Stable Silenolates and Brook-Type Silenes with Exocyclic Structures

Michael Haas†, Roland Fischer†, Michaela Flock†, Stefan Mueller†, Martin Rausch†, Robert Saf‡, Ana Torvisco† and Harald Stueger†*

† Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria

‡ Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria
# Table of Contents

**EXPERIMENTAL SECTION** .......................................................................................................................... 3
  - General Considerations .......................................................................................................................... 3
  - Synthesis of 1b ....................................................................................................................................... 3
  - Synthesis of 1c ......................................................................................................................................... 4
  - Synthesis of [18]-crown-6 adduct of 2a .................................................................................................. 4
  - Synthesis of [18]-crown-6 adduct of 2b .................................................................................................. 5
  - Synthesis of [18]-crown-6 adduct of 2c .................................................................................................. 6
  - Reaction of 2a with iPr_3SiCl ................................................................................................................. 6
  - Reaction of 2b with iPr_3SiCl ................................................................................................................. 7
  - Reaction of 2c with iPr_3SiCl ................................................................................................................. 7
  - Reaction of 3b with MeOH ....................................................................................................................... 8
  - Reaction of 3b with O_2 .......................................................................................................................... 8
  - Photolysis of 3b ....................................................................................................................................... 9
  - X-ray Crystallography ............................................................................................................................ 9
  - Computational Methods ......................................................................................................................... 10

**ANALYTICAL SECTION** ............................................................................................................................. 11
  - Spectroscopy ......................................................................................................................................... 11
  - X-ray Crystallography ............................................................................................................................. 38

**COMPUTATIONAL SECTION** ..................................................................................................................... 43
Experimental Section

General Considerations

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.\(^1\) Commercial KO\textsubscript{t}Bu (97 %), ClCOMes (99 %), ClCOAd (98 %), ClCO\textsubscript{o}-Tol (99 %), iPr\textsubscript{3}SiCl (97 %) and [18]crown-6 (99 %) were used as purchased. Et\textsubscript{3}N (99 %) was dried by distillation from solid KOH, commercial anhydrous MeOH was dried with 3Å molecular sieve.\(^1\)\textsuperscript{H} (299.95 MHz), \textsuperscript{13}C (75.43 MHz) and \textsuperscript{29}Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer in C\textsubscript{6}D\textsubscript{6} or CDCl\textsubscript{3} solution and referenced versus TMS using the internal \textsuperscript{2}H-lock signal of the solvent. (Me\textsubscript{3}Si)\textsubscript{2}Si\textsubscript{6}Me\textsubscript{8}(SiMe\textsubscript{3})\textsubscript{2}\textsuperscript{2} (Me\textsubscript{3}Si)\textsubscript{2}Si\textsubscript{6}Me\textsubscript{8}(SiMe\textsubscript{3})K\textsuperscript{1} and 1a\textsuperscript{3} were synthesized according to published procedures. HRMS spectra were run on a Kratos Profile mass spectrometer. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR Spectrometer from the solid sample. Melting points were determined using a Buechi 535 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. Photolyses were performed by using a 500 W medium pressure mercury lamp (Original HANAU). Sample solutions were photolyzed under an atmosphere of nitrogen in Pyrex Schlenk tubes immersed in cold water to ensure ambient sample temperature and to prevent irradiation with light of wavelengths \(\lambda < 300\) nm. UV absorption spectra were recorded on a Perkin Elmer Lambda 5 spectrometer.

Synthesis of 1b

A solution of (Me\textsubscript{3}Si)\textsubscript{2}Si\textsubscript{6}Me\textsubscript{8}(SiMe\textsubscript{3})K in 20 mL of DME was freshly prepared from 3.00 g (5.16 mmol) of (Me\textsubscript{3}Si)\textsubscript{2}Si\textsubscript{6}Me\textsubscript{8}(SiMe\textsubscript{3})\textsubscript{2} and 0.64 g (5.67 mmol) of KO\textsubscript{t}Bu and slowly added to a solution of 1.04 g (5.67 mmol) 2,4,6-trimethylbenzoylchloride in 50 mL diethyl ether at -80\textdegree C. Subsequently the mixture was stirred for another 30 min at -80 \textdegree C, allowed to warm to room temperature and finally stirred for additional 60 minutes. After aqueous work up with 100 mL of 3 % sulfuric acid the organic layer was separated, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvents were

---

\(^1\) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518.

\(^2\) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. J. Organomet. Chem. 2003, 685, 79.

\(^3\) Stueger, H.; Hasken, B.; Haas, M.; Rausch, M.; Fischer, R.; Torvisco, A. Organometallics 2014, 33, 231.
stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from acetone solution at -30°C afforded 3.30 g (98%) of analytically pure 1b as slightly yellow crystals.

**mp:** 185 °C. **Anal. Found:** C, 49.75; H, 9.33 %. **Calc.:** C, 49.47; H, 9.53 %. **29Si-NMR** (C\(_6\)D\(_6\), TMS, ppm): −8.22, −8.37, −12.46 (SiMe\(_3\)); −37.61, −38.46 (SiMe\(_2\)); −71.14 (SiC=O); −131.67 (Si(SiMe\(_3\))\(_2\)). **13C-NMR** (C\(_6\)D\(_6\), TMS, ppm): 246.17 (C=O); 147.19, 137.41, 131.31, 128.67 (Mes-C); 20.60, 19.86 (Mes-CH\(_3\)); 3.70, 3.64, 1.45 (Si(CH\(_3\))\(_3\)); −0.83, −1.12, −1.99, −2.51 (Si(CH\(_3\))\(_2\)). **1H-NMR** (C\(_6\)D\(_6\), TMS, ppm): 6.55 (s, 2 H, Mes-H); 2.17 (6H, s, Mes-CH\(_3\)); 2.01 (3H, s, Mes-CH\(_3\)); 0.55, 0.43, 0.37, 0.36 (s, 6H each, Si(CH\(_3\))\(_2\)); 0.34, 0.29, 0.07 (s, 9H each, Si(CH\(_3\))\(_3\)). **IR** (neat): \(\nu\) (C=O) = 1608 (m) cm\(^{-1}\). **HRMS:** calc. for [C\(_{27}\)H\(_{62}\)OSi\(_9\)]\(^+\) (M\(^+\)): 654.2724; found: 654.2752. **UV-VIS:** \(\lambda\) [nm] (\(\varepsilon\) [L mol\(^{-1}\) cm\(^{-1}\)]) = 254 (16800), 393 (230).

**Synthesis of 1c**

The procedure followed was that used for 1b with 3.00 g (5.16 mmol) of (Me\(_3\)Si)\(_2\)Si\(_6\)Me\(_8\)(SiMe\(_3\))\(_2\), 0.64 g (5.67 mmol) of KOtBu and 0.88 g (5.67 mmol) 2-methylbenzoylchloride. Yield: 3.00 g (93 %) of analytically pure 1c as slightly yellow crystals.

**mp:** 128 °C. **Anal. Found:** C, 47.54; H, 9.00 %. **Calc.:** C, 47.85; H, 9.32 %. **29Si-NMR** (C\(_6\)D\(_6\), TMS, ppm): −7.66, −8.66, −10.29 (SiMe\(_3\)); −36.51, −37.87 (SiMe\(_2\)); −66.79 (SiC=O); −131.42 (Si(SiMe\(_3\))\(_2\)). **13C-NMR** (C\(_6\)D\(_6\), TMS, ppm): 239.77 (C=O); 145.43, 134.24, 131.64, 130.10, 129.80, 124.85 (o-Tol-C); 20.09 (o-Tol-CH\(_3\)); 3.74, 3.71, 1.84 (Si(CH\(_3\))\(_3\)); −0.89, −1.15, −2.34, −2.67 (Si(CH\(_3\))\(_2\)). **1H-NMR** (C\(_6\)D\(_6\), TMS, ppm): 7.59 - 6.88 (4H, o-Tol-H); 2.40 (3H, o-Tol-CH\(_3\)); 0.45, 0.41, 0.35, 0.28, 0.27, 0.20 (s, 51H, Si(CH\(_3\))\(_2\) + Si(CH\(_3\))\(_3\)). **IR** (neat): \(\nu\) (C=O) = 1601 (m) cm\(^{-1}\). **HRMS:** calc. for [C\(_{25}\)H\(_{58}\)OSi\(_9\)]\(^+\) (M\(^+\)): 626.2411; found: 626.2453. **UV-VIS:** \(\lambda\) [nm] (\(\varepsilon\) [L mol\(^{-1}\) cm\(^{-1}\)]) = 254 (18200), 414 (240).

**Synthesis of [18]-crown-6 adduct of 2a**

300 mg (0.447 mmol) of 1a and 0.124 mg (0.447 mmol) of [18]crown-6 were dissolved in 4 mL of toluene, cooled to −50°C and 46.9 mg (0.447 mmol) of KOtBu were added. After stirring for
additional 30 minutes the mixture was allowed to warm to room temperature and finally stirred for an additional hour. At this time reaction control by $^{29}$Si-NMR showed that the starting material completely had been consumed. For isolation the product was crystallized from toluene at $-30^\circ$C to give 210 mg of the 1 : 1 [18]crown-6 adduct of 2a as red crystals which after filtration contained variable amounts of residual toluene and Me$_3$SiO$_2$Bu and immediately decomposed to uncharacterized material upon the attempted removal of the volatile components in vacuo.

$^{29}$Si-NMR ($C_6D_6$, TMS, ppm): $-8.52$ (SiMe$_3$); $-33.10$, $-35.07$ (SiMe$_2$); $-92.01$ (SiCOAr$_3$); $-131.30$ (Si(SiMe$_3$)$_2$). $^{13}$C-NMR ($C_6D_6$, TMS, ppm): 272.23 (C=O); 69.62 (-CH$_2$-CH$_2$-O-); 50.59 (Ad-C-CO); 39.70, 37.65 (Ad-CH$_2$); 29.30 (Ad-CH); 4.12 (Si(CH$_3$)$_3$); 2.77, $-0.11$ (Si(CH$_3$)$_2$).

$^1$H-NMR ($C_6D_6$, TMS, ppm): 3.23 (-CH$_2$-CH$_2$-O-); 2.3 - 1.5 (Ad-CH$_2$, Ad-CH; partially superimposed by toluene-CH$_3$); 0.74, 0.62 (12H each, s, Si(CH$_3$)$_2$); 0.48 (18H, s, Si(CH$_3$)$_3$).

**Synthesis of [18]-crown-6 adduct of 2b**

The procedure followed was that used for 2a with 300 mg (0.458 mmol) of 1b, 0.127 mg (0.481 mmol) of [18]crown-6 and 53.9 mg (0.481 mmol) of KOrBu. Yield: 240 mg of the 1 : 1 [18]crown-6 adduct of 2b as red crystals which after filtration contained variable amounts of residual toluene and other minor impurities and immediately decomposed to uncharacterized material upon the attempted removal of the volatile components in vacuo.

$^{29}$Si-NMR ($C_6D_6$, TMS, ppm): $-8.79$ (SiMe$_3$); $-35.09$ (broad), $-36.40$ (SiMe$_2$); $-73.11$ (SiC=O); $-131.13$ (Si(SiMe$_3$)$_2$). $^{13}$C-NMR ($C_6D_6$, TMS, ppm): 264.65 (C=O); 152.02, 133.17, 131.87 (Mes-C); 69.82 (-CH$_2$-CH$_2$-O-); 20.85 (Mes-CH$_3$); 20.72 (Mes-CH$_3$); 4.01 (Si(CH$_3$)$_3$); 0.59, 0.54, $-0.47$ (Si(CH$_3$)$_2$). $^1$H-NMR ($C_6D_6$, TMS, ppm): 6.78 (s, 2 H, Mes-H); 3.12 (-CH$_2$-CH$_2$-O-); 2.67 (6H, s, Mes-CH$_3$); 2.16 (3H, s, Mes-CH$_3$); 0.66, 0.65 (s, 24H Si(CH$_3$)$_2$); 0.48 (s, 18H, Si(CH$_3$)$_3$).
Synthesis of [18]-crown-6 adduct of 2c

The procedure followed was that used for 2a with 300 mg (0.478 mmol) of 1c, 0.139 mg (0.526 mmol) of [18]crown-6 and 59.0 mg (0.526 mmol) of KOrBu. Yield: 75 mg of the 1 : 1 [18]crown-6 adduct of 2c as dark red crystals which after filtration contained variable amounts of residual toluene, Me$_3$SiOrBu and (Me$_3$Si)$_2$O and immediately decomposed to uncharacterized material upon the attempted removal of the volatile components in vacuo.

$^{29}$Si-NMR (C$_6$D$_6$, TMS, ppm): −8.78 (SiMe$_3$); −34.26, −36.60 (SiMe$_2$); −66.95 (SiC=O); −131.49 (Si(SiMe$_3$)$_2$). $^{13}$C-NMR (C$_6$D$_6$, TMS, ppm): 265.07 (C=O); 153.68, 131.04, 129.99, 127.04, 125.67, 123.82 (o-Tol-C); 69.57 (-CH$_2$-CH$_2$-O-); 19.81 (o-Tol-CH$_3$); 4.03 (Si(C$_3$H$_3$)$_3$); 0.81, −0.53 (Si(CH$_3$)$_2$). $^1$H-NMR (C$_6$D$_6$, TMS, ppm): 7.65 (d, o-Tol-H); 3.05 (-C$_2$H$_2$-C$_2$-O-); 2.55 (3H, s, o-Tol-CH$_3$); 0.61 (s, 12H, Si(C$_3$H$_3$)$_2$), 0.56 (s, 12H Si(C$_3$H$_3$)$_2$); 0.45 (s, 18H, Si(CH$_3$)$_3$).

Reaction of 2a with iPr$_3$SiCl

A solution of 2a was freshly prepared by stirring a mixture of 46.9 mg (0.447 mmol) of KOrBu and 300 mg (0.447 mmol) of 1a in 5 mL of THF for 1 h at −70°C. Now the resulting red solution was warmed to 0°C and 0.10 g (0.447 mmol) of iPr$_3$SiCl were added drop wise. Immediately the solution turned colorless. After aqueous work up with 100 mL of 3 % sulfuric acid the organic layer was separated, dried over Na$_2$SO$_4$ and the solvents were stripped off with a rotary evaporator. Drying in vacuum (0.001 mbar) and crystallization from acetone solution at −30°C afforded 270 mg (80%) of the analytically pure acylcyclohexasilane 1d as white crystals.

mp: 127 °C. Anal. Found: C, 53.92; H, 10.24 %. Calc.: C, 54.03; H, 10.40 %. $^{29}$Si-NMR (CDCl$_3$, TMS, ppm): −7.29, −8.55 (SiMe$_3$); −33.80, −35.69 (SiMe$_2$); −69.72 (SiC=O); −131.35 (Si(SiMe$_3$)$_2$). $^{13}$C-NMR (CDCl$_3$, TMS, ppm): 250.91 (C=O); 52.00, 37.83, 36.62, 28.10 (Ad-C); 20.45 (CH-(CH$_3$)$_2$), 14.76 (CH-(CH$_3$)$_2$); 4.14, 4.08 (Si(CH$_3$)$_3$); 0.45, −0.18, −0.19, −0.49 (Si(CH$_3$)$_2$). $^1$H-NMR (CDCl$_3$, TMS, ppm): 2.05 (3H, b, Ad-CH); 1.72 (12H, b, Ad-CH$_2$); 1.30 (3H, m, CH-(CH$_3$)$_2$); 1.17 (18H, d, CH-(CH$_3$)$_2$); 0.37, 0.34, 0.30, 0.29, (6H each, s, Si(CH$_3$)$_2$); 0.24, 0.23 (9H each, s, Si(CH$_3$)$_3$). IR (neat): v(C=O) = 1614 (m) cm$^{-1}$. HRMS: calc. for [C$_{34}$H$_{78}$OSi$_9$]$^{+}$ (M$^+$): 754.3976; found: 754.3955.
Reaction of 2b with iPr\textsubscript{3}SiCl

162 mg (0.839 mmol) of iPr\textsubscript{3}SiCl were added drop wise at 0 °C to a solution of 2b in 5 mL of THF freshly prepared from 500 mg (0.763 mmol) of 1b and 94.0 mg (0.839 mmol) of KOtBu according to the procedure described above. Immediately the red solution turned yellow. After removal of the volatile components in vacuo the remaining yellow solid was dissolved in heptane, filtered over dry celite and the solvent was stripped off again. Recrystallization from diethyl ether afforded 330 mg (59%) of the analytically pure silene 3b as yellow crystals.

mp: 85-86 °C (dec). Anal. Found: C, 53.23; H, 10.25 %. Calc.: C, 53.58; H, 10.08 %. \textsuperscript{29}Si-NMR (C\textsubscript{6}D\textsubscript{6}, TMS, ppm): 31.22 (Si=C); 13.08 (iPr\textsubscript{3}SiO); –8.66 (SiMe\textsubscript{3}); –35.57, –35.67, –37.35, –37.57 (SiMe\textsubscript{2}); –132.05 (Si(SiMe\textsubscript{3})\textsubscript{2}). \textsuperscript{13}C-NMR (C\textsubscript{6}D\textsubscript{6}, TMS, ppm): 200.31 (Si=C); 142.96, 136.94, 136.64, 128.62 (Mes-C); 21.27, 20.99 (Mes-CH\textsubscript{3}); 18.31 (CH(CH\textsubscript{3})\textsubscript{2}); 13.96 (CH(CH\textsubscript{3})\textsubscript{2}); 3.48 (Si(CH\textsubscript{3})\textsubscript{3}); –1.30, –1.37, –1.80, –3.12 (Si(CH\textsubscript{3})\textsubscript{2}). \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, TMS, ppm): 6.73 (s, 2 H, Mes-H); 2.54 (6H, s, Mes-CH\textsubscript{3}); 2.07 (3H, s, Mes-CH\textsubscript{3}); 1.01-0.9 (21 H, b, CH(CH\textsubscript{3})\textsubscript{2}); 0.68, 0.40, 0.29, –0.03 (6H each, s Si(CH\textsubscript{3})\textsubscript{2}); 0.28 (18H, Si(CH\textsubscript{3})\textsubscript{3}). IR (neat): v(Si=C) = 1155 (s) cm\textsuperscript{–1}. HRMS: calc. for [C\textsubscript{33}H\textsubscript{74}O\textsubscript{9}Si\textsubscript{9}]\textsuperscript{+} (M\textsuperscript{+}): 738.3663; found: 738.3628. UV-VIS: \lambda [nm] (ε [L mol\textsuperscript{–1} cm\textsuperscript{–1}]) = 308 (3100), 364 (16500).

Reaction of 2c with iPr\textsubscript{3}SiCl

170 mg (0.876 mmol) of iPr\textsubscript{3}SiCl were added drop wise at 0 °C to a solution of 2c in 5 mL of THF freshly prepared from 500 mg (0.797 mmol) of 1c and 94 mg (0.876 mmol) of KOtBu according to the procedure described above. Immediately the red solution turned yellow. After removal of the volatile components in vacuo the remaining yellow solid was dissolved in heptane, filtered over dry celite and the solvent was stripped off again. The target silene 3c was formed along with several unidentified by-products. Purification of the crude material by crystallization was not successful because it decomposed further even at –70°C.

\textsuperscript{29}Si-NMR (C\textsubscript{6}D\textsubscript{6}, TMS, ppm): 36.65 (Si=C); 14.63 (iPr\textsubscript{3}SiO); –8.67, –8.73 (SiMe\textsubscript{3}); –35.21, –35.62, –37.33, –37.57 (SiMe\textsubscript{2}); –132.01 (Si(SiMe\textsubscript{3})\textsubscript{2}).
Reaction of 3b with MeOH

300 mg (0.410 mmol) of 3b were dissolved in 6 mL THF and added drop wise to a mixture of 2 mL of MeOH with 3 drops of Et₃N. After removal of the volatile components on a rotary evaporator 5 mL of pentane were added and the resulting solution was filtered over silica gel. Evaporation of pentane followed by crystallization from acetone at −30°C afforded 190 mg (61%) of analytically pure 4a as white crystals.

mp: 164-165 °C. Anal. Found: C, 53.07; H, 9.60 %. Calc.: C, 52.91; H, 10.16 %. ²⁹Si-NMR (CDCl₃, TMS, ppm): 21.54 (SiOMe); 14.76 (iPr₂SiO); −6.24, −9.41 (SiMe₃); −33.96, −34.45, −39.16, −41.59 (SiMe₂); −131.73 (Si(SiMe₃)₂). ¹³C-NMR (CDCl₃, TMS, ppm): 138.47, 137.90, 135.42, 132.86, 130.20, 128.75 (Mes-C); 70.30 (SiCHMesOSi); 54.49 (OCH₃); 22.71, 21,32, 20,80 (Mes-CH₃); 18.27, 17.99 (CH(CH₃)₂); 12.65 (CH(CH₃)₂); 4.01, 3.84, (Si(CH₃)₃); −0.60, −0.66, −1.71, −2.07, −3.54, −4.43, −4.65, −4.88 (Si(CH₃)₂). ¹H-NMR (CDCl₃, TMS, ppm): 6.76, 6.71 (1H each, s, Mes-H); 5.42 (1H, s, CHMesOSi); 3.49 (3H, s, OCH₃); 2.42, 2.30, 2.22 (3H each, s, Mes-CH₃); 1.01 (12H, b, CH(CH₃)₂ + CH(CH₃)₂); 0.90 (9H, b, CH(CH₃)₂ + CH(CH₃)₂); 0.29, 0.28, −0.06, −0.16 (3H each, s, Si(CH₃)₂); 0.25 (15H, s, Si(CH₃)₂ + Si(CH₃)₃); 0.20 (12H s, Si(CH₃)₂); 0.19 (9H, s, Si(CH₃)₃). HRMS: calc. for [C₃₂H₇₄O₂Si₉]+ (M⁺): 770.3925; found: 770.3910.

Reaction of 3b with O₂

A solution of 300 mg (0.410 mmol) of 3b in 6 mL of THF was stirred in contact with air at room temperature for 2 h. After removal of the volatile components on a rotary evaporator the product was chromatographed twice on silica gel, eluting with gradient (heptane, toluene), to give 100 mg (32%) of a semi-solid residue of slightly impure 4b.

²⁹Si-NMR (CDCl₃, TMS, ppm): 9.59 (iPr₃SiO); 2.83 (OSiO); −7.20, −8.64 (SiMe₃); −35.77, −40.62 (SiMe₂); −132.15 (Si(SiMe₃)₂). ¹³C-NMR (CDCl₃, TMS, ppm): 169.45 (C=O); 139.12, 136.30, 130.87, 128.86 (Mes-C); 29.70, 21.07 (Mes-CH₃); 18.00 (Si(CHCH₃)₃); 13.02 (Si(CHCH₃)₃); 3.74 (Si(CH₃)₃); −1.18, −1.30, −4.76, −4.84 (Si(CH₃)₂). ¹H-NMR (CDCl₃, TMS, ppm): 6.83 (s, 2 H, Mes-H); 2.41 (s, 6H, Mes-CH₃); 2.27 (s, 3H, Mes-CH₃); 1.05 (18 H, b, CH(CH₃)₂ + CH(CH₃)₂); 0.35 (s, 6H, Si(CH₃)₂); 0.32 (s,
6 H Si(CH₃)₂; 0.30 (s, 6H, Si(CH₃)₂); 0.26 (s, 12H, Si(CH₃)₂ + Si(CH₃)₃); 0.25 (s, 12 H Si(CH₃)₂ + Si(CH₃)₃). IR (neat): ν(C=O) = 1609 (s) cm⁻¹; ν(Si-O(CO)R) = 1073, 1034 (s) cm⁻¹. HRMS: calc. for [C₃₃H₇₄O₃Si₉]⁺ (M⁺–CH₃): 755.3327; found: 755.3225.

**Photolysis of 3b**

A solution of 300 mg (0.410 mmol) of 4c in 5 mL of benzene was photolyzed with a 500 W mercury lamp at 25 °C for 12 h. At this time ¹H- and ²⁹Si-NMR analysis showed that the starting material completely had been consumed. After removal of the volatile components on a rotary evaporator 5 mL of pentane were added and the resulting solution was filtered over silica gel. Evaporation of pentane followed by crystallization from acetone at −30 °C afforded 175 mg (58 %) of analytically pure 4c as white crystals.

**mp:** 130-131 °C. **Anal. Found:** C, 53.30; H, 9.65 %. **Calc.:** C, 53.58; H, 10.08 %. **²⁹Si-NMR** (CDCl₃, TMS, ppm): 12.36 (OSi(iPr)₃) −7.45, −8.99 (SiMe₃); −36.45, −36.72, −39.04, −40.75 (SiMe₂); −56.45 (SiH); −131.85 (Si(SiMe₃)₂). **¹³C-NMR** (C₆D₆, TMS, ppm): 149.12, 139.43, 138.49, 132.54, 129.64, 121.52 (aryl-C); 76.31 (SiC(Mes)OSi); 46.83 (aryl-CH₂); 21.73 (aryl-CH₃); 18.38 (CH(CH₃)₂); 18.20 (CH(CH₃)₂); 17.19 (aryl-CH₃); 13.56 (CH(CH₃)₂); 3.59, 3.47, (Si(CH₃)₃); −1.03, −1.12, −1.87, −2.07, −2.76, −4.09, −4.40, −4.67 (Si(CH₃)₂). **¹H-NMR** (CDCl₃, TMS, ppm): 6.74 (1H, s, aryl-H); 6.67 (1H, s, aryl-H); 3.90 (1H, s, SiH); 3.37, 3.32, 3.21, 3.16 (2H, CH₂₈H₆); 2.28, 2.24 (3H each, s, aryl-CH₃); 1.0 -0.9 (21H, b, CH(CH₃)₂+CH(CH₃)₃); 0.34, 0.27, 0.26, 0.19, 0.18, −0.05, −0.36 (3H each, s, Si(CH₃)₂); 0.23 (12H, s, Si(CH₃)₃+Si(CH₃)₂); 0.20 (9H, s, Si(CH₃)₃). IR (neat): ν(Si-H) = 2069 (s) cm⁻¹; HRMS: calc. for [C₃₃H₇₄O₃Si₉]⁺ (M⁺): 738.3684; found: 738.3663.

**X-ray Crystallography**

For X-ray structure analysis suitable crystals were mounted onto the tip of glass fibres using mineral oil. Data collection was performed on a Bruker Kappa Apex II CCD diffractometer at 100 K using graphite-monochromated Mo Kα (λ = 0.71073Å) radiation. Details of the crystal data and structure refinement are provided in Tables S1 – S4. The SHELX version 6.1 program
package was used for the structure solution and refinement.\(^4\) Absorption corrections were applied using the SADABS program.\(^5\) All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the refinement at calculated positions using a riding model as implemented in the SHELXTL program. In the solid state structure of 2a the adamantyl group as well as the crown ether molecule were found disordered over two positions and were accordingly implemented in the structural model. The ratios of occupancy refined to 0.65:0.35 (adamantyl group) and 0.60:0.40 (crown ether), respectively. All non-hydrogen atoms of the disordered parts were refined anisotropically and hydrogen atoms were placed using standard AFIX commands. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1012279 (1d), CCDC-1012280 (2a), CCDC-1012281 (2c), CCDC-1012282 (3b), CCDC-1012283 (4c). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

**Computational Methods**

All calculations were carried out using the Gaussian09 program package\(^6\) on a computing cluster with blade architecture. For all calculations the mPW1PW91 hybrid functional was used\(^7\) together with the 6-31+G** basis set. After structure optimizations the vibrational frequencies were calculated to ensure minimum structures. The same combination of functional and basis set was used to calculate the excited states via time dependent (TD)-DFT. Compound 3b was modeled by substituting the OSiPr\(_3\) group by OSiMe\(_3\).

---

\(^4\) SHELX and SHELXL PC: VERSION 5.03, Bruker AXS, Inc., Madison, WI, 1994.  
\(^5\) SADABS: Area-detection Absorption Correction: Bruker AXS Inc., Madison, WI, 1995.  
\(^6\) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.  
\(^7\) C. Adamo, C.; Barone, V. J. Chem. Phys. 1998, 108, 664.
Analytical Section

Spectroscopy
Figure S1. $^1$H NMR spectrum of 2a-[18]crown-6 (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S2. $^{13}$C NMR spectrum of 2a·[18]crown-6 (C₆D₆ solution, vs. ext. TMS, ppm)
Figure S3. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 2a-[18]crown-6 (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S4. $^1$H NMR spectrum of 2b·[18]crown-6 (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S5. $^{13}$C NMR spectrum of 2b-[18]crown-6 ($C_6D_6$ solution, vs. ext. TMS, ppm)
Figure S6. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 2b-[18]crown-6 (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S7. $^1$H NMR spectrum of 2c·[18]crown-6 (C₆D₆ solution, vs. ext. TMS, ppm)
Figure S8. $^{13}$C NMR spectrum of 2c·[18]crown-6 (C₆D₆ solution, vs. ext. TMS, ppm)
Figure S9. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 2c-[18]crown-6 (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S10. $^1$H NMR spectrum of 1d (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S11. $^{13}$C NMR spectrum of 1d (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S12. $^{29}\text{Si}$ NMR spectrum (INEPT, bb decoupled) of 1d (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S13. $^1$H NMR spectrum of 3b (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S14. $^{13}$C NMR spectrum of 3b (C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S15. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 3b (C₆D₆ solution, vs. ext. TMS, ppm)
Figure S16. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 3c (crude product, C$_6$D$_6$ solution, vs. ext. TMS, ppm)
Figure S17. $^1$H NMR spectrum of 4a (CDCl$_3$ solution, vs. ext. TMS, ppm)

steric bulk hindered rotation:
Mes-H: 2 non-equivalent hydrogens
Mes-CH$_3$: 3 signals due to non equivalent ortho-CH$_3$ groups
Figure S18. $^{13}$C NMR spectrum of 4a (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S19. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 4a (CDCl₃ solution, vs. ext. TMS, ppm)
Figure S20. $^1$H NMR spectrum of 4b after column chromatography (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S21. $^{13}$C NMR spectrum of 4b after column chromatography (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S22. $^{29}$Si NMR spectrum (INEPT, bb decoupled) of 4b after column chromatography (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S23. $^1$H NMR spectrum of 4c (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S24. $^{13}$C NMR spectrum of 4c (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S25. $^{29}\text{Si}$ NMR spectrum (INEPT, bb decoupled) of 4c (CDCl$_3$ solution, vs. ext. TMS, ppm)
Figure S26. UV absorption spectrum of 3b (n-hexane solution).
X-ray Crystallography

**Table S1.** Crystallographic data and structure refinement for 2a·[18]crown-6

|                          | 2a·[18]crown-6                  |
|--------------------------|---------------------------------|
| **Empirical formula**    | C_{37}H_{81}K_{1}O_{7}Si_{8}    |
| **Formula weight**       | 901.84                          |
| **Temperature [K]**      | 100(2)                          |
| **Wavelength [Å]**       | 0.71073                         |
| **Crystal system, space group** | monoclinic, P2(1)/c            |
| **Unit cell dimensions** | a = 21.6510(6) Å; α = 90.00     |
|                          | b = 10.6610(3)Å; β = 92.8930(10) |
|                          | c = 22.4888(6) Å; γ = 90.00     |
| **Volume [Å³]**          | 5184.3(2)                       |
| **Z, Calculated density**| 4, 1.155                        |
| **Absorption coefficient [mm⁻¹]** | 0.327                      |
| **F(000)**               | 1960                            |
| **Crystal size [mm]**    | 0.26 x 0.21 x 0.12              |
| **θ range for data collection [°]** | 2.55 to 29.99                   |
| **Limiting indices**     | −28 ≤ h ≤ 28, −14 ≤ k ≤ 13, −29 ≤ l ≤ 29 |
| **Reflections collected/unique** | 91746/12471 [R(int) = 0.0387]    |
| **Completeness to θ [%]**| 99.7                            |
| **Absorption correction**| SADABS                          |
| **Refinement method**    | Full-matrix least-squares on F² |
| **Max. and min. transmission** | 0.962 and 0.921               |
| **Data / restraints/parameters** | 12463/155/695                |
| **Goodness-of-fit on F²** | 1.105                          |
| **Final R indices [I>2σ(I)]** | R1 = 0.0456; wR2 = 0.1157     |
|                           | R1 = 0.0588; wR2 = 0.1235       |
| **Largest diff. peak and hole [e.Å⁻³]** | 1.030/−0.891                  |
Table S2. Crystallographic data and structure refinement for 2c·[18]crown-6

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | \(C_{34}H_{73}K_1O_7Si_8\)                |
| Formula weight                                | 857.74                                     |
| Temperature [K]                               | 100(2)                                     |
| Wavelength [Å]                                | 0.71073                                    |
| Crystal system, space group                   | monoclinic, P2(1)/c                       |
| Unit cell dimensions                          | \(a = 15.646(3) \text{ Å}; \ a = 90.00\)   |
|                                              | \(b = 10.014(2) \text{ Å}; \ b = 90.487(5)\) |
|                                              | \(c = 31.683(4) \text{ Å}; \ c = 90.00\)   |
| Volume [Å³]                                   | 4964.0(15)                                 |
| Z, Calculated density                         | 4, 1.148                                   |
| Absorption coefficient [mm⁻¹]                 | 0.338                                      |
| \(F(000)\)                                    | 1856                                       |
| Crystal size [mm]                             | 0.27 x 0.21 x 0.16                        |
| \(\theta\) range for data collection [°]     | 1.29 to 28.00                              |
| Limiting indices                              | \(-20 \leq h \leq 20, -13 \leq k \leq 13, -41 \leq l \leq 41\) |
| Reflections collected/unique                  | 209729/11997 [R(int) = 0.0485]              |
| Completeness to \(\theta\) [%]               | 100                                        |
| Absorption correction                         | SADABS                                     |
| Refinement method                             | Full-matrix least-squares on \(F^2\)      |
| Max. and min. transmission                    | 0.9479 and 0.9143                          |
| Data / restraints/parameters                   | 10997/0/466                                |
| Goodness-of-fit on \(F^2\)                    | 1.125                                      |
| Final R indices [I>2σ(I)]                     | \(R1 = 0.0305\); \(wR2 = 0.0742\)         |
| R indices (all data)                           | \(R1 = 0.0427\); \(wR2 = 0.0871\)         |
| Largest diff. peak and hole [e⋅Å⁻³]            | 0.399/−0.239                               |
Table S3. Crystallographic data and structure refinement for 3b

|                         | 3b                        |
|-------------------------|---------------------------|
| Empirical formula       | C$_{33}$H$_{74}$O$_1$Si$_9$|
| Formula weight          | 739.73                    |
| Temperature [K]         | 100(2)                    |
| Wavelength [Å]          | 0.71073                   |
| Crystal system, space group | orthorhombic, P2(1)2(1)2(1) |
| Unit cell dimensions    | a = 9.7222(3) Å; α = 90.00 |
|                        | b = 14.2897(7) Å; β = 90.00 |
|                        | c = 33.2883(16) Å; γ = 90.00 |
| Volume [Å$^3$]          | 4624.7(3)                 |
| Z, Calculated density   | 4, 1.062                  |
| Absorption coefficient [mm$^{-1}$] | 0.281                   |
| F(000)                  | 1624                      |
| Crystal size [mm]       | 0.35 x 0.21 x 0.18        |
| θ range for data collection [°] | 2.18 to 27.81            |
| Limiting indices        | −10 ≤ h ≤ 13, −20 ≤ k ≤ 17, −46 ≤ l ≤ 46 |
| Reflections collected/unique | 52831/13504 [R(int) = 0.0498] |
| Completeness to θ [%]   | 99.8                      |
| Absorption correction   | SADABS                    |
| Refinement method       | Full-matrix least-squares on F$^2$ |
| Max. and min. transmission | 0.951 and 0.932         |
| Data / restraints/parameters | 13504/0/411             |
| Goodness-of-fit on F$^2$ | 1.068                     |
| Final R indices [I>2σ(I)] | R1 = 0.0370; wR2 = 0.0747 |
| R indices (all data)    | R1 = 0.0503; wR2 = 0.0886 |
| Largest diff. peak and hole [e·Å$^{-3}$] | 0.380/−0.284          |
### Table S4. Crystallographic data and structure refinement for 4c

| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| Empirical formula                            | C$_{33}$H$_{74}$O$_{1}$Si$_{9}$ |
| Formula weight                                | 739.73                 |
| Temperature [K]                               | 100(2)                 |
| Wavelength [Å]                                | 0.71073                |
| Crystal system, space group                   | triclinic, P–1         |
| Unit cell dimensions                          | a = 11.3473(18) Å; α = 63.402(5)  |
|                                                | b = 15.109(2) Å; β = 71.052(6)  |
|                                                | c = 16.174(2) Å; γ = 73.938(6)  |
| Volume [Å$^3$]                                | 2316.7(6)              |
| Z, Calculated density                         | 2, 1.060               |
| Absorption coefficient [mm$^{-1}$]            | 0.280                  |
| F(000)                                        | 812                    |
| Crystal size [mm]                             | 0.15 x 0.14 x 0.03     |
| θ range for data collection [°]               | 2.66 to 27.14          |
| Limiting indices                              | −14 ≤ h ≤ 14, −18 ≤ k ≤ 16, −20 ≤ l ≤ 20 |
| Reflections collected/unique                  | 54299/9451 [R(int) = 0.0325] |
| Completeness to θ [%]                         | 100.0                  |
| Absorption correction                         | SADABS                 |
| Refinement method                             | Full-matrix least-squares on F$^2$ |
| Max. and min. transmission                    | 0.992 and 0.959        |
| Data / restraints/parameters                   | 9451/125/414           |
| Goodness-of-fit on F$^2$                       | 0.997                  |
| Final R indices [I>2σ(I)]                     | R1 = 0.0327; wR2 = 0.0787 |
| R indices (all data)                          | R1 = 0.0441; wR2 = 0.0843 |
| Largest diff. peak and hole [e·Å$^{-3}$]      | 0.40/~0.33             |
Figure S28. ORTEP diagram for compound 4c. Thermal ellipsoids are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.
Computational Section

Figure S29. Frontier orbitals and orbital energies in eV for model compound of 3b (top) and 6 (bottom).

Table S5. Experimental absorption data and selected absorption wavelengths and oscillator strengths (atomic units) calculated at the time-dependent DFT mPW1PW91/6-31+G** level of theory for model compound of 3b and 6

|       | calc. | exp. | assignment              |       |       |
|-------|-------|------|-------------------------|-------|-------|
|       | λ(nm) | f    | λmax(nm) | ε (Lmol⁻¹ cm⁻¹) |       |       |
| 3b    | 365   | 0.279| 364      | 16500            | π_{Si=C→π^*_{aryl}} | HOMO-LUMO |
|       | 345   | 0.061| 308      | 3100             | π_{Si=C→π^*_{aryl}} | HOMO-LUMO+1 |
|       | 312   | 0.006| -        | -                | π_{Si=C→π^*_{Si=C}} | HOMO-LUMO+2 |
| 6     | 348   | 0.210| 340ᵃ     | 7400             | π_{Si=C→π^*_{Si=C}} | HOMO-LUMO |

ᵃ Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. J. Am. Chem. Soc. 1982, 104, 5667.
**Table S6.** The Cartesian coordinates for model compound of 3b together with the zero point vibrational energy corrected absolute energies in Hartree.

\[ E = -3746.12871 \text{ a.u.} \]

| Element | X          | Y          | Z          | Energy       | Zero Point Correction | Absolute Energy  |
|---------|------------|------------|------------|--------------|-----------------------|------------------|
| Si      | -3.37054800 | -0.08542800 | 0.04096500 | -3.28821800  | -0.54132700           | -2.39060000     |
| Si      | -5.66795200 | -0.22074200 | -0.65959700| -2.50701400  | 2.09663500            | -0.41124000     |
| Si      | -2.11533100 | -1.67942400 | -1.22548500| 0.14380100   | -1.95951100           | -0.47660700     |
| Si      | -0.11241900 | 2.28767500  | -0.20802100| 1.05365300   | 0.22492700            | -0.31470300     |
| C       | 2.80317800  | 0.39547400  | -0.03799200| 3.32746500   | 1.65934300            | 0.20425500      |
| Si      | 4.87989000  | 2.45229900  | 0.05569600 | -6.51308000  | -1.74350200           | 0.12993900      |
| H       | -7.54172700 | -1.83367400 | -0.24161000| -5.98158100  | -2.66813100           | -0.11735300     |
| H       | -6.55743400 | -1.65944200 | 1.22086300 | -5.80840200  | -0.40198300           | -2.55697800     |
| H       | -6.86540400 | -0.44350900 | -2.84903700| -5.34582500  | 0.44149200            | -3.07948500     |
| H       | -5.32801600 | -1.32249000 | -2.90538400| -6.64434700  | 1.33947800            | -0.14374800     |
| H       | -7.69962400 | 1.22824900  | -0.42355600| -6.59638700  | 1.50687700            | 0.93686500      |
| H       | -6.25740200 | 2.23370400  | -0.64401200| -3.44172000  | -2.41703700           | 2.71660000      |
| H       | -3.45306600 | -2.61160100 | 3.79643500 | -4.36722800  | -2.81723200           | 2.29019400      |
| H       | -2.60196900 | -2.96899100 | 2.28315000 | -1.66305800  | 0.10671300            | 3.15636400      |
| H       | -0.79047500 | -0.12223300 | 2.53570700 | -1.70926800  | 1.19445200            | 3.27717800      |
| H       | -1.50581000 | -0.33395200 | 4.14872500 | -4.73119600  | 0.33793100            | 3.28520700      |
| H       | -5.70365600 | -0.05430800 | 2.96943200 | -4.64465500  | 0.18731000            | 4.36876100      |
| H       | -4.72030500 | 1.41557600  | 3.09172400 | -3.00524700  | 2.62508300            | -2.18699200     |
| H       | -4.09292900 | 2.73834300  | -2.26346400| -2.54680200  | 3.58788100            | -2.44075900     |
| H       | -2.68610400 | 1.88971800  | -2.93122600| -3.26547500  | 3.37927500            | 0.79984700      |
| H       | -2.96161800 | 4.39324100  | 0.51224800 | -4.35975000  | 3.35307000            | 0.78521500      |
| H       | -2.92878200 | 3.20840300  | 1.82757100 | -1.95964200  | -1.09353200           | -3.04618200     |
| H       | -1.49896100 | -1.88367400 | -3.65150800| -2.93662400  | -0.85794600           | -3.48021800     |
| H       | -1.32600300 | -0.20307100 | -3.12071000| -2.98681800  | -3.38846500           | -1.22667800     |
| H       | -2.39426700 | -4.11793200 | -1.79169000| -3.12311400  | -3.77130500           | -0.21067900     |
| H       | -3.97330100 | -3.32001000 | -1.69949700| 1.03757900   | -3.00919800           | -1.80744900     |
| H       | 0.99248100  | -2.52676900 | -2.78838400| 2.08913700   | -3.15493800           | -1.53857100     |
| H       | 0.56561300  | -3.99631100 | -1.88642300| 0.28266000   | -2.91258700           | 1.17735600      |
| Atom | X    | Y    | Z    | Atom | X    | Y    | Z    | Atom | X    | Y    | Z    |
|------|------|------|------|------|------|------|------|------|------|------|------|
| H    | -0.17788200 | -2.36836200 | 2.00590700 | H    | -0.20485800 | -3.89159000 | 1.09382600 |
| H    | 1.33775000 | -3.07978600 | 1.42161200 | C    | 0.31761000 | 3.14165500 | 1.44998000 |
| H    | -0.12530600 | 4.14366300 | 1.49790600 | H    | -0.04267800 | 2.56183800 | 2.30398900 |
| H    | 1.40546800 | 3.22854000 | 1.53187700 | C    | 0.51857800 | 3.40960100 | -1.62975900 |
| H    | 1.60943000 | 3.48843500 | -1.57200500 | H    | 0.25650100 | 2.99775900 | -2.60911800 |
| H    | 0.09202300 | 4.41710700 | -1.55222900 | C    | 6.25350900 | 1.51109100 | 0.95342600 |
| H    | 6.00592700 | 1.35321800 | 2.00764800 | H    | 6.43971700 | 0.53335400 | 0.50060500 |
| H    | 7.18419200 | 2.09041400 | 0.91104900 | C    | 4.54281500 | 4.11697900 | 0.87693500 |
| H    | 4.24800300 | 3.98101700 | 1.92231000 | H    | 5.43347700 | 4.75493500 | 0.85521200 |
| H    | 3.73241000 | 4.64529900 | 0.36510600 | C    | 5.29735700 | 2.66543900 | -1.77832900 |
| H    | 5.56316300 | 1.71356300 | -2.24631400 | H    | 4.45076000 | 3.09225700 | -2.32598300 |
| H    | 6.14973000 | 3.34554800 | -1.89352200 | C    | 3.76778200 | 0.74655600 | 0.03045700 |
| C    | 4.34332000 | -1.30087600 | -1.13787500 | C    | 4.11745100 | -1.27611700 | 1.30430100 |
| C    | 5.25259600 | -2.37028200 | -1.01421800 | C    | 5.02196600 | -2.34288300 | 1.38157800 |
| C    | 5.60188800 | -2.90817300 | 0.23058900 | H    | 5.69361200 | -2.78761300 | -1.91614700 |
| H    | 5.28257900 | -2.74249400 | 2.35852000 | C    | 4.01117600 | -0.79300000 | -2.52327100 |
| H    | 3.27922600 | -1.44717200 | -3.01013400 | H    | 3.57369100 | 0.20628300 | -2.49842500 |
| H    | 4.90485400 | -0.77618100 | -3.15645500 | C    | 3.51679300 | 0.70901300 | 2.56895400 |
| H    | 3.64282100 | 0.37651200 | 2.62273900 | H    | 2.43763800 | -0.89318800 | 2.60627700 |
| H    | 3.97344500 | -1.15686900 | 3.45597700 | C    | 6.56724700 | -4.06453800 | 0.34314800 |
| H    | 7.38257900 | -3.83671500 | 1.03856600 | H    | 6.06340200 | 4.96317700 | 0.71820800 |
| H    | 7.01028500 | -4.31168900 | -0.62535200 |
**Table S7.** The Cartesian coordinates for compound 6 together with the zero point vibrational energy corrected absolute energies in Hartree.

\[ E = -2020.033757 \text{ a.u.} \]

| Element | X       | Y       | Z       | Energy  | Si       | 3.10981400 | 0.28478400 | 1.13220400 |
|---------|---------|---------|---------|---------|---------|------------|------------|------------|
| Si      | 1.42398500 | -2.71745900 | -0.94431200 |       | Si       | 3.10981400 | 0.28478400 | 1.13220400 |
| Si      | 1.25147800 | -0.54038400 | -0.05274400 |       | C       | -0.19248300 | 0.49198000 | -0.10874900 |
| O       | -0.03522600 | 1.82080500 | 0.21967500 |       | Si       | 0.19636500 | 3.11834500 | -0.84103300 |
| C       | 0.73431900 | -4.09395900 | 0.15538700 |       | H       | 1.21589600 | -4.09107000 | 1.13738500 |
| H       | -0.34232400 | -3.99731000 | 0.31241800 |       | H       | 0.92249200 | -5.06816500 | -0.30955500 |
| C       | 0.65929800 | -2.84330000 | -2.67301300 |       | H       | 1.08972800 | -2.09173300 | -3.34076600 |
| H       | 0.87601900 | -3.83177400 | -3.09353800 |       | H       | -0.42521600 | -2.71119900 | -2.67600500 |
| C       | 4.63610600 | 0.56815500 | 0.04760000 |       | H       | 5.47661500 | 0.90630500 | 0.66393200 |
| H       | 4.94269900 | -0.35218400 | -0.45712000 |       | H       | 4.45360000 | 1.32592400 | -0.71882900 |
| C       | 2.71855500 | 1.86744100 | 2.08767300 |       | H       | 2.63867800 | 2.73627900 | 1.43180800 |
| H       | 1.77771300 | 1.77819100 | 2.63601800 |       | H       | 3.52153100 | 2.06919900 | 2.80780900 |
| C       | -1.07109400 | 3.10540700 | -2.22970500 |       | H       | -0.94164900 | 2.23314600 | -2.87798300 |
| H       | -2.09926500 | 3.11388800 | -1.85893500 |       | H       | -0.93474400 | 3.99640000 | -2.85229100 |
| C       | 1.90446600 | 3.05866900 | -1.61674400 |       | H       | 2.08053500 | 2.09615900 | -2.10594200 |
| H       | 1.99032200 | 3.84068100 | -2.37873900 |       | H       | 2.69968200 | 3.21815400 | -0.88476300 |
| C       | -0.01143200 | 4.62462200 | 0.25047800 |       | H       | -1.02120600 | 4.67085900 | 0.66792000 |
| H       | 0.69416800 | 4.60226900 | 1.08538800 |       | H       | 0.16305500 | 5.54476900 | -0.31576800 |
| C       | 3.54897900 | -1.04152900 | 2.41587100 |       | H       | 2.72377100 | -1.19334400 | 3.11760600 |
| H       | 3.78126700 | -2.00722200 | 1.95888800 |       | H       | 4.42723700 | -0.72682600 | 2.99068200 |
| C       | 3.28115000 | -3.03163600 | -1.15763500 |       | H       | 3.73885700 | -2.29766100 | -1.82690100 |
| H       | 3.81947200 | -3.00456600 | -0.20669300 |       | H       | 3.43429200 | -4.02390000 | -1.59612100 |
| C       | -1.63130200 | 0.13779300 | -0.44879600 |       | H       | -1.77893600 | 0.39918700 | -1.51034500 |
| C       | -2.67159100 | 0.96617600 | 0.34908400 |       | C       | -2.00391900 | -1.35314200 | -0.29923800 |
| H       | -2.41395300 | 2.02577600 | 0.28898800 |       | C       | -2.69542800 | 0.53819700 | 1.82188900 |
| C       | -4.05651000 | 0.74268900 | -0.27228300 |       | H       | -1.26951600 | -1.96473600 | -0.83258900 |
| C       | -2.05090500 | -1.77729200 | 1.17604300 |       | C       | -3.39005000 | -1.57838700 | -0.92324000 |
| H       | -3.41176000 | 1.16200700 | 2.37145900 |       | H       | -1.71162500 | 0.70966000 | 2.27597300 |
| C       | -3.09129100 | -0.93941300 | 1.92592100 |       | H       | -4.05764600 | 1.07004600 | -1.32003000 |
| X  | Y  | Z   | X  | Y  | Z   |
|----|----|-----|----|----|-----|
| -4.799968 | 1.354983 | 0.253782 | -4.438997 | -0.739174 | -0.180723 |
| -1.066585 | -1.655313 | 1.639091 | -2.309209 | -2.842102 | 1.240069 |
| -3.374599 | -1.307838 | -1.986788 | -3.652437 | -2.642214 | -0.867633 |
| -3.115548 | -1.241940 | 2.979761 | -4.473977 | -1.155283 | 1.296645 |
| -5.424983 | -0.897325 | -0.634044 | -4.766176 | -2.209326 | 1.385223 |
| -5.229590 | -0.567678 | 1.833383 |