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SUPPORTING INFORMATION

Icosahedral carboranes as scaffolds for congested regioselective polyaryl compounds. The distinct distance tuning of C-C and its antipodal B-B.

Zsolt Kelemen,[a] Ariadna Pepiol,[a] Marius Lupu,[a] Reijo Sillanpää,[b] Mikko M. Hänninen,[b] Francesc Teixidor,[a] Clara Viñas[a,*]

[a] Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus U.A.B. 08193 Bellaterra, Spain.

[b] Department of Chemistry, University of Jyväskylä, FIN-40351, Jyväskylä, Finland.

* clara@icmab.es, Fax: +34 93 580 57 29; Tel: +34 93 580 18 53

Experimental Section:
Synthesis of 9,12-($C_6H_4CH(OCH_3)_2$)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$, **3**
Synthesis of 9,12-(C_6H_4CHO)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$, **4**
Synthesis of 8,10-I_2-9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_8$, **7**
Synthesis of 8,10-Ph_2-9,12-(CH_2=$CHCH_2$)$_2$-1,2-*closo*-$C_2B_{10}H_8$, **9**
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Synthesis of 8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, **11** and 8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$ **10** under microwave irradiation

X-ray structure analysis of compounds **3**, **4**, **9**, **10** and **11**
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Spectroscopic characterization:
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9,12-($C_6H_4CH(OCH_3)_2$)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$, **3**
9,12-(C_6H_4CHO)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$, **4**
8,10-I_2-9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_8$, **7**
8,10-Ph_2-9,12-(CH_2=$CHCH_2$)$_2$-1,2-*closo*-$C_2B_{10}H_8$, **9**
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8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, **11**.

DFT calculations

Table S1 Bond lengths of the B9-B12 and C1-C2 bonds in case of 9,12-(aryl)$_2$-1,2-*closo*-$C_2B_{10}B_{10}$ and some related compounds

Experimental Section

Materials and instrumentation: All *o*-carboranes prepared are air and moisture stable. All manipulations were carried out under inert atmosphere. All solvents for the reactions were distilled from sodium prior to use. Reagents were obtained commercially (PhMgBr solution in THF, allyl-MgBr solution in THF as well) and used as purchased. 1,2-*closo*-$C_2B_{10}H_{12}$ was purchased from Katchem. 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, **1**[1] 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$, **2**,[1] 9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_8$[2] and 8,10-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$, **5**[3] were synthetized as reported at the literature.

IR spectra (v, cm^{-1}; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ATR-IR spectra recorded on a high-resolution spectrometer FT-IR Perkin Elmer Spectrum ONE. The ^1H- and $^1H\{^{11}B\}$-NMR (300.13 MHz), $^{13}C\{^1H\}$-NMR (75.47 MHz) and ^{11}B- and $^{11}B\{^1H\}$-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. The NMR spectra of compound **3**, **4**, **7**, **9, 10** and **11** were recorded on a Bruker Advance III 400SB (^1H- and $^1H\{^{11}B\}$-NMR (400.23 MHz), $^{13}C\{^1H\}$-NMR (100.62 MHz) and ^{11}B- and $^{11}B\{^1H\}$-NMR (128.38 MHz)). All NMR spectra were performed in deuterated solvent at 22 ºC. The ^{11}B- and $^{11}B\{^1H\}$-NMR shifts were referenced to external $BF_3{\cdot}OEt_2$, while the ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$-NMR shifts were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. The LDI-MS spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; exc 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)], and the ESI-MS spectra were recorded using a FIA-ES/MS (Shimadzu AD VP/ API 150) instrument. Elemental analyses were carried out with Flash EA 2000 CHNS, Thermo Fisher Scientific.

Synthesis of 9,12-($C_6H_4CH(OCH_3)_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 3

9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (300 mg, 0.75 mmol) in THF (10 ml), [$PdCl_2(PPh_3)_2$] (53 mg, 10% equiv.) and CuI (15 mg, 10% equiv.) and a solution of 4-benzaldehyde dimethyl acetal magnesium bromide (7.3 ml, 1M, 6.13 mmol), prepared from magnesium turnings (0.32 g) and 4-benzaldehyde dimethyl acetal (1.84 ml), were reacted at 0°C. After 30 min at room temperature the solution was heated under reflux for 3h. Ten drops of water were then added to quench the excess Grignard reagent, the grey precipitate was filtered and the solvent was removed under reduced pressure. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 x 10 ml). The combined organic phase was dried over $MgSO_4$ and filtered. Absorption onto active carbon of the ether solution of the compound was then performed, followed by filtration and removal of the solvent in vacuum. Recrystallization from a mixture of chloroform and hexane gave 9,12-($C_6H_4CH(OCH_3)_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ as white crystals (239 mg, 71%) suitable for X-ray diffraction. Elemental analysis calcd (%) for $C_{20}H_{32}B_{10}O_4$: C= 54.03, H= 7.26; found: C=54.63, H= 6.96. IR (KBr): ν= 3050, 3033 (C_c-H, C_{alkyl}-H), 2929, 2828, 2736 (C_{aryl}-H), 2589 (B-H), 1693 (C-O). ^{1}H NMR ($CDCl_3$): δ= 7.23-7.16 (m, 8H, C_6H_4), 5.29(s, 2H, O-**CH**-O) 3.67 (s, 2H, C_c-H), 3.29 (s, 12H, CH_3), 2.74-2.40 (B-*H*). ^{1}H{^{11}B} (CD_3COCD_3): δ= 7.23-7.16 (m, 8H, C_6H_4), 5.29(s, 2H, O-**CH**-O) 3.67 (s, 2H, C_c-H), 3.29 (s, 12H, CH_3), 2.74 (s, B-H), 2.40 (s, B-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 136.5 (s, C_6H_4), 132.8 (s, C_6H_4), 128.6 (s, C_6H_4), 125.4 (s, C_6H_4), 103.5 (O-CH-O), 53.2 (O-CH_3), 49.3 (C_c-H). ^{11}B NMR ($CDCl_3$): δ= 8.94 (s, 2B-C), -7.9 (d, ^1J(B,H)= 140), -12.9 (br s, B-H).

Synthesis of 9,12-($C_6H_4CHO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 4

A rigorous series of three extractions of 9,12-($C_6H_4CH(OCH_3)_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (100 mg, 0.22 mmol) with Et_2O (15 ml) in aqueous HCl solution (3M) was performed. The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to give 9,12-($C_6H_4CHO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (76 mg, 96%). Elemental analysis calcd (%) for $C_{16}H_{20}B_{10}O_2$: C= 54.53, H= 5.72; found: C=55.07, H= 5.79. IR (KBr): ν= 3067(C_c-H, C_{alkyl}-H), 2826, 2737 (C_{aryl}-H), 2595 (B-H), 1691 (C=O). ^{1}H NMR ($CDCl_3$): δ= 9.91 (s, 2H, CHO), 7.63 (d, 4H, C_6H_4), 7.38 (d, 4H, C_6H_4), 3.81 (s, 2H, C_c-H), 2.81-2.46 (B-*H*). ^{1}H{^{11}B} (CD_3COCD_3): δ= 9.91 (s, 2H, CHO), 7.63 (d, 4H, C_6H_4), 7.38 (d, 4H, C_6H_4), 3.81 (s, 2H, C_c-H), 2.81(s, B-H), 2.51 (s, B-*H*), 2.46 (s, B-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 192.5 (s, CHO), 133.4 (s, C_6H_4), 128.5 (s, C_6H_4), 50.3 (C_c-H). ^{11}B NMR ($CDCl_3$): δ= 6.88 (s, 2B-

C), -9.4 (d, ^1J(B,H)= 146), -14.1 (d, ^1J(B,H)= 155), -16.2 (br s, B-H). Good crystals suitable for X-ray diffraction were grown by diffusion of $CHCl_3$ into hexane.

Synthesis of 9,12-Ph_2-8,10-I_2-1,2-closo-$C_2B_{10}H_8$, 7

A thick-walled Pyrex tube charged with 9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ (50 mg, 0.2 mmol) and iodine (432 mg, 1.7 mmol) was put under vacuum, cooled down with liquid nitrogen and sealed. The tube was then placed in a furnace and the temperature gradually raised to 210ºC during 20 minutes, maintained for 5h and allowed to drop slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture a 50ºC under reduced pressure. The resulting solid was purified by thin layer chromatography (TLC), using chloroform as the eluting solvent, to give 9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ Yield: 67 mg (73%). %). Elemental Analysis for $C_{14}B_{10}H_{18}I_2$: calc: C 30.67, H 3.31; found: C 29.57, H 2.42. IR (KBr): ν [cm^{-1}] = 3045 (s, C_C-H st.), 2972, 2924, 2858 (vs, $\nu s(CH_2)$), 2609 (s, B-H st.), 1430 (vs, $\nu s(C\text{-}C_{phenyl})$). ^{1}H NMR: δ [ppm] =7.52 (d, 1 J(H,H)=9 Hz, 4H, $H_{phenyl\text{-}meta}$), 7.24 (m, 6H, $H_{phenyl\text{-}ortho,para}$), 5.06 (br s, 2H, C_cH), 4.0–1.6 (br m, 6H, BH). ^{1}H{^{11}B} NMR: δ [ppm]=7.52 (d, ^{1}J(H,H)=9 Hz, 4H, $H_{phenyl\text{-}meta}$), 7.24 (m, 6H, $H_{phenyl\text{-}ortho,para}$), 5.06 (br s, 2H, C_cH), 3.36 (br s, 4H, B(4,5,7,11)H), 2.88 (br s, 2H, B(3,6)H).^{13}C{1 H} NMR: δ [ppm] =134.3, 127.9, 126.8 (C_{phenyl}), 52.7 (C_c). ^{11}B NMR: δ [ppm] =5.01 (s, 2B, B(9,12)-Ph), -12.1 (d, ^{1}J(B,H)=164 Hz, 4B, B(4,5,7,11)), -14.8 5 (d, ^{1}J(B,H)=186 Hz, 2B, B(3,6)). -20.1 (s, 2B, B(8,10)-I). ESI MS: m/z (%)= 537 (100) $[M\text{-}BH]^-$, 547 (20) $[M\text{-}H]^-$, 663 (75) $[M\text{-}B+I]^-$.

Synthesis of 8,10-Ph_2-9,12-$(CH_2{=}CHCH_2)_2$-1,2-*closo*-$C_2B_{10}H_8$, 9.

To a stirring solution of 8,10-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$ (120 mg, 0.27 mmol) in THF (5 mL) cooled to 0 ºC in an ice-water bath was added, dropwise, a solution of allylmagnesium chloride in THF (0.55 mL, 2 M, 1.1 mmol). After stirring at room temperature for 30 minutes, *cis*-$[PdCl_2(PPh_3)_2]$ (7.7 mg, 4% equiv.) and CuI (2.1 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux overnight. The solvent was removed and 5 mL of diethyl ether were added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was purified by flash silica gel chromatography, using hexane/chloroform (3:1 by volume) mixture as the eluting solvent, to give 8,10-Ph-9,12-

$(CH_2=CHCH_2)_2$-1,2-*closo*-$C_2B_{10}H_8$. Yield: 130 mg (75%). Elemental Analysis for $C_{20}B_{10}H_{28}$: calc: C 63.82, H 7.45; found: C 63.97, H 7.39. IR (KBr): [cm^{-1}] = 3072 (vs, $_s$($C_{cluster}$-H and =CH_2)), 2954, 2923, 2854 (vs, $_s$(=CH and CH_2)), 2600 (vs, $_s$(B-H)), 1633 (vs, $_s$(C=C)) ^{1}H NMR: [ppm]=7.70 (m, 4H, H_{phenyl}), 7.36 (m, 6H, H_{phenyl}), 5.93 (m, 2H, CH_2=C*H*-CH_2), 4.87-4.82 (m, 4H, C*H*$_2$=CH-CH_2), 4.62 (s, 2H, $C_{cluster}$-*H*), 3.10–1.00 (m, 6H, B-*H*$_{terminal}$), 1.33 (s, 4H, CH_2=CH-C*H*$_2$).^{1}H{^{11}B} NMR: [ppm]=7.70 (m, 4H, H_{phenyl}), 7.36 (m, 6H, H_{phenyl}), 5.93 (m, 2H, CH_2=C*H*-CH_2), 4.87-4.82 (m, 4H, C*H*$_2$=CH-CH_2), 4.62 (s, 2H, $C_{cluster}$-*H*), 2.41 (br s, 4H, B(4,5,7,11)*H*), 2.32 (br s, 2H, B(3,6)*H*), 1.33 (d, ^{3}*J*(B,H)=9.0 Hz, 4H, CH_2=CH-C*H*$_2$).^{13}C{^{1}H} NMR: [ppm] =139.4 (s, CH_2=*C*H-CH_2), 134.3, 127.3 (*C*$_{phenyl}$), 112.4 (s, *C*H$_2$=CH-CH_2), 49.3 (s, *C*$_{cluster}$), 21.4 (br m, CH_2=CH-*C*H$_2$). ^{11}B NMR: [ppm] =7.3 (s, 2B, B(9,12)), 2.2 (s, 2B, B(8,10)-*Ph*), -14.9(d, ^{1}*J*(B,H)=161 Hz, 4B, B(4,5,7,11)), -17.0 (d, ^{1}*J*(B,H)=167 Hz, 2B, B(3,6)). ESI MS: *m*/*z* (%)= 399.4 (100) $[M+23]^+$.

Synthesis of 8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, 11 and 8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$, 10

To a stirring solution of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$ (300 mg, 0.46 mmol) in dry solvent (5 mL, entry 1: 1,4-dioxane, entry 2: toluene, entry 3: diglyme (bis(2-methoxyethyl)ether), entry 4: mesitylene) cooled to 0 ºC in an ice-water bath was added dropwise phenylmagnesium bromide solution in THF (5.6 mL, 1M, 5.6 mmol). After stirring at room temperature for 30 minutes, *cis*-[$PdCl_2(PPh_3)_2$] (25.0 mg, 8% equiv.) and CuI (7.0 mg, 8% equiv.) were added in a single portion. The solvents evaporated under reduced pressure to about one-half volume to remove the THF of the Grignard reagent) and the reaction was heated to reflux for 16 h. The solvent was removed and 20 mL of diethyl ether were added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layers were separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was further purified by silicagel chromatography, using hexane/chloroform (1:1 by volume) eluent. (R_F=0.4 for **11** and R_F=0.5 for **10**) Both compounds (**10** and **11**) were recrystallized from aceton/pentane mixture.

Entry	Solvent	Yield	
		8,9,10,12-Ph_3I-1,2-*closo*-$C_2B_{10}H_8$	8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$
1	dioxane	136 mg (59 %)	38 mg (18 %)
2	toluene	134 mg (59 %)	43 mg (21 %)
3	diglyme	101 mg (44 %)	34 mg (16 %)
4	mesitylene	89 mg (39 %)	26 mg (12 %)
5	toluene (5days)	107 mg (47 %)	71 mg (34 %)

8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$, 10

Elemental Analysis for $C_{26}B_{10}H_{28}$: calc: C 69.61 , H 6.21 ; found: C 71.66, H 5.26. ATR-IR (KBr): ν [cm^{-1}] = 3047 (vs, νs($C_{cluster}$-H)), 2580 (vs, νs(B-H)) ^{1}H NMR: δ [ppm]=7.52-7.27 (m, 15 H, H_{phenyl}), 5.07 (s, 1H, $C_{cluster}$-H), 4.80 (s, 1H, $C_{cluster}$-H). ^{1}H{^{11}B} NMR: δ [ppm]= 7.52-7.27 (m, 15H, H_{phenyl}), 5.07 (s, 1H, $C_{cluster}$-H), 4.80 (s, 1H, $C_{cluster}$-H), 2.74, (br, 2H, B-$H_{terminal}$), 2.54 (br, 4H, B-$H_{terminal}$). ^{13}C{^{1}H} NMR: δ [ppm]=135.7, 135.1, 128.0, 127.9, 127.6 (s C_{phenyl}), 50.0 (s, $C_{cluster}$). ^{11}B NMR: δ [ppm]=4.0 (s, 2B, B(9,12)), -1.1 (s, 2B, B(8,10)), -16.6 (d, ^{1}J(B,H)=195 Hz 4B, B(4,5,7,11)), -18.8 (br, 2B, B(3,6)). LDI MS: m/z (%)=446.7 (100) $[M-1]^-$

8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, 11

Elemental Analysis for $C_{20}B_{10}H_{23}I$: calc: C 48.21, H 4.61 ; found: C 47.40, H 4.68. ATR-IR: ν [cm^{-1}] =3053 (vs, νs($C_{cluster}$-H)), 2594 (s, νs(B-H). ^{1}H NMR: δ [ppm]=7.41-7.34 (m, 6H, H_{phenyl}), 7.21-7.04 (m, 9H, H_{phenyl}), 5.19 (s, 1H, $C_{cluster}$-H), 4.95 (s, 1H, $C_{cluster}$-H), ^{1}H{^{11}B} NMR: δ [ppm]=7.41-7.34 (m, 6H, H_{phenyl}), 7.21-7.04 (m, 9H, H_{phenyl}), 5.19 (s, 1H, $C_{cluster}$-H), 4.95 (s, 1H, $C_{cluster}$-H), 2.97, (br, 2H, B-$H_{terminal}$), 2.86, (br, 2H, B-$H_{terminal}$), 2.58 (br, 2H, B-$H_{terminal}$). ^{13}C{^{1}H} NMR: δ [ppm]=135.2, 134.9, 128.4, 128.3 128.0, 127.7, (s C_{phenyl}), 51.9 (s, $C_{cluster}$), 50.9 (s, $C_{cluster}$). ^{11}B NMR: δ [ppm]=3.46 (s, 1B, B(9)), -1.4 (s, 2B, B(8,10)), -11.7 (s, 1B, B(12)), -16.5 (d, ^{1}J(B,H)=170 Hz, 4B, B(4,5,7,11)), -18.8 (d, ^{1}J(B,H)=194 Hz, 2B, B(3,6)). LDI MS: m/z (%)=496.6 (100) $[M-1]^-$.

Synthesis of 8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, 11 and 8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$ 10 under microwave irradiation

To a stirring solution of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$ (300 mg, 0.46 mmol) in dry toluene cooled to 0 ºC in an ice-water bath was added dropwise phenylmagnesium bromide solution in THF (5.6 mL, 1M, 5.6 mmol). After stirring at room temperature for 30 minutes, *cis*-[$PdCl_2(PPh_3)_2$] (25.0 mg, 8% equiv.) and CuI (7.0 mg, 8% equiv.) were added in a single portion. The solvents evaporated under reduced pressure to about one-half volume to remove the THF of the Grignard reagent). The reaction mixture was transferred to the microwave vial and it was sealed under N_2, than it is was exposed to microwave irradiation at 120 °C (temperature was monitored at the external surface vessel using an in-built infrared sensor system). After 15 min irradiation only the doubly substituted product formed according the ^{1}H NMR spectra of the crude product. After 2 hours **11** and **10** formed with the similar ratio (3:1) to the reaction under reflux (16 h).

X-ray structure analysis of compounds 3, 7, 9, 10 and 11

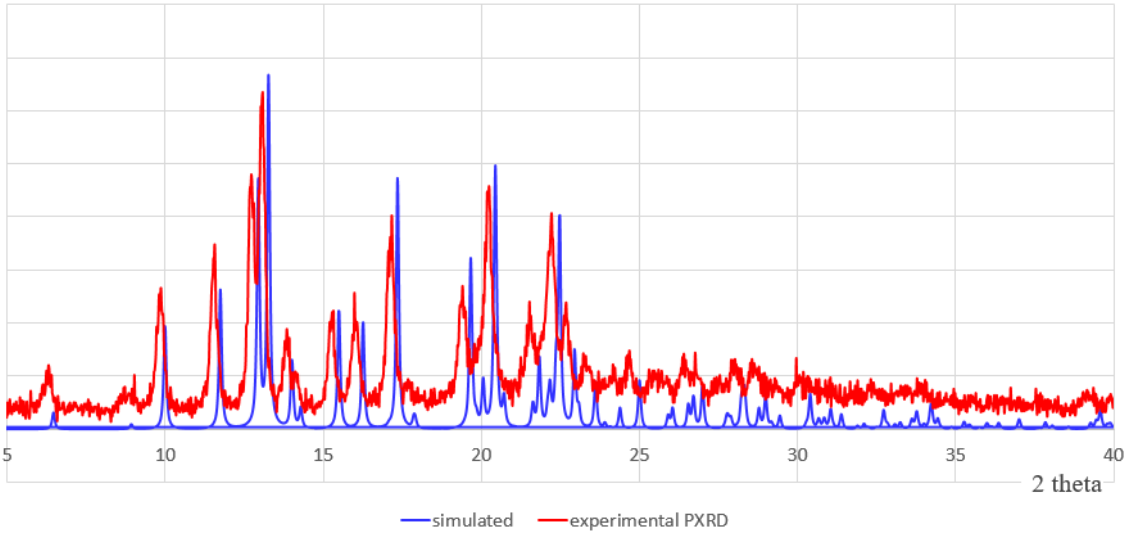
X-ray structure determination for **9** and **11** was carried out on a Bruker D8 QUEST ECO diffractometer using doubly curved silicon crystal Bruker Triumph-monochromated Mo K radiation (=0.71073 Å) with APEX 3 software suite.[4] When needed, the data sets were corrected for absorption using analytical numeric correction using multifaceted crystal was performed as implemented in CrysAlisPro program[5] or SADABS program[6]. The data for compound **3**, **4**, **10** was collected using SuperNova diffractometer equipped with Atlas detector using Cu-Kα radiation with the CrysAlisPro program.[5] An absorption correction using spherical harmonics, was applied as implemented in SCALE3 ABSPACK scaling algorithm.[7] The structure was solved by direct methods using the and refined with the full-matrix least squares method on F[7] using the SHELX and Olex2 program packages.[8,9] Powder X-ray Diffraction (PXRD) patterns of **10** were recorded at room temperature on an X'Pert PRO MPD diffractometer (Panalytical) using Cu $K_Þ$ (I = 1.5405 Å) radiation.

Compound	**3**	**4**	**9**	**10**	**11**
Formula	$C_{20}H_{32}B_{10}O_4$	$C_{16}H_{20}B_{10}O_2$	$C_{18}H_{20}B_{10}$	$C_{26}H_{28}B_{10}$	$C_{20}H_{23}B_{10}I$
M_r	444.56	352.42	344.44	448.58	498.38
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	triclinic
Space group (no.)	*P*-1 (2)	*P*21/*c* (14)	*P*nma	$P2_1$	P1
a (Å)	13.0593(7)	6.9997(2)	28.315(8)	10.0809(3)	8.2721(3)
b (Å)	13.3337(6)	25.3248(7)	21.003(6)	9.02379(19)	8.3343(3)
c (Å)	16.6231(9)	10.7346(3)	8.077(2)	13.9208(3)	9.0538(3)
α (°)	95.700(4)	90	90	90	70.7871(9)
β (°)	110.824(5)	94.777(3)	90	90	71.3375(9)
γ (°)	111.529(4)	90	90	100.834(2)	81.5210(10)
V (Å)	2427.2(2)	1896.27(9)	4804(2)	1243.77(5)	557.811 Å
Z	4	4	8	4	1
D_c (g cm^{-3})	1.217	1.234	0.953	1.198	1.484
T(K)	123	150	298	120	100
μ(mm^{-1})	0.569[d]	0.069	0.048	0.446	0.223
Observed reflections	14258	9536	57992	4729	39095
R_{int}	0.0333	0.0198	0.0896	0.0383	0.0208
Parameters	666	253	1424	468	246
R_1[a]	0.0739 (0.0617)[b]	0.0642 (0.0521)[b]	0.1271	0.0417	0.0105
wR_2[c]	0.1817 (0.1679)	0.01383 (0.1306)	0.2873	0.0989	0.0268

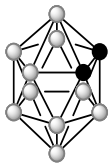
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Values in parentheses for reflections with $I > 2\sigma(I)$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (2F_c^2 + F_o^2)/3$. [d]Cu-Kα radition.

Results of the powder X-ray diffraction of **10**

Solid powder of **10** was obtained from an acetone solution of the compound by fast precipitation by adding hexane. The powder X-ray diffraction (PXRD) of this solid was run (pattern in red) and compared with the calculated pattern from the X-ray structure of the compound **10** (pattern in blue). Both patterns match very well.

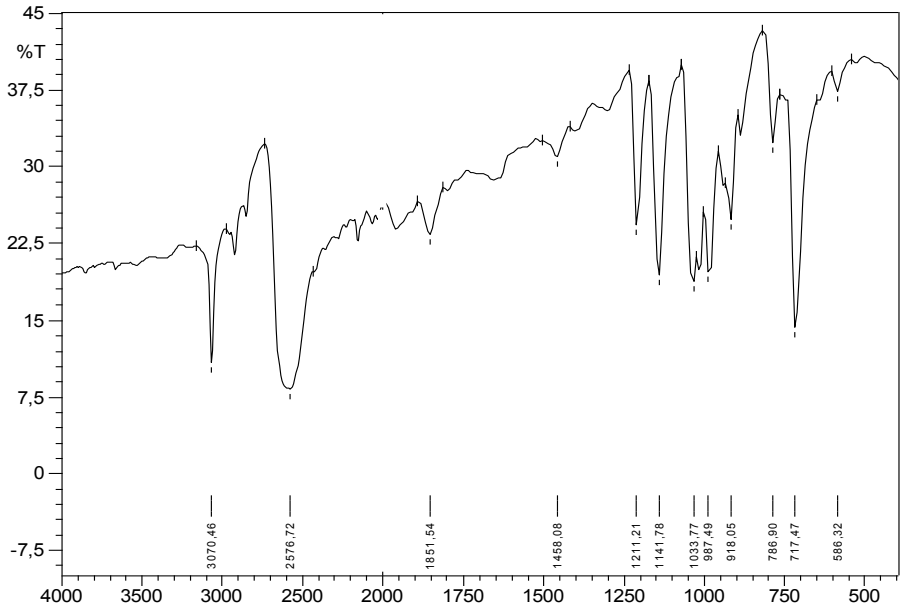


1,2-*closo*-$C_2B_{10}H_{12}$

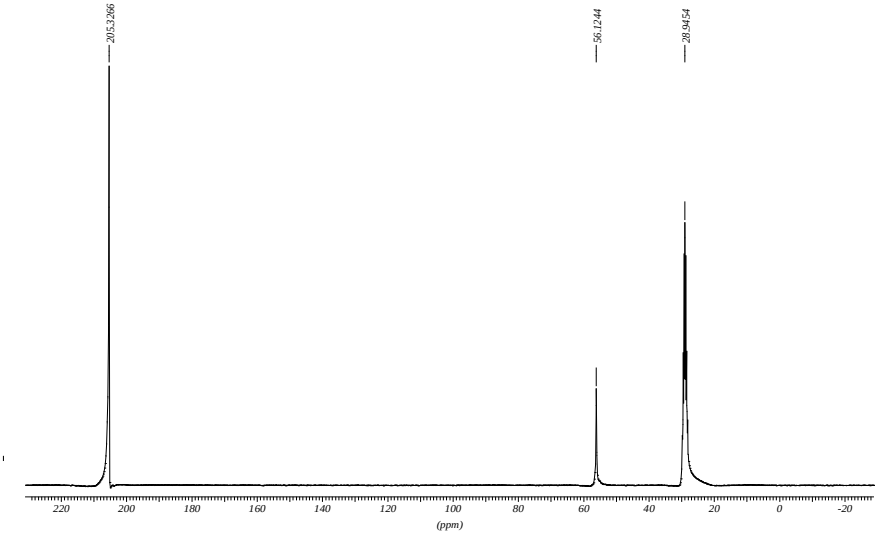


IR (KBr), ν (cm^{-1}) = 3070 (I, ν($C_{clúster}$-H)), 2576 (mI, ν(B-H)). ^{1}H NMR (CD_3COCD_3, 300 MHz, TMS): δ(ppm) = 3.55 (s(a), 2H, $C_{clúster}$-H), 3.50 – 1.00 (m(a), 10H, B-$H_{terminal}$). ^{1}H{^{11}B} NMR (CD_3COCD_3, 300 MHz, TMS): δ(ppm) = 3.55 (s(a), 2H, $C_{clúster}$-H), 2.32 (s(a), 2H, B-$H_{terminal}$), 2.20 (s(a), 2H, B-$H_{terminal}$), 2.11 (s(a), 6H, B-$H_{terminal}$). ^{13}C{^{1}H} NMR (CD_3COCD_3, 75 MHz, TMS): δ(ppm) = 56.12 (s, $C_{clúster}$). ^{11}B NMR (CD_3COCD_3, 96 MHz, $BF_3\cdot Et_2O$): δ = -3.1 (d, 2B, ^1J(B,H) = 147 Hz, B(9,12)), -9.6 (d, 2B, ^1J(B,H) = 150 Hz, B(8,10)), -13.6 (d, 4B, ^1J(B,H) = 166 Hz, B(4,5,7,11)). -14.3 (d, 2B, ^1J(B,H) = 178 Hz, B(3,6)).

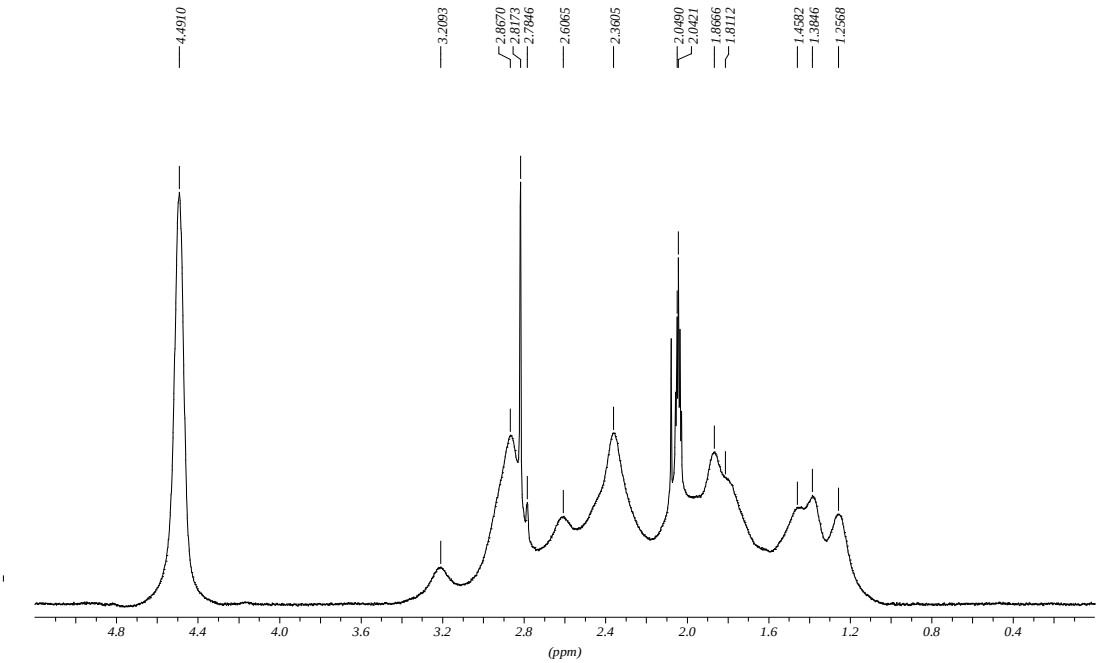
IR



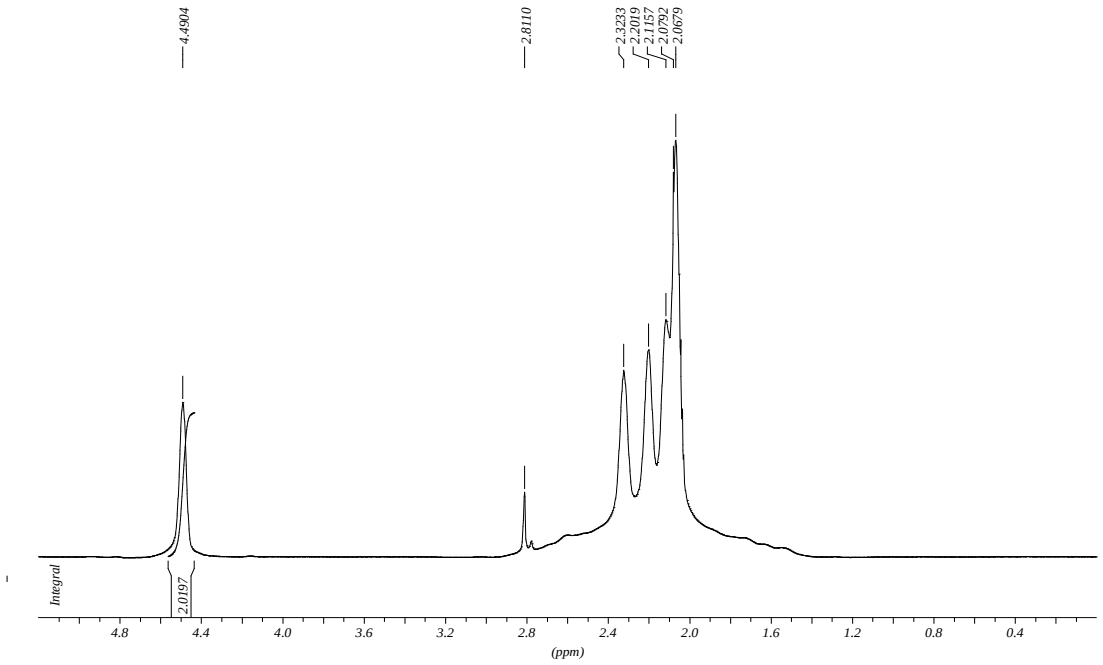
^{13}C{^{1}H}- NMR



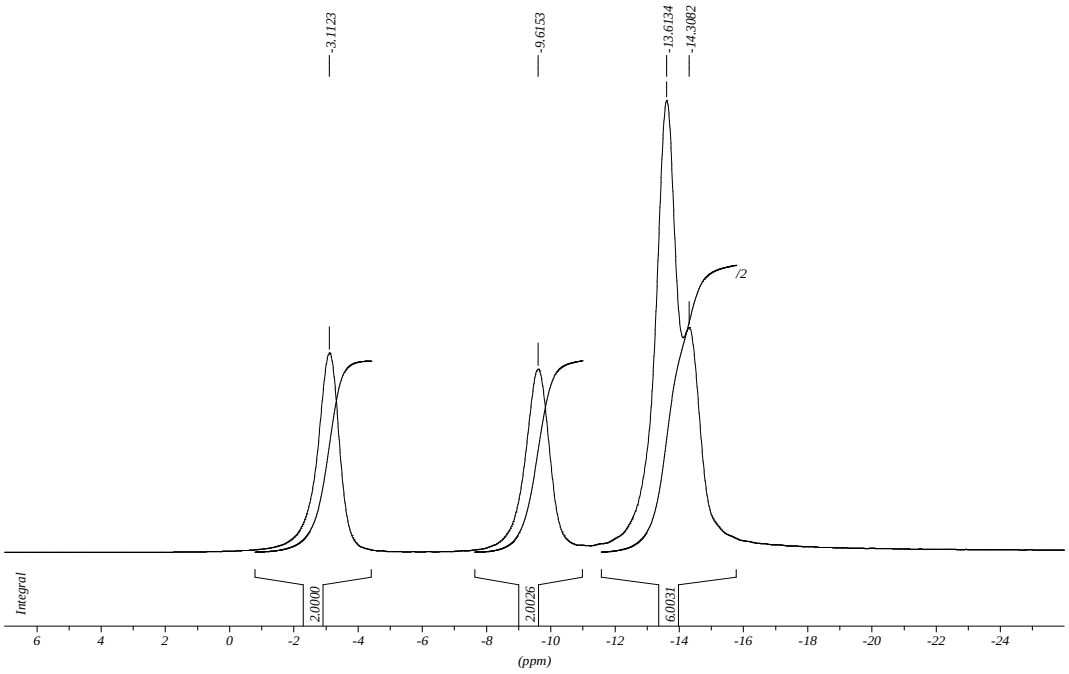
^{1}H-NMR



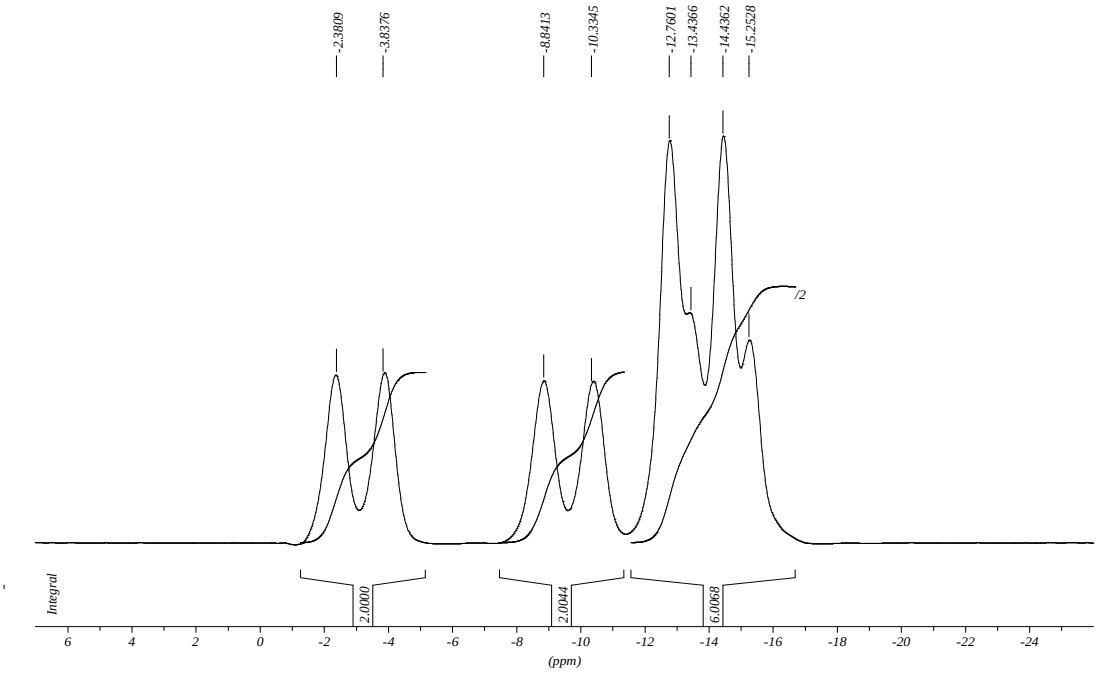
$^{1}H\{^{11}B\}$-NMR



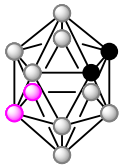
$^{11}B\{^{1}H\}$-NMR



^{11}B-NMR

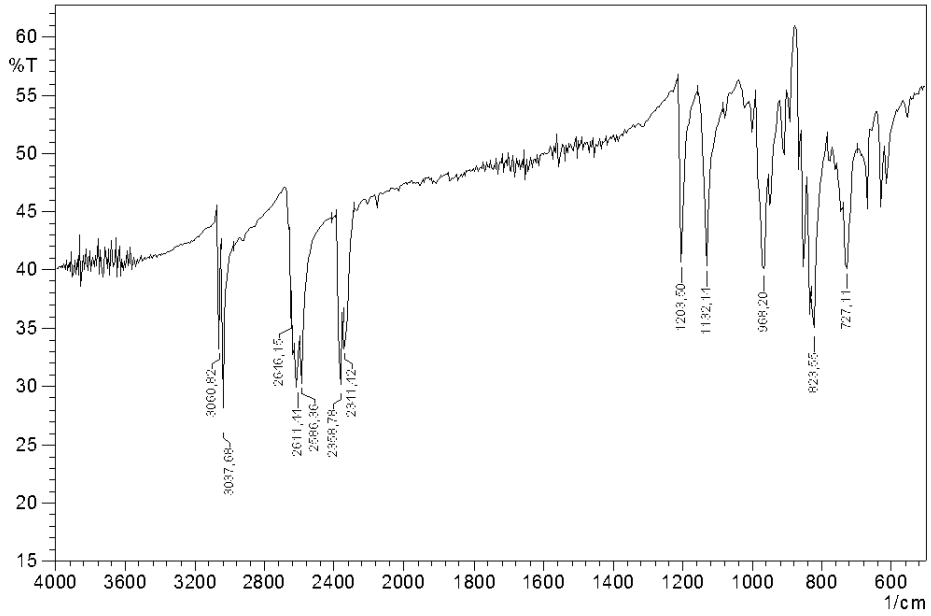


9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$

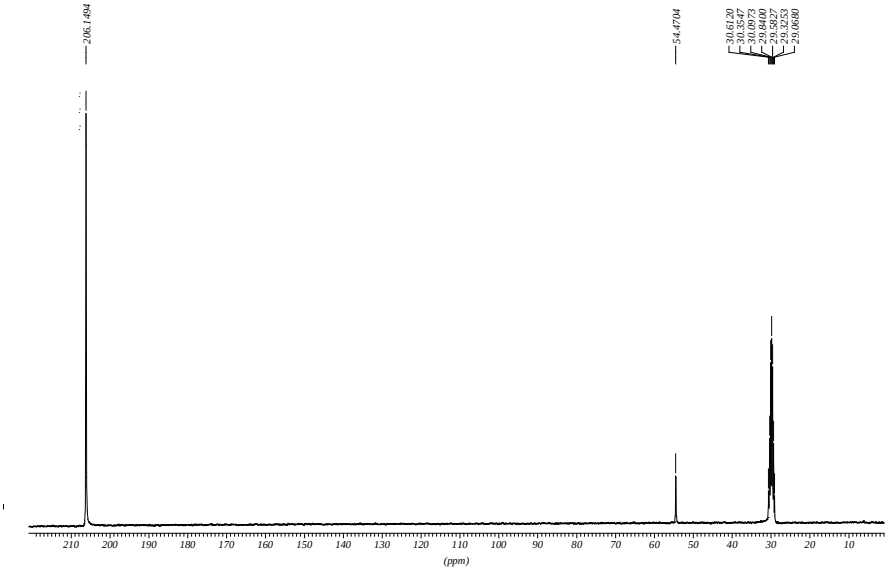


IR (KBr), ν (cm^{-1}) = 3060, 3037 (ml, ν(**$C_{clúster}$-H**)), 2645, 2611, 2586 (ml, ν(**B-H**)). **^{1}H NMR (CD_3COCD_3, 300 MHz, TMS)**: δ(ppm) = 5.15 (s(a), 2H, $C_{clúster}$-**H**), 3.80 – 1.50 (m(a), 8H, B-**$H_{terminal}$**). **^{1}H{^{11}B} NMR (CD_3COCD_3, 300 MHz, TMS)**: δ(ppm) = 5.15 (s(a), 2H, $C_{clúster}$-**H**), 3.50 (s(a), 2H, B-**$H_{terminal}$**), 2.97 (s(a), 2H, B-**$H_{terminal}$**), 2.47 (s(a), 2H, B-**$H_{terminal}$**), 1.82 (s(a), 2H, B-**$H_{terminal}$**). **^{13}C{^{1}H} NMR (CD_3COCD_3, 75 MHz, TMS)**: δ(ppm) = 54.47 (s, **$C_{clúster}$**).**^{11}B NMR (CD_3COCD_3, 96 MHz, BF_3· Et_2O)**: δ = -6.3 (d, 2B, ^1J(B,H) = 156 Hz, B(8,10)), -12.8 (d, 4B, ^1J(B,H) = 167 Hz, B(4,5,7,11)), -14.2 (d, 2B, ^1J(B,H) = 105 Hz, B(3,6)), -14.9 (s(a), 2B, B(9,12)).

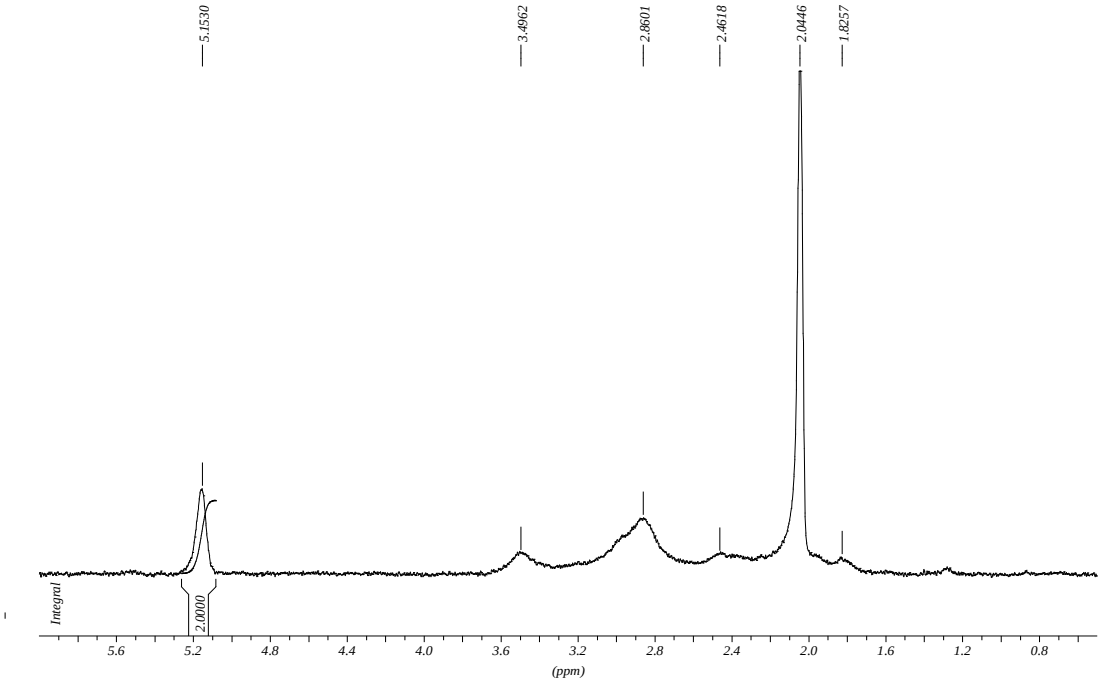
IR



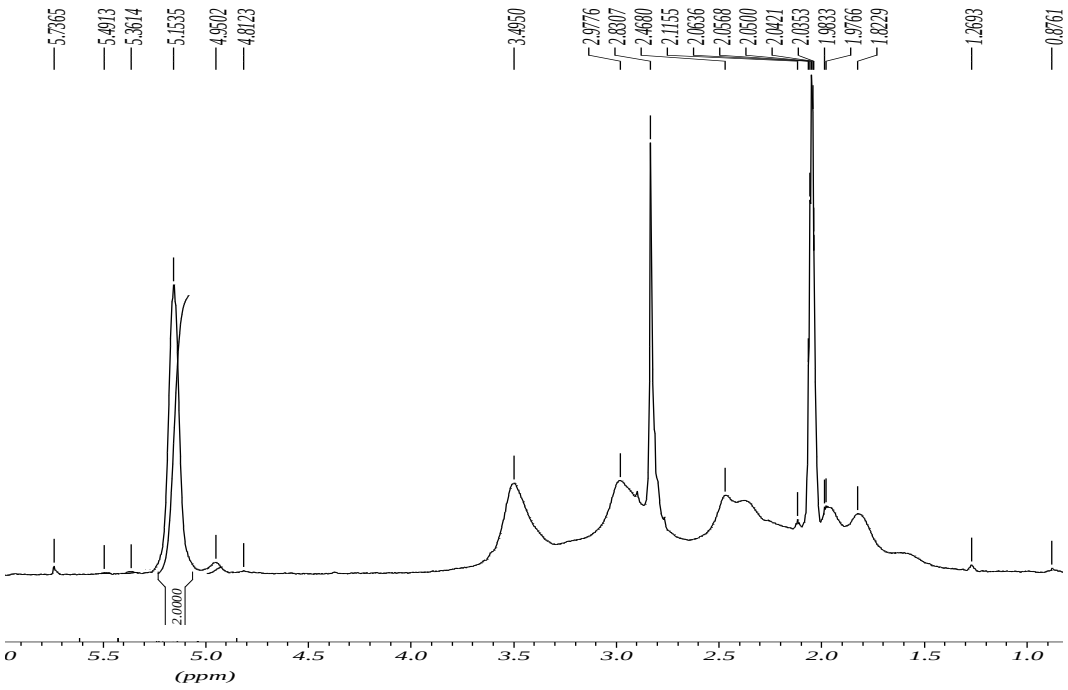
^{13}C{^{1}H}-NMR



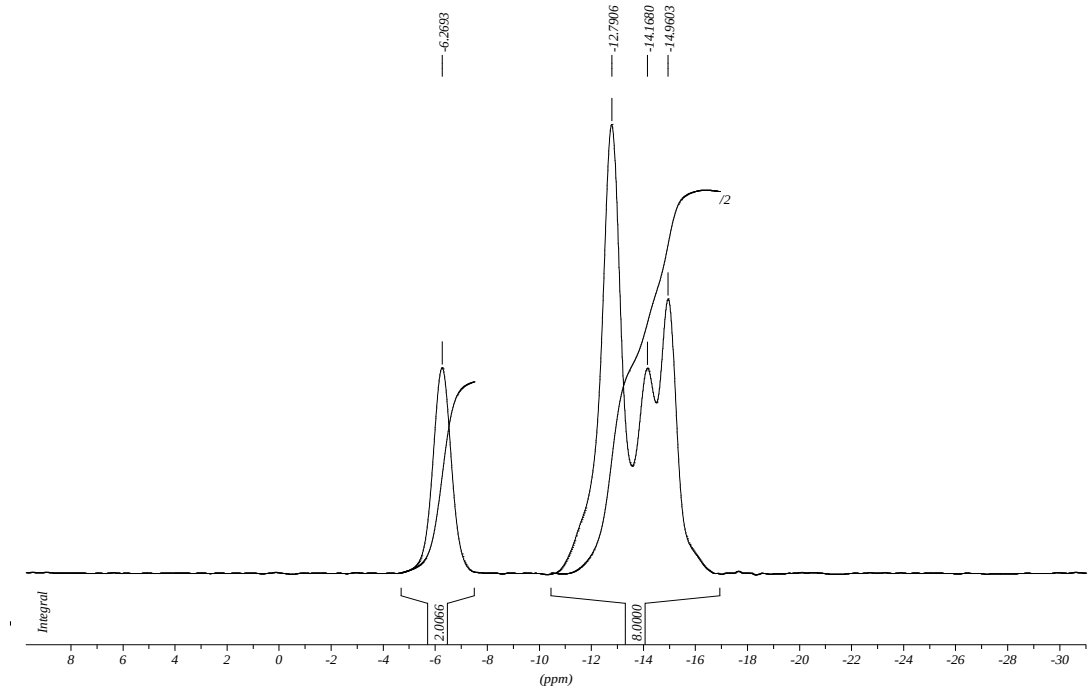
^{1}H-NMR



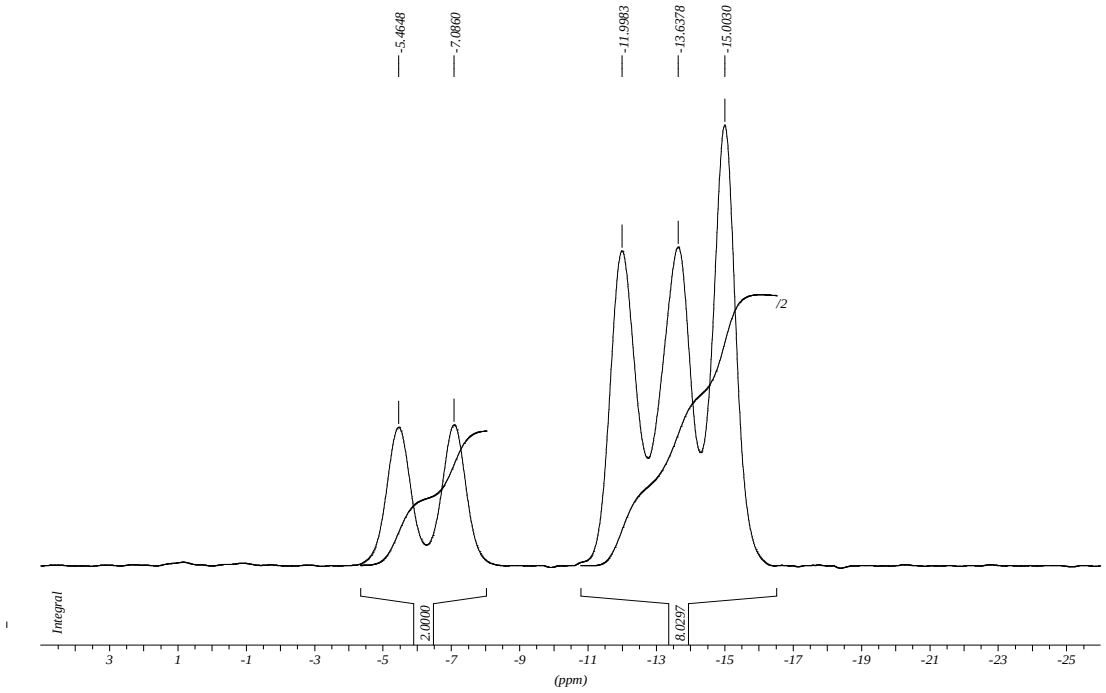
^{1}H{^{11}B}-NMR



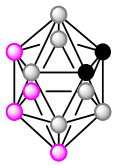
$^{11}B\{^{1}H\}$-NMR



^{11}B-NMR

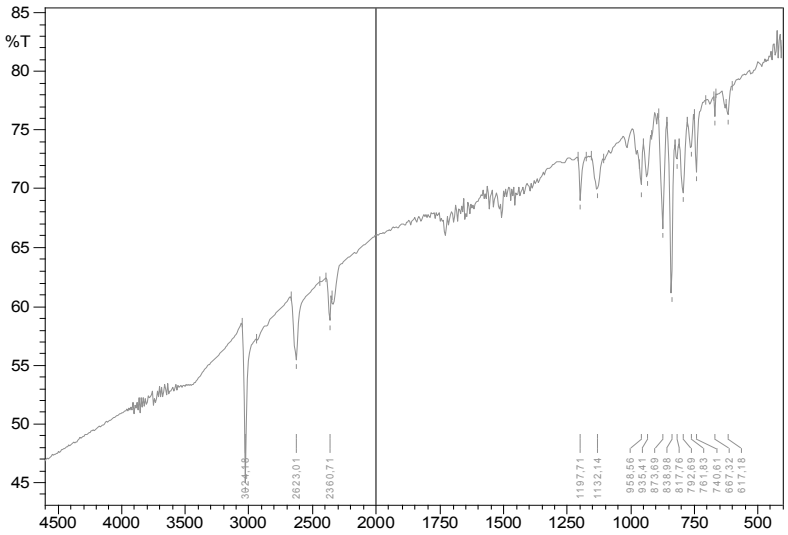


8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$

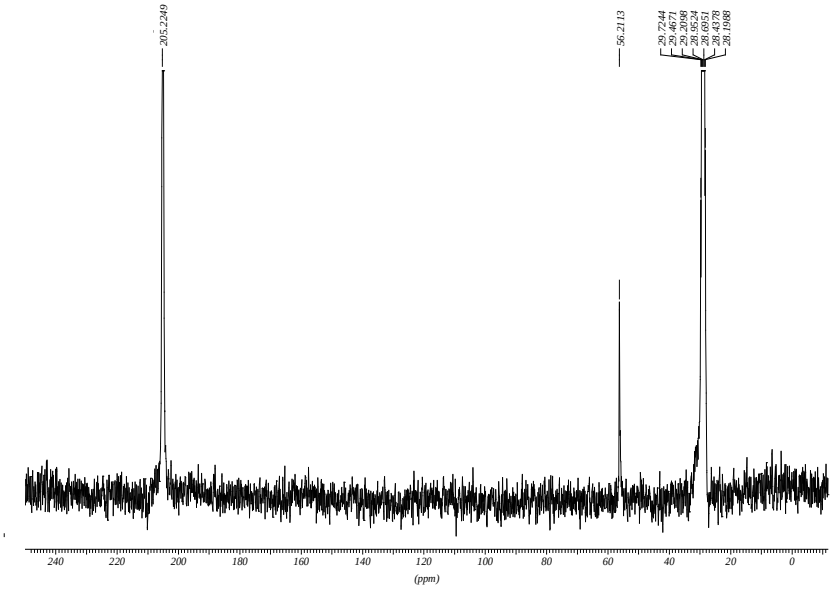


Elemental analysis $C_2B_{10}H_8I_4$: : C, 3.71; H, 1.24. Experimental: C, 3.82; H, 1.05. IR (KBr), ν (cm^{-1}) = 3024 (ml, $\nu(C_{clúster}\text{-}H)$), 2623 (I, ν(B-H)). ^{1}H NMR (CD_3COCD_3, 300 MHz, TMS): δ(ppm) = 5.57 (s(a), 2H, $C_{clúster}$-H), 4.00 – 1.50 (m(a), 6H, B-$H_{terminal}$). $^1H\{^{11}B\}$ NMR (CD_3COCD_3, 300 MHz, TMS): δ(ppm) = 5.57 (s(a), 2H, $C_{clúster}$-H), 3.37 (s(a), 2H, B(3,6)-$H_{terminal}$), 3.02 (s(a), 4H, B(4,5,7,11)-$H_{terminal}$). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 75 MHz, TMS): δ(ppm) = 56.21 ($C_{clúster}$). ^{11}B NMR (CD_3COCD_3, 96 MHz, $BF_3\cdot Et_2O$): δ = -7.1(s(a), 2B, B(9,12)), -9.5 (d, 4B, ^1J(B,H) = 176 Hz, B(4,5,7,11)), -13.2 (d, 2B, ^1J(B,H) = 190 Hz, B(3,6)). -16.3 (s(a), 2B, B(8,10)).

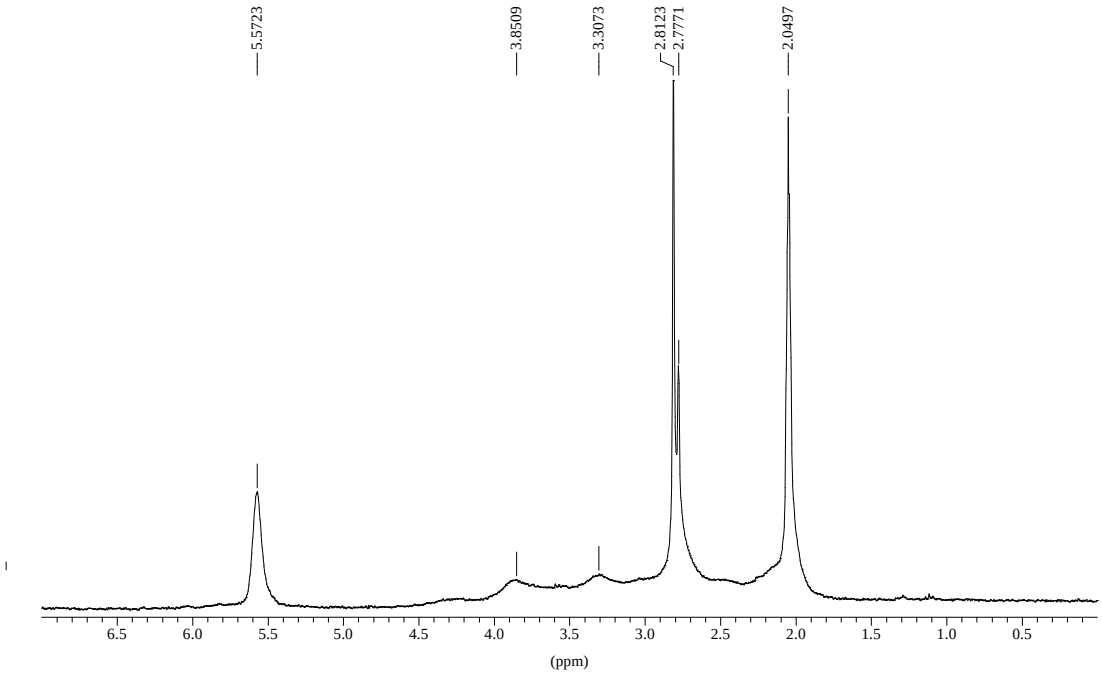
IR



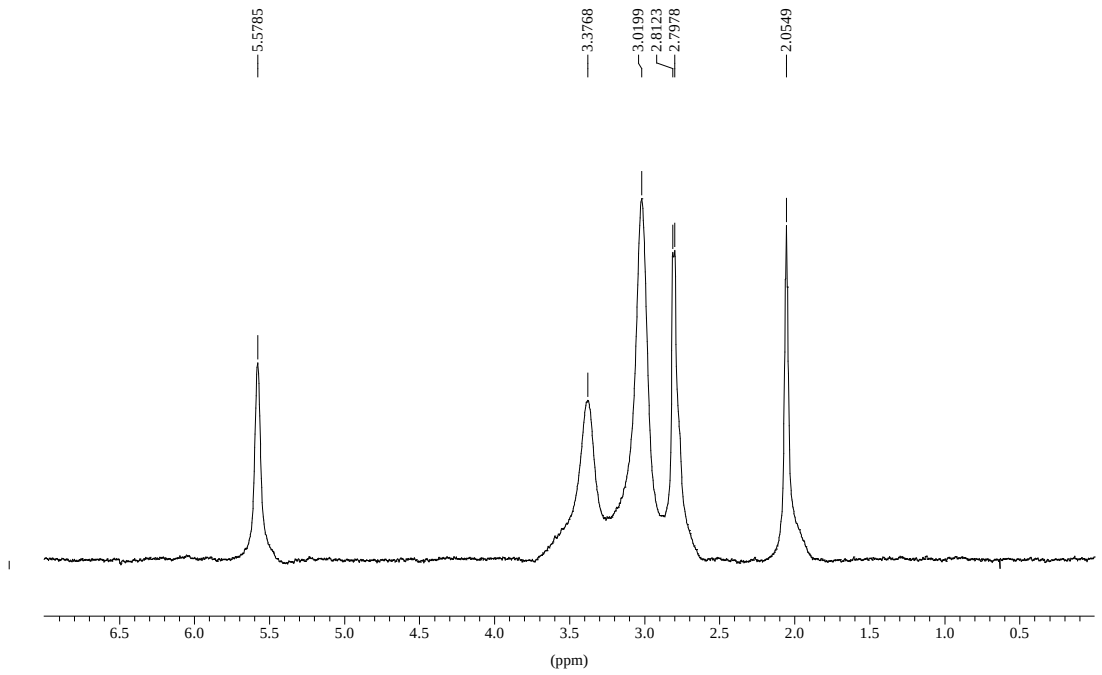
$^{13}C\{^1H\}$-NMR



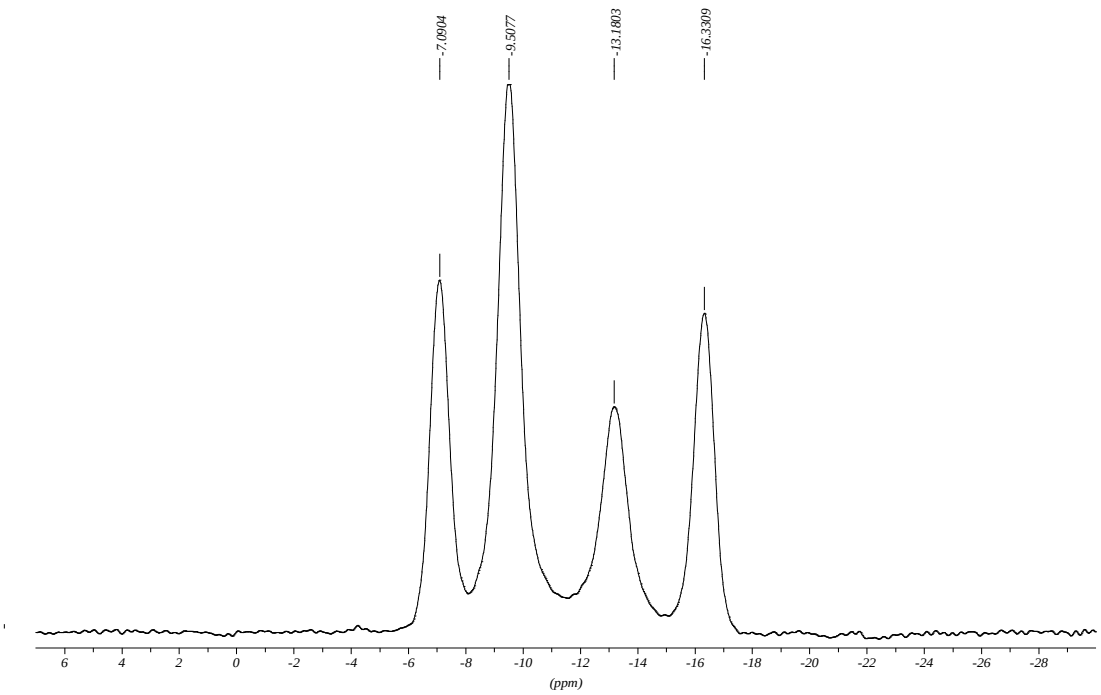
^{1}H-NMR



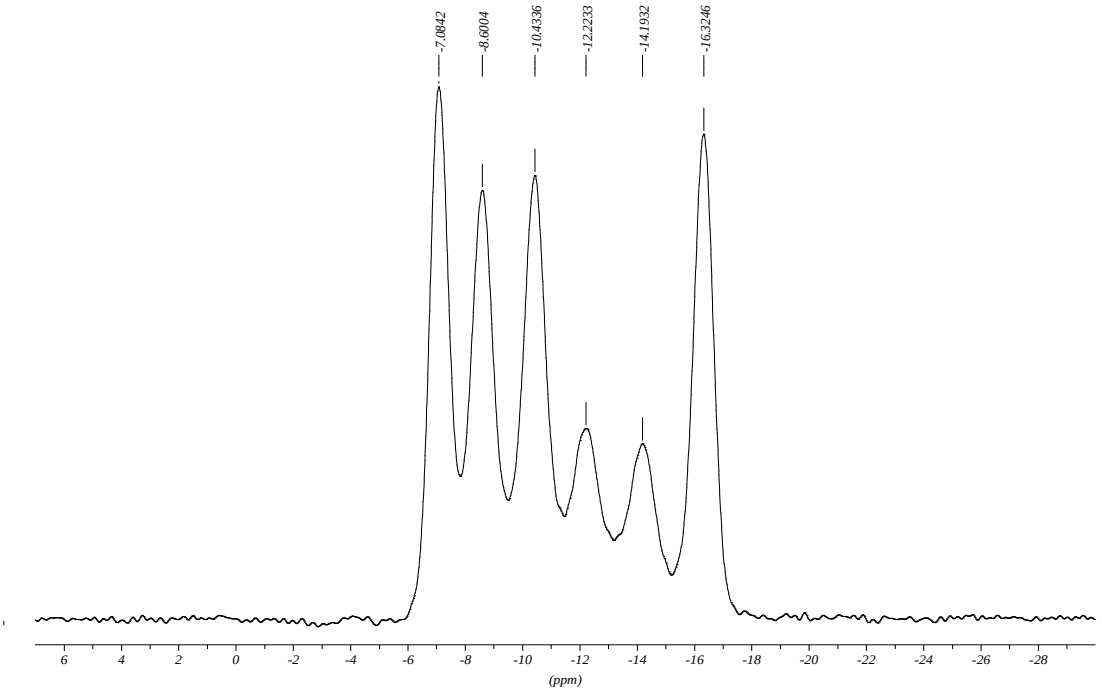
$^{1}H\{^{11}B\}$-NMR



$^{11}B\{^{1}H\}$-NMR



^{11}B-NMR

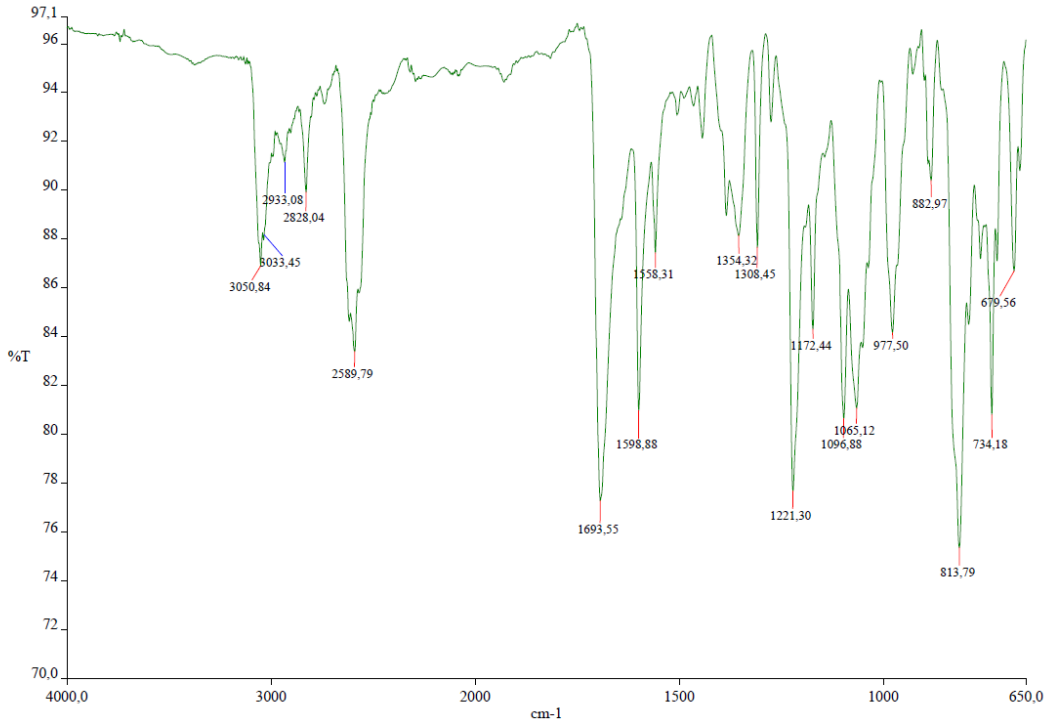


OeClara1(cosy-bis) 211 1 C:\Bruker\TOPSPIN cv
F1 [ppm]
- 18
- 16
- 14
- 12
- 10
- 8
- 6
- 4
F2 [ppm]
- 15
- 10
- 5

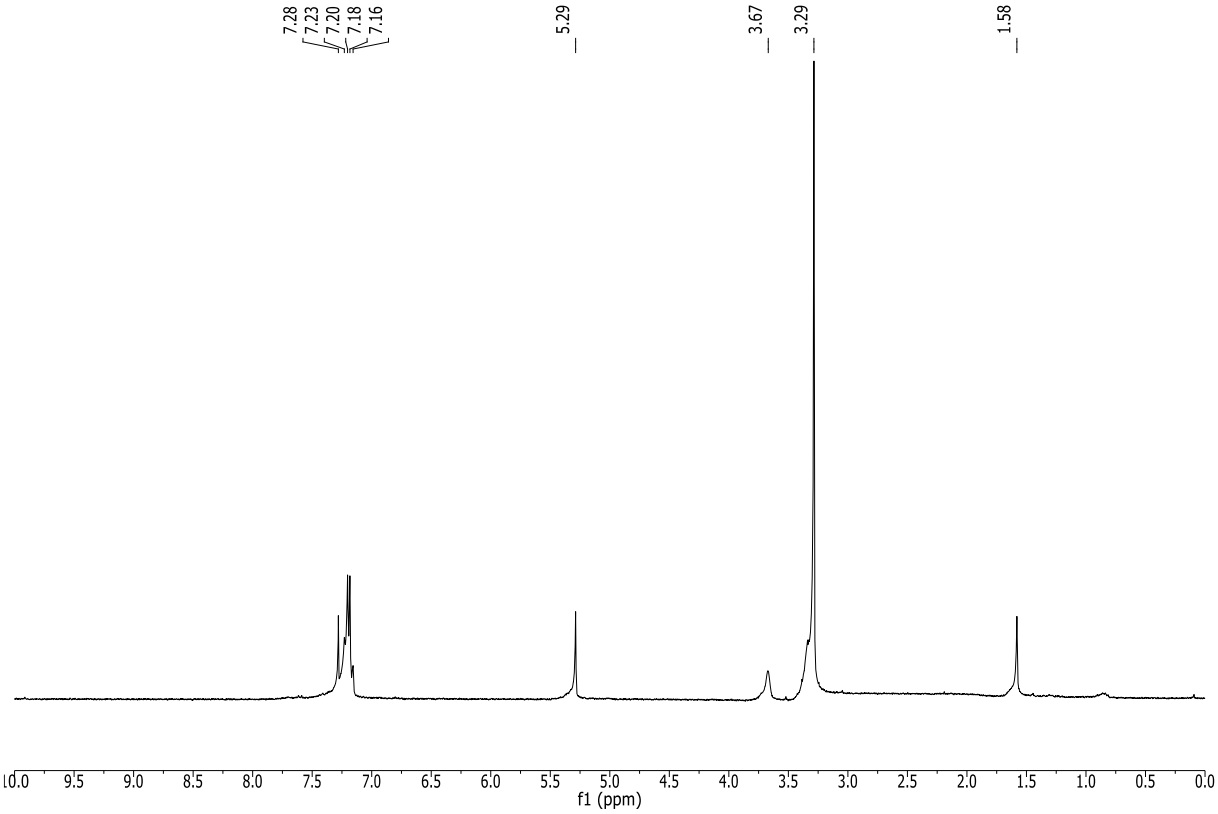
9,12-($C_6H_4CH(OCH_3)_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 3

Elemental analysis calcd (%) for $C_{20}H_{32}B_{10}O_4$: C= 54.03, H= 7.26; found: C=54.63, H= 6.96. IR (KBr): ν= 3050, 3033 (C_c-H, C_{alkyl}-H), 2929, 2828, 2736 (C_{aryl}-H), 2589 (B-H), 1693 (C-O). ^{1}H NMR ($CDCl_3$): δ= 7.23-7.16 (m, 8H, C_6H_4), 5.29(s, 2H, O-CH-O) 3.67 (s, 2H, C_c-H), 3.29 (s, 12H, CH_3), 2.74-2.40 (B-*H*). ^{1}H{^{11}B} (CD_3COCD_3): δ= 7.23-7.16 (m, 8H, C_6H_4), 5.29(s, 2H, O-CH-O) 3.67 (s, 2H, C_c-H), 3.29 (s, 12H, CH_3), 2.74 (s, B-H), 2.40 (s, B-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 136.5 (s, C_6H_4), 132.8 (s, C_6H_4), 128.6 (s, C_6H_4), 125.4 (s, C_6H_4), 103.5 (O-CH-O), 53.2 (O-CH_3), 49.3 (C_c-H). ^{11}B NMR ($CDCl_3$): δ= 8.94 (s, 2B-C), -7.9 (d, ^1J(B,H)= 140), -12.9 (br s, B-H).

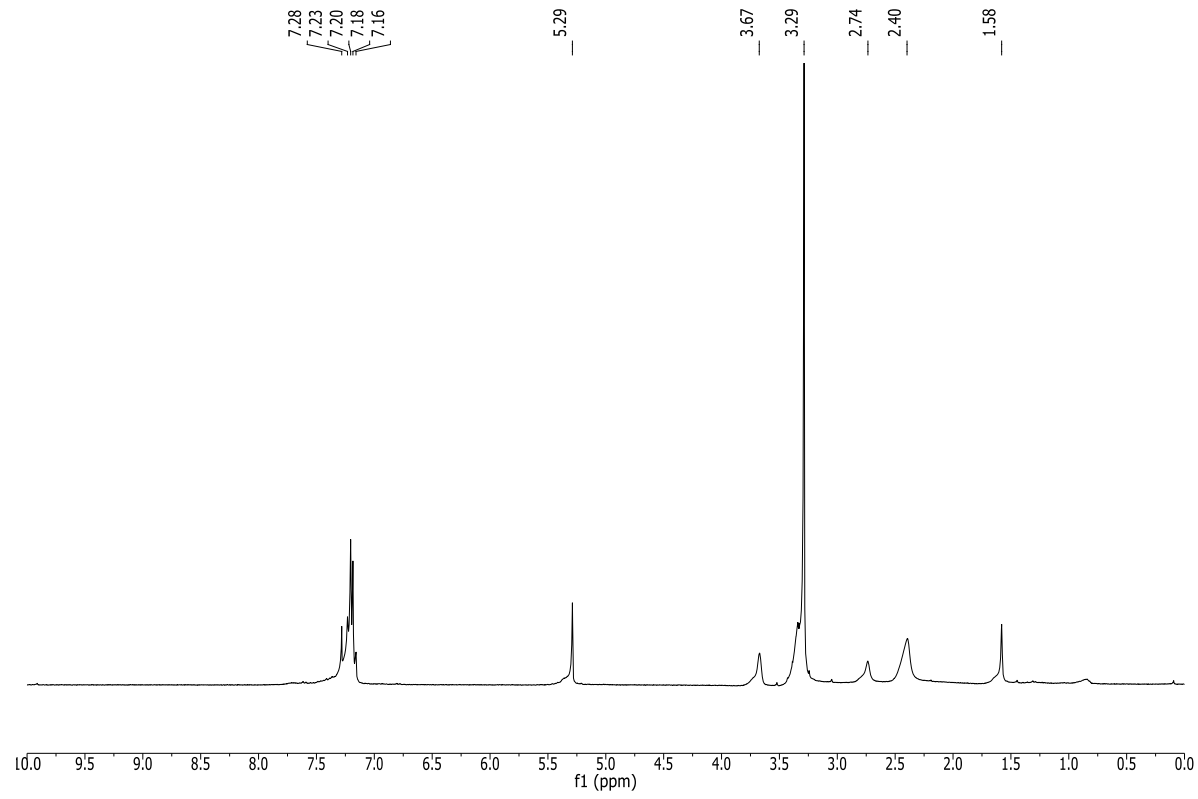
IR



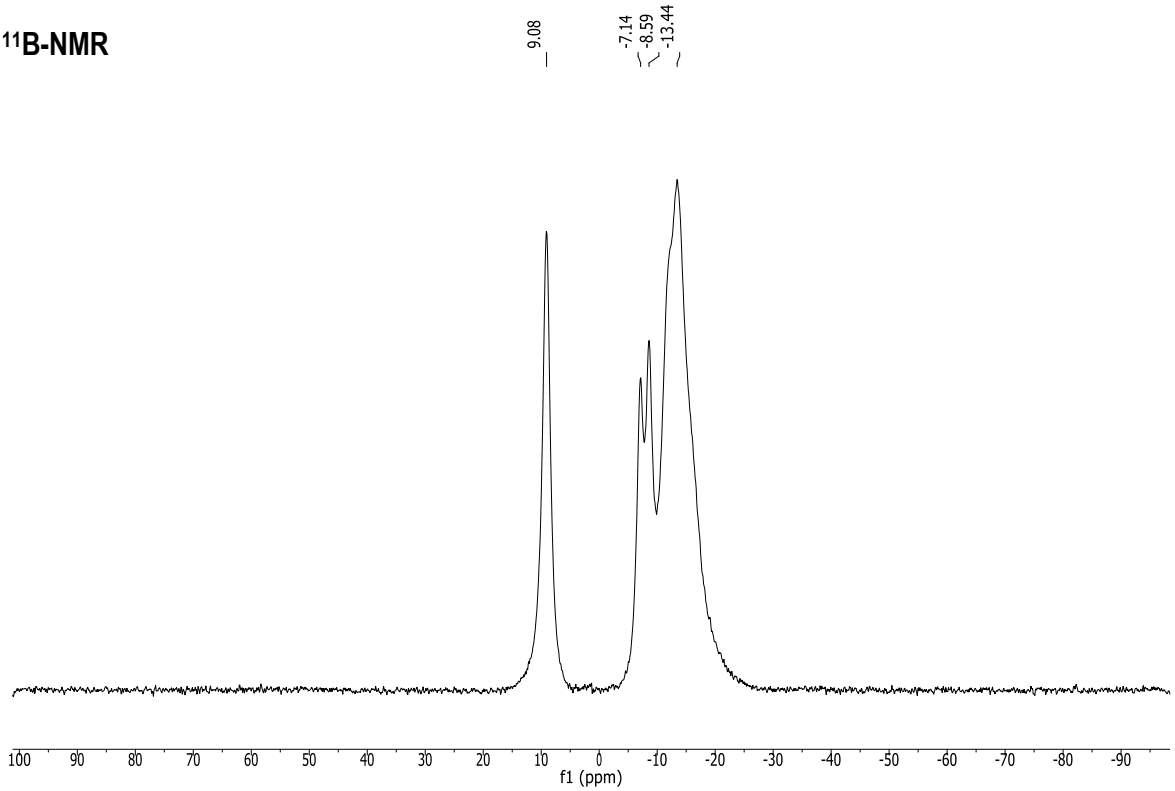
^{1}H-NMR



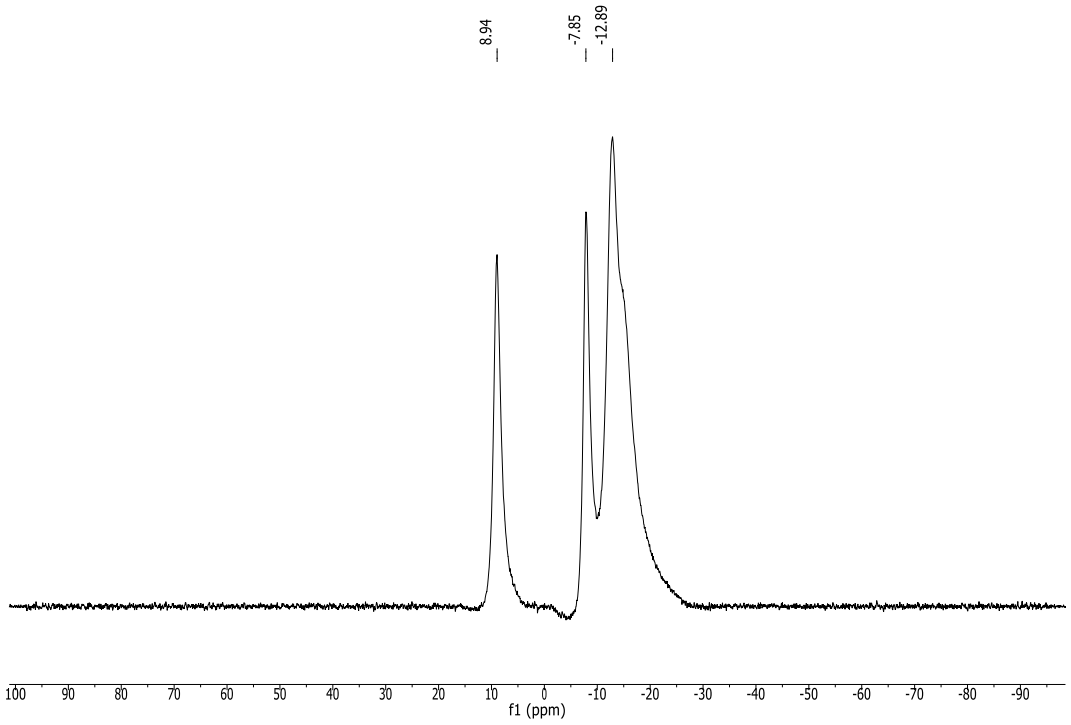
^{1}H{^{11}B}-NMR



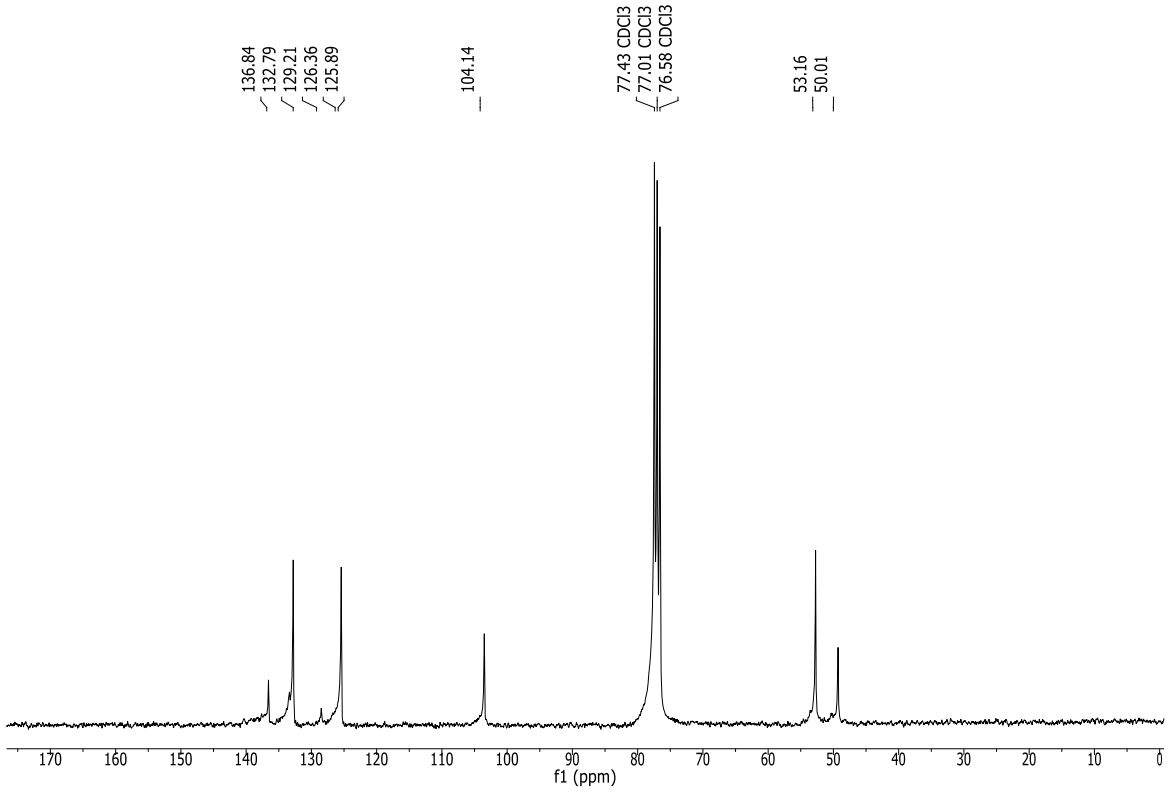
^{11}B-NMR



^{11}B{^{1}H}-NMR



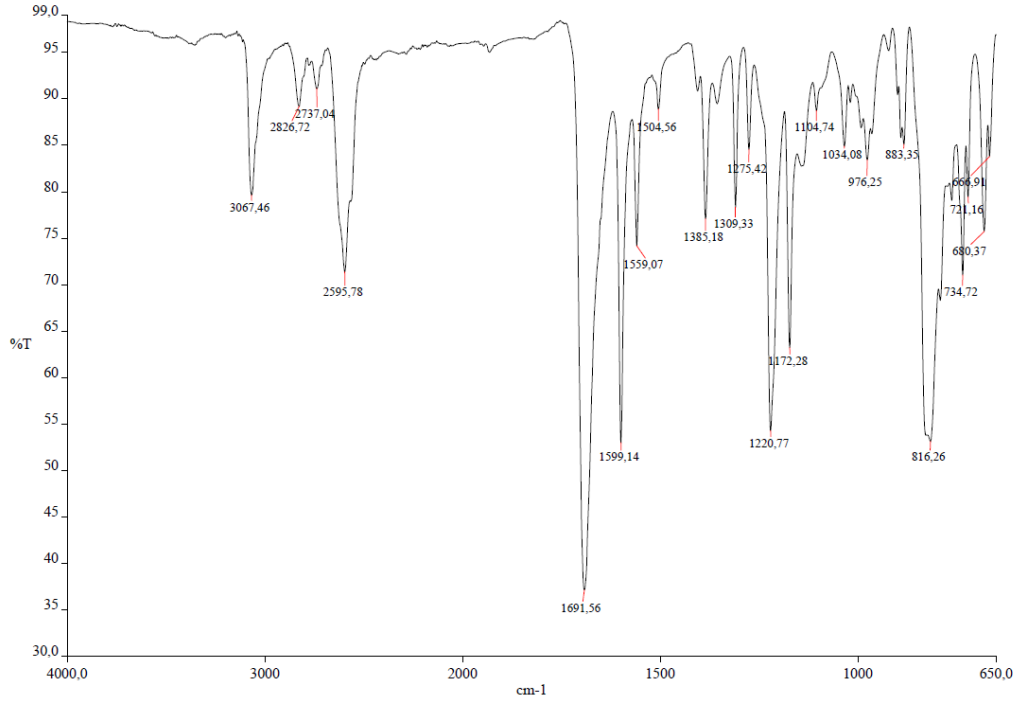
$^{13}C\{^{1}H\}$-NMR


136.84
132.79
129.21
126.36
125.89
104.14
77.43 CDCl3
77.01 CDCl3
76.58 CDCl3
53.16
50.01
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

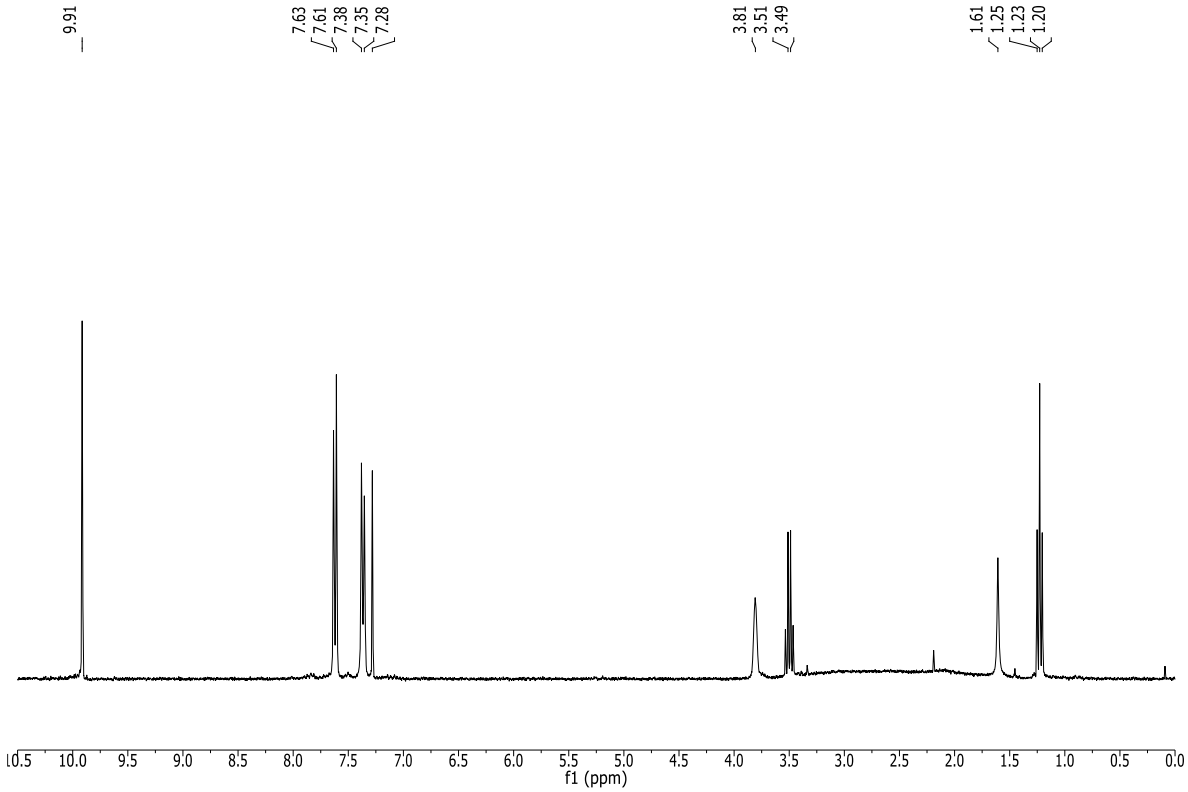
9,12-($C_6H_4CHO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 4

Elemental analysis calcd (%) for $C_{16}H_{20}B_{10}O_2$: C= 54.53, H= 5.72; found: C=55.07, H= 5.79. IR (KBr): ν= 3067(C_c-H, C_{alkyl}-H), 2826, 2737 (C_{aryl}-H), 2595 (B-H), 1691 (C=O). ^{1}H NMR ($CDCl_3$): δ= 9.91 (s, 2H, CHO), 7.63 (d, 4H, C_6H_4), 7.38 (d, 4H, C_6H_4), 3.81 (s, 2H, C_c-H), 2.81-2.46 (B-*H*). ^{1}H{^{11}B} (CD_3COCD_3): δ= 9.91 (s, 2H, CHO), 7.63 (d, 4H, C_6H_4), 7.38 (d, 4H, C_6H_4), 3.81 (s, 2H, C_c-H), 2.81(s, B-H), 2.51 (s, B-*H*), 2.46 (s, B-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 192.5 (s, CHO), 133.4 (s, C_6H_4), 128.5 (s, C_6H_4), 50.3 (C_c-H). ^{11}B NMR ($CDCl_3$): δ= 6.88 (s, 2B-C), -9.4 (d, ^1J(B,H)= 146), -14.1 (d, ^1J(B,H)= 155), -16.2 (br s, B-H).

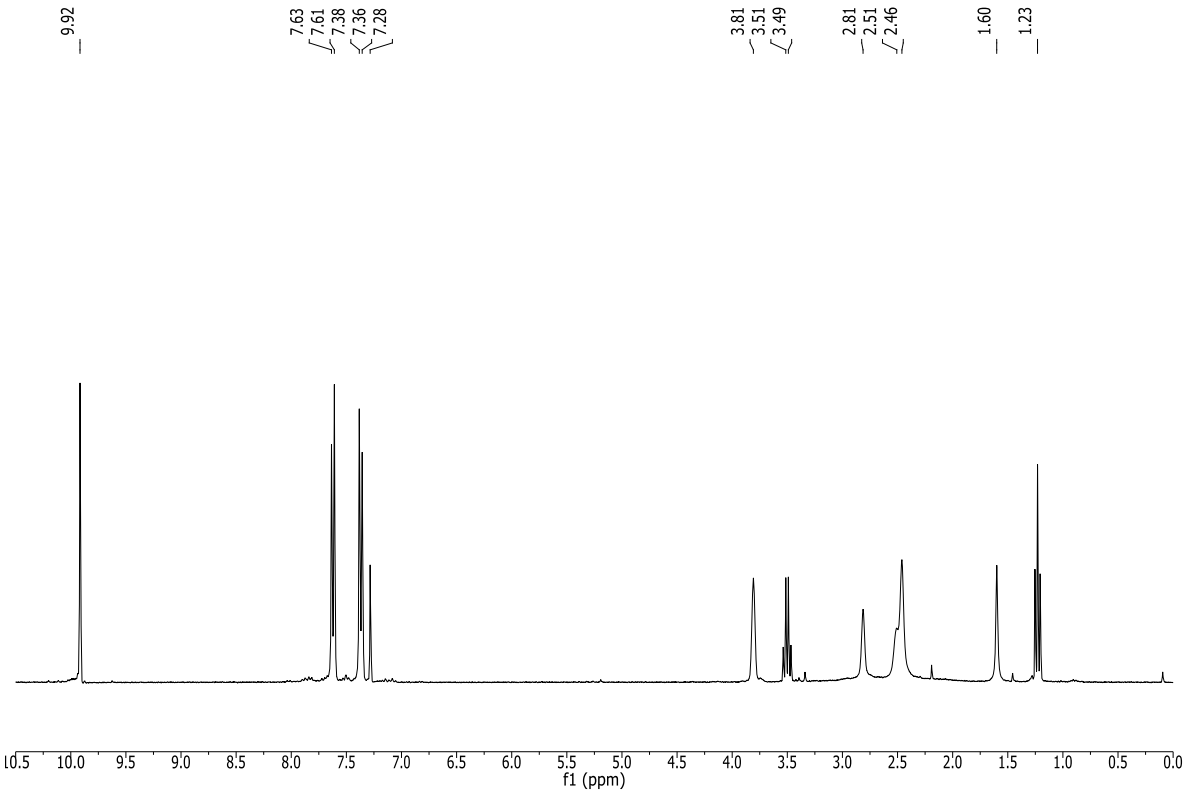
IR



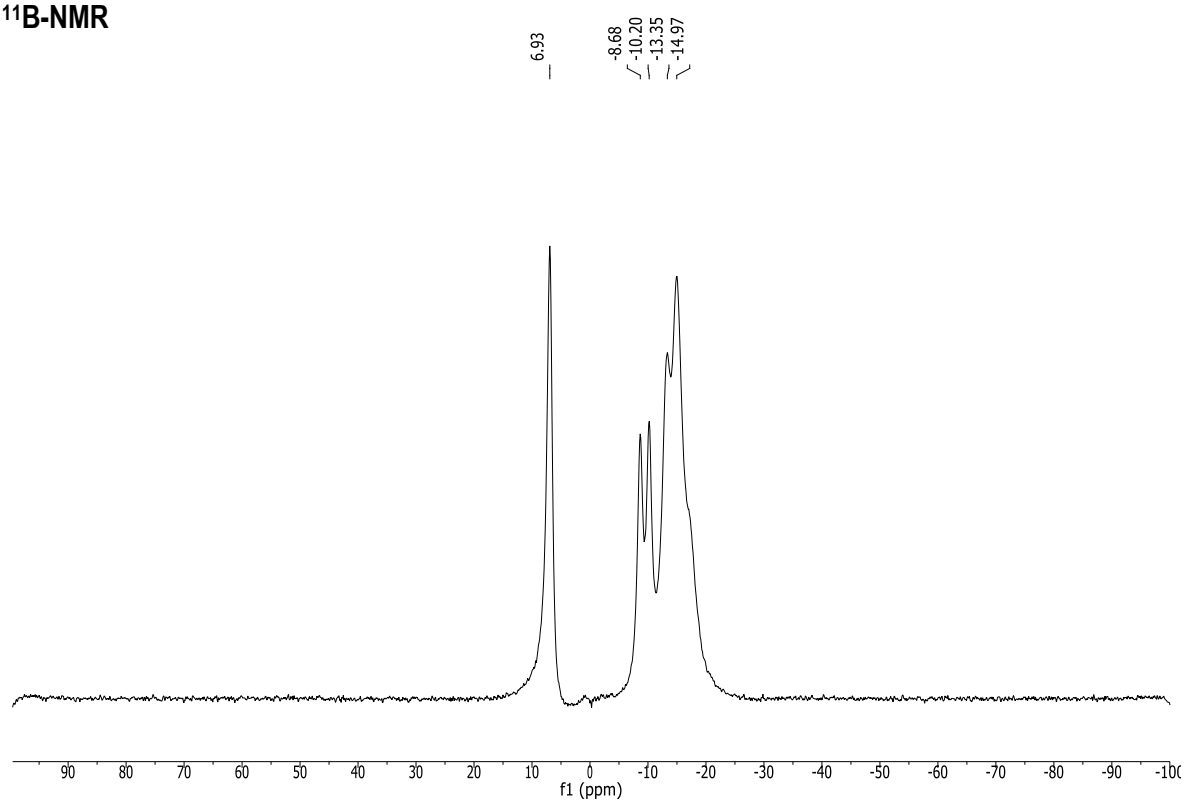
^{1}H-NMR



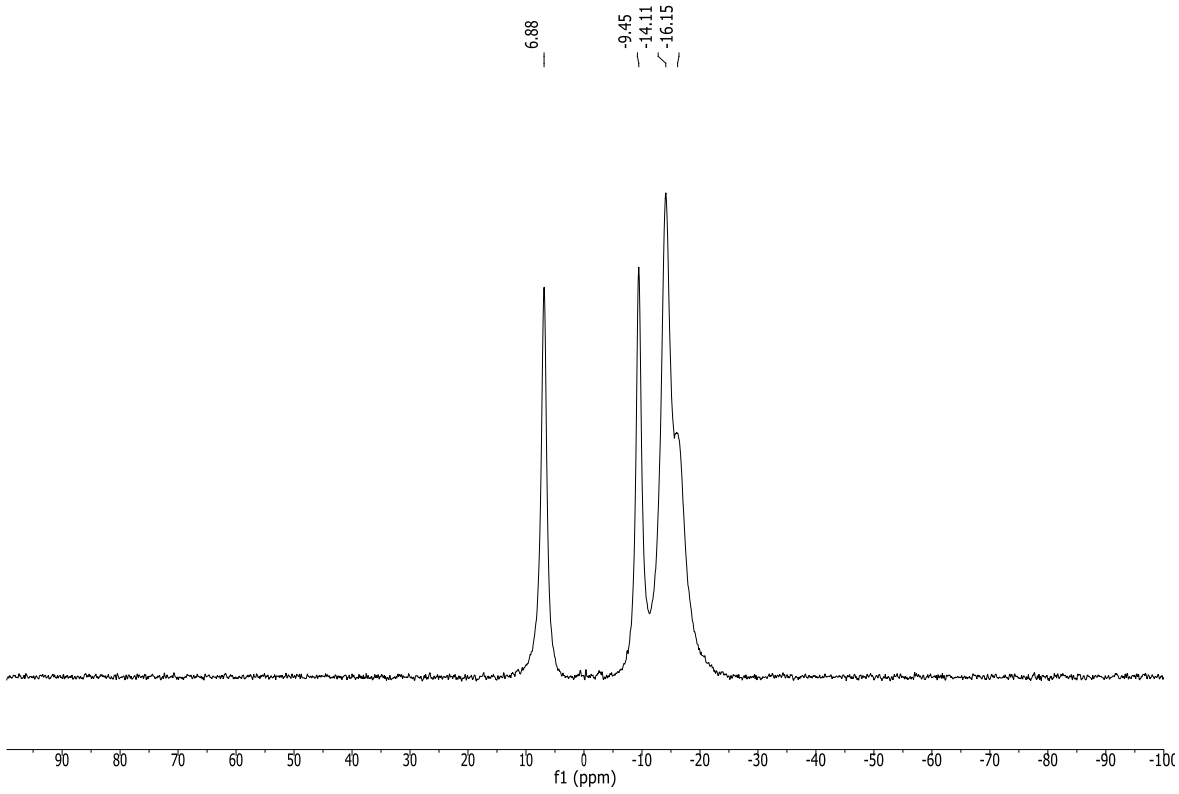
^{1}H{^{11}B}-NMR



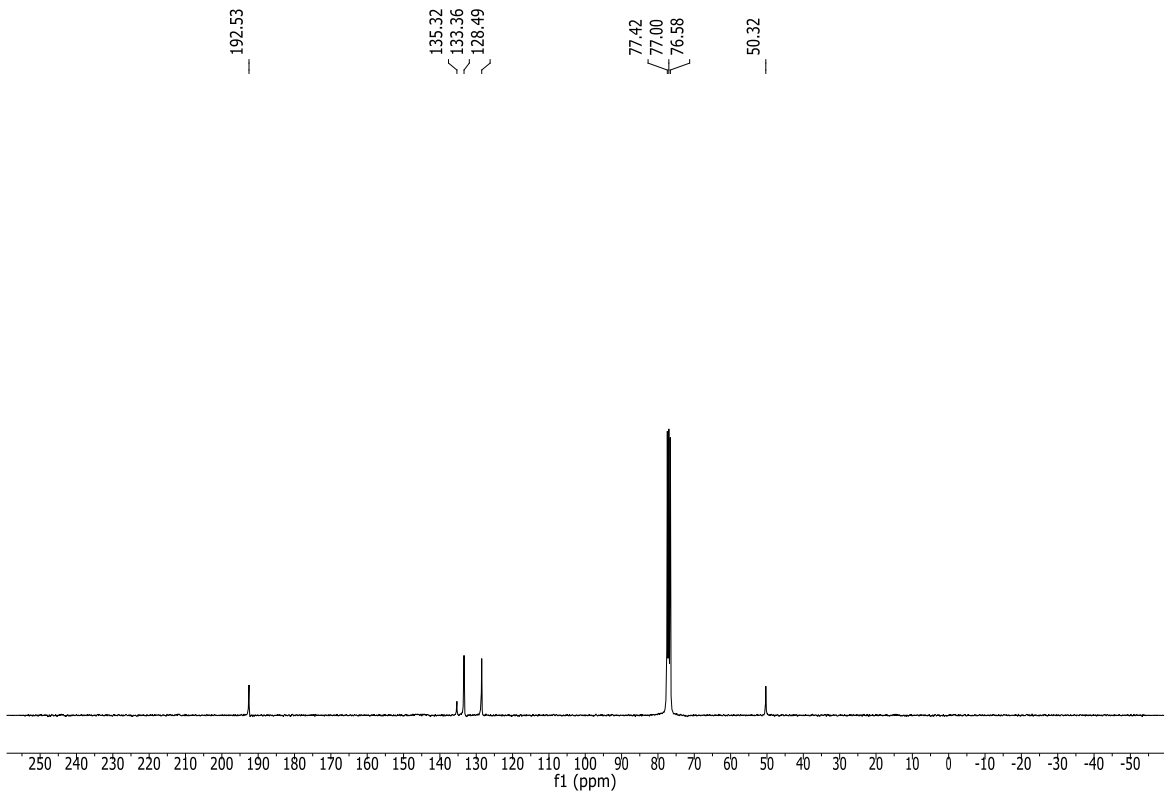
^{11}B-NMR



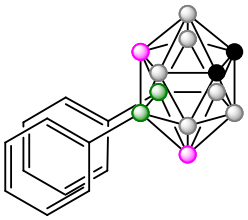
^{11}B{^{1}H}-NMR



$^{13}C\{^{1}H\}$-NMR

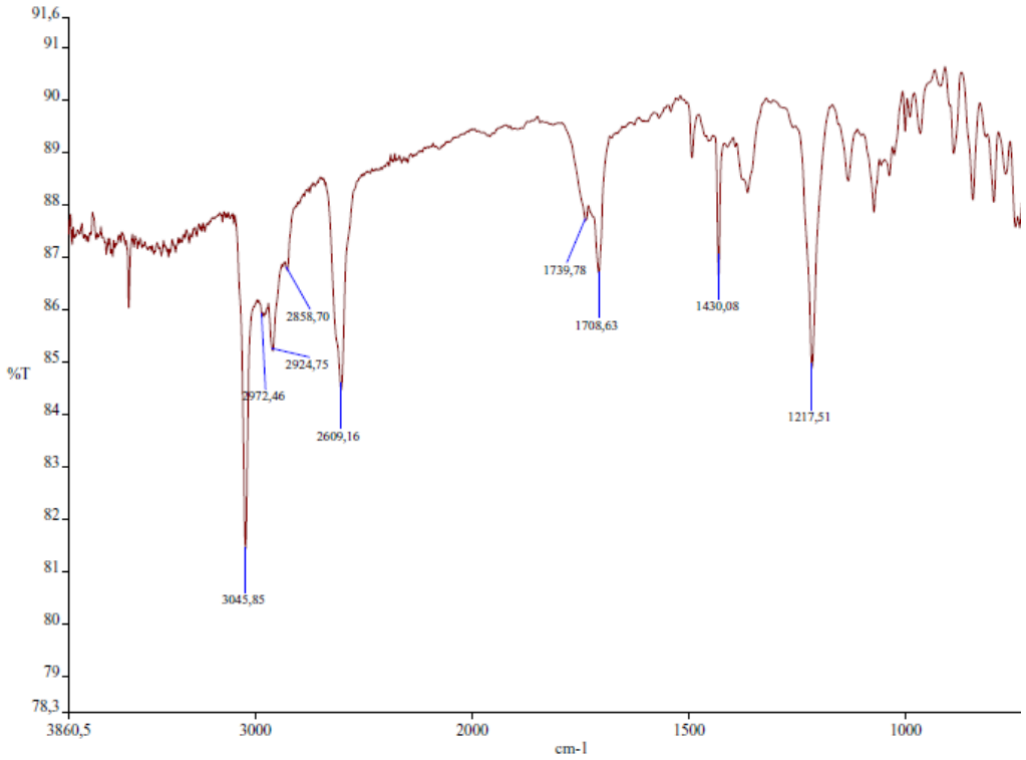

192.53
135.32
133.36
128.49
77.42
77.00
76.58
50.32
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

9,12-Ph_2-8,10-I_2-1,2-*closo*-$C_2B_{10}H_8$

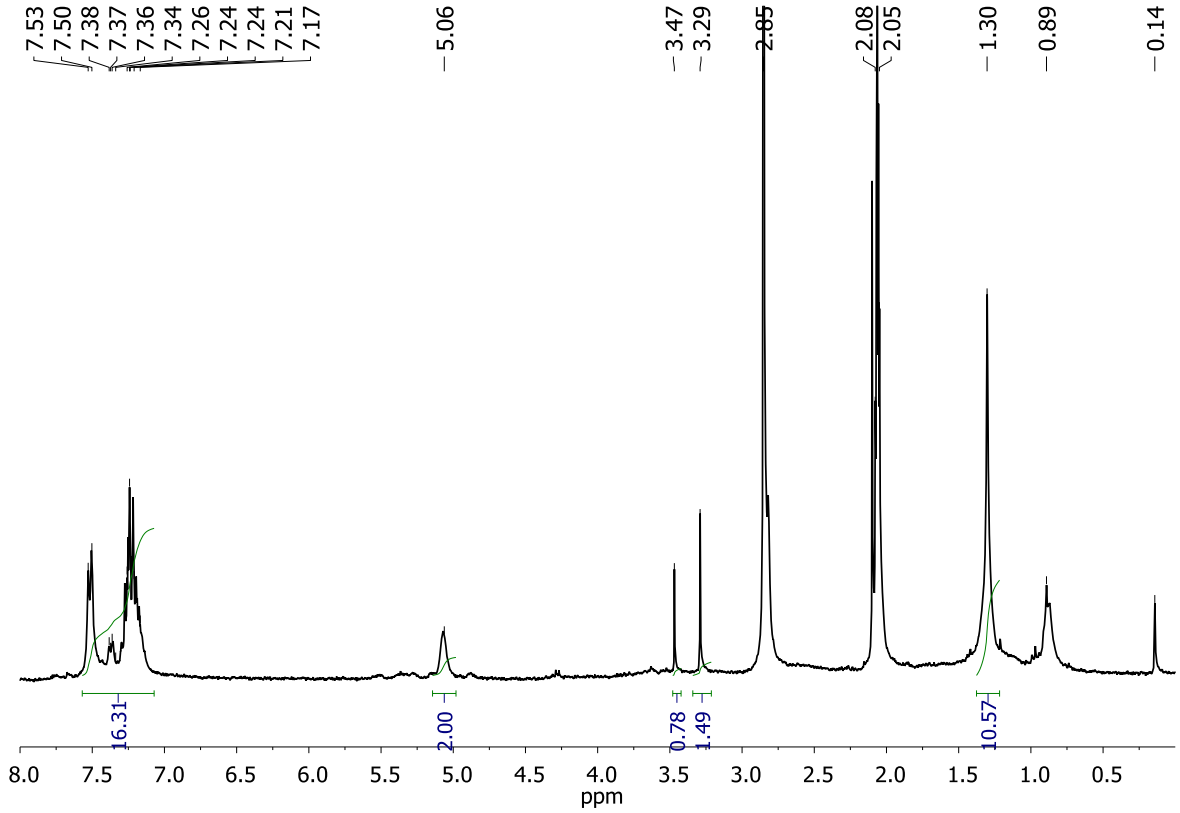


IR (KBr): ν [cm^{-1}] = 3045 (s, $C_{cluster}$-H st.), 2972, 2924, 2858 (vs, $\nu_s(CH_2)$), 2609 (s, B-H st.), 1430 (vs, ν_s(C-C_{phenyl})). ^{1}H NMR: δ [ppm] =7.52 (d, ^{1}J(H,H)=9 Hz, 4H, $H_{phenyl\text{-}meta}$), 7.24 (m, 6H, $H_{phenyl\text{-}ortho,para}$), 5.06 (br s, 2H, $C_{cluster}H$), 4.0–1.6 (br m, 6H, B*H*). ^{1}H{^{11}B} NMR: δ [ppm]=7.52 (d, ^{1}J(H,H)=9 Hz, 4H, $H_{phenyl\text{-}meta}$), 7.24 (m, 6H, $H_{phenyl\text{-}ortho,para}$), 5.06 (br s, 2H, $C_{cluster}H$), 3.36 (br s, 4H, B(4,5,7,11)*H*), 2.88 (br s, 2H, B(3,6)*H*).^{13}C{^{1}H} NMR: δ [ppm] =134.3, 127.9, 126.8 (C_{phenyl}), 52.7 ($C_{cluster}$). ^{11}B NMR: δ [ppm] =5.01 (s, 2B, B(9,12)-*Ph*), -12.1 (d, ^1J(B,H)=164 Hz, 4B, B(4,5,7,11)), -14.8 (d, ^1J(B,H)=186 Hz, 2B, B(3,6)). -20.1 (s, 2B, B(8,10)-*I*). ESI MS: *m/z* (%)= 537 (100) [M-B-H]$^-$, 547 (20) [M-H]$^-$, 663 (75) [M-B+I]$^-$.

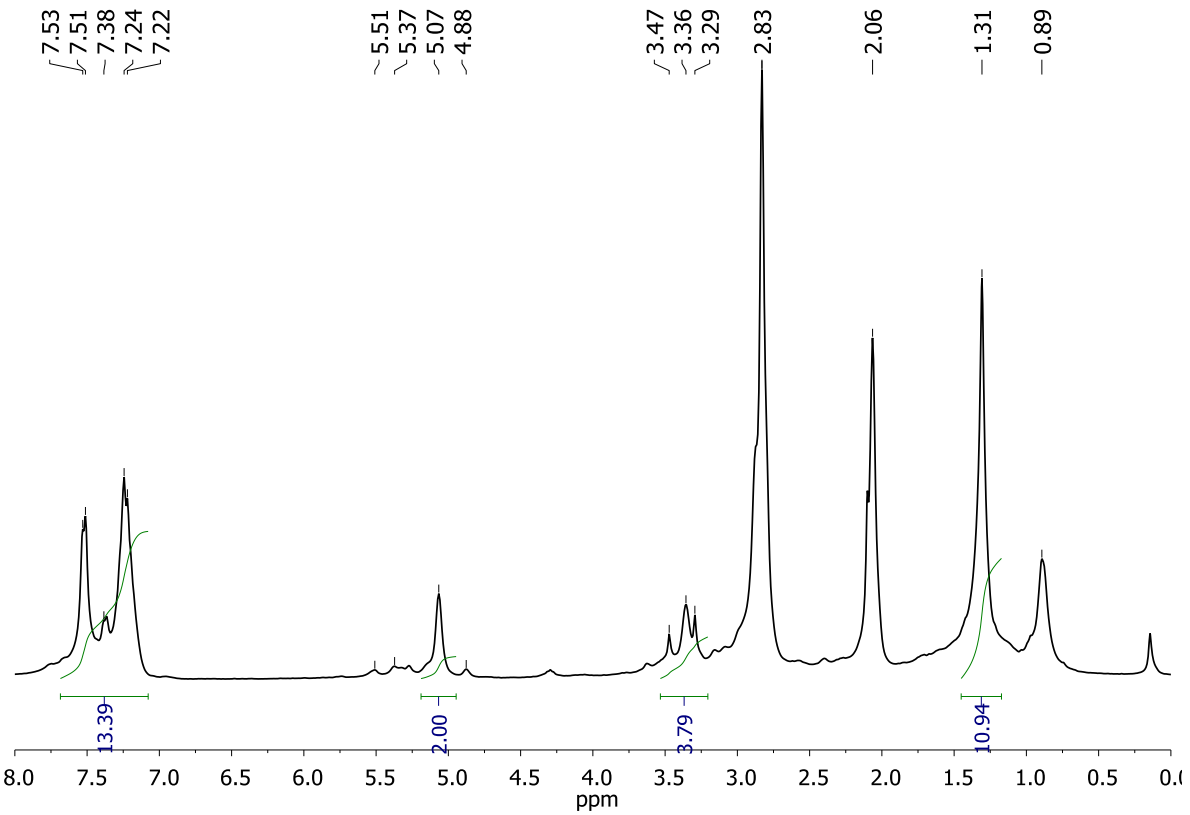
IR



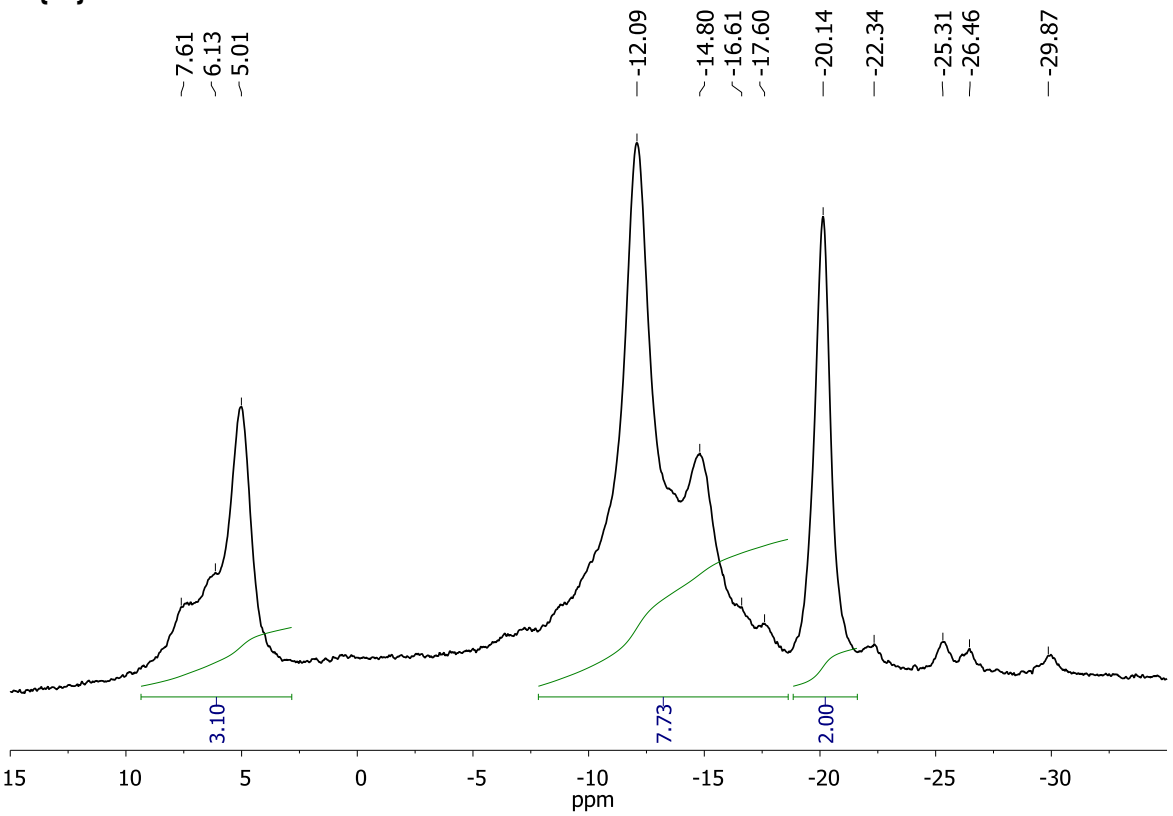
^{1}H-RMN



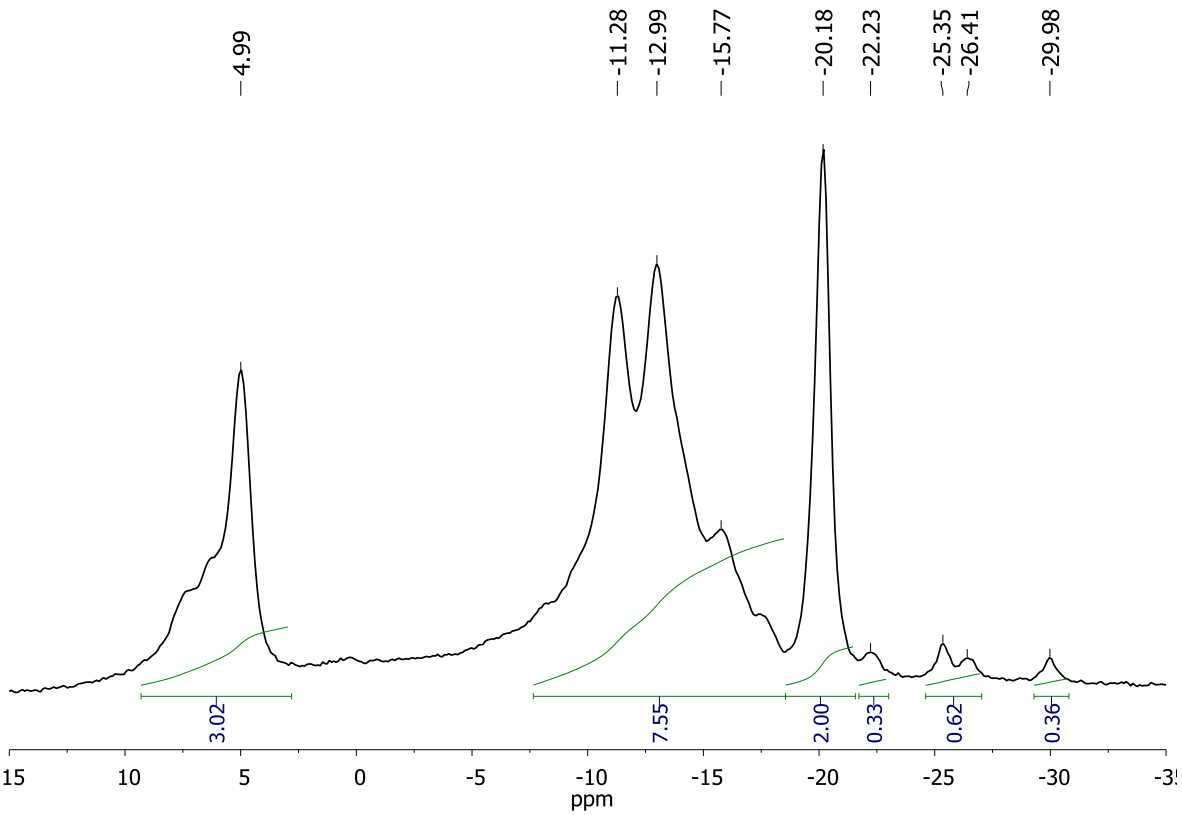
^{1}H{^{11}B}-RMN



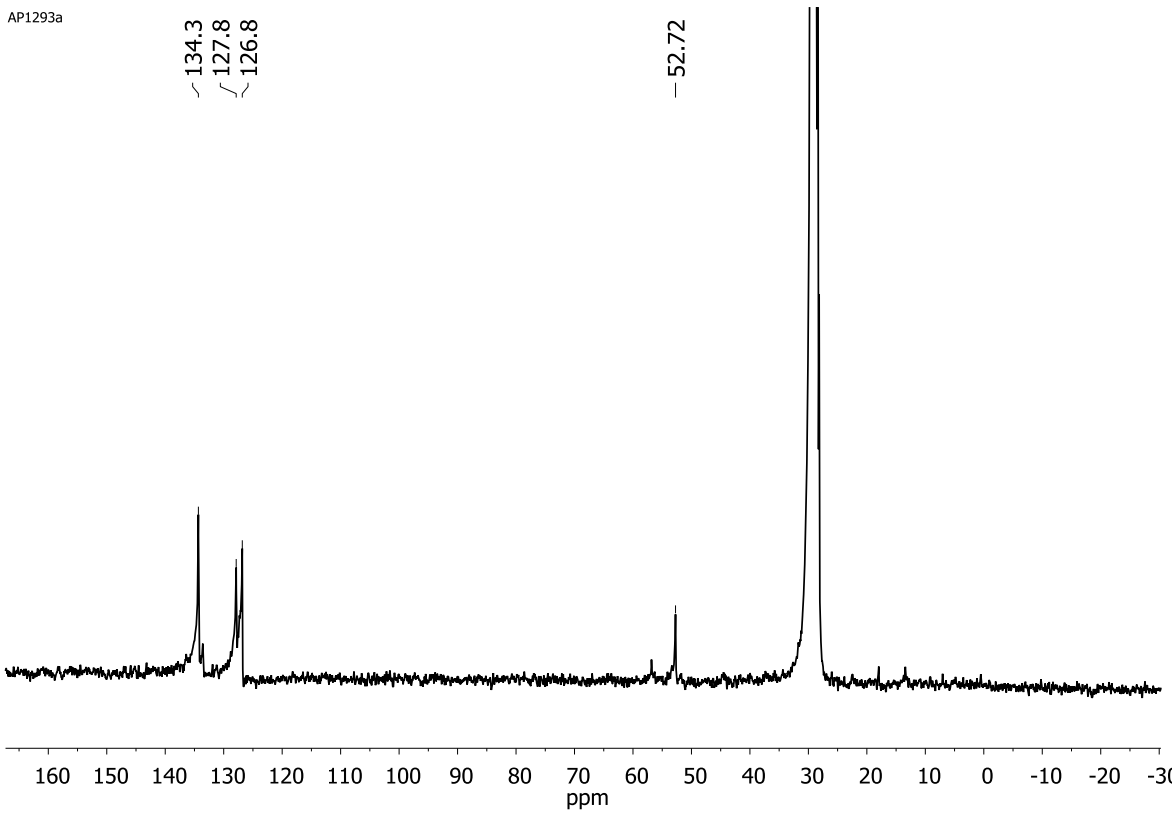
$^{11}B\{^{1}H\}$-RMN



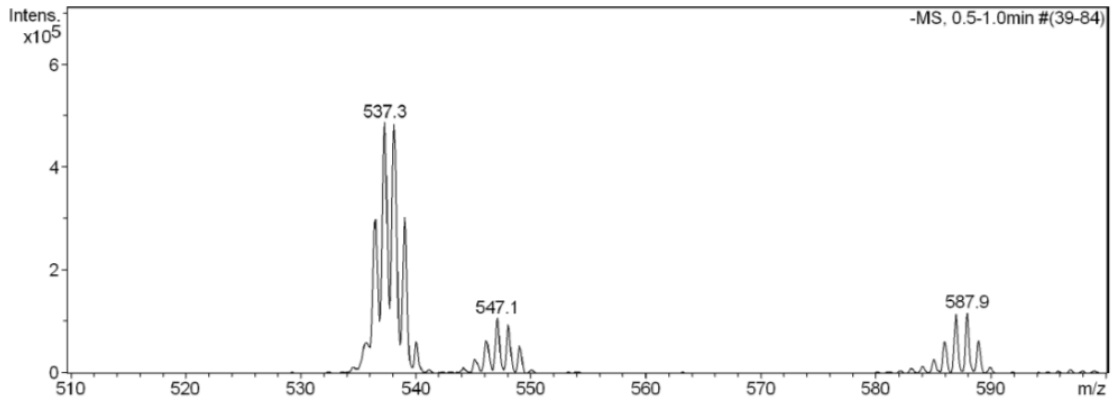
^{11}B-RMN



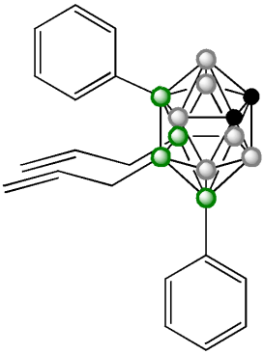
$^{13}C\{^{1}H\}$-RMN



ESI-MS

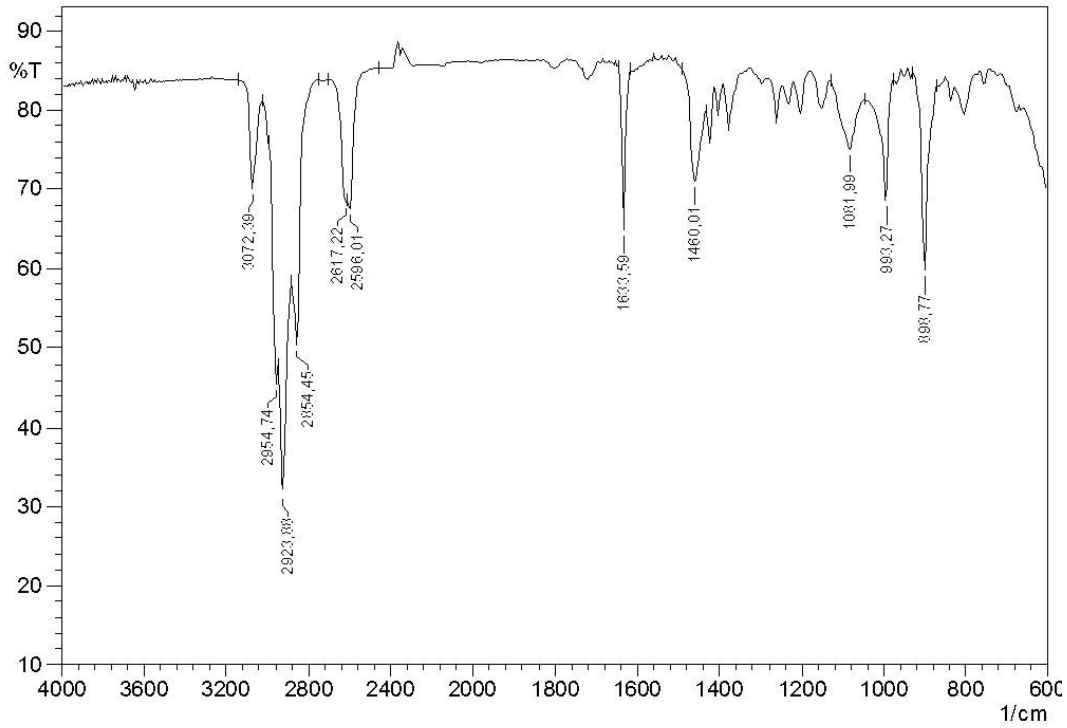


8,10-Ph_2-9,12-$(CH_2{=}CHCH_2)_2$-1,2-*closo*-$C_2B_{10}H_8$

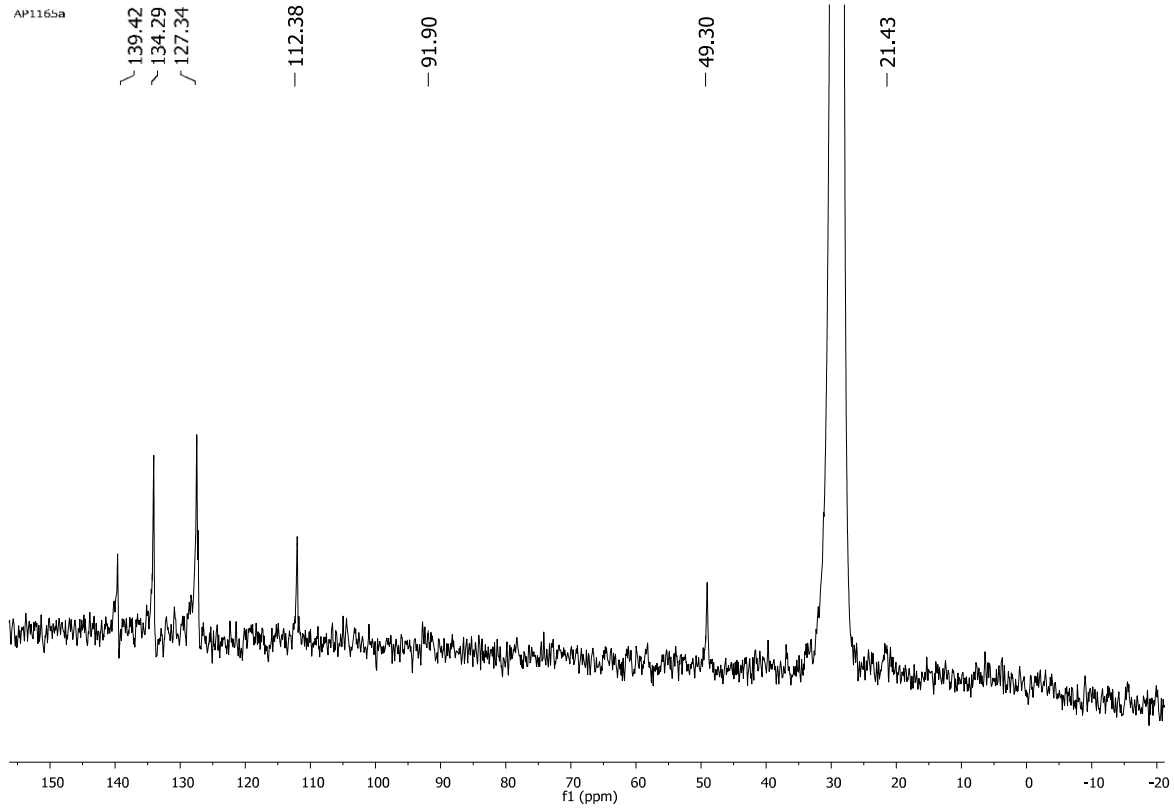


Elemental Analysis for $C_{20}B_{10}H_{28}$: calc: C 63.82, H 7.45; found: C 63.97, H 7.39. IR (KBr): [cm^{-1}] = 3072 (vs, $_s$($C_{cluster}$-H and $=CH_2$)), 2954, 2923, 2854 (vs, $_s$(=CH and CH_2)), 2600 (vs, $_s$(B-H)), 1633 (vs, $_s$(C=C)) ^{1}H NMR: [ppm]=7.70 (m, 4H, H_{phenyl}), 7.36 (m, 6H, H_{phenyl}), 5.93 (m, 2H, $CH_2{=}CH{-}CH_2$), 4.87-4.82 (m, 4H, $CH_2{=}CH{-}CH_2$), 4.62 (s, 2H, $C_{cluster}$-*H*), 3.10–1.00 (m, 6H, B-$H_{terminal}$), 1.33 (s, 4H, $CH_2{=}CH{-}CH_2$).^{1}H{^{11}B} NMR: [ppm]=7.70 (m, 4H, H_{phenyl}), 7.36 (m, 6H, H_{phenyl}), 5.93 (m, 2H, $CH_2{=}CH{-}CH_2$), 4.87-4.82 (m, 4H, $CH_2{=}CH{-}CH_2$), 4.62 (s, 2H, $C_{cluster}$-*H*), 2.41 (br s, 4H, B(4,5,7,11)*H*), 2.32 (br s, 2H, B(3,6)*H*), 1.33 (d, ^3J(B,H)=9.0 Hz, 4H, $CH_2{=}CH{-}CH_2$).^{13}C{^{1}H} NMR: [ppm] =139.4 (s, $CH_2{=}CH{-}CH_2$), 134.3, 127.3 (C_{phenyl}), 112.4 (s, $CH_2{=}CH{-}CH_2$), 49.3 (s, $C_{cluster}$), 21.4 (br m, $CH_2{=}CH{-}CH_2$). ^{11}B NMR: [ppm] =7.3 (s, 2B, B(9,12)), 2.2 (s, 2B, B(8,10)-*Ph*), -14.9(d, ^1J(B,H)=161 Hz, 4B, B(4,5,7,11)), -17.0 (d, ^1J(B,H)=167 Hz, 2B, B(3,6)). ESI MS: *m*/*z* (%)= 399.4 (100) $[M+23]^+$.

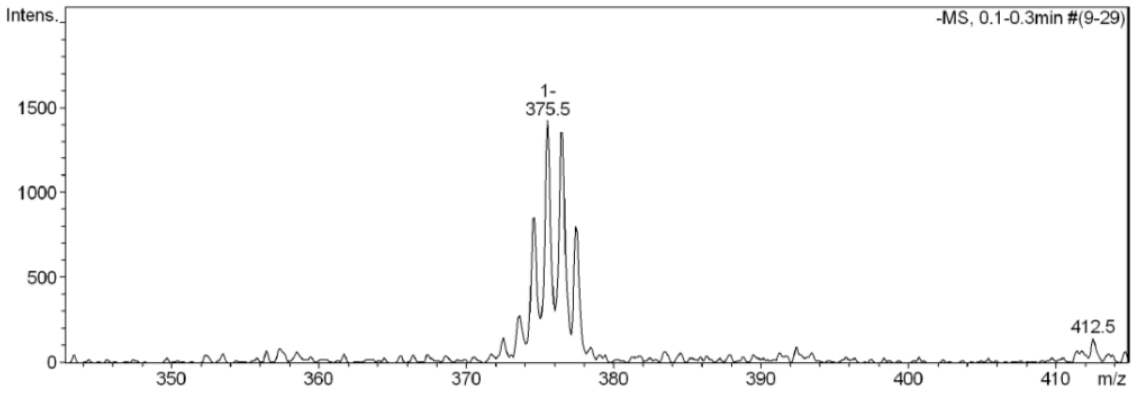
IR



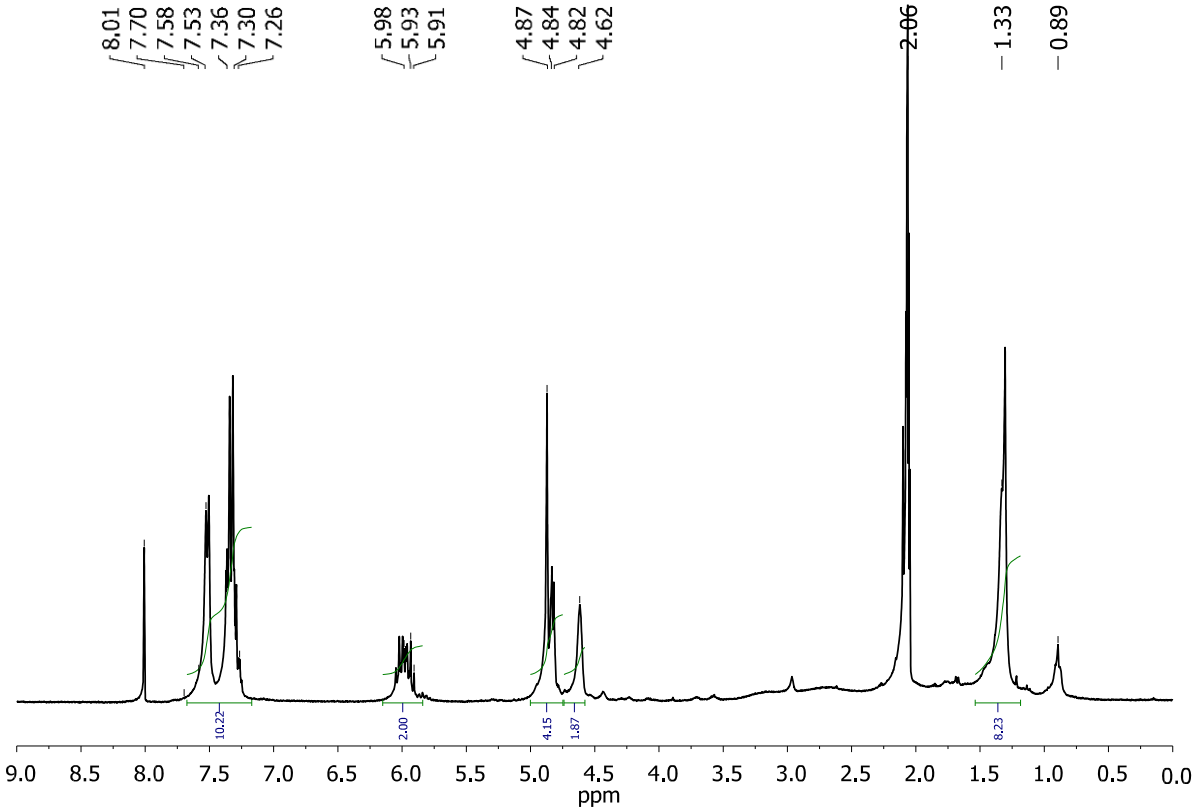
$^{13}C\{^{1}H\}$- NMR



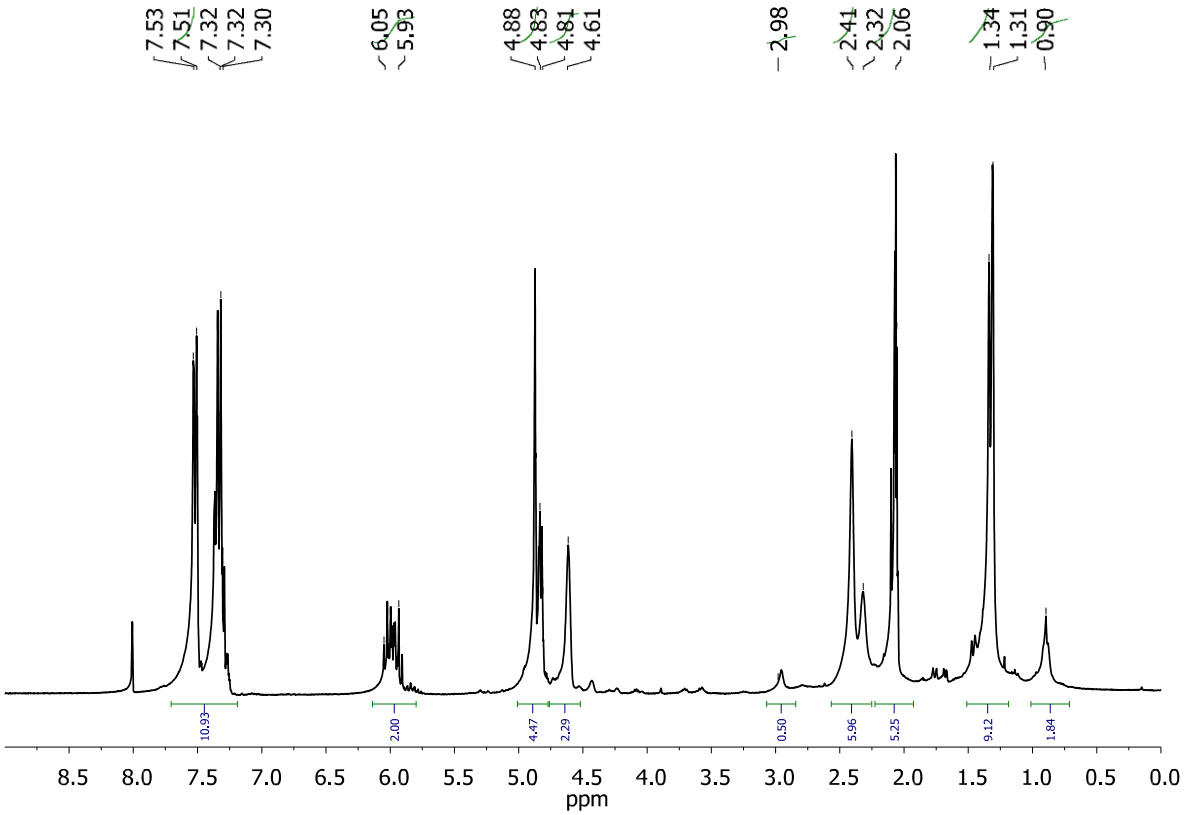
ESI-MS



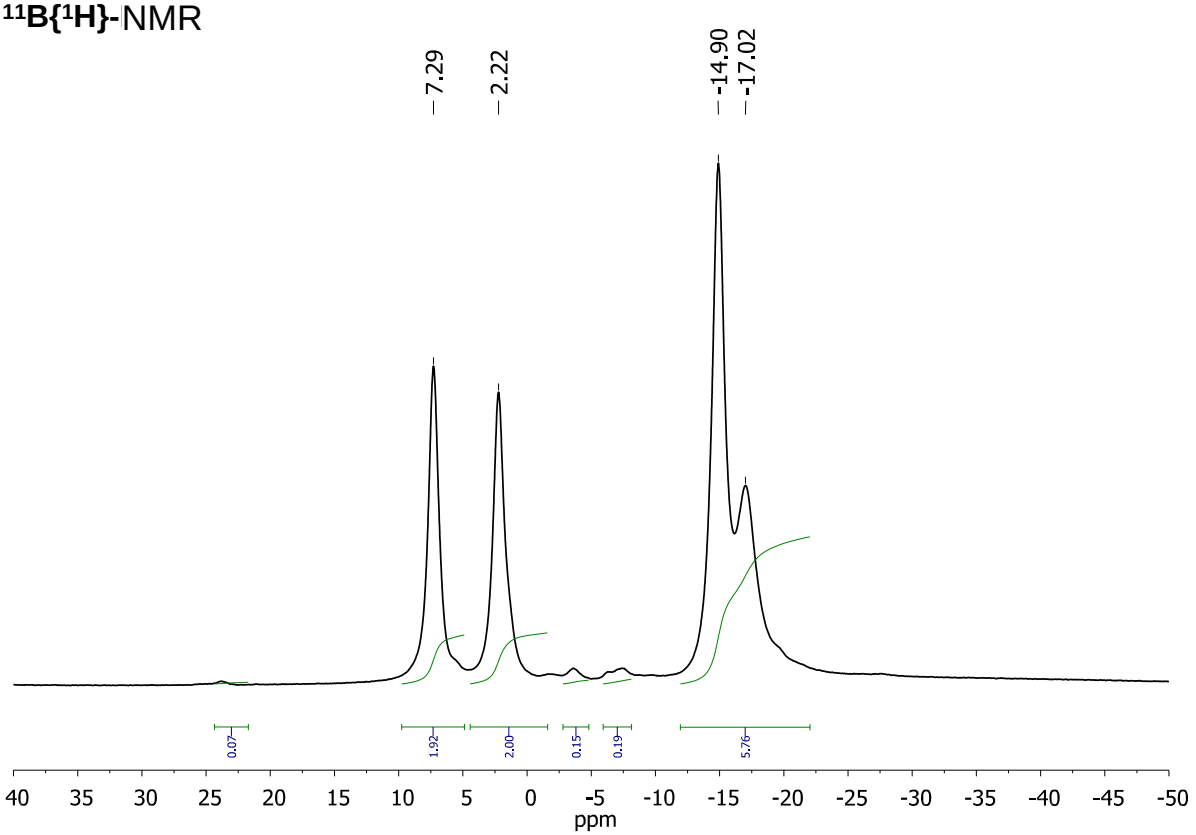
^{1}H-NMR



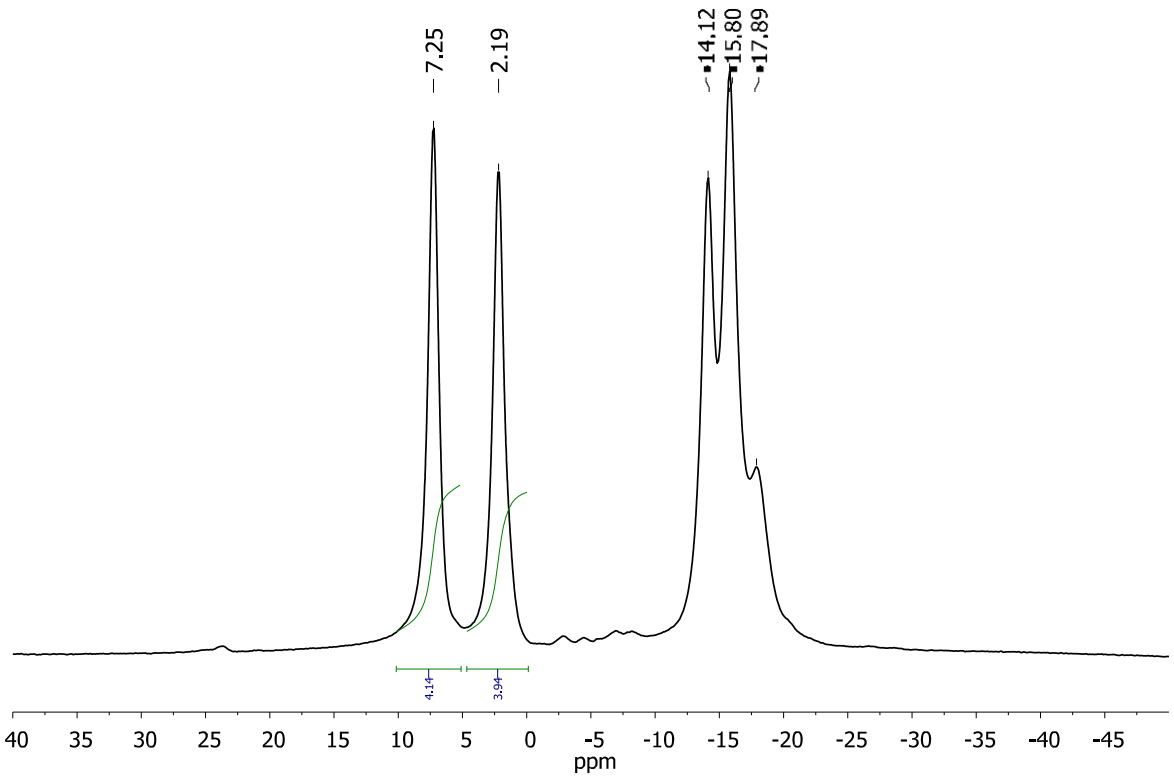
^{1}H{^{11}B}-NMR



$^{11}B\{^{1}H\}$-NMR



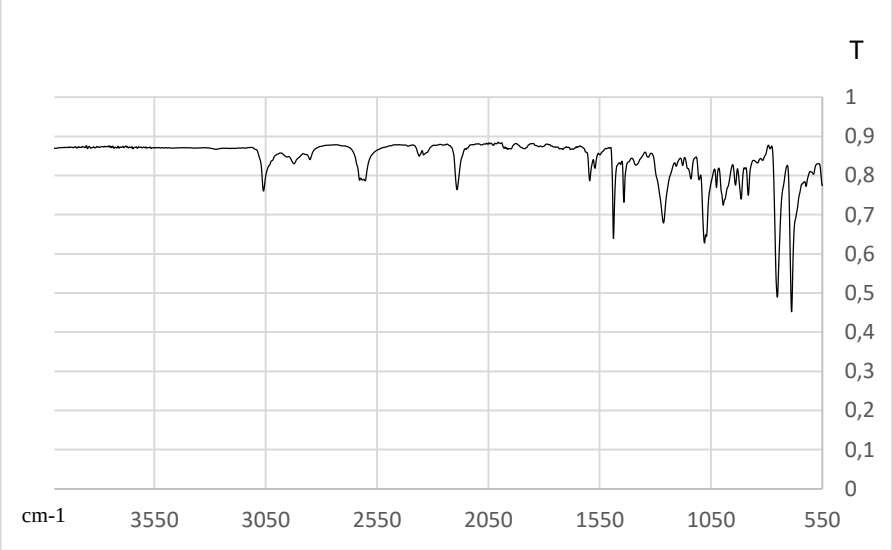
^{11}B-NMR



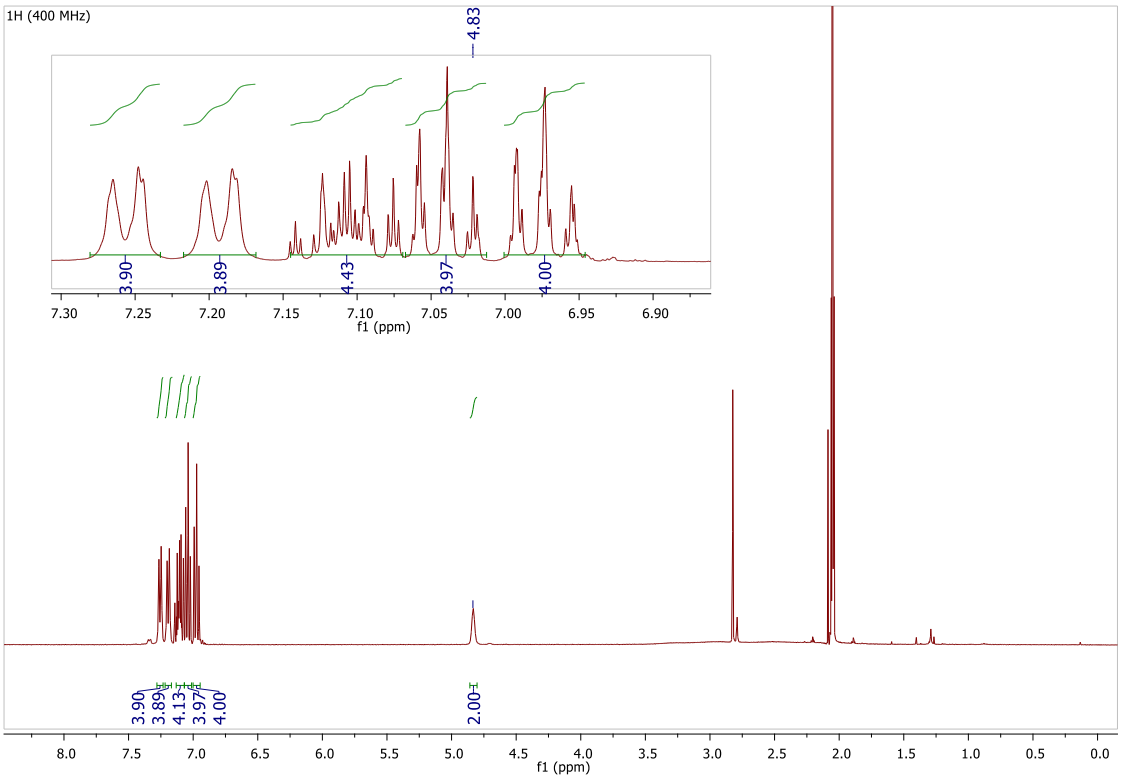
8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$, 10

Elemental Analysis for $C_{26}B_{10}H_{28}$: calc: C 69.61 , H 6.21 ; found: C 71.66, H 5.26. IR (KBr): ν [cm^{-1}] = 3047 (vs, $\nu s(C_{cluster}\text{-}H)$), 2580 (vs, $\nu s(B\text{-}H)$) ^1H NMR: δ [ppm]=7.27-6.95 (m, 15 H, H_{phenyl}), 4.83 (s, 2H, $C_{cluster}$-H), $^1H\{^{11}B\}$ NMR: δ [ppm]= 7.27-6.95 (m, 15H, H_{phenyl}), 4.83 (s, 2H, $C_{cluster}$-H), 2.74, (br, 2H, B-$H_{terminal}$), 2.54 (br, 4H, B-$H_{terminal}$). $^{13}C\{^1H\}$ NMR: δ [ppm]=135.7, 135.1, 128.0, 127.9, 127.6 (s C_{phenyl}), 50.0 (s, $C_{cluster}$). ^{11}B NMR: δ [ppm]=4.0 (s, 2B, B(9,12)), -1.1 (s, 2B, B(8,10)), -16.6 (d, $^1J(B,H)$=195 Hz 4B, B(4,5,7,11)), -18.8 (br, 2B, B(3,6)). LDI MS: m/z (%)=446.714 (100) [M-1]

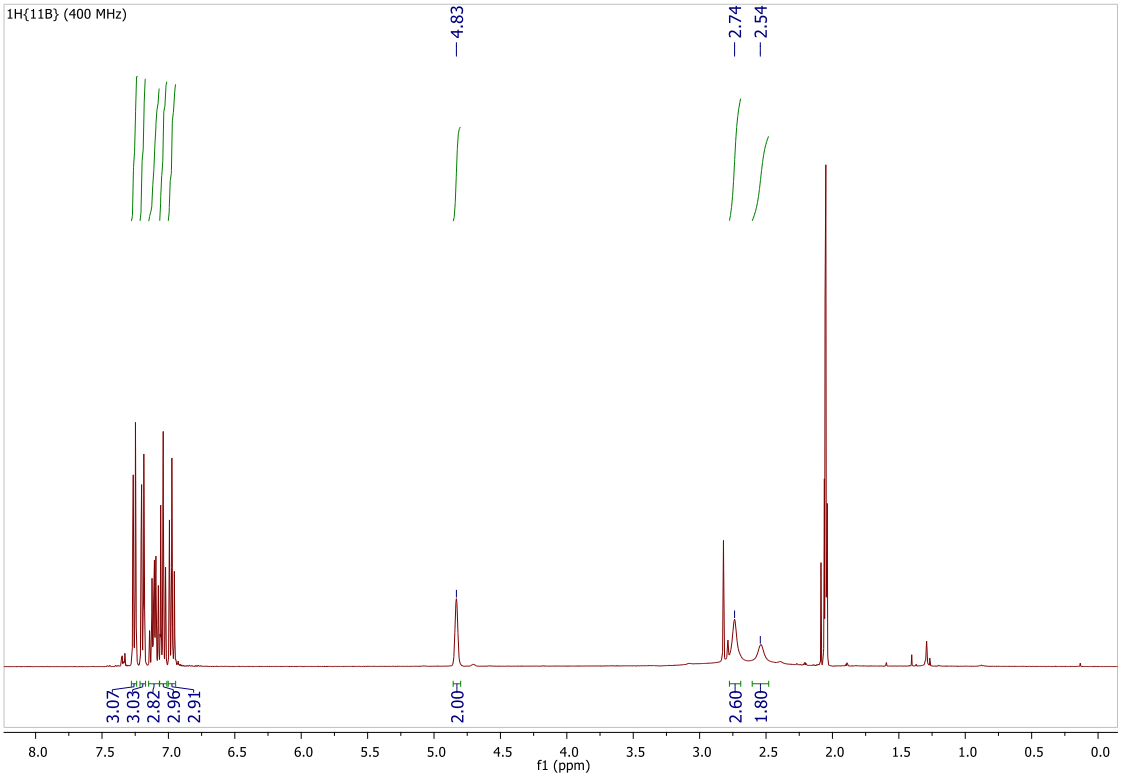
ATR-IR



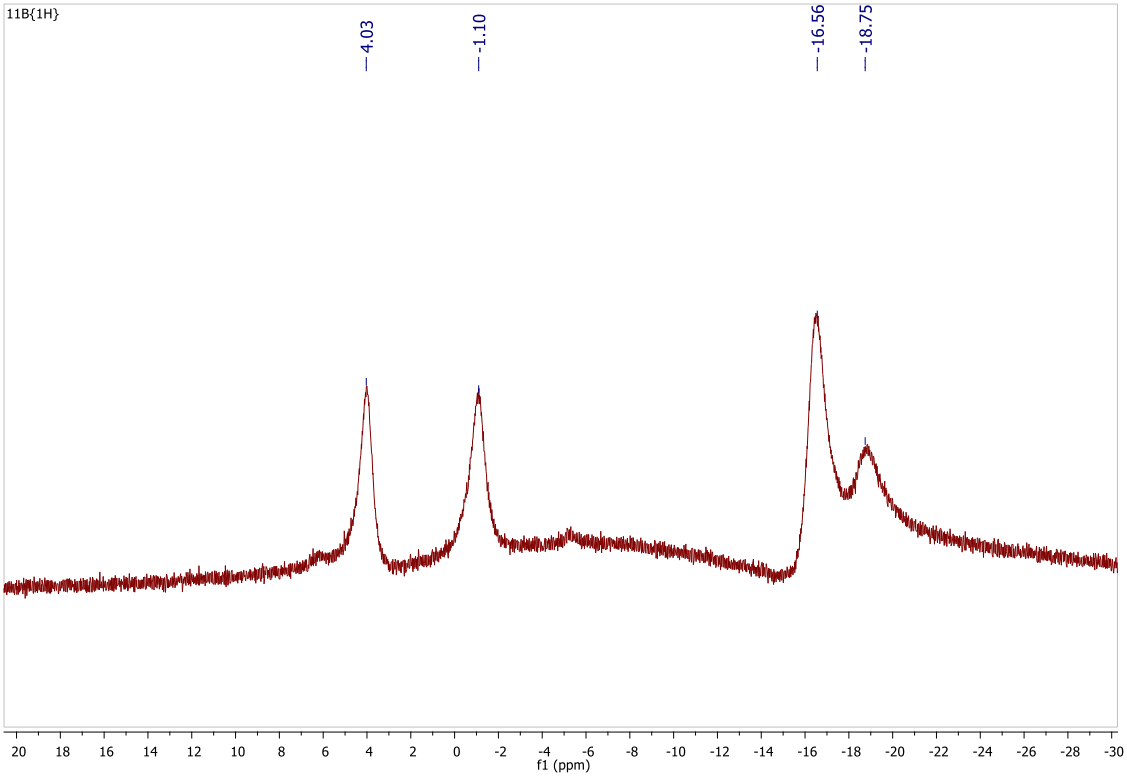
^{1}H NMR



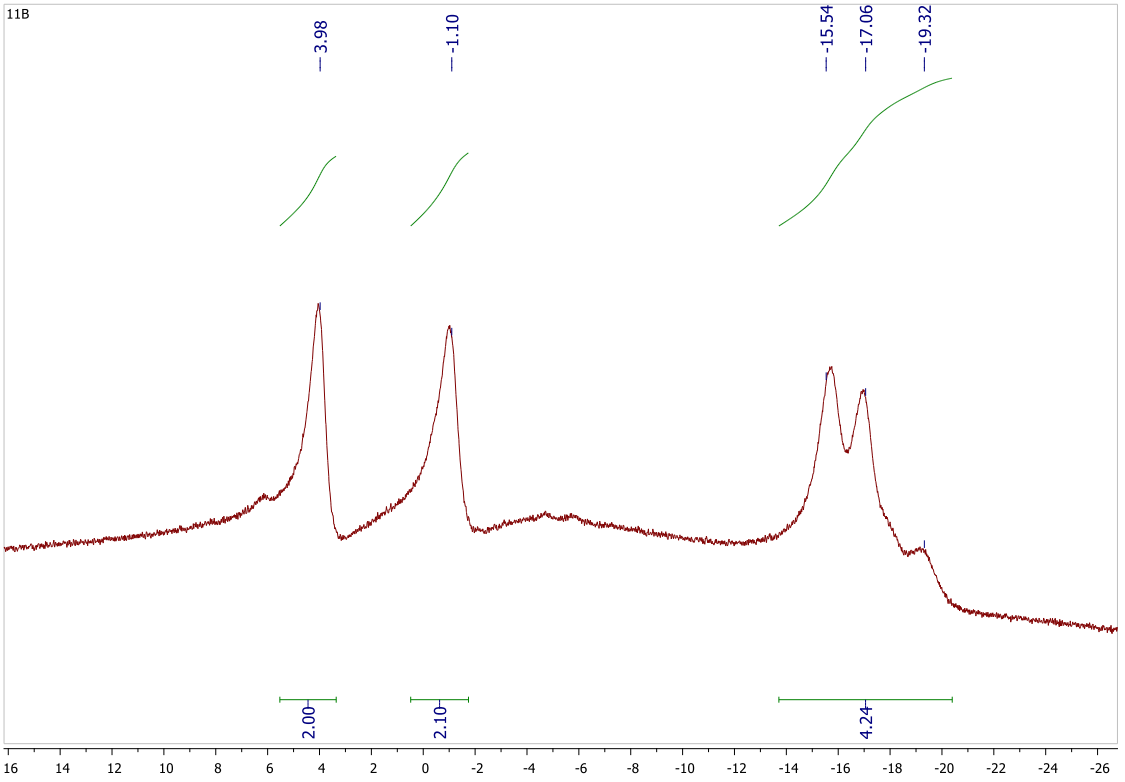
$^{1}H\{^{11}B\}$ NMR



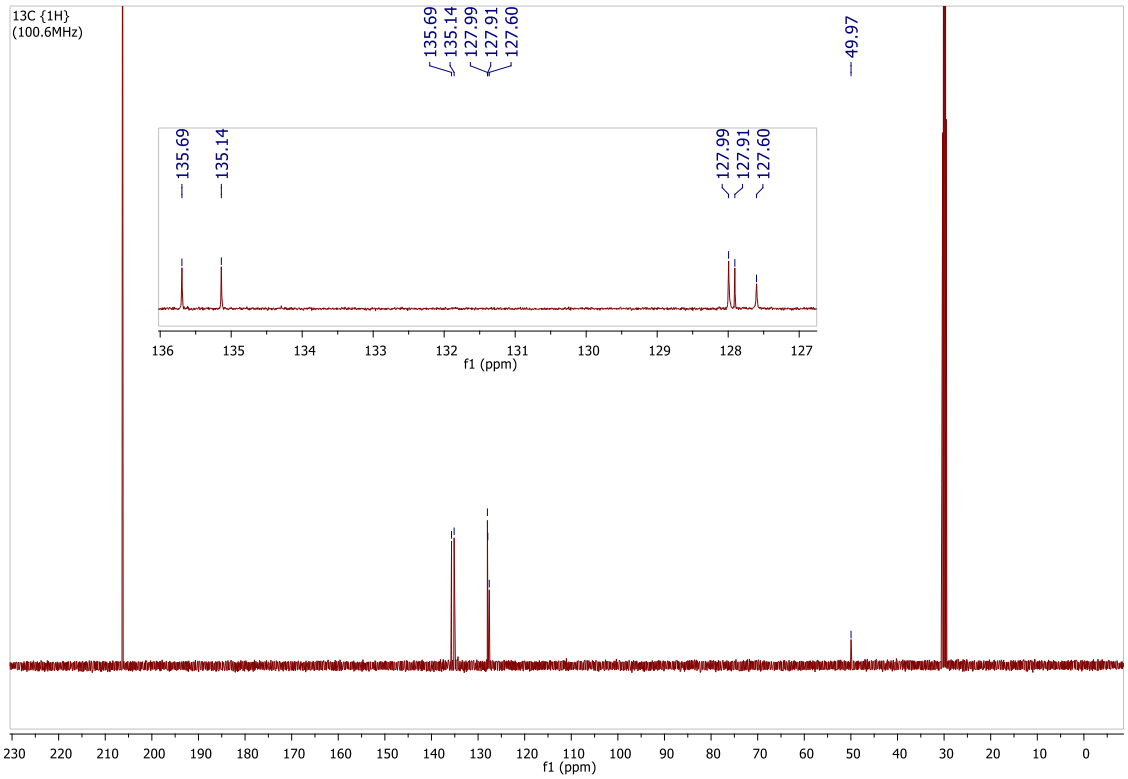
$^{11}B\{^{1}H\}$ NMR



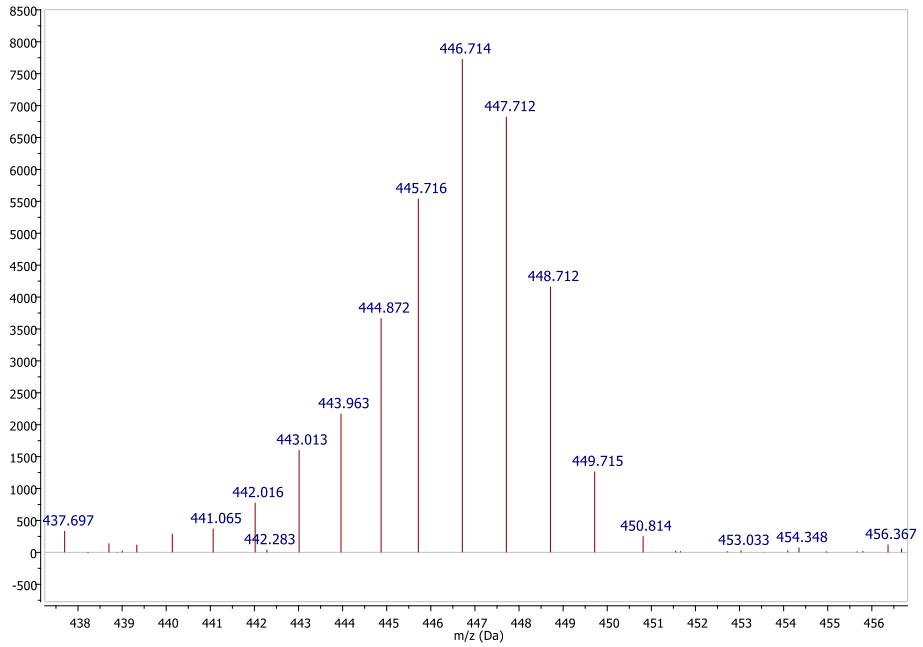
^{11}B NMR



$^{13}C\{^{1}H\}$ NMR



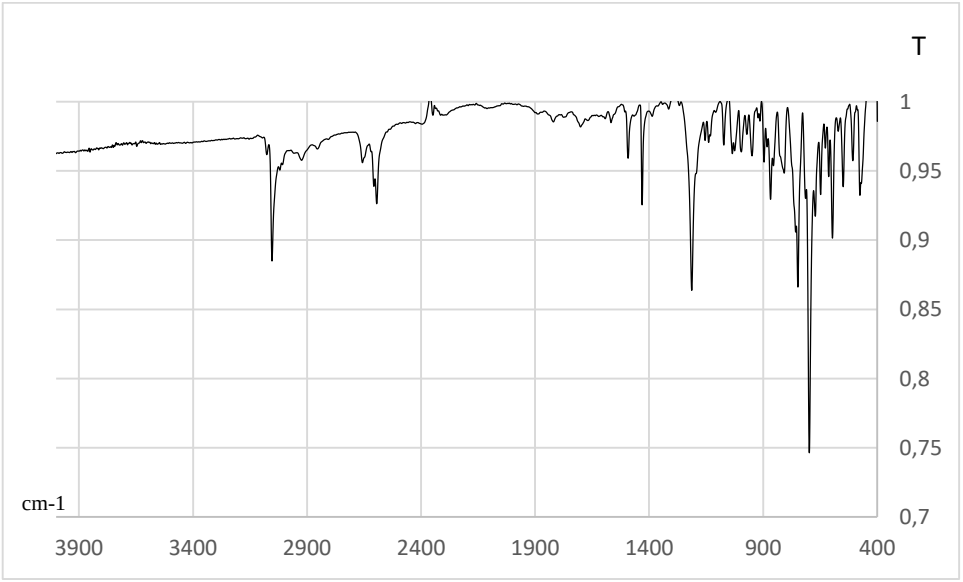
LDI-MS



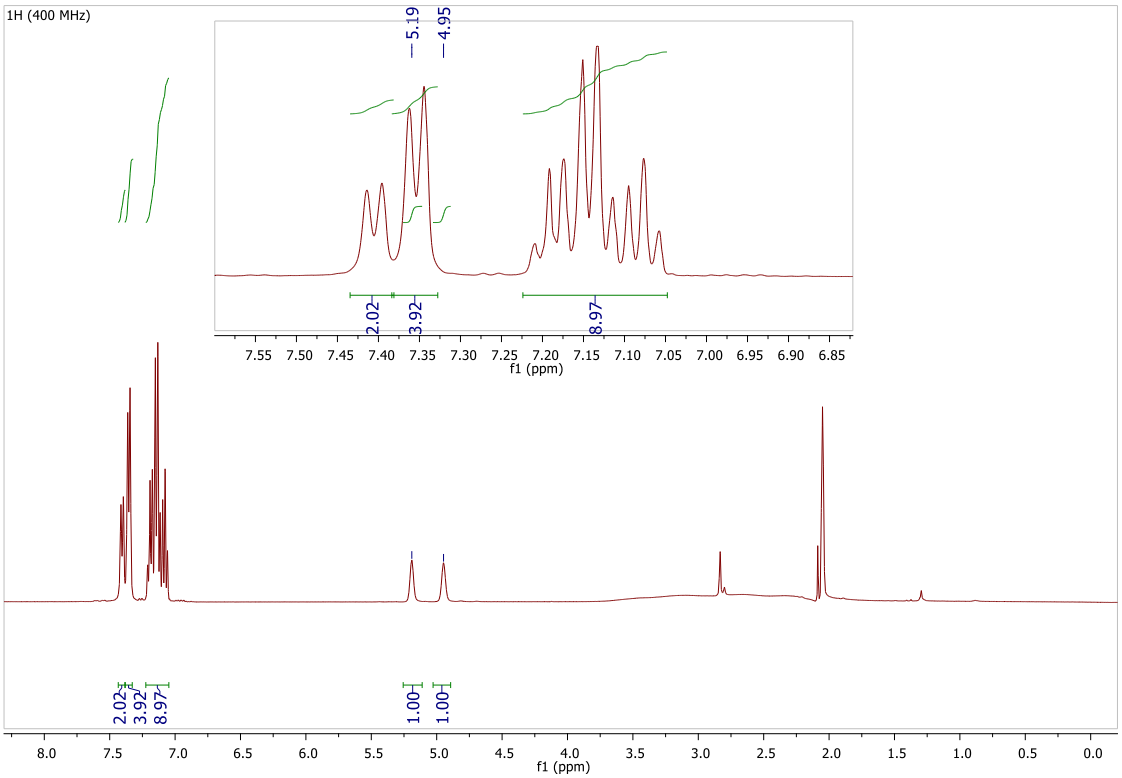
8,10,12-Ph_3-9-I-1,2-*closo*-$C_2B_{10}H_8$, 11

Elemental Analysis for $C_{20}B_{10}H_{23}I$: calc: C 48.21, H 4.61 ; found: C 47.40, H 4.68. IR (KBr): ν [cm^{-1}] =3053 (vs, $\nu s(C_{cluster}-H)$), 2594 (s, νs(B-H). ^1H NMR: δ [ppm]=7.41-7.34 (m, 6H, H_{phenyl}), 7.21-7.04 (m, 9H, H_{phenyl}), 5.19 (s, 1H, $C_{cluster}$-H), 4.95 (s, 1H, $C_{cluster}$-H), $^1H\{^{11}B\}$ NMR: δ [ppm]=7.41-7.34 (m, 6H, H_{phenyl}), 7.21-7.04 (m, 9H, H_{phenyl}), 5.19 (s, 1H, $C_{cluster}$-H), 4.95 (s, 1H, $C_{cluster}$-H), 2.97, (br, 2H, B-$H_{terminal}$), 2.86, (br, 2H, B-$H_{terminal}$), 2.58 (br, 2H, B-$H_{terminal}$). $^{13}C\{^1H\}$ NMR: δ [ppm]=135.2, 134.9, 128.4, 128.3 128.0, 127.7, (s C_{phenyl}), 51.9 (s, $C_{cluster}$), 50.9 (s, $C_{cluster}$). ^{11}B NMR: δ [ppm]=3.46 (s, 1B, B(9)), -1.4 (s, 2B, B(8,10)), -11.7 (s, 1B, B(12)), -16.5 (d, ^1J(B,H)=170 Hz, 4B, B(4,5,7,11)), -18.8 (d, ^1J(B,H)=194 Hz, 2B, B(3,6)). ESI MS: m/z (%)=496.589 (100) $[M-1]^-$.

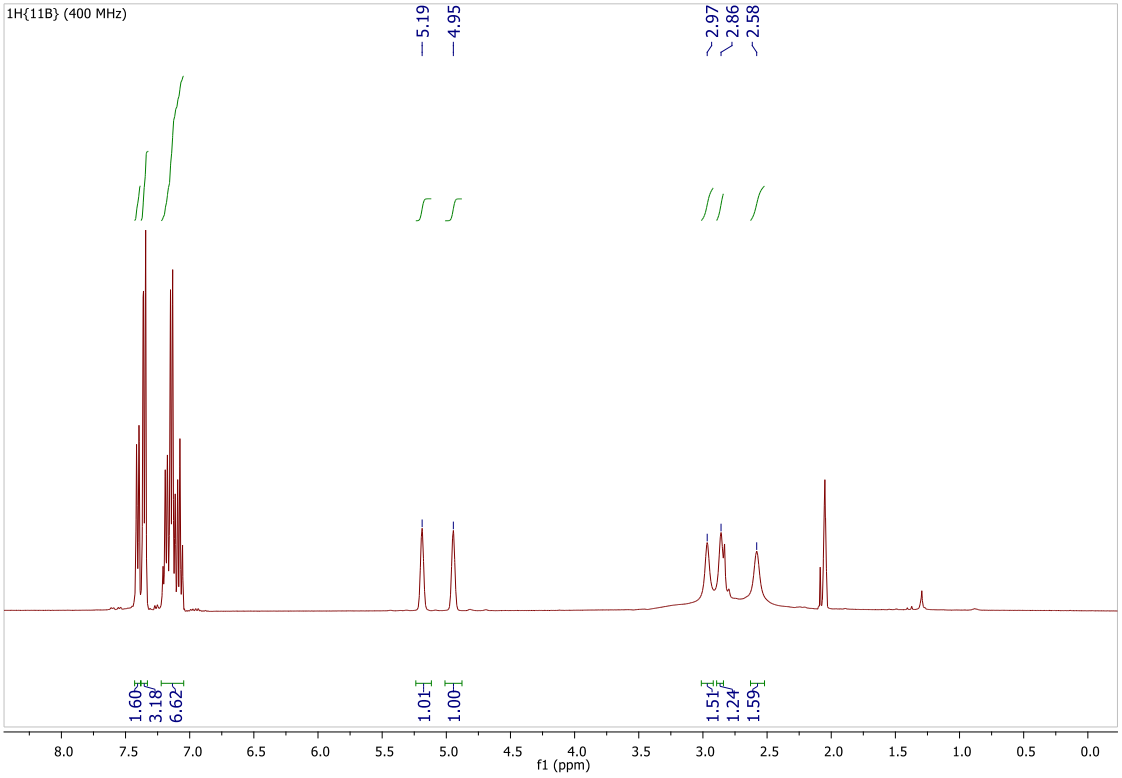
ATR-IR



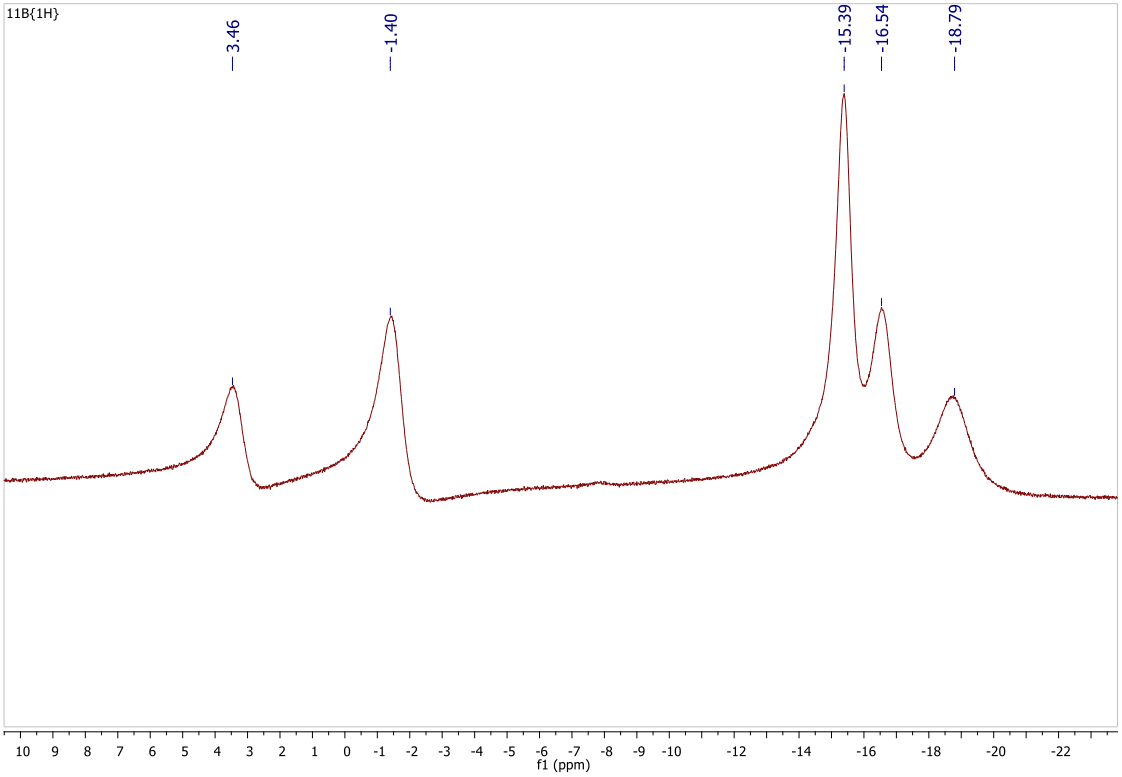
^{1}H NMR



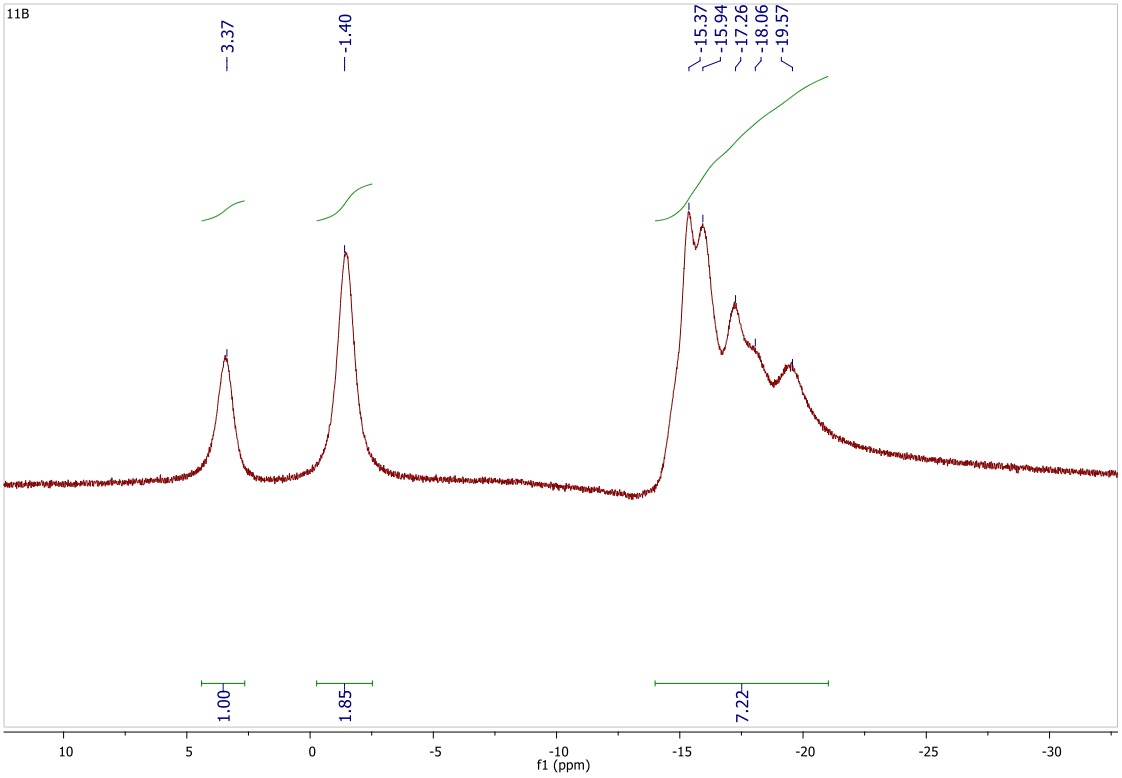
$^{1}H\{^{11}B\}$ NMR



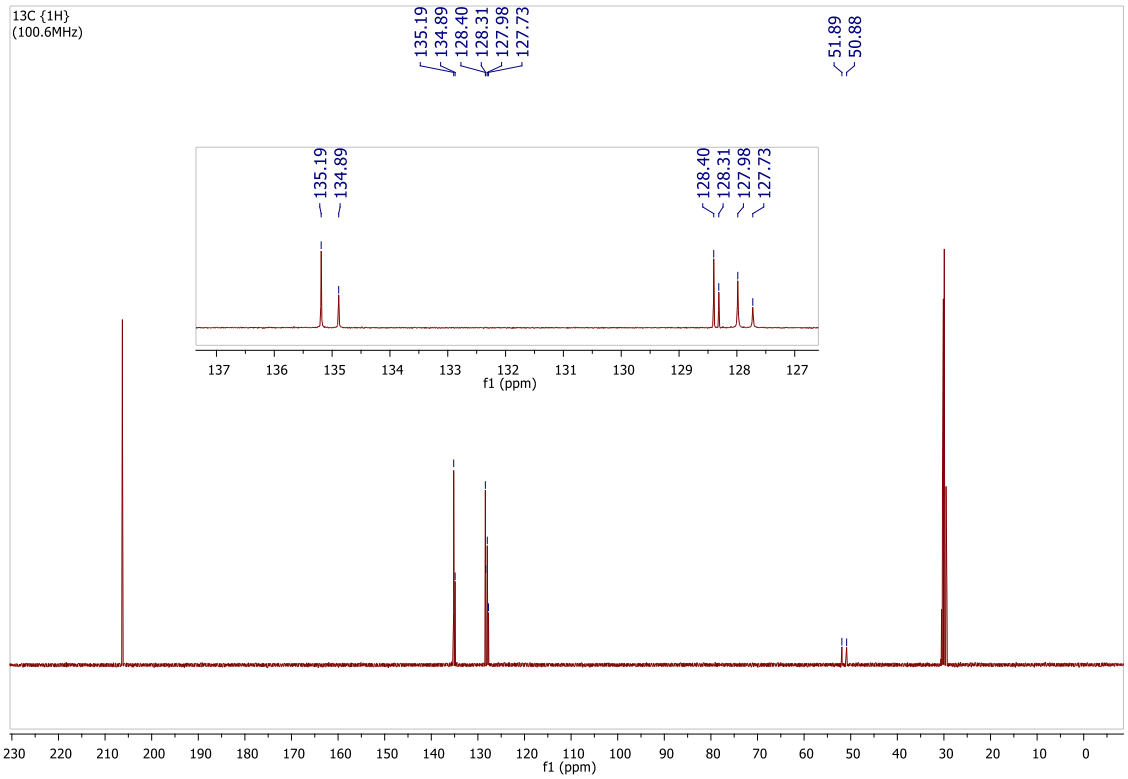
$^{1}H\{^{11}B\}$ NMR



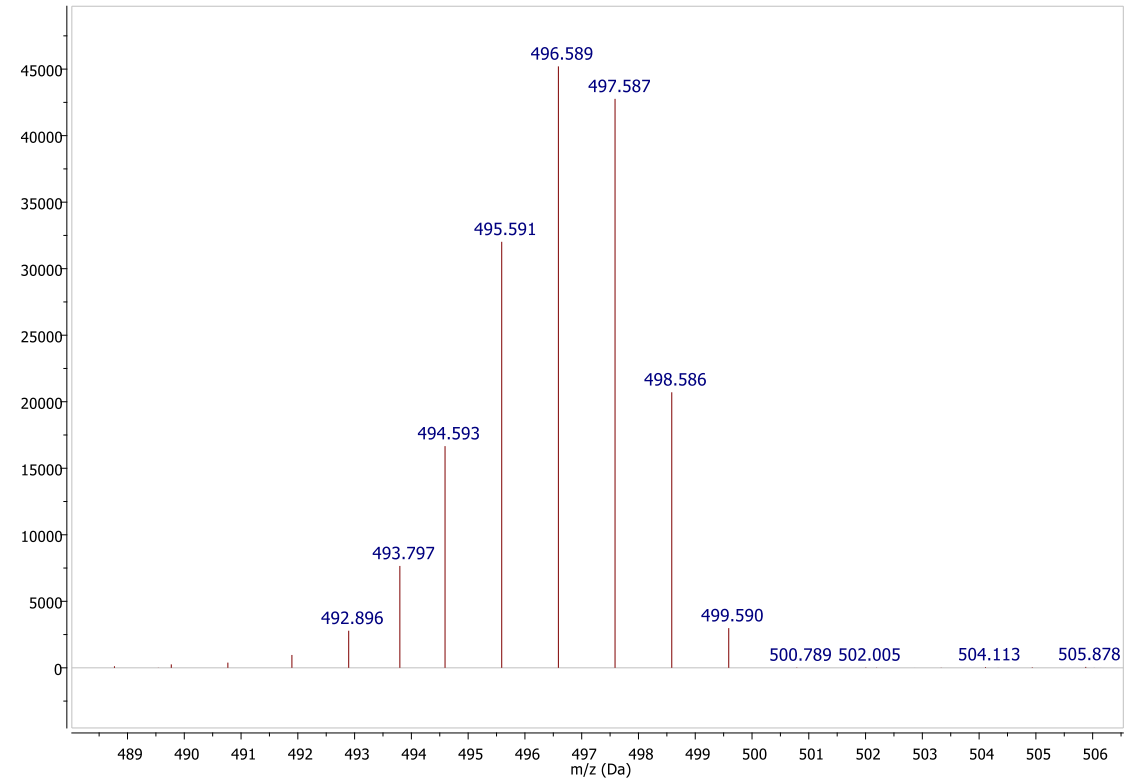
$^{11}B\{^{1}H\}$ NMR



$^{13}C\{^{11}B\}$ NMR

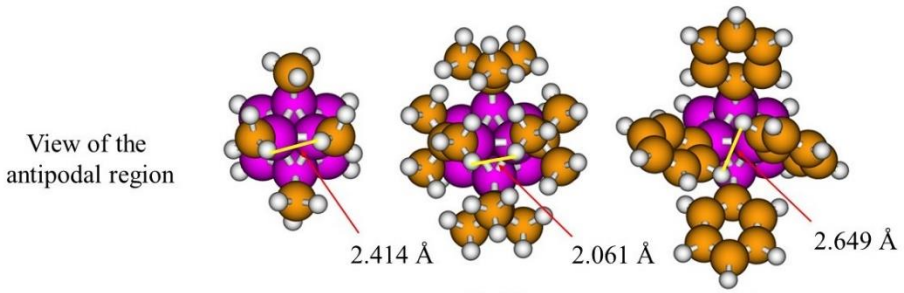


LDI-MS



Details of the DFT calculations

All calculations were carried out with the Gaussian 09 program package[10] at ωB97XD/6-31+G* level of theory as it was implemented in G09. Full geometry optimization calculations were performed and harmonic vibrational frequencies were calculated to establish the nature of the stationary points obtained, as characterized by none negative eigenvalue of the Hessian for minima structures. For the visualization of the molecules and orbitals the MOLDEN[11] and VMD program[12] were used.



	R=Me	R=^{t}Bu	R=Ph
B9-B12 distance	1.791	1.893	1.805
Angle between B9-B12-C_{subst}	122.8°	135.0°	125.8°
Shortest atomic distance between the substiutents	2.414	2.059	2.651

Figure S1. Optimized structures (at ωB97XD/6-31+G* level of theory) of different 8,9,10,12-tetrasubstituted-1,2-*closo*-carboranes (R=Me, tBu, Ph). According the structural parameters the phenyl derivative is not sterically crowded.

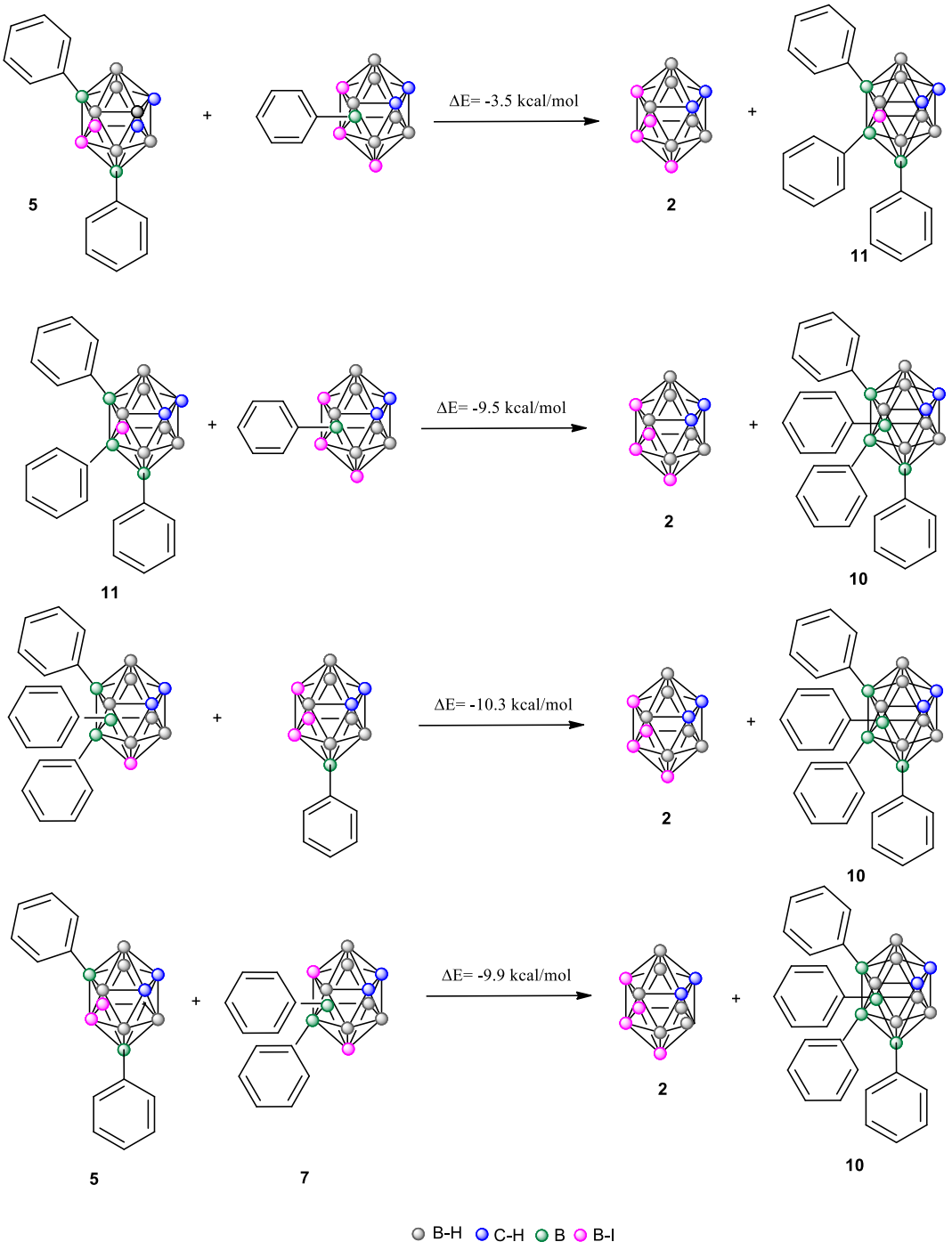


Figure S2. Different isodesmic reactions to estimate the steric repulsion between the substituents of **10**. The negative ΔE values indicate that there is no steric hindrance in the tetra- and threesubstituated products

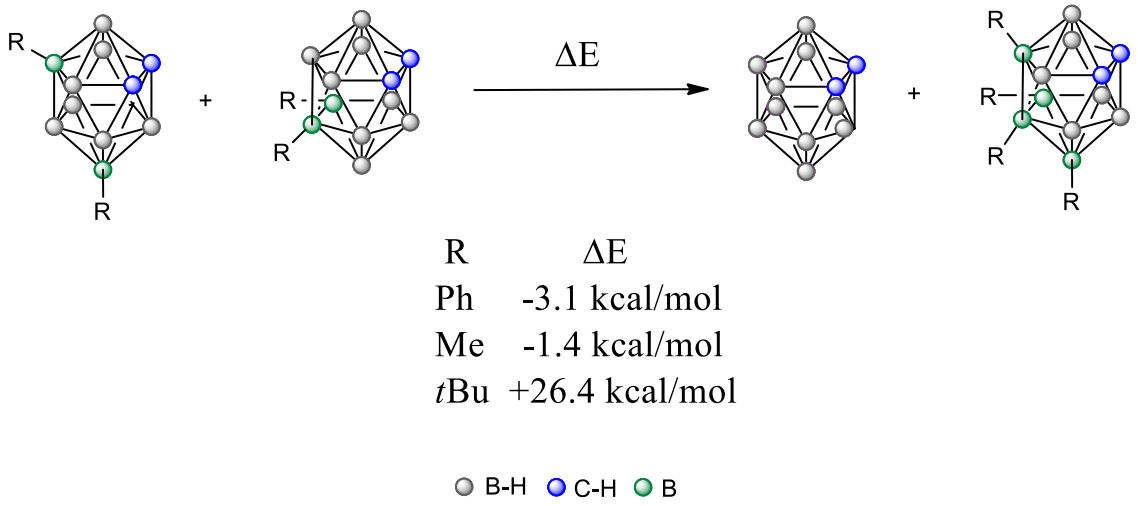


Figure S3. Isodesmic reaction at ωB97XD/6-31+G* level of theory to compare the destabilization effect of the different substituent in the 8,9,10,12-tetrasubstituted-1,2-*closo*-carboranes. Single point calculations at ω-B97XD-cc-pVTZ//ω-B97XD/6-31+G* level of theory give -2.9 kcal/mol isodesmic reaction energy in case of R=Ph, which verifies the accuracy of the 6-31+G* basis set.

The calculated Mulliken charges of boron atoms in the B-I vertices (the position of the B-I in brackets):

compound	**1**	**2**	**5**	**11**
Mulliken charge of the boron atoms in the B-I vertices	0.63 (8, 10)	0.66 (9, 12) 0.11 (8, 10)	0.31 (8, 10)	0.13

XYZ coordinates and total energies (in atomic unit) of the investigated systems

8,9,10,12-tetraiodo-1,2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -375.3438063

C	0.000818	0.803953	3.193500
B	1.454927	-0.003956	2.776206
B	0.890539	-1.440329	1.895633
C	0.000980	-0.811954	3.191717
B	-1.453224	-0.002841	2.776948
B	-0.889524	-1.439867	1.896571
B	-0.000027	-0.899828	0.449820
I	-0.000526	-2.124259	-1.331369
B	-0.889266	1.435489	1.899580
B	0.000474	0.898285	0.451765
I	-0.000083	2.127954	-1.325910
B	0.890719	1.435158	1.899486
B	1.459072	-0.001591	1.010495
I	3.363346	-0.000260	-0.013845
B	-1.458228	-0.001270	1.011370
I	-3.363588	-0.000003	-0.013109
H	-2.341085	-0.004802	3.556849
H	-1.478781	-2.456146	2.042187
H	0.000787	-1.298413	4.159471
H	-1.478148	2.451603	2.047987
H	0.001572	1.287789	4.162579
H	1.480393	2.450901	2.047219
H	2.343234	-0.004050	3.555655
H	1.478976	-2.457043	2.041706

8-Ph-9,10,12-I_3-1.2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -595.507192

C	-0.003275	-0.084997	0.147018
B	0.607162	-1.491636	-0.607692
B	2.333629	-1.468629	-0.194798
C	1.488975	-0.028550	-0.471334
B	1.158655	0.916313	0.919827
B	2.670203	0.008337	0.739581
B	2.485238	-1.554800	1.576938
I	4.270919	-2.461728	2.412029
B	0.021694	-0.090968	1.832296
B	0.822629	-1.632110	2.292212
C	0.420757	-2.349657	3.643723
B	-0.318076	-1.566304	0.909253
B	1.195555	-2.478785	0.733859
I	1.181187	-4.631955	0.444801
B	1.744560	-0.072249	2.261226
I	2.415441	0.918985	4.067467
H	1.062216	2.088428	0.799278
H	3.670720	0.611684	0.547568
H	1.611562	0.525711	-1.393838

H	-0.851476	0.471792	2.401124
H	-0.775160	0.441432	-0.400927
H	-1.417594	-2.005137	0.868783
H	0.183670	-1.798294	-1.668025
H	3.110395	-1.845930	-1.004723
C	1.038250	-3.532590	4.072472
C	0.681889	-4.142332	5.273208
C	-0.305315	-3.580489	6.078545
C	-0.934245	-2.405678	5.671558
C	-0.572794	-1.803039	4.469996
H	1.811872	-3.992175	3.466941
H	1.181318	-5.057453	5.578979
H	-0.582351	-4.052495	7.017218
H	-1.703931	-1.954731	6.291952
H	-1.074929	-0.883948	4.181330

9-Ph-8,10,12-I_3-1.2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -595.508682

C	0.077463	-0.131016	-0.024910
B	0.727154	-1.568988	-0.703128
B	2.416392	-1.539704	-0.173657
C	1.606579	-0.102753	-0.539463
B	1.188035	0.878723	0.800650
B	2.704448	-0.046657	0.748876
B	2.447864	-1.588532	1.602598
I	4.105922	-2.518929	2.641671
B	-0.019626	-0.097084	1.665606
B	0.751621	-1.619787	2.173425
I	0.090752	-2.593333	3.992735
B	-0.298380	-1.589999	0.739776
B	1.214397	-2.548845	0.691150
C	1.201334	-4.123018	0.565045
B	1.677836	-0.073668	2.203443
I	2.263611	0.976707	4.004259
H	1.113760	2.048184	0.643775
H	3.719958	0.546832	0.613093
H	1.798772	0.432086	-1.461460
H	-0.929830	0.460596	2.177902
H	-0.650590	0.387011	-0.637001
H	-1.401684	-2.011264	0.642542
H	0.369363	-1.889134	-1.783986
H	3.250031	-1.925132	-0.922496
C	2.328113	-4.822715	0.112174
C	2.311970	-6.208600	-0.025198
C	1.160552	-6.927203	0.289500
C	0.029937	-6.250896	0.742904
C	0.053953	-4.864828	0.877499
H	3.240518	-4.283273	-0.129154
H	3.200893	-6.726217	-0.374973
H	1.146152	-8.008849	0.186919

H	-0.871772	-6.801689	0.995850
H	-0.836216	-4.359063	1.242801

8,10-Ph$_2$-9,12-I$_2$-1,2-*closo*-C$_2$B$_{10}$H$_8$

E(ωB97XD/6-31+G*)= -815.673479

C	0.170086	-0.298128	0.057615
B	0.078852	-0.043674	4.261991
H	2.969015	0.067690	1.601193
C	1.561327	-0.100495	5.073463
C	2.796821	0.167446	4.076852
B	2.275011	0.432557	2.490194
B	1.325852	1.929604	2.588371
B	-0.041448	1.632941	3.691067
I	-1.988724	2.575020	3.504542
B	2.391874	1.395816	5.205195
B	0.626632	1.290691	5.299749
B	1.402799	2.545870	4.288324
B	2.822888	1.766796	3.528210
B	1.493716	-0.791576	3.503845
B	0.490649	0.323767	2.559984
C	-0.359929	-0.240455	1.353837
C	-1.661494	-0.722857	1.547914
C	-2.406742	-1.240861	0.491374
C	-1.860958	-1.288710	-0.789664
C	-0.568503	-0.814618	-1.004328
C	1.409262	4.069546	4.706585
C	2.349321	4.962988	4.175136
C	2.371977	6.302217	4.557212
C	1.449374	6.778113	5.486469
C	0.506506	5.906512	6.027418
C	0.490485	4.568761	5.639915
I	1.256561	3.280702	0.890095
H	3.106046	1.558125	6.134109
H	0.108616	1.455648	6.353087
H	1.731248	-0.799653	5.882848
H	3.874254	2.271319	3.315767
H	3.714239	-0.369807	4.283020
H	1.662362	-1.957731	3.399440
H	-0.796165	-0.748701	4.639180
H	1.172454	0.076139	-0.134436
H	-0.134492	-0.843353	-2.000023
H	-2.440617	-1.689961	-1.616495
H	-3.415068	-1.604282	0.669724
H	-2.110782	-0.687034	2.536963
H	-0.260729	3.908777	6.066272
H	-0.220172	6.267793	6.749918
H	1.462886	7.822854	5.784781
H	3.109245	6.973832	4.125956
H	3.072806	4.615637	3.442119

8,10-Ph_2-9,12-(allyl)$_2$-1,2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -1256.016381

C	0.783356	1.420733	-1.720111
C	0.106982	1.830401	-0.561922
C	-0.442406	3.120178	-0.564102
C	-0.349049	3.955348	-1.675151
C	0.312585	3.518224	-2.820083
C	0.883745	2.247600	-2.835663
B	0.023623	0.902218	0.723887
B	0.914052	1.409522	2.181132
B	1.457170	-0.029239	3.055222
B	0.857424	-1.443306	2.180404
C	-0.016938	-0.805310	3.477914
B	-1.456494	0.028178	3.055623
B	-0.913622	-1.410319	2.180813
B	-0.023576	-0.902415	0.723495
C	-0.107296	-1.830184	-0.562584
C	-0.784457	-1.420310	-1.720251
C	-0.885018	-2.246742	-2.836121
C	-0.313239	-3.517101	-2.821415
C	0.349158	-3.954445	-1.677012
C	0.442675	-3.119721	-0.565644
B	-1.466546	0.030591	1.283365
C	-2.847992	0.044525	0.511374
C	-3.447127	1.244414	0.107384
C	-4.653690	1.256155	-0.589547
C	-5.292264	0.057339	-0.897344
C	-4.713750	-1.148468	-0.505239
C	-3.506828	-1.149946	0.188377
B	-0.857061	1.442593	2.181161
C	0.017639	0.804074	3.478252
B	1.466713	-0.030997	1.283000
C	2.848070	-0.044673	0.510810
C	3.447615	-1.244508	0.107250
C	4.654223	-1.256119	-0.589597
C	5.292455	-0.057212	-0.897755
C	4.713512	1.148541	-0.506119
C	3.506552	1.149886	0.187438
H	-2.339306	0.047730	3.844206
H	-1.512862	-2.422407	2.340686
H	-0.025576	-1.290428	4.445804
H	-1.425189	2.470182	2.357355
H	0.026485	1.288873	4.446301
H	1.513317	2.421567	2.341211
H	2.340157	-0.049061	3.843596
H	1.425620	-2.470923	2.356223
H	2.961710	-2.190609	0.328164
H	5.092763	-2.202439	-0.894793
H	6.232960	-0.061760	-1.442152
H	5.198501	2.090729	-0.746980

H	3.058973	2.101868	0.461659
H	-2.960949	2.190446	0.328013
H	-5.091914	2.202492	-0.895139
H	-6.232725	0.062006	-1.441819
H	-5.199031	-2.090580	-0.745809
H	-3.059551	-2.101968	0.462932
H	-1.250049	-0.440219	-1.753036
H	-1.415937	-1.895986	-3.717019
H	-0.388687	-4.163342	-3.691882
H	0.792273	-4.946424	-1.646309
H	0.949849	-3.492461	0.321050
H	-0.949014	3.492727	0.322996
H	-0.791687	4.947523	-1.643796
H	0.387908	4.164865	-3.690266
H	1.414035	1.896964	-3.716984
H	1.248448	0.440440	-1.753581

9,12-Ph$_2$-8,10-I$_2$-1.2-*closo*-C$_2$B$_{10}$H$_8$

E(ωB97XD/6-31+G*)= -815.670946

C	0.024614	-0.193204	0.036810
B	-0.030344	-0.187836	1.721397
B	1.668619	-0.086106	2.225419
B	2.666250	0.024400	0.759359
B	2.530918	-1.548635	1.614345
B	1.306846	-2.516375	0.702883
B	-0.259227	-1.682320	0.796403
B	0.823372	-1.683312	2.228747
B	1.102773	0.863282	0.851769
C	1.543159	-0.070223	-0.507470
B	2.432966	-1.462820	-0.176150
B	0.734115	-1.573845	-0.672669
H	0.954337	2.028534	0.716482
I	1.421588	-4.669776	0.397081
H	3.641075	0.680895	0.608077
I	2.169514	1.043691	4.018949
H	1.682903	0.480026	-1.429735
H	-0.953517	0.338847	2.245132
H	-0.740964	0.296542	-0.552189
H	-1.334461	-2.171936	0.705244
H	0.379805	-1.903586	-1.751502
C	0.402191	-2.419275	3.567154
H	3.244850	-1.804411	-0.968685
C	3.793205	-2.210414	2.306546
C	-0.579828	-1.874003	4.407342
C	-0.949797	-2.497544	5.596664
C	-0.339653	-3.690946	5.976808
C	0.639919	-4.249591	5.159058
C	1.003841	-3.619097	3.972004
H	-1.063530	-0.938237	4.140207

H	-1.709984	-2.046107	6.228324
H	-0.622343	-4.179550	6.905326
H	1.128484	-5.176870	5.445749
H	1.780441	-4.068633	3.362239
C	3.937462	-2.247408	3.700561
C	5.041700	-2.847001	4.300724
C	6.034337	-3.430012	3.516421
C	5.911429	-3.408104	2.128831
C	4.803692	-2.805717	1.537036
H	3.172170	-1.814701	4.336237
H	5.121373	-2.861796	5.384314
H	6.894930	-3.901640	3.983049
H	6.674044	-3.865723	1.504593
H	4.727065	-2.812643	0.453037

8,9,10,12-Ph_4-1,2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -1256.0163811

C	0.783356	1.420733	-1.720111
C	0.106982	1.830401	-0.561922
C	-0.442406	3.120178	-0.564102
C	-0.349049	3.955348	-1.675151
C	0.312585	3.518224	-2.820083
C	0.883745	2.247600	-2.835663
B	0.023623	0.902218	0.723887
B	0.914052	1.409522	2.181132
B	1.457170	-0.029239	3.055222
B	0.857424	-1.443306	2.180404
C	-0.016938	-0.805310	3.477914
B	-1.456494	0.028178	3.055623
B	-0.913622	-1.410319	2.180813
B	-0.023576	-0.902415	0.723495
C	-0.107296	-1.830184	-0.562584
C	-0.784457	-1.420310	-1.720251
C	-0.885018	-2.246742	-2.836121
C	-0.313239	-3.517101	-2.821415
C	0.349158	-3.954445	-1.677012
C	0.442675	-3.119721	-0.565644
B	-1.466546	0.030591	1.283365
C	-2.847992	0.044525	0.511374
C	-3.447127	1.244414	0.107384
C	-4.653690	1.256155	-0.589547
C	-5.292264	0.057339	-0.897344
C	-4.713750	-1.148468	-0.505239
C	-3.506828	-1.149946	0.188377
B	-0.857061	1.442593	2.181161
C	0.017639	0.804074	3.478252
B	1.466713	-0.030997	1.283000
C	2.848070	-0.044673	0.510810
C	3.447615	-1.244508	0.107250
C	4.654223	-1.256119	-0.589597

C	5.292455	-0.057212	-0.897755
C	4.713512	1.148541	-0.506119
C	3.506552	1.149886	0.187438
H	-2.339306	0.047730	3.844206
H	-1.512862	-2.422407	2.340686
H	-0.025576	-1.290428	4.445804
H	-1.425189	2.470182	2.357355
H	0.026485	1.288873	4.446301
H	1.513317	2.421567	2.341211
H	2.340157	-0.049061	3.843596
H	1.425620	-2.470923	2.356223
H	2.961710	-2.190609	0.328164
H	5.092763	-2.202439	-0.894793
H	6.232960	-0.061760	-1.442152
H	5.198501	2.090729	-0.746980
H	3.058973	2.101868	0.461659
H	-2.960949	2.190446	0.328013
H	-5.091914	2.202492	-0.895139
H	-6.232725	0.062006	-1.441819
H	-5.199031	-2.090580	-0.745809
H	-3.059551	-2.101968	0.462932
H	-1.250049	-0.440219	-1.753036
H	-1.415937	-1.895986	-3.717019
H	-0.388687	-4.163342	-3.691882
H	0.792273	-4.946424	-1.646309
H	0.949849	-3.492461	0.321050
H	-0.949014	3.492727	0.322996
H	-0.791687	4.947523	-1.643796
H	0.387908	4.164865	-3.690266
H	1.414035	1.896964	-3.716984
H	1.248448	0.440440	-1.753581

8,10,12-Ph_3-9-I-1.2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -1035.836307

C	3.427380	0.993765	0.635465
C	2.819232	-0.253706	0.436990
C	3.483534	-1.181491	-0.376315
C	4.708233	-0.880486	-0.968028
C	5.296607	0.364746	-0.756515
C	4.651697	1.302756	0.047911
B	1.422760	-0.594277	1.094953
B	0.793955	-2.264633	1.200614
B	1.353948	-1.431864	2.656260
B	0.829981	0.255804	2.547642
B	-0.015061	0.510083	0.998094
B	-1.519467	-0.513946	1.032732
C	-2.871461	-0.110865	0.320990
C	-3.571314	-1.023962	-0.479856
C	-4.762539	-0.672084	-1.109458

C	-5.283251	0.610689	-0.949848
C	-4.602601	1.534714	-0.159811
C	-3.411551	1.174178	0.466399
B	-0.941578	0.297994	2.510783
B	-1.557982	-1.354583	2.595271
B	-0.983414	-2.217572	1.165664
B	-0.045847	-1.086050	0.173389
I	-0.045906	-1.434823	-1.981868
C	-0.102151	-0.882127	3.377306
C	-0.125475	-2.301608	2.619135
C	0.082973	1.941247	0.322585
H	-1.576912	-3.179650	0.807625
H	2.213522	-1.826631	3.367363
H	1.424525	1.065254	3.179287
H	-0.127411	-0.910754	4.459598
H	1.351555	-3.256399	0.866682
H	-0.162326	-3.187170	3.241429
H	-2.464901	-1.701531	3.271598
H	-1.527707	1.122810	3.130254
H	-3.174833	-2.025284	-0.628391
H	-5.281494	-1.398385	-1.729183
H	-6.211056	0.889460	-1.442060
H	-4.996523	2.539586	-0.033287
H	-2.890265	1.913837	1.067816
H	2.928583	1.746349	1.241260
H	5.098384	2.279635	0.212325
H	6.249849	0.604360	-1.219932
H	5.199282	-1.616418	-1.599013
H	3.033863	-2.153310	-0.564206
C	0.662977	2.130258	-0.938884
C	0.778414	3.398432	-1.503322
C	0.319026	4.517877	-0.813342
C	-0.248291	4.357268	0.449226
C	-0.357348	3.085162	1.005513
H	1.048527	1.278408	-1.488880
H	1.235399	3.510235	-2.482756
H	0.408531	5.507678	-1.252870
H	-0.603296	5.222304	1.003383
H	-0.793281	2.987865	1.997089

9,10,12-Ph_3-8-I-1.2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -1035.836540

C	-0.474184	-3.127935	0.799097
C	-0.134201	-1.766678	0.824633
C	0.090550	-1.183390	2.078859
C	-0.043717	-1.917518	3.255388
C	-0.399698	-3.263222	3.206320
C	-0.609484	-3.870214	1.969640
B	0.021858	-0.953009	-0.527254
B	-0.662642	-1.603332	-2.043911

B	-1.071918	-0.263114	-3.120162
C	0.410301	-1.121130	-3.255492
B	1.806115	-0.289088	-2.713999
B	1.091355	-1.627050	-1.793055
B	1.550007	-0.116946	-0.976105
I	3.305821	-0.043953	0.306612
B	1.151998	1.224782	-2.063504
B	0.053552	0.850840	-0.696103
C	-0.109519	1.902227	0.481715
C	0.809265	2.950552	0.636350
C	0.678431	3.891557	1.655424
C	-0.384521	3.804931	2.551581
C	-1.307467	2.768986	2.420645
C	-1.167995	1.831427	1.400045
C	0.441629	0.485015	-3.407255
B	-0.601675	1.238884	-2.311882
B	-1.333532	-0.093205	-1.376908
C	-2.819937	-0.018935	-0.837874
H	2.796440	-0.368748	-3.356048
H	1.676884	-2.657362	-1.761067
H	0.535038	-1.694620	-4.165591
H	1.783160	2.212198	-2.242301
H	0.590793	0.875896	-4.406141
H	-1.124801	2.247965	-2.651058
H	-1.841320	-0.333594	-4.016734
H	-1.251529	-2.622302	-2.195531
H	1.653501	3.035070	-0.043019
H	1.411393	4.688218	1.750749
H	-0.490482	4.537042	3.347729
H	-2.137466	2.685043	3.117118
H	-1.892023	1.025696	1.330905
H	0.380546	-0.140307	2.146768
H	0.134833	-1.434277	4.212136
H	-0.504674	-3.836033	4.123782
H	-0.873528	-4.923116	1.914421
H	-0.634745	-3.625826	-0.154573
C	-3.414157	-1.111686	-0.192161
C	-4.714289	-1.039558	0.305285
C	-5.452466	0.133650	0.165048
C	-4.881549	1.230655	-0.478208
C	-3.582135	1.150171	-0.971823
H	-2.851307	-2.031232	-0.057131
H	-5.147353	-1.900603	0.807183
H	-6.463813	0.194861	0.557874
H	-5.444511	2.153561	-0.589045
H	-3.148309	2.024744	-1.449773

8,10-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$

E(ωB97XD/6-31+G*)=-794.024031

C	0.001554	0.008931	-0.000649

C	-0.000620	-0.002380	1.400695
C	1.241014	-0.008062	2.050560
C	2.435789	-0.003889	1.334459
C	2.414679	0.006966	-0.058606
C	1.191480	0.013970	-0.725504
B	-1.347782	-0.022292	2.232432
B	-1.470986	0.522674	3.936738
B	-1.605511	-1.202132	3.550259
C	-3.274720	-1.490283	3.554289
C	-4.025898	-0.658421	2.393435
B	-2.500467	-1.353169	2.026473
B	-2.944194	0.278350	1.490332
B	-2.297276	1.440458	2.661476
B	-4.015421	1.003850	2.707405
B	-4.256816	-0.160931	4.021834
B	-2.677978	-0.474859	4.766300
B	-3.111998	1.176353	4.237497
C	-3.403231	2.341982	5.267903
C	-4.129024	3.480298	4.892466
C	-4.378703	4.512326	5.794382
C	-3.901085	4.428142	7.100476
C	-3.171031	3.308281	7.493195
C	-2.926493	2.281294	6.584151
H	-0.529768	0.948328	4.528379
H	-1.954402	2.526921	2.319265
H	-0.879215	-2.090618	3.853655
H	-5.300880	-0.395500	4.528812
H	-4.953980	1.640253	2.355660
H	-4.878558	-1.140373	1.931349
H	-2.666511	-0.884393	5.880707
H	-3.679365	-2.468617	3.782493
H	-2.481770	-2.308400	1.326680
H	-3.180532	0.438898	0.337958
H	1.276889	-0.013373	3.137286
H	3.384075	-0.008911	1.865331
H	3.344347	0.009981	-0.621167
H	1.162774	0.022885	-1.811900
H	-0.942683	0.015706	-0.540451
H	-4.502725	3.567859	3.874864
H	-4.943202	5.384580	5.475563
H	-4.094225	5.231344	7.806397
H	-2.788196	3.235435	8.507717
H	-2.348055	1.418473	6.906686

9,12-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$

E(ωB97XD/6-31+G*)= -794.027523

C	-0.012345	-0.018235	-0.005325
C	-0.008340	-0.002987	1.395688
C	1.235195	0.023607	2.040871

C	2.428139	0.027119	1.321046
C	2.400701	0.007328	-0.071768
C	1.174676	-0.014834	-0.733629
B	-1.358649	0.038916	2.219244
B	-1.422415	-0.400375	3.946787
B	-2.649395	0.608246	4.738205
C	-2.993341	-0.980879	4.179835
B	-2.221208	-1.435308	2.740047
B	-3.960890	-1.083335	2.768193
C	-4.098997	0.174201	3.932199
B	-3.384413	1.651287	3.504109
B	-4.186761	0.613910	2.301841
B	-2.950412	-0.383651	1.511672
B	-2.588226	1.318059	1.940889
B	-1.647564	1.292750	3.466501
C	-2.394266	2.422209	0.824393
C	-1.245968	3.224187	0.787855
C	-1.053750	4.169514	-0.216566
C	-2.011375	4.332373	-1.215627
C	-3.158945	3.542471	-1.201240
C	-3.342186	2.599341	-0.192176
H	-0.835492	2.119386	3.736840
H	-3.080232	-0.740993	0.384141
H	-4.814095	-1.904627	2.743491
H	-1.883755	-2.566160	2.616764
H	-3.220758	-1.703680	4.953329
H	-5.244830	0.928523	1.864441
H	-4.983389	0.132230	4.555529
H	-3.908989	2.653421	3.862507
H	-2.705293	0.804214	5.905065
H	-0.555783	-0.846694	4.624694
H	-4.240356	1.985612	-0.203804
H	-3.910050	3.656275	-1.978625
H	-1.861459	5.066624	-2.002656
H	-0.150411	4.773504	-0.222716
H	-0.479220	3.098007	1.548056
H	-0.959390	-0.016390	-0.539022
H	1.140789	-0.021069	-1.819757
H	3.328131	0.014138	-0.638196
H	3.378358	0.050581	1.848273
H	1.277543	0.048949	3.127642

8,10-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$

E(ωB97XD/6-31+G*)= -410.669328

C	0.007006	0.011864	0.016449
B	0.010598	0.013247	1.709150
B	1.738515	0.003858	2.171009
B	0.805466	1.536190	2.132047
B	1.180053	2.439054	0.627168
B	-0.327642	1.488085	0.774182

B	0.615512	1.436564	-0.725170
B	2.333062	1.424111	-0.289127
B	2.450406	1.496663	1.474677
B	2.671306	-0.050707	0.645883
C	1.507789	-0.024215	-0.583291
B	1.169052	-0.977076	0.805000
H	3.367206	2.043150	2.004989
H	0.529915	2.111276	3.138898
C	2.259908	-0.677140	3.516881
C	1.180090	4.032251	0.531297
H	0.194442	1.720756	-1.796077
H	3.112047	1.800069	-1.103487
H	1.641817	-0.577442	-1.504485
H	-1.436835	1.909349	0.714405
H	-0.747470	-0.520078	-0.549610
H	-0.873546	-0.546635	2.271439
H	1.081999	-2.149974	0.657902
H	3.675311	-0.655950	0.453531
H	2.568827	0.082868	4.242577
H	1.482956	-1.286582	3.992490
H	3.123810	-1.327047	3.336389
H	1.560451	4.477281	1.457013
H	1.813406	4.391000	-0.288146
H	0.172239	4.430487	0.367203

9,12-Me$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$

E(ωB97XD/6-31+G*)= -410.670549

C	0.014420	0.028568	0.033296
B	0.013830	0.032711	1.728009
B	1.730220	0.029144	2.165580
B	0.809690	1.566259	2.174842
B	1.193237	2.421953	0.645607
B	-0.317321	1.507296	0.792634
B	0.628003	1.451364	-0.708948
B	2.346486	1.434006	-0.266065
B	2.478335	1.521981	1.511961
B	2.679022	-0.038845	0.669899
C	1.515995	-0.012463	-0.563240
B	1.171932	-0.964366	0.825245
C	3.698212	2.255666	2.232716
C	0.453760	2.344431	3.522001
H	2.116269	-0.484534	3.168594
H	1.193554	3.610721	0.569325
H	0.209523	1.734289	-1.780756
H	3.135159	1.802290	-1.074584
H	1.651149	-0.566958	-1.483390
H	-1.427539	1.926267	0.735822
H	-0.741010	-0.501111	-0.533447
H	-0.878908	-0.517379	2.286370

H	1.081765	-2.136469	0.676940
H	3.683705	-0.642378	0.475734
H	-0.587882	2.186145	3.824239
H	1.089642	2.014317	4.351363
H	0.600863	3.424553	3.407414
H	3.361748	3.154585	2.762075
H	4.179316	1.604306	2.971263
H	4.468116	2.566937	1.517327

8,9,10,12-Me_4-1,2-*closo*-$C_2B_{10}H_8$

E(ωB97XD/6-31+G*)= -489.301917

C	0.003061	0.003919	-0.004280
B	-0.000504	-0.000544	1.591586
B	1.517331	0.000111	2.520362
C	1.141548	0.824635	3.949001
B	1.257798	-0.886451	4.029240
B	0.488218	-1.454305	2.537562
C	0.925629	-2.824100	1.844831
B	0.476866	1.437588	2.519843
B	-1.228032	0.914422	2.538449
B	-1.220888	-0.885375	2.558642
B	-0.431232	-1.410118	4.064190
B	-1.473053	0.025553	4.064302
C	0.039158	0.026348	4.822528
B	-0.448820	1.469530	4.028060
C	-2.387441	1.760287	1.839737
C	-2.395491	-1.741637	1.899669
H	0.136987	0.098144	5.898430
H	-0.713320	-2.341798	4.746720
H	2.627228	0.079188	2.101568
H	2.121907	-1.349533	4.695911
H	-0.617473	2.433549	4.697248
H	-2.444987	0.051436	4.748583
H	0.894047	2.470082	2.103310
H	1.892408	1.369222	4.507502
H	-0.395390	-0.932170	-0.412908
H	-0.611543	0.818069	-0.406198
H	1.014675	0.129135	-0.407731
H	-3.370857	-1.258637	2.031282
H	-2.242971	-1.875654	0.822336
H	-2.465632	-2.741408	2.344001
H	0.134797	-3.579160	1.921714
H	1.132639	-2.679709	0.778314
H	1.828744	-3.249374	2.297393
H	-2.866347	1.182611	1.040654
H	-3.172507	2.048183	2.548310
H	-2.000445	2.680757	1.387526

8,10-*t*Bu$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$

E(ωB97XD/6-31+G*)= -646.492531

C	0.013194	0.018845	0.024688
B	0.014503	0.021130	1.715558
B	1.744917	0.008973	2.187441
B	0.808223	1.542162	2.139984
B	1.184828	2.453618	0.637420
B	-0.322622	1.492580	0.782632
B	0.620248	1.446033	-0.714562
B	2.335827	1.428172	-0.279517
B	2.454231	1.502306	1.482347
B	2.672964	-0.043254	0.653448
C	1.509246	-0.017399	-0.573018
B	1.173736	-0.969701	0.817102
H	3.379415	2.043327	2.001285
H	0.518547	2.112572	3.144318
C	2.272255	-0.696567	3.550059
C	1.179648	4.071942	0.526402
H	0.199078	1.728580	-1.786008
H	3.119743	1.787078	-1.095046
H	1.645070	-0.570273	-1.494143
H	-1.436747	1.897407	0.725437
H	-0.742589	-0.512489	-0.540170
H	-0.880226	-0.531552	2.265489
H	1.085871	-2.142471	0.668430
H	3.676262	-0.641892	0.445003
C	2.708767	0.361742	4.577963
C	1.160379	-1.552074	4.182640
C	3.476819	-1.608379	3.256922
C	1.712422	4.708606	1.821754
C	2.068801	4.537860	-0.640062
C	-0.247854	4.593847	0.285263
H	3.817759	-2.099274	4.178693
H	3.226575	-2.395371	2.534401
H	4.322276	-1.040783	2.850808
H	1.528025	-2.043620	5.093738
H	0.292556	-0.942839	4.461214
H	0.810801	-2.336654	3.499820
H	3.063891	-0.125944	5.496301
H	3.523782	0.985597	4.194703
H	1.881094	1.025558	4.851159
H	-0.243692	5.688350	0.190787
H	-0.682736	4.182639	-0.634412
H	-0.916889	4.334700	1.114196
H	2.046340	5.633006	-0.723903
H	3.113150	4.237313	-0.495498
H	1.733230	4.124259	-1.599407

H	1.704824	5.804031	1.736434
H	1.098849	4.436970	2.687828
H	2.741664	4.397261	2.031668

9,12-*t*Bu$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$

E(ωB97XD/6-31+G*)= -646.485343

C	0.028438	0.184372	0.043871
B	0.021576	0.129109	1.730455
B	1.729003	0.087925	2.194263
B	0.825275	1.642350	2.266560
B	1.254813	2.534536	0.754420
B	-0.273162	1.641908	0.852105
B	0.670852	1.619953	-0.640903
B	2.376288	1.547988	-0.195004
B	2.536083	1.588965	1.592469
B	2.676837	0.044502	0.697315
C	1.526001	0.132245	-0.542220
B	1.161079	-0.855638	0.811837
C	3.918839	2.207726	2.208514
C	0.263867	2.348169	3.630648
H	2.090809	-0.498303	3.164713
H	1.266014	3.722471	0.683337
H	0.265411	1.952976	-1.703109
H	3.160174	1.916806	-1.004695
H	1.662210	-0.391061	-1.480263
H	-1.372767	2.087478	0.797122
H	-0.738572	-0.309840	-0.539023
H	-0.884040	-0.436238	2.246565
H	1.050246	-2.021036	0.629802
H	3.667327	-0.577048	0.489259
C	-1.138506	1.810349	3.988086
C	1.153076	2.066560	4.853817
C	0.123472	3.869768	3.438052
C	3.748636	3.648637	2.719046
C	4.452096	1.319435	3.348182
C	5.021964	2.263337	1.129892
H	0.692882	2.486798	5.758627
H	1.281156	0.989835	5.015848
H	2.146862	2.507901	4.761602
H	-1.530041	2.347468	4.862552
H	-1.856308	1.943777	3.170979
H	-1.112932	0.745202	4.243359
H	-0.251396	4.336387	4.359539
H	1.071684	4.350520	3.181751
H	-0.587933	4.103345	2.636235
H	4.718616	4.050483	3.042693
H	3.361483	4.308181	1.933444
H	3.070334	3.715521	3.571286
H	5.379007	1.743509	3.758527
H	3.738536	1.217084	4.170545

H	4.681916	0.308956	2.988101
H	5.962206	2.611627	1.578396
H	5.214772	1.282666	0.680639
H	4.767495	2.959286	0.322871

8,9,10,12-*t*Bu$_4$-1.2-*closo*-C$_2$B$_{10}$H$_8$

E(ωB97XD/6-31+G*)= -960.895637

C	-0.025476	2.125790	-1.223810
B	-0.007221	0.946318	-0.043293
B	0.007215	-0.946334	-0.043295
C	0.025472	-2.125821	-1.223787
B	0.864341	1.426754	1.457216
B	-0.893606	1.405676	1.461704
B	-1.438373	-0.017587	2.337007
C	0.008622	-0.802684	2.759318
B	-0.864338	-1.426733	1.457235
B	0.893607	-1.405660	1.461714
B	1.502787	0.011665	0.551488
C	3.072764	0.020619	0.028984
B	-1.502785	-0.011651	0.551491
C	-3.072763	-0.020605	0.028983
C	-0.008619	0.802716	2.759306
B	1.438353	0.017610	2.337003
H	0.014579	-1.295260	3.723267
H	1.488960	-2.406880	1.673916
H	1.431234	2.446763	1.663684
H	2.319815	0.028369	3.128432
H	-2.319800	-0.028317	3.128475
H	-1.431232	-2.446739	1.663721
H	-1.488959	2.406901	1.673877
H	-0.014576	1.295294	3.723253
C	-0.160113	1.609015	-2.664022
C	-1.181098	3.126723	-1.001532
C	1.244018	3.004050	-1.210778
C	-1.243999	-3.004112	-1.210713
C	0.160075	-1.609081	-2.664015
C	1.181117	-3.126727	-1.001496
C	3.873743	-1.154290	0.637424
C	3.236486	-0.072143	-1.498293
C	3.805205	1.292964	0.514696
C	-3.236481	0.072171	-1.498294
C	-3.805215	-1.292941	0.514701
C	-3.873731	1.154313	0.637419
H	4.855726	1.257102	0.195981
H	3.373437	2.214703	0.122275
H	3.800010	1.368565	1.608275
H	4.285485	0.103799	-1.773408
H	2.970714	-1.062034	-1.875861
H	2.629155	0.657270	-2.037998
H	4.909194	-1.118349	0.272619

H	3.911479	-1.098781	1.731273
H	3.467352	-2.133141	0.373482
H	1.182310	-3.866343	-1.812951
H	2.160952	-2.649067	-0.998362
H	1.071934	-3.677284	-0.062105
H	0.198043	-2.460930	-3.357068
H	-0.690311	-0.992380	-2.958899
H	1.069529	-1.026799	-2.816719
H	-1.137440	-3.800370	-1.959810
H	-1.406911	-3.490614	-0.244574
H	-2.143810	-2.445492	-1.468224
H	1.137481	3.800280	-1.959910
H	1.406942	3.490592	-0.244661
H	2.143817	2.445399	-1.468262
H	-0.198000	2.460845	-3.357103
H	0.690223	0.992227	-2.958877
H	-1.069617	1.026808	-2.816716
H	-1.182291	3.866315	-1.813010
H	-2.160945	2.649084	-0.998366
H	-1.071888	3.677308	-0.062162
H	-4.285481	-0.103760	-1.773414
H	-2.970698	1.062062	-1.875856
H	-2.629156	-0.657244	-2.038005
H	-4.909185	1.118372	0.272621
H	-3.911461	1.098825	1.731269
H	-3.467336	2.133156	0.373453
H	-4.855732	-1.257079	0.195971
H	-3.373445	-2.214684	0.122298
H	-3.800038	-1.368531	1.608282

Table S1 Bond lengths of the B9-B12 and C1-C2 bonds in case of 9,12-(aryl)$_2$-1,2-*closo*-$C_2B_{10}B_{10}$ and some related compounds

Substituents at the 9,12 vertexes of *o*-carborane	d(B9-B12), in Å	Substituents at the 1,2 vertexes of *o*-carborane	d(C1-C2), in Å	Database Identifier
H	1.776[13]	H	1.630[13]	TOKGIJ
C_6H_5-	1.809[2]	H	1.621[2]	TAHBAG
4-CH_3O-C_6H_4-	1.812[2]	H	1.612[2]	TAHBEK
4-Cl-C_6H_4-	1.806/1.814[2]	H	1.609/1.613[2]	TAHBIO
4-OH-C_6H_4-	1.824[2]	H	1.625[2]	TAHBOU
4-F-C_6H_4-	1.807/1.803/1.800/1.781[14]	H	1.620[14]	XEHVUB
2,5-F_2-C_6H_3-	1.803[14]	H	1.628[14]	XEHWAI
4-$COOCH_3$-C_6H_4-	1.808[15]	H	1.637[15]	HIMHEQ
-$C_6H_4CH(OCH_3)_2$ compound **2**	1.804/1.803[16]	H	1.624/1.629[16]	
4-CHO-C_6H_4- compound **3**	1.798[16]	H	1.630[16]	
H	1.760/1.757[17]	1,2-$(C_6H_5)_2$-	1.720/1.733[17]	
H	1.775[18]	3-C_6H_5-1,2-$(C_6H_5)_2$-	1.763[18*]	XILFOP
H	1.774[18]	3-C_6H_5-1,2-$(C_6H_5)_2$-	1.632[18*]	XILFUV
H	1.775[18]	3,6-$(C_6H_5)_2$-1,2-$(C_6H_5)_2$-	1.704[18]	XILGAC
Substituents at the 8,9,10,12 vertexes of *o*-carborane				
$(C_6H_5)_4$ Compound **10**	1.822[16]	H	1.623[16]	
$(C_6H_5)_3I$ Compound **11**	1.824[16]	H	1.629[16]	
4,5,7,8,9,10,11,12-octamethyl-*o*-carborane	1.788[19]	H	1.635[19]	FASPIY

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