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Supporting Information

Derivatization of an especially electron-rich diborane

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1. General details of the synthetic work

All reactions were carried out under a dry argon atmosphere by using standard Schlenk technique. The reagents tetrabutylammonium chloride, tetrabutylammonium thiocyanate and tetrabutylammonium azide were purchased from Sigma-Aldrich, and tetrabutylammonium bromide was delivered by Fluka. All reagents were used without further purification. The compound $B_2(hpp)_2(OTf)_2$ was synthesized according to the literature.[1] All solvents were rigorously dried by the solvent purification system MB SPS-800 MBRAUN and stored over molecular sieves (3 Å and 4 Å) after being degassed by the freeze-pump-thaw method. Infrared spectra (ATR) were recorded on powders with a Bruker Alpha Platinum-ATR machine. BRUKER Avance DPX 200, BRUKER Avance II 400 and BRUKER Avance III 600 devices were used for NMR spectroscopy. NMR spectra were recorded at 298 K and ^{11}B NMR chemical shifts are given in ppm relative to $BF_3{\cdot}Et_2O$. Elemental analyses were performed at the Microanalytical Laboratory of the University of Heidelberg using the vario EL and vario MICRO cube devices from Elementar Analysensysteme GmbH. Mass spectrometric data were taken with JOEL JMS-700 magnetic sector and BRUKER ApexQe hybrid 9.4 T FT-ICR spectrometers at the MS laboratory of the University of Heidelberg.
Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Bruker D8 Venture, dual source (Mo- or Cu-K_α radiation, microfocus X-ray tube, Photon III detector). Data were processed using the standard Bruker software package (SAINT, APEX3).[2] Multiscan absorption correction was applied using the SADABS program.[3] The structures were solved by intrinsic phasing [4] and refined using the SHELXTL software package (2018/3).[5] Graphical handling of the structural data during solution and refinement was performed OLEX2.[6] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally placed at calculated positions and refined with a riding model. CCDC 1580986 (**3**),[7] 2120343 (**5**), 2120345 (**6**), 2120346 (**7**), 2120344 (**8**), 2120349 (**9**), 2120348 (**10**) and 2120347 (**12**) contain the supplementary crystallographic data for this paper.

Table 1. Selected structure parameters (bond lengths in Å, bond angles in °) for the new structurally characterized diboranes **5** - **10** and **12** from SCXRD measurements.

parameter	**5**	**6**	**7**	**8**	**9**	**10**	**12**
B-B	1.712(4)	1.732(7)	1.735(2)	1.716(1)	1.705(8)	1.723(2)	1.697(7)
B-X_1 (Cl/Br [a]/NCS/N_3)	2.100(9)	1.537(8)	1.573(7)	1.904(2)	2.079(9)	1.514(4)	1.608(4)
B-X_2 (OTf/Br)	-	-	-	1.573(5)	1.569(8)	1.582(9)	2.101(2)
B-N (hpp)	1.527(1)	1.535(8)	1.562(1)	1.540(5)	1.534(1)	1.528(7)	1.531(9)
B-B-X_1 (Cl/Br [a]/NCS/N_3)	124.58	125.29	127.22	124.98	123.65	126.62	127.64
B-B-X_2 (OTf/Br)	-	-	-	128.33	128.06	127.21	122.61

[a] X_1 = Br only in the case of diborane **9**.

2. Experimental procedures and analytical data

$B_2(hpp)_2Cl_2$ (3)

In a dry argon-flushed Schlenk flask, tetrabutylammonium chloride (98 mg, 0.35 mmol) was dissolved in 0.5 mL of absolute dichloromethane. A solution of $B_2(hpp)_2(OTf)_2$ (100 mg, 0.17 mmol) in 0.5 ml of absolute dichloromethane was added. The reaction mixture was stirred for 1 d at room temperature, before 1.5 ml of absolute *n*-pentane was added. After storing the solution for 1 d at –20 °C, the solvent was removed from the precipitated solid. The solid was suspended three times in 0.5 ml of absolute tetrahydrofuran and stored for 1 d at –20 °C. Each time the solvent was completely removed from the solid to separate the by-product from the product. The remaining solid was dried in vacuo to give the product in a yield of 36 mg (0.10 mmol, 59 %). C,H,N analysis (%) for $C_{14}H_{24}B_2Cl_2N_6$ (368.91 g mol^{-1}): calcd. C 45.58, H 6.56, N 22.78; found C 45.56, H 6.63, N 22.37. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.51-3.05 (m, 16 H, N-CH_2), 2.01-1.80 (m, 8 H, CH_2) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = 3.68 (2 B, *B*-Cl) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 156.55 (C_q), 47.71 (NCH_2), 39.84 (NCH_2), 22.50 (CH_2) ppm. MS (EI$^+$): m/z (%) = 368.1622 ([M]$^+$, 75%), 333.1929 ([M-Cl]$^+$, 55%), 138.1023 ([hpp]$^+$, 17%). IR (powder): $\tilde{\nu}$ = 2962(w), 2939(w), 2859(w), 1632(w), 1585(s), 1553(s), 1458(w), 1438(w), 1393(w), 1368(w), 1317(s), 1271(m), 1218(m), 1182(w), 1096(m), 1063(w), 1041(m), 1027(m), 995(w), 935(s), 895(w), 860(m), 814(s), 733(s), 718(m), 651(s), 582(s), 480(w), 434(w) cm^{-1}. Crystal data for $B_2(hpp)_2Cl_2$ [7], $C_{14}H_{24}B_2N_6Cl_2$, M_r = 368.91, 0.100 x 0.094 x 0.031 mm, orthorhombic, space group Pbca, a = 8.28705(11), b = 16.6292(3), c = 24.2620(4) Å, α = 90°, β = 90°, γ = 90°, V = 3343.48(9) Å^3, Z = 8, ρ_{cald} = 1.466 Mg·m^{-3}, Cu-$K\alpha$ radiation (λ = 1.54184 Å), T = 120 K, θ_{range} = 3.6 – 71.0°. Reflections collected 113521, independent reflections 3219, R_{int} = 0.0865. Final R indices [$I > 2\sigma(I)$]: R = 0.0382, wR = 0.0929.

$B_2(hpp)_2Br_2$ (5)

In a dry argon-flushed Schlenk flask, tetrabutylammonium bromide (454 mg, 1.41 mmol) was dissolved in 1.5 ml of absolute dichloromethane. A solution of $B_2(hpp)_2(OTf)_2$ (400 mg, 0.67 mmol) in 2.0 ml of absolute dichloromethane was added. The reaction mixture was stirred for 1 d at room temperature. After storing the reaction mixture for 1 d at –20 °C, the solvent was removed from the precipitated solid. The solid was suspended three times in 1.5 ml of absolute tetrahydrofuran and stored for

1 d at –20 °C. Each time the solvent was completely removed from the solid to separate the by-product from the product. The remaining solid was dried in vacuo to give the product in a yield of 205 mg (0.45 mmol, 67 %). C,H,N analysis (%) for $C_{14}H_{24}B_2Br_2N_6$ (457.82 g mol^{-1}): calcd. C 36.73, H 5.28, N 18.36; found C 36.53, H 5.08, N 18.13. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.57-3.08 (m, 16 H, N-C*H*$_2$), 2.06-1.83 (m, 8 H, C*H*$_2$) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = 4.02 (2 B, *B*-Br) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 156.49 (*C*$_q$), 47.70 (N*C*H$_2$), 41.18 (N*C*H$_2$), 22.39 (*C*H$_2$) ppm. MS (EI$^+$): m/z (%) = 138.1026 ([hpp]$^+$, 100%). IR (powder): $\tilde{\nu}$ = 2951(w), 2856(w), 1630(w), 1587(s), 1543(s), 1475(w), 1458(w), 1437(w), 1392(m), 1368(w), 1350(w), 1314(s), 1272(s), 1218(m), 1184(m), 1115(w), 1098(w), 1063(w), 1042(s), 1024(m), 995(w), 944(s), 895(w), 862(m), 819(m), 804(s), 731(s), 717(m), 696(w), 665(w), 634(m), 573(s), 479(m), 457(w), 426(w) cm^{-1}. Crystal data for $B_2(hpp)_2Br_2 \cdot 2CH_2Cl_2$, $C_{16}H_{28}B_2Br_2N_6Cl_4$, M_r = 627.68, 0.221 x 0.14 x 0.052 mm, orthorhombic, space group Pnma, *a* = 22.646(2), *b* = 12.3273(11), *c* = 8.5158(7) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 2377.3(4) Å^3, *Z* = 4, ρ_{cald} = 1.754 Mg·m^{-3}, Mo-K_α radiation (*λ* = 0.71073 Å), T = 100 K, θ_{range} = 2.44 - 28.30°. Reflections collected 23126, independent reflections 3090, R_{int} = 0.0730. Final *R* indices [$I > 2\sigma(I)$]: *R* = 0.0475, *wR* = 0.0668.

$B_2(hpp)_2(NCS)_2$ (6)

In a dry argon-flushed Schlenk flask, tetrabutylammonium thiocyanate (106 mg, 0.35 mmol) was dissolved in 0.5 ml of absolute dichloromethane. A solution of $B_2(hpp)_2(OTf)_2$ (100 mg, 0.17 mmol) in 0.5 ml of absolute dichloromethane was added. The reaction mixture was stirred for 1 d at room temperature, before 1.5 ml of absolute *n*-pentane was added. After storing the solution for 1 d at –20 °C, the solvent was removed from the precipitated solid. The solid was suspended three times in 0.5 ml of absolute tetrahydrofuran and stored for 1 d at –20 °C. Each time the solvent was completely removed from the solid to separate the by-product from the product. The remaining solid was dried in vacuo to give the product in a yield of 49 mg (0.12 mmol, 71 %). C,H,N analysis (%) for $C_{16}H_{24}B_2N_8S_2$ (414.16 g mol^{-1}): calcd. C 46.40, H 5.84, N 27.06; found C 45.80, H 5.66, N 26.79. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 3.37-3.07 (m, 16 H, N-C*H*$_2$), 1.97-1.84 (m, 8 H, C*H*$_2$) ppm. ^{11}B NMR (192 MHz, CD_2Cl_2): δ = −3.28 (2 B, *B*-NCS) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 157.33 (*C*$_q$), 47.55 (N*C*H$_2$), 40.47 (N*C*H$_2$), 22.51 (*C*H$_2$) ppm. MS (EI$^+$): m/z (%) = 414.1734 ([M]$^+$, 100%), 356.1986 ([M-SCN]$^+$, 55%), 138.1020 ([hpp]$^+$, 12%). IR (powder): $\tilde{\nu}$ = 2960(w), 2857(w), 2132(s),

1587(s), 1554(s), 1458(w), 1435(w), 1397(w), 1370(m) 1319(s), 1273(m) 1216(s) 1184(m) 1115(w) 1096(w) 1041(s) 997(w), 937(s), 893(m), 863(m), 824(s), 809(s), 734(s), 699(m), 684(m), 661(s), 587(s), 477(m), 438(w) cm^{-1}. Crystal data for $B_2(hpp)_2(NCS)_2$, $C_{16}H_{24}B_2N_8S_2$, M_r = 414.17, 0.203 x 0.19 x 0.148 mm, monoclinic, space group Cc, a = 12.739(2), b = 15.667(3), c = 10.1279(18) Å, α = 90°, β = 91.214(7)°, γ = 90°, V = 2020.9(6) $Å^3$, Z = 4, ρ_{cald} = 1.361 $Mg \cdot m^{-3}$, Mo-K_α radiation (λ = 0.71073 Å), T = 100 K, θ_{range} = 2.60 - 28.78°. Reflections collected 24812, independent reflections 4620, R_{int} = 0.0726. Final R indices [$I > 2\sigma(I)$]: R = 0.0729, wR = 0.2000.

$B_2(hpp)_2(N_3)_2$ (7)

In a dry argon-flushed Schlenk flask Tetrabutylammonium azide (200 mg, 0.71 mmol) was dissolved in 0.5 ml of absolute dichloromethane. A solution of $B_2(hpp)_2(OTf)_2$ (200 mg, 0.36 mmol) in 1.0 ml of absolute dichloromethane was added. The reaction mixture was stirred for 1 d at room temperature, before 2.0 ml of absolute *n*-pentane was added. After storing the solution for 1 d at –20 °C, the solvent was removed from the precipitated solid. The solid was suspended three times in 1.0 ml of absolute tetrahydrofuran and stored for 1 d at –20 °C. Each time the solvent was completely removed from the solid to separate the by-product from the product. The remaining solid was dried in vacuo to give the product in a yield of 79 mg (0.21 mmol, 62 %). Elemental analysis was not possible due to decomposition of the bisazide. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 3.34-3.06 (m, 16 H, N-CH_2), 2.00-1.82 (m, 8 H, CH_2) ppm. ^{11}B NMR (192 MHz, CD_2Cl_2): δ = 0.71 (2 B, *B*-N_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 157.09 (C_q), 47.71 (NCH_2), 40.10 (NCH_2), 22.74 (CH_2) ppm. MS (EI$^+$): m/z (%) = 382.2413 ([M]$^+$, 1%), 138.1038 ([hpp]$^+$, 93%). IR (powder): $\tilde{\nu}$ =2951(w), 2849(w), 2098(s), 1562(s), 1473(w), 1453(w), 1434(w), 1395(w), 1369(w), 1342(w), 1320(s), 1275(s), 1215(s), 1182(m), 1113(w), 1093(m), 1040(s), 993(w), 934(s), 905(s), 862(w), 824(s), 784(w), 756(s), 720(m), 695(m), 681(m), 637(s), 597(m), 580(s), 480(m), 413(w) cm^{-1}. Crystal data for $B_2(hpp)_2(N_3)_2$, $C_{14}H_{24}B_2N_{12}$, M_r = 382.07, 0.236 x 0.12 x 0.086 mm, monoclinic, space group P21/c, a = 15.8187(18), b = 13.1616(15), c = 8.5854(10) Å, α = 90°, β = 90.123(3)°, γ = 90°, V = 1764.9(4) $Å^3$, Z = 4, ρ_{cald} = 1.438 $Mg \cdot m^{-3}$, Mo-K_α radiation (λ = 0.71073 Å), T = 100 K, θ_{range} = 2.85 - 28.68°. Reflections collected 4563, independent reflections 4563, R_{int} = 9.47. Final R indices [$I > 2\sigma(I)$]: R = 0.1022, wR = 0.2297.

General protocol for the preparation of the equilibria, from which the unsymmetric diboranes precipitated

Option a) In a dry argon-flushed Schlenk flask, equimolar quantities of the tetrabutylammonium salt and the symmetric diborane were dissolved in absolute dichloromethane. The reaction mixture was stirred for 1 h at room temperature before the solvent was removed under vacuo. The remaining solid was dissolved in deuterated dichloromethane and analyzed via NMR spectroscopy.

Option b) In an NMR tube, equimolar quantities of two symmetric substituted diboranes were dissolved in deuterated dichloromethane and analyzed via NMR spectroscopy.

Then, crystals suitable for single-crystal structure determination of the unsymmetric diboranes were grown at -20 °C from the respective equilibrium either directly from a dichloromethane solution or by laying a dichloromethane solution with *n*-pentane.
In solution, the unsymmetric diboranes form instantly equilibria with the corresponding symmetric diboranes. The ^{1}H and ^{13}C NMR chemical shift values for the three compounds present in solution are similar; therefore these shifts are generally not quoted in the following; ^{13}C NMR data are only given for compounds **11** – **13**.

$B_2(hpp)_2(OTf)Cl$ (8)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 6.96 (1 B, *B*-OTf), 1.41 (1 B, *B*-OTf) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = −78.09 ppm. Crystal data for $B_2(hpp)_2(OTf)Cl{\cdot}CH_2Cl_2$, $C_{16}H_{26}B_2N_6Cl_3F_3O_3S$, M_r = 567.46, 0.708 x 0.462 x 0.234 mm, triclinic, space group P−1, a = 9.2288(4), b = 10.8961(5), c = 13.2949(6) Å, α = 77.600(2)°, β = 84.277(2)°, γ = 67.063(2)°, V = 1202.29(10) Å^3, Z = 2, ρ_{cald} = 1.567 Mg·m^{-3}, Mo-K_α radiation (λ = 0.71073 Å), T = 100 K, θ_{range} = 2.40 - 34.34°. Reflections collected 106196, independent reflections 10078, R_{int} = 0.0530. Final R indices [$I > 2\sigma(I)$]: R = 0.0402, wR = 0.0890.

$B_2(hpp)_2(OTf)Br$ (9)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 7.23 (1 B, *B*-OTf), 0.97 (1 B, *B*-Br) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = −78.01 ppm. Crystal data for $B_2(hpp)_2(OTf)Br \cdot CH_2Cl_2$, $C_{16}H_{26}B_2BrN_6Cl_2F_3O_3S$, M_r = 611.92, 0.646 x 0.343 x 0.142 mm, triclinic, space group P−1, *a* = 9.3122(4), *b* = 10.8490(4), *c* = 13.3508(6) Å, *α* = 77.930(2)°, *β* = 84.754(2)°, *γ* = 67.245(2)°, *V* = 1216.24(9) Å^3, *Z* = 2, ρ_{cald} = 1.671 Mg·m^{-3}, Mo-K_α radiation (*λ* = 0.71073 Å), T = 100 K, θ_{range} = 2.073 - 30.600°. Reflections collected 76806, independent reflections 7430, R_{int} = 0.0489. Final *R* indices [$I > 2\sigma(I)$]: *R* = 0.0261, *wR* = 0.0613.

$B_2(hpp)_2B(OTf)(NCS)$ (10)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 5.72 (B, *B*-OTf), −4.72 (B, *B*-NCS) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = −78.00 ppm. Crystal data for $B_2(hpp)_2(OTf)(NCS)$, $C_{16}H_{24}B_2F_3N_7O_3S_2$, M_r = 505.16, 0.23 x 0.136 x 0.118 mm, orthorhombic, space group Pna21, *a* = 49.546(2), *b* = 8.8940(4), *c* = 14.6374(7) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 6450.1(5) Å^3, *Z* = 12, ρ_{cald} = 1.561 Mg·m^{-3}, Mo-K_α radiation (*λ* = 0.71073 Å), T = 100 K, θ_{range} = 2.154 – 29.000°. Reflections collected 144873, independent reflections 17146, R_{int} = 0.0583. Final *R* indices [$I > 2\sigma(I)$]: *R* = 0.0780, *wR* = 0.1983.

$B_2(hpp)_2ClBr$ (11)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 3.91 (B, *B*-Br/Cl) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 156.52 (C_q), 47.71 (N*C*H$_2$), 40.02 (N*C*H$_2$), 39.95 (N*C*H$_2$), 22.43 (*C*H$_2$) ppm.

$B_2(hpp)_2(NCS)Br$ (12)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 3.96 (B, *B*-Br), −3.01 (B, *B*-NCS) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 156.93 (C_q), 47.69 (N*C*H$_2$), 47.50 (N*C*H$_2$), 40.89 (N*C*H$_2$), 40.62 (N*C*H$_2$), 22.42 (*C*H$_2$) ppm. Crystal data for $B_2(hpp)_2(NCS)Br$, $C_{15}H_{23}B_2BrN_7S$, M_r = 434.99, 0.268 x 0.122 x 0.108 mm, orthorhombic, space group Pbca, *a* = 16.7035(10), *b* = 15.5342(9), *c* = 16.8091(10) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 4361.5(4) Å^3, *Z* = 8, ρ_{cald} = 1.325 Mg·m^{-3}, Mo-K_α radiation (*λ* = 0.71073 Å), T = 100 K, θ_{range} = 2.162 - 26.000°. Reflections collected 80071, independent reflections 4282, R_{int} = 0.1664. Final *R* indices [$I > 2\sigma(I)$]: *R* = 0.1105, *wR* = 0.2208.

$B_2(hpp)_2(N_3)Br$ (13)

^{11}B NMR (192 MHz, CD_2Cl_2): δ = 3.92 (1 B, *B*-Br), 0.53 (1 B, *B*-N_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 156.80 (C_q), 47.68 (N*C*H_2), 40.75 (N*C*H_2), 40.15 (N*C*H_2), 22.57 (*C*H_2), 22.48 (*C*H_2) ppm.

3. NMR and IR spectra

$B_2(hpp)_2Cl_2$ (3)

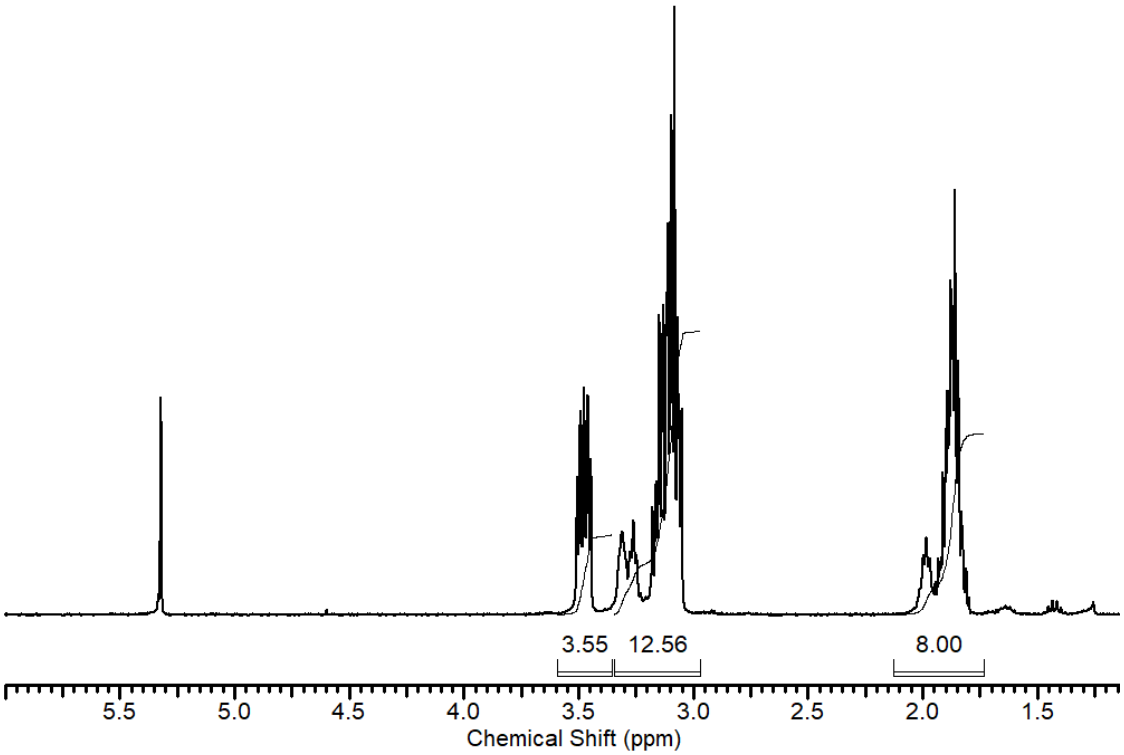


Figure 1: *^1H NMR spectrum of $B_2(hpp)_2Cl_2$ in CD_2Cl_2 (400 MHz).*

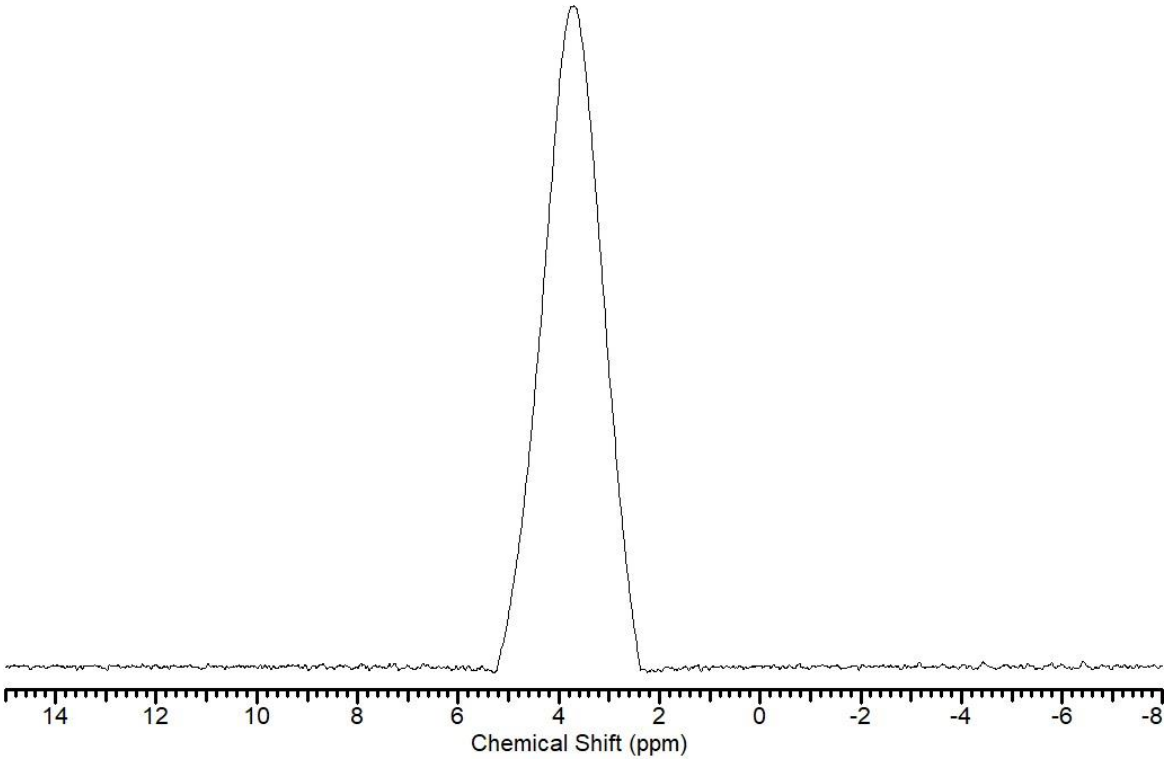


Figure 2: *^{11}B NMR spectrum of $B_2(hpp)_2Cl_2$ in CD_2Cl_2 (128 MHz).*

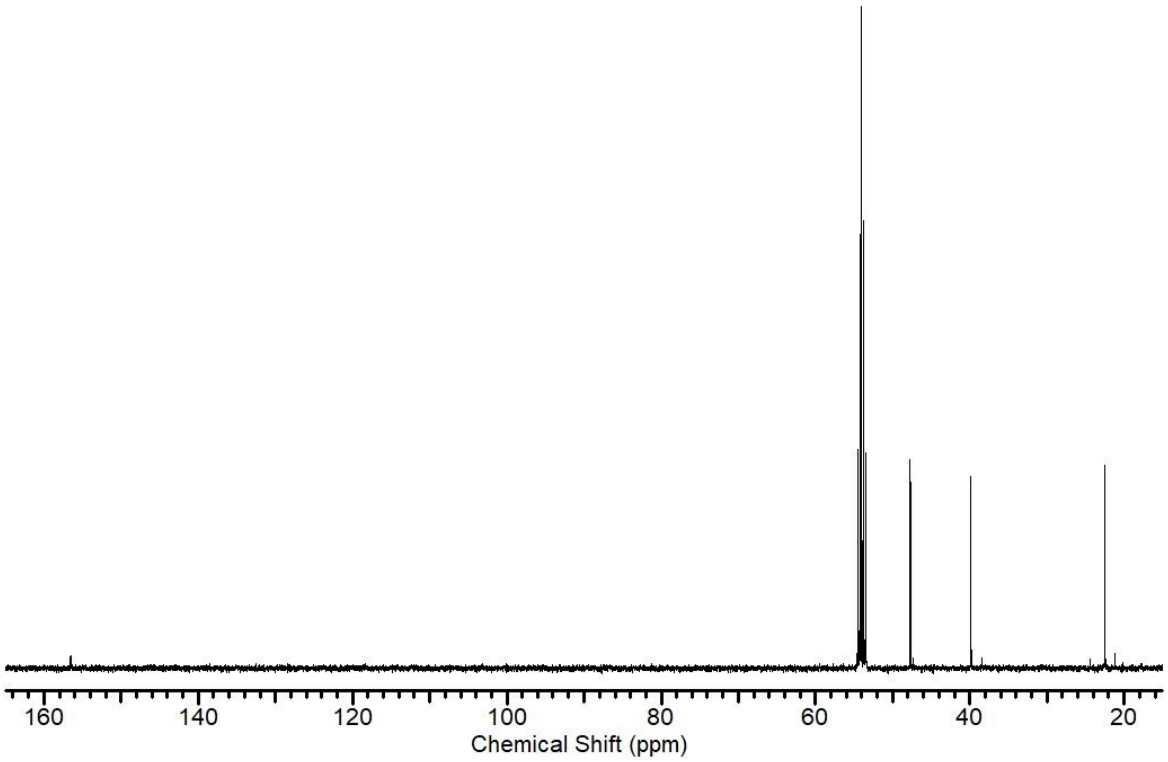


Figure 3: *^{13}C NMR spectrum of $B_2(hpp)_2Cl_2$ in CD_2Cl_2 (100 MHz).*

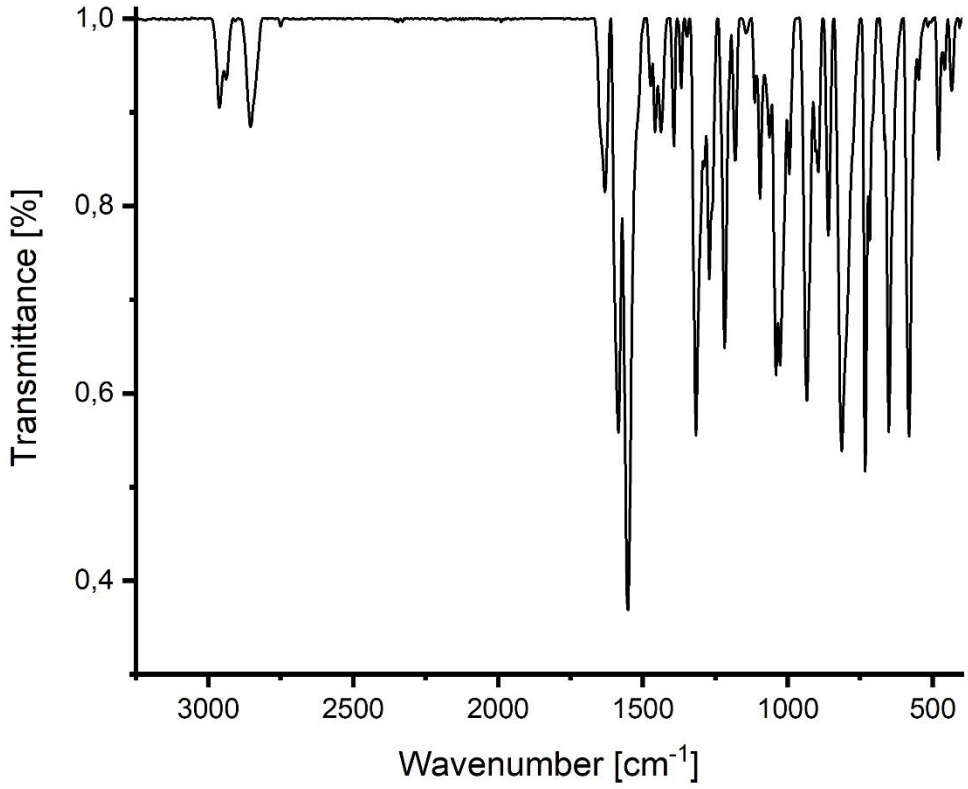


Figure 4: *IR spectrum (ATR) of $B_2(hpp)_2Cl_2$ as powder.*

$B_2(hpp)_2Br_2$ (5)

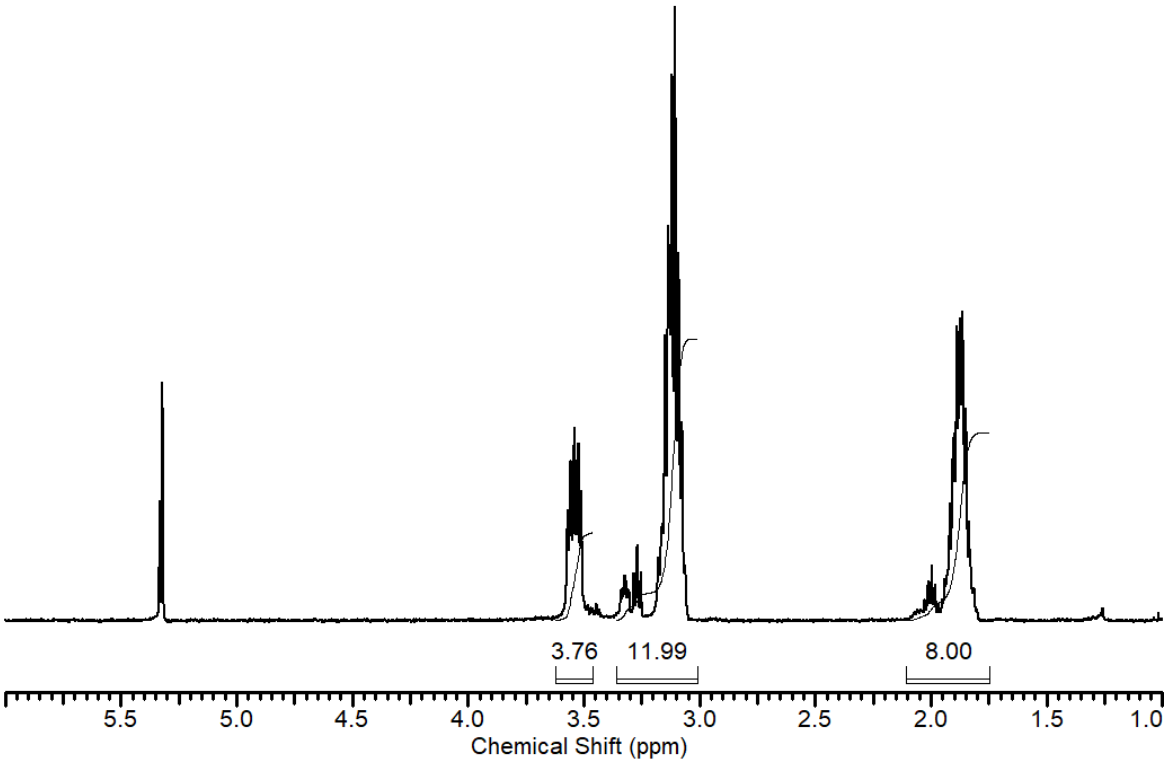


Figure 5: *^1H NMR spectrum of $B_2(hpp)_2Br_2$ in CD_2Cl_2 (400 MHz).*

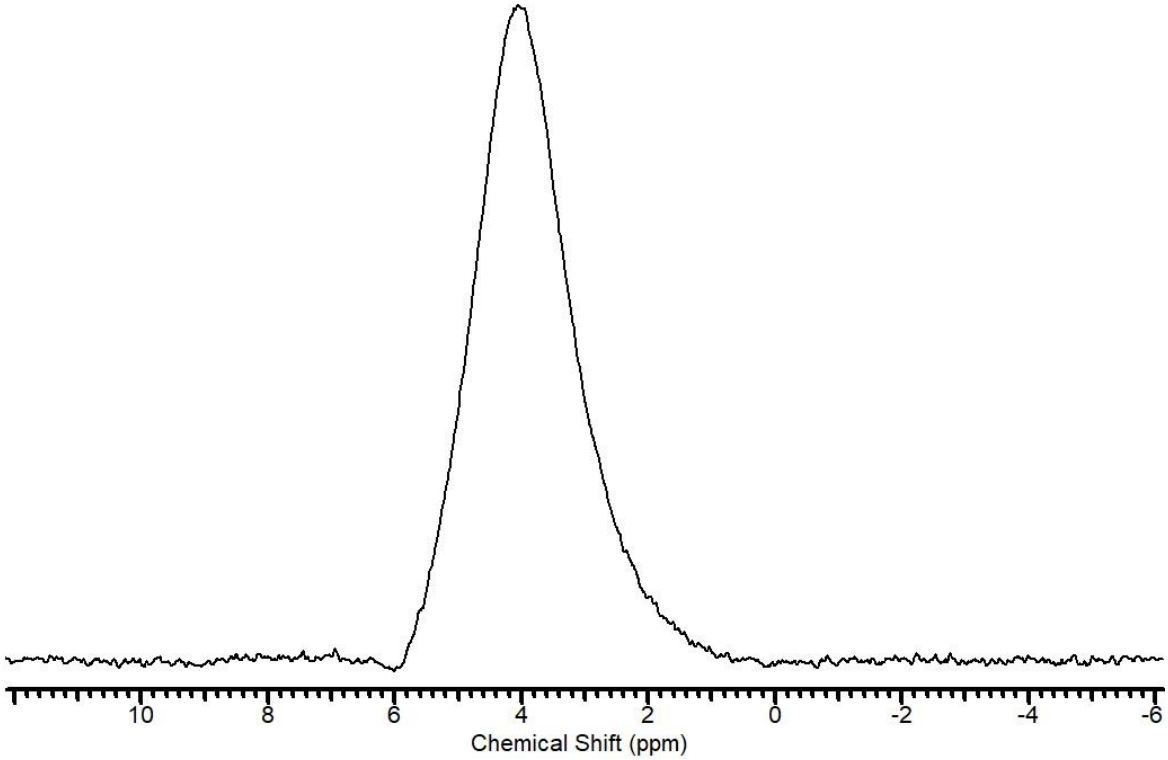


Figure 6: *^{11}B NMR spectrum of $B_2(hpp)_2Br_2$ in CD_2Cl_2 (128 MHz).*

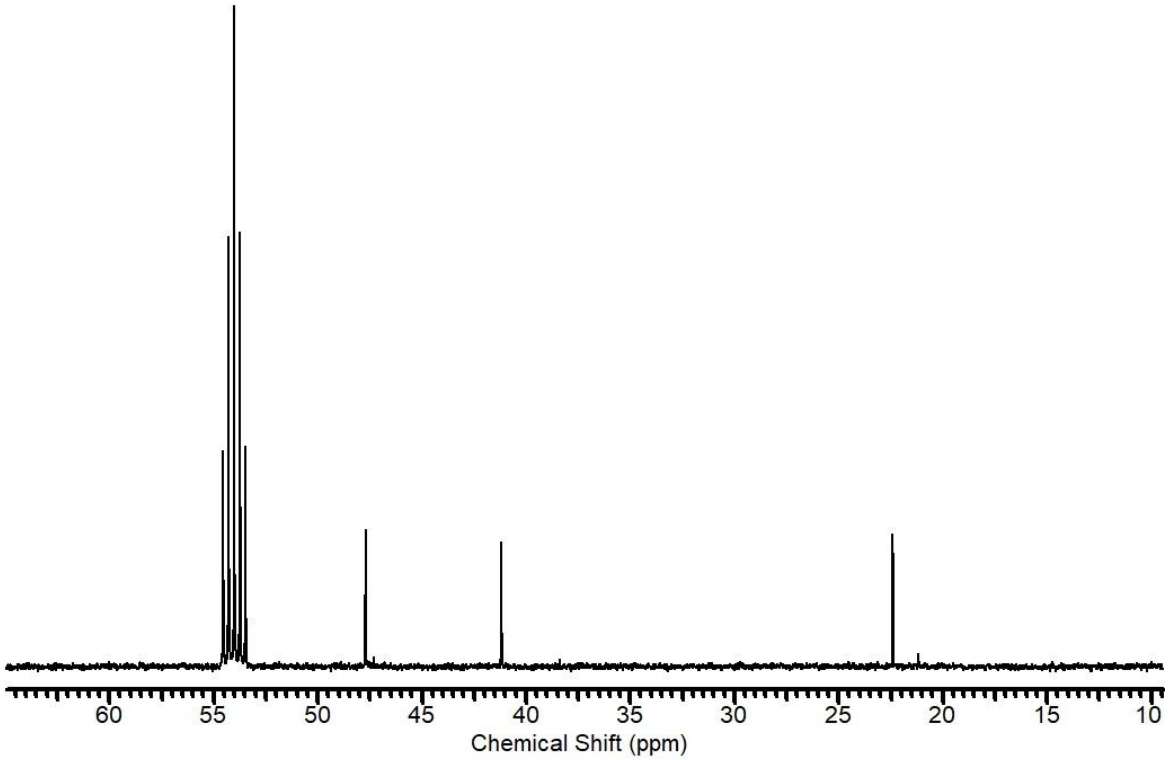


Figure 7: *^{13}C NMR spectrum of $B_2(hpp)_2Br_2$ in CD_2Cl_2 (100 MHz).*

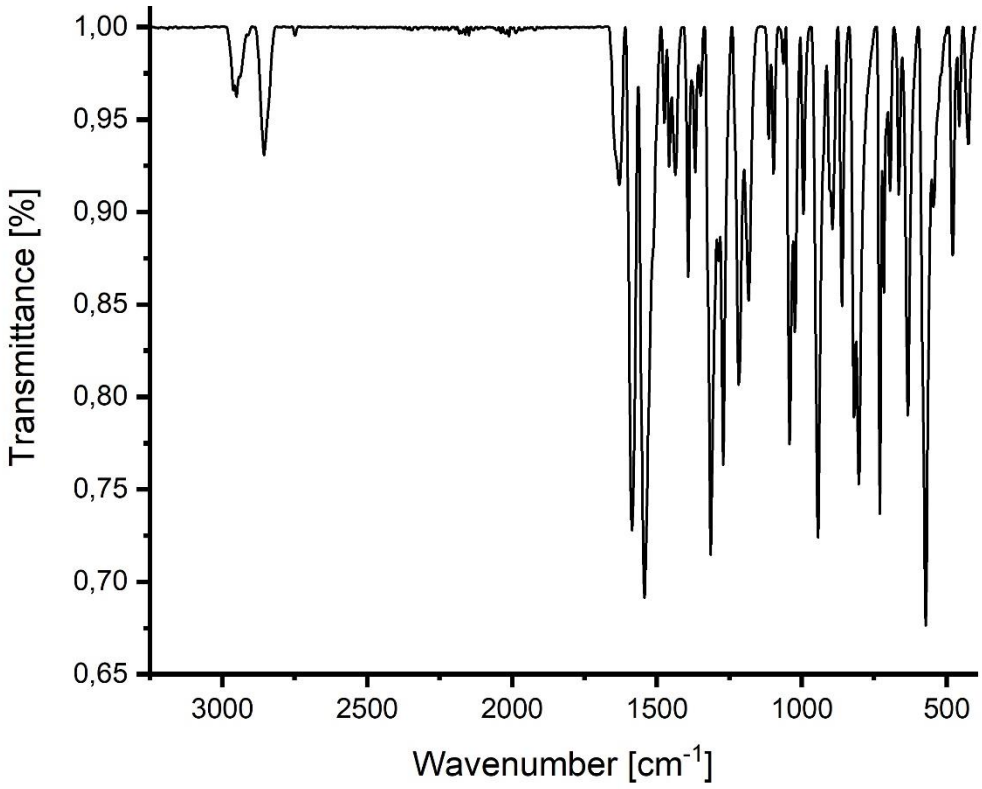


Figure 8: *IR spectrum (ATR) of $B_2(hpp)_2Br_2$ as powder.*

$B_2(hpp)_2(NCS)_2$ (6)

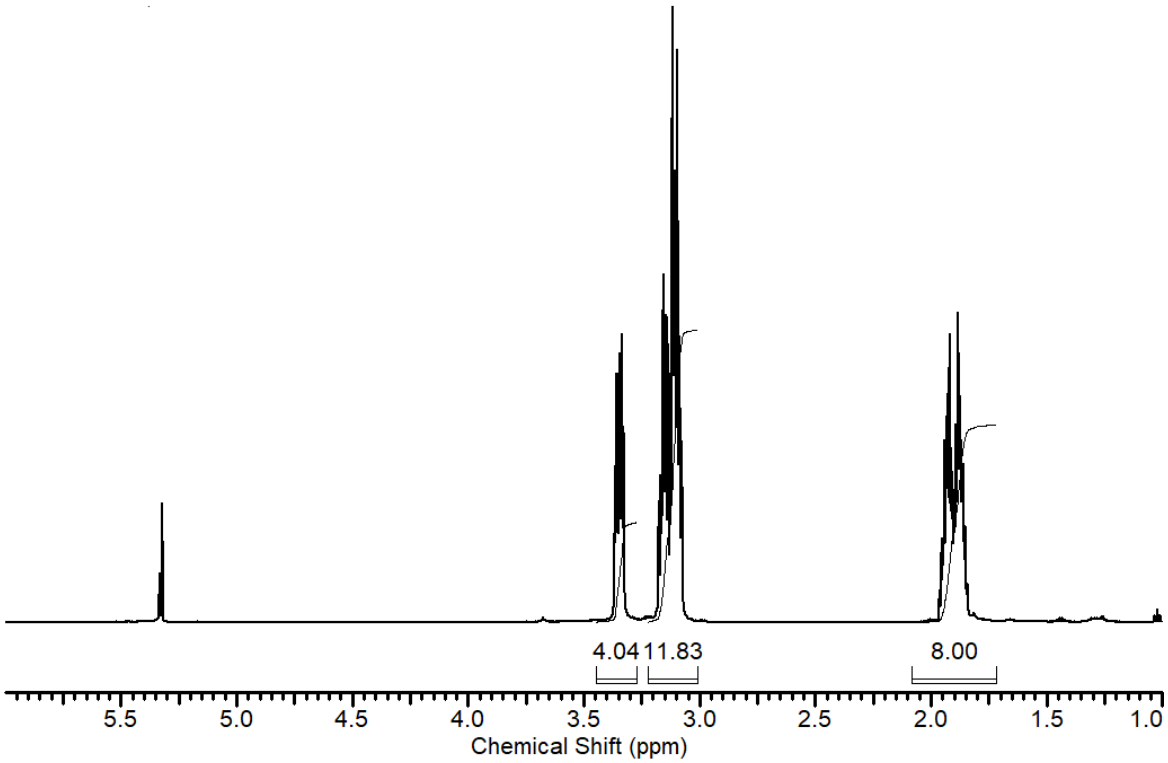


Figure 9: *^1H NMR spectrum of $B_2(hpp)_2(NCS)_2$ in CD_2Cl_2 (600 MHz).*

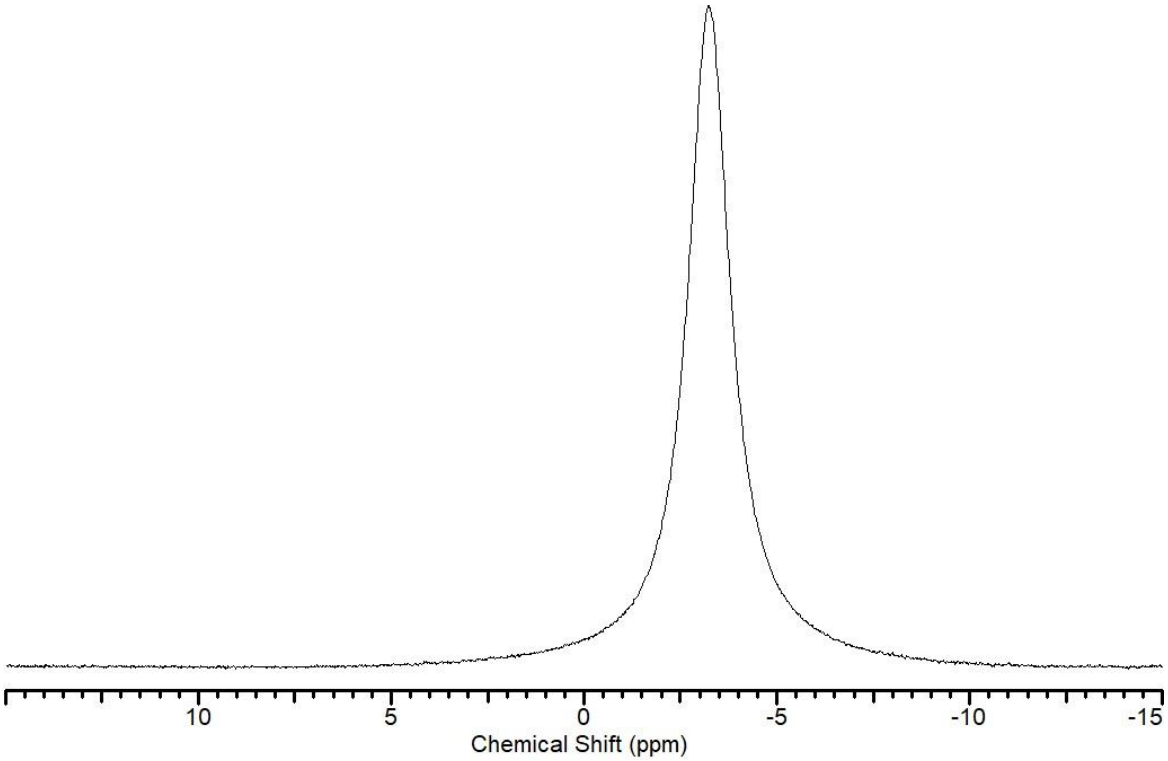


Figure 10: *^{11}B NMR spectrum of $B_2(hpp)_2(NCS)_2$ in CD_2Cl_2 (192 MHz).*

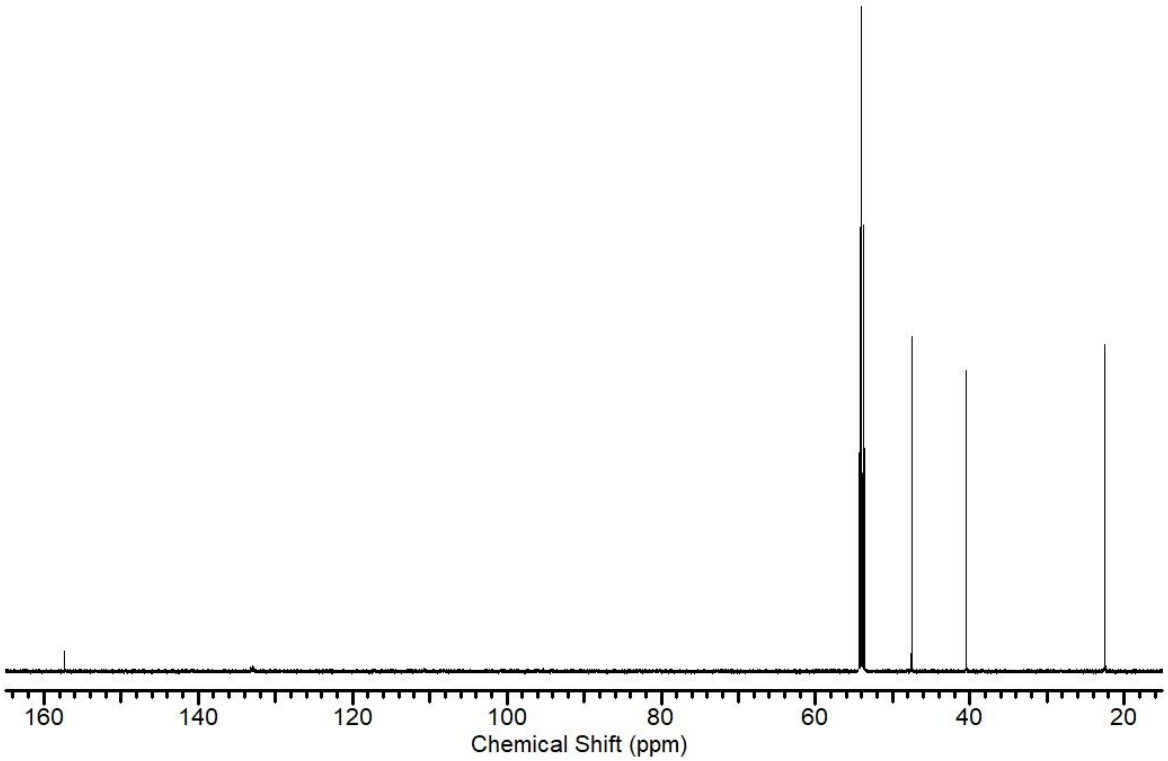


Figure 11: *^{13}C NMR spectrum of $B_2(hpp)_2(NCS)_2$ in CD_2Cl_2 (150 MHz).*

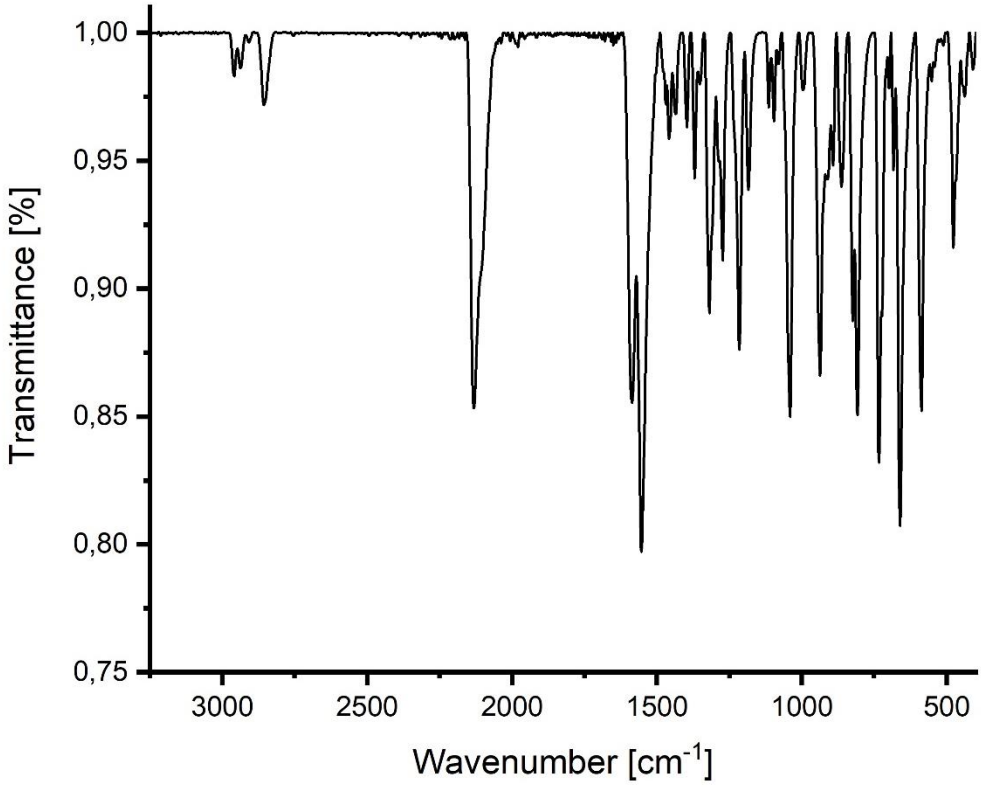


Figure 12: *IR spectrum (ATR) of $B_2(hpp)_2(NCS)_2$ as powder.*

$B_2(hpp)_2(N_3)_2$ (7)

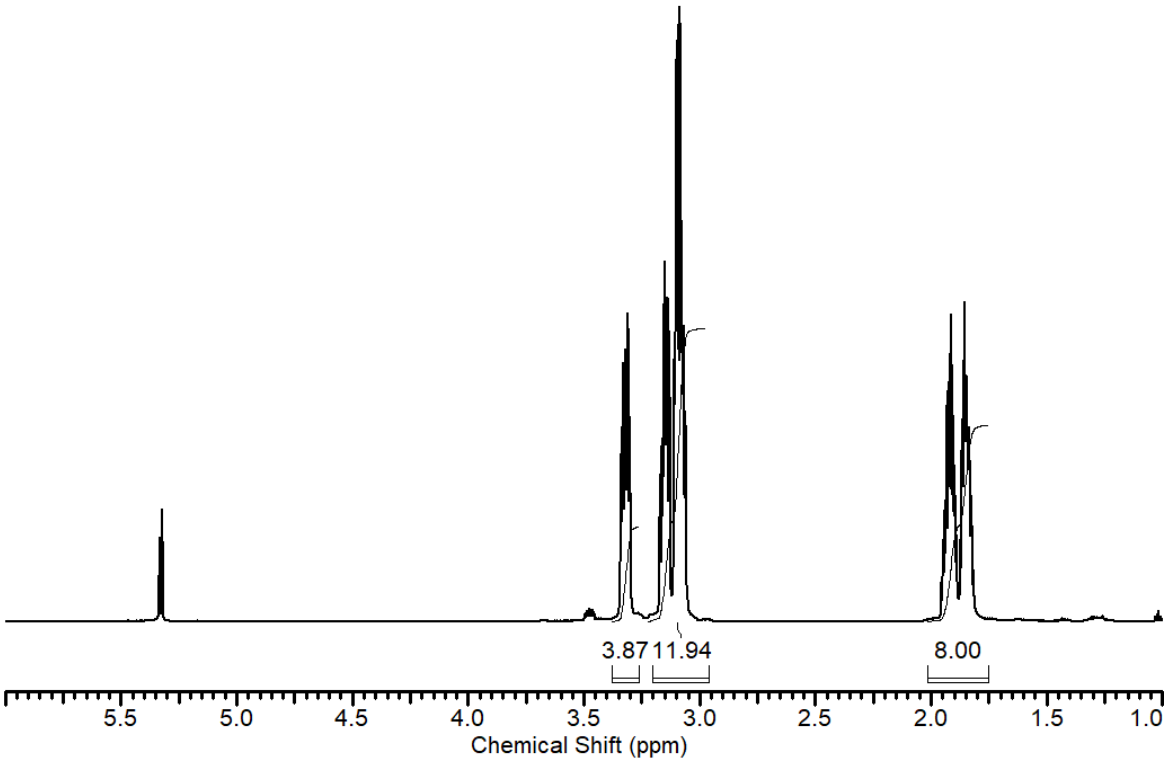


Figure 13: *^1H NMR spectrum of $B_2(hpp)_2(N_3)_2$ in CD_2Cl_2 (600 MHz).*

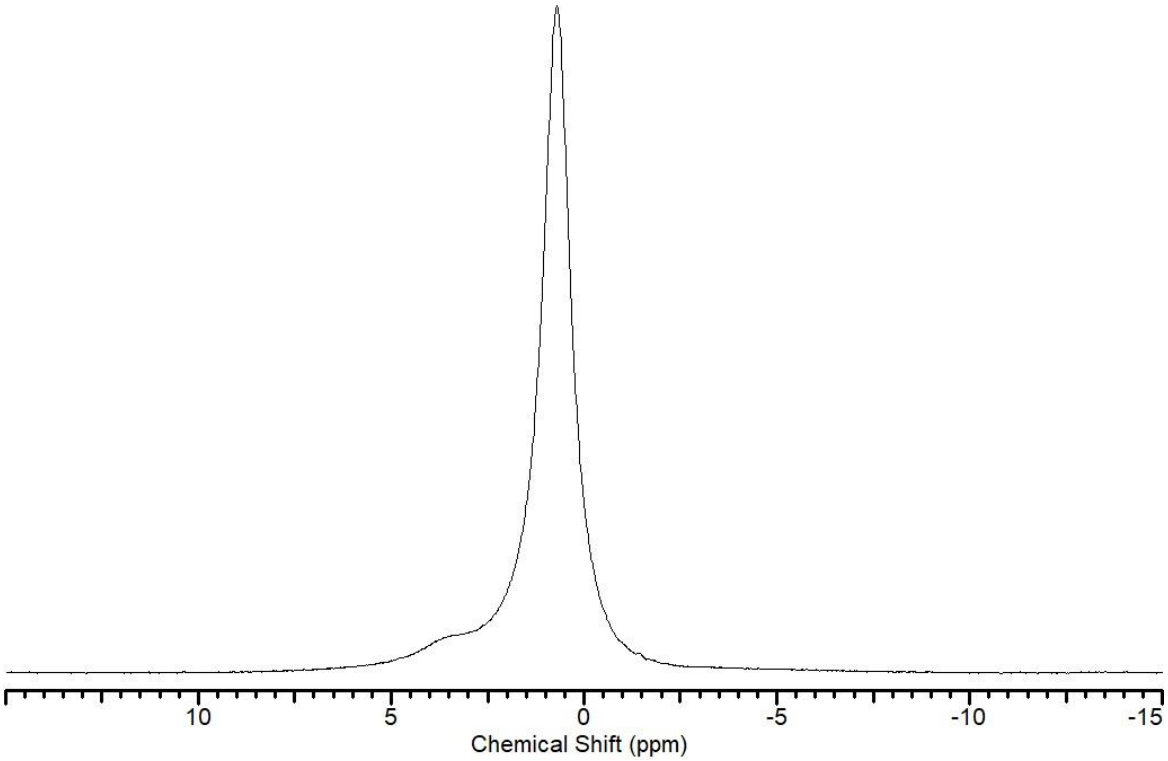


Figure 14: *^{11}B NMR spectrum of $B_2(hpp)_2(N_3)_2$ in CD_2Cl_2 (192 MHz).*

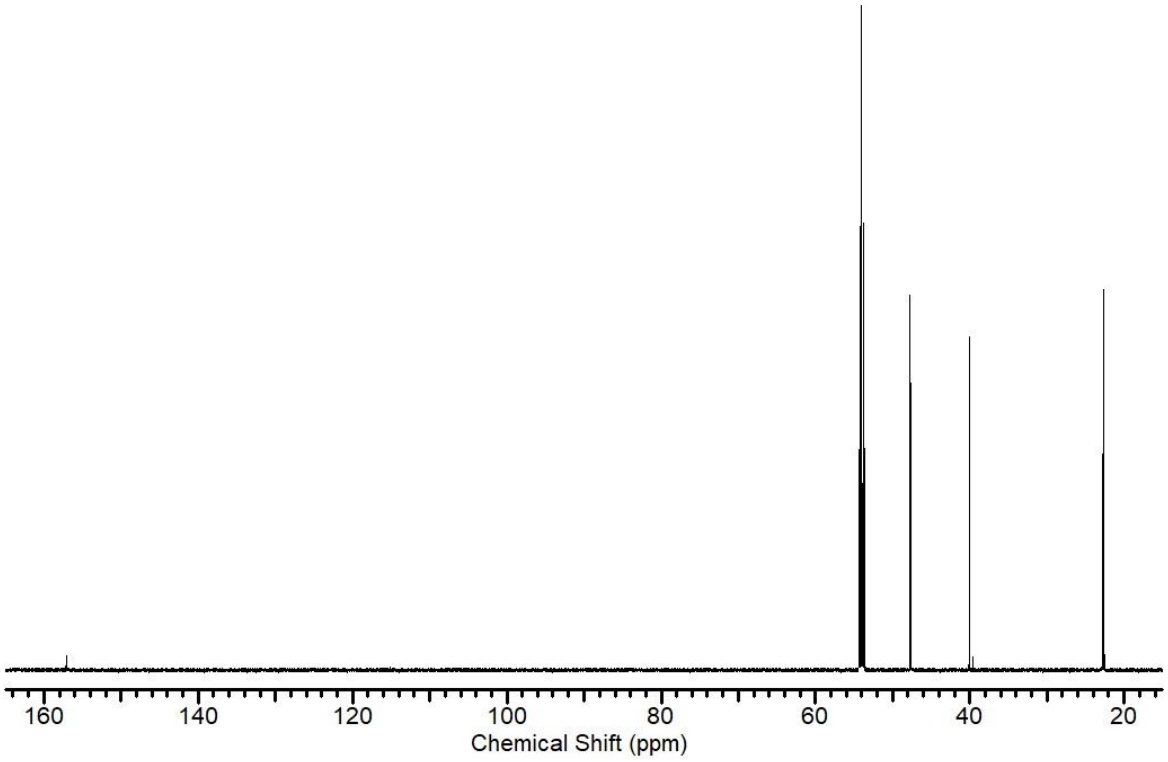


Figure 15: *^{13}C NMR spectrum of $B_2(hpp)_2(N_3)_2$ in CD_2Cl_2 (150 MHz).*

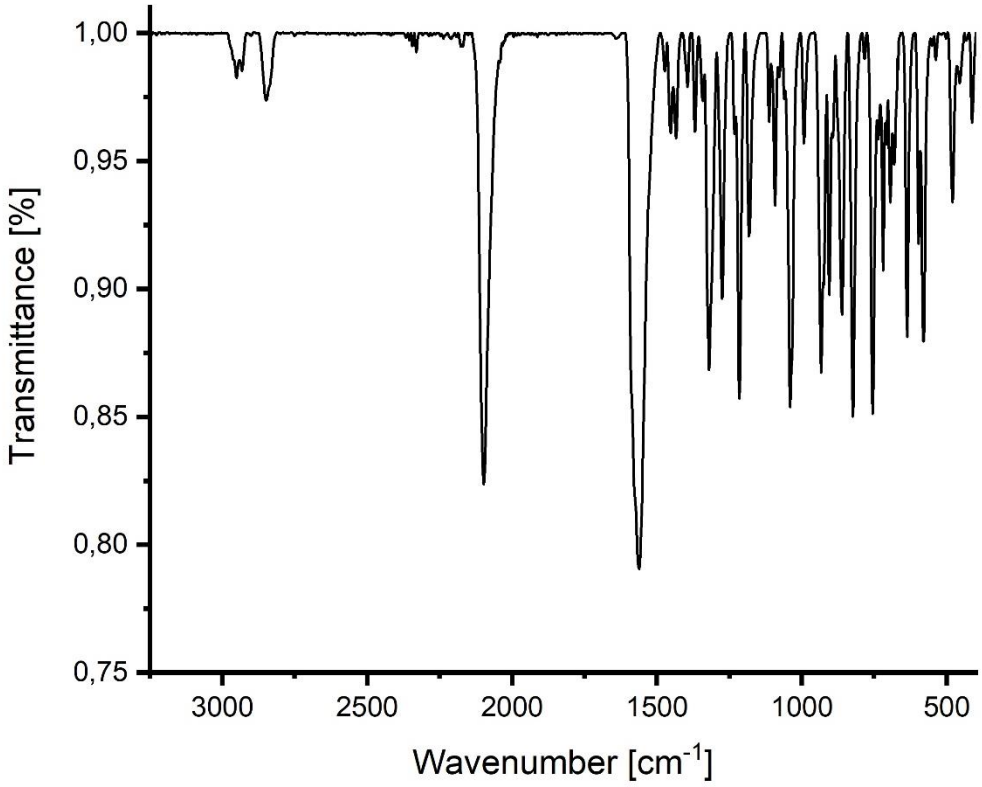


Figure 16: *IR spectrum (ATR) of $B_2(hpp)_2(N_3)_2$ as powder.*

Equilibrium ($B_2(hpp)_2(OTf)_2$ + $B_2(hpp)_2(OTf)Cl$ + $B_2(hpp)_2Cl_2$)

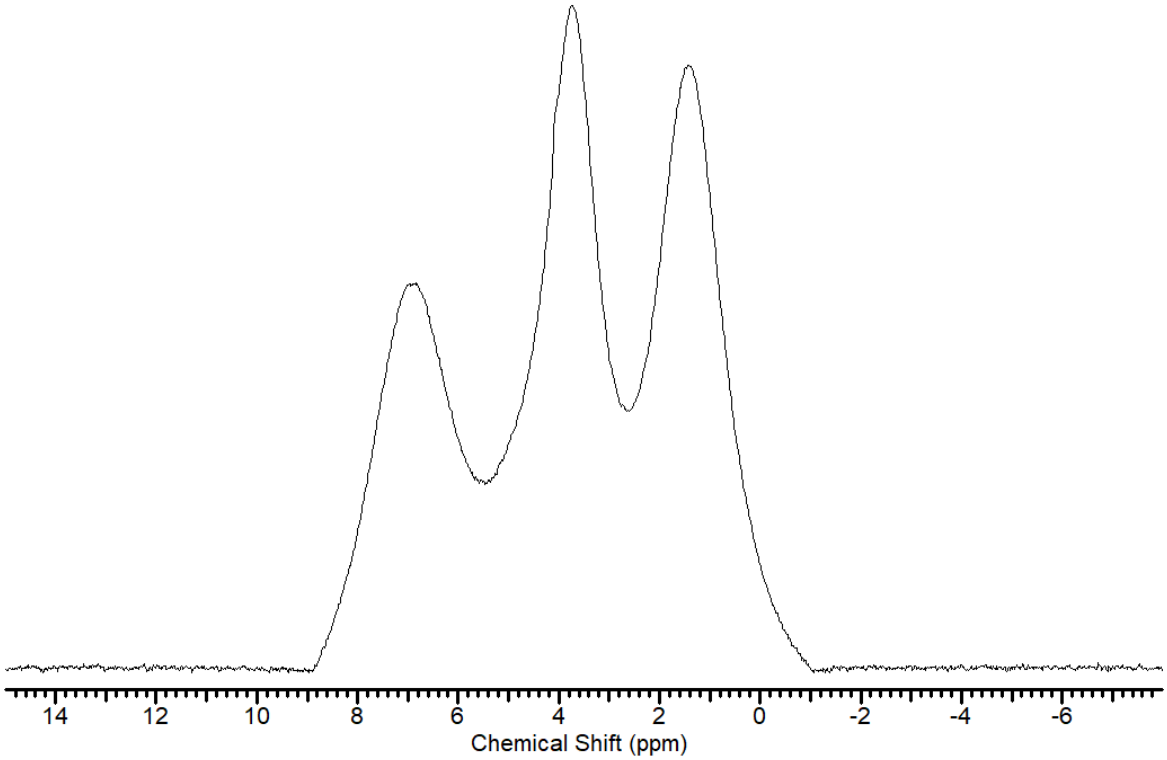


Figure 17: *^{11}B NMR spectrum of the equlibrium **2/3/8** in CD_2Cl_2 (192 MHz).*

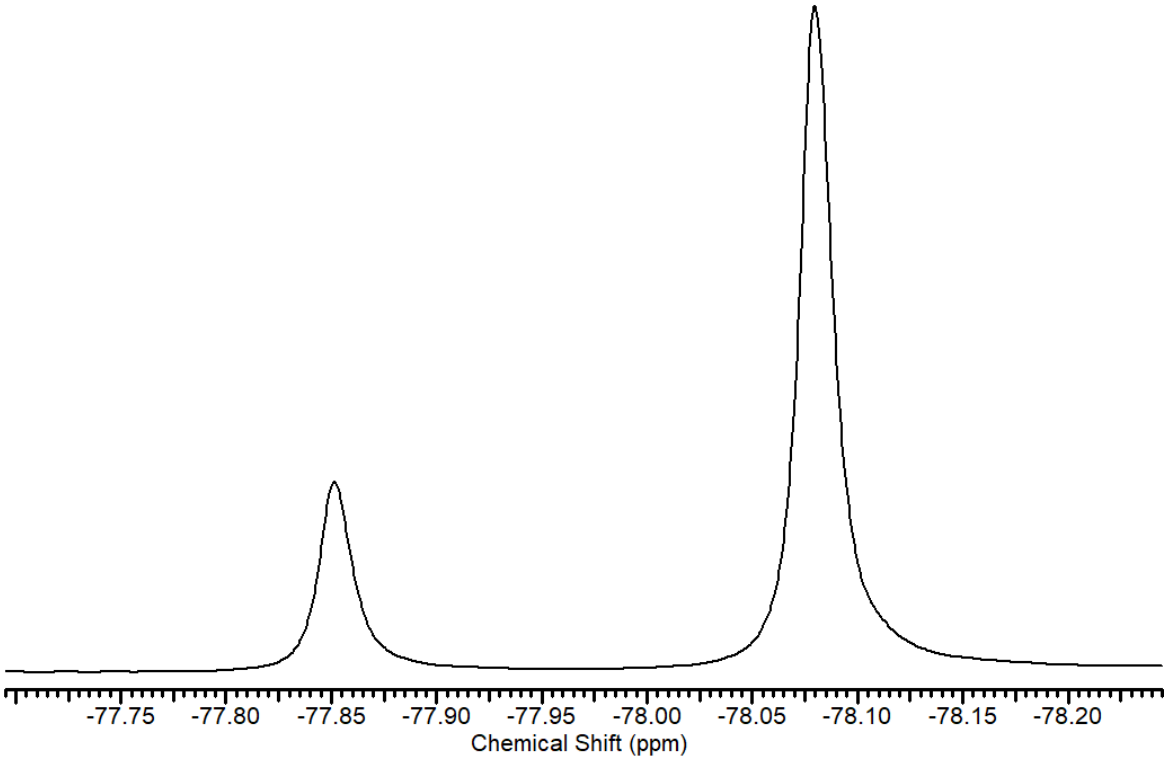


Figure 18: *^{19}F NMR spectrum of the equilibrium **2/3/8** in CD_2Cl_2 (188 MHz).*

Equilibrium ($B_2(hpp)_2(OTf)_2$ + $B_2(hpp)_2(OTf)Br$ + $B_2(hpp)_2Br_2$)

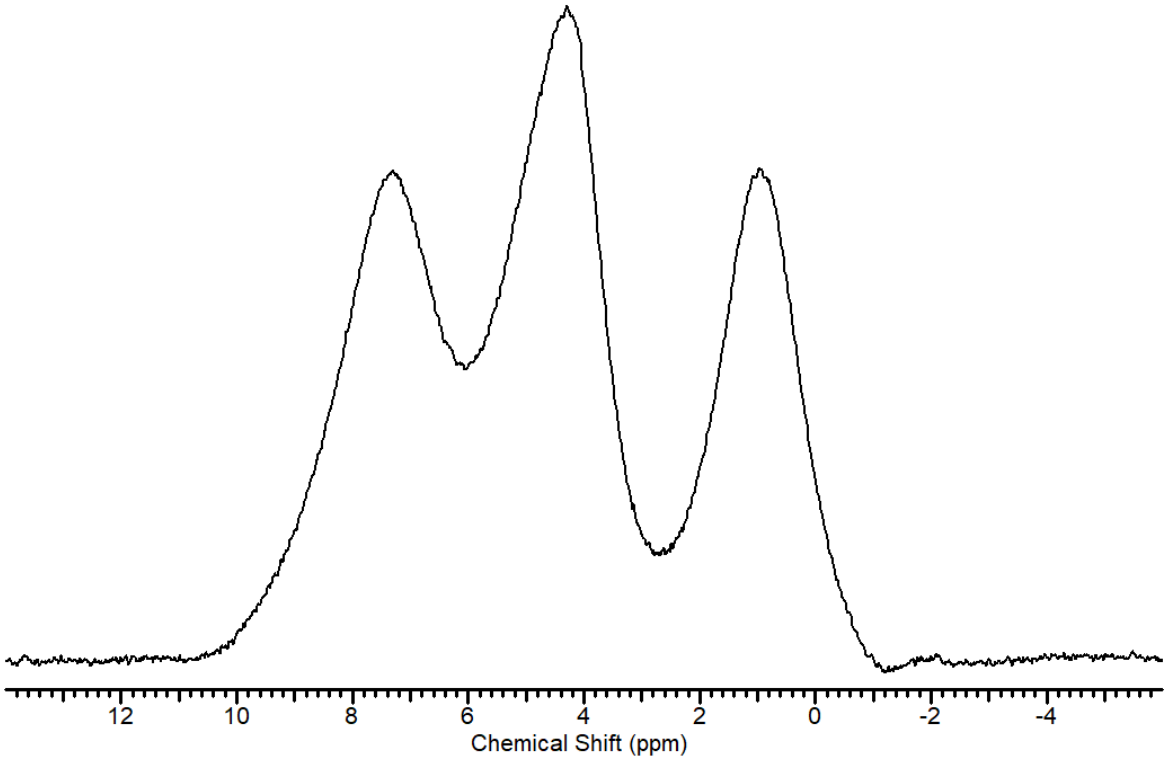


Figure 19: *^{11}B NMR spectrum of the equilibrium **2/5/9** in CD_2Cl_2 (192 MHz).*

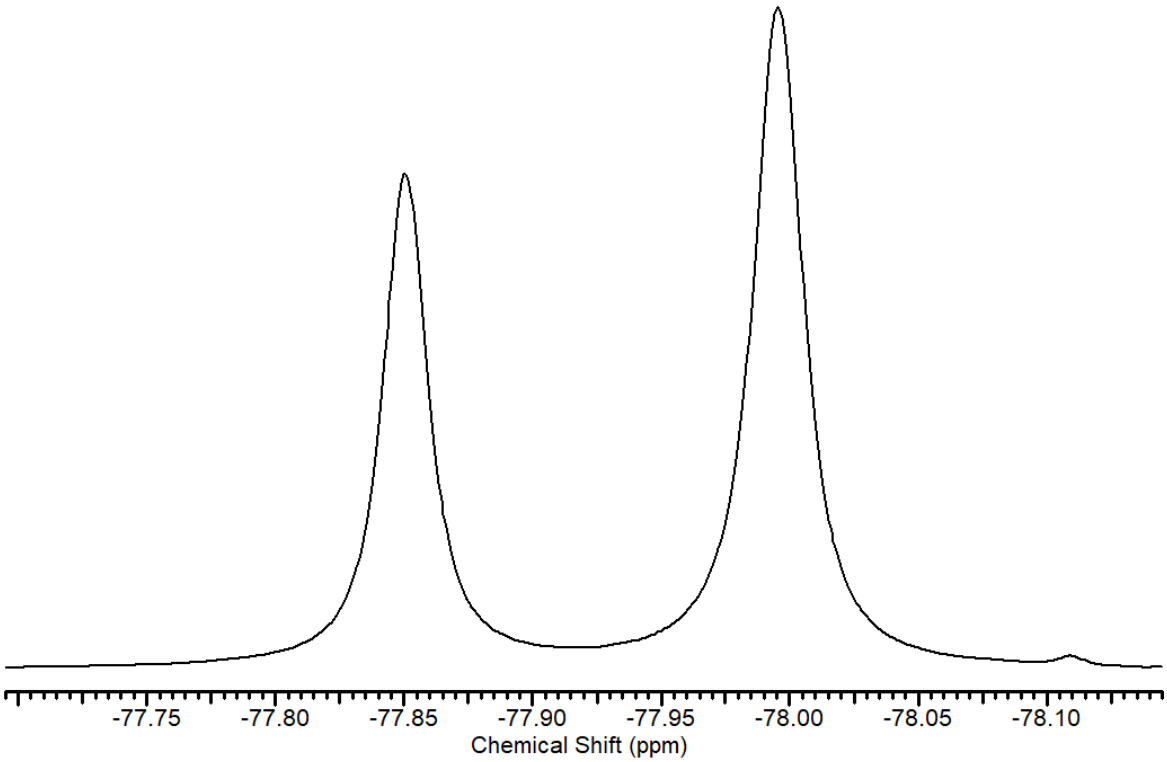


Figure 20: *^{19}F NMR spectrum of the equilibrium **2/5/9** in CD_2Cl_2 (188 MHz).*

Equlibrium ($B_2(hpp)_2(OTf)_2$ + $B_2(hpp)_2(OTf)(NCS)$ + $B_2(hpp)_2(NCS)_2$)

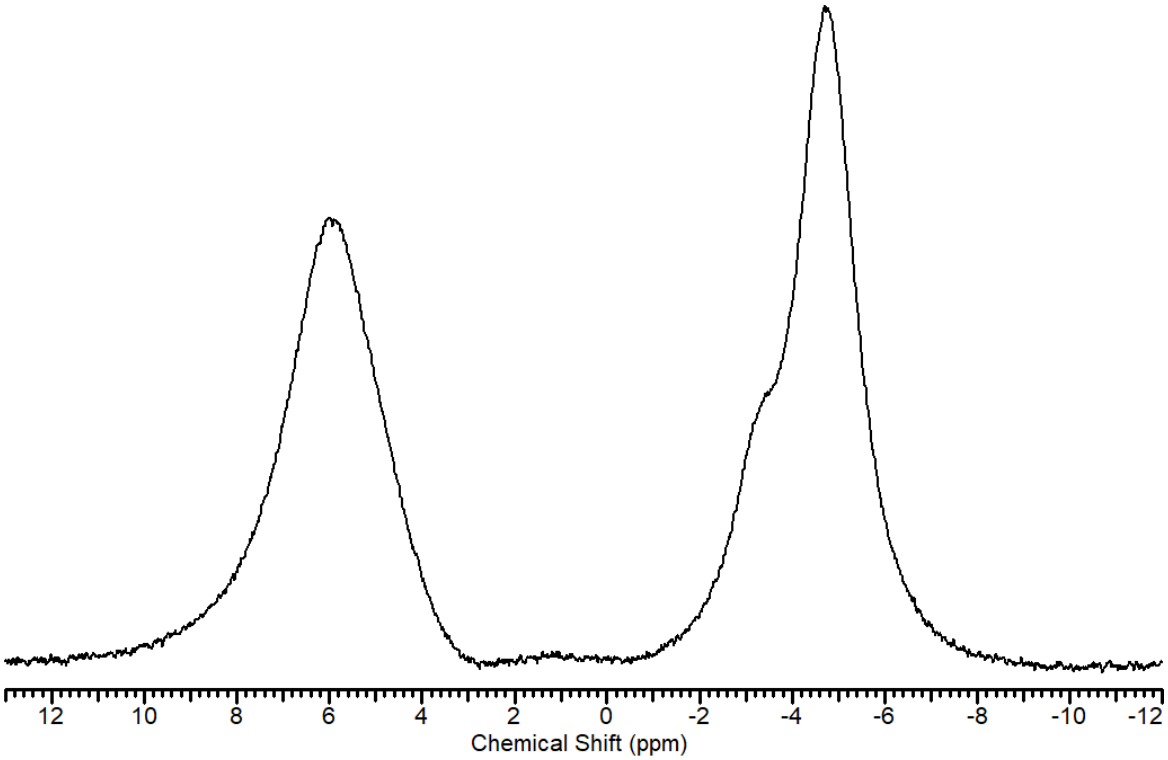


Figure 21: *^{11}B NMR spectrum of the equlibrium **2/6/10** in CD_2Cl_2 (192 MHz).*

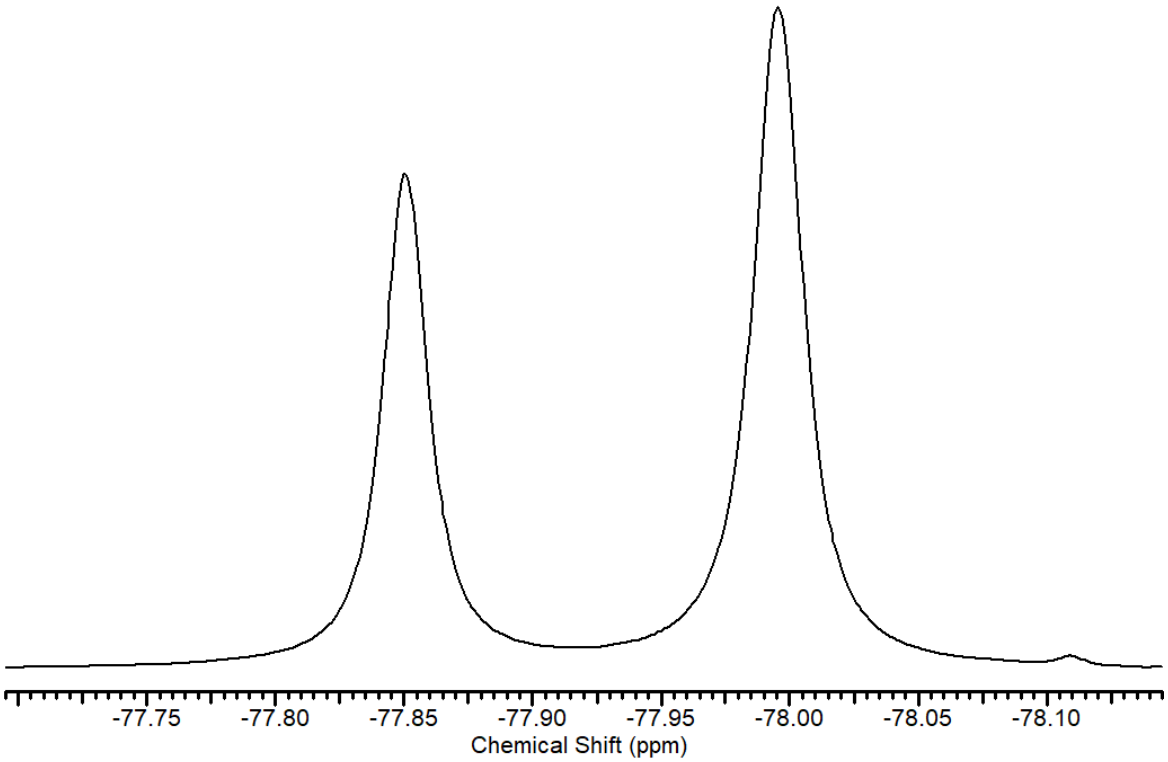


Figure 22: *^{19}F NMR spectrum of the equilibrium **2/6/10** in CD_2Cl_2 (188 MHz).*

Equilibrium ($B_2(hpp)_2(Br)_2$ + $B_2(hpp)_2BrCl$ + $B_2(hpp)_2Cl_2$)

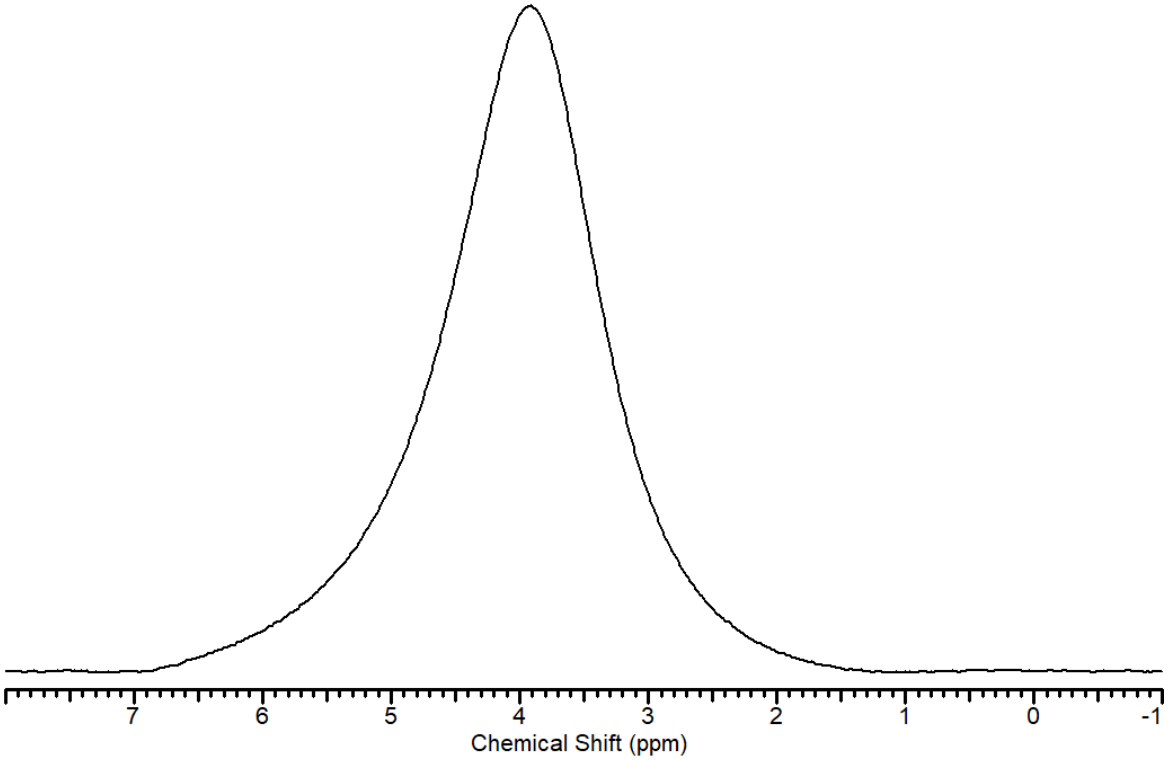


Figure 23: *^{11}B NMR spectrum of the equilibrium **3/5/11** in CD_2Cl_2 (192 MHz).*

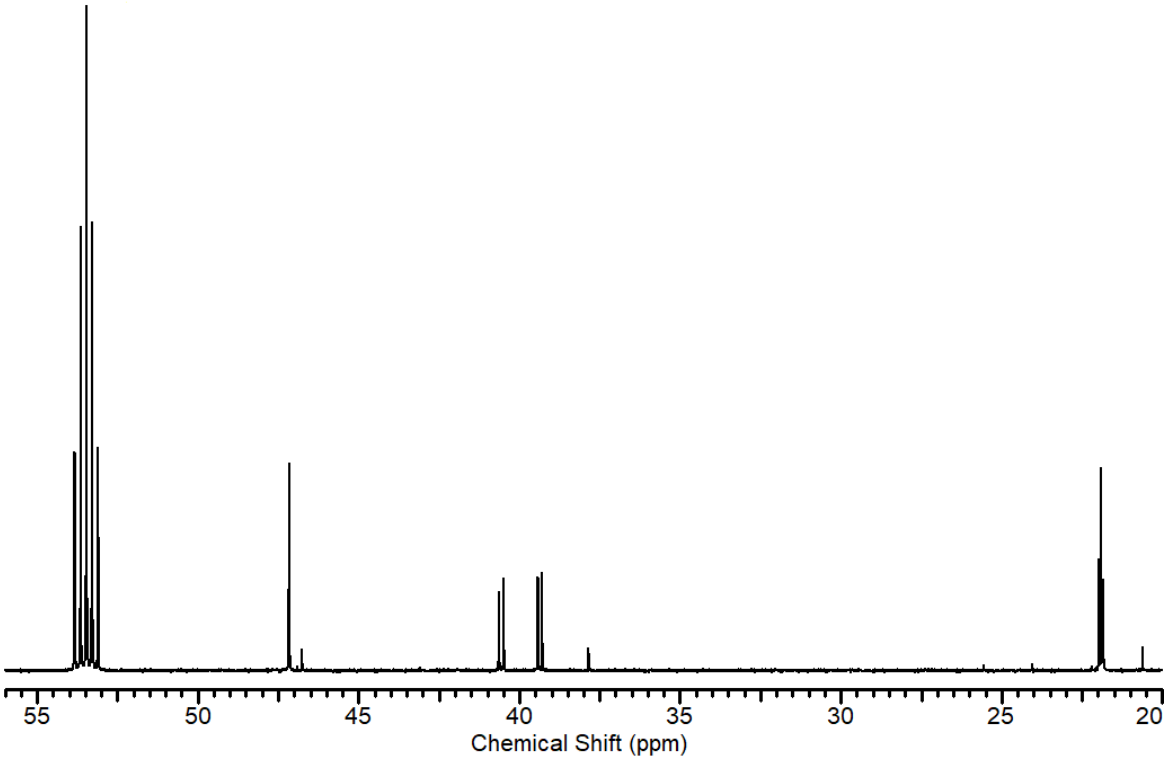


Figure 24: *^{13}C NMR spectrum of the equilibrium **3/5/11** in CD_2Cl_2 (150 MHz).*

Equilibrium ($B_2(hpp)_2Br_2$ + $B_2(hpp)_2Br(NCS)$ + $B_2(hpp)_2(NCS)_2$)

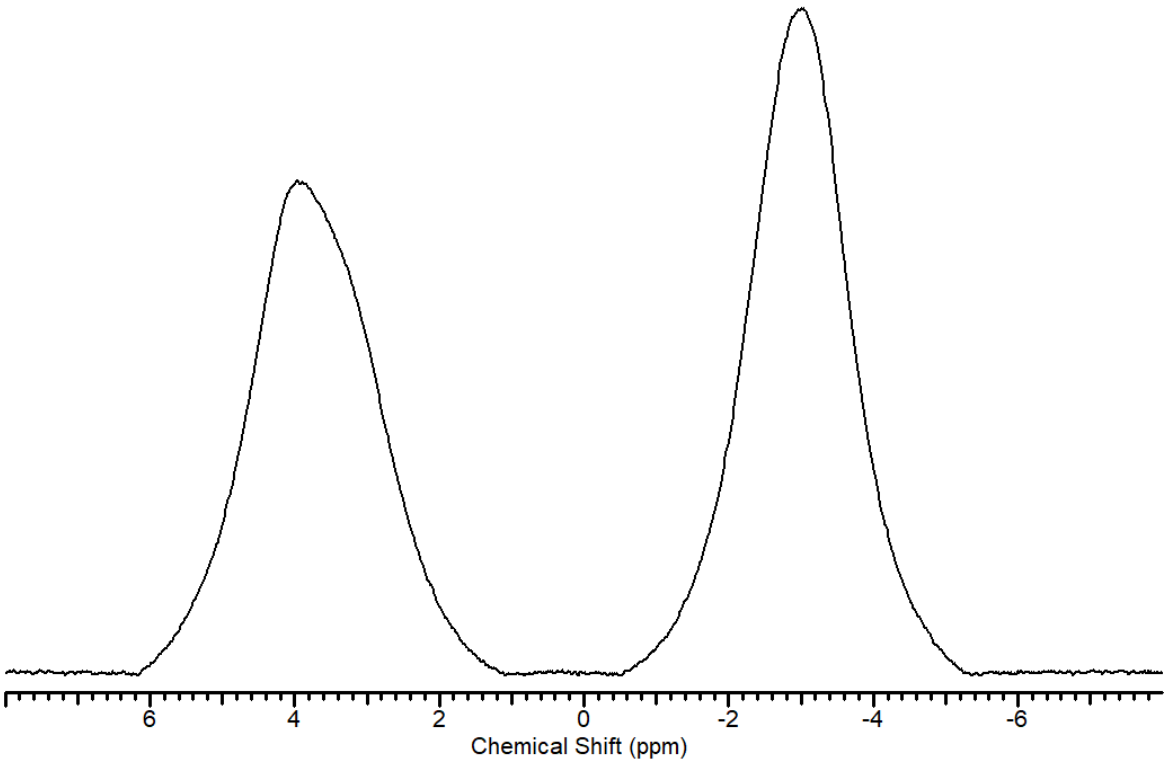


Figure 25: *^{11}B NMR spectrum of the equilibrium **5/6/12** in CD_2Cl_2 (192 MHz).*

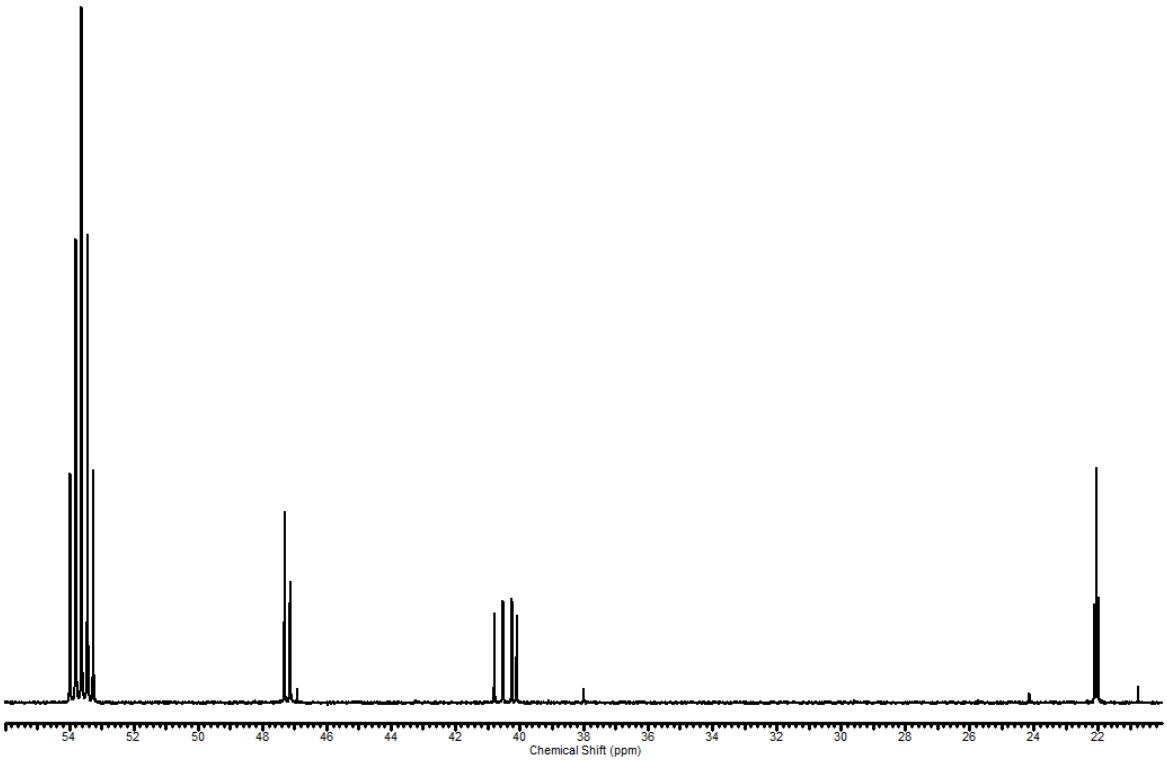


Figure 26: *^{13}C NMR spectrum of the equilibrium **5/6/12** in CD_2Cl_2 (150 MHz).*

Equilibrium ($B_2(hpp)_2Br_2$ + $B_2(hpp)_2Br(N_3)$ + $B_2(hpp)_2(N_3)_2$)

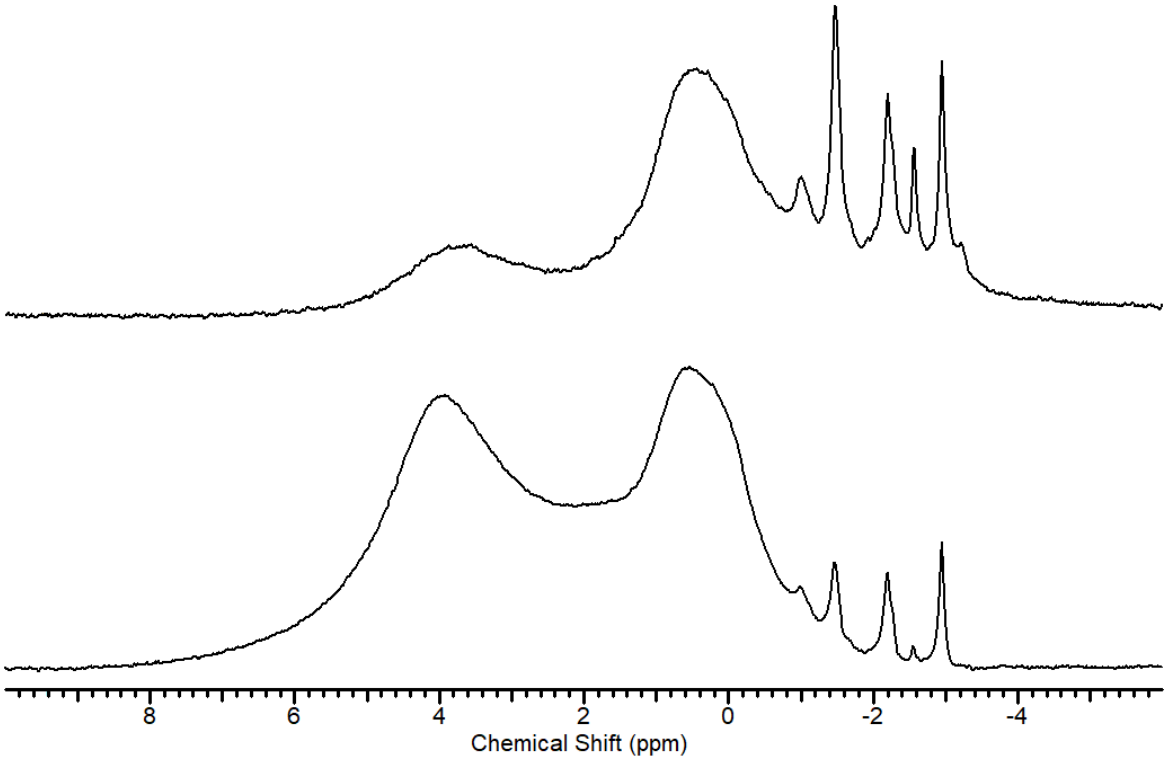


Figure 27: *^{11}B NMR spectra of the equilibrium **5/7/13** after 1 d (bottom) and after 7 d (top) in CD_2Cl_2 (192 MHz).*

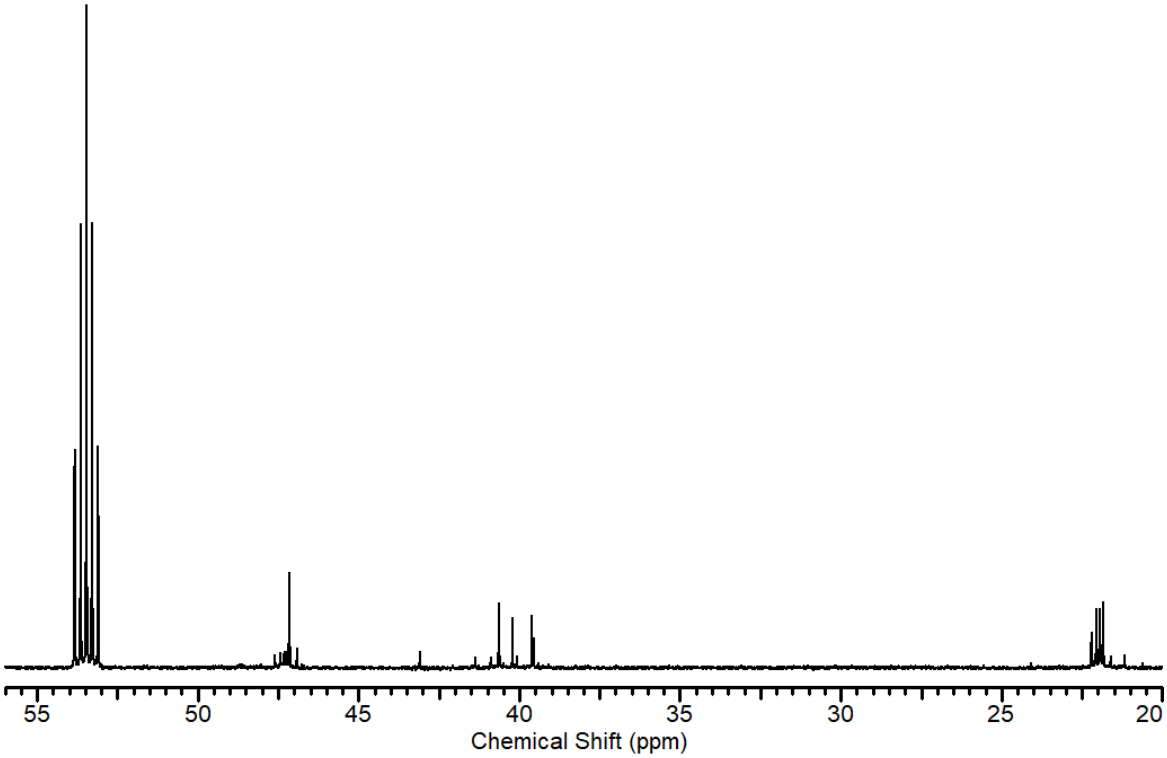


Figure 28: *^{13}C NMR spectrum of the equilibrium **5/7/13** after 1 d in CD_2Cl_2 (150 MHz).*

Comparison of the equilibria with $B_2(hpp)_2(OTf)_2$ (2)

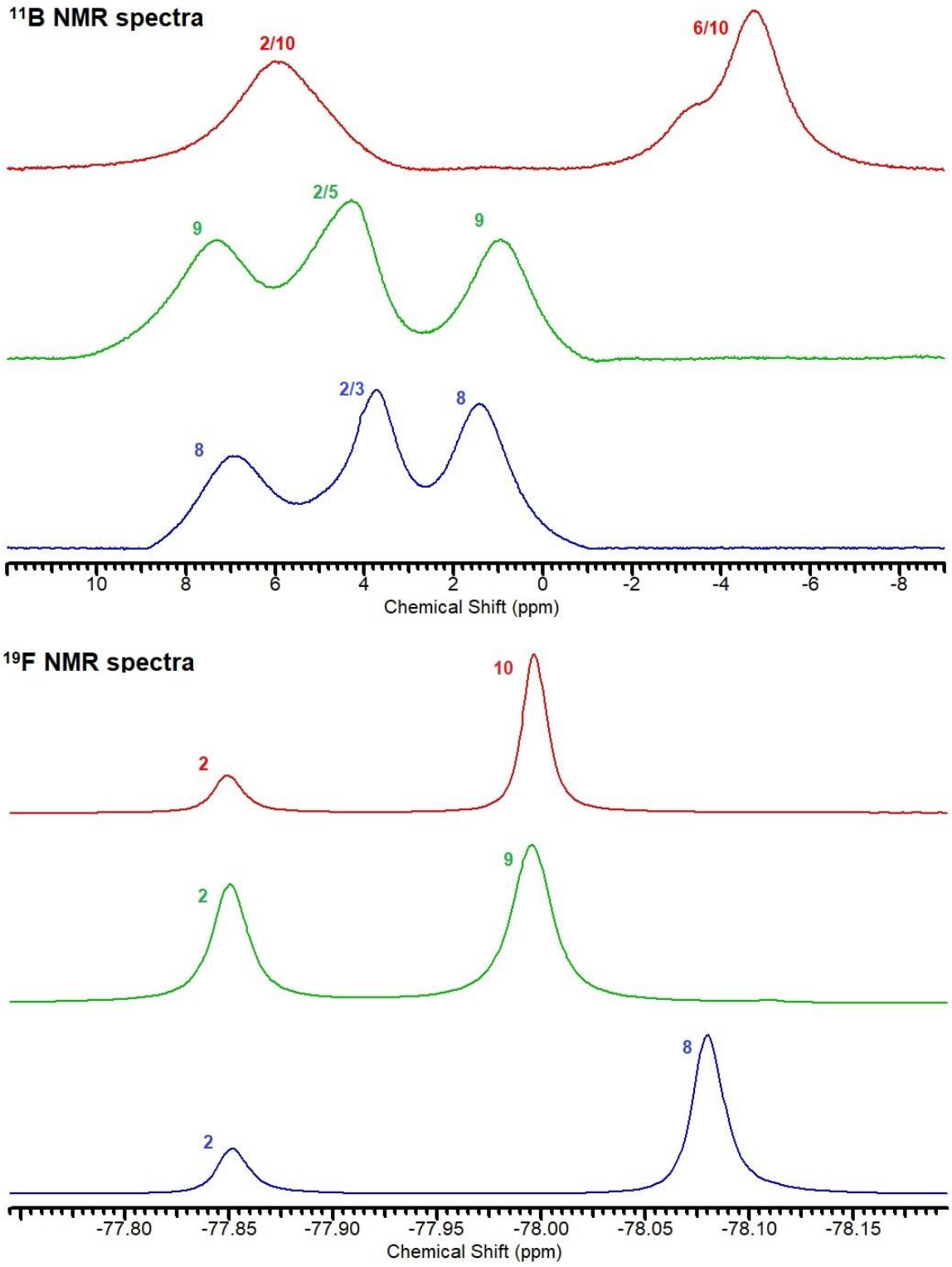


Figure 29: *^{11}B NMR (192 MHz) and ^{19}F NMR (188 MHz) spectra of the equilibria **2**,**3**,**8** (blue); **2,5,9** (green) and **2,6,10** (red) in CD_2Cl_2.*

Comparison of the equilibria with $B_2(hpp)_2Br_2$ (5)

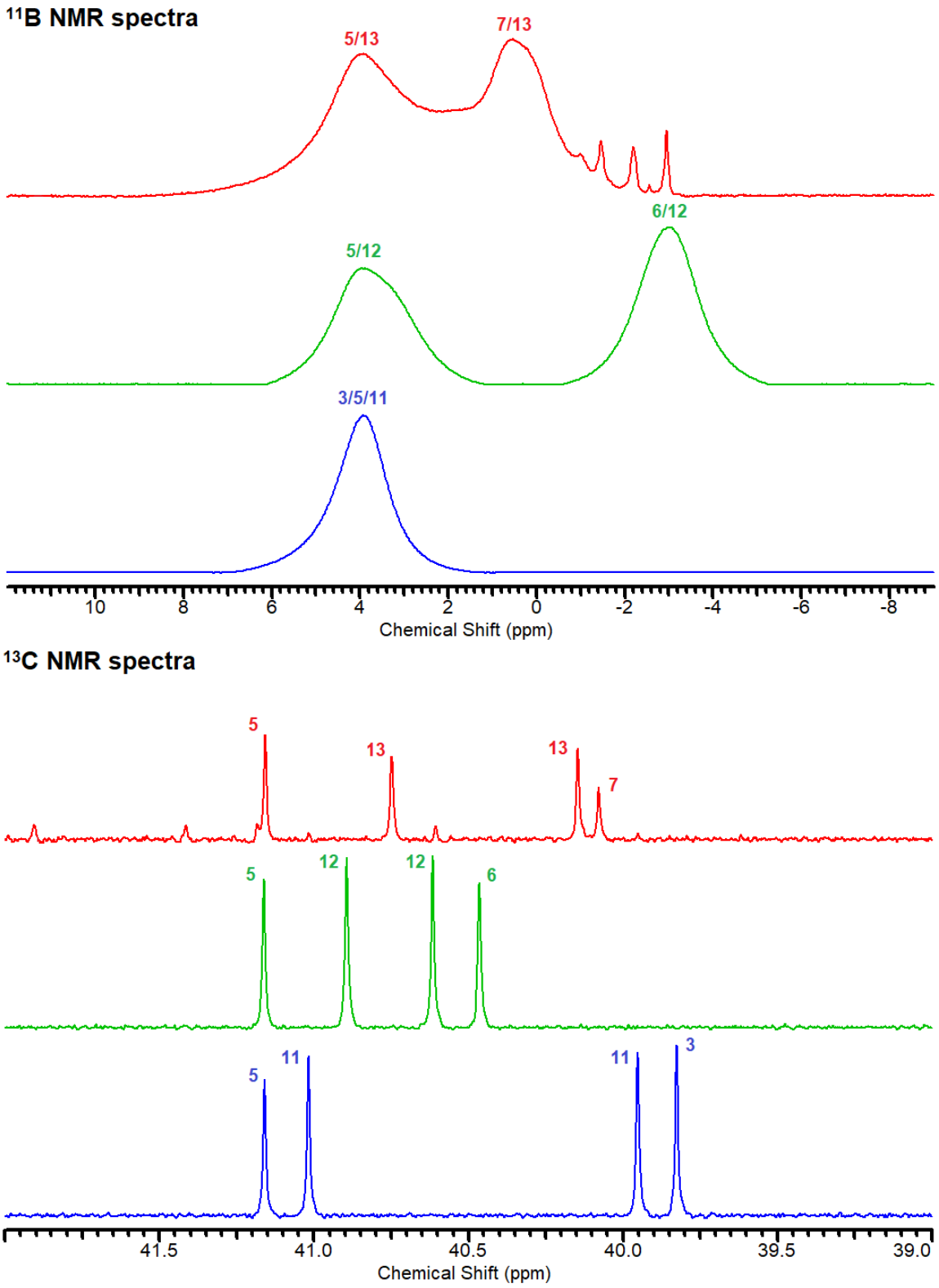


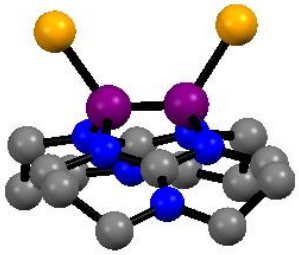
Figure 30: *^{11}B NMR (192 MHz) and ^{13}C NMR (150 MHz) spectra of the equilibria* ***3,5,11*** *(blue);* ***5,6,12*** *(green) and* ***5,7,13*** *(red) in CD_2Cl_2.*

4. Details of the quantum-chemical calculations

DFT calculations were carried out with the Turbomole program.[8,9,10] Structure optimisations were performed at the RI-DFT level of theory [11] with a DFT-D3 dispersions correction [12] using the B3LYP functional [13,14] in combination with the def2-TZVPP basis set.[15] The calculated structures and isodensity surfaces for the orbitals were visualized with the Mercury or Chemcraft software.

$B_2(hpp)_2Br_2$ (5)

Illustration of the calculated minimum structure of **5**. Hydrogen atoms omitted.



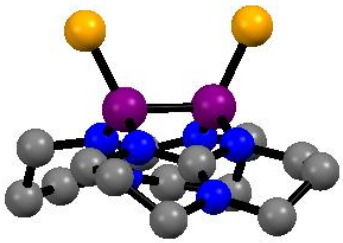
Cartesian coordinates (in Å):

Br	13.591083	5.090134	2.528436
N	13.378409	4.216773	5.359545
N	15.770088	4.217223	4.349223
C	12.905494	5.524080	5.792460
H	12.101975	5.860113	5.129997
H	13.720859	6.237085	5.671697
C	12.430391	5.483893	7.236212
H	13.281063	5.342841	7.907279
H	11.944420	6.423081	7.503106
C	11.458352	4.328295	7.412798
H	11.182447	4.209257	8.462000
H	10.534647	4.518430	6.851224
N	12.074849	3.081831	6.972487
C	12.921276	3.081824	5.904894
C	16.398158	5.520876	4.488932
H	16.335007	5.858498	5.531771
H	15.831148	6.224755	3.880675
C	17.852536	5.475090	4.048070
H	17.899504	5.316800	2.968903
H	18.352722	6.417774	4.273624
C	18.557774	4.330803	4.758767
H	19.566516	4.194539	4.365198

H	18.654435	4.547813	5.830834
N	17.831296	3.081830	4.557040
C	16.477260	3.081823	4.425900
B	14.265141	3.937874	4.120279
Br	13.591084	1.073482	2.528458
N	13.378403	1.946868	5.359551
N	15.770098	1.946417	4.349211
C	12.905477	0.639566	5.792473
H	12.101967	0.303531	5.130002
H	13.720842	-0.073441	5.671725
C	12.430354	0.679759	7.236218
H	13.281020	0.820788	7.907297
H	11.944360	-0.259420	7.503101
C	11.458337	1.835376	7.412805
H	11.182441	1.954423	8.462009
H	10.534625	1.645253	6.851239
C	16.398184	0.642769	4.488896
H	16.335041	0.305130	5.531729
H	15.831181	-0.061107	3.880628
C	17.852560	0.688583	4.048028
H	17.899521	0.846901	2.968865
H	18.352757	-0.254101	4.273557
C	18.557785	1.832861	4.758754
H	19.566529	1.969140	4.365195
H	18.654438	1.615832	5.830818
B	14.265145	2.225756	4.120289

$[B_2(hpp)_2Br_2]^+$

Illustration of the calculated minimum structure of [**5**]$^+$. Hydrogen atoms omitted.



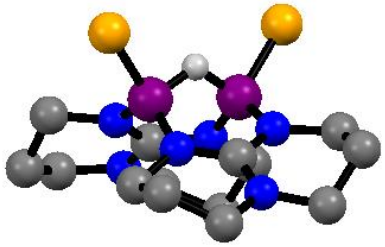
Cartesian coordinates (in Å):

Br	13.617703	5.010193	2.540661
N	13.377326	4.221197	5.359196
N	15.778556	4.221560	4.372297
C	12.851881	5.532586	5.770525
H	12.020054	5.809088	5.118277
H	13.635983	6.272596	5.619868
C	12.417284	5.490590	7.223573
H	13.287144	5.367572	7.871769

H	11.928334	6.425636	7.494803
C	11.459123	4.331052	7.426553
H	11.241388	4.190277	8.484743
H	10.508707	4.517694	6.916573
N	12.045931	3.081805	6.928113
C	12.912625	3.081813	5.901864
C	16.424107	5.537966	4.488335
H	16.365604	5.878731	5.526900
H	15.862086	6.238356	3.874132
C	17.869786	5.464190	4.034214
H	17.908745	5.285284	2.958462
H	18.375299	6.407887	4.236162
C	18.568364	4.335172	4.769320
H	19.566579	4.171934	4.365464
H	18.678705	4.570062	5.832940
N	17.821129	3.081845	4.614981
C	16.486390	3.081849	4.462966
B	14.289033	4.109003	4.162107
Br	13.617807	1.153545	2.540587
N	13.377268	1.942446	5.359119
N	15.778549	1.942150	4.372333
C	12.851812	0.631051	5.770412
H	12.019976	0.354570	5.118168
H	13.635910	-0.108953	5.619713
C	12.417232	0.672983	7.223469
H	13.287111	0.795926	7.871653
H	11.928253	-0.262059	7.494658
C	11.459126	1.832551	7.426553
H	11.241469	1.973303	8.484763
H	10.508667	1.645948	6.916640
C	16.424070	0.625748	4.488472
H	16.365548	0.285059	5.527061
H	15.862045	-0.074675	3.874310
C	17.869751	0.699474	4.034357
H	17.908724	0.878327	2.958596
H	18.375245	-0.244223	4.236358
C	18.568336	1.828513	4.769424
H	19.566571	1.991701	4.365597
H	18.678627	1.593686	5.833064
B	14.289037	2.054693	4.162093

$[B_2(hpp)_2Br_2H]^+$

Illustration of the calculated minimum structure of [(**5**)+H]$^+$. Hydrogen atoms omitted.



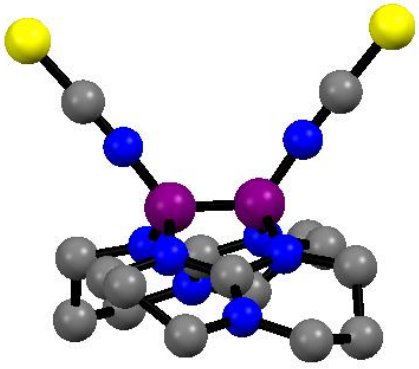
Cartesian coordinates (in Å):

Br	14.084836	5.328443	2.469180
N	13.202372	4.269246	5.099621
N	15.700548	4.016666	4.565031
C	12.436564	5.508569	5.299440
H	11.533385	5.486708	4.684431
H	13.040707	6.338780	4.946295
C	12.093302	5.669668	6.767769
H	13.007907	5.808975	7.347678
H	11.467987	6.549324	6.915571
C	11.357900	4.434088	7.249458
H	11.263037	4.437877	8.335175
H	10.347462	4.397909	6.831056
N	12.077413	3.211111	6.872210
C	12.919447	3.168838	5.825494
C	16.326191	5.237194	5.088890
H	16.298496	5.221499	6.182595
H	15.734627	6.085455	4.752491
C	17.752092	5.342741	4.583671
H	17.740484	5.446727	3.497638
H	18.246525	6.219503	5.000316
C	18.508533	4.091021	4.986979
H	19.458707	4.028985	4.456571
H	18.731482	4.101538	6.058321
N	17.746040	2.874785	4.672223
C	16.418978	2.881861	4.464398
B	14.279171	4.113951	4.056241
Br	13.296633	0.645501	2.856285
N	13.531336	2.025427	5.457468
N	15.740229	1.759290	4.149219
C	13.377471	0.777806	6.225981
H	12.675371	0.127246	5.701543
H	14.342734	0.271019	6.235187
C	12.898866	1.048994	7.638290
H	13.689023	1.512644	8.232169
H	12.625117	0.111400	8.120364
C	11.702723	1.979714	7.574624
H	11.372233	2.261293	8.572742
H	10.858667	1.501044	7.068847

C	16.424591	0.473529	3.928015
H	16.306847	-0.151030	4.818112
H	15.927889	-0.035852	3.107016
C	17.896304	0.677016	3.627890
H	18.022856	1.108764	2.633434
H	18.410052	-0.283407	3.642290
C	18.491393	1.611078	4.664038
H	19.528244	1.845550	4.430740
H	18.472527	1.159224	5.660799
B	14.234018	1.898585	4.115920
H	14.004985	2.992612	3.441561

$B_2(hpp)_2(NCS)_2$ (6)

Illustration of the calculated minimum structure of **6**. Hydrogen atoms omitted.



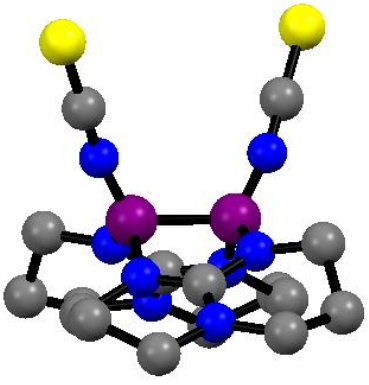
Cartesian coordinates (in Å):

S	6.753306	7.761451	4.989011
S	5.719088	13.636400	1.170386
N	4.966830	11.877141	7.218084
N	4.784894	13.802202	6.040092
N	3.076124	13.241427	7.564825
N	7.553007	12.149277	7.162225
N	7.372999	14.007037	5.880498
N	9.231935	13.797760	7.314692
N	6.404600	10.389173	5.815033
N	5.996579	13.309651	3.913582
C	4.255354	12.976928	6.949573
C	4.512935	10.916439	8.206371
H	4.899815	11.170342	9.202445
H	4.920985	9.942609	7.936613
C	2.991219	10.872518	8.236112
H	2.634533	10.207969	9.023634
H	2.628225	10.487377	7.281173
C	2.448528	12.275156	8.464494
H	1.371363	12.300868	8.283542

H	2.609114	12.585199	9.503944
C	2.326268	14.465007	7.292589
H	1.880405	14.801702	8.231840
H	1.502079	14.242306	6.604548
C	3.222692	15.547049	6.709702
H	3.894346	15.924558	7.484269
H	2.610533	16.379598	6.361585
C	4.047032	14.962169	5.571140
H	3.399147	14.695232	4.727878
H	4.763688	15.691846	5.195397
C	8.072979	13.324850	6.792878
C	8.283053	11.259807	8.048677
H	8.955469	10.608776	7.477619
H	7.563987	10.608043	8.544159
C	9.069687	12.073800	9.066759
H	8.373232	12.616410	9.710271
H	9.676732	11.426237	9.700131
C	9.968836	13.061373	8.338456
H	10.386685	13.788025	9.039636
H	10.812644	12.537003	7.874390
C	9.852270	15.023672	6.815240
H	10.933098	14.865704	6.791919
H	9.660584	15.843253	7.518101
C	7.817217	15.308841	5.418100
H	7.401191	16.107805	6.046416
H	7.431806	15.453686	4.409058
C	6.553369	9.278117	5.460620
C	5.878135	13.443254	2.751549
B	6.264911	11.780556	6.355256
B	6.099139	13.237323	5.407501
C	9.338202	15.379079	5.428218
H	9.731403	14.670797	4.696278
H	9.685449	16.375097	5.151890

$[B_2(hpp)_2(NCS)_2]^+$

Illustration of the calculated minimum structure of [**6**]$^+$. Hydrogen atoms omitted.



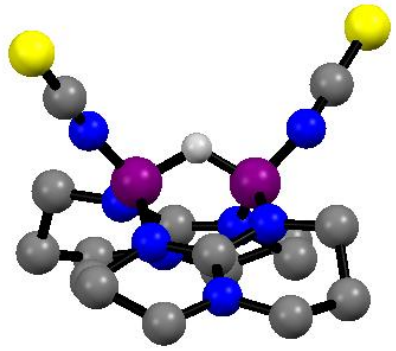
Cartesian coordinates (in Å):

S	5.006535	8.333622	4.405215
S	7.474168	12.896171	1.503205
N	5.104707	12.156813	7.409293
N	4.691647	13.719123	5.816098
N	3.091114	13.365896	7.499882
N	7.652088	11.979135	6.993970
N	7.225335	14.065222	6.209000
N	9.217287	13.684787	7.397467
N	6.062825	10.446001	5.838360
N	6.331508	13.316762	3.983025
C	4.268965	13.086436	6.928064
C	4.789246	11.451215	8.653187
H	5.160914	12.016957	9.512956
H	5.309404	10.494818	8.637090
C	3.284124	11.244186	8.751445
H	3.020036	10.775496	9.698825
H	2.961090	10.579771	7.948124
C	2.579086	12.585849	8.634022
H	1.508285	12.444477	8.480372
H	2.703169	13.173126	9.548653
C	2.206420	14.428259	7.000610
H	1.831201	14.982078	7.863011
H	1.346935	13.955688	6.516548
C	2.919830	15.357964	6.030637
H	3.578279	16.037864	6.574610
H	2.182330	15.961709	5.502764
C	3.747093	14.535226	5.052104
H	3.103779	13.899108	4.437169
H	4.315481	15.170116	4.376978
C	8.057886	13.258998	6.880779
C	8.601571	10.962806	7.449623
H	9.268996	10.670980	6.633471
H	8.039331	10.078802	7.740127
C	9.392711	11.532338	8.619397
H	8.711249	11.740944	9.446320
H	10.133136	10.815267	8.972348
C	10.097224	12.808348	8.183794
H	10.443648	13.374575	9.050198
H	10.974929	12.572908	7.575031
C	9.713685	15.046784	7.161924
H	10.789953	14.981463	6.995954
H	9.558299	15.638780	8.068685
C	7.521642	15.493752	6.081130
H	7.120417	16.040927	6.939594
H	7.017019	15.862146	5.189330
C	5.595385	9.542477	5.218676
C	6.836370	13.131175	2.920118
B	6.257227	11.706329	6.503028
B	6.101930	13.404674	5.400098

C	9.027013	15.691832	5.968930
H	9.379928	15.236024	5.042236
H	9.275173	16.752096	5.935124

$[B_2(hpp)_2(NCS)_2H]^+$

Illustration of the calculated minimum structure of [(**6**)+H]$^+$. Hydrogen atoms omitted.



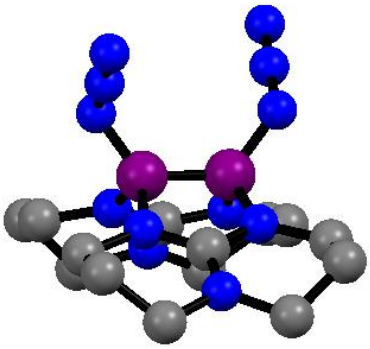
Cartesian coordinates (in Å):

S	4.718846	7.845614	5.599763
S	7.722809	14.125061	1.544775
N	5.121410	12.092006	7.339977
N	4.671926	13.711394	5.775468
N	3.094641	13.265233	7.451228
N	7.677193	11.931396	6.994013
N	7.216144	14.005326	6.122756
N	9.219184	13.671145	7.294733
N	6.172029	10.111228	6.223310
N	6.223820	13.756354	3.836164
C	4.280355	13.026926	6.864643
C	4.797766	11.422596	8.605030
H	5.084927	12.063208	9.444354
H	5.390348	10.513131	8.667367
C	3.312199	11.109622	8.650303
H	3.042482	10.623172	9.586931
H	3.065128	10.426413	7.835997
C	2.542467	12.410419	8.512234
H	1.495674	12.218775	8.269597
H	2.561734	12.972132	9.450727
C	2.212898	14.367044	7.040997
H	1.848459	14.854595	7.947283
H	1.345644	13.938427	6.530457
C	2.923949	15.357817	6.137140
H	3.602682	15.985028	6.718414
H	2.190074	16.010376	5.665644
C	3.716411	14.589651	5.093029
H	3.050378	14.001314	4.455204

H	4.275397	15.257799	4.444381
C	8.052868	13.209560	6.811509
C	8.633632	10.970349	7.552529
H	9.325530	10.630446	6.776415
H	8.079086	10.100404	7.892081
C	9.386206	11.633779	8.693349
H	8.682184	11.905964	9.482140
H	10.120043	10.952922	9.122977
C	10.091833	12.868873	8.163483
H	10.425603	13.510784	8.981106
H	10.978485	12.585455	7.588995
C	9.758365	14.994854	6.950779
H	10.814391	14.867080	6.706001
H	9.704732	15.629312	7.840297
C	7.519017	15.437729	6.022910
H	7.198783	15.946206	6.937400
H	6.941453	15.848548	5.198420
C	5.527657	9.145266	5.947309
C	6.888073	13.904783	2.855768
B	6.296051	11.535796	6.526945
B	6.070384	13.464069	5.260145
C	9.008297	15.629186	5.793855
H	9.288575	15.160749	4.848893
H	9.261960	16.686617	5.729823
H	6.192937	12.131640	5.331875

$B_2(hpp)_2(N_3)_2$ (7)

Illustration of the calculated minimum structure of **7**. Hydrogen atoms omitted.



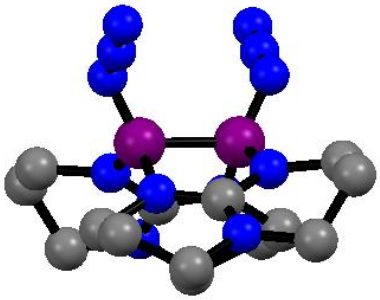
Cartesian coordinates (in Å):

N	5.147271	0.222927	2.209495
N	3.195666	0.849702	1.244906
N	5.221935	1.548753	0.255871
N	4.037905	-1.927496	3.179695
N	2.124840	-1.366712	2.103710
N	2.611779	-3.654497	2.433981

N	4.567804	-0.004399	4.688991
N	4.832856	1.142120	4.964068
N	5.108844	2.200300	5.278690
N	1.505242	0.909685	3.088122
N	0.838355	0.458369	3.989269
N	0.167904	0.082034	4.828167
C	4.532124	0.878761	1.218516
C	6.595934	0.134159	2.285648
H	6.942262	-0.800913	1.825833
H	6.873927	0.092374	3.338914
C	7.253868	1.322395	1.599957
H	8.334729	1.186635	1.544499
H	7.055660	2.229015	2.174805
C	6.677428	1.473957	0.199900
H	7.039555	2.390773	-0.268299
H	6.995008	0.637390	-0.436673
C	4.515968	2.152314	-0.868326
H	4.412591	1.431529	-1.690267
H	5.125260	2.978401	-1.238474
C	3.148204	2.649212	-0.423665
H	3.277042	3.463433	0.292173
H	2.595423	3.037286	-1.280171
C	2.386076	1.508103	0.233625
H	1.482984	1.873753	0.722137
H	2.072618	0.782614	-0.528605
C	2.923241	-2.336453	2.564922
C	5.007142	-2.860616	3.728944
H	5.430151	-2.406064	4.624695
H	5.831433	-3.008510	3.018863
C	4.359713	-4.198842	4.052927
H	5.116971	-4.937700	4.318272
H	3.687292	-4.083285	4.905266
C	3.563288	-4.678846	2.848429
H	4.238124	-4.935450	2.021082
H	2.996868	-5.578617	3.093704
C	1.439064	-4.066250	1.671012
H	1.101307	-5.023444	2.071649
H	1.703822	-4.230667	0.618006
C	0.340491	-3.019428	1.783468
H	-0.014384	-2.974293	2.814883
H	-0.502049	-3.294470	1.147655
C	0.899433	-1.662908	1.380521
H	1.084284	-1.641927	0.298362
H	0.183426	-0.869631	1.596096
B	4.134576	-0.376923	3.251272
B	2.648947	0.068547	2.473482

$[B_2(hpp)_2(N_3)_2]^+$

Illustration of the calculated minimum structure of [**7**]$^+$. Hydrogen atoms omitted.



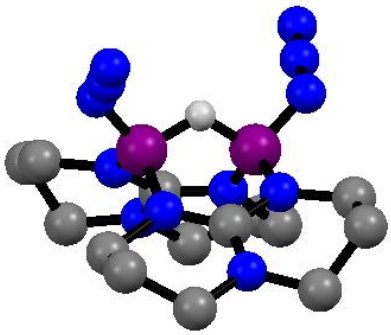
Cartesian coordinates (in Å):

N	5.064629	0.077070	2.038052
N	3.103166	0.991124	1.352302
N	5.074519	1.530612	0.187059
N	4.022849	-1.887840	3.379825
N	2.315001	-1.407227	1.963727
N	2.773509	-3.660075	2.467127
N	4.591935	0.227903	4.548436
N	5.039767	1.363847	4.602356
N	5.449895	2.406714	4.728294
N	1.483578	0.669491	3.206728
N	0.764698	-0.005142	3.929191
N	0.069520	-0.562568	4.620300
C	4.430845	0.879648	1.166443
C	6.490704	-0.227724	1.880266
H	6.615759	-1.118476	1.256980
H	6.894681	-0.458256	2.865357
C	7.212254	0.963200	1.267902
H	8.252337	0.713568	1.060635
H	7.201457	1.796516	1.972398
C	6.517846	1.370017	-0.021999
H	6.907970	2.321738	-0.381427
H	6.690800	0.627095	-0.807086
C	4.315605	2.356272	-0.758404
H	3.955755	1.742267	-1.590226
H	4.999807	3.096707	-1.169058
C	3.159332	3.027776	-0.033623
H	3.555575	3.708132	0.722318
H	2.566826	3.616385	-0.732976
C	2.286725	1.969796	0.620034
H	1.587005	2.416920	1.323876
H	1.699771	1.443128	-0.138611
C	3.031614	-2.351016	2.597205
C	4.777895	-2.760037	4.290617
H	4.905505	-2.230998	5.233294
H	5.774025	-2.930923	3.871140

C	4.061820	-4.083938	4.496577
H	4.723265	-4.788820	4.998865
H	3.183730	-3.942179	5.129237
C	3.624472	-4.640169	3.150280
H	4.489438	-4.887553	2.526556
H	3.040001	-5.549751	3.276528
C	1.709353	-4.148993	1.583296
H	1.286121	-5.043773	2.038765
H	2.142214	-4.443546	0.622036
C	0.634615	-3.091298	1.389072
H	0.077899	-2.954688	2.317670
H	-0.067435	-3.419281	0.623191
C	1.282976	-1.774820	0.988466
H	1.722413	-1.847971	-0.011157
H	0.545214	-0.973744	0.963731
B	4.281036	-0.408194	3.259058
B	2.529915	0.049275	2.379379

$[B_2(hpp)_2(N_3)_2H]^+$

Illustration of the calculated minimum structure of [**7**+(H)]$^+$. Hydrogen atoms omitted.



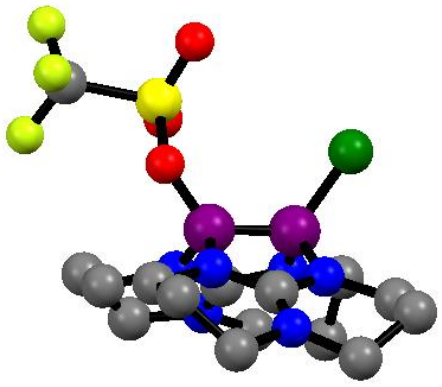
Cartesian coordinates (in Å):

N	5.033987	0.109915	2.109163
N	3.058464	1.030379	1.383559
N	5.046402	1.528212	0.237527
N	4.061142	-1.886296	3.439117
N	2.309585	-1.355908	2.050932
N	2.777534	-3.613085	2.499174
N	5.069833	0.017614	4.658013
N	5.560951	1.134544	4.738229
N	6.042103	2.142684	4.885320
N	1.124138	0.736767	2.900456
N	0.368342	0.080318	3.602568
N	-0.380443	-0.462517	4.246142
C	4.387348	0.898791	1.227522
C	6.441900	-0.239178	1.874721

H	6.500204	-1.087716	1.185715
H	6.869565	-0.559625	2.822386
C	7.191263	0.956158	1.316040
H	8.225601	0.695381	1.094773
H	7.198580	1.758486	2.055274
C	6.498255	1.416185	0.047159
H	6.867324	2.395607	-0.257124
H	6.696650	0.721948	-0.775467
C	4.306253	2.304249	-0.763565
H	3.970704	1.648661	-1.573488
H	4.997828	3.026569	-1.193024
C	3.131394	3.000017	-0.101604
H	3.502089	3.716905	0.633300
H	2.549935	3.550749	-0.839960
C	2.256186	1.960908	0.570681
H	1.521268	2.426203	1.222672
H	1.707557	1.388566	-0.183112
C	3.047695	-2.304888	2.661107
C	4.860030	-2.811539	4.261224
H	5.051619	-2.329639	5.216591
H	5.827644	-2.969549	3.775886
C	4.149199	-4.137431	4.446503
H	4.830950	-4.863668	4.887392
H	3.301148	-4.021977	5.123986
C	3.653575	-4.626054	3.098097
H	4.489804	-4.843567	2.426009
H	3.071831	-5.539853	3.202500
C	1.669263	-4.103303	1.669648
H	1.231309	-4.961819	2.178759
H	2.069711	-4.458521	0.714962
C	0.624169	-3.026556	1.445319
H	0.058057	-2.851903	2.361410
H	-0.075834	-3.350052	0.675811
C	1.324947	-1.745583	1.032304
H	1.825553	-1.873339	0.067322
H	0.613968	-0.929122	0.924330
B	4.394815	-0.410407	3.399946
B	2.393047	0.132051	2.404324
H	3.206192	0.187083	3.456005

$B_2(hpp)_2(OTf)Cl$ (8)

Illustration of the calculated minimum structure of **8**. Hydrogen atoms omitted.



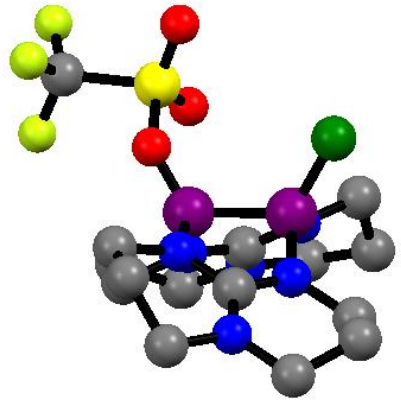
Cartesian coordinates (in Å):

Cl	3.327033	4.767048	12.162157
S	3.061023	3.222525	8.661359
F	3.706295	1.089539	7.205516
F	3.937056	2.976863	6.156829
F	1.953288	2.172319	6.518336
O	4.541782	3.149777	9.034612
O	2.248081	2.397244	9.495414
O	2.648261	4.555329	8.321291
N	6.140643	4.772339	12.051690
N	6.649322	3.574718	10.194067
N	8.100952	3.455113	12.051190
N	4.875505	6.555268	10.632783
N	5.538487	5.441999	8.770848
N	5.082700	7.746303	8.605960
C	6.982477	3.931886	11.443432
C	6.381685	5.265036	13.397654
H	5.412339	5.381383	13.881996
H	6.849338	6.256919	13.352612
C	7.265941	4.308663	14.184007
H	7.565988	4.755343	15.132715
H	6.710073	3.394715	14.402349
C	8.497228	3.962804	13.360181
H	9.144463	4.842779	13.250044
H	9.086476	3.187351	13.852262
C	9.065863	2.659785	11.299767
H	9.595655	2.022921	12.009885
H	9.813267	3.310186	10.826443
C	8.355296	1.818078	10.250051
H	7.723781	1.079299	10.747319
H	9.087255	1.283020	9.644008
C	7.494351	2.719904	9.378022
H	8.132557	3.330214	8.725828
H	6.845856	2.127446	8.732698

C	5.157694	6.602033	9.325179
C	4.342530	7.722163	11.315311
H	4.573280	7.629493	12.375627
H	3.250608	7.745662	11.234099
C	4.953010	8.986727	10.728043
H	4.518360	9.877124	11.183635
H	6.027390	8.998525	10.927011
C	4.709132	9.013742	9.227077
H	3.653302	9.222647	9.017979
H	5.295879	9.805465	8.753993
C	5.183447	7.747023	7.145395
H	6.148504	8.176131	6.851364
H	4.404441	8.409039	6.759042
C	5.019240	6.347413	6.572475
H	5.291932	6.350193	5.516604
H	3.981035	6.026305	6.661104
C	5.890882	5.381397	7.362955
H	5.738427	4.360003	7.022635
H	6.952235	5.622855	7.218694
C	3.174785	2.304779	7.039170
B	4.896216	5.097865	11.170256
B	5.346449	4.257399	9.742926

$[B_2(hpp)_2(OTf)Cl]^+$

Illustration of the calculated minimum structure of [**8**]$^+$. Hydrogen atoms omitted.



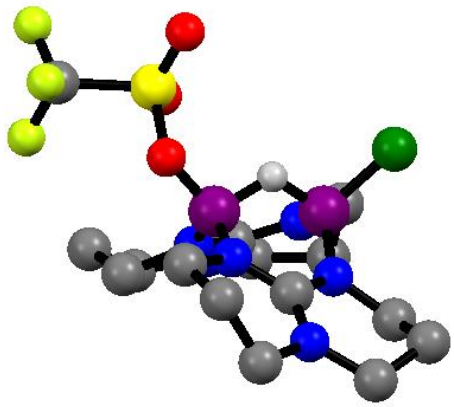
Cartesian coordinates (in Å):

Cl	3.718335	4.358210	12.396121
S	3.005328	3.579547	8.589863
F	3.437615	1.558353	6.943842
F	4.128670	3.480089	6.203557
F	2.002110	3.029178	6.237377
O	4.462020	3.245749	9.066706
O	2.072880	2.785674	9.309321

O	2.833491	4.993772	8.431090
N	6.410373	4.926467	11.848313
N	6.590774	3.370710	10.209621
N	8.263592	3.476350	11.860273
N	4.624795	6.391228	10.697919
N	5.708719	5.442208	8.944676
N	4.992547	7.671746	8.761145
C	7.119780	3.916494	11.326082
C	6.915353	5.685636	12.996621
H	6.056100	6.074244	13.540882
H	7.505607	6.538232	12.649279
C	7.746528	4.774014	13.887961
H	8.205136	5.345326	14.694305
H	7.097015	4.021071	14.337165
C	8.830806	4.095301	13.064555
H	9.603443	4.812491	12.771519
H	9.315190	3.309877	13.643838
C	9.002201	2.397989	11.193314
H	9.635821	1.924008	11.940501
H	9.655968	2.811986	10.419461
C	8.016345	1.399585	10.603344
H	7.442718	0.942880	11.411645
H	8.549471	0.604360	10.083912
C	7.084267	2.110348	9.635114
H	7.607094	2.334373	8.701023
H	6.224953	1.488621	9.389886
C	5.110877	6.535191	9.444544
C	3.638988	7.361119	11.181992
H	3.537576	7.235136	12.256047
H	2.665049	7.156267	10.730057
C	4.132296	8.756053	10.823053
H	3.415792	9.511353	11.144081
H	5.073201	8.950028	11.341356
C	4.327217	8.859457	9.318175
H	3.363153	8.966621	8.813724
H	4.931779	9.730946	9.061853
C	5.416315	7.775536	7.357112
H	6.360228	8.326573	7.319301
H	4.668149	8.371335	6.833242
C	5.551367	6.406666	6.711263
H	6.044535	6.506762	5.745086
H	4.564404	5.977128	6.547154
C	6.348914	5.485973	7.625443
H	6.369251	4.473611	7.226414
H	7.382978	5.828667	7.722015
C	3.149789	2.852178	6.874395
B	4.982678	5.094402	11.347458
B	5.429521	4.140979	9.669900

$[B_2(hpp)_2(OTf)ClH]^+$

Illustration of the calculated minimum structure of [(**8**)+H]$^+$. Hydrogen atoms omitted.



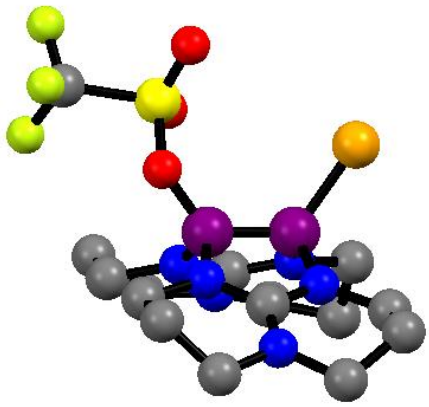
Cartesian coordinates (in Å):

Cl	3.668443	4.866595	12.870722
S	3.084804	3.291952	8.363436
F	3.735018	1.361992	6.682398
F	4.158733	3.364328	5.954124
F	2.108258	2.646171	6.028394
O	4.584604	3.118373	8.805352
O	2.261956	2.389807	9.092262
O	2.759989	4.682476	8.245818
N	6.298412	4.921227	11.908061
N	6.517779	3.368077	10.234384
N	8.167431	3.500545	11.897956
N	4.601802	6.496730	10.785737
N	5.553224	5.415746	8.996861
N	4.960761	7.673358	8.788110
C	7.012724	3.921803	11.358026
C	6.870993	5.696766	13.016589
H	6.051272	6.177047	13.547135
H	7.517174	6.484335	12.615185
C	7.645720	4.778982	13.943611
H	8.113369	5.346686	14.748358
H	6.957405	4.060913	14.394224
C	8.713791	4.056427	13.143236
H	9.538104	4.733759	12.896426
H	9.131269	3.229151	13.718910
C	8.974027	2.490886	11.202733
H	9.619356	2.021305	11.943566
H	9.620036	2.972941	10.460997
C	8.059154	1.469382	10.551024
H	7.494169	0.944374	11.324509
H	8.643202	0.728773	10.004492
C	7.114624	2.180056	9.600357
H	7.652397	2.493232	8.699856

H	6.308113	1.520091	9.287134
C	5.035442	6.548337	9.510958
C	3.825958	7.621184	11.325131
H	3.822966	7.542879	12.408321
H	2.786978	7.551563	10.990017
C	4.462541	8.921216	10.866142
H	3.896760	9.777643	11.233351
H	5.475339	8.993259	11.270052
C	4.493902	8.948803	9.349949
H	3.496087	9.151594	8.948814
H	5.159803	9.733718	8.984525
C	5.270689	7.722044	7.351240
H	6.215737	8.259415	7.222732
H	4.489968	8.313504	6.868714
C	5.345325	6.335517	6.741712
H	5.801359	6.393725	5.753270
H	4.345582	5.916628	6.632824
C	6.162124	5.442864	7.659787
H	6.190778	4.423027	7.281553
H	7.194359	5.799809	7.735151
C	3.284867	2.609563	6.633865
B	4.853587	5.213680	11.530487
B	5.324277	4.064185	9.637076
H	4.516664	4.268860	10.660451

$B_2(hpp)_2(OTf)Br$ (9)

Illustration of the calculated minimum structure of **9**. Hydrogen atoms omitted.



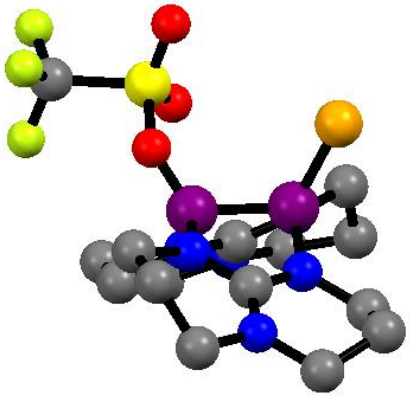
Cartesian coordinates (in Å):

Br	3.170467	4.687083	12.301918
S	3.019190	3.152447	8.701884
F	1.949310	2.064101	6.558702
F	3.714534	1.018164	7.271554
F	3.921910	2.898395	6.205633

O	4.495428	3.100091	9.096963
O	2.205670	2.321826	9.529399
O	2.596046	4.477907	8.346738
N	6.124273	4.774097	12.068741
N	6.612189	3.547998	10.222910
N	8.080572	3.449510	12.067154
N	4.819590	6.525760	10.650319
N	5.472704	5.397479	8.792366
N	4.995020	7.695103	8.607315
C	6.958594	3.920755	11.463548
C	6.398081	5.302524	13.395355
H	5.439880	5.452612	13.892034
H	6.885826	6.282209	13.313055
C	7.273934	4.349289	14.193877
H	7.589564	4.810778	15.130303
H	6.704013	3.450126	14.435878
C	8.492514	3.967413	13.367744
H	9.156372	4.832517	13.241104
H	9.069349	3.187526	13.867512
C	9.031749	2.633280	11.319915
H	9.563913	2.005391	12.036090
H	9.778863	3.269706	10.827855
C	8.304122	1.778260	10.293054
H	7.672129	1.053535	10.809969
H	9.025587	1.226636	9.689378
C	7.441301	2.670833	9.413630
H	8.077086	3.264160	8.743825
H	6.781037	2.072127	8.786445
C	5.087155	6.560068	9.337560
C	4.301985	7.701725	11.330451
H	4.554974	7.620898	12.386491
H	3.208746	7.722899	11.272751
C	4.898853	8.959373	10.715765
H	4.471370	9.853972	11.169713
H	5.977024	8.975850	10.892857
C	4.624955	8.967785	9.219974
H	3.564088	9.167657	9.028980
H	5.197713	9.756792	8.725869
C	5.082490	7.682378	7.145667
H	6.038786	8.122365	6.839603
H	4.290823	8.329658	6.760150
C	4.933335	6.275144	6.587654
H	3.899937	5.941504	6.684241
H	5.201268	6.270923	5.530608
C	5.821063	5.328506	7.383646
H	5.682664	4.302115	7.053381
H	6.878411	5.583895	7.234473
C	3.163562	2.222380	7.088639
B	4.877156	5.081173	11.198480
B	5.301327	4.221404	9.778380

$[B_2(hpp)_2(OTf)Br]^+$

Illustration of the calculated minimum structure of [**9**]$^+$. Hydrogen atoms omitted.



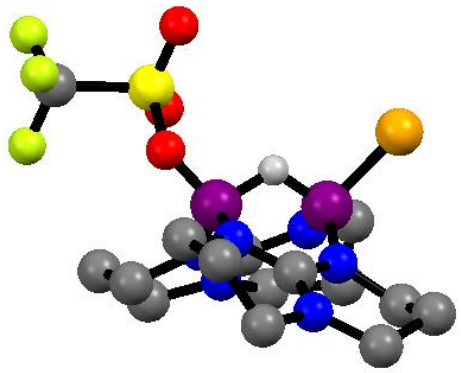
Cartesian coordinates (in Å):

Br	3.595583	4.226849	12.510186
S	2.967308	3.501975	8.634479
F	1.958755	2.922928	6.291235
F	3.414667	1.473963	7.001163
F	4.079791	3.397546	6.242399
O	4.430539	3.190458	9.105529
O	2.048124	2.700648	9.362726
O	2.776934	4.912904	8.467432
N	6.385426	4.922104	11.857531
N	6.560694	3.345390	10.239938
N	8.241808	3.475537	11.880958
N	4.579858	6.360642	10.716224
N	5.649557	5.398470	8.960703
N	4.918284	7.621573	8.760020
C	7.095322	3.906069	11.345728
C	6.897851	5.702164	12.988229
H	6.041781	6.101277	13.529715
H	7.487347	6.547143	12.621838
C	7.732028	4.804434	13.890875
H	8.194217	5.388381	14.686020
H	7.083090	4.059840	14.354570
C	8.812773	4.111359	13.074773
H	9.586065	4.822407	12.768942
H	9.297061	3.333678	13.664477
C	8.978994	2.389050	11.225552
H	9.616296	1.925997	11.976429
H	9.628882	2.793415	10.443461
C	7.991438	1.381850	10.653560
H	7.422241	0.935404	11.470659
H	8.522959	0.580324	10.142266
C	7.053488	2.078043	9.680369

H	7.570735	2.290546	8.740547
H	6.194027	1.451747	9.448105
C	5.050270	6.493391	9.454850
C	3.602718	7.336376	11.206179
H	3.522042	7.224316	12.283494
H	2.620462	7.124314	10.776151
C	4.086723	8.727392	10.820888
H	3.374123	9.484832	11.145471
H	5.036188	8.929849	11.320038
C	4.254926	8.812562	9.311956
H	3.281850	8.907728	8.822634
H	4.850097	9.683868	9.034049
C	5.325679	7.712140	7.350150
H	6.265272	8.269119	7.295818
H	4.567634	8.296949	6.828119
C	5.462830	6.336993	6.718454
H	4.477085	5.899319	6.569743
H	5.945263	6.429193	5.746093
C	6.275983	5.432007	7.634553
H	6.299440	4.415480	7.246690
H	7.308478	5.782985	7.717068
C	3.111731	2.763950	6.923516
B	4.958558	5.069542	11.362327
B	5.387227	4.101678	9.702619

$[B_2(hpp)_2(OTf)BrH]^+$

Illustration of the calculated minimum structure of [(**9**)+H]$^+$. Hydrogen atoms omitted.



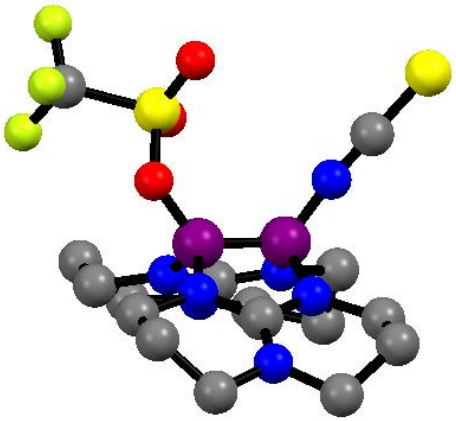
Cartesian coordinates (in Å):

Br	3.539885	4.750272	12.988886
S	3.067044	3.224188	8.402161
F	2.085811	2.554082	6.075920
F	3.726507	1.288458	6.731386
F	4.129654	3.289100	5.987091
O	4.571023	3.067741	8.838877

O	2.257114	2.319010	9.140727
O	2.729066	4.610621	8.276613
N	6.281945	4.912576	11.908751
N	6.512877	3.347773	10.248675
N	8.156578	3.499671	11.917039
N	4.563219	6.458126	10.785176
N	5.518081	5.376606	8.997491
N	4.895969	7.624478	8.775538
C	7.002924	3.911413	11.369656
C	6.850972	5.702919	13.008320
H	6.030083	6.190903	13.528286
H	7.499493	6.483004	12.598812
C	7.619615	4.794629	13.949822
H	8.081968	5.369615	14.751261
H	6.927801	4.082571	14.402362
C	8.692828	4.063874	13.163353
H	9.519524	4.737352	12.918220
H	9.104026	3.240540	13.747610
C	8.969524	2.486814	11.233766
H	9.611333	2.024808	11.981205
H	9.617889	2.964837	10.492859
C	8.060779	1.458038	10.584325
H	7.493961	0.937043	11.357876
H	8.649508	0.716219	10.046274
C	7.118428	2.159138	9.624110
H	7.659472	2.469832	8.725781
H	6.317140	1.494485	9.310421
C	4.988287	6.506432	9.506601
C	3.791073	7.584140	11.327446
H	3.806600	7.515212	12.410347
H	2.747808	7.505317	11.011361
C	4.411934	8.884167	10.847816
H	3.845960	9.738632	11.216643
H	5.429411	8.966746	11.235282
C	4.420656	8.899207	9.331357
H	3.415674	9.086072	8.942970
H	5.071337	9.687886	8.949566
C	5.194118	7.665419	7.335827
H	6.130118	8.213830	7.195796
H	4.402419	8.242293	6.855426
C	5.282324	6.275191	6.736517
H	4.288212	5.842925	6.638280
H	5.730170	6.331352	5.745191
C	6.117267	5.400725	7.655903
H	6.156804	4.378913	7.286243
H	7.144302	5.771559	7.721135
C	3.265353	2.531672	6.676176
B	4.838098	5.178434	11.525191
B	5.311622	4.028710	9.649935
H	4.503680	4.230133	10.681140

$B_2(hpp)_2(OTf)(NCS)$ (10)

Illustration of the calculated minimum structure of **10**. Hydrogen atoms omitted.



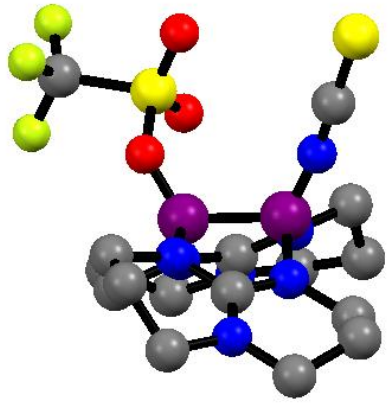
Cartesian coordinates (in Å):

S	3.011030	3.169409	8.772677
F	1.757697	2.137153	6.704522
F	3.533085	1.028338	7.283994
F	3.728074	2.915085	6.226175
O	4.518219	3.094319	9.035733
O	2.262873	2.357374	9.677789
O	2.581788	4.504711	8.463067
N	6.049946	4.712547	12.086178
N	6.610133	3.544473	10.226285
N	8.040098	3.443651	12.101176
N	4.803071	6.500687	10.633535
N	5.491958	5.388595	8.782849
N	4.995460	7.683842	8.602004
C	6.919515	3.898458	11.482890
C	6.243367	5.180433	13.448898
H	5.262962	5.250391	13.921125
H	6.671533	6.190620	13.437905
C	7.148547	4.240693	14.232480
H	7.418742	4.681273	15.192707
H	6.622544	3.304298	14.428378
C	8.402358	3.950587	13.420641
H	9.018061	4.854698	13.328458
H	9.013075	3.191457	13.911484
C	9.034459	2.677625	11.357213
H	9.566866	2.044913	12.068957
H	9.774240	3.349837	10.903186
C	8.359725	1.831721	10.287287
H	7.739656	1.071496	10.766255
H	9.113463	1.322160	9.686098
C	7.489499	2.722133	9.412567

H	8.121183	3.356952	8.777924
H	6.866292	2.121163	8.750354
C	5.090153	6.545886	9.327326
C	4.221022	7.652987	11.301303
H	4.440196	7.576579	12.365876
H	3.129636	7.644854	11.202598
C	4.800247	8.933380	10.716308
H	4.330877	9.812127	11.159529
H	5.870156	8.979076	10.932893
C	4.579844	8.944776	9.211399
H	3.522499	9.124306	8.984233
H	5.153093	9.749175	8.743591
C	5.104511	7.674665	7.141917
H	6.070645	8.101349	6.848478
H	4.326967	8.333085	6.747375
C	4.942474	6.270225	6.580747
H	3.905731	5.946548	6.679965
H	5.206392	6.265651	5.522741
C	5.825033	5.313352	7.370186
H	5.666195	4.288079	7.042823
H	6.884075	5.552256	7.208514
C	3.009988	2.249953	7.148656
B	4.808548	5.038015	11.184227
B	5.304547	4.203626	9.755875
N	3.553262	4.796777	11.963187
C	2.597405	4.703771	12.642161
S	1.305664	4.585957	13.576593

$[B_2(hpp)_2(OTf)(NCS)]^+$

Illustration of the calculated minimum structure of [**9**]$^+$. Hydrogen atoms omitted.



Cartesian coordinates (in Å):

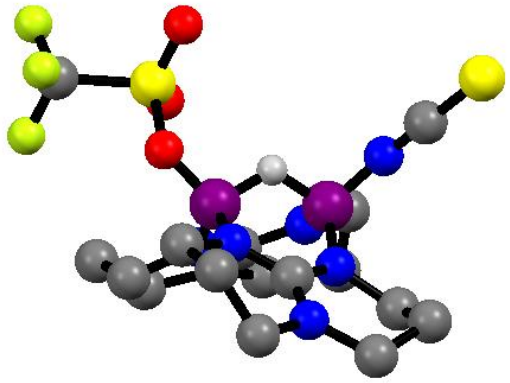
S	2.904242	3.583812	8.702131
F	1.744486	2.976094	6.438829

F	3.214947	1.514000	7.089048
F	3.866903	3.411059	6.254270
O	4.384803	3.248091	9.089824
O	2.012686	2.826267	9.510122
O	2.732699	4.994778	8.514393
N	6.268092	4.915769	11.919742
N	6.497738	3.378767	10.268579
N	8.129552	3.476536	11.960533
N	4.569548	6.430884	10.681954
N	5.640583	5.432033	8.950074
N	4.939669	7.662786	8.716563
C	6.995619	3.917135	11.402195
C	6.743337	5.670489	13.082230
H	5.871224	6.046718	13.615482
H	7.328015	6.534512	12.753208
C	7.572579	4.765438	13.982138
H	8.013474	5.339205	14.796611
H	6.927705	4.002255	14.421005
C	8.675168	4.102203	13.170591
H	9.441309	4.830576	12.887601
H	9.163877	3.323260	13.754955
C	8.893438	2.410275	11.303400
H	9.501660	1.925937	12.065175
H	9.573448	2.837079	10.559455
C	7.933546	1.417809	10.663395
H	7.335967	0.942797	11.443405
H	8.488701	0.635429	10.147512
C	7.029874	2.142313	9.678987
H	7.585605	2.396543	8.771736
H	6.188845	1.516605	9.384711
C	5.052152	6.541241	9.427585
C	3.593771	7.416419	11.149720
H	3.501863	7.318860	12.228536
H	2.613470	7.208451	10.711993
C	4.089805	8.800756	10.754524
H	3.378212	9.567459	11.059090
H	5.034152	9.003313	11.263116
C	4.278630	8.864913	9.246300
H	3.312377	8.962120	8.743771
H	4.883503	9.728929	8.966406
C	5.353440	7.726901	7.307600
H	6.307081	8.258942	7.247176
H	4.611450	8.323644	6.776105
C	5.457279	6.340482	6.693937
H	4.461103	5.921846	6.556844
H	5.935767	6.408682	5.717613
C	6.256237	5.431979	7.618587
H	6.253171	4.409039	7.246003
H	7.297404	5.759826	7.686489
C	2.931248	2.807717	7.002652
B	4.858267	5.116594	11.350332

B	5.347535	4.150173	9.702974
N	3.784666	4.550670	12.117064
C	3.031619	3.844549	12.712642
S	2.025257	2.937042	13.502590

$[B_2(hpp)_2(OTf)(NCS)H]^+$

Illustration of the calculated minimum structure of [(**10**)+H]$^+$. Hydrogen atoms omitted.



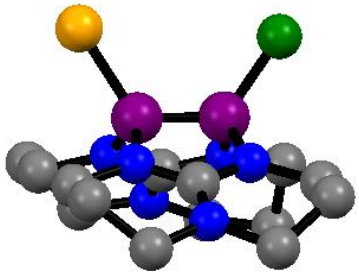
Cartesian coordinates (in Å):

S	3.013696	3.260000	8.290367
F	2.049831	2.582377	5.959093
F	3.669070	1.303772	6.641966
F	4.102562	3.294777	5.888428
O	4.509070	3.092108	8.740991
O	2.182602	2.373372	9.030070
O	2.689510	4.648794	8.148825
N	6.129910	4.912701	11.905153
N	6.388109	3.344531	10.248379
N	7.980952	3.469484	11.967290
N	4.459358	6.483925	10.708840
N	5.472959	5.385094	8.968413
N	4.876139	7.638141	8.713441
C	6.850052	3.901993	11.383785
C	6.667310	5.674353	13.041038
H	5.835186	6.167862	13.538075
H	7.340165	6.454060	12.671798
C	7.391781	4.744079	13.995915
H	7.830498	5.302047	14.822300
H	6.680302	4.029872	14.414001
C	8.484466	4.017348	13.233738
H	9.321330	4.689924	13.022328
H	8.874229	3.185599	13.820772
C	8.803940	2.450683	11.305726
H	9.415017	1.976825	12.071317
H	9.482667	2.924543	10.589622

C	7.906270	1.436584	10.619851
H	7.308219	0.916712	11.370376
H	8.504019	0.691726	10.096041
C	7.005118	2.156352	9.634928
H	7.580346	2.469657	8.758918
H	6.209346	1.502703	9.286251
C	4.935459	6.521161	9.450053
C	3.623819	7.590415	11.189187
H	3.553824	7.516533	12.270270
H	2.611166	7.496515	10.787620
C	4.260970	8.900475	10.758061
H	3.660622	9.749546	11.082499
H	5.245884	8.993413	11.219724
C	4.379864	8.916252	9.244601
H	3.406802	9.115240	8.787096
H	5.063304	9.700026	8.912828
C	5.231313	7.671709	7.286995
H	6.176127	8.212785	7.181813
H	4.463823	8.252045	6.772572
C	5.333285	6.277781	6.697355
H	4.340437	5.852104	6.562263
H	5.819394	6.326789	5.723807
C	6.124985	5.400265	7.651971
H	6.171218	4.377046	7.287123
H	7.151514	5.763675	7.756215
C	3.222667	2.551836	6.572602
B	4.685567	5.227688	11.501679
B	5.210871	4.037630	9.612447
N	3.714656	5.011232	12.562813
C	3.295257	4.405692	13.503579
S	2.713638	3.653605	14.749383
H	4.381236	4.250126	10.597926

$B_2(hpp)_2BrCl$ (11)

Illustration of the calculated minimum structure of **11**. Hydrogen atoms omitted.

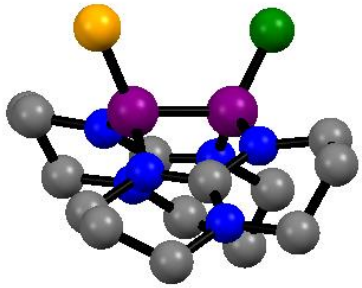


Cartesian coordinates (in Å):

Br	8.865901	5.348787	2.393514
N	6.548955	4.181819	3.847434
N	6.916892	4.529459	6.059611
N	4.696814	4.590629	5.256442
N	8.666635	2.691301	3.711271
N	9.020084	3.006033	5.930865
N	9.792818	1.014830	4.928942
C	6.034362	4.431196	5.059377
C	5.704335	3.978310	2.682358
H	5.523291	2.905932	2.531534
H	6.251164	4.342499	1.813193
C	4.380812	4.711377	2.833719
H	4.555975	5.788354	2.795415
H	3.701600	4.450411	2.021075
C	3.753497	4.348867	4.170753
H	2.867413	4.957409	4.359578
H	3.431558	3.298805	4.169652
C	4.162447	4.729442	6.606256
H	3.923581	3.743892	7.027958
C	5.157888	5.459021	7.495030
H	4.787031	5.493324	8.520273
H	5.272064	6.485990	7.142337
C	6.501796	4.749389	7.434395
H	7.276199	5.342866	7.919666
H	6.440540	3.790222	7.965715
C	9.173429	2.220451	4.858721
C	8.726466	1.897484	2.497463
H	8.690415	2.585501	1.654443
H	7.855311	1.232582	2.424968
C	10.010429	1.080508	2.474168
H	10.050805	0.437103	1.594357
H	10.860374	1.764352	2.432055
C	10.090607	0.229827	3.732406
H	11.093855	-0.188686	3.847967
H	9.394056	-0.614991	3.669547
C	10.287773	0.479538	6.193772
H	10.108298	-0.598850	6.195622
H	11.373031	0.626826	6.252261
C	9.602704	1.139065	7.380884
H	10.107814	0.846072	8.302061
H	8.566234	0.798817	7.443464
C	9.627874	2.650267	7.201124
H	9.072563	3.150380	7.993267
H	10.654719	3.028795	7.254502
B	8.094081	4.118107	3.884301
B	8.381566	4.376096	5.557641
Cl	9.441365	5.763849	6.279905
H	3.226138	5.285740	6.536699

$[B_2(hpp)_2BrCl]^+$

Illustration of the calculated minimum structure of [**11**]$^+$. Hydrogen atoms omitted.



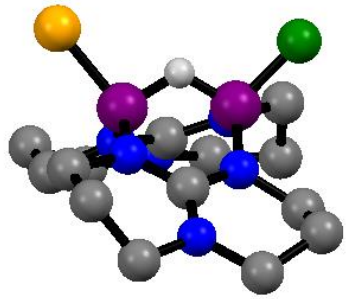
Cartesian coordinates (in Å):

Br	8.354111	5.612538	2.586594
N	6.535067	3.854297	4.081197
N	7.028962	4.735092	6.112284
N	4.768289	4.480066	5.501401
N	8.849725	2.853893	3.573213
N	8.750809	2.836433	5.840965
N	9.722620	1.001364	4.738276
C	6.074124	4.358124	5.235021
C	5.617614	3.302329	3.079433
H	5.462772	2.235148	3.262905
H	6.089533	3.410056	2.104217
C	4.298565	4.059396	3.121215
H	4.464371	5.086590	2.792721
H	3.575857	3.603084	2.445650
C	3.746888	4.052205	4.538232
H	2.903707	4.737109	4.623638
H	3.389081	3.054648	4.810971
C	4.343832	4.988989	6.809644
H	4.306065	4.172821	7.537980
C	5.303650	6.080722	7.257265
H	5.018950	6.456818	8.239142
H	5.250409	6.913604	6.553885
C	6.718355	5.528543	7.311835
H	7.449040	6.331045	7.386186
H	6.843956	4.891062	8.191441
C	9.125827	2.198351	4.721610
C	9.339039	2.359696	2.279920
H	9.585234	3.220909	1.663511
H	8.535751	1.811796	1.777280
C	10.548200	1.462188	2.476710
H	10.827499	1.000529	1.530581
H	11.396492	2.056832	2.821200
C	10.227442	0.388788	3.502927
H	11.122576	-0.175482	3.763442
H	9.489512	-0.320557	3.116553

C	9.981250	0.298615	6.000559
H	9.895486	-0.769789	5.802450
H	11.008514	0.495007	6.321883
C	8.985029	0.727420	7.065102
H	9.259691	0.291453	8.024762
H	7.990212	0.359881	6.804865
C	8.965543	2.244039	7.164168
H	8.160286	2.579248	7.818060
H	9.903597	2.622262	7.580056
B	8.003869	4.076044	3.772992
B	8.415671	4.316726	5.711968
Cl	9.757030	5.421315	6.183591
H	3.333457	5.377747	6.698459

$[B_2(hpp)_2BrClH]^+$

Illustration of the calculated minimum structure of [(**11**)+H]$^+$. Hydrogen atoms omitted.



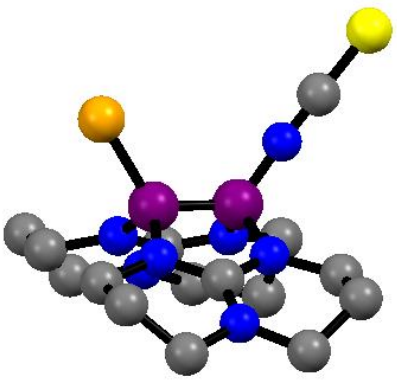
Cartesian coordinates (in Å):

Br	9.103916	4.925891	2.139019
N	6.625505	4.402747	3.714460
N	6.886300	4.266511	5.993058
N	4.727752	4.494168	5.103586
N	8.505178	2.653724	3.921678
N	9.216055	3.169565	6.042255
N	9.803081	1.100021	5.102619
C	6.057910	4.389785	4.937986
C	5.824085	4.558698	2.489526
H	5.660000	3.573516	2.042356
H	6.403162	5.145202	1.781796
C	4.495683	5.224929	2.785433
H	4.650451	6.274206	3.043051
H	3.859830	5.188563	1.901707
C	3.828228	4.510479	3.944240
H	2.917014	5.023473	4.246513
H	3.553739	3.486636	3.671191
C	4.090365	4.501244	6.427287
H	3.662908	3.512566	6.621577

C	5.074730	4.883826	7.515820
H	4.629152	4.702914	8.493342
H	5.320961	5.944613	7.449011
C	6.338452	4.064687	7.340674
H	7.097076	4.369173	8.057892
H	6.137797	3.000308	7.497088
C	9.185768	2.288614	5.024500
C	8.311548	1.673539	2.846380
H	8.039954	2.214808	1.943726
H	7.482928	1.006555	3.102507
C	9.595888	0.889306	2.643062
H	9.478502	0.143100	1.858191
H	10.385418	1.577386	2.337676
C	9.955891	0.202371	3.947593
H	10.991712	-0.141270	3.933705
H	9.323173	-0.674716	4.110696
C	10.439111	0.618445	6.336686
H	10.173364	-0.433480	6.456397
H	11.523822	0.668624	6.205617
C	10.010442	1.430734	7.544384
H	10.661593	1.200875	8.386817
H	8.989469	1.172629	7.832844
C	10.080760	2.908323	7.199244
H	9.737992	3.524775	8.024451
H	11.107656	3.210041	6.976135
B	8.105803	4.095448	3.675418
B	8.390316	4.421829	5.872248
Cl	9.049349	5.871582	6.766415
H	8.627873	4.810178	4.628665
H	3.264513	5.211496	6.389304

$B_2(hpp)_2Br(NCS)$ (12)

Illustration of the calculated minimum structure of **12**. Hydrogen atoms omitted.

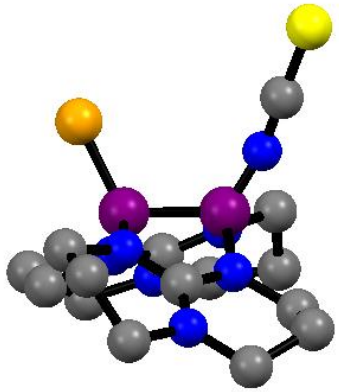


Cartesian coordinates (in Å):

N	5.990070	4.727010	12.078899
N	6.576356	3.643895	10.174893
N	7.993586	3.479907	12.058046
N	4.794918	6.549352	10.636828
N	5.353893	5.425517	8.747868
N	5.039282	7.759659	8.628009
C	6.873138	3.947947	11.445751
C	6.179618	5.155919	13.454145
H	5.198159	5.212152	13.926012
H	6.608173	6.166426	13.475919
C	7.084756	4.195528	14.211517
H	7.347069	4.604838	15.187754
H	6.563132	3.249931	14.371624
C	8.344066	3.941875	13.396509
H	8.954855	4.852668	13.341303
H	8.957124	3.169844	13.863896
C	8.996085	2.736145	11.303126
H	9.513074	2.074384	12.000087
H	9.747231	3.420640	10.887325
C	8.335098	1.936637	10.190975
H	7.705892	1.158755	10.627867
H	9.096485	1.451042	9.579367
C	7.477581	2.863215	9.343093
H	8.117779	3.530944	8.752196
H	6.867133	2.292680	8.643902
C	5.058892	6.597428	9.326205
C	4.326457	7.730324	11.341154
H	4.556973	7.608768	12.399018
H	3.236343	7.820976	11.265825
C	5.003481	8.970784	10.774815
H	4.621397	9.876089	11.247667
H	6.076915	8.916700	10.970624
C	4.758487	9.038817	9.274957
H	3.720190	9.327661	9.072645
H	5.399092	9.795759	8.815199
C	5.188679	7.787335	7.173674
H	6.193598	8.144550	6.918992
H	4.477861	8.517490	6.778638
C	4.939038	6.417145	6.562356
H	3.875335	6.176302	6.610330
H	5.235998	6.425233	5.513039
C	5.714694	5.365408	7.342547
H	5.475765	4.364903	6.985658
H	6.794145	5.518617	7.212267
B	4.761838	5.080289	11.177976
B	5.221618	4.246357	9.738984
N	3.496333	4.873755	11.954314
C	2.505311	4.791276	12.579942
S	1.161333	4.688617	13.445359
Br	4.040818	2.760261	8.892851

$[B_2(hpp)_2Br(NCS)]^+$

Illustration of the calculated minimum structure of [**12**]$^+$. Hydrogen atoms omitted.



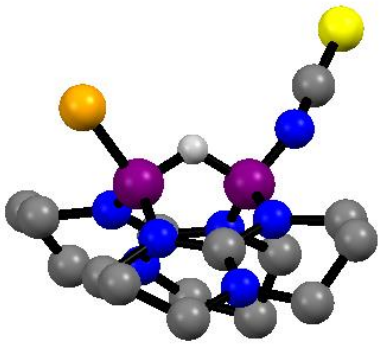
Cartesian coordinates (in Å):

N	6.181572	4.954220	11.874250
N	6.376114	3.476666	10.161280
N	8.010305	3.475695	11.859575
N	4.562664	6.584052	10.681900
N	5.602081	5.598512	8.926042
N	5.057222	7.881371	8.784843
C	6.885177	3.960016	11.314553
C	6.663657	5.643734	13.073999
H	5.794613	6.006641	13.621616
H	7.262822	6.513837	12.789067
C	7.475706	4.686785	13.933384
H	7.924148	5.216247	14.773378
H	6.818503	3.914317	14.336183
C	8.567154	4.045515	13.091424
H	9.341114	4.776458	12.836611
H	9.049064	3.237641	13.641144
C	8.767463	2.429369	11.164867
H	9.352264	1.896890	11.912938
H	9.469743	2.879841	10.456058
C	7.803842	1.489454	10.458328
H	7.188011	0.979622	11.201379
H	8.355259	0.729791	9.905670
C	6.925251	2.281221	9.505437
H	7.502129	2.593748	8.629852
H	6.092038	1.678891	9.149380
C	5.078011	6.718762	9.444651
C	3.715364	7.646687	11.223943
H	3.631536	7.499704	12.297922
H	2.706893	7.580762	10.805251
C	4.355378	8.988183	10.891544
H	3.739055	9.810588	11.253090

H	5.324879	9.056243	11.388522
C	4.527078	9.114229	9.384947
H	3.569512	9.339760	8.907027
H	5.213630	9.926441	9.139870
C	5.504660	7.983444	7.389212
H	6.490498	8.457054	7.371272
H	4.813492	8.648806	6.869968
C	5.543369	6.621220	6.715412
H	4.528704	6.265189	6.530071
H	6.050310	6.704609	5.754723
C	6.260047	5.625262	7.616909
H	6.207788	4.621985	7.198182
H	7.315368	5.889496	7.730879
B	4.783055	5.233875	11.314294
B	5.240380	4.298240	9.621833
N	3.692594	4.731883	12.102597
C	2.819313	4.100535	12.607016
S	1.661669	3.286555	13.289883
Br	3.754802	3.307556	8.769825

$[B_2(hpp)_2Br(NCS)H]^+$

Illustration of the calculated minimum structure of [(**12**)+H]$^+$. Hydrogen atoms omitted.



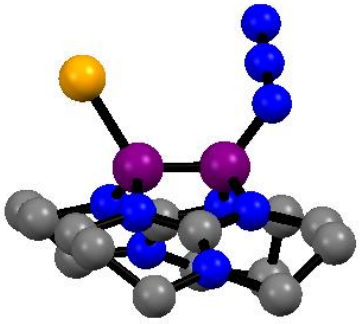
Cartesian coordinates (in Å):

N	5.883411	4.627976	12.250532
N	6.659219	3.875367	10.226620
N	8.014660	3.649596	12.128228
N	4.942114	6.448278	10.647036
N	5.112096	5.235398	8.698459
N	4.981058	7.577699	8.590204
C	6.870393	4.044957	11.545002
C	5.923048	4.740272	13.718510
H	4.928328	4.520417	14.099763
H	6.154770	5.774699	13.988187
C	6.956392	3.806251	14.318179
H	7.109392	4.051372	15.368471

H	6.611108	2.772271	14.263324
C	8.255465	3.943988	13.544904
H	8.674638	4.949153	13.653718
H	9.001656	3.237752	13.903249
C	9.087944	2.964059	11.395689
H	9.480711	2.180200	12.043565
H	9.899825	3.674189	11.211426
C	8.583218	2.376396	10.090794
H	7.958550	1.502760	10.282786
H	9.428538	2.058005	9.481771
C	7.760704	3.424931	9.366520
H	8.380903	4.281989	9.086205
H	7.327647	3.014663	8.457509
C	5.010282	6.436837	9.301530
C	4.779636	7.717438	11.370722
H	5.180550	7.581265	12.374209
H	3.717376	7.955039	11.476366
C	5.506840	8.829871	10.641303
H	5.347508	9.782786	11.144030
H	6.580251	8.629885	10.634310
C	4.979284	8.902034	9.222453
H	3.962098	9.304799	9.205937
H	5.600378	9.556078	8.608821
C	4.895017	7.594654	7.123227
H	5.873464	7.864176	6.714501
H	4.196416	8.386459	6.848809
C	4.432267	6.255754	6.585416
H	3.374051	6.103730	6.805133
H	4.555721	6.230028	5.503566
C	5.246723	5.156174	7.238806
H	4.902994	4.174804	6.926236
H	6.301551	5.245879	6.957768
B	4.707772	5.182727	11.474343
B	5.285158	4.039547	9.606500
N	3.469571	5.215635	12.241367
C	2.323241	5.505539	12.406831
S	0.823839	5.875716	12.678547
Br	4.544662	2.313375	8.878328
H	4.444763	4.216299	10.566657

$B_2(hpp)_2Br(N_3)$ (13)

Illustration of the calculated minimum structure of **13**. Hydrogen atoms omitted.



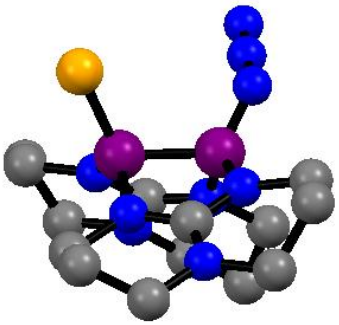
Cartesian coordinates (in Å):

N	6.045302	4.737048	12.151837
N	6.585126	3.641657	10.240308
N	8.053077	3.498196	12.086589
N	4.819146	6.546428	10.714854
N	5.302893	5.391212	8.823090
N	4.989326	7.724432	8.677964
C	6.913640	3.957220	11.501002
C	6.266920	5.173515	13.519528
H	5.294604	5.225969	14.009635
H	6.691176	6.186438	13.525688
C	7.197364	4.222611	14.257851
H	7.483221	4.638352	15.224907
H	6.686116	3.274440	14.435805
C	8.436551	3.971808	13.411376
H	9.039143	4.886646	13.334212
H	9.067721	3.207281	13.867186
C	9.039623	2.757378	11.308942
H	9.582303	2.105340	11.995578
H	9.772932	3.444436	10.865955
C	8.353625	1.943696	10.222340
H	7.742260	1.165647	10.683673
H	9.101081	1.457694	9.593942
C	7.466116	2.857234	9.391140
H	8.085087	3.521983	8.774621
H	6.838545	2.276125	8.715985
C	5.032261	6.573142	9.394820
C	4.406394	7.747714	11.421841
H	4.686591	7.636660	12.468731
H	3.315813	7.860167	11.395722
C	5.074053	8.967732	10.802447
H	4.731902	9.886814	11.279571
H	6.155313	8.898136	10.942740
C	4.751382	9.015610	9.316636
H	3.705994	9.310219	9.164916

H	5.372964	9.759932	8.812011
C	5.062602	7.727256	7.217830
H	6.052456	8.080582	6.904962
H	4.331002	8.450019	6.847436
C	4.783707	6.346568	6.644053
H	3.723944	6.106676	6.749640
H	5.027935	6.335950	5.581182
C	5.597996	5.309181	7.403836
H	5.345548	4.302540	7.074622
H	6.669826	5.462714	7.220350
B	4.799942	5.078683	11.283176
B	5.213994	4.232432	9.840965
Br	4.010817	2.719010	9.060684
N	3.550687	4.872420	12.165384
N	2.452279	5.147874	11.742902
N	1.394864	5.405412	11.412639

$[B_2(hpp)_2Br(N_3)]^+$

Illustration of the calculated minimum structure of [**13**]$^+$. Hydrogen atoms omitted.



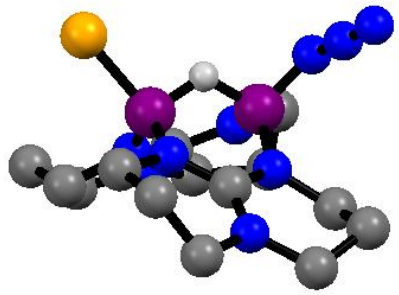
Cartesian coordinates (in Å):

N	5.907222	4.673590	12.272076
N	6.738529	3.979869	10.278233
N	8.054263	3.713947	12.210753
N	5.061902	6.514063	10.648754
N	5.073659	5.241498	8.767650
N	5.004434	7.586669	8.557056
C	6.930920	4.111558	11.600415
C	5.837803	4.676074	13.741008
H	4.828746	4.389963	14.031844
H	6.004486	5.696862	14.097238
C	6.869552	3.735381	14.341280
H	6.961361	3.922520	15.410464
H	6.555416	2.698322	14.210488
C	8.210084	3.940644	13.651328
H	8.598183	4.947505	13.835075

H	8.950130	3.231402	14.016953
C	9.161891	3.110048	11.461150
H	9.623897	2.358719	12.100978
H	9.917411	3.874077	11.253143
C	8.663571	2.478157	10.170985
H	8.066628	1.593354	10.397624
H	9.513390	2.164214	9.565739
C	7.806744	3.477104	9.408134
H	8.412214	4.310719	9.040454
H	7.336845	3.000072	8.549589
C	5.045821	6.478432	9.306196
C	5.082455	7.784758	11.380510
H	5.656446	7.637239	12.295463
H	4.064393	8.058471	11.673870
C	5.702279	8.877705	10.524736
H	5.605885	9.843410	11.019217
H	6.766901	8.679018	10.385268
C	5.009967	8.918300	9.172623
H	3.981582	9.279930	9.268610
H	5.534070	9.590036	8.492861
C	4.846989	7.514443	7.098548
H	5.825333	7.615734	6.619553
H	4.241190	8.368219	6.795256
C	4.173958	6.211176	6.703115
H	3.139072	6.211256	7.050915
H	4.160440	6.115037	5.618267
C	4.921356	5.042396	7.321133
H	4.386794	4.108097	7.166898
H	5.910492	4.938133	6.863869
B	4.806574	5.199810	11.393398
B	5.320088	4.152551	9.773322
Br	4.343391	2.456357	9.487779
N	3.463909	5.006876	11.956301
N	2.485502	5.539718	11.454593
N	1.538995	5.992799	11.042393

$[B_2(hpp)_2Br(N_3)H]^+$

Illustration of the calculated minimum structure of [(**13**)+H]$^+$. Hydrogen atoms omitted.



Cartesian coordinates (in Å):

N	5.998748	4.888081	11.885014
N	6.313321	3.434002	10.130350
N	7.860909	3.460064	11.902812
N	4.475436	6.599036	10.670171
N	5.490338	5.538303	8.905201
N	5.023151	7.830706	8.752123
C	6.742501	3.919251	11.311463
C	6.510643	5.603721	13.062317
H	5.664178	6.059771	13.571707
H	7.171810	6.413843	12.738925
C	7.245617	4.645171	13.979230
H	7.672341	5.174914	14.830162
H	6.547228	3.900310	14.363645
C	8.351389	3.971723	13.189654
H	9.175115	4.668512	13.004861
H	8.758383	3.126703	13.744695
C	8.718842	2.480973	11.225117
H	9.263249	1.937234	11.995167
H	9.457023	2.999263	10.604826
C	7.869634	1.540663	10.393048
H	7.227285	0.950318	11.048958
H	8.503106	0.850401	9.837358
C	7.027713	2.353509	9.431074
H	7.660633	2.789420	8.652020
H	6.289018	1.728419	8.937478
C	4.996785	6.673870	9.431606
C	3.728671	7.742802	11.206946
H	3.638338	7.612565	12.280905
H	2.715206	7.756563	10.796553
C	4.473635	9.019467	10.855507
H	3.939322	9.894336	11.224001
H	5.457725	9.007257	11.328206
C	4.611616	9.110791	9.346480
H	3.661201	9.406030	8.893000
H	5.353592	9.860246	9.064458

C	5.406507	7.914235	7.334844
H	6.369837	8.428346	7.271517
H	4.669127	8.541797	6.831122
C	5.485347	6.544367	6.686085
H	4.486673	6.149816	6.493340
H	6.005558	6.622020	5.732155
C	6.212306	5.601792	7.629133
H	6.254352	4.596913	7.217080
H	7.238631	5.938869	7.803340
B	4.607421	5.290201	11.400799
B	5.155165	4.178968	9.494284
Br	4.008070	3.066037	8.265456
H	4.307464	4.367172	10.440300
N	3.506729	5.109704	12.378803
N	3.541157	4.184832	13.180338
N	3.502126	3.365857	13.951711

5. Acknowledgements

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