Supporting Information:

Site-Selective Functionalization of Si_6R_6 Siliconoids

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Contents

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. NMR spectra were recorded on a Bruker Avance III 300 NMR spectrometer (^{1}H = 300.13 MHz, ^{13}C = 75.46 MHz, ^{29}Si = 59.6 MHz, ^{7}Li = 116.64 MHz, ^{11}B = 96.3 MHz) and/or a Bruker Avance IV 400 NMR spectrometer (^{1}H = 400.13 MHz, ^{13}C = 100.6 MHz, ^{29}Si = 59.6 MHz) UV/Vis spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer in quartz cells with a path length of 0.1 cm. Infrared spectra were measured with a Bruker Vertex 79 in a platinum ATR diamond cell. Elemental analyses were performed on an elemental analyzer Leco CHN-900 and/or an elementar vario Micro Cube. They are mostly low in carbon, which is tentatively attributed to incomplete combustion due to the formation of silicon carbide. Compounds **1, 2** and **3** were prepared according to our published procedures.[21, 22, 31, 32]

General procedure for the synthesis of *privo* and *ligato* functionalized siliconoids **5a-b** and **6a-f**.

The respective compounds are prepared by treating 1 equivalent of the anionic siliconoid **3Li** or **4Li** with 1 equivalent of Me_3SiCl (**5a**, **6a**), benzoylchloride (**5b**, **6b**), pivaloyl chloride (**6c),** $(Me_2N)_2PCl$ (**6d**), $SiCl_4$ (**6e**), or $H_3B{\cdot}SMe_2$ (**6f**) in benzene or toluene at room temperature. After stirring for the indicated period of time, all volatiles are removed in vacuo and the crude product is filtered from hexane and crystallized from hexane or pentane.

***Preparation of ligato*-Trimethylsilyl-2,2,5,5,6-pentakis(2',4',6'-triisopropylphenyl)tetracyclo [2.2.0.0^{1,3}.0^{3,6}]hexasilane (5a)**

Quantities: **3Li**, 325 mg (0.21 mmol); Me_3SiCl 25.24 mg (0.23 mmol); benzene (5 mL); stirring 4 h; crystallization from pentane. Yield: 120 mg (45 %) red crystals. **^{1}H-NMR** (300.13 MHz, tol-d_8, 223 K): δ = 7.61, 7.28 ($C_{10}H_8$), 7.21 (m, overlapping with $C_{10}H_8$, 3 H, Ar-H), 7.09 – 6.81 (m, overlapping with benzene-d_6, 12 H, Tip-CH), 5.32 (sept, $^3J_{HH}$ = 6.44 , 1H, Tip-*i*Pr-$CHMe_2$), 5.07 (sept, $^3J_{HH}$ = 6.44, 1 H, Tip-*i*Pr-$CHMe_2$), 4.44 (sept, $^3J_{HH}$ = 6.44, 2 H, Tip-^{i}Pr-$CHMe_2$), 3.96 (sept, $^3J_{HH}$ = 6.44, 2 H, Tip-^{i}Pr-CH_3), 3.55 (sept, $^3J_{HH}$ = 6.44, 1H, Tip-^{i}Pr-$CHMe_2$), 3.28 (m, overlapping, together 3H, Tip-^{i}Pr-$CHMe_2$), 2.73 (m, overlapping, together 6H, Tip-^{i}Pr-$CHMe_2$), 2.22 (br, 2H, Tip-^{i}Pr-CH_3), 1.98 (br, 2H, Tip-^{i}Pr-CH_3), 1.76 (br, 3H, Tip-^{i}Pr-CH_3), 1.53 - 1.07 (br, together 96H, Tip-^{i}Pr-CH_3), 0.22 (s, 9H, Si-CH_3). **^{13}C-NMR** (75.46 MHz, tol-d_8, 223 K): δ = 156.47, 155.65, 154.41, 154.15, 153.82, 153.15, 152.95, 151.94, 151.59, 150.59, 150.42, 150.14, 148.99, 148.89, 139.32, 139.07 (Ar-C), 133.88, 128.15, 126.06 ($C_{10}H_8$), 123.61, 123.45, 123.21, 123.04, 122.47, 122.08, 121.91, 121.24, 121.05 (Ar-CH), 38.37, 36.22, 36.09, 35.90, 35.14, 34.84, 34.46, 34.25, 32.05, 29.31 (Tip-^{i}Pr-CH), 29.1884, 28.49, 27.26, 26.23, 25.35, 24.96, 24.58, 24.24, 24.05, 23.85, 23.42, 22.80 (Tip-^{i}Pr-CH_3), 22.56 (Tip-*i*Pr-CH_2), 14.12 (Tip-^{i}Pr-CH_3), 2.94 (Si-CH_3). **^{29}Si-NMR** (59.62 MHz, tol-d_8, 223 K): δ = 169.9 (s, *privo*-$SiTip_2$), 25.8 (s, *remoto*-$SiTip_2$), 11.3 (s, *ligato*-SiTip), −3.7 (s, *ligato*-Si-$SiMe_3$), −42.5 (s, $SiMe_3$), −257.8 (s, *nudo*-Si), −266.6 (s, *nudo*-Si). **Elemental analysis** calculated for $C_{81}H_{130}Si_7$: C, 74.81; H, 10.08. Found: C, 74.1; H, 9.95.

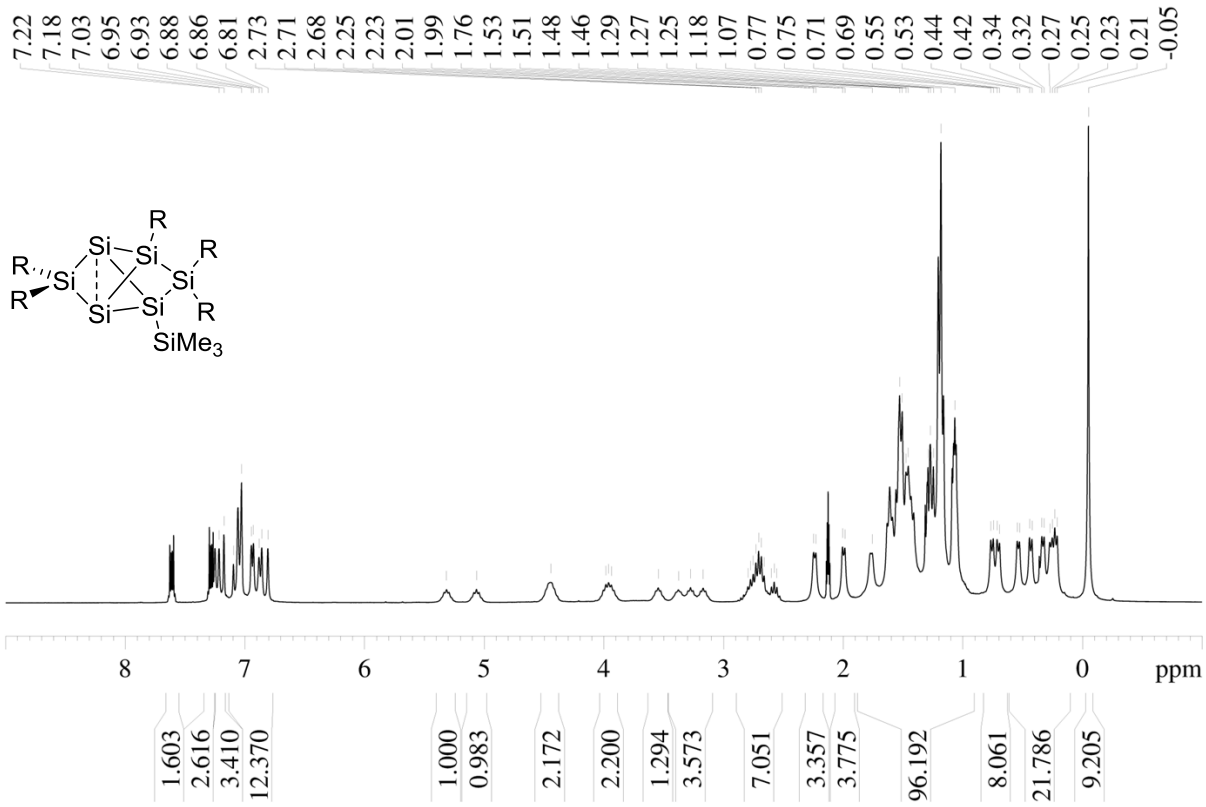

Figure S1: ^{1}H NMR of **5a** in C_6D_6 (300 MHZ).

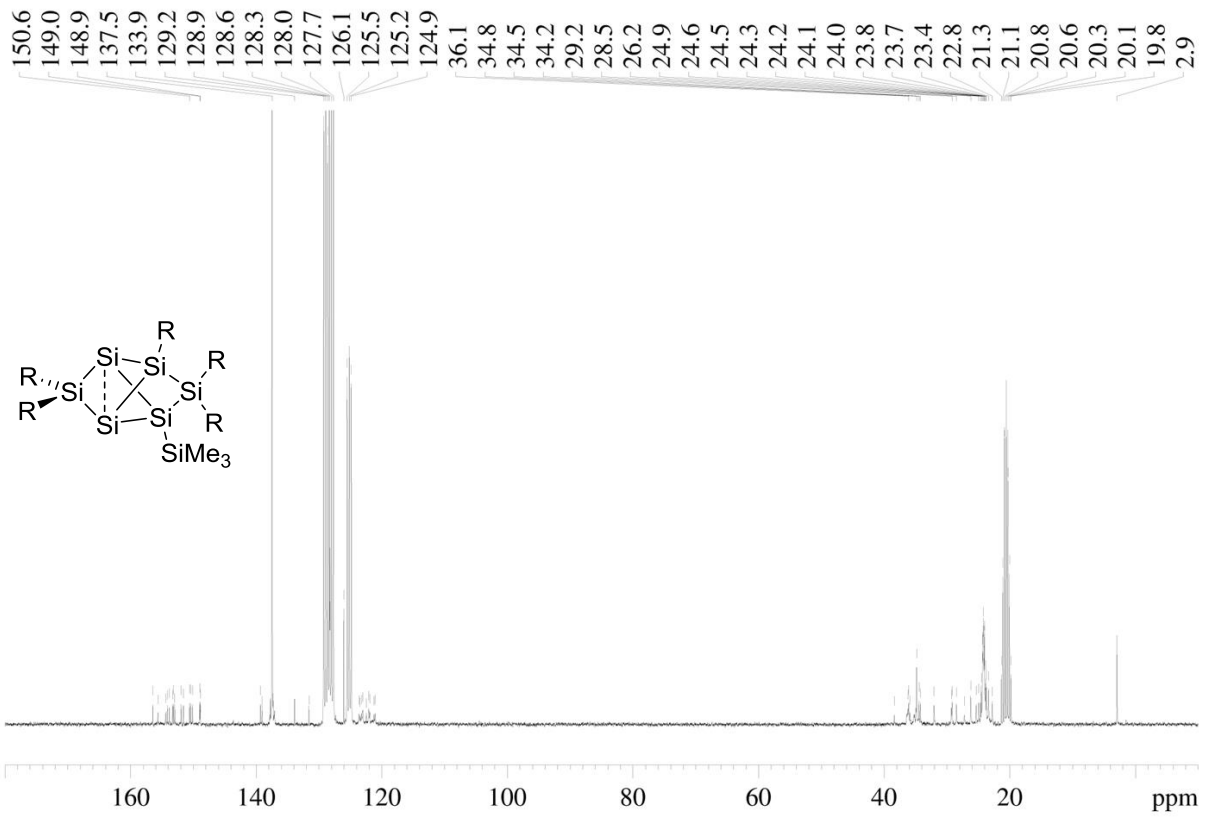

Figure S2: ^{13}C NMR of **5a** in C_6D_6 (75.5 MHZ).

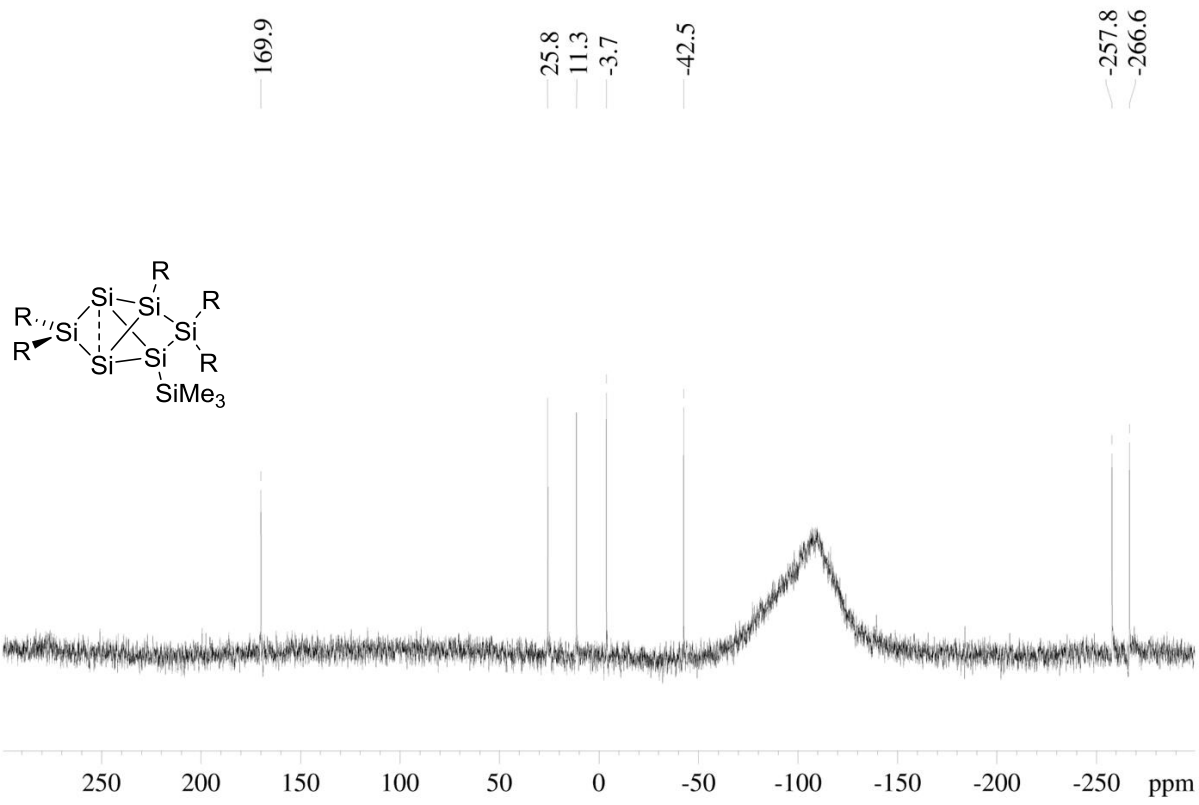

Figure S3: ^{29}Si NMR of **5a** in C_6D_6 (59.6 MHZ).

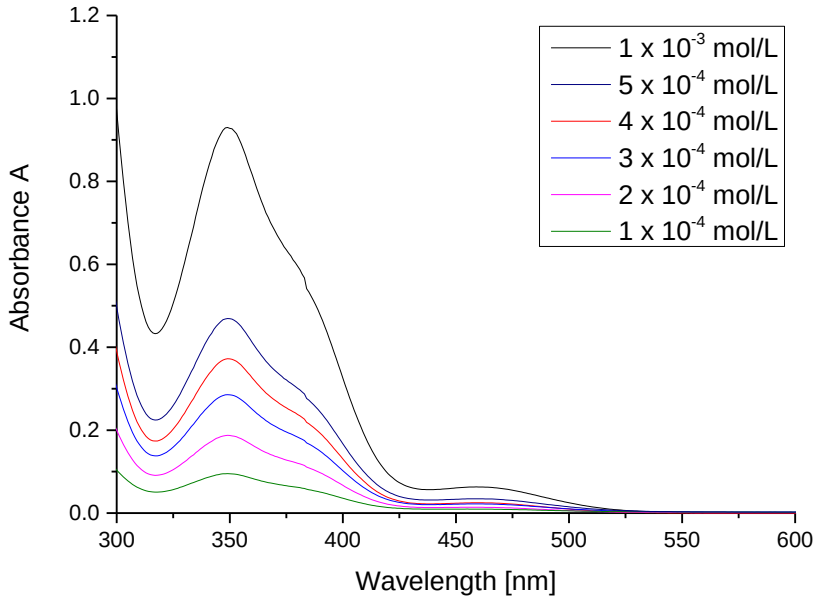

Figure S4: UV-Vis spectrum of **5a** in hexane at different concentrations.

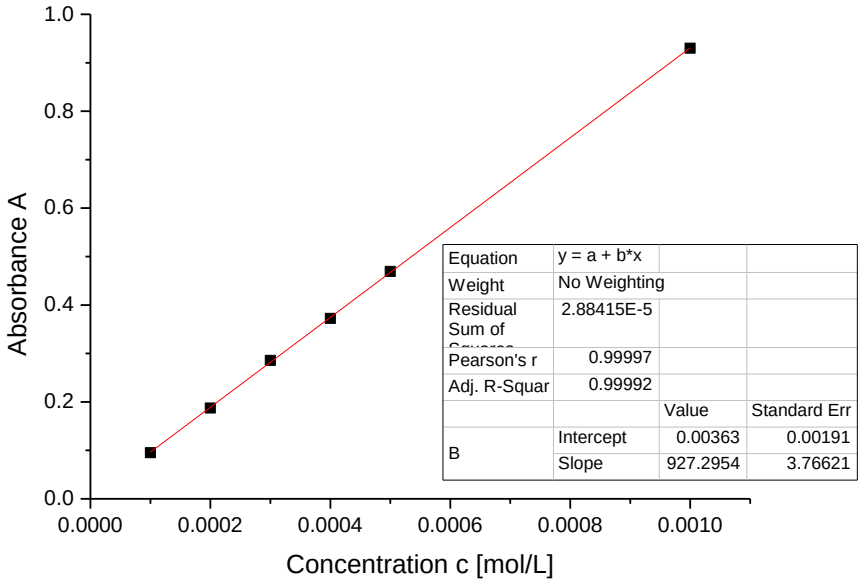

Figure S5: Determination of ε (9273 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 349 nm) of **5a** against concentration.

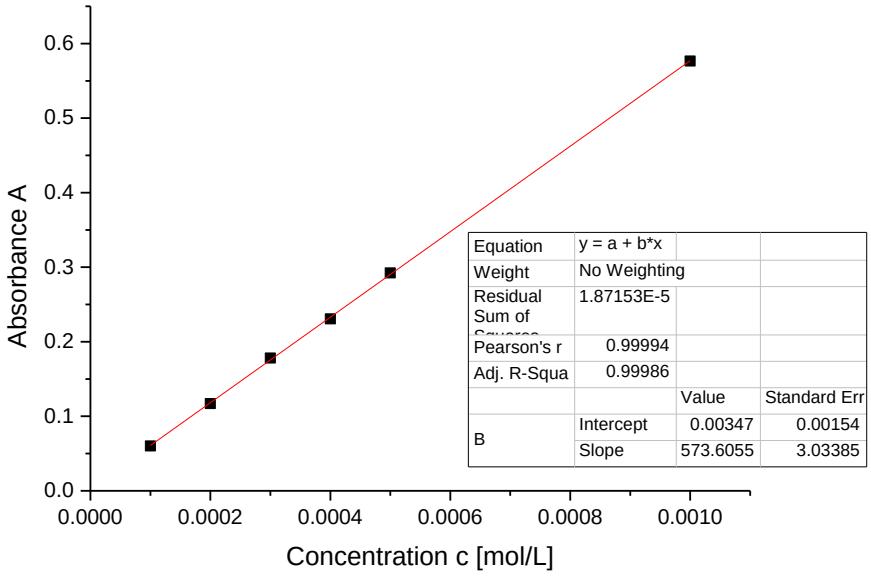

Figure S6: Determination of ε (5736 M^{-1} cm^{-1}) by linear regression of absorptions (λ= 382 nm) of **5a** against concentration.

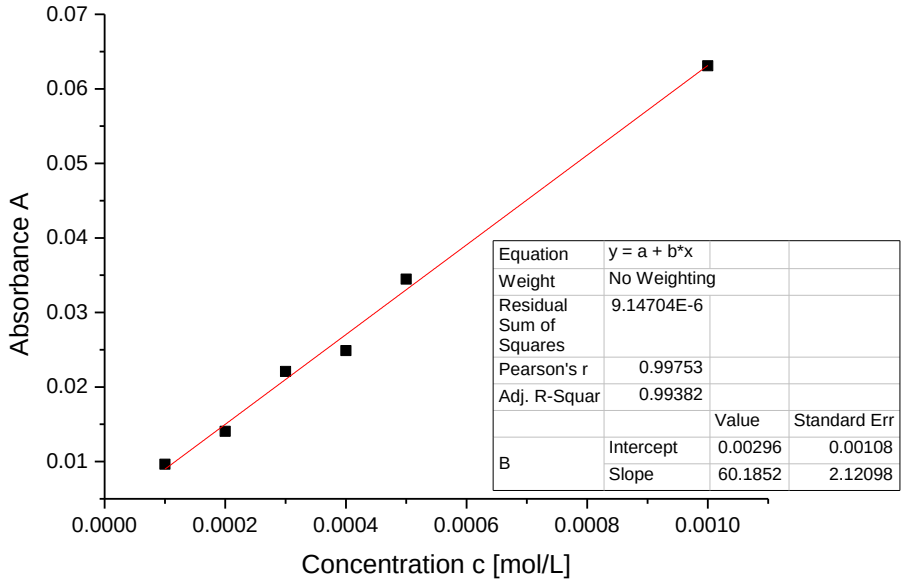

Figure S7: Determination of ε (602 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 459 nm) of **5a** against concentration.

Preparation of ligato-Benzoyl-2,2,5,5,6-pentakis(2',4',6'-triisopropyl-phenyl)tetracyclo [2.2.0.0^{1,3}.0^{3,6}] hexasilane (5b)

Quantities: **3Li**, 500 mg (0.32 mmol); benzoylchloride 49.24 mg (0.35 mmol); benzene; stirring 4 h; crystallization from pentane. Yield: 270 mg (66 %) red crystals.

^{1}H-NMR (300.13 MHz, benzene-d_6, 300 K): δ = 7.87 (m, 1H, Ar-H) 7.62, 7.24 ($C_{10}H_8$), 7.07 - 6.79 (br, overlapping with benzene-d_6, 8H Tip-CH), 6.73 (s, 1H, Tip-CH), 5.05 - 4.82 (m, 2H, Tip-^{i}Pr-$CHMe_2$), 4.38 - 4.13 (m, 2H, Tip-^{i}Pr-$CHMe_2$), 4.03 - 3.48 (m, 4H, Tip-^{i}Pr-$CHMe_2$), 3.22 - 2.89 (m, 2H, Tip-^{i}Pr-$CHMe_2$), 2.82 - 2.48 (m, 5H, Tip-^{i}Pr-$CHMe_2$) 2.33 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, Tip-^{i}Pr-$CHMe_2$), 2.1, 2.07 (br, 3H, Tip-^{i}Pr-CH_3), 1.87 - 0.12 (m, overlapping with hexane, 112H, Tip-^{i}Pr-CH_3). **^{13}C-NMR** (75.46 MHz, benzene-d_6, 300 K): δ = 155.99, 154. 64, 152.59, 151.01, 150.59, 150.23, 149.53, 143.49, 136.75, 136.38, 136.09 (Ar-C), 133.90 ($C_{10}H_8$), 132.42, 128.89 (Ar-CH), 128.19 ($C_{10}H_8$), 127.87, 127.55 (Ar-C), 125.88 ($C_{10}H_8$), 123.55, 123.09, 122.51, 122.24, 122.04, 121.32, 120.99 (br, Ar-CH), 37.61, 36.79, 36.39, 35.99, 35.52, 34.34, 34.59, 34.49, 34.27, 34.17, 33.86 (Tip-^{i}Pr-CH), 28.21, 28.11, 27.34, 27.19, 27.09, 25.54, 24.92, 24.74, 24.28, 24.28, 24.05, 23.86, 23.76, 23.53, 23.24 (Tip-^{i}Pr-CH_3), 22.54 (Tip-^{i}Pr-CH_2), 22.43, 14.11 (Tip-^{i}Pr-CH_3). **^{29}Si-NMR** (59.62 MHz, benzene-d_6, 300 K): δ = 174.7 (s, *privo*-$SiTip_2$), 17.1 (s, *ligato*-SiTip), 8.7 (s, *remoto*-$SiTip_2$), −26.5 (s, *ligato*-Si-C=O), −263.0 (s, *nudo*-Si), −279.0 (s, *nudo*-Si). **Elemental analysis** calculated for $C_{82}H_{120}OSi_6$: C, 76.33; H, 8.91. Found: C, 74.96; H, 9.60.

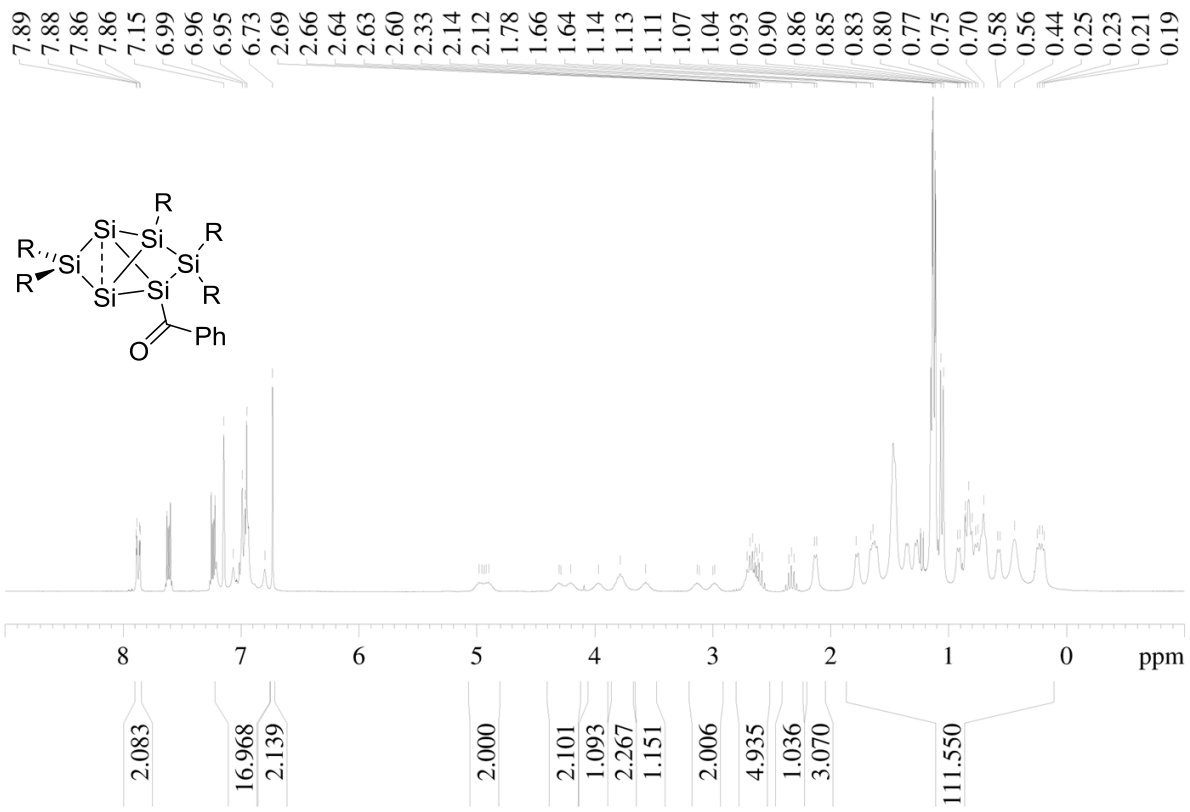

Figure S8: ^{1}H NMR of **5b** in C_6D_6 (300 MHZ).

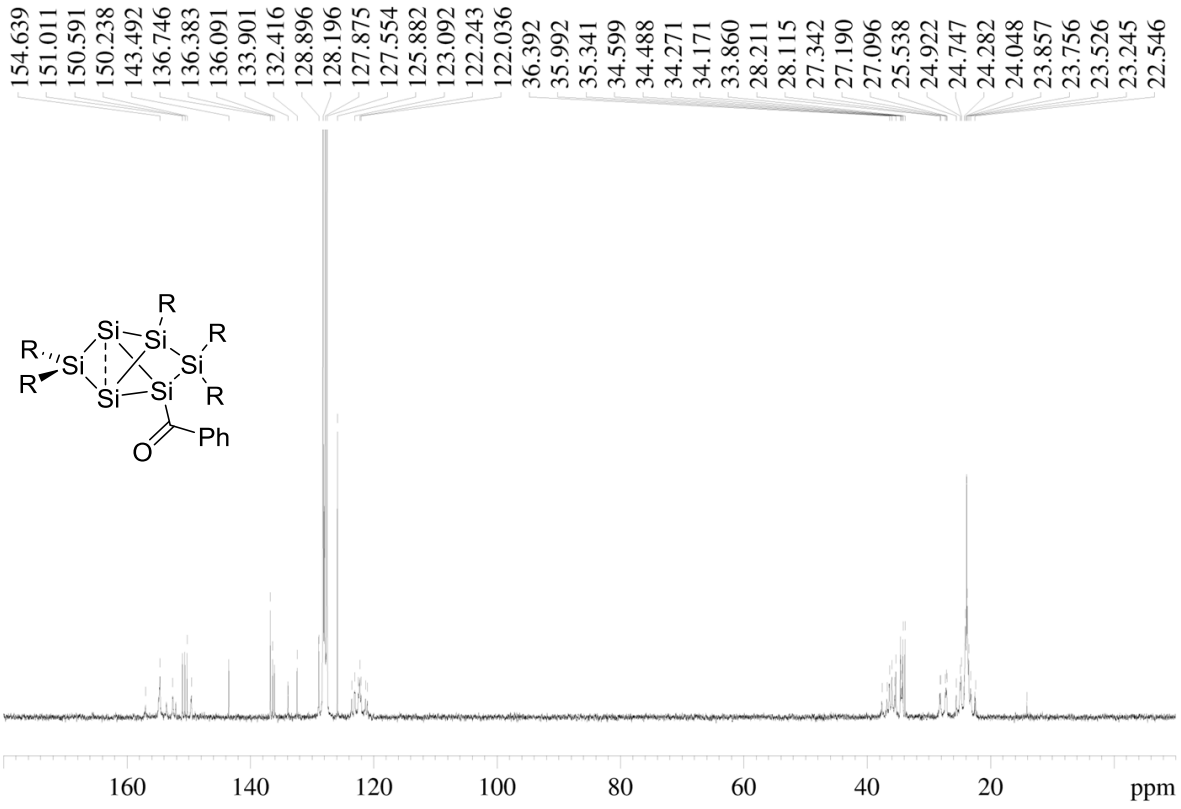

Figure S9: ^{13}C NMR of **5b** in C_6D_6 (75.5 MHZ).

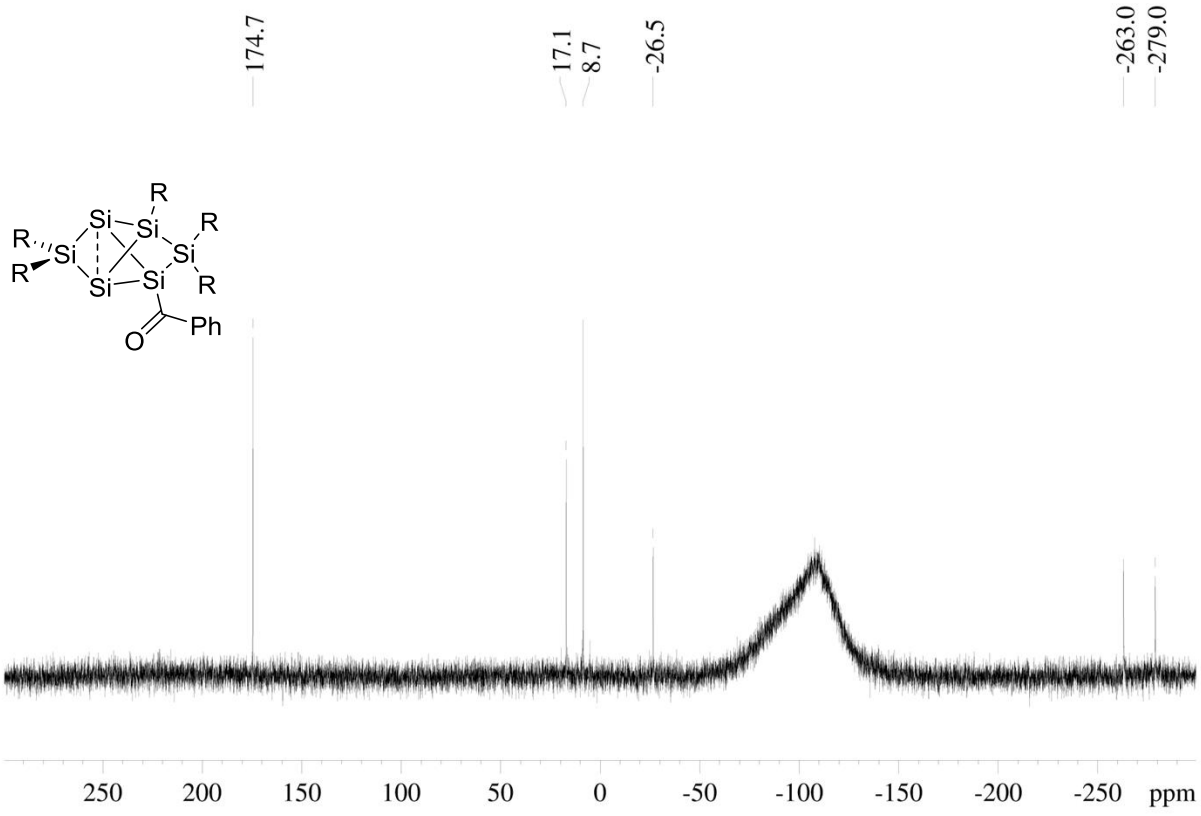

Figure S10: ^{29}Si NMR of **5b** in C_6D_6 (59.6 MHZ).

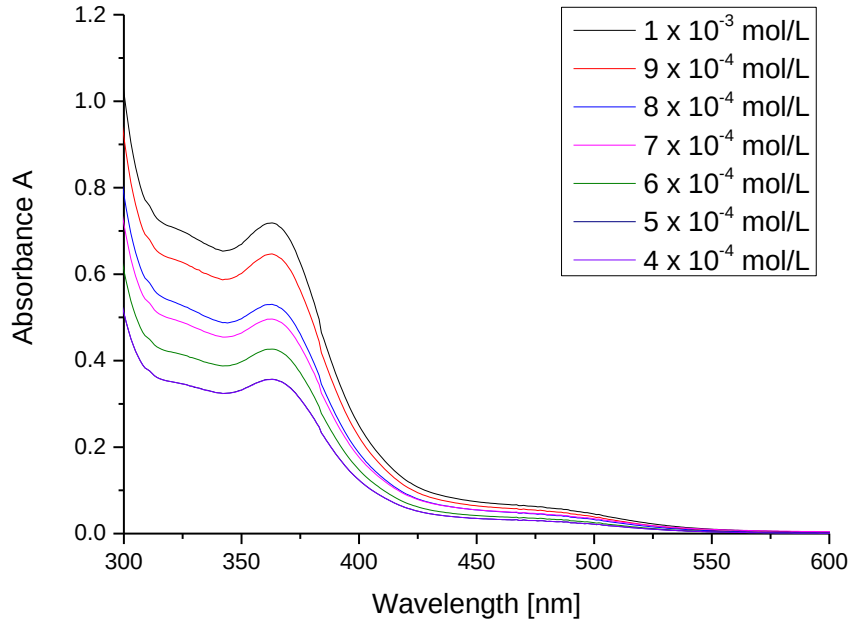

Figure S11: UV-Vis spectrum of **5b** in hexane at different concentrations.

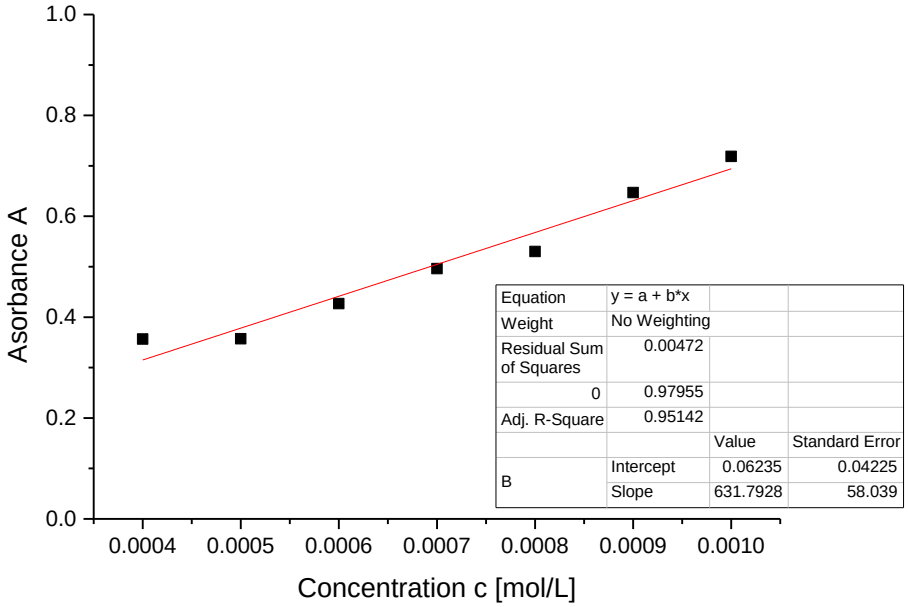

Figure S12: Determination of ε (6318 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 363 nm) of **5b** against concentration.

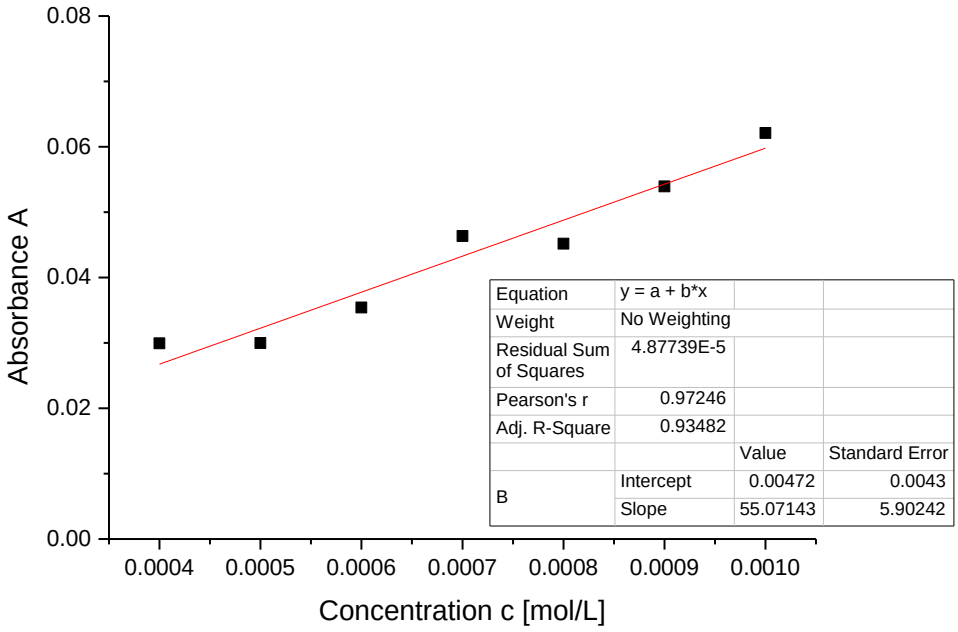

Figure S13: Determination of ε (551 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 477 nm) of **5b** against concentration.

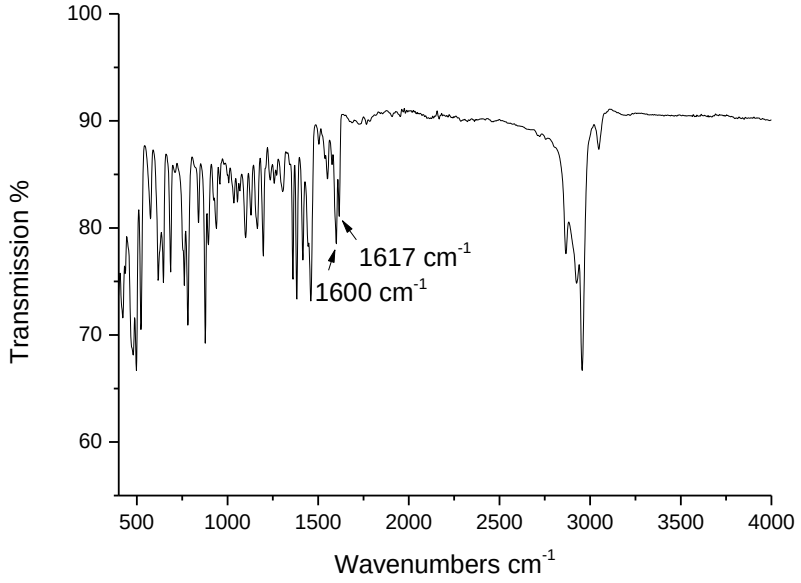

Figure S14: Infrared spectrum of **5b** (powder).

***Preparation of privo*-Lithiated anionic siliconoid 4Li**

***privo*-Lithio-2,4,5,5,6-pentakis(2',4',6'-triisopropylphenyl) tetracyclo [2.2.0.0^{1,3}.0^{3,6}]hexasilane (4Li)**

A solution of 2.39 g of siliconoid **3** (1.72 mmol) in 6 mL of Et_2O is cooled to −78°C. Lithium/naphthalene solution in thf (7.6 mL, 0.5 M, 3.78 mmol) is added dropwise and the resulting reaction mixture allowed warming to room temperature overnight with vigorous stirring. All volatiles are removed in vacuum and the resulting residue is washed three times with hexane. The final product **4Li** remains as pale-orange microcrystals. (1.42 g; 60% yield). **^{1}H NMR** (300.13 MHz, benzene-d_6, 300K): $\delta =$ 7.28 (d, 1H, Tip-H), 7.27 (d, 1H, Tip-H), 7.05 (d, 1H, Tip-H), 7.00 (s, 2H, Tip-H), 6.94 (d, 1H, Tip-H), 6.93 (s, 1H, Tip-H), 6.84, 6.83 (each d, each 1H, Tip-H), 5.45 (sept, 1H, ^{i}Pr-CH), 5.15 – 5.00 (m, 2H, ^{i}Pr-CH), 4.57 (sept, 1H, ^{i}Pr-CH), 4.45 (sept, 1H, ^{i}Pr-CH), 4.18 (sept, 2H, ^{i}Pr-CH), 3.64 (sept, 1H, ^{i}Pr-CH), 3.44 – 3.30 (m, 2H, ^{i}Pr-CH), 3.04 (t, 8H, thf), 2.83 – 2.65 (m, 5H, ^{i}Pr-CH), 2.17, 2.14 (each d, together 6H, ^{i}Pr-CH_3), 1.74 (t, 6H, ^{i}Pr-CH_3), 1.67, 1.62, 1.57 (each d, each 3H, ^{i}Pr-CH_3), 1.50 (d, 9H, ^{i}Pr-CH_3), 1.45 (d, 3H, ^{i}Pr-CH_3) 1.25 – 1.11 (m, 38H, ^{i}Pr-CH_3 and thf), 0.95 (d, 6H, ^{i}Pr-CH_3), 0.75 (t, 6H, ^{i}Pr-CH_3), 0.69 – 0.62 (m, 9H, ^{i}Pr-CH_3) 0.37, 0.34 (each d, together 6H, ^{i}Pr-CH_3). **^{7}Li NMR** (116.6 MHz, benzene-d_6, 300K): $\delta =$ 0.29 (s). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300K): $\delta =$ 158.3, 156.4, 156.1, 156.0, 153.8, 153.5, 152.5, 152.5, 151.0, 149.3, 148.8, 148.4, 148.3, 147.5, 146.3, 140.9, 139.8, 131.7, 131.5 (Ar-C), 123.0, 122.6, 122.4, 122.2, 121.4, 121.3, 120.9, 120.1, 119.8 (Ar-CH), 68.5 (thf), 36.8, 36.7, 36.5, 36.3, 36.1, 36.0, 35.1, 34.9, 34.8, 34.7, 34.6, 30.2, 28.1, 27.8, 27.5, 27.1, 26.7, 25.6 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3), 25.2 (thf), 25.2, 24.9, 24.9, 24.8, 24.7, 24.6, 24.5, 24.3, 24.2 23.6, 22.6, 22.0 (Tip-

^{i}Pr-CH and Tip-^{i}Pr-CH_3). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300K): δ = 267.9 (br, *privo*-SiTipLi), 100.2 (s, *ligato*-Si), 15.3 (s, *remoto*-Si), −43.8 (s, *ligato*-Si), −222.2 (s, *nudo*-Si), −231.4 (s, *nudo*-Si). **Elemental analysis** calculated for $C_{83}H_{131}LiO_2Si_6$: C, 74.60; H, 9.88. Found: C, 72.68; H, 9.51.

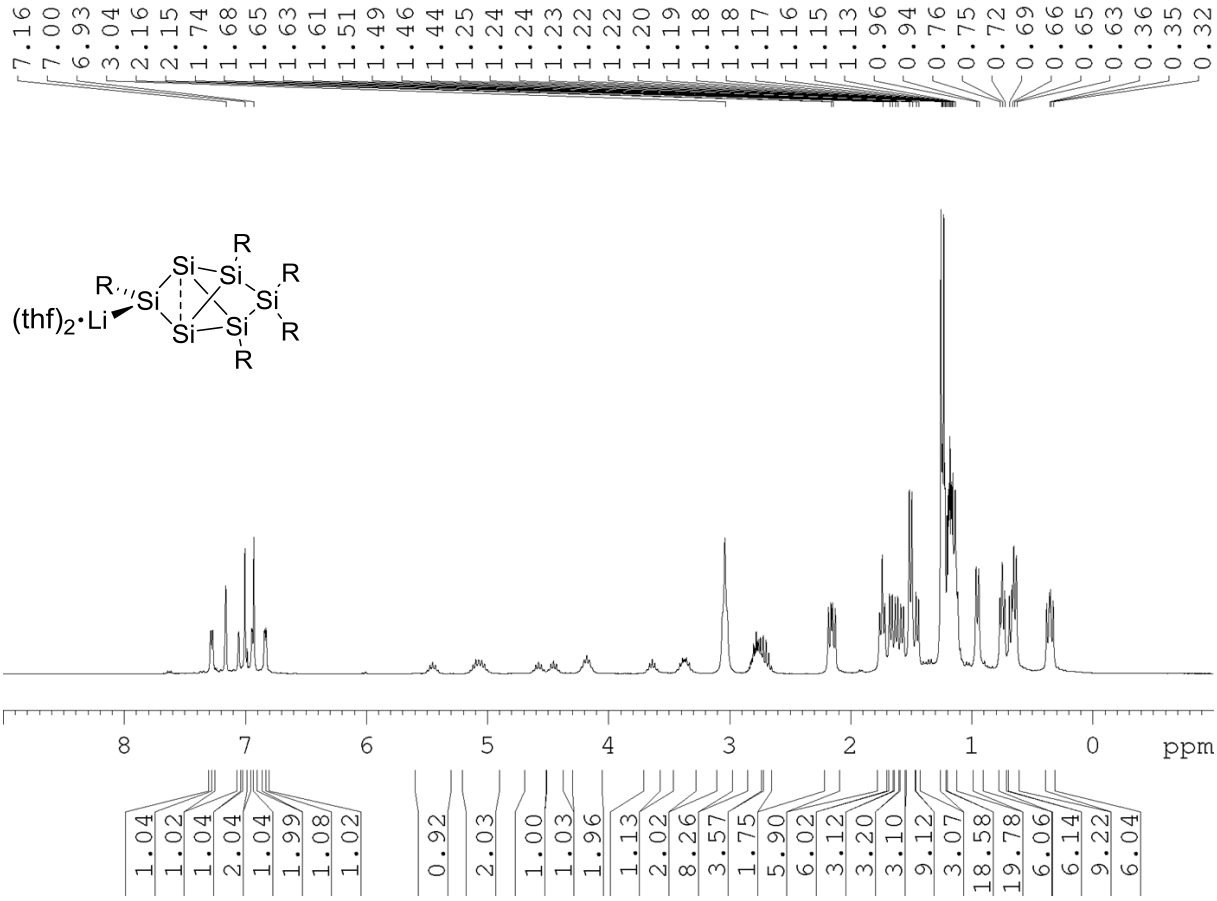

Figure S15: ^{1}H NMR of **4Li** in C_6D_6 (300 MHZ).

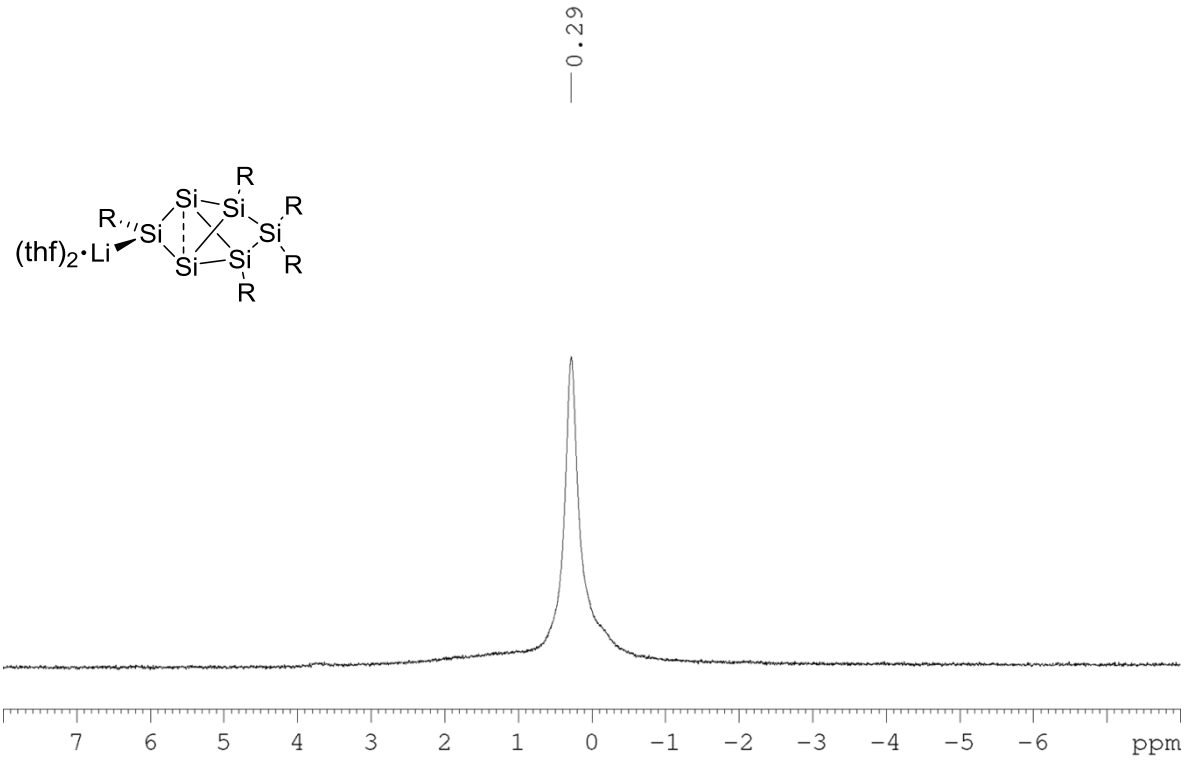

Figure S16: ^{7}Li NMR of **4Li** in C_6D_6 (116.6 MHZ).

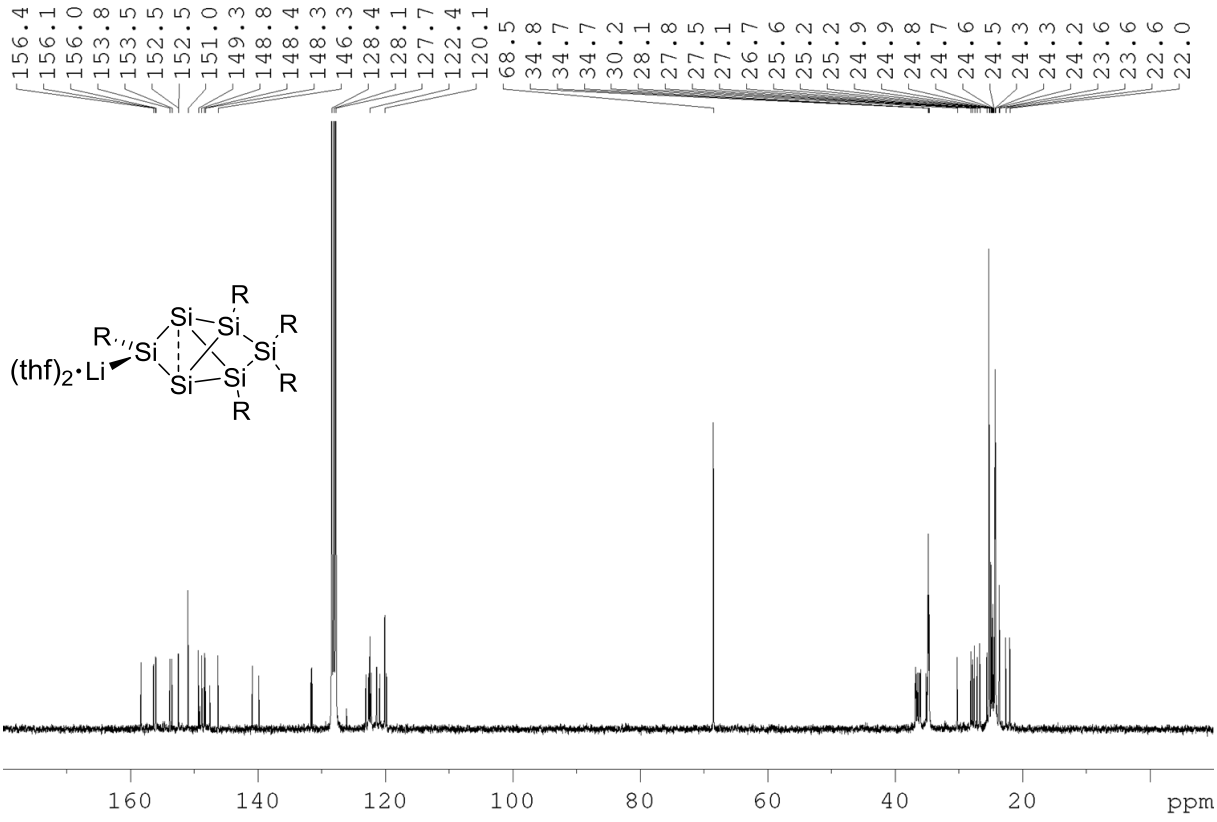

Figure S17: ^{13}C NMR of **4Li** in C_6D_6 (75.5 MHZ).

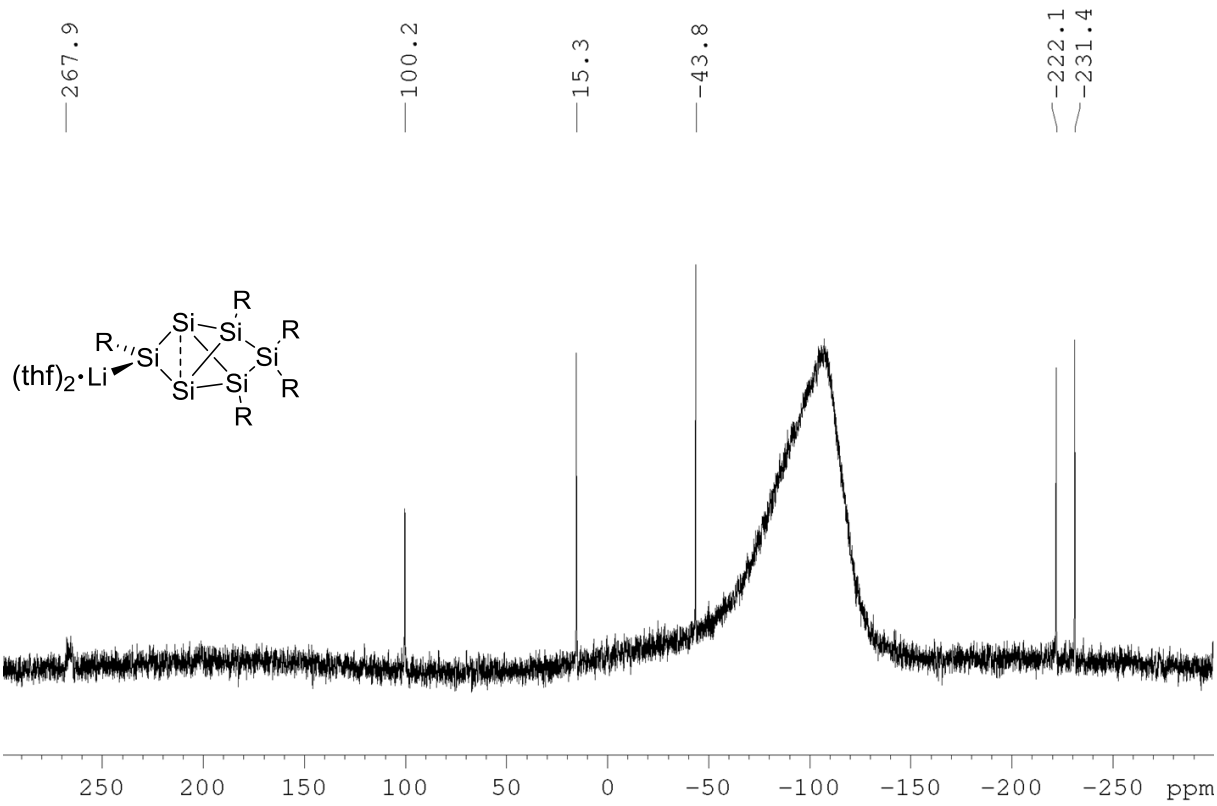

Figure S18: ^{29}Si NMR of **4Li** in C_6D_6 (59.6 MHZ).

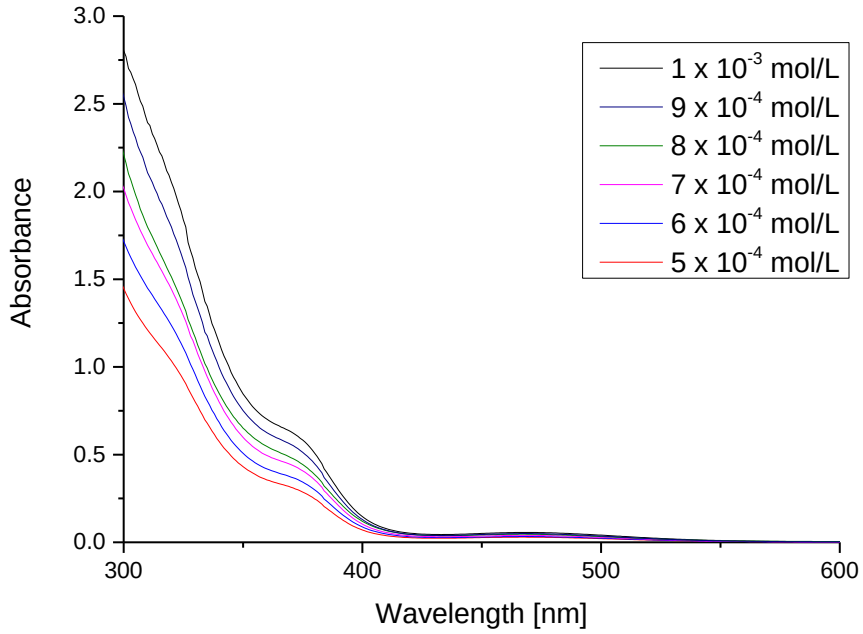

Figure S19: UV-Vis spectrum of **4Li** in hexane at different concentrations.

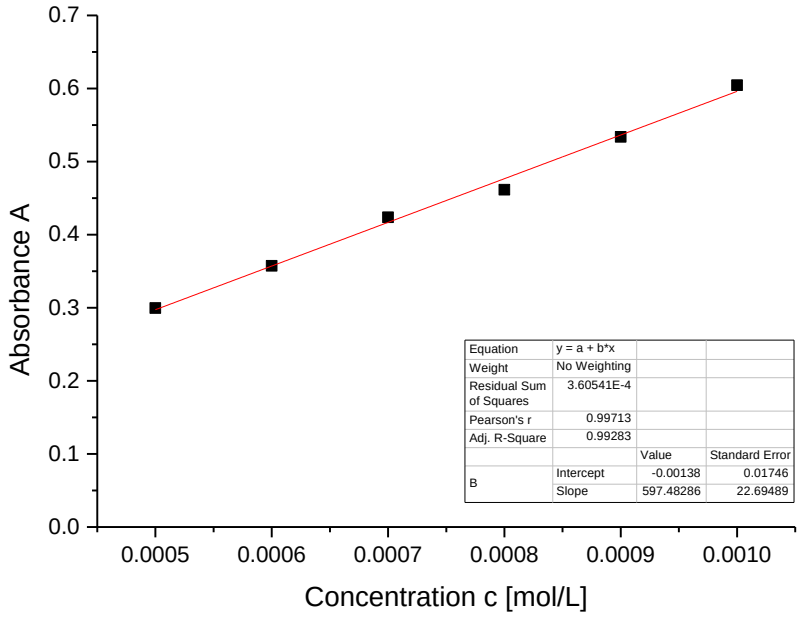

Figure S20: Determination of ε (5974 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 373 nm) of **4Li** against concentration.

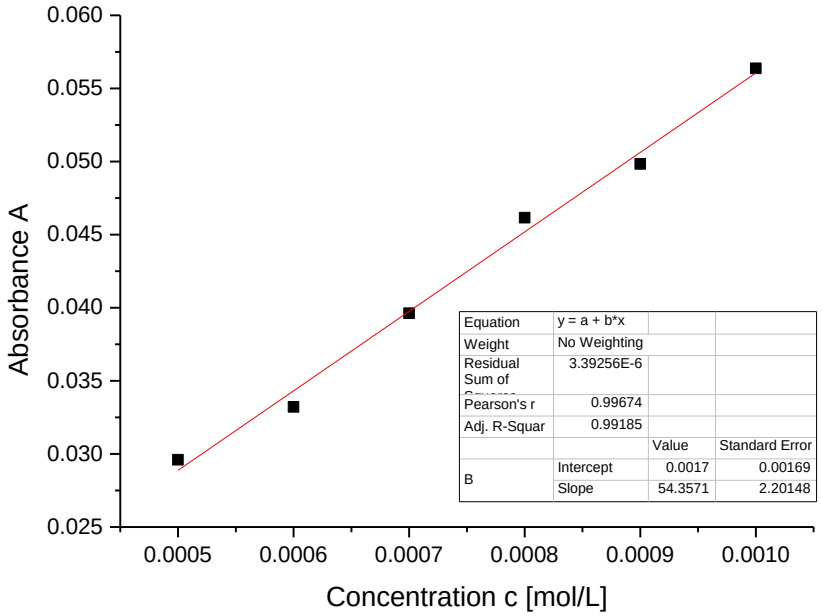

Figure S21: Determination of ε (543 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 468 nm) of **4Li** against concentration.

Preparaion of privo-Trimethylsilyl-2,4,5,5,6-pentakis(2',4',6'-triisopropylphenyl)tetracyclo [2.2.0.0^{1,3}.0^{3,6}]hexasilane (6a)

Quantities: **4Li**, 104 mg (0.078 mmol); Me_3SiCl 11 µL (9.39 mg, 0.086 mmol); toluene (2 mL); stirring 2.5 h; crystallization from hexane. Yield: 65 mg (66 %) orange crystals.

^{1}H NMR (300.13 MHz, benzene-d_6, 300K): δ = 7.27 (d, 2H, Tip-H), 7.07, 7.01, 6.97, 6.91, 6.83 (each d, each 1H, Tip-H), 6.80 (d, 2H, Tip-H), 6.75 (d, 1H, Tip-H), 4.93 (m, 2H, ^{i}Pr-CH), 4.37 (sept, 1H, ^{i}Pr-CH), 4.06 (sept, 2H, ^{i}Pr-CH), 3.74, 3.63 (each m, each 1H, ^{i}Pr-CH), 3.57 (t, 10H, thf), 3.37 (m, 2H, ^{i}Pr-CH), 2.71 (m, 6H, ^{i}Pr-CH), 2.14 (d, 3H, ^{i}Pr-CH_3), 2.05 (d, 3H, ^{i}Pr-CH_3), 1.82 (d, 3H, ^{i}Pr-CH_3), 1.67 (m, 7H, ^{i}Pr-CH_3), 1.57 (m, 14H, ^{i}Pr-CH_3), 1.43 (br, 10H, thf), 1.24, 1.21, 1.20, 1.18, 1.17, 1.16, 1.15, 1.13, 1.11, 1.08 (each d, overall 36H, ^{i}Pr-CH_3), 0.79 (d, 3H, ^{i}Pr-CH_3), 0.67 (t, 6H, ^{i}Pr-CH_3), 0.51 (m, 6H, ^{i}Pr-CH_3), 0.40, 0.38 (each d, overall 6H, ^{i}Pr-CH_3), 0.29 (d, 3H, ^{i}Pr-CH_3), −0.15 (s, 9H, $Si(CH_3)_3$). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300K): δ = 157.1, 156.9, 156.6, 156.1, 153.7, 153.2, 152.6, 152.0, 150.7, 150.2, 149.9, 149.4, 149.2, 138.7, 138.3, 134.8, 129.1, 126.9, 123.7 (Ar-C), 123.1, 122.8, 122.6, 122.4, 122.2, 122.1, 121.7, 121.6, 121.3, 121.0 (Ar-CH), 37.7, 37.6, 37.3, 36.9, 36.7, 36.4, 35.1, 35.0, 34.8, 34.7, 34.6, 34.5, 27.8, 27.6, 27.4, 27.1, 27.0, 26.5, 26.4, 26.2, 25.7, 25.4, 25.3, 25.1, 25.0, 24.9, 24.6, 24.4, 24.3, 24.1, 24.0, 23.9, 22.6 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3), 1.5 ($Si(CH_3)_3$. **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300K): δ = 193.6 (s, *privo*-Si(Tip)$SiMe_3$), 29.2 (s, *remoto*-$SiTip_2$), 22.4 (s, *ligato*-SiTip), −11.2 (s, $SiMe_3$), −15.9 (s, *ligato*-SiTip), −242.0 (s, *nudo*-Si), −253.3 (s, *nudo*-Si). **Elemental analysis** calculated for $C_{78}H_{124}Si_7$: C, 74.45; H, 9.93. Found: C, 71.65; H, 9.83.

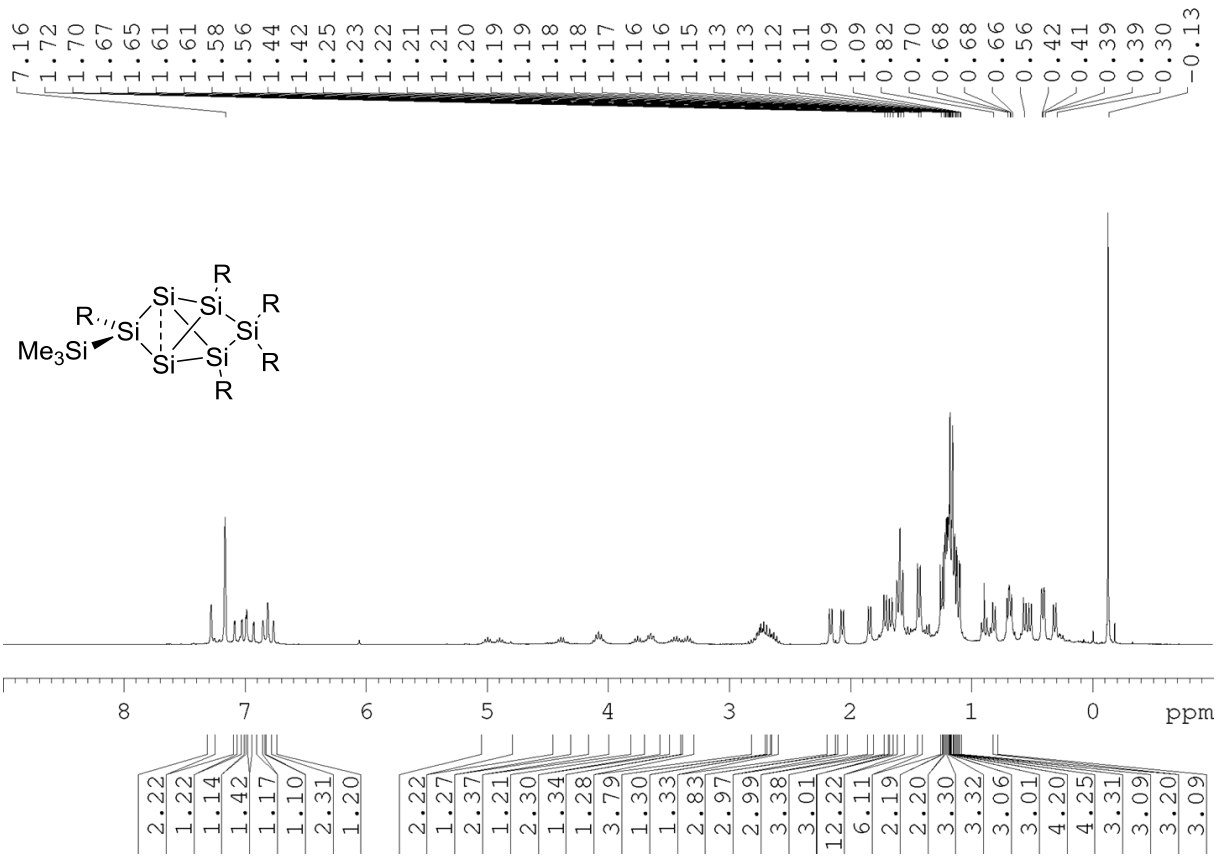

Figure S22: ^{1}H NMR of **6a** in C_6D_6 (300 MHZ).

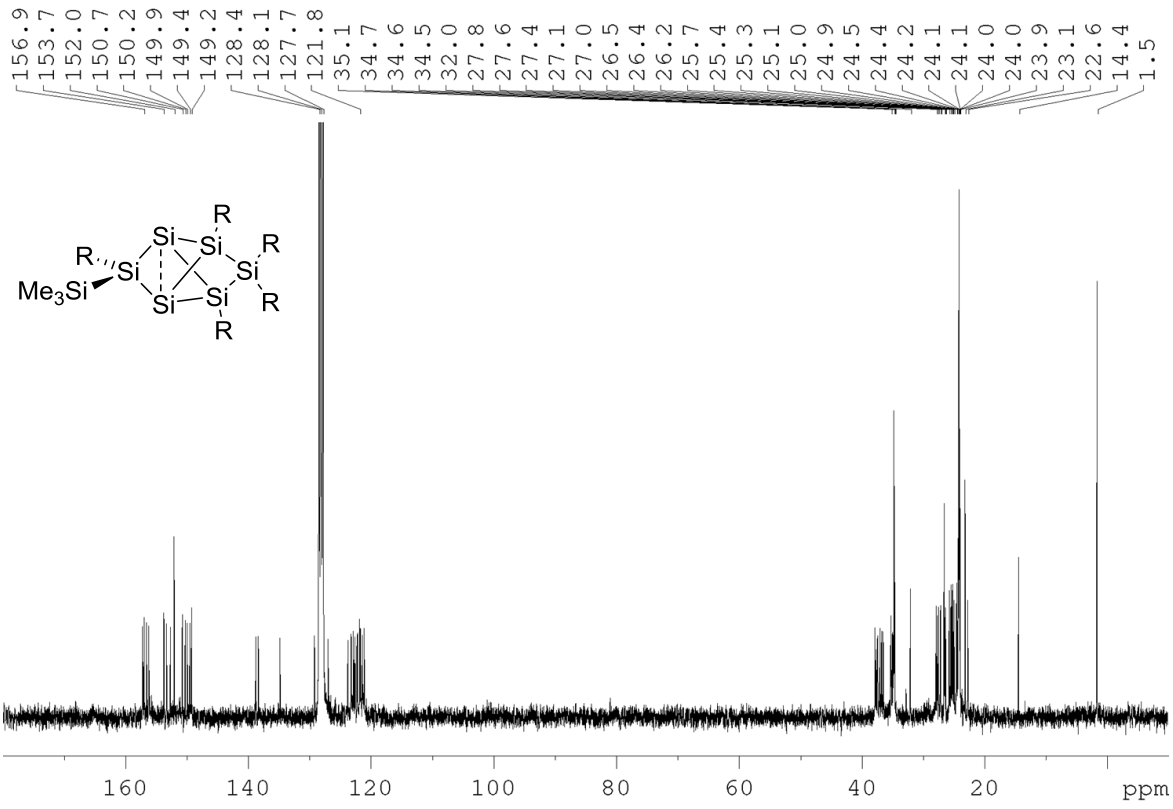

Figure S23: ^{13}C NMR of **6a** in C_6D_6 (75.5 MHZ).

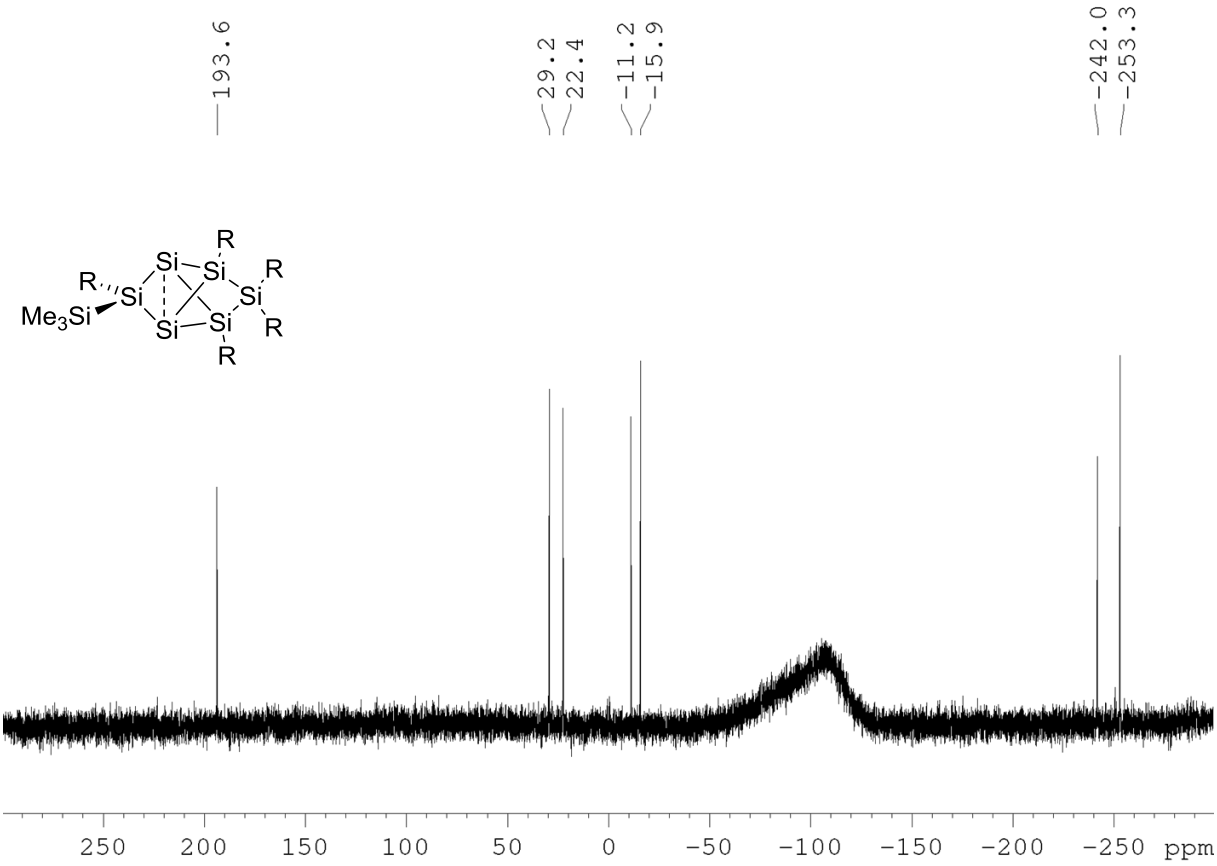

Figure S24: ^{29}Si NMR of **6a** in C_6D_6 (59.6 MHZ).

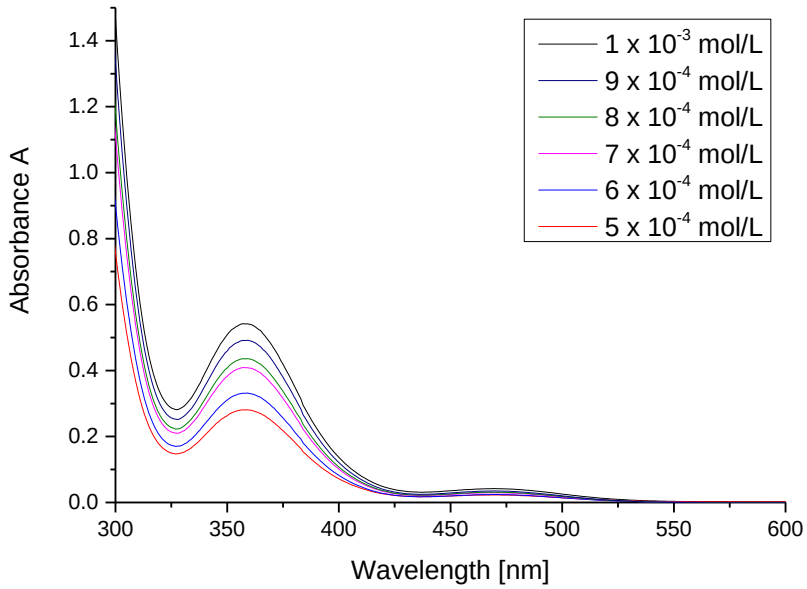

Figure S25: UV-Vis spectrum of **6a** in hexane at different concentrations.

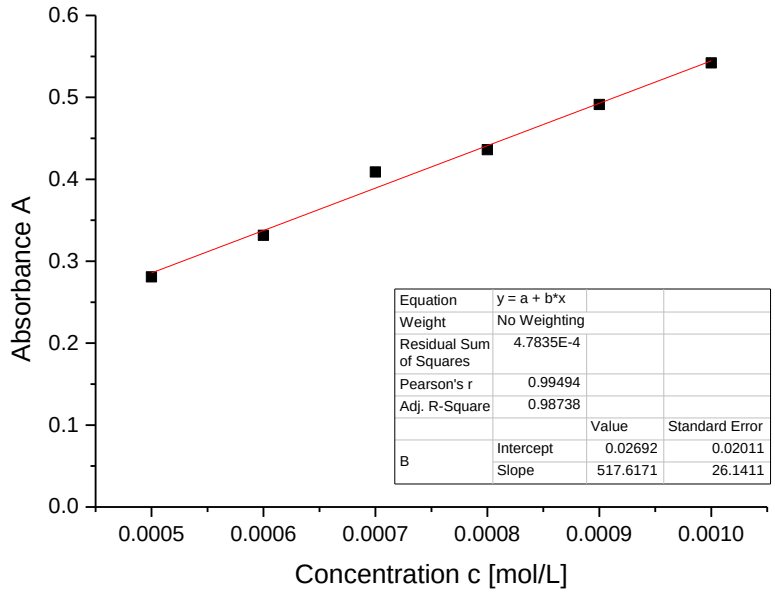

Figure S26: Determination of ε (5176 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 357 nm) of **6a** against concentration.

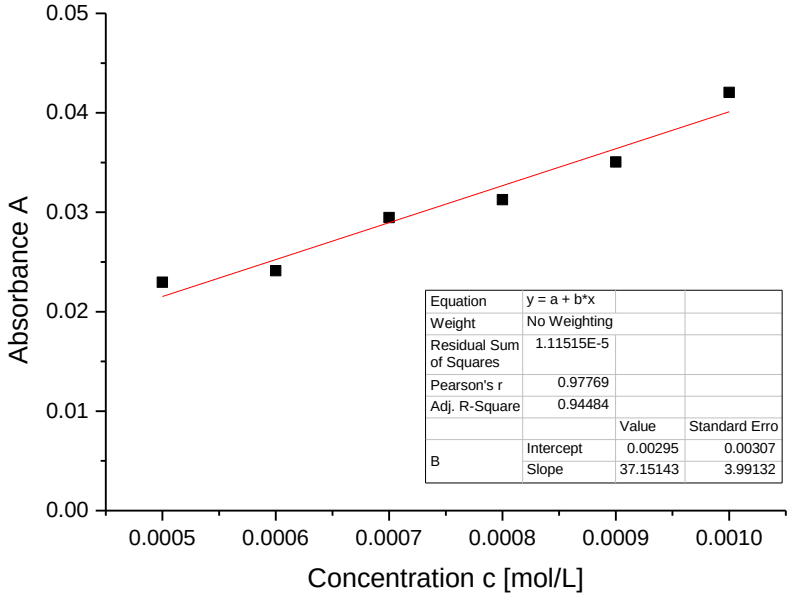

Figure S27: Determination of ε (371 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 469 nm) of **6a** against concentration.

Preparation of privo-Benzoyl-2,4,5,5,6-pentakis(2',4',6'-tri-iso-propylphenyl)tetracyclo [2.2.0.0^{1,3}.0^{3,6}] hexasilane (6b)

Quantities: **4Li**, 89.5 mg (0.06 mmol); benzoyl chloride 7.5 μL (9.1 mg, 0.065 mmol); toluene; stirring 0.5 h; The crude product was thoroughly dried in vacuo and characterized by multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, benzene-d_6, 300K): δ = 7.72 (s), 7.70 (d), 7.26 (d), 7.24 (br), 7.07 (d), 6.96 (d), 6.89 (d), 6.87 (s), 6.81 (t), 6.77 (m), 6.74 (s), 5.06 – 5.02 (m), 4.90 – 4.85 (m), 4.30 – 4.20 (m), 4.15 – 4.02 (m), 3.70 – 3.63 (m), 3.30 – 3.19 (m), 2.86 – 2.55 (m), 2.14 (d), 2.04 (d), 1.87 (d), 1.63 – 1.33 (m), 1.25 – 1.06 (m), 0.80 (d), 0.74 (d), 0.70 – 0.62 (m), 0.47 (d), 0.39 (d), 0.31 (d). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300 K): δ = 226.9 (CO), 156.8, 156.5, 156.1, 156.1, 154.3, 153.7, 153.4, 153.3, 152.2, 152.0, 151.4, 150.8, 150.6, 149.6, 149.5, 149.1, 140.5, 138.5, 138.4, 133.5, 132.4, 128.9, 126.5, 126.1, 123.5, 123.2, 122.9, 122.4, 122.2, 121.9, 121.5, 121.3, 121.2 (Ar-C and Ar-CH), 37.4, 37.1, 36.6, 35.2, 34.8, 34.6, 34.5 (Tip-*i*Pr-CH and Tip-*i*Pr-CH_3), 32.0 (hexane), 27.6, 27.4, 27.1, 26.7, 26.5, 26.1, 25.9, 25.7, 25.6, 25.4, 25.3, 24.9, 24.7, 24.5, 24.1, 24.1, 24.0, 23.9, 23.5, 23.1, 22.9, 22.7, 22.6 (Tip-*i*Pr-CH and Tip-*i*Pr-CH_3), 14.4 (hexane). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300 K): δ = 166.2 (s, *privo*-Si(Tip)COPh), 30.9 (s, *remoto*-$SiTip_2$), −3.6 (s, *ligato*-SiTip), −16.2 (s, *ligato*-SiTip) −269.5 (s, *nudo*-Si) −271.1 (s, *nudo*-Si).

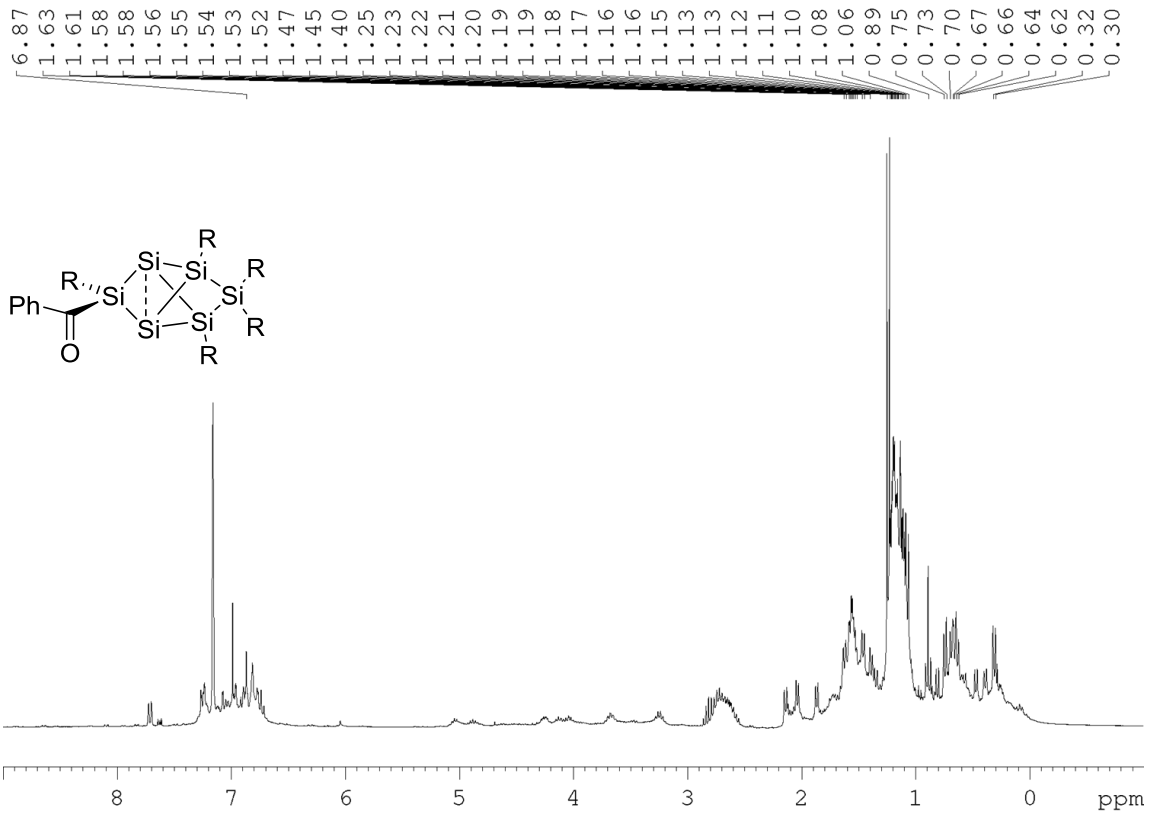

Figure S28: ^{1}H NMR of **6b** in C_6D_6 (300 MHZ).

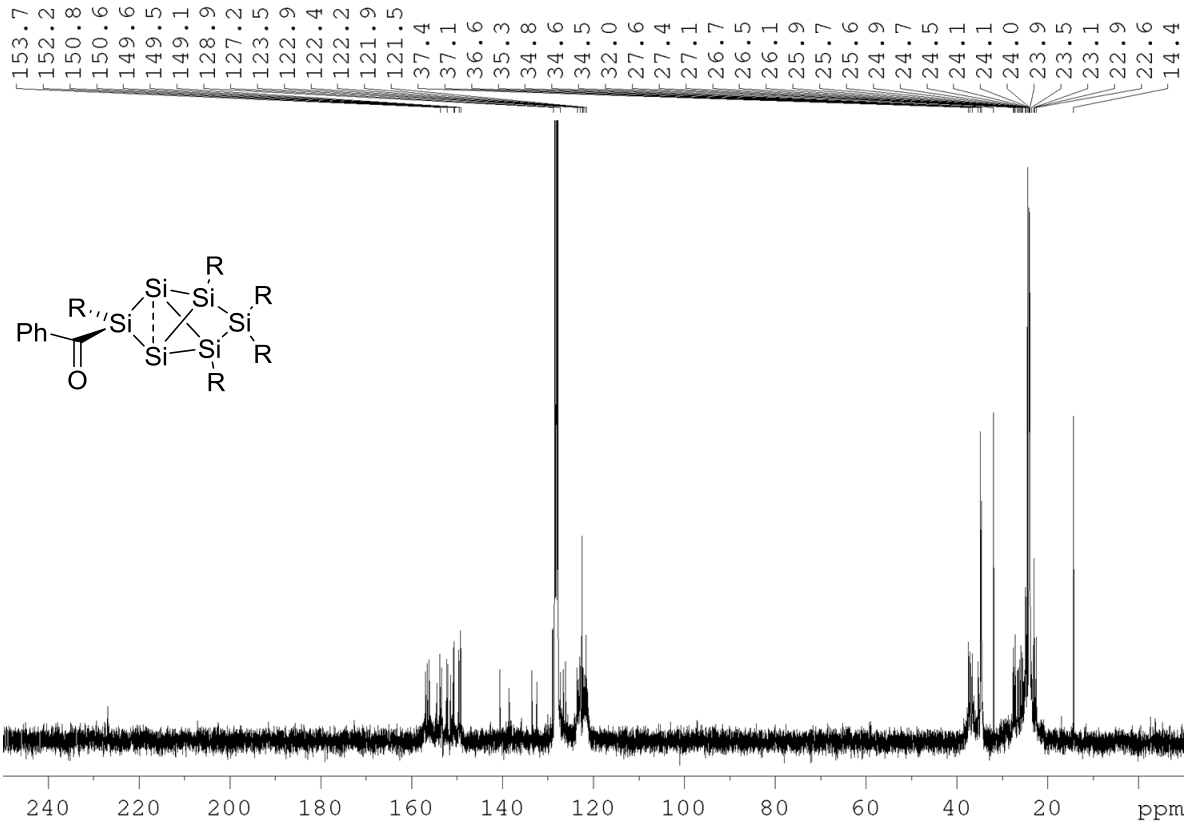

Figure S29: ^{13}C NMR of **6b** in C_6D_6 (75.5 MHZ).

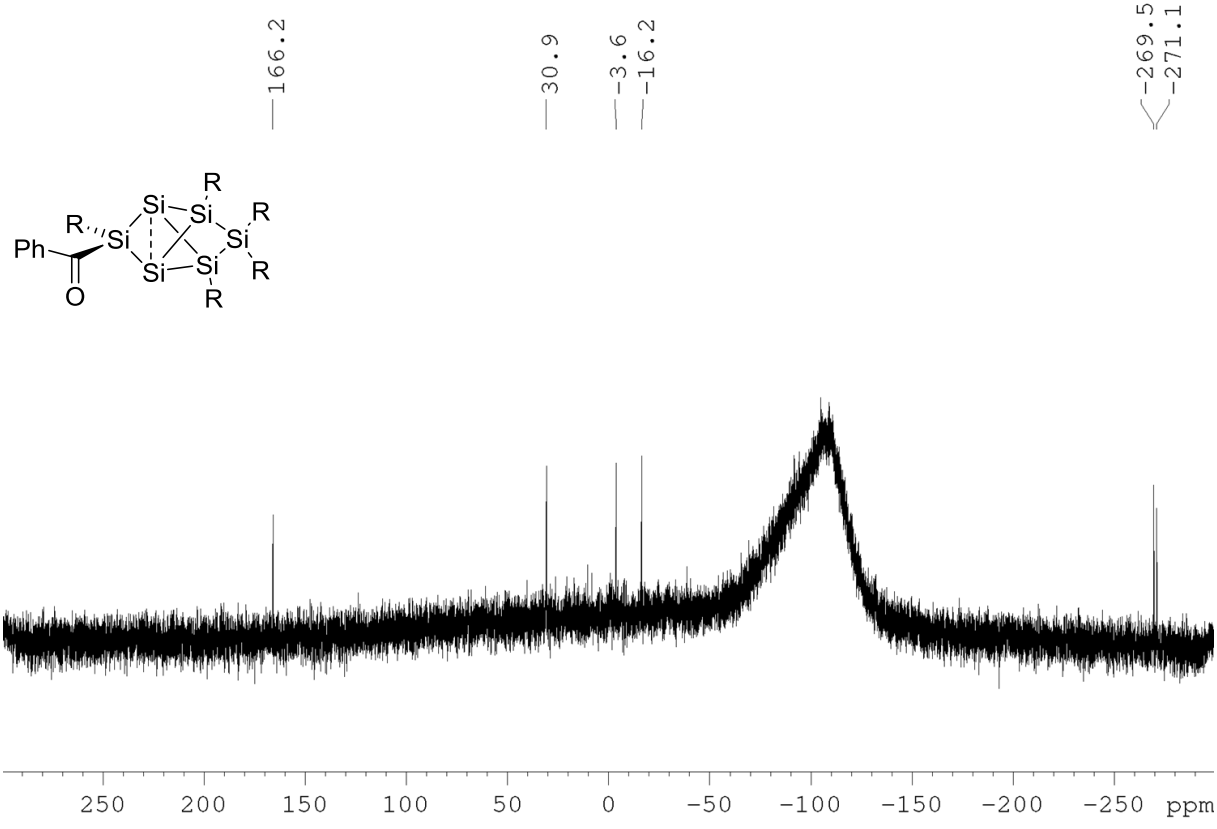

Figure S30: ^{29}Si NMR of **6b** in C_6D_6 (59.6 MHZ).

Preparation of privo-Pivaloyl-2,4,5,5,6-pentakis(2',4',6'-triisopropylphenyl)tetracyclo[2.2.0.0^{1,3}.0^{3,6}] hexasilane (6c)

Quantities: **4Li**, 150.7 mg (0.11 mmol); pivaloyl chloride 13.9 μL (13.6 mg, 0.11 mmol); toluene (2.5 mL); stirring 0.5 h; crystallization from hexane. Yield: 39 mg (27 %) orange crystals.

^{1}H NMR (400.13 MHz, benzene-d_6, 300K): δ = 7.27, 7.25, 7.12, 7.07, 7.01, 6.92, 6.86, 6.85 (each d, each 1H, Tip-H), 6.80 (t, 2H, Tip-H), 5.07, 4.86, 4.35 (each sept, each 1H, ^{i}Pr-CH), 4.18 – 4.06 (m, 2H, ^{i}Pr-CH), 3.96 – 3.87 (m, 2H, ^{i}Pr-CH), 3.65 (s, 1H, ^{i}Pr CH), 3.32 – 3.23 (m, 2H, ^{i}Pr-CH), 2.78 – 2.70 (m, 3H, ^{i}Pr-CH), 2.65 – 2.58 (m, 2H, ^{i}Pr-CH), 2.17, 2.05, 1.81, 1.78 (each d, each 3H, ^{i}Pr-CH_3), 1.64 – 1.56 (m, 12H, ^{i}Pr-CH_3), 1.44, 1.41, 1.32 (each d, each 3H, ^{i}Pr-CH_3), 1.25 – 1.17 (m, 21H, ^{i}Pr-CH_3), 1.11 – 1.08 (m, 12H, ^{i}Pr-CH_3), 0.89 (s, 9H, ^{t}Bu-CH_3), 0.75, 0.69, 0.67, 0.58 (each d, each 3H, ^{i}Pr-CH_3), 0.36 – 0.28 (m, 12H, ^{i}Pr-CH_3). **^{13}C NMR** (100.6 MHz, benzene-d_6, 300K): δ = 238.7 (CO), 157.1, 156.9, 155.9, 155.4, 154.2, 153.8, 153.5, 153.2, 152.1 151.8, 151.6, 150.6, 150.5, 149.5, 149.3, 138.5, 138.4, 133.6, 128.2, 127.9 (Ar-C), 126.6, 123.6, 123.0, 122.9, 122.7, 122.4, 122.2, 122.0, 121.5, 120.6 (Ar-CH), 49.4 (CMe_3), 37.7, 37.5, 37.3, 37.2, 37.0, 36.7, 36.5, 35.3, 35.0, 35.0, 34.7, 34.6, 34.6, 32.0, 29.0, 27.4, 26.8 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3), 26.8 (^{t}Bu-CH_3), 26.2, 26.1, 25.7, 25.7,25.5, 25.4, 25.2, 25.1, 25.0, 24.9, 24.8, 24.5, 24.1, 24.1, 24.1, 24.0, 23.9, 23.6, 23.1, 22.4, 14.4 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300 K): δ = 173.1 (s, *privo*-Si(Tip)CO^{t}Bu) 30.9 (s, *remoto*-$SiTip_2$), −1.7 (s, *ligato*-SiTip), −14.5 (s, *ligato*-SiTip) −263.1 (s, *nudo*-Si) −265.8 (s, *nudo*-Si). Elemental analysis calculated for $C_{80}H_{124}OSi_6$: C, 75.64, H; 9.84. Found: C, 74.29; H, 10.05.

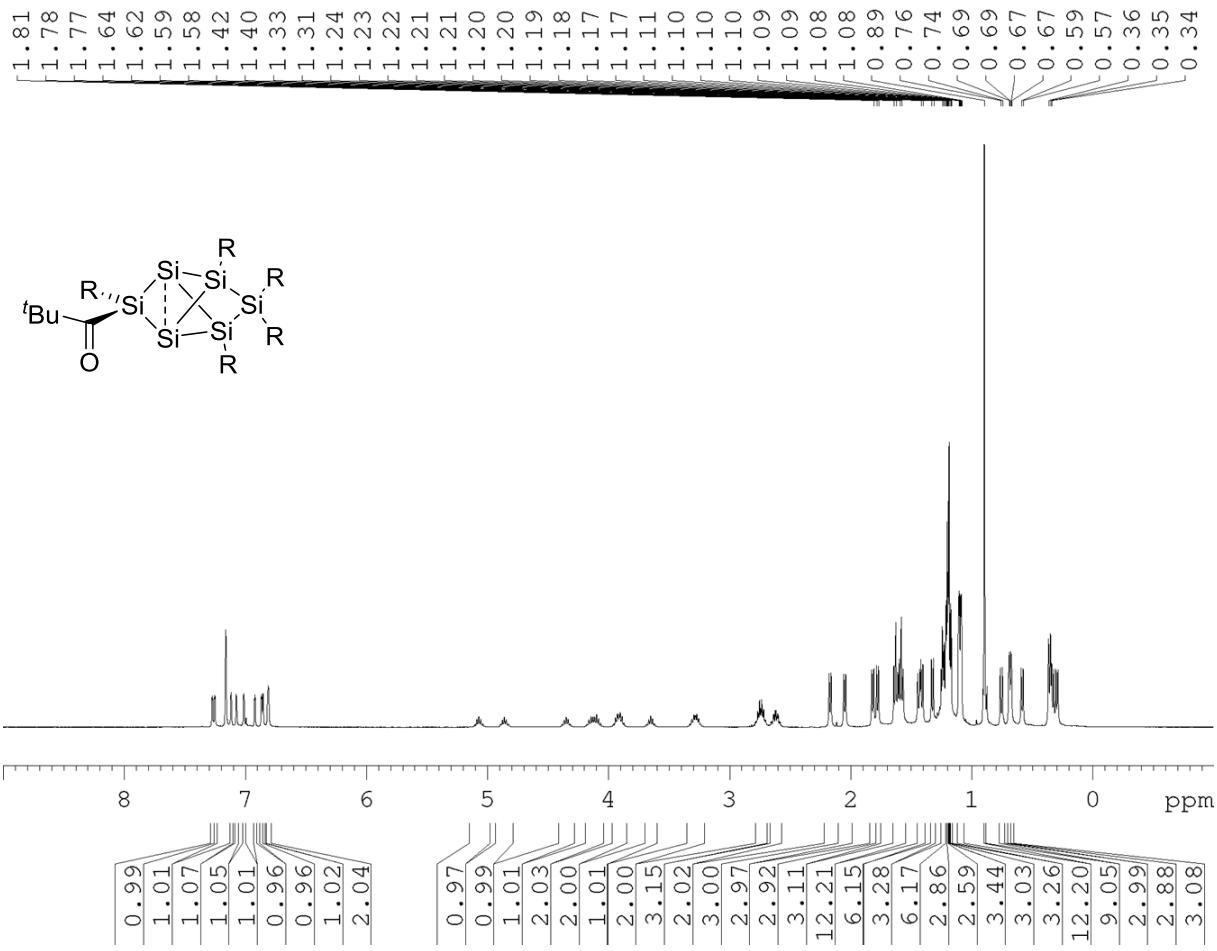

Figure S31: ^{1}H NMR of **6c** in C_6D_6 (400 MHZ).

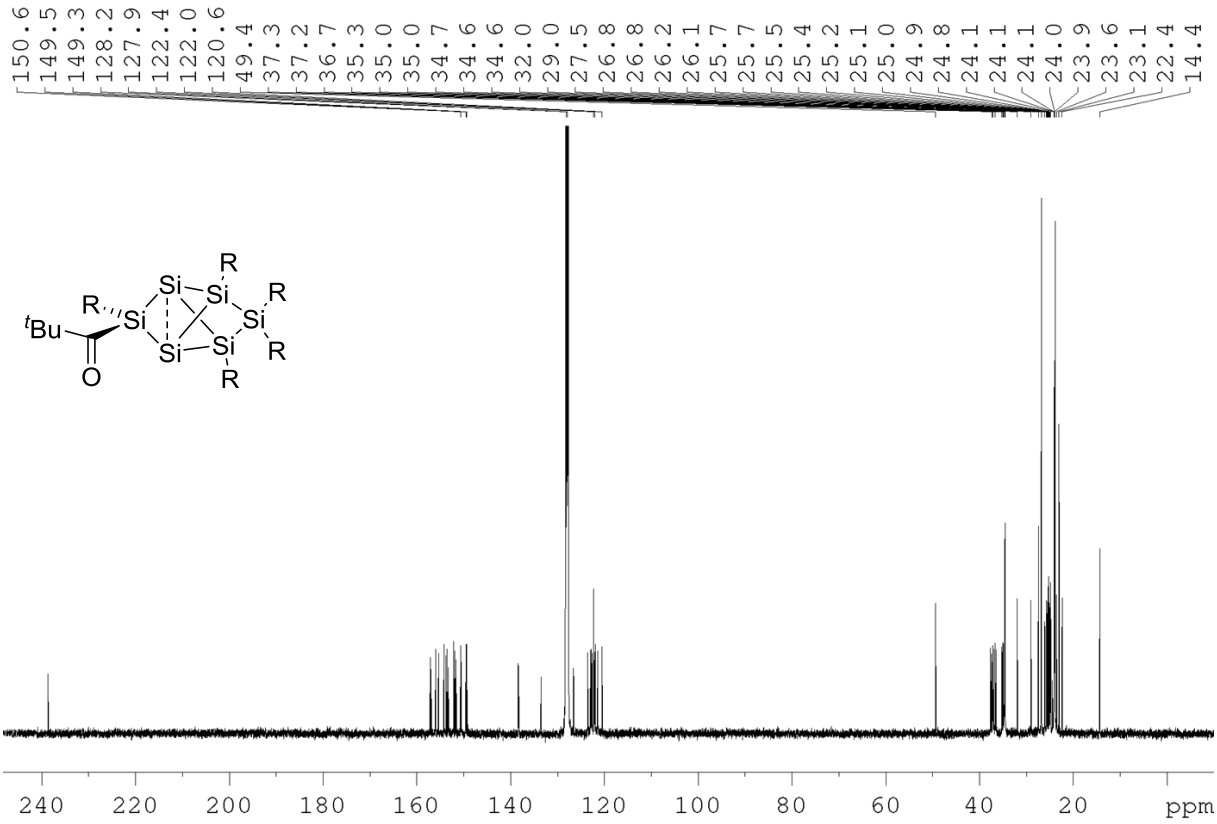

Figure S32: ^{13}C NMR of **6c** in C_6D_6 (100.6 MHZ).

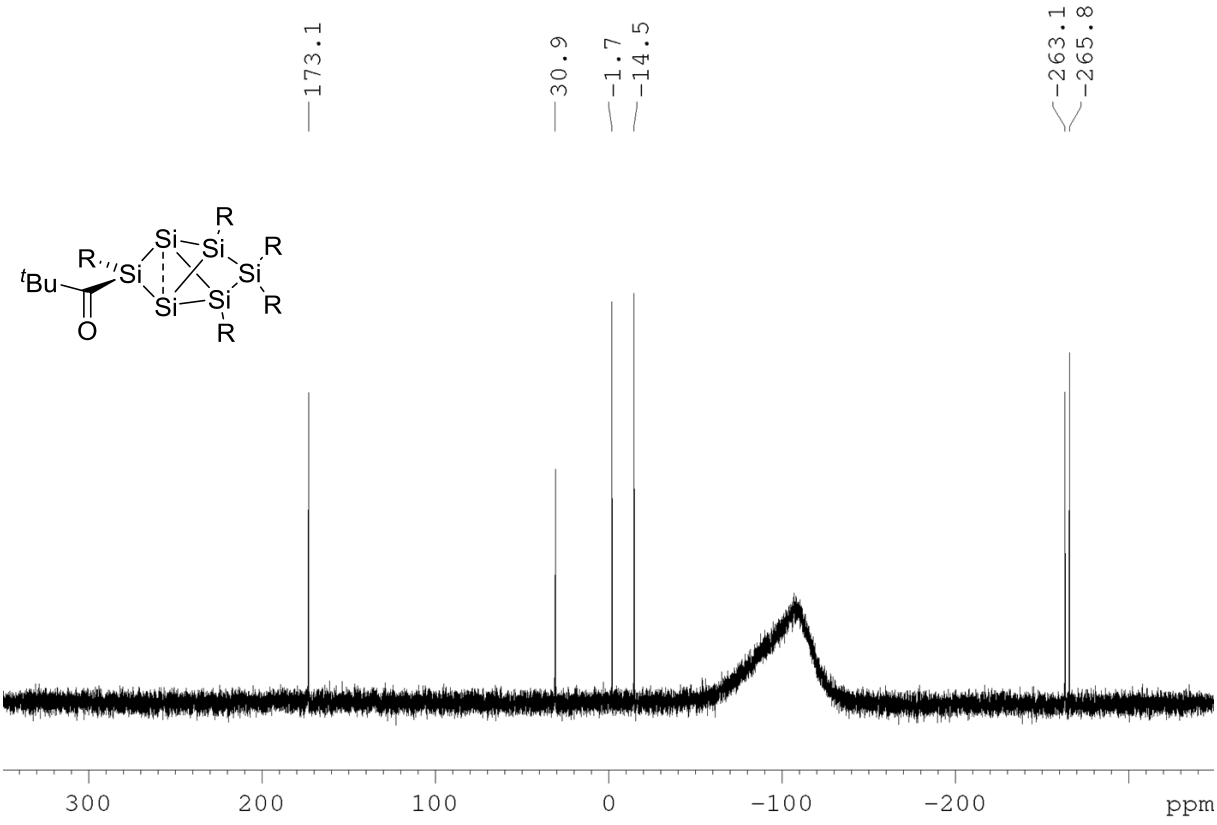

Figure S33: ^{29}Si NMR of **6c** in C_6D_6 (59.6 MHZ).

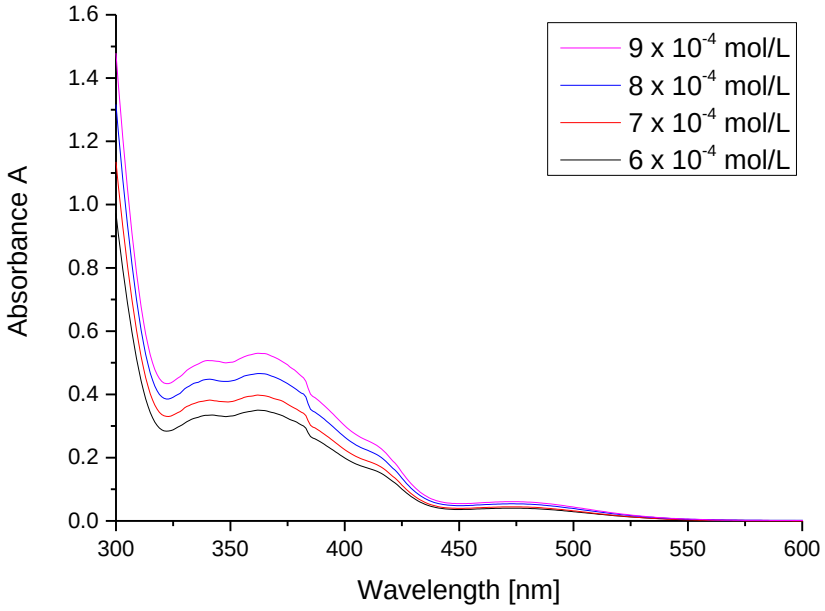

Figure S34: UV-Vis spectrum of **6c** in hexane at different concentrations.

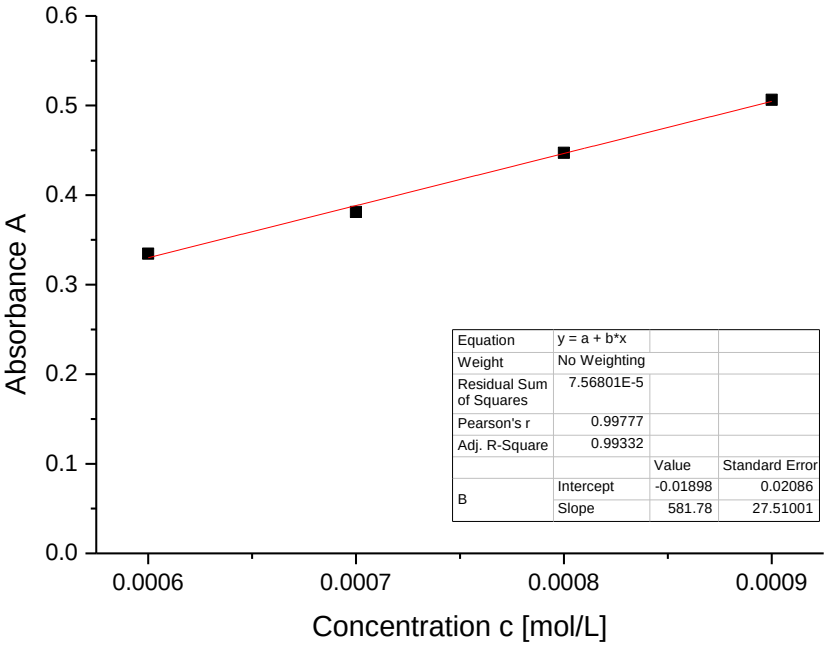

Figure S35: Determination of ε (5817 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 342 nm) of **6c** against concentration.

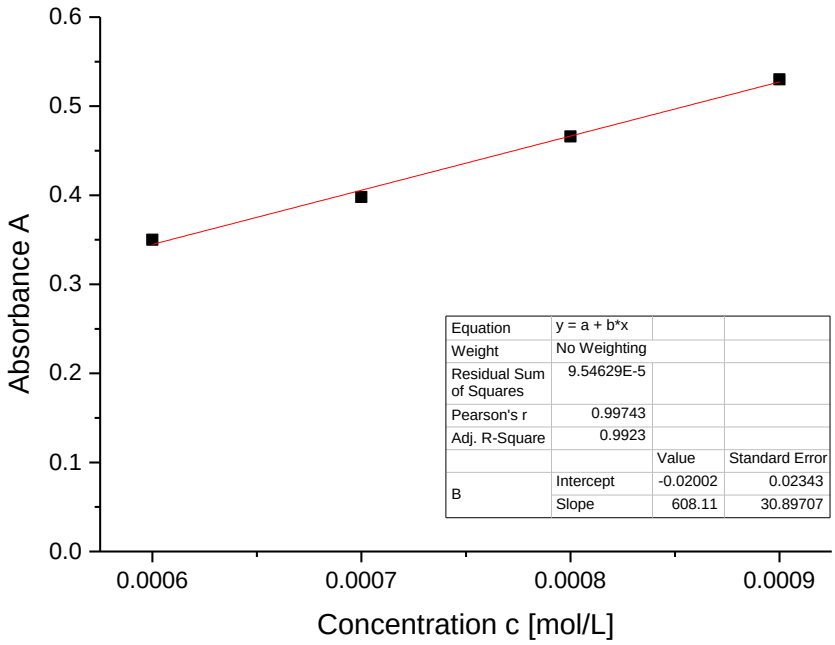

Figure S36: Determination of ε (6081 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 362 nm) of **6c** against concentration.

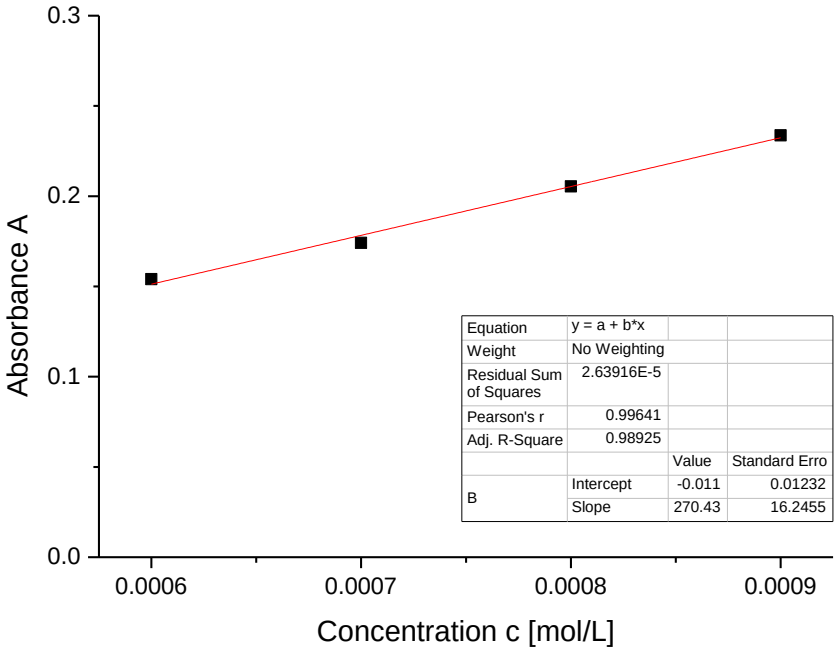

Figure S37: Determination of ε (2704 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 415 nm) of **6c** against concentration.

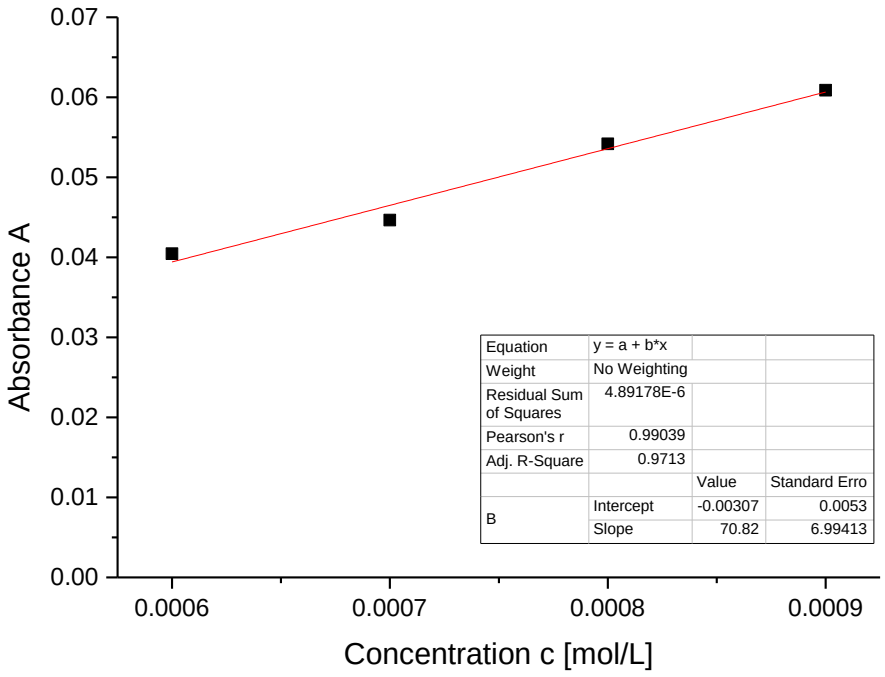

Figure S38: Determination of ε (708 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 473 nm) of **6c** against concentrations.

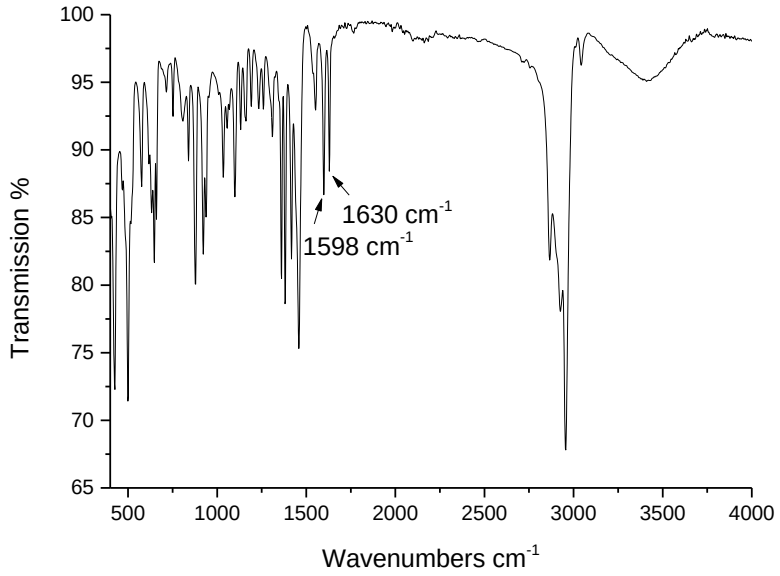

Figure S39: Infrared spectrum of 6c (powder).

***Preparation of privo*-Bis(dimethylamino)phosphanyl-2,4,5,5,6-pentakis(2',4',6'tri¬iso¬propyl¬phenyl)¬tetracyclo[2.2.0.0^{1,3}.0^{3,6}] hexasilane (6d)**

Quantities: **4Li**, 102.8 mg (0.077 mmol); $(Me_2N)_2PCl$ 11.2 µL (11.9 mg, 0.077 mmol); benzene-d_6 (0.6 mL); NMR scale. The crude product was thoroughly dried in vacuum and characterized by multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, benzene-d_6, 300K): δ = 7.28 (d, 2H, Tip-H), 7.09 (s, 1H, Tip-H), 6,99 (s, 1H, Tip-H), 6.91 (s, 1H, Tip-H), 6.87 (s, 1H, Tip-H), 6.81 (s, 2H, Tip-H), 6.79 (s, 1H, Tip-H), 5.06 (sept, 1H, ^{i}Pr-CH), 4.88 (sept, 1H, ^{i}Pr-CH), 4.41 (sept, 1H, ^{i}Pr-CH), 4.19 – 4.08 (m, 2H, ^{i}Pr-CH), 4.01 – 3.95 (m, 2H, ^{i}Pr-CH), 3.65 (sept, 1H, ^{i}Pr-CH), 3.47 (sept, 1H, ^{i}Pr-CH), 3.35 (sept, 1H, ^{i}Pr-CH), 2.78 – 2.65 (m, 5H, ^{i}Pr-CH), 2.58 (d, $^3J_{PH}$ = 9.89 Hz, 6H, $N(CH_3)_2$), 2.30 (d, $^3J_{PH}$ = 9.19 Hz, 6H, $N(CH_3)_2$), 2.19 (d, 3H, ^{i}Pr-CH_3), 2.06 (d, 3H, ^{i}Pr-CH_3), 1.86 (d, 3H, ^{i}Pr-CH_3), 1.79 (d, 3H, ^{i}Pr-CH_3), 1.70 (d, 3H, ^{i}Pr-CH_3), 1.65 – 1.57 (m, 12H, ^{i}Pr-CH_3), 1.44 (t, 6H, ^{i}Pr-CH_3), 1.22 – 1.14 (m, 27H, ^{i}Pr-CH_3), 1.11 – 1.07 (m, 6H, ^{i}Pr-CH_3), 0.84 (d, 3H, ^{i}Pr-CH_3), 0.72 (d, 3H, ^{i}Pr-CH_3), 0.68 (d, 3H, ^{i}Pr-CH_3), 0.55 (d, 3H, ^{i}Pr-CH_3), 0.45 – 0.39 (m, 9H, ^{i}Pr-CH_3), 0.31 (d, 3H, ^{i}Pr-CH_3). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300 K): δ = 157.4, 157.1, 156.9, 156.5, 156.3, 156.0, 155.9, 154.5, 153.7, 153.6, 153.3, 152.0, 151.8, 151.2, 151.0, 150.7, 150.3, 149.9, 149.3, 149.1 (Ar-C), 123.7, 123.1, 122.8, 122.5, 122.2, 122.1, 121.9, 121.7, 121.6, 121.4 (Ar-CH), 47.2 (d, $^2J_{CP}$ = 9.54 Hz, $N(CH_3)_2$), 46.0 (d, ^{2}JC-P = 14.79 Hz, $N(CH_3)_2$), 40.7, 39.5, 38.4, 37.6, 37.4, 37.2, 37.1, 36.9, 36.4, 35.2, 34.8, 34.7, 34.6, 34.5, 28.4, 27.8, 27.4, 26.9, 26.6, 26.4, 26.3, 25.6, 25.4, 25.3, 25.2, 25.1, 25.0, 24.9, 24.8, 24.5, 24.5, 24.1, 24.1, 24.0, 24.0, 22.4 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300 K): δ = 186.5 (d, $^1J_{SiP}$ = 97.44 Hz, *privo*-Si(Tip)P(NMe_2)$_2$), 28.0 (d, $^1J_{SiP}$ = 7.52 Hz, *remoto*-$SiTip_2$), 13.7 (d, $^1J_{SiP}$ = 20.87 Hz, *ligato*-SiTip), −16.9 (s, *ligato*-SiTip), −246.0 (d, $^1J_{SiP}$ = 33.40 Hz, *nudo*-Si), −256.1 (d, $^1J_{SiP}$ = 8.28 Hz, *nudo*-Si). **^{31}P NMR** (121.5 MHz, benzene-d_6, 300 K): δ = 121.3 (s, $^1J_{SiP}$ = 97.44 Hz).

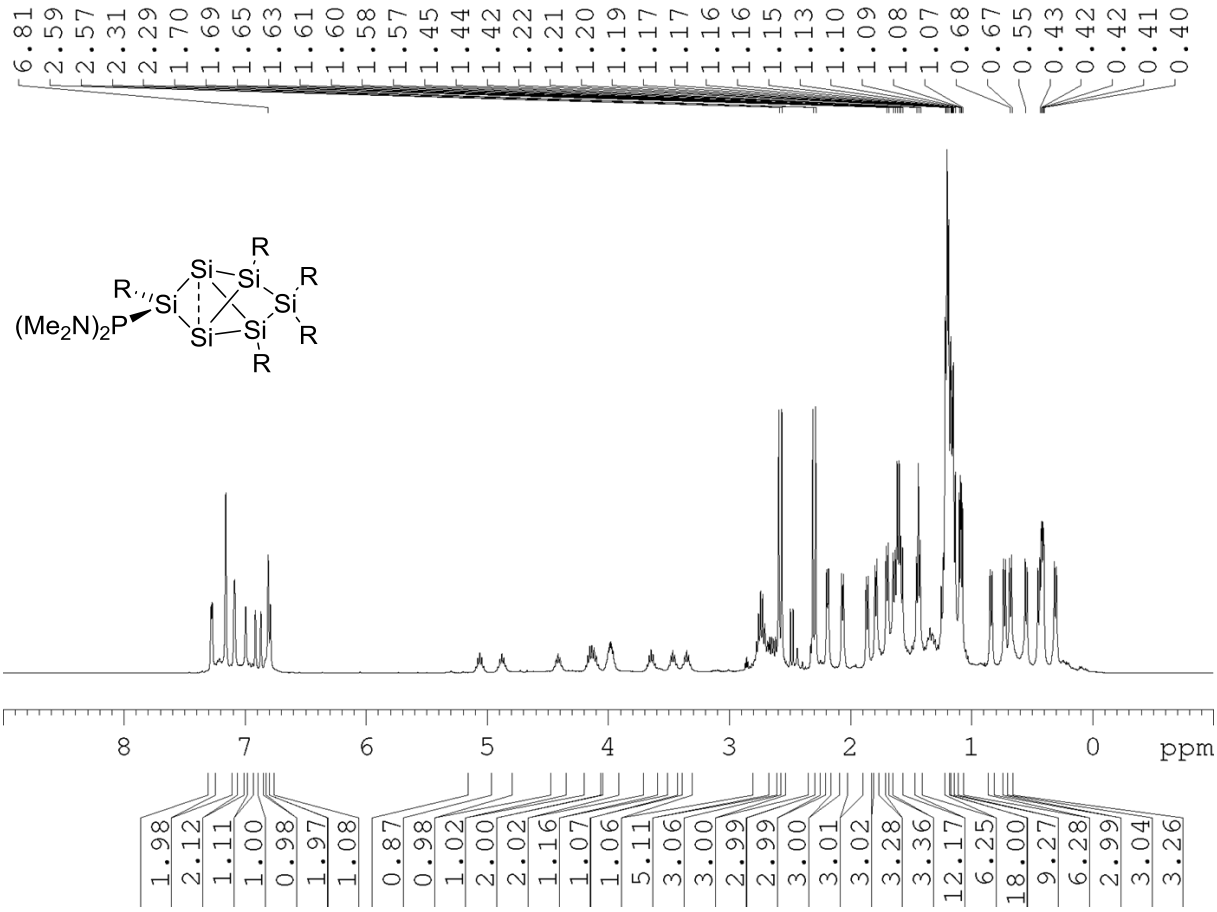

Figure S40: ^{1}H NMR of **6d** in C_6D_6 (400 MHZ).

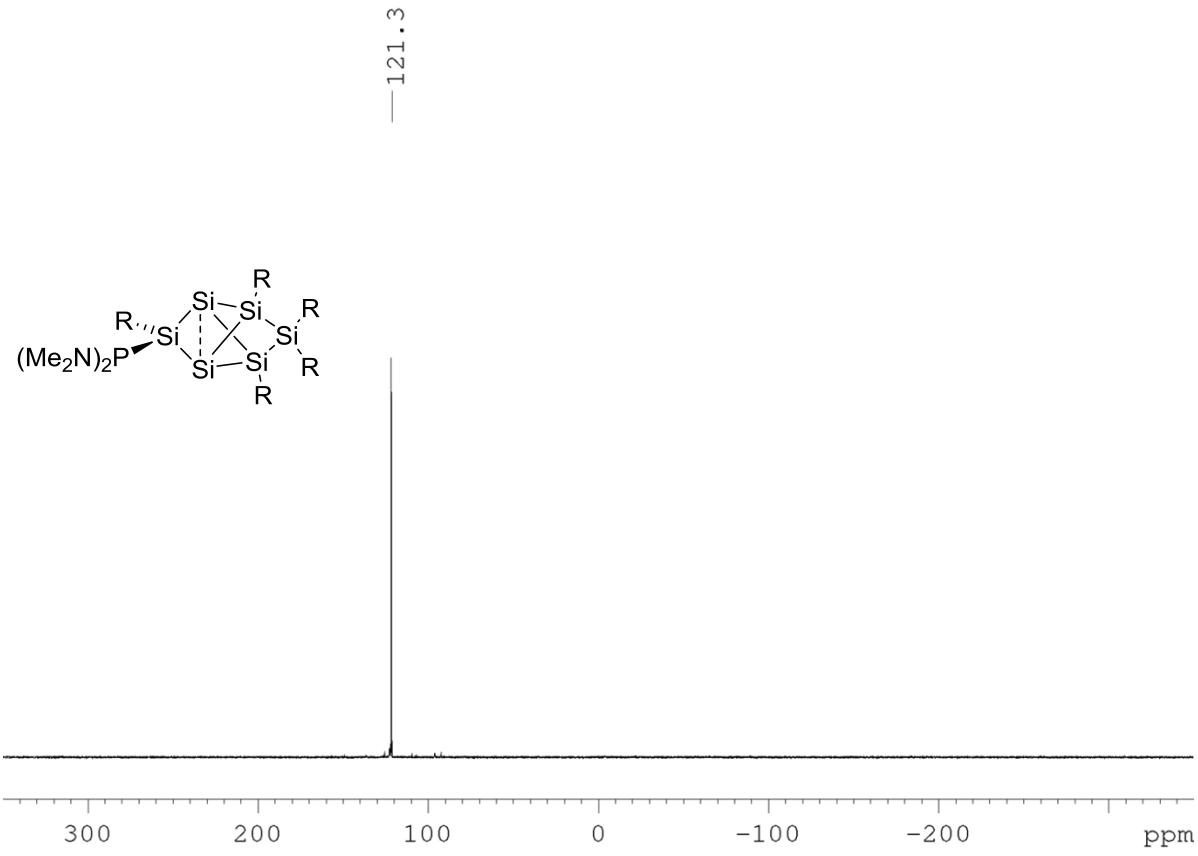

Figure S41: ^{31}P NMR of **6d** in C_6D_6 (121.5 MHZ).

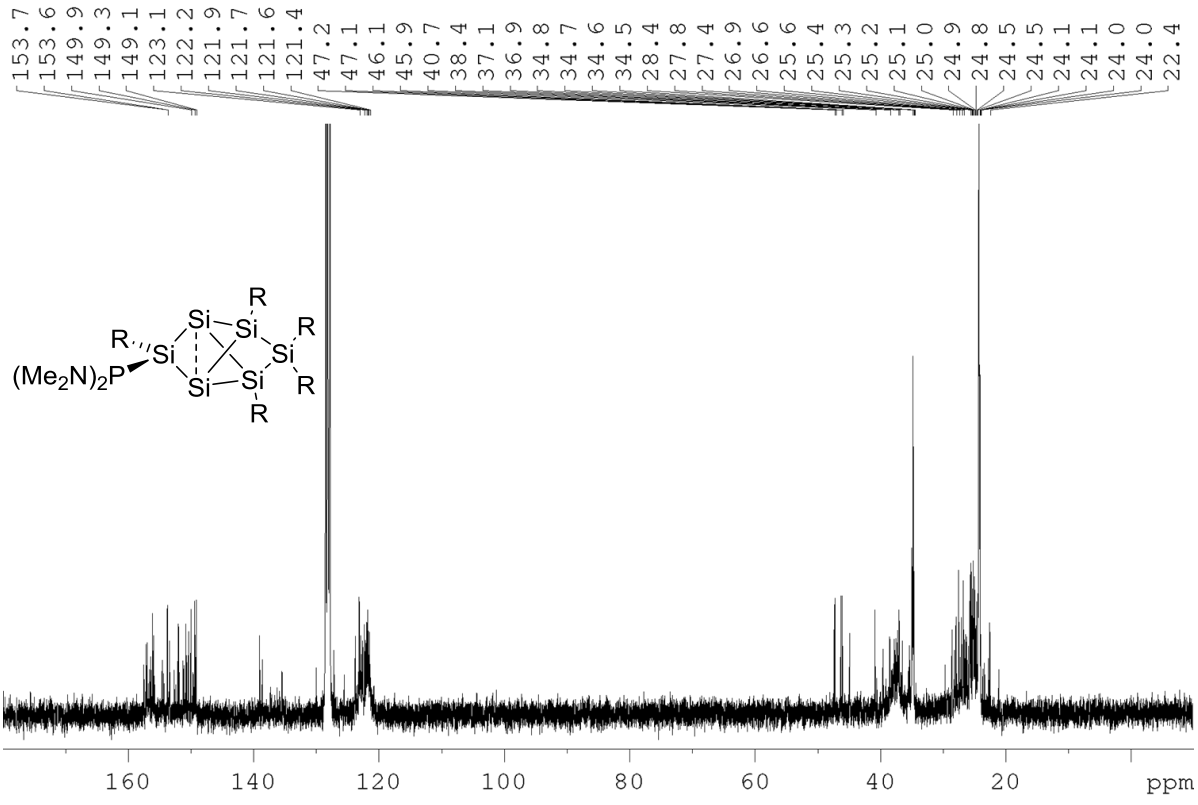

Figure S42: ^{13}C NMR of **6d** in C_6D_6 (75.5 MHZ).

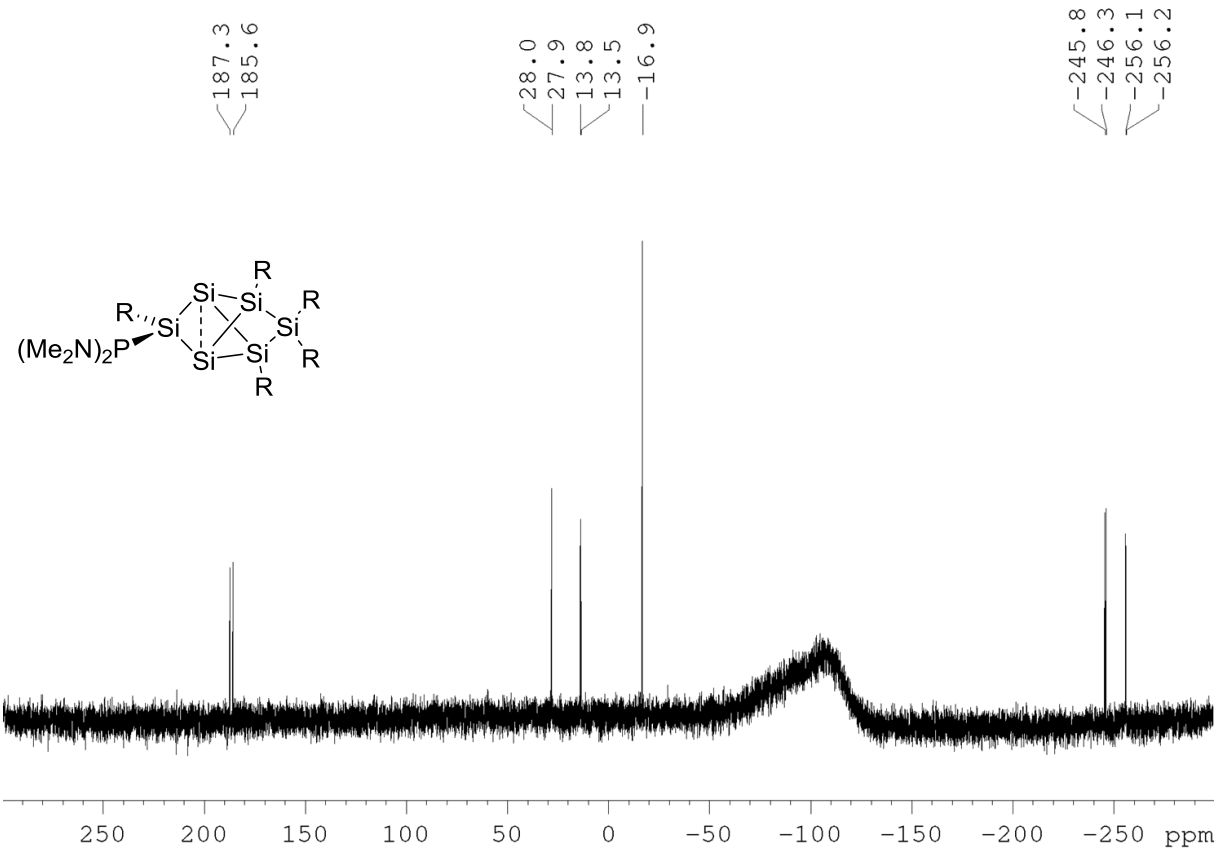

Figure S43: ^{29}Si NMR of **6d** in C_6D_6 (59.6 MHZ).

***privo*-Trichlorosilyl-2,4,5,5,6-pentakis(2',4',6'-tri¬iso¬propyl¬phenyl)tetracyclo[2.2.0.0^{1,3}.0^{3,6}] hexasilane (6e)**

Quantities: **4Li**, 81.8 mg (0.061 mmol); $SiCl_4$ 7.7 µL (11.4 mg, 0.067 mmol); benzene-d_6 (0.6 mL); NMR scale. The crude product was thoroughly dried in vacuo and characterized by multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, benzene-d_6, 300K): δ = 7.25 (s, 2H, Tip-H), 7.10 (d, 1H, Tip-H), 7.04 (d, 1H, Tip-H), 6.97 (d, 1H, Tip-H), 6.90 (d, 1H, Tip-H), 6.82 (d, 1H, Tip-H), 6.78 (s, 2H, Tip-H), 6.74 (d, 1H, Tip-H), 4.89 (sept, 1H, ^{i}Pr-CH), 4.74 (sept, 1H, ^{i}Pr-CH), 4.28 (sept, 1H, ^{i}Pr-CH), 4.01 – 3.79 (m, 3H, ^{i}Pr-CH), 3.72 – 3.52 (m, 2H, ^{i}Pr-CH), 3.39 – 3.20 (m, 2H, ^{i}Pr-CH), 2.78 – 2.52 (m, 5H, ^{i}Pr-CH), 2.13 (d, 3H, ^{i}Pr-CH_3), 2.03 (d, 3H, ^{i}Pr-CH_3), 1.81 (d, 6H, ^{i}Pr-CH_3), 1.62 (d, 3H, ^{i}Pr-CH_3), 1.60 – 1.50 (m, 15H, ^{i}Pr-CH_3), 1.39 (d, 3H, ^{i}Pr-CH_3), 1.24 (d, 3H, ^{i}Pr-CH_3), 1.21 – 1.05 (m, 30H, ^{i}Pr-CH_3), 0.77 (d, 3H, ^{i}Pr-CH_3), 0.65 (d, 6H, ^{i}Pr-CH_3), 0.53 (d, 3H, ^{i}Pr-CH_3), 0.46 (d, 3H, ^{i}Pr-CH_3), 0.38 – 0.35 (m, 6H, ^{i}Pr-CH_3), 0.28 (d, 3H, ^{i}Pr-CH_3). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300 K): δ = 157.0, 156.7, 156.6, 156.2, 154.4, 154.1, 153.8, 153.6, 152.0, 151.8, 151.3, 150.8, 149.9 ,149.7, 137.8, 137.5, 130.1, 127.6, 125.3(Ar-C), 123.9, 123.3, 122.9, 122.8, 122.4, 122.3, 122.2, 122.1, 121.5 (Ar-CH), 38.3, 37.8, 37.6, 37.5, 37.1, 36.5, 36.5, 35.4, 35.1, 34.7, 34.7, 34.6, 34.6, 34.5, 27.8, 27.4, 27.3, 27.1, 27.0, 26.7, 26.5, 26.1, 25.6, 25.2, 25.1, 25.0, 24.6, 24.1,

24.0, 23.9, 23.8, 23.7, 22.9, 22.5 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300 K): δ = 161.7 (privo-Si(Tip)$SiCl_3$), 35.2 (s, *remoto*-$SiTip_2$), 12.0 (s, *ligato*-SiTip), 7.4 ($SiCl_3$), −6.4 (s, *ligato*-SiTip), −251.6 (s, *nudo*-Si), −258.9 (s, *nudo*-Si).

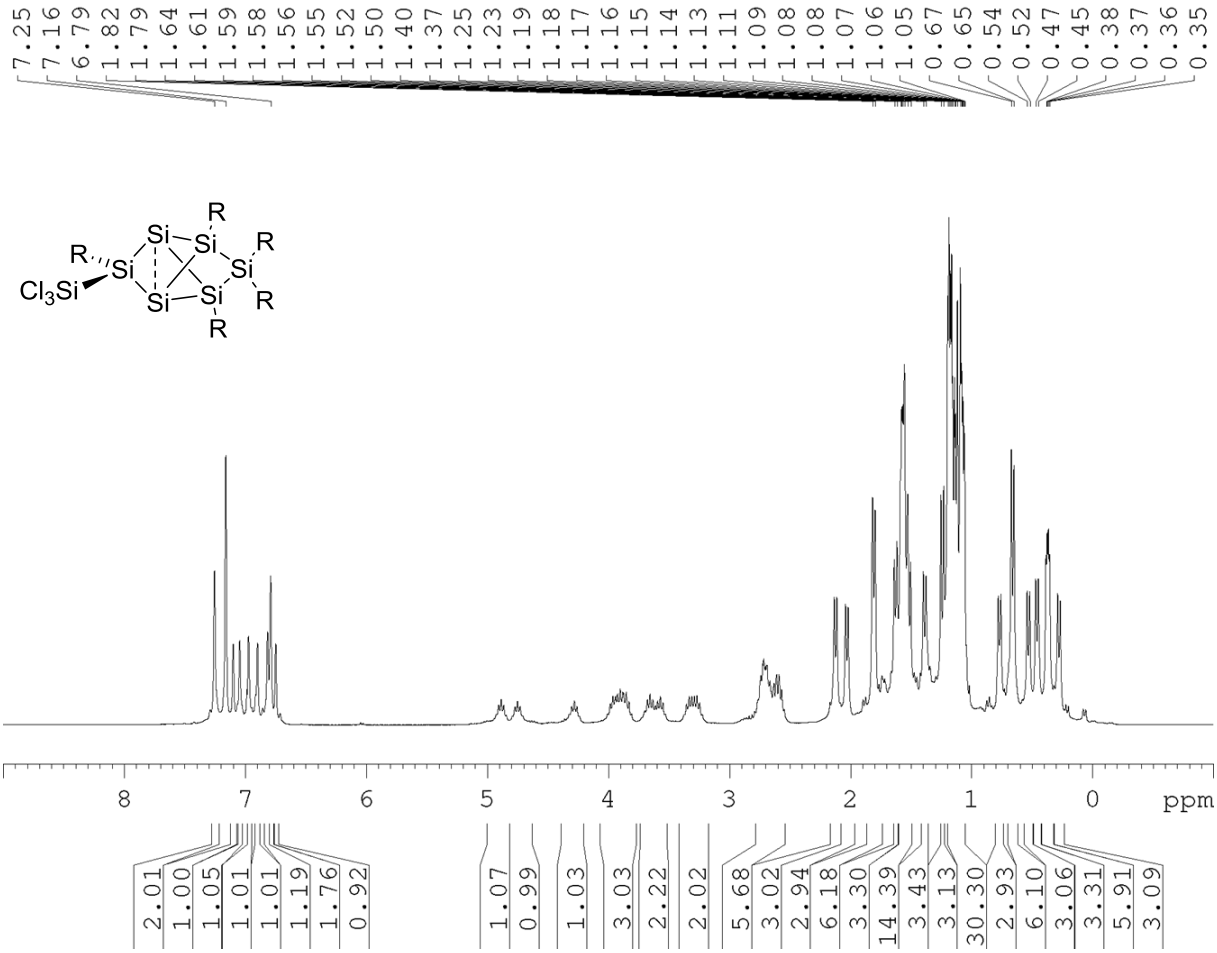

Figure S44: ^{1}H NMR of **6e** in C_6D_6 (300 MHZ).

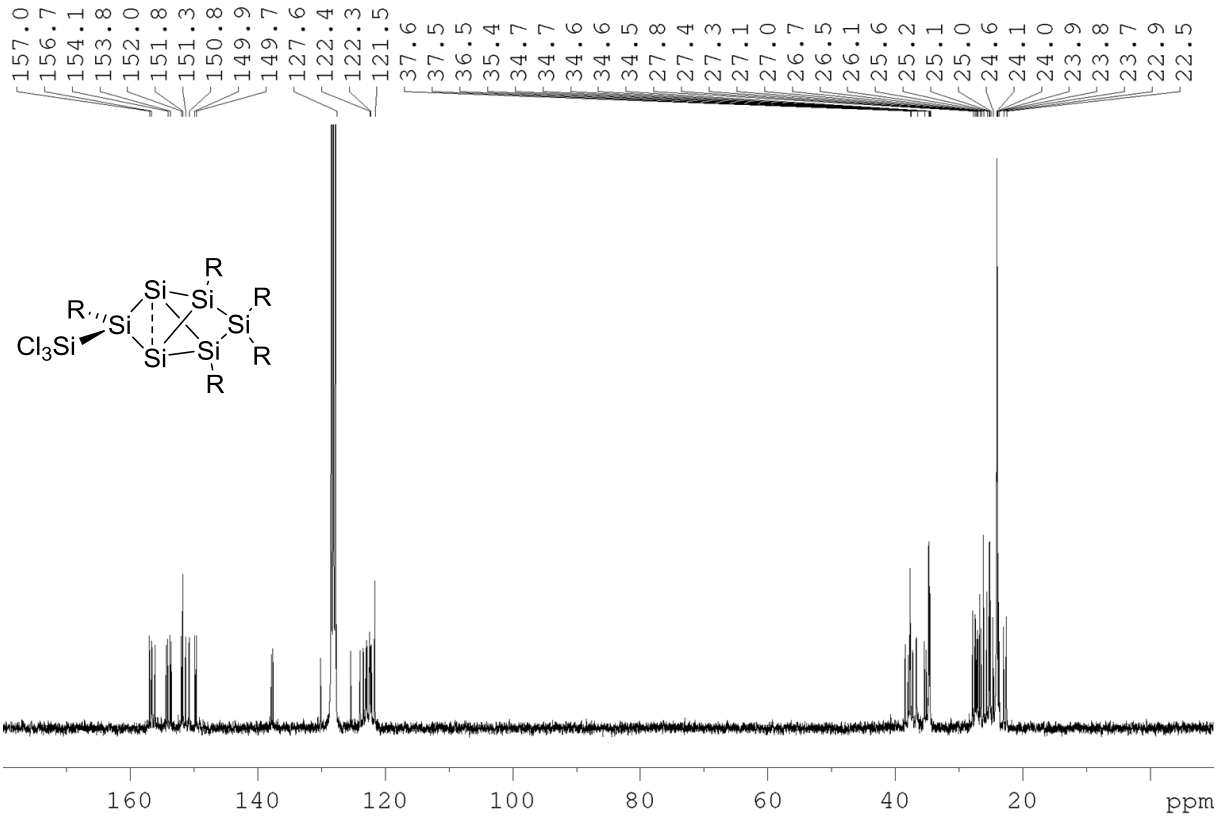

Figure S45: ^{13}C NMR of **6e** in C_6D_6 (75.5 MHZ).

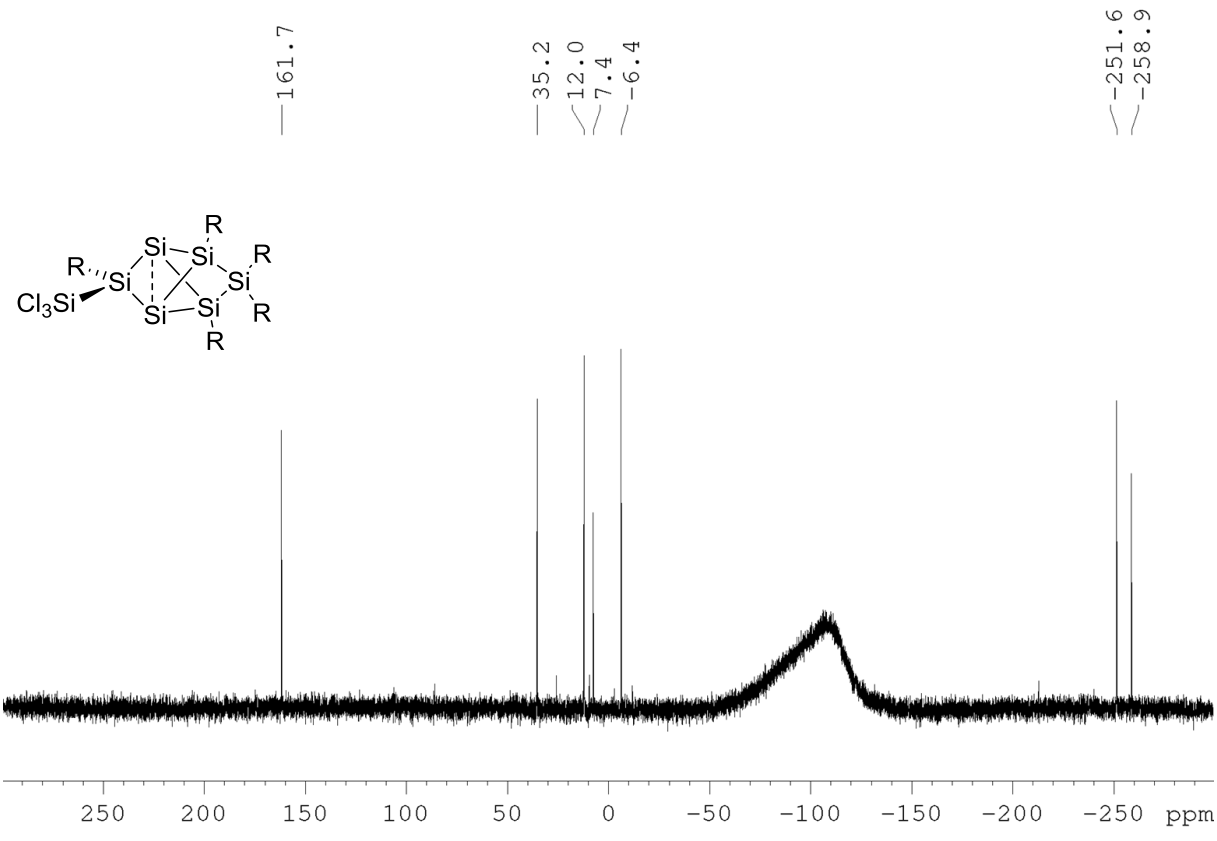

Figure S46: ^{29}Si NMR of **6e** in C_6D_6 (59.6 MHZ).

***Preparation of privo*-Lithium-2,4,5,5,6-pentakis(2',4',6'-triisopropylphenyl)tetracyclo[2.2.0.0^{1,3}.0^{3,6}] hexasilan-2-ylborate (6f)**

Quantities: **4Li**, 53.4 mg (0.04 mmol); $H_3B{\cdot}SMe_2$ 4.2 μL (3.4 mg, 0.04 mmol); toluene (1 mL); stirring 1 h; crystallization from hexane. Yield: 40 mg (78 %) yellow crystals.

^{1}H NMR (300.13 MHz, benzene-d_6, 300K): $\delta =$ 7.27, 7.24, 7.09, 6.97, 6.94 (each d, each 1H, Tip-H), 6.89 (s, 2H, Tip-H), 6.81, 6.80, 6.68 (each d, each 1 H, Tip-H), 5.16, 5.05, 4.77 (each sept, each 1H, ^{i}Pr-CH), 4.30 (m, 3H, ^{i}Pr-CH), 3.79, 3.69 (each sept, each 1H, ^{i}Pr-CH), 3.33 (m, 2H, ^{i}Pr-CH), 3.07 (br, 7H, thf), 2.72 (m, 5H, ^{i}Pr-CH), 2.14, 2.10, 1.78, 1.71 (each d, each 3H, ^{i}Pr-CH_3), 1.61 (m, 12H, ^{i}Pr-CH_3), 1.47, 1.42, 1.37 (each d, each 3H, ^{i}Pr-CH_3), 1.20 (m, 30H, ^{i}Pr-CH_3), 1.19 (m, thf), 0.63 (m, 18H, ^{i}Pr-CH_3), 0.35 (m, 9H, ^{i}Pr-CH_3). **^{7}Li NMR** (116.6 MHz, benzene-d_6, 300K): $\delta =$ −0.58 (s). **^{11}B NMR** (96.3 MHz, benzene-d_6, 300K): $\delta =$ −36.4 (q, $^1J_{BH}$ = 82.3 Hz, BH_3). **^{13}C NMR** (75.5 MHz, benzene-d_6, 300K): $\delta =$ 156.8, 156.5, 156.4, 155.9, 153.5, 153.3, 152.0, 151.9, 149.3, 149.0, 148.8, 148.6, 148.4, 148.1, 142.7, 139.9, 139.4, 130.6, 128.8 (Ar-C), 123.1, 122.7, 122.4, 122.2, 121.6, 121.0, 120.8, 120.3, 119.6 (Ar-CH), 36.9, 36.7, 36.6, 36.1, 35.9, 35.2, 34.7, 34.6, 34.5, 34.4, 33.8, 28.5, 27.5, 27.5, 27.3, 27.0, 26.4, 26.3, 25.7, 25.5, 25.2, 25.1, 25.0, 24.9, 24.8, 24.7, 24.6, 24.4, 24.3, 24.1, 24.0, 24.0, 23.9, 23.9, 23.8, 23.6, 22.5, 22.0 (Tip-^{i}Pr-CH and Tip-^{i}Pr-CH_3). **^{29}Si NMR** (59.6 MHz, benzene-d_6, 300K): $\delta =$ 237.3 (br, *privo*-Si(Tip)BH_3), 21.7 (s, *ligato*-SiTip), 21.1 (s, *remoto*-$SiTip_2$), −28.8 (s, *ligato*-SiTip), −243.3 (s, *nudo*-Si), −255.6 (s, *nudo*-Si). **Elemental analysis** calculated for $C_{79}H_{126}BLiOSi_6$: C, 74.24; H, 9.94. Found: C, 70.10; H, 9.50.

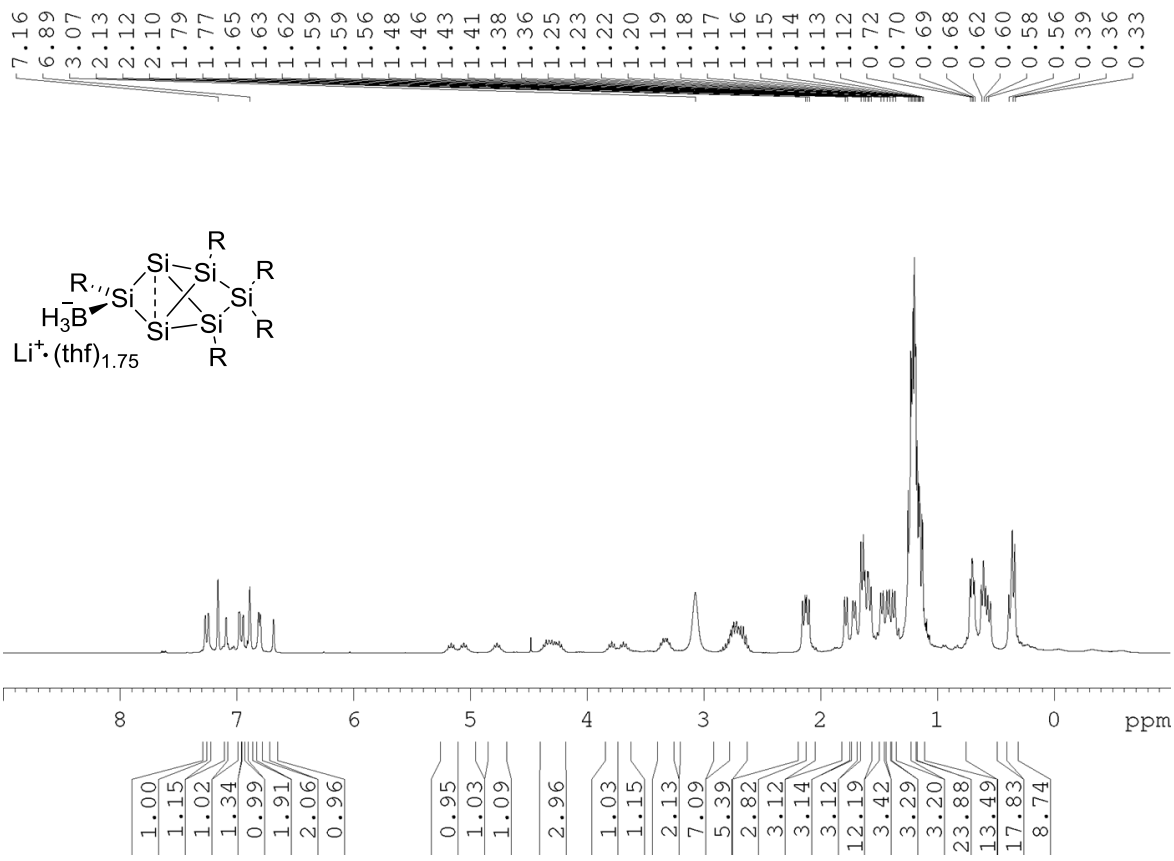

Figure S47: ^{1}H NMR of **6f** in C_6D_6 (300 MHZ).

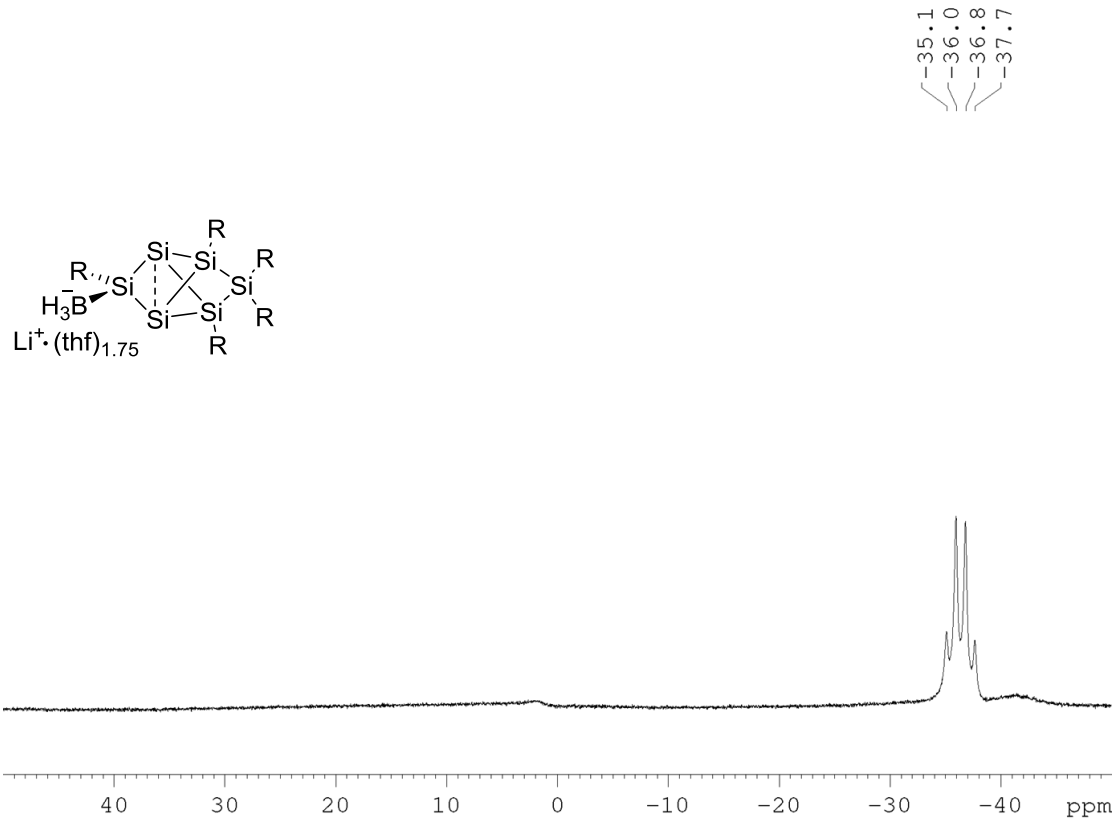

Figure S48: ^{11}B NMR of **6f** in C_6D_6 (96.3 MHZ).

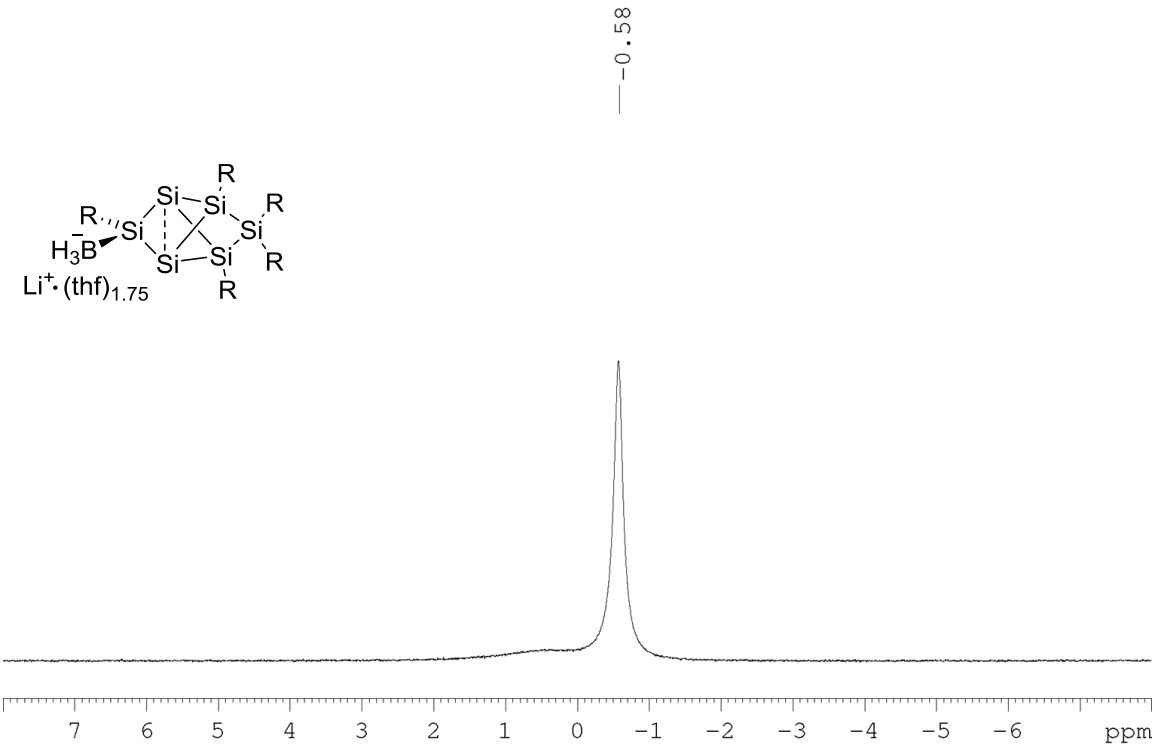

Figure S49: ^{7}Li NMR of **6f** in C_6D_6 (116.6 MHZ).

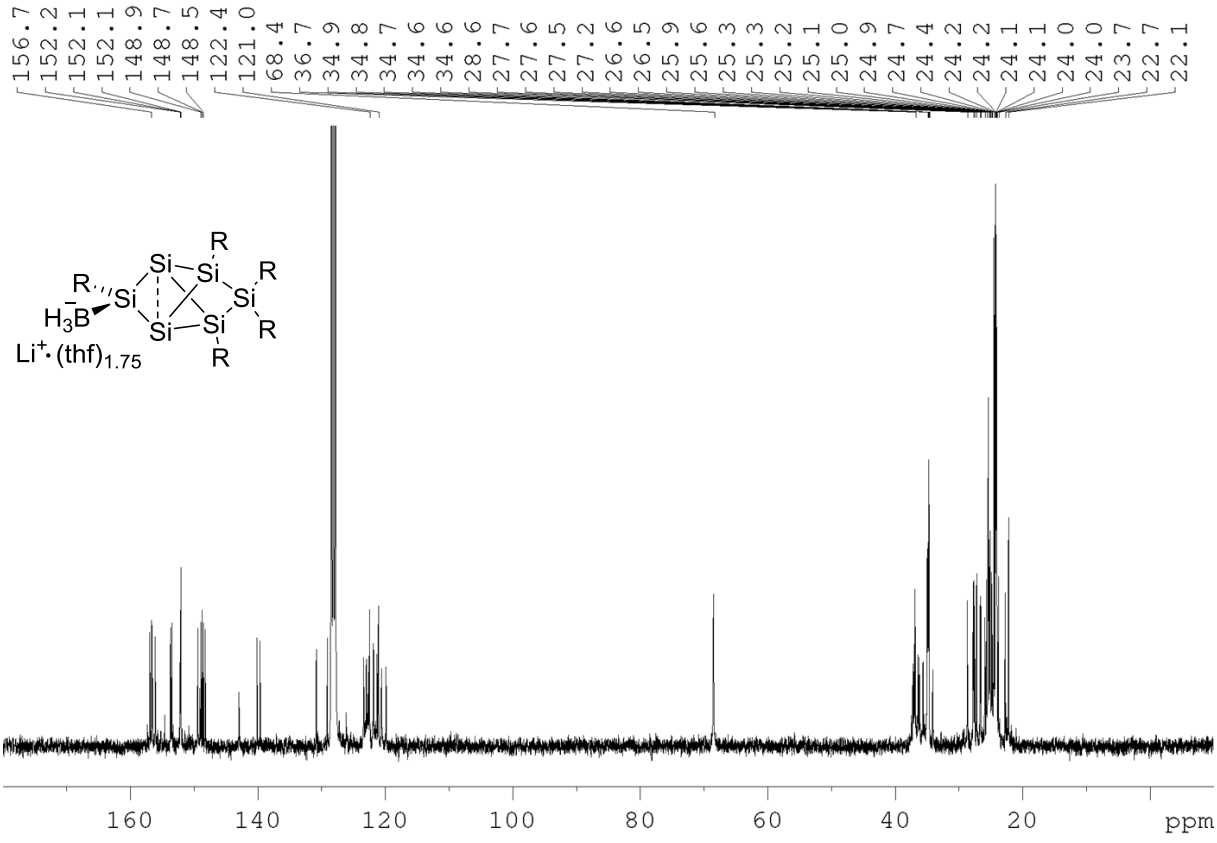

Figure S50: ^{13}C NMR of **6f** in C_6D_6 (75.5 MHZ).

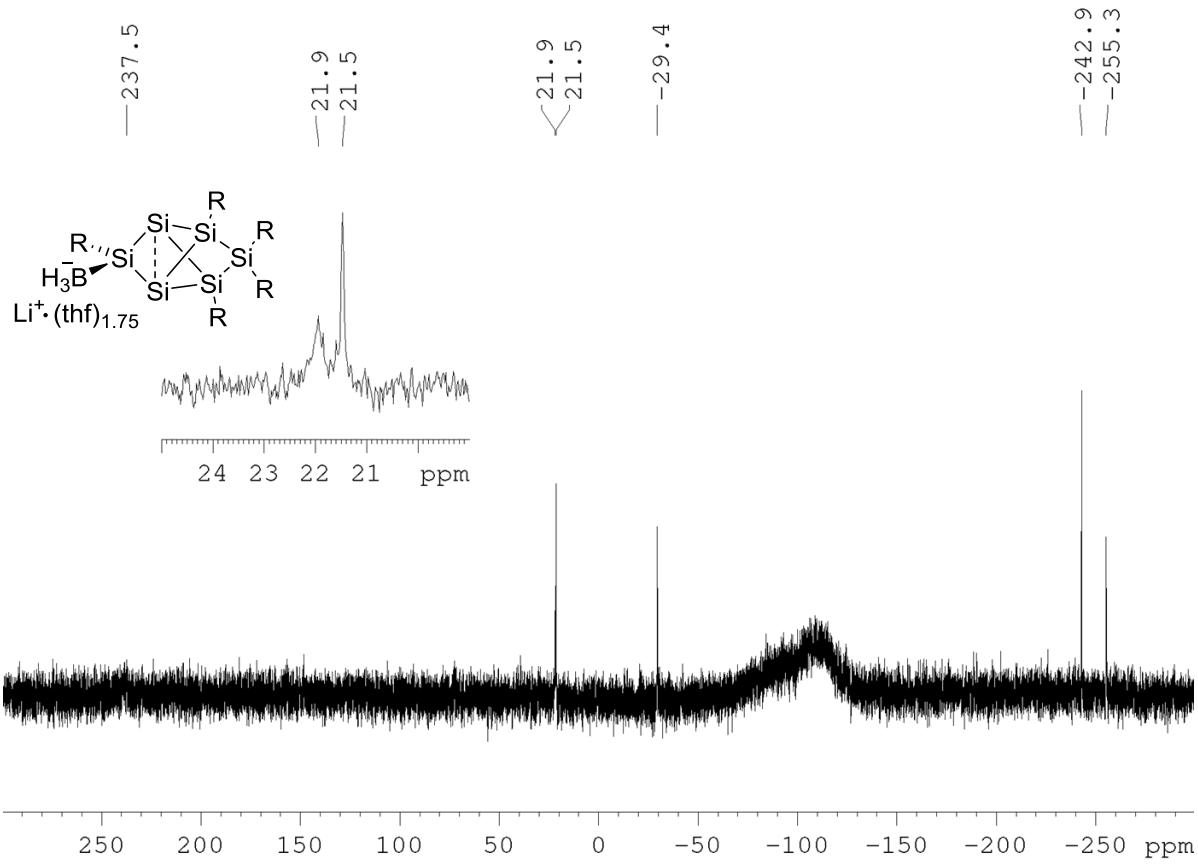

Figure S51: ^{29}Si NMR of **6f** in C_6D_6 (59.6 MHZ; lb = 1)

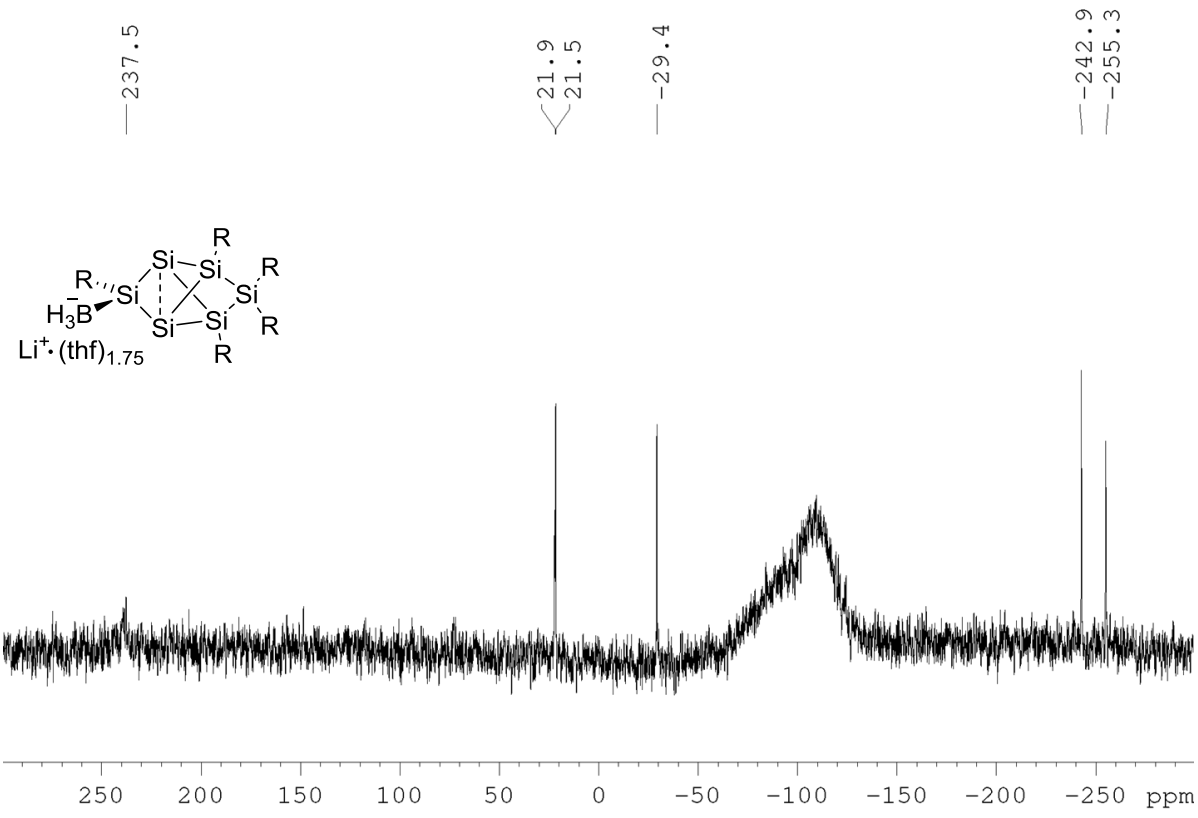

Figure S52: ^{29}Si NMR of **6f** in C_6D_6 (59.6 MHZ; lb = 6)

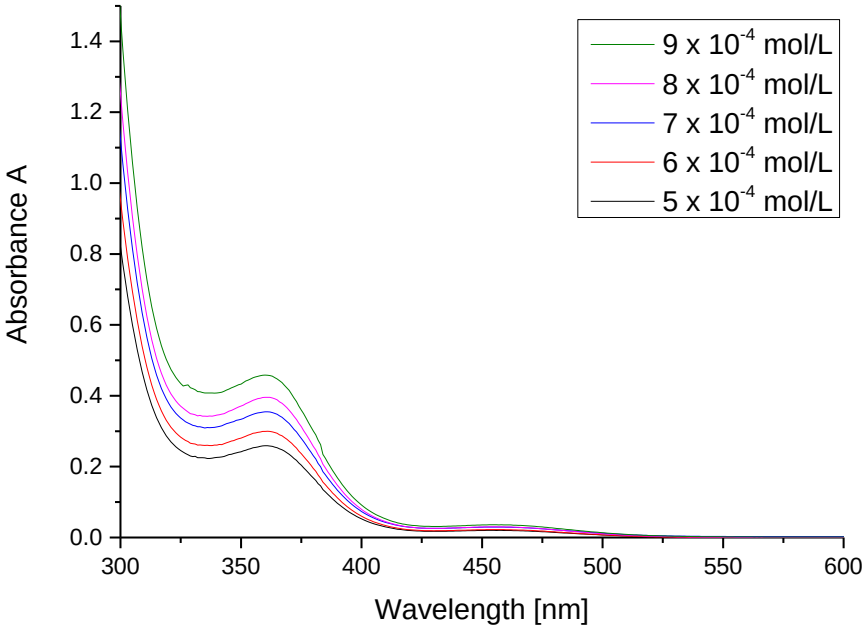

Figure S53: UV-Vis spectrum of **6f** in hexane at different concentrations.

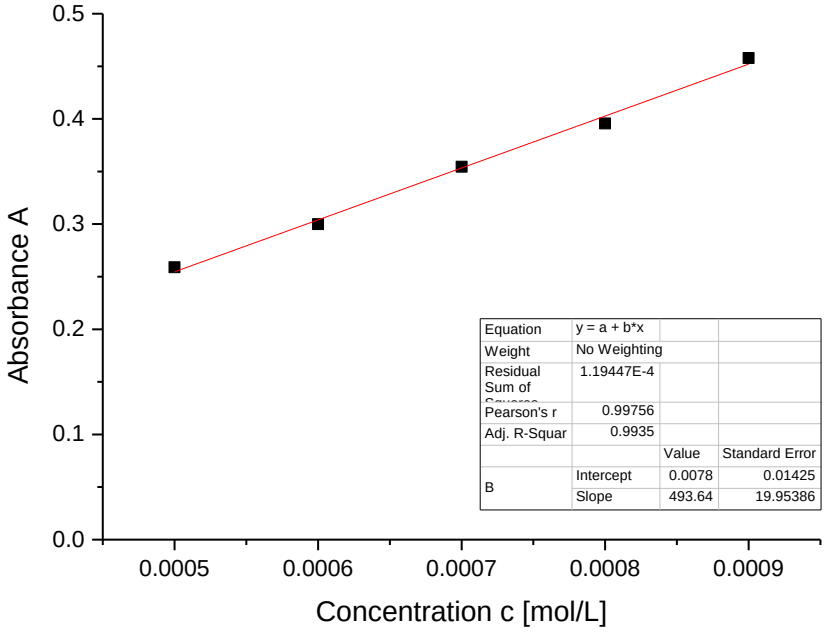

Figure S54: Determination of ε (4936 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 361 nm) of **6f** against concentration.

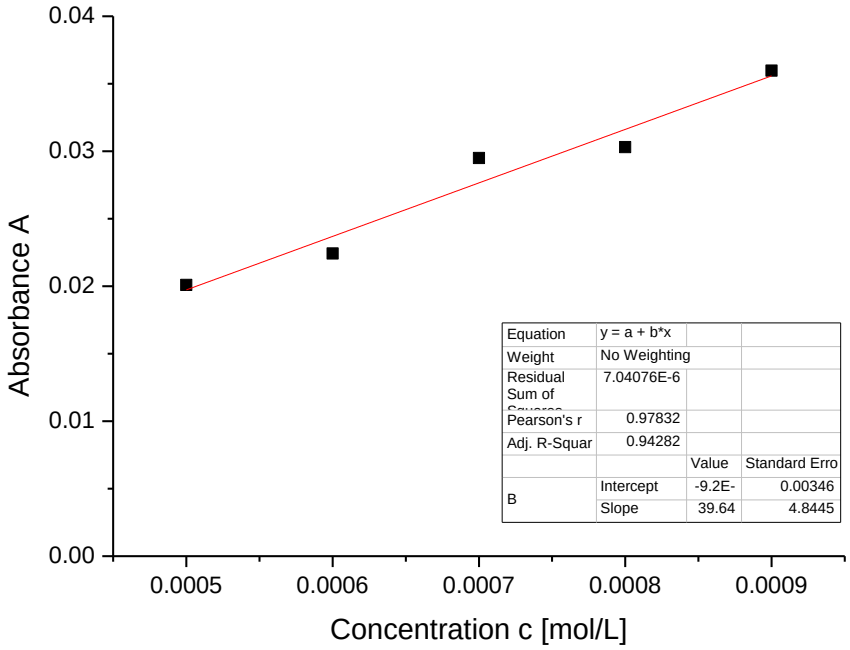

Figure S55: Determination of ε(396 M^{-1} cm^{-1}) by linear regression of absorptions (λ = 454 nm) of **6f** against concentration.

Details on X-ray Diffraction Studies

Table S1. Crystal data and structure refinement for *ligato*-TMS-substituted siliconoid **5a** (CCDC-1877380).

Identification code	sh3711	
Empirical formula	C78 H124 Si7, 0.5(C5 H12)	
Formula weight	1294.47	
Temperature	132(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 38.1514(15) Å	α = 90°.
	b = 12.7134(5) Å	β= 94.456(3)°.
	c = 33.8416(11) Å	γ = 90°.
Volume	16364.7(11) $Å^3$	
Z	8	
Density (calculated)	1.051 Mg/m^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	5688	
Crystal size	0.546 x 0.393 x 0.223 mm^3	
Theta range for data collection	1.071 to 29.218°.	
Index ranges	-52<=h<=52, -17<=k<=17, -46<=l<=46	
Reflections collected	160059	
Independent reflections	22155 [R(int) = 0.0358]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7025	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22155 / 83 / 836	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1036	
R indices (all data)	R1 = 0.0584, wR2 = 0.1118	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.779 and -0.649 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for *ligato*-benzoyl-substituted siliconoid **5b** (CCDC-1877381).

Identification code	sh3716	
Empirical formula	C82 H120 O Si6	
Formula weight	1290.31	
Temperature	132(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.8229(6) Å	α= 90°.
	b = 28.6659(10) Å	β= 107.786(2)°.
	c = 30.7990(12) Å	γ = 90°.
Volume	15824.1(10) $Å^3$	
Z	8	
Density (calculated)	1.083 Mg/m^3	
Absorption coefficient	0.147 mm^{-1}	
F(000)	5632	
Crystal size	0.672 x 0.453 x 0.385 mm^3	
Theta range for data collection	0.993 to 27.929°.	
Index ranges	-22<=h<=24, -37<=k<=35, -40<=l<=40	
Reflections collected	152878	
Independent reflections	37861 [R(int) = 0.0485]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	37861 / 192 / 1743	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0648, wR2 = 0.1395	
R indices (all data)	R1 = 0.1038, wR2 = 0.1598	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.801 and -0.476 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for *privo*-lithiated anionic siliconoid **4Li** (CCDC-1877378).

Identification code	sh3618	
Empirical formula	C87 H139 Li O3 Si6	
Formula weight	1408.45	
Temperature	175(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.2918(16) Å	α= 109.652(5)°.
	b = 16.4145(18) Å	β= 104.243(4)°.
	c = 21.516(3) Å	γ = 99.970(4)°.
Volume	4422.6(9) Å^3	
Z	2	
Density (calculated)	1.058 Mg/m^3	
Absorption coefficient	0.138 mm^{-1}	
F(000)	1544	
Crystal size	0.696 x 0.647 x 0.466 mm^3	
Theta range for data collection	1.362 to 27.284°.	
Index ranges	-18<=h<=18, -21<=k<=20, -27<=l<=27	
Reflections collected	69055	
Independent reflections	19545 [R(int) = 0.0443]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6196	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19545 / 411 / 1006	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1581	
R indices (all data)	R1 = 0.0952, wR2 = 0.1885	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.975 and -0.428 e.Å^{-3}	

Table S4. Crystal data and structure refinement for *privo*-TMS-substituted siliconoid **6a** (CCDC-1877379).

Identification code	sh3668	
Empirical formula	C78 H124 Si7, C6 H14	
Formula weight	1344.57	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 21.0070(7) Å	α= 90°.
	b = 20.4182(7) Å	β= 95.4324(13)°.
	c = 19.9183(7) Å	γ = 90°.
Volume	8505.1(5) $Å^3$	
Z	4	
Density (calculated)	1.050 Mg/m^3	
Absorption coefficient	0.152 mm^{-1}	
F(000)	2960	
Crystal size	0.480 x 0.380 x 0.166 mm^3	
Theta range for data collection	0.974 to 28.755°.	
Index ranges	-27<=h<=28, -27<=k<=25, -24<=l<=26	
Reflections collected	68739	
Independent reflections	22100 [R(int) = 0.0376]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6844	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22100 / 26 / 1278	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1158	
R indices (all data)	R1 = 0.0737, wR2 = 0.1319	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.783 and -0.504 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for *privo*-pivaloyl-substituted siliconoid **6c** (CCDC-1877382).

Identification code	sh3824	
Empirical formula	C80 H124 O Si6, 0.5(C6 H14)	
Formula weight	1313.41	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.3961(3) Å	α= 67.9010(10)°.
	b = 18.2592(5) Å	β= 70.1540(10)°.
	c = 19.4141(4) Å	γ = 76.3090(10)°.
Volume	4106.08(17) $Å^3$	
Z	2	
Density (calculated)	1.062 Mg/m^3	
Absorption coefficient	0.143 mm^{-1}	
F(000)	1442	
Crystal size	0.374 x 0.306 x 0.220 mm^3	
Theta range for data collection	1.179 to 33.864°.	
Index ranges	-20<=h<=20, -28<=k<=28, -30<=l<=30	
Reflections collected	127205	
Independent reflections	33036 [R(int) = 0.0356]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7467 and 0.7205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33036 / 77 / 872	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1381	
R indices (all data)	R1 = 0.0908, wR2 = 0.1578	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.580 and -0.722 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for *privo*-borate-substituted siliconoid **6f** (CCDC-1877383).

Identification code	sh3732	
Empirical formula	C158 H252 B2 Li2 O2 Si12, 2(C6 H6)	
Formula weight	2712.38	
Temperature	192(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.8496(8) Å	α= 90°.
	b = 24.9370(10) Å	β= 99.856(2)°.
	c = 20.3519(9) Å	γ = 90°.
Volume	8925.2(7) $Å^3$	
Z	2	
Density (calculated)	1.009 Mg/m^3	
Absorption coefficient	0.133 mm^{-1}	
F(000)	2968	
Crystal size	0.778 x 0.754 x 0.306 mm^3	
Theta range for data collection	1.158 to 29.617°.	
Index ranges	-24<=h<=24, -34<=k<=22, -28<=l<=28	
Reflections collected	96855	
Independent reflections	25096 [R(int) = 0.0341]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6970	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25096 / 192 / 950	
Goodness-of-fit on F^2	1.403	
Final R indices [I>2sigma(I)]	R1 = 0.0643, wR2 = 0.1752	
R indices (all data)	R1 = 0.0991, wR2 = 0.1926	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.192 and -0.383 $e.Å^{-3}$	

Plot of the Hammett parameter σ_m/σ_p vs ^{29}Si chemical shift of Si2

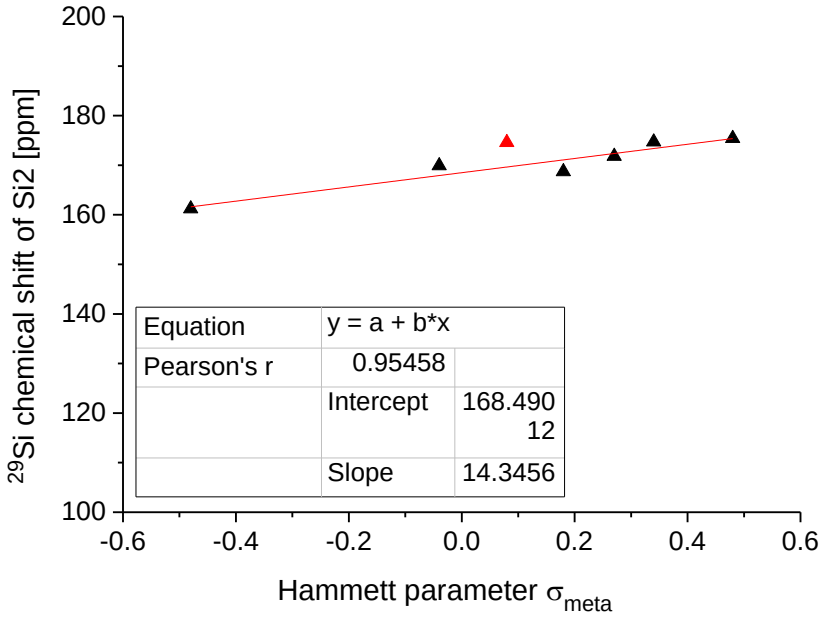

Figure S56: Plot of the Hammett parameter σ_m vs ^{29}Si chemical shift of Si2 for substituents in *ligato* position of **5a-f** and **2**.

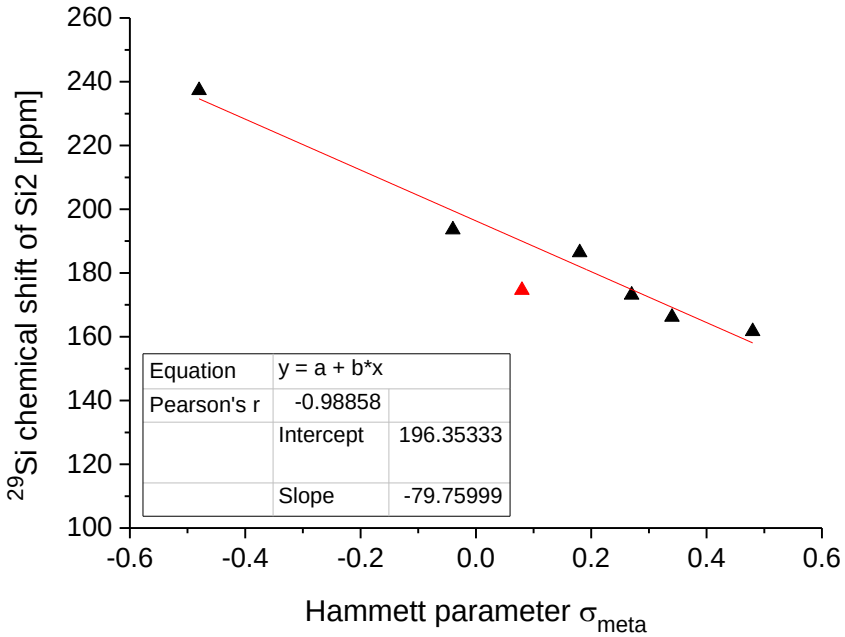

Figure S57: Plot of the Hammett parameter σ_m vs ^{29}Si chemical shift of Si2 for substituents in *privo* position of **6a-f** and **2**.

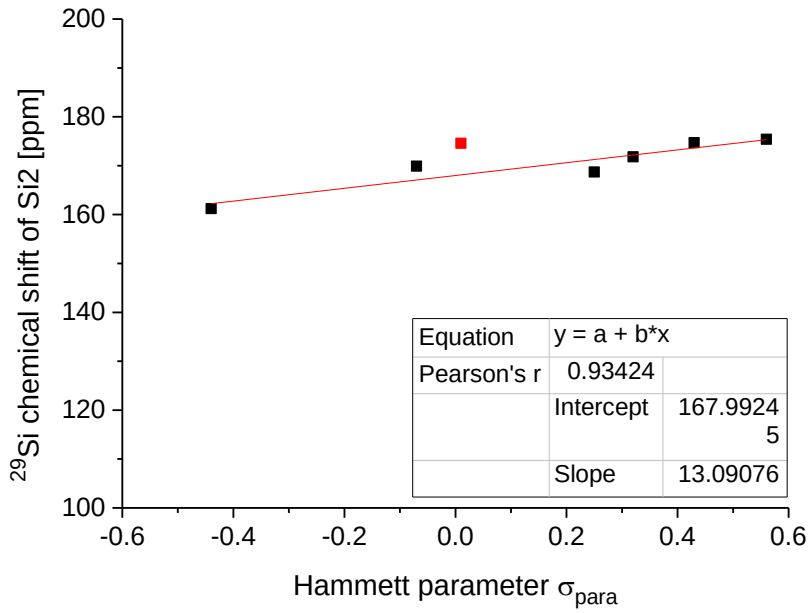

Figure S58: Plot of the Hammett parameter σ_p vs ^{29}Si chemical shift of Si2 for substituents in *ligato* position of **5a-f** and **2**.

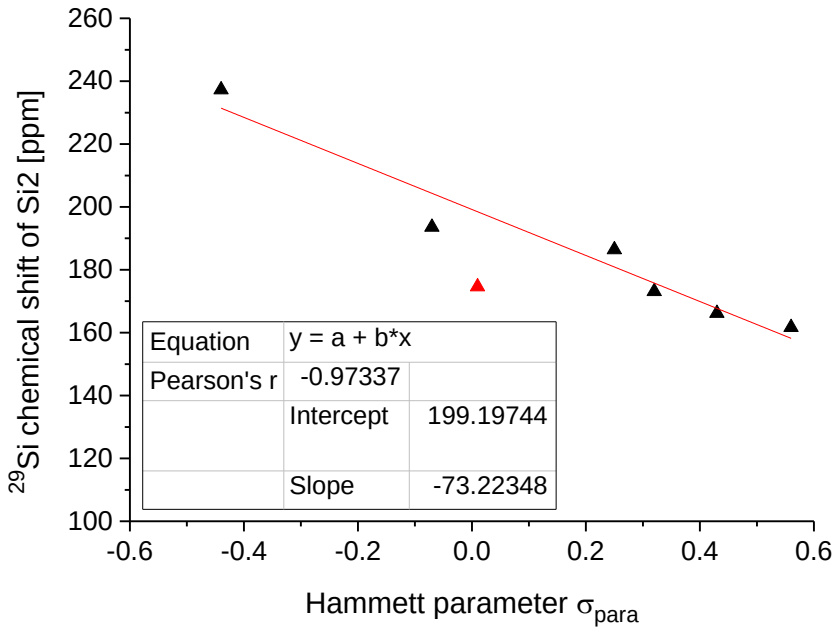

Figure S59: Plot of the Hammett parameter σ_p vs ^{29}Si chemical shift of Si2 for substituents in *privo* position of **6a-f** and **2**.