Superseding β-Diketiminato Ligands: An Amido Imidazoline-2-Imine Ligand Stabilizes the Exhaustive Series of B= X Boranes (X = O, S, Se, Te)

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Abstract: While the C=X bond (X = O, S, Se, Te) in ketones and their heavier chalcogen analogues is an established structural entity, carbon’s neighbor element boron reluctantly forms the respective B=X moieties, which has stimulated the quest for such species in the past few years. Based on the partial success achieved in this area by means of the \(N,N'\)-chelating \(\beta\)-diketiminato ligand (HNacNac), we present a new amido imidazoline-2-imine ligand system (HAmIm), which gives rise to the isolation of an exhaustive series of Lewis acid free, monomeric chalcogeno B=X boranes with documented \(\pi\)-bond character between boron and the chalcogen. The chalcogeno-boranes are isoelectronic and isolobal the respective ketones. The chemical behavior of the oxoborane (B=O) strongly resembles the classical carbonyl reactivity in C=O bonds as demonstrated by four typical textbook examples including imine and ketal formation. The improved stability provided by the HAmIm ligand system arises (i) from the formation of more stable five-membered boron chelates vs. the six-membered NacNac analogues and (ii) from the incorporation of an imidazoline-2-imine moiety providing enhanced \(\sigma\)- and \(\pi\)-donation. We, therefore, propose that the new HAmIm ligand class may supersede the widely employed NacNac system in certain applications.
1. Synthetic and Analytical Procedures

1.1. General Information

All manipulations were performed under dry argon atmosphere using Schlenk techniques or in a glove box (M. Braun 200B model) unless stated otherwise. Solvents were purified and dried using a Solvent Purification System (M. Braun) and stored over molecular sieves (3–4 Å). All commercially available compounds (TCI, abcr, deuter, Sigma Aldrich) were used without further purification. Deuterated solvents were dried over sodium (C₆D₆, THF-d₈) or CaH₂ (CD₂Cl₂, CDCl₃), distilled under argon and stored over molecular sieves (3–4 Å). Compounds 5 [1] and Li₂X (X = Se, Te) [2] were prepared according to literature methods.

NMR spectra were recorded on Bruker Avance II-300, Avance III-HD, Avance III-400 and AVII-500 spectrometer. The chemical shifts (δ) are reported in parts per million (ppm). The residual solvent peak (C₆HD₅, δ = 7.16 ppm, THF-HD₇, δ = 1.72, 3.58 ppm, CHCl₃, δ = 7.26 ppm, CHDCl₂, δ = 5.30 ppm) is used for the referencing of the ¹H-NMR spectra. The ¹³C spectra are internally calibrated by using the ¹³C resonances of the solvent peaks (C₆D₆, δ = 128.06 ppm, THF-D₈, δ = 25.31, 67.21 ppm, CDCl₃, δ = 77.16 ppm, CD₂Cl₂, δ = 53.80 ppm).

For ¹⁷B-NMR spectra an external calibration with BF₃·Et₂O was used. Coupling constants are stated in Hertz (Hz), multiplicities are defined as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), sept (septet) or m (multiplet). If necessary, 2D-NMR experiments (H,H-COSY, H,C-HSQC, H,C-HMBC) were used to aid the assignment of the signals.

IR spectra were recorded on a Bruker Vertex 70 with the KBr disc transmission technique.

Mass spectra were recorded on a Finnigan MAT 8400-MSS I instrument (for electro spray ionization, ESI) or on a Finnigan MAT 4515 instrument (electron impact mode, EI) and are reported as the m/z ratio (in Da).

Elemental analyses were accomplished by combustion and gas chromatographic analysis using a VarioMICRO Tube and HW detection. Values are reported in weight-%.
1.2. Synthesis of HAmIm 1.

1.2.1. Synthesis of Compound 4.

3-Chloro-2-butanone (2, 10.55 g, 99.0 mmol) was added to a solution of 2,6-diisopropylaniline (3, 18.43 g, 104.0 mmol, 1.05 eq.) in CH₂Cl₂ (150 mL), and the mixture was cooled to 0 °C. A solution of titanium tetrachloride (6.40 mL, 5.90 mmol, 0.60 eq.) in CH₂Cl₂ (30 mL) was added dropwise with immediate change of the color from yellowish to deep red. Triethylamine (55.20 mL, 396.0 mmol, 4.00 eq.) was added dropwise to the reaction mixture, and stirring was continued for 1 h at 0 °C and then 3 h at room temperature. The dropwise addition of water (30 mL) quenched the remaining titanium tetrachloride, and the mixture was filtered through a pad of celite. Water (200 mL) was added to the filtrate. The aqueous phase was extracted in a separator funnel with CH₂Cl₂ (3 × 100 mL). The combined organic phases were dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography (pentane / ethyl acetate, 5:95, v/v) to afford a yellowish oil of 4 in analytically pure form (19.10 g, 73 %). Rᵣ = 0.37.

¹H NMR (CD₂Cl₂, 400 MHz, 293 K): δ = 1.27 (3 H, d, ³JHH = 0.6 Hz, CH₃ in iPr), 1.29 (3 H, d, ³JHH = 0.6 Hz, CH₃ in iPr), 1.30 (3 H, d, ³JHH = 1.8 Hz, CH₃ in iPr), 1.32 (3 H, d, ³JHH = 1.8 Hz, CH₃ in iPr), 1.92 (3 H, d, ³JHH = 6.8 Hz, CHCH₂), 1.93 (3 H, s, NCCH₃), 2.85 (2 H, sept, ³JHH = 6.9 Hz, CH in iPr), 4.88 (1 H, q, ³JHH = 6.7 Hz, CHCH₃), 7.19 (1 H, t, ³JHH = 7.6 Hz, aryl-CH), 7.26 (2 H, d, ³JHH = 7.6 Hz, aryl-CH).

¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, 293 K): δ = 16.7 (NCCH₃), 22.3 (CHCH₃), 23.2, 23.3, 23.6, 23.7 (all four CH₃ in iPr), 28.5, 28.6 (both CH in iPr), 61.4 (CHCl), 123.6, 123.6, 124.4 (all three aryl-CH), 136.3, 136.4, 145.7 (all three aryl-C), 169.1 (NCCH₃).

MS (EI): m/z = 265.2 (30 %) [M]+, 202.2 (100 %) [M−CH₃CHCl]+.

Elemental analysis. Calculated for C₁₆H₂₄ClN: C 72.29, H 9.10, N 5.27. Found: C 72.18, H 8.97, N 5.35.
Figure S1. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 293 K) of compound 4.

Figure S2. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 4.
1.2.2. Synthesis of Compound 6, HAmIm-HI.

Imidazole-2-imine (5, 1.00 g, 5.12 mmol, 1 eq.) was added to a solution of compound 4 (1.36 g, 5.12 mmol, 1 eq.) in anhydrous acetone (30 mL). Sodium iodide (767 mg, 5.12 mmol, 1 eq.) was added to the reaction mixture with rapid dissolution of the solid. The clear solution was stirred for 48 h at room temperature with continuous precipitation of colorless sodium chloride. The solvent was removed under vacuum and water (30 mL) was added to yellowish honey-like residue. After stirring for 1 h chloroform (30 mL) was added, and the mixture was transferred into a separatory funnel. The aqueous phase was extracted with chloroform (2 × 20 mL) and was dried over magnesium sulfate and filtered. The filtrate was dried under vacuum to yield 6 (2.26 g, 80 %) as a white powder. Crystals suitable for X-ray crystallography (Figure S3) and elemental analysis were obtained by diffusion of n-pentane into a solution of X in dichloromethane.

$^{1}$H NMR (CD$_2$Cl$_2$, 500 MHz, 293 K): $\delta = 1.00$ (3 H, d, $^{3}$J$_{HH} = 6.9$ Hz, CH$_3$ in iPr), 1.11 (3 H, d, $^{3}$J$_{HH} = 6.9$ Hz, CH$_3$ in iPr), 1.14 (3 H, d, $^{3}$J$_{HH} = 6.9$ Hz, CH$_3$ in iPr), 1.54 (6 H, d, $^{3}$J$_{HH} = 7.1$ Hz, CH$_3$ in iPr), 1.56 (6 H, d, $^{3}$J$_{HH} = 7.1$ Hz, CH$_3$ in iPr), 1.65 (3 H, d, $^{3}$J$_{HH} = 6.8$ Hz, CHCH$_3$), 1.81 (3 H, s, N=CCCH$_3$), 2.28 (6 H, s, CH$_3$, imidazoline backbone), 2.28 (1 H, sept, $^{3}$J$_{HH} = 6.9$ Hz, CHMe$_2$ in Dipp), 4.50 (1 H, qu, $^{3}$J$_{HH} = 6.4$ Hz, CHCH$_3$ in Dipp), 5.03 (2 H, sept, $^{3}$J$_{HH} = 7.0$ Hz, CHMe$_2$ in imidazoline), 6.61 (1 H, d, $^{3}$J$_{HH} = 5.7$ Hz, NH), 7.04–7.13 (3 H, m, aryl-CH).

$^{13}$C($^{1}$H) NMR (CD$_2$Cl$_2$, 125 MHz, 293 K): $\delta = 10.5$ (N=CCCH$_3$), 18.4 (N=HCHCH$_3$), 19.9 (CCCH$_3$, imidazoline backbone), 21.4 (CH$_3$ in iPr), 21.9 (CH$_3$ in iPr), 23.0 (CH$_3$ in iPr), 23.4 (CH$_3$ in iPr), 23.5 (CH$_3$ in iPr), 23.7 (CH$_3$ in iPr), 28.1 (CHMe$_2$ in Dipp), 50.5 (CHMe$_2$ in imidazoline), 60.5 (CHCH$_3$), 123.4 (aryl-CH), 123.5 (CCCH$_3$, imidazoline backbone), 123.5, 124.4 (both aryl-CH), 136.3, 136.5, 143.2 (all three aryl-C), 144.5 (N$_3$C), 171.2 (N=CCCH$_3$).

MS (ESI+): m/z = 425.3 (100 %) [M−I]$^+$

Elemental analysis. Calculated for C$_{22}$H$_{45}$I$_3$: C 58.69, H 8.21, N 10.14. Found: C 58.42, H 7.95, N 9.95.

Figure S3. Molecular structure of compound 6. Thermal ellipsoids are presented at the 50 % level of probability. Carbon bound hydrogen atoms are omitted for clarity. The asymmetric unit contains two crystallographically independent ion pairs, one of which is depicted. Selected bond distances and bond angles are reported in Å or degree (°), respectively. C28–N5 1.344(5), C28–N6 1.346(5), C28–N7 1.371(5), C39–N7 1.472(5), C39–C41 1.515(6), C41–N8 1.267(5), C43–N8 1.425(5), N8–C41–C39 119.1(4).
Figure S4. $^1$H NMR (CD$_2$Cl$_2$, 500 MHz, 293 K) of compound 6.

Figure S5. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 125 MHz, 293 K) of compound 6.
1.2.3. Synthesis of Compound 1, HAmIm.

Hydrogen iodide adduct HAmIm-HI (6, 3.00 g, 5.36 mmol) was dissolved in methanol (10 mL). A portion of hexanes (40 mL) was added followed by a solution of potassium hydroxide (7 mL, 50 % in water) with vigorous stirring. The two-phase mixture was stirred at room temperature for 20 min. The layers were allowed to settle for 5 min. The top phase (hexanes) was separated via cannula and dried over magnesium sulfate. The solvent was removed *in vacuo* (assisted by freeze-drying), which afforded HAmIm 1 (1.07 g, 75%) as an analytically pure, off-white powder.

1H NMR (CD2Cl2, 400 MHz, 293 K): δ = 1.10 (3 H, d, 3JHH = 6.9 Hz CH3 in iPr), 1.12 (3 H, d, 3JHH = 7.0 Hz CH3 in iPr), 1.16 (3 H, d, 3JHH = 7.0 Hz, CH3 in iPr), 1.17 (3 H, d, 3JHH = 6.9 Hz, CH3 in iPr), 1.38 (6 H, d, 3JHH = 7.1 Hz, CH3 in iPr), 1.39 (6 H, d, 3JHH = 7.1 Hz, CH3 in iPr), 1.42 (3 H, d, 3JHH = 6.5 Hz, CHCH3), 1.74 (3 H, s, N=CCH3), 2.03 (6 H, s, CH3, imidazoline backbone), 2.76 (1 H, sept, 3JHH = 7.0 Hz, CHMe2 in Dipp), 2.86 (1 H, sept, 3JHH = 6.8 Hz, CHMe2 in imidazoline), 4.56 (1 H, q, 3JHH = 6.0 Hz, CHCH3), 6.99−7.19 (3 H, m, aryl-CH).

13C{1H} NMR (CD2Cl2, 100 MHz, 293 K): δ = 11.1 (N=CCH3), 16.1 (N=CCCH3), 21.1 (CCH3, imidazoline backbone), 21.4 (CH3 in iPr), 21.6 (CH3 in iPr), 23.3 (CH3 in iPr), 23.5 (CH3 in iPr), 23.8 (CH3 in iPr), 28.1 (CHMe2 in Dipp), 28.2 (CHMe2 in Dipp), 47.5(CHMe2 in imidazoline), 62.6 (CHCH3), 116.7 (CH3, imidazoline backbone), 123.2, 123.3, (both three aryl-CH), 136.5, 136.7, 147.1 (all three aryl-C), 150.9 (N=C), 177.6 (N=CCCH3).

MS (EI): m/z = 424.3 (10 %) [M]+.

Elemental analysis. Calculated for C27H44N4: C 76.36, H 10.44, N 13.19. Found: C 76.41, H 10.41, N 12.60.

![Figure S6. 1H NMR (CD2Cl2, 400 MHz, 293 K) of compound 1.](image-url)
Figure S7. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 1.
1.3. Synthesis of Compounds 7-BBr₄ and 7-Br.

1.3.1. Synthesis of Compound 7-BBr₄.

A side arm flask (the neck should be large in diameter) was charged with hexanes (100 mL), 2,3-dimethyl-2-butenone (Me₂C=CMe₂, dried over CaH₂ and distilled, 6 mL) and boron tribromide (BBr₃, 2.67 mL, 28.26 mmol, 6 eq.). HAmIm 1 (2.00 g, 4.71 mmol, 1 eq.) was dissolved in hexanes (50 mL) and added dropwise to the above mixture. An intense stream of nitrogen was applied during the addition to remove as much as possible hydrogen bromide formed in the reaction. A white precipitate was formed immediately upon addition. After 15 min the mixture was cannula-filtrated. Diethyl ether (50 mL) was added to the solid part. The suspension was stirred for 1 h and then again cannula-filtrated, which gave compound 7-BBr₄ (3.50 g, 4.19 mmol, 89 %) sufficiently pure for further reactions. Crystals suitable for X-ray crystallography (Figure S8) and elemental analysis were obtained by layering pentane with a solution of 7-BBr₄ in dichloromethane.

¹H NMR (CD₂Cl₂, 400 MHz, 293 K): δ = 1.16 (6 H, d, 3JHH = 6.9 Hz, CH₃ in iPr); 1.22 (6 H, d, 3JHH = 6.9 Hz, CH₃ in iPr), 1.56 (6 H, d, 3JHH = 7.0 Hz, CH₃ in iPr), 1.66 (6 H, d, 3JHH = 7.0 Hz, CH₃ in iPr), 1.73 (3 H, q, 5JHH = 0.9 Hz, CCH₃), 1.96 (3 H, q, 5JHH = 1.0 Hz, CCH₃), 2.47 (6 H, s, CH₃, imidazoline backbone), 2.68 (2 H, sept, 3JHH = 6.9 Hz, CHMe₂ in Dipp), (2 H, sept, 3JHH = 7.1 Hz, CHMe₂ in imidazoline), 7.28 (2 H, d, 3JHH = 7.8 Hz, aryl-CH), 7.28 (1 H, t, 3JHH = 7.8 Hz, aryl-CH).

¹³C(¹H) NMR (CD₂Cl₂, 100 MHz, 293 K): δ = 10.7 (CCH₃, imidazoline backbone), 10.8 (CCH₃), 11.4 (CCH₃), 21.4 (CCH₃ in iPr), 21.7 (CCH₃ in iPr), 23.5 (CCH₃ in iPr), 24.5 (CCH₃ in iPr), 29.1 (CHMe₂ in Dipp), 52.1 (CHMe₂ in imidazoline), 115.5 (aryl-C), 119.5 (aryl-C), 124.4 (aryl-CH), 127.1 (aryl-C), 129.4 (aryl-C), 133.0 (aryl-C), 135.2 (aryl-C), 146.3 (NₛC).

¹¹B(¹H) NMR (CD₂Cl₂, 128 MHz, 293 K): δB = −24.2 (BBr₄⁻, ω₁/₂ = 3 Hz), 21.4 (N₂BBr, ω₁/₂ = 152 Hz).

Elemental analysis. Calculated for C₇₂H₄₃BBr₅N₄: C 38.39, H 5.13, N 6.63. Found: C 37.98, H 4.97, N 6.59.

Figure S8. Molecular structure of compound 7-BBr₄. Thermal ellipsoids are presented at the 50 % level of probability. Hydrogen atoms are omitted for clarity. The asymmetric unit in the space group P2₁/c contains one ion pair of 7-BBr₄. Bond distances and bond angles are reported in Å or degree (°), respectively. Br₁–Br₁ 1.913(6), N₃–C₁ 1.379(6), N₃–B₁ 1.429(7), N₄–B₁ 1.399(7), N₄–B₁–N₃ 106.0(4), N₄–B₁–Br₁ 130.0(4), N₃–B₁–Br₁ 123.9(4).
Figure S9. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 293 K) of compound 7-BBr$_4$.

Figure S10. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 7-BBr$_4$. 
Figure S11. $^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 128 MHz, 293 K) of compound 7-BBr$_4$. 
1.3.2. Synthesis of Compound 7-Br.

A side arm flask (the neck should be large in diameter) was charged with dichloromethane (100 mL) and 7-BBr\(_2\) (3.00 g, 4.14 mmol, 1 eq.). Silver tetrafluoroborate (AgBF\(_4\), 1.60 g, 8.28 mmol, 2 eq.) was added in one portion with the application of an intense stream of nitrogen. After 5 min the mixture was cannula-filtered. The solvent of the filtrate was removed in vacuo. Diethyl ether (50 mL) was added to the hone-like residue and stirred for 3 h. The solution was decanted. The solid was dried in vacuo, which gave compound 7-Br (1.90 g, 3.28 mmol, 80 %) sufficiently pure for further reactions. Crystals suitable for X-ray crystallography (Figure S12) and elemental analysis were obtained by layering diethyl ether with a solution of 7-BBr in dichloromethane and were found to have the composition (7-Br)\(_2\)·Et\(_2\)O.

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz, 293 K): \(\delta = 1.13\) (6 H, d, 3\(^J\)HH = 6.9 Hz, CH\(_3\) in iPr), 1.20 (6 H, d, 3\(^J\)HH = 6.9 Hz, CH\(_3\) in iPr), 1.54 (6 H, d, 3\(^J\)HH = 7.0 Hz, CH\(_3\) in iPr), 1.67 (6 H, d, 3\(^J\)HH = 7.0 Hz, CH\(_3\) in iPr), 1.73 (3 H, q, 5\(^J\)HH = 1.0 Hz, CCH\(_3\)), 1.95 (3 H, q, 5\(^J\)HH = 1.0 Hz, CCH\(_3\)), 2.49 (6 H, s, CH\(_3\), imidazoline backbone), 2.67 (2 H, sept, 3\(^J\)HH = 7.0 Hz, CHMe\(_2\) in Dipp), 4.43 (2 H, sept, 3\(^J\)HH = 7.1 Hz, CHMe\(_2\) in imidazoline), 7.26 (2 H, d, 3\(^J\)HH = 7.7 Hz, aryl-CH), 7.40 (1 H, t, 3\(^J\)HH = 7.7 Hz, aryl-CH).

\(^1\)C\(^{13}\)(\(^1\)H) NMR (CD\(_2\)Cl\(_2\), 100 MHz, 293 K): \(\delta = 10.6\) (CCH\(_3\), imidazoline backbone), 10.7 (CCH\(_3\)), 11.3 (CCH\(_3\)), 21.3 (CH\(_3\) in iPr), 21.7 (CH\(_3\) in iPr), 23.4 (CH\(_3\) in iPr), 24.4 (CH\(_3\) in iPr), 29.0 (CHMe\(_2\) in Dipp), 52.1 (CHMe\(_2\) in imidazoline), 119.5, (CCH\(_3\), imidazoline backbone), 124.3 (aryl-CH), 126.9 (CCH\(_3\)), 127.0 (CCH\(_3\)), 129.2 (aryl-CH), 133.0 (aryl-C), 135.0 (aryl-C), 146.3 (N\(_3\)C).

\(^1\)B\(^{11}\)(\(^1\)H) NMR (CD\(_2\)Cl\(_2\), 128 MHz, 293 K): \(\delta_B = 21.2\) (\(\omega_{1/2} = 170\) Hz).

Elemental analysis was performed with samples obtained from the crystallization procedure. Calculated for C\(_{65}\)H\(_{66}\)B\(_2\)Br\(_2\)NaO \(\equiv\) (7-Br)\(_2\)·Et\(_2\)O: C 55.17, H 7.66, N 8.87. Found: C 55.03, H 7.45, N 9.02.

Figure S12. Molecular structures of compound 7-Br. Thermal ellipsoids are presented at the 50 \% level of probability. Hydrogen atoms are omitted for clarity. The full asymmetric unit in the space group P\(_{2}2\) is displayed and contains two crystallographically independent ion pairs of 7-Br and one molecule of diethyl ether. Bond distances and bond angles are reported in Å or degree (\(^\circ\)), respectively. First ion pair: Br1–B1 1.913(3), N1–C1 1.384(4), N1–B1 1.429(4), N4–B1 1.402(4), N4–B1–N1 106.0(2), N4–B1–Br1 128.7(2), N1–B1–Br1 125.4(2). Second ion pair: Br2–B2 1.905(3), N5–C28 1.388(4), N5–B2 1.428(4), N8–B2 1.408(4), N8–B2–N5 105.7(2), N8–B2–Br2 128.3(2), N5–B2–Br2 126.0(2).
Figure S13. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 293 K) of compound 7-Br.

Figure S14. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 7-Br.
Figure S15. $^{11}$B{($^1$H) NMR (CD$_2$Cl$_2$, 128 MHz, 293 K) of compound 7-Br.
1.4. Synthesis of Compounds 8 and 9.

1.4.1. Synthesis of Compound 8.

Compound 7-Br (1.00 g, 1.68 mmol, 1 eq.) dissolved in dichloromethane (60 mL). A mixture of H₂O (29 mg, 1.65 mmol, 1 eq.) and NEt₃ (330 mg, 3.30 mmol, 2 eq.) in dichloromethane (40 mL) was added dropwise under nitrogen flow. The reaction stirred for 2 h. Calcium hydride (CaH₂, 140 mg, 2 eq.) was added and the suspension was stirred for 1 h. Cannula filtration and removal of the solvent in vacuo gave compound 8 (623 mg, 1.176 mmol, 70 %), sufficiently pure for further manipulation. Analytically pure samples for elemental analysis and crystals suitable for X-ray crystallography (Figure S16) were obtained by layering diethyl ether with a solution of compound 3 in dichloromethane.

¹H NMR (CDCl₃, 400 MHz, 293 K): δ = 1.04 (6 H, d, 3JHH = 6.9 Hz, CH₃ in iPr), 1.10 (6 H, d, 3JHH = 7.0 Hz, CH₃ in iPr), 1.47 (3 H, q, 5JHH = 1.0 Hz, CCH₃), 1.49 (12 H, d, 3JHH = 7.1 Hz, CH₃ in iPr), 1.67 (3 H, q, 5JHH = 1.0 Hz, CCH₃), 2.20 (6 H, s, CH₃, imidazoline backbone), 2.78 (2 H, sept, 3JHH = 7.0 Hz, CHMe₂ in Dipp), 4.34 (2 H, sept, 3JHH = 7.1 Hz, CHMe₂ in imidazoline), 7.05−7.21 (3 H, m, Aryl-CH), 7.37 (1 H, s, OH).

¹³C{¹H} NMR (CDCl₃, 100 MHz, 293 K): δ = 10.1 (CCH₃, imidazoline backbone), 10.4 (CCH₃), 10.6 (CCH₃), 21.4 (CH₃ in iPr), 21.5 (CH₃ in iPr), 22.9 (CH₃ in iPr), 24.6 (CH₃ in iPr), 28.5 (CHMe₂ in Dipp), 50.7 (CHMe₂ in imidazole), 112.3 (CCH₃), 122.4 (CCH₃), 123.1 (aryl-CH), 125.4 (CCH₃, imidazoline backbone), 127.5 (aryl-CH), 128.3 (aryl-C), 134.2 (aryl-C), 136.4 (aryl-C), 146.9 (N₃C).

¹¹B{¹H} NMR (CDCl₃, 128 MHz, 293 K): δ = 22.9 (ω₁/₂ = 520 Hz).

Elemental analysis was performed with samples obtained from the crystallization procedure. Calculated for C₂₇H₄₄BBrN₄O: C 61.03, H 8.35, N 10.54. Found: C 61.25, H 8.16, N 10.59.

Figure S16. Molecular structure of compound 8. Thermal ellipsoids are presented at the 50 % level of probability. Carbon bound hydrogen atoms and the anion (Br⁻) are omitted for clarity. The asymmetric unit contains two crystallographically independent molecules, only one of which is depicted. Bond distances and bond angles are reported in Å or degree (°), respectively. O1−B1 1.353(9), N1−B1(1) 1.422(10), N4−B1 1.421(9), N1−C1 1.356(9), O1−B1−N4 127.1(7), O1−B1−N1 125.8(7), N4−B1−N1 107.1(6).
Figure S17. $^1$H NMR (CDCl$_3$, 400 MHz, 293 K) of compound 8.

Figure S18. $^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz, 293 K) of compound 8.
Figure S19. $^{11}$B($^1$H) NMR (CDCl$_3$, 128 MHz, 293 K) of compound 8.
1.4.2. Synthesis of Compound 9.

Compound 3 (200 mg, 0.37 mmol, 1 eq.) was dissolved in THF (10 mL) and a solution of lithium hexamethyl disilylamide (LiHMDS, 472 µL, 1 M in THF, 2 eq.) was added with stirring. After 1 h a small amount of a precipitate was formed, which was removed by cannula-filtration. Layering of n-pentane over the THF crude solution afforded crystals suitable for X-ray crystallography, which showed the intercalation of an undefined amount of THF in the void volume of the lattice, and was thus treated with the SQUEEZE-tool in OLEX2, see Figure S20.

The filtrate was further reduced to dryness in vacuo. The final compound 9 can only hardly be redissolved in THF, but readily dissolves in dichloromethane. Samples for NMR characterization and elemental analysis were obtained by dissolution of the material in dichloromethane (5 mL) and precipitation of product 9 upon addition of n-pentane (10 mL), which afforded 9 as a white powder (120 mg, 0.22 mmol, 60 %).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 293 K): $\delta$ = 0.87 (6 H, d, $^3$$J_{HH}$ = 6.9 Hz, CH$_3$ in iPr), 1.10 (6 H, d, $^3$$J_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.34 (6 H, d, $^3$$J_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.44 (3 H, s, CCH$_3$), 1.45 (6 H, d, $^3$$J_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.65 (3 H, s, CCH$_3$), 2.24 (6 H, s, CH$_3$, imidazoline backbone), 2.95 (2 H, sept, $^3$$J_{HH}$ = 7.0 Hz, CHMe$_2$ in Dipp), 4.53 (2 H, sept, $^3$$J_{HH}$ = 7.3 Hz, CHMe$_2$ in imidazole), 7.08 (2 H, d, $^3$$J_{HH}$ = 7.7 Hz, aryl-CH), 7.26 (1 H, t, $^3$$J_{HH}$ = 7.6 Hz, aryl-CH).

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): $\delta$ = 10.4 (CCH$_3$, imidazoline backbone), 10.8 (CCH$_3$), 11.0 (CCH$_3$), 21.5 (CH$_3$ in iPr), 21.9 (CH$_3$ in iPr), 23.3 (CH$_3$ in iPr), 25.2 (CH$_3$ in iPr), 28.3(CHMe$_2$ in Dipp), 50.2 (CHMe$_2$ in imidazoline), 111.4 (CCH$_3$), 122.3 (CCH$_3$), 123.9 (aryl-CH), 124.6 (CCH$_3$, imidazoline backbone), 127.1 (aryl-CH), 137.0 (aryl-C), 139.8 (aryl-C), 147.8 (N$_3$C).

$^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 128 MHz, 293 K): $\delta$ = 21.6 ($\omega_{1/2}$ = 700 Hz).

Elemental analysis. Calculated for C$_{27}$H$_{43}$BBrLiN$_4$O: C 60.35, H 8.07, N 10.43. Found: C 60.56, H 8.24, N 10.27.

Figure S20. Molecular structure of compound 9. The dimer is located on a center of inversion. Thermal ellipsoids are presented at the 50 % level of probability. Hydrogen atoms are omitted for clarity. Bond distances and bond angles are reported in Å or degree (°), respectively. O1–B1 1.3040(17), N1–B1 1.489(2) N4–B1 1.4523(18), Br1–Li1 2.402(3), O1–Li 1.804(3), O1–B1–N4 131.45(13), O1–B1–N1 126.06(13), N4–B1–N1 102.49(11).
**Figure S21.** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 293 K) of compound 9.

**Figure S22.** $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 9.
Figure S23. $^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 128 MHz, 293 K) of compound 9.
1.5. Synthesis of Compound 10.

Compound 8 (350 mg, 0.66 mmol, 1 eq.) was dissolved in THF (10 mL).

Potassium hexamethyl disilylamide (KHMS, 131 mg, 1 eq.) and 2.2.2-cryptand (C18N2H26O6, 248 mg, 1 eq.) were dissolved in THF (5 mL) at room temperature. This solution was added to the solution aforementioned at ambient temperature and stirring was continued for 30 min with formation of a white precipitate, which was removed by cannula-filtration. The solvent was removed to dryness.

The solid residue was treated following the aforementioned procedure with two additional cycles. The final solid was then extracted with Et2O (15 mL). The extract was concentrated to 2-3 mL and subjected to layering with pentane, which afforded colorless crystals of compound 10 (163 mg, 0.36 mmol, 55%).

1H NMR (THF-d8, 400 MHz, 293 K): δ = 1.16 (6 H, d, 3JHH = 7.0 Hz, CH3 in iPr), 1.22 (6 H, d, 3JHH = 6.8 Hz, CH3 in iPr), 1.46 (3 H, s, CCH3), 1.52 (6 H, d, 3JHH = 7.2 Hz, CH3 in iPr), 1.57 (6 H, d, 3JHH = 7.0 Hz, CH3 in iPr), 1.75 (3 H, s, CCH3), 2.28 (6 H, s, CH3, imidazoline backbone), 3.24 (2 H, sept, 3JHH = 6.9 Hz, CHMe2 in Dipp), 4.71 (2 H, sept, 3JHH = 7.1 Hz, CHMe2 in imidazoline), 7.03–7.10 (3 H, m, aryl-CH), 7.29 (6 H, s, 1×C6H6).

13C{1H} NMR (THF-d8, 100 MHz, 293 K): δ = 10.4 (CCH3, imidazoline backbone), 10.7 (CCH3), 10.9 (CCH3), 21.3 (CH3 in iPr), 21.8 (CH3 in iPr), 23.1 (CH3 in iPr), 25.2 (CH3 in iPr), 29.0 (CHMe2 in Dipp), 51.2 (CHMe2 in imidazoline), 111.9, 121.6 (aryl-CH), 123.0, 123.1, 124.8, 126.7 (aryl-CH), 140.6, 148.0 (N3C).

11B{1H} NMR (CD2Cl2, 128 MHz, 293 K): δ = 21.4 (ω1/2 = 600 Hz).

IR: v = 1667 cm⁻¹ (B=O), see Figure S27.

Elemental analysis. Calculated for C27H43BN4O: C 71.99, H 9.62, N 12.44. Found: C 72.05, H 9.85, N 12.21.
Figure S25. $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 100 MHz, 293 K) of compound 10.

Figure S26. $^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 128 MHz, 293 K) of compound 10.
Figure S27. FT-IR spectrum (KBr disc) of compound 10.
1.6. Synthesis of Compound 11.

Compound 7-Br (200 mg, 0.33 mmol, 1 eq.) was suspended in 1,2-dimethoxyethane (10 mL) and Li2S (30 mg, 1.34 mmol, 2 eq.) was added. The suspension was heated to 50 °C overnight. Volatile components were removed in vacuo, and the product 11 was extracted with benzene (15 mL) in the form of its adduct with lithium bromide. The addition of 12-crown-4 (C8H16O4, 5.8 mg, 0.33 mmol, 1 eq.) to the benzene solution and stirring for 30 min led to a precipitate of lithium bromide crown ether complex, which was removed by cannula-filtration. The filtrate was condensed to a volume of ca. 5 mL under reduced pressure. Slow solvent evaporation gave colorless crystals (also suitable for X-ray crystallography) of the composition 6 ∙ C6H6 (107 mg, 0.196 mmol, 60%).

1H NMR (THF-d8, 400 MHz, 293 K): δ = 1.12 (6 H, d, 3JHH = 7.0 Hz, CH3 in iPr), 1.28 (6 H, d, 3JHH = 6.8 Hz, CH3 in iPr), 1.51 (3 H, d, 3JHH = 1.0 Hz, C(CH3)), 1.55 (6H, d, 3JHH = 7.2 Hz, CH3 in iPr), 1.67 (6 H, d, 3JHH = 7.0 Hz, CH3 in iPr), 1.79 (3 H, d, 3JHH = 1.0 Hz, C(CH3)), 2.36 (6 H, s, CH3imidazoline backbone), 3.18 (2 H, sept, 3JHH = 6.9 Hz, CHMe2 in Dipp), 4.67 (2 H, sept, 3JHH = 7.1 Hz, CHMe2 in imidazoline), 7.03−7.11 (3 H, m, aryl-CH), 7.29 (6 H, s, 1 × C6H6).

13C{1H} NMR (THF-d8, 100 MHz, 293 K): δ = 10.0 (CCH3, imidazoline backbone), 11.3 (CCH3), 11.4 (CCH3), 21.5 (CH3 in iPr), 21.7 (CH3 in iPr), 23.6 (CH3 in iPr), 25.5 (CH3 in iPr), 29.3 (CHMe2 in Dipp), 51.3 (CHMe2 in imidazoline), 113.4, 123.0 (aryl-CH), 124.3 (2 sorts of carbon atoms, overlap), 126.5 (aryl-CH), 129.0 (C6H6), 140.4 (aryl-C), 148.1 (N3C).

11B{1H} NMR (THF-d8, 128 MHz, 293 K): δ = 35.2 (ω1/2 = 320 Hz).

IR: see Figure S31.

Elemental analysis was performed with samples obtained from the crystallization procedure. Calculated for C33H49BN3S: 6 ∙ C6H6: C 72.77, H 9.07, N 10.29. Found: C 72.34, H 8.89, N 10.11.

Figure S28. 1H NMR (THF-d8, 400 MHz, 293 K) of compound 11 ∙ C6H6.
Figure S29. $^{13}$C($^1$H) NMR (THF-$d_8$, 100 MHz, 293 K) of compound 11 $\cdot$ C$_6$H$_6$.

Figure S30. $^{11}$B($^1$H) NMR (THF-$d_8$, 128 MHz, 293 K) of compound 11 $\cdot$ C$_6$H$_6$. 
Figure S31. FT-IR spectrum (KBr disc) of compound \( \text{11} \cdot \text{C}_6\text{H}_6 \).
1.7. Synthesis of Compound 12.

Compound 7-Br (200 mg, 0.33 mmol, 1 eq.) was suspended in 1,2-dimethoxyethane (10 mL) and Li$_2$Se (61 mg, 0.66 mmol, 2 eq.) was added. The suspension was heated to 50 °C overnight. Volatile components were removed in vacuo, and the product 12 was extracted with benzene (15 mL) in the form of its adduct with lithium bromide. The addition of 12-crown-4 (C$_8$H$_{16}$O$_4$, 5.8 mg, 0.33 mmol, 1 eq.) to the benzene solution and stirring for 30 min led to a precipitate of lithium bromide crown ether complex, which was removed by cannula-filtration. The filtrate was condensed to a volume of ca. 5 mL under reduced pressure. Slow solvent evaporation gave colorless crystals (also suitable for X-ray crystallography) of the composition 12 · 3 C$_6$H$_6$ (135 mg, 0.181 mmol, 55 %).

For the measurement of NMR and FT-IR spectra samples of compound 12 · 3 C$_6$H$_6$ were dried in vacuo, which led to the complete loss of the co-crystallized solvent C$_6$H$_6$.

$^1$H NMR (THF-d$_8$, 400 MHz, 293 K): $\delta$ = 1.10 (6 H, d, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.27 (6 H, d, $^3$J$_{HH}$ = 6.8 Hz, CH$_3$ in iPr), 1.51 (3 H, d, $^3$J$_{HH}$ = 1.0 Hz, CCH$_3$), 1.53 (6H, d, $^3$J$_{HH}$ = 7.2 Hz, CH$_3$ in iPr), 1.69 (6 H, d, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.78 (3 H, d, $^3$J$_{HH}$ = 1.0 Hz, CCH$_3$), 2.33 (6 H, s, CH$_3$ in imidazoline backbone), 3.13 (2 H, sept, $^3$J$_{HH}$ = 6.9 Hz, CHMe$_2$ in Dipp), 4.64 (2 H, sept, $^3$J$_{HH}$ = 7.1 Hz, CHMe$_2$ in imidazoline), 7.01–7.11 (3 H, m, aryl-CH).

$^{13}$C($^1$H) NMR (THF-d$_8$, 100 MHz, 293 K): $\delta$ = 10.1 (CCH$_3$, imidazoline backbone), 11.5 (CCH$_3$), 11.5 (CCH$_3$), 21.6 (CH$_3$ in iPr), 21.9 (CH$_3$ in iPr), 23.8 (CH$_3$ in iPr), 26.3 (CH$_3$ in iPr), 29.4 (CHMe$_2$ in Dipp), 51.6 (CHMe$_2$ in imidazoline), 115.0, 123.2 (aryl-CH), 123.5, 124.5, 125.0, 126.7 (aryl-CH), 140.3, 148.0 (N$_3$C).

$^{11}$B($^1$H) NMR (THF-d$_8$, 128 MHz, 293 K): $\delta$ = 35.8 ($\omega_{1/2}$ = 330 Hz).

IR: see Figure S35.

Elemental analysis was performed with samples of 12 · 3 C$_6$H$_6$ as obtained from the crystallization procedure. Calculated for C$_{45}$H$_{51}$BN$_3$Se: $\equiv$ 12 · 3 C$_6$H$_6$: C 72.28, H 8.22, N 7.49. Found: C 72.59, H 8.79, N 8.05.

Figure S32. $^1$H NMR (THF-d$_8$, 400 MHz, 293 K) of compound 12.
Figure S33. $^{13}$C($^{1}$H) NMR (THF-d$_8$, 100 MHz, 293 K) of compound 12.

Figure S34. $^{11}$B($^{1}$H) NMR (THF-d$_8$, 128 MHz, 293 K) of compound 12. The spectrum additionally shows the external reference Et$_2$O·BF$_3$ with a referenced chemical shift of $\delta_B = 0.000$ ppm.
Figure S35. FT-IR spectrum (KBr disc) of compound 12.
1.8. Synthesis of Compound 13.

Compound 7-Br (200 mg, 0.33 mmol, 1 eq.) was suspended in 1,2-dimethoxy-ethane (10 mL) and Li₂Te (93 mg, 0.66 mmol, 2 eq.) was added. The suspension was stirred ambient temperature for 48 h. Volatile components were removed in vacuo, and the product 13 was extracted with benzene (15 mL) by cannula-filtration. The filtrate was condensed to a volume of ca. 5 mL under reduced pressure. Slow solvent evaporation gave colorless crystals (also suitable for X-ray crystallography) of the composition 13 · 3 C₆H₆ (58 mg, 0.075 mmol, 23 %).

In contrast to compounds 11 and 12 the NMR spectra were measured in C₆D₆, in which compound 13 shows limited solubility and prevented the record of meaningful ¹³C{¹H} NMR spectra. More polar solvents (THF-d₈ and CD₂Cl₂) lead to decomposition of 13.

¹H NMR (C₆D₆, 300 MHz, 293 K): δ = 0.89 (6 H, d, 3JHH = 7.2 Hz, CH₃ in iPr), 1.30 (6 H, d, 3JHH = 7.0 Hz, CH₃ in iPr), 1.42 (6 H, s, CH₃, imidazole backbone), 1.56 (3 H, s, CCH₃), 1.66 (6 H, d, 3JHH = 7.0 Hz, CH₃ in iPr), 1.72 (3 H, s, CCH₃), 1.76 (6 H, d, 3JHH = 6.9 Hz, CH₃ in iPr), 3.54 (2 H, sept, 3JHH = 6.9 Hz, CHMe₂ in Dipp), 4.63 (2 H, sept, 3JHH = 7.2 Hz, CHMe₂ in imidazole), 7.29−7.34 (3 H, m, aryl-CH).

¹¹B{¹H} NMR (C₆D₆, 96 MHz, 293 K): δ = 30.2 (ω₁/₂ = 680 Hz).

IR: see Figure S38.

Elemental analysis was performed with samples obtained from the crystallization procedure. Calculated for C₄₅H₆₁BN₄Te: ≡ 13 · 3 C₆H₆: C 67.87, H 7.72, N 7.04. Found: C 68.33, H 8.26, N 6.54.

Figure S36. ¹H NMR (C₆D₆, 300 MHz, 293 K) of compound 13 · 3 C₆H₆.
Figure S37. $^{11}$B($^1$H) NMR (CD$_6$$_6$, 96 MHz, 293 K) of compound $13 \cdot 3$ C$_6$H$_6$. The spectrum additionally shows the external reference Et$_2$O • BF$_3$ with a referenced chemical shift of $\delta_B = 0.000$ ppm.

Figure S38. FT-IR spectrum (KBr disc) of compound $13 \cdot 3$ C$_6$H$_6$. 

1.9. Synthesis of Compound 14.

Compound 10 (250 mg, 0.55 mmol, 1 eq.) was dissolved in 1,2-dimethoxyethane (10 mL). A portion of tert-butylamine (tBuNH$_2$, C$_4$H$_{11}$N, 120 mg, 0.66 mmol, 3 eq.) and the water trapping reagent MgSO$_4$ (300 mg) were added. The suspension was stirred for 2 h and all volatile components were removed in vacuo. The solid was extracted with benzene (15 mL) and HBF$_4$·Et$_2$O (90 mg, 1 eq.) was added. Slow solvent evaporation gave colorless crystals of compound 14 (212 mg, 65 %), which were also suitable for X-ray crystallography.

$^1$H NMR (CDCl$_3$, 400 MHz, 293 K): δ = 0.83 [9 H, s, (CH$_3$)$_3$], 1.16 (6 H, d, $^3$J$_{HH}$ = 7.2 Hz, CH$_3$ in iPr), 1.20 (6 H, d, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.53 (3 H, s, CCH$_3$), 1.62 (6 H, d, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$ in iPr), 1.63 (6 H, d, $^3$J$_{HH}$ = 6.9 Hz, CH$_3$ in iPr), 1.73 (3 H, s, CCH$_3$), 2.14 (1 H, s, NH), 2.48 (6 H, s, CH$_3$, imidazoline backbone), 2.91 (2 H, sept, $^3$J$_{HH}$ = 6.9 Hz, CHMe$_2$ in Dipp), 4.57 (2 H, sept, $^3$J$_{HH}$ = 7.2 Hz, CHMe$_2$ in imidazoline), 7.20 (2 H, d, $^3$J$_{HH}$ = 9.0 Hz, aryl-CH), 7.32 (1 H, t, $^3$J$_{HH}$ = 9.0 Hz, aryl-CH).

$^{13}$C{¹H} NMR (CDCl$_3$, 100 MHz, 293 K): δ = 10.5 (C(CH$_3$), imidazoline backbone), 10.8 (C(CH$_3$), 11.1 (CCH$_3$), 21.2 (CH$_3$ in iPr), 21.6 (CH$_3$ in iPr), 23.9 (CH$_3$ in iPr), 24.3 (CH$_3$ in iPr), 28.2 (CHMe$_2$ in Dipp), 32.7 [C(CH$_3$)$_3$], 49.5 (CHMe$_2$ in imidazoline), 50.7 [C(CH$_3$)$_3$], 114.7, 124.0 (aryl-CH), 124.5, 126.2, 128.2 (aryl-CH), 135.1, 137.9, 147.0 (N$_3$C).

$^{11}$B{¹H} NMR (CDCl$_3$, 128 MHz, 293 K): δ$_B$ = 22.9 ($\omega_{1/2}$ = 650 Hz, B=N), −1.0 ($\omega_{1/2}$ = 3 Hz, BF$_4$). Element analysis was performed with crystalline samples dried in vacuo for 24 h. Calculated for C$_{31}$H$_{53}$B$_2$F$_4$N$_5$: C 62.75, H 9.00, N 11.80. Found: C 62.48, H 8.86, N 11.66.

Figure S39. $^1$H NMR (CDCl$_3$, 400 MHz, 293 K) of compound 14.
Figure S40. $^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz, 293 K) of compound 14.

Figure S41. $^{11}$B($^1$H) NMR (CDCl$_3$, 128 MHz, 293 K) of compound 14.
1.10. Synthesis of Compound 15.

Compound 10 (250 mg, 0.55 mmol, 1 eq.) was dissolved in 1,2-dimethoxyethane (10 mL). Catechol [(1,2-(HO):C_{6}H_{4}, 73 mg, 0.66 mmol, 1.2 eq.] and the water trapping reagent MgSO_{4} (300 mg) were added. The suspension was vigorously stirred at ambient temperature for 6 h. The solvent was removed in vacuo and the solid extracted with CHCl_{3} (20 mL) and filtered over Celite. The solution was reduced in vacuo (to ca. 0.5 mL) and layered with n-pentane (20 mL). Slow solvent diffusion gave colorless crystals, which were also found suitable for X-ray crystallographic analysis. The colorless crystals were found to have the composition 15∙CHCl_{3} (278 mg, 75 %). For NMR measurements and elemental analysis the crystalline samples were finely ground to powder with mortar and pestle and dried in high vacuum for 24 h to remove CHCl_{3} trapped in the crystal lattice.

\[ ^{1}H \text{ NMR (C}_{6}D_{6}, 400 MHz, 293 K): } \delta = 0.92 \text{ (6 H, d, } J_{HH} = 7.2 \text{ Hz, CH}_{3} \text{ in iPr), 1.25 (6 H, s, CH}_{3}, \text{ imidazoline backbone), 1.26 (6 H, d, } J_{HH} = 7.0 \text{ Hz, CH}_{3} \text{ in iPr), 1.37 (6 H, d, } J_{HH} = 7.0 \text{ Hz, CH}_{3} \text{ in iPr), 1.59 (6 H, d, } J_{HH} = 6.9 \text{ Hz, CH}_{3} \text{ in iPr), 1.72 (3 H, s, CCH}_{3}, 1.75 (3 H, s, CCH}_{3}), 4.20 (2 H, sept, } J_{HH} = 6.9 \text{ Hz, CHMe}_{2} \text{ in Dipp), 5.41 (2 H, sept, } J_{HH} = 7.1 \text{ Hz, CHMe}_{2} \text{ in imidazoline), 6.57–6.60 (2 H, m, aryl-CH in catechol), 6.68–6.71 (2 H, m, aryl-CH in catechol), 7.29–7.34 (3 H, m, aryl-CH).} \]

\[ ^{13}C\{^{1}H\} \text{ NMR (C}_{6}D_{6}, 100 MHz, 293 K): } \delta = 9.7 \text{ (CCH}_{3}, \text{ imidazoline backbone), 12.3 (CCH}_{3}, 12.6 (CCH}_{3}, 21.4 (CH}_{3} \text{ in iPr), 22.0 (CH}_{3} \text{ in iPr), 25.5 (CH}_{3} \text{ in iPr), 26.2 (CH}_{3} \text{ in iPr), 28.6 (CHMe}_{2} \text{ in Dipp), 49.3 (CHMe}_{2} \text{ in imidazoline), 106.5, 108.3 (aryl-CH), 118.0 (aryl-CH), 122.0, 123.7 (aryl-CH), 126.5 (aryl-CH), 139.9, 146.0 (NCH}_{3}), 150.6, 153.8.} \]

\[ ^{11}B\{^{1}H\} \text{ NMR (C}_{6}D_{6}, 128 MHz, 293 K): } \delta_{B} = 12.0 \text{ (} \omega_{1/2} = 47 \text{ Hz).} \]

Elemental analysis. Calculated for C_{33}H_{47}BN_{4}O_{2}: C 73.05, H 8.73, N 10.33. Found: C 73.23, H 8.66, N 10.35.
Figure S43. \[^{13}C(\text{H})\] NMR (CD\(_6\), 100 MHz, 293 K) of compound 15.

Figure S44. \[^{11}B(\text{H})\] NMR (CD\(_6\), 128 MHz, 293 K) of compound 15.
1.11. Synthesis of Compound 16.

Compound 10 (250 mg, 0.55 mmol, 1 eq.) was dissolved in toluene (10 mL). Trimethylsilyl cyanide (Me3SiCN, 120 mg, 1.21 mmol, 2.2 eq.) was added and the resulting solution was stirred at ambient temperature for 6 h. The solution was reduced in vacuo (to ca. 0.5 mL) and layered with n-pentane (20 mL). Slow solvent diffusion gave colorless crystals of compound 16, which were also found suitable for X-ray crystallographic analysis (147 mg, 55%).

$^1$H NMR (CDCl$_3$, 400 MHz, 293 K): $\delta = 1.26$ (6 H, d, $^3$$J_{HH} = 7.2$ Hz, CH$_3$ in iPr), 1.45 (6 H, d, $^3$$J_{HH} = 7.0$ Hz, CH$_3$ in iPr), 1.54 (3 H, s, CCH$_3$), 1.63 (6 H, d, $^3$$J_{HH} = 7.0$ Hz, CH$_3$ in iPr), 1.79 (3 H, s, CCH$_3$), 1.80 (6 H, d, $^3$$J_{HH} = 6.9$ Hz, CH$_3$ in iPr), 2.43 (6 H, s, CH$_3$, imidazoline backbone), 3.63 (2 H, sept, $^3$$J_{HH} = 6.9$ Hz, CHMe$_2$ in Dipp), 5.37 (2 H, sept, $^3$$J_{HH} = 7.1$ Hz, CHMe$_2$ in imidazoline), 7.24–7.35 (3 H, m, aryl-CH).

$^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz, 293 K): $\delta = 10.1$ (CCH$_3$, imidazoline backbone), 11.6 (CCH$_3$), 12.2 (CCH$_3$), 21.3 (CH$_3$ in iPr), 22.4 (CH$_3$ in iPr), 25.0 (CH$_3$ in iPr), 25.4 (CH$_3$ in iPr), 27.9 (CHMe$_2$ in Dipp), 49.5 (CHMe$_2$ in imidazoline), 123.1, 123.6 (aryl-CH), 123.8, 126.3, 128.0, 137.9 (aryl-CH), 148.9 (N$_3$C), 150.1, not observed B–C≡N.

$^{11}$B($^1$H) NMR (CDCl$_3$, 128 MHz, 293 K): $\delta_B = -8.5$ ($\omega_{1/2} = 54$ Hz).

Elemental analysis. Calculated for C$_{29}$H$_{43}$BN$_6$: C 71.60, H 8.91, N 17.27. Found: C 71.25, H 8.85, N 17.35.

Figure S45. $^1$H NMR (CDCl$_3$, 400 MHz, 293 K) of compound 16.
Figure S46. $^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz, 293 K) of compound 16.

Figure S47. $^{11}$B($^1$H) NMR (CDCl$_3$, 128 MHz, 293 K) of compound 16.
1.12. *Synthesis of Thioborane 11 from Oxoborane 10*

Compound 10 (250 mg, 0.55 mmol, 1 eq.) was dissolved in 1,2-dimethoxyethane (10 mL), and the water trapping reagent MgSO₄ (300 mg) was added. Hydrogen sulfide (H₂S, anhydrous) was bubbled through the suspension for 5 min. The reaction was stirred at ambient temperature for 6 h and filtered over Celite. All volatile material was removed *in vacuo* to afford a colorless solid 11 (218 mg, 85 %). The ¹H and ¹¹B{¹H} NMR spectra recorded in THF-d₈ were identical to those of compound 11.
3. Quantum Mechanical Calculations

3.1. Detailed computational methods

All four compounds 10-13 (X = O, S, Se, Te) were optimized using several different combinations of DFT methods and basis sets, to assess the impact of the choice of DFT functional / basis set on the obtained results. The starting points for all calculations were the respective crystal structures. We used modern ωB97XD, [3] M06 [4] and CAM-B3LYP [5] functionals with two basis sets: a double-zeta 6-31G** basis set on all atoms and LANL2DZ ECP [6] on Te (if present) and a triple-zeta 6-311G++** basis set on all atoms and def2-TZVP ECP on Te (if present). The influence of the effective core potentials on the result for the Te system was investigated with additional calculations for this system using the same basis sets but with replacement of the LANL2DZ ECP by the WTBS basis set [7,8] obtained from the basis set exchange. [9] Since the results from all chosen combinations of DFT functional and basis sets were similar, we decided to base the discussion on the ωB97XD/6-311G++** (with WTBS on Te atom if present) calculations. Selected results from all other methods are presented below. All calculations were performed using Gaussian 09 software [10]. We used ultrafine grid for DFT and standard optimization and convergence parameters as implemented in Gaussian 09. Bond indices, partial charges and orbital localization calculations using Foster-Boys approach [11] were performed using the Multiwfn Version 3.7 software [12]. Orbital visualization was performed using the VMD ver. 1.9.3 software [13].
3.2. Computational Results for Compounds 10–13.

The B=X computationally obtained bond distances calculated at different levels of theory are presented in Table S1. A comparison with the structural metrics obtained from crystal structures suggests excellent accuracy with the bond lengths obtained from the medium-sized basis sets. It is worth noting, however, that the calculations were performed for the isolated molecules, while the experimental bond lengths are from crystal structures, where molecules interact with their neighbors and are densely packed, shortening their bond lengths.

The chemical character of the B=X bond was assessed by Meyer and Wiberg bond indices calculations, Tables S2 and S3. Both methods quite consistently assign the double bond to all studied systems in virtually all combinations of DFT methods and basis sets.

The natural population analysis (NPA) partial charges for B and X atoms are presented in Table 4. Similarly to the previously studied oxoborane case [14] the results for the B-O system suggest a double bond which is heavily polarized towards oxygen (NPA partial charge of -1.02 for O and 1.02 for B). The description is similar for all other B-X cases, but as shown previously the polarization become weaker as the terminal heteroatom becomes heavier, since for S the NPA partial charge is equal to -0.72, for Se it is equal to -0.58 to finally reach -0.31 for Te.

Tables S6 and S7 lists Meyer and Wiberg bond indices for the previously synthesized systems bearing a B=X bond, discussed in this work. The previously synthesized compounds are termed as stated:
Table S1. Experimental and computed bond lengths in Å obtained compounds 5-8 with various density functionals. * The bond length was calculated as the average value resulting from three crystallographically independent molecules with the individual bond lengths as stated: B1–Te1 2.151(6) Å, B2–Te2 2.124(7) Å, B3–Te3 2.143(6) Å. m stands for the double-zeta basis set (6-31G** basis set on all atoms and LANL2DZ ECP on Te), t for the triple-zeta basis set (6-311++G** basis set on all atoms and def2-TZVP ECP on Te) and w stands for the triple zeta basis set 6-311++G** for all atoms with the WTBS basis set for Te.

| Bond length [Å] | B=O (10) | B=S (11) | B=Se (12) | B=Te (13) |
|-----------------|----------|----------|-----------|----------|
| Exp. bond length | 1.2867(16) | 1.754(1) | 1.909(2) | 2.139(7)* |
| ωB97X-D/d       | 1.279    | 1.749    | 1.880    | 2.128    |
| ωB97X-D/t       | 1.296    | 1.783    | 1.904    | 2.121    |
| ωB97X-D/w       | -        | -        | -        | 2.155    |
| M06/d           | 1.274    | 1.750    | 1.880    | 2.133    |
| M06/t           | 1.289    | 1.784    | 1.906    | 2.128    |
| M06/w           | -        | -        | -        | 2.159    |
| CAM-B3LYP/d     | 1.276    | 1.750    | 1.884    | 2.134    |
| CAM-B3LYP/t     | 1.292    | 1.781    | 1.904    | 2.121    |
| CAM-B3LYP/w     | -        | -        | -        | 2.156    |

Table S2. Calculated Meyer bond indices.

| Bond order      | B=O (10) | B=S (11) | B=Se (12) | B=Te (13) |
|-----------------|----------|----------|-----------|----------|
| ωB97X-D/d       | 1.79     | 1.56     | 1.49      | 1.50     |
| ωB97X-D/t       | 1.78     | 1.68     | 1.65      | 1.37     |
| ωB97X-D/w       | -        | -        | -         | 1.61     |
| M06/d           | 1.78     | 1.57     | 1.47      | 1.52     |
| M06/t           | 1.80     | 1.69     | 1.60      | 1.36     |
| M06/w           | -        | -        | -         | 1.61     |
| CAM-B3LYP/d     | 1.84     | 1.54     | 1.47      | 1.45     |
| CAM-B3LYP/t     | 1.82     | 1.69     | 1.65      | 1.37     |
| CAM-B3LYP/w     | -        | -        | -         | 1.57     |
Table S3. Calculated Wiberg bond indices

| Bond order | B=O (10) | B=S (11) | B=Se (12) | B=Te (13) |
|------------|----------|----------|-----------|-----------|
| ωB97X-D/d  | 2.13     | 1.77     | 1.69      | 1.52      |
| ωB97X-D/t  | 1.86     | 1.75     | 1.69      | 1.53      |
| ωB97X-D/w  | -        | -        | -         | 1.69      |
| M06/d      | 2.13     | 1.78     | 1.70      | 1.55      |
| M06/t      | 1.88     | 1.76     | 1.68      | 1.55      |
| M06/w      | -        | -        | -         | 1.70      |
| CAM-B3LYP/d| 2.14     | 1.76     | 1.68      | 1.50      |
| CAM-B3LYP/t| 1.88     | 1.76     | 1.68      | 1.53      |
| CAM-B3LYP/w| -        | -        | -         | 1.69      |

Table S4. Calculated partial charges located on B and X atoms.

| ωB97X-D/w | B=O (10) | B=S (11) | B=Se (12) | B=Te (13) |
|-----------|----------|----------|-----------|-----------|
| Hirschfeld B | 0.13     | 0.06     | 0.04      | 0.02      |
| Hirschfeld X | -0.47    | -0.48    | -0.46     | -0.44     |
| Mulliken B  | 0.83     | 0.54     | 0.39      | 0.54      |
| Mulliken X  | -0.64    | -0.60    | -0.40     | -0.53     |
| Becke B     | 0.64     | 0.44     | 0.43      | 0.43      |
| Becke X     | -0.78    | -1.06    | -1.10     | -1.20     |
| NAO B       | 1.02     | 0.64     | 0.50      | 0.22      |
| NAO X       | -1.02    | -0.72    | -0.58     | -0.31     |
Table S5. Calculated frequencies of B=X stretch vibrations [cm$^{-1}$].

| $\tilde{\nu}$ (B=X) [cm$^{-1}$] | B=O (10) | B=S (11) | B=Se (12) | B=Te (13) |
|----------------------------------|----------|----------|-----------|-----------|
| $\omega$B97X-D/d                 | 1692     | 1279     | 1279      | 1278      |
| $\omega$B97X-D/t                 | 1651     | 1283     | 1280      | 1276      |
| $\omega$B97X-D/w                 | -        | -        | -         | 1283      |
| M06/d                            | 1692     | 1257     | 1255      | 1248      |
| M06/t                            | 1648     | 1261     | 1258      | 1254      |
| M06/w                            | -        | -        | -         | 1257      |
| CAM-B3LYP/d                      | 1693     | 1275     | 1276      | 1274      |
| CAM-B3LYP/t                      | 1640     | 1275     | 1272      | 1268      |
| CAM-B3LYP/w                      | -        | -        | -         | 1272      |
Table S6. Calculated Meyer bond indices for previously synthesized systems at the \( \omega B97X-D/t \) level of theory.

| Bond order       | B=O | B=S | B=Se | B=Te |
|------------------|-----|-----|------|------|
| Cowley neutral   | 1.35| -   | -    | -    |
| Cui neutral      | 1.20| -   | -    | -    |
| Kinjo neutral    | 1.27| -   | -    | -    |
| Rivard neutral   | 1.36| -   | -    | -    |
| Cui anionic      | 1.38| -   | -    | -    |
| Aldridge anionic | 1.73| 1.63| -    | -    |
| Inoue cationic   | -   | 1.85| -    | -    |
| Cui neutral      | -   | 1.95| -    | -    |
| Braunschweig neutral | - | 2.04| -    | -    |
| Braunschweig Mn  | -   | 1.72| 1.78 | 1.71 |

Table S7. Calculated Wiberg bond indices for previously synthesized systems at the \( \omega B97X-D/t \) level of theory.

| Bond order       | B=O | B=S | B=Se | B=Te |
|------------------|-----|-----|------|------|
| Cowley neutral   | 1.48| -   | -    | -    |
| Cui neutral      | 1.38| -   | -    | -    |
| Kinjo neutral    | 1.44| -   | -    | -    |
| Rivard neutral   | 1.54| -   | -    | -    |
| Cui anionic      | 1.57| -   | -    | -    |
| Aldridge anionic | 1.80| 1.69| -    | -    |
| Inoue cationic   | -   | 1.87| -    | -    |
| Cui neutral      | -   | 1.91| -    | -    |
| Braunschweig neutral | - | 2.02| -    | -    |
| Braunschweig Mn  | -   | 1.84| 1.80 | 1.82 |
A thorough investigation of the molecular orbitals was performed for compounds 10-13 to obtain a full description of the newly synthesized systems in terms of molecular orbitals theory. Selected orbitals for compound 10 are presented in Figure S39 and include the HOMO−4, HOMO−1, HOMO and LUMO orbitals. The π-bond to support the B=O double bond character can be attributed to the HOMO−4 orbital spanning over the large part of the B,N heterocyclic ring with a partial contribution of the HOMO−1 p-orbital, which is mostly localized on the O atom.

Figure S39. Selected molecular orbitals of compound 10.
In the case of compound 11 the picture is quite similar, although the order of some crucial orbitals is slightly different, Figure S40. A $\pi$-orbital similar to that of HOMO−4 for compound 10 systems is in this case the HOMO−2 orbital, while the HOMO−1, HOMO and LUMO orbitals are very similar to those of compound 10. The $\pi$-bond between the B and S atoms can be attributed to the HOMO−2 orbital spanning over the large part of the B,N-heterocyclic ring with a partial contribution of the HOMO−1 $p$-orbital, which is highly localized on the S atom.

The analysis compound 12 reveals a similar pattern of orbitals close to the HOMO and LUMO as found for compound 11. The main difference is that the HOMO−2 orbital is now antibonding with respect to the B and Se atoms, and the bonding character can be attributed to the HOMO−1 and HOMO orbitals, which both are now slightly more localized on the Se atom, and slightly less on the B atom compared to compound 10.
The order of the orbitals for compound 13 is similar except for the fact that HOMO−2 does not span over the Te atom, most likely due to a relatively long distance from the diazaborole ring to the Te atom. On the other hand the HOMO−1, HOMO and LUMO are again very similar and the B-Te double bond may be attributed to the HOMO−1 and HOMO orbitals, which are highly localized on the Te atom.

Table S8. Orbital localization of selected molecular orbitals using the Foster-Boys localization method at the ωB97XD level of theory with the 6-311++G**/WTBS basis set.

| Atom | B-O HOMO−4 | B-O HOMO−1 | B-S HOMO−1 | B-S HOMO | B-Se HOMO−1 | B-Se HOMO | B-Te HOMO−1 | B-Te HOMO |
|------|------------|------------|-------------|----------|-------------|-----------|-------------|-----------|
| B    | 22.4%      | 8.2%       | 5.3%        | 9.5%     | 4.8%        | 8.1%      | 3.3%        | 5.8%      |
| O    | 71.9%      | 87.0%      | 89.1%       | 82.1%    | 89.4%       | 83.4%     | 91.4%       | 85.7%     |
3.3. Cartesian coordinates for systems 10-13 and the previously reported compounds.

Cartesian coordinates of optimized systems at the wB97XD/6-311G++** (with WTBS on Te atom if present) level of theory.

### Compound 10

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| O1| 3.153233  | 16.821655 | 2.315123  |
| N2| 2.866975  | 17.006273 | 4.820467  |
| N3| 3.638787  | 19.268070 | 5.011371  |
| N4| 1.503991  | 18.96143  | 5.92644   |
| N5| 2.614752  | 14.911325 | 3.917108  |
| C6| 2.685959  | 18.346277 | 4.855933  |
| H8| 5.065113  | 17.824472 | 4.791749  |
| C9| 3.14979   | 16.60943  | 2.582644  |
| H10| 2.614752 | 14.911325 | 3.917108  |
| C13| 6.037085  | 19.618378 | 5.185212  |
| H14| 6.180312  | 20.655935 | 4.884841  |
| H15| 7.004523  | 19.120518 | 5.109176  |
| H16| 5.723626  | 19.593280 | 6.230150  |
| C17| 3.049541  | 20.540070 | 4.583994  |
| C18| 3.803162  | 21.804158 | 4.350449  |
| H19| 4.405419  | 22.086369 | 5.215869  |
| H20| 3.111192  | 22.620552 | 4.19526   |
| H21| 4.467036  | 21.722828 | 3.491497  |
| C22| 1.721805  | 20.372414 | 4.849958  |
| H23| 6.052771  | 21.402693 | 4.974230  |
| H24| -0.177939 | 21.212221 | 4.293661  |
| H25| 1.053546  | 22.384995 | 4.731267  |
| C27| 0.222474  | 18.249119 | 4.954280  |
| H28| 0.490731  | 17.230614 | 5.233536  |
| C29| -0.276909 | 18.216118 | 3.68483   |
| H30| -0.571426 | 19.209229 | 3.162787  |
| H31| -1.143186 | 17.556747 | 3.433873  |
| H32| 0.503915  | 17.832575 | 2.849558  |
| C33| -0.809045 | 18.749716 | 5.962762  |
| H34| -0.358916 | 18.895620 | 6.945586  |
| H35| -1.594144 | 17.998903 | 6.059582  |
| H36| -1.282060 | 19.679558 | 5.650555  |
| C37| 2.445177  | 16.096313 | 5.848176  |
| C38| 2.346797  | 16.546202 | 7.266934  |
| H39| 3.301149  | 16.950956 | 7.620838  |
| H40| 2.076811  | 15.716533 | 7.91927   |
| H41| 1.593360  | 17.329512 | 7.409668  |
| C42| 2.330431  | 14.866865 | 5.294648  |
| C43| 1.995260  | 13.571638 | 5.956245  |
| H44| 1.123673  | 13.110482 | 5.485320  |
| H45| 1.778918  | 13.709259 | 7.014770  |
| H46| 2.818131  | 12.857828 | 5.864805  |
| C47| 2.526909  | 13.763781 | 3.077978  |
| C48| 3.642105  | 12.915000 | 2.956922  |
| C49| 4.949330  | 13.288234 | 3.639404  |
| H50| 4.698652  | 13.859198 | 4.536221  |
| C51| 5.785967  | 12.078668 | 4.074834  |
| H52| 5.197589  | 11.382967 | 4.677336  |
| H53| 6.638915  | 12.411653 | 4.670578  |
| H54| 6.183466  | 11.532076 | 3.216120  |
| C55| 5.759813  | 14.222951 | 2.719194  |
| H56| 6.059054  | 13.690472 | 1.812131  |
| H57| 6.664511  | 14.569159 | 3.227157  |
| H58| 5.167381  | 15.089879 | 2.421050  |
C59  3.537188  11.788080  2.140131
H60  4.381543  11.120745  2.031989
C61  2.359342  11.517179  1.450464
H62  2.293245  10.640986  0.818427
C63  1.274426  12.378300  1.558720
H64  0.371864  12.171268  0.998545
C65  1.339304  13.513341  2.372009
C66  0.184120  14.500988  2.426756
H67  0.336385  15.128310  3.308579
H68  0.236941  15.420252  1.191755
H69  0.131926  14.831314  0.276145
C70  1.189758  15.953354  1.160199
C71  0.578207  16.149397  3.308579
C72  2.946396  16.274828  3.471523

Compound 11

S1  2.967476  17.041719  1.726802
N2  2.659524  17.033089  4.620312
N3  3.651898  19.227259  4.807688
N4  1.475753  19.135508  4.626148
N5  2.570142  14.935668  3.793232
C6  2.590058  18.392227  4.705630
C7  5.047808  18.722057  4.816921
H8  4.920701  17.642876  4.901731
C9  5.739020  19.000227  3.482865
H10 5.124374  18.622852  2.664522
H11 6.696342  18.476946  3.463654
C13 5.935169  20.063269  3.334266
C14 5.816600  19.218756  6.040448
C15 6.082777  20.271154  5.958902
H15 6.745144  18.648014  6.129577
H16 6.238506  19.073563  6.954316
C17 3.187641  20.544756  4.782698
C18 4.063766  21.744291  4.901304
H19 4.418197  21.888645  5.923521
H20 3.512578  22.638218  4.615016
H21 4.932734  21.676769  4.249501
C22 1.825003  20.487206  4.670864
C23 0.842869  21.607292  4.636662
H24 0.110146  21.479570  3.841705
H25 1.397851  22.548895  4.455013
H26 0.303874  21.702942  5.580938
C27 0.149742  18.514742  4.375540
H28 0.338738  17.448816  4.502070
C29 0.287071  18.736208  2.927936
H30 0.526397  19.781698  2.727052
H31 1.180824  18.142212  2.731503
H32 0.500365  18.406927  2.248466
C33 0.882483  18.844277  5.416821
H34 0.483272  18.853256  6.428075
H35 1.753327  18.292106  5.336473
H36 1.222732  19.679555  5.263505
C37 2.433132  16.130783  5.710660
C38 2.327744  16.633717  7.109454
H39 3.237358  17.157724  7.422969
H40 2.168420  15.810307  7.804336
H41 1.492009  17.331348  7.233450
C42 2.394208  14.882441  5.195171
C43 2.216490  13.576065  5.892448
H44 1.322207  13.058202  5.537260
H45 2.125280  13.712759  6.969447
| Compound 12 | 76 |
|-------------|----|
| Se1         | 2.971733  | 17.084545  | 1.590476  |
| N2          | 2.681423   | 17.039900  | 4.594264  |
| N3          | 3.649080   | 19.245296  | 4.788629  |
| N4          | 1.473104   | 19.127888  | 4.618324  |
| N5          | 2.591951   | 14.940129  | 3.777237  |
| C6          | 2.606429   | 18.398617  | 4.681188  |
| C7          | 5.051701   | 18.758858  | 4.796483  |
| H8          | 4.938600   | 17.670506  | 4.847986  |
| C9          | 5.756048   | 19.084993  | 3.480552  |
| H10         | 5.150947   | 18.734230  | 2.643391  |
| H11         | 6.713845   | 18.563032  | 3.453341  |
| H12         | 5.953242   | 20.152388  | 3.370691  |
| C13         | 5.798878   | 19.231026  | 6.042995  |
| H14         | 6.046959   | 20.291298  | 5.997897  |
| H15         | 6.735177   | 18.677696  | 6.122869  |
| H16         | 5.215564   | 19.044283  | 6.945928  |
| C17         | 3.167870   | 20.556803  | 4.781815  |
| C18         | 4.027753   | 21.766602  | 4.914233  |
| H19         | 4.381095   | 21.903086  | 5.937949  |
| H20         | 3.463730   | 22.656334  | 4.640104  |
| H21         | 4.896676   | 21.720007  | 4.260890  |
| C22         | 1.805482   | 20.483105  | 4.675520  |
| C23         | 0.809489   | 21.591360  | 4.662968  |
| H24         | 0.066722   | 21.459124  | 3.878402  |
| H25         | 1.310330   | 22.540087  | 4.478748  |
| H26         | 0.283589   | 21.675338  | 5.615728  |
| C27         | 0.149983   | 18.494116  | 4.384959  |
| H28         | 0.356427   | 17.428675  | 4.484950  |
| C29         | -0.327906  | 18.737467  | 2.954232  |
| H30         | -0.598138  | 19.780533  | 2.782461  |
| H31         | -1.211381  | 18.125374  | 2.766615  |
| H32         | 0.450196   | 18.441336  | 2.249061  |
| C   | X   | Y   | Z   |
|-----|-----|-----|-----|
| C33 | -0.861197 | 18.888868 | 5.460237 |
| H34 | -0.437905 | 18.777161 | 6.459523 |
| H35 | -1.728437 | 18.232019 | 7.393033 |
| H36 | -1.212804 | 19.826549 | 7.787450 |
| C37 | 2.469275  | 16.140381 | 5.690878 |
| C38 | 2.379836  | 16.647469 | 7.089343 |
| C39 | 3.295561  | 17.166245 | 7.393033 |
| C40 | 2.221838  | 15.826549 | 7.787450 |

**Compound 13**

| 76  | 17.184420 | 5.460237 |
|-----|-----------|----------|
| Te1 | 2.765005  | 1.293162 |
| N2  | 2.526083  | 4.521722 |
| N3  | 3.632097  | 4.760119 |
| N4  | 1.451402  | 4.605376 |
| N5  | 2.496049  | 3.731024 |
| C6  | 2.536427  | 4.629741 |
| C7  | 5.003767  | 4.746220 |
| C8  | 4.828279  | 3.452828 |
| C9  | 5.737199  | 3.721402 |
| C10 | 6.112918  | 2.594035 |
| H11 | 6.649953  | 3.392738 |
| H12 | 6.021524  | 3.409415 |
| C13 | 5.769991  | 6.017299 |
| H14 | 6.073083  | 6.028352 |
| H15 | 6.675550  | 6.067869 |
| H16 | 5.175178  | 6.908997 |
| C17 | 3.234753  | 4.804470 |
| C18 | 4.169323  | 4.974315 |
| H19 | 4.534898  | 5.999940 |
| Atom | Cx  | Cy  | Cz  |
|------|-----|-----|-----|
| H20  | 3.660690 | 22.612795 | 4.736477 |
| H21  | 5.030242  | 21.603954 | 4.313598 |
| C22  | 1.869721  | 20.548407 | 4.707766 |
| C23  | 0.947865  | 21.718504 | 4.745571 |
| H24  | 0.186773  | 21.660929 | 3.970305 |
| H25  | 1.506854  | 22.638065 | 4.582250 |
| H26  | 0.443815  | 21.806532 | 5.709734 |
| C27  | 0.028294  | 18.681660 | 4.392420 |
| H28  | 0.230261  | 17.602028 | 4.417417 |
| H29  | -0.444524 | 19.070263 | 5.536362 |
| C30  | -0.040023 | 18.859266 | 6.506263 |
| H31  | -1.769436 | 18.455400 | 5.455144 |
| H32  | -1.129789 | 20.123644 | 5.499835 |
| C33  | 0.019982  | 16.816049 | 7.031417 |
| H34  | 0.232704  | 17.250877 | 7.305459 |
| H40  | 2.233463  | 15.860986 | 7.741167 |
| H41  | 1.464653  | 17.340385 | 7.177951 |
| C42  | 2.688157  | 14.906681 | 5.140871 |
| C43  | 2.285332  | 13.605610 | 5.861989 |
| H44  | 1.911922  | 13.049534 | 5.530636 |
| H45  | 2.705449  | 12.758495 | 6.937857 |
| C46  | 3.159588  | 12.979940 | 5.669086 |
| C47  | 2.485881  | 13.758460 | 2.940032 |
| C48  | 3.701150  | 13.121258 | 2.643351 |
| H49  | 5.030252  | 13.687491 | 3.119607 |
| C50  | 4.810350  | 14.516973 | 3.794280 |
| C51  | 5.853244  | 12.651849 | 3.902587 |
| H52  | 5.284271  | 12.240203 | 4.740378 |
| H53  | 6.761782  | 13.112684 | 4.298208 |
| H54  | 6.156164  | 11.818530 | 3.264375 |
| C55  | 5.830449  | 14.259015 | 1.936513 |
| H56  | 6.089085  | 13.469358 | 1.225647 |
| H57  | 6.759974  | 14.714203 | 2.289871 |
| H58  | 5.247203  | 15.017588 | 1.413366 |
| C59  | 3.668521  | 11.963287 | 1.863298 |
| H60  | 4.595287  | 11.463729 | 1.611740 |
| C61  | 2.464436  | 11.452565 | 1.393643 |
| H62  | 2.456800  | 10.557929 | 0.784892 |
| C63  | 1.271103  | 12.096965 | 1.699694 |
| H64  | 0.338158  | 11.701129 | 1.316508 |
| C65  | 1.259886  | 13.257551 | 2.473584 |
| C66  | -0.052164 | 13.969589 | 2.767327 |
| H67  | 0.165033  | 14.784786 | 3.460105 |
| C68  | -0.627384 | 14.598112 | 1.486595 |
| H69  | -0.875763 | 13.826565 | 0.752649 |
| H70  | 0.096653  | 15.280572 | 1.040108 |
| H71  | -1.540659 | 15.155734 | 1.713066 |
| C72  | -1.074334 | 13.040995 | 3.442957 |
| H73  | -1.975051 | 13.600052 | 3.708308 |
| H74  | -0.666699 | 12.595825 | 4.355285 |
| H75  | -1.373647 | 12.227708 | 2.775111 |
| B76  | 2.590320  | 16.306839 | 3.253974 |

Cowley neutral B=O

| Atom | Cx  | Cy  | Cz  |
|------|-----|-----|-----|
| C    | 8.544594 | 2.771318 | 1.191427 |
| C    | 7.182562 | 3.382104 | 1.184765 |
| C    | 6.240369 | 3.062859 | 0.212080 |
| C    | 4.964404 | 3.619958 | 0.193961 |
| C    | 3.963707 | 3.263891 | -0.854330 |
| C    | 3.328582 | 5.118845 | 1.204553 |
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| C       | 3.125635 | 6.373963 | 0.648813 |
| C       | 1.928931  | 7.042738  | 0.821273 |
| C       | 0.920019  | 6.450911  | 1.564180 |
| C       | 1.098846  | 5.192093  | 2.115044 |
| C       | 2.301877  | 4.537354  | 1.934279 |
| C       | 7.772433  | 4.641951  | 3.185657 |
| C       | 7.815284  | 3.941601  | 4.381739 |
| C       | 8.611609  | 4.364698  | 5.428409 |
| C       | 9.372524  | 5.517351  | 5.284929 |
| C       | 9.343253  | 6.226248  | 4.098533 |
| C       | 8.543145  | 5.788248  | 3.060904 |
| B       | 5.537970  | 4.912647  | 2.228132 |
| F       | 4.139127  | 6.947567  | -0.074822 |
| F       | 1.739033  | 8.274451  | 0.268520 |
| F       | -0.264289 | 7.103051  | 1.737546 |
| F       | 0.095402  | 4.609798  | 2.831708 |
| F       | 2.500654  | 3.294108  | 2.478450 |
| F       | 7.052006  | 2.807549  | 4.512543 |
| F       | 8.647766  | 3.659880  | 6.597277 |
| F       | 10.158521 | 5.938197  | 6.313027 |
| F       | 10.098244 | 7.355021  | 3.959226 |
| F       | 8.499884  | 6.490543  | 1.882512 |
| Al      | 4.586923  | 6.871561  | 4.377936 |
| Cl      | 6.248377  | 7.156245  | 5.791360 |
| Cl      | 3.986405  | 8.675105  | 3.280967 |
| Cl      | 2.827125  | 5.865090  | 5.224632 |
| O       | 5.215322  | 5.759568  | 3.159571 |
| N       | 4.621416  | 4.507469  | 1.155788 |
| N       | 6.854217  | 4.269278  | 2.154153 |
| H       | 6.507755  | 2.357021  | -0.555651 |
| H       | 9.312404  | 3.545710  | 1.146793 |
| H       | 8.674925  | 2.103911  | 0.344782 |
| H       | 4.382471  | 2.562409  | -1.569701 |
| H       | 8.701487  | 2.202148  | 2.109708 |
| H       | 3.637262  | 4.156937  | -1.390211 |
| H       | 3.081219  | 2.811126  | -0.398265 |

**Cui neutral B=O**

| 108 |
|-----|
| B   | 6.886578  | 7.847994  | 10.968885 |
| B   | 8.649926  | 8.302809  | 8.866345 |
| N   | 5.889118  | 6.752266  | 11.038531 |
| N   | 6.922175  | 8.673757  | 12.202507 |
| O   | 7.565537  | 8.089871  | 9.871543 |
| C   | 4.024871  | 5.527721  | 12.119227 |
| H   | 3.271250  | 5.884808  | 11.414362 |
| H   | 4.317259  | 4.541408  | 11.774825 |
| C   | 5.169014  | 6.494797  | 12.155167 |
| C   | 5.448749  | 7.184992  | 13.326577 |
| H   | 4.924440  | 6.919579  | 14.228868 |
| C   | 6.307823  | 8.272320  | 13.344196 |
| C   | 6.528880  | 9.015125  | 14.625609 |
| H   | 7.499112  | 8.731562  | 15.036970 |
| H   | 5.763459  | 8.755238  | 15.352365 |
| H   | 6.537884  | 10.093251 | 14.845217 |
| C   | 5.612757  | 5.923667  | 9.873584 |
| C   | 6.056504  | 4.591274  | 9.877869 |
| C   | 5.622179  | 3.766315  | 8.838886 |
| H   | 5.948241  | 2.735686  | 8.808990 |
| C   | 4.817703  | 4.258441  | 7.822279 |
| H   | 4.506308  | 3.608765  | 7.016901 |
| C   | 4.452027  | 5.599548  | 7.807185 |
| C   | 3.869120  | 5.977533  | 6.980317 |
| C   | 4.840758  | 6.464493  | 8.832011 |
| C   | 7.044538  | 4.040585  | 10.905084 |
| Symbol | X       | Y       | Z       |
|-------|---------|---------|---------|
| H     | 7.341501| 4.852045| 11.570281|
| C     | 8.323346| 3.542722| 10.203786|
| H     | 8.700806| 4.279441| 9.500629 |
| C     | 8.130793| 2.621503| 9.649374 |
| H     | 6.470302| 2.899842| 11.765174|
| H     | 5.666247| 3.227194| 12.425470|
| C     | 7.259351| 2.484813| 12.395045|
| H     | 6.087005| 2.092586| 11.136909|
| C     | 4.450292| 7.940278| 8.807734 |
| H     | 5.298022| 8.507077| 9.193292 |
| C     | 3.225717| 8.228189| 9.695453 |
| H     | 2.377970| 7.608140| 9.393723 |
| C     | 4.208155| 8.477534| 7.391224 |
| H     | 5.029145| 8.215332| 7.247272 |
| C     | 4.141207| 9.565706| 7.423308 |
| H     | 3.278232| 8.097957| 6.961337 |
| C     | 7.484006| 10.020974| 12.182176|
| C     | 6.606483| 11.066701| 11.819367|
| C     | 7.095854| 12.370773| 11.882627|
| H     | 6.457853| 13.194175| 11.601521|
| C     | 8.410341| 12.627594| 12.258474|
| H     | 8.778419| 13.644289| 12.267978|
| C     | 9.248899| 11.582217| 12.612268|
| H     | 10.266636| 11.792443| 12.911732|
| C     | 8.795922| 10.257691| 12.613076|
| C     | 5.158084| 10.811312| 11.403058|
| C     | 5.121470| 9.839476| 10.908403|
| C     | 4.211013| 10.761861| 12.618826|
| C     | 4.433651| 9.942257| 13.299919|
| H     | 3.181387| 10.634542| 12.278111|
| C     | 4.269112| 11.697808| 13.179672|
| C     | 4.618277| 11.844987| 10.402748|
| C     | 4.437642| 12.808989| 10.883666|
| C     | 3.660450| 11.499882| 10.009010|
| H     | 5.297180| 11.947799| 9.569103 |
| C     | 9.715111| 9.164279| 13.139271|
| H     | 9.166379| 8.221903| 13.135528|
| C     | 10.167428| 9.458998| 14.583188|
| H     | 10.691944| 8.593347| 14.992014|
| H     | 3.532218| 9.700184| 15.241975|
| H     | 10.857104| 10.305144| 14.608487|
| C     | 10.949118| 8.976519| 12.247827|
| H     | 10.669723| 8.759930| 11.228577|
| C     | 11.556386| 8.147141| 12.615977|
| H     | 11.571937| 9.874257| 12.237340|
| C     | 9.863367| 7.230278| 9.143246 |
| C     | 10.029642| 6.472987| 10.292248|
| C     | 11.073126| 5.583666| 10.488542|
| C     | 12.003715| 5.393387| 9.489450 |
| C     | 11.884576| 6.118353| 8.316464 |
| C     | 10.835911| 7.004974| 8.172097 |
| C     | 8.032900| 7.986649| 7.357592 |
| C     | 7.677608| 6.679721| 7.036823 |
| C     | 7.161164| 6.279279| 5.818074 |
| C     | 6.965230| 7.220250| 4.827419 |
| C     | 7.327867| 8.529333| 5.072413 |
| C     | 7.858383| 8.882160| 6.304120 |
| C     | 9.154247| 9.861250| 8.999126 |
| C     | 10.452410| 10.333026| 9.136959 |
| C     | 10.773079| 11.677148| 9.263344 |
| C     | 9.774705| 12.624549| 9.205543 |
| C     | 8.468166| 12.211045| 9.027628 |
| C     | 8.191689| 10.863885| 8.954944 |
| F     | 9.142317| 6.565398| 11.367307|
| F     | 11.168873| 4.874033| 11.665065|
|  | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| F | 13.036379 | 4.505806  | 9.659054  |
| F | 12.810827 | 5.951096  | 7.317132  |
| F | 10.796160 | 7.728132  | 6.992989  |
| F | 12.810827 | 5.951096  | 7.317132  |
| F | 10.796160 | 7.728132  | 6.992989  |
| F | 11.536495 | 9.469418  | 9.184338  |
| F | 12.075451 | 12.067424 | 9.470356  |
| F | 10.062119 | 13.957948 | 9.365614  |
| F | 7.892110  | 5.667698  | 7.956070  |
| F | 6.847120  | 4.962052  | 5.579137  |
| F | 6.432929  | 6.856436  | 3.615904  |
| F | 7.160755  | 9.47250    | 4.088774  |
| F | 8.240605  | 10.208223 | 6.402594  |
| F | 11.536495 | 9.469418  | 9.184338  |
| F | 12.075451 | 12.067424 | 9.470356  |
| F | 10.062119 | 13.957948 | 9.365614  |
| F | 7.462022  | 13.148420 | 8.958062  |
| F | 6.862111  | 10.516252 | 8.760147  |

### Kinjo neutral B=O

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| A1| 2.828470  | 1.720735  | 3.662546  |
| B | 1.974390  | 4.269302  | 5.119063  |
| C | 3.624078  | 5.754189  | 2.907765  |
| H | 3.505762  | 4.908821  | 2.541571  |
| C | 4.615671  | 6.331058  | 2.122414  |
| H | 4.815285  | 5.918832  | 1.143952  |
| C | 5.338878  | 7.429342  | 2.586187  |
| H | 6.103044  | 7.87692   | 1.966813  |
| C | 5.082313  | 7.99437   | 3.856097  |
| H | 5.651755  | 8.77691   | 4.230513  |
| C | 4.111537  | 7.353330  | 4.664953  |
| C | 3.968453  | 7.713651  | 5.676282  |
| C | 3.377169  | 6.268879  | 4.181545  |
| C | 0.796321  | 5.637806  | 6.585404  |
| C | -0.125410 | 6.226714  | 7.637102  |
| C | 0.092484  | 7.749992  | 7.732726  |
| H | 1.114764  | 7.999898  | 8.027098  |
| H | -0.569428 | 8.147984  | 8.500730  |
| H | -0.158307 | 8.260064  | 6.798868  |
| C | -1.597844 | 5.953580  | 7.266410  |
| H | -1.844778 | 6.352015  | 6.281277  |
| H | -2.239608 | 6.439217  | 8.002808  |
| H | -1.815564 | 4.888143  | 7.767898  |
| C | 0.186116  | 5.588880  | 9.007891  |
| H | -0.041378 | 4.525378  | 9.006391  |
| H | -0.433205 | 6.068684  | 9.766900  |
| H | 1.233042  | 5.722769  | 9.284119  |
| C | 0.226743  | 3.188916  | 6.46018   |
| C | -0.934375 | 2.798951  | 5.958418  |
| C | -1.478496 | 3.576817  | 4.767626  |
| H | -1.064002 | 4.589712  | 4.800384  |
| C | -3.009684 | 3.713009  | 4.790708  |
| H | -3.494354 | 2.753442  | 4.602538  |
| H | -3.331817 | 4.397789  | 4.003878  |
| H | -3.373803 | 4.092479  | 5.747039  |
| C | -1.017044 | 2.935437  | 3.446768  |
| H | 0.067056  | 2.929194  | 3.360466  |
| H | -1.421779 | 3.484492  | 2.594314  |
| H | -1.353294 | 1.899234  | 3.384422  |
| C | -1.552060 | 1.613642  | 6.358638  |
| H | -2.437739 | 1.274754  | 5.840904  |
| C | -1.023581 | 0.842066  | 7.384427  |
| H | -1.505138 | -0.084626 | 7.663495  |
| C | 0.139802  | 1.237946  | 8.029533  |
| H | 0.559852  | 0.609979  | 8.802115  |
| C | 0.797555  | 2.414850  | 7.668741  |
| H | 2.124726  | 2.778241  | 8.322294  |
| H | 2.332662  | 3.831278  | 8.115291  |
| C | 2.105245  | 2.608240  | 9.850030  |
| H | 1.258953  | 3.122043  | 10.309320 |
### Supporting Information

|  |  |  |  |
|---|---|---|---|
| H | 3.025272 | 3.011252 | 10.277772 |
| H | 2.052298 | 1.554991 | 10.131096 |
| C | 3.267991 | 1.951944 | 7.704179 |
| H | 3.088991 | 0.884172 | 7.842452 |
| C1 | 1.499448 | 0.137442 | 4.422920 |
| Cl | 4.943030 | 1.305204 | 4.086448 |
| Cl | 2.484335 | 2.162166 | 1.522418 |
| N | 2.382195 | 5.646134 | 4.978898 |
| N | 1.645793 | 6.395195 | 5.890939 |
| H | 1.710120 | 7.396274 | 5.902902 |
| N | 0.938286 | 4.360102 | 6.184261 |
| O | 2.389900 | 3.201046 | 4.495317 |

**Rivard neutral B=O**

|  |  |  |  |
|---|---|---|---|
| Cl | 7.037125 | 5.659092 | 14.637034 |
| F | 3.858655 | 6.309061 | 14.127839 |
| F | 4.006465 | 8.850300 | 15.033345 |
| F | 4.200317 | 9.357350 | 17.743482 |
| F | 4.228067 | 7.255687 | 19.523361 |
| F | 4.069056 | 4.710989 | 18.656482 |
| F | 1.366353 | 4.402129 | 16.966398 |
| F | -1.086555 | 4.332236 | 15.810851 |
| F | -1.356263 | 3.618595 | 13.156094 |
| F | 0.897930 | 2.985067 | 11.685211 |
| F | 3.320947 | 3.076316 | 12.773160 |
| F | 2.089392 | 1.546826 | 16.564505 |
| F | 2.868776 | -0.429300 | 18.193825 |
| F | 5.397328 | -0.441704 | 19.300628 |
| F | 7.145801 | 1.606908 | 18.718237 |
| F | 6.412373 | 3.599358 | 17.048155 |
| O | 4.983021 | 3.764769 | 14.647302 |
| N | 6.842888 | 2.098815 | 12.809504 |
| N | 6.889488 | 3.892877 | 11.596738 |
| C | 6.608022 | 3.428569 | 12.832959 |
| C | 7.260346 | 1.720314 | 11.541622 |
| H | 7.508801 | 0.702333 | 11.317121 |
| C | 7.277250 | 2.841165 | 10.779235 |
| H | 7.525942 | 2.988392 | 9.748811 |
| C | 6.814003 | 1.211393 | 13.953248 |
| C | 5.758980 | 0.298916 | 14.070810 |
| C | 5.801190 | -0.586521 | 15.151274 |
| H | 5.001954 | -1.302284 | 15.282624 |
| C | 6.851268 | -0.555797 | 16.058880 |
| H | 6.864646 | -1.246646 | 16.809880 |
| C | 7.878819 | 0.371182 | 15.918560 |
| H | 8.671165 | 0.397060 | 16.650441 |
| C | 7.883127 | 1.283694 | 14.863761 |
| C | 4.628024 | 0.227090 | 13.057698 |
| H | 4.642944 | 1.139702 | 12.462563 |
| C | 3.248517 | 0.160310 | 13.726607 |
| H | 2.468042 | 0.274144 | 12.972381 |
| H | 3.085489 | -0.794002 | 14.231989 |
| H | 3.126700 | -0.954031 | 14.458756 |
| C | 4.826776 | -0.910170 | 12.110912 |
| H | 4.032232 | -0.995517 | 11.363065 |
| H | 5.784670 | -0.924689 | 11.588622 |
| H | 4.798087 | -1.910129 | 12.668425 |
| C | 9.032829 | 2.270684 | 14.692280 |
| H | 8.660222 | 3.153185 | 14.169891 |
| C | 9.598742 | 2.774910 | 16.026270 |
| H | 8.805813 | 3.137103 | 16.678393 |
| H | 10.151766 | 1.993932 | 16.552155 |
| H | 10.290904 | 3.597680 | 15.839594 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 10.141810 | 1.656557  | 13.817193 |
| H       | 9.765503  | 1.360836  | 12.835663 |
| H       | 10.947616 | 2.378391  | 13.668374 |
| H       | 11.560659 | 0.771340  | 14.302615 |
| C       | 6.862819  | 5.280559  | 11.184958 |
| C       | 5.665608  | 5.813640  | 10.690887 |
| C       | 5.682749  | 7.156518  | 11.06215  |
| H       | 4.778243  | 7.611266  | 9.929777  |
| C       | 6.842353  | 7.935553  | 10.408142 |
| H       | 8.017051  | 7.347680  | 10.892425 |
| C       | 8.905929  | 6.028741  | 12.96343  |
| C       | 4.118652  | 4.963002  | 10.51263  |
| H       | 4.495605  | 4.097016  | 11.17454  |
| C       | 3.122690  | 5.691150  | 10.904758 |
| H       | 2.294529  | 4.986612  | 10.87608  |
| H       | 3.193670  | 6.106289  | 11.90865  |
| H       | 2.892111  | 6.509643  | 10.209542 |
| C       | 4.335558  | 4.437533  | 9.069923  |
| H       | 5.224887  | 3.864917  | 8.796212  |
| H       | 3.467020  | 3.789411  | 8.957676  |
| H       | 4.239701  | 5.269335  | 8.365340  |
| C       | 9.345847  | 5.383010  | 11.803414 |
| H       | 9.085837  | 4.506917  | 12.402571 |
| C       | 10.155061 | 6.317230  | 12.714355 |
| H       | 9.980137  | 5.763985  | 13.167209 |
| H       | 10.582956 | 7.148154  | 12.15417  |
| H       | 9.536214  | 6.723700  | 13.512883 |
| C       | 10.210404 | 4.901833  | 10.622497 |
| H       | 11.117645 | 4.417654  | 10.98102  |
| C       | 9.675852  | 4.189117  | 9.923278  |
| H       | 10.503318 | 5.748110  | 9.997121  |
| C       | 3.986123  | 5.396899  | 16.348666 |
| C       | 3.953487  | 6.499245  | 15.50280  |
| C       | 4.026142  | 7.810031  | 15.931525 |
| C       | 4.124845  | 8.065904  | 17.286442 |
| C       | 4.141938  | 7.007661  | 18.175110 |
| C       | 4.068177  | 5.708377  | 17.699145 |
| C       | 2.459328  | 3.773652  | 14.933259 |
| C       | 1.289207  | 4.074794  | 15.624663 |
| C       | 0.026462  | 4.029737  | 15.06581  |
| C      | -0.112980 | 3.671446  | 13.737241 |
| C       | 1.014816  | 3.356139  | 13.008470 |
| C       | 2.263408  | 3.420232  | 13.606130 |
| C       | 4.217514  | 2.680002  | 16.73457  |
| C       | 3.370133  | 1.637734  | 17.085238 |
| C       | 3.737155  | 0.604311  | 17.934875 |
| C       | 4.995502  | 0.598549  | 18.498300 |
| C       | 5.873467  | 1.621456  | 18.194882 |
| C       | 5.476928  | 2.612555  | 17.323183 |
| B       | 6.053155  | 4.222223  | 14.086368 |
| B       | 3.901097  | 3.897878  | 15.62085  |

Cui anionic B=O

107

B   4.836925  8.240474  6.623679
O   5.925091  8.813451  6.126100
N   4.546461  8.168507  8.057336
N   3.808400  7.619626  5.772351
C   3.035010  7.760678  9.923894
C   3.340387  7.679716  8.607659
C   2.453214  7.033189  7.650101
C   2.682960  6.994258  6.320914
C   1.749323  6.279394  5.382297
C   5.524913  8.650746  8.982713
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| H       | 11.506494| 12.138134| 3.597722 |
| H       | 9.942880 | 12.739568| 3.066368 |
| H       | 10.553427| 11.201066| 2.452452 |
| C       | 9.286574 | 9.593388 | 7.771656 |
| H       | 8.231625 | 9.388358 | 7.967079 |
| C       | 9.774715 | 10.611876| 8.798054 |
| H       | 10.848352| 10.784181| 8.733938 |
| H       | 9.553989 | 10.230077| 9.791862 |
| H       | 9.248894 | 11.559991| 8.682498 |
| C       | 10.048126| 8.271122 | 7.074787 |
| H       | 9.659342 | 7.579135 | 8.804245 |
| H       | 9.910149 | 7.820328 | 7.074787 |
| H       | 11.118114| 8.409051 | 7.653495 |
| C       | 7.577774 | 10.868015| 3.323476 |
| H       | 6.662748 | 12.044691| 3.665443 |
| H       | 5.983410 | 12.241222| 2.835505 |
| H       | 7.239805 | 12.949430| 3.86307 |
| C       | 6.810200 | 9.582780 | 3.037875 |
| H       | 7.490545 | 8.772929 | 2.772445 |
| H       | 6.125207 | 9.740041 | 2.205487 |
| C       | 6.224380 | 9.267723 | 3.904429 |
| C       | 1.572921 | 6.550075 | 8.047958 |
| H       | 2.102443 | 7.349499 | 10.282971|
| H       | 0.956716 | 5.785494 | 5.943971 |
| H       | 1.291271 | 6.965918 | 4.666692 |
| H       | 2.282977 | 5.525456 | 4.799106 |

Aldridge anionic B=O

| 66 |
|---|
| O  | 0.670547 | 8.538561 | 2.475101 |
| N  | -0.277634| 6.541799 | 1.215905 |
| N  | 1.925600 | 7.055688 | 0.840989 |
| C  | 0.272376 | 5.628218 | 0.297374 |
| H  | -0.320894| 4.846297 | -0.148155|
| C  | 1.568238 | 5.936528 | 0.072002 |
| H  | 2.271666 | 5.454233 | -0.587013|
| C  | -1.630993| 6.489421 | 1.618138 |
| C  | -2.083202| 5.408400 | 2.403067 |
| C  | -3.438224| 5.337117 | 2.736383 |
| H  | -3.806120| 4.510240 | 3.329960 |
| C  | -4.321203| 6.334412 | 2.336407 |
| H  | -5.369535| 6.269579 | 2.602890 |
| C  | -3.852077| 7.430525 | 1.618819 |
| H  | -4.543059| 8.216930 | 1.345939 |
| C  | -2.507706| 7.532783 | 1.251421 |
| C  | -1.963281| 8.736883 | 0.492493 |
| H  | -1.034456| 9.012884 | 1.000319 |
| C  | -1.633750| 8.381583 | -0.968949|
| H  | -2.544811| 8.111776 | -1.514409|
| H  | -0.935128| 7.547100 | -1.022003|
| H  | -1.175312| 9.239474 | -1.470096|
| C  | -2.880889| 9.964101 | 0.542067 |
| H  | -2.365581| 10.817760| 0.094922 |
| H  | -3.135584| 10.226173| 1.571015 |
| H  | -3.809491| 9.807165 | -0.017751|
| C  | -1.063411| 4.428537 | 2.970894 |
| H  | -0.317202| 4.232301 | 2.199247 |
| C  | -1.657596| 3.079155 | 3.392932 |
| H  | -2.320496| 3.183187 | 4.256839 |
| H  | -0.854057| 2.395428 | 3.678507 |
| H  | -2.225900| 2.619903 | 2.580132 |
| C  | -0.324406| 5.093893 | 4.149881 |
| H  | 0.101715 | 6.052362 | 3.851507 |
### Supporting Information

#### Aldridge anionic B=S

| Element | X  | Y  | Z     |
|---------|----|----|-------|
| C       | 4.908763 | 11.128324 | 11.337128 |
| H       | 4.427881  | 10.186723  | 11.133328  |
| N       | 4.189926  | 12.227994  | 11.835954  |
| S       | 4.699056  | 15.029623  | 12.621474  |
| B       | 5.075001  | 13.383210  | 12.007093  |
| C       | 2.826915  | 12.114324  | 12.220320  |
| N       | 6.359422  | 12.828127  | 11.563698  |
| C       | 6.198541  | 11.486023  | 11.172755  |
| H       | 7.029132  | 10.904427  | 10.806954  |
| C       | 1.815973  | 12.320940  | 11.265531  |
| C       | 0.483589  | 12.194366  | 11.664958  |
| H       | 0.308986  | 12.361388  | 10.946256  |
| C       | 0.160309  | 11.873906  | 12.979758  |
| H       | 0.877935  | 11.784119  | 13.275855  |
| C       | 2.514952  | 11.803978  | 13.554666  |
| C       | 1.170221  | 11.685333  | 13.915940  |
| H       | 0.913730  | 11.455734  | 14.943403  |
| C       | 3.610618  | 11.635009  | 14.596364  |
| H       | 4.566076  | 11.735669  | 14.080715  |
| C       | 3.544262  | 12.756132  | 15.645271  |
| H       | 3.631127  | 13.725076  | 15.157400  |
| H       | 4.367735  | 12.656740  | 16.358170  |
| C       | 2.602510  | 12.720347  | 16.202859  |
| C       | 3.573471  | 10.242521  | 15.245681  |
| H       | 2.646290  | 10.087345  | 15.805738  |
| H       | 4.409000  | 10.129813  | 15.942124  |
| H       | 3.648828  | 9.458374   | 14.488856  |
| C       | 2.177571  | 12.752027  | 9.852734   |
| C       | 3.222970  | 12.484277  | 9.692065   |
| C       | 2.078486  | 14.283679  | 9.733630   |
| H       | 2.406385  | 14.611733  | 8.742474   |
### Inoue cationic B=S

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| S | 15.462345 | 12.438124 | 5.901269 |
| B | 15.568816 | 10.785980 | 5.329226 |
| N | 16.375877 | 9.663504 | 5.854743 |
| N | 14.873816 | 10.142471 | 4.192808 |
| N | 18.475519 | 9.460435 | 7.028489 |
| N | 16.718369 | 9.913029 | 8.240955 |
| N | 14.873799 | 11.770135 | 2.457643 |
| N | 12.767929 | 10.469226 | 3.058261 |
| C | 16.376996 | 8.508420 | 4.931183 |
| H | 16.438467 | 7.563913 | 5.469998 |
| H | 17.211712 | 8.567234 | 4.229628 |
| C | 15.035863 | 8.672512 | 4.212373 |
| H | 15.058720 | 8.257827 | 3.205504 |
| H | 14.227002 | 8.195624 | 4.769813 |
| C | 17.141110 | 9.690266 | 6.972936 |
| C | 18.901289 | 9.548221 | 8.352173 |
| H | 19.929435 | 9.403829 | 8.619416 |
| C | 17.812583 | 9.839919 | 9.101295 |
| H | 17.701288 | 9.995383 | 10.155802 |
| C | 19.300984 | 9.225986 | 5.871926 |
| C | 19.616452 | 10.305721 | 5.039303 |
| C | 20.358199 | 10.028208 | 3.888751 |
| H | 20.617785 | 10.849295 | 3.232763 |
| C | 20.777921 | 8.736151 | 3.571146 |
| C | 20.449685 | 7.691363 | 4.439222 |
| H | 20.777106 | 6.684582 | 4.208103 |
| C | 19.708868 | 7.913266 | 5.600550 |
| C | 19.171046 | 11.709374 | 5.343646 |
### Cui neutral B=S

|   |   |   |   |   |
|---|---|---|---|---|
| C | 2.93903 | 2.623313 | 0.916864 |
| B | 3.359785 | 1.776663 | -0.613321 |
| N | 2.037759 | 3.113296 | 1.567497 |
| N | 4.885713 | 2.959253 | 1.758328 |
| C | 0.687990 | 4.212222 | 3.311155 |
| H | 0.181072 | 4.889472 | 2.623413 |
| H | 0.03649 | 4.717077 | 4.262454 |
| H | 0.019532 | 3.362139 | 3.460368 |
| C | 2.003698 | 3.762938 | 2.747175 |
| C | 3.185076 | 4.015751 | 3.436720 |
| H | 3.144350 | 4.536230 | 4.378985 |
| C | 4.417947 | 3.611422 | 2.935181 |
| C | 5.676411 | 3.896363 | 3.699287 |
| H | 6.203445 | 2.974869 | 3.941882 |
| H | 5.449904 | 4.428285 | 4.621374 |
| C | 0.784446 | 2.869940 | 0.878367 |
| C | 0.089970 | 1.687758 | 1.147708 |
| C | -1.131584 | 1.488643 | 0.502324 |
| H | -1.684178 | 0.577060 | 0.688402 |
| C | -1.629246 | 2.436470 | -0.385732 |
| H | -2.574742 | 2.265796 | -0.882480 |
| C | -0.906209 | 3.594887 | -0.650305 |
| H | -1.283755 | 4.319598 | -1.359681 |
| C | 0.319197 | 3.829562 | -0.024466 |
| C | 0.675353 | 0.646036 | 2.063550 |
| H | -0.014238 | -0.187219 | 2.194078 |
| H | 0.910315 | 1.047460 | 3.052997 |
| C | 1.603942 | 0.260120 | 1.636375 |
| C | 1.146383 | 0.546011 | -0.344868 |
| H | 1.402151 | 5.621712 | 0.548703 |
| H | 0.61593 | 5.706515 | -1.029703 |
| H | 2.082577 | 4.740499 | -0.818081 |
| C | 5.790126 | 2.553926 | 1.269314 |
| C | 6.280904 | 1.297013 | 1.632159 |
| C | 7.553003 | 0.939868 | 1.182010 |
| H | 7.951562 | -0.031686 | 1.443156 |
| C | 8.296869 | 1.808530 | 0.390330 |
| H | 9.278950 | 1.515663 | 0.044509 |
| C | 7.774293 | 3.045407 | 0.027356 |
| H | 8.344779 | 3.709632 | -0.608505 |
| C | 6.505942 | 3.438166 | 0.458002 |
| C | 5.434812 | 0.345929 | 2.436019 |
| H | 5.986668 | -0.564923 | 2.665579 |
| H | 4.563920 | 0.073559 | 1.865176 |
| H | 5.099450 | 0.783957 | 3.79906 |
| C | 5.897046 | 4.744998 | 0.024344 |
| C | 5.013937 | 4.553792 | -0.589886 |
| H | 6.605285 | 5.326277 | -0.565064 |
| H | 5.581144 | 5.358018 | 0.872715 |
### Braunschweig neutral B=S

| Atom | X    | Y    | Z    |
|------|------|------|------|
| S    | 3.138952 | 3.519824 | 3.321982 |
| B    | 4.755125  | 2.862243  | 3.106795  |
| N    | 5.912749  | 3.833716  | 3.635605  |
| C    | 6.514011  | 4.836427  | 2.948431  |
| H    | 4.225889  | 0.625969  | 2.475269  |
| N    | 6.399754  | 3.911340  | 4.898914  |
| C    | 6.023723  | 0.665021  | 3.50487   |
| H    | 6.352129  | -0.290886 | 3.109003  |
| H    | 5.407533  | 0.448493  | 4.407118  |
| H    | 6.919166  | 1.203777  | 3.858649  |
| C    | 6.158216  | 1.735736  | 1.268579  |
| H    | 6.487428  | 0.788633  | 0.828237  |
| H    | 7.055793  | 2.289434  | 1.564398  |
| H    | 5.640487  | 2.302756  | 0.490454  |
| C    | 4.031006  | 0.625969  | 2.005113  |
| H    | 4.374332  | -0.322794 | 1.576632  |
| H    | 3.449860  | 1.160728  | 1.252299  |
| H    | 3.355521  | 0.411880  | 2.834758  |
| C    | 7.375555  | 5.543515  | 3.782269  |
| H    | 7.941041  | 6.385510  | 3.433567  |
| C    | 7.304071  | 4.964441  | 5.003273  |
| H    | 7.794968  | 5.203249  | 5.926477  |
| C    | 6.236245  | 5.172535  | 1.555486  |
| H    | 6.940183  | 4.674523  | 0.891717  |
| H    | 6.306880  | 6.250273  | 1.430371  |
| C    | 6.223063  | 4.857477  | 1.318126  |
| C    | 5.975798  | 3.061424  | 6.007174  |
| H    | 5.979169  | 3.646882  | 6.923639  |
| H    | 6.388285  | 2.204801  | 6.110728  |
| H    | 4.962179  | 2.719041  | 5.813650  |

### Braunschweig neutral Mn B=S

| Atom | X    | Y    | Z    |
|------|------|------|------|
| Mn   | 6.489238 | 8.604581 | 8.850635 |
| O    | 9.285944  | 9.028765  | 9.602175  |
| C    | 8.155855  | 8.785025  | 9.342692  |
| S    | 5.761532  | 7.001646  | 10.555193 |
| B    | 6.760183  | 5.579380  | 10.887014 |
| C    | 6.668651  | 7.481146  | 7.566882  |
| O    | 7.115350  | 6.829068  | 6.609201  |
| C    | 6.436044  | 4.445109  | 11.959147 |
| C    | 6.332156  | 3.078159  | 11.237700 |
| H    | 6.128836  | 2.287014  | 11.966102 |
| H    | 7.261824  | 2.819733  | 10.721371 |
| H    | 5.518229  | 3.076604  | 10.508602 |
| C    | 5.937184  | 4.360758  | 12.981008 |
| H    | 7.395123  | 3.597288  | 13.709872 |
| H    | 7.709475  | 5.298557  | 13.530490 |
| H    | 8.845904  | 4.125994  | 12.495608 |
| C    | 5.152990  | 4.707971  | 12.717327 |
| H    | 4.938395  | 3.908284  | 13.442052 |
| H    | 4.277907  | 4.758594  | 12.031464 |
| H    | 5.164665  | 5.658101  | 13.252372 |
| C    | 4.580987  | 9.312780  | 8.049864  |
| H    | 3.839230  | 8.709051  | 7.559940  |
| C    | 4.614954  | 9.645777  | 9.426599  |
| H    | 3.940998  | 9.269277  | 10.175244 |
| C    | 5.731501  | 10.482966 | 9.673887  |
| H    | 6.006225  | 10.913934 | 10.619106 |
| C    | 6.396662  | 10.692783 | 8.419104  |
| H    | 7.256949  | 11.317643 | 8.257362  |
| C    | 5.689495  | 9.973374  | 7.420336  |
| H    | 5.920053  | 9.958068  | 6.370002  |
### SUPPORTING INFORMATION

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|-------|-------|-------|
| N       | 9.296449 | 5.979034 | 10.312641 |
| C       | 8.089911  | 5.437679  | 10.029888 |
| N       | 8.207600  | 4.870362  | 8.807922  |
| C       | 9.488863  | 5.076361  | 8.310443  |
| H       | 10.229694 | 4.463292  | 7.043103  |
| C       | 10.155297 | 6.070999  | 12.294888 |
| H       | 8.707349  | 7.074551  | 11.983050 |
| C       | 9.627821  | 6.716211  | 11.529706 |
| H       | 10.229694 | 7.579053  | 11.263117 |
| H       | 10.155297 | 6.070999  | 12.294888 |
| H       | 8.707349  | 7.074551  | 11.983050 |

| Braunschweig neutral Mn B=Se |
|-------------------------------|
| 45 Se  | 1.066006 | 4.559700  | 2.448042 |
| O      | 2.610727 | 4.635385  | 6.377499 |
| C      | 2.383635 | 5.234914  | 5.380938 |
| Mn     | 2.047270 | 6.286148  | 4.027820 |
| B      | 2.028762 | 2.953959  | 2.259804 |
| C      | 3.689575 | 6.258154  | 3.436748 |
| O      | 4.818610 | 6.360888  | 3.091469 |
| C      | 1.612371 | 1.724553  | 1.330961 |
| C      | 0.308885 | 1.966373  | 0.558067 |
| H      | 0.066855 | 2.096405  | -0.061450 |
| H      | 0.390202 | 2.840064  | -0.090054 |
| H      | 0.524593 | 2.143953  | 1.240610 |
| C      | 2.751487 | 1.452203  | 0.312594 |
| H      | 2.489466 | 0.595932  | -0.316662 |
| H      | 3.696645 | 1.217656  | 0.811439 |
| H      | 2.908772 | 2.311987  | -0.343052 |
| C      | 1.447652 | 0.459439  | 2.209474 |
| H      | 1.184666 | -0.397453 | 1.581459 |
| H      | 0.649738 | 0.592035  | 2.944049 |
| H      | 2.370831 | 0.208221  | 2.740339 |
| H      | 0.262110 | 7.323148  | 4.858703 |
| H      | 0.498558 | 6.745552  | 5.441163 |
| C      | 0.240913 | 7.438044  | 3.456881 |
| H      | -0.515832 | 7.074179  | 2.784417 |
| C      | 1.409699 | 8.144481  | 3.074314 |
| C      | 1.662298 | 8.464524  | 2.080198 |
| H      | 2.164512 | 8.401682  | 4.267252 |
| H      | 3.084935 | 8.954986  | 4.364187 |
| C      | 1.455980 | 7.840548  | 5.364587 |
| H      | 1.751756 | 7.895951  | 6.398104 |
| C      | 3.361866 | 2.830942  | 3.106489 |
| N      | 3.473422 | 2.397603  | 4.383455 |
| C      | 4.776220 | 2.575993  | 4.833090 |
| H      | 5.064081 | 2.337334  | 5.837654 |
| N      | 4.593696 | 3.257921  | 2.744498 |
| C      | 5.477234 | 3.114334  | 3.807511 |
| H      | 6.497257 | 3.436994  | 3.741082 |
| C      | 4.945262 | 3.825397  | 1.444758 |
| H      | 5.609408 | 4.668294  | 1.598617 |
| H      | 4.037947 | 4.192627  | 0.969157 |
| H      | 5.407945 | 3.068406  | 0.815674 |
| C      | 2.388285 | 1.861017  | 5.192918 |
| H      | 2.467970 | 2.255286  | 6.200236 |
| H      | 2.412778 | 0.773195  | 5.193736 |
| H      | 1.438040 | 2.201601  | 4.776122 |
### Supporting Information

#### Braunschweig Neutral Mn B=Te

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Te      | 1.304180 | 1.988061 | 9.954670 |
| O       | -2.661073 | 0.392295 | 9.256698 |
| C       | -1.536470 | 0.387853 | 8.881526 |
| Mn      | 0.079772  | 0.206388 | 8.254023 |
| B       | 0.222078  | 3.810279 | 10.067756 |
| C       | -0.166610 | 1.314126 | 6.930756  |
| O       | -0.342316 | 1.962827 | 5.954195  |
| C       | 1.780710  | 0.877887 | 7.429627  |
| H       | 2.592755  | 0.451131 | 6.870259  |
| C       | 0.541688  | -1.362337| 6.891791  |
| H       | 0.264051  | -1.365887| 5.852956  |
| C       | -0.231985 | -1.878939| 7.964240  |
| H       | -1.197924 | -2.343840| 7.880766  |
| C       | 0.523232  | -1.718690| 9.174105  |
| H       | 0.223756  | -2.034637| 10.156454 |
| C       | 1.758622  | -1.115585| 8.827793  |
| H       | 2.537713  | -0.847252| 9.518875  |
| C       | 0.603964  | 5.087309 | 10.941830 |
| H       | 0.773822  | 6.307415 | 10.000453 |
| C       | 1.011964  | 7.198016 | 10.589834 |
| H       | -0.140874 | 6.518006 | 9.438904  |
| C       | 1.589116  | 6.149069 | 9.290881  |
| H       | 1.895010  | 4.913307 | 11.758153 |
| C       | 2.103106  | 5.820259 | 12.335012 |
| H       | 2.749245  | 4.716070 | 11.108248 |
| C       | 1.812789  | 4.075666 | 12.452853 |
| H       | -0.561462 | 5.393704 | 11.917412 |
| C       | -0.323050 | 6.282360 | 12.509606 |
| H       | -0.725786 | 4.565228 | 12.610175 |
| C       | -1.495677 | 5.592993 | 11.384267 |
| H       | -1.090044 | 3.879586 | 9.186418  |
| N       | -2.329638 | 3.466241 | 9.542120  |
| C       | -3.190295 | 3.557604 | 8.455178  |
| H       | -4.209541 | 3.231522 | 8.519495  |
| N       | -1.176687 | 4.253464 | 7.887723  |
| C       | -2.469419 | 4.049835 | 7.420694  |
| H       | -2.735676 | 4.238492 | 6.399765  |
| C       | -2.710754 | 2.954217 | 10.856077 |
| H       | -3.366064 | 2.100151 | 10.719818 |
| H       | -3.196851 | 3.734583 | 11.438372 |
| C       | -1.816751 | 2.614611 | 11.372563 |
| H       | -0.073951 | 4.755837 | 7.071948  |
| H       | -0.139671 | 4.309078 | 6.085317  |
| H       | 0.865160  | 4.443724 | 7.521344  |
| H       | -0.110961 | 5.842006 | 7.015542  |
4. X-ray Crystallographic Analysis

4.1. General Information

Data collections were performed by mounting single crystals on glass fibers or MiTeGen mounts in perfluorinated oil. Diffractometers used for intensity measurements (at 100 K) were Oxford Diffraction Xcalibur E with Mo $K\alpha$ radiation or Rigaku XtaLAB Synergy S Single Source with either Mo $K\alpha$ or Cu $K\alpha$ micro sources. Absorption correction was applied based on multi-scan methods. Data reduction was performed using the program CrystallisPro.[15] The structures were solved with SHELXT-14/5.[16] and refined anisotropically on $F^2$ using the programs SHELXL-14/7 and SHELXL-17/1 [17] employing the graphical surfaces WINGX [18] or Olex² Crystallography Software.[19]
4.2. Compound 6.

CCDC entry code: 2027614
Empirical formula: C_{27}H_{45}I_{4}N_{4}
Formula weight: 552.57
Temperature: 100.00(10) K
Wavelength: 1.54184 Å
Crystal system: Triclinic
Space group: P-1, Z = 4
Unit cell dimensions: 
\[ \begin{array}{c}
\alpha = 11.2124(2) \text{ Å} \\
\beta = 16.0192(3) \text{ Å} \\
\gamma = 16.5432(3) \text{ Å}
\end{array} \]
\[ \begin{array}{c}
\alpha = 71.246(2)^\circ \\
\beta = 89.5310(10)^\circ \\
\gamma = 88.9930(10)^\circ 
\end{array} \]
Volume: 2813.18(9) Å³
Density (calculated): 1.305 g/cm³
Absorption coefficient: 9.079 mm⁻¹
F(000): 1152
Theta range for data collection: 2.821 to 74.492°.
Index ranges: -14<=h<=14, -18<=k<=20, -20<=l<=20
Reflections collected: 57855
Independent reflections: 11401 [R(int) = 0.0563]
Completeness to theta = 67.684°: 99.8 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.38687
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 11401 / 2 / 609
Goodness-of-fit on F²: 1.018
Final R indices [I>2sigma(I)]: R₁ = 0.0592, wR₂ = 0.1626
R indices (all data): R₁ = 0.0638, wR₂ = 0.1668
Largest diff. peak and hole: 3.200 and -1.642 e.Å⁻³
4.3. Compound 7-BBr₄.

CCDC entry code: 2027606
Empirical formula: C₂₇H₄₃B₂Br₅N₄
Formula weight: 844.82
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: \(P2_1/c\), \(Z = 4\)
Unit cell dimensions:
\[a = 8.5096(2) \text{ Å}, \quad \alpha = 90^\circ\]
\[b = 16.1289(4) \text{ Å}, \quad \beta = 98.289(2)^\circ\]
\[c = 25.3325(6) \text{ Å}, \quad \gamma = 90^\circ\]
Volume: 3440.58(14) Å³
Density (calculated): 1.631 g/cm³
Absorption coefficient: 5.863 mm⁻¹
\(F(000): 1672\)
Theta range for data collection: 2.526° to 26.370°
Completeness to theta = 25.242°: 99.9 %
Index ranges: -10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -31 ≤ l ≤ 31
Reflections collected: 11825
Independent reflections: 11825 (Rint = 0.0942)
Max. and min. transmission: 0.991 and 0.923
Refinement method: Full-matrix least-squares on \(F^2\)
Data / restraints / parameters: 11825 / 0 / 350
Goodness-of-fit on \(F^2\): 1.045
Final R indices [I>2sigma(I)]: \(R_1 = 0.0365, \quad wR_2 = 0.1056\)
R indices (all data): \(R_1 = 0.0412, \quad wR_2 = 0.1079\)
Largest diff. peak and hole: 1.479 and -1.686 e.Å⁻³
4.4. Compound 7-Br.

CCDC entry code: 2027609
Empirical formula: C_{58}H_{98}Br_4N_8O ≡ (7-Br)_2 · Et_2O
Formula weight: 1262.68
Temperature: 100.0(3) K
Wavelength: 0.71073 Å
Crystal system: Trigonal
Space group: P32, Z = 3
Unit cell dimensions:
\[
\begin{align*}
    a &= 17.67270(10) \text{ Å} & \alpha &= 90^\circ \\
    b &= 17.67270(10) \text{ Å} & \beta &= 90^\circ \\
    c &= 17.60890(10) \text{ Å} & \gamma &= 120^\circ
\end{align*}
\]
Volume: 4762.87(6) Å³
Density (calculated): 1.321 g/cm³
Absorption coefficient: 2.578 mm⁻¹
F(000): 1974
Theta range for data collection: 2.579 to 26.371°.
Index ranges: -22<=h<=22, -22<=k<=22, -22<=l<=22
Reflections collected: 191395
Independent reflections: 12987 [R(int) = 0.0401]
Completeness to theta = 25.242°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.78069
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 12987 / 1 / 685
Goodness-of-fit on F²: 1.069
Final R indices [I>2sigma(I)]: R₁ = 0.0230, wR₂ = 0.0634
R indices (all data): R₁ = 0.0236, wR₂ = 0.0637
Absolute structure parameter: 0.005(5)
Largest diff. peak and hole: 0.674 and -0.491 e.Å⁻³
4.5. Compound 8.

CCDC entry code: 2027607
Empirical formula: C_{27}H_{44}BBrN_{4}O
Formula weight: 531.38
Temperature: 298(2) K
Wavelength: 0.71073 Å
Crystal system: Triclinic
Space group: P1, Z = 2
Unit cell dimensions:
\[ a = 8.73270(10) \text{ Å} \quad \alpha = 117.516(2)^\circ \]
\[ b = 13.5981(2) \text{ Å} \quad \beta = 99.7310(10)^\circ \]
\[ c = 13.6474(2) \text{ Å} \quad \gamma = 94.4720(10)^\circ \]
Volume: 1393.84(4) Å³
Density (calculated): 1.266 g/cm³
Absorption coefficient: 1.500 mm⁻¹
F(000): 564
Theta range for data collection: 2.694 to 31.122°.
Index ranges: -12 <= h <= 12, -18 <= k <= 19, -19 <= l <= 18
Reflections collected: 62119
Independent reflections: 13881 [R(int) = 0.0275]
Completeness to theta = 25.242°: 99.9 %
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 13881 / 3 / 569
Goodness-of-fit on F²: 1.044
Final R indices [I>2sigma(I)]: R₁ = 0.0355, wR₂ = 0.0894
R indices (all data): R₁ = 0.0438, wR₂ = 0.0941
Absolute structure parameter: 0.486(13)
Largest diff. peak and hole: 0.845 and -0.470 e.Å⁻³
### 4.6. Compound 9.

| Property                                    | Value                                      |
|---------------------------------------------|--------------------------------------------|
| CCDC entry code                             | 2027610                                    |
| Empirical formula                           | C$_{54}$H$_{86}$B$_2$Br$_2$Li$_2$N$_8$O$_2$ |
| Formula weight                              | 1074.62                                    |
| Temperature                                 | 100(2) K                                   |
| Wavelength                                  | 1.54184 Å                                  |
| Crystal system                              | Monoclinic                                 |
| Space group                                 | $C2/c$, \(Z = 4\)                         |
| Unit cell dimensions                        | \(a = 25.176(3) \text{ Å}, \ a = 90^\circ\) |
|                                           | \(b = 10.81621(10) \text{ Å}, \ b = 90.2610(10)^\circ\) |
|                                           | \(c = 23.3489(3) \text{ Å}, \ c = 90^\circ\) |
| Volume                                      | 6358.24(12) Å$^3$                          |
| Density (calculated)                        | 1.123 g/cm$^3$                             |
| Absorption coefficient                      | 1.925 mm$^{-1}$                            |
| F(000)                                      | 2272                                       |
| Theta range for data collection             | 3.511 to 77.585$^\circ$                    |
| Index ranges                                | -31$\leq$h$\leq$31, -13$\leq$k$\leq$13, -26$\leq$l$\leq$29 |
| Reflections collected                       | 128887                                     |
| Independent reflections                     | 6719 [R(int) = 0.0490]                     |
| Completeness to theta                       | 67.684$^\circ$                             |
| Refinement method                           | Full-matrix least-squares on F$^2$         |
| Data / restraints / parameters              | 6719 / 0 / 328                             |
| Goodness-of-fit on F$^2$                    | 1.101                                      |
| Final R indices [I>2sigma(I)]               | R$_1$ = 0.0322, wR$_2$ = 0.0909            |
| R indices (all data)                        | R$_1$ = 0.0338, wR$_2$ = 0.0921            |
| Largest diff. peak and hole                 | 0.345 and -0.740 e.Å$^{-3}$                |
4.7. Compound 10.

| Parameter                        | Value                        |
|----------------------------------|------------------------------|
| CCDC entry code                  | 2027611                      |
| Empirical formula                | C_{27}H_{43}BN_{4}O          |
| Formula weight                   | 450.46                       |
| Temperature                      | 100(2) K                     |
| Wavelength                       | 1.54184 Å                    |
| Crystal system                   | Trigonal                     |
| Space group                      | R-3, Z = 18                  |
| Unit cell dimensions             |                             |
| a = 29.5459(4) Å                | α = 90°                      |
| b = 29.5459(4) Å                | β = 90°                      |
| c = 16.7972(2) Å                | γ = 120°                     |
| Volume                           | 12698.8(4) Å³               |
| Density (calculated)             | 1.060 g/cm³                  |
| Absorption coefficient           | 0.495 mm⁻¹                   |
| F(000)                           | 4428                         |
| Theta range for data collection  | 2.991 to 77.627°             |
| Index ranges                     | -34<=h<=37, -37<=k<=37, -21<=l<=21 |
| Reflections collected            | 87610                        |
| Independent reflections          | 5987 [R(int) = 0.0381]        |
| Completeness to theta = 67.684° | 100.0 %                      |
| Refinement method                | Full-matrix least-squares on F² |
| Data / restraints / parameters   | 5987 / 0 / 310               |
| Goodness-of-fit on F²            | 1.044                        |
| Final R indices [I>2sigma(I)]    | R₁ = 0.0473, wR₂ = 0.1290    |
| R indices (all data)             | R₁ = 0.0501, wR₂ = 0.1311    |
| Largest diff. peak and hole      | 0.249 and -0.291 e.Å⁻³       |
### 4.8. Compound 11.

CCDC entry code: 2027608  
Empirical formula: $C_{33}H_{49}BN_4S \equiv 11 \cdot C_6H_6$  
Formula weight: 544.63  
Temperature: 99.9(6) K  
Wavelength: 1.54184 Å  
Crystal system: Monoclinic  
Space group: $P2_1/c$, $Z = 4$  
Unit cell dimensions:  
\[
\begin{align*}
  a &= 10.6234(2) \text{ Å} \quad \alpha = 90^\circ \\
  b &= 24.7853(6) \text{ Å} \quad \beta = 92.8606(18)^\circ \\
  c &= 12.4183(2) \text{ Å} \quad \gamma = 90^\circ 
\end{align*}
\]
Volume: 3265.72(11) Å$^3$  
Density (calculated): 1.108 g/cm$^3$  
Absorption coefficient: 1.066 mm$^{-1}$  
F(000): 1184  
Theta range for data collection: 3.567 to 77.631°  
Index ranges: -13 ≤ h ≤ 13, -31 ≤ k ≤ 31, -15 ≤ l ≤ 15  
Reflections collected: 13121  
Independent reflections: 13121 [R(int) = 0.0590]  
Completeness to theta = 67.684°: 100.0 %  
Refinement method: Full-matrix least-squares on $F^2$  
Data / restraints / parameters: 13121 / 0 / 365  
Goodness-of-fit on $F^2$: 1.045  
Final R indices [I>2sigma(I)]: $R_1 = 0.0338$, $wR_2 = 0.0925$  
R indices (all data): $R_1 = 0.0355$, $wR_2 = 0.0936$  
Largest diff. peak and hole: 0.262 and -0.194 e.Å$^{-3}$
4.9. Compound 12.

CCDC entry code: 2027612
Empirical formula: C_{45}H_{61}BN_{4}Se \equiv 12 \cdot 3 C_{6}H_{6}
Formula weight: 747.74
Temperature: 298(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: Pnma, Z = 4
Unit cell dimensions:
\[ a = 18.1400(2) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 24.8754(3) \text{ Å} \quad \beta = 90^\circ \]
\[ c = 9.40470(10) \text{ Å} \quad \gamma = 90^\circ \]
Volume: 4243.77(8) Å³
Density (calculated): 1.170 g/cm³
Absorption coefficient: 0.919 mm⁻¹
F(000): 1592
Theta range for data collection: 2.573 to 31.009°
Index ranges: -24<=h<=22, -33<=k<=33, -11<=l<=12
Reflections collected: 92625
Independent reflections: 6204 [R(int) = 0.0297]
Completeness to theta = 25.242°: 99.9 %
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 6204 / 3 / 284
Goodness-of-fit on F²: 1.042
Final R indices [I>2sigma(I)]: R₁ = 0.0400, wR₂ = 0.1057
R indices (all data): R₁ = 0.0482, wR₂ = 0.1102
Largest diff. peak and hole: 0.798 and -0.549 e.Å⁻³
4.10. **Compound 13.**

---

**CCDC entry code:** 2027613  
**Empirical formula:** C_{45}H_{61}BN_{4}Te \equiv 13 \cdot 3 C_{6}H_{6}  
**Formula weight:** 796.38  
**Temperature:** 100.00(10) K  
**Wavelength:** 0.71073 Å  
**Crystal system:** Orthorhombic  
**Space group:** P2_12_12_1, Z = 12  
**Unit cell dimensions:**  
  \[ a = 18.3769(4) \text{ Å}, \quad a = 90^\circ \]  
  \[ b = 24.6599(6) \text{ Å}, \quad \beta = 90^\circ \]  
  \[ c = 28.6576(6) \text{ Å}, \quad \gamma = 90^\circ \]  
**Volume:** 12986.8(5) Å³  
**Density (calculated):** 1.222 g/cm³  
**Absorption coefficient:** 0.721 mm⁻¹  
**F(000):** 4992  
**Theta range for data collection:** 2.541 to 31.247°.  
**Index ranges:**  
  \(-25 \leq h \leq 23, \quad -33 \leq k \leq 34, \quad -38 \leq l \leq 41\)  
**Reflections collected:** 303639  
**Independent reflections:** 36459 [R(int) = 0.0487]  
**Completeness to theta = 25.242°:** 99.8 %  
**Refinement method:** Full-matrix least-squares on F²  
**Data / restraints / parameters:** 36459 / 72 / 1391  
**Goodness-of-fit on F²:** 1.035  
**Final R indices [I>2sigma(I)]:** R₁ = 0.0659, wR₂ = 0.1711  
**R indices (all data):** R₁ = 0.0899, wR₂ = 0.1856  
**Largest diff. peak and hole:** 2.765 and -0.656 e.Å⁻³
### 4.11. Compound 14.

| Property                                    | Value                                      |
|---------------------------------------------|--------------------------------------------|
| CCDC entry code:                           | 2045657                                    |
| Empirical formula:                         | C31 H53 B2 F4 N5                          |
| Formula weight:                            | 593.40                                     |
| Temperature:                               | 100(2) K                                   |
| Wavelength:                                | 1.54184 Å                                  |
| Crystal system:                            | Monoclinic                                 |
| Space group:                               | $P2_1/c$, $Z = 8$                          |
| Unit cell dimensions:                      |                                           |
| $a = 8.9678(2)$ Å                          | $\alpha = 90^\circ$                       |
| $b = 24.5277(4)$ Å                         | $\beta = 91.361(2)^\circ$                 |
| $c = 33.6924(7)$ Å                         | $\gamma = 90^\circ$                       |
| Volume:                                    | 7408.9(3) Å                                |
| Density (calculated):                      | 1.064 g/cm$^3$                             |
| Absorption coefficient:                    | 0.622 mm$^{-1}$                            |
| F(000):                                    | 2560                                       |
| Theta range for data collection:           | 2.228 to 77.664°                           |
| Index ranges:                              | $-11 \leq h \leq 11$, $-31 \leq k \leq 29$, $-41 \leq l \leq 42$ |
| Reflections collected:                     | 150934                                     |
| Independent reflections:                   | 5534 [R(int) = 0.0894]                     |
| Completeness to theta = 67.684°:           | 99.9 %                                     |
| Refinement method:                         | Full-matrix least-squares on F$^2$         |
| Data / restraints / parameters:            | 15534 / 0 / 832                            |
| Goodness-of-fit on F$^2$:                   | 1.027                                      |
| Final R indices [I>2sigma(I)]:             | $R_1 = 0.0895$, $wR_2 = 0.2387$            |
| R indices (all data):                      | $R_1 = 0.0995$, $wR_2 = 0.2458$            |
| Largest diff. peak and hole:               | 0.699 and -0.434 e.Å$^3$                   |
4.12. Compound 15.

CCDC entry code: 2045658
Empirical formula: C$_{34}$H$_{48}$BCl$_3$N$_4$O$_2$ ≡ 15 · CHCl$_3$
Formula weight: 661.92
Temperature: 100.00(10) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$, $Z = 2$
Unit cell dimensions:

\[
\begin{align*}
a &= 10.3013(3) \text{ Å} & \alpha &= 90^\circ \\
b &= 17.8595(3) \text{ Å} & \beta &= 113.336(3)^\circ \\
c &= 10.4602(3) \text{ Å} & \gamma &= 90^\circ 
\end{align*}
\]
Volume: 1767.00(9) Å$^3$
Density (calculated): 1.244 g/cm$^3$
Absorption coefficient: 0.295 mm$^{-1}$
F(000): 704
Theta range for data collection: 2.611 to 31.638°.
Index ranges: -14<=h<=14, -25<=k<=24, -14<=l<=14
Reflections collected: 83739
Independent reflections: 10226 [R(int) = 0.0469]
Completeness to theta = 25.242°: 99.8 %
Refinement method: Full-matrix least-squares on $F^2$
Data / restraints / parameters: 10226 / 1 / 410
Goodness-of-fit on $F^2$: 1.061
Final R indices [I>2sigma(I)]: $R_1 = 0.0358$, $wR_2 = 0.0936$
R indices (all data): $R_1 = 0.0384$, $wR_2 = 0.0951$
Absolute structure parameter: 0.32(4)
Largest diff. peak and hole: 0.588 and -0.407 e.Å$^{-3}$
4.13. Compound 16.

CCDC entry code: 2045659
Empirical formula: C_{29}H_{43}BN_{6}
Formula weight: 486.50
Temperature: 100(2) K
Wavelength: 1.54184 Å
Crystal system: Monoclinic
Space group: $I2/a$, $Z = 8$
Unit cell dimensions:

| Parameter | Value                      |
|-----------|----------------------------|
| $a$       | 15.98950(10) Å             |
| $b$       | 11.87200(10) Å             |
| $c$       | 30.8634(2) Å               |
| $\alpha$  | 90°                        |
| $\beta$   | 92.0010(10)°               |
| $\gamma$  | 90°                        |

Volume: 5855.14(7) Å³
Density (calculated): 1.104 g/cm³
Absorption coefficient: 0.508 mm⁻¹
F(000): 2112
Theta range for data collection: 2.865 to 77.485°.
Index ranges: -19≤h≤20, -14≤k≤15, -39≤l≤37
Reflections collected: 60598
Independent reflections: 6157 [R(int) = 0.0287]
Completeness to theta = 67.684°: 100.0%
Refinement method: Full-matrix least-squares on $F^2$
Data / restraints / parameters: 6157 / 0 / 337
Goodness-of-fit on $F^2$: 1.046
Final R indices (I>2sigma(I)): $R_1 = 0.0437$, $wR_2 = 0.1108$
R indices (all data): $R_1 = 0.0463$, $wR_2 = 0.1137$
Largest diff. peak and hole: 0.291 and -0.265 e.Å⁻³
Author Contributions

Hadi Dolati (lead synthetic work, writing of original draft), Lars Denker (synthetic work, X-ray crystallographic work including structural solution), Dr. Bartosz Trzaskowski (computational work, formal analysis, funding acquisition, project administration), Dr. René Frank (synthetic work, formal analysis, funding acquisition, project administration).

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