

Supplementary information

Synthesis and structure of 3-aryldiazo derivatives of *ortho*-carborane

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Materials and Instruments.

3-Diazonium derivative of *ortho*-carborane [3-N₂-*o*-C₂B₁₀H₁₁][BF₄] [1] and Grignard reagents 4-BrMgC₆H₄NMe₂ [2] and 2-BrMgC₆H₄Me [3] were prepared according to the literature procedures. 4-Methoxyphenylmagnesium bromide (1.0 M in THF) and cesium fluoride were purchased from Sigma-Aldrich and P&M Invest, respectively. Tetrahydrofuran and diethyl ether were dried as described in the literature [4]. Analytical TLC was performed using silica gel on aluminum plates Merck F254 and visualized with 0.5 % PdCl₂ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (¹H), 128.4 MHz (¹¹B) and 100.0 MHz (¹³C) were recorded with Bruker Avance-400 and Varian Inova-400 spectrometers. Chemical shifts for ¹H and ¹³C NMR spectra were referenced to Me₄Si as an internal standard. Chemical shifts values for ¹¹B NMR spectra were referenced relative to external BF₃·Et₂O. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. Adsorption spectra were registered using spectrophotometer SF-2000 (LOMO, Russia). High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a negative ion mode, mass range from *m/z* 50 to *m/z* 3000.

3-(4'-N,N-dimethylaminophenyldiazo)-1,2-dicarba-*closo*-dodecarborane 3-(4'-Me₂N-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (1)

130 mg (0.5 mmol) [3-N₂-*o*-C₂B₁₀H₁₁][BF₄] was placed in a 25 mL two-neck flask under argon atmosphere, cooled to –78 °C and THF (10 mL) was added. Then a 0.5 M solution of *p*-Me₂NC₆H₄MgBr in THF (3 mL, 1.5 mmol) was added dropwise to the flask. The reaction

mixture immediately darkened, and cooling bath was removed. The reaction was stirred overnight, then water (20 mL) was added. The product was extracted with diethyl ether (3×20 mL). The organic fractions were separated, combined, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was washed with hot hexane (3×10 mL), the filtrate was evaporated and subjected to column chromatography on silica (eluent diethyl ether—petroleum ether, 2 : 1 (v/v)). The first, second and third fractions were collected and concentrated on a rotary evaporator to obtain compounds **1** (78 mg, 54%), **1a** (24 mg, 21%) and **1b** (29 mg, 20%), respectively.

Compound 1. ¹H NMR (CDCl₃, ppm): 7.74 (2H, d, *J* = 9.1 Hz, C₆H₄), 6.70 (2H, d, *J* = 9.1 Hz, C₆H₄), 3.82 (2H, br.s, CH_{carb.}), 3.10 (6H, s, N(CH₃)₂). ¹¹B NMR (CDCl₃, ppm): -2.6 (1B, s), -3.2 (2B, d, *J* = 152 Hz), -9.8 (1B, d, *J* = 158 Hz), -13.6 (6B, d, *J* = 156 Hz). IR (CHCl₃, cm⁻¹): 3060 (C_{carb}-H), 3043 (C_{aryl}-H), 2952-2808 (C_{Me}-H), 2640, 2590 (B-H), 1603 ((C=C)_{aryl}). UV (CHCl₃, nm): 461.

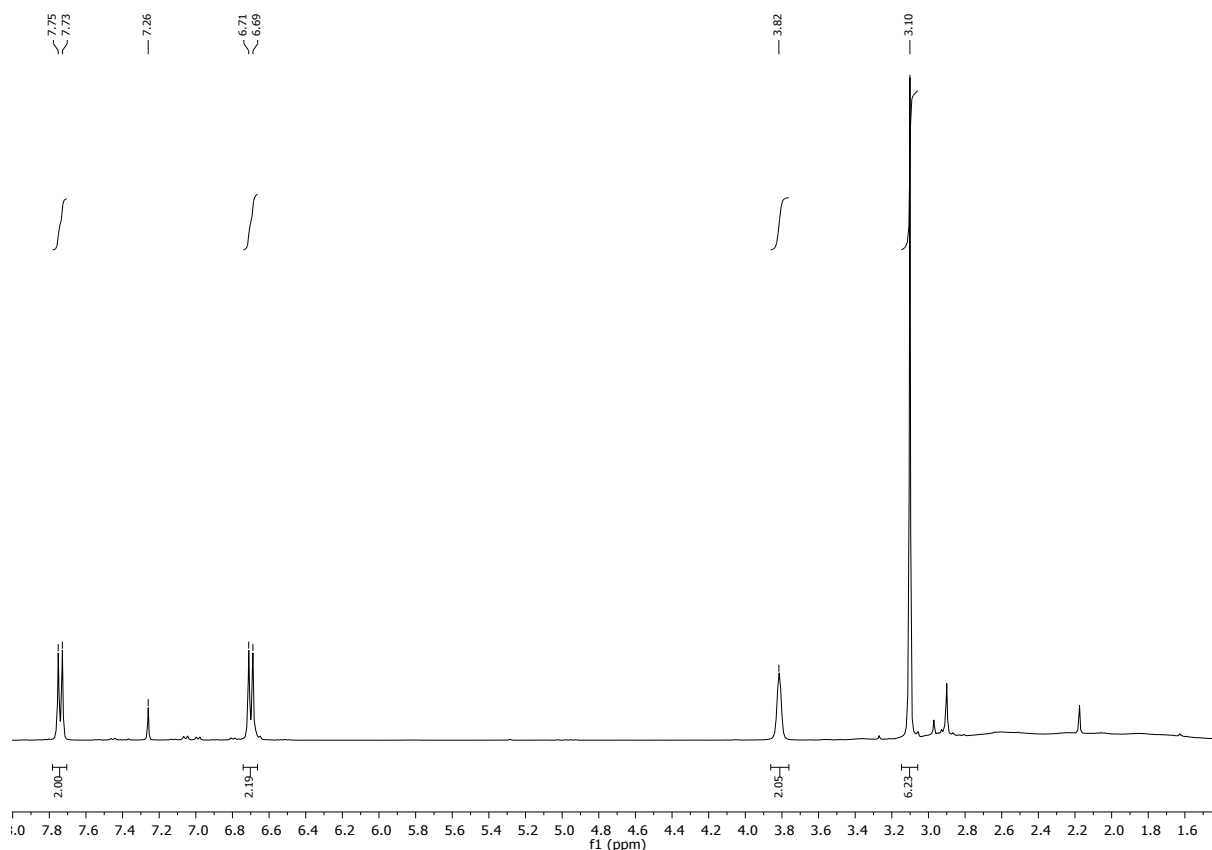


Fig. S1. ¹H NMR spectrum of 3-(4'-Me₂N-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**1**).

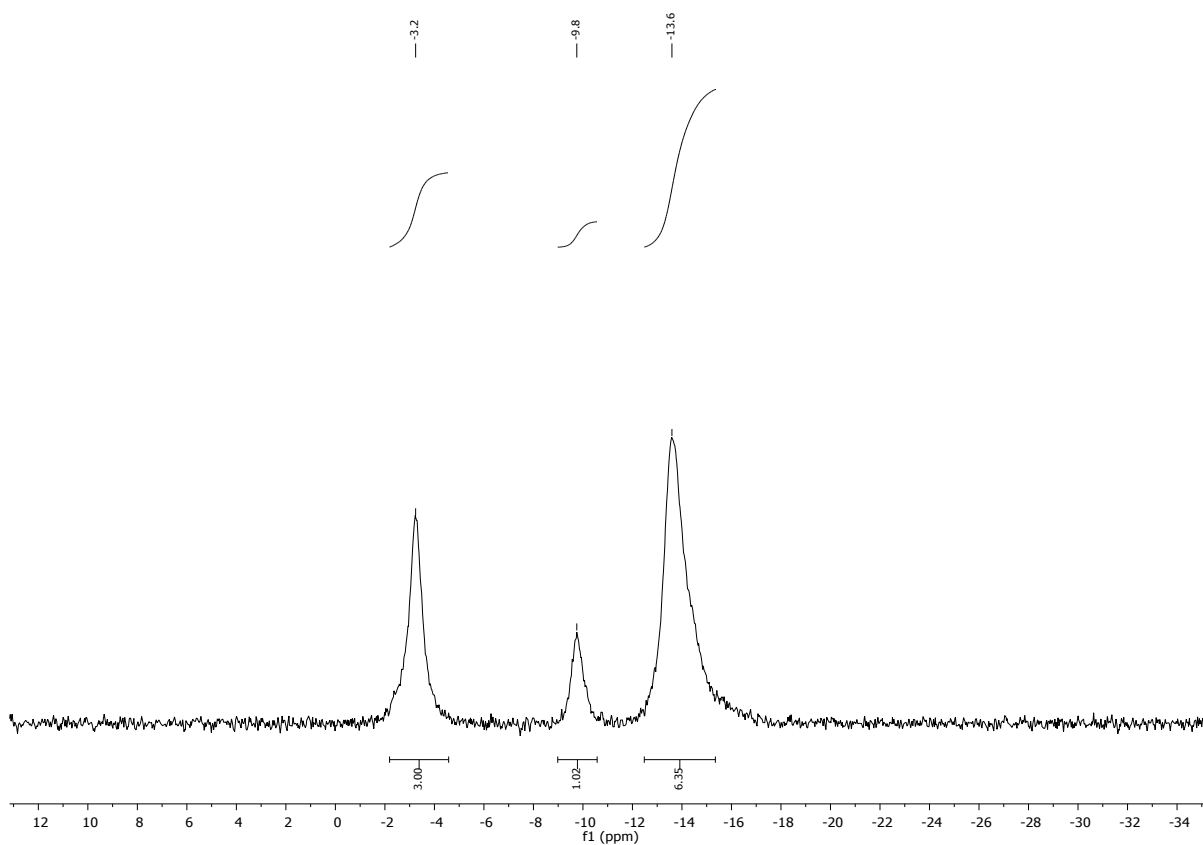


Fig. S2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 3-(4'-Me₂N-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**1**).

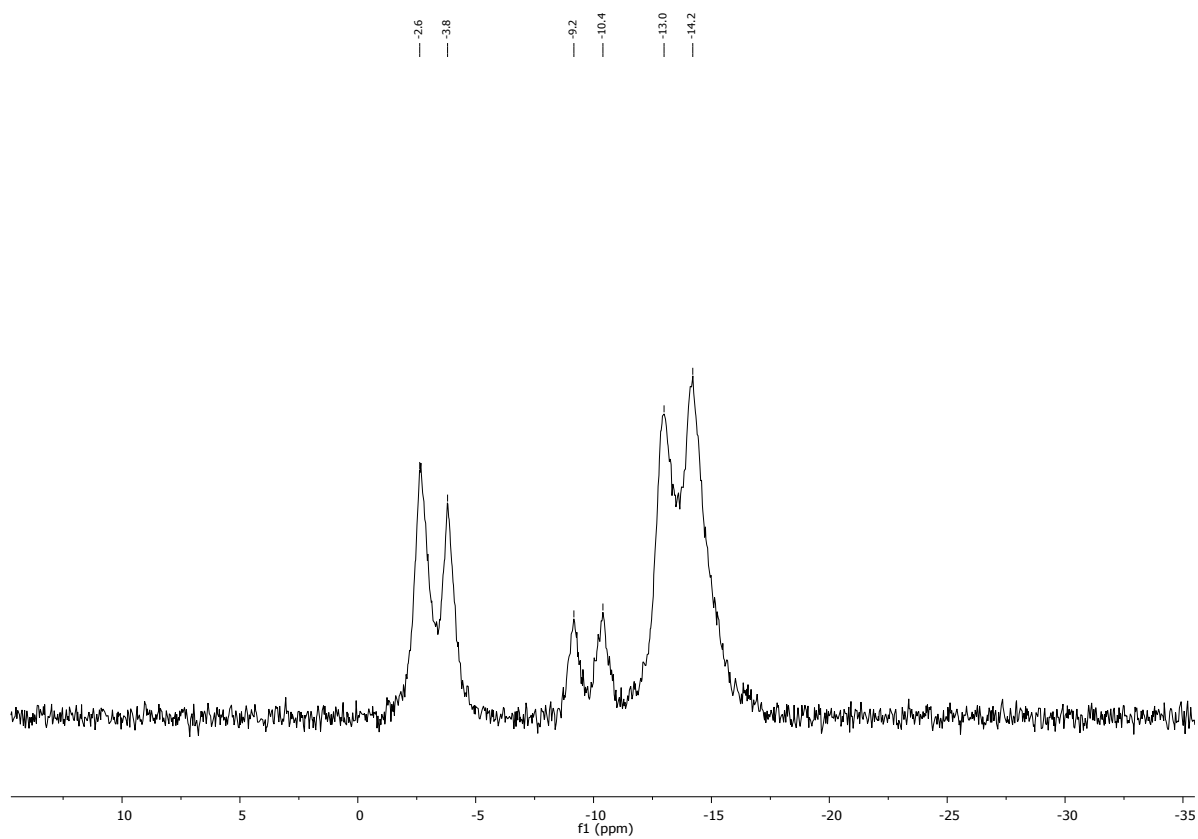


Fig. S3. ^{11}B NMR spectrum of 3-(4'-Me₂N-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**1**).

Compound 1a (3-bromo-1,2-dicarbha-*closo*-dodecarborane 3-Br-1,2-C₂B₁₀H₁₁).

The spectral data correspond to those described in the literature [5,6]. ¹H NMR (CDCl₃, ppm): 3.85 (2H, br.s, CH_{carb}). ¹¹B NMR (CDCl₃, ppm): -2.1 (2B, d, *J* = 154 Hz), -8.3 (1B, d, *J* = 153 Hz), -11.9 (2B, d, *J* = 175 Hz), -12.4 (1B, s), -13.4 (4B, d, *J* = 180 Hz).

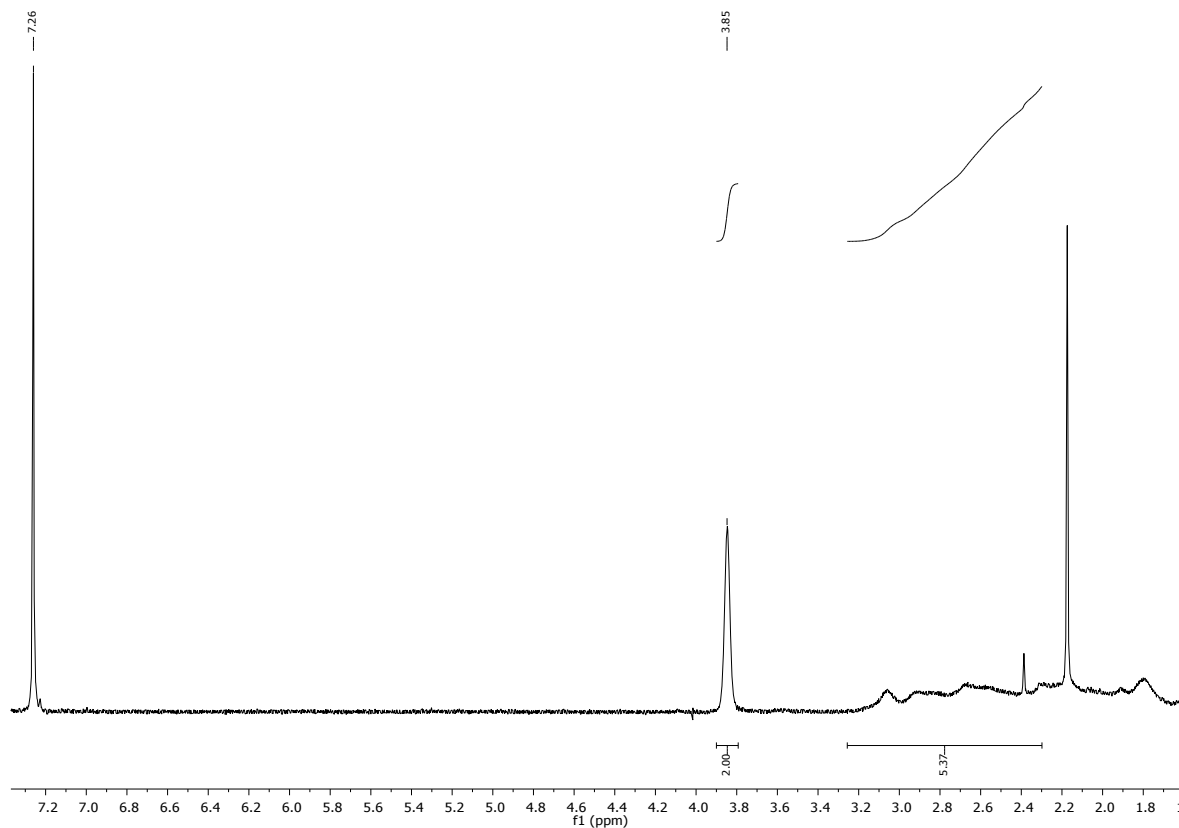


Fig. S4. ¹H NMR spectrum of 3-Br-1,2-C₂B₁₀H₁₁ (**1a**).

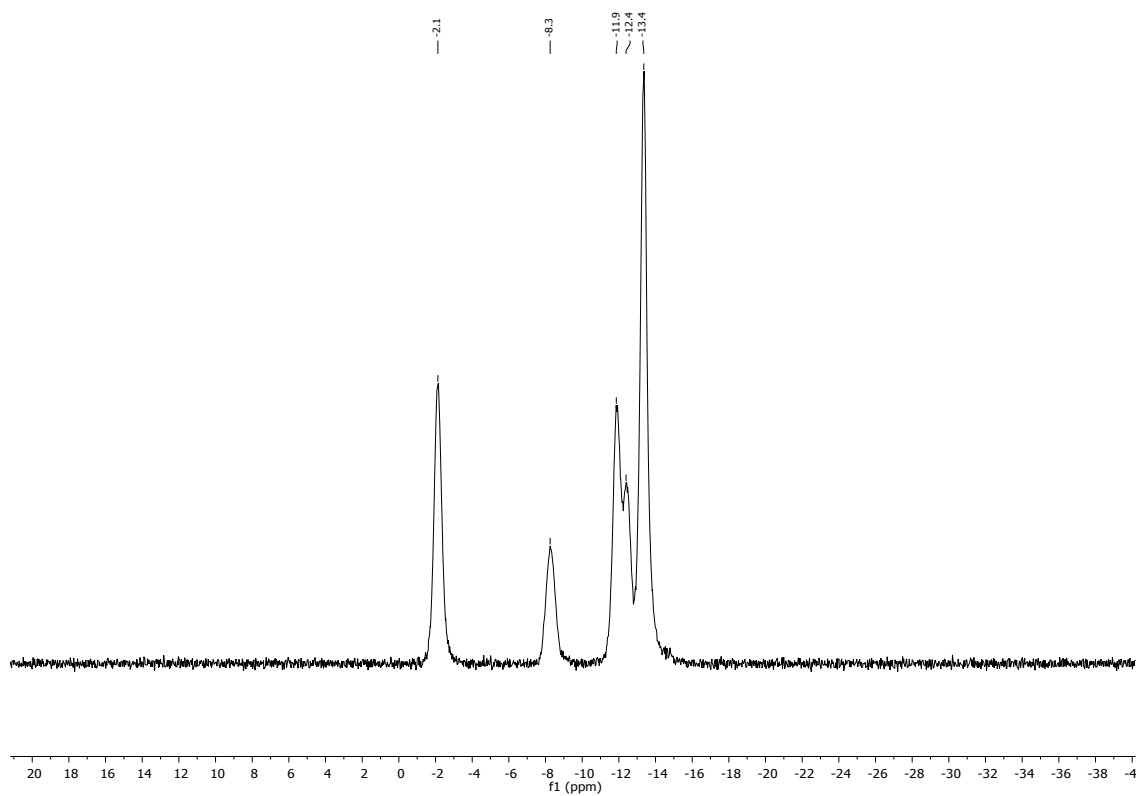


Fig. S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**1a**).

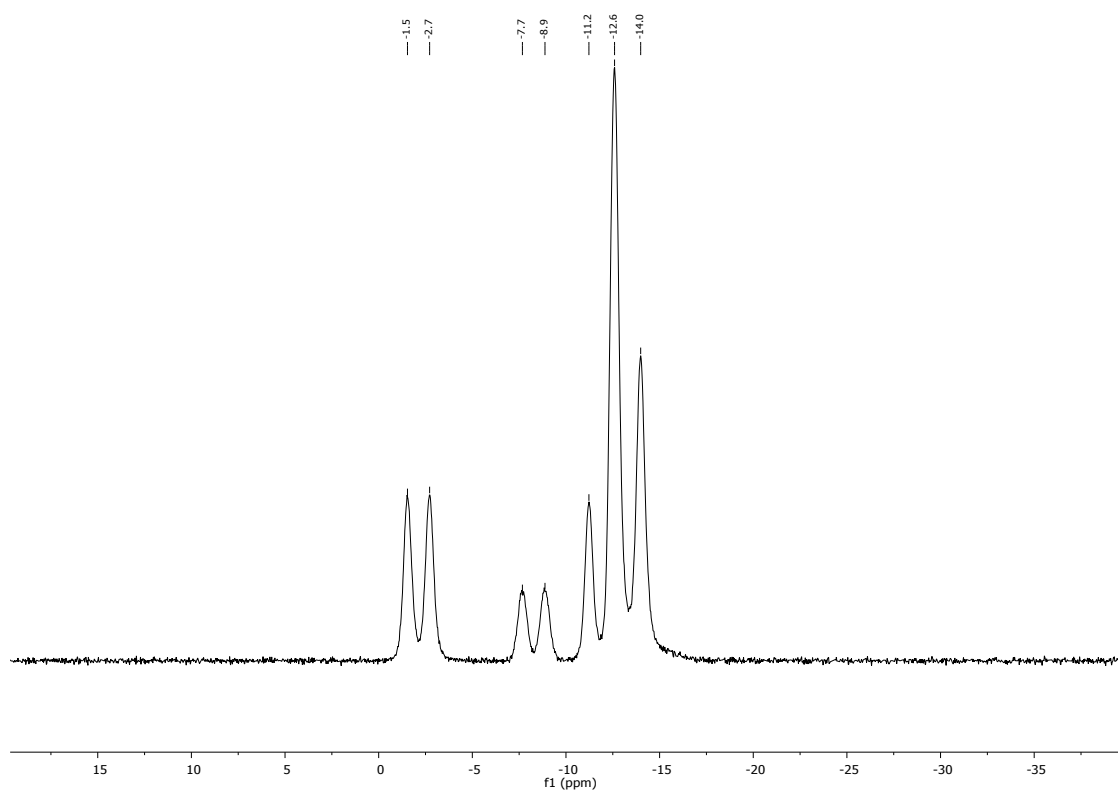


Fig. S6. ^{11}B NMR spectrum of 3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**1a**).

Compound 1b (3-(4'-bromobutoxy)-1,2-dicarba-closo-dodecarborane 3-Br(CH₂)₄O-1,2-C₂B₁₀H₁₁). ¹H NMR (CDCl₃, ppm): 3.93 (2H, t, *J* = 6.1 Hz, OCH₂), 3.57 (2H, br.s, C_H_{carb}), 3.45 (2H, t, CH₂ *J* = 6.7 Hz, CH₂Br), 1.96 (2H, m, CH₂CHBr), 1.79 (2H, m, OCH₂CH₂). ¹¹B NMR (CDCl₃, ppm): 1.0 (1B, s), -5.3 (2B, d, *J* = 146 Hz), -12.9 (1B, d, *J* = 147 Hz), -14.7 (3B, d, *J* = 158 Hz), -15.8 (2B, d, *J* = 160 Hz), -19.7 (1B, d, *J* = 144 Hz). ¹³C{¹H} NMR (CDCl₃, ppm): 69.1 (OCH₂), 55.8 (C_{carb}), 33.4 (CH₂Br), 29.6 (OCH₂CH₂), 29.2 (CH₂CH₂Br).

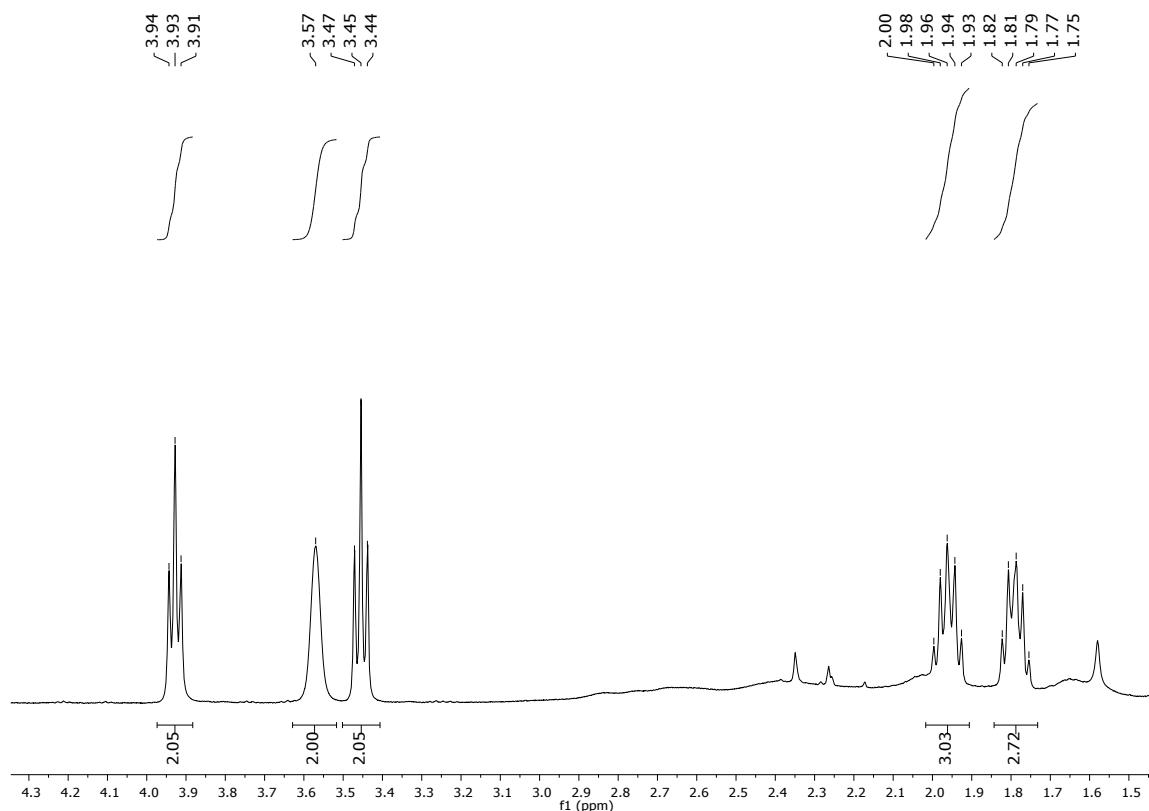


Fig. 7S. ¹H NMR spectrum of 3-Br(CH₂)₄O-1,2-C₂B₁₀H₁₁ (**1b**).

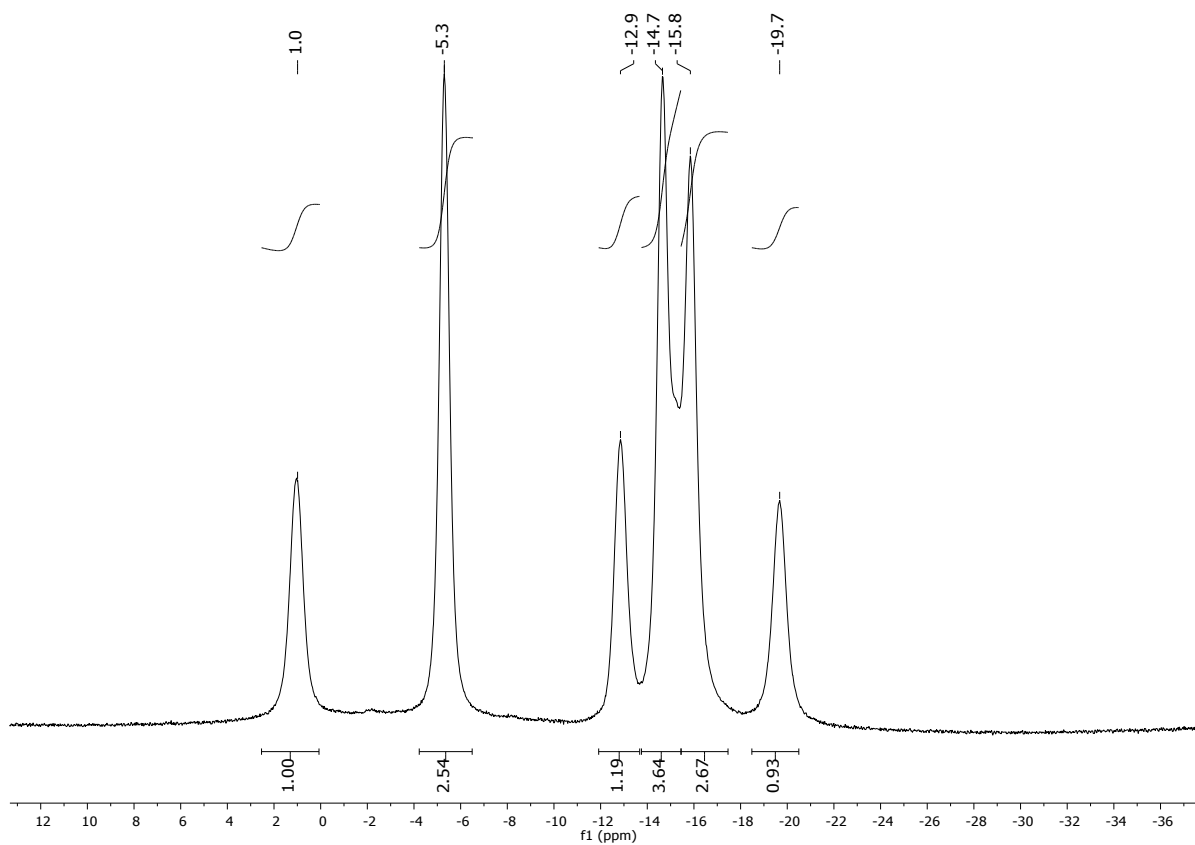


Fig. 8S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 3-Br(CH₂)₄O-1,2-C₂B₁₀H₁₁ (**1b**).

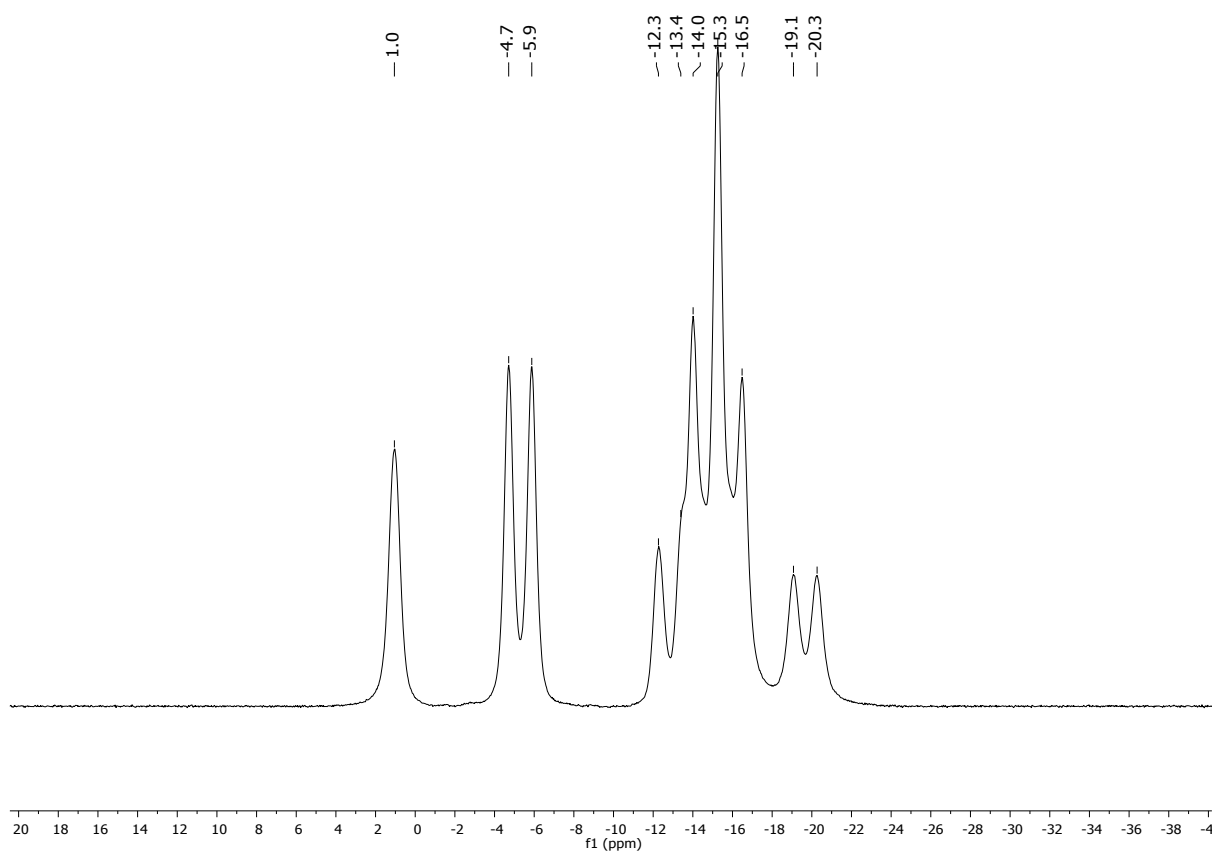


Fig. 9S. ^{11}B NMR spectrum of 3-Br(CH₂)₄O-1,2-C₂B₁₀H₁₁ (**1b**).

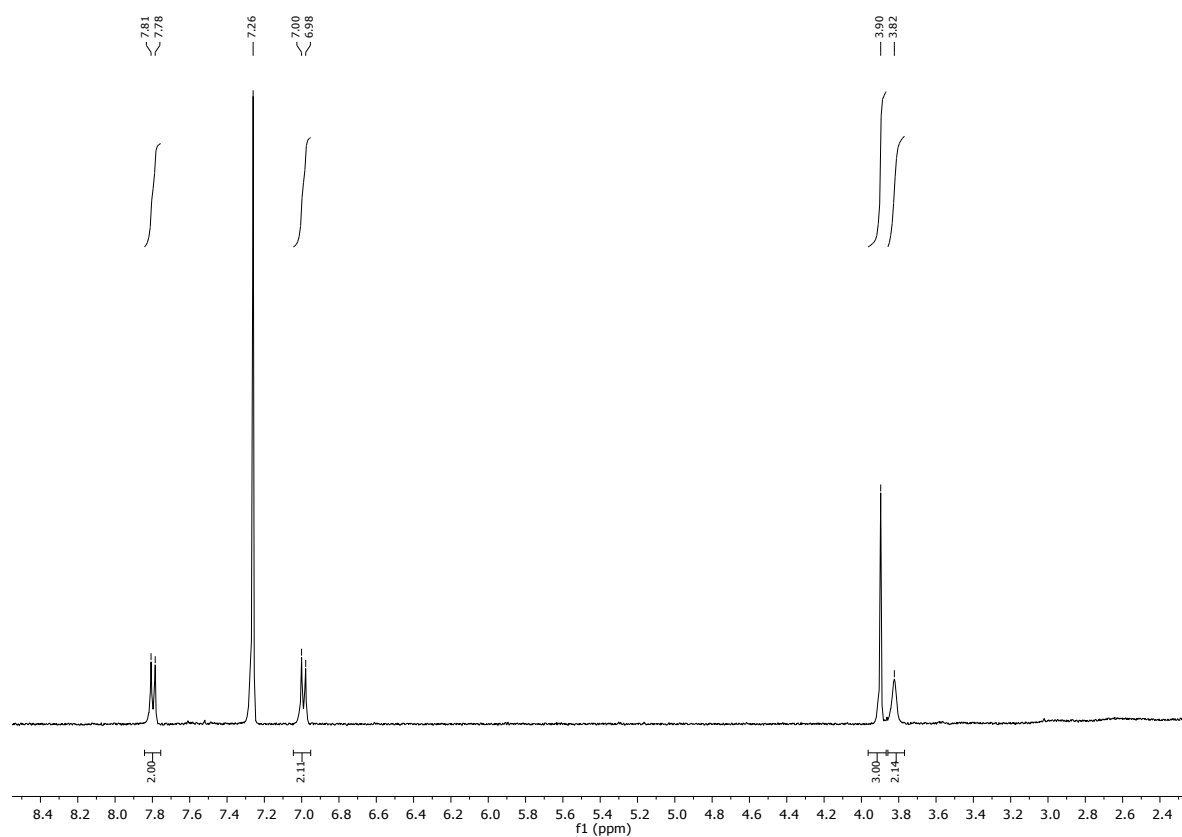


Fig. 11S. ^1H NMR spectrum of 3-(4'-MeO-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**2**).

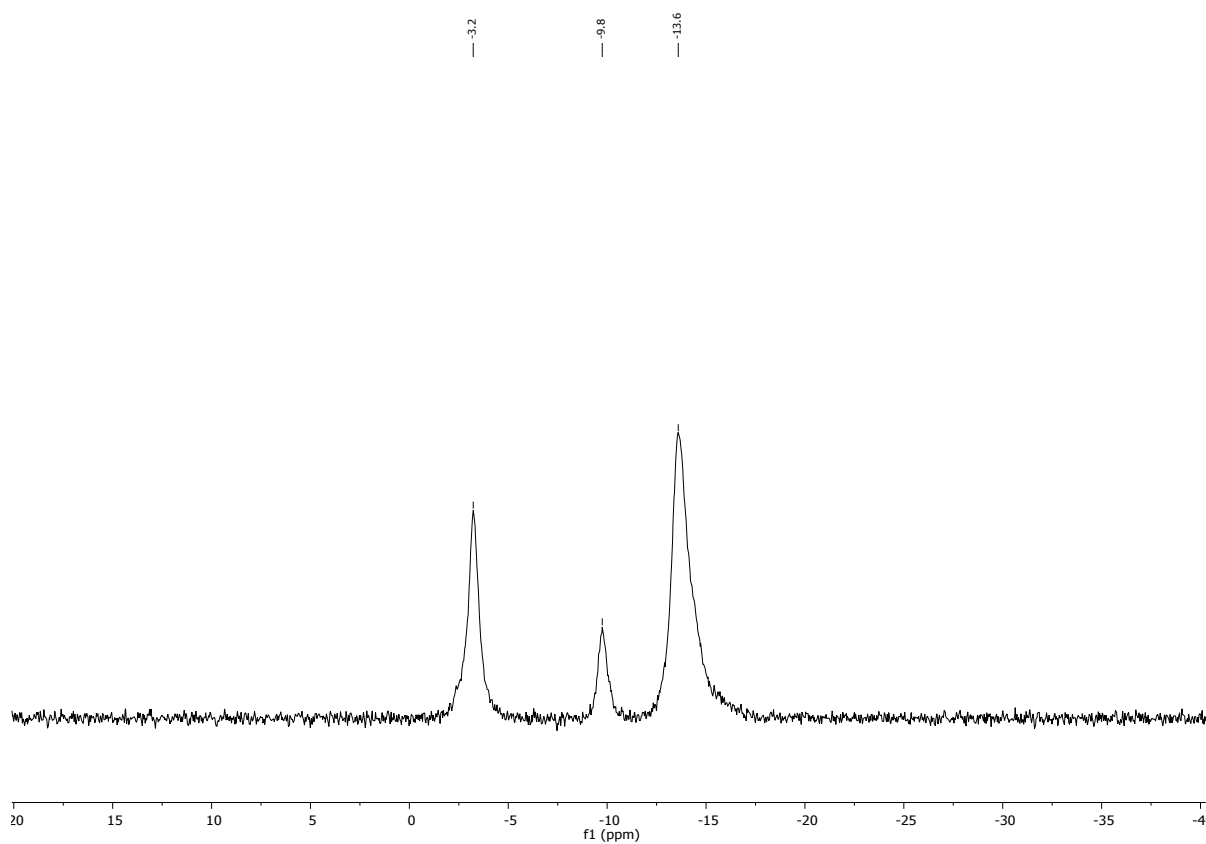


Fig. 12S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 3-(4'-MeO-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**2**).

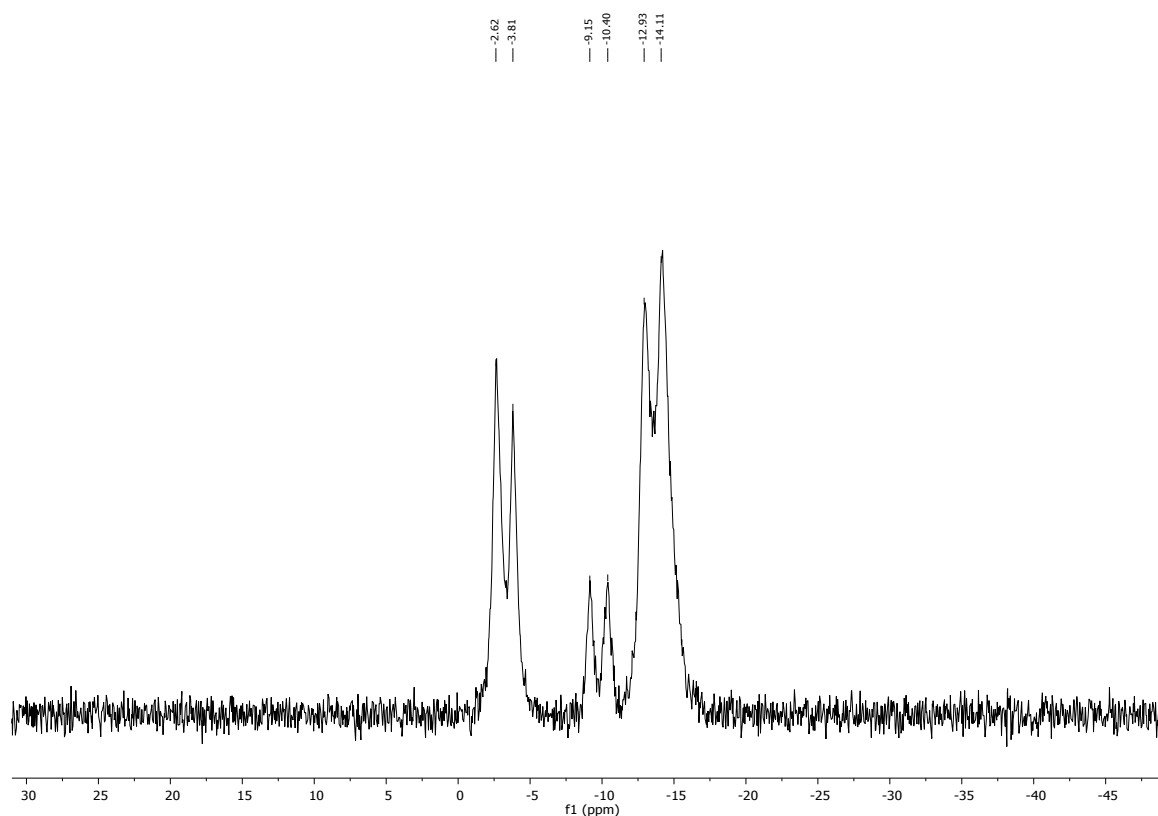


Fig. 13S. ^{11}B NMR spectrum of 3-(4'-MeO-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**2**).

3-(2'-methylphenyldiazo)-1,2-dicarb-*clos*-dodecarborane 3-(2'-Me-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (3**).**

130 mg (0.5 mmol) [3-N₂-o-C₂B₁₀H₁₁][BF₄] was placed in a 25 mL two-neck flask under argon atmosphere, cooled to -30 °C and diethyl ether (5 mL) was added. Then a 2.0 M solution of *o*-MeC₆H₄MgBr in Et₂O (0.75 mL, 1.5 mmol) was added dropwise to the resulting suspension. The reaction mixture first darkened and then turned red, cooling was removed, and the mixture was stirred for 12 h. Then water (20 mL) was added, the product was extracted with diethyl ether (3×20 mL). The organic fractions were separated, combined, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The resulting residue was washed with hot hexane (3×10 mL), the filtrate was evaporated and subjected to column chromatography (eluent diethyl ether—hexane, 1 : 1 (v/v)). The boron-containing fraction was collected and concentrated on a rotary evaporator to obtain a pink compound **1** (61 mg, 47%). ^1H NMR (CDCl₃, ppm): 7.42 (1H, t, $J = 4.2$ Hz, C₆H₄), 7.36 (1H, d, $J = 4.2$ Hz, C₆H₄), 7.23 (2H, m, C₆H₄), 3.80 (2H, br.s, CH_{carb}), 2.76 (3H, s, CH₃). ^{11}B NMR (CDCl₃, ppm): -2.4 (1B, s), -3.1 (2B, d, $J = 140$ Hz), -9.6 (1B, d, $J = 160$ Hz), -13.6 (6B, d, $J = 163$ Hz). IR (CHCl₃, cm⁻¹): 3068 (C_{carb}-H), 3020 (C_{aryl}-H), 2957-2853 (C_{Me}-H), 2600, 2583 (B-H), 1600 ((C-C)_{aryl}). UV (CHCl₃, nm): 525.

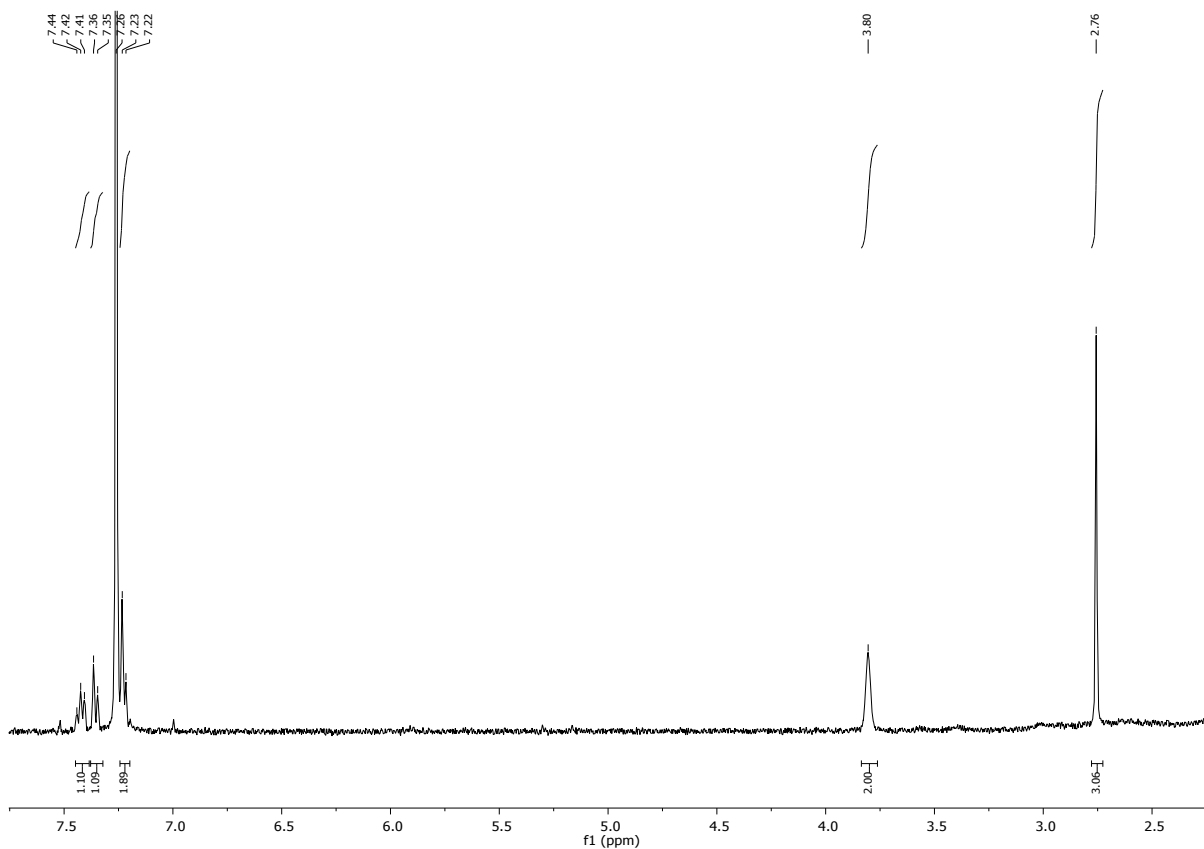


Fig. 14S. ^1H NMR spectrum of 3-(2'-Me-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**3**).

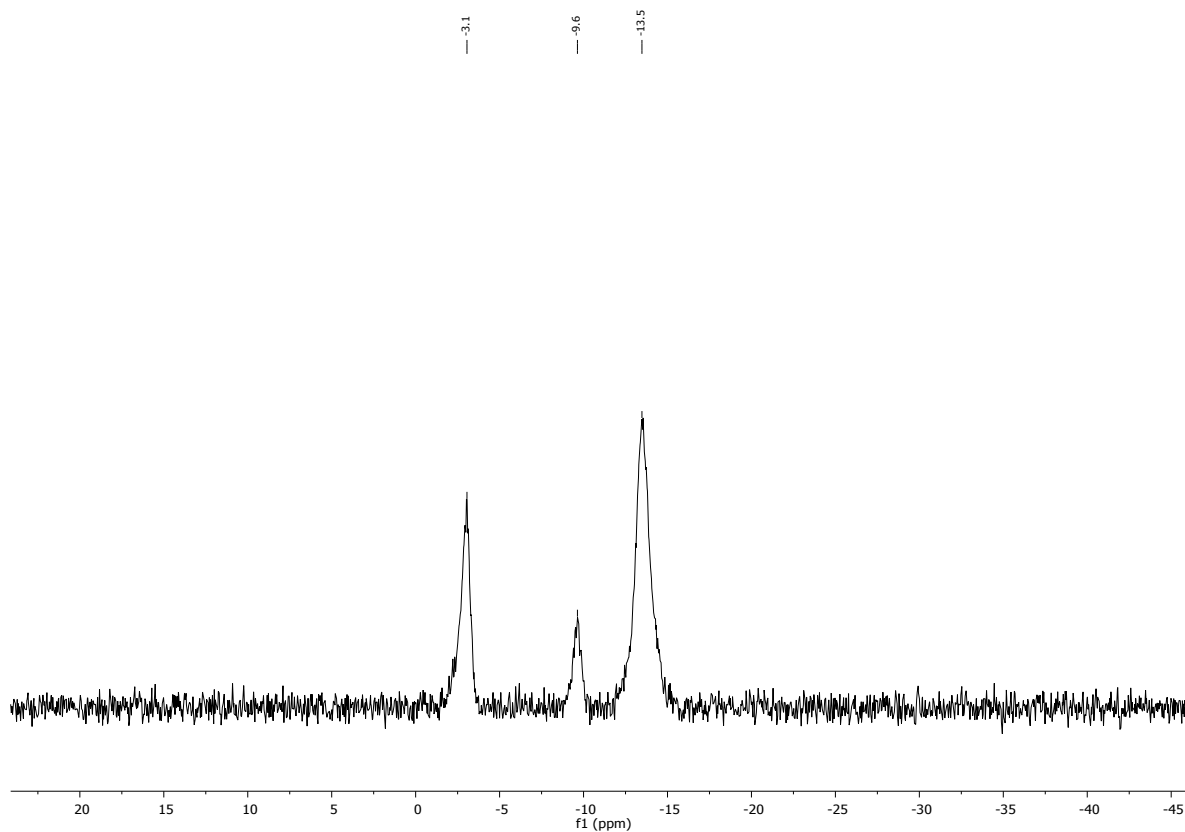


Fig. 15S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 3-(2'-Me-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**3**).

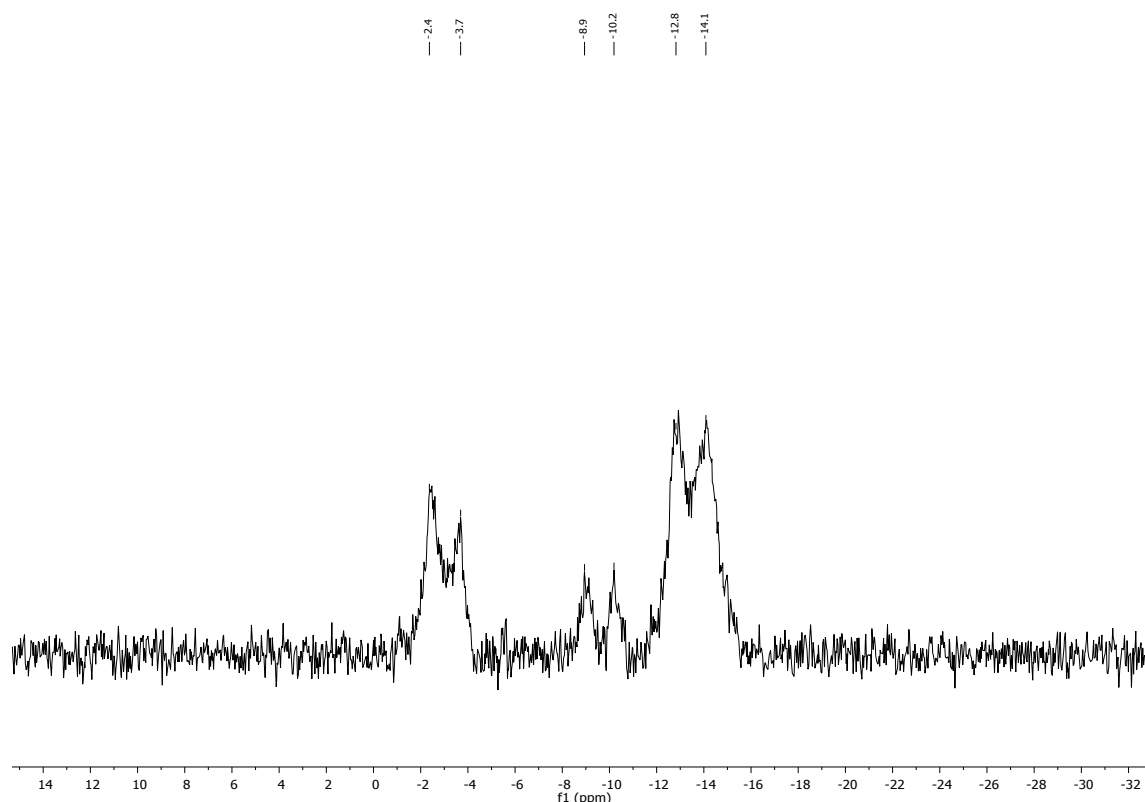


Fig. 16S. ^{11}B NMR spectrum of 3-(2'-Me-C₆H₄N=N)-1,2-C₂B₁₀H₁₁ (**3**).

Cesium 3-(4'-N,N-dimethylaminophenyldiazo)-7,8-dicarba-*nido*-undecaborate Cs[3-(4'-Me₂NC₆H₄N=N)-7,8-C₂B₉H₁₁] (4**).**

Cesium fluoride (136 mg, 0.88 mmol) was added to a solution of compound **1** (65 mg, 0.22 mmol) in ethanol (10 mL) and the reaction mixture was heated under reflux for 16 h. Then, the reaction mixture was cooled to room temperature and evaporated on a rotary evaporator, the residue was dissolved in acetone (20 mL), the precipitate was filtered off, and the filtrate was evaporated again to obtain a pink compound **4** (90 mg, 99%). ^1H NMR (acetone-*d*₆, ppm): 7.57 (2H, d, $J = 8.9$ Hz, C₆H₄), 6.72 (2H, d, $J = 8.9$ Hz, C₆H₄), 3.00 (6H, s, N(CH₃)₂), 2.04 (2H, br.s, CH_{carb}), -2.51 (1H, br.s, BHB). ^{11}B NMR (acetone-*d*₆, ppm): -4.8 (1B, s), -11.1 (2B, d, $J = 137$ Hz), -16.8 (2B, d, $J = 136$ Hz), -22.6 (2B, d, $J = 149$ Hz), -36.0 (1B, d, $J = 159$ Hz), -37.5 (1B, d, $J = 146$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone-*d*₆, ppm): 151.9 (N₂C_{Ar}), 147.4 (C_{Ar}NMe₂), 122.8 (C_{Ar}H), 111.1 (C_{Ar}H), 45.6 (C_{carb}), 39.6 (N(CH₃)₂). IR (acetone, cm⁻¹): 3071 (C_{carb}-H), 3036 (C_{aryl}-H), 2924-2810 (C_{Me}-H), 2549, 2530, 2499 (B-H), 1697, 1684 ((C=C)_{aryl}). UV (acetone, nm): 470. HRMS (ESI), found m/z 281.2581 [M]⁻; C₁₀H₂₁B₉N₃; calculated for C₁₀H₂₁B₉N₃: [M]⁻ = 281.2622.

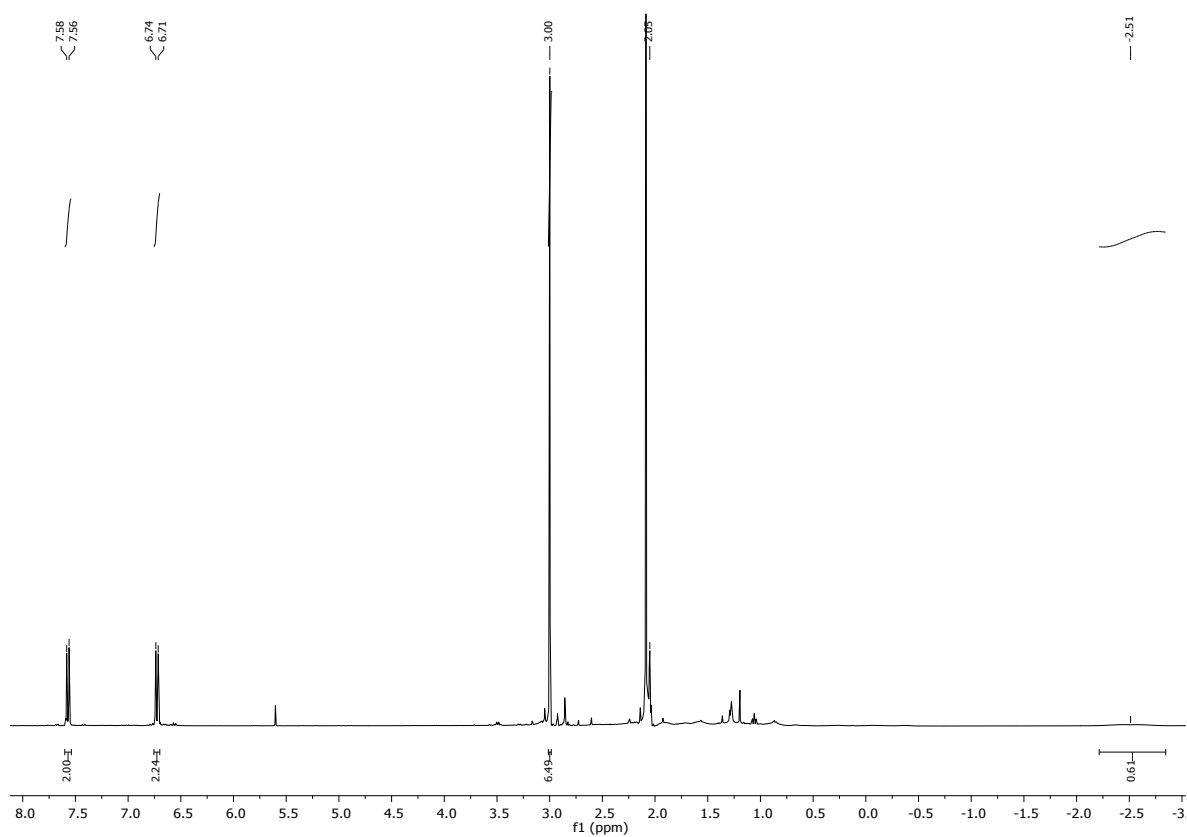


Fig. 17S. ^1H NMR spectrum of $\text{Cs}[3-(4'\text{-Me}_2\text{NC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**4**).

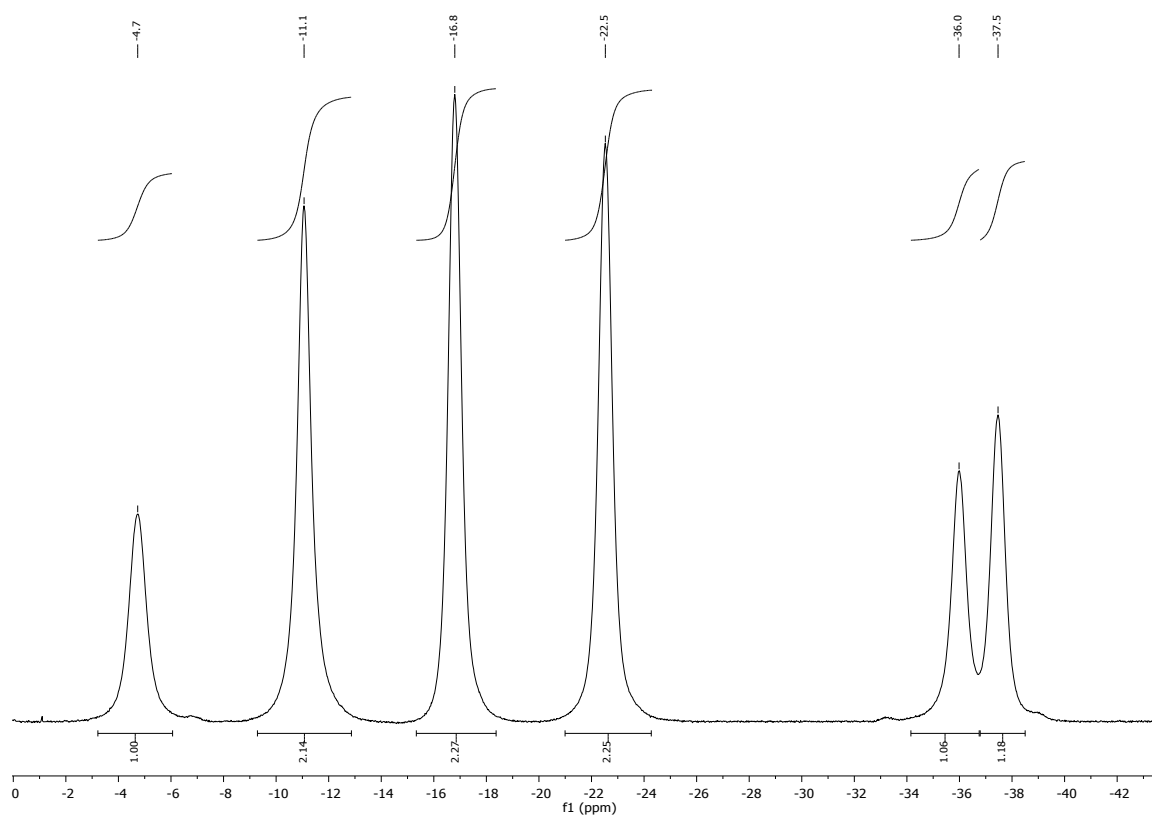


Fig. 18S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(4'\text{-Me}_2\text{NC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**4**).

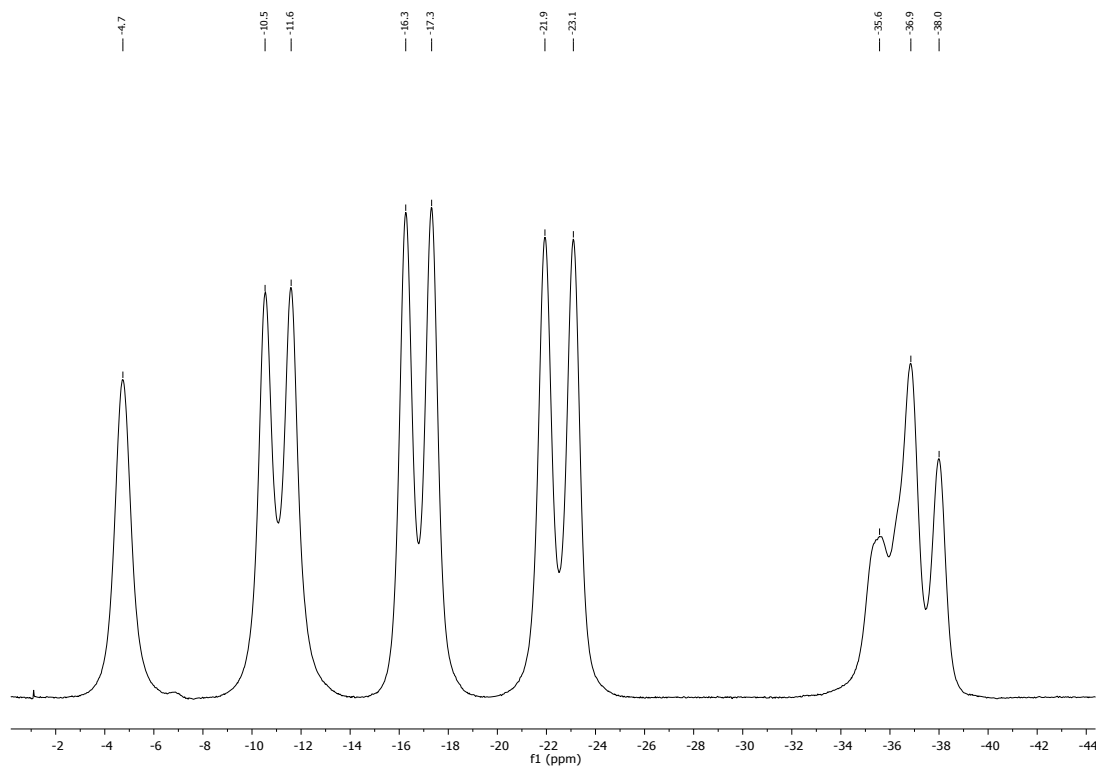


Fig. 19S. ^{11}B NMR spectrum of $\text{Cs}[3-(4'\text{-Me}_2\text{NC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**4**).

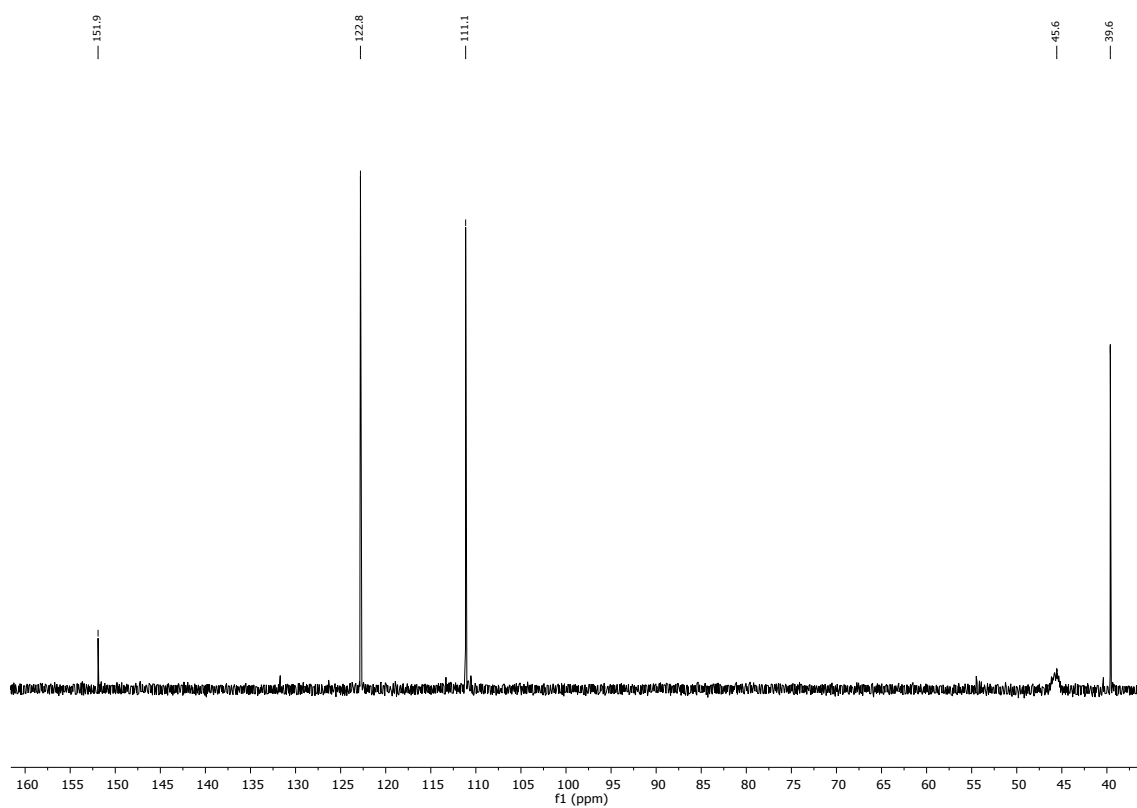


Fig. 20S. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(4'\text{-Me}_2\text{NC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**4**).

Cesium 3-(4'-methoxyphenyldiazo)-7,8-dicarba-*nido*-undecaborate Cs[3-(4'-MeO-C₆H₄N=N)-7,8-C₂B₉H₁₁] (5)

The synthesis was carried out similarly to the procedure described above using compound **2** (40 mg, 0.16 mmol) and CsF (97 mg, 0.64 mmol). The yield of red compound **5** was 64 mg (99%). ¹H NMR (acetone-*d*₆, ppm): 7.63 (2H, d, *J* = 8.9 Hz, C₆H₄), 6.98 (2H, d, *J* = 8.9 Hz, C₆H₄), 3.84 (3H, s, CH₃O), 2.87 (2H, br.s, CH_{carb}), -2.52 (1H, br.s, BHB). ¹¹B NMR (acetone-*d*₆, ppm): -4.9 (1B, s), -11.0 (2B, d, *J* = 137 Hz), -16.7 (2B, d, *J* = 136 Hz), -22.6 (2B, d, *J* = 151 Hz), -36.8 (1B, d, *J* = 125 Hz), -37.5 (1B, d, *J* = 155 Hz). ¹³C{¹H} NMR (acetone-*d*₆, ppm): 161.2 (MeOC_{Ar}), 150.1 (C_{Ar}N₂), 122.7 (C_{Ar}H), 113.5 (C_{Ar}H), 54.9 (OCH₃), 45.9 (C_{carb}). IR (acetone, cm⁻¹): 3073 (C_{carb}-H), 3005 (C_{aryl}-H), 2956-2841 (C_{Me}-H), 2528, 2507 (B-H), 1601, 1582 ((C=C)_{aryl}), 1252 (H₃C-O). UV (acetone, nm): 495. HRMS (ESI), found *m/z* 268.2295 [M]⁻; C₉H₁₈B₉N₂O; calculated for C₉H₁₈B₉N₂O: [M]⁻ = 268.2305.

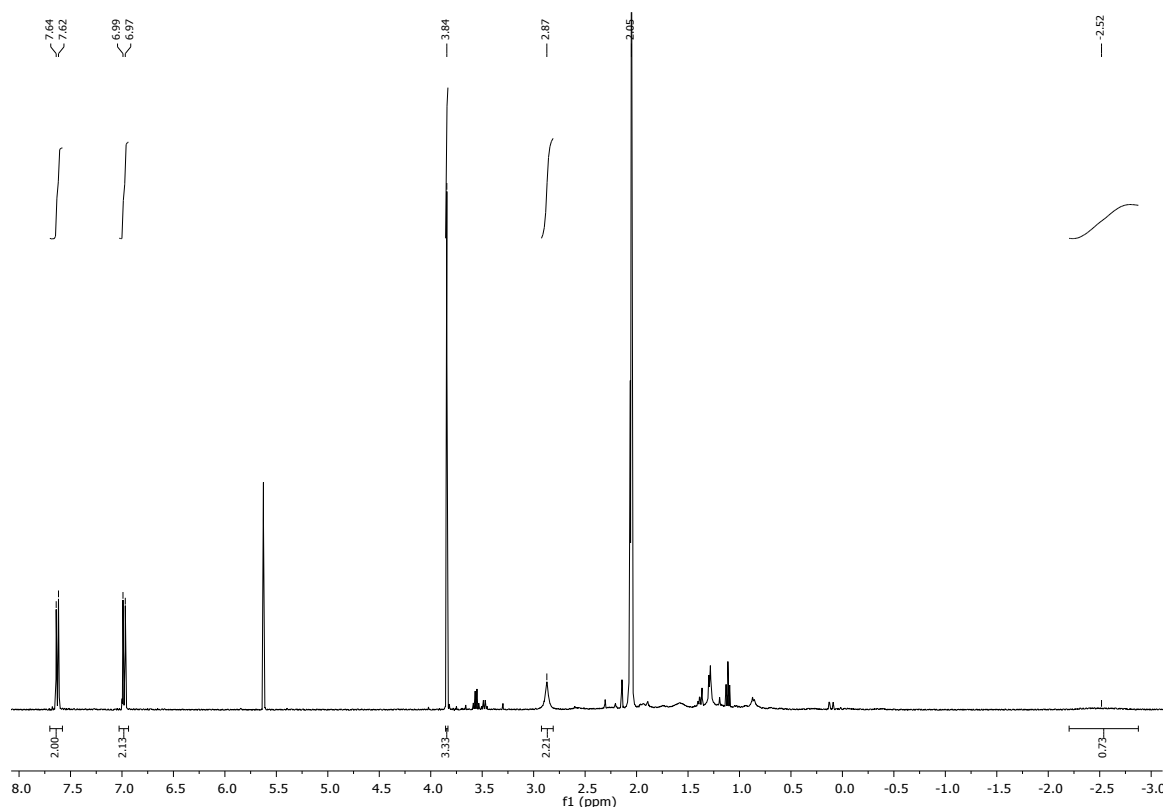


Fig. 21S. ¹H NMR spectrum of Cs[3-(4'-MeOC₆H₄N=N)-7,8-C₂B₉H₁₁] (**5**).

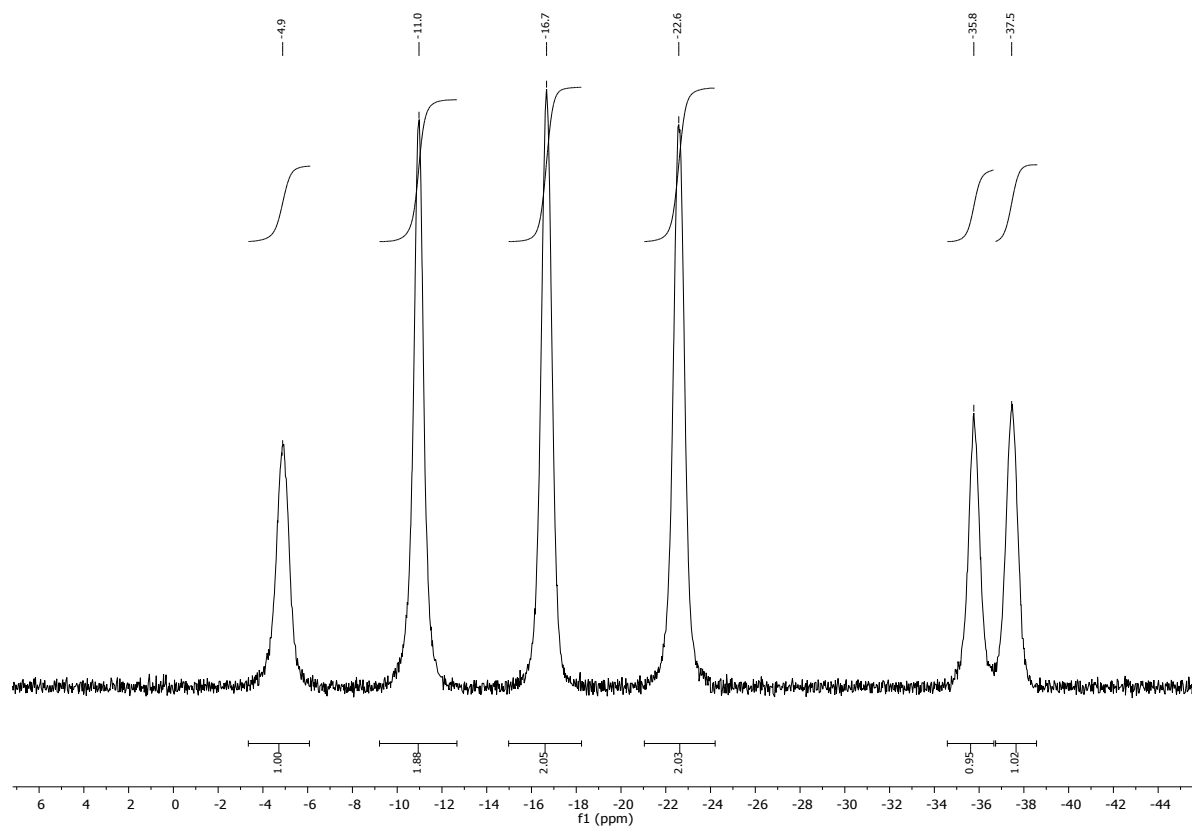


Fig. 22S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(4'\text{-MeOC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**5**).

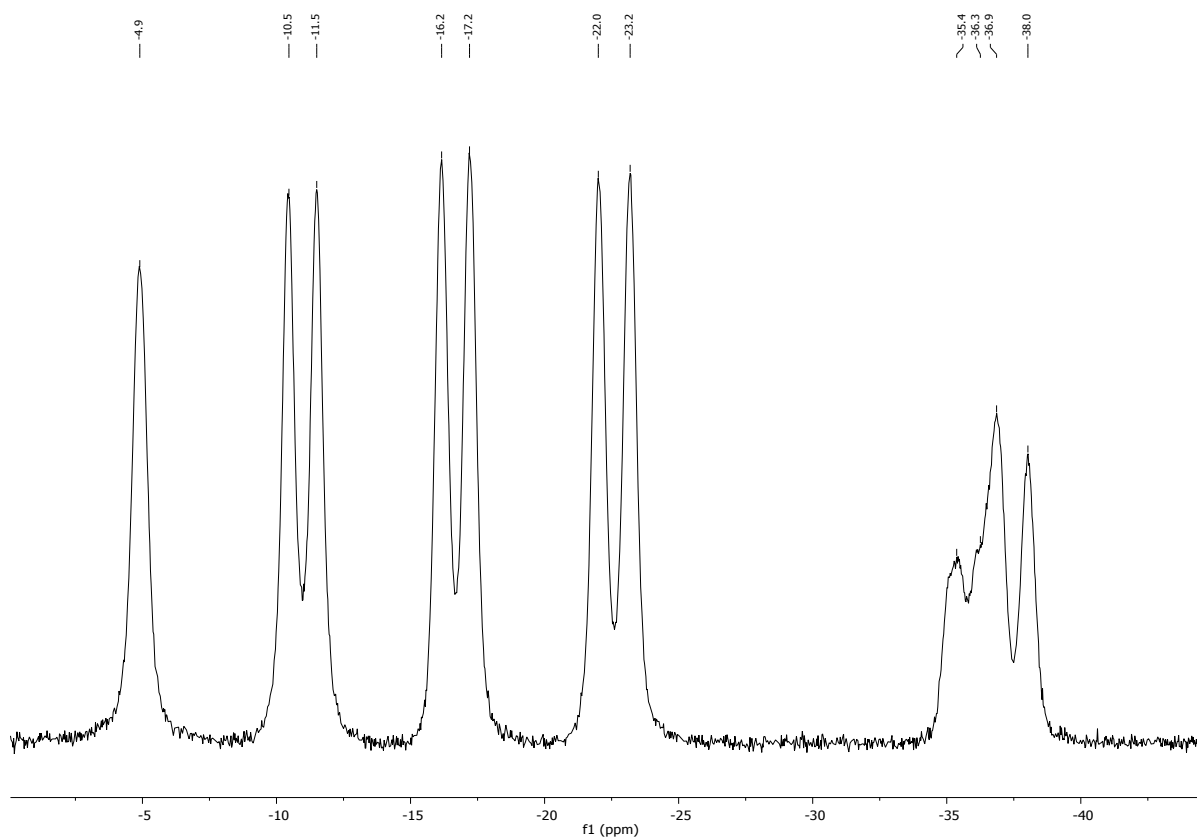


Fig. 23S. ^{11}B NMR spectrum of $\text{Cs}[3-(4'\text{-MeOC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**5**).

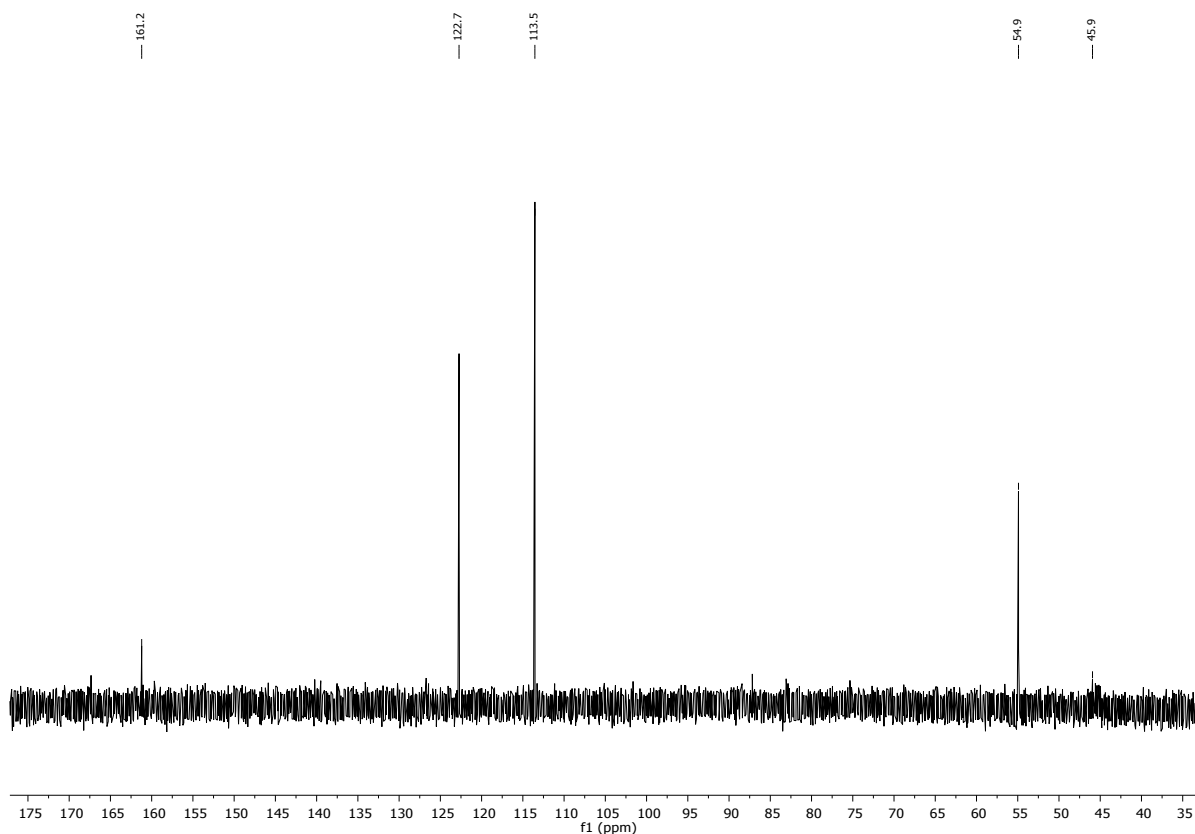


Fig. 24S. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(4'\text{-MeOC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**5**).

Cesium 3-(2'-methylphenyldiazo)-7,8-dicarba-*nido*-undecaborate $\text{Cs}[3-(2'\text{-Me-C}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**6**).

The synthesis was carried out similarly to the procedure described above using compound **3** (47 mg, 0.18 mmol) and CsF (55 mg, 0.72 mmol). The yield of pink compound **6** was 68 mg (98%). ^1H NMR (acetone- d_6 , ppm): 7.27 (1H, m, C_6H_4), 7.14 (1H, m, C_6H_4), 7.02 (2H, d, $J = 7.8$ Hz, C_6H_4), 2.91 (2H, br.s, CH_{carb}), 2.65 (3H, s, CH_3), -2.51 (1H, br.s, BHB). ^{11}B NMR (acetone- d_6 , ppm): -4.9 (1B, s), -10.8 (2B, d, $J = 137$ Hz), -16.6 (2B, d, $J = 136$ Hz), -22.6 (2B, d, $J = 150$ Hz), -35.6 (1B, d, $J = 131$ Hz), -37.3 (1B, d, $J = 155$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , ppm): 152.9 ($\text{C}_{\text{Ar}}\text{N}_2$), 136.5 ($\text{CH}_3\text{C}_{\text{Ar}}$), 130.9 ($\text{C}_{\text{Ar}}\text{H}$), 129.7 ($\text{C}_{\text{Ar}}\text{H}$), 125.9 ($\text{C}_{\text{Ar}}\text{H}$), 112.5 ($\text{C}_{\text{Ar}}\text{H}$), 45.7 (C_{carb}), 16.2 (CH_3). IR (acetone, cm^{-1}): 3056 ($\text{C}_{\text{carb}}\text{-H}$), 3025 ($\text{C}_{\text{aryl}}\text{-H}$), 2973-2855 ($\text{C}_{\text{Me}}\text{-H}$), 2526 (B-H), 1699 ($(\text{C}=\text{C})_{\text{aryl}}$), 1254 ($\text{H}_3\text{C-O}$). UV (acetone, nm): 517. HRMS (ESI), found m/z 252.2359 [M] $^-$; $\text{C}_9\text{H}_{18}\text{B}_9\text{N}_2$; calculated for $\text{C}_9\text{H}_{18}\text{B}_9\text{N}_2$: [M] $^-$ = 252.2356.

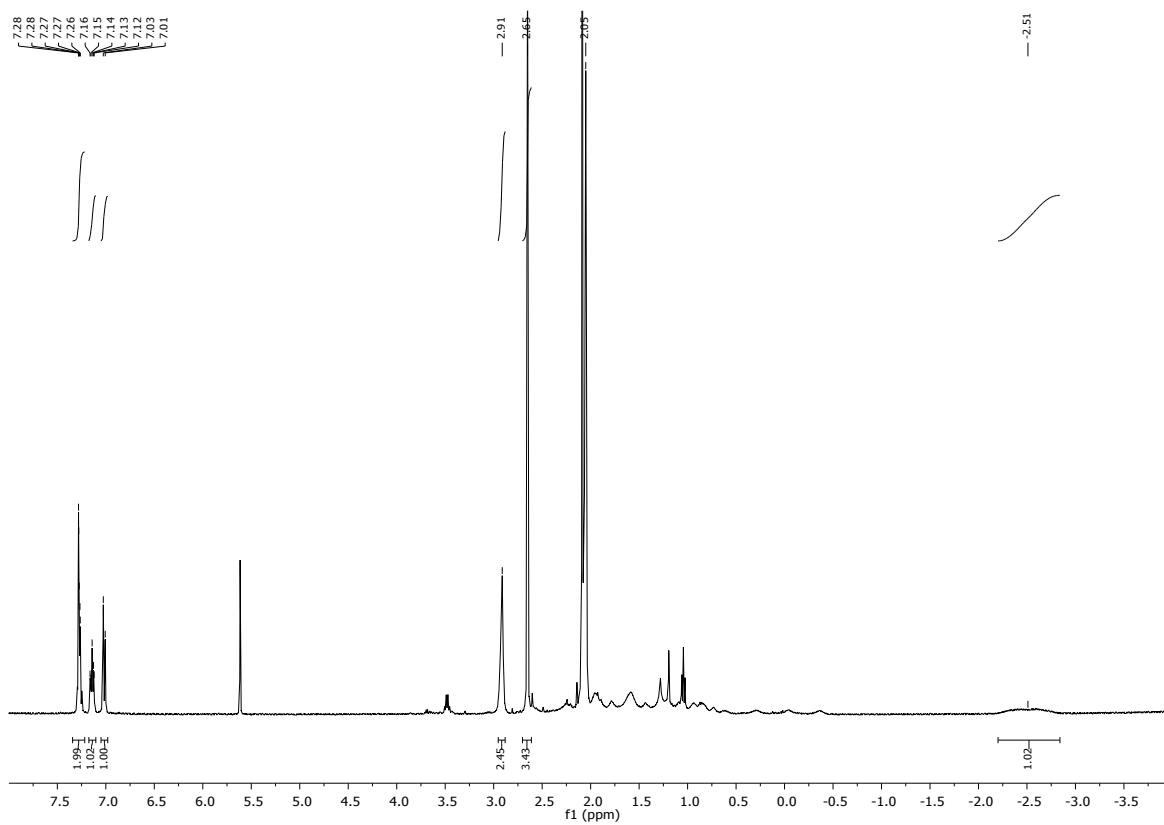


Fig. 25S. ^1H NMR spectrum of $\text{Cs}[3-(2'\text{-MeC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**6**).

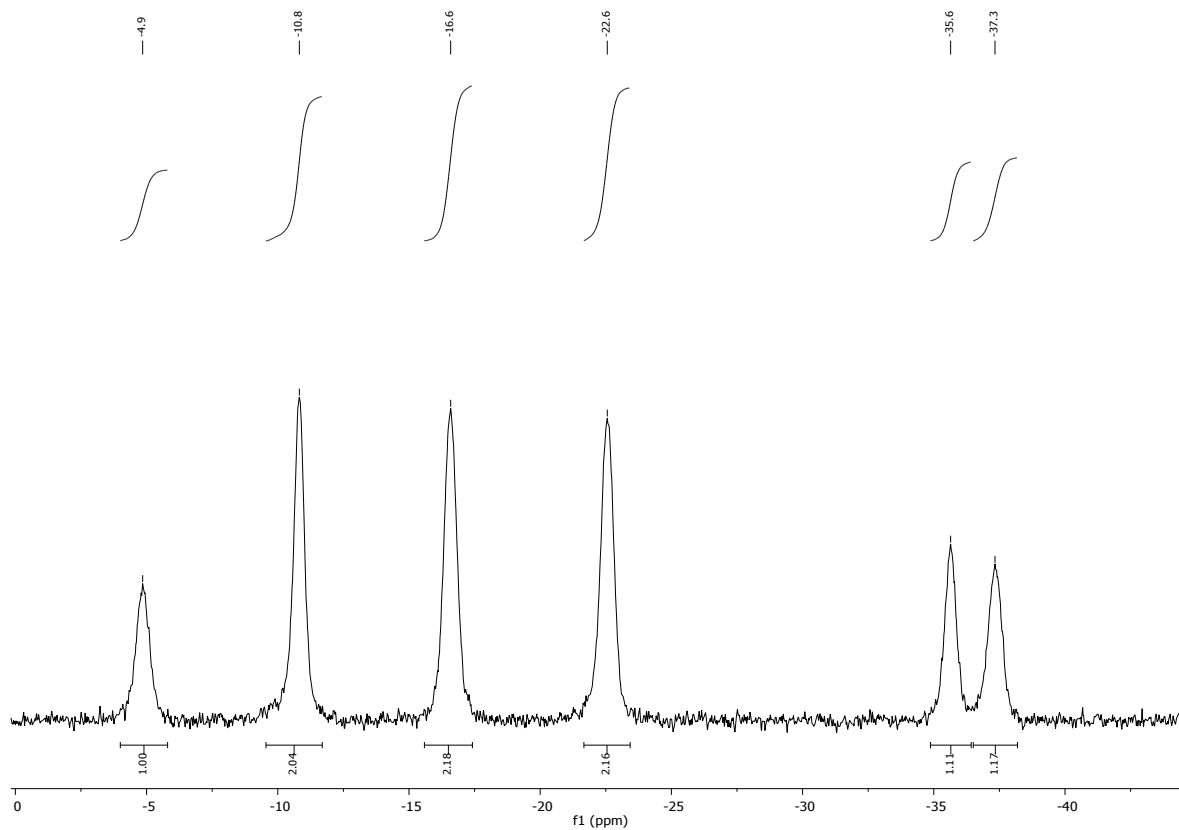


Fig. 26S. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(2'\text{-MeC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**6**).

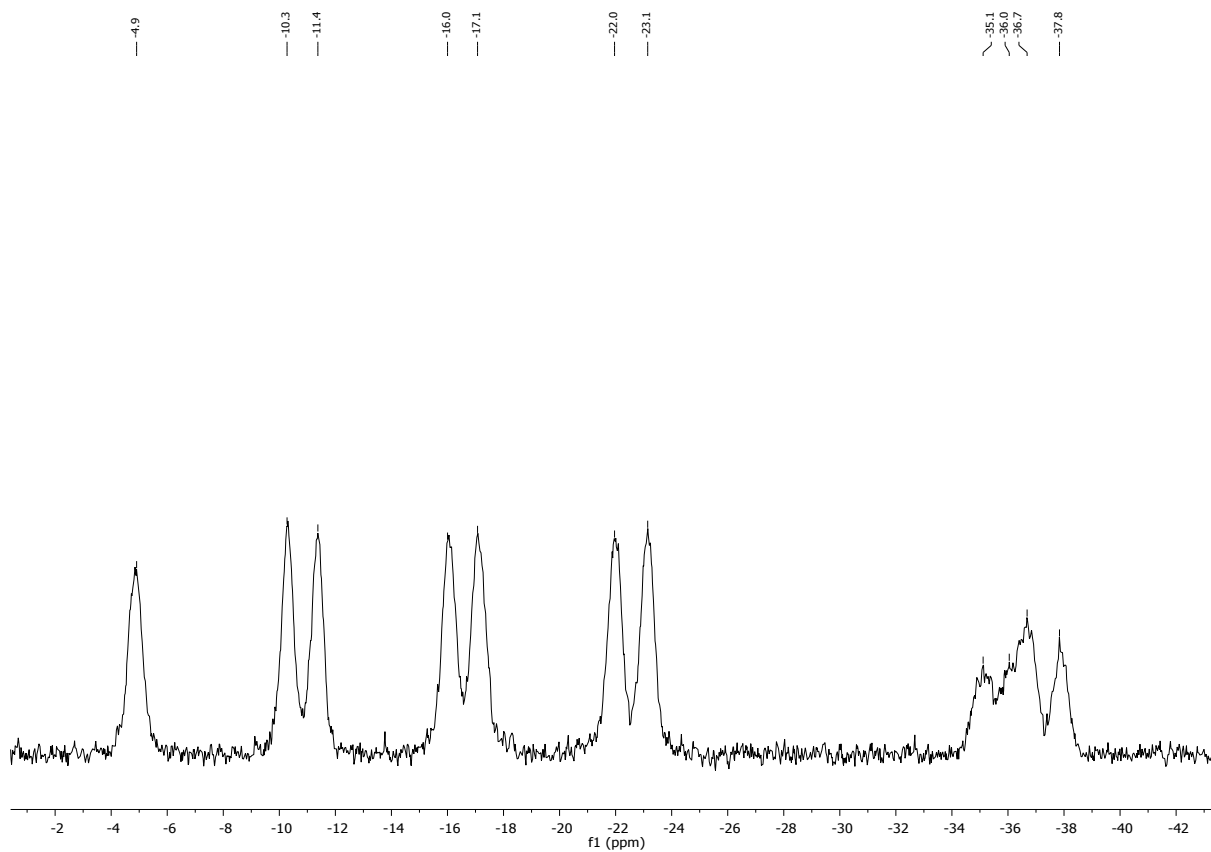


Fig. 27S. ^{11}B NMR spectrum of $\text{Cs}[3-(2'\text{-MeC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**6**).

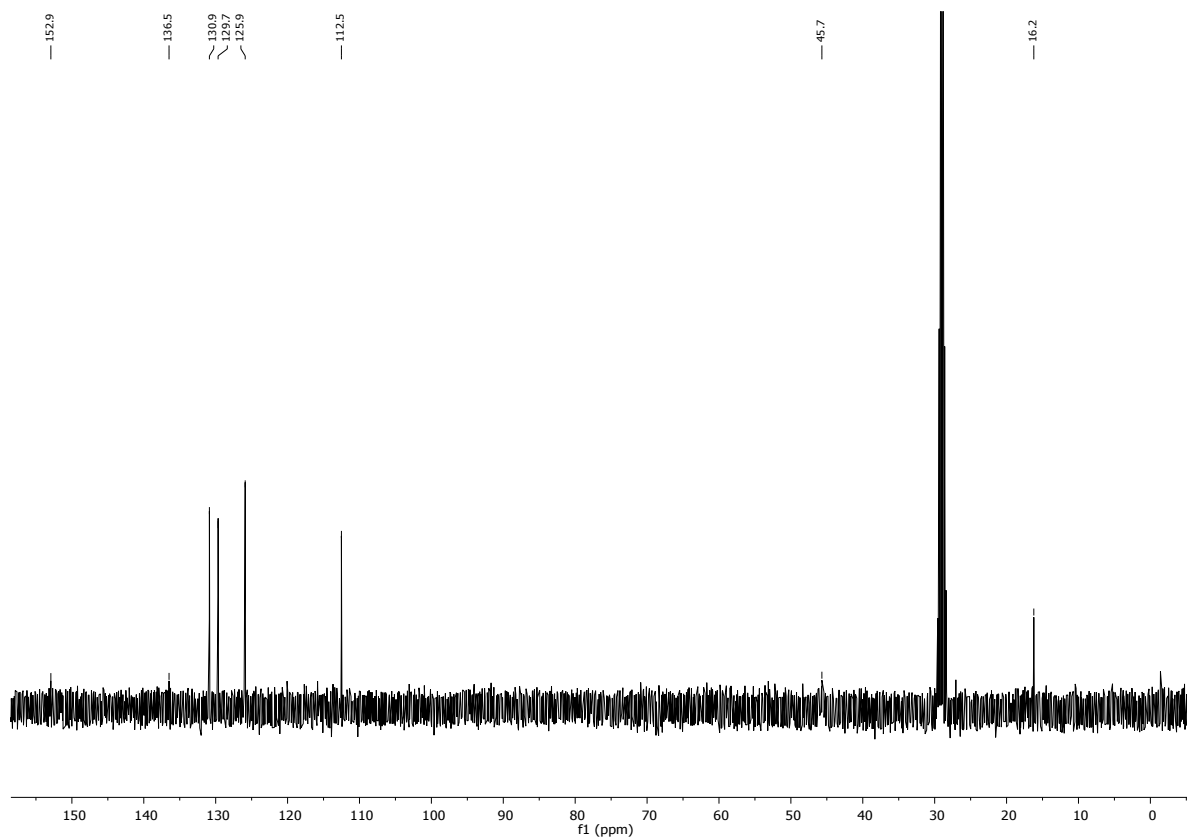


Fig. 28S. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Cs}[3-(2'\text{-MeC}_6\text{H}_4\text{N}=\text{N})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**6**).

Table S1. ¹H NMR chemical shifts of the *p*-MeOC₆H₄ group in the corresponding arylazo derivatives of carboranes and arenes (in CDCl₃).

Compound	Chemical shifts, ppm	Reference
1-(<i>p</i> -MeOC ₆ H ₄)-N=N-1,2-C ₂ B ₁₀ H ₁₁	7.74, 6.97, 3.89	[7]
1-(<i>p</i> -MeOC ₆ H ₄)-N=N-1,7-C ₂ B ₁₀ H ₁₁	7.71, 6.94, 3.87	[8]
1,2-(<i>p</i> -MeOC ₆ H ₄) ₂ -N=N-1,7-C ₂ B ₁₀ H ₁₀	7.72, 6.94, 3.88	[8]
1,7-(<i>p</i> -MeOC ₆ H ₄) ₂ -N=N-1,7-C ₂ B ₁₀ H ₁₀	7.73, 6.95, 3.88	[8]
1-(<i>p</i> -MeOC ₆ H ₄)-N=N-3-Cp*-3,1,2-IrC ₂ B ₉ H ₁₀	7.69, 6.95, 3.88	[9]
1-(<i>p</i> -MeOC ₆ H ₄)-N=N-3-Cp*-3,1,2-RhC ₂ B ₉ H ₁₀	7.71, 6.95, 3.88	[9]
1,2-(<i>p</i> -MeOC ₆ H ₄) ₂ -N=N-3-Cp*-3,1,2-IrC ₂ B ₉ H ₉	7.80, 7.00, 3.90	[9]
3-(<i>p</i> -MeOC ₆ H ₄)-N=N-1,2-C ₂ B ₁₀ H ₁₁	7.80, 6.99, 3.88	This work
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₅	7.93, 7.02, 3.89	[10]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -Me	7.90, 7.00, 3.88	[10]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -OMe	7.88, 6.99, 3.87	[10]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -F	7.91, 7.01, 3.89	[10]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -NO ₂	7.97, 7.04, 3.92	[11]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -CF ₃	7.95, 7.03, 3.91	[11]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -CN	7.98, 7.06, 3.94	[11]
<i>p</i> -MeOC ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -COOMe	7.93, 7.00, 3.87	[12]

X-ray experiments for compounds **1**, **2**, **3** were carried out using SMART APEX2 CCD diffractometer ($\lambda(\text{Mo-K}\alpha)=0.71073 \text{ \AA}$, graphite monochromator, ω -scans) at 120K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [13]. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program [14]. The CCDC numbers (1995638, 1995639, 1995640 for **1**, **2**, **3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for 1: C₁₀H₂₁B₁₀N₃ are triclinic, space group *P*-1: $a = 13.4382(13) \text{ \AA}$, $b = 14.3212(13) \text{ \AA}$, $c = 19.2290(18) \text{ \AA}$, $\alpha = 71.551(2)^\circ$, $\beta = 89.699(2)^\circ$, $\gamma = 75.284(2)^\circ$, $V = 3383.9(6) \text{ \AA}^3$, $Z = 8$, $M = 291.40$, $d_{\text{cryst}} = 1.144 \text{ g}\cdot\text{cm}^{-3}$. $wR2=0.1721$ calculated on F^2_{hkl} for all 14444 independent reflections with $2\theta < 53.7^\circ$, ($GOF=1.008$, $R=0.0627$ calculated on F_{hkl} for 8383 reflections with $I > 2\sigma(I)$).

Crystallographic data for 2: C₉H₁₈B₁₀N₂O are monoclinic, space group $P2_1/c$: $a = 12.3986(17)\text{\AA}$, $b = 19.258(3)\text{\AA}$, $c = 6.6169(9)\text{\AA}$, $\beta = 99.327(3)^\circ$, $V = 1559.1(4)\text{\AA}^3$, $Z = 4$, $M = 278.35$, $d_{\text{cryst}} = 1.186\text{ g}\cdot\text{cm}^{-3}$. $wR2=0.1373$ calculated on F^2_{hkl} for all 2963 independent reflections with $2\theta < 52^\circ$, ($GOF=0.989$, $R=0.0522$ calculated on F_{hkl} for 1868 reflections with $I > 2\sigma(I)$).

Crystallographic data for 3: C₉H₁₈B₁₀N₂ are orthorhombic, space group $Pbcn$: $a = 19.235(3)\text{\AA}$, $b = 7.0992(11)\text{\AA}$, $c = 21.796(3)\text{\AA}$, $V = 2976.4(8)\text{\AA}^3$, $Z = 8$, $M = 262.35$, $d_{\text{cryst}} = 1.171\text{ g}\cdot\text{cm}^{-3}$. $wR2=0.1561$ calculated on F^2_{hkl} for all 4170 independent reflections with $2\theta < 59.2^\circ$, ($GOF=1.003$, $R=0.0580$ calculated on F_{hkl} for 2265 reflections with $I > 2\sigma(I)$).

Table S2. Selected bond lengths (Å) and torsion angles (°) of compounds **1**, **2**, **3**.

Bond/Tors.angle	1				2	3	Mean Xray*
	Mol. A	Mol. A'	Mol. A''	Mol. (d)			
B8-B3-N1-N2	-177.5(2)	-179.7(2)	179.2(2)	178.1(2)	-154.0(2)	131.6(2)	
B3-N1-N2-C3	179.1(2)	179.3(2)	179.6(2)	-178.5(2)	179.7(2)	177.7(2)	
N1-N2-C3-C4	-179.6(2)	177.6(2)	-178.4(2)	177.8(2)	178.8(2)	157.9(2)	
N2-C3	1.411(3)	1.407(3)	1.416(3)	1.416(3)	1.435(2)	1.432(2)	
N1-N2	1.270(3)	1.274(3)	1.274(3)	1.271(3)	1.262(2)	1.259(2)	
B3-N1	1.479(3)	1.482(3)	1.479(3)	1.488(3)	1.490(3)	1.491(3)	
B3-C1	1.734(4)	1.736(4)	1.736(4)	1.739(4)	1.739(3)	1.718(3)	1.722
B3-C2	1.738(4)	1.735(4)	1.732(4)	1.727(4)	1.729(3)	1.727(3)	1.722
B3-B4	1.779(4)	1.771(4)	1.783(4)	1.775(4)	1.776(3)	1.771(3)	1.773
B3-B7	1.777(4)	1.783(4)	1.780(4)	1.779(4)	1.780(3)	1.785(3)	1.773
B3-B8	1.758(4)	1.758(4)	1.766(4)	1.759(4)	1.762(3)	1.762(3)	1.765
C1-C2	1.618(3)	1.627(3)	1.619(3)	1.631(3)	1.622(3)	1.630(3)	1.676
C1-B6	1.718(4)	1.719(4)	1.718(4)	1.721(4)	1.718(3)	1.717(3)	1.722
C2-B6	1.714(4)	1.720(4)	1.718(4)	1.730(4)	1.725(3)	1.715(3)	1.722
B5-B6	1.781(4)	1.776(4)	1.769(5)	1.769(4)	1.783(4)	1.780(3)	1.773
B6-B10	1.768(4)	1.767(4)	1.766(5)	1.766(4)	1.765(3)	1.776(3)	1.765
B6-B11	1.769(4)	1.778(4)	1.767(5)	1.781(4)	1.784(4)	1.781(3)	1.773

* statistically average bond lengths in X-ray studied carborane cages [15] are given for a comparison

Calculations

Optimization of compound **1** has led to the structure being close to the experimental one and it is characterized by approximate C_s symmetry (the B8-B3-N1-N2 torsion angle is -179.9°) (Fig. S1). Redistribution of the bond lengths in carborane cage due to p -Me₂NC₆H₄-N=N substituent is provided in Table 2S.

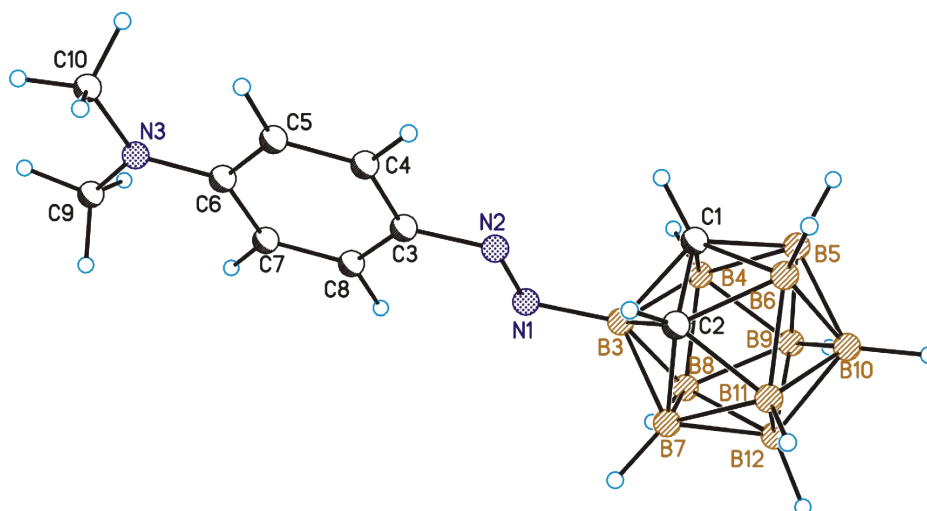


Fig. 29S. General view of optimized structure of compound **1**.

Table S3. Selected bond lengths (Å) for unsubstituted *ortho*-carborane and compound **1** as obtained from PBE0/6-311G(df,pd) calculation.

	<i>ortho</i> -carborane	Compound 1
B3-C1	1.707	1.722
B3-C2	1.707	1.722
B3-B4	1.770	1.772
B3-B7	1.770	1.771
B3-B8	1.760	1.761
C1-C2	1.612	1.602
C1-B6	1.707	1.703
C2-B6	1.707	1.703
B5-B6	1.770	1.771
B6-B10	1.760	1.762
B6-B11	1.770	1.771

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