

**SUPPORTING INFORMATION:**

**Dehydربorylation of Terminal Alkynes Using Lithium  
Aminoborohydrides**

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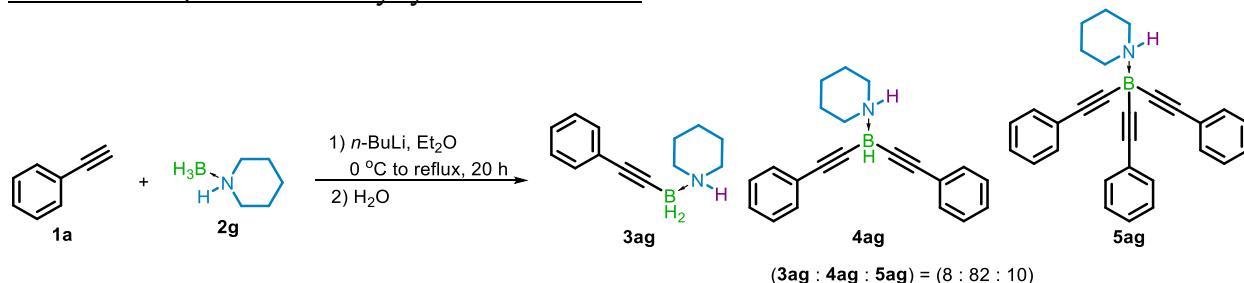
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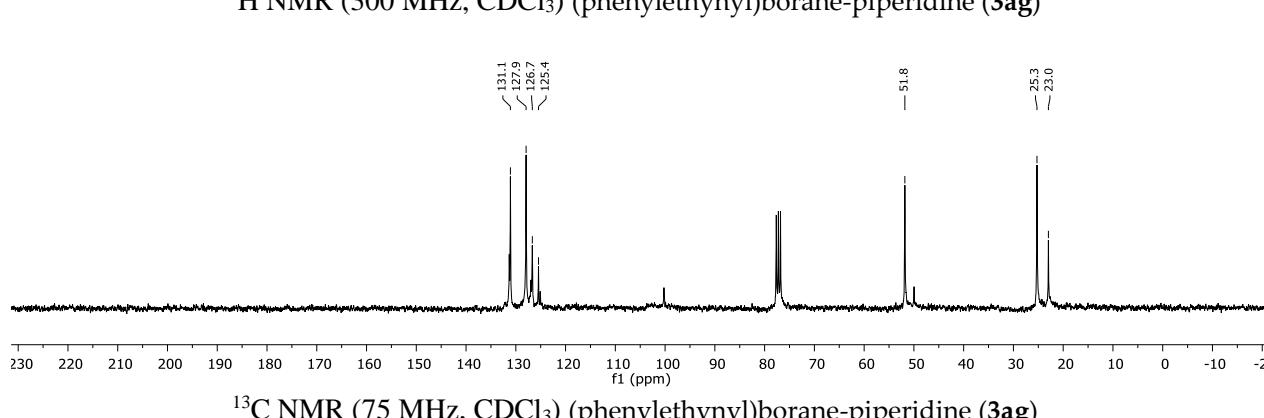
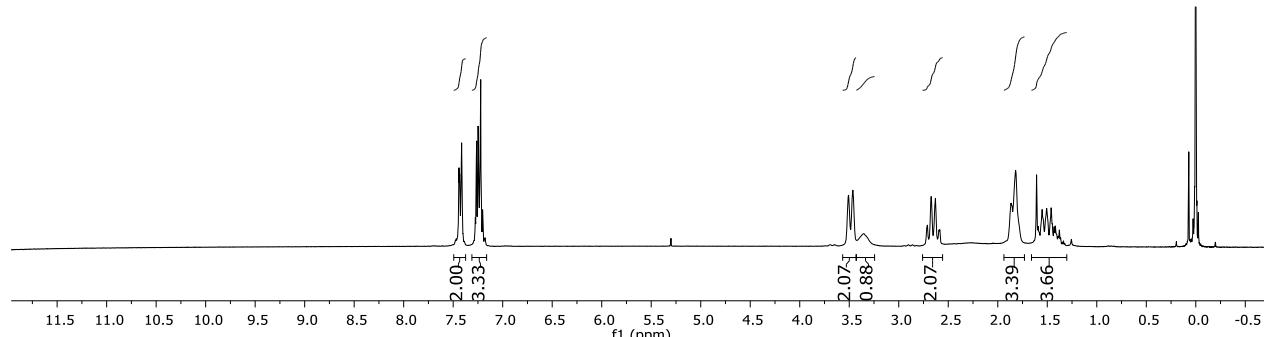
**Initial mono-, di- and trialkynylborane-amines:**

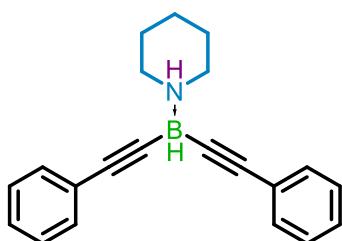
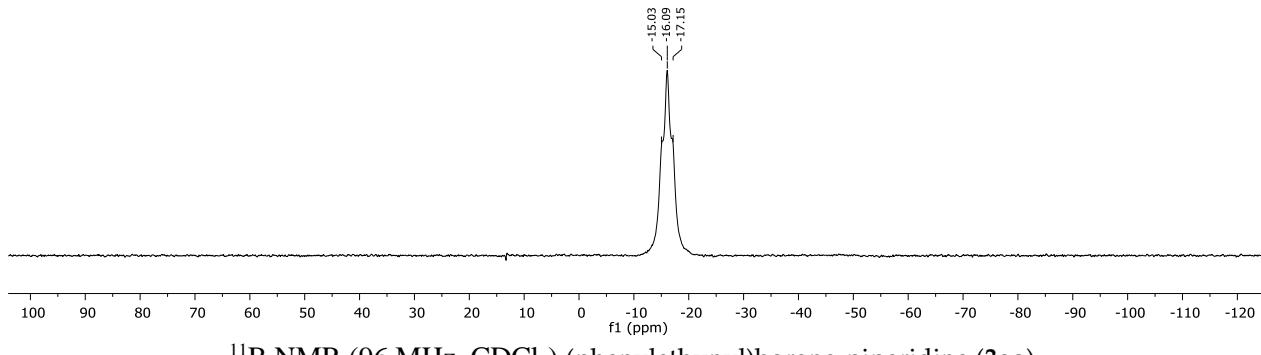


**Scheme S1.** Initial reaction of terminal alkyne and amine-borane.

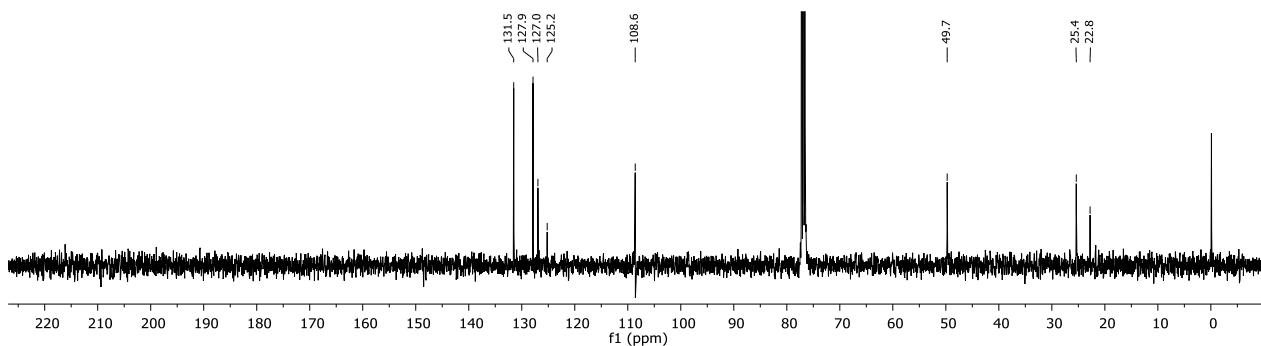
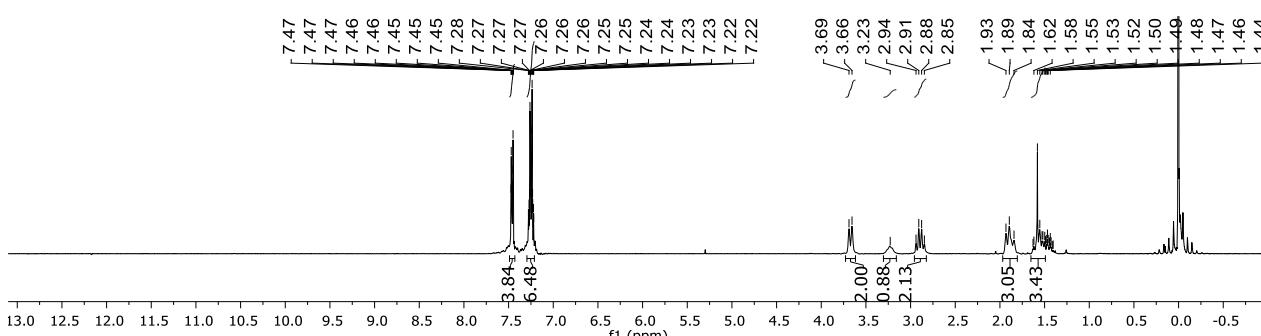
**Characterization**

**(phenylethynyl)borane-piperidine (3ag);** Melting point: 145–147 °C (DSC). **<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.49 – 7.37 (m, 2H), 7.31 – 7.16 (m, 3H), 3.49 (d, *J* = 13.4 Hz, 2H), 3.35 (s, 1H), 2.76 – 2.56 (m, 2H), 1.84 (d, *J* = 14.1 Hz, 3H), 1.66 – 1.30 (m, 4H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 131.1, 127.9, 126.7, 125.4, 51.8, 25.3, 23.0. **<sup>11</sup>B NMR** (96 MHz, Chloroform-*d*) δ -16.09 (*t*, *J* = 102.1 Hz). **HRMS (ESI)** calcd for C<sub>13</sub>H<sub>18</sub>NNa (M+Na)<sup>+</sup>: *m/z*, 221.1466, found 221.1462.

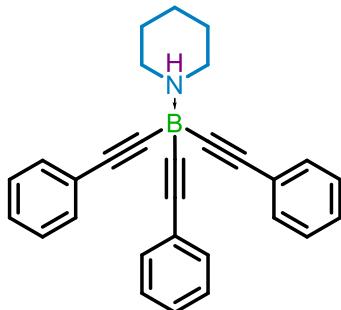
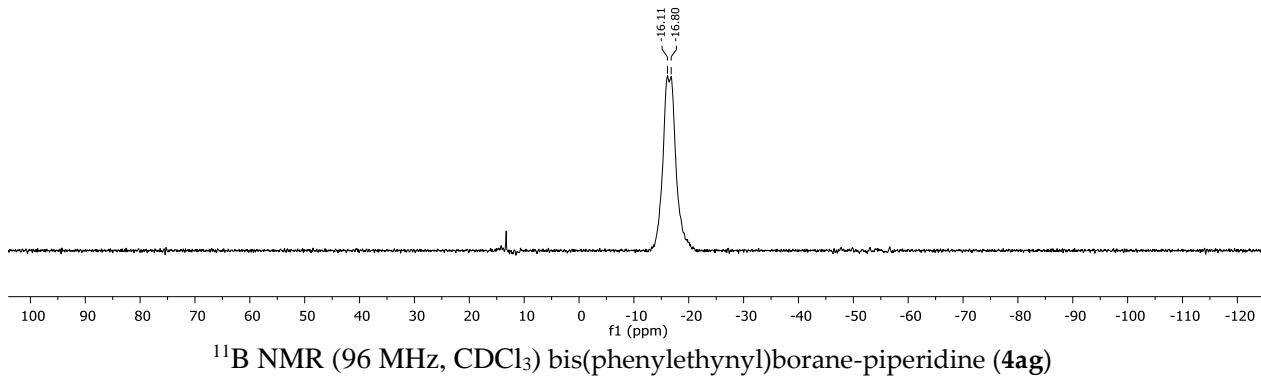




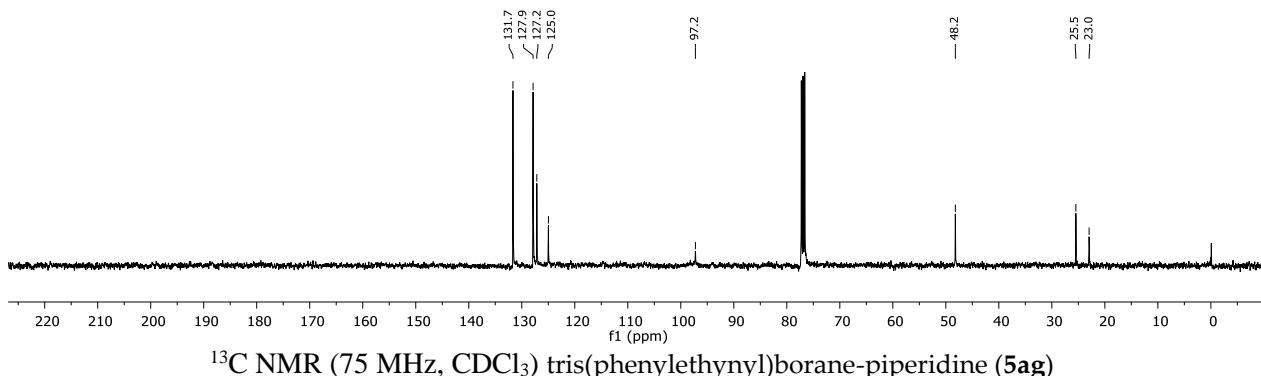
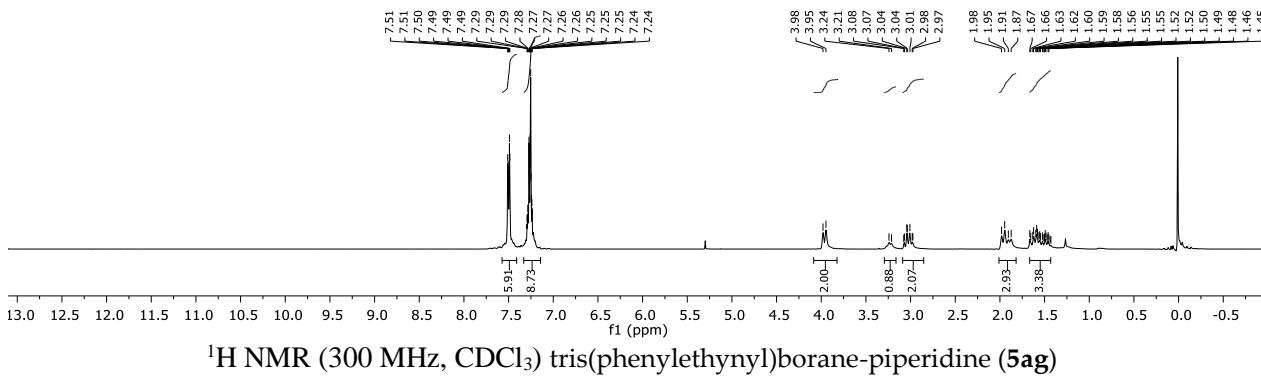
bis(phenylethynyl)borane-piperidine (**4ag**); Melting point: 105-107 °C (DSC). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 4H), 7.29 – 7.21 (m, 6H), 3.67 (d, *J* = 13.5 Hz, 2H), 3.23 (s, 1H), 2.89 (q, *J* = 12.4 Hz, 2H), 1.89 (t, *J* = 18.0 Hz, 3H), 1.65 – 1.49 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 131.5, 127.9, 127.0, 125.2, 108.6, 49.7, 25.4, 22.8. <sup>11</sup>B NMR (96 MHz, Chloroform-*d*) δ -16.42 (d, *J* = 102.1 Hz). HRMS (ESI) calcd for C<sub>21</sub>H<sub>22</sub>BNNa (M+Na)<sup>+</sup>: *m/z*, 321.1779, found 321.1775.

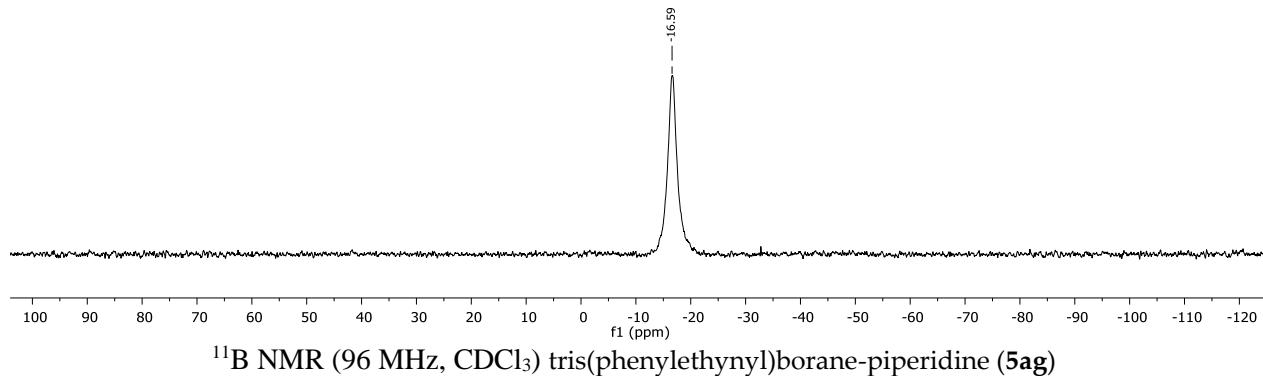


<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) bis(phenylethynyl)borane-piperidine (**4ag**)



tris(phenylethynyl)borane-piperidine (**5ag**); Melting point: 232–235 °C (DSC). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.41 (m, 6H), 7.33 – 7.14 (m, 9H), 3.96 (d, *J* = 13.3 Hz, 2H), 3.23 (d, *J* = 11.4 Hz, 1H), 3.09 – 2.85 (m, 2H), 1.93 (dd, *J* = 29.9, 13.5 Hz, 3H), 1.67 – 1.43 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 131.66, 127.86, 127.16, 124.97, 48.20, 25.47, 22.97. <sup>11</sup>B NMR (96 MHz, Chloroform-*d*) δ -16.59. HRMS (ESI) calcd for C<sub>29</sub>H<sub>26</sub>BNNa (M+Na)<sup>+</sup>: *m/z*, 421.2092, found 421.2086.





### Reaction optimization:

**Table S1.** Examination of order of reagent addition

Addition Type <sup>a</sup>	Equivalency DMAB:nBuLi:Alkyne	Alkyne Conversion <sup>b,c</sup>
LAB formation	1:1:0.3	69%
Acetylide formation	1:1:0.3	70%
Parallel addition	1:1:0.3	70%
LAB formation	1:1:0.5	51%
Acetylide formation	1:1:0.5	48%
Parallel addition	1:1:0.5	50%

<sup>a</sup>The reactions were carried out using diethyl ether as the solvent and 4-methoxyphenylacetylene as the alkyne. <sup>b</sup>Isolated yield, but without complete chromatographic separation. <sup>c</sup>Alkyne conversion includes both mono- and di- substituted products

**Table S2.** Examination of reagent equivalency

Conditions <sup>a</sup>	Equivalency DMAB:nBuLi:Alkyne	Product Ratio <sup>b</sup>	Alkyne Conversion <sup>c,d</sup>
rt, 48 h	1:1:1	78:22	68%
rt, 24 h	1:1:0.8	94:6	75%
rt, 24 h	1: 0.9325:0.8	91:9	56%
rt, 24 h	1:1:0.65	92:8	66%
rt, 24 h	1: 0.875:0.65	87:3	82%
rt, 24 h	1:1:0.5	87:13	98%
rt, 24 h	1:0.9325:0.5	85:15	99%
rt, 24 h	1:0.75:0.5	90:10	74%
rt, 24 h	1:1:0.3	99:1	66%

<sup>a</sup>The reactions were carried out using diethyl ether as the solvent and 4-methoxyphenylacetylene as the alkyne. <sup>b</sup>Ratio is of mono- substituted to di- substituted product. <sup>c</sup>Isolated yield, but without complete chromatographic separation. <sup>d</sup>Alkyne conversion includes both mono- and di- substituted products

**Table S3.** Examination of reaction duration

Conditions <sup>a</sup>	Product Ratio <sup>b</sup>	Alkyne Conversion <sup>c,d</sup>
6 h	97:3	70%
12 h	94:6	78%
24 h	85:15	95%

<sup>a</sup>The reactions were carried out at room temperature, using diethyl ether as the solvent, dimethylamine-borane as the amine-borane, and 4-methoxyphenylacetylene as the alkyne. <sup>b</sup>Ratio is of mono- substituted to di- substituted product. <sup>c</sup>Isolated yield, but without complete chromatographic separation. <sup>d</sup>Alkyne conversion includes both mono- and di- substituted products

**Table S4.** Examination of reaction solvent<sup>a</sup>

Solvent	Product Ratio <sup>b</sup>	Alkyne Conversion <sup>c,d</sup>
Diethyl ether	85:15	95%
Tetrahydrofuran	73:27	51%
Dimethoxymethane	80:20	30%
Dichloromethane	87:13	80%
<b>Toluene</b>	<b>100:0</b>	<b>79%</b>
<b>Pentane</b>	<b>99:1</b>	<b>92%</b>
Triethylamine	85:15	80%

<sup>a</sup>The reactions were carried out at room temperature, using dimethylamine-borane as the amine-borane, and 4-methoxyphenylacetylene as the alkyne. <sup>b</sup>Ratio is of mono- substituted to di- substituted product. <sup>c</sup>Isolated yield, but without complete chromatographic separation. <sup>d</sup>Alkyne conversion includes both mono- and di- substituted products

**Table S5.** Final reaction conditions standardization<sup>a</sup>

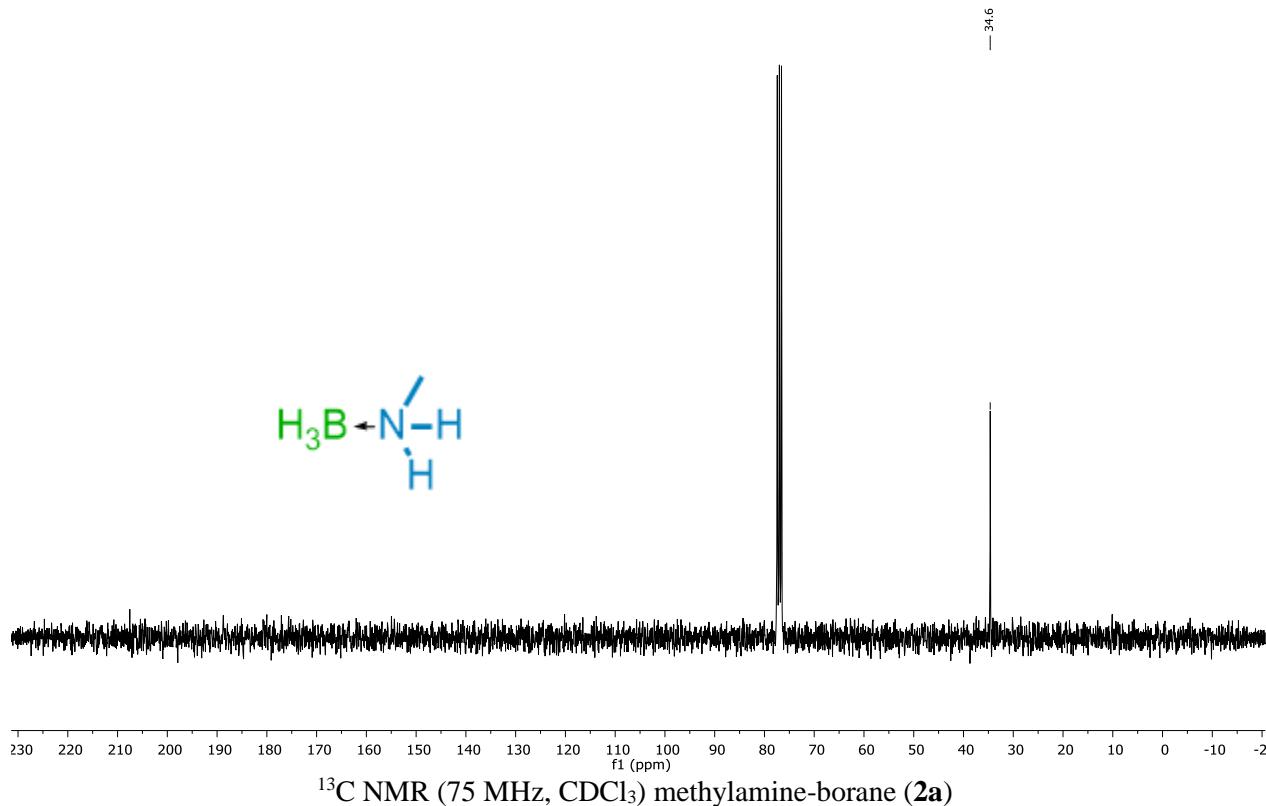
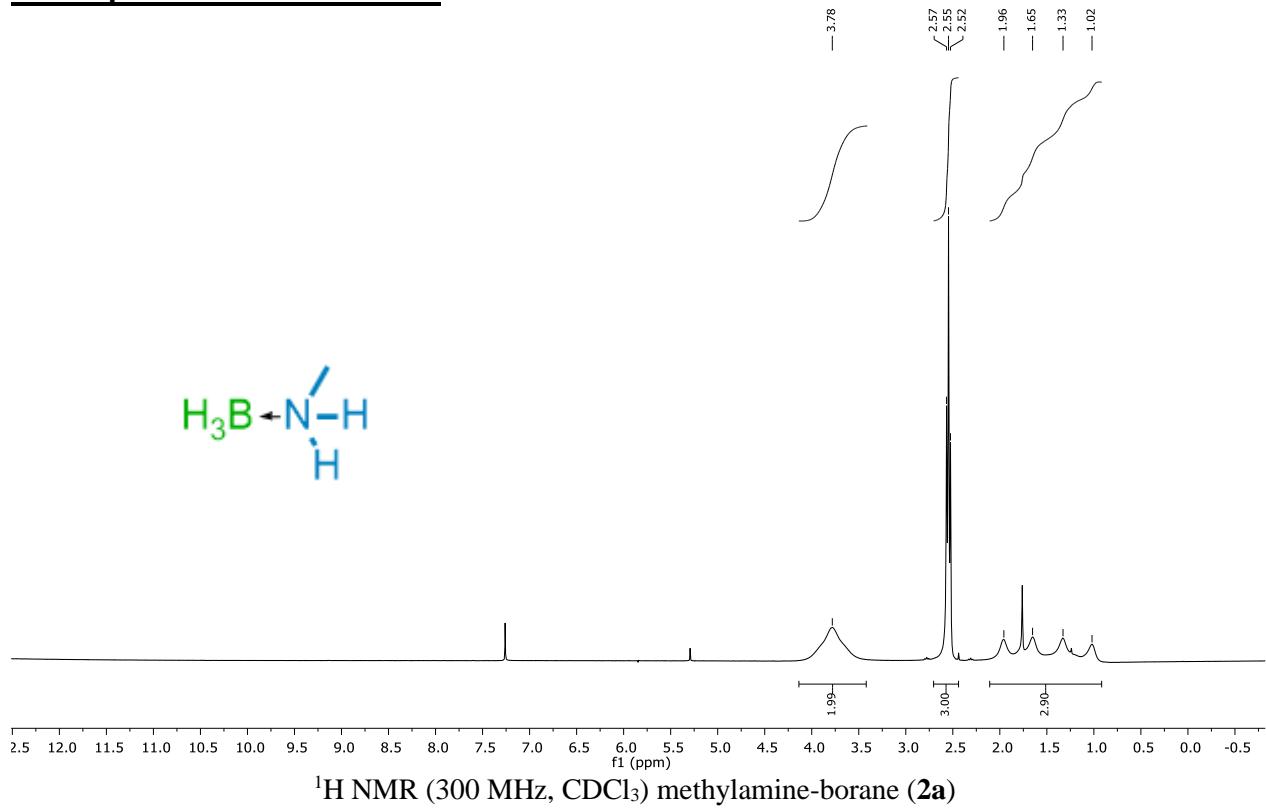
Reaction Conditions	Equivalency DMAB:nBuLi:Alkyne	Product Ratio <sup>b</sup>	Alkyne Conversion <sup>c,d</sup>
rt, 24 h, pentane (0.33 M)	2:1.865:1	99:1	59%
rt, 36 h, pentane (1 M)	2:1.865:1	99:1	99%
rt, 24 h, pentane (neat)	2:1.865:1	99:1	98%
reflux, 24 h, pentane	2:1.865:1	99:1	86%
<b>reflux, 2 h, pentane</b>	<b>2:1.865:1</b>	<b>99:1</b>	<b>97%</b>
reflux 2 h, hexane	2:1.865:1	99:1	91%
reflux 18 h, pentane	2:1.865:1	99:1	72%
rt, 24 h, toluene	2:1.865:1	99:1	86%
60 °C, 24 h, toluene	2:1.865:1	99:1	94%
60 °C, 4 h, toluene	2:1.865:1	99:1	87%
reflux, 24 h, toluene	2:1.865:1	99:1	82%
60 °C, 16 h, toluene	2:1.865:1.5	99:1	79%
60 °C, 16 h, toluene	1:0.9325:1	94:6	62%

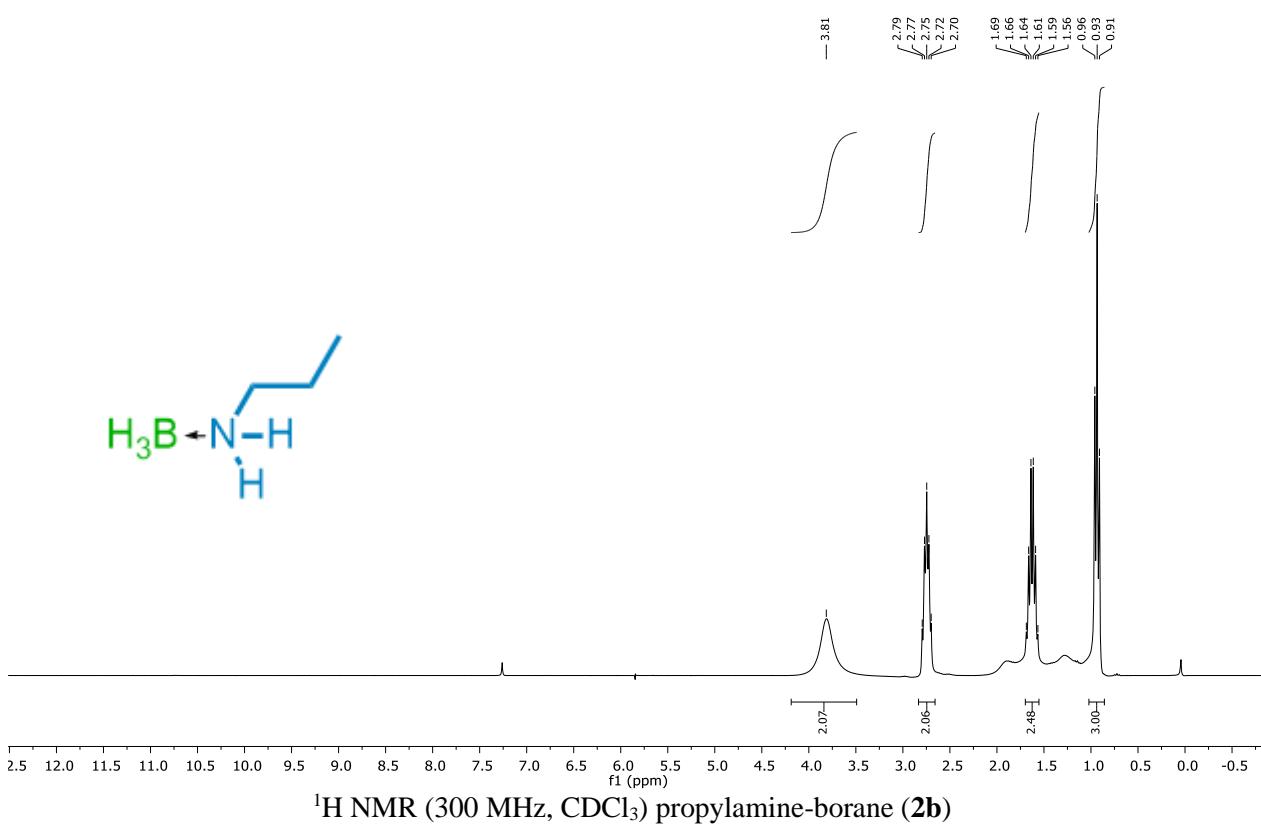
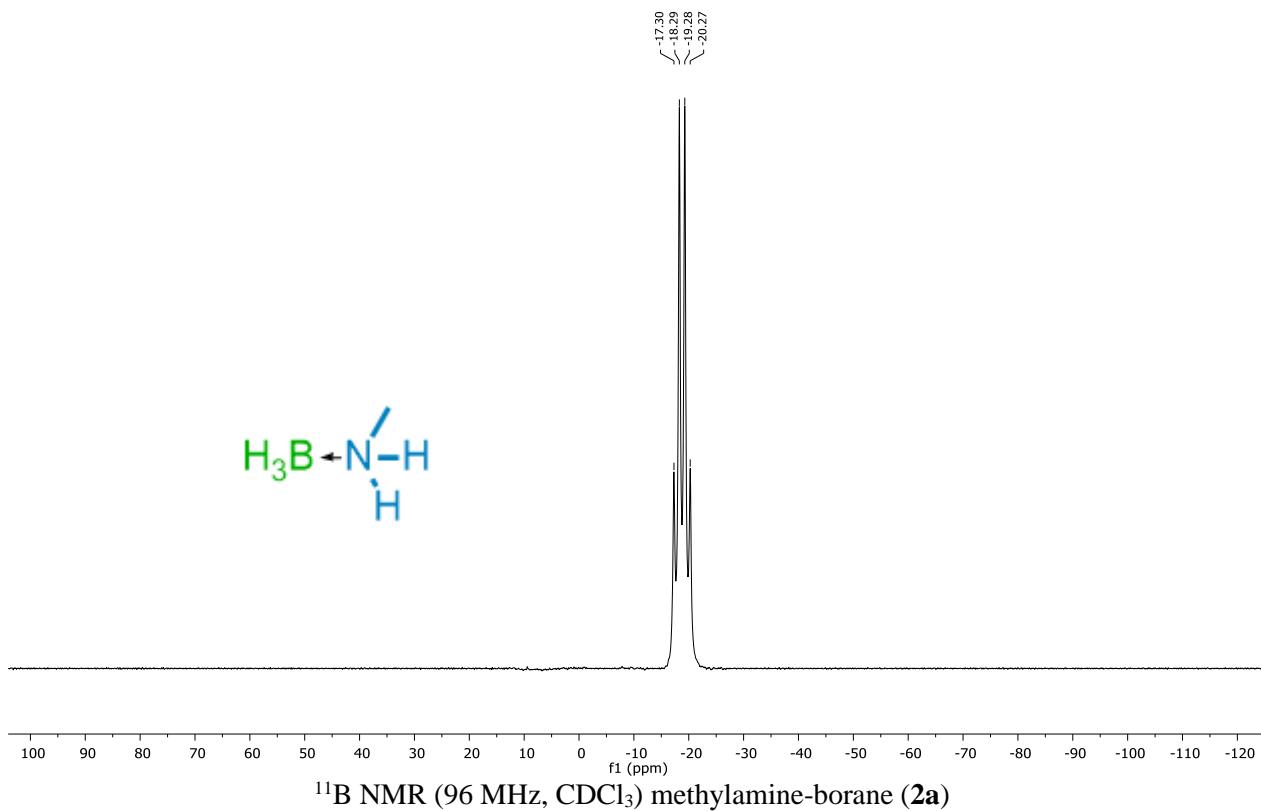
<sup>a</sup>The reactions were carried out using dimethylamine-borane as the amine-borane, and 4-methoxyphenylacetylene as the alkyne. <sup>b</sup>Ratio is of mono- substituted to di- substituted product. <sup>c</sup>Isolated yield, but without complete chromatographic separation. <sup>d</sup>Alkyne conversion includes both mono- and di- substituted products

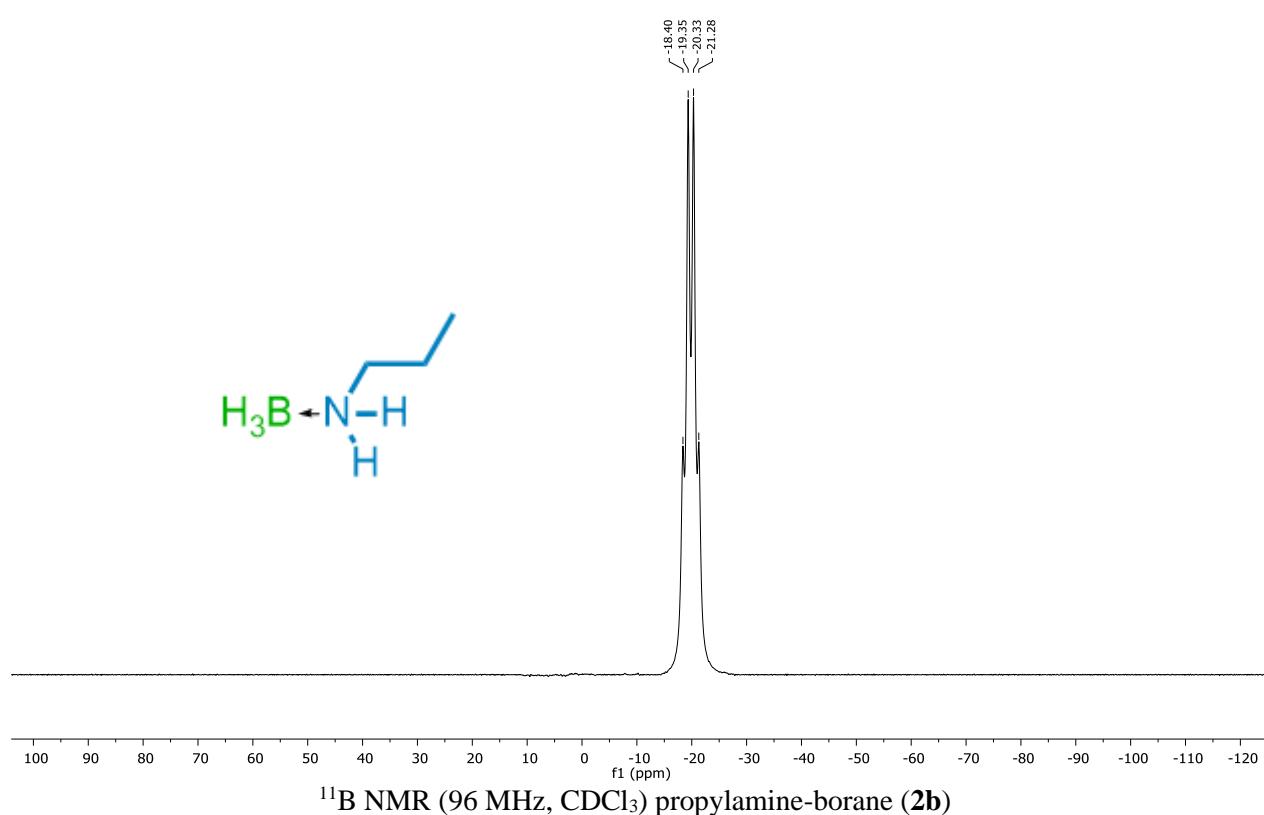
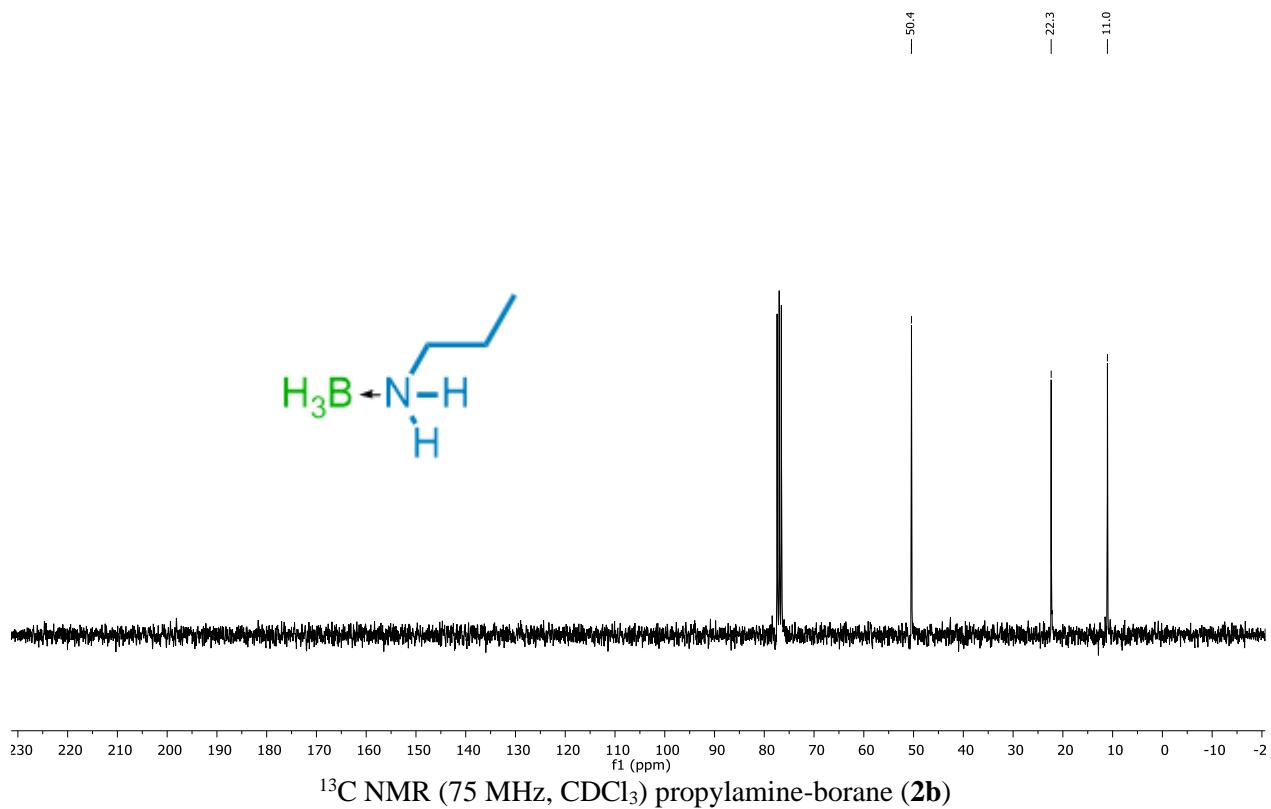
**Table S6.** Optimization of Dibromide Conversion

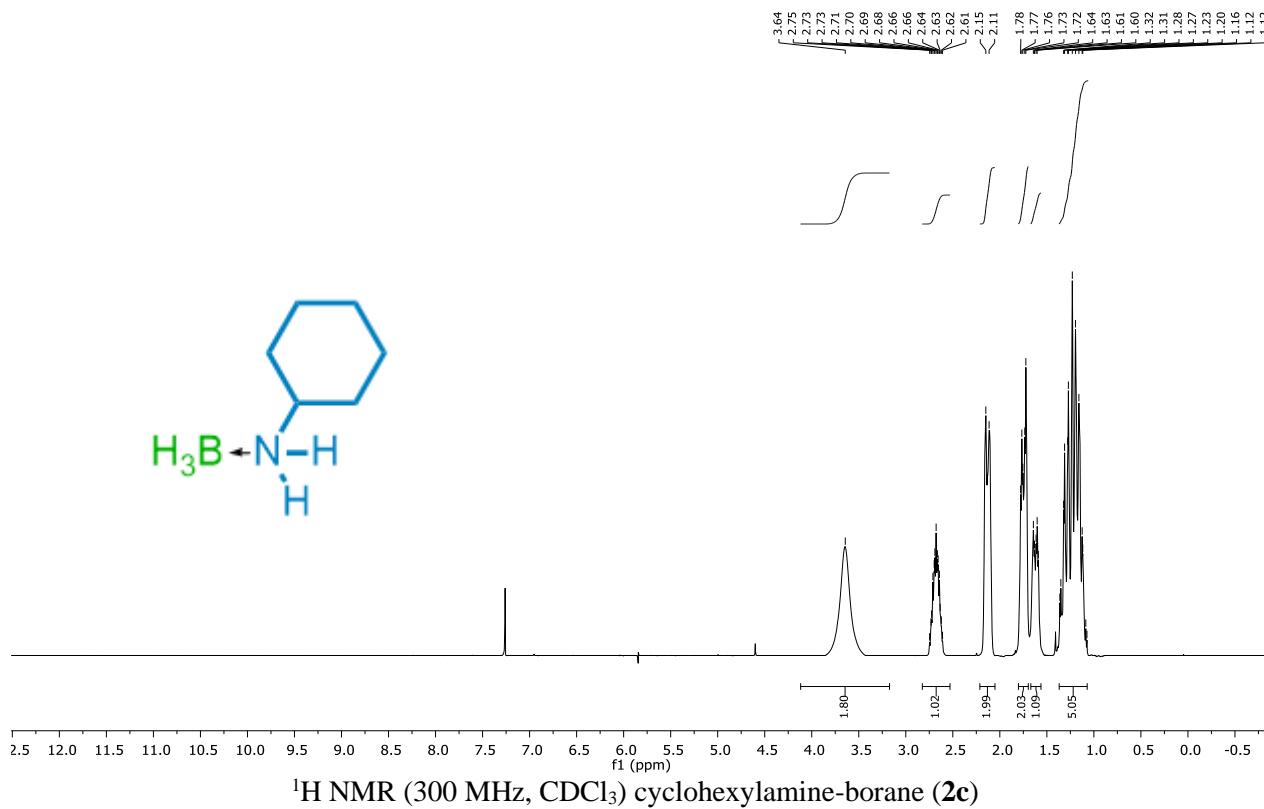
Reaction Conditions	Equivalency DMAB:nBuLi:Dibromide	Product Ratio <sup>b</sup>	Alkyne Conversion <sup>c,d</sup>
1h -78 °C, 1h 0 °C, 2h reflux	2:3.865:1	99:1	10%
1h -78 °C, 1h 0 °C, 2h reflux	2:2.865:1	99:1	62%
1h -78 °C, 1h 0 °C, 4h reflux	2:2.865:1	99:1	60%
1h -78 °C, 1h 0 °C, 2h reflux	2:2.3:1	99:1	89%

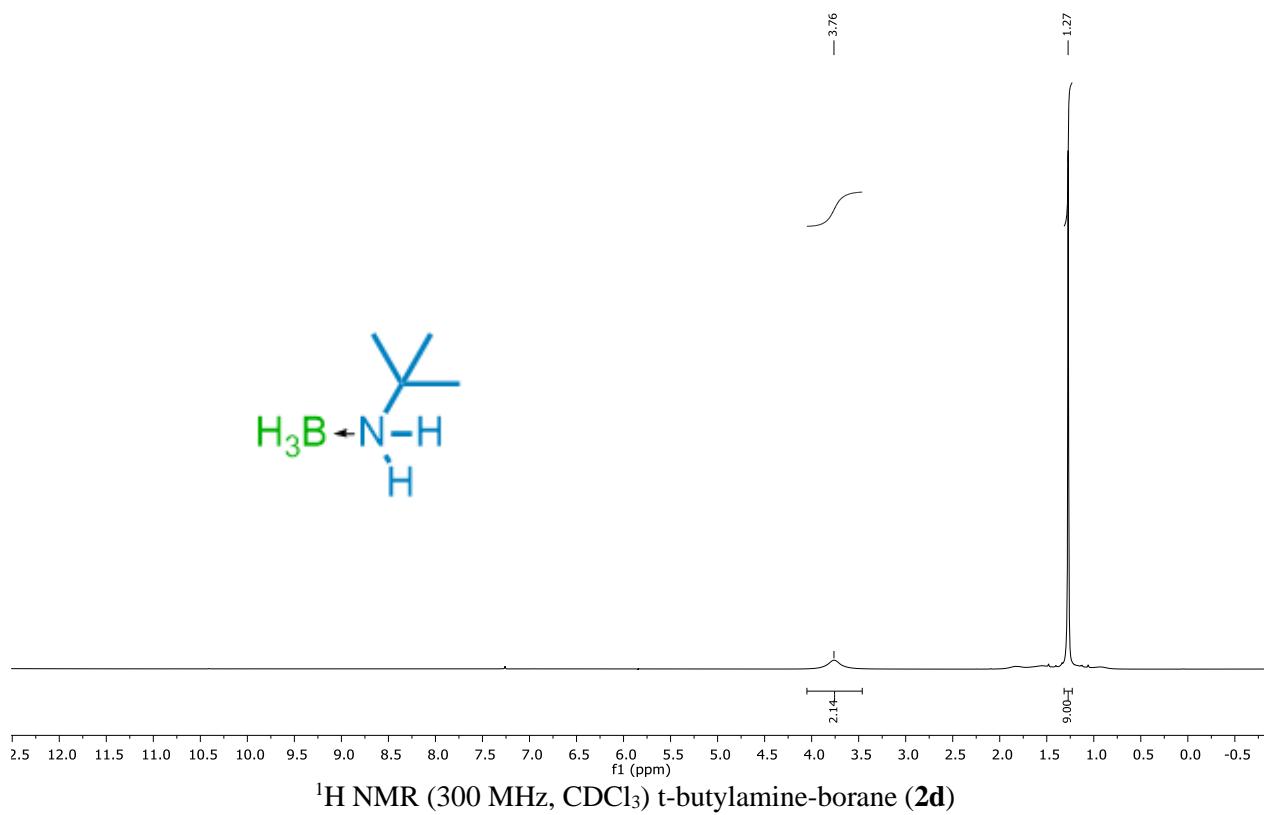
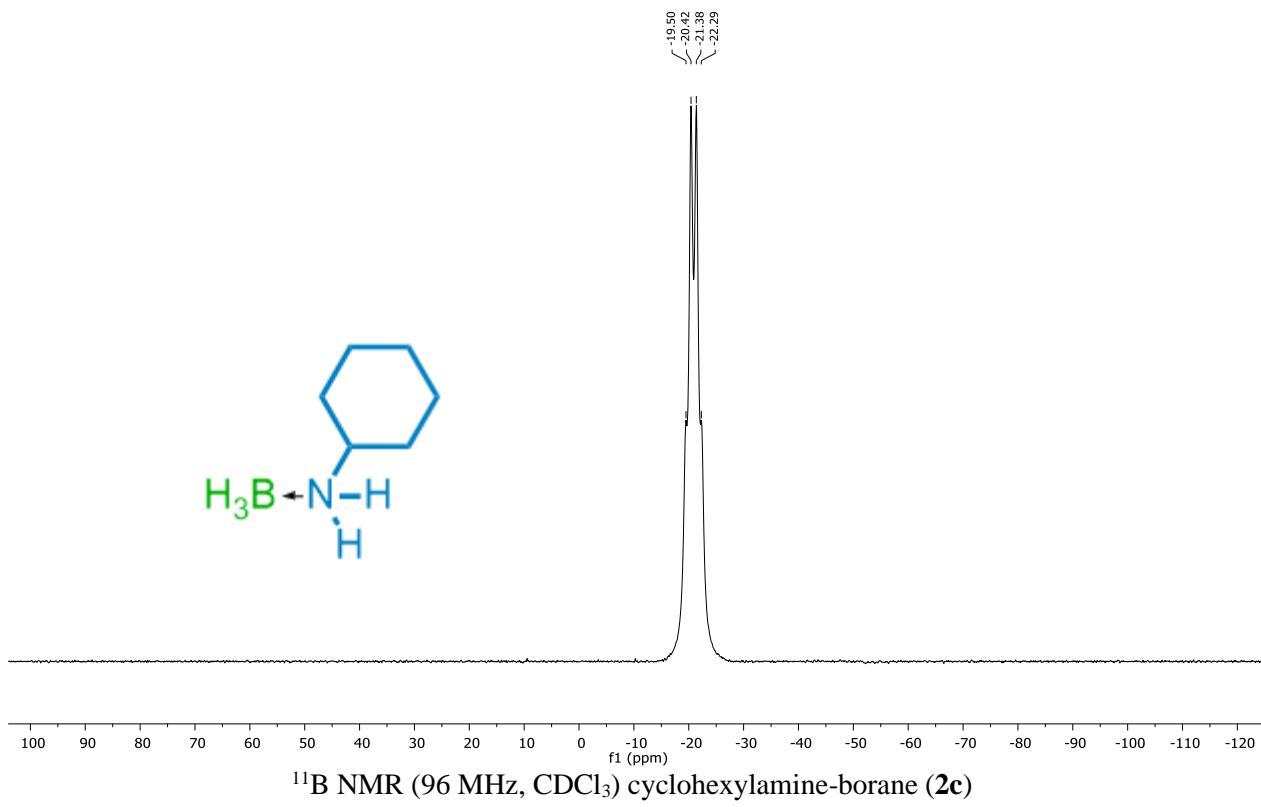
## NMR spectra of amine-boranes

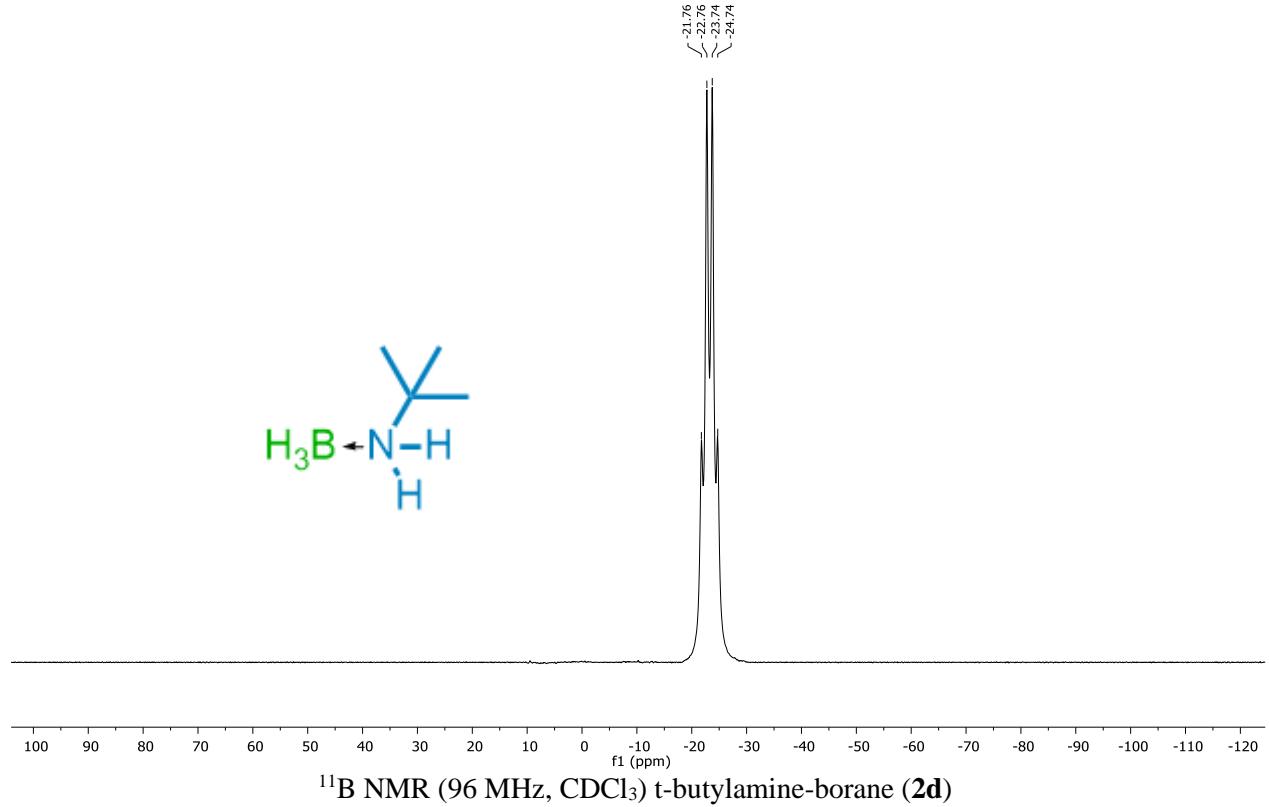
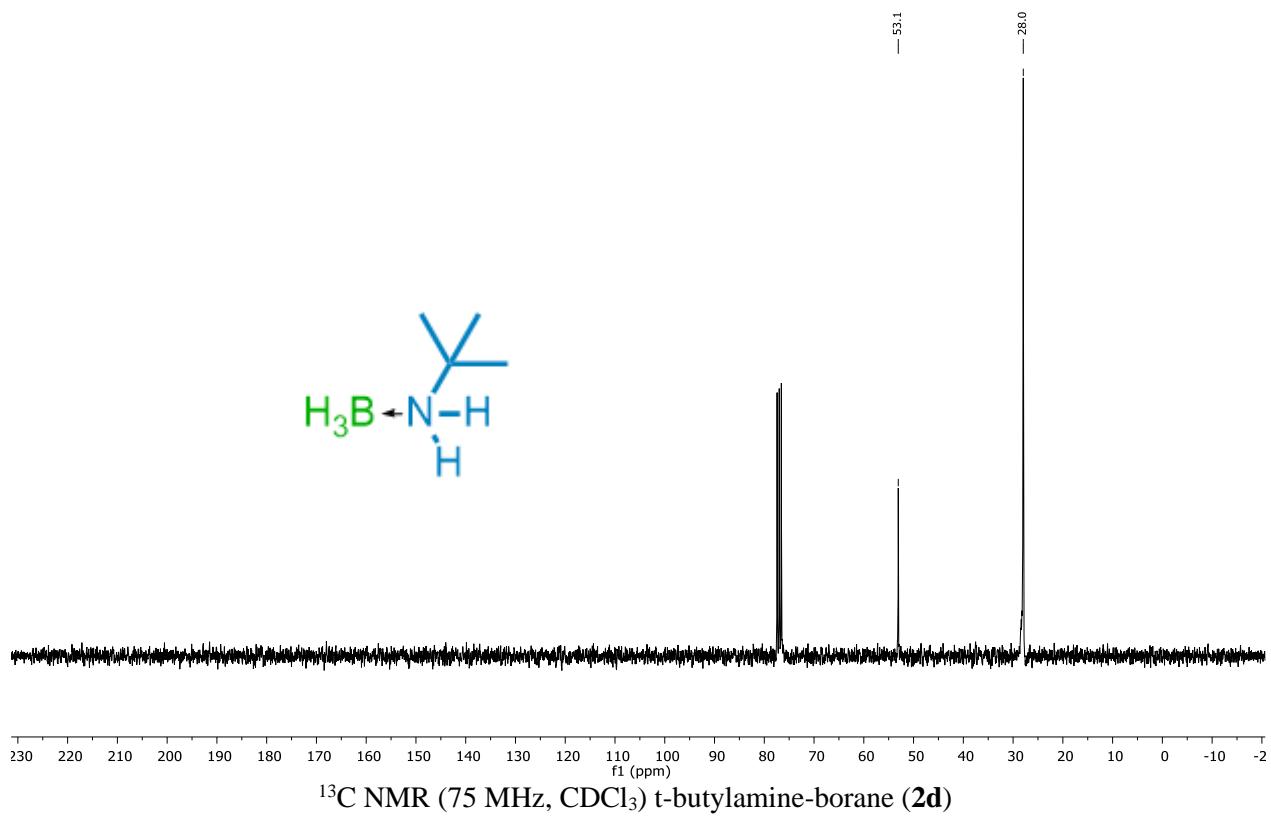


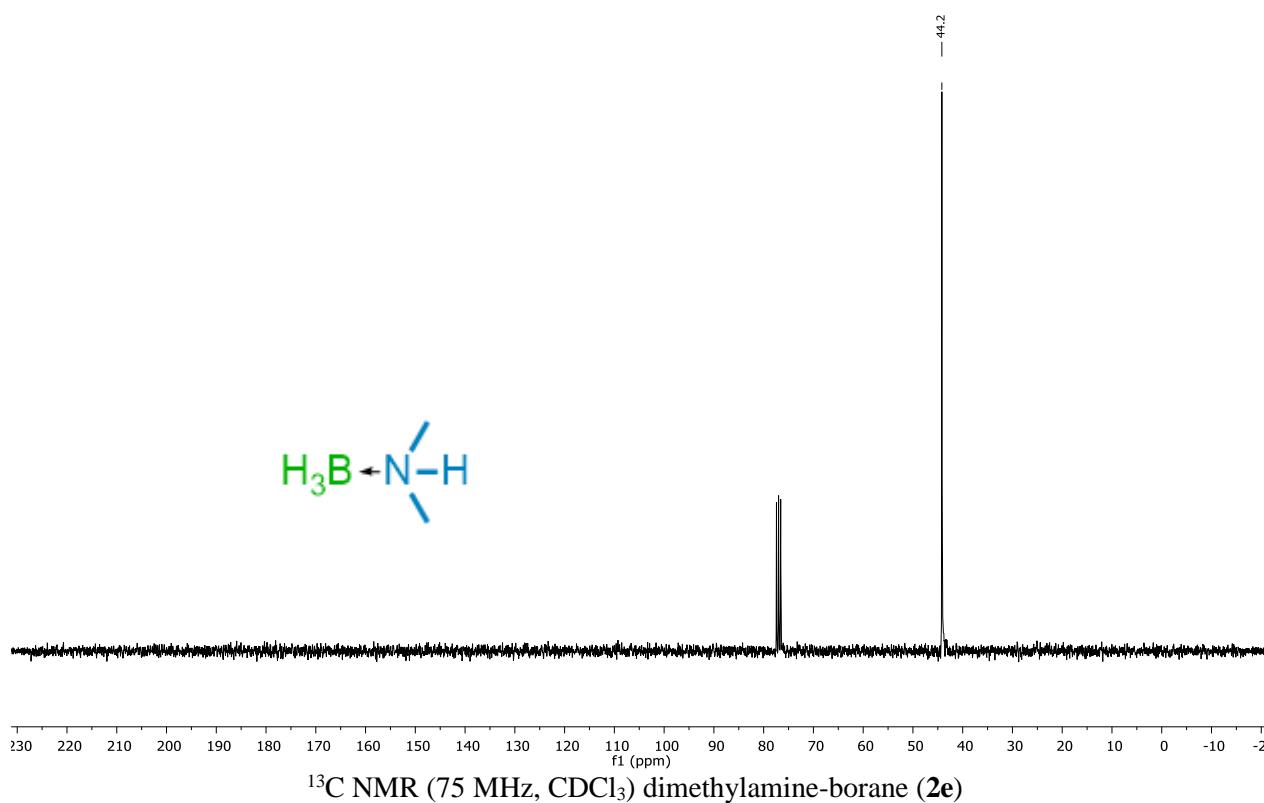
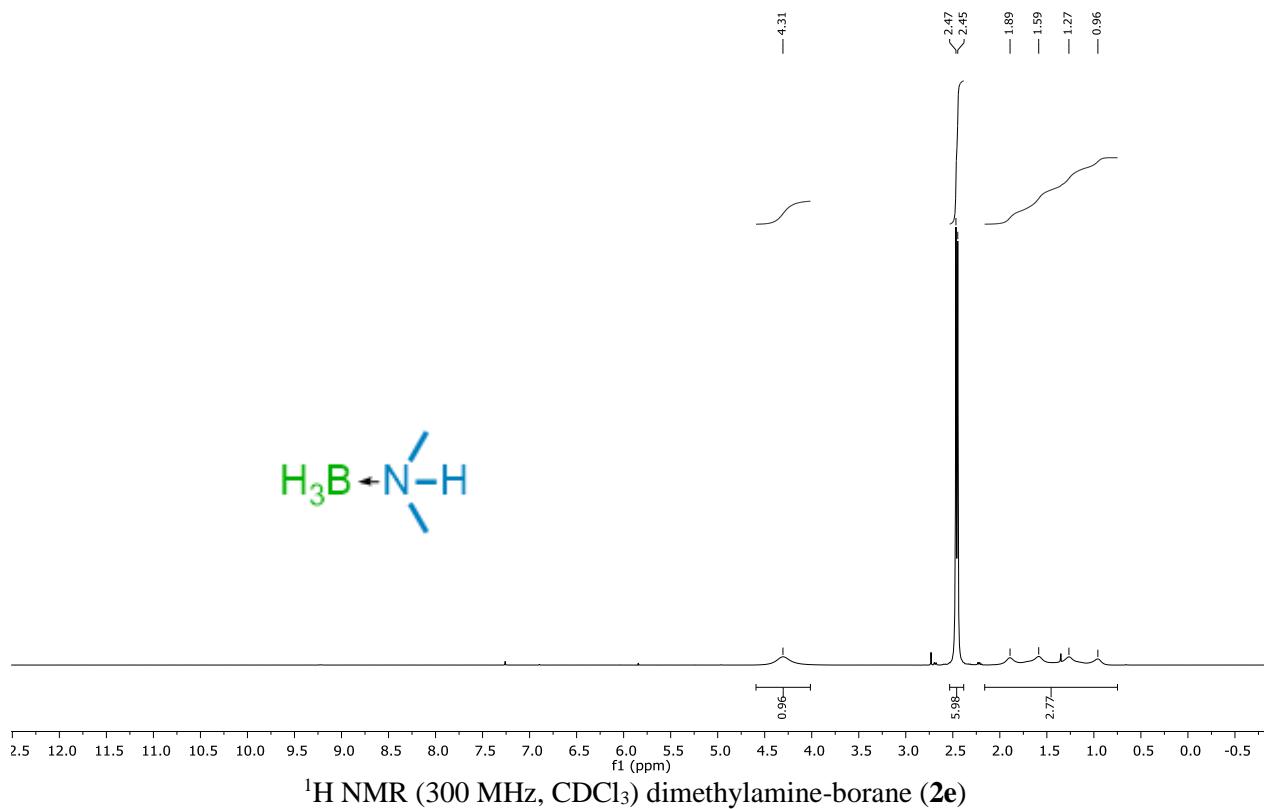


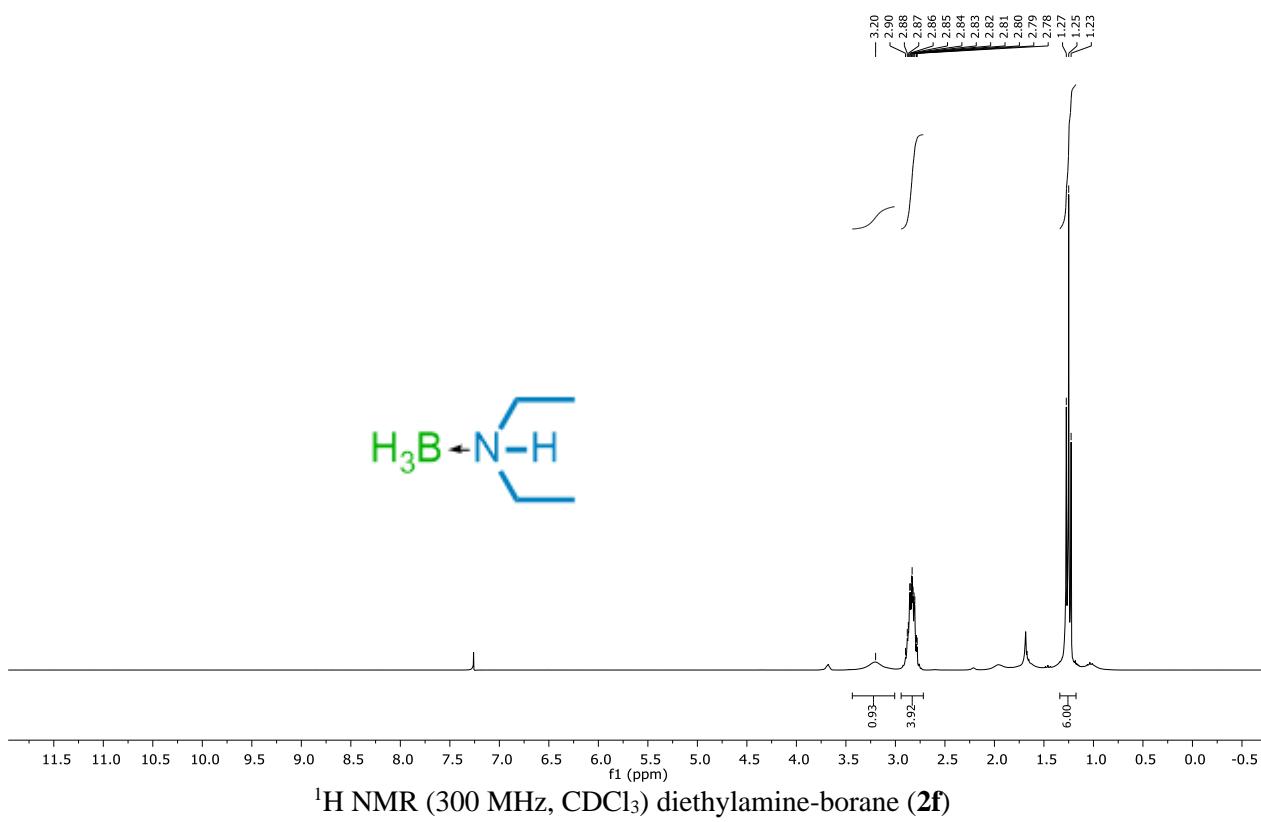
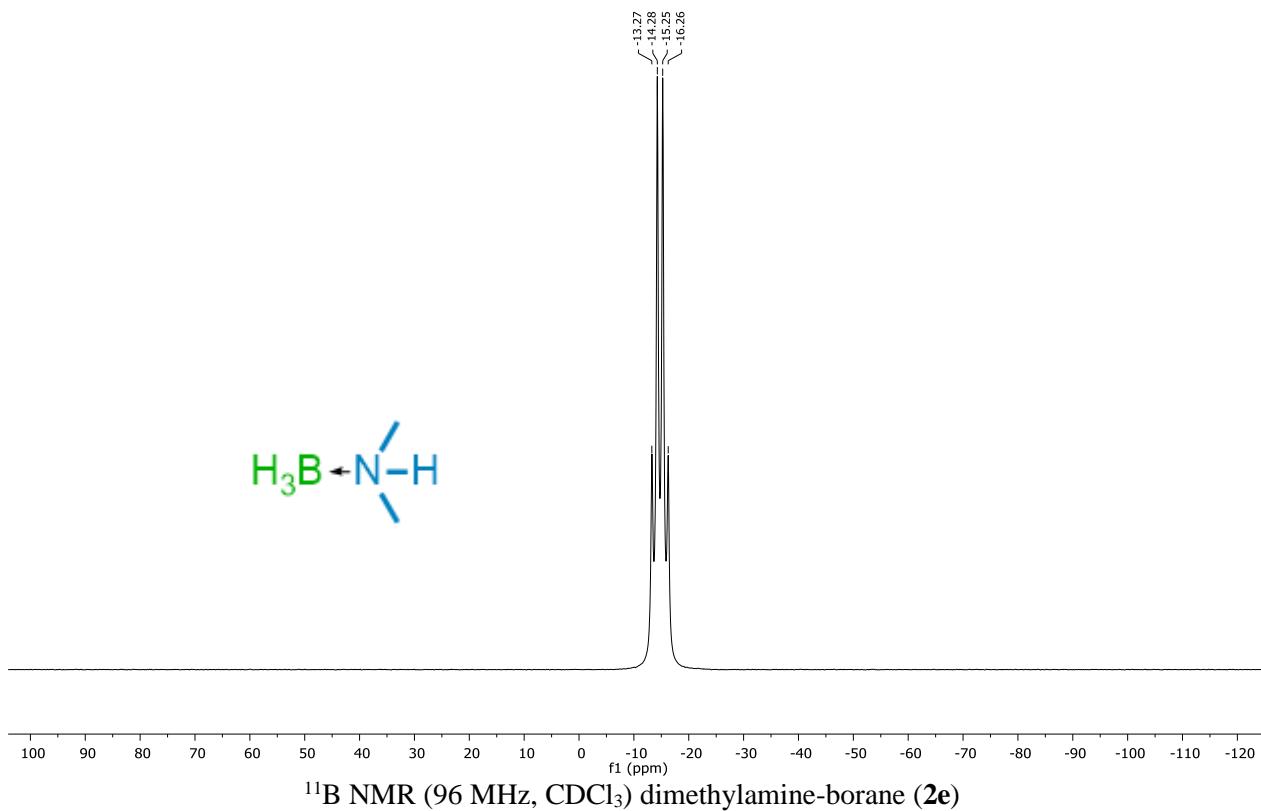


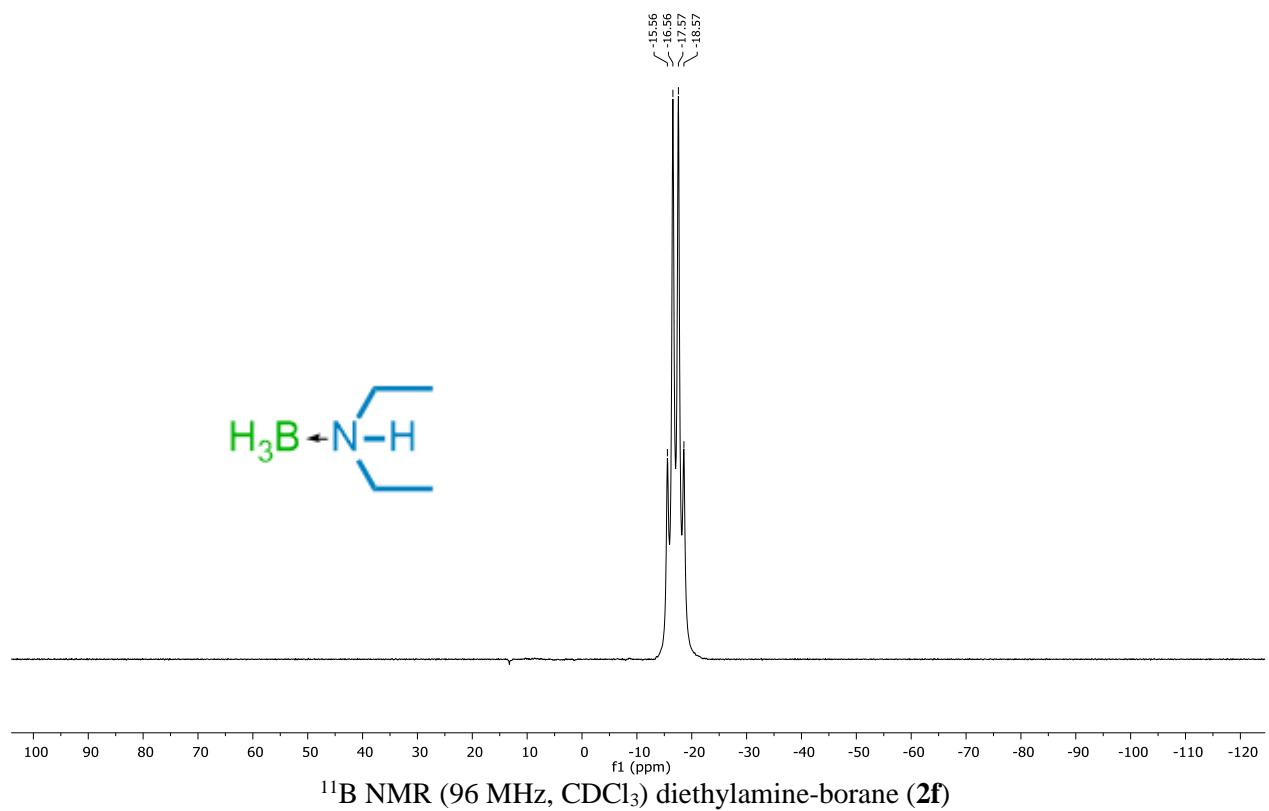
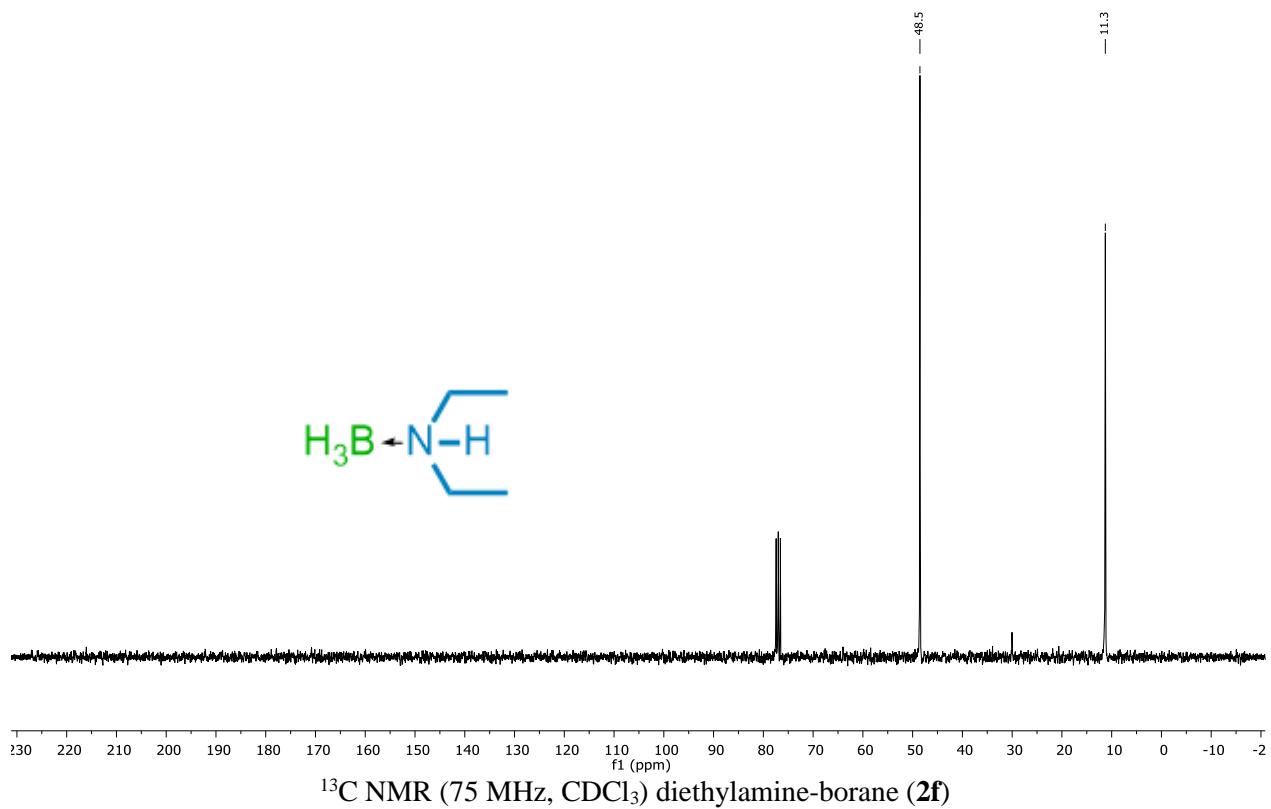


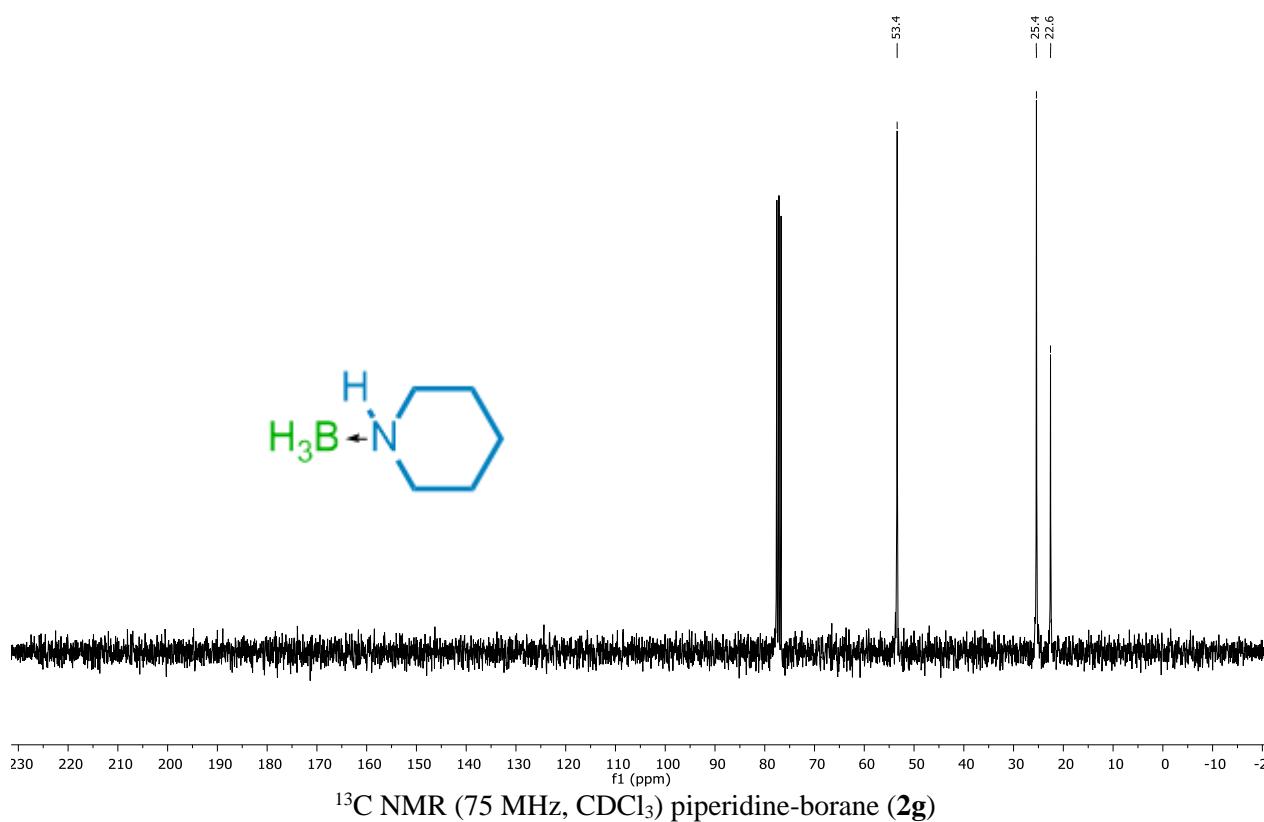
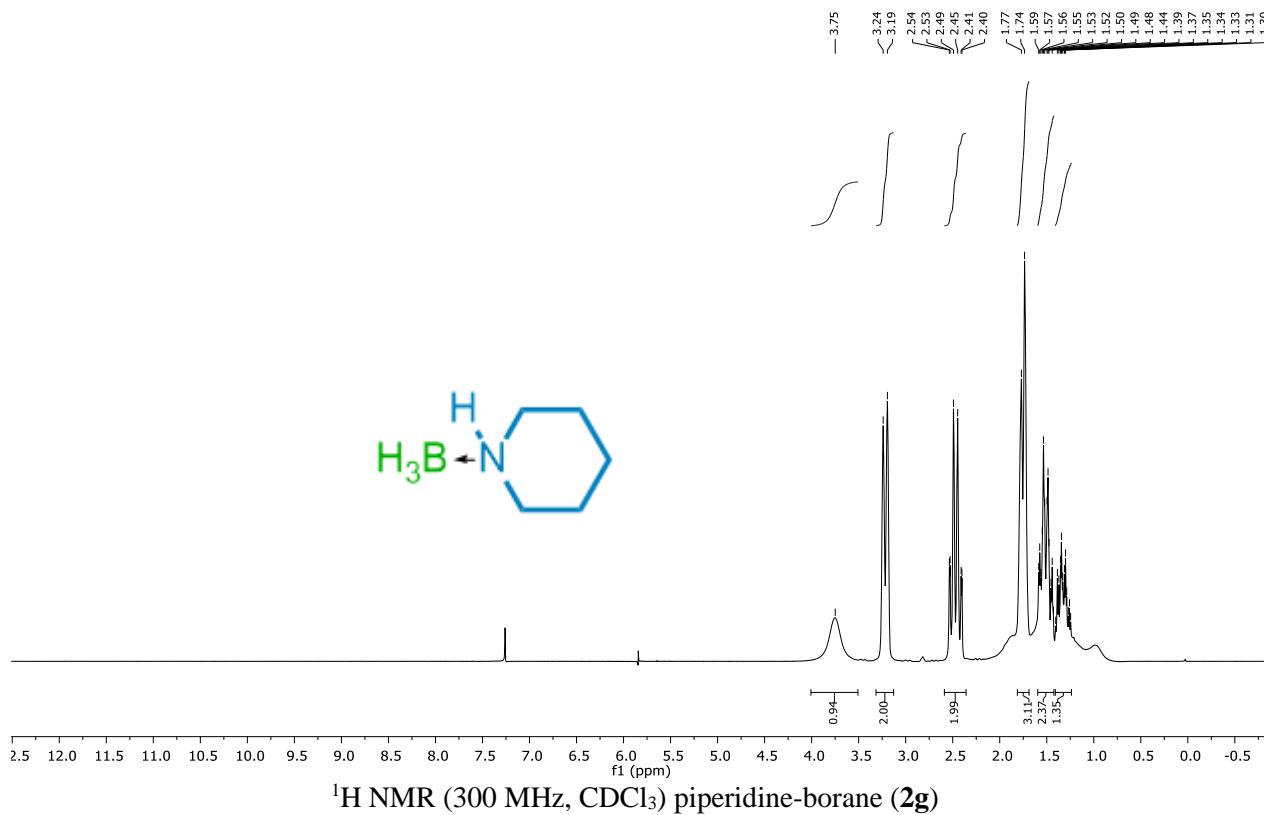


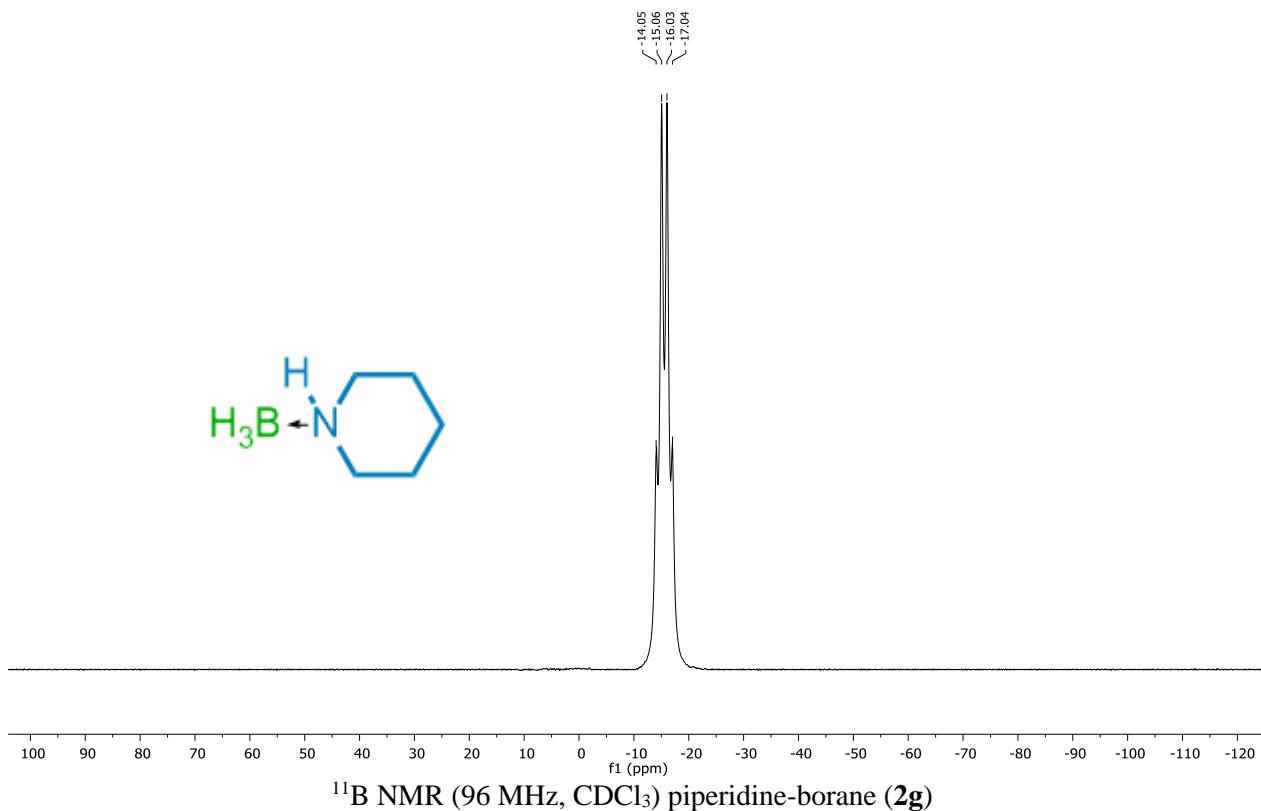




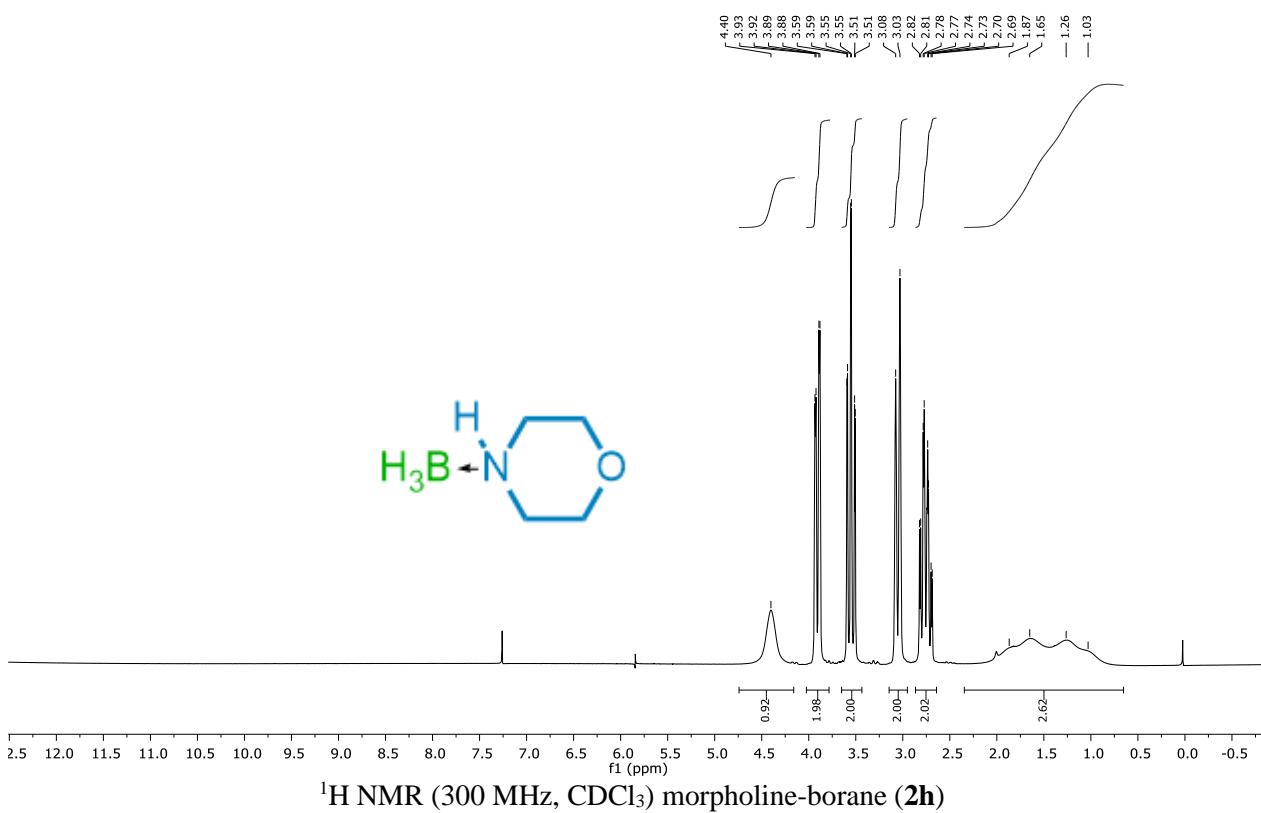


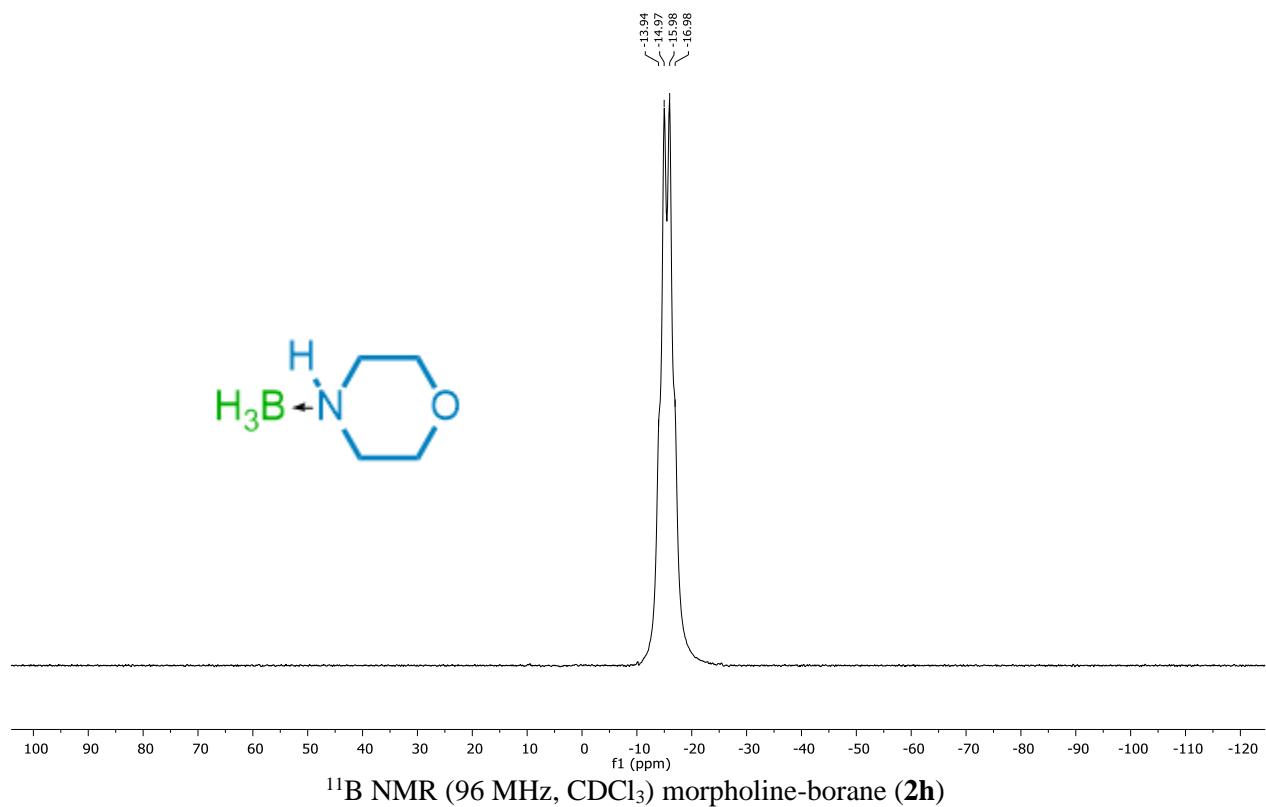
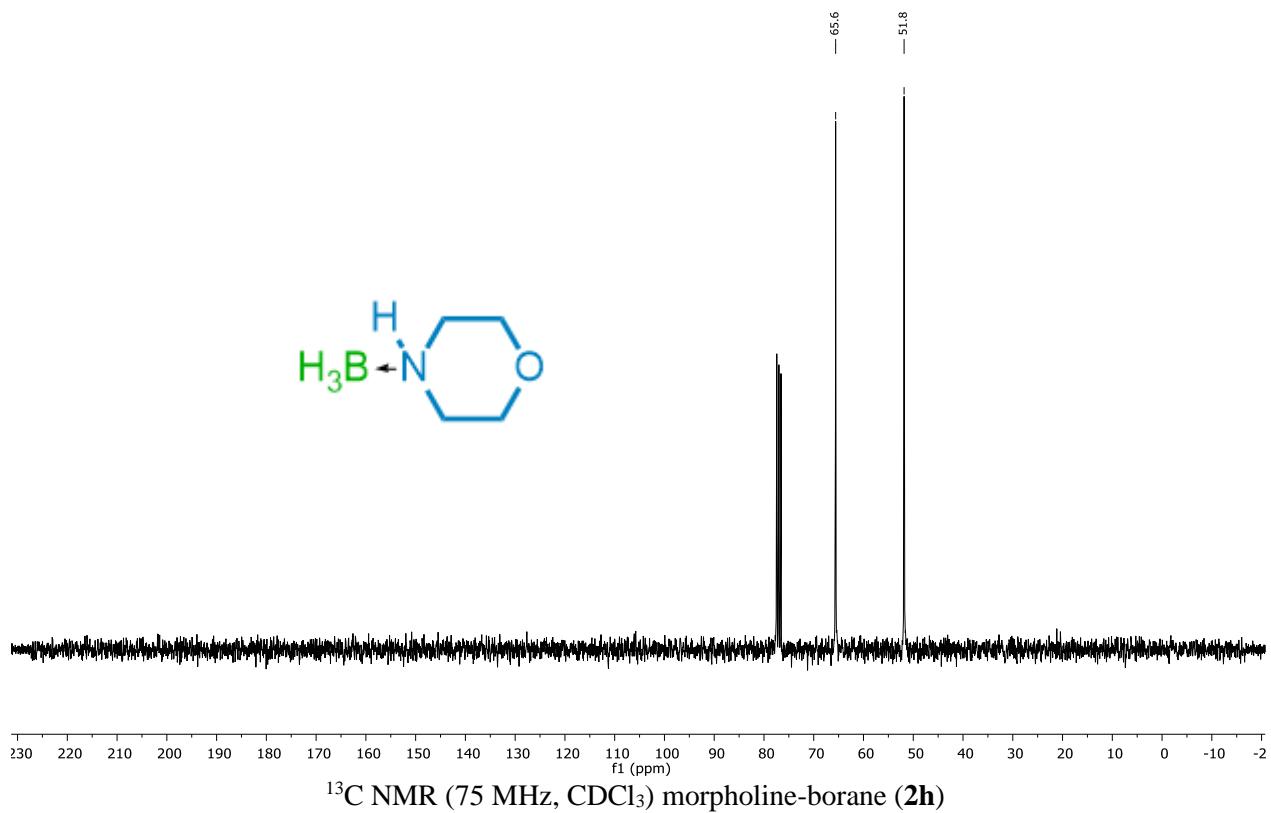


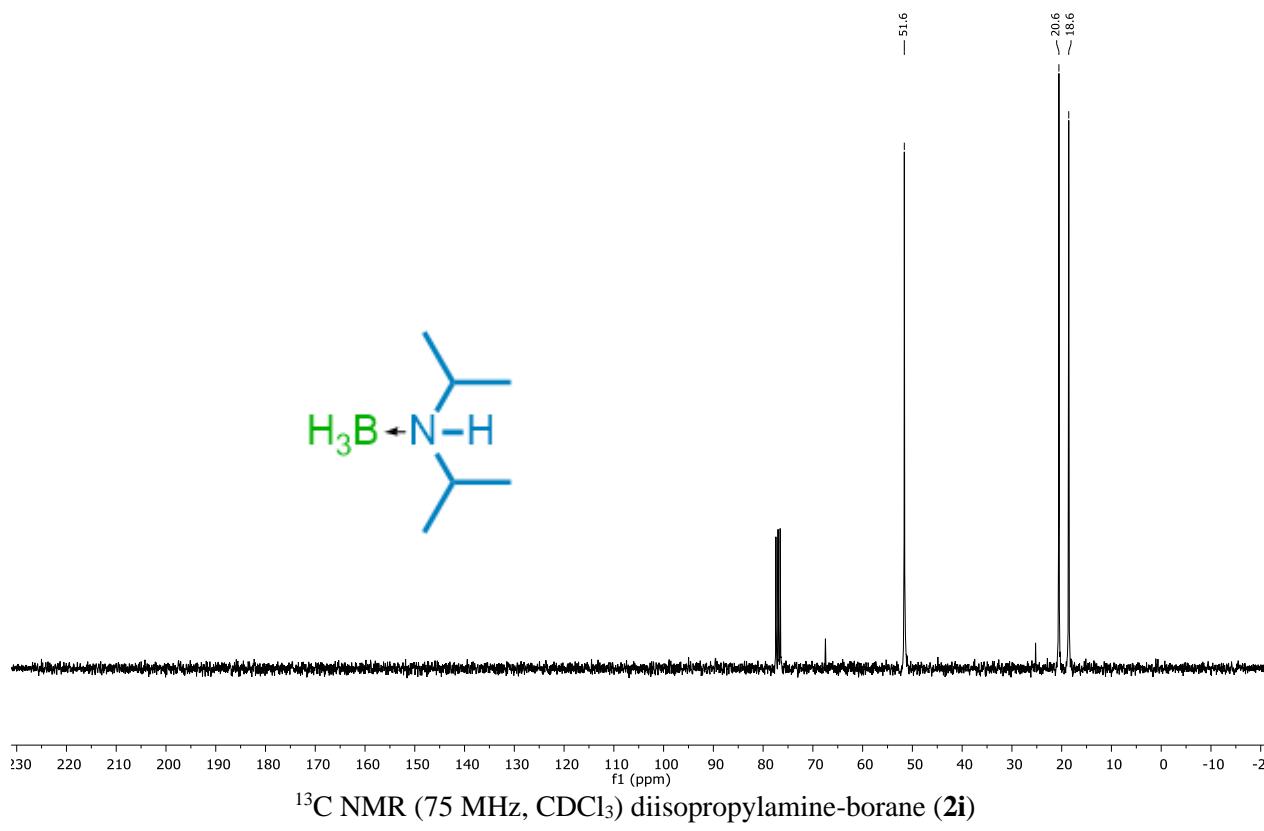
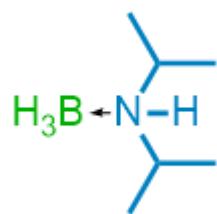
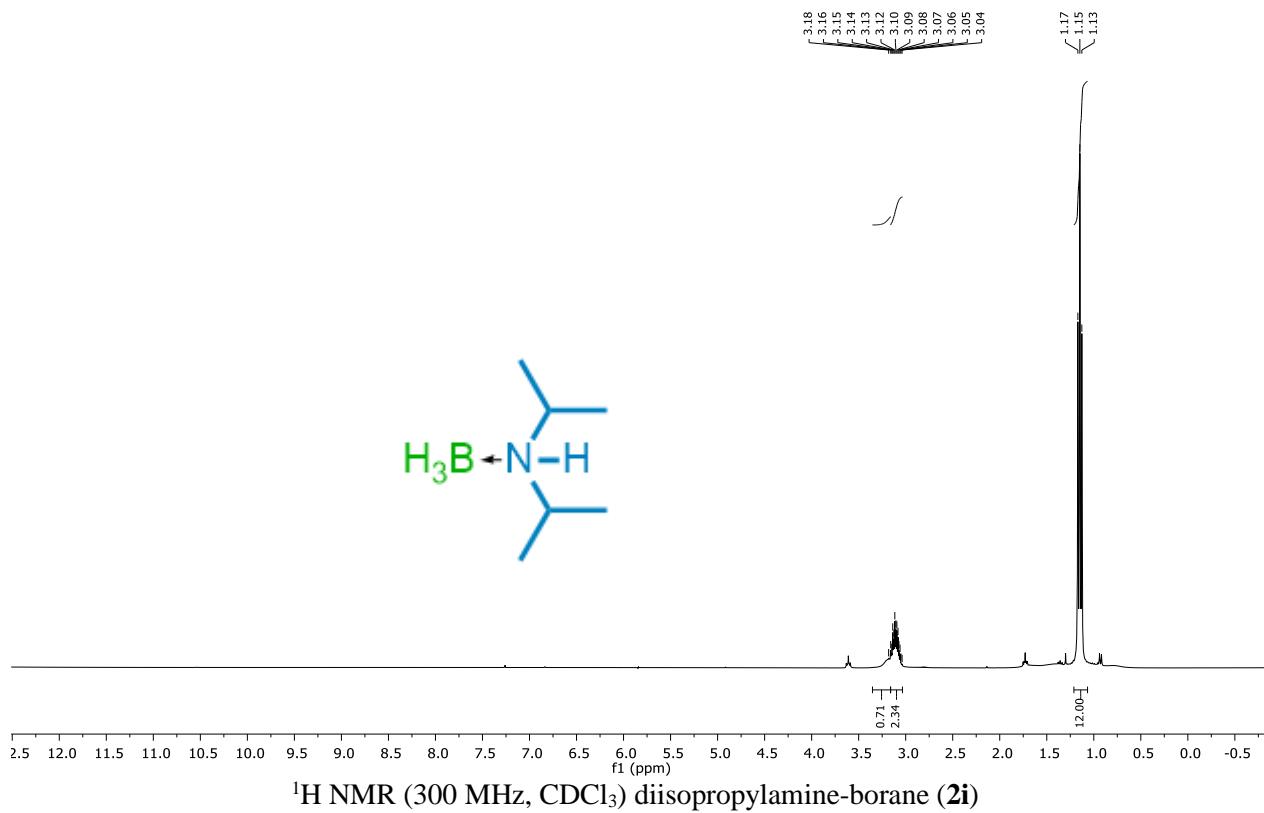
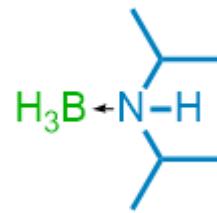


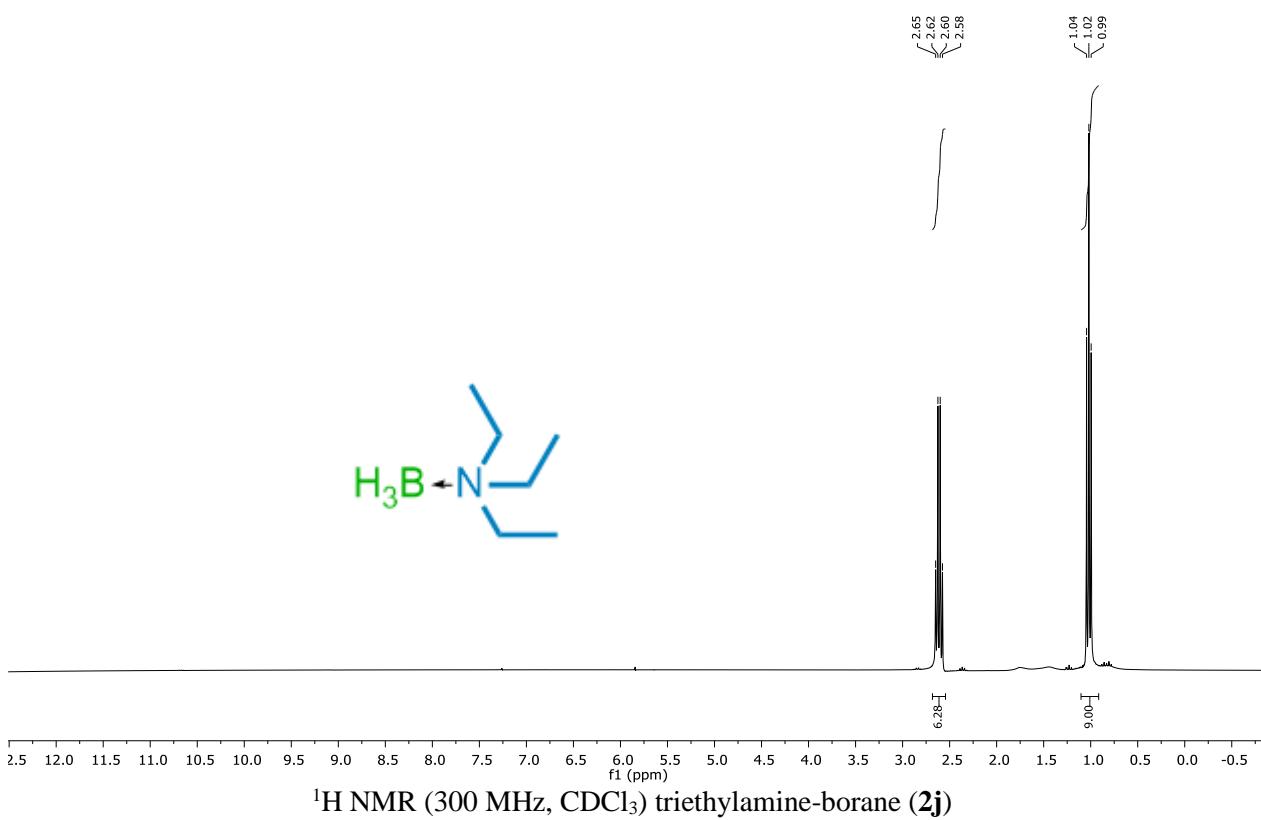
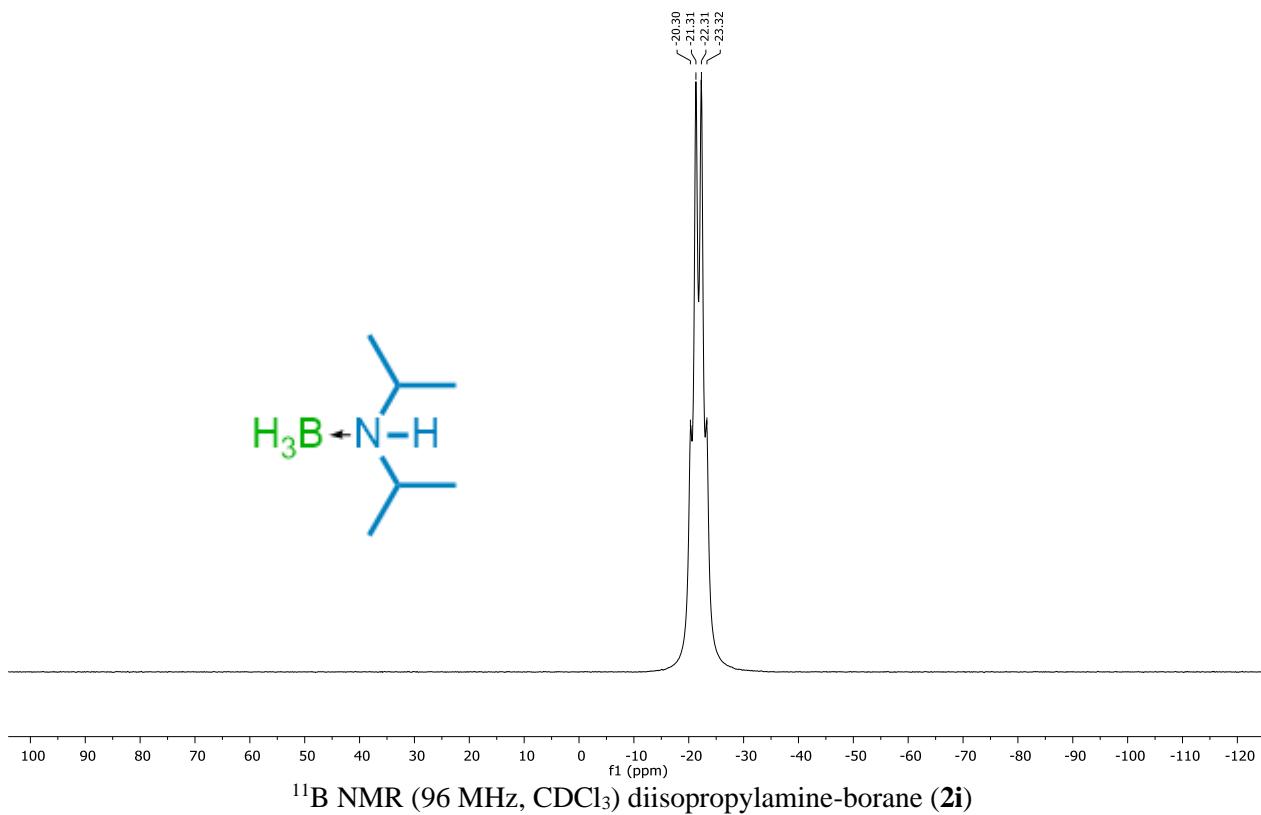


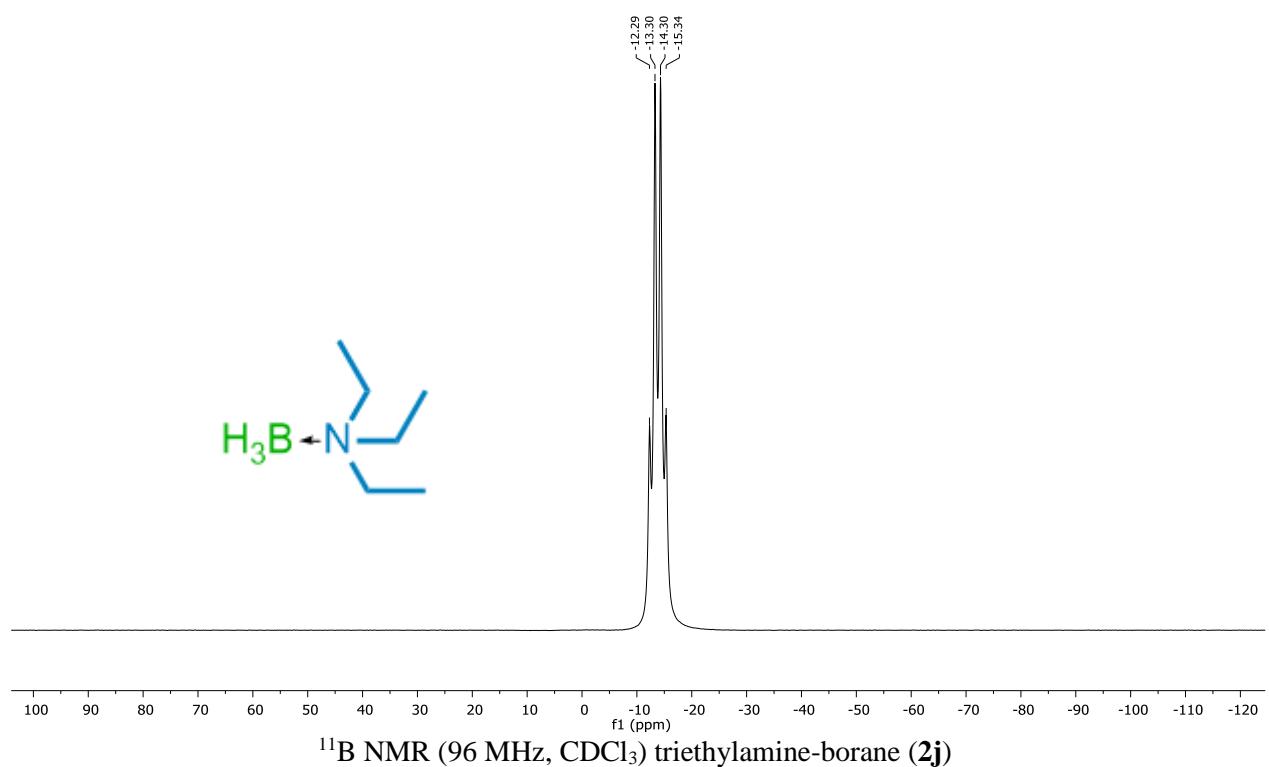
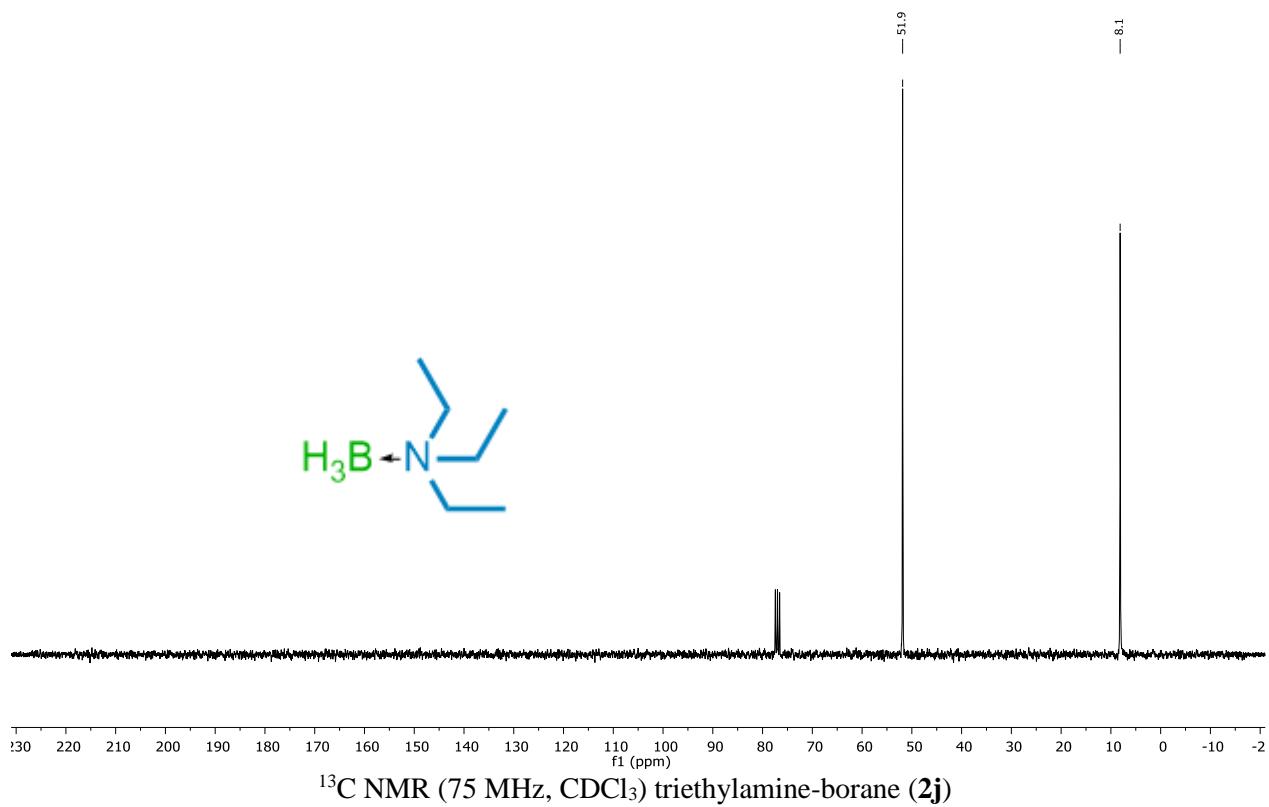
<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) piperidine-borane (**2g**)



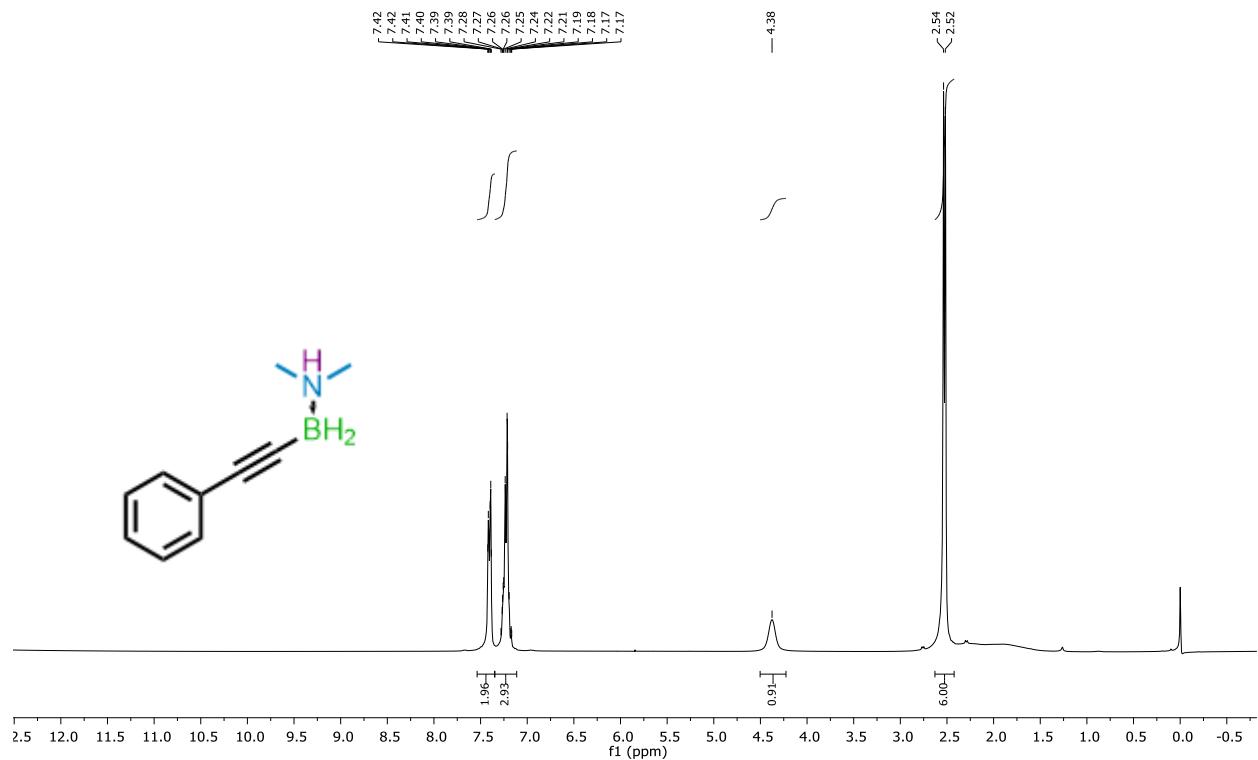




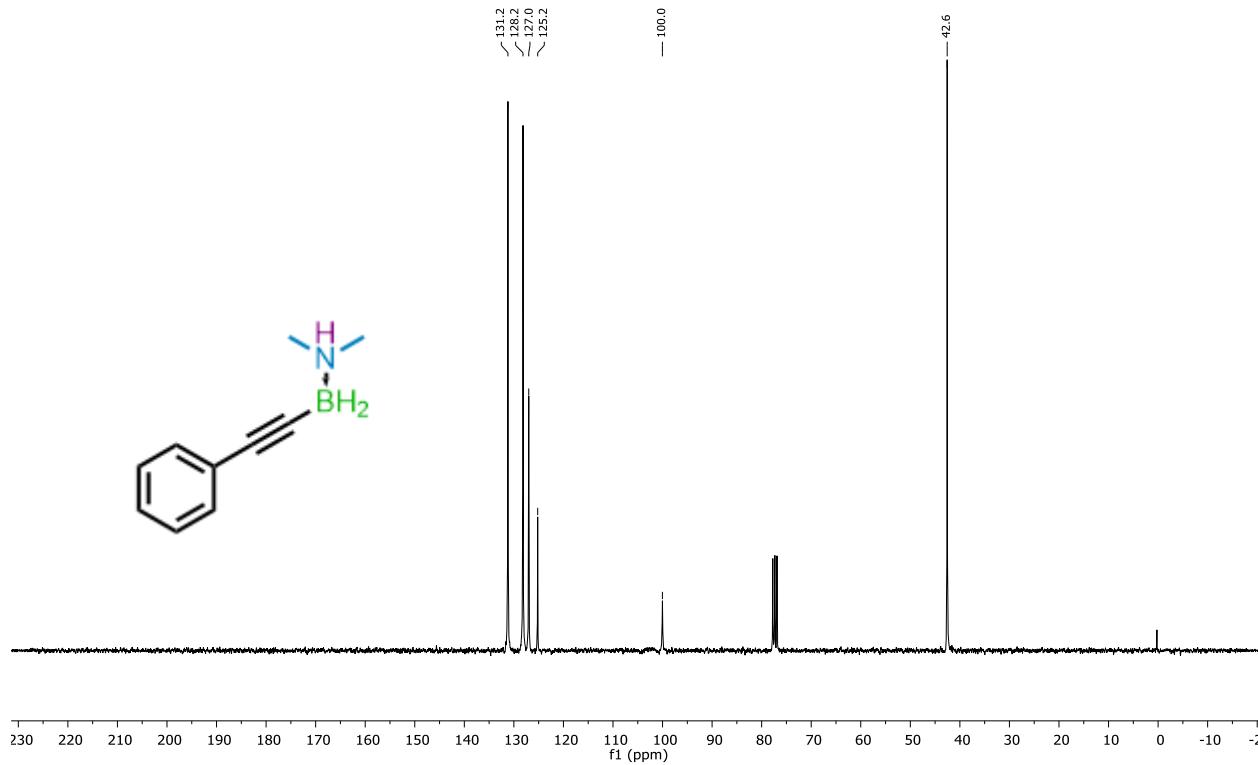




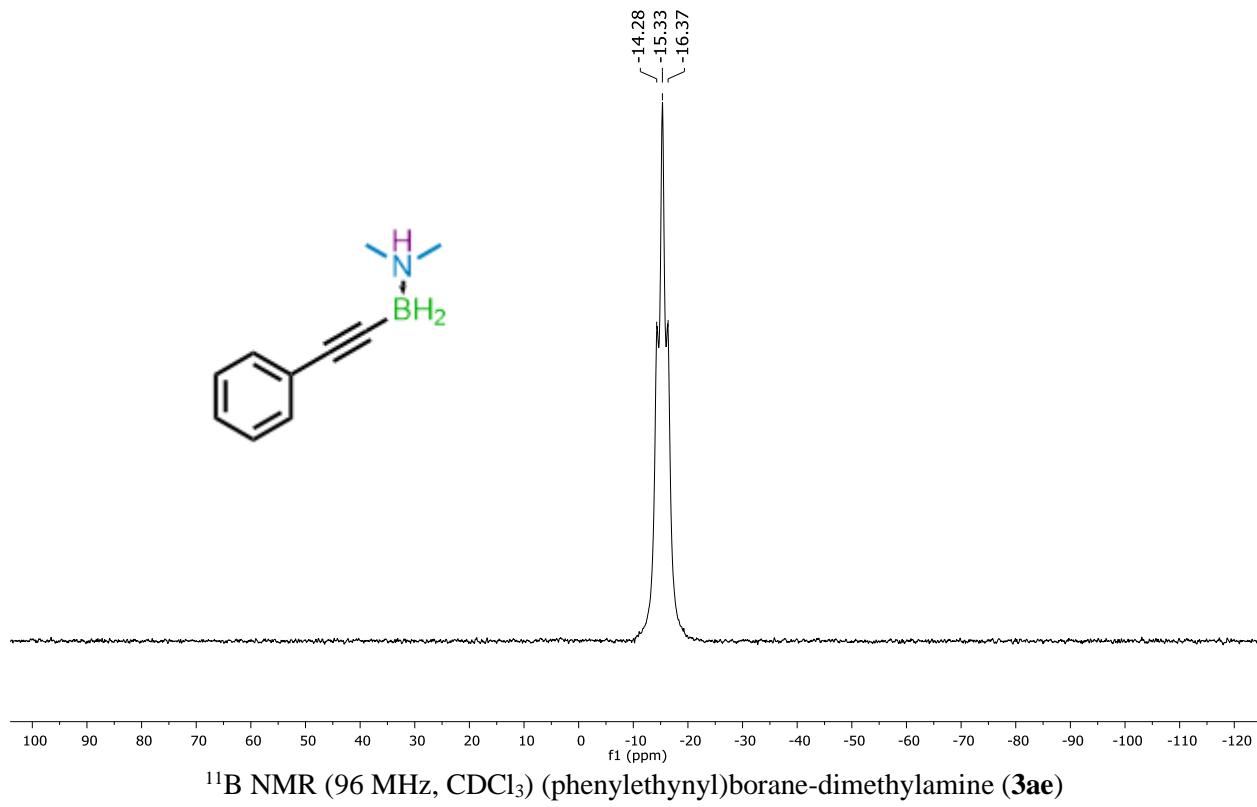
**NMR spectra of alkynylborane-amines from terminal alkynes**



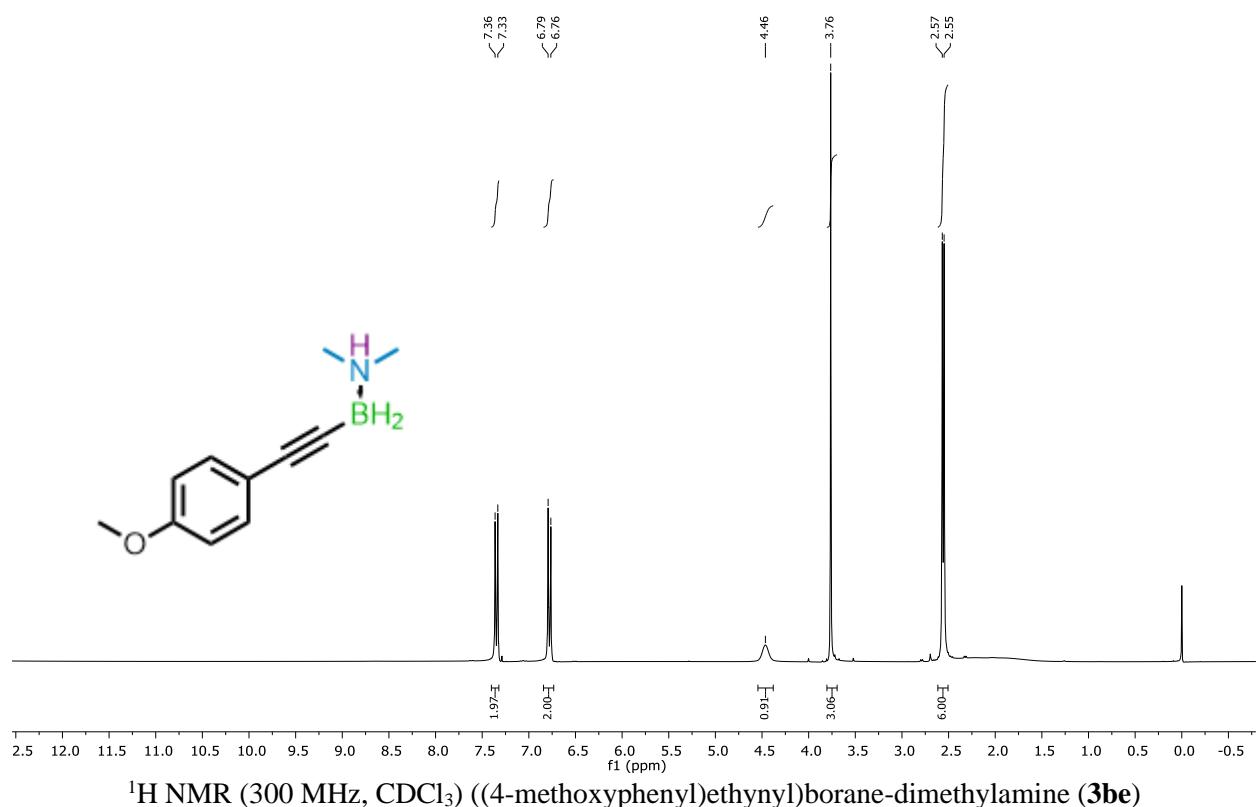
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) (phenylethynyl)borane-dimethylamine (**3ae**)



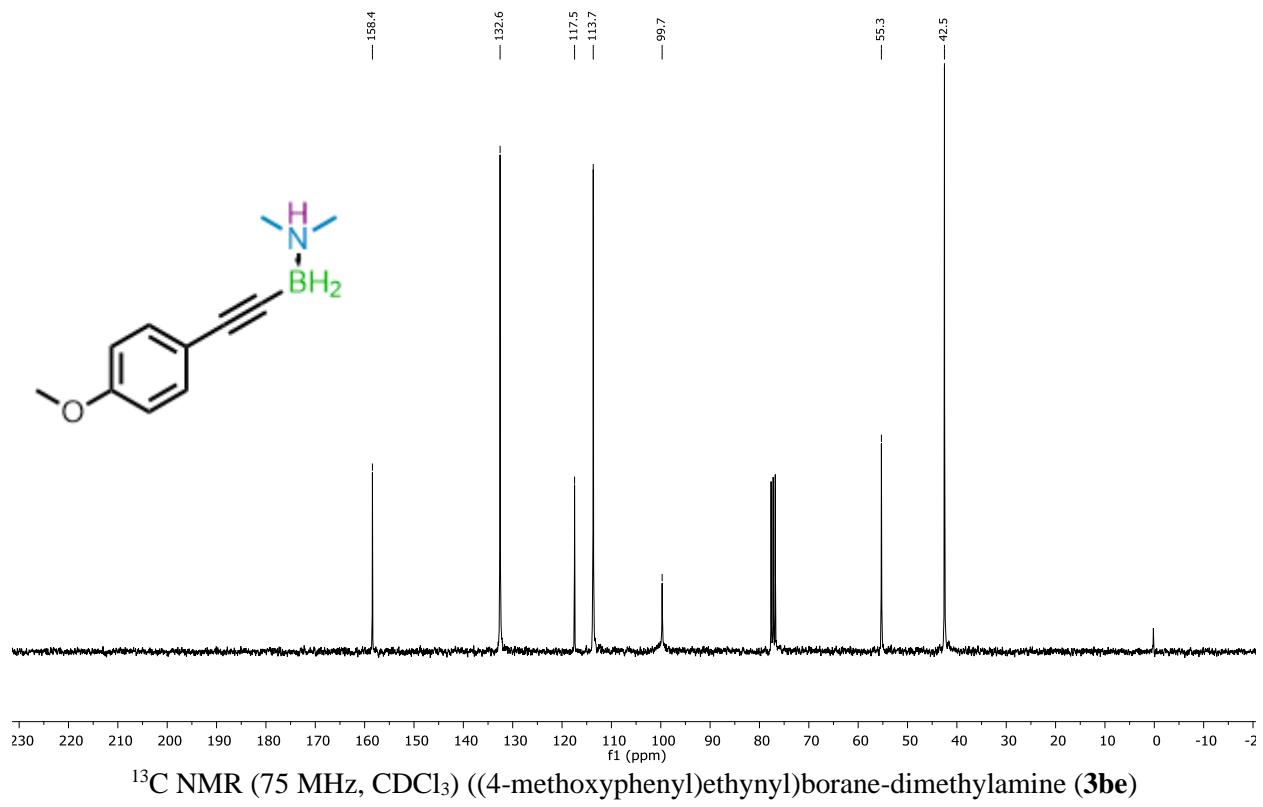
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) (phenylethynyl)borane-dimethylamine (**3ae**)



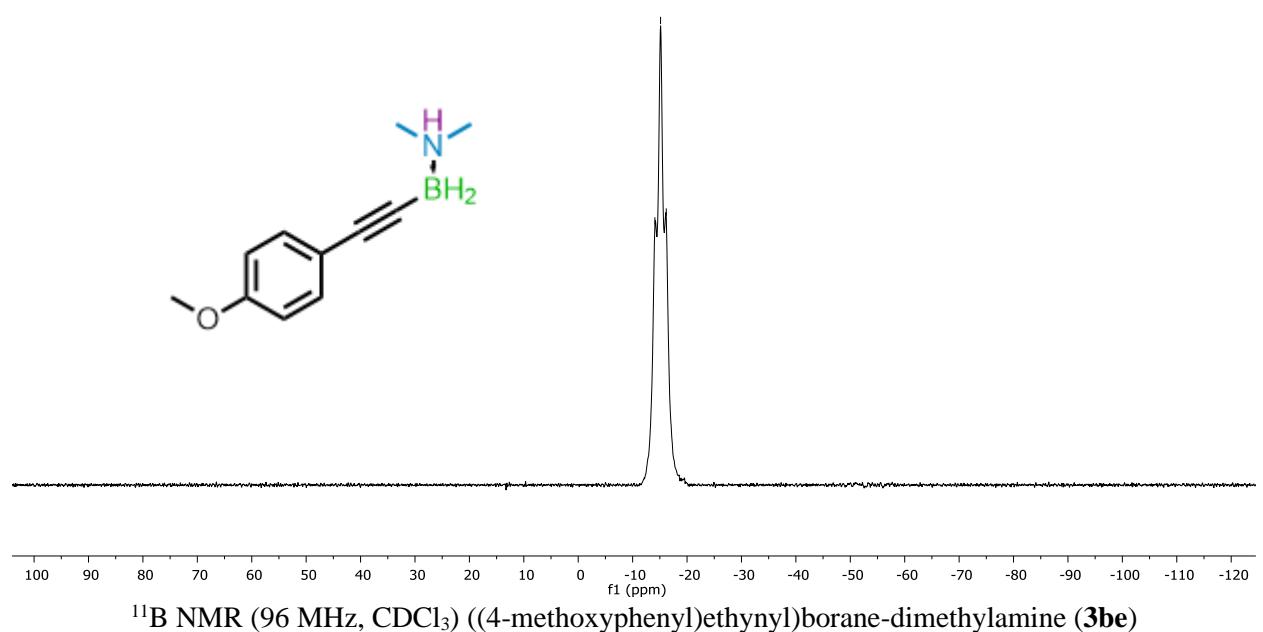
$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ) (phenylethyynyl)borane-dimethylamine (**3ae**)



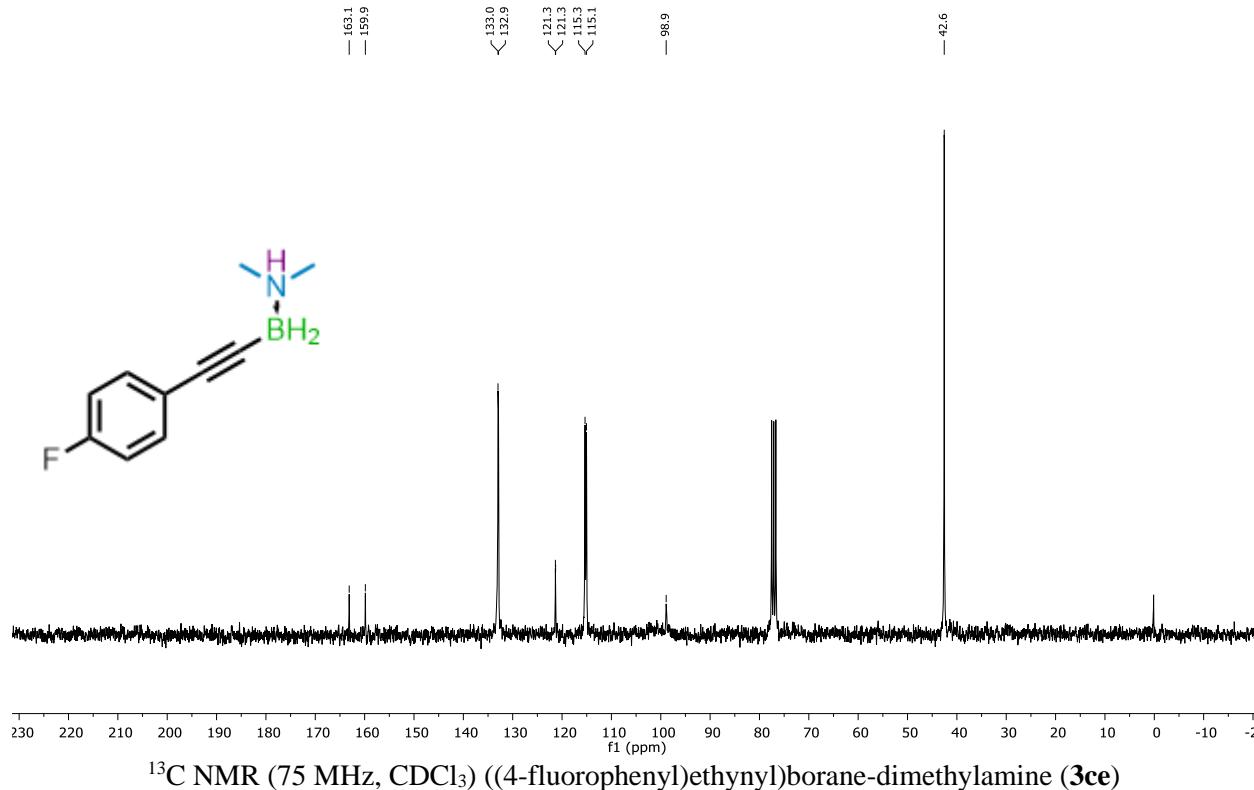
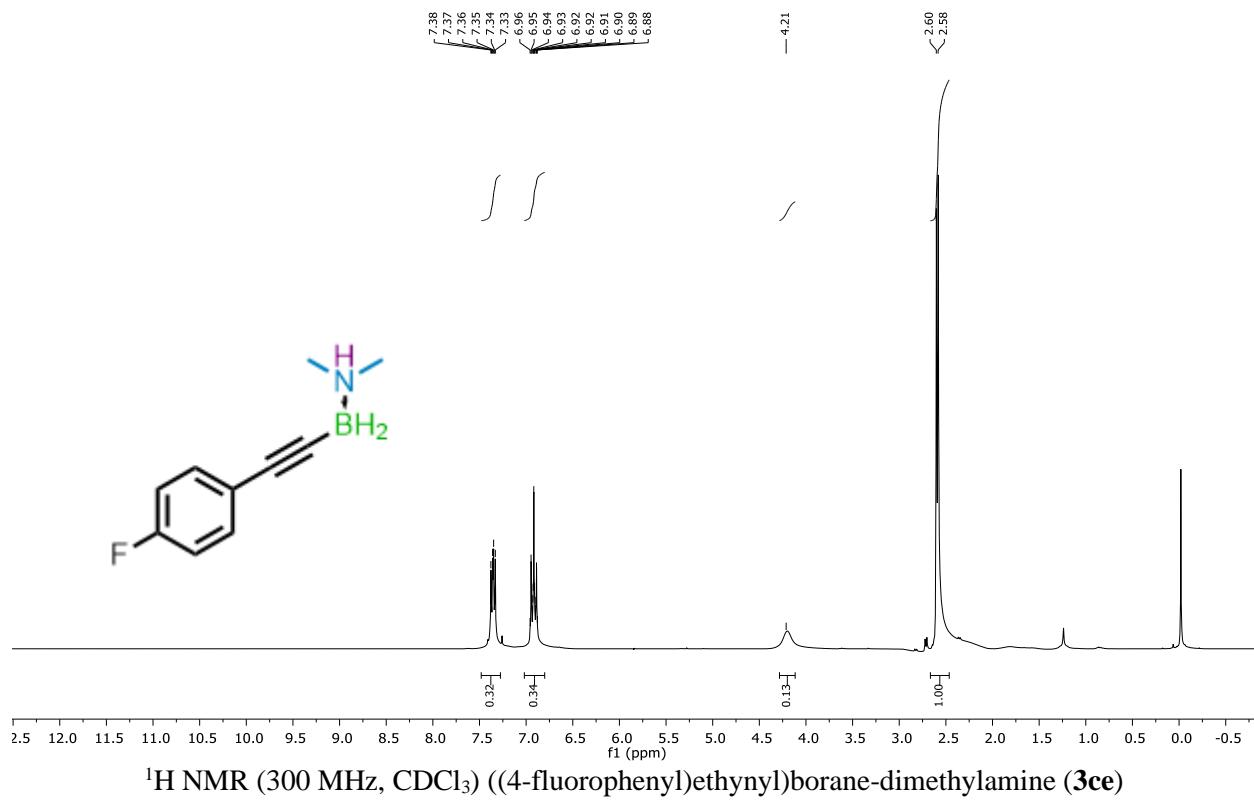
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) ((4-methoxyphenyl)ethynyl)borane-dimethylamine (**3be**)

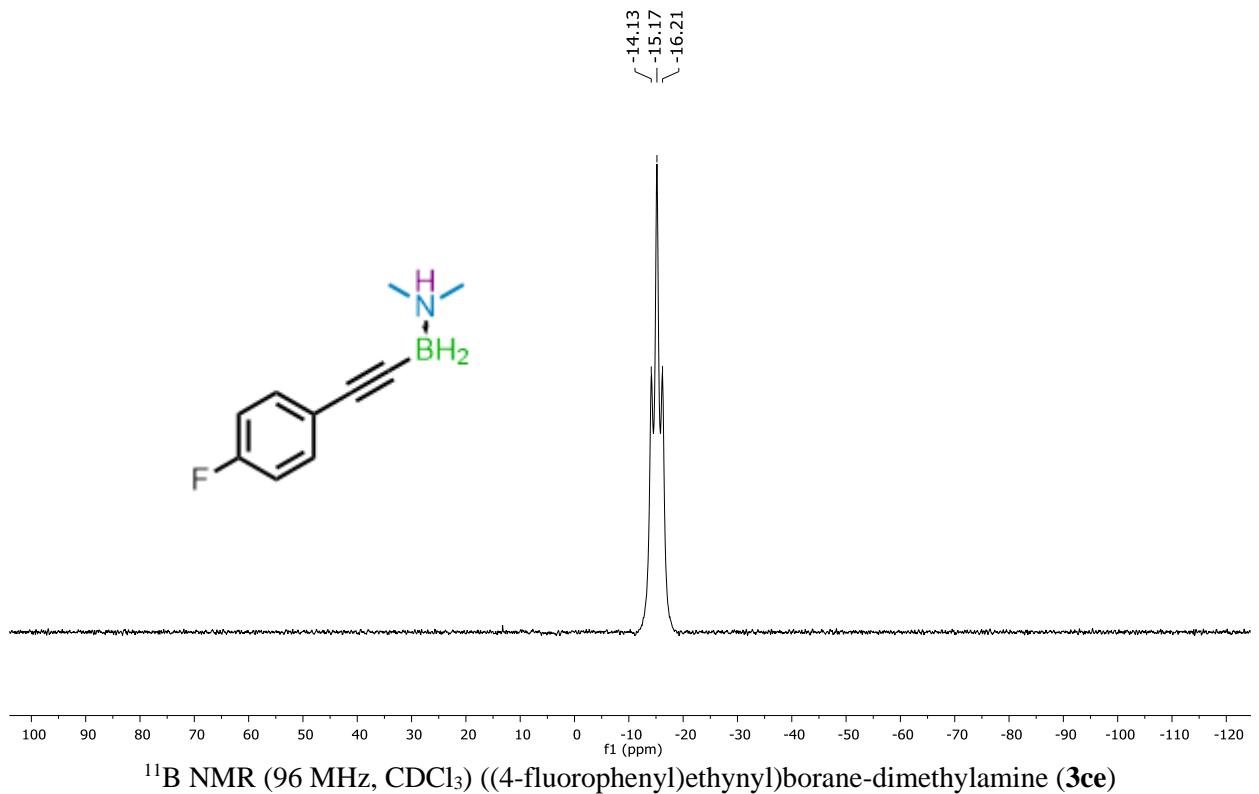


<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) ((4-methoxyphenyl)ethynyl)borane-dimethylamine (**3be**)

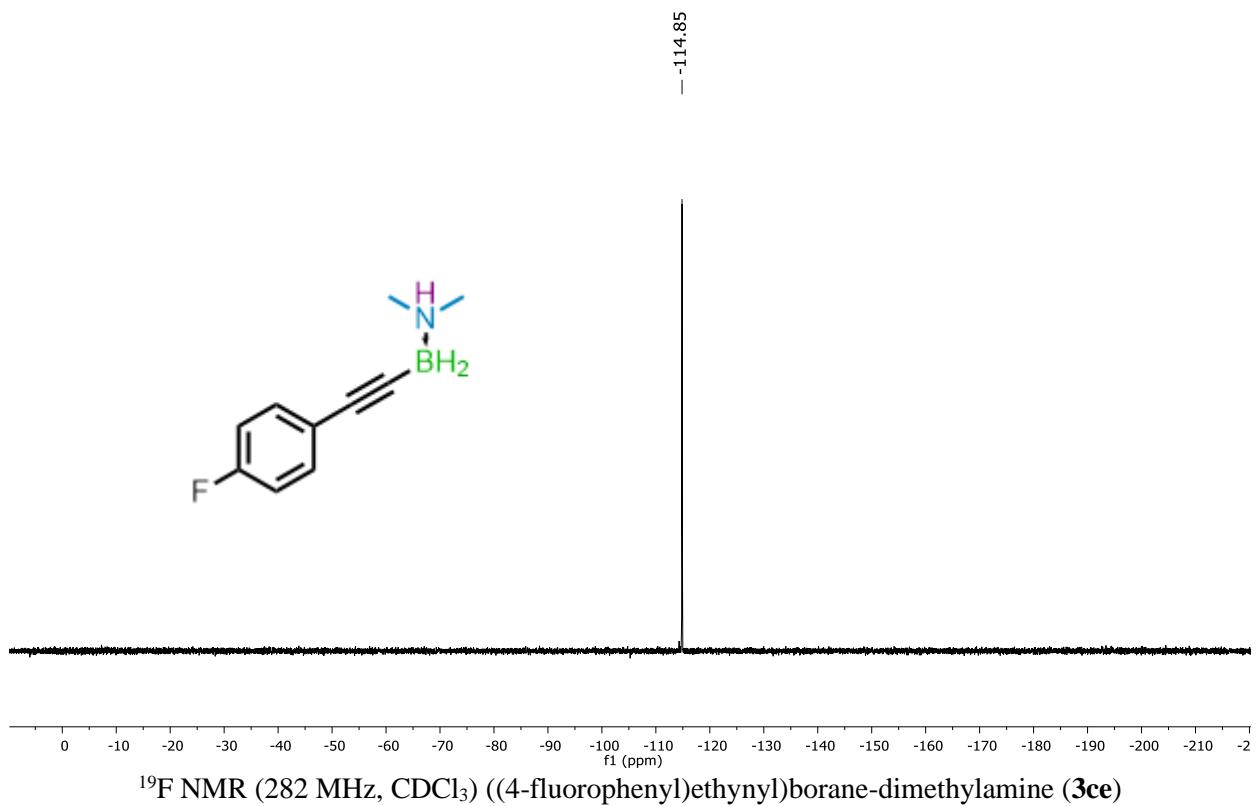


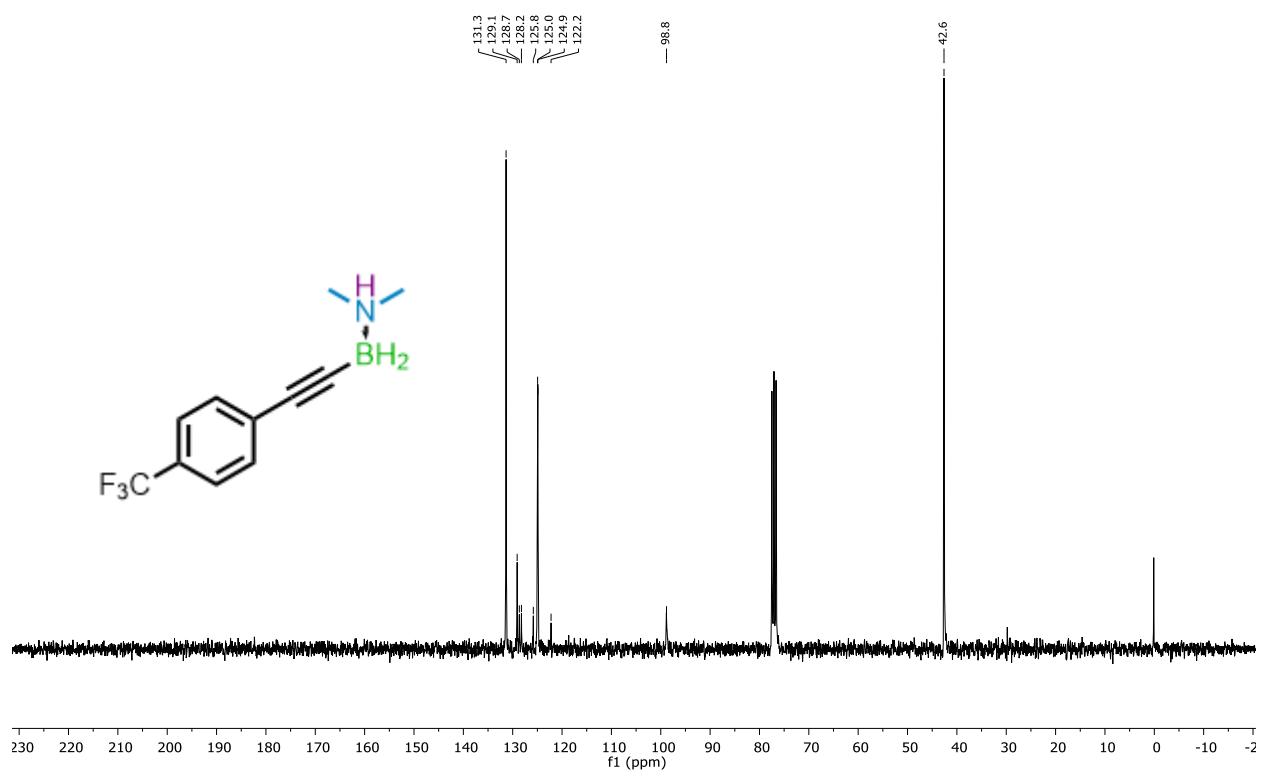
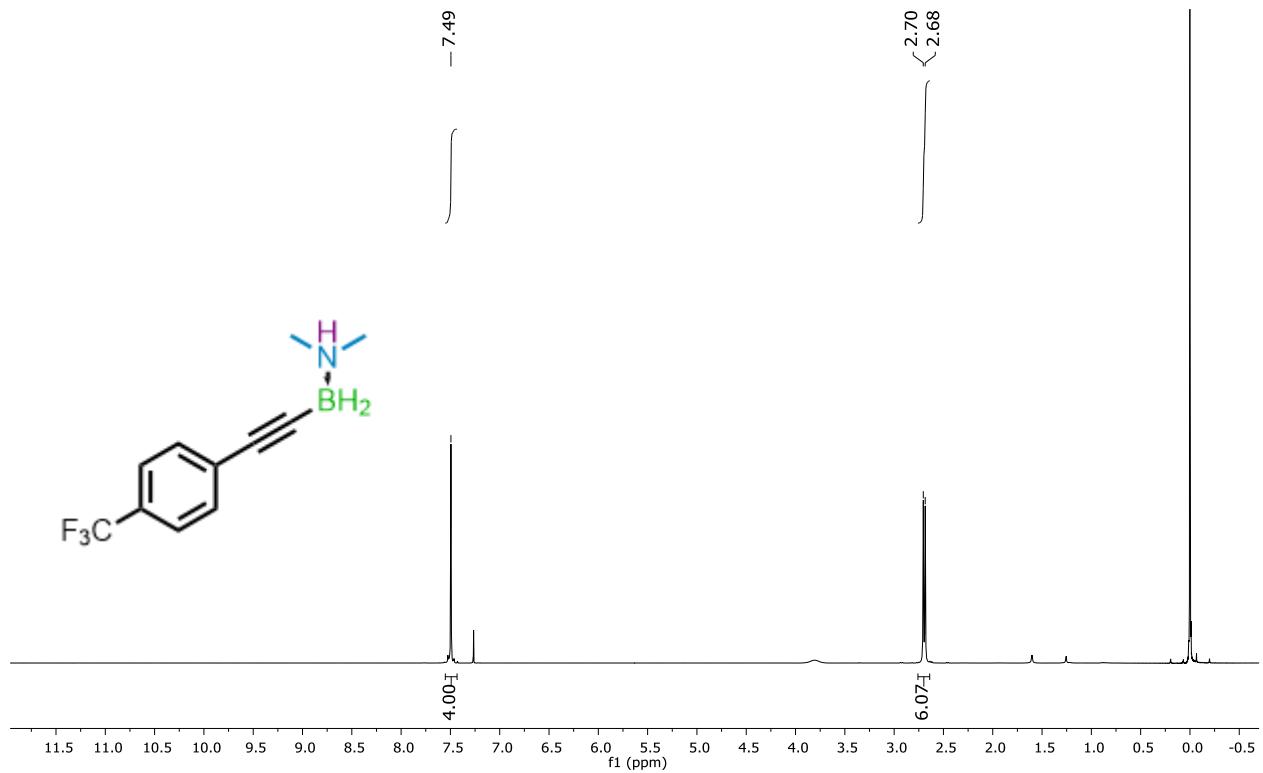
<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) ((4-methoxyphenyl)ethynyl)borane-dimethylamine (**3be**)

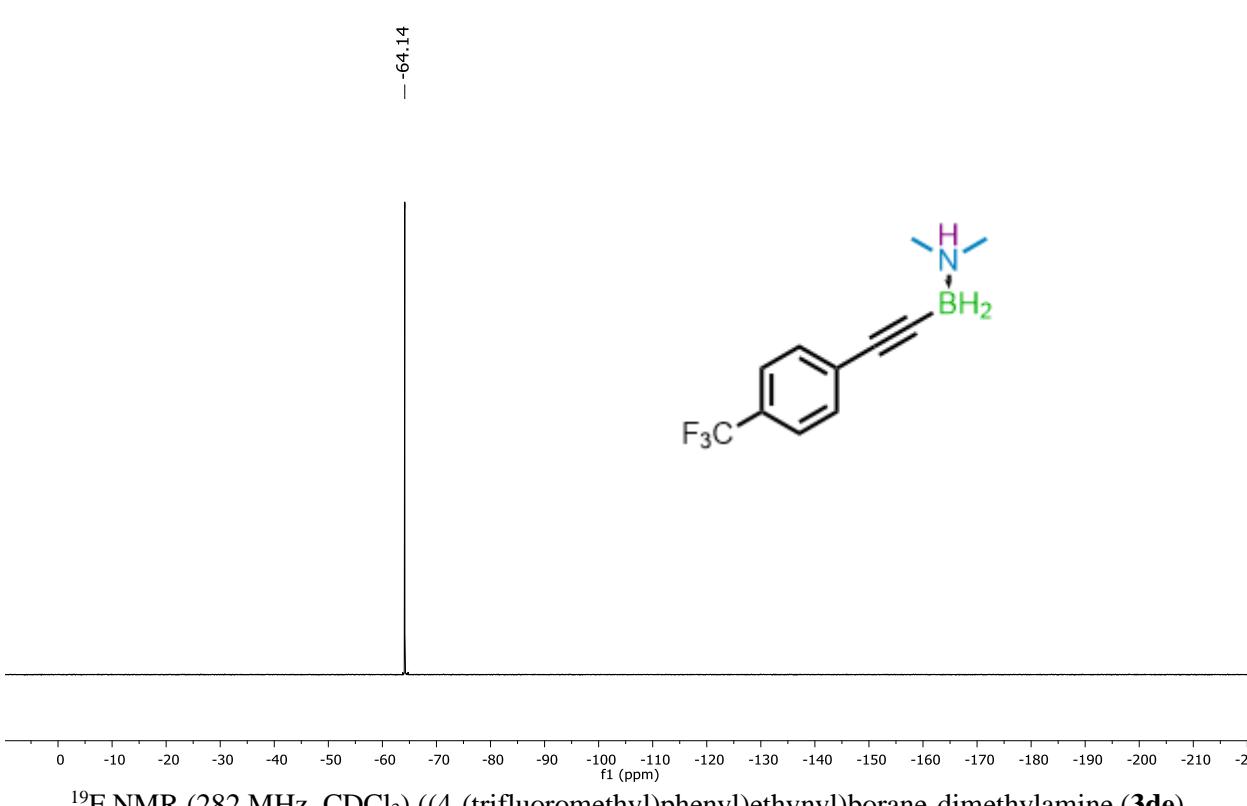
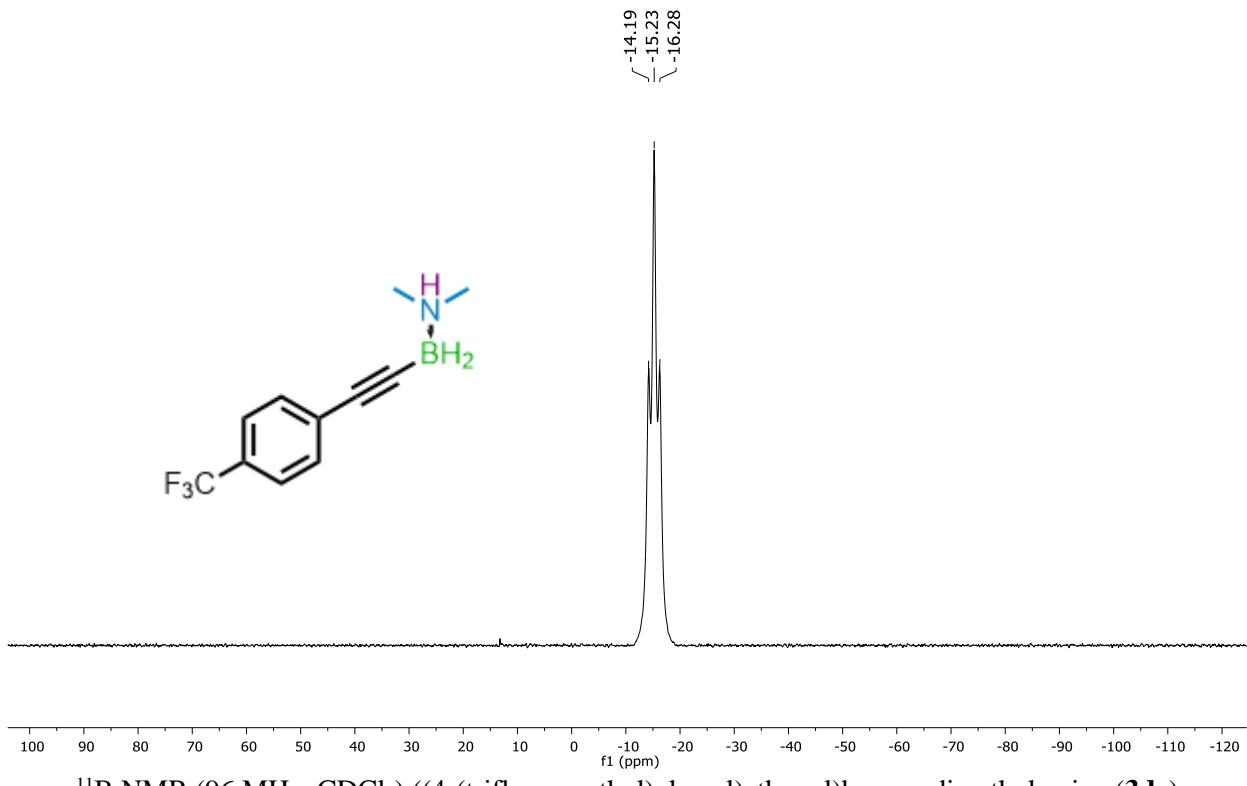


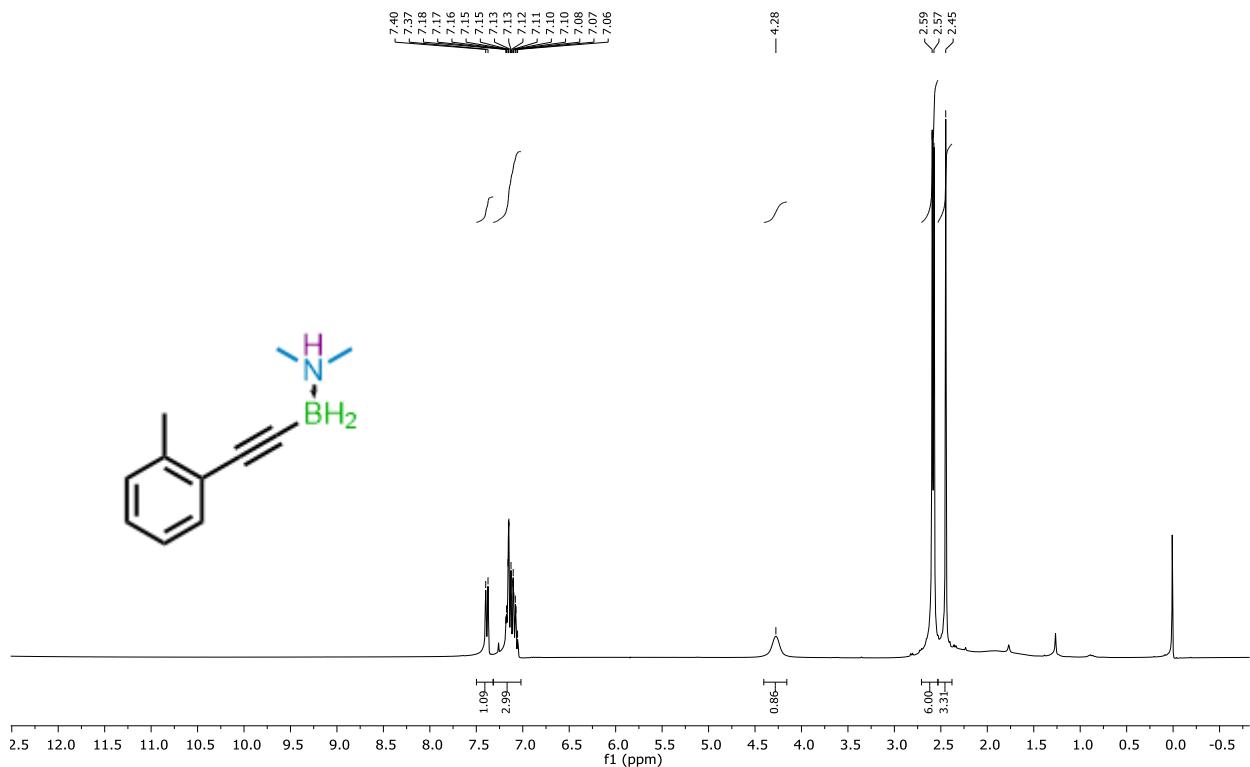


$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ) ((4-fluorophenyl)ethynyl)borane-dimethylamine (**3ce**)

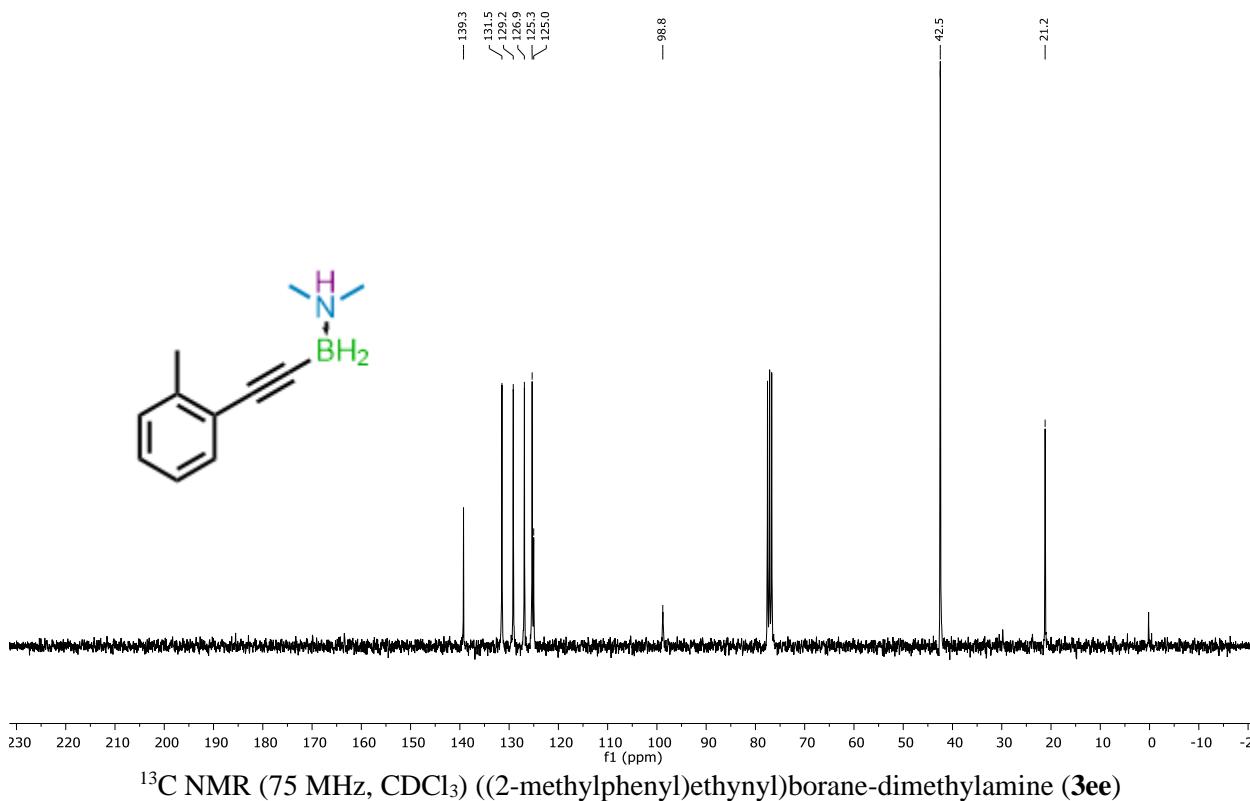




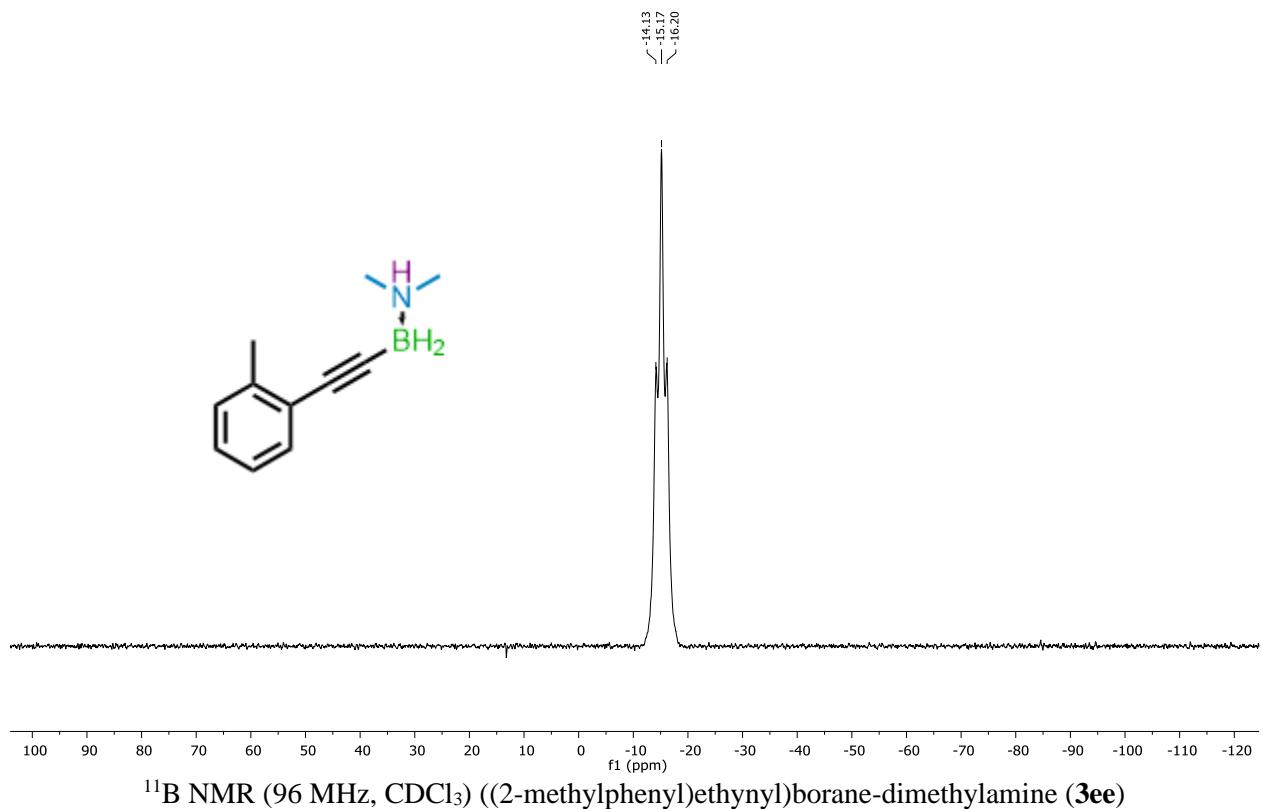




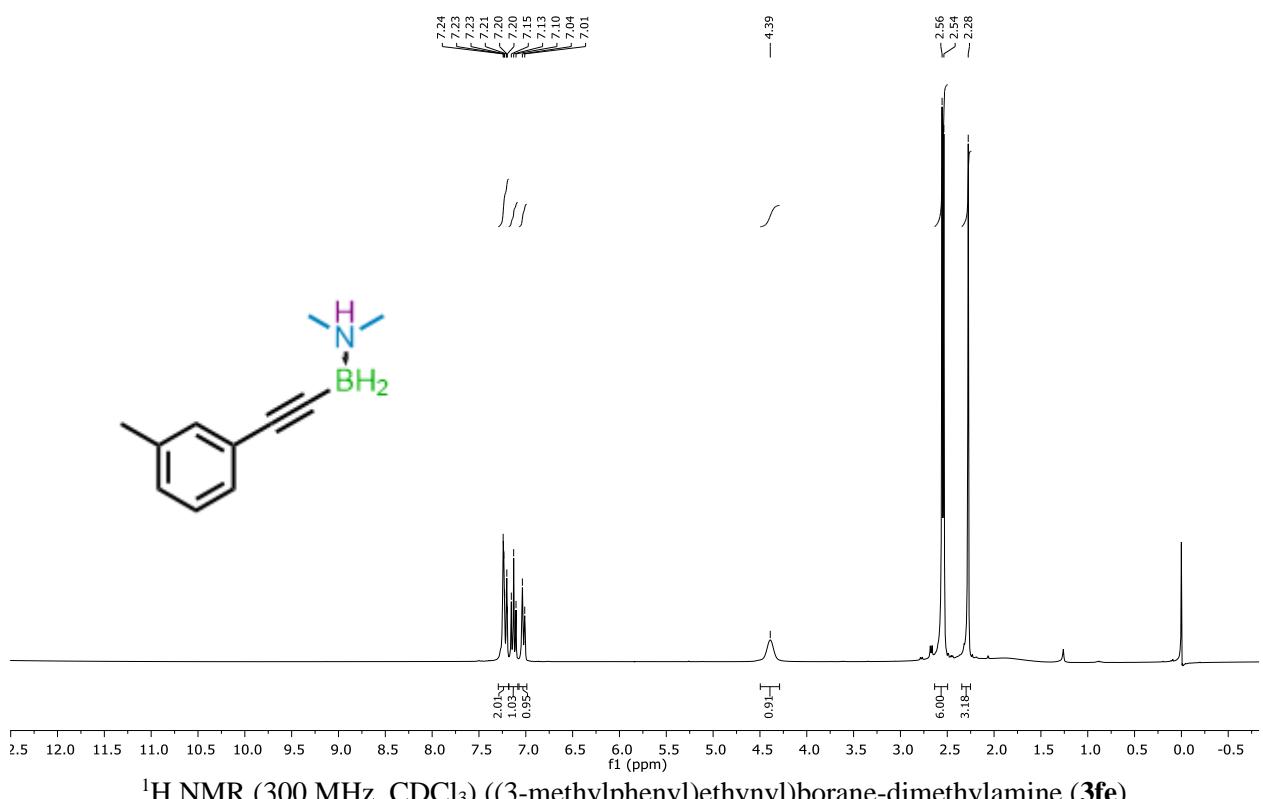
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) ((2-methylphenyl)ethynyl)borane-dimethylamine (**3ee**)



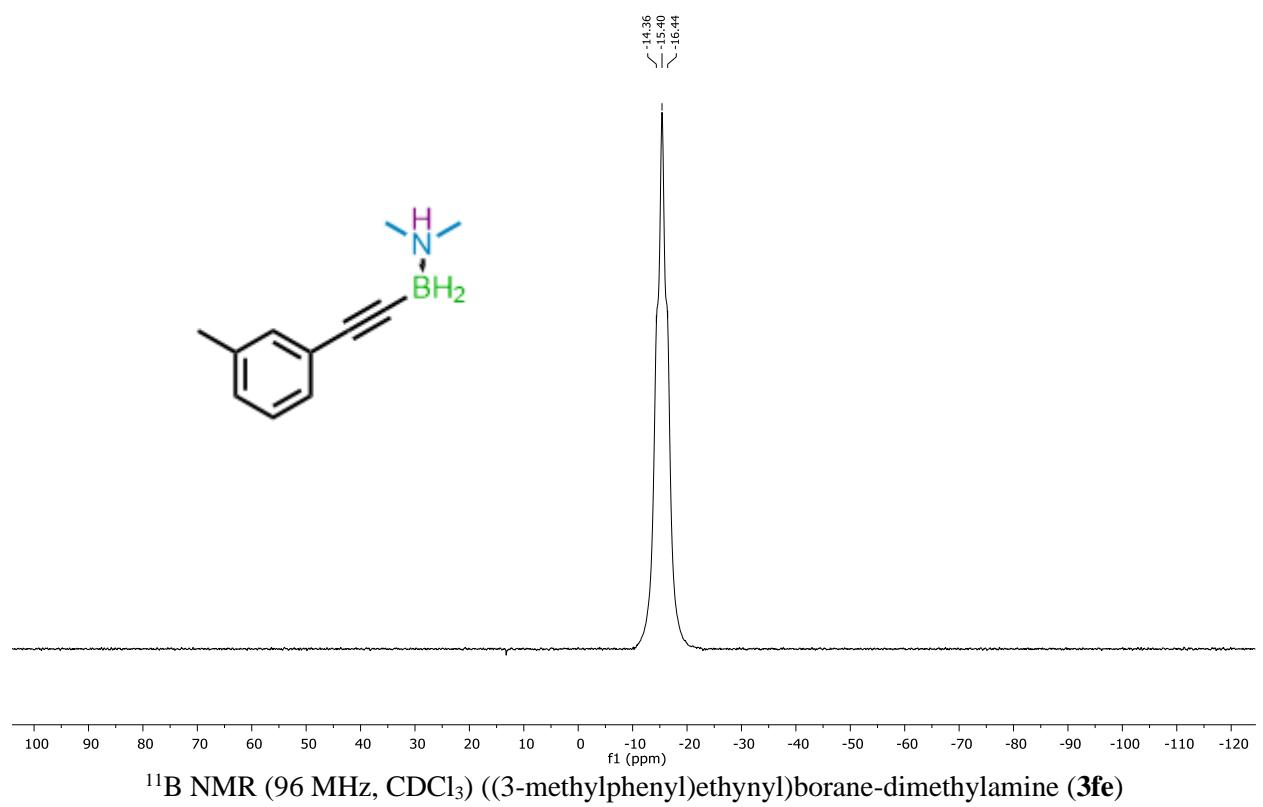
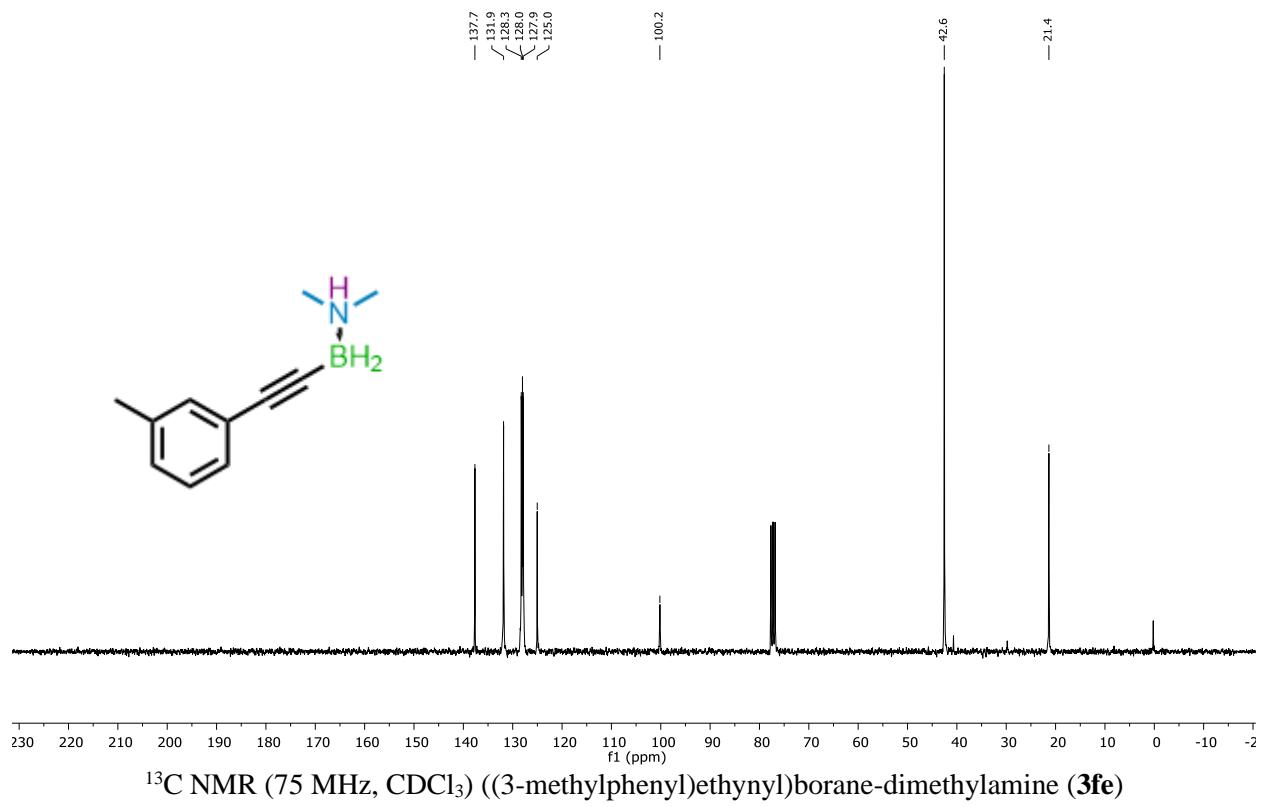
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) ((2-methylphenyl)ethynyl)borane-dimethylamine (**3ee**)

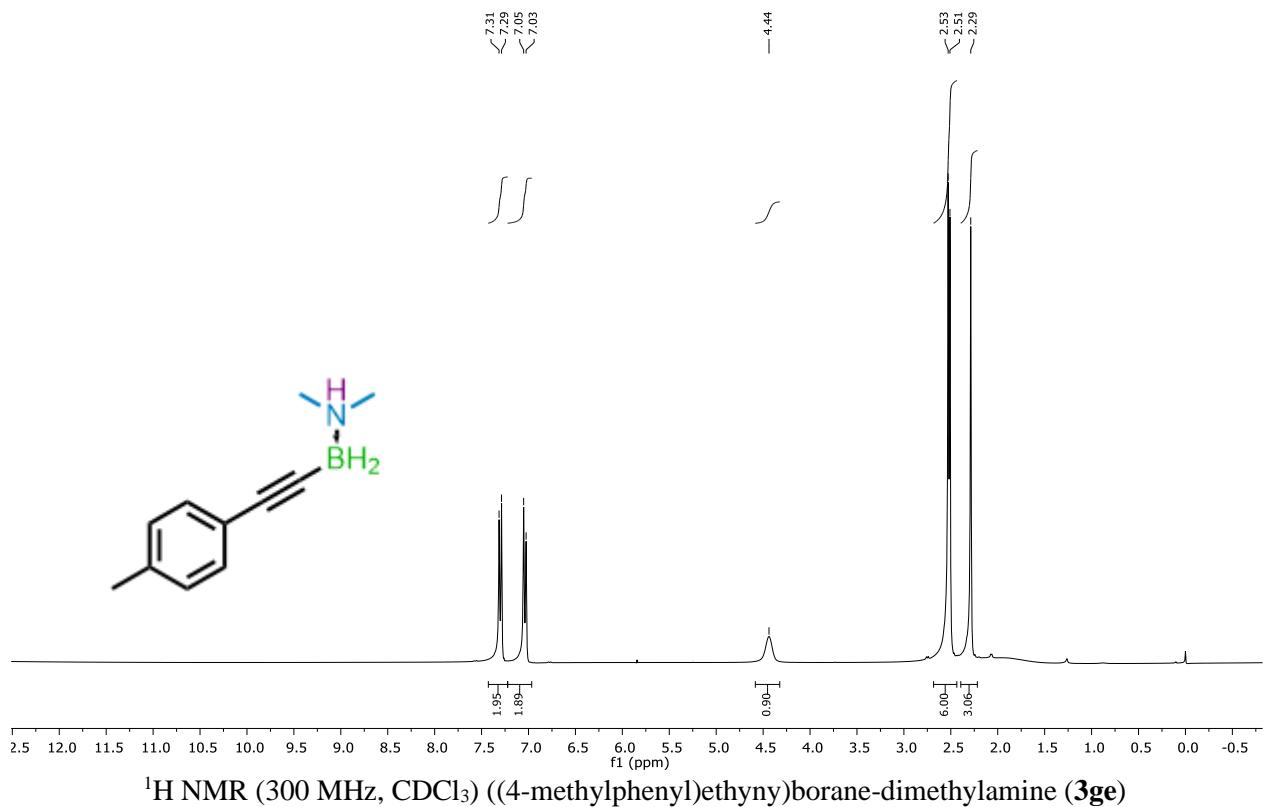


<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) ((2-methylphenyl)ethynyl)borane-dimethylamine (**3ee**)

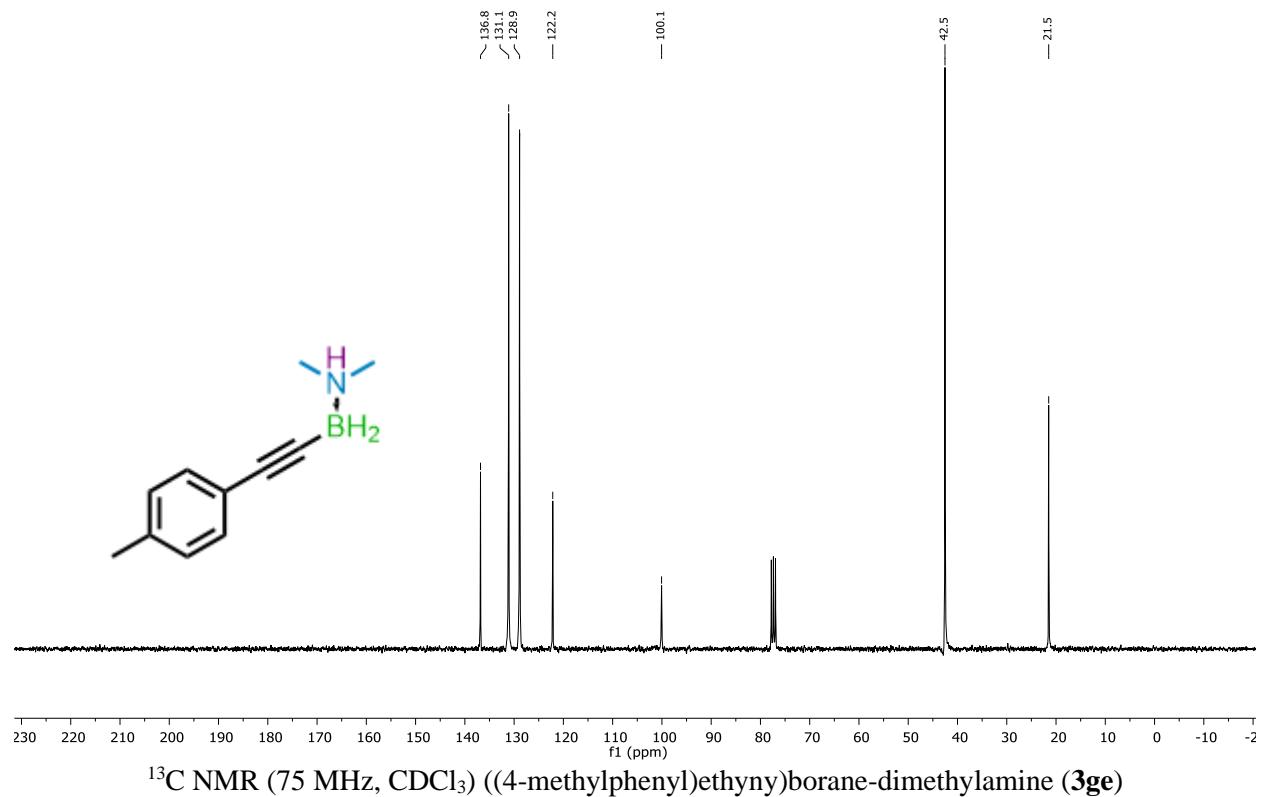


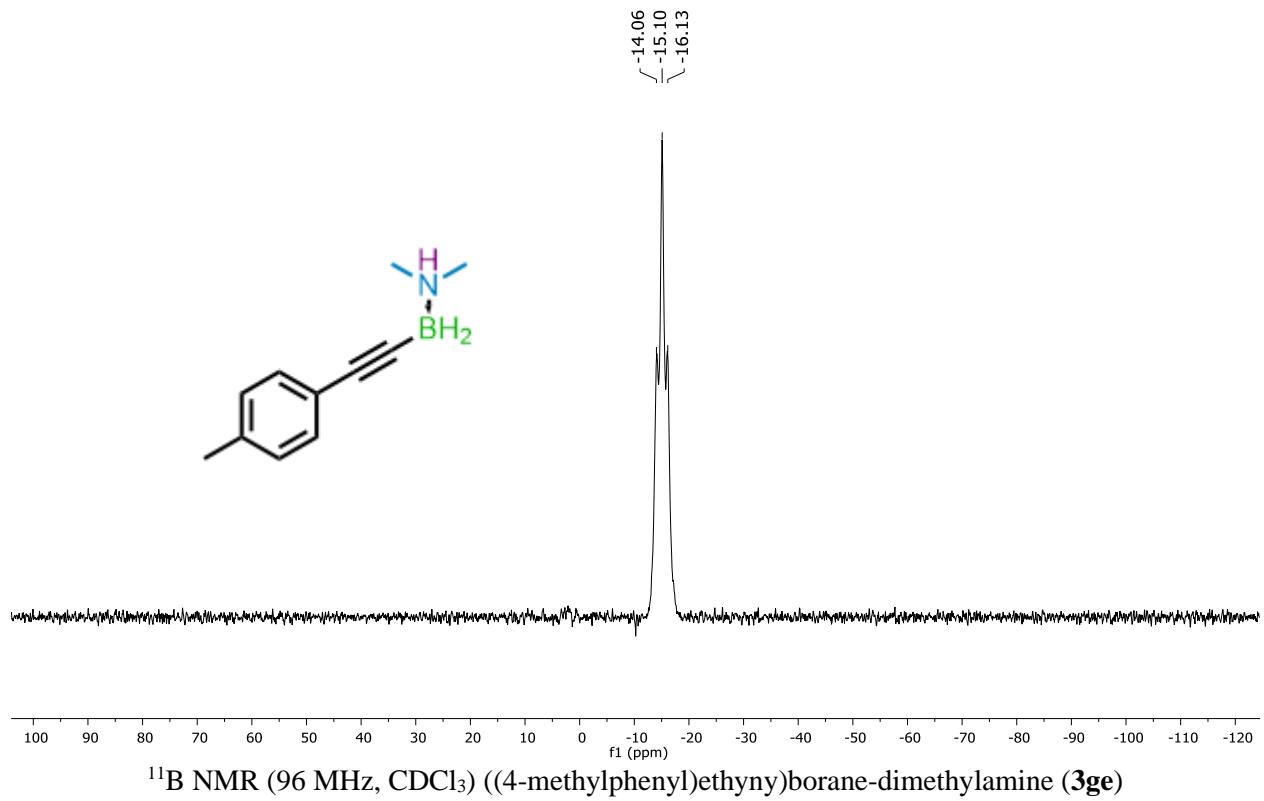
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) ((3-methylphenyl)ethynyl)borane-dimethylamine (**3fe**)



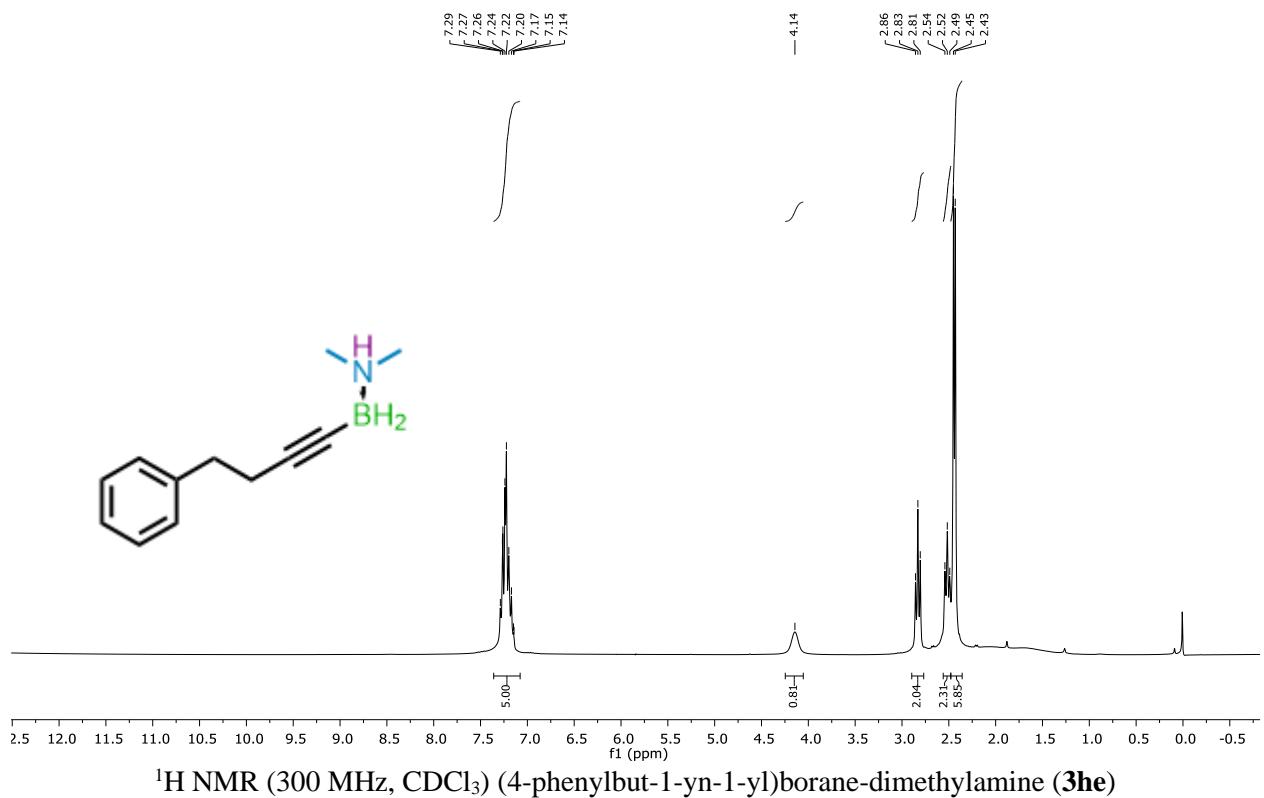


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) ((4-methylphenyl)ethynyl)borane-dimethylamine (**3ge**)

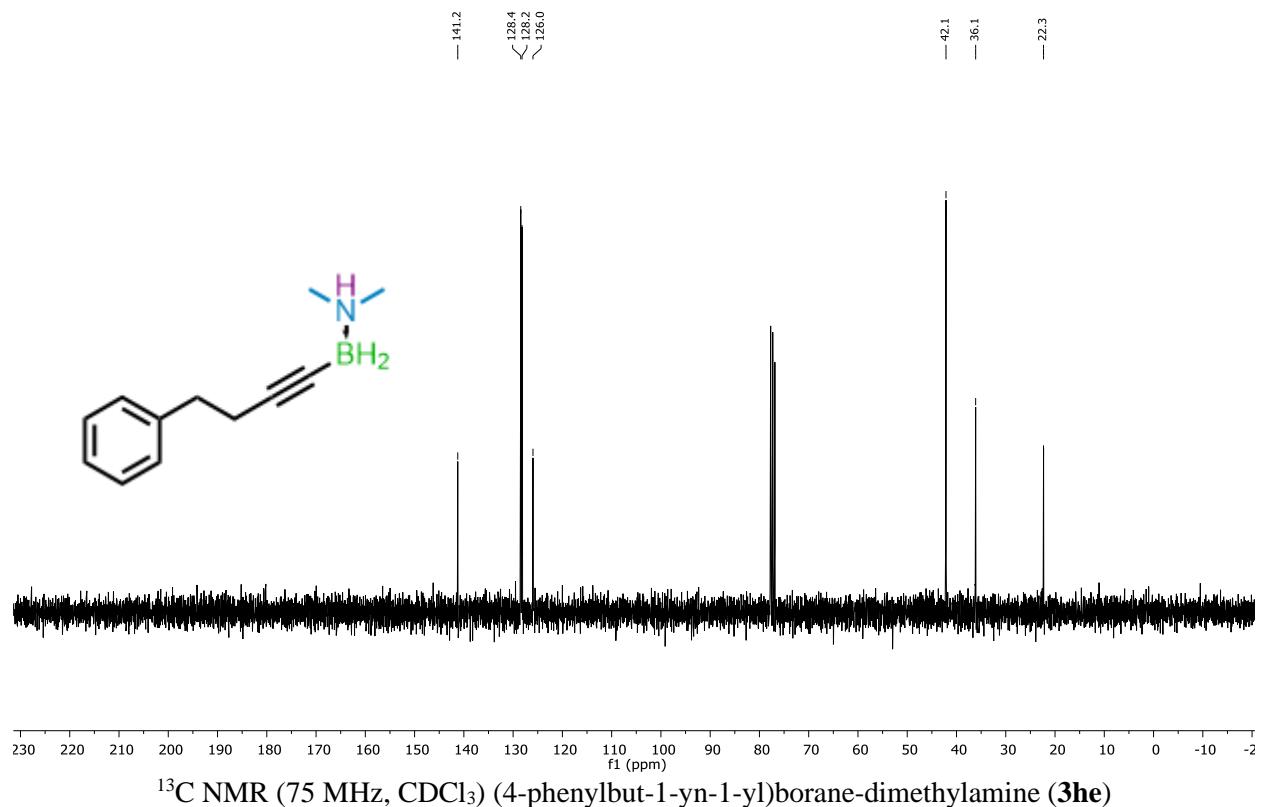




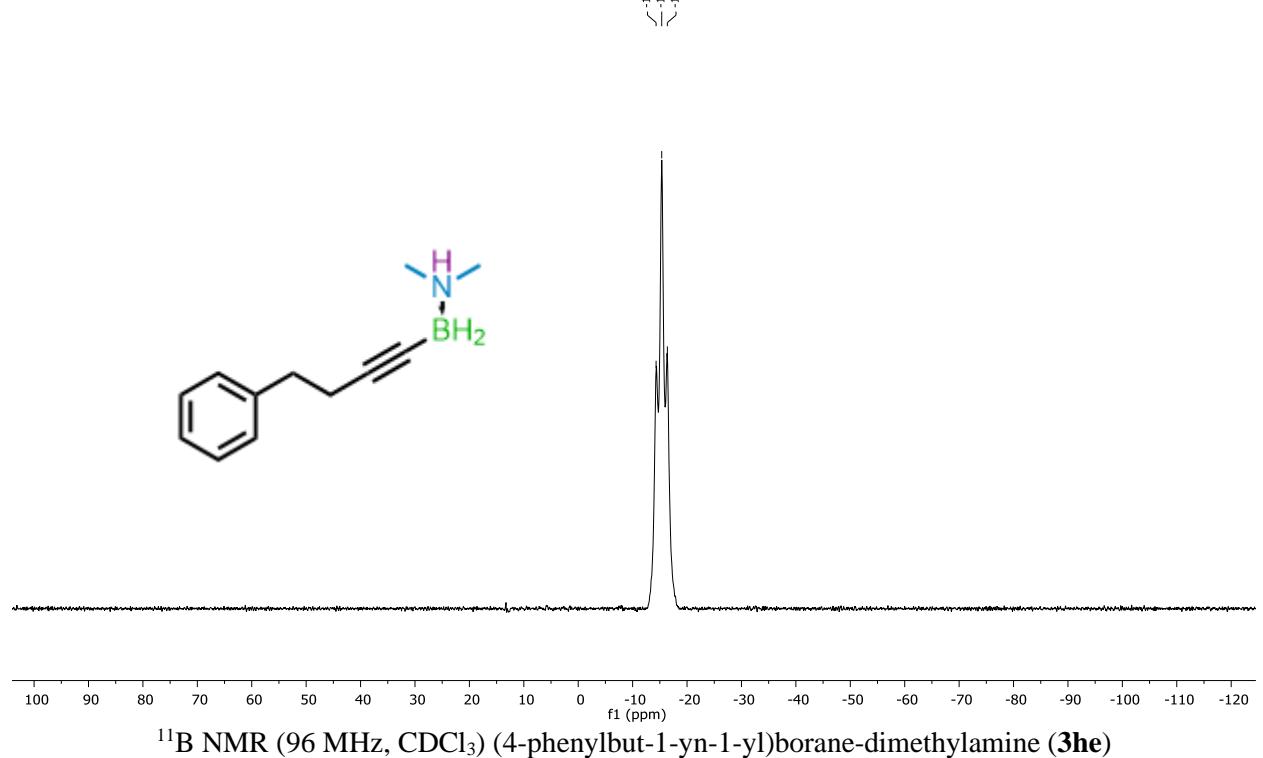
$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ) ((4-methylphenyl)ethynyl)borane-dimethylamine (**3ge**)



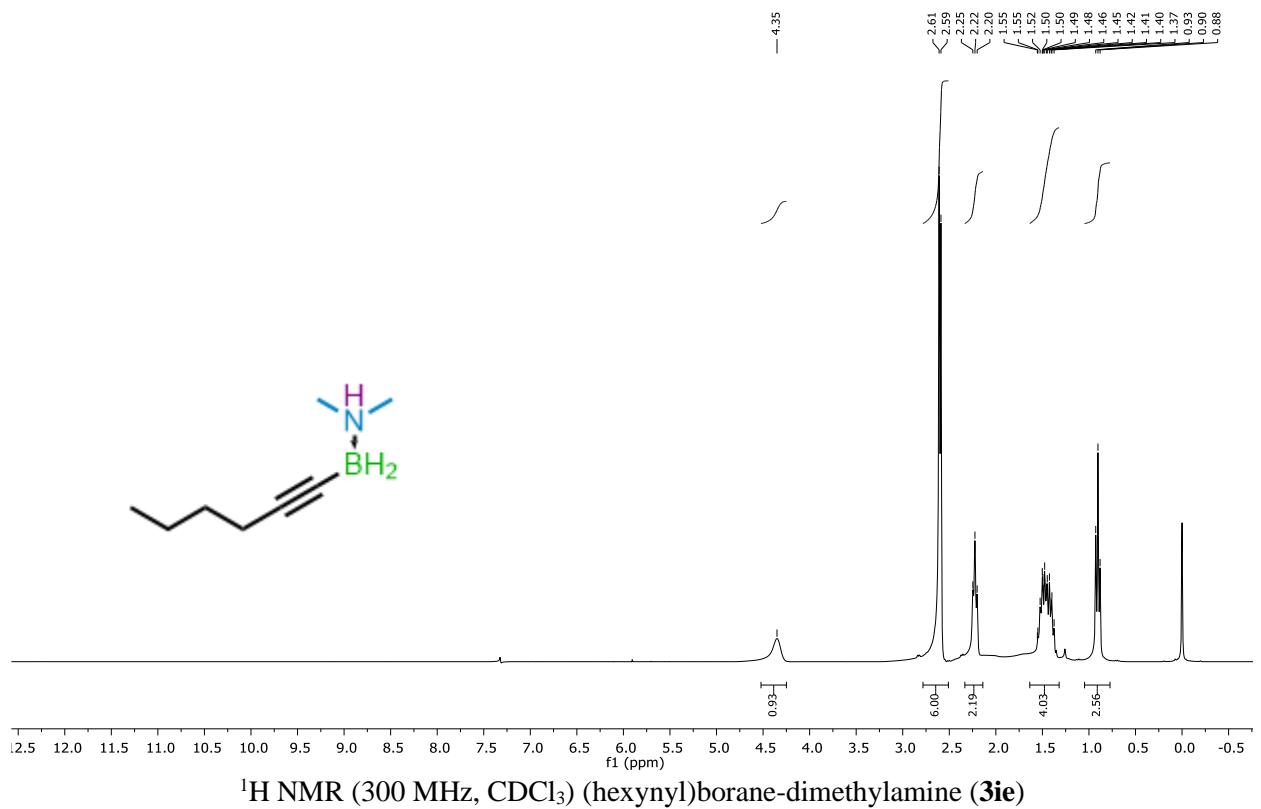
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) (4-phenylbut-1-yn-1-yl)borane-dimethylamine (**3he**)



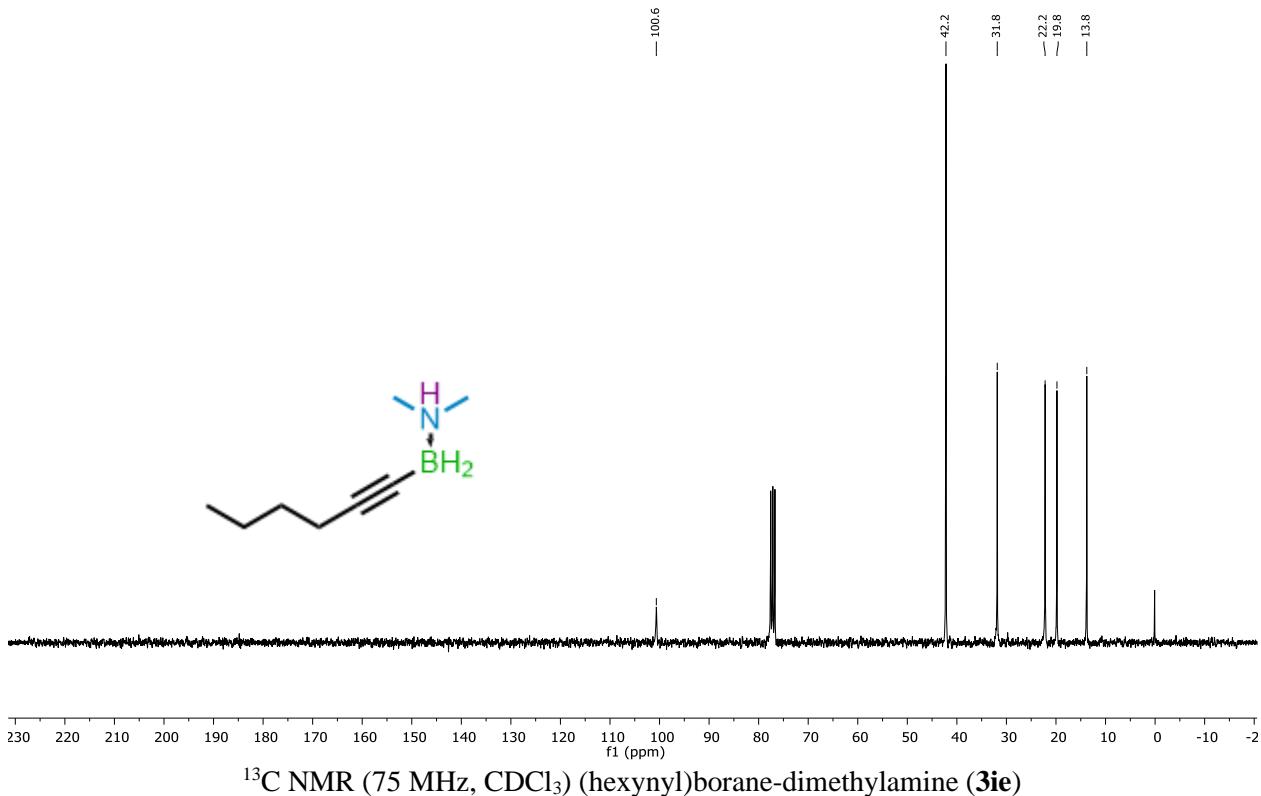
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) (4-phenylbut-1-yn-1-yl)borane-dimethylamine (**3he**)

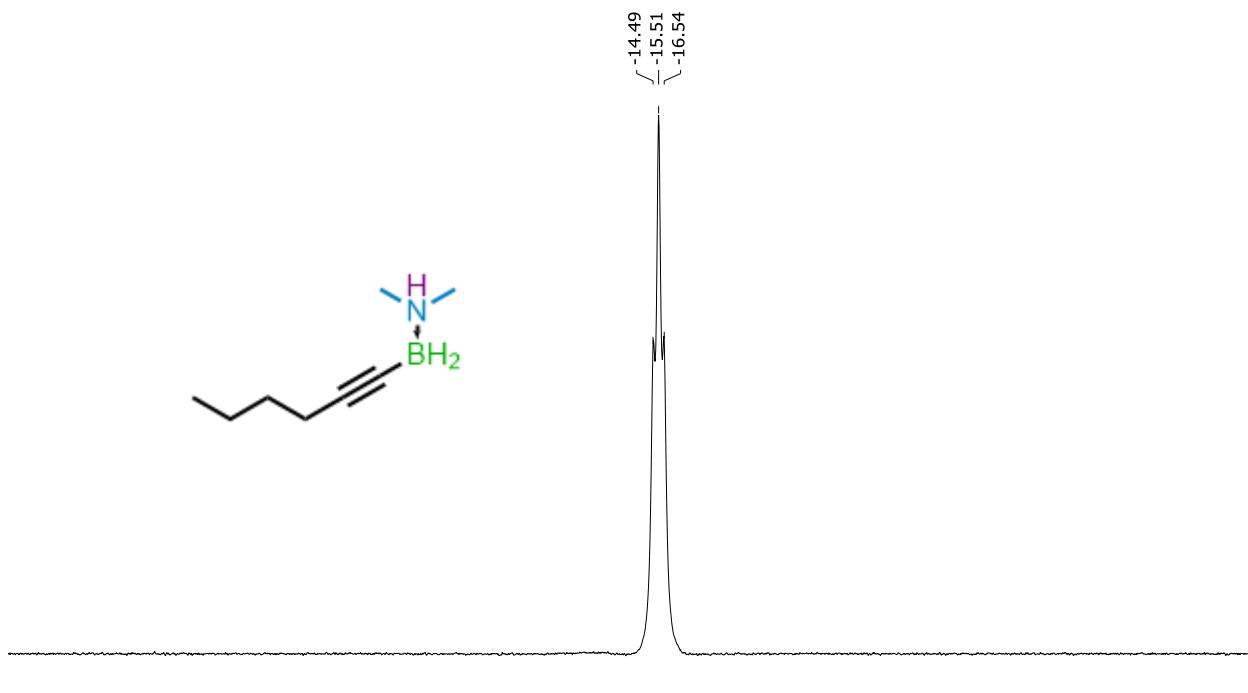


$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ) (4-phenylbut-1-yn-1-yl)borane-dimethylamine (**3he**)

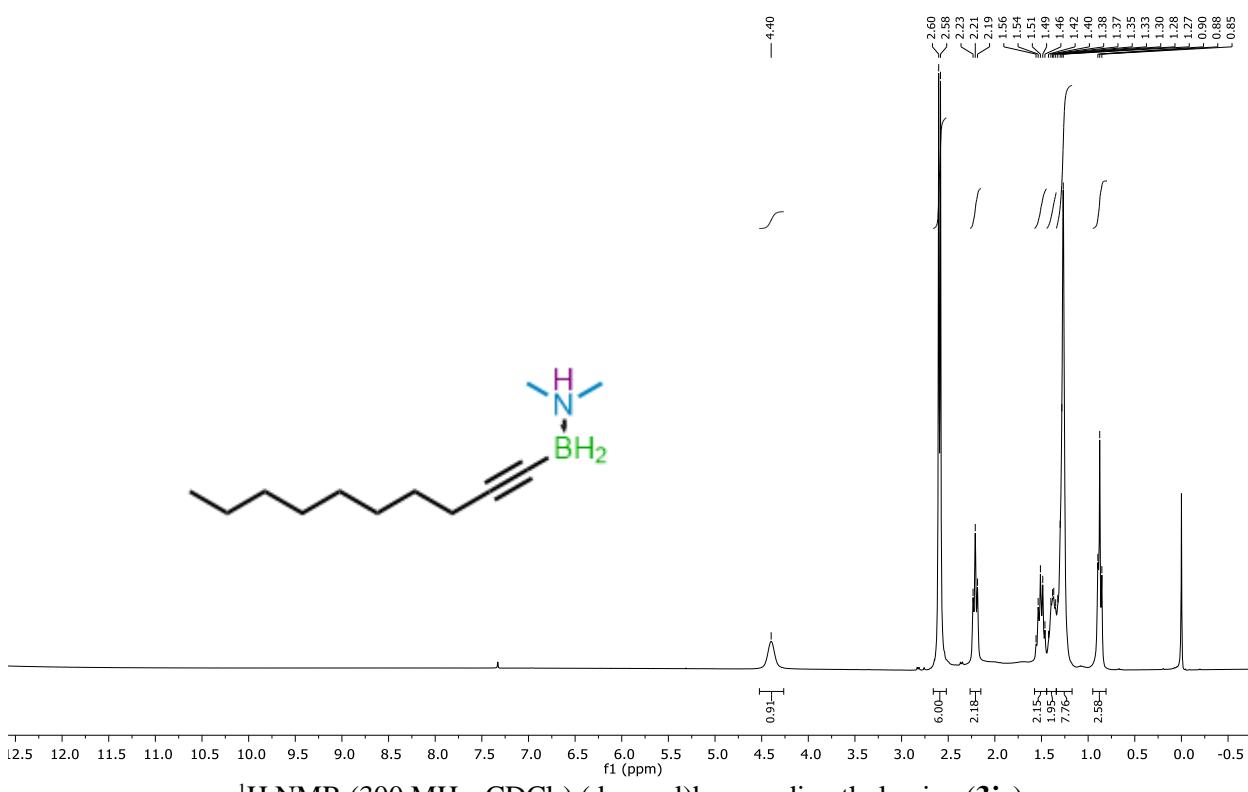


<sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ) (hexynyl)borane-dimethylamine (**3ie**)

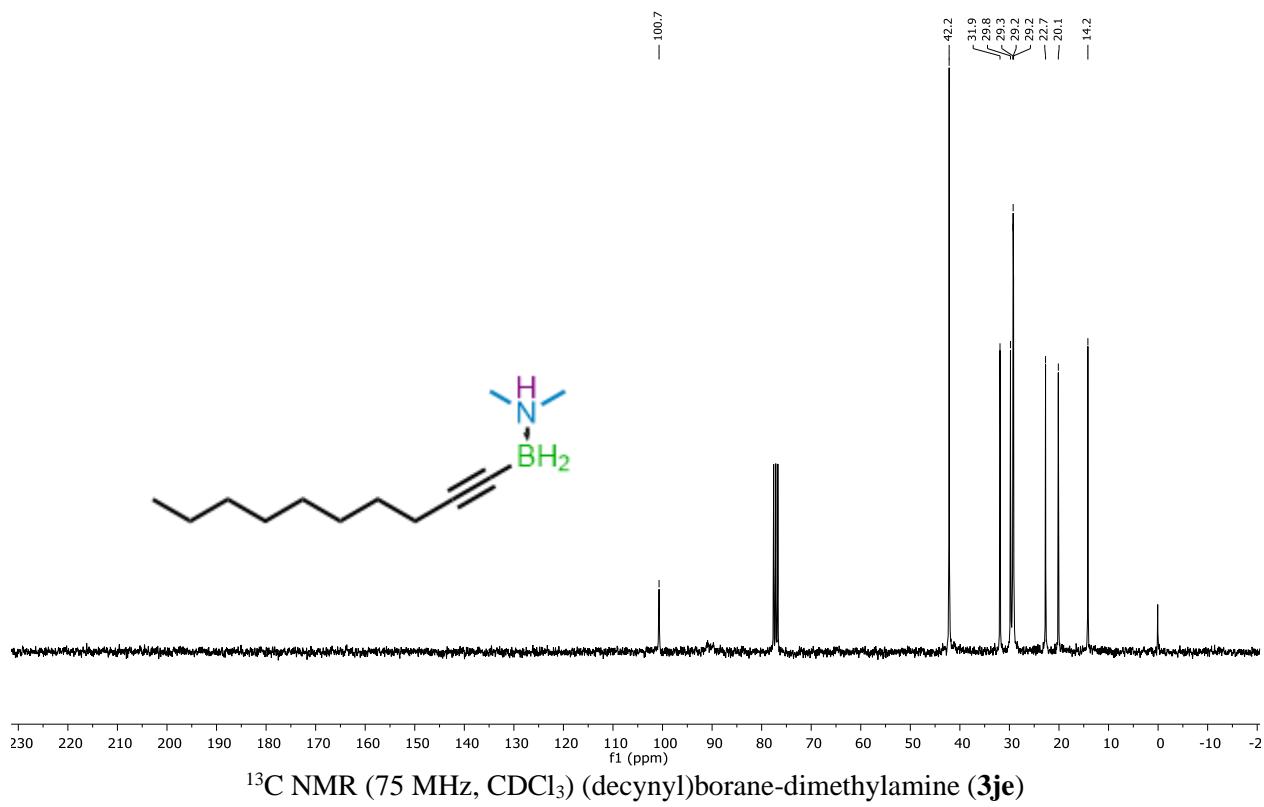




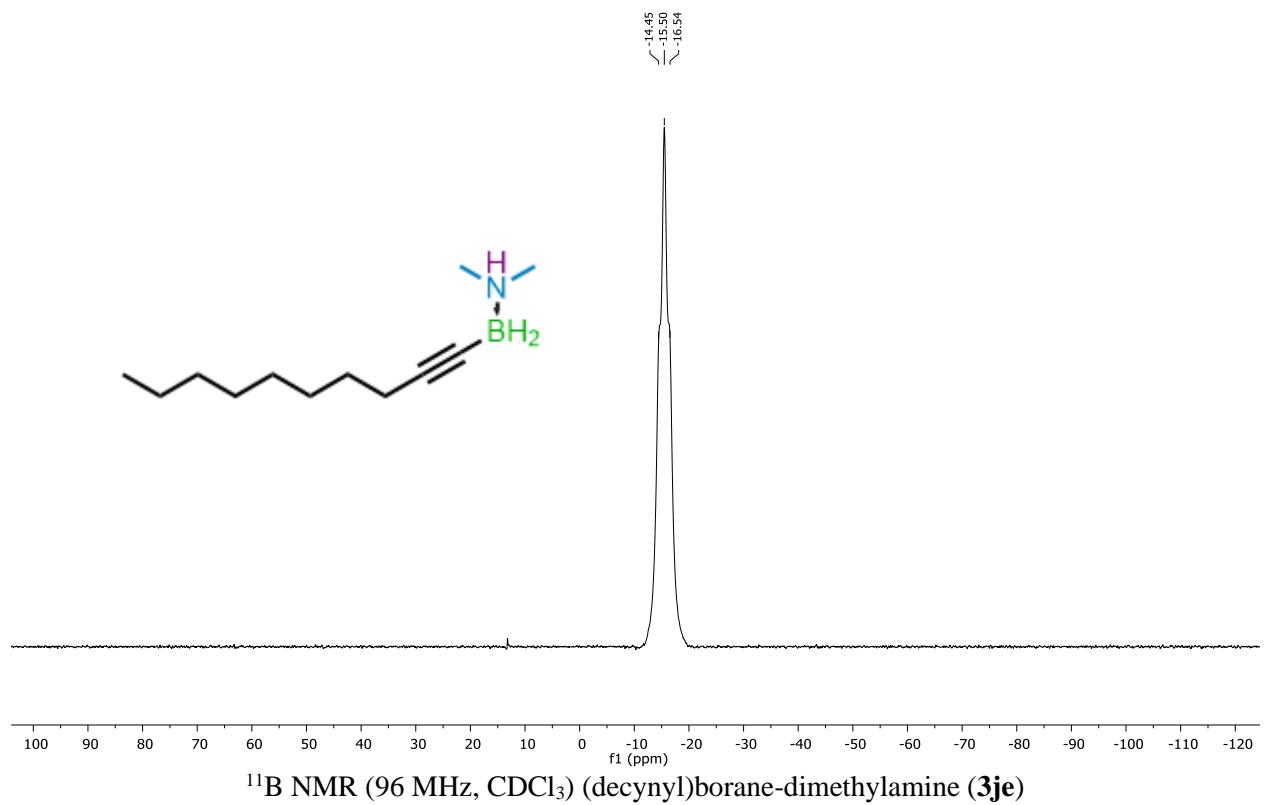
<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) (hexynyl)borane-dimethylamine (**3ie**)

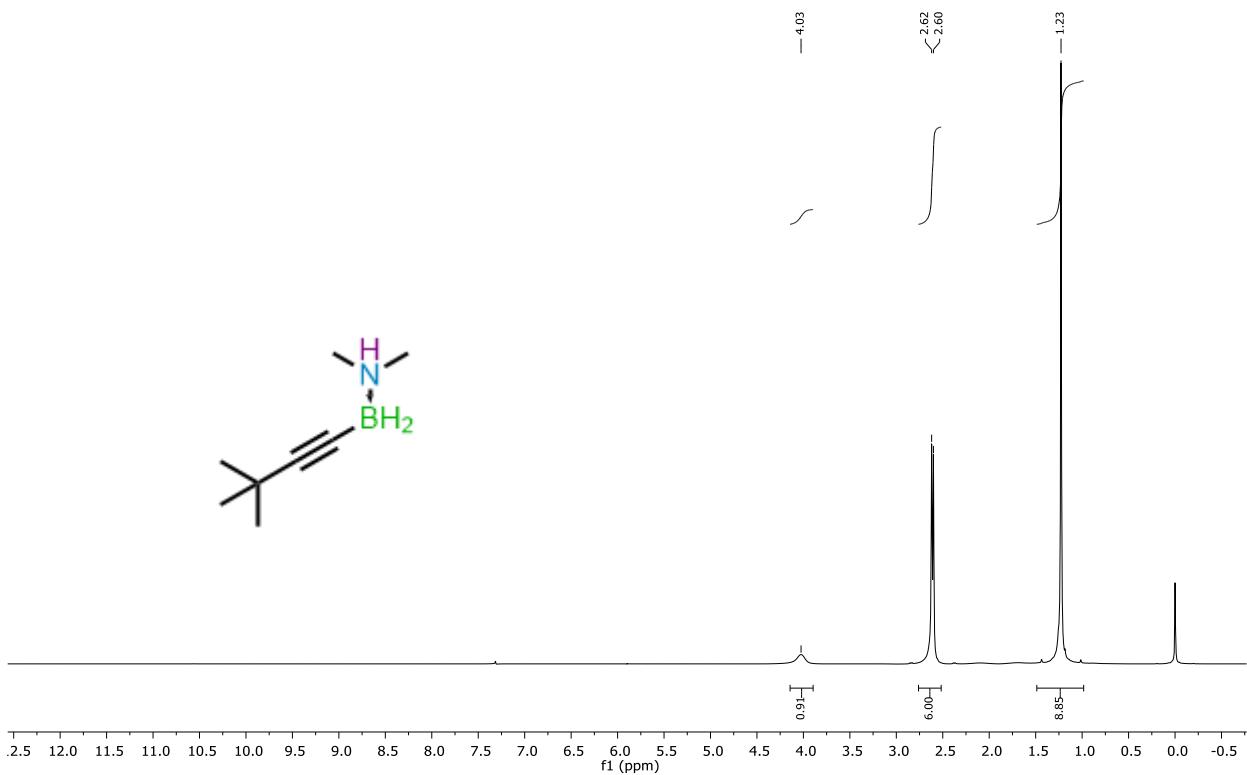


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) (decynyl)borane-dimethylamine (**3je**)

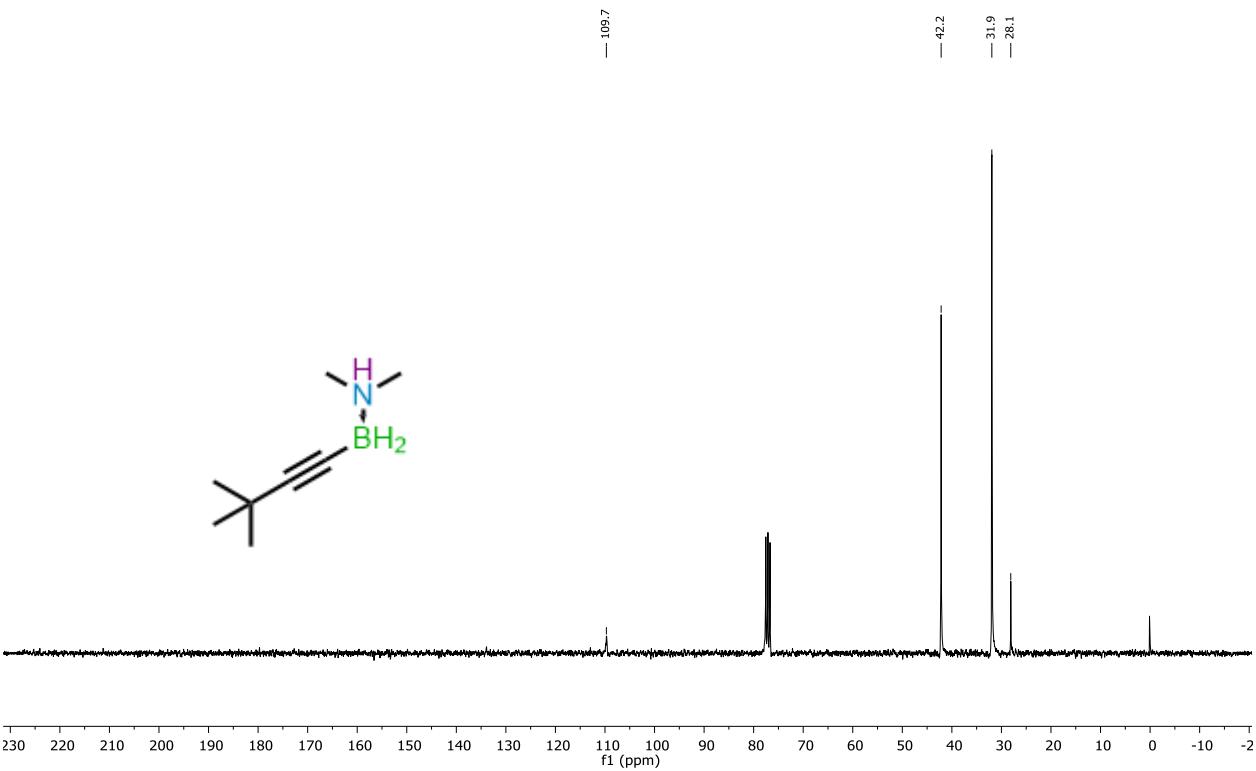


$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) (decynyl)borane-dimethylamine (**3je**)

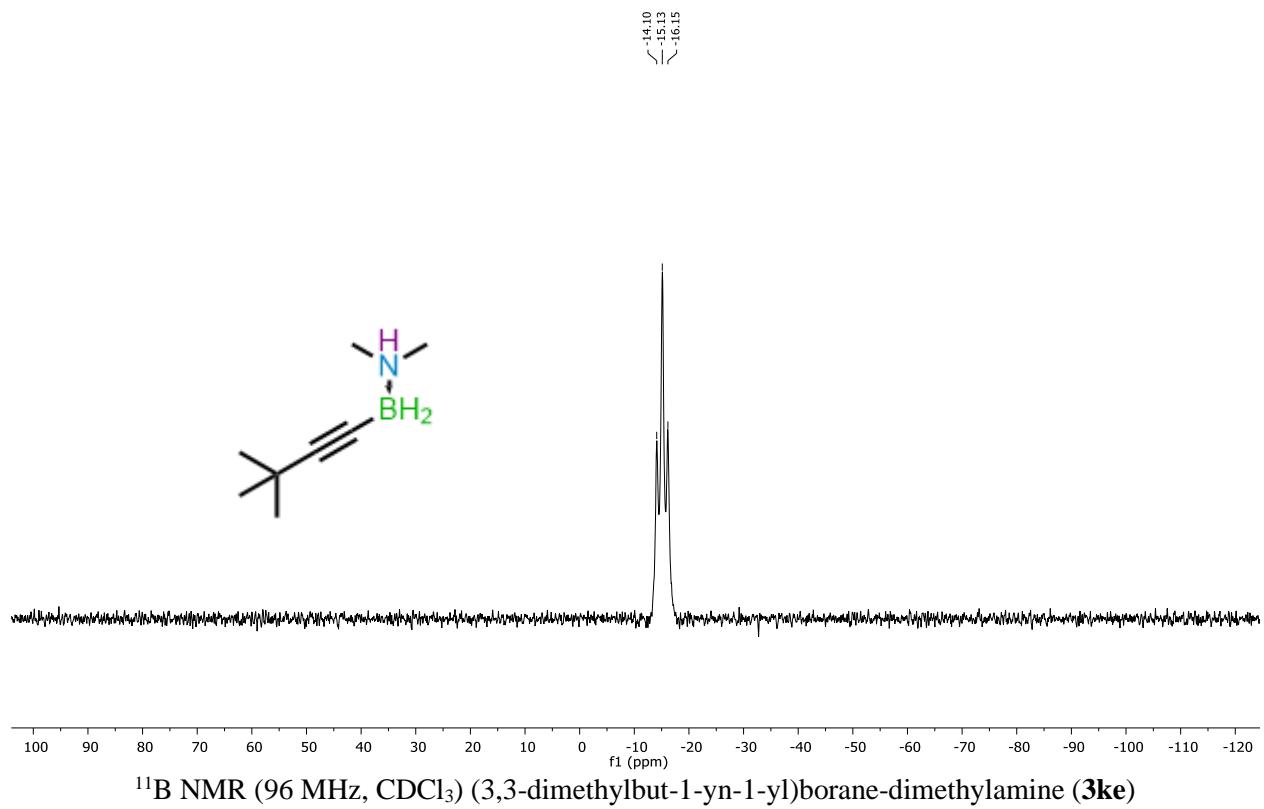




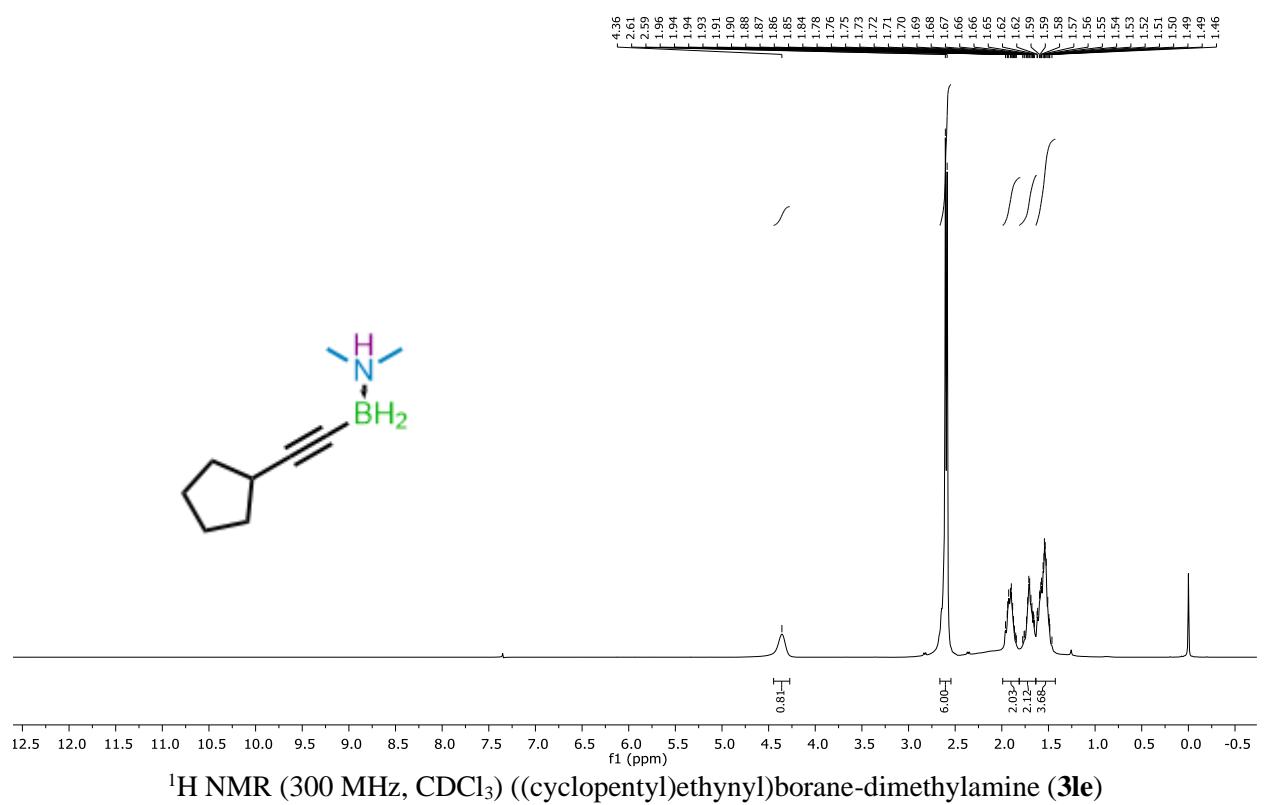
<sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ) (3,3-dimethylbut-1-yn-1-yl)borane-dimethylamine (**3ke**)



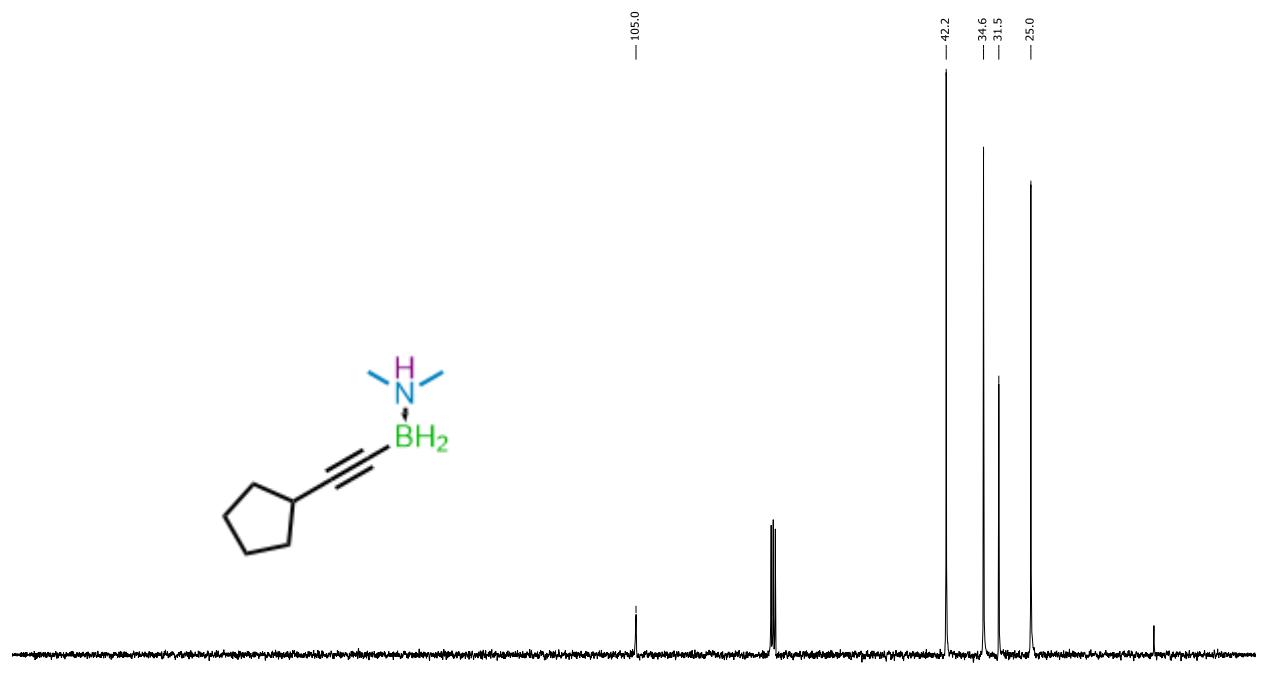
<sup>13</sup>C NMR (75 MHz,  $\text{CDCl}_3$ ) (3,3-dimethylbut-1-yn-1-yl)borane-dimethylamine (**3ke**)



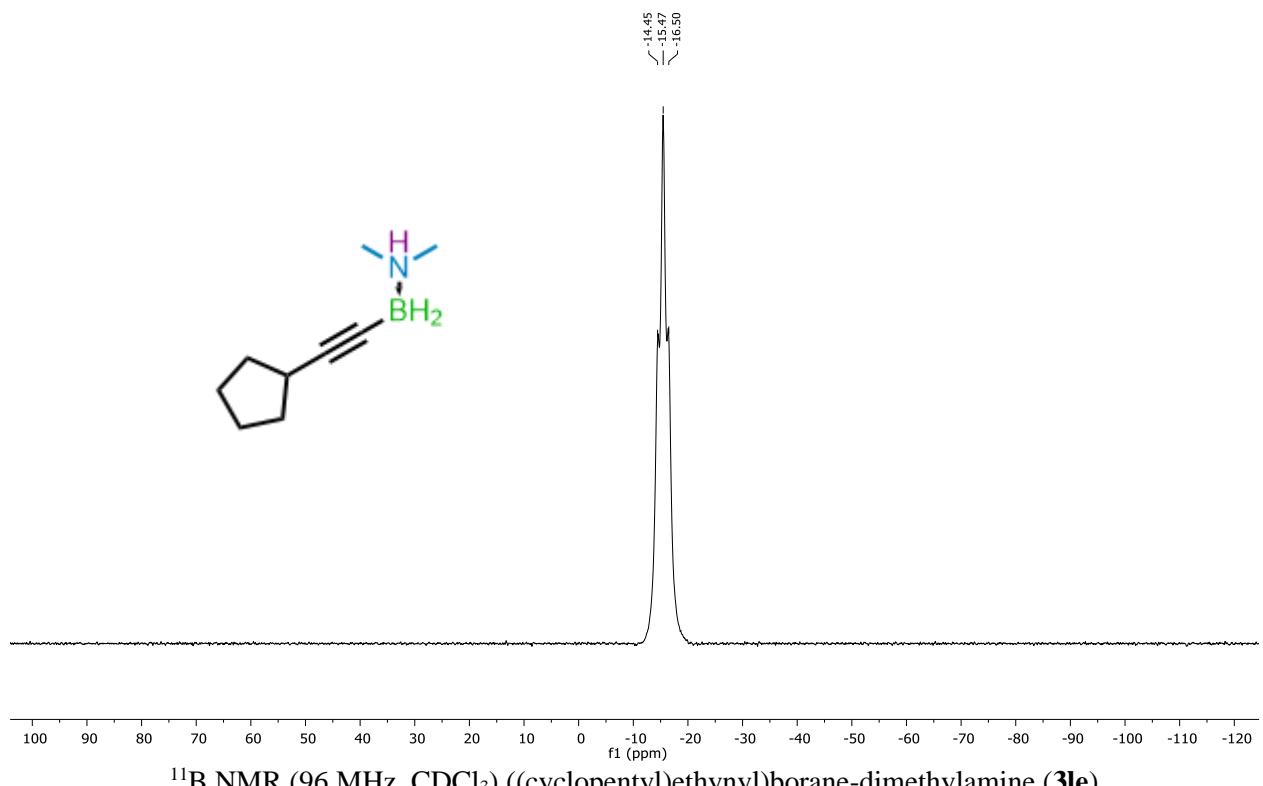
$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ) (3,3-dimethylbut-1-yn-1-yl)borane-dimethylamine (**3ke**)



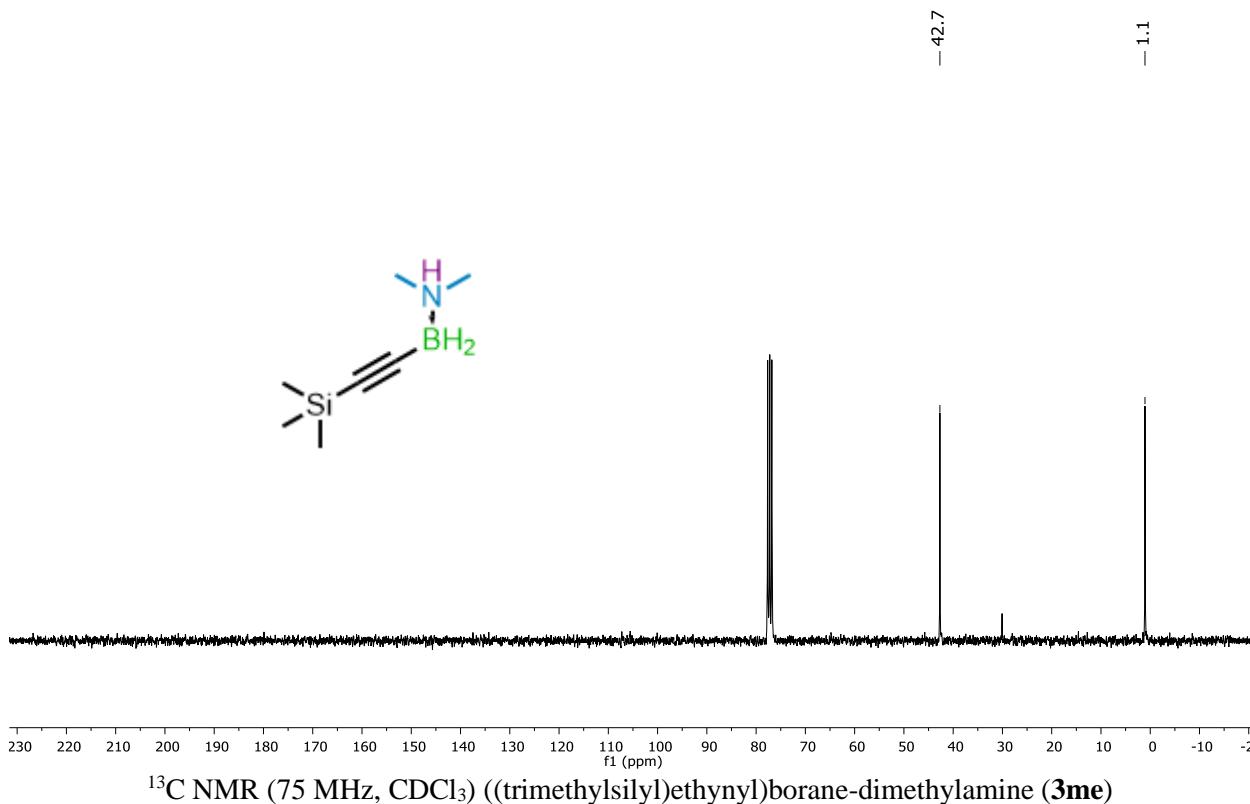
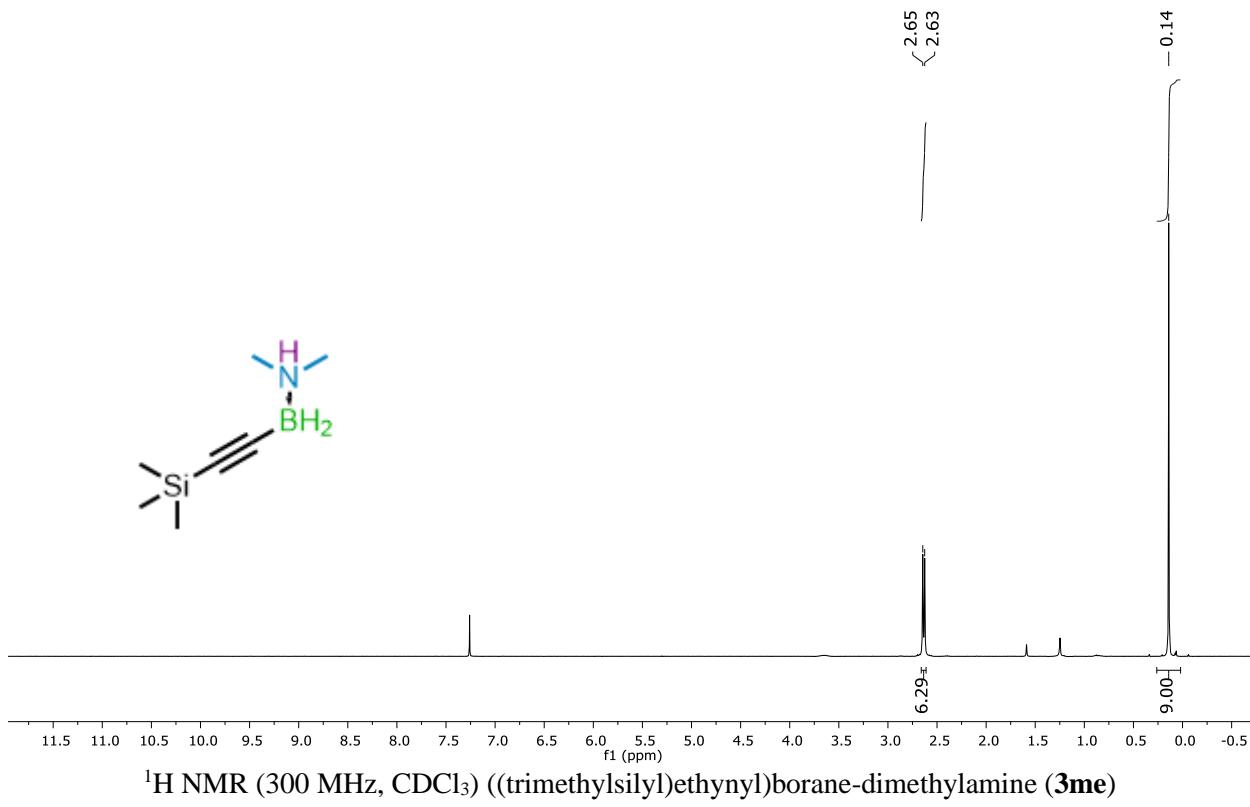
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) ((cyclopentyl)ethynyl)borane-dimethylamine (**3le**)

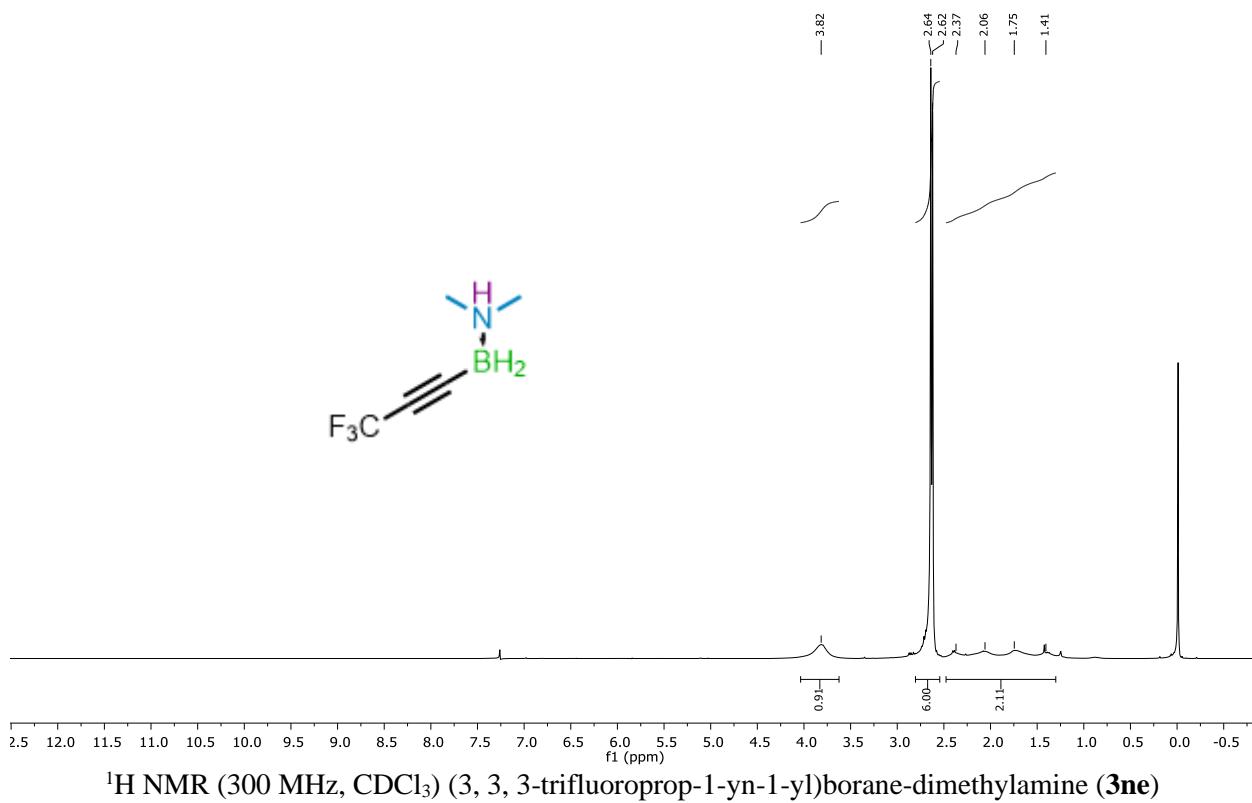
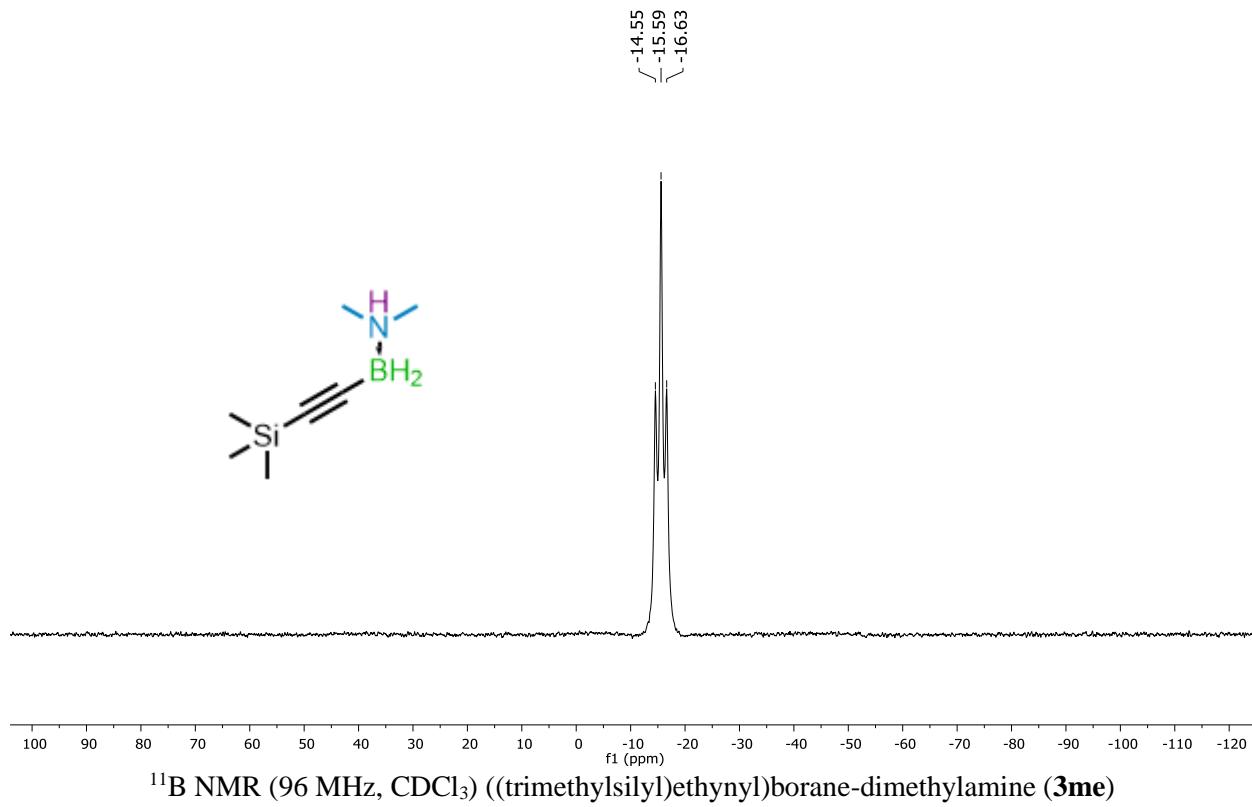


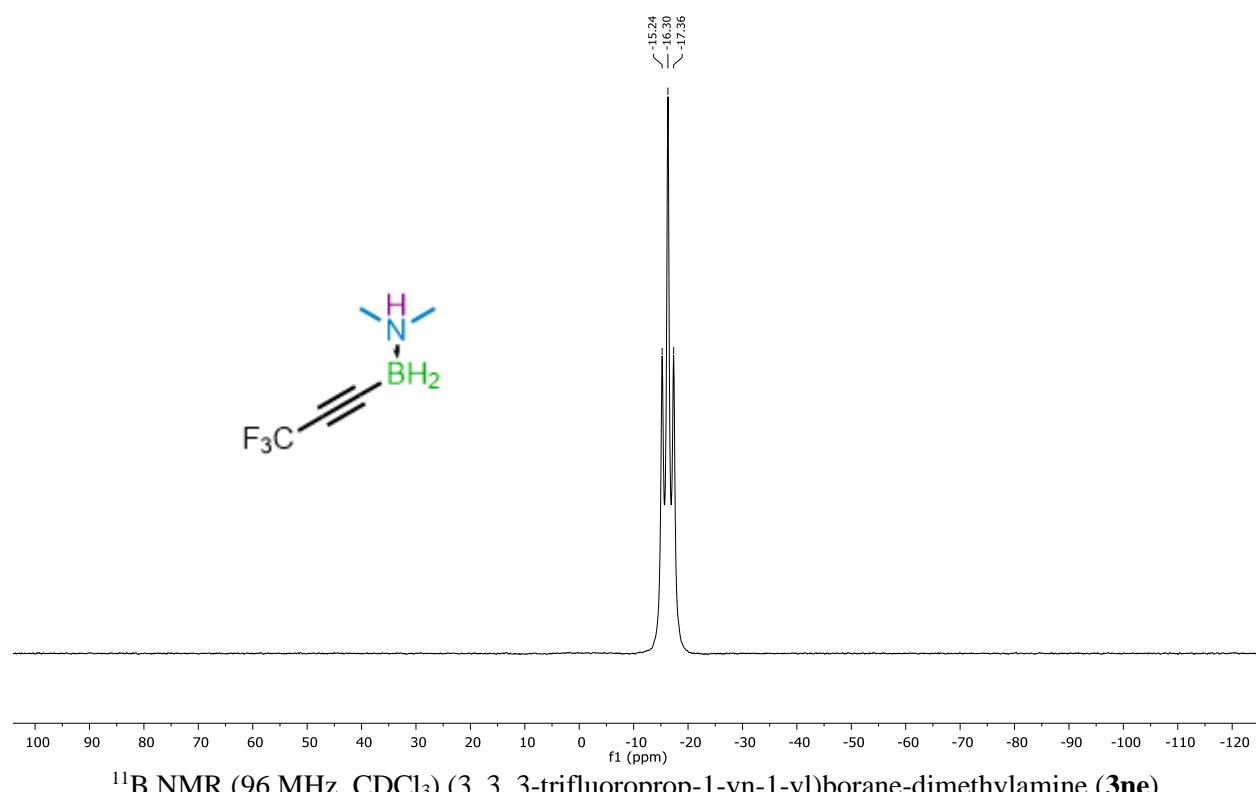
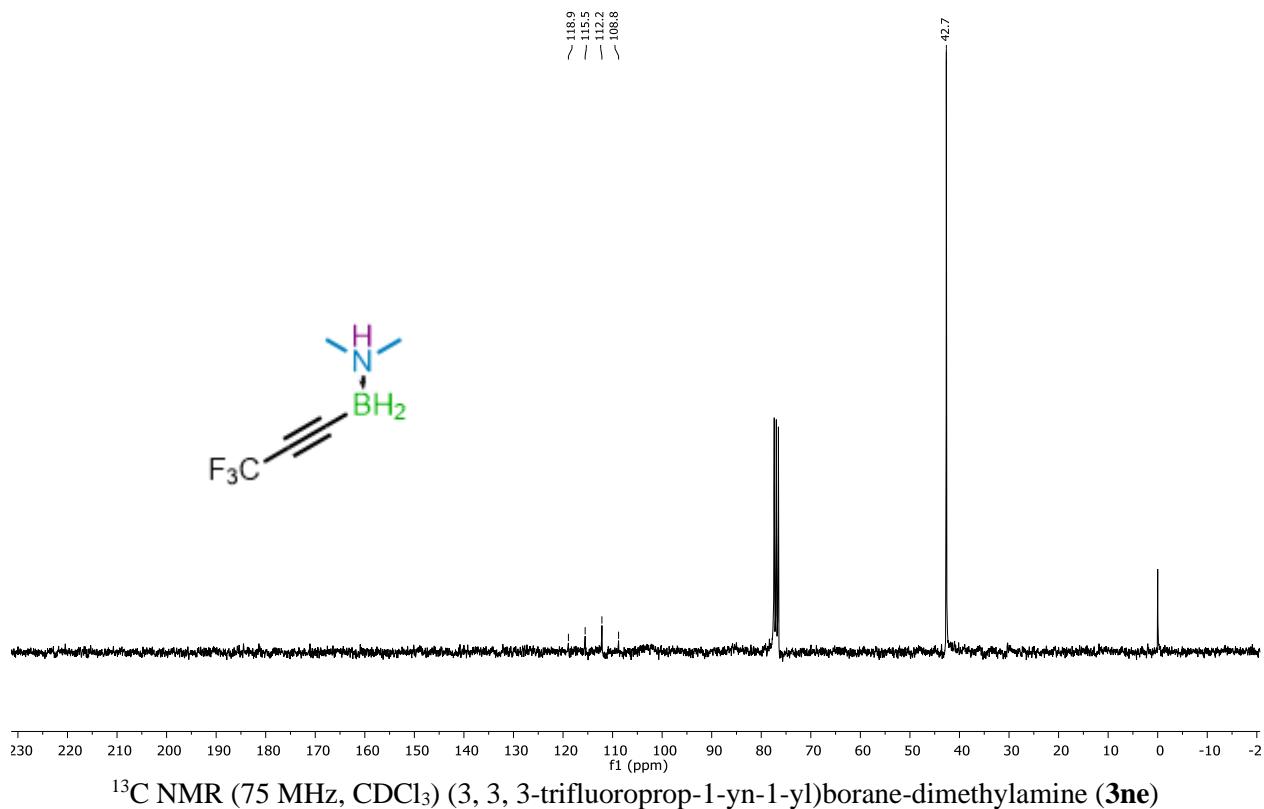
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) ((cyclopentyl)ethynyl)borane-dimethylamine (**3le**)

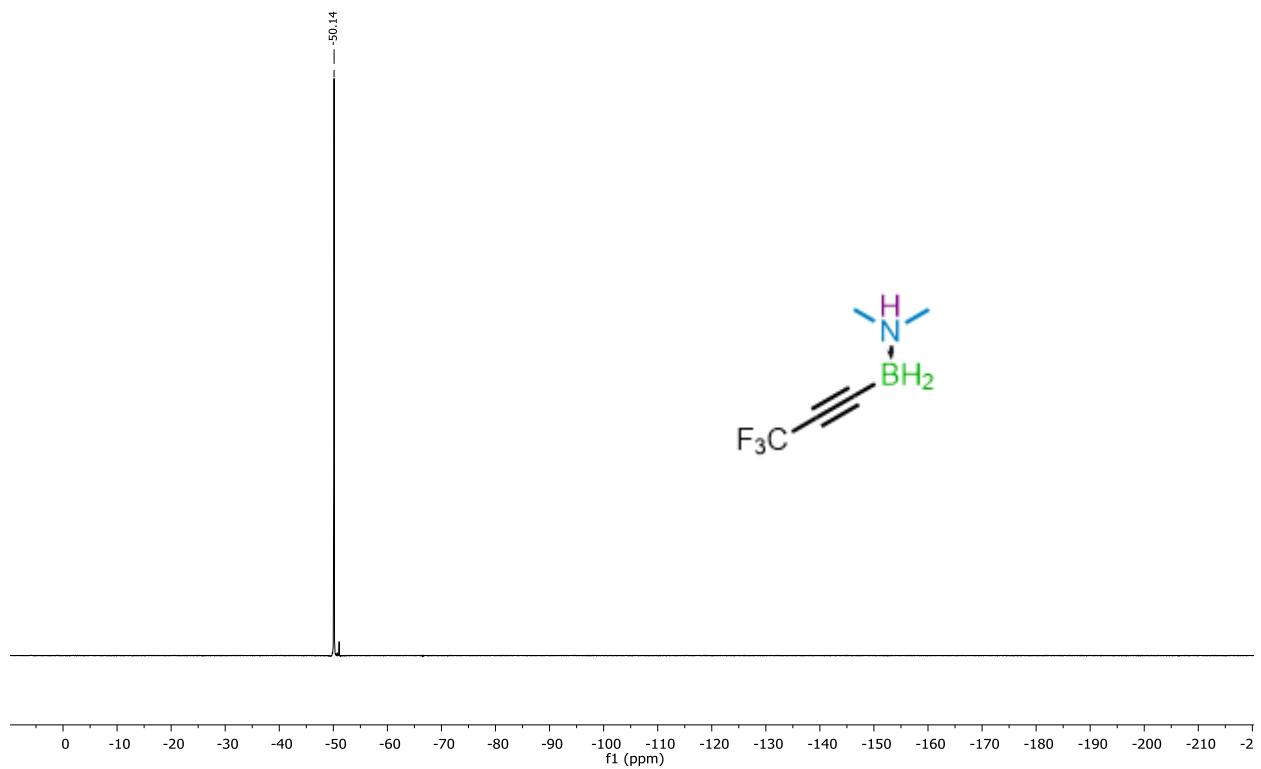


<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) ((cyclopentyl)ethynyl)borane-dimethylamine (**3le**)

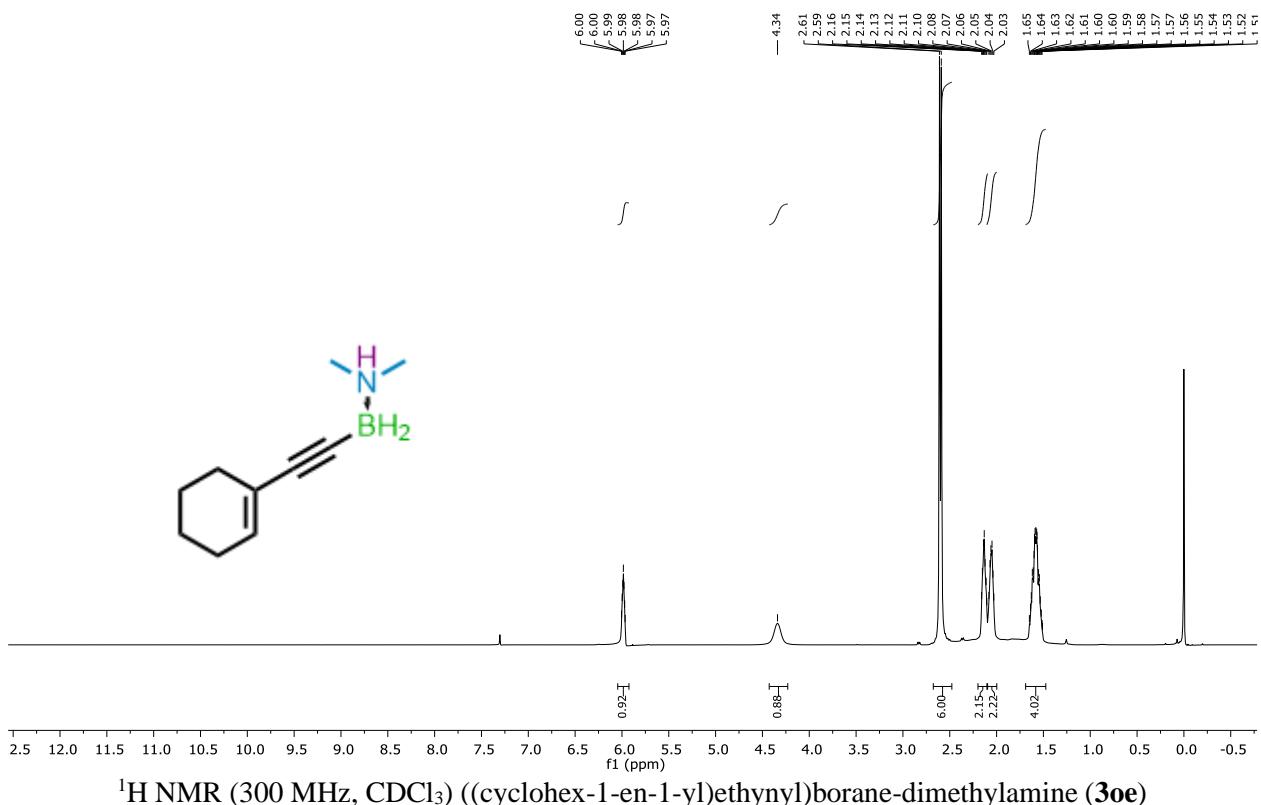




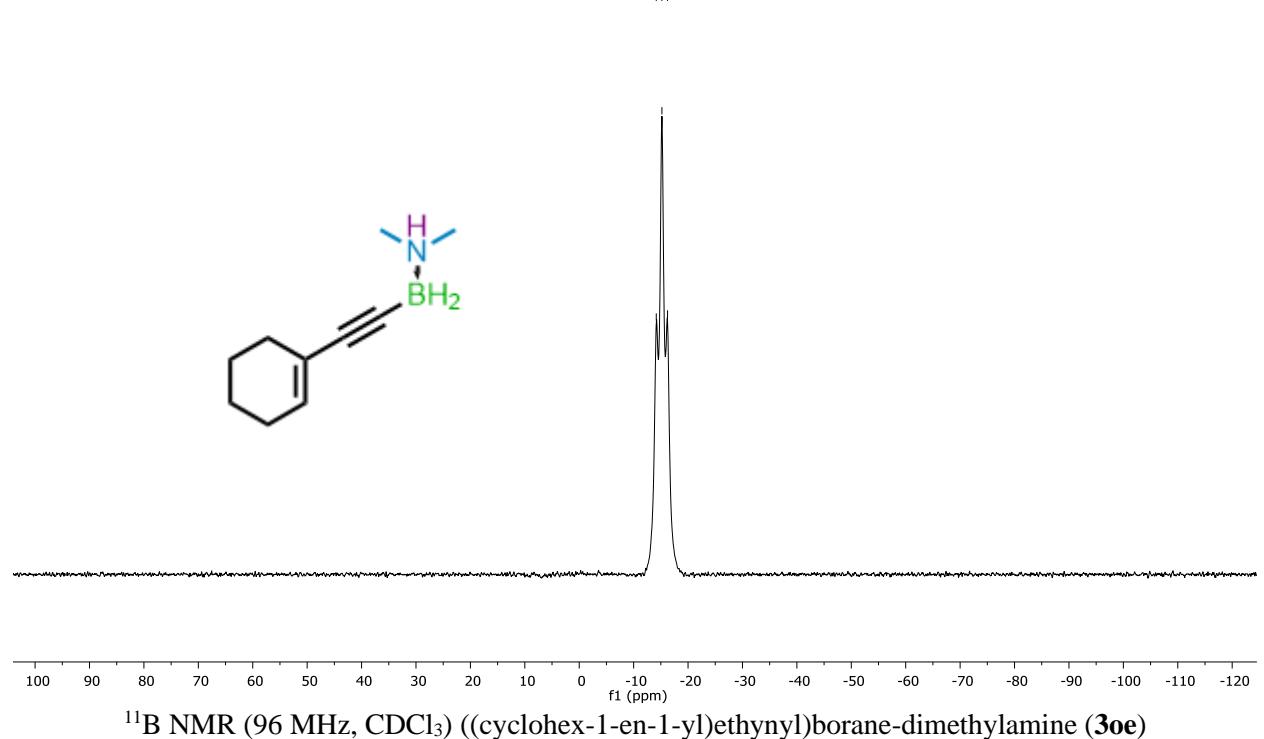
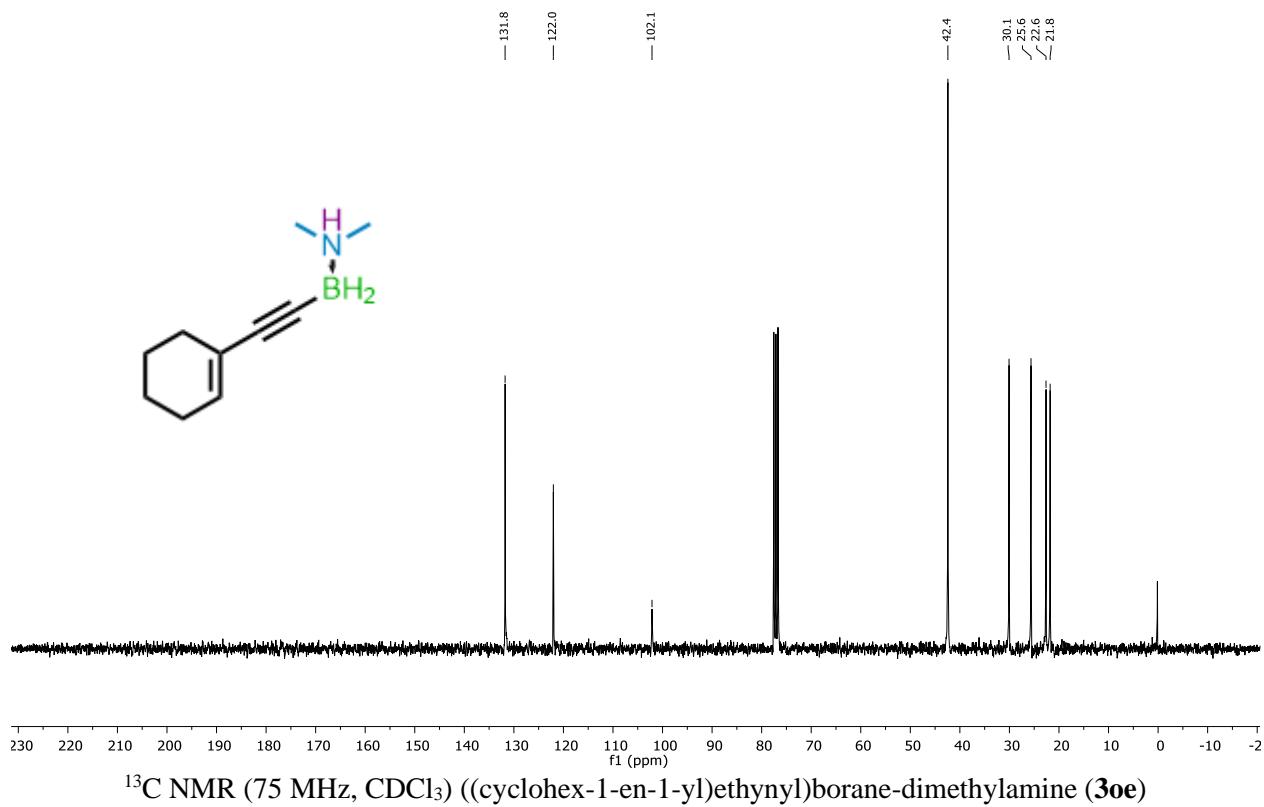


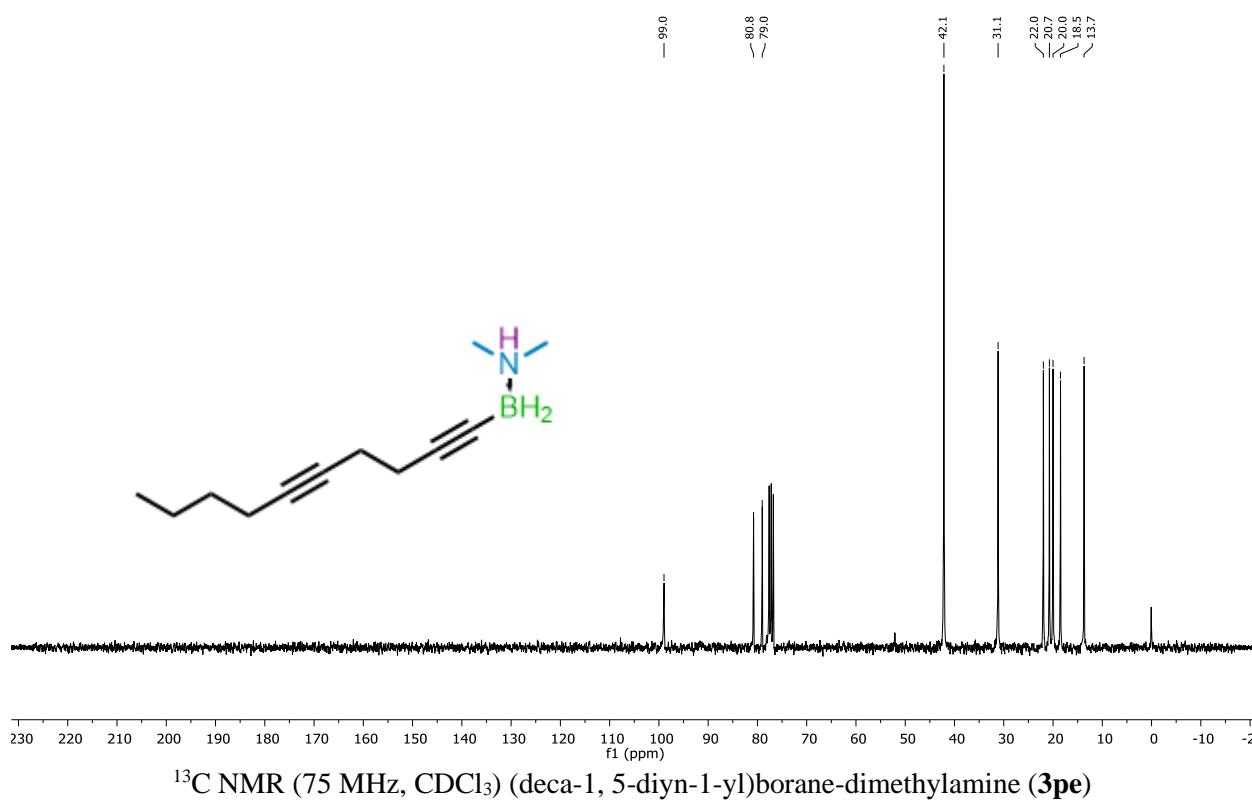
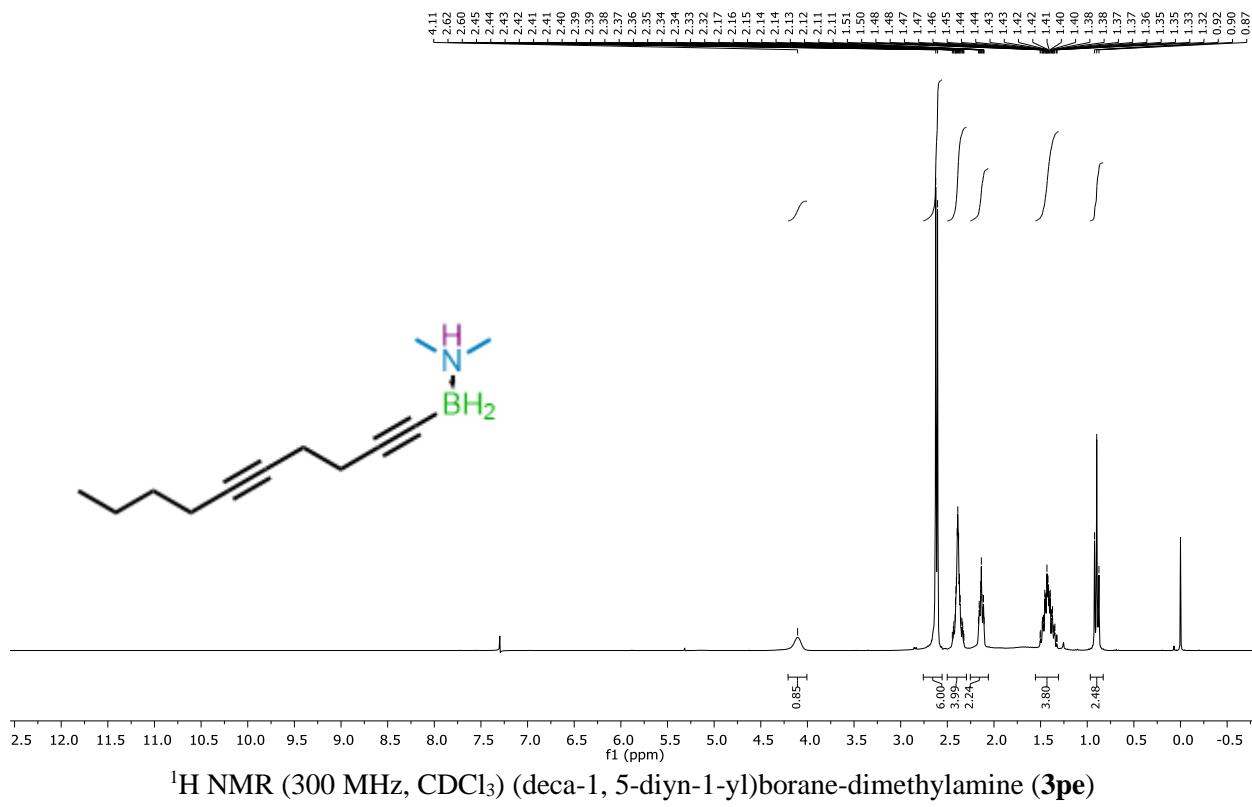


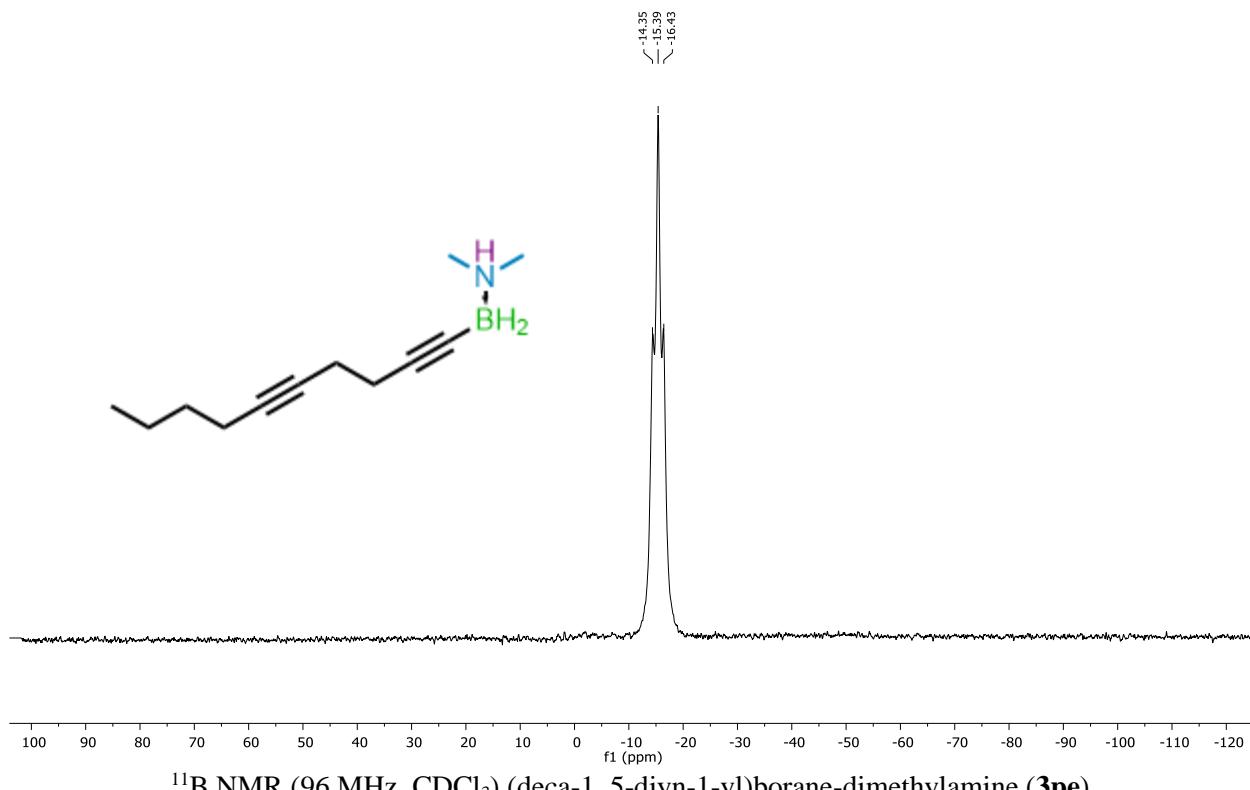
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ) (3, 3, 3-trifluoroprop-1-yn-1-yl)borane-dimethylamine (**3ne**)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) ((cyclohex-1-en-1-yl)ethynyl)borane-dimethylamine (**3oe**)

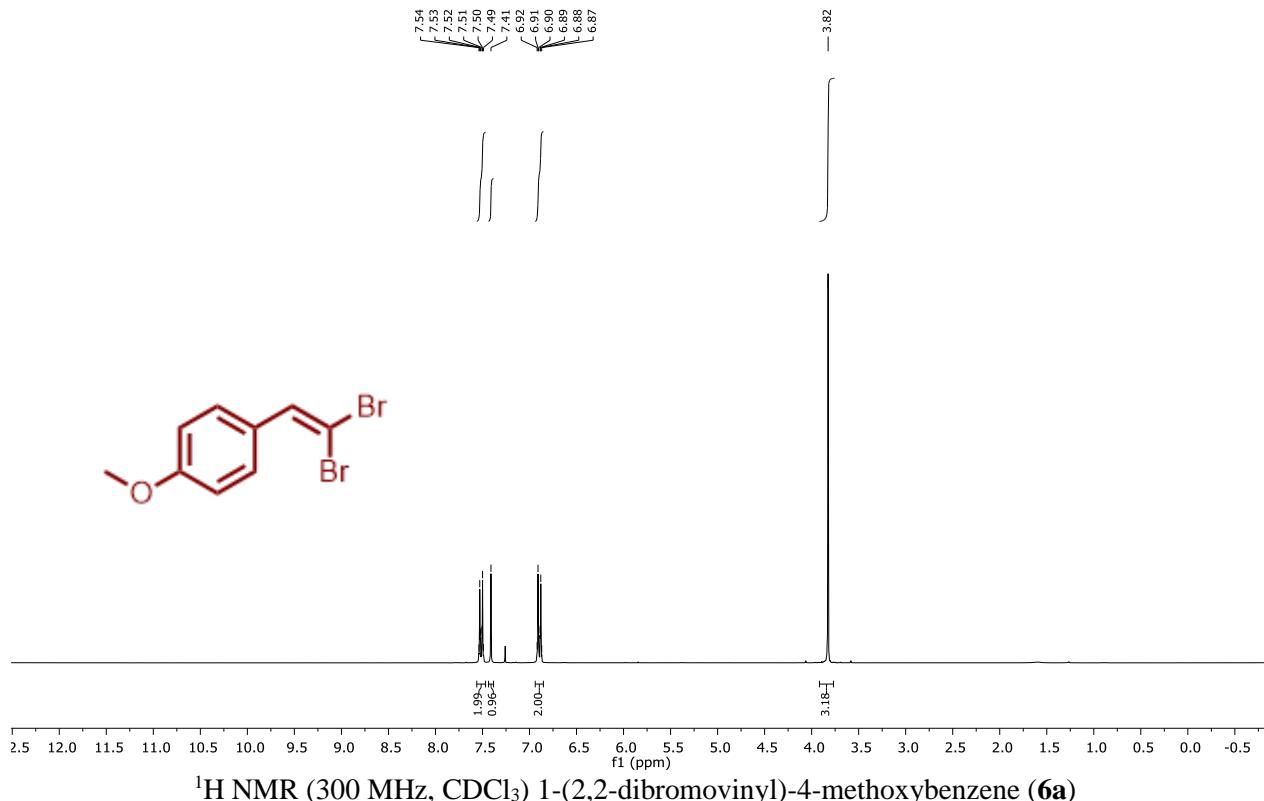




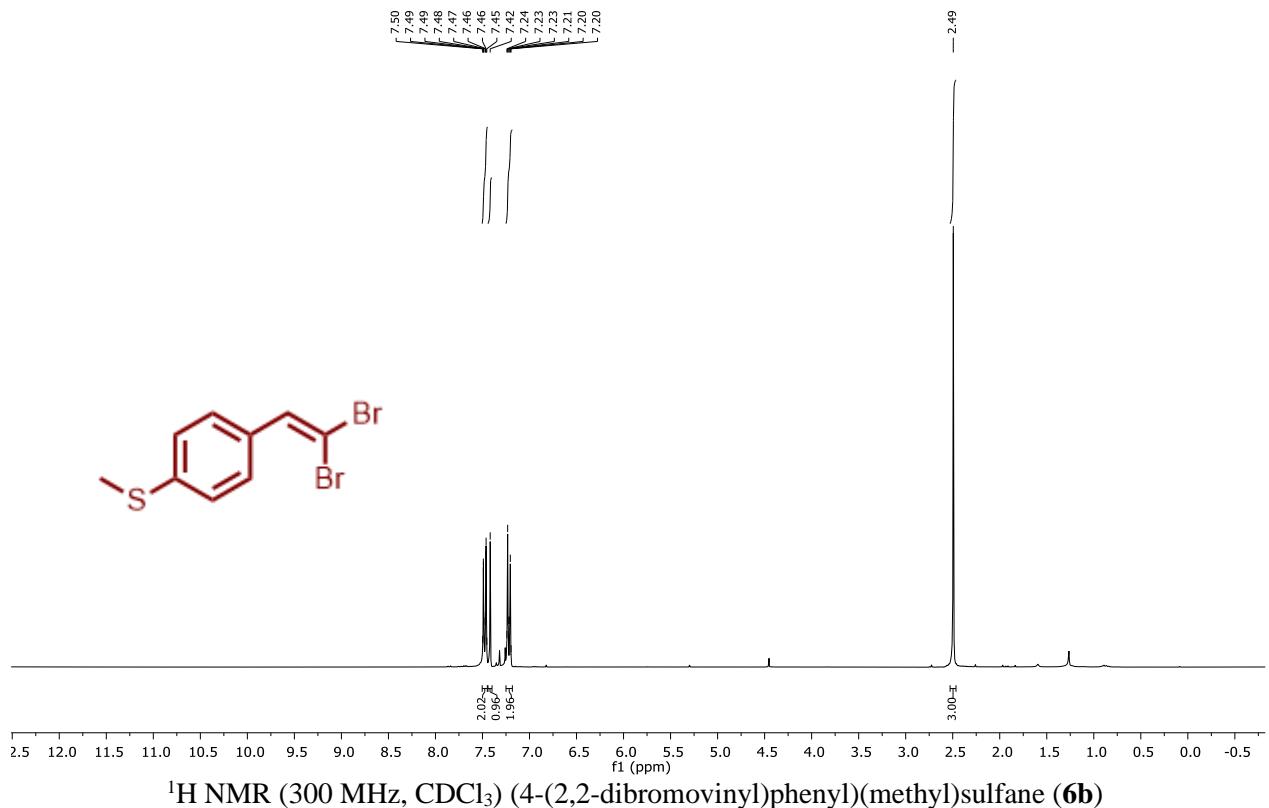
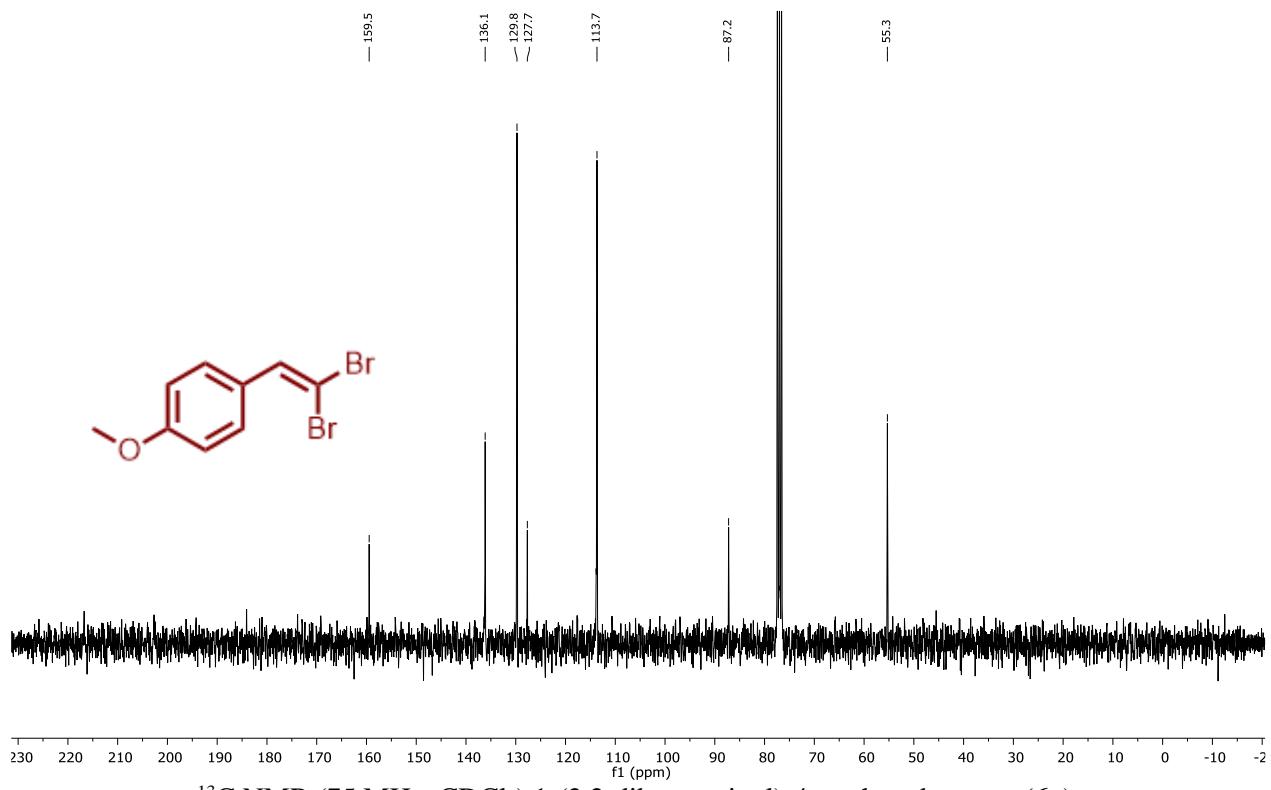


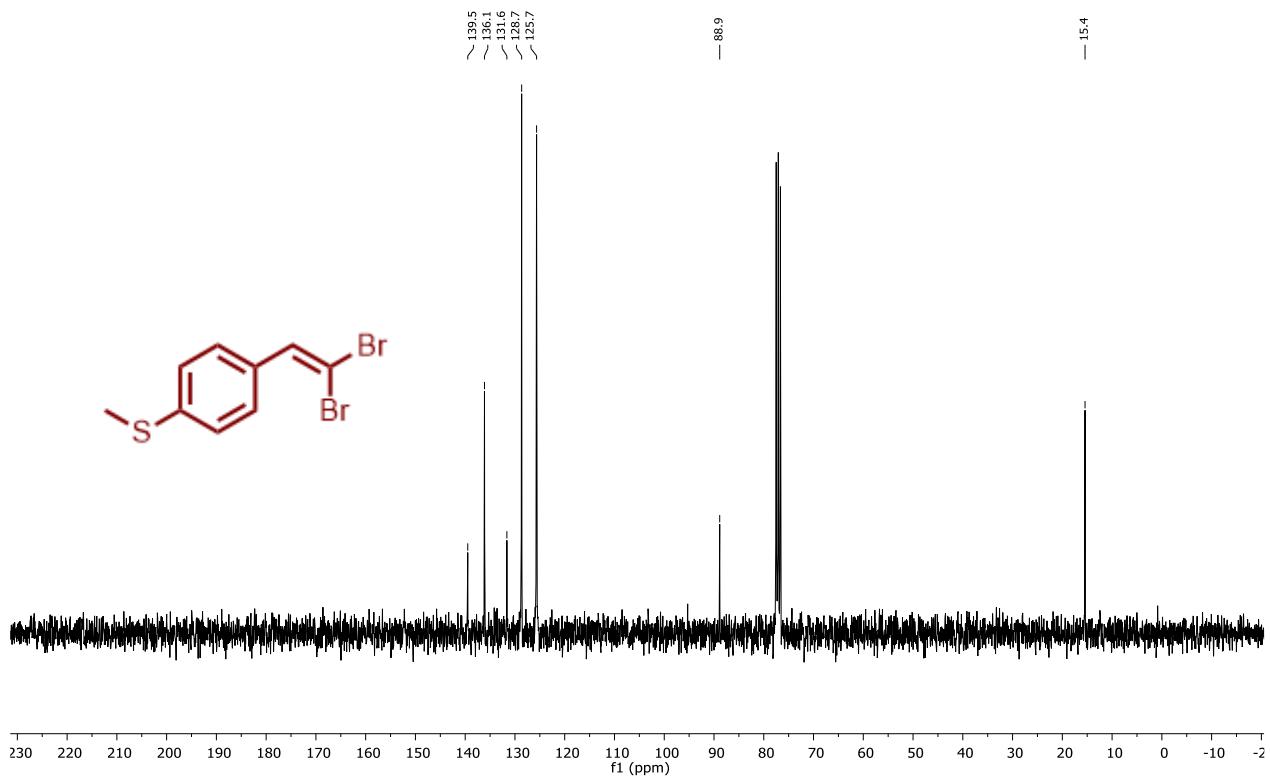
<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) (deca-1, 5-diyn-1-yl)borane-dimethylamine (**3pe**)

### NMR spectra of dibromides

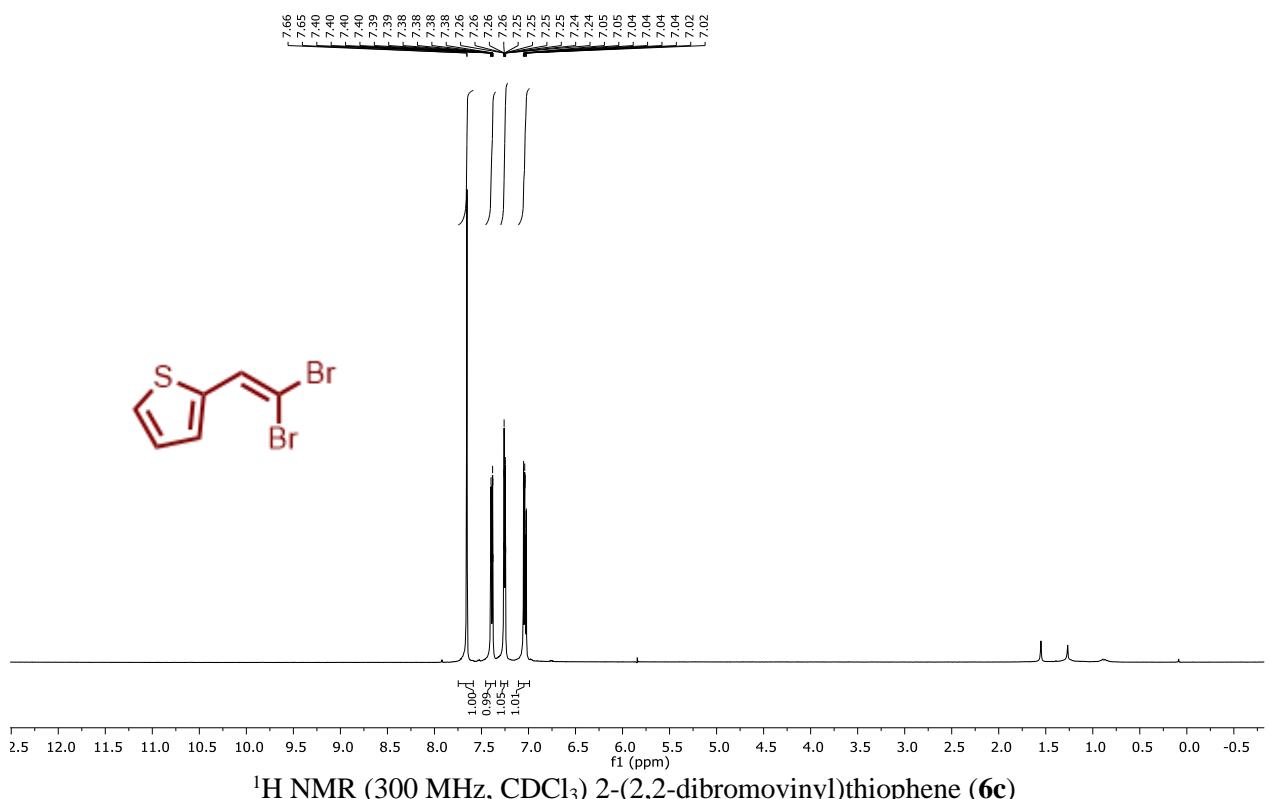


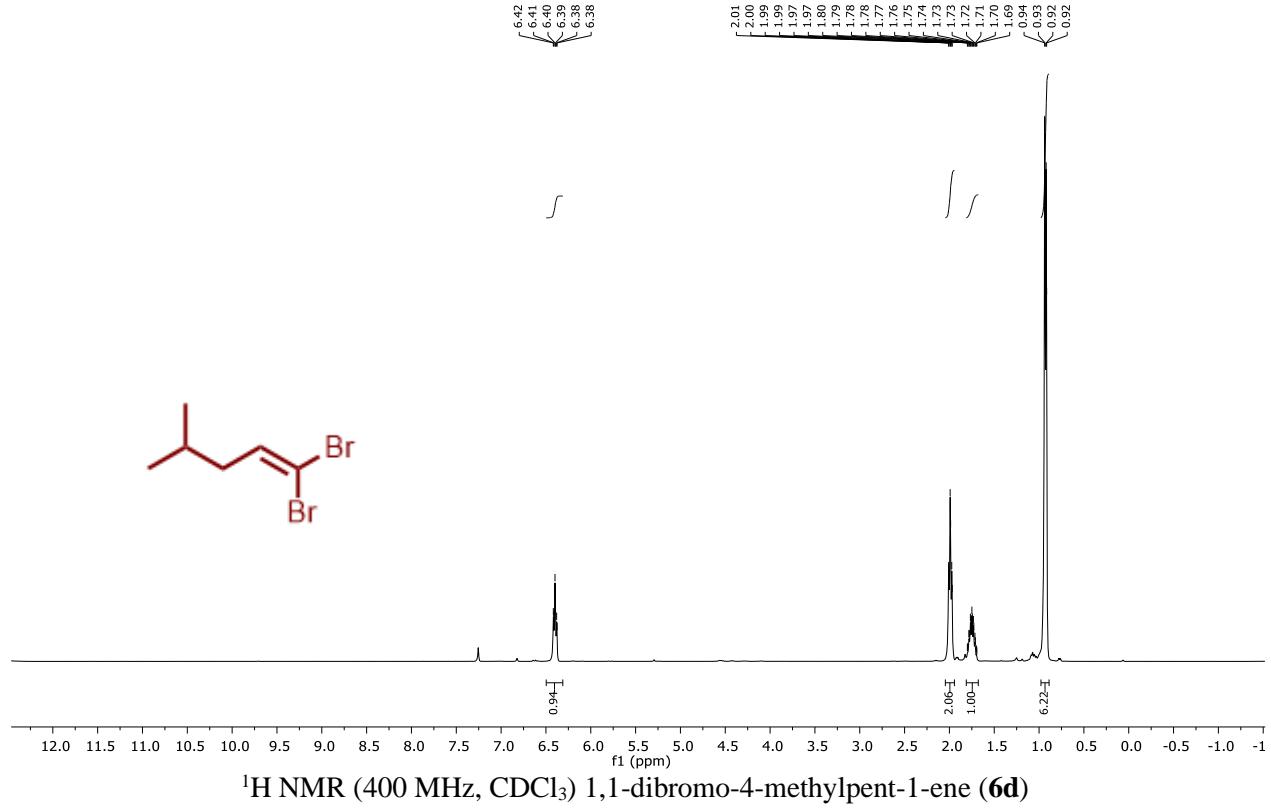
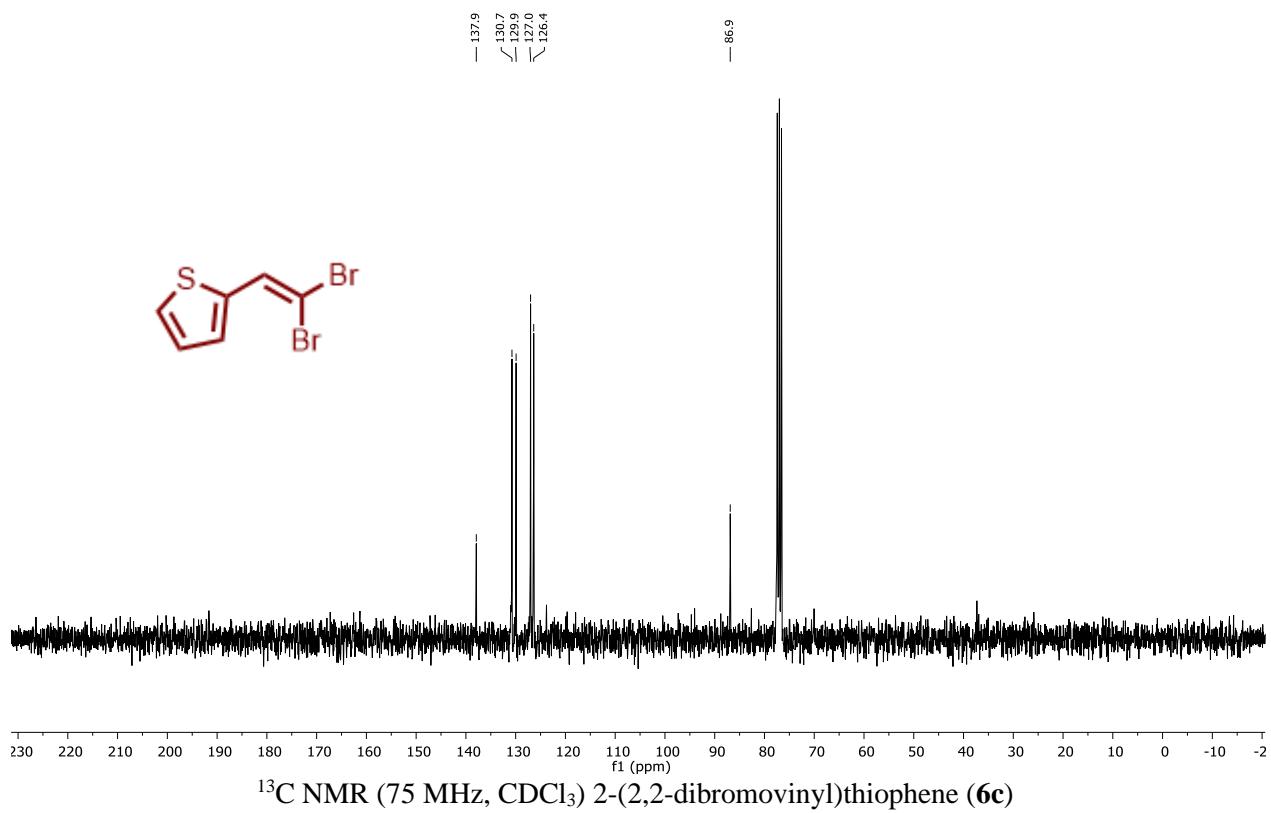
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 1-(2,2-dibromovinyl)-4-methoxybenzene (**6a**)

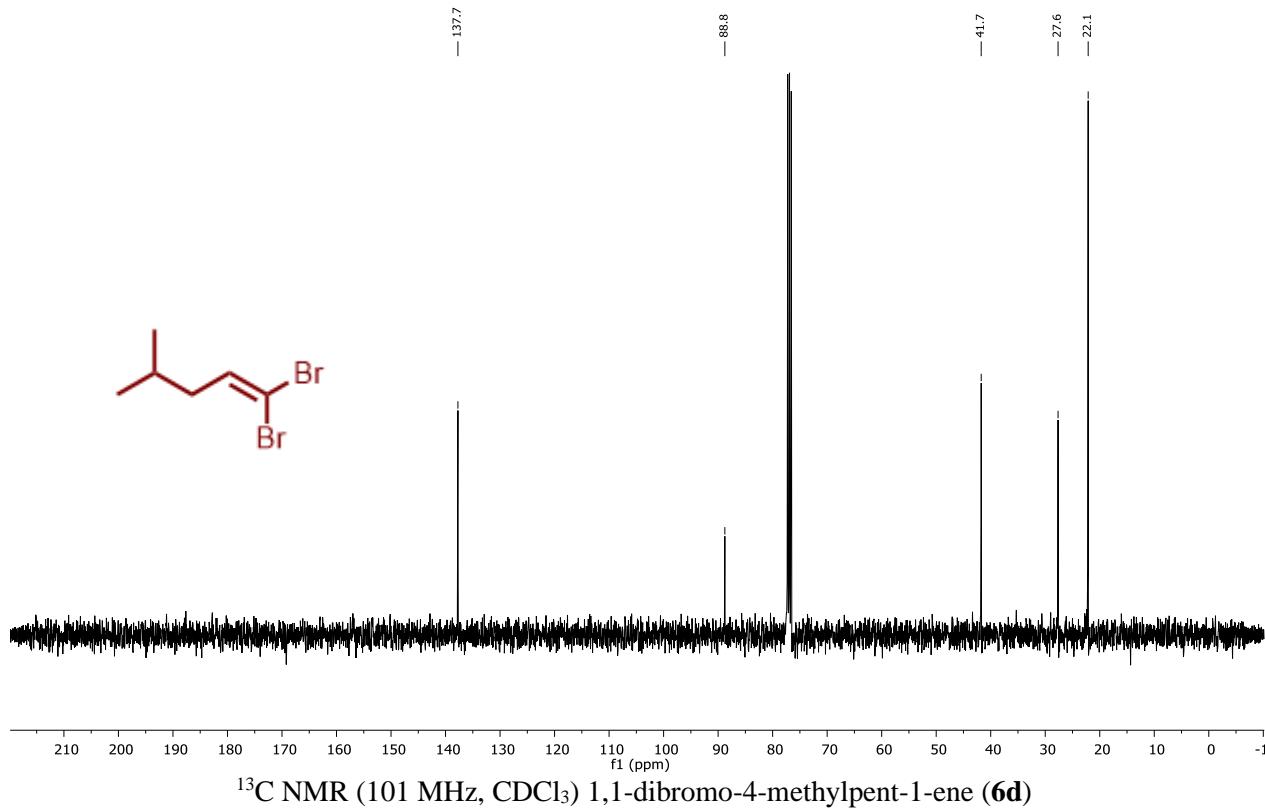




<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) (4-(2,2-dibromovinyl)phenyl)(methyl)sulfane (**6b**)







### NMR spectra of alkynylborane-amines from dibromides

