Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Oxidation Reactions of a Versatile, Two-Coordinate, Acyclic Iminosiloxysilylene

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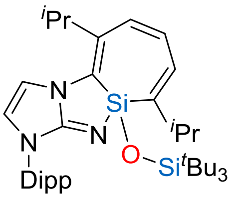
1. Experimental Section

1.1 General Methods and Instrumentation

All manipulations were carried out under exclusion of H_2O and O_2 under an atmosphere of argon 4.6 (≥99.996%; *Westfalen AG*) using standard *Schlenk* techniques or in a *LABstar* glovebox from *MBraun Inertgas-Systeme GmbH* with H_2O and O_2 levels below 0.5 ppm. The glassware used was heat dried under fine vacuum prior to use with *Triboflon III* grease (mixture of polytetrafluoroethylene (PTFE) and perfluoropolyether (PFPE)) from *Freudenberg & Co. KG* as sealant. All solvents were refluxed over sodium/benzophenone, freshly distilled under argon and deoxygenated before use. Deuterated benzene was obtained from *Sigma-Aldrich Chemie GmbH*, dried over Na/K alloy, flask-to-flask condensed, deoxygenated by three freeze-pump-thaw cycles and stored over 3 Å molecular sieves in the glovebox. All NMR samples were prepared under argon in *J. Young* PTFE valve NMR tubes. The NMR spectra were recorded on *Bruker AV400US* (^{1}H: 400.13 MHz, ^{11}B 128.38 MHz), *Avance Neo 400* (^{1}H: 400.23 MHz, ^{13}C: 100.65 MHz, ^{31}P: 162.01 MHz), *AV500* (^{1}H: 500.13 MHz) or *AV500C* (^{1}H: 500.36 MHz, ^{13}C: 125.83 MHz, ^{19}F: 470.77 MHz, ^{29}Si: 99.41 MHz, ^{31}P: 202.57 MHz) spectrometers at ambient temperature (300 K). The ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. ^{1}H and ^{13}C{^{1}H} NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the deuterated solvent as internal standard (C_6D_6: $\delta(^1H) = 7.16$ ppm and $\delta(^{13}C) = 128.1$ ppm).[S1] The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad and combinations thereof (*e.g.* dd = doublet of doublets). Some NMR spectra include resonances for silicone grease (C_6D_6: $\delta(^1H) = 0.29$ ppm, $\delta(^{13}C) = 1.4$ ppm and $\delta(^{29}Si) = -21.8$ ppm) derived from *B. Braun Melsungen AG Sterican®* cannulas. Quantitative elemental analyses (EA) were carried out using a *EURO EA* (*HEKAtech*) instrument equipped with a CHNS combustion analyzer at the *Laboratory for Microanalysis* at the *TUM Catalysis Research Center*. Elemental analyses provided partially and reproducibly low carbon percentages (~1% deviation), presumably due to the formation of incombustible SiC compounds. Melting Points (m.p.) were determined in sealed glass capillaries under inert gas by a *Büchi M-565* melting point apparatus. Mass spectra (Liquid Injection Field Desorption Ionization (LIFDI)-MS) were recorded on a *Waters Micromass LCT TOF* mass spectrometer equipped with a LIFDI-ion source (*LIFDI-700*) from *Linden CMS GmbH*. The samples were provided as filtered solution in toluene. Photochemical experiments were carried out using an *Asahi Spectra Co., Ltd. MAX-302* Xenon

Light Source at λ_{max} = 340 nm. Unless otherwise stated, all commercially available reagents were purchased from *abcr GmbH* or *Sigma-Aldrich Chemie GmbH* and used without further purification. Carbon dioxide (CO_2) 5.0 (≥99.999%), dinitrogen monoxide (N_2O) 5.0 (≥99.999%) and oxygen (O_2) 5.0 (≥99.999%) were purchased from *Westfalen AG* and used as received. The compounds iminosiloxysilylene (IDippN)(^{t}Bu$_3$SiO)Si: (**1**)[S2], 1,3,4,5-tetramethylimidazolin-2-ylidene (IMe$_4$)[S3] and 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (I^{i}Pr$_2$Me$_2$)[S3] were prepared as described in the corresponding references. Azido(di-*tert*-butylmethyl)silane (^{t}Bu$_2$MeSiN$_3$) was synthesized *via* a modified literature procedure (*vide infra*).[S4] White phosphorus (P_4) was sublimed and stored at –35 °C in the dark in the glovebox.

1.2 Synthesis of Iminosiloxysilepin 2



2
$C_{39}H_{63}N_3OSi_2$
646.12 g/mol

A *J. Young* PTFE valve NMR tube was charged with a solution of silylene **1** (50.0 mg, 77.4 µmol) in C_6D_6 (0.5 mL). After irradiation (λ_{max} = 340 nm) at room temperature for 4 h, quantitative conversion was detected by ^{1}H NMR spectroscopy. Removal of the solvent *in vacuo* provided iminosiloxysilepin **2** as a pale yellow solid (50.0 mg, 77.4 µmol, quantitative yield). Compound **2** is completely stable as a solid and in solution at ambient and elevated temperatures (≤130 °C).

m.p.: 181-182 °C.

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.20–7.14 (m, 2H, *m*-/*p*-C$_{Dipp}$*H̲*, overlapping with solvent signal), 7.07 (dd, ^4J = 1.9 Hz, ^3J = 7.3 Hz, 1H, *m*-C$_{Dipp}$*H̲*), 6.83 (d, ^3J = 7.2 Hz, 1H, C$_{silepin}$*H̲*), 6.70 (d, ^3J = 2.9 Hz, 1H, NC*H̲*), 6.55 (d, ^3J = 13.2 Hz, 1H, C$_{silepin}$*H̲*), 6.42 (dd, ^3J = 13.2 Hz, ^3J = 6.9 Hz, 1H, C$_{silepin}$*H̲*), 5.87 (d, ^3J = 2.9 Hz, 1H, NC*H̲*), 3.34 (sept, ^3J = 6.9 Hz, 1H, C*H̲*(CH$_3$)$_2$), 3.06 (sept, ^3J = 7.1 Hz, 1H, C*H̲*(CH$_3$)$_2$), 2.97 (sept, ^3J = 6.7 Hz, 1H, C*H̲*(CH$_3$)$_2$), 2.87 (sept, ^3J = 6.9 Hz, 1H, C*H̲*(CH$_3$)$_2$), 1.40 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.37 (d, ^3J = 7.0 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.36 (d, ^3J = 6.7 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.25 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.22 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.20 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$), 1.13 (s, 27H, C(C*H̲*$_3$)$_3$), 1.07 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$), 0.93 (d, ^3J = 6.9 Hz, 3H, CH(C*H̲*$_3$)$_2$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 157.6 (*C̲*), 151.1 (*C̲*), 148.0 (*C̲*), 147.5 (*C̲*), 133.9 (*C̲*), 133.8 (*C̲*), 132.1 (*C̲*H), 132.0 (*C̲*), 129.7 (*C̲*H), 128.6 (*C̲*H), 126.6 (*C̲*H), 124.3 (*C̲*H), 123.9 (*C̲*H), 117.1 (N*C̲*H), 110.5 (N*C̲*H), 36.1 (*C̲*H(CH$_3$)$_2$), 30.2 (C(*C̲*H$_3$)$_3$), 29.5 (*C̲*H(CH$_3$)$_2$), 28.9 (*C̲*H(CH$_3$)$_2$), 28.7 (*C̲*H(CH$_3$)$_2$), 25.5 (CH(*C̲*H$_3$)$_2$), 25.1 (CH(*C̲*H$_3$)$_2$), 24.7 (CH(*C̲*H$_3$)$_2$), 23.9

(CH($\underline{C}$H$_3$)$_2$), 23.7 (CH($\underline{C}$H$_3$)$_2$), 23.2 ($\underline{C}$(CH$_3$)$_3$), 23.2 (CH($\underline{C}$H$_3$)$_2$), 22.1 (CH($\underline{C}$H$_3$)$_2$), 22.0 (CH($\underline{C}$H$_3$)$_2$).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 4.7 (<u>*Si*</u>^{t}Bu$_3$), –15.5 (<u>*silepin Si*</u>).

Anal. Calcd. [%] for C$_{39}$H$_{63}$N$_3$OSi$_2$: C, 72.50; H, 9.83; N, 6.50. Found [%]: C, 72.25; H, 9.80; N, 6.49.

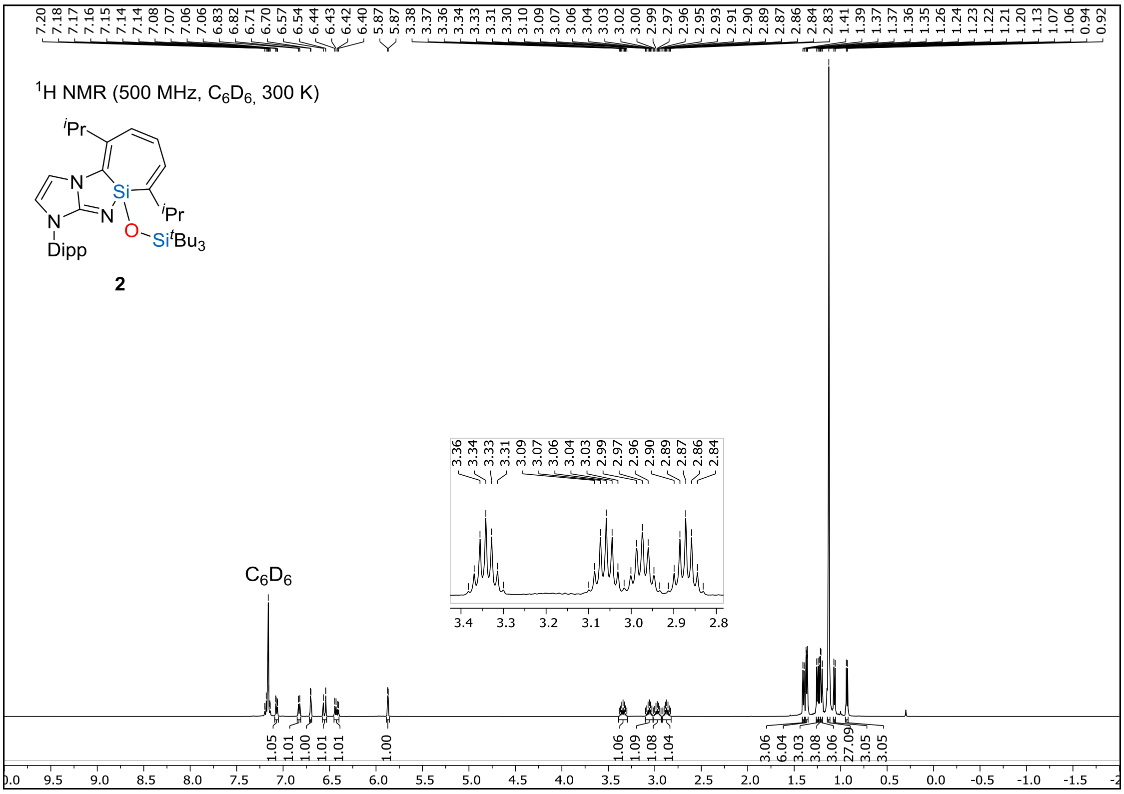


Figure S1. ^{1}H NMR spectrum of iminosiloxysilepin **2** in C$_6$D$_6$ at 300 K.

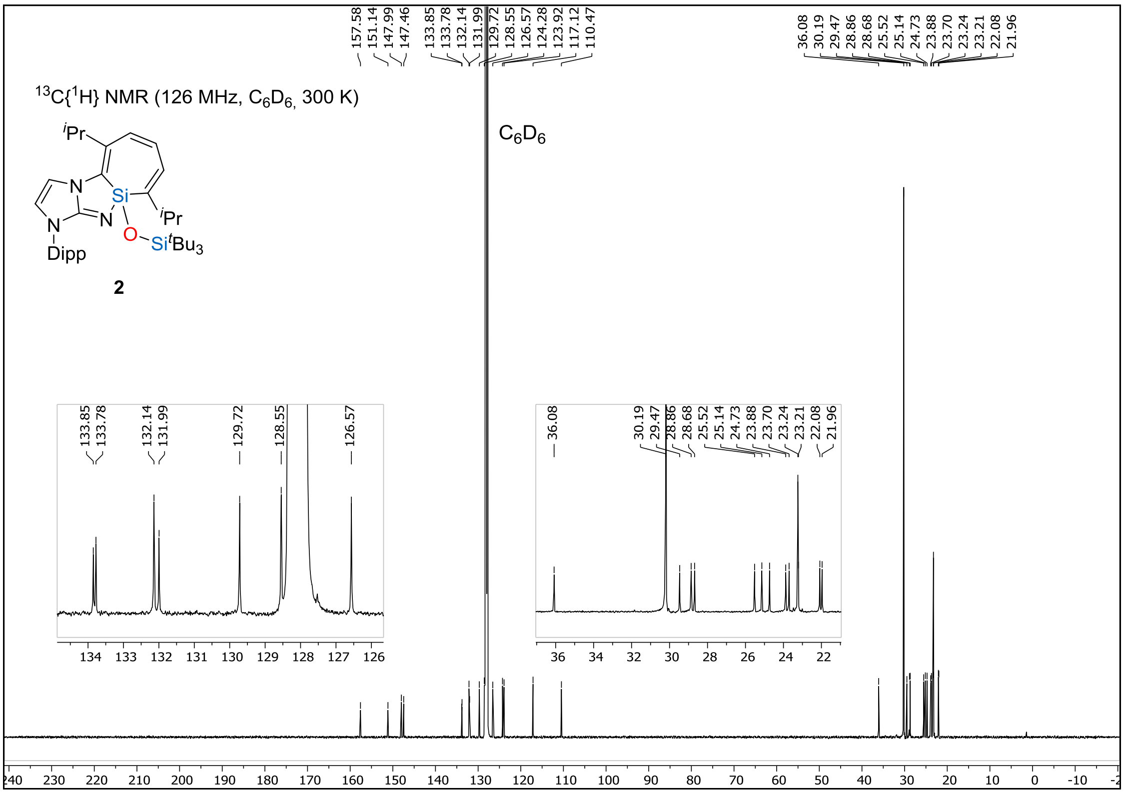


Figure S2. ^{13}C{^{1}H} NMR spectrum of iminosiloxysilepin **2** in C_6D_6 at 300 K.

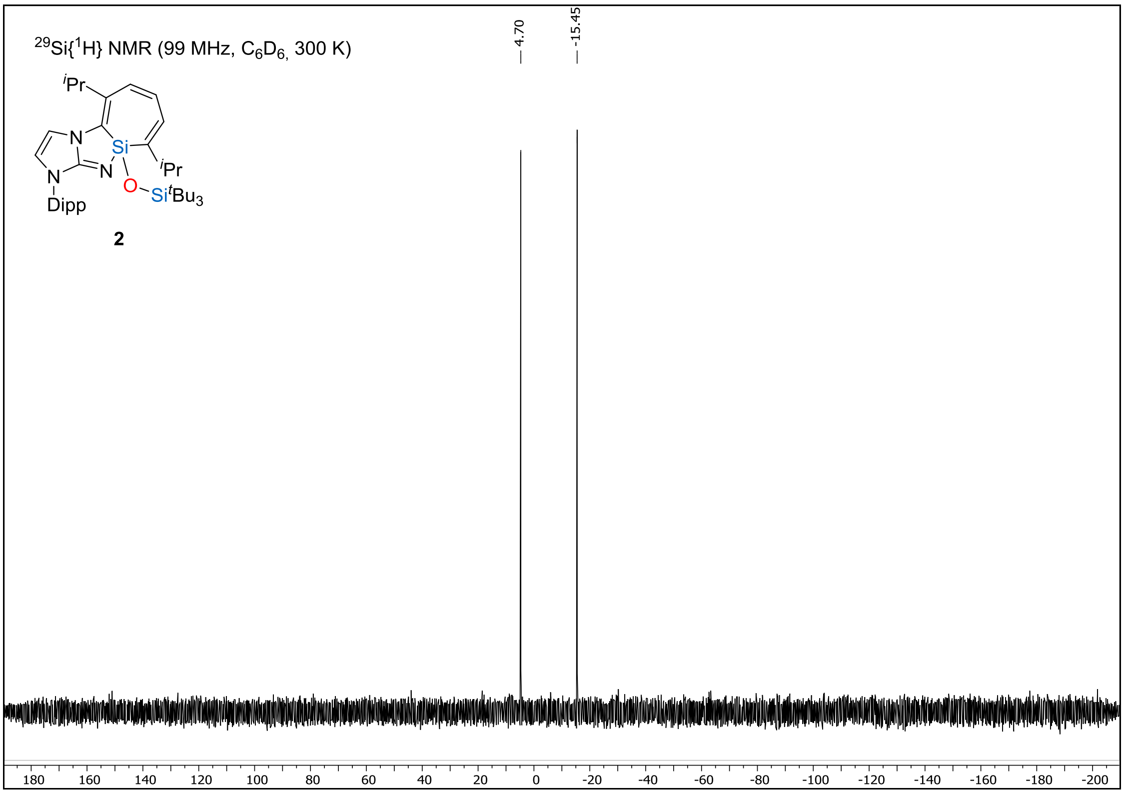


Figure S3. ^{29}Si{^{1}H} NMR spectrum of iminosiloxysilepin **2** in C_6D_6 at 300 K.

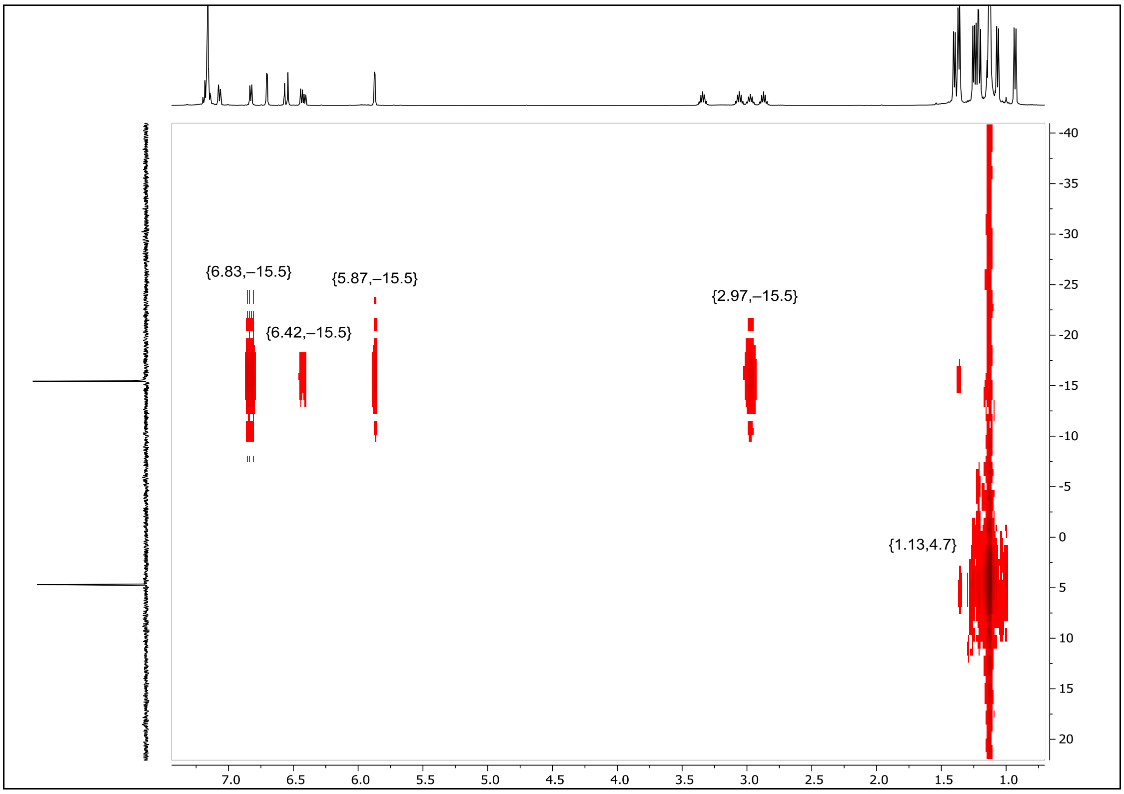
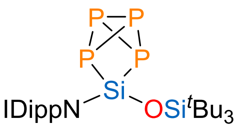


Figure S4. ^{1}H/^{29}Si HMBC NMR spectrum of iminosiloxysilepin **2** in C_6D_6 at 300 K.

1.3 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si(P_4) (3)



3

$C_{39}H_{63}N_3OP_4Si_2$

770.02 g/mol

To a mixture of silylene **1** (100 mg, 155 µmol, 1.0 eq.) and P_4 (19.2 mg, 155 µmol, 1.0 eq.) was added benzene (3 mL). The Reaction mixture was stirred for 3 h whereby a color change from colorless to orange was observed. After removal of the solvent *in vacuo*, (IDippN)(^{t}Bu$_3$SiO)Si(P_4) (**3**) was obtained as a pale orange solid (119 mg, 155 µmol, quantitative yield). Colorless crystals, suitable for single-crystal X-ray diffraction (SC-XRD) analysis, were obtained by cooling a saturated *n*-hexane solution of **3** to –35 °C for several days. Compound **3** is completely stable as a solid and in solution at ambient temperature.

Note: Compound **3** reacts selectively with an equimolar amount of silylene **1** to form a new product, which is most likely ((IDippN)(^{t}Bu$_3$SiO)Si)$_2$(P_4), but the reaction is extremely slow (only ~10% conversion after 10 days at 110 °C in benzene detected) and thus was not further studied. A similar reaction between an $R_2Si(P_4)$ cage compound and a silylene R_2Si: was reported previously.[S5]

m.p.: 120-121 °C (decomposition; color change from pale orange to orange).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.23–7.18 (m, 6H, $C_{ar}\underline{H}$), 6.01 (s, 2H, $NC\underline{H}$), 3.25 (sept, ^3J = 6.9 Hz, 4H, $C\underline{H}(CH_3)_2$), 1.49 (d, ^3J = 6.9 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.17 (s, 27H, $C(C\underline{H}_3)_3$), 1.14 (d, ^3J = 6.9 Hz, 12H, $CH(C\underline{H}_3)_2$).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 146.5 (*o*-$\underline{C}_{ar}$), 141.7 (N$\underline{C}$N), 134.7 (*ipso*-$\underline{C}_{ar}$), 130.1 (*p*-$\underline{C}_{ar}$H), 125.5 (*m*-$\underline{C}_{ar}$H), 115.5 (N$\underline{C}$H), 30.7 (C($\underline{C}H_3)_3$), 29.1 ($\underline{C}$H($CH_3)_2$), 24.9 (CH($\underline{C}H_3)_2$), 23.5 (CH($\underline{C}H_3)_2$), 23.4 (CH($\underline{C}H_3)_2$), 23.0 ($\underline{C}(CH_3)_3$).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 5.1 ($\underline{Si}^t$Bu$_3$), –87.9 (broad s, $\underline{Si}P_4$).

$^{31}P\{^1H\}$ NMR (203 MHz, C_6D_6, 300 K): δ [ppm] = 152.1 (dd, $^1J(P_2P_1)$ = 157.6 Hz, $^1J(P_3P_1)$ = 149.6 Hz, 2P, Si$\underline{P}_1$), –327.7 (dt, $^1J(P_2P_3)$ = 181.6 Hz, $^1J(P_1P_3)$ = 149.6 Hz, 1P, $\underline{P}_3$), –337.0 (dt, $^1J(P_3P_2)$ = 181.6 Hz, $^1J(P_1P_2)$ = 157.6 Hz, 1P, $\underline{P}_2$). The assignment of the observed resonances to the respective ^{31}P nuclei can be found in **Figure S8** (*vide infra*).

Anal. Calcd. [%] for $C_{39}H_{63}N_3OP_4Si_2$: C, 60.83; H, 8.25; N, 5.46. Found [%]: C, 60.53; H, 8.24; N, 5.30.

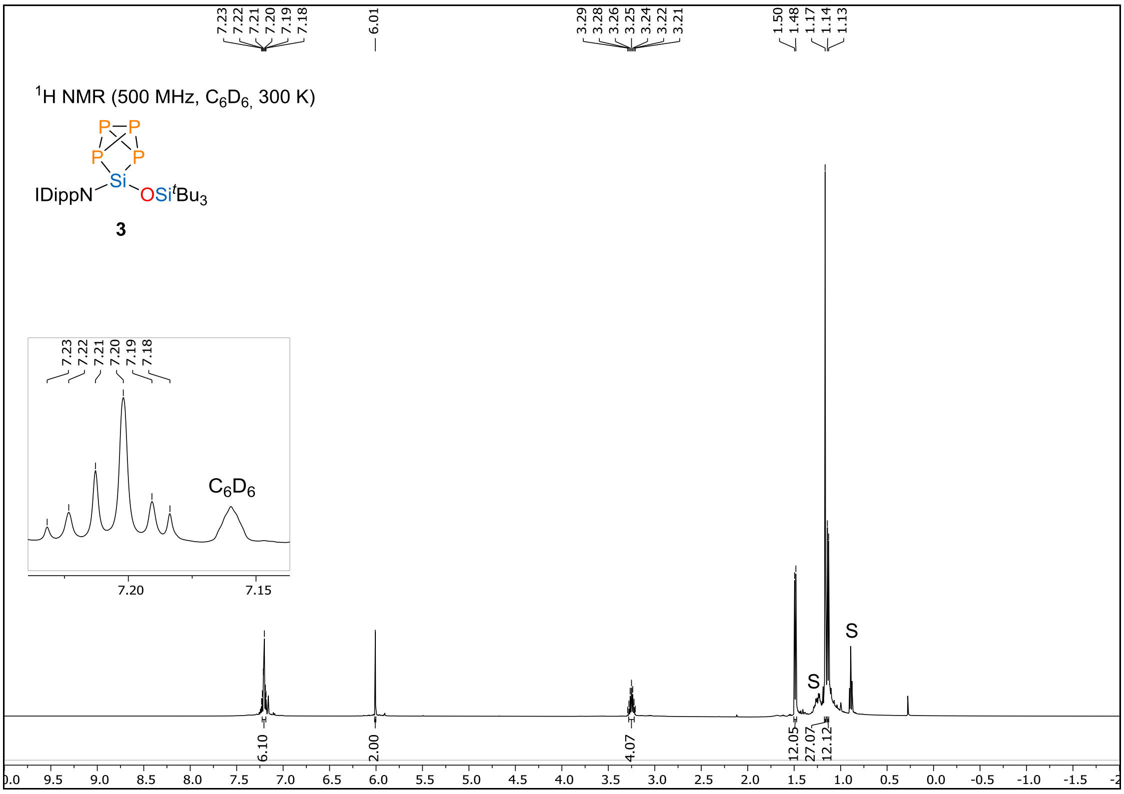


Figure S5. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(P$_4$) (**3**) in C_6D_6 at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

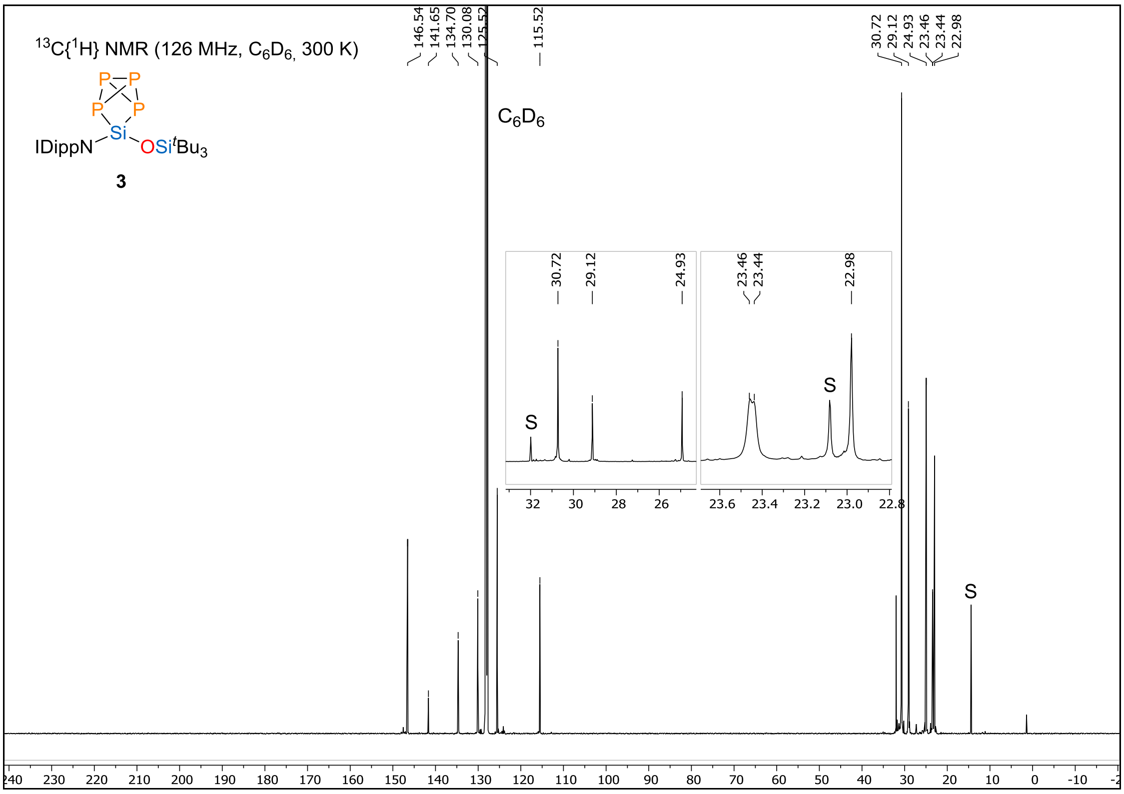


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(P$_4$) (**3**) in C_6D_6 at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

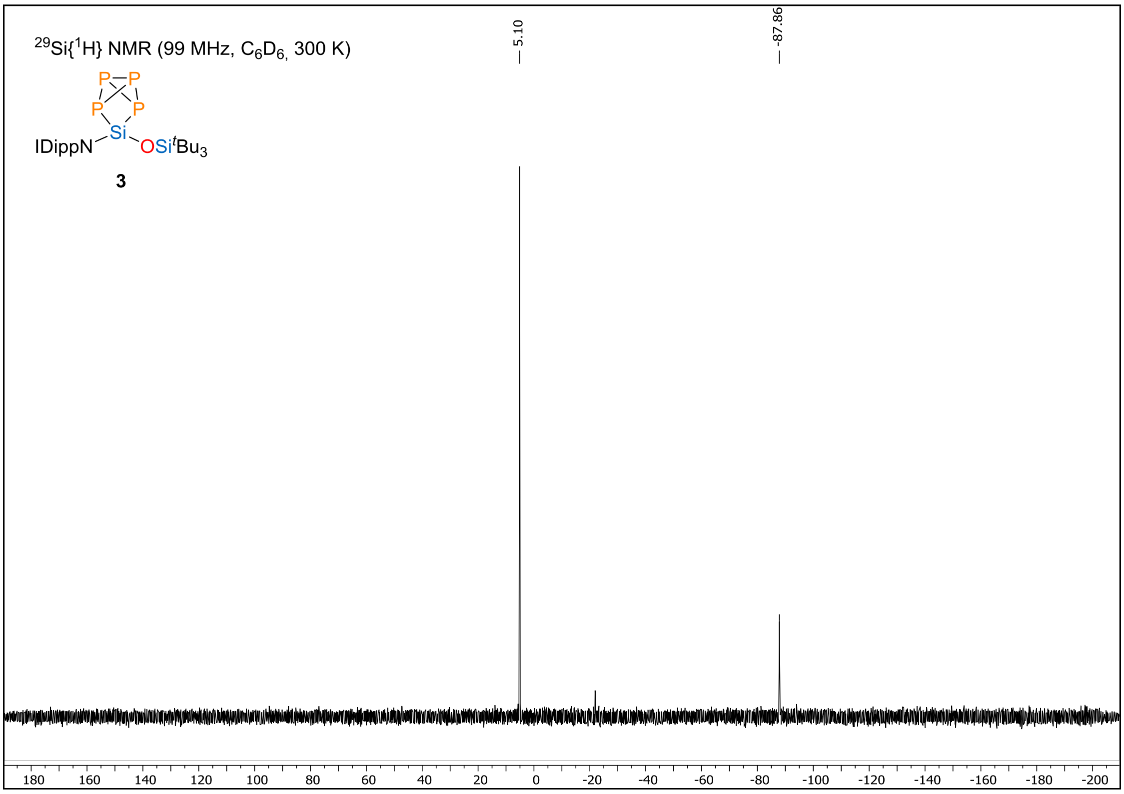


Figure S7. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(P$_4$) (**3**) in C_6D_6 at 300 K.

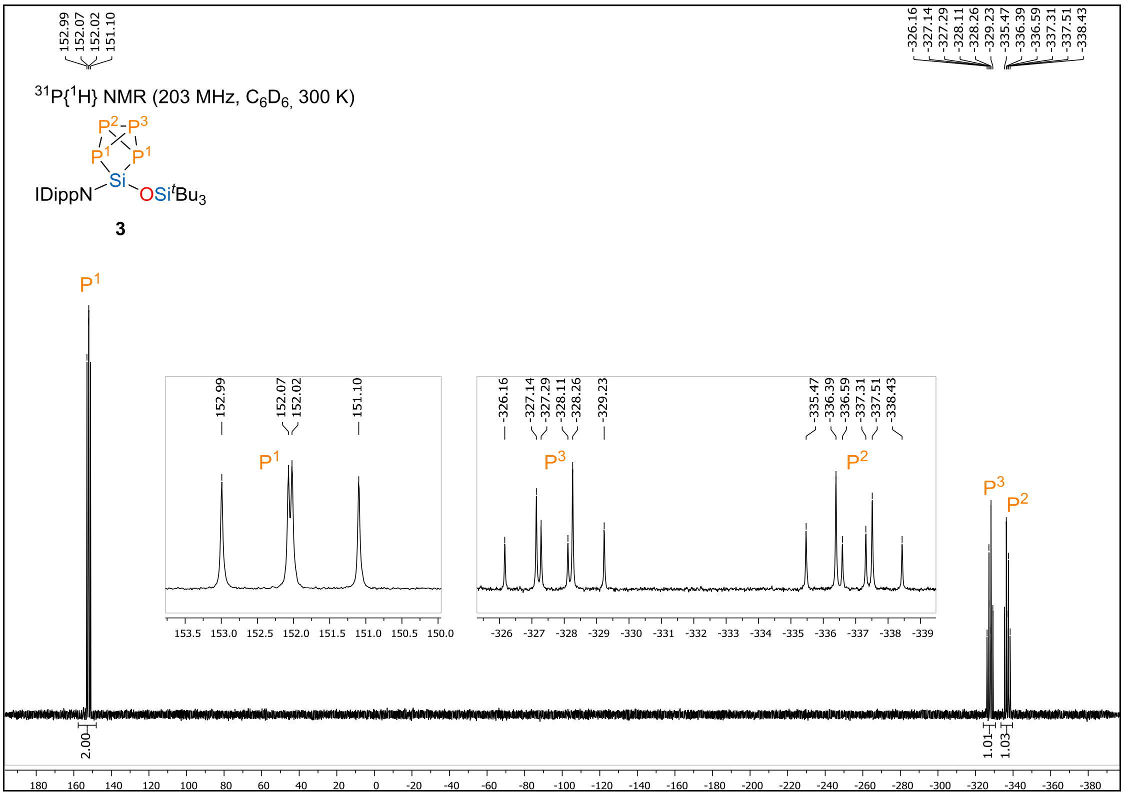
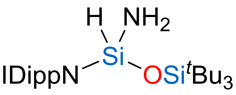


Figure S8. $^{31}P\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(P$_4$) (**3**) in C_6D_6 at 300 K.

1.4 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (4)



4

$C_{39}H_{66}N_4OSi_2$

663.15 g/mol

To a cooled (–80 °C) solution of silylene **1** (300 mg, 464 µmol, 1.0 eq.) in *n*-hexane (10 mL) was added a 0.4 M NH_3 solution in 1,4-dioxane (1.16 mL, 7.91 mg, 464 µmol, 1.0 eq.) under vigorous stirring. An immediate precipitation (1,4-dioxane) was observed. After stirring was continued at –80 °C for one hour, the solution was warmed to ambient temperature. All volatiles were removed *in vacuo*, affording crude aminosilane **4** as a colorless solid. Multinuclear and 2D NMR analysis clearly revealed **4** as the major product. However, all further purification attempts via crystallization, sublimation or washing were unsuccessful so far.

Note: Since the central silicon atom is chiral, the small by-product could be a stereoisomer of **4**. In addition, (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (**4**) reacts with excessive amounts of ammonia to an unidentified mixture of products, presumably also including elimination of the imino ligand under formation of IDippNH and (H$_2$N)(^{t}Bu$_3$SiO)Si(H)(NH$_2$). A similar σ-bond metathesis reaction between an Si–N bond and ammonia was previously observed.[S6]

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.24–7.21 (m, 2H, *p*-C$_{ar}$*H*), 7.14–7.11 (m, 4H, *m*-C$_{ar}$*H*), 5.95 (s, 2H, NC*H*), 4.81 (s, 1H, Si*H*, $^1J_{SiH}$ = 243.8 Hz), 3.20 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 3.09 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.42 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d,

^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.18 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.17 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.06 (s, 27H, C(C$\underline{H}_3$)$_3$), –0.14 (br s, 2H. N$\underline{H}_2$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 148.2 (*o*-$\underline{C}_{ar}$), 148.0 (*o*-$\underline{C}_{ar}$), 143.7 (N$\underline{C}$N), 134.6 (*ipso*-$\underline{C}_{ar}$), 130.0 (*p*-$\underline{C}_{ar}$H), 124.2 (*m*-$\underline{C}_{ar}$H), 124.0 (*m*-$\underline{C}_{ar}$H), 114.2 (N$\underline{C}$H), 30.2 (C($\underline{C}H_3$)$_3$), 29.1 ($\underline{C}$H(CH$_3$)$_2$), 25.5 (CH($\underline{C}H_3$)$_2$), 24.0 (CH($\underline{C}H_3$)$_2$), 23.2 ($\underline{C}$(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 1.3 ($\underline{Si}^t$Bu$_3$), –66.5 ($\underline{Si}$NH$_2$).

^{29}Si INEPT NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 1.3 ($\underline{Si}^t$Bu$_3$), –66.5 (d, $^1J_{HSi}$ = 243.8 Hz, $\underline{Si}$NH$_2$).

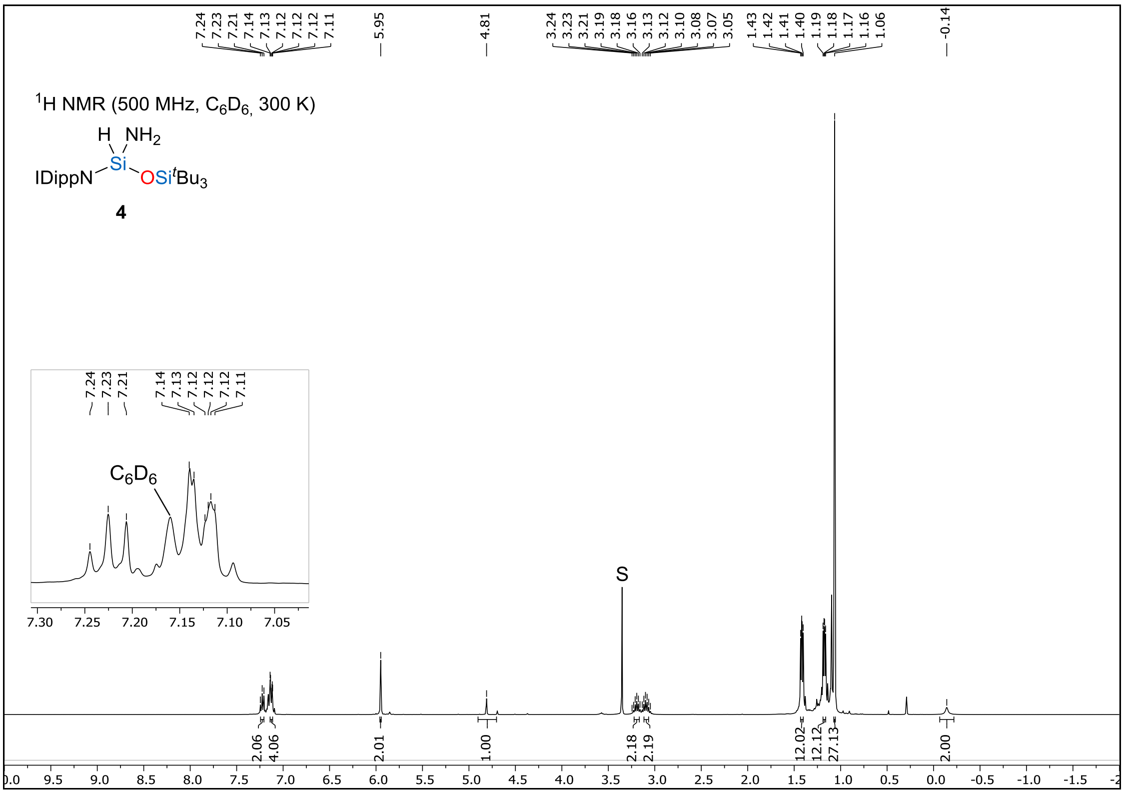


Figure S9. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (**4**) in C_6D_6 at 300 K. Residual 1,4-dioxane is marked with an S.

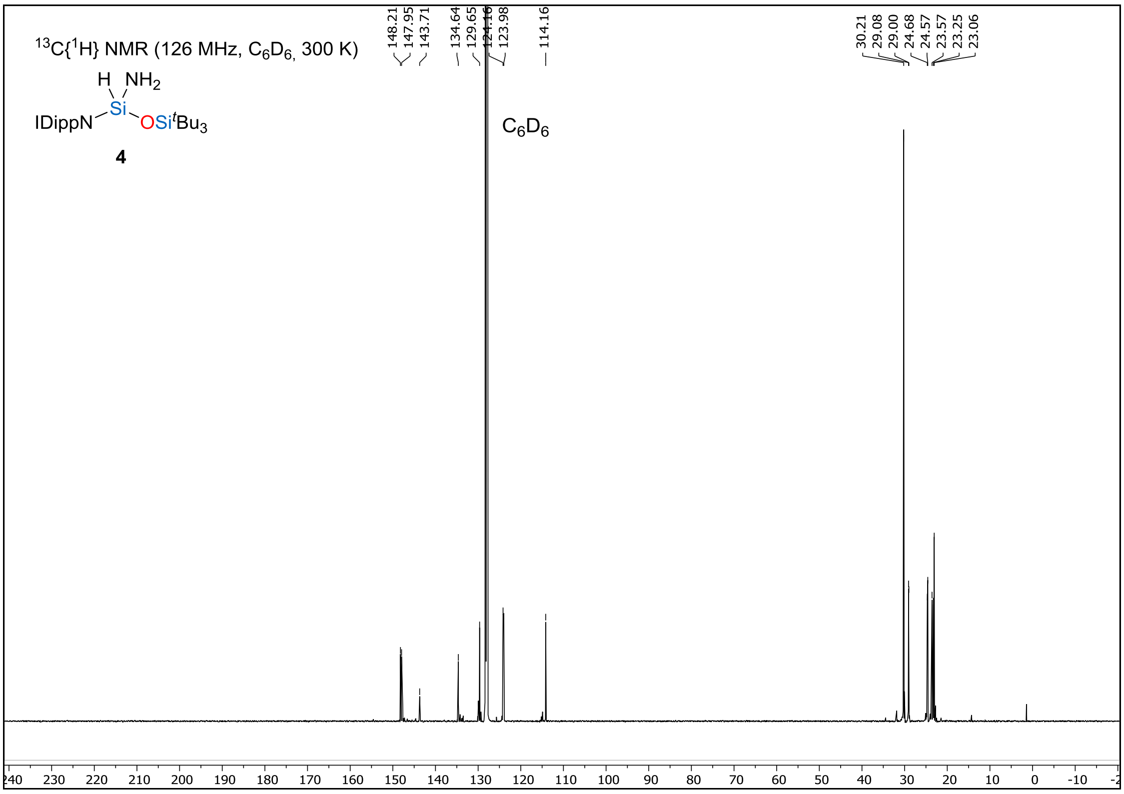


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (**4**) in C_6D_6 at 300 K.

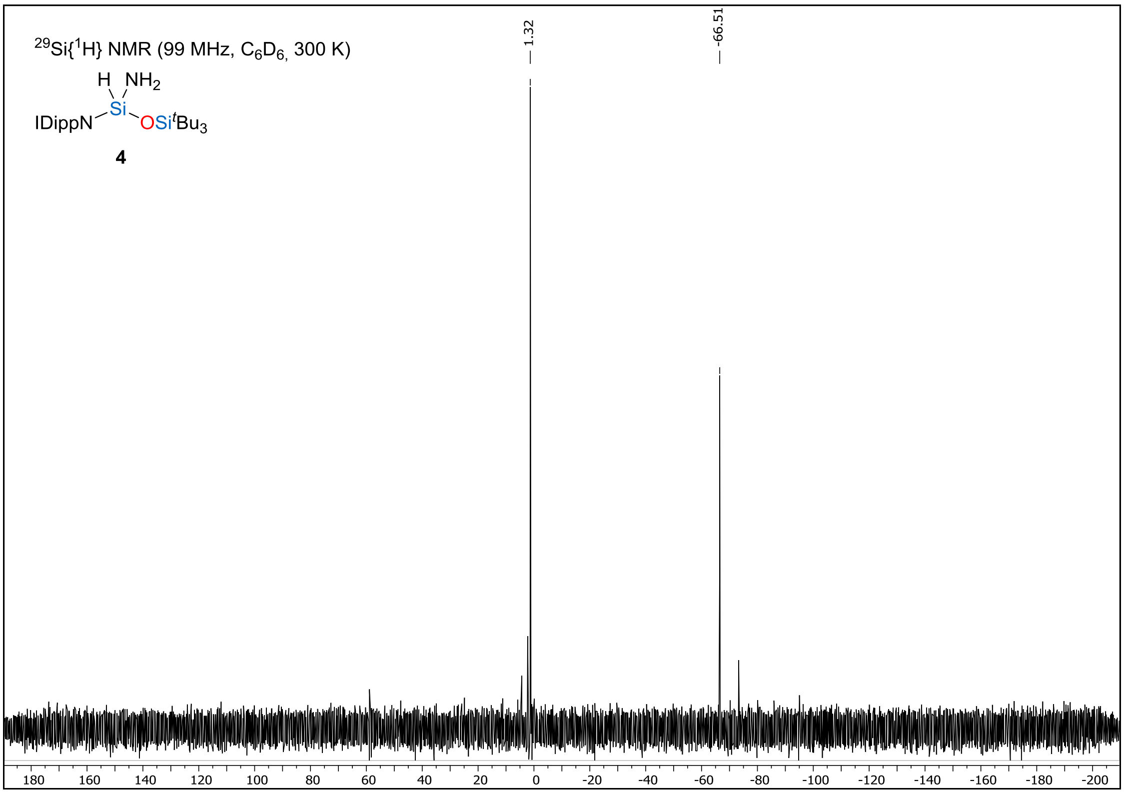


Figure S11. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (**4**) in C_6D_6 at 300 K.

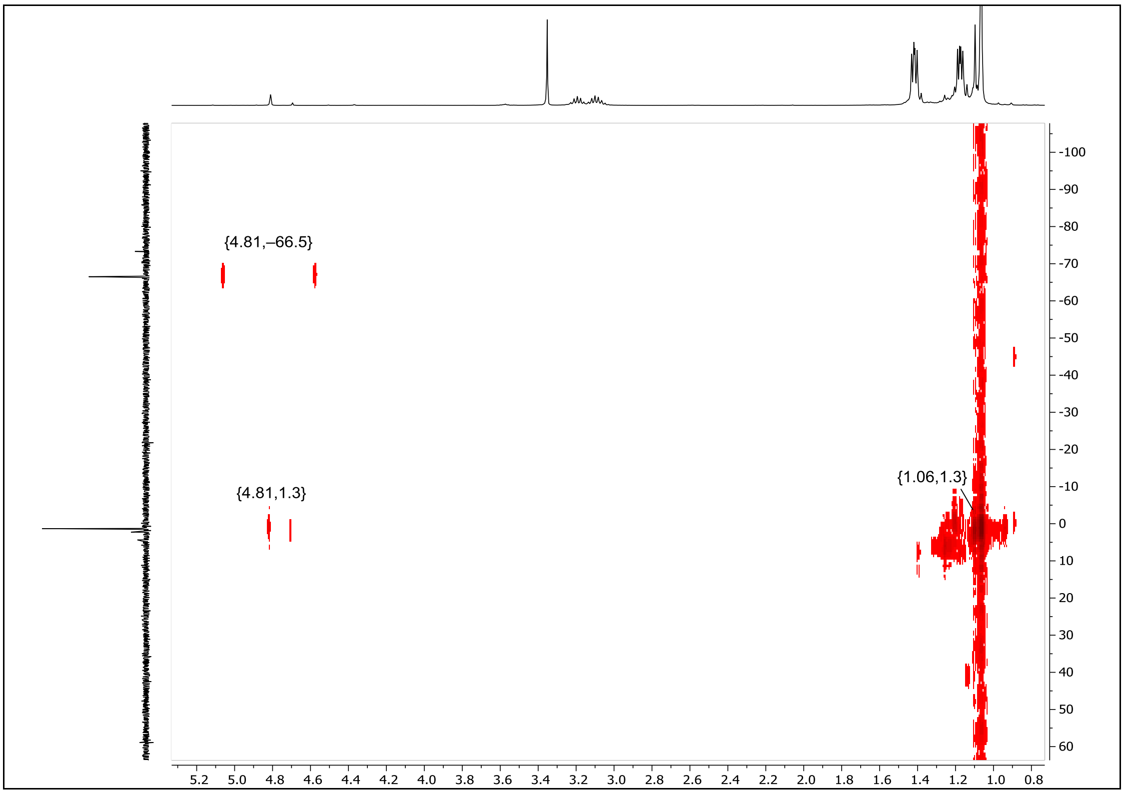
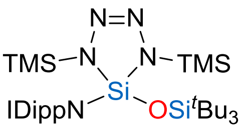


Figure S12. ^{1}H/^{29}Si HMBC NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(H)(NH$_2$) (**4**) in C_6D_6 at 300 K.

1.5 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si(NTMSN)$_2$ (5)



5

$C_{45}H_{81}N_7OSi_4$

848.53 g/mol

To a stirred solution of silylene **1** (50.0 mg, 77.4 µmol, 1.0 eq.) in benzene (2 mL) was added TMSN$_3$ (20.5 µL, 17.8 mg, 155 µmol, 2.0 eq.). After an immediately observed gas evolution (N_2), the reaction mixture was stirred for further 30 min. Removal of all volatiles *in vacuo* provided silatetrazoline **5** as a colorless solid (65.7 mg, 77.4 µmol, quantitative yield).

m.p.: 263-264 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.22–7.19 (m, 2H, *p*-C$_{ar}$$\underline{H}$), 7.16–7.13 (m, 4H, *m*-C$_{ar}$$\underline{H}$, overlapping with solvent signal), 5.89 (s, 2H, NC$\underline{H}$), 3.30 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.18 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 1.46 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.43 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.16 (s, 27H, C(C$\underline{H}_3$)$_3$), 1.09 (pseudo t, ^3J = 6.9 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 0.28 (s, 9H, $\underline{TMS}$), 0.24 (s, 9H, $\underline{TMS}$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 147.4 (*o*-$\underline{C}_{ar}$), 147.4 (*o*-$\underline{C}_{ar}$), 141.9 (N$\underline{C}$N), 135.8 (*ipso*-$\underline{C}_{ar}$), 129.7 (*p*-$\underline{C}_{ar}$H), 125.0 (*m*-$\underline{C}_{ar}$H), 124.7 (*m*-$\underline{C}_{ar}$H), 116.5 (N$\underline{C}$H), 31.0 (C($\underline{C}$H$_3$)$_3$), 29.5 ($\underline{C}$H(CH$_3$)$_2$), 29.1 ($\underline{C}$H(CH$_3$)$_2$), 26.3 (CH($\underline{C}$H$_3$)$_2$), 25.8 (CH($\underline{C}$H$_3$)$_2$), 23.2 (CH($\underline{C}$H$_3$)$_2$), 23.1 ($\underline{C}$(CH$_3$)$_3$), 23.1 (CH($\underline{C}$H$_3$)$_2$), 6.6 ($\underline{TMS}$), 6.4 ($\underline{TMS}$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 4.7 (*Si*^{t}Bu$_3$), 2.3 (*TMS*), 0.7 (*TMS*), –90.6 (*Si*(NTMSN)$_2$).

Anal. Calcd. [%] for $C_{45}H_{81}N_7OSi_4$: C, 63.70; H, 9.62; N, 11.56. Found [%]: C, 63.86; H, 9.86; N, 11.29.

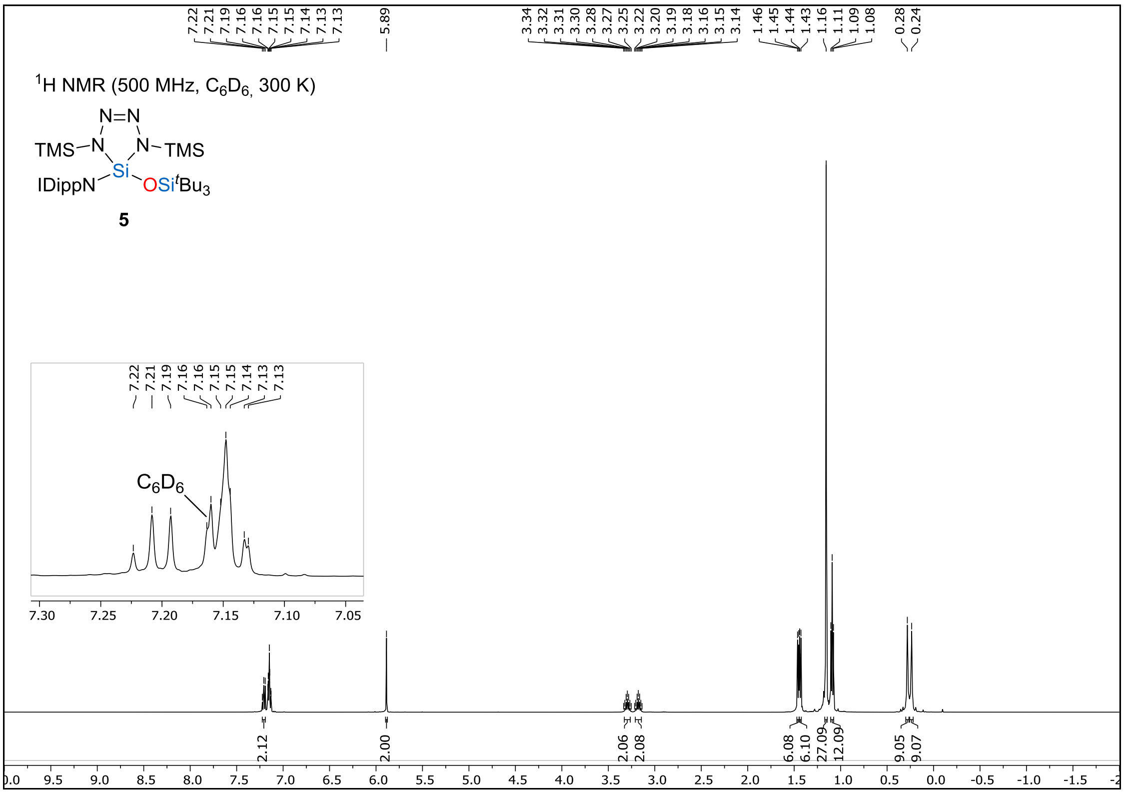


Figure S13. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(NTMSN)$_2$ (**10**) in C_6D_6 at 300 K.

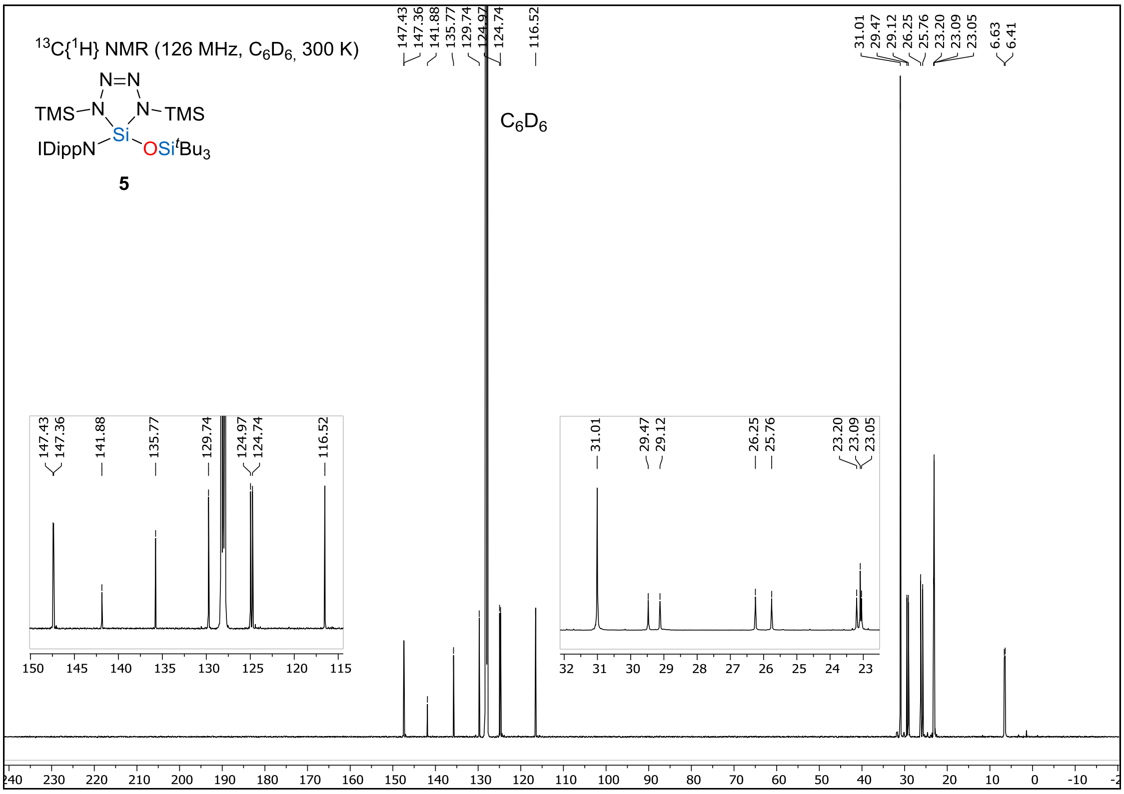


Figure S14. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(NTMSN)$_2$ (**5**) in C_6D_6 at 300 K.

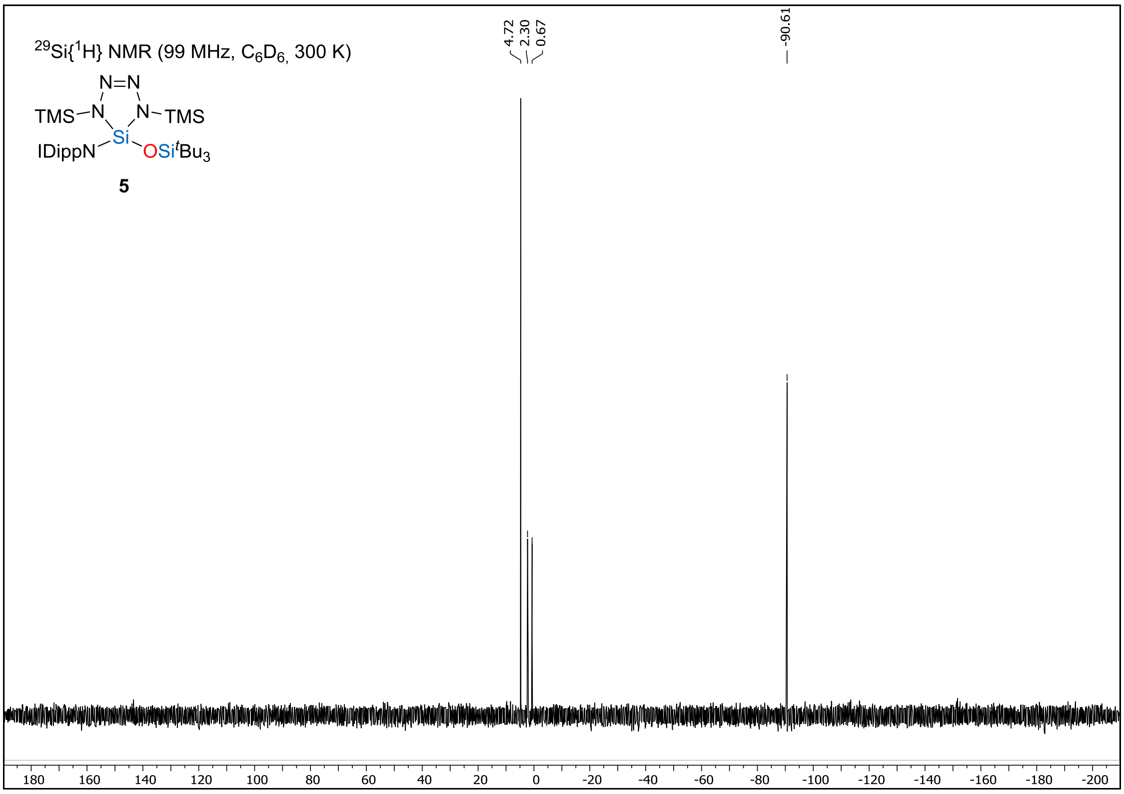


Figure S15. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(NTMSN)$_2$ (**5**) in C_6D_6 at 300 K.

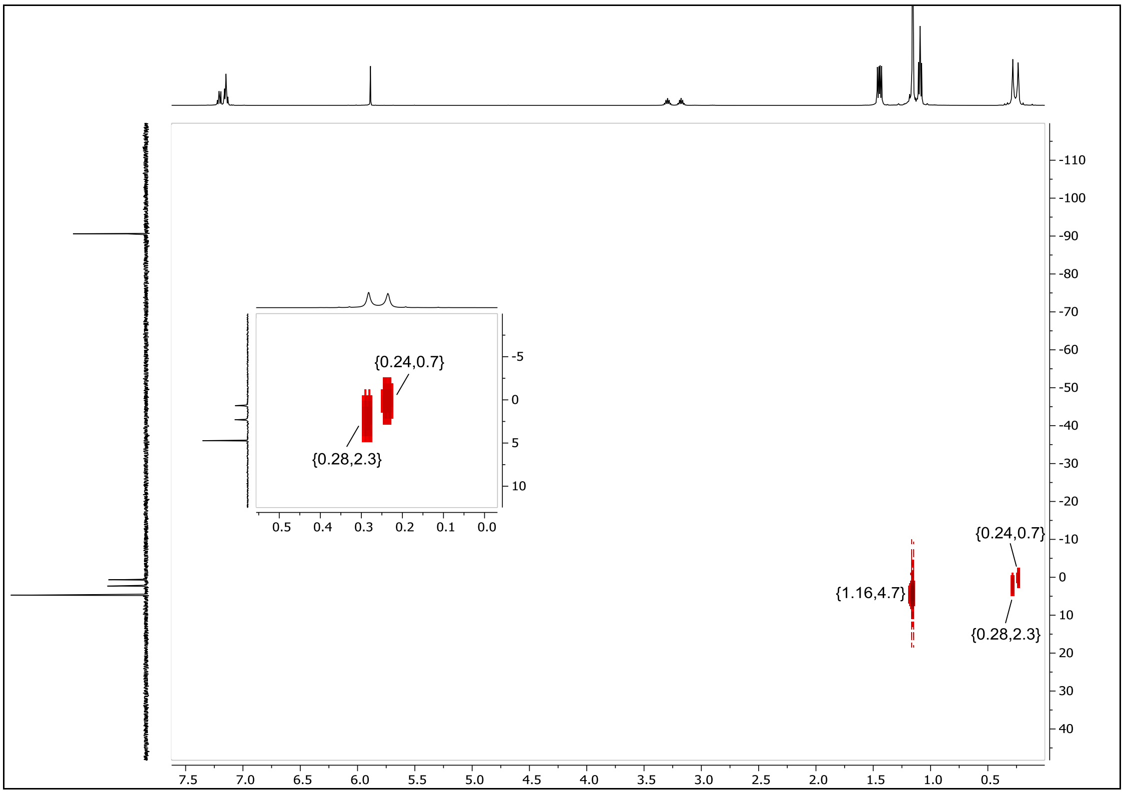
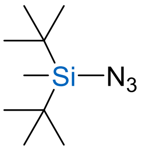


Figure S16. ^{1}H/^{29}Si HMBC NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(NTMSN)$_2$ (**5**) in C_6D_6 at 300 K.

1.6 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (6)

Synthesis of Azido(di-*tert*-butylmethyl)silane ^{t}Bu$_2$MeSiN$_3$

The following procedure represents a modified version of a method that has already been reported.[S4]



$C_9H_{21}N_3Si$
199.37 g/mol

To a mixture of ^{t}Bu$_2$MeSiBr (3.00 g, 12.6 mmol, 1.0 eq.) and NaN$_3$ (2.47 g, 37.9 mmol, 3.0 eq) was added THF (20 mL). The resulting colorless suspension was heated under reflux for 48 h. Subsequently, the product solution was flask-to-flask condensed (50 °C / 5.0×10^{-3} mbar) to remove excess sodium azide. Removal of THF *in vacuo* at 0 °C provided analytically pure ^{t}Bu$_2$MeSiN$_3$ as a colorless liquid (2.14 g, 10.7 mmol, 85%).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 0.90 (s, 18H, C(C$\underline{H}_3$)$_3$), –0.01 (s, 3H, SiC$\underline{H}_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 27.4 (C($\underline{C}$H$_3$)$_3$), 21.0 ($\underline{C}$(CH$_3$)$_3$), –9.0 (Si$\underline{C}$H$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 17.7 ($\underline{Si}$CH$_3$).

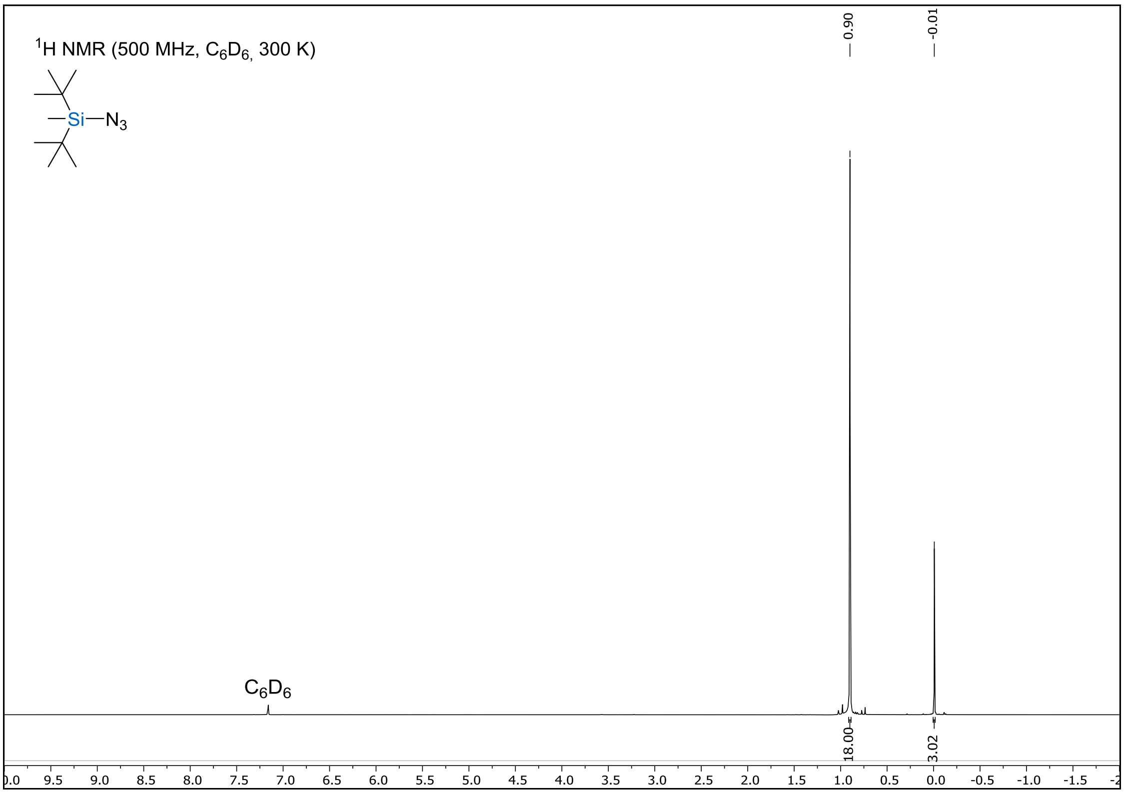


Figure S17. ^{1}H NMR spectrum of ^{t}Bu$_2$MeSiN$_3$ in C_6D_6 at 300 K.

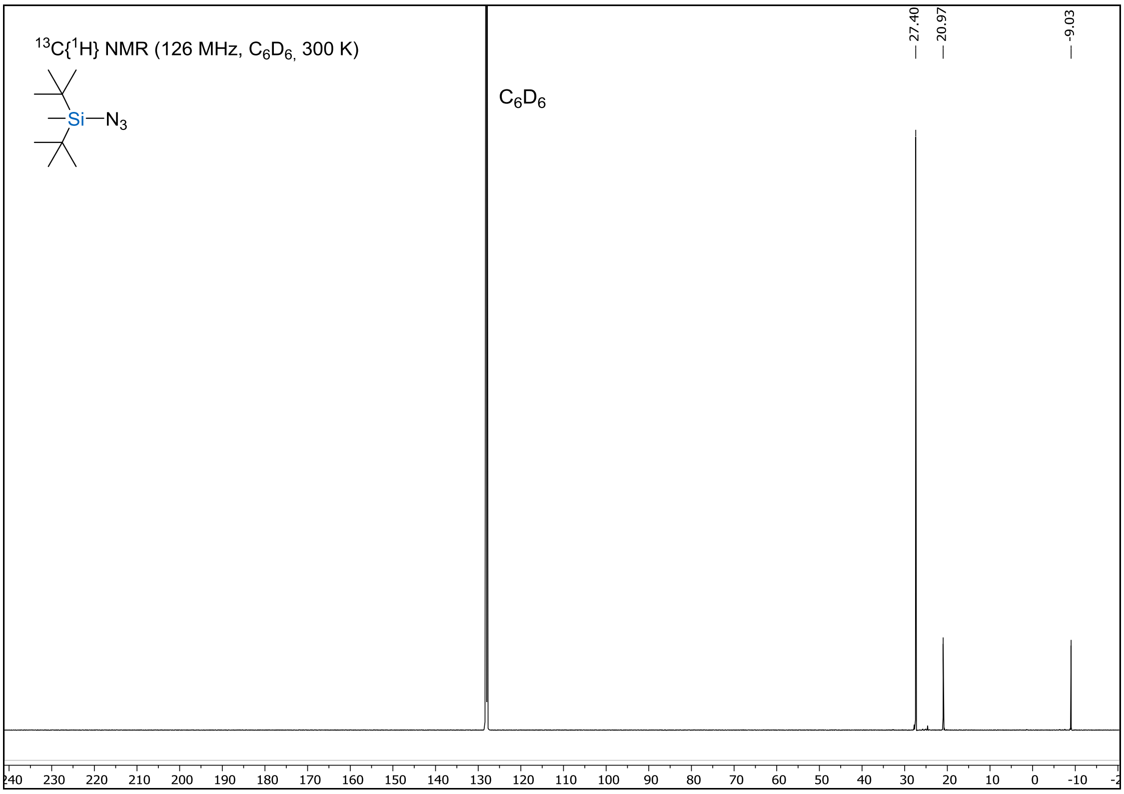


Figure S18. ^{13}C{^{1}H} NMR spectrum of ^{t}Bu$_2$MeSiN$_3$ in C_6D_6 at 300 K.

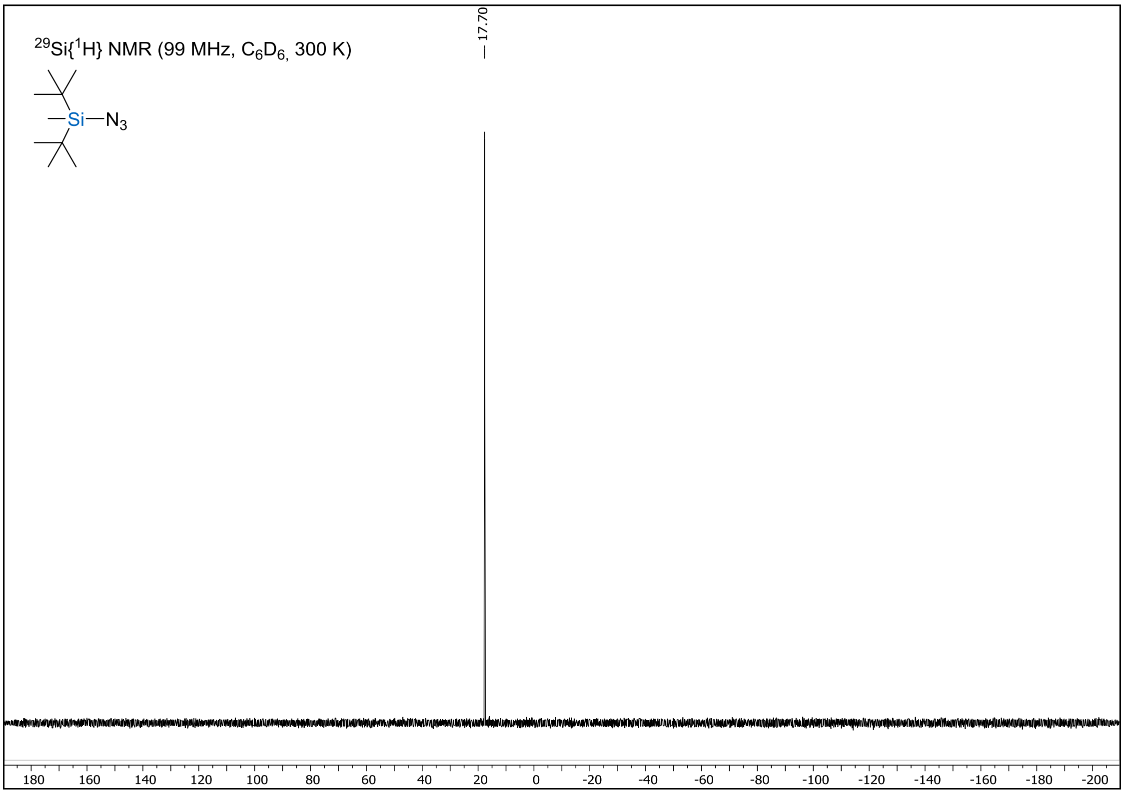
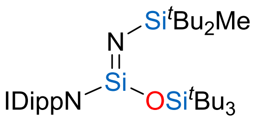


Figure S19. ^{29}Si{^{1}H} NMR spectrum of ^{t}Bu$_2$MeSiN$_3$ in C_6D_6 at 300 K.

Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (6)



6

$C_{48}H_{84}N_4OSi_3$

817.48 g/mol

To a stirred solution of silylene **1** (300 mg, 464 µmol, 1.0 eq.) in benzene (10 mL) was added a solution of ^{t}Bu$_2$MeSiN$_3$ (92.6 mg, 464 µmol, 1.0 eq.) in benzene (1 mL). After an immediately observed gas evolution (N_2), the reaction mixture was stirred for an additional hour. Removal of all volatiles *in vacuo* afforded silaimine **6** as a colorless solid (380 mg, 464 µmol, quantitative yield). Crystals, suitable for SC-XRD analysis were obtained by cooling a concentrated *n*-hexane solution of **6** to –35 °C for several days. Silaimine **6** is completely stable as a solid and in solution at ambient temperature.

Note: At high temperatures a very slow decomposition to an unidentified mixture of products was observed (~5% decomposition after 24 h at 130 °C).

m.p.: 302-303 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.21–7.18 (m, 2H, *p*-C$_{ar}$$\underline{H}$), 7.13–7.11 (m, 4H, *m*-C$_{ar}$$\underline{H}$), 6.01 (s, 2H, NC$\underline{H}$), 3.15 (sept, $^{3}J = 6.9$ Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.40 (d, $^{3}J = 6.9$ Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.14 (s, 18H, Si$\underline{^{t}Bu_2}$Me), 1.11 (s, 27H, Si$\underline{^{t}Bu_3}$), 1.08 (d, $^{3}J = 6.9$ Hz, 12H, CH(C$\underline{H}_3$)$_2$), 0.16 (s, 3H, Si^{t}Bu$_2$$\underline{Me}$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 146.5 (*o*-$\underline{C}_{ar}$), 141.1 (N$\underline{C}$N), 133.5 (*ipso*-$\underline{C}_{ar}$), 129.9 (*p*-$\underline{C}_{ar}$H), 125.0 (*m*-$\underline{C}_{ar}$H), 115.5 (N$\underline{C}$H), 30.3 (Si(C($\underline{C}H_3)_3)_3$), 29.7 (Si(C($\underline{C}H_3)_3)_2$Me), 29.0 ($\underline{C}H(CH_3)_2$), 25.2 (CH($\underline{C}H_3)_2$), 23.5 (CH($\underline{C}H_3)_2$), 23.2 (Si($\underline{C}(CH_3)_3)_3$), 21.2 (Si($\underline{C}(CH_3)_3)_2$Me), –6.6 (Si(C($CH_3)_3)_2$*$\underline{Me}$*).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 6.8 (*$\underline{Si}$*^{t}Bu$_3$), –6.7 (*$\underline{Si}$*^{t}Bu$_2$Me), –50.1 (*$\underline{Si}$*=N).

Anal. Calcd. [%] for $C_{48}H_{84}N_4OSi_3$: C, 70.52; H, 10.36; N, 6.85. Found [%]: C, 70.35; H, 10.17; N, 6.84.

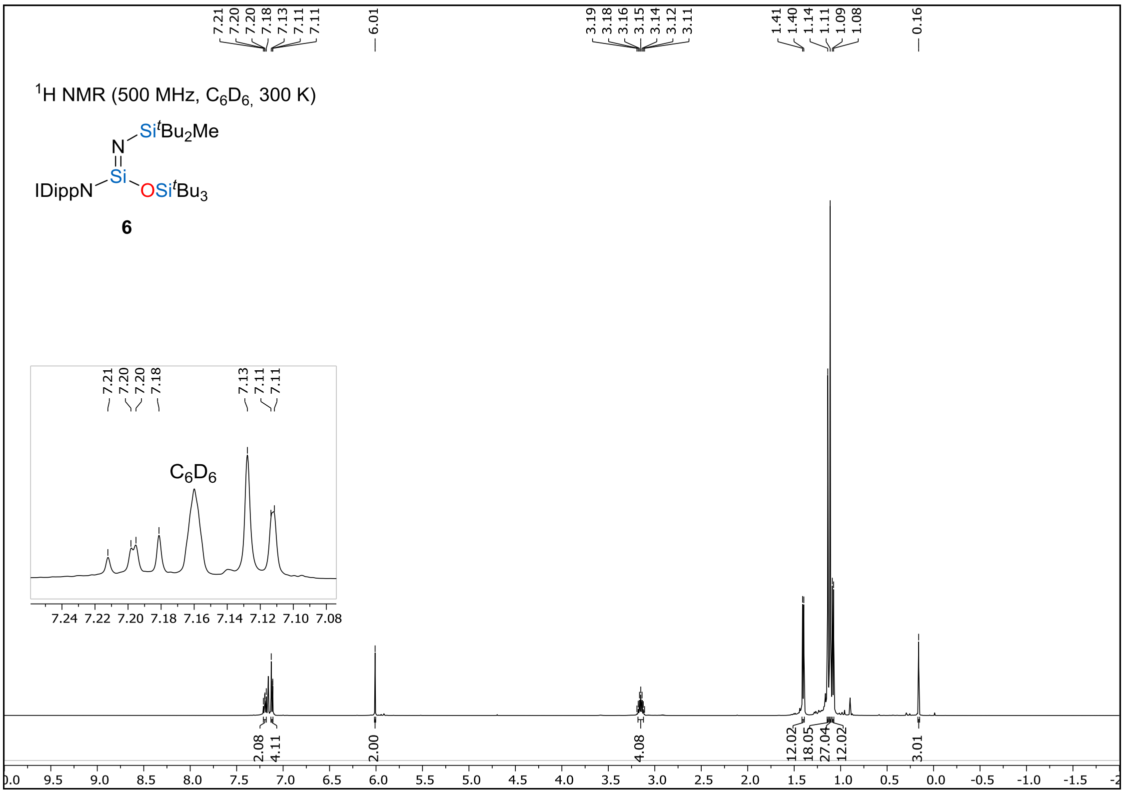


Figure S20. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (**6**) in C_6D_6 at 300 K.

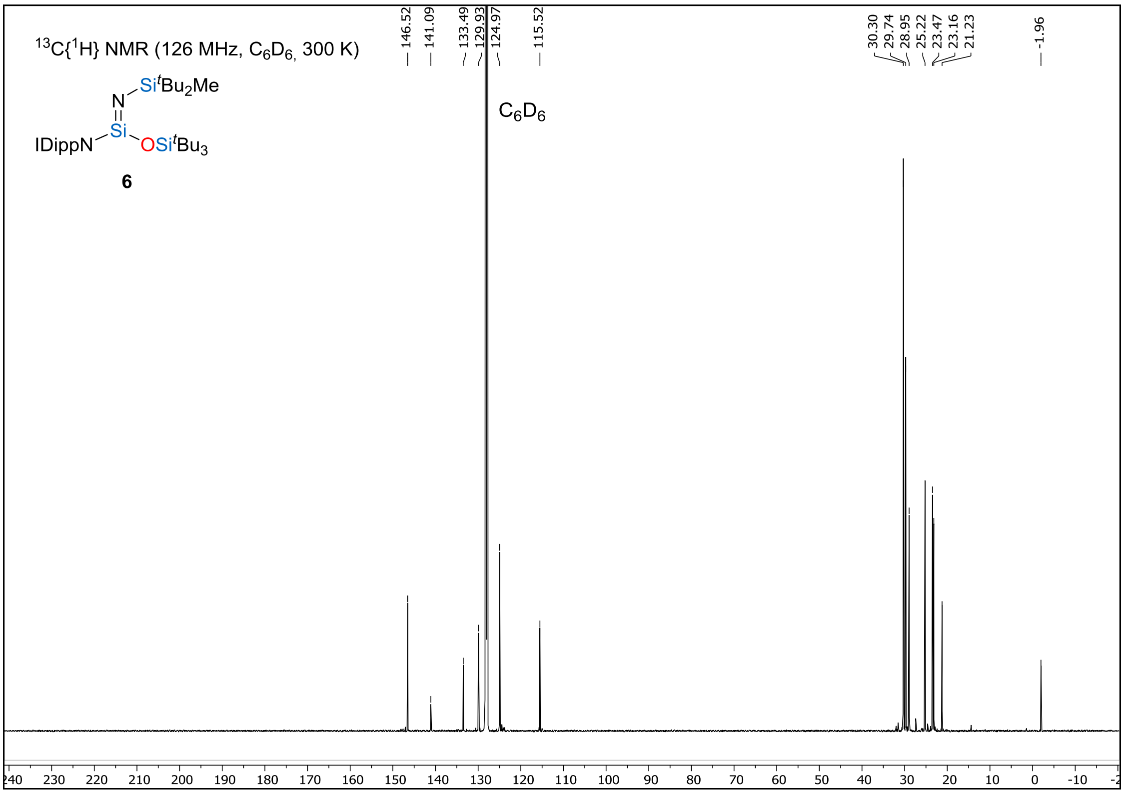


Figure S21. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (**6**) in C_6D_6 at 300 K.

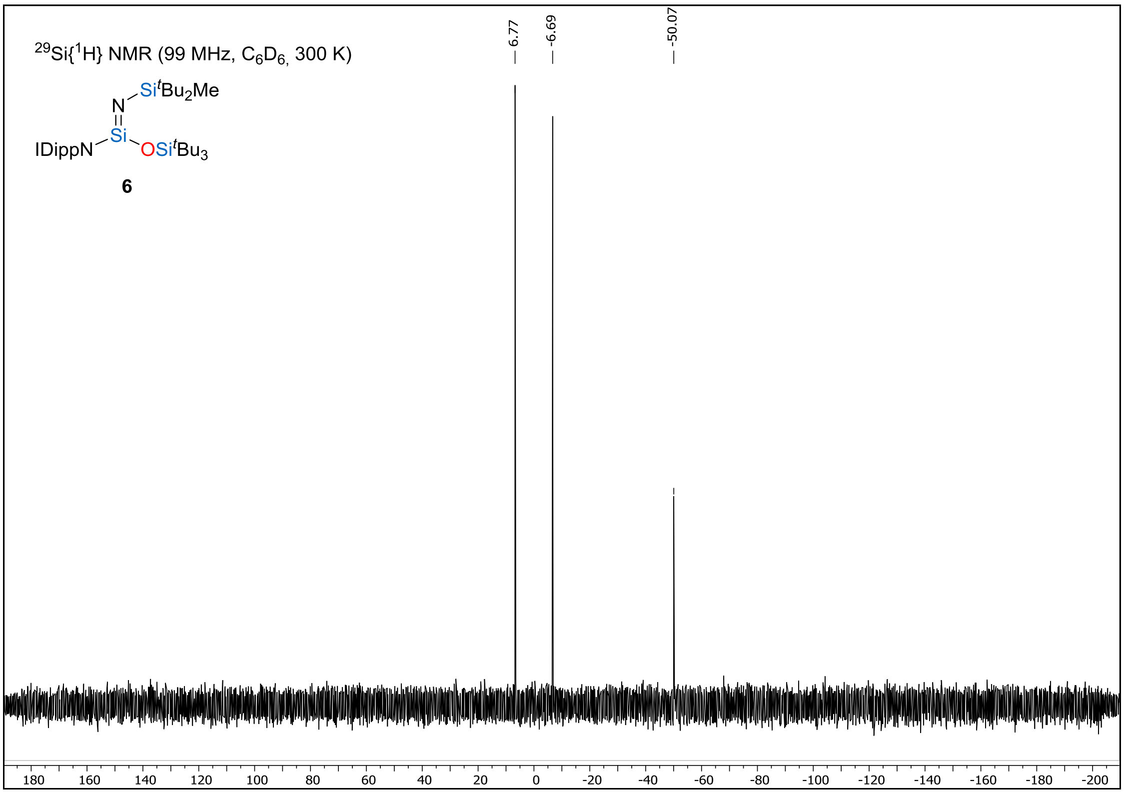


Figure S22. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (**6**) in C_6D_6 at 300 K.

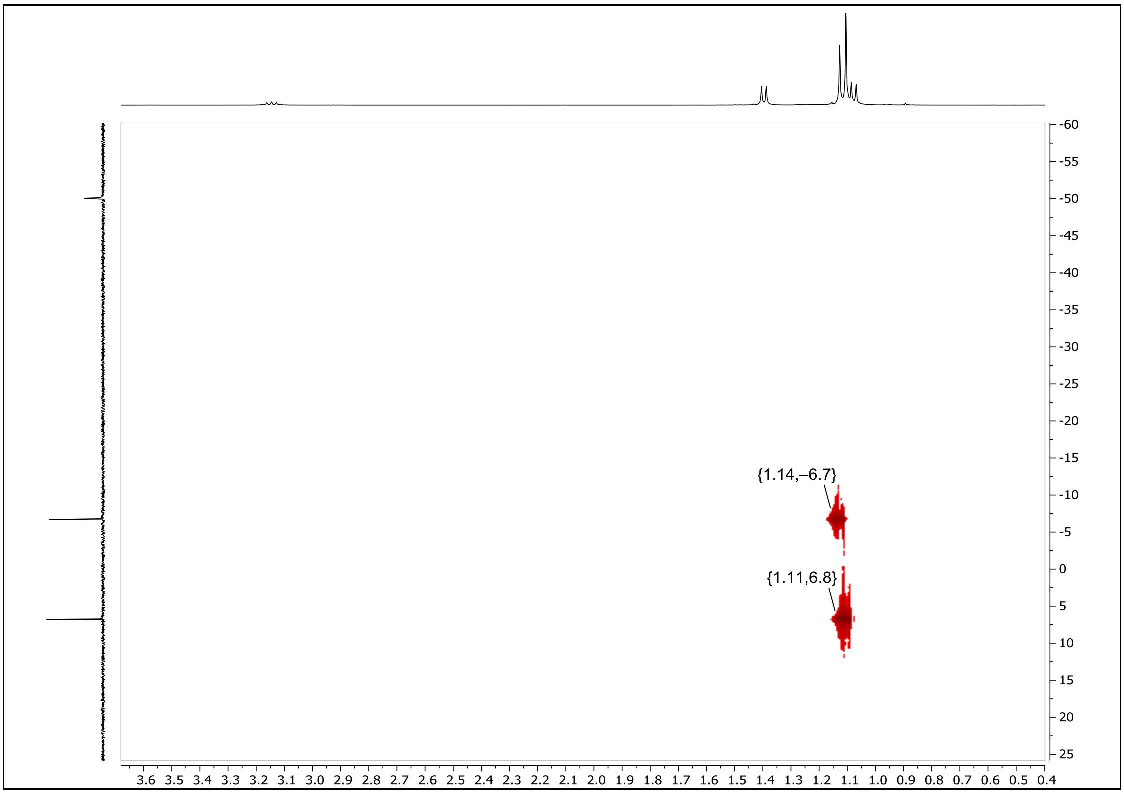
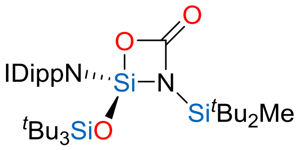


Figure S23. ^{1}H/^{29}Si HMBC NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=NSi^{t}Bu$_2$Me (**6**) in C_6D_6 at 300 K.

1.7 Synthesis of Azaoxasiletane (7)



7

$C_{49}H_{84}N_4O_3Si_3$

861.49 g/mol

A solution of silaimine **6** (75.0 mg, 91.8 µmol) in benzene (3 mL) was degassed and subsequently exposed to CO_2 (1 bar) under vigorous stirring at room-temperature. After stirring for additional 30 min, all volatiles were removed *in vacuo*. Azaoxasiletane **7** was afforded as a colorless solid (79.0 mg, 91.8 µmol, quantitative yield). Suitable crystals for SC-XRD analysis were obtained by cooling a saturated toluene solution of **7** to –35 °C for several days. Azaoxasiletane **7** is completely stable as a solid and in solution at room-temperature.

Note: At high temperatures a very slow decomposition to an unidentified mixture of products was observed (~10% decomposition after 24 h at 130 °C).

m.p.: 202-203 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.26–7.23 (m, 2H, *p*-C$_{ar}$*H*), 7.19–7.11 (m, 4H, *m*-C$_{ar}$*H*, overlapping with solvent signal), 6.05 (s, 2H, NC*H*), 3.21 (sept, ^{3}J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 3.09 (sept, ^{3}J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.50 (d, ^{3}J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, ^{3}J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (s, 9H, Si^{t}*Bu*$_2$Me), 1.08 (s, 36H, Si^{t}*Bu*$_3$ + Si^{t}*Bu*$_2$Me), 1.06 (d, ^{3}J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, ^{3}J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.09 (s, 3H, Si^{t}Bu$_2$*Me*).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 156.7 ($\underline{C}$=O), 146.9 (*o*-$\underline{C}_{ar}$), 146.6 (*o*-$\underline{C}_{ar}$), 143.0 (N$\underline{C}$N), 134.0 (*ipso*-$\underline{C}_{ar}$), 130.1 (*p*-$\underline{C}_{ar}$H), 124.9 (*m*-$\underline{C}_{ar}$H), 124.7 (*m*-$\underline{C}_{ar}$H), 116.3 (N$\underline{C}$H), 30.3 ($Si(C(\underline{C}H_3)_3)_3$), 29.2 ($Si(C(\underline{C}H_3)_3)_2Me$), 29.1 ($\underline{C}H(CH_3)_2$), 29.0 ($\underline{C}H(CH_3)_2$), 25.8 ($CH(\underline{C}H_3)_2$), 25.7 ($CH(\underline{C}H_3)_2$), 23.3 ($CH(\underline{C}H_3)_2$), 23.0 ($Si(\underline{C}(CH_3)_3)_3$), 22.9 ($CH(\underline{C}H_3)_2$), 20.3 ($Si(\underline{C}(CH_3)_3)_2Me$), 20.3 ($Si(\underline{C}(CH_3)_3)_2Me$), –5.9 ($Si(C(CH_3)_3)_2\underline{Me}$).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 8.4 ($\underline{Si}{}^tBu_2Me$), 7.7 ($\underline{Si}{}^tBu_3$), –89.6 ($\underline{Si}$OC=O).

Anal. Calcd. [%] for $C_{49}H_{84}N_4O_3Si_3$: C, 68.32; H, 9.83; N, 6.50. Found [%]: C, 67.71; H, 9.70; N, 6.73.

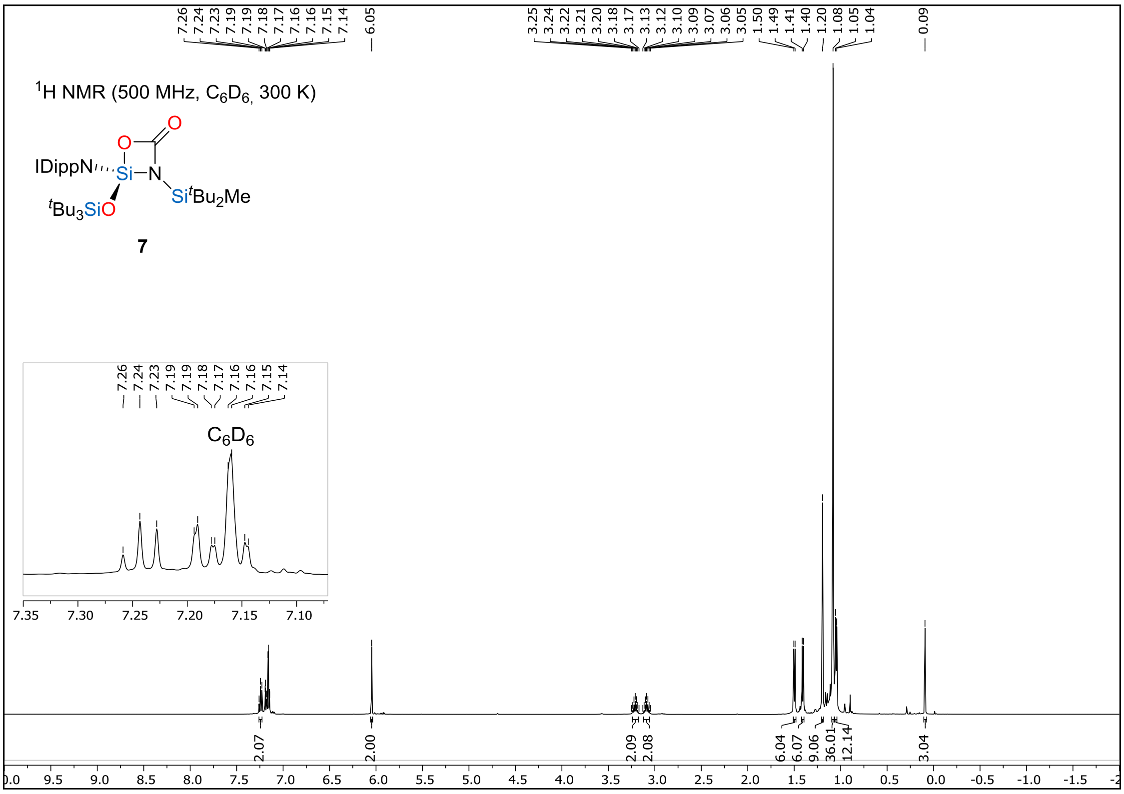


Figure S24. ^{1}H NMR spectrum of azaoxasiletane **7** in C_6D_6 at 300 K.

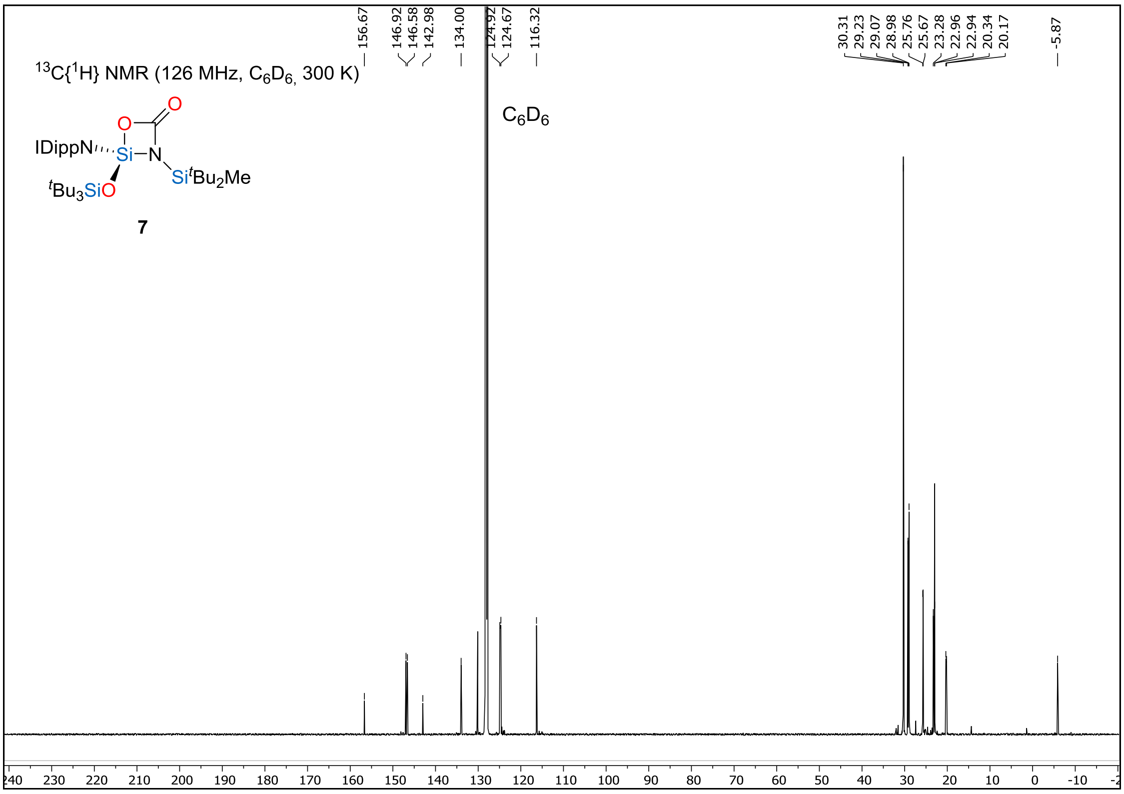


Figure S25. ^{13}C{^{1}H} NMR spectrum of azaoxasiletane **7** in C$_6$D$_6$ at 300 K.

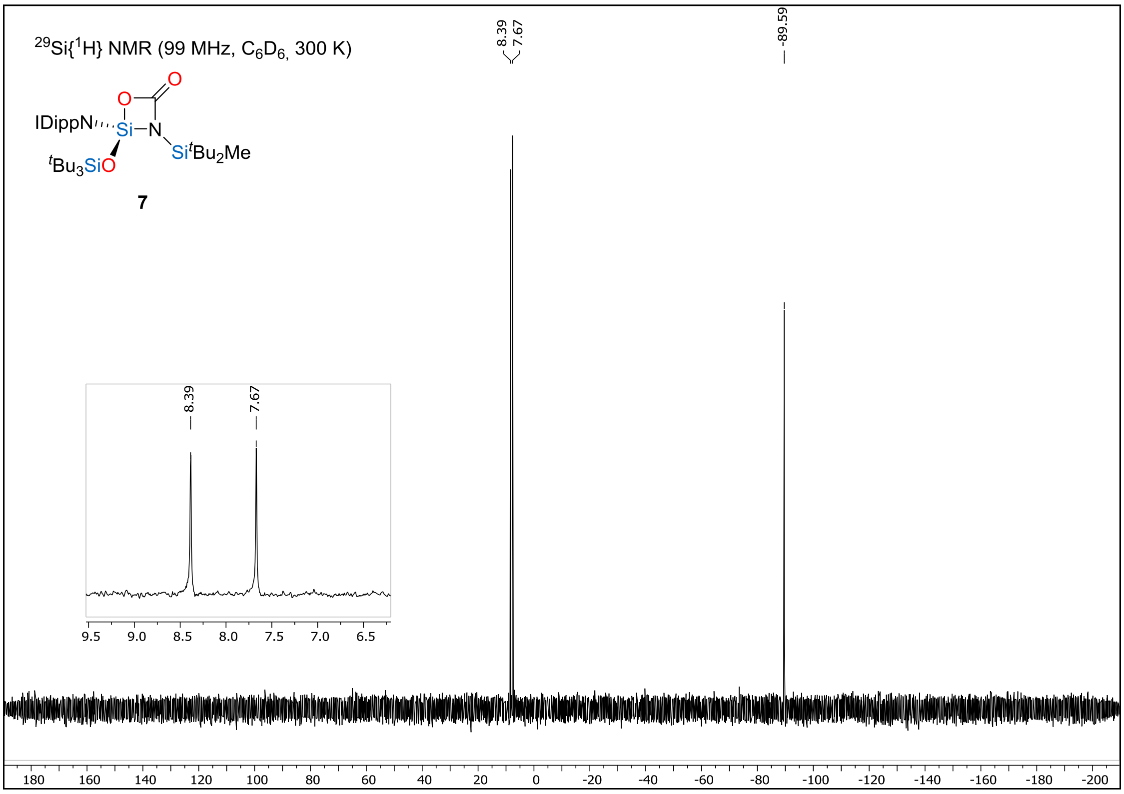


Figure S26. ^{29}Si{^{1}H} NMR spectrum of azaoxasiletane **7** in C$_6$D$_6$ at 300 K.

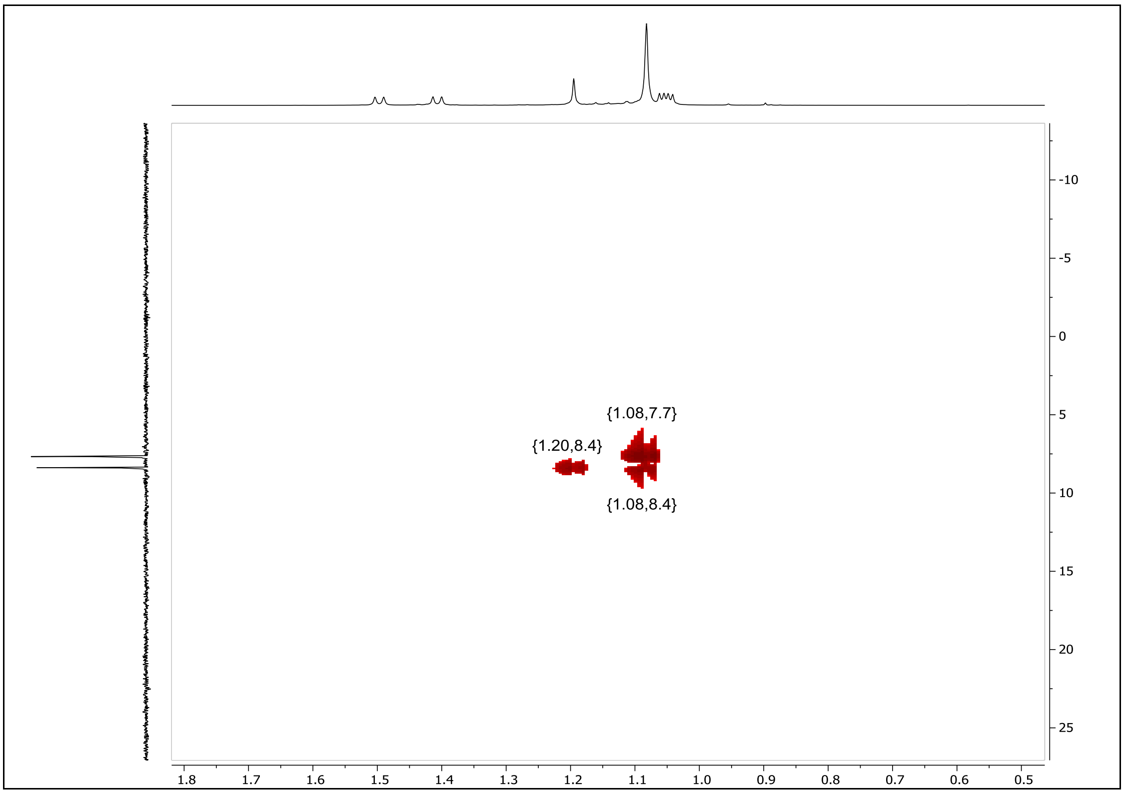
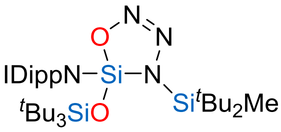


Figure S27. ^{1}H/^{29}Si HMBC NMR spectrum of azaoxasiletane **7** in C_6D_6 at 300 K.

1.8 Synthesis of Oxatriazasilole (8)



8

$C_{48}H_{84}N_6O_2Si_3$

861.50 g/mol

A solution of silaimine **6** (75.0 mg, 91.8 µmol) in benzene (3 mL) was degassed and subsequently exposed to N_2O (1 bar) under vigorous stirring at ambient temperature. After an additional hour of stirring, all volatiles were removed *in vacuo*. Oxatriazasilole **8** was provided as a colorless solid (79.0 mg, 91.8 µmol, quantitative yield). Heterocycle **8** is completely stable as a solid and in solution at ambient and elevated temperatures (≤130 °C).

m.p.: 350-351 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.24–7.19 (m, 4H, m-C$_\mathrm{ar}\underline{H}$), 7.13–7.11 (m, 2H, p-C$_\mathrm{ar}\underline{H}$), 5.98 (s, 2H, NC$\underline{H}$), 3.36 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.04 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 1.47 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.39 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.13 (s, 27H, Si$\underline{^t Bu_3}$), 1.12–1.09 (m, 21H, Si$\underline{^t Bu_2}$Me + CH(C$\underline{H}_3$)$_2$), 1.05 (s, 9H, Si$\underline{^t Bu_2}$Me), 0.18 (s, 3H, Si^{t}Bu$_2\underline{Me}$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 147.8 (o-$\underline{C}_\mathrm{ar}$), 146.8 ($o$-$\underline{C}_\mathrm{ar}$), 142.1 (N$\underline{C}$N), 134.9 ($ipso$-$\underline{C}_\mathrm{ar}$), 129.8 ($p$-$\underline{C}_\mathrm{ar}$H), 125.0 ($m$-$\underline{C}_\mathrm{ar}$H), 124.1 ($m$-$\underline{C}_\mathrm{ar}$H), 116.0 (N$\underline{C}$H), 30.4 (Si(C($\underline{C}H_3$)$_3$)$_3$), 29.3 ($\underline{C}$H(CH$_3$)$_2$), 29.2 ($\underline{C}$H(CH$_3$)$_2$), 28.6 (Si(C($\underline{C}H_3$)$_3$)$_2$Me), 28.4

$\mathrm{(Si(C(\underline{C}H_3)_3)_2Me)}$, 25.9 $\mathrm{(CH(\underline{C}H_3)_2)}$, 25.3 $\mathrm{(CH(\underline{C}H_3)_2)}$, 23.9 $\mathrm{(CH(\underline{C}H_3)_2)}$, 23.0 $\mathrm{(Si(\underline{C}(CH_3)_3)_3)}$, 22.8 $\mathrm{(CH(\underline{C}H_3)_2)}$, 20.6 $\mathrm{(Si(\underline{C}(CH_3)_3)_2Me)}$, 20.5 $\mathrm{(Si(\underline{C}(CH_3)_3)_2Me)}$, –4.3 $\mathrm{(Si(C(CH_3)_3)_2\underline{\mathit{Me}})}$.

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 9.8 ($\underline{\mathit{Si}}{}^t\mathrm{Bu}_3$), 3.7 ($\underline{\mathit{Si}}{}^t\mathrm{Bu}_2\mathrm{Me}$), –103.7 ($\underline{\mathit{Si}}\mathrm{ON}_3$).

Anal. Calcd. [%] for $C_{48}H_{84}N_6O_2Si_3$: C, 66.92; H, 9.83; N, 9.76. Found [%]: C, 67.56; H, 9.74; N, 9.52.

LIFDI-MS: calculated for **8** ($C_{48}H_{84}N_6O_2Si_3$): 860.5964

observed: 860.5765

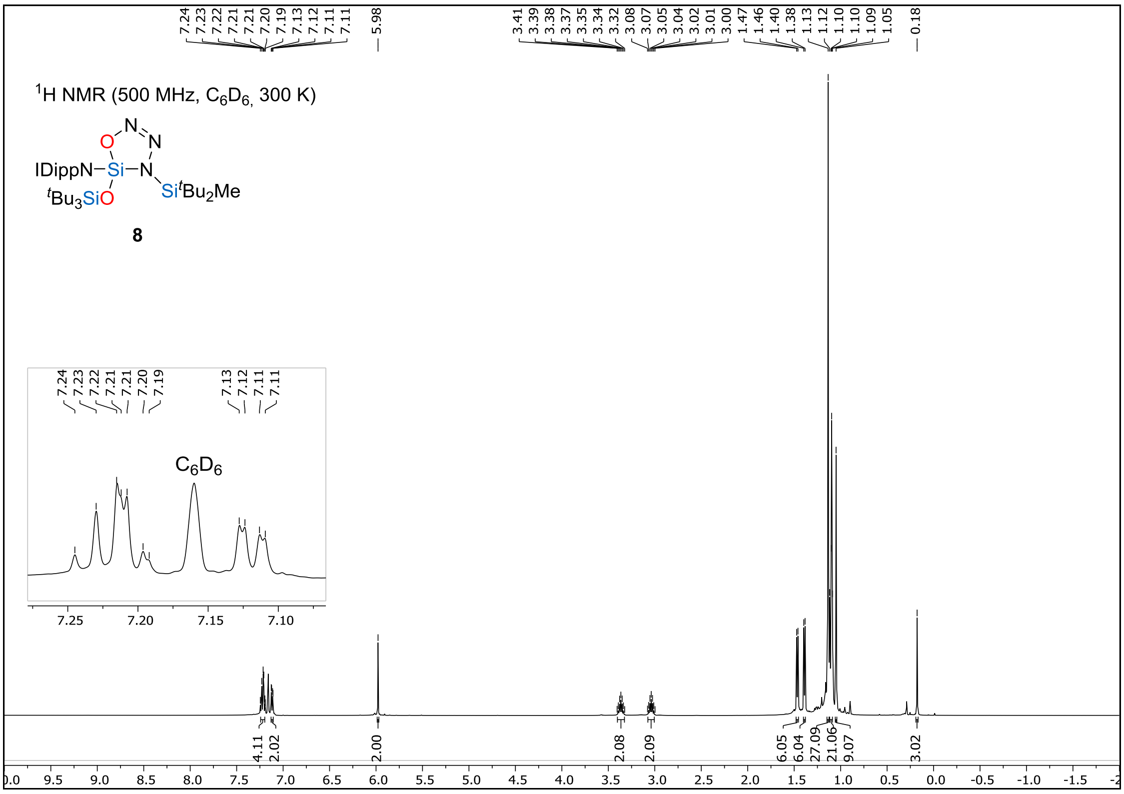


Figure S28. ^{1}H NMR spectrum of oxatriazasilole **8** in C_6D_6 at 300 K.

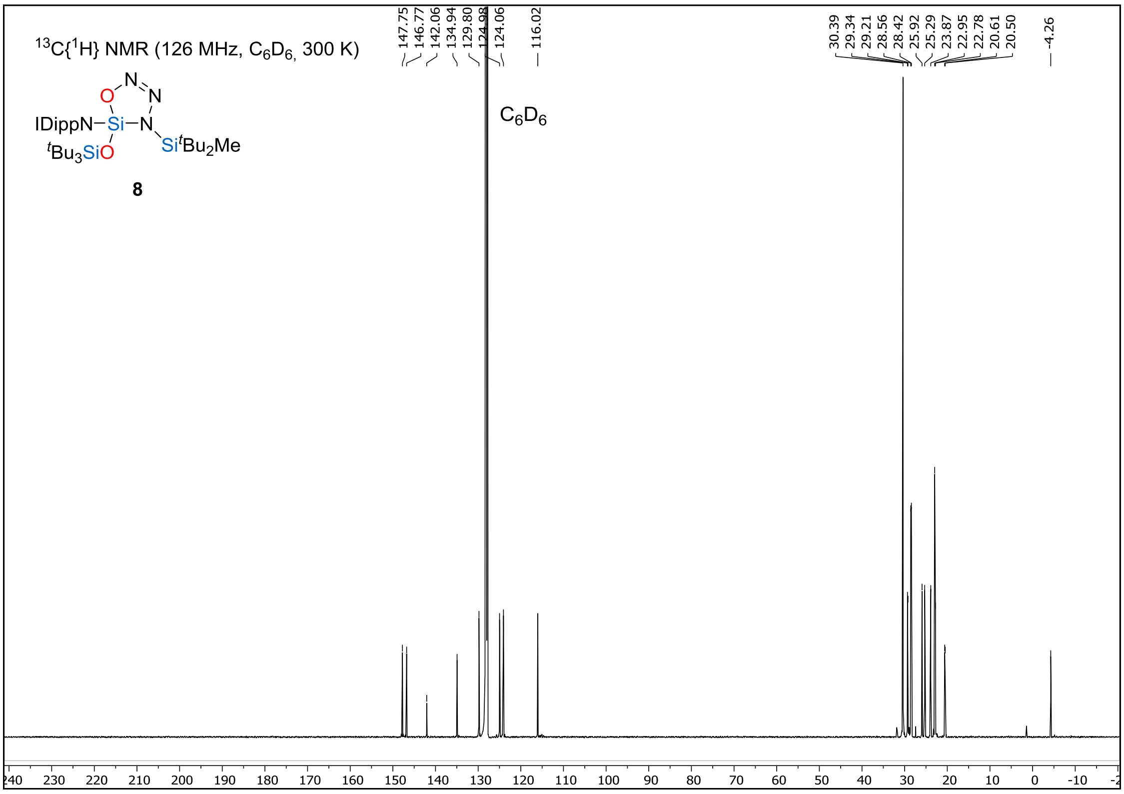


Figure S29. $^{13}C\{^1H\}$ NMR spectrum of oxatriazasilole **8** in C_6D_6 at 300 K.

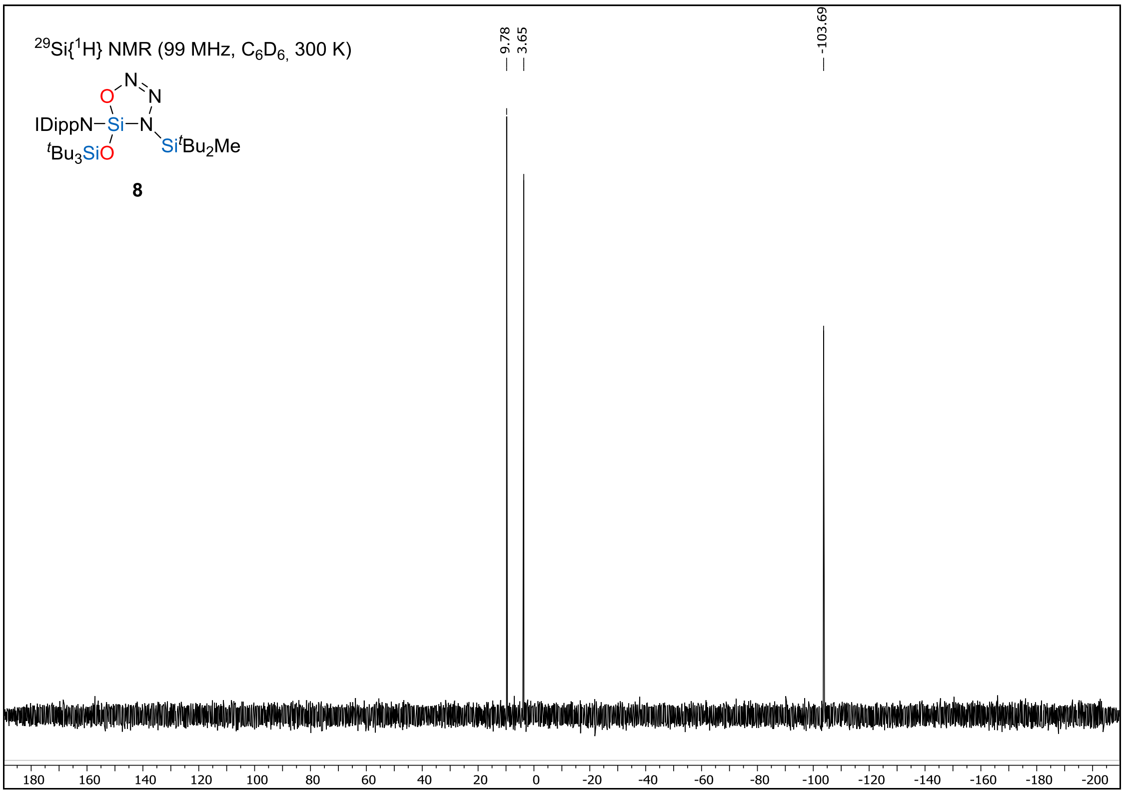


Figure S30. $^{29}Si\{^1H\}$ NMR spectrum of oxatriazasilole **8** in C_6D_6 at 300 K.

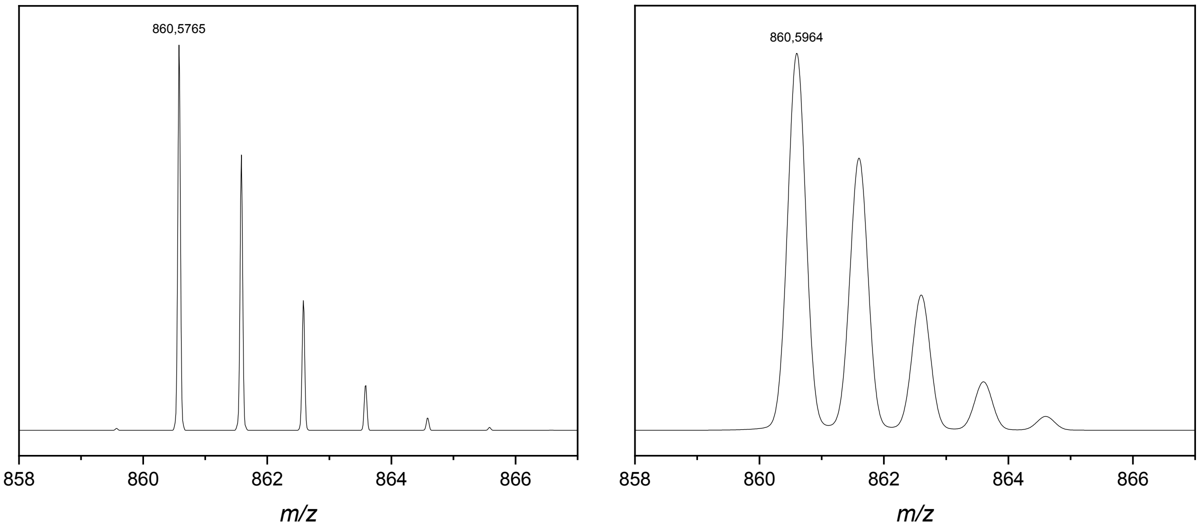
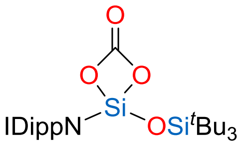


Figure S31. LIFDI-MS spectrometry (detail view with isotope pattern) of oxatriazasilole **8**. Measured (left; m/z = 860.5765) and simulated (right; m/z = 860.5964) mass spectrum.

1.9 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (9)



9

$C_{40}H_{63}N_3O_4Si_2$

706.13 g/mol

A solution of silylene **1** (100 mg, 155 µmol) in toluene (3 mL) was frozen in liquid nitrogen and degassed. The solution was cooled to –80 °C and exposed to CO_2 (1 bar) under vigorous stirring. Subsequently, the reaction mixture was warmed to ambient temperature and the excess of CO_2 and the solvent were removed *in vacuo*. Crystallization of the residue from *n*-hexane at –35 °C provided silicon carbonate complex **9** as colorless crystals (91.5 mg, 130 µmol, 84%), which were suitable for SC-XRD analysis. Compound **9** is completely stable as a solid and in solution at room temperature.

Note: Silicon carbonate complex **9** reacts with another equivalent of CO_2 in a slow equilibrium reaction after several days to compound **9′**. Unfortunately, complete conversion and isolation of **9′** was not possible, as heating of the reaction mixture or removal of CO_2 selectively regenerates **9**. Presumably CO_2 inserts into the Si–N bond; for NMR characterization of **9′** see below.

m.p.: 177-178 °C (gas formation, sticky colorless oil).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.30 (t, $^3J = 7.8$ Hz, 2H, *p*-C$_{ar}$$\underline{H}$), 7.16 (d, $^3J = 7.8$ Hz, 4H, *m*-C$_{ar}$$\underline{H}$, overlapping with solvent signal), 5.93 (s, 2H, NC$\underline{H}$), 2.88 (sept, $^3J = 6.9$ Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.41 (d, $^3J = 6.9$ Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.10 (d, $^3J = 6.9$ Hz, 12H, CH(C$\underline{H}_3$)$_2$), 0.97 (s, 27H, C(C$\underline{H}_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 149.5 (O$_2$$\underline{C}$=O), 146.7 (*o*-$\underline{C}$$_{ar}$), 146.2 (N$\underline{C}$N), 132.4 (*ipso*-$\underline{C}$$_{ar}$), 130.8 (*p*-$\underline{C}$$_{ar}$H), 124.7 (*m*-$\underline{C}$$_{ar}$H), 115.5 (N$\underline{C}$H), 29.7 (C($\underline{C}H_3$)$_3$), 29.2 ($\underline{C}$H(CH$_3$)$_2$), 24.6 (CH($\underline{C}H_3$)$_2$), 23.2 (CH($\underline{C}H_3$)$_2$), 22.9 ($\underline{C}$(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 7.4 (<u>*Si*</u>^{t}Bu$_3$), –90.9 (<u>*Si*</u>O_2C=O).

Anal. Calcd. [%] for $C_{40}H_{63}N_3O_4Si_2$: C, 68.04; H, 8.99; N, 5.95. Found [%]: C, 68.01; H, 9.13; N, 5.94.

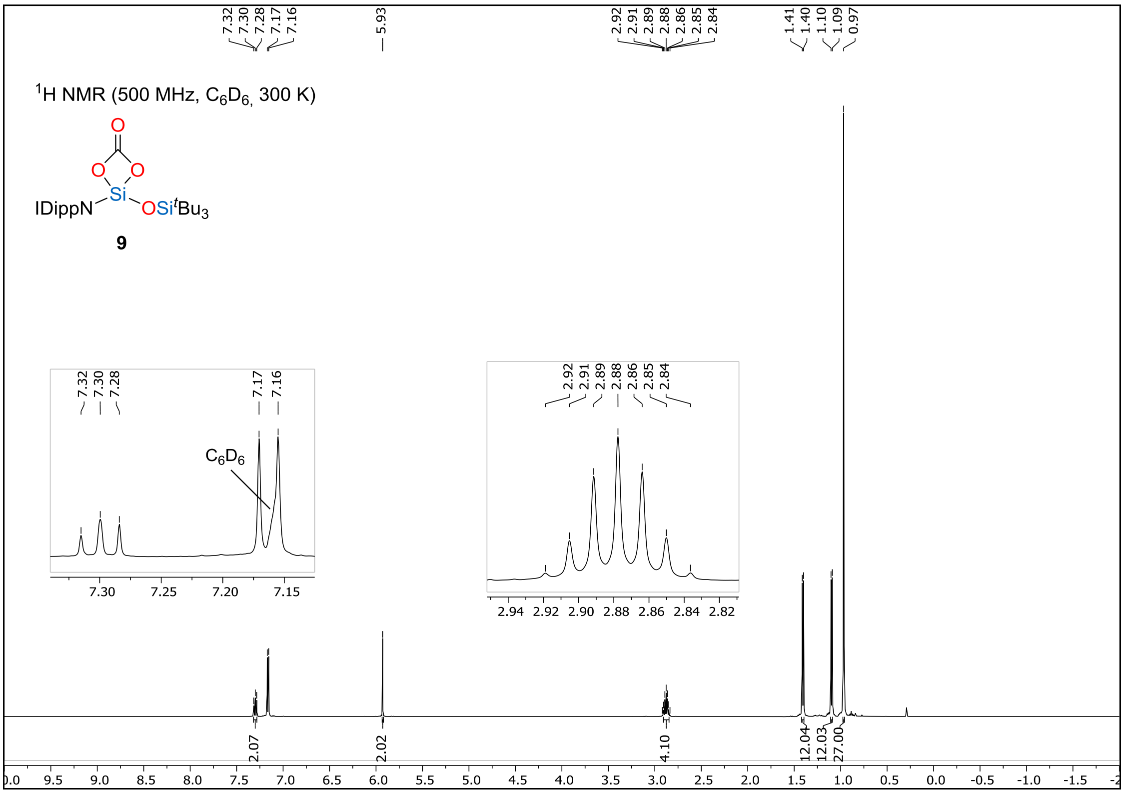


Figure S32. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O_2C=O) (**9**) in C_6D_6 at 300 K.

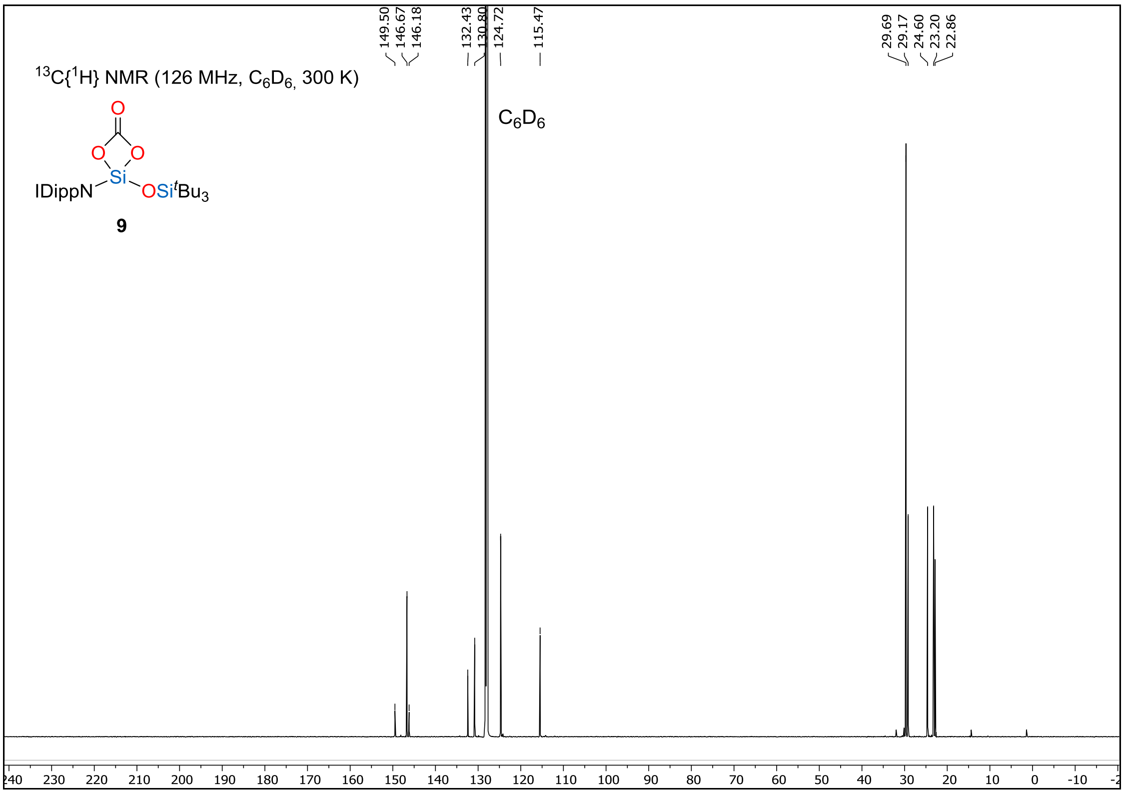


Figure S33. ^{13}C{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) in C$_6$D$_6$ at 300 K.

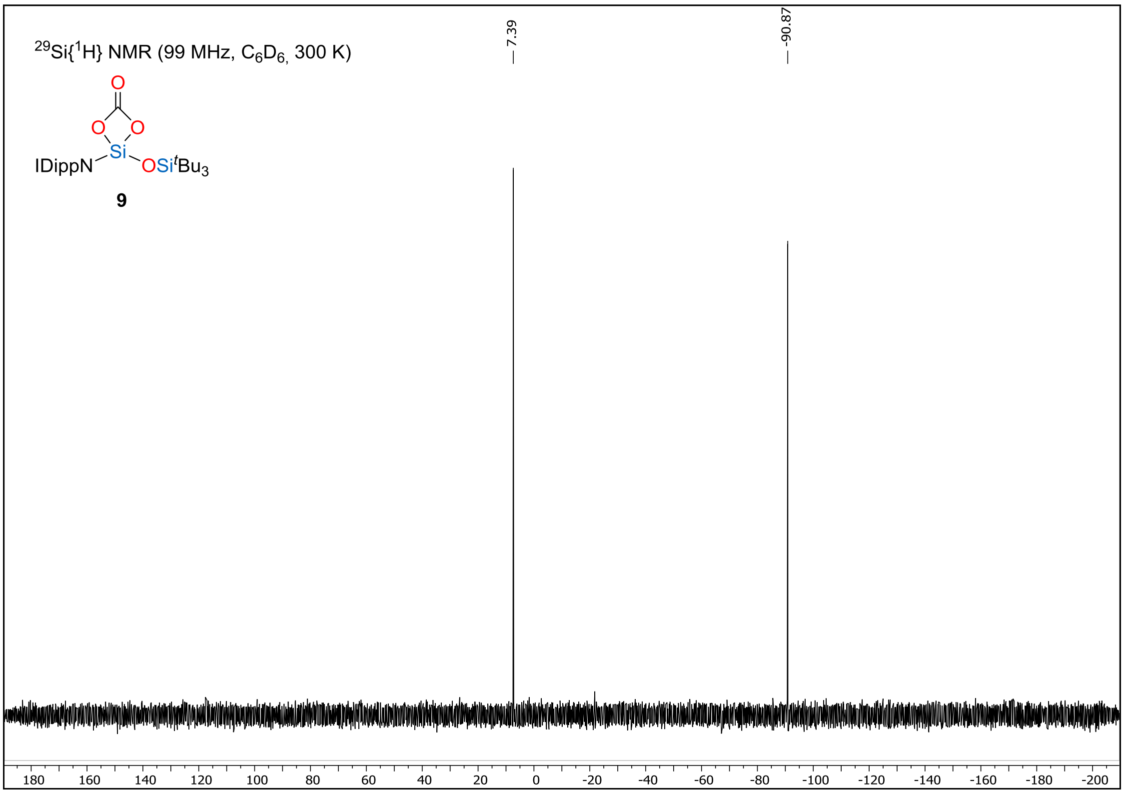


Figure S34. ^{29}Si{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) in C$_6$D$_6$ at 300 K.

Multinuclear NMR Characterization of Compound 9′:

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.26 (t, $^3J = 7.8$ Hz, 2H, p-C$_{\text{ar}}\underline{H}$), 7.04 (d, $^3J = 7.8$ Hz, 4H, m-C$_{\text{ar}}\underline{H}$), 6.05 (s, 2H, NC$\underline{H}$), 2.58 (sept, $^3J = 6.9$ Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.33 (d, $^3J = 6.9$ Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.09 (s, 27H, C(C$\underline{H}_3$)$_3$) 0.97 (d, $^3J = 6.7$ Hz, 12H, CH(C$\underline{H}_3$)$_2$, overlapping with C(C$\underline{H}_3$)$_3$ resonance of **9**).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 163.1 ($\underline{C}$=O), 152.5 (O$_2\underline{C}$=O), 148.8 (N$\underline{C}$N), 145.7 (o-$\underline{C}_{\text{ar}}$), 131.9 ($p$-$\underline{C}_{\text{ar}}$H), 130.2 ($ipso$-$\underline{C}_{\text{ar}}$), 124.8 ($m$-$\underline{C}_{\text{ar}}$H), 119.2 (N$\underline{C}$H), 29.9 (C($\underline{C}H_3$)$_3$), 29.4 ($\underline{C}$H(CH$_3$)$_2$), 24.8 (CH($\underline{C}H_3$)$_2$), 23.3 (CH($\underline{C}H_3$)$_2$), 23.1 ($\underline{C}$(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.1 ($\underline{Si}^t$Bu$_3$), −126.9 ($\underline{Si}$O$_2$C=O).

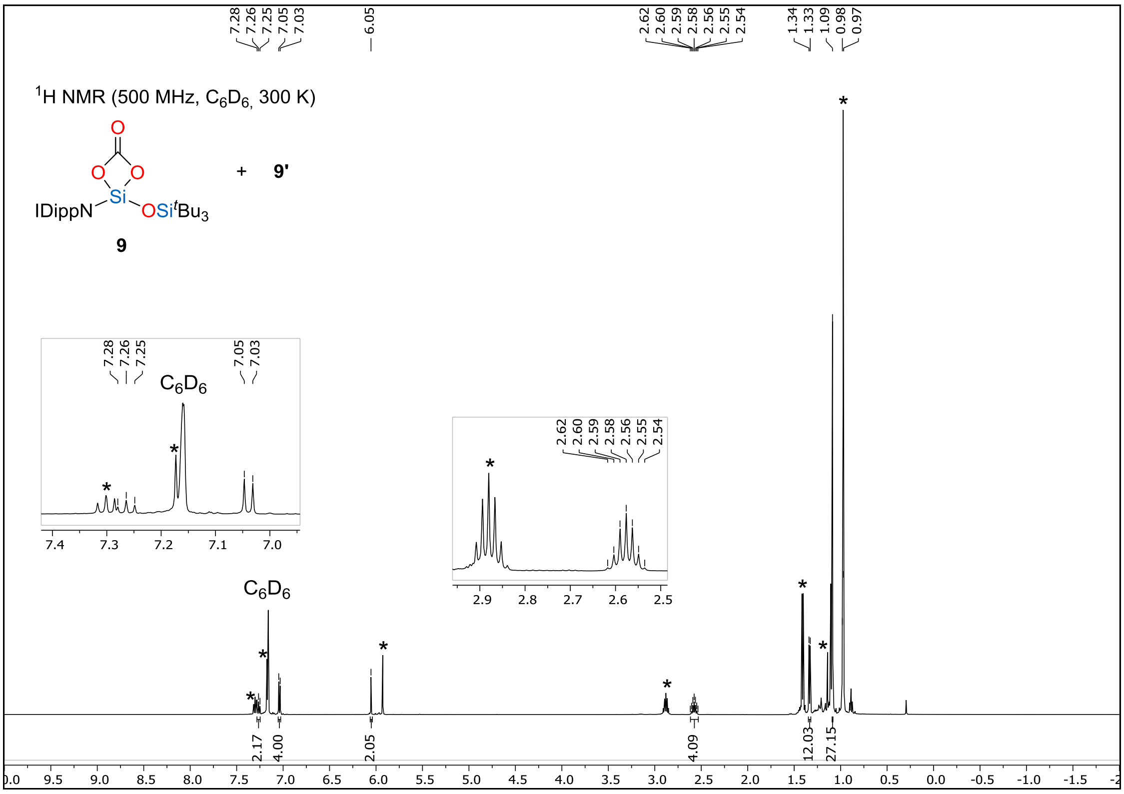


Figure S35. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) and **9′** in C$_6$D$_6$ at 300 K. The respective resonances of compound **9** are marked with asterisks *.

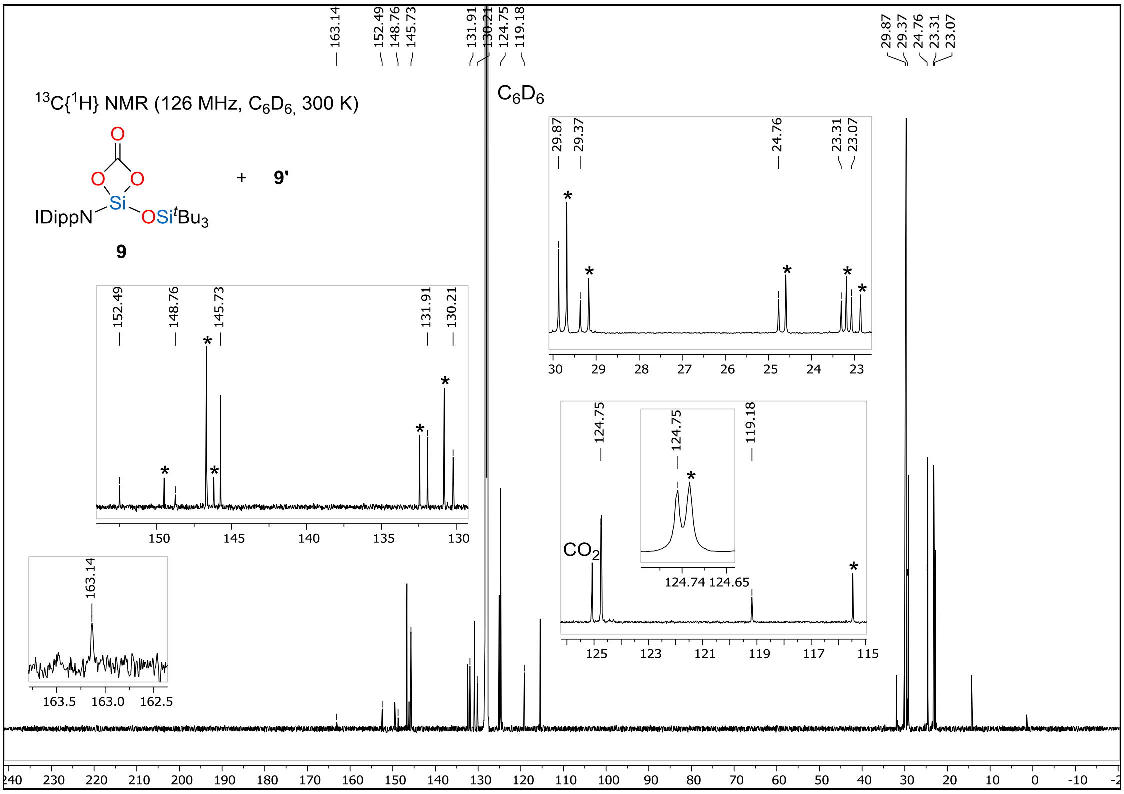


Figure S36. ^{13}C{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) and **9′** in C$_6$D$_6$ at 300 K. The respective resonances of compound **9** are marked with asterisks *.

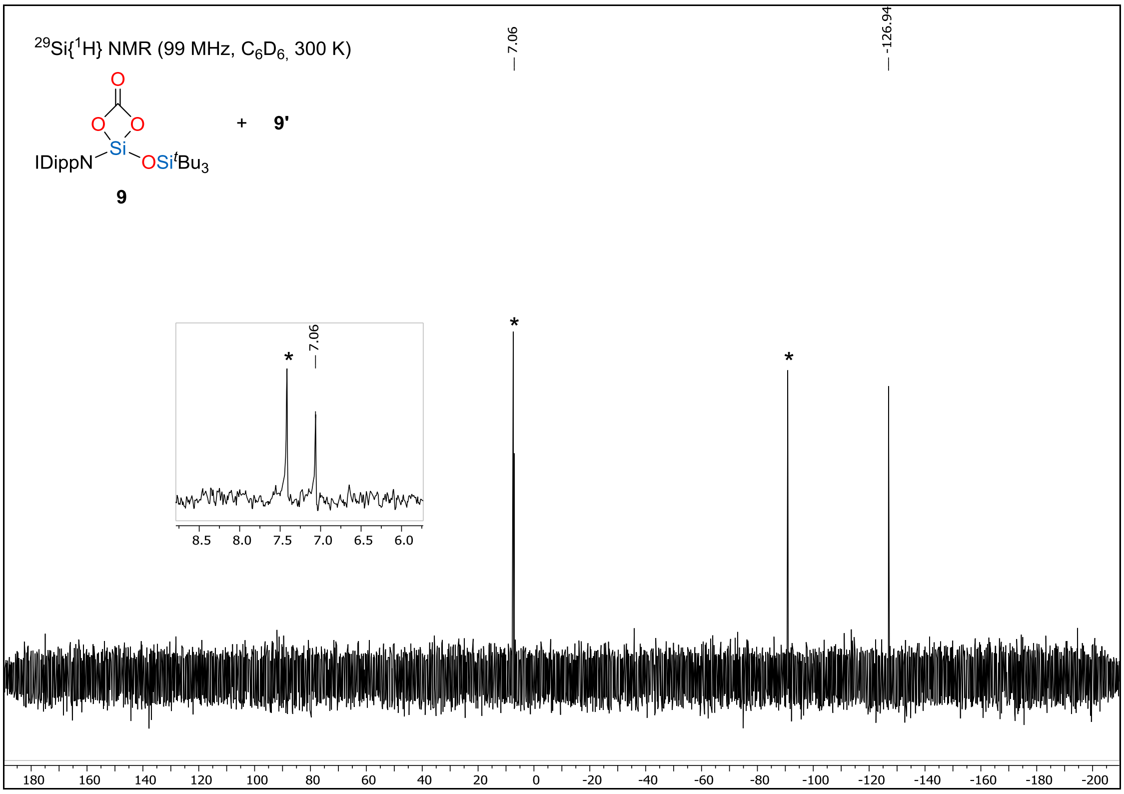
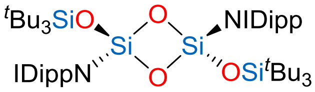


Figure S37. ^{29}Si{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) and **9′** in C$_6$D$_6$ at 300 K. The respective resonances of compound **9** are marked with asterisks *.

1.10 Synthesis of *trans*-Cyclodisiloxane [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (10a)



10a

$C_{78}H_{126}N_6O_4Si_4$

1324.24 g/mol

A solution of silylene **1** (300 mg, 464 µmol) in *n*-hexane (6 mL) was frozen in liquid nitrogen and degassed. The solution was cooled to –80 °C and exposed to N_2O (1 bar) under vigorous stirring. Subsequently, the reaction mixture was warmed to ambient temperature with concomitant formation of a fine white precipitate. The solid was separated *via* filtration, washed with *n*-hexane and dried *in vacuo* to give pure *trans*-cyclodisiloxane **10a** as a white powder (247 mg, 187 µmol, 81%). Suitable crystals for SC-XRD analysis were obtained by cooling an *n*-hexane/toluene solution of **10a** to –35 °C for several days. Compound **10a** is completely stable as a solid and in solution even under air and moisture.

m.p.: 335-336 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.27 (*pseudo* t, ^3J = 7.6 Hz, 4H, *p*-C$_{ar}$*H*), 7.17 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 4H, *m*-C$_{ar}$*H*), 7.02 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 4H, *m*-C$_{ar}$*H*), 5.83 (s, 4H, NC*H*), 3.48 (sept, ^3J = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 2.90 (sept, ^3J = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 1.43 (d, ^3J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.20 (s, 54H, C(C*H*$_3$)$_3$), 1.15 (d, ^3J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, ^3J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.10 (d, ^3J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 148.8 (*o*-*C*$_{ar}$), 147.3 (*o*-*C*$_{ar}$), 145.1 (N*C*N), 136.1 (*ipso*-*C*$_{ar}$), 129.5 (*p*-*C*$_{ar}$H), 125.2 (*m*-*C*$_{ar}$H), 124.2 (*m*-*C*$_{ar}$H), 116.5 (N*C*H), 31.1 (C(*C*H$_3$)$_3$), 29.1 (*C*H(CH$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 27.5 (CH(*C*H$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.2 (*C*(CH$_3$)$_3$), 22.6 (CH(*C*H$_3$)$_2$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 5.6 (*Si*^{t}Bu$_3$), –83.5 (*Si*$_2$O$_2$).

Anal. Calcd. [%] for $C_{78}H_{126}N_6O_4Si_4$: C, 70.75; H, 9.59; N, 6.35. Found [%]: C, 70.99; H, 9.90; N, 6.16.

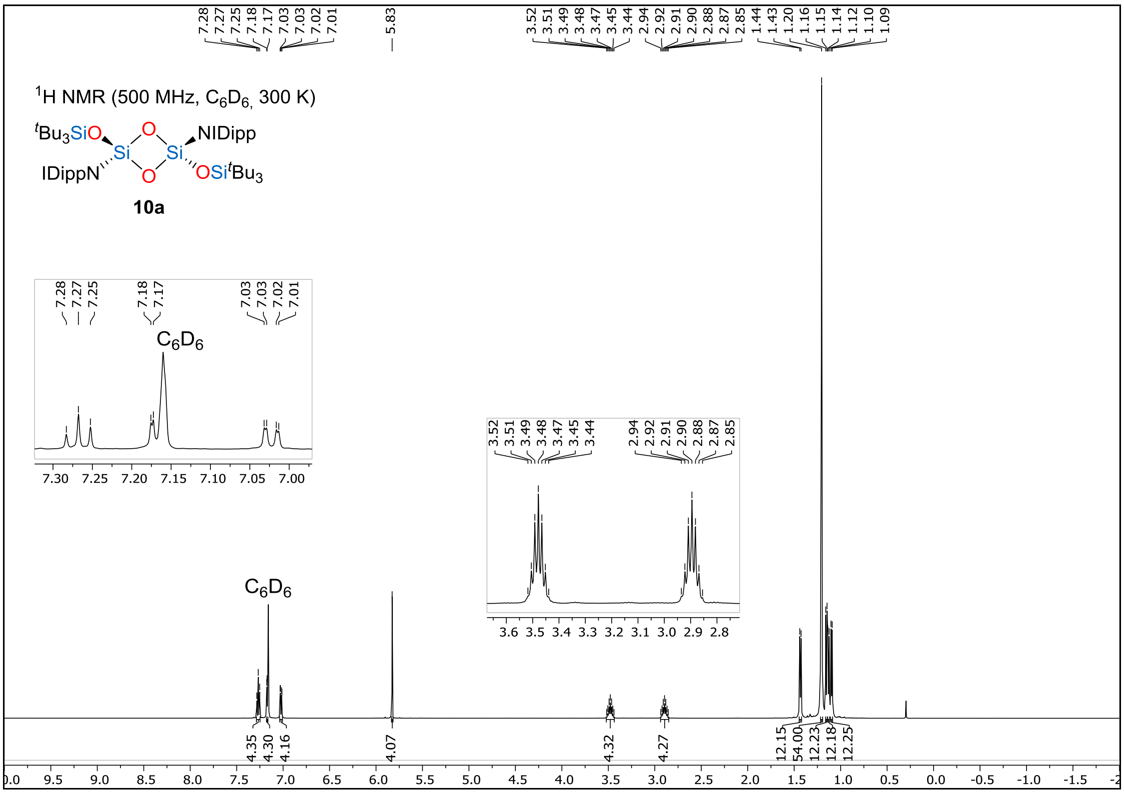


Figure S38. ^{1}H NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (**10a**) in C_6D_6 at 300 K.

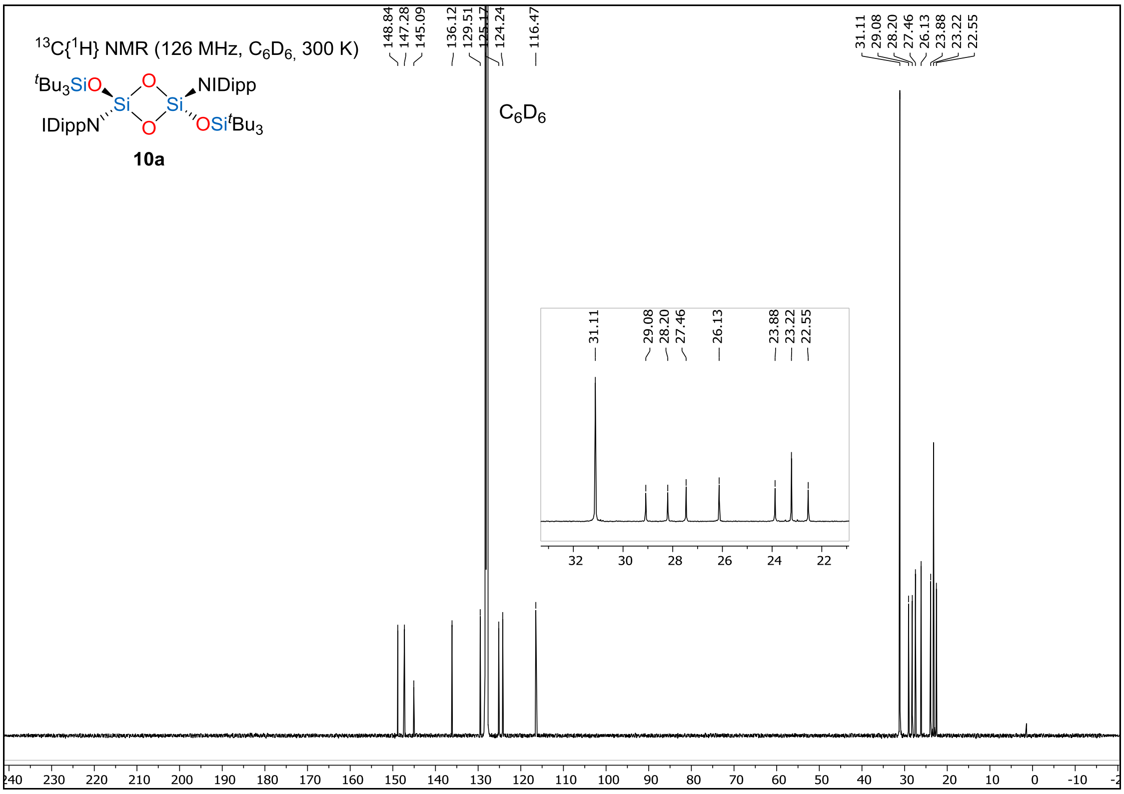


Figure S39. ^{13}C{^{1}H} NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (**10a**) in C_6D_6 at 300 K.

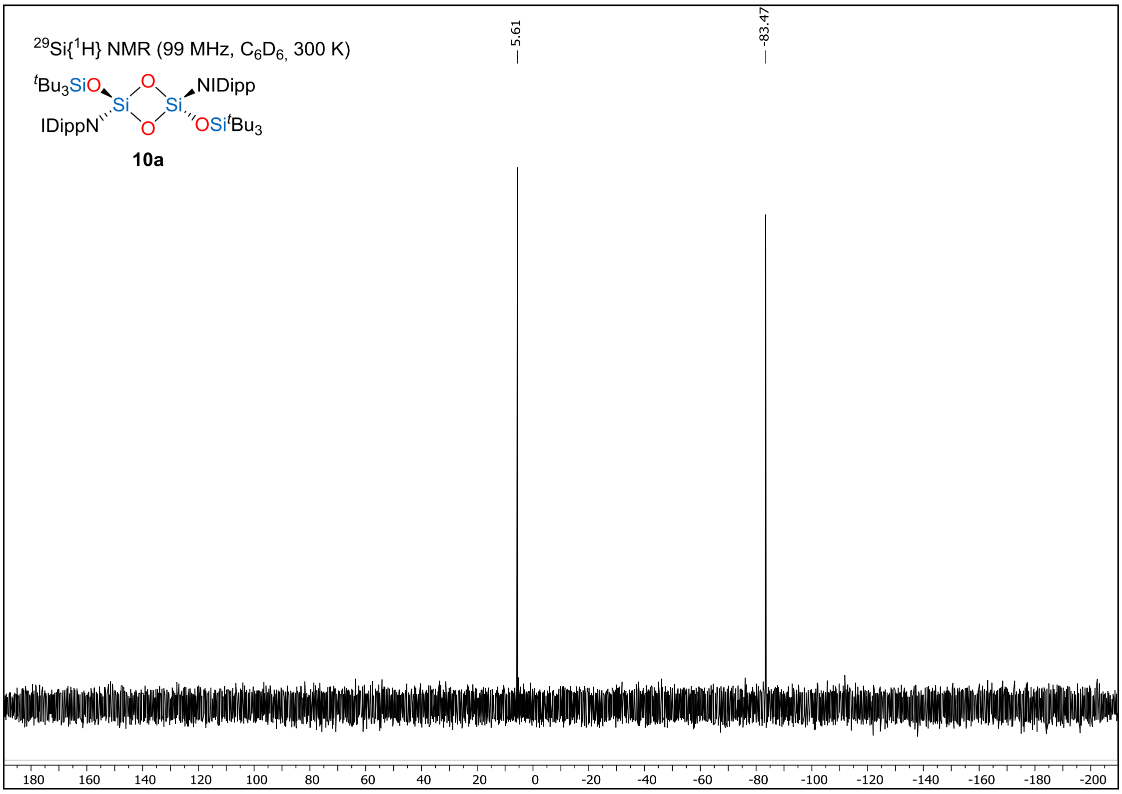
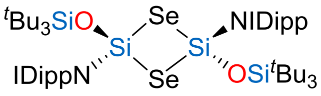


Figure S40. ^{29}Si{^{1}H} NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (**10a**) in C$_6$D$_6$ at 300 K.

1.11 Synthesis of Silicon Diselenide [(IDippN)(^{t}Bu$_3$SiO)Si=Se]$_2$ (10b)



10b

$C_{78}H_{126}N_6O_2Se_2Si_4$

1450.17 g/mol

To a solution of silylene **1** (100 mg, 155 µmol, 1.0 eq.) in toluene (3 mL) was added gray selenium powder (12.2 mg, 155 µmol, 1.0 eq.) at room temperature. Quantitative conversion of **1** to silicon diselenide **10b** was detected by ^{1}H NMR spectroscopy after stirring the reaction mixture for 3 days. Subsequently, the solvent was removed *in vacuo* and the residue recrystallized from *n*-hexane/toluene at –35 °C providing **10b** as colorless crystals (95.7 mg, 66.0 mmol, 85%) suitable for SC-XRD analysis. Compound **10b** is completely stable as a solid, but decomposes (or dimerizes) extremely slowly in solution to an unidentified species, which thus was not investigated in more detail.

<u>*Note:*</u> The NMR data obtained indicate that **10b** presumably exists as monomer **10b′** in solution. The significantly downfield-shifted ^{29}Si NMR resonance for the SiSe moiety compared to that observed for the SiO moiety in **10a** (δ = –83.5 ppm) along with the decreased signal splitting in the ^{1}H NMR suggest a monomer with a three-coordinate Si nucleus.

m.p.: 100-101 °C (decomposition; color change from colorless to red).

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.20–7.17 (m, 2H, *p*-C$_{\mathrm{ar}}\underline{H}$), 7.13–7.11 (m, 4H, *m*-C$_{\mathrm{ar}}\underline{H}$), 6.08 (s, 2H, NC$\underline{H}$), 3.15 (sept, ^3J = 6.9 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.49 (d, ^3J = 6.9 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.10 (d, ^3J = 6.9 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.06 (s, 27H, C(C$\underline{H}_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 147.7 (N$\underline{C}$N), 147.3 (*o*-$\underline{C}_{\mathrm{ar}}$), 132.7 (*ipso*-$\underline{C}_{\mathrm{ar}}$), 130.5 (*p*-$\underline{C}_{\mathrm{ar}}$H), 124.4 (*m*-$\underline{C}_{\mathrm{ar}}$H), 116.3 (N$\underline{C}$H), 30.0 (C($\underline{C}H_3$)$_3$), 29.1 ($\underline{C}$H(CH$_3$)$_2$), 25.4 (CH($\underline{C}H_3$)$_2$), 23.8 (CH($\underline{C}H_3$)$_2$), 23.2 ($\underline{C}$(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 8.8 ($\underline{Si}^t$Bu$_3$), 6.2 ($\underline{Si}$Se).

Anal. Calcd. [%] for C$_{78}$H$_{126}$N$_6$O$_2$Se$_2$Si$_4$: C, 64.60; H, 8.76; N, 5.80. Found [%]: C, 66.42; H, 8.82; N, 5.59.

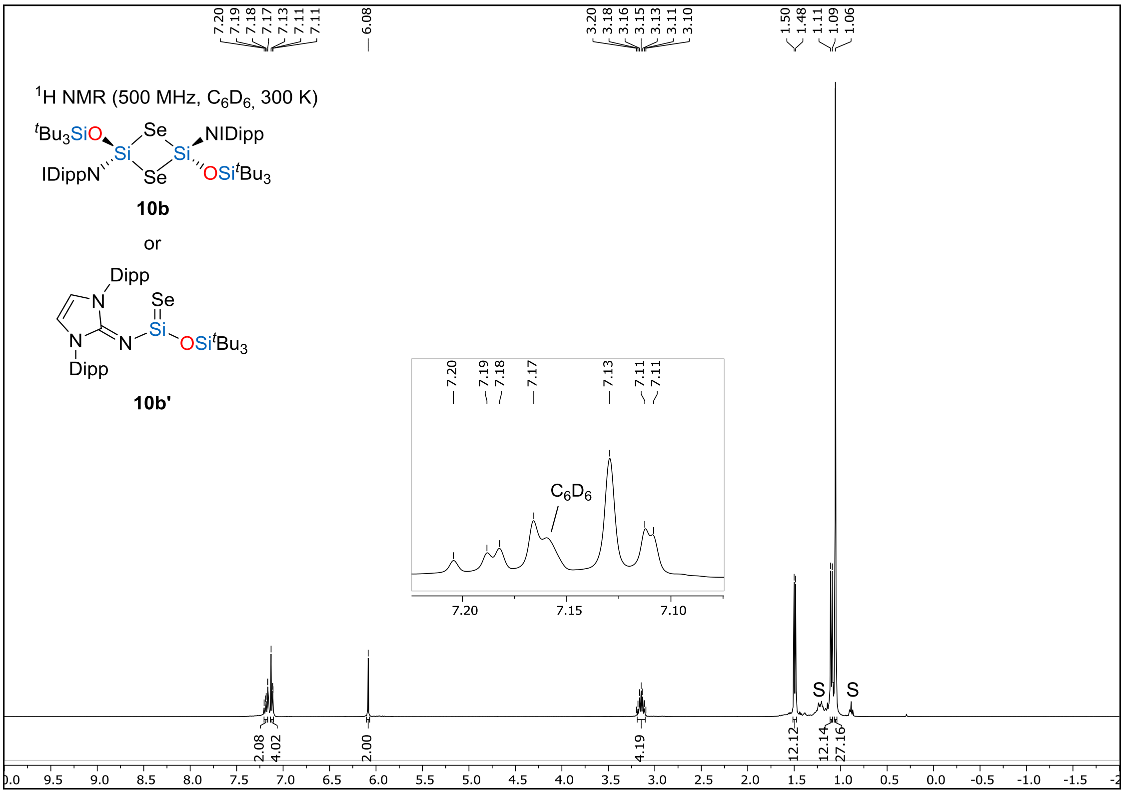


Figure S41. ^{1}H NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=Se]$_2$ (**10b**) in C$_6$D$_6$ at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

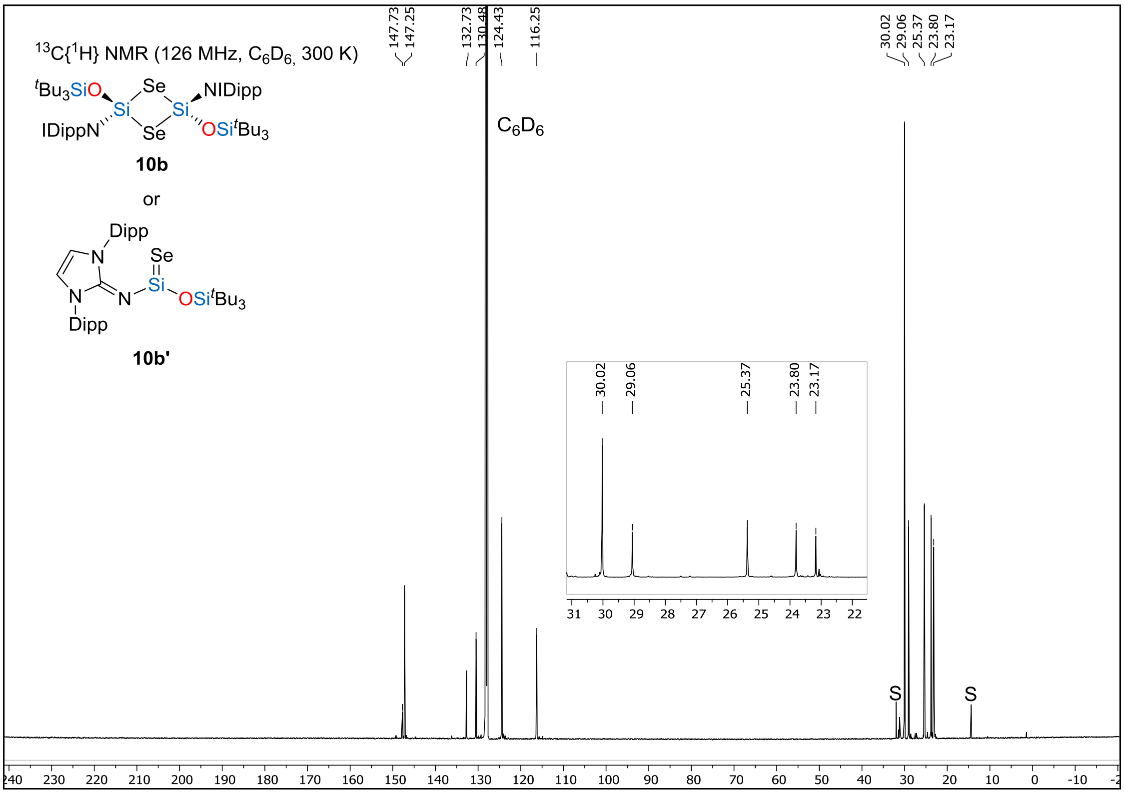


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=Se]$_2$ (**10b**) in C_6D_6 at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

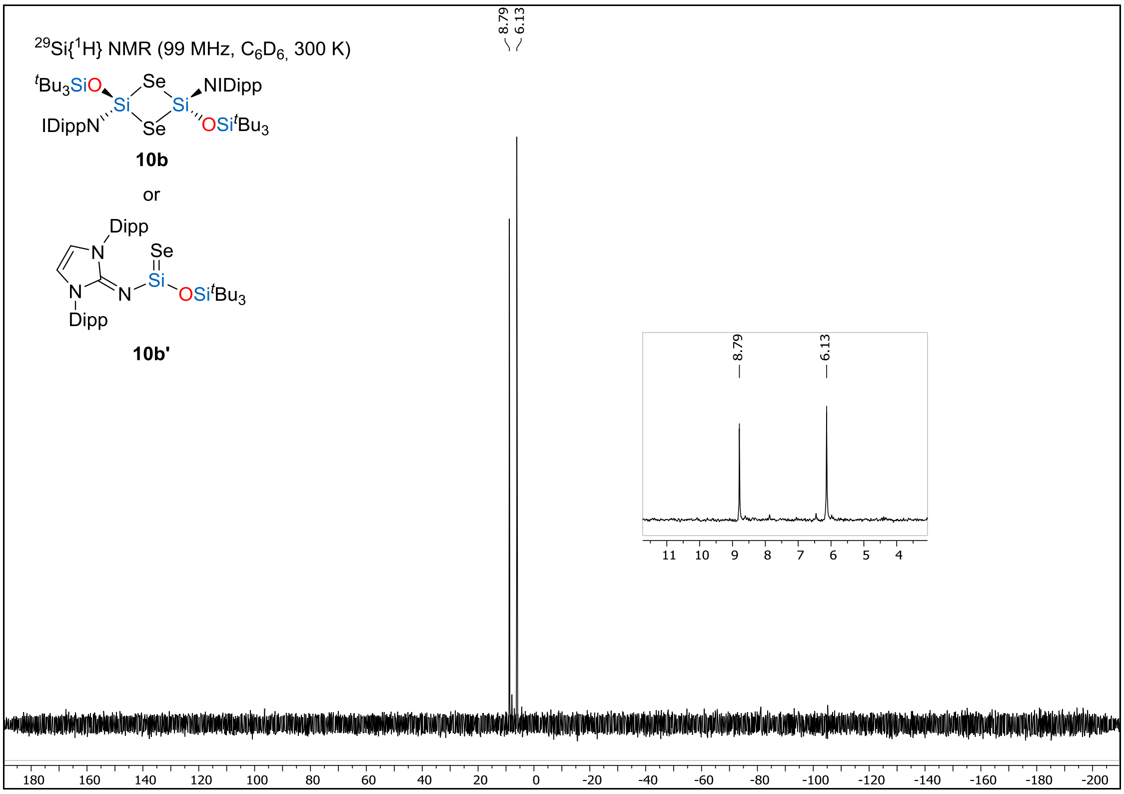
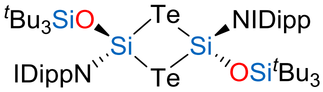


Figure S43. $^{29}Si\{^{1}H\}$ NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=Se]$_2$ (**10b**) in C_6D_6 at 300 K.

1.12 Synthesis of Silicon Ditelluride (IDippN)(^{t}Bu$_3$SiO)Si=Te (10c)



10c

$C_{78}H_{126}N_6O_2Te_2Si_4$

1547.45 g/mol

To a solution of silylene **1** (100 mg, 155 µmol, 1.0 eq.) in toluene (3 mL) was added crystalline tellurium (19.8 mg, 155 µmol, 1.0 eq.) at ambient temperature. Quantitative conversion of **1** to silicon ditelluride **10c** was detected by ^{1}H NMR spectroscopy after stirring the reaction mixture for 2 weeks (The reaction time can be significantly shortened by carrying out the reaction at elevated temperatures, so that after heating the reaction mixture to 50 °C for 3 d quantitative conversion was already achieved). Subsequent removal of the solvent afforded **10c** as an off-white solid (119.8 mg, 155 µmol, quantitative yield). Compound **10c** is completely stable as a solid and in solution at ambient temperature.

Note: The NMR data obtained indicate that **10c** presumably exists as monomer **10c′** in solution. The significantly downfield-shifted ^{29}Si NMR resonance for the SiTe moiety compared to that observed for the SiO moiety in **10a** ($\delta = -83.5$ ppm) along with the decreased signal splitting in the ^{1}H NMR suggest a monomer with a three-coordinate Si nucleus.

m.p.: 220-221 °C (decomposition; color change from colorless to black).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.21–7.17 (m, 2H, *p*-C$_{ar}$*H*), 7.14–7.11 (m, 4H, *m*-C$_{ar}$*H*), 6.09 (s, 2H, NC*H*), 3.16 (sept, $^3J = 6.9$ Hz, 4H, C*H*(CH$_3$)$_2$), 1.50 (d, $^3J = 6.9$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.08 (d, $^3J = 6.9$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.06 (s, 27H, C(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 147.1 (*o*-*C*$_{ar}$), 146.9 (N*C*N), 132.8 (*ipso*-*C*$_{ar}$), 130.5 (*p*-*C*$_{ar}$H), 124.5 (*m*-*C*$_{ar}$H), 116.5 (N*C*H), 30.2 (C(*C*H$_3$)$_3$), 29.1 (*C*H(CH$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.2 (*C*(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 10.1 (*Si*^{t}Bu$_3$), –14.6 (*Si*Te).

Anal. Calcd. [%] for $C_{78}H_{126}N_6O_2Te_2Si_4$: C, 60.54; H, 8.21; N, 5.43. Found [%]: C, 60.46; H, 8.27; N, 5.41.

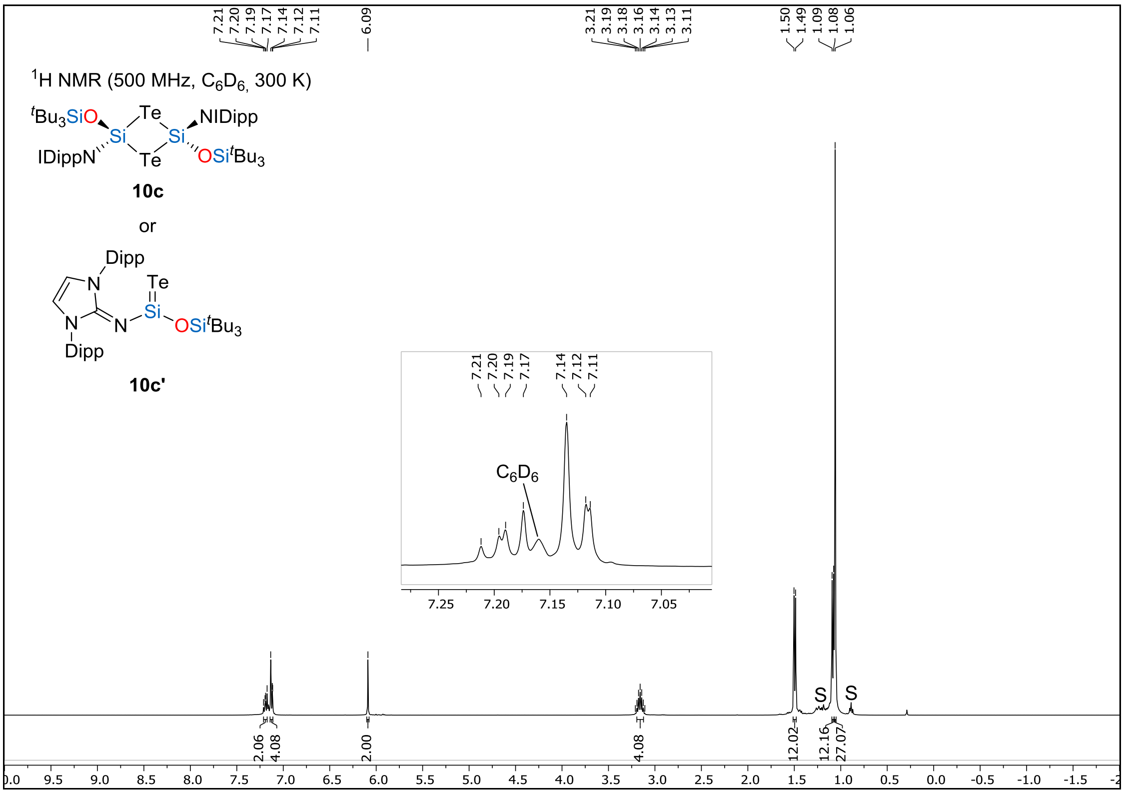


Figure S44. ^{1}H NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=Te]$_2$ (**10c**) in C_6D_6 at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

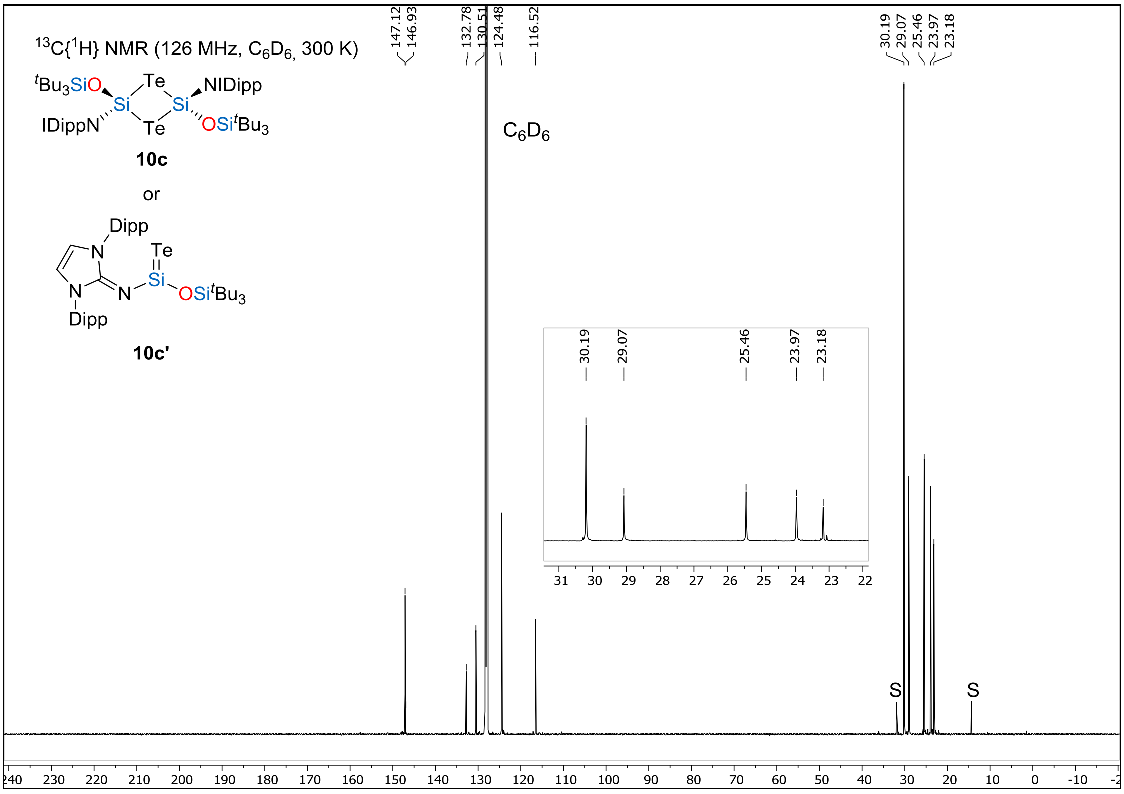


Figure S45. ^{13}C{^{1}H} NMR spectrum of [(IDippN)(^{t}Bu$_3$SiO)Si=Te]$_2$ (**10c**) in C_6D_6 at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

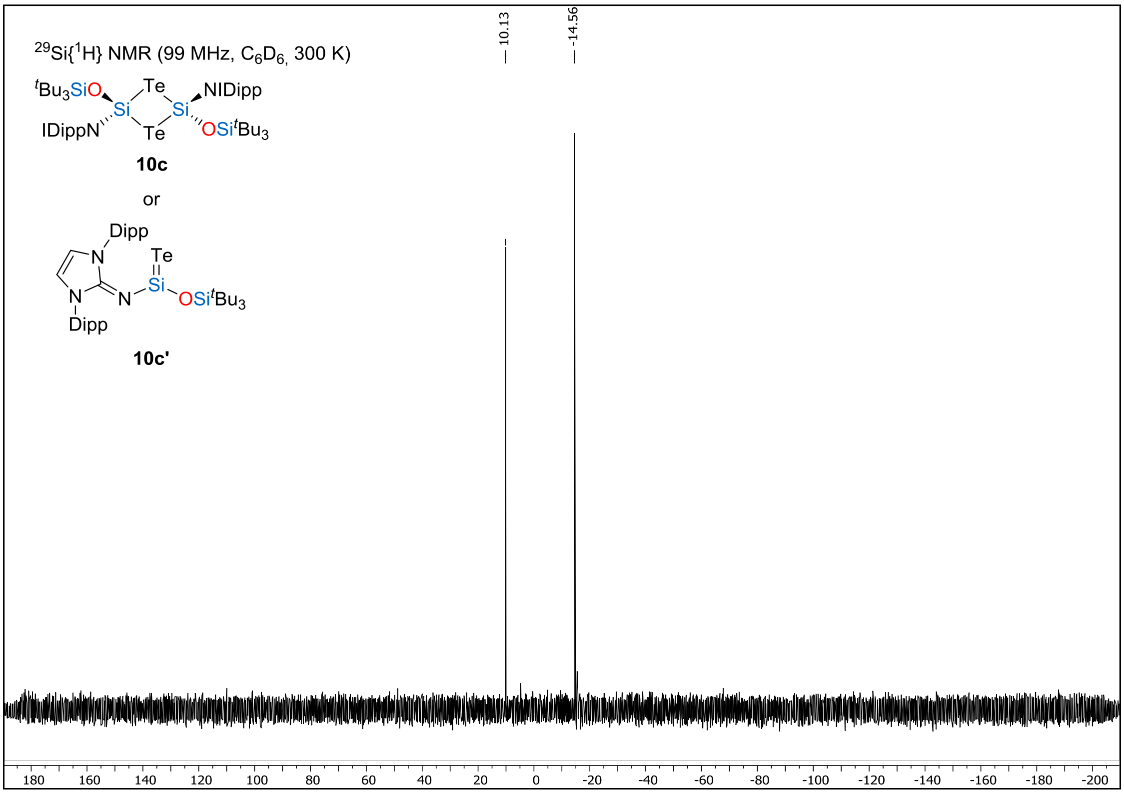
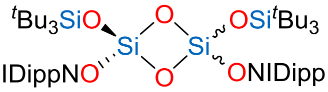


Figure S46. $^{29}Si\{^1H\}$ NMR spectrum of $[(IDippN)(^tBu_3SiO)Si{=}Te]_2$ (**10c**) in C_6D_6 at 300 K.

1.13 Synthesis of *cis*/*trans*-Cyclodisiloxane $[(IDippNO)(^tBu_3SiO)Si{=}O]_2$ (11)



cis/*trans*-**11**
$C_{78}H_{126}N_6O_6Si_4$
1356.24 g/mol

A solution of silylene **1** (100 mg, 155 µmol) in toluene (3 mL) was frozen in liquid nitrogen and degassed. The solution was cooled to –80 °C and exposed to O_2 (1 bar) under vigorous stirring. Subsequently, the reaction mixture was warmed to ambient temperature and the excess of O_2 and the solvent were removed *in vacuo*. Crystallization of the residue from *n*-hexane/toluene at –35 °C provided *cis*/*trans*-cyclodisiloxane **11** as colorless crystals (73.2 mg, 54.0 µmol, 70%), which were suitable for SC-XRD analysis (*cis*-**11**). Compound **11** is completely stable as a solid and in solution even under air and moisture.

Note: *cis*/*trans*-Cyclodisiloxane **11** is insoluble in *n*-hexane and sparingly soluble in benzene. Based on the results of SC-XRD analyses, we assume that the main product of the reaction is the *cis*-isomer formed under kinetic control. The *cis*/*trans*-ratio of **11** was calculated by ^1H NMR spectroscopy to about 71/29. The assignment of the resonances in the ^1H and ^{13}C NMR spectra proved to be difficult/impossible because many of them superimpose. Hence, in the following only those signals are given that could be clearly assigned. Carrying out the reaction at higher temperatures leads to a less selective oxygenation and formation of by-products.

m.p.: 298-299 °C (decomposition; color change from colorless to yellow).

Major isomer *cis*-cyclodisiloxane 11 (~71%):

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 6.13 (d, ^3J = 2.6 Hz, 1H, NC$\underline{H}$), 5.59 (d, ^3J = 2.6 Hz, 1H, NC$\underline{H}$), 1.48 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.48 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.08 (s, 27H, C(C$\underline{H}_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 6.9 ($\underline{Si}^t$Bu$_3$), –84.5 ($\underline{Si}_2$O$_2$).

Minor isomer *trans*-cyclodisiloxane 11 (~29%):

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 5.79 (d, ^3J = 2.6 Hz, 1H, NC$\underline{H}$), 5.66 (d, ^3J = 2.6 Hz, 1H, NC$\underline{H}$), 1.02 (s, 27H, C(C$\underline{H}_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 3.9 ($\underline{Si}^t$Bu$_3$).

Anal. Calcd. [%] for $C_{78}H_{126}N_6O_6Si_4$: C, 69.08; H, 9.36; N, 6.20. Found [%]: C, 68.12; H, 9.55; N, 6.05.

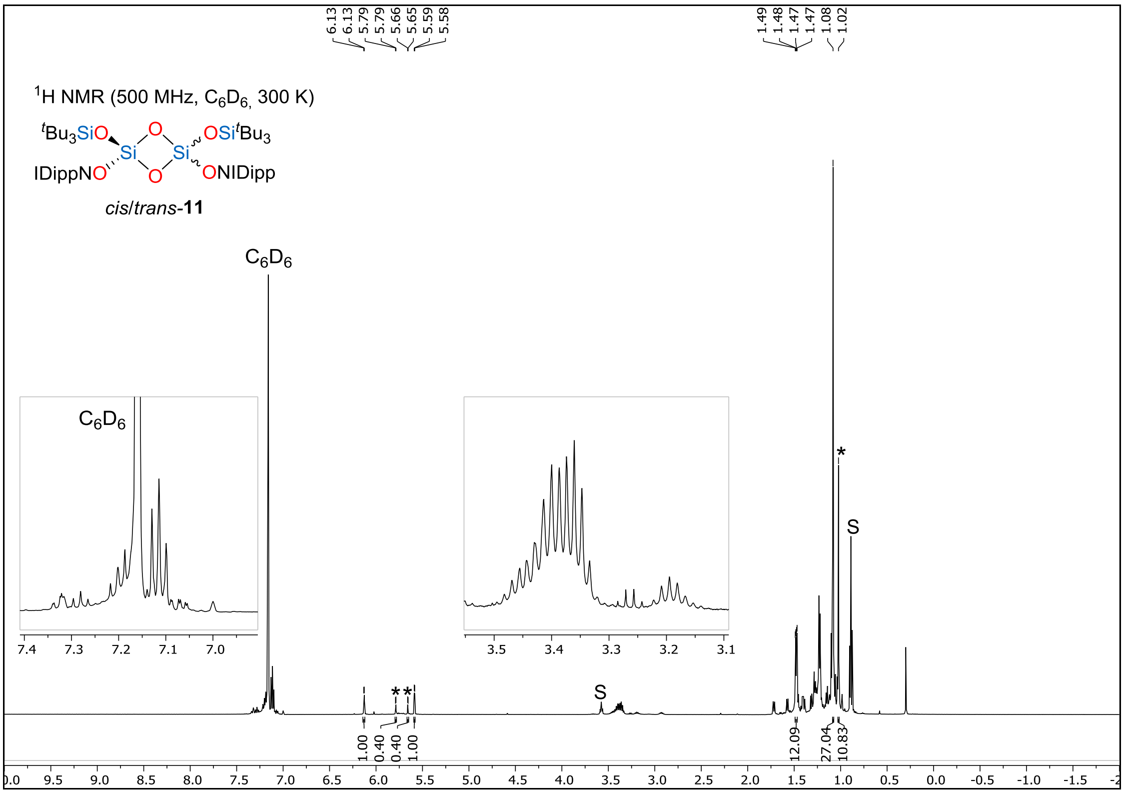


Figure S47. ^{1}H NMR spectrum of [(IDippNO)(^{t}Bu$_3$SiO)Si=O]$_2$ (**11**) in C_6D_6 at 300 K. Unambiguously assigned resonances for the minor *trans*-product and residual solvent are labeled with asterisks * and S, respectively.

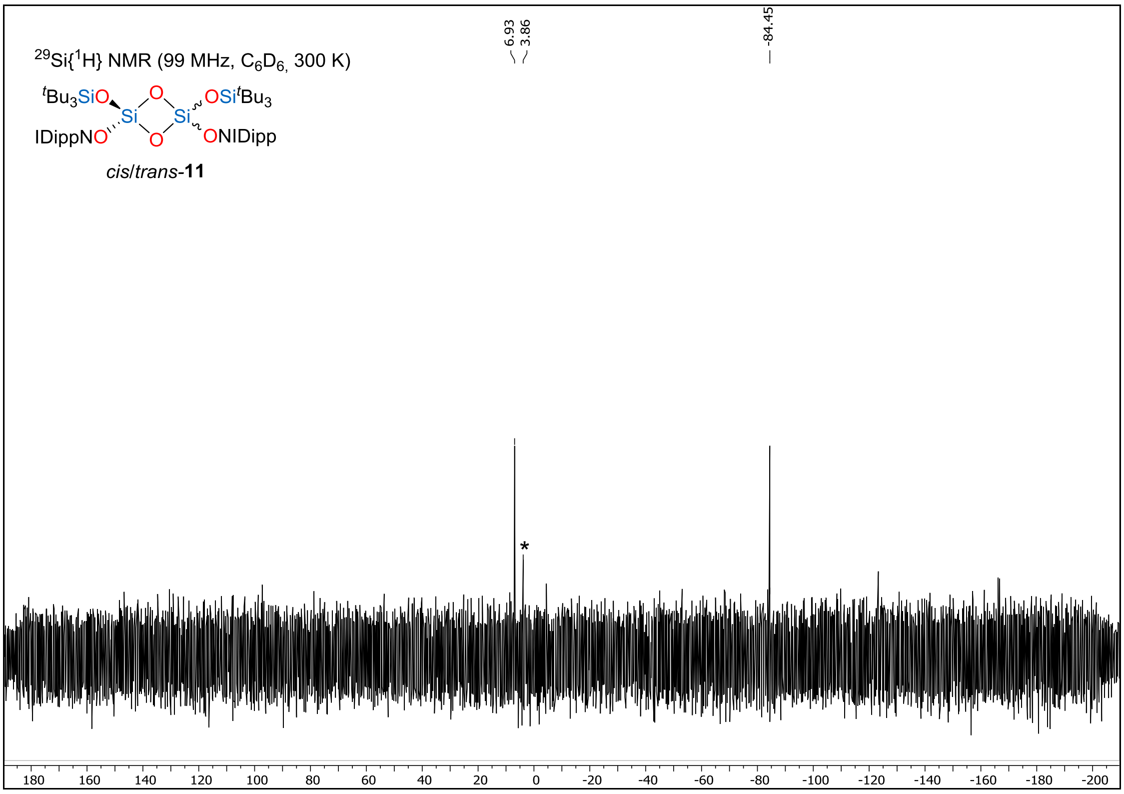


Figure S48. ^{29}Si{^{1}H} NMR spectrum of [(IDippNO)(^{t}Bu$_3$SiO)Si=O]$_2$ (**11**) in C_6D_6 at 300 K. The unambiguously assigned resonance for the minor *trans*-product is labeled with an asterisk *.

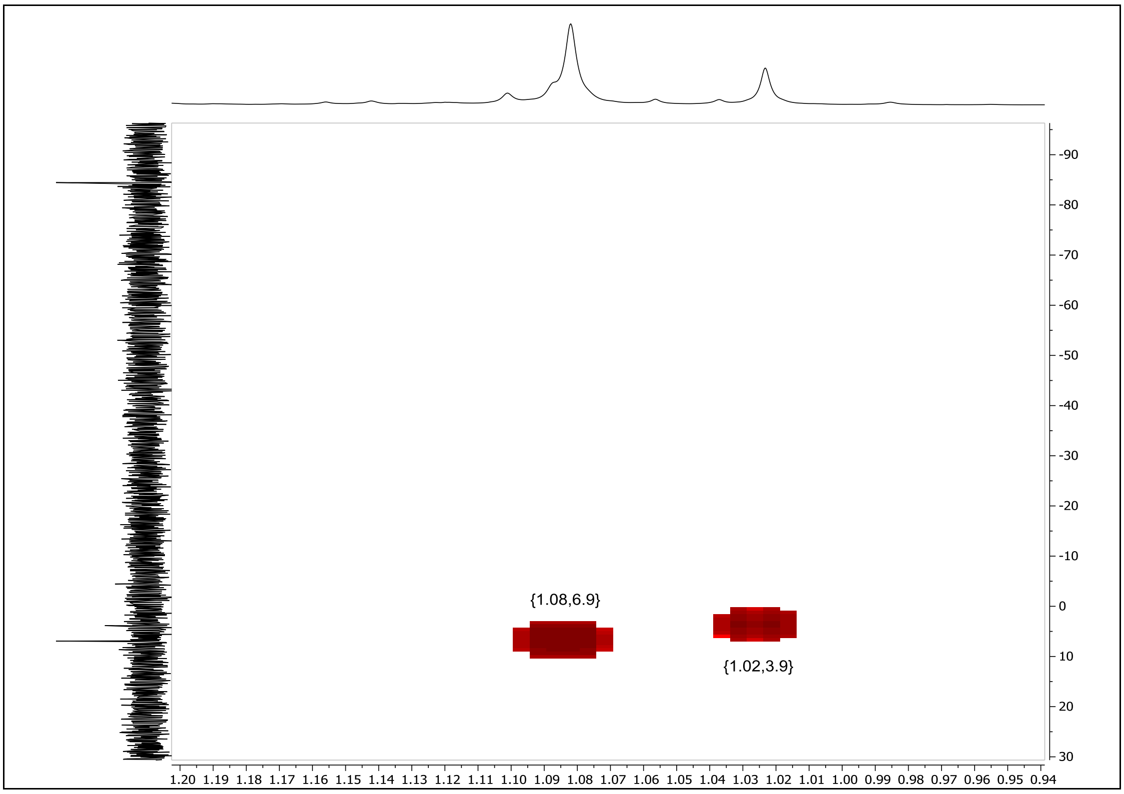
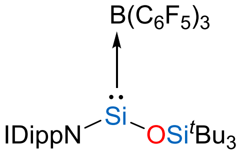


Figure S49. ^{1}H/^{29}Si HMBC NMR spectrum of [(IDippNO)(^{t}Bu$_3$SiO)Si=O]$_2$ (**11**) in C_6D_6 at 300 K.

1.14 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si(B(C$_6$F$_5$)$_3$) (12a)



12a

$C_{57}H_{63}BF_{15}N_3OSi_2$
1158.11 g/mol

To a solution of silylene **1** (100 mg, 155 µmol, 1.0 eq.) in *n*-hexane (3 mL) was added a solution of B(C$_6$F$_5$)$_3$ (BCF) (79.2 mg, 155 µmol, 1.0 eq.) in *n*-hexane (1 mL) at room temperature. After stirring the resulting colorless solution for 30 min, the solvent was removed *in vacuo*. Crystallization of the residue from *n*-hexane at –35 °C afforded silylene-BCF adduct **12a** as colorless crystals (149 mg, 129 µmol, 83%), which were suitable for SC-XRD analysis. Compound **12a** is completely stable as a solid and in solution at room-temperature.

Note: Due to coupling with the ^{11}B nucleus (high quadrupole moment and spin ^{11}B = 3/2), several resonances are broadened in the NMR spectra or were not observable at all.

m.p.: 200-201 °C (decomposition; color change from colorless to orange).

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.16–7.11 (m, 4H, *m*-C$_{\text{ar}}$*H*, overlapping with solvent signal), 6.80 (br s, 2H, *p*-C$_{\text{ar}}$*H*), 5.98 (s, 2H, NC*H*), 3.15–3.09 (m, 2H, C*H*(CH$_3$)$_2$), 2.96–2.85 (m, 2H, C*H*(CH$_3$)$_2$), 1.31–1.12 (m, 12H, CH(C*H*$_3$)$_2$), 0.91–0.87 (m, 12H, CH(C*H*$_3$)$_2$), 0.81 (s, 27H, C(C*H*$_3$)$_3$).

^{11}B{^{1}H} NMR (128 MHz, C$_6$D$_6$, 300 K): δ [ppm] = –20.3.

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 149.6 (*C*F), 148.9 (*o*-*C*$_{\text{ar}}$), 147.7 (*C*F), 147.5 (*o*-*C*$_{\text{ar}}$), 147.0 (*C*F), 146.0 (*C*F), 145.4 (N*C*N), 138.8 (*C*F), 136.7 (*C*F), 132.8 (*ipso*-*C*$_{\text{ar}}$), 130.4 (*p*-*C*$_{\text{ar}}$H), 124.7 (*m*-*C*$_{\text{ar}}$H), 124.5 (*m*-*C*$_{\text{ar}}$H), 117.2 (N*C*H), 30.1 (*C*H(CH$_3$)$_2$), 29.7 (C(*C*H$_3$)$_3$), 28.5 (*C*H(CH$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$), 22.4 (*C*(CH$_3$)$_3$).

^{19}F{^{1}H} NMR (471 MHz, C$_6$D$_6$, 300 K): δ [ppm] = –127.6, –157.7, –162.1.

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 11.4 (*Si*^{t}Bu$_3$)

The resonance for the low-valent Si atom (*silylene Si*) was not observed.

Anal. Calcd. [%] for $C_{57}H_{63}BF_{15}N_3OSi_2$: C, 59.12; H, 5.48; N, 3.63. Found [%]: C, 58.19; H, 5.72; N, 3.58.

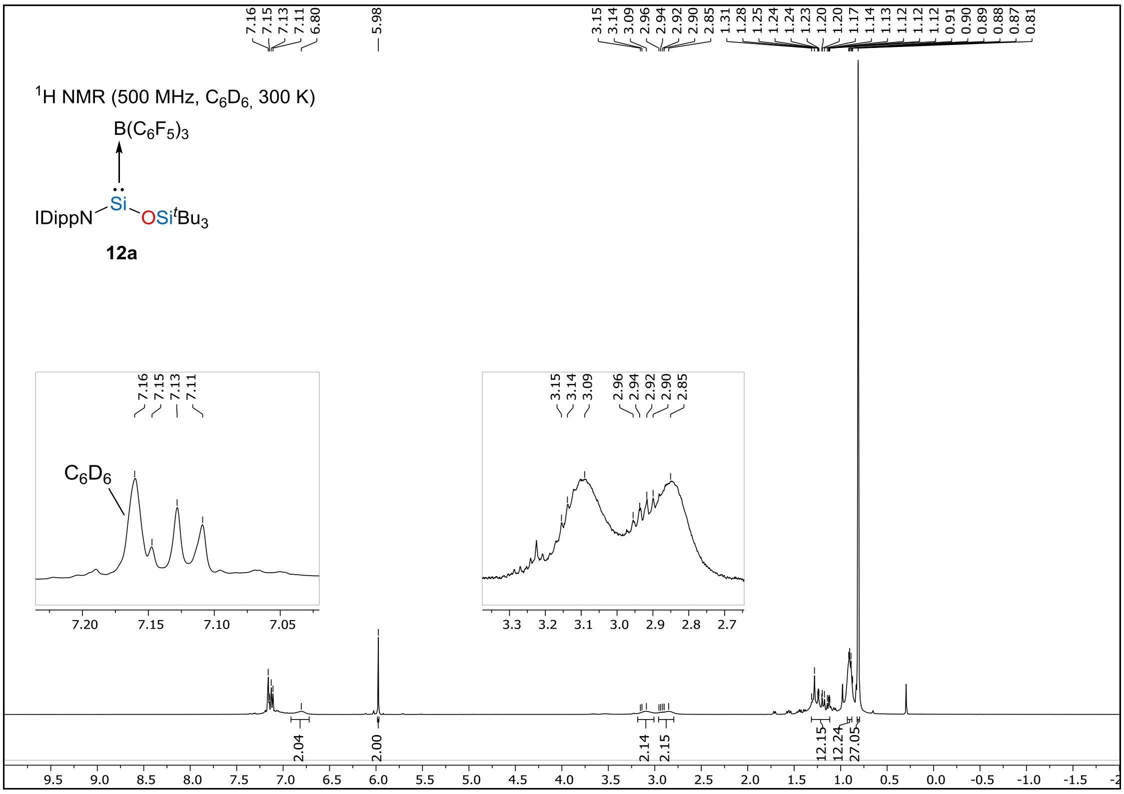


Figure S50. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(B(C$_6$F$_5$)$_3$) (**12a**) in C_6D_6 at 300 K.

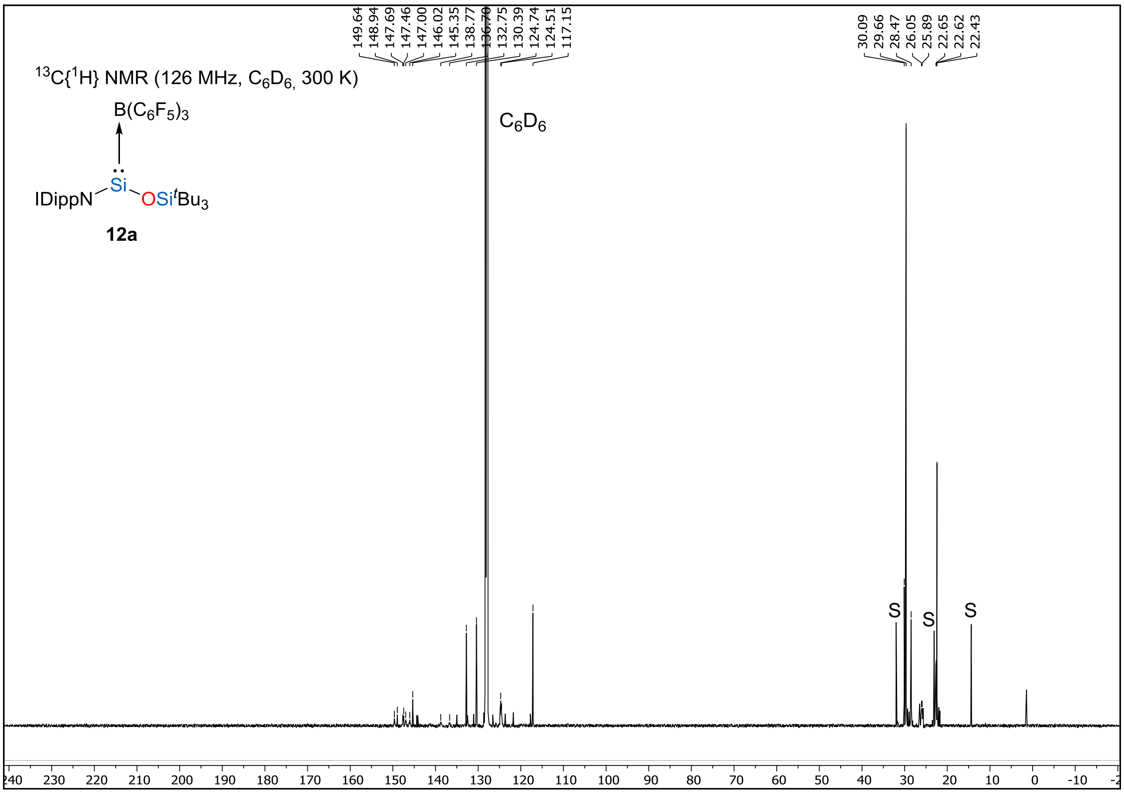


Figure S51. ^{13}C{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(B(C$_6$F$_5$)$_3$) (**12a**) in C_6D_6 at 300 K. Residual *n*-hexane is labeled with S.

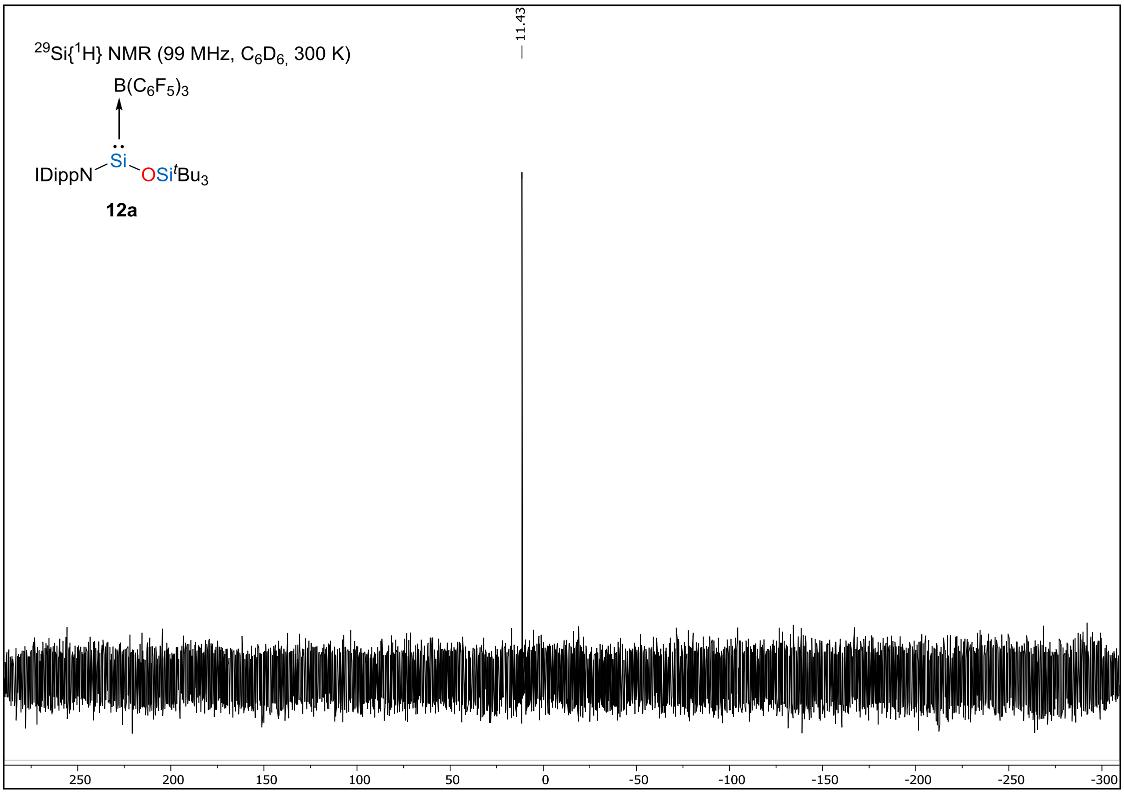
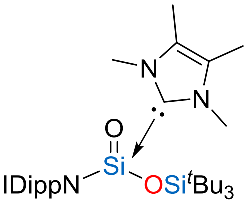


Figure S52. ^{29}Si{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si(B(C$_6$F$_5$)$_3$) (**12a**) in C$_6$D$_6$ at 300 K.

1.15 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si=O(IMe$_4$) (13a)



13a
$C_{46}H_{75}N_5O_2Si_2$
786.31 g/mol

A thick-walled, pressurizeable Schlenk flask with a rubber septum, containing a solution of silylene **1** (150 mg, 232 µmol, 1.0 eq.) in *n*-pentane (10 mL) was cooled to –130 °C. A precooled (–80 °C) solution of IMe$_4$ (28.8 mg, 232 µmol, 1.0 eq.) in toluene (0.5 mL) was added under vigorous stirring. A color change from colorless to yellow indicated formation of the NHC-stabilized silylene ((IDippN)(^{t}Bu$_3$SiO)Si(IMe$_4$)). Subsequently, the rubber septum was replaced by a PTFE-sealed screw cap and the reaction mixture was stirred for 30 min at –130 °C. The mixture was then frozen in liquid nitrogen, degassed and warmed to –130 °C. The solution was carefully exposed to N$_2$O (1 bar; **DANGER**: possible condensation of N$_2$O) and warmed to room-temperature, whereby a color change from yellow to colorless was observed. After removal of all volatiles *in vacuo*, the residue was washed with *n*-hexane. The IMe$_4$-stabilized silanoic ester derivative **13a** was afforded as a colorless solid (165 mg, 210 µmol, 90%). Colorless crystals, suitable for SC-XRD analysis, were obtained by cooling a saturated toluene solution of **13a** to –35 °C for several days. NHC adduct **13a** is completely stable as a solid and in solution at ambient and elevated temperatures (≤130 °C).

Note: The observed unusual broad splitting of the NHC wingtip methyl protons ($\Delta\delta$ = 1.03 ppm) in the ^{1}H NMR spectrum presumably originates from hydrogen bonding of one methyl C–H proton to the oxygen atom of the Si=O bond. This assumption is supported by the solid-state structure of **13a** (*vide infra*), which revealed a close O···H distance of 2.153 Å, being much shorter than the sum of the van der Waals radii of hydrogen and oxygen (2.72 Å).[S7]

m.p.: 209-210 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.21 (t, ^3J = 7.8 Hz, 2H, p-C$_{ar}\underline{H}$), 7.12–7.09 (m, 4H, m-C$_{ar}\underline{H}$), 6.03 (s, 2H, NC$\underline{H}$), 4.22 (s, 3H, N$_{NHC}$C$\underline{H}_3$), 3.38 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.29 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.19 (s, 3H, N$_{NHC}$C$\underline{H}_3$), 1.40 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.37–1.34 (m, 12H, CH(C$\underline{H}_3$)$_2$ + C$_{NHC}$C$\underline{H}_3$), 1.22 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.22 (d, ^3J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.17 (s, 27H, C(C$\underline{H}_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 159.6 (carbene C), 148.6 (o-$\underline{C}_{ar}$), 148.5 (o-$\underline{C}_{ar}$), 144.1 (N$\underline{C}$N), 136.0 (*ipso*-$\underline{C}_{ar}$), 128.8 (p-$\underline{C}_{ar}$H), 124.7 ($\underline{C}_{NHC}$CH$_3$), 123.6 (m-$\underline{C}_{ar}$H), 123.5 (m-$\underline{C}_{ar}$H + $\underline{C}_{NHC}$CH$_3$), 114.7 (N$\underline{C}$H), 33.8 (N$_{NHC}\underline{C}$H$_3$), 33.4 (N$_{NHC}\underline{C}$H$_3$), 30.7 (C($\underline{C}$H$_3$)$_3$), 29.2 ($\underline{C}$H(CH$_3$)$_2$), 29.1 ($\underline{C}$H(CH$_3$)$_2$), 25.2 (CH($\underline{C}$H$_3$)$_2$), 25.1 (CH($\underline{C}$H$_3$)$_2$), 23.4 ($\underline{C}$(CH$_3$)$_3$), 23.3 (CH($\underline{C}$H$_3$)$_2$), 22.9 (CH($\underline{C}$H$_3$)$_2$), 7.8 (C$_{NHC}\underline{C}$H$_3$), 7.8 (C$_{NHC}\underline{C}$H$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 1.3 (Si^tBu$_3$), –88.5 (central Si).

Anal. Calcd. [%] for $C_{46}H_{75}N_5O_2Si_2$: C, 70.27; H, 9.61; N, 8.91. Found [%]: C, 69.13; H, 9.78; N, 8.98.

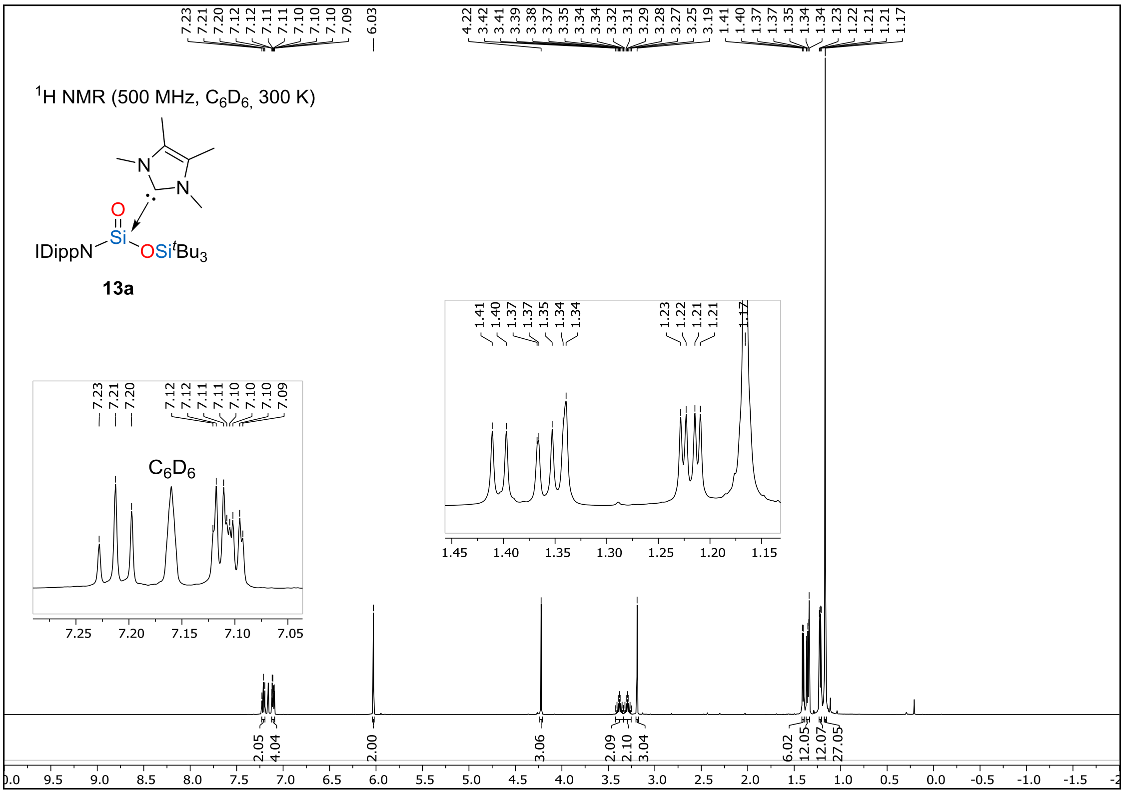


Figure S53. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(IMe$_4$) (**13a**) in C$_6$D$_6$ at 300 K.

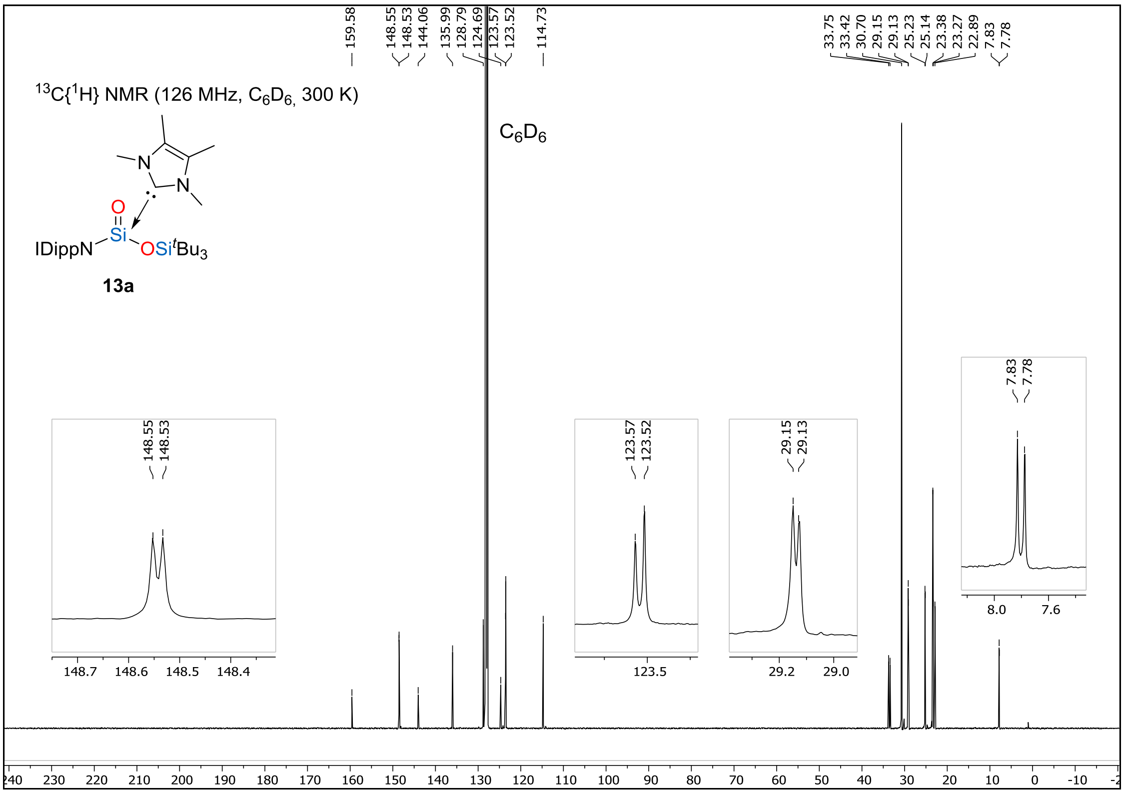


Figure S54. ^{13}C{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(IMe$_4$) (**13a**) in C$_6$D$_6$ at 300 K.

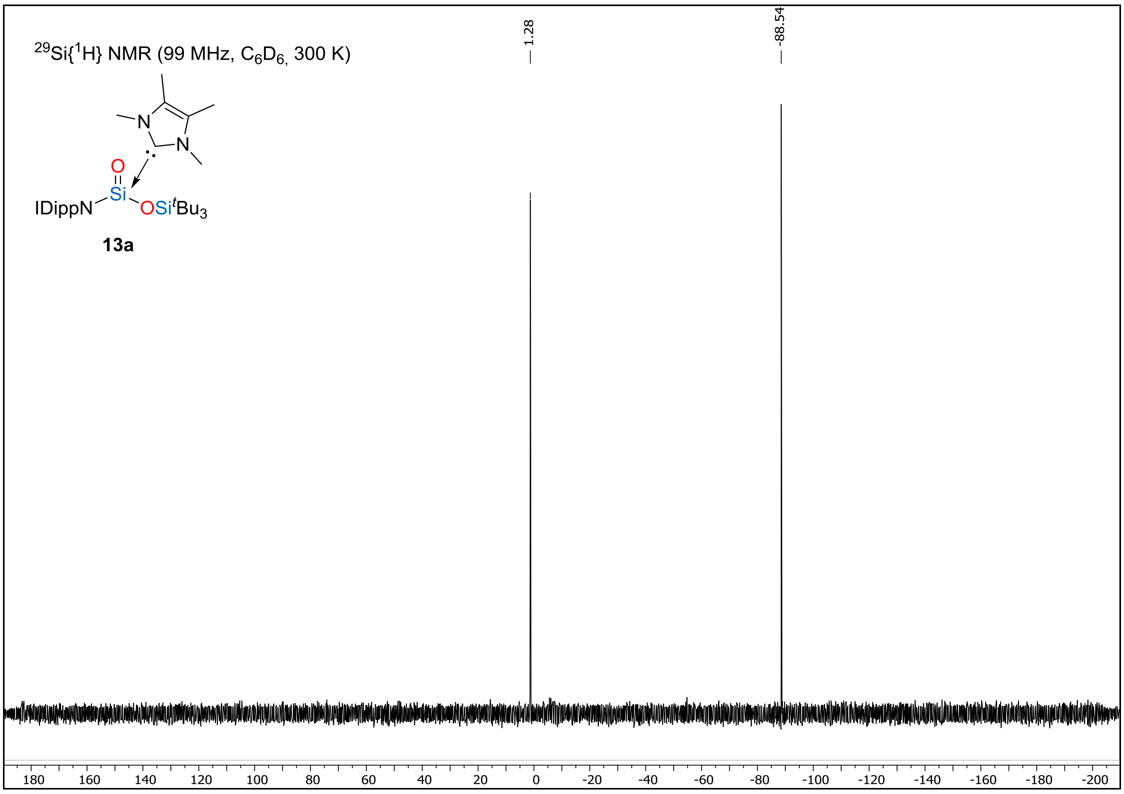
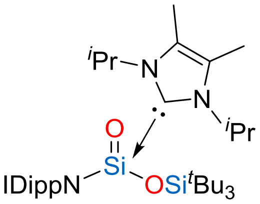


Figure S55. ^{29}Si{^{1}H} NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(IMe$_4$) (**13a**) in C$_6$D$_6$ at 300 K.

1.16 Synthesis and Reactivity of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (13b)



13b

$C_{50}H_{83}N_5O_2Si_2$

842.42 g/mol

Benzene (5 mL) was added to a mixture of silylene **1** (100 mg, 155 µmol, 1.0 eq.) and I^{i}Pr$_2$Me$_2$ (27.9 mg, 155 µmol, 1.0 eq.) in a thick-walled, pressurizeable Schlenk flask. The solution was then frozen in liquid nitrogen, degassed and exposed to N$_2$O (1 bar) at room-temperature. Subsequently, the reaction mixture was stirred for 30 min. Removal of all volatiles *in vacuo* provided the I^{i}Pr$_2$Me$_2$-stabilized silanoic ester derivative **13b** as a colorless solid (130 mg, 155 µmol, quantitative yield). NHC adduct **13b** is completely stable as a solid and in solution at ambient and elevated temperatures (≤130 °C). Note: The observed unusual broad splitting of the NHC wingtip methine protons ($\Delta\delta$ = 2.74 ppm) in the ^{1}H NMR spectrum presumably originates from hydrogen bonding of one isopropyl C–H proton to the oxygen atom of the Si=O bond.

m.p.: 242-243 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 8.53 (sept, ^3J = 6.9 Hz, 1H, N$_{NHC}$C*H*(CH$_3$)$_2$), 7.32–7.26 (m, 4H, C$_{ar}$*H*), 7.07–7.05 (m, 2H, C$_{ar}$*H*), 5.89 (s, 2H, NC*H*), 5.79 (sept, ^3J = 6.9 Hz, 1H, N$_{NHC}$C*H*(CH$_3$)$_2$), 3.54 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 3.10 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.71 (br s, 6H, CH(C*H*$_3$)$_2$), 1.63 (s, 3H, C$_{NHC}$C*H*$_3$), 1.60 (s, 3H, C$_{NHC}$C*H*$_3$), 1.40 (d, ^3J = 6.9 Hz, 3H, N$_{NHC}$CH(C*H̲*$_3$)$_2$), 1.34 (d, ^3J = 6.9 Hz, 3H, N$_{NHC}$CH(C*H̲*$_3$)$_2$), 1.23 (s, 27H, C(C*H̲*$_3$)$_3$), 1.22 (d, ^3J = 6.9 Hz, 6H, CH(C*H̲*$_3$)$_2$), 1.16 (d, ^3J = 6.9 Hz, 6H, CH(C*H̲*$_3$)$_2$), 1.13 (d, ^3J = 6.9 Hz, 3H, N$_{NHC}$CH(C*H̲*$_3$)$_2$), 1.05 (br s, 6H, CH(C*H̲*$_3$)$_2$), 0.81 (d, ^3J = 6.9 Hz, 3H, N$_{NHC}$CH(C*H̲*$_3$)$_2$).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 158.5 (*carbene C̲*), 149.4 (*o*-C̲$_{ar}$), 147.4 (*o*-C̲$_{ar}$), 144.5 (NC̲N), 136.5 (*ipso*-C̲$_{ar}$), 129.2 (*p*-C̲$_{ar}$H), 126.8 (C̲$_{NHC}$CH$_3$), 124.5 (C̲$_{NHC}$CH$_3$), 123.9 (*m*-C̲$_{ar}$H), 115.7 (NC̲H), 50.4 (N$_{NHC}$C̲H(CH$_3$)$_2$), 48.7 (N$_{NHC}$C̲H(CH$_3$)$_2$), 30.9 (C(C̲H$_3$)$_3$), 29.5 (C̲H(CH$_3$)$_2$), 28.5 (C̲H(CH$_3$)$_2$), 26.0 (CH(C̲H$_3$)$_2$), 25.7 (CH(C̲H$_3$)$_2$), 23.6 (CH(C̲H$_3$)$_2$), 23.4 (C̲(CH$_3$)$_3$), 23.1 (CH(C̲H$_3$)$_2$), 22.8 (N$_{NHC}$CH(C̲H$_3$)$_2$), 22.6 (N$_{NHC}$CH(C̲H$_3$)$_2$), 21.8 (N$_{NHC}$CH(C̲H$_3$)$_2$), 21.7 (N$_{NHC}$CH(C̲H$_3$)$_2$), 10.4 (C$_{NHC}$C̲H$_3$), 10.3 (C$_{NHC}$C̲H$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 1.6 (*Si*^{t}Bu$_3$), –86.7 (*central Si̲*).

Anal. Calcd. [%] for $C_{50}H_{83}N_5O_2Si_2$: C, 71.29; H, 9.93; N, 8.31. Found [%]: C, 70.40; H, 9.94; N, 8.26.

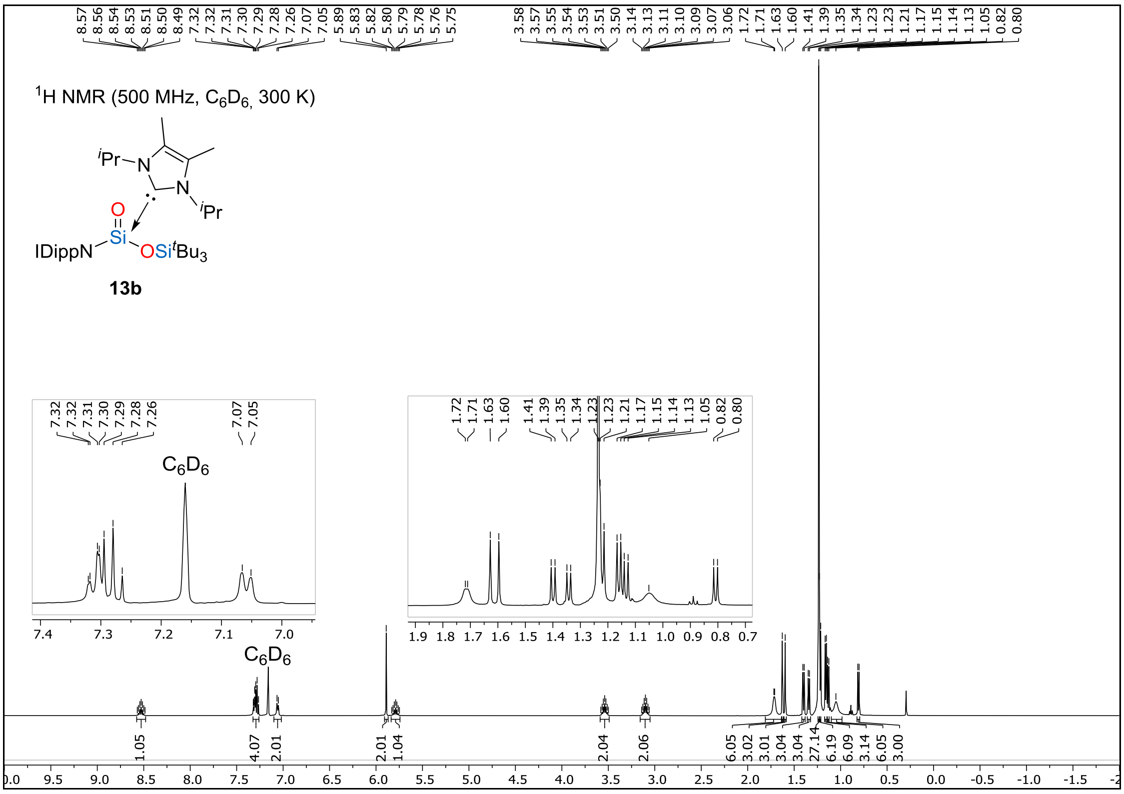


Figure S56. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) in C$_6$D$_6$ at 300 K.

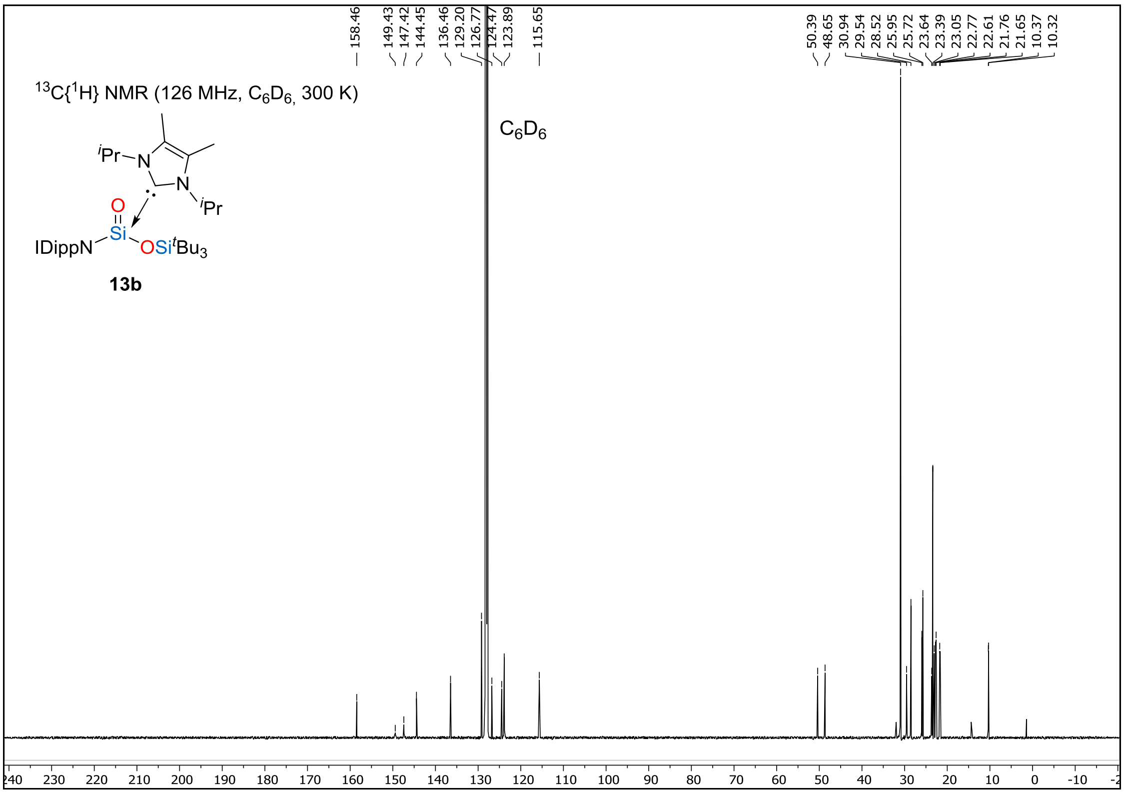


Figure S57. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) in C_6D_6 at 300 K.

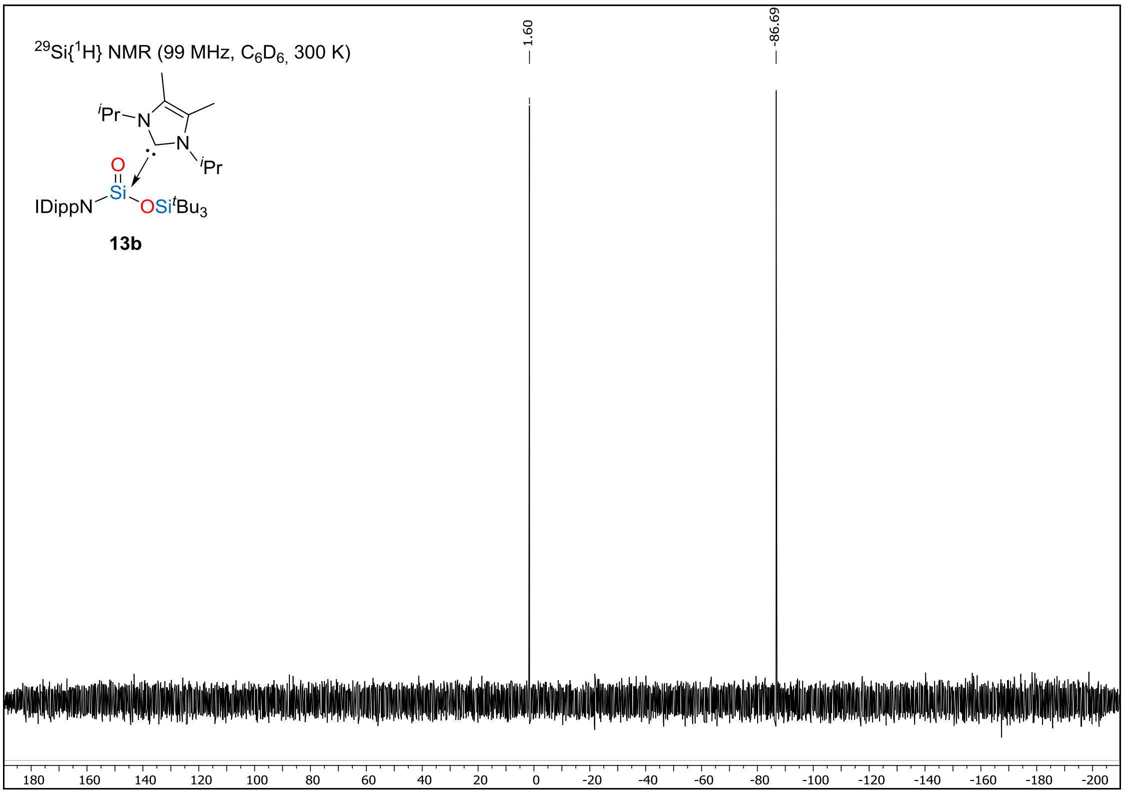


Figure S58. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) in C_6D_6 at 300 K.

Reactivity Investigations

Due to the convenient access to (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**), this NHC-stabilized silanoic ester derivative was subjected to some subsequent reactions.

Ligand Substitution (NHC Exchange Reaction)

A substitution of a weaker σ-donor by a stronger Lewis base is often observed for NHC-supported organosilicon compounds.[S8] Therefore, a possible ligand exchange reaction was investigated:

A *J. Young* PTFE valve NMR tube was charged with a mixture of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) (20.0 mg, 23.7 µmol, 1.0 eq.) and IMe$_4$ (2.95 mg, 23.7 µmol, 1.0 eq.) in C_6D_6 (0.5 mL). Since no reaction was detected after 1 d at room-temperature *via* ^{1}H NMR spectroscopy, we exposed the sample to elevated temperatures. Full conversion of **13b** to the IMe$_4$-stabilized silanoic ester derivative (IDippN)(^{t}Bu$_3$SiO)Si=O(IMe$_4$) (**13a**) with concomitant formation of free I^{i}Pr$_2$Me$_2$ was observed after 1 d at 110 °C.
Note: NHC adduct **13a** can be separated from I^{i}Pr$_2$Me$_2$ and isolated after removing the solvent *in vacuo* and washing the residue with cold *n*-hexane.

NHC Abstraction Reactions

To prove the intermediary formation of (IDippN)(^{t}Bu$_3$SiO)Si=O (**10a′**) during the synthesis of *trans*-cyclodisiloxane [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (**10a**), we wanted to abstract the NHC and observe subsequent dimerization affording **10a**. For this purpose, the reaction of **13b** toward common NHC abstraction reagents, such as CO_2 or BR_3 compounds, was studied:

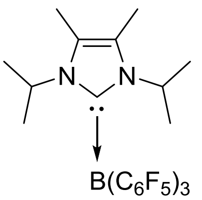
A *J. Young* PTFE valve NMR tube was charged with a solution of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) (20.0 mg, 23.7 µmol) in C_6D_6 (0.5 mL), degassed and exposed to CO_2 (1 bar). Immediate full conversion of **13b** to silicon carbonate complex (IDippN)(^{t}Bu$_3$SiO)Si(O$_2$C=O) (**9**) with simultaneous formation of the NHC-CO$_2$ adduct I^{i}Pr$_2$Me$_2$·CO$_2$ was detected by ^{1}H NMR spectroscopy.

Since NHC abstraction with CO_2 worked, but not the dimerization to **10a**, but the [2+2] cycloaddition reaction providing **9** was observed, we turned to the Lewis acids $B(C_6F_5)_3$ and BPh_3.

Interestingly, addition of an equimolar amount of BCF to **13b** at room temperature resulted in the unselective formation of novel silicon-containing products, but only a conversion of 50% was detected. The addition of a second equivalent of BCF then led to full conversion. The formation of a mixture of products, containing the desired NHC-borane adduct I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ and a compound bearing a Si–F bond, was identified by multinuclear and 2D NMR spectroscopy. However, purification and isolation was not possible so far. The reaction most likely proceeds via NHC-abstraction and simultaneous formation of I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ and the Lewis acid-stabilized silanoic ester derivative (IDippN)(^{t}Bu$_3$SiO)Si=O(B(C$_6$F$_5$)$_3$), which undergoes subsequent bond activation and rearrangement reactions.

By-product NHC-borane adduct I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$:

For the sake of comparison, the Lewis acid/base-complex I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ was separately synthesized and characterized *via* multinuclear NMR spectroscopy:



I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$
$C_{29}H_{20}BF_{15}N_2$
692.28 g/mol

To a solution of BCF (28.4 mg, 55.5 µmol, 1.0 eq.) in benzene (0.5 mL) was added a solution of I^{i}Pr$_2$Me$_2$ (10.0 mg, 55.5 µmol, 1.0 eq.) in benzene (0.5 mL). Subsequently, the reaction mixture was stirred for 30 min. Removal of the solvent *in vacuo* afforded the NHC-borane adduct I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ as a colorless solid (38.4 mg, 55.5 µmol, quantitative yield).

Note: Due to coupling with the ^{11}B nucleus (high quadrupole moment and spin ^{11}B = 3/2) and the ^{19}F atoms, several resonances are broadened in the NMR spectra.

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 4.69 (sept, ^{3}J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 1.42 (s, 6H, C$\underline{H}_3$), 1.02 (d, ^{3}J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 0.52 (d, ^{3}J = 6.9 Hz, 6H, CH(C$\underline{H}_3$)$_2$).

^{11}B{^{1}H} NMR (128 MHz, C$_6$D$_6$, 300 K): δ [ppm] = –16.5.

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 158.6–157.0 (m, $\underline{\text{carbene } C}$), 150.2–146.6 (m, $\underline{C}_{\text{ar}}$), 141.1–140.8 (m, $\underline{C}_{\text{ar}}$), 139.1–138.3 (m, $\underline{C}_{\text{ar}}$), 137.0–136.2 (m, $\underline{C}_{\text{ar}}$), 126.6 ($\underline{C}CH_3$), 49.9 ($\underline{C}$H(CH$_3$)$_2$), 49.9 ($\underline{C}$H(CH$_3$)$_2$), 21.3 (CH($\underline{C}H_3$)$_2$), 21.3 (CH($\underline{C}H_3$)$_2$), 20.3 (br s, CH($\underline{C}H_3$)$_2$), 10.2 (C$\underline{C}H_3$).

^{19}F{^{1}H} NMR (471 MHz, C$_6$D$_6$, 300 K): δ [ppm] = –126.4 to –126.4 (m, 2F, *o*-C$_{\text{ar}}\underline{F}$), –130.3 to –130.4 (m, 2F, *o*-C$_{\text{ar}}\underline{F}$), –132.3 to –132.3 (m, 2F, *o*-C$_{\text{ar}}\underline{F}$), –157.6 (t, $^{3}J_{\text{FF}}$ = 21.7 Hz, 1F, *p*-C$_{\text{ar}}\underline{F}$), –158.2 (t, $^{3}J_{\text{FF}}$ = 21.7 Hz, 2F, *p*-C$_{\text{ar}}\underline{F}$), –162.7 (t, $^{3}J_{\text{FF}}$ = 21.7 Hz, 2F, *m*-C$_{\text{ar}}\underline{F}$), –164.4 (dt, $^{3}J_{\text{FF}}$ = 21.7 Hz, $^{4}J_{\text{FF}}$ = 7.8 Hz, 2F, *m*-C$_{\text{ar}}\underline{F}$), –165.1 to –165.2 (m, 2F, *m*-C$_{\text{ar}}\underline{F}$).

The spectroscopic data are consistent with those previously reported.[S9]

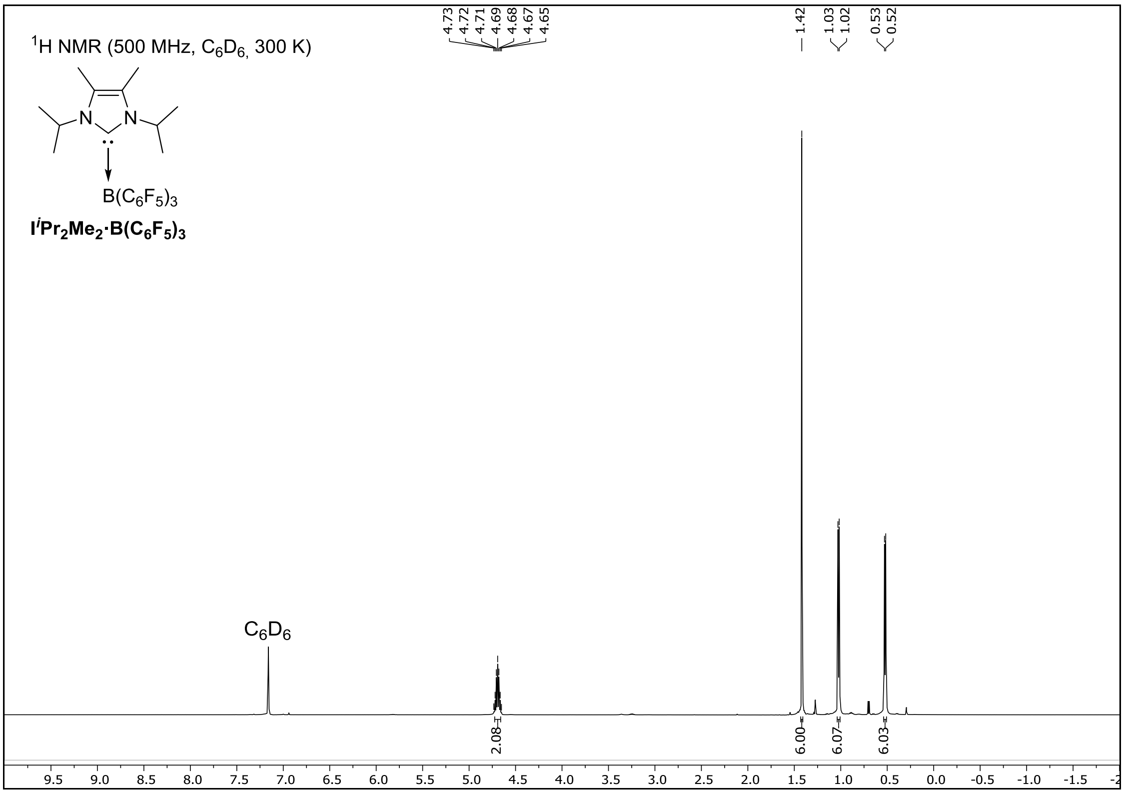


Figure S59. ^{1}H NMR spectrum of I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ at 300 K.

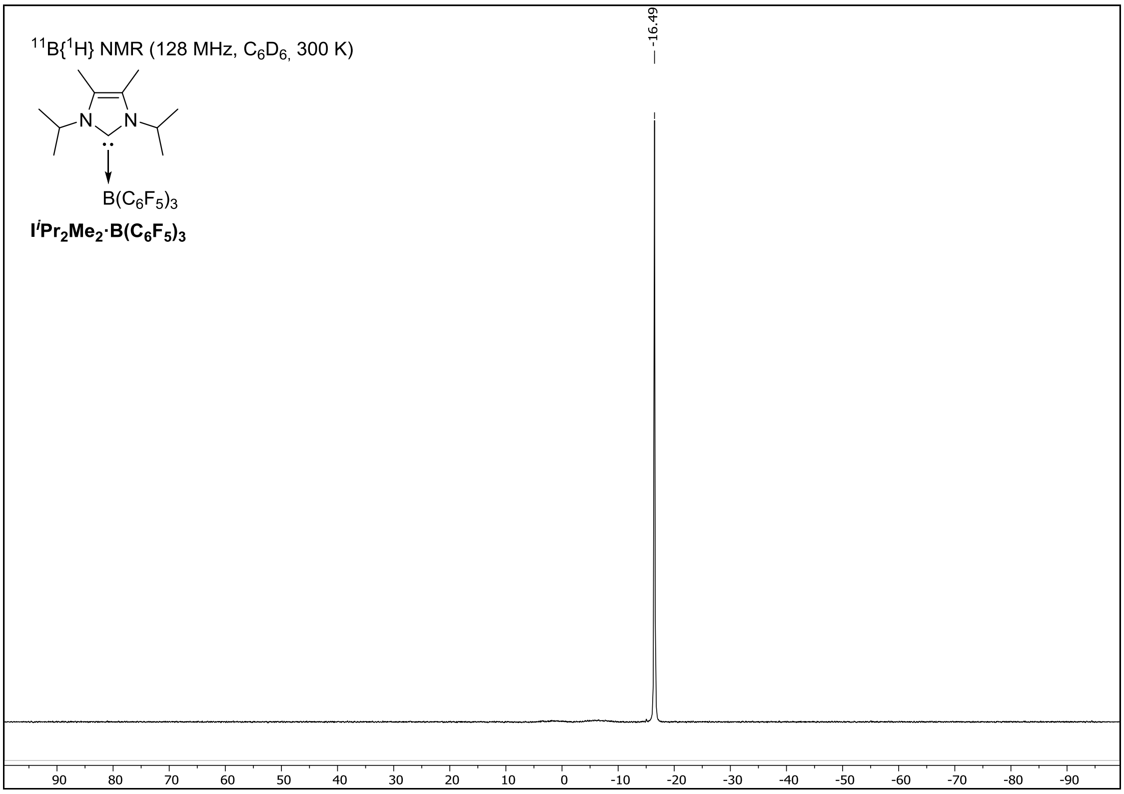


Figure S60. ^{11}B{^{1}H} NMR spectrum of I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ at 300 K.

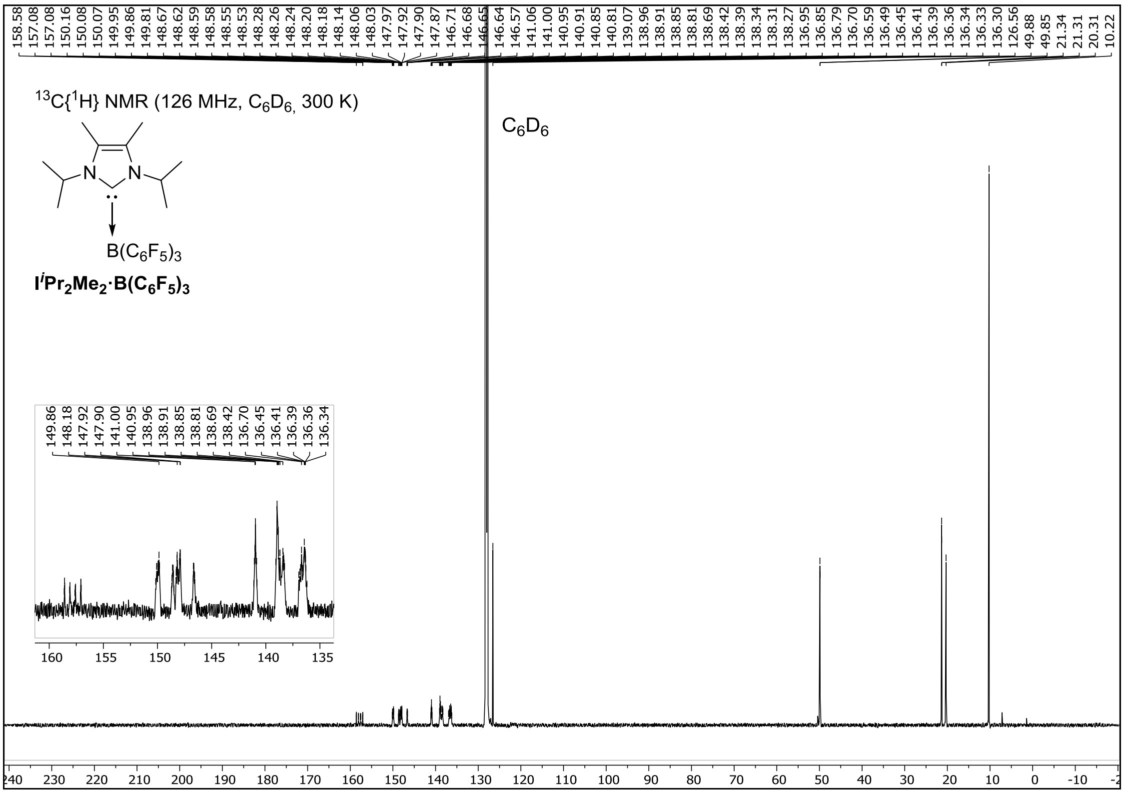


Figure S61. ^{13}C{^{1}H} NMR spectrum of I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ at 300 K.

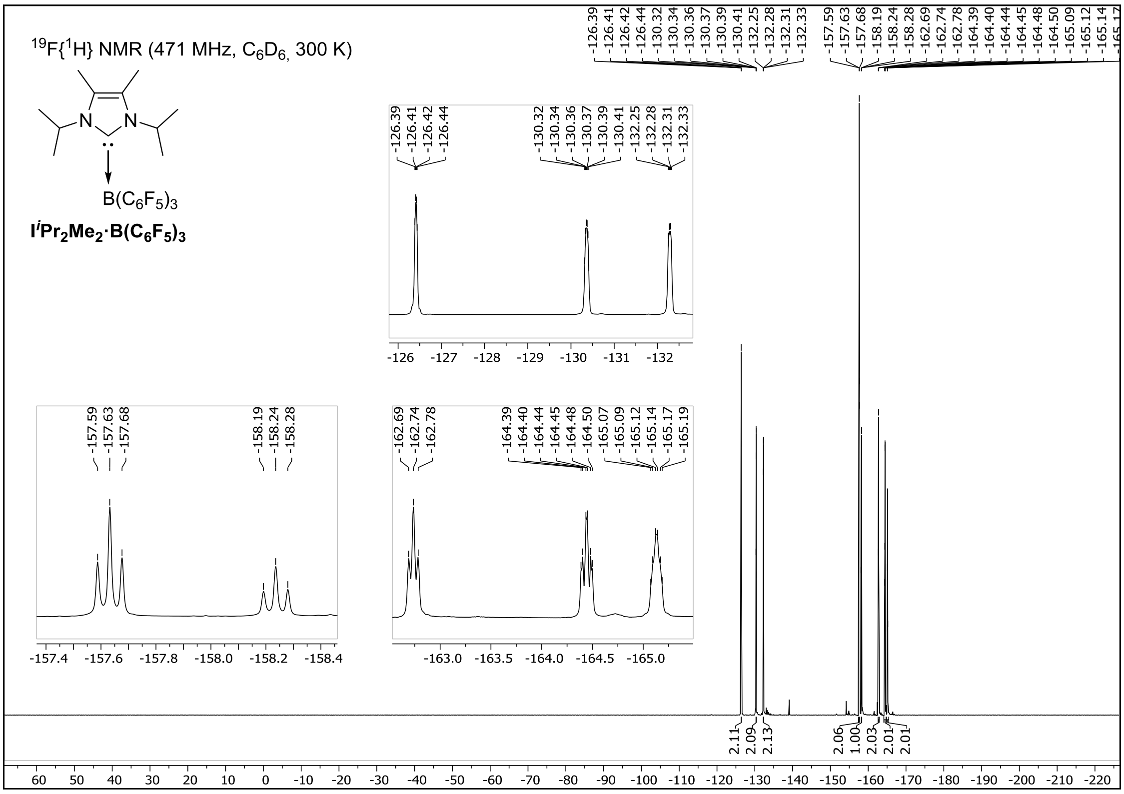


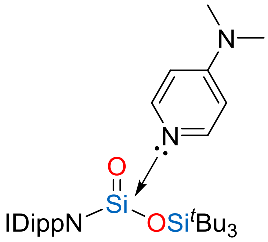
Figure S62. ^{19}F{^{1}H} NMR spectrum of I^{i}Pr$_2$Me$_2$·B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ at 300 K.

In contrast to the reaction of **13b** with BCF, treatment of **13b** with BPh$_3$ resulted in the clean formation of a sole product, but again two equivalents and additionally elevated temperatures were required to achieve full conversion. In analogy to a recent report by Iwamoto *et al.* on the rearrangement of a BCF-stabilized silanone to an aryl(boryloxy)silane, the intermediary formed Lewis acid-stabilized silanoic ester derivative (IDippN)(^{t}Bu$_3$SiO)Si=O(BPh$_3$) isomerized to aryl(boryloxy)silane **14**.[S10]

A *J. Young* PTFE valve NMR tube was charged with a mixture of (IDippN)(^{t}Bu$_3$SiO)Si=O(I^{i}Pr$_2$Me$_2$) (**13b**) (20.0 mg, 23.7 µmol, 1.0 eq.) and BPh$_3$ (11.5 mg, 47.5 µmol, 2.0 eq.) in C$_6$D$_6$ (0.5 mL). Since no reaction was detected after 1 d at room-temperature *via* ^{1}H NMR spectroscopy, we exposed the sample to elevated temperatures. Full conversion of **13b** to aryl(boryloxy)silane **14** with concomitant formation of I^{i}Pr$_2$Me$_2$·BPh$_3$ was observed after 2 h at 130 °C.

Note: It was not possible to separate aryl(boryloxy)silane **14** from the I^{i}Pr$_2$Me$_2$·BPh$_3$ adduct, however pure **14** can be obtained *via* exposure of the *in-situ* generated (IDippN)(^{t}Bu$_3$SiO)Si(BPh$_3$) (**12b**) to N$_2$O (*vide infra*).

1.17 Synthesis of (IDippN)(^{t}Bu$_3$SiO)Si=O(DMAP) (13c)



13c

C$_{46}$H$_{73}$N$_5$O$_2$Si$_2$

784.29 g/mol

Benzene (5 mL) was added to a mixture of silylene **1** (100 mg, 155 µmol, 1.0 eq.) and DMAP (18.9 mg, 155 µmol, 1.0 eq.) in a thick-walled, pressurizeable Schlenk flask. The solution was then frozen in liquid nitrogen, degassed and exposed to N$_2$O (1 bar) at room-temperature. Subsequently, the reaction mixture was stirred for 30 min. Removal of all volatiles *in vacuo* provided the DMAP-stabilized silanoic ester derivative **13c** as a colorless solid (121 mg, 155 µmol, quantitative yield). DMAP adduct **13c** is completely stable as a solid and in solution at ambient temperature.

Note: At high temperatures isomerization to an unidentified product was observed, but the reaction is extremely slow (only ~10% conversion after 10 days at 135 °C) and thus was not further studied. However, ^{1}H NMR spectroscopy indicated aromatic C–H bond activation of DMAP.

m.p.: 253-254 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 8.37 (d, ^3J = 6.8 Hz, 2H, *o*-C$_{\mathrm{DMAP}}\underline{H}$), 7.20–7.17 (m, 3H, C$_{\mathrm{ar}}\underline{H}$), 7.15–7.14 (m, 2H, C$_{\mathrm{ar}}\underline{H}$), 7.14–7.13 (m, 1H, C$_{\mathrm{ar}}\underline{H}$), 6.48 (d, ^3J = 6.8 Hz, 2H, *m*-C$_{\mathrm{DMAP}}\underline{H}$), 6.02 (s, 2H, NC$\underline{H}$), 3.48 (sept, ^3J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.36 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.59 (s, 6H, N(C*H*$_3$)$_2$), 1.55 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.52 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.17 (s, 27H, C(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 156.0 (*p*-*C*$_{\mathrm{DMAP}}$), 148.2 (*o*-*C*$_{\mathrm{ar}}$), 148.1 (*o*-*C*$_{\mathrm{ar}}$), 145.7 (*o*-*C*$_{\mathrm{DMAP}}$H), 143.2 (N*C*N), 135.7 (*ipso*-*C*$_{\mathrm{ar}}$), 129.2 (*p*-*C*$_{\mathrm{ar}}$H), 124.0 (*m*-*C*$_{\mathrm{ar}}$H), 123.8 (*m*-*C*$_{\mathrm{ar}}$H), 114.5 (N*C*H), 106.3 (*m*-*C*$_{\mathrm{DMAP}}$H), 39.4 (N(*C*H$_3$)$_2$), 30.7 (C(*C*H$_3$)$_3$), 29.2 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 23.4 (*C*(CH$_3$)$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 0.6 (*Si*^{t}Bu$_3$), –87.8 (*central Si*).

Anal. Calcd. [%] for C$_{46}$H$_{73}$N$_5$O$_2$Si$_2$: C, 70.45; H, 9.38; N, 8.93. Found [%]: C, 70.14; H, 9.55; N, 8.66.

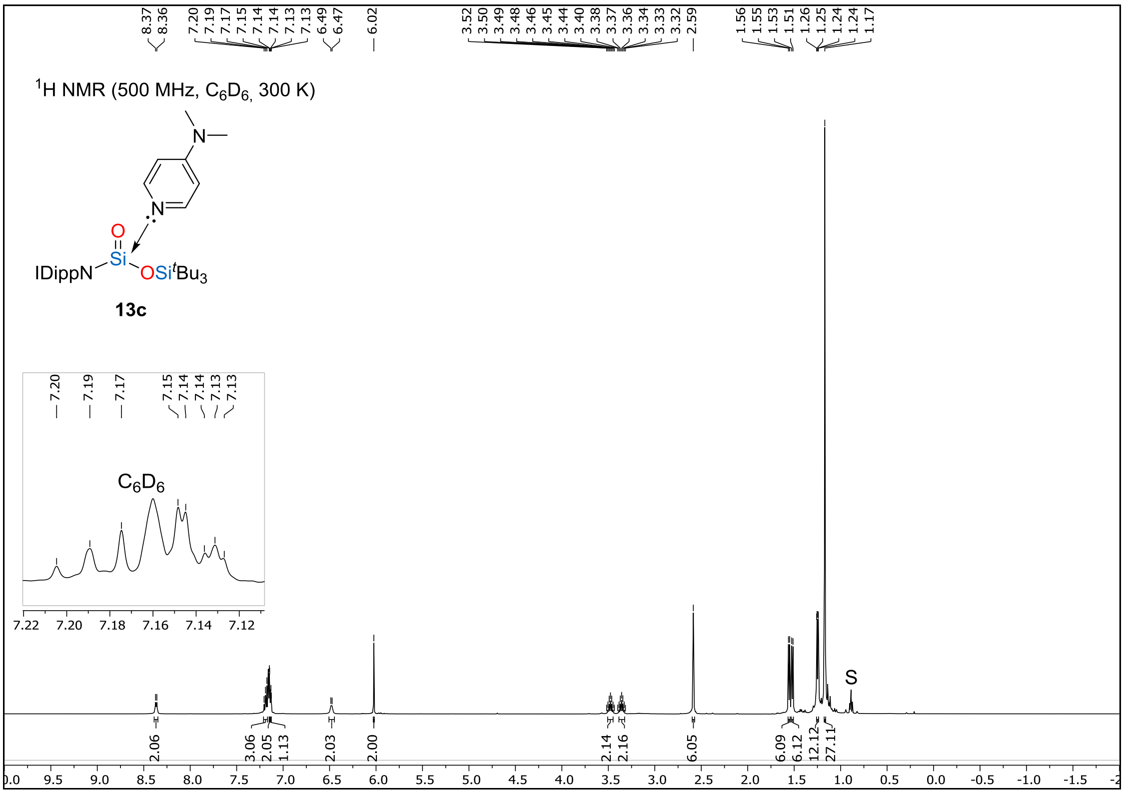


Figure S63. ^{1}H NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(DMAP) (**13c**) in C$_6$D$_6$ at 300 K. Residual *n*-hexane (from starting material) is labeled with S.

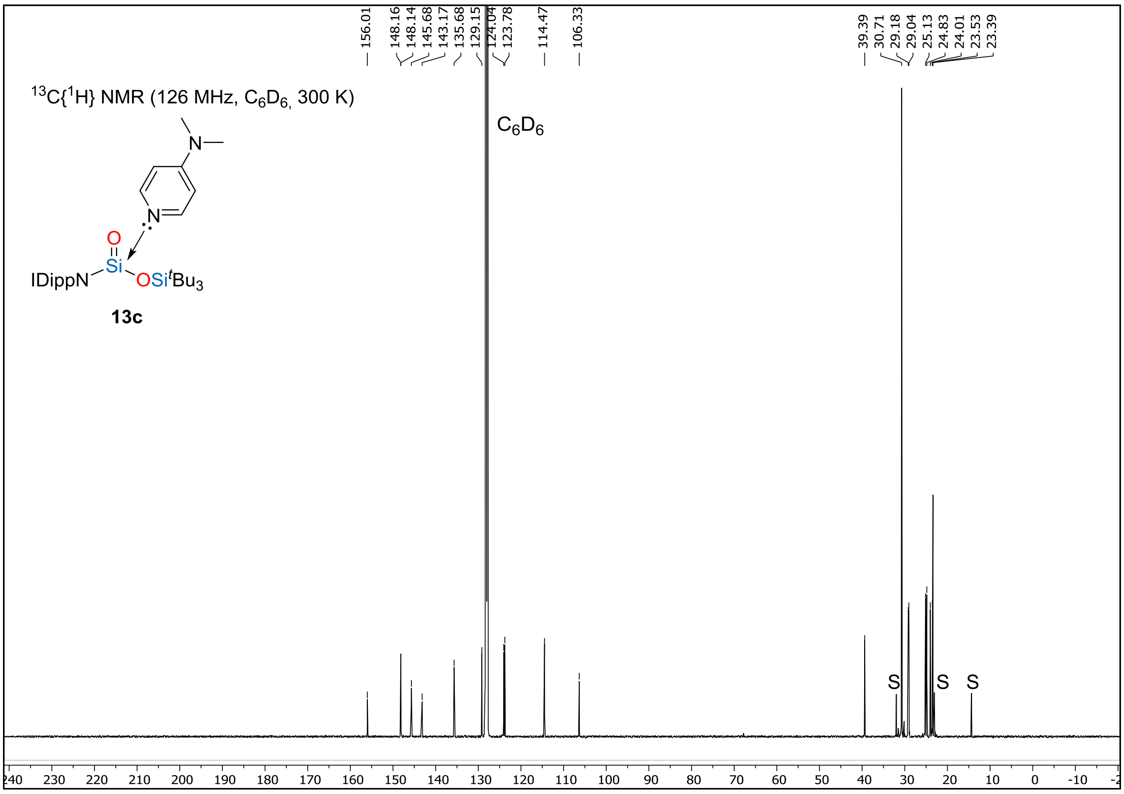


Figure S64. $^{13}C\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(DMAP) (**13c**) in C_6D_6 at 300 K. Residual *n*-hexane is labeled with S.

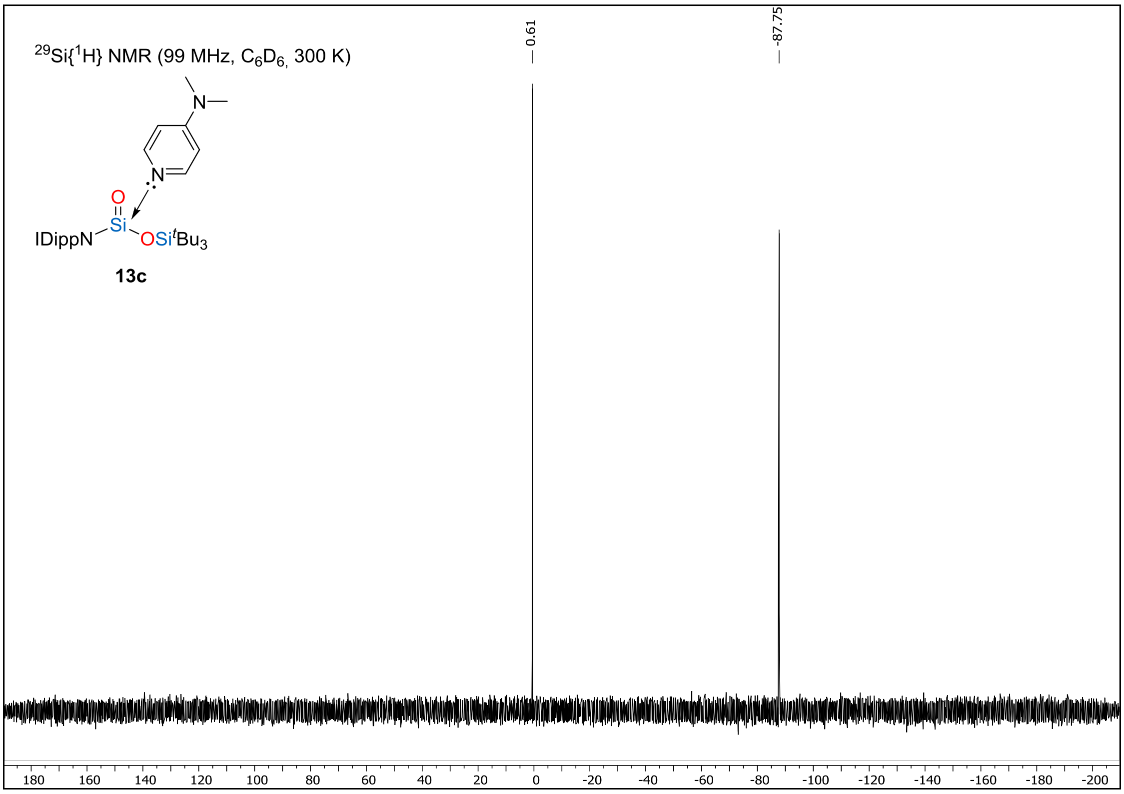
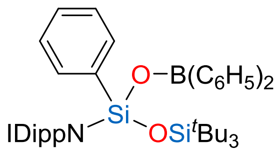


Figure S65. $^{29}Si\{^1H\}$ NMR spectrum of (IDippN)(^{t}Bu$_3$SiO)Si=O(DMAP) (**13c**) in C_6D_6 at 300 K.

1.18 Synthesis of Aryl(boryloxy)silane 14



14

$C_{57}H_{78}BN_3O_2Si_2$

904.25 g/mol

Benzene (5 mL) was added to a mixture of silylene **1** (100 mg, 155 µmol, 1.0 eq.) and BPh_3 (37.5 mg, 155 µmol, 1.0 eq.) in a thick-walled, pressurizeable Schlenk flask. The resulting reaction mixture was stirred for 30 min. An observed color change to yellow indicated formation of the silylene-borane adduct (IDippN)(^{t}Bu$_3$SiO)Si(BPh$_3$) (**12b**). The solution was then frozen in liquid nitrogen, degassed and exposed to N_2O (1 bar) at room-temperature. Subsequently, the reaction mixture was stirred for 30 min. Removal of all volatiles *in vacuo* provided aryl(boryloxy)silane **14** as a colorless solid (140 mg, 155 µmol, quantitative yield). Compound **14** is completely stable as a solid and in solution at ambient and elevated temperatures (≤130 °C).

m.p.: 188-189 °C (decomposition; color change from colorless to yellow).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 7.86–7.84 (m, 4H, $C_{ar}\underline{H}$), 7.66–7.64 (m, 2H, $C_{ar}\underline{H}$), 7.34–7.23 (m, 8H, $C_{ar}\underline{H}$), 7.14–7.12 (m, 2H, $C_{ar}\underline{H}$), 7.00–6.99 (m, 3H, $C_{ar}\underline{H}$), 6.92–6.90 (m, 2H, $C_{ar}\underline{H}$), 6.04 (s, 2H, $NC\underline{H}$), 3.29 (sept, ^3J = 6.9 Hz, 2H, $C\underline{H}(CH_3)_2$), 3.19 (sept, ^3J = 6.9 Hz, 2H, $C\underline{H}(CH_3)_2$), 1.21 (d, ^3J = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.12 (d, ^3J = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.09 (d, ^3J = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.09 (d, ^3J = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 0.88 (s, 27H, $C(C\underline{H}_3)_3$).

^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 300 K): In an inexplicable way no ^{11}B NMR resonance could be detected for compound **14**.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 147.3 (*o*-$\underline{C}_{Dipp}$), 147.2 (*o*-$\underline{C}_{Dipp}$), 144.8 ($N\underline{C}N$), 139.4 ($\underline{C}_{ar}$), 137.1 ($\underline{C}_{ar}H$), 135.7 ($\underline{C}_{ar}H$), 134.7 (*ipso*-$\underline{C}_{Dipp}$), 130.4 ($\underline{C}_{ar}H$), 129.8 ($\underline{C}_{ar}H$), 128.9 (*p*-$\underline{C}_{Dipp}H$), 127.3 ($\underline{C}_{ar}H$), 127.1 ($\underline{C}_{ar}H$), 124.4 (*m*-$\underline{C}_{Dipp}H$), 124.3 (*m*-$\underline{C}_{Dipp}H$), 115.6 ($N\underline{C}H$), 30.4 ($C(\underline{C}H_3)_3$), 29.1 ($\underline{C}H(CH_3)_2$), 29.0 ($\underline{C}H(CH_3)_2$), 26.1 ($CH(\underline{C}H_3)_2$), 26.1 ($CH(\underline{C}H_3)_2$), 22.9 ($\underline{C}(CH_3)_3$), 22.8 ($CH(\underline{C}H_3)_2$), 22.3 ($CH(\underline{C}H_3)_2$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 300 K): δ [ppm] = 2.5 ($\underline{Si}^t$Bu$_3$), –81.4 ($\underline{Si}$O).

Anal. Calcd. [%] for $C_{57}H_{78}BN_3O_2Si_2$: C, 75.71; H, 8.69; N, 4.65. Found [%]: C, 75.62; H, 8.63; N, 4.67.

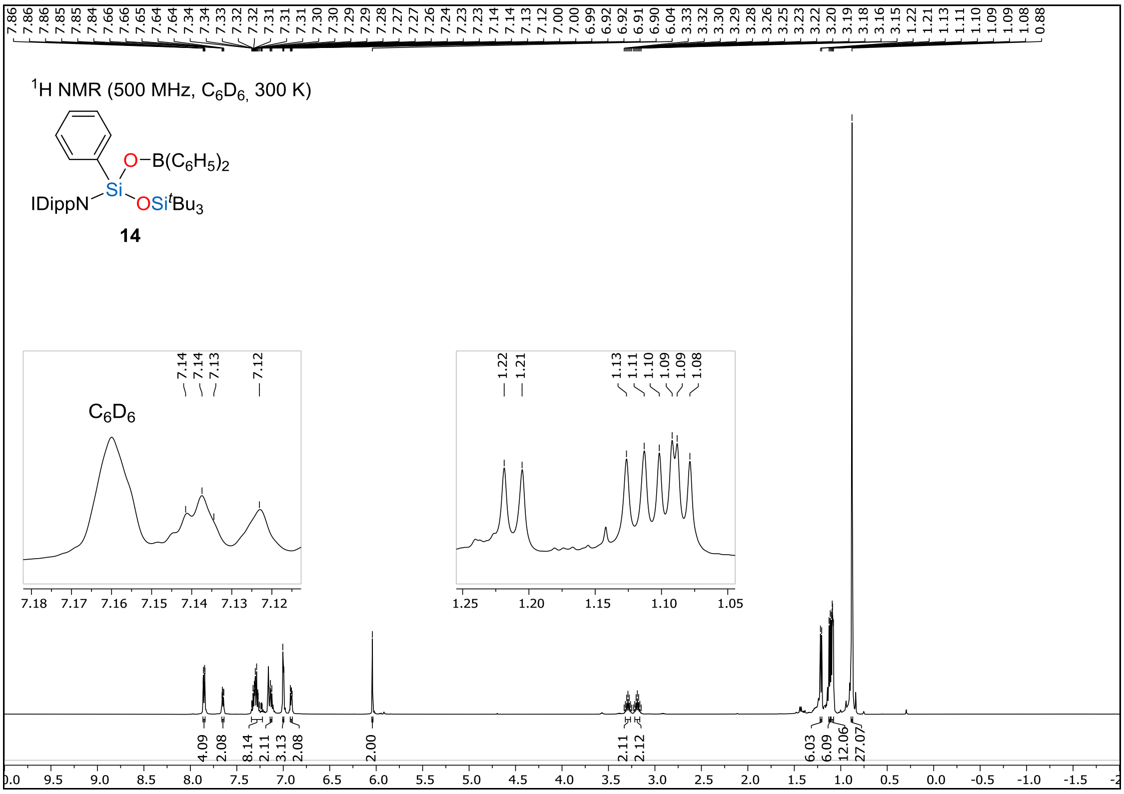


Figure S66. ^{1}H NMR spectrum of aryl(boryloxy)silane **14** in C_6D_6 at 300 K.

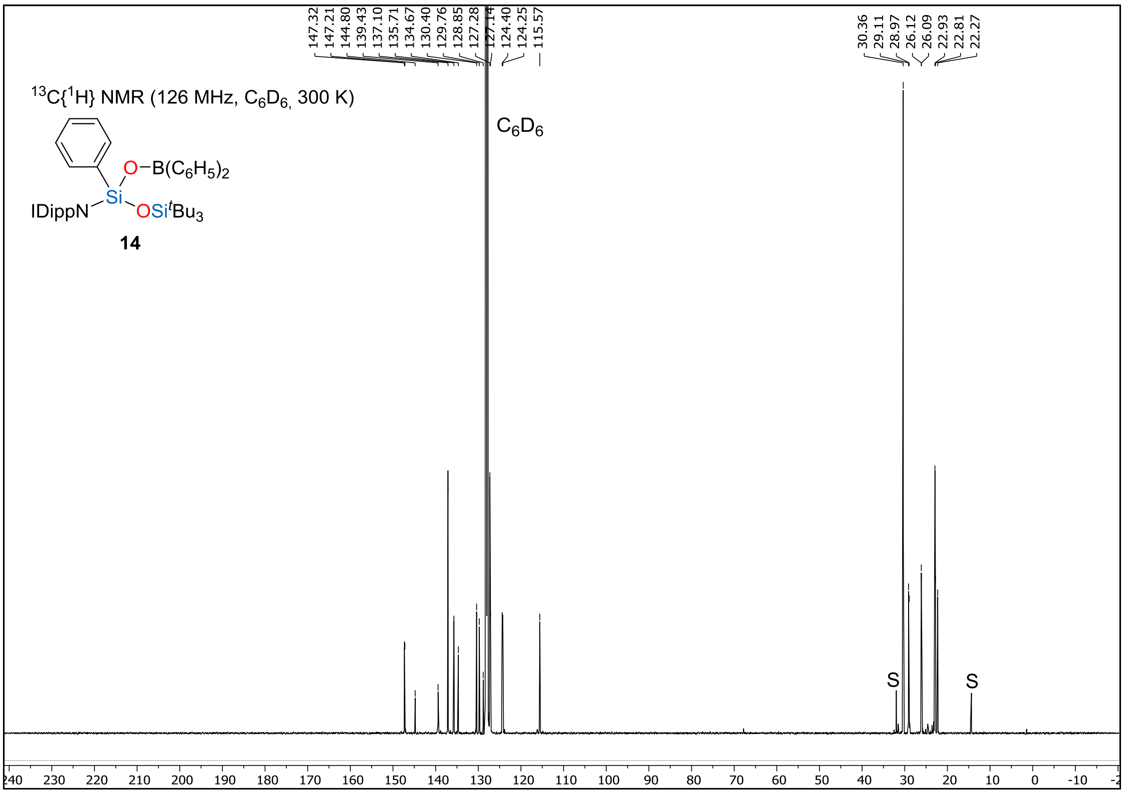


Figure S67. ^{13}C{^{1}H} NMR spectrum of aryl(boryloxy)silane **14** in C_6D_6 at 300 K. Residual *n*-hexane is labeled with S.

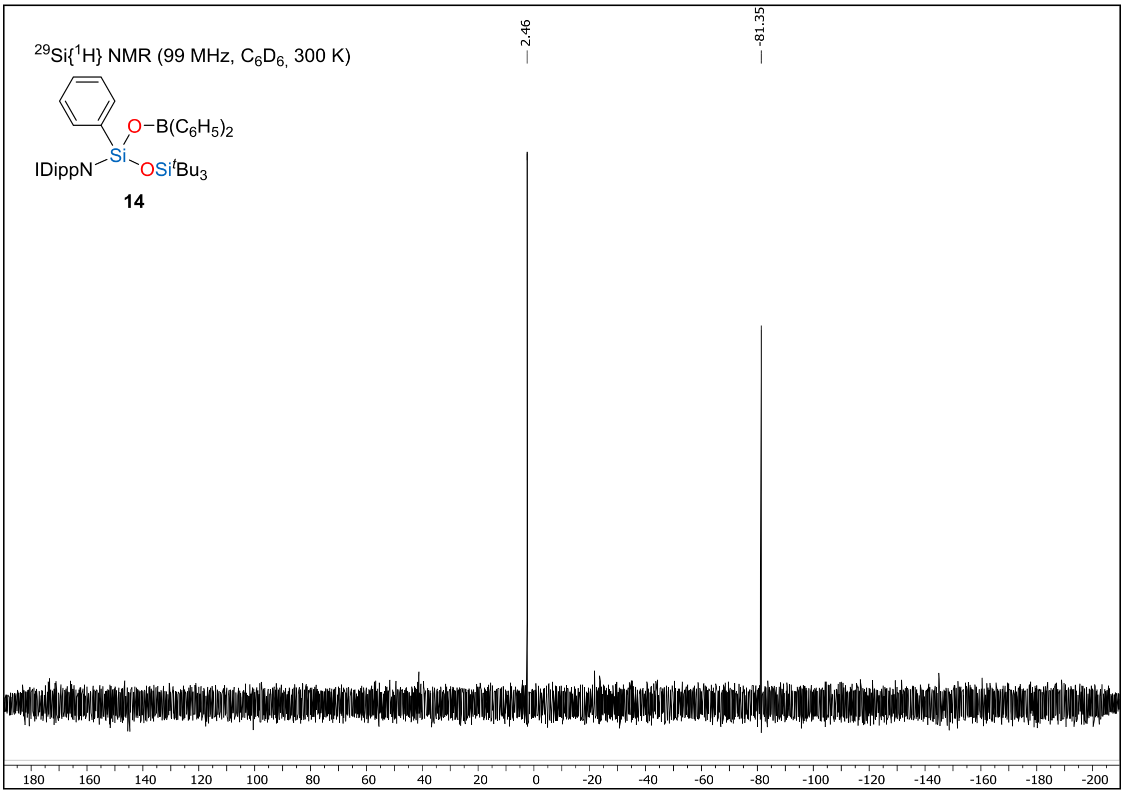


Figure S68. ^{29}Si{^{1}H} NMR spectrum of aryl(boryloxy)silane **14** in C_6D_6 at 300 K.

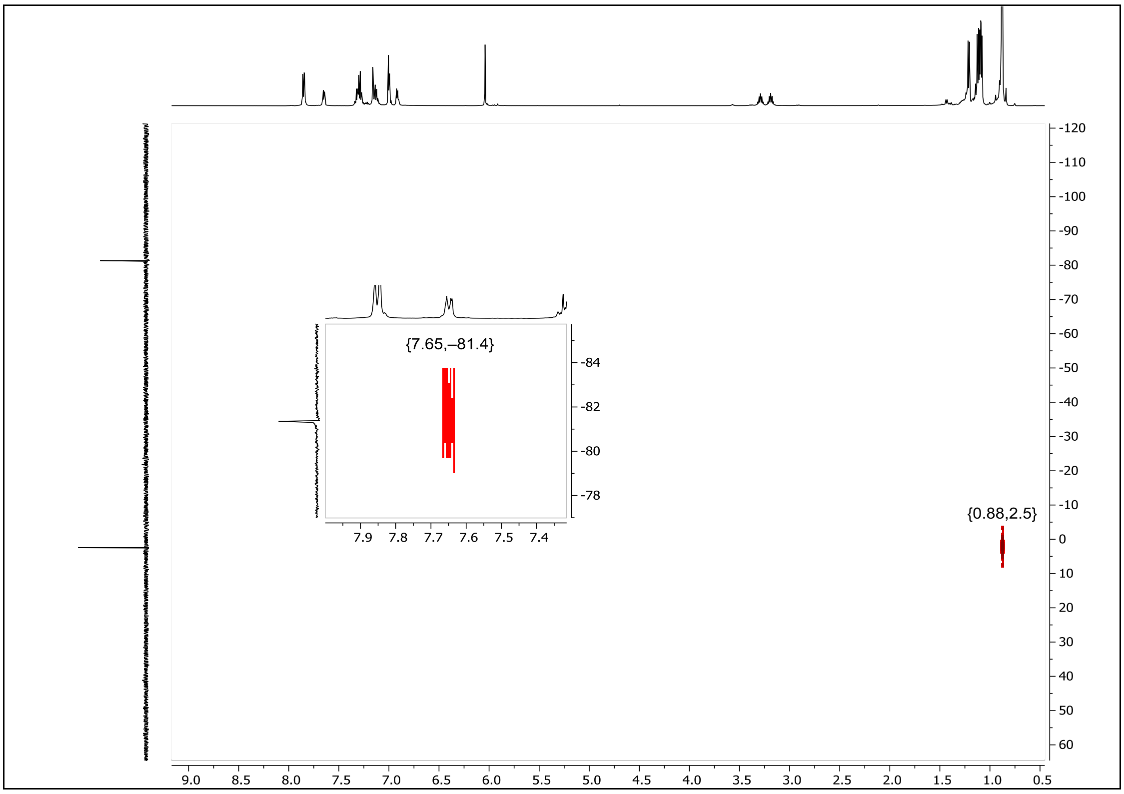


Figure S69. ^{1}H/^{29}Si HMBC NMR spectrum of aryl(boryloxy)silane **14** in C_6D_6 at 300 K.

2. X-ray Crystallographic Data

General Information

The X-ray intensity data of **3** was collected on an X-ray single crystal diffractometer equipped with a CMOS detector (*Bruker Photon-100*), a rotating anode (*Bruker TXS*) with MoKα radiation (λ = 0.71073 Å) and a *Helios* mirror optic by using the *APEX III* software package.[S11] The X-ray intensity data of **6**, **7**, **9**, **11**, **12a** and **13a** were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (*Bruker Photon-100*), an IMS microsource with MoKα radiation (λ = 0.71073 Å) and a *Helios* mirror optic by using the *APEX III* software package.[S11] The measurements were performed on single crystals coated with the perfluorinated ether *Fomblin® Y*. The crystals were fixed on the top of a microsampler, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using *SAINT*.[S12] Absorption corrections, including odd and even ordered spherical harmonics were performed using *SADABS*.[S12] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the *APEX III* software in conjunction with *SHELXL-2014*[S13] and *SHELXLE*.[S14] All H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\cdot U_{\mathrm{eq}}(\mathrm{C})$. Full-matrix least-squares refinements were carried out by minimizing $\Delta w(F_o^2-F_c^2)^2$ with *SHELXL-97*[S15] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S16] The images of the crystal structures were generated by *Mercury*.[S17] The CCDC numbers CCDC-1983560 (**13a**), CCDC-1983561 (**3**), CCDC-1983562 (**12a**), CCDC-1983563 (**11**), CCDC-1983564 (**7**), CCDC-1983565 (**6**), and CCDC-1983579 (**9**) contain the supplementary crystallographic data for the structures. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* https://www.ccdc.cam.ac.uk/structures/.

Single Crystal X-ray Structure Determinations

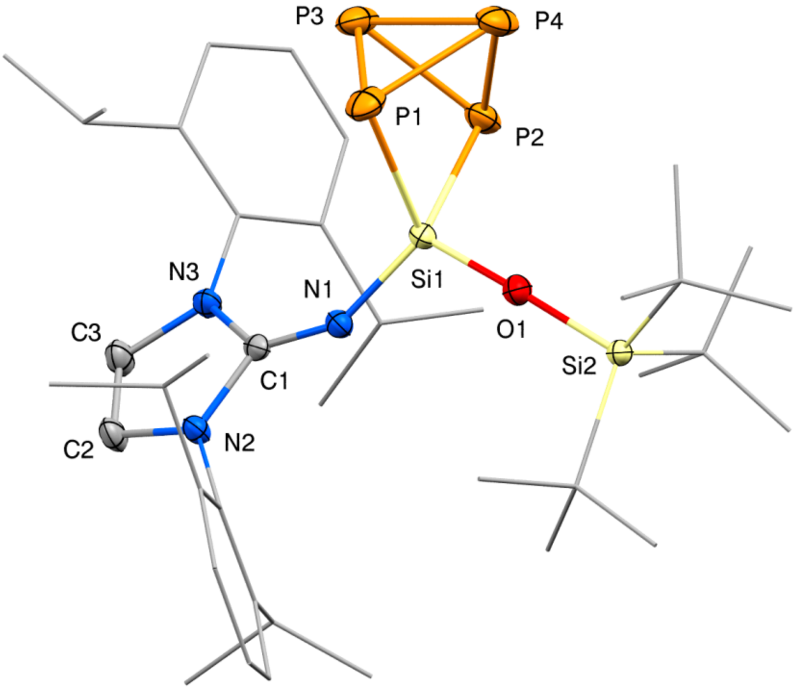


Figure S70. Molecular structure of **3** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.617(1), Si1–P1 2.256(1), Si1–P2 2.270(1), Si1–N1 1.657(1), N1–C1 1.280(2), Si2–O1 1.639(1), P1–P3 2.241(1), P1–P4 2.227(1), P2–P3 2.222(1), P2–P4 2.360(1), P3–P4 2.162(1); N1–Si1–O1 109.1(1), Si1–N1–C1 149.0(1), Si1–O1–Si2 166.7(1), P1–Si1–P2 86.7(1).

Table S1. Crystal data and structure refinement for compound **3**.

Chemical formula	$C_{39}H_{63}N_3OP_4Si_2$	
Formula weight	770.02 g/mol	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal size	0.112 × 0.179 × 0.242 mm	
Crystal habit	clear colorless fragment	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 18.2755(11) Å	α = 90(5)°
	b = 10.7417(7) Å	β = 90.804(2)°
	c = 22.0169(15) Å	γ = 90(5)°
Volume	4321.7(5) $Å^3$	
Z	4	
Density (calculated)	1.183 g/cm^3	
Absorption coefficient	0.263 mm^{-1}	
F(000)	1656	
Diffractometer	Bruker D8 Venture	
Radiation source	TXS rotating anode, Mo	
Theta range for data collection	2.23 to 25.35°	
Index ranges	–22<=h<=22, –12<=k<=12, –26<=l<=26	
Reflections collected	79231	
Independent reflections	7897 [R(int) = 0.0367]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7260 and 0.7452	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	Σ w($F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7897 / 489 / 39	
Goodness-of-fit on F^2	1.040	
Final R indices	6837 data; I>2σ(I)	R1 = 0.0348, wR2 = 0.0866
	all data	R1 = 0.0427, wR2 = 0.0917
Weighting scheme	w = 1/[$\sigma^2(F_o^2) + (0.0398P)^2 + 4.0672P$]	
	where P = ($F_o^2 + 2F_c^2$)/3	
Largest diff. peak and hole	0.646 and –0.457 $eÅ^{-3}$	
R.M.S. deviation from mean	0.052 $eÅ^{-3}$	

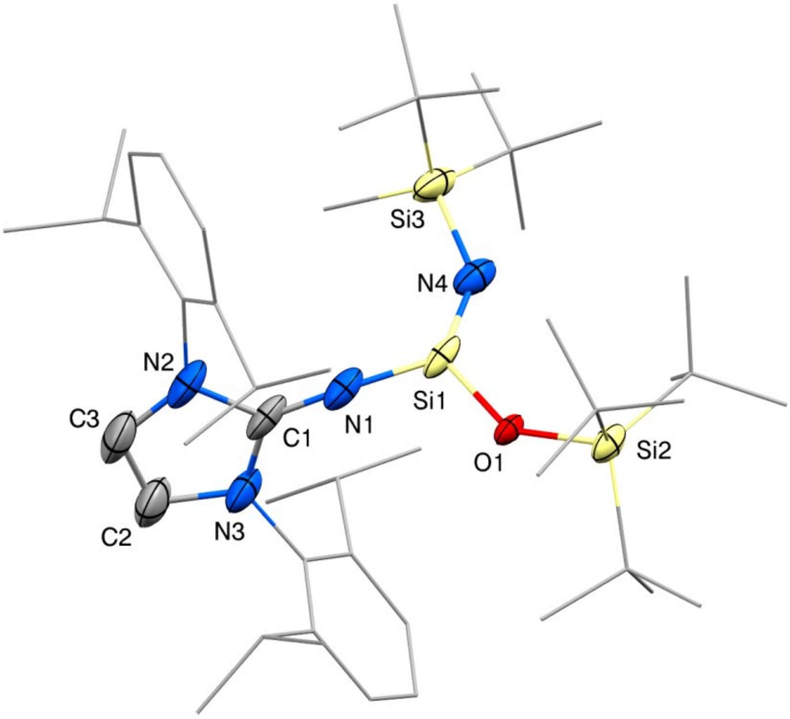


Figure S71. Molecular structure of **6** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.618(3), Si1–N1 1.623(2), Si1–N4 1.573(2), N1–C1 1.275(4), Si2–O1 1.651(5), N4–Si3 1.693(2); N1–Si1–O1 107.0(1), N1–Si1–N4 130.7(1), N4–Si1–O1 122.2(1), Si1–N1–C1 153.9(2), Si1–O1–Si2 143.6(3), Si1–N4–Si3 139.4(1).

Table S2. Crystal data and structure refinement for compound **6**.

Chemical formula	$C_{48}H_{84}N_4OSi_3$	
Formula weight	817.48 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 × 0.181 × 0.290 mm	
Crystal habit	clear colorless fragment	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.2094(8) Å	$\alpha = 90°$
	b = 18.7067(12) Å	$\beta = 91.315(2)°$
	c = 20.3570(13) Å	$\gamma = 90°$
Volume	5029.0(5) $Å^3$	
Z	4	
Density (calculated)	1.080 g/cm^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	1800	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.18 to 25.35°	
Index ranges	–15<=h<=15, –22<=k<=22, –24<=l<=24	
Reflections collected	182252	
Independent reflections	9197 [R(int) = 0.0728]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7209 and 0.7450	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9197 / 818 / 549	
Goodness-of-fit on F^2	1.125	
Final R indices	8326 data; $I>2\sigma(I)$	R1 = 0.0662, wR2 = 0.1423
	all data	R1 = 0.0730, wR2 = 0.1462
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 5.7268P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.379 and –0.381 $eÅ^{-3}$	
R.M.S. deviation from mean	0.044 $eÅ^{-3}$	

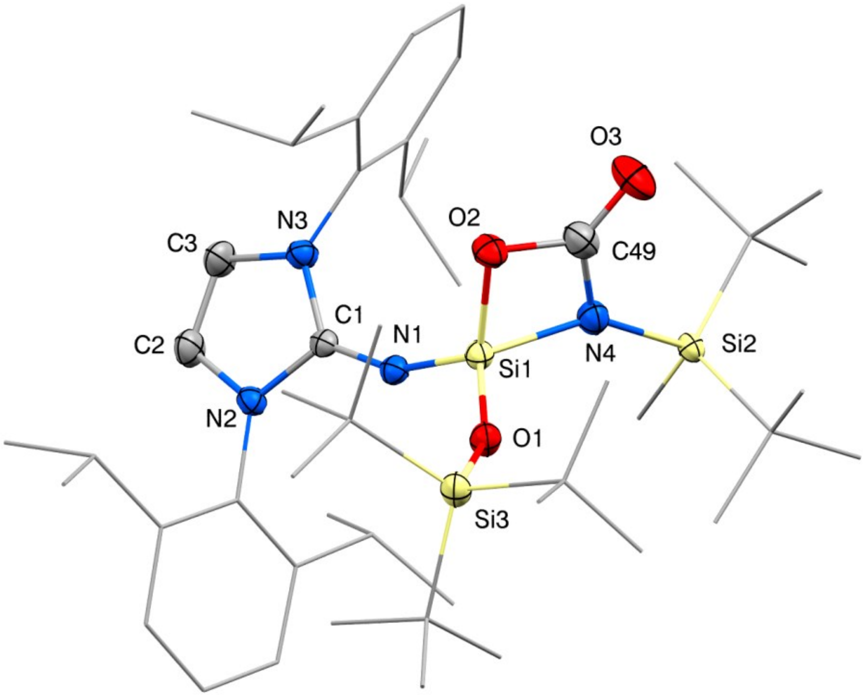


Figure S72. Molecular structure of **7** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.613(1), Si1–O2 1.699(1), Si1–N1 1.620(1), Si1–N4 1.764(2), N1–C1 1.286(2), Si2–N4 1.787(2), Si3–O1 1.656(1), N4–C49 1.399(3), O2–C49 1.387(2), C49–O3 1.195(2); N1–Si1–O1 112.7(1), Si1–N1–C1 154.8(1), Si1–O1–Si3 152.5(1), O2–Si1–N4 78.6(1), Si1–O2–C49 90.2(1), Si1–N4–C49 87.2(1), O2–C49–N4 103.9(2).

Table S3. Crystal data and structure refinement for compound **7**.

Chemical formula	$C_{49}H_{84}N_4O_3Si_3$	
Formula weight	861.49 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.236 × 0.297 × 0.373 mm	
Crystal habit	clear colorless fragment	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.5215(6) Å	α = 90°
	b = 17.5358(8) Å	β = 93.012(2)°
	c = 22.5862(10) Å	γ = 90°
Volume	5348.0(4) $Å^3$	
Z	4	
Density (calculated)	1.070 g/cm^3	
Absorption coefficient	0.129 mm^{-1}	
F(000)	1888	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.14 to 25.35°	
Index ranges	–16<=h<=16, –21<=k<=21, –27<=l<=27	
Reflections collected	102378	
Independent reflections	9793 [R(int) = 0.0444]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.6620 and 0.7453	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9197 / 654 / 102	
Goodness-of-fit on F^2	1.055	
Final R indices	8633 data; I>2σ(I)	R1 = 0.0452, wR2 = 0.1149
	all data	R1 = 0.0523, wR2 = 0.1208
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 4.5428P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	1.091 and –0.396 $eÅ^{-3}$	
R.M.S. deviation from mean	0.046 $eÅ^{-3}$	

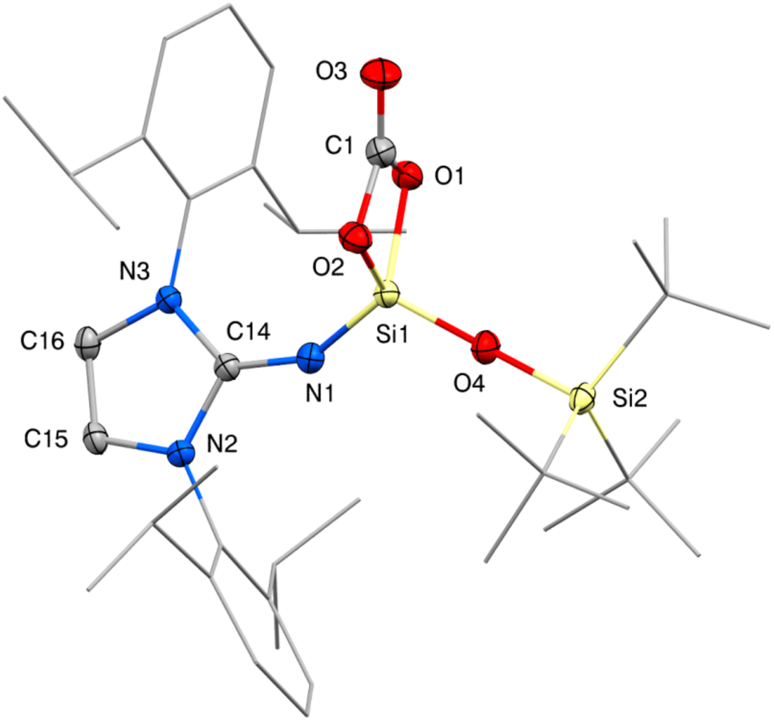


Figure S73. Molecular structure of **9** with ellipsoids set at 50% probability (one out of two independent molecules in the asymmetric unit). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.712(2), Si1–O2 1.712(2), Si1–O4 1.585(2), Si1–N1 1.609(2), N1–C14 1.299(3), Si2–O4 1.648(2), O1–C1 1.360(3), O2–C1 1.362(3), C1–O3 1.196(3); N1–Si1–O4 112.5(1), O1–Si1–O2 78.0(1), Si1–N1–C14 150.0(2), Si1–O4–Si2 165.1(1), O1–C1–O2 104.6(2).

Table S4. Crystal data and structure refinement for compound **9**.

Chemical formula	$C_{40}H_{63}N_3O_4Si_2$	
Formula weight	706.13 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.466 × 0.495 × 0.585 mm	
Crystal habit	clear colorless fragment	
Crystal system	orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 16.804(2) Å	$\alpha = 90°$
	b = 14.1855(18) Å	$\beta = 90°$
	c = 34.372(4) Å	$\gamma = 90°$
Volume	8193.4(17) $Å^3$	
Z	8	
Density (calculated)	1.145 g/cm^3	
Absorption coefficient	0.128 mm^{-1}	
F(000)	3072	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	1.97 to 25.70°	
Index ranges	–20<=h<=20, –17<=k<=17, –41<=l<=41	
Reflections collected	323173	
Independent reflections	15568 [R(int) = 0.0428]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7017 and 0.7460	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	15568 / 918 / 1	
Goodness-of-fit on F^2	1.084	
Final R indices	15207 data; $I>2\sigma(I)$	R1 = 0.0290, wR2 = 0.0722
	all data	R1 = 0.0301, wR2 = 0.0729
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 2.9609P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.258 and –0.220 $eÅ^{-3}$	
R.M.S. deviation from mean	0.035 $eÅ^{-3}$	

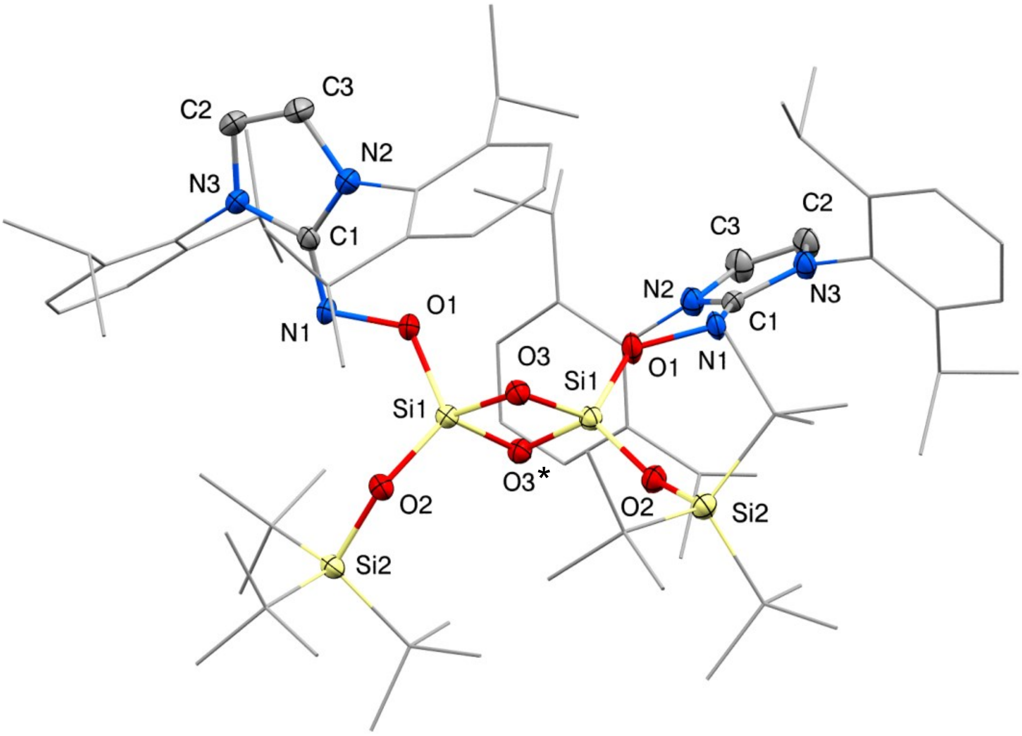


Figure S74. Molecular structure of **11** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.623(2), Si1–O2 1.601(2), Si1–O3 1.659(2), Si1–O3* 1.673(2), N1–O1 1.449(3), N1–C1 1.305(2), Si2–O2 1.682(2); O1–Si1–O2 114.5(1), O3–Si1–O3* 88.8(1), Si1–O2–Si2 146.7(1), Si1–O1–N1 125.3(1), O1–N1–C1 106.7(1).

Table S5. Crystal data and structure refinement for compound **11**.

Chemical formula	$C_{78}H_{126}N_6O_6Si_4$	
Formula weight	1356.24 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.331 × 0.394 × 0.411 mm	
Crystal habit	clear colorless fragment	
Crystal system	monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 26.09(2) Å	$\alpha = 90°$
	b = 13.509(11) Å	$\beta = 107.52(4)°$
	c = 27.21(3) Å	$\gamma = 90°$
Volume	9148(14) $Å^3$	
Z	4	
Density (calculated)	0.985 g/cm^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	2960	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.49 to 25.39°	
Index ranges	$-31<=h<=31, -16<=k<=16, -32<=l<=32$	
Reflections collected	156212	
Independent reflections	8320 [R(int) = 0.0668]	
Coverage of independent reflections	98.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.6421 and 0.7831	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8320 / 0 / 441	
Goodness-of-fit on F^2	1.054	
Final R indices	7002 data; $I>2\sigma(I)$	R1 = 0.0484, wR2 = 0.1120
	all data	R1 = 0.0606, wR2 = 0.1177
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 14.5084P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.387 and -0.340 $eÅ^{-3}$	
R.M.S. deviation from mean	0.045 $eÅ^{-3}$	

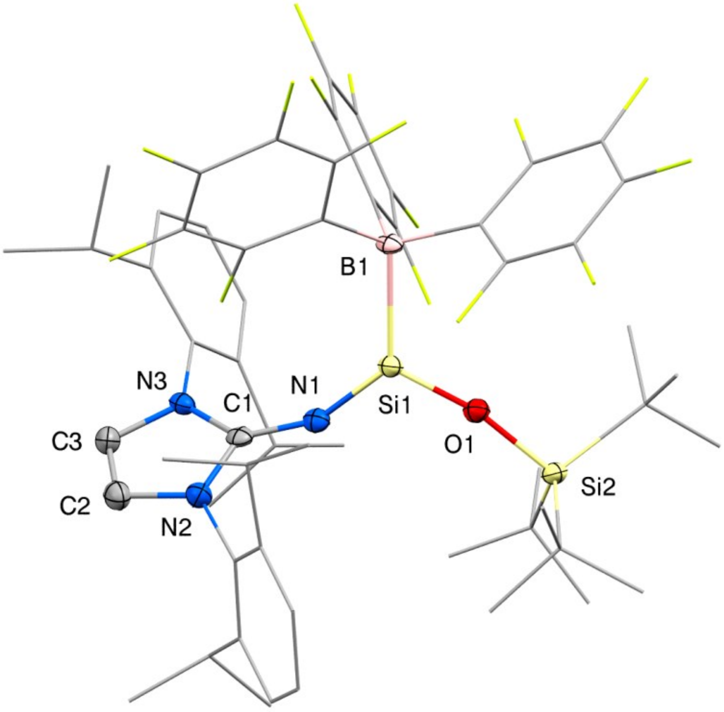


Figure S75. Molecular structure of **12a** with ellipsoids set at 50% probability. Hydrogen atoms and cocrystallized toluene are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–B1 2.086(3), Si1–O1 1.598(2), Si1–N1 1.621(2), N1–C1 1.296(4), Si2–O1 1.676(2); B1–Si1–O1 116.5(1), B1–Si1–N1 128.9(1) N1–Si1–O1 114.2(1), Si1–N1–C1 150.8(3), Si1–O1–Si2 164.7(2).

Table S6. Crystal data and structure refinement for compound **12a**.

Chemical formula	$C_{57}H_{63}BF_{15}N_3OSi_2$	
Formula weight	1158.11 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.184 × 0.200 × 0.254 mm	
Crystal habit	clear colorless fragment	
Crystal system	hexagonal	
Space group	P 65	
Unit cell dimensions	a = 21.6490(15) Å	$\alpha = 90°$
	b = 21.6490(15) Å	$\beta = 90°$
	c = 24.0739(18) Å	$\gamma = 120°$
Volume	9771.3(18) $Å^3$	
Z	6	
Density (calculated)	1.275 g/cm^3	
Absorption coefficient	0.139 mm^{-1}	
F(000)	3912	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	1.88 to 25.68°	
Index ranges	–26<=h<=26, –26<=k<=26, –29<=l<=29	
Reflections collected	482120	
Independent reflections	12388 [R(int) = 0.0715]	
Coverage of independent reflections	100%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8224 and 0.7438	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/5 (Sheldrick, 2016)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	12388 / 911 / 208	
Goodness-of-fit on F^2	1.096	
Final R indices	12202 data; $I>2\sigma(I)$	R1 = 0.0387, wR2 = 0.0983
	all data	R1 = 0.0393, wR2 = 0.0987
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 4.9609P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.363 and –0.315 $eÅ^{-3}$	
R.M.S. deviation from mean	0.045 $eÅ^{-3}$	

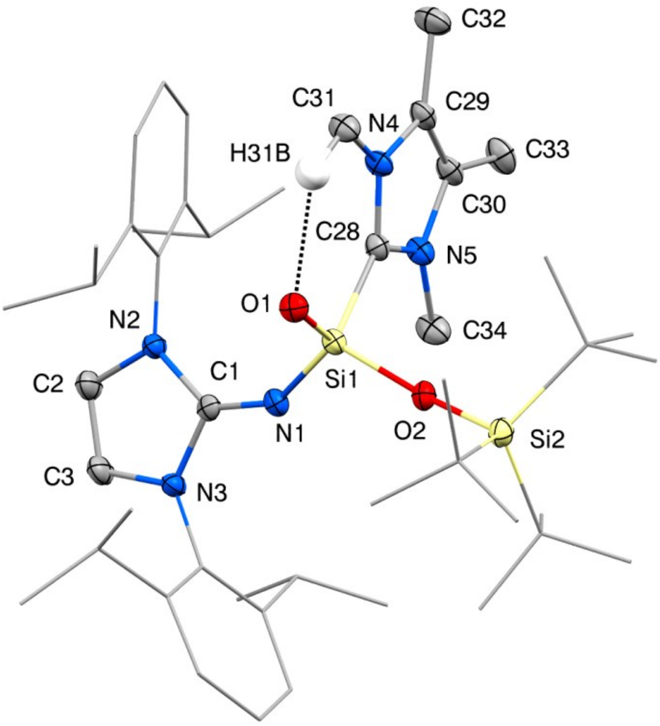


Figure S76. Molecular structure of **13a** with ellipsoids set at 50% probability. Hydrogen atoms, except for H31B involved in hydrogen bonding (visualized by the dashed line), and cocrystallized toluene are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.554(2), Si1–O2 1.653(2), Si1–C28 1.935(3), Si1–N1 1.684(2), N1–C1 1.271(3), Si2–O2 1.626(2); N1–Si1–O2 104.2(1), O1–Si1–O2 115.5(1), Si1–N1–C1 146.1(2), Si1–O2–Si2 151.6(1).

Table S7. Crystal data and structure refinement for compound **13a**.

Chemical formula	$C_{46}H_{75}N_5O_2Si_2$	
Formula weight	786.31 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.103 × 0.127 × 0.274 mm	
Crystal habit	clear colorless fragment	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 12.3466(7) Å	$\alpha = 90°$
	b = 16.0952(9) Å	$\beta = 90°$
	c = 26.4133(15) Å	$\gamma = 90°$
Volume	5248.9(5) Å^3	
Z	4	
Density (calculated)	1.112 g/cm^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	1920	
Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.217 to 25.349°	
Index ranges	–14<=h<=14, –19<=k<=19, –31<=l<=31	
Reflections collected	55732	
Independent reflections	9603 [R(int) = 0.0416]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7153 and 0.7450	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9603 / 581 / 0	
Goodness-of-fit on F^2	1.066	
Final R indices	8376 data; $I>2\sigma(I)$	R1 = 0.0366, wR2 = 0.0814
	all data	R1 = 0.0493, wR2 = 0.0896
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.2905P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.210 and –0.218 eÅ^{-3}	
R.M.S. deviation from mean	0.041 eÅ^{-3}	

Preliminary Measurement Results as Structural Evidence

For the following two cases the crystal quality was unfortunately not sufficient for a complete refinement process and subsequent analysis of the structural data. Nevertheless, the preliminary structures obtained serve as evidence for the respective molecular structures in the solid state.

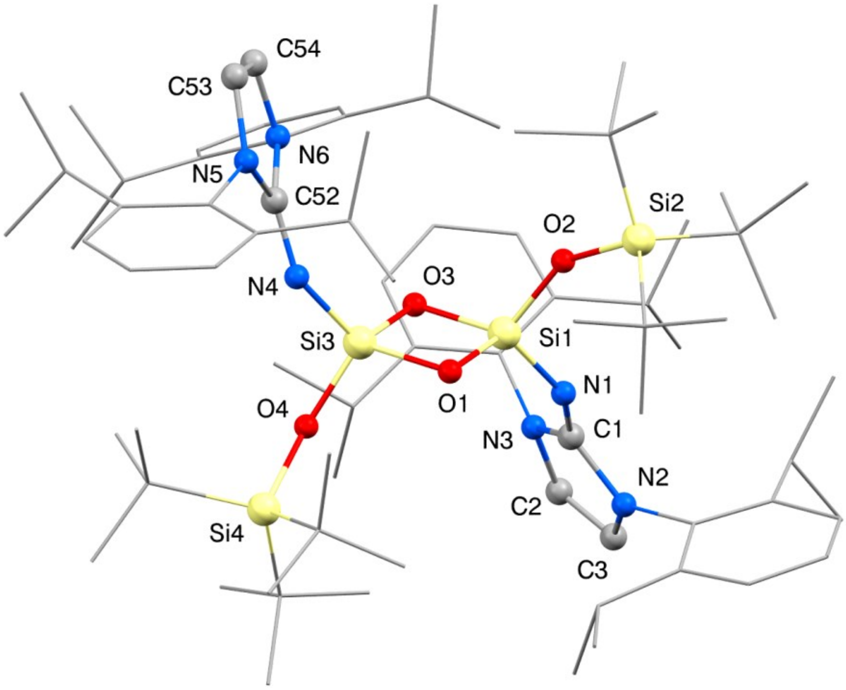


Figure S77. Molecular structure of *trans*-Cyclodisiloxane [(IDippN)(^{t}Bu$_3$SiO)Si=O]$_2$ (**10a**) in the ball-and-stick representation. Hydrogen atoms are omitted for clarity.

Table S8. Structural information for compound **10a**.

Chemical formula	$C_{78}H_{126}N_6O_4Si_4$	
Formula weight	1324.24 g/mol	
Crystal habit	clear colorless fragment	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 14.221(8) Å	α = 89.052(6)°
	b = 14.221(8) Å	β = 89.052(6)°
	c = 45.50(2) Å	γ = 68.589°
Volume	8563.96 Å^3	

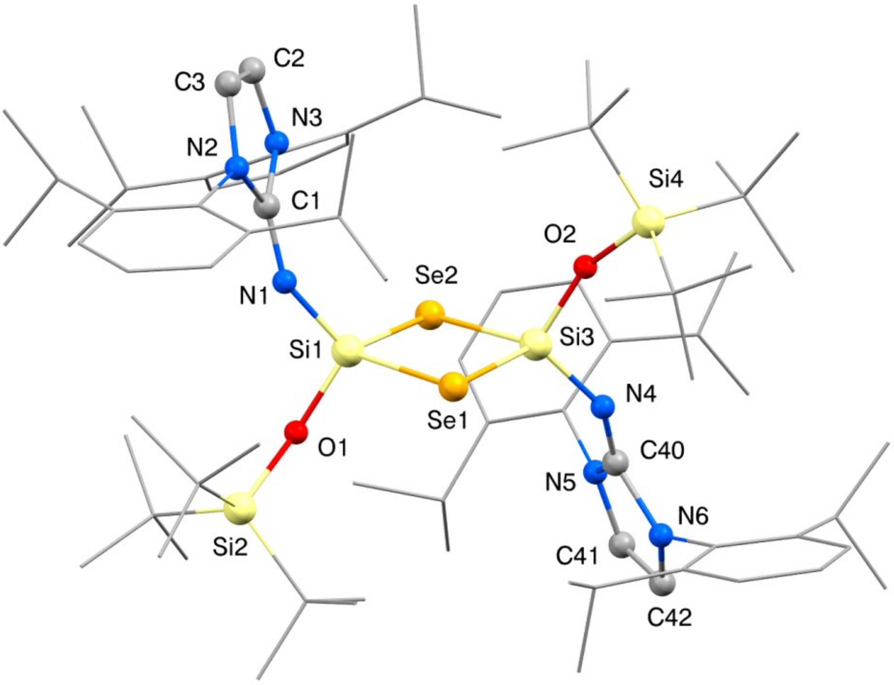


Figure S78. Molecular structure of Silicon Diselenide $[(\mathrm{IDippN})(^{t}\mathrm{Bu}_3\mathrm{SiO})\mathrm{Si{=}Se}]_2$ (**10b**) in the ball-and-stick representation. Hydrogen atoms are omitted for clarity.

Table S9. Structural information for compound **10b**.

Chemical formula	$C_{78}H_{126}N_6O_2Se_2Si_4$	
Formula weight	1450.17 g/mol	
Crystal habit	clear colorless fragment	
Crystal system	triclinic	
Space group	$P\,\bar{1}$	
Unit cell dimensions	a = 13.118(13) Å	α = 72.28(3)°
	b = 16.152(16) Å	β = 75.65(3)°
	c = 20.61(2) Å	γ = 76.26(3)°
Volume	3967.27 $Å^3$	

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