Pathway bifurcations in the cage rearrangement of metallacarboranes: experimental and computational evidence

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SUPPORTING INFORMATION

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Experimental Section

General Considerations

All reactions were carried out under argon atmosphere using standard Schlenk techniques with subsequent work-up in air. All solvents were purified and degassed by standard procedures. Starting materials 1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$,[1] NMe_4[7,8-$(CH_2)_3$-7,8-$C_2B_9H_{10}$],[1] 1,2-CH_2OCH_2-1,2-$C_2B_{10}H_{10}$,[2] $[(cod)RhCl]_2$[3] and $[(cod)IrCl]_2$[4] were prepared as described in the literature. The compound NMe_4[7,8-CH_2OCH_2-7,8-$C_2B_9H_{10}$] was prepared similar to preparation of NMe_4[7,8-$(CH_2)_3$-7,8-$C_2B_9H_{10}$][1] from the corresponding 1,2-CH_2OCH_2-1,2-$C_2B_{10}H_{10}$ carborane. ^1H and $^{11}B\{^1H\}$ NMR spectra (δ in ppm) were recorded on a Bruker Avance-400 spectrometer operating at 400.13 and 128.38 MHz, respectively.

10-SMe_2-7,8-$(CH_2)_3$-7,8-*nido*-$C_2B_9H_9$ (1) and **10-SMe_2-7,8-CH_2OCH_2-7,8-$C_2B_9H_{10}$ (2)** were prepared according to the modified method**:**[5]

A dark-red solution of 163 mg (1 mmol) of anhydrous $FeCl_3$ in 4 ml of dry benzene and 0.3 ml (4.1 mmol) of dimethyl sulfide was added dropwise over a period of 5 min to a preheated to 80 °C suspension of 100 mg (0.4 mmol) of NMe_4[7,8-$(CH_2)_3$-7,8-$C_2B_9H_{10}$] or NMe_4[7,8-CH_2OCH_2-7,8-$C_2B_9H_{10}$] in 3 ml of dry benzene. The reaction mixture was additionally stirred for 1 h at 80 °C, precipitated salts were filtered off and washed with benzene. After the evaporation of benzene *in vacuo* a residue was chromatographed on SiO_2 with a mixture CH_2Cl_2 − petroleum ether (1:1) as eluent. The solvent was removed *in vacuo* and the product was crystallized from toluene – heptane at −6 °C.

10-SMe_2-7,8-$(CH_2)_3$-7,8-*nido*-$C_2B_9H_9$ (1): yield 83 mg (88%). ^1H ($CDCl_3$) δ: 2.55 (s, 6H, SMe_2), 2.26−2.18 (m, 2H, CH_2), 1.99−1.94 (m, 2H, CH_2), 1.75−1.66 (m, 1H, CH_2), 1.59−1.51 (m, 1H, CH_2), −0.49 ÷ −1.23 (m, 1H). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: −11.6 (2B), −14.7 (1B), −17.6 (2B), −19.3 (2B), −25.9 (1B, $BSMe_2$), −35.2 (1B). Anal. Calcd for $C_7H_{21}B_9S$: C, 35.84; H, 9.02%. Found: C, 36.35; H, 8.98%.

10-SMe_2-7,8-CH_2OCH_2-7,8-$C_2B_9H_9$ (2): yield 42 mg (45%). ^1H (acetone-d_6) δ: 3.97 (d, 2H, CH_2, $^2J_{HH}$ = 8.5 Hz), 3.72 (d, 2H, CH_2, $^2J_{HH}$ = 8.5 Hz), 2.72 (s, 6H, SMe_2), −0.50 ÷ −1.35 (m, 1H). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: −12.8 (2B), −15.1 (1B), −18.2 (4B), −24.8 (1B, $BSMe_2$), −35.9 (1B). Anal. Calcd for $C_6H_{19}B_9SO$: C, 30.46; H, 8.09%. Found: C, 31.11; H, 8.11%.

9-SMe_2-7,8-$(CH_2)_3$-7,8-*nido*-$C_2B_9H_9$ (3) and **9-SMe_2-7,8-CH_2OCH_2-7,8-$C_2B_9H_9$ (4)** were prepared according to the modified method**:**[6]

A mixture of 1,2-CH_2XCH_2-1,2-$C_2B_{10}H_{10}$ (X = CH_2 or O, 1.07 mmol) and KOH (200 mg, 3.57 mmol) was refluxed in ethanol (5 ml) for 6 hours. The clear mixture was cooled to room

temperature, diluted with a solution of NH_4Cl (200 mg, 3.74 mmol) in H_2O (5 ml) to neutralize the excess of KOH and dimethyl sulfide (1 ml) was added. After the addition of a solid $Fe(NO_3)_3 \times 9H_2O$ (1 g, 2.48 mmol) reaction was stirred for 24 h. The precipitated product was filtered off, washed with water and dried.

9-SMe$_2$-7,8-(CH$_2$)$_3$-7,8-*nido*-C$_2$B$_9$H$_9$ (3): yield 208 mg (88%). ^{1}H (acetone-d$_6$) δ: 2.93 (s, 3H, SMe), 2.70 (s, 3H, SMe), 2.33−2.28 (m, 2H, CH_2), 2.00−1.91 (m, 2H, CH_2), 1.79−1.72 (m, 1H, CH_2), 1.60−1.52 (m, 1H, CH_2), −2.98 (br s, 1H). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: −7.5 (1B), −8.4 (1B), −9.6 (1B), −16.7 (2B), −20.5 (1B), −29.2 (2B), −35.2 (1B). Anal. Calcd for $C_7H_{21}B_9S$: C, 35.84; H, 9.02%. Found: C, 35.18; H, 8.73%.

9-SMe$_2$-7,8-CH$_2$OCH$_2$-7,8-C$_2$B$_9$H$_9$ (4): yield 171 mg (67%). ^{1}H (acetone-d$_6$) δ: 4.19 (d, 1H, CH_2, $^2J_{HH}$ = 8.8 Hz), 4.07 (d, 1H, CH_2, $^2J_{HH}$ = 8.1 Hz), 3.89 (d, 1H, CH_2, $^2J_{HH}$ = 8.8 Hz), 3.83 (d, 1H, CH_2, $^2J_{HH}$ = 8.1 Hz), 2.97 (s, 3H, SMe), 2.74 (s, 3H, SMe), −2.92 (br s, 1H). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: −7.4 (1B), −8.6 (1B), −9.9 (1B), −16.1 (1B), −17.7 (1B), −21.0 (1B), −28.7 (2B), −35.5 (1B). Anal. Calcd for $C_6H_{19}B_9SO$: C, 30.46; H, 8.09%. Found: C, 31.33; H, 8.02%.

Synthesis of rhoda- and iridacarborane complexes.

A solution of carborane (0.32 mmol) in THF (5 ml) was added carefully to a sodium hydride (hydrogen evoluation) and heated at 60 °C for 1 hour. The clear solution was decantated from exess of NaH, added to the mixture of $TlPF_6$ (112 mg, 0.32 mmol) and $[(cod)MCl]_2$ (0.15 mmol). After stirring the reaction mixture at 60 °C for 2 hours suspension was filtered, solution evaporated to drines *in vacuo* and products were crystallized from methanol as yellow or pale-yellow (rhodium and iridium complexes respectively) solids.

1,2-(CH$_2$)$_3$-3,3-(cod)-8-SMe$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_8$ (1a): yield 80%. ^{1}H (acetone-d$_6$) δ: 4.17 (br s, 4H, CH-cod), 3.27−3.14 (m, 1H, CH_2-carb), 2.73−2.67 (m, 2H, CH_2-carb), 2.63 (s, 6H, SMe_2), 2.51−2.29 (m, 7H, CH_2 cod+carb), 2.17−2.11 (m, 4H, CH_2 cod+carb). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: 6.5 (1B, $BSMe_2$), −12.7 (2B), −14.4 (2B), −15.8 (2B), −19.6 (2B). Anal. Calcd for $C_{15}H_{32}B_9RhS$: C, 40.51; H, 7.25%. Found: C, 40.41; H, 7.26%.

1,2-(CH$_2$)$_3$-3,3-(cod)-8-SMe$_2$-3,1,2-*closo*-IrC$_2$B$_9$H$_8$ (1b): yield 60%. ^{1}H (acetone-d$_6$) δ: 3.76 (br s, 4H, CH-cod), 2.91−2.81 (m, 1H, CH_2-carb), 2.69−2.65 (m, 4H, CH_2-cod), 2.54 (s, 6H, SMe_2), 2.36−2.21 (m, 6H, CH_2 cod+carb) 2.16−2.05 (m, 3H, CH_2 cod+carb). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: 2.7 (1B, $BSMe_2$), −9.6 (1B), −12.7 (3B), −15.8 (2B), −19.5 (2B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.78; H, 6.09%.

1,2-O(CH$_2$)$_2$-3,3-(cod)-8-SMe$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_8$ (2a): yield 57%. ^{1}H (acetone-d$_6$) δ: 4.73 (d, 2H, CH$_2$-carb, $^2J_{HH}$ = 8 Hz), 4.24 (br s, 4H, CH-cod), 4.20 (d, 2H, CH$_2$-carb, $^2J_{HH}$ = 8 Hz), 2.68 (s, 6H, SMe$_2$), 2.46 (m, 4H, CH$_2$-cod), 2.14 (m, 4H, CH$_2$-cod). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: 7.4 (1B, BSMe$_2$), −12.5 (1B), −13.8 (1B), −15.4 ÷ −16.2 (3B), −20.4 (3B). Anal. Calcd for C$_{14}$H$_{30}$B$_9$RhSO: C, 37.65; H, 6.77%. Found: C, 37.74; H, 6.56%.

1,2-O(CH$_2$)$_2$-3,3-(cod)-8-SMe$_2$-3,1,2-*closo*-IrC$_2$B$_9$H$_8$ (2b): yield 52%. ^{1}H (CDCl$_3$) δ: 4.68 (d, 2H, CH$_2$-carb, $^2J_{HH}$ = 8.3 Hz), 4.47 (d, 2H, CH$_2$-carb, $^2J_{HH}$ = 8.3 Hz), 3.87 (br s, 4H, CH-cod), 2.50 (s, 6H, SMe$_2$), 2.29 (m, 4H, CH$_2$-cod), 2.15 (m, 4H, CH$_2$-cod). ^{11}B{^{1}H} NMR (CDCl$_3$) δ: 3.7 (1B, BSMe$_2$), −10.2 (1B), −14.2 ÷ −15.3 (5B), −20.9 (2B). Anal. Calcd for C$_{14}$H$_{30}$B$_9$IrSO: C, 31.37; H, 5.64%. Found: C, 31.32; H, 5.78%.

1,2-(CH$_2$)$_3$-3,3-(cod)-4-SMe$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_8$ (3a): yield 56%. ^{1}H (CDCl$_3$) δ: 4.33−4.29 (m, 2H, CH-cod), 3.91 (br s, 2H, CH-cod), 3.37−3.30 (m, 1H, CH$_2$-carb), 3.00 (s, 3H, SMe), 2.65−2.57 (m, 3H, CH$_2$ cod+carb), 2.54 (s, 3H, SMe), 2.42−2.31 (m, 5H, CH$_2$ cod+carb), 2.22−2.17 (m, 3H, CH$_2$ cod+carb), 2.02−1.96 (m, 2H, CH$_2$ cod+carb). ^{11}B{^{1}H} NMR (CDCl$_3$) δ: −3.5 (1B), −7.8 (1B, BSMe$_2$), −11.7 (1B), −14.3 (2B), −16.0 ÷ −16.8 (3B), −20.5 (1B). Anal. Calcd for C$_{15}$H$_{32}$B$_9$RhS: C, 40.51; H, 7.25%. Found: C, 40.36; H, 7.28%.

1,2-(CH$_2$)$_3$-3,3-(cod)-4-SMe$_2$-3,1,2-*closo*-IrC$_2$B$_9$H$_8$ (3b): yield 82%. ^{1}H (CDCl$_3$) δ: 4.00−3.96 (m, 2H, CH-cod), 3.45−3.39 (m, 2H, CH-cod), 3.21−3.14 (m, 1H, CH$_2$-carb), 3.03−2.97 (m, 1H, CH$_2$-carb), 2.84 (s, 3H, SMe), 2.76−2.67 (m, 3H, CH$_2$ cod+carb), 2.54 (s, 3H, SMe), 2.50−2.34 (m, 4H, CH$_2$ cod+carb), 2.29−1.98 (m, 3H, CH$_2$ cod+carb), 1.80−1.71 (m, 2H, CH$_2$ cod+carb). ^{11}B{^{1}H} NMR (CDCl$_3$) δ: −5.6 (1B), −6.8 (1B, BSMe$_2$), −10.1 (1B), −11.3 (1B), −15.6 ÷ −16.3 (3B), −18.6 (1B)), −20.9 (1B). Anal. Calcd for C$_{15}$H$_{32}$B$_9$IrS: C, 33.74; H, 6.04%. Found: C, 33.75; H, 5.90%.

1,2-O(CH$_2$)$_2$-3,3-(cod)-4-SMe$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_8$ (4a): yield 75%. ^{1}H (acetone-d$_6$) δ: 5.99 (d, 1H, CH$_2$-carb, $^2J_{HH}$ = 8 Hz), 4.41−4.37 (m, 2H, CH-cod), 4.22 (d, 1H, CH$_2$-carb, $^2J_{HH}$ = 8 Hz), 4.23−4.17 (m, 2H, CH-cod), 4.01 (br s, 2H, CH$_2$-carb), 3.12 (s, 3H, SMe), 2.75−2.65 (m, 2H, CH$_2$-cod), 2.66 (s, 3H, SMe), 2.51−2.45 (m, 2H, CH$_2$-cod), 2.36−2.22 (m, 2H, CH$_2$-cod), 1.96−1.81 (m, 2H, CH$_2$-cod). ^{11}B{^{1}H} NMR (acetone-d$_6$) δ: −4.9 (1B), −5.8 (1B, BSMe$_2$), −11.8 (1B), −13.5 (2B), −14.7 (1B), −17.5 (1B), −18.7 (1B), −23.4 (1B). Anal. Calcd for C$_{14}$H$_{30}$B$_9$RhSO: C, 37.65; H, 6.77%. Found: C, 37.78; H, 6.53%.

1,2-O(CH$_2$)$_2$-3,3-(cod)-4-SMe$_2$-3,1,2-*closo*-IrC$_2$B$_9$H$_8$ (4b): yield 90%. ^{1}H (CDCl$_3$) δ: 4.82 (d, 1H, CH$_2$-carb, $^2J_{HH}$ = 6.4 Hz), 4.66 (d, 1H, CH$_2$-carb, $^2J_{HH}$ = 6.4 Hz), 4.42 (d, 1H, CH$_2$-carb, $^2J_{HH}$ = 7.2 Hz), 4.14−4.11 (m, 3H, CH$_2$-carb+ CH-cod), 3.73−3.69 (m, 2H, CH-cod), 2.90 (s, 3H, SMe), 2.86−2.81 (m, 2H, CH$_2$-cod), 2.56 (s, 3H, SMe), 2.52−2.46 (m, 2H, CH$_2$-cod), 2.27−2.19 (m, 2H, CH$_2$-cod), 1.75−1.66 (m, 2H, CH$_2$-cod). ^{11}B{^{1}H} NMR (CDCl$_3$) δ: −5.4 (2B, BSMe$_2$), −10.3

(1B), −11.6 (1B), −13.8 (1B), −15.7 (2B), −21.2 (1B), −23.5 (1B). Anal. Calcd for $C_{14}H_{30}B_9IrSO$: C, 31.37; H, 5.64%. Found: C, 31.48; H, 5.60%.

Thermal isomerization of 1,2-$(CH_2)_3$-3,3-(cod)-4-SMe_2-3,1,2-$IrC_2B_9H_8$ (3b):

A solution of 1,2-$(CH_2)_3$-3,3-(cod)-4-SMe_2-3,1,2-$IrC_2B_9H_8$ (80 mg) in *o*-xylene (5 ml) was heated at 144 °C for 7 hours. The solvent was removed *in vacuo* and the residue was chromatographed on SiO_2 with a mixture benzene – petroleum ether (1:2) as eluent. Two mobile colourless bands were subsequently collected as solids after removal of the solvent *in vacuo* and crystallization from diethyl ether – petroleum ether.

1,2-$(CH_2)_3$-4,4-(cod)-8-SMe_2-4,1,2-*closo*-IrC_2B_9H (5): yield 7 mg (9%). ^{1}H ($CDCl_3$) δ: 4.00−3.97 (m, 2H, CH-cod), 3.86−3.82 (m, 2H, CH-cod), 2.69−2.57 (m, 4H, CH_2 cod+carb), 2.54 (s, 3H, SMe), 2.40−2.15 (m, 8H, CH_2 cod+carb), 2.34 (s, 3H, SMe), 2.03−1.98 (m, 1H, CH_2 cod+carb), 0.92−0.86 (m, 1H, CH_2 carb). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −0.3 (1B, $BSMe_2$), −5.9 (1B), −9.6 (2B), −11.1 (1B), −16.8 (1B), −20.0 (1B), −21.6 (1B), −22.0 (1B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.89; H, 6.14%.

1,2-$(CH_2)_3$-4,4-(cod)-9-SMe_2-4,1,2-*closo*-$IrC_2B_9H_8$ (6): yield 10 mg (13%). ^{1}H ($CDCl_3$) δ: 4.19−4.15 (m, 2H, CH-cod), 3.51−3.46 (m, 2H, CH-cod), 2.70−2.66 (m, 2H, CH_2 cod+carb), 2.60 (s, 3H, SMe), 2.46 (s, 3H, SMe), 2.38−1.86 (m, 12H, CH_2 cod+carb), 2.03−1.98 (m, 1H, CH_2 cod+carb), 0.92−0.86 (m, 1H, CH_2 carb). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −3.57 (1B, $BSMe_2$), −7.3 (1B), −8.1 (1B), −9.7 (2B), −16.8 (1B), −18.1 (1B), −20.1 (1B), −23.3 (1B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.65; H, 6.11%.

Thermal isomerization of 1,2-O$(CH_2)_2$-3,3-(cod)-4-SMe_2-3,1,2-*closo*-$IrC_2B_9H_8$ (4b):

A solution of 1,2-O$(CH_2)_2$-3,3-(cod)-4-SMe_2-3,1,2-*closo*-$IrC_2B_9H_8$ (100 mg) in *o*-xylene (5 ml) was heated at 135 °C for 4 hours. The solvent was removed *in vacuo* and the residue was chromatographed on SiO_2 with a mixture ethyl acetate – petroleum ether (1:2) as eluent. Four mobile colourless bands were subsequently collected as solids after removal of the solvent *in vacuo* and crystallization from diethyl ether – petroleum ether.

1,2-O$(CH_2)_2$-4,4-(cod)-8-SMe_2-4,1,2-*closo*-$IrC_2B_9H_8$ (7): yield 22 mg (22%). R_f = 0.49. ^{1}H ($CDCl_3$) δ: 4.52 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.5 Hz), 4.23 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.5 Hz), 4.00 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.5 Hz), 3.96(br s, 4H, CH-cod), 3.91 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.5 Hz), 2.62−2.57 (m, 2H, CH_2-cod), 2.59 (s, 3H, SMe), 2.40−2.14 (m, 6H, CH_2-cod), 2.36 (s, 3H, SMe).

$^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: −0.4 (1B, $BSMe_2$), −4.8 (1B), −9.4 (2B), −11.6 (1B), −16.4 (1B), −20.9 (1B), −22.4 (1B), −24.1 (1B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.89; H, 6.14%.

1,2-O(CH$_2$)$_2$-4,4-(cod)-9-SMe$_2$-4,1,2-*closo*-IrC$_2$B$_9$H$_8$ (8): yield 31 mg (31%). R_f = 0.33. ^1H ($CDCl_3$) δ: 4.44 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.2 Hz), 4.22−4.19 (m, 2H, CH-cod), 4.03−3.97 (m, 2H, CH-cod), 3.83 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.2 Hz), 3.64 (br s, 2H, CH-cod), 2.80−2.65 (m, 2H, CH_2-cod), 2.63 (s, 3H, SMe), 2.50 (s, 3H, SMe), 2.45−2.38 (m, 2H, CH_2-cod), 2.30−2.20 (m, 4H, CH_2-cod). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: −3.5 (1B, $BSMe_2$), −6.7 (2B), −10.2 (2B), −16.3 (1B), −19.3 (1B), −20.8 (1B), −25.2 (1B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.81; H, 5.94%.

1,2-O(CH$_2$)$_2$-4,4-(cod)-5-SMe$_2$-4,1,2-*closo*-IrC$_2$B$_9$H$_8$ (9): yield 10 mg (10%). R_f = 0.11. ^1H (CD_2Cl_2) δ: 4.28 (d, 1H, CH_2-carb, $^2J_{HH}$ = 8.2 Hz), 3.85−3.79 (m, 3H, CH_2-carb+CH-cod), 3.73−3.68 (m, 2H, CH-cod), 3.44 (d, 1H, CH_2-carb, $^2J_{HH}$ = 9.6 Hz), 3.10−3.05 (m, 2H, CH_2-cod), 2.99 (d, 1H, CH_2-carb, $^2J_{HH}$ = 9.6 Hz), 2.89 (s, 3H, SMe), 2.67 (s, 3H, SMe), 2.64−2.57 (m, 2H, CH_2-cod), 2.43−2.35 (m, 2H, CH_2-cod), 2.08−2.00 (m, 2H, CH_2-cod). $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ: −1.7 (1B), −5.8 (1B), −6.5 (1B), −9.0 (2B), −16.9 (1B), −22.0 (1B), −22.8 (1B), −23.8 (1B). Anal. Calcd for $C_{15}H_{32}B_9IrS$: C, 33.74; H, 6.04%. Found: C, 33.66; H, 5.93%.

1,2-O(CH$_2$)$_2$-3,3-(cod)-8-SMe$_2$-3,1,2-*closo*-IrC$_2$B$_9$H$_8$ (2b): yield 5 mg (5%). R_f= 0.43.

NMR Spectra

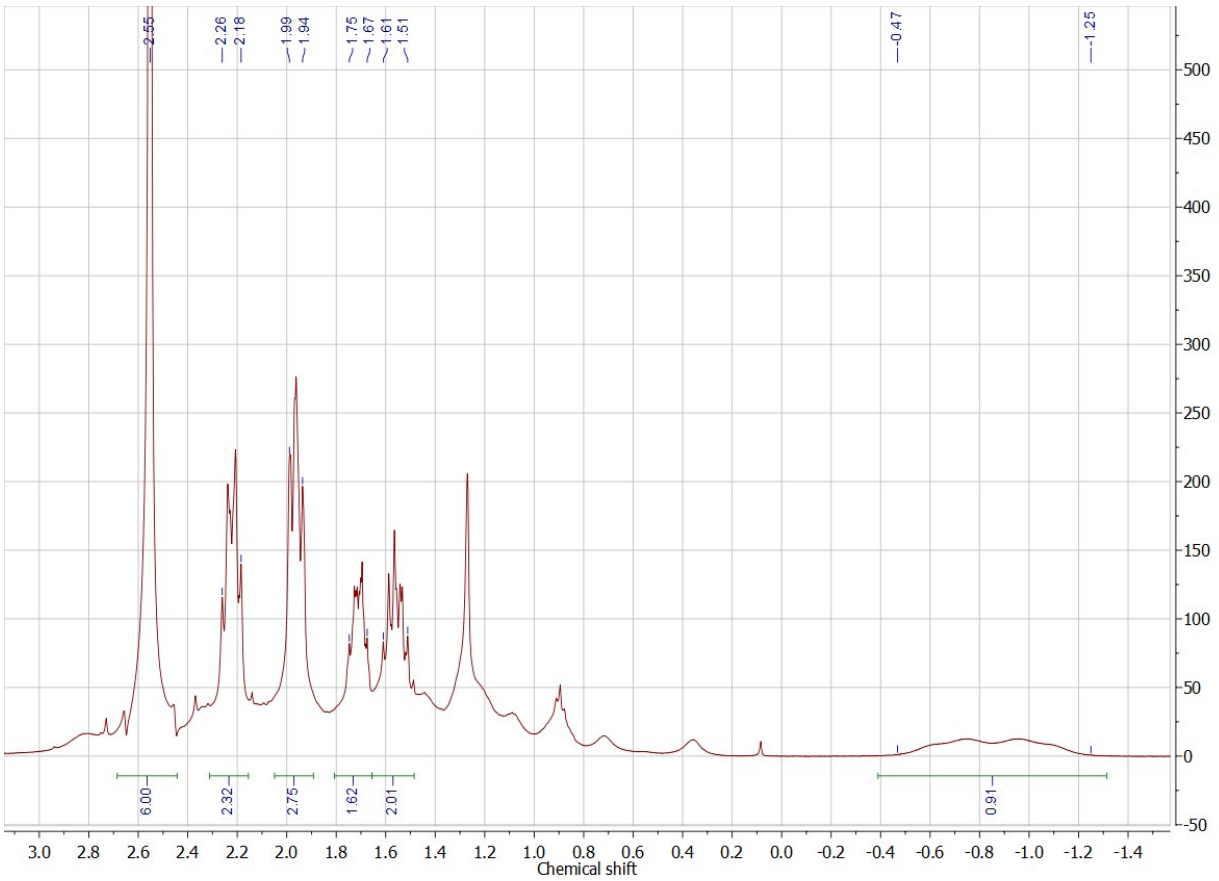


Figure S1. The ^{1}H NMR spectrum of **1** in $CDCl_3$.

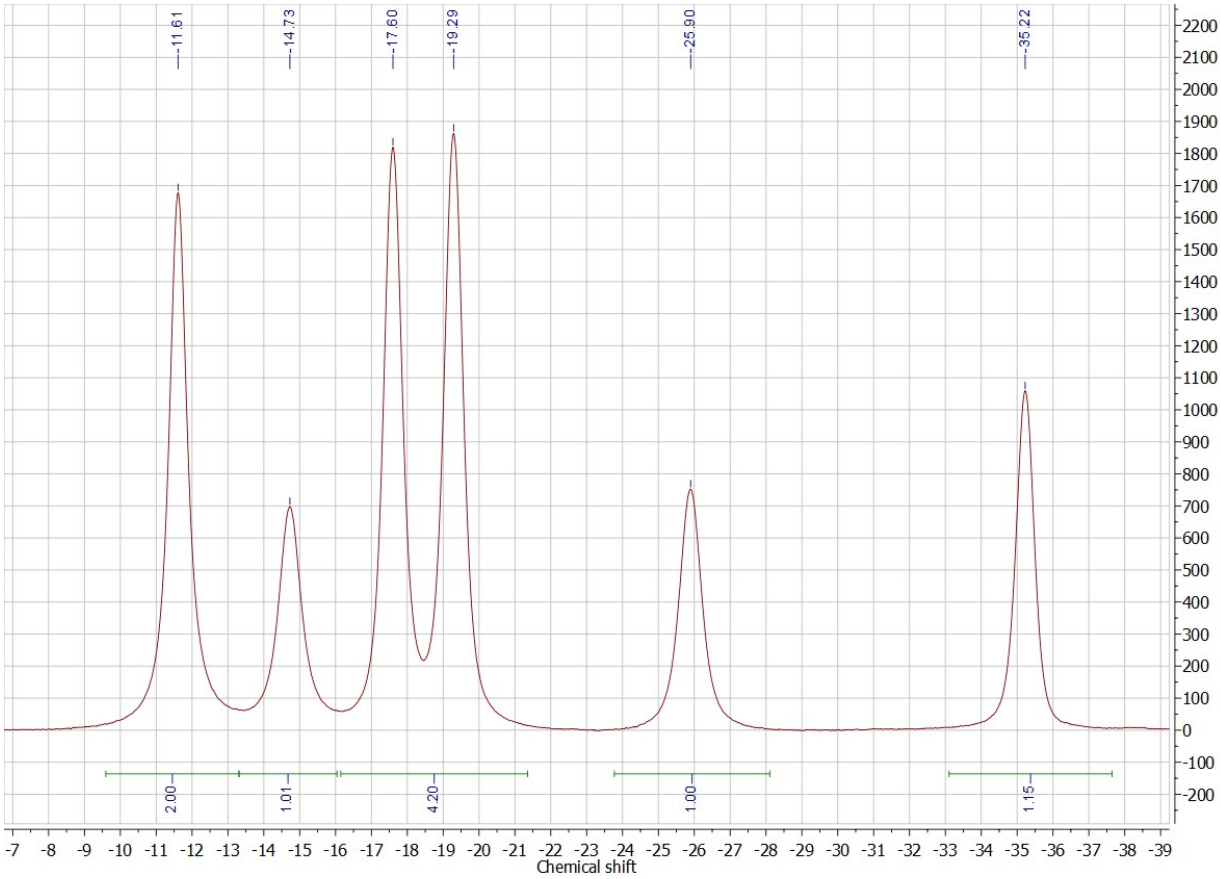


Figure S2. The $^{11}B\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

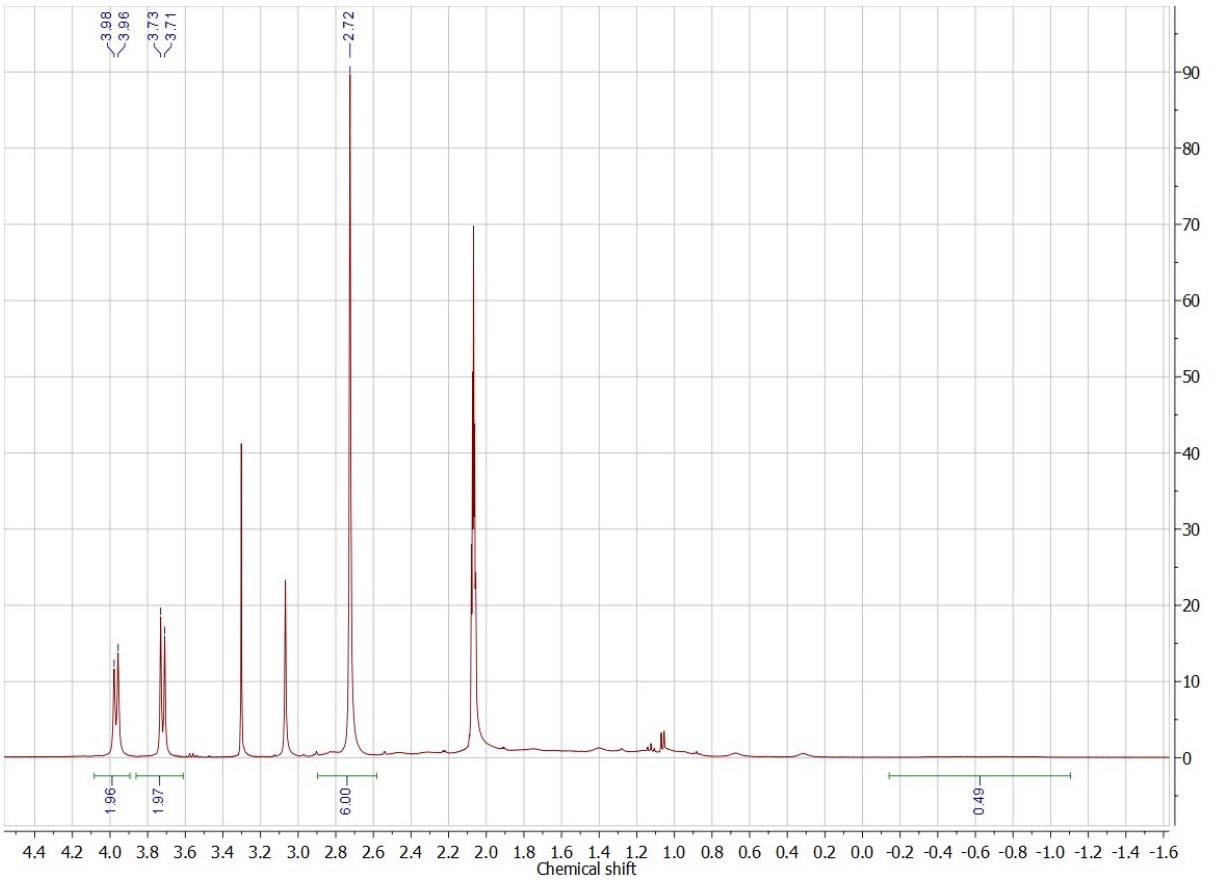


Figure S3. The ^{1}H NMR spectrum of **2** in acetone-d_6.

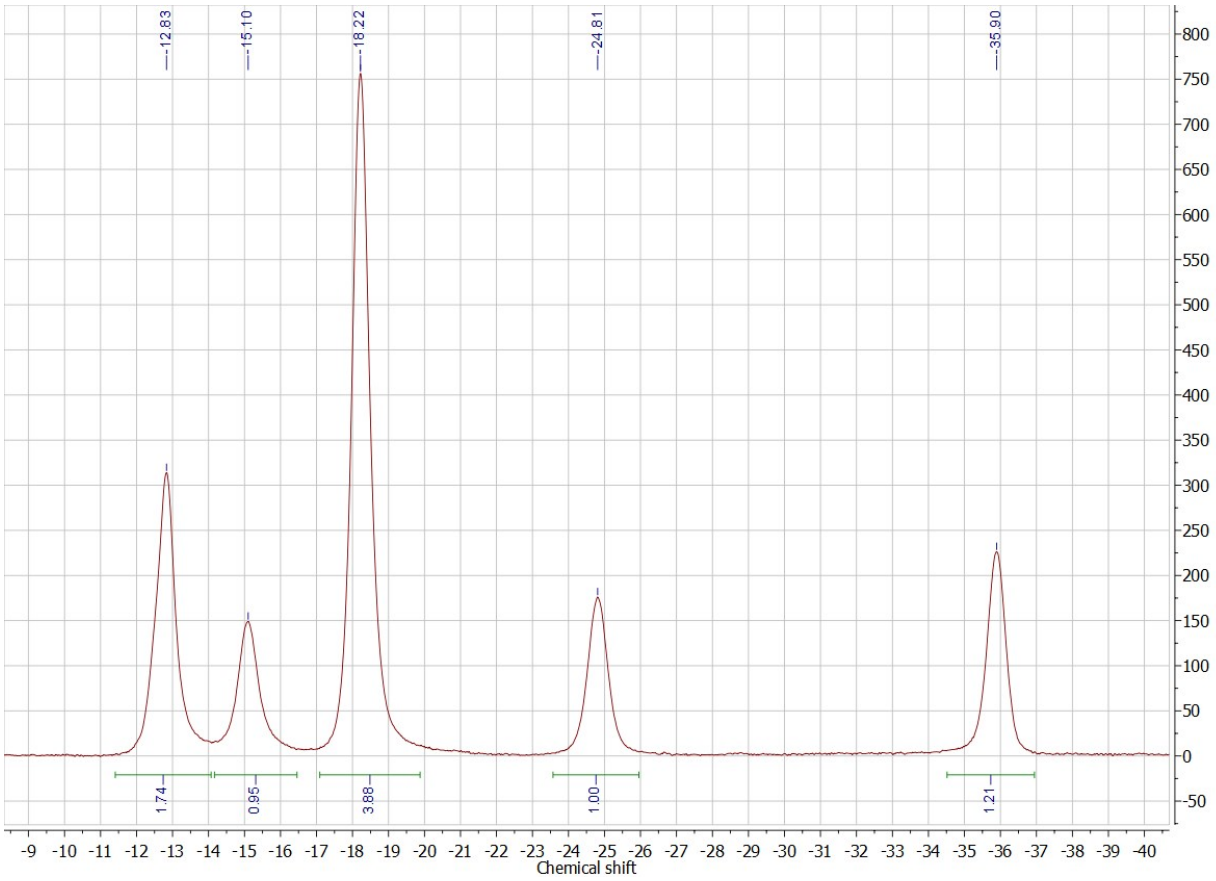


Figure S4. The $^{11}B\{^{1}H\}$ NMR spectrum of **2** in acetone-d_6.

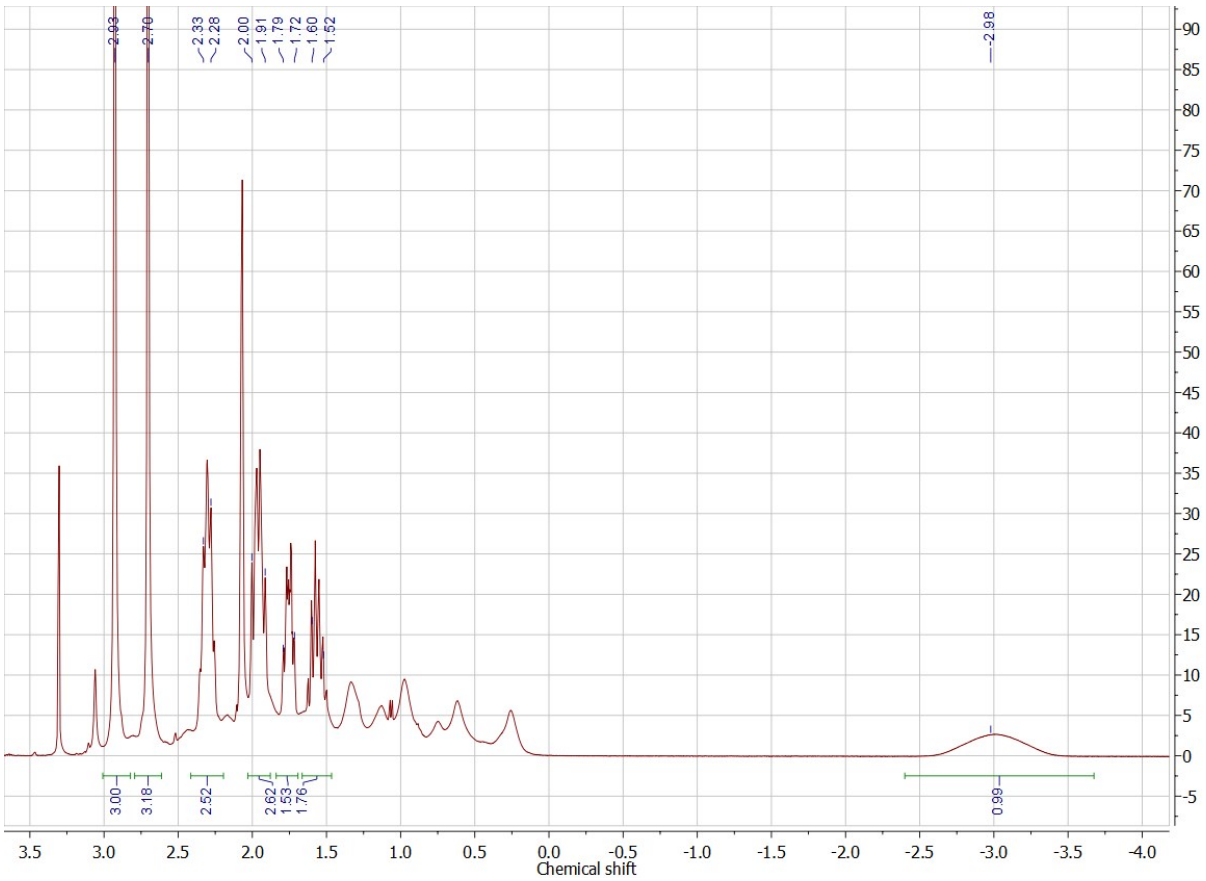


Figure S5. The ^{1}H NMR spectrum of **3** in acetone-d_6.

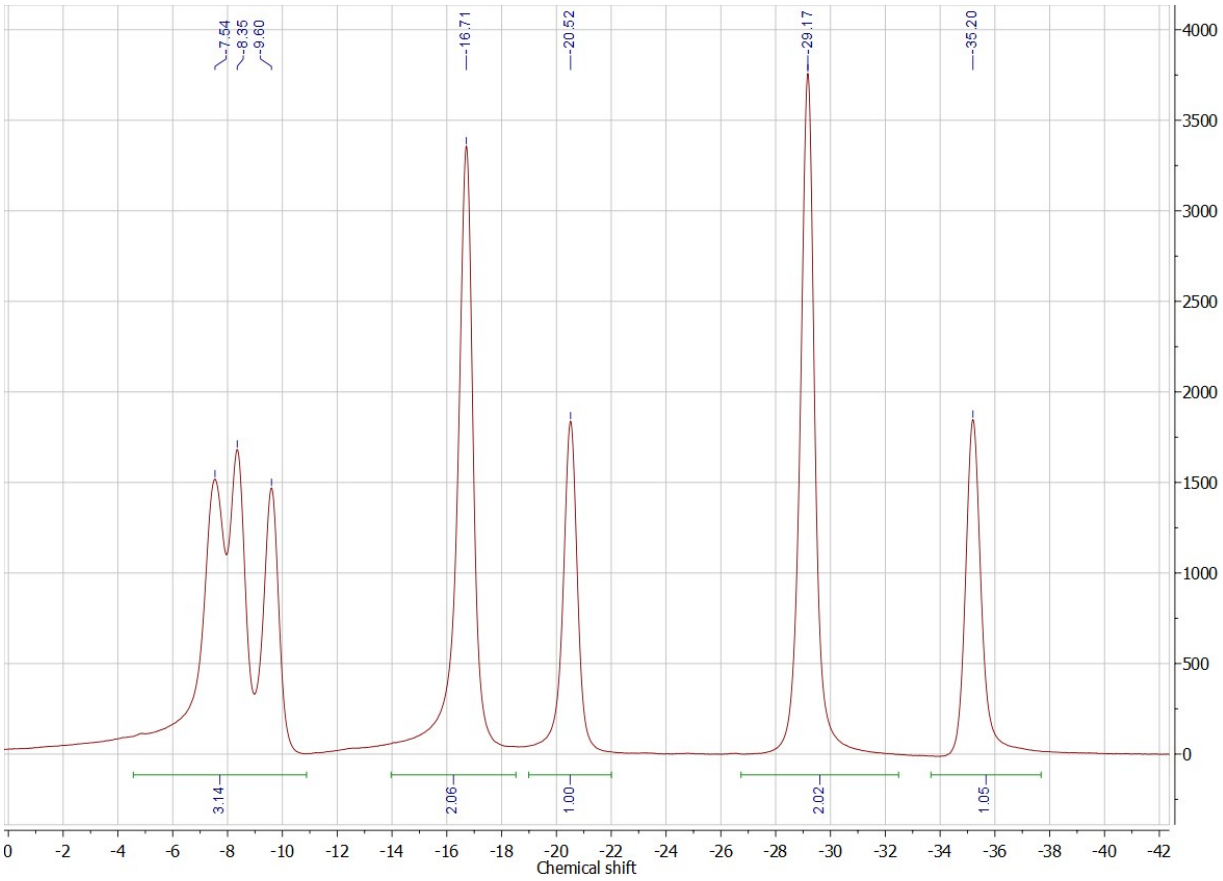


Figure S6. The $^{11}B\{^{1}H\}$ NMR spectrum of **3** in acetone-d_6.

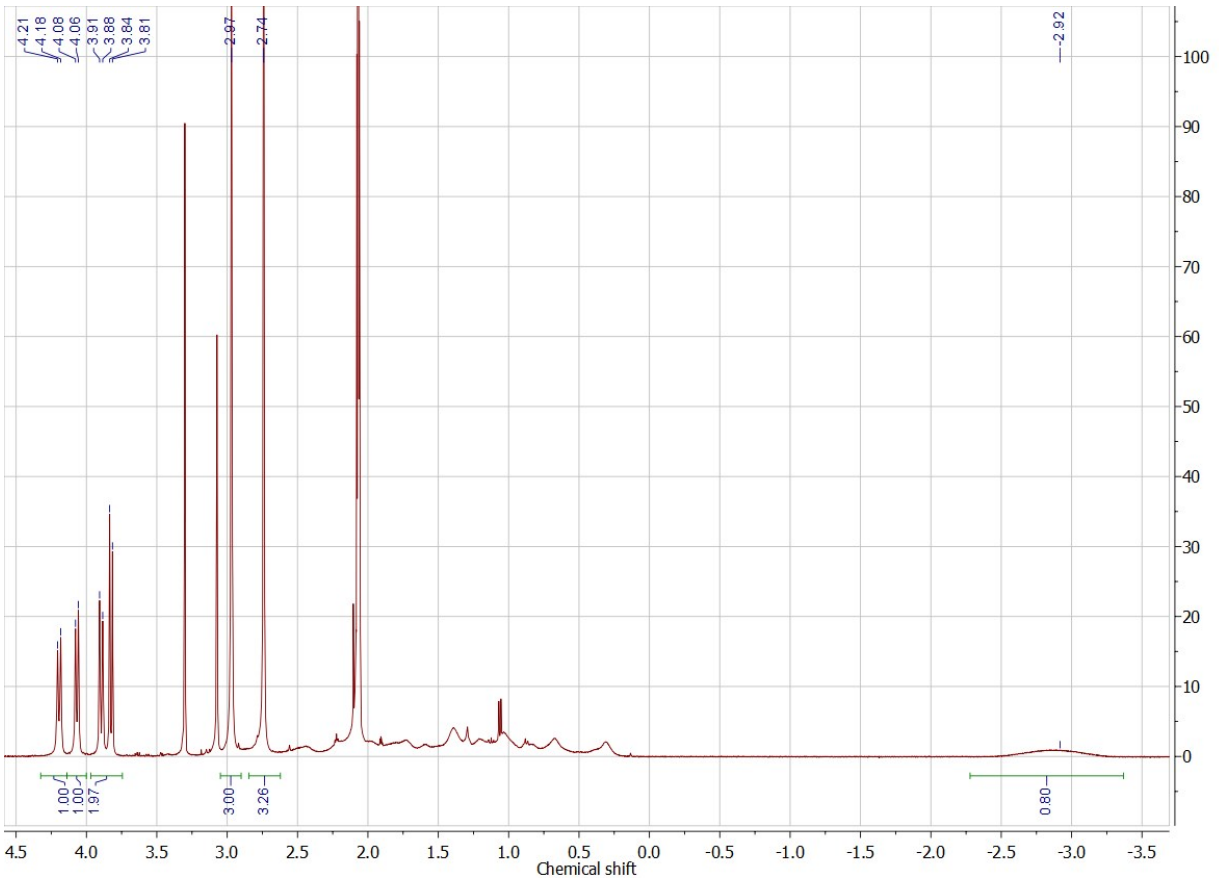


Figure S7. The ^{1}H NMR spectrum of **4** in acetone-d_6.

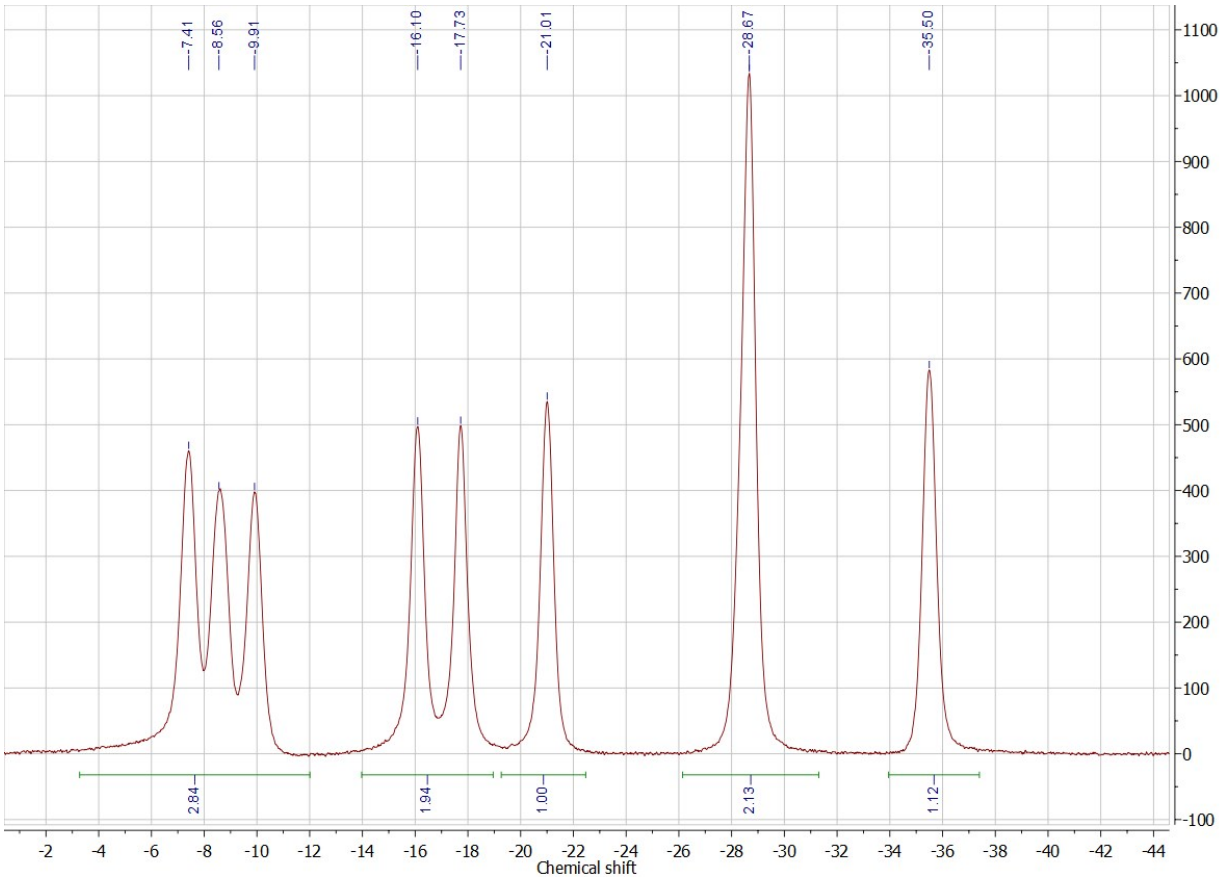


Figure S8. The $^{11}B\{^{1}H\}$ NMR spectrum of **4** in acetone-d_6.

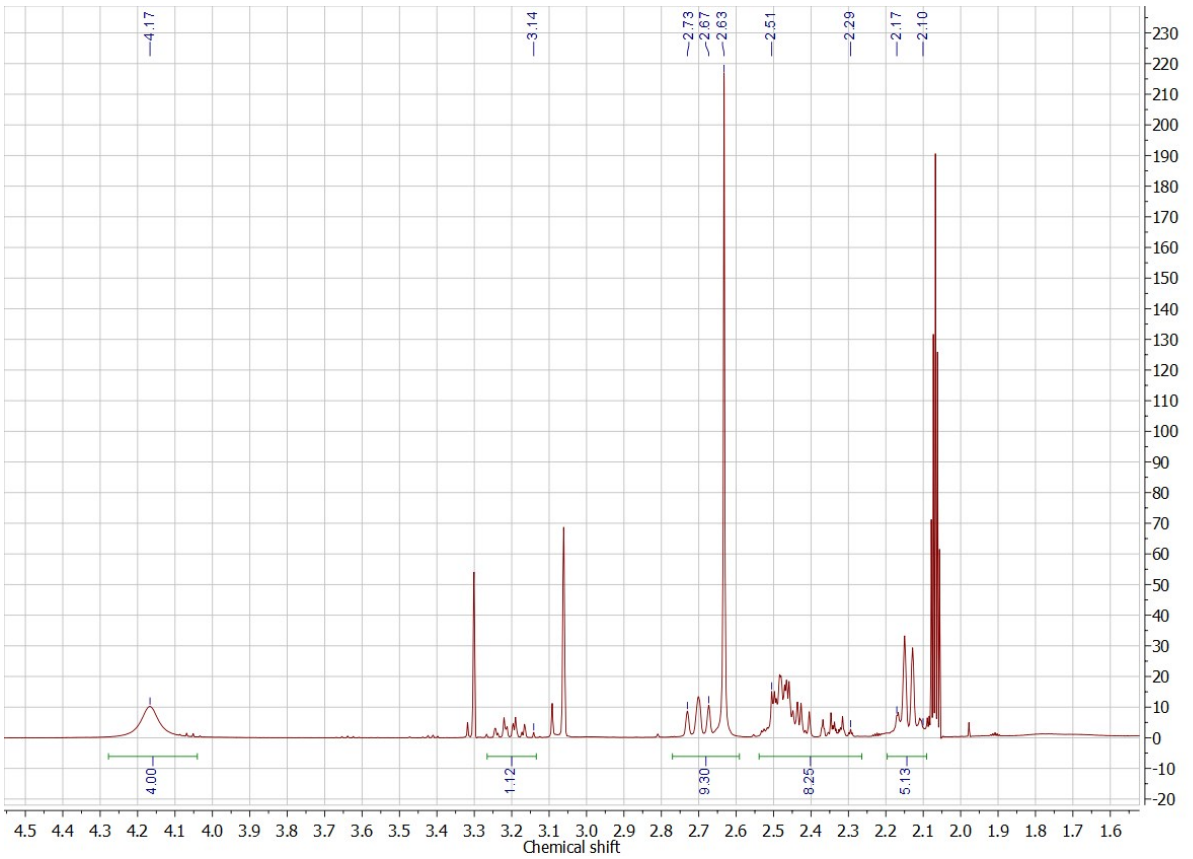


Figure S9. The ^{1}H NMR spectrum of **1a** in acetone-d_6.

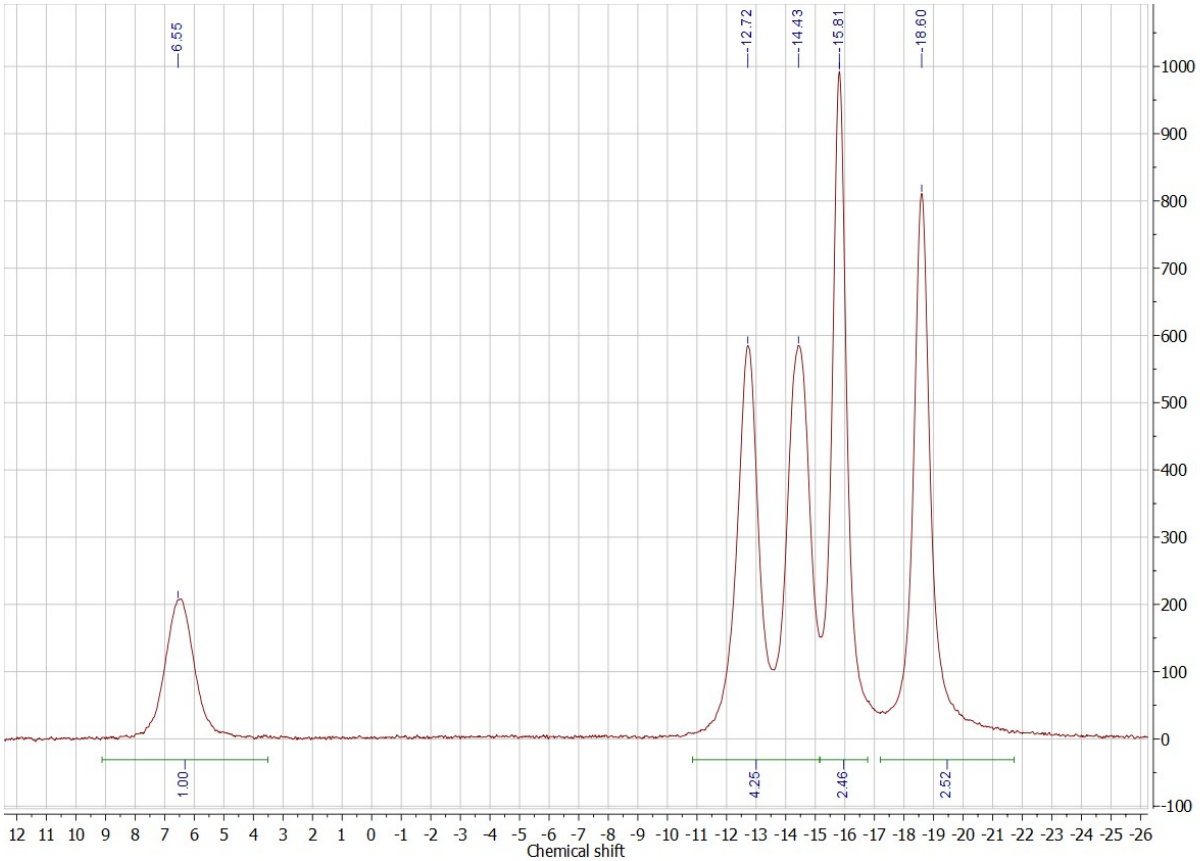


Figure S10. The $^{11}B\{^{1}H\}$ NMR spectrum of **1a** in acetone-d_6.

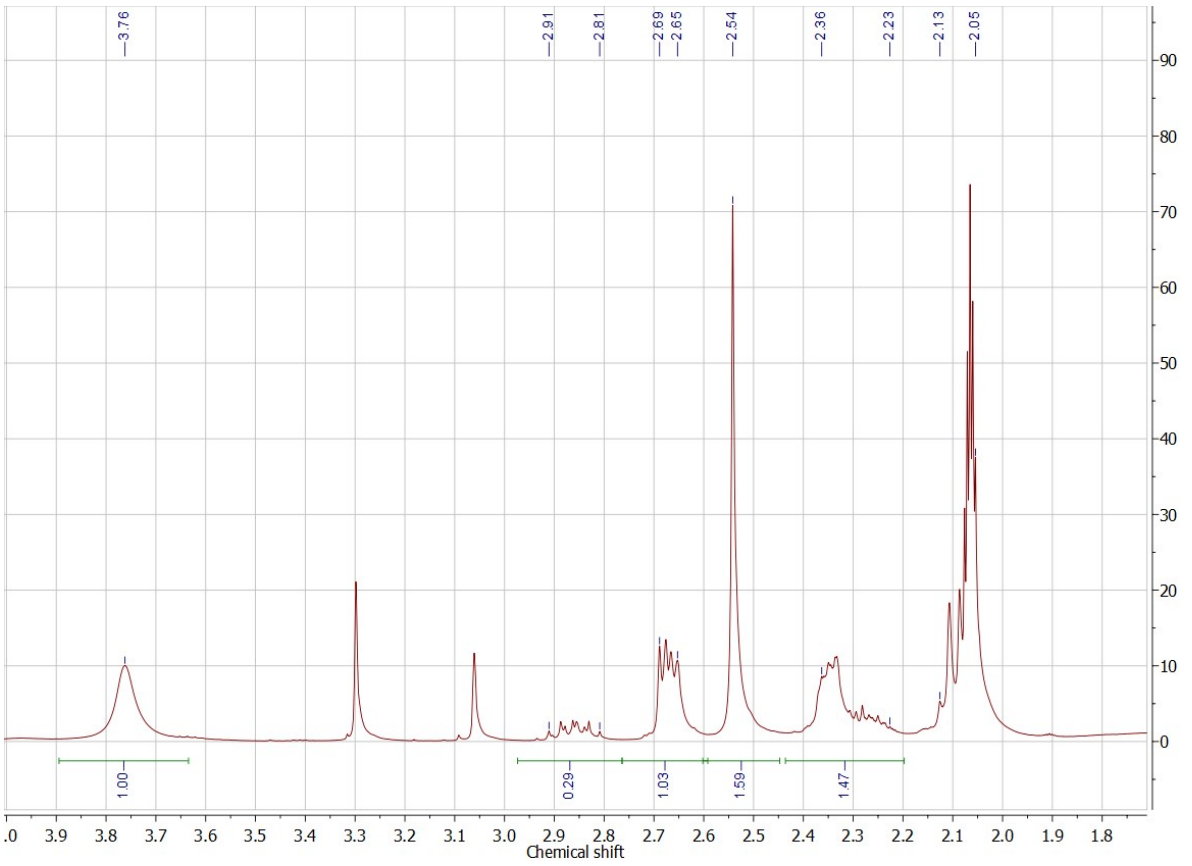


Figure S11. The ^{1}H NMR spectrum of **1b** in acetone-d_6.

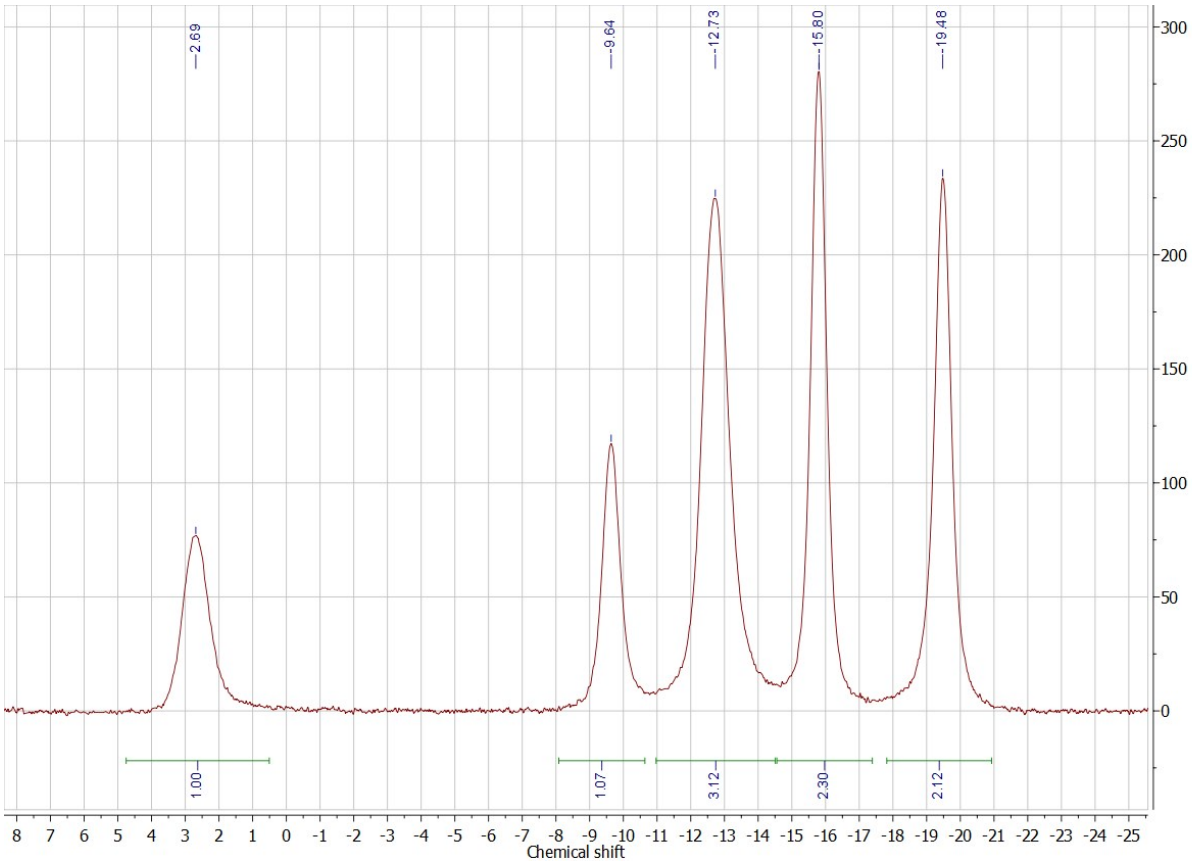


Figure S12. The $^{11}B\{^{1}H\}$ NMR spectrum of **1b** in acetone-d_6.

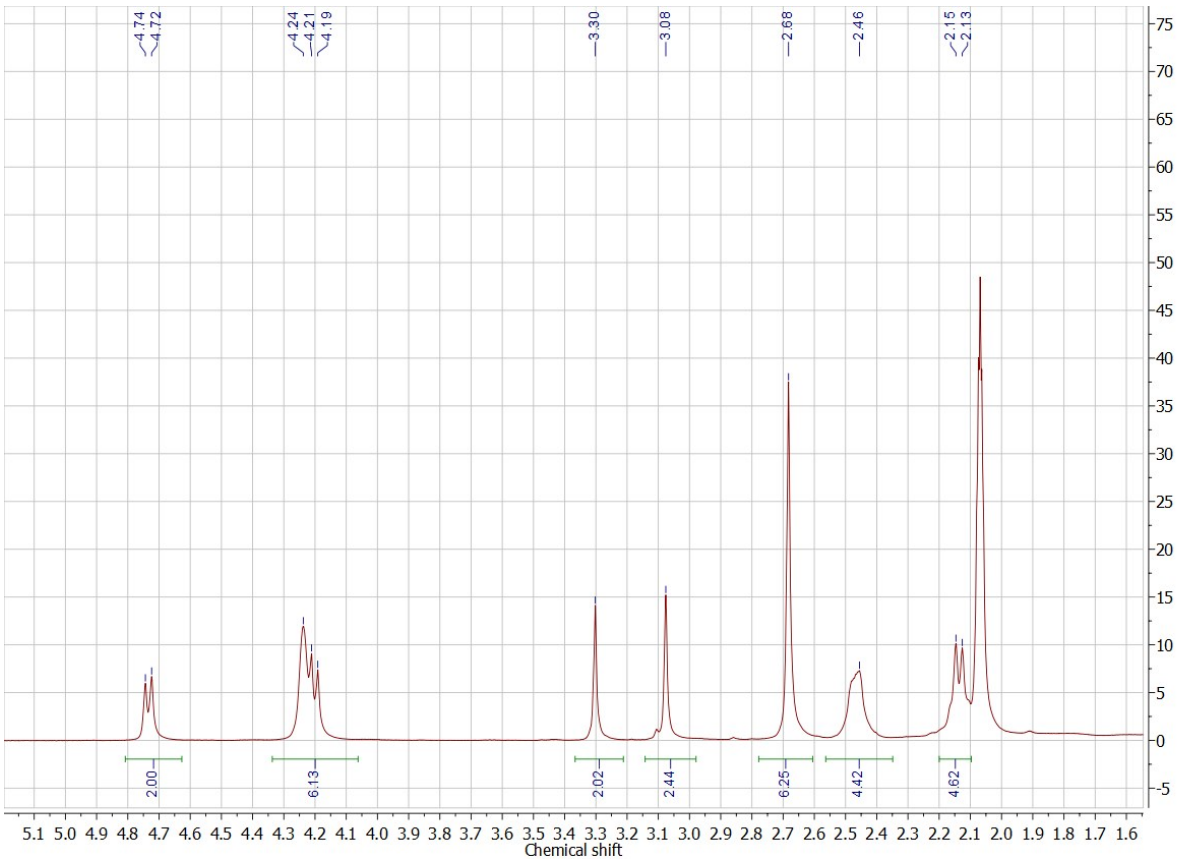


Figure S13. The ^{1}H NMR spectrum of **2a** in acetone-d_6.

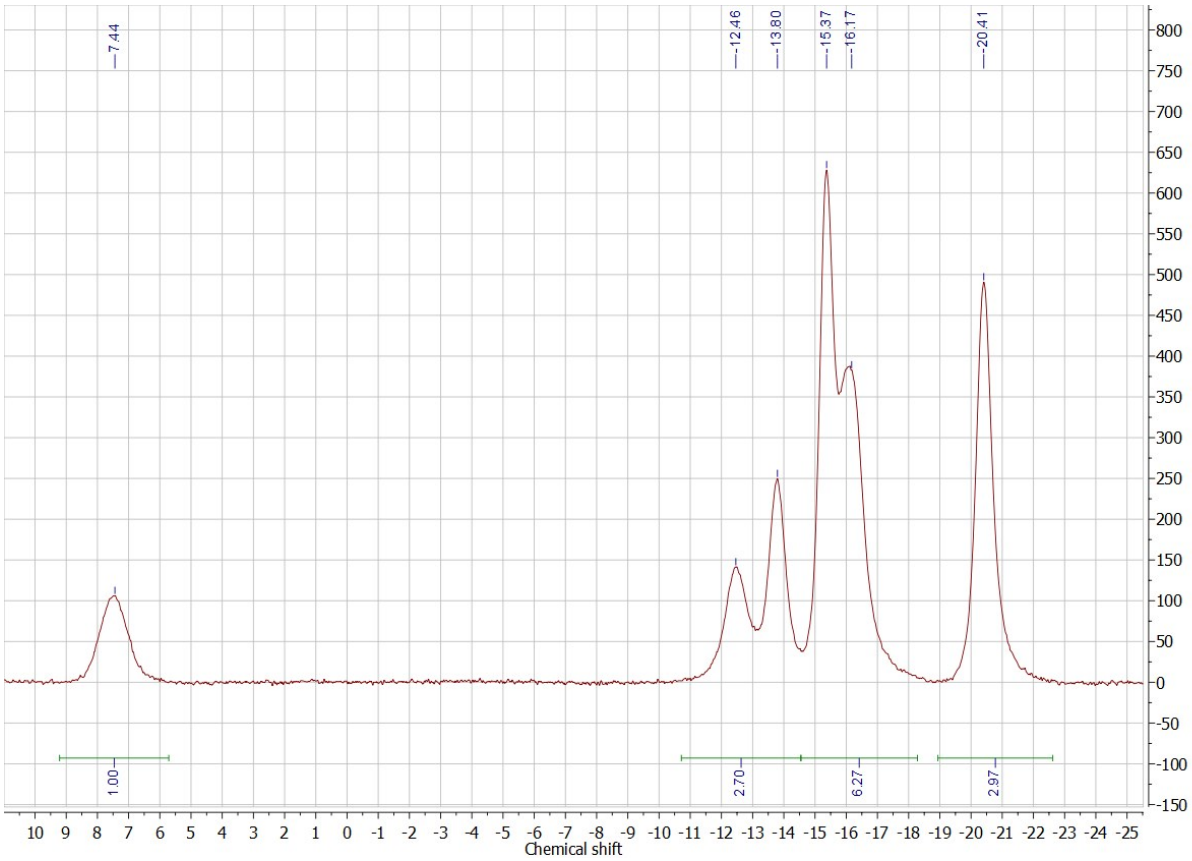


Figure S14. The $^{11}B\{^{1}H\}$ NMR spectrum of **2a** in acetone-d_6.

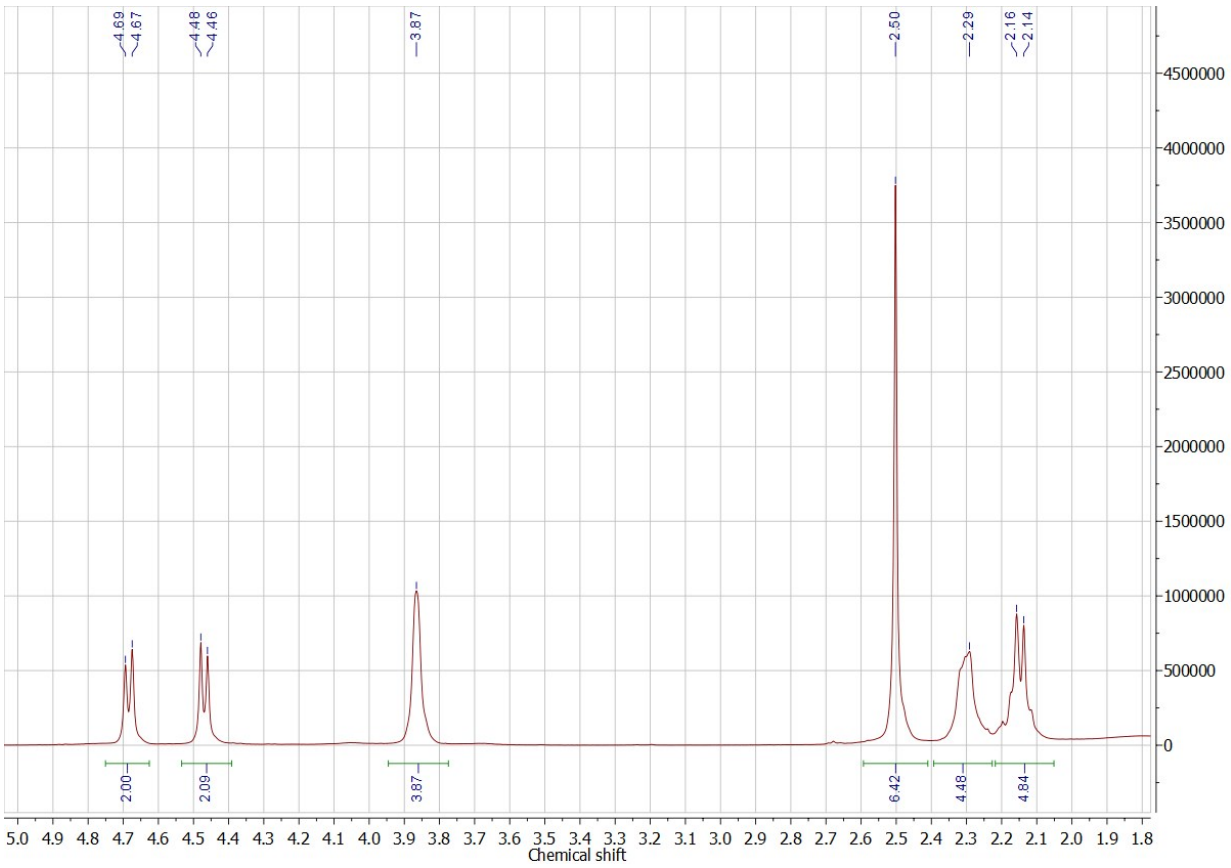


Figure S15. The ^{1}H NMR spectrum of **2b** in acetone-d_6.

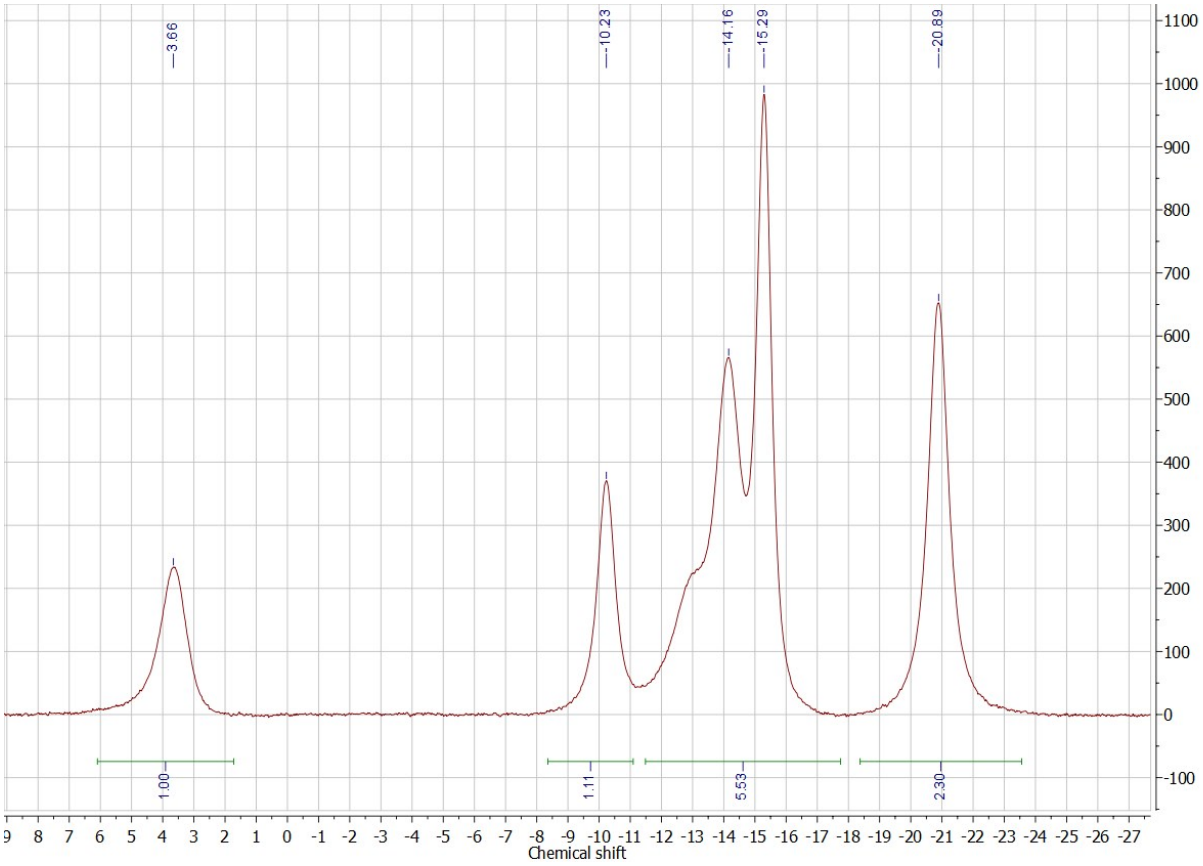


Figure S16. The $^{11}B\{^{1}H\}$ NMR spectrum of **2b** in acetone-d_6.

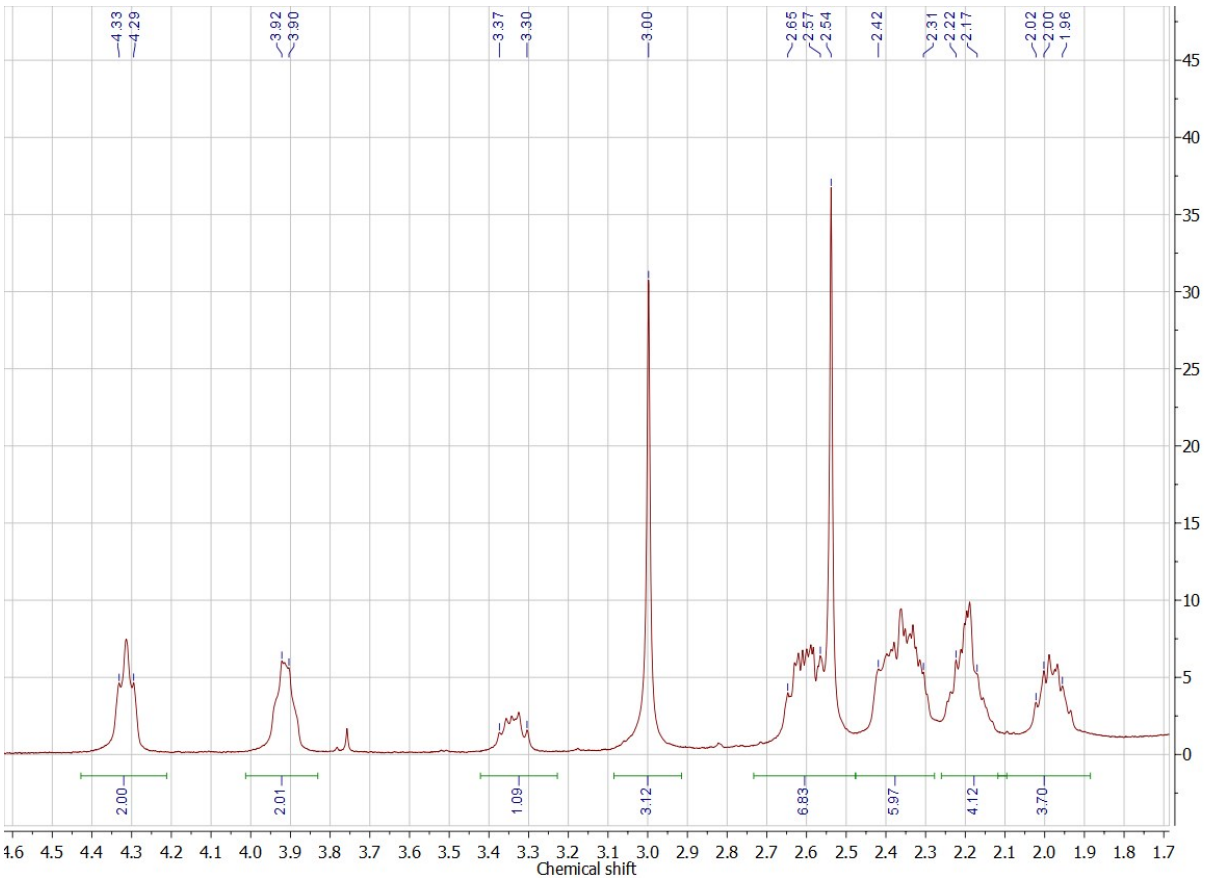


Figure S17. The ^{1}H NMR spectrum of **3a** in $CDCl_3$.

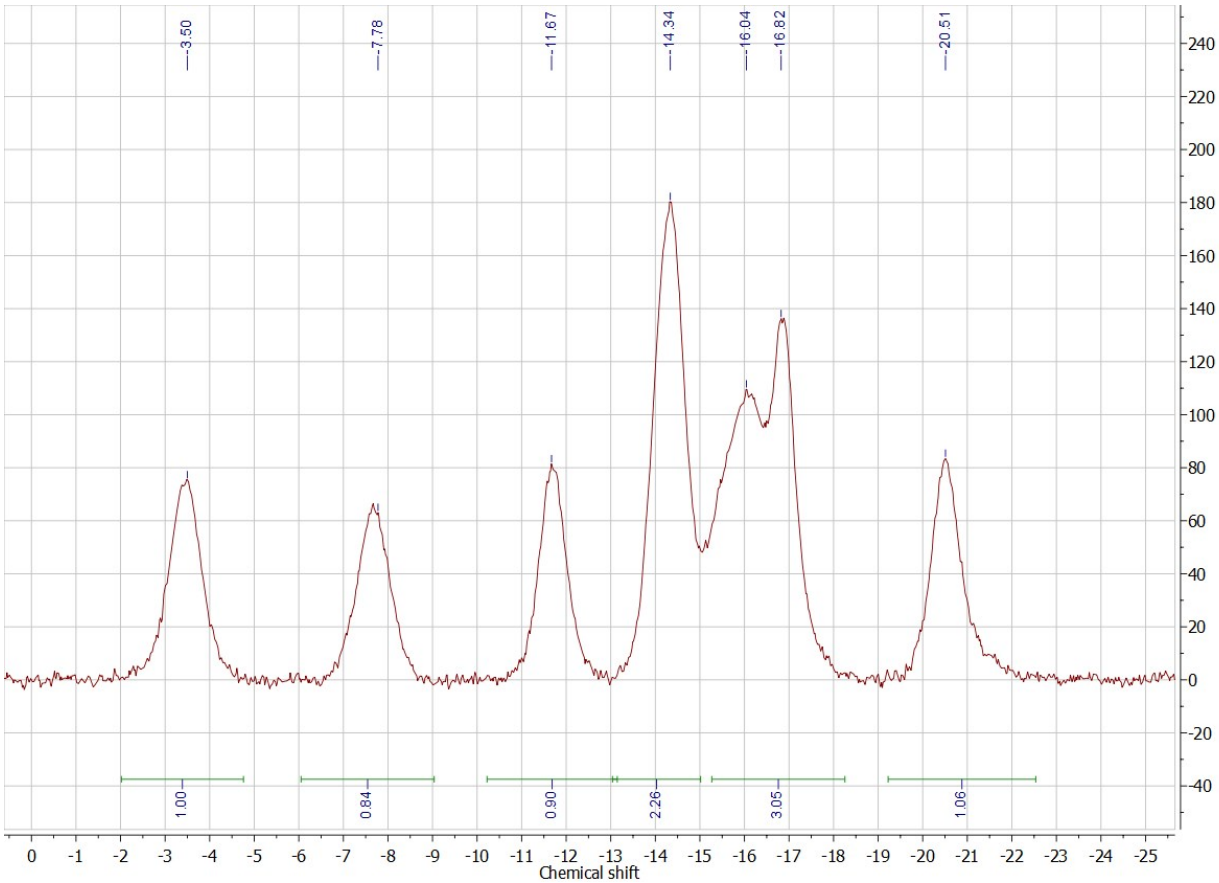


Figure S18. The $^{11}B\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

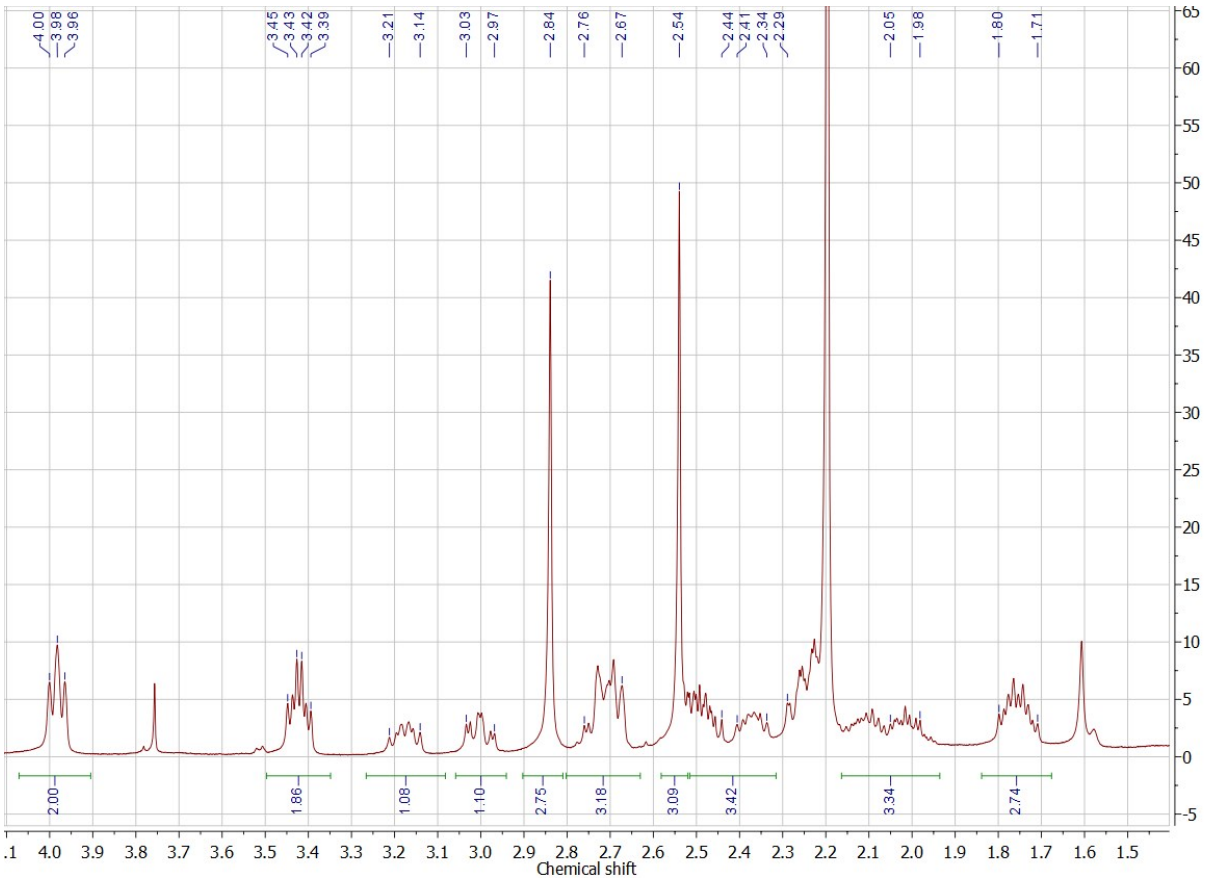


Figure S19. The ^{1}H NMR spectrum of **3b** in $CDCl_3$.

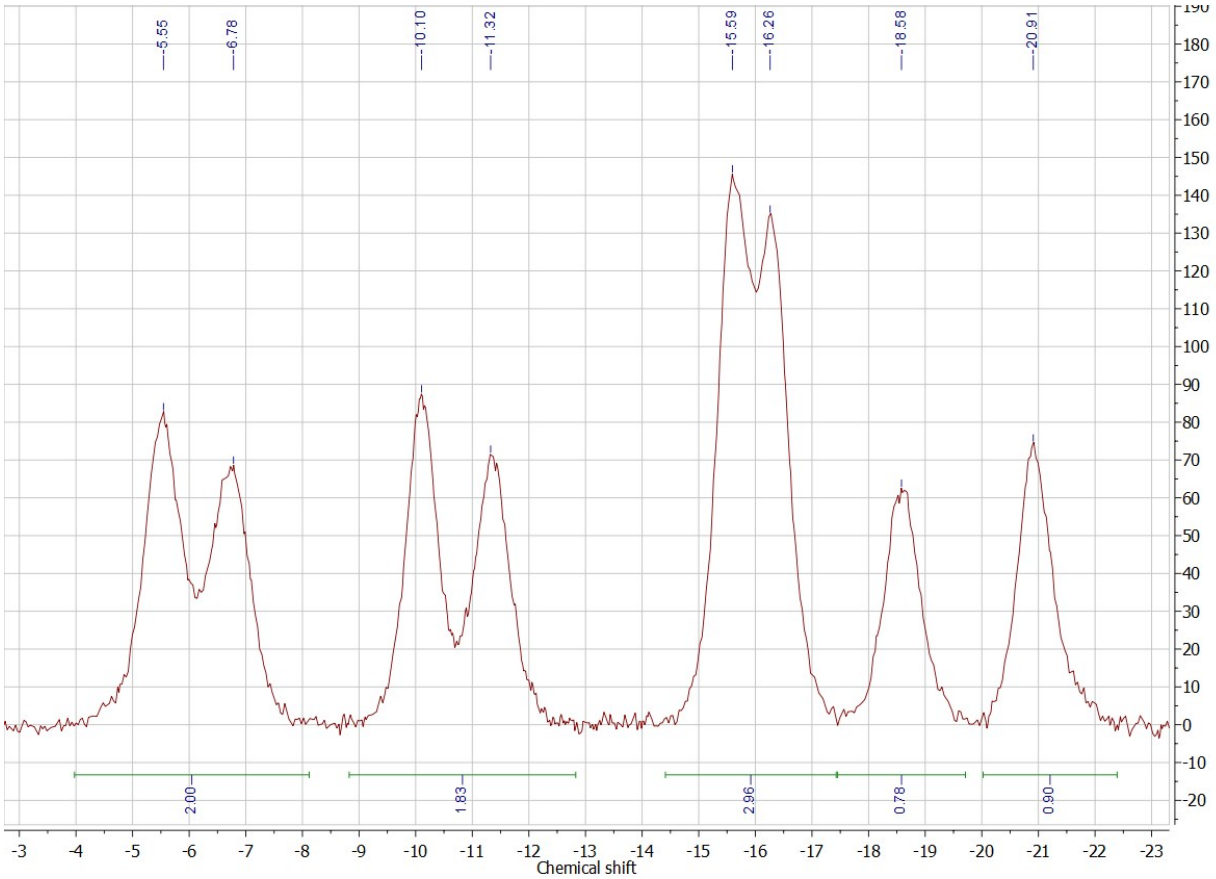


Figure S20. The $^{11}B\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

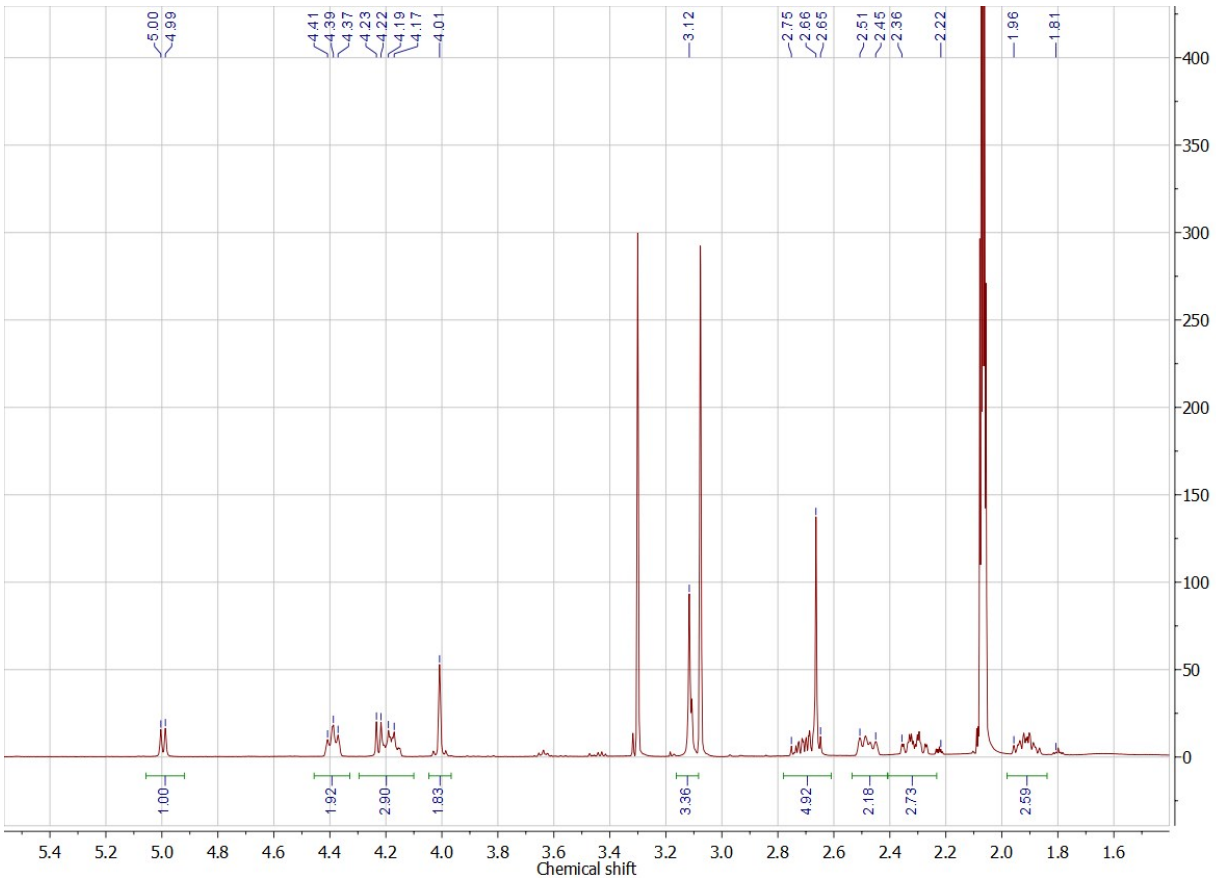


Figure S21. The ^{1}H NMR spectrum of **4a** in acetone-d_6.

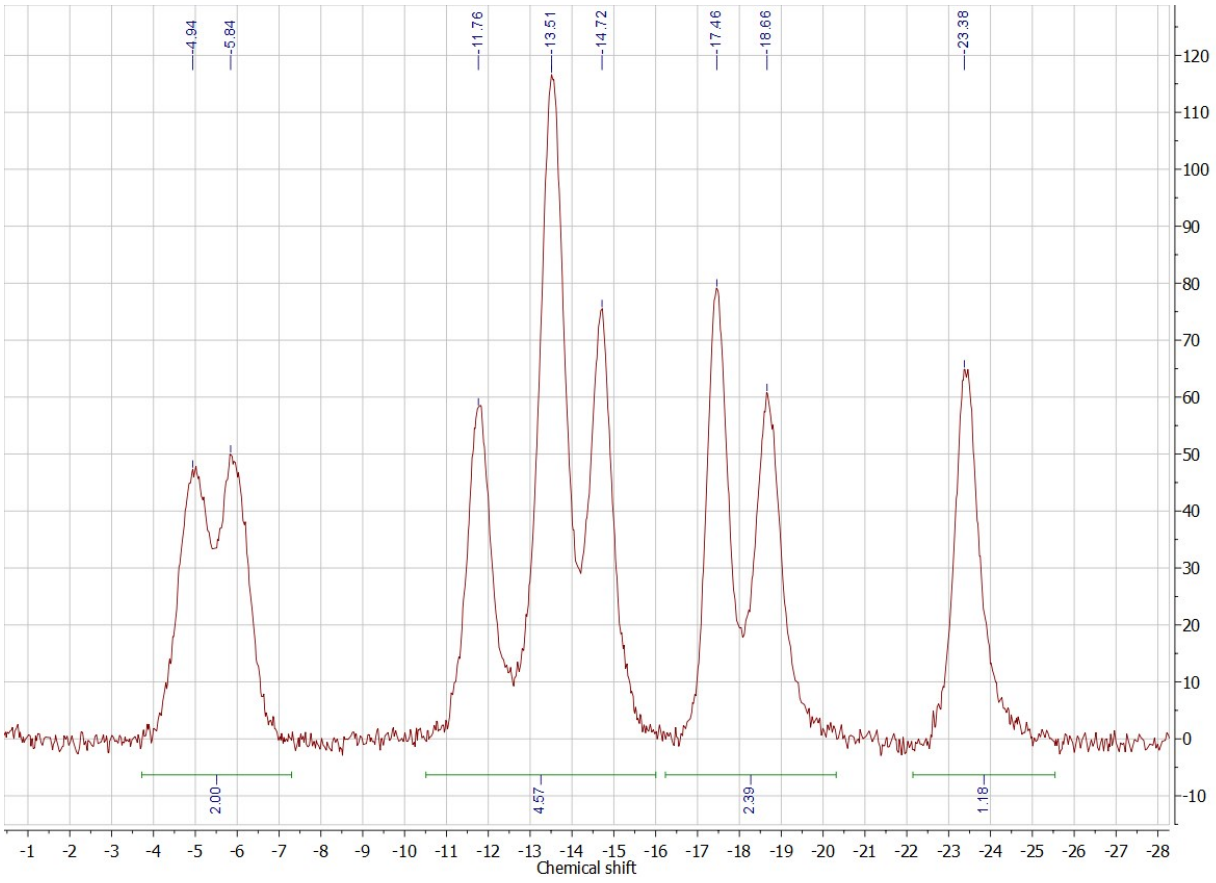


Figure S22. The $^{11}B\{^{1}H\}$ NMR spectrum of **4a** in acetone-d_6.

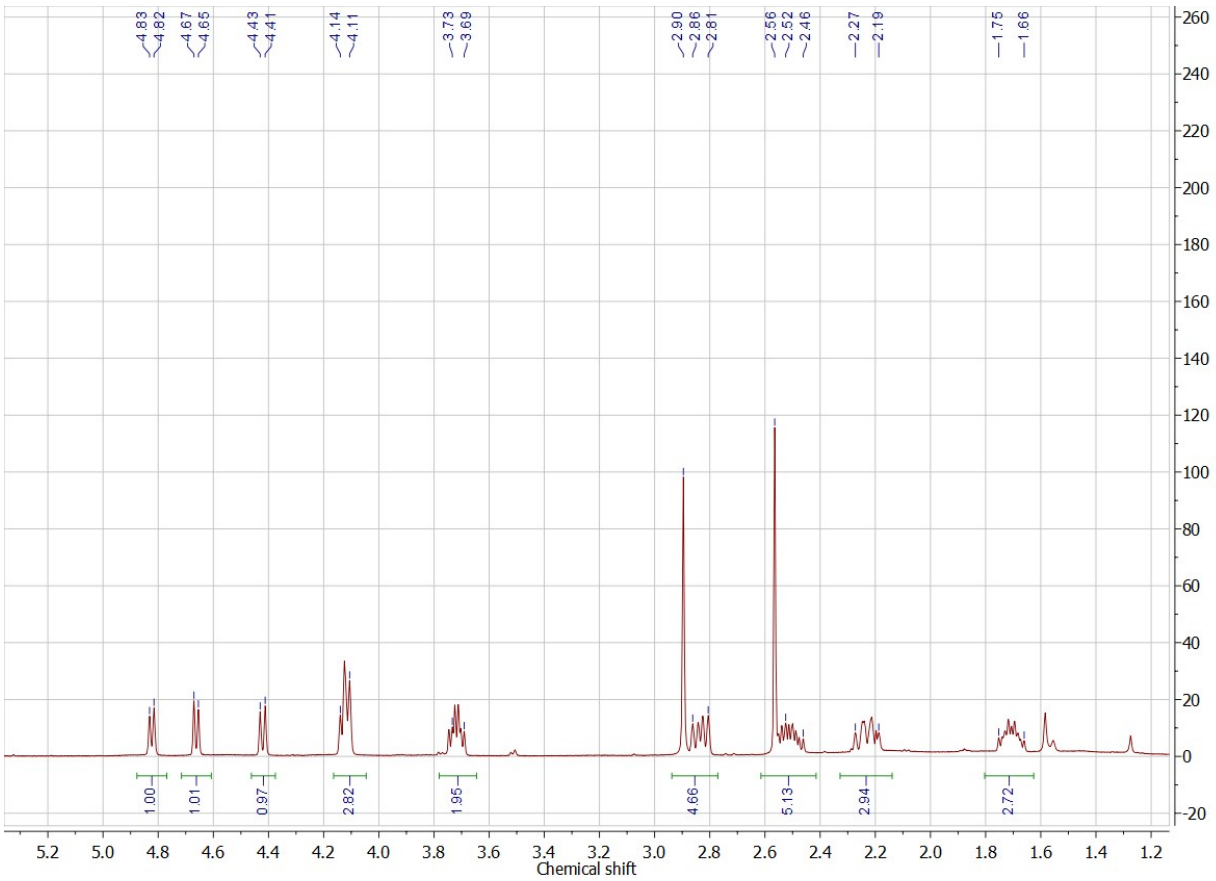


Figure S23. The ^{1}H NMR spectrum of **4b** in $CDCl_3$.

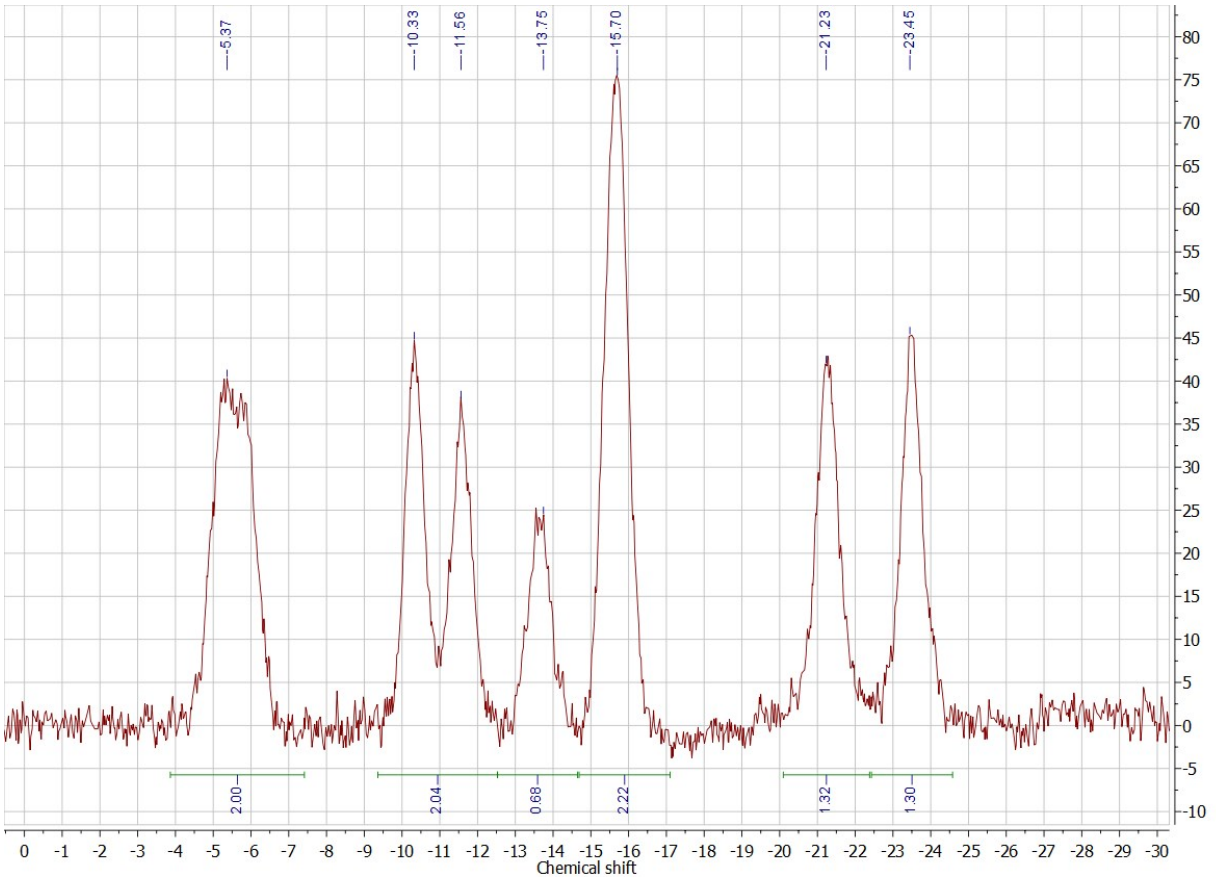


Figure S24. The $^{11}B\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$.

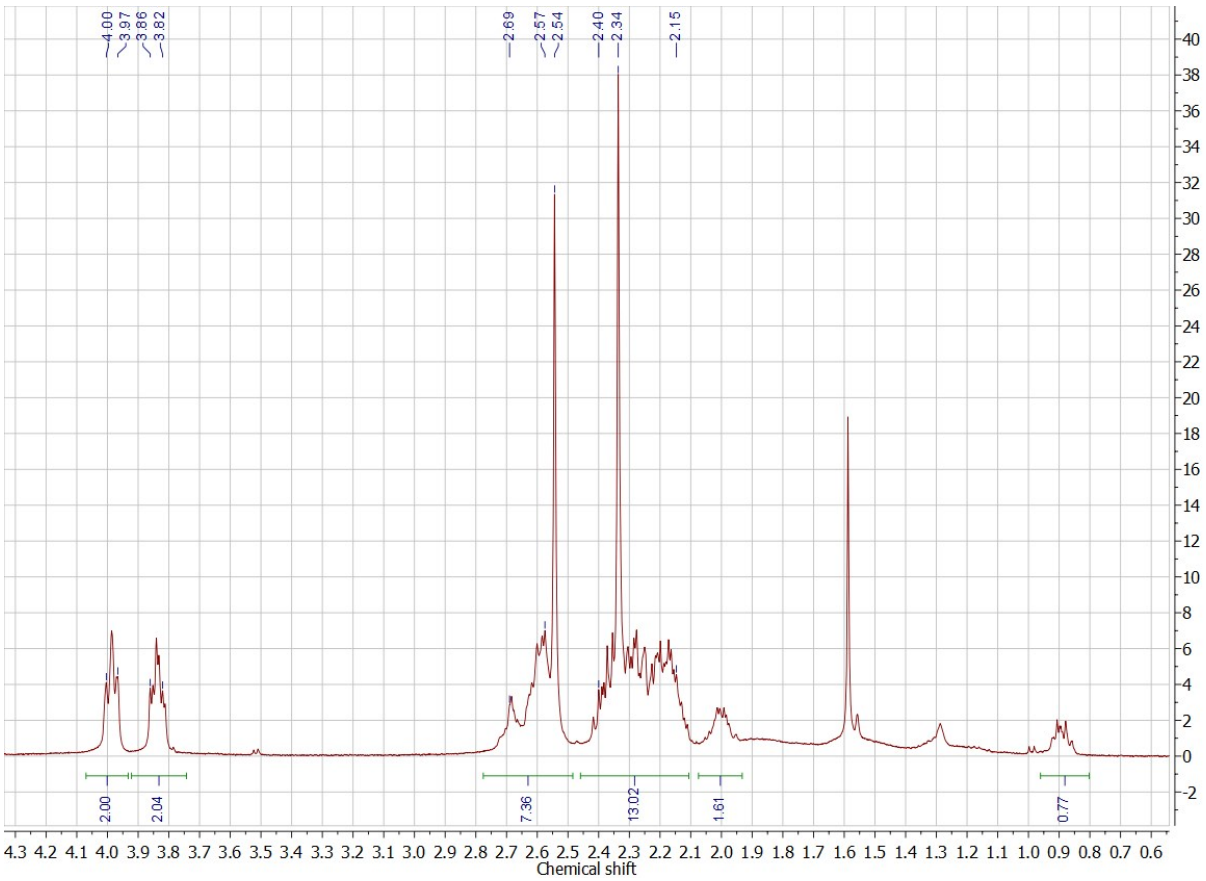


Figure S25. The ^{1}H NMR spectrum of **5** in $CDCl_3$.

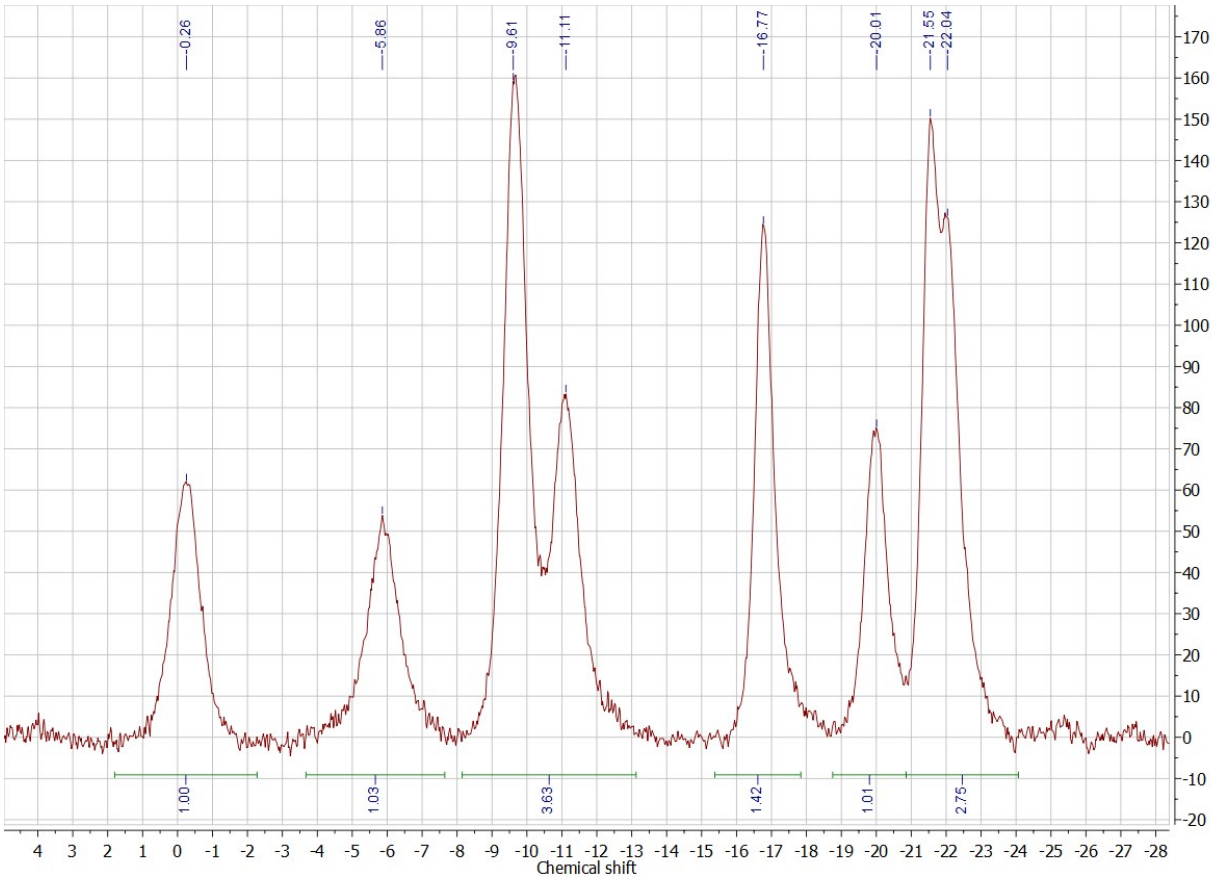


Figure S26. The $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

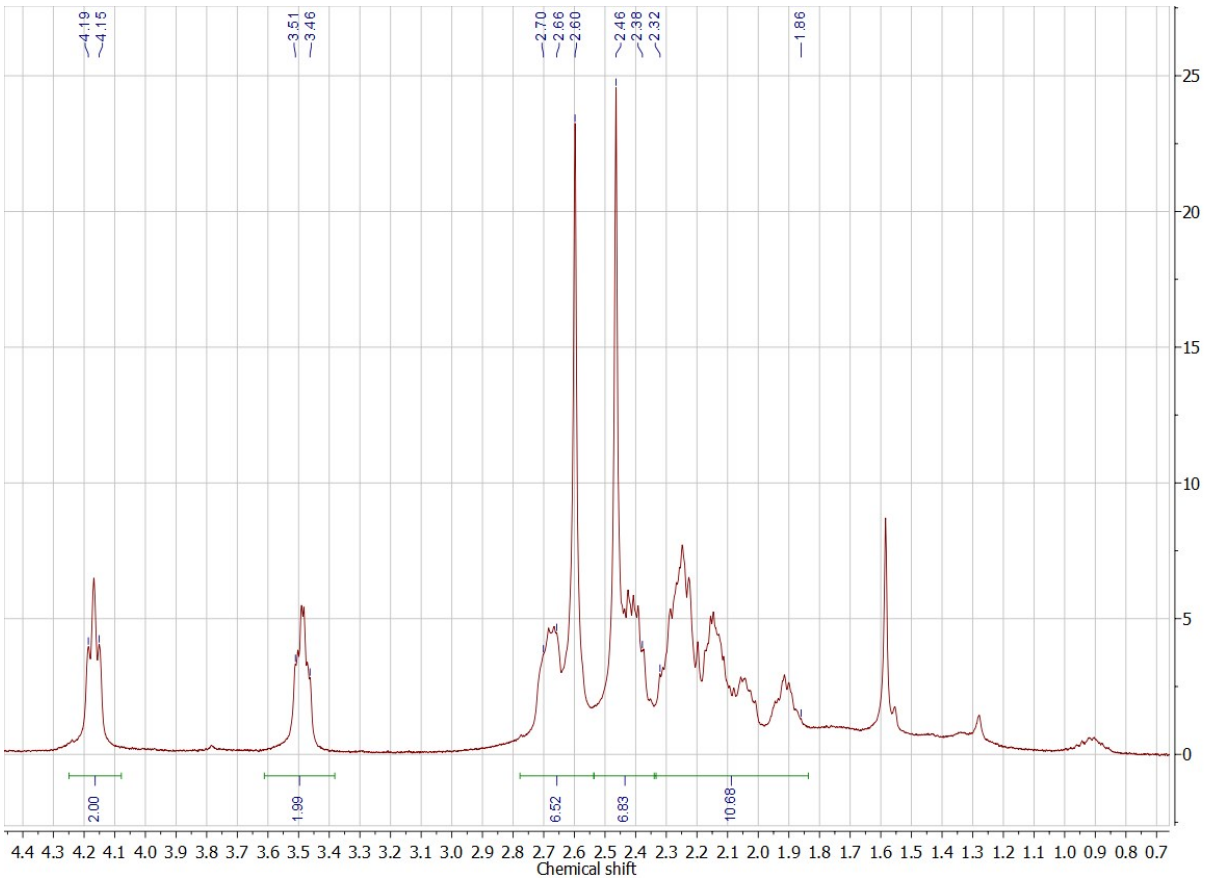


Figure S27. The ^{1}H NMR spectrum of **6** in $CDCl_3$.

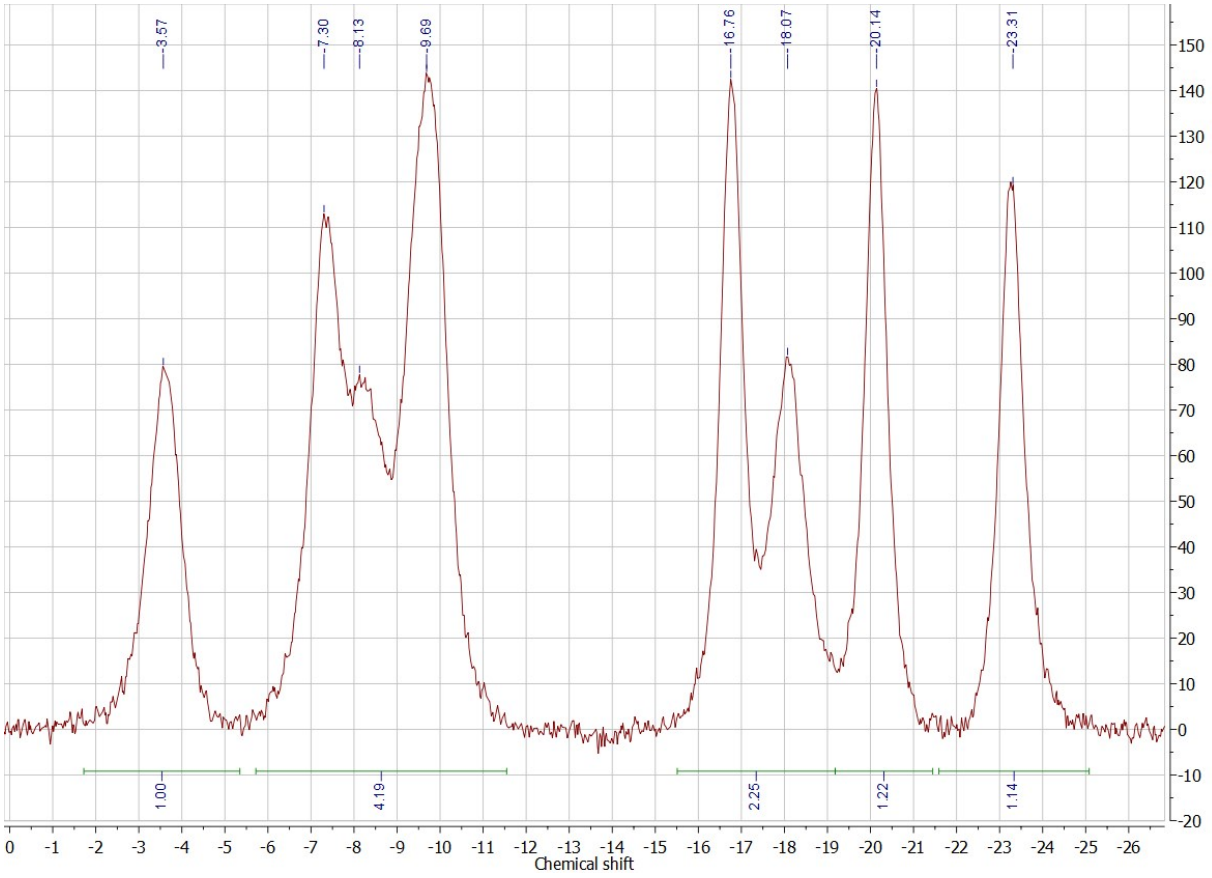


Figure S28. The $^{11}B\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

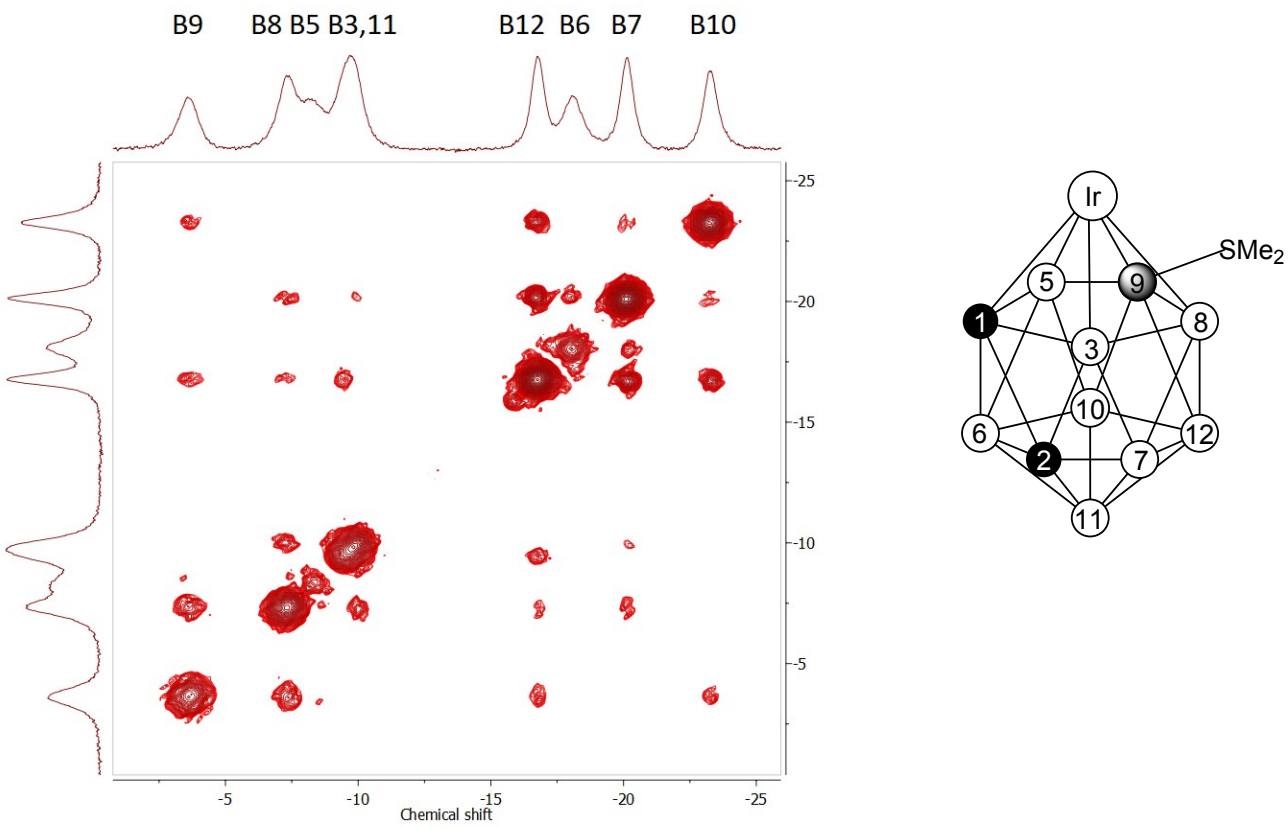


Figure S29. The $^{11}B\{^{1}H\} - ^{11}B\{^{1}H\}$ COSY NMR spectrum of **6** in $CDCl_3$.

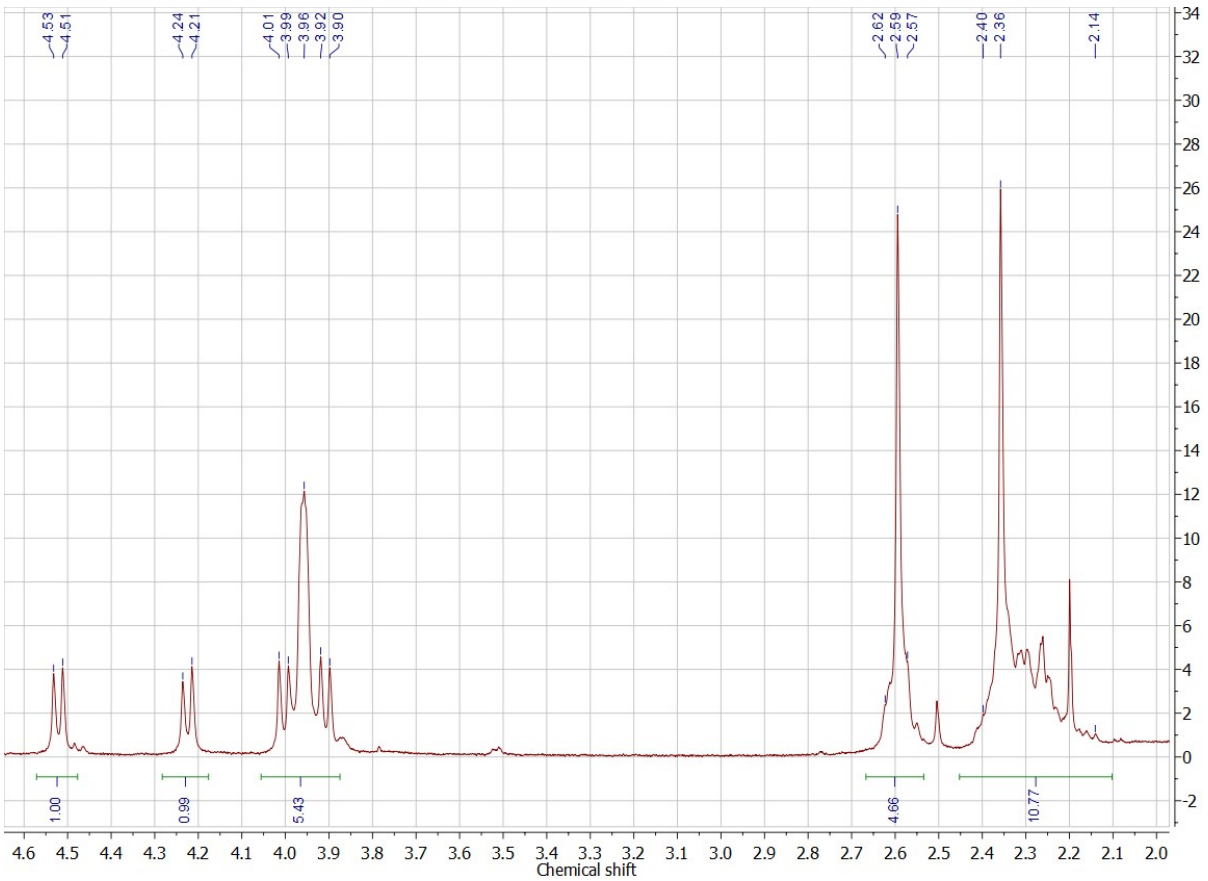


Figure S30. The ^{1}H NMR spectrum of **7** in $CDCl_3$.

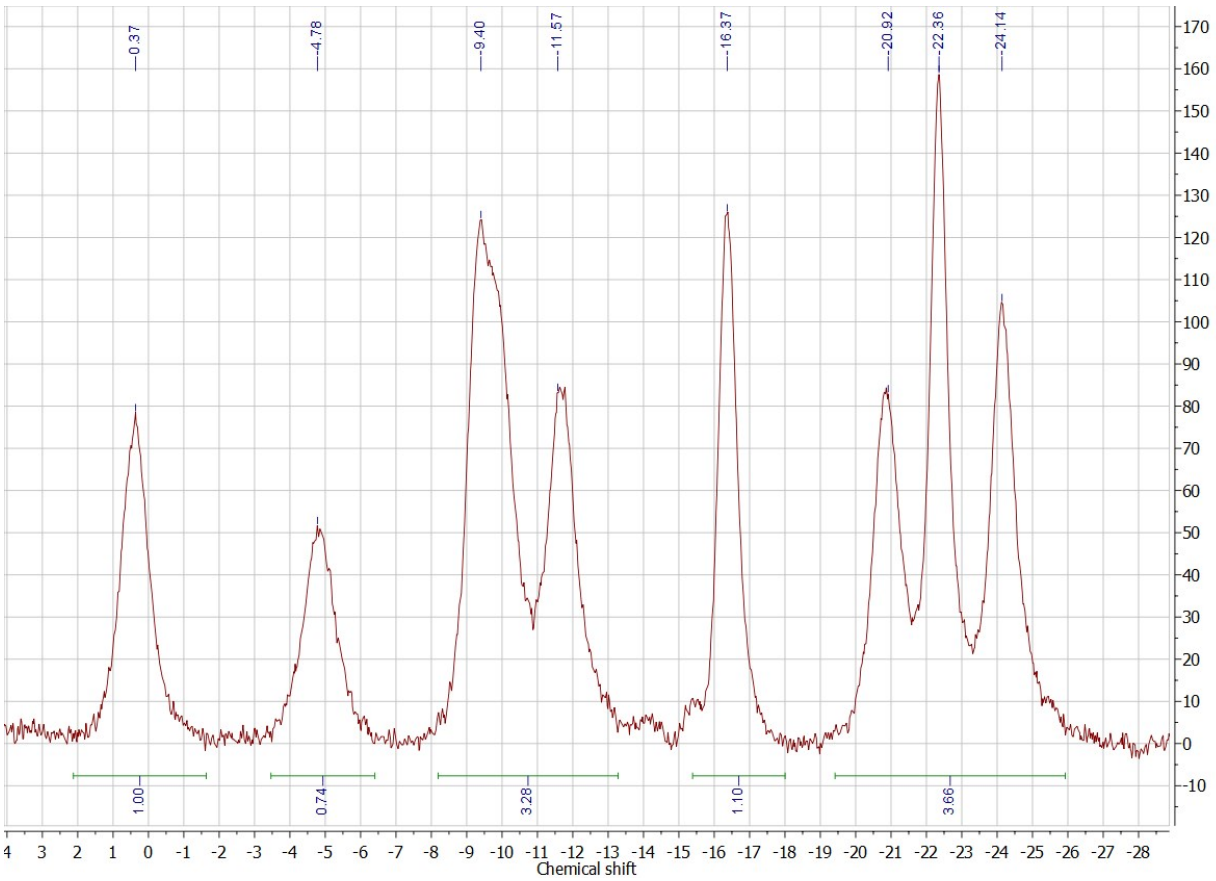


Figure S31. The $^{11}B\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

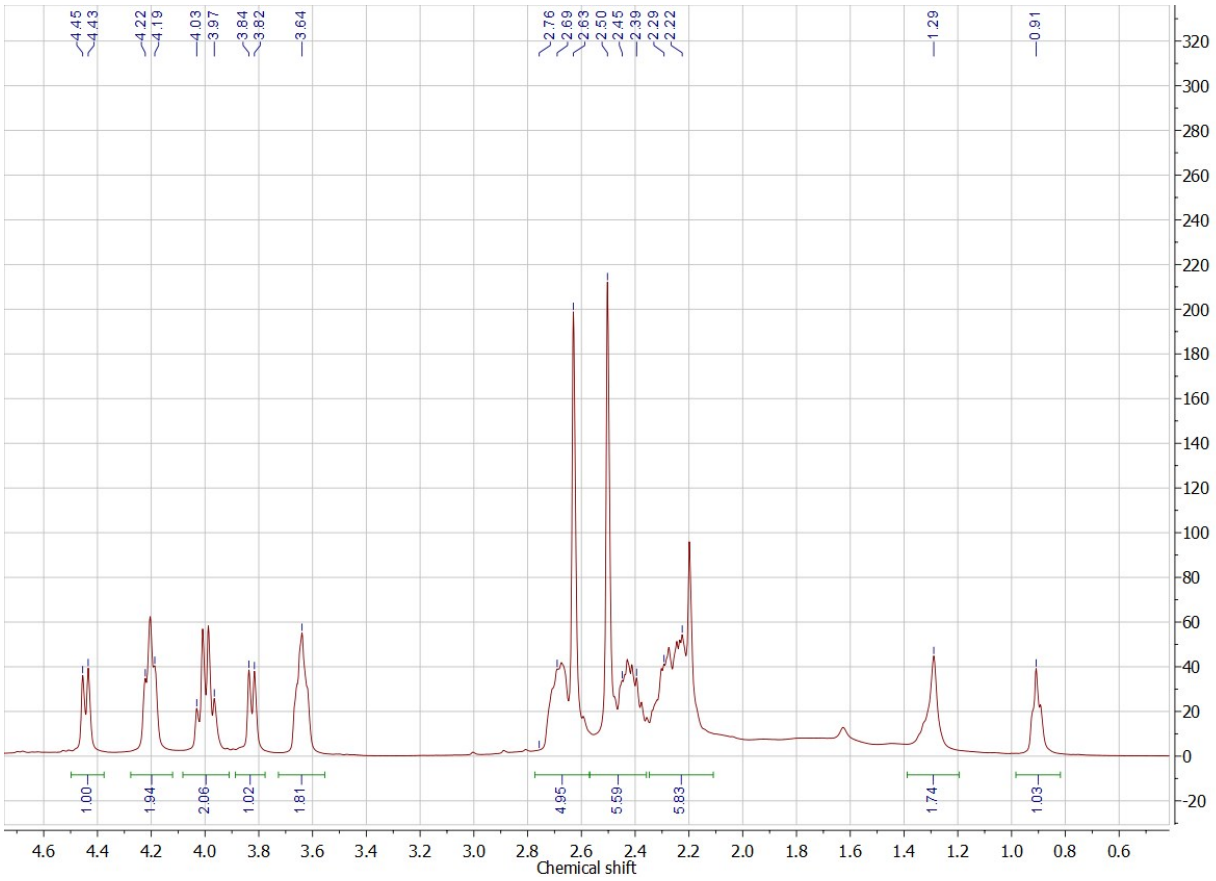


Figure S32. The ^{1}H NMR spectrum of **8** in $CDCl_3$.

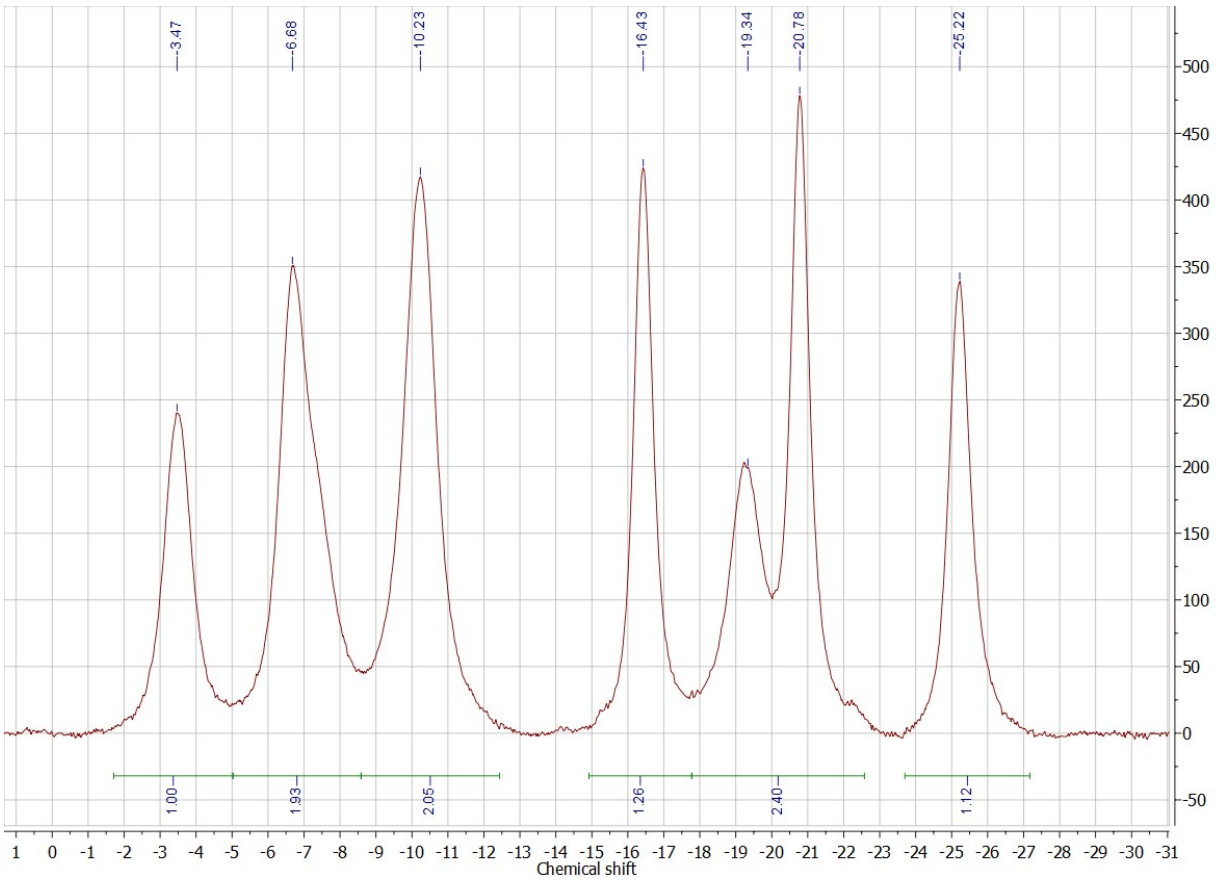
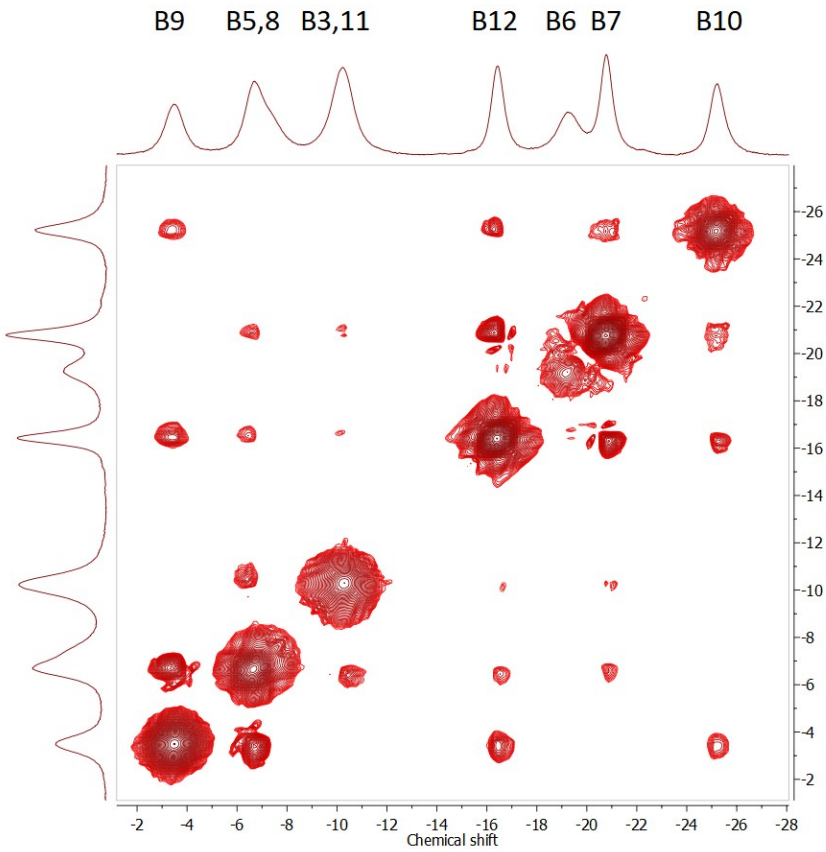


Figure S33. The $^{11}B\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.



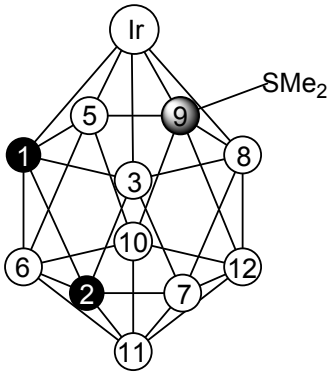


Figure S34. The $^{11}B\{^{1}H\} - ^{11}B\{^{1}H\}$ COSY NMR spectrum of **8** in $CDCl_3$.

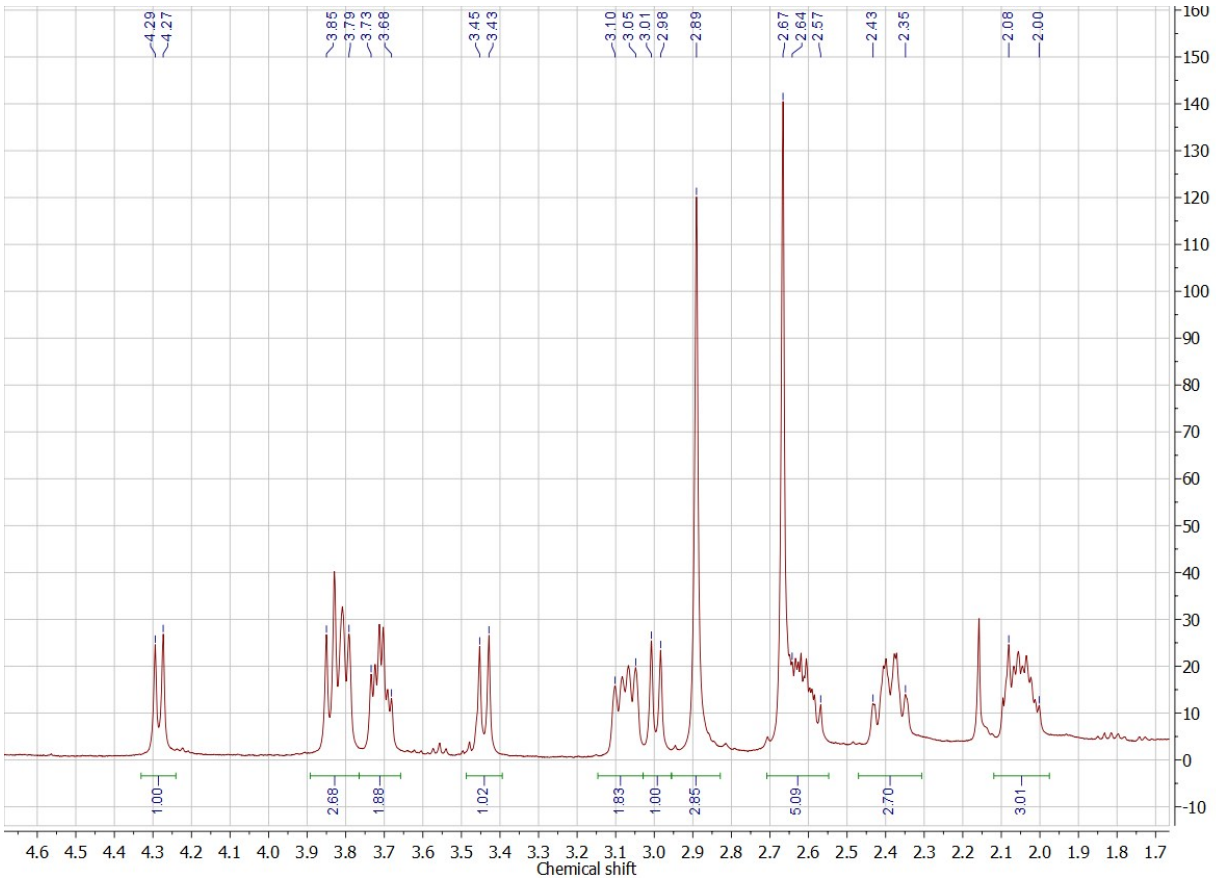


Figure S35. The ^{1}H NMR spectrum of **9** in CD_2Cl_2.

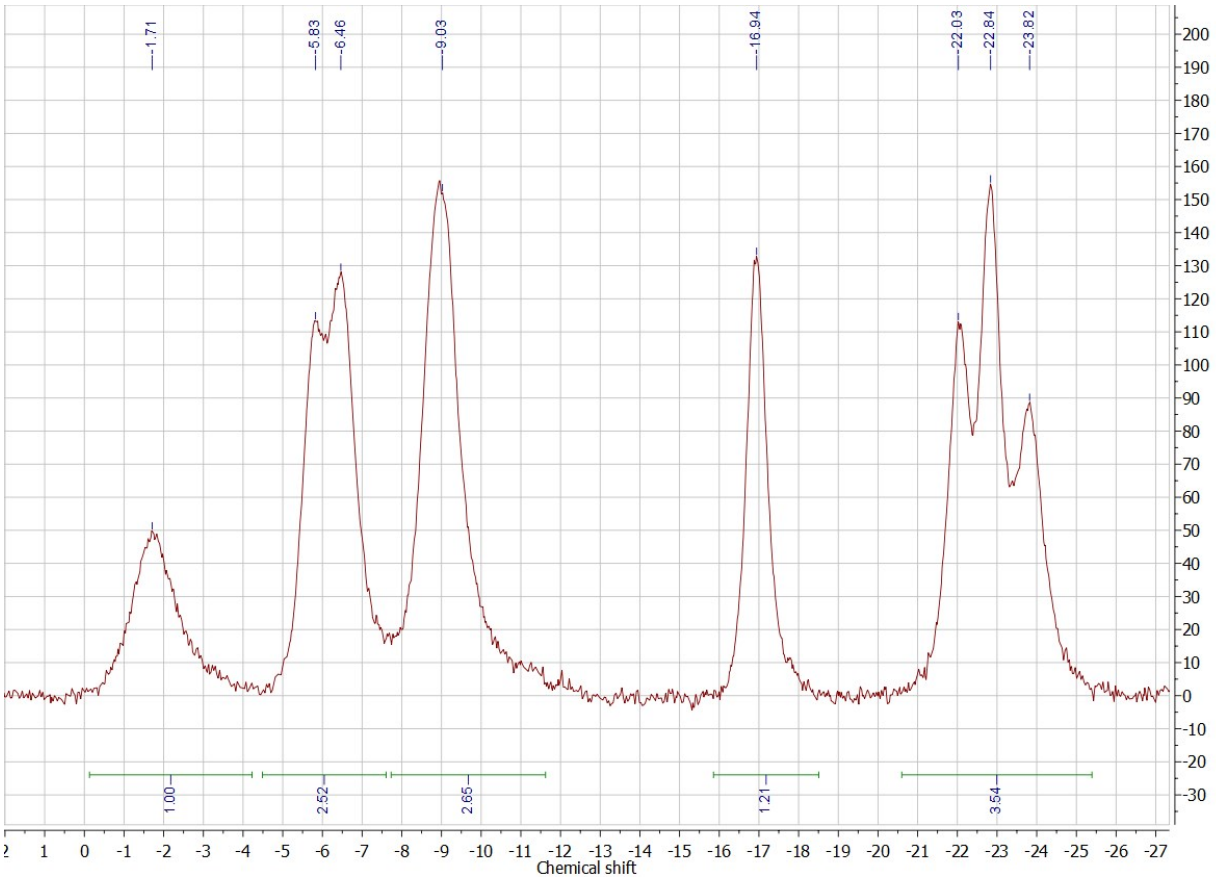


Figure S36. The $^{11}B\{^{1}H\}$ NMR spectrum of **9** in CD_2Cl_2.

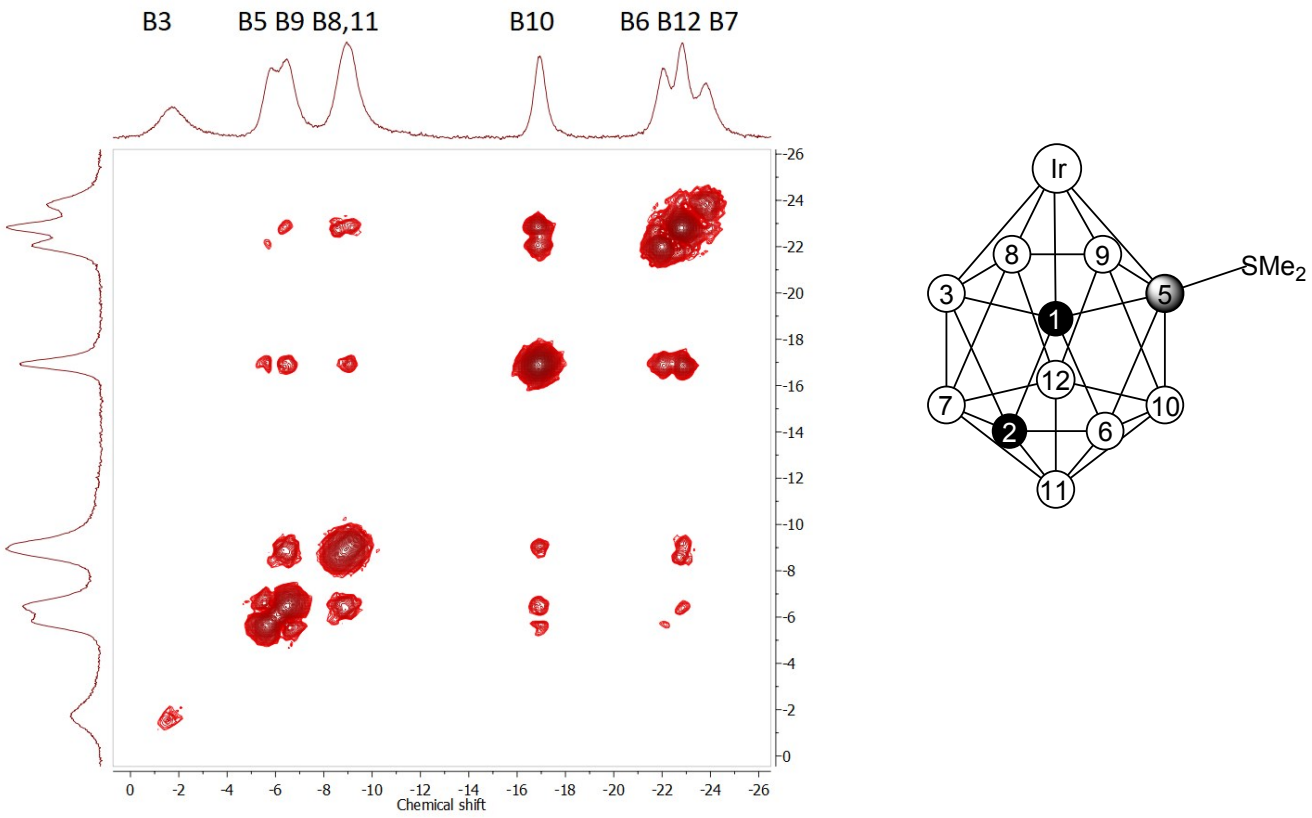


Figure S37. The $^{11}B\{^1H\} - ^{11}B\{^1H\}$ COSY NMR spectrum of **9** in CD_2Cl_2.

Single Crystal XRD (SC-XRD) data

Crystals of **5**, **6** and **8** were grown by slow gas phase diffusion of petroleum ether into a solution of complexes in C_6H_6–CH_2Cl_2 mixture. X-ray diffraction data were collected at 120 with Bruker Apex2 DUO diffractometer using graphite monochromated Mo-Kα radiation (lλ = 0.71073 Å, ω-scans). Using Olex2,[7] the structures were solved with the ShelXT[8] structure solution program using Intrinsic Phasing and refined with the XL[9] refinement package using Gauss-Newton minimisation. Hydrogen atoms of the BH groups were found in difference Fourier synthesis while positions of others were calculated, and they all were refined in the isotropic approximation within the riding model. Crystallographic data and structure refinement parameters are given in Table S1. CCDC 2019951, 2019952 and 2019950 contain the supplementary crystallographic data for **5**, **6** and **8** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and structure refinement parameters for **5**, **6** and **8.**

Compound	**5**	**6**	**8**
Empirical formula	$C_{15}H_{32}B_9IrS$	$C_{15}H_{32}B_9IrS$	$C_{14}H_{30}B_9IrOS$
Formula weight	533.95	533.95	535.93
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	16.9917(14)	7.7089(9)	7.6152(4)
b (Å)	14.5337(12)	15.4832(18)	15.4766(8)
c (Å)	16.3704(13)	17.075(2)	16.6390(8)
β (°)	99.389(2)	94.072(2)	97.3260(10)
V (Å^3)	3988.5(6)	2032.9(4)	1945.02(17)
D_{calc} (g cm^{-3})	1.778	1.745	1.830
Linear absorption, μ (cm^{-3})	67.96	66.67	69.72
F(000)	2080	1040	1040
$2\theta_{max}$, °	52	52	54
Reflections measured	63723	19576	16954
Independent reflections	6862 (R_{int} = 0.0291)	4002 (R_{int} = 0.0326)	4247 (R_{int} = 0.0532)
Observed reflections ($I > 2\sigma(I)$)	7844	3630	3442
Parameters	473	237	237

R_1 (on F for obs. refls)	0.0166	0.0185	0.0246
wR_2 (on F2 for all refls)	0.0399	0.0426	0.0554
Goodness-of-fit	1.029	1.059	1.032
Largest diff. peak and hole (e $Å^{-3}$)	1.105 and −0.472	1.951 and −0.399	0.878 and −0.880

Computational Methods

All calculations were performed using Orca programm (version 4.2.1)[10] on PBE/def2-TZVP[11] level on all atoms with ECP on iridium atom (TightOpt, TightScf and Grid4 options were used). The geometry optimizations were carried out without symmetry constraints, and analytical hessians were computed to confirm the nature of the stationary points to yield one imaginary frequency for the transition states and none for the minima. The nature of all transition states was investigated by the analysis of vectors associated with the imaginary frequency and by the calculations of the Intrinsic Reaction Roordinate (IRC).[12] The ChemCraft program[13] was used for molecular modeling and visualization.

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