Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Phenylene-bridged cross-conjugated 1,2,3-trisilacyclopentadienes

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# 1. Experimental details

General Considerations

All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk or glovebox techniques. Solvents were distilled and degassed by reflux over sodium/benzophenone under argon. Benzene-$d_6$ and Toluene-$d_8$ were dried over potassium and distilled under argon before use. Cyclotrisilene **1** (1,1,2,3 tetra(2,4,6-triisopropylphenyl)trisilacyclopropene) was prepared according to published procedures.[ref] Phenylacetylene was purified before use by distillation under argon in vacuum and kept in a Schlenk tube filled with argon atmosphere. 1,4-diethynylbenzene was purified before use by sublimation in vacuum. Other chemicals were obtained commercially and used as supplied.

NMR spectroscopy were recorded on a Bruker Avance **III** 300 MHz spectrometer. $^{1}$H and $^{13}$C NMR spectra were referenced to residual signals of the solvent. $^{29}$Si and referenced to external $SiMe_4$. UV/vis spectra were acquired using a Perkin-Elmer Lambda 35 spectrometer using quartz cells with a path length of 0.1 cm. Melting points were determined under argon in sealed NMR tubes and are thus uncorrected. Elemental analyses were performed on a Leco CHN-900 analyzer.

Synthesis of 4-phenyl-1,1,2,3-tetrakis(2,4,6-triisopropylphenyl)-1*H*-1,2,3-trisilole **2a**

Cyclotrisilene **1** (300 mg, 0.334 mmol) was dissolved in 8 mL thf at room temperature, the resulting orange solution was cooled to −20°C. Phenylacetylene (36.7 µl, 0.334 mmol) was introduced via micro syringe to the cyclotrisilene solution. A color change from orange to dark-red occurred after phenylacetylene was added. After stirring the reaction mixture in cooling bath over one hour, removal of the solvent thf under vacuum, a red foam residue was obtained, which was redissolved in hexane. The thus obtained red solution was concentrated to ~3 mL and kept at room temperature over three days. Red crystals of **2a** (yield: 0.20 g, 59.9%) formed and were separated by solvent decantation and dried in vacuum. M. p. 178-180°C, decomposition.

**$^{1}$H NMR** (300.13 MHz, $C_6D_6$, 300 K): δ 7.43 (s, 1H, SiPhC=C*H*Si); 7.27 (s, 1H, Tip-*H*); 7.25 (s, 1H, Tip-*H*); 7.09 (br. 1H, Tip-*H*); 7.06, 7.03 (s, 2H, Tip-*H*); 6.95, 6.82 (m, 5H, Ph-*H*); 4.01 (br, 6H, $^{i}$Pr-C*H*); 2.73 (m, 6H, $^{i}$Pr-C*H*); 1.28, 1.26 (br, 9H, $^{i}$Pr-C*H*$_3$); 1.24, 1.23 (d, 12H, $^{i}$Pr-C*H*$_3$); 1.21 (d, 12H, $^{i}$Pr-C*H*$_3$); 1.24, 1.18 (d, 6H, $^{i}$Pr-C*H*$_3$); 1.16 (d, 12H, $^{i}$Pr-C*H*$_3$); 1.13 (d, 12H, $^{i}$Pr-C*H*$_3$); 1.11, 1.07 (br, 9H, $^{i}$Pr-C*H*$_3$) ppm.

**$^{13}$C{$^{1}$H} NMR** (75.47 MHz, $C_6D_6$, 300 K): δ 160.73 (SiPh*C*=CHSi); 145.49 (SiPhC=*C*HSi); 157.16, 155.22, 151.76, 150.94, 149.28, 147.41 (Tip-*C*); 135.04 (Ph-*C*); 131.70 (Tip-*C*H); 126.92, 122.03, 121.72, 121.42 (Tip-*C*H and Ph-*C*H); 38.98, 37.78, 35.48, 34.58, 34.55, 34.48, 31.79 ($^{i}$Pr-*C*H); 26.84, 25.51, 24.66, 24.35, 24.10, 23.97, 23.86, 22.88 ($^{i}$Pr-*C*H$_3$) ppm.

**$^{29}$Si{$^{1}$H} NMR** (59.6 MHz, $C_6D_6$, 300 K): δ 111.9, 34.08 (Tip*Si*=*Si*Tip), −27.02 (*Si*Tip$_2$) ppm.

**UV/Vis** (hexane) $\lambda_{max}$ (ε) 493 nm (3719 $M^{-1}cm^{-1}$).

**Elemental Analysis** Calc. for $C_{68}H_{98}Si_3$: C, 81.69; H, 9.88; Found: C, 81.13; H, 10.25.

Synthesis of 4,5-diphenyl-1,1,2,3-tetrakis(2,4,6-triisopropylphenyl)-1*H*-1,2,3-trisilole **2b**

Cyclotrisilene **1** (300 mg, 0.334 mmol) and diphenylacetylene (59.5 mg, 0.334 mmol) were mixed and dissolved in toluene at room temperature. The resulting dark-red mixture was stirred at room temperature over ten hours. Afterwards toluene was removed under vacuum, the dark-red residue was extracted with pentane (2*5 mL). After filtration the filtrate was concentrated to ~5 mL and stored at –20°C overnight. Crude crystals of **2b** thus formed were separated by solvent decantation and dried in vacuum (yield: 200 mg, 56%). Recrystallization with pentane resulted in spectroscopically pure red crystals of **2b** (yield: 145 mg, 40.3%). M. p. 122-124°C.

**$^1$H NMR** (300.13 MHz, $C_6D_6$, 300 K): δ 7.37 (s, 1H, Tip-*H*); 7.24 (s, 1H, Tip-*H*); 7.14 (overlapped with solvent, 1H, Tip-*H*); 7.01 (s, 1H, Tip-*H*); 6.88 (s, 1H, Tip-*H*); 6.85 (s, 1H, Tip-*H*); 6.83 (s, 2H, Tip-*H*); 6.82-6.78 (m, 2H, Ph-*H*); 6.65 (m, 4H, Ph-*H*); 6.45 (m, 1H, Ph-*H* ); 5.22 (m, 1H, $^i$Pr-C*H*); 4.62 (m, 2H, $^i$Pr-C*H*); 4.07, 3.92 (m, 2H, $^i$Pr-C*H*); 3.37, 3.22 (m, 2H, $^i$Pr-C*H*); 2.81 (m, 5H, $^i$Pr-C*H*); 2.18 (d, 6H, $^i$Pr-C$H_3$ ), 2.19 (d, 3H, $^i$Pr-C$H_3$); 1.58 (d, 6H, $^i$Pr-C$H_3$); 1.48, 1.40, 1.33 (each d, 9H, $^i$Pr-C$H_3$); 1.24, 1.21, 1.19, 1.17, 1.15 (br, 27H, $^i$Pr-C$H_3$); 1.07 (d, 6H, $^i$Pr-C$H_3$); 0.53 (d, 3H, $^i$Pr-C$H_3$); 0.40 (br, 6H, $^i$Pr-C$H_3$); 0.16, 0.03 (each d, 6H, $^i$Pr-C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (75.47 MHz, $C_6D_6$, 300 K): δ 164.86, 143.16 (–Ph*C*=*C*Ph–); 157.85, 157.48, 157.12, 156.51, 155.75, 155.46, 155.22, 153.24, 151.92, 151.24, 150.84 , 149.84, 149.09 (Tip-*C*); 145.09, 137.16, 134.61, 131.80 (Tip-*C*); 130.81, 128.68, 128.64, 128.47 (Tip-*C*H, Ph*C*H); 126.52, 125.01, 124.57 (Ph*C*H); 123.23, 122.88, 122.81, 122.15, 122.05, 121.06, 120.98, 120.82 (Tip-*C*H); 39.67, 38.71, 38.44, 36.89, 36.68, 36.60, 35.85 ($^i$Pr-*C*H); 34.94, 34.56, 34.48, 34.45, 34.41, 34.27 ($^i$Pr-*C*H); 28.44, 27.55, 27.12, 26.62, 26.52, 26.47, 25.63, 25.20, 24.59, 24.39, 24.35, 24.11, 24.08, 24.06, 23.99, 23.80, 23.76, 23.73, 23.57, 23.51, 23.20, 22.55, 22.43 ($^i$Pr-*C*$H_3$) ppm.

**$^{29}$Si{$^1$H} NMR** (59.6 MHz, $C_6D_6$, 300 K): δ 106.8, 43.30 (Tip*Si*=*Si*Tip), –19.8 (*Si*$Tip_2$) ppm.

**UV/Vis** (hexane) $\lambda_{max}$ (ε) 495 nm (6237 $M^{-1}cm^{-1}$).

**Elemental Analysis** Calc. for $C_{74}H_{102}Si_3$. C, 82.61; H, 9.56; Found: C, 81.58; H, 9.00.

Synthesis of 1,4-bis(1,1,2,3-tetrakis(2,4,6-triisopropylphenyl)-1*H*-1,2,3-trisilol-4-yl)-benzene **3**

Cyclotrisilene **1** (300 mg, 0.334 mmol) and 1,4-diethynylbenzene (21 mg, 0.167 mmol) were mixed and dissolved in thf (10 mL) at room temperature. The resulting red mixture was stirred overnight at room temperature. After removal of toluene in vacuum, the red-brown residue was dissolved in 10 mL hexane. The resulting hexane solution was concentrated to ~3 mL and kept at room temperature. Microcrystals of **3** deposited after one day (yield: 0.33 g, 52%). Pure purple crystals of **3** were isolated by recrystallization from pentane at ambient temperature. M. p. 184-186°C, decomposition.

**$^1$H NMR** (300.13 MHz, $C_6D_6$, 300 K): δ 7.27 (s. 2H, PhC=C*H*); 7.14 (overlapped with solvent, 4H, Ph-*H*); 7.07 (br, 4H, Tip-*H*); 7.04 (s, 4H, Tip-*H*); 7.00 (s, 8H, Tip-*H*); 3.97 (br,

12H, $^{i}$Pr-C*H*); 2.82 (m, 12H, $^{i}$Pr-C*H*); 1.28, 1.26 (d, 24H, $^{i}$Pr-C$H_3$); 1.23-1.17 (d, total 72H, $^{i}$Pr-C$H_3$); 1.01, 1.09 (br, 24H, $^{i}$Pr-C$H_3$) ppm.

**$^{13}$C{$^{1}$H} NMR**(75.47 MHz, $C_6D_6$, 300 K): δ 160.21 (Ph*C*=CHSi); 146.84 (PhC=*C*HSi); 157.18, 155.15, 154.69, 151. 57, 150.87, 149. 23, 144.25 (Tip-*C*); 135.05, 131.57 (Tip-*C*); 126.94, 122.00, 121.66, 121.27 (Ph-*C*H); 38.91, 37.83, 35.38, 34.70, 34.52, 34.47 ($^{i}$Pr-*C*H); 26.92, 25.49, 24.55, 24.38, 24.08, 24.02, 23.94, 23.85, 23.66 ($^{i}$Pr-*C*$H_3$) ppm.

**$^{29}$Si{$^{1}$H} NMR** (59.6 MHz, $C_6D_6$, 300 K): δ 109.68, 32.97 (Tip*Si*=*Si*Tip), −26.97 (*Si*$Tip_2$) ppm.

**UV/Vis** (hexane) $\lambda_{max}$ (ε) 495 nm (7484 $M^{-1}cm^{-1}$).

**Elemental Analysis** Calc. for $C_{130}H_{190}Si_6$. C, 81.26; H, 9.97 Found: C, 80.52; H, 9.73

## 2. Plots of NMR spectra

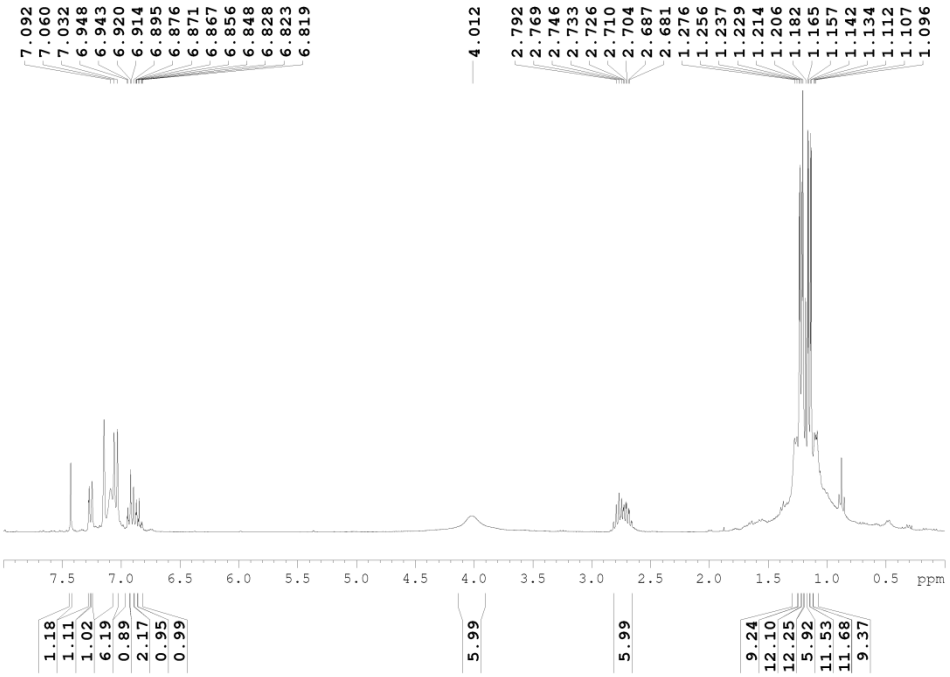



**Figure S1.** $^{1}$H NMR (300.13 MHz, $C_6D_6$, 300 K) of **2a**.

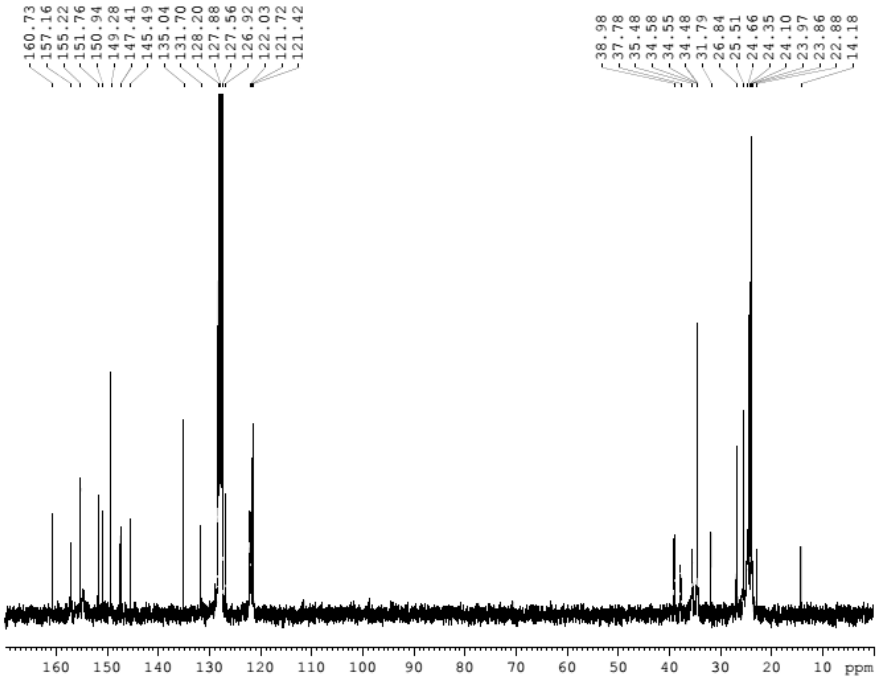



**Figure S2.** $^{13}$C{$^{1}$H} NMR (75.47 MHz, $C_6D_6$, 300 K) of **2a**.

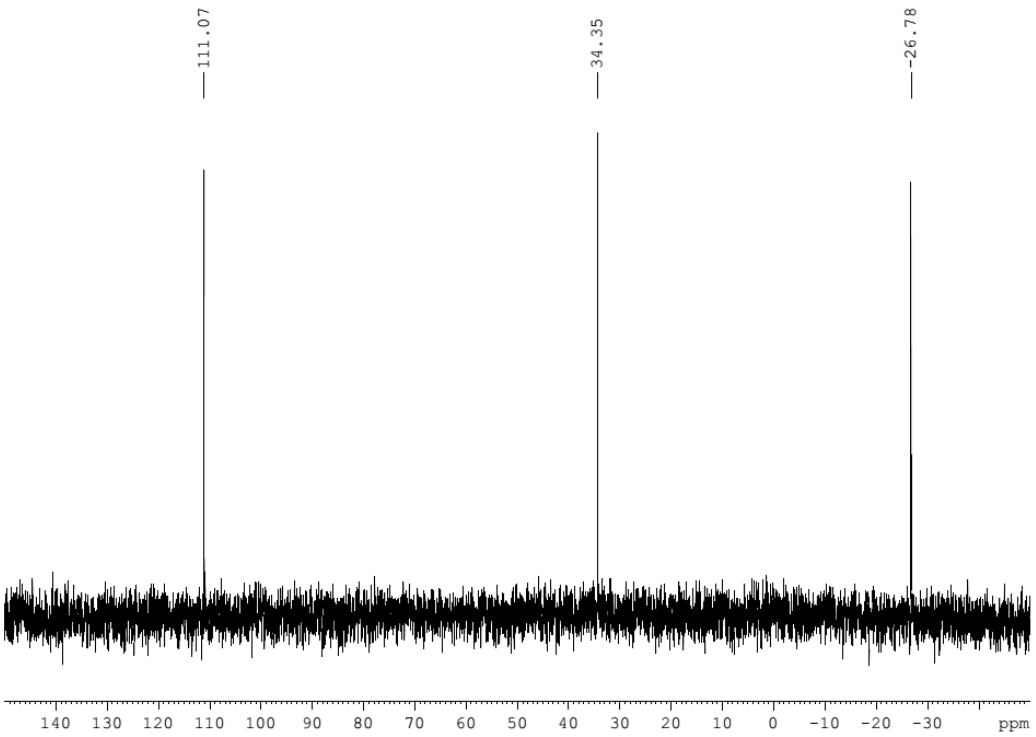



**Figure S3.** $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, $C_6D_6$, 300 K) of **2a**.

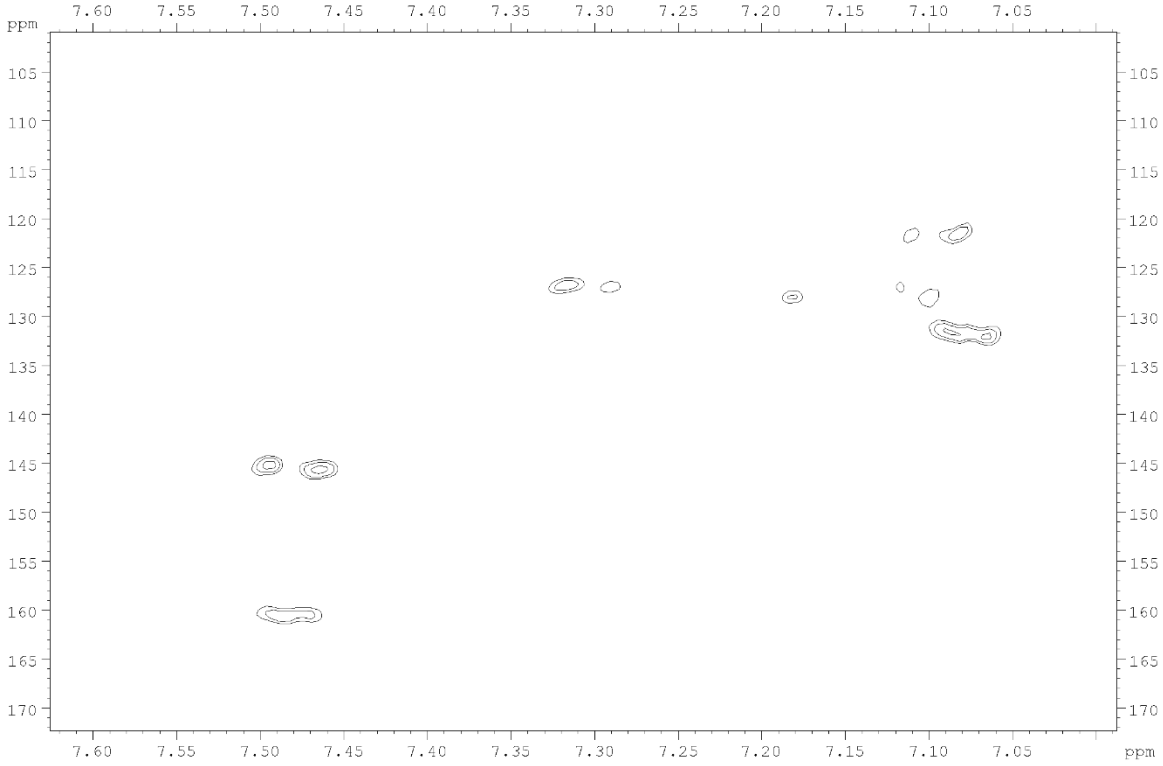



**Figure S4.** $^{1}H/^{13}C$ HMBC ($C_6D_6$, 300 K) of **2a**.

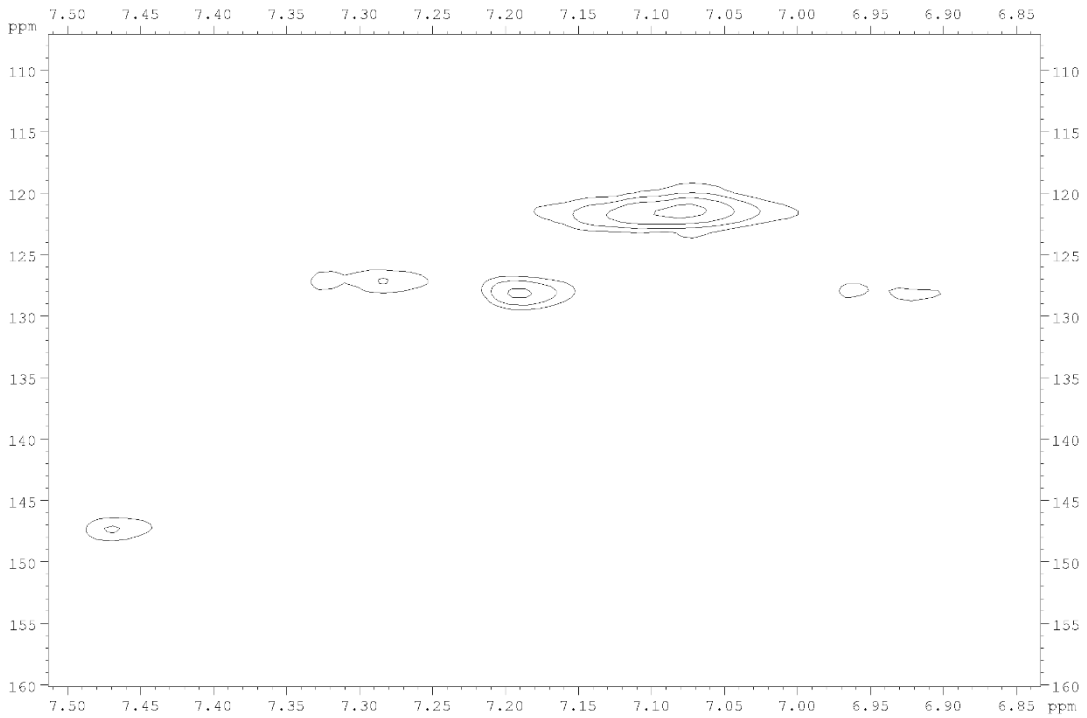



**Figure S5.** $^{1}H/^{13}C$ HMQC ($C_6D_6$, 300 K) of **2a**.

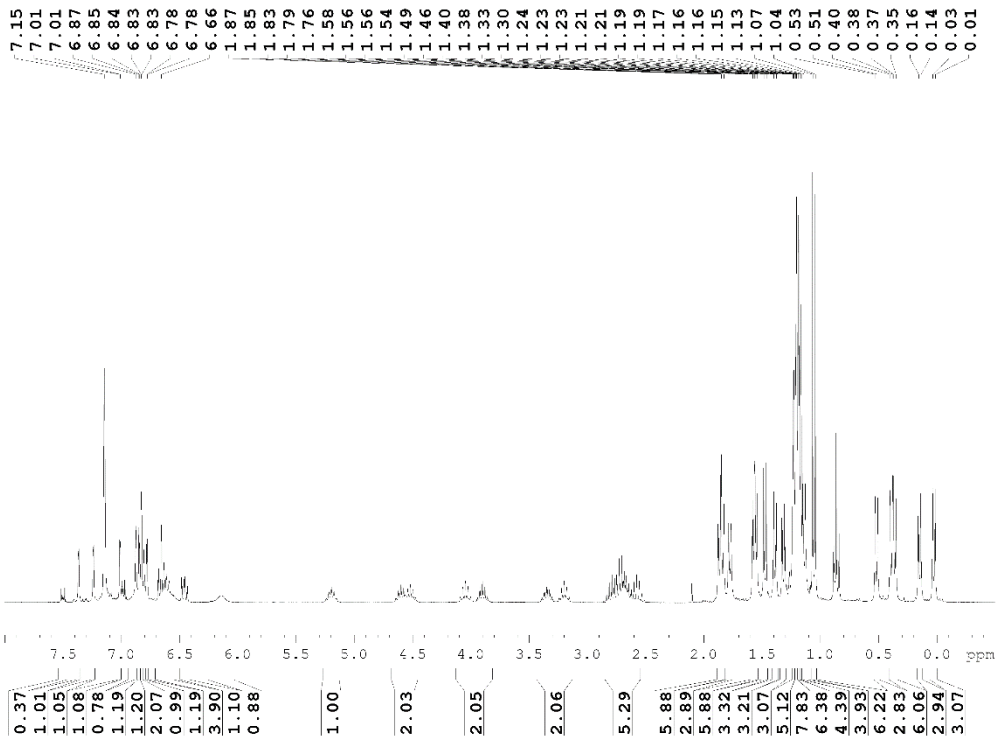



**Figure S6.** $^{1}H$ NMR (59.6 MHz, $C_6D_6$, 300 K) of **2b**.

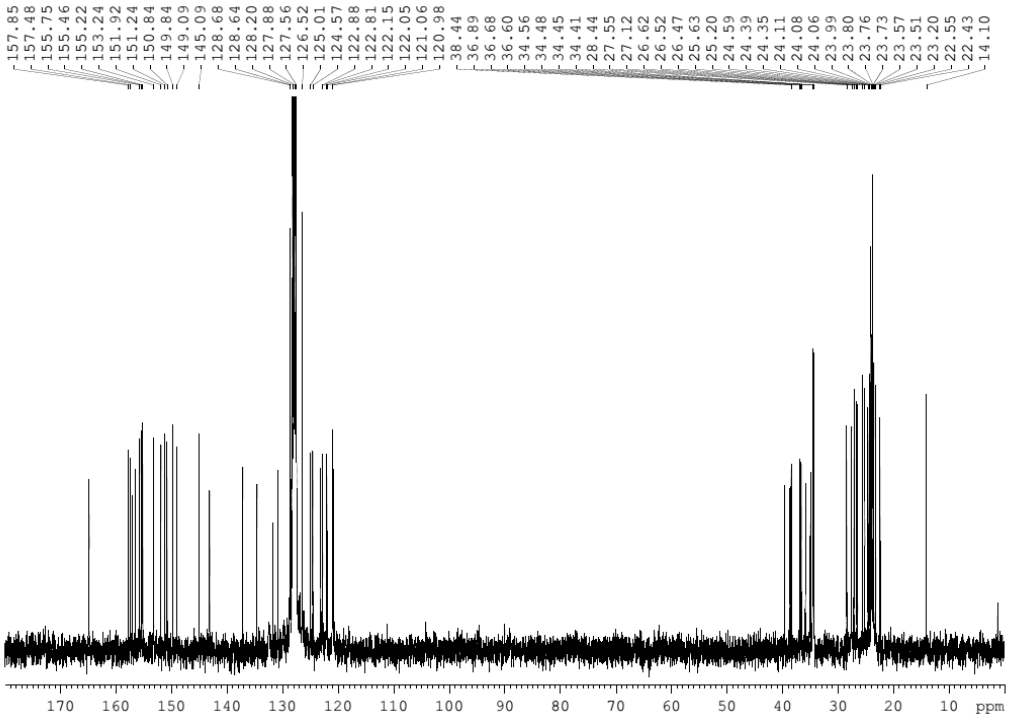



**Figure S7.** $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $C_6D_6$, 300 K) of **2b**.

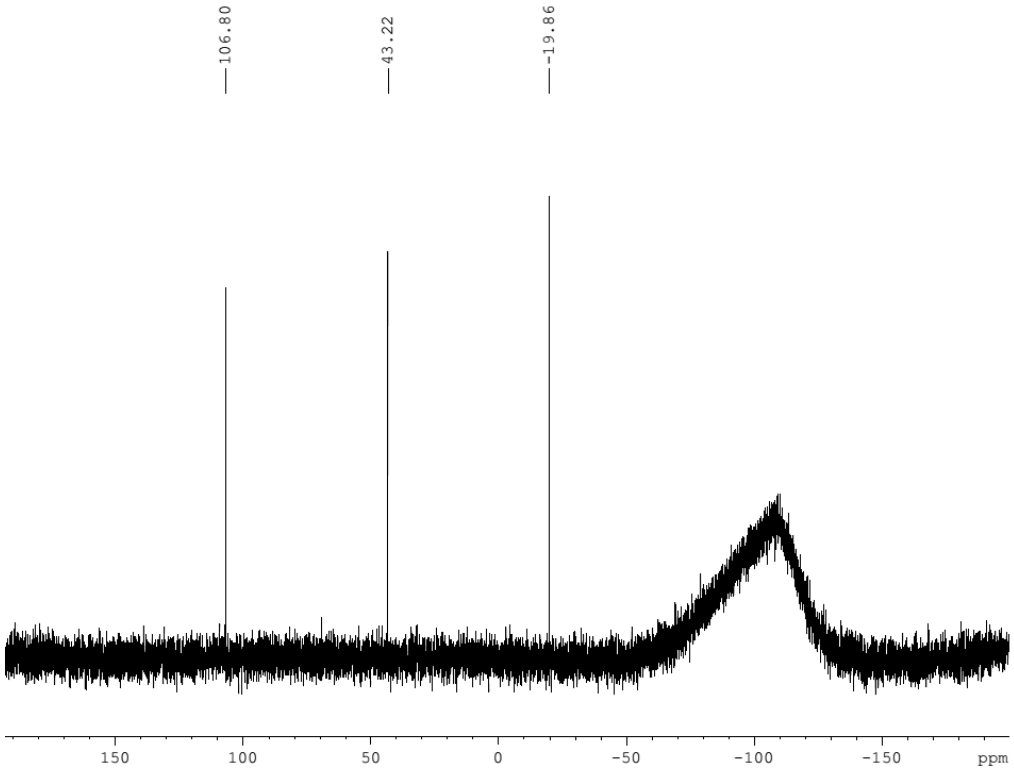



**Figure S8.** $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, $C_6D_6$, 300 K) of **2b**.

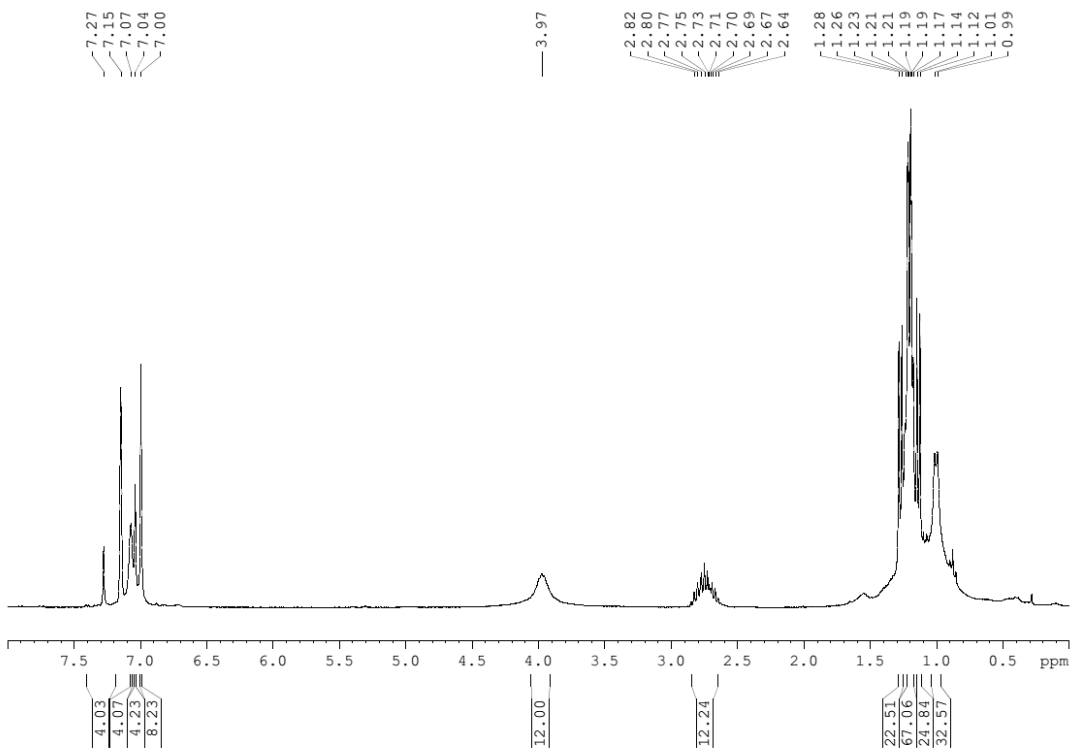



**Figure S9.** $^{1}$H NMR (300.13 MHz, $C_6D_6$, 300 K) of **3**.

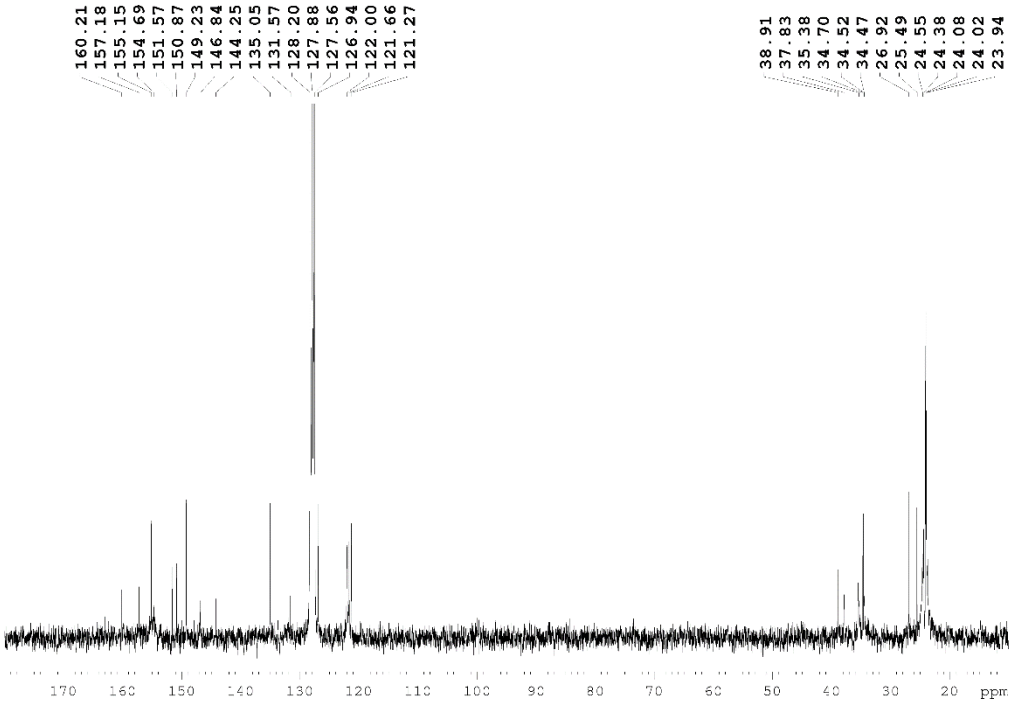



**Figure S10.** $^{13}$C{$^{1}$H} NMR (75.47 MHz, $C_6D_6$, 300 K) of **3**.

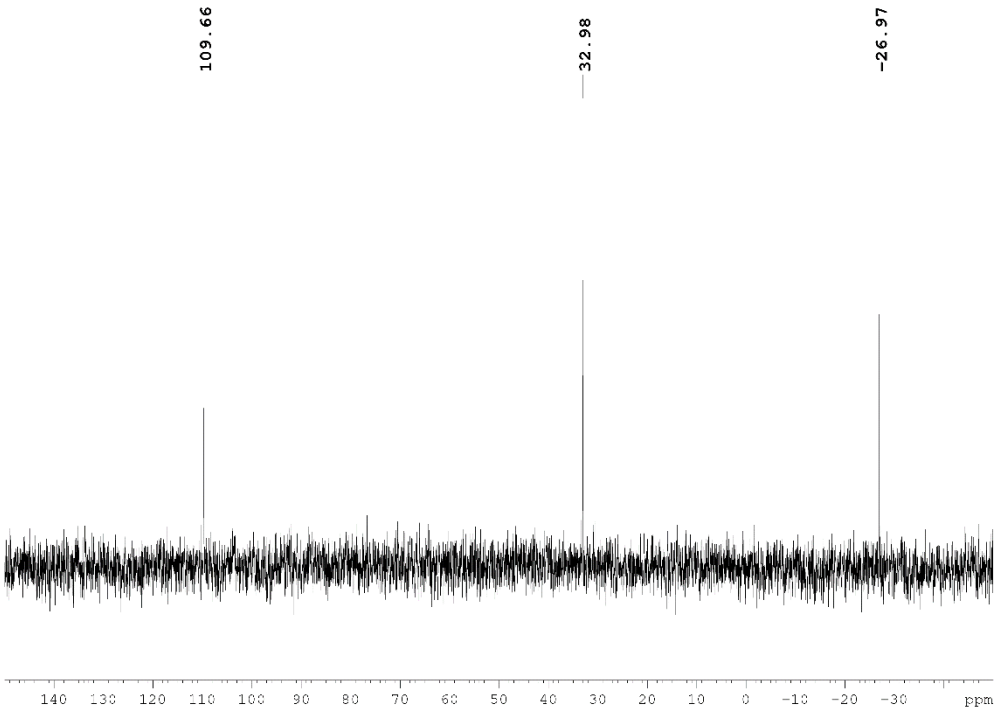



**Figure S11.** $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, $C_6D_6$, 300 K) of **3**.

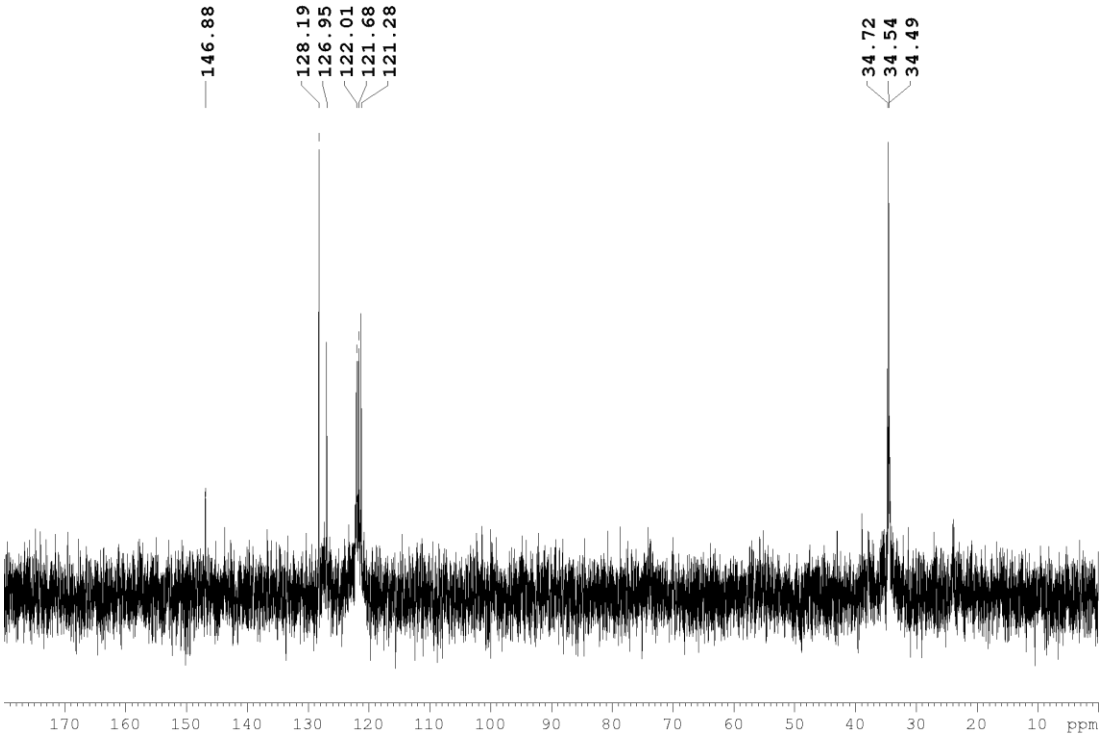



**Figure S12.** $^{13}C$ DEPT-90 ($C_6D_6$, 300 K) of **3**.

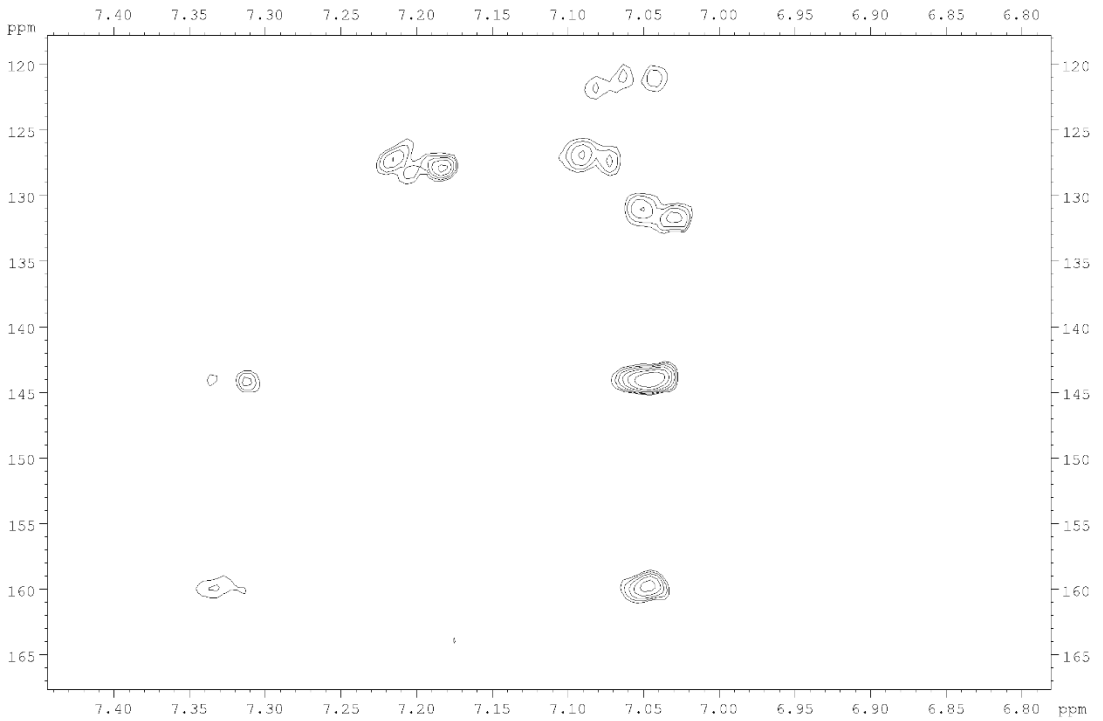



**Figure S13.** $^{1}H/^{13}C$ HMBC ($C_6D_6$, 300 K) of **3**.

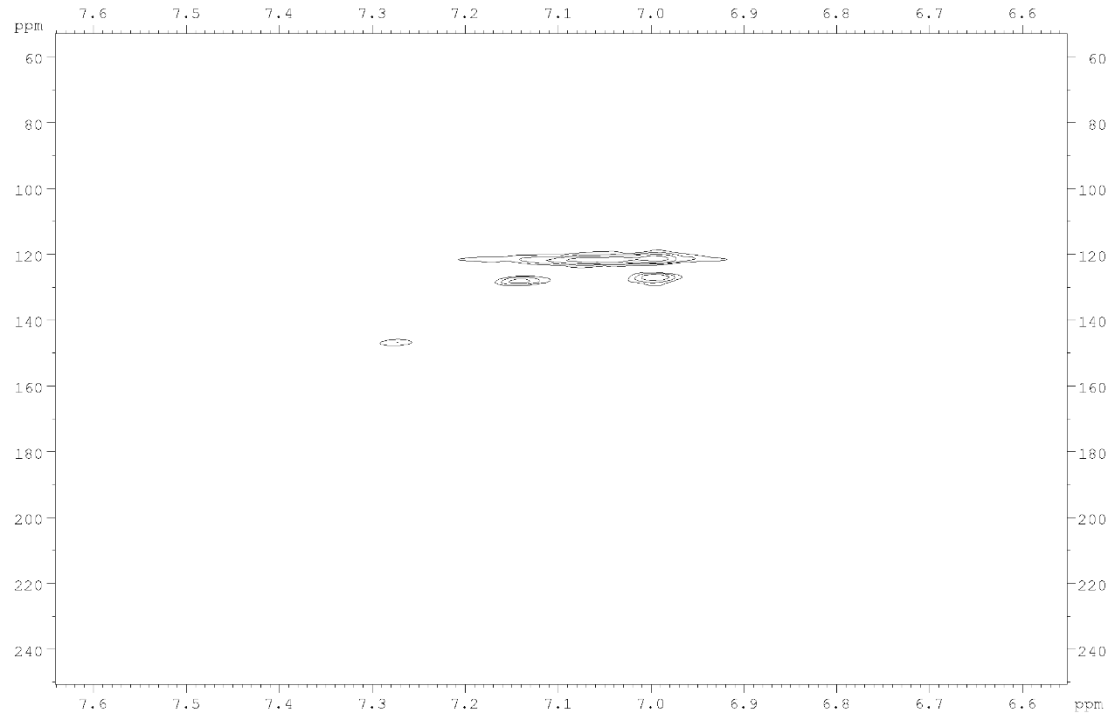



**Figure S14.** $^{1}H/^{13}C$ HMQC ($C_6D_6$, 300 K) of **3**.

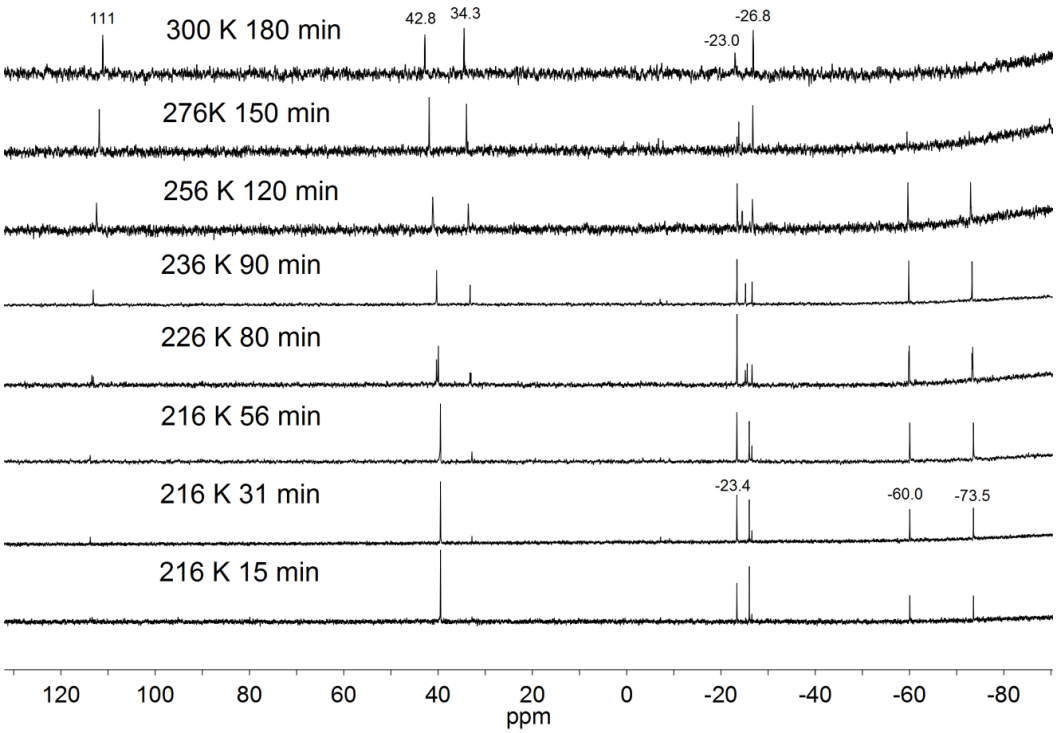



**Figure S15.** $^{29}Si\{^{1}H\}$ VT-NMR (toluene-$d_8$) of reaction of **1** with phenylacetylene.

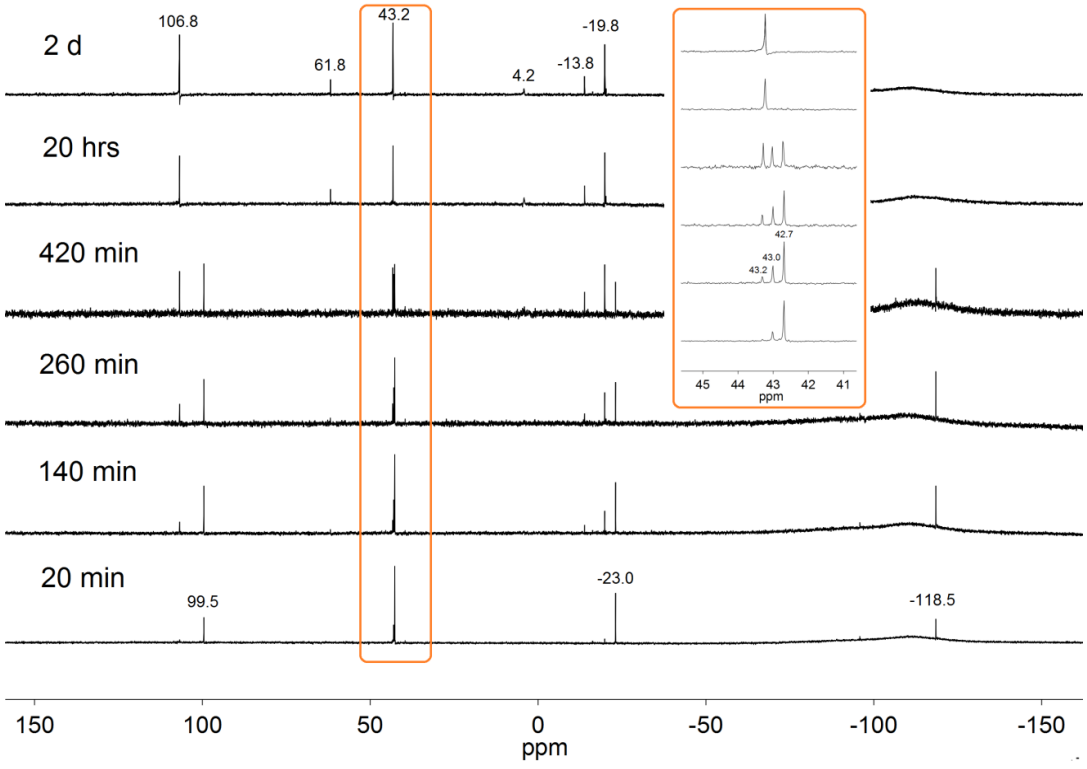



**Figure S16.** $^{29}Si$ NMR group ($C_6D_6$, 300 K) of reaction of **1** with diphenylacetylene.

## 3. Absorption spectra

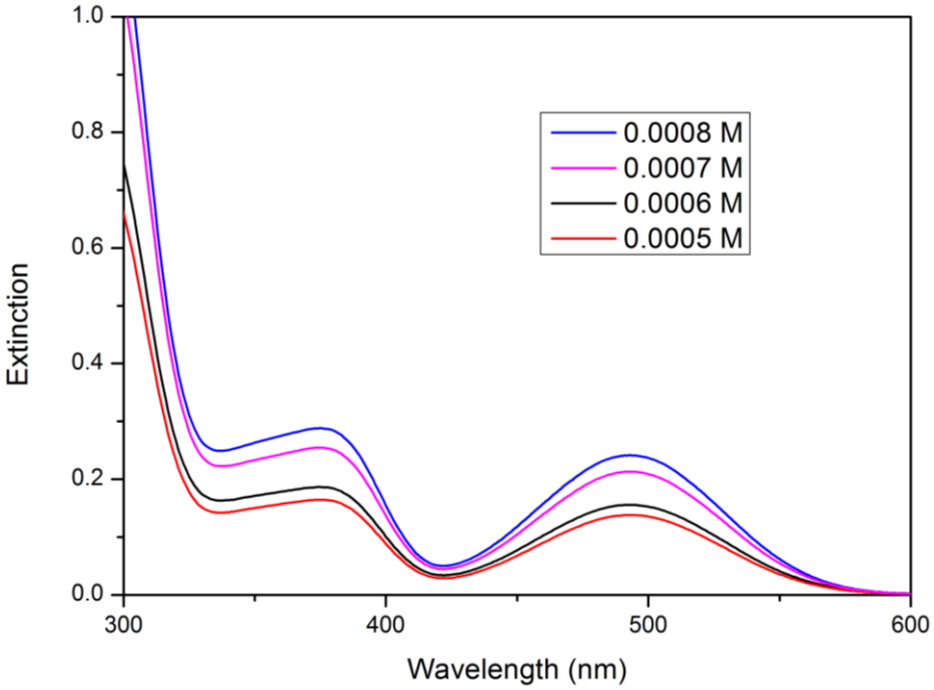



**Figure S17.** UV/Vis spectra of **2a** in hexane at different concentrations (0.0005-0.0008 M) ($\lambda_{max}$ = 493 nm)

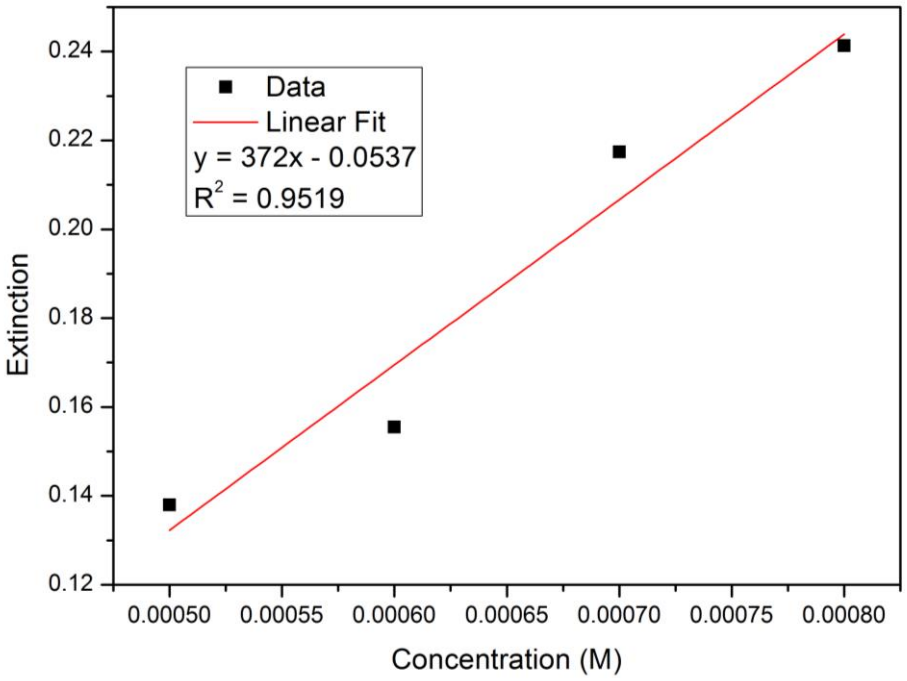



**Figure S18.** Determination of ε (3719 $M^{-1}cm^{-1}$) by linear regression of extinction ($\lambda_{max}$ = 493 nm) of **2a** in hexane against concentration.

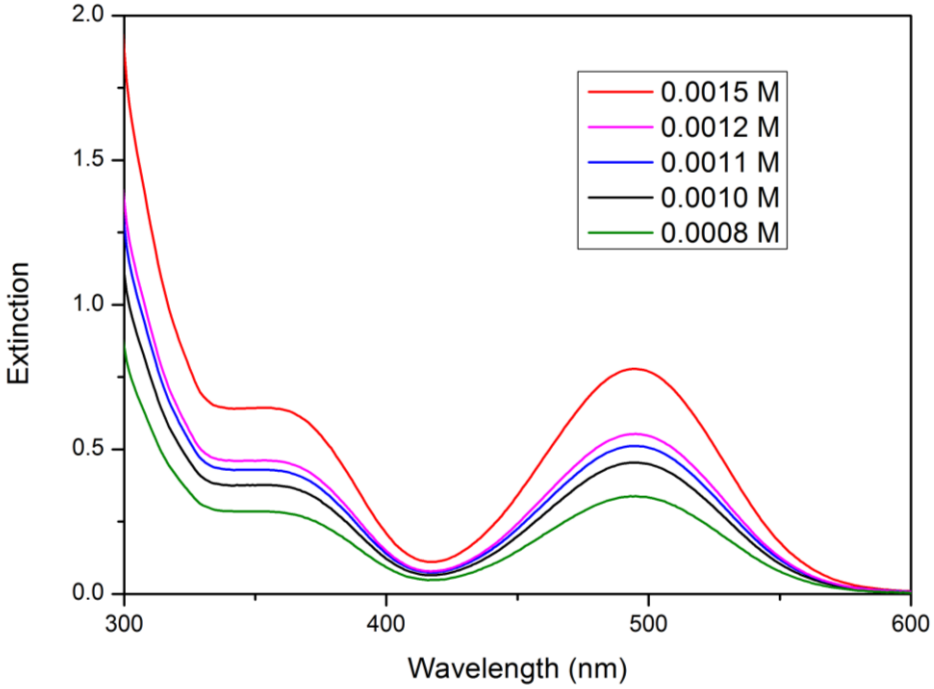



**Figure S19.** UV/Vis spectra of **2b** in hexane at different concentrations (0.0008-0.0015 M) ($\lambda_{max}$ = 495 nm)

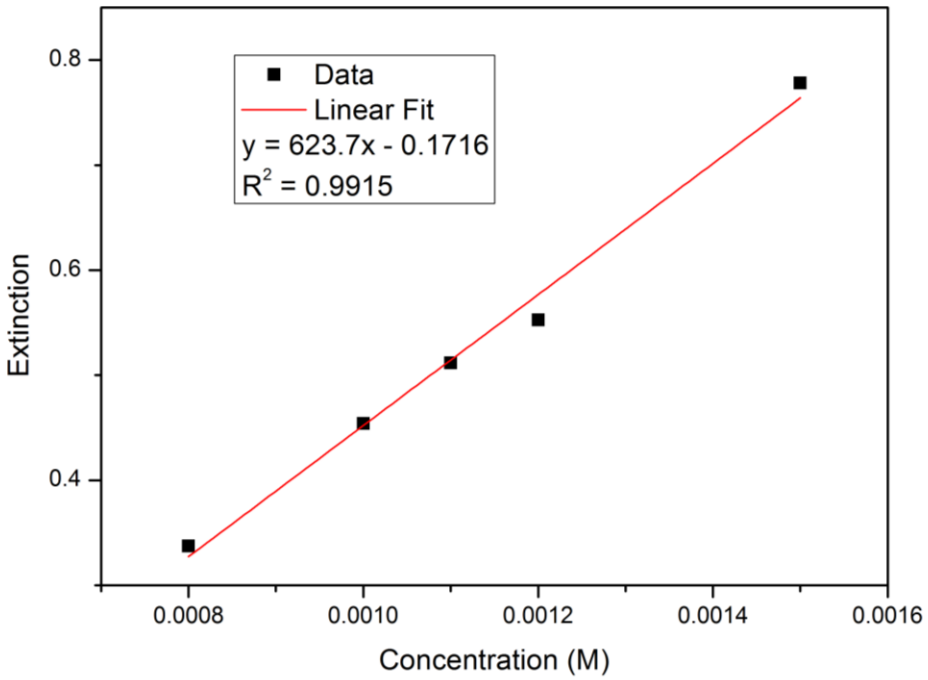



**Figure S20:** Determination of ε (6237 $M^{-1}cm^{-1}$) by linear regression of extinction ($\lambda_{max}$ = 495 nm) of **2b** in hexane against concentration.

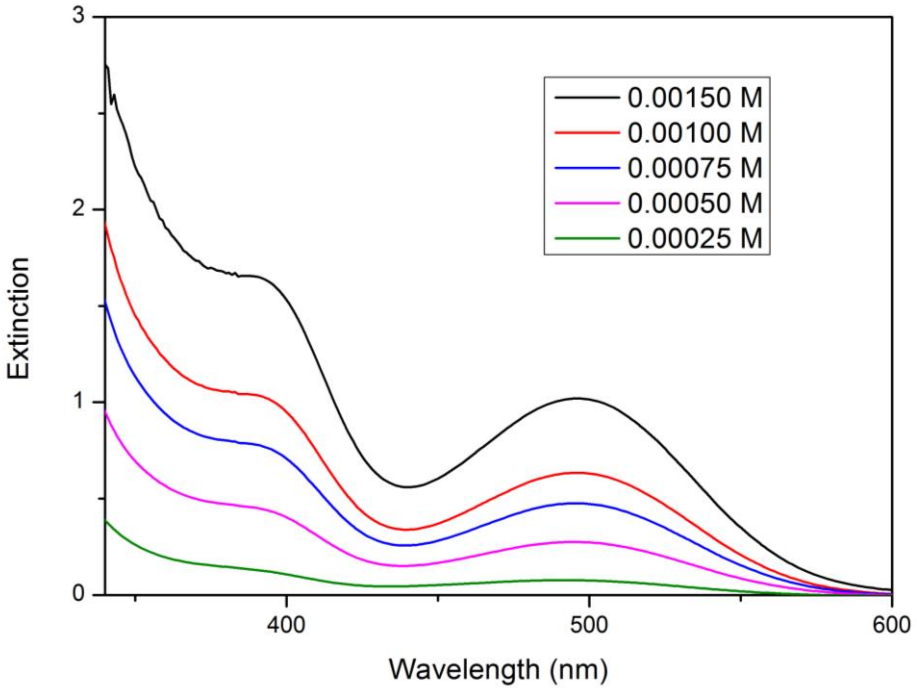



**Figure S21:** UV/Vis spectra of **3** in hexane at different concentrations (0.00025-0.0015 M) ($\lambda_{max}$ = 495 nm)

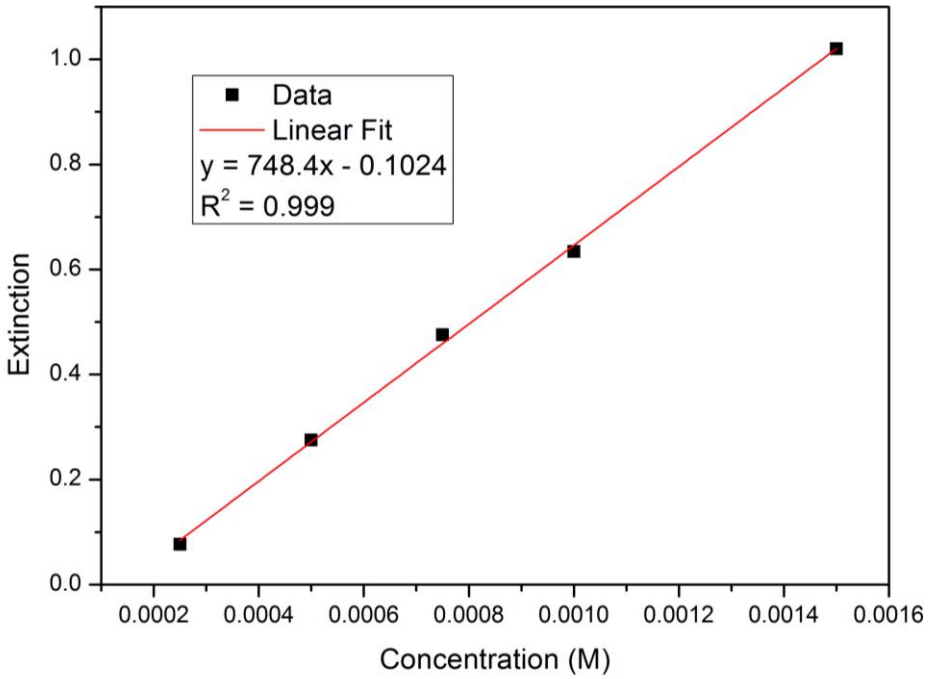



**Figure S22:** Determination of ε (7484 $M^{-1}cm^{-1}$) by linear regression of extinction ($\lambda_{max}$ = 495 nm) of **3** in hexane against concentration.

## 4. X-Ray Crystallographic Details

**Table S1**. Crystal data and structure refinement for **2a**.

| | | |
|---|---|---|
| Identification code | sh3624 | |
| Empirical formula | $C_{68}H_{98}Si_3$ | |
| Formula weight | 999.73 | |
| Temperature | 182(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | a = 19.538(12) Å | a= 90° |
| | b = 14.015(9) Å | b= 108.596(14)° |
| | c = 24.330(14) Å | g = 90° |
| Volume | 6315(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.052 $Mg/m^3$ | |
| Absorption coefficient | 0.112 $mm^{-1}$ | |
| F(000) | 2192 | |
| Crystal size | 0.432 x 0.365 x 0.135 mm | |
| Theta range for data collection | 1.170 to 25.680°. | |
| Index ranges | −23<=h<=23, −17<=k<=13, −26<=l<=29 | |
| Reflections collected | 43839 | |
| Independent reflections | 11997 [R(int) = 0.1859] | |
| Completeness to theta = 25.242° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.5657 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11997 / 24 / 673 | |
| Goodness-of-fit on $F^2$ | 0.976 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0835, wR2 = 0.1676 | |
| R indices (all data) | R1 = 0.2225, wR2 = 0.2255 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.717 and −0.345 $e.Å^{-3}$ | |

**Table S2**. Crystal data and structure refinement for **2b**.

| | | |
|---|---|---|
| Identification code | sh3605a | |
| Empirical formula | $C_{74}H_{102}Si_3$ x 1/4 ($C_5H_{12}$) | |
| Formula weight | 1093.86 | |
| Temperature | 163(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 18.411(4) Å | a = 110.122(5)° |
| | b = 20.736(5) Å | b = 100.632(10)° |
| | c = 22.030(5) Å | g = 100.340(10)° |
| Volume | 7488(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 0.970 $Mg/m^3$ | |
| Absorption coefficient | 0.099 $mm^{-1}$ | |
| F(000) | 2394 | |
| Crystal size | 0.42 x 0.33 x 0.25 mm | |
| Theta range for data collection | 1.021 to 26.401°. | |
| Index ranges | −23<=h<=22, −25<=k<=25, −27<=l<=27 | |
| Reflections collected | 105345 | |
| Independent reflections | 29453 [R(int) = 0.1472] | |
| Completeness to theta = 25.242° | 97.1% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6885 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 29453 / 864 / 1454 | |
| Goodness-of-fit on $F^2$ | 1.316 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1177, wR2 = 0.2918 | |
| R indices (all data) | R1 = 0.2873, wR2 = 0.3379 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.670 and −0.415 $e.Å^{-3}$ | |

**Table S3**. Crystal data and structure refinement for **3**.

| | | |
|---|---|---|
| Identification code | sh3843b | |
| Empirical formula | $C_{130}H_{190}Si_6$ x $C_5H_{12}$ | |
| Formula weight | 1993.49 | |
| Temperature | 224(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 40.86(3) Å | a = 90° |
| | b = 14.207(9) Å | b = 96.47(3)° |
| | c = 23.479(16) Å | g = 90° |
| Volume | 13542(16) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 0.978 $Mg/m^3$ | |
| Absorption coefficient | 0.105 $mm^{-1}$ | |
| F(000) | 4384 | |
| Crystal size | 0.304 x 0.280 x 0.194 mm | |
| Theta range for data collection | 1.003 to 26.371°. | |
| Index ranges | −50<=h<=50, −14<=k<=17, −25<=l<=29 | |
| Reflections collected | 59910 | |
| Independent reflections | 13830 [R(int) = 0.0655] | |
| Completeness to theta = 25.242° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7456 and 0.6864 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 13830 / 384 / 788 | |
| Goodness-of-fit on $F^2$ | 1.738 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0819, wR2 = 0.2357 | |
| R indices (all data) | R1 = 0.1178, wR2 = 0.2478 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.680 and −0.332 $e.Å^{-3}$ | |

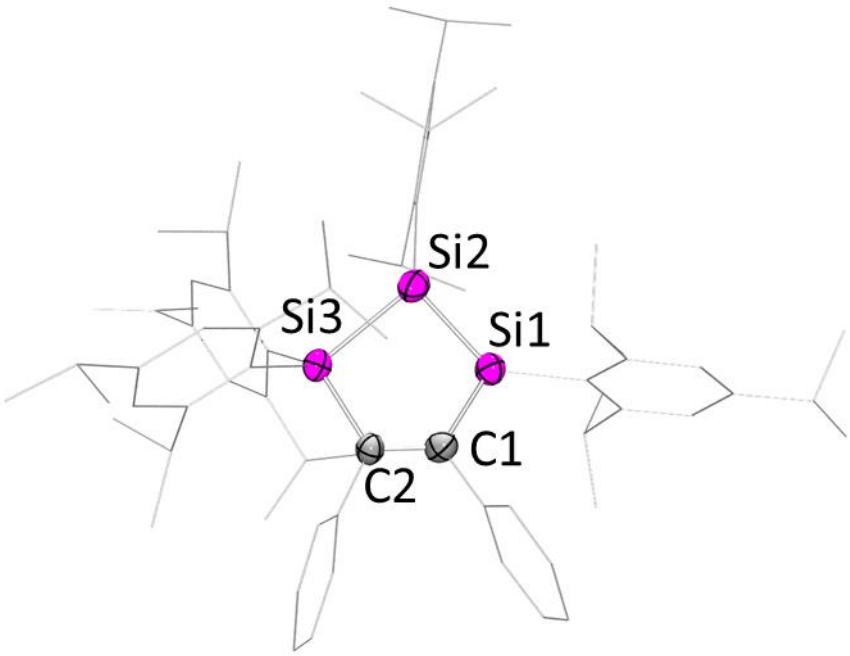
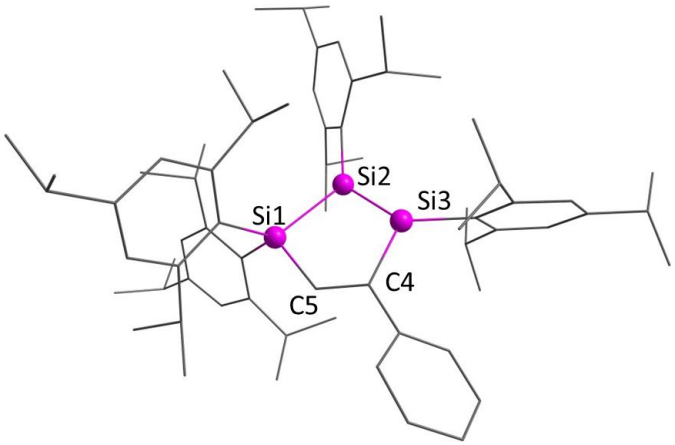



**Figure S23:** Molecular structure of **2b** x 1/4 ($C_5H_{12}$). Thermal ellipsoids at 50%, hydrogen atoms and co-crystallized $C_5H_{12}$ molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Si2 2.184(3), Si2-Si3 2.425(3), Si1-C1 1.881(7), Si3-C2 1.930(7), C1-C2 1.367(9); Si1-Si2-Si3 93.0(1), C1-Si1-Si2 104.0(2), Si2-Si3-C2 98.3(2), Si3-C2-C1 120.3(5), C2-C1-Si1 121.7(5).

## 5. Computational Details

Structural optimizations of **2** and **3** were carried out at the B3LYP/6-311G(d,p) level of theory[2], using the Gaussian 09 program package.[3] Subsequent frequency analysis ensured the presence of local minima. Optimized structures were plotted using ChemCraft 1.8.[4] Data from TD-DFT calculations was processed and visualized with the GaussSum[5].




| Bond lengths [Å] | Bond angles[°] | $\tau_{Si2=Si3}$ 26.2° |
|---|---|---|
| Si1-Si2 2.431 | Si3-Si2-Si1 94.0 | |
| Si2-Si3 2.187 | Si2-Si1-C5 95.6 | |
| Si1-C5 1.897 | Si1-C5-C4 126.6 | |
| C5-C4 1.354 | C5-C4-Si3 117.8 | |
| C4-Si3 1.908 | C4-Si3-Si2 104.3 | |

**Figure S24.** Optimized structure of **2a** including selected bond lengths and angles.

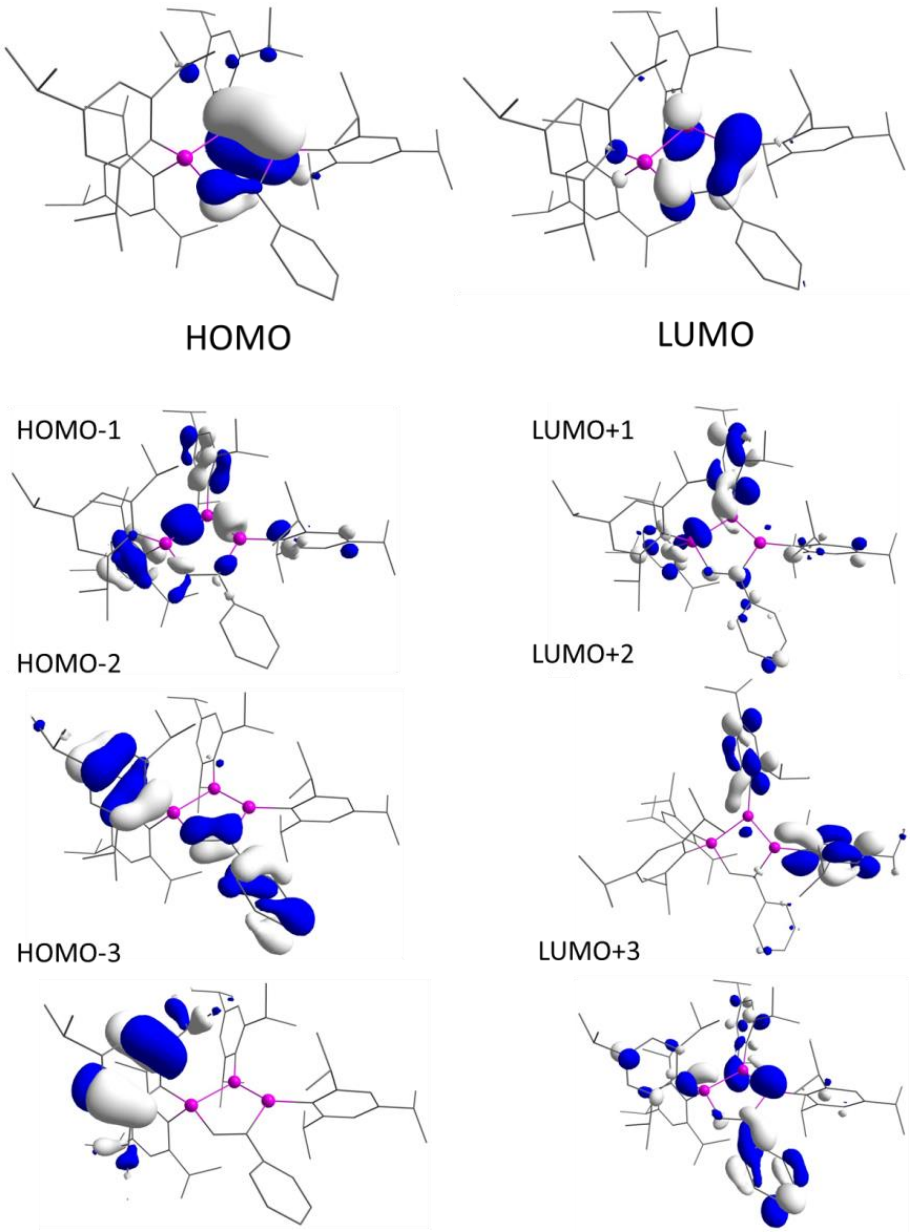



**Figure S25.** Selected frontier orbitals of **2a**.

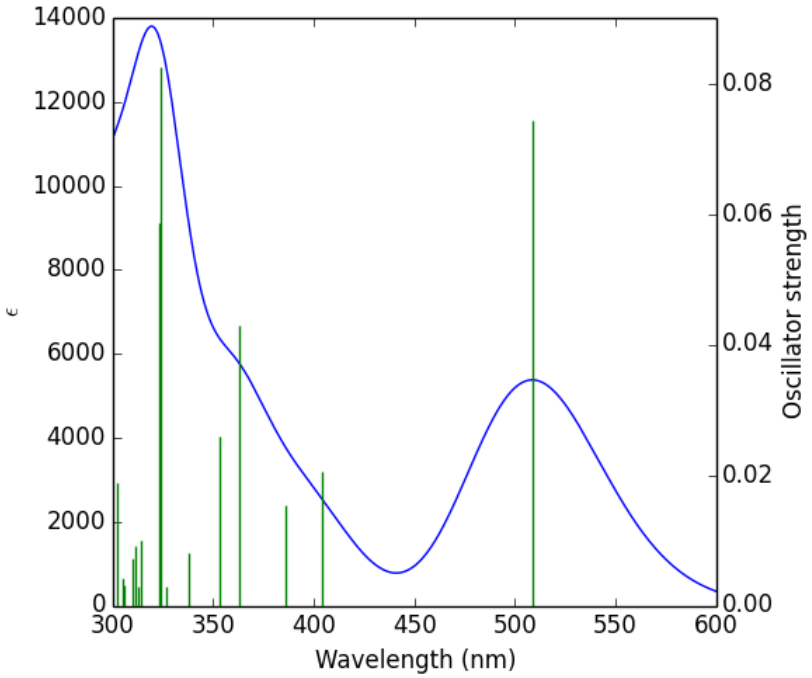
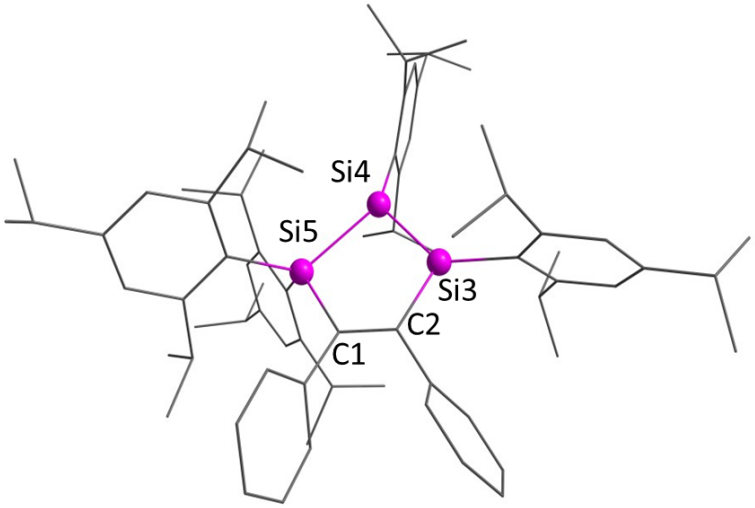



**Figure S26.** Calculated transitions (vertical bars) and simulated UV/vis absorption spectrum of **2a**.

**Table S4**: Principal electronic transitions and optical parameters of the theoretical calculations of **2a** (only contributions ≥10% are displayed).

| Transition No. | $\lambda_{calc.}$ (nm) | Transition energy (eV) | transitions | f | Contribution |
|---|---|---|---|---|---|
| 1 | 508.76 | 2.44 | H→L | 0.0742 | 97% |
| 2 | 404.36 | 3.07 | H→L+1 | 0.0205 | 94% |
| 3 | 386.30 | 3.21 | H→L+2 | 0.0153 | 97% |
| 4 | 363.05 | 3.42 | H→L+3 | 0.0428 | 78% |
| 5 | 353.54 | 3.51 | H-1→L | 0.0259 | 84% |
| 6 | 337.69 | 3.67 | H→L+4 | 0.0080 | 94% |
| 7 | 326.71 | 3.79 | H→L+5 | 0.0029 | 91% |
| 8 | 323.84 | 3.83 | H-2→L | 0.0825 | 45% |
| | | | H→L+6 | | 45% |
| 9 | 323.05 | 3.84 | H-2→L | 0.0585 | 36% |
| | | | H→L+6 | | 48% |




| Bond lengths [Å] | Bond angles [°] | $\tau_{Si=Si}$ 40.5° |
|---|---|---|
| Si3-Si4 2.183 | Si4-Si5-C1 96.6 | |
| Si4-Si5 2.470 | Si5-C1-C2 122.1 | |
| Si5-C1 1.961 | C1-C2-Si3 121.8 | |
| C1-C2 1.370 | C2-Si3-Si4 104.9 | |
| Si3-C2 1.901 | Si3-Si4-Si5 94.1 | |

**Figure S27.** Optimized structure of **2b** including selected bond lengths and angles.

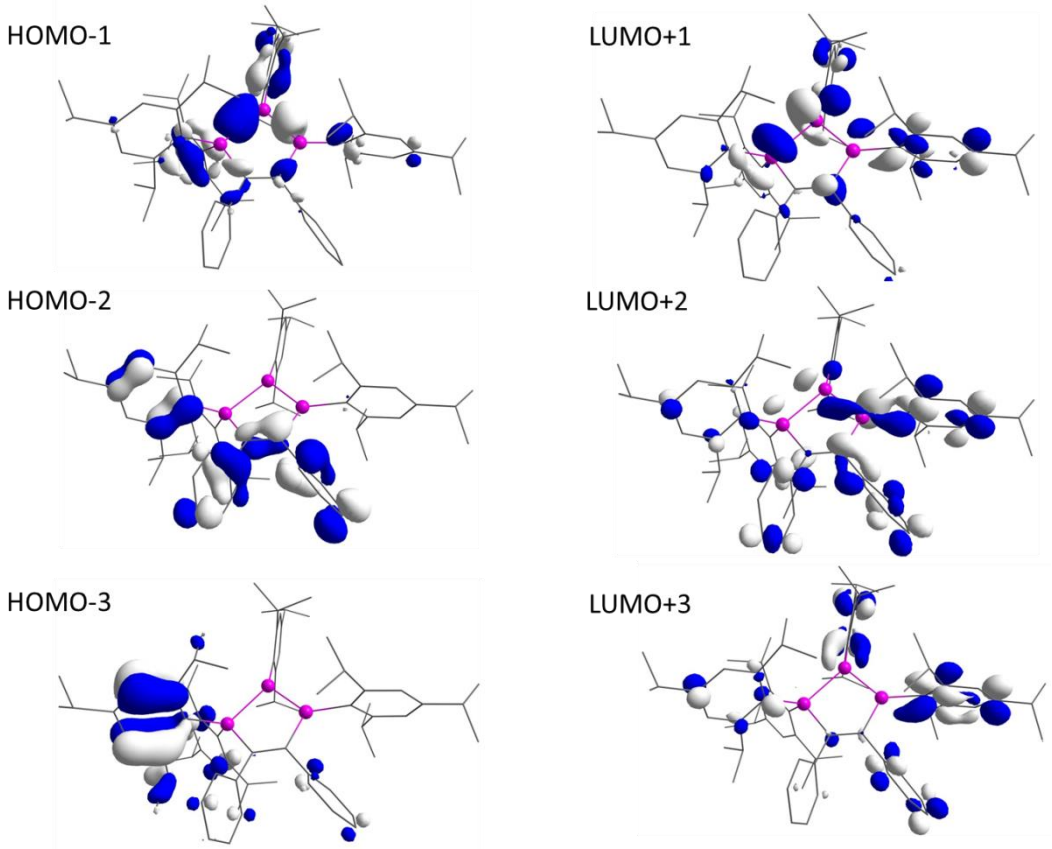



**Figure S28.** Selected frontier orbitals of **2b**.

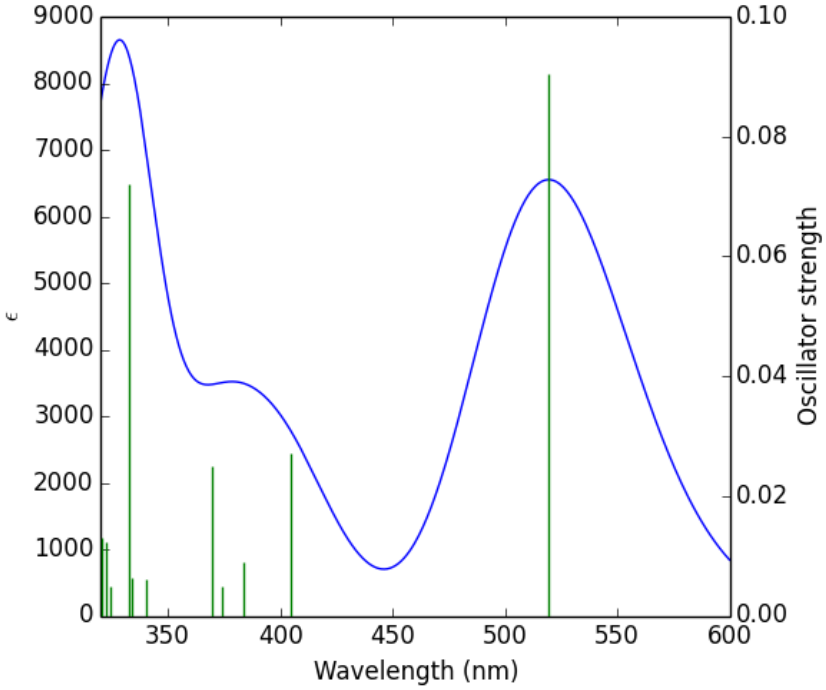
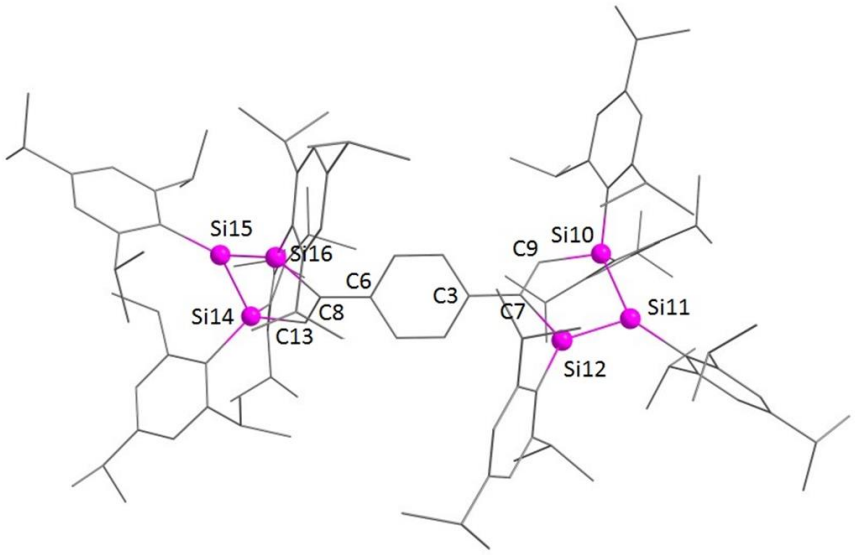



**Figure S29** Calculated transitions (vertical bars) and simulated UV/vis absorption spectrum of **2b**.

**Table S5**: Principal electronic transitions and optical parameters of the theoretical calculations of **2b** (only contributions ≥10% are displayed).

| Transition No. | $\lambda_{calc.}$ (nm) | Transition energy (eV) | transitions | f | Contribution |
|---|---|---|---|---|---|
| 1 | 519.49 | 2.39 | H→L | 0.0904 | 95% |
| 2 | 404.60 | 3.06 | H→L+1 | 0.0272 | 87% |
| 3 | 383.63 | 3.22 | H-1→L+1 | 0.0090 | 75% |
| | | | H→L+2 | | 17% |
| 4 | 373.81 | 3.32 | H-1→L | 0.0050 | 87% |
| 5 | 369.70 | 3.35 | H→L+2 | 0.0250 | 15% |
| | | | H→L+3 | | 69% |
| 6 | 340.46 | 3.44 | H→L+4 | 0.0062 | 94% |
| 7 | 333.95 | 3.71 | H→L+5 | 0.0063 | 89% |
| 8 | 332.74 | 3.73 | H-2→L | 0.072 | 85% |




| Bond lengths [Å] | Bond angles [°] | $\tau_{Si=Si}$ 19.1° |
|---|---|---|
| Si10-Si11 2.418, Si11-Si12 2.173 | Si12-Si11-Si10 95.7 | |
| C8-C13 1.364, Si2-C7 1.904 | Si11-Si10-C9 97.8 | |
| Si16-C8 1.901, C8-C6 1.489 | Si10-C9-C7 127.8 | |
| C7-C9 1.361, C7-C3 1.490 | C9-C7-Si12 117.3 | |
| Si14-Si15 2.432, Si15-Si16 2.172 | C7-Si12-Si11 104.5 | |

**Figure S30.** Optimized structure of **3** including selected bond lengths and angles.

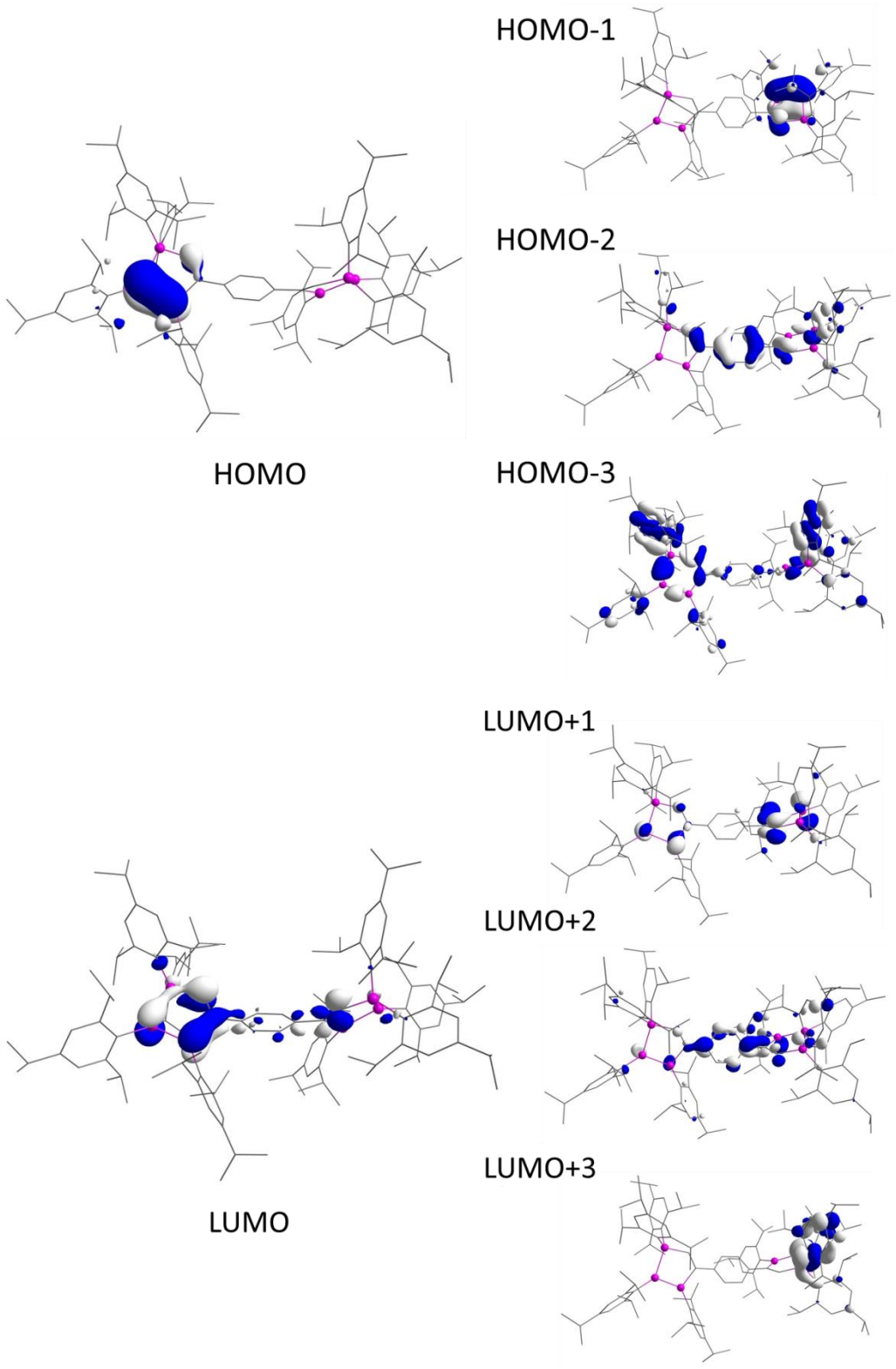



**Figure S31.** Selected frontier orbitals of **3**.

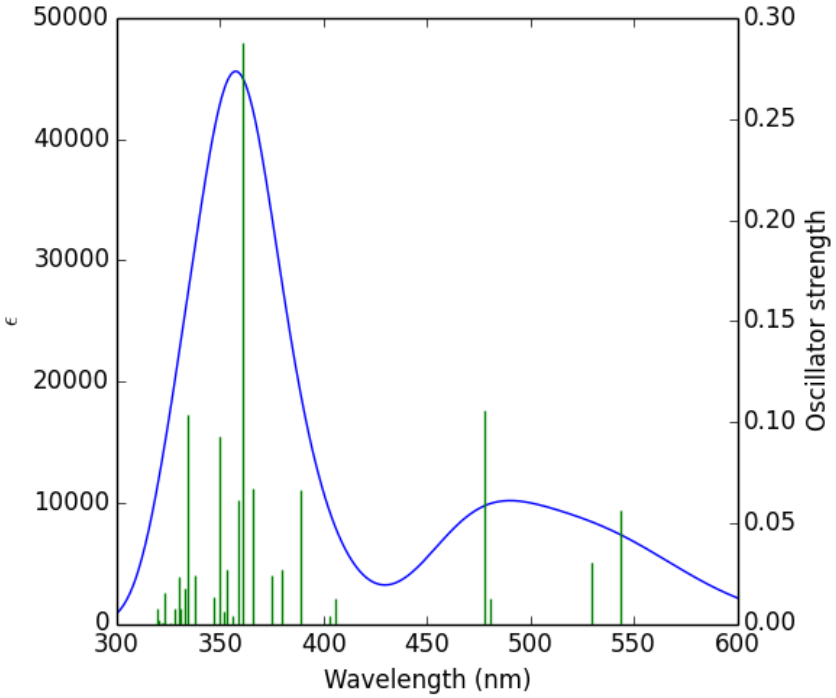
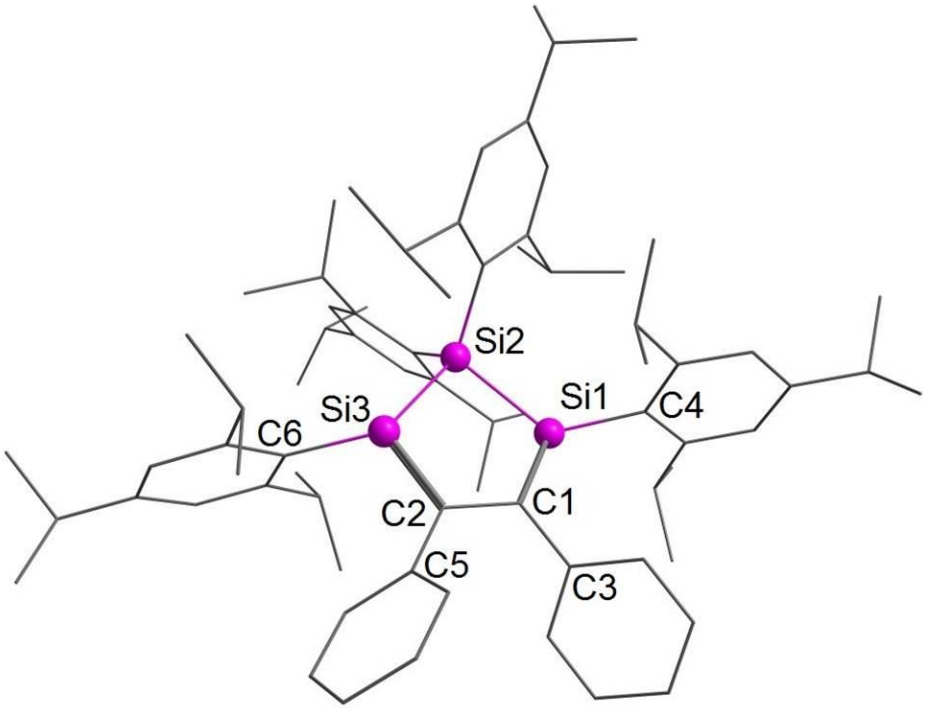



**Figure S32:** Calculated transitions (vertical bars) and simulated UV/vis absorption spectrum of **3**.

**Table S6**: Principal electronic transitions and optical parameters of the theoretical calculations of **3** (only contributions ≥10% are displayed).

| Transition No. | $\lambda_{calc.}$ (nm) | Transition energy (eV) | transitions | f | Principal Contributions |
|---|---|---|---|---|---|
| 1 | 543.38 | 2.28 | H→L | 0.0561 | 93% |
| 2 | 529.73 | 2.34 | H-1→L | 0.0306 | 85% |
| | | | H-1→L+1 | | 10% |
| 3 | 480.58 | 2.58 | H-1→L+1 | 0.0124 | 42% |
| | | | H→L+1 | | 48% |
| 4 | 477.98 | 2.59 | H-1→L+1 | 0.1055 | 45% |
| | | | H→L+1 | | 48% |
| 5 | 405.47 | 3.06 | H→L+2 | 0.0129 | 14% |
| | | | H→L+4 | | 77% |
| 6 | 403.03 | 3.08 | H-1→L+2 | 0.0042 | 12% |
| | | | H-1→L+3 | | 79% |
| 7 | 388.68 | 3.19 | H-1→L+2 | 0.0661 | 53% |
| | | | H-1→L+5 | | 16% |
| 8 | 380.24 | 3.26 | H→L+2 | 0.0266 | 57% |
| | | | H→L+4 | | 10% |
| | | | H→L+5 | | 11% |
| 9 | 374.96 | 3.31 | H→L+6 | 0.0240 | 86% |
| 10 | 366.18 | 3.39 | H-2→L | 0.0670 | 32% |
| | | | H-2→L+1 | | 11% |
| | | | H-1→L+5 | | 22% |
| | | | H-1→L+8 | | 10% |
| 11 | 360.78 | 3.44 | H-2→L | 0.2880 | 30% |
| | | | H-1→L+2 | | 10% |
| | | | H-1→L+5 | | 19% |

Structural optimizations of **10b** and **11b** were carried out using the Gaussian 09 program package[3] and the functional BP86[6] with Grimme dispersion corrections D3[7] in combination with the def2-SVP basis set.[8] Subsequent frequency analysis ensured the presence of local minima. $^{29}$Si NMR chemical shifts were computed use the functional M06-2X[9] with the Grimme dispersion corrections D3[7] in combination with the def2-TZVPP basis set[10] using the GIAO method.[11]




| Bond lengths [Å] | Bond angles [°] | Distortion angle |
|---|---|---|
| Si1-Si2 2.3757 | Si3-Si2-Si1 87.9 | $\Psi_{C6\text{-}Si3\text{-}C2\text{-}C5} = 37.0^{\circ}$ |
| Si2-Si3 2.3773 | Si2-Si1-C1 105.3 | $\Psi_{C4\text{-}Si1\text{-}C1\text{-}C3} = 35.6^{\circ}$ |
| C1-C2 1.4531 | Si1-C1-C2 120.3 | |
| Si1-C1 1.8175 | Si3-C2-C1 120.1 | |
| Si3-C2 1.8163 | | |

**Figure S33:** Optimized structure of **10b**, selected bond lengths and angles included.

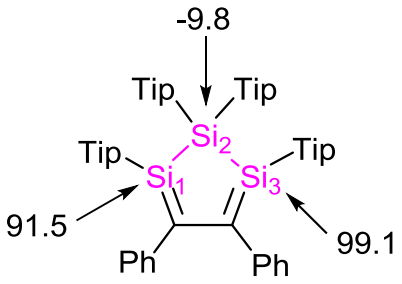



**Figure S34:** Calculated $^{29}$Si NMR chemical shifts (ppm) of **10b** at the (M06-2X(D3)/def2-TZVPP level of theory.

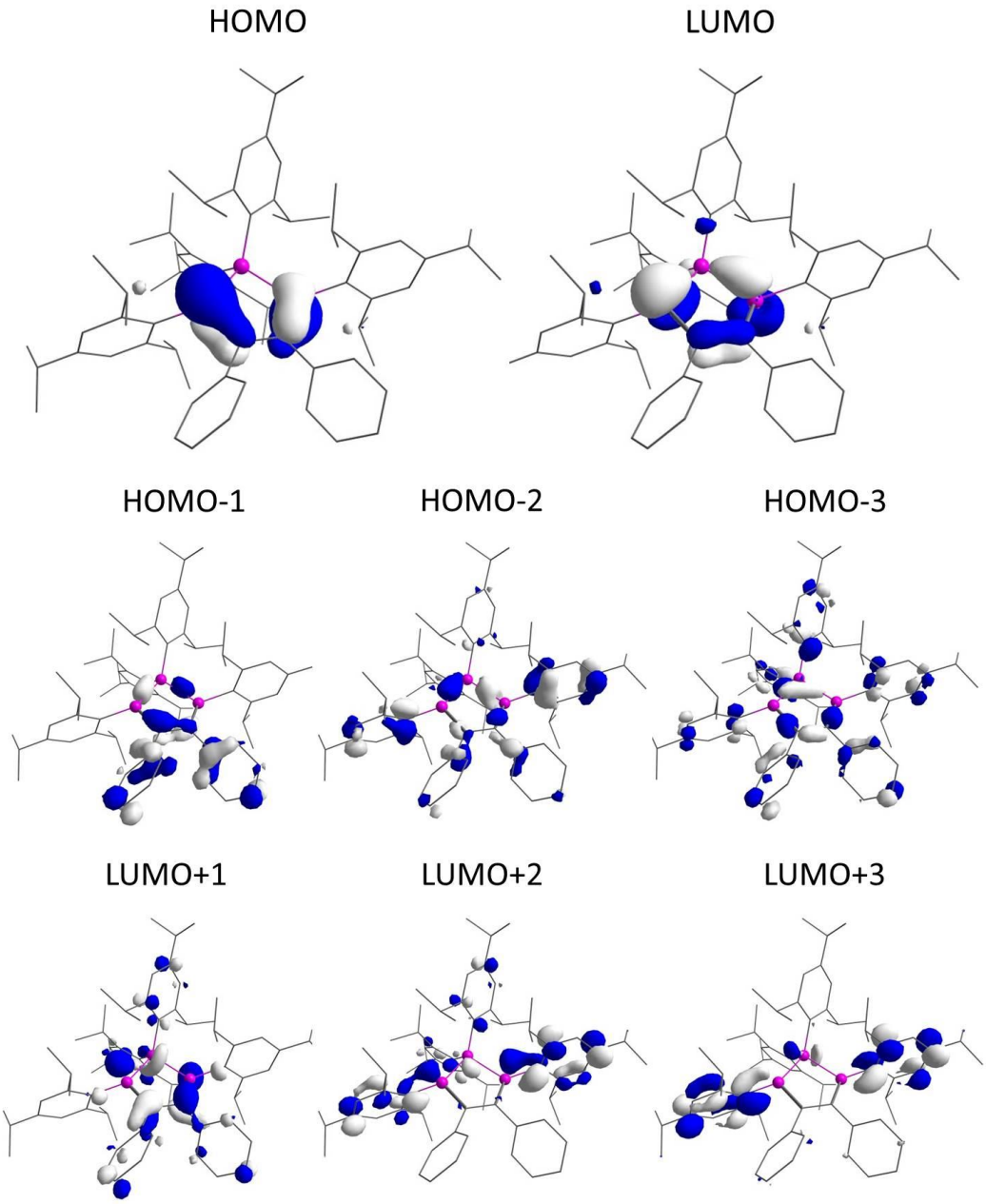
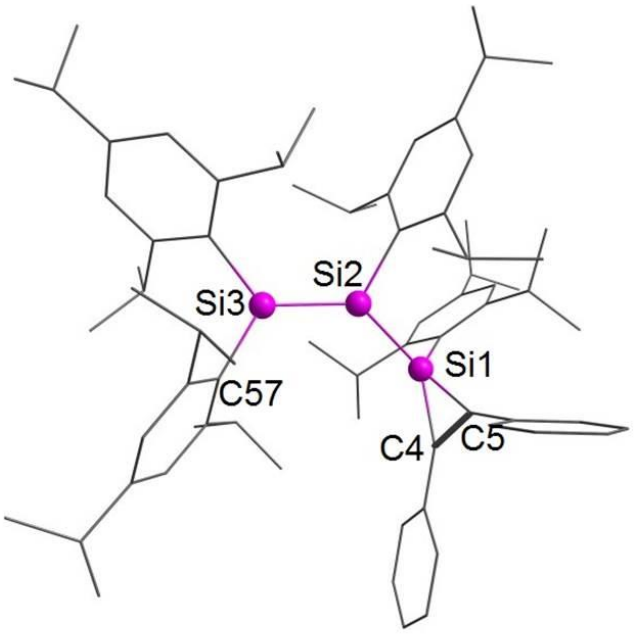



**Figure S35:** Selected frontier orbitals of **10b** (contour value = 0.04).




| Bond lengths [Å] | Bond angles [°] | Distortion angle |
|---|---|---|
| Si1-Si2 2.3316 | Si3-Si2-Si1 133.9 | $\psi_{C57\text{-}Si3\text{-}Si2\text{-}Si1} = 34.2°$ |
| Si2-Si3 2.1884 | Si2-Si1-C4 128.2 | |
| Si1-C4 1.8526 | Si2-Si1-C5 113.8 | |
| Si1-C5 1.8669 | C4-Si1-C5 42.8 | |
| C4-C5 1.3577 | | |

**Figure S36:** Optimized structure of **11b** including selected bond lengths and angles.

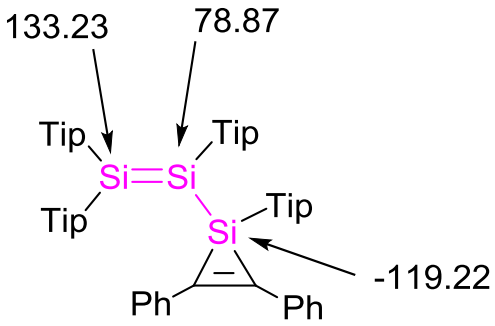



**Figure S37:** Calculated $^{29}$Si NMR chemical shifts (ppm) of **11b** at the (M06-2X(D3)/def2-TZVPP level of theory.

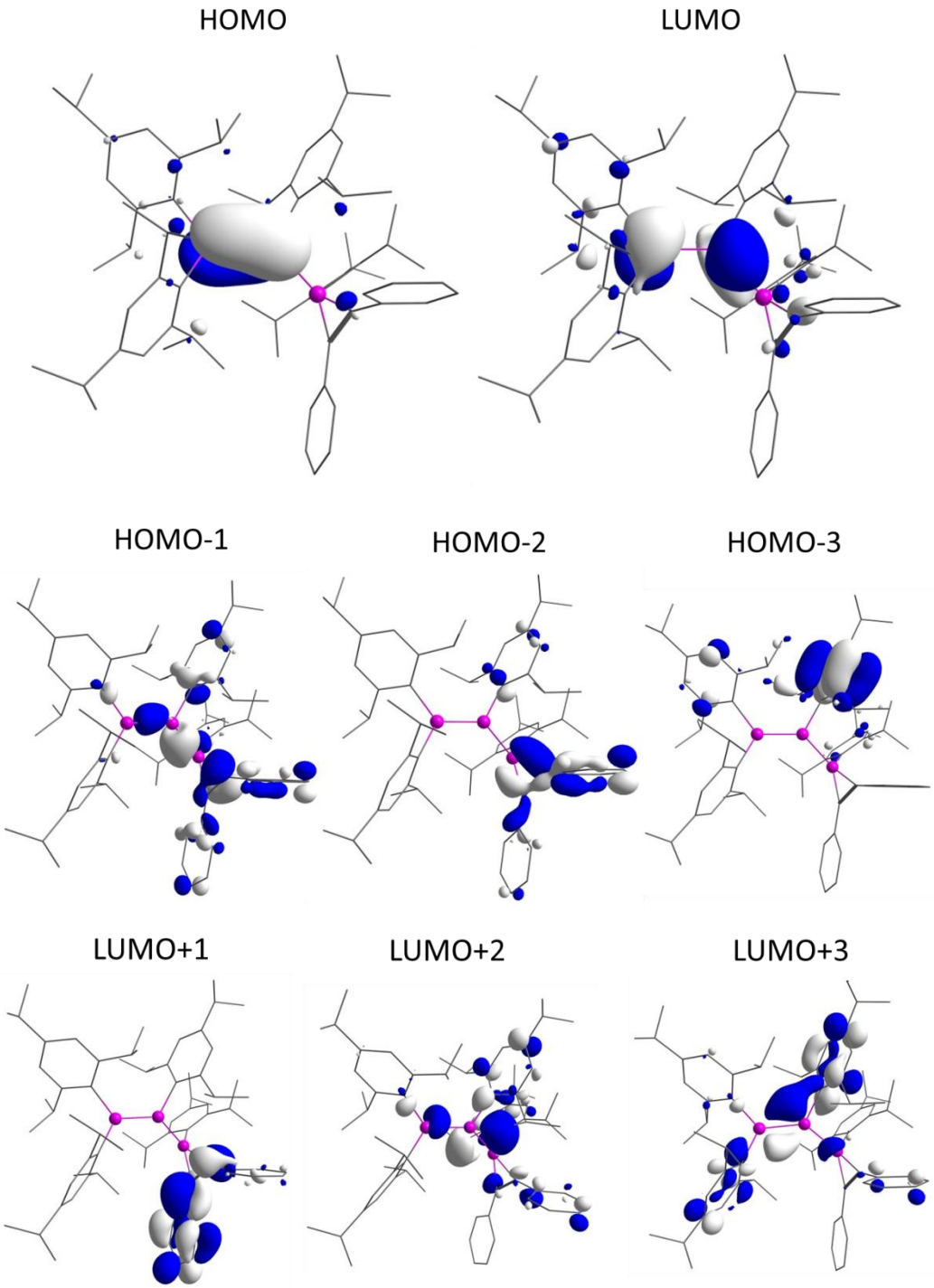



**Figure S38:** Selected frontier orbitals of **11b** (contour value = 0.04).

**Table S7.** Optimized structure of **2a** (Cartesian coordinates).

| | X | Y | Z |
|---|---|---|---|
| Si | -1.247234077 | -0.785395004 | -0.275137588 |
| Si | 0.474115273 | 0.918237586 | -0.081489892 |
| Si | 2.103124344 | -0.534098783 | 0.061056545 |
| C | 1.298847036 | -2.192074854 | -0.433866126 |
| C | -0.046979358 | -2.221570008 | -0.575891149 |
| C | 2.074793559 | -3.450650628 | -0.627727426 |
| H | -0.487239206 | -3.188257613 | -0.806018814 |
| C | 1.620330555 | -4.661087662 | -0.077998368 |
| C | 2.309831656 | -5.850719716 | -0.288588910 |
| C | 3.475162452 | -5.861167527 | -1.053691113 |
| C | 3.944900322 | -4.668168339 | -1.597685251 |
| C | 3.257661506 | -3.476613789 | -1.379749776 |
| C | -2.291499543 | -1.521906751 | 1.214311278 |
| C | -2.508436222 | -0.376356477 | -1.712214585 |
| C | -2.476939063 | -0.828174873 | -3.072414628 |
| C | -3.561277704 | -0.529207375 | -3.911279918 |
| C | -4.671953190 | 0.206397960 | -3.518386766 |
| C | -4.663374184 | 0.698143365 | -2.221041016 |
| C | -3.618506181 | 0.438851049 | -1.330030319 |
| C | -3.144094803 | -2.633902772 | 0.948367917 |
| C | -3.926959604 | -3.179148208 | 1.971750663 |
| C | -3.913799035 | -2.693939471 | 3.272820889 |
| C | -3.062242465 | -1.626751645 | 3.534727299 |
| C | -2.257934831 | -1.041249066 | 2.551606883 |
| C | 0.331045411 | 2.792769805 | 0.342546194 |
| C | 4.009278428 | -0.431230635 | 0.037819780 |
| C | 0.723639855 | 3.275610087 | 1.631888056 |
| C | 0.290077340 | 4.524679722 | 2.075411670 |
| C | -0.493841528 | 5.367086584 | 1.291757083 |
| C | -0.734942028 | 4.959602787 | -0.012347251 |
| C | -0.305044975 | 3.727593314 | -0.527425535 |
| C | 4.644496299 | 0.117332177 | -1.112995975 |
| C | 6.036142102 | 0.229525056 | -1.160759292 |

| | | | |
|---|---|---|---|
| C | 6.850739831 | -0.192385244 | -0.115661445 |
| C | 6.223012316 | -0.745216528 | 0.996460641 |
| C | 4.834513186 | -0.878118129 | 1.111360257 |
| C | 1.753598453 | 2.545951005 | 2.484832012 |
| C | 3.161407594 | 2.910981181 | 1.962581772 |
| C | 1.681872541 | 2.829025156 | 3.993681780 |
| C | -0.996259702 | 6.697154602 | 1.831601254 |
| C | -2.533413896 | 6.776703224 | 1.822656555 |
| C | -0.375166523 | 7.893168211 | 1.086609377 |
| C | -0.450599377 | 3.666866351 | -2.059898342 |
| C | 0.632792721 | 4.577489785 | -2.686722869 |
| C | -0.428306649 | 2.317687023 | -2.765925791 |
| C | 3.877013564 | 0.603189471 | -2.343635213 |
| C | 3.990876056 | 2.128746985 | -2.512187396 |
| C | 4.305467459 | -0.118341948 | -3.635116557 |
| C | 4.374128461 | -1.491431412 | 2.444398081 |
| C | 3.809709230 | -0.444223052 | 3.417209526 |
| C | 3.440198330 | -2.703514378 | 2.341249677 |
| C | 8.366140644 | -0.073673733 | -0.175595328 |
| C | 8.963662141 | -0.941507849 | -1.298271874 |
| C | 8.824323103 | 1.390358775 | -0.301587248 |
| C | -5.811558483 | 0.486341632 | -4.485963479 |
| C | -7.159470199 | -0.036620555 | -3.958528049 |
| C | -5.900038136 | 1.981501727 | -4.844138243 |
| C | -3.756688384 | 1.128200058 | 0.032770326 |
| C | -3.829759766 | 2.660880541 | -0.111522820 |
| C | -4.971170829 | 0.616018606 | 0.829197926 |
| C | -1.380589025 | -1.617566170 | -3.824889504 |
| C | 0.043612251 | -1.054475618 | -3.731606843 |
| C | -1.431235939 | -3.143695248 | -3.616431520 |
| C | -4.781688300 | -3.321145498 | 4.353577667 |
| C | -3.933820302 | -3.979126225 | 5.457305960 |
| C | -5.780418836 | -2.313549222 | 4.950785123 |
| C | -3.280919227 | -3.326345130 | -0.410381027 |
| C | -2.842428946 | -4.802605449 | -0.344736588 |
| C | -4.705639343 | -3.215279287 | -0.986124439 |

| | | | |
|---|---|---|---|
| C | -1.355445586 | 0.089932630 | 3.036008927 |
| C | -0.288353574 | -0.452077601 | 4.004614804 |
| C | -2.142468085 | 1.249873524 | 3.674471681 |
| H | 0.731583239 | -4.657581037 | 0.542258627 |
| H | 1.941582574 | -6.769997649 | 0.153912430 |
| H | 4.014324508 | -6.787521089 | -1.217255255 |
| H | 4.851806429 | -4.661448429 | -2.192438356 |
| H | 3.642056399 | -2.557388219 | -1.800820029 |
| H | -3.528860052 | -0.889410576 | -4.935340619 |
| H | -5.489974929 | 1.313074935 | -1.883702617 |
| H | -4.573550209 | -4.020261337 | 1.743283640 |
| H | -3.012749004 | -1.232174196 | 4.543608699 |
| H | 0.575249087 | 4.862713857 | 3.064449209 |
| H | -1.261555958 | 5.629222895 | -0.685601403 |
| H | 6.492369674 | 0.654451099 | -2.048172329 |
| H | 6.842761637 | -1.091532467 | 1.818463148 |
| H | 1.611646444 | 1.472367601 | 2.334564554 |
| H | 3.936978131 | 2.401520309 | 2.538457940 |
| H | 3.285879449 | 2.635438550 | 0.914348599 |
| H | 3.326003086 | 3.989561532 | 2.048289204 |
| H | 2.342222955 | 2.141564499 | 4.528383380 |
| H | 0.672968725 | 2.705435323 | 4.392295587 |
| H | 2.017198230 | 3.842042785 | 4.234020894 |
| H | -0.670318077 | 6.757910024 | 2.876371946 |
| H | -2.873131048 | 7.714137546 | 2.273160879 |
| H | -2.974414515 | 5.949600454 | 2.384387375 |
| H | -2.926888043 | 6.735073803 | 0.802930980 |
| H | -0.695040597 | 8.836712995 | 1.538831692 |
| H | 0.716574270 | 7.853486320 | 1.117386093 |
| H | -0.679715809 | 7.908292679 | 0.036061991 |
| H | -1.420639154 | 4.125544670 | -2.285684605 |
| H | 0.503581057 | 4.625371669 | -3.772478176 |
| H | 0.591016431 | 5.594696725 | -2.293258264 |
| H | 1.630620904 | 4.180695227 | -2.481750237 |
| H | -0.628530161 | 2.470132447 | -3.831601742 |
| H | -1.188187268 | 1.633857029 | -2.392387953 |

| | | | |
|---|---|---|---|
| H | 0.546613232 | 1.832476068 | -2.684598080 |
| H | 2.817159595 | 0.378103026 | -2.187998665 |
| H | 3.403433037 | 2.464313122 | -3.371677105 |
| H | 3.627243469 | 2.653927443 | -1.626091163 |
| H | 5.028178613 | 2.434362356 | -2.677450509 |
| H | 3.674349319 | 0.200271569 | -4.469804697 |
| H | 4.211988943 | -1.202844901 | -3.541937964 |
| H | 5.342264519 | 0.104782476 | -3.902355513 |
| H | 5.294243219 | -1.867233801 | 2.902987890 |
| H | 3.608313433 | -0.903759312 | 4.389852121 |
| H | 4.515674956 | 0.375594522 | 3.568531772 |
| H | 2.872507148 | -0.027850129 | 3.045766775 |
| H | 3.334175266 | -3.165449624 | 3.327850126 |
| H | 3.829556424 | -3.454969990 | 1.653711003 |
| H | 2.436352475 | -2.428656227 | 2.009965864 |
| H | 8.751807669 | -0.457637984 | 0.775767465 |
| H | 10.056526457 | -0.891688689 | -1.283646314 |
| H | 8.668939359 | -1.987947815 | -1.186754632 |
| H | 8.627871341 | -0.602949320 | -2.282827318 |
| H | 9.916054186 | 1.455825965 | -0.271632647 |
| H | 8.423889916 | 2.000529925 | 0.511766225 |
| H | 8.491029915 | 1.831480215 | -1.245379089 |
| H | -5.585527195 | -0.059274567 | -5.409404465 |
| H | -7.948666204 | 0.116046096 | -4.700773659 |
| H | -7.107379684 | -1.104134791 | -3.730910742 |
| H | -7.457923628 | 0.485473582 | -3.044890346 |
| H | -6.686385262 | 2.155530413 | -5.584904512 |
| H | -4.955780974 | 2.344382639 | -5.257860177 |
| H | -6.132363618 | 2.586058185 | -3.962420158 |
| H | -2.867124489 | 0.917148507 | 0.627534805 |
| H | -3.805510108 | 3.134202750 | 0.874127699 |
| H | -2.990674767 | 3.051268483 | -0.687189210 |
| H | -4.754237093 | 2.973359050 | -0.604929560 |
| H | -5.015057764 | 1.099173866 | 1.809333221 |
| H | -4.923765973 | -0.461207789 | 0.987126875 |
| H | -5.905023092 | 0.844555353 | 0.307517418 |

| | | | |
|---|---|---|---|
| H | -1.655303520 | -1.484194141 | -4.875358685 |
| H | 0.711776235 | -1.653681697 | -4.358676898 |
| H | 0.073928731 | -0.028059043 | -4.100229000 |
| H | 0.446466451 | -1.069460621 | -2.722238568 |
| H | -0.802721563 | -3.634061187 | -4.366254838 |
| H | -2.450957942 | -3.518737193 | -3.737280803 |
| H | -1.064227958 | -3.452964371 | -2.640884954 |
| H | -5.364683378 | -4.113992731 | 3.870856973 |
| H | -4.574520064 | -4.480343093 | 6.189281552 |
| H | -3.248451615 | -4.720442108 | 5.039028503 |
| H | -3.335411207 | -3.235694861 | 5.992056609 |
| H | -6.431110845 | -2.803470848 | 5.681367121 |
| H | -6.410644333 | -1.874296994 | 4.173545063 |
| H | -5.262704694 | -1.496551911 | 5.461904934 |
| H | -2.629171943 | -2.831022313 | -1.123856481 |
| H | -2.851534658 | -5.246543605 | -1.344680708 |
| H | -1.834267370 | -4.905616029 | 0.063387636 |
| H | -3.513954129 | -5.393125861 | 0.284313822 |
| H | -4.751289930 | -3.686800701 | -1.972236431 |
| H | -5.007163005 | -2.172682984 | -1.098271047 |
| H | -5.437620937 | -3.715488559 | -0.345726490 |
| H | -0.826202370 | 0.494961175 | 2.171549714 |
| H | 0.392261055 | 0.341283922 | 4.319993507 |
| H | 0.301542668 | -1.242037499 | 3.535113429 |
| H | -0.749212933 | -0.871575990 | 4.903463304 |
| H | -1.473510915 | 2.082079198 | 3.906364237 |
| H | -2.916482502 | 1.626109351 | 3.002396768 |
| H | -2.629349546 | 0.946339168 | 4.605527210 |

**Table S8.** Optimized structure of **2b** (Cartesian coordinates).

| | X | Y | Z |
|---|---|---|---|
| C | -0.194246876 | -2.064816547 | -0.428085620 |
| C | 1.172386919 | -1.970403097 | -0.456455935 |
| Si | 2.075820544 | -0.394538320 | 0.104691890 |
| Si | 0.494204101 | 0.950954414 | 0.778935586 |
| Si | -1.332634903 | -0.544138847 | 0.053817479 |
| C | 3.975757658 | -0.594015083 | 0.325798294 |
| C | 0.674579144 | 2.874510624 | 0.915103142 |
| C | -2.801648584 | -1.325387593 | 1.127712014 |
| C | -2.234611455 | 0.513223910 | -1.320793430 |
| C | -0.787477390 | -3.432857049 | -0.645767126 |
| C | 2.036976780 | -3.094388253 | -0.958120157 |
| C | -2.080958564 | 0.339340098 | -2.722098347 |
| C | -2.839937072 | 1.110014892 | -3.610338574 |
| C | -3.763831488 | 2.058565905 | -3.188292666 |
| C | -3.882341363 | 2.254614386 | -1.815663340 |
| C | -3.142788952 | 1.524674422 | -0.880318607 |
| C | -3.914351914 | -1.884337423 | 0.417365100 |
| C | -5.048858389 | -2.323525705 | 1.112624975 |
| C | -5.158565776 | -2.286714908 | 2.491794921 |
| C | -4.047151701 | -1.822755892 | 3.184496158 |
| C | -2.885446384 | -1.358723511 | 2.555771392 |
| C | -1.252835302 | -4.179566587 | 0.446874621 |
| C | -1.631313899 | -5.512085489 | 0.300289473 |
| C | -1.574610456 | -6.126717984 | -0.948958167 |
| C | -1.146314578 | -5.389221909 | -2.049498866 |
| C | -0.756645677 | -4.060813957 | -1.898699712 |
| C | 2.138326157 | -4.345926049 | -0.336724830 |
| C | 2.951097606 | -5.344477644 | -0.865604723 |
| C | 3.675589187 | -5.122365967 | -2.034690211 |
| C | 3.578973465 | -3.887560776 | -2.670034714 |
| C | 2.774135717 | -2.886684706 | -2.131814927 |
| C | 4.828093541 | -0.122157836 | -0.710230895 |

| | | | |
|---|---|---|---|
| C | 6.198897973 | -0.390888727 | -0.683718549 |
| C | 6.791874101 | -1.107853606 | 0.346718109 |
| C | 5.964538281 | -1.518027014 | 1.386846054 |
| C | 4.585800721 | -1.278393325 | 1.422491968 |
| C | 1.008447538 | 3.471538900 | 2.160918469 |
| C | 1.136283018 | 4.862018131 | 2.258796649 |
| C | 0.963857676 | 5.710203366 | 1.174550979 |
| C | 0.665943077 | 5.118720771 | -0.050031954 |
| C | 0.514898489 | 3.739682664 | -0.207746398 |
| C | 0.229598973 | 3.253976940 | -1.626095269 |
| C | 1.310770310 | 2.688869508 | 3.434471029 |
| C | 1.102128299 | 7.217173962 | 1.327226574 |
| C | 4.337675605 | 0.752149665 | -1.860601903 |
| C | 3.917556336 | -1.750081530 | 2.724081539 |
| C | 8.278148099 | -1.430515792 | 0.356914661 |
| C | -6.418026726 | -2.760774367 | 3.199719227 |
| C | -1.809163191 | -0.943146430 | 3.568612392 |
| C | -4.008745070 | -2.117968210 | -1.099143216 |
| C | -1.118794917 | -0.667458027 | -3.352433839 |
| C | -3.403411404 | 1.876892418 | 0.590273054 |
| C | -4.614488298 | 2.825029392 | -4.191367229 |
| C | 4.830149384 | 2.200305391 | -1.663991758 |
| C | 4.745461672 | 0.237310040 | -3.252833568 |
| C | 3.402206811 | -0.583459913 | 3.577372477 |
| C | 2.871463145 | -2.859702371 | 2.574398293 |
| C | 8.655223773 | -2.386464438 | -0.790055119 |
| C | 9.150203365 | -0.162702101 | 0.332317189 |
| C | 0.466196457 | 3.152370754 | 4.636157587 |
| C | 2.809796495 | 2.786713302 | 3.778990115 |
| C | 2.252269554 | 7.780378525 | 0.473072143 |
| C | -0.220780887 | 7.944797918 | 1.025516002 |
| C | -0.869021049 | 4.060195026 | -2.339483765 |
| C | 1.511548138 | 3.288285851 | -2.474637714 |
| C | -4.280770661 | -3.598611175 | -1.437879558 |
| C | -5.099677481 | -1.260143198 | -1.768567671 |

| | | | |
|---|---|---|---|
| C | -6.153435615 | -3.993834247 | 4.082716408 |
| C | -7.081612351 | -1.631981271 | 4.008873797 |
| C | -0.446355231 | -1.615772042 | 3.374574779 |
| C | -1.720463268 | 0.575106712 | 3.778127058 |
| C | -3.066526589 | 3.344426763 | 0.917702747 |
| C | -4.853749060 | 1.576612280 | 1.016520189 |
| C | -6.103901872 | 2.453820336 | -4.065681224 |
| C | -4.419178326 | 4.348468815 | -4.095367528 |
| C | -1.805548799 | -1.598565564 | -4.370076059 |
| C | 0.087098752 | 0.031155732 | -4.007814099 |
| H | -2.714474083 | 0.954040009 | -4.676902304 |
| H | -4.583562163 | 2.997329440 | -1.450582352 |
| H | -5.881781733 | -2.721177145 | 0.543469755 |
| H | -4.071371133 | -1.818851882 | 4.269376200 |
| H | -1.290873875 | -3.720993622 | 1.425375407 |
| H | -1.968435034 | -6.069757451 | 1.167401805 |
| H | -1.865171311 | -7.164973696 | -1.063621177 |
| H | -1.097591954 | -5.851959843 | -3.029149371 |
| H | -0.383403257 | -3.519726908 | -2.757860209 |
| H | 1.564064657 | -4.547792258 | 0.556442742 |
| H | 3.009345024 | -6.304757871 | -0.364811935 |
| H | 4.303983334 | -5.903719305 | -2.447193941 |
| H | 4.129501794 | -3.700351010 | -3.585617116 |
| H | 2.695640924 | -1.932967500 | -2.640514868 |
| H | 6.816392471 | -0.022885489 | -1.495403914 |
| H | 6.413996301 | -2.049116572 | 2.220487619 |
| H | 1.389128676 | 5.298422237 | 3.219250974 |
| H | 0.543192175 | 5.753787515 | -0.919378376 |
| H | -0.107797337 | 2.216855462 | -1.566147610 |
| H | 1.077976046 | 1.635247247 | 3.244669877 |
| H | 1.349844462 | 7.408130165 | 2.377761711 |
| H | 3.240637006 | 0.762729369 | -1.827006926 |
| H | 4.732689164 | -2.199765731 | 3.299375644 |
| H | 8.483097601 | -1.951475781 | 1.299139163 |
| H | -7.124554926 | -3.063431960 | 2.418136215 |

| | | | |
|---|---|---|---|
| H | -2.176017949 | -1.331797946 | 4.523532883 |
| H | -3.055468261 | -1.862569214 | -1.555771799 |
| H | -0.721638147 | -1.291485048 | -2.552567880 |
| H | -2.759238398 | 1.259419712 | 1.215316529 |
| H | -4.282937171 | 2.514922644 | -5.189264480 |
| H | 4.502791607 | 2.840828158 | -2.486732854 |
| H | 4.456834298 | 2.626038722 | -0.729692748 |
| H | 5.922762542 | 2.231732122 | -1.630945030 |
| H | 4.240554900 | 0.817554232 | -4.030464981 |
| H | 4.487613697 | -0.814330596 | -3.387763284 |
| H | 5.821441715 | 0.338326257 | -3.420305499 |
| H | 3.062238745 | -0.951470171 | 4.550929379 |
| H | 4.193859902 | 0.148210876 | 3.749932182 |
| H | 2.565186635 | -0.075542574 | 3.097824915 |
| H | 1.982500136 | -2.526517309 | 2.039066295 |
| H | 2.549539420 | -3.196027168 | 3.565018289 |
| H | 3.289337289 | -3.714895621 | 2.042627330 |
| H | 9.713019248 | -2.660251957 | -0.731858406 |
| H | 8.061686875 | -3.303014198 | -0.750279987 |
| H | 8.483537294 | -1.920555605 | -1.764902102 |
| H | 10.209573936 | -0.424138343 | 0.411709151 |
| H | 8.900782231 | 0.504537731 | 1.161079888 |
| H | 9.016067252 | 0.395454659 | -0.598755485 |
| H | 0.619502244 | 2.482823922 | 5.487655757 |
| H | -0.599184198 | 3.168208590 | 4.401111955 |
| H | 0.751059063 | 4.156968993 | 4.960409968 |
| H | 3.042598691 | 2.191214232 | 4.665781358 |
| H | 3.433183768 | 2.431993632 | 2.956163647 |
| H | 3.090186316 | 3.822923262 | 3.988579834 |
| H | 2.376340542 | 8.852367328 | 0.653530505 |
| H | 3.197306168 | 7.283792456 | 0.706735155 |
| H | 2.058009793 | 7.643764327 | -0.594679693 |
| H | -0.118257787 | 9.019858013 | 1.201488710 |
| H | -1.029427643 | 7.571114271 | 1.658532554 |
| H | -0.521388823 | 7.804426456 | -0.016861820 |

| | | | |
|---|---|---|---|
| H | -1.147296763 | 3.556851539 | -3.267193354 |
| H | -1.766687917 | 4.155328316 | -1.730374477 |
| H | -0.525035888 | 5.064843611 | -2.602465918 |
| H | 1.312168359 | 2.933159973 | -3.489821662 |
| H | 2.288844153 | 2.665581873 | -2.038656791 |
| H | 1.900081113 | 4.308705860 | -2.546191850 |
| H | -4.171680586 | -3.755373908 | -2.514846538 |
| H | -3.596203053 | -4.270213628 | -0.926936905 |
| H | -5.301417380 | -3.887774071 | -1.172051580 |
| H | -5.116633839 | -1.452611975 | -2.845262680 |
| H | -4.941267362 | -0.194998130 | -1.619861720 |
| H | -6.087872406 | -1.516332081 | -1.375189136 |
| H | -7.084628132 | -4.354408845 | 4.530129422 |
| H | -5.717522204 | -4.809255768 | 3.500178581 |
| H | -5.462446388 | -3.758553765 | 4.897671888 |
| H | -8.020797190 | -1.976521825 | 4.452158229 |
| H | -7.299877645 | -0.768642506 | 3.375574844 |
| H | -6.434054288 | -1.293527059 | 4.823122111 |
| H | 0.221448911 | -1.350048973 | 4.199428577 |
| H | -0.551557933 | -2.703757762 | 3.372805591 |
| H | 0.052188949 | -1.317166036 | 2.453742817 |
| H | -1.056168758 | 0.796156363 | 4.616395135 |
| H | -2.705870619 | 0.987489684 | 4.011423231 |
| H | -1.334708394 | 1.101714197 | 2.904676315 |
| H | -3.217882464 | 3.529308503 | 1.985489723 |
| H | -2.032645470 | 3.592120604 | 0.679663463 |
| H | -3.716484391 | 4.035059763 | 0.372711361 |
| H | -5.562281655 | 2.206415473 | 0.470405055 |
| H | -4.980803861 | 1.786189390 | 2.082602543 |
| H | -5.121348433 | 0.534786671 | 0.844628845 |
| H | -6.693493647 | 2.957183694 | -4.837955706 |
| H | -6.252662593 | 1.376411377 | -4.169806029 |
| H | -6.503547961 | 2.753067879 | -3.092276222 |
| H | -5.007688293 | 4.858502146 | -4.863954539 |
| H | -3.371225844 | 4.624996980 | -4.231006489 |

| | | | |
|---|---|---|---|
| H | -4.742239544 | 4.732143853 | -3.123248924 |
| H | -1.097146656 | -2.348764814 | -4.733764802 |
| H | -2.654395177 | -2.124762021 | -3.929233341 |
| H | -2.167534386 | -1.049311568 | -5.243161770 |
| H | 0.776265373 | -0.710084376 | -4.424339248 |
| H | 0.635924217 | 0.634535127 | -3.284182457 |
| H | -0.229892692 | 0.687152025 | -4.824566077 |

**Table S9.** Optimized structure of **3** (Cartesian coordinates).

| | X | Y | Z |
|---|---|---|---|
| C | 0.707915713 | -0.138968184 | 1.168327235 |
| C | -0.681847087 | -0.198084363 | 1.197989324 |
| C | -1.464698664 | 0.504300006 | 0.264177949 |
| C | -0.784938017 | 1.303862102 | -0.670936256 |
| C | 0.605812338 | 1.343026584 | -0.717042385 |
| C | 1.389509181 | 0.602825440 | 0.186290963 |
| C | -2.945777279 | 0.348482191 | 0.209179152 |
| C | 2.872135846 | 0.548433919 | 0.064413238 |
| C | -3.484182977 | -0.895098168 | 0.334036527 |
| Si | -5.326133080 | -1.378802041 | 0.291801987 |
| Si | -6.115280242 | 0.872616067 | -0.104653836 |
| Si | -4.147064473 | 1.792585677 | -0.104406149 |
| C | 3.441929327 | 0.440095837 | -1.169765894 |
| Si | 5.232510046 | -0.079419846 | -1.521090019 |
| Si | 5.875991423 | -0.324022525 | 0.811355096 |
| Si | 4.018187021 | 0.497859833 | 1.579638132 |
| C | -5.436911575 | -2.414550314 | 1.977971273 |
| C | -5.912835124 | -2.604347413 | -1.151921534 |
| C | -3.435389813 | 3.554811084 | -0.272896654 |
| C | -7.739949013 | 1.634756229 | -0.790989466 |
| C | 6.490560523 | 1.184667139 | -2.314292769 |
| C | 5.015997217 | -1.699519734 | -2.633877462 |
| C | 7.552427752 | -0.605209859 | 1.713265135 |
| C | 3.287289897 | 0.959996185 | 3.271351226 |
| C | -3.374560883 | 4.122995824 | -1.576610333 |
| C | -2.773696992 | 5.373567047 | -1.773423872 |
| C | -2.221356496 | 6.104801897 | -0.728671928 |
| C | -2.311280305 | 5.555313026 | 0.552431716 |
| C | -2.907325947 | 4.316939614 | 0.818627790 |
| C | -8.428090896 | 2.663248138 | -0.088901284 |
| C | -9.610104486 | 3.197141097 | -0.619870022 |
| C | -10.158119757 | 2.763671015 | -1.823307723 |
| C | -9.468307262 | 1.767578972 | -2.515275685 |
| C | -8.282043426 | 1.201597154 | -2.037936078 |

| | | | |
|---|---|---|---|
| C | -5.116965131 | -2.950266168 | -2.307537625 |
| C | -5.527619805 | -4.000004930 | -3.145968477 |
| C | -6.694911578 | -4.730890401 | -2.966600091 |
| C | -7.505042946 | -4.327155053 | -1.917478588 |
| C | -7.169886895 | -3.294737199 | -1.022629922 |
| C | -4.914098687 | -3.746836268 | 1.915898057 |
| C | -5.141455618 | -4.658271016 | 2.957367520 |
| C | -5.850444544 | -4.327298317 | 4.103048498 |
| C | -6.229183104 | -2.991833474 | 4.227011582 |
| C | -6.004183817 | -2.022242845 | 3.238038619 |
| C | 7.807769375 | 0.680234800 | -2.558812933 |
| C | 8.757299048 | 1.455600641 | -3.240243743 |
| C | 8.486178471 | 2.733841293 | -3.704472491 |
| C | 7.229327788 | 3.254021063 | -3.398925992 |
| C | 6.236212801 | 2.551245132 | -2.699315272 |
| C | 4.657905254 | -2.931519936 | -1.987181201 |
| C | 4.924643142 | -4.162011756 | -2.597651871 |
| C | 5.445204999 | -4.260661063 | -3.885955220 |
| C | 5.539745425 | -3.070737522 | -4.599870697 |
| C | 5.294366623 | -1.806068960 | -4.037391704 |
| C | 8.389012426 | 0.408020328 | 2.275689405 |
| C | 9.598390724 | 0.036408689 | 2.880946684 |
| C | 10.044935411 | -1.280305936 | 2.967911186 |
| C | 9.219062449 | -2.261660085 | 2.427930598 |
| C | 7.998512584 | -1.956768850 | 1.815104248 |
| C | 3.184669797 | 0.021687440 | 4.332863335 |
| C | 2.566980223 | 0.403091726 | 5.530633258 |
| C | 2.045719143 | 1.679954242 | 5.732899302 |
| C | 2.176315410 | 2.603094623 | 4.692624573 |
| C | 2.789143676 | 2.277949833 | 3.479843792 |
| C | -2.978323457 | 3.962844796 | 2.313533918 |
| C | -2.289235914 | 2.659446857 | 2.740222192 |
| C | -4.413834048 | 4.047743115 | 2.860892438 |
| C | -1.559922945 | 7.452932851 | -0.976057244 |
| C | -2.290837458 | 8.594437976 | -0.244629278 |
| C | -0.063604381 | 7.430492243 | -0.611162029 |

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| C | -3.966105211 | 3.448120886 | -2.814114444 |
| C | -2.926649320 | 3.220874469 | -3.927107313 |
| C | -5.176824746 | 4.243048282 | -3.341276581 |
| C | -7.608466459 | 0.168316317 | -2.939032121 |
| C | -8.550776937 | -0.975060560 | -3.359469256 |
| C | -7.013996728 | 0.844459874 | -4.189601153 |
| C | -7.932209744 | 3.279411818 | 1.216387939 |
| C | -7.427626854 | 4.716873517 | 0.980876461 |
| C | -8.998072103 | 3.259013390 | 2.328304588 |
| C | -11.453338119 | 3.359923411 | -2.355983072 |
| C | -11.256556204 | 4.041806270 | -3.722622487 |
| C | -12.579132871 | 2.310404612 | -2.418542412 |
| C | -3.810364700 | -2.314272083 | -2.849094918 |
| C | -8.344566670 | -3.089094194 | -0.028599793 |
| C | -8.391877974 | -4.168868358 | 1.073701501 |
| C | -8.587169197 | -1.703337330 | 0.560075141 |
| C | -3.853904669 | -0.795438455 | -3.049807906 |
| C | -2.504658108 | -2.811347884 | -2.196279839 |
| C | -7.074061785 | -5.867925703 | -3.903264354 |
| C | -7.208965999 | -7.206027267 | -3.153225767 |
| C | -8.352053946 | -5.551158085 | -4.702540799 |
| C | -6.128666468 | -5.352535585 | 5.192116455 |
| C | -5.391449163 | -5.014500085 | 6.501885868 |
| C | -7.638301578 | -5.529815890 | 5.437697879 |
| C | -6.261998338 | -0.595004163 | 3.763060784 |
| C | -7.536005847 | 0.127369786 | 3.299552103 |
| C | -5.012518570 | 0.289903470 | 3.652657365 |
| C | -3.987199290 | -4.273950577 | 0.813265955 |
| C | -2.555385018 | -4.444007730 | 1.366389448 |
| C | -4.466026361 | -5.587666658 | 0.168791679 |
| C | 2.928146823 | 3.386045865 | 2.437304756 |
| C | 1.370383498 | 2.048959295 | 7.046333056 |
| C | 3.738071521 | -1.399173031 | 4.248387612 |
| C | 4.918371439 | -1.588274580 | 5.220906057 |
| C | 2.655722168 | -2.470765364 | 4.476339676 |
| C | 1.569335172 | 3.926374683 | 1.957716189 |

| | | | |
|---|---|---|---|
| C | 3.815886337 | 4.537072566 | 2.948877580 |
| C | 2.116408630 | 3.179631140 | 7.779088391 |
| C | -0.114408179 | 2.405768766 | 6.844391927 |
| C | 8.113123751 | 1.915887378 | 2.327841886 |
| C | 11.373043833 | -1.616573497 | 3.630277390 |
| C | 7.185666114 | -3.148684765 | 1.312785010 |
| C | 7.931616483 | -3.977655806 | 0.251501692 |
| C | 6.738998181 | -4.038937982 | 2.488733403 |
| C | 7.860084949 | 2.576468070 | 0.966490714 |
| C | 7.041844469 | 2.277181229 | 3.372641652 |
| C | 11.181056051 | -2.492285066 | 4.882621500 |
| C | 12.356570075 | -2.270893037 | 2.642228355 |
| C | 5.144433579 | -0.718401831 | -5.126816204 |
| C | 4.086475958 | 0.335751089 | -4.807060592 |
| C | 6.437406361 | -0.084892135 | -5.671811874 |
| C | 3.771984940 | -2.963884867 | -0.740722511 |
| C | 2.296000471 | -2.834550100 | -1.186956492 |
| C | 3.900429033 | -4.221462169 | 0.136057729 |
| C | 5.772466625 | -5.610251150 | -4.507466787 |
| C | 4.823960201 | -5.953390210 | -5.671934484 |
| C | 7.244292285 | -5.691415509 | -4.952260823 |
| C | 8.336097135 | -0.684245821 | -2.087770562 |
| C | 5.031030661 | 3.466305713 | -2.357822005 |
| C | 9.524212457 | 3.534851106 | -4.476671492 |
| C | 9.055269390 | 3.841026765 | -5.911543773 |
| C | 9.923747788 | 4.825856794 | -3.738007194 |
| C | 3.702170528 | 3.238090526 | -3.100473299 |
| C | 4.815204646 | 3.641809866 | -0.848511107 |
| C | 8.743989552 | -1.619308370 | -3.243077307 |
| C | 9.544163338 | -0.504780146 | -1.142922997 |
| H | 1.276727295 | -0.696321736 | 1.905453543 |
| H | -1.172966141 | -0.789917755 | 1.964528070 |
| H | -1.352193353 | 1.888442389 | -1.387133831 |
| H | 1.095415368 | 1.961782762 | -1.462569434 |
| H | -2.789767930 | -1.696862360 | 0.582573403 |
| H | 2.758453507 | 0.348133008 | -2.016595868 |

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|---|---|---|---|
| H | -2.735272945 | 5.788353849 | -2.777557753 |
| H | -1.907897548 | 6.117024251 | 1.390934715 |
| H | -10.122312502 | 3.984235199 | -0.072573820 |
| H | -9.860406648 | 1.423009043 | -3.467951904 |
| H | -4.896314887 | -4.253622519 | -3.994107614 |
| H | -8.462219706 | -4.823413101 | -1.777083493 |
| H | -4.744830607 | -5.665429679 | 2.864439719 |
| H | -6.695831817 | -2.669226952 | 5.154360939 |
| H | 9.742821240 | 1.036440115 | -3.421979578 |
| H | 7.010075154 | 4.274617711 | -3.700595246 |
| H | 4.684465554 | -5.077923682 | -2.067201665 |
| H | 5.779366567 | -3.110338883 | -5.660650308 |
| H | 10.223631953 | 0.820640585 | 3.302138076 |
| H | 9.525793215 | -3.302137944 | 2.485986555 |
| H | 2.488479498 | -0.322312830 | 6.336836807 |
| H | 1.796494619 | 3.611776253 | 4.830357314 |
| H | -2.419912298 | 4.763805342 | 2.812826210 |
| H | -2.251658937 | 2.609063303 | 3.834324100 |
| H | -1.265584161 | 2.605153879 | 2.364733753 |
| H | -2.821127890 | 1.770451648 | 2.397424657 |
| H | -4.412926985 | 3.904163204 | 3.947374479 |
| H | -4.854936417 | 5.025138537 | 2.646443892 |
| H | -5.055962789 | 3.280083111 | 2.421857067 |
| H | -1.633279581 | 7.652192057 | -2.053358531 |
| H | -1.835473625 | 9.561145166 | -0.485648775 |
| H | -3.346919627 | 8.634514580 | -0.528461797 |
| H | -2.242049088 | 8.466422644 | 0.842137707 |
| H | 0.407593583 | 8.389568803 | -0.852569880 |
| H | 0.465144114 | 6.643497140 | -1.157772806 |
| H | 0.081333178 | 7.248399071 | 0.459163891 |
| H | -4.334936366 | 2.459136170 | -2.513227552 |
| H | -3.378135221 | 2.671618812 | -4.760058376 |
| H | -2.072070159 | 2.639516094 | -3.566868366 |
| H | -2.541662891 | 4.165468590 | -4.325862686 |
| H | -5.610495312 | 3.754693587 | -4.219981118 |
| H | -5.958776176 | 4.324414195 | -2.580130706 |

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|---|---|---|---|
| H | -4.887026096 | 5.257717950 | -3.635164898 |
| H | -6.778374049 | -0.279708811 | -2.383226143 |
| H | -7.983413252 | -1.756775077 | -3.873296824 |
| H | -9.045983864 | -1.431795264 | -2.499516083 |
| H | -9.328782060 | -0.625179601 | -4.046752961 |
| H | -6.545428160 | 0.102327261 | -4.844848235 |
| H | -6.259407380 | 1.586306575 | -3.917521701 |
| H | -7.792741164 | 1.353678319 | -4.767778474 |
| H | -7.081447565 | 2.681666544 | 1.563589064 |
| H | -7.092964049 | 5.168231854 | 1.920184795 |
| H | -6.589080467 | 4.737371785 | 0.278434381 |
| H | -8.223581193 | 5.348700585 | 0.572003426 |
| H | -8.560009810 | 3.586233714 | 3.277526100 |
| H | -9.411062031 | 2.256956456 | 2.471790407 |
| H | -9.830966718 | 3.934826168 | 2.106574823 |
| H | -11.766237134 | 4.135050858 | -1.643908852 |
| H | -12.186666553 | 4.515609925 | -4.055064896 |
| H | -10.480145174 | 4.811390532 | -3.673433144 |
| H | -10.960962449 | 3.318342642 | -4.490230939 |
| H | -13.517969618 | 2.769292591 | -2.747722395 |
| H | -12.747813993 | 1.852291952 | -1.439173873 |
| H | -12.335466698 | 1.508279659 | -3.123721119 |
| H | -3.748713609 | -2.712294005 | -3.867552266 |
| H | -9.225650917 | -3.276953202 | -0.655214876 |
| H | -9.349847389 | -4.112265295 | 1.603595351 |
| H | -8.302665886 | -5.173171062 | 0.648504083 |
| H | -7.594517188 | -4.041251417 | 1.805492267 |
| H | -9.548151165 | -1.702921698 | 1.087319840 |
| H | -8.637072834 | -0.927839920 | -0.206145762 |
| H | -7.833298578 | -1.428394824 | 1.291753278 |
| H | -4.066218513 | -0.244931794 | -2.137645513 |
| H | -2.889998906 | -0.442723992 | -3.434691622 |
| H | -4.620895338 | -0.533366110 | -3.783209716 |
| H | -1.654414475 | -2.512347541 | -2.819488419 |
| H | -2.498110365 | -3.904135570 | -2.127813966 |
| H | -2.330833659 | -2.401677131 | -1.203824959 |

| | | | |
|---|---|---|---|
| H | -6.253294325 | -5.975479920 | -4.624983967 |
| H | -7.420892492 | -8.021900895 | -3.852907524 |
| H | -6.290319322 | -7.450645535 | -2.611377771 |
| H | -8.026686880 | -7.172347886 | -2.425073337 |
| H | -8.574802483 | -6.356299311 | -5.411348292 |
| H | -8.245233750 | -4.619837227 | -5.267303286 |
| H | -9.217993299 | -5.442191123 | -4.040544468 |
| H | -5.737280783 | -6.313932534 | 4.833522556 |
| H | -5.556208711 | -5.796553821 | 7.251240806 |
| H | -4.313612947 | -4.921375303 | 6.336966085 |
| H | -5.746883869 | -4.068826976 | 6.925227615 |
| H | -7.820099787 | -6.310353867 | 6.184666386 |
| H | -8.158767458 | -5.810354340 | 4.516957496 |
| H | -8.091591740 | -4.603652071 | 5.807353323 |
| H | -6.412512488 | -0.740958286 | 4.838900177 |
| H | -7.671416590 | 1.034235223 | 3.898346085 |
| H | -8.420596741 | -0.501662748 | 3.438691307 |
| H | -7.495142198 | 0.435181263 | 2.253500743 |
| H | -5.166693435 | 1.228874627 | 4.195426119 |
| H | -4.141736478 | -0.213194731 | 4.084489887 |
| H | -4.783328416 | 0.542335733 | 2.617411810 |
| H | -3.932079674 | -3.543126956 | 0.011297105 |
| H | -1.866791816 | -4.730839817 | 0.564012490 |
| H | -2.183915311 | -3.519613415 | 1.819447598 |
| H | -2.516751925 | -5.223329091 | 2.134739891 |
| H | -3.798960618 | -5.864943683 | -0.654477172 |
| H | -5.475983641 | -5.489096019 | -0.233531651 |
| H | -4.461313784 | -6.417718851 | 0.882877041 |
| H | 3.436809664 | 2.958325431 | 1.564659870 |
| H | 1.409842139 | 1.159090928 | 7.688382754 |
| H | 4.126068439 | -1.544606481 | 3.233741546 |
| H | 5.323369293 | -2.603205279 | 5.147108115 |
| H | 5.726896950 | -0.884213659 | 5.002401881 |
| H | 4.608179240 | -1.431231007 | 6.259736846 |
| H | 3.076955175 | -3.472309155 | 4.336539604 |
| H | 1.823047024 | -2.354615493 | 3.775102032 |

| | | | |
|---|---|---|---|
| H | 2.243388325 | -2.426039869 | 5.489877666 |
| H | 1.712750388 | 4.686622015 | 1.181847899 |
| H | 0.946916744 | 3.132865376 | 1.539285588 |
| H | 1.016542007 | 4.395787596 | 2.779035692 |
| H | 3.978001343 | 5.274532207 | 2.155290960 |
| H | 4.791136728 | 4.172851174 | 3.280669715 |
| H | 3.347370099 | 5.055511343 | 3.792525384 |
| H | 1.648036307 | 3.386646185 | 8.747496251 |
| H | 3.163183571 | 2.914161790 | 7.955875609 |
| H | 2.101510316 | 4.108250036 | 7.198230051 |
| H | -0.598224085 | 2.604809888 | 7.806928089 |
| H | -0.653964240 | 1.590546401 | 6.352704399 |
| H | -0.226862422 | 3.301824290 | 6.224358437 |
| H | 9.045375839 | 2.357372274 | 2.700625297 |
| H | 11.817368251 | -0.667149141 | 3.956937908 |
| H | 6.278032991 | -2.753666040 | 0.837487038 |
| H | 7.289088250 | -4.777857777 | -0.130100418 |
| H | 8.234146905 | -3.361961262 | -0.599259891 |
| H | 8.831493296 | -4.446483845 | 0.664451337 |
| H | 6.141581462 | -4.885241414 | 2.136241214 |
| H | 6.137704180 | -3.472179707 | 3.204691276 |
| H | 7.602061509 | -4.445392227 | 3.026462431 |
| H | 7.744497926 | 3.658745708 | 1.095218022 |
| H | 8.696363547 | 2.407997830 | 0.281653793 |
| H | 6.955020452 | 2.201876433 | 0.487487937 |
| H | 6.992113978 | 3.364782835 | 3.497781117 |
| H | 7.283477067 | 1.837859637 | 4.346054867 |
| H | 6.049962888 | 1.926514871 | 3.081405074 |
| H | 12.140656973 | -2.672543866 | 5.379333862 |
| H | 10.508999358 | -2.013676180 | 5.601448339 |
| H | 10.752945360 | -3.466738696 | 4.623643551 |
| H | 13.325138169 | -2.448814520 | 3.122097916 |
| H | 12.520388799 | -1.634592961 | 1.767231181 |
| H | 11.980141056 | -3.236241448 | 2.286741832 |
| H | 4.733869304 | -1.288227460 | -5.970398390 |
| H | 4.410594563 | 0.998121554 | -4.009441388 |

| | | | |
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| H | 3.897789264 | 0.960193828 | -5.687553521 |
| H | 3.139820384 | -0.127845128 | -4.511826218 |
| H | 6.206621738 | 0.486275488 | -6.578663190 |
| H | 7.170580064 | -0.851264781 | -5.942563826 |
| H | 6.903608290 | 0.593267805 | -4.959090374 |
| H | 4.005989998 | -2.102188229 | -0.110627758 |
| H | 1.634187347 | -2.767356036 | -0.316846847 |
| H | 2.133779069 | -1.947612570 | -1.801035616 |
| H | 2.000107197 | -3.711824387 | -1.773848817 |
| H | 3.395086800 | -4.056545376 | 1.093321118 |
| H | 4.938980321 | -4.482091071 | 0.343675896 |
| H | 3.424740740 | -5.091684899 | -0.329209055 |
| H | 5.620565555 | -6.367223858 | -3.726399532 |
| H | 5.037846829 | -6.953810594 | -6.064199820 |
| H | 3.778206615 | -5.929070758 | -5.350413002 |
| H | 4.935665211 | -5.242012276 | -6.497419877 |
| H | 7.478217734 | -6.689456978 | -5.339003359 |
| H | 7.922039169 | -5.480707765 | -4.119335622 |
| H | 7.458498261 | -4.968159647 | -5.746603352 |
| H | 7.551804434 | -1.196864717 | -1.522979944 |
| H | 5.357593355 | 4.451706486 | -2.707769291 |
| H | 10.421865508 | 2.906691919 | -4.550516441 |
| H | 9.836974256 | 4.367722675 | -6.469935628 |
| H | 8.809665370 | 2.921891138 | -6.452163104 |
| H | 8.162256218 | 4.475426983 | -5.910490128 |
| H | 10.716570986 | 5.351940896 | -4.280977247 |
| H | 10.287129254 | 4.608806008 | -2.728857708 |
| H | 9.074008985 | 5.510857004 | -3.646412539 |
| H | 3.028632974 | 4.073776429 | -2.877305897 |
| H | 3.849261890 | 3.211879382 | -4.183693032 |
| H | 3.195756023 | 2.322995888 | -2.797110662 |
| H | 4.018257232 | 4.373341961 | -0.670539252 |
| H | 5.724063576 | 4.009819157 | -0.366310548 |
| H | 4.525657038 | 2.709859504 | -0.365322074 |
| H | 9.143168483 | -2.556616588 | -2.839451641 |
| H | 7.901218690 | -1.866223982 | -3.887281090 |

| | | | |
|---|---|---|---|
| H | 9.529698755 | -1.168317991 | -3.858323870 |
| H | 9.824354860 | -1.464077632 | -0.697486973 |
| H | 9.329429191 | 0.188772871 | -0.329893522 |
| H | 10.416311528 | -0.129436032 | -1.688341325 |

**Table S10.** Coordinates of optimized structure of **10b**.

symmetry c1

| | | | |
|---|---|---|---|
| C | -1.028043000 | -1.483610000 | -4.697822000 |
| C | 0.189264000 | 0.489775000 | -3.681251000 |
| C | -0.382595000 | -0.916688000 | -3.422990000 |
| C | 3.170027000 | 2.060309000 | -2.712517000 |
| C | 1.385264000 | -2.693299000 | -3.647801000 |
| C | 3.099280000 | -5.938094000 | -3.788622000 |
| C | 3.168648000 | -4.443079000 | -4.156572000 |
| C | 0.663351000 | -1.836797000 | -2.791091000 |
| C | -3.711894000 | -2.759096000 | -1.074886000 |
| C | 4.628876000 | -3.952829000 | -4.256761000 |
| C | -0.813496000 | 2.407581000 | -0.103730000 |
| C | 2.377830000 | -3.572767000 | -3.187622000 |
| C | 0.569554000 | 2.443111000 | 0.340461000 |
| C | -1.617415000 | -4.108264000 | -1.632680000 |
| C | 3.317003000 | 0.716190000 | -1.969870000 |
| C | -2.190634000 | -2.899341000 | -0.866215000 |
| C | 3.961631000 | -0.353125000 | -2.868596000 |
| C | 0.951623000 | -1.852907000 | -1.389603000 |
| C | 4.050094000 | 0.900835000 | -0.643007000 |
| C | 8.159792000 | 2.577677000 | -0.385714000 |
| C | 2.649768000 | -3.580084000 | -1.810623000 |
| C | 5.450603000 | 1.029897000 | -0.659795000 |
| C | -1.795212000 | -2.944680000 | 0.609838000 |
| C | 1.971625000 | -2.735697000 | -0.912170000 |
| C | 3.355812000 | 0.987686000 | 0.601476000 |
| C | -0.828070000 | -2.061766000 | 1.183729000 |
| C | 6.198925000 | 1.241972000 | 0.514509000 |
| C | -2.408372000 | -3.930749000 | 1.408242000 |
| C | 7.717564000 | 1.370154000 | 0.465963000 |
| C | 4.100187000 | 1.193521000 | 1.798478000 |
| C | 5.502373000 | 1.320937000 | 1.731039000 |
| C | 3.375486000 | 2.762772000 | 3.663485000 |
| C | 2.353049000 | -2.836429000 | 0.564054000 |
| C | 3.414414000 | 1.307659000 | 3.157230000 |
| C | -0.527754000 | -2.189758000 | 2.578428000 |
| C | -2.127326000 | -4.063437000 | 2.774897000 |
| C | 3.854197000 | -2.593808000 | 0.815463000 |
| C | 8.374857000 | 0.063806000 | -0.025833000 |
| C | 1.875890000 | -4.173278000 | 1.165740000 |
| C | -3.826443000 | -4.399645000 | 4.607320000 |
| C | -0.195155000 | -0.014679000 | 3.847681000 |
| C | -1.189161000 | -3.178480000 | 3.333112000 |

| | | | |
|---|---|---|---|
| C | -2.850502000 | -5.093809000 | 3.633712000 |
| C | 0.473367000 | -1.295726000 | 3.313818000 |
| C | 4.033496000 | 0.365416000 | 4.204268000 |
| C | -1.872133000 | -6.021869000 | 4.380024000 |
| C | 1.235689000 | -2.017669000 | 4.438057000 |
| H | -1.882089000 | -0.849680000 | -5.003036000 |
| H | -0.320430000 | -1.500411000 | -5.553533000 |
| H | -0.569516000 | 1.145100000 | -4.158350000 |
| H | 1.071118000 | 0.433943000 | -4.352850000 |
| H | -1.403308000 | -2.516041000 | -4.543331000 |
| H | 2.745261000 | 1.910216000 | -3.725893000 |
| H | 0.501719000 | 0.981494000 | -2.737385000 |
| H | 1.173191000 | -2.676085000 | -4.727600000 |
| H | 2.048358000 | -6.287354000 | -3.722332000 |
| H | 2.702342000 | -4.320860000 | -5.160243000 |
| H | -3.936462000 | -2.595051000 | -2.149981000 |
| H | -1.200183000 | -0.787979000 | -2.674917000 |
| H | 2.496013000 | 2.749922000 | -2.164943000 |
| H | 5.199685000 | -4.546044000 | -5.002354000 |
| H | 4.156072000 | 2.558793000 | -2.826795000 |
| H | 3.624082000 | -6.556427000 | -4.547127000 |
| H | -1.834665000 | -4.022774000 | -2.718002000 |
| H | 5.146191000 | -4.049769000 | -3.278267000 |
| H | 4.673625000 | -2.884529000 | -4.551931000 |
| H | -4.120581000 | -1.897672000 | -0.509938000 |
| H | -4.257321000 | -3.673749000 | -0.760203000 |
| H | 3.300056000 | -0.578565000 | -3.729176000 |
| H | 3.581970000 | -6.137017000 | -2.808102000 |
| H | -1.739819000 | -1.985450000 | -1.306726000 |
| H | 2.294354000 | 0.352244000 | -1.728640000 |
| H | -2.069379000 | -5.055343000 | -1.267747000 |
| H | 4.939286000 | -0.019530000 | -3.277121000 |
| H | -0.517963000 | -4.179730000 | -1.511221000 |
| H | 7.700385000 | 3.518271000 | -0.018288000 |
| H | 5.978379000 | 0.966282000 | -1.625049000 |
| H | 7.861236000 | 2.450656000 | -1.448179000 |
| H | 4.118399000 | -1.300485000 | -2.316343000 |
| H | 9.263603000 | 2.697577000 | -0.361284000 |
| H | -3.142791000 | -4.612463000 | 0.948291000 |
| H | 3.427248000 | -4.254917000 | -1.418014000 |
| H | 2.873020000 | 3.432473000 | 2.939542000 |
| H | 1.821041000 | -2.025068000 | 1.102357000 |
| H | -4.548592000 | -3.758588000 | 4.061425000 |
| H | -0.597596000 | 0.608583000 | 3.024786000 |

| | | | |
|---|---|---|---|
| H | 4.186837000 | -1.631152000 | 0.378621000 |
| H | 2.353001000 | 0.990602000 | 2.993861000 |
| H | 4.404584000 | 3.149215000 | 3.825800000 |
| H | 0.783945000 | -4.306322000 | 1.028728000 |
| H | 2.831193000 | 2.826599000 | 4.629609000 |
| H | 6.075031000 | 1.489023000 | 2.658278000 |
| H | 4.480353000 | -3.405387000 | 0.387893000 |
| H | -3.454843000 | -5.725574000 | 2.944327000 |
| H | 2.393899000 | -5.030482000 | 0.685012000 |
| H | 1.231555000 | -0.962483000 | 2.566050000 |
| H | 9.482526000 | 0.139795000 | 0.004873000 |
| H | 8.082813000 | -0.160826000 | -1.073876000 |
| H | 8.067873000 | -0.799590000 | 0.599563000 |
| H | -4.398161000 | -5.144997000 | 5.200054000 |
| H | -1.031160000 | -0.265063000 | 4.534293000 |
| H | 0.534037000 | 0.607760000 | 4.407906000 |
| H | -3.276570000 | -3.749214000 | 5.320713000 |
| H | 4.057250000 | -2.558763000 | 1.906802000 |
| H | 2.089508000 | -4.214747000 | 2.254062000 |
| H | -0.966766000 | -3.261661000 | 4.407353000 |
| H | 4.077430000 | -0.679235000 | 3.833365000 |
| H | 5.067417000 | 0.673458000 | 4.468611000 |
| H | 3.442090000 | 0.382339000 | 5.143677000 |
| H | -1.169967000 | -6.514734000 | 3.676559000 |
| H | 1.672041000 | -2.975151000 | 4.088182000 |
| H | -2.421551000 | -6.812154000 | 4.933766000 |
| H | 2.059168000 | -1.378444000 | 4.808017000 |
| H | -1.265281000 | -5.459666000 | 5.121654000 |
| H | 0.585156000 | -2.237319000 | 5.310710000 |
| Si | 0.020472000 | -0.839070000 | -0.041184000 |
| Si | 1.454979000 | 0.899465000 | 0.709636000 |
| H | 8.063869000 | 1.549082000 | 1.508816000 |
| C | 1.198542000 | 3.732611000 | 0.768629000 |
| C | 2.488346000 | 4.136986000 | 0.345238000 |
| C | 0.516056000 | 4.569171000 | 1.691256000 |
| C | 3.068759000 | 5.325730000 | 0.818784000 |
| C | 1.098402000 | 5.751025000 | 2.169194000 |
| C | 2.379782000 | 6.139235000 | 1.733722000 |
| H | 3.050555000 | 3.505370000 | -0.354080000 |
| H | -0.483521000 | 4.270227000 | 2.042007000 |
| H | 4.074337000 | 5.611374000 | 0.470859000 |
| H | 0.547466000 | 6.374996000 | 2.891210000 |
| H | 2.837313000 | 7.068562000 | 2.108532000 |
| C | -1.548874000 | 3.672836000 | -0.421632000 |

| | | | |
|---|---|---|---|
| C | -2.867025000 | 3.930049000 | 0.029476000 |
| C | -0.943084000 | 4.638771000 | -1.268079000 |
| C | -3.547780000 | 5.100763000 | -0.344790000 |
| C | -1.625230000 | 5.803166000 | -1.647185000 |
| C | -2.933541000 | 6.043554000 | -1.185953000 |
| H | -3.373017000 | 3.197535000 | 0.671176000 |
| H | 0.077536000 | 4.456162000 | -1.637716000 |
| H | -4.572833000 | 5.269765000 | 0.022029000 |
| H | -1.131381000 | 6.530242000 | -2.311801000 |
| H | -3.469335000 | 6.958780000 | -1.483851000 |
| C | -4.157632000 | 0.353724000 | -4.096702000 |
| C | -3.611190000 | 1.276378000 | -2.993746000 |
| C | -3.727037000 | 2.762304000 | -3.385588000 |
| C | -4.252196000 | 0.998233000 | -1.636304000 |
| C | -8.448156000 | -0.358811000 | -1.028366000 |
| C | -5.655497000 | 1.011779000 | -1.529979000 |
| C | -3.462854000 | 0.758974000 | -0.474078000 |
| C | -6.311015000 | 0.789983000 | -0.305164000 |
| C | -7.833108000 | 0.797971000 | -0.213546000 |
| C | -4.110989000 | 0.523469000 | 0.773139000 |
| C | -5.518205000 | 0.546527000 | 0.830940000 |
| C | -3.857916000 | -0.904303000 | 2.875735000 |
| C | -3.323598000 | 0.285129000 | 2.059434000 |
| C | -8.424543000 | 2.158900000 | -0.633686000 |
| C | -3.244847000 | 1.567372000 | 2.913116000 |
| H | -3.627351000 | 0.531587000 | -5.055613000 |
| H | -4.041084000 | -0.715255000 | -3.823834000 |
| H | -5.236413000 | 0.538475000 | -4.285371000 |
| H | -3.208098000 | 2.956094000 | -4.348354000 |
| H | -2.519511000 | 1.058171000 | -2.873187000 |
| H | -4.791742000 | 3.056298000 | -3.507488000 |
| H | -8.040106000 | -1.338376000 | -0.704702000 |
| H | -6.257013000 | 1.207902000 | -2.432683000 |
| H | -8.228105000 | -0.245429000 | -2.111327000 |
| H | -3.281062000 | 3.418911000 | -2.613676000 |
| H | -9.552312000 | -0.385170000 | -0.910831000 |
| H | -3.969324000 | -1.806120000 | 2.241663000 |
| H | -2.286539000 | 0.021709000 | 1.754086000 |
| H | -4.840698000 | -0.679663000 | 3.342370000 |
| H | -3.152168000 | -1.160060000 | 3.691264000 |
| H | -6.021025000 | 0.370938000 | 1.796359000 |
| H | -9.527108000 | 2.169464000 | -0.501123000 |
| H | -8.215101000 | 2.376111000 | -1.702699000 |
| H | -7.994919000 | 2.986907000 | -0.033241000 |

| | | | |
|---|---|---|---|
| H | -2.634505000 | 2.345351000 | 2.411021000 |
| H | -4.257738000 | 1.985254000 | 3.094976000 |
| H | -2.780604000 | 1.358816000 | 3.898457000 |
| H | -8.096175000 | 0.632880000 | 0.855562000 |
| Si | -1.565241000 | 0.835828000 | -0.616987000 |

**Table S11.** Coordinates of optimized structure of **11b**.

symmetry c1

| | | | |
|---|---|---|---|
| Si | -1.997000000 | 1.460000000 | -0.008000000 |
| Si | -0.318985000 | -0.145199000 | 0.204364000 |
| Si | 1.810213000 | -0.191805000 | -0.298862000 |
| C | -1.970759872 | 3.226023952 | 0.551647315 |
| C | -2.339601632 | 2.402980977 | 1.566508233 |
| C | -2.509108616 | 2.473465539 | 3.020142160 |
| C | -3.770316625 | 2.568881908 | 3.651983085 |
| C | -3.865030599 | 2.596769431 | 5.053134056 |
| C | -2.708139560 | 2.523005613 | 5.849341110 |
| C | -1.447385551 | 2.428691259 | 5.230585183 |
| C | -1.345534579 | 2.406465739 | 3.831398206 |
| C | -3.296182273 | 0.769564656 | -1.213872939 |
| C | -3.091984361 | 0.978347169 | -2.607447174 |
| C | -4.024192249 | 0.462630907 | -3.529691582 |
| C | -5.158269051 | -0.256634934 | -3.117312760 |
| C | -5.329201959 | -0.480741454 | -1.737451508 |
| C | -4.413013061 | -0.001371159 | -0.781874060 |
| C | -1.879871574 | 1.743498900 | -3.137426049 |
| C | -0.903997352 | 0.822949316 | -3.896430056 |
| C | -2.296513911 | 2.953792843 | -3.995359376 |
| C | -6.140818927 | -0.826040315 | -4.134779107 |
| C | -6.060499526 | -2.366840340 | -4.176505407 |
| C | -7.582794047 | -0.344189409 | -3.879924604 |
| C | -4.663738951 | -0.287618592 | 0.695780262 |
| C | -5.708646194 | 0.695782757 | 1.258147201 |
| C | -5.060978563 | -1.750256405 | 0.958759888 |
| C | -1.256104566 | -1.774528850 | 0.561240823 |
| C | -1.560072345 | -2.713704061 | -0.462492132 |
| C | -2.148849015 | -3.947195830 | -0.114191755 |
| C | -2.459702898 | -4.270704440 | 1.216780610 |
| C | -2.221906128 | -3.298347283 | 2.208544530 |
| C | -1.648735461 | -2.050136464 | 1.908667137 |
| C | -1.264804462 | -2.404630601 | -1.925783481 |
| C | -2.466900411 | -2.684550928 | -2.842680142 |
| C | 0.011825711 | -3.110249811 | -2.418022732 |
| C | -3.077547538 | -5.616558205 | 1.576105112 |
| C | -2.173284307 | -6.412586905 | 2.539005970 |
| C | -4.502215569 | -5.447190950 | 2.143207959 |
| C | -1.491876707 | -1.005056197 | 3.018831978 |
| C | -0.197361642 | -1.181842960 | 3.832560142 |
| C | -2.713304706 | -0.924790484 | 3.952113919 |
| C | 2.905338596 | -1.755219072 | -0.492943701 |

| | | | |
|---|---|---|---|
| C | 3.825032629 | -1.730081103 | -1.587311651 |
| C | 4.804861370 | -2.734703229 | -1.704839737 |
| C | 4.903459072 | -3.790803270 | -0.785131902 |
| C | 3.957718035 | -3.835468172 | 0.254196026 |
| C | 2.962579288 | -2.853528094 | 0.419161087 |
| C | 3.786849939 | -0.643753906 | -2.660881452 |
| C | 3.502057820 | -1.231003290 | -4.056802107 |
| C | 5.060297165 | 0.222789735 | -2.637185463 |
| C | 5.995686799 | -4.847138422 | -0.905803042 |
| C | 6.962788787 | -4.783569002 | 0.294870051 |
| C | 5.409883434 | -6.262836075 | -1.081694621 |
| C | 1.970868210 | -3.045133099 | 1.562656851 |
| C | 2.651147158 | -3.114731802 | 2.943664791 |
| C | 1.101105890 | -4.294109606 | 1.322111450 |
| C | 2.931436400 | 1.349915574 | -0.178036269 |
| C | 2.924470700 | 2.413493623 | -1.125983095 |
| C | 3.927294957 | 3.402070290 | -1.062016978 |
| C | 4.945411928 | 3.380436956 | -0.094959977 |
| C | 4.923941633 | 2.340630914 | 0.852854873 |
| C | 3.938757372 | 1.336712190 | 0.836053740 |
| C | 1.840946764 | 2.556891084 | -2.192392962 |
| C | 2.395642845 | 2.738298514 | -3.617241748 |
| C | 0.903285057 | 3.716340911 | -1.813787704 |
| C | 6.036788205 | 4.444888648 | -0.074466775 |
| C | 6.019710385 | 5.254705203 | 1.238195120 |
| C | 7.425672050 | 3.825786574 | -0.335588425 |
| C | 3.991128063 | 0.253937987 | 1.912660545 |
| C | 5.250888838 | -0.621741186 | 1.771391608 |
| C | 3.841593183 | 0.843432462 | 3.327873193 |
| C | -1.710226249 | 4.657743854 | 0.401010727 |
| C | -1.811873442 | 5.277156426 | -0.867651955 |
| C | -1.363047430 | 5.453114184 | 1.522902840 |
| C | -1.570491804 | 6.650874326 | -1.015156479 |
| C | -1.112429792 | 6.824628081 | 1.370547318 |
| C | -1.214694980 | 7.428226654 | 0.102528654 |

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