Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Thiaborane clusters with the exoskeletal B-H group

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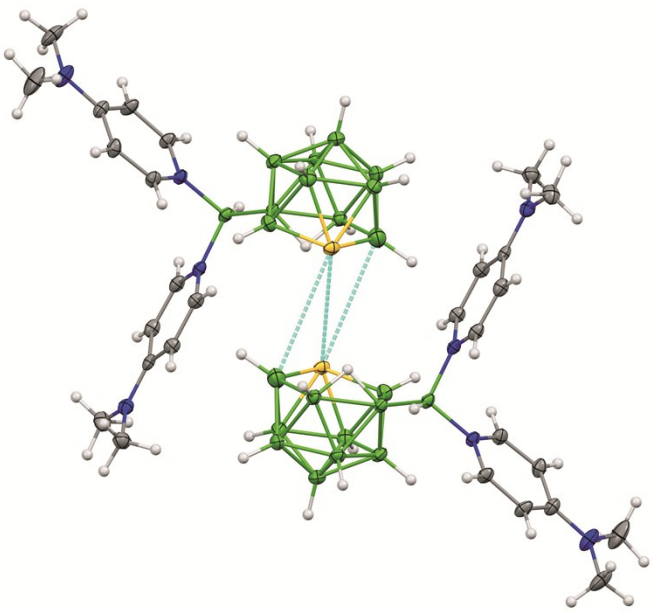


Fig. S1: Supramolecular architecture of **2a**, highlighting S...BH and S...S contacts.

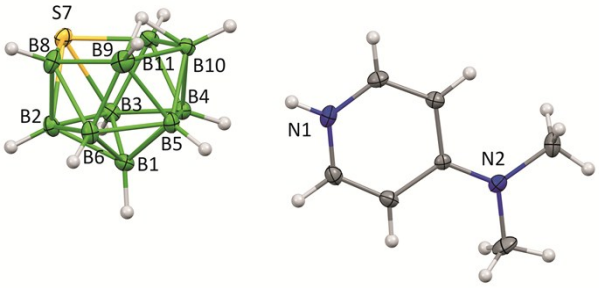


Fig. S2: Molecular structure of **3a**.

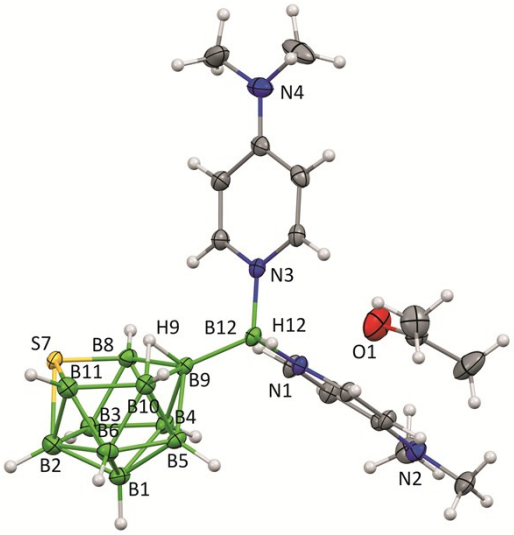


Fig. S3: Molecular structure of **4a**. Selected structural parameters [Å, °]: B9-B12 1.725(2), B12-N1 1.602(2), B12-N3 1.601(2), N1-B12-N3 105.35(12).

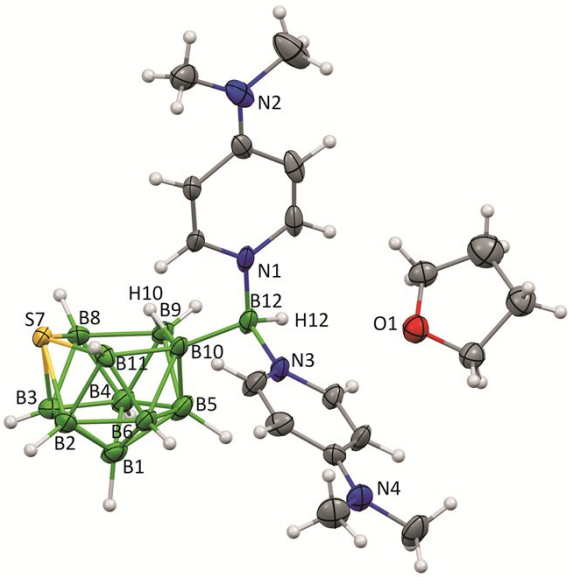


Fig. S4: Molecular structure of **4a**. Selected structural parameters [Å, °]: B10-B12 1.757(10), B12-N1 1.591(10), B12-N3 1.607(7), N1-B12-N3 105.0(6).

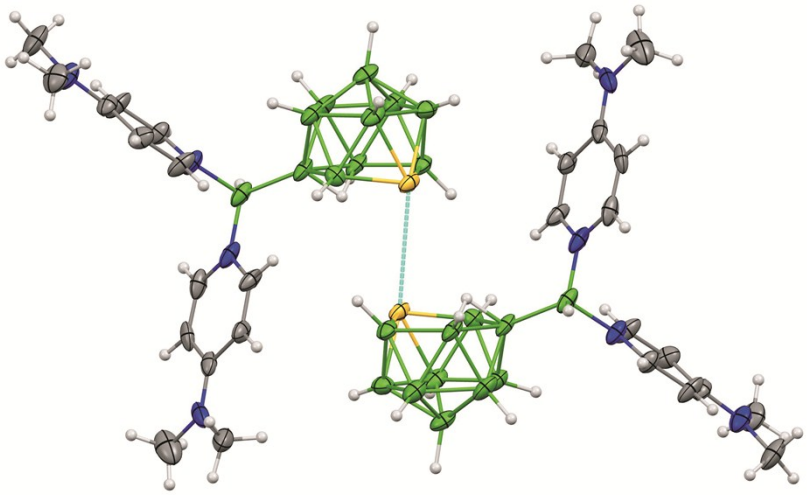


Fig. S5: Supramolecular architecture of **4a'**, highlighting S...BH and S...S contacts.

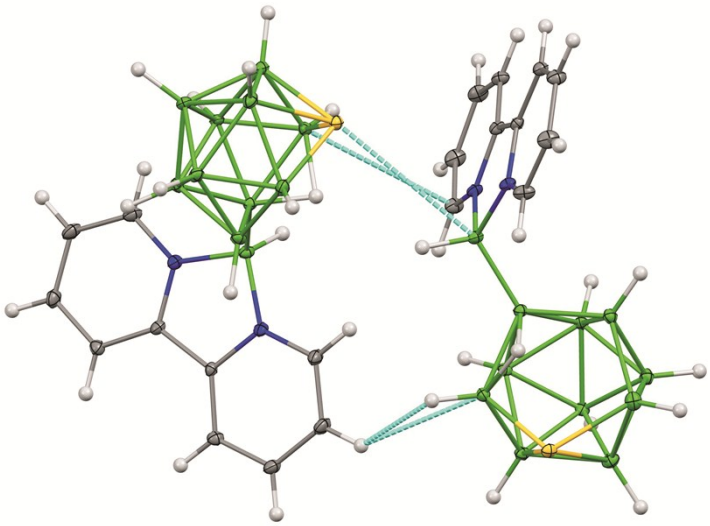


Fig. S6: Supramolecular architecture of **5a**, highlighting S...BH and C-H...H-B contacts.

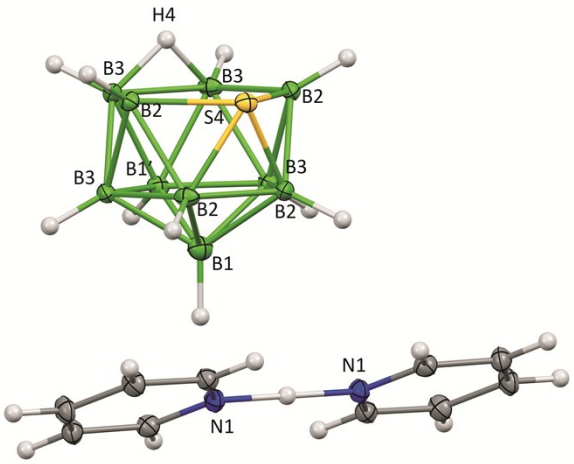


Fig. S7: Molecular structure of **6a**.

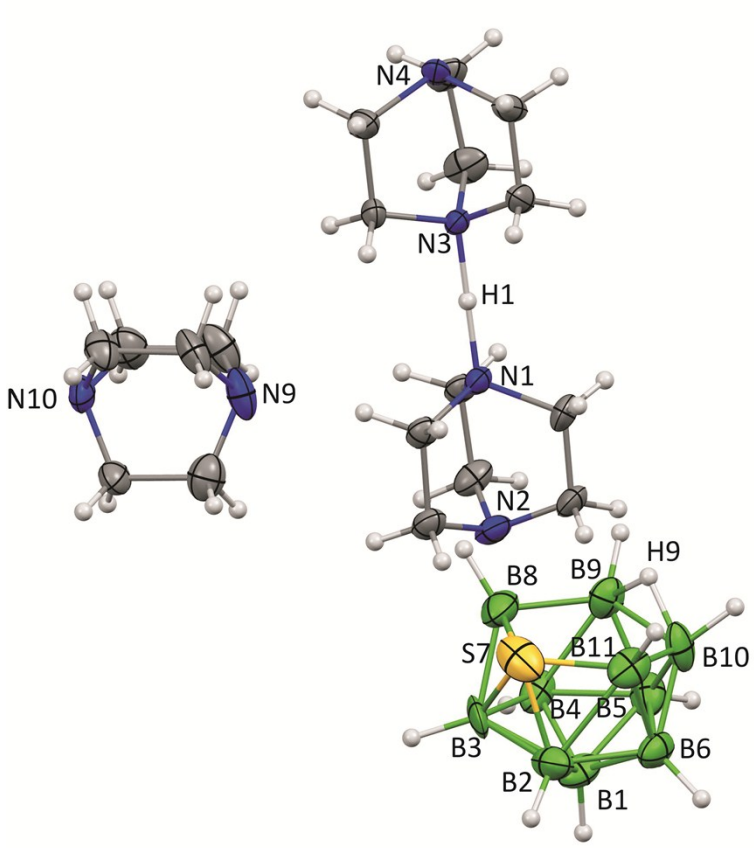


Fig. S8: Molecular structure of **7a**.

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-$SB_{11}H_{11}$,[S1] 12-I-1-$SB_{11}H_{10}$,[S1] 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 ($CDCl_3$: $\delta(^{1}H)$ = 7.24 ppm and $\delta(^{13}C)$ = 77.23 ppm; acetone-d6: $\delta(^{1}H)$ = 2.05 ppm and $\delta(^{13}C)$ = 29.92 ppm; CD_2Cl_2: $\delta(^{1}H)$ = 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 [^{11}B–^{11}B]-COSY (and ^{1}H-{^{11}B(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_α radiation; λ =1.54178 Å) or Mo (Mo/K_α radiation; λ = 0.71073 Å) microfocus X-ray (IμS) 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.[S2]

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 0.93Å and 1.1 Å for terminal and 1.25 Å for bridging B-H bonds.

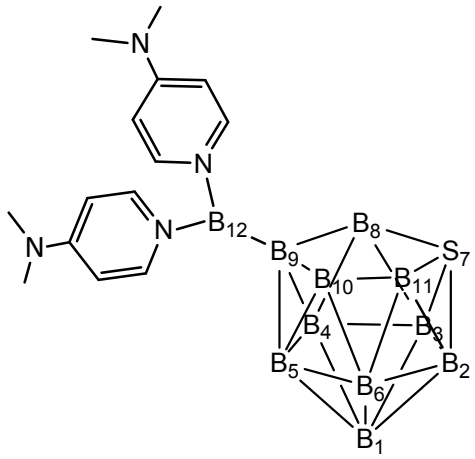
$R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | |F_o| - |F_c| | / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data. Crystallographic data for structural 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[S3] were calculated at B3LYP/cc-pVTZ level of theory.

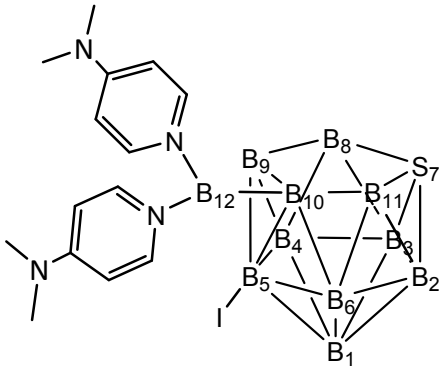
Synthesis of *nido*-9-BH(DMAP)$_2$-7-SB$_{10}$H$_{10}$ (2a)



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

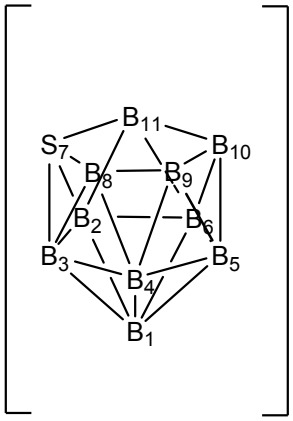
solution of 1-$SB_{11}H_{11}$ (43 mg, 0.27 mmol) in diethyl ether (10 mL). Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried *in vacuo*. Yield 104 mg (96 %). Obtained powder can be recrystallised from boiling acetone (THF) giving adduct **4a** (**4a'**). **Mp** 155 °C. **Anal. Calc**. for $C_{14}H_{31}B_{11}N_4S$ (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-d6, 500 MHz): δ = 3.18 (s, 12H, NCH_3), 6.81 (m, 4H, Ar*H*), 8.20 (d, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, 2H, Ar*H*), 8.26 (d, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, 2H, Ar*H*) ppm.**^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -35.8 (d, $^1J(^1H\text{-}^{11}B)$ = 135 Hz, 1B, B1), -17.6 (d, $^1J(^1H\text{-}^{11}B)$ = 142 Hz, 2B, B5,10), -16.1 (d, $^1J(^1H\text{-}^{11}B)$ = 137 Hz, 2B, B2,3), -11.4 (m, 3B, B8,9,11), -5.4 (m, 2B, B4,6), 5.0 (m broad, 1B, B12)m. **^{13}C{^{1}H} NMR** (25 °C, acetone-d6, 125.76 Hz): δ = 39.3 (s, N*C*H_3), 106.8, 149.8, 154.4 (s, Ar*C*) ppm.

Synthesis of *nido*-5-I-10-BH(DMAP)$_2$-7-$SB_{10}H_9$ (2b)



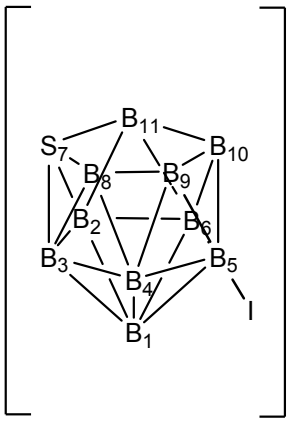
This synthetic procedure was performed under argon atmosphere. Solution of 4-dimethylaminopyridine (33 mg, 0.27 mmol) was added at ambient temperature to a stirred solution of 12-I-1-$SB_{11}H_{10}$ (39 mg, 0.14 mmol) in diethyl ether (10 mL). Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried *in vacuo*. Yield 69 mg (95 %). **Mp** 205 °C. **Anal. Calc**. for $C_{14}H_{30}B_{11}IN_4S$ (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-d6, 500 MHz): δ = 3.04 (s, 6H, NCH_3), 3.07 (s, 6H, NCH_3), 6.64 (d, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 2H, Ar*H*), 6.70 (d, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 2H, Ar*H*), 8.18 (d, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 2H, Ar*H*), 8.43 (d, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 2H, Ar*H*) ppm. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -33.9 (d, $^1J(^1H\text{-}^{11}B)$ = 163 Hz, 1B, B1), -23.3 (s, 1B, B5), -17.7 (m broad, 2B, B2,3), -14.0 (m broad, 2B, 9,10), -11.8 (m broad, 2B, B8,11), -4.6 (m, 2B, B4,6), 5.9 (m broad, 1B, B12) ppm. **^{13}C{^{1}H} NMR** (25 °C, acetone-d6, 125.76 Hz): δ = 39.9, 40.0 (s, N*C*H_3), 107.6, 107.9, 146.9, 147.6, 156.7, 156.9 (s, Ar*C*) ppm.

Synthesis of[(DMAP)H][*nido*-7- $SB_{10}H_{11}$] (3a)



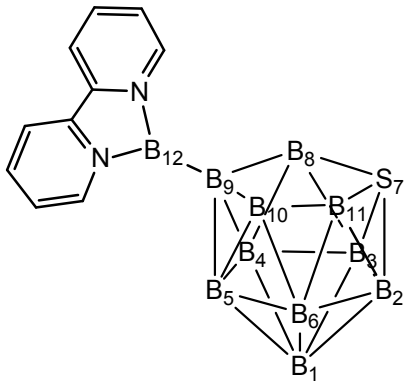
Solution of DMAP (34 mg, 0.28mmol) in methanol (10 mL) was added at ambient temperature to a stirred solution of 1-$SB_{11}H_{11}$ (45 mg, 0.28 mmol) in methanol (10 mL). The reaction mixture was stirred overnight and evaporated *in vacuo* giving **3a** in the form of colourless powder. Yield 74 mg (97 %). **Mp** 196 °C with decomposition. **Anal. Calc**. for $C_7H_{22}B_{10}N_2S$ (274.44): C 30.6, H 8.1, N 10.2; found C 30.7, H 8.3, N 10.3.**^{1}H NMR** (25 °C, acetone-d6, 500 MHz): δ = 3.17 (s, 6H, CH_3), 6.84 (d, ^3J(^{1}H-^{1}H) = 6.8 Hz, 2H, Ar*H*), 8.25 (d, ^3J(^{1}H-^{1}H) = 6.8 Hz, 2H, Ar*H*), 10.28 (s, 1H, N*H*) ppm. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -36.7 (d, ^1J(^{1}H-^{11}B) = 141 Hz, 1B, B1), -17.8 (m, 5B, B2,3,5,9,10), -12.3 (d, ^1J(^{1}H-^{11}B) = 147 Hz, 2B, B8,11), -6.2 (d, ^1J(^{1}H-^{11}B) = 138 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, acetone-d6, 125.76 Hz): δ = 39.7 (s, *C*H_3), 107.8, 145.3, 157.0 (s, Ar*C*) ppm.

Synthesis of [(DMAP)H][*nido*-5-I-7-$SB_{10}H_{10}$] (3b)



Solution of DMAP (17 mg, 0.14mmol) 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 $C_7H_{22}B_{10}IN_2S$ (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-d6, 500 MHz): δ = 3.18 (s, 6H, CH_3), 6.86 (d, $^3J(^1H\text{-}^1H)$ = 6.7 Hz, 2H, Ar*H*), 8.26 (d, $^3J(^1H\text{-}^1H)$ = 6.7 Hz, 2H, Ar*H*) ppm, N*H* not observed. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -35.2 (d, $^1J(^1H\text{-}^{11}B)$ = 145 Hz, 1B, B1), -27.0 (s, 1B, B5), -18.0 (d, $^1J(^1H\text{-}^{11}B)$ = 167 Hz, 2B, B2,3), -15.9 (d, $^1J(^1H\text{-}^{11}B)$ = 140 Hz, 2B, B9,10), -12.1 (d, $^1J(^1H\text{-}^{11}B)$ = 156 Hz, 2B, B8,11), -5.8 (d, $^1J(^1H\text{-}^{11}B)$ = 145 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, acetone-d6, 125.76 Hz): δ = 47.1 (s, *C*H_2) ppm.

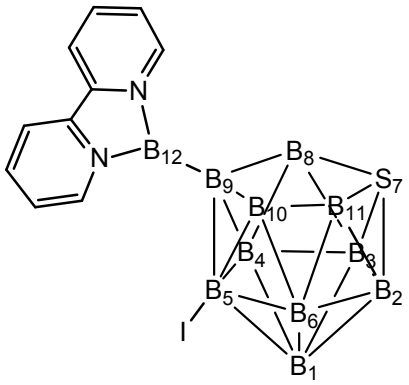
Synthesis of *nido*-9-B(H)bipy-7-$SB_{10}H_{10}$ (5a)



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 $C_{10}H_{19}B_{11}N_2S$ (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-d6, 500 MHz): δ = 8.13 (m, 2H, Ar*H*), 8.55 (m, 2H Ar*H*), 8.91 (d, $^1J(^1H\text{-}^1H)$ = 10 Hz, 2H, Ar*H*), 8.95 (d, $^1J(^1H\text{-}^1H)$ = 7.2 Hz, 1H, Ar*H*), 9.10 (d, $^1J(^1H\text{-}^1H)$ = 7.2 Hz, 1H, Ar*H*) ppm. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ= -35.9 (d, $^1J(^1H\text{-}^{11}B)$ = 140 Hz, 1B, B1), -18.0 (d, $^1J(^1H\text{-}^{11}B)$ = 144 Hz, 2B, B5,10), -16.8 (d, $^1J(^1H\text{-}^{11}B)$ = 143 Hz, 2B, B2,3), -10.6 (m, 3B, B8,9,11), -6.4 (m, 2B, B4,6), 2.0 (m broad, 1B, B12) ppm. **^{13}C{^{1}H}**

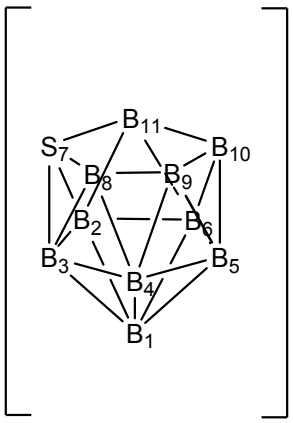
NMR (25 °C, acetone-d6, 125.76 Hz): δ = 122.7, 127.5, 141.5, 143.4, 143.8, 145.2, 145.4 (s, Ar*C*) ppm.

Synthesis of *nido*-9-B(H)bipy-5-I-7-$SB_{10}H_9$ (5b)



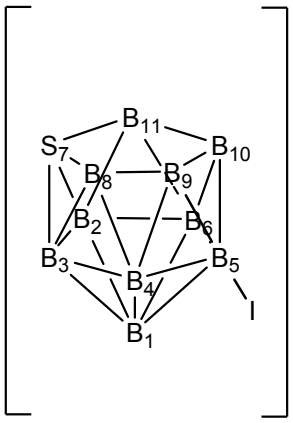
This synthetic procedure was performed under argon atmosphere. To a solution of 12-I-1-$SB_{11}H_{10}$ (50 mg, 0.17 mmol) in diethyl ether (10 mL), solution of 2,2'-bipyridyl (27 mg, 0.17 mmol) was added at ambient temperature and left for 1 day without stirring yielding yellow crystals of **5b**. The crystals were decanted and dried *in vacuo*. Yield 72 mg (94 %).**Mp** 205 with decomposition. **Anal. Calc**. for $C_{10}H_{18}B_{11}IN_2S$ (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): δ = 8.17 (m, 2H, Ar*H*), 8.62 (m, 2H Ar*H*), 8.94 (m, 2H, Ar*H*), 9.04 (m, 2H, Ar*H*) ppm. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -33.7 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 152 Hz, 1B, B1), -25.4 (s, 1B, B5), -17.1 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 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): δ = 122.8, 127.6, 142.1, 143.7, 143.9, 146.5, 146.7 (s, Ar*C*) ppm.

Synthesis of [(py)$_2$H][*nido*-7- SB$_{10}$H$_{11}$] (6a)



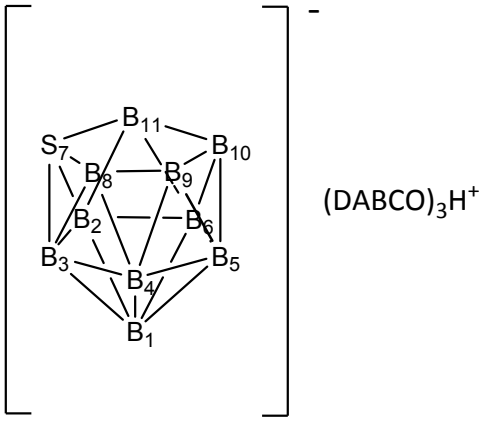
Pyridine (0.22 mL, 2.71 mmol) was added at -30 °C to a stirred solution of 1-SB$_{11}$H$_{11}$ (44 mg, 0.27 mmol) in methanol (10 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The colourless solution was evaporated *in vacuo* giving **6a** in the form of colourless 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, Ar*H*), 8.38 (t, ^3J(^{1}H-^{1}H) = 7.6 Hz, 2H, Ar*H*), 8.94 (d, ^3J(^{1}H-^{1}H) = 6.2 Hz, 4H, Ar*H*), 10.55 (s, 1H, N*H*) ppm. **^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ= -36.8 (d, ^1J(^{1}H-^{11}B) = 141 Hz, 1B, B1), -18.1 (m, 5B, B2,3,5,9,10), -12.4 (d, ^1J(^{1}H-^{11}B) = 147 Hz, 2B, B8,11), -6.3 (d, ^1J(^{1}H-^{11}B) = 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, Ar*C*) ppm.

Synthesis of [(py)$_2$H][*nido*-5-I-7-SB$_{10}$H$_{10}$] (6b)



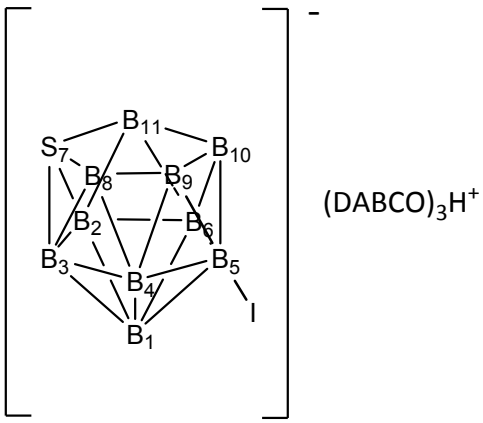
Pyridine (0.11 mL, 1.35 mmol) was added at -30 °C to a stirred solution of 12-I-1-$SB_{11}H_{10}$ (39 mg, 0.14 mmol) in methanol (10 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The colourless solution was evaporated *in vacuo* giving **6b** in the form of colourless powder. Yield 66 mg (95 %). **Mp** 180 °C. **Anal. Calc**. for $C_{10}H_{21}B_{10}IN_2S$ (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-d6, 500 MHz): δ = 7.87 (t, $^3J(^1H\text{-}^1H)$ = 6.4 Hz, 4H, Ar*H*), 8.35 (t, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 2H, Ar*H*), 8.92 (d, $^3J(^1H\text{-}^1H)$ = 6.8 Hz, 4H, Ar*H*), 11.71 (s, 1H, N*H*) ppm.**^{11}B NMR** (25 °C, acetone-d6, 160.42 MHz): δ = -35.2 (d, $^1J(^1H\text{-}^{11}B)$ = 153 Hz, 1B, B1), -27.0 (s, 1B, B5), -18.0 (d, $^1J(^1H\text{-}^{11}B)$ = 167 Hz, 2B, B2,3), -15.8 (d, $^1J(^1H\text{-}^{11}B)$ = 135 Hz, 2B, B9,10), -12.1 (d, $^1J(^1H\text{-}^{11}B)$ = 140 Hz, 2B, B8,11), -5.8 (d, $^1J(^1H\text{-}^{11}B)$ = 140 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, acetone-d6, 125.76 Hz): δ = 126.8, 142.9, 146.8 (s, Ar*C*) ppm.

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



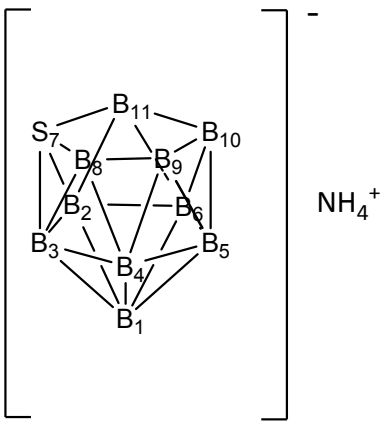
To a stirred solution of 1-$SB_{11}H_{11}$ (48 mg, 0.30 mmol) in diethyl ether (10 mL), solution of DABCO (99 mg, 0.89 mmol) in diethylether (10 mL) was added at ambient temperature. Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried *in vacuo*. Yield 130 mg (90 %). **Mp** 228 °C. **Anal. Calc**. for $C_{18}H_{48}B_{10}N_6S$ (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-d8, 500 MHz): δ = 2.95 (s, 36H, CH_2), 10.11 (s, 1H, N*H*) ppm. **^{11}B NMR** (25 °C, THF-d8, 160.42 MHz): δ = -36.9 (d, $^1J(^1H\text{-}^{11}B)$ = 143 Hz, 1B, B1), -18.1 (d, $^1J(^1H\text{-}^{11}B)$ = 137 Hz, 5B, B2,3,5,9,10), -12.3 (d, $^1J(^1H\text{-}^{11}B)$ = 148 Hz, 2B, B8,11), -6.4 (d, $^1J(^1H\text{-}^{11}B)$ = 137 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, THF-d8, 125.76 Hz): δ = 47.0 (s, CH_2) ppm.

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



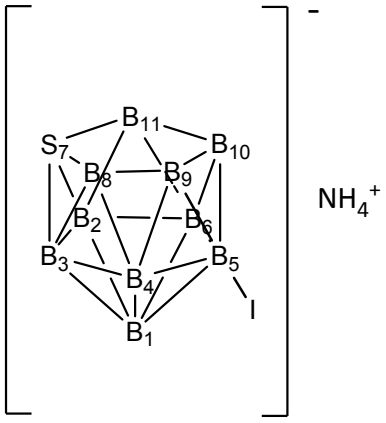
To a stirred solution of 12-I-1-SB$_{11}$H$_{10}$(35 mg, 0.12 mmol) in diethyl ether (10 mL), solution of DABCO (27 mg, 0.24 mmol) in diethylether (10 mL) was added at ambient temperature. Colourless precipitate was formed immediately. After 30 minutes of stirring, the suspension was filtered off and the solid was dried *in vacuo*. Yield 66 mg (88 %). **Mp** 80 °C. **Anal. Calc**. for $C_{18}H_{47}B_{10}IN_6S$ (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-d8, 500 MHz): δ = 2.96 (s, 36H, CH_2), 9.66 (s, 1H, N*H*) ppm. **^{11}B NMR** (25 °C, THF-d8, 160.42 MHz): δ = -35.3 (d, $^1J(^1H\text{-}^{11}B)$ = 147 Hz, 1B, B1), -26.9 (s, 1B, B5), -18.1 (d, $^1J(^1H\text{-}^{11}B)$ = 163 Hz, 2B, B2,3), -16.1 (d, $^1J(^1H\text{-}^{11}B)$ = 130 Hz, 2B, B9,10), -12.2 (d, $^1J(^1H\text{-}^{11}B)$ = 145 Hz, 2B, B8,11), -6.0 (d, $^1J(^1H\text{-}^{11}B)$ = 144 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, THF-d8, 125.76 Hz): δ = 47.1 (s, *C*H$_2$) 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%).**Mp** 198 °C with decomposition. **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 °C, THF-d8, 500 MHz): δ = 6.81 (s broad, 4H, NH_4) ppm. **^{11}B NMR** (25 °C, THF-d8, 160.42 MHz): δ= -36.9 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 141 Hz, 1B, B1), -18,1 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 141 Hz, 5B, B2,3,5,9,10), -12.3 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 148 Hz, 2B, B8,11), -6.4 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 138 Hz, 2B, B4,6) ppm.

Synthesis of NH_4[*nido*-5-I-7-$SB_{10}H_{10}$] (8b)



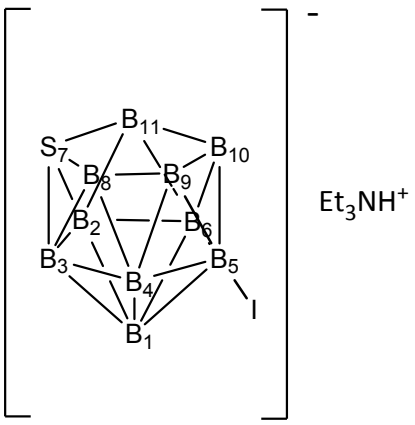
This synthetic procedure was performed under argon atmosphere. To a stirred solution of 12-I-1-$SB_{11}H_{10}$ (51 mg, 0.18 mmol) in THF (10 mL), solution of ammonia (4.4 mL, 1.8 mmol, 0.4M solution in THF) was added at ambient temperature and stirred overnight. The volatiles

were removed*in vacuo* and the colourless residue was washed with diethyl ether (2 mL) to give **8b** in the form of colourless powder. Yield 42 mg (80%). **Mp.** 195 °C with decomposition. **Anal. Calc**. for $H_{14}B_{10}INS$ (295.20): H4.8, N 4.7; found H 4.9, N 4.8. **^{1}H NMR** (25 °C, THF-d8, 500 MHz): δ = 6.31 (s broad, 4H, NH_4) ppm. **^{11}B NMR** (25 °C, CD_3CN, 160.42 MHz): δ = -35.3 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 147 Hz, 1B, B1), -26.9 (s, 1B, B5), -18.0 (d, , $^{1}J(^{1}H\text{-}^{11}B)$ = 165 Hz, 2B, B2,3), -15.9 (d, , $^{1}J(^{1}H\text{-}^{11}B)$ = 135 Hz, 2B, B9,10),-12.1 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 143 Hz, 2B, B8,11), -5.9 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 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-$SB_{11}H_{10}$ (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

$C_{14}H_{30}B_{11}IN_4S$ (379.36): C 19.0, H 6.9, N 3.7; found C 19.1, H 7.0, N 3.8. **^{1}H NMR** (25 °C, CD_3CN, 500 MHz): δ = 1.44 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.3 Hz, 9H, CH_3), 3.25 (q,$^{3}J(^{1}H\text{-}^{1}H)$ = 7.3 Hz, 6H, CH_2), 8.37 (s broad, 1H, N*H*) ppm. **^{11}B NMR** (25 °C, CD_3CN, 160.42 MHz): δ = -35.1 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 146 Hz, 1B, B1), -27.0 (s, 1B, B5), -17.8 (d, , $^{1}J(^{1}H\text{-}^{11}B)$ = 171 Hz, 2B, B2,3), -15.9 (d, , $^{1}J(^{1}H\text{-}^{11}B)$ = 144 Hz, 2B, B9,10),-11.9 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 150 Hz, 2B, B8,11), -5.9 (d, $^{1}J(^{1}H\text{-}^{11}B)$ = 146 Hz, 2B, B4,6) ppm. **^{13}C{^{1}H} NMR** (25 °C, CD_3CN, 125.76 Hz): δ = 9.1 (s, *C*H_3), 47.3 (s, *C*H_2) ppm.

TABLE S1: Selected crystallographic parameters

Compound reference	**2a**	**2b**	**3a**	**4a**	**4a'**
Chemical formula	$C_{14}H_{31}B_{11}N_4SCH_2Cl_2$	$C_{14}H_{30}B_{11}IN_4S$	$C_7H_{22}B_{10}N_2S$	$C_{13}H_{29}B_{11}N_4S{\cdot}C_4H_8O$	$C_{14}H_{31}B_{11}N_4S{\cdot}C_4H_8O$
Formula Mass	491.32	532.29	274.42	464.47	478.50
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	8.8688(3)	10.9419(6)	8.7985(5)	8.4015(5)	8.831(3)
b/Å	10.1323(4)	13.0988(7)	12.6301(6)	11.3344(7)	10.884(2)
c/Å	15.8068(6)	17.6099(11)	14.4822(7)	15.3636(9)	15.634(3)
α/°	72.8750(10)	90	90	72.113(2)	71.461(5)
β/°	77.9390(10)	99.408(2)	101.517(2)	78.085(2)	76.041(12)
γ/°	76.3180(10)	90	90	68.708(2)	71.517(12)
Unit cell volume/Å^3	1304.00(8)	2490.0(2)	1576.94(14)	1289.81(14)	1334.7(6)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	*P*-1	$P2_1/n$	$P2_1/c$	*P*-1	P-1
No. of formula units per unit cell, *Z*	2	4	4	2	2
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	0.342	1.380	0.186	0.145	0.142
No. of reflections measured	79833	69717	29752	55773	2691
No. of independent reflections	6017	5734	3630	5940	2161
R_{int}	0.0291	0.0501	0.0571	0.0521	0.1347
Final R_1 values ($I > 2\sigma(I)$)	0.0508	0.0306	0.0540	0.0468	0.0813
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1429	0.0664	0.1405	0.1181	0.1882
Final R_1 values (all data)	0.0545	0.0409	0.0664	0.0596	0.1401
Final $wR(F^2)$ values (all data)	0.1456	0.0711	0.1484	0.1248	0.2108
Goodness of fit on F^2	1.146	1.102	1.068	1.070	1.086

TABLE S1 - continuation: Selected crystallographic parameters

Compound reference	**5a**	**6a**	**7a**
Chemical formula	$C_{10}H_{19}B_{11}N_2S$	$B_{10}H_{11}S{\cdot}C_{10}H_{11}N_2$	$B_{10}H_{11}S{\cdot}C_{12}H_{25}N_4{\cdot}C_6H_{12}N_2$
Formula Mass	318.24	310.45	488.78
Crystal system	Monoclinic	Monoclinic	Trigonal
a/Å	18.868(2)	8.2222(7)	22.2424(5)
b/Å	8.9391(9)	16.0093(12)	22.2424(5)
c/Å	19.9161(19)	6.8094(5)	14.5434(3)
α/°	90	90	90
β/°	93.607(4)	98.739(5)	90
γ/°	90	90	120
Unit cell volume/Å^3	3352.4(6)	885.93(12)	6231.0(3)
Temperature/K	150(2)	150(2)	150(2)
Space group	*C2/c*	C2/m	$P3_1$
No. of formula units per unit cell, *Z*	8	2	9
Radiation type	MoKα	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	0.184	0.173	1.166
No. of reflections measured	34726	9319	73941
No. of independent reflections	3838	905	16651
R_{int}	0.1052	0.0667	0.0846
Final R_1 values ($I > 2\sigma(I)$)	0.0852	0.0552	0.1139
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2162	0.1421	0.2926
Final R_1 values (all data)	0.0983	0.0655	0.1335
Final $wR(F^2)$ values (all data)	0.2242	0.1494	0.3213
Goodness of fit on F^2	1.064	0.986	1.286

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