Supporting Information for:

Thiaborane clusters with the exoskeletal B-H group

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**Fig. S2:** Molecular structure of 3a.

**Fig. S3:** Molecular structure of 4a. Selected structural parameters [Å, °]: B9-B12 1.725(2), B12-N1 1.602(2), B12-N3 1.601(2), N1-B12-N3 105.35(12).
Fig. S4: Molecular structure of 4a. Selected structural parameters [Å, °]: B10-B12 1.757(10), B12-N1 1.591(10), B12-N3 1.607(7), N1-B12-N3 105.0(6).

Fig. S5: Supramolecular architecture of 4a’, highlighting S...BH and S...S contacts.
Fig. S6: Supramolecular architecture of 5a, highlighting S...BH and C-H...H-B contacts.

Fig. S7: Molecular structure of 6a.
Fig. S8: Molecular structure of 7a.
Experimental Part

Synthesis

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. Solvents were dried using a Pure Solv–Innovative Technology equipment under argon gas atmosphere. Starting compounds 1-SB_{12}H_{11}, 12-I-1-SB_{11}H_{10} were prepared according to the published procedures or obtained from commercial sources. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

NMR spectroscopy

$^1$H, $^{11}$B and $^{13}$C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer or Bruker Ultrashield 400 MHz, using 5 mm tuneable broad-band probe. Appropriate chemical shifts in $^1$H and $^{13}$C NMR spectra were related to the residual signals of the solvents (CDCl$_3$: $\delta(^1H) = 7.24$ ppm and $\delta(^{13}C) = 77.23$ ppm; acetone-d$_6$: $\delta(^1H) = 2.05$ ppm and $\delta(^{13}C) = 29.92$ ppm; CD$_2$Cl$_2$: $\delta(^1H) = 5.33$ ppm and $\delta(^{13}C) = 54.24$ ppm). $^{11}$B NMR spectra were NMR spectra were recorded with a Varian Mercury 400 Plus Instrument. Standard [11B−11B]-COSY (and $^1$H-{11B(selective)}) NMR experiments led to complete assignments of all resonances to individual cage BH units, at least in the well resolved area. $^{11}$B chemical shifts were related to external standard BF$_3$•OEt$_2$ ($\delta(^{11}B) = 0.0$ ppm).

sc-XRD

Full-sets of diffraction data for 2a, 2b, 3a, 4a, 4a', 5a, 6a and 7a were collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Cu (Cu/K$_\alpha$ radiation; $\lambda$ =1.54178 Å) or Mo (Mo/K$_\alpha$ radiation; $\lambda$ = 0.71073 Å) microfocus X-ray (μS) sources, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection.

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2$ U$_{eq}$ (pivot atom) or of 1.5U$_{eq}$ (methyl). H atoms in methyl, methylene, methine, vinylidene moieties and hydrogen
atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98, 0.93 and 0.93 Å and 1.1 Å for terminal and 1.25 Å for bridging B-H bonds.

\[
R_{\text{int}} = \frac{\sum |F_o^2 - F_{o,\text{mean}}^2|}{\sum F_o^2}, \quad \text{GOF} = \left[ \frac{\sum (w(F_o^2 - F_c^2)^2)}{N_{\text{diffrs}} - N_{\text{params}}} \right]^{1/2} \text{ for all data}, \quad R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \text{ for observed data}, \quad wR(F^2) = \left[ \frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2} \right]^{1/2} \text{ for all data}.
\]

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1895084-1895091. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

In the case of crystal of 4a', only poor quality material which revealed weak diffraction pattern was obtained, which was the reason, only low completeness to desired theta angle was obtained - A alert in the checkcif procedure. In this particular case, the result confirms analogous composition as found for 4a, and it had no further influence to the quality of the final model. For 2a and 4a, the positions of the sulfur atom in the cage is disordered to the two positions with nearly equal occupancy. Disorder of one of the boron atoms in the molecule of nido-7a is treated by standard methods.

**Computational part**

The gas-phase basicity values were calculated at B3LYP/cc-pVTZ level of theory.

**Synthesis of nido-9-BH(DMAP)\_2-7-SB\_10H\_10 (2a)**

This synthetic procedure was performed under argon atmosphere. A solution of 4-dimethylaminopyridine (65 mg, 0.53 mmol) was added at ambient temperature to a stirred
solution of 1-SB$_{11}$H$_{11}$ (43 mg, 0.27 mmol) in diethyl ether (10 mL). Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried in vacuo. Yield 104 mg (96 %). Obtained powder can be recrystallised from boiling acetone (THF) giving adduct 4a (4a'). **Mp** 155 °C. **Anal. Calc.** for C$_{14}$H$_{31}$B$_{11}$N$_4$S (406.41): C 41.4, H 7.7, N 13.8; found C 41.5, H 7.9, N 14.9. **$^1$H NMR** (25 °C, acetone-d$_6$, 500 MHz): $\delta$ = 3.18 (s, 12H, NC$_{3}$H$_3$), 6.81 (m, 4H, ArH), 8.20 (d, $^3$J($^1$H-$^1$H) = 7.5 Hz, 2H, ArH), 8.26 (d, $^3$J($^1$H-$^1$H) = 7.5 Hz, 2H, ArH) ppm. **$^{11}$B NMR** (25 °C, acetone-d$_6$, 160.42 MHz): $\delta$ = -35.8 (d, $^1$J($^1$H-$^{11}$B) = 135 Hz, 1B, B$_1$), -17.6 (d, $^1$J($^1$H-$^{11}$B) = 142 Hz, 2B, B$_5$,10), -16.1 (d, $^1$J($^1$H-$^{11}$B) = 137 Hz, 2B, B$_2$,3), -11.4 (m, 3B, B$_8$,9,11), -5.4 (m, 2B, B$_4$,6), 5.0 (m broad, 1B, B$_{12}$) ppm. **$^{13}$C{$_1$H} NMR** (25 °C, acetone-d$_6$, 125.76 Hz): $\delta$ = 39.3 (s, NCH$_3$), 106.8, 149.8, 154.4 (s, ArC) ppm.

**Synthesis of nido-5-I-10-BH(DMAP)$_2$-7-SB$_{10}$H$_9$ (2b)**

This synthetic procedure was performed under argon atmosphere. Solution of 4-dimethylaminopyridine (33 mg, 0.27 mmol) was added at ambient temperature to a stirred solution of 12-I-1-SB$_{11}$H$_{10}$ (39 mg, 0.14 mmol) in diethyl ether (10 mL). Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried in vacuo. Yield 69 mg (95 %). **Mp** 205 °C. **Anal. Calc.** for C$_{14}$H$_{30}$B$_{11}$N$_3$S (532.31): C 31.6, H 5.7, N 10.5; found C 31.5, H 5.8, N 10.3. **$^1$H NMR** (25 °C, acetone-d$_6$, 500 MHz): $\delta$ = 3.04 (s, 6H, NC$_{3}$H$_3$), 3.07 (s, 6H, NC$_{3}$H$_3$), 6.64 (d, $^3$J($^1$H-$^1$H) = 7.6 Hz, 2H, ArH), 6.70 (d, $^3$J($^1$H-$^1$H) = 7.6 Hz, 2H, ArH), 8.18 (d, $^3$J($^1$H-$^1$H) = 7.6 Hz, 2H, ArH), 8.43 (d, $^3$J($^1$H-$^1$H) = 7.6 Hz, 2H, ArH) ppm. **$^{11}$B NMR** (25 °C, acetone-d$_6$, 160.42 MHz): $\delta$ = -33.9 (d, $^1$J($^1$H-$^{11}$B) = 163 Hz, 1B, B$_1$), -23.3 (s, 1B, B$_5$), -17.7 (m broad, 2B, B$_2$,3), -14.0 (m broad, 2B, B, 9,10), -11.8 (m broad, 2B, B$_8$,11), -4.6 (m, 2B, B$_4$,6), 5.9 (m broad, 1B, B$_{12}$) ppm. **$^{13}$C{$_1$H} NMR** (25 °C, acetone-d$_6$, 125.76 Hz): $\delta$ = 39.9, 40.0 (s, NCH$_3$), 107.6, 107.9, 146.9, 147.6, 156.7, 156.9 (s, ArC) ppm.
Synthesis of [(DMAP)H][\textit{nido-7- SB}_{10}H_{11}] (3a)

Solution of DMAP (34 mg, 0.28 mmol) in methanol (10 mL) was added at ambient temperature to a stirred solution of 1-SB_{11}H_{11} (45 mg, 0.28 mmol) in methanol (10 mL). The reaction mixture was stirred overnight and evaporated \textit{in vacuo} giving 3a in the form of colourless powder. Yield 74 mg (97 %). \textbf{Mp} 196 °C with decomposition. \textbf{Anal. Calc.} for C_{7}H_{22}B_{10}N_{2}S (274.44): C 30.6, H 8.1, N 10.2; found C 30.7, H 8.3, N 10.3. \textbf{\textsuperscript{1}H NMR} (25 °C, acetone-d\textsubscript{6}, 500 MHz): \(\delta = 3.17\) (s, 6H, CH\textsubscript{3}), 6.84 (d, \(3J(\text{\textsuperscript{1}H-\textsuperscript{1}H}) = 6.8\) Hz, 2H, ArH), 8.25 (d, \(3J(\text{\textsuperscript{1}H-\textsuperscript{1}H}) = 6.8\) Hz, 2H, ArH), 10.28 (s, 1H, NH) ppm. \textbf{\textsuperscript{11}B NMR} (25 °C, acetone-d\textsubscript{6}, 160.42 MHz): \(\delta = -36.7\) (d, \(1J(\text{\textsuperscript{1}H-\textsuperscript{11}B}) = 141\) Hz, 1B, B1), -17.8 (m, 5B, B2,3,5,9,10), -12.3 (d, \(1J(\text{\textsuperscript{1}H-\textsuperscript{11}B}) = 147\) Hz, 2B, B8,11), -6.2 (d, \(1J(\text{\textsuperscript{1}H-\textsuperscript{11}B}) = 138\) Hz, 2B, B4,6) ppm. \textbf{\textsuperscript{13}C\{}\textsuperscript{1}H\}\textsuperscript{NMR} (25 °C, acetone-d\textsubscript{6}, 125.76 Hz): \(\delta = 39.7\) (s, CH\textsubscript{3}), 107.8, 145.3, 157.0 (s, ArC) ppm.

Synthesis of [(DMAP)H][\textit{nido-5-I-7-SB}_{10}H_{10}] (3b)
Solution of DMAP (17 mg, 0.14 mmol) in methanol (10 mL) was added at ambient temperature to a stirred solution of 12-I-1-SB$_{11}$H$_{10}$ (40 mg, 0.14 mmol) in methanol (10 mL). The reaction mixture was stirred overnight and evaporated in vacuo giving 3a in the form of colourless powder. Yield 53 mg (96 %). Mp 190 °C with decomposition. Anal. Calc. for C$_7$H$_{22}$B$_{10}$IN$_2$ (274.44): C 30.6, H 8.1, N 10.2; found C 30.5, H 8.2, N 10.1. $^1$H NMR (25 °C, acetone-d$_6$, 500 MHz): $\delta$ = 3.18 (s, 6H, C$_3$H$_3$), 6.86 (d, $^3$J(H-H) = 6.7 Hz, 2H, ArH), 8.26 (d, $^3$J(H-H) = 6.7 Hz, 2H, ArH) ppm, NH not observed. $^{11}$B NMR (25 °C, acetone-d$_6$, 160.42 MHz): $\delta$ = -35.2 (d, $^1$J(H-11B) = 145 Hz, 1B, B1), -27.0 (s, 1B, B5), -18.0 (d, $^1$J(H-11B) = 167 Hz, 2B, B2,3), -15.9 (d, $^1$J(H-11B) = 140 Hz, 2B, B9,10), -12.1 (d, $^1$J(H-11B) = 156 Hz, 2B, B8,11), -5.8 (d, $^1$J(H-11B) = 145 Hz, 2B, B4,6) ppm. $^{13}$C($^1$H) NMR (25 °C, acetone-d$_6$, 125.76 Hz): $\delta$ = 47.1 (s, CH$_2$) ppm.

This synthetic procedure was performed under argon atmosphere. To a solution of 1-SB$_{11}$H$_{11}$ (40 mg, 0.25 mmol) in acetone/diethyl ether (1:3, 10 mL), solution of 2,2′-bipyridyl (39 mg, 0.25 mmol) was added at ambient temperature and left for 1 day without stirring yielding yellow single crystals of 5a. The crystals were decanted and dried in vacuo. Yield 75 mg (95 %). Mp 215 °C with decomposition. Anal. Calc. for C$_{10}$H$_{19}$B$_{11}$N$_2$S (318.26): C 37.7, H 6.0, N 8.8; found C 37.8, H 6.1, N 8.7. $^1$H NMR (25 °C, acetone-d$_6$, 500 MHz): $\delta$ = 8.13 (m, 2H, ArH), 8.55 (m, 2H ArH), 8.91 (d, $^1$J(H-H) = 10 Hz, 2H, ArH), 8.95 (d, $^1$J(H-H) = 7.2 Hz, 1H, ArH), 9.10 (d, $^1$J(H-H) = 7.2 Hz, 1H, ArH) ppm. $^{11}$B NMR (25 °C, acetone-d$_6$, 160.42 MHz): $\delta$ = -35.9 (d, $^1$J(H-11B) = 140 Hz, 1B, B1), -18.0 (d, $^1$J(H-11B) = 144 Hz, 2B, B5,10), -16.8 (d, $^1$J(H-11B) = 149 Hz, 2B, B8,11), -5.8 (d, $^1$J(H-11B) = 145 Hz, 2B, B4,6) ppm. $^{13}$C($^1$H)
**NMR** (25 °C, acetone-d6, 125.76 Hz): $\delta = 122.7, 127.5, 141.5, 143.4, 143.8, 145.2, 145.4$ (s, ArC) ppm.

**Synthesis of nido-9-B(H)bipy-5-I-7-SB$_{10}$H$_9$ (5b)**

This synthetic procedure was performed under argon atmosphere. To a solution of 12-I-1-SB$_{11}$H$_{10}$ (50 mg, 0.17 mmol) in diethyl ether (10 mL), solution of 2,2'-bipyridyl (27 mg, 0.17 mmol) was added at ambient temperature and left for 1 day without stirring yielding yellow crystals of 5b. The crystals were decanted and dried in vacuo. Yield 72 mg (94 %). **Mp** 205 with decomposition. **Anal. Calc.** for C$_{10}$H$_{18}$B$_{11}$IN$_2$S (444.15): C 27.0, H 4.1, N 6.3; found C 27.0, H 4.3, N 6.1. **$^1$H NMR** (25 °C, acetone-d6, 500 MHz): $\delta = 8.17$ (m, 2H, ArH), 8.62 (m, 2H ArH), 8.94 (m, 2H, ArH), 9.04 (m, 2H, ArH) ppm. **$^{11}$B NMR** (25 °C, acetone-d6, 160.42 MHz): $\delta = -33.7$ (d, $^{1}J(\text{H-}^{11}\text{B}) = 152$ Hz, 1B, B1), -25.4 (s, 1B, B5), -17.1 (d, $^{1}J(\text{H-}^{11}\text{B}) = 143$ Hz, 3B, B2,3,10), -11.7 (m, 3B, B8,9,11), -5.4 (m, 2B, B4,6), 2.1 (m broad, 1B, B12) ppm. **$^{13}$C{($^1$H)} NMR** (25 °C, acetone-d6, 125.76 Hz): $\delta = 122.8, 127.6, 142.1, 143.7, 143.9, 146.5, 146.7$ (s, ArC) ppm.
Synthesis of [(py)$_2$H][nido-7-SB$_{10}$H$_{11}$] (6a)

Pyridine (0.22 mL, 2.71 mmol) was added at -30 °C to a stirred solution of 1-SB$_{11}$H$_{11}$ (44 mg, 0.27 mmol) in methanol (10 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The colourless solution was evaporated in vacuo giving 6a in the form of colourless powder. Yield 100 mg (95 %). Mp 175 °C. Anal. Calc. for C$_{10}$H$_{22}$B$_{10}$N$_2$S (310.47): C 38.7, H 7.1, N 9.0; found C 38.8, H 7.3, N 9.1. $^1$H NMR (25 °C, acetone-d6, 500 MHz): δ = 7.90 (t, $^3J(^1$H-$^1$H) = 7.6 Hz, 4H, ArH), 8.38 (t, $^3J(^1$H-$^1$H) = 7.6 Hz, 2H, ArH), 8.94 (d, $^3J(^1$H-$^1$H) = 6.2 Hz, 4H, ArH), 10.55 (s, 1H, NH) ppm. $^{11}$B NMR (25 °C, acetone-d6, 160.42 MHz): δ = -36.8 (d, $^1J(^{11}$B-$^1$H) = 141 Hz, 1B, B1), -18.1 (m, 5B, B2,3,5,9,10), -12.4 (d, $^1J(^{11}$B-$^1$H) = 147 Hz, 2B, B8,11), -6.3 (d, $^1J(^{11}$B-$^1$H) = 137 Hz, 2B, B4,6) ppm. $^{13}$C{$^1$H} NMR (25 °C, acetone-d6, 125.76 Hz): δ = 127.0, 143.3, 146.5 (s, ArC) ppm.

Synthesis of [(py)$_2$H][nido-5-1-7-SB$_{10}$H$_{10}$] (6b)
Pyridine (0.11 mL, 1.35 mmol) was added at -30 °C to a stirred solution of 12-I-1-SB$_{11}$H$_{10}$ (39 mg, 0.14 mmol) in methanol (10 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The colourless solution was evaporated in vacuo giving 6b in the form of colourless powder. Yield 66 mg (95 %). **Mp** 180 °C. **Anal. Calc.** for C$_{10}$H$_{21}$B$_{10}$N$_2$S (436.37): C 27.5, H 4.9, N 6.4; found C 27.6, H 5.9, N 8.1. **$^1$H NMR** (25 °C, acetone-d$_6$, 500 MHz): $\delta$ = 7.87 (t, J($^1$H-1$^1$H) = 6.4 Hz, 4H, Ar H), 8.35 (t, J($^1$H-1$^1$H) = 7.6 Hz, 2H, Ar H), 8.92 (d, J($^1$H-1$^1$H) = 6.8 Hz, 4H, Ar H), 11.71 (s, 1H, NH) ppm. **$^{11}$B NMR** (25 °C, acetone-d$_6$, 160.42 MHz): $\delta$ = -35.2 (d, J($^1$H-11$^1$B) = 153 Hz, 1B, B1), -27.0 (s, 1B, B5), -18.0 (d, J($^1$H-11$^1$B) = 167 Hz, 2B, B2,3), -15.8 (d, J($^1$H-11$^1$B) = 135 Hz, 2B, B9,10), -12.1 (d, J($^1$H-11$^1$B) = 140 Hz, 2B, B8,11), -5.8 (d, J($^1$H-11$^1$B) = 140 Hz, 2B, B4,6) ppm. **$^{13}$C($^1$H) NMR** (25 °C, acetone-d$_6$, 125.76 Hz): $\delta$ = 126.8, 142.9, 146.8 (s, Ar C) ppm.

**Synthesis of [(DABCO)$_3$H][nido-7- SB$_{10}$H$_{11}$] (7a)**

![Chemical Structure](image)

To a stirred solution of 1-SB$_{11}$H$_{11}$ (48 mg, 0.30 mmol) in diethyl ether (10 mL), solution of DABCO (99 mg, 0.89 mmol) in diethylether (10 mL) was added at ambient temperature. Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried in vacuo. Yield 130 mg (90 %). **Mp** 228 °C. **Anal. Calc.** for C$_{18}$H$_{48}$B$_{10}$N$_6$S (488.79): C 44.2, H 9.9, N 17.2; found C 44.4, H 10.1, N 17.1. **$^1$H NMR** (25 °C, THF-d$_8$, 500 MHz): $\delta$ = 2.95 (s, 36H, CH$_2$), 10.11 (s, 1H, NH) ppm. **$^{11}$B NMR** (25 °C, THF-d$_8$, 160.42 MHz): $\delta$ = -36.9 (d, J($^1$H-11$^1$B) = 143 Hz, 1B, B1), -18.1 (d, J($^1$H-11$^1$B) = 137 Hz, 5B, B2,3,5,9,10), -12.3 (d, J($^1$H-11$^1$B) = 148 Hz, 2B, B8,11), -6.4 (d, J($^1$H-11$^1$B) = 137 Hz, 2B, B4,6) ppm. **$^{13}$C($^1$H) NMR** (25 °C, THF-d$_8$, 125.76 Hz): $\delta$ = 47.0 (s, CH$_2$) ppm.
Synthesis of [(DABCO)$_3$H][nido-5-I-7-SB$_{10}$H$_{10}$] (7b)

To a stirred solution of 12-I-1-SB$_{11}$H$_{10}$ (35 mg, 0.12 mmol) in diethyl ether (10 mL), solution of DABCO (27 mg, 0.24 mmol) in diethylether (10 mL) was added at ambient temperature. Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried in vacuo. Yield 66 mg (88 %). Mp 80 °C. Anal. Calc. for C$_{18}$H$_{47}$B$_{10}$IN$_6$S (614.89): C 35.2, H 7.7, N 13.7; found C 35.4, H 7.6, N 13.8. $^1$H NMR (25 °C, THF-d$_8$, 500 MHz): $\delta = 2.96$ (s, 36H, CH$_2$), 9.66 (s, 1H, NH) ppm. $^{11}$B NMR (25 °C, THF-d$_8$, 160.42 MHz): $\delta = -35.3$ (d, $^1J(^{1}$H-$^{11}$B) = 147 Hz, 1B, B1), -26.9 (s, 1B, B5), -18.1 (d, $^1J(^{1}$H-$^{11}$B) = 163 Hz, 2B, B2,3), -16.1 (d, $^1J(^{1}$H-$^{11}$B) = 130 Hz, 2B, B9,10), -12.2 (d, $^1J(^{1}$H-$^{11}$B) = 145 Hz, 2B, B8,11), -6.0 (d, $^1J(^{1}$H-$^{11}$B) = 144 Hz, 2B, B4,6) ppm. $^{13}$C($^1$H) NMR (25 °C, THF-d$_8$, 125.76 Hz): $\delta = 47.1$ (s, CH$_2$) ppm.

Synthesis of NH$_4$[nido-7-SB$_{10}$H$_{11}$] (8a)
This synthetic procedure was performed under argon atmosphere. To a stirred solution of 1-SB$_{11}$H$_{11}$ (60 mg, 0.37 mmol) in THF (10 mL), solution of ammonia (9.3 mL, 3.7 mmol, 0.4M solution in THF) was added at ambient temperature and stirred overnight. The volatiles were removed in vacuo and the colourless residue was washed with diethyl ether (2 mL) to give 9a in the form of colourless powder. Yield 85 mg (90%).

**Anal.** Calc. for H$_{15}$B$_{10}$NS (169.3): H 8.9, N 8.3; found H 9.0, N 8.2. $^1$H NMR (25 ºC, THF-d$_8$, 500 MHz): $\delta = 6.81$ (s, broad, 4H, NH$_4^+$) ppm. $^{11}$B NMR (25 ºC, THF-d$_8$, 160.42 MHz): $\delta = -36.9$ (d, $^1J(^1$H-$^{11}$B) = 141 Hz, 1B, B1), -18.1 (d, $^1J(^1$H-$^{11}$B) = 141 Hz, 5B, B2,3,5,9,10), -12.3 (d, $^1J(^1$H-$^{11}$B) = 148 Hz, 2B, B8,11), -6.4 (d, $^1J(^1$H-$^{11}$B) = 138 Hz, 2B, B4,6) ppm.

**Synthesis of NH$_4$[nido-5-I-7-SB$_{10}$H$_{10}$] (8b)**

This synthetic procedure was performed under argon atmosphere. To a stirred solution of 12-I-1-SB$_{11}$H$_{11}$ (51 mg, 0.18 mmol) in THF (10 mL), solution of ammonia (4.4 mL, 1.8 mmol, 0.4M solution in THF) was added at ambient temperature and stirred overnight. The volatiles were removed in vacuo and the colourless residue was washed with diethyl ether (2 mL) to give 9a in the form of colourless powder. Yield 85 mg (90%).

**Calc.** for H$_{15}$B$_{10}$NS (169.3): H 8.9, N 8.3; found H 9.0, N 8.2. $^1$H NMR (25 ºC, THF-d$_8$, 500 MHz): $\delta = 6.81$ (s, broad, 4H, NH$_4^+$) ppm. $^{11}$B NMR (25 ºC, THF-d$_8$, 160.42 MHz): $\delta = -36.9$ (d, $^1J(^1$H-$^{11}$B) = 141 Hz, 1B, B1), -18.1 (d, $^1J(^1$H-$^{11}$B) = 141 Hz, 5B, B2,3,5,9,10), -12.3 (d, $^1J(^1$H-$^{11}$B) = 148 Hz, 2B, B8,11), -6.4 (d, $^1J(^1$H-$^{11}$B) = 138 Hz, 2B, B4,6) ppm.
were removed *in vacuo* and the colourless residue was washed with diethyl ether (2 mL) to give 8b in the form of colourless powder. Yield 42 mg (80%). **Mp.** 195 °C with decomposition.  
**Anal. Calc.** for H$_3$B$_{10}$NS (295.20): H 4.8, N 4.7; found H 4.9, N 4.8.  
**$^1$H NMR** (25 °C, THF-d$_8$, 500 MHz): $\delta$ = 6.31 (s broad, 4H, NH$_4$) ppm.  
**$^{11}$B NMR** (25 °C, CD$_3$CN, 160.42 MHz): $\delta$ = -35.3 (d, $^1J(1^H-11^B)$ = 147 Hz, 1B, B1), -26.9 (s, 1B, B5), -18.0 (d, , $^1J(1^H-11^B)$ = 165 Hz, 2B, B2,3), -15.9 (d, , $^1J(1^H-11^B)$ = 135 Hz, 2B, B9,10),-12.1 (d, $^1J(1^H-11^B)$ = 143 Hz, 2B, B8,11), -5.9 (d, $^1J(1^H-11^B)$ = 143 Hz, 2B, B4,6) ppm.

**Synthesis of [HNEt$_3$][nido-7-SB$_{10}$H$_{11}$] (9a)**

To a stirred solution of 1-SB$_{11}$H$_{11}$ (110 mg, 0.68 mmol) in diethyl ether (10 mL), triethylamine (0.95 mL, 6.8 mmol) was added at ambient temperature. Colourless precipitate was formed immediately. After 12 hours of stirring, the suspension was filtered off and the solid was extracted with chloroform (25 mL). The solvent was removed *in vacuo* to give 8a in the form of colourless powder. Yield 169 mg (98%). Analytical data were in agreement with the literature.

**Synthesis of [HNEt$_3$][nido-5-I-7-SB$_{10}$H$_{10}$] (9b)**

To a stirred solution of 12-I-1-SB$_{11}$H$_{11}$ (72 mg, 0.17 mmol) in diethyl ether (10 mL), triethylamine (0.24 mL, 1.7 mmol) was added at ambient temperature. Colourless precipitate was formed immediately. After 2 hours of stirring, the suspension was filtered off and the solid was extracted with chloroform (20 mL). The solvent was removed *in vacuo* to give 8b in the form of colourless powder. Yield 63 mg (67%). **Mp** 220 °C. **Anal. Calc.** for
C_{14}H_{30}B_{11}N_{4}S (379.36): C 19.0, H 6.9, N 3.7; found C 19.1, H 7.0, N 3.8. \(^1H\) NMR (25 °C, CD\(_3\)CN, 500 MHz): \(\delta = 1.44\) (t, \(^3J(^1H-^1H) = 7.3\) Hz, 9H, CH\(_3\)), 3.25 (q, \(^3J(^1H-^1H) = 7.3\) Hz, 6H, CH\(_2\)), 8.37 (s broad, 1H, NH) ppm. \(^11B\) NMR (25 °C, CD\(_3\)CN, 160.42 MHz): \(\delta = -35.1\) (d, \(^1J(^1H-^{11}B) = 146\) Hz, 1B, B1), -27.0 (s, 1B, B5), -17.8 (d, \(^1J(^1H-^{11}B) = 171\) Hz, 2B, B2,3), -15.9 (d, \(^1J(^1H-^{11}B) = 144\) Hz, 2B, B9,10), -11.9 (d, \(^1J(^1H-^{11}B) = 150\) Hz, 2B, B8,11), -5.9 (d, \(^1J(^1H-^{11}B) = 146\) Hz, 2B, B4,6) ppm. \(^13C\{^1H\}\) NMR (25 °C, CD\(_3\)CN, 125.76 Hz): \(\delta = 9.1\) (s, CH\(_3\)), 47.3 (s, CH\(_2\)) ppm.
<table>
<thead>
<tr>
<th>Compound reference</th>
<th>Chemical formula</th>
<th>Formula Mass</th>
<th>Crystal system</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>α/°</th>
<th>β/°</th>
<th>γ/°</th>
<th>Unit cell volume/Å³</th>
<th>Temperature/K</th>
<th>Space group</th>
<th>No. of formula units per unit cell, Z</th>
<th>Radiation type</th>
<th>Absorption coefficient, μ/mm⁻¹</th>
<th>No. of reflections measured</th>
<th>No. of independent reflections</th>
<th>R_{int}</th>
<th>Final R₁ values (I &gt; 2σ(I))</th>
<th>Final wR(F²) values (I &gt; 2σ(I))</th>
<th>Final R₁ values (all data)</th>
<th>Final wR(F²) values (all data)</th>
<th>Goodness of fit on F²</th>
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<tbody>
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<td>2a</td>
<td>C_{14}H_{31}B_{11}N_{4}SCH_{2}Cl_{2}</td>
<td>491.32</td>
<td>Triclinic</td>
<td>8.8688(3)</td>
<td>10.1323(4)</td>
<td>15.8068(6)</td>
<td>72.8750(10)</td>
<td>77.9390(10)</td>
<td>76.3180(10)</td>
<td>1304.00(8)</td>
<td>150(2)</td>
<td>P-1</td>
<td>2</td>
<td>MoKα</td>
<td>0.342</td>
<td>79833</td>
<td>6017</td>
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<td>2b</td>
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<td>532.29</td>
<td>Monoclinic</td>
<td>10.9419(6)</td>
<td>13.0988(7)</td>
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<td>99.408(2)</td>
<td>90</td>
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<td>150(2)</td>
<td>P2₁/n</td>
<td>4</td>
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<td>90</td>
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<td>8.4015(5)</td>
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**TABLE S1 - continuation: Selected crystallographic parameters**

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<th>Compound reference</th>
<th>5a (\text{C}<em>{10}\text{H}</em>{19}\text{B}<em>{11}\text{N}</em>{2}\text{S})</th>
<th>6a (\text{B}<em>{10}\text{H}</em>{11}\text{S}\text{C}<em>{10}\text{H}</em>{11}\text{N}_{2})</th>
<th>7a (\text{B}<em>{10}\text{H}</em>{11}\text{S}\text{C}<em>{12}\text{H}</em>{25}\text{N}<em>{4}\text{C}</em>{6}\text{H}<em>{12}\text{N}</em>{2})</th>
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<tr>
<td>Chemical formula</td>
<td>(\text{C}<em>{10}\text{H}</em>{19}\text{B}<em>{11}\text{N}</em>{2}\text{S})</td>
<td>(\text{B}<em>{10}\text{H}</em>{11}\text{S}\text{C}<em>{10}\text{H}</em>{11}\text{N}_{2})</td>
<td>(\text{B}<em>{10}\text{H}</em>{11}\text{S}\text{C}<em>{12}\text{H}</em>{25}\text{N}<em>{4}\text{C}</em>{6}\text{H}<em>{12}\text{N}</em>{2})</td>
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<td>(\beta/°)</td>
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<td>(\gamma/°)</td>
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<td>150(2)</td>
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<td>(\text{C2/m})</td>
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<td>No. of formula units per unit cell, (Z)</td>
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<td>MoK(\alpha)</td>
<td>CuK(\alpha)</td>
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<td>(R_{\text{int}}) values ((I &gt; 2\sigma(I)))</td>
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<td>Goodness of fit on (F^2)</td>
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<td>0.986</td>
<td>1.286</td>
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References

