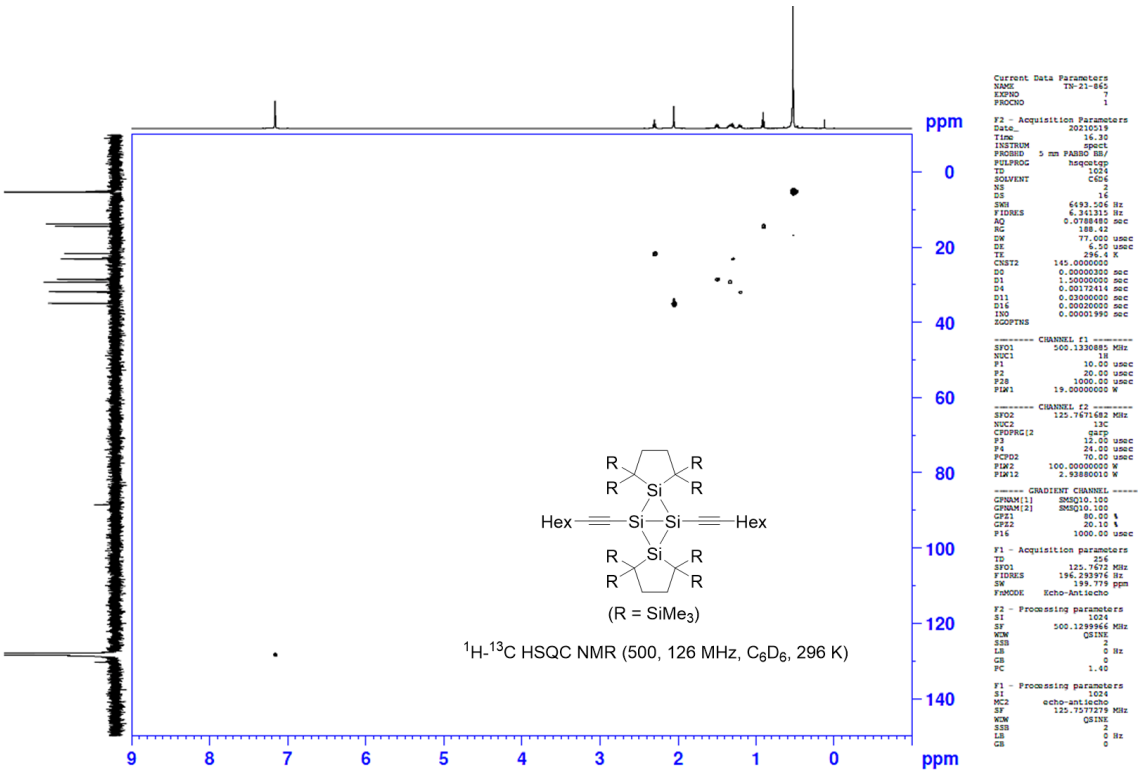


Figure 5-11. ^{1}H-^{13}C HSQC NMR spectrum of **3** in C_6D_6 at 296 K.

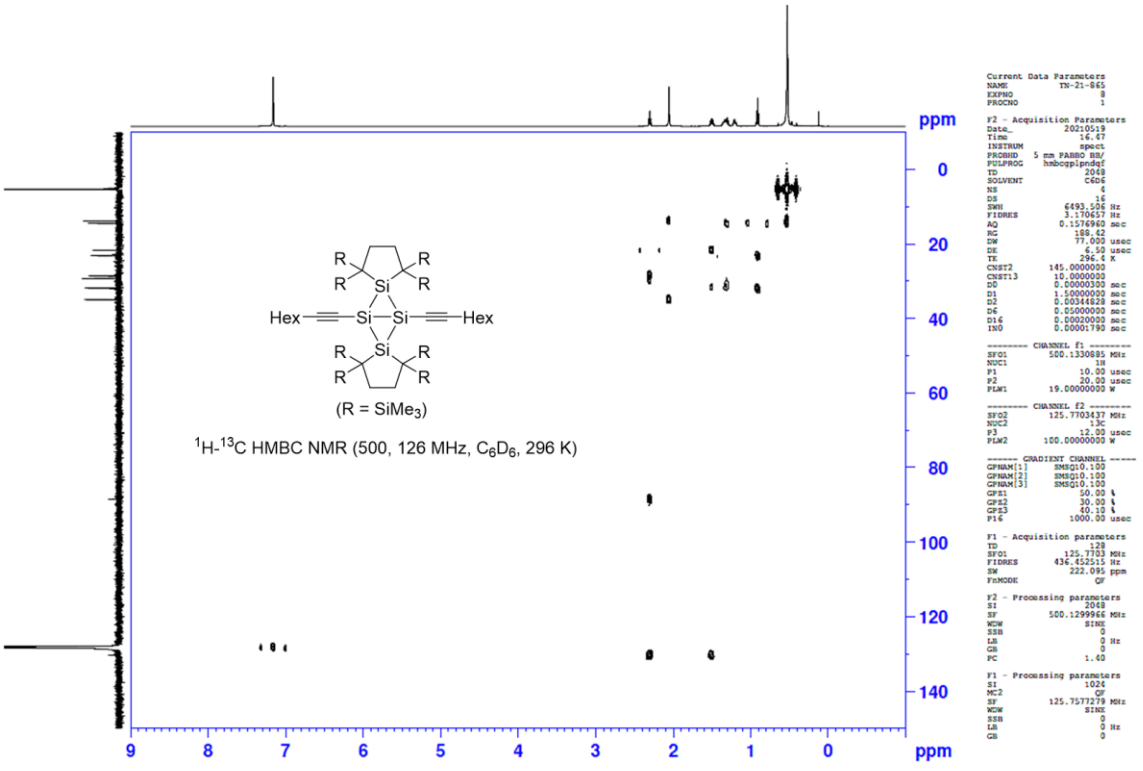


Figure 5-12. ^{1}H-^{13}C HMBC NMR spectrum of **3** in C_6D_6 at 296 K.

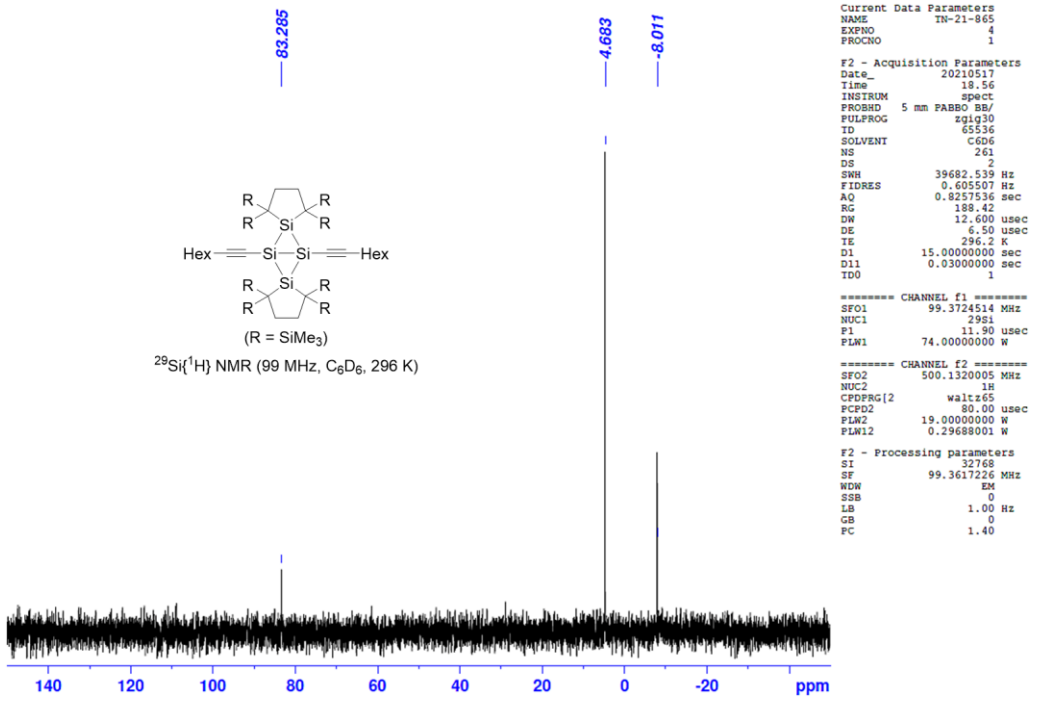


Figure 5-13. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 296 K.

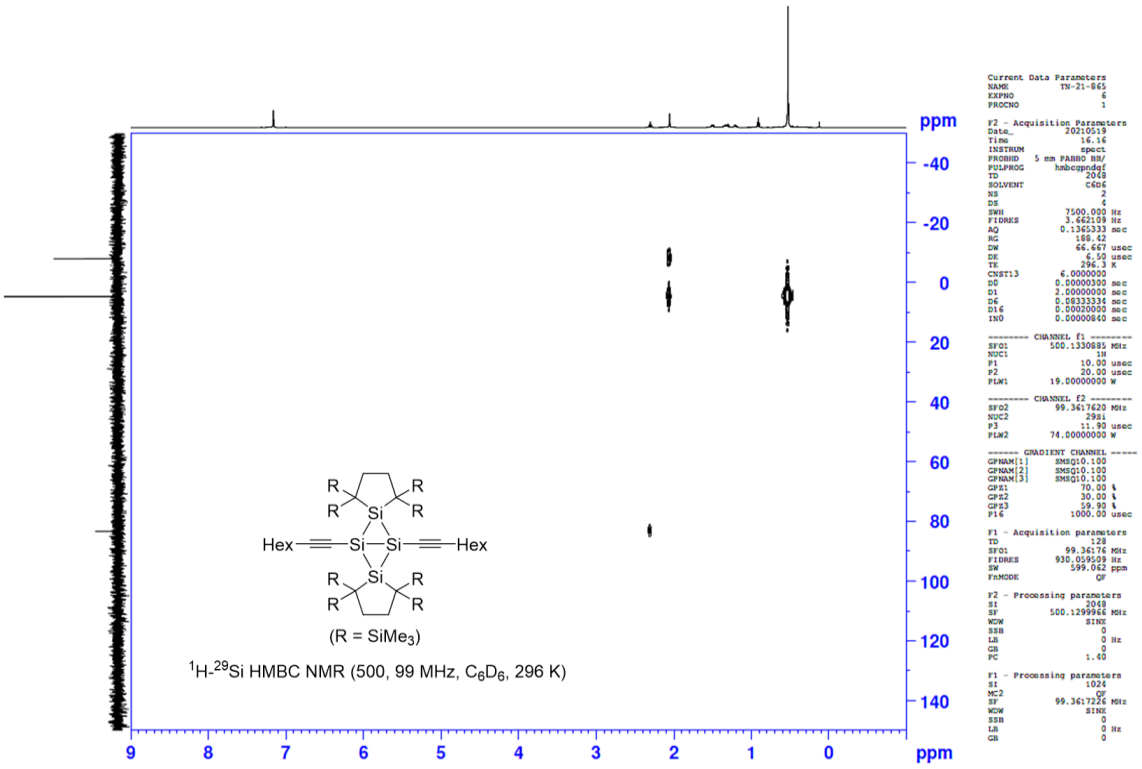


Figure 5-14. ^{1}H-^{29}Si HMBC NMR spectrum of **3** in C_6D_6 at 296 K.

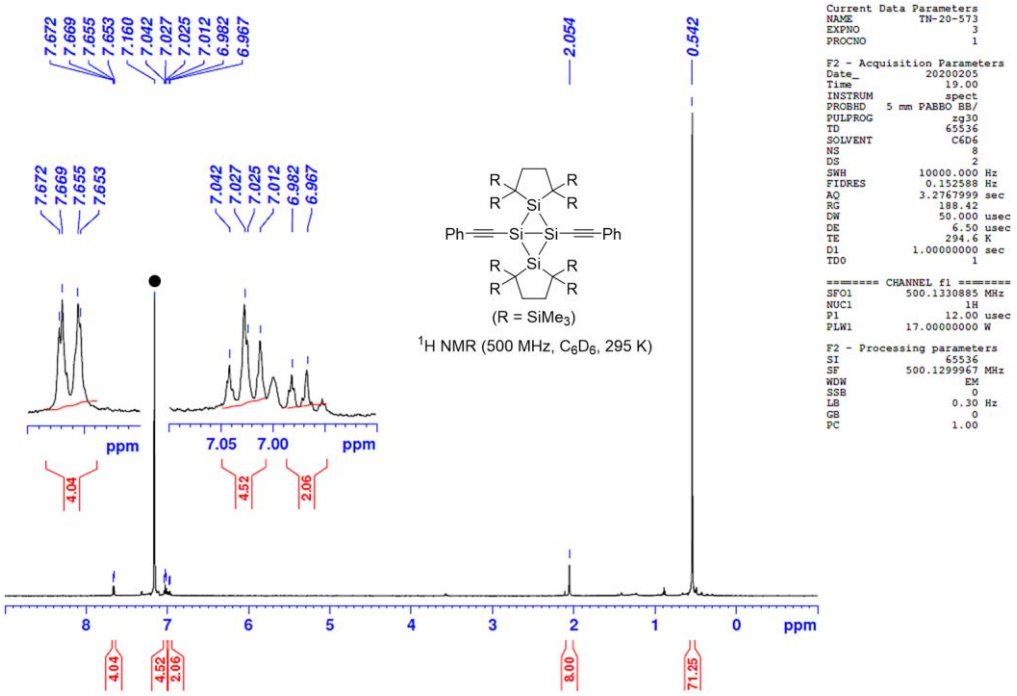


Figure 5-15. ^{1}H NMR spectrum of **4** in C_6D_6 at 295 K (● = C_6HD_5).

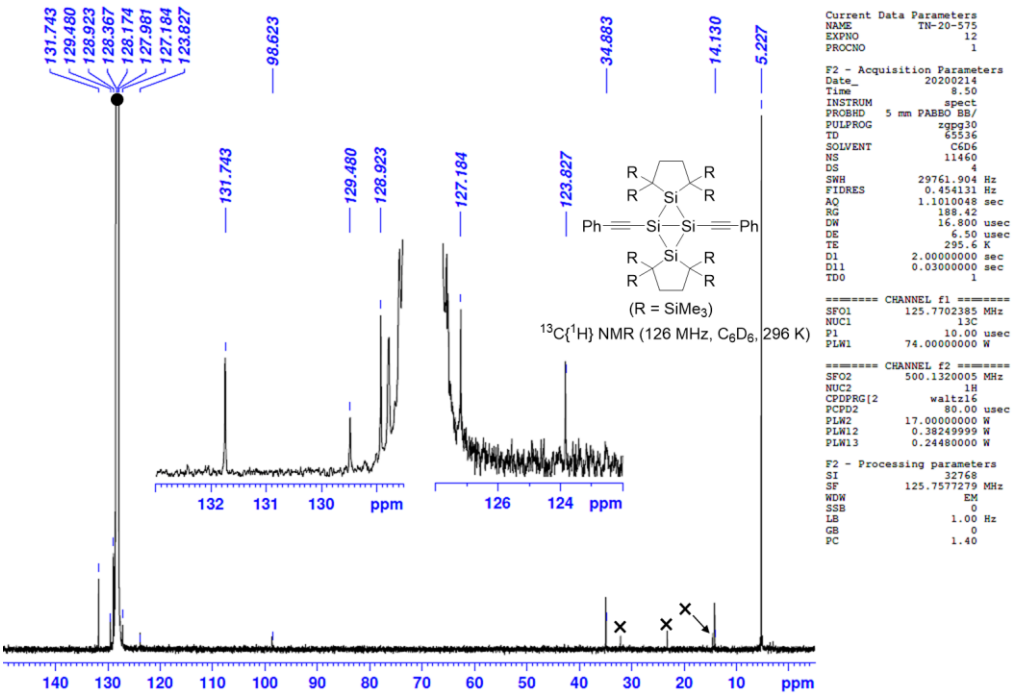


Figure 5-16. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 in 296 K (● = C_6D_6, × = hexane).

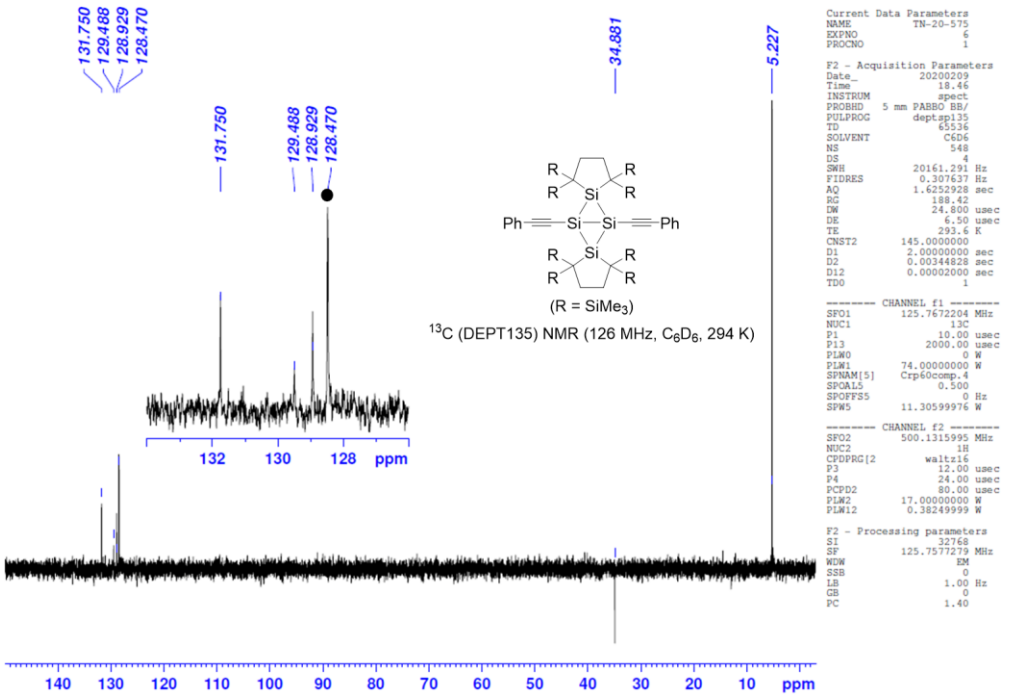


Figure 5-17. ^{13}C (DEPT135) NMR spectrum of **4** in C_6D_6 at 294 K (● = C_6D_6).

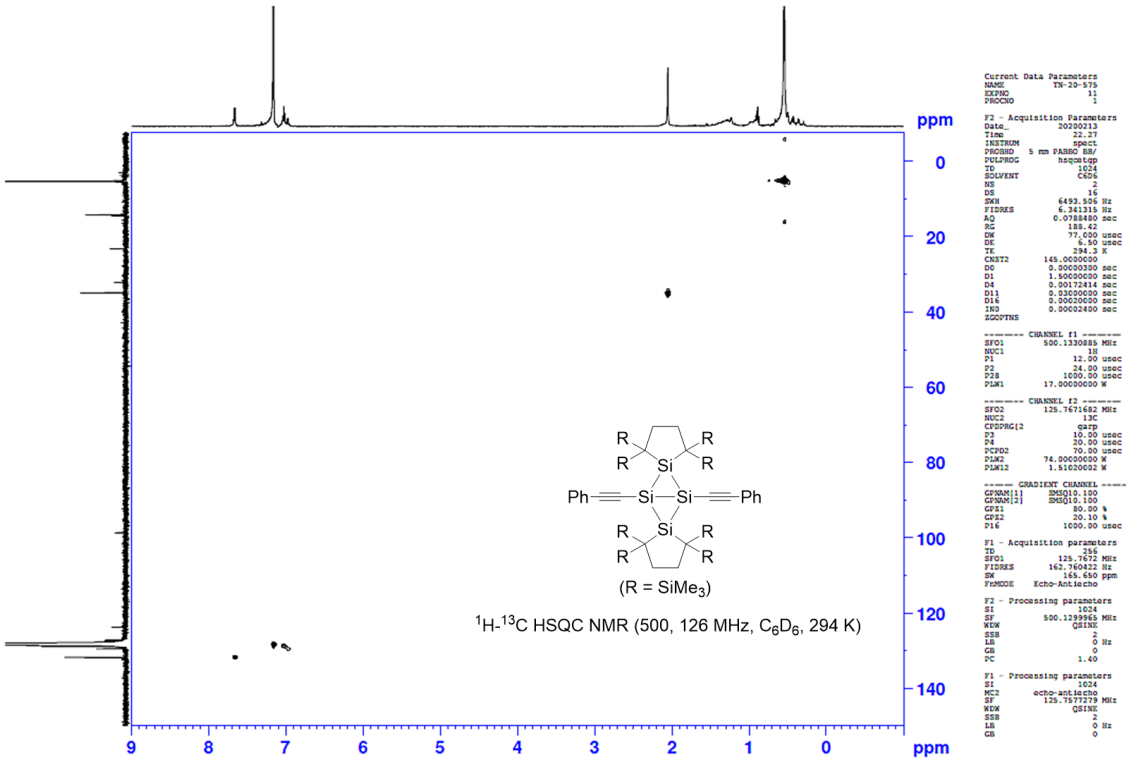


Figure 5-18. ^{1}H-^{13}C HSQC NMR spectrum of **4** in C_6D_6 at 294 K.

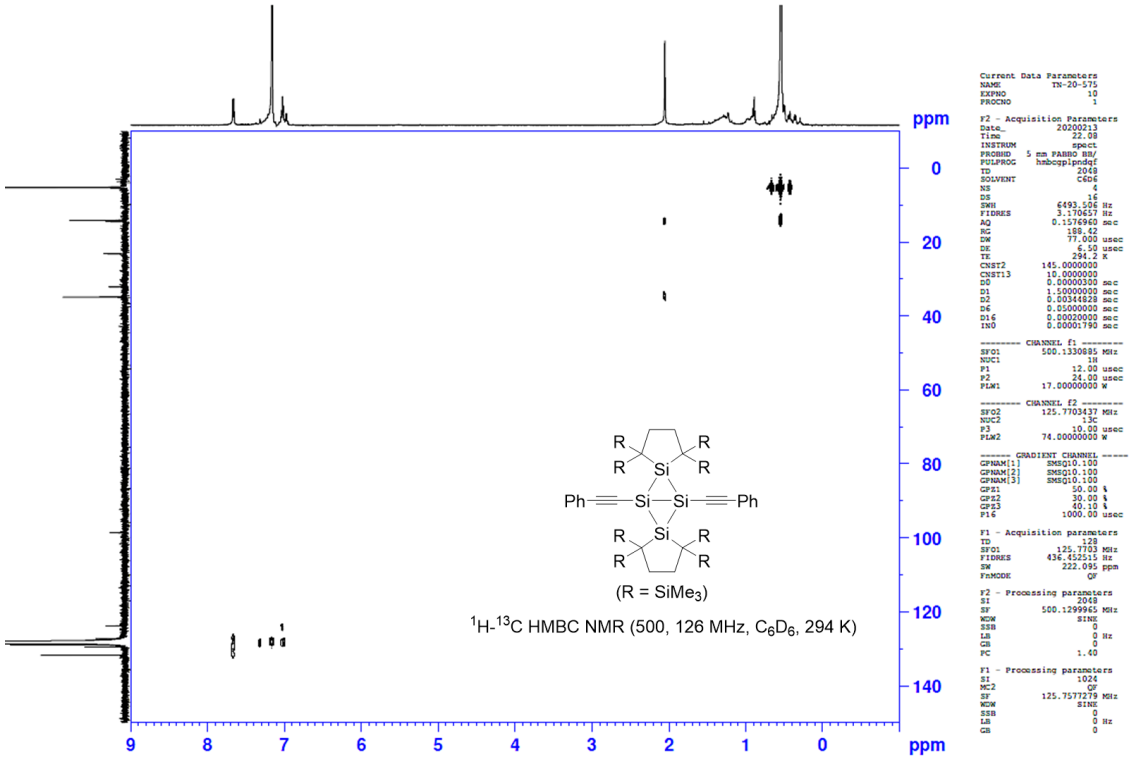


Figure 5-19. ^{1}H-^{13}C HMBC NMR spectrum of **4** in C_6D_6 at 294 K.

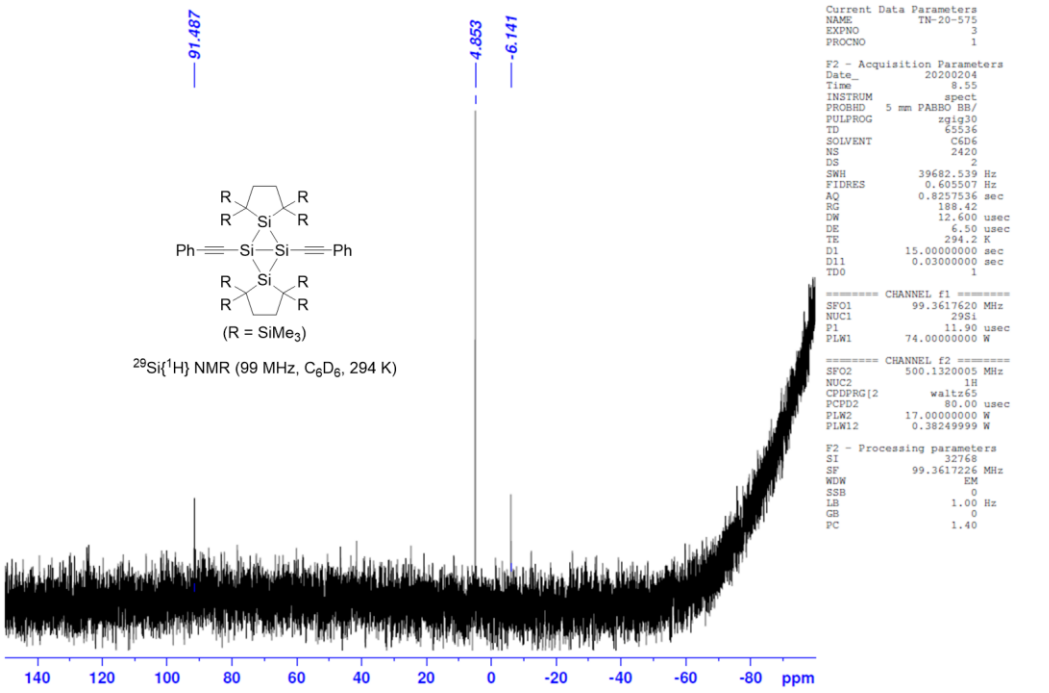


Figure 5-20. $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 294 K.

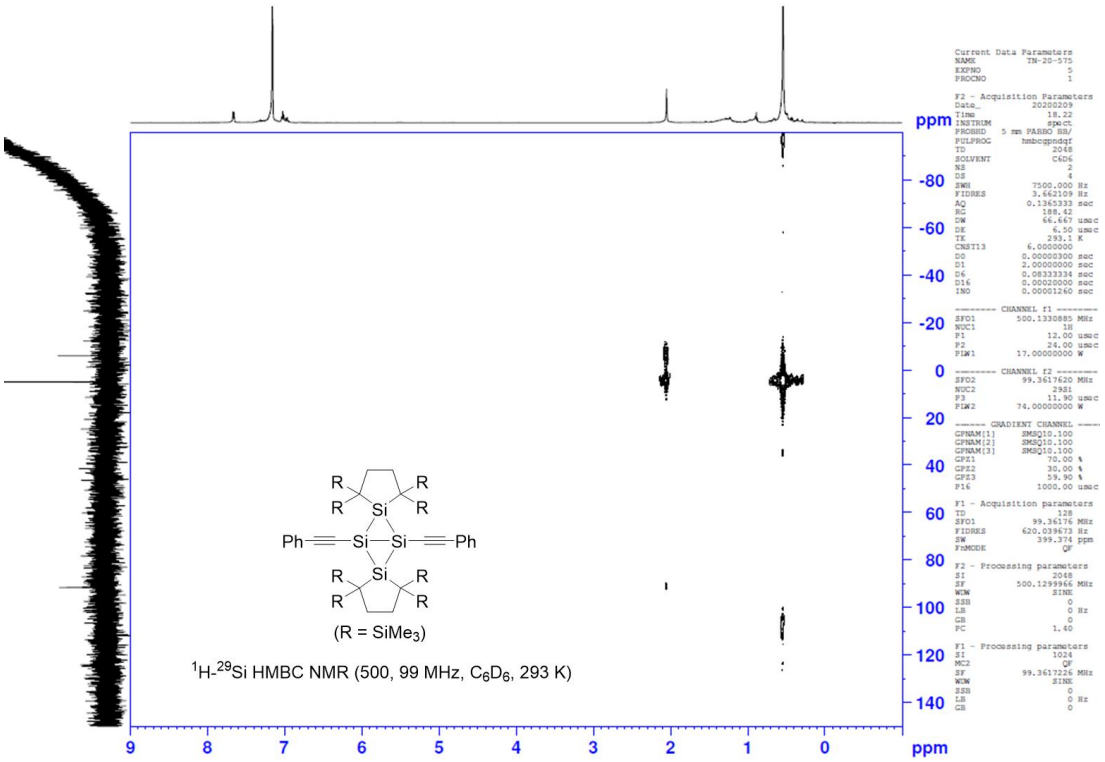


Figure 5-21. ^{1}H-^{29}Si HMBC NMR spectrum of **4** in C_6D_6 at 293 K.

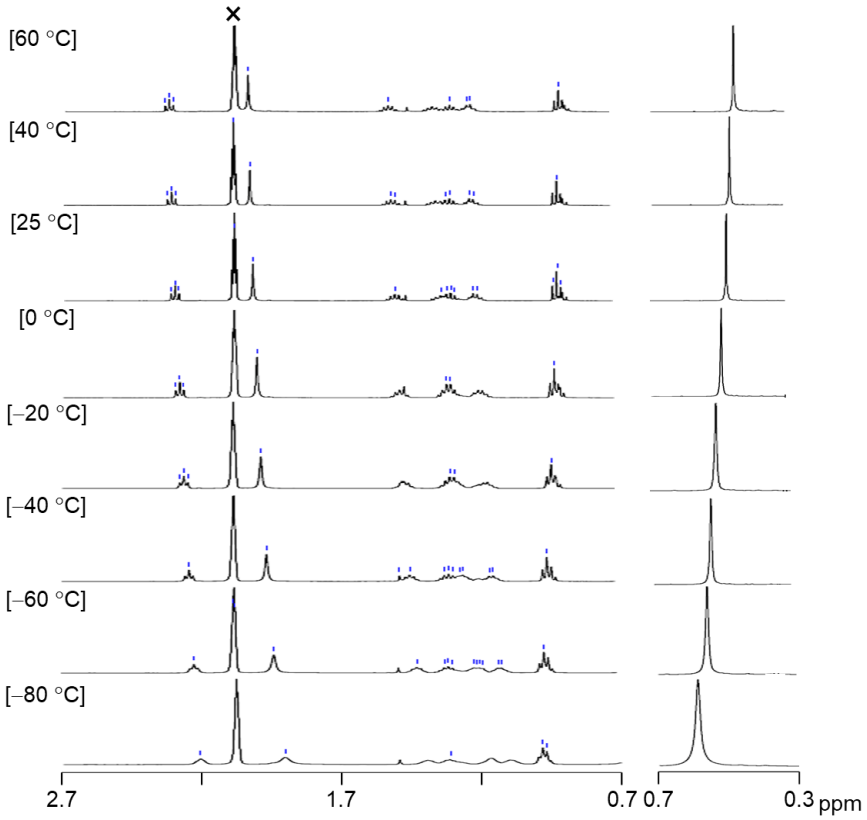


Figure 5-22. ^{1}H NMR spectra of **3** in toluene-d_8 at variable temperatures (× = C_7D_7H).

Table 5-2. ^{29}Si Chemical Shifts of **3** at Variable Temperatures.

Temperature/°C	^{29}Si chemical shift/ppm[a,b]			note
	Bridgehead Si	Bridge Si	$SiMe_3$	
60	87.6	–7.3	4.8	TN880_NMR27
50	86.3	–7.5	4.6	TN880_NMR25
40	85.3	–7.7	4.6	TN880_NMR23
30	84.4	–8.0	4.6	TN880_NMR21
25	83.4	–8.1	4.5	TN880_NMR2
0	80.4	–8.6	4.6	TN880_NMR18
–10	78.9	–8.8	4.6	TN880_NMR17
–20	77.1	–9.2	4.6	TN880_NMR9
–30	75.3	–9.4	4.5	TN880_NMR15
–40	73.2	–9.6	4.4	TN880_NMR5

[a]These values were obtained by measurement of the ^{1}H-^{29}Si HMBC 2D NMR spectra in toluene-d_8. [b]Spectral resolution is 0.39 ppm.

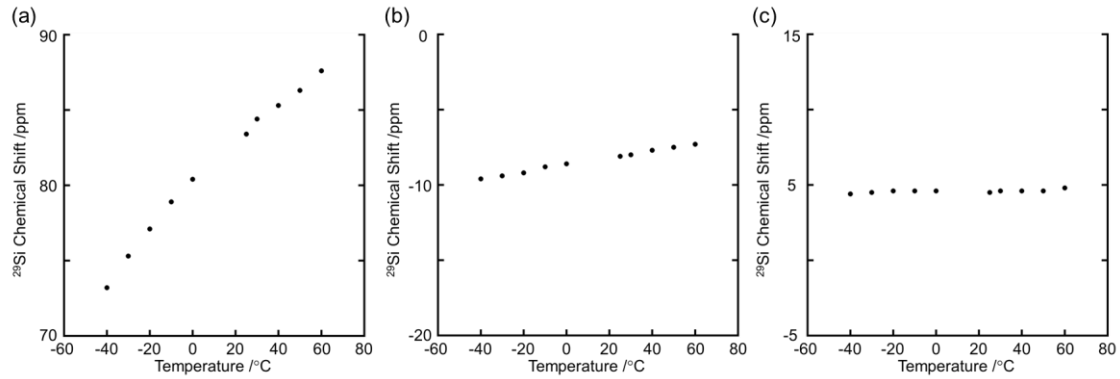


Figure 5-23. A plot of observed ^{29}Si chemical shift of **3** vs measurement temperature (a: bridgehead Si, b: bridge Si, c: $SiMe_3$).

X-ray Diffraction Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere using the following conditions; from hexamethyldisiloxane at room temperature for **3**, from toluene at −27 °C for **4**. For data collection, the single crystals coated by Apiezon grease were mounted on the glass fibre and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer using a graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[18] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2018/3).[19] Molecular structure was analysed by Yadokari-XG software.[20]

Crystal data of **3** [tn87a] (100 K) [CCDC-2095782]: $C_{48}H_{106}Si_{12}$; Fw 1020.40; triclinic; *P*-1, a = 11.9028(5) Å, b = 12.0034(5) Å, c = 12.1944(5) Å, α = 79.1540(10)°, β = 81.4440(10)°, γ = 62.7870(10)°, V = 1517.81(11) Å^3, Z = 1, D_{calc} = 1.116 Mg/m^3, $R1$ = 0.0304 ($I > 2\sigma(I)$), $wR2$ = 0.0786 (all data), GOF = 1.045.

Crystal data of **4** [tn53b] (100 K) [CCDC-2095783]: $C_{48}H_{90}Si_{12}$; Fw 1004.27; monoclinic; $P2_1/c$, a = 10.9137(5) Å, b = 23.4184(12) Å, c = 11.4842(6) Å, β = 90.4870(10)˚, V = 2935.0(3) Å^3, Z = 2, D_{calc} = 1.136 Mg/m^3, $R1$ = 0.0400 ($I > 2\sigma(I)$), $wR2$ = 0.1013 (all data), GOF = 1.076.

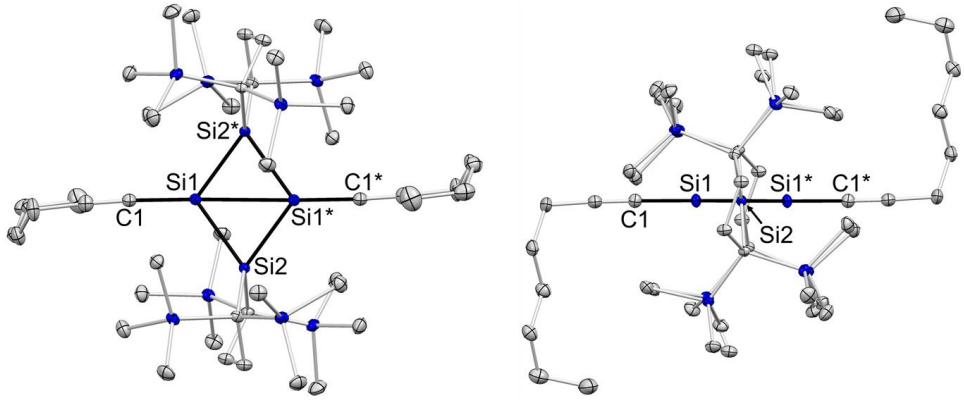


Figure 5-24. ORTEPs of **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

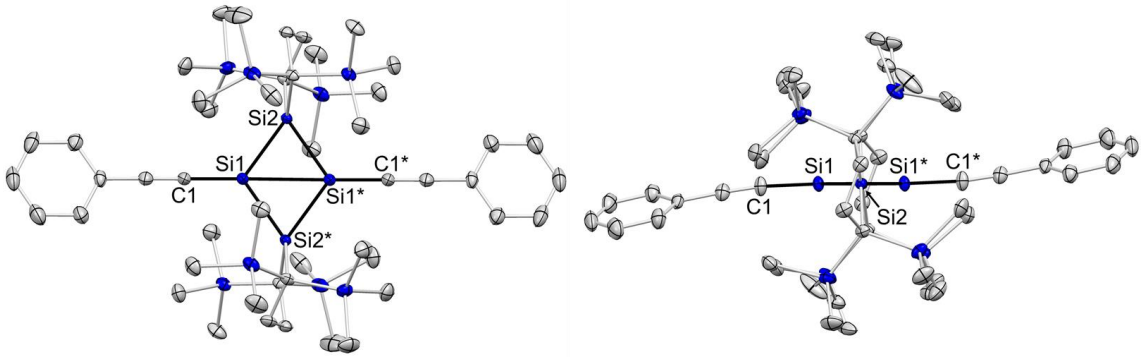


Figure 5-25. ORTEPs of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

UV-vis Absorption Spectrum [TN575,840,865,867]

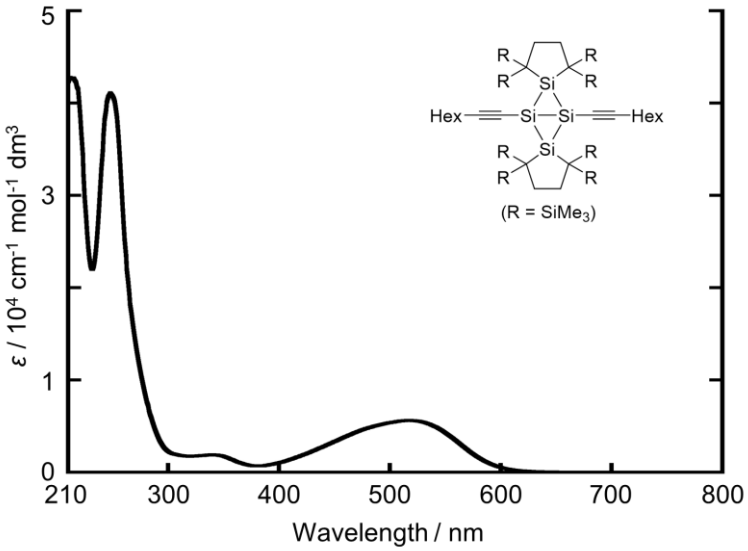


Figure 5-26. UV-vis absorption spectrum of **3** in hexane at room temperature. [TN865]

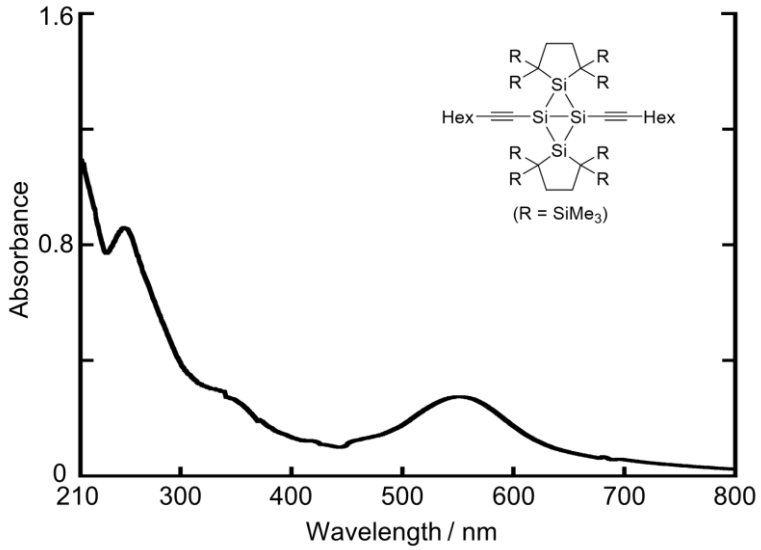


Figure 5-27. UV-vis absorption spectrum of **3** in a KBr matrix at room temperature. [TN867]

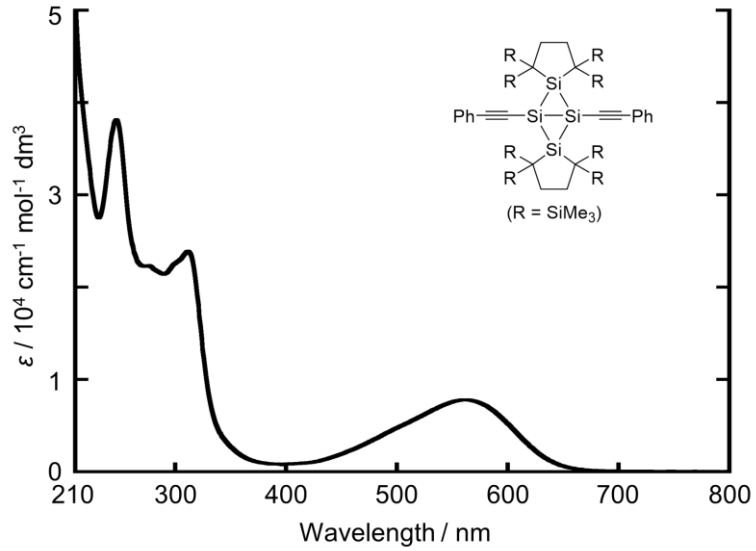


Figure 5-28. UV-vis absorption spectrum of **4** in hexane at room temperature. [TN575]

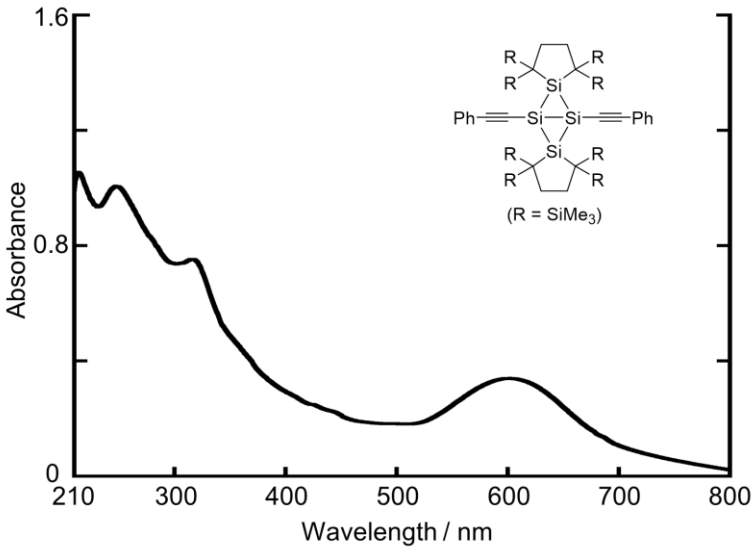


Figure 5-29. UV-vis absorption spectrum of **4** in a KBr matrix at room temperature. [TN840]

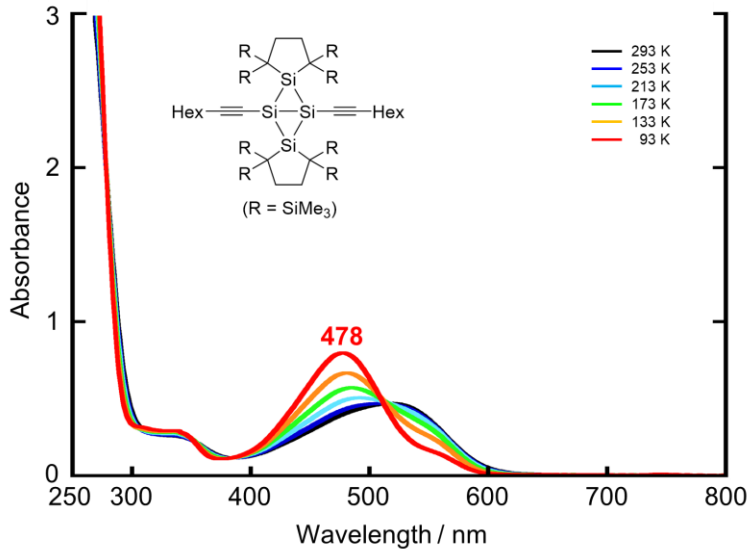


Figure 5-30. Variable-temperature UV-vis absorption spectra of **3** in 3-methylpentane at 40 K intervals from 293 K to 93 K. [TN868]

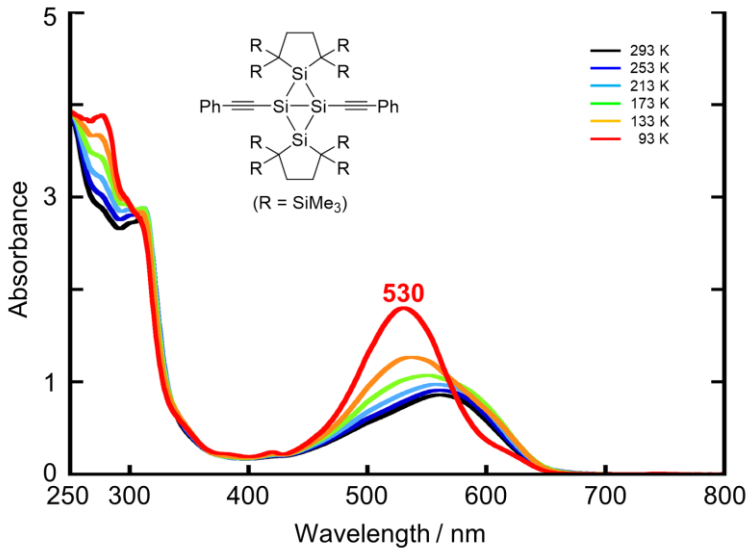
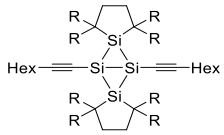


Figure 5-31. Variable-temperature UV-vis absorption spectra of **4** in 3-methylpentane at 40 K intervals from 293 K to 93 K. [TN600]

Computational Study

All theoretical calculations were performed using a Gaussian 09[21] program or GRRM14 program.[22] Geometry optimization was carried out at the ωB97XD/6-311G(d) (**3**$_{opt}$) and ωB97XD/6-311G(d)/SCRF(solvent = heptane) (**5**$_p$, **5**$_c$, **5′**$_c$, and **5″**$_c$) level of theory. Frontier Kohn-Sham orbitals and their energy levels of **3**$_{cry}$, **4**$_{cry}$, **5**$_p$, and **5**$_c$ were shown in Figure 5-33. The atomic coordinates and energies of the optimized structures are summarized in Tables 5-3 to 5-7. Isotropic chemical shielding tensors were calculated at the GIAO/M06L/6-311+G(2df,p) level of theory (Table 5-8). Absolute isotropic shielding tensors of ^{29}Si nucleus in tetramethylsilane were calculated to be 361.4 (GIAO/M06L/6-311+G(2df,p)). Natural bond orbital (NBO)[23] calculations of **3**$_{cry}$ and **4**$_{cry}$ were performed at the ωB97XD/6-311G(d) level of theory. Excitation energies and oscillator strengths of **3**$_{cry}$, **4**$_{cry}$, **5**$_p$, and **5**$_c$ were calculated at the M06-2X/6-311G(d) level of theory (Tables 5-9 to 5-12).

Table 5-3. Atomic Coordinates of $\mathbf{3_{opt}}$ at the ωB97XD/6-311G(d) Level of Theory

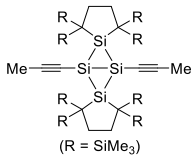


$\mathbf{3_{opt}}$

Atom	X	Y	Z
Si	8.610380718170	6.498495310301	5.143408053425
Si	10.308061120633	5.030261574750	4.654310108240
C	7.263354816674	7.008900040901	4.043101807602
C	6.399374147260	7.463406145583	3.325612236707
C	5.406003580097	8.105713172431	2.476349101843
H	4.412251475881	7.952587449850	2.910616038169
H	5.399292015310	7.618055995860	1.494597733493
C	5.681946973551	9.610738995122	2.313252990534
H	4.871438785885	10.041997857386	1.714881740107
H	5.637461174930	10.089136852713	3.297835246590
C	7.027852045953	9.909420681740	1.660570048507
H	7.092164819681	9.386776660900	0.696755062557
H	7.824840192809	9.491539862577	2.281661020323
C	7.257141189827	11.402715926290	1.438802224323
H	6.469584263006	11.788641097634	0.780060192209
H	7.140977409942	11.934749267895	2.392227018590
C	8.623960431966	11.736825437830	0.835471015968
H	8.775535452159	11.132218848056	-0.067338726601
H	8.622400519359	12.780609502593	0.503140886066
C	9.792997991096	11.524300968560	1.794648347424
H	9.701022352331	12.169778963483	2.674373051807
H	10.747936899291	11.757116707006	1.315767387616
H	9.848220800822	10.492182847717	2.146951875025
C	11.753635688567	5.244665024884	3.384433418214
C	11.701701387481	3.880841372800	2.606923745628
H	11.048779819663	3.949235611124	1.733867170393
H	12.683411691492	3.607291482747	2.204985604427
C	11.178933230631	2.757131092661	3.508514776679
H	11.943366095889	2.514871329918	4.248969886329
H	11.034498922313	1.845799656718	2.919971788637
C	9.866831592633	3.209138588360	4.220134193459
Si	11.646998301826	6.713603558407	2.141354068055
C	12.026078994340	6.056666496539	0.412033038754
H	11.214823559360	5.450407058031	-0.000889295424
H	12.935384350811	5.449845182594	0.383885060783
H	12.173221994790	6.901261390627	-0.268918570002
C	12.862640520967	8.131930600348	2.428850619672
H	12.669497954258	8.869932793624	1.641727433674
H	13.917065661054	7.861658657001	2.359990593523
H	12.710274266910	8.641328716158	3.379947461756
C	9.996825659135	7.610332331555	2.032874936471
H	9.786388830288	8.198271479289	2.929199367444
H	9.134117676969	6.975059517598	1.846202916972
H	10.065508714373	8.317510620466	1.198175416645
Si	13.474209830794	5.316681956172	4.226089942358
C	13.698235112969	6.861182539316	5.289098050677
H	14.054096684745	6.588521389064	6.285836500882
H	12.767419974760	7.415314983281	5.422167542552
H	14.421384817575	7.552713458835	4.849418707320
C	14.831892689630	5.235022092269	2.908265550836
H	15.792808909185	5.484417743292	3.371634442149
H	14.698417029539	5.906215931227	2.058801484757
H	14.929887386070	4.220774034791	2.509717958616
Si	9.564810861627	2.070165469929	5.716131952162
C	13.867254213890	3.824816812744	5.310446466852
H	14.820657700318	4.023306144469	5.814127032036
H	13.999371174757	2.909474585313	4.727069155833
H	13.129840756541	3.636964882123	6.089218370975
C	8.183897657938	2.647163352836	6.848870172852
H	8.218712681315	2.082136187497	7.785060819863
H	7.189185604814	2.512202002116	6.422291292523
H	8.294296360724	3.703978276004	7.096850140441
C	9.155174653881	0.312300158438	5.166478251704
H	9.098491406431	-0.332837551674	6.049913486210
H	9.926841951661	-0.103960677711	4.511719918466
H	8.197084103163	0.231718232511	4.646886869981
C	11.103122032137	1.900151967685	6.789271123405
H	11.414857188703	2.841614604534	7.243753406963
H	11.960586867195	1.484438987766	6.253954469324
H	10.870653143015	1.213293755904	7.609058650941
Si	8.420738461426	3.063819277205	2.967977704197
C	8.249044254484	4.467081171921	1.723390520732
H	7.536084723921	4.136808730656	0.959048154073
H	9.171229130457	4.731970281929	1.203500809453
H	7.834290451213	5.369015783884	2.174402060741
C	6.730216256974	2.966140351419	3.788974073418
H	6.552370197063	3.801269781336	4.471447936791
H	6.561399523214	2.037475462320	4.338837299948
H	5.964569753515	3.023701193241	3.008024274419
C	8.664561093902	1.527291211573	1.898187370947
H	8.894506209094	0.619706649258	2.458585931462
H	9.463390871476	1.676620878284	1.164925933193
H	7.745896023767	1.340285343334	1.331878788984
Si	10.595806263704	5.823582071174	6.802238271676
Si	8.898125861241	7.291815806725	7.291336216861
C	11.942832165201	5.313177340573	7.902544517499
C	12.806812834614	4.858671235891	8.620034088393
C	13.800183401777	4.216364209044	9.469297223257
H	14.793935505993	4.369489931624	9.035030286931
H	13.806894966564	4.704021385615	10.451048591607
C	13.524240008323	2.711338386353	9.632393334566
H	14.334748195989	2.280079524088	10.230764584993
H	13.568725806944	2.232940528761	8.647811078511
C	12.178334935921	2.412656699735	10.285076276593
H	12.114022162193	2.935300720575	11.248891262543
H	11.381346789065	2.830537518898	9.663985304777
C	11.949045792048	0.919361455185	10.506844100777
H	12.736602718868	0.533436283841	11.165586132891
H	12.065209571932	0.387328113580	9.553419306510
C	10.582226549909	0.585251943645	11.110175309132
H	10.430651529715	1.189858533419	12.012985051701
H	10.583786462515	-0.458532121118	11.442505439034
C	9.413188990778	0.797776412914	10.150997977676
H	9.505164629543	0.152298417992	9.271273273294
H	8.458250082583	0.564960674469	10.629878937484
H	9.357966181053	1.829894533758	9.798694450076
C	7.452551293307	7.077412356591	8.561212906887
C	7.504485594393	8.441236008675	9.338722579472
H	8.157407162211	8.372841770350	10.211779154707
H	6.522775290382	8.714785898728	9.740660720673
C	8.027253751243	9.564946288813	8.437131548422
H	7.262820885985	9.807206051557	7.696676438771
H	8.171688059561	10.476277724757	9.025674536463
C	9.339355389241	9.112938793115	7.725512131641
Si	7.559188680049	5.608473823067	9.804292257045
C	7.180107987535	6.265410884936	11.533613286347
H	7.991363422515	6.871670323443	11.946535620525
H	6.270802631064	6.872232198881	11.561761264317
H	7.032964987084	5.420815990847	12.214564895102
C	6.343546460907	4.190146781127	9.516795705428
H	6.536689027616	3.452144587851	10.303918891426
H	5.289121320820	4.460418724473	9.585655731577
H	6.495912714964	3.680748665316	8.565698863345
C	9.209361322739	4.711745049920	9.912771388629
H	9.419798151586	4.123805902186	9.016446957656
H	10.072069304905	5.347017863876	10.099443408128
H	9.140678267501	4.004566761009	10.747470908455
Si	5.731977151080	7.005395425302	7.719556382742
C	5.507951868905	5.460894842159	6.656548274423
H	5.152090297130	5.733555992411	5.659809824218
H	6.438767007115	4.906762398194	6.523478782548
H	4.784802164300	4.769363922639	7.096227617780
C	4.374294292244	7.087055289206	9.037380774264
H	3.413378072689	6.837659638183	8.574011882952
H	4.507769952335	6.415861450248	9.886844840343
H	4.276299595804	8.101303346683	9.435928366485
Si	9.641376120247	10.251911911546	6.229514372938
C	5.338932767984	8.497260568731	6.635199858248
H	4.385529281556	8.298771237006	6.131519293064
H	5.206815807117	9.412602796161	7.218577169267
H	6.076346225333	8.685112499352	5.856427954125
C	11.022289323937	9.674914028639	5.096776152248
H	10.987474300559	10.239941193977	4.160585505238
H	12.017001377060	9.809875379358	5.523355032578
H	10.911890621150	8.618099105471	4.848796184659
C	10.051012327993	12.009777223037	6.779168073396
H	10.107695575443	12.654914933149	5.895732838891
H	9.279345030213	12.426038059186	7.433926406635
H	11.009102878711	12.090359148963	7.298759455120
C	8.103064949737	10.421925413790	5.156375201696
H	7.791329793171	9.480462776941	4.701892918138
H	7.245600114679	10.837638393709	5.691691855776
H	8.335533838859	11.108783625571	4.336587674160
Si	10.785448520448	9.258258104269	8.977668620903
C	10.957142727390	7.854996209553	10.222255804369
H	11.670102257953	8.185268650819	10.986598171027
H	10.034957851417	7.590107099546	10.742145515648
H	11.371896530661	6.953061597590	9.771244264359
C	12.475970724900	9.355937030055	8.156672251683
H	12.653816784811	8.520807600139	7.474198388309
H	12.644787458660	10.284601919155	7.606809025153
H	13.241617228360	9.298376188234	8.937622050681
C	10.541625887973	10.794786169901	10.047458954153
H	10.311680772780	11.702370732216	9.487060393638
H	9.742796110399	10.645456503191	10.780720391907
H	11.460290958107	10.981792038141	10.613767536116

E+ZPVE = -5365.613969 au, Free E (298.15 K) = -5365.733000 au.
Job name: TN120da

Table 5-4. Atomic Coordinates of $\mathbf{5_p}$ at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) Level of Theory

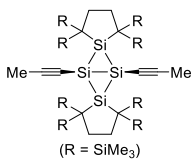


$\mathbf{5_p}$

Atom	X	Y	Z
Si	-1.331054133558	-0.036204068321	-0.148426239565
Si	0.032654071593	-1.869939988902	0.095367941890
C	-3.137542722239	-0.043985554198	-0.318778608211
C	-4.345389218970	-0.001098395951	-0.400745606235
C	-0.240126534784	-3.032633113961	1.601726422263
C	0.501936638482	-4.314767668018	1.114069022172
H	1.578514215595	-4.201529801145	1.253605881338
H	0.218072057126	-5.199359777203	1.692602189846
C	0.216742415279	-4.553479049967	-0.373211908213
H	-0.811539864032	-4.907988561337	-0.471016608958
H	0.836039484671	-5.378895317537	-0.740973339337
C	0.446029284377	-3.241099809564	-1.206434728667
Si	2.294165866112	-3.257800585076	-1.714854932714
C	3.489770773757	-3.434021522610	-0.267920971955
H	4.506380479625	-3.329386840958	-0.665069091127
H	3.430204618579	-4.419485569085	0.202038032272
H	3.368511149962	-2.673678031943	0.502416656606
C	2.655241752951	-4.809588838604	-2.739996200235
H	1.920725810827	-5.036728683020	-3.514086259305
H	2.734712823682	-5.691504838129	-2.097385953563
H	3.625085988468	-4.691914553301	-3.235842117391
C	2.805277801650	-1.718571137573	-2.682184728618
H	3.723202502009	-1.297999957686	-2.264237844717
H	2.049973363183	-0.931613164757	-2.648250867652
H	2.985292263598	-1.945119215790	-3.735876819108
Si	-0.608521176060	-3.285620495945	-2.819178287412
C	-1.188328542731	-5.060713650643	-3.102480551793
H	-1.970056904356	-5.371332844406	-2.403496898821
H	-0.372261185998	-5.784613474899	-3.024365388099
H	-1.607683704039	-5.143981391237	-4.110423201091
C	-2.144805924174	-2.199260041247	-2.858881989016
H	-2.675952237473	-2.424239874578	-3.791207312700
H	-1.908755677243	-1.133019126266	-2.881992039448
H	-2.842399142965	-2.367530263562	-2.040738469167
C	0.292018272395	-2.786221595544	-4.404427522323
H	-0.432716732350	-2.893475824262	-5.219585079850
H	1.154766590337	-3.401957511784	-4.661714829626
H	0.613038810974	-1.744615338980	-4.402118194548
Si	0.559436407463	-2.446252713799	3.228081360207
C	-0.037955261033	-0.764406414428	3.814972458423
H	0.655838475201	-0.374229301530	4.566476753538
H	-1.031045470422	-0.789421022224	4.265867585610
H	-0.066742192311	-0.046726730809	2.993627424775
C	0.244560006217	-3.680846096718	4.620034455114
H	0.573266501819	-4.690502814250	4.355354802254
H	-0.806008151028	-3.737851829574	4.916298364441
H	0.814137295797	-3.375518820378	5.504262690372
C	2.434899310686	-2.326925651834	3.093574033371
H	2.774396399585	-1.568505716555	2.385183419307
H	2.909573477690	-3.274196370943	2.825187870319
H	2.823533808898	-2.040527275900	4.077179343940
Si	-2.084440133196	-3.475984498904	1.883413858342
C	-2.974086581781	-2.264889289366	3.016666717864
H	-2.871840085186	-1.230839910089	2.677246674082
H	-2.643274445583	-2.314484620026	4.056599525856
H	-4.043116586903	-2.503064574320	3.004475397351
C	-2.214847281676	-5.208417969332	2.622857013655
H	-1.553952428547	-5.387194028826	3.472423941019
H	-2.005310336124	-5.975766018227	1.870882582301
H	-3.242974816438	-5.370534359203	2.964132963394
C	-3.168913454514	-3.555043770196	0.345282795722
H	-4.116370066141	-4.020595975234	0.640860910189
H	-2.761350766215	-4.154321732407	-0.470451935813
H	-3.408975360609	-2.564154248724	-0.039953526932
Si	1.331054133558	0.036204068321	0.148426239565
Si	-0.032654071593	1.869939988902	-0.095367941890
C	3.137542722239	0.043985554198	0.318778608211
C	4.345389218970	0.001098395951	0.400745606235
C	0.240126534784	3.032633113961	-1.601726422263
C	-0.501936638482	4.314767668018	-1.114069022172
H	-1.578514215595	4.201529801145	-1.253605881338
H	-0.218072057126	5.199359777203	-1.692602189846
C	-0.216742415279	4.553479049967	0.373211908213
H	0.811539864032	4.907988561337	0.471016608958
H	-0.836039484671	5.378895317537	0.740973339337
C	-0.446029284377	3.241099809564	1.206434728667
Si	-2.294165866112	3.257800585076	1.714854932714
C	-3.489770773757	3.434021522610	0.267920971955
H	-4.506380479625	3.329386840958	0.665069091127
H	-3.430204618579	4.419485569085	-0.202038032272
H	-3.368511149962	2.673678031943	-0.502416656606
C	-2.655241752951	4.809588838604	2.739996200235
H	-1.920725810827	5.036728683020	3.514086259305
H	-2.734712823682	5.691504838129	2.097385953563
H	-3.625085988468	4.691914553301	3.235842117391
C	-2.805277801650	1.718571137573	2.682184728618
H	-3.723202502009	1.297999957686	2.264237844717
H	-2.049973363183	0.931613164757	2.648250867652
H	-2.985292263598	1.945119215790	3.735876819108
Si	0.608521176060	3.285620495945	2.819178287412
C	1.188328542731	5.060713650643	3.102480551793
H	1.970056904356	5.371332844406	2.403496898821
H	0.372261185998	5.784613474899	3.024365388099
H	1.607683704039	5.143981391237	4.110423201091
C	2.144805924174	2.199260041247	2.858881989016
H	2.675952237473	2.424239874578	3.791207312700
H	1.908755677243	1.133019126266	2.881992039448
H	2.842399142965	2.367530263562	2.040738469167
C	-0.292018272395	2.786221595544	4.404427522323
H	0.432716732350	2.893475824262	5.219585079850
H	-1.154766590337	3.401957511784	4.661714829626
H	-0.613038810974	1.744615338980	4.402118194548
Si	-0.559436407463	2.446252713799	-3.228081360207
C	0.037955261033	0.764406414428	-3.814972458423
H	-0.655838475201	0.374229301530	-4.566476753538
H	1.031045470422	0.789421022224	-4.265867585610
H	0.066742192311	0.046726730809	-2.993627424775
C	-0.244560006217	3.680846096718	-4.620034455114
H	-0.573266501819	4.690502814250	-4.355354802254
H	0.806008151028	3.737851829574	-4.916298364441
H	-0.814137295797	3.375518820378	-5.504262690372
C	-2.434899310686	2.326925651834	-3.093574033371
H	-2.774396399585	1.568505716555	-2.385183419307
H	-2.909573477690	3.274196370943	-2.825187870319
H	-2.823533808898	2.040527275900	-4.077179343940
Si	2.084440133196	3.475984498904	-1.883413858342
C	2.974086581781	2.264889289366	-3.016666717864
H	2.871840085186	1.230839910089	-2.677246674082
H	2.643274445583	2.314484620026	-4.056599525856
H	4.043116586903	2.503064574320	-3.004475397351
C	2.214847281676	5.208417969332	-2.622857013655
H	1.553952428547	5.387194028826	-3.472423941019
H	2.005310336124	5.975766018227	-1.870882582301
H	3.242974816438	5.370534359203	-2.964132963394
C	3.168913454514	3.555043770196	-0.345282795722
H	4.116370066141	4.020595975234	-0.640860910189
H	2.761350766215	4.154321732407	0.470451935813
H	3.408975360609	2.564154248724	0.039953526932
C	5.793599493075	-0.063961220567	0.496721143826
H	6.258133328280	0.301945632480	-0.422539494171
H	6.155150968836	0.548575146422	1.326315959336
H	6.123062888803	-1.093011593766	0.661275806267
C	-5.793599493075	0.063961220567	-0.496721143826
H	-6.155150968836	-0.548575146422	-1.326315959336
H	-6.258133328280	-0.301945632480	0.422539494171
H	-6.123062888803	1.093011593766	-0.661275806267

E+ZPVE = -4972.787402 au, Free E (298.15 K) = -4972.896005 au.
Job name: TN116db

Table 5-5. Atomic Coordinates of $\mathbf{5_c}$ at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) Level of Theory



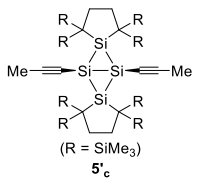
$\mathbf{5_c}$

Atom	X	Y	Z
Si	-1.270443952028	0.073947483656	-0.260878495385
Si	0.103133829755	1.887382596035	0.096545600198
C	-2.815720540426	0.191502341269	-1.196469486215
C	-3.874773589161	0.287632270266	-1.774704689073
C	0.179284621581	3.267891998925	-1.256860817385
C	0.797535540580	4.431837825224	-0.416693216917
H	1.878328647798	4.302896225070	-0.341380926931

H	0.644344470133	5.404639522156	-0.894431030623
C	0.209701553680	4.446200148803	0.994499558336
H	-0.824479726606	4.797233884705	0.927681469316
H	0.726994842055	5.190882295657	1.608592125763
C	0.267969537649	3.019223115567	1.647633074745
Si	1.980855908730	2.782973020607	2.476651083424
C	3.451928578408	2.973007547261	1.316048225806
H	4.358291648322	2.825728255282	1.914430124819
H	3.535222934312	3.954532497844	0.844653673429
H	3.465027368253	2.213742009220	0.531677308257
C	2.256009032211	4.098248686158	3.804277907150
H	1.532952271660	4.067888642977	4.621562501152
H	2.239998088993	5.109633196832	3.386912768887
H	3.248551232121	3.951111250535	4.243569804466
C	2.169870357196	1.068680970647	3.236273465528
H	3.162993293377	0.668568976092	3.014188529202
H	1.447411483628	0.360899002640	2.827504495411
H	2.051697453462	1.071215931561	4.321687188606
Si	-1.084789133345	2.960268161325	3.015148993706
C	-1.359894916761	4.718045892166	3.650284642055
H	-1.846209208022	5.362675584980	2.913084152858
H	-0.431828648499	5.208259097873	3.955363633429
H	-2.015264968013	4.680578701215	4.527019565709
C	-2.786338814061	2.335602583105	2.492296016782
H	-3.313257075040	1.998747792147	3.390947865971
H	-2.764921513886	1.492301987237	1.800837177846
H	-3.388754853781	3.122993098653	2.037782638031
C	-0.634573250190	1.956801823248	4.547438715927
H	-1.498600359786	1.991640619584	5.219771638244
H	0.217699080395	2.355988058607	5.100045457011
H	-0.436415620652	0.906318800111	4.343262745008
Si	1.326299058652	3.011958105502	-2.770944902899
C	1.032234764376	1.438973434183	-3.753614304193
H	1.811259541463	1.359818617153	-4.520176699189
H	0.068668107616	1.430549390002	-4.265021361426
H	1.088926091988	0.538323117458	-3.143597736074
C	1.175074827244	4.447517906025	-3.993315132390
H	1.397182380136	5.408537991317	-3.519692253634
H	0.205743468536	4.532713888160	-4.487945601334
H	1.925387741735	4.298359935711	-4.777803752434
C	3.147389095437	3.085309471319	-2.292297705054
H	3.431947994846	2.379359677773	-1.515646203929
H	3.448878519341	4.087720602432	-1.975432638095
H	3.736023079801	2.838919811734	-3.183331015731
Si	-1.557994695518	3.811925352882	-1.878324478205
C	-2.110449927372	2.869487976853	-3.413704223416
H	-2.032769993392	1.788411729342	-3.285711202252
H	-1.558824805142	3.147084525558	-4.314439030426
H	-3.166327898988	3.097824818740	-3.595659857644
C	-1.558803313076	5.658510569932	-2.276753516734
H	-0.756835663719	5.985461880074	-2.939094975724
H	-1.504001362778	6.259487915077	-1.363495445036
H	-2.508512686583	5.907946768502	-2.762680824910
C	-2.955795719979	3.659014604031	-0.629559193128
H	-3.880868868606	3.971498858783	-1.127830984527
H	-2.817593178482	4.323070925561	0.226856255863
H	-3.118780034855	2.648269610391	-0.260960369242
Si	1.270443952028	-0.073947483656	-0.260878495385
Si	-0.103133829755	-1.887382596035	0.096545600198
C	2.815720540426	-0.191502341269	-1.196469486215
C	3.874773589161	-0.287632270266	-1.774704689073
C	-0.267969537649	-3.019223115567	1.647633074745
C	-0.209701553680	-4.446200148803	0.994499558336
H	-0.726994842055	-5.190882295657	1.608592125763
H	0.824479726606	-4.797233884705	0.927681469316
C	-0.797535540580	-4.431837825224	-0.416693216917
H	-0.644344470133	-5.404639522156	-0.894431030623
H	-1.878328647798	-4.302896225070	-0.341380926931
C	-0.179284621581	-3.267891998925	-1.256860817385
Si	-1.326299058652	-3.011958105502	-2.770944902899
C	-3.147389095437	-3.085309471319	-2.292297705054
H	-3.736023079801	-2.838919811734	-3.183331015731
H	-3.448878519341	-4.087720602432	-1.975432638095
H	-3.431947994846	-2.379359677773	-1.515646203929
C	-1.175074827244	-4.447517906025	-3.993315132390
H	-0.205743468536	-4.532713888160	-4.487945601334
H	-1.397182380136	-5.408537991317	-3.519692253634
H	-1.925387741735	-4.298359935711	-4.777803752434
C	-1.032234764376	-1.438973434183	-3.753614304193
H	-1.811259541463	-1.359818617153	-4.520176699189
H	-1.088926091988	-0.538323117458	-3.143597736074
H	-0.068668107616	-1.430549390002	-4.265021361426
Si	1.557994695518	-3.811925352882	-1.878324478205
C	1.558803313076	-5.658510569932	-2.276753516734
H	1.504001362778	-6.259487915077	-1.363495445036
H	0.756835663719	-5.985461880074	-2.939094975724
H	2.508512686583	-5.907946768502	-2.762680824910
C	2.955795719979	-3.659014604031	-0.629559193128
H	3.880868868606	-3.971498858783	-1.127830984527
H	3.118780034855	-2.648269610391	-0.260960369242
H	2.817593178482	-4.323070925561	0.226856255863
C	2.110449927372	-2.869487976853	-3.413704223416
H	3.166327898988	-3.097824818740	-3.595659857644
H	1.558824805142	-3.147084525558	-4.314439030426
H	2.032769993392	-1.788411729342	-3.285711202252
Si	-1.980855908730	-2.782973020607	2.476651083424
C	-2.169870357196	-1.068680970647	3.236273465528
H	-3.162993293377	-0.668568976092	3.014188529202
H	-2.051697453462	-1.071215931561	4.321687188606
H	-1.447411483628	-0.360899002640	2.827504495411
C	-2.256009032211	-4.098248686158	3.804277907150
H	-2.239998088993	-5.109633196832	3.386912768887
H	-1.532952271660	-4.067888642977	4.621562501152
H	-3.248551232121	-3.951111250535	4.243569804466
C	-3.451928578408	-2.973007547261	1.316048225806
H	-3.465027368253	-2.213742009220	0.531677308257
H	-3.535222934312	-3.954532497844	0.844653673429
H	-4.358291648322	-2.825728255282	1.914430124819
Si	1.084789133345	-2.960268161325	3.015148993706
C	0.634573250190	-1.956801823248	4.547438715927
H	0.436415620652	-0.906318800111	4.343262745008
H	-0.217699080395	-2.355988058607	5.100045457011
H	1.498600359786	-1.991640619584	5.219771638244
C	1.359894916761	-4.718045892166	3.650284642055
H	0.431828648499	-5.208259097873	3.955363633429
H	1.846209208022	-5.362675584980	2.913084152858
H	2.015264968013	-4.680578701215	4.527019565709
C	2.786338814061	-2.335602583105	2.492296016782
H	3.313257075040	-1.998747792147	3.390947865971
H	3.388754853781	-3.122993098653	2.037782638031
H	2.764921513886	-1.492301987237	1.800837177846
C	5.120544294905	-0.399931237455	-2.512728310702
H	5.841050148517	-1.018328515147	-1.971689680136
H	4.943358096455	-0.859544894946	-3.488877527933
H	5.566164572204	0.585121067882	-2.673406697411
C	-5.120544294905	0.399931237455	-2.512728310702
H	-5.841050148517	1.018328515147	-1.971689680136
H	-4.943358096455	0.859544894946	-3.488877527933
H	-5.566164572204	-0.585121067882	-2.673406697411

E+ZPVE = -4972.790314 au, Free E (298.15 K) = -4972.897349 au.
Job name: TN117bb

Table 5-6. Atomic Coordinates of **5′$_c$** at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) Level of Theory



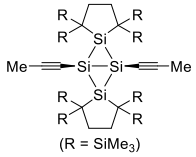
5′$_c$

Atom	X	Y	Z
Si	-1.876461367697	0.034013722833	-0.124559427253
Si	-3.826739073314	-1.928493545467	1.478730051435
Si	-2.876110516473	-2.883232572513	-1.329013150227
Si	-2.746438810114	2.423954041246	-2.000937833945
Si	-3.114514799643	2.882198452370	1.095788294633
Si	0.109406678163	-0.335576424525	-1.254801809382
C	-3.221891377236	-1.345488386818	-0.247515237088
C	-4.455002169202	0.864829009602	-0.388850609196
H	-4.897469353410	0.787670094180	0.606002151370
H	-5.165677406553	1.459143073237	-0.973592839137
C	-4.356994181252	-0.547297531919	-0.961616816964
H	-4.151284637291	-0.483212502216	-2.031878376356
H	-5.325748152485	-1.049743509981	-0.872129386460
C	-3.043990384923	1.559840516442	-0.316826567614
C	0.390994771982	-2.058414273595	-3.716733875593
C	-4.295568052713	-4.129854307549	-1.227198522949
H	-5.250204192221	-3.680942469473	-1.517971680290
H	-4.428097780528	-4.599455407875	-0.250749978414
H	-4.089365004247	-4.931595989137	-1.945576649829
C	0.274904438378	-1.377291334848	-2.723687575572
C	-3.694248411626	-0.657992142151	2.859381317809
H	-4.225268827291	0.270314372848	2.642058468463
H	-2.663239129609	-0.418646804645	3.117527393496
H	-4.158716241370	-1.088881662631	3.753881040382
C	-1.299530875574	-3.803794091042	-0.862959646973
H	-0.802884379111	-4.189647725540	-1.757395337979
H	-1.514862073212	-4.650511357020	-0.206431657911
H	-0.582069774542	-3.163855944882	-0.347061646532
C	-5.670651185372	-2.326817105114	1.412168185814
H	-5.955301281123	-3.008939298999	0.609830344977
H	-6.268158070394	-1.415909325820	1.303688721376
H	-5.966899421734	-2.790582558473	2.359267550460
C	-2.085488713004	2.515322330770	2.630890065315
H	-2.048417900575	3.425283426074	3.240076621788
H	-1.056153908230	2.231798562145	2.412783992349
H	-2.521441835457	1.729417200090	3.247499667922
C	-2.651074879568	1.271033357880	-3.490787968172
H	-2.550327219566	1.904379745279	-4.380056014871
H	-3.543822029360	0.659521845162	-3.637479849263

H	-1.782835526930	0.608179875916	-3.474659363245
C	-4.219336502710	3.552644376999	-2.377735630702
H	-4.704272589090	3.962513766516	-1.488819028116
H	-4.984041711777	3.010761569807	-2.942529233552
H	-3.902083625274	4.397915793354	-2.997107490256
C	-2.888522383507	-2.428397765829	-3.159692093145
H	-2.451191465292	-3.254566041799	-3.730900095409
H	-2.324043377602	-1.532246401890	-3.407397159376
H	-3.914841682756	-2.296552763396	-3.516280045787
C	-2.660247538772	4.651277090462	0.603836300605
H	-2.923686240446	5.282579957900	1.460078439781
H	-3.214626875240	5.034612191528	-0.254911412383
H	-1.598965404146	4.802460761601	0.417600630120
C	-1.132225336890	3.394059176821	-2.053668874065
H	-0.795858410364	3.476706615040	-3.092057216666
H	-0.341510098288	2.882081914447	-1.501224725807
H	-1.215400320319	4.405047580639	-1.654726382044
C	-2.887256291633	-3.445010731334	2.085884023975
H	-3.104829894810	-3.586725962632	3.150144270184
H	-1.806485775306	-3.321742273615	1.993333157276
H	-3.168494191563	-4.365835500160	1.570734387157
C	-4.901531995186	3.068441320517	1.688101534478
H	-5.286506902639	2.206493316841	2.238497081999
H	-5.593573892556	3.269471994108	0.864796387361
H	-4.947285721972	3.925637533193	2.367936339209
Si	1.889013215252	0.156474177040	0.113697302939
Si	3.182046090464	2.695438199085	-1.403137973853
Si	2.266344860869	3.014648507102	1.599790598660
Si	3.328560458222	-2.165596789198	1.800463396976
Si	3.733375359985	-2.217271362874	-1.301711137397
Si	-0.071167767276	-0.304709609106	1.259319570424
C	2.883074034948	1.787740794400	0.277239527657
C	4.599070914224	-0.116924197062	0.276033570287
H	4.997169242860	0.057464339630	-0.729202481015
H	5.430989851312	-0.547164805999	0.844002561255
C	4.223802528056	1.237589960591	0.876189289739
H	4.119829615321	1.108547850814	1.958635741407
H	5.048721838977	1.942082212256	0.741063134407
C	3.376017726078	-1.095133779315	0.210841429253
C	-0.302973379657	-1.766164786396	3.889786389297
C	3.665366453217	4.238055911423	1.945659664692
H	4.435561259009	3.770598495609	2.566896169035
H	4.159664885711	4.613767592063	1.046714459581
H	3.286186862520	5.103665994252	2.498839754133
C	-0.200656436841	-1.225711154711	2.811999748107
C	2.324649331294	1.954799416291	-2.905005908961
H	2.668494894645	2.504787131564	-3.788558943911
H	2.525291420933	0.901786408177	-3.079017028846
H	1.241301887517	2.081287330734	-2.853183718893
C	0.697372946912	3.918922959774	1.118006082733
H	0.186894972768	4.278946466339	2.015054109300
H	0.866344639183	4.776378808136	0.467729966337
H	0.009486190226	3.243622505815	0.606579281318
C	5.032726386045	2.775900482745	-1.766693175993
H	5.570098399368	3.367579334786	-1.019190702162
H	5.520660592846	1.800437734407	-1.828442967345
H	5.176469649872	3.271716970288	-2.732179366704
C	3.783695526014	-1.282998637078	-2.936157575234
H	4.247427481579	-1.946501664731	-3.674711984801
H	2.793306296090	-1.030098194498	-3.310226321040
H	4.391342797893	-0.374683396722	-2.902934589158
C	3.198184339936	-1.106073677442	3.349579531170
H	3.087798599270	-1.767936950399	4.215638907320
H	4.110193599429	-0.521012657164	3.505791167825
H	2.347858427910	-0.427939765022	3.355602478554
C	4.929976311923	-3.135963026697	2.074959358352
H	4.951471128153	-4.077395666204	1.521993276870
H	5.837797529739	-2.581199064965	1.824310829196
H	4.991394300859	-3.390354600671	3.138807125557
C	1.915752727817	2.239995760765	3.282907366576
H	1.615623027946	3.053855191082	3.953015428211
H	1.101869445962	1.511636888882	3.285486486497
H	2.791782027399	1.766758405661	3.731197629851
C	2.568444793504	-3.681422319100	-1.492624427935
H	2.592265519751	-4.023716233758	-2.532800853293
H	2.872181835845	-4.523426533699	-0.865589658906
H	1.532119066184	-3.440800983646	-1.256410415656
C	1.957122882048	-3.458561467163	1.769900970706
H	1.651286054428	-3.695475473385	2.792869846634
H	1.061009351453	-3.141835757109	1.235627177341
H	2.307494298383	-4.383591108160	1.306101842227
C	2.598203370400	4.492054677197	-1.497054114925
H	3.018473614296	4.902789029050	-2.422185849918
H	1.511903262689	4.560158147313	-1.588894250238
H	2.915355020873	5.145695211193	-0.683390416990
C	5.488700658605	-2.913164439884	-1.180826540571
H	6.230273130700	-2.141313753013	-0.954975883620
H	5.603891834079	-3.706993532514	-0.443393644826
H	5.755311008969	-3.337072298549	-2.155066616158
C	-0.435035454158	-2.461243391901	5.158702795370
H	-1.269740541106	-2.058961593276	5.738361539145
H	-0.620086525896	-3.525960750996	4.992164986755
H	0.474605111463	-2.361495970844	5.756299019240
C	0.536250494094	-2.914572090666	-4.880658490148
H	0.503114564018	-3.966999371200	-4.585382428660
H	-0.268030978293	-2.737421791349	-5.599039114475
H	1.490729417461	-2.732208120956	-5.381378140510

E+ZPVE = -4972.786789 au, Free E (298.15 K) = -4972.895845 au.
Job name: TN121bb

Table 5-7. Atomic Coordinates of **5′′$_c$** at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) Level of Theory



5′′$_c$

Atom	X	Y	Z
Si	-0.001789529906	1.316596867587	0.026563551419
Si	-1.908954419203	-0.006953808013	0.173237584884
Si	0.001789529906	-1.316596867587	0.026563551419
Si	1.908954419203	0.006953808013	0.173237584884
C	0.017925076934	2.755035525009	-1.075154734196
C	0.054639261368	3.755681339566	-1.754750689393
C	-0.017925076934	-2.755035525009	-1.075154734196
C	-0.054639261368	-3.755681339566	-1.754750689393
C	-3.128039594438	-0.007903972926	1.668000574397
C	-3.241090306010	-0.018896441985	-1.245956580013
C	3.128039594438	0.007903972926	1.668000574397
C	3.241090306010	0.018896441985	-1.245956580013
Si	2.842273817163	1.341115611133	3.005421714946
Si	3.380014662188	-1.710221175891	2.514729219658
Si	3.550575717255	1.735405589849	-2.077329810781
Si	3.051997760119	-1.278173185921	-2.647352595744
Si	-3.380014662188	1.710221175891	2.514729219658
Si	-2.842273817163	-1.341115611133	3.005421714946
Si	-3.550575717255	-1.735405589849	-2.077329810781
Si	-3.051997760119	1.278173185921	-2.647352595744
C	2.830427191563	3.104330614421	2.348356135326
H	1.981640426279	3.306667371568	1.691074504193
H	3.741738674440	3.401106876652	1.828374650781
H	2.725859804179	3.765180252586	3.216177666044
C	4.271695243003	1.297660521785	4.238538576332
H	4.158779887801	2.121482988826	4.951018767709
H	5.235364191445	1.434394061051	3.737758428567
H	4.329624848653	0.374000139384	4.818449574892
C	1.213112191048	1.194258505176	3.915002277423
H	1.043863533826	2.111953472388	4.487825830925
H	1.143482723929	0.354765803940	4.604061364944
H	0.396892536806	1.102697245633	3.195399981173
C	2.449412228028	-1.946900726614	4.134581792400
H	1.366552172642	-1.899673144095	4.018459405476
H	2.734641043669	-1.244982174833	4.920401582117
H	2.690262196596	-2.951822298227	4.498314109888
C	5.208917912550	-1.943910051643	2.925368951684
H	5.317041452318	-2.863096344382	3.510962805633
H	5.633174235744	-1.128930068722	3.516688942792
H	5.824573088584	-2.062259072114	2.028661623386
C	2.943603421796	-3.226063819247	1.489377973526
H	3.087442243816	-4.105524159398	2.126964987605
H	3.602762182884	-3.347003347741	0.629370004891
H	1.912936422429	-3.255851156923	1.129931766096
C	4.463511690828	0.377911098698	0.933177470954
H	4.517643448594	1.457163688414	0.756671605737
H	5.340344351431	0.132554460561	1.535905075942
C	4.518975534219	-0.338288986324	-0.415959085841
H	4.570902849191	-1.417338294442	-0.231507926749
H	5.438098376580	-0.083967240255	-0.951547611134
C	3.382279544207	3.261149944195	-0.988990691208
H	3.375553094908	4.133947910473	-1.652124409375
H	4.241599492030	3.376940263961	-0.324831152265
H	2.475193016818	3.309270548349	-0.394207999337
C	5.353859550829	1.874603247410	-2.631372143749
H	5.731423626301	1.039646975668	-3.220677386340
H	6.020446660749	2.006949330467	-1.773524071461
H	5.448862602506	2.778213567985	-3.244228504222
C	2.459644901310	2.019073857123	-3.586723960527
H	2.771656950921	1.432465627095	-4.453551122127
H	2.535253137680	3.075015417165	-3.867900291375
H	1.406837803797	1.808932878227	-3.394996290070
C	1.428343543923	-1.161671226634	-3.589457205442
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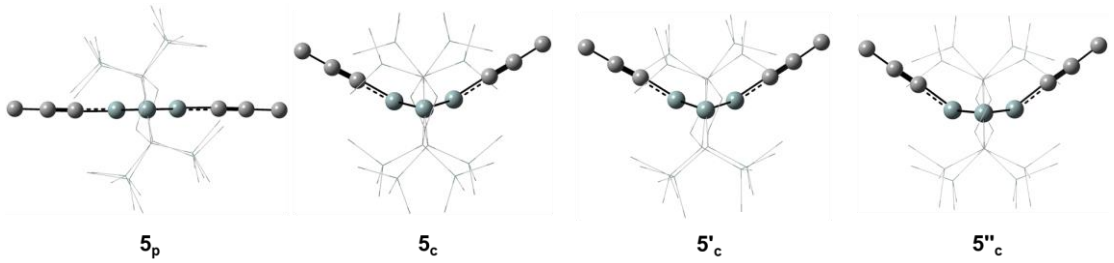
H	1.477628704664	-0.446021238742	-4.411967236340
H	0.595003056651	-0.874034165571	-2.951066056484
C	3.280571637238	-3.040435698348	-2.026853941400
H	3.123586093402	-3.710074197788	-2.880297586336
H	2.574068465730	-3.333688272559	-1.254082486446
H	4.296899835237	-3.221404086224	-1.664588475792
C	4.427134834235	-1.129518448606	-3.936562595928

H	5.423424996063	-1.212854707601	-3.492306029561
H	4.396563817141	-0.214767762449	-4.531492727959
H	4.316505607347	-1.969110131368	-4.632152815028
C	-3.280571637238	3.040435698348	-2.026853941400
H	-2.574068465730	3.333688272559	-1.254082486446
H	-4.296899835237	3.221404086224	-1.664588475792
H	-3.123586093402	3.710074197788	-2.880297586336
C	-1.428343543923	1.161671226634	-3.589457205442
H	-1.181709865742	2.140482198969	-4.012091128983
H	-1.477628704664	0.446021238742	-4.411967236340
H	-0.595003056651	0.874034165571	-2.951066056484
C	-4.427134834235	1.129518448606	-3.936562595928
H	-5.423424996063	1.212854707601	-3.492306029561
H	-4.396563817141	0.214767762449	-4.531492727959
H	-4.316505607347	1.969110131368	-4.632152815028
C	-5.353859550829	-1.874603247410	-2.631372143749
H	-5.448862602506	-2.778213567985	-3.244228504222
H	-5.731423626301	-1.039646975668	-3.220677386340
H	-6.020446660749	-2.006949330467	-1.773524071461
C	-2.459644901310	-2.019073857123	-3.586723960527
H	-2.535253137680	-3.075015417165	-3.867900291375
H	-1.406837803797	-1.808932878227	-3.394996290070
H	-2.771656950921	-1.432465627095	-4.453551122127
C	-3.382279544207	-3.261149944195	-0.988990691208
H	-4.241599492030	-3.376940263961	-0.324831152265
H	-2.475193016818	-3.309270548349	-0.394207999337
H	-3.375553094908	-4.133947910473	-1.652124409375
C	-4.518975534219	0.338288986324	-0.415959085841
H	-4.570902849191	1.417338294442	-0.231507926749
H	-5.438098376580	0.083967240255	-0.951547611134
C	-4.463511690828	-0.377911098698	0.933177470954
H	-4.517643448594	-1.457163688414	0.756671605737
H	-5.340344351431	-0.132554460561	1.535905075942
C	-2.943603421796	3.226063819247	1.489377973526
H	-3.087442243816	4.105524159398	2.126964987605
H	-3.602762182884	3.347003347741	0.629370004891
H	-1.912936422429	3.255851156923	1.129931766096
C	-2.449412228028	1.946900726614	4.134581792400
H	-1.366552172642	1.899673144095	4.018459405476
H	-2.734641043669	1.244982174833	4.920401582117
H	-2.690262196596	2.951822298227	4.498314109888
C	-5.208917912550	1.943910051643	2.925368951684
H	-5.317041452318	2.863096344382	3.510962805633
H	-5.633174235744	1.128930068722	3.516688942792
H	-5.824573088584	2.062259072114	2.028661623386
C	-4.271695243003	-1.297660521785	4.238538576332
H	-4.158779887801	-2.121482988826	4.951018767709
H	-5.235364191445	-1.434394061051	3.737758428567
H	-4.329624848653	-0.374000139384	4.818449574892
C	-2.830427191563	-3.104330614421	2.348356135326
H	-1.981640426279	-3.306667371568	1.691074504193
H	-3.741738674440	-3.401106876652	1.828374650781
H	-2.725859804179	-3.765180252586	3.216177666044
C	-1.213112191048	-1.194258505176	3.915002277423
H	-1.043863533826	-2.111953472388	4.487825830925
H	-1.143482723929	-0.354765803940	4.604061364944
H	-0.396892536806	-1.102697245633	3.195399981173
C	0.099486007009	4.919819410484	-2.621040666250
H	-0.852789674440	5.456074045214	-2.604346748894
H	0.887634266805	5.609912414268	-2.309095512825
H	0.303030031727	4.616078732431	-3.651938140622
C	-0.099486007009	-4.919819410484	-2.621040666250
H	0.852789674440	-5.456074045214	-2.604346748894
H	-0.887634266805	-5.609912414268	-2.309095512825
H	-0.303030031727	-4.616078732431	-3.651938140622

E+ZPVE = -4972.783104 au, Free E (298.15 K) = -4972.888189 au.
Job name: TN124bb



5$_p$ **5**$_c$ **5'**$_c$ **5''**$_c$

Figure 5-32. Molecular structures (side view) of **5**$_p$**,** **5**$_c$, **5′**$_c$, and **5′′**$_c$ optimized at the ωB97XD/6-311G(d)/SCRF(solvent = heptane) level of theory.

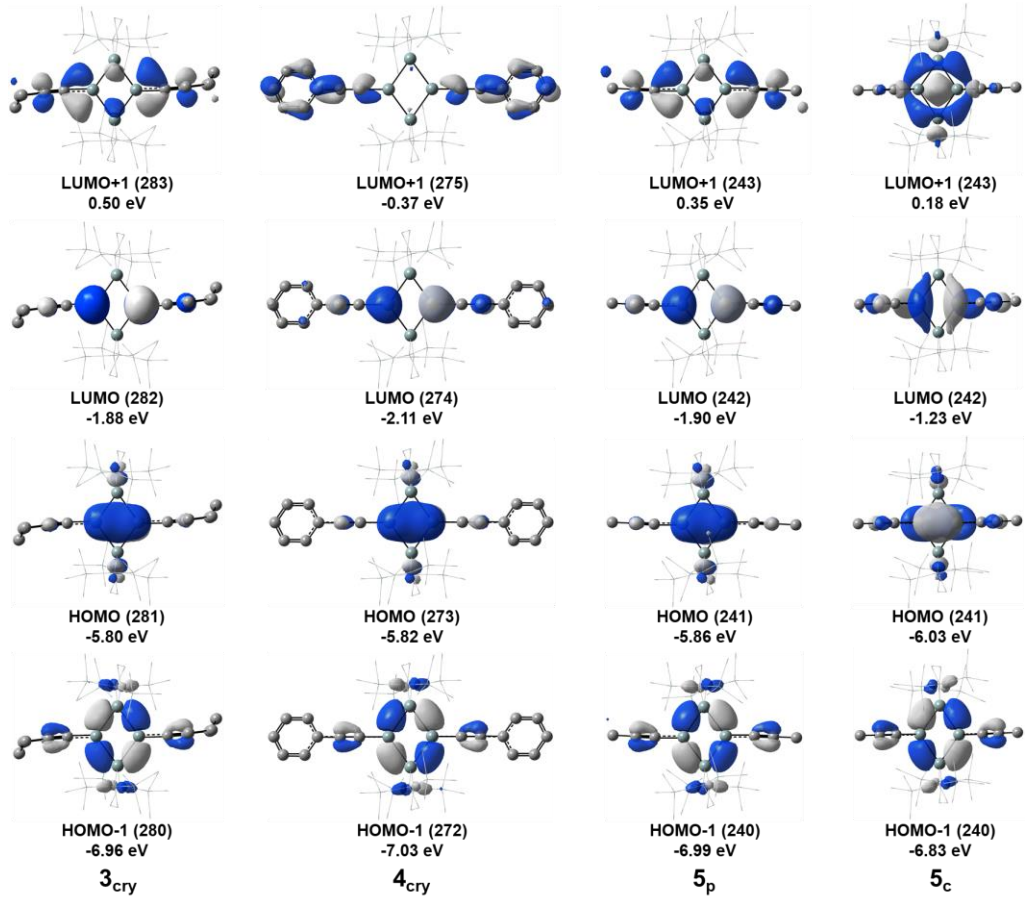


Figure 5-33. Frontier Kohn-Sham orbitals of $\mathbf{3}_{cry}$, $\mathbf{4}_{cry}$, $\mathbf{5}_{p}$, and $\mathbf{5}_{c}$ at the M06-2X/6-311G(d) level of theory (isosurface level: 0.04 e·a.u.$^{-3}$).

Table 5-8. Theoretical Isotropic ^{29}Si Chemical Shifts of $\mathbf{3}_{cry}$, $\mathbf{4}_{cry}$, $\mathbf{5}_{p}$, $\mathbf{5}_{c}$, $\mathbf{5'}_{c}$, and $\mathbf{5''}_{c}$

Compound	$SiMe_3$	Bridge Si	Bridgehead Si	note
$\mathbf{3}_{cry}$[a,b]	7.5 (353.9)[c]	−17.1 (378.5)	137.2 (224.2)	nmrTN120_tn87a2
$\mathbf{4}_{cry}$[a,b]	8.0 (353.4)[c]	−15.9 (377.3)	129.9 (231.5)	nmr_TN100_tn53b_a
$\mathbf{5}_{p}$[a,b]	3.6 (357.8)[c]	−21.3 (382.7)	133.7 (227.7)	nmrTN116db1
$\mathbf{5}_{c}$[a,b]	2.7 (358.7)[c]	−15.3 (376.7)	−25.7 (387.1)	nmrTN117bb1
$\mathbf{5'}_{c}$[a,b]	3.6 (357.8)[c]	−16.8 (378.2)	−29.4 (390.8)	nmrTN121bb1
		−17.5 (378.9)	−44.9 (406.3)	
$\mathbf{5''}_{c}$[a,b]	3.7 (357.7)[c]	18.2 (343.2)	−27.4 (388.8)	nmrTN124bb1

[a]GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [b]The absolute chemical shift is shown in the parentheses. [c]Average values.

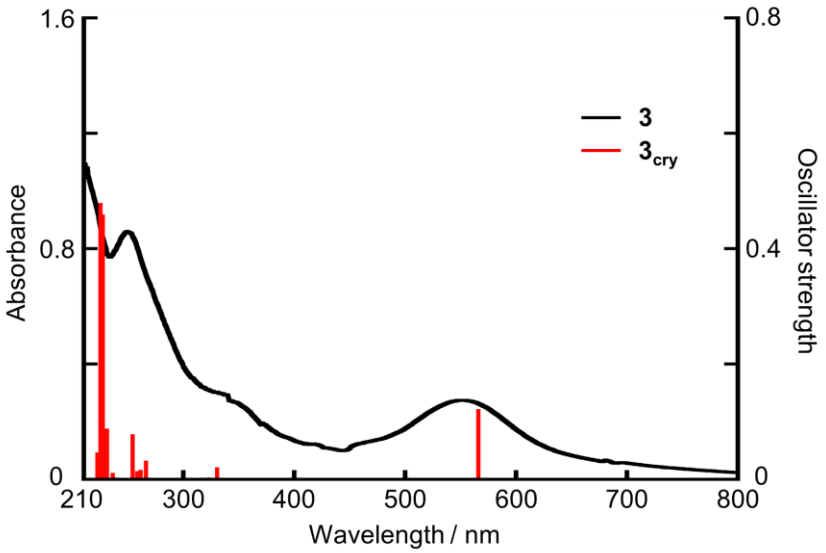


Figure 5-34. Experimental UV-vis absorption spectrum of **3** in a KBr matrix at room temperature (black) and theoretical band positions of $\mathbf{3}_{cry}$ calculated at the TD-M06-2X/6-311G(d) level of theory (red bar). [tdTN120_tn87a2]

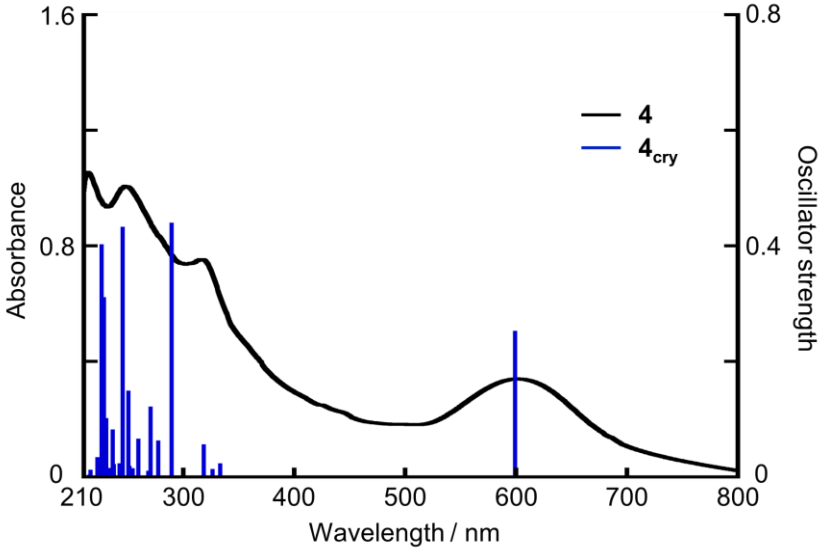


Figure 5-35. Experimental UV-vis absorption spectrum of **4** in a KBr matrix at room temperature (black) and theoretical band positions of $\mathbf{4}_{cry}$ calculated at the TD-M06-2X/6-311G(d) level of theory (blue bar). [td_TN100_tn53b_d]

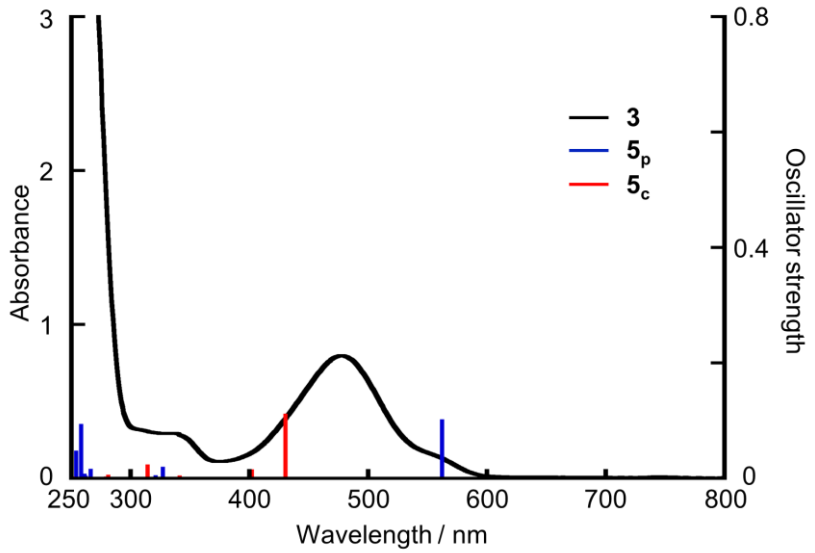


Figure 5-36. Experimental UV-vis absorption spectrum of **3** in 3-methylpentane at 93 K (black) and theoretical band positions of $\mathbf{5_p}$ (blue bar) and $\mathbf{5_c}$ (red bar) calculated at the TD-M06-2X/6-311G(d) level of theory. [tdTN116db1, tdTN117bb1]

Table 5-9. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{3_{cry}}$ (The 281th orbital is highest occupied orbital shown in Figure 5-33) [tdTN120_tn87a2]

Excited State 1: Singlet-A 2.1894 eV 566.29 nm f=0.1218
<S**2>=0.000
281 -> 282 0.70400

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5365.40034799
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.4748 eV 500.98 nm f=0.0000
<S**2>=0.000
280 -> 282 0.69830

Excited State 3: Singlet-A 3.7583 eV 329.90 nm f=0.0211
<S**2>=0.000
272 -> 282 -0.11190
276 -> 282 -0.14545
279 -> 282 0.34366
281 -> 284 0.56640

Excited State 4: Singlet-A 3.8429 eV 322.63 nm f=0.0034
<S**2>=0.000
272 -> 282 -0.10406
279 -> 282 0.51078
281 -> 284 -0.38319
281 -> 286 -0.18874

Excited State 5: Singlet-A 3.8683 eV 320.51 nm f=0.0000
<S**2>=0.000
281 -> 283 0.69629

Excited State 6: Singlet-A 3.9886 eV 310.85 nm f=0.0005
<S**2>=0.000
269 -> 282 -0.11870
272 -> 282 0.15346
274 -> 282 0.16207
276 -> 282 0.56065
277 -> 282 0.13700
279 -> 282 0.19980
281 -> 286 0.14294

Excited State 7: Singlet-A 4.0500 eV 306.13 nm f=0.0000
<S**2>=0.000
281 -> 285 0.70060

Excited State 8: Singlet-A 4.5832 eV 270.52 nm f=0.0000
<S**2>=0.000
278 -> 282 0.69377

Excited State 9: Singlet-A 4.6547 eV 266.36 nm f=0.0325
<S**2>=0.000
274 -> 282 0.22164
276 -> 282 -0.21454
277 -> 282 0.59868
280 -> 283 -0.12008

Excited State 10: Singlet-A 4.7524 eV 260.89 nm f=0.0164
<S**2>=0.000
255 -> 282 0.14380
269 -> 282 0.31318
270 -> 282 0.14869
279 -> 282 0.17967
281 -> 286 0.46183
281 -> 289 0.15284

Excited State 11: Singlet-A 4.7605 eV 260.44 nm f=0.0000
<S**2>=0.000
256 -> 282 -0.16463
257 -> 282 0.34415
269 -> 288 0.11172
273 -> 282 0.43028
275 -> 282 -0.30276

Excited State 12: Singlet-A 4.7677 eV 260.05 nm f=0.0000
<S**2>=0.000
257 -> 282 0.13972
273 -> 282 0.23849
275 -> 282 0.62722

Excited State 13: Singlet-A 4.7722 eV 259.80 nm f=0.0142
<S**2>=0.000
255 -> 282 -0.12009
269 -> 282 -0.26273
270 -> 282 -0.11321
274 -> 282 0.31873
276 -> 282 -0.21253
277 -> 282 -0.28704
281 -> 286 0.31550
281 -> 287 0.12555

Excited State 14: Singlet-A 4.8005 eV 258.27 nm f=0.0142
<S**2>=0.000
255 -> 282 0.11407
269 -> 282 0.23811
270 -> 282 0.10089
274 -> 282 0.52493
277 -> 282 -0.14357
281 -> 286 -0.19927
281 -> 287 -0.13629

Excited State 15: Singlet-A 4.8771 eV 254.21 nm f=0.0782
<S**2>=0.000
269 -> 282 0.14900
280 -> 285 0.20220
281 -> 286 -0.10455
281 -> 287 0.61429

Excited State 16: Singlet-A 5.1165 eV 242.32 nm f=0.0000
<S**2>=0.000
280 -> 284 0.66376
281 -> 288 0.11058

Excited State 17: Singlet-A 5.2006 eV 238.41 nm f=0.0000
<S**2>=0.000
259 -> 282 -0.22107
264 -> 282 0.21226
268 -> 282 -0.29507
271 -> 282 -0.23482
273 -> 282 -0.17298
280 -> 284 -0.11026
281 -> 288 0.35385

Excited State 18: Singlet-A 5.2046 eV 238.22 nm f=0.0033
<S**2>=0.000
270 -> 282 0.17445
272 -> 282 0.58762
276 -> 282 -0.21049
279 -> 282 0.11894
280 -> 283 0.11051

Excited State 19: Singlet-A 5.2604 eV 235.69 nm f=0.0115
<S**2>=0.000
280 -> 285 -0.23388
281 -> 289 -0.26698
281 -> 291 0.55664

Excited State 20: Singlet-A 5.2709 eV 235.23 nm f=0.0000
<S**2>=0.000
256 -> 282 0.12117
257 -> 282 -0.14016
268 -> 282 0.15479
271 -> 282 0.28056
273 -> 282 0.27884
281 -> 288 0.48373

Excited State 21: Singlet-A 5.3194 eV 233.08 nm f=0.0000
<S**2>=0.000
256 -> 282 0.15550
257 -> 282 -0.21130
259 -> 282 -0.16737
264 -> 282 0.29810
266 -> 282 0.17928
268 -> 282 -0.23600
271 -> 282 0.17912
273 -> 282 0.28890
281 -> 288 -0.26773

Excited State 22: Singlet-A 5.3742 eV 230.70 nm f=0.0880
<S**2>=0.000
258 -> 282 -0.32587
260 -> 282 -0.10605
265 -> 282 -0.17302
267 -> 282 0.20476
270 -> 282 0.10968
272 -> 282 -0.16309
274 -> 282 0.13197
280 -> 283 0.42104

Excited State 23: Singlet-A 5.4201 eV 228.75 nm f=0.0000
<S**2>=0.000
256 -> 282 -0.17279
257 -> 282 0.23432
263 -> 282 0.24785
271 -> 282 0.52129
273 -> 282 -0.21217

Excited State 24: Singlet-A 5.4285 eV 228.39 nm f=0.0781
<S**2>=0.000
260 -> 282 -0.13783
262 -> 282 -0.13464
267 -> 282 -0.20803
269 -> 282 -0.19029
270 -> 282 0.52955
272 -> 282 -0.14596
280 -> 283 -0.12165
280 -> 285 0.17297

Excited State 25: Singlet-A 5.4490 eV 227.53 nm f=0.4592
<S**2>=0.000
265 -> 282 -0.12161
267 -> 282 0.12269
270 -> 282 -0.11577
280 -> 285 0.56332
281 -> 287 -0.17080
281 -> 289 -0.11404
281 -> 291 0.18586

Excited State 26: Singlet-A 5.4997 eV 225.44 nm f=0.0000
<S**2>=0.000
280 -> 286 0.62932
280 -> 289 0.19356

Excited State 27: Singlet-A 5.5168 eV 224.74 nm f=0.4792
<S**2>=0.000
258 -> 282 0.26110
265 -> 282 0.29279
267 -> 282 -0.19871
280 -> 283 0.48146
280 -> 285 0.13678

Excited State 28: Singlet-A 5.5678 eV 222.68 nm f=0.0000
<S**2>=0.000
259 -> 282 -0.19050
261 -> 282 0.18507
263 -> 282 0.14678
264 -> 282 0.37656
266 -> 282 -0.10314
268 -> 282 0.48430

Excited State 29: Singlet-A 5.5727 eV 222.48 nm f=0.0465
<S**2>=0.000
258 -> 282 -0.35256
265 -> 282 0.56120
267 -> 282 0.12014
270 -> 282 -0.14496

Excited State 30: Singlet-A 5.7273 eV 216.48 nm f=0.0000
<S**2>=0.000
261 -> 282 0.11943
263 -> 282 0.47840
264 -> 282 -0.29406
266 -> 282 0.33956
271 -> 282 -0.12746

Excited State 31: Singlet-A 5.7308 eV 216.35 nm f=0.0000
<S**2>=0.000
256 -> 282 0.11080
259 -> 282 0.20557
261 -> 282 0.52110
263 -> 282 0.12175
266 -> 282 -0.26795
268 -> 282 -0.23503

Excited State 32: Singlet-A 5.7361 eV 216.15 nm f=0.0014
<S**2>=0.000
258 -> 282 0.33816
262 -> 282 0.19579
265 -> 282 0.16902
267 -> 282 0.48797
270 -> 282 0.20504

Excited State 33: Singlet-A 5.8225 eV 212.94 nm f=0.0000
<S**2>=0.000
257 -> 282 0.12520
259 -> 282 0.12420
261 -> 282 0.22432
263 -> 282 -0.31923
264 -> 282 0.10886
266 -> 282 0.43929
280 -> 287 -0.25035

Excited State 34: Singlet-A 5.8448 eV 212.13 nm f=0.0027
<S**2>=0.000
254 -> 282 0.10154
260 -> 282 0.20497
262 -> 282 0.60464
267 -> 282 -0.23013
269 -> 282 -0.12183

Excited State 35: Singlet-A 5.8712 eV 211.17 nm f=0.0000
<S**2>=0.000
261 -> 282 0.19107
266 -> 282 0.20316
280 -> 287 0.57925

280 -> 289 0.15781

Excited State 36: Singlet-A 5.8878 eV 210.58 nm f=0.0000
<S**2>=0.000
281 -> 290 0.40951
281 -> 292 -0.35153
281 -> 293 0.13856
281 -> 298 0.19211
281 -> 301 0.23320
281 -> 302 0.17527

Excited State 37: Singlet-A 5.9040 eV 210.00 nm f=0.0269
<S**2>=0.000
260 -> 282 0.20922
269 -> 282 -0.13841
281 -> 289 0.34130
281 -> 291 0.23239
281 -> 294 -0.21222
281 -> 296 -0.28585
281 -> 308 -0.11670
281 -> 312 -0.14696

Excited State 38: Singlet-A 5.9217 eV 209.37 nm f=0.0055
<S**2>=0.000
260 -> 282 0.56885
262 -> 282 -0.17938
267 -> 282 0.16987
270 -> 282 0.11938
281 -> 289 -0.16570

Excited State 39: Singlet-A 5.9401 eV 208.73 nm f=0.0000
<S**2>=0.000
259 -> 282 0.52188
261 -> 282 -0.23785
263 -> 282 0.19947
264 -> 282 0.29277
271 -> 282 -0.14241

Excited State 40: Singlet-A 5.9778 eV 207.41 nm f=0.0148
<S**2>=0.000
281 -> 286 -0.22638
281 -> 289 0.41552
281 -> 291 0.19039
281 -> 294 0.20051
281 -> 296 0.25911
281 -> 297 -0.13955
281 -> 312 0.13744

Excited State 41: Singlet-A 6.0316 eV 205.56 nm f=0.0071
<S**2>=0.000
254 -> 282 0.30898
255 -> 282 -0.29883
269 -> 282 0.31892
280 -> 288 -0.25077
281 -> 294 -0.11275
281 -> 296 -0.12536

Excited State 42: Singlet-A 6.0476 eV 205.01 nm f=0.0000
<S**2>=0.000
281 -> 290 0.49939
281 -> 292 0.30250
281 -> 293 -0.29032
281 -> 301 -0.11985

Excited State 43: Singlet-A 6.1234 eV 202.48 nm f=0.0000
<S**2>=0.000
256 -> 282 0.57212
257 -> 282 0.36532
261 -> 282 -0.11366

Excited State 44: Singlet-A 6.1365 eV 202.04 nm f=0.0134
<S**2>=0.000
254 -> 282 0.54152
255 -> 282 0.24840
260 -> 282 -0.15662
272 -> 282 -0.15633
279 -> 284 -0.10229
280 -> 288 0.19146

Excited State 45: Singlet-A 6.1659 eV 201.08 nm f=0.0025
<S**2>=0.000
255 -> 282 0.45960
280 -> 288 -0.43761

Excited State 46: Singlet-A 6.1921 eV 200.23 nm f=0.0000
<S**2>=0.000
281 -> 292 0.40174
281 -> 293 0.47295
281 -> 298 0.21848

Excited State 47: Singlet-A 6.2427 eV 198.61 nm f=0.1251
<S**2>=0.000
272 -> 284 -0.11497
274 -> 284 -0.10660
276 -> 284 -0.29830
279 -> 284 0.54962

Excited State 48: Singlet-A 6.2710 eV 197.71 nm f=0.0000
<S**2>=0.000
256 -> 282 -0.10329
257 -> 282 0.18860
258 -> 283 0.31777
259 -> 291 -0.12378
264 -> 291 0.11510
272 -> 283 -0.15035
274 -> 283 0.14571
276 -> 283 -0.14234
277 -> 283 0.15638
279 -> 283 0.10981
281 -> 298 0.10463

Excited State 49: Singlet-A 6.3279 eV 195.93 nm f=0.0000
<S**2>=0.000
253 -> 282 -0.13453
272 -> 283 -0.15667
274 -> 283 -0.15691
276 -> 283 -0.30566
279 -> 283 0.46880
280 -> 286 0.11150
280 -> 291 0.12557

Excited State 50: Singlet-A 6.3397 eV 195.57 nm f=0.0000
<S**2>=0.000
253 -> 282 0.47822
276 -> 285 0.17198
279 -> 285 0.42721
280 -> 291 0.10679

Excited State 51: Singlet-A 6.3483 eV 195.30 nm f=0.0052
<S**2>=0.000
252 -> 282 0.68416

Excited State 52: Singlet-A 6.3488 eV 195.29 nm f=0.0000
<S**2>=0.000
253 -> 282 0.45835
258 -> 283 -0.10717
276 -> 285 -0.17048
279 -> 283 0.12927
279 -> 285 -0.38768
281 -> 292 0.11576

Excited State 53: Singlet-A 6.3696 eV 194.65 nm f=0.0090
<S**2>=0.000
255 -> 282 0.11659
258 -> 291 -0.13504
259 -> 283 0.20693
264 -> 283 -0.19193
268 -> 283 0.16221
278 -> 285 0.13284
280 -> 288 0.31499
281 -> 295 0.14857
281 -> 297 0.10067
281 -> 306 0.18517

Excited State 54: Singlet-A 6.4165 eV 193.23 nm f=0.0000
<S**2>=0.000
278 -> 284 -0.11736
281 -> 290 -0.14307
281 -> 292 0.15494
281 -> 293 -0.35959
281 -> 298 0.45208
281 -> 301 0.14164
281 -> 302 0.14926
281 -> 303 -0.11872

Excited State 55: Singlet-A 6.4448 eV 192.38 nm f=0.6027
<S**2>=0.000
276 -> 284 0.48132
277 -> 284 0.17457
279 -> 284 0.29965
281 -> 294 0.22084

Excited State 56: Singlet-A 6.4861 eV 191.15 nm f=0.1196
<S**2>=0.000

276 -> 284 -0.16703
277 -> 284 -0.10127
279 -> 284 -0.10664
281 -> 294 0.45652
281 -> 295 0.38594
281 -> 297 0.12275
281 -> 312 -0.10000

Excited State 57: Singlet-A 6.5251 eV 190.01 nm f=0.0000
<S**2>=0.000
251 -> 282 -0.18996
276 -> 283 0.20785
276 -> 285 -0.33431
280 -> 289 -0.18940
280 -> 291 0.40090

Excited State 58: Singlet-A 6.5429 eV 189.50 nm f=0.0000
<S**2>=0.000
241 -> 282 -0.12968
249 -> 282 0.11904
251 -> 282 0.62977
280 -> 291 0.10763

Excited State 59: Singlet-A 6.5593 eV 189.02 nm f=0.0012
<S**2>=0.000
278 -> 285 0.11749
281 -> 294 -0.29651
281 -> 295 0.31558
281 -> 296 0.41927
281 -> 305 0.13950

Excited State 60: Singlet-A 6.6176 eV 187.36 nm f=0.0000
<S**2>=0.000
275 -> 284 0.11561
276 -> 283 -0.12246
276 -> 285 -0.14926
278 -> 284 0.56146
281 -> 298 0.18486

Excited State 61: Singlet-A 6.6351 eV 186.86 nm f=0.0162
<S**2>=0.000
274 -> 284 -0.12304
276 -> 284 -0.11128
277 -> 284 0.24624
278 -> 285 0.31532
281 -> 295 -0.28166
281 -> 297 0.31211
281 -> 306 0.12596

Excited State 62: Singlet-A 6.6603 eV 186.15 nm f=0.0001
<S**2>=0.000
275 -> 284 0.14674
276 -> 283 0.15403
276 -> 285 0.28218
278 -> 284 0.17577
279 -> 283 0.15394
281 -> 300 0.28868
281 -> 301 0.20141
281 -> 302 0.20002
281 -> 304 0.16239
281 -> 311 0.10881

Excited State 63: Singlet-A 6.6607 eV 186.14 nm f=0.0311
<S**2>=0.000
274 -> 284 -0.11544
277 -> 284 0.37873
278 -> 285 0.10598
281 -> 295 0.21505
281 -> 296 -0.22102
281 -> 297 -0.37123
281 -> 305 -0.10152
281 -> 308 0.12553

Excited State 64: Singlet-A 6.6885 eV 185.37 nm f=0.0073
<S**2>=0.000
276 -> 284 -0.11548
277 -> 284 0.36359
278 -> 283 0.16130
278 -> 285 -0.34302
281 -> 296 0.12392
281 -> 297 0.23002
281 -> 306 -0.15532

Table 5-10. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{4}_{\mathbf{cry}}$ (The 273th orbital is highest occupied orbital shown in Figure 5-33) [td_TN100_tn53b_d]

Excited State 1: Singlet-A 2.0683 eV 599.46 nm f=0.2531
<S**2>=0.000
273 -> 274 0.70253
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5355.85581669
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.4338 eV 509.42 nm f=0.0000
<S**2>=0.000
272 -> 274 0.69128

Excited State 3: Singlet-A 3.5927 eV 345.10 nm f=0.0000
<S**2>=0.000
273 -> 275 0.54687
273 -> 277 0.39382
273 -> 280 -0.14822

Excited State 4: Singlet-A 3.7244 eV 332.90 nm f=0.0235
<S**2>=0.000
260 -> 274 0.10504
265 -> 274 -0.11439
269 -> 274 -0.37159
273 -> 276 0.15090
273 -> 278 0.52565

Excited State 5: Singlet-A 3.8058 eV 325.78 nm f=0.0139
<S**2>=0.000
269 -> 274 0.46444
271 -> 274 0.17930
273 -> 278 0.39781
273 -> 282 -0.16517

Excited State 6: Singlet-A 3.8962 eV 318.22 nm f=0.0566
<S**2>=0.000
254 -> 274 -0.11254
260 -> 274 -0.12464
265 -> 274 0.40284
267 -> 274 -0.30580
271 -> 274 -0.34001
272 -> 275 -0.10428
273 -> 278 0.12889
273 -> 282 -0.12747

Excited State 7: Singlet-A 4.0407 eV 306.84 nm f=0.0000
<S**2>=0.000
273 -> 275 -0.16230
273 -> 277 0.29352
273 -> 280 -0.16112
273 -> 281 0.59153

Excited State 8: Singlet-A 4.2487 eV 291.81 nm f=0.0000
<S**2>=0.000
273 -> 275 -0.38431
273 -> 277 0.41740
273 -> 280 -0.12836
273 -> 281 -0.35826

Excited State 9: Singlet-A 4.2873 eV 289.19 nm f=0.4400
<S**2>=0.000
265 -> 274 0.24723
267 -> 274 -0.24980
269 -> 274 -0.20276
271 -> 274 0.53926

Excited State 10: Singlet-A 4.3311 eV 286.26 nm f=0.0000
<S**2>=0.000
240 -> 274 0.10632
270 -> 274 0.64426

Excited State 11: Singlet-A 4.4757 eV 277.02 nm f=0.0634
<S**2>=0.000
244 -> 274 0.10564
264 -> 274 -0.14064
265 -> 274 0.13539

272 -> 275 0.11886
273 -> 276 0.55163
273 -> 278 -0.11255
273 -> 283 0.13621
273 -> 284 -0.14103

Excited State 12: Singlet-A 4.4769 eV 276.94 nm f=0.0000
<S**2>=0.000
268 -> 274 0.68956

Excited State 13: Singlet-A 4.5948 eV 269.83 nm f=0.1220
<S**2>=0.000
244 -> 274 0.14681
253 -> 274 0.15208
254 -> 274 0.12377
264 -> 274 -0.26872
265 -> 274 0.24810
267 -> 274 0.30395
269 -> 274 -0.12778
272 -> 275 0.25537
273 -> 276 -0.23240
273 -> 282 -0.12188

Excited State 14: Singlet-A 4.6313 eV 267.71 nm f=0.0106
<S**2>=0.000
244 -> 274 -0.10742
253 -> 274 -0.11278
254 -> 274 -0.12052
264 -> 274 0.16503
265 -> 274 0.33405
267 -> 274 0.46356
272 -> 275 -0.19983
273 -> 276 0.15259

Excited State 15: Singlet-A 4.6386 eV 267.29 nm f=0.0000
<S**2>=0.000
261 -> 274 0.16217
266 -> 274 0.65404

Excited State 16: Singlet-A 4.7365 eV 261.76 nm f=0.0000
<S**2>=0.000
244 -> 275 -0.10417
246 -> 274 -0.23948
247 -> 274 -0.25549
253 -> 275 -0.12415
261 -> 274 0.39774
266 -> 274 -0.24187
270 -> 274 0.14825
272 -> 276 -0.14520

Excited State 17: Singlet-A 4.7933 eV 258.66 nm f=0.0664
<S**2>=0.000
264 -> 274 -0.22088
265 -> 274 0.10323
269 -> 274 0.18215
273 -> 278 0.11476
273 -> 282 0.56737
273 -> 285 -0.10833

Excited State 18: Singlet-A 4.8816 eV 253.98 nm f=0.0153
<S**2>=0.000
244 -> 274 0.12292
253 -> 274 0.14658
254 -> 274 0.10206
264 -> 274 0.53631
265 -> 274 0.13823
272 -> 275 0.22937
273 -> 282 0.17956

Excited State 19: Singlet-A 4.9323 eV 251.37 nm f=0.0192
<S**2>=0.000
262 -> 274 0.36958
262 -> 276 0.13036
263 -> 275 0.19007
270 -> 280 -0.14392
271 -> 279 -0.13658
273 -> 279 0.40983
273 -> 283 0.23572

Excited State 20: Singlet-A 4.9356 eV 251.20 nm f=0.0000
<S**2>=0.000
262 -> 275 0.21034
263 -> 274 0.40911
263 -> 276 0.14436
270 -> 279 -0.17070
271 -> 280 -0.14071
273 -> 277 0.15536
273 -> 280 0.40836

Excited State 21: Singlet-A 4.9528 eV 250.33 nm f=0.1494
<S**2>=0.000
253 -> 274 -0.10538
262 -> 274 -0.17485
272 -> 275 0.14065
272 -> 281 -0.22063
273 -> 279 -0.15687
273 -> 283 0.51844
273 -> 284 0.11692

Excited State 22: Singlet-A 5.0674 eV 244.67 nm f=0.4331
<S**2>=0.000
244 -> 274 -0.12720
253 -> 274 -0.22746
254 -> 274 -0.14857
260 -> 274 -0.19832
272 -> 275 0.43787
272 -> 277 0.19371
273 -> 276 0.13478
273 -> 283 -0.22155

Excited State 23: Singlet-A 5.0972 eV 243.24 nm f=0.0000
<S**2>=0.000
272 -> 276 0.19025
272 -> 278 0.64463

Excited State 24: Singlet-A 5.1128 eV 242.50 nm f=0.0000
<S**2>=0.000
243 -> 274 -0.11701
246 -> 274 0.21341
247 -> 274 0.10981
257 -> 274 0.13996
259 -> 274 0.23793
261 -> 274 0.51016
272 -> 276 0.18470

Excited State 25: Singlet-A 5.1273 eV 241.81 nm f=0.0237
<S**2>=0.000
245 -> 274 -0.15853
258 -> 274 0.28933
260 -> 274 0.51652
265 -> 274 0.12933
269 -> 274 0.14885
272 -> 275 0.15755
273 -> 282 -0.13633

Excited State 26: Singlet-A 5.2284 eV 237.13 nm f=0.0000
<S**2>=0.000
259 -> 274 -0.13017
262 -> 275 -0.11177
263 -> 274 -0.43140
273 -> 277 0.18603
273 -> 280 0.48043

Excited State 27: Singlet-A 5.2293 eV 237.09 nm f=0.0222
<S**2>=0.000
262 -> 274 -0.43459
263 -> 275 -0.11707
273 -> 279 0.52004

Excited State 28: Singlet-A 5.2635 eV 235.55 nm f=0.0821
<S**2>=0.000
253 -> 274 0.11331
270 -> 277 0.12019
273 -> 276 0.17137
273 -> 283 -0.11467
273 -> 284 0.58527

Excited State 29: Singlet-A 5.2682 eV 235.35 nm f=0.0000
<S**2>=0.000
246 -> 274 -0.12746
249 -> 274 0.12082
250 -> 274 0.12985
259 -> 274 0.58375
261 -> 274 -0.12718
272 -> 276 -0.11797
273 -> 280 0.10418

Excited State 30: Singlet-A 5.3128 eV 233.37 nm f=0.0157
<S**2>=0.000
248 -> 274 0.12693
251 -> 274 0.12770
254 -> 274 0.26577
256 -> 274 0.12034
258 -> 274 0.51968

260 -> 274 -0.29434

Excited State 31: Singlet-A 5.3854 eV 230.22 nm f=0.1019
<S**2>=0.000
251 -> 274 0.17423
253 -> 274 -0.18172
254 -> 274 0.40137
256 -> 274 -0.35521
258 -> 274 -0.12376
272 -> 277 0.25605
272 -> 280 -0.11000
272 -> 281 0.13620

Excited State 32: Singlet-A 5.4184 eV 228.82 nm f=0.0000
<S**2>=0.000
249 -> 274 -0.12238
250 -> 274 0.17424
255 -> 274 -0.37302
257 -> 274 0.52913

Excited State 33: Singlet-A 5.4380 eV 227.99 nm f=0.3114
<S**2>=0.000
253 -> 274 0.24587
256 -> 274 0.32589
272 -> 277 0.41967
272 -> 280 -0.17266
272 -> 281 0.23404
273 -> 283 0.10571

Excited State 34: Singlet-A 5.4938 eV 225.68 nm f=0.0000
<S**2>=0.000
246 -> 274 -0.11081
247 -> 274 -0.11556
250 -> 274 0.13920
271 -> 275 0.11689
272 -> 276 0.29163
272 -> 278 -0.15754
272 -> 282 0.48426
272 -> 285 -0.11498

Excited State 35: Singlet-A 5.4973 eV 225.54 nm f=0.4028
<S**2>=0.000
254 -> 274 -0.12611
256 -> 274 -0.11193
272 -> 277 -0.21578
272 -> 281 0.56595
273 -> 283 0.16371
273 -> 284 0.13853

Excited State 36: Singlet-A 5.5617 eV 222.93 nm f=0.0000
<S**2>=0.000
249 -> 274 -0.27670
250 -> 274 0.49449
252 -> 274 -0.17830
255 -> 274 -0.13013
257 -> 274 -0.29882

Excited State 37: Singlet-A 5.5740 eV 222.43 nm f=0.0000
<S**2>=0.000
250 -> 274 0.34925
252 -> 274 0.38873
255 -> 274 0.40334
257 -> 274 0.14675
259 -> 274 -0.14025

Excited State 38: Singlet-A 5.5806 eV 222.17 nm f=0.0345
<S**2>=0.000
248 -> 274 -0.15605
251 -> 274 0.29035
253 -> 274 -0.15843
254 -> 274 0.21893
256 -> 274 0.44610
258 -> 274 -0.20065
260 -> 274 0.14024
272 -> 277 -0.16720

Excited State 39: Singlet-A 5.6223 eV 220.52 nm f=0.0000
<S**2>=0.000
270 -> 276 -0.17862
270 -> 284 0.12113
271 -> 275 -0.32318
271 -> 277 -0.22009
272 -> 276 -0.23978
272 -> 282 0.33186

Excited State 40: Singlet-A 5.6594 eV 219.08 nm f=0.0000
<S**2>=0.000
249 -> 274 0.18843
252 -> 274 0.47396
255 -> 274 -0.38436
257 -> 274 -0.22993
259 -> 274 0.10188

Excited State 41: Singlet-A 5.6771 eV 218.39 nm f=0.0006
<S**2>=0.000
244 -> 274 -0.10403
248 -> 274 0.10779
251 -> 274 0.54505
253 -> 274 0.31186
254 -> 274 -0.16582
256 -> 274 -0.13613

Excited State 42: Singlet-A 5.7390 eV 216.04 nm f=0.0124
<S**2>=0.000
248 -> 274 -0.12415
251 -> 274 -0.16540
253 -> 274 0.12666
254 -> 274 0.15114
270 -> 275 0.32965
270 -> 277 0.24024
271 -> 276 0.18350
271 -> 284 -0.14148
272 -> 277 -0.16006
273 -> 284 -0.17410

Excited State 43: Singlet-A 5.7409 eV 215.97 nm f=0.0000
<S**2>=0.000
246 -> 274 -0.10380
249 -> 274 0.42952
250 -> 274 0.14144
252 -> 274 -0.25499
271 -> 277 -0.13252
272 -> 276 0.24702
272 -> 282 -0.17311
272 -> 283 0.10966

Excited State 44: Singlet-A 5.7632 eV 215.13 nm f=0.0040
<S**2>=0.000
248 -> 274 0.62640
253 -> 274 -0.16431
258 -> 274 -0.15993

Excited State 45: Singlet-A 5.8018 eV 213.70 nm f=0.0000
<S**2>=0.000
246 -> 274 0.21220
247 -> 274 0.24676
249 -> 274 0.38089
250 -> 274 0.16967
252 -> 274 -0.10737
271 -> 275 0.11154
271 -> 277 0.12008
272 -> 276 -0.24832
272 -> 282 0.12781

Excited State 46: Singlet-A 5.8960 eV 210.29 nm f=0.0059
<S**2>=0.000
262 -> 274 0.29265
262 -> 275 -0.12286
262 -> 276 -0.19634
263 -> 274 0.17447
263 -> 275 -0.21203
263 -> 276 -0.11716
270 -> 279 0.12934
270 -> 280 0.20690
271 -> 279 0.22638
271 -> 280 0.12160
272 -> 279 0.11044
272 -> 280 0.16906
273 -> 279 0.12644

Excited State 47: Singlet-A 5.8961 eV 210.28 nm f=0.0021
<S**2>=0.000
262 -> 274 -0.17421
262 -> 275 -0.21076
262 -> 276 0.11684
263 -> 274 0.29297
263 -> 275 0.12368
263 -> 276 -0.19668
270 -> 279 0.21856
270 -> 280 -0.12237
271 -> 279 -0.13292
271 -> 280 0.20728
272 -> 279 0.18683
272 -> 280 -0.10009

273 -> 280 0.11795

Excited State 48: Singlet-A 5.9102 eV 209.78 nm f=0.0000
<S**2>=0.000
269 -> 275 -0.20496
272 -> 276 -0.10083
272 -> 283 0.55473
272 -> 284 0.12467:

Table 5-11. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{5_p}$ (The 241th orbital is highest occupied orbital shown in Figure 5-33) [tdTN116db1]

Excited State 1: Singlet-AU 2.2067 eV 561.84 nm f=0.1023
<S**2>=0.000
241 -> 242 0.70320
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4973.38334234
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-AG 2.4947 eV 496.98 nm f=0.0000
<S**2>=0.000
240 -> 242 0.69761

Excited State 3: Singlet-AU 3.7962 eV 326.60 nm f=0.0203
<S**2>=0.000
232 -> 242 -0.11554
239 -> 242 0.40747
241 -> 244 0.53048

Excited State 4: Singlet-AG 3.8037 eV 325.96 nm f=0.0000
<S**2>=0.000
241 -> 243 0.69593

Excited State 5: Singlet-AU 3.8590 eV 321.29 nm f=0.0053
<S**2>=0.000
239 -> 242 0.47933
241 -> 244 -0.44044
241 -> 246 -0.13289
241 -> 250 0.10706

Excited State 6: Singlet-AU 4.0402 eV 306.88 nm f=0.0013
<S**2>=0.000
231 -> 242 0.11222
232 -> 242 -0.16820
234 -> 242 -0.20897
235 -> 242 0.56404
237 -> 242 0.15898
239 -> 242 -0.12028
241 -> 246 -0.10514

Excited State 7: Singlet-AG 4.1716 eV 297.21 nm f=0.0000
<S**2>=0.000
241 -> 245 0.69945

Excited State 8: Singlet-AG 4.5873 eV 270.28 nm f=0.0000
<S**2>=0.000
236 -> 242 0.21117
238 -> 242 0.66342

Excited State 9: Singlet-AU 4.6594 eV 266.09 nm f=0.0164
<S**2>=0.000
234 -> 242 -0.30170
235 -> 242 -0.26762
237 -> 242 0.53884
240 -> 243 -0.12741

Excited State 10: Singlet-AG 4.7251 eV 262.40 nm f=0.0000
<S**2>=0.000
217 -> 242 0.24737
230 -> 242 0.10699
233 -> 242 -0.30194
236 -> 242 0.48650
238 -> 242 -0.18233

Excited State 11: Singlet-AU 4.7350 eV 261.84 nm f=0.0044
<S**2>=0.000
214 -> 242 -0.14281
215 -> 242 0.12641
231 -> 242 0.49660
232 -> 242 -0.10758
237 -> 242 -0.12469
239 -> 242 0.10400
240 -> 248 0.10915
241 -> 247 -0.23882

Excited State 12: Singlet-AG 4.7352 eV 261.83 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.25453
223 -> 242 0.11513
230 -> 242 -0.11841
231 -> 248 0.10068
233 -> 242 0.35785
236 -> 242 0.45293
238 -> 242 -0.12637

Excited State 13: Singlet-AU 4.7500 eV 261.02 nm f=0.0082
<S**2>=0.000
234 -> 242 0.53368
235 -> 242 0.10919
237 -> 242 0.39784
240 -> 243 0.11637

Excited State 14: Singlet-AU 4.8080 eV 257.87 nm f=0.0943
<S**2>=0.000
231 -> 242 0.17320
234 -> 242 -0.11134
240 -> 245 -0.13426
241 -> 246 0.35087
241 -> 247 0.48987
241 -> 250 -0.15387

Excited State 15: Singlet-AU 4.8747 eV 254.34 nm f=0.0481
<S**2>=0.000
231 -> 242 -0.13400
235 -> 242 0.14767
239 -> 242 0.13217
241 -> 246 0.44400
241 -> 247 -0.37809
241 -> 250 -0.19876

Excited State 16: Singlet-AG 5.1141 eV 242.43 nm f=0.0000
<S**2>=0.000
228 -> 242 0.16061
240 -> 244 0.36013
240 -> 247 -0.10339
241 -> 248 0.49761
241 -> 249 -0.12182

Excited State 17: Singlet-AG 5.1658 eV 240.01 nm f=0.0000
<S**2>=0.000
240 -> 244 0.57666
241 -> 248 -0.31451

Excited State 18: Singlet-AU 5.2126 eV 237.85 nm f=0.0122
<S**2>=0.000
231 -> 242 0.11669
240 -> 245 0.15999
241 -> 250 -0.25697
241 -> 251 0.58118

Excited State 19: Singlet-AG 5.2389 eV 236.66 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.12481
218 -> 242 0.15327
223 -> 242 0.12710
227 -> 242 0.18246
228 -> 242 0.37490
230 -> 242 -0.29461
233 -> 242 -0.22153
241 -> 248 -0.28931

Excited State 20: Singlet-AU 5.2443 eV 236.41 nm f=0.0185
<S**2>=0.000
215 -> 242 0.11509
229 -> 242 0.19343
231 -> 242 0.10580
232 -> 242 0.51726
235 -> 242 0.18701
239 -> 242 0.12706
240 -> 243 -0.24190
241 -> 246 -0.10139

Excited State 21: Singlet-AG 5.3108 eV 233.46 nm f=0.0000
<S**2>=0.000

216 -> 242 0.13891
217 -> 242 0.24133
218 -> 242 0.13602
225 -> 242 0.12937
227 -> 242 0.22910
228 -> 242 0.25647
230 -> 242 0.11278
233 -> 242 0.45019

Excited State 22: Singlet-AU 5.3218 eV 232.97 nm f=0.1734
<S**2>=0.000
220 -> 242 0.20634
222 -> 242 -0.10460
224 -> 242 0.19561
232 -> 242 0.29104
234 -> 242 -0.17225
240 -> 243 0.47610

Excited State 23: Singlet-AU 5.4813 eV 226.19 nm f=0.2998
<S**2>=0.000
219 -> 242 -0.11721
220 -> 242 -0.35847
224 -> 242 -0.22192
229 -> 242 0.35863
240 -> 243 0.36568

Excited State 24: Singlet-AU 5.5035 eV 225.28 nm f=0.5221
<S**2>=0.000
240 -> 245 0.64322
241 -> 247 0.15419
241 -> 251 -0.13459

Excited State 25: Singlet-AG 5.5684 eV 222.66 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.12905
223 -> 242 0.28303
228 -> 242 0.20273
230 -> 242 0.52207
240 -> 246 0.20599
240 -> 250 -0.11135

Excited State 26: Singlet-AU 5.5741 eV 222.43 nm f=0.0369
<S**2>=0.000
219 -> 242 0.11661
222 -> 242 -0.20625
224 -> 242 0.30211
226 -> 242 -0.13857
229 -> 242 0.50989
232 -> 242 -0.16862
240 -> 243 -0.11296

Excited State 27: Singlet-AG 5.5827 eV 222.09 nm f=0.0000
<S**2>=0.000
223 -> 242 -0.11117
228 -> 242 -0.11658
230 -> 242 -0.18230
240 -> 246 0.52403
240 -> 250 -0.28277
240 -> 251 -0.13312

Excited State 28: Singlet-AG 5.6516 eV 219.38 nm f=0.0000
<S**2>=0.000
218 -> 242 0.12562
223 -> 242 0.15149
225 -> 242 -0.12386
227 -> 242 0.53547
228 -> 242 -0.34560

Excited State 29: Singlet-AU 5.7248 eV 216.57 nm f=0.0019
<S**2>=0.000
219 -> 242 -0.15276
220 -> 242 -0.21450
222 -> 242 -0.14579
224 -> 242 0.37032
226 -> 242 0.50138

Excited State 30: Singlet-AG 5.7835 eV 214.38 nm f=0.0000
<S**2>=0.000
221 -> 242 0.16732
240 -> 247 0.57145
240 -> 251 -0.15427
241 -> 248 0.12104
241 -> 249 0.23329

Excited State 31: Singlet-AU 5.8061 eV 213.54 nm f=0.0031
<S**2>=0.000
241 -> 246 0.33719
241 -> 250 0.54929
241 -> 251 0.22086

Excited State 32: Singlet-AG 5.8165 eV 213.16 nm f=0.0000
<S**2>=0.000
240 -> 247 -0.25665
241 -> 248 0.12887
241 -> 249 0.58937
241 -> 252 -0.13999

Excited State 33: Singlet-AG 5.8716 eV 211.16 nm f=0.0000
<S**2>=0.000
216 -> 242 -0.14516
218 -> 242 0.17381
221 -> 242 0.50039
225 -> 242 0.33833
228 -> 242 -0.19830
240 -> 247 -0.11927

Excited State 34: Singlet-AG 5.8916 eV 210.44 nm f=0.0000
<S**2>=0.000
216 -> 242 0.11244
217 -> 242 0.13257
218 -> 242 0.12304
221 -> 242 -0.21444
223 -> 242 0.48129
225 -> 242 0.30097
227 -> 242 -0.16932
228 -> 242 -0.14451
230 -> 242 -0.12343

Excited State 35: Singlet-AU 5.9072 eV 209.89 nm f=0.0024
<S**2>=0.000
219 -> 242 0.29298
220 -> 242 0.26152
222 -> 242 0.18141
224 -> 242 -0.16098
226 -> 242 0.40241
229 -> 242 0.17061
240 -> 248 -0.12168

Excited State 36: Singlet-AG 5.9228 eV 209.33 nm f=0.0000
<S**2>=0.000
234 -> 243 -0.10147
241 -> 249 0.17047
241 -> 252 0.48467
241 -> 257 -0.25178
241 -> 259 -0.24412

Excited State 37: Singlet-AU 5.9262 eV 209.21 nm f=0.0112
<S**2>=0.000
220 -> 242 0.14694
224 -> 242 -0.12536
226 -> 242 0.20142
228 -> 243 -0.12080
231 -> 242 -0.17085
240 -> 248 0.24149
241 -> 254 -0.12188
241 -> 255 -0.14943
241 -> 256 -0.23403
241 -> 258 0.20364
241 -> 262 0.17846
241 -> 277 -0.10815

Excited State 38: Singlet-AU 5.9636 eV 207.90 nm f=0.0005
<S**2>=0.000
214 -> 242 0.12231
222 -> 242 0.59701
224 -> 242 0.30521

Excited State 39: Singlet-AG 5.9762 eV 207.46 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.21713
218 -> 242 -0.26691
221 -> 242 -0.20533
223 -> 242 -0.18617
225 -> 242 0.48281
227 -> 242 0.16539

Excited State 40: Singlet-AU 6.0244 eV 205.80 nm f=0.0274
<S**2>=0.000
219 -> 242 -0.10824
231 -> 242 -0.17614
239 -> 244 -0.13921
240 -> 248 0.37634
240 -> 249 -0.10359
241 -> 254 0.17141

241 -> 255 0.14975
241 -> 256 0.23098
241 -> 258 -0.23228
241 -> 277 0.10192

Excited State 41: Singlet-AU 6.0648 eV 204.43 nm f=0.0006
<S**2>=0.000
215 -> 242 -0.14998
219 -> 242 0.52631
220 -> 242 -0.35279
229 -> 242 -0.10678
240 -> 248 0.12588

Excited State 42: Singlet-AG 6.0783 eV 203.98 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.14309
218 -> 242 0.50696
221 -> 242 -0.23340
223 -> 242 -0.22244
227 -> 242 -0.15482
230 -> 242 0.14232
241 -> 252 0.10786

Excited State 43: Singlet-AG 6.1331 eV 202.16 nm f=0.0000
<S**2>=0.000
216 -> 242 0.28144
217 -> 242 0.20227
219 -> 243 0.11198
220 -> 243 0.23351
221 -> 242 0.12697
224 -> 243 0.13786
228 -> 251 -0.12075
229 -> 243 -0.10730
232 -> 243 -0.10785
234 -> 243 0.18758
235 -> 243 0.11900
241 -> 252 0.18733

Excited State 44: Singlet-AG 6.1928 eV 200.21 nm f=0.0000
<S**2>=0.000
216 -> 242 0.56970
217 -> 242 -0.29728
221 -> 242 0.14871

Excited State 45: Singlet-AU 6.1965 eV 200.09 nm f=0.0027
<S**2>=0.000
210 -> 242 -0.12042
214 -> 242 0.36758
215 -> 242 -0.16213
218 -> 243 0.10369
227 -> 243 0.10583
228 -> 243 0.14394
231 -> 242 0.15776
240 -> 248 0.34593

Excited State 46: Singlet-AU 6.2194 eV 199.35 nm f=0.0543
<S**2>=0.000
212 -> 242 -0.10484
214 -> 242 0.22781
215 -> 242 0.42452
219 -> 242 0.14839
232 -> 242 -0.12365
235 -> 244 -0.14506
239 -> 244 -0.36560

Excited State 47: Singlet-AG 6.2270 eV 199.11 nm f=0.0000
<S**2>=0.000
232 -> 243 -0.15815
234 -> 243 -0.12160
235 -> 243 0.21776
239 -> 243 0.53860
240 -> 246 -0.10936
240 -> 250 0.11000
241 -> 253 0.11096

Excited State 48: Singlet-AU 6.2445 eV 198.55 nm f=0.0885
<S**2>=0.000
214 -> 242 0.22044
215 -> 242 0.34210
235 -> 244 0.13265
239 -> 244 0.48205

Excited State 49: Singlet-AG 6.2688 eV 197.78 nm f=0.0000
<S**2>=0.000
235 -> 243 -0.10484
239 -> 243 -0.11219
241 -> 252 0.20319
241 -> 253 0.53499
241 -> 257 0.20818
241 -> 259 0.11316
241 -> 261 -0.22053

Excited State 50: Singlet-AU 6.2842 eV 197.29 nm f=0.0011
<S**2>=0.000
214 -> 242 0.38113
215 -> 242 -0.25749
218 -> 243 -0.14367
227 -> 243 -0.13825
228 -> 243 -0.19207
231 -> 242 0.12092
240 -> 248 -0.15705
241 -> 254 0.15860
241 -> 262 0.12347

Excited State 51: Singlet-AG 6.3593 eV 194.96 nm f=0.0000
<S**2>=0.000
240 -> 251 -0.14062
241 -> 252 0.22696
241 -> 253 -0.37301
241 -> 257 0.38157
241 -> 259 0.17682
241 -> 261 -0.11947
241 -> 263 0.13492

Excited State 52: Singlet-AU 6.4024 eV 193.65 nm f=0.0253
<S**2>=0.000
241 -> 254 0.60067
241 -> 255 -0.16767
241 -> 256 -0.15970

Excited State 53: Singlet-AG 6.4244 eV 192.99 nm f=0.0000
<S**2>=0.000
213 -> 242 0.46720
239 -> 245 0.32069
240 -> 250 0.10689
240 -> 251 -0.19465
241 -> 252 0.11084
241 -> 253 0.10003
241 -> 259 0.10140
241 -> 261 0.15245

Excited State 54: Singlet-AG 6.4252 eV 192.97 nm f=0.0000
<S**2>=0.000
213 -> 242 0.45211
239 -> 245 -0.33911
240 -> 250 -0.12353
240 -> 251 0.25772
241 -> 257 0.11423

Excited State 55: Singlet-AU 6.4294 eV 192.84 nm f=0.0040
<S**2>=0.000
212 -> 242 0.66889
214 -> 242 0.10287

Excited State 56: Singlet-AU 6.4909 eV 191.01 nm f=0.5873
<S**2>=0.000
234 -> 244 -0.18053
235 -> 244 0.51583
237 -> 244 0.27100
239 -> 244 -0.20438

Excited State 57: Singlet-AG 6.4968 eV 190.84 nm f=0.0000
<S**2>=0.000
213 -> 242 -0.19830
235 -> 243 0.12489
235 -> 245 -0.11810
238 -> 244 0.13840
240 -> 251 0.21444
241 -> 252 0.23000
241 -> 259 0.28503
241 -> 261 0.34790
241 -> 266 0.16813

Excited State 58: Singlet-AG 6.5378 eV 189.64 nm f=0.0000
<S**2>=0.000
211 -> 242 0.29070
235 -> 243 0.12264
235 -> 245 -0.28458
237 -> 245 -0.10397
239 -> 245 0.26967
240 -> 247 0.10368
240 -> 250 -0.11180
240 -> 251 0.23526
241 -> 257 0.14140

241 -> 259 -0.14317
241 -> 261 -0.16878

Excited State 59: Singlet-AU 6.5543 eV 189.16 nm f=0.0085
<S**2>=0.000
228 -> 243 0.10336
235 -> 244 -0.11023
236 -> 245 -0.13304
238 -> 245 -0.20551
241 -> 254 -0.10600
241 -> 258 -0.17203
241 -> 262 0.46113
241 -> 269 0.13327

Excited State 60: Singlet-AG 6.5685 eV 188.75 nm f=0.0000
<S**2>=0.000
211 -> 242 0.60663
235 -> 245 0.10552
239 -> 245 -0.13609
241 -> 261 0.15102

Excited State 61: Singlet-AU 6.5799 eV 188.43 nm f=0.0068
<S**2>=0.000
241 -> 255 0.46670
241 -> 256 -0.33198
241 -> 258 -0.12107
241 -> 260 -0.26285
241 -> 265 -0.12997
241 -> 268 -0.12985
241 -> 269 -0.10721

Excited State 62: Singlet-AG 6.6134 eV 187.47 nm f=0.0000
<S**2>=0.000
237 -> 243 -0.12314
238 -> 244 0.57621
241 -> 259 -0.19648
241 -> 264 0.14006

Excited State 63: Singlet-AU 6.6220 eV 187.23 nm f=0.0075
<S**2>=0.000
235 -> 244 0.11683
237 -> 244 -0.32953
238 -> 243 0.11206
241 -> 255 0.17857
241 -> 256 -0.19705
241 -> 260 0.18518
241 -> 268 0.38835

Excited State 64: Singlet-AU 6.6512 eV 186.41 nm f=0.0293
<S**2>=0.000
235 -> 244 -0.22195
237 -> 244 0.43283
238 -> 243 -0.16889
241 -> 255 0.12503
241 -> 258 0.10873
241 -> 260 0.22639
241 -> 268 0.26698

Table 5-12. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{5_c}$ (The 241th orbital is highest occupied orbital shown in Figure 5-33) [tdTN117bb1]

Excited State 1: Singlet-B 2.8807 eV 430.39 nm f=0.1121
<S**2>=0.000
240 -> 244 0.11038
241 -> 242 0.68779
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4973.36122781
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-B 3.0836 eV 402.08 nm f=0.0154
<S**2>=0.000
240 -> 242 0.68349

Excited State 3: Singlet-A 3.6377 eV 340.83 nm f=0.0051
<S**2>=0.000
241 -> 243 0.68177

Excited State 4: Singlet-B 3.9458 eV 314.22 nm f=0.0239
<S**2>=0.000
241 -> 244 0.68675

Excited State 5: Singlet-A 4.4118 eV 281.03 nm f=0.0064
<S**2>=0.000
232 -> 242 0.10939
235 -> 242 -0.10778
236 -> 242 0.14713
239 -> 242 0.37873
240 -> 243 -0.12879
241 -> 245 0.50112

Excited State 6: Singlet-B 4.4502 eV 278.61 nm f=0.0031
<S**2>=0.000
240 -> 244 -0.11076
241 -> 246 0.68716

Excited State 7: Singlet-A 4.4545 eV 278.33 nm f=0.0005
<S**2>=0.000
230 -> 242 -0.15400
235 -> 242 0.24366
236 -> 242 0.19983
238 -> 242 0.26328
239 -> 242 -0.11046
240 -> 243 0.40438
240 -> 245 -0.18803
241 -> 245 0.20342

Excited State 8: Singlet-A 4.6600 eV 266.06 nm f=0.0022
<S**2>=0.000
232 -> 242 0.12124
236 -> 242 0.22133
238 -> 242 0.11880
239 -> 242 0.41889
240 -> 243 0.14957
241 -> 245 -0.39424
241 -> 247 0.16781

Excited State 9: Singlet-A 4.7530 eV 260.85 nm f=0.0003
<S**2>=0.000
230 -> 242 0.12674
235 -> 242 -0.14607
236 -> 242 -0.20533
238 -> 242 -0.20735
240 -> 243 0.50789
241 -> 247 -0.10472
241 -> 248 0.18969

Excited State 10: Singlet-A 4.9405 eV 250.95 nm f=0.0033
<S**2>=0.000
236 -> 242 0.16771
238 -> 242 0.12912
240 -> 243 -0.11207
240 -> 245 -0.22795
241 -> 247 -0.20701
241 -> 248 0.51714

Excited State 11: Singlet-B 5.0316 eV 246.41 nm f=0.0800
<S**2>=0.000
220 -> 242 -0.15552
233 -> 242 -0.13708
234 -> 242 -0.17730
240 -> 244 0.50759
240 -> 246 -0.16854
241 -> 249 -0.23084

Excited State 12: Singlet-A 5.0345 eV 246.27 nm f=0.0000
<S**2>=0.000
235 -> 242 0.10882
236 -> 242 0.13622
238 -> 242 0.17092
239 -> 242 -0.15252
240 -> 245 0.59365
241 -> 248 0.15557

Excited State 13: Singlet-B 5.1029 eV 242.97 nm f=0.0830
<S**2>=0.000
220 -> 242 0.20965
228 -> 242 0.13064
233 -> 242 0.16677
240 -> 244 0.36343

240 -> 246 0.21087
241 -> 249 0.28153
241 -> 252 0.13035

Excited State 14: Singlet-A 5.1506 eV 240.72 nm f=0.0340
<S**2>=0.000
230 -> 242 0.23169
235 -> 242 -0.17731
236 -> 242 0.19175
239 -> 242 -0.26696
241 -> 247 0.40820
241 -> 251 0.16325

Excited State 15: Singlet-A 5.2160 eV 237.70 nm f=0.0286
<S**2>=0.000
230 -> 242 -0.20667
235 -> 242 0.17139
236 -> 242 -0.29717
241 -> 245 0.10026
241 -> 247 0.35842
241 -> 248 0.24745
241 -> 251 0.23554

Excited State 16: Singlet-B 5.2824 eV 234.71 nm f=0.0596
<S**2>=0.000
220 -> 242 -0.24135
223 -> 242 -0.11962
228 -> 242 -0.10305
233 -> 242 -0.23519
237 -> 242 0.14784
240 -> 246 0.13548
241 -> 249 0.44825
241 -> 252 0.15671

Excited State 17: Singlet-A 5.4026 eV 229.49 nm f=0.0031
<S**2>=0.000
230 -> 242 0.12587
235 -> 242 -0.15429
236 -> 242 -0.36545
238 -> 242 0.54506

Excited State 18: Singlet-B 5.4068 eV 229.31 nm f=0.0167
<S**2>=0.000
234 -> 242 0.13139
237 -> 242 0.66565

Excited State 19: Singlet-B 5.4541 eV 227.32 nm f=0.4391
<S**2>=0.000
234 -> 242 -0.18123
240 -> 246 0.57976
241 -> 249 -0.25283

Excited State 20: Singlet-B 5.5190 eV 224.65 nm f=0.1602
<S**2>=0.000
234 -> 242 0.58873
237 -> 242 -0.11400
240 -> 244 0.18455
240 -> 246 0.19538

Excited State 21: Singlet-A 5.5699 eV 222.60 nm f=0.0003
<S**2>=0.000
214 -> 242 -0.10602
230 -> 242 0.31700
235 -> 242 0.52325
239 -> 242 0.12570
240 -> 247 -0.14223

Excited State 22: Singlet-A 5.6766 eV 218.41 nm f=0.0010
<S**2>=0.000
222 -> 242 -0.24592
227 -> 242 0.30682
229 -> 242 0.15718
230 -> 244 -0.13721
231 -> 242 -0.24365
232 -> 242 0.19878
235 -> 244 0.11550
240 -> 248 -0.24179
241 -> 247 -0.10671

Excited State 23: Singlet-B 5.7749 eV 214.70 nm f=0.0022
<S**2>=0.000
218 -> 242 0.14634
225 -> 242 -0.13744
236 -> 243 -0.16220
239 -> 243 -0.28114
240 -> 249 0.44743
240 -> 252 0.21729

Excited State 24: Singlet-A 5.7930 eV 214.03 nm f=0.0050
<S**2>=0.000
230 -> 242 0.21025
240 -> 247 0.58135
240 -> 251 0.24741

Excited State 25: Singlet-B 5.9399 eV 208.73 nm f=0.0215
<S**2>=0.000
218 -> 242 0.10455
225 -> 242 -0.13500
228 -> 242 -0.21012
233 -> 242 0.43844
234 -> 242 -0.11304
239 -> 243 0.25358
241 -> 250 0.14646
241 -> 252 -0.12144
241 -> 258 0.11466

Excited State 26: Singlet-B 5.9629 eV 207.93 nm f=0.0551
<S**2>=0.000
218 -> 242 -0.21465
219 -> 242 -0.10846
223 -> 242 -0.10302
225 -> 242 0.23621
226 -> 242 0.10844
228 -> 242 0.22567
240 -> 244 -0.10055
240 -> 249 0.30333
241 -> 250 0.16256
241 -> 252 -0.18518
241 -> 258 0.15249

Excited State 27: Singlet-A 5.9746 eV 207.52 nm f=0.0022
<S**2>=0.000
222 -> 242 0.10547
227 -> 242 -0.13856
232 -> 242 0.53176
236 -> 242 -0.11242
238 -> 242 -0.10446
239 -> 242 -0.11306
241 -> 247 -0.13316
241 -> 251 0.26522

Excited State 28: Singlet-A 5.9857 eV 207.13 nm f=0.0019
<S**2>=0.000
232 -> 242 -0.28106
241 -> 247 -0.23187
241 -> 248 -0.20597
241 -> 251 0.48972
241 -> 259 0.11130

Excited State 29: Singlet-B 5.9979 eV 206.71 nm f=0.0290
<S**2>=0.000
218 -> 242 -0.12107
220 -> 242 -0.18204
223 -> 242 -0.11341
225 -> 242 0.12373
226 -> 242 0.10030
233 -> 242 0.40144
236 -> 243 -0.13141
239 -> 243 -0.30270
240 -> 249 -0.13356
241 -> 250 -0.18662

Excited State 30: Singlet-B 6.0244 eV 205.80 nm f=0.0705
<S**2>=0.000
220 -> 242 -0.13070
235 -> 243 -0.12127
239 -> 243 0.30861
240 -> 249 0.24686
241 -> 249 -0.16546
241 -> 250 -0.17730
241 -> 252 0.27879
241 -> 258 -0.19756

Excited State 31: Singlet-B 6.0802 eV 203.91 nm f=0.0064
<S**2>=0.000
241 -> 250 0.57953
241 -> 252 0.29203

Excited State 32: Singlet-A 6.1250 eV 202.42 nm f=0.0718
<S**2>=0.000
227 -> 242 0.15211
229 -> 242 0.14016
231 -> 242 -0.24188
239 -> 244 0.15439

240 -> 248 0.45150
240 -> 251 0.11586
241 -> 257 -0.11601
241 -> 259 0.14530

Excited State 33: Singlet-A 6.1557 eV 201.41 nm f=0.0084
<S**2>=0.000
227 -> 244 0.10791
230 -> 242 0.19191
231 -> 244 -0.12642
232 -> 244 0.16159
236 -> 244 0.20397
238 -> 244 0.10803
239 -> 244 0.32308
240 -> 248 -0.20623
241 -> 251 0.16082
241 -> 259 -0.12785

Excited State 34: Singlet-A 6.1894 eV 200.32 nm f=0.0057
<S**2>=0.000
222 -> 242 -0.25156
227 -> 242 0.25477
229 -> 242 -0.20912
231 -> 242 0.50354
232 -> 242 0.11570

Excited State 35: Singlet-B 6.2363 eV 198.81 nm f=0.4857
<S**2>=0.000
235 -> 243 0.19539
236 -> 243 0.36067
238 -> 243 0.43114
239 -> 243 -0.20915
241 -> 252 0.10600

Excited State 36: Singlet-B 6.2608 eV 198.03 nm f=0.0041
<S**2>=0.000
218 -> 244 -0.20244
220 -> 242 0.15796
222 -> 248 0.12876
225 -> 244 0.19314
227 -> 248 -0.14076
228 -> 242 0.26209
228 -> 244 0.13556
231 -> 248 0.10146
234 -> 244 -0.20909
241 -> 252 0.23452

Excited State 37: Singlet-A 6.2669 eV 197.84 nm f=0.0198
<S**2>=0.000
222 -> 244 0.15115
227 -> 244 -0.15810
230 -> 242 -0.12657
236 -> 244 0.12234
239 -> 244 0.31272
239 -> 246 -0.11686
240 -> 248 -0.17429
241 -> 253 0.18241
241 -> 254 0.15612
241 -> 257 -0.14961
241 -> 259 0.26609

Excited State 38: Singlet-A 6.2963 eV 196.91 nm f=0.0001
<S**2>=0.000
222 -> 244 -0.11743
227 -> 244 0.12281
236 -> 244 -0.17527
238 -> 244 -0.11199
239 -> 244 -0.23323
241 -> 253 0.48383
241 -> 254 0.10776
241 -> 259 0.13889
241 -> 260 -0.10550

Excited State 39: Singlet-B 6.3533 eV 195.15 nm f=0.0106
<S**2>=0.000
218 -> 242 0.14107
219 -> 242 0.22938
220 -> 242 -0.11711
223 -> 242 -0.17694
225 -> 242 -0.22705
226 -> 242 0.11683
228 -> 242 0.46878
241 -> 252 -0.10010

Excited State 40: Singlet-A 6.3574 eV 195.02 nm f=0.0282
<S**2>=0.000
222 -> 244 0.11124
227 -> 244 -0.12293
238 -> 244 0.10598
240 -> 248 0.19594
241 -> 253 0.38363
241 -> 254 -0.20592
241 -> 257 0.20031
241 -> 259 -0.22364
241 -> 260 -0.10166

Excited State 41: Singlet-A 6.3930 eV 193.94 nm f=0.0028
<S**2>=0.000
217 -> 242 0.13096
224 -> 242 0.26177
227 -> 242 -0.11173
229 -> 242 0.54406
231 -> 242 0.25428

Excited State 42: Singlet-B 6.4063 eV 193.54 nm f=0.0127
<S**2>=0.000
236 -> 243 -0.23238
238 -> 243 0.21292
241 -> 249 -0.11983
241 -> 250 -0.10328
241 -> 252 0.25476
241 -> 255 0.23456
241 -> 256 -0.22711
241 -> 258 0.25523
241 -> 262 0.18188
241 -> 265 0.12425

Excited State 43: Singlet-B 6.4148 eV 193.28 nm f=0.0051
<S**2>=0.000
219 -> 242 -0.22667
223 -> 242 0.13274
225 -> 242 -0.32942
226 -> 242 0.53334

Excited State 44: Singlet-A 6.4503 eV 192.22 nm f=0.0012
<S**2>=0.000
237 -> 243 0.62383
237 -> 245 0.12165
238 -> 244 -0.13661

Excited State 45: Singlet-B 6.4607 eV 191.91 nm f=0.0227
<S**2>=0.000
235 -> 243 -0.11891
236 -> 243 -0.35402
237 -> 244 -0.13827
238 -> 243 0.38769
239 -> 243 0.10901
241 -> 252 -0.10980
241 -> 255 -0.17753
241 -> 256 0.17873
241 -> 258 -0.14410
241 -> 262 -0.13429

Excited State 46: Singlet-B 6.5334 eV 189.77 nm f=0.1185
<S**2>=0.000
219 -> 242 -0.23106
221 -> 242 -0.12569
223 -> 242 -0.12038
235 -> 243 0.27400
236 -> 243 -0.13518
236 -> 245 0.10536
239 -> 245 0.38377
240 -> 249 -0.12897
241 -> 262 -0.12000

Excited State 47: Singlet-A 6.5393 eV 189.60 nm f=0.0000
<S**2>=0.000
217 -> 242 -0.16295
224 -> 242 0.55972
227 -> 242 -0.23868
229 -> 242 -0.19214
230 -> 242 0.10426
231 -> 242 -0.11693

Excited State 48: Singlet-B 6.5823 eV 188.36 nm f=0.0023
<S**2>=0.000
219 -> 242 0.25194
220 -> 242 -0.10257
221 -> 242 0.27649
223 -> 242 0.31988
225 -> 242 0.17627
226 -> 242 0.17458
235 -> 243 0.33012
238 -> 245 -0.10267

Excited State 49: Singlet-B 6.5909 eV 188.12 nm f=0.0212
<S**2>=0.000
218 -> 242 -0.15622
221 -> 242 -0.15798
223 -> 242 -0.13603
225 -> 242 -0.25148
226 -> 242 -0.17396
235 -> 243 0.35801
236 -> 245 -0.15278
238 -> 245 -0.15509
239 -> 243 0.10976
239 -> 245 -0.14523
241 -> 255 -0.14774

Excited State 50: Singlet-A 6.5910 eV 188.11 nm f=0.0014
<S**2>=0.000
222 -> 242 0.43342
224 -> 242 0.19480
227 -> 242 0.35232
234 -> 243 0.18685
239 -> 246 -0.17672

Excited State 51: Singlet-A 6.6125 eV 187.50 nm f=0.0105
<S**2>=0.000
222 -> 242 -0.31750
227 -> 242 -0.16636
234 -> 243 0.41592
235 -> 244 -0.15740
238 -> 246 0.10956
239 -> 246 -0.24134
241 -> 254 -0.10410

Excited State 52: Singlet-B 6.6320 eV 186.95 nm f=0.0047
<S**2>=0.000
218 -> 242 -0.13852
219 -> 242 0.36839
220 -> 242 0.32346
223 -> 242 -0.35970
226 -> 242 0.19562
228 -> 242 -0.18024

Excited State 53: Singlet-A 6.6437 eV 186.62 nm f=0.0538
<S**2>=0.000
234 -> 243 0.36164
235 -> 246 -0.11344
236 -> 244 0.22899
236 -> 246 -0.18629
238 -> 244 0.11296
238 -> 246 -0.18544
239 -> 244 -0.17592
239 -> 246 0.26838
240 -> 248 -0.10182

Excited State 54: Singlet-B 6.6667 eV 185.98 nm f=0.0171
<S**2>=0.000
218 -> 242 0.27524
220 -> 242 0.13271
223 -> 242 -0.11196
225 -> 242 0.10982
226 -> 242 0.11050
241 -> 256 -0.12100
241 -> 258 -0.27015
241 -> 261 -0.19104
241 -> 262 0.29479
241 -> 265 0.18712

Excited State 55: Singlet-B 6.7094 eV 184.79 nm f=0.0452
<S**2>=0.000
215 -> 242 0.10157
218 -> 242 0.32516
219 -> 242 -0.23725
223 -> 242 -0.20508
225 -> 242 0.12400
239 -> 245 -0.26847
241 -> 258 0.21257
241 -> 262 -0.14316

Excited State 56: Singlet-A 6.7118 eV 184.73 nm f=0.0410
<S**2>=0.000
235 -> 244 -0.12118
236 -> 244 -0.11381
238 -> 244 -0.23402
239 -> 244 0.15138
239 -> 246 0.15544
241 -> 253 0.11695
241 -> 254 -0.26048
241 -> 257 -0.25178
241 -> 259 -0.12517
241 -> 260 0.28491
241 -> 268 0.11867
241 -> 270 0.10813

Excited State 57: Singlet-A 6.7222 eV 184.44 nm f=0.0068
<S**2>=0.000
235 -> 246 0.10348
236 -> 244 0.10142
239 -> 246 -0.16442
240 -> 251 -0.12836
241 -> 254 0.36545
241 -> 259 -0.20559
241 -> 260 0.38057

Excited State 58: Singlet-A 6.7284 eV 184.27 nm f=0.0332
<S**2>=0.000
236 -> 244 -0.10515
240 -> 247 -0.23321
240 -> 248 -0.11977
240 -> 251 0.50425
240 -> 259 0.10685
241 -> 254 0.21083
241 -> 257 0.10302
241 -> 259 -0.13986

Excited State 59: Singlet-B 6.7481 eV 183.73 nm f=0.0068
<S**2>=0.000
218 -> 242 -0.10338
219 -> 242 -0.13533
221 -> 242 0.49172
223 -> 242 -0.14141
225 -> 242 -0.18242
226 -> 242 -0.12894
238 -> 245 -0.12120
241 -> 255 0.19509
241 -> 258 -0.13185
241 -> 261 0.15142

Excited State 60: Singlet-A 6.7517 eV 183.64 nm f=0.0135
<S**2>=0.000
235 -> 244 -0.10334
236 -> 244 -0.14352
238 -> 244 -0.28992
239 -> 244 0.16524
239 -> 246 0.23284
240 -> 251 -0.18653
241 -> 254 0.29593
241 -> 257 0.16300
241 -> 259 -0.13087
241 -> 260 -0.19878
241 -> 268 -0.10479

Excited State 61: Singlet-B 6.7584 eV 183.45 nm f=0.0065
<S**2>=0.000
221 -> 242 -0.23518
225 -> 242 0.11679
239 -> 245 -0.17798
241 -> 255 0.35334
241 -> 258 -0.32191
241 -> 261 0.22636
241 -> 265 -0.13869

Excited State 62: Singlet-A 6.7755 eV 182.99 nm f=0.0088
<S**2>=0.000
216 -> 242 0.19051
217 -> 242 -0.20198
229 -> 242 0.11597
236 -> 246 0.14409
241 -> 257 0.32138
241 -> 259 0.21263
241 -> 260 0.27533
241 -> 263 0.19231
241 -> 264 -0.12039

Excited State 63: Singlet-B 6.7827 eV 182.79 nm f=0.0861
<S**2>=0.000
240 -> 250 0.49767
240 -> 252 -0.21626
240 -> 255 0.10366
240 -> 258 0.22370
241 -> 256 0.10299

Excited State 64: Singlet-A 6.7945 eV 182.48 nm f=0.0191
<S**2>=0.000
216 -> 242 -0.29769

217 -> 242	0.42491	229 -> 242	-0.15546
224 -> 242	0.13779	238 -> 246	-0.11579
227 -> 242	0.10817	241 -> 257	0.18478
		241 -> 260	0.16822

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Chapter 6

Reactions of a Bicyclo[1.1.0]tetrasil-1(3)-ene with Nucleophilic Reagents

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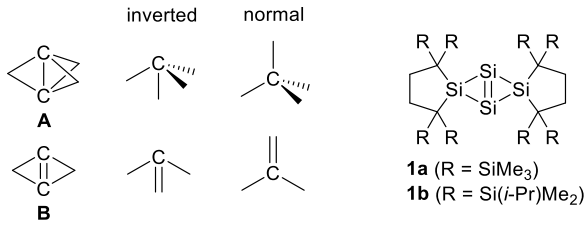
6-1. Introduction

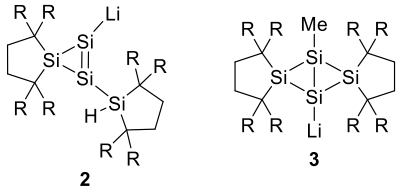
A molecule containing a distorted structure often exhibits unexpected reactivity. For example, [1.1.1]propellane has a nonclassical single bond between bridgehead carbon atoms that adopt an inverted (or hemispheroidal) geometry (Chart 6-1, **A**),[1,2] which exhibits diradical or ionic characters. Bicyclo[1.1.0]but-1(3)-ene has a strained bridgehead C=C double bond in the bicyclic framework, whereby the orientation of the double bond is diametrically opposite to that of typical double bonds in acyclic alkenes (Chart 6-1, **B**).[3] Although **B** and its derivatives have been proposed as reactive intermediates and the formal 1,2-addition of nucleophiles to the bridgehead C=C bond has been reported, the reactivity of such compounds containing an inverted double bond has not been investigated in detail.

Chart 6-1. [1.1.1]Propellane (**A**), Bicyclo[1.1.0]but-1(3)-ene (**B**), and Bicyclo[1.1.0]tetrasil-1(3)-ene **1**



Recently, we synthesized bicyclo[1.1.0]tetrasil-1(3)-enes **1a** and **1b** as the first isolable silicon analogues of bicyclo[1.1.0]but-1(3)-ene (Chart 6-1).[4] Experimental and theoretical studies disclosed that **1** has a planar Si_4 bicyclic structure with the bridgehead Si=Si bond comprised of a π-bond and an inverted σ-bond as found between bridgehead silicon atoms in pentasila[1.1.1]propellane.[5] Although halogen abstraction of **1a** from alkyl halides provided 1,3-dihalobicyclo[1.1.0]tetrasilanes that contain an unsupported bridgehead Si−Si π-bond,[6] the reactivity of **1** for other reagents remains to be elucidated. In this chapter, the author reports the reactions of **1a** with lithium aluminum hydride ($LiAlH_4$) and methyl lithium (MeLi). The reduction of **1a** with $LiAlH_4$ provides unexpectedly cyclotrisilenide **2** as the first disilenide with a cyclotrisilene moiety (Chart 6-2),[7,8] while the reaction of **1a** with MeLi afforded the corresponding 1-methyl-3-lithiobicyclo[1.1.0]tetrasilane **3** (Chart 6-2).

Chart 6-2. Structures of Compound **2** and **3** (R = $SiMe_3$)

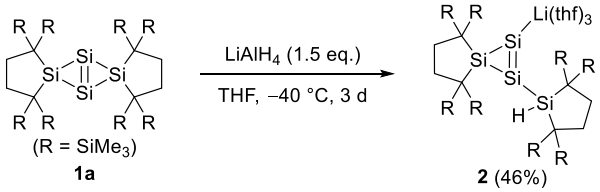


6-2. Results and Discussion

6-2-1. Reaction of 1a with $LiAlH_4$

The reaction of **1a** with $LiAlH_4$ in THF at −40 °C afforded cyclotrisilenide **2** as a reddish-orange solid in 46% yield (Scheme 6-1).[9,10] The molecular structure of **2** was determined using a combination of multinuclear NMR spectroscopy and single-crystal X-ray diffraction (XRD) analysis. Compound **2** was very air- and moisture-sensitive, but stable in a benzene solution at room temperature for several days.

Scheme 6-1. Reduction of **1a** with $LiAlH_4$



6-2-2. Molecular Structure and NMR Spectra of Cyclotrisilenide 2

Recrystallization from pentane at −27 °C provided red crystals of **2** suitable for single-crystal XRD analysis (Figure 6-1a). In the crystalline state, **2** exists as a contact ion pair, and the lithium atom coordinates to three THF molecules. The Si1−Li1 distance [2.655(5) Å] is similar to those of typical sp^3-type silyllithiums (2.64−2.70 Å)[11] and within those of previously reported sp^2-type silyllithiums (2.598(9)−2.853(3) Å).[12,13] The Si=Si bond distance [Si1−Si2: 2.182(2) Å] is slightly shorter than those in previously reported disilenides (2.192−2.209 Å),[12] and comparable to those of reported cyclotrisilenes (2.118−2.186 Å).[14] The geometry around the unsaturated silicon atoms is almost planar [the angle sums of Si1 and Si2 atoms are 359.64° and 359.81°]. The ^{29}Si NMR resonances in benzene-d_6 due to the Si1 and Si2 nuclei [281.0 and

168.1 ppm, respectively, Figure 6-1b] fall in the range for the reported disilenides (100.5−328.4 ppm).[12] The broadening of the signal at 281.0 ppm might arise from the coupling between the ^{29}Si and ^{7}Li nuclei.

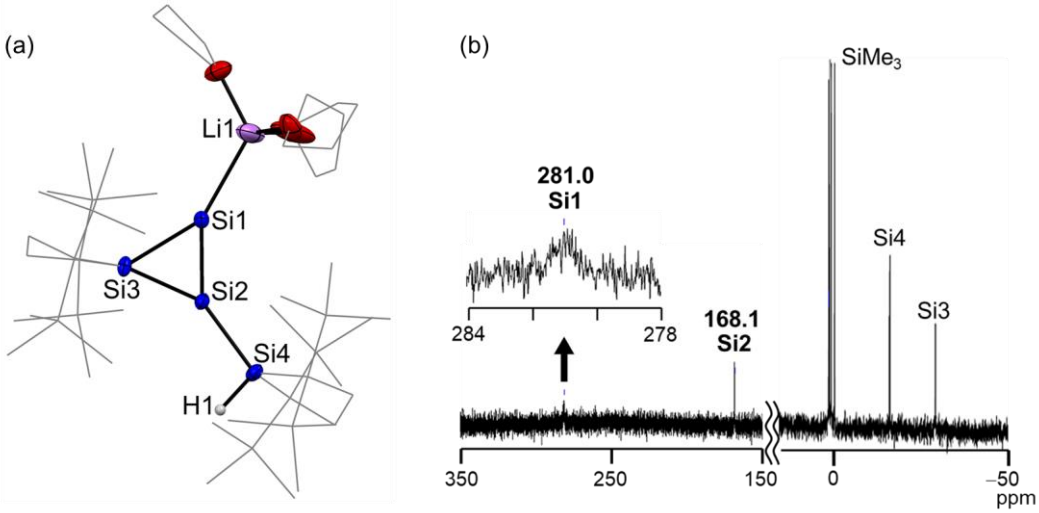


Figure 6-1. (a) ORTEP of **2** with thermal ellipsoids at 50% probability; hydrogen atoms, cocrystallized solvent (pentane), and disordered atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Li1 2.655(5), Si1−Si2 2.182(2), Si1−Si3 2.403(2), Si2−Si3 2.2690(8), Si2−Si4 2.3651(8), Li1−Si1−Si2−Si4 −2.2(4). (b) ^{29}Si NMR spectrum of **2** in benzene-d_6 at room temperature.

6-2-3. Theoretical Study

Theoretical calculations provided further insight into the structure of **2**. The optimized structure of **2** (**2**$_{opt}$) calculated at the B3LYP-D3/6-311G(d) level of theory is in good agreement with the structure of **2** observed in the crystalline state. The ^{29}Si NMR chemical shifts of the unsaturated Si1 and Si2 nuclei in **2**$_{opt}$ calculated at the M06L/6-311+G(2df,p) level of theory (276.9 ppm, 177.5 ppm) is consistent with the observed values of **2** (281.0 ppm, 168.1 ppm) in benzene-d_6, suggesting that even in benzene solution, **2** adopts a contact ion pair structure similar to that observed in the solid state.

6-2-4. UV-vis Absorption Spectra of 2

The author found the remarkable solvatochromism of **2**. When **2** was dissolved in hexane, the color of the solution was orange and the longest-wavelength absorption band was observed at 530 nm (ε = 200 cm^{-1}mol^{-1}dm^3; Figure 6-2a). Conversely, for a yellowish green THF solution of **2**, the longest-wavelength absorption band appeared at 574 nm (ε = 200 cm^{-1}mol^{-1}dm^3; Figure

6-2a). The solvent-dependent color change of **2** is reversible. Similar solvatochromism has been observed in the isolable silenyl lithium reported by Apeloig, in which the color change of the solution arises from the differences in structure between the contact ion pair and the solvent-separated ion pair.[13] The TD-DFT calculations suggest that the color change of the solution of **2** is also explained by the structure in solution as follows. The predicted longest-wavelength absorption band positions [528 nm ($\mathbf{2}_{opt}$) and 569 nm ($\mathbf{2'}_{opt}$, free anion of **2**)][15] at the B3LYP-D3/6-311+G(d)/SCRF(solvent = heptane ($\mathbf{2}_{opt}$), THF ($\mathbf{2'}_{opt}$)) level of theory are consistent with the observed absorption wavelengths (See Figures 6-61 and 6-62). In addition, there absorptions are attributed to a symmetry-forbidden HOMO–LUMO transition: the HOMO is the in-plane anionic lone pair orbital and the LUMO is the π*(Si=Si) orbitals (Figure 6-2b,c), which is in agreement with the observed small ε values.

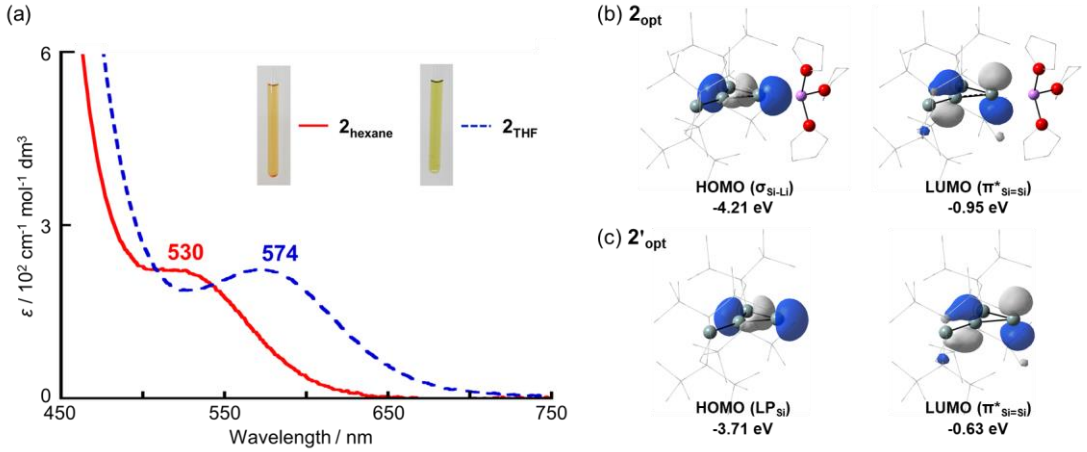


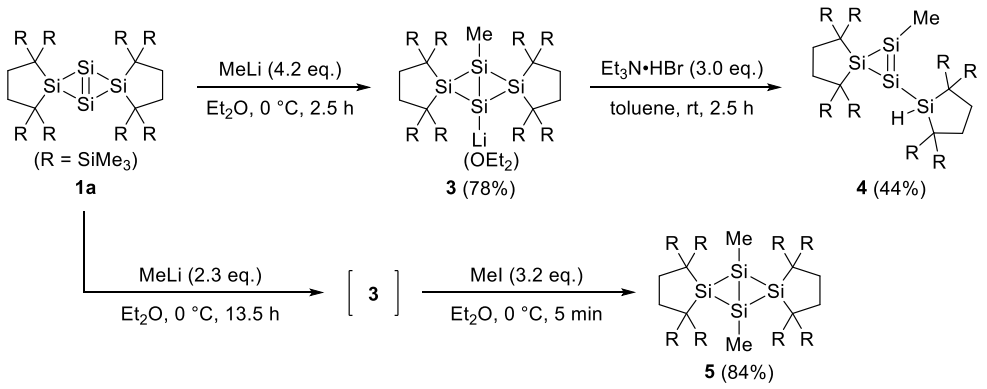
Figure 6-2. (a) UV-vis spectra of **2** at room temperature (red line: in hexane, blue dash line: in THF). (b) Frontier Kohn-Sham orbitals of $\mathbf{2}_{opt}$ at the B3LYP-D3/6-311+G(d)/SCRF(solvent = heptane)//B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}). (c) Frontier Kohn-Sham orbitals of $\mathbf{2'}_{opt}$ at the B3LYP-D3/6-311+G(d)/SCRF(solvent = THF)//B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}).

6-2-5. Reaction of 1a with MeLi

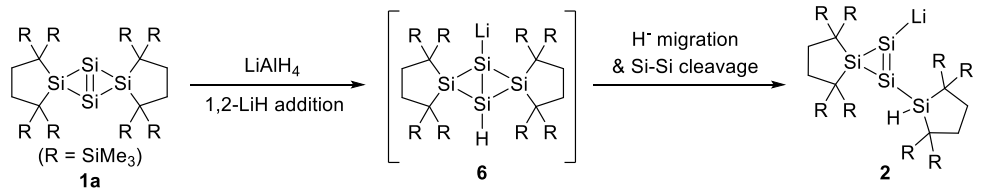
The reaction of **1a** with MeLi provided further insight into the mechanism for the formation of **2**. When **1a** was treated with MeLi in Et_2O solution at 0 °C, 1-methyl-3-lithiobicyclo[1.1.0]tetrasilane **3** was obtained as a pale yellow solid in 78% yield (Scheme 6-2). In this reaction, 1,2-addition of MeLi to the bridgehead Si=Si bond in **1a** occurred similar to the reaction of an acyclic disilene with MeLi.[16] While no isomerization of **3**

was observed in solution, the protonation of **3** with Et_3N·HBr led to full conversion into cyclotrisilene **4** with Me group on the unsaturated silicon atom (NMR yield: 97%, Scheme 6-2), which was isolated as a pale yellow solid in 44% yield. Conversely, when compound **1a** was treated with MeLi followed by MeI, 1,3-dimethylbicyclo[1.1.0]tetrasilane **5** was obtained in 84% yield (2 steps, Scheme 6-2). Compound **5** is stable even at 60 °C. These results indicate that after protonation of **3**, the intramolecular hydride migration from the bridgehead silicon atom to the bridge silicon atom accompanied by the ring-opening affords **4**. These results suggest that the reduction of **1a** with $LiAlH_4$ afforded the corresponding 1,2-LiH adduct **6** as an initial product and the subsequent hydride migration and ring-opening provided cyclotrisilenide **2** (Scheme 6-3). As a 1,3-dichlorobicyclo[1.1.0]tetrasilane undergoes a similar isomerization involving the chlorine migration and the ring opening to afford the corresponding cyclotrisilene,[6b] relatively high migratory aptitude of hydride[17] and the release of the ring strain may be responsible for the observed transformation to cyclotrisilene derivatives such as **2** and **4**.

Scheme 6-2. Reaction of **1a** with MeLi



Scheme 6-3. Possible Mechanism for Generation of **2**



6-2-6. Molecular Structure of 3

Recrystallization from toluene at −27 °C afforded orange crystals of **3** suitable for single-crystal XRD analysis (Figure 6-3).[18] In the single crystals of **3**, two crystallographically independent molecules exhibiting similar structural characteristics were found in the asymmetric unit. Compound **3** exists as a contact ion pair in the crystalline state. Interestingly, the lithium atom was solvated by only one Et_2O molecule, which is consistent with the fact that the ratio of silyl anion moiety: Et_2O is observed to be 1:1 in the ^1H NMR spectrum of **3** (Figure 6-12). The Si1−Si2 distance in **3** [avg. 2.564 Å] is much longer than those of previously reported bicyclo[1.1.0]tetrasilanes with bent structures (2.35−2.47 Å)[19] and those of 1-lithio-1,3-disilabicyclo[1.1.0]butane (2.3840(16) Å)[20a] and potassium pentasilatricyclo [2.1.0.0^{2,5}]pentan-1-ide (2.3801(6) Å).[20b] The Si2−Li1 distance [avg. 2.524 Å] is shorter than typical Si−Li bond lengths in sp^3-type silyllithiums (2.64−2.70 Å)[11] and those of sp^2-type silyllithiums (2.598(9)−2.853(3) Å).[12,13]

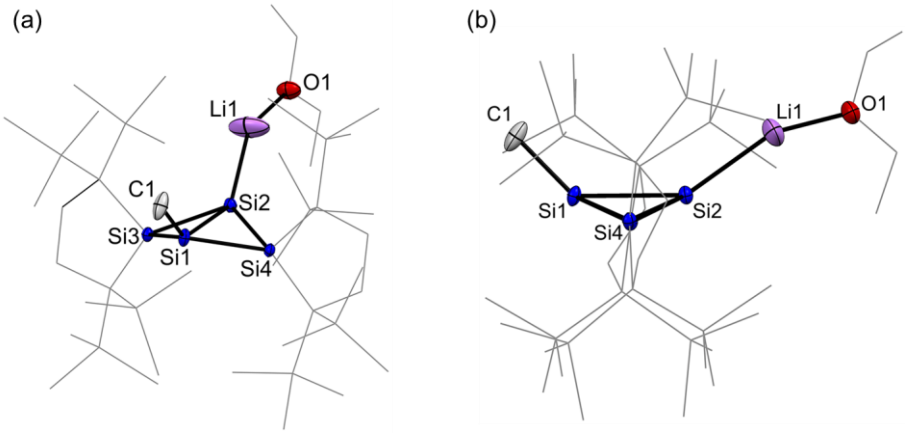


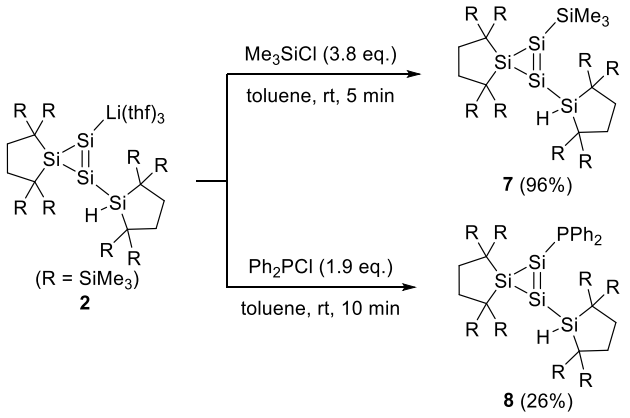
Figure 6-3. ORTEPs of **3** (a: perspective view, b: side view) with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. One of the two crystallographically independent molecules is shown. Selected bond lengths (Å) and angles (deg): Si1−C1 1.912(2), Si1−Si2 2.5577(8), Si1−Si3 2.3205(7), Si1−Si4 2.3054(7), Si2−Si3 2.3148(7), Si2−Si4 2.3189(7), Si2−Li1 2.502(5), C1−Si1−Si2 133.92(9), Si1−Si2−Li1 143.63(14), Si2−Li1−O1 152.3(3), Si3−Si1−Si2−Si4 144.42(3).

6-2-7. Reactions of 2 with Electrophiles

Compound **2** readily reacted with Me_3SiCl in toluene to provide Me_3Si-substituted cyclotrisilene **7** in 96% yield (Scheme 6-4). In addition, treatment of **2** with Ph_2PCl afforded phosphanyl-substituted cyclotrisilene **8** in 80% NMR yield, which was isolated as orange

crystals in 26% yield (Scheme 6-4). Compounds **7** and **8** were characterized by a combination of multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal XRD analysis. Compound **8** is the first example of a cyclotrisilene with a phosphanyl substituent on the unsaturated silicon atom.

Scheme 6-4. Reactions of **2** with Electrophiles



6-2-8. Molecular Structure and Electronic Property of Cyclotrisilene 8

Single-crystal XRD analysis of **8** (Figure 6-4a) disclosed that the geometry around the unsaturated Si2 atom is perfectly planar [the angle sums of the Si2 atom is 360.00°], while a slight pyramidalization of Si1 is observed [the angle sums of the Si1 atom is 355.99°]. The Si1−Si2 distance [2.1451(7) Å] falls within the range of the Si=Si double bond in reported cyclotrisilenes (2.118−2.186 Å)[14] and is comparable to those of phosphanyl-substituted acyclic disilenes (2.1542−2.1968 Å).[21,22] The Si1−P1 distance [2.2746(7) Å] is similar to those of reported phosphanyl disilenes (2.2367(12)−2.3126(10) Å).[21] In the ^{29}Si NMR spectrum of **8** in benzene-d_6, signals assigned to the Si1 and Si2 nuclei were observed at 141.3 and 107.0 ppm, respectively, which were downfield shifted compared with those of reported acyclic phosphanyl disilenes (52.5−111.7 ppm).[21] The ^1J(Si,P) coupling constant of Si1 nucleus [214.8 Hz] is significantly larger than those of reported phosphanyl disilenes [^1J(Si,P) = 115−133 Hz],[21] suggesting an increased s-character of the orbital of the silicon atom in the P−Si bond.[23] The UV-vis absorption spectrum of **8** in hexane exhibits a longest-wavelength absorption band at 430 nm, which is bathochromically shifted compared with those of **4** and **7** [373 and 414 nm].

The HOMO of the optimized structure of **8** (**8**$_{opt}$) calculated at B3LYP-D3/6-311G(d) level of theory represents the interactions between the π-orbital of the Si=Si bond and the lone pair orbital on the phosphorous atom of the PPh_2 moiety (Figure 6-4b). These results suggested the presence of the n−π interaction between the phosphorus lone pair and the Si=Si bond in **8**.

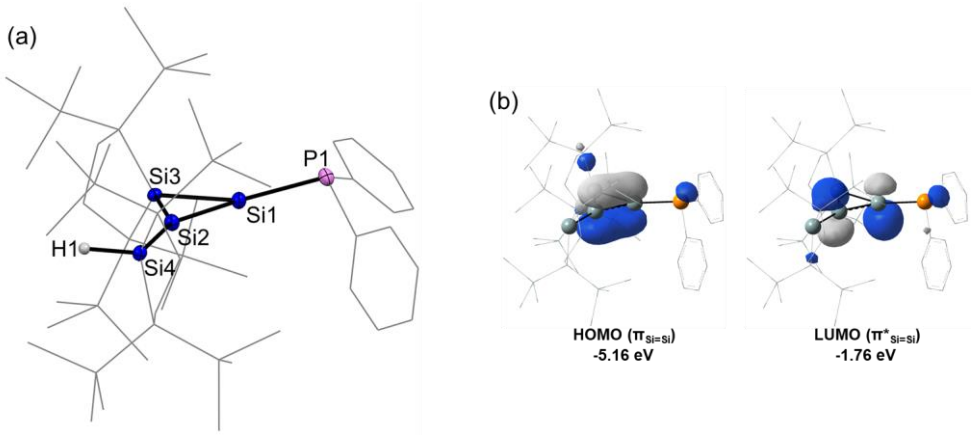


Figure 6-4. (a) ORTEP of **8** with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Si2 2.1451(7), Si1−Si3 2.3256(7), Si1−P1 2.2746(7), Si2−Si3 2.3500(6), Si2−Si4 2.3871(7), Si4−Si2−Si1−P1 −17.37(9). (b) Frontier Kohn-Sham orbitals of **8**$_{opt}$ at the B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}).

6-3. Conclusion

In conclusion, the author investigated the reactions of **1a** with nucleophiles such as $LiAlH_4$ and MeLi. The reduction of **1a** with $LiAlH_4$ provided the first isolable cyclotrisilenide **2** as a reddish-orange solid. In the crystalline state, **2** exists as a contact ion pair structure, and the UV-Vis absorption spectra changed depending on the solvent. The reaction of **1a** with MeLi afforded 1,2-adduct **3** and its protonation led to the generation of cyclotrisilene **4**, suggesting that **2** should be formed via the 1,2-addition of LiH to the bridgehead Si=Si bond of **1a** and subsequent intramolecular hydride migration accompanied by ring-opening. Silyl and phosphanyl-substituted cyclotrisilenes **7** and **8** were successfully obtained from the reactions of **2** with the corresponding chlorosilane and chlorophosphine, respectively.

6-4. Experimental Section

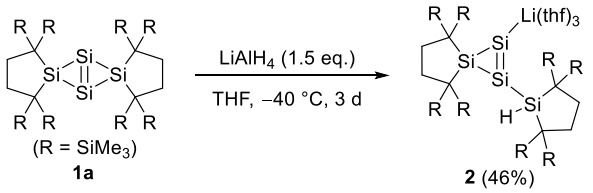
General Procedures

All reactions involving air-sensitive compounds were performed under argon or nitrogen atmosphere using a high-vacuum line and a standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. Reactions at lower temperatures were performed using an EYELA PSL-1400 cryobath. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C shifts of the solvents: C_6D_6 (^{1}H: δ 7.16 and ^{13}C: δ 128.0).[24] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). The sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4T spectrometer and a JEOL JMS-T100GCV spectrometer. UV-vis spectra were recorded on a JASCO V-770 spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer.

Materials

Dry and degassed hexane, THF, and toluene were prepared using a VAC 103991 solvent purifier. Benzene-d_6 was dried by molecular sieves 4Å after degassing through three freeze-pump-thaw cycles. Hexamethyldisiloxane and Et_2O were dried by lithium aluminum hydride after degassing through three freeze-pump-thaw cycles. To treat cyclotrisilenide **2** and silyl anion **3**, benzene-d_6, hexane, and toluene were further dried by potassium graphite (KC_8). Tetrasilabicyclo[1.1.0]but-1(3)-ene[4b] **1a** and KC_8[25] were prepared according to published procedure. Lithium aluminum hydride, a diethyl ether solution of methyllithium, triethylamine hydrobromide, iodomethane, chlorotrimethylsilane, and chlorodiphenylphosphine were commercially available and used without further purification.

Reaction of 1a with Lithium Aluminum Hydride ($LiAlH_4$) [TN790,808]

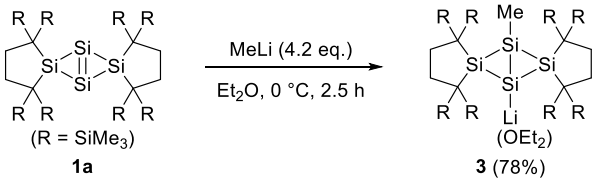


To a Schlenk tube (30 mL) equipped with a magnetic stir bar, compound **1a** (119.9 mg, 150 μmol) and $LiAlH_4$ (8.6 mg, 227 μmol) were placed. To the mixture dry and degassed THF (10.0 mL) was introduced via a vacuum line under reduced pressure and then the mixture was stirred at −40 °C for 3 days. The resulting suspension turned from orange to yellow green. After the volatiles were removed in vacuo at 0 °C, hexane was added to the residue and the resulting insoluble material was filtered off. The volatile was removed under reduced pressure. After hexane was added to the resulting residue, a reddish orange solid was formed and the suspension was left to stand at −27 °C for 1 day. Pure **2** (71.1 mg, 69.2 μmol) was obtained in 46% yield after removing the upper layer by pipetting.

2: a reddish orange solid; mp 167-169 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 296 K) 0.46 (s, 18H, SiC*H*$_3$), 0.53 (s, 18H, SiC*H*$_3$), 0.587 (s, 18H, SiC*H*$_3$), 0.593 (s, 18H, SiC*H*$_3$), 1.34-1.38 (m, 12H, C*H*$_2$ (THF)), 2.11-2.24 (m, 4H, C*H*$_2$), 2.28-2.38 (m, 4H, C*H*$_2$), 3.43-3.49 (m, 12H, C*H*$_2$ (THF)), 5.37 (s, 1H, Si-*H*); ^{13}C NMR (126 MHz, C_6D_6, 296 K); 3.4 (Si*C*H$_3$), 5.0 (Si*C*H$_3$), 5.1 (Si*C*H$_3$), 5.3 (Si*C*H$_3$), 9.8 (*C*), 11.2 (*C*), 25.5 (*C*H$_2$ (THF)), 34.6 (*C*H$_2$), 35.1 (*C*H$_2$), 68.8 (*C*H$_2$ (THF)); ^{29}Si NMR (99 MHz, C_6D_6, 296 K) −27.9 (*Si*), −14.0 (*Si*H), 2.7 (*Si*Me$_3$), 3.6 (*Si*Me$_3$), 4.1 (*Si*Me$_3$), 4.4 (*Si*Me$_3$), 168.1 (*Si*=Si-Li), 281.0 (Si=*Si*-Li); ^{7}Li NMR (194 MHz, C_6D_6, 296 K) 0.13; UV-vis (hexane, 293 K) λ_{max}/nm (ε) 530 (sh, 2.0×10^2), 426 (sh, 1.9×10^3), 359 (5.7×10^3), 250 (sh, 2.1×10^4); UV-vis (THF, 293 K) λ_{max}/nm (ε) 574 (2.0×10^2), 441 (sh, 1.6×10^3), 370 (7.2×10^3), 308 (8.7×10^3), 262 (sh, 2.2×10^4).

We have tried to measure the mass spectrum (FD) and elemental analysis of **2**, but sampling of **2** for measurement was unsuccessful due to extremely high sensitivity of **2** toward moisture and oxygen.

Reaction of 1a with Methyllithium [TN773,780,834]

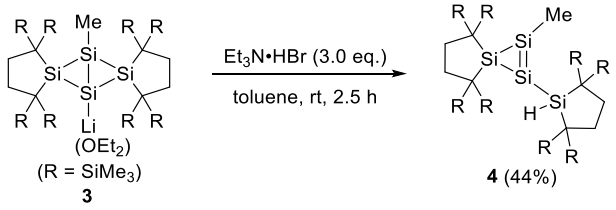


To a Schlenk tube (30 mL) equipped with a magnetic stir bar, tetrasilabicyclo[1.1.0]but-1(3)-ene **1a** (59.9 mg, 74.7 μmol) and dry and degassed Et_2O (5.0 mL) were placed. To the Schlenk tube, a diethyl ether solution of methyllithium (316.1 μmol, (290 μL, 1.09 M)) was added at 0 °C and the mixture was stirred at 0 °C for 2.5 hours. After the volatiles were removed in vacuo at 0 °C, toluene was added to the residue and the insoluble material was filtered off. The filtrate was concentrated in vacuo. After hexane was added to the resulting residue, a pale yellow solid was formed and the suspension was left to stand at –27 °C for 1 day. Pure **3** (52.3 mg, 58.2 μmol) was obtained in 78% yield after removing the upper layer by pipetting.

3: a pale yellow solid; mp 115-117 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 292 K) 0.47 (s, 36H, SiC*H*$_3$), 0.52 (s, 36H, SiC*H*$_3$), 0.84 (s, 3H, SiC*H*$_3$), 0.88 (t, *J* = 7.1 Hz, 6H, C*H*$_3$ (ether)), 2.08-2.23 (m, 8H, C*H*$_2$), 2.98 (q, *J* = 7.1 Hz, 4H, C*H*$_2$ (ether)); ^{13}C NMR (126 MHz, C_6D_6, 293 K) 2.0 (Si*C*H$_3$), 5.4 (Si*C*H$_3$), 6.0 (Si*C*H$_3$), 12.0 (*C*), 14.9 (*C*H$_3$ (ether)), 36.2 (*C*H$_2$), 66.9 (*C*H$_2$ (ether)); ^{29}Si NMR (99 MHz, C_6D_6, 292 K) –80.6 (*Si*-Me), 2.9 (*Si*Me$_3$), 3.1 (*Si*Me$_3$), 16.5 (*Si*); ^{7}Li NMR (194 MHz, C_6D_6, 295 K) 0.53 (broad); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 373 (2.1×10^3), 298 (sh, 1.0×10^4), 236 (2.8×10^4); Anal. Calcd for $C_{37}H_{93}LiOSi_{12}$: C, 49.48; H, 10.44%. Found: C, 49.66; H, 10.25%.

We failed to measure the mass spectrum (APCI, ESI and FD) of **3** because **3** is extremely reactive toward moisture and oxygen and decomposes during sampling for measurement.

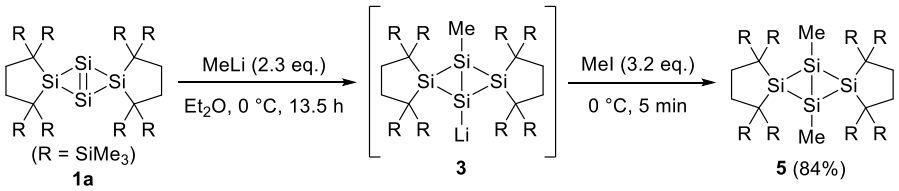
Reaction of 3 with Triethylamine Hydrobromide [TN842,844,845,847]



To a round-bottomed stock bottle (10 mL) equipped with a magnetic stir bar, silyl anion **3** (30.3 mg, 33.7 μmol) and dry and degassed toluene (3.0 mL) were placed. To the stock bottle, triethylamine hydrobromide (18.1 mg, 99.4 μmol) was added at room temperature and the mixture was stirred for 2.5 hours at room temperature. The resulting suspension turned from orange to yellow gradually. After the volatiles were removed in vacuo, hexane was added to the residue and the insoluble material was filtered off. The filtrate was concentrated in vacuo. After hexamethyldisiloxane was added to the resulting residue, a pale yellow solid was formed and the suspension was left to stand at −27 °C for 1 day. Pure **4** (12.0 mg, 14.7 μmol) was obtained in 44% yield after removing the upper layer by pipetting.

4: a pale yellow solid; mp 133-136 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 296 K) 0.30 (s, 18H, SiC*H*$_3$), 0.33 (s, 18H, SiC*H*$_3$), 0.42 (s, 18H, SiC*H*$_3$), 0.45 (s, 18H, SiC*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 1.82-2.05 (m, 8H, C*H*$_2$), 4.95 (s, 1H, Si*H*); ^{13}C NMR (126 MHz, C_6D_6, 296 K) 3.1 (Si*C*H$_3$), 3.5 (Si*C*H$_3$), 4.2 (*C*H$_3$), 4.5 (Si*C*H$_3$), 4.6 (Si*C*H$_3$), 10.3 (*C*), 14.3 (*C*), 33.8 (*C*H$_2$), 34.6 (*C*H$_2$); ^{29}Si NMR (99 MHz, C_6D_6, 295 K) −16.5 (*Si*H), 2.8 (*Si*Me$_3$), 2.9 (*Si*Me$_3$), 3.9 (*Si*Me$_3$), 5.0 (*Si*Me$_3$), 9.4 (*Si*), 56.0 (*Si*=Si-Me), 154.3 (Si=*Si*-Me); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 373 (2.5×10^3), 293 (sh, 1.1×10^4), 237 (3.1×10^4), 216 (4.0×10^4); HRMS (FD) Calcd for $C_{33}H_{84}Si_{12}$ [M^+], 816.38042; Found, 816.37997; Anal. Calcd for $C_{33}H_{84}Si_{12}$: C, 48.45; H, 10.35%. Found: C, 48.11; H, 10.06%.

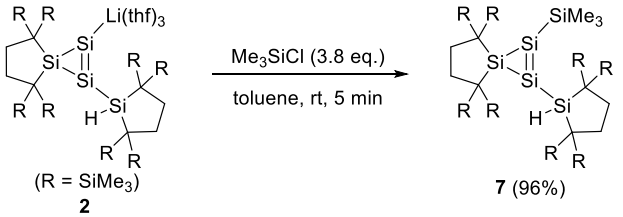
Reaction of 3 with Iodomethane [TN760,762,765]



To a Schlenk tube (30 mL) equipped with a magnetic stir bar, compound **1a** (60.1 mg, 74.9 μmol) and dry and degassed Et_2O (5.0 mL) were placed. To the mixture a diethyl ether solution of methyllithium (174 μmol, (160 μL, 1.09 M)) was added at 0 °C and then the mixture was stirred for 13.5 hours at 0 °C. The resulting solution turned from orange suspension to orange solution. To the reaction mixture iodomethane (ca. 34 mg, 240 μmol) was added at 0 °C. The resulting solution turned from orange solution to yellow suspension immediately. After the volatiles were removed in vacuo at 0 °C, hot toluene was added to the residue and the insoluble material was filtered off. The filtrate was concentrated in vacuo and the residue was washed with hexane to provide a yellow solid of **5** (52.3 mg, 62.9 μmol) in 84% yield.

5: a yellow solid; mp 196-198 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 333 K) 0.36 (s, 72H, SiC*H*$_3$), 1.37 (s, 6H, SiC*H*$_3$ (bridgehead)), 1.98 (s, 8H, C*H*$_2$); ^{13}C NMR (125 MHz, C_6D_6, 333 K), 5.2 (Si*C*H$_3$), 9.5 (Si*C*H$_3$), 13.4 (*C*), 35.1 (*C*H$_2$); ^{29}Si NMR (99 MHz, C_6D_6, 333 K) −14.6 (*Si*), 3.6 (*Si*Me$_3$), 81.6 (*Si*-Me); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 422 (sh, 0.8 × 10^3), 349 (1.5 × 10^3), 292 (2.4 × 10^3), 267 (sh, 7.0 × 10^3), 247 (1.8 × 10^4); HRMS (APCI_positive) Calcd for $C_{34}H_{86}Si_{12}$ [(M+H)$^+$], 831.40335; Found, 831.40347; Anal. Calcd for $C_{34}H_{86}Si_{12}$: C, 49.08; H, 10.42. Found: C, 48.70; H, 10.15%.

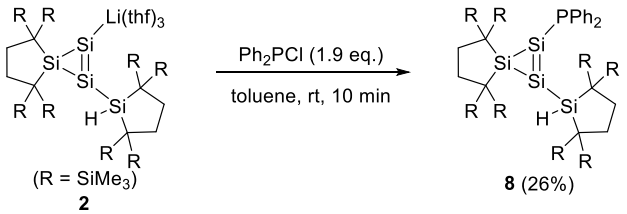
Reaction of 2 with Chlorotrimethylsilane [TN827,828,835]



To a Schlenk tube (10 mL) equipped with a magnetic stir bar, cyclotrisilenide **2** (20.0 mg, 19.5 μmol) and dry and degassed toluene (3.0 mL) were placed. To the Schlenk tube, chlorotrimethylsilane (8.1 mg, 74.6 μmol) was added at room temperature and the mixture was stirred for 5 minutes. The resulting solution turned from red to yellow immediately. After the volatiles were removed in vacuo, hexane was added to the residue and the insoluble material was filtered off. The filtrate was purified by recrystallization from hexane at –27 °C to provide orange crystals of **7** (16.4 mg, 18.7 μmol) in 96% yield.

7: orange crystals; mp 225-227 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 296 K) 0.30 (s, 18H, SiC*H*$_3$), 0.36 (s, 18H, SiC*H*$_3$), 0.42 (s, 18H, SiC*H*$_3$), 0.44 (s, 18H, SiC*H*$_3$), 0.50 (s, 9H, SiC*H*$_3$), 1.88-2.08 (m, 8H, C*H*$_2$), 5.24 (s, 1H, Si*H*); ^{13}C NMR (126 MHz, C_6D_6, 297 K) 2.5 (Si*C*H$_3$), 3.4 (Si*C*H$_3$), 3.8 (Si*C*H$_3$), 4.8 (Si*C*H$_3$), 5.0 (Si*C*H$_3$), 10.6 (*C*), 13.4 (*C*), 34.0 (*C*H$_2$), 34.9 (*C*H$_2$); ^{29}Si NMR (99 MHz, C_6D_6, 296 K) −16.1 (*Si*H), −10.0 (*Si*), −4.3 (Si=Si-*Si*Me$_3$), 3.3 (*Si*Me$_3$), 3.6 (*Si*Me$_3$), 4.4 (*Si*Me$_3$), 5.1 (*Si*Me$_3$), 121.6 (*Si*=Si-SiMe$_3$), 163.4 (Si=*Si*-SiMe$_3$); UV-vis (hexane, 293 K) λ_{max}/nm (ε) 414 (3.7×10^3), 306 (1.1×10^4), 247 (sh, 2.3×10^4), 221 (3.9×10^4); HRMS (FD) Calcd for $C_{35}H_{90}Si_{13}$ [M^+], 874.40429; Found, 874.40400; Anal. Calcd for $C_{35}H_{90}Si_{13}$: C, 47.98; H, 10.35%. Found: C, 48.01; H, 10.27%.

Reaction of 2 with Chlorodiphenylphosphine [TN817,821,825,829]



To a Schlenk tube (10 mL) equipped with a magnetic stir bar, cyclotrisilenide **2** (19.9 mg, 19.4 μmol) and dry and degassed toluene (3.0 mL) were placed. To the Schlenk tube, chlorodiphenylphosphine (7.9 mg, 35.8 μmol) was added at room temperature and the mixture was stirred for 10 minutes. The resulting solution turned from red to orange immediately. After the volatiles were removed in vacuo, hexane was added to the residue and the insoluble material was filtered off. The filtrate was concentrated in vacuo and the residue was purified by

recrystallization from hexamethyldisiloxane at room temperature to provide orange crystals of **8** (5.0 mg, 5.1 μmol) in 26% yield.

8: orange crystals; mp 155-157 ˚C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 296 K) 0.30 (s, 36H, SiC*H*$_3$), 0.35 (s, 18H, SiC*H*$_3$), 0.45 (s, 18H, SiC*H*$_3$), 1.82-2.03 (m, 8H, C*H*$_2$), 5.17 (s, 1H, Si*H*), 7.02-7.07 (m, 2H, *p*-C*H*), 7.10-7.15 (m, 4H, *m*-C*H*), 7.74-7.80 (m, 4H, *o*-C*H*); ^{13}C NMR (126 MHz, C_6D_6, 297 K); 3.4 (Si*C*H$_3$), 3.7 (Si*C*H$_3$), 4.7 (Si*C*H$_3$), 5.0 (Si*C*H$_3$), 10.7 (*C*), 15.9 (*C*), 34.1 (*C*H$_2$), 34.8 (*C*H$_2$), 128.8 (*p*-*C*H), 129.1 (d, $^{3}J_{CP}$ = 7.1 Hz, *m*-*C*H), 135.3 (d, $^{1}J_{CP}$ = 22.7 Hz, *ipso*-*C*), 136.1 (d, $^{2}J_{CP}$ = 19.0 Hz, *o*-*C*H); ^{29}Si NMR (99 MHz, C_6D_6, 296 K) −15.1 (d, $^{3}J_{SiP}$ = 3.1 Hz, *Si*H), 3.2 (*Si*Me$_3$), 3.3 (*Si*Me$_3$), 4.0 (*Si*Me$_3$), 5.2 (*Si*Me$_3$), 18.5 (d, $^{2}J_{SiP}$ = 9.0 Hz, *Si* in three-membered ring), 107.0 (d, $^{2}J_{SiP}$ = 11.4 Hz, *Si*=Si-P), 141.3 (d, $^{1}J_{SiP}$ = 214.8 Hz, Si=*Si*-P); ^{31}P NMR (202 MHz, C_6D_6, 296 K) −23.2; UV-vis (hexane, 293 K) λ_{max}/nm (ε) 430 (5.2×10^3), 319 (1.7×10^4), 284 (2.3×10^4), 219 (sh, 6.1×10^4); HRMS (FD) Calcd for $C_{44}H_{91}Si_{12}P$ [M^+], 986.40895; Found, 986.40854; Anal. Calcd for $C_{44}H_{91}Si_{12}P$: C, 53.48; H, 9.28%. Found: C, 53.61; H, 9.28%.

NMR spectra

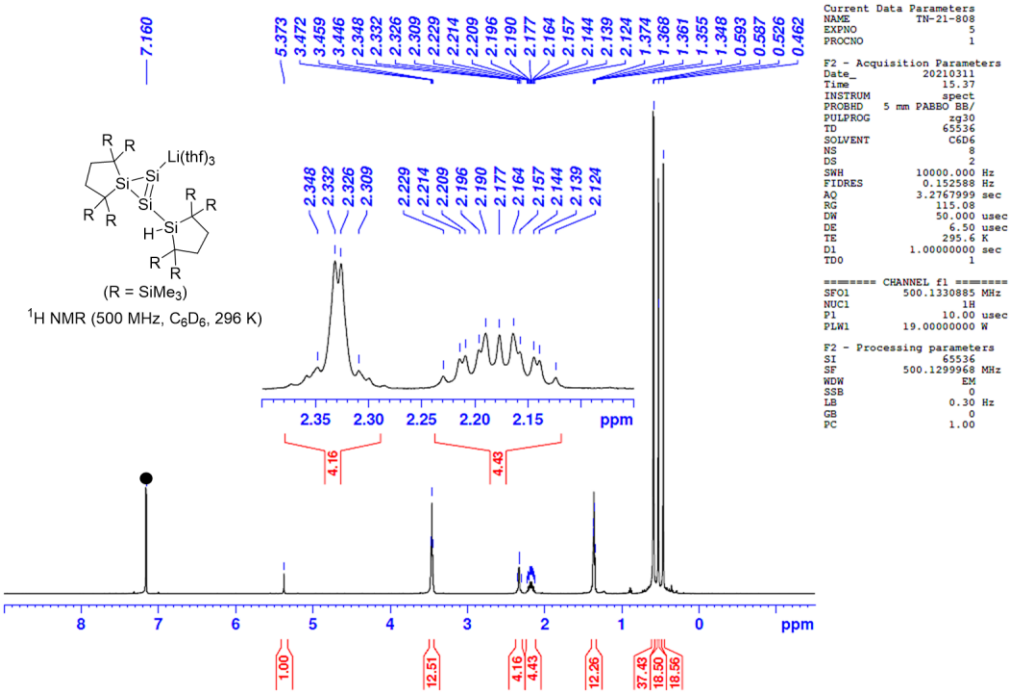


Figure 6-5. ^{1}H NMR spectrum of **2** in C_6D_6 at 296 K (● = C_6HD_5).

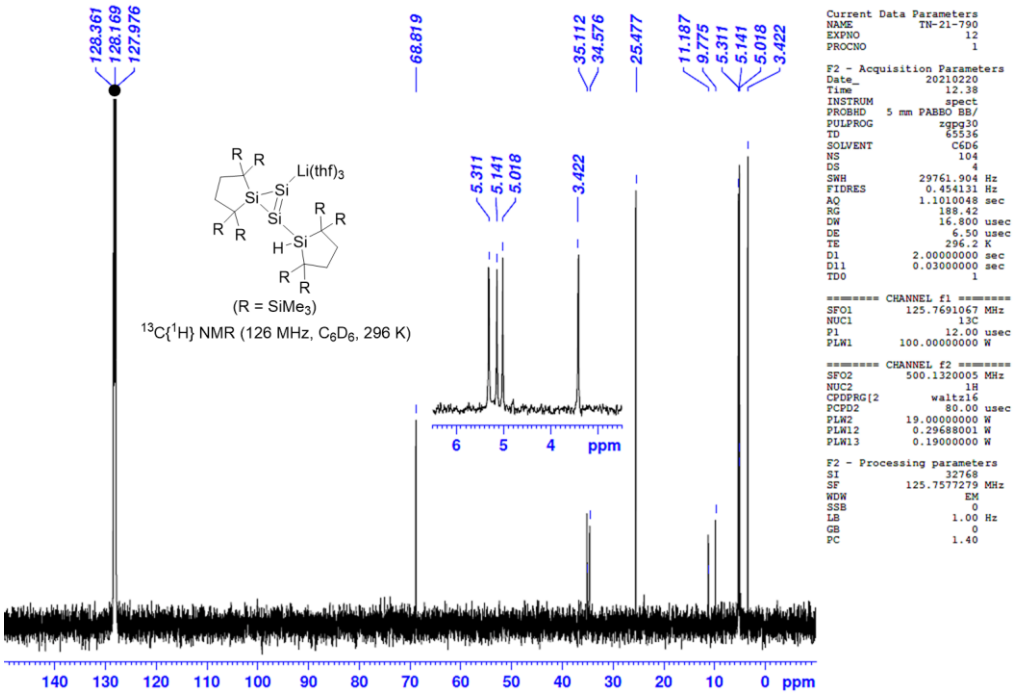


Figure 6-6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 in 296 K (● = C_6D_6).

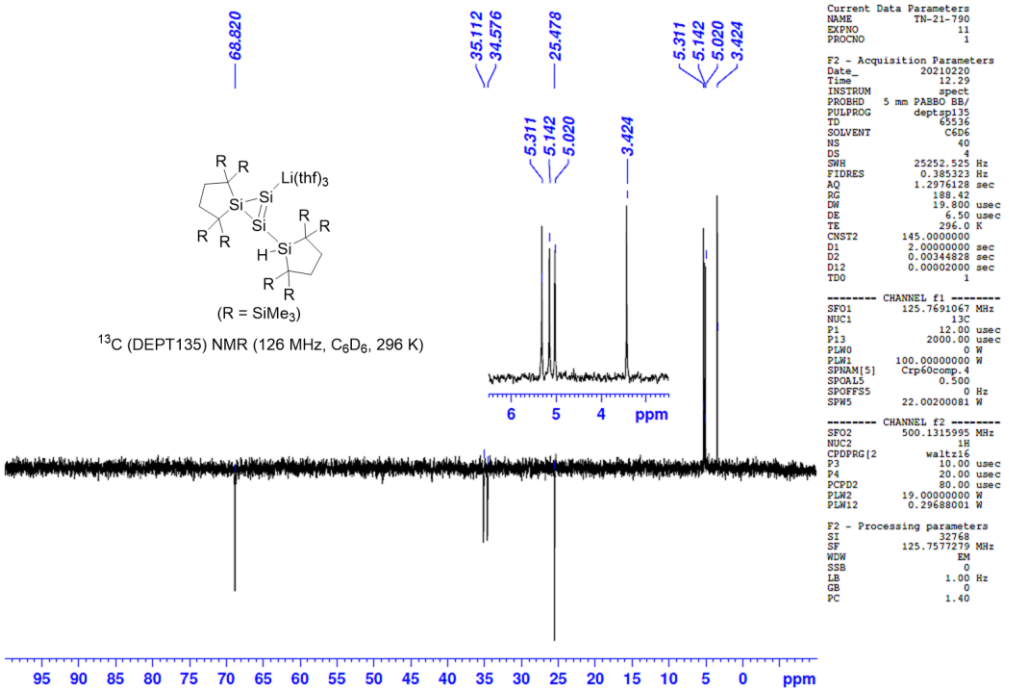


Figure 6-7. ^{13}C (DEPT135) NMR spectrum of **2** in C_6D_6 at 296 K.

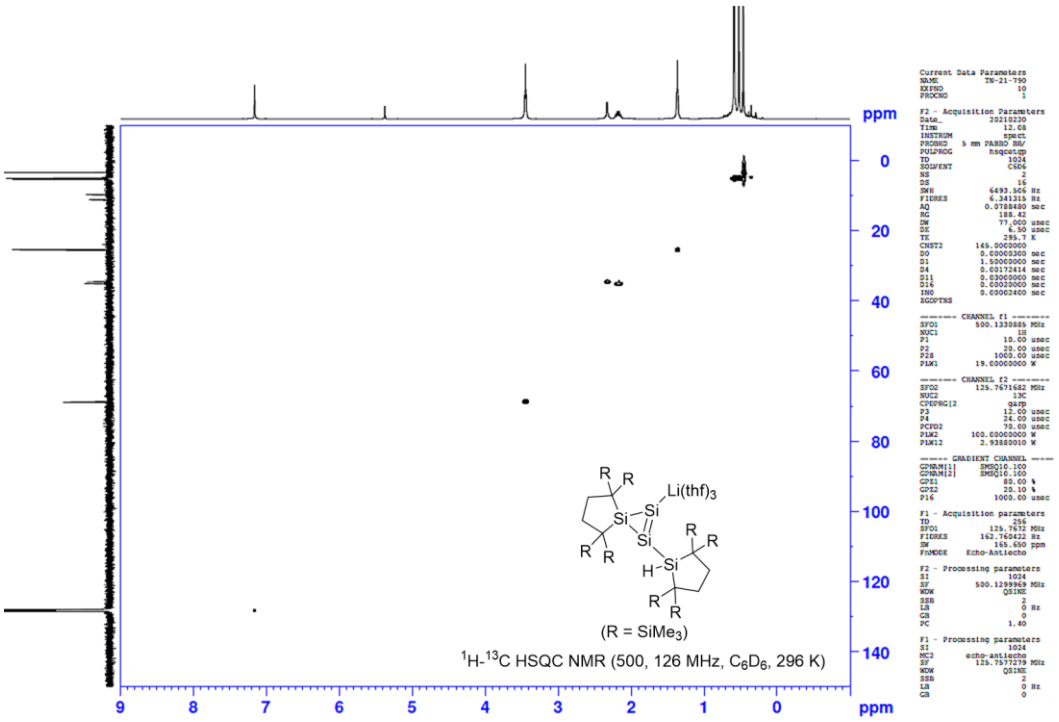


Figure 6-8. ^{1}H-^{13}C HSQC NMR spectrum of **2** in C_6D_6 at 296 K.

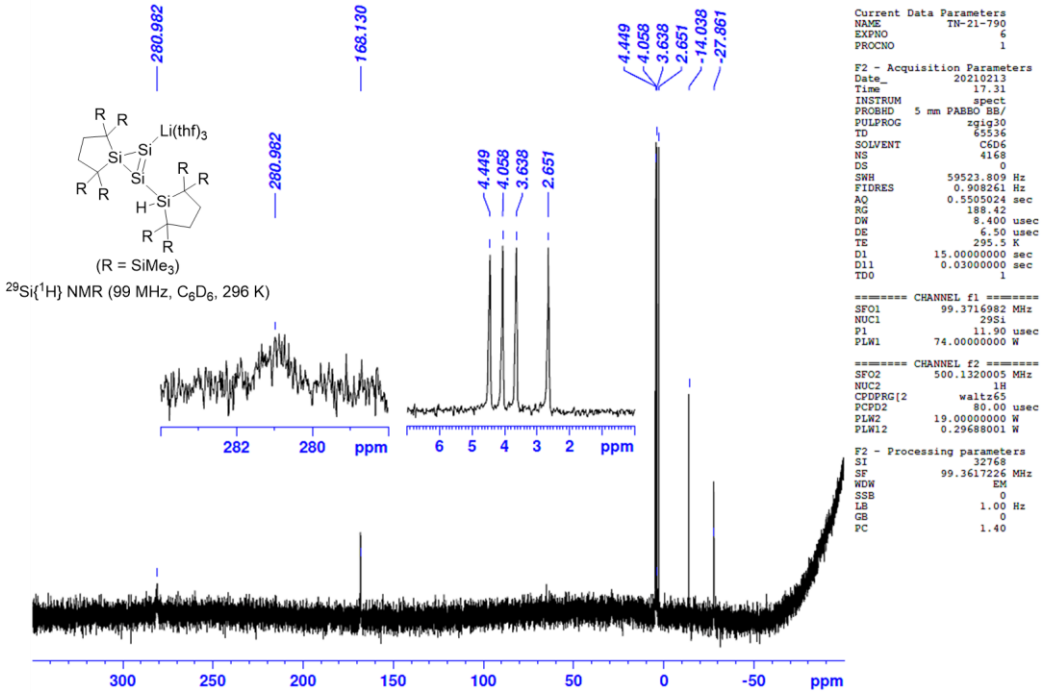


Figure 6-9. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 296 K.

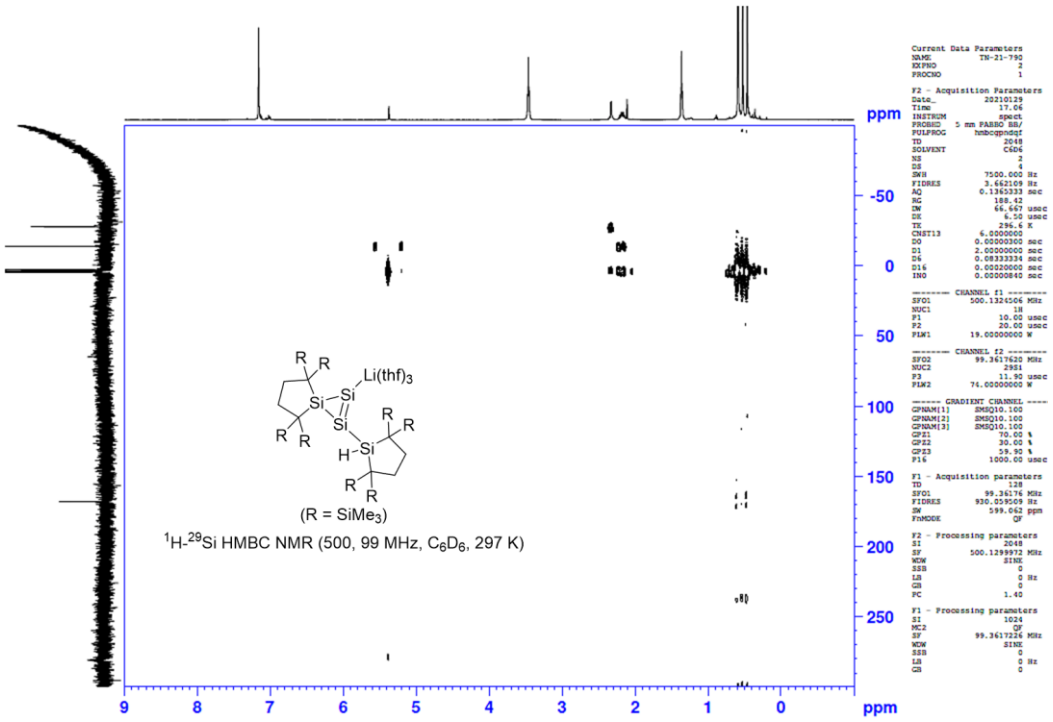


Figure 6-10. ^{1}H-^{29}Si HMBC NMR spectrum of **2** in C_6D_6 at 297 K.

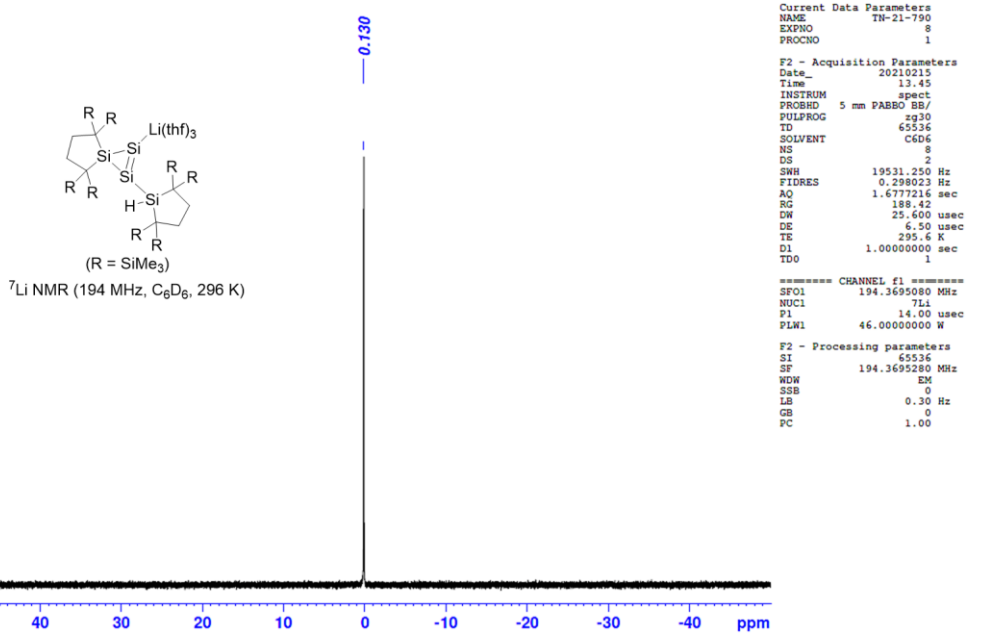


Figure 6-11. ^{7}Li NMR spectrum of **2** in C_6D_6 at 296 K.

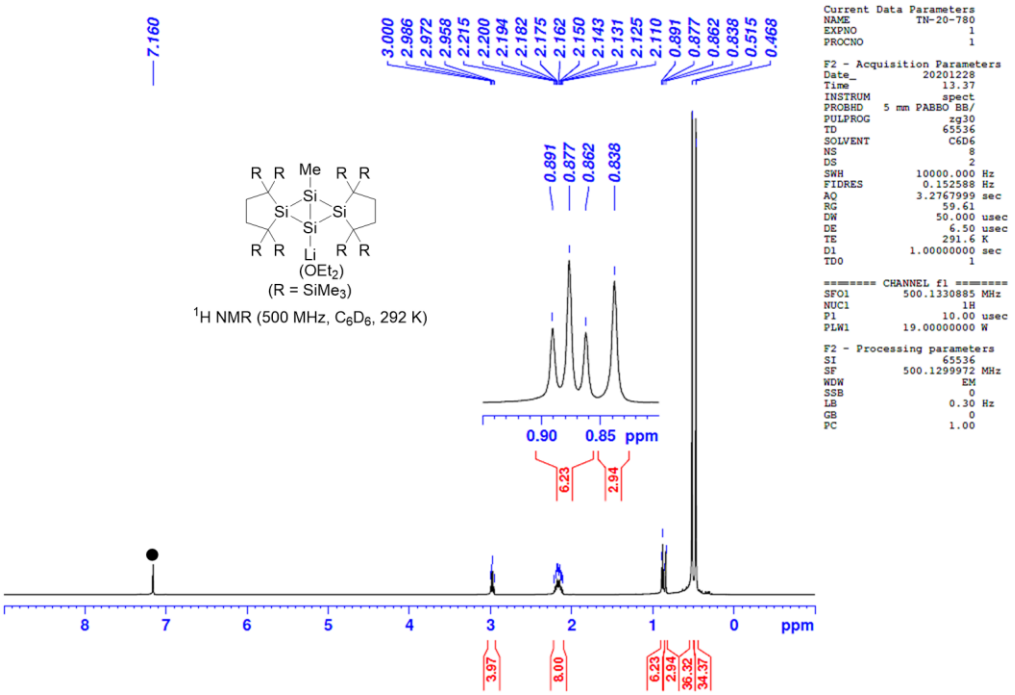


Figure 6-12. ^{1}H NMR spectrum of **3** in C_6D_6 at 292 K (● = C_6HD_5).

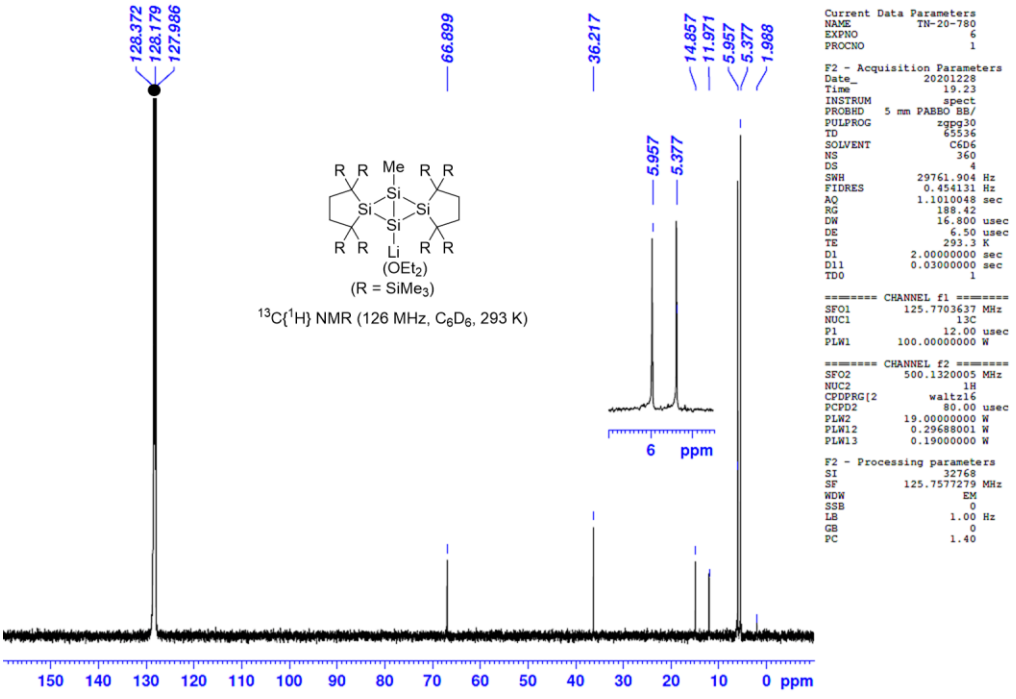


Figure 6-13. ^{13}C{^{1}H} NMR spectrum of **3** in C_6D_6 in 293 K (● = C_6D_6).

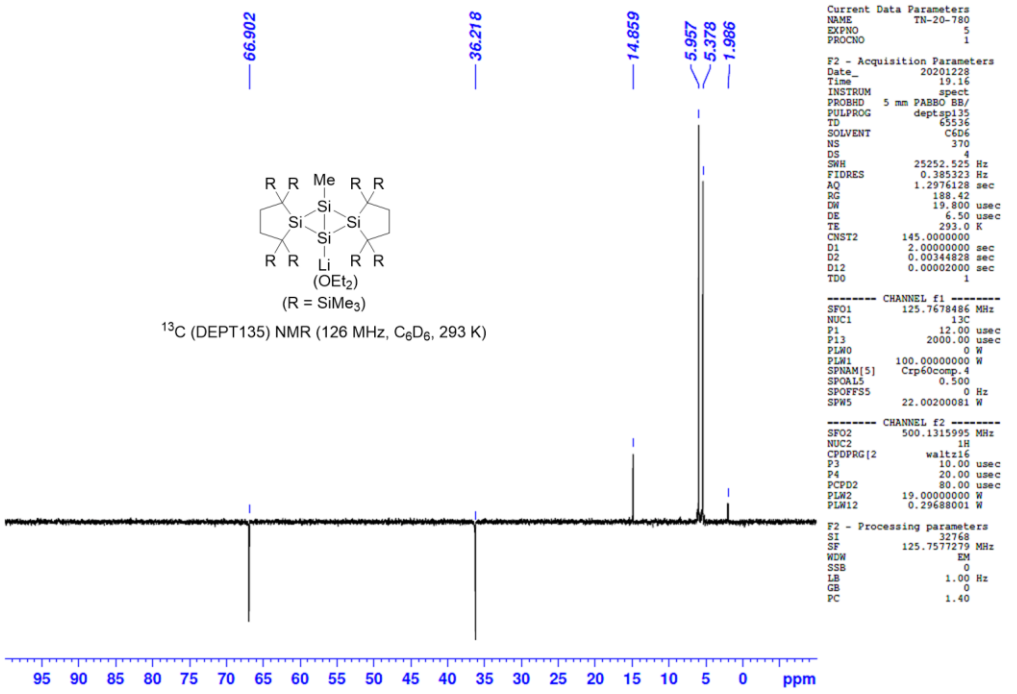


Figure 6-14. ^{13}C (DEPT135) NMR spectrum of **3** in C_6D_6 at 293 K.

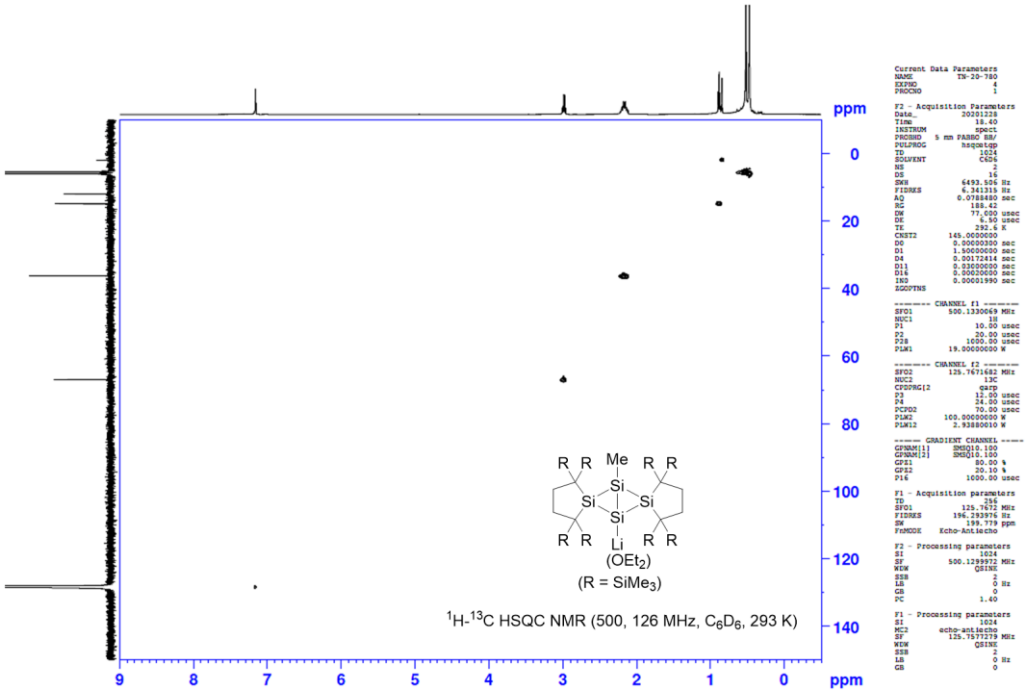


Figure 6-15. ^{1}H-^{13}C HSQC NMR spectrum of **3** in C_6D_6 at 293 K.

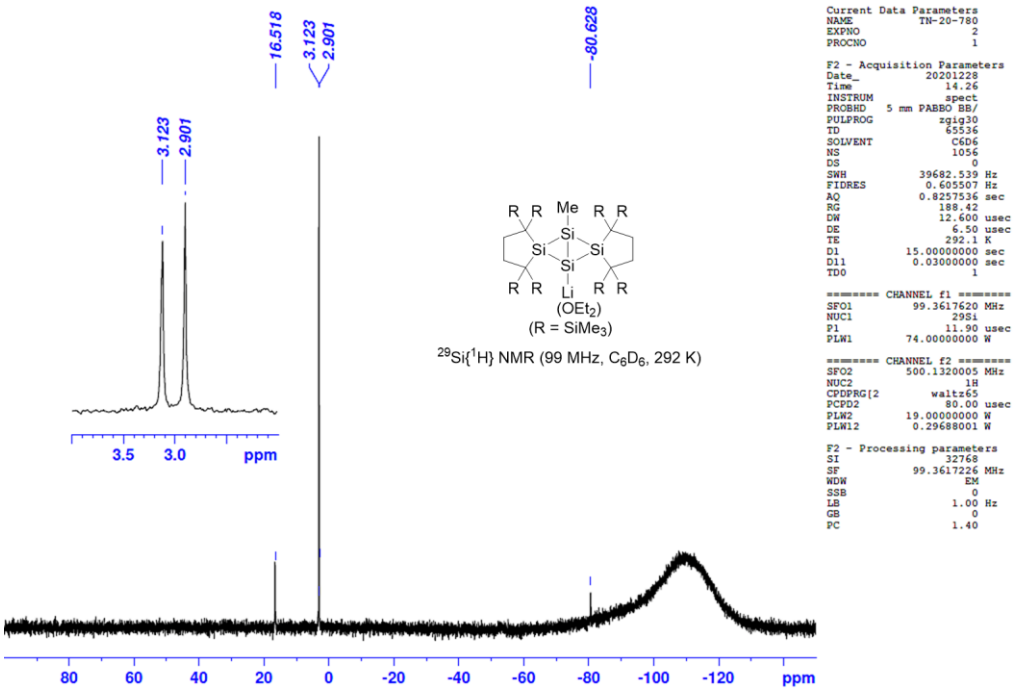


Figure 6-16. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 292 K.

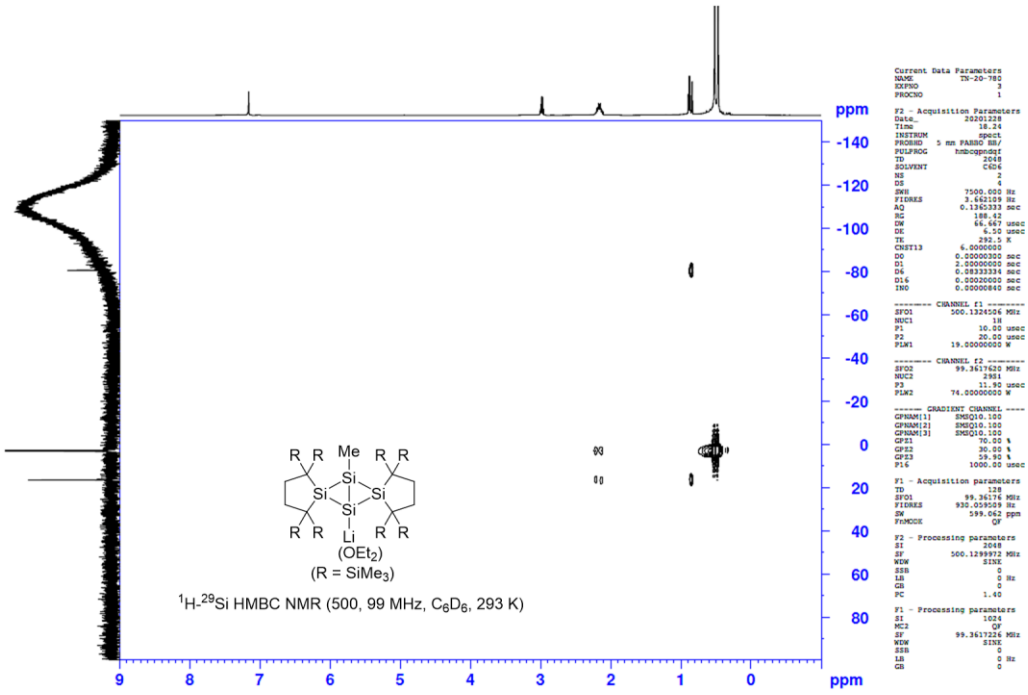


Figure 6-17. ^{1}H-^{29}Si HMBC NMR spectrum of **3** in C_6D_6 at 293 K.

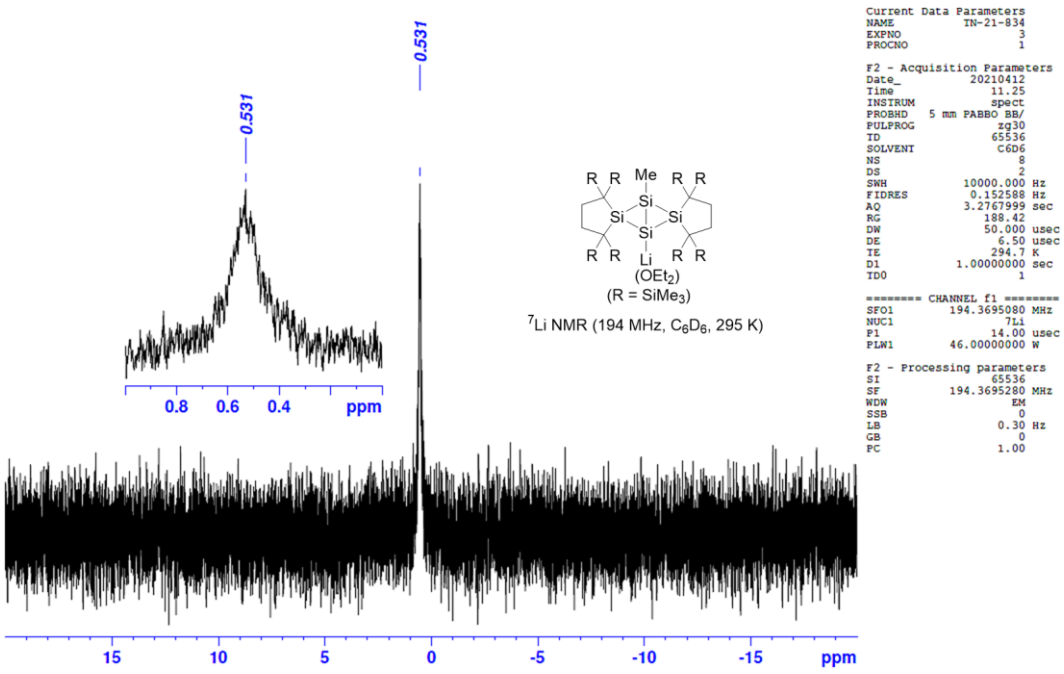


Figure 6-18. ^{7}Li NMR spectrum of **3** in C_6D_6 at 295 K.

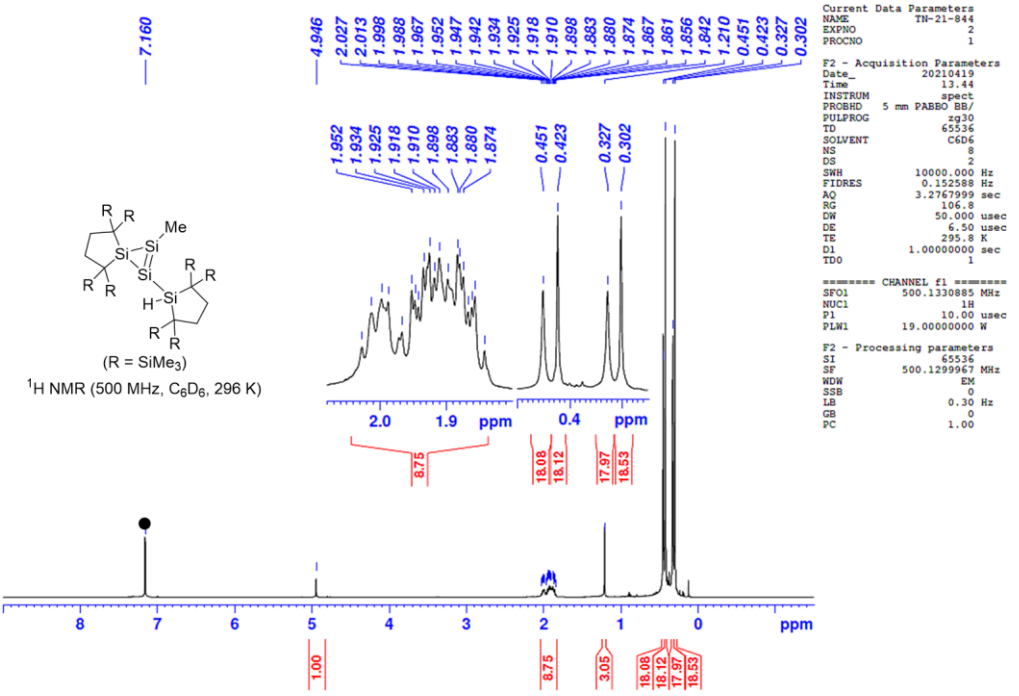


Figure 6-19. ^{1}H NMR spectrum of **4** in C_6D_6 at 296 K (● = C_6HD_5).

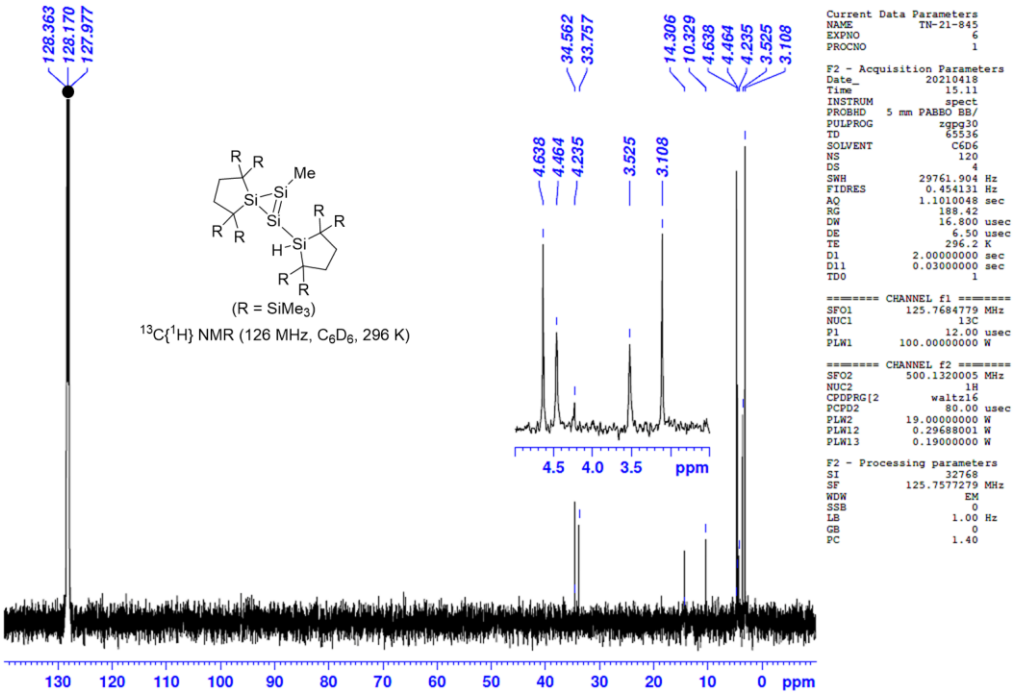


Figure 6-20. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 in 296 K (● = C_6D_6).

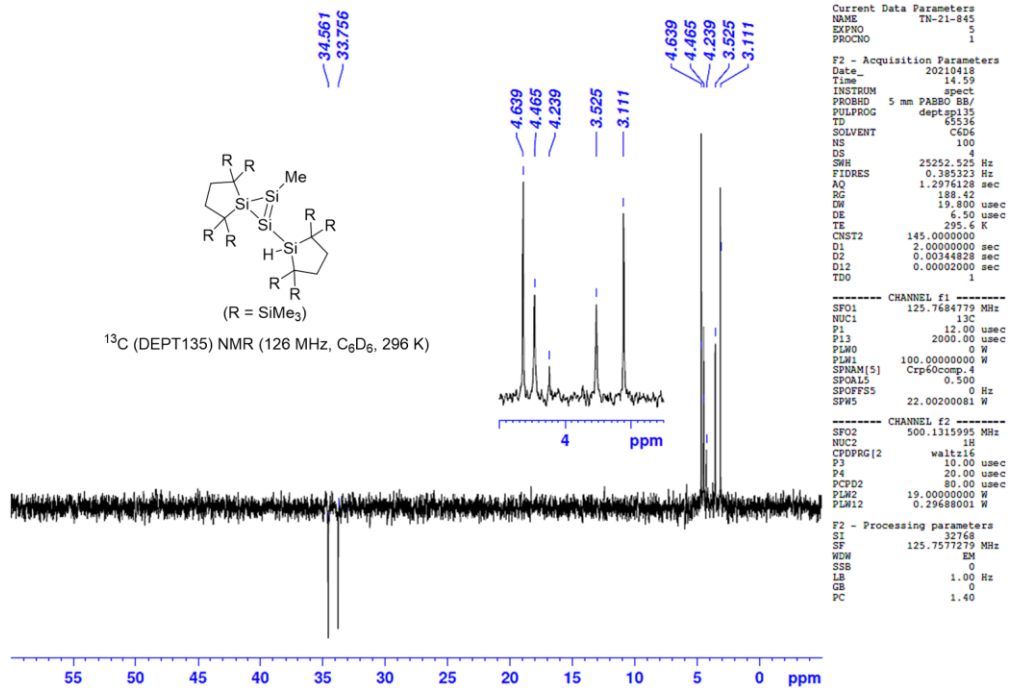


Figure 6-21. ^{13}C (DEPT135) NMR spectrum of **4** in C_6D_6 at 296 K.

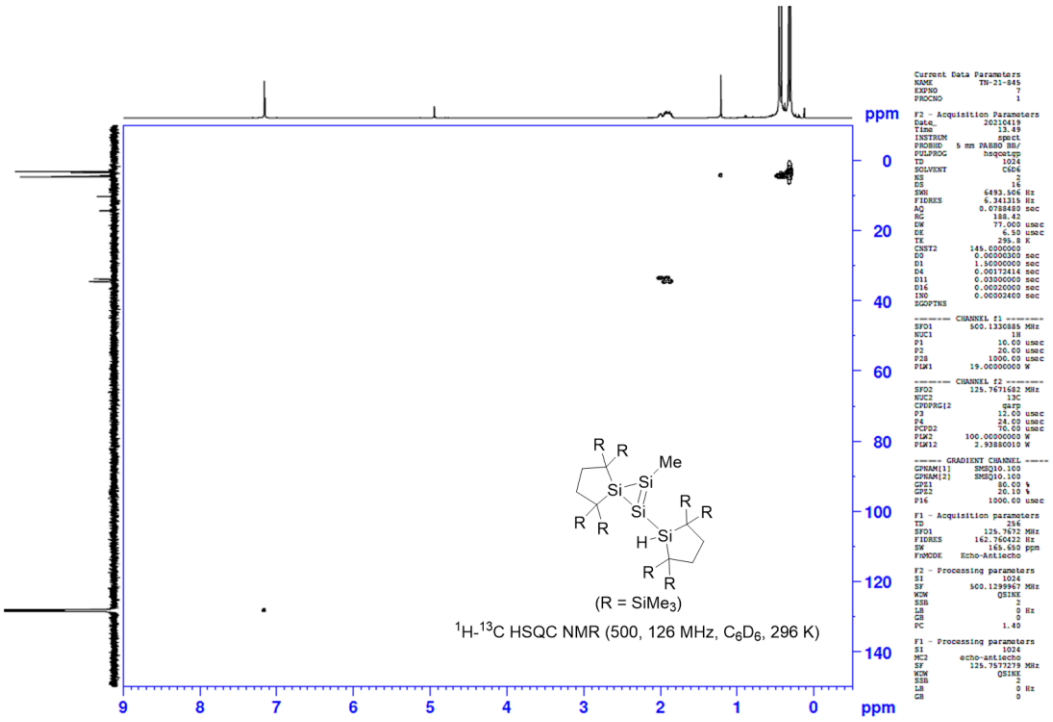


Figure 6-22. ^{1}H-^{13}C HSQC NMR spectrum of **4** in C_6D_6 at 296 K.

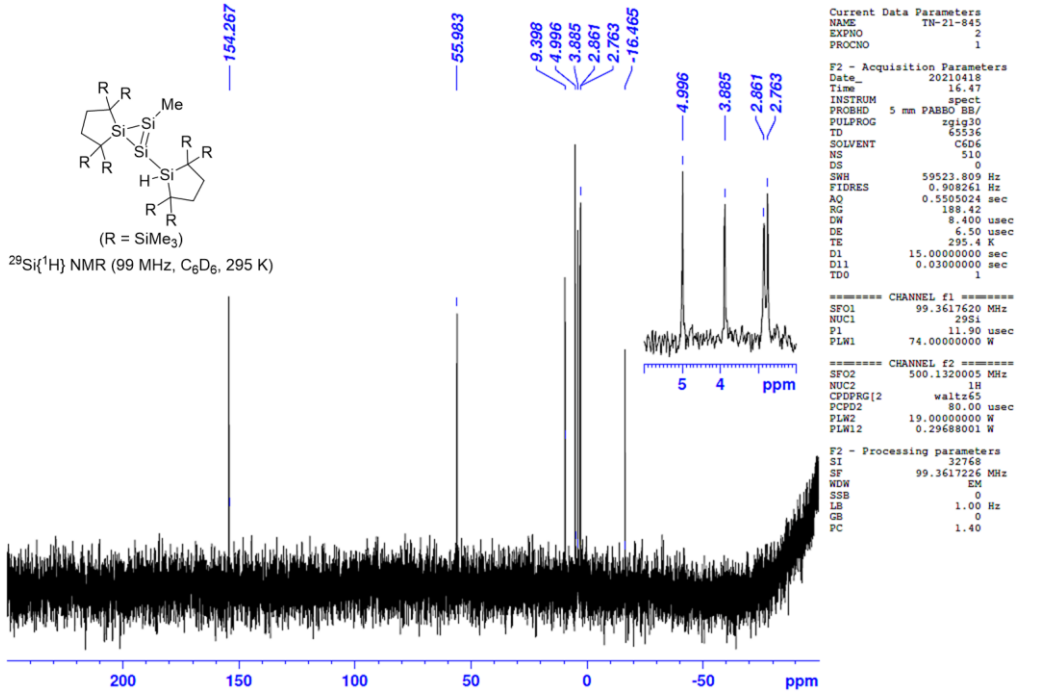


Figure 6-23. $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 295 K.

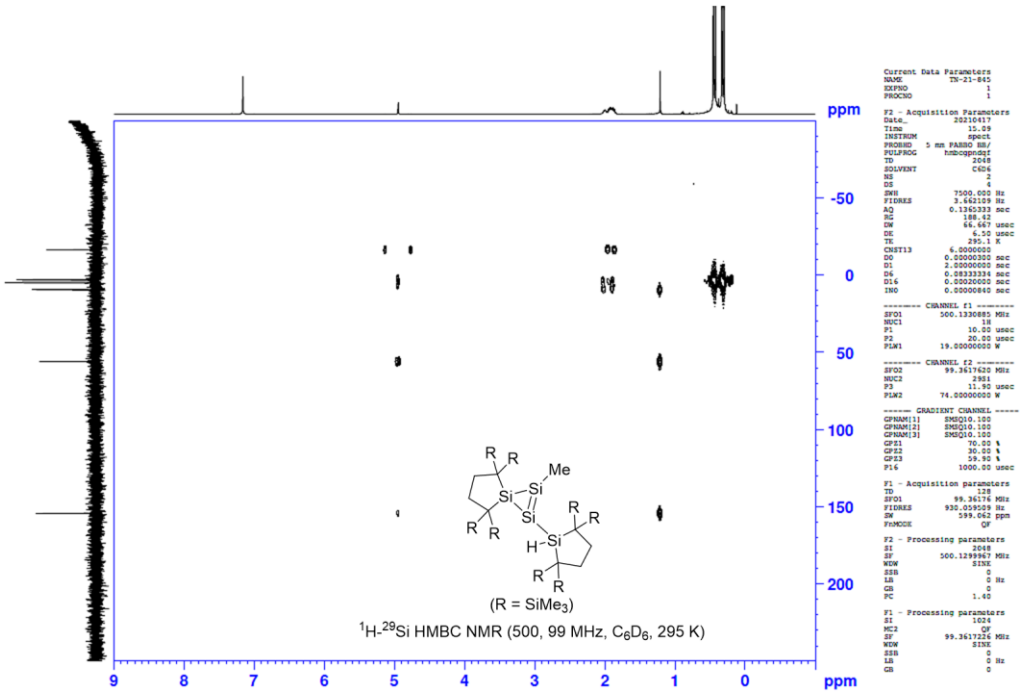


Figure 6-24. ^{1}H-^{29}Si HMBC NMR spectrum of **4** in C_6D_6 at 295 K.

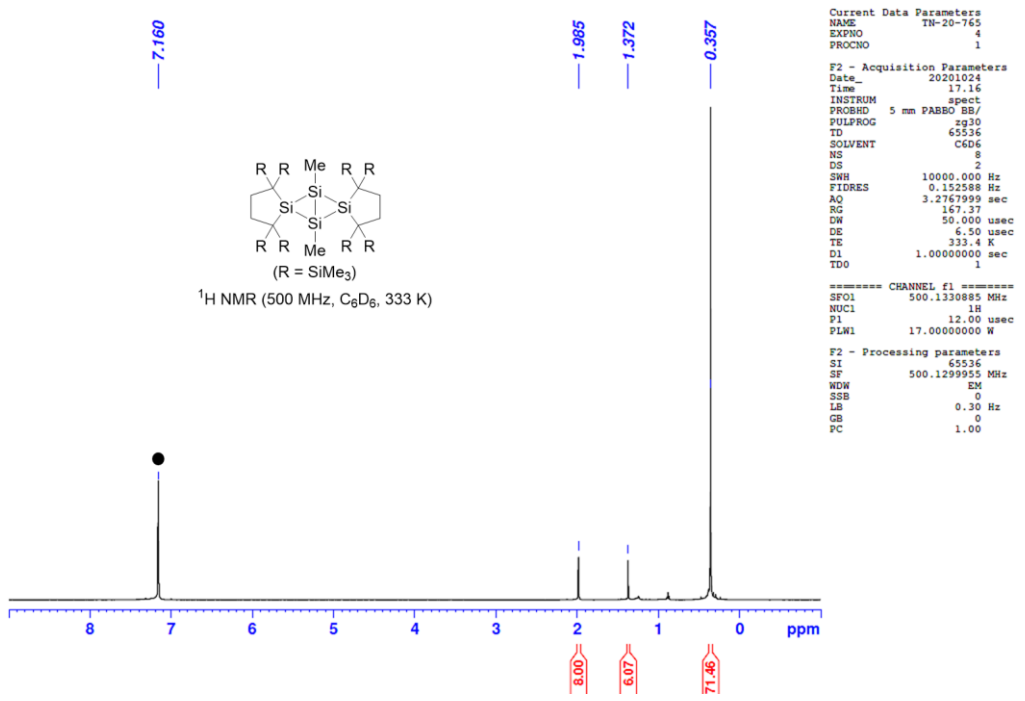


Figure 6-25. ^{1}H NMR spectrum of **5** in C_6D_6 at 333 K (● = C_6HD_5).

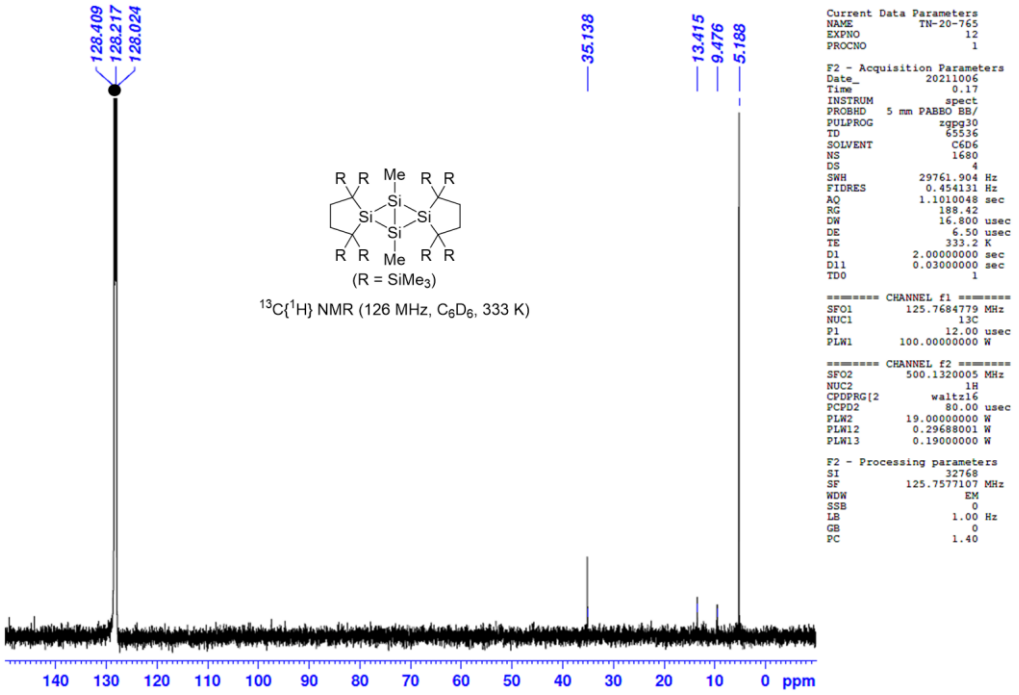


Figure 6-26. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 in 333 K (● = C_6D_6).

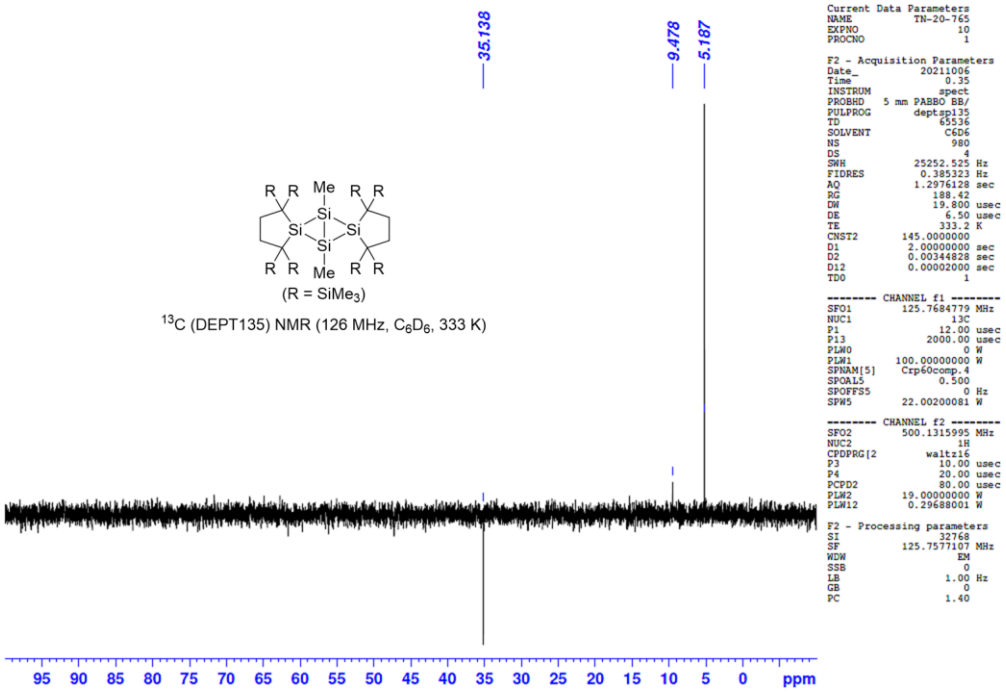


Figure 6-27. ^{13}C (DEPT135) NMR spectrum of **5** in C_6D_6 at 333 K.

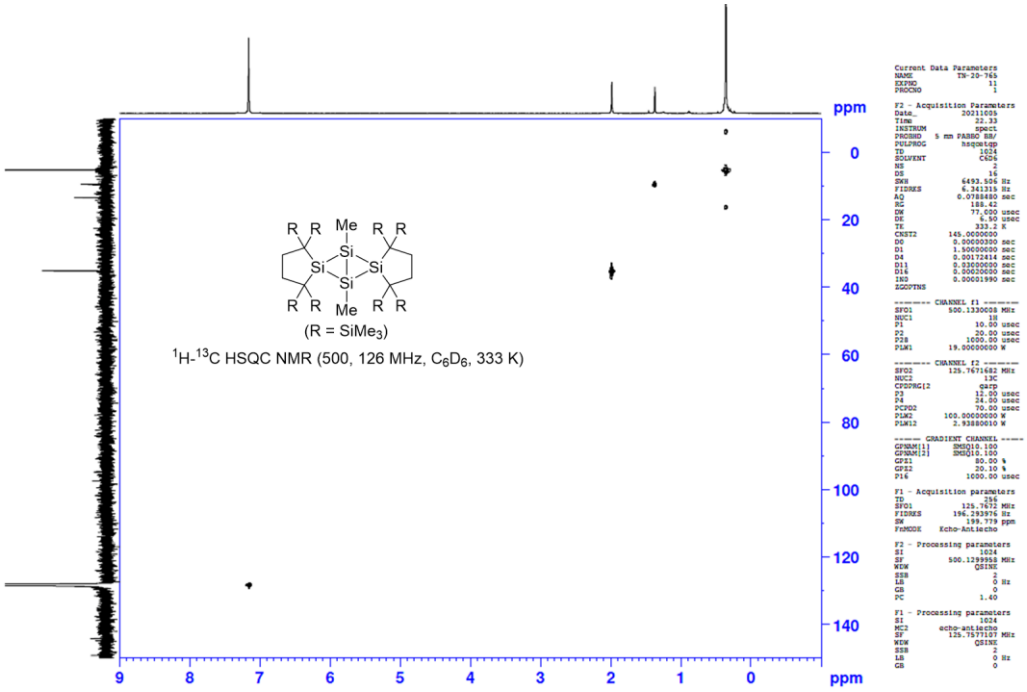


Figure 6-28. ^{1}H-^{13}C HSQC NMR spectrum of **5** in C_6D_6 at 333 K.

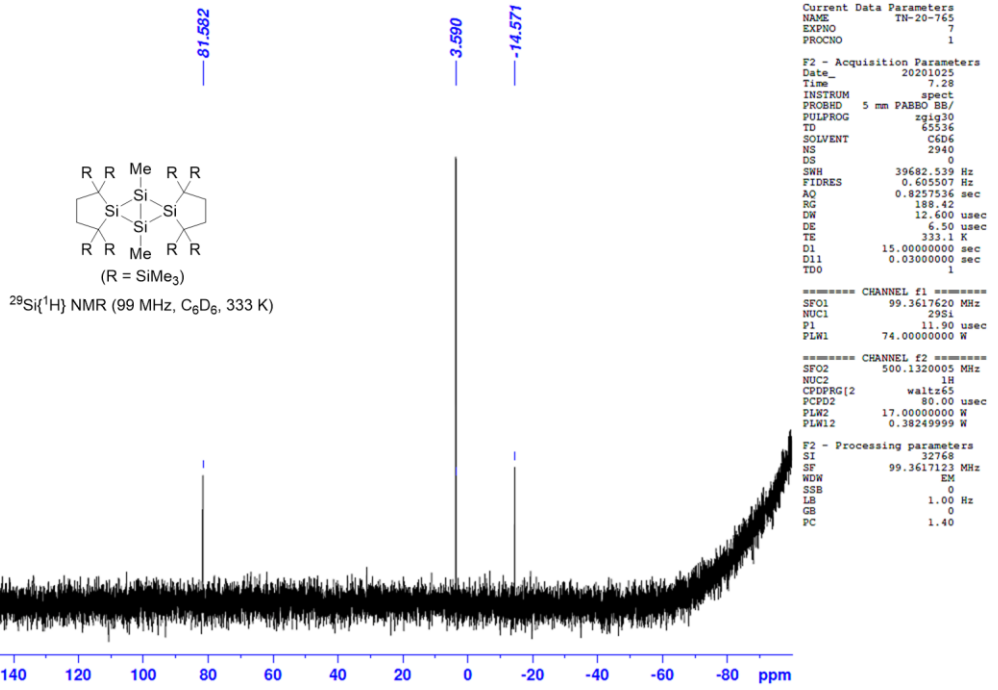


Figure 6-29. $^{29}Si\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 333 K.

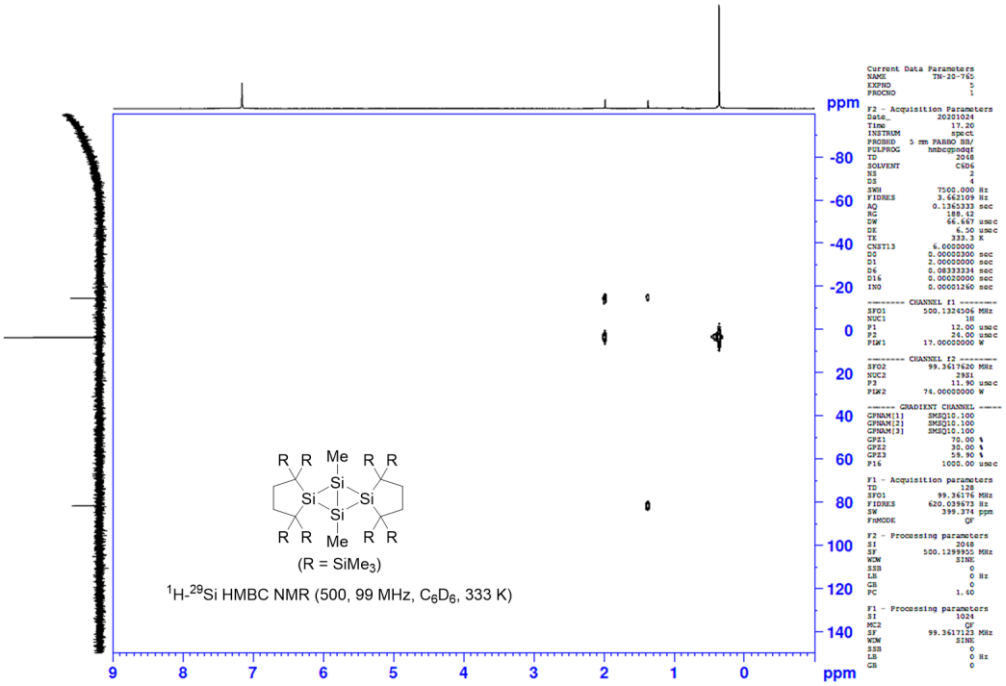


Figure 6-30. ^{1}H-^{29}Si HMBC NMR spectrum of **5** in C_6D_6 at 333 K.

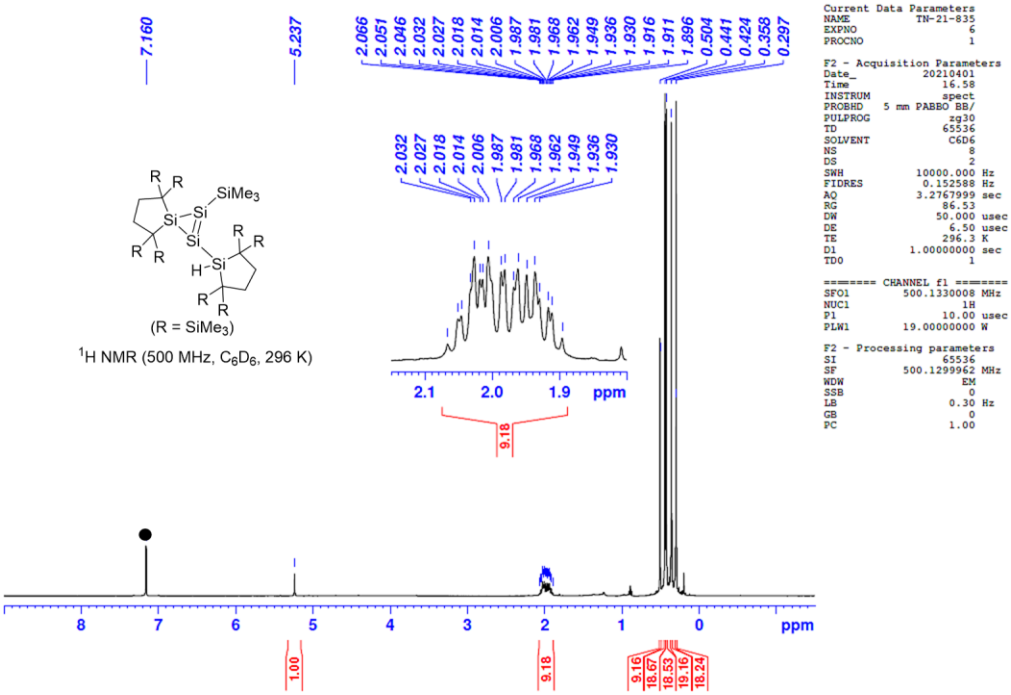


Figure 6-31. ^{1}H NMR spectrum of **7** in C_6D_6 at 296 K (● = C_6HD_5).

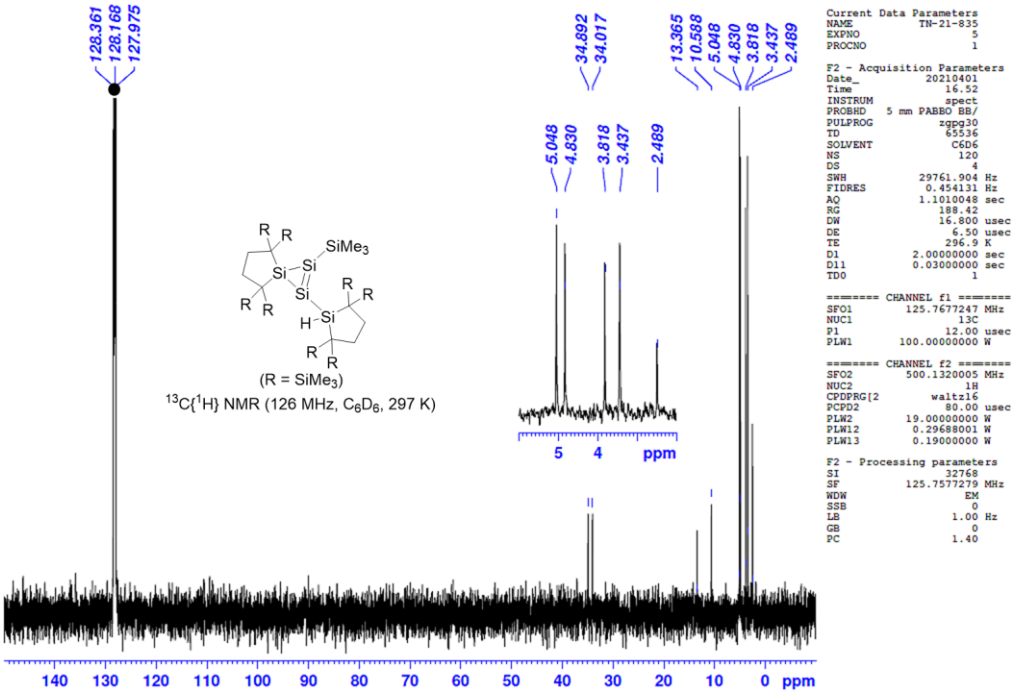


Figure 6-32. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 in 297 K (● = C_6D_6).

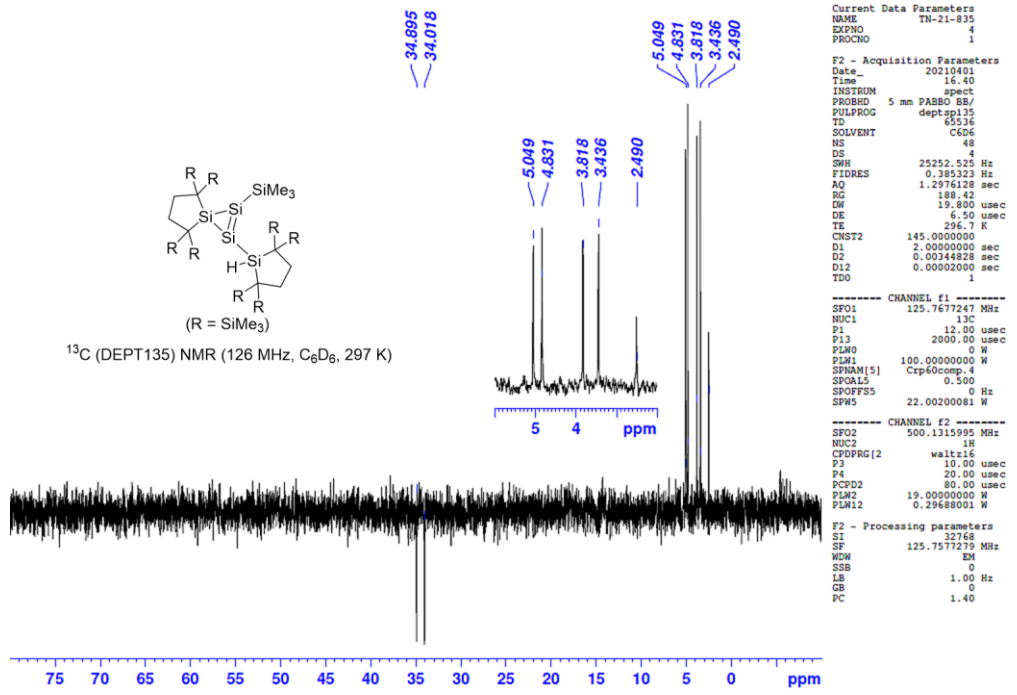


Figure 6-33. ^{13}C (DEPT135) NMR spectrum of **7** in C_6D_6 at 297 K.

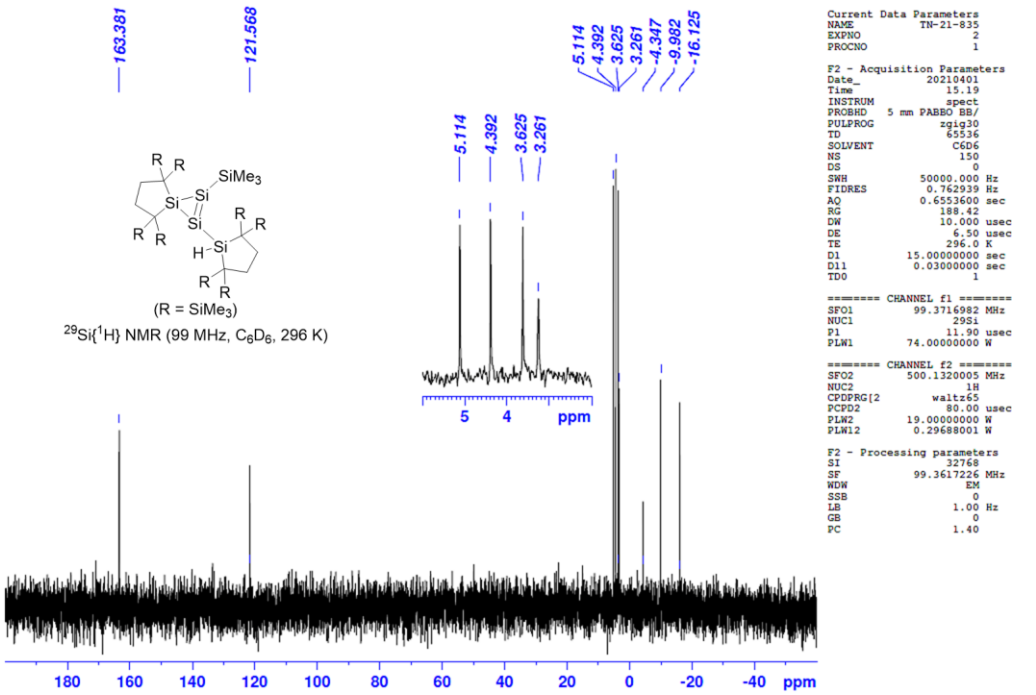


Figure 6-34. $^{29}Si\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 296 K.

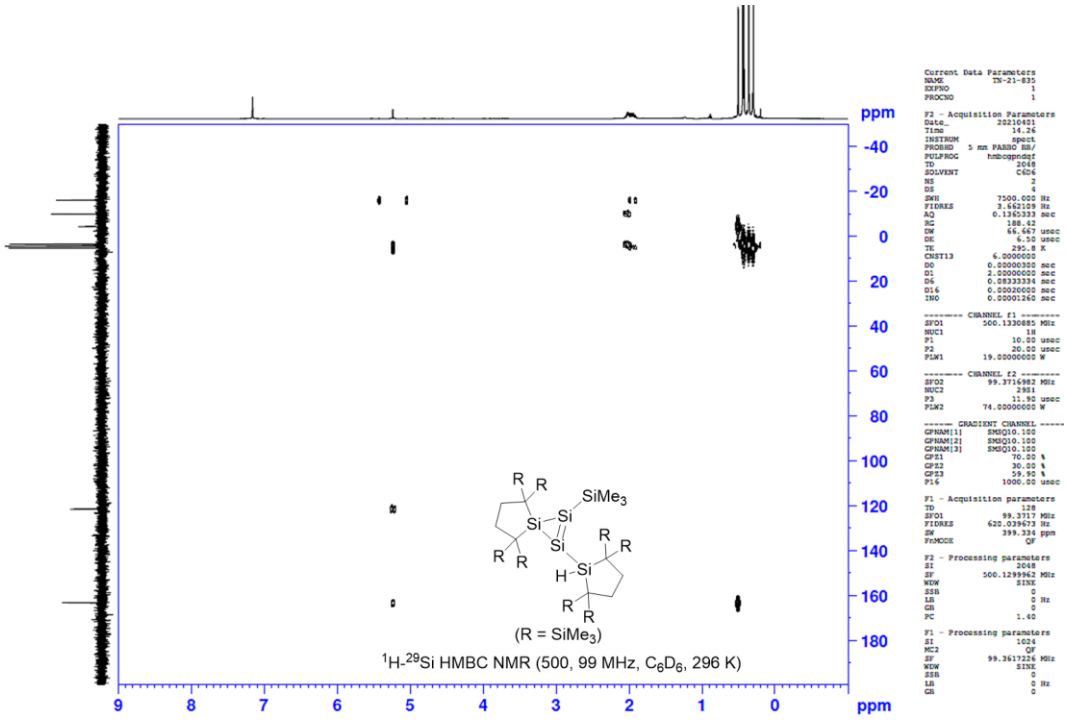


Figure 6-35. ^{1}H-^{29}Si HMBC NMR spectrum of **7** in C_6D_6 at 296 K.

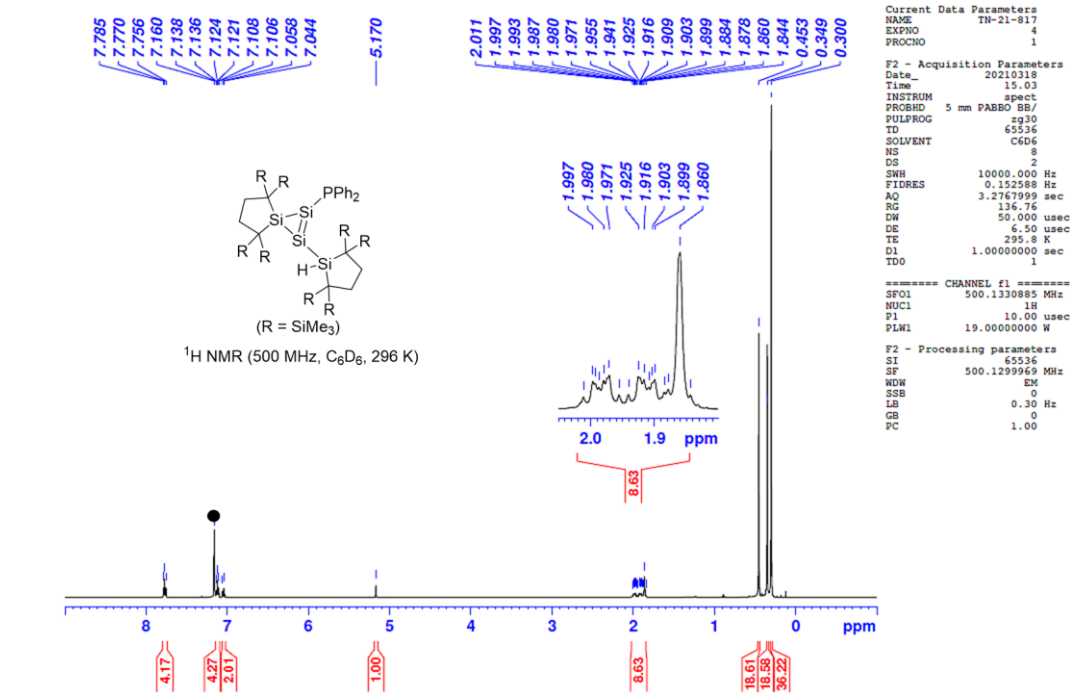


Figure 6-36. ^{1}H NMR spectrum of **8** in C_6D_6 at 296 K (● = C_6HD_5).

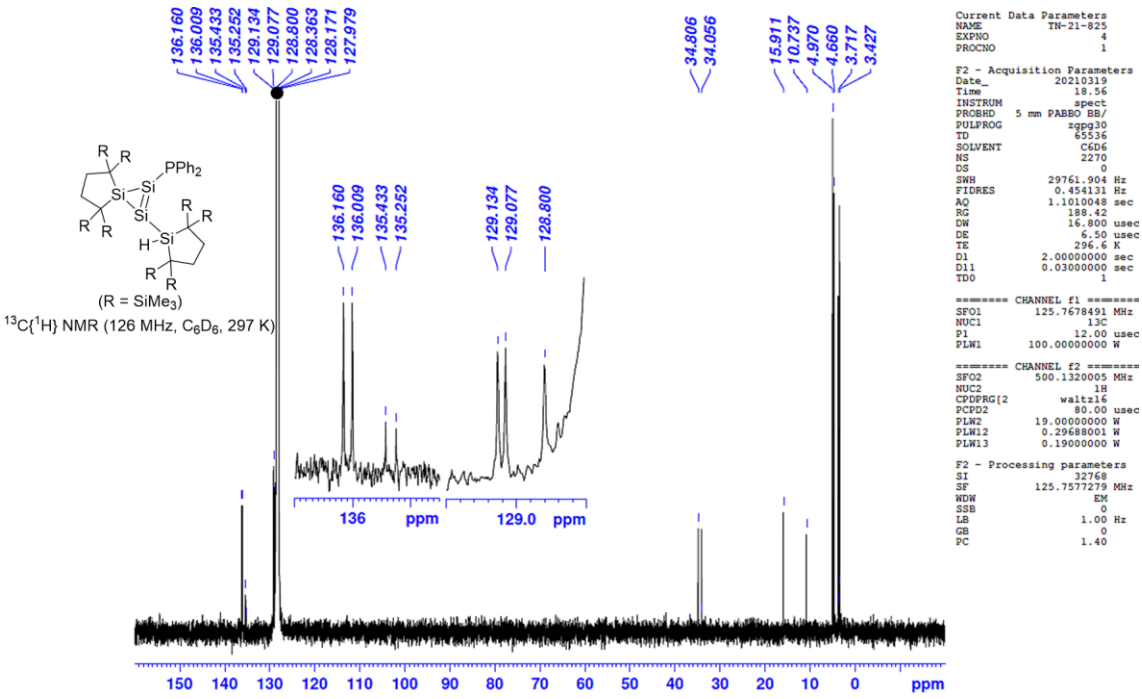


Figure 6-37. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 in 297 K (● = C_6D_6).

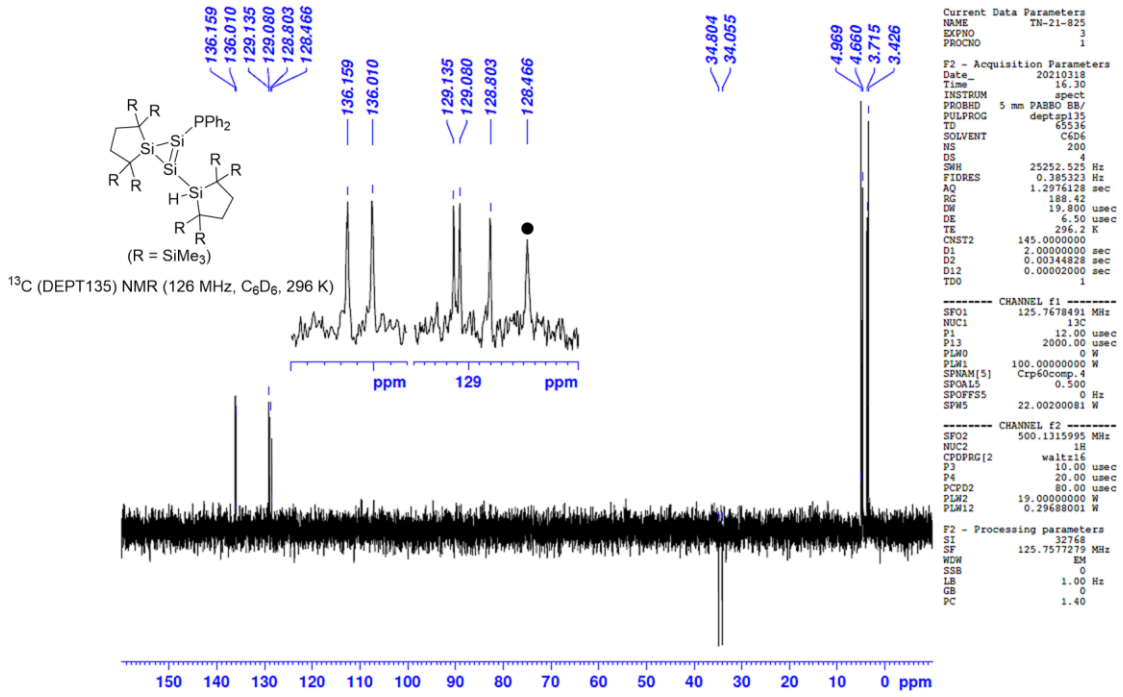


Figure 6-38. ^{13}C (DEPT135) NMR spectrum of **8** in C_6D_6 at 296 K (● = C_6D_6).

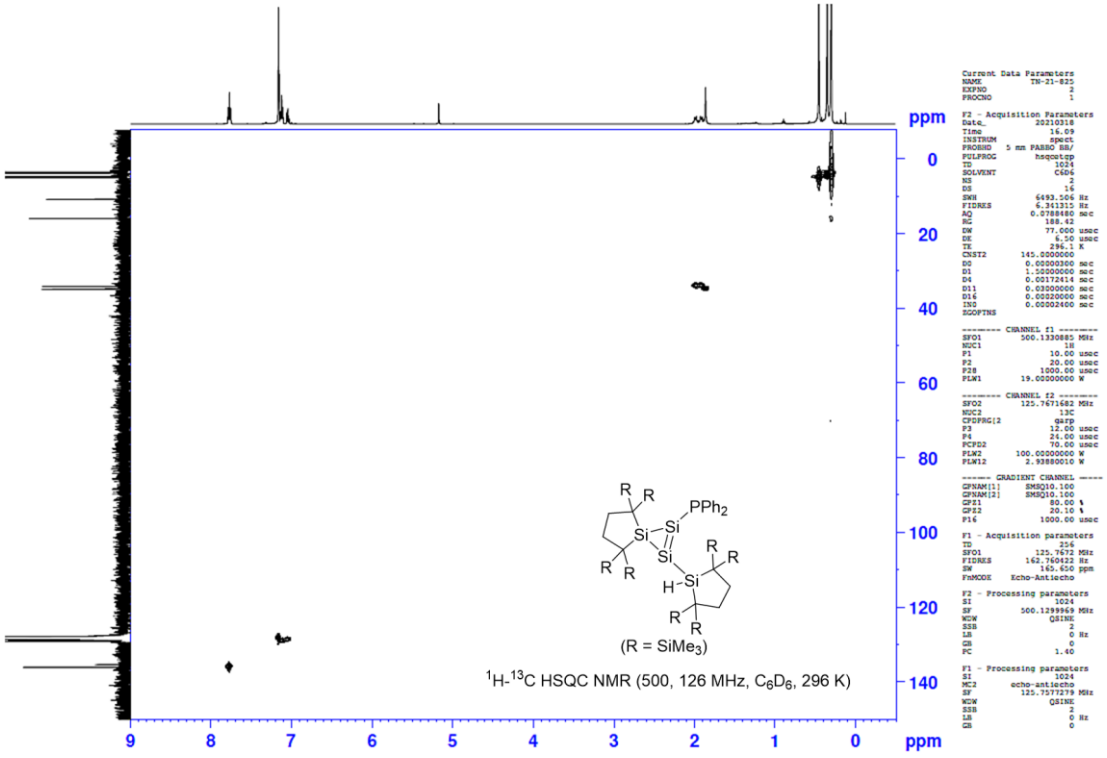


Figure 6-39. ^{1}H-^{13}C HSQC NMR spectrum of **8** in C_6D_6 at 296 K.

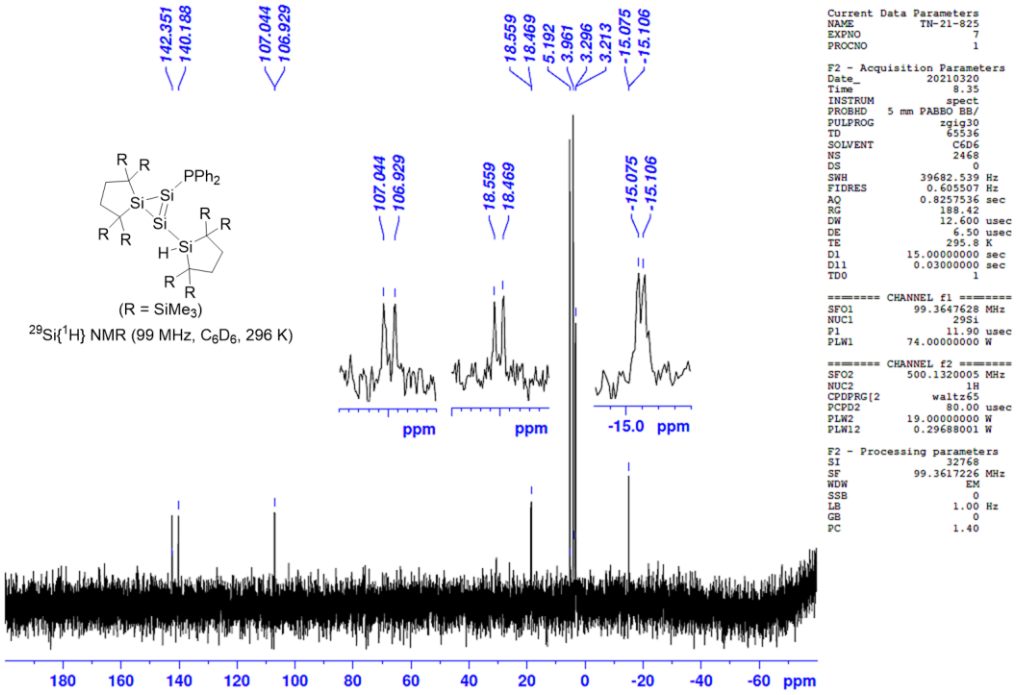


Figure 6-40. $^{29}Si\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 at 296 K.

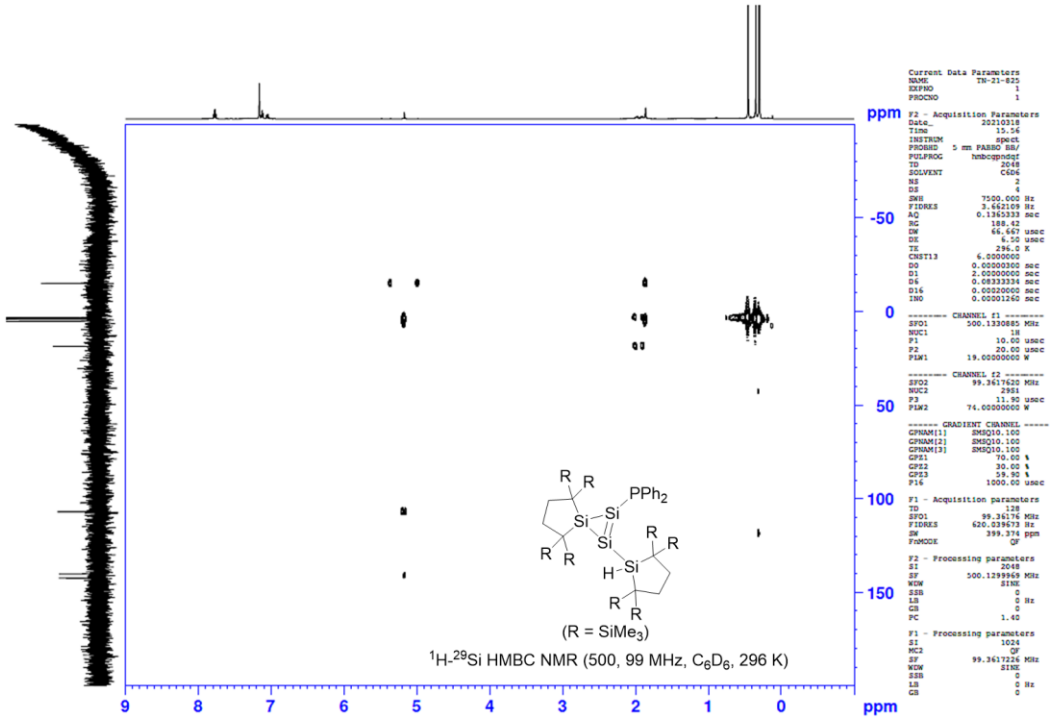


Figure 6-41. ^{1}H-^{29}Si HMBC NMR spectrum of **8** in C_6D_6 at 296 K.

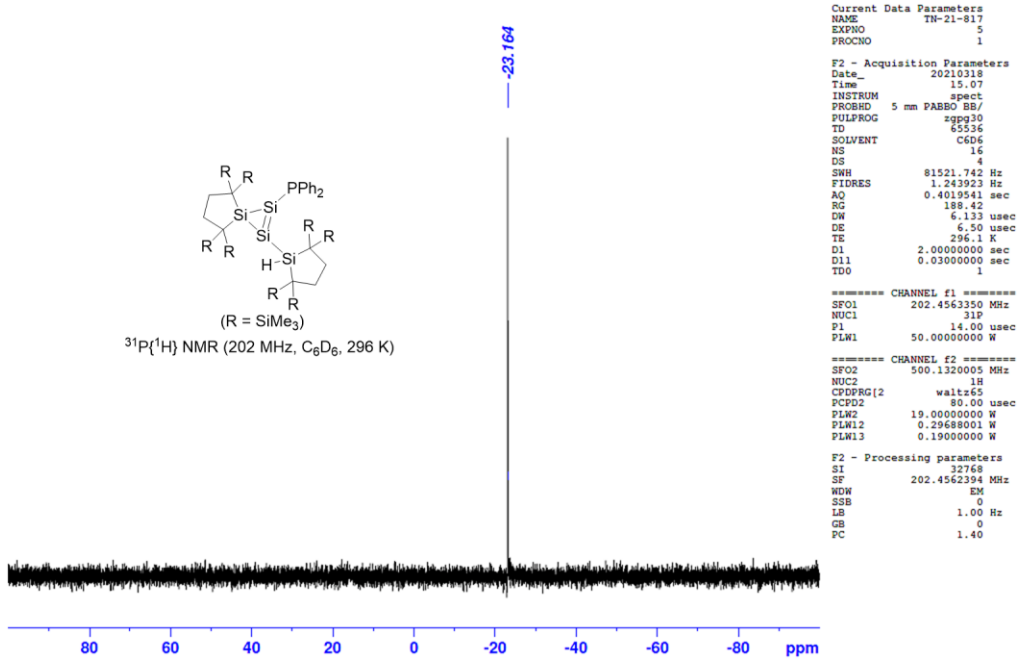


Figure 6-42. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 at 296 K.

X-ray Diffraction Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere using the following conditions; from pentane at −27 °C for cyclotrisilenide **2**, from toluene at −27 °C for silyl anion $\mathbf{3_{CIP}}$ (contact ion pair), from Et_2O at −27 °C for silyl anion $\mathbf{3_{SSIP}}$ (solvent-separated ion pair), from toluene at −27 °C for cyclotrisilene **4**, from benzene at room temperature for bicyclo[1.1.0]tetrasilane **5**, from hexane at −27 °C for cyclotrisilene **8**. For data collection, the single crystals coated by Apiezon grease were mounted on the glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer using a graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[26] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2014).[27] Molecular structure was analysed by Yadokari-XG software.[28]

Crystal data of cyclotrisilenide **2** [tn33f] (100 K) [CCDC-2109131]: $C_{44}H_{105}LiO_3Si_{12}$; Fw 1026.28; Monoclinic, $P2_1/c$, a = 13.0239(5) Å, b = 26.5332(9) Å, c = 20.0854(7) Å, β = 101.5760(10)˚, V = 6799.6(4) Å^3, Z = 4, D_{calc} = 1.073 Mg/m^3, $R1$ = 0.0458 ($I > 2\sigma(I)$), $wR2$ = 0.1243 (all data), GOF = 1.052.

Crystal data of silyl anion $\mathbf{3_{CIP}}$ [tn66a] (100 K) [CCDC-2109132]: $C_{37}H_{93}LiOSi_{12}$; Fw 898.11; Triclinic; P-1, a = 15.6180(15) Å, b = 18.3260(18) Å, c = 19.5473(19) Å, α = 79.580(2)˚, β = 85.086(2)˚, γ = 81.005(2)˚, V = 5425.3(9) Å^3, Z = 4, D_{calc} = 1.100 Mg/m^3, $R1$ = 0.0410 ($I > 2\sigma(I)$), $wR2$ = 0.1113 (all data), GOF = 1.030.

Crystal data of silyl anion $\mathbf{3_{SSIP}}$ [tn64b] (100 K) [CCDC-2109133]: $C_{49}H_{123}LiO_4Si_{12}$; Fw 1120.48; Orthorhombic, $Pna2_1$, a = 28.3355(18) Å, b = 16.0930(10) Å, c = 14.9192(10) Å, V = 6803.2(8) Å^3, Z = 4, D_{calc} = 1.094 Mg/m^3, $R1$ = 0.0408 ($I > 2\sigma(I)$), $wR2$ = 0.1123 (all data), GOF = 1.074.

Crystal data of cyclotrisilene **4** [tn50a] (100 K) [CCDC-2109134]: $C_{33}H_{84}Si_{12}$; Fw 818.06; Monoclinic, $P2_1/n$, a = 16.0494(9) Å, b = 16.6272(9) Å, c = 18.9919(10) Å, β = 99.6730(10)°, V = 4996.1(5) Å^3, Z = 4, D_{calc} = 1.088 Mg/m^3, $R1$ = 0.0355 ($I > 2\sigma(I)$), $wR2$ = 0.0940 (all data), GOF = 1.025.

Crystal data of bicyclo[1.1.0]tetrasilane **5** [tn63ba] (100 K) [CCDC-2114373]: $C_{34}H_{86}Si_{12}$; Fw 832.10; Triclinic, P-1, a = 11.9706(5) Å, b = 12.7911(7) Å, c = 17.8378(7) Å, α = 101.2600(10)˚, β = 100.1120(10)°, γ = 108.7420(10)˚, V = 2451.7(2) Å^3, Z = 2, D_{calc} = 1.127 Mg/m^3, $R1$ = 0.0378 ($I > 2\sigma(I)$), $wR2$ = 0.0922 (all data), GOF = 1.015.

Crystal data of cyclotrisilene **8** [tn83a] (100 K) [CCDC-2109135]: $C_{44}H_{91}Si_{12}P$; Fw 988.21; Monoclinic, $P2_1/n$, a = 11.5263(6) Å, b = 29.5998(16) Å, c = 17.3317(10) Å, β = 103.9400(10)°, V = 5739.0(5) Å^3, Z = 4, D_{calc} = 1.144 Mg/m^3, $R1$ = 0.0326 ($I > 2\sigma(I)$), $wR2$ = 0.0881 (all data), GOF = 1.040.

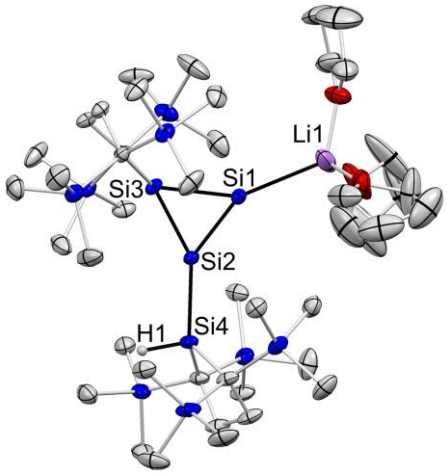


Figure 6-43. ORTEP of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, co-crystallized solvent, and disordered atoms are omitted for clarity.

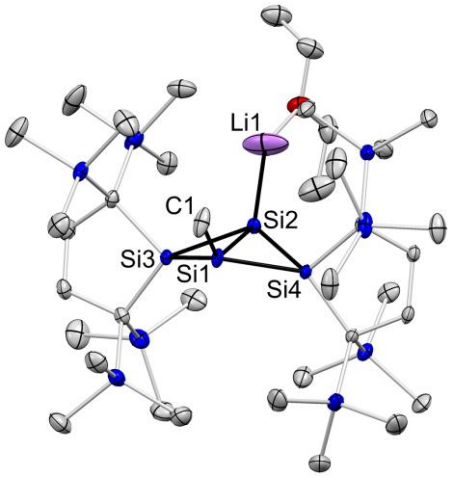


Figure 6-44. ORTEP of $\mathbf{3_{CIP}}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

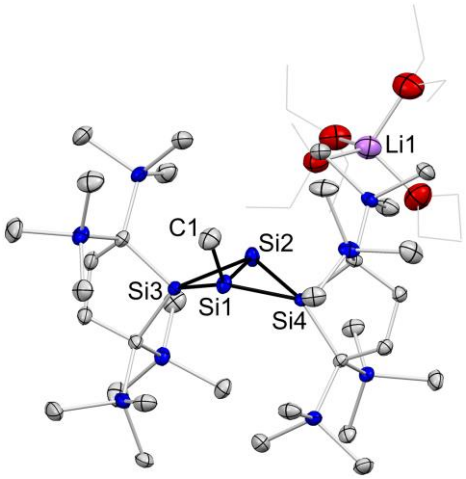


Figure 6-45. ORTEP of $\mathbf{3_{SSIP}}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

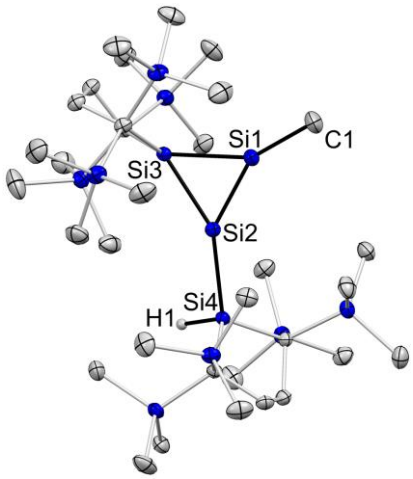


Figure 6-46. ORTEP of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

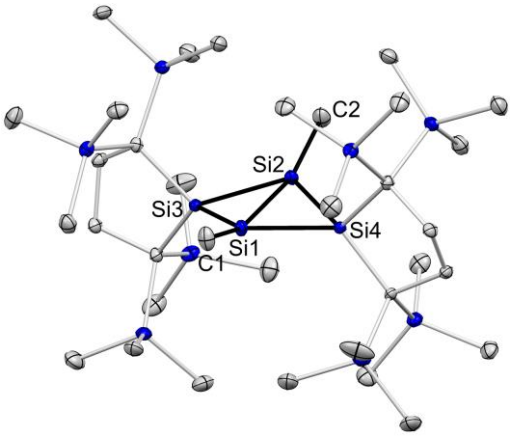


Figure 6-47. ORTEP of **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

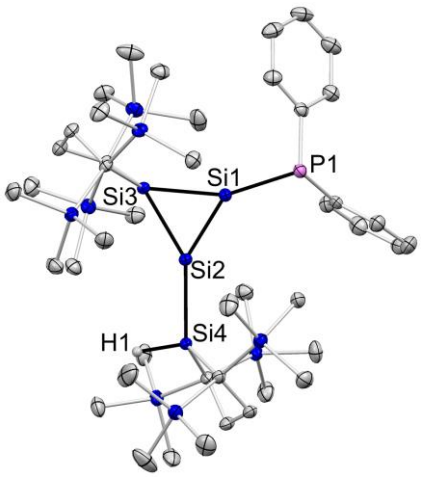


Figure 6-48. ORTEP of **8**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

UV-vis Absorption Spectrum

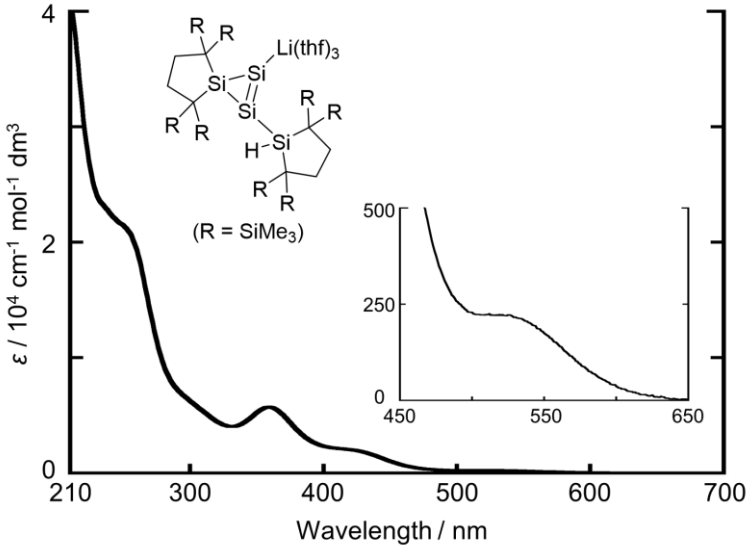


Figure 6-49. UV-vis absorption spectrum of **2** in hexane at room temperature [TN790].

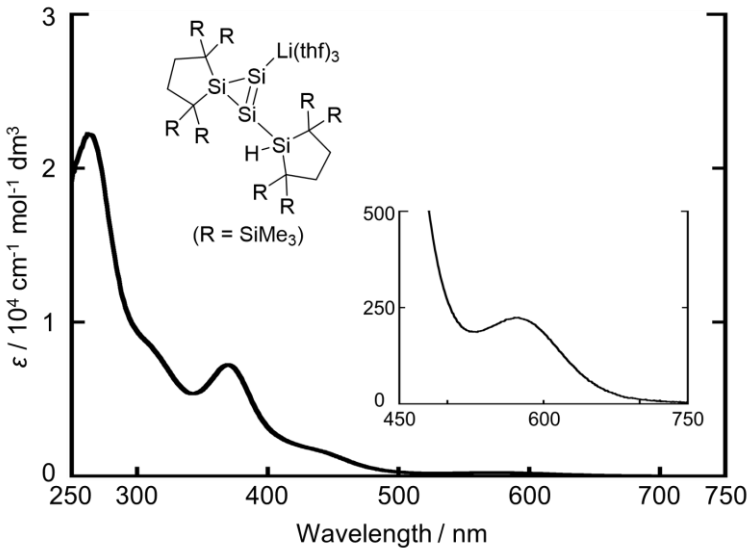


Figure 6-50. UV-vis absorption spectrum of **2** in THF at room temperature [TN790].

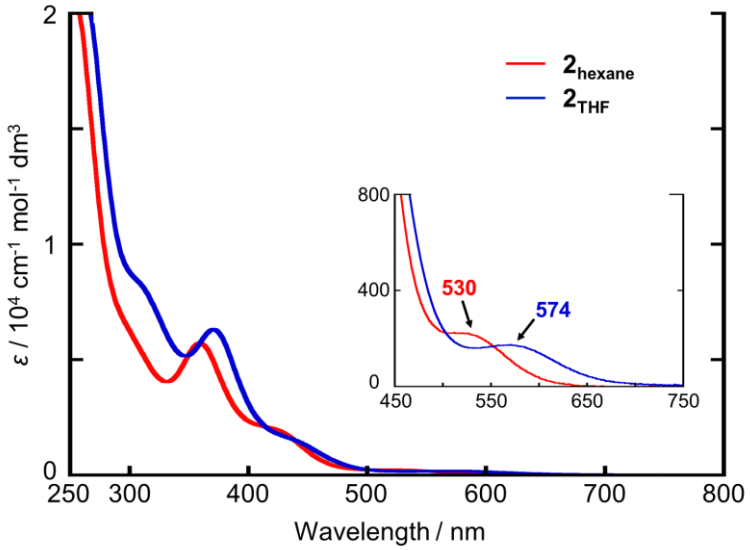


Figure 6-51. UV-vis absorption spectra of **2** at room temperature (red: hexane, blue: THF).

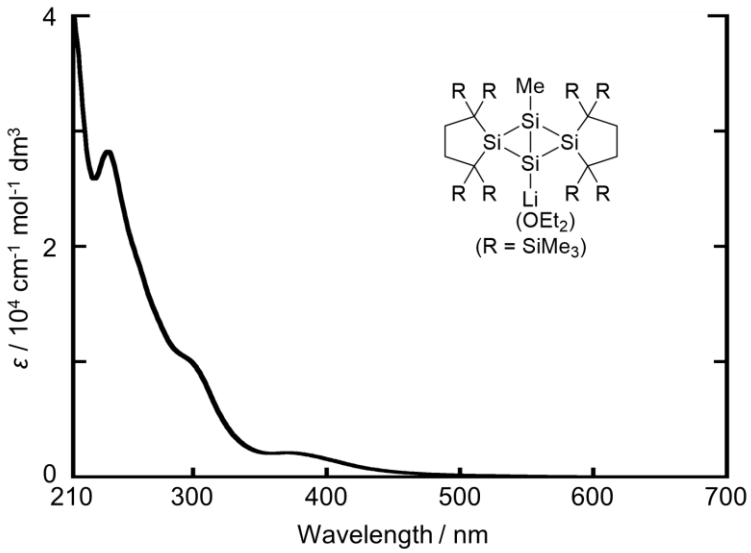


Figure 6-52. UV-vis absorption spectrum of **3** in hexane at room temperature [TN780].

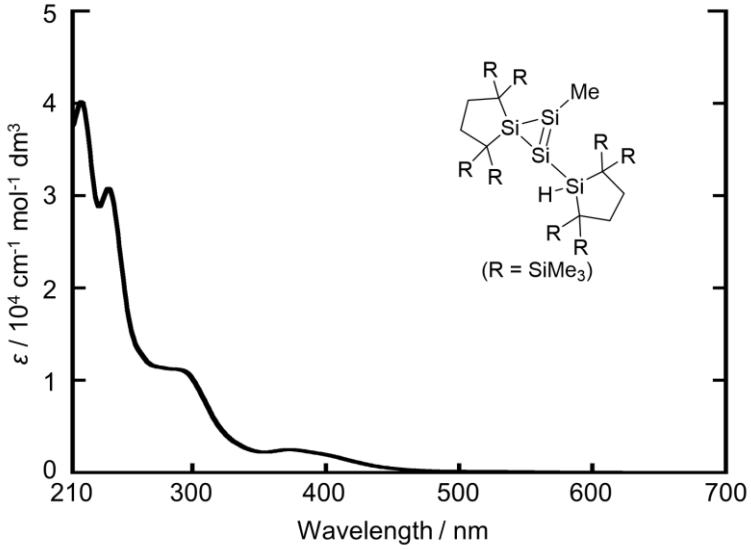


Figure 6-53. UV-vis absorption spectrum of **4** in hexane at room temperature [TN845].

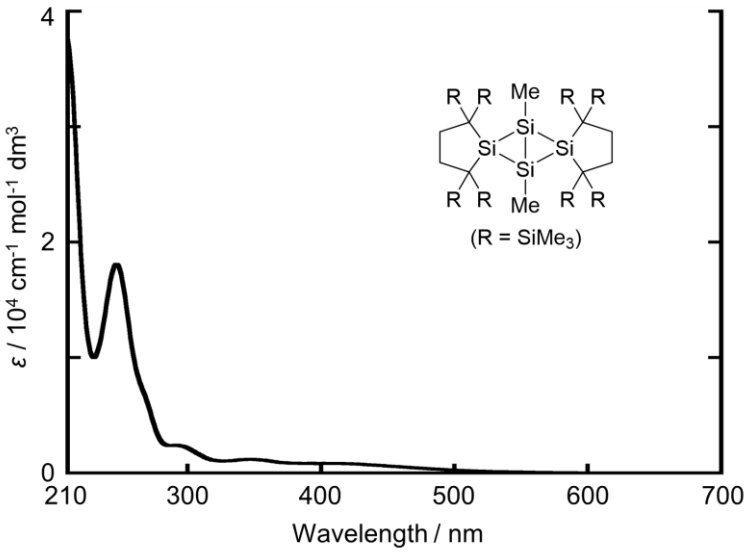


Figure 6-54. UV-vis absorption spectrum of **5** in hexane at room temperature [TN765].

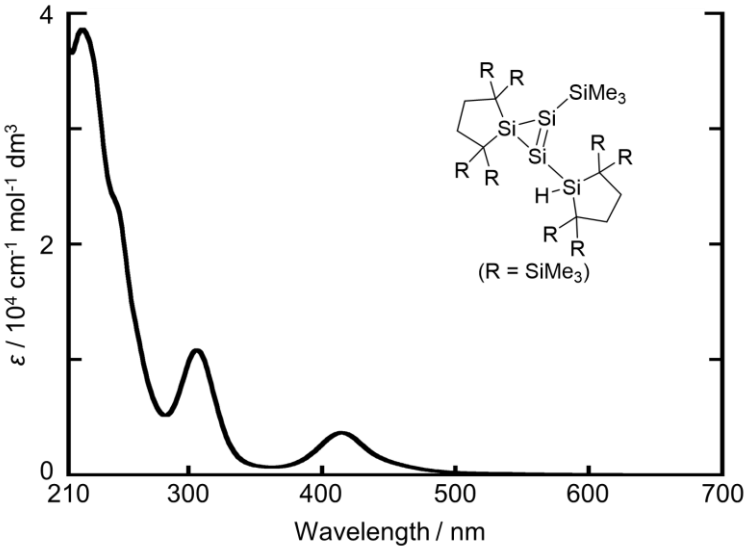


Figure 6-55. UV-vis absorption spectrum of **7** in hexane at room temperature [TN835].

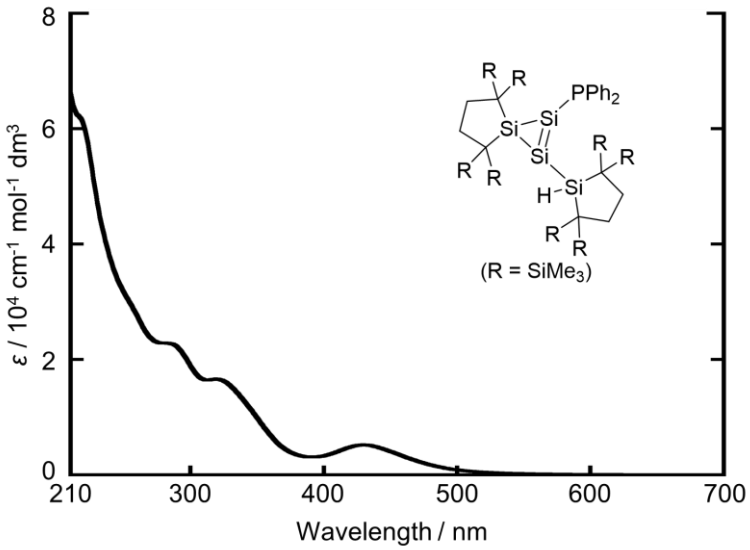
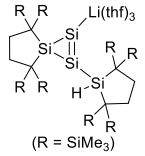


Figure 6-56. UV-vis absorption spectrum of **8** in hexane at room temperature [TN825].

Computational Study

All theoretical calculations were performed using a Gaussian 09[29] program or GRRM14 program.[30] Geometry optimization was carried out at the B3LYP-D3/6-311G(d) (**2**$_{opt}$, **2′**$_{opt}$ (free anion of **2**), and **8**$_{opt}$) and M06-2X/6-311G(d) (**3**$_{opt}$) level of theory. Frontier Kohn-Sham orbitals and their energy levels of **2**$_{opt}$, **2′**$_{opt}$, and **8**$_{opt}$ were shown in Figures 6-57 to 6-59. The optimized structures of model cyclotrisilene **9** with an $SiMe_3$ group and a PMe_2 group on the Si=Si double bond and methyl groups on the saturated ring silicon atom at the B3LYP-D3/6-311G(d) level of theory was shown in Figure 6-60. The atomic coordinates and energies of the optimized structures are summarized in Tables 6-1 to 6-6. Isotropic chemical shielding tensors were calculated at the GIAO/M06L/6-311+G(2df,p) level of theory (Tables 6-7 and 6-8). Absolute isotropic shielding tensors of ^{29}Si nucleus in tetramethylsilane were calculated to be 361.4 (GIAO/M06L/6-311+G(2df,p)). Excitation energies and oscillator strengths were calculated at the B3LYP-D3/6-311+G(d)/SCRF(solvent = heptane) (**2**$_{opt}$) and B3LYP-D3/6-311+G(d)/SCRF(solvent = THF) (**2′**$_{opt}$) level of theory (Tables 6-9 and 6-10). Natural bond orbital (NBO)[31] calculation of **8**$_{opt}$ was performed at the B3LYP-D3/6-311G(d) level of theory (Table 6-11).

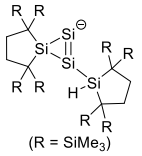
Table 6-1. Atomic Coordinates of Cyclotrisilenide $\mathbf{2_{opt}}$ at the B3LYP-D3/6-311G(d) Level of Theory



Atom	X	Y	Z
Si	4.024002480248	10.717873381792	5.121179003724
Si	2.092000258213	10.150166883217	5.974214746097
Si	2.023584572771	11.727859791619	4.336664126023
Li	6.584278763353	10.429070719138	5.366587736384
Si	0.969175023987	8.859078942263	7.625279465549
C	2.344180623003	6.515669243275	4.662771044360
H	2.667762905544	7.558500923079	4.636451809996
H	1.497420392878	6.411156722021	3.986154422360
H	3.156848870959	5.902455818288	4.258991181896
C	1.419421279566	4.107103557578	6.274729981066
H	2.232930246634	3.538911241015	5.810521122340
H	0.529317807887	3.949912976349	5.663312904630
H	1.233625129039	3.653680328852	7.252578183220
C	3.634049971592	5.794351051833	7.291914740933
H	4.297158033545	5.178755938104	6.673845573902
H	3.561394452100	5.305377727334	8.266655660336
H	4.119946078444	6.756997432884	7.431581526821
Si	1.963622133593	5.922794269444	6.410097524907
Si	-1.093808336346	6.601203092186	6.655250366900
C	-1.793485756067	5.023982267368	7.442806330711
H	-2.720187016297	4.745706144577	6.929796501239
H	-2.045211524331	5.176376889174	8.496190085109
H	-1.118288322708	4.169163189883	7.386732543180
C	-1.119489091796	6.385985020612	4.775838941356
H	-0.614153403895	5.487500908066	4.417658794299
H	-0.682614747143	7.242863820766	4.262338129056
H	-2.164356505407	6.320096489690	4.454372605351
C	-2.401184682432	7.932818667562	6.975321816837
H	-2.236621049147	8.833445220640	6.381365861346
H	-2.486151595921	8.237217522114	8.019018715135
H	-3.371062281795	7.517095841654	6.678565613149
C	0.666210354899	6.954874801351	7.377342348120
C	0.691227235488	6.467222763862	8.879245937122
H	-0.296472672346	6.577989960247	9.328417205909
H	0.915628134147	5.396165139382	8.950557707699
C	1.699013824913	7.263208081510	9.732327005597
H	2.708580157528	6.914336760466	9.499735241267
H	1.546205427109	7.020490737218	10.791545107226
C	1.589138051497	8.809270592619	9.471723900694
Si	0.244604654278	9.565991846100	10.625496458313
C	-1.273385058279	8.448979206002	10.813324385950
H	-1.988923202220	8.954001909009	11.471092218963
H	-1.031200119699	7.490324189810	11.280442941402
H	-1.787536753621	8.247339924230	9.873834365388
C	0.859277249512	9.768064978881	12.410360782498
H	1.577325417615	10.582111575322	12.531706318714
H	1.315421464493	8.857856330285	12.808180656586
H	-0.002352778050	10.002968937851	13.044392254140
C	-0.380158473215	11.257802409588	10.074624485798
H	-1.011051174202	11.676183845995	10.866491166719
H	-0.983956073004	11.200866034036	9.168655646872
H	0.419676202802	11.973927520074	9.883554208753
C	4.000186273190	9.031502656028	11.491715523474
H	5.079353494996	9.222179299899	11.502357926896
H	3.868368192528	7.954962614720	11.637326817025
H	3.572619288740	9.535137791383	12.358198840679
C	3.202661769559	11.487881055649	9.819631476932
H	4.202740916683	11.923214591414	9.903166061788
H	2.616073261598	11.877158642346	10.655138753014
H	2.758783997460	11.864091061445	8.896061815990
Si	3.292757700129	9.601186883694	9.822813111440
C	4.639713571901	9.055718722041	8.609918520644
H	4.352521263563	9.143077993180	7.562731254397
H	4.956328223265	8.029697012453	8.810765432339
H	5.520664429165	9.688858994321	8.749803417272
C	1.338898736979	11.536106645526	2.510498993912
Si	2.727218543050	11.140412344671	1.261859598324
C	3.977333900372	12.560167729767	1.147515954189
H	4.788604049023	12.282895603329	0.465516201288
H	4.417851965383	12.788038565559	2.117252195319
H	3.528888943491	13.478166417890	0.758853218673
C	3.750003716616	9.584367956059	1.610175402399
H	3.169430805124	8.662758115453	1.569297733576
H	4.222447629555	9.628417316999	2.594110432635
H	4.542553997694	9.507800057589	0.856227678541
C	2.043468068281	10.962253624108	-0.502235737091
H	1.453572686389	11.831864778789	-0.806068476195
H	1.415682686239	10.078379229311	-0.635549714914
H	2.876854751642	10.876755436826	-1.208287293427
C	0.467263486684	8.524736994685	1.943355646422
H	1.197959731800	8.153754222070	2.662672466944
H	0.905040373552	8.439110338386	0.946364622649
H	-0.395731203939	7.852314773994	1.973454154807
C	-1.160530725387	10.113428012898	3.917215935775
H	-2.052305830236	9.521823123134	3.683934849930
H	-1.496497026069	11.067182555409	4.324707925657
H	-0.618329950772	9.604269508717	4.713704937170
Si	-0.099142968224	10.280896594296	2.359071070051
C	-1.281320526931	10.814276678958	0.972553120799
H	-0.765675914077	11.002914216365	0.028316923797
H	-1.841263140488	11.718591598102	1.226639855986
H	-2.015941396942	10.021845189984	0.793338876753
C	0.783928978365	12.971788544665	2.183692213321
H	0.875496290200	13.213952515075	1.117594255533
H	-0.285642522023	13.019006411214	2.387245291254
C	1.471874938966	14.073047049365	3.016921804626
H	0.909188803049	15.008939753171	2.908557610635
H	2.455538603037	14.276380554047	2.582313954448
C	1.621688414114	13.645057582515	4.514808411263
C	-0.259099970759	12.839193170517	6.945052438229
H	-1.040729809131	13.235138789023	7.601284949213
H	0.647307467133	12.728243365085	7.543550691302
H	-0.557363199924	11.837203345213	6.633750036912
Si	0.002800281076	14.002687395584	5.488195836259
C	-1.555238756241	13.968846662974	4.403865664392
H	-1.789900138596	13.000640015382	3.963306030527
H	-1.501807756909	14.700342251100	3.592100729945
H	-2.407432749024	14.251212997768	5.031487909777
C	7.108612651037	12.257098328620	9.151010251480
H	6.589088935743	11.568305971109	9.822610255981
H	7.070331987192	13.251552531779	9.598400129169
C	-0.082095587543	15.757990850703	6.216220397635
H	-1.071537458265	15.880217866522	6.670292367271
H	0.022309509935	16.536206776413	5.456168921893
H	0.654089221966	15.952696744839	6.998838965404
C	3.305865421454	14.263897006099	7.104158910165
H	4.172055871223	14.802985197295	7.502825293780
H	3.471232591419	13.196251352370	7.257370614524
H	2.439271792523	14.549705457074	7.704848698365
C	2.903978298524	16.495154537455	4.994096442379
H	2.288715170709	16.995007114361	5.741781799409
H	2.476619531379	16.720911457048	4.012236389470
H	3.895597189320	16.959714281903	5.024257467440
C	4.753003217438	14.270668332668	4.423706008593
H	4.761474133871	14.625929943496	3.389872323971
H	5.037499548416	13.218165661414	4.432526403985
H	5.523381846042	14.837076713226	4.960613653797
C	8.537669649438	11.761590883431	8.884497057463
H	9.030537121525	11.361712589127	9.772617901094
H	9.156525747599	12.572031870735	8.486920030883
C	8.303506172670	10.698007894770	7.815237698226
H	9.150983940886	10.546568096966	7.143187159738
H	8.028045124318	9.732995789387	8.253985832226
O	7.194938256615	11.187314823874	7.032950575252
C	6.481507962007	12.224228059231	7.757999046051
H	5.421897215159	11.974534550280	7.748858752943
H	6.619876448030	13.168101895141	7.221980732918
O	7.614822288440	11.421435529628	4.033562187296
C	7.232799076695	11.471906456386	2.632987272501
H	6.177723662830	11.209146991518	2.559448399529
H	7.825306249337	10.724182625752	2.095068993503
C	8.304249501308	12.638899402274	4.402768564978
H	9.140170398617	12.368484672560	5.050313915633
H	7.613748405173	13.277508187998	4.961498279332
C	8.715313858913	13.285013048040	3.083638442323
H	8.845437491051	14.365150944262	3.173066878227
H	9.655464597843	12.856335149093	2.722560772478
C	7.549900953643	12.890421415893	2.165391694797
H	7.800737096509	12.930032296546	1.104115844781
H	6.693656052874	13.544827808757	2.336054182308
O	7.119819896293	8.568784842665	5.145307966210
C	6.127121150264	7.518824524549	5.219291090563
H	5.235920015870	7.947388313132	5.670795012011
H	6.510933398871	6.723846584959	5.867446437894
C	5.916648165127	7.037384966504	3.770404700863
H	4.965978868939	7.392999278805	3.375508014318
H	5.909434387028	5.946916514546	3.719147191371
C	7.105747272468	7.650483897304	2.987599419811
H	7.614124818622	6.928190088020	2.345796211409
H	6.755574100477	8.470627387408	2.357798860778
C	8.019165722136	8.188499446860	4.091306791219
H	8.703028479583	7.414684033650	4.464619074319
H	8.594649559694	9.072919848495	3.819871314135
Si	3.083560749287	14.620239036106	5.262578401794
H	-0.362510953155	9.518919214594	7.653193248678

E+ZPVE = -5446.902126 au, Free E (298.15 K) = -5447.031888 au.
Job name: TN110aa

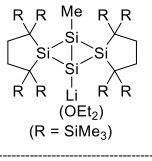
Table 6-2. Atomic Coordinates of Cyclotrisilenide **2′$_{opt}$** at the B3LYP-D3/6-311G(d) Level of Theory



Atom	X	Y	Z
Si	4.070748781004	10.610834035828	5.030377952106
Si	2.119244064366	10.172026520648	5.983540605594
Si	2.024142291334	11.725197587875	4.357453615800
Si	0.927962658027	8.884504405400	7.568409407941
C	2.254050295214	6.617552977420	4.481954959229
H	2.309558206359	7.703972972211	4.393596782499
H	1.464377222169	6.250610307995	3.826880736293
H	3.204030110926	6.223750336198	4.103619950487
C	1.723741053719	4.197106819626	6.237851383320
H	2.567688142373	3.699232017804	5.747736915495
H	0.825327968098	3.936703246492	5.672827544833
H	1.626441138953	3.757635903942	7.234987465366
C	3.788499096656	6.237515905646	7.032195974014
H	4.481214429241	5.628046348590	6.441285157611
H	3.855401108699	5.894037052320	8.067243826957
H	4.147682435389	7.265522534332	6.985301376367
Si	2.065177199884	6.071697601142	6.276546638392
Si	-1.034559018065	6.516982581316	6.603277310992
C	-1.631137501069	4.886176045332	7.380418914135
H	-2.523201073723	4.535735470054	6.849662396184
H	-1.909223668248	5.010205904478	8.430992829432
H	-0.883627808082	4.092028541180	7.330503040273
C	-1.107410425589	6.285768193141	4.726725881074
H	-0.575467641220	5.401812464599	4.369408363956
H	-0.717786614701	7.150391791103	4.189147637083
H	-2.158471802187	6.173258458352	4.438429655918
C	-2.419203263127	7.766309201177	6.944449930456
H	-2.319616716606	8.661727502251	6.328501144638
H	-2.490564967934	8.092111404362	7.982181148109
H	-3.370940551078	7.288319760006	6.682884167304
C	0.703999747870	6.960966137930	7.301034215682
C	0.773303543535	6.430770920491	8.786376491363
H	-0.220762880820	6.436290561044	9.235300116614
H	1.095183411018	5.383144260004	8.828319818380
C	1.696380836859	7.286180787746	9.674853145926
H	2.735437752306	7.034352271735	9.445271795230
H	1.553562755335	6.996747417093	10.724712973260
C	1.457607187138	8.820897748965	9.454216697410
Si	0.017083184136	9.436218820846	10.562275842721
C	-1.378689027203	8.163166627990	10.755250621076
H	-2.150893344412	8.597185288830	11.400262267194
H	-1.031341485052	7.246635377638	11.241505319618
H	-1.859199857574	7.883806228057	9.818506476666
C	0.532139489502	9.732287974934	12.370102692867
H	1.166635003320	10.611916268363	12.497998855369
H	1.053440070629	8.878129670179	12.809688905568
H	-0.376723524498	9.900191387255	12.958899644938
C	-0.768363124259	11.053861352086	9.989137036449
H	-1.423410295660	11.435319838786	10.780617904161
H	-1.370175139505	10.930248250493	9.088056249517
H	-0.029249354412	11.825907868760	9.772723209773
C	3.707166390862	9.222508458915	11.623928952106
H	4.786294997797	9.404333058881	11.671687387405
H	3.556542165328	8.154053888450	11.807761614960
H	3.248451872854	9.766729748261	12.449588412562
C	2.863078289730	11.611550876921	9.865468244872
H	3.827873218621	12.107324297443	10.011486178392
H	2.184955263041	11.975564535289	10.642095886383
H	2.479541676208	11.940872405534	8.898033451702
Si	3.082467915117	9.736858021989	9.896514529234
C	4.540653553015	9.280718021654	8.791756865862
H	4.371069951061	9.462474136013	7.730862513468
H	4.844901971254	8.239899249269	8.927066943611
H	5.391737312470	9.903912226421	9.089615059241
C	1.221419331322	11.588016484590	2.556712668026
Si	2.533986641982	11.143896469150	1.245712667243
C	3.864229462990	12.481072519687	1.080127233259
H	4.577118270785	12.182019970243	0.303307157907
H	4.423154880132	12.607977622581	2.007681970036
H	3.456197079386	13.453505236738	0.790471459672
C	3.469313616990	9.523286425702	1.509245182761
H	2.829123251180	8.658449782610	1.679894938619
H	4.149149105490	9.596343871063	2.361356650870
H	4.074906166300	9.317600648876	0.618176481125
C	1.741307625654	11.054067234465	-0.488957518718
H	1.200386326168	11.971106322322	-0.742412033951
H	1.043537195386	10.221182985155	-0.604502996028
H	2.528147271787	10.925619528058	-1.240964296461
C	0.139886755587	8.634078017119	1.910599792559
H	0.847121408476	8.147983323208	2.582485226029
H	0.548979353115	8.576701589688	0.899724392751
H	-0.782082348846	8.042882215446	1.921906467323
C	-1.234219313860	10.179164316173	4.075625778937
H	-2.179046948617	9.664308675742	3.866000307868
H	-1.468238951315	11.114136095006	4.585129532912
H	-0.666789745524	9.574266299659	4.782625942051
Si	-0.270032974343	10.400312878981	2.461082837852
C	-1.529576750277	11.043031270951	1.183719274076
H	-1.062324865153	11.278973848526	0.224273211005
H	-2.051035073561	11.942053496639	1.524619092179
H	-2.291433765745	10.276789015384	1.001636496173
C	0.713603482949	13.046932884511	2.265358307565
H	0.773321050175	13.298498695559	1.198321351230
H	-0.343794068853	13.138482773512	2.511761405643
C	1.479310826084	14.110200358891	3.078798433193
H	0.953197895009	15.071416019231	2.996081856742
H	2.453424486479	14.270203056599	2.607009600662
C	1.672005108735	13.663657769082	4.563650315096
C	-0.137408608994	12.921024127720	7.083279099138
H	-0.909312159238	13.333476156458	7.741985033582
H	0.779608542121	12.820997504731	7.666464879823
H	-0.438354012795	11.912677513513	6.798426008152
Si	0.110808405509	14.051266776996	5.597830379090
C	-1.504121606714	14.041645086567	4.590411110329
H	-1.768772402544	13.075795447268	4.161172910371
H	-1.479639353231	14.773189087531	3.776820658678
H	-2.320962979834	14.332791961732	5.260520112532
C	0.080228343987	15.816567852249	6.319458258976
H	-0.893220893659	15.968053123070	6.799782542728
H	0.191459668014	16.589754809898	5.554833701137
H	0.844894049926	15.987558381064	7.080625974730
C	3.509717470715	14.200282398422	7.075138805057
H	4.379652849806	14.757716833825	7.439531370385
H	3.712935293657	13.135860636211	7.210903301227
H	2.662227719428	14.459200507412	7.715509999532
C	3.048776511631	16.469298622121	5.033744022418
H	2.502836743828	16.966096415374	5.836371340865
H	2.556876036800	16.728355357781	4.090704528416
H	4.053045108014	16.906266281675	5.001222438323
C	4.800912471460	14.202709193332	4.305776800177
H	4.750848144465	14.537133302925	3.265851101812
H	5.074245965690	13.147045902642	4.313806914545
H	5.614981578946	14.761320089029	4.782848342866
Si	3.202464478260	14.577276734360	5.249796981137
H	-0.436753827708	9.480604319862	7.550955166330

E+ZPVE = -4742.118981 au, Free E (298.15 K) = -4742.222773 au.
Job name: TN112ac

Table 6-3. Atomic Coordinates of Silyl Anion **3$_{opt}$** at the M06-2X/6-311G(d) Level of Theory

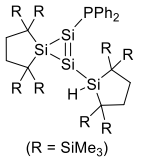


Atom	X	Y	Z
Si	12.995120510875	14.626934134415	-0.377914250760
Si	14.010367723791	12.990762676301	1.269362071146
Si	15.214121442606	14.690299104252	0.258392819639
Si	12.450447475996	12.395532288092	-0.343287818506
C	11.666613555734	16.000747204595	-0.233837205136
H	10.909938450331	15.856620978448	-1.009113561085
H	12.111027221018	16.986156359354	-0.388731648339
H	11.158583877104	16.015999309257	0.729930106442
Li	14.511269197691	12.926068258195	3.713866142297
C	12.473469165016	10.960531361976	-1.668087059403
C	11.147801355771	10.181945720722	-1.340160806909
H	10.322658560952	10.539811042283	-1.960492292331
H	11.241256353560	9.113361192761	-1.572778328676
C	10.739925389141	10.367561901468	0.123202389927
H	11.442503664680	9.826324550108	0.761700037566
H	9.756514226326	9.914984399172	0.292223277441
C	10.758804893517	11.884132495213	0.483199911060
Si	12.480148125770	11.363541386878	-3.556992437366
C	11.061584983120	10.423465975999	-4.394054861839
H	10.064992584387	10.790934133627	-4.139575903006
H	11.081601783526	9.352184235757	-4.175185847985
H	11.174497399303	10.536290543531	-5.476670565193
C	13.995355727341	10.751514243199	-4.517855113029
H	13.748160600567	10.871204043284	-5.578312265790
H	14.237468500188	9.698988476744	-4.365447483685
H	14.892790559235	11.339098346985	-4.337998359159

C	12.279326567166	13.175498657109	-4.066528050274
H	12.818723713724	13.330298294779	-5.005653186608
H	12.673013688432	13.887073595979	-3.338168925617
H	11.233288701240	13.425586258013	-4.248252969026
Si	13.906632038468	9.767457073682	-1.266825471547
C	13.926315353522	9.140095519545	0.518898254790
H	14.843230874292	8.555894345131	0.656408304174
H	13.087709997824	8.476941159343	0.745460671168
H	13.934595925021	9.950100326323	1.249294269033
C	13.723682427666	8.178768161085	-2.297111751216
H	13.022539291540	8.276963855568	-3.128812347039
H	13.369885078451	7.354602697246	-1.671939979850
H	14.685535321608	7.873110253206	-2.719222596261
C	15.589800528945	10.555466065431	-1.567973406297
H	15.595787946295	11.606379533193	-1.264845858510
H	15.887633790448	10.499878582122	-2.615597061439
H	16.357381097979	10.045259016819	-0.977704762920
Si	9.249822600132	12.737242372520	-0.316985963135
C	8.616978121672	14.218757260983	0.667941029311
H	9.397701796415	14.942283994253	0.901012545229
H	8.135083785891	13.936913302940	1.606087802117
H	7.865956973455	14.737003845538	0.063614100785
C	7.808599632244	11.522455952354	-0.463692945823
H	7.536988809258	11.058146806606	0.486751797182
H	8.017297136705	10.720444295362	-1.177393620486
H	6.927157690121	12.057112183801	-0.831012895021
C	9.558997161821	13.359712562189	-2.066173094119
H	8.688368252960	13.927515246186	-2.409852882031
H	9.702821715210	12.536969921897	-2.769583673613
H	10.431642631319	14.009348555368	-2.142765771455
Si	10.613478708355	11.987106894783	2.366860748110
C	8.917220719475	11.362929279795	2.937955698424
H	8.728180336012	10.344399567907	2.586157817381
H	8.076890070775	11.983557105214	2.622593381596
H	8.901517531089	11.330605265811	4.032573066075
C	11.781886687555	10.780234243347	3.246968092692
H	12.818071907418	10.860051903601	2.918322680319
H	11.458498993394	9.743796892906	3.113857926892
H	11.746112762865	10.994420115154	4.321591710706
C	10.841082439860	13.720806268526	3.091007027418
H	11.378494191804	13.668225351041	4.044369634692
H	9.880432646153	14.202299835461	3.288945699431
H	11.417598248674	14.366106523241	2.426599199900
C	15.782860696003	16.030394151418	1.605837704199
C	17.220357799781	16.388763520843	1.104302363409
H	17.547723709496	17.374883765896	1.453086386166
H	17.954146905262	15.672312487326	1.501352364170
C	17.279316038510	16.317006912838	-0.423329577577
H	18.297327302942	16.509636563420	-0.773319829433
H	16.664011310067	17.128150760791	-0.825992789290
C	16.739573828014	14.937600132016	-0.921129686507
Si	18.140747559573	13.621485308092	-0.780920491707
C	17.949655564463	12.325785241341	0.582403760059
H	16.916280418741	12.011091538053	0.744122317642
H	18.356791820561	12.674928090206	1.531723588974
H	18.524193008349	11.440434084366	0.291545382703
C	18.479777715987	12.572843841321	-2.320938741836
H	19.435144266015	12.069879736599	-2.135369089864
H	18.583591088860	13.123364053327	-3.256067799477
H	17.733525089850	11.791184075690	-2.462059653911
C	19.800309163059	14.477814901950	-0.461541116220
H	19.821195805677	15.099482770493	0.436398238924
H	20.111162209344	15.102908901213	-1.303329322125
H	20.563908397487	13.703487831398	-0.337677464439
Si	16.286843548541	15.190098482977	-2.748462203318
C	15.015556103638	16.540155745895	-3.095739016405
H	14.915477873397	16.605304431135	-4.184890222854
H	15.321063329094	17.528977549666	-2.747586666337
H	14.025180837969	16.318069659444	-2.693409970618
C	15.605190131458	13.627628140811	-3.528564301473
H	14.882169440675	13.159181249574	-2.853875330406
H	16.370625826069	12.891145607407	-3.767238797571
H	15.073905367039	13.868847858694	-4.452785251413
C	17.831864998128	15.811567329727	-3.653391294267
H	18.755815623166	15.298515052451	-3.380607892790
H	17.978630587892	16.875880387281	-3.445384771179
H	17.707989999658	15.712171007436	-4.736145903579
Si	16.002886156734	15.403315768151	3.372223608781
C	14.417831444762	15.222158438398	4.421561176616
H	14.629798487195	14.604683311961	5.305289003052
H	13.536623606053	14.837037778660	3.897269816471
H	14.118895136461	16.195070823420	4.816038335218
C	16.894428259081	13.732313090447	3.527522940773
H	17.960092850333	13.873554510219	3.329965314037
H	16.564744885623	12.938707713227	2.854312880609
H	16.829103487715	13.379733487980	4.565054226961
C	17.130957434502	16.524948294713	4.388717400354
H	17.363647114756	16.034181221269	5.339462942667
H	16.698287093575	17.497940034457	4.619437205742
H	18.081511491981	16.700078932710	3.877274665801
Si	14.697059814117	17.597514406502	1.636575242893
C	12.997702616366	17.272226626765	2.397448219966
H	12.236095157922	17.879344783443	1.902765799592
H	12.984490621145	17.544216924007	3.455053085948
H	12.691226727163	16.228891320819	2.314442638591
C	14.482334440101	18.373672528796	-0.065164592845
H	14.213205792132	17.650750135344	-0.834325481108
H	15.391317080504	18.888662237981	-0.388891902220
H	13.687548464925	19.125161546536	-0.017675335963
C	15.459983169896	18.974962961436	2.693457928511
H	14.999459188556	19.924471716039	2.402327257648
H	16.539266381037	19.090799714375	2.567519022080
H	15.260079397412	18.842996321026	3.759129098886
O	14.383498160704	11.800463797186	5.202934406297
C	14.759080194000	10.418156325203	5.135003640825
H	13.852565115193	9.828187043893	4.964524853147
H	15.194889463961	10.123036581484	6.094220404718
C	15.750980355426	10.229747935705	4.009025924760
H	15.329336672963	10.551945948582	3.052318227848
H	16.005159691602	9.172880843004	3.913829495030
H	16.670441012845	10.788164248212	4.193743040331
C	13.533890789103	12.117668396907	6.309752345210
H	12.842674570596	11.284372768675	6.471243001234
H	12.940269387800	12.982387672362	6.003454143520
C	14.337037173367	12.428832229957	7.558698882484
H	14.931473547723	11.572171555509	7.880247620560
H	13.667381433016	12.698150134732	8.377646481081
H	15.012945546088	13.267545414832	7.380596919785

E+ZPVE = -5021.195762 au, Free E (298.15 K) = -5021.305308 au.
Job name: TN107ca

Table 6-4. Atomic Coordinates of Cyclotrisilene **8**$_{opt}$ at the B3LYP-D3/6-311G(d) Level of Theory



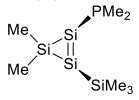
(R = $SiMe_3$)

Atom	X	Y	Z
Si	0.119169386403	16.878955547727	10.707247098637
Si	0.142052942680	18.865800812973	11.498723450820
Si	0.413807379583	17.090689404036	13.012244676783
P	-0.442363307453	15.810818073935	8.751996381235
Si	-0.105513619243	21.211965142089	11.203324118842
C	0.673836923678	16.663583809829	7.545187810535
C	0.091693237685	17.091264625998	6.344052412134
H	-0.970053538389	16.939264453764	6.180863155885
C	0.859639287468	17.711177582195	5.360436959013
H	0.390991655581	18.039781862913	4.438491320687
C	2.223354200648	17.907329025142	5.561074716287
H	2.823949589625	18.385667161326	4.794049355159
C	2.812326362557	17.498277877302	6.756407236872
H	3.872253668738	17.657913800896	6.924641974405
C	2.043772763651	16.891782015377	7.745376031537
H	2.513933644996	16.591694000534	8.675323371587
C	0.310673815745	14.134945333307	8.987619500722
C	1.501147914179	13.686631806663	8.402430309457
H	2.068937298316	14.337619766130	7.749553626361
C	1.972246318510	12.399871069052	8.657775078957
H	2.899206422088	12.071031513701	8.198324420328
C	1.270371573278	11.543577572044	9.503020761067
H	1.648207287933	10.547656429074	9.709876010947
C	0.070907683839	11.971675548503	10.070357142792
H	-0.494218315428	11.312202348712	10.721021649415
C	-0.412160130349	13.247311955982	9.798327640865
H	-1.361604401523	13.558285125114	10.221175201176
C	1.213402990751	22.275450500503	10.285819170463
C	0.270420251530	23.375403575090	9.649360870085
H	0.106266763800	24.188667271100	10.358140466392
H	0.742743351348	23.846156911818	8.779729988076
C	-1.104828033834	22.806140363555	9.247242777320
H	-0.991551913486	22.235818705086	8.321618846955
H	-1.780339671547	23.633866261611	9.000599320266
C	-1.707698985320	21.887634765761	10.371856615667
Si	2.235339109187	21.467952155019	8.868627453283
C	1.200223196707	20.964977234874	7.373449848036
H	1.886928649787	20.624878139049	6.592591938117
H	0.617061906215	21.787990041334	6.953113341367
H	0.527958219821	20.133326707161	7.573673129193
C	3.206867476723	19.937570070295	9.378404003953
H	2.552748534771	19.122806393069	9.693964959767
H	3.926504102128	20.122812588325	10.173139633239
H	3.764890219081	19.582115343505	8.507420640137
Si	2.410816115664	23.159732169053	11.525551836723
C	3.474350568557	22.718230774527	8.156614507256
H	4.260036989856	23.020507646221	8.850996209448
H	2.986966204064	23.626711446394	7.791393356168
H	3.967084714758	22.255192194751	7.294990611625
C	4.034894425544	22.235026572327	11.819234381916

H	4.573135706809	22.741261675790	12.627579996067
H	4.698050710808	22.214042241049	10.952798559157
H	3.870371287563	21.205574682722	12.139755365663
C	2.824413694051	24.889041953750	10.870277265184
H	1.965638869586	25.562882383201	10.936420684652
H	3.168447117818	24.895561866360	9.835471179066
H	3.619899889300	25.324614978543	11.484053250568
C	1.711645325090	23.441490007940	13.262651005157
H	1.670868964327	22.525472497494	13.854388682891
H	0.716816845405	23.888465257375	13.278272235654
H	2.384746643562	24.134619295676	13.779877337953
Si	-2.846870797125	20.593637550518	9.527000092921
C	-1.905109514730	19.432992590828	8.368152749514
H	-0.973769586192	19.042046784243	8.773877555871
H	-1.682480576239	19.911415850783	7.411768528776
H	-2.542056127590	18.567901958462	8.155707940249
C	-3.766565274884	19.531940502844	10.784978496937
H	-4.421035952928	18.824757675560	10.265861177896
H	-4.388057076575	20.107066573644	11.475033810771
H	-3.065091415243	18.938142500868	11.374328447352
C	-4.094093164632	21.435001683684	8.372181114995
H	-4.446797682864	20.697785950077	7.643094774324
H	-3.634739438882	22.249101264771	7.803387627698
H	-4.971802253289	21.837998664764	8.876536333349
Si	-2.689695020381	22.927308782531	11.665413302649
C	-1.919790650097	24.632340883920	11.956294259452
H	-2.540031182414	25.171422244769	12.680292720184
H	-1.894048274168	25.236794438313	11.045182794708
H	-0.909526754195	24.596484789261	12.364419065977
H	-0.117451422650	21.582876447723	12.640582979198
C	-4.454531422522	23.326440419501	11.103084774720
H	-5.111398448307	22.454492392169	11.077861054967
H	-4.488374342775	23.800291352358	10.119025168308
H	-4.885888753046	24.034093439196	11.819202870572
C	-2.825923613035	22.051702353971	13.334195076399
H	-3.693394630197	22.432129613241	13.883200999569
H	-1.944900895285	22.211366084126	13.958784411025
H	-2.956364970040	20.974543834449	13.231447435867
C	-0.847669257761	16.528745201226	14.371491592176
C	0.093761954968	15.699428646364	15.319925419404
H	-0.322017860095	15.599054638581	16.326326553652
H	0.199297706416	14.681239045640	14.942298307459
C	1.498147536541	16.326809049415	15.393140686991
H	2.172733328080	15.667548335523	15.952250625648
H	1.434283850439	17.247244159007	15.987137322381
C	2.046150910324	16.640690524710	13.954832524905
Si	-1.655353682604	17.985465124278	15.349055080493
C	-1.966102850944	17.462364087162	17.144149611429
H	-2.566625054380	18.233542313393	17.638267738736
H	-1.034490236021	17.373950301158	17.710868628078
H	-2.504277701779	16.517855353473	17.240317948600
C	-3.311337562116	18.540409011416	14.625905603433
H	-3.624176340146	19.451813392462	15.144241206903
H	-4.110154697101	17.807170699445	14.748987101648
H	-3.244672647880	18.779607803325	13.564738583557
C	-0.620009968076	19.556201522219	15.490749804909
H	-0.319937187828	19.982083712387	14.533281213470
H	0.279374620919	19.395506280550	16.087345816804
H	-1.217956267177	20.313529622952	16.008531312676
Si	-2.236894043939	15.359829679165	13.734508603672
C	-3.287178616457	16.031134572941	12.314102794399
H	-3.896632599595	15.210841752837	11.919484877621
H	-2.683474637246	16.411453223862	11.487486196853
H	-3.970458679355	16.826714894622	12.608661048455
C	-1.524324141161	13.720715635177	13.122242036868
H	-2.327214643065	13.144532361872	12.650182290290
H	-1.118449825525	13.104508082434	13.927459906948
H	-0.742069637957	13.856676723837	12.377457720121
C	-3.400484883045	14.856446315764	15.145149301201
H	-4.007073007217	15.671817892349	15.543090742867
H	-2.846973079201	14.416561494491	15.980175898680
H	-4.090587052239	14.089072217484	14.778347768178
Si	2.943829000095	15.095939048541	13.217943047813
C	4.632867121679	14.808440259789	14.037645750721
H	5.026115865880	13.857761557232	13.661649181502
H	4.551943358686	14.711699779193	15.123955925382
H	5.381813088189	15.572603041177	13.825345203849
C	2.062534079439	13.453765284291	13.527945840516
H	1.108291139894	13.364202281403	13.014424575449
H	1.904342645666	13.246311526705	14.589749494148
H	2.707153311557	12.658361474977	13.138038484290
C	3.220387351537	15.214023225653	11.349346227859
H	3.330802262114	16.236626092909	10.989010110119
H	2.398735889345	14.749962210161	10.800640662990
H	4.129969710657	14.667754461411	11.077868794616
Si	3.333200115607	18.069522756572	14.083630015212
C	4.448052993092	18.204049671330	12.563871077607
H	3.862876648726	18.394995409964	11.662880247557
H	5.063967205051	17.323251170843	12.376457815130
H	5.126513359711	19.053072936690	12.695846068776
C	4.402935878295	17.837714006326	15.631757842757
H	5.083090812064	18.691808155418	15.720432384732
H	5.011338296242	16.934279276549	15.635106638666
H	3.789928580972	17.825586457787	16.537817239599
C	2.615246901839	19.800290358789	14.327300908001
H	3.453263107416	20.504017638838	14.337536125496
H	2.097672083610	19.914421517163	15.278559670160
H	1.933978399922	20.114031767545	13.537052353330

E+ZPVE = -5546.687948 au, Free E (298.15 K) = -5546.806547 au.
Job name: TN126aa

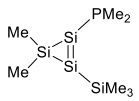
Table 6-5. Atomic Coordinates of Model Cyclotrisilene **9** (*cis*-bent) at the B3LYP-D3/6-311G(d) Level of Theory



Atom	X	Y	Z
Si	-0.485640413711	2.147586385438	-0.770078670931
Si	0.623818368308	0.332738231553	-0.426200487610
Si	-1.703234273313	0.247313940475	-0.292374098053
P	-0.328155786773	4.415298965997	-0.714944931849
Si	2.710925069144	-0.518957960615	0.273697467031
C	-2.604683659050	0.002700977422	1.357113513140
H	-3.614101658615	0.425938321303	1.316899451018
H	-2.708976726673	-1.063345589673	1.587163365936
H	-2.070034660058	0.477794970713	2.181733525268
C	-2.731883286889	-0.611871426886	-1.630361329965
H	-2.831953145930	-1.681068766567	-1.413969567121
H	-3.741854723963	-0.190603157271	-1.676554744934
H	-2.271944592391	-0.505738871098	-2.614318436355
C	1.492766004964	4.601623089372	-1.107996477325
H	1.793623086704	4.080777094266	-2.019906691295
H	1.717875136038	5.665325648118	-1.222979683361
H	2.087071240252	4.220255185590	-0.275937326458
C	-1.057486312253	4.877718539185	-2.378168404412
H	-2.122938532347	4.640667393318	-2.391192217642
H	-0.954280535347	5.957667132082	-2.514372708776
H	-0.575555287323	4.371677626409	-3.217444506841
C	2.565838202447	-1.104438237599	2.065529169432
H	3.522495464600	-1.508609332426	2.414802666991
H	2.284470587226	-0.286328786366	2.733500192554
H	1.815119247535	-1.892274645687	2.171700190869
C	3.232448786539	-1.968190813594	-0.821718925250
H	3.334502106767	-1.666516825823	-1.867574824900
H	4.198161456103	-2.369087769873	-0.494580388464
H	2.504889715538	-2.783520625666	-0.782567339686
C	3.979464212442	0.876189223015	0.144106224373
H	3.706345118964	1.722254529397	0.780253536024
H	4.970148136590	0.528358935928	0.456425448525
H	4.065036544474	1.246694089560	-0.880975969931

E+ZPVE = -1778.675567 au, Free E (298.15 K) = -1778.731279 au.
Job name: ti636MIN01G

Table 6-6. Atomic Coordinates of Model Cyclotrisilene **9** (planar) at the B3LYP-D3/6-311G(d) Level of Theory



Atom	X	Y	Z
Si	-1.450621449652	0.077567005375	0.075796322995
Si	0.681376785434	0.247163380647	0.275172484848
Si	-0.541948909657	2.179856257943	-0.175737385319
P	-3.248720810648	-1.324508692034	0.116353471176
Si	2.727091631844	-0.858884795591	0.676802477615
C	-0.452936545255	3.048082942264	-1.857649393888
H	-1.368205410695	3.617261684316	-2.052676343811
H	0.382996414971	3.755666041562	-1.884620205987
H	-0.318240399656	2.331488950785	-2.669817740447
C	-0.785016942261	3.525935218716	1.136761760033
H	0.047171056270	4.238222078320	1.119452623967
H	-1.702911351588	4.093413038636	0.949088668324
H	-0.846340034717	3.099739023798	2.139753471099
C	-2.457875058428	-2.775268425652	0.998003347443

H	-1.972566944238	-2.497209296966	1.936324184554
H	-3.231433631248	-3.518643047666	1.208946096252
H	-1.716494955238	-3.240413955748	0.345761443473
C	-4.204906843023	-0.574578313504	1.544069639638
H	-4.582392731075	0.409212809069	1.258881625680
H	-5.066938768566	-1.213162646833	1.755489637562
H	-3.612797111625	-0.472429678529	2.456083331330
C	3.887191719425	-0.623225787573	-0.796384444971
H	4.842790874503	-1.128391525358	-0.617324971723
H	3.459233450220	-1.034320368950	-1.714408364618
H	4.099816598442	0.434320512360	-0.975118356175
C	3.529260710105	-0.144943547691	2.232427525030
H	2.891618928330	-0.276750604983	3.110470085373
H	4.483745469246	-0.643549584645	2.434320617756
H	3.730347779765	0.924633004922	2.126784723783
C	2.353736348339	-2.695144383309	0.922653158200
H	1.891332407047	-3.131575033353	0.033283159797
H	3.274823623630	-3.251850096504	1.126806611732
H	1.673312410000	-2.856572593828	1.762972189279

E+ZPVE = -1778.675170 au, Free E (298.15 K) = -1778.731764 au.
Job name: ti636MIN01Gplanar

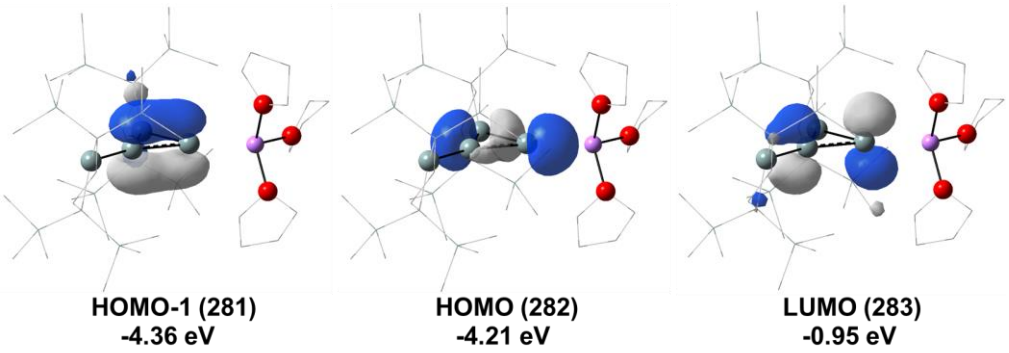


Figure 6-57. Frontier Kohn-Sham orbitals of $\mathbf{2}_{opt}$ at the B3LYP-D3/6-311+G(d)/SCRF(solvent = heptane)//B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}). [td_TN110aab3]

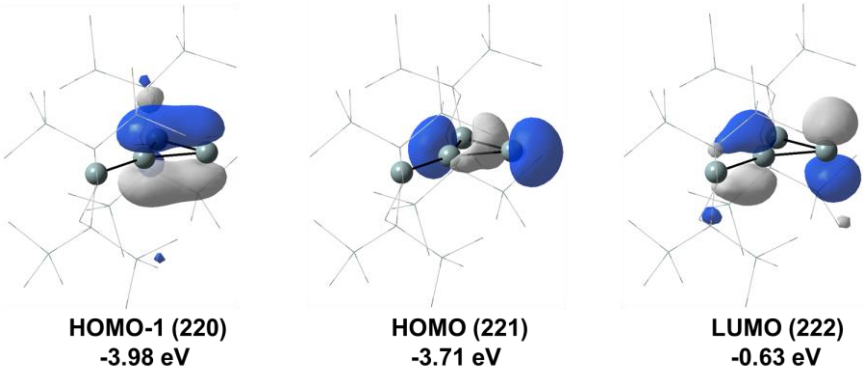


Figure 6-58. Frontier Kohn-Sham orbitals of $\mathbf{2'}_{opt}$ at the B3LYP-D3/6-311+G(d)/SCRF(solvent = THF)//B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}). [td_b_TN112ac]

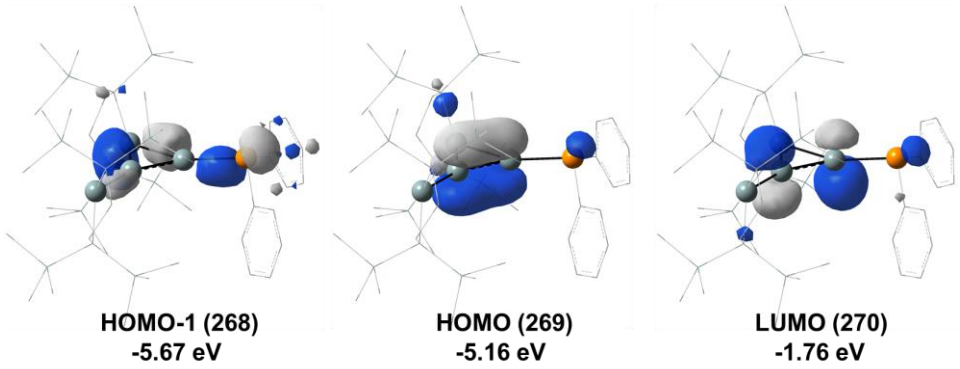


Figure 6-59. Frontier Kohn-Sham orbitals of $\mathbf{8}_{opt}$ at the B3LYP-D3/6-311G(d) level of theory (isosurface level: 0.05 e·au^{-3}). [TN126aa]

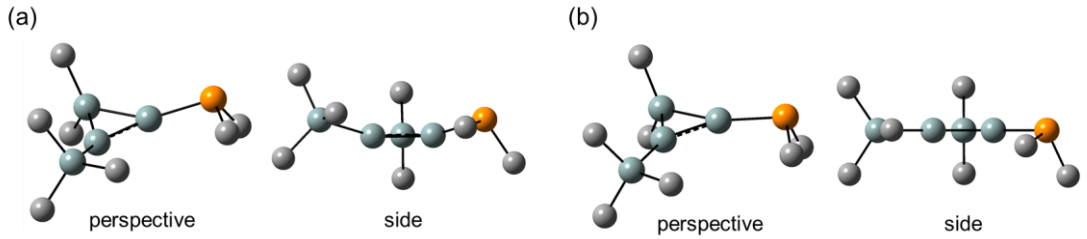
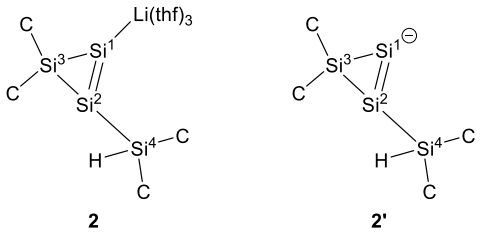


Figure 6-60. Structures of model cyclotrisilene **9**. (a) fully-optimized *cis*-bent structure. (b) partially-optimized planar structure.

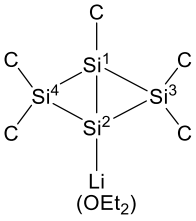
Table 6-7. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of **2**, $\mathbf{2}_{opt}$ and $\mathbf{2'}_{opt}$



Cpd	$SiMe_3$	Si1	Si2	Si3	Si4	note
2[a]	2.7, 3.6, 4.1, 4.4	281.0	168.1	−27.9	−14.0	TN790_NMR6
$\mathbf{2}_{opt}$[b,c]	3.4 (358.0)[d]	276.9 (84.5)	177.5 (183.9)	−39.1 (400.5)	−14.7 (376.1)	nmr_TN110aa
$\mathbf{2'}_{opt}$[b,c]	2.9 (358.5)[d]	325.7 (35.7)	154.8 (206.6)	−43.1 (404.5)	−14.9 (376.3)	nmr_TN112ac1

[a]Experimental ^{29}Si chemical shifts of **2** in benzene-d_6 at room temperature. [b]GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [c]The absolute chemical shift is shown in the parentheses. [d]Average values.

Table 6-8. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of **3** and $\mathbf{3}_{opt}$



Cpd	$SiMe_3$	Si1	Si2	Si3, S4	note
3[a]	2.9, 3.1	−80.6	-[e]	16.5	TN780_NMR2
$\mathbf{3}_{opt}$[b,c]	0.8 (360.6)[d]	−108.4 (469.8)	−98.9 (460.3)	10.8 (350.6), 17.6 (343.8)	nmr_TN107ca

[a]Experimental ^{29}Si chemical shifts of **2** in benzene-d_6 at room temperature. [b]GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. [c]The absolute chemical shift is shown in the parentheses. [d]Average values. [e]Not observed.

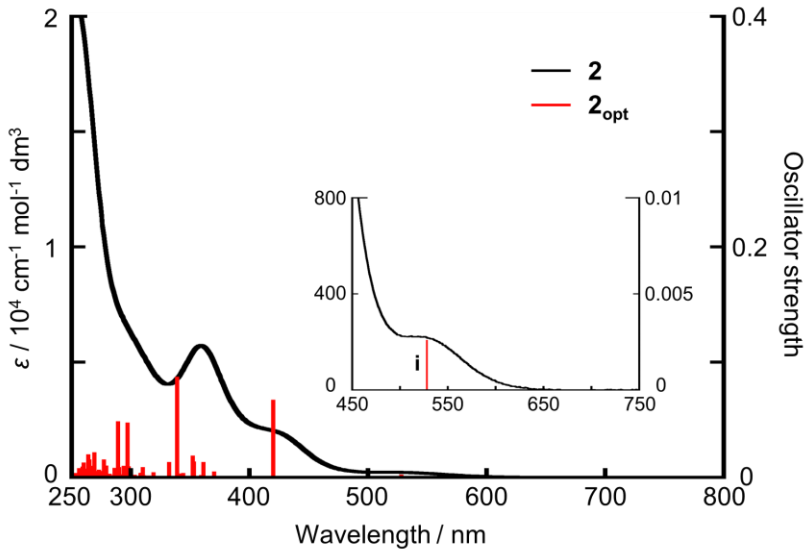


Figure 6-61. Experimental UV-vis absorption spectrum of **2** in hexane at room temperature (black) and calculated band positions of $\mathbf{2}_{opt}$ at the TD-B3LYP-D3/6-311G+(d)/SCRF(solvent = heptane) level of theory (red bar). i: σ(Si⁻Li) → π*(Si–Si) transition. [td_TN110aab3]

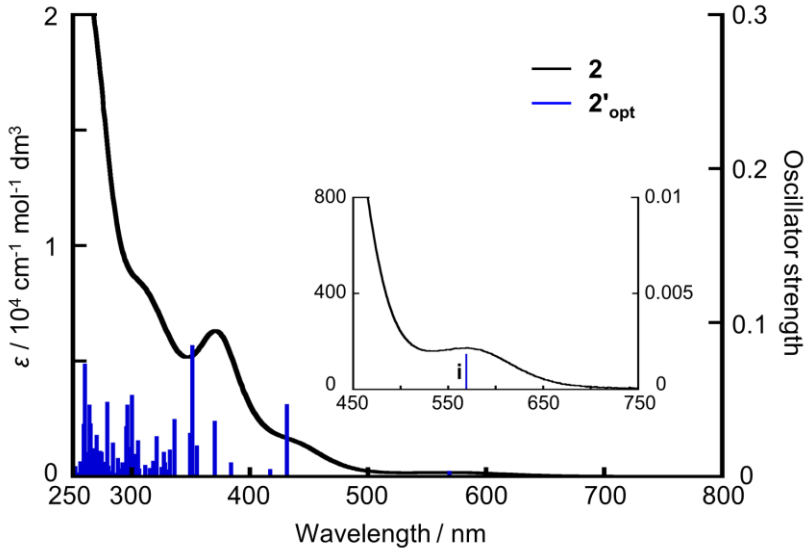


Figure 6-62. Experimental UV-vis absorption spectrum of **2** in THF at room temperature (black) and calculated band positions of $\mathbf{2'}_{opt}$ at the TD-B3LYP-D3/6-311G+(d)/SCRF(solvent = THF) level of theory (blue bar). i: σ anionic lone pair(Si) → π*(Si–Si) transition. [td_b_TN112ac]

Table 6-9. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{2}_{opt}$ (The 282th orbital is highest occupied orbital shown in Figure 6-57) [td_TN110aab3]

Excited State 1:	Singlet-A	2.3470 eV	528.26 nm	f=0.0026	
<S**2>=0.000					
282 -> 283	0.70393				
Excited State 2:	Singlet-A	2.9489 eV	420.44 nm	f=0.0673	
<S**2>=0.000					
281 -> 283	0.66352				
282 -> 289	-0.12841				
Excited State 3:	Singlet-A	3.0389 eV	407.99 nm	f=0.0006	
<S**2>=0.000					
280 -> 283	0.70096				
Excited State 4:	Singlet-A	3.1888 eV	388.81 nm	f=0.0012	
<S**2>=0.000					
282 -> 284	0.70251				
Excited State 5:	Singlet-A	3.3485 eV	370.27 nm	f=0.0052	
<S**2>=0.000					
281 -> 284	0.70116				
Excited State 6:	Singlet-A	3.4322 eV	361.23 nm	f=0.0135	
<S**2>=0.000					
282 -> 285	0.63844				

282 -> 286 -0.13106
282 -> 287 0.18413
282 -> 289 -0.11504

Excited State 7: Singlet-A 3.4574 eV 358.60 nm f=0.0021 <S**2>=0.000
282 -> 285 0.17878
282 -> 286 0.67262

Excited State 8: Singlet-A 3.5142 eV 352.81 nm f=0.0138 <S**2>=0.000
281 -> 285 -0.26026
281 -> 286 0.13708
281 -> 287 -0.20528
281 -> 288 -0.20023
281 -> 289 0.28026
281 -> 292 -0.12025
282 -> 285 -0.15894
282 -> 286 0.11131
282 -> 287 0.38180
282 -> 289 -0.12344

Excited State 9: Singlet-A 3.5216 eV 352.07 nm f=0.0188 <S**2>=0.000
281 -> 285 0.18911
281 -> 286 -0.15952
281 -> 287 0.18516
281 -> 288 0.17609
281 -> 289 -0.24595
281 -> 292 0.10714
282 -> 285 -0.15258
282 -> 287 0.45769
282 -> 289 -0.11721

Excited State 10: Singlet-A 3.6052 eV 343.90 nm f=0.0038 <S**2>=0.000
281 -> 285 0.54061
281 -> 286 0.37730
281 -> 287 -0.10091
282 -> 287 0.11332
282 -> 289 0.10155

Excited State 11: Singlet-A 3.6270 eV 341.84 nm f=0.0033 <S**2>=0.000
281 -> 285 -0.27982
281 -> 286 0.53356
281 -> 287 0.26009
281 -> 288 0.11949
281 -> 289 -0.18142

Excited State 12: Singlet-A 3.6597 eV 338.78 nm f=0.0874 <S**2>=0.000
281 -> 283 0.11080
281 -> 285 -0.12458
281 -> 286 -0.13366
282 -> 287 0.28206
282 -> 288 -0.27251
282 -> 289 0.46319
282 -> 291 -0.15277
282 -> 292 -0.15337

Excited State 13: Singlet-A 3.7313 eV 332.28 nm f=0.0135 <S**2>=0.000
281 -> 287 0.57847
281 -> 288 -0.19654
281 -> 289 0.26502
281 -> 292 -0.12273

Excited State 14: Singlet-A 3.8440 eV 322.54 nm f=0.0004 <S**2>=0.000
282 -> 288 0.60890
282 -> 289 0.32543

Excited State 15: Singlet-A 3.8835 eV 319.26 nm f=0.0045 <S**2>=0.000
282 -> 290 0.66210
282 -> 291 -0.18254

Excited State 16: Singlet-A 3.9126 eV 316.88 nm f=0.0010 <S**2>=0.000
282 -> 289 0.27534
282 -> 291 0.36565
282 -> 292 0.51708

Excited State 17: Singlet-A 3.9413 eV 314.57 nm f=0.0017 <S**2>=0.000
282 -> 290 0.18584
282 -> 291 0.52936
282 -> 292 -0.41206

Excited State 18: Singlet-A 3.9815 eV 311.40 nm f=0.0018 <S**2>=0.000
280 -> 284 0.16097
281 -> 288 0.55294
281 -> 289 0.37395

Excited State 19: Singlet-A 3.9859 eV 311.06 nm f=0.0088 <S**2>=0.000
280 -> 284 0.66330
281 -> 288 -0.12854
281 -> 289 -0.10495
282 -> 293 0.12308

Excited State 20: Singlet-A 4.0071 eV 309.41 nm f=0.0040 <S**2>=0.000
280 -> 284 -0.14666
282 -> 293 0.67177

Excited State 21: Singlet-A 4.0218 eV 308.28 nm f=0.0038 <S**2>=0.000
281 -> 290 0.65400
281 -> 291 -0.15128

Excited State 22: Singlet-A 4.0649 eV 305.01 nm f=0.0013 <S**2>=0.000
281 -> 288 -0.11606
281 -> 289 0.26643
281 -> 291 0.33765
281 -> 292 0.53870

Excited State 23: Singlet-A 4.0894 eV 303.18 nm f=0.0022 <S**2>=0.000
281 -> 290 0.18034
281 -> 291 0.55298
281 -> 292 -0.37118

Excited State 24: Singlet-A 4.1447 eV 299.14 nm f=0.0069 <S**2>=0.000
281 -> 293 0.48464
281 -> 302 -0.12132
282 -> 294 0.27959
282 -> 297 0.13259
282 -> 302 -0.22313

Excited State 25: Singlet-A 4.1532 eV 298.53 nm f=0.0096 <S**2>=0.000
281 -> 292 -0.10054
281 -> 293 0.43028
282 -> 294 -0.35524
282 -> 297 -0.15642
282 -> 302 0.22080

Excited State 26: Singlet-A 4.1799 eV 296.62 nm f=0.0476 <S**2>=0.000
280 -> 285 0.37517
280 -> 286 -0.21387
280 -> 287 0.24874
280 -> 288 0.24789
280 -> 289 -0.31451
280 -> 291 0.10039
280 -> 292 0.13578
282 -> 294 0.15734

Excited State 27: Singlet-A 4.2103 eV 294.48 nm f=0.0102 <S**2>=0.000
282 -> 294 0.46476
282 -> 297 -0.31803
282 -> 298 0.20536
282 -> 299 -0.13201
282 -> 302 0.20782
282 -> 303 0.12063
282 -> 308 -0.11112

Excited State 28: Singlet-A 4.2336 eV 292.86 nm f=0.0004 <S**2>=0.000
280 -> 285 -0.18757
282 -> 295 0.60852
282 -> 296 -0.22359
282 -> 297 0.12032

Excited State 29: Singlet-A 4.2461 eV 292.00 nm f=0.0028 <S**2>=0.000
280 -> 285 0.44687
280 -> 286 0.49716

282 -> 295 0.12720

Excited State 30: Singlet-A 4.2488 eV 291.81 nm f=0.0012
<S**2>=0.000
280 -> 286 0.12083
281 -> 291 -0.11709
281 -> 293 0.23497
281 -> 294 -0.27742
281 -> 297 -0.15276
281 -> 302 0.39518
281 -> 303 0.16089
281 -> 304 0.11554

Excited State 31: Singlet-A 4.2698 eV 290.37 nm f=0.0075
<S**2>=0.000
280 -> 286 0.13809
282 -> 295 0.20238
282 -> 296 0.61708
282 -> 299 -0.10981

Excited State 32: Singlet-A 4.2724 eV 290.19 nm f=0.0089
<S**2>=0.000
280 -> 285 -0.27682
280 -> 286 0.37025
280 -> 287 0.27700
280 -> 288 0.14564
280 -> 289 -0.19848
282 -> 295 -0.20654
282 -> 298 -0.10694
282 -> 299 0.15545
282 -> 302 0.10238

Excited State 33: Singlet-A 4.2904 eV 288.98 nm f=0.0487
<S**2>=0.000
280 -> 285 0.13515
280 -> 286 -0.14797
282 -> 294 0.11441
282 -> 296 0.19071
282 -> 297 0.19120
282 -> 299 0.43555
282 -> 301 0.13426
282 -> 302 0.28227

Excited State 34: Singlet-A 4.3018 eV 288.22 nm f=0.0009
<S**2>=0.000
282 -> 297 0.40636
282 -> 298 0.55597

Excited State 35: Singlet-A 4.3194 eV 287.04 nm f=0.0031
<S**2>=0.000
281 -> 294 0.12760
281 -> 299 -0.10360
282 -> 295 0.10066
282 -> 297 -0.26366
282 -> 298 0.28154
282 -> 299 0.42936
282 -> 301 -0.16922
282 -> 302 -0.17969

Excited State 36: Singlet-A 4.3273 eV 286.51 nm f=0.0083
<S**2>=0.000
281 -> 294 0.39338
281 -> 297 -0.26662
281 -> 298 0.21090
281 -> 299 -0.23615
281 -> 303 0.10657
281 -> 308 -0.17264
281 -> 315 0.10069
282 -> 297 0.12051
282 -> 299 -0.18514

Excited State 37: Singlet-A 4.3690 eV 283.78 nm f=0.0002
<S**2>=0.000
280 -> 287 -0.16795
281 -> 294 0.37860
281 -> 295 0.28616
281 -> 296 -0.14235
281 -> 297 0.14697
281 -> 298 -0.10282
281 -> 299 0.20057
281 -> 302 0.22229
282 -> 300 -0.19808

Excited State 38: Singlet-A 4.3771 eV 283.26 nm f=0.0003
<S**2>=0.000
280 -> 287 -0.41873
280 -> 288 0.15139
280 -> 289 -0.21102
282 -> 300 0.44674

Excited State 39: Singlet-A 4.3796 eV 283.09 nm f=0.0020
<S**2>=0.000
280 -> 287 0.34881
280 -> 288 -0.11485
280 -> 289 0.16608
281 -> 294 0.12654
281 -> 295 0.20700
282 -> 300 0.45075
282 -> 302 -0.10462

Excited State 40: Singlet-A 4.3907 eV 282.38 nm f=0.0031
<S**2>=0.000
281 -> 294 -0.22819
281 -> 295 0.56304
281 -> 299 -0.23111
281 -> 302 -0.14861
282 -> 300 -0.10442

Excited State 41: Singlet-A 4.4171 eV 280.69 nm f=0.0004
<S**2>=0.000
281 -> 295 0.11620
281 -> 296 0.66632
281 -> 302 0.11016

Excited State 42: Singlet-A 4.4436 eV 279.02 nm f=0.0103
<S**2>=0.000
282 -> 297 -0.11968
282 -> 301 0.61562
282 -> 302 -0.24130

Excited State 43: Singlet-A 4.4502 eV 278.60 nm f=0.0020
<S**2>=0.000
281 -> 297 0.41034
281 -> 298 0.52708
281 -> 300 0.10947

Excited State 44: Singlet-A 4.4620 eV 277.87 nm f=0.0155
<S**2>=0.000
281 -> 298 0.19225
282 -> 301 -0.18724
282 -> 302 -0.16601
282 -> 303 0.47615
282 -> 304 0.13995
282 -> 308 -0.19564
282 -> 310 -0.11015
282 -> 312 0.11590
282 -> 315 0.12475

Excited State 45: Singlet-A 4.4699 eV 277.38 nm f=0.0057
<S**2>=0.000
281 -> 295 0.13817
281 -> 297 -0.32879
281 -> 298 0.23290
281 -> 299 0.49725
281 -> 301 -0.16073
281 -> 302 -0.11367

Excited State 46: Singlet-A 4.5201 eV 274.30 nm f=0.0047
<S**2>=0.000
281 -> 298 -0.14188
281 -> 299 0.10316
281 -> 300 0.63987
281 -> 302 -0.10304

Excited State 47: Singlet-A 4.5295 eV 273.72 nm f=0.0068
<S**2>=0.000
281 -> 299 0.10464
281 -> 300 -0.17125
282 -> 302 -0.12626
282 -> 304 0.45847
282 -> 305 0.21012
282 -> 306 -0.20390
282 -> 310 0.15521
282 -> 314 0.13541
282 -> 322 0.11330

Excited State 48: Singlet-A 4.5771 eV 270.88 nm f=0.0055
<S**2>=0.000
281 -> 299 -0.14539
281 -> 300 0.13661
281 -> 302 0.11446
281 -> 303 -0.22821
281 -> 304 -0.14465
281 -> 308 0.17873

281 -> 315 -0.11728
282 -> 303 -0.27909
282 -> 304 0.37189
282 -> 306 0.19349

Excited State 49: Singlet-A 4.5942 eV 269.87 nm f=0.0051
<S**2>=0.000
281 -> 297 -0.18247
281 -> 301 0.64067
281 -> 302 -0.16896

Excited State 50: Singlet-A 4.6002 eV 269.52 nm f=0.0014
<S**2>=0.000
281 -> 299 0.11414
281 -> 303 0.25027
281 -> 304 0.14095
281 -> 308 -0.16982
281 -> 315 0.10360
282 -> 302 0.13219
282 -> 303 -0.18696
282 -> 306 0.36734
282 -> 308 -0.15056
282 -> 310 -0.19231
282 -> 313 -0.10476

Excited State 51: Singlet-A 4.6054 eV 269.22 nm f=0.0218
<S**2>=0.000
281 -> 303 -0.10735
282 -> 302 0.10348
282 -> 304 -0.25245
282 -> 305 0.46574
282 -> 308 -0.30233
282 -> 314 0.12281

Excited State 52: Singlet-A 4.6296 eV 267.81 nm f=0.0101
<S**2>=0.000
280 -> 288 0.56316
280 -> 289 0.37231
280 -> 290 -0.14794

Excited State 53: Singlet-A 4.6525 eV 266.49 nm f=0.0061
<S**2>=0.000
282 -> 303 0.21063
282 -> 305 0.38282
282 -> 306 0.34431
282 -> 308 0.33432
282 -> 313 0.11846

Excited State 54: Singlet-A 4.6699 eV 265.50 nm f=0.0155
<S**2>=0.000
280 -> 289 0.21743
280 -> 290 0.64413
280 -> 292 0.11977

Excited State 55: Singlet-A 4.6880 eV 264.47 nm f=0.0199
<S**2>=0.000
281 -> 303 0.37727
281 -> 304 -0.36023
281 -> 305 -0.27824
281 -> 306 0.13403
281 -> 314 -0.13271

Excited State 56: Singlet-A 4.7033 eV 263.61 nm f=0.0042
<S**2>=0.000
280 -> 289 0.13586
280 -> 291 0.20827
280 -> 292 0.24002
282 -> 307 0.54108
282 -> 310 0.15463

Excited State 57: Singlet-A 4.7095 eV 263.27 nm f=0.0075
<S**2>=0.000
280 -> 288 -0.14206
280 -> 289 0.17183
280 -> 290 -0.12953
280 -> 291 0.26091
280 -> 292 0.48415
282 -> 307 -0.32027

Excited State 58: Singlet-A 4.7192 eV 262.72 nm f=0.0076
<S**2>=0.000
281 -> 304 -0.14211
282 -> 304 -0.10741
282 -> 305 -0.16603
282 -> 306 0.30407
282 -> 307 -0.25816
282 -> 308 -0.28356
282 -> 310 0.34911
282 -> 311 -0.14703

Excited State 59: Singlet-A 4.7282 eV 262.22 nm f=0.0052
<S**2>=0.000
280 -> 291 0.11431
281 -> 302 -0.21748
281 -> 303 0.15947
281 -> 304 0.39958
281 -> 305 -0.21044
281 -> 308 0.27257
281 -> 310 0.11758
281 -> 312 -0.11457
281 -> 313 0.11386

Excited State 60: Singlet-A 4.7349 eV 261.85 nm f=0.0067
<S**2>=0.000
280 -> 290 0.10726
280 -> 291 0.55112
280 -> 292 -0.33210
282 -> 309 0.13737

Excited State 61: Singlet-A 4.7414 eV 261.49 nm f=0.0054
<S**2>=0.000
280 -> 291 -0.17041
281 -> 303 -0.16615
281 -> 304 0.24747
281 -> 305 -0.10949
281 -> 306 0.28840
281 -> 310 -0.11674
282 -> 305 -0.10785
282 -> 309 0.41808
282 -> 314 0.14942

Excited State 62: Singlet-A 4.7541 eV 260.80 nm f=0.0129
<S**2>=0.000
281 -> 303 0.13155
281 -> 305 0.12135
281 -> 306 -0.28661
281 -> 310 0.15581
282 -> 309 0.47411
282 -> 311 -0.12687
282 -> 312 0.11013
282 -> 313 0.13759

Excited State 63: Singlet-A 4.7717 eV 259.83 nm f=0.0094
<S**2>=0.000
281 -> 306 -0.15347
282 -> 311 0.40129
282 -> 312 -0.26155
282 -> 313 -0.32880
282 -> 314 0.18409

Excited State 64: Singlet-A 4.7898 eV 258.85 nm f=0.0031
<S**2>=0.000
280 -> 293 -0.12327
281 -> 303 0.18299
281 -> 305 0.50275
281 -> 306 0.36919
281 -> 308 0.16433

Excited State 65: Singlet-A 4.7959 eV 258.52 nm f=0.0069
<S**2>=0.000
280 -> 292 -0.10746
280 -> 293 0.66254
281 -> 306 0.10021

Excited State 66: Singlet-A 4.8095 eV 257.79 nm f=0.0010
<S**2>=0.000
282 -> 310 0.35475
282 -> 311 0.28864
282 -> 312 0.51778

Excited State 67: Singlet-A 4.8276 eV 256.83 nm f=0.0001
<S**2>=0.000
282 -> 309 -0.18010
282 -> 310 -0.20512
282 -> 312 0.14282
282 -> 313 0.30742
282 -> 314 0.47866
282 -> 322 0.11848

Excited State 68: Singlet-A 4.8350 eV 256.43 nm f=0.0081
<S**2>=0.000
282 -> 308 -0.21319
282 -> 311 0.40835
282 -> 312 -0.19110

282 -> 313 0.40272
282 -> 314 -0.17279

Excited State 69: Singlet-A 4.8545 eV 255.40 nm f=0.0007
<S**2>=0.000
278 -> 283 0.11814
281 -> 307 0.65805
281 -> 309 -0.10077

Excited State 70: Singlet-A 4.8597 eV 255.13 nm f=0.0029
<S**2>=0.000
278 -> 283 -0.17521
281 -> 302 -0.13243
281 -> 304 -0.11393
281 -> 305 -0.15995
281 -> 306 0.28154
281 -> 308 -0.26768
281 -> 310 0.41216
281 -> 311 -0.16651

Excited State 71: Singlet-A 4.8924 eV 253.42 nm f=0.0039
<S**2>=0.000
278 -> 283 0.57419
281 -> 307 -0.18346
281 -> 308 -0.12949
281 -> 309 -0.16478
281 -> 310 0.12926
281 -> 312 -0.10879
281 -> 313 -0.13578

Excited State 72: Singlet-A 4.8972 eV 253.17 nm f=0.0025
<S**2>=0.000
281 -> 305 -0.11703
281 -> 309 0.60049
281 -> 314 0.21021

Table 6-10. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **2′$_{opt}$** (The 221th orbital is highest occupied orbital shown in Figure 6-58) [td_b_TN112ac]

Excited State 1: Singlet-A 2.1775 eV 569.39 nm f=0.0037
<S**2>=0.000
221 -> 222 0.70535

Excited State 2: Singlet-A 2.8781 eV 430.79 nm f=0.0471
<S**2>=0.000
219 -> 222 0.17402
220 -> 222 0.64279
221 -> 228 -0.11182
221 -> 229 0.10784

Excited State 3: Singlet-A 2.9738 eV 416.93 nm f=0.0048
<S**2>=0.000
219 -> 222 0.68051
220 -> 222 -0.15401

Excited State 4: Singlet-A 3.2282 eV 384.06 nm f=0.0092
<S**2>=0.000
221 -> 223 0.66597
221 -> 224 0.17480

Excited State 5: Singlet-A 3.3541 eV 369.65 nm f=0.0362
<S**2>=0.000
220 -> 222 0.13581
221 -> 223 -0.18281
221 -> 224 0.60704
221 -> 228 0.22853

Excited State 6: Singlet-A 3.4914 eV 355.12 nm f=0.0202
<S**2>=0.000
220 -> 223 0.61724
220 -> 224 0.21372
220 -> 230 0.10639
221 -> 225 -0.17167

Excited State 7: Singlet-A 3.5084 eV 353.39 nm f=0.0016
<S**2>=0.000
220 -> 223 0.14904
221 -> 225 0.66725

Excited State 8: Singlet-A 3.5285 eV 351.38 nm f=0.0854
<S**2>=0.000
221 -> 224 0.20719
221 -> 226 0.50191
221 -> 227 0.11225
221 -> 228 -0.25202
221 -> 229 0.26788

Excited State 9: Singlet-A 3.5323 eV 351.00 nm f=0.0130
<S**2>=0.000
220 -> 223 -0.27084
220 -> 224 0.43264
220 -> 228 0.32354
220 -> 229 -0.25454
220 -> 230 0.10772

Excited State 10: Singlet-A 3.5452 eV 349.72 nm f=0.0283
<S**2>=0.000
221 -> 224 -0.19370
221 -> 226 0.42429
221 -> 227 -0.14553
221 -> 228 0.36189
221 -> 229 -0.14324
221 -> 230 0.23290

Excited State 11: Singlet-A 3.6954 eV 335.51 nm f=0.0373
<S**2>=0.000
221 -> 227 0.47061
221 -> 228 0.36531
221 -> 229 0.33047

Excited State 12: Singlet-A 3.7304 eV 332.36 nm f=0.0176
<S**2>=0.000
220 -> 224 0.11955
221 -> 227 -0.44478
221 -> 228 0.12154
221 -> 229 0.47062

Excited State 13: Singlet-A 3.7465 eV 330.94 nm f=0.0045
<S**2>=0.000
220 -> 224 0.46745
220 -> 225 -0.11973
220 -> 227 0.15058
220 -> 228 -0.26141
220 -> 229 0.33512
220 -> 230 -0.12638
221 -> 227 0.13399
221 -> 229 -0.11041

Excited State 14: Singlet-A 3.7814 eV 327.88 nm f=0.0091
<S**2>=0.000
220 -> 225 0.59563
220 -> 226 0.11908
221 -> 230 0.24689
221 -> 232 -0.13436

Excited State 15: Singlet-A 3.7853 eV 327.54 nm f=0.0161
<S**2>=0.000
220 -> 225 -0.31278
221 -> 226 -0.12712
221 -> 228 -0.19057
221 -> 230 0.50873
221 -> 232 -0.19268

Excited State 16: Singlet-A 3.8106 eV 325.37 nm f=0.0062
<S**2>=0.000
220 -> 223 -0.10440
220 -> 225 -0.13305
220 -> 226 0.64105
220 -> 230 0.11238
220 -> 232 -0.10794

Excited State 17: Singlet-A 3.8606 eV 321.15 nm f=0.0262
<S**2>=0.000
221 -> 229 0.11585
221 -> 230 0.24094
221 -> 231 0.46674
221 -> 232 0.39661

Excited State 18: Singlet-A 3.8975 eV 318.11 nm f=0.0103
<S**2>=0.000
221 -> 230 -0.16254

221 -> 231 0.45647
221 -> 232 -0.45469
221 -> 235 0.12837
221 -> 238 -0.10475

Excited State 19: Singlet-A 3.9336 eV 315.19 nm f=0.0056
<S**2>=0.000
220 -> 227 0.23539
220 -> 228 0.48355
220 -> 229 0.36538
220 -> 236 -0.12836
220 -> 240 -0.15659

Excited State 20: Singlet-A 3.9900 eV 310.74 nm f=0.0075
<S**2>=0.000
220 -> 227 0.60517
220 -> 229 -0.30739

Excited State 21: Singlet-A 4.0482 eV 306.27 nm f=0.0052
<S**2>=0.000
220 -> 226 -0.14455
220 -> 227 0.12037
220 -> 228 -0.15091
220 -> 230 0.46707
220 -> 231 -0.10103
220 -> 232 -0.29088
221 -> 233 -0.19740

Excited State 22: Singlet-A 4.0676 eV 304.81 nm f=0.0235
<S**2>=0.000
219 -> 223 0.13586
220 -> 230 0.21917
220 -> 231 -0.12428
221 -> 233 0.37575
221 -> 235 -0.15102
221 -> 236 0.30147
221 -> 238 0.12375
221 -> 239 0.12459
221 -> 240 0.21883

Excited State 23: Singlet-A 4.0890 eV 303.21 nm f=0.0122
<S**2>=0.000
219 -> 223 -0.18996
220 -> 230 0.13209
220 -> 231 0.10579
221 -> 233 0.47310
221 -> 234 0.16158
221 -> 236 -0.25345
221 -> 240 -0.20619
221 -> 241 0.10054

Excited State 24: Singlet-A 4.1090 eV 301.74 nm f=0.0147
<S**2>=0.000
219 -> 223 0.26394
220 -> 229 0.11615
220 -> 230 0.34084
220 -> 231 0.31560
220 -> 232 0.33620
221 -> 233 -0.11302

Excited State 25: Singlet-A 4.1270 eV 300.42 nm f=0.0531
<S**2>=0.000
219 -> 223 0.38836
219 -> 224 0.21475
220 -> 230 -0.13969
220 -> 232 -0.25430
221 -> 234 0.36544
221 -> 236 -0.14123

Excited State 26: Singlet-A 4.1329 eV 299.99 nm f=0.0192
<S**2>=0.000
219 -> 223 -0.28733
220 -> 231 -0.15569
220 -> 232 0.12980
221 -> 232 -0.11675
221 -> 233 -0.13693
221 -> 234 0.46891
221 -> 235 -0.10633
221 -> 237 0.13664
221 -> 238 0.14924
221 -> 240 0.15383

Excited State 27: Singlet-A 4.1533 eV 298.52 nm f=0.0050
<S**2>=0.000
221 -> 233 0.16717
221 -> 234 0.13372
221 -> 235 0.62400
221 -> 236 0.15092

Excited State 28: Singlet-A 4.1690 eV 297.40 nm f=0.0026
<S**2>=0.000
219 -> 223 -0.23099
219 -> 224 0.44844
219 -> 228 0.27693
219 -> 229 -0.23364
219 -> 230 0.10862
220 -> 231 -0.15611
221 -> 234 -0.14417

Excited State 29: Singlet-A 4.1895 eV 295.94 nm f=0.0468
<S**2>=0.000
219 -> 223 -0.23505
220 -> 231 0.49857
220 -> 232 -0.26938
221 -> 236 0.26158

Excited State 30: Singlet-A 4.2049 eV 294.86 nm f=0.0327
<S**2>=0.000
221 -> 232 -0.11174
221 -> 234 -0.18709
221 -> 235 0.16636
221 -> 236 -0.31094
221 -> 237 0.45398
221 -> 238 0.21251
221 -> 240 0.15952

Excited State 31: Singlet-A 4.2475 eV 291.90 nm f=0.0093
<S**2>=0.000
221 -> 236 -0.15715
221 -> 237 -0.41512
221 -> 238 0.41982
221 -> 239 0.17732
221 -> 240 0.12975
221 -> 241 0.12075

Excited State 32: Singlet-A 4.2642 eV 290.76 nm f=0.0053
<S**2>=0.000
220 -> 229 0.11245
220 -> 231 0.12529
220 -> 236 0.19071
220 -> 239 0.10263
220 -> 240 0.17328
221 -> 236 -0.24559
221 -> 237 -0.15695
221 -> 238 -0.17723
221 -> 240 0.35522
221 -> 241 -0.25169

Excited State 33: Singlet-A 4.2877 eV 289.16 nm f=0.0049
<S**2>=0.000
220 -> 228 0.11351
220 -> 229 0.16599
220 -> 234 -0.16062
220 -> 236 0.32591
220 -> 239 0.14536
220 -> 240 0.29887
220 -> 241 -0.10473
221 -> 237 0.10667
221 -> 238 0.12955
221 -> 239 0.11748
221 -> 240 -0.20687
221 -> 241 0.18772

Excited State 34: Singlet-A 4.2992 eV 288.39 nm f=0.0120
<S**2>=0.000
221 -> 237 0.10241
221 -> 238 -0.25206
221 -> 239 0.57505

Excited State 35: Singlet-A 4.3516 eV 284.91 nm f=0.0024
<S**2>=0.000
219 -> 224 0.11318
219 -> 229 0.12777
220 -> 233 0.62387
220 -> 235 -0.15274

Excited State 36: Singlet-A 4.3708 eV 283.67 nm f=0.0221
<S**2>=0.000
219 -> 224 0.43494
219 -> 225 -0.12375
219 -> 227 0.15598
219 -> 228 -0.24740
219 -> 229 0.34985
219 -> 230 -0.14227

220 -> 233 -0.19255

Excited State 37: Singlet-A 4.3871 eV 282.61 nm f=0.0035
<S**2>=0.000
220 -> 232 -0.17991
220 -> 234 0.53375
220 -> 237 0.15067
220 -> 238 0.15054
220 -> 240 0.15511
221 -> 238 -0.10953
221 -> 239 -0.10063
221 -> 240 0.11170
221 -> 241 0.17323

Excited State 38: Singlet-A 4.3986 eV 281.87 nm f=0.0006
<S**2>=0.000
219 -> 225 0.67091
219 -> 226 0.11625

Excited State 39: Singlet-A 4.4074 eV 281.31 nm f=0.0035
<S**2>=0.000
220 -> 234 -0.24815
221 -> 238 -0.22410
221 -> 239 -0.18472
221 -> 240 0.29128
221 -> 241 0.45681
221 -> 243 -0.11008

Excited State 40: Singlet-A 4.4211 eV 280.44 nm f=0.0070
<S**2>=0.000
219 -> 225 -0.11031
219 -> 226 0.29521
220 -> 233 0.17093
220 -> 235 0.55667
220 -> 236 0.12428

Excited State 41: Singlet-A 4.4353 eV 279.54 nm f=0.0485
<S**2>=0.000
219 -> 226 0.57998
220 -> 235 -0.30544

Excited State 42: Singlet-A 4.4765 eV 276.97 nm f=0.0008
<S**2>=0.000
220 -> 234 -0.19785
220 -> 235 0.14181
220 -> 236 -0.39362
220 -> 237 0.41380
220 -> 238 0.16935
220 -> 240 0.16874

Excited State 43: Singlet-A 4.4885 eV 276.23 nm f=0.0096
<S**2>=0.000
221 -> 239 -0.11646
221 -> 241 -0.12929
221 -> 242 0.52733
221 -> 243 -0.19643
221 -> 245 -0.18063
221 -> 247 0.24221

Excited State 44: Singlet-A 4.5302 eV 273.68 nm f=0.0004
<S**2>=0.000
220 -> 234 -0.11850
220 -> 236 0.31220
220 -> 237 0.37490
220 -> 239 -0.32984
220 -> 240 -0.29355

Excited State 45: Singlet-A 4.5333 eV 273.50 nm f=0.0160
<S**2>=0.000
219 -> 228 0.12075
220 -> 234 -0.14566
220 -> 237 -0.24794
220 -> 238 0.50027
220 -> 239 -0.18058
220 -> 241 0.11802
220 -> 245 0.12152
221 -> 242 0.11343

Excited State 46: Singlet-A 4.5414 eV 273.01 nm f=0.0168
<S**2>=0.000
220 -> 237 0.21591
220 -> 239 0.27202
220 -> 240 -0.18705
220 -> 241 0.18108
220 -> 243 -0.11257
220 -> 247 0.11514
221 -> 241 0.17392
221 -> 242 0.21515
221 -> 243 0.31165
221 -> 247 -0.17284

Excited State 47: Singlet-A 4.5545 eV 272.22 nm f=0.0084
<S**2>=0.000
219 -> 227 0.14269
219 -> 228 0.25711
219 -> 229 0.16220
220 -> 239 0.22356
221 -> 243 -0.31700
221 -> 244 0.14896
221 -> 245 0.34710

Excited State 48: Singlet-A 4.5627 eV 271.73 nm f=0.0120
<S**2>=0.000
220 -> 238 -0.17015
220 -> 239 -0.15710
220 -> 240 0.13066
220 -> 241 -0.14392
221 -> 242 0.34724
221 -> 243 0.15553
221 -> 245 0.34168
221 -> 247 -0.26444

Excited State 49: Singlet-A 4.5963 eV 269.75 nm f=0.0270
<S**2>=0.000
219 -> 227 0.42063
219 -> 228 0.35038
220 -> 238 -0.21358
220 -> 239 -0.16091
221 -> 243 0.22201
221 -> 245 -0.13271
221 -> 247 0.13663

Excited State 50: Singlet-A 4.6119 eV 268.84 nm f=0.0119
<S**2>=0.000
221 -> 243 0.22945
221 -> 244 0.60316
221 -> 247 0.21609

Excited State 51: Singlet-A 4.6182 eV 268.47 nm f=0.0105
<S**2>=0.000
219 -> 227 0.46638
219 -> 228 -0.22966
219 -> 229 -0.39766
221 -> 243 -0.10317
221 -> 244 0.10458
221 -> 247 -0.11394

Excited State 52: Singlet-A 4.6433 eV 267.02 nm f=0.0183
<S**2>=0.000
219 -> 228 -0.13188
220 -> 238 0.11722
221 -> 243 0.18143
221 -> 244 -0.20911
221 -> 245 0.31097
221 -> 246 0.31073
221 -> 247 0.36113

Excited State 53: Singlet-A 4.6818 eV 264.82 nm f=0.0010
<S**2>=0.000
220 -> 241 0.11223
221 -> 243 -0.12001
221 -> 244 0.14010
221 -> 245 -0.14756
221 -> 246 0.56476
221 -> 247 -0.18684

Excited State 54: Singlet-A 4.6879 eV 264.48 nm f=0.0345
<S**2>=0.000
219 -> 226 -0.11375
219 -> 229 0.18951
219 -> 230 0.42818
219 -> 232 -0.16483
220 -> 239 0.14695
220 -> 240 -0.18709
220 -> 241 -0.25208
221 -> 245 -0.14014
221 -> 247 -0.13434

Excited State 55: Singlet-A 4.6951 eV 264.07 nm f=0.0466
<S**2>=0.000
219 -> 228 -0.16462
219 -> 230 0.44882
220 -> 239 -0.16111
220 -> 240 0.19627

220 -> 241 0.34331
220 -> 243 -0.12607

Excited State 56: Singlet-A 4.7184 eV 262.77 nm f=0.0104
<S**2>=0.000
220 -> 238 0.18636
220 -> 239 -0.22058
220 -> 241 -0.26636
220 -> 242 0.35734
220 -> 243 -0.11117
220 -> 245 -0.27153
220 -> 247 0.27211

Excited State 57: Singlet-A 4.7490 eV 261.07 nm f=0.0158
<S**2>=0.000
219 -> 230 0.11043
219 -> 231 0.27851
219 -> 232 0.23347
221 -> 248 0.54524

Excited State 58: Singlet-A 4.7586 eV 260.55 nm f=0.0734
<S**2>=0.000
219 -> 231 0.43040
219 -> 232 0.25033
220 -> 241 -0.18407
221 -> 248 -0.39092

Excited State 59: Singlet-A 4.7958 eV 258.53 nm f=0.0341
<S**2>=0.000
219 -> 230 0.10522
219 -> 231 -0.39641
219 -> 232 0.48834
220 -> 241 -0.10211
220 -> 242 -0.13742

Excited State 60: Singlet-A 4.8035 eV 258.11 nm f=0.0053
<S**2>=0.000
219 -> 232 0.11721
220 -> 242 0.48310
220 -> 243 -0.12281
220 -> 245 0.37714
220 -> 247 -0.17219
220 -> 250 0.10175

Excited State 61: Singlet-A 4.8143 eV 257.54 nm f=0.0078
<S**2>=0.000
220 -> 241 0.12712
220 -> 242 0.14216
220 -> 243 0.38221
220 -> 244 -0.13258
220 -> 245 -0.17875
220 -> 247 -0.14532
221 -> 246 -0.13069
221 -> 250 -0.19570
221 -> 251 0.27478
221 -> 252 -0.15149
221 -> 253 0.11369

Excited State 62: Singlet-A 4.8233 eV 257.05 nm f=0.0043
<S**2>=0.000
220 -> 241 0.11031
220 -> 242 0.19327
220 -> 243 0.36128
220 -> 247 -0.10459
221 -> 246 0.13572
221 -> 248 -0.10387
221 -> 250 0.30452
221 -> 251 -0.27259
221 -> 252 0.16215
221 -> 253 -0.11964

Excited State 63: Singlet-A 4.8372 eV 256.32 nm f=0.0098
<S**2>=0.000
217 -> 222 0.20832
218 -> 222 -0.12602
221 -> 249 0.55541
221 -> 250 0.23497
221 -> 255 0.11120

Excited State 64: Singlet-A 4.8534 eV 255.46 nm f=0.0020
<S**2>=0.000
217 -> 222 0.22256
218 -> 222 -0.11579
221 -> 249 -0.33533
221 -> 250 0.40993
221 -> 251 0.23740
221 -> 252 -0.17268
221 -> 253 0.15482
221 -> 259 -0.11650

Excited State 65: Singlet-A 4.8673 eV 254.73 nm f=0.0025
<S**2>=0.000
217 -> 222 0.46997
218 -> 222 -0.33104
220 -> 242 0.10293
221 -> 250 -0.22714
221 -> 251 -0.18631

Excited State 66: Singlet-A 4.8808 eV 254.02 nm f=0.0004
<S**2>=0.000
220 -> 243 0.24531
220 -> 244 0.57958
220 -> 247 0.22624

Excited State 67: Singlet-A 4.9107 eV 252.48 nm f=0.0068
<S**2>=0.000
220 -> 243 0.14466
220 -> 244 -0.19466
220 -> 245 0.22713
220 -> 246 0.21994
220 -> 247 0.29520
221 -> 251 0.31118
221 -> 252 0.26089
221 -> 253 -0.20450

Excited State 68: Singlet-A 4.9131 eV 252.35 nm f=0.0056
<S**2>=0.000
220 -> 243 -0.12361
220 -> 244 0.26601
220 -> 245 -0.21567
220 -> 246 -0.16306
220 -> 247 -0.25933
221 -> 251 0.29246
221 -> 252 0.32037
221 -> 253 -0.21332

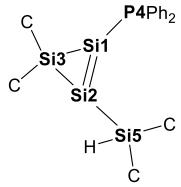
Excited State 69: Singlet-A 4.9500 eV 250.47 nm f=0.0013
<S**2>=0.000
218 -> 222 0.11867
219 -> 233 0.35582
219 -> 235 -0.13082
219 -> 236 0.17533
220 -> 246 -0.21523
221 -> 252 0.24820
221 -> 253 0.26210
221 -> 254 -0.10944
221 -> 255 -0.11755

Excited State 70: Singlet-A 4.9573 eV 250.10 nm f=0.0026
<S**2>=0.000
219 -> 233 0.37716
219 -> 235 -0.14349
219 -> 236 0.10833
220 -> 246 0.27733
220 -> 247 -0.11648
221 -> 252 -0.25937
221 -> 253 -0.28234

Excited State 71: Singlet-A 4.9651 eV 249.71 nm f=0.0045
<S**2>=0.000
220 -> 245 -0.11725
220 -> 246 0.48345
220 -> 247 -0.16235
221 -> 252 0.26504
221 -> 253 0.30383

Excited State 72: Singlet-A 4.9799 eV 248.97 nm f=0.0017
<S**2>=0.000
217 -> 222 0.25182
218 -> 222 0.40684
219 -> 233 -0.32229
219 -> 234 -0.23063
219 -> 236 0.21556
219 -> 240 0.11171

Table 6-11. Natural Bond Orbital (NBO) Analysis for $\mathbf{8_{opt}}$



NBO	NBO[a] analysis			
	occ.,[a]	population	hybrids	WBI[a]
Si1-Si2	1.938	48.84% (Si1)	s 31.24%, p 68.40%, d 0.35% ($sp^{2.19}d^{0.01}$) (Si1)	1.7338
		51.16% (Si2)	s 31.00%, p 68.66%, d 0.34% ($sp^{2.21}d^{0.01}$) (Si2)	
Si1-Si2	1.791	46.41% (Si1)	s 0.08%, p 99.51%, d 0.41% ($sp^{99.99}d^{5.12}$) (Si1)	-
		53.59% (Si2)	s 0.07%, p 99.65%, d 0.28% ($sp^{99.99}d^{3.83}$) (Si2)	
Si1-Si3	1.888	56.83% (Si1)	s 33.70%, p 66.07%, d 0.23% ($sp^{1.96}d^{0.01}$) (Si1)	1.0038
		43.17% (Si3)	s 19.93%, p 79.54%, d 0.53% ($sp^{3.99}d^{0.03}$) (Si3)	
Si1-P4	1.934	46.16% (Si1)	s 34.80%, p 64.92%, d 0.28% ($sp^{1.87}d^{0.01}$) (Si1)	0.9010
		53.84% (P4)	s 13.78%, p 85.75%, d 0.47% ($sp^{6.22}d^{0.03}$) (P4)	
Si2-Si3	1.857	54.56% (Si2)	s 27.91%, p 71.77%, d 0.32% ($sp^{2.57}d^{0.01}$) (Si2)	0.9907
		45.44% (Si3)	s 24.18%, p 75.34%, d 0.48% ($sp^{3.12}d^{0.02}$) (Si3)	
Si2-Si5	1.970	56.08% (Si2)	s 40.80%, p 59.01%, d 0.19% ($sp^{1.45}$) (Si2)	0.9231
		43.92% (Si5)	s 25.11%, p 74.39%, d 0.50% ($sp^{2.96}d^{0.02}$) (P4)	

[a]NBO: natural bond orbital. occ.: occupancy. WBI: Wiberg bond indices. JOB number: nbo1TN126aa

2-5. Reference and Notes

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