

## Supporting information

### **Unlocking the Chemistry of the Octahydrotriborate Anion: Robust Synthesis, Structural Elucidation, and Unprecedented Protonation Stability of Diamine-Substituted Derivatives**

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## Contents

<b>NMR data</b> .....	<b>3</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>] (1)</b> .....	<b>5</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>] (2)</b> .....	<b>6</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>4</sub>H<sub>9</sub>] (3)</b> .....	<b>8</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>9</sub>H<sub>19</sub>] (4)</b> .....	<b>9</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>7</sub>H<sub>14</sub>NH<sub>3</sub>]CF<sub>3</sub>COO (5)</b> .....	<b>11</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>8</sub>H<sub>16</sub>NH<sub>3</sub>]CF<sub>3</sub>COO (6)</b> .....	<b>12</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>9</sub>H<sub>18</sub>NH<sub>3</sub>]CF<sub>3</sub>COO (7)</b> .....	<b>14</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>10</sub>H<sub>20</sub>NH<sub>3</sub>]CF<sub>3</sub>COO (8)</b> .....	<b>15</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>12</sub>H<sub>24</sub>NH<sub>3</sub>]CF<sub>3</sub>COO (9)</b> .....	<b>17</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>]Cl (10)</b> .....	<b>18</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]Cl (11)</b> .....	<b>20</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NHC<sub>6</sub>H<sub>5</sub>] (12)</b> .....	<b>21</b>
<b>[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>2</sub>]I (13)</b> .....	<b>23</b>
<b>IR data</b> .....	<b>25</b>
<b>X-Ray Diffraction data</b> .....	<b>25</b>

## NMR data

**Table S1.**  $^{11}\text{B}$  values of chemical shifts of substituted derivatives obtained in this work

Substituent	2B, $\delta$ , ppm	1B, $\delta$ , ppm	Solvent
i-PrNH <sub>2</sub>	-8.33	-30.10	CDCl <sub>3</sub>
BuNH <sub>2</sub>	-8.18	-29.80	CDCl <sub>3</sub>
C <sub>9</sub> H <sub>19</sub> NH <sub>2</sub>	-8.18	-29.80	CDCl <sub>3</sub>
C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	-10.23	-30.55	CDCl <sub>3</sub>
ethylenediamine	-10.86	-29.16	THF
1,2-propylenediamine	-10.11	-29.32	THF
N, N-dimethylaminopropylamine	-8.88	-29.35	THF
	-18.81	-20.60	
N, N-diethylaminoethylamine	-10.42	-29.45	THF
1,7-diaminoheptane	-11.50	-29.50	THF
1,8-diaminooctane	-13.09	-31.20	THF
1,9-diaminononane	-13.05	-31.09	THF
1,10-diaminodecane	-13.20	-31.09	THF
1,12-diaminododecane	-11.83	-29.91	THF
<i>ortho</i> -phenylenediamine	-10.07	-28.75	THF
<i>ortho</i> -N-phenylphenylenediamine	-8.76	-28.49	CDCl <sub>3</sub>

**Table S2.**  $^1\text{H}$  values of chemical shifts of pure ligands and products

Ligand formula	Group	Free ligand, ppm	Compound, ppm	Shift, ppm	Solvent
NH <sub>2</sub> C <sub>6</sub> H <sub>11</sub>	NH <sub>2</sub>	1.18	1.68	0.70	CDCl <sub>3</sub>
	CH	2.62	3.49	0.87	
NH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	NH <sub>2</sub>	1.22	1.73	0.51	CDCl <sub>3</sub>
	CH <sub>2</sub>	3.10	3.28	0.18	
	CH <sub>3</sub>	1.07	1.44 (1.42)	0.37 (0.35)	
NH <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	NH <sub>2</sub>	1.42	1.57	0.15	CDCl <sub>3</sub>

	CH <sub>2</sub>	2.68	2.87	0.19	
<b>NH<sub>2</sub>C<sub>9</sub>H<sub>19</sub></b>	NH <sub>2</sub>	1.14	2.21	1.07	CDCl <sub>3</sub>
	CH <sub>2</sub>	2.67	3.43	0.76	
<b>NH<sub>2</sub>C<sub>7</sub>H<sub>14</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	10.87	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.09	4.86	3.77	
	CH <sub>2</sub>	2.62	3.63	1.01	
<b>NH<sub>2</sub>C<sub>8</sub>H<sub>16</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	10.90	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.09	4.86	3.77	
	CH <sub>2</sub>	2.62	3.62	1.00	
<b>NH<sub>2</sub>C<sub>9</sub>H<sub>18</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	10.87	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.13	4.86	3.65	
	CH <sub>2</sub>	2.67	3.63	1.01	
<b>NH<sub>2</sub>C<sub>10</sub>H<sub>20</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	10.86	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.15	4.86	3.61	
	CH <sub>2</sub>	2.68	3.64	0.96	
<b>NH<sub>2</sub>C<sub>12</sub>H<sub>24</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	10.87	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.18	4.86	3.68	
	CH <sub>2</sub>	2.70	3.62	0.92	
<b>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	8.89	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	4.36	7.78	3.31	
<b>NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	12.30	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	4.18	5.97	1.79	
	CH <sub>2</sub>	2.50	3.35	0.85	
	CH <sub>2</sub>	2.72	3.17	0.45	
<b>NH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>2</sub></b>	NH <sub>3</sub> <sup>+</sup>	-	12.45	-	THF-d <sub>8</sub>
	NH <sub>2</sub>	1.15	4.51	3.36	
	CH <sub>2</sub>	2.74	3.66	0.92	
	CH <sub>2</sub>	2.25	2.73	0.48	

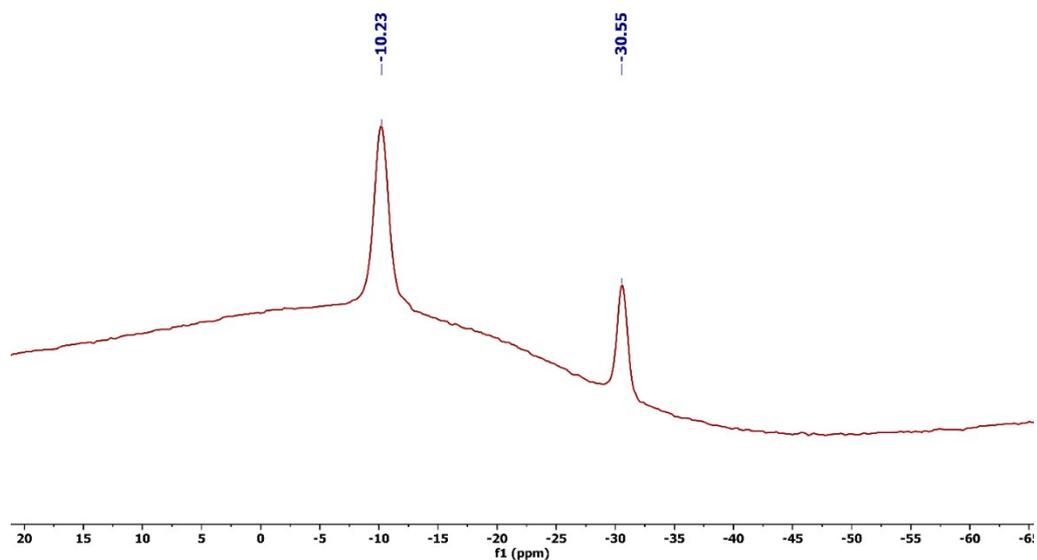


Fig. S1  $^{11}\text{B}$  NMR spectra of (**1**) in  $\text{CDCl}_3$

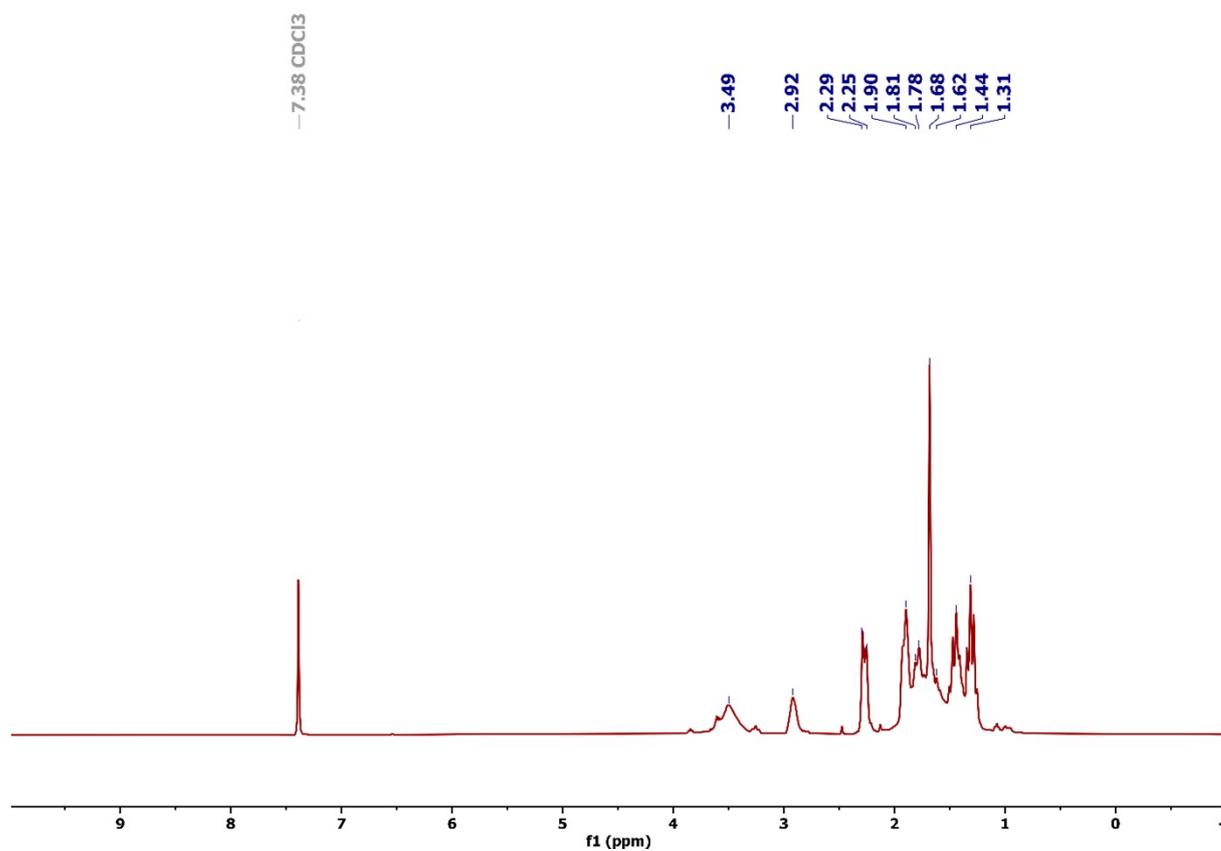


Fig. S2  $^1\text{H}$  NMR spectra of (**1**) in  $\text{CDCl}_3$

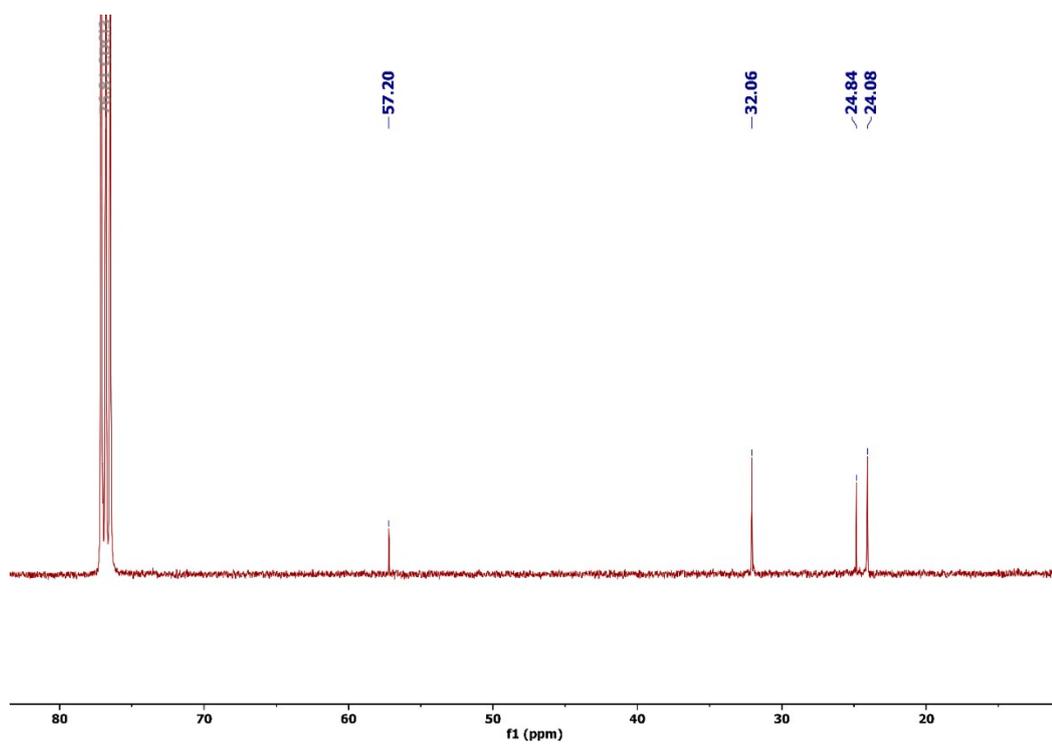


Fig. S3 <sup>13</sup>C<sup>1</sup>H NMR spectra of (1) in CDCl<sub>3</sub>

[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>] (2)

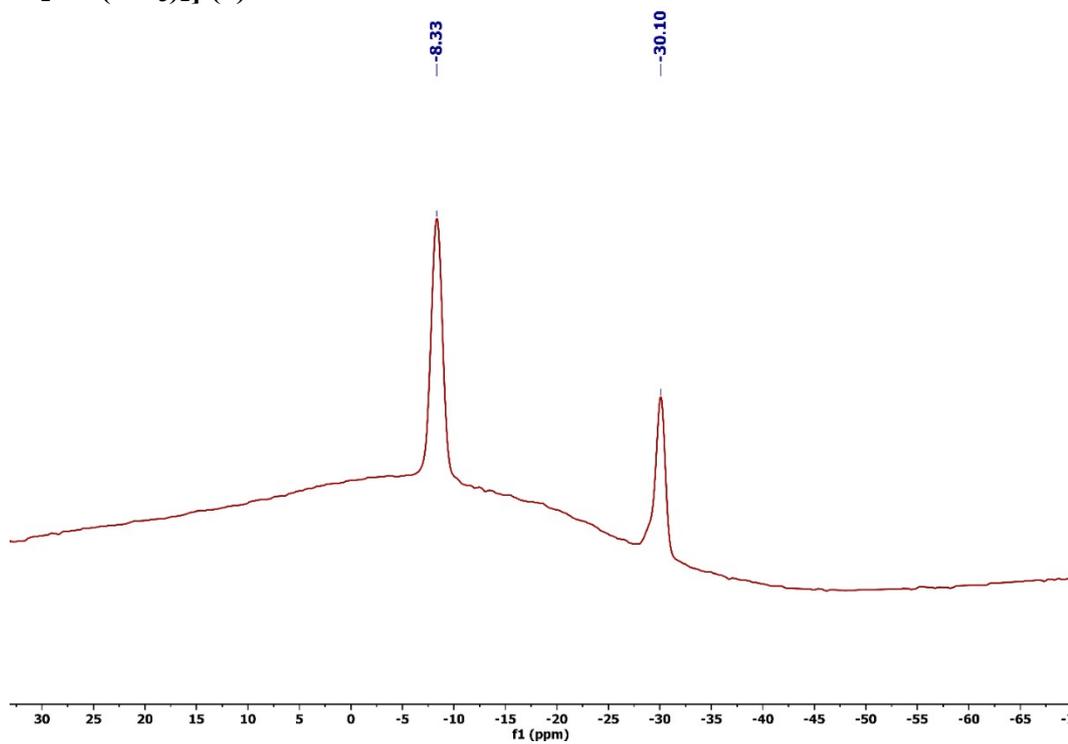


Fig. S4 <sup>11</sup>B NMR spectra of (2) in CDCl<sub>3</sub>

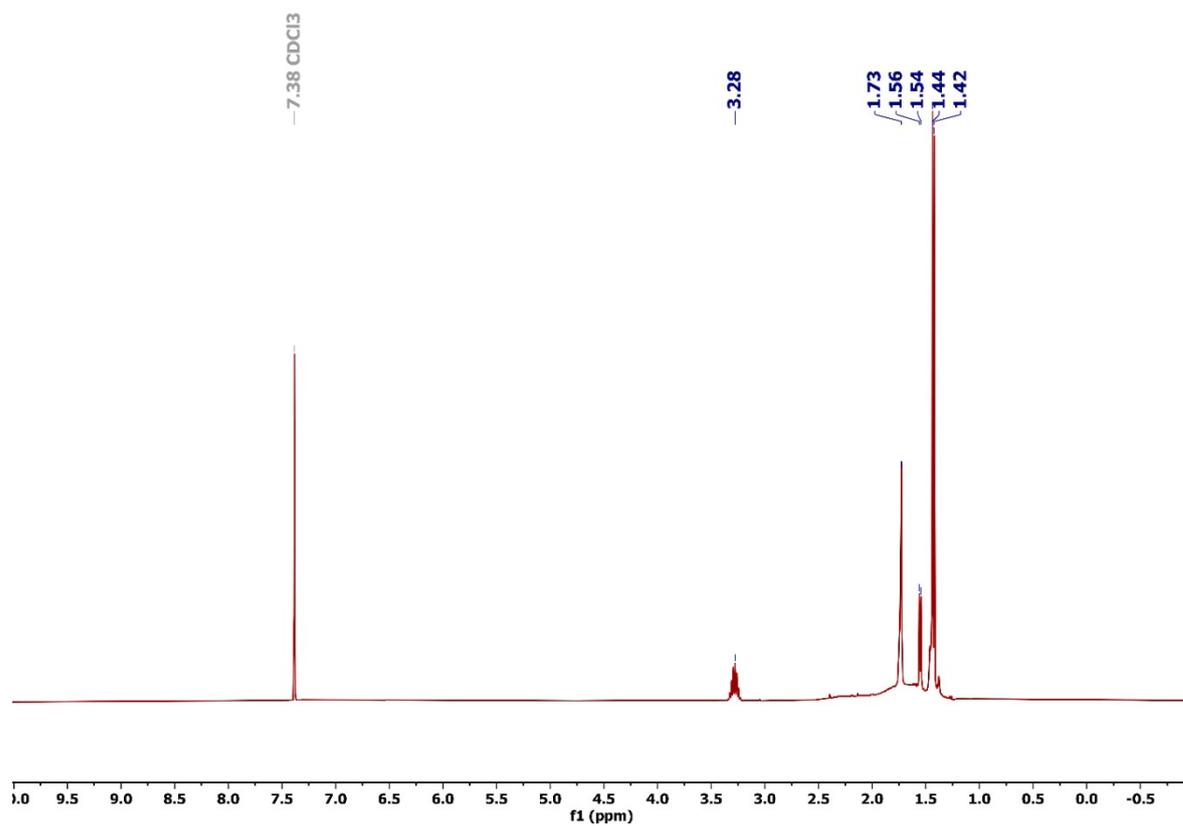


Fig. S5 <sup>1</sup>H NMR spectra of **(2)** in CDCl<sub>3</sub>

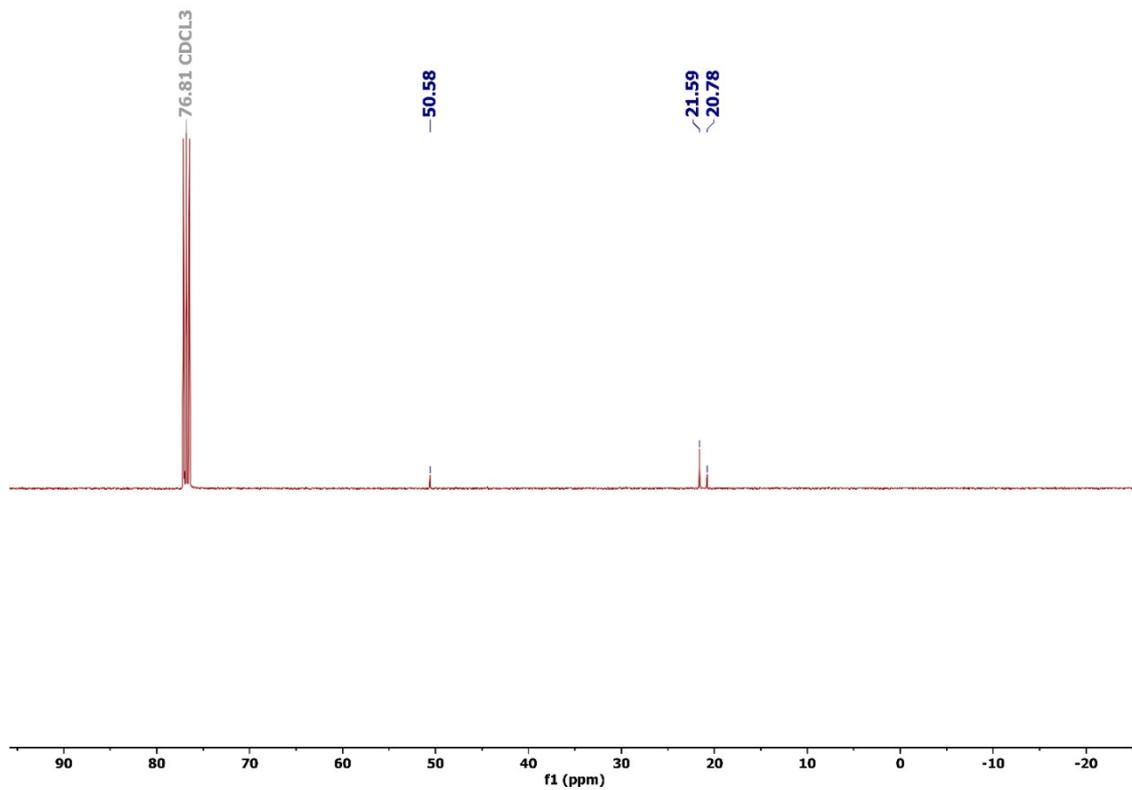


Fig. S6 <sup>13</sup>C NMR spectra of **(2)** in CDCl<sub>3</sub>

[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>4</sub>H<sub>9</sub>] (3)

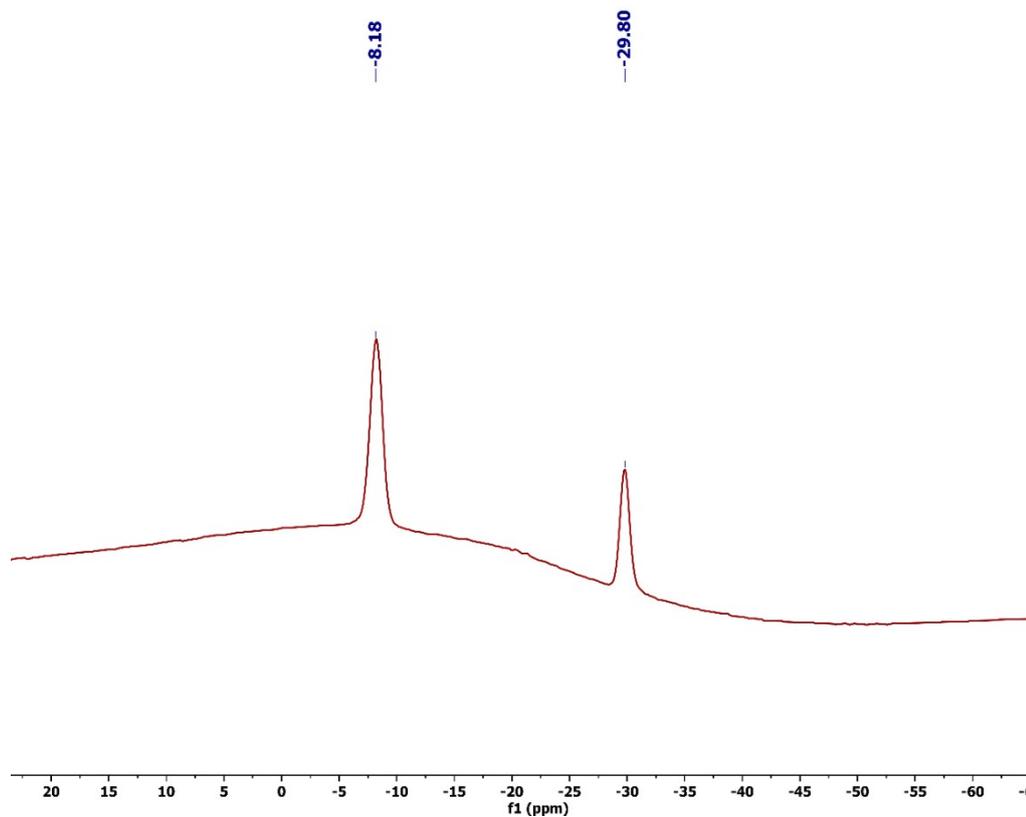


Fig. S7 <sup>11</sup>B NMR spectra of (3) in CDCl<sub>3</sub>

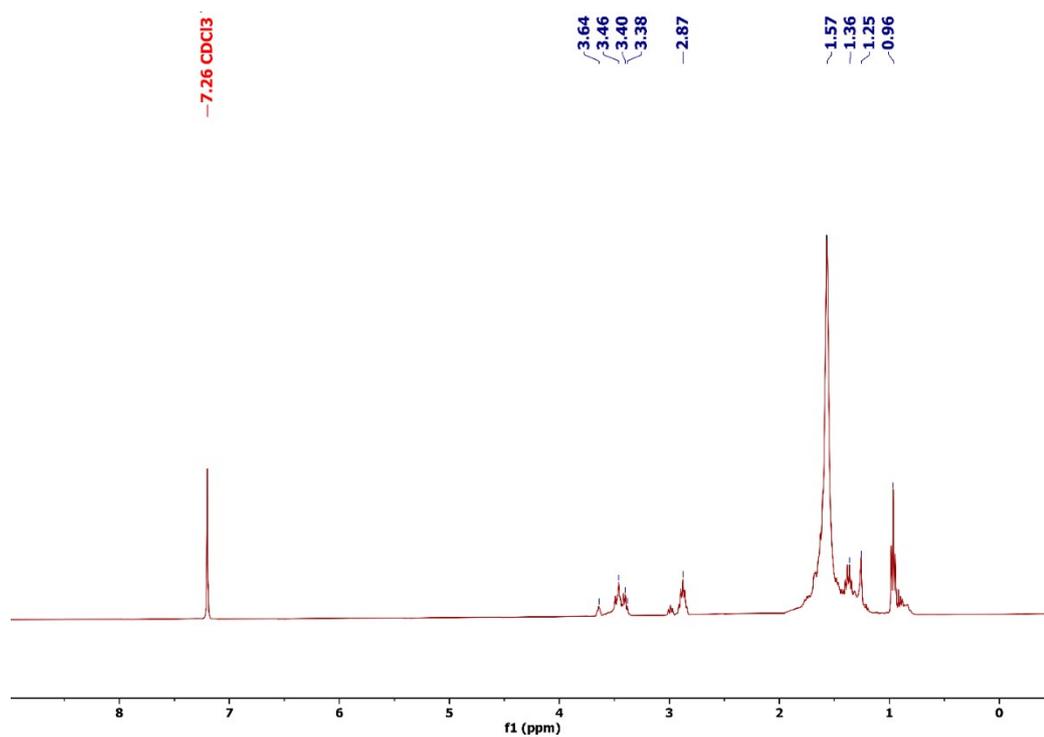


Fig. S8  $^1\text{H}$  NMR spectra of **(3)** in  $\text{CDCl}_3$

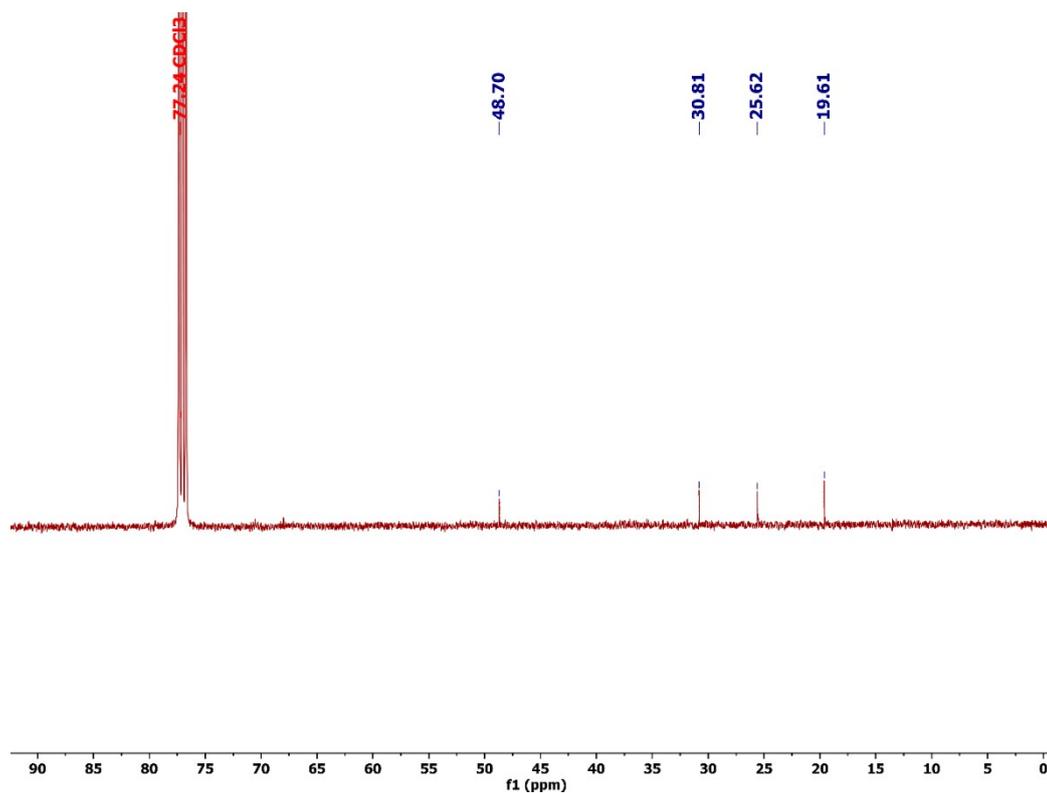


Fig. S9  $^{13}\text{C}$  NMR spectra of **(3)** in  $\text{CDCl}_3$

$[\text{B}_3\text{H}_7\text{NH}_2\text{C}_9\text{H}_{19}]$  (**4**)

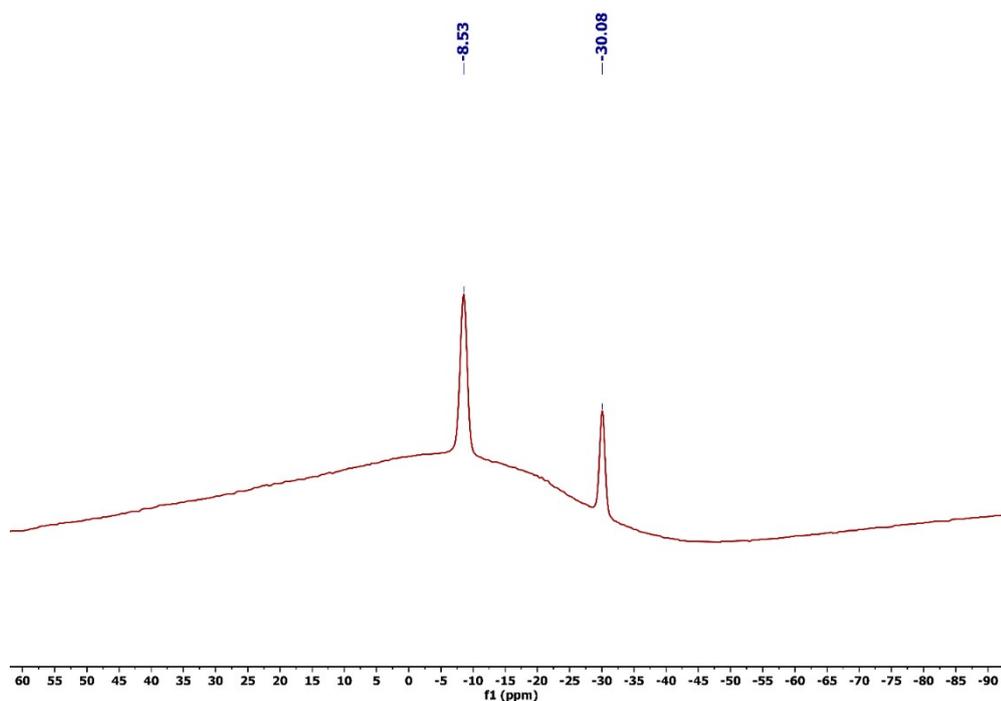


Fig. S10  $^{11}\text{B}$  NMR spectra of **(4)** in  $\text{CDCl}_3$

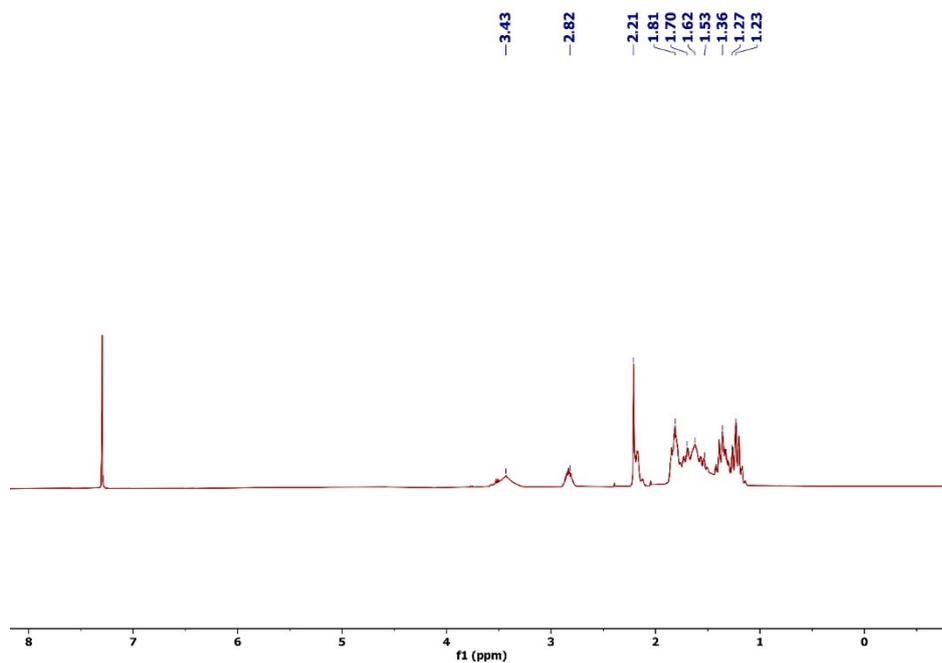


Fig. S11  $^1\text{H}$  NMR spectra of **(4)** in  $\text{CDCl}_3$

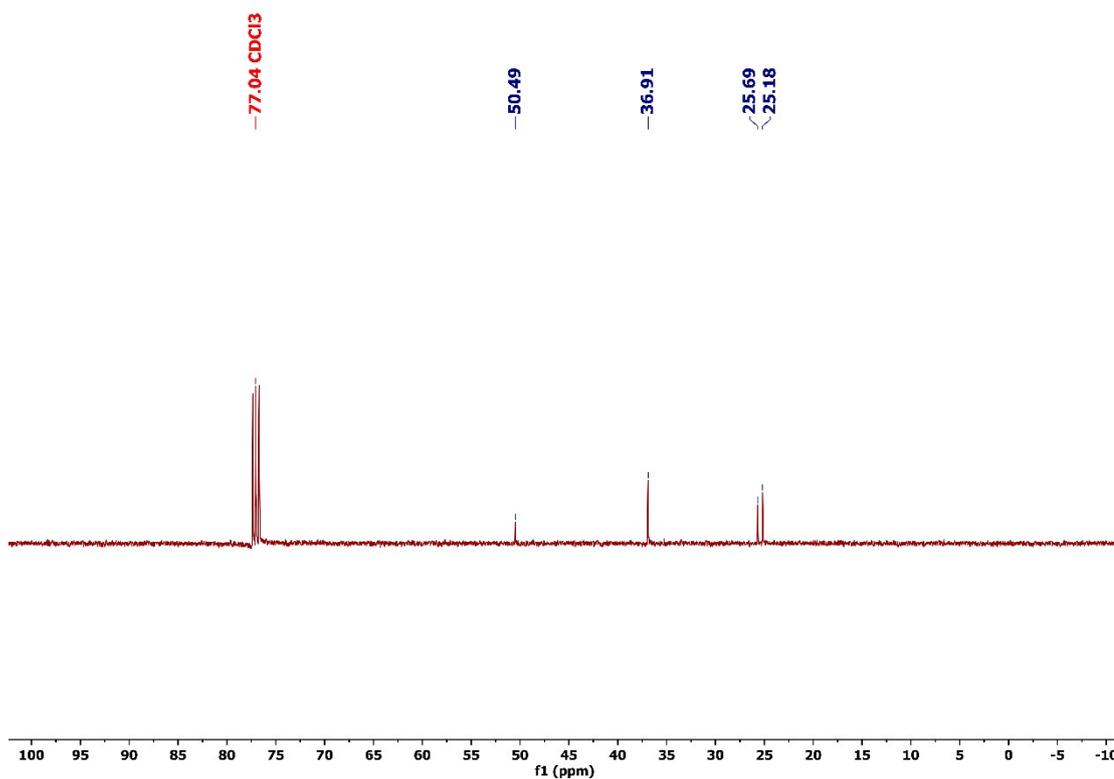


Fig. S12  $^{13}\text{C}$  NMR spectra of **(4)** in  $\text{THF-d}_8$

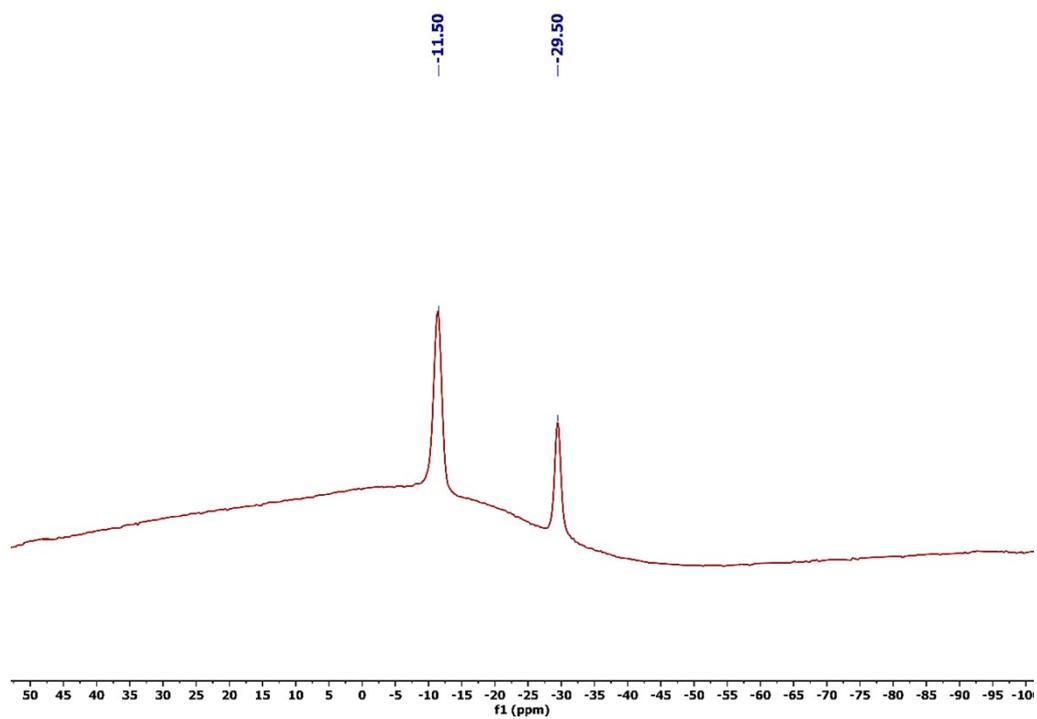


Fig. S13 <sup>11</sup>B NMR spectra of (**5**) in THF-d<sub>8</sub>

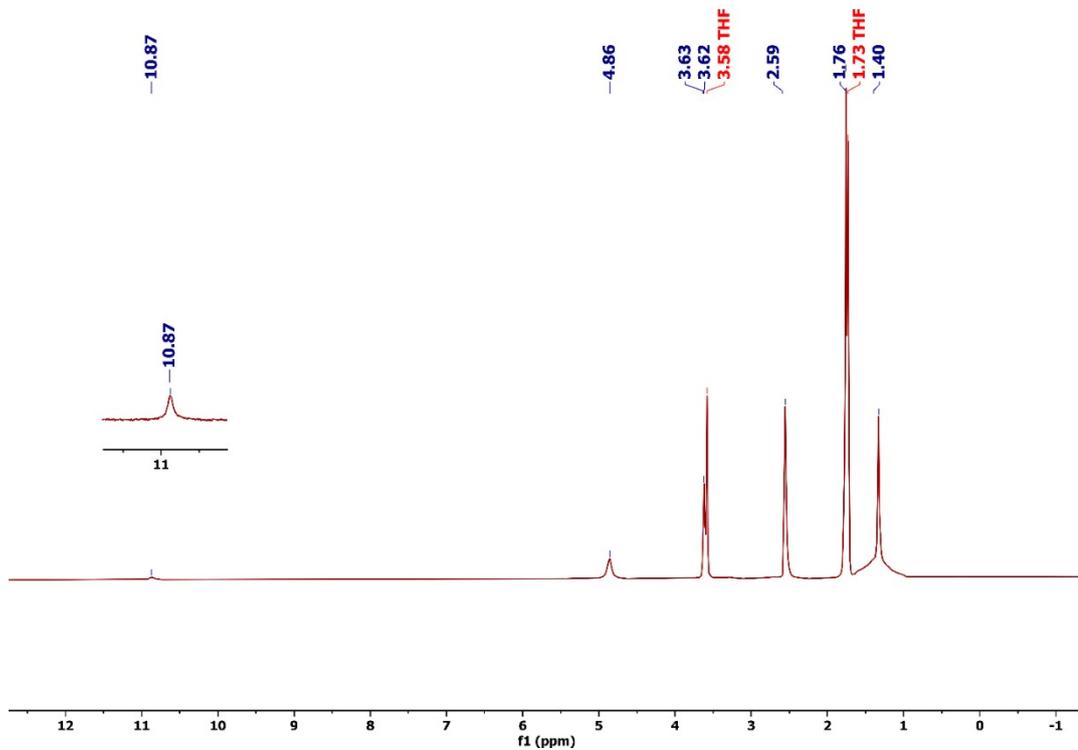


Fig. S14 <sup>1</sup>H NMR spectra of (**5**) in THF-d<sub>8</sub>

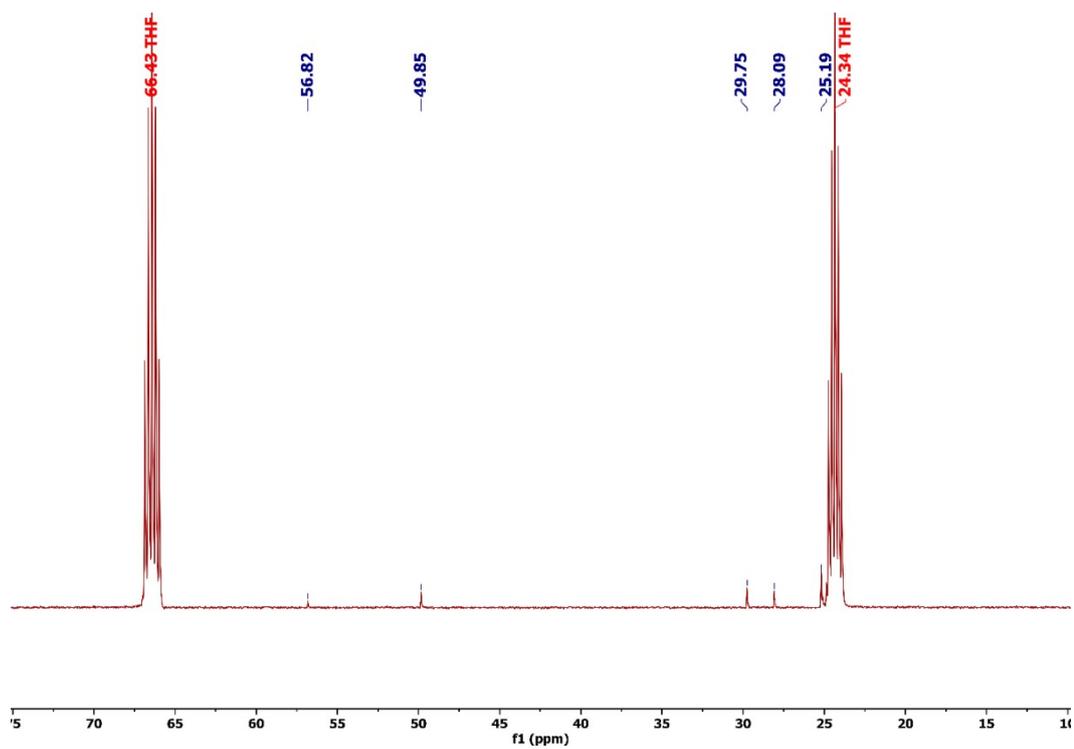


Fig. S15  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **(5)** in  $\text{THF-d}_8$

$[\text{B}_3\text{H}_7\text{NH}_2\text{C}_8\text{H}_{16}\text{NH}_3]\text{CF}_3\text{COO}$  (**6**)

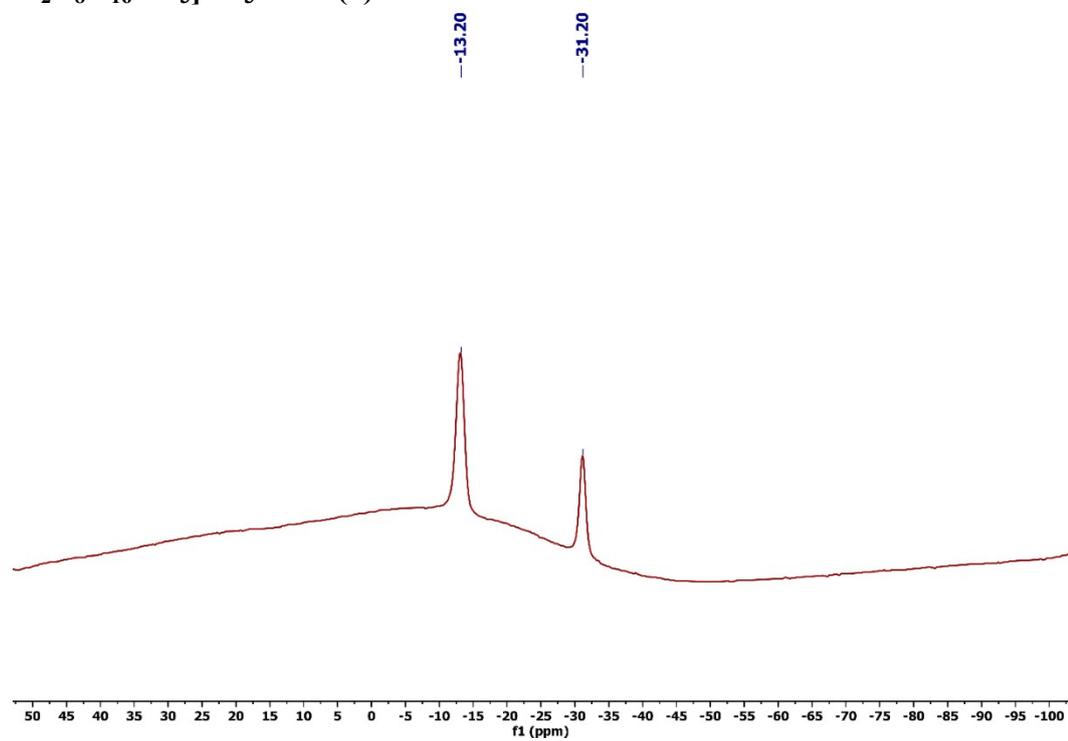


Fig. S16  $^{11}\text{B}$  NMR spectra of **(6)** in  $\text{THF-d}_8$

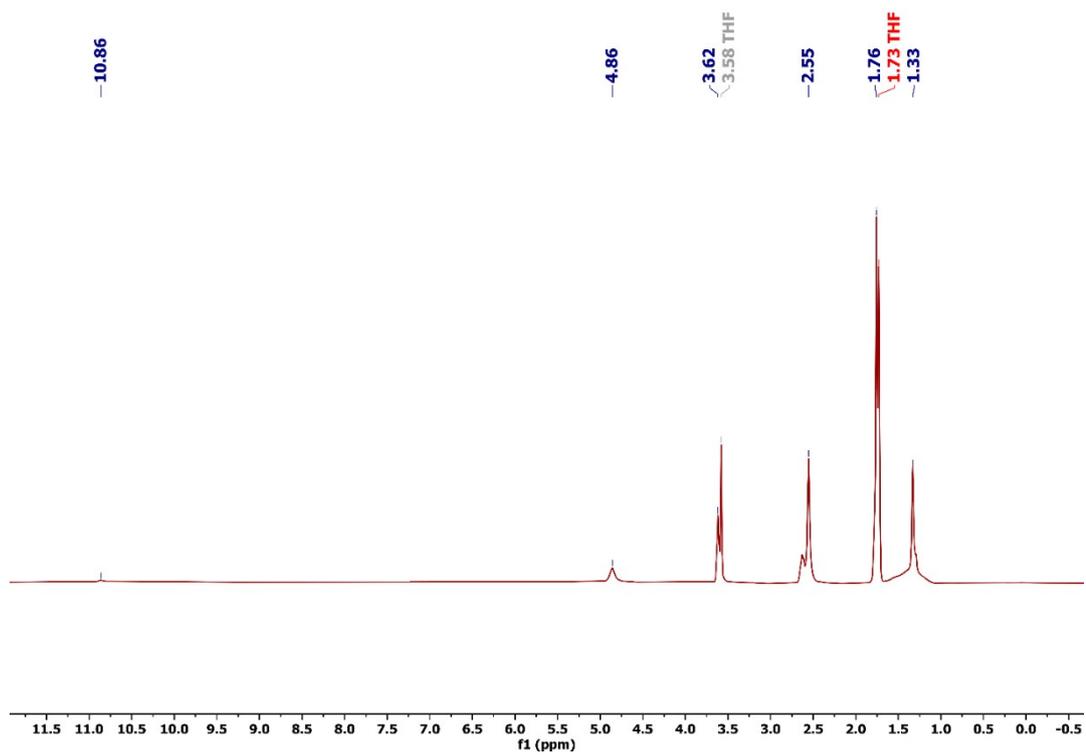


Fig. S17  $^1\text{H}$  NMR spectra of **(6)** in THF- $\text{d}_8$

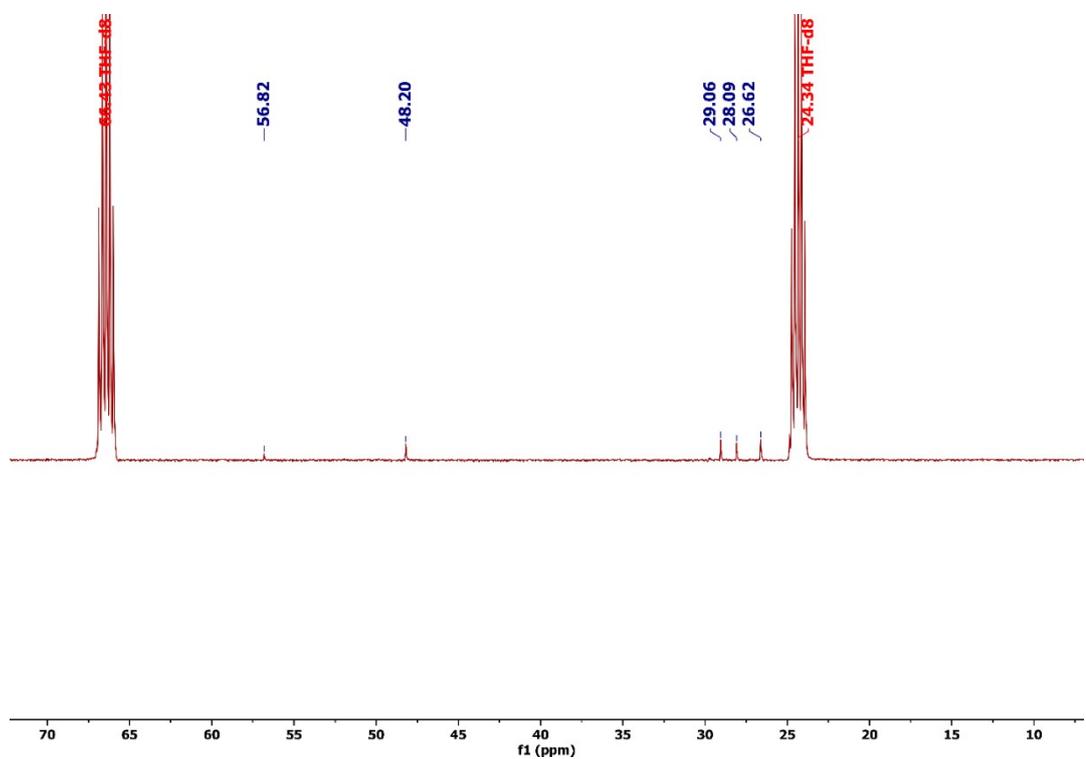


Fig. S18  $^{13}\text{C}$  NMR spectra of **(6)** in THF- $\text{d}_8$

$[B_3H_7NH_2C_9H_{18}NH_3]CF_3COO$  (7)

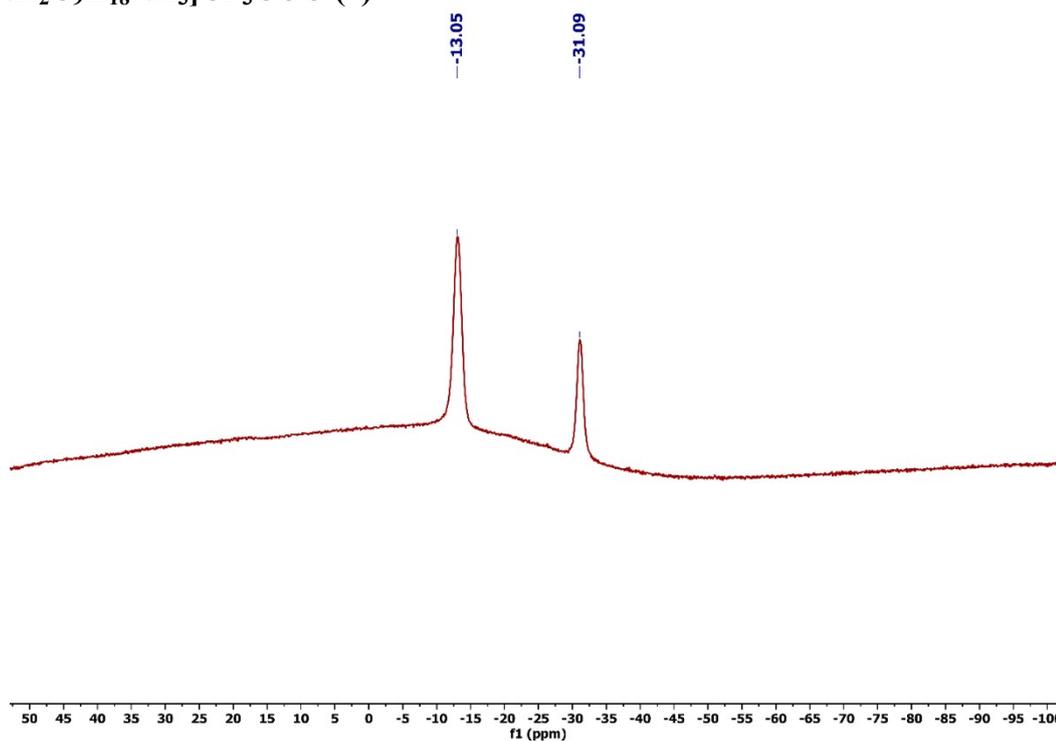


Fig. S19 <sup>11</sup>B NMR spectra of (7) in THF-d<sub>8</sub>

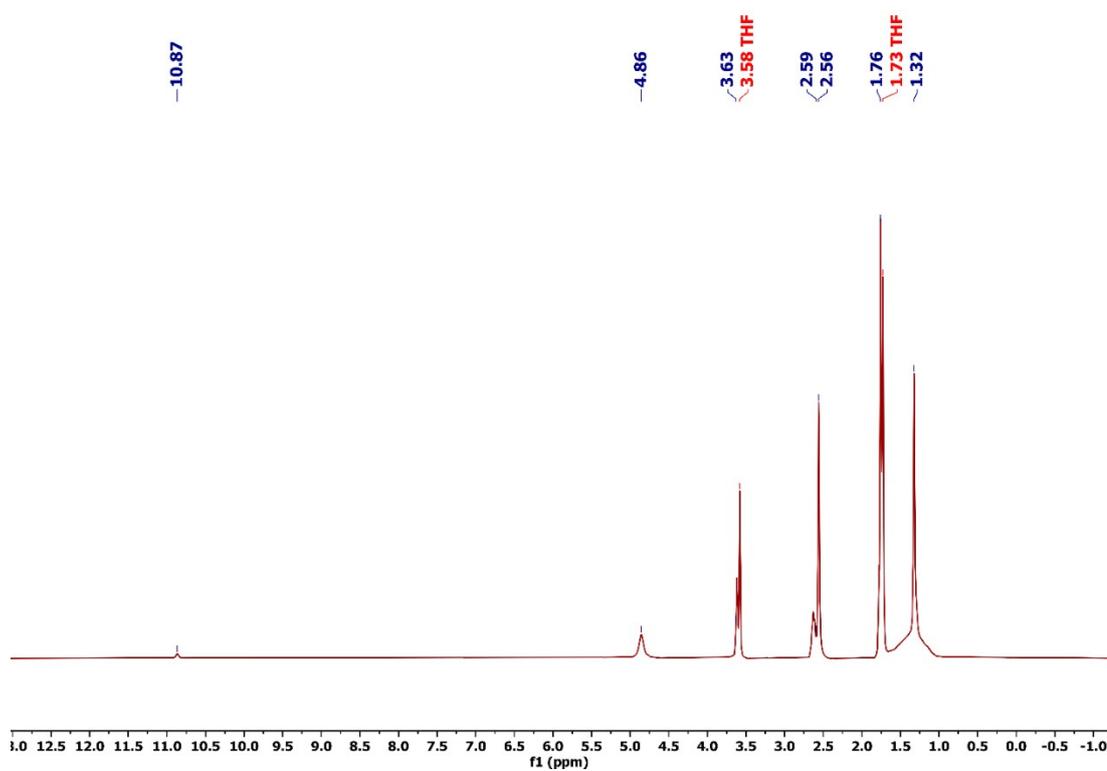


Fig. S20 <sup>1</sup>H NMR spectra of (7) in THF-d<sub>8</sub>

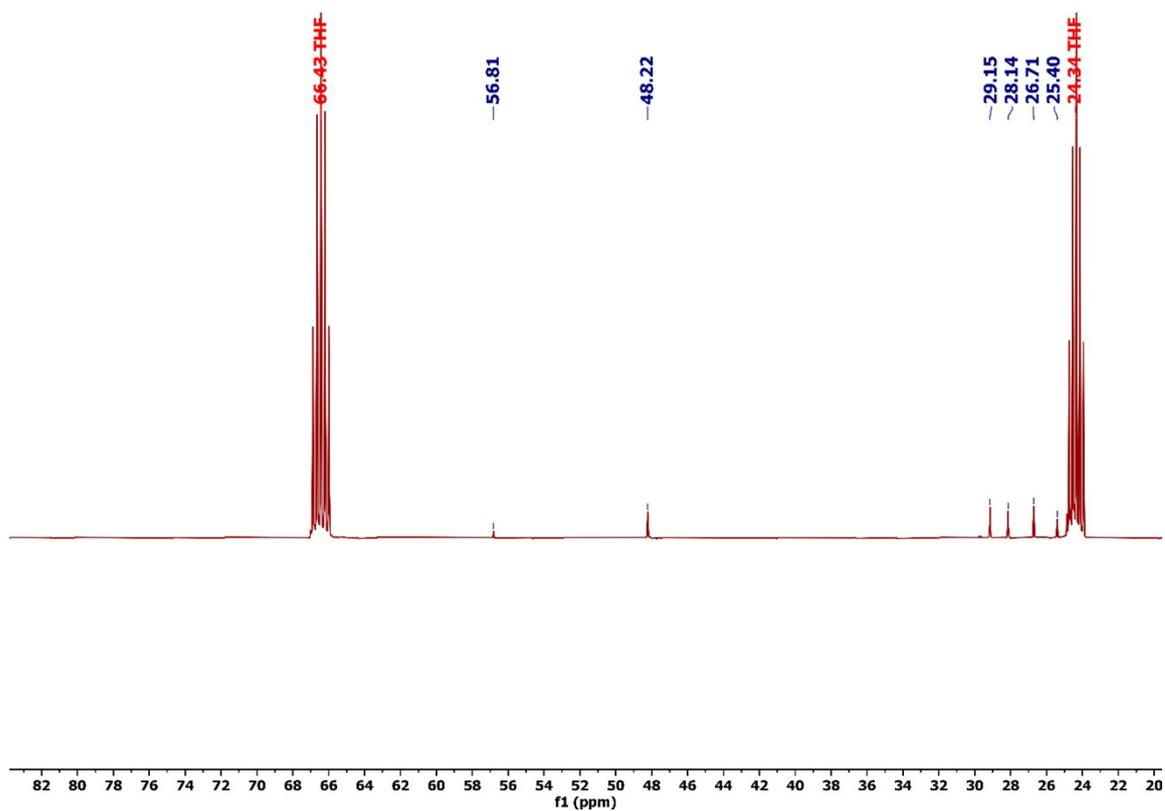


Fig. S21 <sup>13</sup>C<sup>1</sup>H NMR spectra of (7) in THF-d<sub>8</sub>

[B<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>C<sub>10</sub>H<sub>20</sub>NH<sub>3</sub>]<sup>+</sup>CF<sub>3</sub>COO<sup>-</sup> (8)

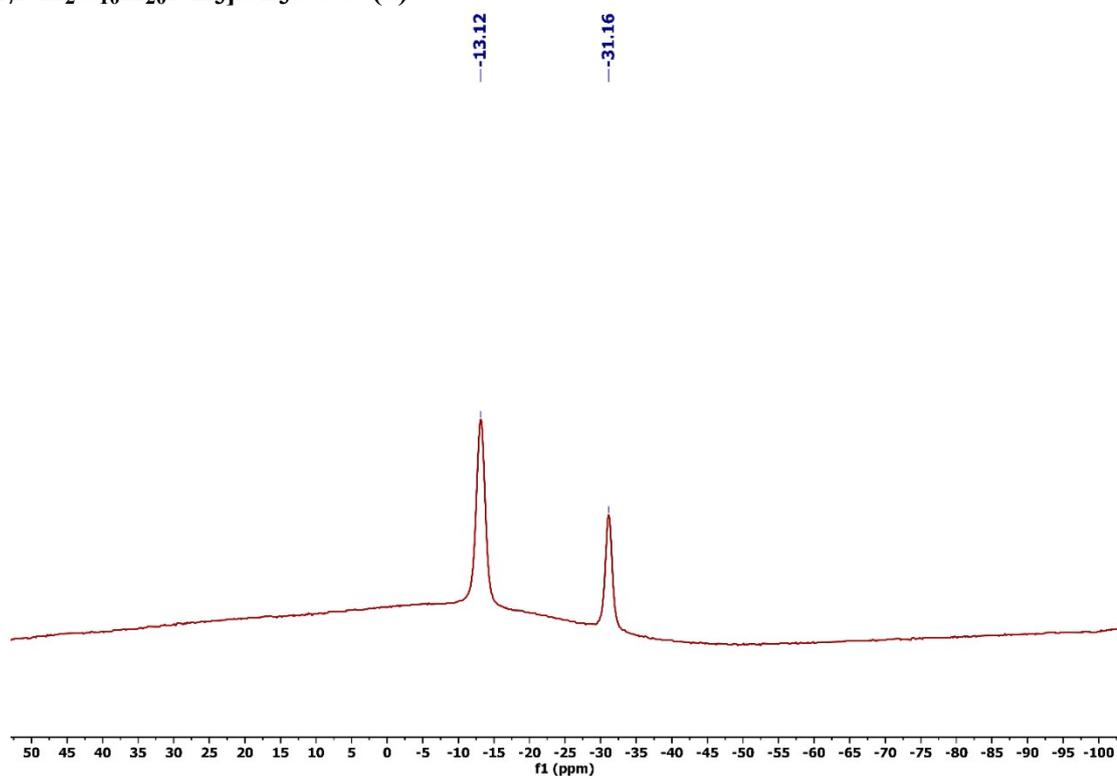


Fig. S22  $^{11}\text{B}$  NMR spectra of **(8)** in THF- $\text{d}_8$

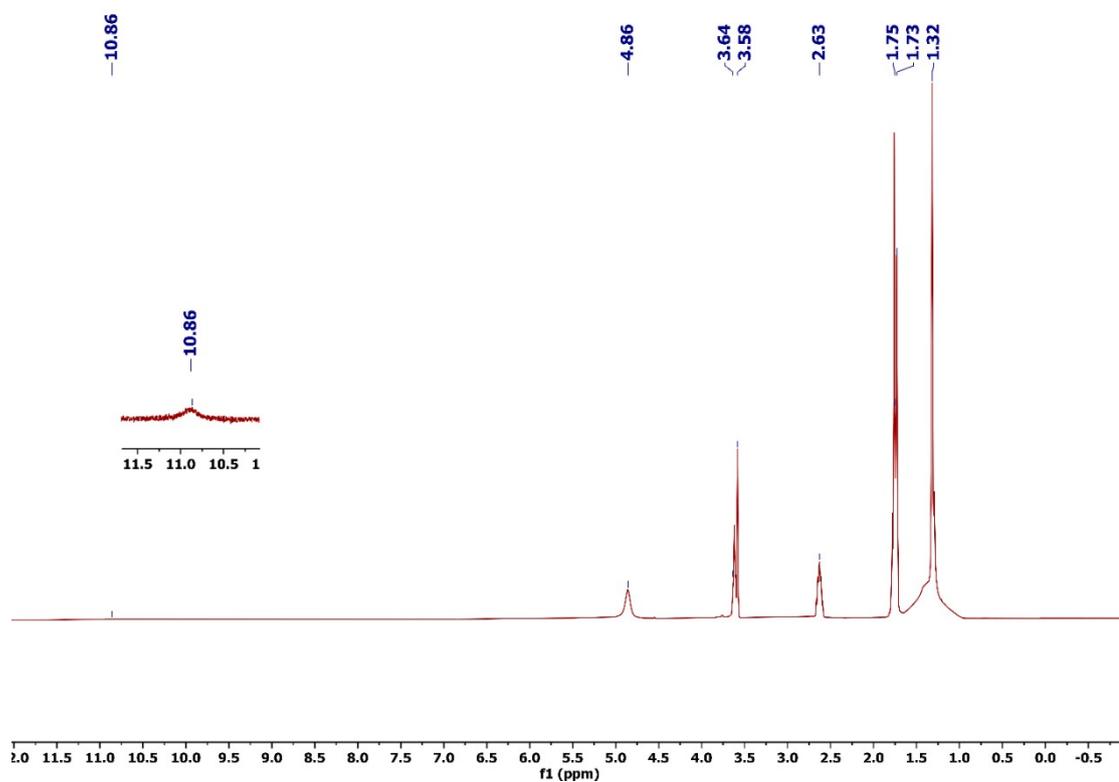


Fig. S23  $^1\text{H}$  NMR spectra of **(8)** in THF- $\text{d}_8$

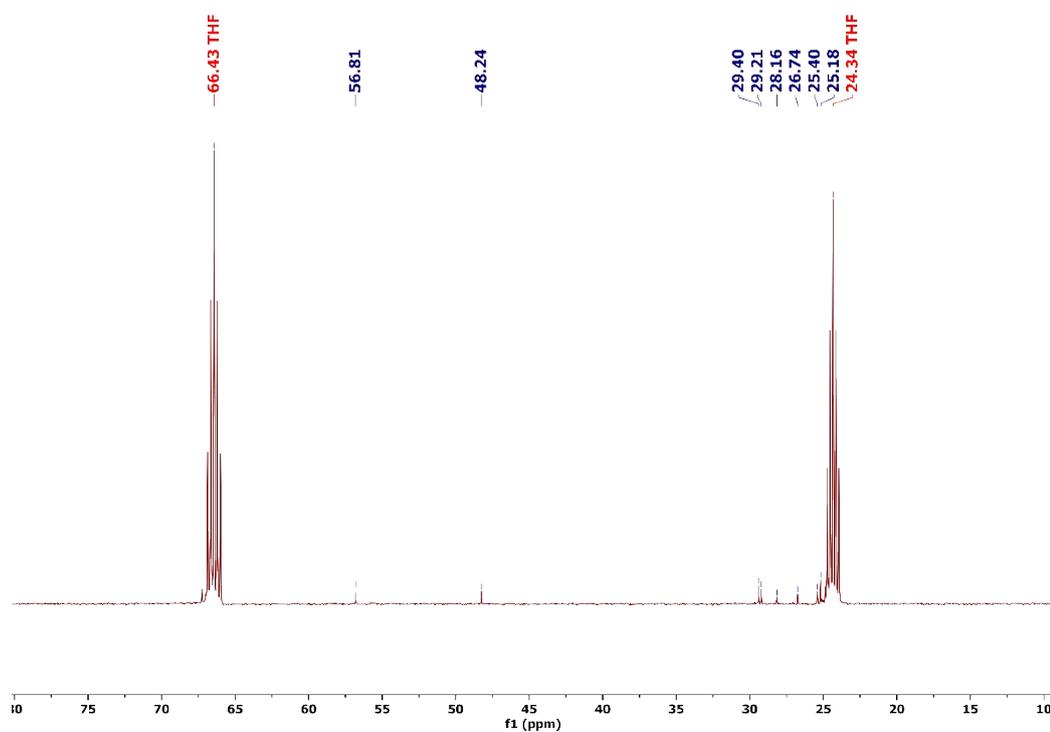


Fig. S24  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **(8)** in THF- $\text{d}_8$

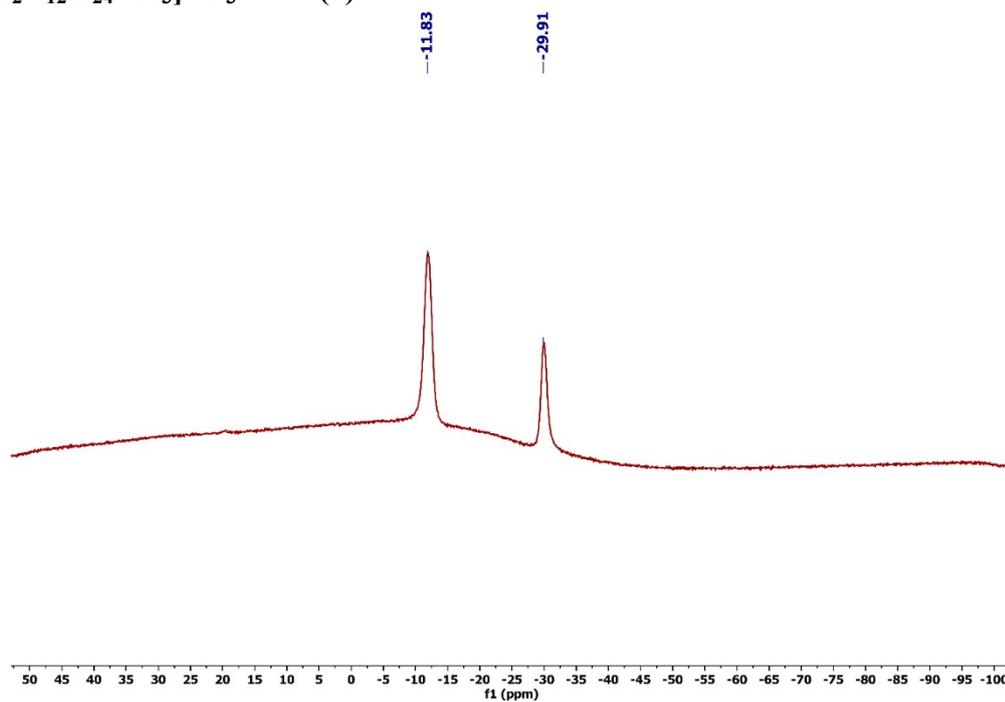


Fig. S25 <sup>11</sup>B NMR spectra of (**9**) in THF-d<sub>8</sub>

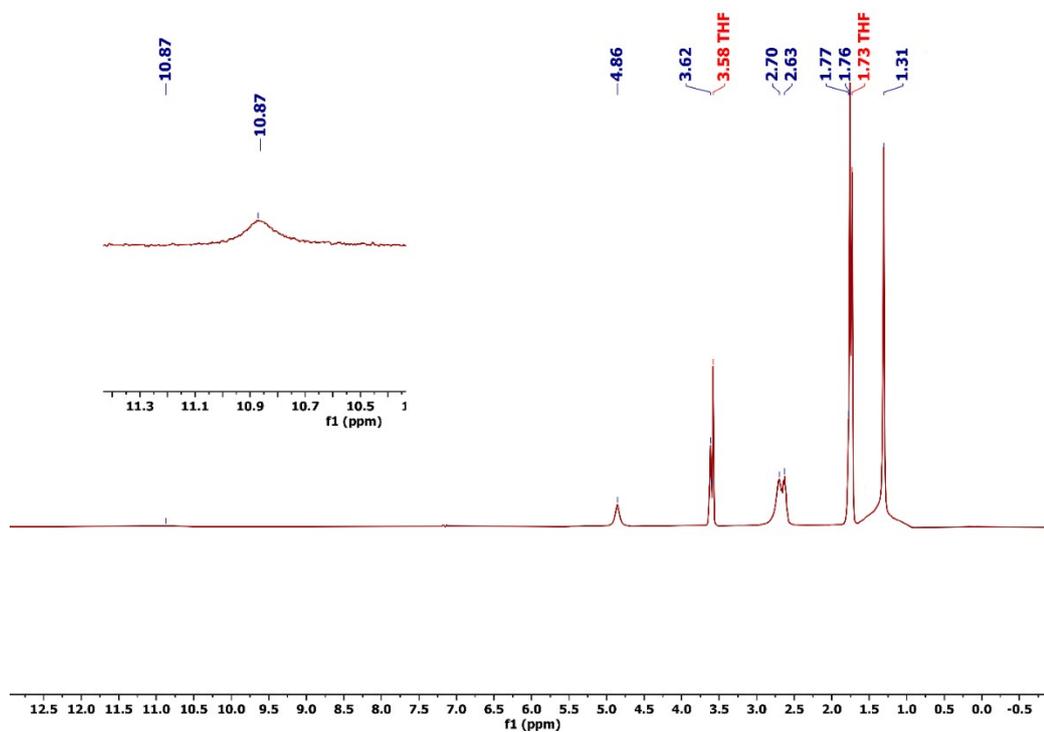


Fig. S26 <sup>1</sup>H NMR spectra of (**9**) in THF-d<sub>8</sub>

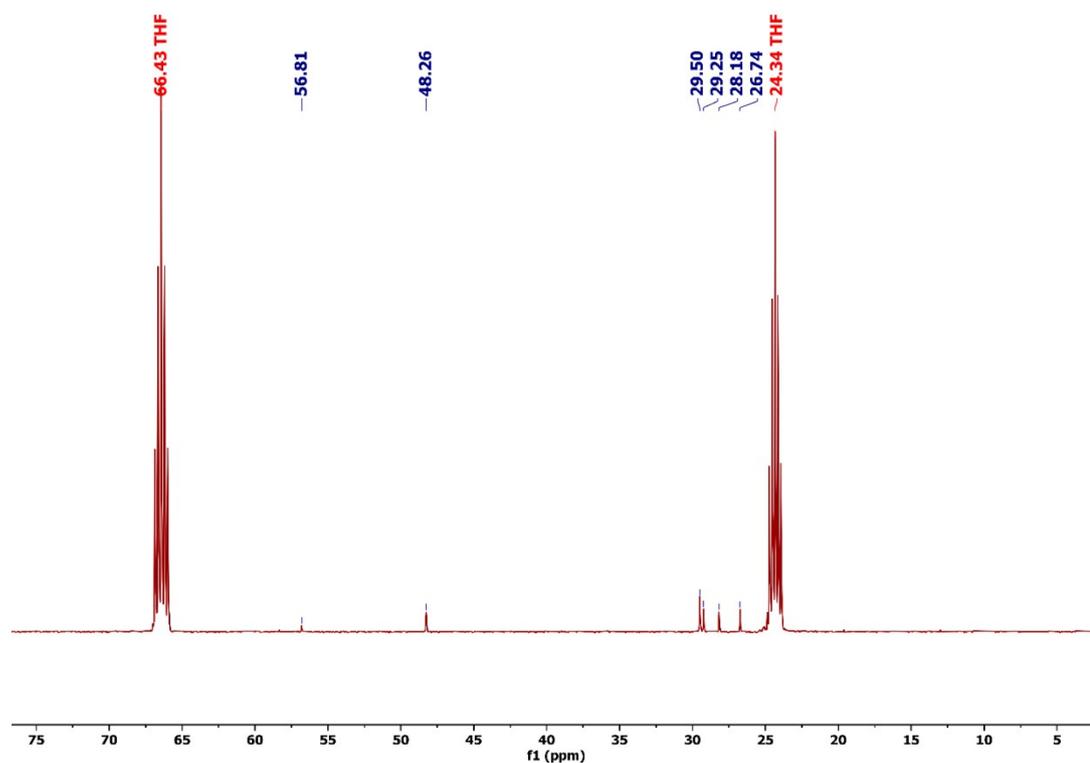


Fig. S27  $^{13}\text{C}^1\text{H}$  NMR spectra of **(9)** in  $\text{THF-d}_8$

$[\text{B}_3\text{H}_7\text{NH}_2\text{C}_6\text{H}_4\text{NH}_3]\text{Cl}$  (**10**)

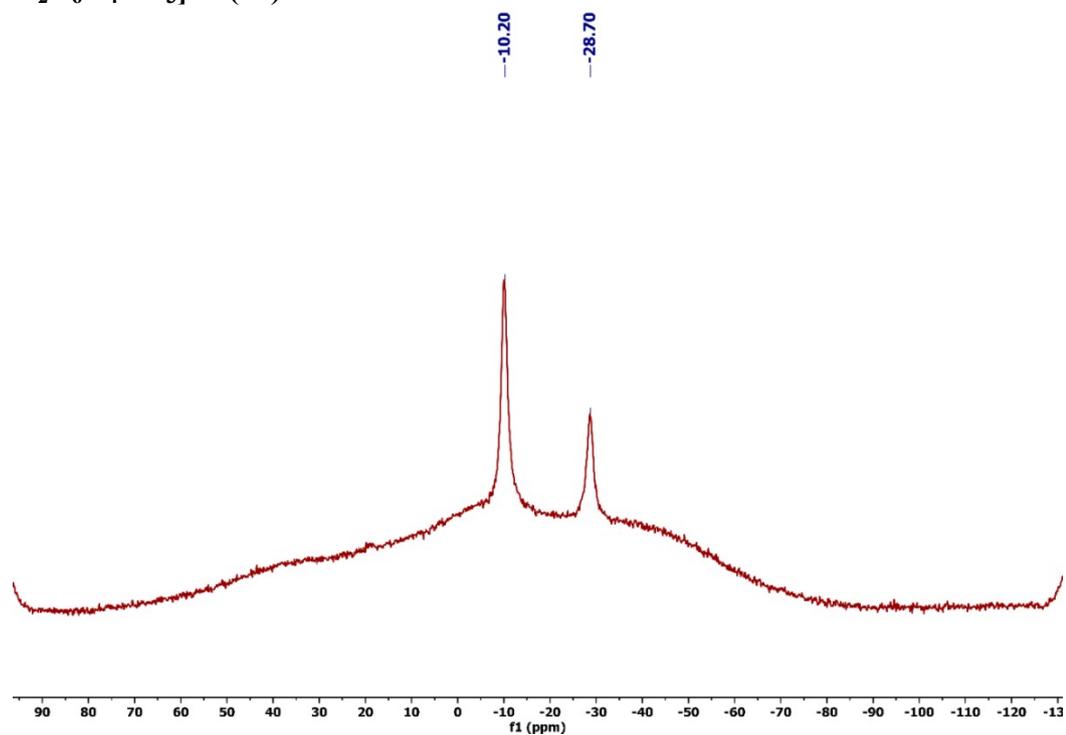


Fig. S28  $^{11}\text{B}$  NMR spectra of **(10)** in  $\text{THF-d}_8$

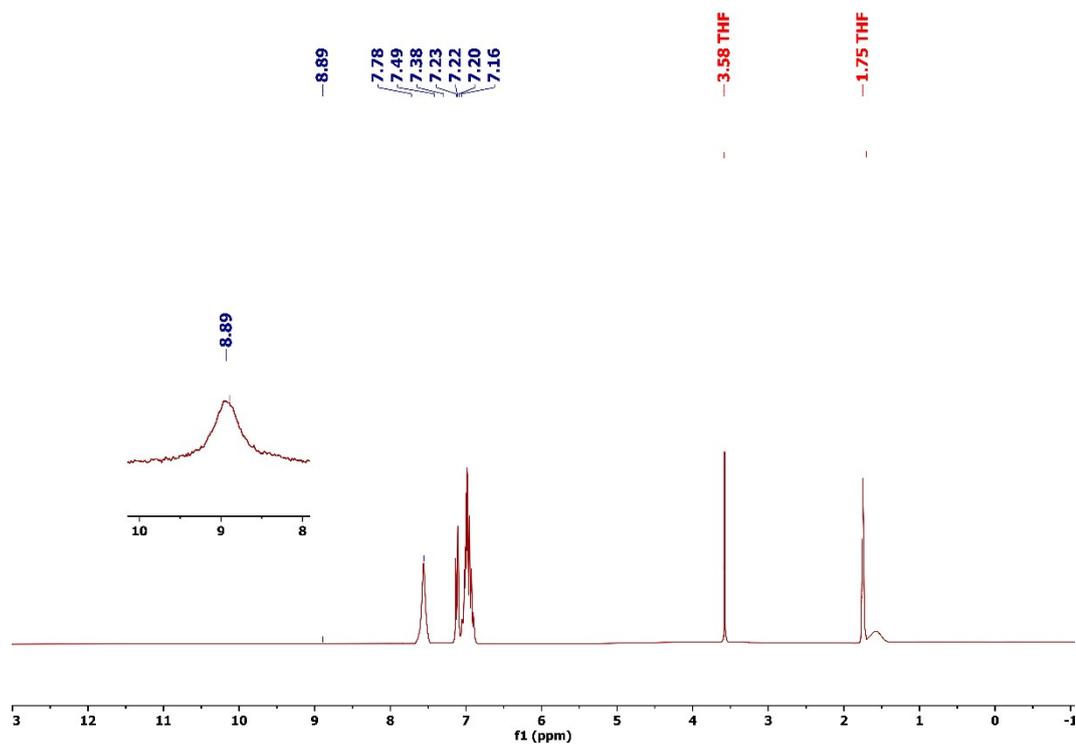


Fig. S29  $^1\text{H}$  NMR spectra of **(10)** in  $\text{THF-d}_8$

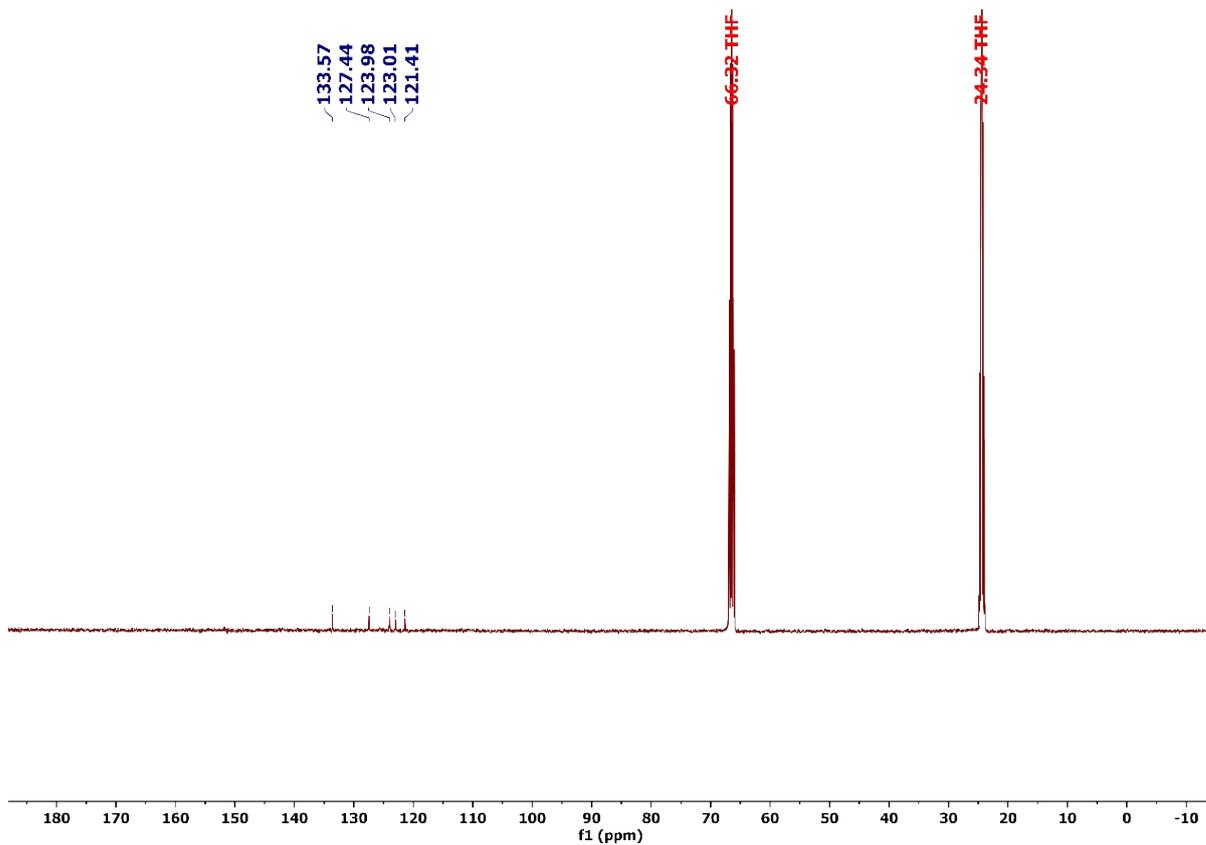


Fig. S30  $^{13}\text{C}$  NMR spectra of **(10)** in  $\text{THF-d}_8$

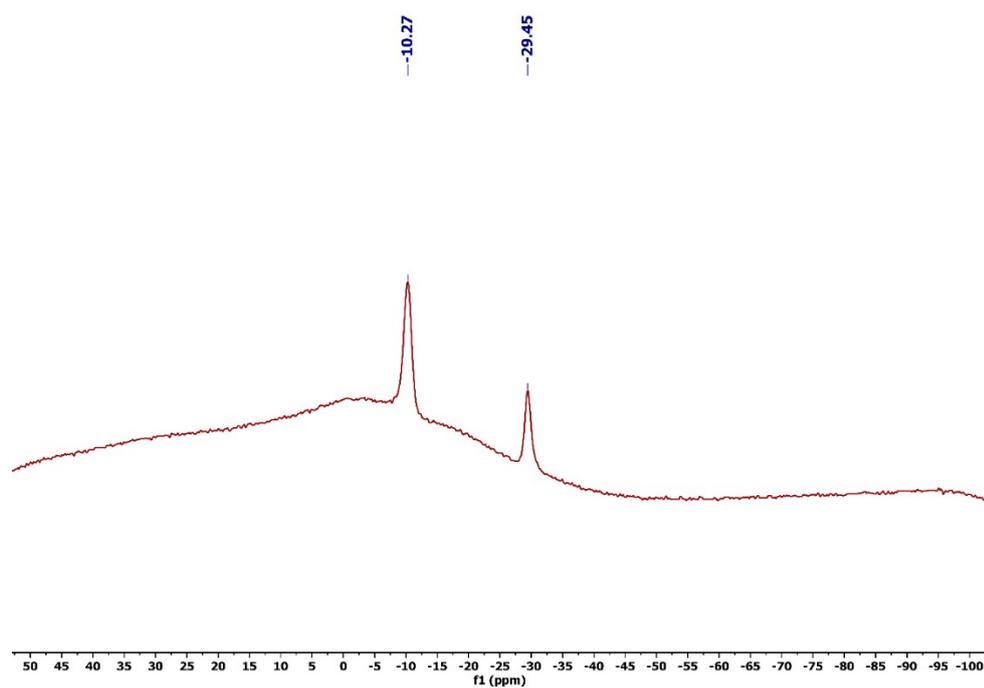


Fig. S31  $^{11}B$  NMR spectra of (**11**) in THF- $d_8$

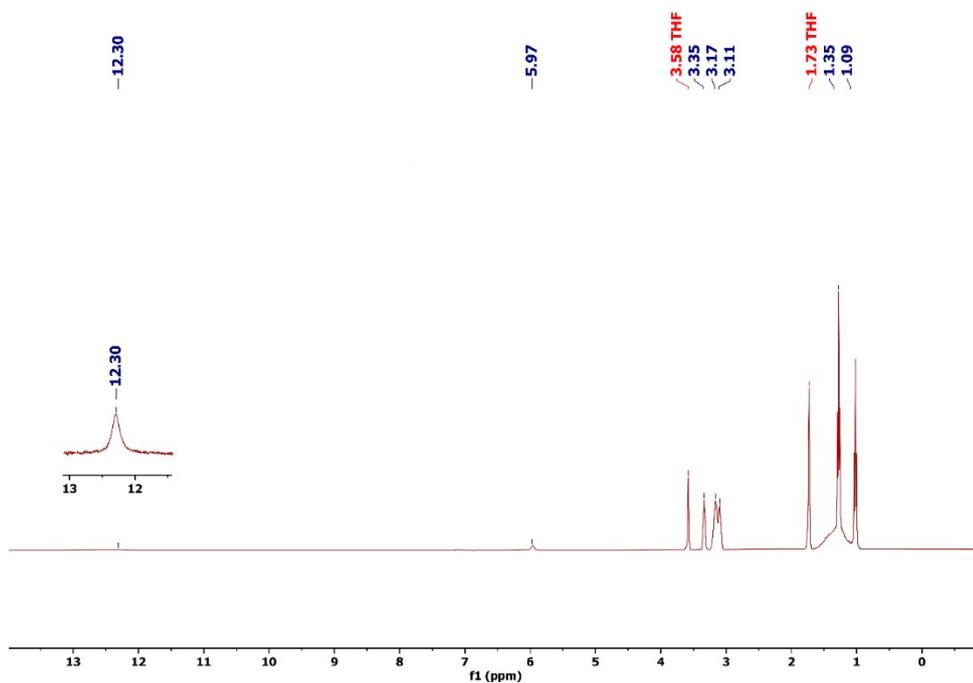


Fig. S32  $^1H$  NMR spectra of (**11**) in THF- $d_8$

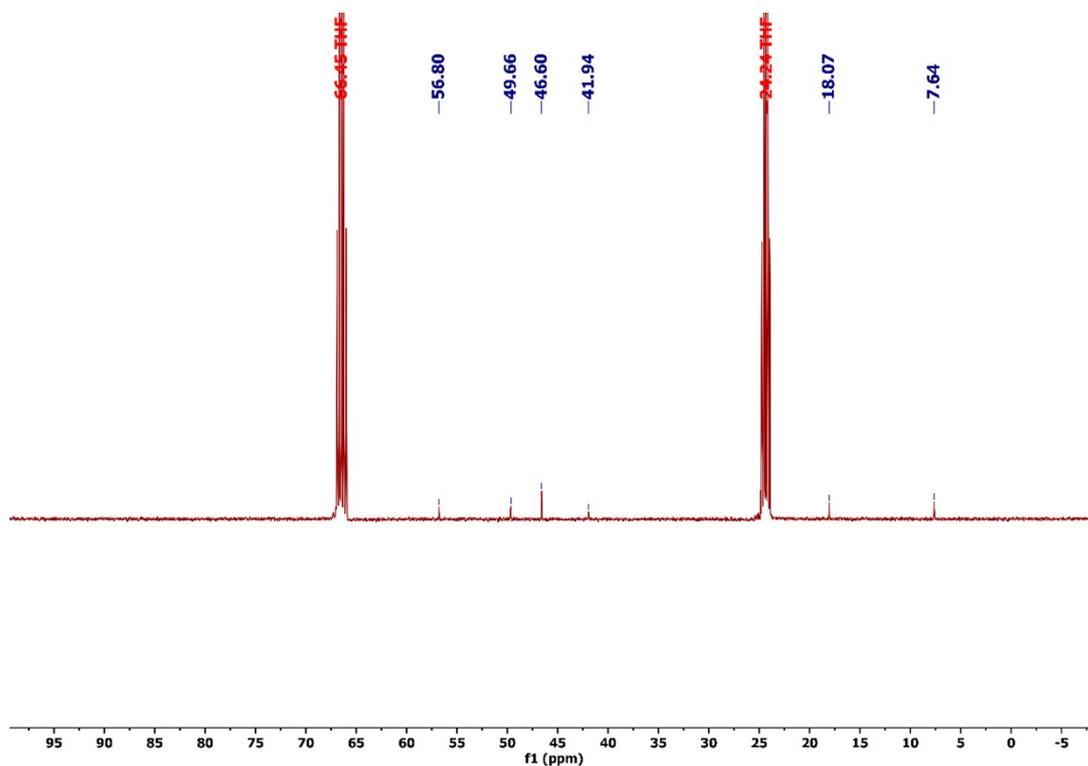


Fig. S33  $^{13}\text{C}$  NMR spectra of (11) in THF- $\text{d}_8$

$[\text{B}_3\text{H}_7\text{NH}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5]$  (12)

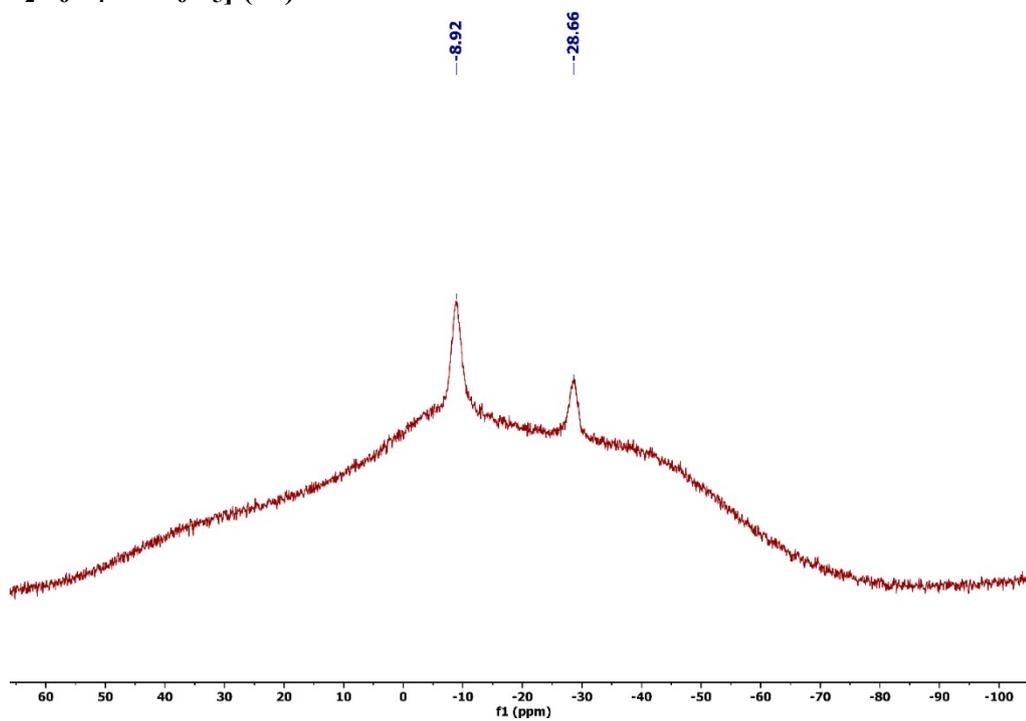


Fig. S34  $^{11}\text{B}$  NMR spectra of (12) in THF- $\text{d}_8$

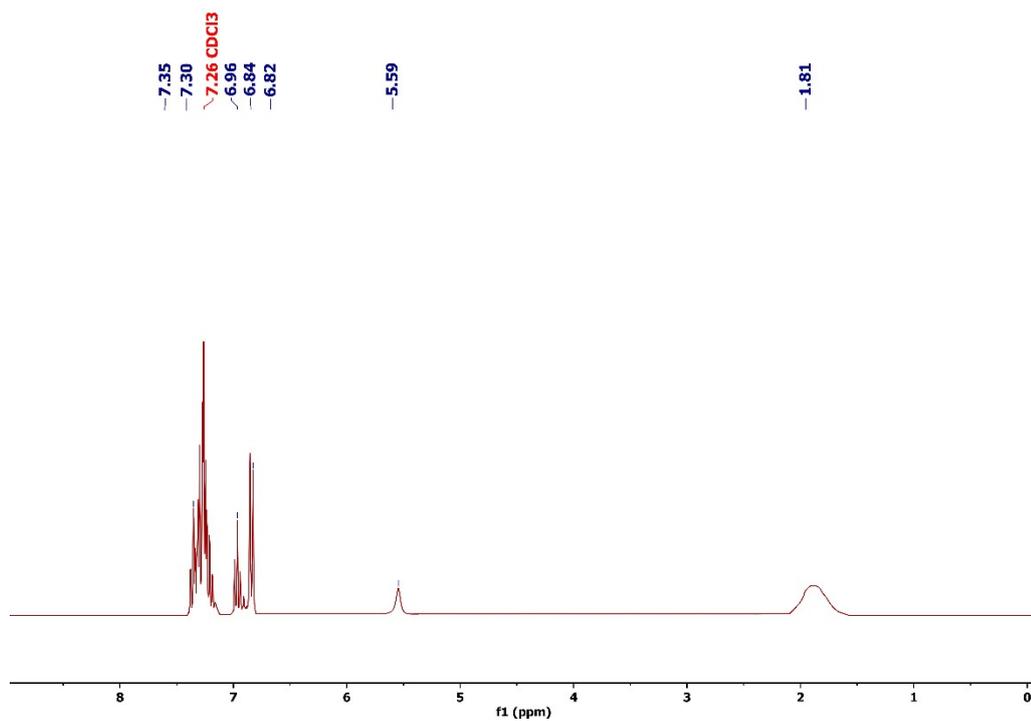


Fig. S35 <sup>1</sup>H NMR spectra of (12) in THF-d<sub>8</sub>

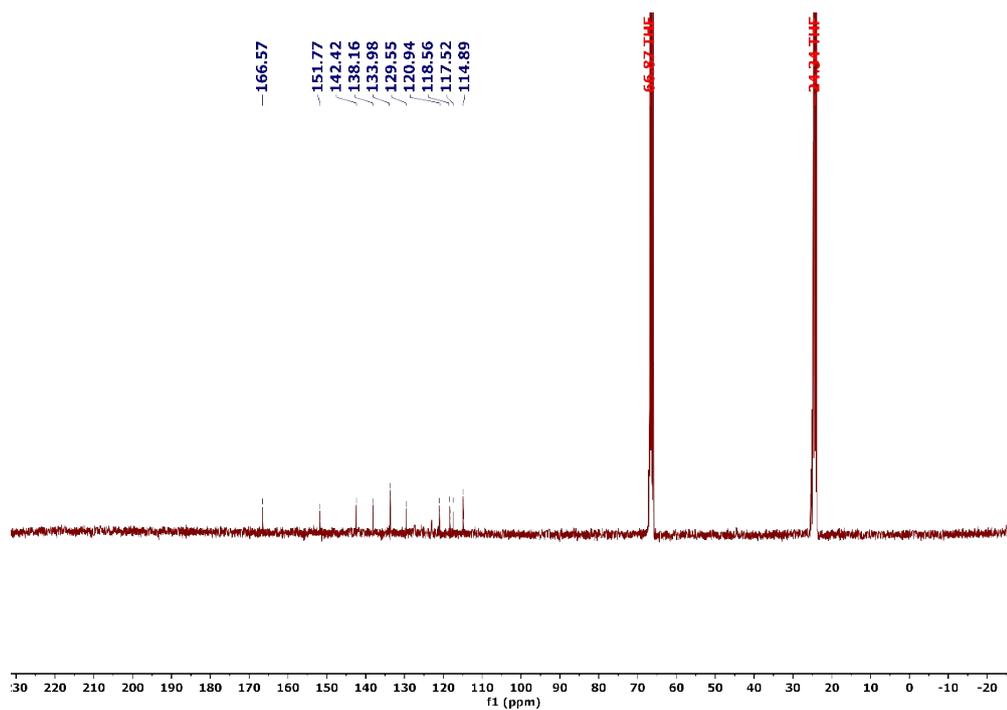


Fig. S36 <sup>13</sup>C NMR spectra of (12) in THF-d<sub>8</sub>

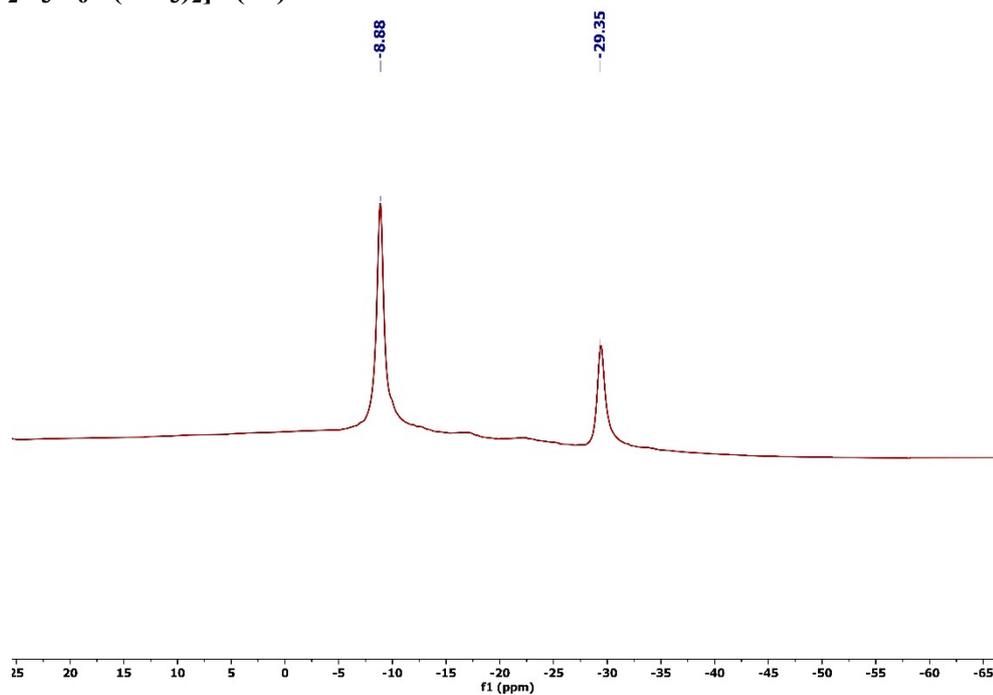


Fig. S37 <sup>11</sup>B NMR spectra of (**13**) in THF-d<sub>8</sub>

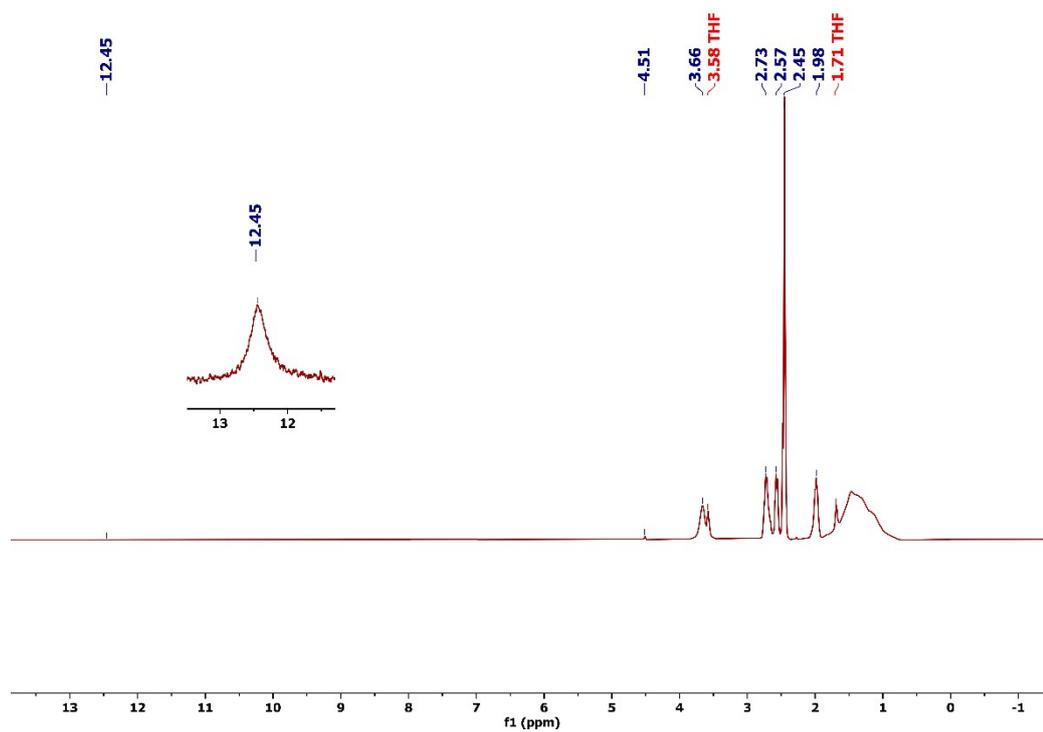


Fig. S38 <sup>1</sup>H NMR spectra of (**13**) in THF-d<sub>8</sub>

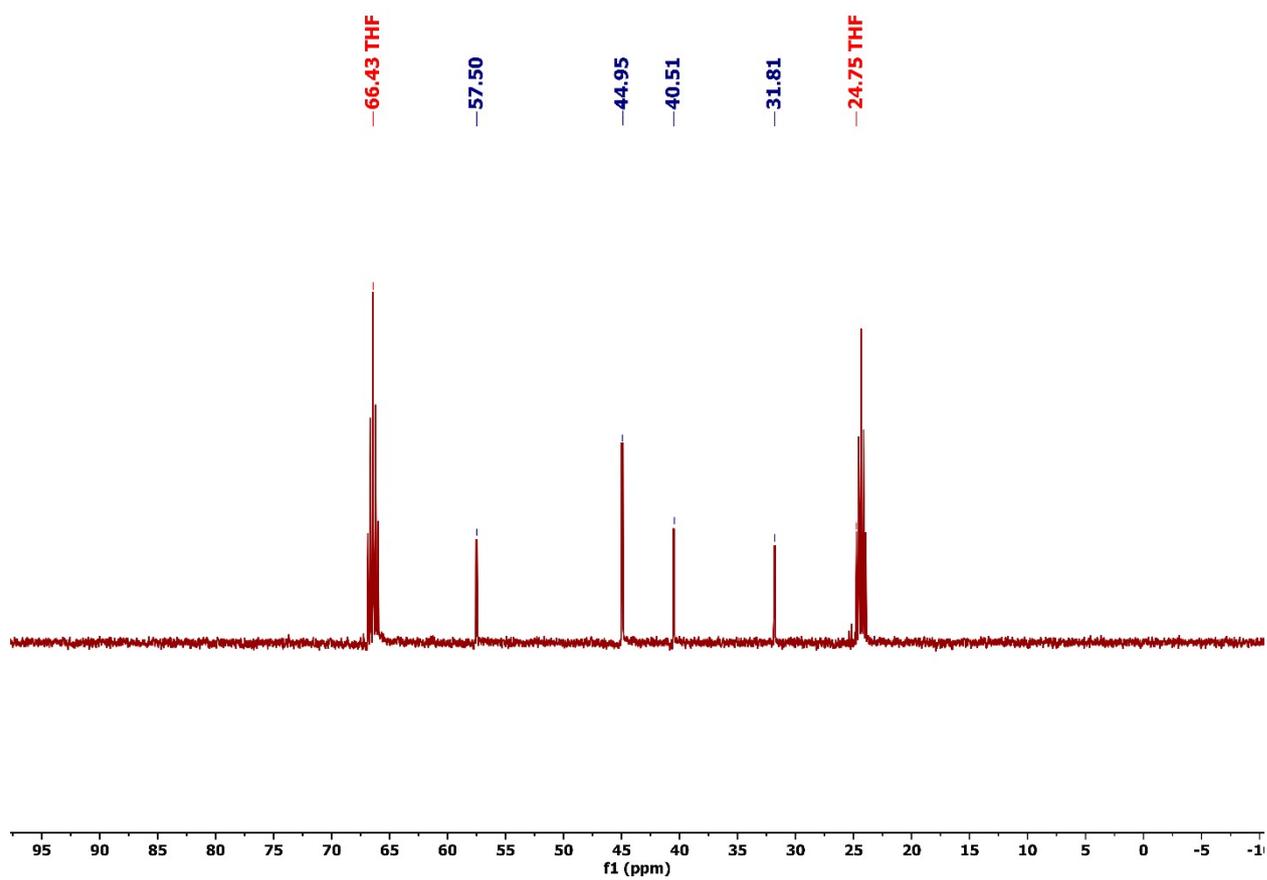


Fig. S39  $^{13}\text{C}$  NMR spectra of **(13)** in  $\text{THF-d}_8$

## IR data

**Table S3.** Selected maxima of absorption bands in the IR spectra of octahydrotriborate derivatives.

Complexes	$\nu(\text{B-H}), \text{cm}^{-1}$	$\nu(\text{N-H}), \text{cm}^{-1}$	$\nu(\text{B-N}), \text{cm}^{-1}$
1	2502, 2430, 2333 2018	3318	1181
2	2495, 2428, 2328 2026	3324	1192
3	2510, 2433, 2336 2024	3321	1165
4	2498, 2455, 2341 2019	3258	1198
5	2503, 2429, 2334 2021	3364	1162
6	2504, 2424, 2336 2020	3283	1166
7	2497, 2434, 2340 2003	3282	1161
8	2501, 2434, 2330 2007	3283	1155
9	2505, 2421, 2324 1998	3276	1158
10	2512, 2489, 2435 1961	3227	1112
11	2521, 2483, 2441 1999	3156	1160
12	2510, 2473, 2430 1998	3234	1123
13	2523, 2473, 2434 2003	3229	1162

## X-Ray Diffraction data

**Table S4.** Hydrogen-bond geometry of 1a

D-H...A	d(D-H), Å	d(H-A), Å	d(D-A), Å	D-H-A, °
N1-H1A...Cl11	0.93(3)	2.43(3)	3.260(2)	147(2)
N1-H1B...Cl12	0.88(3)	2.42(3)	3.303(2)	178(2)
N2-H2A...Cl11	0.91(3)	2.33(3)	3.225(2)	168(2)
N2-H2B...Cl1	0.88(3)	2.33(3)	3.207(2)	173(2)

Table S5. Selected bond length for compounds 1, 11–13, Å.

Bond	1	11	12	13
N–C	1.505(2)	1.486(1)	1.460(3)	1.494(4)
B–N	1.590(2)	1.601(1)	1.632(3)	1.598(5)
B1–B2(B3)	1.819(2)	1.840(1)	1.848(4)	1.850(6)
	1.803(2)	1.852(1)	1.834(4)	1.857(6)
B2–B3	1.752(2)	1.721(1)	1.730(4)	1.730(6)
B2–Hbr	1.21(2)	1.27(1)	1.20(3)	1.23(5)
B3–Hbr	1.37(2)	1.23(1)	1.25(3)	1.26(4)
av. B1–H	1.17(2)	1.09(1)	1.01(2)	1.04(4)
	1.08(2)	1.09(1)	1.06(2)	1.16(4)
av. B2(3)–Hterm	1.14	1.1	1.1	1.11

Table S6. Hydrogen-bond geometry of 11 and 13

Compound	D–H...A	d(D–H)/Å	d(H–A)/Å	d(D–A)/Å	D–H–A/°
11	N1–H1A...Cl1 <sup>1</sup>	0.880(10)	2.434(10)	3.3041(6)	169.9(8)
	N1–H1B...Cl1 <sup>2</sup>	0.880(10)	2.443(10)	3.2701(6)	156.8(8)
	N2–H2...Cl1	0.876(10)	2.249(10)	3.0874(6)	160.2(9)
	<sup>1</sup> 1–X,1–Y,1–Z; <sup>2</sup> +X,-1+Y,+Z				
13	N1–H1A...I1 <sup>1</sup>	0.97(4)	2.72(4)	3.629(3)	156(3)
	N2–H2...I1	0.84(4)	2.78(5)	3.505(3)	146(4)
	<sup>1</sup> 1–X,1–Y,1–Z				

Table S7. Crystal data and structure refinement for all compounds studied.

Compound	1a	1	11	12	13
Empirical formula	C <sub>12</sub> H <sub>28</sub> BClN <sub>2</sub>	C <sub>6</sub> H <sub>20</sub> B <sub>3</sub> N	C <sub>6</sub> H <sub>24</sub> B <sub>3</sub> ClN <sub>2</sub>	C <sub>12</sub> H <sub>19</sub> B <sub>3</sub> N <sub>2</sub>	C <sub>5</sub> H <sub>22</sub> B <sub>3</sub> IN <sub>2</sub>
Formula weight	246.62	138.66	192.15	223.72	269.57
Temperature, K	150.00	100.00	100.00	100.00	100.00
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	triclinic

Space group	Pbca	Pbca	P2 <sub>1</sub> /c	Pbca	P-1
<b>a, Å</b>	10.9652(18)	9.3751(7)	10.7640(3)	7.6448(6)	7.4110(4)
<b>b, Å</b>	10.781(2)	9.4843(7)	7.0083(2)	18.0943(14)	8.4211(5)
<b>c, Å</b>	25.738(11)	21.4916(15)	16.6109(5)	19.011(2)	10.3215(7)
<b>β, °</b>	90	90	97.7510(10)	90	94.477(3)
<b>Volume, Å<sup>3</sup></b>	3042.7(15)	1911.0(2)	1241.63(6)	2629.8(4)	622.53(7)
<b>Z</b>	8	8	4	8	2
<b>d<sub>calc</sub>, g/cm<sup>3</sup></b>	1.077	0.964	1.028	1.130	1.438
<b>μ, mm<sup>-1</sup></b>	0.231	0.051	0.264	0.064	2.525
<b>F(000)</b>	1088.0	624.0	424.0	960.0	268.0
<b>Radiation</b>	MoKα (λ = 0.71073)				
<b>Index ranges</b>	-13 ≤ h ≤ 14, -15 ≤ k ≤ 11, -17 ≤ l ≤ 36	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -23 ≤ l ≤ 23	-9 ≤ h ≤ 9, -23 ≤ k ≤ 22, -24 ≤ l ≤ 18	-9 ≤ h ≤ 9, -10 ≤ k ≤ 9, -12 ≤ l ≤ 12
<b>Reflections collected</b>	11014	23559	72620	14171	5261
<b>Independent reflections</b>	4228 [R <sub>int</sub> = 0.0502]	2308 [R <sub>int</sub> = 0.0809,]	3485 [R <sub>int</sub> = 0.0367]	3010 [R <sub>int</sub> = 0.0643]	2405 [R <sub>int</sub> = 0.0287]
<b>Goodness-of-fit on F<sup>2</sup></b>	1.010	1.041	1.030	1.030	1.033
<b>Final R indexes [I ≥ 2σ (I)]</b>	R <sub>1</sub> = 0.0520, wR <sub>2</sub> = 0.1160	R <sub>1</sub> = 0.0525, wR <sub>2</sub> = 0.1200	R <sub>1</sub> = 0.0223, wR <sub>2</sub> = 0.0617	R <sub>1</sub> = 0.0645, wR <sub>2</sub> = 0.1392	R <sub>1</sub> = 0.0286, wR <sub>2</sub> = 0.0687
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.1188, wR <sub>2</sub> = 0.1590	R <sub>1</sub> = 0.0719, wR <sub>2</sub> = 0.1317	R <sub>1</sub> = 0.0241, wR <sub>2</sub> = 0.0626	R <sub>1</sub> = 0.0960, wR <sub>2</sub> = 0.1585	R <sub>1</sub> = 0.0316, wR <sub>2</sub> = 0.0705