

## SUPPLEMENTARY MATERIALS FOR

### **Novel Synthetic Approach to the Charge-Compensated Phosphonio-*nido*-Carboranes. Synthesis and Structural Characterization of Neutral Mono and Bis(Phosphonio) *nido*- *ortho*-Carboranes**

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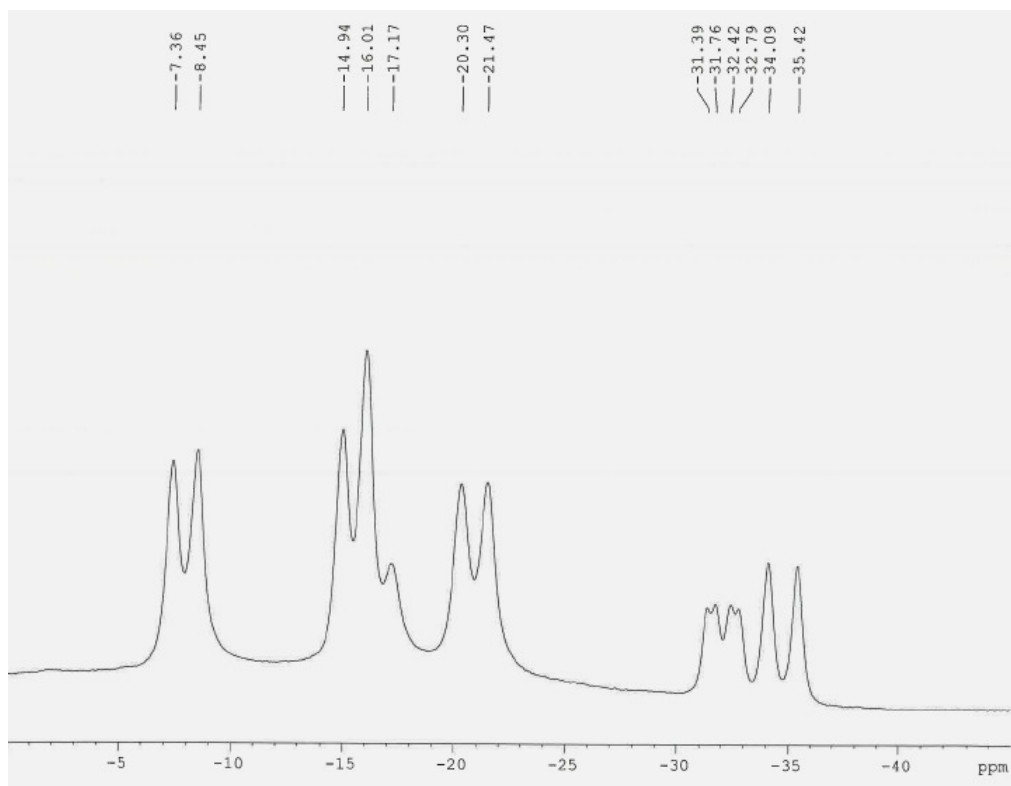
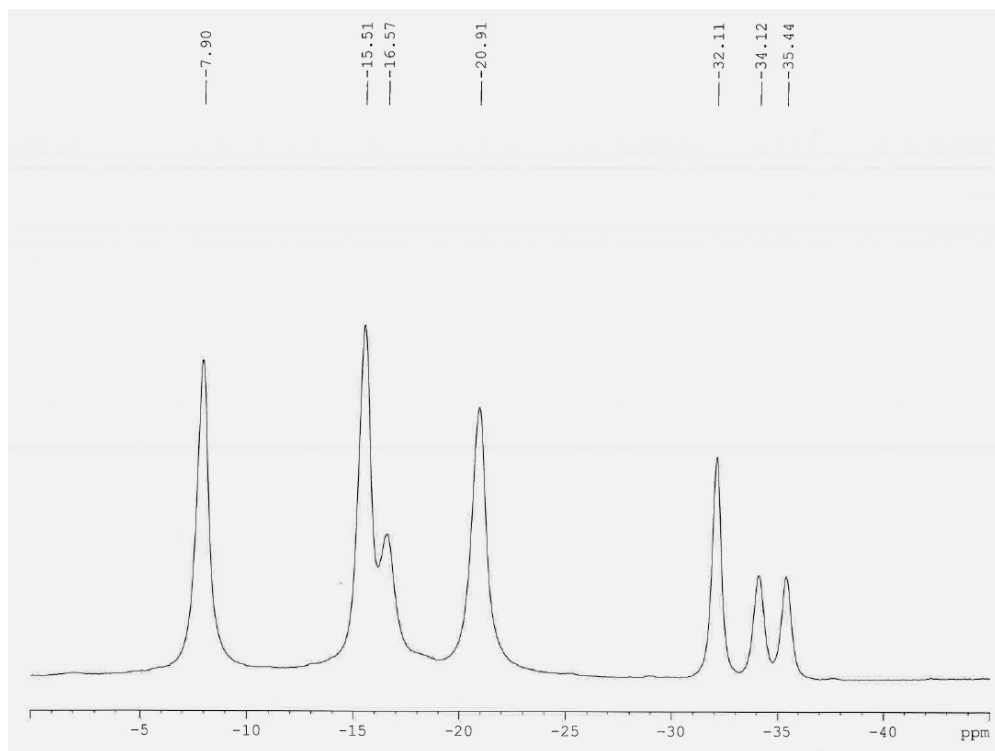
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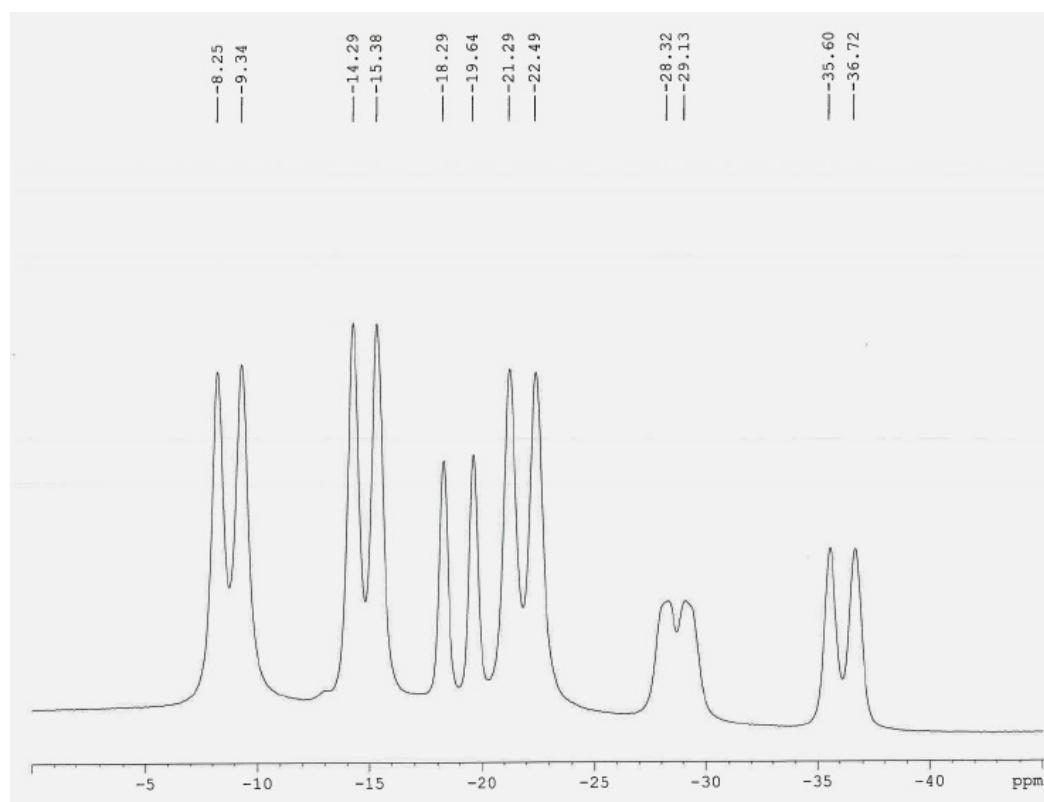
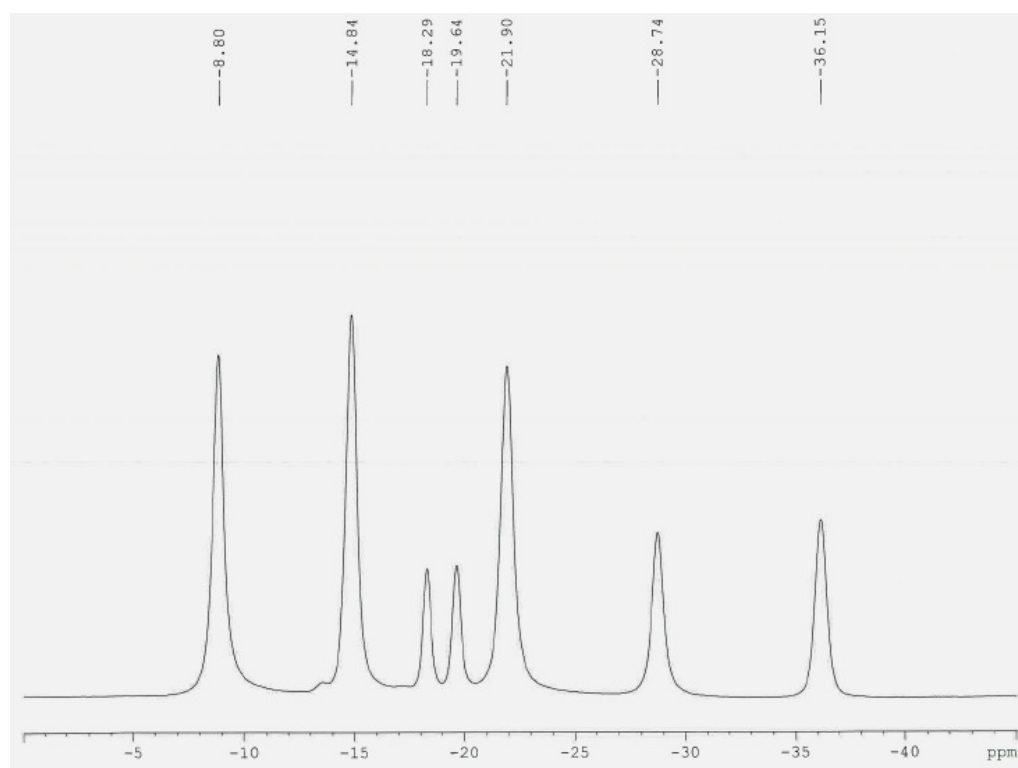
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## I. Boron NMR spectra of compounds 2a-d, 4, 6, 8, 9, 10, and 12

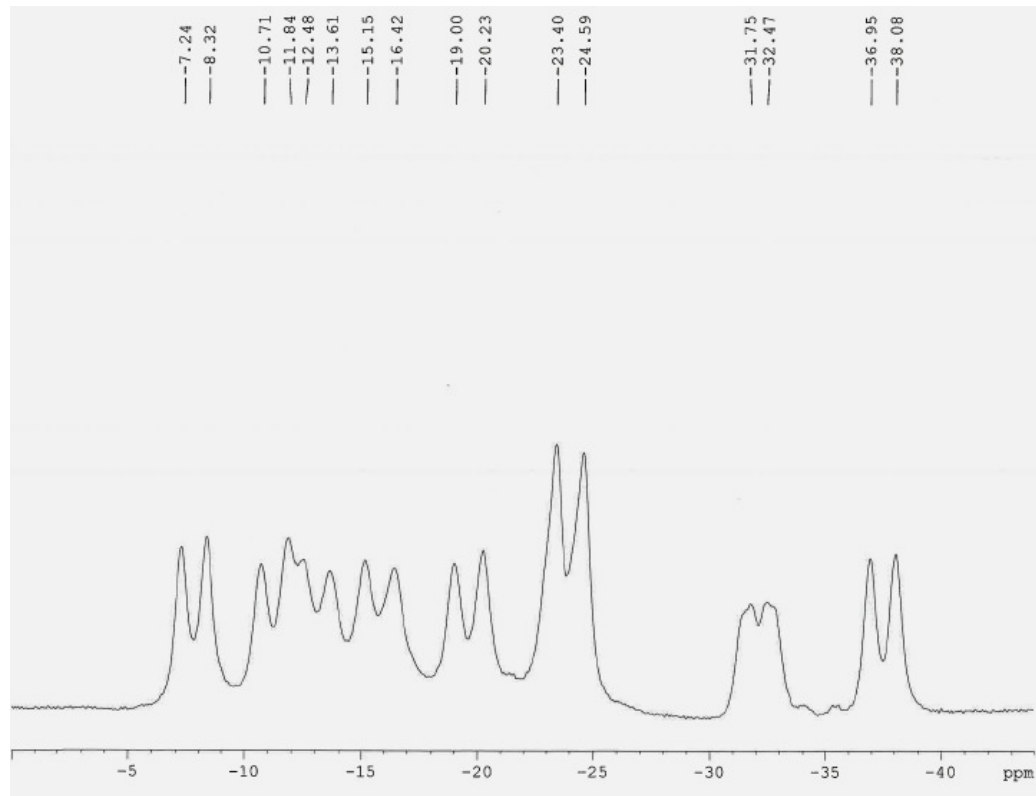
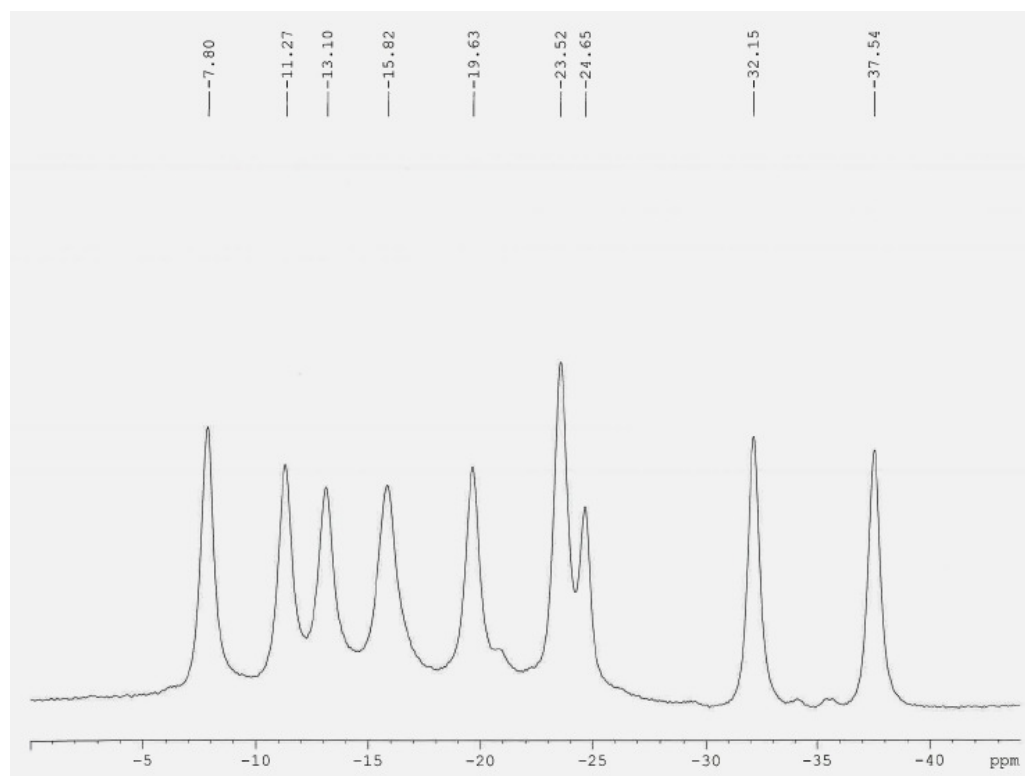
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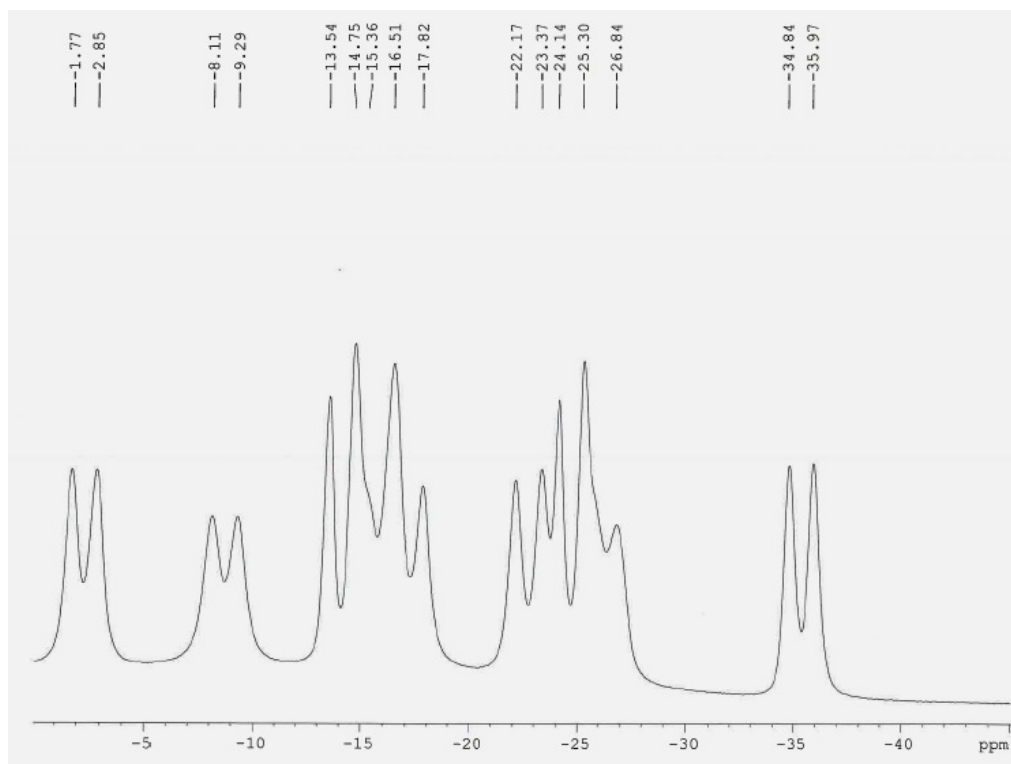
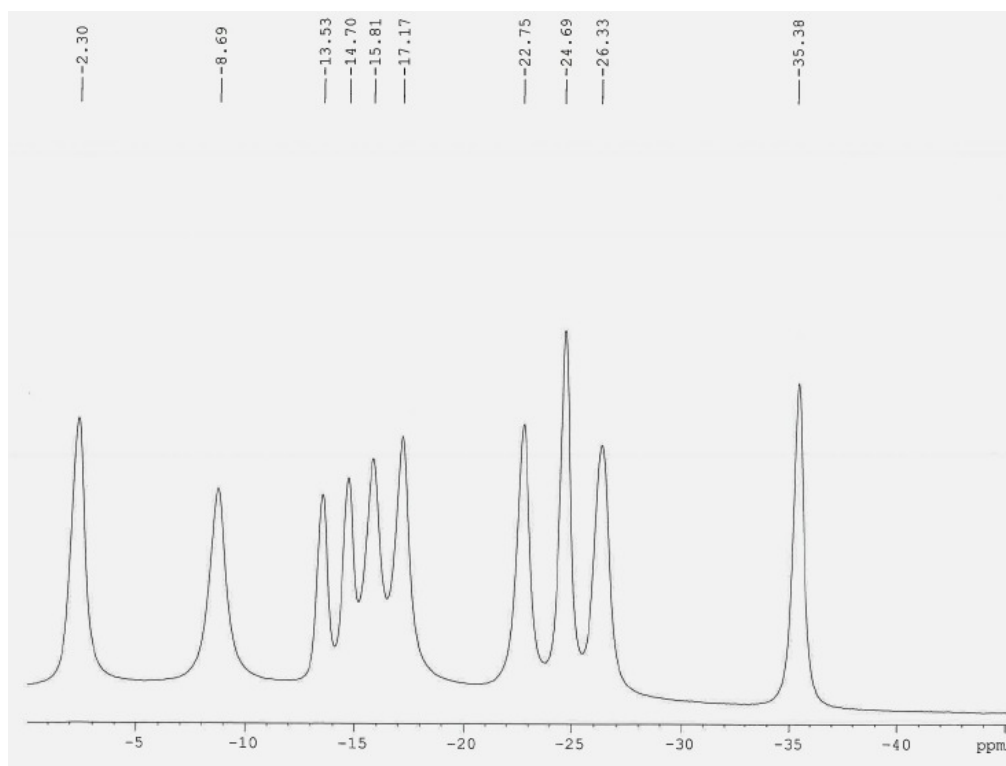
**Boron NMR spectra of compound 2b.**



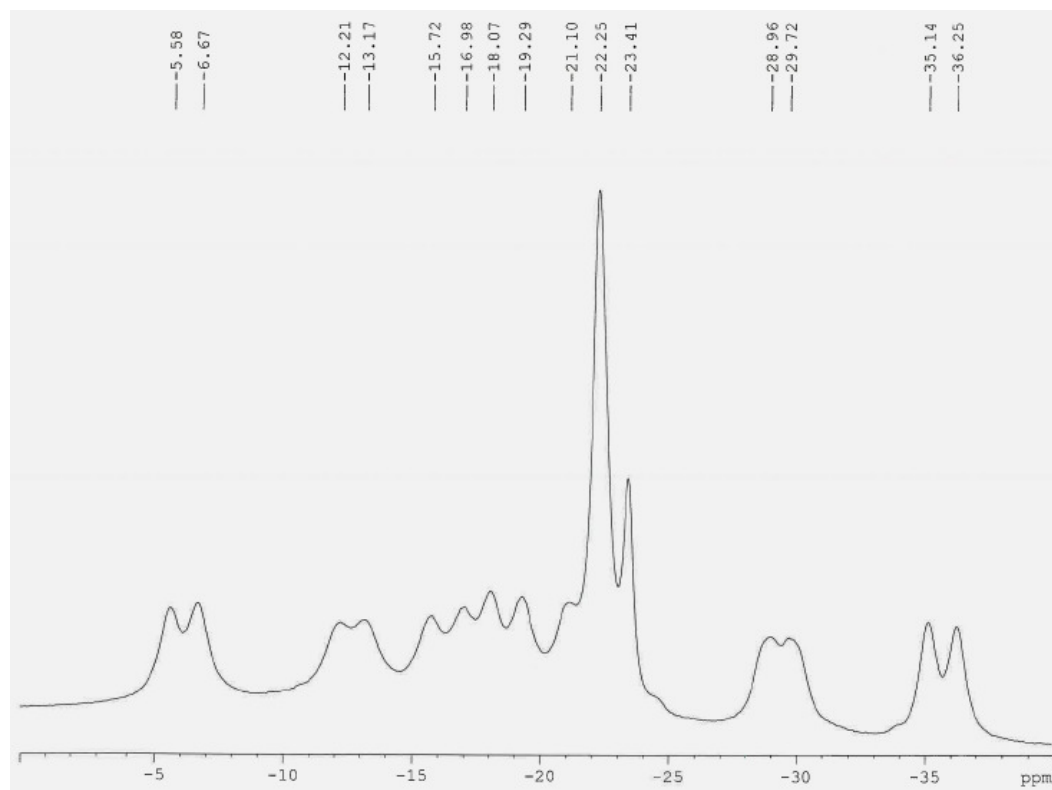
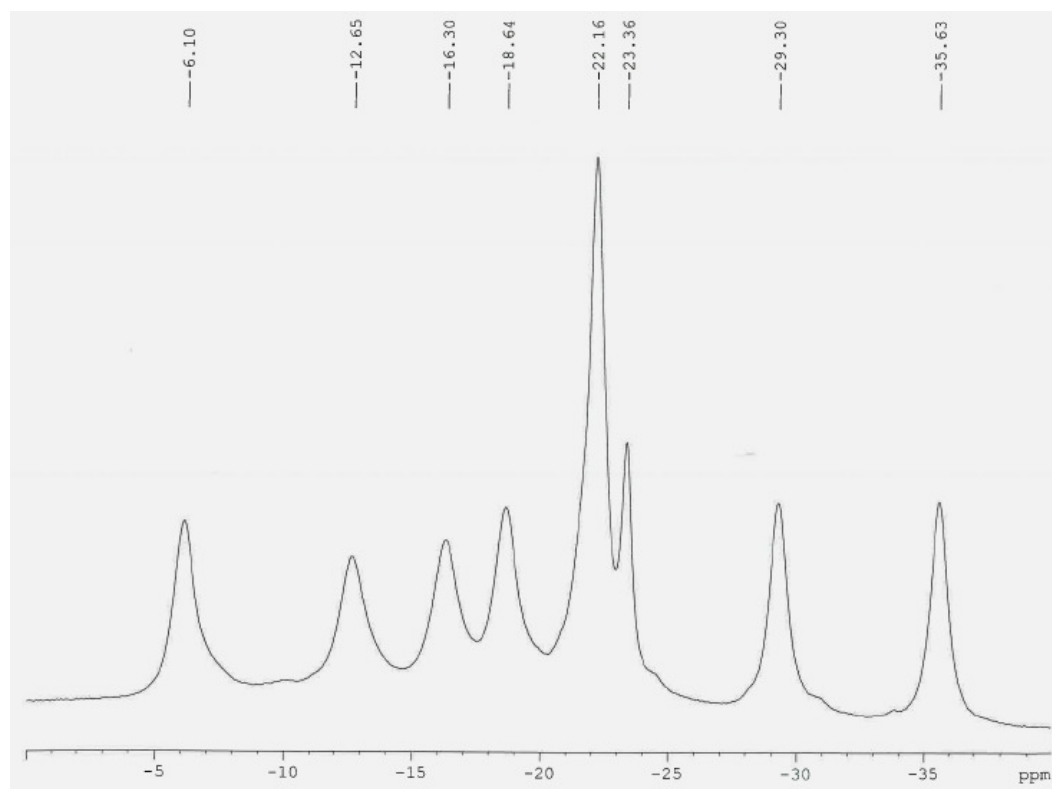
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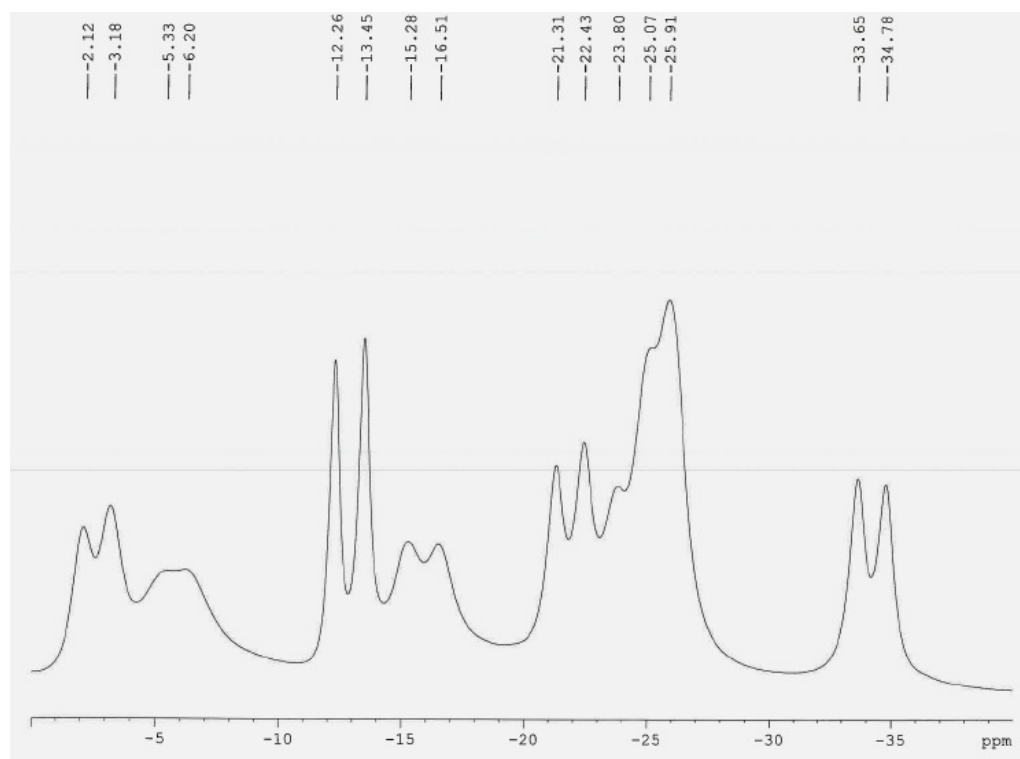
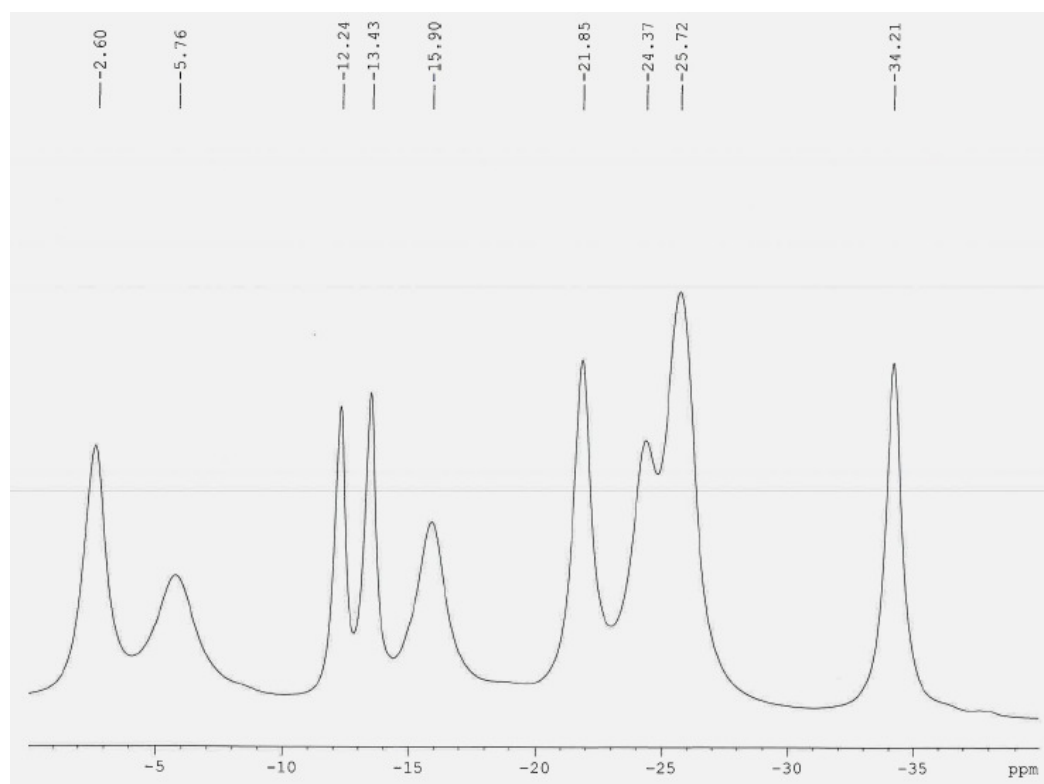
**Boron NMR spectra of compound 2d.**



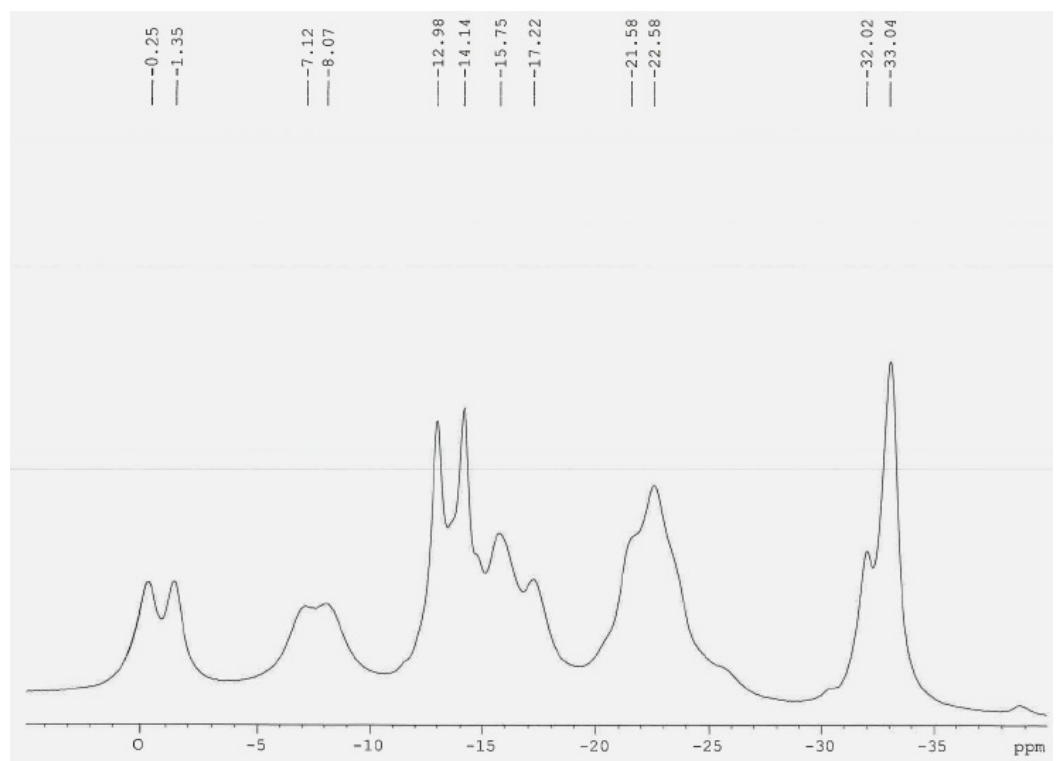
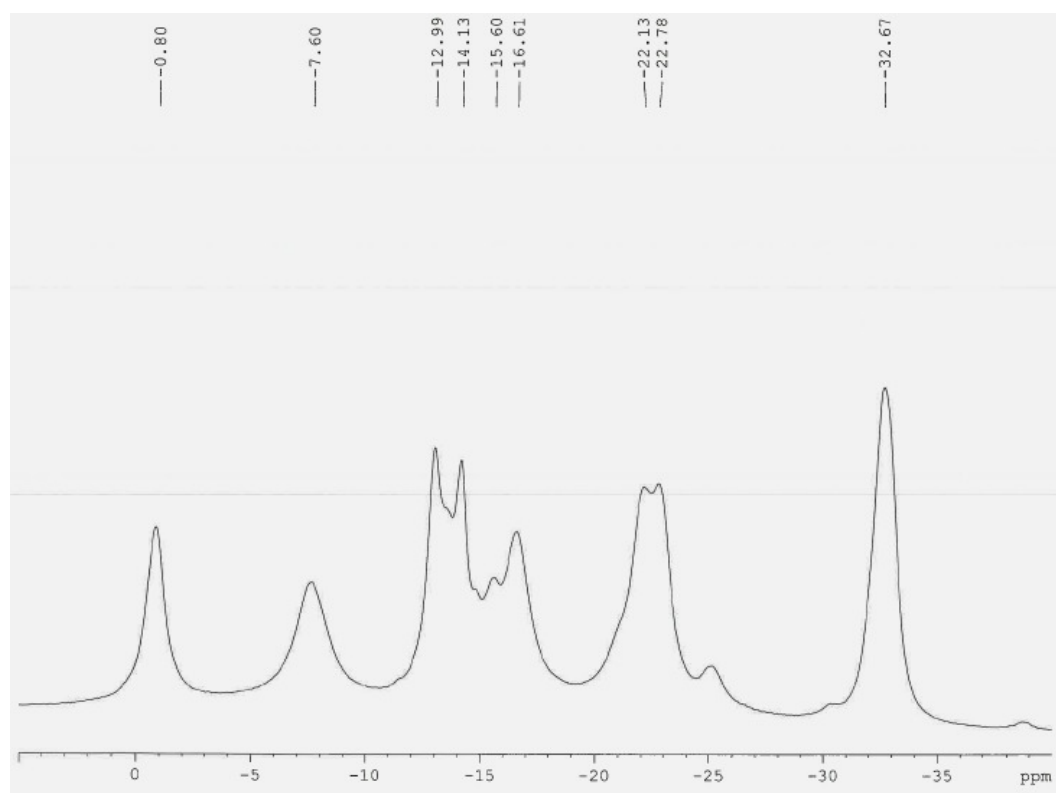
**Boron NMR spectra of compound 4.**



**Boron NMR spectra of compound 6.**

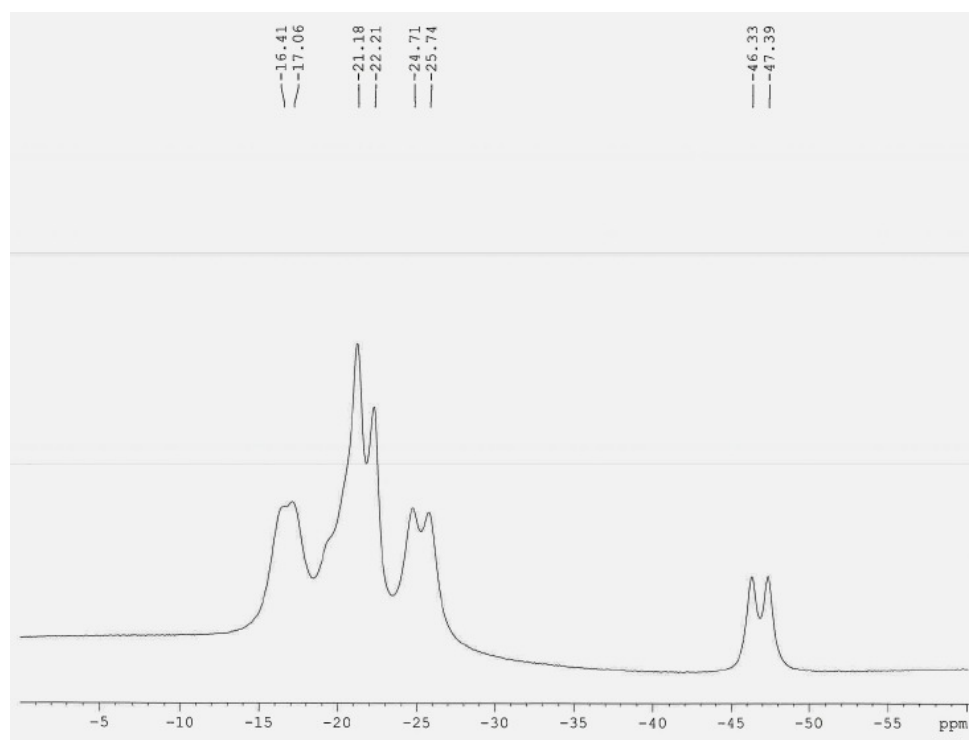
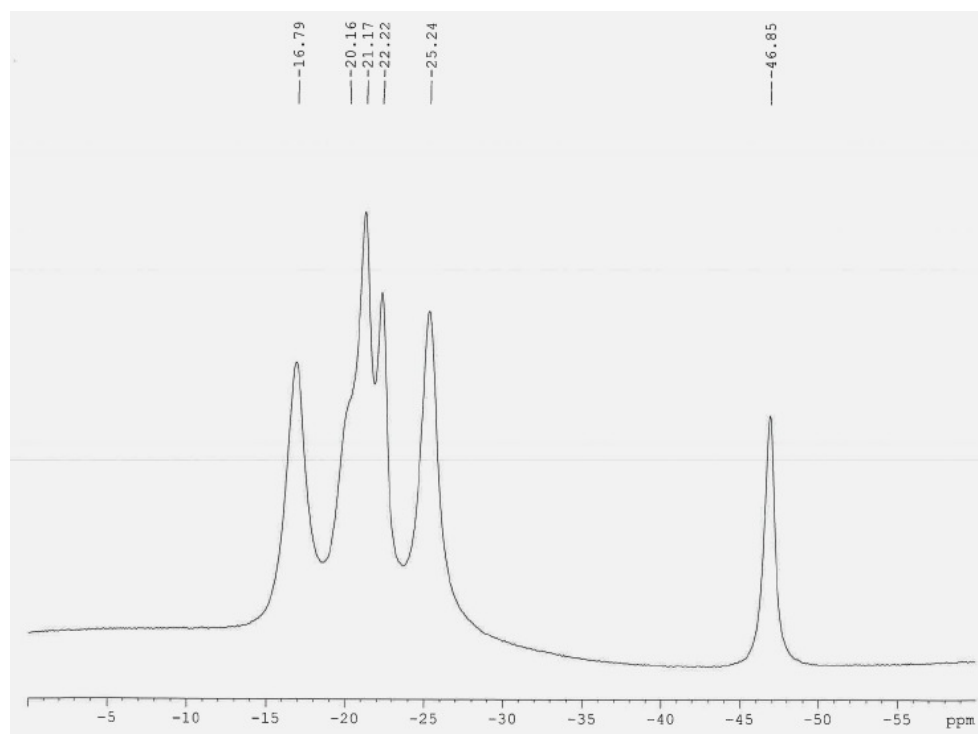


**Boron NMR spectra of compound 8.**

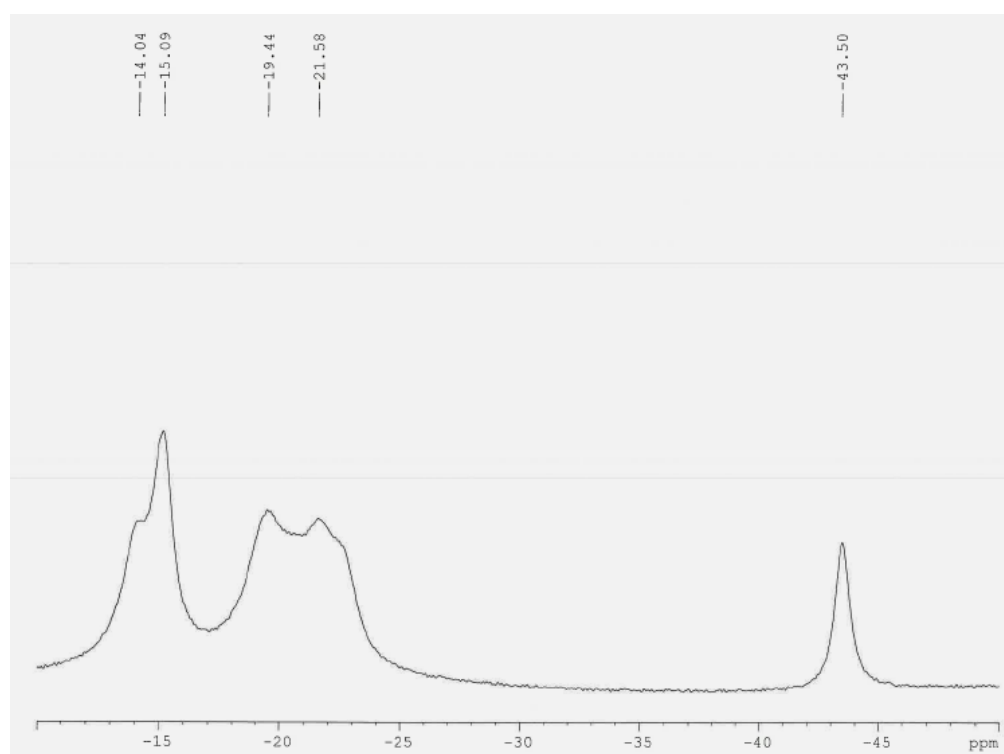
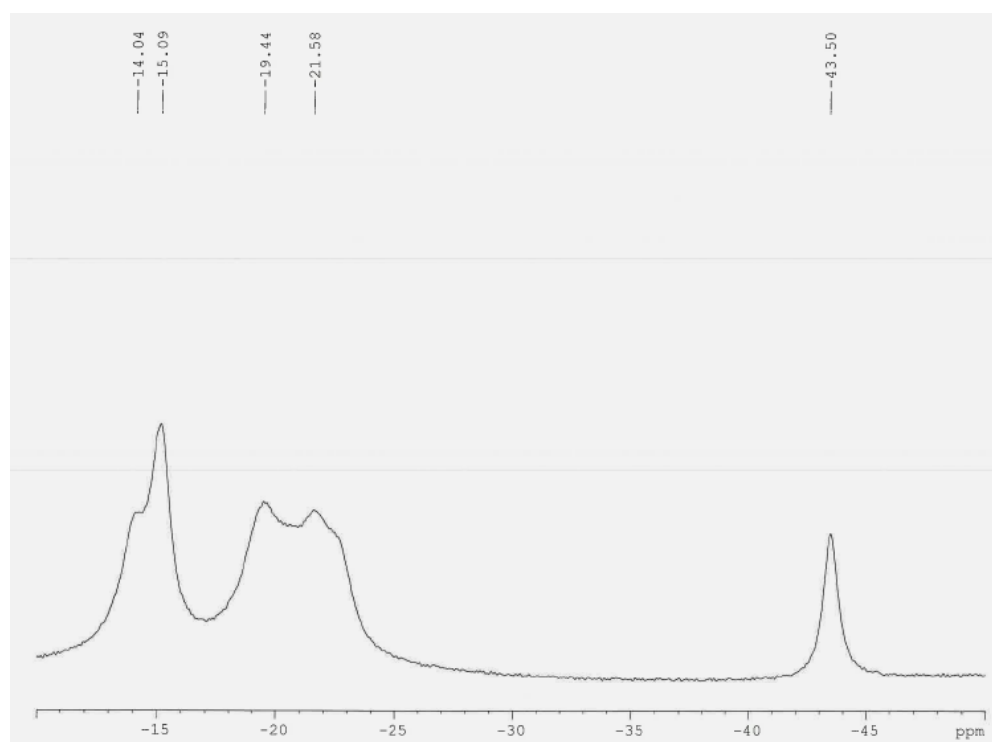




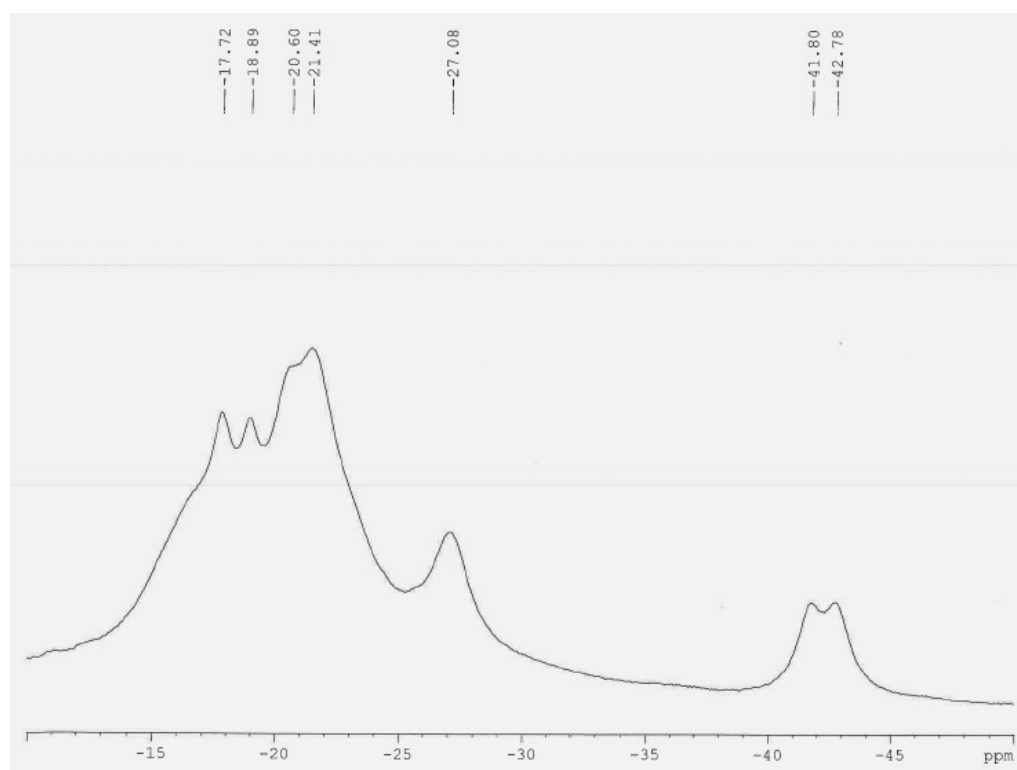
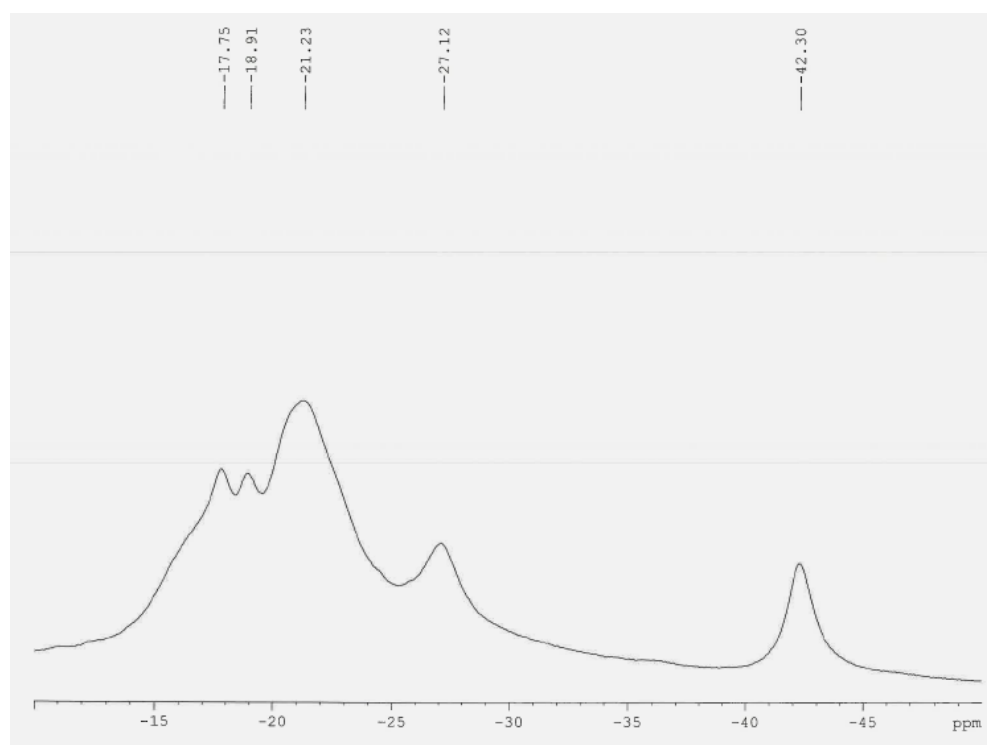
**Boron NMR spectra of compound 9.**



**Boron NMR spectra of compound 10.**



**Boron NMR spectra of compound 12.**



## II. X-ray experimental

**X-ray Diffraction Experiment for compound 2c.** X-ray quality crystals of the compound **2c** were obtained by the slow vapor diffusion of hexane into dichloromethane. Colorless block of **2c** was coated with paratone oil and mounted onto a MiTeGen MicroMount fiber. Complete and redundant data were collected on a single flash-cooled crystal ( $T = 100$  K with an Oxford Cryostream LT device) using a Bruker X8 Prospector Ultra X-ray diffractometer system with a three-circle goniometer and an APEX II CCD area detector mounted on D8-platform and equipped with a Cu-I $\mu$ S ( $\lambda = 1.54178$  Å) microfocus X-ray source operated at 30 W. The frames were collected with a scan width of  $0.5^\circ$  in  $\omega$  and an exposure time of 20 s/frame. The intensity datasets consisted of  $\phi$  and  $\omega$  scans at a crystal to detector distance of 4.00 cm. The APEX II<sup>1</sup> and SAINT<sup>2</sup> software packages were used for data collection and data integration. The data were corrected for absorption effects using the SADABS empirical method.<sup>3</sup> The structures were solved and refined using the Bruker SHELXTL<sup>4</sup> software package. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms, except for those on carbon atoms of triphenylphosphonium ligand, were located in difference Fourier maps and were refined individually. The H-atoms of triphenylphosphonium ligand were included at geometrically idealized positions; thus, the refinement was mixed. The crystallographic data and the details of data collection and structure refinement are provided in Table 1S.

**Table 1S.** Crystallographic details for **2c**.

compound	<b>2c</b>
empirical formula	C <sub>20</sub> H <sub>26</sub> B <sub>9</sub> P
Fw	394.67
crystal size (mm <sup>3</sup> )	0.18 × 0.12 × 0.07
crystal system	triclinic
space group	<i>P</i> 1
<i>a</i> (Å)	9.7892(3)
<i>b</i> (Å)	9.9725(2)
<i>c</i> (Å)	12.1570(3)
$\alpha$ (deg)	71.2550(10)
$\beta$ (deg)	87.3180(10)
$\gamma$ (deg)	74.6270(10)
<i>V</i> (Å <sup>3</sup> )	1082.68(5)
<i>Z</i>	2
<i>T</i> (K)	100(2)
$\lambda$ (Å)	1.54178
<i>d</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	1.211
$\mu$ (mm <sup>-1</sup> )	1.121
$\theta_{\max}$ (deg)	66.46
unique data	14889
observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3634
Parameters	315
GOF <sup>a</sup> on <i>F</i> <sup>2</sup>	1.054
<i>R</i> 1 <sup>b</sup> , <i>wR</i> 2 <sup>c</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0358, 0.0960
<i>R</i> 1 <sup>b</sup> , <i>wR</i> 2 <sup>c</sup> (all data)	0.0362, 0.0964
$\Delta\rho_{\max,\min}$ (e·Å <sup>-3</sup> )	0.4749, -0.259
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.68 /0.75

<sup>a</sup> GOF =  $[\Sigma[w(F_o^2 - F_c^2)^2]/(\text{N}_{\text{obs}} - \text{N}_{\text{params}})]^{1/2}$ .

<sup>b</sup> *R*1 =  $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ . <sup>c</sup> *wR*2 =  $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ .

**X-ray Diffraction Experiment for compounds 6, 8, 9, and 12.** Data for **8** and **12** were collected at 100K using a Bruker X8 Prospector Ultra X-ray diffractometer system equipped with a Cu-I $\mu$ S ( $\lambda = 1.54178 \text{ \AA}$ ) microfocus X-ray source operated at 30 W. The intensity datasets consisted of  $\phi$  and  $\omega$  scans at a crystal to detector distance of 4.00 cm. Data for **6** and **9** were collected at 100K using a Bruker SMART diffractometer updated with an Apex II detector and MoK $\alpha$  ( $\lambda=0.71073 \text{ \AA}$ ) radiation from a sealed tube source and graphite monochromator. The intensity datasets consisted of  $\omega$  scans at a crystal to detector distance of 6.00 cm. The APEX II<sup>1</sup> and SAINT<sup>2</sup> software packages were used for data collection and data integration. The data were corrected for absorption effects using the SADABS empirical method.<sup>3</sup> The structures were solved and refined using the Bruker SHELXTL<sup>4</sup> software package or the equivalent SHELX<sup>5</sup> software. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally included at calculated positions using a riding mode, except for bridging H atoms on the carborane cage, which were located in difference maps and refined with isotropic thermal parameters. The crystallographic data and the details of data collection and structure refinement are provided in Table 2S.

**Table 2S.** Crystallographic details for **6**, **8**, **9**, and **12**.

compound	<b>6</b>	<b>8</b>	<b>9</b>	<b>12</b>
Empirical formula	C <sub>20</sub> H <sub>25</sub> B <sub>9</sub> IP	C <sub>20</sub> H <sub>25</sub> B <sub>9</sub> IP	C <sub>40.50</sub> H <sub>44</sub> B <sub>9</sub> Cl <sub>5</sub> P <sub>2</sub>	C <sub>38</sub> H <sub>38</sub> B <sub>9</sub> IP <sub>2</sub>
Formula weight	520.56	520.56	867.23	780.81
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å	1.54178 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P -1	P 21/c	P 21/n	P 21/n
Unit cell dimensions	a = 9.3173(18) Å	a = 16.2403(4) Å	a = 10.2000(7) Å	a = 9.7556(4) Å
	b = 10.190(2) Å	b = 22.5110(5) Å	b = 25.2671(16) Å	b = 25.5594(9) Å
	c = 14.362(3) Å	c = 13.1895(3) Å	c = 16.6713(11) Å	c = 15.4202(6) Å
	α = 74.626(2)°	α = 90°	α = 90°	α = 90°
	β = 89.288(2)°	β = 93.3890(10)°	β = 90.0600(10)°	β = 95.005(2)°
Volume	γ = 63.652(2)°	γ = 90°	γ = 90°	γ = 90°
	1169.4(4) Å <sup>3</sup>	4813.46(19) Å <sup>3</sup>	4296.6(5) Å <sup>3</sup>	3830.3(3) Å <sup>3</sup>
Z	2	8	4	4
Density (calculated)	1.478 Mg/m <sup>3</sup>	1.437 Mg/m <sup>3</sup>	1.341 Mg/m <sup>3</sup>	1.354 Mg/m <sup>3</sup>
Absorption coefficient	1.444 mm <sup>-1</sup>	11.097 mm <sup>-1</sup>	0.443 mm <sup>-1</sup>	7.548 mm <sup>-1</sup>
F(000)	516	2064	1788	1576
Crystal size	0.400 x 0.400 x 0.050	0.500 x 0.120 x 0.020	0.500 x 0.350 x 0.250	0.350 x 0.200 x 0.050
	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>
Theta range for data collection	2.330 to 27.516°	2.725 to 72.166°	1.463 to 26.372°	3.357 to 65.079°
Index ranges	-12 ≤ h ≤ 12	-16 ≤ h ≤ 18	-12 ≤ h ≤ 12	-11 ≤ h ≤ 11
	-13 ≤ k ≤ 13	-27 ≤ k ≤ 25	-31 ≤ k ≤ 31	0 ≤ k ≤ 31
	-18 ≤ l ≤ 18	-16 ≤ l ≤ 13	-20 ≤ l ≤ 20	0 ≤ l ≤ 18
Reflections collected	13502	50559	47325	34627

Independent reflections	5259 [R(int) = 0.0273]	9134 [R(int) = 0.0260]	8795 [R(int) = 0.0394]	6240 [R(int) = 0.0575]
Completeness to theta	25.242° = 99.8%	67.679° = 98.4%	25.242° = 100.0%	67.679° = 90.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.93 and 0.66	0.81 and 0.10	0.90 and 0.84	0.70 and 0.41
Refinement method	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least- squares on F <sup>2</sup>
Data / restraints / parameters	5259 / 1 / 288	9134 / 0 / 587	8795 / 6 / 561	6240 / 0 / 459
Goodness-of-fit on F <sup>2</sup>	1.055	1.053	1.032	1.157
Final R indices [I>2sigma(I)]	R1 = 0.0494 wR2 = 0.1242	R1 = 0.0348 wR2 = 0.0921	R1 = 0.0423 wR2 = 0.0992	R1 = 0.0727 wR2 = 0.1467
R indices (all data)	R1 = 0.0550 wR2 = 0.1291	R1 = 0.0359 wR2 = 0.0929	R1 = 0.0533 wR2 = 0.1064	R1 = 0.0911 wR2 = 0.1496
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole	5.413 and -1.341 e.Å <sup>-3</sup>	1.789 and -0.569 e.Å <sup>-3</sup>	0.602 and -0.680 e.Å <sup>-3</sup>	2.556 and -1.256 e.Å <sup>-3</sup>



## References

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- (1) Bruker, Apex 2 v APEX 2010.7; Bruker AXS Inc.: Madison, WI, 2010.
- (2) Bruker, SAINT v 7.68A; Bruker AXS Inc.: Madison, WI, 2009.
- (3) Sheldrick, G. M. SADABS 2008/1; Gottingen, 2008.
- (4) Sheldrick, G. M. SHELXTL, v 2008/4; Bruker AXS, Inc.: Madison, WI, 2008.
- (5) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.