

# **Nickel-Assisted Complete Cleavage of CO by a Silylene/Siliconoid Hybrid under Formation of an Si=C Enol Ether bridge**

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## **Electronic Supplementary Information**

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## 1. General

All manipulations were carried out under a protective atmosphere of argon, by using a glovebox or standard Schlenk techniques. Ethereal solvents were dried by heating to reflux over Na/benzophenone and distilled and stored under an atmosphere of argon. Hydrocarbons were dried over sodium or potassium. Solution NMR spectra were recorded on a Bruker Avance IV 400 NMR spectrometer ( $^1\text{H}$  = 400.13 MHz,  $^{13}\text{C}$  = 100.6 MHz,  $^{29}\text{Si}$  = 79.49 MHz) and solid state NMR spectra on a Bruker Avance III 400 WB spectrometer ( $^{29}\text{Si}$  = 79.53 MHz). UV/Vis spectra were recorded on a Shimadzu UV-2600 spectrometer in quartz cells with a path length of 0.1 cm. Elemental analyses were performed on an elemental analyzer Leco CHN-900 and/or an elemental vario Micro Cube. Compound **1** was prepared according to our published procedure.<sup>1</sup>

## 2. Preparation, data and spectra (NMR, UV-vis, IR)

### *Ligato-privo* Si=C Enol ether bridged Si<sub>6</sub> siliconoid

**Route A:** Compound **2** is prepared by treating 1 equivalent of the *ligato*-siylene-functionalized siliconoid **1** (350 mg ; 0.237 mmol) with 1 equivalent of Bis(cycloocta-1,5-dien)nickel (74.41 mg ; 0.259 mmol) under CO atmosphere in 8 mL benzene. The suspension was slightly heated to 50°C until the color changed from bright red to brown. The mixture was stirred over night at room temperature until the color changed to green. All volatiles (caution, Ni(CO)<sub>4</sub> !) were removed in vacuo and the crude product is extracted with 6 mL hexane. The hexane solution is concentrated and compound **2** is crystallized at -26°C as green crystals in 66 % yield (230 mg ; 0.156 mmol).

**Route B:** Compound **2** is prepared by treating 1 equivalent of the *ligato*-siylene-functionalized siliconoid **1** (250 mg ; 0.173 mmol) with 10 mol% of Bis(cycloocta-1,5-dien)nickel (4.76 mg ; 0.0173 mmol) under CO atmosphere in 8 mL benzene at 45°C over two days. The color changed from a bright red suspension to a green solution. All volatiles were removed in vacuo and the crude product is filtered from 6 mL hexane. Compound **2** is crystallized as green crystals at -26°C in 44 % yield (112 mg ; 0.076 mmol).

**$^1\text{H}$ -NMR** (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K)  $\delta$  = 7.631 (0.074H, C<sub>10</sub>H<sub>8</sub>), 7.340 – 7.337 (m, 1H, Ar-H), 7.251 – 7.235 (m, 2H, Ar-H), 7.1838 (bs, 1H, Ar-H), 7.037 – 6.972 (m, 5H, Ar-H), 6.889 – 6.813 (m, 4H, Ar-H), 6.705 – 6.664 (m, 1H, Ar-H), 6.549 – 6.529 (m, 1H, Ar-H), 5.371 – 5.249 (m, 2H, Tip-*i*Pr-CH<sub>2</sub>), 4.815 (bs, 1H, Tip-*i*Pr-CH<sub>2</sub>), 4.584 (bs, 1H, Tip-*i*Pr-CH<sub>2</sub>), 4.453 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 4.335 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 4.115 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 3.865 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 3.362 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 3.207 (sept, 1H,  $^3J_{\text{HH}}$  = 6.25 Hz, Tip-*i*Pr-CH<sub>2</sub>), 2.9358 – 2.617 (m, 5H, Tip-*i*Pr-CH<sub>2</sub>), 2.222 (d, 3H,  $^3J_{\text{HH}}$  = 6.32 Hz, Tip-*i*Pr-CH<sub>2</sub>), 2.089 (d, 3H,  $^3J_{\text{HH}}$  = 6.32 Hz, Tip-*i*Pr-CH<sub>2</sub>), 1.850 (bs, 3H, Tip-*i*Pr-CH<sub>3</sub>), 1.706 – 1.666 (m, 10H, Tip-*i*Pr-CH<sub>3</sub>), 1.585 – 1.453 (m, 30H, Tip-*i*Pr-CH<sub>3</sub> overlapping with C(CH<sub>3</sub>)<sub>2</sub>), 1.315 – 1.216 (m, 26H, Tip-*i*Pr-CH<sub>3</sub>), 1.126 – 1.046 (m, 14H, Tip-*i*Pr-CH<sub>3</sub>), 0.8925 (t, 3H, hexane), 0.835 – 0.745 (m, 16H, Tip-*i*Pr-CH<sub>3</sub>), 0.621 (s, 9H, C(CH<sub>3</sub>)<sub>2</sub>), 0.560 (d, 3H,  $^3J_{\text{HH}}$  = 6.32 Hz, Tip-*i*Pr-CH<sub>3</sub>), 0.400 (d, 3H,  $^3J_{\text{HH}}$  = 6.32 Hz, Tip-*i*Pr-CH<sub>3</sub>), 0.252 (d, 3H,  $^3J_{\text{HH}}$  = 6.32 Hz, Tip-*i*Pr-CH<sub>3</sub>) ppm.

**$^{13}\text{C}$ -NMR** (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K)  $\delta$  = 175.66 (Ph-C), 156.99, 155.36, 153.51, 152.63, 152.54, 151.61, 149.79, 149.38, 148.50, 148.33, 147.20 (s, each 1C, Ar-C), 141.67, 140.67, 140.19, 139.60 (s, each 1C, Ar-CH), 135.54 (s, 1C, Ar-CH), 130.60, 129.91, 128.25, 127.80, 127.60, 127.20, 125.70 (s, each 1C, Ar-CH), 122.90, 122.49, 122.36, 121.91, 121.53, 121.01, 120.78, 120.41, 118.65 (s, each 1C, Ar-CH), 54.46, 53.11 (s, each 1C, C(CH<sub>3</sub>)<sub>2</sub>), 36.80, 35.78, 35.38 (s, each 1C, Tip-*i*Pr-CH), 34.88, 34.41, 34.37, 34.32, 34.25, 34.18 (s, each 1C, Tip-*i*Pr-CH), 32.30, 31.61, 31.16, 30.10 (s, each 1C, Tip-*i*Pr-CH), 28.06, 27.87, 27.58, 27.20, 26.80 (s, each 1C, Tip-*i*Pr-CH<sub>3</sub>),

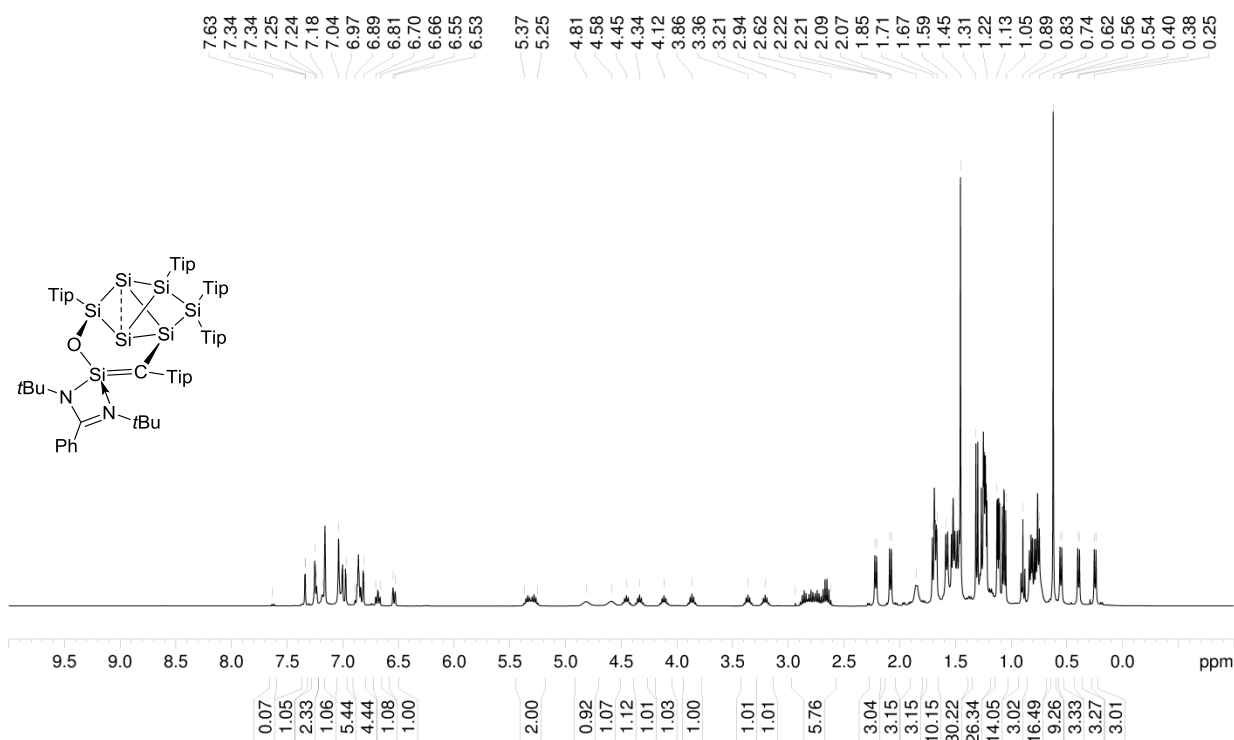
25.54 (s, 1C, Tip-*i*Pr-CH<sub>3</sub>), 25.32 (bs, 1C, Tip-*i*Pr-CH<sub>3</sub>), 24.76, 24.64, 24.50, 24.45, 24.15, 24.05, 23.98, 23.85, 23.83, 23.69, 23.62, 23.54, 23.54, 23.36 (s, each 1C, Tip-*i*Pr-CH<sub>3</sub>), 22.89, 22.87 (bs, each 1C, Tip-*i*Pr-CH<sub>3</sub>), 22.70, 21.78 (s, each 1C, Tip-*i*Pr-CH<sub>3</sub>), 14.02, 12.11 (s, each 1C, NHC-*i*pr-CH<sub>3</sub>) ppm.

<sup>29</sup>Si-NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K)  $\delta$  = 160.9 (s, *privo*-Si(Tip)<sub>2</sub>), 30.4 (s, *ligato*-SiTip), -22.7 (s, *remoto*-Si(Tip)<sub>2</sub>), -33.6 (s, *ligato*-Si-NHSi), -35.1 (NHSi), -268.2 (s, *nudo*-Si), -300.5 (s, *nudo*-Si) ppm.

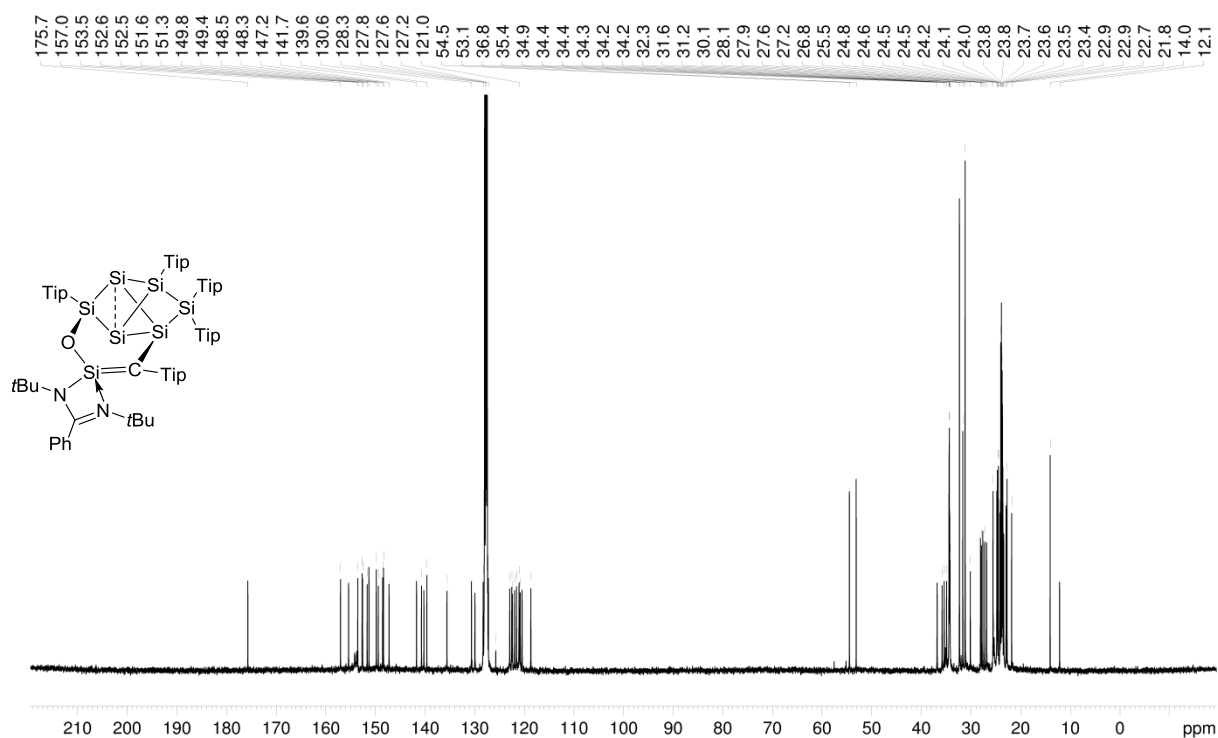
CP-MAS <sup>29</sup>Si-NMR (79.53 MHz, 13KHz, 300K)  $\delta$  = 160.9 (s, *privo*-Si(Tip)<sub>2</sub>), 28.6 (s, *ligato*-SiTip), -22.5 (s, *remoto*-Si(Tip)<sub>2</sub>), -34.4 (s, *ligato*-Si-NHSi), -37.9 (NHSi), -267.5 (s, *nudo*-Si), -303.4 (s, *nudo*-Si) ppm.

**Elemental analysis:** calculated for C<sub>91</sub>H<sub>138</sub>N<sub>2</sub>O<sub>Si</sub><sub>7</sub>: C: 74.22 % ; H: 9.45 % ; N: 1.90 %. Found: C: 73.89 % ; H: 9.00 % ; N: 1.85 %.

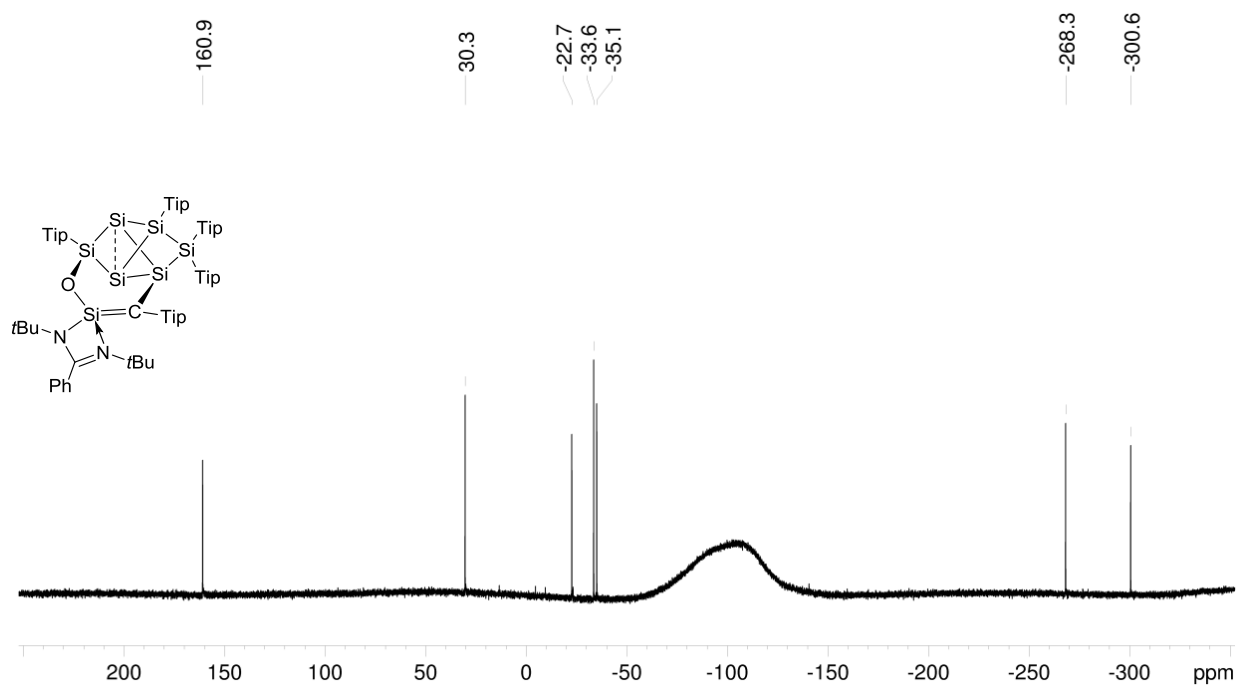
**UV/VIS** (hexane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 638 nm (3640 M<sup>-1</sup> cm<sup>-1</sup>).



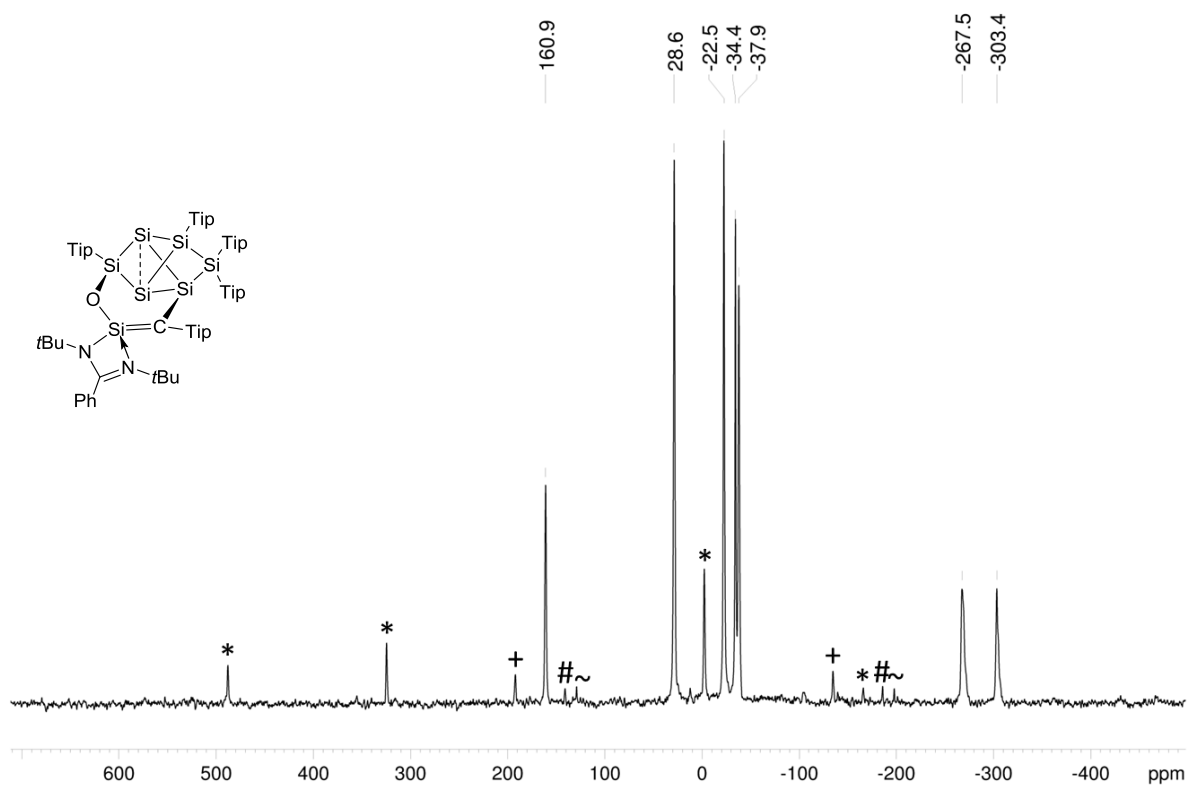
**Figure S1.** <sup>1</sup>H NMR of 2 in C<sub>6</sub>D<sub>6</sub> (400.13 MHz, 300 K).



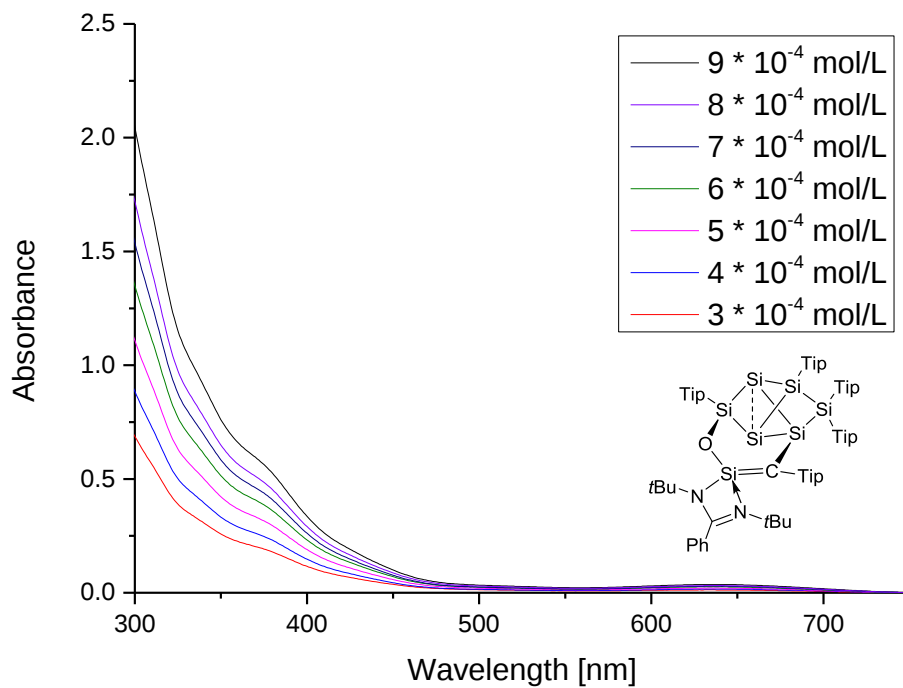
**Figure S2.** <sup>13</sup>C NMR of **2** in C<sub>6</sub>D<sub>6</sub> (100.61 MHz, 300 K).



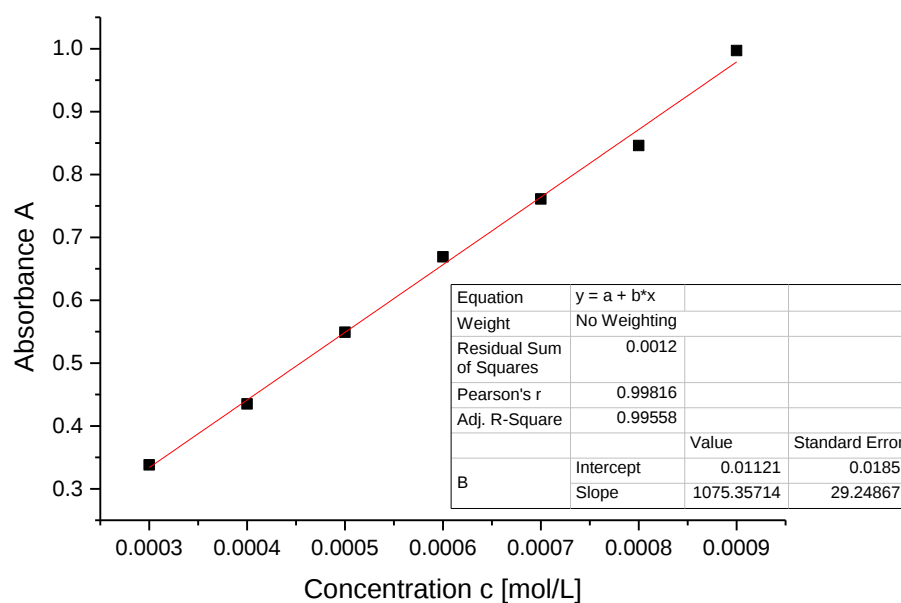
**Figure S3.** <sup>29</sup>Si NMR of **2** in C<sub>6</sub>D<sub>6</sub> (79.49 MHz, 300 K).



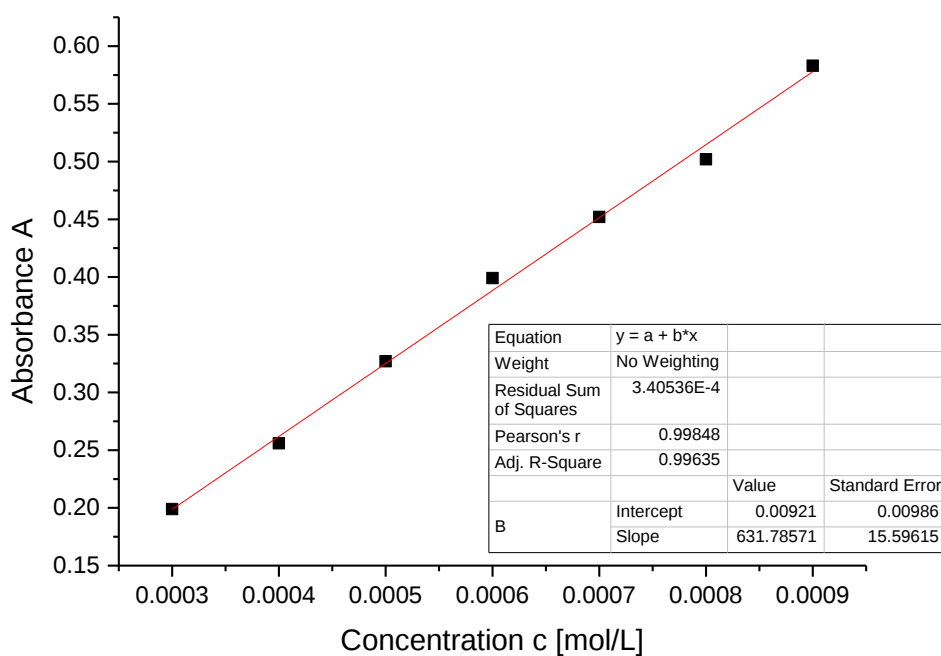
**Figure S4.** CP-MAS  $^{29}\text{Si}$  NMR of **2** (79.53 MHz, 13 KHz, 300 K) with side spinning bands of: \* *privo*-Si(Tip) $_2$  (160.9 ppm), + *ligato*-SiTip (28.6 ppm), # *remoto*-Si(Tip) $_2$  (-22.5 ppm), ~ *ligato*-Si-NHSi (-34.4 ppm).



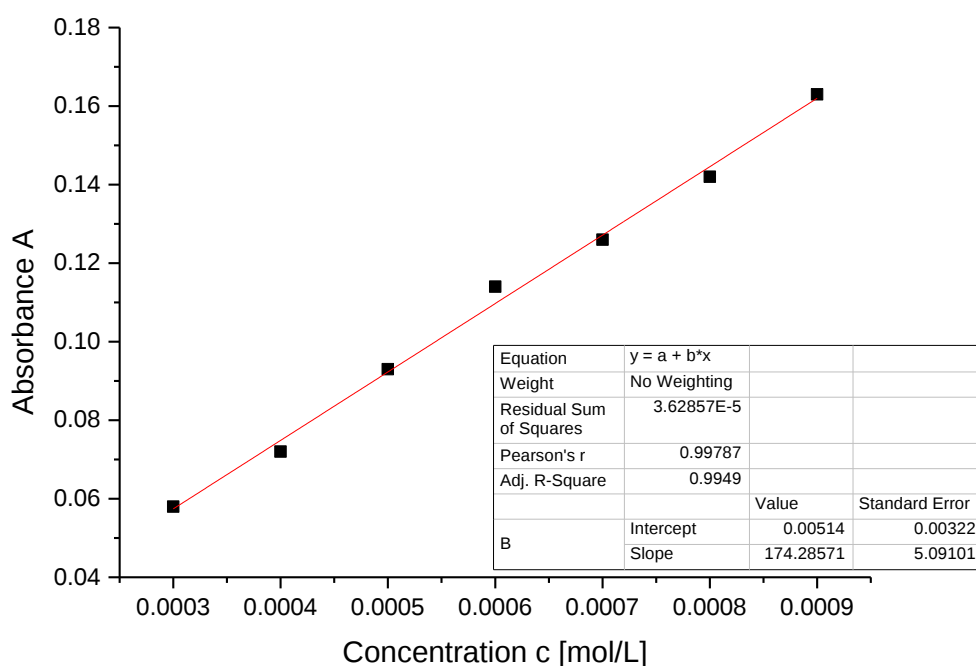
**Figure S5.** UV-Vis spectrum of **2** in hexane at different concentrations ( $9 \times 10^{-4}$  mol/L to  $3 \times 10^{-4}$  mol/L).



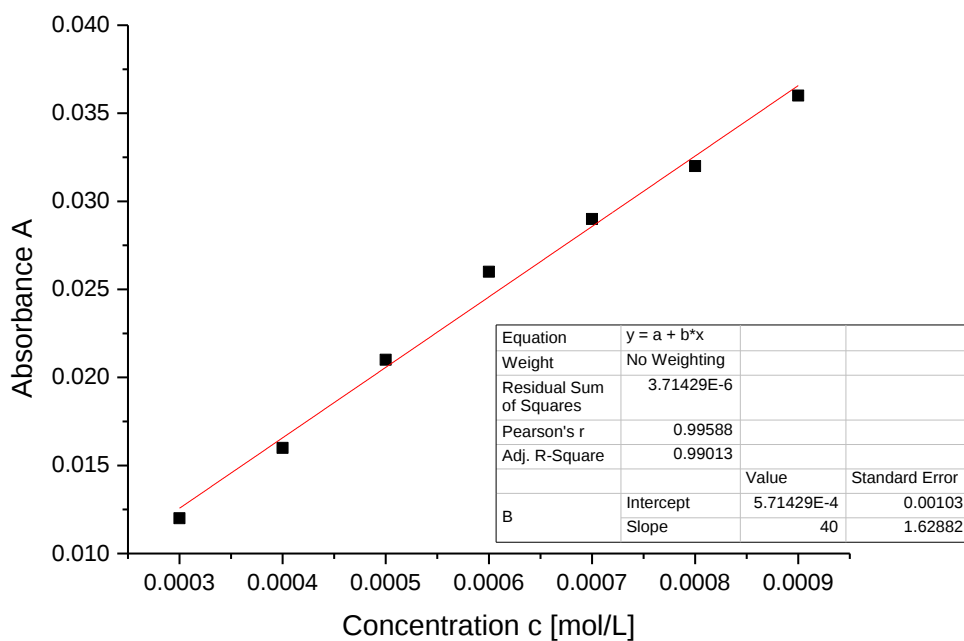
**Figure S6.** Determination of  $\varepsilon = 10750 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  by linear regression of absorptions ( $\lambda = 334 \text{ nm}$ ) of **2** against concentration.



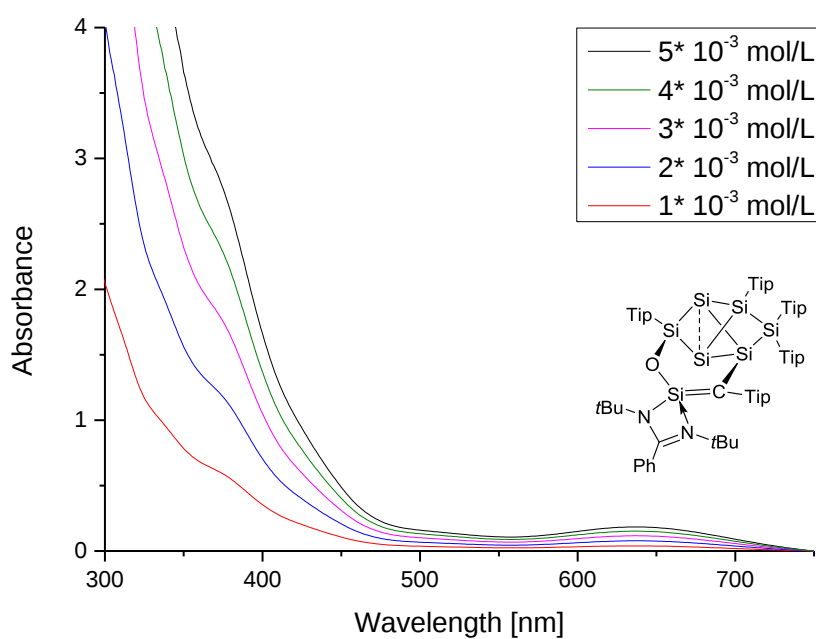
**Figure S7.** Determination of  $\varepsilon = 6310 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  by linear regression of absorptions ( $\lambda = 372 \text{ nm}$ ) of **2** against concentration.



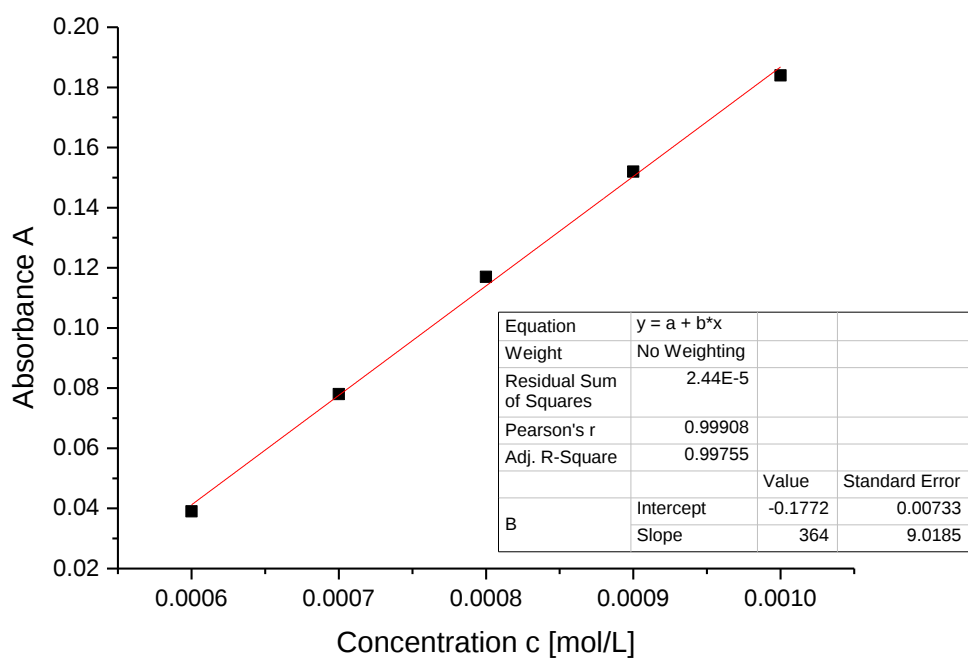
**Figure S8.** Determination of  $\epsilon = 1740 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  by linear regression of absorptions ( $\lambda = 432 \text{ nm}$ ) of **2** against concentration.



**Figure S9.** Determination of  $\epsilon = 400 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  by linear regression of absorptions ( $\lambda = 638 \text{ nm}$ ) of **2** against concentration.



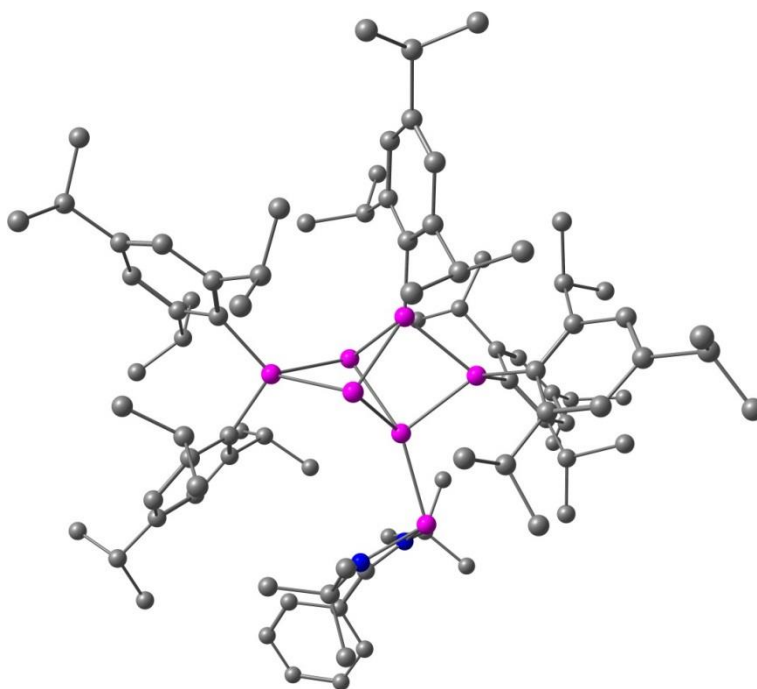
**Figure S9.** UV-Vis spectrum of **2** in hexane at different concentrations ( $5 \times 10^{-3}$  mol/L to  $1 \times 10^{-3}$  mol/L).



**Figure S10.** Determination of  $\epsilon = 3640$  ( $M^{-1} \text{ cm}^{-1}$ ) by linear regression of absorptions ( $\lambda = 638$  nm) of **2** against concentration.

### 3. Computational Details

Structural and geometry optimizations of **1**, [Int-a], [Int-b], [Int-c], and **2** were performed using the Gaussian09 program package<sup>[2]</sup> together with TurboMole V7.0.<sup>[3]</sup> All geometry optimizations were computed using the BP86<sup>[4,5]</sup> functional with Grimme dispersion correctors D3<sup>[6]</sup> and the Becke-Johnson damping function<sup>[7]</sup> in combination with the def2-SVP basis set.<sup>[8]</sup> To ensure the presence of a local minimum on the potential energy surface, the subsequent analysis of the frequency and molecular orbitals was performed at the same level of theory. The UV-Vis absorption spectrum was computed to determine the transition states using the CAM-B3LYP<sup>[9]</sup> functional with Grimme dispersion correctors D3 and the Becke-Johnson damping function with the def2-SVPP basis set. The optimized structures were plotted using ChemCraft 1.8.<sup>[10]</sup> The data from TD-DFT calculations were analysed with the GaussSum<sup>[11]</sup> and OriginPro 9.0 programmes.<sup>[12]</sup>



**Figure S11.** Optimized structure at the BP86-D3(BJ)/def2-SVP level of theory for **1**. Bond distances are in [Å]. Hydrogen atoms omitted for clarity.

**Table S1.** Atomic coordinates of the optimized structure **1** at the BP86-D3(BJ)/def2-SVP level of theory.

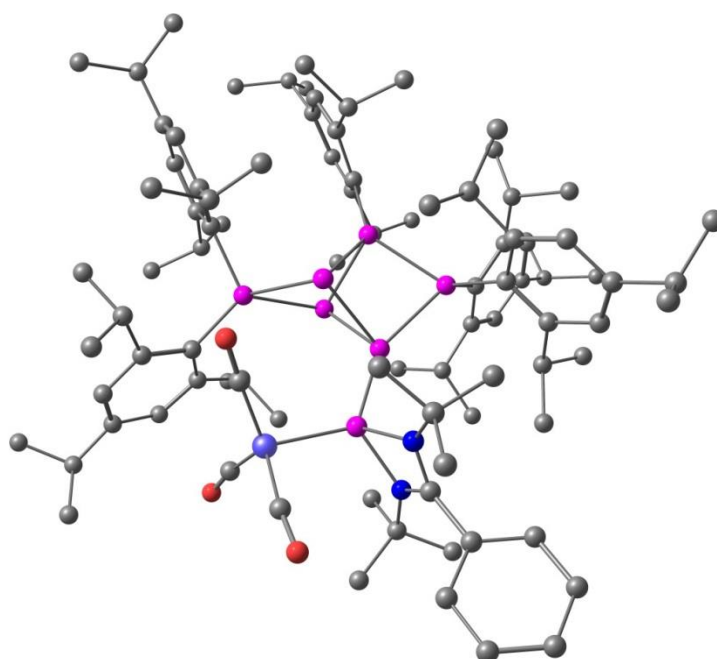
|    |              |              |              |
|----|--------------|--------------|--------------|
| Si | 0.195667586  | 0.874853889  | -1.286999097 |
| Si | 0.442345407  | 0.434597390  | 1.483541342  |
| Si | -0.005494444 | -1.282998236 | -0.226109021 |
| Si | -1.525057674 | 1.235562893  | 0.384707451  |
| Si | 2.024725025  | 1.652778196  | 0.151599169  |
| Si | -2.348830326 | -0.971624427 | 0.104663537  |
| Si | 0.504210056  | -3.411499333 | -1.226091160 |
| N  | 2.378764497  | -3.298549370 | -1.636938201 |
| N  | 1.579065461  | -4.427863796 | 0.015058554  |
| C  | 2.706537885  | -4.235416806 | -0.709409114 |
| C  | 3.058723066  | -2.889972670 | -2.883626866 |
| C  | 2.079714850  | -1.937034614 | -3.596185924 |
| H  | 1.847284887  | -1.063046983 | -2.953122809 |
| H  | 1.123547410  | -2.454789572 | -3.825094492 |
| H  | 2.512369152  | -1.573625054 | -4.549189434 |
| C  | 4.353710358  | -2.121705059 | -2.566722408 |
| H  | 4.153818976  | -1.326366947 | -1.824714859 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 4.755177340  | -1.646248154 | -3.484376835 |
| H | 5.136503889  | -2.791171970 | -2.163807099 |
| C | 3.342265592  | -4.112838918 | -3.780176747 |
| H | 4.064251763  | -4.804592256 | -3.302472897 |
| H | 3.771585380  | -3.789168347 | -4.750990066 |
| H | 2.403515672  | -4.669566225 | -3.981672764 |
| C | 1.265733304  | -5.236511050 | 1.210348836  |
| C | 0.184709798  | -4.451524084 | 1.982989493  |
| H | -0.164883193 | -5.021830275 | 2.866413630  |
| H | -0.704295828 | -4.253558007 | 1.350378418  |
| H | 0.572244503  | -3.470418574 | 2.320358283  |
| C | 0.701265188  | -6.608808301 | 0.777204584  |
| H | 1.474241619  | -7.207070963 | 0.254981461  |
| H | -0.161985975 | -6.484830962 | 0.095470642  |
| H | 0.362125984  | -7.184588391 | 1.662975457  |
| C | 2.490596287  | -5.461022160 | 2.118911977  |
| H | 2.966011752  | -4.503840780 | 2.400128790  |
| H | 3.254326716  | -6.103293371 | 1.641110250  |
| H | 2.157984033  | -5.966018760 | 3.048467436  |
| C | 3.974549795  | -5.004695912 | -0.620698708 |
| C | 5.185195647  | -4.392897965 | -0.230768745 |
| H | 5.199392107  | -3.320439073 | 0.010308445  |
| C | 6.362536988  | -5.152649018 | -0.142061354 |
| H | 7.299132617  | -4.667370758 | 0.171654538  |
| C | 6.348330907  | -6.523204938 | -0.451775402 |
| H | 7.274275362  | -7.114968033 | -0.381286218 |
| C | 5.148694540  | -7.135513551 | -0.856841198 |
| H | 5.132718034  | -8.206326152 | -1.113167350 |
| C | 3.968745329  | -6.381826240 | -0.938621377 |
| H | 3.029747818  | -6.852689267 | -1.266023495 |
| C | -2.503872084 | 2.855432620  | 0.572470843  |
| C | -3.297050725 | 3.309409331  | -0.526554474 |
| C | -3.998322887 | 4.522964383  | -0.413075780 |
| H | -4.599174913 | 4.868886503  | -1.268475469 |
| C | -3.952517865 | 5.306116845  | 0.753218492  |
| C | -3.197977038 | 4.829663880  | 1.837399544  |
| H | -3.170906860 | 5.429384875  | 2.761082872  |
| C | -2.478133935 | 3.620824581  | 1.774535308  |
| C | -3.399284679 | 2.534182817  | -1.840341447 |
| H | -3.129581080 | 1.478146587  | -1.620797168 |
| C | -2.401307532 | 3.058844983  | -2.885115267 |
| H | -1.357173651 | 2.911153550  | -2.548539984 |
| H | -2.558960087 | 4.141572840  | -3.075558951 |
| H | -2.526763954 | 2.522839665  | -3.847953150 |
| C | -4.815479659 | 2.523816055  | -2.439665538 |
| H | -5.580804288 | 2.245491656  | -1.691779136 |
| H | -4.864395005 | 1.781930846  | -3.261142963 |
| H | -5.088303404 | 3.513056803  | -2.865403907 |
| C | -4.682849711 | 6.639314523  | 0.833504143  |
| H | -4.545887066 | 7.021368008  | 1.869910993  |
| C | -4.053874597 | 7.665519439  | -0.130274846 |
| H | -4.543125803 | 8.657719743  | -0.032918145 |
| H | -4.162380487 | 7.337332229  | -1.185817459 |
| H | -2.970149225 | 7.790235034  | 0.070048759  |
| C | -6.195309992 | 6.484445086  | 0.586842884  |
| H | -6.644313343 | 5.755306307  | 1.291805455  |
| H | -6.400900910 | 6.124593179  | -0.443462837 |
| H | -6.718977130 | 7.455609324  | 0.711280809  |
| C | -1.651606476 | 3.187231179  | 2.981652448  |
| H | -1.566779733 | 2.079541174  | 2.927741637  |
| C | -2.294235019 | 3.539158651  | 4.332636424  |
| H | -1.746746100 | 3.039549001  | 5.158690344  |
| H | -3.355506739 | 3.220626809  | 4.377572992  |
| H | -2.259731964 | 4.630095190  | 4.537443546  |
| C | -0.222808491 | 3.751002904  | 2.889356527  |
| H | 0.401651867  | 3.388720734  | 3.733281408  |
| H | -0.230215002 | 4.861246543  | 2.916312811  |
| H | 0.279275212  | 3.446481770  | 1.950963919  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 2.382306714  | 3.523930766  | 0.463277372  |
| C | 1.768391529  | 4.589047948  | -0.265741687 |
| C | 2.297108076  | 5.890536812  | -0.174331514 |
| H | 1.829734824  | 6.688467575  | -0.772534176 |
| C | 3.382284796  | 6.212600965  | 0.654726001  |
| C | 3.917534243  | 5.181294981  | 1.438325306  |
| H | 4.740397203  | 5.417630684  | 2.133327024  |
| C | 3.443074366  | 3.858074887  | 1.360837098  |
| C | 0.534614498  | 4.428836440  | -1.149858521 |
| H | 0.117040017  | 3.413839752  | -0.969873866 |
| C | 0.888677433  | 4.541209552  | -2.645074376 |
| H | 1.424053369  | 5.491285807  | -2.853812046 |
| H | -0.024478763 | 4.524024521  | -3.272425229 |
| H | 1.537494958  | 3.706300333  | -2.975030631 |
| C | -0.560650071 | 5.439123059  | -0.762863875 |
| H | -0.807663507 | 5.373328758  | 0.314414407  |
| H | -1.490374455 | 5.238026841  | -1.326899151 |
| H | -0.255555774 | 6.483242213  | -0.984352796 |
| C | 3.945351027  | 7.625407010  | 0.710733756  |
| H | 4.768630724  | 7.616054014  | 1.459811870  |
| C | 2.889704811  | 8.641810346  | 1.186670091  |
| H | 2.470612448  | 8.353421446  | 2.172265114  |
| H | 2.044256920  | 8.707920725  | 0.469581971  |
| H | 3.329475992  | 9.657117598  | 1.279870301  |
| C | 4.550908524  | 8.033383089  | -0.646723640 |
| H | 5.327053848  | 7.311072020  | -0.972411265 |
| H | 5.014640825  | 9.040794011  | -0.590205547 |
| H | 3.771298010  | 8.065538704  | -1.437127566 |
| C | 4.089843716  | 2.843926496  | 2.296028226  |
| H | 3.624028664  | 1.861102240  | 2.093359553  |
| C | 3.779881926  | 3.165663819  | 3.770096957  |
| H | 4.197187337  | 2.382681170  | 4.437724438  |
| H | 2.685463544  | 3.216645189  | 3.940409665  |
| H | 4.215815376  | 4.139623870  | 4.077025514  |
| C | 5.600786391  | 2.716276276  | 2.033690992  |
| H | 6.053362588  | 1.927513096  | 2.668482950  |
| H | 6.127706064  | 3.667039646  | 2.259642756  |
| H | 5.799922034  | 2.455597197  | 0.975482885  |
| C | 3.743085787  | 0.851314471  | -0.175004388 |
| C | 4.395412399  | -0.074505973 | 0.698730651  |
| C | 5.709596241  | -0.488116544 | 0.413565544  |
| H | 6.204174293  | -1.186650712 | 1.106299163  |
| C | 6.426119804  | -0.008754716 | -0.698074355 |
| C | 5.779787687  | 0.902668895  | -1.545651458 |
| H | 6.325567713  | 1.292971793  | -2.421006796 |
| C | 4.460030560  | 1.333526265  | -1.306902511 |
| C | 3.725459216  | -0.632266354 | 1.950462301  |
| H | 2.897507720  | 0.060437390  | 2.214435741  |
| C | 3.079564781  | -1.988486004 | 1.654604905  |
| H | 3.857291610  | -2.763165550 | 1.504467789  |
| H | 2.449081686  | -1.951531684 | 0.745380906  |
| H | 2.433398460  | -2.307099138 | 2.497726622  |
| C | 4.642229933  | -0.731152743 | 3.180271858  |
| H | 4.047780163  | -1.023335686 | 4.070521476  |
| H | 5.143703960  | 0.230706932  | 3.404234963  |
| H | 5.430524141  | -1.502870489 | 3.051858674  |
| C | 7.876625336  | -0.403766802 | -0.939075443 |
| H | 8.136161800  | -0.067230527 | -1.967693678 |
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| H | 9.146405725  | -2.183642536 | -1.130577847 |
| H | 7.427660140  | -2.462736147 | -1.574055365 |
| H | 7.904915787  | -2.314019322 | 0.148220986  |
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| H | 8.576465264  | 0.049221431  | 1.093255521  |
| H | 8.667055488  | 1.438461569  | -0.031061081 |
| H | 9.870006029  | 0.106200217  | -0.151760039 |
| C | 3.842973677  | 2.334451162  | -2.275637286 |
| H | 2.806771586  | 2.531371299  | -1.924638150 |

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| C | 3.705542985  | 1.749219855  | -3.690858364 |
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| H | 3.199534206  | 2.470388108  | -4.366697511 |
| H | 3.108020060  | 0.815994334  | -3.673521437 |
| C | 4.584923207  | 3.681623448  | -2.259349861 |
| H | 4.627210121  | 4.096612555  | -1.232423486 |
| H | 4.067044940  | 4.421113611  | -2.904151699 |
| H | 5.625347359  | 3.574313382  | -2.633323635 |
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| C | -5.046449463 | -0.500570654 | -0.685209564 |
| C | -6.153146472 | -0.498360588 | -1.556412854 |
| H | -7.147837878 | -0.226485629 | -1.164769429 |
| C | -6.034907372 | -0.834474823 | -2.913820677 |
| C | -4.755893761 | -1.162840630 | -3.399147696 |
| H | -4.634850075 | -1.417382015 | -4.464756526 |
| C | -3.625343050 | -1.198408782 | -2.562231381 |
| C | -5.284389679 | -0.136081062 | 0.781930761  |
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| C | -5.911394756 | 1.257436975  | 0.964925958  |
| H | -6.035525451 | 1.481919684  | 2.045071806  |
| H | -6.915860860 | 1.323712975  | 0.495767874  |
| H | -5.271862704 | 2.050781925  | 0.532811628  |
| C | -6.110241680 | -1.222263785 | 1.497261559  |
| H | -5.614551456 | -2.210548664 | 1.438855626  |
| H | -7.120480843 | -1.313226460 | 1.044664921  |
| H | -6.241907701 | -0.973581356 | 2.570988958  |
| C | -7.251087821 | -0.840214121 | -3.830219600 |
| H | -8.128318652 | -0.563924922 | -3.203335884 |
| C | -7.125875540 | 0.213620184  | -4.947494021 |
| H | -6.979805368 | 1.229207146  | -4.526675815 |
| H | -8.036022043 | 0.230310446  | -5.583559026 |
| H | -6.259481730 | -0.003930336 | -5.607696652 |
| C | -7.511934791 | -2.245592798 | -4.406139192 |
| H | -6.672829435 | -2.574373941 | -5.055294671 |
| H | -8.436778028 | -2.259747554 | -5.020730041 |
| H | -7.621062676 | -2.995511076 | -3.596232211 |
| C | -2.280966328 | -1.582582643 | -3.172582235 |
| H | -1.576143625 | -1.744804924 | -2.326624472 |
| C | -1.703016866 | -0.432505472 | -4.012808156 |
| H | -1.587349562 | 0.484689936  | -3.401622838 |
| H | -2.364983578 | -0.187895388 | -4.871242432 |
| H | -0.701593426 | -0.697476427 | -4.411675883 |
| C | -2.330294152 | -2.891554809 | -3.976965314 |
| H | -1.305745857 | -3.197695579 | -4.274025588 |
| H | -2.933566836 | -2.786772448 | -4.903632789 |
| H | -2.763093635 | -3.717972014 | -3.379415015 |
| C | -2.881892826 | -2.252914664 | 1.442141145  |
| C | -3.259180922 | -3.563118198 | 0.998715238  |
| C | -3.609848492 | -4.544440592 | 1.943664326  |
| H | -3.903224031 | -5.542858469 | 1.582470468  |
| C | -3.586645874 | -4.300284856 | 3.327155946  |
| C | -3.213362914 | -3.017218006 | 3.750024973  |
| H | -3.191684486 | -2.804374699 | 4.832327594  |
| C | -2.868784704 | -1.995551690 | 2.842062766  |
| C | -3.339621748 | -3.961636266 | -0.477751129 |
| H | -2.801662835 | -3.188976649 | -1.063994342 |
| C | -4.800108950 | -3.999241152 | -0.967601446 |
| H | -5.367341647 | -4.791359967 | -0.433598384 |
| H | -4.842827905 | -4.219285721 | -2.054508528 |
| H | -5.314590772 | -3.035360049 | -0.800506798 |
| C | -2.645440249 | -5.296748079 | -0.788451092 |
| H | -1.574878214 | -5.266464588 | -0.507892393 |
| H | -2.687492325 | -5.504901273 | -1.877491679 |
| H | -3.122925914 | -6.152626767 | -0.267430976 |
| C | -3.919899083 | -5.396979066 | 4.329390197  |
| H | -3.918643869 | -4.925356632 | 5.337699836  |
| C | -5.320452362 | -5.991823930 | 4.092207535  |
| H | -5.570848400 | -6.741751385 | 4.871829146  |

|   |              |              |             |
|---|--------------|--------------|-------------|
| H | -5.380459210 | -6.502812299 | 3.108003158 |
| H | -6.099144569 | -5.202172706 | 4.107404797 |
| C | -2.833964370 | -6.491932150 | 4.324647890 |
| H | -1.834257459 | -6.063239363 | 4.542904004 |
| H | -2.775621033 | -6.988371161 | 3.332696543 |
| H | -3.048267101 | -7.274056812 | 5.083510201 |
| C | -2.494123459 | -0.640575791 | 3.431109076 |
| H | -2.282619711 | 0.037970777  | 2.576254451 |
| C | -3.642757639 | -0.014776226 | 4.241051972 |
| H | -3.918638281 | -0.645052578 | 5.112509061 |
| H | -4.550772896 | 0.114529436  | 3.619768459 |
| H | -3.349103583 | 0.981397531  | 4.627976015 |
| C | -1.205347888 | -0.729751106 | 4.266700145 |
| H | -1.357282059 | -1.341341700 | 5.181691991 |
| H | -0.868852283 | 0.279870997  | 4.585447225 |
| H | -0.384031674 | -1.193217638 | 3.681193836 |



**Figure S12.** Optimized structure at the BP86-D3(BJ)/def2-SVP level of theory for **[Int-a]**. Bond distances are in [Å]. Hydrogen atoms omitted for clarity.

**Table S2.** Atomic coordinates of the optimized structure **[Int-a]** at the BP86-D3(BJ)/def2-SVP level of theory.

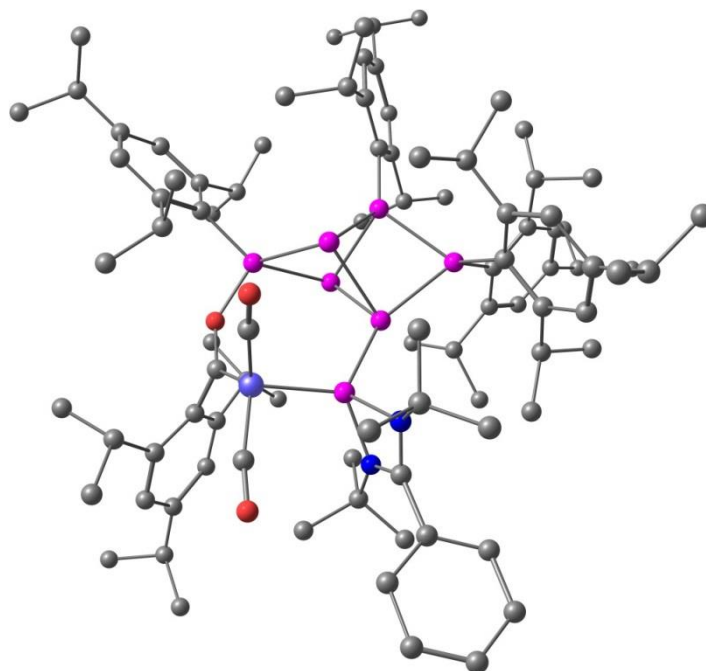
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| Si | -0.508008891 | -0.384384659 | 1.376911730  |
| Si | 1.157734292  | -0.362849993 | -0.401577706 |
| Si | -0.796302903 | 1.811629930  | 0.334519654  |
| Si | -2.377380603 | -1.355010502 | 0.037105785  |
| Si | 1.536129162  | 1.979486927  | -0.109659327 |
| Si | 2.043140346  | -2.502210817 | -0.042035773 |
| N  | 3.572842778  | -2.408584148 | 1.069701556  |
| N  | 3.603699897  | -2.840234226 | -1.044913989 |
| C  | 4.372647082  | -2.820762704 | 0.066078931  |
| C  | 3.851429045  | -2.139770990 | 2.494755540  |
| C  | 4.421279763  | -0.715123340 | 2.617988412  |
| H  | 5.399777567  | -0.633676108 | 2.104131358  |
| H  | 4.568363928  | -0.439814276 | 3.681500981  |
| H  | 3.734751267  | 0.023899041  | 2.162527099  |

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| H | 4.846642532  | -3.023288961 | 4.209448263  |
| H | 5.852698151  | -3.061419251 | 2.731559290  |
| C | 2.502551195  | -2.236695312 | 3.227402108  |
| H | 1.736888734  | -1.600104321 | 2.737839116  |
| H | 2.611023376  | -1.895805372 | 4.275744467  |
| H | 2.128402665  | -3.277895789 | 3.230572235  |
| C | 5.786032984  | -3.279799515 | 0.183317692  |
| C | 6.851764636  | -2.356726005 | 0.194255231  |
| H | 6.640112205  | -1.284673728 | 0.094309841  |
| C | 8.174536781  | -2.807925108 | 0.325222008  |
| H | 8.999861833  | -2.079083123 | 0.329782414  |
| C | 8.443617486  | -4.181495665 | 0.450984710  |
| H | 9.481644169  | -4.533887210 | 0.555504341  |
| C | 7.382443849  | -5.103626186 | 0.449860926  |
| H | 7.584511451  | -6.180152557 | 0.561708981  |
| C | 6.058164130  | -4.658876331 | 0.317632748  |
| H | 5.223813764  | -5.373112113 | 0.355001797  |
| C | 3.855663119  | -3.338284221 | -2.408413589 |
| C | 2.690079202  | -2.802783860 | -3.257093503 |
| H | 2.797840953  | -3.111621100 | -4.315649348 |
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| C | 5.190281612  | -2.799127589 | -2.955962718 |
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| H | 4.682877615  | -5.301005839 | -1.855129305 |
| H | 3.914254863  | -5.252682087 | -3.474303603 |
| O | -0.687018609 | -3.507293830 | 2.872502756  |
| O | 3.078384996  | -5.946470741 | 1.171278187  |
| O | -0.357824725 | -5.380834503 | -2.079299488 |
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| H | -4.879462332 | 4.355188456  | 1.955844997  |
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| C | -1.776240180 | 3.358228848  | -2.387919993 |
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| C | -2.466448865 | 2.489924824  | -3.452736931 |
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| H | -2.633487596 | 1.456505470  | -3.082039103 |
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| C | -1.382413676 | 4.724318067  | -2.979896548 |
| H | -0.657656384 | 4.582302626  | -3.807299452 |
| H | -0.898420485 | 5.368855464  | -2.222548827 |
| H | -2.263769475 | 5.267798051  | -3.381746014 |
| C | -6.083352597 | 5.098771329  | -0.354861449 |
| H | -6.236148982 | 5.748003449  | 0.537655314  |
| C | -7.176391806 | 4.009204750  | -0.321387922 |
| H | -7.095143148 | 3.388456834  | 0.592809845  |
| H | -7.071533217 | 3.329588849  | -1.192336129 |
| H | -8.191531044 | 4.458306490  | -0.351226029 |
| C | -6.221630528 | 5.979790281  | -1.604698342 |
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| H | -5.421394457 | 6.746332260  | -1.656506768 |
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| H | -1.784850153 | 2.457204472  | 2.719817794  |

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| H | -1.382471435 | 4.591205234  | 4.102021921  |
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| H | -0.329330958 | -1.641302426 | -4.243479625 |
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| C | -3.923622263 | -0.627028023 | 0.925926373  |
| C | -4.087334707 | -0.569395112 | 2.351224282  |
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| H | -5.380644211 | 0.031423891  | 3.975838384  |
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| C | -6.122698248 | 0.440627258  | 0.682898567  |
| H | -6.928051675 | 0.817389505  | 0.032753055  |
| C | -4.977527920 | -0.134289975 | 0.101613904  |
| C | -3.097774140 | -1.151789716 | 3.370373096  |
| H | -2.333922265 | -1.727206875 | 2.811379635  |
| C | -2.343627678 | -0.070862955 | 4.162404665  |
| H | -1.853807404 | 0.659673745  | 3.490029327  |
| H | -1.554511790 | -0.538127293 | 4.787613360  |
| H | -3.028692882 | 0.485034911  | 4.833885450  |
| C | -3.753539922 | -2.122677131 | 4.371241688  |
| H | -4.434687627 | -1.593212121 | 5.070324691  |
| H | -2.969445985 | -2.615662112 | 4.981815627  |
| H | -4.340499501 | -2.911088329 | 3.867632199  |
| C | -7.551482747 | 1.117189372  | 2.677785653  |
| H | -8.188444618 | 1.446240157  | 1.826305084  |
| C | -7.256261957 | 2.355892144  | 3.543329107  |
| H | -6.709983975 | 3.127552156  | 2.964449271  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -6.630445830 | 2.094319358  | 4.422277262  |
| H | -8.196671789 | 2.807619989  | 3.923052419  |
| C | -8.340470150 | 0.054394237  | 3.467293782  |
| H | -9.295897398 | 0.470638045  | 3.850806378  |
| H | -7.757760907 | -0.308684469 | 4.340287856  |
| H | -8.573975962 | -0.824533795 | 2.832501343  |
| C | -4.952192009 | -0.301759600 | -1.414525210 |
| H | -3.895045438 | -0.499260940 | -1.705121335 |
| C | -5.391682160 | 0.960267595  | -2.171422431 |
| H | -5.202893578 | 0.845829199  | -3.258492425 |
| H | -4.848460658 | 1.855196601  | -1.811605339 |
| H | -6.479291481 | 1.147496856  | -2.048363780 |
| C | -5.793811095 | -1.523554599 | -1.832549121 |
| H | -5.753144512 | -1.674295432 | -2.931468765 |
| H | -6.856891358 | -1.375385572 | -1.546565040 |
| H | -5.432189885 | -2.452136065 | -1.350771522 |
| C | 2.987289805  | 2.295042184  | 1.107212661  |
| C | 4.301235316  | 2.234749035  | 0.552950161  |
| C | 5.425105154  | 2.471670765  | 1.366484298  |
| H | 6.432800985  | 2.433599558  | 0.919541230  |
| C | 5.308007225  | 2.743819750  | 2.736263385  |
| C | 4.013201028  | 2.781972403  | 3.277973345  |
| H | 3.896267133  | 2.980586114  | 4.354504510  |
| C | 2.858282324  | 2.575555048  | 2.499840823  |
| C | 4.564912671  | 1.910729752  | -0.913643470 |
| H | 3.593361932  | 1.677447143  | -1.387392937 |
| C | 5.160516122  | 3.118745885  | -1.657209870 |
| H | 5.316385423  | 2.889920313  | -2.731626004 |
| H | 6.141804510  | 3.410546036  | -1.227137894 |
| H | 4.482154376  | 3.992830683  | -1.594804468 |
| C | 5.414657343  | 0.642037469  | -1.063991315 |
| H | 4.905381995  | -0.216936145 | -0.583296307 |
| H | 6.418478591  | 0.760418213  | -0.604401674 |
| H | 5.568574261  | 0.391260958  | -2.133957476 |
| C | 6.537966337  | 2.970536085  | 3.604561995  |
| H | 7.419899544  | 2.951032675  | 2.925587997  |
| C | 6.505507928  | 4.349518613  | 4.290336646  |
| H | 6.395124411  | 5.164954046  | 3.546701384  |
| H | 7.437564380  | 4.528466943  | 4.866522732  |
| H | 5.654737335  | 4.425828073  | 5.000062198  |
| C | 6.713684617  | 1.833567375  | 4.630421184  |
| H | 5.854729875  | 1.795524738  | 5.333660203  |
| H | 7.635342736  | 1.978144219  | 5.232596874  |
| H | 6.778785219  | 0.846983414  | 4.128460384  |
| C | 1.516634601  | 2.615854537  | 3.225219935  |
| H | 0.716038171  | 2.692009683  | 2.455526895  |
| C | 1.391144735  | 3.822629283  | 4.169372268  |
| H | 1.496783580  | 4.782419766  | 3.624331200  |
| H | 2.159713400  | 3.801209754  | 4.969038827  |
| H | 0.405509300  | 3.817871265  | 4.672695636  |
| C | 1.284045785  | 1.301736974  | 3.989908418  |
| H | 0.294350911  | 1.302470848  | 4.490532152  |
| H | 2.065777104  | 1.149530722  | 4.764318554  |
| H | 1.313579088  | 0.430832087  | 3.305609913  |
| C | 1.756633396  | 3.197019069  | -1.580059754 |
| C | 1.740296657  | 4.581791536  | -1.229947211 |
| C | 1.984978173  | 5.558008337  | -2.212199099 |
| H | 1.987857786  | 6.619801747  | -1.916572409 |
| C | 2.212268305  | 5.220413420  | -3.556325383 |
| C | 2.190811189  | 3.859210962  | -3.896058558 |
| H | 2.360447995  | 3.581066113  | -4.949582689 |
| C | 1.981803141  | 2.842001858  | -2.942938243 |
| C | 1.490450074  | 5.066630838  | 0.199452485  |
| H | 1.214911963  | 4.182870452  | 0.816434784  |
| C | 0.298395870  | 6.037015932  | 0.282756155  |
| H | 0.449264995  | 6.928899364  | -0.360603038 |
| H | 0.164404728  | 6.399895791  | 1.322325599  |
| H | -0.643170120 | 5.541422970  | -0.027923141 |

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|----|--------------|--------------|--------------|
| C  | 2.766265592  | 5.671713605  | 0.813861051  |
| H  | 3.077314804  | 6.585344158  | 0.264075959  |
| H  | 3.605533866  | 4.949209169  | 0.786523951  |
| H  | 2.596628146  | 5.954970227  | 1.873581700  |
| C  | 2.466825195  | 6.291537330  | -4.607805599 |
| H  | 2.610241781  | 5.764535317  | -5.577720402 |
| C  | 3.757974200  | 7.076899921  | -4.306394366 |
| H  | 4.629861341  | 6.396703370  | -4.220020875 |
| H  | 3.672533606  | 7.634786677  | -3.349823032 |
| H  | 3.971202537  | 7.815734021  | -5.107423694 |
| C  | 1.256125070  | 7.232613026  | -4.760821735 |
| H  | 1.430240700  | 7.977134617  | -5.565981821 |
| H  | 1.063154982  | 7.792997021  | -3.821591931 |
| H  | 0.334682603  | 6.666290973  | -5.005545490 |
| C  | 2.027482552  | 1.399545144  | -3.448906450 |
| H  | 2.010610667  | 0.729797536  | -2.559307254 |
| C  | 3.304534974  | 1.081612505  | -4.248668187 |
| H  | 3.346943731  | -0.000196517 | -4.491823667 |
| H  | 4.220485667  | 1.340995142  | -3.684197737 |
| H  | 3.336662785  | 1.634688547  | -5.210432660 |
| C  | 0.780321295  | 1.062761222  | -4.279974647 |
| H  | 0.661009039  | 1.765713437  | -5.131114642 |
| H  | -0.136688572 | 1.115378908  | -3.659745906 |
| H  | 0.847495039  | 0.033947068  | -4.689678130 |
| Ni | 0.757629444  | -4.296672422 | 0.426724476  |



**Figure S13.** Optimized structure at the BP86-D3(BJ)/def2-SVP level of theory for **[Int-b]**. Bond distances are in [Å]. Hydrogen atoms omitted for clarity.

**Table S3.** Atomic coordinates of the optimized structure **[Int-b]** at the BP86-D3(BJ)/def2-SVP level of theory.

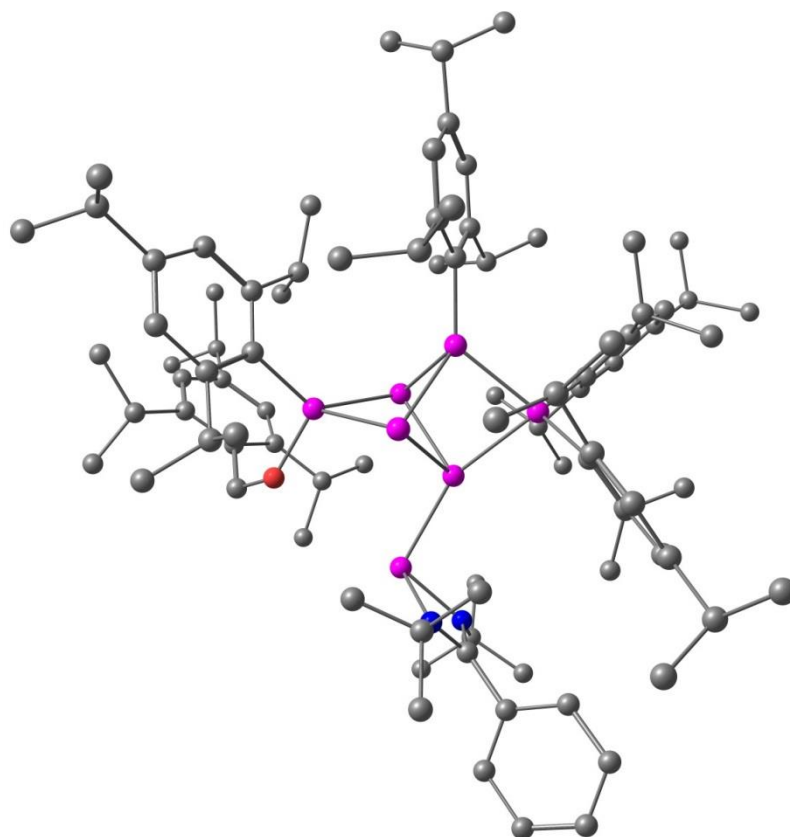
|    |              |              |              |
|----|--------------|--------------|--------------|
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| Si | -0.405382530 | 0.791797276  | -1.484921966 |
| Si | 0.161345197  | -0.884224919 | 0.195456507  |
| Si | -2.368903374 | 0.632919909  | -0.124929889 |
| Si | 0.518955696  | 2.587102543  | -0.202232053 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| Si | -2.064284110 | -1.705186545 | 0.093265745  |
| Si | 2.369395488  | -1.229801619 | -0.449911486 |
| N  | 2.560464480  | -2.875736886 | -1.361110857 |
| N  | 3.317148009  | -2.448858527 | 0.614187568  |
| C  | 3.389528783  | -3.337566625 | -0.395770468 |
| C  | 2.390747768  | -3.272757748 | -2.775384088 |
| C  | 2.176959086  | -4.791573929 | -2.916309737 |
| H  | 3.076380346  | -5.370306627 | -2.634284425 |
| H  | 1.945947488  | -5.024411659 | -3.975606101 |
| H  | 1.319102285  | -5.126702500 | -2.301560388 |
| C  | 3.620772229  | -2.827692990 | -3.593032361 |
| H  | 3.774182650  | -1.735763846 | -3.500242570 |
| H  | 3.479494741  | -3.073397887 | -4.665603274 |
| H  | 4.536863774  | -3.341186922 | -3.238212168 |
| C  | 1.124416996  | -2.544699554 | -3.259855570 |
| H  | 0.240314038  | -2.861350298 | -2.672774551 |
| H  | 0.931991839  | -2.769166880 | -4.327448386 |
| H  | 1.236096219  | -1.447085830 | -3.158889636 |
| C  | 4.296128454  | -4.515942762 | -0.462949885 |
| C  | 3.833115014  | -5.813564435 | -0.161491128 |
| H  | 2.779088483  | -5.963499136 | 0.107846344  |
| C  | 4.717906180  | -6.901355741 | -0.199311495 |
| H  | 4.350611798  | -7.911065091 | 0.041488738  |
| C  | 6.067439655  | -6.703512402 | -0.541862411 |
| H  | 6.759939260  | -7.559243449 | -0.571533517 |
| C  | 6.529827380  | -5.411861382 | -0.846671999 |
| H  | 7.584693541  | -5.250975850 | -1.118130339 |
| C  | 5.651187931  | -4.316805960 | -0.806174747 |
| H  | 6.004376438  | -3.302371565 | -1.043113193 |
| C  | 3.932459603  | -2.380672107 | 1.948381290  |
| C  | 2.948343783  | -1.560772291 | 2.797568638  |
| H  | 3.348863067  | -1.415682838 | 3.819797708  |
| H  | 1.963907848  | -2.065559591 | 2.863081850  |
| H  | 2.793215827  | -0.561323238 | 2.343521773  |
| C  | 4.110193249  | -3.778476723 | 2.568214630  |
| H  | 4.407698206  | -3.669643838 | 3.630975507  |
| H  | 4.893643600  | -4.367894536 | 2.055703225  |
| H  | 3.160153486  | -4.350059501 | 2.530971087  |
| C  | 5.282342858  | -1.637218300 | 1.872213332  |
| H  | 5.144460609  | -0.613735625 | 1.471173332  |
| H  | 5.997278584  | -2.175632877 | 1.220150071  |
| H  | 5.725729214  | -1.548854796 | 2.884842487  |
| O  | 2.197760228  | 2.702278198  | 0.230590673  |
| O  | 2.402533054  | 0.781065979  | -3.933037194 |
| O  | 5.952664338  | -1.037423315 | -1.385230015 |
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| C  | 2.782891071  | 0.760452425  | -2.824245416 |
| C  | 5.037542806  | -0.309863570 | -1.276212670 |
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| C  | -5.834557955 | 2.426895951  | 1.385697416  |
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| C  | -6.383984330 | 3.125435574  | 0.296182030  |
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| H  | -6.158709342 | 3.574140812  | -1.803605581 |
| C  | -4.550573312 | 2.285278218  | -1.114063448 |
| C  | -4.114164168 | 0.973917108  | 2.516619440  |
| H  | -3.383431544 | 0.207029831  | 2.178409444  |
| C  | -3.360363290 | 1.976208404  | 3.409465557  |
| H  | -4.032415369 | 2.798479543  | 3.734287380  |
| H  | -2.502291083 | 2.428570649  | 2.871487471  |
| H  | -2.967852061 | 1.477078051  | 4.319567588  |
| C  | -5.188425962 | 0.232976247  | 3.329258955  |
| H  | -4.704875502 | -0.392134332 | 4.107058784  |
| H  | -5.790792721 | -0.440571455 | 2.691448994  |
| H  | -5.879041971 | 0.934853969  | 3.843140828  |
| C  | -7.637675244 | 3.973522873  | 0.459536057  |
| H  | -7.888506582 | 4.377066231  | -0.546912884 |

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| H | -8.266340355 | 5.827535350  | 1.463461733  |
| C | -8.837571320 | 3.136302880  | 0.941572863  |
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| H | -9.756960962 | 3.756281161  | 0.997394787  |
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| H | -3.269885331 | 1.340827620  | -2.528639770 |
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| C | 5.650083697  | 2.286095850  | 0.824636137  |
| C | 6.637258299  | 2.153842051  | 1.811391488  |
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| C | 6.314651951  | 1.885047410  | 3.155012317  |
| C | 4.955664883  | 1.846212541  | 3.507799078  |
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| C | 3.920535810  | 2.003981288  | 2.565726957  |
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| H | 6.216897990  | 4.754798243  | -1.544266178 |
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| H | 7.498829876  | 2.563378283  | -2.157529401 |
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| C | 8.286266683  | 0.469138501  | 3.873359172  |
| H | 9.044429882  | 0.301374580  | 4.667168745  |
| H | 8.828251239  | 0.615154640  | 2.915187272  |
| H | 7.678891219  | -0.453431119 | 3.773725007  |
| C | 8.248283187  | 2.962101243  | 4.387021537  |
| H | 7.611512138  | 3.832309167  | 4.646637710  |
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| H | 8.998790461  | 2.827538173  | 5.194377222  |
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| H | 1.831713132  | 1.570465633  | 2.314833979  |
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| H | 2.670148323  | 2.035996056  | 5.250073852  |
| H | 2.551571413  | 0.415733862  | 4.492809789  |
| H | 1.105092242  | 1.464727557  | 4.613054391  |
| C | 2.024182661  | 3.570885721  | 3.095762336  |
| H | 0.944917735  | 3.627998414  | 3.347496208  |
| H | 2.184339404  | 4.076179312  | 2.126171241  |
| H | 2.588953197  | 4.124615239  | 3.875618838  |
| C | 0.086080633  | 4.362822044  | -0.662738586 |
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| H | 0.924288701  | 6.499409636  | -3.227307507 |
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| H | -0.034414418 | 3.188030305  | -3.944520298 |

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| C | -1.467693828 | 8.367407654  | -3.461582277 |
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| H | 0.317306628  | 10.299347216 | -2.505639108 |
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| C | -1.572383196 | 4.762157183  | 1.289123161  |
| H | -1.324668801 | 3.690743717  | 1.461457146  |
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| H | -3.445420172 | 4.265700297  | 0.242953412  |
| H | -3.412948496 | 5.915969547  | 0.943350915  |
| C | -1.109597927 | 5.552625599  | 2.527092975  |
| H | -1.570365623 | 5.140884519  | 3.449680975  |
| H | -1.406610882 | 6.620285785  | 2.450934812  |
| H | -0.008774877 | 5.517614862  | 2.642214438  |
| C | -2.101006132 | -2.995923612 | -1.318264095 |
| C | -1.589330664 | -4.286425629 | -0.989257337 |
| C | -1.521161072 | -5.286883411 | -1.977125728 |
| H | -1.129223545 | -6.283466795 | -1.712271959 |
| C | -1.936060324 | -5.056611566 | -3.298670192 |
| C | -2.438142079 | -3.782019898 | -3.610829031 |
| H | -2.766981479 | -3.574778910 | -4.642154351 |
| C | -2.527378148 | -2.752608437 | -2.655218196 |
| C | -1.116201287 | -4.633168106 | 0.420478821  |
| H | -1.124514619 | -3.697396428 | 1.013294256  |
| C | -2.081846317 | -5.610965010 | 1.111418339  |
| H | -1.753585694 | -5.826445880 | 2.149642342  |
| H | -2.135106198 | -6.575192052 | 0.562799182  |
| H | -3.103862976 | -5.185391649 | 1.163813787  |
| C | 0.340078187  | -5.117380297 | 0.442482203  |
| H | 0.997429459  | -4.364765289 | -0.035753570 |
| H | 0.464728147  | -6.079808803 | -0.098024689 |
| H | 0.686245545  | -5.271923279 | 1.486025184  |
| C | -1.846065345 | -6.149887640 | -4.354344418 |
| H | -1.368761802 | -7.029914062 | -3.867832339 |
| C | -3.246557044 | -6.580414132 | -4.832855639 |
| H | -3.876879730 | -6.910964859 | -3.982206233 |
| H | -3.179756741 | -7.415734866 | -5.561415974 |
| H | -3.772553398 | -5.739335737 | -5.332373456 |
| C | -0.952094770 | -5.725923317 | -5.535125814 |
| H | -1.385012349 | -4.858597842 | -6.076774712 |
| H | -0.838332774 | -6.553797363 | -6.265997278 |
| H | 0.057676834  | -5.430897105 | -5.184790086 |
| C | -3.060048496 | -1.403169484 | -3.124741881 |
| H | -3.109449701 | -0.742976611 | -2.230713720 |
| C | -4.479584459 | -1.497206207 | -3.709842444 |
| H | -5.191616530 | -1.927576475 | -2.978912426 |
| H | -4.505142640 | -2.133957819 | -4.618965619 |
| H | -4.848049239 | -0.492323561 | -3.996823744 |
| C | -2.091316489 | -0.745974961 | -4.123561229 |
| H | -2.433569522 | 0.273039813  | -4.400479371 |
| H | -2.009327126 | -1.342186431 | -5.056774140 |
| H | -1.070878922 | -0.657211870 | -3.696174415 |
| C | -3.080224474 | -2.352808585 | 1.578571988  |
| C | -4.454607700 | -2.631570566 | 1.314881716  |
| C | -5.268878986 | -3.161193457 | 2.331241549  |
| H | -6.324518513 | -3.383638326 | 2.104774615  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -4.778594143 | -3.399838690 | 3.626664808  |
| C  | -3.432608912 | -3.092731880 | 3.882424973  |
| H  | -3.039142577 | -3.266442499 | 4.897872197  |
| C  | -2.572391315 | -2.583252471 | 2.889063257  |
| C  | -5.079289346 | -2.399063450 | -0.060541655 |
| H  | -4.321801086 | -1.883127830 | -0.689847903 |
| C  | -6.296376232 | -1.458391389 | -0.014684199 |
| H  | -7.121495382 | -1.879387907 | 0.597717514  |
| H  | -6.693075227 | -1.291897711 | -1.037882440 |
| H  | -6.023734271 | -0.468857106 | 0.402232880  |
| C  | -5.404995889 | -3.740378702 | -0.742968906 |
| H  | -6.155032142 | -4.311234575 | -0.155756388 |
| H  | -4.495788385 | -4.365811536 | -0.843976206 |
| H  | -5.821094628 | -3.581186114 | -1.759317002 |
| C  | -5.680791588 | -3.954733334 | 4.720577811  |
| H  | -5.051975920 | -4.067546992 | 5.632067434  |
| C  | -6.224917036 | -5.348296505 | 4.351950457  |
| H  | -5.399654903 | -6.055556821 | 4.130609214  |
| H  | -6.875007159 | -5.299983522 | 3.452771756  |
| H  | -6.831462804 | -5.770432785 | 5.180678479  |
| C  | -6.821336997 | -2.974213999 | 5.057304534  |
| H  | -7.446719252 | -3.361194564 | 5.889237205  |
| H  | -7.485932609 | -2.818257553 | 4.181258975  |
| H  | -6.424239638 | -1.982395920 | 5.354341614  |
| C  | -1.125976736 | -2.289501222 | 3.281170655  |
| H  | -0.565931445 | -2.070618102 | 2.344026683  |
| C  | -0.433087684 | -3.481609519 | 3.963770110  |
| H  | 0.641147302  | -3.260959365 | 4.133788273  |
| H  | -0.501497122 | -4.399166996 | 3.346304484  |
| H  | -0.881159491 | -3.709243722 | 4.953478047  |
| C  | -1.034736767 | -1.024065474 | 4.149748174  |
| H  | -1.576146514 | -1.154853123 | 5.110909290  |
| H  | -1.479981033 | -0.152685076 | 3.627607209  |
| H  | 0.022200048  | -0.773519933 | 4.376356662  |
| Ni | 3.468600035  | 0.531491870  | -1.203361082 |



**Figure S14.** Optimized structure at the BP86-D3(BJ)/def2-SVP level of theory for **[Int-c]**. Bond distances are in [Å]. Hydrogen atoms omitted for clarity.

**Table S4.** Atomic coordinates of the optimized structure **[Int-c]** at the BP86-D3(BJ)/def2-SVP level of theory.

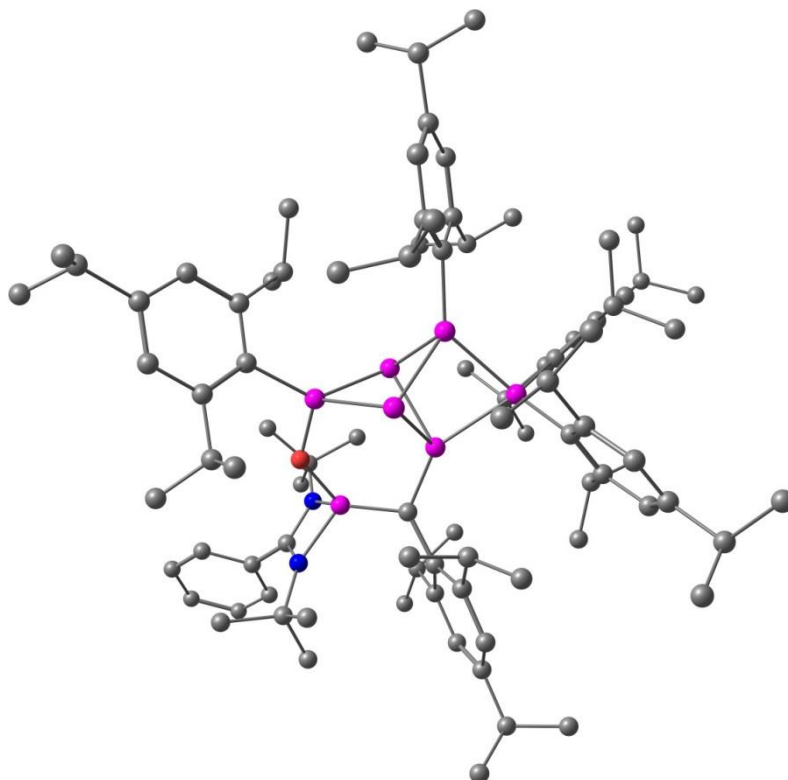
|    |              |              |              |
|----|--------------|--------------|--------------|
| Si | 0.951428118  | 0.001146030  | -1.272718793 |
| Si | 0.174149641  | 0.634396668  | 1.396216412  |
| Si | -1.205511092 | 0.862508110  | -0.618995123 |
| Si | 0.289063589  | -1.550658401 | 0.456933950  |
| Si | 2.137757757  | 1.353673287  | 0.299886646  |
| Si | -1.985345861 | -1.379609597 | -0.151103621 |
| Si | -1.378949544 | 3.274692944  | -0.796021259 |
| N  | -2.650041504 | 3.673398340  | 0.625116507  |
| N  | -3.204521543 | 3.554722272  | -1.457767526 |
| C  | -3.668992453 | 3.886891647  | -0.229928960 |
| C  | -2.600064750 | 3.686293527  | 2.098870214  |
| C  | -3.102817358 | 2.326289180  | 2.617979638  |
| H  | -4.164751026 | 2.165388837  | 2.351036535  |
| H  | -3.012113446 | 2.257954119  | 3.720801652  |
| H  | -2.520343234 | 1.502197592  | 2.163753668  |
| C  | -3.429813666 | 4.834497676  | 2.711268941  |
| H  | -3.164329827 | 5.806894262  | 2.248756198  |
| H  | -3.210316081 | 4.897595094  | 3.796732967  |
| H  | -4.518736569 | 4.678115364  | 2.598280184  |
| C  | -1.120473054 | 3.895960311  | 2.477748440  |
| H  | -0.479972475 | 3.107209821  | 2.029784859  |
| H  | -0.993551272 | 3.849908349  | 3.577843286  |
| H  | -0.751736457 | 4.876310775  | 2.114082811  |
| C  | -5.034800880 | 4.360146656  | 0.126280030  |
| C  | -5.983629991 | 3.424410766  | 0.589036065  |
| H  | -5.706905215 | 2.362727415  | 0.664011099  |
| C  | -7.268706883 | 3.850312254  | 0.959725664  |
| H  | -8.003105843 | 3.113577908  | 1.320945050  |
| C  | -7.613430353 | 5.210512608  | 0.874464891  |
| H  | -8.620892076 | 5.544258037  | 1.168117544  |

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|---|--------------|--------------|--------------|
| C | -6.668212522 | 6.146141383  | 0.416325723  |
| H | -6.933244438 | 7.213091465  | 0.354025977  |
| C | -5.382655349 | 5.723982294  | 0.043644179  |
| H | -4.635110393 | 6.454466930  | -0.301771185 |
| C | -3.643763118 | 3.955019392  | -2.807789056 |
| C | -3.020543272 | 2.912483065  | -3.755789804 |
| H | -3.224304130 | 3.162044151  | -4.816454441 |
| H | -3.423147249 | 1.904481365  | -3.539976309 |
| H | -1.918444453 | 2.873926772  | -3.617090563 |
| C | -5.176045580 | 3.965086296  | -2.977071165 |
| H | -5.419359665 | 4.111830544  | -4.049185552 |
| H | -5.652709951 | 4.784899649  | -2.408010917 |
| H | -5.627662087 | 3.011179216  | -2.648831873 |
| C | -3.079149361 | 5.358298325  | -3.126467131 |
| H | -1.975348385 | 5.368972465  | -3.016380345 |
| H | -3.500230584 | 6.115003746  | -2.433132792 |
| H | -3.333924462 | 5.661758988  | -4.163212766 |
| O | 2.056040423  | 3.151133083  | 0.033641612  |
| C | 2.791781550  | 3.940162270  | -0.695526853 |
| C | 1.326350156  | -3.101935352 | 0.817471146  |
| C | 1.623683994  | -3.987405166 | -0.263255711 |
| C | 2.456249201  | -5.096851357 | -0.035797820 |
| H | 2.685307500  | -5.768838692 | -0.878270739 |
| C | 3.008555968  | -5.368695865 | 1.228345942  |
| C | 2.682488620  | -4.506286007 | 2.287225157  |
| H | 3.097988484  | -4.719556345 | 3.285473152  |
| C | 1.845647444  | -3.386478700 | 2.112129094  |
| C | 1.089201171  | -3.762850230 | -1.676550118 |
| H | 0.273753624  | -3.008988300 | -1.606677459 |
| C | 2.183865436  | -3.184071816 | -2.589522798 |
| H | 3.063256221  | -3.860884046 | -2.632230413 |
| H | 2.530035899  | -2.196299948 | -2.222680116 |
| H | 1.807866559  | -3.050118454 | -3.624647574 |
| C | 0.469379984  | -5.025147586 | -2.297446437 |
| H | -0.045322733 | -4.764317533 | -3.244299378 |
| H | -0.283402340 | -5.480196898 | -1.626380051 |
| H | 1.236955407  | -5.793103956 | -2.531033890 |
| C | 3.946865363  | -6.548880353 | 1.439394990  |
| H | 4.183919652  | -6.583008264 | 2.526377845  |
| C | 5.271336892  | -6.339096288 | 0.678237071  |
| H | 5.758318119  | -5.388211339 | 0.975600421  |
| H | 5.097488746  | -6.295607444 | -0.417873504 |
| H | 5.980796141  | -7.170426973 | 0.875010732  |
| C | 3.283860161  | -7.886910954 | 1.062102274  |
| H | 3.040462054  | -7.924993936 | -0.020766462 |
| H | 2.339361440  | -8.039495774 | 1.623272527  |
| H | 3.959837424  | -8.739919861 | 1.281579374  |
| C | 1.540435025  | -2.502823409 | 3.316821173  |
| H | 0.637475130  | -1.909477528 | 3.055759853  |
| C | 1.219225620  | -3.313514281 | 4.583568857  |
| H | 0.457289492  | -4.094852591 | 4.386388445  |
| H | 0.835857918  | -2.646533947 | 5.383753815  |
| H | 2.121172050  | -3.817123633 | 4.990523021  |
| C | 2.676644620  | -1.498749267 | 3.572321427  |
| H | 3.636987130  | -2.021834770 | 3.765187902  |
| H | 2.452403697  | -0.858658864 | 4.450645068  |
| H | 2.831530683  | -0.834825313 | 2.701433288  |
| C | 3.672752866  | 3.275459880  | -1.676663315 |
| C | 5.078849647  | 3.248718765  | -1.440929927 |
| C | 5.923672939  | 2.756901049  | -2.445614442 |
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| C | 3.137020053  | 2.822802931  | -2.921338931 |
| C | 5.622498110  | 3.776414328  | -0.116914526 |
| H | 4.854295456  | 3.557704900  | 0.653769720  |
| C | 6.906932634  | 3.079476382  | 0.349315453  |

|   |              |              |              |
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| H | 6.780667767  | 1.978380724  | 0.371738805  |
| H | 7.165965903  | 3.409795218  | 1.375828462  |
| H | 7.773132501  | 3.322166376  | -0.302717834 |
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| H | 6.546703107  | 5.585595406  | -0.948759688 |
| H | 6.123826666  | 5.711449208  | 0.794833764  |
| H | 4.827612223  | 5.791070169  | -0.451022381 |
| C | 6.362518573  | 1.797210839  | -4.771759448 |
| H | 5.724224552  | 1.504035695  | -5.635327748 |
| C | 7.317364519  | 2.907341198  | -5.253603295 |
| H | 7.955792263  | 2.549775665  | -6.089160952 |
| H | 7.990873328  | 3.238023156  | -4.434599080 |
| H | 6.754293891  | 3.796968340  | -5.602448008 |
| C | 7.140962013  | 0.545424462  | -4.323485939 |
| H | 6.452511885  | -0.269520289 | -4.022905229 |
| H | 7.794389657  | 0.769518739  | -3.453590981 |
| H | 7.790729550  | 0.167622914  | -5.141090364 |
| C | 1.641072372  | 2.945165417  | -3.199185071 |
| H | 1.100113732  | 2.588670045  | -2.293498230 |
| C | 1.250950510  | 4.423753412  | -3.388170649 |
| H | 1.767255920  | 4.859409446  | -4.269917437 |
| H | 1.527996893  | 5.018044249  | -2.490553339 |
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| C | 1.150142721  | 2.077810907  | -4.362172003 |
| H | 0.042336830  | 2.108441840  | -4.413762710 |
| H | 1.450714425  | 1.017359327  | -4.232607954 |
| H | 1.537071214  | 2.430679330  | -5.341562301 |
| C | 3.727477234  | 1.041827927  | 1.266020589  |
| C | 3.963356468  | 1.837758776  | 2.427639022  |
| C | 5.108468063  | 1.589462799  | 3.205920412  |
| H | 5.283221451  | 2.204771848  | 4.103483085  |
| C | 6.014147696  | 0.562493196  | 2.890484109  |
| C | 5.735223554  | -0.246798919 | 1.775188197  |
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| C | 4.605015459  | -0.041214841 | 0.964079608  |
| C | 2.956141464  | 2.871201895  | 2.941087853  |
| H | 2.160743999  | 2.998309847  | 2.181329756  |
| C | 2.260174653  | 2.346122759  | 4.211743336  |
| H | 1.743618689  | 1.385863731  | 4.004888331  |
| H | 1.500436485  | 3.072506673  | 4.569117953  |
| H | 2.984747743  | 2.172555336  | 5.035090525  |
| C | 3.570985805  | 4.265454240  | 3.149049585  |
| H | 4.397119715  | 4.249836346  | 3.891094145  |
| H | 2.801838066  | 4.974481357  | 3.519103569  |
| H | 3.969591864  | 4.671673260  | 2.197919304  |
| C | 7.231116089  | 0.290350694  | 3.764022601  |
| H | 7.798197828  | -0.535139833 | 3.278672436  |
| C | 6.805970166  | -0.195938151 | 5.164121221  |
| H | 6.150655106  | -1.088286737 | 5.095646236  |
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| H | 7.691101931  | -0.460421411 | 5.780325860  |
| C | 8.164240315  | 1.512583325  | 3.849165913  |
| H | 9.066682156  | 1.280785180  | 4.452978263  |
| H | 7.654748830  | 2.375563456  | 4.327869061  |
| H | 8.495267778  | 1.835651576  | 2.841599021  |
| C | 4.317442841  | -0.995819924 | -0.191709110 |
| H | 3.210057298  | -1.119790289 | -0.227180103 |
| C | 4.899750565  | -2.401683036 | 0.003182591  |
| H | 4.524080381  | -3.077775395 | -0.789037442 |
| H | 4.598770908  | -2.835977529 | 0.977552842  |
| H | 6.008758026  | -2.406415119 | -0.059815488 |
| C | 4.757604422  | -0.383297234 | -1.531008732 |
| H | 4.510971692  | -1.059090372 | -2.376153324 |
| H | 5.852147807  | -0.204476612 | -1.537669269 |
| H | 4.261959352  | 0.587927470  | -1.720504232 |
| C | -3.451966015 | -1.100190357 | 1.058786360  |
| C | -4.669716040 | -0.678731328 | 0.442837998  |
| C | -5.765639815 | -0.293515850 | 1.237468820  |

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| C | -4.513151632 | -0.740322194 | 3.236524733  |
| H | -4.445664441 | -0.769004818 | 4.336276243  |
| C | -3.394719842 | -1.148919141 | 2.482790578  |
| C | -4.844628071 | -0.675302593 | -1.073902101 |
| H | -3.839870438 | -0.801138731 | -1.524184579 |
| C | -5.693200160 | -1.873149865 | -1.535946453 |
| H | -5.766868300 | -1.899664211 | -2.643273660 |
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| C | -5.369966948 | 0.658266351  | -1.614643731 |
| H | -4.679626027 | 1.482342740  | -1.346366487 |
| H | -6.381861430 | 0.907169839  | -1.231797845 |
| H | -5.441798897 | 0.622677778  | -2.721667078 |
| C | -6.885215729 | 0.182133207  | 3.476590865  |
| H | -7.726488172 | 0.362592978  | 2.769514438  |
| C | -7.347212074 | -0.881639116 | 4.489619824  |
| H | -7.585665587 | -1.840240300 | 3.985316065  |
| H | -8.251781790 | -0.542010157 | 5.036408499  |
| H | -6.560135371 | -1.086483439 | 5.245739483  |
| C | -6.566180481 | 1.520923810  | 4.172201323  |
| H | -5.712518939 | 1.410151872  | 4.873770513  |
| H | -7.438714599 | 1.885179270  | 4.754664800  |
| H | -6.292614946 | 2.304732843  | 3.437012524  |
| C | -2.183573870 | -1.659602672 | 3.263284808  |
| H | -1.406492426 | -1.941107511 | 2.518617968  |
| C | -2.531206418 | -2.919257169 | 4.079151087  |
| H | -2.953038210 | -3.715382829 | 3.437575500  |
| H | -3.280266932 | -2.694077962 | 4.867170831  |
| H | -1.627529837 | -3.320283797 | 4.579678341  |
| C | -1.575952566 | -0.584974709 | 4.180894975  |
| H | -0.705463304 | -0.988743374 | 4.737079769  |
| H | -2.314294208 | -0.222897620 | 4.926664340  |
| H | -1.225095974 | 0.293754525  | 3.601216770  |
| C | -2.407428552 | -2.754972605 | -1.416838032 |
| C | -2.702184725 | -4.041467989 | -0.875087404 |
| C | -3.041608638 | -5.103926769 | -1.731236814 |
| H | -3.276404705 | -6.086890517 | -1.290868536 |
| C | -3.077273052 | -4.950551253 | -3.127312322 |
| C | -2.758848543 | -3.687975030 | -3.650964924 |
| H | -2.771019683 | -3.557541268 | -4.745901683 |
| C | -2.430547941 | -2.589481581 | -2.830904349 |
| C | -2.684652590 | -4.315267430 | 0.627642826  |
| H | -2.333612067 | -3.390713314 | 1.133696178  |
| C | -1.683258250 | -5.417755570 | 1.015716052  |
| H | -1.951112882 | -6.396496144 | 0.564592558  |
| H | -1.663461395 | -5.551644081 | 2.117529676  |
| H | -0.656262203 | -5.156682794 | 0.691392576  |
| C | -4.107670481 | -4.603667628 | 1.140347227  |
| H | -4.551414561 | -5.475682381 | 0.615828600  |
| H | -4.770039717 | -3.729465104 | 0.978162988  |
| H | -4.106923616 | -4.832923368 | 2.226089007  |
| C | -3.429745439 | -6.116611281 | -4.040721081 |
| H | -3.404066869 | -5.729178445 | -5.083915270 |
| C | -4.854544757 | -6.636547296 | -3.769434824 |
| H | -5.603322738 | -5.824070668 | -3.866800343 |
| H | -4.941260927 | -7.050790316 | -2.742576078 |
| H | -5.125062061 | -7.445562788 | -4.480275268 |
| C | -2.387060202 | -7.246860488 | -3.935626633 |
| H | -2.621541065 | -8.071939843 | -4.640816750 |
| H | -2.364745110 | -7.676016146 | -2.911484439 |
| H | -1.367278397 | -6.875464527 | -4.162928857 |
| C | -2.091474904 | -1.269321867 | -3.519199514 |
| H | -2.026270651 | -0.483850626 | -2.733001404 |
| C | -3.166166643 | -0.829145733 | -4.528083506 |
| H | -2.913988310 | 0.163150106  | -4.954217414 |
| H | -4.164965163 | -0.756709284 | -4.052679953 |

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| H | -3.250641742 | -1.538681601 | -5.377505925 |
| C | -0.707682679 | -1.343115994 | -4.185684659 |
| H | -0.674052110 | -2.142803668 | -4.955883846 |
| H | 0.081047813  | -1.560683781 | -3.437515153 |
| H | -0.450823463 | -0.380778410 | -4.672458972 |



**Figure S15.** Optimized structure at the BP86-D3(BJ)/def2-SVP level of theory for **2**. Bond distances are in [Å]. Hydrogen atoms omitted for clarity.

**Table S5.** Atomic coordinates of the optimized structure **2** at the BP86-D3(BJ)/def2-SVP level of theory.

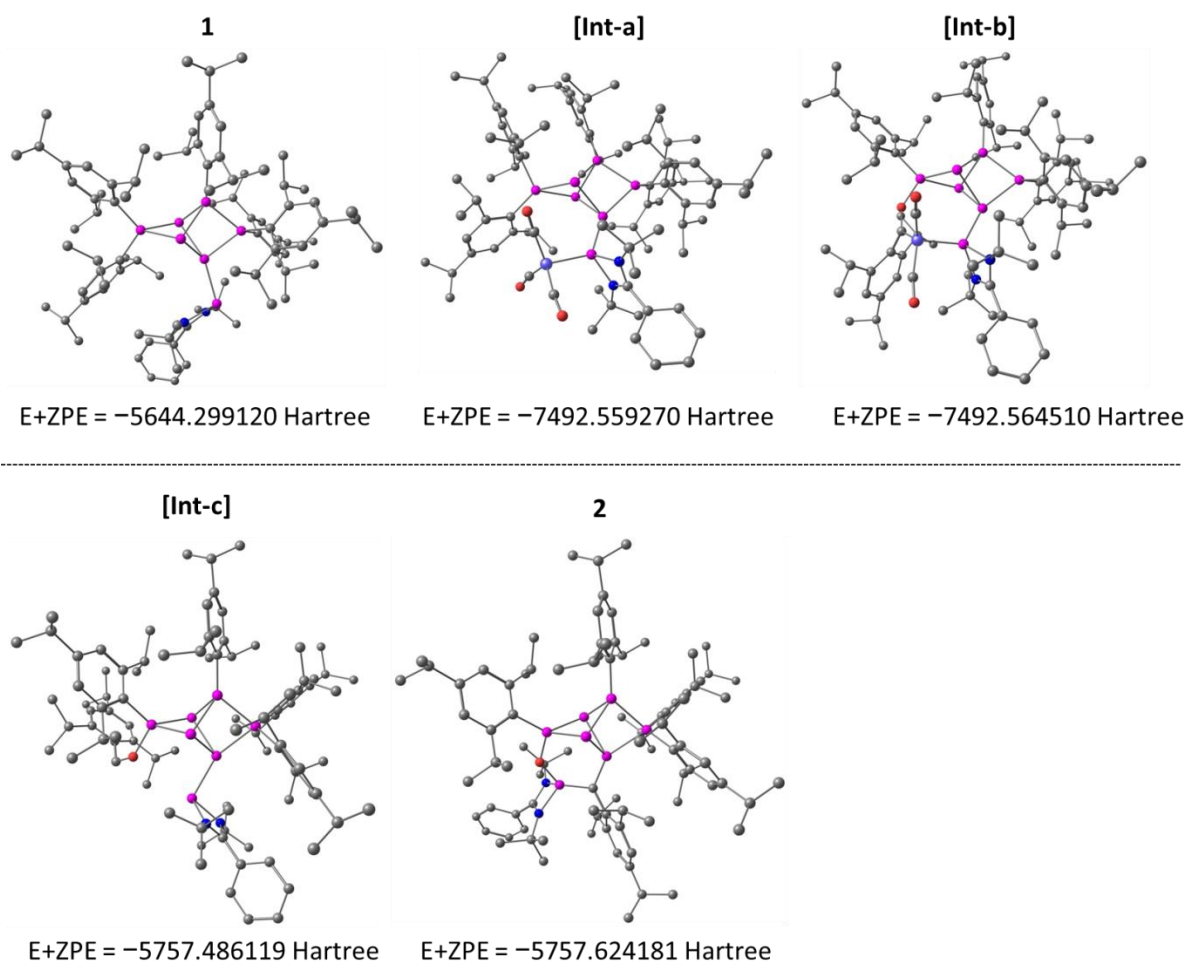
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| Si | 1.131875771  | 2.354461370  | -0.245938360 |
| Si | -0.196145250 | 0.911266358  | -1.577540235 |
| Si | 0.329461783  | -0.734942488 | 0.114545351  |
| Si | -1.964683924 | -1.410728717 | 0.099931412  |
| Si | -2.114939792 | 0.958765700  | -0.219253802 |
| Si | 3.140670196  | 0.111823616  | 0.480115129  |
| N  | 4.061722269  | 0.516315373  | 2.093590935  |
| N  | 4.973114847  | 0.023666896  | 0.185738421  |
| O  | 2.678617033  | 1.676843172  | 0.068535785  |
| C  | 2.095040733  | -1.273118666 | 0.138497604  |
| C  | 1.313665825  | 4.159311100  | -0.760924266 |
| C  | 2.239149181  | 4.506121005  | -1.789913993 |
| C  | 2.273453334  | 5.829037578  | -2.266488420 |
| H  | 2.987039139  | 6.090113048  | -3.064489844 |
| C  | 1.404778310  | 6.819648339  | -1.773410960 |
| C  | 0.471512137  | 6.452835000  | -0.787878242 |
| H  | -0.227881298 | 7.217705203  | -0.414940899 |
| C  | 0.398795272  | 5.143347522  | -0.279020569 |
| C  | 3.109103481  | 3.449852910  | -2.474829170 |
| H  | 3.154001313  | 2.566019804  | -1.808674724 |
| C  | 4.563151479  | 3.900095752  | -2.691994226 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 5.164987797  | 3.067782263  | -3.113349473 |
| H | 5.031742304  | 4.216445447  | -1.737235948 |
| H | 4.640551436  | 4.748145083  | -3.404879225 |
| C | 2.447265026  | 3.002454808  | -3.794449091 |
| H | 3.026868400  | 2.183548829  | -4.271038600 |
| H | 2.380769158  | 3.845514241  | -4.514761009 |
| H | 1.419133708  | 2.627049715  | -3.610371922 |
| C | 1.443742387  | 8.241354511  | -2.318884493 |
| C | 1.017563013  | 8.281340943  | -3.800019259 |
| H | 0.012848522  | 7.832896033  | -3.939748003 |
| H | 1.729229528  | 7.712930598  | -4.435688740 |
| H | 0.988019105  | 9.325070622  | -4.178183116 |
| C | -0.635891689 | 4.807215689  | 0.795340176  |
| H | -0.916853962 | 3.739098760  | 0.654176911  |
| C | -0.002742747 | 4.925601800  | 2.194666145  |
| H | -0.729795245 | 4.646178045  | 2.985288166  |
| H | 0.335957669  | 5.966235141  | 2.384327240  |
| H | 0.877487054  | 4.257263216  | 2.291841905  |
| C | -1.945400271 | 5.602988827  | 0.698460506  |
| H | -2.372413269 | 5.556027945  | -0.322668281 |
| H | -1.813908017 | 6.670949056  | 0.974721219  |
| H | -2.699269471 | 5.170820473  | 1.387463895  |
| C | -3.546605651 | 2.202225024  | -0.142295579 |
| C | -3.903357881 | 2.994704594  | -1.272832492 |
| C | -4.884721566 | 3.994513435  | -1.128031917 |
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| C | -5.534840640 | 4.233966685  | 0.093437777  |
| C | -5.189344005 | 3.428311945  | 1.193129572  |
| H | -5.690495588 | 3.594018419  | 2.160463313  |
| C | -4.213166717 | 2.420243669  | 1.101343836  |
| C | -3.214013263 | 2.827307902  | -2.623879240 |
| H | -2.794677907 | 1.798236829  | -2.639901166 |
| C | -2.021781387 | 3.793430684  | -2.754883815 |
| H | -1.471421723 | 3.621381921  | -3.703870827 |
| H | -1.299265679 | 3.660223335  | -1.925848817 |
| H | -2.361544212 | 4.850787890  | -2.739809391 |
| C | -4.168466290 | 2.957950858  | -3.821731179 |
| H | -3.654978982 | 2.653969745  | -4.757700436 |
| H | -4.513956093 | 4.003150285  | -3.968347319 |
| H | -5.067883078 | 2.320752176  | -3.697770794 |
| C | -6.562074489 | 5.349933674  | 0.227105397  |
| H | -6.701348384 | 5.784121754  | -0.788274104 |
| C | -6.037364713 | 6.471055631  | 1.146497367  |
| H | -6.758412477 | 7.313981436  | 1.200735066  |
| H | -5.067126180 | 6.865938225  | 0.782092663  |
| H | -5.878265456 | 6.095824934  | 2.179741796  |
| C | -7.928771044 | 4.822411548  | 0.702625131  |
| H | -8.308611404 | 4.027136535  | 0.029221518  |
| H | -8.680268726 | 5.639226038  | 0.733771736  |
| H | -7.861473510 | 4.392435660  | 1.724361674  |
| C | -3.860251621 | 1.636786105  | 2.364111288  |
| H | -3.246140788 | 0.762012847  | 2.054910354  |
| C | -3.002614868 | 2.504436336  | 3.302751250  |
| H | -3.544657130 | 3.429721483  | 3.591961073  |
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| H | -2.745498629 | 1.952501962  | 4.230456631  |
| C | -5.084237005 | 1.078658288  | 3.108521423  |
| H | -5.739505444 | 0.494675964  | 2.435617485  |
| H | -5.691924472 | 1.885040112  | 3.571516823  |
| H | -4.751276034 | 0.398142475  | 3.918256813  |
| C | -3.103237245 | -1.880270241 | 1.572577230  |
| C | -4.498743512 | -1.992717496 | 1.281462617  |
| C | -5.401342291 | -2.359587552 | 2.294239798  |
| H | -6.470076230 | -2.456283915 | 2.042060750  |
| C | -4.983634901 | -2.593450818 | 3.615141275  |
| C | -3.618627024 | -2.442799087 | 3.898126022  |
| H | -3.278930918 | -2.608027052 | 4.934175281  |
| C | -2.671911283 | -2.099108714 | 2.910345427  |

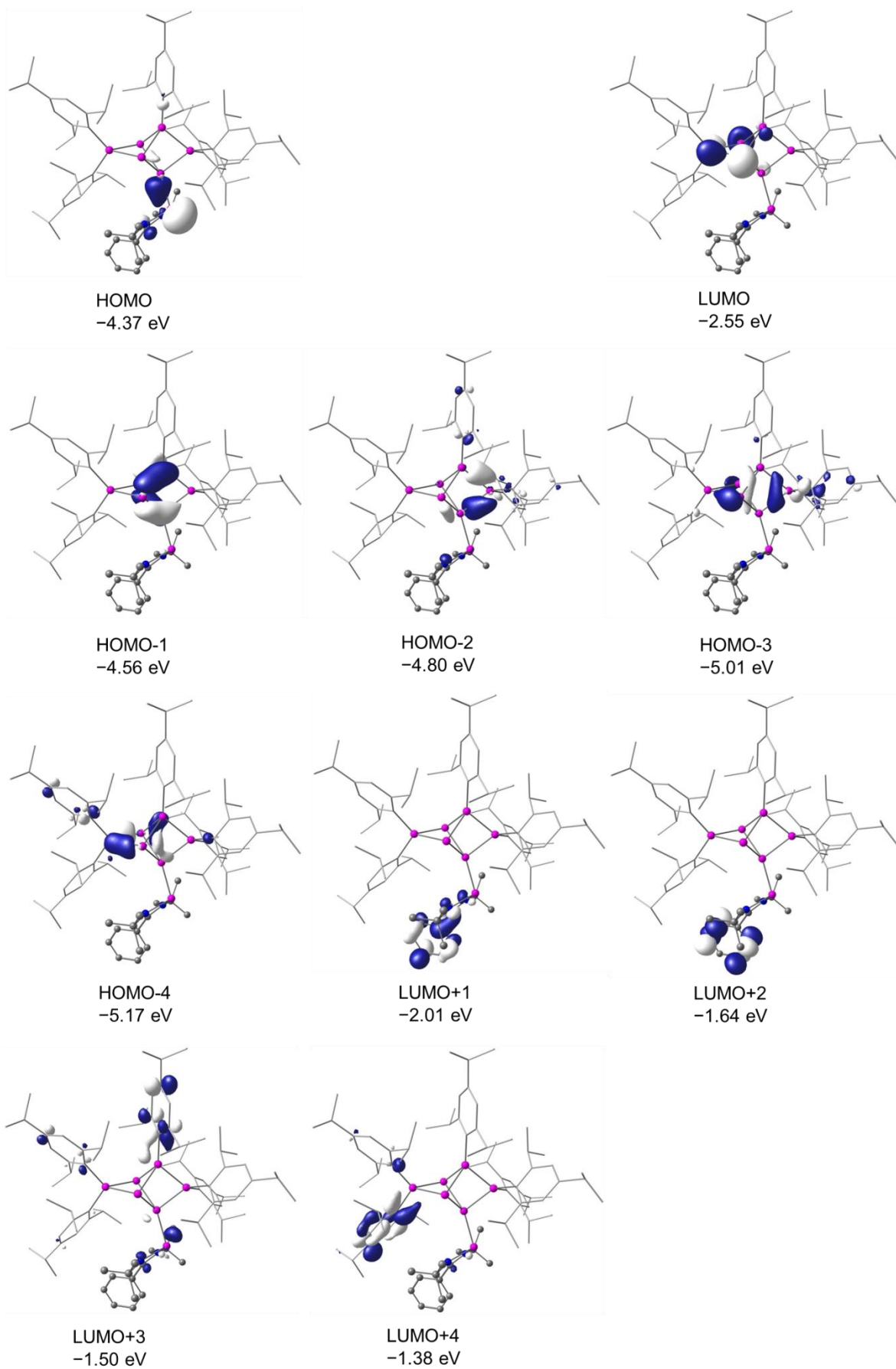
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| H | -6.408835870 | -3.494062790 | -0.138726082 |
| H | -4.757582477 | -3.827266034 | -0.764274381 |
| H | -5.929131667 | -2.919544131 | -1.769189512 |
| C | -6.146424281 | -0.653458749 | -0.140900736 |
| H | -6.522267924 | -0.505206665 | -1.174774551 |
| H | -5.737071758 | 0.316180524  | 0.205276603  |
| H | -7.019450270 | -0.910312919 | 0.495318877  |
| C | -5.976441965 | -2.986751076 | 4.700510520  |
| C | -7.032005159 | -1.887609464 | 4.929330705  |
| H | -7.646846838 | -1.726774194 | 4.018551634  |
| H | -6.555836812 | -0.919143220 | 5.184207266  |
| H | -7.721463105 | -2.163388044 | 5.755007057  |
| C | -6.635478993 | -4.344982431 | 4.390968865  |
| H | -7.238875203 | -4.293210878 | 3.459929746  |
| H | -7.313613076 | -4.656043312 | 5.213568618  |
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| H | -0.593192154 | -1.803212339 | 2.452397262  |
| C | -0.702409221 | -3.206322783 | 4.091161421  |
| H | -1.302058894 | -3.428305193 | 4.998191821  |
| H | 0.346406253  | -3.061786505 | 4.416218336  |
| H | -0.736756243 | -4.100674885 | 3.438123876  |
| C | -1.053463117 | -0.699182579 | 4.232909320  |
| H | -1.308746630 | 0.215876237  | 3.659893224  |
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| H | -1.713770626 | -0.737428394 | 5.125102554  |
| C | -2.224477017 | -2.721182738 | -1.277566184 |
| C | -1.911635910 | -4.064577302 | -0.915609104 |
| C | -2.141397501 | -5.109194454 | -1.831950871 |
| H | -1.905065095 | -6.145840704 | -1.538821600 |
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| C | -2.940256954 | -3.543143662 | -3.469837876 |
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| H | -0.122953075 | -6.161235158 | -0.129178564 |
| H | 0.379961549  | -5.372718511 | 1.396865083  |
| H | 0.742407692  | -4.592293604 | -0.173332972 |
| C | -2.407266724 | -5.207336667 | 1.280787545  |
| H | -3.344035166 | -4.625146880 | 1.387765023  |
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| H | -2.653565713 | -6.173713581 | 0.791990071  |
| C | -2.876100717 | -6.016193336 | -4.096633537 |
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| H | -2.057782273 | -4.993015933 | -5.863093680 |
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| H | -5.240452415 | -1.257781300 | -2.956300497 |
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| C | 2.293564509  | -3.155689061 | -1.565464331 |

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| C | 1.894620486  | -1.265926893 | -3.226647115 |
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| H | 2.223611997  | -0.497696582 | -2.500418832 |
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| C | 4.440396201  | -6.364242685 | -1.648739801 |
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| C | 3.376287609  | -7.452936608 | -1.889381700 |
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| C | 3.786221443  | -2.884599891 | 1.989024035  |
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| C | 4.707410706  | 0.800234367  | 4.497843630  |
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| H | 5.671987031  | 1.321333334  | 4.352005555  |
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| H | 3.168623312  | 3.113074110  | 4.136712966  |
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| H | 1.572915469  | 0.676381760  | 2.971144655  |
| H | 1.952002297  | 0.937074158  | 4.703090556  |
| H | 2.422530482  | -0.602623056 | 3.890459455  |
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| C | 7.089062584  | 2.018450581  | 1.954568177  |
| H | 6.511534251  | 2.799854684  | 1.437955956  |
| C | 8.334131136  | 2.313375609  | 2.530854943  |
| H | 8.734808697  | 3.336982128  | 2.470076709  |
| C | 9.066571822  | 1.305159841  | 3.182684414  |
| H | 10.042864899 | 1.538900501  | 3.634831823  |
| C | 8.551497782  | -0.000848803 | 3.256943979  |
| H | 9.121431998  | -0.792014096 | 3.767992753  |
| C | 7.306127546  | -0.302397864 | 2.684315451  |
| H | 6.888042382  | -1.316802777 | 2.752630461  |
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| C | 6.879210043  | 0.789225496  | -1.216543289 |
| H | 7.452992913  | 0.548965377  | -2.134676500 |
| H | 7.606237352  | 0.946250605  | -0.397185105 |
| H | 6.329632271  | 1.736517347  | -1.389965591 |
| C | 6.647613504  | -1.652979733 | -0.549938894 |
| H | 5.926416723  | -2.466608899 | -0.333101465 |

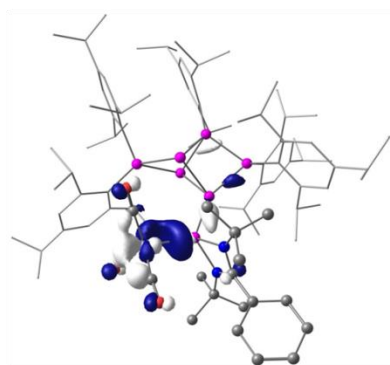
|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 7.308432589  | -1.506597918 | 0.327095929  |
| H | 7.282563707  | -1.970300473 | -1.402174583 |
| C | 5.007740459  | -0.613880810 | -2.136020997 |
| H | 4.303707204  | -1.444547700 | -1.937690735 |
| H | 5.632865222  | -0.890647205 | -3.007881727 |
| H | 4.424183639  | 0.291354370  | -2.400833971 |
| C | 2.822705806  | 8.895979312  | -2.111493393 |
| H | 3.611522385  | 8.360995983  | -2.681653483 |
| H | 3.116241045  | 8.884597980  | -1.041901367 |
| H | 2.817360269  | 9.950754244  | -2.458454579 |
| H | 0.698853727  | 8.830132305  | -1.738204777 |
| H | -5.396113173 | -3.099804742 | 5.643715419  |
| H | -2.655447547 | -6.959196031 | -3.548003388 |



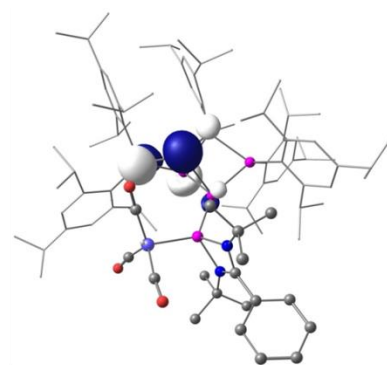
**Figure S16::** Free Gibbs energies in Hartree of **1**, **[Int-a]**, **[Int-b]**, **[Int-c]** and **2**.



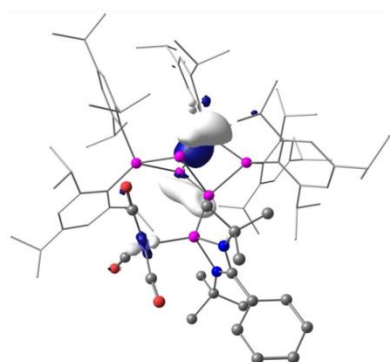
**Figure S17:** Selected molecular orbitals of **1** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value 0.051840).



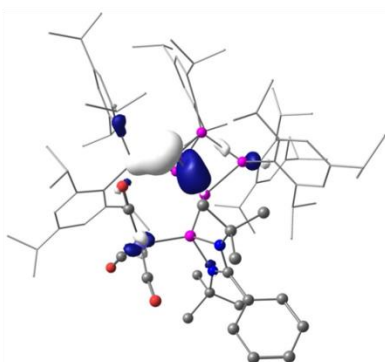
HOMO  
-4.47 eV



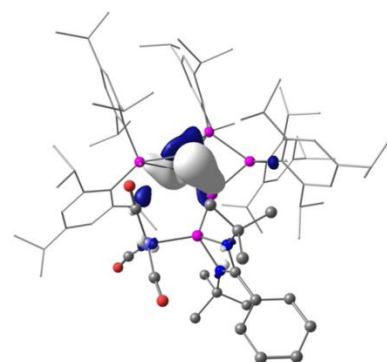
LUMO  
-2.61 eV



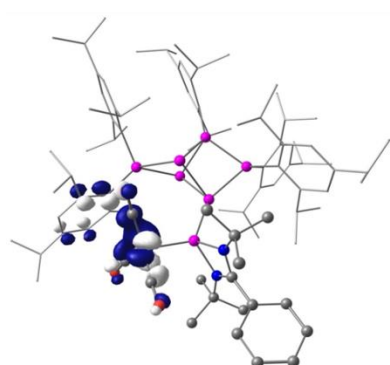
HOMO-1  
-4.81 eV



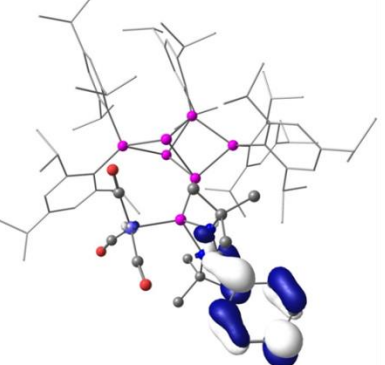
HOMO-2  
-4.97 eV



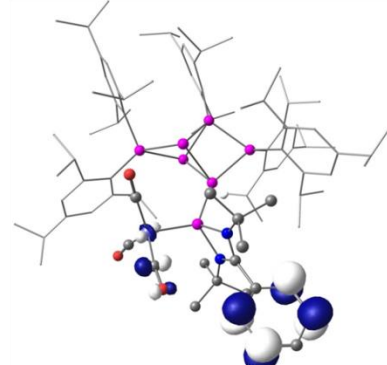
HOMO-3  
-5.04 eV



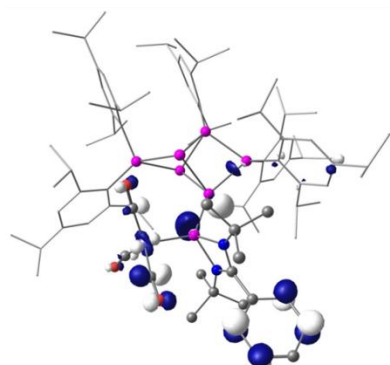
HOMO-4  
-5.17 eV



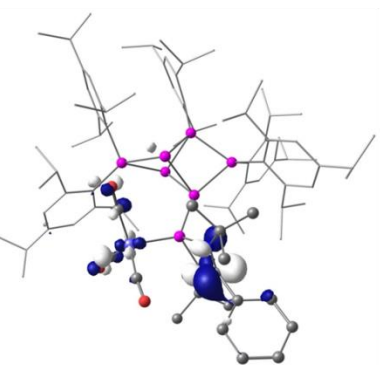
LUMO+1  
-1.95 eV



LUMO+2  
-1.68 eV

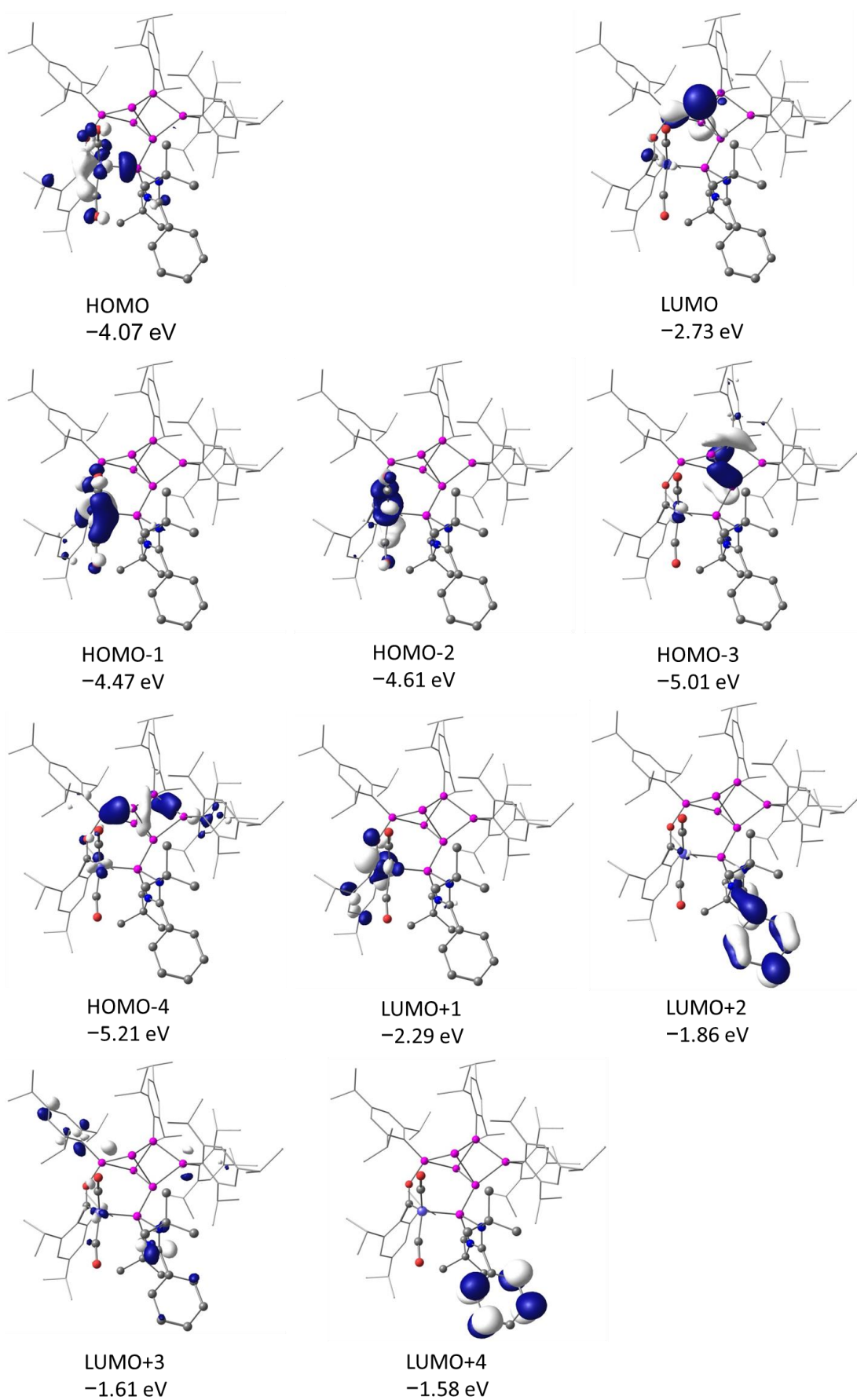


LUMO+3  
-1.63 eV

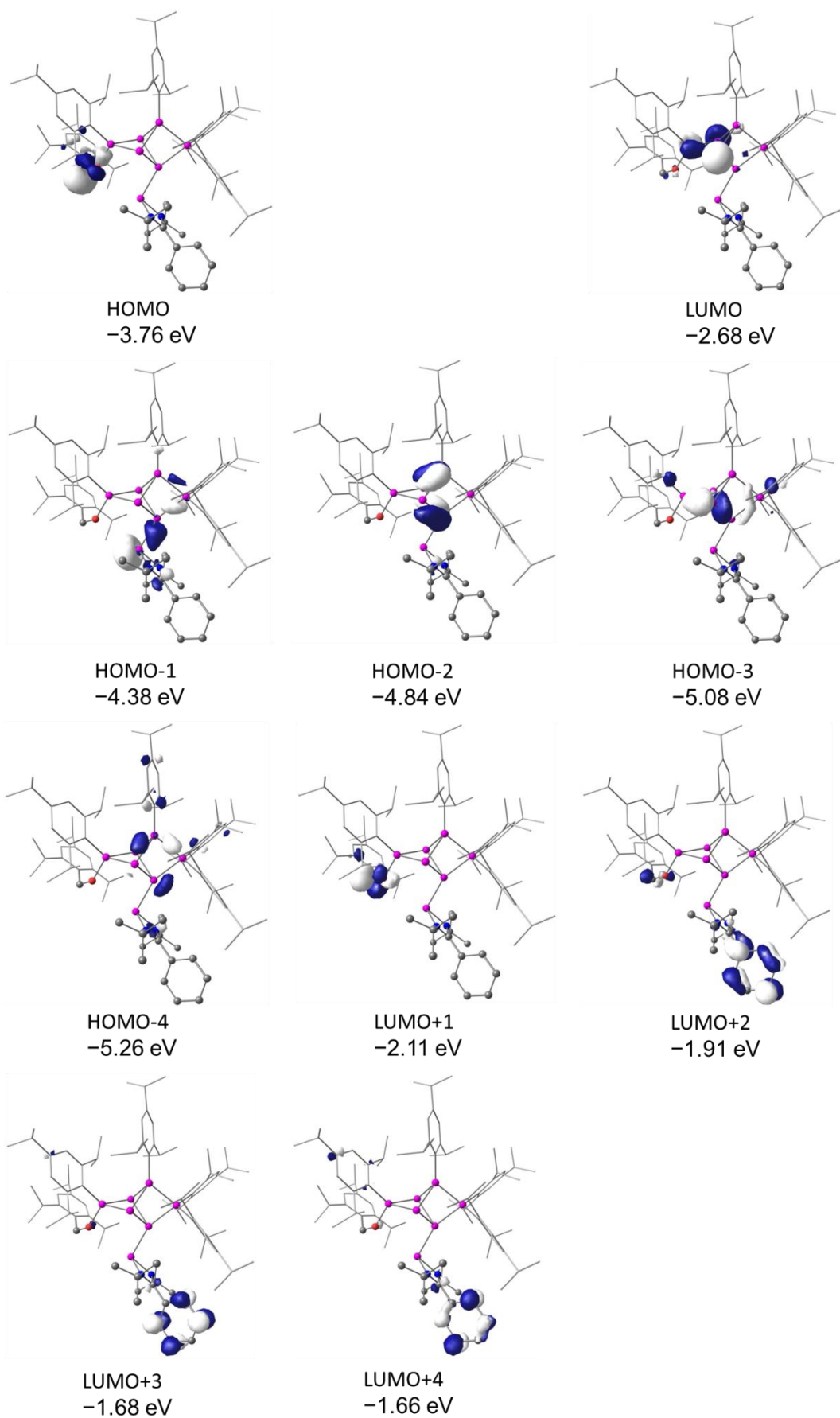


LUMO+4  
-1.56 eV

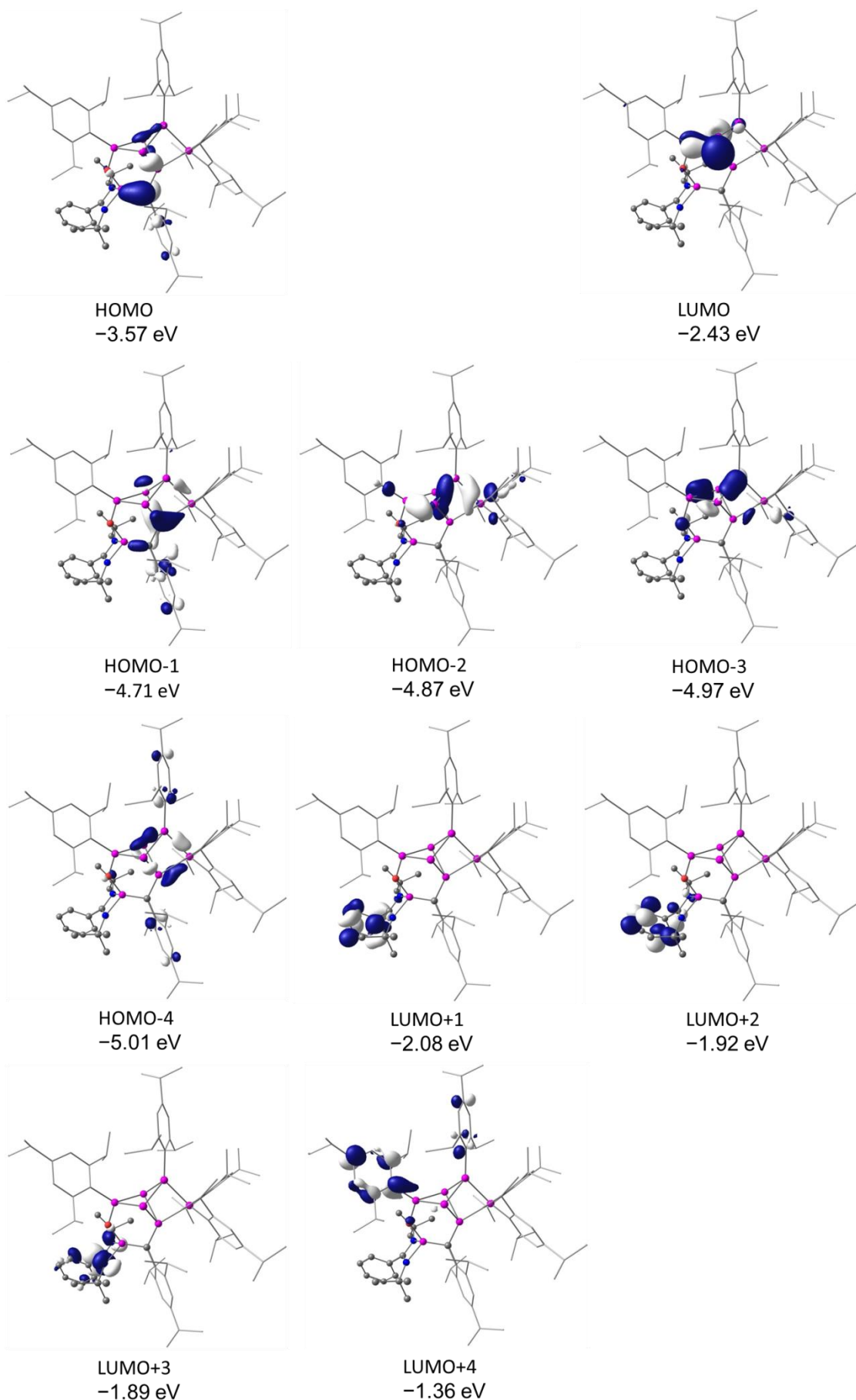
**Figure S18:** Selected molecular orbitals of **[Int-a]** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value 0.051840).



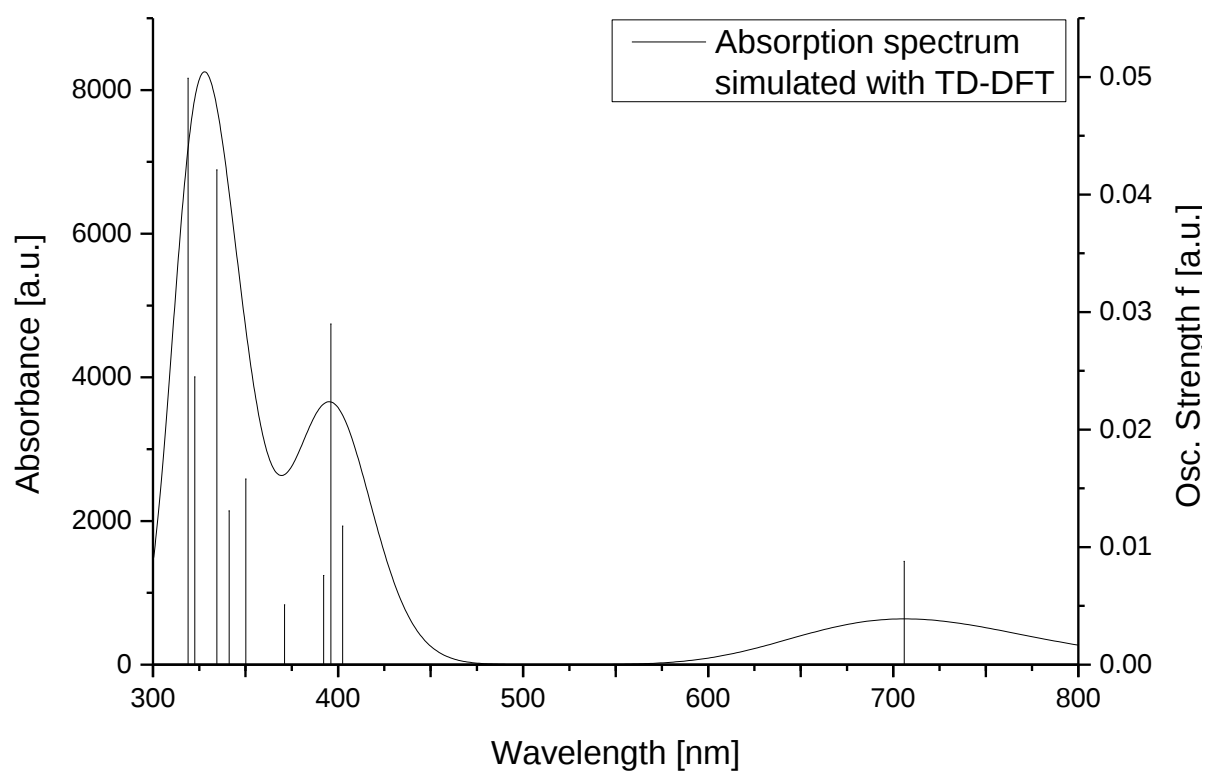
**Figure S19:** Selected molecular orbitals of **[Int-b]** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value 0.051840).



**Figure S20:** Selected molecular orbitals of **[Int-c]** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value 0.051840).



**Figure S21:** Selected molecular orbitals of **2** at the BP86-D3(BJ)/def2-SVP level of theory (isocontour value 0.051840).

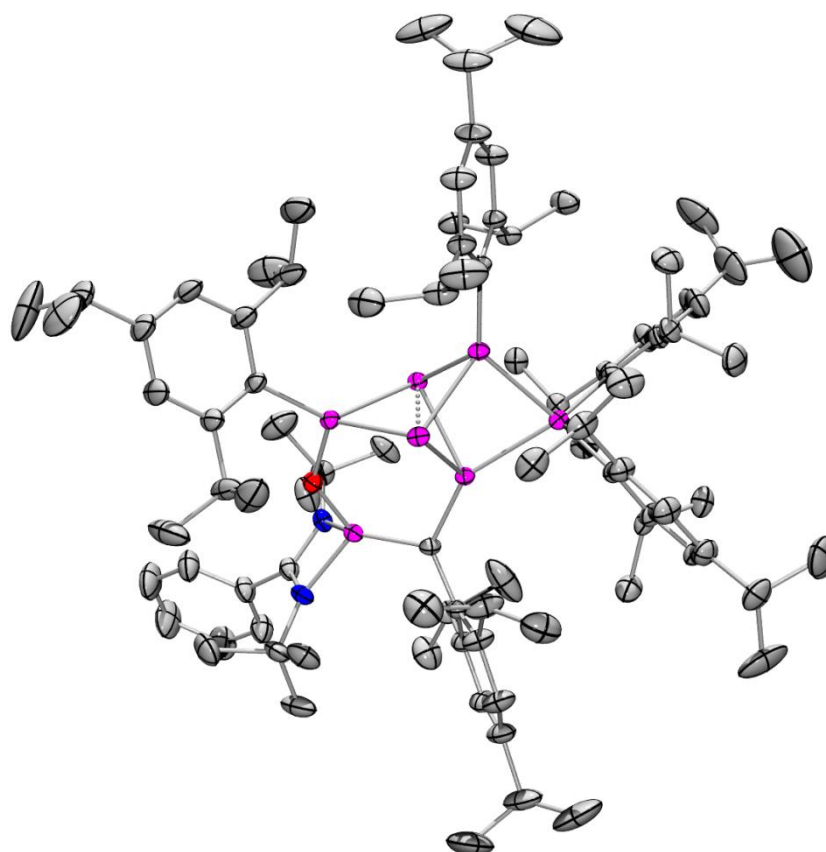


**Figure S22.** Calculated transitions (vertical bars) and simulated UV-Vis absorption spectrum of siliconoid 2.

**Table S6:** Selected electronic transitions and optical parameters of the TD-DFT calculations of siliconoid **2**.

| Transition No. | $\lambda_{\text{calc. max}}$ [nm] | Transitions                | $f$    | Contribution [%] |
|----------------|-----------------------------------|----------------------------|--------|------------------|
| <b>1</b>       | 705                               | HOMO $\rightarrow$ LUMO    | 0.0088 | 91               |
|                |                                   | HOMO-1 $\rightarrow$ LUMO  |        | 4                |
| <b>2</b>       | 402                               | HOMO-3 $\rightarrow$ LUMO  | 0.0118 | 57               |
|                |                                   | HOMO-2 $\rightarrow$ LUMO  |        | 19               |
|                |                                   | HOMO-1 $\rightarrow$ LUMO  |        | 11               |
|                |                                   | HOMO $\rightarrow$ LUMO+3  |        | 3                |
|                |                                   |                            |        |                  |
| <b>3</b>       | 396                               | HOMO-4 $\rightarrow$ LUMO  | 0.029  | 22               |
|                |                                   | HOMO-3 $\rightarrow$ LUMO  |        | 13               |
|                |                                   | HOMO-1 $\rightarrow$ LUMO  |        | 51               |
|                |                                   | HOMO-2 $\rightarrow$ LUMO  |        | 3                |
| <b>4</b>       | 392                               | HOMO $\rightarrow$ LUMO+3  | 0.0076 | 78               |
|                |                                   | HOMO-4 $\rightarrow$ LUMO  |        | 3                |
|                |                                   | HOMO $\rightarrow$ LUMO+7  |        | 2                |
| <b>5</b>       | 371                               | HOMO-3 $\rightarrow$ LUMO  | 0.0051 | 17               |
|                |                                   | HOMO-2 $\rightarrow$ LUMO  |        | 59               |
|                |                                   | HOMO-15 $\rightarrow$ LUMO |        | 2                |
|                |                                   | HOMO-5 $\rightarrow$ LUMO  |        | 9                |
|                |                                   | HOMO-4 $\rightarrow$ LUMO  |        | 3                |
|                |                                   | HOMO-1 $\rightarrow$ LUMO  |        | 2                |

#### 4. Details on X-ray Diffraction Studies



**Figure S23.** Molecular structure of siliconoid **2** in the solid state. Hydrogen atoms omitted for clarity. Thermal ellipsoids represent 50% probability.

**Table S7.** Crystal data and structure refinement for **2** (CCDC: 2016837).

|                        |                                                                                                    |                  |
|------------------------|----------------------------------------------------------------------------------------------------|------------------|
| Identification code    | sh3999b                                                                                            |                  |
| Empirical formula      | C <sub>91</sub> H <sub>138</sub> N <sub>2</sub> O Si <sub>7</sub> , C <sub>7</sub> H <sub>14</sub> |                  |
| Formula weight         | 1558.83                                                                                            |                  |
| Temperature            | 133(2) K                                                                                           |                  |
| Wavelength             | 0.71073 Å                                                                                          |                  |
| Crystal system         | Monoclinic                                                                                         |                  |
| Space group            | P <sub>2</sub> <sub>1</sub> /c                                                                     |                  |
| Unit cell dimensions   | a = 13.0001(3) Å                                                                                   | α = 90°.         |
|                        | b = 28.8076(8) Å                                                                                   | β = 93.4546(9)°. |
|                        | c = 26.4244(6) Å                                                                                   | γ = 90°.         |
| Volume                 | 9878.0(4) Å <sup>3</sup>                                                                           |                  |
| Z                      | 4                                                                                                  |                  |
| Density (calculated)   | 1.048 Mg/m <sup>3</sup>                                                                            |                  |
| Absorption coefficient | 0.140 mm <sup>-1</sup>                                                                             |                  |
| F(000)                 | 3416                                                                                               |                  |
| Crystal size           | 0.343 x 0.083 x 0.028 mm <sup>3</sup>                                                              |                  |
|                        | S39                                                                                                |                  |

|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| Theta range for data collection   | 1.925 to 29.594°.                           |
| Index ranges                      | -18<=h<=18, -40<=k<=33, -36<=l<=35          |
| Reflections collected             | 159316                                      |
| Independent reflections           | 27713 [R(int) = 0.0382]                     |
| Completeness to theta = 25.242°   | 99.9 %                                      |
| Absorption correction             | Semi-empirical from equivalents             |
| Max. and min. transmission        | 0.7459 and 0.7132                           |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 27713 / 311 / 1110                          |
| Goodness-of-fit on F <sup>2</sup> | 1.039                                       |
| Final R indices [I>2sigma(I)]     | R1 = 0.0492, wR2 = 0.1436                   |
| R indices (all data)              | R1 = 0.0613, wR2 = 0.1541                   |
| Extinction coefficient            | n/a                                         |
| Largest diff. peak and hole       | 1.489 and -0.380 e.Å <sup>-3</sup>          |

PLAT097 B LEVEL ALERT: The largest peaks of residual electron density are located near the co-crystallized hexane molecule indicating some unresolved disorder.

## 5. References

- [1] N. E. Poitiers, L. Giarrana, K. I. Leszczyńska, V. Huch, M. Zimmer, D. Scheschkewitz, *Angew. Chem. Int. Ed.* 2020, **59**, 8532-8536.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Najajima, Y. Honda, O. Kitao, H. Nikai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratman, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian09, Revision C.01*. Gaussian, Inc.: Wallingford CT, 2009.
- [3] TURBOMOLE V7.0 2015 a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007; TURBOMOLE GmbH, since 2007, available from <http://www.turbomole.com>; Karlsruhe.
- [4] A. D. Becke, *Phys. Rev. A* 1988, **38** (6), 3098-3100.
- [5] J. P. Perdew, *Phys. Rev. B* 1986, **33** (12), 8822-8824.
- [6] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132** (15), 154104.
- [7] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* 2011, **32** (7), 1456-1465.
- [8] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7** (18), 3297-3305.
- [9] T. Yanai, D. Tew, N. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51-57 .
- [10] <https://www.chemcraftprog.com/>
- [11] N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, *J. Comput. Chem.* 2008, **29**, 839-845.
- [12] <http://www.OriginLab.com>.

## Author Contributions

N. P. Conceptualization: Equal, Data curation: Lead; Formal analysis: Lead; Investigation: Lead; Methodology: Lead; Validation: Lead; Visualization: Lead; Writing original draft: Lead; Writing review & editing: Lead. V.H. Data curation (X-ray): Lead; Formal analysis (X-ray): Lead, X-ray structures: Lead. M. Z. CP/MAS NMR studies: Lead. D. S. Conceptualization: Lead, Funding acquisition: Lead; Methodology: Supporting; Project administration: Lead; Resources: Lead; Supervision: Lead; Writing original draft: Supporting; Writing review & edition: Supporting.