Supporting Information

Synthesis of Functionalized Hydrazines: Facile Homogeneous (N-Heterocyclic Carbene)-Pd(0) Catalyzed Diboration and Silaboration of Azobenzenes**

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General Methods, Instrumentation and Starting Materials

The manipulation of air sensitive compounds and their spectroscopic measurements were undertaken using standard Schlenk line techniques under pre-dried argon (using a BASF R2-11(G) catalyst and 4 Å molecular sieves), or in a MBraun glovebox under N₂ (O₂ < 10.0 ppm). All glassware was dried in a 160 °C oven prior to use. All solvents used for air sensitive compounds were dried by vacuum distillation followed by distillation over potassium or stored over activated 4 Å molecular sieves under an Ar atmosphere. Deuterated benzene, C₆D₆, was degassed and dried by refluxing over potassium for 3 days, vacuum transferred into ampoules and stored under N₂.

NMR spectra were recorded on a Varian VNMRS 400 (¹H 399.5 MHz; ¹³C{¹H} 100.46 MHz; ²⁹Si{¹H} 79.4 MHz; ¹¹B{¹H} 128.2 MHz; ¹⁹F 375.9 MHz). Chemical shifts are reported in ppm and are referenced to the residue solvent peak. All spectra carried out on the Varian VNMRS 400 were recorded at 303 K. Elemental analyses were carried out at the Elemental Analysis Service, London Metropolitan University.
Synthesis and Catalysis

Synthesis of 1,2-di-p-tolylidiazene\(^{[1]}\)

\(p\)-Toluidine (0.331 g, 3.09 mmol), copper(I) bromide (0.013 g, 0.09 mmol) and pyridine (22.5 \(\mu\)l, 0.28 mmol) were dissolved in toluene (5 ml). The resulting reaction mixture was heated to 60 °C under an atmosphere of air for 3 d. At this point the reaction mixture was cooled to room temperature and filtered through a plug of silica. The resulting filtrate was concentrated and the crude mixture was purified by flash chromatography (elucent: 100% hexane). Yield: 0.110 g, 34%. \(^1\)H NMR (399.5 MHz, \(\text{C}_6\text{D}_6\)): \(\delta = 7.81\) (d, \(^3J_{HH} = 8.0\) Hz, 4H), 7.30 (d, \(^3J_{HH} = 8.0\) Hz, 4H), 2.43 (s, 6H). \(^{13}\)C\(^{[1]}\)H NMR (100.46 MHz, CDCl\(_3\)): 151.0, 141.3, 129.9, 122.9, 21.6.

Synthesis of 1,2-bis(4-fluorophenyl)diazene\(^{[1]}\)

4-Fluoroaniline (94.6 \(\mu\)l, 1.00 mmol), copper(I) bromide (0.004 g, 0.03 mmol) and pyridine (8.9 \(\mu\)l, 0.11 mmol) were dissolved in toluene (4 ml). The resulting reaction mixture was heated to 60 °C for 48 h under 1 atmosphere of air. Upon cooling, the reaction mixture was filtered through a plug of silica, the filtrate volatiles were removed in vacuo and the crude solid was purified by flash chromatography (elucent: 100% hexane). Yield: 0.100 g, 92%. \(^1\)H NMR (399.5 MHz, CDCl\(_3\)): \(\delta = 7.92\) (m, 4H), 7.20 (m, 4H). \(^1\)H NMR (399.5 MHz, C\(_6\)D\(_6\)): \(\delta = 7.76\) (m, 4H), 6.78 (m, 4H). \(^{13}\)C\(^{[1]}\)H NMR (100.46 MHz, CDCl\(_3\)): \(\delta = 164.6\) (d, \(^4J_{CF} = 251.2\) Hz), 148.2 (d, \(^4J_{CF} = 2.6\) Hz), 125.0 (d, \(^3J_{CF} = 9.0\) Hz), 116.2 (d, \(^2J_{CF} = 23.1\) Hz). \(^{19}\)F NMR (375.9 MHz, CDCl\(_3\)): \(\delta = -109.38\) (m).

Synthesis of Pd(ITMe)\(_2\)(PhC≡CPh) (1)

1 was synthesised following previous literature preparation.\(^{[2]}\)
**Stock solution of 1**

Stock solutions were made in batches; in a glovebox 5mg of 1 was dissolved in 2 ml of C₆D₆ (9.38 µmol, 4.69 x 10⁻³ M)

**Synthesis of 1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2)**

*In C₆D₆*

PhN=NPh (0.025 g, 0.14 mmol), B₂pin₂ (0.041 g, 0.16 mmol) and 1 (0.001 g, 2.62 µmol) were dissolved in C₆D₆ (0.7 ml). The resulting reaction mixture was stirred at room temperature for 2 h. At this point the reaction mixture was filtered by cannula and all volatiles were then removed in vacuo. The resulting off-white solid was recrystallized in hexane at −30 °C. On decanting the volatiles, the colourless crystals were dried under a high vacuum to give a white powder.

*In toluene*

In an ampoule, azobenzene (0.101 g, 0.55 mmol), bis(pinacalato) diboron (0.109 g, 0.43 mmol) and 1 (0.001 g, 2.06 µmol) were dissolved in toluene (2 ml). The resulting reaction mixture was stirred at ambient temperature under an N₂ atmosphere for 2 h. At this stage the reaction mixture was filtered via cannula and the filtrates volatiles were removed in vacuo. The resulting crude solid was re-crystallized in hexane (3 x 5 ml), which resulted in isolation of an off white powder. Yield: 0.119 g, 63%. ¹H NMR (399.5 MHz, C₆D₆): δ = 7.76 (m, 4H, Ph), 7.16 (m, 4H, Ph), 6.81 (m, 2H, p-Ph), 1.12 (s, 12H, Bpin), 1.08 (s, 12H, Bpin). ¹³C{¹H} NMR (100.46 MHz, C₆D₆): δ = 146.5 (i-Ph), 129.2 (Ph), 121.6 (p-Ph), 117.0 (Ph), 83.5 (C, Bpin), 24.8 (CH₃, Bpin), 24.4 (CH₃, Bpin). ¹¹B{¹H} NMR (128.2 MHz, C₆D₆): δ = 25.84. Elem. Anal. Calcd for C₂₄H₃₄O₆N₂B₂: C, 66.09%; H, 7.86%; N, 6.42%. Found: C, 66.41%; H, 7.56%; N, 6.62%.
Synthesis of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-m-tolylhydrazine (3)

3,3’-dimethylazobenzene (0.025 g, 0.12 mmol), B$_2$pin$_2$ (0.041 g, 0.16 mmol) and 1 (0.32 mg, 0.59 µmol) were dissolved in C$_6$D$_6$ (0.7 ml). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 2.5 h. At this point the volatiles were removed in vacuo. The resulting off-white solid was recrystallized in toluene/hexane (1:3, 5.0 ml) and then hexane (2 x 2.0 ml) at −30 °C. Yield: 0.040 g, 72%. $^1$H NMR (399.5 MHz, C$_6$D$_6$): $\delta$ = 7.63 (m, 2H, 6-Ph), 7.63 (s, 2H, 2-Ph), 7.13 (m, 2H, 5-Ph), 6.68 (d, $^J_{HH}$ = 7.4 Hz, 2H, 4-Ph), 2.11 (s, 6H, Me), 1.14 (s, 12H, Bpin), 1.11 (s, 12H, Bpin). $^{13}$C{$^1$H} NMR (100.46 MHz, C$_6$D$_6$): $\delta$ = 146.7 (1-Ph), 138.6 (3-Ph), 129.1 (5-Ph), 122.5 (4-Ph), 117.7 (2-Ph), 114.5 (6-Ph), 83.5 (C, Bpin), 24.9 (CH$_3$, Bpin), 24.4 (CH$_3$, Bpin), 21.9 (Me). $^{11}$B{$^1$H} NMR (128.2 MHz, C$_6$D$_6$): $\delta$ = 25.54. Elem. Anal. Calcd for C$_{26}$H$_{38}$O$_4$N$_2$B$_2$: C, 67.27%; H, 8.25%; N, 6.03%. Found: C, 67.33%; H, 8.27%; N, 6.10%.

Synthesis of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-p-tolylhydrazine (4)

1,2-di-p-Tolyl diazene (0.025 g, 0.11 mmol), B$_2$pin$_2$ (0.033 g, 0.13 mmol) and 1 (0.30 mg, 0.56 µmol) were dissolved in C$_6$D$_6$ (0.7 ml). The resulting reaction mixture was stirred at room temperature under a N$_2$ atmosphere for 3 h. At this point, the volatiles were removed in vacuo and the crude reaction mixture was recrystallized in hexane (3 x 2 ml) at −30 °C resulting in the isolation of a white powder. Yield: 0.040 g, 75%. $^1$H NMR (399.5 MHz, C$_6$D$_6$, 400 MHz): $\delta$ = 7.69 (m, 4H, o-PhMe), 7.00 (m, 4H, m-PhMe), 2.07 (s, 6H, PhMe), 1.15 (s, 12H, Bpin), 1.11 (s, 12H, Bpin). $^{13}$C{$^1$H} NMR (100.46 MHz, C$_6$D$_6$): $\delta$ = 144.2 (i-PhMe), 130.4 (p-PhMe), 129.7 (m-PhMe), 117.3 (o-PhMe), 83.4 (C, Bpin), 24.9 (CH$_3$, Bpin), 24.5 (CH$_3$, Bpin), 20.6
(PhMe). $^{11}$B{${}^1$H} NMR (128.2 MHz, C$_6$D$_6$): $\delta = 25.53$. Elem. Anal. Calcd for C$_{26}$H$_{38}$O$_4$N$_2$B$_2$: C, 67.27%; H, 8.25%; N, 6.03%. Found: C, 67.19%; H, 8.27%; N, 6.12%.

Synthesis of 1-(4-methoxyphenyl)-2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5)

1-(4-Methoxyphenyl)-2-phenyldiazene (0.099 g, 0.46 mmol), B$_2$pin$_2$ (0.144 g, 0.61 mmol) and 1 (0.001 g, 0.24 µmol) were dissolved in C$_6$D$_6$ (0.7 ml). The resulting reaction mixture was stirred at room temperature under a N$_2$ atmosphere for 4 h. At this stage the sample was filtered via a cannula, the filtrate volatiles were removed in vacuo and the resulting off-white solid was recrystallized in hexane (3 x 4 ml). Yield: 0.170 g, 79%. $^1$H NMR (399.5 MHz, C$_6$D$_6$): $\delta = 7.77$ (m, 2H, m-Ph), 7.62 (m, 2H, PhOMe), 7.18 (m, 2H, o-Ph), 6.83 (m, 1H, p-Ph), 6.75 (m, 2H, PhOMe), 3.28 (s, 3H, OMe), 1.15 (s, 6H, Bpin), 1.14 (s, 6H, Bpin), 1.11 (s, 6H, Bpin), 1.10 (s, 6H, Bpin). $^{13}$C{${}^1$H} NMR (100.46 MHz, C$_6$D$_6$): $\delta = 155.2$ (p-PhOMe), 146.7 (i-Ph), 139.7 (i-PhOMe), 129.1 (o-Ph), 121.5 (p-Ph), 118.6 (PhOMe), 117.2 (m-Ph), 114.6 (PhOMe), 83.5 (C, Bpin), 55.0 (OMe), 24.9 (CH$_3$, Bpin), 24.5 (CH$_3$, Bpin). $^{11}$B{${}^1$H} NMR (128.2 MHz, C$_6$D$_6$): $\delta = 25.30$. Elem. Anal. Calcd for C$_{25}$H$_{36}$O$_5$N$_2$B$_2$: C, 64.41%; H, 7.78%; N, 6.01%. Found: C, 64.28%; H, 7.65%; N, 6.09%.

Synthesis of N-(4-(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)hydrazinyl)-2-methylphenyl)acetamide (6)

4-Aacetamido-2',3-dimethylazobenzene (0.120 g, 0.45 mmol), B$_2$pin$_2$ (0.144 g, 0.57 mmol) and 1 (0.001 g, 2.25 µmol) were dissolved in toluene (1.5 ml). The resulting reaction mixture was heated to 80 °C under a N$_2$ atmosphere for 22 h. At this point, the reaction mixture was cooled to room temperature, dissolved in dioxane (15 ml) and filtered via cannula. The filtrate volatiles were removed in vacuo. The off white solid was recrystallized in toluene/hexane (5:1, 2 x 5
ml) at −30 °C and then washed with hexane (5 ml). Yield: 0.169 g, 72%. ¹H NMR (399.5 MHz, C₆D₆): δ = 7.92 (d, ³J_HH = 8.7 Hz, 1H, [1]5-PhH), 7.74 (m, 1H, [2]4-PhH), 7.63 (d, ³J_HH = 8.7 Hz, [1]6-PhH), 7.47 (s, 1H, [1]2-PhH), 7.06 (m, 2H, [2]3-PhH/[2]5-PhH), 6.88 (m, 1H, [2]6-PhH), 5.84 (s, 1H, C(O)NH), 2.63 (s, 3H, [2]2-PhMe), 1.83 (s, 3H, [1]3-PhMe), 1.51 (s, 3H, MeC(O)NH−), 1.15 (s, 12H, Bpin), 1.13 (s, 12H, Bpin). ¹³C{¹H} NMR (100.46 MHz, C₆D₆): δ = 166.7 (C(O)NH), 144.9 ([2]1-Ph), 143.8 ([1]1-Ph), 132.9 ([2]2-Ph), 131.5, 131.4 ([2]3-Ph, 129.8, 126.6 ([2]5-Ph), 125.0 ([2]6-Ph), 124.7 ([2]4-Ph), 124.2 ([1]5-Ph), 122.0 ([1]2-Ph), 118.6 ([1]6-Ph), 83.5 (C, Bpin), 25.1 (CH₃, Bpin), 25.1 (CH₃, Bpin), 24.6 (CH₃, Bpin), 24.4 (Bpin), 23.6 (MeC(O)NH), 19.8 ([2]2-PhMe), 18.1 ([1]3-PhMe). ¹¹B{¹H} (128.2 MHz, C₆D₆): δ = 25.22. Elem. Anal. Calcd for C₂₈H₄₁O₅N₃B₂: C, 64.52%; H, 7.93%; N, 8.06%. Found: C, 64.66%; H, 8.07%; N, 8.21%.

Synthesis of 1,2-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1,2-diphenylhydrazine (7)

Azobenzene (0.025 g, 0.14 mmol), 5,5,5′,5′-tetramethyl-2,2′-bi(1,3,2-dioxaborinane) (0.035 g, 0.15 mmol) and 1 (0.001 g, 2.63 µmol) were dissolved in C₆D₆ (0.7 ml). The resulting reaction mixture was heated to 80 °C under an N₂ atmosphere for 48 h. At this stage, the reaction mixture was cooled to room temperature, the volatiles were removed in vacuo. The resulting brown oily solid was recrystallized in toluene/hexane (2:3, 2 ml) and then hexane (2 x 2 ml) at −30 °C. A colourless crystalline solid was obtained as a result. Yield: 0.043 g, 77%. ¹H NMR (399.5 MHz, C₆D₆): δ = 7.83 (d, ³J_HH = 8.1 Hz, 4 H, Ph), 7.23 (m, 4H, Ph), 6.86 (pseudo t, ³J_HH = 7.3 Hz, 2H, p-Ph), 3.37 (m, 8H, CH₂), 0.63 (s, 12H, CH₃). ¹³C{¹H} NMR (100.46 MHz, C₆D₆): δ = 147.1 (i-Ph), 128.5 (Ph), 120.8 (p-Ph), 118.0 (Ph), 72.2 (CH₂), 31.4 (C{CH₃}₂), 21.1 (CH₃). ¹¹B{¹H} NMR (128.2 MHz, C₆D₆): δ = 21.32. Elem. Anal. Calcd for C₂₂H₃₆O₄N₂B₂: C, 64.75%; H, 7.41%; N, 6.86%. Found: C, 64.66%; H, 7.44%; N, 6.90%.
Synthesis of 1,2-bis(benzo[d][1,3,2]dioxaborol-2-yl)-1,2-diphenylhydrazine (8)

In C₆D₆

Azobenzene (0.025 g, 0.14 mmol), 2,2'-bibenzo[d][1,3,2]dioxaborole (0.035 g, 0.15 mmol) and 1 (0.001 g, 2.63 µmol) were dissolved in C₆D₆ (0.7 ml). The resulting reaction mixture was heated at 80 °C under a N₂ atmosphere for 24 h. At this stage the volatiles were removed in vacuo, the crude brown oily solid was then recrystallized in toluene/hexane (1:3, 2 ml) and then toluene (1 x 5 ml) at −30 °C. This resulted in the isolation of an off-white powdered solid.

In toluene

Azobenzene (0.060 g, 0.32 mmol), 2,2'-bibenzo[d][1,3,2]dioxaborole (0.078 g, 0.33 mmol) and 1 (0.003 g, 6.38 µmol) were dissolved in toluene (1.5 ml). The resulting reaction mixture was heated to 80 °C and stirred at this temperature under a N₂ atmosphere for 24 h. The volatiles were removed in vacuo and the crude oily solid was recrystallized in toluene (3 x 3 ml) at −30 °C. The resulting off-white powder was washed with hexane (3 x 3 ml). Yield: 0.089 g, 66%.

¹H NMR (399.5 MHz, C₆D₆): δ = 7.70 (d, 3J_HH = 8.3 Hz, 4H, N{o-Ph}), 7.13 (m, 4H, N{m-Ph}), 6.87 (dd, J = 8.3 Hz, 6.6 Hz, 2H, N{p-Ph}), 6.81 (m, 4H, cat-3-Ph), 6.64 (m, 4H, cat-2-Ph). ¹³C{¹H} NMR (100.46 MHz, C₆D₆): δ = 148.8 (cat-1-Ph), 144.3 (N{i-Ph}), 129.7 (N{m-Ph}), 123.6 (N{p-Ph}), 122.7 (cat-2-Ph), 117.7 (N{o-Ph}), 112.5 (cat-3-Ph). ¹¹B{¹H} (128.2 MHz, C₆D₆): δ = 26.65. Elem. Anal. Calcd for C₂₄H₁₈O₄N₂B₂: C, 68.63%; H, 4.32%; N, 6.67%. Found: C, 68.63%; H, 4.38%; N, 6.59%.

Synthesis of 1-(dimethyl(phenyl)silyl)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (9)

In C₆D₆

Azobenzene (0.025 g, 0.14 mmol), PhMe₂SiBpin (46.0 µl, 0.17 mmol) and 1 (0.36 mg, 0.68 µmol) were dissolved in C₆D₆ (0.7 ml). The resulting reaction mixture was stirred at room
temperature for 2 h. At this point the volatiles were removed in vacuo and the resulting oily solid was washed with cold hexane (4 x 1 ml). Upon drying the resulting white powder was obtained without further purification.

In toluene
Azobenzene (0.070 g, 0.38 mmol), PhMe₂SiBpin (0.120 g, 0.46 mmol) and 1 (0.001 g, 1.31 µmol) were dissolved in toluene (1.5 ml). The reaction mixture was stirred at room temperature under a N₂ atmosphere for 2 h. At this stage the volatiles were removed in vacuo, the resulting oily solid was stirred in deionized H₂O overnight and a white powder was obtained upon filtering. Yield: 0.148 g, 87%. ¹H NMR (399.5 MHz, C₆D₆): δ = 7.85 (m, 2H, SiMe₂Ph), 7.68 (m, 2H, o-Ph{1}), 7.23 (m, 3H, SiMe₂Ph), 7.16 (m, 2H, m-Ph{1}), 7.03 (m, 4H, o- and m-Ph{2}), 6.85 (m, 1H, p-Ph{1}), 6.68 (m, 1H, p-Ph{2}), 1.05 (s, 6H, Bpin), 1.01 (s, 6H, Bpin), 0.61 (s, 3H, SiMe₂Ph), 0.58 (s, 3H, SiMe₂Ph). ¹³C{¹H} NMR (100.46 MHz, C₆D₆): δ = 149.8 (i-Ph{2}), 147.5 (i-Ph{1}), 138.3 (SiMe₂i-Ph), 134.8 (SiMe₂Ph), 129.7 (SiMe₂p-Ph), 129.3 (Ph{2}), 129.1 (m-Ph{1}), 128.1 (SiMe₂Ph), 121.9 (p-Ph{1}), 119.1 (p-Ph{2}), 118.0 (o-Ph{1}), 114.1 (Ph{2}), 83.6 (C, Bpin), 24.8 (CH₃, Bpin), 24.4 (CH₃, Bpin), −0.7 (SiMe₂Ph), −0.8 (SiMe₂Ph). ¹¹B{¹H} NMR (128.2 MHz, C₆D₆): δ = 25.78. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆): δ = 4.59. Elem. Anal. Caled for C₂₆H₃₃O₂N₂SiB: C, 70.26%; H, 7.48%; N, 6.30%. Found: C, 70.18%; H, 7.50%; N, 6.30%.

Synthesis of 1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-m-tolylhydrazine (10)
1,2-di-m-Tolyldiazene (0.024 g, 0.11 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (0.040 g, 0.15 mmol) and 1 (0.30 mg, 0.56 µmol) were dissolved in C₆D₆ (0.7 ml). The resulting reaction mixture was stirred at room temperature under a N₂ atmosphere. After 2.5 h, the volatiles were removed in vacuo, deionized H₂O (100 ml) was
added and the crude reaction mixture was stirred at room temperature for 15 h. The product was obtained cleanly as a white powder on filtering the precipitate. Yield: 0.052 g, 98%. $^1$H NMR (399.5 MHz, C$_6$D$_6$): $\delta =$ 7.88 (m, 2H, SiMe$_2$-o-Ph), 7.62 (dd, $J =$ 8.3, 2.2 Hz, 1H, [2]Ph(6)), 7.55 (s, 1H, [2]Ph(2)), 7.24 (m, 3H, SiMe$_2$m/p-Ph), 7.15 (m, 1H, [2]Ph(5)), 6.96 (m, 3H, [1]Ph(2/5/6)), 6.71 (m, 1H, [2]Ph(4)), 6.53 (m, 1H, [1]Ph(4)), 2.13 (s, 3H, [2]Me), 2.01 (s, 3H, [1]Me), 1.08 (s, 6H, Bpin), 1.04 (s, 6H, Bpin), 0.67 (s, 3H, SiMe$_2$Ph), 0.62 (s, 3H, SiMe$_2$Ph). $^{13}$C{$^1$H} NMR (100.46 MHz, C$_6$D$_6$): $\delta =$ 149.9 ([1]Ph(1)), 147.6 ([2]Ph(1)), 138.7 ([1]Ph(3)), 138.6 ([2]Ph(3)), 138.5 (SiMe$_2$-Ph), 134.9 (SiMe$_2$-o-Ph), 129.7 (SiMe$_2$p-Ph), 129.3, 129.1 ([2]Ph(5)), 128.1 (SiMe$_2$m-Ph), 122.7 ([2]Ph(4)), 120.1 ([1]Ph(4)), 118.4 ([2]Ph(2)), 115.3 ([2]Ph(6)), 114.6, 111.5, 83.5 (C, Bpin), 24.8 (CH$_3$, Bpin), 24.4 (CH$_3$, Bpin), 21.8 ([1]Me), 21.8 ([2]Me), −0.6 (SiMe$_2$Ph), −0.9 (SiMe$_2$Ph). $^{11}$B{$^1$H} NMR (128.2 MHz, C$_6$D$_6$): $\delta =$ 25.84. $^{29}$Si{$^1$H} NMR (79.4 MHz, C$_6$D$_6$): $\delta =$ 4.40. Elem. Anal. Calcd for C$_{28}$H$_{37}$N$_2$O$_2$SiB: C, 71.17%; H, 7.89%; N, 5.93%. Found: C, 71.06%; H, 7.74%; N, 5.75%.

**Synthesis of 1-(dimethyl(phenyl)silyl)-1,2-bis(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (11)**

1,2-bis(4-Fluorophenyl)diazene (0.027 g, 0.12 mmol), PhMe$_2$SiBpin (0.038 g, 0.14 mmol) and 1 (0.33 mg, 0.62 µmol) were dissolved in C$_6$D$_6$ (0.7 ml). The resulting reaction mixture was stirred at room temperature for 1.5 h under a N$_2$ atmosphere. At this stage the volatiles were removed in vacuo, deionized H$_2$O (100 ml) was added and the reaction mixture was stirred for a further 24 h at room temperature. The H$_2$O was then decanted and the off white solid was dried under a high vacuum. Yield: 0.050 g, 84%. $^1$H NMR (399.5 MHz, C$_6$D$_6$): $\delta =$ 7.68 (m, 2H, SiMe$_2$-o-Ph), 7.37 (m, 2H, [2]o-PhF), 7.17 (m, 3H, SiMe$_2$m/p-Ph), 6.74 (m, 2H, [1]o-PhF), 6.74 (m, 2H, [2]m-PhF), 6.60 (m, 2H, [1]m-PhF), 0.97 (s, 6H, Bpin), 0.92 (s, 6H, Bpin), 0.48 (s, 3H, SiMe$_2$Ph), 0.43 (s, 3H, SiMe$_2$Ph). $^{13}$C{$^1$H} NMR (100.46 MHz, C$_6$D$_6$): $\delta =$ 159.8 (d,
$^{1}J_{CF} = 239.7$ Hz, $[2]p$-PhF), 158.3 (d, $^{1}J_{CF} = 236.7$ Hz, $[1]p$-PhF), 145.6 ($[1]i$-PhF), 143.3 ($[2]i$-PhF), 137.8 (SiMe$_3$-Ph), 134.6 (SiMe$_2$-Ph), 130.0 (SiMe$_2$-p-Ph), 128.2 (SiMe$_2$-m-Ph), 119.1 (d, $^{2}J_{CF} = 7.6$ Hz, $[2]o$-PhF), 115.8 (d, $^{2}J_{CF} = 21.9$ Hz, $[2]m$-PhF), 115.6 (d, $^{2}J_{CF} = 21.9$ Hz, $[1]m$-PhF), 114.7 (d, $^{3}J_{CF} = 7.6$ Hz, $[1]o$-PhF), 83.7 (C, Bpin), 24.8 (CH$_3$, Bpin), 24.3 (CH$_3$, Bpin), −0.8 (SiMe$_2$Ph), −1.1 (SiMe$_2$Ph).

$^{11}$B$^{[1]}$H NMR (128.2 MHz, C$_6$D$_6$): δ = 25.35.

$^{19}$F$^{[1]}$H NMR (375.9 MHz, C$_6$D$_6$): δ = −122.60 (m), −126.70 (m).

$^{29}$Si$^{[1]}$H NMR (79.4 MHz, C$_6$D$_6$): δ = 4.85. Elem. Anal. Calcd for C$_{26}$H$_{31}$O$_2$N$_2$F$_2$SiB: C, 65.00%; H, 6.50%; N, 5.83%. Found: C, 64.81%; H, 6.39%; N, 6.00%.

**Synthesis of 1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-p-tolylhydrazine (12)**

1,2-di-p-Tolylidiazene (0.031 g, 0.15 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (45.0 µl, 0.17 mmol) and I (0.40 mg, 0.74 µmmol) were dissolved in C$_6$D$_6$ (0.7 ml). The resulting reaction was stirred at room temperature under a N$_2$ atmosphere for 8 h. At this stage the volatiles were removed in vacuo, deionized H$_2$O (80 ml) was added and the precipitated mixture was stirred at room temperature for 16 h. The H$_2$O was decanted resulting in isolation of a white powder. Yield: 0.069 g, 91%. $^{1}$H NMR (399.5 MHz, C$_6$D$_6$): δ = 7.90 (m, 2H, SiMe$_2$-o-Ph), 7.64 (m, 2H, $[2]o$-PhMe), 7.26 (m, 3H, SiMe$_2$m,p-Ph), 7.00 (m, 4H, $[1]o$-PhMe and $[2]m$-PhMe), 6.82 (m, 2H, $[1]m$-PhMe), 2.10 (s, 3H, $[2]$PhMe), 2.04 (s, 3H, $[1]$PhMe), 1.07 (s, 6H, Bpin), 1.03 (s, 6H, Bpin), 0.65 (s, 3H, SiMe$_2$Ph), 0.62 (s, 3H, SiMe$_2$Ph). $^{13}$C$^{[1]}$H NMR (100.46 MHz, C$_6$D$_6$): δ = 147.5 ($[1]i$-PhMe), 145.2 ($[2]i$-PhMe), 138.7 (SiMe$_3$i-Ph), 134.8 (SiMe$_2$-o-Ph), 130.8 ($[2]p$-PhMe), 129.9 ($[1]m$-PhMe), 129.7 ($[2]m$-PhMe), 129.7 ($[1]$SiMe$_2$p-Ph), 127.9 (SiMe$_2$m-Ph), 127.7 ($[1]$p-PhMe), 118.1 ($[2]$o-PhMe), 114.1 ($[1]$o-PhMe), 83.4 (C, Bpin), 24.8 (CH$_3$, Bpin), 24.4 (CH$_3$, Bpin), 20.6 ($[1]$PhMe), 20.4 ($[2]$PhMe), −0.6 (SiMe$_2$Ph), −0.8 (SiMe$_2$Ph). $^{11}$B$^{[1]}$H NMR (128.2 MHz, C$_6$D$_6$): δ = 25.81.
\[ \text{Reaction of 1-(4-methoxyphenyl)-2-phenyldiazene and PhMe}_2\text{SiBpin} \]

1-(4-Methoxyphenyl)-2-phenyldiazene (0.025 g, 0.12 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (35.0 µl, 0.13 mmol) and 1 (0.31 mg, 0.59 µmol) were dissolved in \( \text{C}_6\text{D}_6 \) (0.7 ml). The resulting reaction mixture was stirred at room temperature for 24 h under a \( \text{N}_2 \) atmosphere. Crude NMR analysis at this stage showed a mixture of inseparable regioisomers (see \(^1\text{H} \) NMR spectrum below).

\[ \text{Hydrolysis of 2 to form 1,2-diphenylhydrazine} \]

To 2 (0.014 g, 31.49 µmol) degassed deionized \( \text{H}_2\text{O} \) (10 ml) was added. The resulting reaction mixture was stirred for 48 h at room temperature under an argon atmosphere. At this stage the \( \text{H}_2\text{O} \) was filtered off and the resulting white powder was dried in vacuo. Yield: 0.005 g, 90%.

\(^1\text{H} \) NMR (399.5 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 7.08 \) (m, 4H), 6.76 (m, 2H), 6.62 (m, 4H), 4.71 (s, 2H).

\(^{13}\text{C} \{^1\text{H}\} \) NMR (100.46 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 149.4, 129.5, 120.0, 112.7. \)

\( \text{NMR resonances agree with that found for 1,2-diphenylhydrazine}\[^{3}\] \)

\[ \text{Based driven alcoholysis of 9 to form 1,2-diphenylhydrazine} \]

9 (0.025 g, 0.06 mmol) and KOrBu (0.013 g, 0.12 mmol) was dissolved in \( \text{iPrOH/toluene} \) (1:1, 2 ml). The resulting reaction mixture was stirred at room temperature for 22 h under an \( \text{N}_2 \) atmosphere. The volatiles were removed in vacuo and the product extracted with hexane (2 x 1 ml). Colourless crystals were obtained on recrystallizing the hexane extracts at \( -30 \) °C. Yield: 0.009 g, 85%. [See above for NMR assignment]
Spectroscopic Data

1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2)
1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-m-tolyldiazine (3)
1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-p-tolylhydrazine (4)
1-(4-methoxyphenyl)-2-phenyl-1,2-bis(4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5)
N-(4-(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)hydrazinyl)-2-methylphenyl)acetamide (6)
1,2-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1,2-diphenylhydrazine (7)
1,2-bis(benzo[d][1,3,2]dioxaborol-2-yl)-1,2-diphenylhydrazine (8)
1-(dimethyl(phenyl)silyl)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (9)
1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-m-tolylhydrazine (10)
1-(dimethyl(phenyl)silyl)-1,2-bis(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-
dioxaborolan-2-yl)hydrazine (11)
1-(dimethylphenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-p-tolylhydrazine (12)
Reaction of 1-(4-methoxyphenyl)-2-phenyldiazene and PhMe$_2$SiBpin (Crude)

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{N} \\
& \quad \text{N} \quad \text{N}
\end{align*}
\]

+ PhMe$_2$Si—Bpin → 0.5 mol% 1 \\
C$_6$D$_6$, r.t., 24 h → PhMe$_2$Si—Bpin + PhMe$_2$Si—Bpin

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{N} \\
& \quad \text{N} \quad \text{N}
\end{align*}
\]
1,2-diphenylhydrazine
**X-ray Crystallography Data**

The crystal data of 2 was collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo\(_{\text{K}a}\) radiation. The structure was solved using intrinsic phasing method (SHELXT\(^{[4]}\)), refined with the SHELXL program,\(^{[5]}\) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. Single crystal X-ray diffraction data for 4, 9 and 11 were collected at the University of Sussex on an Agilent Technologies Xcalibur Gemini Ultra diffractometer (\(\lambda\text{CuK}\alpha = 1.54184\)) equipped with a Eos CCD area detector. The data were collected at 173 K using an Oxford Cryosystems Cobra low temperature device. Data were processed using CrysAlisPro, and the unit cell parameters were refined against all data. Semi empirical absorption corrections were carried out using the MULTI-SCAN program.\(^{[6]}\) The structures were solved by using an intrinsic phasing method (SHELXT\(^{[4]}\)), and refined F0 by full matrix least squares refinement using SHELXL-2013,\(^{[7]}\) within OLEX2.\(^{[8]}\) All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added at calculated positions and refined using riding models with isotropic displacement parameters based on the equivalent isotropic displacement parameter (Ueq) of the parent atoms. The cif files for 2, 4, 9 and 11 have been deposited with the CCDC and have been given the deposition numbers 1501645, 1501646, 1501647 and 1501648 respectively.
Crystal Structure Information for 2

![Crystal structure diagram](image)

**Table S1 Crystal data and structure refinement for 2.**

| Property                  | Value               |
|---------------------------|---------------------|
| Empirical formula         | C_{24}H_{34}B_{2}N_{2}O_{4} |
| Formula weight            | 436.15              |
| Temperature/K             | 103.15              |
| Crystal system            | orthorhombic        |
| Space group               | P2_12_12_1          |
| a/Å                       | 11.248(3)           |
| b/Å                       | 12.019(6)           |
| c/Å                       | 17.861(4)           |
| α/°                       | 90                  |
| β/°                       | 90                  |
| γ/°                       | 90                  |
| Volume/Å³                 | 2414.6(15)          |
| Z                         | 4                   |
\( \rho_{\text{calc}} / \text{cm}^3 \) 1.200
\( \mu / \text{mm}^{-1} \) 0.079
F(000) 936.0
Crystal size/mm\(^3\) 0.129 × 0.116 × 0.105
Radiation MoK\( \alpha \) (\( \lambda = 0.71073 \))
2\( \Theta \) range for data collection/° 4.084 to 52.744
Index ranges -14 \( \leq \) h \( \leq \) 9, -15 \( \leq \) k \( \leq \) 10, -14 \( \leq \) l \( \leq \) 22
Reflections collected 10281
Independent reflections 4865 [R\(_{\text{int}}\) = 0.0530, R\(_{\text{sigma}}\) = 0.0865]
Data/restraints/parameters 4865/522/383
Goodness-of-fit on F\(^2\) 1.017
Final R indexes [I\( \geq \)2\( \sigma \) (I)] R\(_1\) = 0.0483, wR\(_2\) = 0.0890
Final R indexes [all data] R\(_1\) = 0.0756, wR\(_2\) = 0.0982
Largest diff. peak/hole / e Å\(^{-3}\) 0.16/-0.21
Flack parameter -0.2(10)

Table S2 Fractional Atomic Coordinates (\( \times 10^4 \)) and Equivalent Isotropic Displacement Parameters (Å\(^2 \times 10^3 \)) for 2. U\(_{\text{eq}}\) is defined as \( 1/3 \) of the trace of the orthogonalised U\(_{\text{ij}}\) tensor.

| Atom | x        | y         | z      | U(eq) |
|------|----------|-----------|--------|-------|
| O1   | 1114.0(17) | 7254.9(18) | 7147(1) | 16.7(5) |
| N1   | 2296(2)   | 6083(2)   | 6285.0(12) | 16.3(6) |
| C1   | 2720(3)   | 6894(3)   | 5769.0(15) | 15.2(7) |
| B1   | 1542(3)   | 6249(3)   | 6921.5(17) | 15.1(8) |
|    |    |    |    |    |
|----|----|----|----|----|
| O2 | 1185.4(17) | 5370.2(18) | 7358.4(10) | 18.3(5) |
| N2 | 2790(2) | 5001(2) | 6218.1(12) | 15.4(6) |
| C2 | 3577(3) | 6625(3) | 5235.9(16) | 23.1(8) |
| C3 | 3974(3) | 7422(3) | 4736.0(16) | 30.7(9) |
| C4 | 3528(3) | 8491(3) | 4748.4(17) | 24.1(8) |
| C5 | 2680(3) | 8758(3) | 5276.1(15) | 23.7(8) |
| C6 | 2281(3) | 7976(3) | 5782.7(16) | 19.2(8) |
| C7 | 2178(3) | 4256(3) | 5737.4(15) | 16.7(7) |
| C8 | 2568(3) | 3158(3) | 5657.3(15) | 19.4(8) |
| C9 | 1964(3) | 2444(3) | 5183.3(16) | 23.2(8) |
| C10 | 963(3) | 2790(3) | 4790.9(15) | 24.3(8) |
| C11 | 589(3) | 3870(3) | 4870.3(15) | 24.6(8) |
| C12 | 1192(3) | 4605(3) | 5331.1(14) | 19.4(8) |
| C13 | 296(3) | 7045(3) | 7766.4(15) | 18.2(8) |
| C14 | 669(3) | 5864(3) | 8035.9(15) | 19.2(8) |
| C15 | -954(3) | 7096(3) | 7438.6(16) | 26.2(9) |
| C16 | 447(3) | 7954(3) | 8344.6(16) | 23.0(8) |
| C17 | -351(3) | 5138(3) | 8294.8(17) | 27.4(8) |
| C18 | 1651(3) | 5865(3) | 8619.8(15) | 26.6(9) |
| B3 | 3900(50) | 4890(60) | 6710(40) | 15.8(18) |
| O3 | 4130(13) | 5519(14) | 7265(8) | 16.0(17) |
| C19 | 5129(14) | 4933(16) | 7651(9) | 18.4(16) |
| C20 | 5680(15) | 4239(16) | 7020(9) | 18.7(16) |
| Atom | U₁₁   | U₂₂   | U₃₃   | U₁₂  | U₁₃  | U₂₃  |
|------|-------|-------|-------|------|------|------|
| O1   | 15.2(11) | 19.4(14) | 15.5(9) | -0.7(9) | 3.7(9) | 0.1(10) |
| N1   | 14.2(13) | 17.2(17) | 17.6(11) | 0.1(12) | 0.8(10) | 3.9(13) |
| C1   | 11.7(15) | 19(2) | 14.7(14) | 0.4(13) | -2.1(12) | -0.3(15) |
| B1   | 11.1(17) | 18(2) | 16.5(16) | -0.3(15) | -4.6(13) | 0.1(17) |
| O2   | 20.6(11) | 16.8(14) | 17.4(10) | -1.6(9) | 4.0(9) | -1.3(10) |
| N2   | 14.7(13) | 15.3(17) | 16.2(11) | -1.8(11) | 0.3(10) | 4.3(12) |

Table S3 Anisotropic Displacement Parameters (Å²×10³) for 2. The Anisotropic displacement factor exponent takes the form: \(-2\pi²[h^2a^∗^2U₁₁+2hkab^∗U₁₂+…]\).
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C2 | 19.9(17) | 24(2) | 25.9(16) | 1.0(15) | 6.7(13) | 4.6(16) |
| C3 | 25.2(19) | 40(3) | 26.8(16) | 4.1(17) | 12.0(15) | 5.0(18) |
| C4 | 19.5(17) | 30(2) | 23.3(16) | 10.1(15) | -0.6(14) | -4.7(16) |
| C5 | 25.2(18) | 23(2) | 22.8(15) | 3.5(15) | -0.9(14) | 1.6(17) |
| C6 | 17.1(16) | 23(2) | 17.1(14) | 0.0(14) | 1.2(13) | 1.7(16) |
| C7 | 13.1(15) | 25(2) | 12.3(13) | 0.2(13) | 5.1(12) | -1.5(15) |
| C8 | 15.5(17) | 26(2) | 16.3(15) | 0.6(14) | 2.9(12) | 1.2(16) |
| C9 | 22.9(18) | 23(2) | 23.3(15) | -4.1(16) | 6.3(14) | -3.4(15) |
| C10| 23.1(18) | 33(2) | 16.9(14) | -7.3(15) | 2.4(14) | -10.3(17) |
| C11| 19.9(17) | 38(3) | 15.5(14) | 2.2(16) | -2.7(13) | -1.0(17) |
| C12| 19.2(16) | 22(2) | 16.9(14) | 1.2(13) | 0.5(13) | 4.3(15) |
| C13| 13.8(16) | 25(2) | 16.0(14) | -0.7(14) | 4.1(12) | -3.4(15) |
| C14| 22.2(17) | 20(2) | 15.4(14) | -1.2(13) | 3.2(12) | 1.1(15) |
| C15| 17.3(18) | 34(3) | 27.7(16) | 2.7(16) | 3.4(14) | -2.6(17) |
| C16| 26.6(18) | 19(2) | 23.3(15) | -1.5(15) | 10.0(14) | 0.7(17) |
| C17| 32(2)   | 23(2) | 27.7(16) | -0.3(16) | 12.0(15) | -5.5(18) |
| C18| 27.8(19) | 31(3) | 20.9(15) | 1.3(15) | -1.6(14) | 2.6(18) |
| B3 | 13(3)   | 18(3) | 16(3)   | 1(3)   | -1(3)   | 1(3)   |
| O3 | 12(3)   | 18(3) | 17(3)   | 1(3)   | -2(3)   | 2(3)   |
| C19| 15(3)   | 20(3) | 20(3)   | 0(3)   | -3(2)   | 2(3)   |
| C20| 15(3)   | 21(3) | 20(3)   | 0(3)   | -3(2)   | 0(3)   |
| O4 | 13(3)   | 19(3) | 17(3)   | 1(3)   | -2(3)   | 2(3)   |
| C21| 20(6)   | 23(7) | 21(7)   | -1(6)  | -3(6)   | 0(6)   |
Table S4 Bond Lengths for 2.

| Atom | Atom | Length/Å  | Atom | Atom | Length/Å  |
|------|------|-----------|------|------|-----------|
| O1   | B1   | 1.362(4)  | C13  | C15  | 1.525(4)  |
| O1   | C13  | 1.461(3)  | C13  | C16  | 1.513(4)  |
| N1   | C1   | 1.423(4)  | C14  | C17  | 1.513(4)  |
| N1   | B1   | 1.433(4)  | C14  | C18  | 1.519(4)  |
| N1   | N2   | 1.419(4)  | B3   | O3   | 1.28(6)   |
| C1   | C2   | 1.393(4)  | B3   | O4   | 1.39(7)   |
| C1   | C6   | 1.391(4)  | O3   | C19  | 1.49(2)   |
| B1   | O2   | 1.373(4)  | C19  | C20  | 1.53(2)   |
| O2   | C14  | 1.468(3)  | C19  | C21  | 1.45(5)   |

C22  21(6)  24(6)  27(6)  -3(5)  5(5)  -1(6)
C23  23(6)  24(6)  24(5)  2(5)  -1(5)  4(6)
C24  14(7)  23(6)  24(7)  -2(5)  -7(6)  0(5)
B2   13(3)  17(3)  15(2)  -1(2)  3(2)  0(2)
O13  14.1(15) 17.7(16) 17.5(15) -0.4(13) -2.6(12) 2.9(13)
C119 15.0(16) 21.1(19) 19.8(17) -0.7(15) -3.6(14) 1.4(16)
C120 14.6(17) 22(2)  20.7(17) 0.7(16) -4.6(14) 0.2(16)
O14  14.1(16) 18.2(16) 19.0(16) -0.5(13) -3.4(12) 1.0(13)
C121 19(2)  22(4)  17(3)  5(2)  -3(2)  -2(3)
C122 21(2)  26(3)  26(2)  0(2)  1.6(17)  -3(2)
C123 21(2)  31(3)  23(2)  7(2)  0.2(17)  2(2)
C124 18(4)  24(4)  27(3)  0(3)  -1(2)  2(3)
N2  C7  1.419(4)  C19  C23  1.52(3)
N2  B3  1.54(6)  C20  O4  1.51(2)
N2  B2  1.410(14)  C20  C22  1.50(3)
C2  C3  1.384(4)  C20  C24  1.52(6)
C3  C4  1.379(5)  B2  O13  1.394(13)
C4  C5  1.379(4)  B2  O14  1.369(16)
C5  C6  1.380(4)  O13  C119  1.467(5)
C7  C8  1.398(5)  C119  C120  1.537(6)
C7  C12  1.390(4)  C119  C121  1.506(11)
C8  C9  1.384(4)  C119  C122  1.531(6)
C9  C10  1.390(4)  C120  O14  1.476(5)
C10  C11  1.371(5)  C120  C123  1.527(6)
C11  C12  1.385(4)  C120  C124  1.523(13)
C13  C14  1.556(5)

Table S5 Bond Angles for 2.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| B1   | O1   | C13  | 107.0(2) | C17  | C14  | C13  | 114.6(3) |
| C1   | N1   | B1   | 128.1(3) | C17  | C14  | C18  | 110.0(3) |
| N2   | N1   | C1   | 116.2(2) | C18  | C14  | C13  | 114.1(3) |
| N2   | N1   | B1   | 115.2(2) | O3   | B3   | N2   | 124(5)   |
| C2   | C1   | N1   | 121.0(3) | O3   | B3   | O4   | 121(5)   |
| C6   | C1   | N1   | 120.6(3) | O4   | B3   | N2   | 115(4)   |
| C6   | C1   | C2   | 118.4(3) | B3   | O3   | C19  | 103(3)   |
| Bond | Bond | Angle | Bond | Bond | Angle |
|------|------|-------|------|------|-------|
| O1   | B1   | N1    | 124.6(3) | O3   | C19  | C20  | 102.8(12) |
| O1   | B1   | O2    | 114.3(3) | O3   | C19  | C23  | 103.5(14) |
| O2   | B1   | N1    | 121.1(3) | C21  | C19  | O3   | 112(3)    |
| B1   | O2   | C14   | 105.8(2) | C21  | C19  | C20  | 118(3)    |
| N1   | N2   | B3    | 111(3)   | C21  | C19  | C23  | 102(2)    |
| C7   | N2   | N1    | 116.1(2) | C23  | C19  | C20  | 117.6(18) |
| C7   | N2   | B3    | 133(3)   | O4   | C20  | C19  | 100.8(13) |
| B2   | N2   | N1    | 115.5(6) | O4   | C20  | C24  | 105(3)    |
| B2   | N2   | C7    | 128.4(6) | C22  | C20  | C19  | 117.2(18) |
| C3   | C2   | C1    | 120.2(3) | C22  | C20  | O4   | 103.8(14) |
| C4   | C3   | C2    | 121.1(3) | C22  | C20  | C24  | 117(3)    |
| C5   | C4   | C3    | 118.6(3) | C24  | C20  | C19  | 110(2)    |
| C4   | C5   | C6    | 121.0(3) | B3   | O4   | C20  | 100(3)    |
| C5   | C6   | C1    | 120.6(3) | O13  | B2   | N2   | 119.4(12) |
| C8   | C7   | N2    | 120.4(3) | O14  | B2   | N2   | 127.6(9)  |
| C12  | C7   | N2    | 120.8(3) | O14  | B2   | O13  | 113.0(9)  |
| C12  | C7   | C8    | 118.8(3) | B2   | O13  | C119 | 105.3(7)  |
| C9   | C8   | C7    | 119.6(3) | O13  | C119 | C120 | 102.1(3)  |
| C8   | C9   | C10   | 121.3(3) | O13  | C119 | C121 | 108.7(6)  |
| C11  | C10  | C9    | 118.7(3) | O13  | C119 | C122 | 106.8(3)  |
| C10  | C11  | C12   | 121.0(3) | C121 | C119 | C120 | 116.6(4)  |
| C11  | C12  | C7    | 120.6(3) | C121 | C119 | C122 | 109.3(5)  |
| O1   | C13  | C14   | 102.9(2) | C122 | C119 | C120 | 112.6(4)  |
| A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|
| O1  | C13 | C15 |     | 106.4(2)|
| O1  | C13 | C16 |     | 108.8(2)|
| C15 | C13 | C14 |     | 113.8(3)|
| C16 | C13 | C14 |     | 114.7(2)|
| C16 | C13 | C15 |     | 109.6(3)|
| O2  | C14 | C13 |     | 102.7(2)|
| O2  | C14 | C17 |     | 108.6(3)|
| O2  | C14 | C18 |     | 106.2(2)|

Table S6 Torsion Angles for 2.

| A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|
| O1  | C13 | C14 |     | -12.8(3)|
| O1  | C13 | C14 | O2  | -26.3(3)|
| O1  | C13 | C14 | C17 | -143.8(2)|
| O1  | C13 | C14 | C18 | 88.1(3) |
| N1  | C1  | C2  | C3  | 179.7(3)|
| N1  | C1  | C6  | C5  | -179.2(3)|
| N1  | B1  | O2  | C14 | 167.5(3)|
| N1  | N2  | C7  | C8  | -177.5(2)|
| N1  | N2  | C7  | C12 | 3.3(4) |
| N1  | N2  | B3  | O3  | 21(7) |
| N1  | N2  | B3  | O4  | -168(4)|
| N1  | N2  | B2  | O13 | -11.8(14)|
| N1  | N2  | B2  | O14 | 170.1(11)|

| A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|
| C8  | C9  | C10 | C11 | 1.2(4)  |
| C9  | C10 | C11 | C12 | 0.1(4)  |
| C10 | C11 | C12 | C7  | -1.5(4) |
| C12 | C7  | C8  | C9  | -0.5(4) |
| C13 | O1  | B1  | N1  | 174.6(3)|
| C13 | O1  | B1  | O2  | -5.2(3) |
| C15 | C13 | C14 | O2  | 88.4(3) |
| C15 | C13 | C14 | C17 | -29.1(3)|
| C15 | C13 | C14 | C18 | -157.1(2)|
| C16 | C13 | C14 | O2  | -144.2(2)|
| C16 | C13 | C14 | C17 | 98.3(3) |
| C16 | C13 | C14 | C18 | -29.8(3)|
| B3  | N2  | C7  | C8  | 2(4)    |
| C1 | N1 | B1 | O1 | -1.3(5) | B3 | N2 | C7 | C12 | -177(4) |
| C1 | N1 | B1 | O2 | 178.4(3) | B3 | O3 | C19 | C20 | 24(4) |
| C1 | N1 | N2 | C7 | -90.6(3) | B3 | O3 | C19 | C21 | 152(4) |
| C1 | N1 | N2 | B3 | 90(3) | B3 | O3 | C19 | C23 | -99(4) |
| C1 | N1 | N2 | B2 | 92.0(8) | O3 | B3 | O4 | C20 | -19(6) |
| C1 | C2 | C3 | C4 | -0.6(5) | O3 | C19 | C20 | O4 | -34.4(17) |
| B1 | O1 | C13 | C14 | 19.6(3) | O3 | C19 | C20 | C22 | 77.4(18) |
| B1 | O1 | C13 | C15 | -100.4(3) | O3 | C19 | C20 | C24 | -145(3) |
| B1 | O1 | C13 | C16 | 141.6(3) | C19 | C20 | O4 | B3 | 31(3) |
| B1 | N1 | C1 | C2 | 171.3(3) | O4 | B3 | O3 | C19 | -3(6) |
| B1 | N1 | C1 | C6 | -9.1(4) | C21 | C19 | C20 | O4 | -158(2) |
| B1 | N1 | N2 | C7 | 96.6(3) | C21 | C19 | C20 | C22 | -46(3) |
| B1 | N1 | N2 | B3 | -83(3) | C21 | C19 | C20 | C24 | 91(4) |
| B1 | N1 | N2 | B2 | -80.8(8) | C22 | C20 | O4 | B3 | -91(3) |
| B1 | O2 | C14 | C13 | 23.7(3) | C23 | C19 | C20 | O4 | 78.5(18) |
| B1 | O2 | C14 | C17 | 145.5(3) | C23 | C19 | C20 | C22 | -169.7(16) |
| B1 | O2 | C14 | C18 | -96.3(3) | C23 | C19 | C20 | C24 | -32(3) |
| N2 | N1 | C1 | C2 | -0.4(4) | C24 | C20 | O4 | B3 | 146(4) |
| N2 | N1 | C1 | C6 | 179.2(2) | B2 | N2 | C7 | C8 | -0.5(9) |
| N2 | N1 | B1 | O1 | 170.5(3) | B2 | N2 | C7 | C12 | -179.7(9) |
| N2 | N1 | B1 | O2 | -9.8(4) | B2 | O13 | C119 | C120 | -28.4(8) |
| N2 | C7 | C8 | C9 | -179.7(2) | B2 | O13 | C119 | C121 | -152.2(8) |
| N2 | C7 | C12 | C11 | -179.1(3) | B2 | O13 | C119 | C122 | 89.9(8) |
Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å²×10^3) for 2.

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H2   | 3890 | 5891 | 5216 | 28    |
| H3   | 4564 | 7230 | 4378 | 37    |
| H4   | 3800 | 9032 | 4400 | 29    |
| H5   | 2366 | 9491 | 5291 | 28    |
| H6   | 1700 | 8178 | 6144 | 23    |
|  |  |  |  |  |
|---|---|---|---|---|
| H8 | 3243 | 2903 | 5927 | 23 |
| H9 | 2239 | 1701 | 5125 | 28 |
| H10 | 547 | 2290 | 4474 | 29 |
| H11 | -94 | 4117 | 4605 | 30 |
| H12 | 930 | 5354 | 5370 | 23 |
| H15A | -1539 | 7014 | 7841 | 39 |
| H15B | -1057 | 6493 | 7075 | 39 |
| H15C | -1070 | 7814 | 7189 | 39 |
| H16A | -23 | 7773 | 8790 | 35 |
| H16B | 174 | 8663 | 8136 | 35 |
| H16C | 1288 | 8015 | 8482 | 35 |
| H17A | -774 | 5510 | 8704 | 41 |
| H17B | -40 | 4423 | 8471 | 41 |
| H17C | -899 | 5012 | 7877 | 41 |
| H18A | 1340 | 6154 | 9094 | 40 |
| H18B | 2307 | 6337 | 8448 | 40 |
| H18C | 1941 | 5103 | 8694 | 40 |
| H21A | 6553 | 5293 | 8281 | 32 |
| H21B | 5429 | 6070 | 8451 | 32 |
| H21C | 6200 | 6264 | 7710 | 32 |
| H22A | 6676 | 4329 | 6063 | 36 |
| H22B | 7183 | 5093 | 6723 | 36 |
| H22C | 6032 | 5477 | 6265 | 36 |
|   |     |     |     |     |
|---|-----|-----|-----|-----|
| H23A | 5116 | 3939 | 8591 | 35  |
| H23B | 3971 | 3761 | 8073 | 35  |
| H23C | 4072 | 4842 | 8592 | 35  |
| H24A | 6411 | 2670 | 6915 | 30  |
| H24B | 5490 | 2759 | 7596 | 30  |
| H24C | 6794 | 3279 | 7675 | 30  |
| H12A | 6628 | 5523 | 8158 | 29  |
| H12B | 5281 | 5875 | 8322 | 29  |
| H12C | 6102 | 6643 | 7804 | 29  |
| H12D | 7183 | 5159 | 6769 | 37  |
| H12E | 6446 | 6236 | 6521 | 37  |
| H12F | 6123 | 5045 | 6177 | 37  |
| H12G | 4307 | 3002 | 8125 | 37  |
| H12H | 3988 | 4294 | 8209 | 37  |
| H12I | 5216 | 3827 | 8535 | 37  |
| H12J | 6071 | 2463 | 7378 | 35  |
| H12K | 6957 | 3463 | 7575 | 35  |
| H12L | 6541 | 3269 | 6728 | 35  |
Crystal Structure data for 4

Table S8 Crystal data and structure refinement for 4.

| Property                  | Value                     |
|---------------------------|---------------------------|
| Empirical formula         | C_{26}H_{38}B_{2}N_{2}O_{4} |
| Formula weight            | 464.20                    |
| Temperature/K             | 173                       |
| Crystal system            | orthorhombic              |
| Space group               | P2_12_12_1                |
| a/A                       | 11.3842(5)                |
| b/A                       | 12.2242(5)                |
| c/A                       | 19.0048(8)                |
| \(\alpha/°\)              | 90                        |
| \(\beta/°\)               | 90                        |
| \(\gamma/°\)              | 90                        |
| Volume/A^3                | 2644.75(19)               |
| Z                         | 4                         |
\( \rho_{\text{calc}}/\text{cm}^3 \) = 1.166
\( \mu/\text{mm}^{-1} \) = 0.606
\( F(000) \) = 1000.0
Crystal size/\text{mm}^3 = 0.1 \times 0.1 \times 0.1
Radiation = CuK\( \alpha \) (\( \lambda = 1.54184 \))

2\( \Theta \) range for data collection/° = 8.6 to 142.618
Index ranges = -10 \( \leq h \leq 13 \), -15 \( \leq k \leq 13 \), -23 \( \leq l \leq 19 \)
Reflections collected = 14413
Independent reflections = 5038 [\( R_{\text{int}} = 0.0599 \), \( R_{\text{sigma}} = 0.0593 \)]
Data/restraints/parameters = 5038/0/317
Goodness-of-fit on \( F^2 \) = 0.970
Final R indexes [\( I \geq 2\sigma (I) \)] = \( R_1 = 0.0503 \), \( wR_2 = 0.1226 \)
Final R indexes [all data] = \( R_1 = 0.0681 \), \( wR_2 = 0.1288 \)
Largest diff. peak/hole / e \( \text{Å}^{-3} \) = 0.21/-0.21
Flack parameter = 0.1(2)

Table S9 Fractional Atomic Coordinates (\( \times 10^4 \)) and Equivalent Isotropic Displacement Parameters (\( \text{Å}^2 \times 10^3 \)) for 4. \( U_{\text{eq}} \) is defined as 1/3 of the trace of the orthogonalised \( U_{11} \) tensor.

| Atom | \( x \)        | \( y \)        | \( z \)        | \( U(\text{eq}) \) |
|------|----------------|----------------|----------------|-------------------|
| O001 | -4065.2(18)    | -4837.4(16)    | -5013.9(11)    | 34.0(5)           |
| O002 | -1272.6(19)    | -5008.8(15)    | -5013.6(11)    | 35.5(5)           |
| O003 | -4323.5(19)    | -6564.8(16)    | -4566.2(11)    | 36.2(5)           |
| O004 | -1226(2)       | -3151.7(16)    | -4845.9(11)    | 38.5(5)           |
|   |   |   |   |   |
|---|---|---|---|---|
| N005 | -2384(2) | -4287.2(18) | -4017.1(13) | 29.0(5) |
| N006 | -2938(2) | -5321.0(19) | -3961.5(12) | 28.9(5) |
| C007 | -2441(3) | -6076(2) | -3472.4(15) | 30.0(6) |
| C008 | -2660(2) | -3514(2) | -3485.5(15) | 28.2(6) |
| C009 | -3422(3) | -3777(2) | -2933.3(16) | 35.2(7) |
| C00A | -2172(3) | -2470(2) | -3493.5(16) | 33.7(6) |
| C00B | -5024(3) | -5332(3) | -5414.6(17) | 37.0(7) |
| C00C | -1322(3) | -5925(3) | -3203.7(16) | 36.9(7) |
| C00D | -3221(3) | -1962(3) | -2434.5(16) | 39.1(7) |
| C00E | -3696(3) | -3002(3) | -2425.1(16) | 40.1(7) |
| C00F | -4857(3) | -6574(2) | -5270.2(16) | 36.7(7) |
| C00G | -3077(3) | -6981(3) | -3256.1(18) | 40.0(7) |
| C00H | -2457(3) | -1716(3) | -2977.9(17) | 39.3(7) |
| C00I | -696(3) | -4553(3) | -5635.4(17) | 38.0(7) |
| C00J | -340(3) | -3387(3) | -5386.5(17) | 39.7(7) |
| C00K | -847(3) | -6680(3) | -2739.8(18) | 44.1(8) |
| C00L | -1618(3) | -4536(3) | -6215.7(17) | 49.2(9) |
| C00M | -1464(3) | -7601(3) | -2531.7(18) | 45.7(8) |
| C00N | -2587(4) | -7728(3) | -2792.9(19) | 47.2(8) |
| C00O | -6164(3) | -4876(3) | -5123(2) | 44.8(8) |
| B00P | -3764(3) | -5579(3) | -4503.9(17) | 28.8(6) |
| C00Q | -4899(3) | -5006(3) | -6180.8(18) | 49.2(9) |
| B00R | -1638(3) | -4134(3) | -4620.8(18) | 31.6(7) |
Table S10 Anisotropic Displacement Parameters (Å²×10³) for 4. The Anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁+2hkab*U₁₂+...].

| Atom  | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| O001  | 36.3(11) | 34.2(10) | 31.5(11) | 4.6(8) | -6.5(9) | -4.0(8) |
| O002  | 43.5(12) | 33.3(9) | 29.8(10) | -1.7(8) | 8.3(9) | -2.2(8) |
| O003  | 42.7(11) | 33.7(10) | 32.2(11) | 5.1(8) | -10.4(10) | -5.1(9) |
| O004  | 49.9(13) | 34.2(10) | 31.6(11) | -3.2(8) | 17.4(10) | -5.3(9) |
| N005  | 32.2(12) | 30.6(11) | 24.2(11) | -0.5(9) | 1.8(10) | -5.7(9) |
| N006  | 32.1(12) | 30.2(11) | 24.3(11) | 4.7(9) | -1.1(10) | -4.6(9) |
| C007  | 33.7(15) | 32.9(13) | 23.3(12) | -1(1) | 0.2(12) | 1.9(11) |
| C008  | 26.6(13) | 36.1(14) | 22.0(12) | 2.1(10) | -0.1(11) | 0.3(11) |
| C009  | 39.1(16) | 35.5(14) | 31.1(15) | 5.9(12) | 6.5(13) | 0.6(12) |
| C00A  | 34.0(15) | 39.1(14) | 27.9(13) | -2.8(12) | 5.3(12) | -6.6(12) |
| C00B  | 37.7(15) | 41.6(15) | 31.7(15) | 3.7(13) | -12.7(13) | -3.2(13) |
| C00C  | 37.0(16) | 41.2(15) | 32.4(15) | -1.0(12) | -5.3(13) | -2.1(13) |
| C00D  | 42.8(17) | 48.4(17) | 26.0(15) | -2.5(13) | 3.2(13) | 4.8(14) |
|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| C00E | 47.4(18) | 44.3(16) | 28.7(15) | 6.2(13) | 9.1(14) | 4.9(14) |
| C00F | 40.1(16) | 37.8(15) | 32.3(16) | -3.6(12) | -12.7(13) | -2.0(13) |
| C00G | 40.4(16) | 42.7(17) | 36.9(16) | 10.9(13) | -6.3(14) | -5.4(13) |
| C00H | 42.3(17) | 41.0(15) | 34.7(16) | -5.6(13) | 3.6(14) | -6.1(14) |
| C00I | 41.0(16) | 43.1(16) | 29.9(15) | -3.7(13) | 11.1(13) | -4.1(13) |
| C00J | 44.5(17) | 44.9(16) | 29.8(15) | -4.7(13) | 15.0(14) | -6.7(14) |
| C00K | 45.2(18) | 49.8(18) | 37.5(17) | -4.4(14) | -13.7(15) | 4.0(15) |
| C00L | 57(2) | 59(2) | 31.2(17) | -6.3(15) | 4.3(16) | -11.3(18) |
| C00M | 62(2) | 44.7(17) | 30.2(15) | 2.0(14) | -11.8(16) | 6.5(16) |
| C00N | 59(2) | 42.7(17) | 39.7(17) | 11.0(13) | -3.6(16) | -2.9(16) |
| C00O | 38.7(17) | 45.0(16) | 50.7(19) | 0.5(15) | -9.0(15) | 1.6(13) |
| B00P | 27.9(14) | 32.1(15) | 26.4(15) | -0.3(12) | -1.4(13) | -0.6(12) |
| C00Q | 51(2) | 59(2) | 36.6(18) | 8.6(16) | -13.4(16) | -2.7(17) |
| B00R | 31.8(16) | 35.2(15) | 28.0(16) | -0.4(13) | 3.1(14) | -2.3(12) |
| C00S | 53(2) | 45.1(17) | 56(2) | 3.3(15) | -18.5(18) | -10.1(16) |
| C00T | 48(2) | 72(2) | 47(2) | -10.8(19) | 10.0(18) | -14.7(18) |
| C00U | 60(2) | 53.2(19) | 46(2) | -12.1(16) | -7.9(18) | 10.3(17) |
| C00V | 56(2) | 54(2) | 52(2) | -9.1(17) | 19.0(18) | 1.9(17) |
| C00W | 73(3) | 45.7(18) | 40.1(19) | 1.2(15) | 24.1(19) | -6.7(18) |
| C00X | 76(3) | 59(2) | 46(2) | -16.3(18) | 17(2) | -1(2) |
| C00Y | 96(4) | 65(3) | 54(2) | 15(2) | -29(2) | 13(2) |
### Table S11 Bond Lengths for 4.

| Atom Atom | Length/Å | Atom Atom | Length/Å |
|-----------|----------|-----------|----------|
| O001 C00B | 1.462(4) | C00B C00F | 1.554(4) |
| O001 B00P | 1.370(4) | C00B C00O | 1.517(5) |
| O002 C00I | 1.462(4) | C00B C00Q | 1.517(4) |
| O002 B00R | 1.369(4) | C00C C00K | 1.386(5) |
| O003 C00F | 1.469(3) | C00D C00E | 1.381(5) |
| O003 B00P | 1.369(4) | C00D C00H | 1.383(5) |
| O004 C00J | 1.468(4) | C00D C00X | 1.510(5) |
| O004 B00R | 1.358(4) | C00F C00S | 1.512(5) |
| N005 N006 | 1.416(3) | C00F C00U | 1.521(5) |
| N005 C008 | 1.419(4) | C00G C00N | 1.385(5) |
| N005 B00R | 1.440(4) | C00I C00J | 1.555(4) |
| N006 C007 | 1.426(4) | C00I C00L | 1.523(5) |
| N006 B00P | 1.431(4) | C00I C00V | 1.513(5) |
| C007 C00C | 1.385(4) | C00J C00T | 1.511(5) |
| C007 C00G | 1.385(4) | C00J C00W | 1.512(5) |
| C008 C009 | 1.399(4) | C00K C00M | 1.384(5) |
| C008 C00A | 1.392(4) | C00M C00N | 1.381(5) |
| C009 C00E | 1.389(4) | C00M C00Y | 1.506(5) |
| C00A C00H | 1.384(4) |          |          |
| Atom Atom Atom | Angle/° | Atom Atom Atom | Angle/° |
|----------------|---------|----------------|---------|
| B00P O001 C00B | 106.4(2) | O003 C00F C00S | 108.9(3) |
| B00R O002 C00I | 106.2(2) | O003 C00F C00U | 106.1(3) |
| B00P O003 C00F | 106.1(2) | C00S C00F C00B | 114.1(3) |
| B00R O004 C00J | 106.5(2) | C00S C00F C00U | 111.3(3) |
| N006 N005 C008 | 116.3(2) | C00U C00F C00B | 113.7(3) |
| N006 N005 B00R | 116.0(2) | C00N C00G C007 | 120.3(3) |
| C008 N005 B00R | 127.7(2) | C00D C00H C00A | 122.1(3) |
| N005 N006 C007 | 116.7(2) | O002 C00I C00J | 102.7(2) |
| N005 N006 B00P | 115.8(2) | O002 C00I C00L | 106.3(3) |
| C007 N006 B00P | 126.0(2) | O002 C00I C00V | 108.4(3) |
| C00C C007 N006 | 121.3(3) | C00L C00I C00J | 112.8(3) |
| C00C C007 C00G | 118.5(3) | C00V C00I C00J | 114.8(3) |
| C00G C007 N006 | 120.2(3) | C00V C00I C00L | 110.9(3) |
| C009 C008 N005 | 121.2(3) | O004 C00J C00I | 102.3(2) |
| C00A C008 N005 | 121.0(3) | O004 C00J C00T | 106.5(3) |
| C00A C008 C009 | 117.8(3) | O004 C00J C00W | 108.9(3) |
| C00E C009 C008 | 120.3(3) | C00T C00J C00I | 113.9(3) |
| C00H C00A C008 | 120.6(3) | C00T C00J C00W | 110.6(3) |
| O001 C00B C00F | 102.7(2) | C00W C00J C00I | 114.1(3) |
| O001 C00B C00O | 107.2(3) | C00M C00K C00C | 121.7(3) |
| O001 C00B C00Q | 108.7(3) | C00K C00M C00Y | 121.5(4) |
Table 13 Torsion Angles for 4.

| A     | B     | C     | D     | Angle/° | A     | B     | C     | D     | Angle/° |
|-------|-------|-------|-------|---------|-------|-------|-------|-------|---------|
| O001  | C00B  | C00F  | O003  | 29.5(3) | C00H  | C00D  | C00E  | C009  | 0.4(5)  |
| O001  | C00B  | C00F  | C00S  | 146.6(3)| C00I  | O002  | B00R  | O004  | -9.5(4) |
| O001  | C00B  | C00F  | C00U  | -84.2(3)| C00I  | O002  | B00R  | N005  | 171.4(3) |
| O002  | C00I  | C00J  | O004  | -27.4(3)| C00J  | O004  | B00R  | O002  | -9.3(4)  |
| O002  | C00I  | C00J  | C00T  | 87.0(3) | C00J  | O004  | B00R  | N005  | 169.8(3) |
| O002  | C00I  | C00J  | C00W  | -144.8(3)| C00K  | C00M  | C00N  | C00G  | 1.4(6)   |
| N005  | N006  | C007  | C00C  | -16.1(4)| C00L  | C00I  | C00J  | O004  | 86.7(3)  |
| N005  | N006  | C007  | C00G  | 163.9(3)| C00L  | C00I  | C00J  | C00T  | -158.9(3) |
| N005  | N006  | B00P  | O001  | -4.8(4) | C00L  | C00I  | C00J  | C00W  | -30.7(4) |
| N005  | N006  | B00P  | O003  | 175.3(3)| C00O  | C00B  | C00F  | O003  | -85.9(3) |
| N005  | C008  | C009  | C00E  | -178.9(3)| C00O  | C00B  | C00F  | C00S  | 31.2(4)  |
| N005  | C008  | C00A  | C00H  | 179.2(3)| C00O  | C00B  | C00F  | C00U  | 160.4(3) |
| N006 N005 C008 C009 | 1.1(4) | B00P O001 C00B C00F | -22.7(3) |
|---------------------|-------|---------------------|-----------|
| N006 N005 C008 C00A | -179.4(3) | B00P O001 C00B C00O | 97.2(3) |
| N006 N005 B00R O002 | -15.1(4) | B00P O001 C00B C00Q | -144.4(3) |
| N006 N005 B00R O004 | 165.9(3) | B00P O003 C00F C00B | -26.1(3) |
| N006 C007 C00C C00K | -178.7(3) | B00P O003 C00F C00S | -146.9(3) |
| N006 C007 C00G C00N | 178.6(3) | B00P O003 C00F C00U | 93.1(3) |
| C007 N006 B00P O001 | -170.3(3) | B00P N006 C007 C00C | 149.3(3) |
| C007 N006 B00P O003 | 9.7(5) | B00P N006 C007 C00G | -30.6(4) |
| C007 C00C C00K C00M | 0.2(5) | C00Q C00B C00F O003 | 147.2(3) |
| C007 C00G C00N C00M | 0.0(6) | C00Q C00B C00F C00S | -95.7(4) |
| C008 N005 N006 C007 | -79.6(3) | C00Q C00B C00F C00U | 33.5(4) |
| C008 N005 N006 B00P | 113.4(3) | B00R O002 C00I C00J | 22.7(3) |
| C008 N005 B00R O002 | 167.3(3) | B00R O002 C00I C00L | -96.0(3) |
| C008 N005 B00R O004 | -11.8(5) | B00R O002 C00I C00V | 144.7(3) |
| C008 C009 C00E C00D | -1.2(5) | B00R O004 C00J C00I | 22.6(3) |
| C008 C00A C00H C00D | 0.6(5) | B00R O004 C00J C00T | -97.2(3) |
| C009 C008 C00A C00H | -1.4(5) | B00R O004 C00J C00W | 143.6(3) |
| C00A C008 C009 C00E | 1.6(5) | B00R N005 N006 C007 | 102.5(3) |
| C00B O001 B00P O003 | 6.9(3) | B00R N005 N006 B00P | -64.5(3) |
| C00B O001 B00P N006 | -173.0(3) | B00R N005 C008 C009 | 178.8(3) |
| C00C C007 C00G C00N | -1.4(5) | B00R N005 C008 C00A | -1.8(5) |
| C00C C00K C00M C00N | -1.5(5) | C00V C00I C00J O004 | -144.9(3) |
| C00C C00K C00M C00Y | 179.3(4) | C00V C00I C00J C00T | -30.5(4) |
| Atom    | x     | y     | z     | U(eq) |
|---------|-------|-------|-------|-------|
| H009    | -3753 | -4489 | -2906 | 42    |
| H00A    | -1638 | -2273 | -3856 | 40    |
| H00C    | -877  | -5302 | -3338 | 44    |
| H00E    | -4227 | -3192 | -2059 | 48    |
| H00G    | -3853 | -7091 | -3426 | 48    |
| H00H    | -2118 | -1006 | -2998 | 47    |
| H00K    | -79   | -6562 | -2560 | 53    |
| H00B    | -1904 | -5281 | -6299 | 74    |
| H00D    | -1269 | -4246 | -6649 | 74    |
| H00F    | -2276 | -4069 | -6072 | 74    |
| H00N    | -3037 | -8344 | -2651 | 57    |
| H00I    | -6229 | -5063 | -4623 | 67    |
| H00J    | -6829 | -5191 | -5380 | 67    |
| H00L    | -6169 | -4078 | -5177 | 67    |
| H00M    | -4989 | -4211 | -6225 | 74    |
| H00O    | -5505 | -5373 | -6460 | 74    |

Table S14 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 4.
|   |   |   |   |   |
|---|---|---|---|---|
| H00P | -4121 | -5222 | -6352 | 74 |
| H00Q | -5814 | -7994 | -5177 | 77 |
| H00R | -6425 | -7114 | -5681 | 77 |
| H00S | -6468 | -6956 | -4846 | 77 |
| H00T | 933 | -2630 | -4791 | 84 |
| H00U | 1466 | -3440 | -5371 | 84 |
| H00V | 886 | -3925 | -4670 | 84 |
| H00W | -3243 | -6683 | -5763 | 80 |
| H00X | -4291 | -7167 | -6230 | 80 |
| H00Y | -3791 | -7855 | -5579 | 80 |
| H00Z | 844 | -5372 | -5426 | 81 |
| H   | 757 | -4961 | -6224 | 81 |
| HA  | 21 | -6006 | -5973 | 81 |
| H00 | -1237 | -2428 | -6096 | 80 |
| HB  | 51 | -2753 | -6362 | 80 |
| HC  | -109 | -1829 | -5773 | 80 |
| H0AA | -3994 | -545 | -2081 | 91 |
| HD  | -2782 | -812 | -1690 | 91 |
| HE  | -3945 | -1481 | -1493 | 91 |
| H1AA | -82 | -8427 | -2086 | 107 |
| HF  | -1247 | -9154 | -2143 | 107 |
| HG  | -1144 | -8230 | -1549 | 107 |
Crystal structure data for 9

Table S15 Crystal data and structure refinement for 9.

| Property                        | Value                       |
|---------------------------------|-----------------------------|
| Empirical formula               | C_{26}H_{33}BN_{2}O_{2}Si    |
| Formula weight                  | 444.44                      |
| Temperature/K                   | 173                         |
| Crystal system                  | monoclinic                  |
| Space group                     | P2\textsubscript{1}         |
| a/Å                             | 8.51365(19)                 |
| b/Å                             | 12.4441(3)                  |
| c/Å                             | 11.7153(3)                  |
| α/°                             | 90                          |
| β/°                             | 91.067(2)                   |
| γ/°                             | 90                          |
| Volume/Å\textsuperscript{3}     | 1240.96(5)                  |
Z  2
ρ_{calc} g/cm^3  1.189
μ/mm^1  1.019
F(000)  476.0
Crystal size/mm^3  0.15 × 0.15 × 0.075
Radiation  CuKα (λ = 1.54184)
2θ range for data collection/°  7.548 to 14.2434
Index ranges  -8 ≤ h ≤ 10, -9 ≤ k ≤ 15, -14 ≤ l ≤ 14
Reflections collected  7442
Independent reflections  3705 [R_{int} = 0.0367, R_{sigma} = 0.0437]
Data/restraints/parameters  3705/1/295
Goodness-of-fit on F^2  1.043
Final R indexes [I>=2σ(I)]  R_1 = 0.0574, wR_2 = 0.1581
Final R indexes [all data]  R_1 = 0.0634, wR_2 = 0.1604
Largest diff. peak/hole / e Å^{-3}  0.64/-0.31
Flack parameter  -0.01(4)

Table S16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 9. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

| Atom | x       | y       | z       | U(eq)   |
|------|---------|---------|---------|---------|
| Si01 | 3706.9(10) | 4459.8(8) | 9065.1(7) | 24.5(3) |
| O002 | 3205(3) | 3624(3) | 5077(2) | 34.9(6) |
| O003 | 4720(3) | 4885(3) | 6013(2) | 32.7(6) |
|       |        |        |        |        |
|-------|--------|--------|--------|--------|
| **N1** | 2359(3) | 4266(3) | 6970(2) | 25.5(7) |
| **N2** | 2713(3) | 5008(3) | 7855(2) | 25.4(6) |
| **C006** | 2068(4) | 6032(3) | 7735(3) | 25.3(7) |
| **C007** | 1055(4) | 3579(3) | 7156(3) | 26.9(8) |
| **C008** | 2291(4) | 6799(4) | 8586(3) | 29.8(8) |
| **C009** | -84(4)  | 3868(4) | 7939(3) | 32.1(8) |
| **C00A** | 5511(4) | 5267(3) | 9430(3) | 28.0(8) |
| **C00B** | 935(5)  | 2584(4) | 6608(3) | 31.9(8) |
| **C00C** | 6307(5) | 5854(4) | 8619(3) | 35.7(9) |
| **C00D** | 1634(5) | 7818(4) | 8492(4) | 36.1(9) |
| **C00E** | 1167(4) | 6327(4) | 6763(3) | 32.3(8) |
| **C00F** | 6194(4) | 5173(4) | 10522(3)| 32.7(8) |
| **C00G** | 8395(4) | 6236(4) | 9962(4) | 39.8(10) |
| **C00H** | 517(5)  | 7345(4) | 6670(4) | 38.6(9) |
| **C00I** | -286(6) | 1900(4) | 6848(4) | 42.7(10) |
| **C00J** | 7736(5) | 6340(4) | 8886(4) | 42.1(10) |
| **C00K** | 7623(5) | 5656(4) | 10783(4)| 38.9(10) |
| **C00L** | 745(5)  | 8105(4) | 7526(4) | 38.9(9) |
| **C00M** | 2396(5) | 4411(5) | 10324(3)| 39.4(9) |
| **C00N** | 4341(6) | 3999(5) | 4263(4) | 45.5(11) |
| **C00O** | -1298(5) | 3156(4) | 8178(3) | 39.6(10) |
| **B1** | 3417(4) | 4252(4) | 6027(3) | 25.9(9) |
| **C00Q** | -1396(5) | 2165(4) | 7647(4) | 42.5(10) |
Table S17 Anisotropic Displacement Parameters (Å²×10³) for 9. The Anisotropic

displacement factor exponent takes the form: -2π²[h²a*²U₁₁+2hka*b*U₁₂+…].

| Atom  | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| Si01  | 26.6(4) | 23.5(5) | 23.5(4) | 1.1(4) | 0.7(3) | -4.6(4) |
| O002  | 41.4(13) | 36.8(17) | 26.8(12) | -9.1(12) | 6.8(10) | -3.7(13) |
| O003  | 35.2(12) | 36.7(17) | 26.4(12) | -6.2(11) | 5.2(10) | -3.0(12) |
| N1    | 28.7(12) | 23.0(18) | 24.9(12) | -6.6(12) | 2.7(10) | -2.2(12) |
| N2    | 30.3(13) | 24.5(17) | 21.3(12) | -2.6(12) | 0.7(10) | -0.9(13) |
| C006  | 27.1(14) | 23(2)  | 25.5(15) | -0.1(14) | 5.8(12) | -3.9(14) |
| C007  | 27.5(14) | 27(2)  | 26.2(15) | -2.1(14) | -3.2(13) | -0.9(16) |
| C008  | 35.2(17) | 26(2)  | 28.9(16) | -1.2(15) | 3.6(14) | -1.1(16) |
| C009  | 28.0(15) | 38(2)  | 30.7(17) | -6.6(16) | -0.4(13) | -1.5(16) |
| C00A  | 30.9(16) | 23(2)  | 30.1(16) | -3.2(14) | 0.0(13) | -0.2(15) |
| C00B  | 34.7(17) | 28(2)  | 33.0(18) | -4.9(16) | -1.0(15) | -1.4(16) |
| C00C  | 38.5(18) | 37(2)  | 31.4(18) | -1.8(16) | 1.2(15) | -7.6(18) |
| C00D  | 47(2)  | 22(2)  | 39(2)  | 0.8(17) | 8.0(17) | -2.7(18) |
| C00E  | 36.6(17) | 33(2)  | 27.2(17) | 1.5(16) | 1.8(14) | 2.5(17) |
Table S18 Bond Lengths for 9.

| Atom  | Atom | Length/Å | Atom  | Atom | Length/Å |
|-------|------|----------|-------|------|----------|
| Si01  | N2   | 1.773(3) | C00A  | C00C | 1.386(6) |
| Si01  | C00A | 1.878(4) | C00A  | C00F | 1.400(5) |
| Si01  | C00M | 1.867(4) | C00B  | C00I | 1.377(6) |
Table S19 Bond Angles for 9.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N2   | Si01 | C00A | 110.64(16) | C008 | C00D | C00L | 120.6(4) |
| N2   | Si01 | C00M | 111.12(17) | C00H | C00E | C006 | 120.8(4) |
| N2   | Si01 | C00S | 106.52(17) | C00K | C00F | C00A | 120.9(4) |
| C00M | Si01 | C00A | 109.62(18) | C00J | C00G | C00K | 119.7(4) |
| C00S | Si01 | C00A | 107.55(17) | C00E | C00H | C00L | 121.0(4) |
| C00S | Si01 | C00M | 111.3(2) | C00B | C00I | C00Q | 121.3(5) |
| Bond | Distance | Angle | Diagonal Angle | Bond | Distance | Angle | Diagonal Angle |
|------|----------|-------|----------------|------|----------|-------|----------------|
| B1 O002 C00N | 105.8(3) | C00G C00J C00C | 120.4(4) |
| B1 O003 C00R | 106.0(3) | C00G C00K C00F | 120.1(4) |
| N2 N1 C007 | 115.8(3) | C00H C00L C00D | 118.5(4) |
| N2 N1 B1 | 116.3(3) | O002 C00N C00R | 103.2(3) |
| C007 N1 B1 | 127.8(3) | O002 C00N C00T | 104.6(4) |
| N1 N2 Si01 | 115.3(2) | O002 C00N C00U | 110.7(5) |
| C006 N2 Si01 | 127.9(2) | C00R C00N C00T | 108.8(4) |
| C006 N2 N1 | 116.3(3) | C00U C00N C00R | 120.7(4) |
| N2 C006 C00E | 121.9(3) | C00U C00N C00T | 107.6(4) |
| C008 C006 N2 | 120.4(3) | C00Q C00O C009 | 121.0(4) |
| C008 C006 C00E | 117.7(4) | O002 B1 N1 | 123.8(3) |
| C009 C007 N1 | 120.0(4) | O003 B1 O002 | 114.6(3) |
| C009 C007 C00B | 119.0(4) | O003 B1 N1 | 121.6(3) |
| C00B C007 N1 | 120.9(3) | C00I C00Q C00O | 118.7(4) |
| C00D C008 C006 | 121.3(4) | O003 C00R C00N | 103.2(3) |
| C00O C009 C007 | 119.7(4) | O003 C00R C00V | 105.0(3) |
| C00C C00A Si01 | 122.3(3) | O003 C00R C00W | 111.7(5) |
| C00C C00A C00F | 118.1(4) | C00N C00R C00V | 107.0(5) |
| C00F C00A Si01 | 119.2(3) | C00W C00R C00N | 119.6(4) |
| C00I C00B C007 | 120.2(4) | C00W C00R C00V | 109.2(5) |
| C00A C00C C00J | 120.8(4) | | |
Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 9.

| Atom  | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| H008  | 2904 | 6622 | 9246 | 36    |
| H009  | -33  | 4547 | 8309 | 39    |
| H00B  | 1699 | 2378 | 6069 | 38    |
| H00C  | 5870 | 5925 | 7871 | 43    |
| H00D  | 1791 | 8325 | 9090 | 43    |
| H00E  | 1005 | 5822 | 6164 | 39    |
| H00F  | 5672 | 4772 | 11091| 39    |
| H00G  | 9378 | 6564 | 10139| 48    |
| H00H  | -95  | 7525 | 6011 | 46    |
| H00I  | -368 | 1233 | 6456 | 51    |
| H00J  | 8262 | 6745 | 8323 | 51    |
| H00K  | 8071 | 5588 | 11528| 47    |
| H00L  | 306  | 8804 | 7456 | 47    |
| H00A  | 2050 | 5141 | 10511| 59    |
| H00M  | 2971 | 4105 | 10979| 59    |
| H00N  | 1478 | 3963 | 10143| 59    |
| H00O  | -2070| 3355 | 8714 | 48    |
| H00Q  | -2211| 1676 | 7828 | 51    |
| H00P  | 3446 | 2657 | 8425 | 55    |
| H00R  | 4905 | 2749 | 9300 | 55    |
| H00S  | 5079 | 3143 | 8008 | 55    |
Table S21 Crystal data and structure refinement for 11.

Empirical formula \( \text{C}_{26}\text{H}_{31}\text{BF}_2\text{N}_2\text{O}_2\text{Si} \)
Formula weight 480.43
Temperature/K 173
Crystal system monoclinic
Space group P2₁
a/Å 8.58378(17)
b/Å 12.6067(2)
c/Å 11.7191(2)
α/° 90
β/° 90.5690(18)
γ/° 90
Volume/Å³ 1268.10(4)
Z 2
ρcalc g/cm³ 1.258
μ/mm⁻¹ 1.154
F(000) 508.0
Crystal size/mm³ 0.4 × 0.3 × 0.25
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 7.544 to 142.394
Index ranges -8 ≤ h ≤ 10, -15 ≤ k ≤ 14, -14 ≤ l ≤ 12
Reflections collected 7720
Independent reflections 4491 [Rint = 0.0345, Rsigma = 0.0509]
Data/restraints/parameters 4491/1/313
Goodness-of-fit on F² 1.061
Final R indexes [I≥2σ (I)]  \( R_1 = 0.0635, \ wR_2 = 0.1735 \)

Final R indexes [all data]  \( R_1 = 0.0716, \ wR_2 = 0.1806 \)

Largest diff. peak/hole / e Å⁻³ 0.77/-0.39

Flack parameter  -0.01(3)

### Table S22 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 11. \( U_{eq} \) is defined as 1/3 of of the trace of the orthogonalised \( U_{1J} \) tensor.

| Atom | \( x \)   | \( y \)   | \( z \)   | \( U(eq) \) |
|------|----------|----------|----------|------------|
| Si01 | 6314.9(13) | 5851.2(10) | 912.9(9) | 28.8(3) |
| F002 | 9733(4) | 1286(3) | 2653(3) | 54.6(9) |
| O003 | 6749(5) | 6756(3) | 4860(3) | 41.0(8) |
| O004 | 5278(4) | 5478(3) | 3968(3) | 39.1(8) |
| F005 | 12559(4) | 8715(3) | 2000(4) | 64.6(11) |
| N006 | 7631(4) | 6058(3) | 3004(3) | 31.4(9) |
| N007 | 7287(4) | 5324(3) | 2128(3) | 29.2(8) |
| C008 | 7917(5) | 4306(4) | 2271(4) | 28.2(9) |
| C009 | 8804(6) | 4039(4) | 3241(4) | 34.5(10) |
| C00A | 8938(5) | 6728(4) | 2804(4) | 31.5(9) |
| C00B | 4527(5) | 5049(4) | 567(4) | 30.9(9) |
| C00C | 7708(6) | 3534(4) | 1427(4) | 33.4(10) |
| C00D | 10079(5) | 6397(4) | 2048(4) | 34.7(10) |
| C00E | 8320(6) | 2519(4) | 1555(5) | 37.2(10) |
| C00F | 9163(6) | 2275(4) | 2528(5) | 37.9(11) |
Table S23 Anisotropic Displacement Parameters (Å²×10³) for 11. The Anisotropic displacement factor exponent takes the form: -2π²[h²a*₂U₁₁+2hka*b*U₁₂+…].

| Atom | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|------|------|------|------|------|------|------|
| Si01 | 29.0(5) | 30.5(6) | 26.9(5) | 0.6(5) | 2.6(4) | -4.5(5) |
|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| F002 | 60 (2) | 35.5 (16) | 68 (2) | 8.6 (16) | 0.4 (16) | 10.4 (16) |
| O003 | 47.3 (19) | 46 (2) | 29.8 (17) | -11.6 (16) | 7.5 (14) | -2.8 (17) |
| O004 | 36.2 (18) | 48 (2) | 33.1 (17) | -8.5 (15) | 6.6 (13) | -0.9 (15) |
| F005 | 49 (2) | 48 (2) | 96 (3) | 7 (2) | 10.4 (19) | -16.4 (17) |
| N006 | 33.3 (18) | 32 (2) | 29.2 (17) | -7.5 (15) | 3.9 (14) | -1.9 (15) |
| N007 | 31.9 (18) | 30 (2) | 25.8 (16) | -4.4 (15) | 2.3 (13) | -3.7 (16) |
| C008 | 25.6 (19) | 32 (2) | 27 (2) | -1.2 (18) | 6.3 (16) | -2.7 (17) |
| C009 | 36 (2) | 38 (3) | 30 (2) | 0 (2) | 4.9 (19) | -3 (2) |
| C00A | 27 (2) | 37 (2) | 30 (2) | -0.2 (19) | -2.0 (16) | -1.4 (19) |
| C00B | 31 (2) | 29 (2) | 33 (2) | -2.2 (18) | 2.9 (18) | 0.6 (17) |
| C00C | 34 (2) | 33 (2) | 32 (2) | -1.7 (19) | 3.0 (18) | -2.4 (19) |
| C00D | 33 (2) | 35 (2) | 37 (2) | -7 (2) | 2.4 (18) | 0 (2) |
| C00E | 40 (2) | 32 (2) | 40 (2) | -4 (2) | 7 (2) | -3 (2) |
| C00F | 36 (2) | 32 (2) | 45 (3) | 7 (2) | 7 (2) | 2 (2) |
| C00G | 35 (2) | 42 (3) | 39 (3) | 5 (2) | 2 (2) | 2 (2) |
| C00H | 29 (2) | 40 (3) | 66 (3) | -11 (3) | -2 (2) | 0 (2) |
| C00I | 38 (2) | 40 (3) | 36 (2) | 0 (2) | 2 (2) | -8 (2) |
| C00J | 30 (2) | 48 (3) | 45 (3) | 1 (2) | 0 (2) | -5 (2) |
| C00K | 37 (2) | 34 (3) | 40 (3) | -5 (2) | -3 (2) | -1 (2) |
| C00L | 44 (3) | 34 (2) | 38 (2) | 3 (2) | -4 (2) | 0 (2) |
| C00M | 34 (2) | 42 (3) | 55 (3) | 7 (2) | -1 (2) | -9 (2) |
| C00N | 40 (3) | 46 (3) | 54 (3) | -4 (3) | 13 (2) | -14 (2) |
| C00O | 43 (3) | 31 (2) | 58 (3) | 1 (2) | -8 (2) | -1 (2) |
Table S24 Bond Lengths for 1

| Atom  | Atom  | Length/Å | Atom  | Atom  | Length/Å |
|-------|-------|----------|-------|-------|----------|
| Si01  | N007  | 1.773(4) | C00B  | C00I  | 1.401(7) |
| Si01  | C00B  | 1.878(5) | C00B  | C00L  | 1.391(7) |
| Si01  | C00Q  | 1.869(5) | C00C  | C00E  | 1.391(7) |
| Si01  | C00S  | 1.855(6) | C00D  | C00J  | 1.400(7) |
| F002  | C00F  | 1.348(6) | C00E  | C00F  | 1.380(8) |
| O003  | B00R  | 1.373(6) | C00F  | C00G  | 1.374(8) |
| O003  | C00U  | 1.450(7) | C00H  | C00N  | 1.372(9) |
| O004  | B00R  | 1.352(7) | C00H  | C00P  | 1.372(9) |
| O004  | C00T  | 1.455(6) | C00I  | C00N  | 1.383(7) |
| F005  | C00M  | 1.355(6) | C00J  | C00M  | 1.379(8) |
| N006  | N007  | 1.412(5) | C00K  | C00O  | 1.386(8) |
N006 C00A    1.426(6)   C00L C00P    1.394(8)
N006 B00R    1.433(6)   C00M C00O    1.360(9)
N007 C008    1.402(6)   C00T C00U    1.513(9)
C008 C009    1.403(7)   C00T C00W    1.436(12)
C008 C00C    1.397(7)   C00T C00X    1.611(12)
C009 C00G    1.397(7)   C00U C00V    1.591(12)
C00A C00D    1.392(7)   C00U C00Y    1.423(11)
C00A C00K    1.396(7)

Table 25 Bond Angles for 11.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| N007 | Si01 | C00B | 110.4(2) |
| N007 | Si01 | C00Q | 111.1(2) |
| N007 | Si01 | C00S | 106.1(2) |
| C00Q | Si01 | C00B | 110.7(2) |
| C00S | Si01 | C00B | 107.6(2) |
| C00S | Si01 | C00Q | 110.9(3) |
| B00R | O003 | C00U | 105.6(4) |
| B00R | O004 | C00T | 106.0(4) |
| N007 | N006 | C00A | 115.4(4) |
| N007 | N006 | B00R | 116.5(4) |
| C00A | N006 | B00R | 128.0(4) |
| N006 | N007 | Si01 | 115.6(3) |
| C008 | N007 | Si01 | 128.1(3) |
| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H009 | 8988 | 4555 | 3817 | 41    |
| H00C | 7136 | 3706 | 754  | 40    |
| H00D | 10025| 5709 | 1719 | 42    |
| H00E | 8160 | 2000 | 978  | 45    |

Table S26 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11.
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| H00G | 10008 | 2840 | 4030 | 46  |
| H00H | 681  | 3769 | -71  | 54  |
| H00I | 4181 | 4405 | 2147 | 46  |
| H00J | 12084 | 6866 | 1249 | 49  |
| H00K | 8280 | 7959 | 3825 | 44  |
| H00L | 4355 | 5518 | -1092 | 47  |
| H00N | 1809 | 3599 | 1725 | 56  |
| H00O | 10358 | 9079 | 3378 | 53  |
| H00P | 1950 | 4720 | -1480 | 53  |
| H00A | 8524 | 6374 | -166 | 66  |
| H00B | 7070 | 6180 | -1006 | 66  |
| H00F | 8029 | 5191 | -508 | 66  |
| H00M | 4967 | 7153 | 1976 | 61  |
| H00Q | 5109 | 7529 | 677  | 61  |
| H00R | 6573 | 7634 | 1526 | 61  |
| H00S | 6920 | 4994 | 5910 | 117 |
| H00T | 5791 | 5218 | 6962 | 117 |
| H00U | 7371 | 5880 | 6834 | 117 |
| H00V | 2611 | 4829 | 4870 | 170 |
| H00W | 2988 | 5233 | 6137 | 170 |
| H00X | 4073 | 4357 | 5559 | 170 |
| H00Y | 3761 | 7399 | 4480 | 146 |
| H   | 2324 | 6751 | 4991 | 146 |
|   | HA  | H00Z | HB  | HC  |
|---|-----|------|-----|-----|
|   | 2890| 6133 | 4460| 4707|
|   | 6524| 7461 | 6923| 7808|
|   | 3717| 6879 | 7032| 6072|
|   | 146 | 136  | 136 | 136 |
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