

Supporting Information for *B*-Cyanodicarba-*closo*-dodecaboranes: Facile Synthesis and Spectroscopic Features

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1. Materials and methods

Carboranes were purchased from Katchem spol. s r. o. (Czech Republic). CuCN ($\geq 99.0\%$) was purchased from Sigma-Aldrich (product code: 61176), Pd(PPh₃)₄ (98%) was purchased from Carbolution (product code: CC03013). DMF (99.99%) from Fisher Chemical was used for the cyanation reactions. All other chemicals were purchased from Sigma Aldrich, Acros or Alfa Aesar. CH₂Cl₂ was distilled prior to usage. All other chemicals were used without further purification. All reactions were performed without exclusion of moisture or air. Column chromatography was performed on silica 60 (0.006 – 0.200 mm, Acros). The microwave reactions were carried out in a CEM *Discover* device (Model 908010). Analytical thin layer chromatography (TLC) was performed on TLC plates F254 (Merck) stained with solutions of PdCl₂ in CH₃OH or AgNO₃ in H₂O. Melting points were measured using a Büchi-545 melting point device and represent uncorrected values.

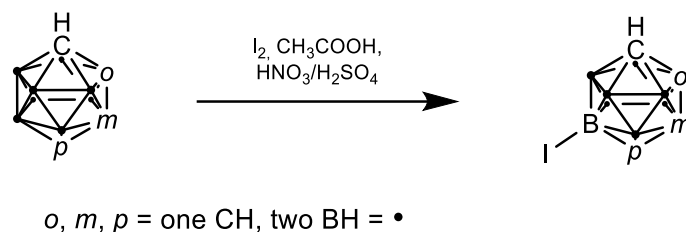
High resolution mass spectra (HR-MS) were recorded on a micrOTOF-Q mass spectrometer (Bruker) with ESI-source coupled with a HPLC Dionex Ultimate 3000 (Thermo Scientific) using EC50/2 Nucleodur C18 Gravity 3 μ m column (Marcherey-Nagel). The column temperature was 25 °C. 1 μ l of sample solution (1 mg/mL in CH₃OH) was injected to a flow of 0.3 mL/min. HPLC started with 90% H₂O containing 2 mM NH₄OAc. The gradient started after 1 min to 100% CH₃CN in 9 min, followed by 5 min flushing with 100% CH₃CN. Positive or negative full scan MS was observed from 50 – 1000 *m/z*. The data were processed using the QuantAnalysis program (Bruker).

¹H NMR, ¹³C NMR and ¹¹B NMR spectra were recorded in CDCl₃ on a Bruker Ascend 600 MHz NMR-spectrometer operating at 600.18 MHz (¹H), 192.56 MHz (¹¹B), 150.93 MHz (¹³C). Chemical shifts (δ) are reported in ppm and are referenced to the chemical shift of the residual solvent proton present in chloroform δ (CHCl₃) = 7.26 ppm for the ¹H NMR spectra and to the solvent ¹³C signal δ (CDCl₃) = 77.16 ppm for the ¹³C NMR spectra. ¹¹B NMR spectra were referenced to the external standard BF₃·OEt₂. Multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; vbr, very broad. Coupling constants (*J*) are shown in hertz (Hz). ¹H- and ¹³C NMR signals of nuclei adjacent to cluster boron atoms are observed as broader signals. The number of boron atoms and the ¹J_{B,H} could not always be determined unambiguously, due to the broad and overlapping signals.

The infrared spectra were recorded as solid samples on an ALPHA-T (Bruker) with a Platinum ATR Module using Opus software. IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000-385 cm⁻¹ (s, strong; m, medium; w, weak).

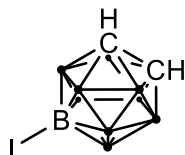
Caution: Cyanides are toxic. Prussic acid (HCN) is a toxic, colorless, bitter-almond-smelling and volatile chemical. Cyanides inhibit the enzyme cytochrome-c-oxidase in the respiratory chain by blocking the oxygen utilization in the cell. Antidotes for cyanide intoxication are 4-dimethylaminophenol-hydrochloride (4-DMAP), sodium thiosulfate and hydroxycobalamin.¹⁻³ Cyanide-containing samples should always be treated with base to avoid the formation of HCN. Oxidizing agents (e.g. NaOCl) can be used to destroy cyanides.⁴ All manipulations with cyanides should be performed in a well-ventilated hood using safety equipment (lab coat, glasses and gloves)! It should be noted that the alternative route described in 1999⁵ required more hazardous or toxic chemicals such as EtMgBr, Cr(VI), SOCl₂, which would clearly argue for using the method described here.

2. Iodination procedure



B-Iododicarba-*closo*-dodecaboranes were prepared according to a literature procedure reported by Himmelsbach and Finze.⁶ In brief, a 1:1 mixture of concentrated H₂SO₄ and concentrated HNO₃ was added dropwise to a mixture of the respective C₂B₁₀H₁₂ (1.0 eq.) and I₂ (0.5 eq.) in AcOH. The reaction was heated to 60 °C for 3 h. Then, the colorless mixture was allowed to cool to room temperature and poured into ice water. The white precipitate was filtered, washed with water and dried under reduced pressure to yield the *B*-iododicarba-*closo*-dodecaboranes as white solids. The iodinated products were obtained in higher than 94% isolated yields and used without further purification.

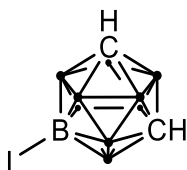
9-Iodo-1,2-dicarba-*closo*-dodecaborane (1o)



¹H NMR (CDCl₃, 600 MHz) δ = 3.86 (s, 1H, CH_{cluster}), 3.66 (s, 1H, CH_{cluster}), 3.23–1.75 (vbr, 9H, B₁₀H₉); **¹³C-APT NMR** (CDCl₃, 151 MHz) δ = 55.0 (C_{cluster}H), 50.8 (C_{cluster}H); **¹¹B NMR** (CDCl₃, 193 MHz) δ = -0.9 (d, ¹J_{B,H} \approx 152 Hz, 2B), -7.5 (d, ¹J_{B,H} \approx 155 Hz, 2B), -12.7 (d, ¹J_{B,H} \approx 143 Hz, 2B), -13.6 (d, ¹J_{B,H} \approx 148 Hz, 2B), -14.7 (d, ¹J_{B,H} \approx 183 Hz, 1B), -16.6 (s, 1B, B-I).

IR (cm⁻¹): $\tilde{\nu}$ = 3068 (m, ν (C_{cluster}H)), 3047 (s, ν (C_{cluster}H)), 2640 (m, ν (BH)), 2611 (s, ν (BH)), 2581 (s, ν (BH)), 2363 (w), 1206 (m), 1137 (m), 1030 (m), 968 (m), 852 (m), 832 (s), 724 (s), 620 (s).

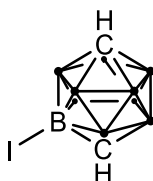
9-Iodo-1,7-dicarba-*closo*-dodecaborane (1m)



^1H NMR (CDCl_3 , 600 MHz) δ = 3.05 (s, 2H, $\text{CH}_{\text{cluster}}$), 3.20–2.11 (vbr, 9H, B_{10}H_9); **^{13}C -APT NMR** (CDCl_3 , 151 MHz) δ = 56.3 (s, $\text{C}_{\text{clusterH}}$); **^{11}B NMR** (CDCl_3 , 193 MHz) δ = –5.3 (d, $^1J_{\text{B,H}} \approx 168$ Hz, 2B), –8.2 (d, $^1J_{\text{B,H}} \approx 156$ Hz, 1B), –11.8 (d, $^1J_{\text{B,H}} \approx 176$ Hz, 2B), –13.0 (d, $^1J_{\text{B,H}} \approx 183$ Hz, 2B), –16.8 (d, $^1J_{\text{B,H}} \approx 184$ Hz, 1B), –18.9 (d, $^1J_{\text{B,H}} \approx 184$ Hz, 1B), –23.6 (s, 1B, B-I).

IR (cm^{-1}): $\tilde{\nu}$ = 3048 (s, $\nu(\text{C}_{\text{clusterH}}$)), 2611 (s, $\nu(\text{BH})$), 2602 (s, $\nu(\text{BH})$), 2589 (s, $\nu(\text{BH})$), 2574, (s, $\nu(\text{BH})$), 829 (s), 752 (s), 725 (s), 614 (m), 420 (m).

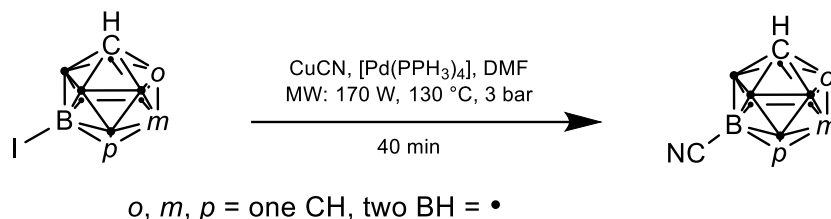
2-Iodo-1,12-dicarba-*closo*-dodecaborane (1p)



^1H NMR (CDCl_3 , 600 MHz) δ = 3.21 (s, 1H, $\text{CH}_{\text{cluster}}$), 2.89 (s, 1H, $\text{CH}_{\text{cluster}}$), 3.08–1.64 (vbr, 9H, B_{10}H_9); **^{13}C -APT NMR** (CDCl_3 , 151 MHz) δ = 68.1 ($\text{C}_{\text{clusterH}}$), 65.5 ($\text{C}_{\text{clusterH}}$). **^{11}B NMR** (CDCl_3 , 193 MHz) δ = –11.8 (d, $^1J_{\text{B,H}} \approx 170$ Hz, 2B), –12.8 to –15.3 (m, 6B), –16.4 (d, $^1J_{\text{B,H}} \approx 167$ Hz, 1B), –28.4 (s, 1B, B-I).

IR (cm^{-1}): $\tilde{\nu}$ = 3046 (m, $\nu(\text{C}_{\text{clusterH}}$)), 3038 (m, $\nu(\text{C}_{\text{clusterH}}$)), 2608 (s, $\nu(\text{BH})$), 1165 (m), 1154 (m), 1116 (w), 1075 (m), 946 (m), 901 (m), 842 (s), 807 (m), 726 (s), 617 (m).

3. Cyanation procedure

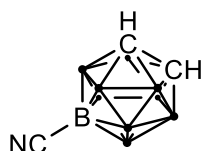


B-Iododicarba-*closo*-dodecaborane (50.0 mg, 185 μmol , 1.00 eq.), CuCN (34.8 mg, 0.39 mmol, 2.10 eq.), Pd(PPh₃)₄ (17.1 mg, 15.2 μmol , 8 mol%) and DMF (1 mL) were added to a microwave vessel (8 cm, ϕ = 1 cm) and closed with a cap. The microwave parameters (CEM *Discover* microwave) were set to 170 W, 130 $^\circ\text{C}$, 10 bar maximum and the reaction was heated for 40 min. The pressure during the reaction process did not exceed 3 bar. The reaction mixture was filtered to remove the solids, which were then washed with CH₂Cl₂. The combined solutions were evaporated to dryness. The crude product was purified by silica gel flash chromatography (CH₂Cl₂/C₆H₁₂) to yield the *B*-cyanodicarba-*closo*-dodecaboranes as white solids.

Upscale: In the used microwave vessel (8 cm, ϕ = 1 cm) an upscale up to 200 mg *B*-iododicarba-*closo*-dodecaborane (in 2.5 mL DMF) was possible giving the same yields as observed for the 50 mg reactions. If larger vessels are used, the microwave parameters might need to be adjusted to reach similar conditions inside the reaction vessel (130 $^\circ\text{C}$, 3 bar).

3.1 Experimental and analytical data of *B*-cyanodicarba-*closo*-dodecaboranes

9-Cyano-1,2-dicarba-*closo*-dodecaborane (2o)



Solvent for silica gel flash chromatography: CH₂Cl₂; **R_f**: 0.70 (CH₂Cl₂).

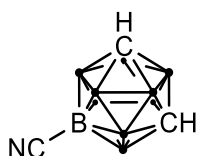
Yield: 26.2 mg (155 μmol , 84%, white solid); **mp:** 241–242 $^\circ\text{C}$.

¹H NMR (CDCl₃, 600 MHz) δ = 3.69 (s, 1H, CH_{cluster}), 3.64 (s, 1H, CH_{cluster}), 2.96–1.64 (vbr, 9H, B₁₀H₉); **¹³C-APT NMR** (CDCl₃, 151 MHz) δ = 123.7 (q, vbr, ¹J_{C,B} \approx 97 Hz, CN), 54.5 (C_{cluster}H), 53.9 (C_{cluster}H); **¹¹B NMR** (CDCl₃, 193 MHz) δ = -1.9 (d, ¹J_{B,H} \approx 160 Hz, 1B), -8.3 (s, 1B, B-CN), -8.8 (d, ¹J_{B,H} \approx 156 Hz, 2B), -13.7 (d, ¹J_{B,H} \approx 158 Hz, 4B), -14.8 (d, ¹J_{B,H} \approx 190 Hz, 2B).

HR-MS (neg) for $C_3B_{10}H_{10}N^- [M-H]^-$, calc'd: 168.1816 found: 168.1816.

IR (cm^{-1}): $\tilde{\nu} = 3070$ (m, $\nu(C_{cluster}H)$), 3045 (s, $\nu(C_{cluster}H)$), 2954 (w), 2924 (m), 2853 (w), 2643 (m, $\nu(BH)$), 2619 (s, $\nu(BH)$), 2599 (s, $\nu(BH)$), 1207 (m), 1155 (m), 1024 (s), 1009 (m), 926 (m), 832 (m), 729 (s), 419 (m).

9-Cyano-1,7-dicarba-closo-dodecaborane (2m)



Solvent for silica gel flash chromatography: CH_2Cl_2 ; **R_f** : 0.62 (CH_2Cl_2).

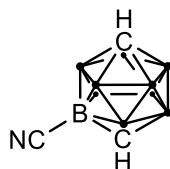
Yield: 26.4 mg (156 μ mol, 84%, white solid); **mp:** 199 – 203 $^{\circ}C$.

1H NMR ($CDCl_3$, 600 MHz) $\delta = 3.06$ (s, 2H, $CH_{cluster}$), 3.04–1.82 (vbr, 9H, $B_{10}H_9$); **^{13}C -APT NMR** ($CDCl_3$, 151 MHz) $\delta = 123.0$ (q, $^1J_{C,B} = 101$ Hz, CN), 55.2 ($C_{cluster}H$); **^{11}B NMR** ($CDCl_3$, 193 MHz) $\delta = -6.0$ (d, $^1J_{B,H} = 170$ Hz, 2B), -9.6 (d, $^1J_{B,H} \approx 157$ Hz, 1B), -12.8 (d, $^1J_{B,H} \approx 164$ Hz, 2B), -13.1 (d, $^1J_{B,H} \approx 164$ Hz, 2B), -15.0 (s, 1B, B-CN), -16.6 (d, $^1J_{B,H} \approx 192$ Hz, 1B), -16.9 (d, $^1J_{B,H} \approx 194$ Hz, 1B).

HR-MS (neg) for $C_3B_{10}H_{10}N^- [M-H]^-$, calc'd: 168.1816 found: 168.1828.

IR (cm^{-1}): $\tilde{\nu} = 3049$ (s, $\nu(C_{cluster}H)$), 2607 (s, $\nu(BH)$), 2585 (s, $\nu(BH)$), 1436 (w), 1175 (m), 1119 (m), 1065 (m), 1007 (m), 976 (m), 893 (m), 828 (w), 812 (m), 776 (w), 755 (m), 720 (s), 694 (s), 588 (w), 540 (s), 416 (m).

2-Cyano-1,12-dicarba-closo-dodecaborane (2p)



Solvent for silica gel flash chromatography: (CH_2Cl_2/C_6H_{12}); 7/3; **R_f** : 0.73 (CH_2Cl_2).

Yield: 27.9 mg, (165 μ mol, 89%, white solid); **mp:** 206 – 207 $^{\circ}C$.

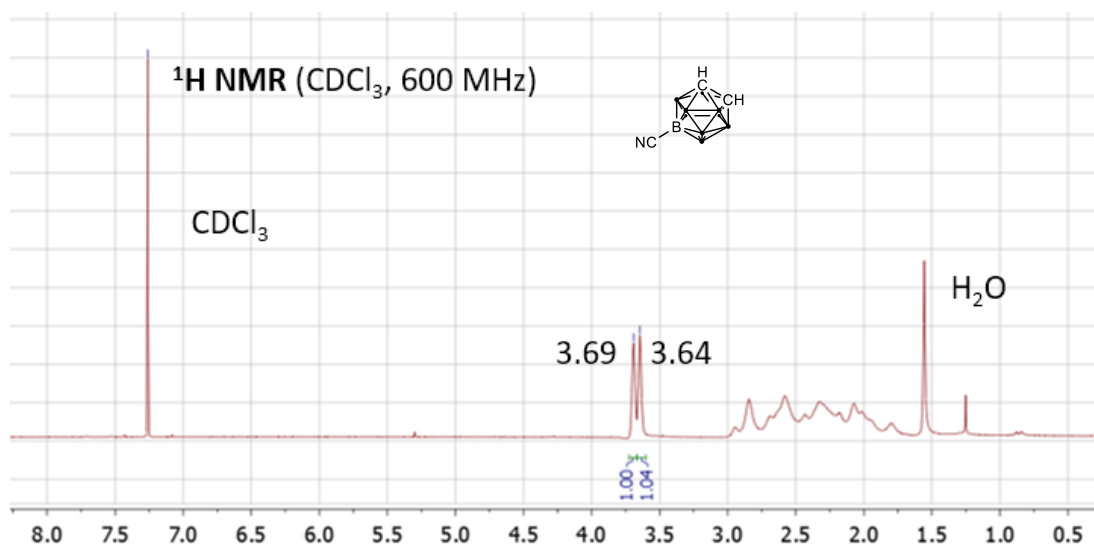
^1H NMR (CDCl_3 , 600 MHz) δ = 3.14 (s, 1H, $\text{CH}_{\text{cluster}}$), 2.92 (s, 1H, $\text{CH}_{\text{cluster}}$), 2.89–1.78 (vbr, 9H, B_{10}H_9); **^{13}C NMR** (CDCl_3 , 151 MHz) δ = 122.0 (q, $^1J_{\text{C,B}}$ = 107 Hz, CN), 65.9 ($\text{C}_{\text{clusterH}}$), 64.9 ($\text{C}_{\text{clusterH}}$); **^{11}B NMR** (CDCl_3 , 193 MHz) δ = –13.9 to –14.3 (m, vbr, 9B), –19.2 (s, 1B, B-CN).

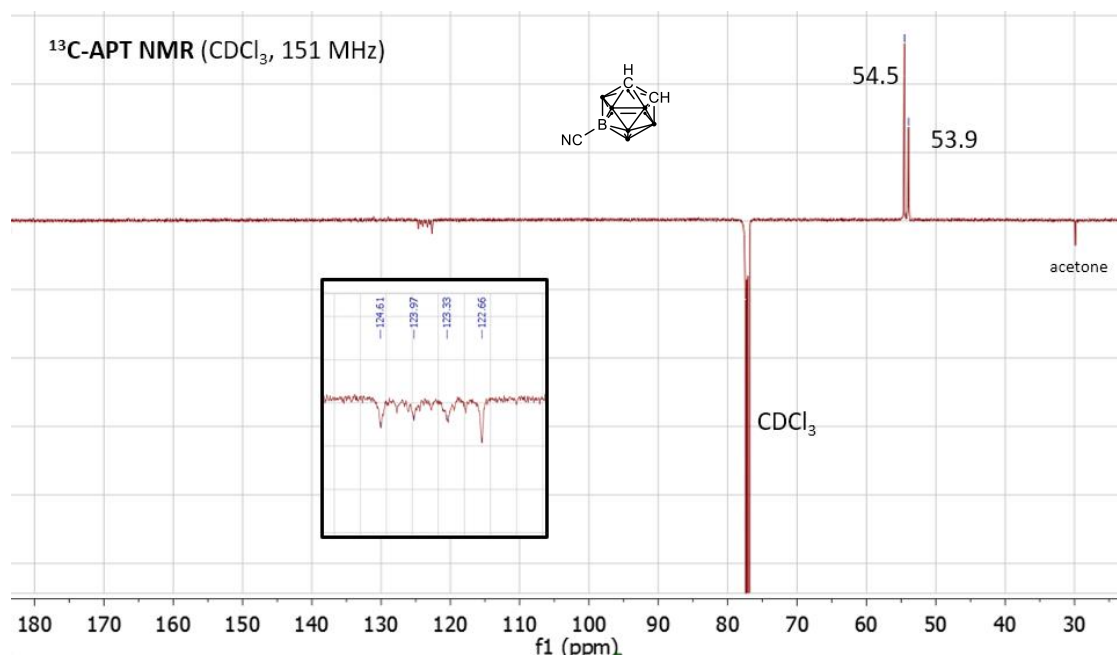
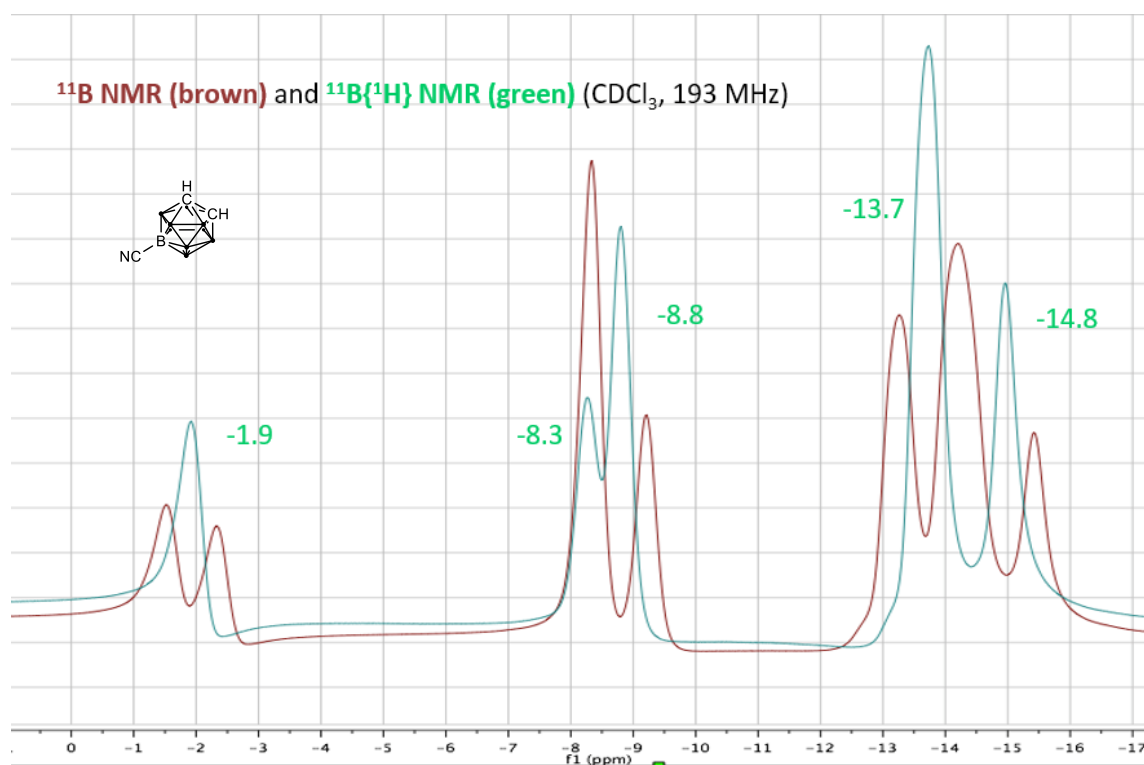
HR-MS (neg) for $\text{C}_3\text{B}_{10}\text{H}_{10}\text{N}^- [\text{M-H}]^-$, calc'd: 168.1816 found: 168.1824

IR (cm^{-1}): $\tilde{\nu}$ = 3049 (w, $\nu(\text{C}_{\text{clusterH}}$)), 2962 (w, $\nu(\text{C}_{\text{clusterH}}$)), 2627 (m, $\nu(\text{BH})$), 2616 (s, $\nu(\text{BH})$), 2598 (m, $\nu(\text{BH})$), 2360 (w), 2323 (w), 1733 (w), 1684 (w), 1636 (w), 1507 (m), 1260 (m), 1180 (m), 1091 (m), 1059 (s), 969 (s), 881 (m), 800 (s), 734 (s).

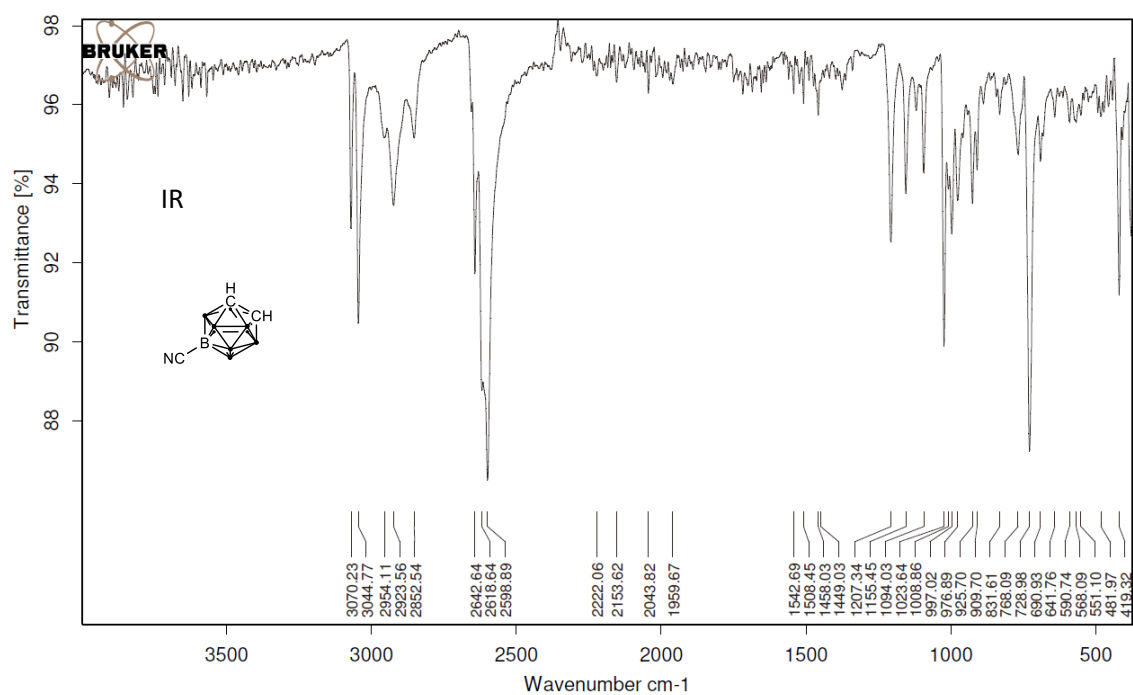
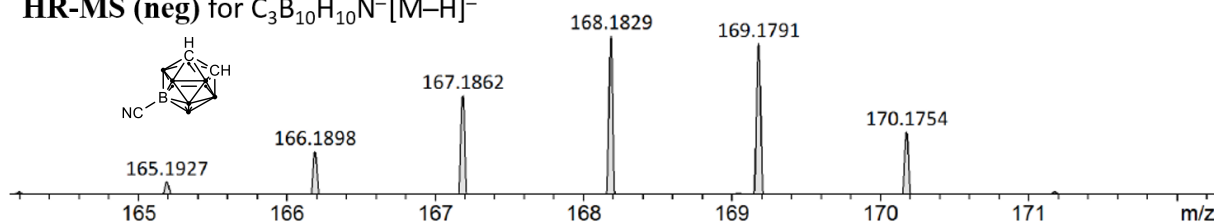
3.2 NMR-, IR-, HR-MS spectra of *B*-cyanodicarba-*closo*-dodecaboranes

9-Cyano-1,2-dicarba-*closo*-dodecaborane (2o)

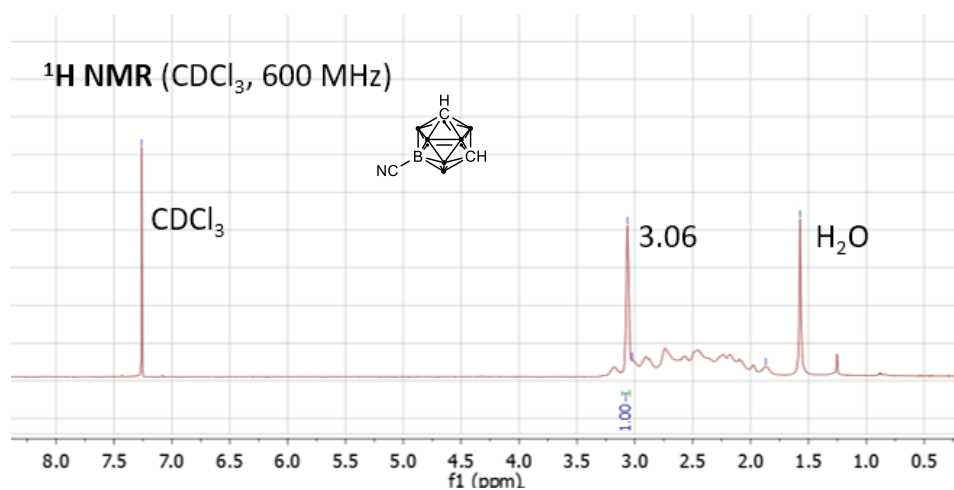




HR-MS (neg) for $C_3B_{10}H_{10}N^- [M-H]^-$



9-Cyano-1,7-dicarba-*closo*-dodecaborane (2m)



Chemical structure of nidoheptaborane (1) is shown in the top left corner. The structure is a nidoheptaborane cage with a cyano group (NC) attached to one of the boron atoms.

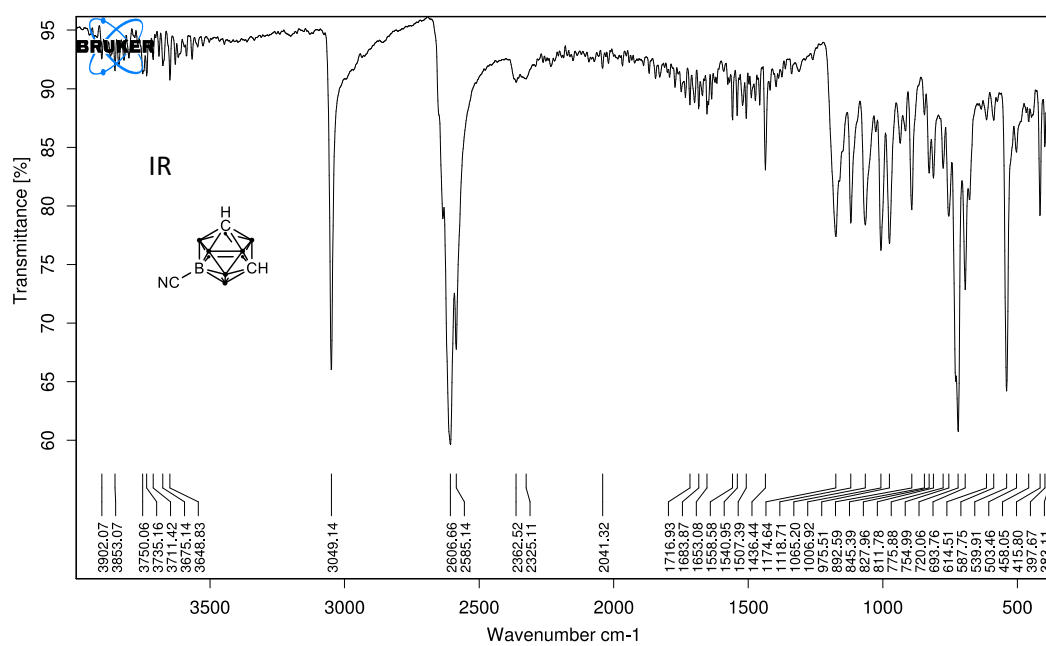
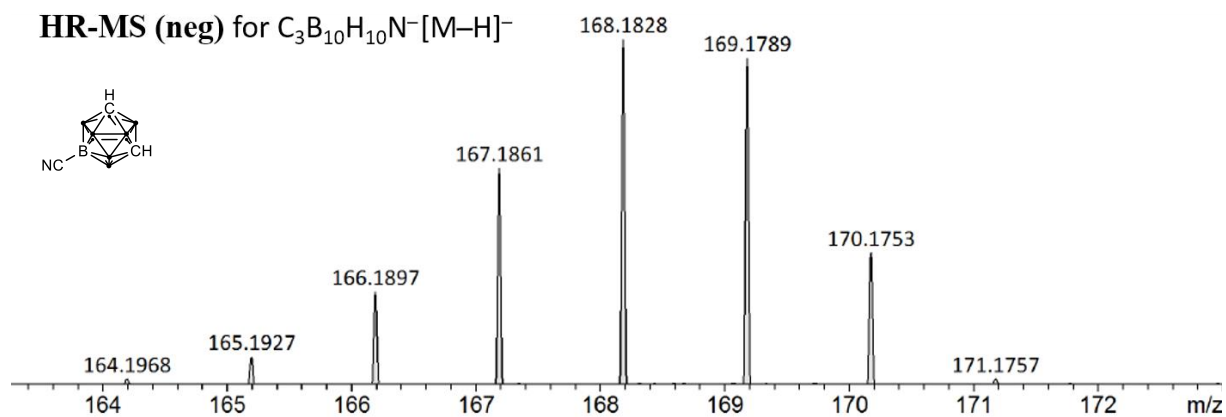
The ^{13}C NMR spectrum shows two traces (red and blue) with the following chemical shift values (ppm) labeled in green:

- 6.0
- 9.6
- 12.8
- 13.1
- 15.0
- 16.6
- 16.9

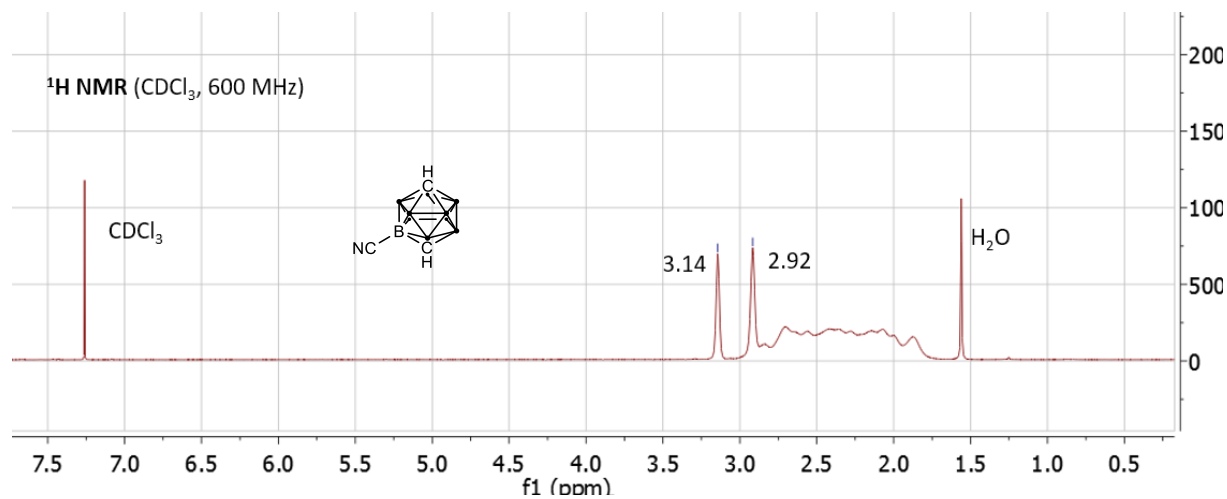
Chemical structure: N#CC1=CC=CC2=C1N=CN=C2

¹³C NMR spectrum (CDCl₃) showing peaks at 124.05, 123.38, 122.71, and 122.05 ppm. The solvent peak (CDCl₃) is at 77.0 ppm. The x-axis is labeled f1 (ppm).

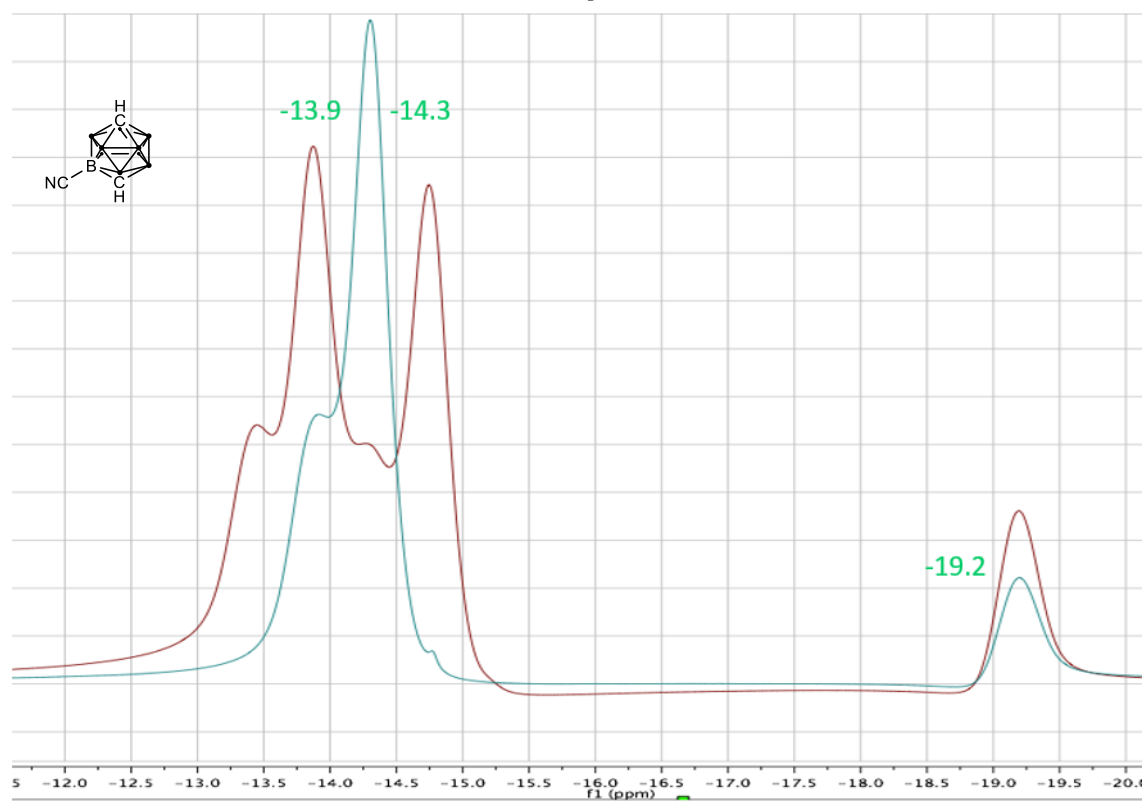
HR-MS (neg) for $C_3B_{10}H_{10}N^-[M-H]^-$

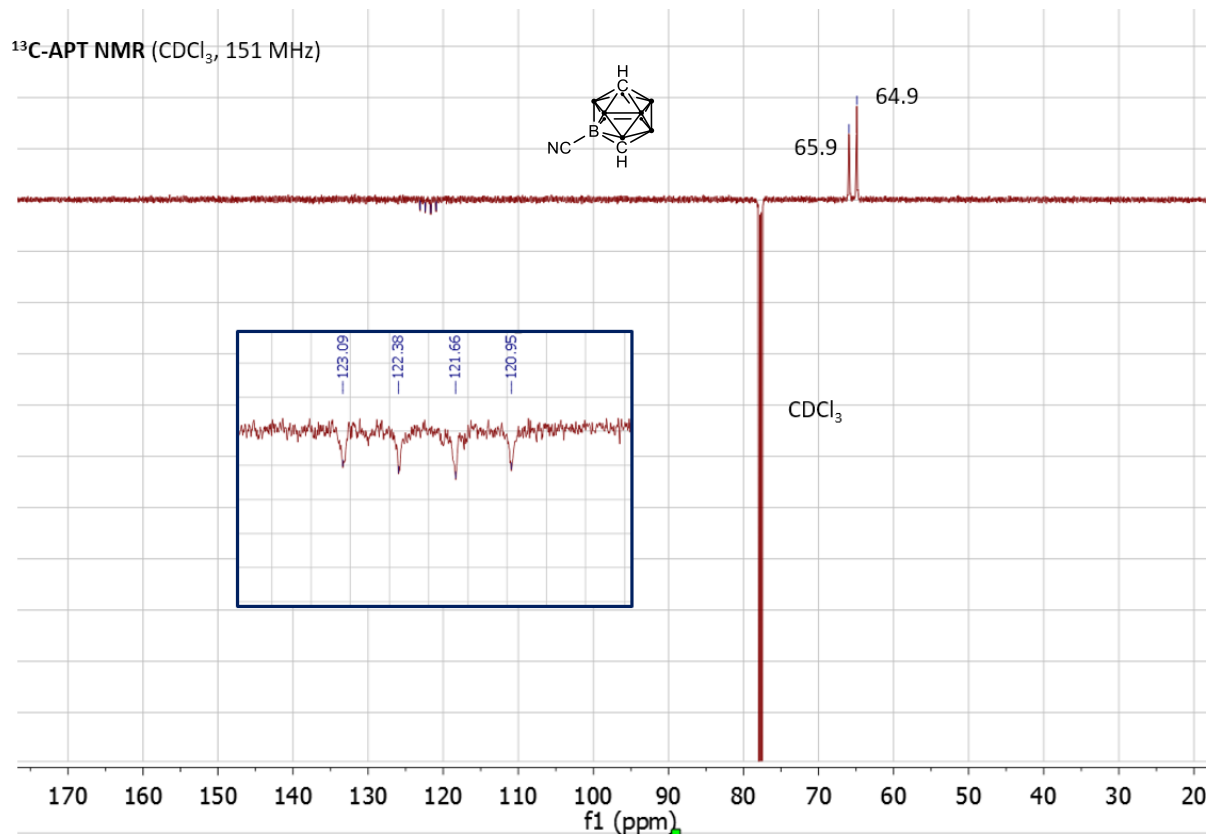


2-Cyano-1,12-dicarba-*closo*-dodecaborane (2p)

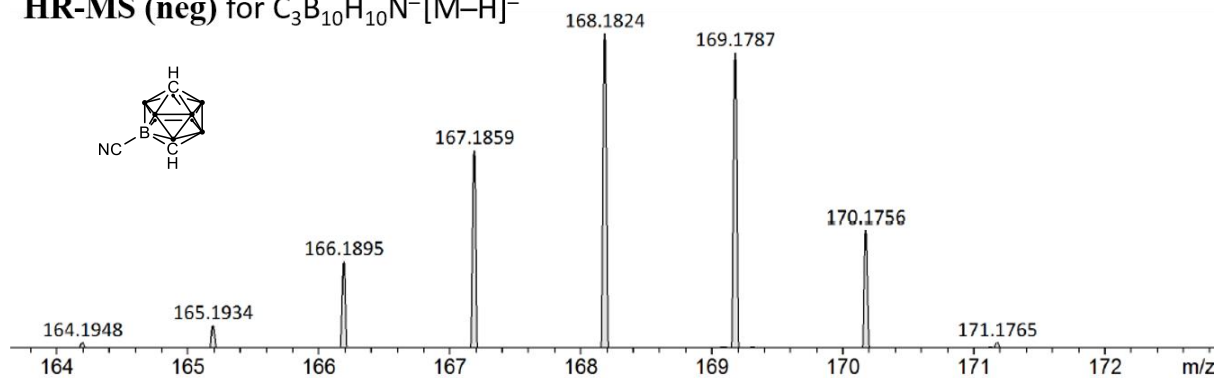


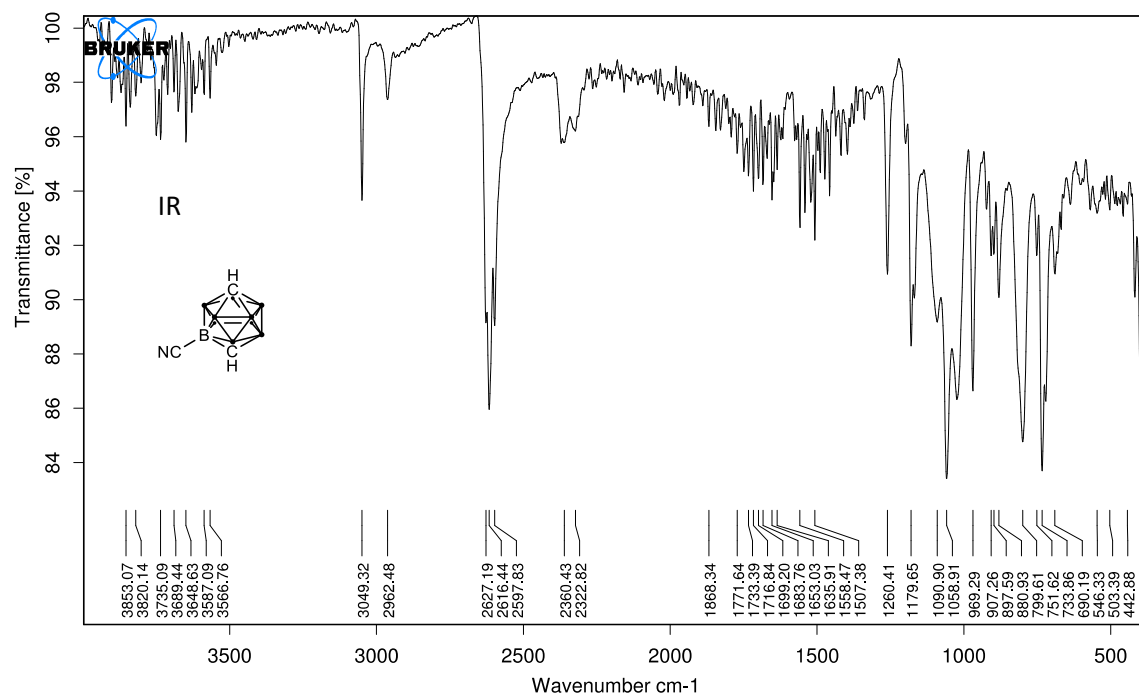
^{11}B NMR (brown) and $^{11}\text{B}\{^1\text{H}\}$ NMR (green) (CDCl_3 , 193 MHz)





HR-MS (neg) for C₃B₁₀H₁₀N⁻[M-H]⁻





4. References

- (1) Way, J. L., *Ann. Rev. Pharmacol. Toxicol.* **1984**, 24, 451-481.
- (2) Petrikovics, I.; Budai, M.; Kovacs, K.; Thompson, D. E., *World J. Methodol.* **2015**, 5, 88-100.
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