

Electronic Supporting Information

Tuning a Modular System – Synthesis and Characterisation of a Boron-rich s-Triazine-based Carboxylic Acid and Amine Bearing a Galactopyranosyl Moiety

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1. Additional Synthetic Procedures and Characterisation of 4, 8, 9 and SP1, SP2 and SP3

1,2:3,4-Di-O-isopropylidene-6-deoxy- α -D-galactopyranosyl-6-triflate (4)¹: 7.50 g (28.8 mmol, 1.00 eq.) 1,2:3,4-di-O-isopropylidene- α -D-galactopyranose were mixed with 7.6 mL (6.98 g, 57.6 mmol, 2.00 eq.) absolute 2,4,6-collidine. The mixture was dissolved in 300 mL absolute CH₂Cl₂. 7.7 mL (13.0 g, 46.1 mmol, 1.60 eq.) trifluoromethanesulfonic anhydride were added dropwise over 30 minutes at ambient temperature to this solution. The reaction mixture turned deep yellow during the addition. Over a stirring period of 4 h at ambient temperature, the mixture turned orange. The reaction was quenched by pouring it onto 300 mL of ice-cold water. The layers were separated and the water layer was extracted twice with 100 mL CHCl₃. The combined organic layers were washed twice with 250 mL of an aqueous 17% KHSO₄ solution. The organic layer was washed twice with 200 mL of ice-cold H₂O, twice with 250 mL of a saturated NaHCO₃ solution, once with 300 mL ice-cold H₂O and finally once with 300 mL of a saturated NaCl solution. The organic layer was dried over Na₂SO₄. The solution was concentrated under reduced pressure. TLC showed the product at an R_f value of 0.46 (*n*-hexane/ethyl acetate, 3:1 (v/v)). The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, 3:1, (v/v)), yielding 10.54 g (26.80 mmol, 93%) of a yellow oil, which slowly solidified at 4 °C. ¹H NMR (CDCl₃): δ = 1.34 (s, 3H, C^{9/9'} or 11/11'H₃), 1.34 (s, 3H, C^{9/9'} or 11/11'H₃), 1.45 (s, 3H, C^{9/9'} or 11/11'H₃), 1.53 (s, 3H, C^{9/9'} or 11/11'H₃), 4.12 (ddd, ³J_{HH} = 7.0 Hz, ³J_{HH} = 4.7 Hz, ³J_{HH} = 2.0 Hz, 1H, C⁵H), 4.25 (dd, ³J_{HH} = 7.8 Hz, ³J_{HH} = 2.0 Hz, 1H, C⁴H), 4.36 (dd, ³J_{HH} = 5.0 Hz, ³J_{HH} = 2.6 Hz, 1H, C²H), 4.55 to 4.68 (m, 3H, C³H, C⁶H₂), 5.54 ppm (d, ³J_{HH} = 4.9 Hz, 1H, C¹H). ¹³C{¹H} NMR (CDCl₃): δ = 24.4 (s, CH₃, C^{9/9'} or 11/11'H₃), 24.8 (s, CH₃, C^{9/9'} or 11/11'H₃), 25.8 (s, CH₃, C^{9/9'} or 11/11'H₃), 25.9 (s, CH₃, C^{9/9'} or 11/11'H₃), 66.1 (s, CH, C⁵H), 70.2 (s, CH, C²H), 70.4 (s, CH, C⁴H), 70.6 (s, C³H), 74.6 (s, CH₂, C⁶H₂), 96.1 (s, CH, C¹H), 109.1 (s, C_q, C_q⁸ or ¹⁰(CH₃)₂), 110.1 (s, C_q, C_q⁸ or ¹⁰(CH₃)₂), 118.6 ppm (q, ¹J_{CF} = 320 Hz, C_q, C_q⁷F₃).¹

tert-Butyl[4-chloro-6-(1,7-dicarba-c/oso-dodecaboran-9-ylthio)-1,3,5-triazin-2-yl]glycinate (8) and tert-butyl[4,6-bis(dicarba-c/oso-dodecaboran-9-ylthio)-1,3,5-triazin-2-yl]glycinate (9): As mentioned in the main text, the synthesis of **9** was problematic. Results from NMR and mass spectrometry experiments showed the presence of **8** and **9**. The mixture could not be efficiently separated.

A 250 mL two-necked round bottom flask, equipped with a condenser, was charged with 1.02 g (3.65 mmol, 1.00 eq.) *tert*-butyl[4,6-dichloro-1,3,5-triazin-2-yl]glycinate (**7**) and 1.37 g

¹ Numbering schemes for all compounds are given in chapter 2.

(7.77 mmol, 2.13 eq.) 9-mercapto-1,7-dicarba-closo-dodecaborane(12) (**1**). The flask was evacuated and purged with nitrogen three times, respectively. The mixture was dissolved in 80 mL absolute MeCN and cooled to 0 °C. 1.55 mL (1.18 g, 9.11 mmol, 2.50 eq.) DIPEA were added dropwise to this mixture. The mixture was stirred for 5 min at 0 °C and then warmed to room temperature. After 30 min of stirring at room temperature, the mixture was heated to 80 °C for 1 d. Monitoring by TLC (ethyl acetate/*n*-hexane, 1:3, v/v) showed a conversion but still some starting material. The reaction mixture was cooled to room temperature and all volatile components were removed under reduced pressure. The residue was dissolved in 75 mL Et₂O and 40 mL saturated NH₄Cl solution. The aqueous layer was extracted three times with 75 mL ethyl acetate. The combined organic layers were washed with 30 mL saturated NaCl solution and dried over MgSO₄, filtered off and the solvent was removed under reduced pressure. The raw product was purified by column chromatography (ethyl acetate/*n*-hexane, 1:3 to 3:1, v/v). 544 mg (3.09 mmol) of unreacted **1** were recovered and 1.47 g of a mixture of **8** and **9** in a ratio of ca. 1:2 were isolated. The following analytical data were obtained from this mixture. Assignment of the NMR data was not possible due to overlapping signals. IR (KBr): $\tilde{\nu}$ = 3429 (s), 3271 (s), 3151 (m), 3071 (m), 3021 (m), 2982 (m), 2935 (w), 2608 (s), 1742 (s), 1615 (s), 1550 (s), 1496 (m), 1418 (s), 1397 (m), 1370 (m), 1336 (w), 1313 (s), 1231 (s), 1168 (s), 1144 (s), 1061 (w), 994 (w), 974 (w), 955 (w), 846 (s), 801 (m), 756 (w), 733 (w), 628 (w), 562 (w) cm⁻¹. ¹H NMR (acetone-*d*₆): δ = 1.45 (s, C(CH₃)₃), 1.46 (s, C(CH₃)₃), 1.55 to 3.61 (m, vbr, B₁₀H₉), 3.76 (s, br, CH, CH_{Cluster}), 3.82 (s, br, CH, CH_{Cluster}), 4.06 (d, ³J_{HH} = 6.2 Hz, CH₂), 4.25 (d, ³J_{HH} = 6.5 Hz, CH₂), 7.53 ppm (m, NH). ¹³C{¹H} NMR (acetone-*d*₆): δ = 28.2 (s, CH₃, C(CH₃)₃), 28.3 (s, CH₃, C(CH₃)₃), 43.8 (s, CH₂), 43.9 (s, CH₂), 56.0 (s, br, CH, CH_{Cluster}), 81.97 (s, C_q), 82.04 (s, C_q), 166.2 (s, C_q), 168.96 (s, C_q), 169.02 (s, C_q), 169.3 (s, C_q), 182.9 ppm (s, C_qO). ¹¹B{¹H} NMR (acetone-*d*₆): δ = -18.3 (s, br, B), -16.9 (s, B), -13.9 (s, br, B), -12.8 (s, br, B), -10.4 (s, B), -5.8 (s, br, B), -3.7 ppm (s, BS). ¹¹B NMR (acetone-*d*₆): δ = -17.6 (m, B), -13.3 (m, B), -10.5 (d, ¹J_{BH} = 151 Hz, B), -5.8 (d, ¹J_{BH} = 166 Hz, B), -3.7 ppm (s, BS). HRMS (ESI+): C₁₁H₂₃B₁₀CIN₄O₂S (**8**), m/z calcd: 420.22754 ([M+H]⁺); found: 420.22790 (100%); C₁₃H₃₄B₂₀N₄O₂S₂ (**9**), m/z calcd: 560.41715 ([M+H]⁺); found: 560.41731 (72%). Colourless crystals of **8** suitable for X-ray structure determination were obtained from acetone at room temperature. Colourless crystals of **9** suitable for X-ray structure determination were obtained from chloroform at room temperature. Crystallographic data are given in Table S1, and the molecular structures are depicted in Figure S1. The fact, that both compounds were crystallised from different solvents indicates the possibility of separation by recrystallisation from the corresponding solvent.

***tert*-Butyl-*N*-[4-chloro-6-(1,7-dicarba-*c*loso-dodecaboran-9-ylthio)-1,3,5-triazin-2-yl]-*N*-(1',2':3',4'-di-*O*-isopropylidene-6'-deoxy- α -D-galactopyranos-6'-yl)glycinate (SP1):** An attempt to prepare **12** in a one-pot synthesis using DIPEA as a base failed and only produced the mono-substituted derivative *tert*-butyl-*N*-(4-chloro-6-(1,7-dicarba-*c*loso-dodecaboran-9-ylthio)-1,3,5-triazin-2-yl)-*N*-(1',2':3',4'-di-*O*-isopropylidene-6'-deoxy- α -D-galactopyranos-6'-yl)glycinate (**SP1**) in 15% yield besides **11**.

A 100 mL Schlenk flask was charged with 0.23 g (1.34 mmol, 1.00 eq.) *tert*-butyl glycinate hydrochloride. The flask was evacuated and purged with nitrogen three times. The ester was suspended in 35 mL absolute tetrahydrofuran, 0.64 mL (0.49 g, 3.76 mmol, 2.81 eq.) DIPEA were added and the mixture was cooled to $-20\text{ }^{\circ}\text{C}$. A solution of 0.50 g (1.27 mmol, 0.95 eq.) 1,2:3,4-di-*O*-isopropylidene-6-deoxy- α -D-galactopyranosyl-6-triflate (**4**) in 25 mL absolute tetrahydrofuran was added slowly. The mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 2 h and then warmed to room temperature and stirred for 3 d. Monitoring by TLC (ethyl acetate/*n*-hexane, 1:2, v/v) showed residual starting material; therefore, the temperature was increased to $50\text{ }^{\circ}\text{C}$ for 7 h. After no starting material was observed by TLC, 0.34 mL (0.26 g, 2.01 mmol, 1.50 eq.) DIPEA and 0.27 g (1.47 mmol, 1.10 eq.) cyanuric chloride were dissolved in 15 mL absolute tetrahydrofuran in a 100 mL Schlenk flask. This mixture was cooled to $0\text{ }^{\circ}\text{C}$ and the initial reaction mixture was added dropwise to this solution at $0\text{ }^{\circ}\text{C}$. After 30 min of stirring at $0\text{ }^{\circ}\text{C}$, the reaction mixture was warmed to room temperature and stirred for 2 d. A 250 mL round bottom flask was charged with 0.59 g (3.35 mmol, 2.50 eq.) 9-mercapto-1,7-dicarba-*c*loso-dodecaborane(12) (**1**), evacuated and purged with nitrogen. **1** was dissolved in 20 mL absolute tetrahydrofuran and 0.57 mL (0.43 g, 3.35 mmol, 2.50 eq.) DIPEA were added. The triazine solution was slowly added to this solution at room temperature and the mixture was stirred at $60\text{ }^{\circ}\text{C}$ for 5 d. The reaction mixture was cooled to room temperature and quenched by addition of 25 mL distilled H₂O and 25 mL saturated NaCl solution. The aqueous layer was extracted once with 50 mL ethyl acetate. The organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The raw product was purified by column chromatography using the Isolera 1 system with a SNAP Ultra 50 g cartridge and ethyl acetate and *n*-hexane as the eluents in 1:3 (v/v) to 2:1 (v/v) ratio and a flow rate of 18 mL/min. 261 mg (0.50 mmol, 37%) of **11** and 134 mg (0.20 mmol, 15%) of **SP1** were isolated. **11**: T_m: 122–124 $^{\circ}\text{C}$ (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3441 (s), 2984 (m), 2937 (w), 1741 (s), 1568 (s), 1489 (s), 1458 (w), 1417 (w), 1372 (m), 1328 (m), 1289 (w), 1228 (s), 1172 (s), 1114 (m), 1071 (s), 1003 (m), 980 (m), 906 (w), 883 (w), 848 (m), 800 (m), 773 (w), 746 (w), 651 (w), 599 (w), 551 (w), 512 (w) cm⁻¹. ¹H NMR (acetone-*d*₆): δ = 1.30 (s, 3H, C¹⁵ or ¹⁵H₃), 1.34 (s, 3H, C¹⁶ or ¹⁶H₃), 1.42 (s, 3H, C¹⁵ or ¹⁵H₃), 1.44 (s, 3H, C¹⁶ or ¹⁶H₃), 1.47 (s, 9H, C(C¹H₃)₃), 3.81 (qd, ²J_{HH} = 14.2 Hz, ³J_{HH} = 6.9 Hz, 2H, 2xC⁷HH), 4.25 (m, 1H, C⁴HH), 4.28 to 4.45 (m, 4H, C⁸H, C¹⁰H, C¹¹H, C⁴HH), 4.65 (dd, ³J_{HH} = 7.9 Hz, ³J_{HH} = 2.5 Hz, 1H, C⁹H),

5.48 ppm (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H, C^{12}H). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): $\delta = 24.7, 25.2, 26.29$ and 26.34 (s, CH_3 , C^{15}H_3 , $\text{C}^{15'}\text{H}_3$, C^{16}H_3 and $\text{C}^{16'}\text{H}_3$), 28.2 (s, CH_3 , $\text{C}(\text{C}^1\text{H}_3)_3$), 50.5 (s, CH_2 , C^7H_2), 52.4 (s, CH_2 , C^4H_2), 65.7 (s, CH , C^8H), 71.3 (s, CH , C^{11}H), 71.7 (s, CH , C^9H), 71.8 (s, CH , C^{10}H), 82.5 (s, C_q , C_q^2), 97.3 (s, CH , C^{12}H), 109.4 (s, C_q , C_q^{14}), 110.0 (s, C_q , C_q^{13}), 166.6 (s, C_q , C_q^5N), 168.0 (s, C_q , $2\times\text{C}_q^6\text{Cl}$), 170.4 ppm (s, C_q , C_q^3O). LRMS (ESI+): $\text{C}_{21}\text{H}_{30}\text{Cl}_2\text{N}_4\text{O}_2$, m/z calcd: 521.2 ($[\text{M}+\text{H}]^+$); found: 521.2 (21%); m/z calcd: 543.1 ($[\text{M}+\text{Na}]^+$); found: 543.1 (55%).

SP1: T_m : $185\text{--}188^\circ\text{C}$ (acetone, decomp.). IR (KBr): $\tilde{\nu} = 3429$ (s), 3271 (s), 3151 (w), 3072 (w), 3021 (m), 2982 (m), 2934 (w), 2608 (s), 1742 (s), 1615 (s), 1550 (s), 1496 (m), 1418 (s), 1397 (m), 1370 (m), 1336 (w), 1314 (s), 1231 (s), 1169 (s), 1144 (s), 1069 (w), 998 (w), 975 (w), 956 (w), 846 (s), 801 (m), 756 (m), 733 (m), 629 (w), 562 (w), 423 (w) cm^{-1} . ^1H NMR (acetone- d_6): $\delta = 1.30$ (s, 3H, C^{16} or $^{16'}\text{H}_3$), 1.35 (s, 3H, C^{17} or $^{17'}\text{H}_3$), 1.42 (m, 6H, C^{16} or $^{16'}\text{H}_3$, C^{17} or $^{17'}\text{H}_3$), 1.46 (s, 9H, $\text{C}(\text{C}^7\text{H}_3)_3$), 1.66 to 3.55 (m, br, 9H, B_{10}H_9), 3.71 (m, 1H, C^8HH), 3.82 (s, br, 2H, $2\times\text{C}^1\text{H}$), 3.99 to 4.13 (m, 2H, C^8HH , C^4HH), 4.21 to 4.28 (m, 2H, C^9H , C^{11}H), 4.36 (m, 1H, C^{12}H), 4.45 (m, 1H, C^4HH), 4.65 (m, 1H, C^{10}H), 5.48 ppm (dd, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HH}} = 5.0$ Hz, 1H, C^{13}H). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): $\delta = 24.6, 25.2, 26.3$ and 26.4 (s, CH_3 , C^{16}H_3 , $\text{C}^{16'}\text{H}_3$, C^{17}H_3 and $\text{C}^{17'}\text{H}_3$), 28.3 (s, CH_3 , $\text{C}(\text{C}^7\text{H}_3)_3$), 49.6 (s, CH_2 , C^8H_2), 51.3 (s, CH_2 , C^4H_2), 56.0 (s, br, CH , $2\times\text{C}^1\text{H}$), 65.9 (s, CH , C^9H), 71.4 (s, CH , C^{12}H), 71.7 (s, CH , C^{10}H), 71.9 (s, CH , C^{11}H), 82.0 (s, C_q , $\text{C}_q^6(\text{CH}_3)_3$), 97.3 (s, CH , C^{13}H), 109.3 (s, C_q , C_q^{15}), 109.9 (s, C_q , C_q^{14}), 165.6 (s, C_q , C_q^3N), 166.2 (s, br, C_q , C_q^{18}S), 168.8 (s, C_q , C_q^2Cl), 169.3 ppm (s, C_q , C_q^5O). $^{11}\text{B}\{^1\text{H}\}$ NMR (acetone- d_6): $\delta = -18.3$ (s, br, 1B), -16.9 (s, 1B), -13.9 (s, 2B), -12.8 (s, br, 2B), -10.4 (s, 1B), -5.8 (s, br, 2B), -3.8 ppm (s, 1B, BS). ^{11}B NMR (acetone- d_6): $\delta = -17.6$ (m, 2B), -13.3 (m, 4B), -10.4 (d, $^1J_{\text{BH}} = 152$ Hz, 1B), -5.8 (d, $^1J_{\text{BH}} = 167$ Hz, 2B), -3.8 ppm (s, 1B, BS). LRMS (ESI+): $\text{C}_{23}\text{H}_{41}\text{B}_{10}\text{ClN}_4\text{O}_7\text{S}$, m/z calcd: 662.3 ($[\text{M}+\text{H}]^+$); found: 662.3 (100%); m/z calcd: 684.3 ($[\text{M}+\text{Na}]^+$); found: 684.3 (34%). Colourless crystals of **SP1** suitable for X-ray structure determination were obtained from acetone at room temperature. Crystallographic data are given in Table S2, and the molecular structure is depicted in Figure S2.

***N*-Ethyl-*N*-isopropyl-4,6-bis(1,7-dicarba-*c*/oso-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (SP2):** An attempt to prepare **5** directly in a one-pot synthesis using DIPEA as a base failed and only produced the side product *N*-ethyl-*N*-isopropyl-4,6-bis(1,7-dicarba-*c*/oso-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (**SP2**) in 10% yield.

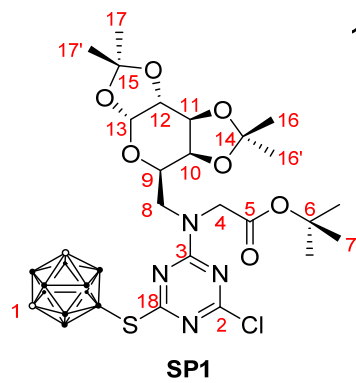
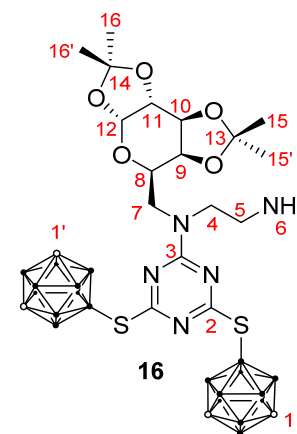
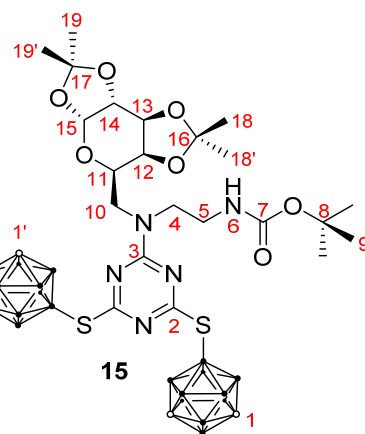
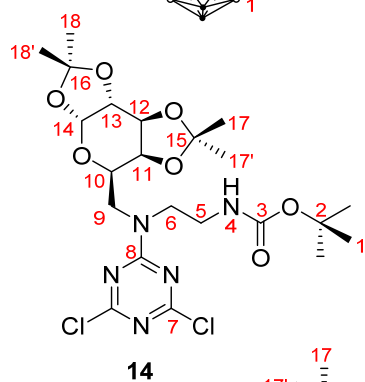
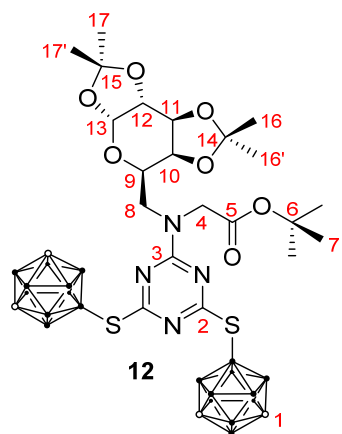
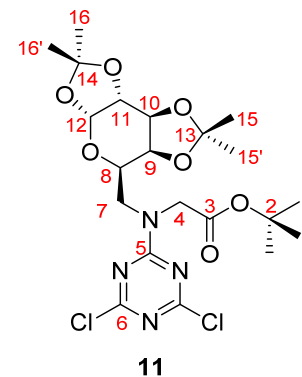
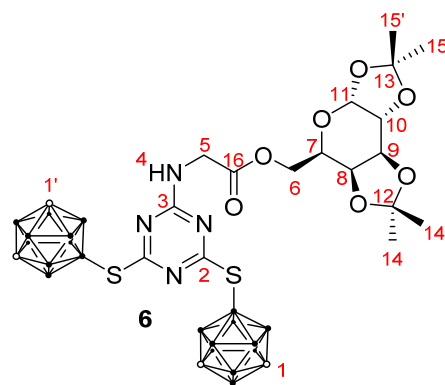
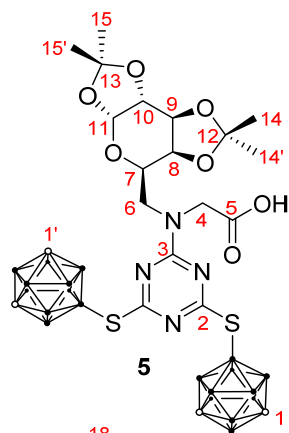
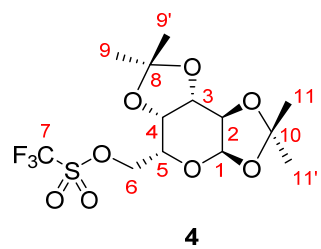
A 250 mL round bottom flask was charged with 1.01 g (2.57 mmol, 0.42 eq.) triflate **4** and 0.51 g (6.72 mmol, 1.10 eq.) glycine, evacuated and purged with nitrogen. This mixture was suspended in 80 mL absolute MeCN and 2.70 mL (2.06 g, 15.9 mmol, 2.59 eq.) DIPEA were added. The mixture was stirred for 2 d at room temperature and for 1 d at 85 °C. Reaction monitoring by TLC showed residual **4**; therefore, 1.65 g (11.9 mmol, 1.94 eq.) K₂CO₃ were added. The mixture was stirred for 4 h at 85 °C. Subsequently, 1.13 g (6.13 mmol, 1.00 eq.) cyanuric chloride and 0.85 g (6.15 mmol, 1.00 eq.) K₂CO₃ were added. The mixture was stirred for 1 d at 85 °C. Afterwards, 3.28 g (18.6 mmol, 3.03 eq.) 9-mercapto-1,7-dicarba-*c*/oso-dodecaborane (**1**), 5.45 g (39.4 mmol, 6.43 eq.) K₂CO₃ and additional 20 mL absolute MeCN were added to the mixture. The reaction mixture was stirred for 3 d at 85 °C. The mixture was cooled to room temperature and 40 mL saturated NaCl solution were added. The aqueous layer was extracted three times with 30 mL ethyl acetate. The organic layer was washed twice with 30 mL saturated NaCl solution. The organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The raw product was purified by column chromatography (1:6, ethyl acetate/*n*-hexane, v/v) and 2.00 g (11.3 mmol) 9-mercapto-1,7-dicarba-*c*/oso-dodecaborane (**1**) and 311 mg (0.60 mmol; R_f = 0.29, 1:6, v/v, ethyl acetate/*n*-hexane) **SP2** were obtained in 61% and 10% yield, respectively. Colourless crystals of **SP2** suitable for X-ray structure determination were obtained from CHCl₃ at room temperature. Crystallographic data are given in Table S3, and the molecular structure is depicted in Figure S3. T_m: 228–231 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3446 (m), 3059 (m), 3041 (m), 2969 (m), 2933 (w), 2873 (w), 2622 (s), 2605 (s), 2563 (m), 1634 (w), 1534 (s), 1518 (s), 1470 (s), 1436 (m), 1376 (w), 1350 (w), 1333 (w), 1320 (w), 1296 (m), 1243 (s), 1204 (w), 1170 (s), 1085 (w), 1062 (m), 1027 (w), 993 (w), 953 (m), 920 (w), 863 (m), 844 (m), 799 (m), 758 (m), 733 (w), 676 (w), 626 (w), 608 (w), 579 (w), 508 (w) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.19 (m, 9 H, 3xCH₃), 1.67 to 3.45 (m, br, 18 H, 2xB₁₀H₉), 2.96 (s, br, 4 H, 4xCH_{cluster}), 3.51 (q, ³J_{HH} = 7.0 Hz, 2 H, CH₂), 5.23 ppm (sept, ³J_{HH} = 6.8 Hz, 1 H, CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃): δ = 15.4 (s, CH₃, CH₂CH₃), 20.7 (s, CH₃, CH(CH₃)₂), 36.0 (s, CH₂, CH₂CH₃), 45.8 (s, CH, CH(CH₃)₂), 53.7, 53.9 (s, br, CH, 4xCH_{cluster}), 161.9 (s, C_q, C_qN), 177.5, 178.1 ppm (s, C_q, 2xC_qS). ¹¹B{¹H} NMR (CDCl₃): δ = -19.0 (s, br, 1 B), -17.5 (s, 1 B), -14.1 (s, 2 B), -12.9 (s, br, 2 B), -10.1 (s, 1 B), -5.6 (s, br, 2 B), -3.0 ppm (s, 1 B, BS). ¹¹B NMR (CDCl₃): δ = -18.2 (m, br, 1 B), -13.5 (m, br, 4 B), -10.1 (d, ¹J_{BH} = 153 Hz, 1 B), -5.6 (d, br, ¹J_{BH} = 166 Hz, 2 B), -3.0 ppm (s, 1 B, BS). LRMS (ESI⁺): C₁₂H₃₄B₂₀N₄S₂, m/z calcd: 516.4 ([M+H]⁺); found: 516.4 (100%), m/z calcd: 538.4 ([M+Na]⁺); found: 538.4 (10%), LRMS (ESI⁻): C₁₂H₃₄B₂₀N₄S₂,

m/z calcd: 550.4 ([M+Cl]⁻); found: 550.4 (100%).

4,6-Bis(1,7-dicarba-closo-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (SP3): During work-up of **16**, side product 4,6-bis(1,7-dicarba-closo-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (**SP3**) was obtained in less than 5% yield.

A 25 mL Schlenk flask was charged with 0.50 g (0.60 mmol, 1.00 eq.) **15**. The starting material was dissolved in 10 mL absolute CH₂Cl₂ and 2.40 mL (3.55 g, 31.5 mmol, 51.9 eq.) trifluoroacetic acid was added. This mixture was stirred for 4 h. Afterwards, all volatile compounds were removed under reduced pressure and the crude product was dissolved again in CH₂Cl₂. This step was repeated three times. The raw product was purified by column chromatography (ethyl acetate/acetone, 1:1, v/v). Additional recrystallisation from MeOH was carried out. Final purification by column chromatography (100% acetone) gave 397 mg (0.54 mmol) **16** in 91% yield. Side product **SP3** was obtained in <5% yield (ca. 13 mg, ca. 0.03 mmol, R_f = 0.95, 100% acetone). Colourless crystals of **SP3** suitable for X-ray structure determination were obtained from MeCN at 4 °C. Crystallographic data are given in Table S3, and the molecular structure is depicted in Figure S4. T_m: 163°C (methanol, decomposition). IR (KBr): $\tilde{\nu}$ = 3429 (s), 3302 (m), 3181 (m), 3051 (m), 2609 (s), 2253 (w), 1633 (s), 1508 (s), 1385 (w), 1300 (s), 1254 (m), 1198 (m), 1160 (m), 1106 (m), 1066 (w), 1008 (m), 991 (m), 951 (m), 917 (w), 864 (m), 847 (s), 805 (m), 758 (m), 730 (m), 626 (w), 602 (w), 551 (w) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.35 to 3.50 (m, br, 18 H, 2xB₁₀H₉), 2.96 (s, br, 4 H, 4xCH_{cluster}), 5.14 ppm (s, 2 H, NH₂). ¹³C{¹H} NMR (CDCl₃): δ = 53.8 (s, CH, 4xCH_{cluster}), 164.0 (s, C_q, C_qNH₂), 179.4 ppm (s, C_q, 2xC_qS). ¹¹B{¹H} NMR (CDCl₃): δ = -18.8 (s, br, 2 B), -17.4 (s, 2 B), -14.1 (s, 4 B), -12.9 (s, br, 4 B), -10.1 (s, 2 B), -5.6 (s, br, 4 B), -3.2 ppm (s, 2 B, 2xBS). ¹¹B NMR (CDCl₃): δ = -20.2 to -16.1 (m, br, 4 B), -15.2 to -11.8 (m, br, 8 B), -10.1 (d, ¹J_{BH} = 154 Hz, 2 B), -5.6 (d, ¹J_{BH} = 168 Hz, 4 B), -3.2 ppm (s, 2 B, 2xBS). HRMS (ESI⁺): C₇H₂₄B₂₀N₄S₂, m/z calcd: 446.3491 ([M+H]⁺); found: 446.3504 (100%), m/z calcd: 912.6759 ([2M+Na]⁺); found: 912.6718 (55%), m/z calcd: 468.3310 ([M+Na]⁺); found: 468.3325 (50%).

2. Numbering Scheme for Assignment of NMR Data



• B/BH
◦ CH

3. Crystallographic Data of Compounds 6, 8, 9, 11, 12, SP1, SP2 and SP3

Table S1: Crystallographic data of compounds 6, 8 and 9.

Parameters	6 ^a	8 ^b	9 ^c
Empirical formula	C _{22.50} H ₄₇ B ₂₀ N ₄ O _{7.50} S ₂	C ₁₁ H ₂₃ B ₁₀ ClN ₄ O ₂ S	C _{14.25} H _{35.25} B ₂₀ Cl _{3.75} N ₄ O ₂ S ₂
Formula weight	773.96	418.94	707.97
Temperature	130(2) K	130(2) K	130(2) K
Wavelength	71.073 pm	71.073 pm	71.073 pm
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2</i> ₁	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> / <i>c</i>
Unit cell dimensions	a = 1122.40(3) pm b = 3037.83(7) pm c = 1243.49(4) pm α = 90° β = 106.902(3)° γ = 90°	a = 713.10(3) pm b = 1889.79(6) pm c = 1651.78(5) pm α = 90° β = 101.482(3)° γ = 90°	a = 2235.91(7) pm b = 1344.47(3) pm c = 2540.62(8) pm α = 90° β = 102.651(3)° γ = 90°
Volume	4.0567(2) nm ³	2.1814(1) nm ³	7.4520(4) nm ³
Z	4	4	8
Density (calculated)	1.267 Mg/m ³	1.276 Mg/m ³	1.262 Mg/m ³
Absorption coefficient	0.178 mm ⁻¹	0.286 mm ⁻¹	0.437 mm ⁻¹
F(000)	1608	864	2884
Crystal size	0.4 x 0.2 x 0.1 mm ³	0.3 x 0.05 x 0.05 mm ³	0.25 x 0.15 x 0.02 mm ³
θ-range for data collection	2.01 to 28.31°	2.155 to 32.479°	2.044 to 28.460°
Index ranges	-14 ≤ h ≤ 14, -40 ≤ k ≤ 39, -15 ≤ l ≤ 14	-10 ≤ h ≤ 10, -28 ≤ k ≤ 28, -24 ≤ l ≤ 24	-28 ≤ h ≤ 29, -17 ≤ k ≤ 17, -31 ≤ l ≤ 31
Reflections collected	36542	25594	53687
Independent reflections	17888 [R(int) = 0.0395]	7280 [R(int) = 0.0552]	16081 [R(int) = 0.0966]
Completeness to theta	100.0%; θ = 26.38°	100.0 %; θ = 30.51°	99.9 %; θ = 25.35°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.99777	1 and 0.98829	1.00000 and 0.99279
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	17888 / 1 / 1275	7280 / 0 / 354	16081 / 88 / 890
Goodness-of-fit on F²	0.987	1.028	1.015
Final R indices [I > 2σ(I)]	R ₁ = 0.0452, wR ₂ = 0.0732	R ₁ = 0.0518, wR ₂ = 0.0964	R ₁ = 0.0814, wR ₂ = 0.1792
R indices (all data)	R ₁ = 0.0682, wR ₂ = 0.0802	R ₁ = 0.0941, wR ₂ = 0.1101	R ₁ = 0.1813, wR ₂ = 0.2268
Absolute structure parameter	0.04(3)	-	-

<i>(Table S1 continued)</i>			
Residual electron density	0.215 and $-0.208 \text{ e}\cdot\text{\AA}^{-3}$	0.299 and $-0.282 \text{ e}\cdot\text{\AA}^{-3}$	1.085 and $-0.712 \text{ e}\cdot\text{\AA}^{-3}$
CCDC Nr	1958031	1958032	1958033

Comments:

^a Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ Excluding methyl hydrogen atoms, all H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Carborane C atoms were localised from a bond length and isotropic displacement parameter analysis. Dimers are formed through intermolecular NH \cdots N donor-acceptor bonds.

^b Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Intermolecular NH \cdots N hydrogen donor-acceptor bonds were detectable. Carborane C atoms were located with a displacement parameter and bond length analysis.

^c Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms, except overlapping disordered atoms, with SHELXL-2018.³ All hydrogen atoms were calculated on idealised positions. One carborane molecule with disordered substituent (O3, O4, C19 to C24) in the vicinity of a twofold axis (0.5; y; 0.25) with a ratio of 50% is observable. Two chloroform molecules of the asymmetric unit are highly disordered as well and are treated as fourfold (C28, Cl4 to Cl6) and twofold (C29, Cl7 to Cl9) disordered to get reasonable refinement parameters. These results are comparable with a "squeezed" solution. All carborane C atoms were localised with a bond length and a displacement parameter analysis. With intermolecular NH \cdots N hydrogen donor-acceptor bond dimers are formed.

Table S2: Crystallographic data of compounds **11**, **12** and **SP1**.

Parameters	11^a	12^b	SP1^c
Empirical formula	C ₂₁ H ₃₀ Cl ₂ N ₄ O ₇	C ₂₅ H ₅₂ B ₂₀ N ₄ O ₇ S ₂	C ₂₃ H ₄₁ B ₁₀ ClN ₄ O ₇ S
Formula weight	521.39	801.02	661.21
Temperature	130(2) K	130(2) K	130(2) K
Wavelength	71.073 pm	71.073 pm	71.073 pm
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2</i> ₁	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁	<i>P2</i> ₁
Unit cell dimensions	a = 1101.39(2) pm b = 2213.85(3) pm c = 1132.11(2) pm α = 90° β = 105.800(2)° γ = 90°	a = 1018.85(2) pm b = 1675.41(3) pm c = 2468.31(5) pm α = 90° β = 90° γ = 90°	a = 1194.41(2) pm b = 1108.47(2) pm c = 1360.80(3) pm α = 90° β = 103.622(2)° γ = 90°
Volume	2.65614(8) nm ³	4.2134(1) nm ³	1.75098(6) nm ³
Z	4	4	2
Density (calculated)	1.304 Mg/m ³	1.263 Mg/m ³	1.254 Mg/m ³
Absorption coefficient	0.289 mm ⁻¹	0.173 mm ⁻¹	0.214 mm ⁻¹
F(000)	1096	1672	692
Crystal size	0.40 x 0.20 x 0.15 mm ³	0.3 x 0.25 x 0.03 mm ³	0.40 x 0.40 x 0.30 mm ³
θ-range for data collection	1.840 to 32.262°	2.05 to 30.18°	2.044 to 32.596°
Index ranges	-15 ≤ h ≤ 16, -33 ≤ k ≤ 33, -16 ≤ l ≤ 16	-13 ≤ h ≤ 14, -22 ≤ k ≤ 21, -34 ≤ l ≤ 34	-17 ≤ h ≤ 17, -16 ≤ k ≤ 16, -20 ≤ l ≤ 19
Reflections collected	46570	42274	25654
Independent reflections	17504 [R(int) = 0.0341]	11457 [R(int) = 0.0745]	11515 [R(int) = 0.0239]
Completeness to theta	100.0 %; θ = 30.51°	100.0%; θ = 28.29°	100.0 %; θ = 30.51°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88446	1 and 0.99061	1.00000 and 0.99527
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	17504 / 7 / 853	11457 / 0 / 731	11515 / 7 / 579
Goodness-of-fit on F²	1.020	1.015	1.018
Final R indices [I>2σ(I)]	R ₁ = 0.0390, wR ₂ = 0.0649	R ₁ = 0.0500, wR ₂ = 0.0754	R ₁ = 0.0382, wR ₂ = 0.0796
R indices (all data)	R ₁ = 0.0590, wR ₂ = 0.0716	R ₁ = 0.0904, wR ₂ = 0.0861	R ₁ = 0.0477, wR ₂ = 0.0847
Absolute structure parameter	-0.03(1)	0.08(3)	-0.06(2)
Residual electron density	0.229 and -0.236 e·Å ⁻³	0.264 and -0.256 e·Å ⁻³	0.291 and -0.276 e·Å ⁻³
CCDC Nr	1958034	1958035	1958036

Comments:

^a Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure determination is in accordance with α -D-galactopyranose derivative.

^b Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Carborane C atoms were localised from bond length and displacement parameter analysis.

^c Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps were calculated at the final stage of the structure refinement. Carborane C atoms were localised from bond length and displacement parameter analysis.

Table S3: Crystallographic data of compounds **SP2** and **SP3**.

Parameters	SP2 ^a	SP3 ^b
Empirical formula	C ₁₂ H ₃₄ B ₂₀ N ₄ S ₂	C ₉ H ₂₇ B ₂₀ N ₅ S ₂
Formula weight	514.75	485.67
Temperature	130(2) K	130(2) K
Wavelength	71.073 pm	71.073 pm
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>C2/c</i>
Unit cell dimensions	a = 672.40(2) pm b = 1905.79(5) pm c = 2172.11(6) pm α = 90° β = 98.581(2)° γ = 90°	a = 3223.82(6) pm b = 1254.64(2) pm c = 1308.72(2) pm α = 90° β = 104.795(2)° γ = 90°
Volume	2.7523(1) nm ³	5.1179(2) nm ³
Z	4	8
Density (calculated)	1.242 Mg/m ³	1.261 Mg/m ³
Absorption coefficient	0.208 mm ⁻¹	0.221 mm ⁻¹
F(000)	1064	1984
Crystal size	0.25 x 0.10 x 0.05 mm ³	0.40 x 0.35 x 0.30 mm ³
Θ-range for data collection	1.896 to 30.346°	1.750 to 30.751°
Index ranges	-8 ≤ h ≤ 9, -25 ≤ k ≤ 26, -26 ≤ l ≤ 30	-45 ≤ h ≤ 45, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	28590	72445
Independent reflections	7407 [R(int) = 0.0752]	7553 [R(int) = 0.0652]
Completeness to theta	99.7 %; θ = 28.29°	100.0 %; θ = 28.29°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.99569	1.00000 and 0.76523
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7407 / 12 / 479	7553 / 6 / 433
Goodness-of-fit on F ²	1.100	1.017
Final R indices [I > 2σ(I)]	R ₁ = 0.0651, wR ₂ = 0.1217	R ₁ = 0.0507, wR ₂ = 0.1222
R indices (all data)	R ₁ = 0.1068, wR ₂ = 0.1346	R ₁ = 0.0787, wR ₂ = 0.1362
Residual electron density	0.300 and -0.360 e·Å ⁻³	0.436 and -0.247 e·Å ⁻³
CCDC Nr	1958037	1958038

Comments:

^a Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Restraints were used to model methyl hydrogen atoms for C(7) and C(10). Carborane C atoms were identified and localised with a bond length and displacement parameter analysis.

^b Structure solution with SHELXT-2014² (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018.³ All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Carborane C atoms were localised with bond length and displacement parameter analysis. Intermolecular hydrogen donor-acceptor bonds between NH \cdots N and NH \cdots S were detected.

4. Additional Molecular Structures of 8, 9, SP1, SP2 and SP3

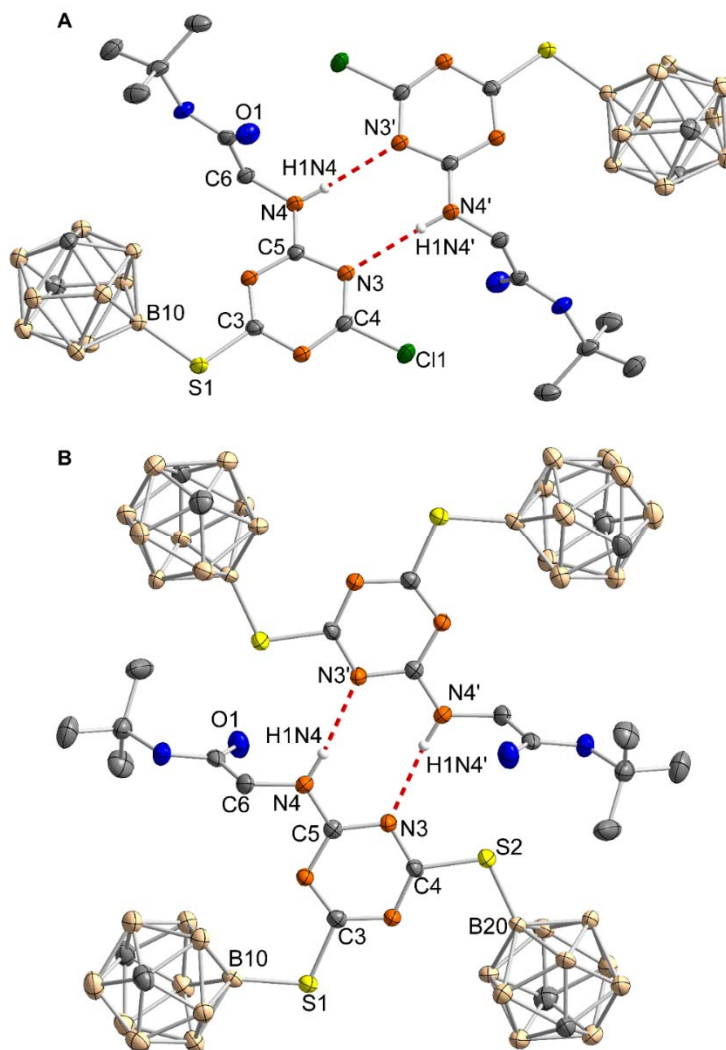


Figure S1: Molecular structures of **8** (A) and **9** (B). Compound **8** crystallises with one molecule in the asymmetric unit and forms dimers via hydrogen bonds. Compound **9** crystallises with two symmetry-independent molecules in the asymmetric unit. The glycinate moiety of the second molecule and co-crystallised chloroform molecules are disordered (not shown). Hydrogen atoms, except the hydrogen atoms attached to the secondary amine group which are drawn with a fixed atom radius of 13.5 pm, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths, distances (pm) and bond angles ($^{\circ}$) (bond lengths and angles of the disordered molecule of **9** are given in brackets []): (**8**) N4–H1N4 84.1(2), H1N4 \cdots N3' 220.3(2), N4 \cdots N3' 303.0(2), N4–C5 133.2(2), Cl1–C4 173.3(2), S1–C3 174.1(2), S1–B10 186.8(2); N4–H1N4 \cdots N3' 167.7(2), H1N4–N4–C5 115(1), C5–N4–C6 123.8(1), C6–N4–H1N4 120(1), C3–S1–B10 106.6(7). (**9**) N4–H1N4 88.0(4) [88.0(4)], H1N4 \cdots N3' 206.4(4) [208.0(3)], N4 \cdots N3' 293.8(6) [296.0(5)], N4–C5 133.8(5) [132.9(5)], S1–C3 174.7(4) [174.7(5)], S1–B10 186.0(5) [185.6(5)], S2–C4 174.2(4) [174.5(5)], S2–B20 185.8(5) [186.0(5)]; N4–H1N4 \cdots N3' 172.6(3) [177.7(3)], H1N4–N4–C5 118.3(4) [118.1(4)], C5–N4–C6 123.5(4) [123.9(4)], C6–N4–H1N4 118.3(4) [118.0(4)], C3–S1–B10 106.8(2) [106.8(2)], C4–S2–B20 107.9(2) [107.9(2)].

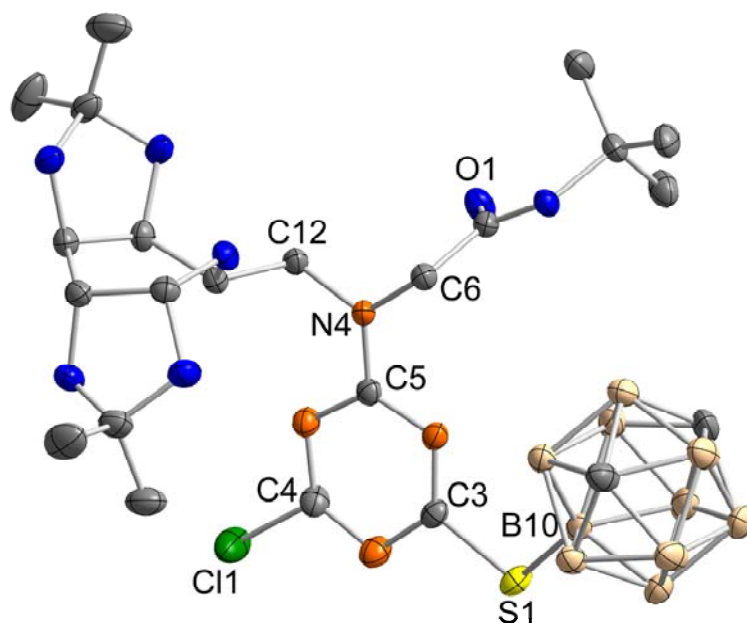


Figure S2: Molecular structure of **SP1**. The compound crystallises with one molecule in the asymmetric unit. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond length (pm) and bond angles ($^{\circ}$): N4–C5 134.0(2), C4–Cl1 173.3(2), S1–C3 175.2(2), S1–B10 185.8(3); C5–N4–C6 121.1(2), C6–N4–C12 118.4(2), C12–N4–C5 120.5(2), C3–S1–B10 106.0(1).

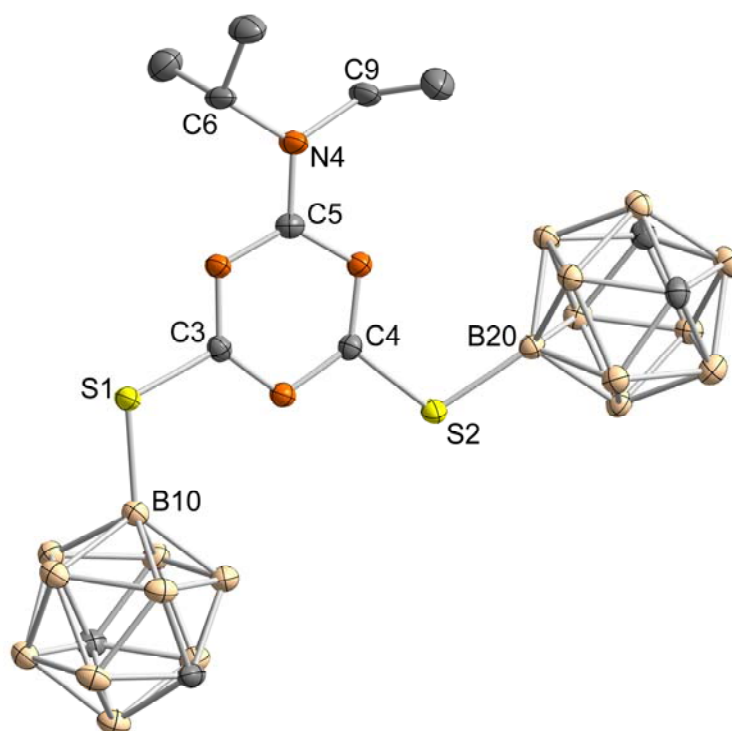


Figure S3: Molecular structure of **SP2**. The compound crystallises with one molecule in the asymmetric unit. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond length (pm) and bond angles ($^{\circ}$): S1–B10 180.6(3), S1–C3 175.4(3), S2–B20 186.3(3), S2–C4 176.0(3), N4–C5 133.7(3), N4–C6 146.9(3), N4–C9 147.0(4); C3–S1–B10 108.5(1), C4–S2–B20 109.6(1), C5–N4–C6 120.2(2), C6–N4–C9 119.3(2), C5–N4–C9 119.8(2).

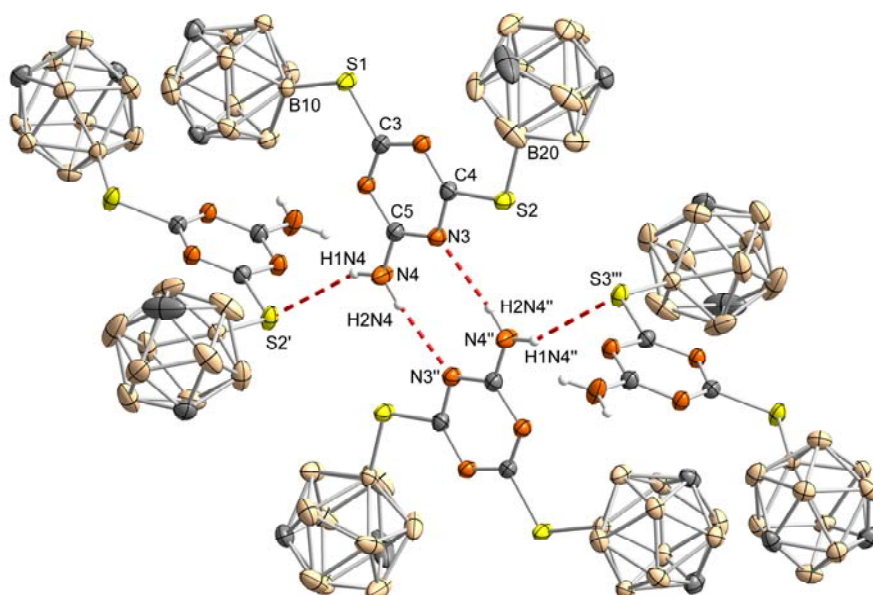


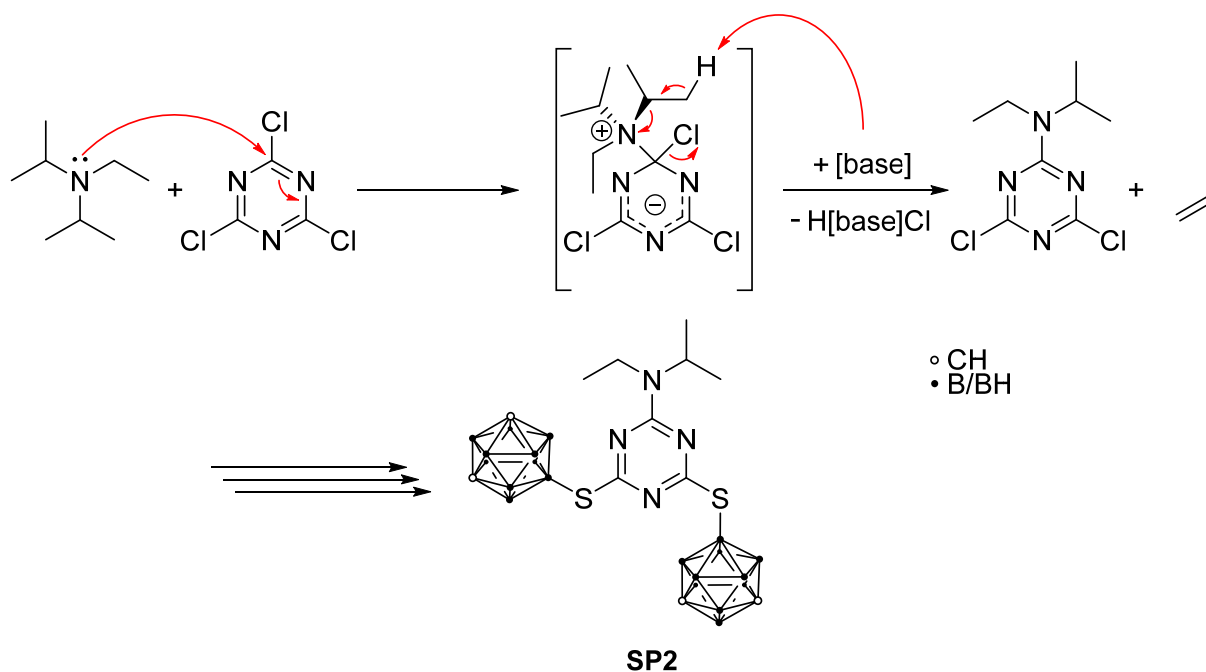
Figure S4: Molecular structure of **SP3** including the hydrogen bonds between the primary amine group and a sulfur atom of one thioether group and one nitrogen atom of the triazine ring. Hydrogen atoms of the primary amine group are drawn with a fixed atom radius of 13.5 pm; all other hydrogen atoms and acetonitrile are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond length (pm) and bond angles ($^{\circ}$): S1–B10 186.8(2), S1–C3 174.7(2), S2–B20 186.0(2), S2–C4 174.8(2), N4–C5 133.2(2), N4–H1N4 87(3), N4–H2N4 85(2), H1N4–S2' 270(3), H2N4–N3'' 220(3), N4 \cdots S2' 349.3(2), N4 \cdots N3'' 304.7(2); C3–S1–B10 109.0(8), C4–S2–B20 109.4(8), C5–N4–H1N4 119(2), C5–N4–H2N4 123(2), H1N4–N4–H2N4 118(2), N4–H1N4 \cdots S2' 152(2), N4–H2N4 \cdots N3'' 173(2).

5. Proposed Mechanism for the Formation of *N*-Ethyl-*N*-isopropyl-4,6-bis(1,7-dicarba-*c*/oso-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (SP2)

An attempt to prepare **5** directly in a one-pot synthesis using DIPEA as a base failed and only produced the side product *N*-ethyl-*N*-isopropyl-4,6-bis(1,7-dicarba-*c*/oso-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (**SP2**) in 10% yield.

It is possible that the organic base DIPEA was not 100% pure and some secondary amine species reacted with the cyanuric chloride followed by substitution with two molecules of **1**. However, no similar observations were made during the preparation of **11** and **14**, where cyanuric chloride and DIPEA were used as well. Thus, it is very unlikely that an impurity in DIPEA was responsible for this side reaction.

However, a mechanism similar to the *Hofmann elimination*⁴ could have occurred. DIPEA was present in higher concentrations, because glycine and not *tert*-butyl glycinate hydrochloride was used, and was thus available as a nucleophile. Cyanuric chloride is a very reactive compound and also serves as a chlorinating agent.^{5,6} In the literature, the carboxylic acid is deprotonated by the base triethylamine and forms a carboxylate anion, which is a weak nucleophile. Cyanuric chloride undergoes a reaction with the carboxylate to form the carboxylic acid chloride with simultaneously formation of a cyanuric acid derivative.⁶ Based on the high reactivity of cyanuric chloride, it can be assumed that DIPEA attacked the *s*-triazine derivative at elevated temperatures and an ammonium species was formed. β -Hydrogen elimination of one of the isopropyl groups facilitated by additional base results in formation of the Zaitsev product propene and compound **SP2**. Scheme S1 shows the proposed mechanism for this reaction. The Gibbs free enthalpy of the reaction calculated at the SMD(acetonitrile)//RI-BLYP-D3BJ/DZVP-DFT level with ORCA 4.1.0 is $-133.17 \text{ kJ mol}^{-1}$. None of the optimised geometries exhibited imaginary frequencies. Thus, the first reaction step shown in Scheme S1 is energetically favoured. However, the cationic intermediate and the corresponding transition states have not been calculated. The fact that the yield of **SP2** is only about 10% indicates that this reaction is not the preferred one.



Scheme S1: Proposed mechanism of the formation of **SP2** following a *Hofmann elimination*-like process (base = DIPEA or K_2CO_3).

6. Proposed Mechanism for the Formation of 4,6-Bis(1,7-dicarba-*c*-closo-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (**SP3**)

During work-up of **16**, the side product 4,6-bis(1,7-dicarba-*c*-closo-dodecaboran-9-ylthio)-1,3,5-triazine-2-amine (**SP3**) was obtained in less than 5% yield by two column chromatography steps and one recrystallisation step for purification (a: column 1: ethyl acetate, 100% to acetone, 100%; b: recrystallisation from methanol; c: column 2: acetone, 100%). After the recrystallisation step in methanol (reflux conditions), new impurities were observed by TLC, and the second column chromatography became necessary. Obviously, the raw product mixture underwent some unexpected side reaction in or with methanol. The very first band from the second column chromatography contained the side product **SP3**, which was crystallised from acetonitrile and characterised, also by X-ray crystallography.

In Scheme S2, a mechanism for the formation of **SP3** is proposed. A process based on a fragmentation reaction, similar to that observed by Chou *et al.*, could have occurred here as well.⁷ The tertiary amine derivative **15** obviously underwent the desired deprotection reaction to give **16**. It can be assumed that during the following recrystallisation from methanol, the tertiary amine group was protonated (**i1**). Subsequently, a process similar to the one observed by Chou *et al.* took place. Due to the electron-withdrawing effect of the ammonium cation and the carborane-substituted triazine ring, the primary amino group attacked the activated methylene group of the protected monosaccharide. This led to simultaneous

7. Peptide analytics: RP-HPLC and mass spectrometry

Table S4: Peptide conjugates nomenclature

Conjugate	Name
sBB2L	sBB2L
17	#4-EG ₃ -sBB2L
18	5*-EG ₃ -sBB2L
19	(5*)-Dap(5*)-EG ₃ -sBB2L

Column 1: Phenomenex Jupiter® 4u Proteo C12 90 Å (250 mm × 4.6 mm, 4 μm, 90 Å), flow rate: 0.6 mL/min

Column 2: Kinetex XB-C18 column (Phenomenex, C₁₈, 250 mm × 4.6 mm, 5 μm 100 Å) flow rate: 1.5 mL/min

Column 3: Phenomenex Aeris® Peptide 3.6u XB-C18 (250 mm × 4.6 mm, 3.6 μm, 100 Å), flow rate: 1.55 mL/min

Linear gradients: eluent A: 0.1% (v/v) TFA in H₂O, eluent B: 0.08% (v/v) TFA in ACN

Gradient A: 20% to 70% eluent B in A over 40 min

Gradient B: 30% to 80% eluent B in A over 40 min

Gradient C: 40% to 90% eluent B in A over 40 min

Table S5. Analysis of the prepared peptides by analytical RP-HPLC.

conjugate	HPLC analysis I				HPLC analysis II				purity
	column	gradient	elution at %ACN	t _R [min]	column	gradient	elution at %ACN	t _R [min]	
sBB2L	1	A	37.6	22.1	2	A	28.4	14.7	> 95 %
17	1	C	72.3	25.8	3	C	63.9	19.1	> 95 %
18	1	B	61.3	25.0	2	B	51.4	17.1	> 95 %
19	1	C	71.8	25.4	2	C	65.3	20.2	> 95 %

Table S6. Analysis of the pure peptides by MALDI-ToF MS.

Conjugate	M _{exact} (calc.) [Da]	M _{exact} (exp.) [M+H] ⁺
sBB2L	1040.56	1041.6
17	1748.95	1750.0
18	1894.05	1895.0
19	2630.48	2631.5

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