Supporting Information

A Striking Mode of Activation of Carbon Disulfide with a Cooperative Bis(silylene)

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1. **General Considerations**

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or inside a MBraun glovebox. Solvents were dried by standard methods and freshly distilled prior to use. The NMR spectra were recorded on Bruker spectrometers Avance II 500 (\(^1\)H, 500.1 MHz; \(^{13}\)C\{\(^1\)H\}, 125.8 MHz; \(^{29}\)Si\{\(^1\)H\}, 99.0 MHz), 400 (\(^1\)H, 400.1 MHz; \(^{13}\)C\{\(^1\)H\}, 99.4 MHz; \(^{29}\)Si\{\(^1\)H\}, 79.5 MHz) and 200 (\(^1\)H, 200.1 MHz; \(^{13}\)C\{\(^1\)H\}, 50.3 MHz) with residual solvent signals as internal reference (\(^1\)H NMR: benzene-\(d_6\), 7.16 ppm, THF-\(d_8\), 1.73 ppm, 3.58 ppm; \(^{13}\)C\{\(^1\)H\} NMR: benzene-\(d_6\) 128.1 ppm, THF-\(d_8\), 25.3 ppm, 67.2 ppm). High-resolution ESI (electrospray ionization) or APCI (atmospheric-pressure chemical ionization) mass spectra were measured on an Orbitrap LTQ XL by Thermo Scientific. Elemental analyses were recorded in a Thermo Flash EA 1112 Organic elemental analyzed and HEKAtech EuroEA 3000. The ATR/IR spectroscopic measurements were recorded on a Thermo Fisher Scientific Spectrometer inside a glovebox. Vibration modes are given in wavenumbers (cm\(^{-1}\)). Abbreviations: (vs) very strong, (s) strong, (m) middle, (w) weak and (br) broad. Commercially available reagents were purchased from Sigma-Aldrich, Acros, Alfa-Assar or abcr and used as received. The starting materials 1,4-bis(2-bromophenyl) benzene,\(^1\) \(N,N'\)-di-tert-butyl(phenylimidinato)-chlorosilylene,\(^2\) phenyl-substituted NHSi,\(^3\) 2-(methylamino)pyridine-substituted silylene 5,\(^4\) 2-bromobiphenyl and 1,4-terphenyl bridged bis(silylene)\(^5\) 1 were prepared according to reported literature procedures.
Molecule Index of new Compounds:

Single crystal X-ray structure analyses: Crystals were mounted on a glas capillary in perfluorinated oil and measured in a cold N$_2$ flow. The data for all compounds were collected on an Agilent Technologies SuperNova device (single source) at 150 K (Cu-K$_\alpha$ radiation, $\lambda = 1.54184$ Å). All structures were solved by direct methods and refined on F$^2$ with the SHELX-97 software. All atoms except for hydrogen atoms were calculated and considered isotopically according to a riding model. Compound 6 crystallized with free yet severely disordered diethylether molecules in the asymmetric unit which were treated using the SQUEEZE routine in PLATON. The CCDC numbers CCDC 2116268 (S2), 2099865 (2Mes), 2116269 (3), 2099867 (4), 2099866 (6), 2099868 (8), 2099864 (9) and 2116270 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
2. Syntheses and Characterization

2.1 Compound S1

To a suspension of mesityl lithium (8.00 g, 63.5 mmol, 1.0 equiv.) in Et₂O (200 ml) \(N,N'-\text{Di-}t\text{-butylcarbodiimid}\) (12.5 ml, 10.0 g, 64.8 mmol, 1.0 equiv.) was added at \(-78 \degree C\). After warming up to room temperature, the reaction was stirred for 3 h. The suspension was added to a solution of trichlorosilane (9.80 ml, 13.2 g, 97.1 mmol, 1.5 equiv) in Et₂O (50 ml) at \(-78 \degree C\). The mixture was warmed up to room temperature and stirred overnight. The solution was filtered and concentrated and then kept at at \(-30 \degree C\) overnight affording S1 as colorless crystals suitable for X-ray diffraction analysis. After removal of Et₂O by filtration, compound S1 was obtained in 51% (12.0 g, 32.1 mmol) isolated yields. Compound S1 is not air stable and generally good soluble in organic solvents except for \(\alpha\)hexane.

\(^1H\) NMR (500.1 MHz, \(C_6D_6\), 298 K): \(\delta/\text{ppm} = 6.80\) (s, 1H, SiH), 6.46 (d, \(^4J_{HH} = 0.5\) Hz, 2H, \(H_A\)), 2.07 (s, 6H, o-MesCH₃), 1.96 (s, 3H, p-MesCH₃), 1.16 (s, 18H, 2x NC(CH₃)₃).

\(^{13}C\{^1H\}\) NMR (50.3 MHz, \(C_6D_6\), 298 K): \(\delta/\text{ppm} = 171.2\) (s, \(C_{\text{quart}},\) NCN), 140.3 (s, p-MesCCH₃, \(C_{\text{quart}}\)), 135.8 (s, 2x o-MesCCH₃, \(C_{\text{quart}}\)), 130.0 (s, \(C_{\text{quart}},\) \(C_{Ar}\), 128.7 (s, \(C_{Ar}\)), 128.6 (s, \(C_{Ar}\)), 55.8 (s, \(C_{\text{quart}},\) 2x NC(CH₃)₃), 30.7 (s, 9x NC(CH₃)₃), 21.3 (s, p-MesCCH₃), 20.7 (s, 2x o-MesCCH₃).

\(^{1}H,^{29}Si\{^1H\}\) NMR (99.0 MHz, \(C_6D_6\), 298 K, optimized for \(J = 200\) Hz): \(\delta/\text{ppm} = 6.79/–96.7\) (SiH).

2.2 Synthesis of compound S2

A mixture of S1 (12 g, 32.1 mmol, 1.0 equiv.) and LiHMDS-Et₂O (7.80 g, 32.1 mmol, 1.0 equiv.) was dissolved in cold Et₂O (200 ml) and cooled to \(-78 \degree C\). After warming up to room temperature, the mixture was stirred for 1 h turning from yellow to orange. After the solution was filtered and concentrated under reduced pressure, the solution was kept at \(-30 \degree C\) overnight affording S2 as colorless crystals. Et₂O was removed by filtration and the title compound S2 was obtained in 75% (8.5 g, 32.4 mmol) isolated yields. Single crystals suitable for X-ray diffraction analysis of S2 were obtained from a concentrated solution in Et₂O at \(-30 \degree C\). Compound S2 is not air stable and generally good soluble in organic solvents except for \(\alpha\)hexane.

\(^1H\) NMR (500.1 MHz, \(C_6D_6\), 298 K): \(\delta/\text{ppm} = 6.52\) (s, 1H, \(H_A\)), 6.49 (s, 1H, \(H_A\)), 2.26 (s, 3H, MesCH₃), 2.02 (s, 3H, MesCH₃), 1.97 (s, 3H, MesCH₃), 1.12 (s, 18H, NC(CH₃)).

\(^{13}C\{^1H\}\) NMR (125.8 MHz, \(C_6D_6\), 298 K): \(\delta/\text{ppm} = 166.9\) (s, \(C_{\text{quart}},\) NCN), 139.8
(s, C\textsubscript{qurt}, p-MesCCH\textsubscript{3}), 136.8 (s, C\textsubscript{qurt}, o-MesCCH\textsubscript{3}), 135.0 (s, C\textsubscript{qurt}, o-MesCCH\textsubscript{3}), 129.8 (s, C\textsubscript{qurt}, C\textsubscript{Ar}), 128.6 (s, C\textsubscript{Ar}), 128.5 (s, C\textsubscript{Ar}), 54.1 (s, C\textsubscript{qurt}, 2x NC(CH\textsubscript{3})\textsubscript{3}), 30.7 (s, 9x NC(CH\textsubscript{3})\textsubscript{3}), 21.1 (s, MesCH\textsubscript{3}), 21.0 (s, m-MesCH\textsubscript{3}), 20.6 (s, MesCH\textsubscript{3}).

\(^{29}\text{Si}\{^{1}\text{H}\}\text{NMR}\ (99.0\ MHz, \text{C}_6\text{D}_6, 298\ K): \delta/\text{ppm} = 18.3\ (s).

### 2.3 Compound 3

To a suspension of 2-bromobiphenyl (212 \mu l, 1.23 mmol, 1.0 equiv.) and Et\textsubscript{2}O (5 ml) at \(-78\ ^\circ\text{C}\) \(\text{^n} \text{BuLi}\ (615 \mu l, 2.0\ M\ solution\ in\ THF,\ 1.23\ mmol,\ 1.0\ equiv.)\) was added via syringe. After stirring for 30 min at room temperature, all volatiles were removed under reduced pressure. The residue was redissolved in Et\textsubscript{2}O (5 ml) and added to a solution of \(N,N\)-di-tert-butyl(mesitylamidinato) chlorosilylene S2 in Et\textsubscript{2}O (10 ml) at \(-78\ ^\circ\text{C}\). After stirring for 1 hour at room temperature, the solution was filtered and Et\textsubscript{2}O was slowly removed under reduced pressure without heating. The title compound 3 was obtained quantitatively (598 mg, 1.23 mmol) and was isolated as a crystalline orange solid. Single crystals suitable for X-ray diffraction analysis of 3 were obtained from a concentrated solution of 3 in Et\textsubscript{2}O at \(-30\ ^\circ\text{C}\). Compound 3 is not stable in solution and slowly reacts to a silane via an intramolecular C-H activation reaction. Do not heat during work-up. 3 is stable in the solid state under an inert atmosphere for months.

\(^{1}\text{H}\text{NMR}\ (500.1\ MHz, \text{C}_6\text{D}_6, 298\ K): \delta/\text{ppm} = 7.98\ (\text{dd}, \ J_{HH} = 7.3\ Hz, \ J_{IH} = 1.3\ Hz, 1\ H, H\textsubscript{Ar}), 7.82\ (\text{dd}, \ J_{HH} = 8.2\ Hz, \ J_{IH} = 1.3\ Hz, 2\ H, H\textsubscript{Ar}), 7.46\ (\text{dd}, \ J_{HH} = 7.6\ Hz, \ J_{IH} = 1.5\ Hz, 1\ H, H\textsubscript{Ar}), 7.40 - 7.37\ (m, 3\ H, H\textsubscript{Ar}), 7.31\ (\text{tt}, \ J_{HH} = 7.3\ Hz, \ J_{IH} = 1.5\ Hz, 1\ H, H\textsubscript{Ar}), 7.25 - 7.21\ (m, 3\ H, H\textsubscript{Ar}, 1\ H), 6.63\ (s, 1\ H, m-MesH), 6.53\ (s, 1\ H, m-MesH), 2.56\ (s, 3\ H, p-MesCH\textsubscript{3}), 2.06\ (s, 3\ H, p-MesCH\textsubscript{3}), 2.02\ (s, 3\ H, p-MesCH\textsubscript{3}), 1.04\ (s, 18\ H, NC(CH\textsubscript{3})\textsubscript{3}). \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\ (125.8\ MHz, \text{C}_6\text{D}_6, 298\ K): \delta/\text{ppm} = 157.3\ (s, \text{C}_{\text{qurt}}, \text{NCN}), 152.1\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}}), 146.1\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}}), 144.7\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}}), 139.1\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}}), 137.6\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}})136.7\ (s, \text{C}_{\text{qurt}}, \text{C}_{\text{Ar}}), 132.8\ (s, \text{C}_{\text{Ar}}), 131.4\ (s, \text{C}_{\text{Ar}}), 130.2\ (s, \text{C}_{\text{Ar}}), 128.8\ (s, \text{C}_{\text{Ar}}), 128.7\ (s, \text{C}_{\text{Ar}}), 128.6\ (s, \text{C}_{\text{Ar}}), 126.7\ (s, \text{C}_{\text{Ar}}), 125.8\ (s, \text{C}_{\text{Ar}}), 53.4\ (s, \text{C}_{\text{qurt}}, \text{NC}(\text{CH}\textsubscript{3})\textsubscript{3}), 30.9\ (s, \text{NC}(\text{CH}\textsubscript{3})\textsubscript{3}), 21.9\ (s, \text{MesCH}_3), 21.0\ (s, \text{MesCH}_3), 20.7\ (s, \text{MesCH}_3).

\(^{29}\text{Si}\{^{1}\text{H}\}\text{NMR}\ (79.5\ MHz, \text{C}_6\text{D}_6, 298\ K,\ \text{optimized\ for\ J} = 7\ Hz): \delta/\text{ppm} = 7.98/17.1\ (\text{SiH}_{\text{Ar}}), 7.46/17.1\ (\text{SiH}_{\text{Ar}}), 7.37/17.1\ (\text{SiH}_{\text{Ar}}), 1.04/17.1\ (\text{SiNC}(\text{CH}\textsubscript{3})\textsubscript{3}).

\textbf{S2}
2.4 Compound 1\textsuperscript{Mes}

A diethlyether suspension (10 ml) of 1,4-bis(2-bromophenyl) benzene\textsuperscript{[1]} (400 mg, 1.03 mmol, 1.0 equiv.) was cooled –78 °C and sBuLi (1.53 ml, 1.3 M in cyclohexane, 2.00 mmol, 2.0 equiv.) was added via syringe. After warming up to room temperature, the solution turned from slight yellow to a suspension containing a white precipitate. After stirring for 4 h at room temperature, the suspension was cooled to –78 °C and a solution of N,N′-di-tert-butyl(mesitylamidinato)-chlorosilylene S\textsubscript{2} (674 mg, 2.00 mmol, 2.0 equiv.) in Et\textsubscript{2}O (10 ml) was added via syringe. The cooling bath was removed and the suspension was stirred overnight to give a yellow suspension. All volatiles were removed under reduced pressure and the residue was washed with Et\textsubscript{2}O (3x 2 ml). After removal of the solvent under reduced pressure, the residue was washed with THF (2x 3 ml) under removal of the residual metathesis salt (LiCl). The product was dried under reduced pressure and 1\textsuperscript{Mes} was obtained as a yellow solid in 56 % (480 mg, 0.577 mmol) isolated yields. Single crystals suitable for X-ray diffraction analysis of 1\textsuperscript{Mes} could not be obtained after several attempts. 1\textsuperscript{Mes} is not air stable and not soluble in C\textsubscript{6}D\textsubscript{6} and THF-d\textsubscript{8}. NMR date was recorded in the solid state.

\textsuperscript{13}C\{\textsuperscript{1}H\} CP/MAS-NMR (10 kHz, 298 K): δ/ppm = 159.3 (s, C\textsubscript{quart}, NCN), 150.5 (s, C\textsubscript{Ar}), 146.2 (s, C\textsubscript{Ar}), 141.6 (s, C\textsubscript{Ar}), 139.2 (s, C\textsubscript{Ar}), 137.6 (s, C\textsubscript{Ar}), 136.3 (s, C\textsubscript{Ar}), 133.5 (s, C\textsubscript{Ar}), 131.5 (s, C\textsubscript{Ar}), 129.9 (s, C\textsubscript{Ar}), 127.9 (s, C\textsubscript{Ar}), 125.4 (s, C\textsubscript{Ar}), 53.7 (s, C\textsubscript{quart}, 4x NC(CH\textsubscript{3})\textsubscript{3}), 31.7 (s, 4x NC(CH\textsubscript{3})\textsubscript{3}), 22.4 .3 (s, 2x o-MesCH\textsubscript{3}), 20.1 (s, p-MesCH\textsubscript{3}). \textsuperscript{29}Si\{\textsuperscript{1}H\} CP/MAS NMR (10 kHz, 298 K): δ/ppm = 16.5 (s, 2x Si).FT-IR (ATR): ṽ (cm\textsuperscript{-1}) = 3043 (w), 2296 (w), 2921 (w), 2868 (w), 1609 (w), 1581 (w), 1453 (w), 1430 (w), 1395 (vs), 1389 (vs), 1359 (s), 1296 (w), 1267 (w), 1224 (w), 1206 (s); APCI-MS m/z (%): Calcd. for [C\textsubscript{54}H\textsubscript{70}N\textsubscript{4}Si\textsubscript{2}+H\textsuperscript{+}]: 831.5212, found: 831.5208. Melting Point: T = 297°C.

2.5 Compound 2\textsuperscript{Ph} (PhTpSi\textsubscript{2}CS\textsubscript{2})

To a solution of 1,4-terphenyl bis(silylene) 1\textsuperscript{Ph} (50 mg, 0.0669 mmol, 1.0 equiv.) in toluene (5 ml) at room temperature an excess of CS\textsubscript{2} was added via syringe. The pale yellow solution was stirred for 30 min at room temperature. After filtration the solution was concentrated under reduced pressure and kept at room temperature overnight to give compound 2\textsuperscript{Ph} as yellow crystalline material in 63 % (35 mg, 0.0425 mmol) isolated yields after filtration. Single crystals suitable for X-ray diffraction analysis could not be obtained after several attempts. Compound 2\textsuperscript{Ph} is not air stable and generally not good soluble in common organic solvents.
1H NMR (500.1 MHz, THF-δ6, 298 K): δ/ppm = 7.98 (d, 3JHH = 7.3 Hz, 1H, HAr), 7.82 (d, 3JHH = 7.2 Hz, 1H, HAr), 7.79 – 7.76 (m, 1H, HAr), 7.69 (t, 3JHH = 8.7 Hz, 2H, HAr), 7.57 – 7.48 (m, 4H, HAr), 7.47 – 7.36 (m, 4H, HAr), 7.35 – 7.28 (m, 3H, HAr), 7.23 (td, 3JHH = 7.2 Hz, 4JHH = 1.5 Hz, 1H, HAr), 7.19 (t, 3JHH = 7.2 Hz, 1H, HAr), 6.60 (dd, 3JHH = 5.8 Hz, 4JHH = 3.3 Hz, 1H, C(sp3)H), 6.35 (d, 3JHH = 5.8 Hz, 1H, C(sp3)H), 3.11 (d, 3JHH = 11.0 Hz, 1H, SiCH3), 2.23 (dd, 4JHH = 3.3 Hz, 3JHH = 11.0 Hz, 1H, (Si)(S)2 CCH3), 1.28 (d, 3JHH = 11.0 Hz, 18H, 2x NC(CH3)3, 1.00 (s, 9H, NC(CH3)3), 0.92 (s, 9H, NC(CH3)3). 13C{1H} NMR (125.8 MHz, THF-δ6, 298 K): δ/ppm = 176.8 (s, Cquart, NCN), 171.0 (s, Cquart, NCN), 152.3 (s, Cquart), 150.9 (s, Cquart), 145.1 (s, Cquart), 143.5 (s, Cquart), 140.4 (s, Cquart), 136.5 (s, Cquart, CAr), 135.3 (s, CAr), 135.1 (s, CAr), 134.6 (s, CAr), 134.1 (s, Cquart), 131.0 (s, CAr), 130.9 (s, CAr), 130.6 (s, CAr), 130.4 (s, CAr), 130.3 (s, CAr), 129.9 (s, CAr), 129.6 (s, CAr), 129.3 (s, CAr), 129.1 (s, CAr), 128.6 (s, CAr), 128.5 (s, CAr), 128.4 (s, CAr), 128.8 (s, CAr), 126.2 (s, CAr), 126.1 (s, CAr), 124.4 (s, CAr), 122.4 (s, C(sp3)H), 115.7 (s, C(sp3)H), 55.1 (s, Cquart, NC(CH3)3), 55.1 (s, Cquart, NC(CH3)3), 55.0 (s, Cquart, NC(CH3)3), 54.6 (s, Cquart, NC(CH3)3), 50.6 (s, SiC(sp3)), 43.9 (s, CquartSi2), 35.8 (s, CC(sp3)H), 33.3 (s, NC(CH3)3), 32.2 (s, NC(CH3)3), 31.8 (s, NC(CH3)3), 31.6 (s, NC(CH3)3). 29Si{1H} NMR (99.0 MHz, THF-δ6, 298 K): δ/ppm = –35.7 (s), –114.4 (s). 1H, 29Si HMQC (500.1/79.5 MHz, THF-δ6, 298 K, optimized for J = 7 Hz): δ/ppm = 3.15/–114.4 (SiCCH3), 7.38/–114.3 (SiCCHAr) 2.28/–35.7 (SiCCHAr). FT-IR (ATR): ʋ (cm⁻¹) = 3046 (w), 2969 (w), 2927 (w), 1582 (w), 1536 (w), 1494 (w), 1481 (w), 1441 (w), 1379 (vs), 1362 (vs), 1254 (w), 1199 (s), 1155 (w), 1124 (w), 1081 (w), 1047 (w), 10020 (w). ESI-MS: m/z (%): Calcd. for [C49H38N4S2Si2+H]⁺: 823.3714, found: 823.3715. Melting Point: T > 370°C (Decomposition).

2.6 Compound 2Mes (MesTpSi2CS2)

To a solution of bis(silylene) 1Mes (50 mg, 0.0601 mmol, 1.0 equiv.) in toluene (5 ml) at room temperature an excess of CS2 was added via syringe. The pale yellow solution was stirred for 30 min. The solution was filtered and concentrated under reduced pressure. The title compound crystallized overnight at room temperature. After removal of the solvent by filtration, 2Mes was obtained as yellow plates in 73 % (40 mg, 0.0441 mmol) isolated yields. Single crystals suitable for X-ray diffraction analysis of 2Mes were obtained from a concentrated solution of 2Mes in toluene at room
temperature. Compound 2\textsuperscript{Mes} is not air stable and generally not good soluble in common organic solvents.

\textbf{\textsuperscript{1}H NMR} (500.1 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta/\text{ppm} = 8.29 - 8.27\) (m, 1H, \(H_{Ar}\)), 8.23 - 8.21 (m, 1H, \(H_{Ar}\)), 7.81 - 7.80 (m, 1H, \(H_{Ar}\)), 7.73 - 7.72 (m, 1H, \(H_{Ar}\)), 7.45 - 7.38 (m, 2H, \(H_{Ar}\)), 7.35 - 7.29 (m, 2H, \(H_{Ar}\)), 6.97 (dd, \(^3J_{HH} = 5.8\) Hz, \(^4J_{HH} = 3.3\) Hz, 1H, C(sp\textsuperscript{2})H), 6.87 (d, \(^3J_{HH} = 5.8\) Hz, 1H, C(sp\textsuperscript{2})H), 6.61 (d, \(^3J_{HH} = 7.7\) Hz, 2H, \(H_{Ar}\)), 6.57 (s, 1H, \(H_{Ar}\)), 6.52 (s, 1H, \(H_{Ar}\)), 3.69 (d, \(^3J_{HH} = 10.9\) Hz, 1H, SiCH\textsubscript{3}), 2.71 (dd, \(^3J_{HH} = 11.2\) Hz, \(^4J_{HH} = 3.2\) Hz, 1H, SiCCH\textsubscript{2}), 2.52 (s, 3H, o-MesCH\textsubscript{3}), 2.42 (s, 3H, o-MesCH\textsubscript{3}), 2.37 (s, 3H, o-MesCH\textsubscript{3}), 2.31 (s, 3H, o-MesCH\textsubscript{3}), 2.01 (d, \(^4J_{HH} = 7.0\) Hz, 6H, p-MesCH\textsubscript{3}), 1.44 (s, 9H, NC(CH\textsubscript{3})\textsubscript{3}), 1.38 (s, 9H, NC(CH\textsubscript{3})\textsubscript{3}), 1.11 (s, 9H, NC(CH\textsubscript{3})\textsubscript{3}), 0.88 (s, 9H, NC(CH\textsubscript{3})\textsubscript{3}). \textbf{\textsuperscript{13}C\textsuperscript{\textsuperscript{1}H} NMR} (125.8 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta/\text{ppm} = 177.1\) (s, C\textsubscript{quart}, NCN), 169.7 (s, C\textsubscript{quart}, NCN), 151.9 (s, C\textsubscript{quart}), 150.7 (s, C\textsubscript{quart}), 144.6 (s, C\textsubscript{quart}), 143.0 (s, C\textsubscript{quart}), 140.5 (s, C\textsubscript{quart}), 139.6 (s, C\textsubscript{quart}), 139.2 (s, C\textsubscript{quart}), 136.5 (s, C\textsubscript{quart}), 136.4 (s, C\textsubscript{quart}), 136.3 (s, C\textsubscript{quart}), 134.9 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 134.8 (s, C\textsubscript{Ar}), 134.7 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 134.2 (s, C\textsubscript{Ar}), 132.6 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 130.6 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 130.4 (s, C\textsubscript{Ar}), 129.4 (s, C\textsubscript{Ar}), 129.2 (s, C\textsubscript{Ar}), 128.5 (s, C\textsubscript{Ar}), 128.3 (s, C\textsubscript{Ar}), 126.8 (s, C\textsubscript{Ar}), 126.6 (s, C\textsubscript{Ar}), 125.9 (s, C\textsubscript{Ar}), 125.2 (C(sp\textsuperscript{2})H), 122.7 (s, C\textsubscript{Ar}), 115.9 (C(sp\textsuperscript{2})H), 55.0 (s, C\textsubscript{quart}, NC(CH\textsubscript{3})\textsubscript{3}), 54.7 (s, C\textsubscript{quart}, NC(CH\textsubscript{3})\textsubscript{3}), 54.6 (s, C\textsubscript{quart}, NC(CH\textsubscript{3})\textsubscript{3}), 54.0 (s, C\textsubscript{quart}, NC(CH\textsubscript{3})\textsubscript{3}), 49.6 (s, SiC(sp\textsuperscript{3})), 42.1 (s, C\textsubscript{quart}Si\textsubscript{2}), 34.9 (s, SiC(sp\textsuperscript{3})H), 31.9 (s, NC(CH\textsubscript{3})\textsubscript{3}), 30.7 (s, NC(CH\textsubscript{3})\textsubscript{3}), 30.6 (s, NC(CH\textsubscript{3})\textsubscript{3}), 30.02 (s, NC(CH\textsubscript{3})\textsubscript{3}), 23.3 (s, MesCH\textsubscript{3}), 21.9 (s, MesCH\textsubscript{3}), 21.3 (s, MesCH\textsubscript{3}), 21.1 (s, MesCH\textsubscript{3}), 20.8 (s, MesCH\textsubscript{3}). \textbf{\textsuperscript{29}Si\textsuperscript{\textsuperscript{1}H} NMR} (99.0 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta/\text{ppm} = -36.9\) (s), -112.2. (s). \textbf{\textsuperscript{1}H,\textsuperscript{29}Si HMQC} (500.1/79.5 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K, optimized for \(J = 7\) Hz) \(\delta/\text{ppm} = 2.70/-36.9\) (SiCCH\textsubscript{3}), 8.28/-36.9 (SiCCH\textsubscript{3}), 3.68/-112.2 (SiCCH\textsubscript{3}), 8.23/-112.2 (SiCCH\textsubscript{3}). \textbf{FT-IR (ATR)}: \(\tilde{\nu} \) (cm\textsuperscript{-1}) = 3048 (w), 2995 (w), 2975 (w), 2870 (w), 1611 (w), 1583 (w), 1523 (w), 1441 (w), 1431 (w), 1389 (vs), 1360 (s), 1307 (w), 1254 (s), 1228 (s), 1217 (w), 1198 (vs), 1155 (w), 1126 (w), 1068 (s), 1047 (w), 1028 (w), 1021 (w). \textbf{Elemental Analysis} (%): Calcd. for C\textsubscript{55}H\textsubscript{70}N\textsubscript{4}S\textsubscript{2}Si\textsubscript{2}: 6.17 (N), 72.80 (C), 7.78 (H), 7.07 (S) found: 6.24 (N), 71.91 (C), 7.67 (H), 7.12 (S). The reduced C content stems from SiC formation. \textbf{ESI-MS}: m/z (%): Calcd. for [C\textsubscript{55}H\textsubscript{70}N\textsubscript{4}S\textsubscript{2}Si\textsubscript{2}+H\textsuperscript{+}]: 907.4653, found: 907.4637. \textbf{Melting Point}: T > 270 °C (Decomposition).
Table S1. Comparison of the chemical shifts of 2\textsuperscript{Ph} and 2\textsuperscript{Mes}.

| Atom | \(\delta(2\textsuperscript{Ph})\) | \(J\) [Hz] | \(\delta(2\textsuperscript{Mes})\) | \(J\) [Hz] |
|------|-----------------|----------|-----------------|----------|
| Si1  | -114.3          | -        | -112.2          | -        |
| Si2  | -35.7           | -        | -36.9           | -        |
| C1   | 43.9            | -        | 42.1            | -        |
| H\(^a\) | 3.11 (d) | \(3^2J_{HH} = 11.0\) | 3.69 (d) | \(3^2J_{HH} = 10.9\) |
| H\(^b\) | 2.23 (dd) | \(3^2J_{HH} = 11.0\) | 2.71 (dd) | \(3^2J_{HH} = 11.2\), \(4^2J_{HH} = 3.3\) |
| H\(^c\) | 6.60 (dd) | \(3^2J_{HH} = 5.8\), \(4^2J_{HH} = 3.3\) | 6.97 (dd) | \(3^2J_{HH} = 5.8\), \(4^2J_{HH} = 3.3\) |
| H\(^d\) | 6.35 (d) | \(3^2J_{HH} = 5.8\) | 6.87 (d) | \(3^2J_{HH} = 5.8\) |

2.7 Compound 4

A suspension of biphenyl-substituted silylene 3 (260 mg, 0.53 mmol, 1.0 equiv.) in Et\(_2\)O (4 ml) was cooled to -78 °C and an excess of CS\(_2\) was added dropwise via syringe. The supernatant violet solution was filtered after 30 min at -78 °C. The residual pink solid 4 was dried under reduced pressure and isolated in yields of 77% (230 mg, 0.41 mmol). Single crystals suitable for X-ray diffraction analysis of 4 were obtained from a concentrated solution of 4 in toluene at -30 °C overnight. Compound 4 is not air stable and generally good soluble in organic solvents except for \(^7\)hexane.

\(^1\)H NMR (500.1 MHz, C\(_6\)D\(_6\), 298 K): \(\delta/\text{ppm} = 8.26\) (d, \(3^2J_{HH} = 7.3\) Hz, 1H, \(H_{Ar}\)), 7.52 (d, \(3^2J_{HH} = 7.3\) Hz, 2H, \(H_{Ar}\)), 7.33 – 7.22 (m, 5H, \(H_{Ar}\)), 7.18 – 7.16 (m, 5H, \(H_{Ar}\)), 6.50 (s, 1H, \(m\)-Mes\(H\)), 6.46 (s, 1H, \(m\)-Mes\(H\)), 2.22 (s, 3H, \(p\)-Mes\(CH_3\)), 2.14 (s, 3H, \(o\)-Mes\(CH_3\)), 1.95 (s, 3H, \(o\)-Mes\(CH_3\)), 1.15 (s, 18H, 2x NC(CH\(_3\))\(_3\)). \(^{13}\)C\(^{1}\)H NMR (125.8 MHz, C\(_6\)D\(_6\), 298 K): \(\delta/\text{ppm} = 274.8\) (s, \(C_{quart}, SiCS_2\)), 182.1 (s, \(C_{quart}, NCN\)), 150.9 (s, \(C_{quart}, C_{Ar}\)), 143.0 (s, \(C_{quart}, C_{Ar}\)), 140.8 (s, \(C_{quart}, C_{Ar}\)), 136.3 (s, \(C_{quart}, C_{Ar}\)), 135.5 (s, \(C_{Ar}\)), 134.4 (s, \(C_{quart}, C_{Ar}\)), 132.4 (s, \(C_{quart}, C_{Ar}\)), 131.1 (s, \(C_{Ar}\)), 130.1 (s, \(C_{Ar}\)), 129.5 (s, \(C_{Ar}\)), 128.3 (s, \(C_{Ar}\)), 126.3 (s, \(C_{Ar}\)), 125.6 (s, \(C_{Ar}\)), 124.6 (s, \(p\)-Mes\(CH_3\)), 121.8 (s, 2x NC(CH\(_3\))\(_3\)), 30.3 (s, 2x NC(CH\(_3\))\(_3\)), 22.2 (s, \(p\)-Mes\(CH_3\)), 21.8 (s, \(o\)-Mes\(CH_3\)), 20.9 (s, \(o\)-Mes\(CH_3\)). \(^1\)H,\(^{29}\)Si HMQC NMR (400.1/79.5 MHz, C\(_6\)D\(_6\), 298 K, optimized for \(J = 5\) Hz): \(\delta/\text{ppm} = 7.25/ 90.9\) (\(SiH_{Ar}\)). FT-IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)): 3051 – 2870 (w), 1611 (w), 1538 (vw), 1555 (vw), 1505 (w), 1464 – 1444 (w), 1424 (w), 1380 -1362 (s), 1301 (vw), 1275 (w), 1234 (w), 1193 (s), 1156 (w), 1122 (w), 1076 (s), 1032 (w), 1007 (vw), 909 (w).
997 (w), 948 (vw), 904 – 884 (w), 853 (s), 814 (vw), 789 (w), 776 (vs), 748 (s).

**Elemental Analysis (%)**: Calcd. for C$_{31}$H$_{58}$N$_2$S$_2$Si + C$_{3.5}$H$_4$: 4.98 (N), 70.41 (C), 8.24 (H), 11.39 (S), found: 5.18 (N), 69.70 (C), 8.61 (H), 10.92 (S). The reduced C content stems from Si-C formation. ESI- and APCI-HR MS analyses show merely molecular fragments. **Melting Point**: T = 119°C.

### 2.8 Compound 6 (dithiasilolane)

To a suspension of thiasilirane 4 (50.0 mg, 0.089 mmol, 1.0 equiv.) in Et$_2$O (5 ml) 2-(methylamino)pyridine-substituted silylene$^{[4]}$ 5 (32.6 mg, 0.089 mmol, 1.0 equiv.) was added at room temperature and stirred for 30 min. The orange solution was filtered and afterwards concentrated under reduced pressure. Compound 6 was obtained as orange crystal rods from the concentrated solution in Et$_2$O overnight at −30 °C in 41 % (32.4 mg, 0.036 mmol, 1.0 equiv.) isolated yields. Single crystals suitable for X-ray diffraction analysis of 6 were obtained from a concentrated solution of 6 in Et$_2$O at −30 °C. Compound 6 is not stable in solution and shows poor solubility in polar solvents such as Et$_2$O and THF. Due to the observation of additional resonance signals in the $^1$H and $^{13}$C NMR spectra a full assignment was not possible.

$^{29}$Si($^1$H) NMR (79.5 MHz, Tol-$d_8$, 223 K) δ/ppm = −71.3 (s, Si1), −73.5 (s, Si1).

$^1$H,$^{29}$Si HMQC NMR (500.1/79.5 MHz, Tol-$d_8$, 223 K, optimized for J = 7 Hz): δ/ppm = 7.43/−71.3 (SiCC$_3$H$_4$), 3.15/−73.5 (SINCH$_3$). **FT-IR (ATR)**: $\tilde{\nu}$ (cm$^{-1}$): 3079 – 2864 (w), 1605 – 591 (w), 1520 (w), 1509 (w), 1489 – 1478 (w), 1458 (w), 1442 (w), 1392-1380 (s), 1361 (s), 1317 (vw), 1288 (s), 1247 (s), 1220 (vw), 1196 (s), 1178 (w), 1150 – 1116 (vw), 1085 (w), 1057 – 1050 (w), 1032 (vw), 2021 (w), 1007 (w), 925 (vw), 909 – 904 (vw), 881 (vw), 867-848 (w), 828 (w), 791- 783 (w), 775 – 738 (s), 703 (vs).

**Elemental Analysis (%)**: Calcd. for C$_{52}$H$_{68}$N$_6$S$_2$Si$_2$ + C$_{4}$H$_{10}$O: 8.65 (N), 69.23 (C), 8.09 (H), 6.60 (S), found: 8.88 (N), 69.32 (C), 8.18 (H), 6.44 (S). **ESI-MS**: (m/z): Calcd. for [C$_{52}$H$_{68}$N$_6$S$_2$Si$_2$] = 897.4558, found: 897.4552. **Melting Point**: T = 109°C.

### 2.9 Compound 8 (thiadisiletane-3-thione)

A suspension of thiasilirane 4 (30.0 mg, 0.053 mmol, 1.0 equiv.) in Et$_2$O (4 ml) was cooled to −78°C and a solution of phenyl-substituted silylene 7 (21.4 mg, 0.057 mmol, 1.0 equiv.) in Et$_2$O (1 ml) was added dropwise. The dark green mixture was warmed up to room temperature and stirred for 15 min. The resulting light green solution was filtered and concentrated under reduced pressure. Single crystals suitable for X-ray
diffraction analysis of 8 were obtained from a concentrated solution of 8 in C₆D₆ at room temperature. The obtained light green crystal rods were washed with cold Et₂O (2x 1 ml) and dried under reduced pressure to obtain compound 8 in 26% (12.8 mg, 0.0136 mmol) isolated yields. Compound 8 is air stable for 1 h and shows good solubility in common organic solvents.

**¹H NMR** (500.1 MHz, C₆D₆, 298 K): δ/ppm = 8.76 (d, 3J_HH = 6.5 Hz, 2H, HAr), 8.03 (d, 3J_HH = 7.2 Hz, 2H, HAr), 7.95 (d, 3J_HH = 7.5 Hz, 1H, HAr), 7.31 (t, 3J_HH = 7.7 Hz, 3H, HAr), 7.23 – 7.17 (m, 4H, HAr), 7.12 (d, 3J_HH = 7.5 Hz, 1H, HAr), 6.96 (t, 3J_HH = 7.5 Hz, 1H, HAr), 6.59 (s, 1H, HAr), 6.54 – 6.49 (m, 4H, HAr), 2.90 (s, 3H, o-MesCH₃), 2.83 (s, 3H, o-MesCH₃), 2.23 (s, 3H, o-MesCH₃), 2.14 (s, 3H, o-MesCH₃), 2.01 (s, 3H, p-MesCH₃), 1.99 (s, 3H, p-MesCH₃), 1.59 (s, NC(CH₃)₃), 1.32 (s, 9H, NC(CH₃)₃), 1.23 (s, 9H, NC(CH₃)₃), 0.92 (s, 9H, NC(CH₃)₃). **¹³C{¹H} NMR** (125.8 MHz, C₆D₆, 298 K): δ/ppm = 267.3 (s, C_quart, SiC(Si)Si), 172.4 (s, C_quart, NCN), 170.9 (s, C_quart, NCN), 149.5 (s, C_quart, CAr), 146.3 (s, C_quart, CAr), 145.3 (s, C_quart, CAr), 142.1 (s, C_quart, CAr), 139.9 (s, C_quart, CAr), 139.2 (s, C_quart, CAr), 138.9 (s, C_quart, CAr), 138.7 (s, 2x CAr), 137.6 (s, C_quart, CAr), 137.3 (s, CAr), 136.6 (s, C_quart, CAr), 135.8 (s, CAr), 133.5 (s, C_quart, CAr), 132.2 (s, C_quart, CAr), 131.7 (s, CAr), 131.4 (s, CAr), 129.3 (s, CAr), 128.9 (s, CAr), 128.7 (s, CAr), 128.4 (s, C_quart, CAr), 128.2 (s, CAr), 128.1 (s, CAr), 128.0 (s, CAr), 127.7 (s, CAr), 127.1 (s, CAr), 127.0 (s, CAr), 126.7 (s, CAr), 124.7 (s, CAr), 57.0 (s, C_quart, NC(CH₃)₃), 56.1 (s, C_quart, NC(CH₃)₃), 55.7 (s, C_quart, NC(CH₃)₃), 55.1 (s, C_quart, NC(CH₃)₃), 32.2 (s, NC(CH₃)₃), 31.3 (s, NC(CH₃)₃), 29.6 (s, NC(CH₃)₃), 29.2 (s, NC(CH₃)₃), 22.4 (s, 2x o-MesCH₃), 21.5 (s, 2x o-MesCH₃), 20.0 (s, 2x p-MesCH₃). **²⁹Si{¹H} NMR** (79.5 MHz, C₆D₆, 298 K): δ/ppm = −59.7 (s, Si₂), −67.4 (s, Si₃).

**¹H,²⁹Si HMQC NMR** (400.1/79.5 MHz, C₆D₆, 298 K, optimized for J = 7 Hz): δ/ppm = 8.76/−59.7 (SiCCH₃), 7.95/−67.4 (SiCCH₃), 7.12/−67.4(SiCCH₃). **FT-IR (ATR):** ν (cm⁻¹) : 3038 – 2867 (w), 1658 (vw), 1612 (vw), 1550 – 1524 (w), 1476-1425 (w) 1391 (w), 1362 (w), 1306 (w), 1230 – 1082 (vs), 1060 (w), 983 (s), 949 (vw), 918 (vw). **ESI-MS:** (m/z): Calcd. for [C₈S₅H₇2N₄S₂Si₂] = 909.4810, found: 909.4810. **Melting Point:** T = 135°C.

### 2.10 Compound 9 (trithia-silabicyclo[3.2.0]-dithione)

To a solution of dithiasilolane 6 (40.0 mg, 0.045 mmol, 1.0 equiv.) in toluene (2 ml) an excess of CS₂ was added dropwise at room temperature. After stirring for 30 min at room temperature the pink solution was filtered and concentrated under reduced
pressure. Single crystals suitable for X-ray diffraction analysis of 9 were obtained from a concentrated solution of 9 in toluene at –30 °C after one week. The isolated crystals of compound 9 were found to be completely insoluble in common organic solvents (benzene, toluene). Compound 9 could only be isolated in very small quantities.

1H,29Si HMQC-NMR (500.1/79.5 MHz, Tol-d8, 298 K, optimized for J = 7 Hz): δ/ppm = 2.91/−143.4 (SNCH3). **Elemental Analysis:** Calcd. for C24H30N4S5Si + C7H8: 9.36 (N), 56.84 (C), 5.85 (H), 24.47 (S), found: 9.80 (N), 56.78 (C), 5.64 (H), 24.23 (S).

**In situ** NMR spectroscopic analysis of the reaction mixture indicates the stoichiometric formation of the corresponding silathione 10.

1H NMR (500.1 MHz, C6D6, 298 K): δ/ppm = 8.37 (d, 3JHH = 6.9 Hz, 1H, HA), 7.67 – 7.60 (m, 2H, HA), 7.31 (t, 3JHH = 7.6 Hz, 2H, HA), 7.24 (d, 4JHH = 1.3 Hz, 4H, HA), 6.53 (d, 3JHH = 12.6 Hz, 2H, HA), 2.32 (s, 3H, o-MesCH3), 2.18 (d, 4JHH = 4.5 Hz 3H, o-MesCH3), 1.99 (s, 3H, sp-MesCH3), 1.10 (s, 18H, 2x NC(CH3)3). 1H,29Si HMQC NMR (500.1/79.5 MHz, Tol-d8, 298 K, optimized for J = 7 Hz): δ/ppm = 8.37/4.4 (SiCCH3).

29Si[1H] NMR (79.5 MHz, Tol-d8, 298 K) δ/ppm = 4.9.

### 2.11 Compound 10

In a Y. Young NMR tube 4 (10.0 mg, 0.019 mmol, 1.0 equiv.) was dissolved in C6D6 (0.5 ml) and heated to 50 °C for 4 h. The color of the solution changed with increasing conversion from red to dark brown. After removal of the solvent under reduced pressure, the residue was re-dissolved in Et2O (1.0 ml). The solution was filtered and transferred to a 5 ml Schlenk tube. The solvent was reduced to a volume of 0.2 ml upon which a dark red solution was obtained. Single crystals suitable for X-ray diffraction analysis of 10 were obtained after one week at –30 °C as colorless blocks. The conversion of thiasilirane 4 to silathione 10 is quantitative as observed by 1H NMR spectroscopy showing the formation of 10 as sole product.

1H NMR (500.1 MHz, C6D6, 298 K): δ/ppm = 8.39 (dd, 3JHH = 7.3 Hz, 4JHH = 2.5 Hz, 1H, HA), 7.73 (dt, 3JHH = 8.0 Hz, 4JHH = 1.6 Hz, 2H, HA), 7.36 (t, 3JHH = 7.6 Hz, 2H, HA), 7.30 – 7.20 (m, 4H, HA), 6.52 (s, 1H, m-MesH), 6.48 (s, 1H, m-MesH), 2.33(s, 3H, p-MesCH3), 2.17 (s, 3H, p-MesCH3), 1.97 (s, 3H, p-MesCH3), 1.11 (s, 18H, NC(CH3)3). 13C[1H] NMR (125.6 MHz, C6D6, 298 K): δ/ppm = 176.0 (s, Cquart, NCN),
152.0 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 143.4 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 140.3 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 137.0 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 135.3 (s, C\textsubscript{Ar}), 135.0 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 133.8 (s, C\textsubscript{quart}, C\textsubscript{Ar}), 132.6 (s, C\textsubscript{Ar}), 131.1 (s, C\textsubscript{Ar}), 130.4 (s, C\textsubscript{Ar}), 129.4 (s, C\textsubscript{Ar}), 128.5 (s, C\textsubscript{Ar}), 127.6 (s, C\textsubscript{Ar}), 127.5 (s, C\textsubscript{Ar}), 126.2 (s, C\textsubscript{Ar}), 55.5 (s, C\textsubscript{quart}, NC(CH\textsubscript{3})\textsubscript{3}), 30.5 (s, NC(CH\textsubscript{3})\textsubscript{3}), 21.6 (s, MesCH\textsubscript{3}), 21.5 (s, MesCH\textsubscript{3}), 21.1 (s, MesCH\textsubscript{3}). ¹\textsubscript{H},²\textsubscript{9}Si HMQC NMR (400.1/79.4 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K, optimized for J = 4 Hz): δ/ppm = 7.29/ 5.9(SiH\textsubscript{Ar}). ²\textsubscript{9}Si{¹\textsubscript{H}} NMR (79.5 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): δ/ppm = 5.1 (s).

3. NMR Spectra

3.1 Compound S1

![NMR Spectra of Compound S1](image)

Figure S1. ¹\textsubscript{H} NMR spectrum of compound S1 in C\textsubscript{6}D\textsubscript{6} under 1 bar N\textsubscript{2} at 298 K.
Figure S2. $^{13}$C($^1$H) NMR spectrum of compound S1 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S3. $^1$H,$^{29}$Si HMQC NMR spectrum (optimized for $J_{SH} = 200$ Hz) of compound S1 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
3.2 Compound S2

Figure S4. $^1$H NMR spectrum of compound S2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S5. $^{13}$C($^1$H) NMR spectrum of compound S2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
**Figure S6.** $^{29}$Si($^1$H) NMR spectrum of compound S2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

**3.3 Compound 2$^{Ph}$**

**Figure S7.** $^1$H NMR spectrum of compound 2$^{Ph}$ in THF-$d_8$ under 1 bar N$_2$ at 298 K.
Figure 8. $^{13}$C($^1$H) NMR spectrum of compound 2$^{Ph}$ in THF-$_d_8$ under 1 bar N$_2$ at 298 K.

Figure S9. $^{29}$Si($^1$H) NMR spectrum of compound 2$^{Ph}$ in THF-$_d_8$ under 1 bar N$_2$ at 298 K.
**Figure S10.** $^1$H, $^{29}$Si HMQC NMR spectrum (optimized for $J_{\text{Si,H}} = 7$ Hz) of compound 2Ph in THF-$d_8$ under 1 bar $N_2$ at 298 K.

**Figure S11.** $^1$H, $^{13}$C HSQC NMR spectrum of compound 2Ph in THF-$d_8$ under 1 bar $N_2$ at 298 K.
Figure S12. Section of $^{13}$C($^1$H) NMR spectrum (bottom) and $^{13}$C 135 DEPT spectrum (top) of compound $2^{Ph}$.

3.4 Compound $2^{Mes}$

Figure S13. $^1$H NMR spectrum of compound $2^{Mes}$ in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S14. $^{13}$C{$^1$H} NMR spectrum of compound $\text{2}^{\text{Mes}}$ in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S15. $^{29}$Si{$^1$H} NMR spectrum of compound $\text{2}^{\text{Mes}}$ in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S16. $^{13}$C($^1$H) NMR spectrum of compound $^2$Mes in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S17. $^1$H,$^29$Si HMQC NMR spectrum (optimized for $J_{\text{Si,H}} = 7$ Hz) of compound $^2$Mes in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S18. $^1$H, $^{13}$C HSQC NMR spectrum of compound 2$^{\text{Mes}}$ in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S19. Section of $^{13}$C{'H}) NMR spectrum (bottom) and $^{13}$C 135 DEPT spectrum (top) of compound 2$^{\text{Mes}}$. 
3.5 Compound 3

Figure S20. $^1$H NMR spectrum of compound 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S21. $^{13}$C($^1$H) NMR spectrum of compound 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S22. $^{29}\text{Si}(^1\text{H})$ NMR spectrum of compound 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S23. $^1\text{H},^{29}\text{Si}$ NMR spectrum (optimized for $J_{\text{Si,H}} = 7$ Hz) of compound 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
3.6 Compound 4

Figure S24. $^1$H NMR spectrum of compound 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S25. $^{13}$C NMR spectrum of compound 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
3.7 Compound 6

Figure S27. $^{29}$Si($^1$H) NMR spectrum of compound 6 in Tol-$d_8$ under 1 bar N$_2$ at 223 K.
Figure S28. $^1$H,$^{29}$Si HMOC NMR spectrum (optimized for $J_{Si,H} = 7$ Hz) of compound 6 in Tol-$d_8$ under 1 bar $N_2$ at 223 K.

3.8 Compound 8

Figure S29. $^1$H NMR spectrum of compound 8 in CsD$_8$ under 1 bar $N_2$ at 298 K.
Figure S30. $^{13}$C NMR spectrum of compound 8 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S31. $^{29}$Si($^1$H) NMR spectrum of compound 8 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
3.9 Compound 10

Figure S33. $^1$H NMR spectrum of compound 10 in C₆D₆ under 1 bar N₂ at 298 K.
Figure S34. $^{13}$C($^1$H) NMR spectrum of compound 10 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S35. $^{29}$Si($^1$H) NMR spectrum of compound 10 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S36. $^1H,^{29}Si$ NMR spectrum (optimized for $J_{Si,H} = 4$ Hz) of compound 10 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

4. FT-IR Spectra

4.1 Compound 1$^{Mes}$

Figure S37. Solid state FT-IR spectrum of compound 1$^{Mes}$. 

$\star = C_6D_6$
4.2 Compound $2^{Ph}$

Figure S38. Solid state FT-IR spectrum of compound $2^{Ph}$.

4.3 Compound $2^{Mes}$

Figure S39. Solid state FT-IR spectrum of compound $2^{Mes}$. 
4.4 Compound 3

**Figure S40.** Solid state FT-IR spectrum of compound XX.

4.5 Compound 4

**Figure S41.** Solid state FT-IR spectrum of compound 4.
4.6 Compound 6

Figure S42. Solid state FT-IR spectrum of compound 6.

4.7 Compound 7

Figure S43. Solid state FT-IR spectrum of compound 7.
4.8 Compound 8

Figure S44. Solid state FT-IR spectrum of compound 8.

5. Calculations

5.1 Compound 2 – DFT

Figure S45. Calculated potential energy surface of the metal free intramolecular de-aromatization.

All quantum chemical calculations were carried out using Gaussian 09.\textsuperscript{[7]} The geometries of all compounds were optimized at B3LYP\textsuperscript{[8]} -D3\textsuperscript{[9]}/def2-SVP\textsuperscript{[10]} basis set for all other atoms. Analytical frequencies were computed to verify the stationary points. Thermochemistry at 298.15 K.
Calculated cartesian coordinates and energies of A

E(B3LYP) \(-2660.579296\) \(\text{E}_\text{h}\)
Sum of electronic and zero-point Energies \(-2659.629404\) \(\text{E}_\text{h}\)
Sum of electronic and thermal Energies \(-2659.575030\) \(\text{E}_\text{h}\)
Sum of electronic and thermal Enthalpies \(-2659.574086\) \(\text{E}_\text{h}\)
Sum of electronic and thermal Free Energies \(-2659.719427\) \(\text{E}_\text{h}\)

Number of imaginary frequencies: 0.

Si \(\begin{array}{ccc}
-2.91897 \\ 1.62058 \\ -2.74520 \\ -3.99651 \\ 3.17950 \\ 1.94554 \\ 3.94713 \\ -0.78695 \\ -2.12107 \\ -3.43543 \\ 2.42613 \\ 2.90640 \\ -3.89115 \\ 1.63451 \\ -2.53269 \\ -4.22773 \\ -4.64130 \\ -2.02570 \\ -0.25135 \\ -1.58965 \\ -5.49925
\end{array}\) \begin{array}{ccc}
0.87777 \\ 1.75632 \\ -0.40434 \\ -0.68089 \\ 0.72627 \\ 0.36744 \\ 0.59831 \\ 4.25755 \\ 4.01404 \\ -1.32093 \\ 3.27393 \\ -0.16937 \\ 3.44533 \\ 4.40684 \\ 3.94642 \\ 2.08460 \\ -1.19735 \\ 0.46589 \\ 4.46603 \\ 4.24309 \\ 1.64593
\end{array}\) \begin{array}{ccc}
0.54007 \\ -0.34069 \\ -0.87795 \\ 0.84650 \\ -0.77730 \\ 0.94429 \\ -2.02739 \\ 1.55799 \\ 1.23019 \\ -0.19486 \\ 0.57732 \\ 0.18799 \\ -0.48360 \\ 0.90435 \\ -0.11115 \\ -0.25273 \\ 2.06585 \\ -2.16159 \\ -0.78130 \\ -1.10810 \\ -0.66865
\end{array}\)
|   |   |   |
|---|---|---|
| C | 0.18083 | 4.42017 |
| C | 1.30629 | -0.07882 |
| C | 3.77508 | 3.28004 |
| C | -6.06018 | 3.83772 |
| C | -4.80328 | 4.30021 |
| C | -6.41152 | 2.50406 |
| C | 2.19464 | 5.47830 |
| C | 4.33379 | 4.35518 |
| C | 3.53857 | 5.45956 |
| H | -5.77438 | 0.59850 |
| H | -7.39306 | 2.13286 |
| H | -6.76419 | 4.51750 |
| H | -4.51992 | 5.34094 |
| H | 4.39877 | 2.41095 |
| H | 5.38628 | 4.33065 |
| H | 3.96414 | 6.30553 |
| H | 1.56508 | 6.33606 |
| H | -0.47318 | 4.24484 |
| H | -2.84752 | 3.81845 |
| H | 0.48258 | 4.62223 |
| H | -1.89646 | 4.22046 |
| C | -2.89384 | -1.13967 |
| H | -3.87723 | -0.64781 |
| H | -2.40265 | -1.05159 |
| H | -3.04806 | -2.20839 |
| C | -0.68296 | -1.20900 |
| H | -0.06247 | -0.71622 |
| H | -0.83691 | -2.26091 |
| H | -0.12829 | -1.18868 |
| C | -1.75288 | 0.99026 |
| H | -1.20171 | 1.01796 |
| H | -2.69665 | 1.54224 |
| H | -1.13392 | 1.50104 |
| C | -5.81616 | -2.13363 |
|   |   |   |   |
|---|---|---|---|
| H | -5.47519 | -3.08011 | 1.29050 |
| H | -6.37595 | -2.37310 | 2.64757 |
| H | -6.50671 | -1.64892 | 1.02221 |
| C | -3.62073 | -1.92439 | 2.96369 |
| H | -4.08902 | -2.23222 | 3.91255 |
| H | -3.23041 | -2.82632 | 2.47038 |
| H | -2.77416 | -1.25834 | 3.19022 |
| C | -5.18769 | 0.03452 | 2.81000 |
| H | -4.37212 | 0.73062 | 3.06469 |
| H | -5.91612 | 0.57588 | 2.18783 |
| H | -5.67958 | -0.26835 | 3.74686 |
| C | 0.56160 | 1.14355 | 2.75679 |
| H | -0.20049 | 1.49897 | 2.04639 |
| H | 0.04264 | 0.87550 | 3.68996 |
| H | 1.26469 | 1.96342 | 2.96648 |
| C | 0.29242 | -1.20857 | 1.92305 |
| H | -0.23089 | -1.48182 | 2.85304 |
| H | -0.46212 | -0.87173 | 1.19705 |
| H | 0.79175 | -2.10945 | 1.53787 |
| C | 2.36149 | -0.53924 | 3.21540 |
| H | 1.87888 | -0.73133 | 4.18652 |
| H | 2.86342 | -1.46486 | 2.90245 |
| H | 3.12358 | 0.24285 | 3.35770 |
| C | 3.26715 | -0.39024 | -2.99492 |
| H | 3.79757 | -0.41489 | -3.96054 |
| H | 3.26569 | -1.41002 | -2.58377 |
| H | 2.22435 | -0.08719 | -3.17556 |
| C | 3.96345 | 2.00179 | -2.65939 |
| H | 2.93813 | 2.34839 | -2.86697 |
| H | 4.43902 | 2.72825 | -1.98344 |
| H | 4.51727 | 1.98948 | -3.61050 |
| C | 5.39862 | 0.16315 | -1.75407 |
| H | 5.86511 | 0.82331 | -1.00627 |
| H | 5.45621 | -0.87109 | -1.39036 |
Calculated cartesian coordinates and energies of TS(A-B)

E(B3LYP)  \(-3494.831523\text{ E}_h\)
Sum of electronic and zero-point Energies  \(-3493.872902\text{ E}_h\)
Sum of electronic and thermal Energies  \(-3493.815017\text{ E}_h\)
Sum of electronic and thermal Enthalpies  \(-3493.814072\text{ E}_h\)
Sum of electronic and thermal Free Energies  \(-3493.966023\text{ E}_h\)

Number of imaginary frequencies: 1, \(\nu = -164.9\text{ cm}^{-1}\).

|     |        |        |        |
|-----|--------|--------|--------|
| S   | -0.22176 | -1.69461 | 0.93309 |
| S   | -0.10426 | 0.47401  | 3.16218 |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| Si      | 2.56126 | 0.88035 | -0.23202 |
| Si      | -2.37824 | 1.00573 | 0.40417 |
| N       | 3.73953 | -0.02652 | 0.97447 |
| N       | 3.57367 | -0.49646 | -1.11545 |
| N       | -3.76074 | -0.25865 | 0.70284 |
| N       | -2.68531 | -0.02489 | -1.14383 |
| C       | -0.37484 | -0.42374 | 1.88049 |
| C       | -4.46403 | -0.75331 | 1.90149 |
| C       | -0.61680 | 4.44892 | -1.43757 |
| C       | 0.77181 | 4.42400 | -1.57776 |
| C       | 4.04115 | -0.95308 | 0.05837 |
| C       | -3.37894 | 2.62710 | 0.04065 |
| C       | -3.54697 | -0.81895 | -0.49847 |
| C       | 3.05288 | 3.72911 | -0.77631 |
| C       | -2.72604 | 3.86349 | -0.21340 |
| C       | 1.58993 | 3.91467 | -0.55649 |
| C       | 3.64969 | 2.44910 | -0.63081 |
| C       | 3.36370 | -1.18401 | -2.40067 |
| C       | 4.16633 | 0.12772 | 2.37516 |
| C       | -0.41475 | 3.53697 | 0.78333 |
| C       | 0.97242 | 3.51583 | 0.64232 |
| C       | 5.03251 | 2.33928 | -0.87311 |
| C       | -1.23832 | 3.96439 | -0.27266 |
| C       | -2.14094 | -0.05521 | -2.51153 |
| C       | -4.78754 | 2.60876 | 0.00277 |
| C       | 5.20473 | 4.69052 | -1.40080 |
| C       | 3.83654 | 4.83102 | -1.16953 |
| C       | 5.80913 | 3.43693 | -1.24870 |
| C       | -3.49065 | 5.01055 | -0.49681 |
| C       | -5.53849 | 3.75558 | -0.26659 |
| C       | -4.88499 | 4.96514 | -0.51632 |
| H       | 5.51024 | 1.35911 | -0.77372 |
| H       | 6.88198 | 3.31891 | -1.42714 |
| H       | 5.80119 | 5.55864 | -1.69476 |
| | x      | y      | z      |
|--|--------|--------|--------|
| H | -0.22638 | 0.77171 | -1.83278 |
| H | -0.58436 | 1.04883 | -3.56049 |
| H | -1.41978 | 2.00117 | -2.31515 |
| C | -1.54234 | -1.42730 | -2.87134 |
| H | -0.98924 | -1.35267 | -3.82056 |
| H | -0.84211 | -1.75186 | -2.08873 |
| H | -2.31465 | -2.19830 | -2.99223 |
| C | -3.25438 | 0.32525 | -3.50508 |
| H | -2.85130 | 0.38906 | -4.52835 |
| H | -4.05744 | -0.42689 | -3.50268 |
| H | -3.68800 | 1.30086 | -3.23670 |
| C | -3.84054 | -2.05841 | 2.43235 |
| H | -4.31202 | -2.33856 | 3.38762 |
| H | -3.98838 | -2.88947 | 1.72928 |
| H | -2.76155 | -1.93274 | 2.59941 |
| C | -4.31198 | 0.34437 | 2.96999 |
| H | -3.25021 | 0.50371 | 3.21718 |
| H | -4.73499 | 1.29819 | 2.62037 |
| H | -4.83468 | 0.05141 | 3.89294 |
| C | -5.95885 | -0.96963 | 1.60157 |
| H | -6.42093 | -0.04723 | 1.21747 |
| H | -6.11082 | -1.76816 | 0.86240 |
| H | -6.48858 | -1.25859 | 2.52283 |
| C | 4.59774 | -2.31063 | 0.33259 |
| C | 3.74311 | -3.31042 | 0.82474 |
| C | 5.95025 | -2.60648 | 0.11320 |
| C | 4.23747 | -4.58994 | 1.08732 |
| H | 2.69063 | -3.07452 | 1.00142 |
| C | 6.44437 | -3.88593 | 0.38269 |
| H | 6.61398 | -1.82850 | -0.27045 |
| C | 5.58868 | -4.87974 | 0.86809 |
| H | 3.56548 | -5.36313 | 1.46813 |
| H | 7.50089 | -4.10710 | 0.21209 |
| H | 5.97513 | -5.88047 | 1.07714 |
|  | X   | Y   | Z   |
|---|-----|-----|-----|
| C | -4.11272 | -2.10379 | -1.00182 |
| C | -5.33094 | -2.10379 | -1.69663 |
| C | -3.43107 | -3.31349 | -0.80029 |
| C | -5.86242 | -3.30077 | -2.18497 |
| H | -5.86259 | -1.16198 | -1.85020 |
| C | -3.96568 | -4.50814 | -1.28702 |
| H | -2.47926 | -3.30697 | -0.26643 |
| C | -5.18113 | -4.50440 | -1.98026 |
| H | -6.81168 | -3.29211 | -2.72615 |
| H | -3.42894 | -5.44640 | -1.12659 |
| H | -5.59676 | -5.44036 | -2.36180 |
Calculated cartesian coordinates and energies of B

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| S    | 0.27046 | -1.28136| 0.17882 |
| S    | 0.33866 | 1.02847 | -1.83232|
| Si   | -2.66637| 0.61960 | 0.19204 |
| Si   | 2.56338 | 0.77715 | -0.08890|
| N    | -3.64389| -0.47467| -1.01275|
| N    | -3.63411| -0.74399| 1.11506 |
| N    | 3.76466 | -0.29144| -1.01100|
| N    | 3.45568 | -0.30588| 1.12421 |
| C    | 0.89317 | 0.11429 | -0.52288|
| C    | 4.04272 | -0.58073| -2.43930|
| C    | 0.34055 | 3.05443 | 1.26061 |
| C    | -1.04923| 3.01688 | 1.36276 |
| C    | -3.92340| -1.35679| -0.04448|
| C    | 3.20299 | 2.53458 | 0.00511 |
| C    | 4.02979 | -0.97073| 0.11466 |
| C    | -3.34173| 3.45153 | 0.41044 |
| C    | 2.44181 | 3.73022 | 0.06126 |
| C    | -1.86381| 3.64990 | 0.40623 |
| C    | -3.87489| 2.13727 | 0.37819 |
| C    | -3.62609| -1.23240| 2.50008 |
| C    | -3.70565| -0.56451| -2.48027|

E(B3LYP) = -3494.866599 E_h
Sum of electronic and zero-point Energies = -3493.906109 E_h
Sum of electronic and thermal Energies = -3493.848358 E_h
Sum of electronic and thermal Enthalpies = -3493.847414 E_h
Sum of electronic and thermal Free Energies = -3493.999178 E_h
Number of imaginary frequencies: 0.
|   |   |   |   |
|---|---|---|---|
| C | 0.15640 | 4.42851 | -0.71194 |
| C | -1.23515 | 4.38292 | -0.61226 |
| C | -5.27393 | 1.99402 | 0.35731 |
| C | 0.96361 | 3.73438 | 0.20249 |
| C | 3.39658 | -0.57544 | 2.57804 |
| C | 4.61020 | 2.63079 | -0.05766 |
| C | -5.58790 | 4.39072 | 0.37834 |
| C | -4.20347 | 4.56391 | 0.39648 |
| C | -6.12833 | 3.09885 | 0.36378 |
| C | 3.11436 | 4.96523 | -0.00226 |
| C | 5.26215 | 3.86266 | -0.09438 |
| C | 4.50463 | 5.03757 | -0.08116 |
| H | -5.69996 | 0.98542 | 0.32263 |
| H | -7.21335 | 2.95872 | 0.35060 |
| H | -6.24720 | 5.26329 | 0.37959 |
| H | -3.77744 | 5.57120 | 0.41557 |
| H | 5.21051 | 1.71822 | -0.10225 |
| H | 6.35307 | 3.90575 | -0.14428 |
| H | 4.99815 | 6.01226 | -0.11919 |
| H | 2.52291 | 5.88301 | 0.03772 |
| H | 0.94807 | 2.55920 | 2.01830 |
| H | -1.51447 | 2.49926 | 2.20318 |
| H | 0.62420 | 4.95851 | -1.54509 |
| H | -1.84927 | 4.87269 | -1.37214 |
| C | -5.08671 | -1.07125 | -2.93207 |
| H | -5.88618 | -0.44774 | -2.50138 |
| H | -5.16197 | -1.02066 | -4.02985 |
| H | -5.25769 | -2.11433 | -2.63218 |
| C | -2.58677 | -1.46850 | -3.03284 |
| H | -1.61086 | -1.13688 | -2.64823 |
| H | -2.74445 | -2.51771 | -2.74525 |
| H | -2.56899 | -1.41919 | -4.13393 |
| C | -3.50070 | 0.86992 | -3.00154 |
| H | -3.54962 | 0.88585 | -4.10136 |
|   | 1st Column | 2nd Column | 3rd Column |
|---|------------|------------|------------|
| H | -4.27474   | 1.54373    | -2.60365   |
| H | -2.51282   | 1.25155    | -2.70000   |
| C | -5.03671   | -1.69434   | 2.91007    |
| H | -5.34815   | -2.58271   | 2.34332    |
| H | -5.05744   | -1.95386   | 3.98069    |
| H | -5.76865   | -0.89117   | 2.73172    |
| C | -2.60474   | -2.36839   | 2.70888    |
| H | -2.53334   | -2.62375   | 3.77883    |
| H | -2.89595   | -3.27756   | 2.16502    |
| H | -1.61164   | -2.05479   | 2.35308    |
| C | -3.21954   | -0.03018   | 3.37188    |
| H | -2.20268   | 0.30475    | 3.11126    |
| H | -3.91138   | 0.81260    | 3.22179    |
| H | -3.22600   | -0.30676   | 4.43728    |
| C | 2.34662    | 0.39513    | 3.14142    |
| H | 1.36502    | 0.20432    | 2.67948    |
| H | 2.25112    | 0.25974    | 4.22879    |
| H | 2.64146    | 1.44040    | 2.95754    |
| C | 2.95860    | -2.01801   | 2.88477    |
| H | 2.76279    | -2.11675   | 3.96381    |
| H | 2.03666    | -2.25126   | 2.33221    |
| H | 3.73376    | -2.74908   | 2.61966    |
| C | 4.77132    | -0.27468   | 3.20032    |
| H | 4.72415    | -0.38274   | 4.29525    |
| H | 5.53593    | -0.97153   | 2.82646    |
| H | 5.08725    | 0.75368    | 2.96470    |
| C | 2.99714    | -1.56778   | -2.99056   |
| H | 3.17095    | -1.73248   | -4.06565   |
| H | 3.06933    | -2.53986   | -2.48190   |
| H | 1.97996    | -1.17332   | -2.85676   |
| C | 3.93589    | 0.76424    | -3.17991   |
| H | 2.93392    | 1.20291    | -3.05941   |
| H | 4.67955    | 1.48197    | -2.80123   |
| H | 4.11455    | 0.61176    | -4.25492   |
|   |   |   |   |
|---|---|---|---|
| C | 5.46210 | -1.14173 | -2.62792 |
| H | 6.20849 | -0.49991 | -2.13363 |
| H | 5.56600 | -2.16243 | -2.23809 |
| H | 5.69503 | -1.17070 | -3.70309 |
| C | -4.24717 | -2.80154 | -0.22987 |
| C | -3.19470 | -3.70892 | -0.43530 |
| C | -5.56807 | -3.26955 | -0.20576 |
| C | -3.46675 | -5.06735 | -0.61366 |
| H | -2.16743 | -3.33537 | -0.44871 |
| C | -5.83717 | -4.62949 | -0.38611 |
| H | -6.38566 | -2.56195 | -0.05061 |
| C | -4.78719 | -5.53011 | -0.59038 |
| H | -2.64320 | -5.76830 | -0.77227 |
| H | -6.87019 | -4.98592 | -0.36848 |
| H | -4.99785 | -6.59330 | -0.73187 |
| C | 4.72999 | -2.27672 | 0.20799 |
| C | 6.09427 | -2.35815 | 0.51215 |
| C | 3.98312 | -3.44319 | -0.01605 |
| C | 6.71484 | -3.60801 | 0.58465 |
| H | 6.67124 | -1.44560 | 0.67593 |
| C | 4.60941 | -4.68858 | 0.05963 |
| H | 2.91339 | -3.36103 | -0.22401 |
| C | 5.97430 | -4.77255 | 0.35724 |
| H | 7.78040 | -3.67198 | 0.81739 |
| H | 4.02781 | -5.59760 | -0.11073 |
| H | 6.46184 | -5.74885 | 0.41437 |

**Calculated cartesian coordinates and energies of TS(B-C)**

E(B3LYP) \hspace{1cm} -3494.863172 \text{E}_h

Sum of electronic and zero-point Energies \hspace{1cm} -3493.902655 \text{E}_h

Sum of electronic and thermal Energies \hspace{1cm} -3493.846028 \text{E}_h

Sum of electronic and thermal Enthalpies \hspace{1cm} -3493.845084 \text{E}_h

Sum of electronic and thermal Free Energies \hspace{1cm} -3493.992411 \text{E}_h

Number of imaginary frequencies: 1, \( \nu = -84.9 \text{ cm}^{-1} \).
| Element | x   | y    | z    |
|---------|-----|------|------|
| S       | -0.0975 | -0.93804 | 0.38027 |
| S       | -0.09718 | 1.23520 | -1.63633 |
| Si      | -2.38105 | 0.67833 | 0.01390 |
| Si      | 2.40449 | 0.80287 | -0.04645 |
| N       | -3.27791 | -0.56738 | -1.07586 |
| N       | -3.32567 | -0.62019 | 1.07534 |
| N       | 3.53765 | -0.31679 | -1.03325 |
| N       | 3.21887 | -0.41004 | 1.09732 |
| C       | 0.70303 | 0.33199 | -0.43470 |
| C       | 3.67751 | -0.60526 | -2.47884 |
| C       | 0.41262 | 3.05784 | 1.31023 |
| C       | -0.98217 | 3.01655 | 1.33112 |
| C       | -3.59002 | -1.33599 | -0.01929 |
| C       | 3.23068 | 2.48653 | 0.03652 |
| C       | 3.77565 | -1.04909 | 0.05857 |
| C       | -3.19774 | 3.47899 | 0.24322 |
| C       | 2.56456 | 3.72855 | 0.19758 |
| C       | -1.73946 | 3.73052 | 0.38002 |
| C       | -3.65529 | 2.14464 | 0.10552 |
| C       | -3.42716 | -0.95165 | 2.50355 |
| C       | -3.36124 | -0.82267 | -2.52614 |
| C       | 0.33447 | 4.58314 | -0.55902 |
| C       | -1.06298 | 4.55374 | -0.52749 |
| C       | -5.03743 | 1.93279 | -0.05048 |
| C       | 1.08790 | 3.80376 | 0.32920 |
| C       | 3.23871 | -0.68773 | 2.54963 |
| C       | 4.63814 | 2.48540 | -0.06896 |
| C       | -5.47749 | 4.30856 | 0.03854 |
| C       | -4.11222 | 4.54728 | 0.19417 |
| C       | -5.94531 | 2.99367 | -0.07893 |
| C       | 3.32099 | 4.91444 | 0.20610 |
| C       | 5.37754 | 3.66783 | -0.03337 |
| C       | 4.71142 | 4.89045 | 0.09465 |
| H       | -5.40944 | 0.90932 | -0.16202 |
H -7.0156  2.80030  -0.19653
H -6.17946  5.14671  0.01444
H -3.74155  5.57117  0.29632
H 5.16606  1.53811  -0.20700
H 6.46697  3.63694  -0.11728
H 5.27630  5.82622  0.11546
H 2.79815  5.86687  0.32273
H 0.97846  2.51932  2.06908
H -1.49257  2.45716  2.11418
H 0.84743  5.16319  -1.33005
H -1.63403  5.10288  -1.28019
C -4.64588  -1.59007  -2.89040
H -5.53108  -1.10215  -2.45234
H -4.76538  -1.59799  -3.98494
H -4.62105  -2.63401  -2.55260
C -2.12324  -1.60004  -3.01239
H -1.20718  -1.06679  -2.72138
H -2.09895  -2.60842  -2.57462
H -2.14601  -1.70362  -4.10962
C -3.41326  0.55674  -3.20994
H -3.48031  0.43393  -4.30213
H -4.28763  1.12880  -2.86441
H -2.50776  1.13827  -2.98957
C -4.91166  -1.07090  2.90002
H -5.38371  -1.93601  2.41356
H -5.01022  -1.20261  3.98962
H -5.45782  -0.16136  2.60571
C -2.66789  -2.24152  2.87150
H -2.67306  -2.37780  3.96500
H -3.12851  -3.13099  2.42167
H -1.62286  -2.17900  2.53288
C -2.79868  0.22474  3.27107
H -1.73240  0.32012  3.01662
H -3.30936  1.16797  3.02292
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -2.88456 | 0.06099 | 4.35595 |
| C    | 2.31880  | 0.36075 | 3.19396 |
| H    | 1.29941  | 0.26760 | 2.78782 |
| H    | 2.27732  | 0.20820 | 4.28256 |
| H    | 2.69516  | 1.37948 | 3.01026 |
| C    | 2.69200  | -2.09092 | 2.86654 |
| H    | 2.57369  | -2.20145 | 3.95580 |
| H    | 1.71101  | -2.22188 | 2.38631 |
| H    | 3.37119  | -2.88280 | 2.52376 |
| C    | 4.67196  | -0.52182 | 3.08473 |
| H    | 4.68383  | -0.63565 | 4.18005 |
| H    | 5.34511  | -1.28132 | 2.66116 |
| H    | 5.06493  | 0.47604  | 2.83417 |
| C    | 2.56271  | -1.56614 | -2.93497 |
| H    | 2.63075  | -1.72951 | -4.02221 |
| H    | 2.65762  | -2.54287 | -2.43872 |
| H    | 1.57316  | -1.14687 | -2.70298 |
| C    | 3.51906  | 0.74572  | -3.19871 |
| H    | 2.53205  | 1.18948  | -2.99314 |
| H    | 4.29501  | 1.45683  | -2.87695 |
| H    | 3.60568  | 0.60166  | -4.28613 |
| C    | 5.06213  | -1.19124 | -2.80025 |
| H    | 5.86229  | -0.55315 | -2.39283 |
| H    | 5.18874  | -2.20627 | -2.40135 |
| H    | 5.18904  | -1.24328 | -3.89243 |
| C    | -3.98138 | -2.77343 | -0.06417 |
| C    | -2.97378 | -3.73750 | -0.23067 |
| C    | -5.31681 | -3.17983 | 0.05735 |
| C    | -3.30473 | -5.09367 | -0.27242 |
| H    | -1.93593 | -3.40501 | -0.30789 |
| C    | -5.64436 | -4.53779 | 0.01258 |
| H    | -6.10131 | -2.42841 | 0.16859 |
| C    | -4.63951 | -5.49635 | -0.15172 |
| H    | -2.51649 | -5.84038 | -0.39767 |
Calculated cartesian coordinates and energies of C

\[
\begin{align*}
\text{H} & : (-6.6844, -4.84775, 0.10304) \\
\text{H} & : (-4.89681, -6.55809, -0.18592) \\
\text{C} & : (4.44291, -2.37609, 0.10073) \\
\text{C} & : (5.82772, -2.49070, 0.27765) \\
\text{C} & : (3.65479, -3.52640, -0.0546) \\
\text{C} & : (6.42384, -3.75415, 0.29625) \\
\text{H} & : (6.43719, -1.59139, 0.38885) \\
\text{C} & : (4.25694, -4.78618, -0.03889) \\
\text{H} & : (2.57342, -3.42332, -0.17120) \\
\text{C} & : (5.64042, -4.90179, 0.13569) \\
\text{H} & : (7.50425, -3.84216, 0.43300) \\
\text{H} & : (3.64227, -5.68131, -0.15966) \\
\text{H} & : (6.10910, -5.88884, 0.14803)
\end{align*}
\]

E(B3LYP) \quad -3494.878431 \text{ E}_h

Sum of electronic and zero-point Energies \quad -3493.916430 \text{ E}_h

Sum of electronic and thermal Energies \quad -3493.859813 \text{ E}_h

Sum of electronic and thermal Enthalpies \quad -3493.858869 \text{ E}_h

Sum of electronic and thermal Free Energies \quad -3494.005707 \text{ E}_h

Number of imaginary frequencies: 0.

\[
\begin{align*}
\text{S} & : (-0.52084, -0.32524, 0.79504) \\
\text{S} & : (-0.52465, 1.56521, -1.35669) \\
\text{Si} & : (-2.23807, 0.74791, -0.10430) \\
\text{Si} & : (2.24946, 0.91995, 0.00413) \\
\text{N} & : (-3.13040, -0.47512, -1.20445) \\
\text{N} & : (-3.39631, -0.54519, 0.94029) \\
\text{N} & : (3.38781, -0.27974, -0.96939)
\end{align*}
\]
|  |  |  |  
|---|---|---|---|
| N | 2.97755 | -0.35870 | 1.14972 |
| C | 0.54549 | 0.67039 | -0.24142 |
| C | 3.40849 | -0.65339 | -2.39968 |
| C | 0.54194 | 3.24674 | 1.49826 |
| C | -0.84656 | 3.19446 | 1.56653 |
| C | -3.64451 | -1.18986 | -0.17948 |
| C | 3.20812 | 2.55327 | -0.03379 |
| C | 3.58564 | -0.99953 | 0.12990 |
| C | -3.06318 | 3.57030 | 0.45639 |
| C | 2.63940 | 3.83114 | 0.23916 |
| C | -1.62922 | 3.90503 | 0.64112 |
| C | -3.44882 | 2.23698 | 0.15635 |
| C | -3.74064 | -0.84159 | 2.34094 |
| C | -3.12322 | -0.72487 | -2.66609 |
| C | 0.39783 | 4.82941 | -0.31491 |
| C | -0.99687 | 4.80649 | -0.22581 |
| C | -4.82039 | 1.99705 | -0.06981 |
| C | 1.18117 | 3.99443 | 0.49442 |
| C | 3.06299 | -0.58758 | 2.60943 |
| C | 4.59698 | 2.48650 | -0.27435 |
| C | -5.37999 | 4.31950 | 0.28874 |
| C | -4.03153 | 4.58993 | 0.51296 |
| C | -5.77675 | 3.01185 | -0.00777 |
| C | 3.46476 | 4.96879 | 0.22709 |
| C | 5.40974 | 3.62231 | -0.25565 |
| C | 4.83719 | 4.87259 | -0.01236 |
| H | -5.15465 | 0.98852 | -0.32016 |
| H | -6.82971 | 2.78274 | -0.19427 |
| H | -6.11861 | 5.12367 | 0.34536 |
| H | -3.70663 | 5.60697 | 0.74828 |
| H | 5.04993 | 1.51903 | -0.50399 |
| H | 6.48323 | 3.53193 | -0.44275 |
| H | 5.45758 | 5.77287 | -0.00314 |
| H | 3.01344 | 5.94354 | 0.42916 |
H  1.13577  2.68348  2.21243
H  -1.33003  2.55888  2.30955
H   0.88135  5.43680  -1.08466
H  -1.59687  5.37869  -0.93752
C  -4.31470  -1.58225  -3.13185
H  -5.26790  -1.17938  -2.75678
H  -4.34866  -1.56347  -4.23182
H  -4.23551  -2.63170  -2.82379
C  -1.80248  -1.41221  -3.06172
H  -0.95000  -0.78719  -2.76200
H  -1.71598  -2.39202  -2.56680
H  -1.76324  -1.57118  -4.15175
C  -3.24389   0.64577  -3.36286
H  -3.27144   0.50887  -4.45510
H  -4.16677   1.15725  -3.04932
H  -2.38749   1.29086  -3.13025
C  -5.27026  -0.85452   2.53051
H  -5.73481  -1.70087   2.00714
H  -5.51849  -0.94651   3.59982
H  -5.71009   0.08144   2.15284
C  -3.12991  -2.17847   2.80322
H  -3.29489  -2.31421   3.88406
H  -3.58319  -3.03361   2.28320
H  -2.04617  -2.18777   2.61150
C  -3.15254   0.29997   3.19172
H  -2.05765   0.33016   3.09758
H  -3.55519   1.27215   2.87100
H  -3.40945   0.15001   4.25151
C   2.29037   0.55482   3.28473
H   1.24288   0.56487   2.94781
H   2.30302   0.41905   4.37669
H   2.75358   1.52772   3.05994
C   2.39993  -1.92400   2.99291
H   2.34757  -2.01366   4.08940
|   |   |   |   |
|---|---|---|---|
| H | 1.37682 | -1.96500 | 2.58974 |
| H | 2.96815 | -2.78450 | 2.61540 |
| C | 4.52935 | -0.54933 | 3.07674 |
| H | 4.57727 | -0.61307 | 4.17517 |
| H | 5.10845 | -1.38902 | 2.66824 |
| H | 5.00709 | 0.39236 | 2.76362 |
| C | 2.32884 | -1.71855 | -2.67402 |
| H | 2.24065 | -1.90450 | -3.75627 |
| H | 2.58170 | -2.67228 | -2.18810 |
| H | 1.35791 | -1.37142 | -2.28947 |
| C | 3.06392 | 0.62880 | -3.17904 |
| H | 2.05505 | 0.98754 | -2.92093 |
| H | 3.78587 | 1.42931 | -2.95826 |
| H | 3.08422 | 0.42767 | -4.26080 |
| C | 4.79558 | -1.15496 | -2.83348 |
| H | 5.57365 | -0.41862 | -2.57729 |
| H | 5.05384 | -2.11305 | -2.36314 |
| H | 4.80964 | -1.30273 | -3.92468 |
| C | -4.24418 | -2.54973 | -0.29609 |
| C | -3.36386 | -3.64043 | -0.36201 |
| C | -5.62627 | -2.76696 | -0.34557 |
| C | -3.86600 | -4.93800 | -0.47985 |
| H | -2.28801 | -3.45609 | -0.31196 |
| C | -6.12568 | -4.06630 | -0.46609 |
| H | -6.31034 | -1.91677 | -0.30838 |
| C | -5.24767 | -5.15294 | -0.53458 |
| H | -3.17695 | -5.78477 | -0.52987 |
| H | -7.20512 | -4.23035 | -0.51072 |
| H | -5.64051 | -6.16826 | -0.63021 |
| C | 4.28949 | -2.30810 | 0.20654 |
| C | 5.69047 | -2.35882 | 0.25277 |
| C | 3.55090 | -3.50098 | 0.20061 |
| C | 6.34580 | -3.59119 | 0.29912 |
| H | 6.26311 | -1.42888 | 0.24977 |
Calculated cartesian coordinates and energies of TS(C-D)

|   | Calculated cartesian coordinates | Energies |   |
|---|----------------------------------|----------|---|
|   | C                                | -4.73195 | 0.23671 |
|   | H                                | -3.45656 | 0.17004 |
|   | C                                | -4.77936 | 0.28823 |
|   | H                                | -3.62397 | 0.33881 |
|   | H                                | -5.65773 | 0.22799 |
|   | H                                | -5.74318 | 0.31967 |
|   | S                                | -0.37054 | 0.68920 |
|   | S                                | -0.44616 | 0.68920 |
|   | Si                               | 1.32490  | -1.59964 |
|   | Si                               | -2.21649 | 1.00780 |
|   | N                                | 0.87199  | -0.16098 |
|   | N                                | 0.95582  | 0.15199 |
|   | N                                | 0.56642  | -0.16291 |
|   | C                                | -1.36728 | 0.95462 |
|   | C                                | 2.61169  | 0.95462 |
|   | C                                | 2.61911  | 1.18582 |
|   | C                                | -3.54626 | -0.00510 |
|   | C                                | -1.12806 | -0.00510 |
|   | C                                | 2.56959  | 0.60195 |
|   | C                                | -3.31986 | 0.07185 |
|   | C                                | 3.47347  | -0.31443 |
|   | C                                | 3.72699  | 0.85488 |
|   | C                                | 3.69657  | 0.14812 |
|   | C                                | 2.12112  | -0.56819 |

E(B3LYP) \(-3494.853950 \text{E}_h\)

- Sum of electronic and zero-point Energies \(-3493.892996 \text{E}_h\)
- Sum of electronic and thermal Energies \(-3493.837189 \text{E}_h\)
- Sum of electronic and thermal Enthalpies \(-3493.836245 \text{E}_h\)
- Sum of electronic and thermal Free Energies \(-3493.981237 \text{E}_h\)

Number of imaginary frequencies: 1, \(\nu = -279.0 \text{ cm}^{-1}\).
|   | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | H     | H     | H     | H     | H     | H     | H     | H     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | -3.77250 | -0.41343 | 2.41567 |   | -2.88690 | -1.17598 | -2.47869 |   | 0.26082 | 4.69824 | -0.08811 |   | -1.14036 | 4.69892 | -0.34629 |   | -4.91977 | 1.82753 | -1.05187 |   | 0.85938 | 3.70682 | 0.66729 |   | 3.04553 | -0.81915 | 2.58344 |   | 4.51025 | 2.63102 | 0.72508 |   | -5.51623 | 4.17761 | -1.03623 |   | -4.24611 | 4.49603 | -0.55927 |   | -5.85697 | 2.83848 | -1.28061 |   | 2.99388 | 4.91138 | 1.23055 |   | 5.15134 | 3.81143 | 1.10227 |   | 4.38283 | 4.95423 | 1.35475 |   | -5.19383 | 0.78955 | -1.26069 |   | -6.85508 | 2.58839 | -1.65207 |   | -6.24933 | 4.96996 | -1.21175 |   | -3.97734 | 5.53504 | -0.34917 |   | 5.10982 | 1.74137 | 0.50843 |   | 6.23963 | 3.84375 | 1.19809 |   | 4.87091 | 5.88501 | 1.65653 |   | 2.39808 | 5.80271 | 1.44013 |   | 0.43481 | 2.11587 | 2.08268 |   | -1.97611 | 2.36388 | 1.82530 |   | 0.88322 | 5.47497 | -0.54062 |   | -1.55930 | 5.44432 | -1.02675 |   | -4.08948 | -2.05863 | -2.87169 |   | -5.04286 | -1.54843 | -2.66624 |   | -4.03848 | -2.25580 | -3.95359 |   | -4.09858 | -3.02920 | -2.36253 |   | -1.58571 | -1.99111 | -2.61180 |   | -0.72878 | -1.37919 | -2.30239 |   | -1.62403 | -2.88350 | -1.96821 |   | -1.44088 | -2.32163 | -3.65354 |
|     | X       | Y       | Z       |
|-----|---------|---------|---------|
| C   | -2.8714 | 0.01460 | -3.4595 |
| H   | -2.8064 | -0.3591 | -4.4932 |
| H   | -3.7896 | 0.6120  | -3.3611 |
| H   | -2.0107 | 0.6687  | -3.2850 |
| C   | -5.3063 | -0.3569 | 2.5248  |
| H   | -5.7785 | -1.2548 | 2.1028  |
| H   | -5.6156 | -0.2881 | 3.5812  |
| H   | -5.6938 | 0.5259  | 1.9908  |
| C   | -3.2283 | -1.7017 | 3.0679  |
| H   | -3.4342 | -1.6899 | 4.1503  |
| H   | -3.6919 | -2.6053 | 2.6527  |
| H   | -2.1388 | -1.7654 | 2.9212  |
| C   | -3.1969 | 0.7814  | 3.1909  |
| H   | -2.0988 | 0.7866  | 3.1356  |
| H   | -3.5845 | 1.7307  | 2.7937  |
| H   | -3.4891 | 0.7142  | 4.2497  |
| C   | 2.2177  | 0.2259  | 3.3476  |
| H   | 1.1727  | 0.2059  | 3.0033  |
| H   | 2.2345  | 0.0007  | 4.4242  |
| H   | 2.6273  | 1.2380  | 3.2054  |
| C   | 2.4241  | -2.2097 | 2.7994  |
| H   | 2.3561  | -2.4192 | 3.8783  |
| H   | 1.4113  | -2.2357 | 2.3712  |
| H   | 3.0296  | -3.0040 | 2.3419  |
| C   | 4.5029  | -0.7832 | 3.0764  |
| H   | 4.5404  | -0.9906 | 4.1570  |
| H   | 5.1183  | -1.5398 | 2.5685  |
| H   | 4.9449  | 0.2099  | 2.8996  |
| C   | 2.4839  | -1.0792 | -2.9621 |
| H   | 2.5563  | -1.1176 | -4.0604 |
| H   | 2.5820  | -2.1062 | -2.5803 |
| H   | 1.4904  | -0.6909 | -2.6930 |
| C   | 3.4198  | 1.2585  | -2.9376 |
| H   | 2.4243  | 1.6631  | -2.6919 |
H  4.18557  1.93020  -2.51968
H  3.51546  1.25757  -4.03361
C  4.98092  -0.69969  -2.77481
H  5.77229  -0.10511  -2.29177
H  5.11525  -1.75330  -2.49679
H  5.11164  -0.62250  -3.86501
C  -4.20425  -2.46619  0.08319
C  -3.39250  -3.59923  0.24269
C  -5.59228  -2.61918  -0.02095
C  -3.96581  -4.87138  0.29841
H  -2.31130  -3.46876  0.32718
C  -6.16422  -3.89287  0.03141
H  -6.22242  -1.73908  -0.16371
C  -5.35296  -5.02093  0.19120
H  -3.32804  -5.74989  0.42489
H  -7.24766  -4.00510  -0.05714
H  -5.80156  -6.01675  0.23120
C  4.23233  -2.28239  -0.03349
C  5.61956  -2.44968  0.06839
C  3.40465  -3.39228  -0.26084
C  6.17752  -3.72446  -0.05470
H  6.25956  -1.58112  0.23693
C  3.96883  -4.66314  -0.39173
H  2.32350  -3.25093  -0.32832
C  5.35385  -4.83081  -0.28758
H  7.25932  -3.85323  0.02726
H  3.32336  -5.52583  -0.57267
H  5.79253  -5.82658  -0.38775
Calculated cartesian coordinates and energies of D

\[ E(\text{B3LYP}) = -3494.882471 \text{ E}_h \]

Sum of electronic and zero-point Energies
\[ -3493.918920 \text{ E}_h \]

Sum of electronic and thermal Energies
\[ -3493.863538 \text{ E}_h \]

Sum of electronic and thermal Enthalpies
\[ -3493.862593 \text{ E}_h \]

Sum of electronic and thermal Free Energies
\[ -3494.005775 \text{ E}_h \]

Number of imaginary frequencies: 0.

| atom | x    | y    | z    |
|------|------|------|------|
| S    | -0.30419 | -0.24790 | 1.03354 |
| S    | -0.00869 | 1.22372 | -1.49879 |
| Si   | -2.05274 | 0.98707 | -0.20496 |
| Si   | 2.45879  | 0.90202 | 0.36394 |
| N    | -2.70975 | -0.67634 | -1.00266 |
| N    | -3.35369 | 0.04518 | 0.94120 |
| N    | 3.22196  | -0.19336 | -0.88420 |
| N    | 3.04151  | -0.60974 | 1.22565 |
| C    | 0.62967  | 1.12866 | 0.23668 |
| C    | 3.52080  | -0.16156 | -2.33864 |
| C    | 0.21050  | 2.46942 | 0.95086 |
| C    | -1.29877 | 2.63441 | 0.67966 |
| C    | -3.45659 | -0.95201 | 0.06317 |
| C    | 3.29518  | 2.46337 | 0.85461 |
| C    | 3.34503  | -1.15963 | 0.04140 |
| C    | -2.98827 | 3.50978 | -0.91329 |
| C    | 2.51652  | 3.65823 | 0.89661 |
| C    | -1.68451 | 3.72783 | -0.26742 |
| C    | -3.33546 | 2.14632 | -1.06099 |
| C    | -3.97403 | 0.16447 | 2.27716 |
| C    | -2.43381 | -1.45660 | -2.22765 |
| C   | 0.53796 | 4.70903 | -0.13298 |
|-----|---------|---------|----------|
| C   | -0.82481| 4.72501 | -0.60410 |
| C   | -4.54149| 1.83358 | -1.70269 |
| C   | 1.07718 | 3.66456 | 0.55610  |
| C   | 3.04479 | -1.15065| 2.60692  |
| C   | 4.67066 | 2.49779 | 1.15472  |
| C   | -5.02767| 4.18732 | -2.03391 |
| C   | -3.82951| 4.52450 | -1.40417 |
| C   | -5.38655| 2.83950 | -2.18338 |
| C   | 3.18297 | 4.85133 | 1.26191  |
| C   | 5.30417 | 3.68934 | 1.49821  |
| C   | 4.54507 | 4.86789 | 1.54951  |
| H   | -4.82802| 0.78500 | -1.82917 |
| H   | -6.32812| 2.57825 | -2.67550 |
| H   | -5.69140| 4.97428 | -2.40299 |
| H   | -3.55458| 5.57422 | -1.26832 |
| H   | 5.25385 | 1.57188 | 1.11269  |
| H   | 6.37123 | 3.70560 | 1.73259  |
| H   | 5.02227 | 5.80969 | 1.83444  |
| H   | 2.60590 | 5.77450 | 1.34501  |
| H   | 0.36481 | 2.30093 | 2.03144  |
| H   | -1.84865| 2.79844 | 1.61290  |
| H   | 1.18616 | 5.53682 | -0.43660 |
| H   | -1.11364| 5.48408 | -1.33556 |
| C   | -3.56935| -2.42152| -2.62917 |
| H   | -4.53844| -1.90198| -2.67138 |
| H   | -3.35265| -2.81237| -3.63549 |
| H   | -3.66724| -3.28279| -1.95805 |
| C   | -1.13153| -2.25813| -2.02348 |
| H   | -0.32913| -1.58209| -1.70178 |
| H   | -1.27233| -3.02352| -1.24363 |
| H   | -0.83630| -2.76365| -2.95798 |
| C   | -2.27046| -0.46495| -3.39876 |
| H   | -2.04814| -1.01881| -4.32438 |
|   | x   | y   | z    |
|---|-----|-----|------|
| H | -3.1943 | 0.1114 | -3.5504 |
| H | -1.4510 | 0.2402 | -3.2242 |
| C | -5.5096 | 0.2499 | 2.1645 |
| H | -5.9483 | -0.7010 | 1.8362 |
| H | -5.9504 | 0.4959 | 3.1443 |
| H | -5.7933 | 1.0355 | 1.4471 |
| C | -3.5596 | -1.0021 | 3.1988 |
| H | -3.9014 | -0.8077 | 4.2282 |
| H | -3.9960 | -1.9574 | 2.8808 |
| H | -2.4628 | -1.0986 | 3.2063 |
| C | -3.4735 | 1.4645 | 2.9228 |
| H | -2.3817 | 1.4387 | 3.0433 |
| H | -3.7489 | 2.3389 | 2.3158 |
| H | -3.9296 | 1.5825 | 3.9177 |
| C | 2.4198 | 0.0638 | 3.4976 |
| H | 1.3699 | 0.1078 | 3.2127 |
| H | 2.4476 | -0.3851 | 4.5494 |
| H | 2.9769 | 0.8829 | 3.4168 |
| C | 2.2216 | -2.4444 | 2.7221 |
| H | 2.1257 | -2.7188 | 3.7839 |
| H | 1.2168 | -2.2868 | 2.3050 |
| H | 2.7008 | -3.2845 | 2.2013 |
| C | 4.5041 | -1.3920 | 3.0332 |
| H | 4.5399 | -1.7279 | 4.0810 |
| H | 4.9768 | -2.1691 | 2.4149 |
| H | 5.0923 | 0.4649 | 2.9472 |
| C | 2.5015 | -0.9955 | -3.1310 |
| H | 2.6846 | -0.8745 | -4.2101 |
| H | 2.5867 | -2.0650 | -2.8917 |
| H | 1.4818 | -0.6552 | -2.9036 |
| C | 3.4334 | 1.3160 | -2.7569 |
| H | 2.4191 | 1.7139 | -2.5975 |
| H | 4.1513 | 1.9282 | -2.1884 |
| H | 3.6705 | 1.4126 | -3.8268 |
|   |   |   |   |
|---|---|---|---|
| C | 4.95195 | -0.67161 | -2.58232 |
| H | 5.67663 | -0.11065 | -1.97068 |
| H | 5.05044 | -1.74173 | -2.35442 |
| H | 5.21594 | -0.53101 | -3.64156 |
| C | -4.20708 | -2.22698 | 0.26878 |
| C | -3.51087 | -3.34912 | 0.74196 |
| C | -5.56752 | -2.33968 | -0.04326 |
| C | -4.17030 | -4.56964 | 0.90209 |
| H | -2.45027 | -3.25293 | 0.98462 |
| C | -6.22581 | -3.56189 | 0.11448 |
| H | -6.10440 | -1.47029 | -0.42805 |
| C | -5.52923 | -4.67887 | 0.58671 |
| H | -3.62208 | -5.43931 | 1.27323 |
| H | -7.28618 | -3.64353 | -0.13703 |
| H | -6.04511 | -5.63467 | 0.70857 |
| C | 3.57993 | -2.60137 | -0.22199 |
| C | 4.84103 | -3.20090 | -0.12612 |
| C | 2.45116 | -3.36683 | -0.55768 |
| C | 4.97478 | -4.57102 | -0.36940 |
| H | 5.71536 | -2.59789 | 0.12698 |
| C | 2.59398 | -4.73391 | -0.79808 |
| H | 1.47157 | -2.88498 | -0.60996 |
| C | 3.85367 | -5.33671 | -0.70449 |
| H | 5.95877 | -5.04030 | -0.29830 |
| H | 1.71608 | -5.32997 | -1.05784 |
| H | 3.96208 | -6.40746 | -0.89374 |

**Calculated cartesian coordinates and energies of TS(D-E)**

E(B3LYP) \(-3494.877599 \text{E}_h\)

Sum of electronic and zero-point Energies \(-3493.914041 \text{E}_h\)

Sum of electronic and thermal Energies \(-3493.859314 \text{E}_h\)

Sum of electronic and thermal Enthalpies \(-3493.858370 \text{E}_h\)

Sum of electronic and thermal Free Energies \(-3494.000593 \text{E}_h\)

Number of imaginary frequencies: 1, \(\nu = -90.8 \text{ cm}^{-1}\).
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| S       | -0.38517 | -0.29437 | 0.68962  |
| S       | 0.29848  | 1.50207  | -1.66072 |
| Si      | -2.25829 | 0.93988  | -0.04677 |
| Si      | 2.40115  | 0.94881  | 0.20301  |
| N       | -2.88328 | -0.62253 | -1.04649 |
| N       | -3.41410 | -0.13524 | 1.00144  |
| N       | 3.26055  | -0.22566 | -0.90292 |
| N       | 3.01381  | -0.48076 | 1.22696  |
| C       | 0.58474  | 1.15514  | 0.12537  |
| C       | 3.63724  | -0.30566 | -2.34060 |
| C       | 0.12411  | 2.40288  | 0.95904  |
| C       | -1.39325 | 2.55352  | 0.73908  |
| C       | -3.55105 | -1.04234 | 0.01473  |
| C       | 3.21744  | 2.52956  | 0.68156  |
| C       | 3.42141  | -1.09370 | 0.11423  |
| C       | -3.15996 | 3.48637  | -0.73039 |
| C       | 2.39779  | 3.67163  | 0.91629  |
| C       | -1.83556 | 3.69231  | -0.12964 |
| C       | -3.54616 | 2.13183  | -0.84675 |
| C       | -3.83914 | -0.21794 | 2.41488  |
| C       | -2.66586 | -1.20922 | -2.38572 |
| C       | 0.35276  | 4.73890  | 0.06848  |
| C       | -1.01745 | 4.74295  | -0.38652 |
| C       | -4.79011 | 1.83859  | -1.42573 |
| C       | 0.94089  | 3.65855  | 0.64968  |
| C       | 2.93662  | -0.92232 | 2.63772  |
| C       | 4.60674  | 2.59973  | 0.89107  |
| C       | -5.23838 | 4.19750  | -1.75745 |
| C       | -4.00599 | 4.51408  | -1.18990 |
| C       | -5.63579 | 2.85621  | -1.87434 |
| C       | 3.03474  | 4.84401  | 1.38199  |
| C       | 5.21347  | 3.77423  | 1.33257  |
| C       | 4.41279  | 4.89741  | 1.58049  |
| H       | -5.10487 | 0.79641  | -1.53472 |
|      | x    | y    | z    |
|------|------|------|------|
| H    | -6.60594 | 2.61135 | -2.31638 |
| H    | -5.90048 | 4.99566 | -2.10466 |
| H    | -3.70514 | 5.55928 | -1.07976 |
| H    | 5.22374  | 1.71503 | 0.70190  |
| H    | 6.29379  | 3.81652 | 1.49164  |
| H    | 4.86861  | 5.82207 | 1.94526  |
| H    | 2.42468  | 5.72065 | 1.60976  |
| H    | 0.29768  | 2.15851 | 2.02215  |
| H    | -1.90116 | 2.68426 | 1.70653  |
| H    | 0.96771  | 5.60855 | -0.18037 |
| H    | -1.34147 | 5.55355 | -1.04412 |
| C    | -3.82519 | -2.10652 | -2.85843 |
| H    | -4.79055 | -1.58375 | -2.77702 |
| H    | -3.66436 | -2.35430 | -3.91896 |
| H    | -3.89412 | -3.05055 | -2.30421 |
| C    | -1.35172 | -2.01477 | -2.35976 |
| H    | -0.52477 | -1.37201 | -2.02808 |
| H    | -1.43445 | -2.86448 | -1.66341 |
| H    | -1.12842 | -2.40915 | -3.36452 |
| C    | -2.53607 | -0.04408 | -3.38498 |
| H    | -2.28386 | -0.43944 | -4.38135 |
| H    | -3.47810 | 0.51733  | -3.46055 |
| H    | -1.74179 | 0.64709  | -3.07619 |
| C    | -5.37324 | -0.31146 | 2.52749  |
| H    | -5.75443 | -1.27028 | 2.15427  |
| H    | -5.67956 | -0.22111 | 3.58182  |
| H    | -5.84661 | 0.50205  | 1.95606  |
| C    | -3.16547 | -1.40968 | 3.12496  |
| H    | -3.38464 | -1.38098 | 4.20444  |
| H    | -3.52676 | -2.37150 | 2.73730  |
| H    | -2.07476 | -1.35842 | 2.98405  |
| C    | -3.38498 | 1.07351  | 3.11118  |
| H    | -2.28898 | 1.15557  | 3.10039  |
| H    | -3.81633 | 1.95848  | 2.61981  |
|   | X    | Y    | Z    |
|---|------|------|------|
| H | -3.71730 | 1.06713 | 4.16017 |
| C | 2.15211  | 0.16574 | 3.39023 |
| H | 1.11956  | 0.22090 | 3.01481 |
| H | 2.12013  | -0.07424 | 4.46343 |
| H | 2.63069  | 1.15083 | 3.27547 |
| C | 2.19808  | -2.26482 | 2.77529 |
| H | 2.03755  | -2.48496 | 3.84213 |
| H | 1.21872  | -2.20772 | 2.27770 |
| H | 2.77170  | -3.09677 | 2.34452 |
| C | 4.36103  | -1.01667 | 3.21399 |
| H | 4.31873  | -1.24600 | 4.29010 |
| H | 4.93894  | -1.81352 | 2.72476 |
| H | 4.89387  | -0.06167 | 3.08405 |
| C | 2.53915  | -1.03456 | -3.13196 |
| H | 2.78629  | -1.03019 | -4.20541 |
| H | 2.45210  | -2.08232 | -2.80762 |
| H | 1.57492  | -0.52845 | -2.97993 |
| C | 3.77722  | 1.14560  | -2.83311 |
| H | 2.83079  | 1.69309  | -2.71164 |
| H | 4.56796  | 1.67282  | -2.27590 |
| H | 4.04525  | 1.14863  | -3.90052 |
| C | 4.99025  | -1.01770 | -2.51530 |
| H | 5.75757  | -0.58043 | -1.85630 |
| H | 4.92921  | -2.09532 | -2.31664 |
| H | 5.32454  | -0.89198 | -3.55607 |
| C | -4.27804 | -2.34181 | 0.11520 |
| C | -3.55098 | -3.51191 | 0.37736 |
| C | -5.65981 | -2.41822 | -0.10220 |
| C | -4.20278 | -4.74644 | 0.42589 |
| H | -2.47311 | -3.44560 | 0.54043 |
| C | -6.30889 | -3.65421 | -0.05967 |
| H | -6.22094 | -1.50643 | -0.31696 |
| C | -5.58215 | -4.81987 | 0.20491 |
| H | -3.63149 | -5.65484 | 0.63270 |
### Calculated cartesian coordinates and energies of E

![Diagram of molecule]

|   |   |   |   |
|---|---|---|---|
| H | -7.38586 | -3.70815 | -0.23669 |
| H | -6.09128 | -5.78637 | 0.23755 |
| C | 3.83706  | -2.51357 | -0.00974 |
| C | 5.13659  | -2.94194 | 0.28773 |
| C | 2.86692  | -3.43622 | -0.43082 |
| C | 5.46757  | -4.29299 | 0.15922 |
| H | 5.89150  | -2.21721 | 0.59837 |
| C | 3.20352  | -4.78584 | -0.55184 |
| H | 1.85211  | -3.09002 | -0.64081 |
| C | 4.50266  | -5.21517 | -0.25924 |
| H | 6.48354  | -4.62589 | 0.38412 |
| H | 2.44721  | -5.50475 | -0.87550 |
| H | 4.76415  | -6.27157 | -0.35766 |

**E(B3LYP)**: -3494.907661 Eₚₜₜ

- Sum of electronic and zero-point Energies: -3493.944193 Eₚₜₜ
- Sum of electronic and thermal Energies: -3493.888609 Eₚₜₜ
- Sum of electronic and thermal Enthalpies: -3493.887665 Eₚₜₜ
- Sum of electronic and thermal Free Energies: -3494.032396 Eₚₜₜ

Number of imaginary frequencies: 0.

|   |   |   |   |
|---|---|---|---|
| S | 0.59546 | 0.21227 | -0.79352 |
| S | -1.42487 | -2.00399 | -1.62096 |
| Si| 2.50206  | -0.76330 | -0.26746 |
| Si| -2.39706 | -0.85393 | -0.04962 |
| N | 3.39194  | 0.95134  | -1.07323 |
| N | 3.41428  | 0.26564  | 0.99279 |
| N | -4.02457 | -0.20573 | -0.83424 |
|   |   |   |   |
|---|---|---|---|
| N | -2.75702 | 0.96324 | 0.46163 |
| C | -0.54377 | -1.06636 | -0.20566 |
| C | -4.75577 | 2.17332 | -0.48572 |
| C | -4.43637 | 3.09578 | -1.49156 |
| C | -4.92213 | -0.69015 | -1.90527 |
| C | 0.10578 | -1.92754 | 0.90666 |
| C | 1.58480 | -2.21312 | 0.65518 |
| C | 3.72364 | 1.28667 | 0.15182 |
| C | -2.90835 | -1.96999 | 1.38054 |
| C | 4.16695 | 2.63854 | 0.60394 |
| C | -3.86878 | 0.99550 | -0.27728 |
| C | -5.27353 | 4.18993 | -1.72883 |
| C | -5.91376 | 2.35572 | 0.28322 |
| C | -6.42794 | 4.36941 | -0.96110 |
| C | 3.01922 | -3.34790 | -1.03732 |
| C | -2.03789 | -3.01605 | 1.80195 |
| C | 1.82574 | -3.44273 | -0.18456 |
| C | 3.53544 | -2.03572 | -1.21437 |
| C | 3.19212 | 3.48217 | 1.16009 |
| C | 3.81168 | -0.00551 | 2.39806 |
| C | -6.74462 | 3.45155 | 0.04704 |
| C | 3.37236 | 1.75137 | -2.31972 |
| C | -0.25203 | -4.37407 | 0.70727 |
| C | 0.95446 | -4.48073 | -0.09475 |
| C | 2.46221 | 2.99042 | -2.19714 |
| C | 4.70091 | -1.85706 | -1.97219 |
| C | -0.70617 | -3.18068 | 1.17468 |
| C | 2.82266 | 0.84091 | -3.43540 |
| C | 5.48795 | 3.08689 | 0.49111 |
| C | 4.79824 | 2.18943 | -2.71055 |
| C | 2.54293 | 0.04935 | 3.27154 |
| C | -2.22196 | 1.93680 | 1.43905 |
| C | -4.16377 | -1.84728 | 1.99669 |
| C | 4.81501 | -4.23688 | -2.40843 |
| C   | 4.55804    | -1.35769    | 2.42563    |
| C   | 3.66399    | -4.44003    | -1.64974   |
| C   | 3.53850    | 4.76302     | 1.59392    |
| C   | -4.32189   | -0.30808    | -3.27247   |
| C   | 5.34415    | -2.94655    | -2.56502   |
| C   | -3.31479   | 2.42157     | 2.41133    |
| C   | -2.46873   | -3.89701    | 2.81156    |
| C   | 4.86108    | 5.20697     | 1.48359    |
| C   | 4.76843    | 1.03963     | 2.99950    |
| C   | -1.13732   | 1.21793     | 2.26152    |
| C   | -1.58584   | 3.12767     | 0.69809    |
| C   | -5.00472   | -2.22182    | -1.75991   |
| C   | 5.83400    | 4.36667     | 0.93346    |
| C   | -6.35062   | -0.12745    | -1.78765   |
| C   | -4.57505   | -2.72164    | 3.00684    |
| C   | -3.72264   | -3.75508    | 3.40859    |
| H   | 5.11193    | -0.85248    | -2.09490   |
| H   | 6.25564    | -2.79685    | -3.15013   |
| H   | 5.31551    | -5.09051    | -2.87403   |
| H   | 3.27477    | -5.45175    | -1.51130   |
| H   | 6.86874    | 4.70781     | 0.84953    |
| H   | 2.77412    | 5.41685     | 2.02117    |
| H   | -4.84594   | -1.05804    | 1.66542    |
| H   | -5.55647   | -2.60245    | 3.47390    |
| H   | -4.03164   | -4.44805    | 4.19600    |
| H   | -1.79320   | -4.69068    | 3.14100    |
| H   | -7.64551   | 3.58860     | 0.64993    |
| H   | -5.02154   | 4.90363     | -2.51687   |
| H   | 0.04922    | -1.29586    | 1.81029    |
| H   | 2.07118    | -2.40456    | 1.62690    |
| H   | -0.87607   | -5.26493    | 0.82328    |
| H   | 1.11020    | -5.39332    | -0.67906   |
| H   | 1.45206    | 2.69683     | -1.87671   |
| H   | 2.85960    | 3.72166     | -1.48035   |
| Symbol | X-coordinate | Y-coordinate | Z-coordinate |
|--------|--------------|--------------|--------------|
| H      | 2.38158      | 3.48967      | -3.17580     |
| H      | 3.44566      | -0.05531     | -3.55847     |
| H      | 1.79832      | 0.51317      | -3.21307     |
| H      | 2.81413      | 1.38965      | -4.38982     |
| H      | 5.20287      | 2.93448      | -2.01376     |
| H      | 5.48022      | 1.32536      | -2.73728     |
| H      | 4.78746      | 2.64334      | -3.71395     |
| H      | 2.02483      | 0.92119      | 3.23375      |
| H      | 1.83828      | -0.81826     | 2.93254      |
| H      | 2.80274      | -0.26576     | 4.31974      |
| H      | 3.95390      | -2.17932     | 2.02287      |
| H      | 5.47536      | -1.29445     | 1.82034      |
| H      | 4.83889      | -1.61903     | 3.45802      |
| H      | -4.29645     | 0.78753      | -3.38677     |
| H      | -3.29499     | -0.69010     | -3.36270     |
| H      | -4.93201     | -0.72178     | -4.09141     |
| H      | -4.05572     | 3.06503      | 1.92065      |
| H      | -3.83497     | 1.56184      | 2.86276      |
| H      | -2.85527     | 3.00740      | 3.22260      |
| H      | 5.68614      | 1.14474      | 2.40472      |
| H      | 4.30919      | 2.02959      | 3.10659      |
| H      | 5.05901      | 0.69610      | 4.00390      |
| H      | -1.54600     | 0.32535      | 2.75909      |
| H      | -0.29399     | 0.91803      | 1.62693      |
| H      | -0.75474     | 1.89806      | 3.03812      |
| H      | -0.81728     | 2.76701      | -0.00216     |
| H      | -2.34056     | 3.69727      | 0.13637      |
| H      | -1.11042     | 3.81418      | 1.41750      |
| H      | -4.01830     | -2.69514     | -1.84712     |
| H      | -5.42421     | -2.49283     | -0.77891     |
| H      | -5.65593     | -2.63526     | -2.54502     |
| H      | -6.75421     | -0.28123     | -0.77516     |
| H      | -6.40781     | 0.94186      | -2.02665     |
| H      | -7.00111     | -0.66064     | -2.49788     |
5.2 Compound 6 – NBO

Natural population analysis on heterocycle 6 at the B3LYP-D3(BJ) / def2-TZVP // B3LYP-D3(BJ) / def2-SVP level using NBO 6\(^{[11]}\) in Gaussian 16 A.03.\(^{[12]}\) Natural populations in the mesoionic heterocycles Münchnones and Montrealones are given for reference, as well as the pyrido-annealed aza-analogues for as close a comparison as possible.

![Münchnone and Montrealone](image)

\[\text{Figure S46. NBO Analysis of compound 6 and five membered heteroatom containing compounds.}\]
Figure S47. NB-Orbital 212: $\pi$(C–N) of compound 6.
Figure 48. NB-HOMO (237): component of pyridine π-system, anion, of compound 6.
Figure S49. NB-LUMO (238): π*(C–N) of compound 6.

Electronic energy of 6 at B3LYP-D3(BJ) / def2-SVP: 3724.8544727 Hartree

Electronic energy of 6 at B3LYP-D3(BJ) / def2-TZVP: -3727.8609604 Hartree

Number of imaginary frequencies: 0

xyz coordinates for 6

|   | x       | y       | z       |
|---|---------|---------|---------|
| S | 0.781494| -0.32375| -1.29905|
| S | -0.75493| -1.02141| 1.59521 |
| Si| -1.24583| -0.78997| -0.53680|
| Si| 2.13828 | -0.24927| 0.43905 |
| N | 3.47549 | 0.63026 | -0.81724|
| N | -3.19469| -0.82596| 0.22981 |
| N | 1.61643 | -1.90938| 2.49379 |
|   |   |   |   |   |
|---|---|---|---|---|
| N | 2.41357700 | 1.56924900 | 0.82917600 |
| N | -2.19098900 | 0.81132700 | -0.77259900 |
| N | 3.44472100 | -1.22698800 | 1.26591500 |
| C | -3.31490700 | 0.43590100 | -0.10124200 |
| C | 3.84849900 | 3.09391700 | -0.56036900 |
| C | -1.67566700 | -2.07407200 | -1.87897200 |
| C | 3.27928100 | 1.77068500 | -0.18600000 |
| C | -1.84191300 | 2.09569000 | -1.43722400 |
| C | -4.43980500 | 1.33477200 | 0.30236700 |
| C | -5.60709600 | 1.45656800 | -0.47470300 |
| C | 3.07074400 | 3.99443100 | -1.30068100 |
| C | 0.31658900 | -3.63322800 | -1.43722400 |
| C | 0.99344500 | -1.04473900 | 1.63866800 |
| C | 5.13986400 | 3.45870800 | -0.15984300 |
| C | -4.30717300 | 2.04950000 | 1.51316200 |
| C | 2.26348000 | 2.36026900 | 2.07461100 |
| C | 1.02313900 | -2.65744500 | 3.48871100 |
| C | 4.07629800 | 0.38647000 | -2.15033400 |
| C | 2.99895300 | -2.03204700 | 2.28173200 |
| C | -0.89928800 | -3.20853900 | -2.22054100 |
| C | -6.64068900 | 2.28102300 | -0.01516300 |
| C | 0.28418900 | -3.90494000 | -0.09908800 |
| C | 3.58192400 | 5.24851700 | -1.63552800 |
| C | -2.79236000 | -1.77853700 | -2.68212800 |
| C | -3.04671400 | 1.99802800 | 2.34124600 |
| C | 5.64571100 | 4.71852400 | -0.48764900 |
| C | -5.36630400 | 2.86142200 | 1.93165800 |
| C | -4.10645100 | -1.72879900 | 0.95691100 |
| C | -6.54502600 | 2.98826600 | 1.18711700 |
| C | 1.52471800 | -3.82757100 | -2.16579000 |
| C | 5.56013300 | 0.79818000 | -2.18345400 |
| C | -3.00453000 | 3.09641300 | -1.52448100 |
| C | 3.97407100 | -1.12400700 | -2.40831800 |
| C | 4.86802500 | 5.61492500 | -1.22615100 |
|  | X          | Y          | Z          |
|---|------------|------------|------------|
| C | 3.31508300 | 1.13570400 | -3.25927000|
| C | 3.73956500 | -2.91631700| 3.05838900 |
| C | -0.69875300| 2.77197600 | -0.66179000|
| C | -5.76186300| 0.77441500 | -1.81087100|
| C | 1.75538700 | -3.54245000| 4.26191800 |
| C | 2.67346500 | -4.24852600| -1.49674300|
| C | 2.13440700 | 3.87152400 | 1.81271100 |
| C | -3.46047700| -3.12444300| 0.93456700 |
| C | 3.12974100 | -3.68800200| 4.05959500 |
| C | 4.87331900 | -1.24307300| 1.03082700 |
| C | 2.63024900 | -4.50490200| -0.12322300|
| C | -1.27510300| -3.99182100| -3.32890800|
| C | 1.42833400 | -4.34589600| 0.56832700 |
| C | 0.98273200 | 1.90329800 | 2.78719600 |
| C | 3.47836900 | 2.08145000 | 2.97830900 |
| C | -3.15287800| -2.55543500| -3.78215300|
| C | -2.38835800| -3.67786100| -4.10584000|
| C | -5.47610200| -1.83086000| 0.26395500 |
| C | -1.41353000| 1.77691900 | -2.88210300|
| C | -4.29187500| -1.28217100| 2.41780900 |
| C | -7.68510800| 3.83977500 | 1.68393300 |
| H | -0.04703100| -2.50397100| 3.60381500 |
| H | 1.23114700 | -4.11015400| 5.03277800 |
| H | 3.72249100 | -4.37426300| 4.66546900 |
| H | 4.80654300 | -3.01247900| 2.86640600 |
| H | 5.22438800 | -2.23591000| 0.69514000 |
| H | 5.12332700 | -0.50862800| 0.26427400 |
| H | 5.42955800 | -0.98268700| 1.94901800 |
| H | 4.40891500 | 2.42654500 | 2.50165900 |
| H | 3.37691300 | 2.60356600 | 3.94287200 |
| H | 3.56911400 | 1.00257900 | 3.17429600 |
| H | 0.81011600 | 2.53633700 | 3.67040500 |
| H | 0.11382600 | 1.98159100 | 2.12084200 |
| H | 1.05255000 | 0.85816700 | 3.10918800 |
| H          | 3.06569300 | 4.32959800 | 1.46129400 |
| H          | 1.34570500 | 4.07419000 | 1.07436100 |
| H          | 1.85622000 | 4.36849800 | 2.75445300 |
| H          | 5.74600300 | 2.75408000 | 0.41266700 |
| H          | 6.65125700 | 4.99946000 | -0.16685200|
| H          | 5.26468600 | 6.59965200 | -1.48380400|
| H          | 2.97177300 | 5.94591100 | -2.21402500|
| H          | 2.06214700 | 3.70685300 | -1.60081000|
| H          | 3.70845400 | 0.83913800 | -4.24414700|
| H          | 2.24542000 | 0.89052500 | -3.21956500|
| H          | 3.43598600 | 2.22328200 | -3.16566100|
| H          | 4.51920300 | -1.69890300 | -1.64772600|
| H          | 2.92773500 | -1.45121200 | -2.39226000|
| H          | 4.40324100 | -1.36490200 | -3.39255700|
| H          | 6.12713000 | 0.32463000 | -1.36764300|
| H          | 6.00680800 | 0.47078000 | -3.13482000|
| H          | 5.68888400 | 1.88534300 | -2.11152700|
| H          | 0.17189600 | 2.11235300 | -0.58232100|
| H          | -0.39656600| 3.70255800 | -1.16870300|
| H          | -1.03196800| 3.03240000 | 0.35301700 |
| H          | -2.64569300| 3.97014500 | -2.08882100|
| H          | -2.40577300| 1.13878100 | 2.10790000 |
| H          | -2.44503300| 2.90803400 | 2.17807400 |
| H          | -3.28704700| 1.96059100 | 3.41440400 |
| H          | -2.49511700| -3.11319200| 1.45660900 |
| H          | -4.12025800| -3.84856400| 1.43550000 |
| H          | -3.29301800| -3.46009200| -0.09839700|
| H          | -4.99519700| 0.01134400 | -1.98046600|
| H          | -6.74417000| 0.28560600 | -1.89449900|
| H          | -5.69273600| 1.50731000 | -2.63212600|
| H          | -7.54704100| 2.37420400 | -0.62067100|
| H          | -5.26498700| 3.41211700 | 2.87156700 |
| H          | -6.07474300| -2.61677200| 0.74978200 |
| H          | -6.04087700| -0.89318900| 0.33294000 |
|   | Column 1 | Column 2 | Column 3 | Column 4 |
|---|----------|----------|----------|----------|
| H | -5.353999700 | -2.10225300 | -0.79481600 |
| H | -3.385336000 | -0.894061000 | -2.453704000 |
| H | -4.023966000 | -2.282994000 | -4.383695000 |
| H | -2.657064000 | -4.307383000 | -4.957833000 |
| H | -0.679052000 | -4.875577000 | -3.568040000 |
| H | 1.564040000 | -3.609380000 | -3.235184000 |
| H | -0.647149000 | -3.779527000 | 0.450826000 |
| H | 1.382893000 | -4.560202000 | 1.636625000 |
| H | 3.608955000 | -4.367646000 | -2.049005000 |
| H | 3.526368000 | -4.829278000 | 0.410491000 |
| H | -3.864504000 | 2.685495000 | -2.066507000 |
| H | -3.343326000 | 3.449959000 | -0.543985000 |
| H | -2.248539000 | 1.318842000 | -3.433736000 |
| H | -1.122721000 | 2.703516000 | -3.401530000 |
| H | -0.561117000 | 1.088081000 | -2.906282000 |
| H | -4.826565000 | -0.324810000 | 2.480912000 |
| H | -4.880264000 | -2.034610000 | 2.966030000 |
| H | -3.316983000 | -1.176122000 | 2.914146000 |
| H | -7.319844000 | 4.739354000 | 2.202661000 |
| H | -8.340538000 | 4.159178000 | 0.860120000 |
| H | -8.308531000 | 3.280746000 | 2.403225000 |
6. Crystallographic Data

6.1 Compound S2

| Property                          | Value                                      |
|----------------------------------|--------------------------------------------|
| Empirical formula                | C_{18}H_{29}ClN_{2}Si                      |
| Formula weight                   | 336.97                                     |
| Temperature                      | 150(2) K                                   |
| Wavelength                       | 1.54184 Å                                  |
| Crystal system                   | Triclinic                                  |
| Space group                      | P-1                                        |
| Unit cell dimensions             | a = 8.8957(6) Å, α = 101.429(5)°.          |
|                                  | b = 9.1640(6) Å, β = 102.349(5)°.          |
|                                  | c = 12.6005(7) Å, γ = 95.939(6)°.          |
| Volume                           | 972.05(11) Å³                              |
| Z                                | 2                                          |
| Density (calculated)             | 1.151 Mg/m³                                |
| Absorption coefficient           | 2.303 mm⁻¹                                 |
| F(000)                           | 364                                        |
| Crystal size                     | 0.350 x 0.190 x 0.130 mm³                  |
| Theta range for data collection  | 3.687 to 67.494°.                          |
| Index ranges                     | -10<=h<=10, -10<=k<=10, -12<=l<=15          |
| Reflections collected            | 6294                                       |
| Independent reflections          | 3424 [R(int) = 0.0353]                      |
| Completeness to theta = 67.494°  | 98.0 %                                     |
| Absorption correction            | Semi-empirical from equivalents            |
| Max. and min. transmission       | 1.00000 and 0.65607                        |
| Refinement method                | Full-matrix least-squares on F²            |
| Data / restraints / parameters    | 3424 / 0 / 227                             |
| Goodness-of-fit on F²             | 1.101                                      |
| Final R indices [I>2sigma(I)]    | R1 = 0.0647, wR2 = 0.1760                   |
|                                  | R1 = 0.0753, wR2 = 0.1828                  |
| Largest diff. peak and hole      | 0.555 and -0.271 e.Å³                      |
6.2 Compound $2^{Mes}$

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | C$_{69}$H$_{86}$N$_4$S$_2$Si$_2$ (including 2 toluene molecules) |
| Formula weight                        | 1091.71                                    |
| Temperature                           | 150(2) K                                   |
| Wavelength                            | 1.54184 Å                                  |
| Crystal system                        | Triclinic                                  |
| Space group                           | $P-1$                                      |
| Unit cell dimensions                  | $\begin{align*}
a &= 14.7039(9) \text{ Å} \\
b &= 14.9136(8) \text{ Å} \\
c &= 16.8768(11) \text{ Å}
\end{align*}$
|                                        | $\begin{align*}
\alpha &= 104.274(5)^\circ \\
\beta &= 95.168(5)^\circ \\
\gamma &= 115.468(5)^\circ
\end{align*}$ |
| Volume                                | 3155.7(4) Å                                |
| Z                                     | 2                                          |
| Density (calculated)                  | 1.149 mg/m$^3$                             |
| Absorption coefficient                | 1.447 mm$^{-1}$                            |
| F(000)                                | 1176                                       |
| Crystal size                          | 0.120 x 0.100 x 0.040 mm$^3$               |
| Theta range for data collection       | 2.772 to 61.498°                          |
| Index range                           | $-17 \leq h \leq 16, -17 \leq k \leq 17, -20 \leq l \leq 19$ |
| Reflections collected                 | 21271                                      |
| Independent reflections, $R_{int}$    | 11330 [R(int) = 0.0395]                    |
| Completeness to theta = 61.498°       | 99.6 %                                     |
| Refinement method                     | Full-matrix least-squares on $F^2$         |
| Data / restraints / parameters        | 11330 / 0 / 714                            |
| Goodness-of-fit on $F^2, S$            | 1.017                                      |
| Final R indices [$I>2\sigma(I)$]      | $R_1 = 0.0649, wR_2 = 0.1721$              |
| R Indices (all data)                  | $R_1 = 0.0897, wR_2 = 0.1958$              |
| Largest diff. peak and hole           | 0.866 and -0.405 e.Å$^3$                   |
### 6.3 Compound 3

| Property                        | Value                      |
|--------------------------------|----------------------------|
| Empirical formula              | C₅₄H₄₈N₂Si                 |
| Formula weight                 | 454.71                     |
| Temperature                    | 150(2) K                   |
| Wavelength                     | 1.54184 Å                  |
| Crystal system                 | Orthorhombic               |
| Space group                    | P₂₁₂₁₂₁                    |
| Unit cell dimensions           | a = 9.07710(10) Å, α = 90° |
|                               | b = 14.34970(10) Å, β = 90°|
|                               | c = 20.6941(2) Å, γ = 90° |
| Volume                         | 2695.48(4) Å³              |
| Z                              | 4                          |
| Density (calculated)           | 1.120 Mg/m³                |
| Absorption coefficient         | 0.896 mm⁻¹                 |
| F(000)                         | 984                        |
| Crystal size                   | 0.320 x 0.250 x 0.050 mm³  |
| Theta range for data collection| 3.748 bis 67.464°          |
| Index range                    | -10→h→10, -17→k→12, -24→l→24|
| Reflections collected          | 18272                      |
| Independent reflections, Rᵢₙ | 4829 [Rᵢₙ = 0.0189]         |
| Completeness                   | 99.8 %                     |
| Absorption correction          | semi empirical (multi scan)|
| Max. and min. transmission     | 1.00000 und 0.76492        |
| Refinement method              | Full-matrix least-squares on F²|
| Data / restraints / parameters | 4829 / 0 / 307             |
| Goodness-of-fit on F², S       | 1.050                      |
| Final R indices [I>2σ(I)]      | R₁ = 0.0289, wR₂ = 0.0784  |
| R Indices (all data)           | R₁ = 0.0295, wR₂ = 0.0812  |
| Largest diff. peak and hole    | 0.292 und -0.162 e.Å³      |
6.4 Compound 4

- Empirical formula: C_{34.50}H_{42}N_{2}S_{2}Si (including 0.5 toluene molecules)
- Formula weight: 576.91
- Temperature: 150(2) K
- Wavelength: 1.54184 Å
- Crystal system: Monoclinic
- Space group: Pc
- Unit cell dimensions:
  - a = 10.97620(10) Å, α = 90 °
  - b = 16.7272(2) Å, β = 102.2820(10)°
  - c = 17.8380(2) Å, γ = 90 °
- Volume: 3200.12(6) Å³
- Z: 4
- Density (calculated): 1.197 Mg/m³
- Absorption coefficient: 2.048 mm⁻¹
- F(000): 1236
- Crystal size: 0.100 x 0.050 x 0.030 mm³
- Theta range for data collection: 2.642 to 67.497°
- Index range: -13≤h≤13, -20≤k≤19, -21≤l≤21
- Reflections collected: 21463
- Independent reflections, R_{int}: 9179 [R_{int} = 0.0243]
- Completeness: 99.5 %
- Absorption correction: semi empirical (multi scan)
- Max. und Min. Transmission: 1.00000 and 0.62662
- Refinement method: Full-matrix least-squares on F²
- Data / restraints / parameters: 9179/ 101 / 731
- Goodness-of-fit on F², S: 1.028
- Final R indices [I>2σ(I)]: R₁ = 0.0322, wR₂ = 0.0825
- R Indices (all data): R₁ = 0.0380, wR₂ = 0.0886
- Largest diff. peak and hole: 0.254 and -0.296 e.Å⁻³
6.5 Compound 6

Empirical formula \( C_{52}H_{68}N_6S_2Si_2 \)
Formula weight 897.42
Temperature 150(2) K
Wavelength 1.54184 Å
Crystal system Monoclinic
Space group \( P2_1/n \)
Unit cell dimensions
\[ a = 16.8842(5) \text{ Å}, \quad \alpha = 90°. \]
\[ b = 17.6363(4) \text{ Å}, \quad \beta = 100.291(3)°. \]
\[ c = 17.9120(6) \text{ Å}, \quad \gamma = 90°. \]
Volume 5247.9(3) Å³
Z 4
Density (calculated) 1.136 Mg/m³
Absorption coefficient 1.649 mm⁻¹
F(000) 1928
Crystal size 0.210 x 0.120 x 0.050 mm³
Theta range for data collection 3.314 to 67.497°.
Index ranges \( -20 \leq h \leq 17, \quad -20 \leq k \leq 21, \quad -21 \leq l \leq 21 \)
Reflections collected 36328
Independent reflections, \( R_{int} \) 9441 \( [R_{int} = 0.0819] \)
Completeness to theta = 67.497° 99.9 %
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 9441 / 0 / 575
Goodness-of-fit on \( F^2, S \) 0.994
Final R indices \( [I>2\sigma(I)] \) \( R_1 = 0.0538, \quad wR_2 = 0.1238 \)
R indices (all data) \( R_1 = 0.0827, \quad wR_2 = 0.1387 \)
Largest diff. peak and hole 0.399 and -0.266 e.Å⁻³
6.6 Compound 8

Empirical formula

\[ \text{C}_{73}\text{H}_{90}\text{N}_4\text{S}_2\text{Si}_2 \] (including 3 benzene molecules)

Formula weight

1143.78

Temperature

150(2) K

Wavelength

1.54184 Å

Crystal system

Triclinic

Space group

\text{P}-1

Unit cell dimensions

\[ \begin{align*}
\text{a} &= 13.8712(5) \text{ Å} \quad \alpha = 82.195(4)^\circ. \\
\text{b} &= 15.6328(7) \text{ Å} \quad \beta = 87.552(3)^\circ. \\
\text{c} &= 15.7624(7) \text{ Å} \quad \gamma = 75.047(4)^\circ. \\
\end{align*} \]

Volume

3271.6(2) Å³

Z

2

Density (calculated)

1.161 Mg/m³

Absorption coefficient

1.418 mm⁻¹

F(000)

1232

Crystal size

0.050 x 0.040 x 0.030 mm³

Theta range for data collection

2.830 to 67.499°.

Index ranges

-14<=h<=16, -18<=k<=18, -18<=l<=18

Reflections collected

22803

Independent reflections, \( R_{\text{int}} \)

11766 [\( R_{\text{int}} = 0.0402 \)]

Completeness to theta = 67.499°

99.6 %

Refinement method

Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters

11766 / 0 / 748

Goodness-of-fit on \( F^2, S \)

1.025

Final R indices [I>2\( \sigma(I) \)]

\( R_1 = 0.0442, \) w\( R_2 = 0.1086 \)

R indices (all data)

\( R_1 = 0.0608, \) w\( R_2 = 0.1219 \)

Largest diff. peak and hole

0.330 and -0.400 e.Å⁻³
6.7 Compound 9

Empirical formula: \( \text{C}_{31}\text{H}_{38}\text{N}_4\text{S}_5\text{Si} \) (including 1 toluene molecule)

Formula weight: 655.04

Temperature: 150(2) K

Wavelength: 1.54184 Å

Crystal system: Triclinic

Space group: \( P-1 \)

Unit cell dimensions:
- \( a = 10.4013(4) \text{ Å} \)
- \( b = 11.3810(4) \text{ Å} \)
- \( c = 14.4360(5) \text{ Å} \)
- \( \alpha = 97.345(3)^\circ \)
- \( \beta = 103.185(3)^\circ \)
- \( \gamma = 96.635(3)^\circ \)

Volume: 1631.56(10) Å\(^3\)

Z: 2

Density (calculated): 1.333 Mg/m\(^2\)

Absorption coefficient: 3.840 mm\(^-1\)

\( F(000) \): 692

Crystal size: 0.020 x 0.020 x 0.010 mm\(^3\)

Theta range for data collection: 3.185 to 67.496°

Index ranges:
- \( -12 \leq h \leq 12 \)
- \( -13 \leq k \leq 13 \)
- \( -17 \leq l \leq 10 \)

Reflections collected: 11109

Independent reflections, \( R_{int} \): 5884 \([R_{int} = 0.0253]\)

Completeness to theta = 67.496°: 99.8 %

Refinement method: Full-matrix least-squares on \( F \)

Data / restraints / parameters: 5884 / 0 / 378

Goodness-of-fit on \( F^2 \), S: 1.038

Final \( R \) indices \([I>2\sigma(I)]\): \( R_1 = 0.0339 \), \( wR_2 = 0.0902 \)

\( R \) indices (all data): \( R_1 = 0.0394 \), \( wR_2 = 0.0958 \)

Largest diff. peak and hole: 0.432 and -0.309 e.Å\(^{-3}\)
### 6.8 Compound 10

![Compound 10](image)

| Property                          | Value                                      |
|-----------------------------------|--------------------------------------------|
| Empirical formula                 | C\textsubscript{30}H\textsubscript{38}N\textsubscript{2}SSi |
| Formula weight                    | 486.77                                     |
| Temperature                       | 150(2) K                                   |
| Wavelength                        | 1.54184 Å                                  |
| Crystal system                    | Triclinic                                  |
| Space group                       | P-1                                        |
| Unit cell dimensions              | a = 9.0115(3) Å                           |
|                                  | b = 18.9015(7) Å                          |
|                                  | c = 19.3421(8) Å                          |
| Volume                            | 3167.4(2) Å                               |
| Z                                 | 4                                          |
| Density (calculated)              | 1.021 Mg/m\textsuperscript{3}             |
| Absorption coefficient            | 1.390 mm\textsuperscript{-1}              |
| F(000)                            | 1048                                       |
| Crystal size                      | 0.080 x 0.040 x 0.020 mm\textsuperscript{3} |
| Theta range for data collection   | 2.975 to 67.499°                           |
| Index ranges                      | -10\leq h \leq 10, -21\leq k \leq 22, -23\leq l \leq 23 |
| Reflections collected             | 22180                                      |
| Independent reflections           | 11426 [R(int) = 0.0417]                     |
| Completeness to theta = 67.499°   | 99.9 %                                     |
| Absorption correction             | Semi-empirical from equivalents           |
| Max. and min. transmission        | 1.00000 and 0.40424                        |
| Refinement method                 | Full-matrix least-squares on F\textsuperscript{2} |
| Data / restraints / parameters    | 11426 / 0 / 631                            |
| Goodness-of-fit on F\textsuperscript{2} | 0.976                                      |
| Final R indices [I>2sigma(I)]     | R1 = 0.0450, wR2 = 0.1119                  |
| R indices (all data)              | R1 = 0.0621, wR2 = 0.1216                  |
| Extinction coefficient            | n/a                                        |
| Largest diff. peak and hole       | 0.202 and -0.310 e.A\textsuperscript{-3}   |
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