

## Selective Functionalization of a Bis-silylene

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## Experimental

All syntheses and manipulations were carried out under strict exclusion of air and moisture in an inert atmosphere of dry nitrogen or argon gas using glove-box or Schlenk-line techniques. The bis-silylene (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi:)<sub>2</sub> (**1**) (Ar = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) was prepared<sup>1</sup> as reported earlier. Me<sub>3</sub>NO (Aldrich) was dried over 4 Å molecular sieves in anhydrous acetonitrile. N<sub>2</sub>O was passed through anhydrous P<sub>2</sub>O<sub>5</sub>, Sicapent (P<sub>2</sub>O<sub>5</sub> with Indicator), and activated 3 Å molecular sieves. C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> were dried over K-benzophenone ketyl and distilled under dry argon prior to use. All other solvents were dried and purified by a MBRAUN solvent purification system (MB SPS 800). <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded using a Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometer. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen.

**Synthesis of (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)(2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi:) (2) and (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)<sub>2</sub> (3):** A 100 mL yellow toluene solution of (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi:)<sub>2</sub> (**1**) (0.64 g, 0.61 mmol) was bubbled with dry N<sub>2</sub>O for 5-10 minutes at -78 °C. After 1 h, the yellow solution was slowly warmed to room temperature with constant stirring. The yellow color of the solution turned to colorless after 1 h. After overnight stirring, all volatiles were removed under vacuum to obtain a white solid. The solid was washed two times with *n*-pentane (20 mL) and the residue was dissolved in benzene (10 mL), filtered and stored in a freezer at 4 °C for one week to obtain colorless crystals of (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)(2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi:) (**2**) in 62% (0.41g) yield. Elemental analysis (%) calcd for C<sub>72</sub>H<sub>100</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>: C, 79.94; H, 9.32; N, 2.59; found: C, 79.87; H, 9.30; N, 2.55. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.03 (d, 24H, *J* = 6.4 Hz, CHMe<sub>2</sub>); 1.26 (m, 24H, CHMe<sub>2</sub>); 1.34 (d, 24H, *J* = 6.8 Hz, CHMe<sub>2</sub>); 2.82 (q, 6H, CHMe<sub>2</sub>); 2.89 (q, 4H, CHMe<sub>2</sub>); 2.97 (br, 2H, OH); 3.02 (q, 2H, CHMe<sub>2</sub>); 6.83 (t, 2H, *J* = 6.8 Hz, *p*-C<sub>6</sub>H<sub>3</sub>); 7.05 (d, 4H, *J* = 6.8 Hz, *m*-C<sub>6</sub>H<sub>3</sub>); 7.16 (s, 6H, *m*-C<sub>6</sub>H<sub>2</sub> + C<sub>6</sub>H<sub>6</sub>); 7.25 (s, 2H, *m*-C<sub>6</sub>H<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 23.53, 24.31, 24.76, 26.11 (CHMe<sub>2</sub>); 30.91, 31.44, 34.65, 34.79 (CHMe<sub>2</sub>); 117.71, 120.53, 121.57, 125.30, 129.65, 131.97, 133.80, 134.05, 137.17, 139.85, 142.46, 147.81, 148.02, 148.58 (C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>2</sub>) ppm. <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 111.16, -62.42 ppm. IR (Nujol, cm<sup>-1</sup>): 3580, 3328 (ν Si-OH).

**Isolation of (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)<sub>2</sub> (3):** The *n*-pentane soluble part of the reaction of **1** with N<sub>2</sub>O was stored in a freezer at 4 °C for two days and filtered cold (to remove the residual amount of compound **2** as colorless crystals). The filtrate was concentrated to 10 mL and stored in a freezer at -35 °C for one week. Colorless crystals of **3** (0.05 g, 8%) were obtained. Elemental analysis (%) calcd for C<sub>72</sub>H<sub>102</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: C, 77.50; H, 9.21; N, 2.51; found: C, 77.49; H, 9.19; N, 2.46. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.00 (d, 24H, *J* = 6.4 Hz, CHMe<sub>2</sub>); 1.29 (m, 48 H, CHMe<sub>2</sub>); 2.97 (m, 16H, CHMe<sub>2</sub>, OH); 6.86 (t, 2H, *J* = 6.8 Hz, *p*-C<sub>6</sub>H<sub>3</sub>); 7.02-7.26 (m, 12H, *m*-C<sub>6</sub>H<sub>3</sub>, *m*-C<sub>6</sub>H<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 24.33, 24.75 (CHMe<sub>2</sub>); 30.91, 34.79 (CHMe<sub>2</sub>); 117.70, 121.45, 125.31, 133.81, 142.56, 147.91, 148.23 (C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>2</sub>) ppm. <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ -68.26 ppm. IR (Nujol, cm<sup>-1</sup>): 3600, 3335 (ν Si-OH).

**Reaction of 1 with Me<sub>3</sub>NO to (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)<sub>2</sub> (3):** To a mixture of **1** (0.52 g, 0.49 mmol) and Me<sub>3</sub>NO (0.16 g, 2.13 mmol) was added 40 mL pre-cooled (−78 °C) toluene. The reaction mixture was allowed to warm to room temperature and continued to stir overnight. Removal of the volatiles under vacuum gave white solid, which was dissolved in 20 mL *n*-pentane and stored at −35 °C for one week to afford colorless crystals of **3** (0.35 g, 63 %).

**Reaction of 2 with Me<sub>3</sub>NO to (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)<sub>2</sub> (3):** To a Schlenk flask containing a mixture of **2** (0.20 g, 0.18 mmol) and Me<sub>3</sub>NO (0.05 g, 0.66 mmol) was added 15 mL toluene and the resulting solution was stirred overnight at room temperature. Removal of the volatiles under vacuum afforded white solid, which was extracted in 10 mL *n*-pentane and stored at −35 °C for one week to give colorless crystals of **3** (0.09 g, 47%).

**Reaction of 1 with N<sub>2</sub>O in toluene-d<sub>8</sub>:** To a 10 mL toluene-d<sub>8</sub> solution of **1** (0.52 g, 0.49 mmol) was bubbled dry N<sub>2</sub>O for 5 minutes at −78 °C. The resulting reaction mixture was stirred overnight at room temperature. The solution was concentrated to 5 mL, filtered and stored at −35 °C for 10 days to yield colorless crystals (0.29 g, 56 %). <sup>1</sup>H NMR (500 MHz, toluene-d<sub>8</sub>, 25 °C): δ 1.00 (d, 12H, CHMe<sub>2</sub>); 1.02 (d, 12H, CHMe<sub>2</sub>); 1.26 (m, 24H, CHMe<sub>2</sub>); 1.35 (d, 12H, *J* = 6.8 Hz, CHMe<sub>2</sub>); 1.37 (d, 12H, *J* = 6.8 Hz, CHMe<sub>2</sub>); 2.75-3.00 (m, 14H, CHMe<sub>2</sub>, OH); 6.84 (t, 2H, *J* = 6.8 Hz, *p*-C<sub>6</sub>H<sub>3</sub>); 7.00-7.04 (m, 4H, C<sub>6</sub>H<sub>3</sub>) 7.12 (s, 4H, C<sub>6</sub>H<sub>2</sub>); 7.13 (s, 4H, C<sub>6</sub>H<sub>2</sub>) ppm <sup>13</sup>C NMR (125 MHz, toluene-d<sub>8</sub>, 25 °C): δ 23.53, 23.85, 24.21, 24.32, 25.68, 26.09 (CHMe<sub>2</sub>); 31.45, 31.66, 34.50, 34.70 (CHMe<sub>2</sub>); 120.46, 121.32, 121.51, 122.28, 123.52, 131.93, 132.38, 134.01, 135.37, 136.35, 137.41, 142.42, 146.16, 147.00, 147.22, 147.73, 148.78 (C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>2</sub>) ppm. <sup>29</sup>Si NMR (99 MHz, toluene-d<sub>8</sub>, 25 °C): δ 110.96, −63.03 ppm. IR (Nujol, cm<sup>−1</sup>): 3580, 3330 (ν Si–OH). <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra (measured in C<sub>6</sub>D<sub>6</sub>) of this compound exhibit resonances as those observed for the compound **2** prepared in toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), which indicates the formation of similar product (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(OH)<sub>2</sub>)(2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi:) (**2**).

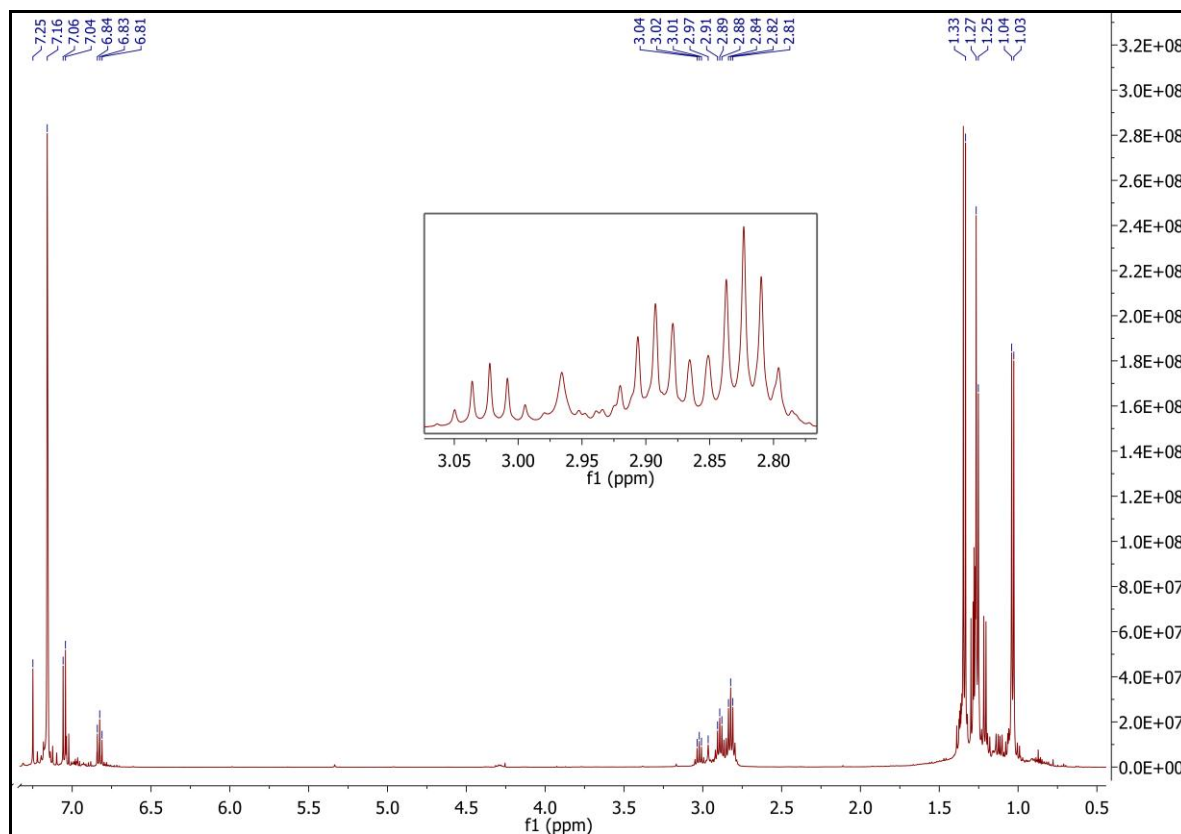


Chart 1:  $^1\text{H}$  NMR spectrum of the compound **2** in  $\text{C}_6\text{D}_6$ .

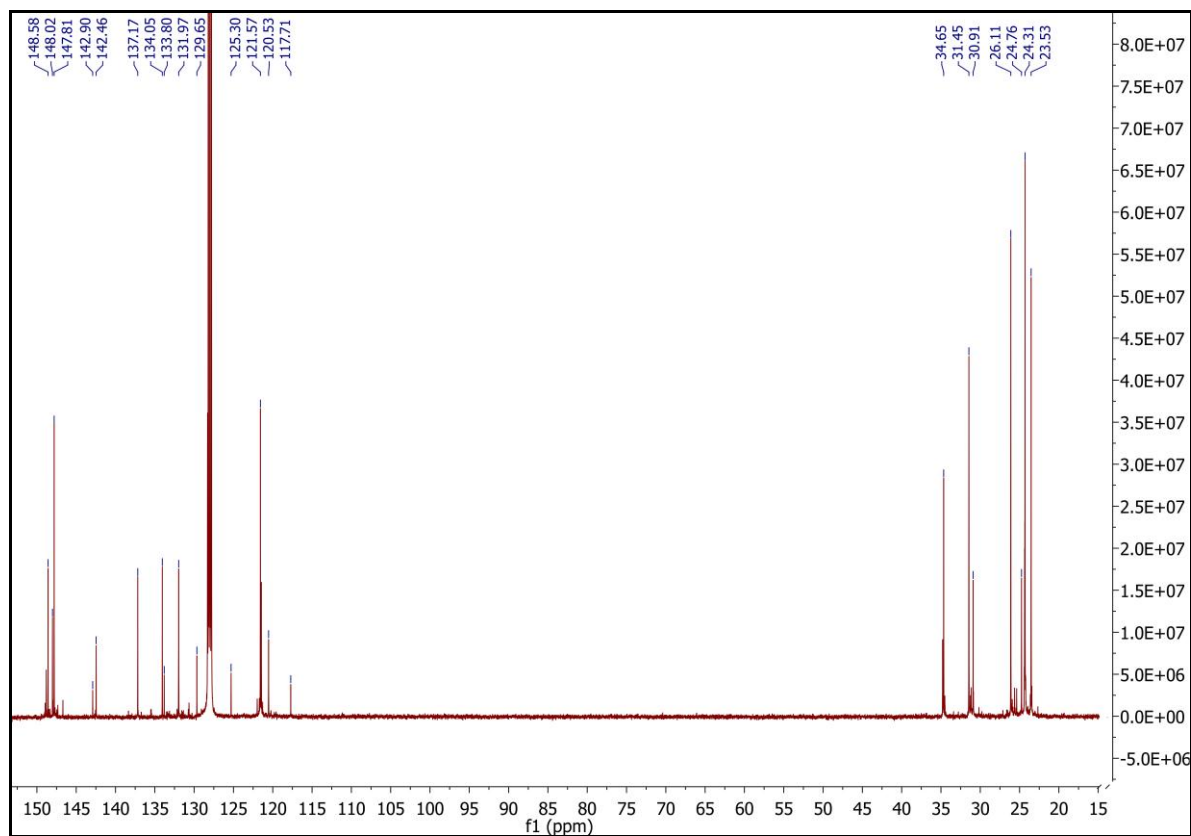
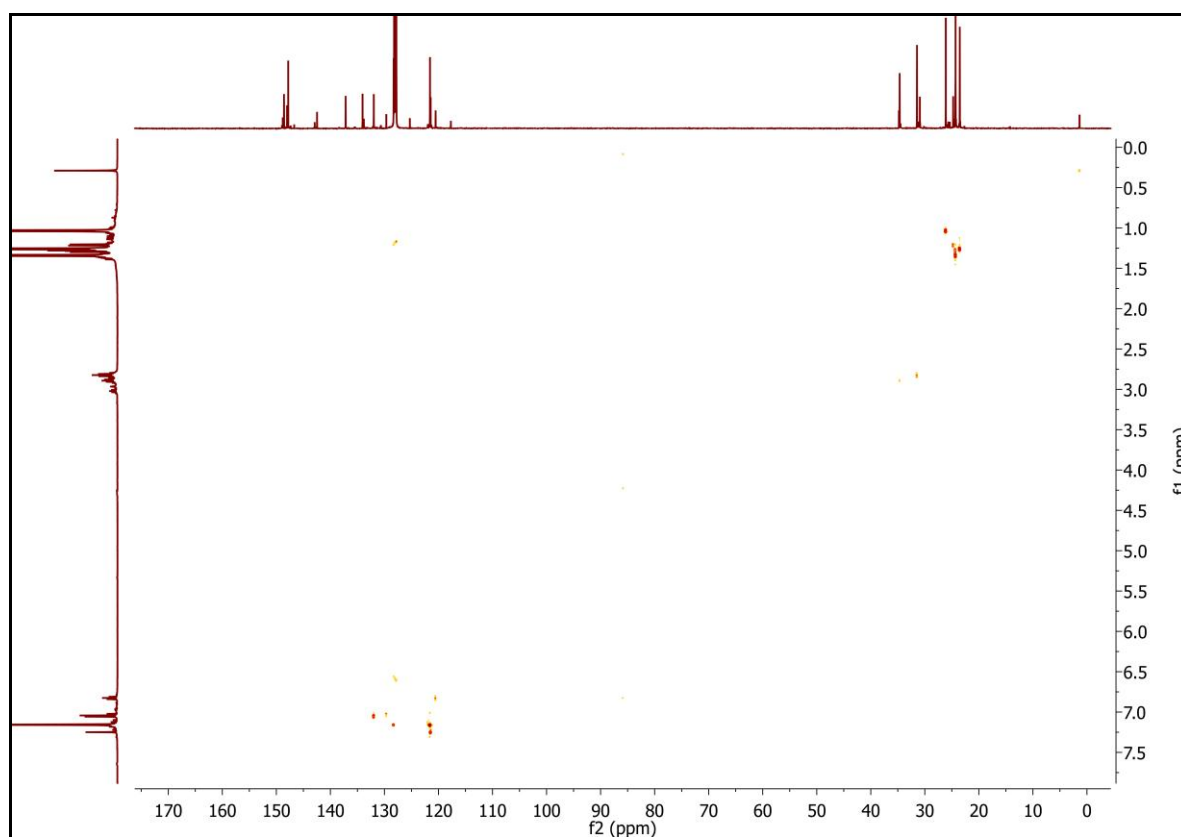
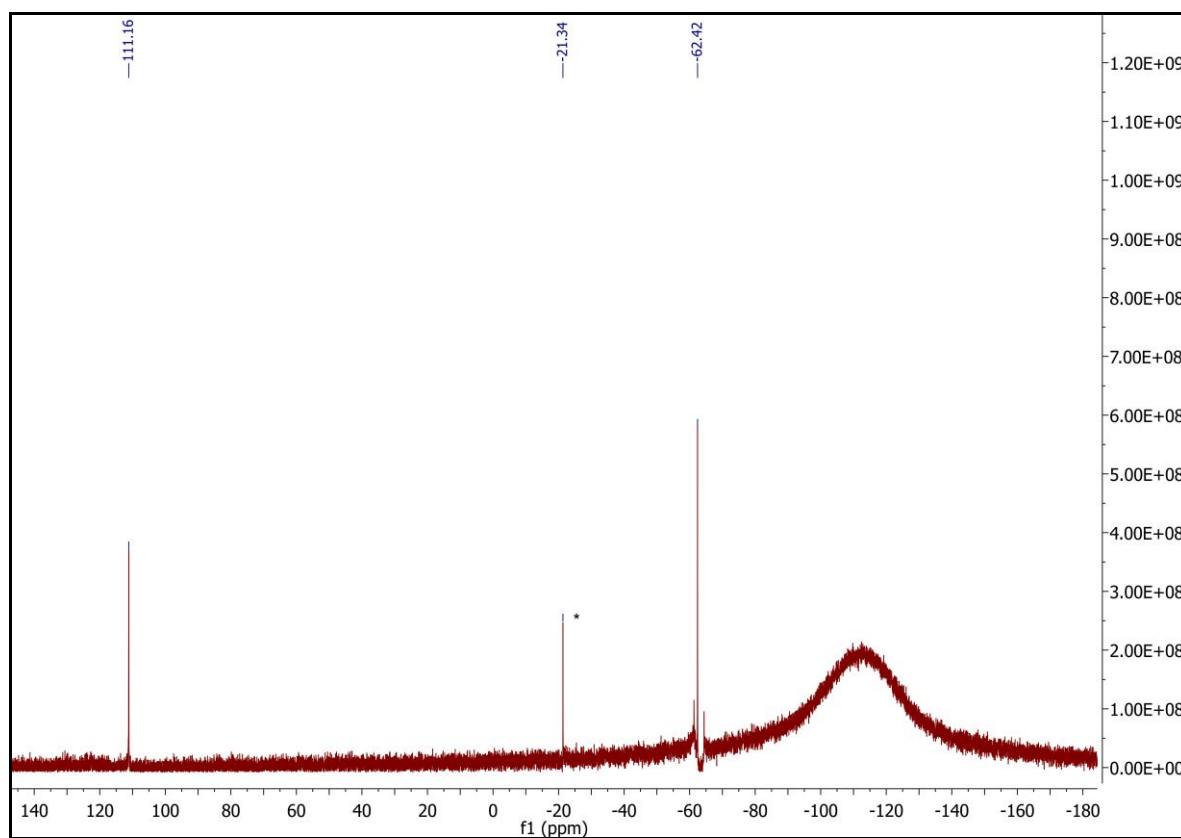


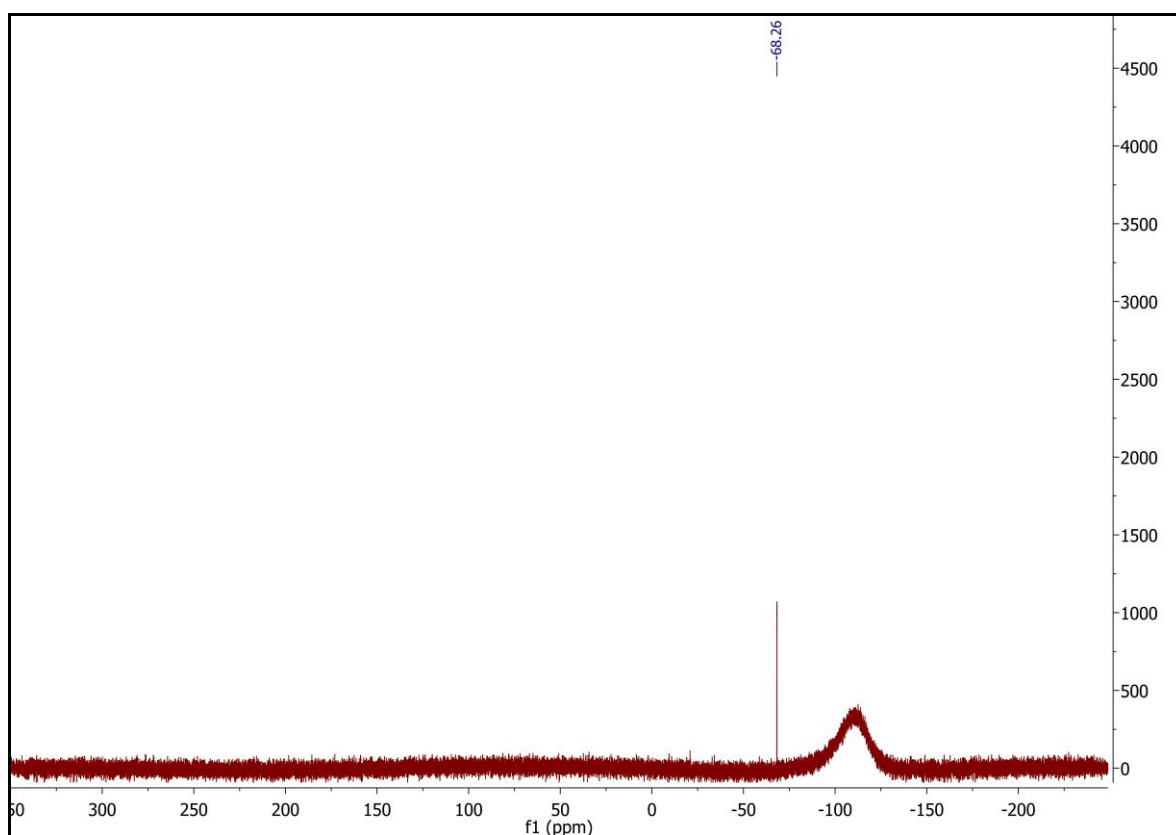
Chart 2:  $^{13}\text{C}$  NMR spectrum of the compound **2** in  $\text{C}_6\text{D}_6$ .



**Chart 3:**  $^1\text{H}$ - $^{13}\text{C}$  COSY NMR spectrum of the compound **2** in  $\text{C}_6\text{D}_6$ .



**Chart 4:**  $^{29}\text{Si}$  NMR spectrum of the compound **2** in  $\text{C}_6\text{D}_6$  (\* Silicon grease).

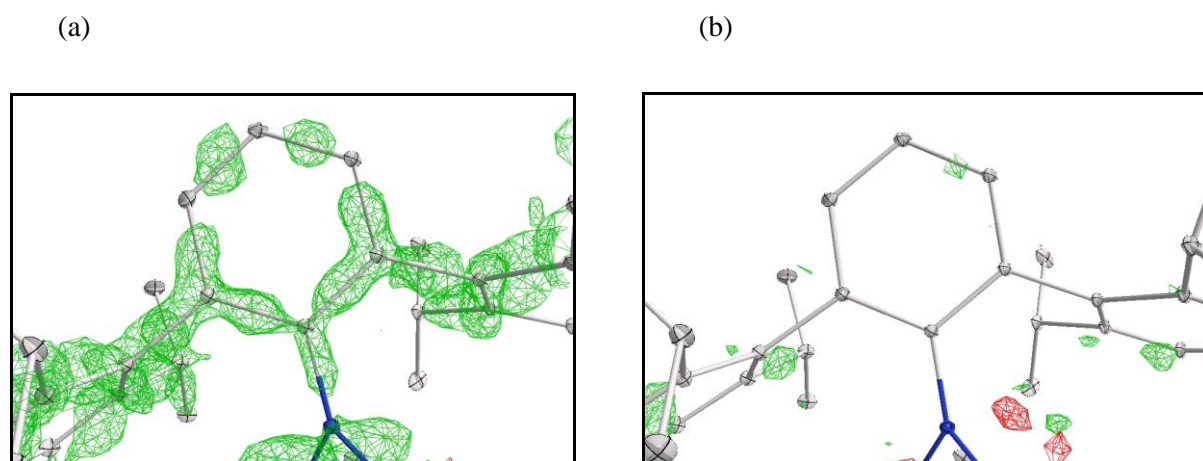


**Chart 5:**  $^{29}\text{Si}$  NMR spectrum of the compound **3** in  $\text{C}_6\text{D}_6$ .

### X-ray crystallography

Single-crystal X-ray diffraction data for compounds **2** and **3** were collected on a Bruker diffractometer equipped with a SMART 6000 CCD detector using Cu  $K\alpha$  radiation from a 5kW rotating anode equipped with INCOATEC mirror optics. Integration was performed with SAINT<sup>2</sup> version 7.61A. An empirical multi-scan absorption correction was performed with SADABS.<sup>3</sup> Merged data for **2** (the space group is  $P2_1/n$ ) are close to complete (98.5%) for the resolution that can be reached with Cu  $K\alpha$ . Structure solution, and an initial structure refinement with the independent atom model (IAM) using the observed intensities ( $I$ ) after scaling, were performed with the programs SHELXS and SHELXL-97.<sup>4</sup> Hydrogen atoms were included using a riding model. This IAM refinement was repeated with the XDLSM routine of the program suite XD<sup>5</sup>. Refinement against  $F$ , the default in XD, gave essentially the same result. Small differences arise only from the different weighting scheme  $w=1/\sigma^2$  and subtle differences in the spherical scattering factor and leading to a  $R(F)$  value of 4.7% for 12378 observed out of a total number of 14094 reflections ( $3\sigma$  cutoff of  $I$ ). Like in SHELXL hydrogen-atom positions were constrained to ride on their parent atoms and isotropic displacement parameters of hydrogen atoms were constrained to 1.2 or 1.5 times the values of the respective non-hydrogen atoms. Constraints (and input files for invariom refinement) were generated with the preprocessor program InvariomTool.<sup>6</sup>

In a subsequent step an invariom refinement<sup>7</sup> was performed with the same refinement choices (i.e. refinement on  $F$  with  $w=1/\sigma^2$  and 12378 reflections). In invariom refinement the valence electron density of all atoms is taken from a database of aspherical scattering factors defined according to the Hansen/Coppens multipole model.<sup>8</sup> Including the scattering contribution of the valence electron density reduced the  $R(F)$  by almost 1% to 3.9%. The physical significance of the anisotropic displacement parameters also improves. This can be shown by the average difference of the mean-square displacement amplitudes in bond direction (DMSDA). Average DMSDA values after invariom refinement (only bonds in between ordered atoms, no solvent,  $12.0 \text{ \AA}^2$ ) are significantly smaller than those from IAM refinement ( $14.7 \text{ \AA}^2$ ). In addition the improvement of the structural model can also be illustrated by comparing the residual electron density map from IAM and invariom refinement. This becomes most obvious for the phenyl ring as shown in Figure S1. After invariom refinement, the features in the bonding region are included in the model and absent from the residual density map.



**Figure S1.** Part of the molecular structure of **2** with anisotropic displacement parameters depicted at 10% probability. (a) Shows the un-modelled bonding residual electron density remaining from IAM refinement, whereas (b) illustrates the reduction of residual density in the same region after invariom refinement.<sup>7</sup> Residual electron density features are shown at a level of  $0.14 \text{ e\AA}^{-3}$ .

**Table 1.** Crystallographic and Structure Refinement Data for Compounds **2** and **3**.

	<b>2</b> · benzene	<b>3</b>
Formula	C <sub>78</sub> H <sub>106</sub> N <sub>2</sub> O <sub>2</sub> Si <sub>2</sub>	C <sub>159</sub> H <sub>236.4</sub> N <sub>4</sub> O <sub>4.4</sub> Si <sub>4</sub>
Formula weight	1159.83	2386.86
Crystal size/mm	0.02 x 0.01 x 0.01	0.03 x 0.01 x 0.01
Crystal system	monoclinic	triclinic
Space group, Z	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 4	<i>P</i> $\bar{1}$ , 1
<i>T</i> / °C	-173	-173
<i>a</i> /Å	13.2600(2)	13.1045(2)
<i>b</i> /Å	22.6118(4)	16.8836(2)
<i>c</i> /Å	23.3990(4)	17.1428(2)
<i>α</i> /deg	90	83.143(1)
<i>β</i> /deg	90.5820(10)	82.555(1)
<i>γ</i> /deg	90	77.087(1)
<i>V</i> /Å <sup>3</sup>	7015.4(2)	3649.70(8)
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.098	1.0856
Wavelength/ Å	1.54178	1.54178
Abs. coeff/mm <sup>-1</sup>	0.797	0.777
<i>θ</i> range/deg	2.717 to 72.21	2.61 to 67.40
Refl. collected/ indep.	161632 / 13733	58445 / 12849
max. and min. transmission	0.7536 and 0.6815	0.4683 and 0.3900
<i>R</i> ( <i>F</i> ) [ <i>I</i> >3σ( <i>I</i> )]	0.0391	0.0528
<i>R</i> <sub>int</sub> ( <i>I</i> )	0.0313	0.0310
<i>wR</i> 2 (all data) [ <i>I</i> >3σ( <i>I</i> )]	0.0419	0.0544
Largest diff. peak and hole/e Å <sup>3</sup>	0.398 and -0.442	0.376 and -0.458



As has been recently observed for a similar Si system<sup>1</sup> the Si<sub>2</sub>N<sub>2</sub> core of **2** shows dynamic disorder. Two main occupancies occurred and were included in our model. After invariom refinement further phenyl-ring disorder became apparent. This disorder was not taken into account, since the minimal residual electron density is only around 0.40 electrons. The same procedures (measurement with the SMART 6000 diffractometer, initial full-matrix least-squares refinement with SHELXL and XD, subsequent invariom refinement) were applied for compound **3**, which crystallizes in space group *P* $\bar{1}$ . Here, invariom refinement led to a drop in the *R*-Factor of approximately 0.5%. Like in **2**, the Si<sub>2</sub>N<sub>2</sub> core shows dynamic disorder, which was again described by two split positions of the (OH)<sub>2</sub> groups with the Si and N-atoms unaltered. Some un-modelled electron density remained at both the dynamically disordered Si-O fragment and the pentane solvent. Hence two different conformations were used to describe the disordered electron density. As in compound **2** the signal for the disordered groups became slightly stronger in the invariom refinement when compared to the corresponding IAM refinement. We think that for structures like **2** and **3**, where we seek to chemically interpret and understand residual electron density, invariom refinements are especially useful, since bonding and lone-pair electron density are taken into account already. Full crystal data for both structures are summarized in Table 1.

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