

## Chiral Carbene–Borane Adducts: Precursors for Borenium Catalysts for Asymmetric FLP Hydrogenations

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### Supporting Information

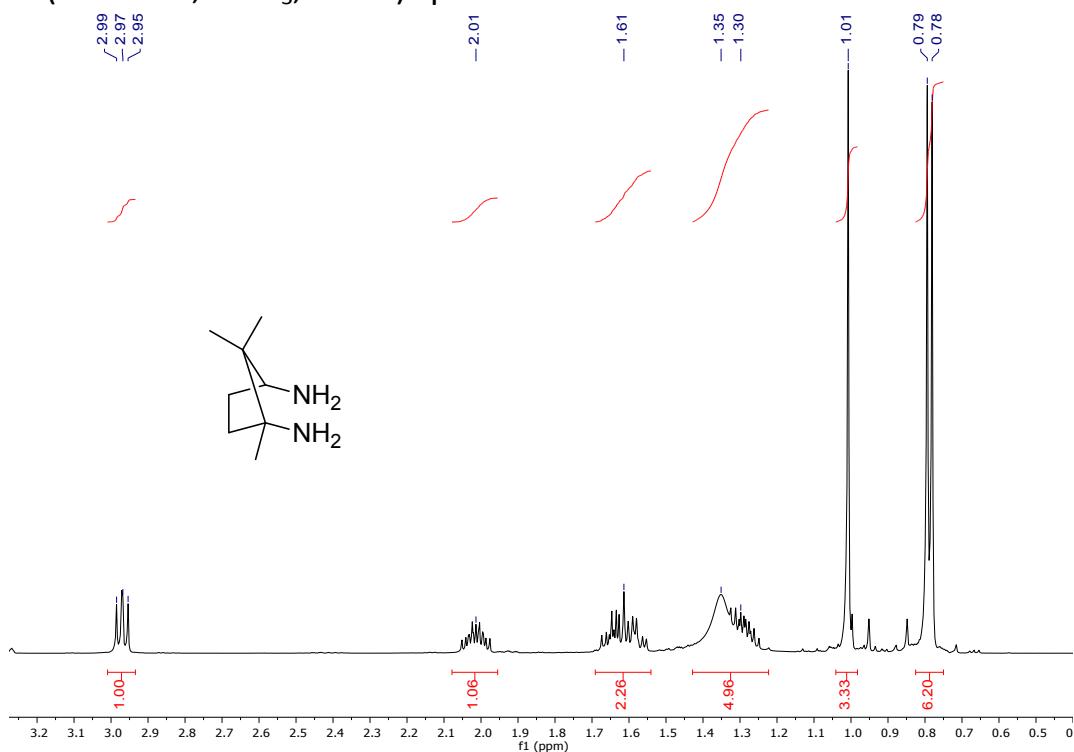
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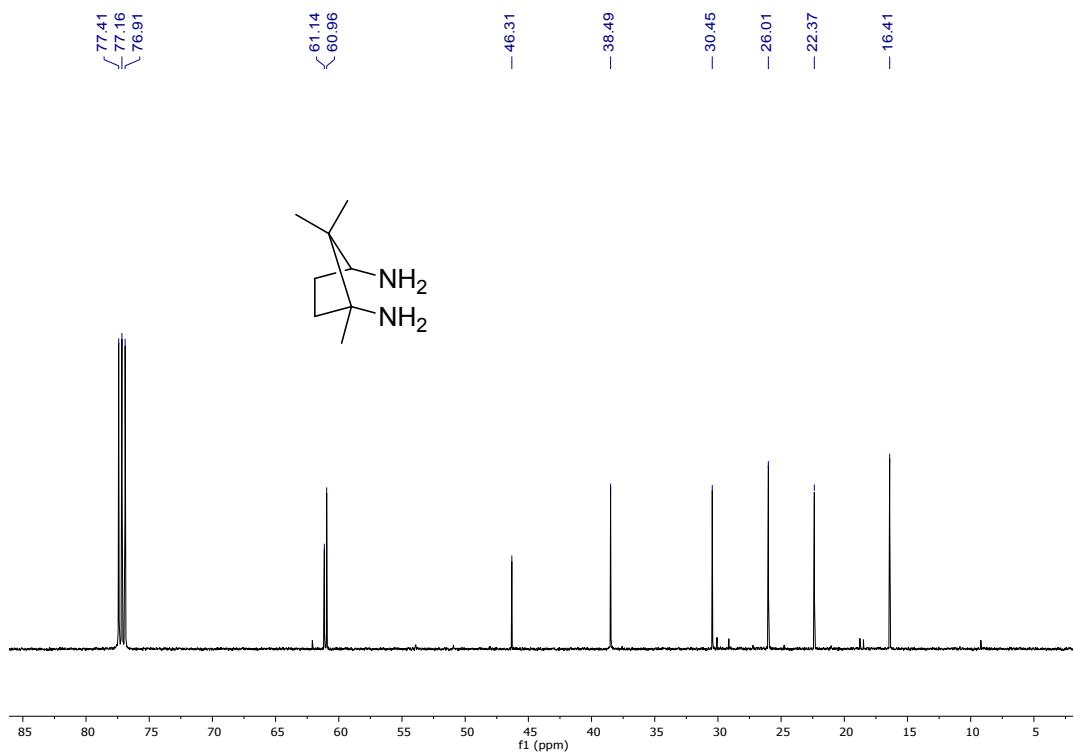
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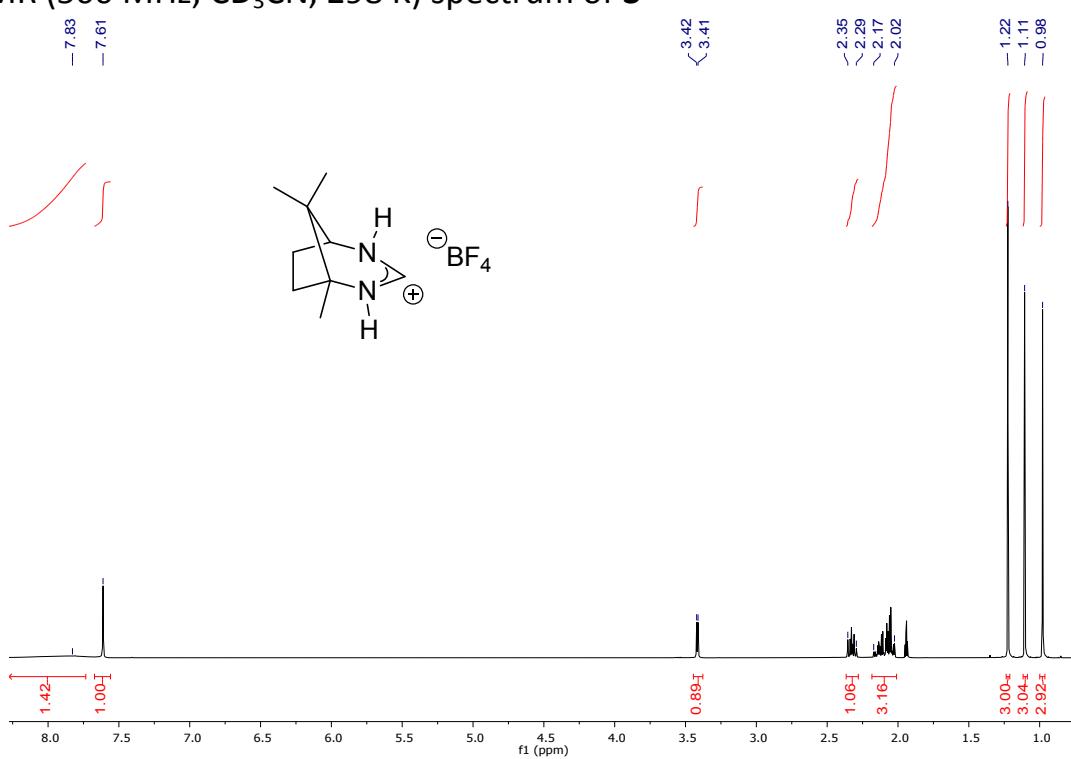
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **2**



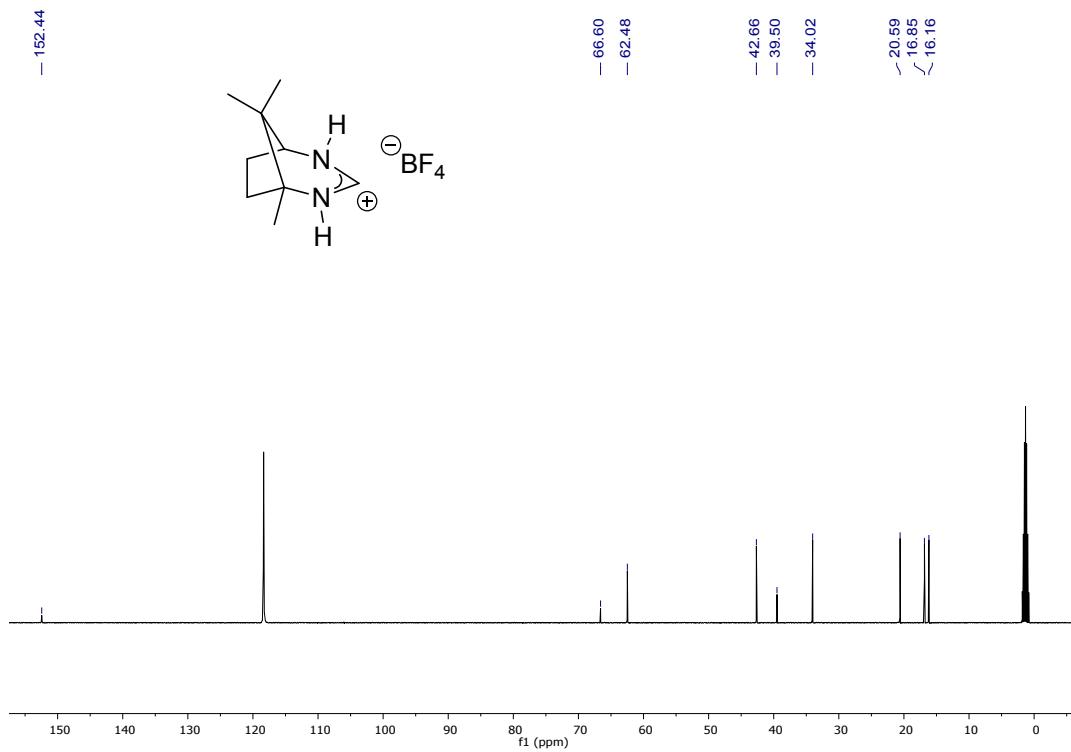
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **2**



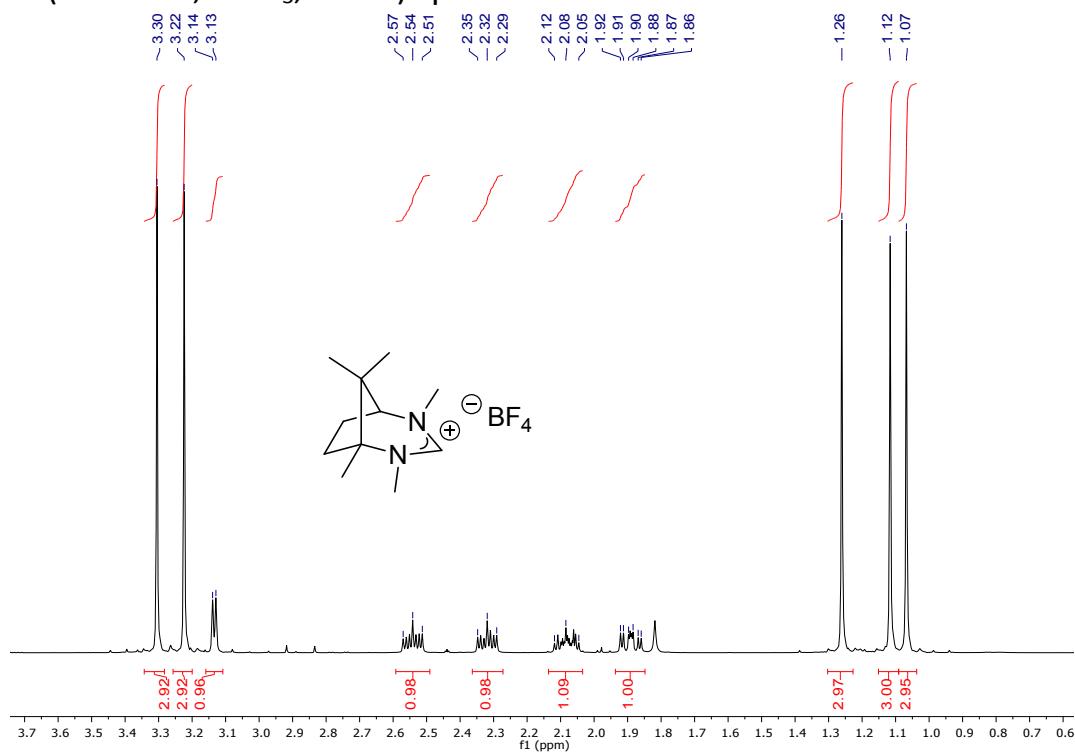
<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) spectrum of **3**



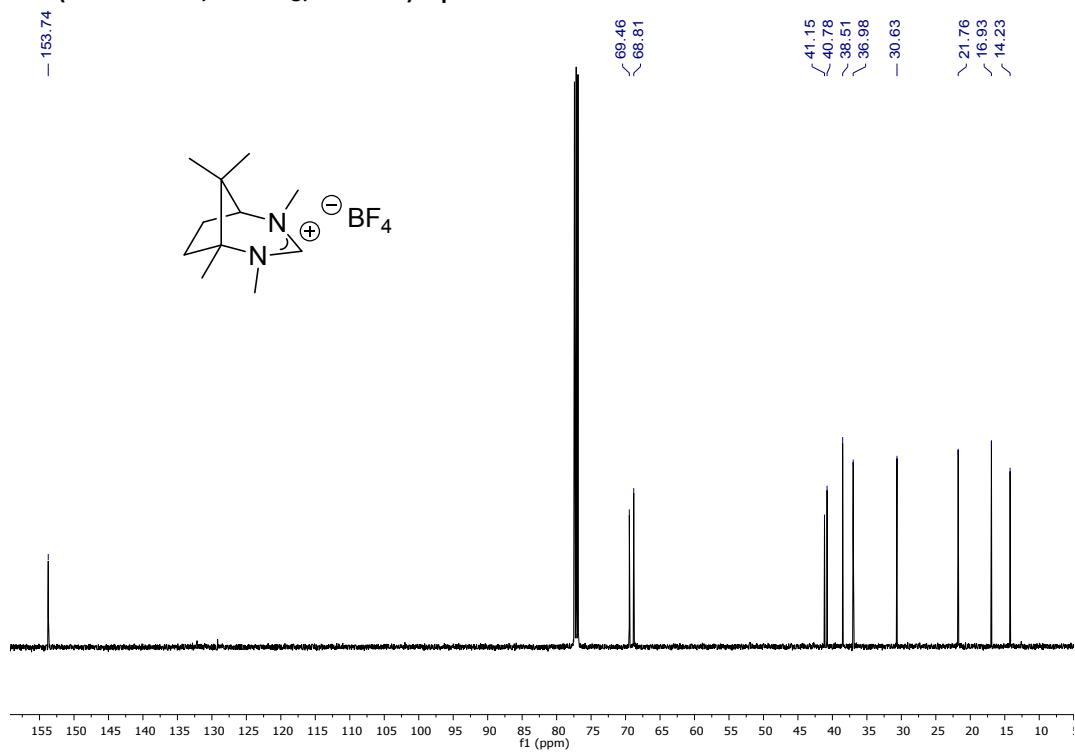
<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298 K) spectrum of **3**



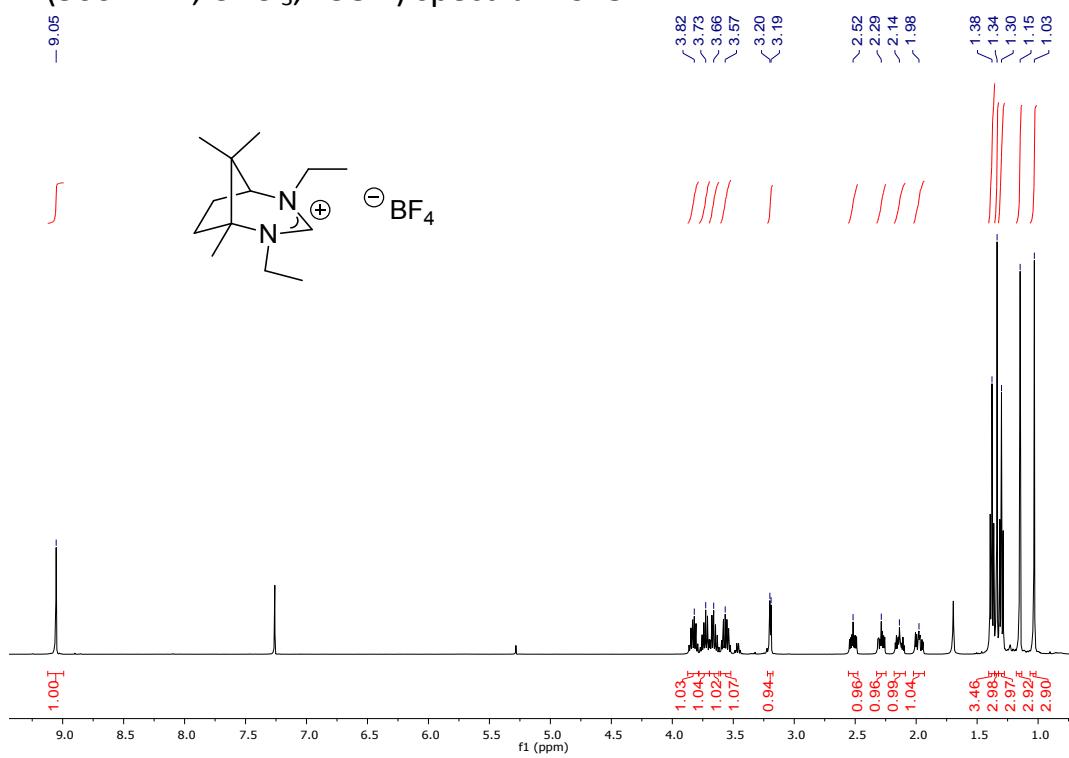
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **4**



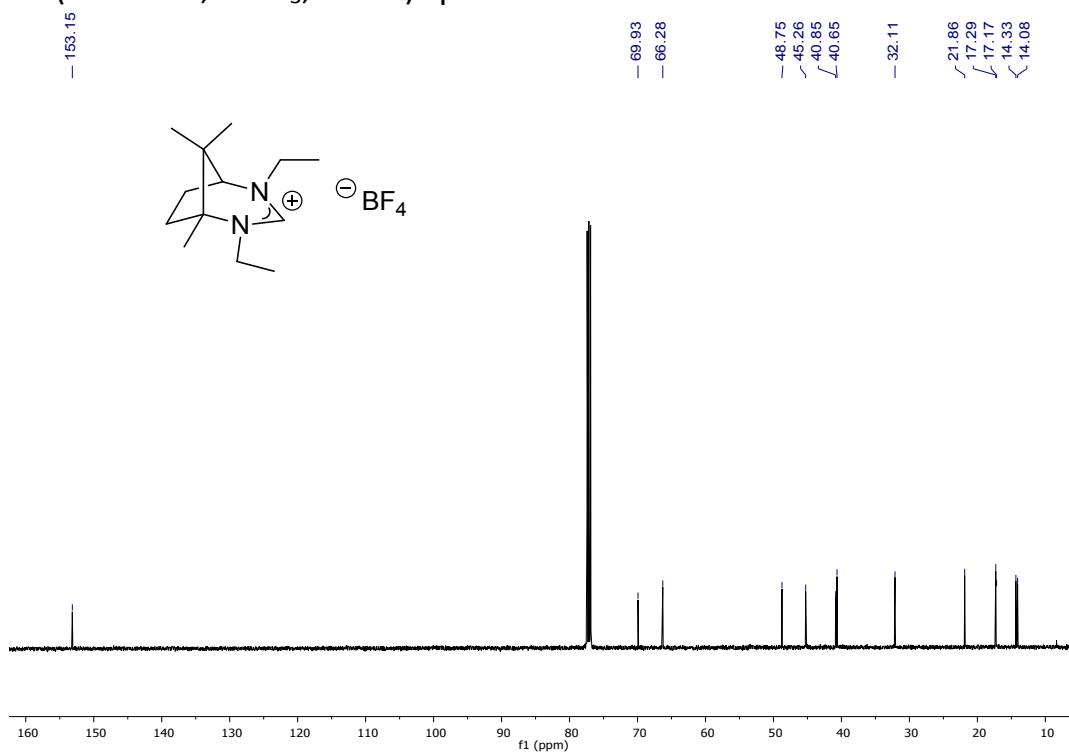
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **4**



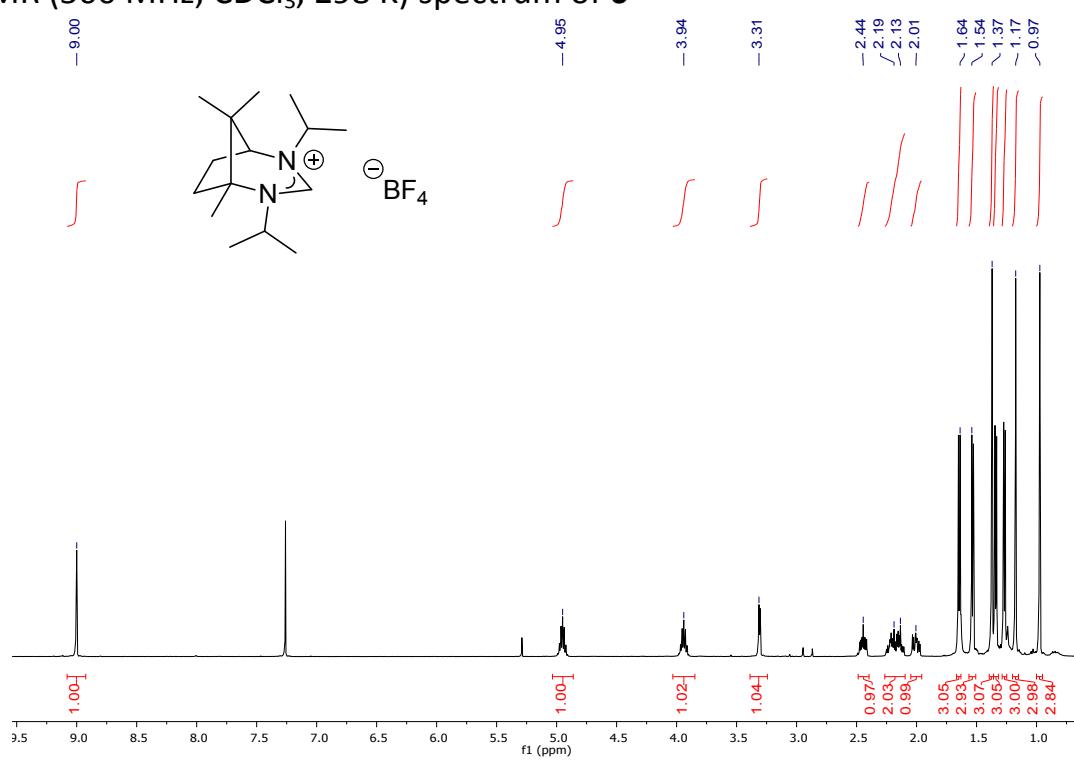
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 5



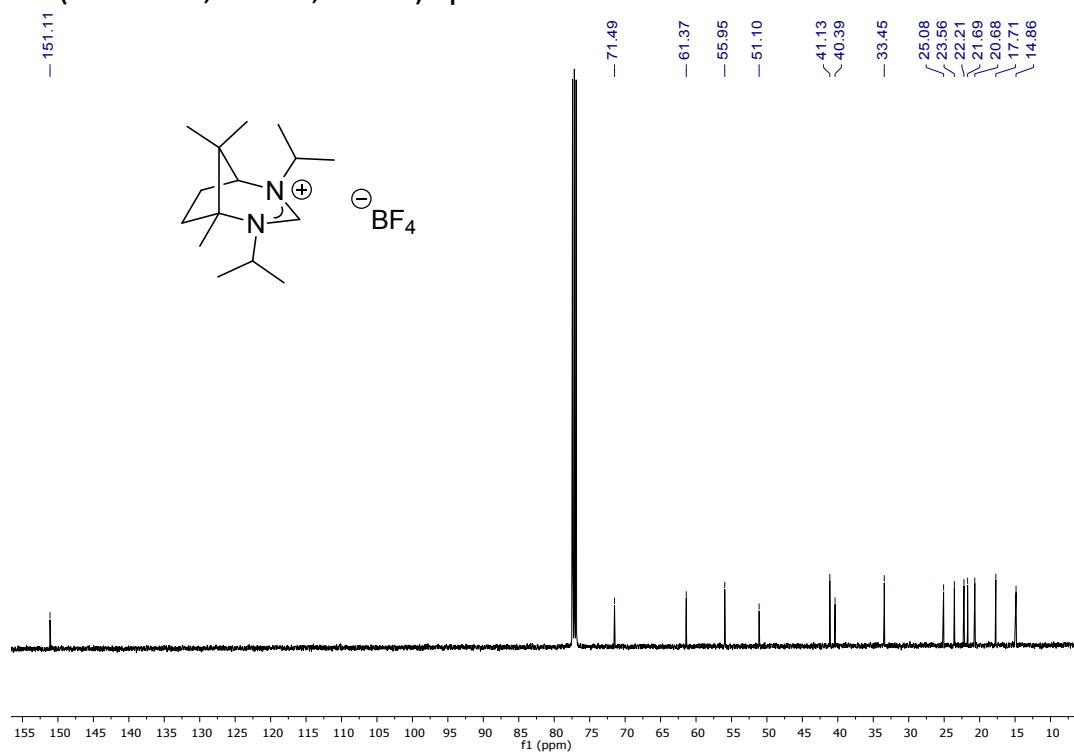
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 5



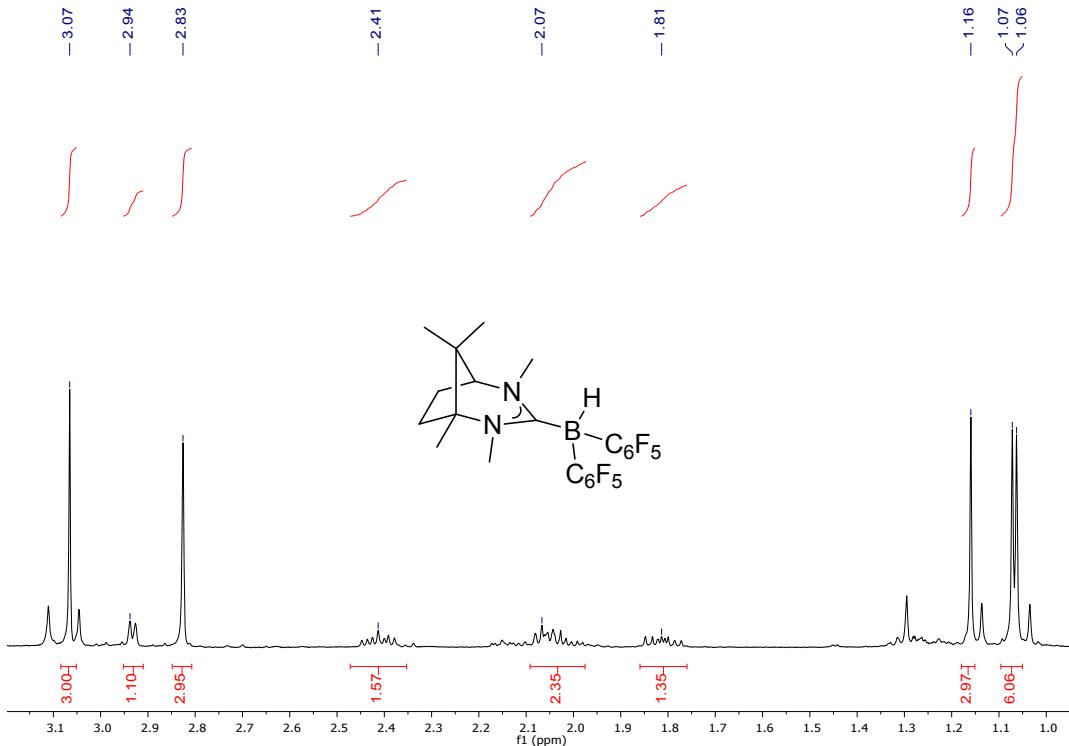
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **6**



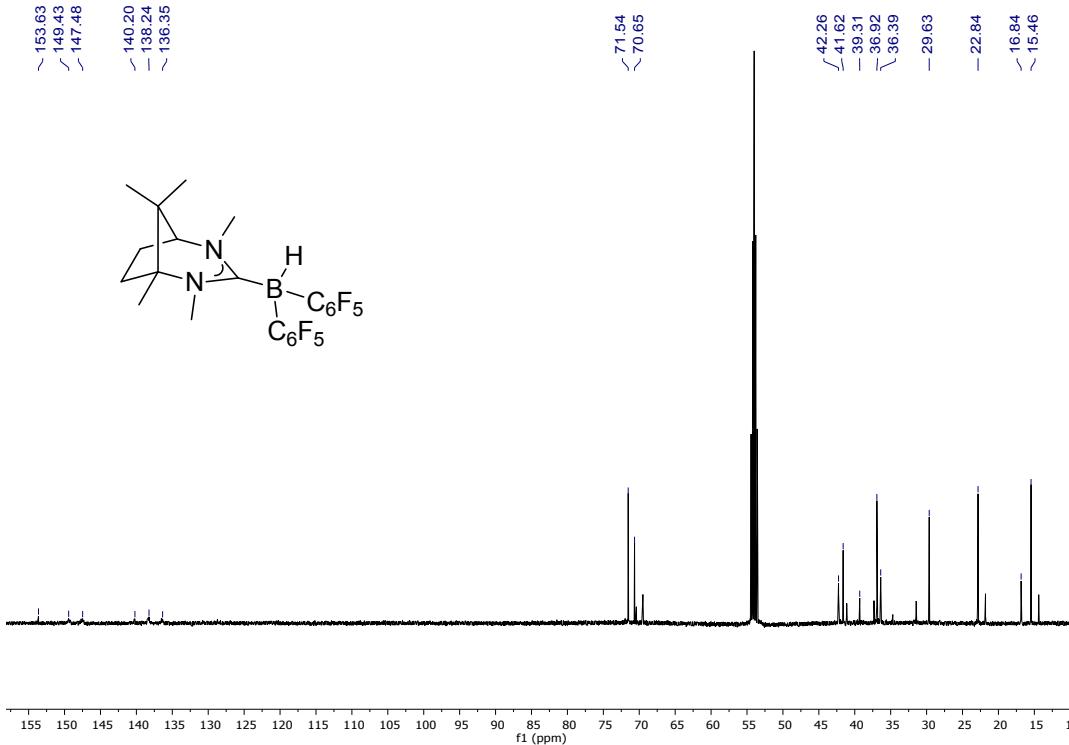
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **6**



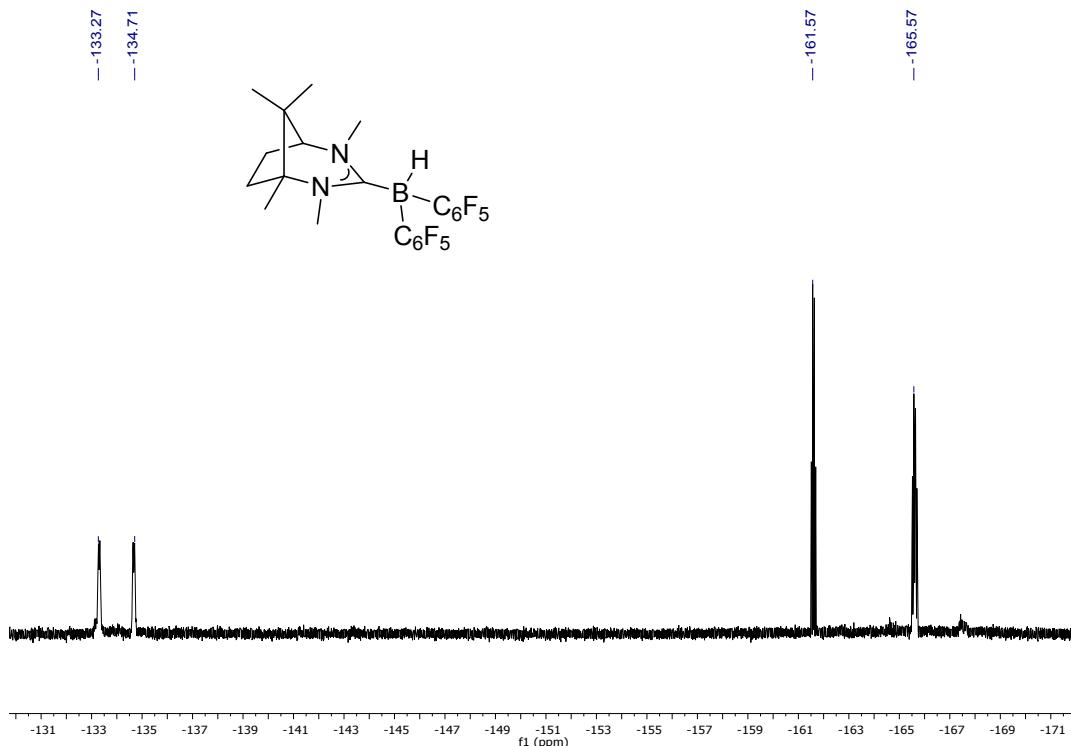
<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **7**



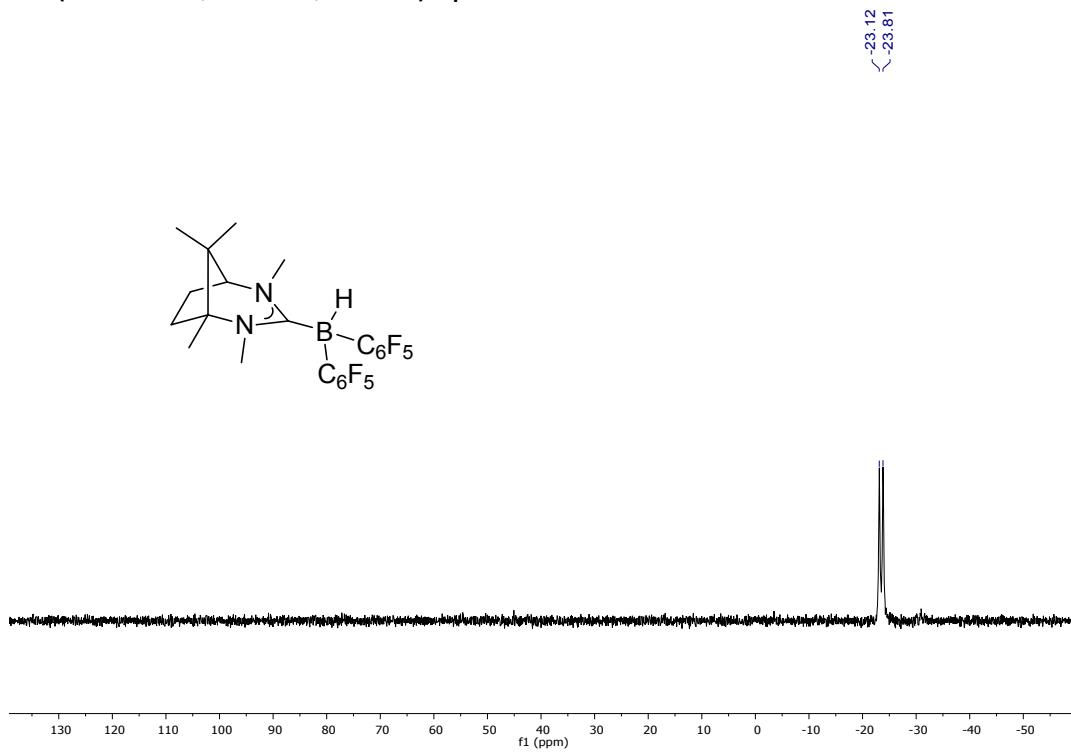
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **7**



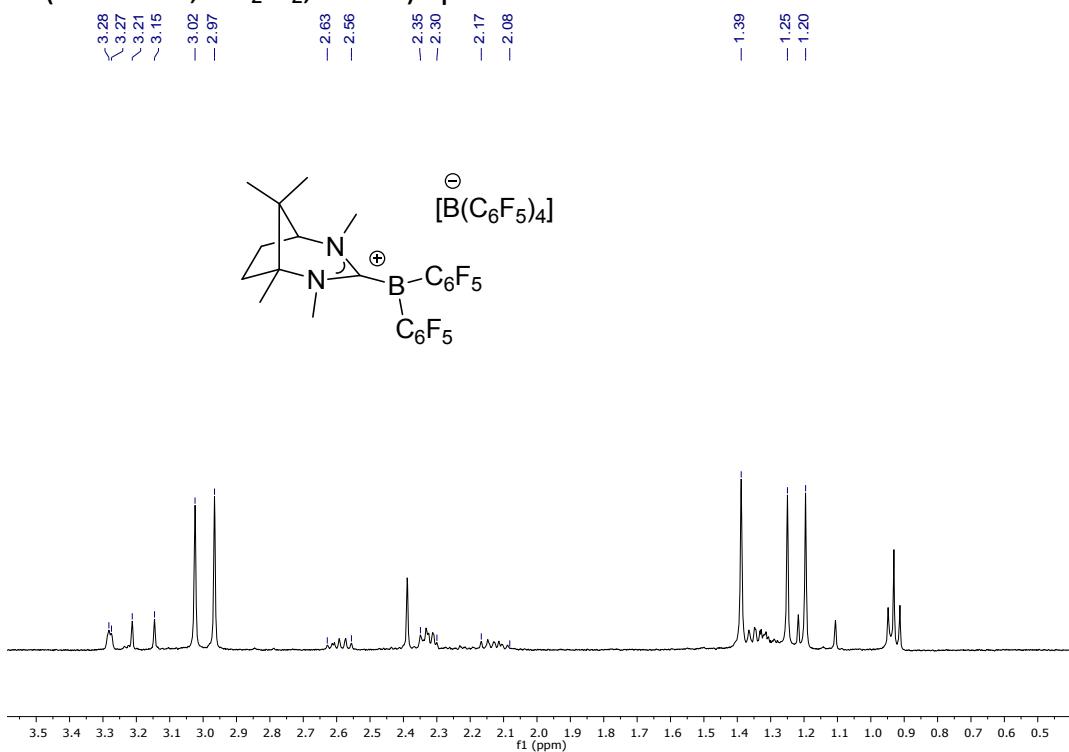
<sup>19</sup>F NMR (377 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **7**



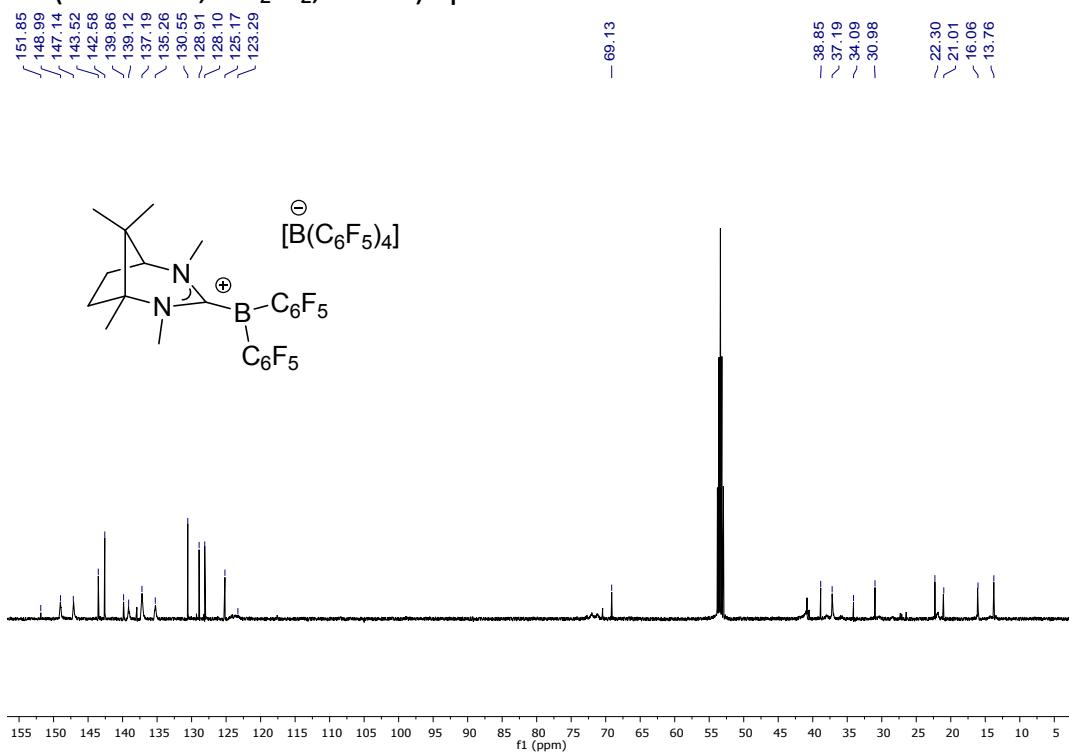
<sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **7**



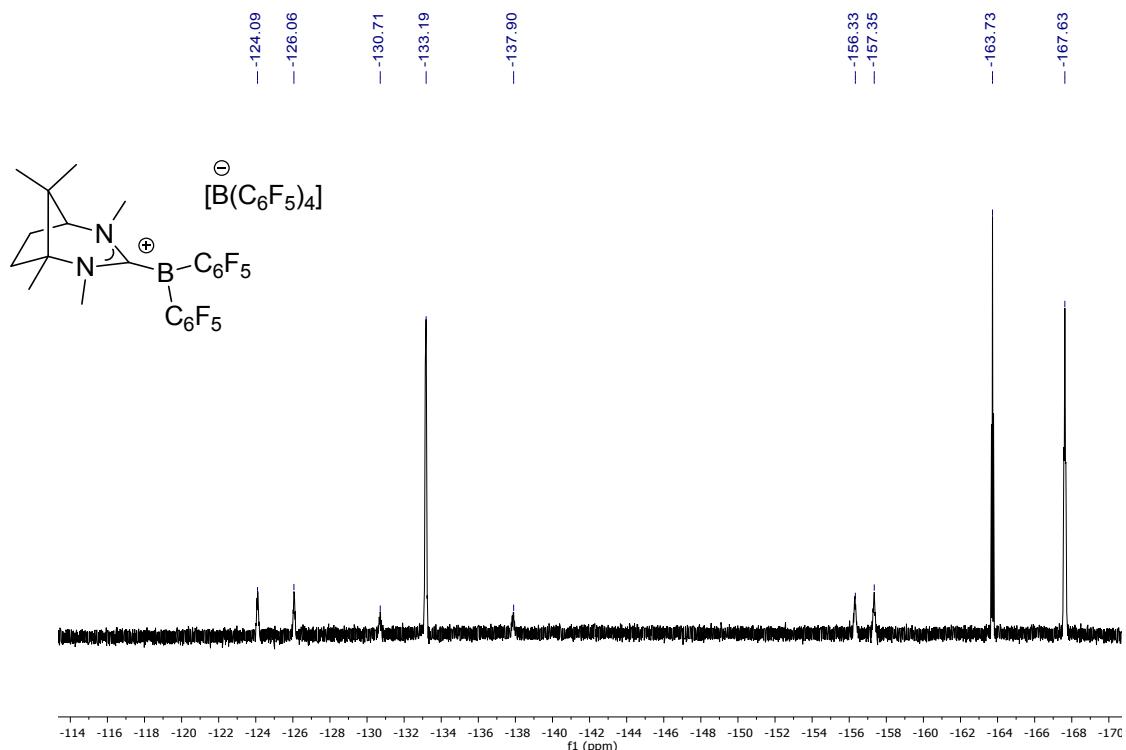
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **8**



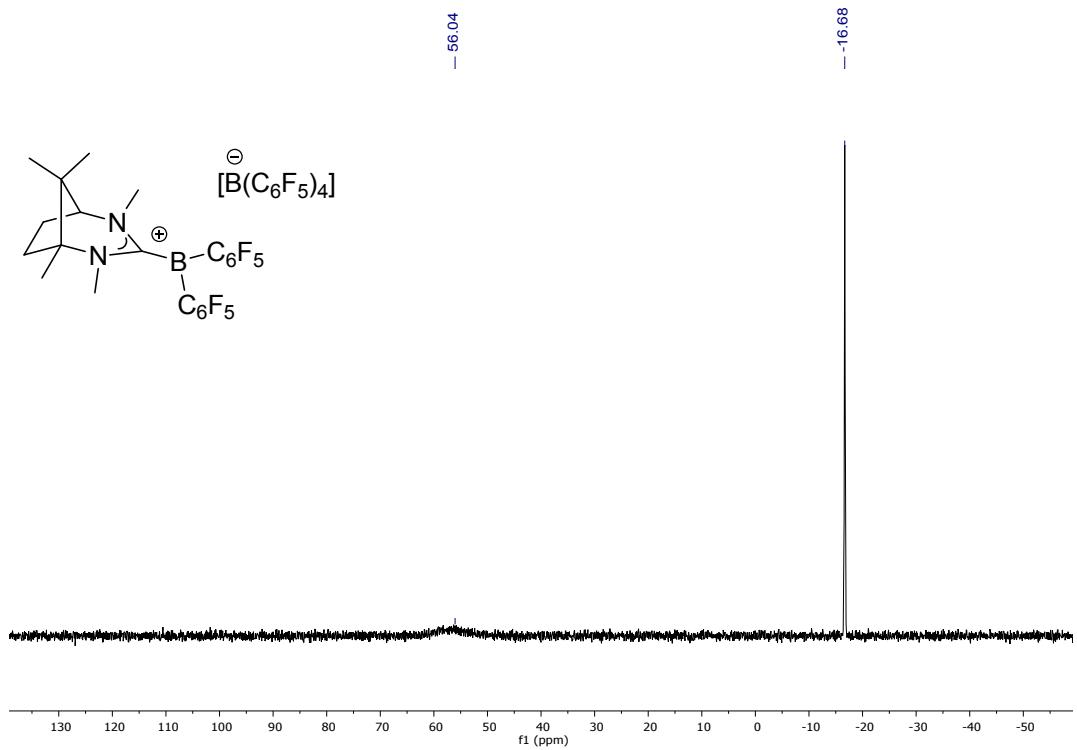
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **8**



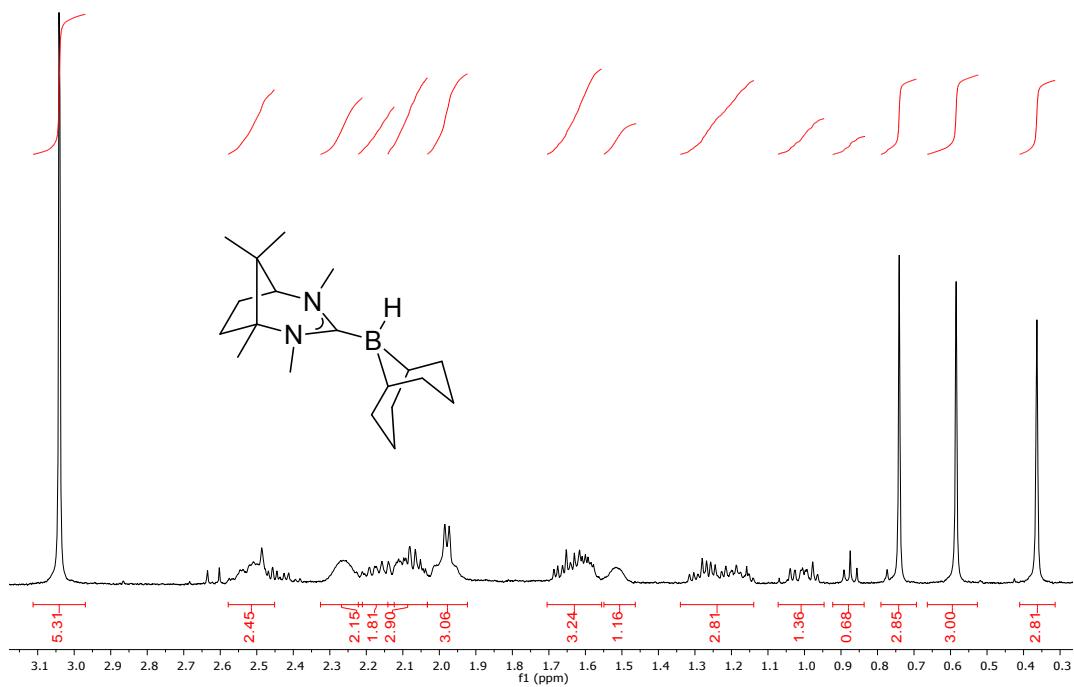
<sup>19</sup>F NMR (377 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **8**



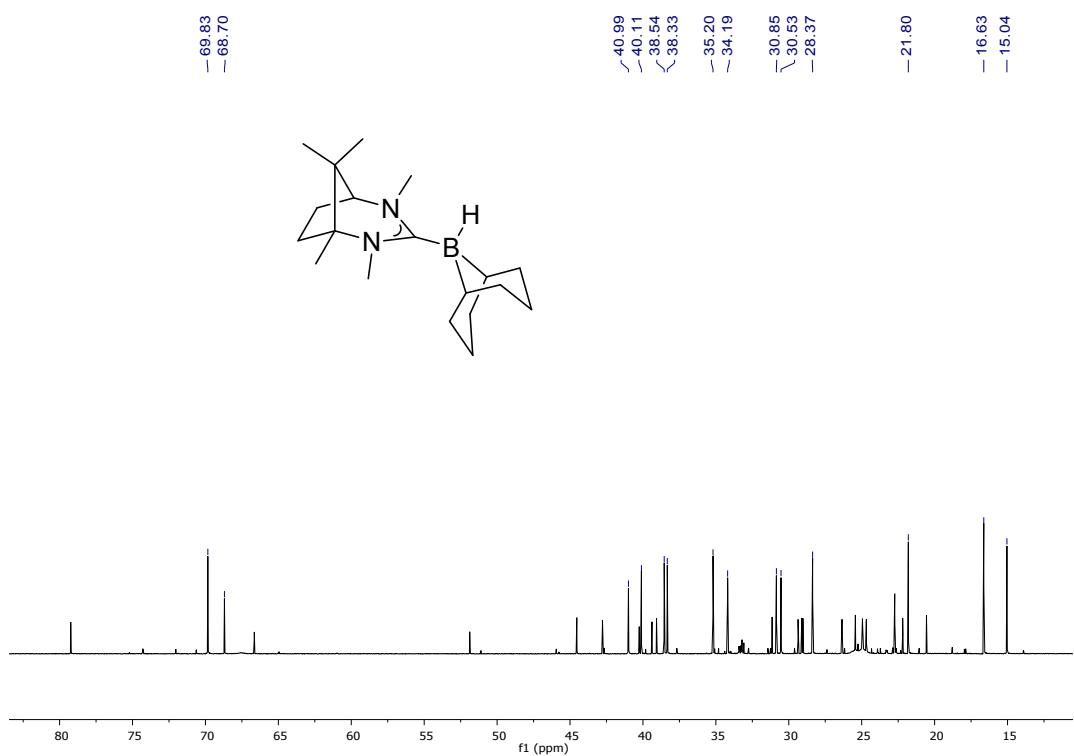
<sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **8**



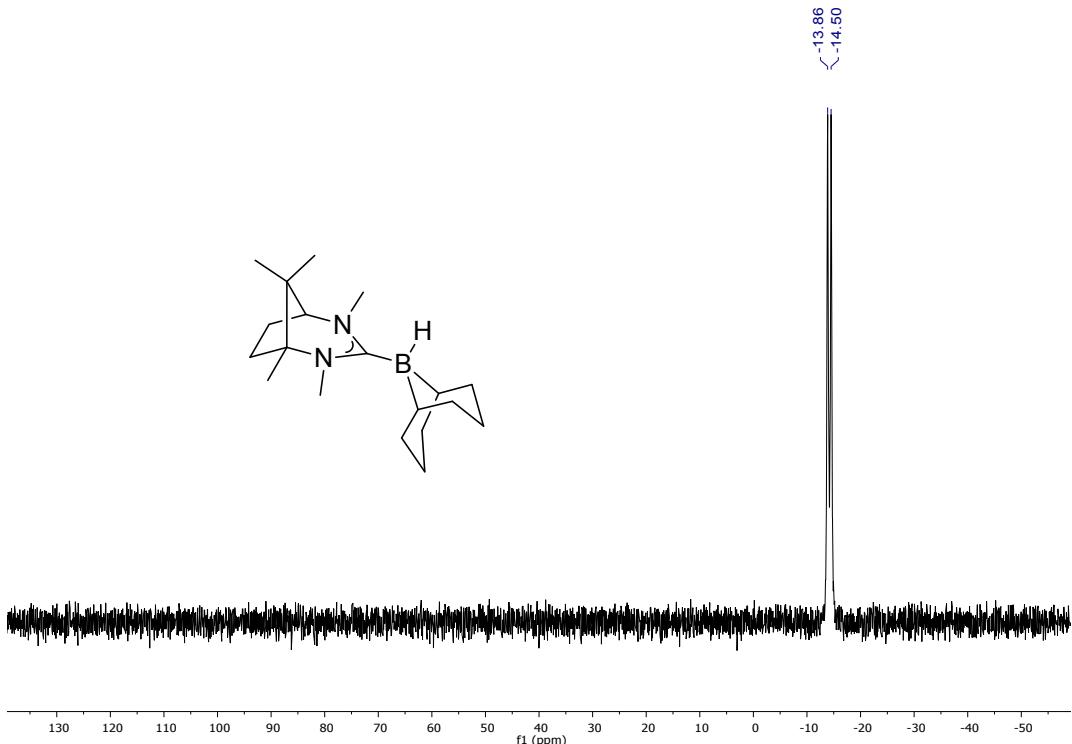
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **9**



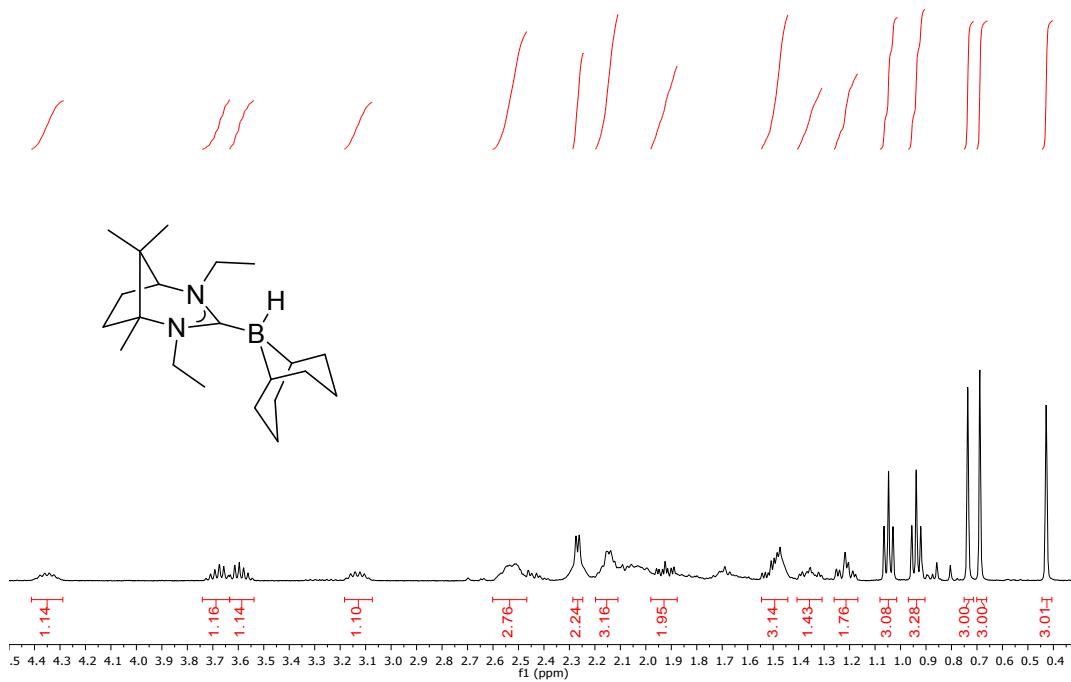
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **9**



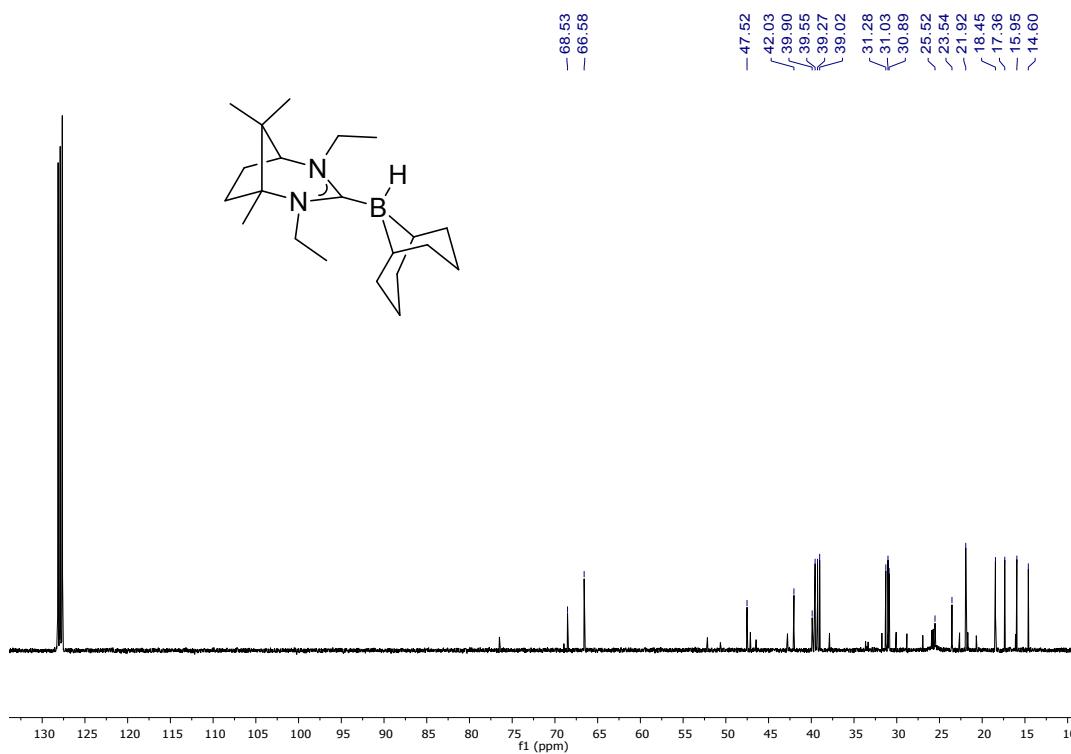
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **9**



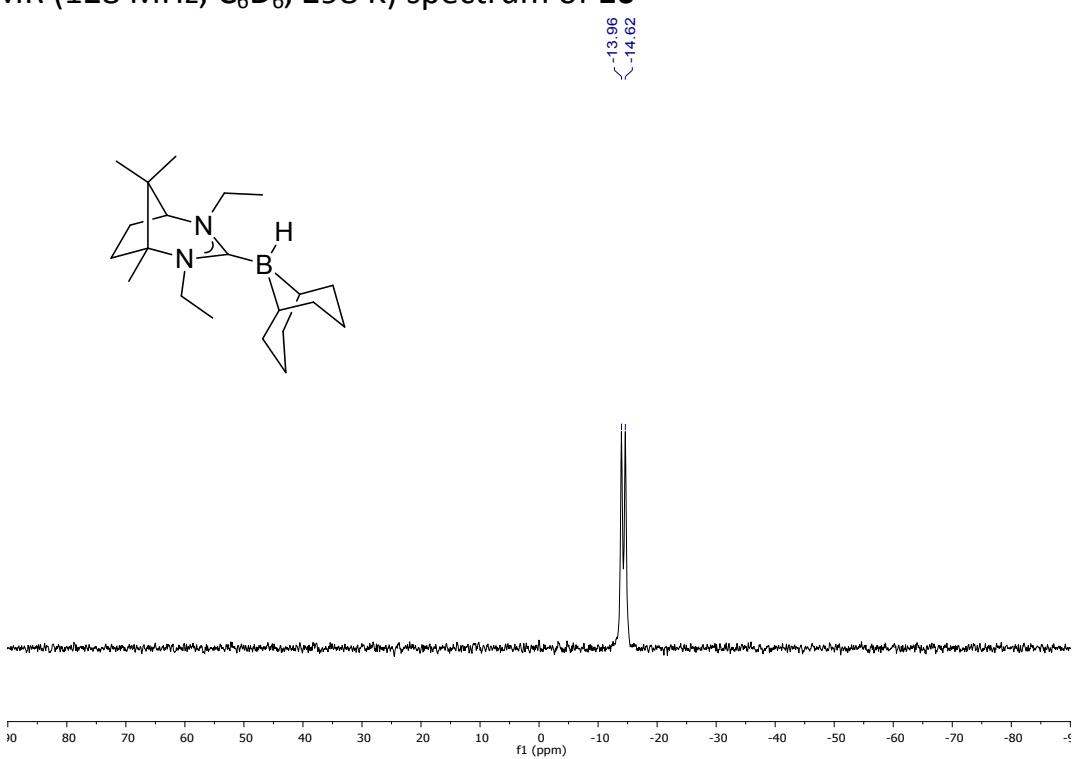
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **10**



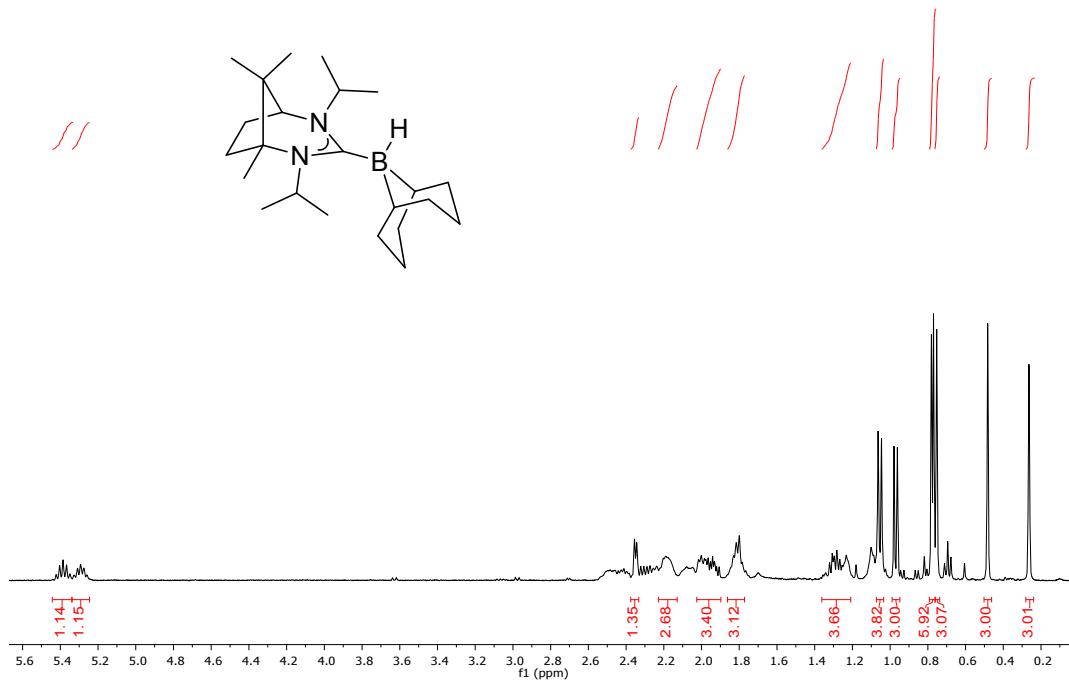
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **10**



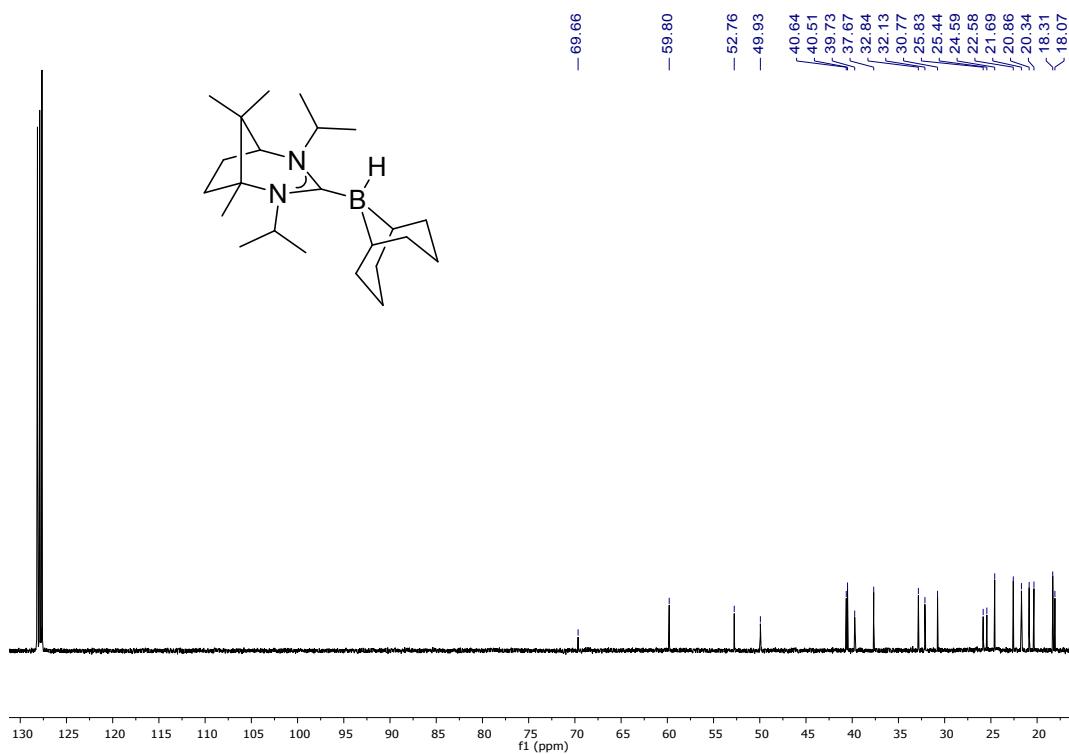
<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **10**



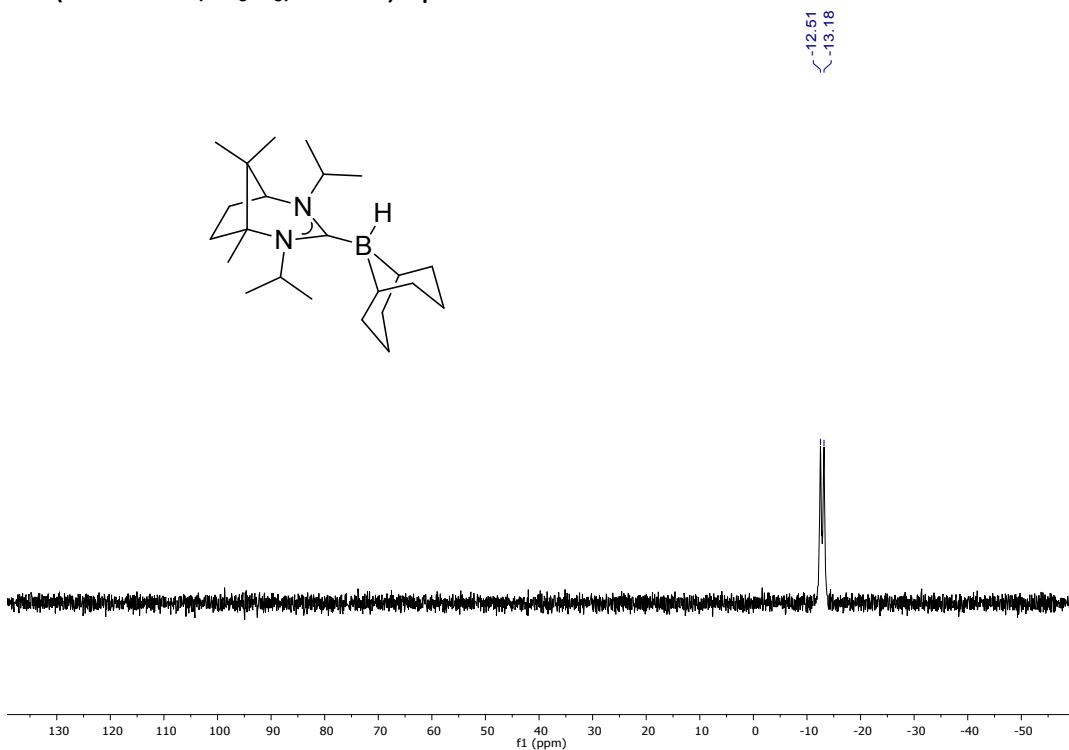
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **11**



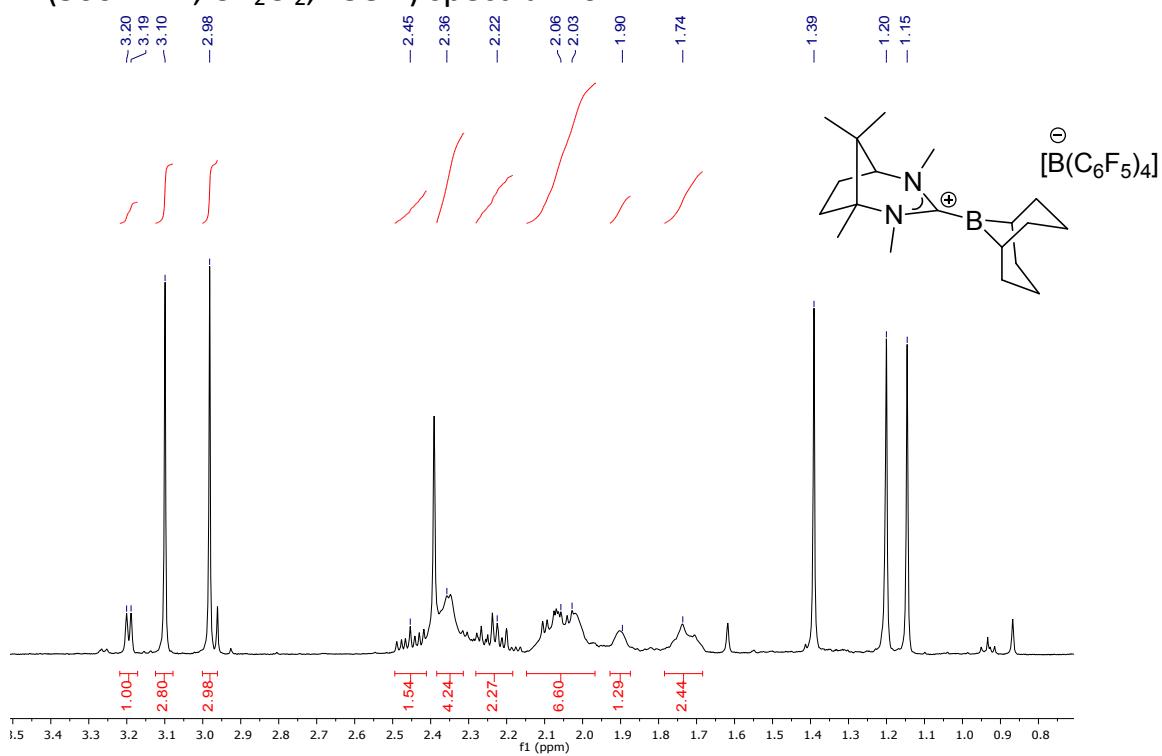
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **11**



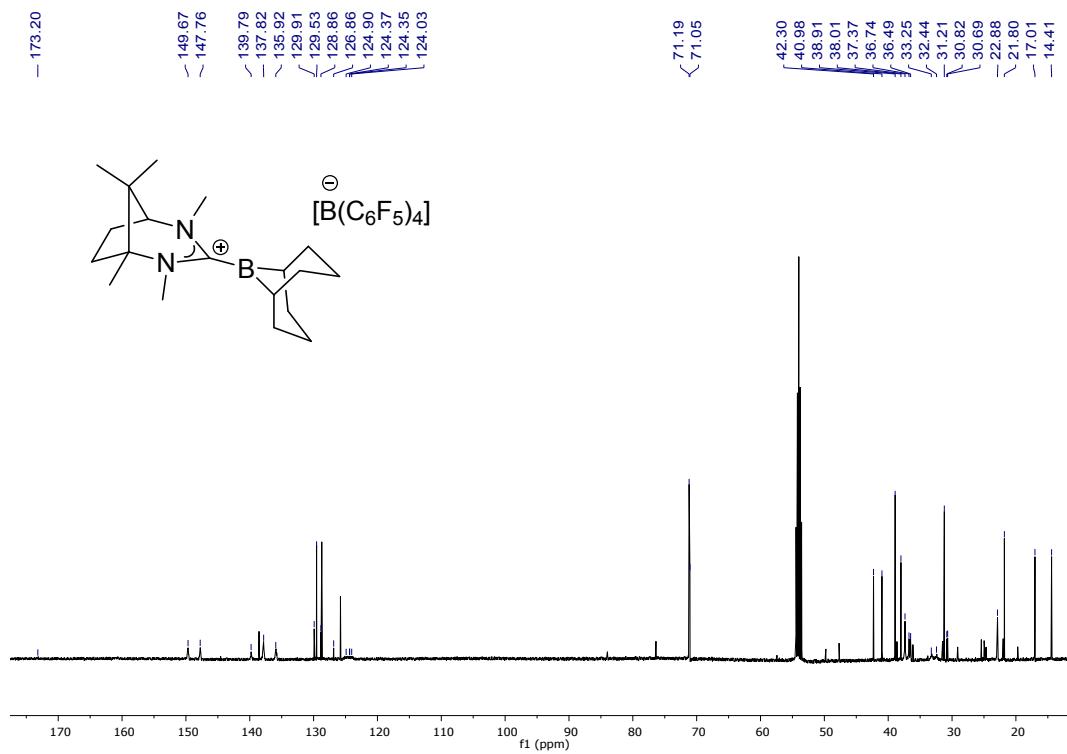
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **11**



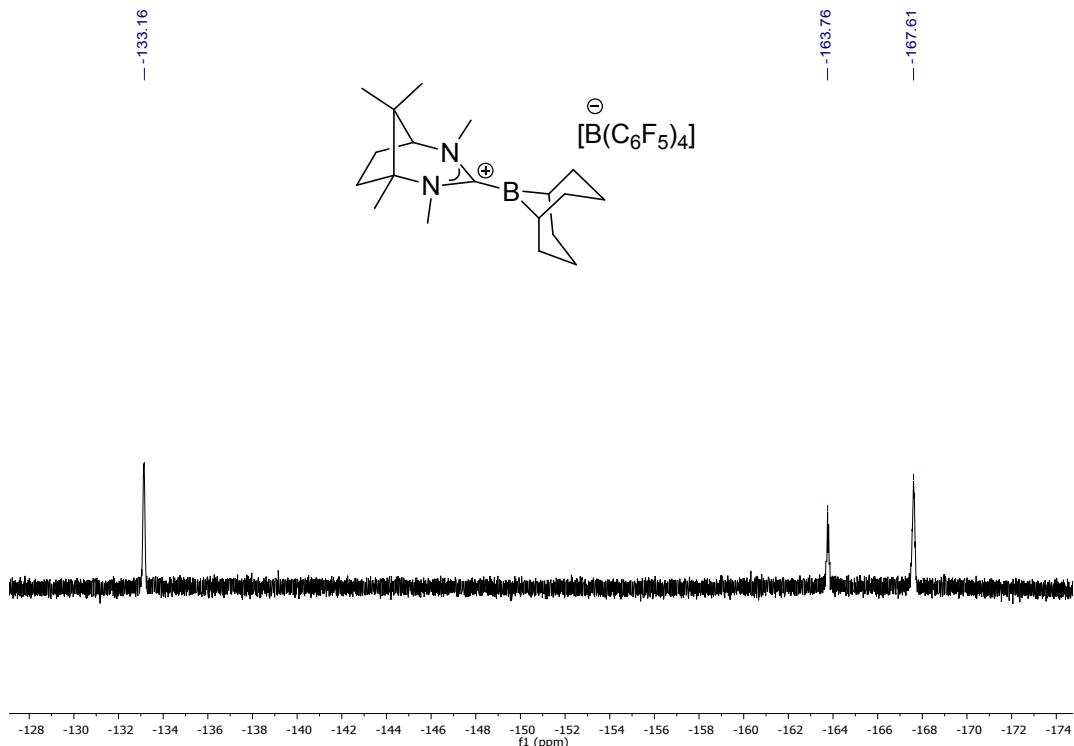
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **12**



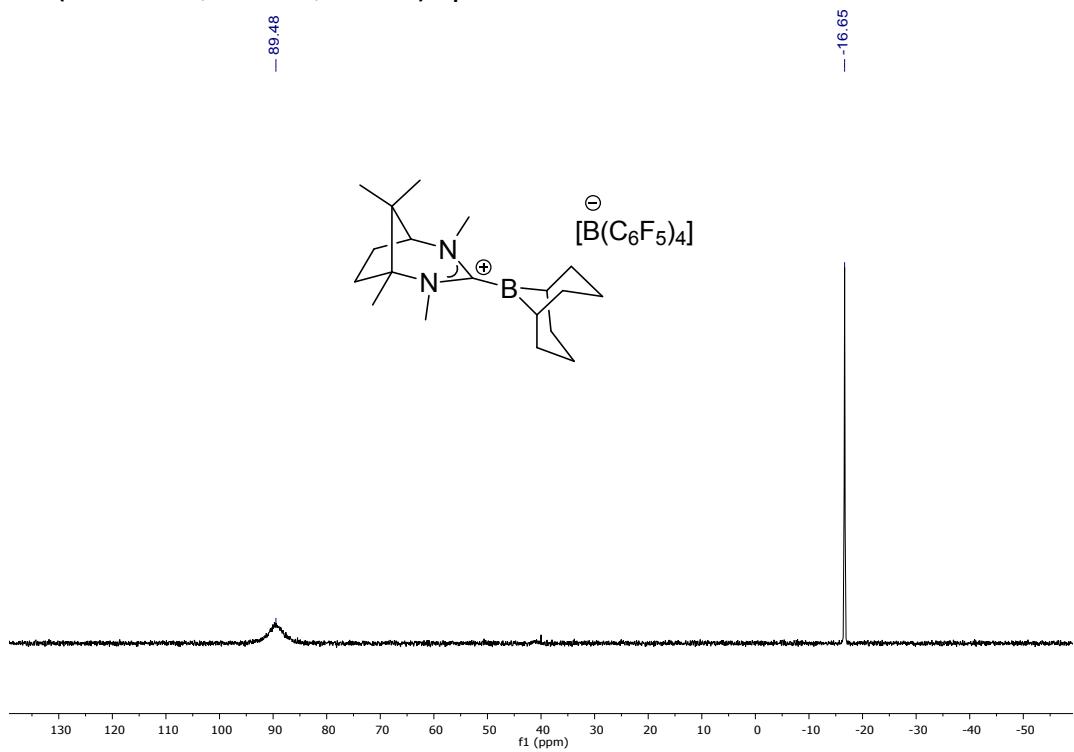
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **12**



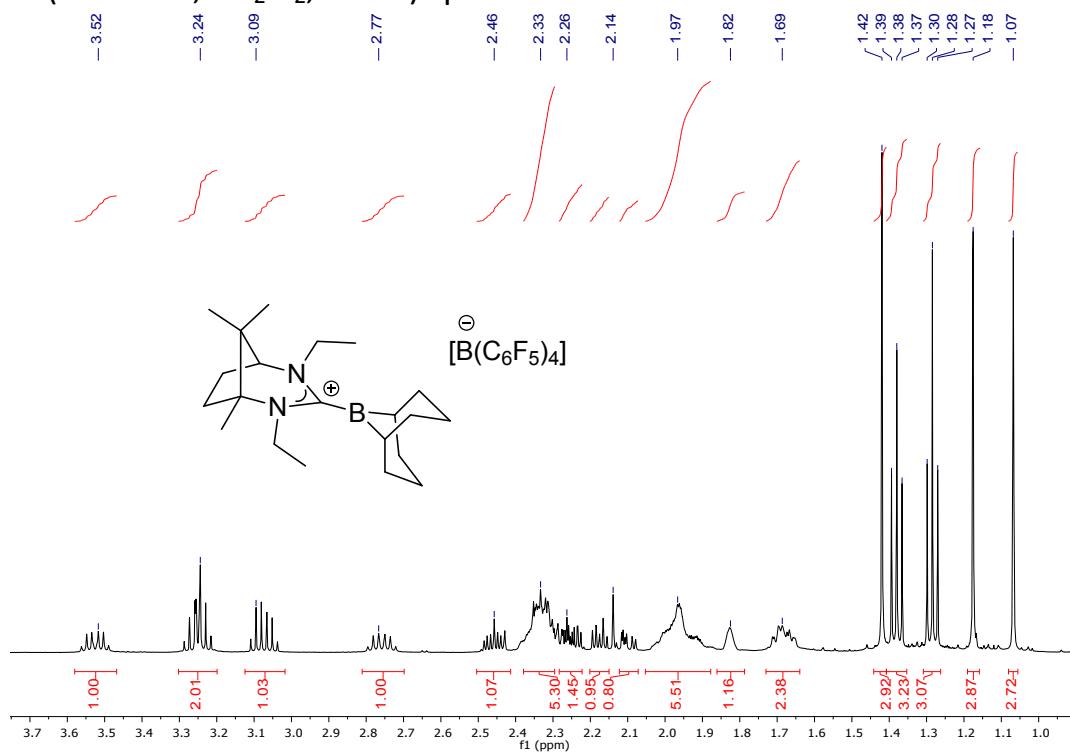
<sup>19</sup>F NMR (377 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **12**



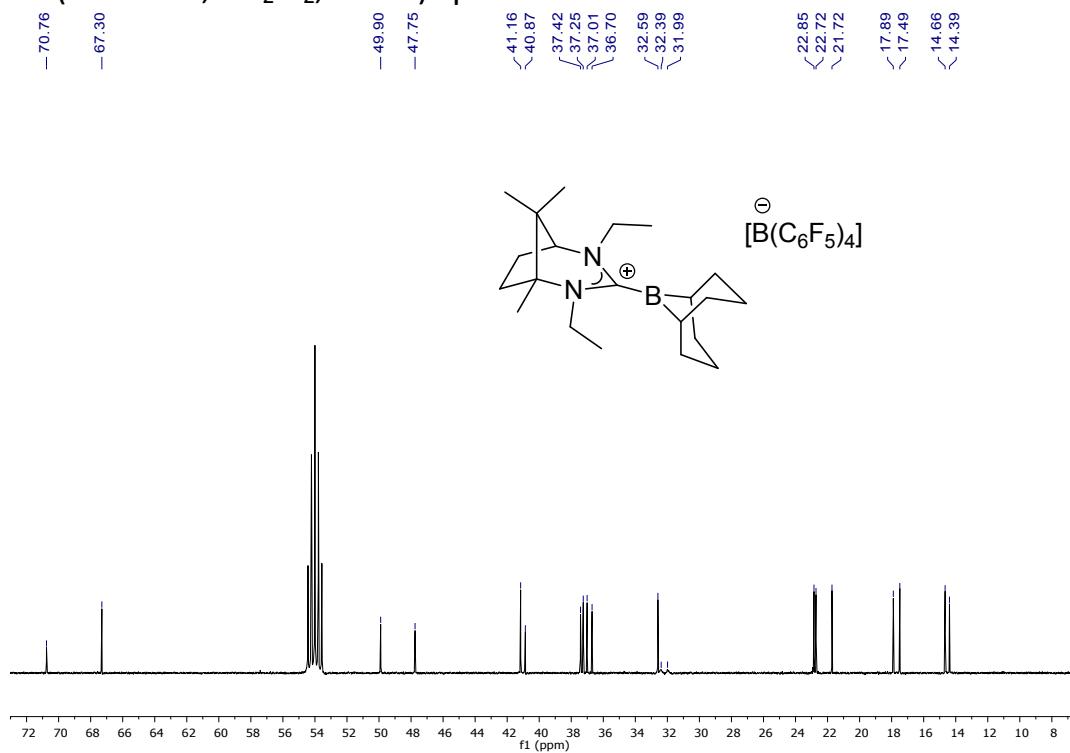
<sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **12**



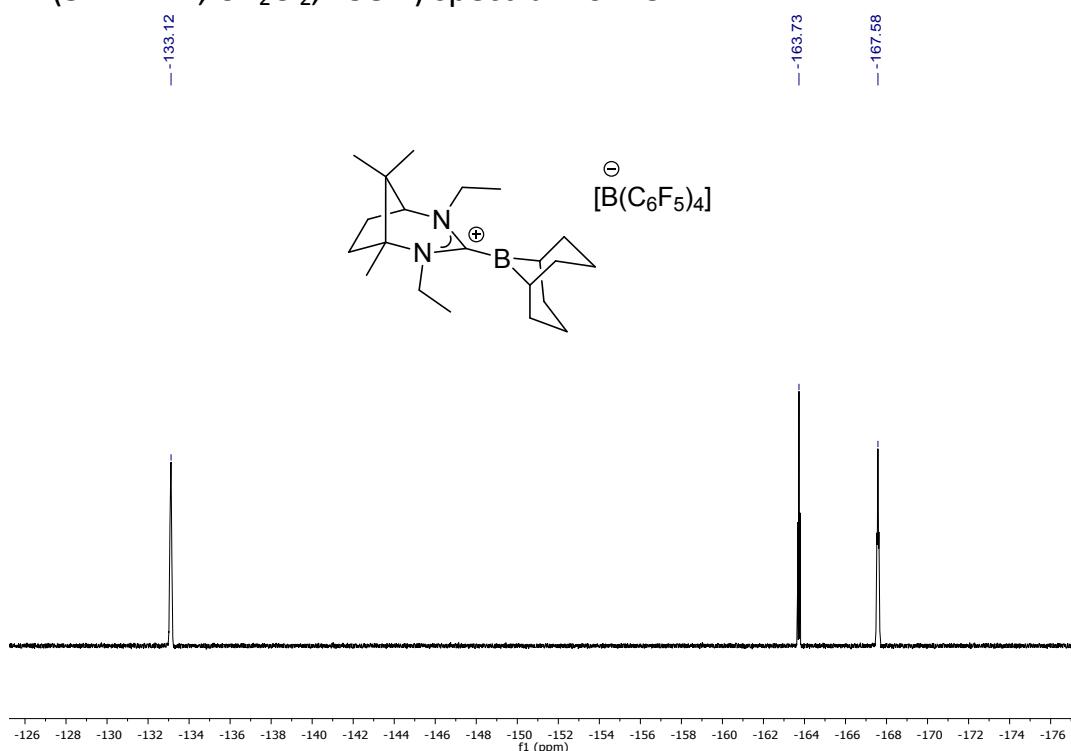
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **13**



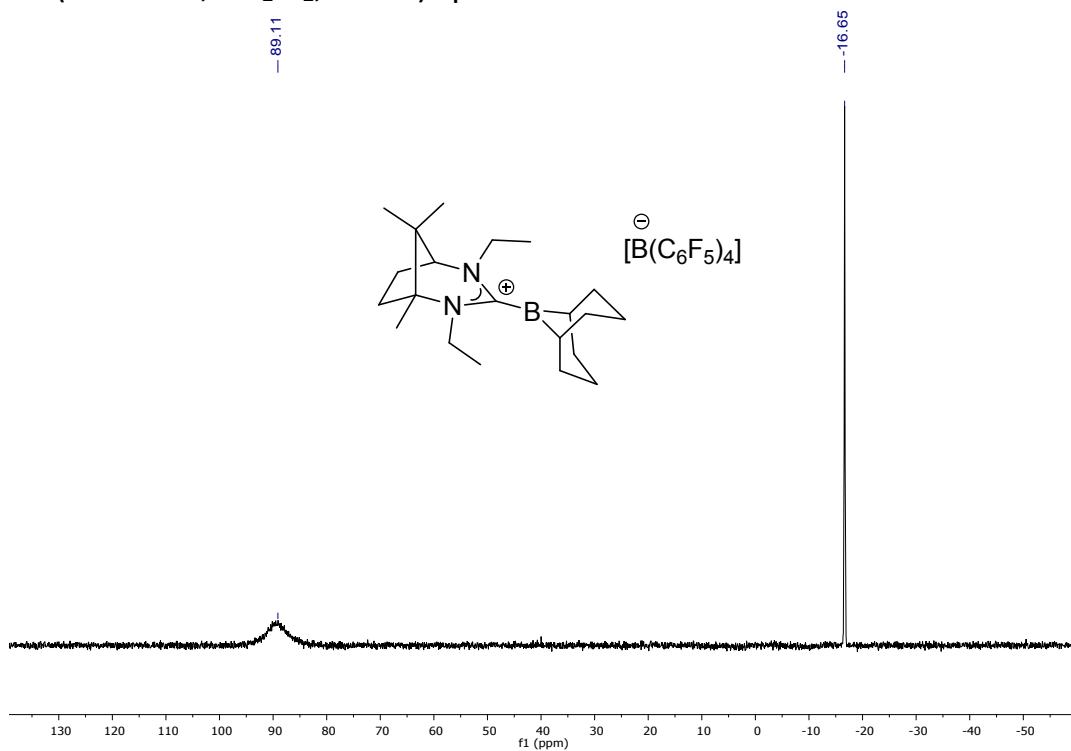
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **13**



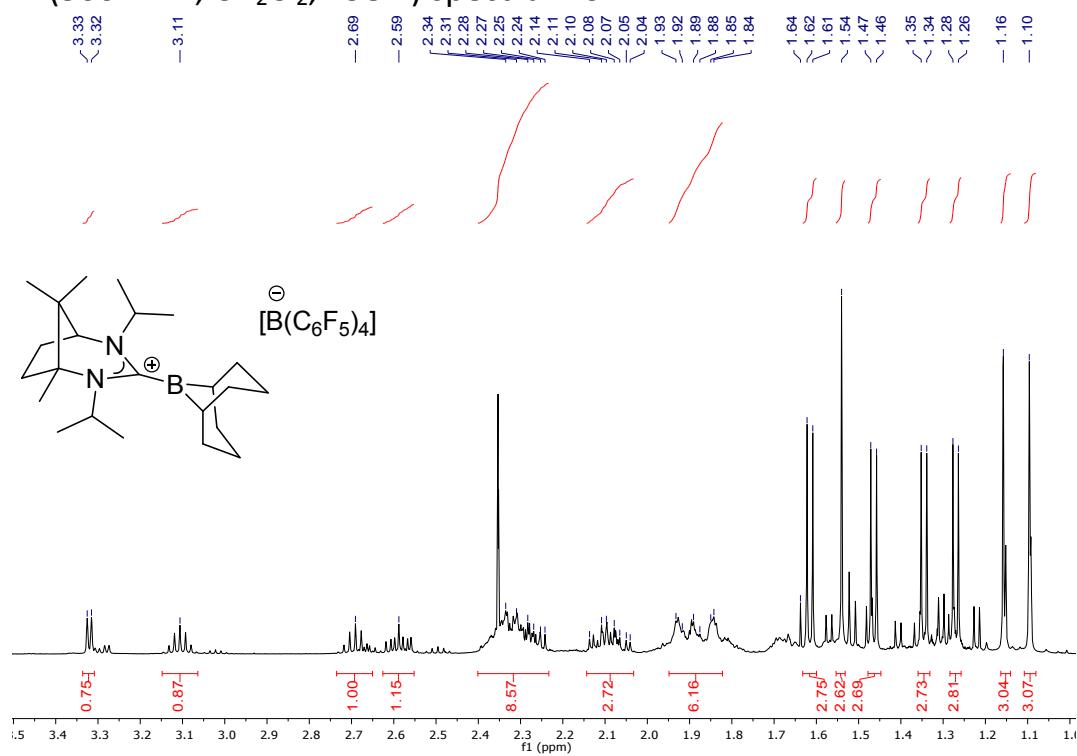
<sup>19</sup>F NMR (377 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **13**



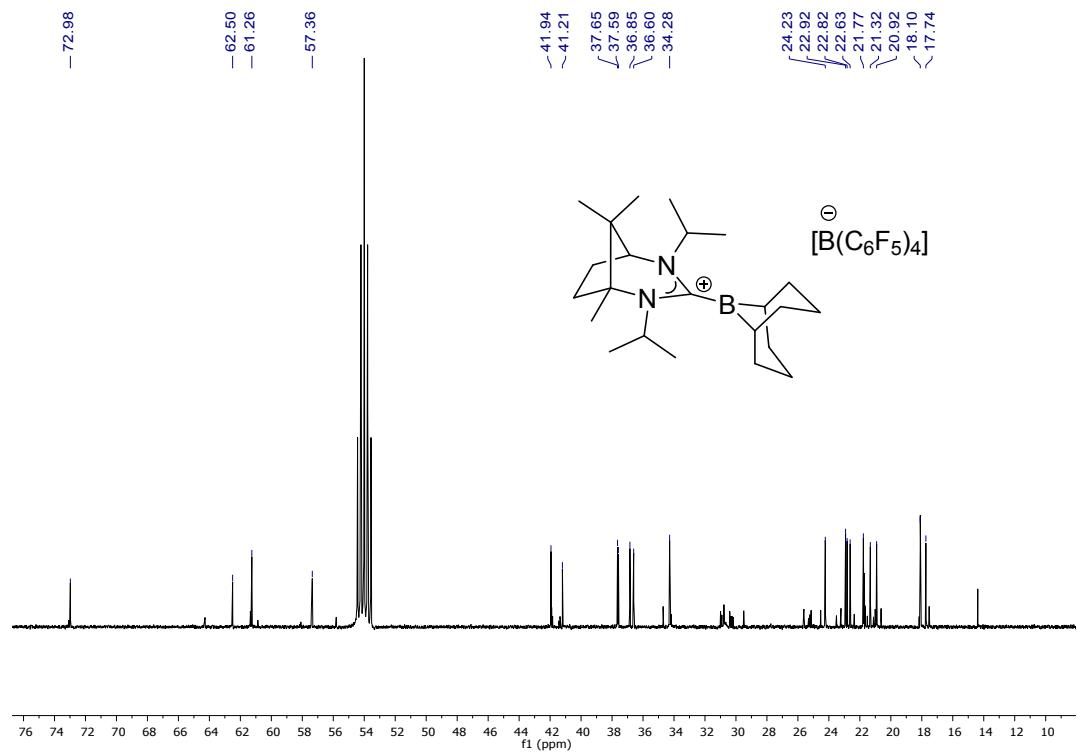
<sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **13**



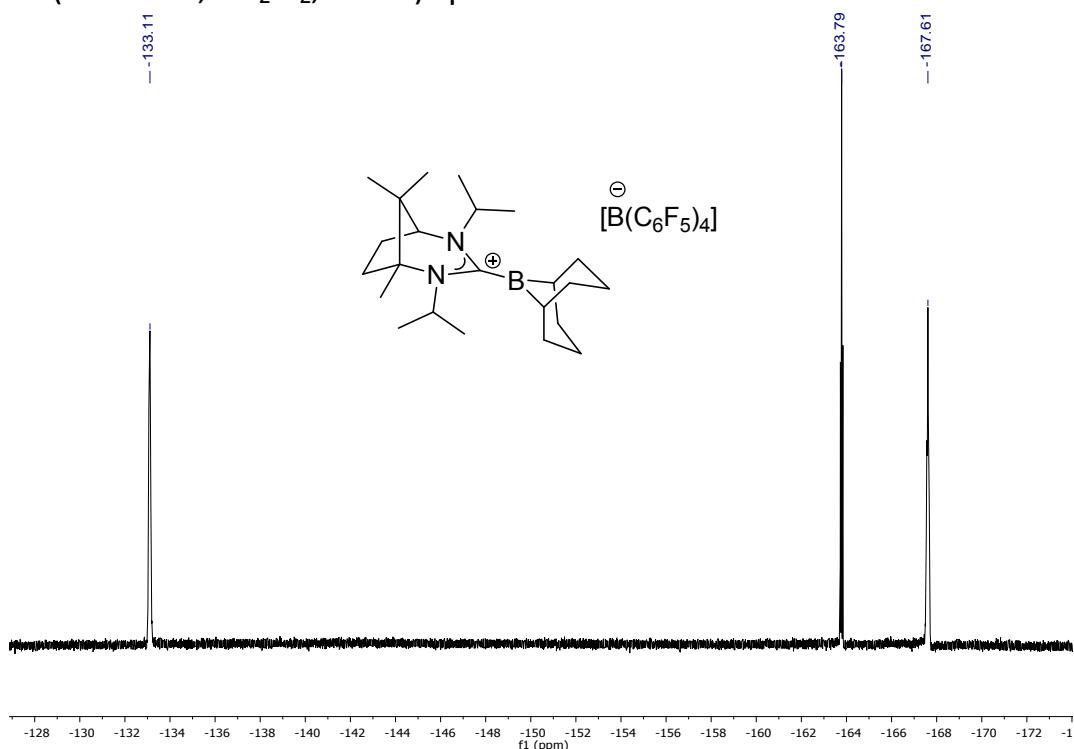
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **14**



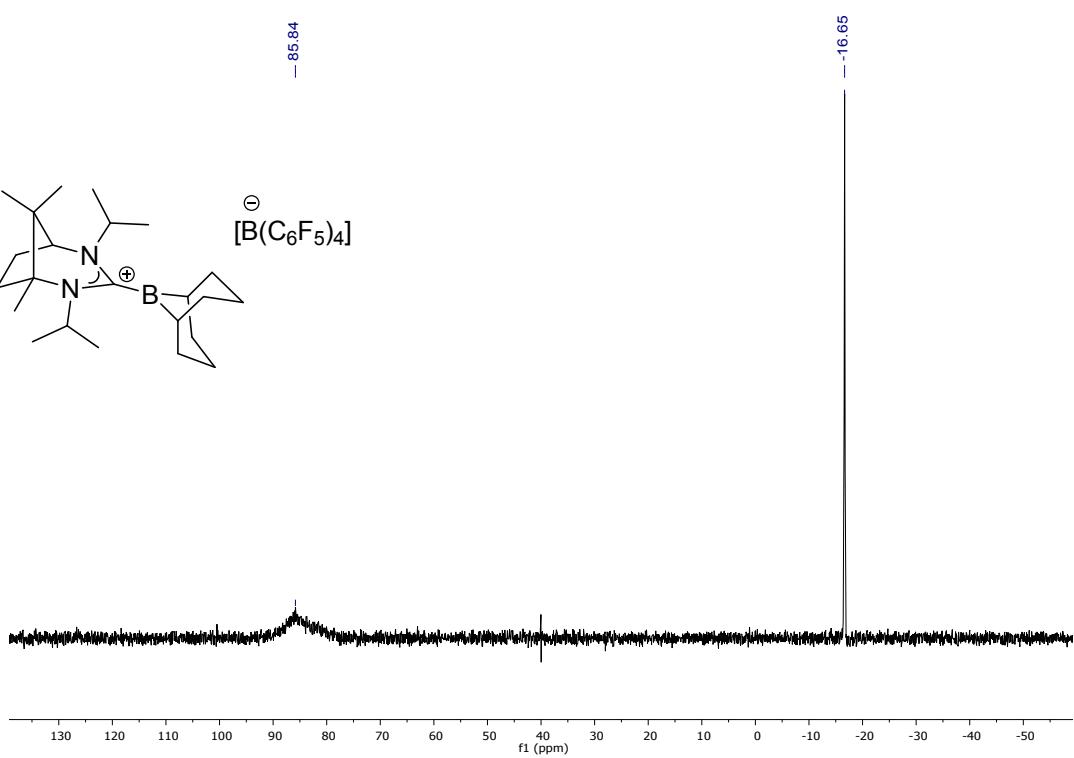
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **14**



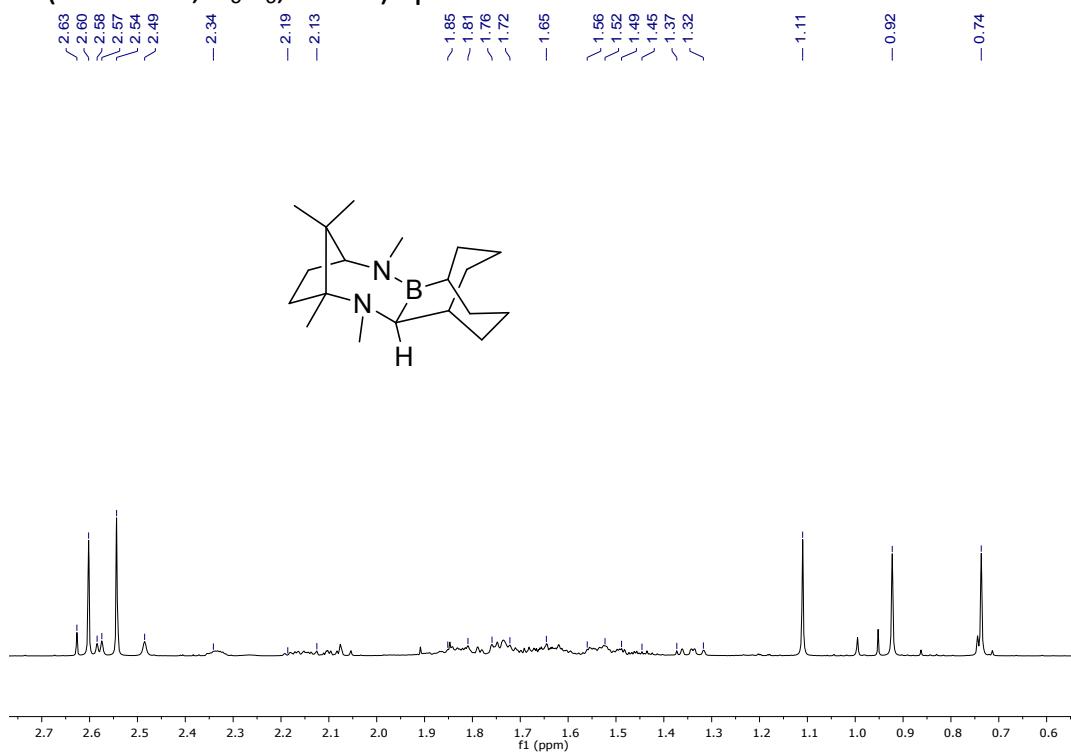
$^{19}\text{F}$  NMR (377 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **14**



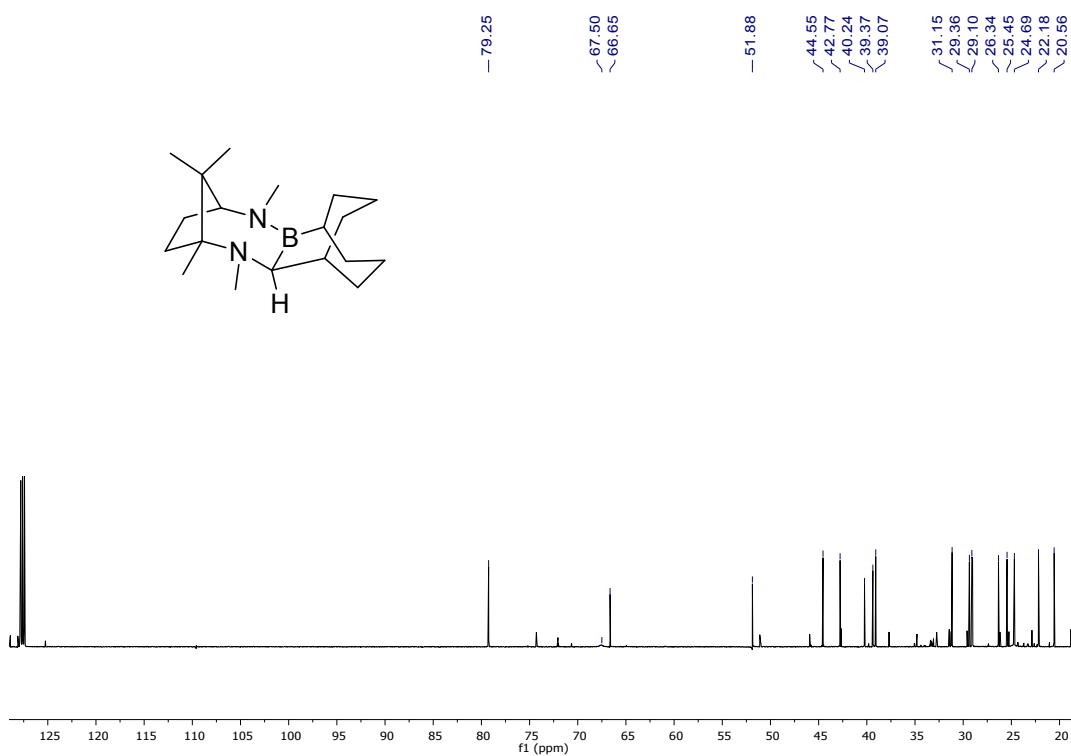
$^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **14**



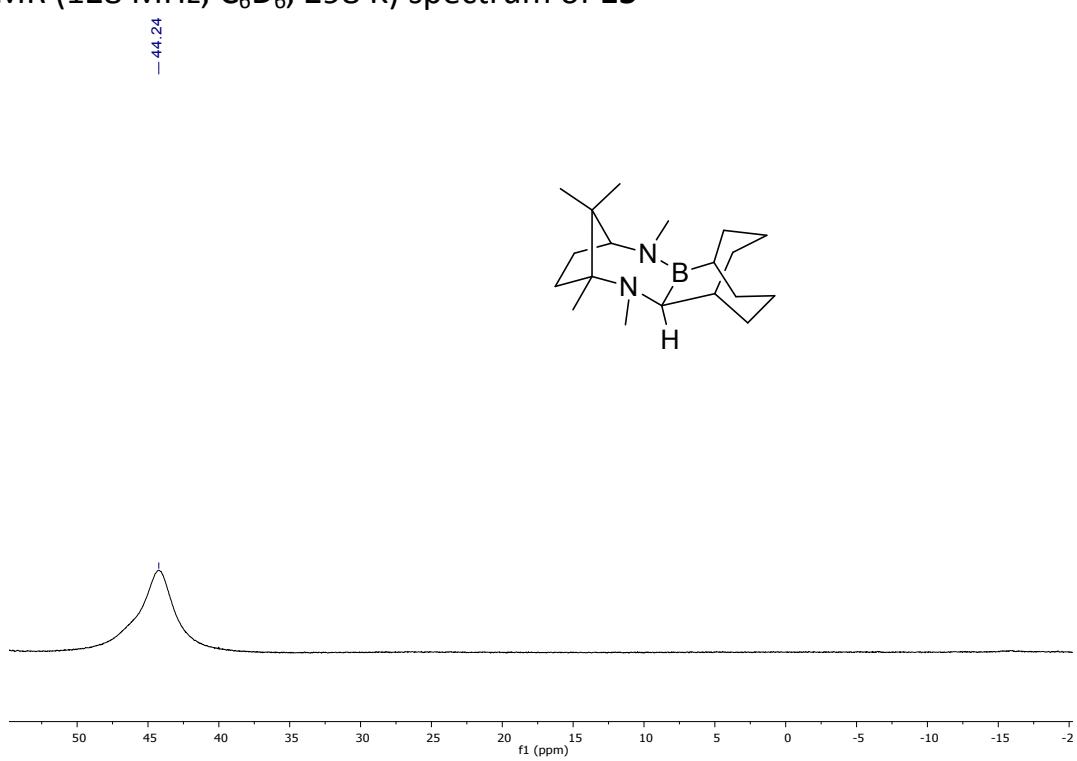
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **15**



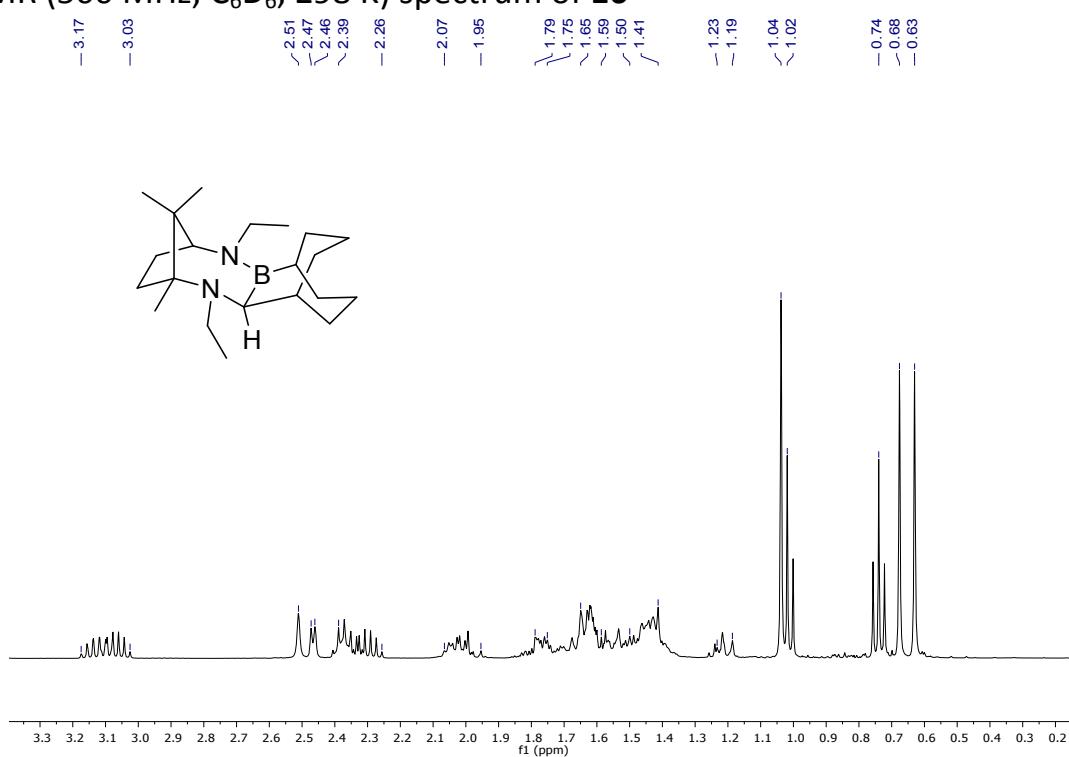
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **15**



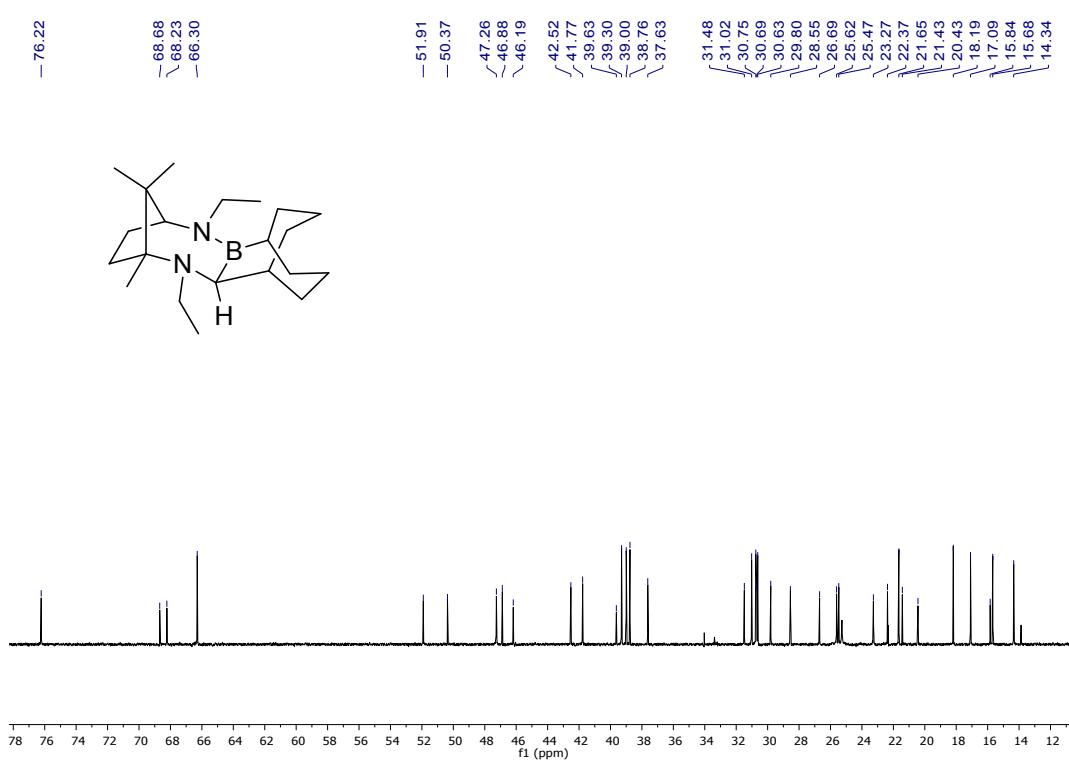
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **15**



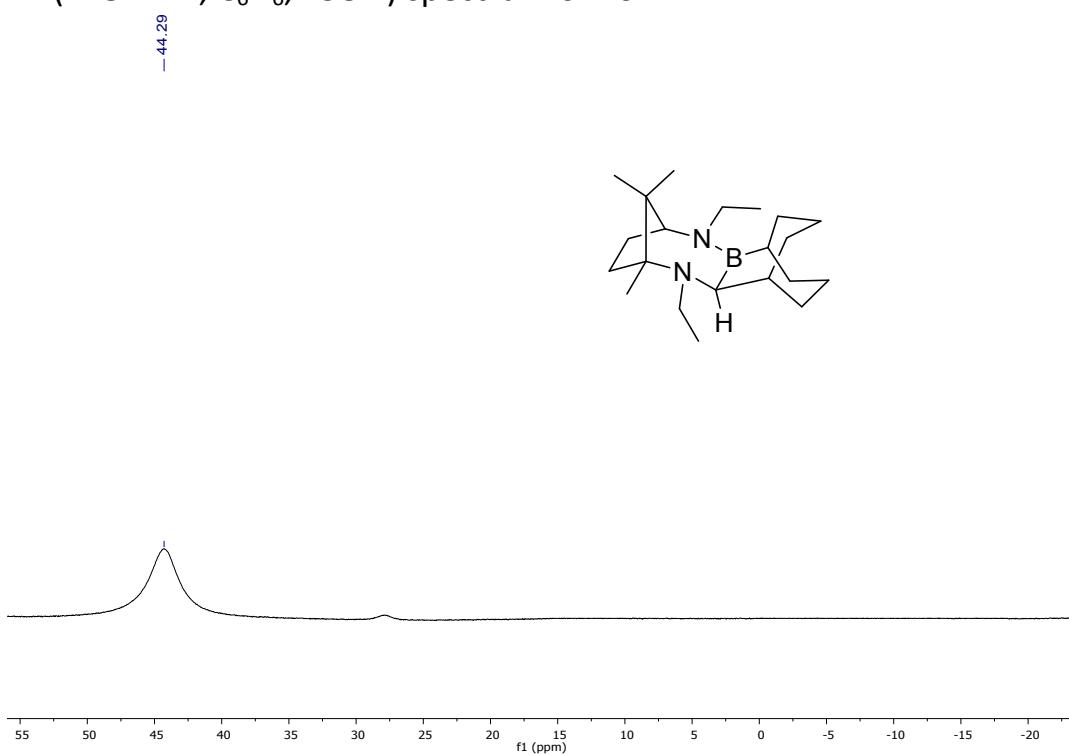
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **16**



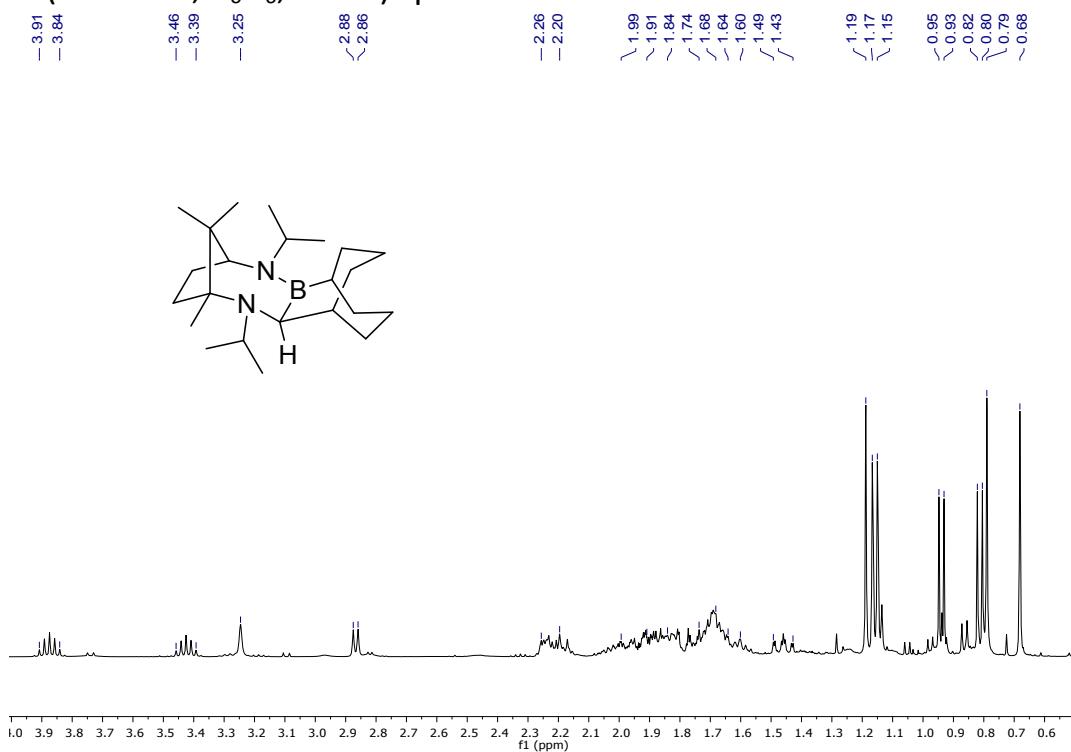
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **16**



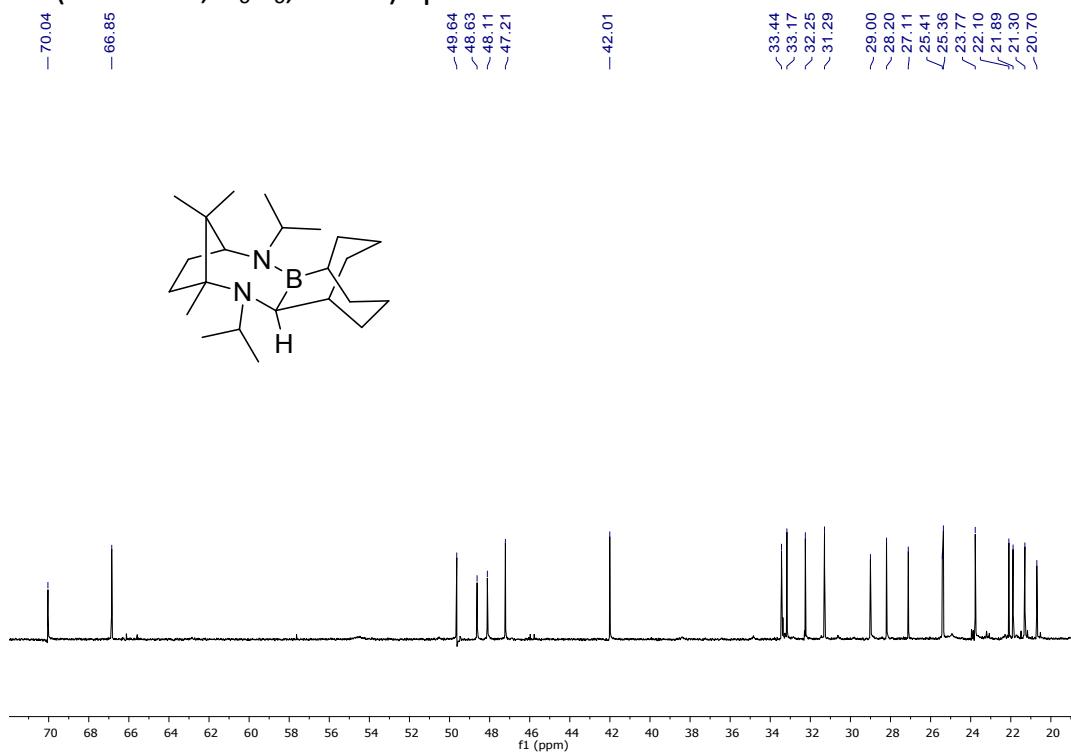
<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **16**



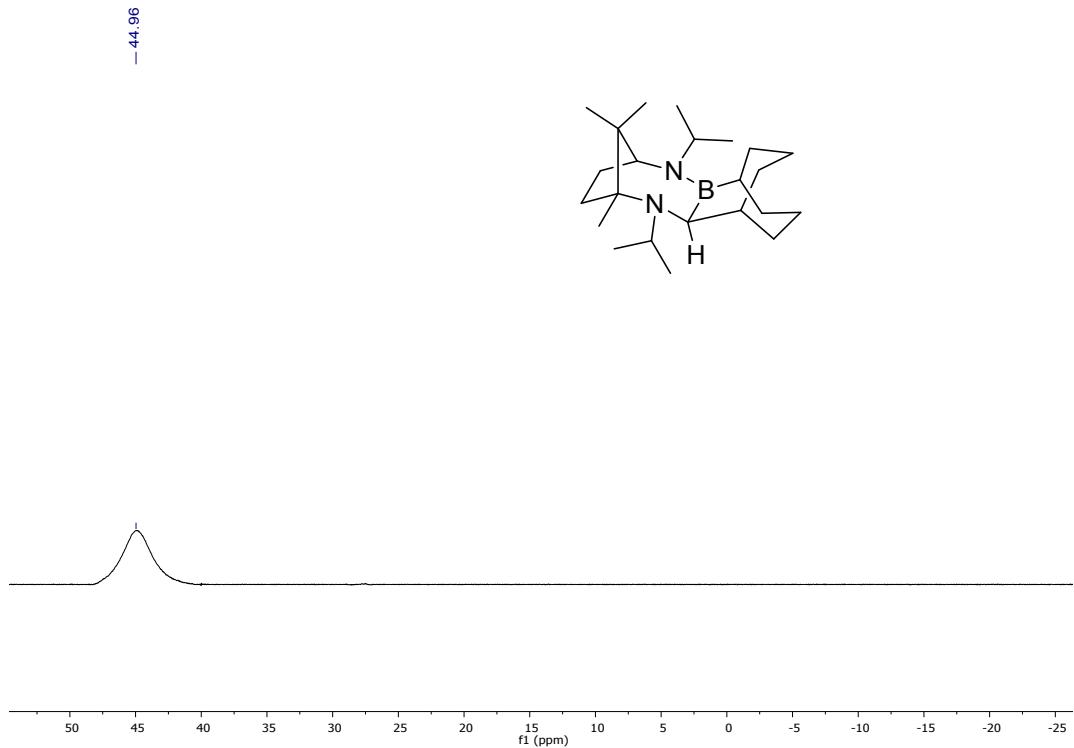
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **17**



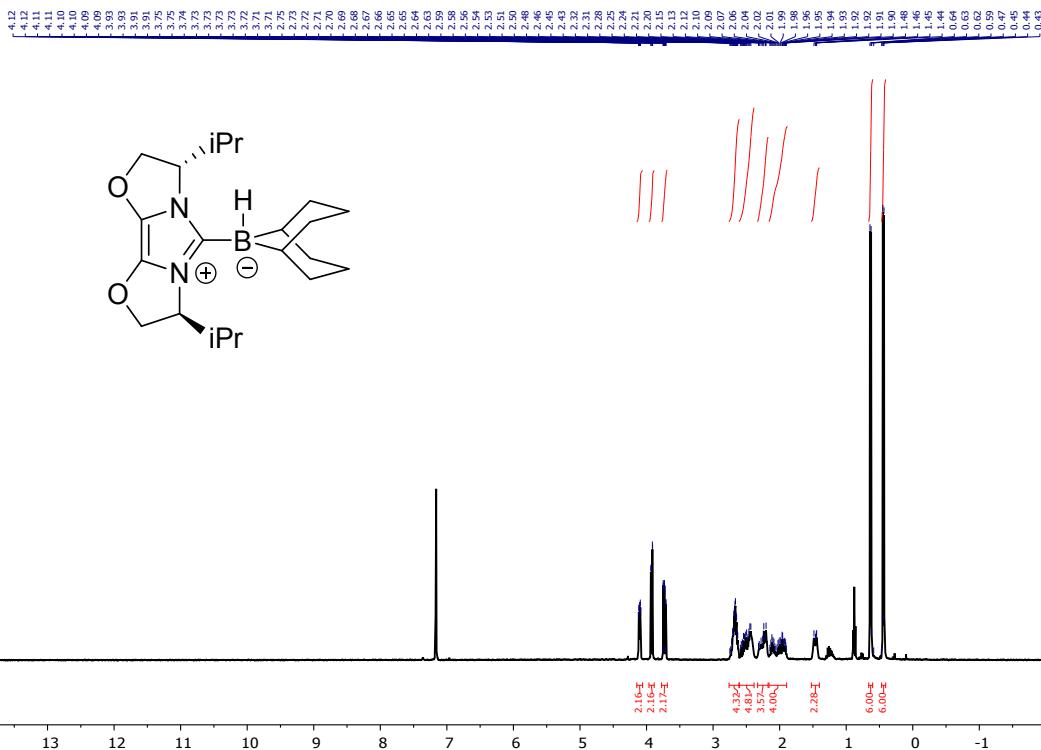
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **17**



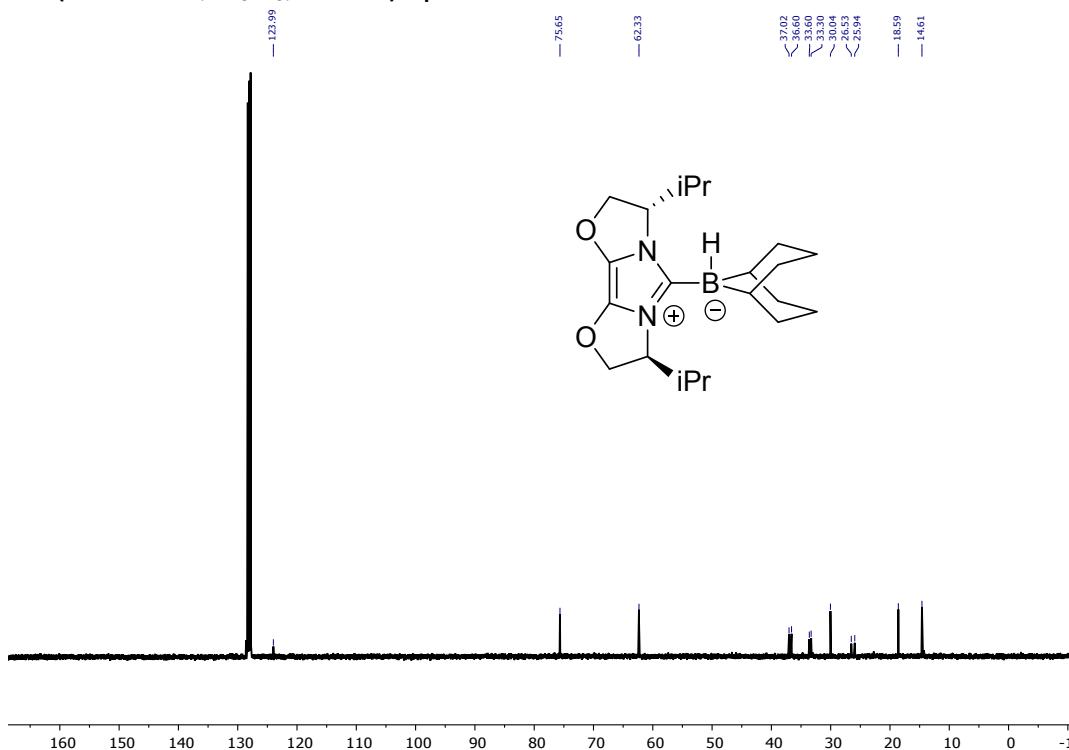
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **17**



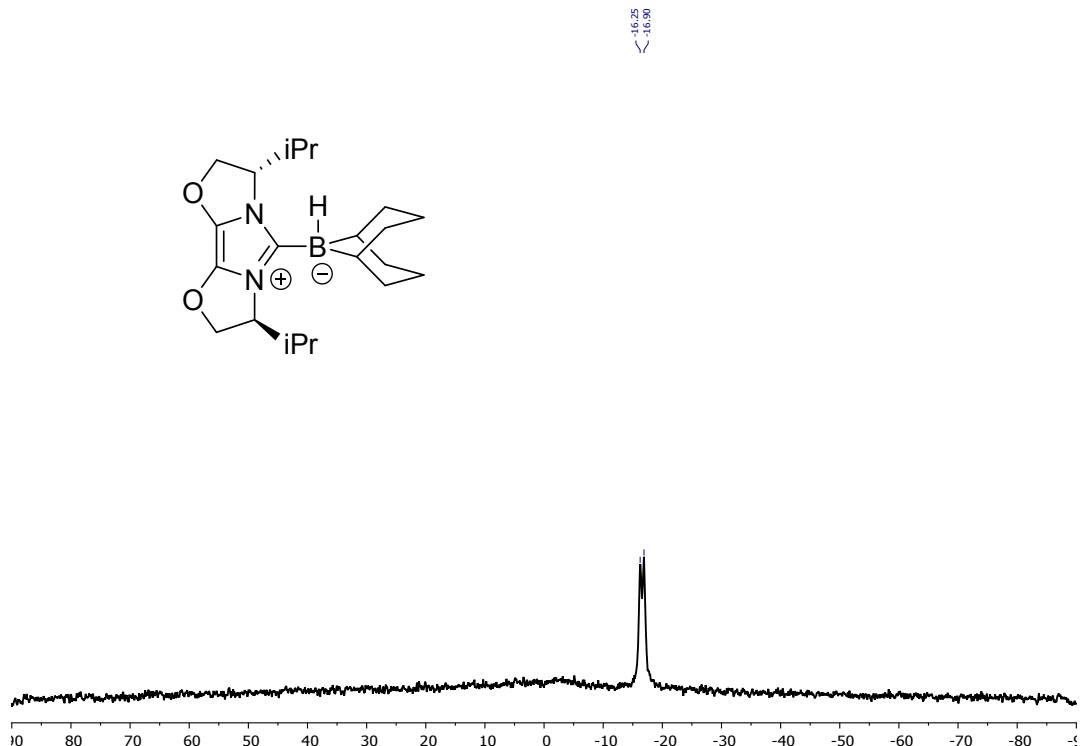
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **20**



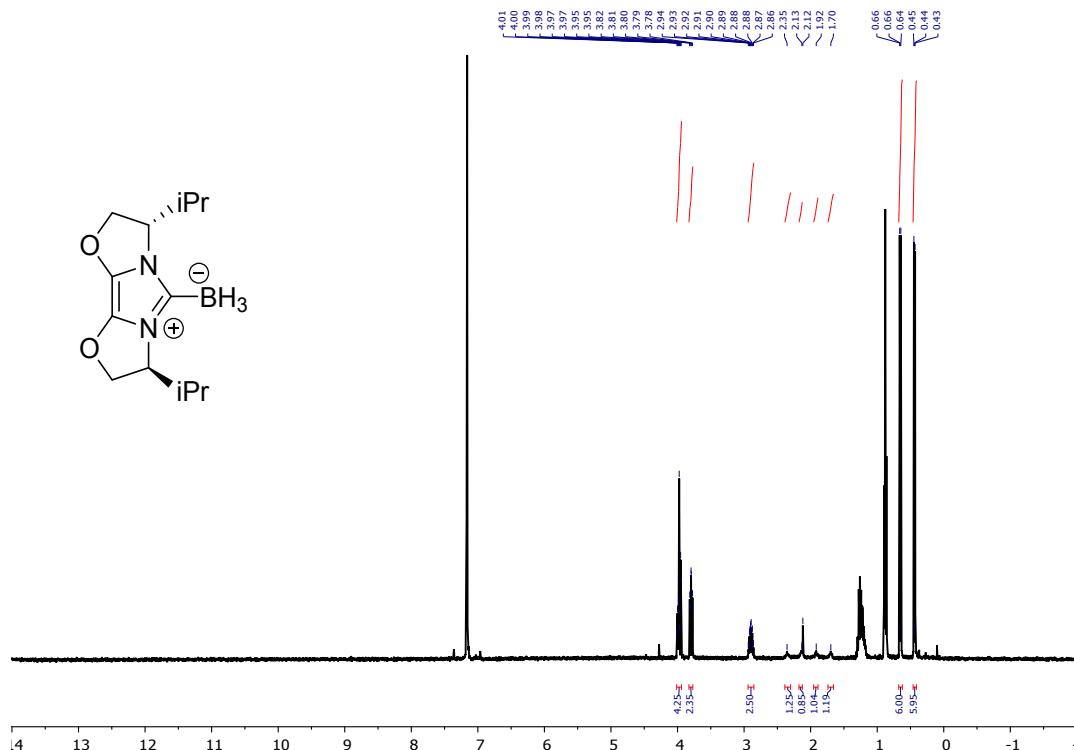
<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **20**



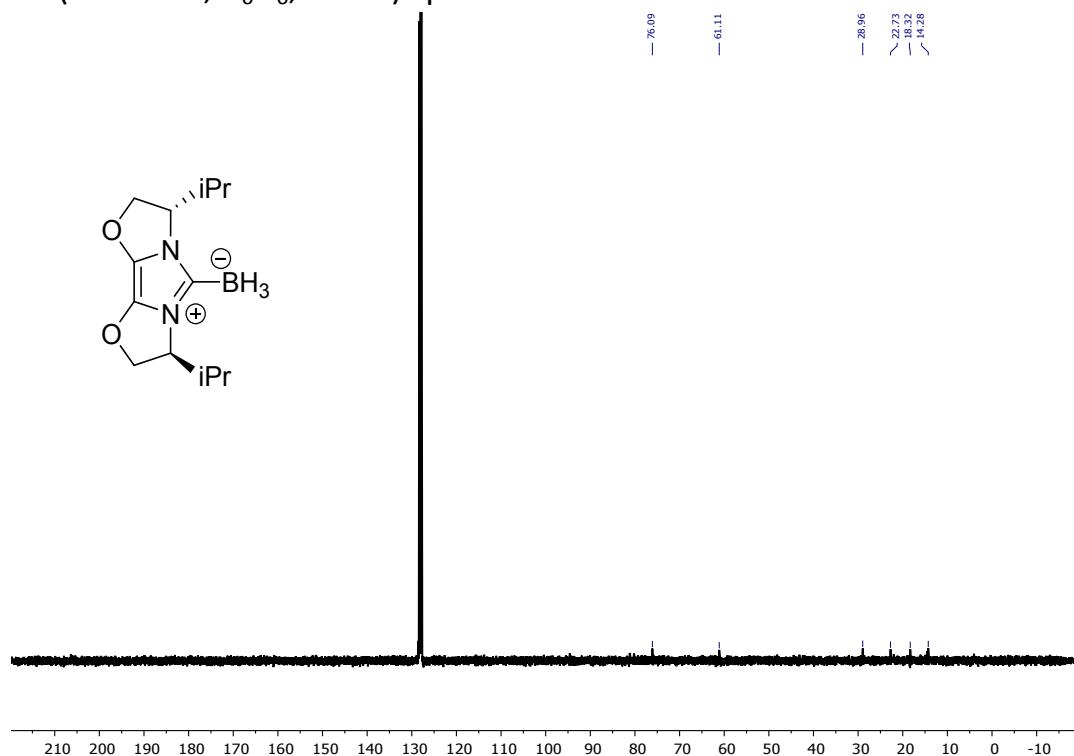
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **20**



<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **21**

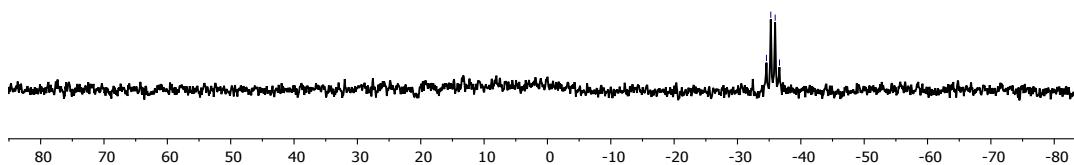
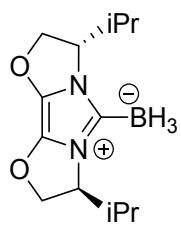


<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **21**

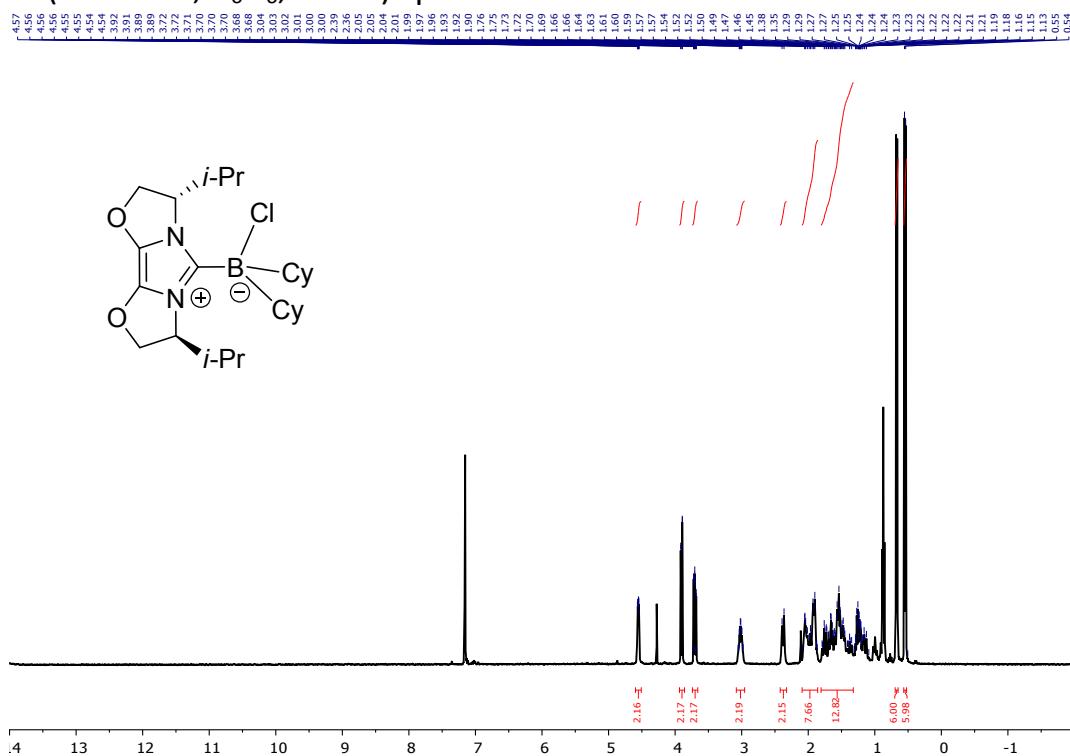


$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **21**

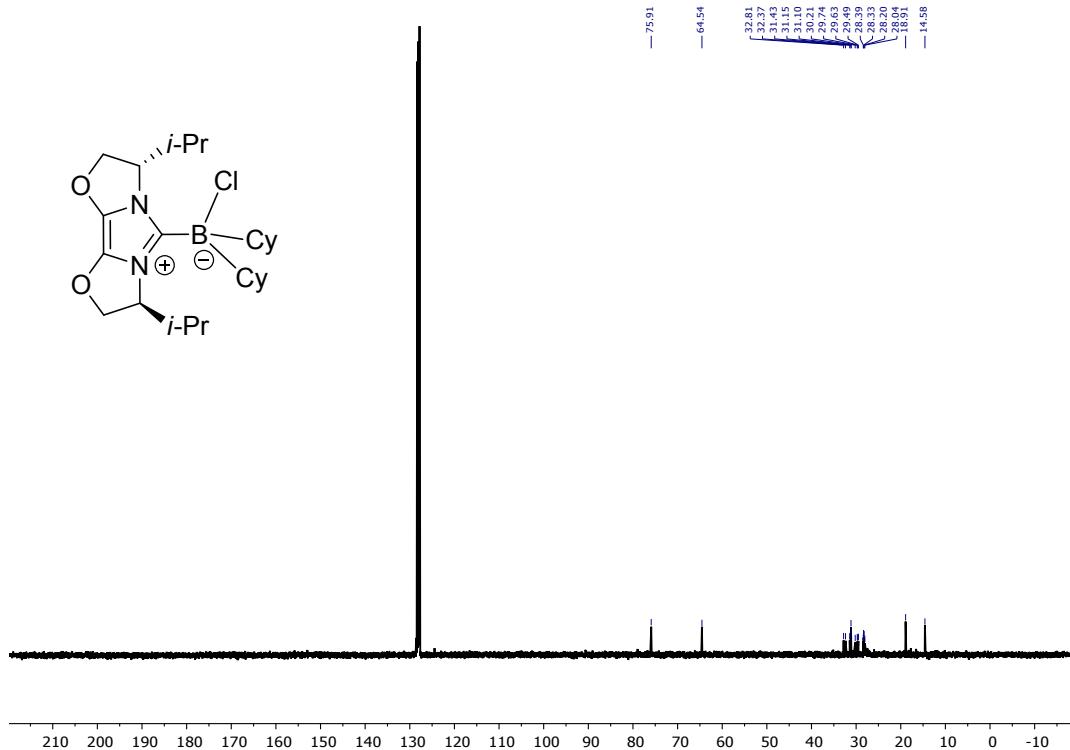
34.57  
35.36  
35.95  
36.63



<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **22**

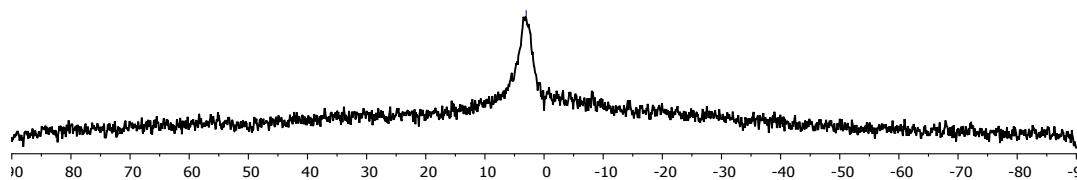
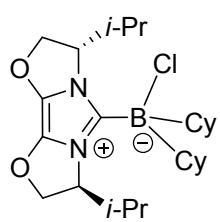


**<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of 22**

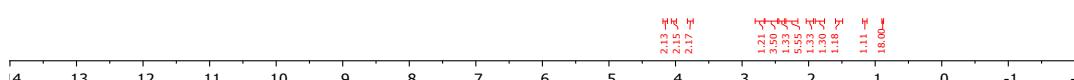
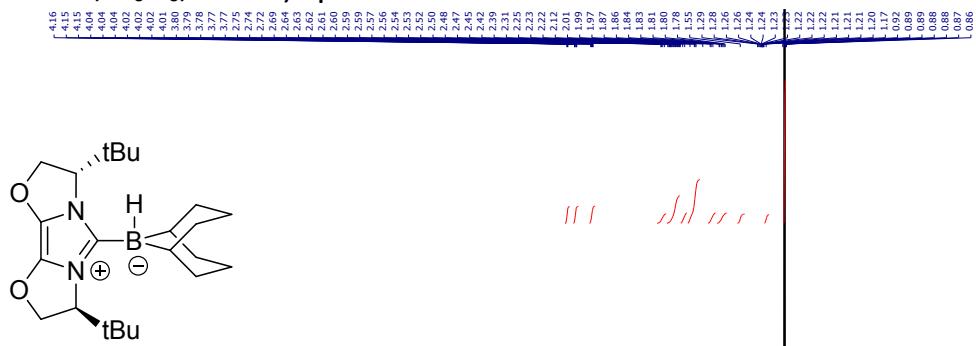


$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **22**

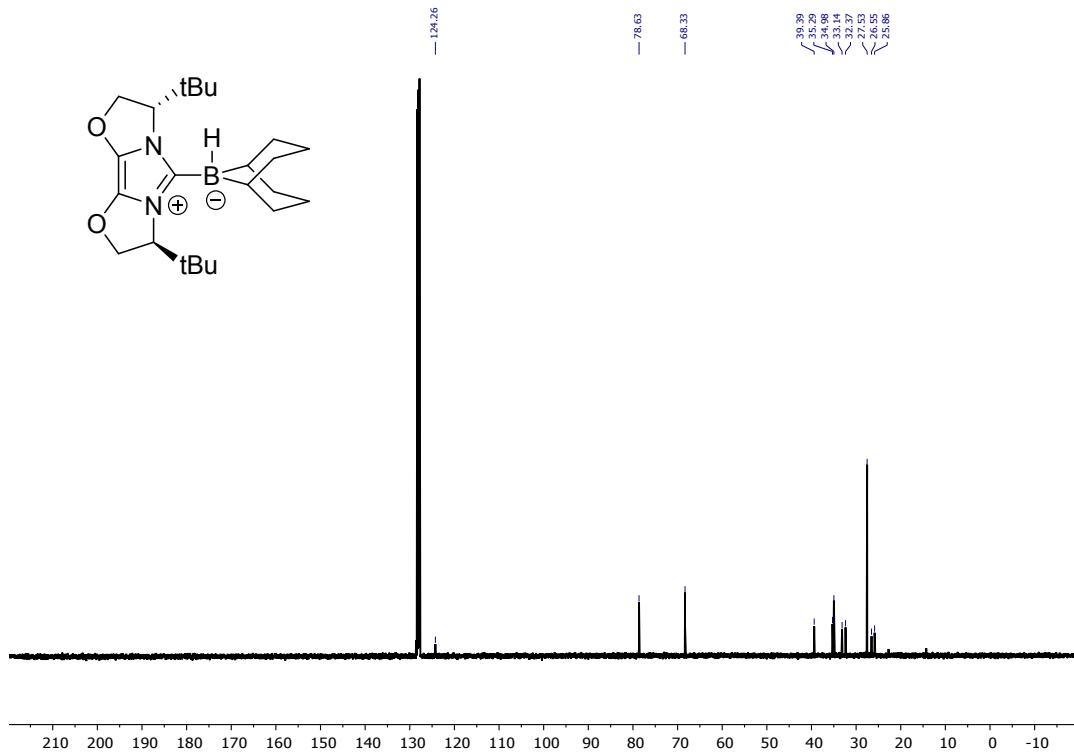
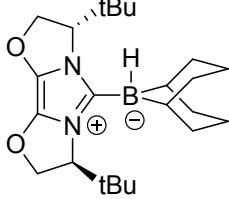
— 3.02



<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **23**

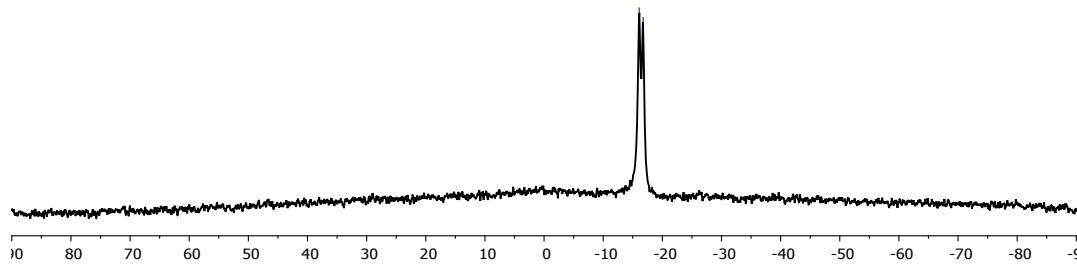
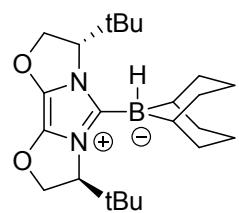


<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **23**

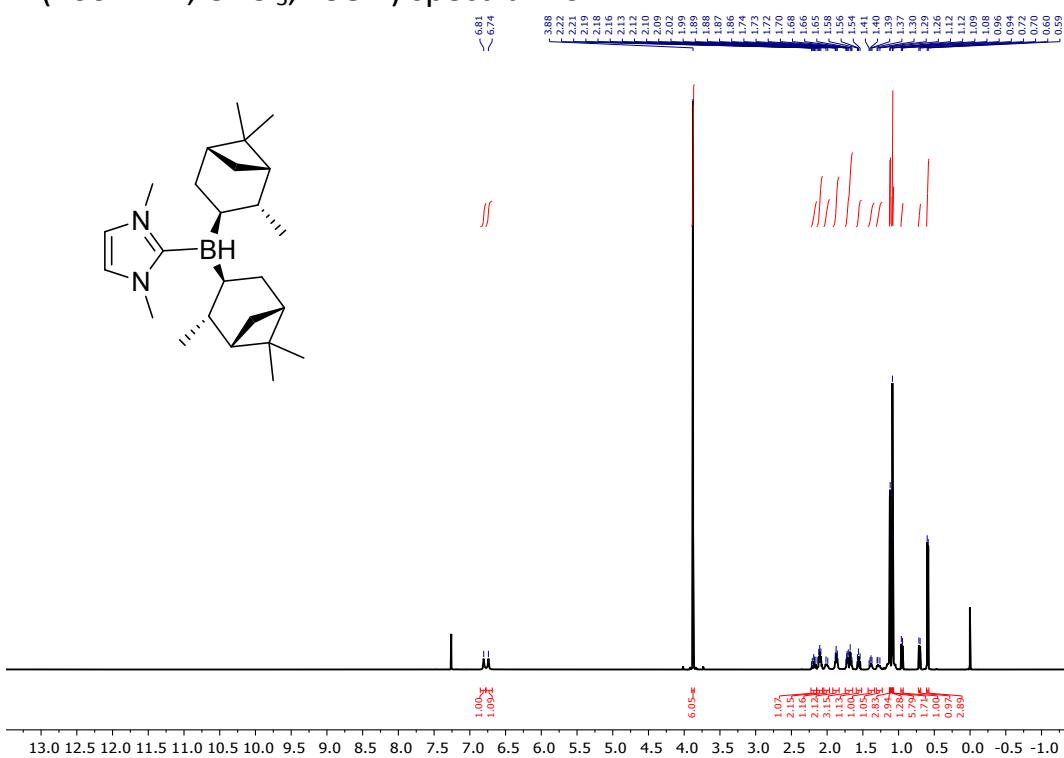


<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **23**

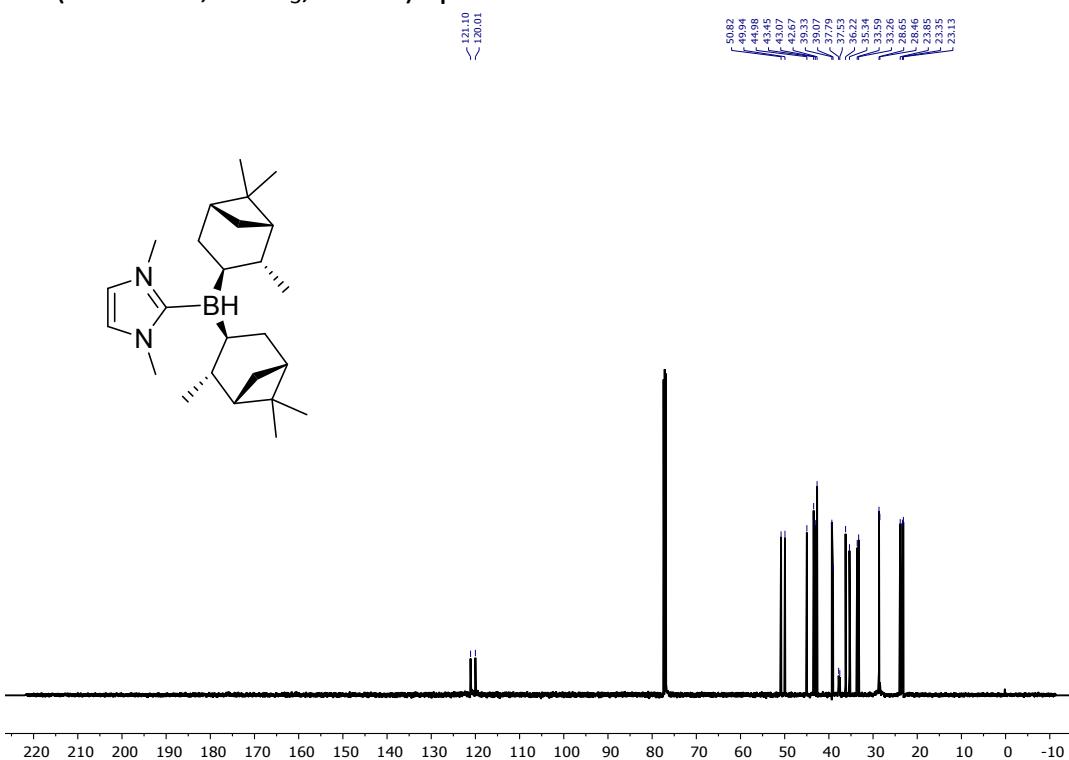
<-16.08  
<-16.75



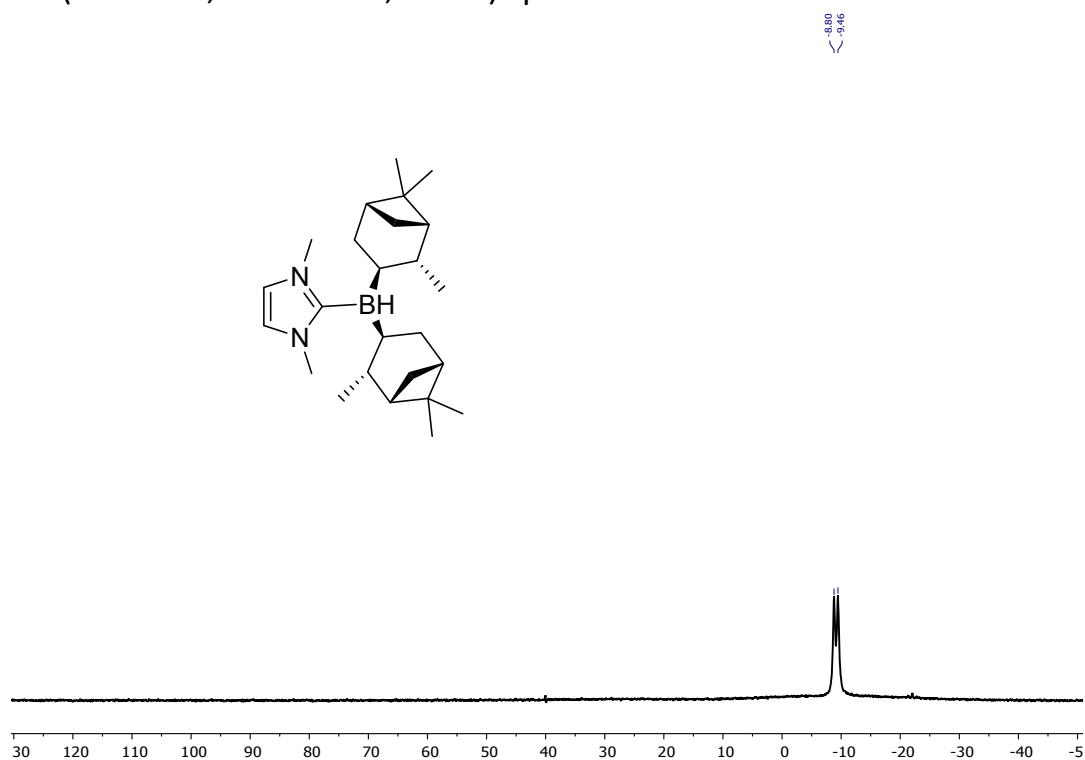
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **24**



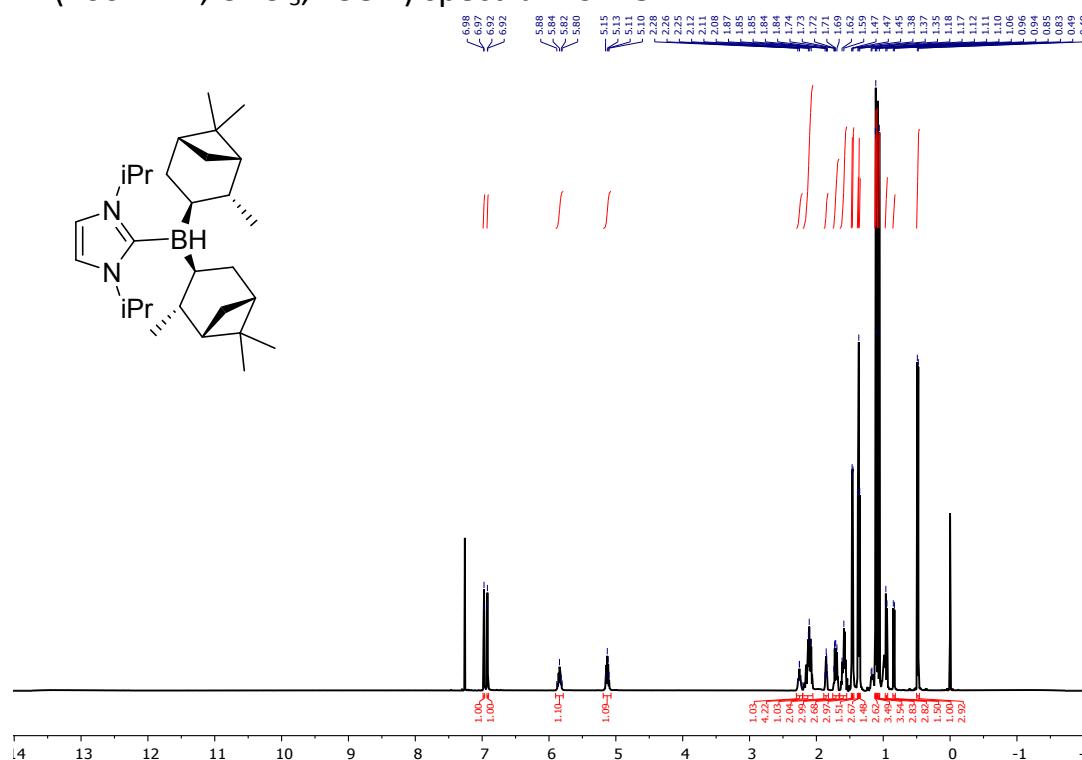
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **24**



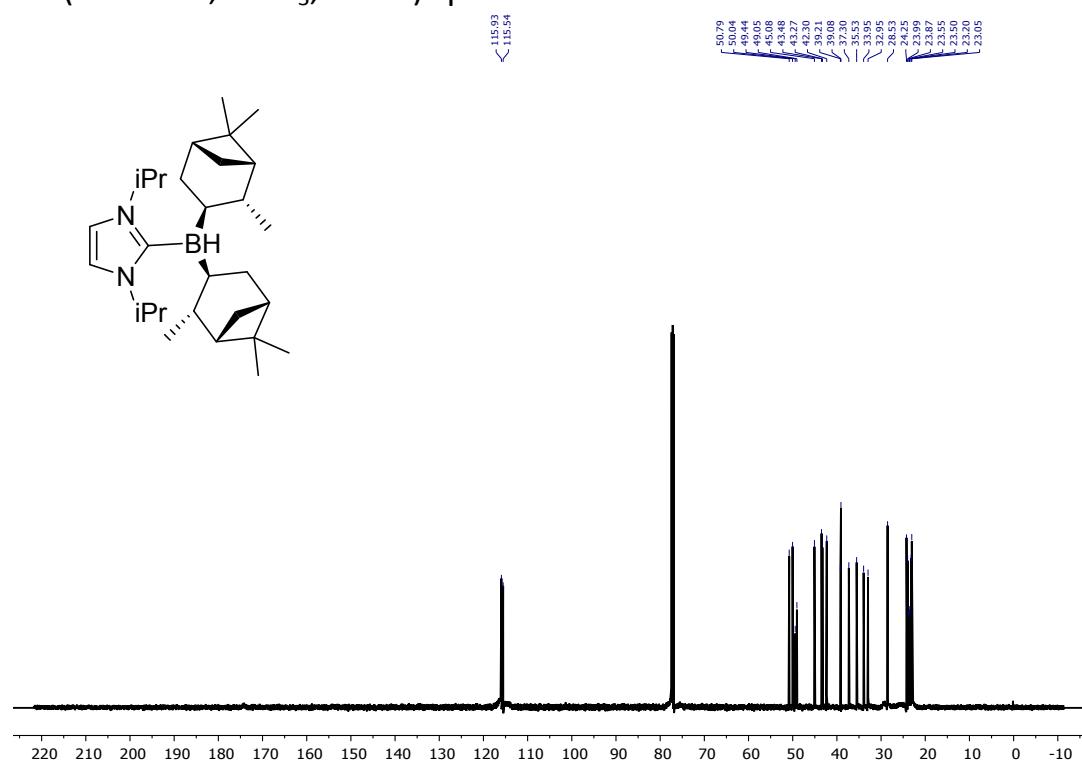
$^{11}\text{B}$  NMR (128 MHz,  $\text{d}^8\text{-toluene}$ , 298 K) spectrum of **24**



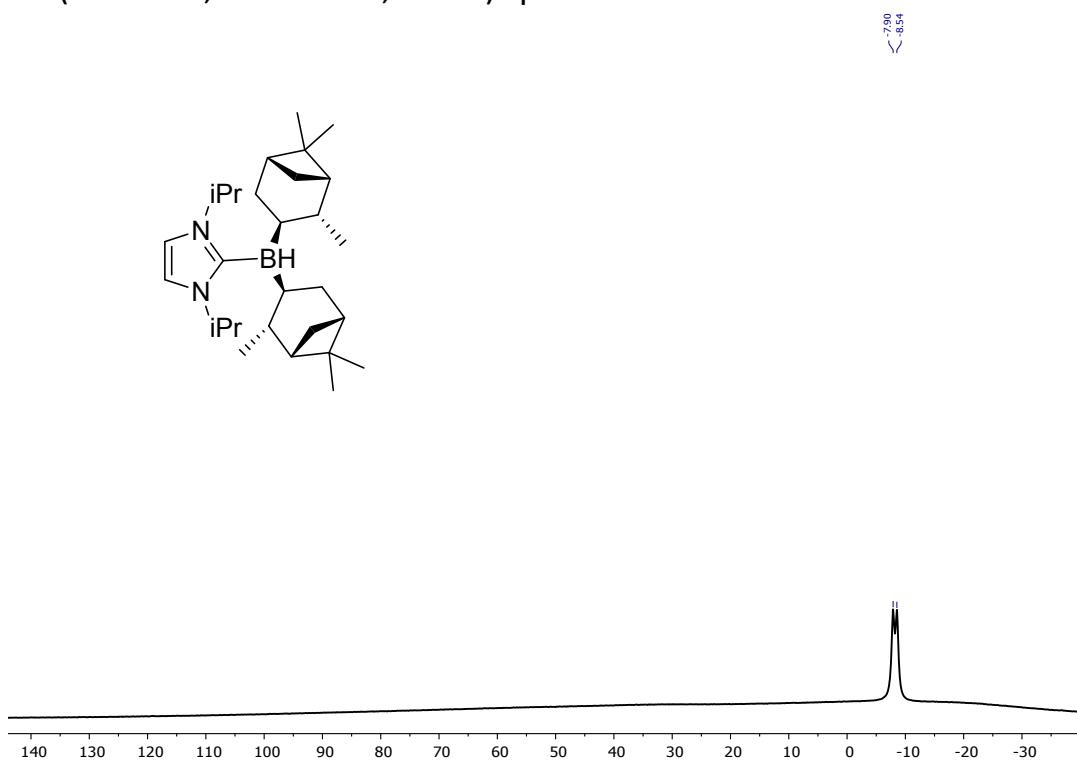
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **25**



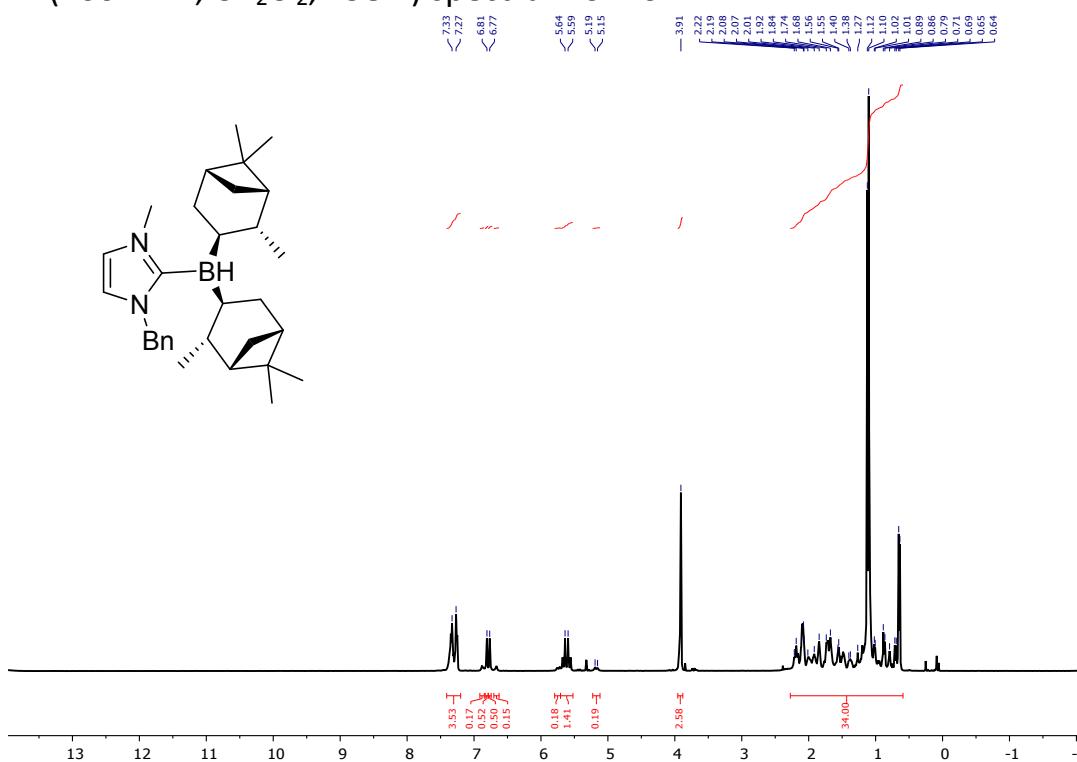
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **25**



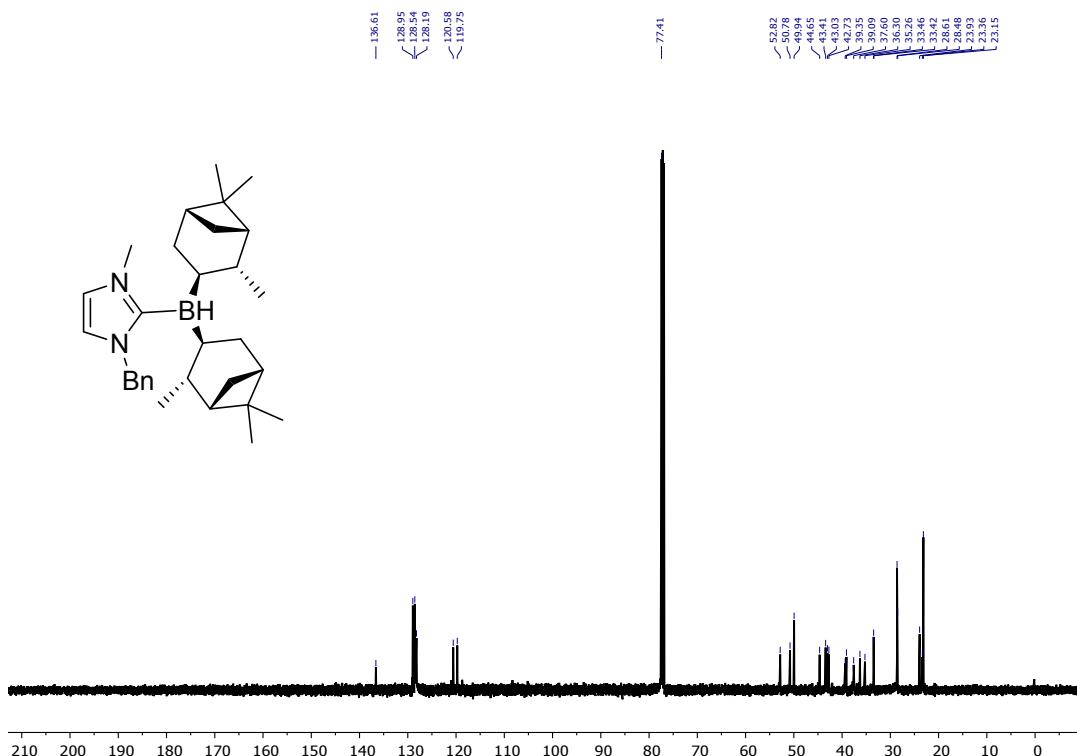
$^{11}\text{B}$  NMR (128 MHz, d<sup>8</sup>-toluene, 298 K) spectrum of **25**



<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **26**

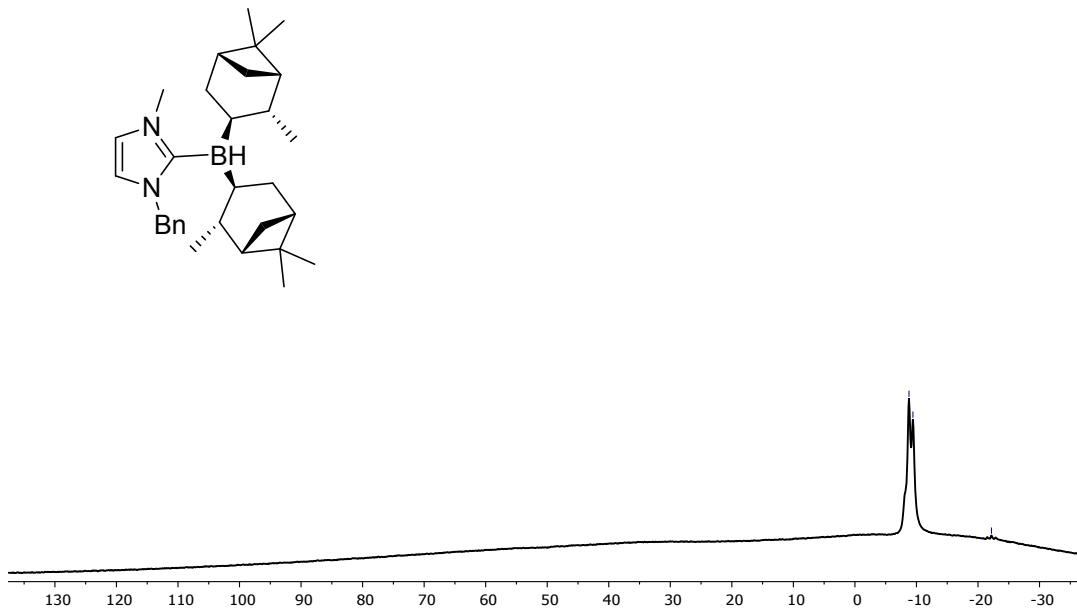


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **26**

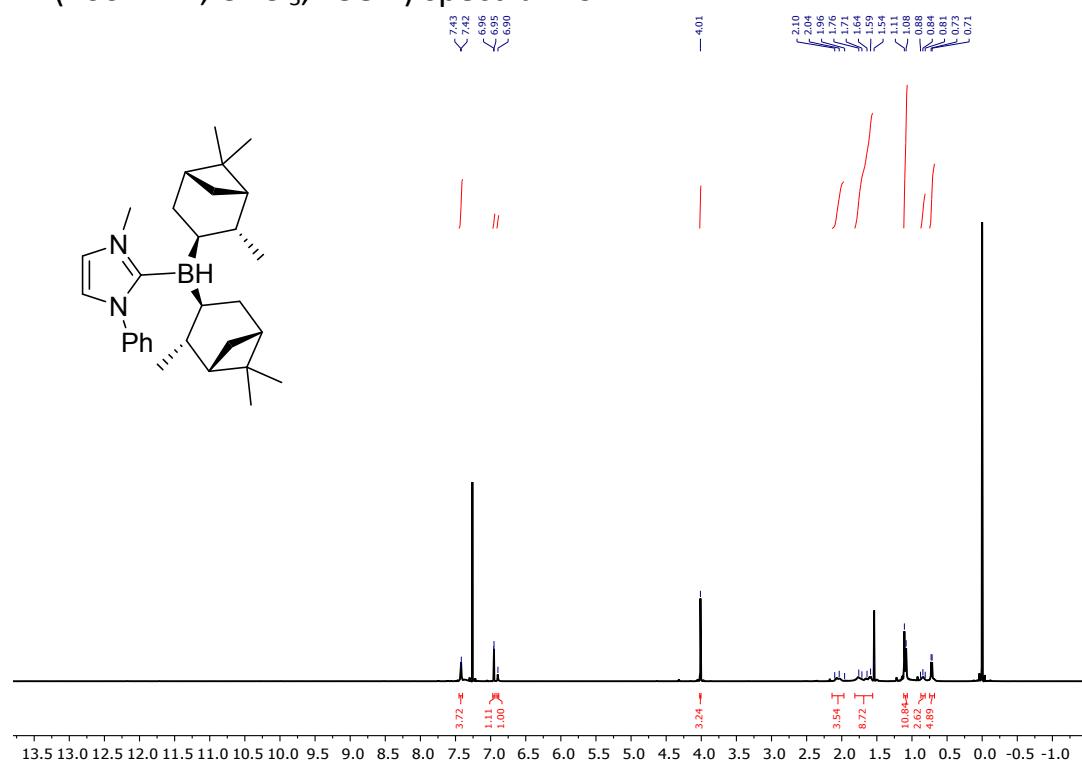


$^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **26**

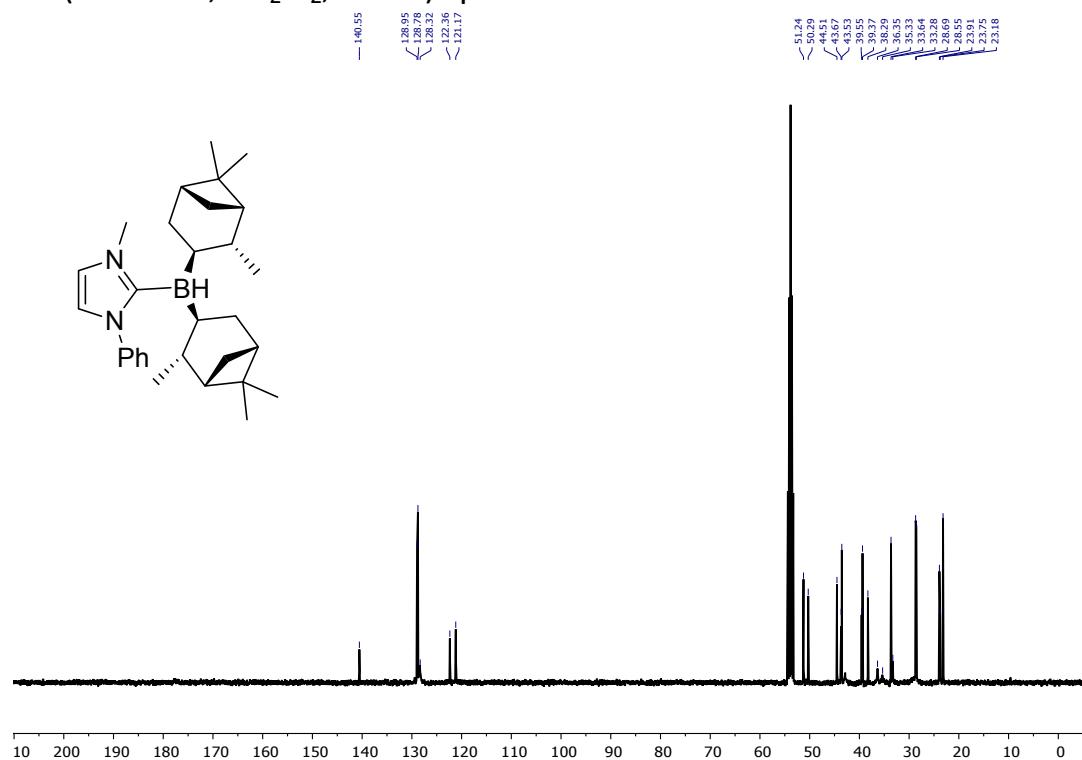
<-8.79  
<-9.43  
— -22.19



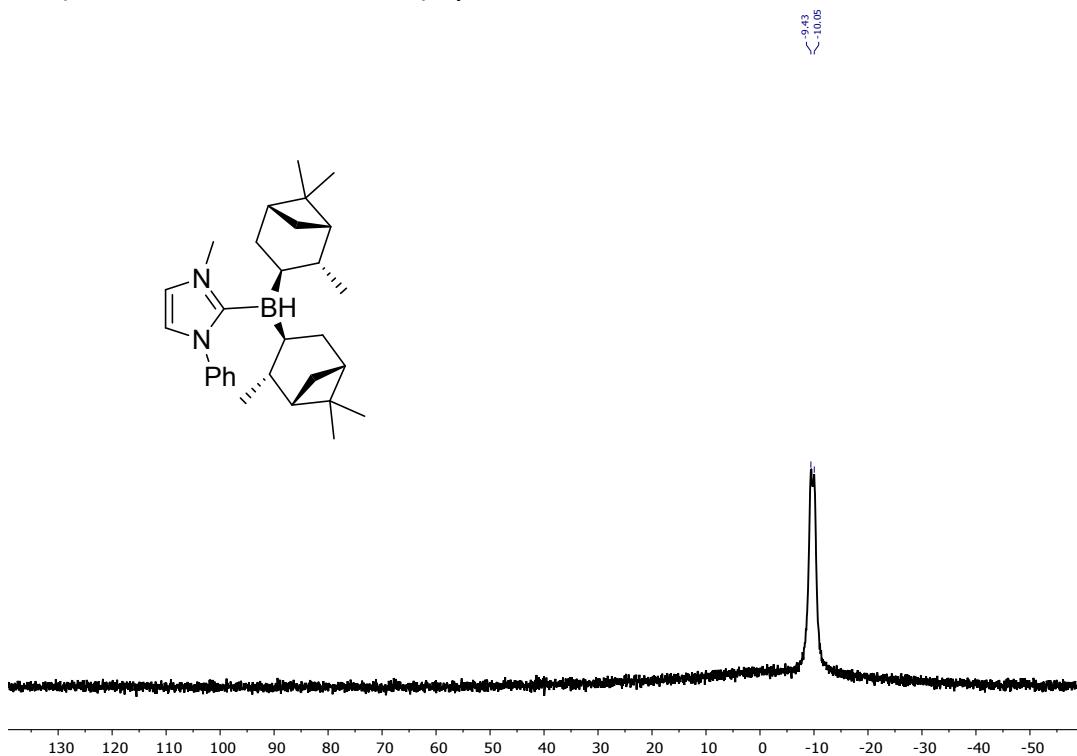
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **27**



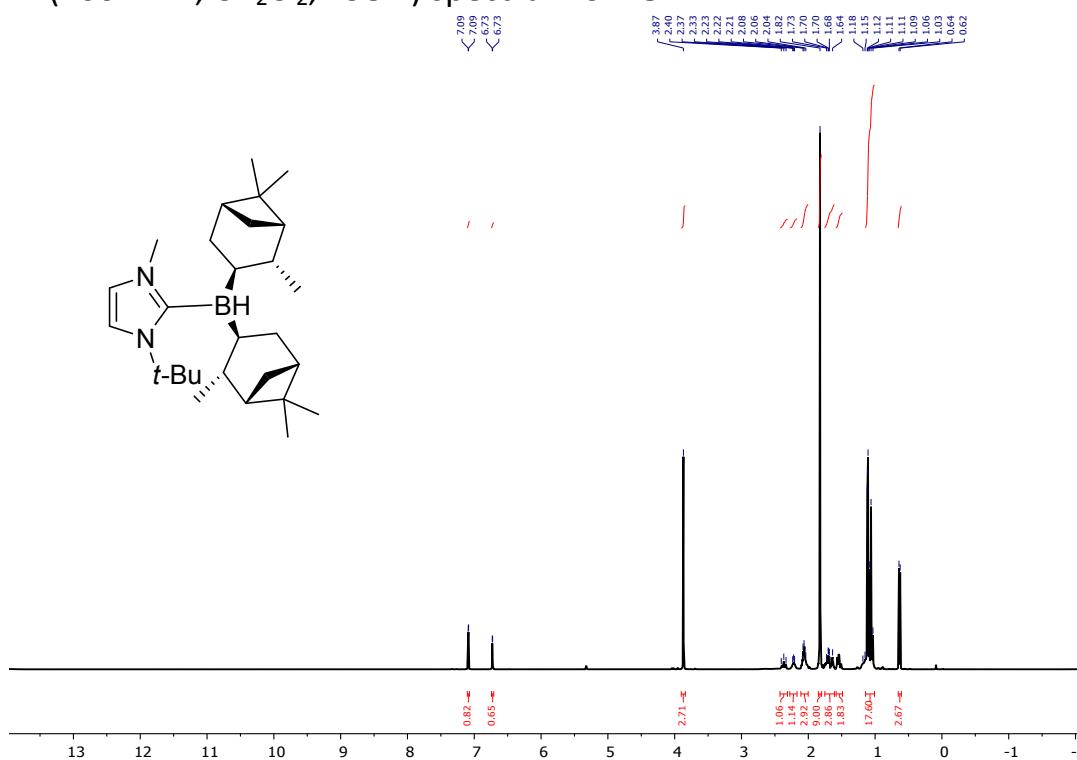
<sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **27**



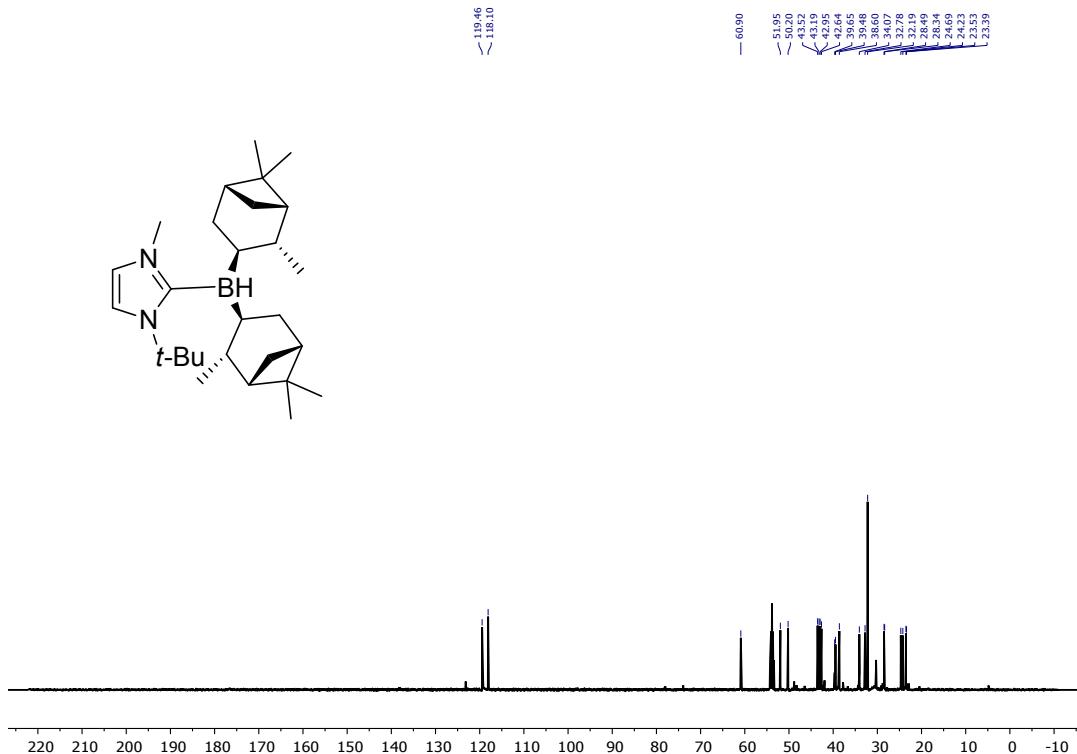
<sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **27**



<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **28**

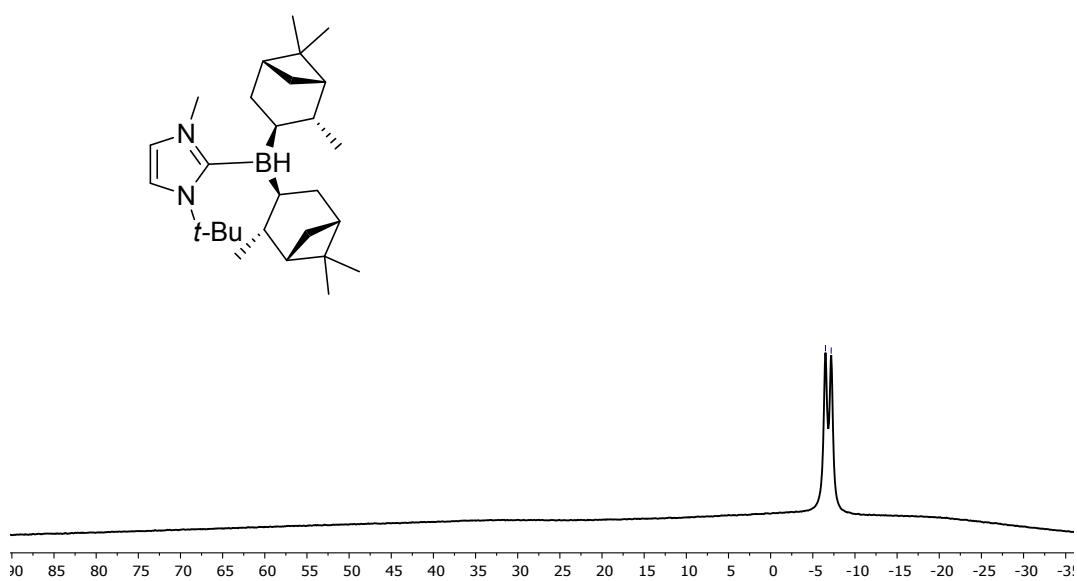


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **28**

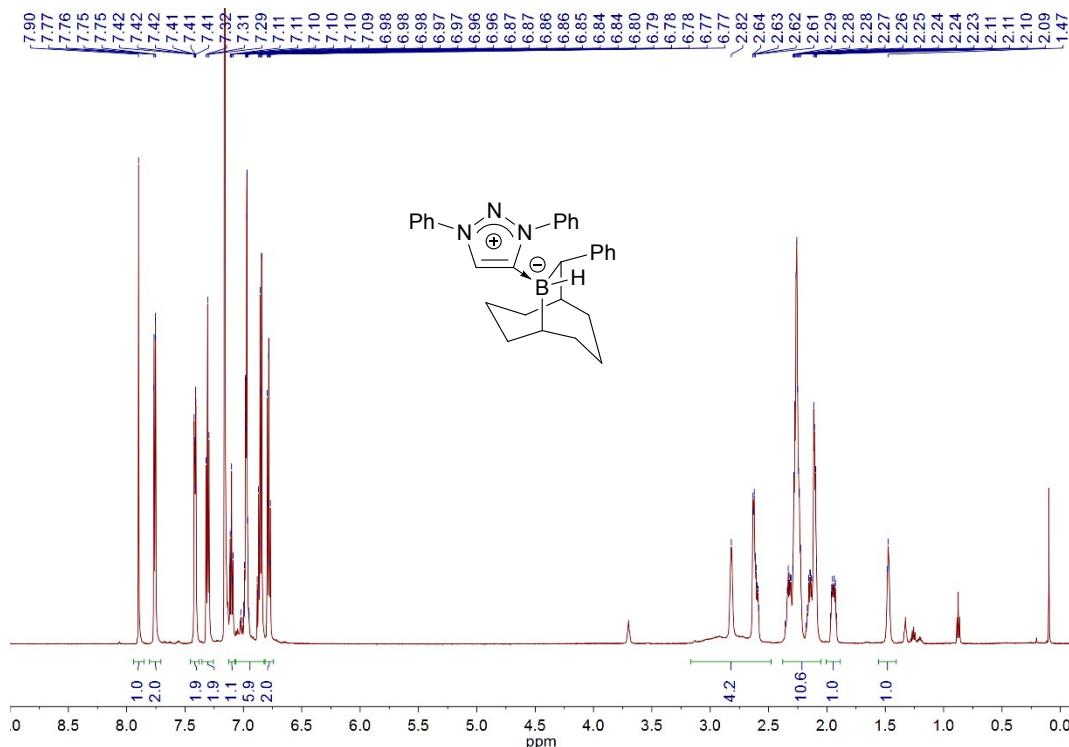


$^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **28**

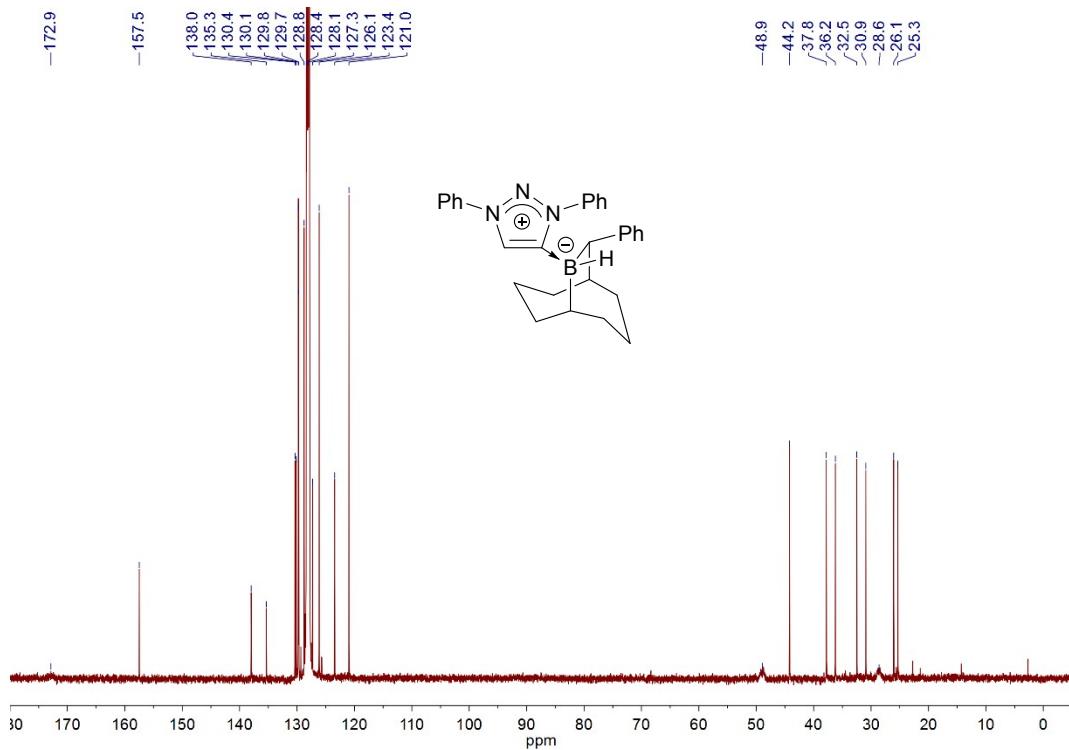
$\sim -6.50$   
 $\sim -7.18$



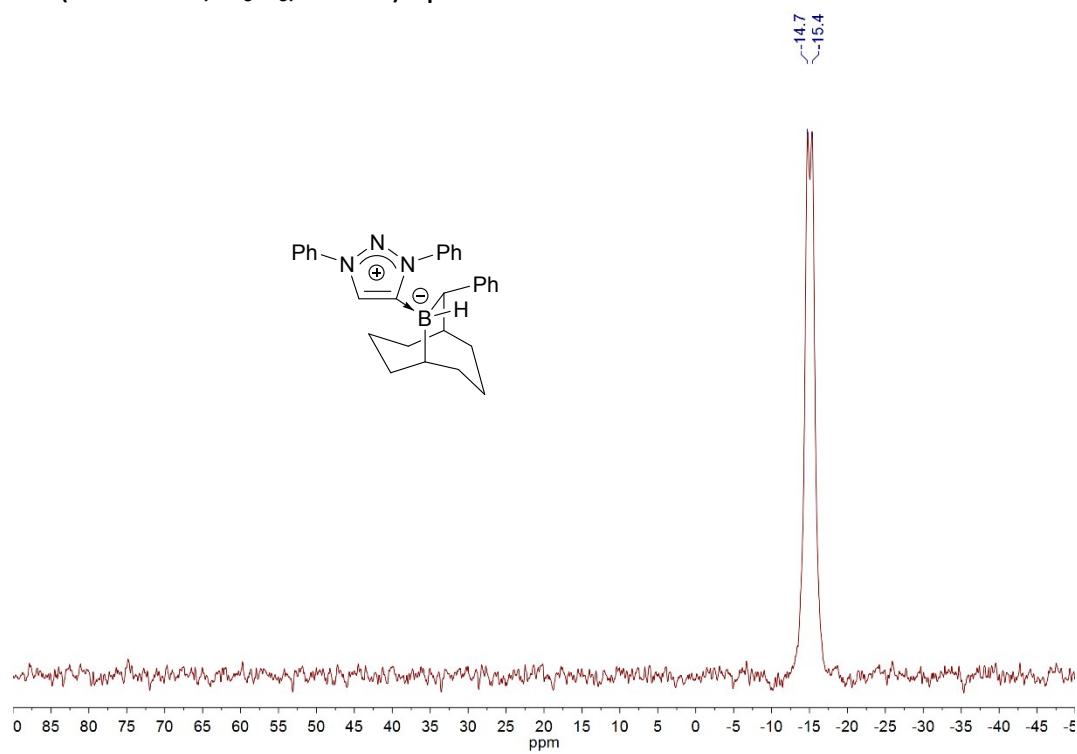
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **29**



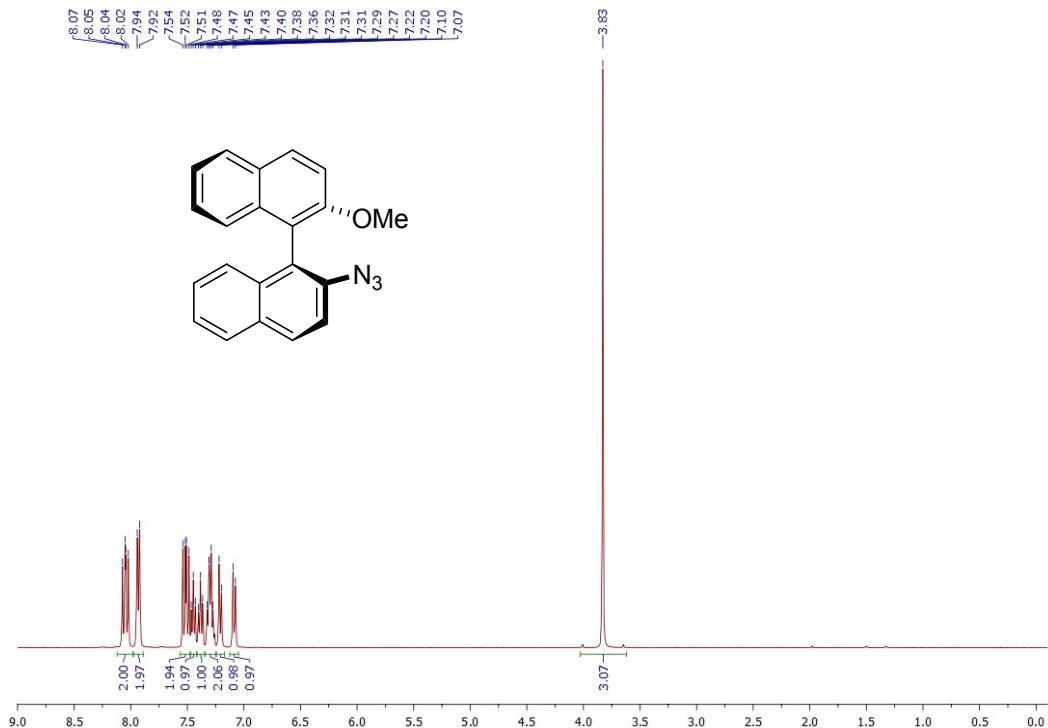
**<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectrum of **29****



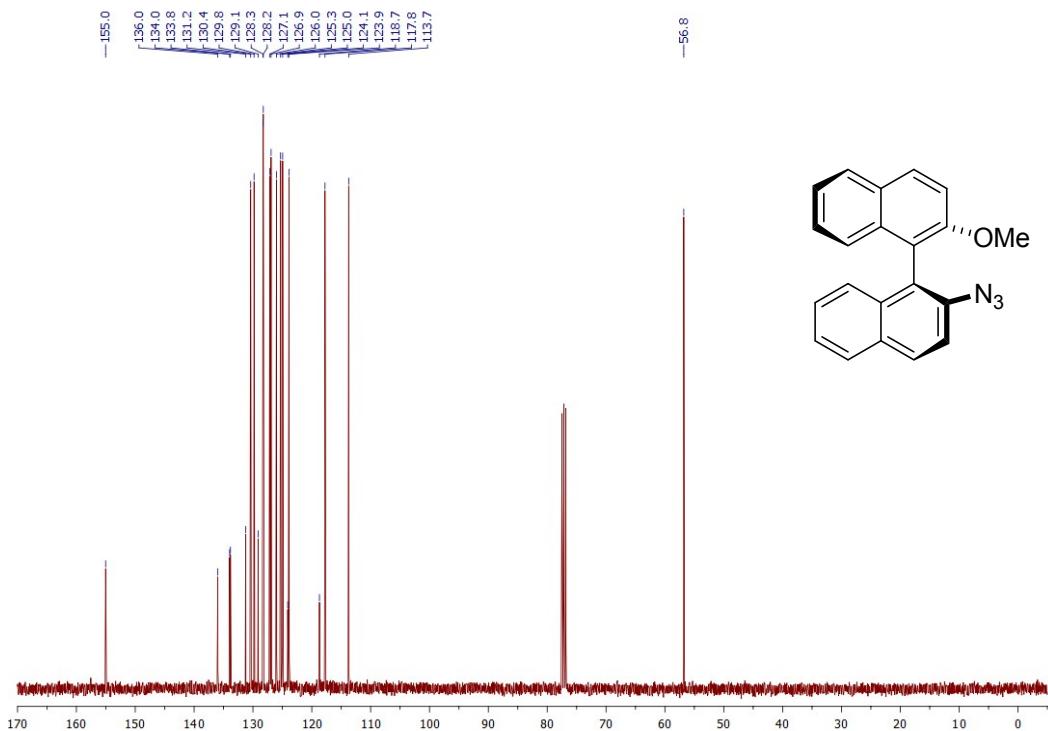
$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectrum of **29**



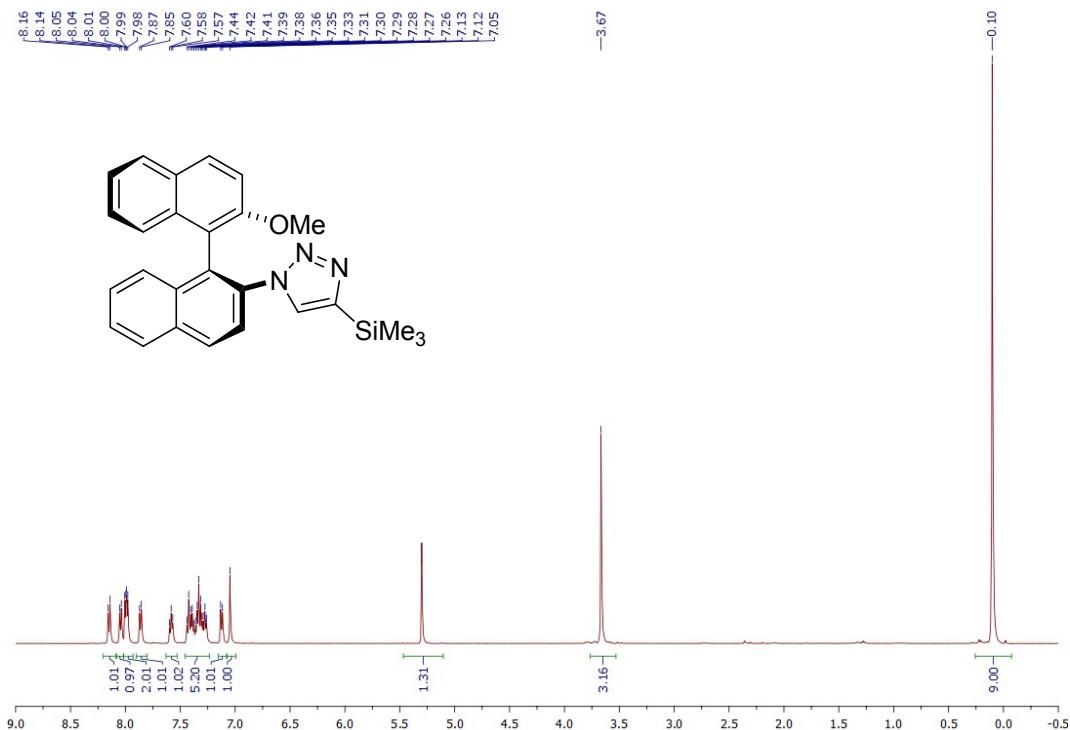
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **30**



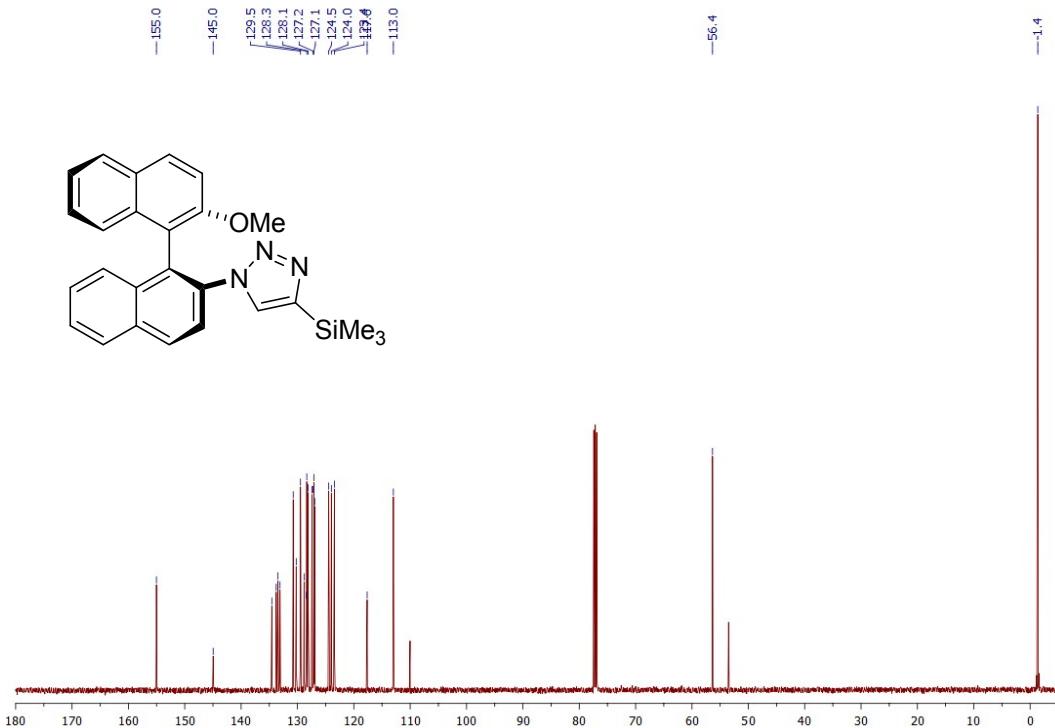
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **30**



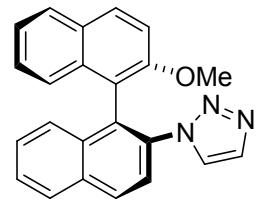
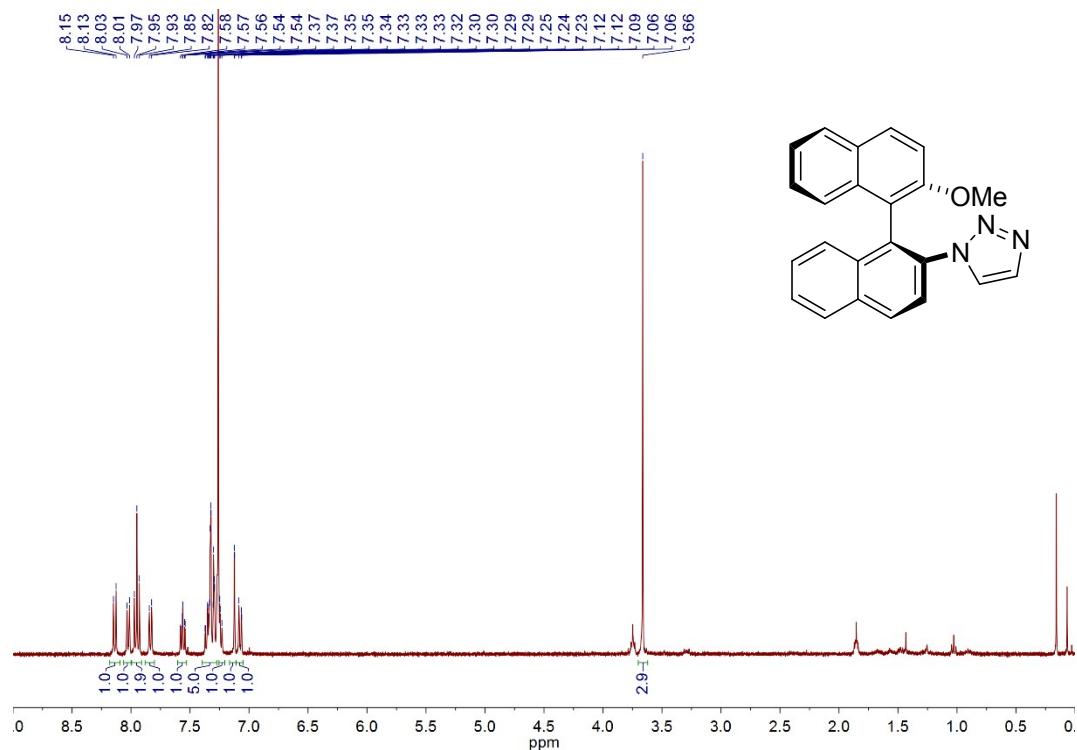
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **31**



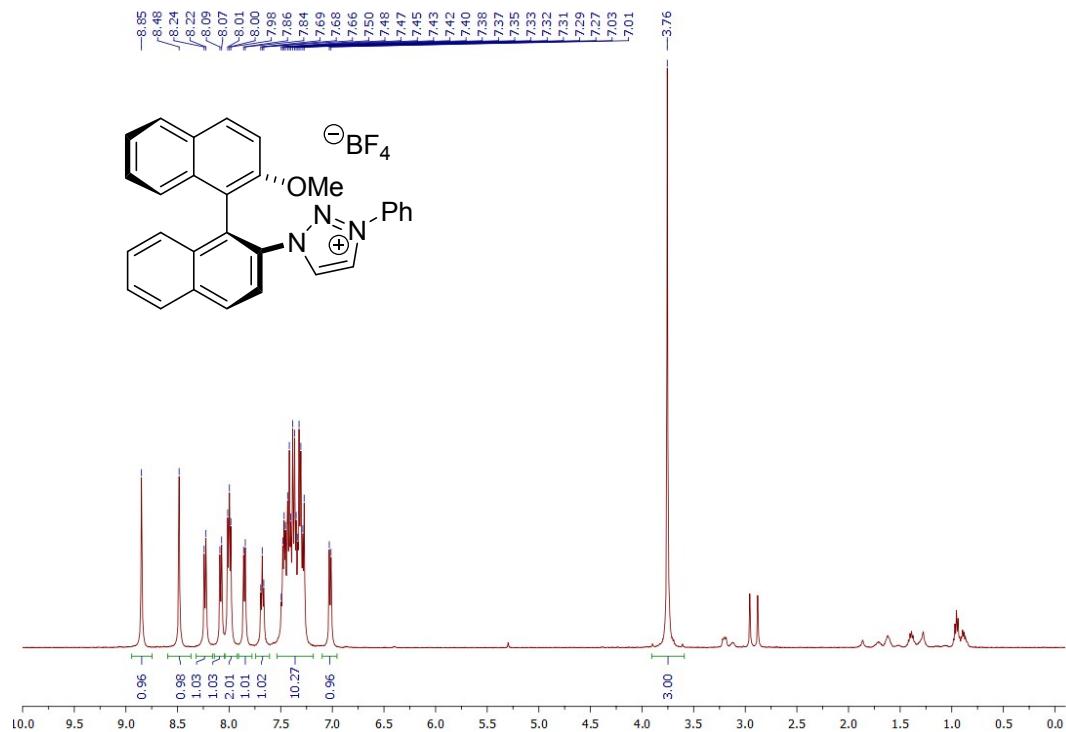
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **31**



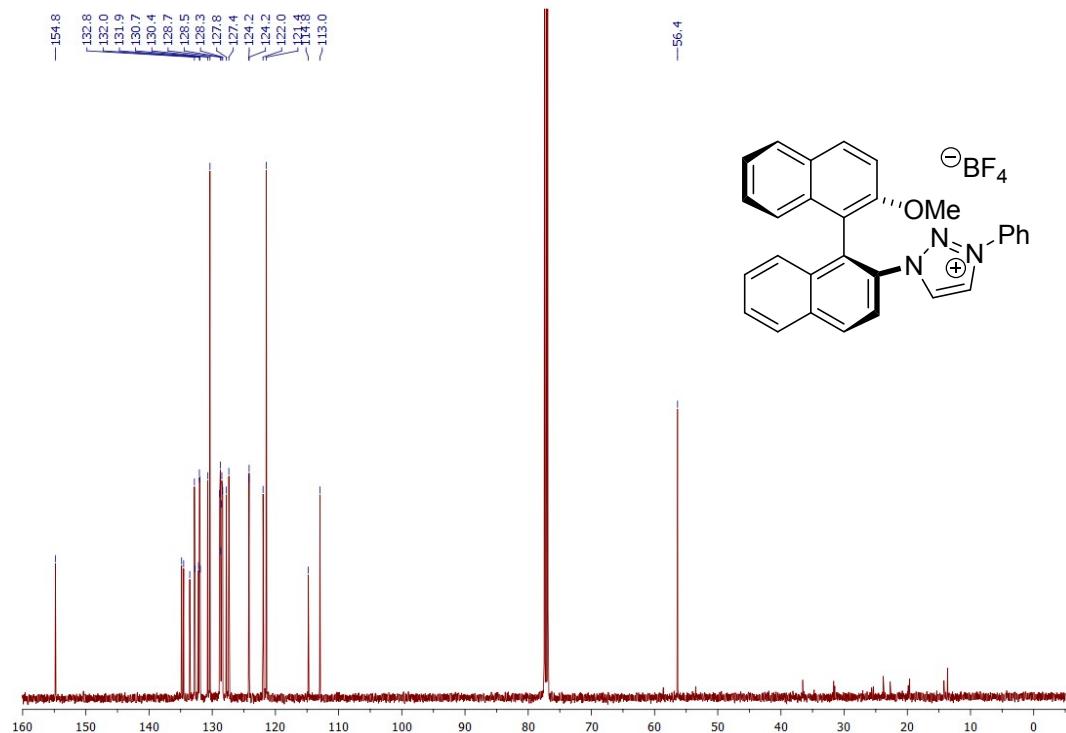
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **32**



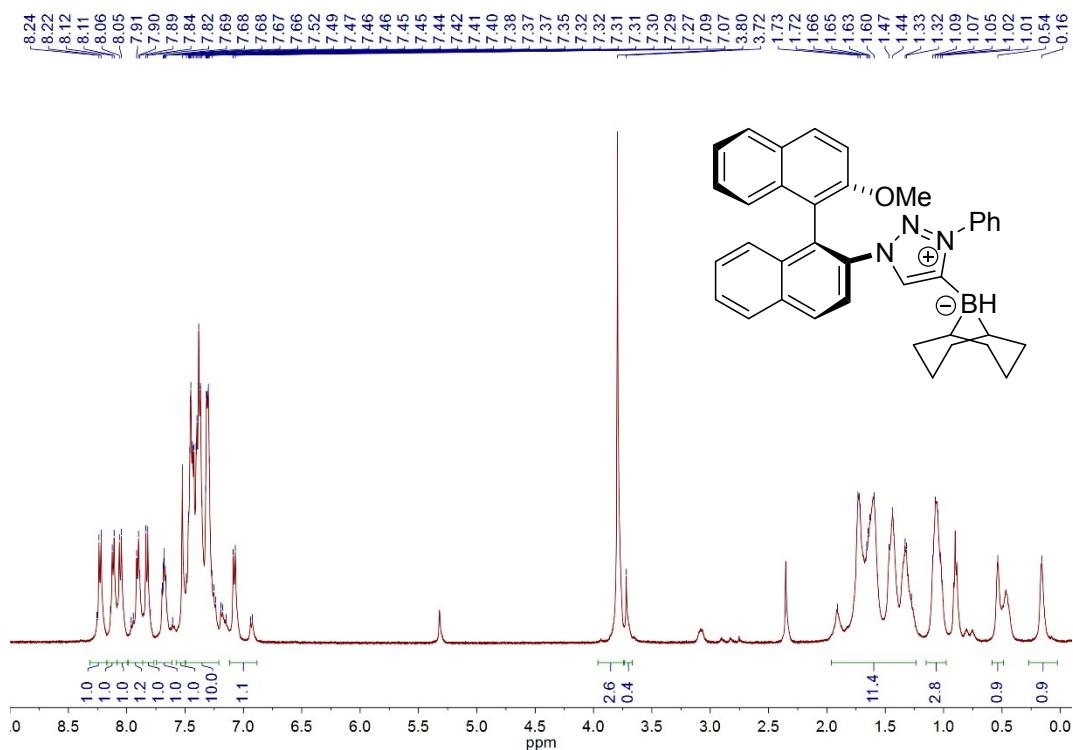
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **33**



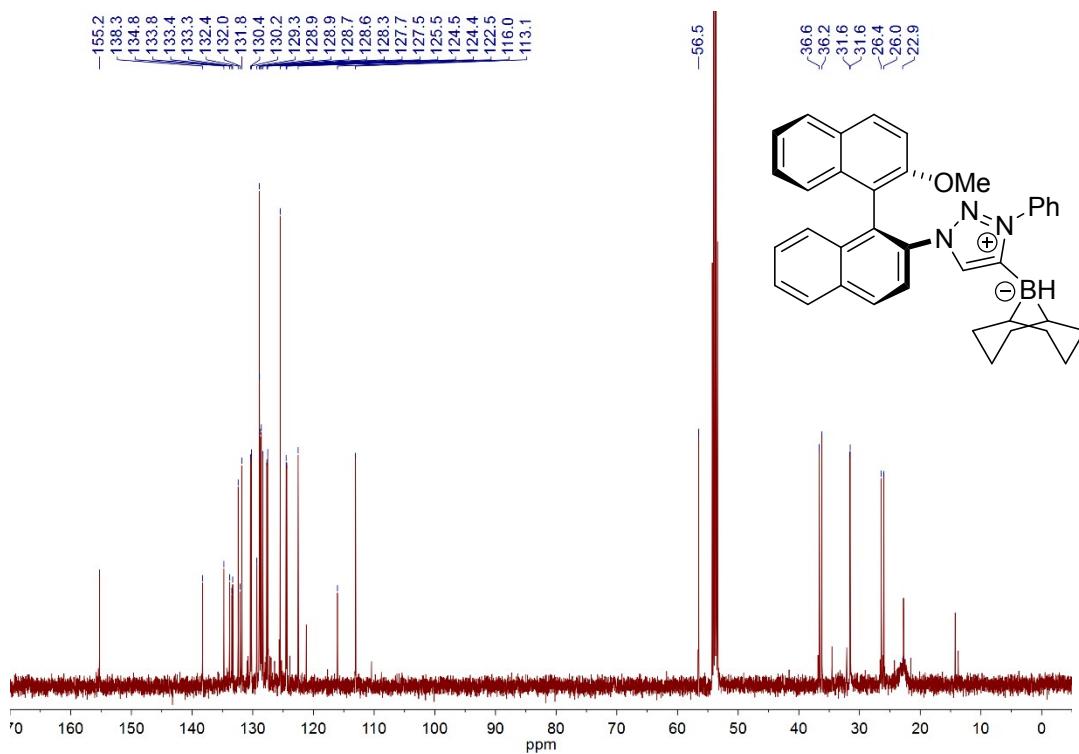
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K) spectrum of **33**



<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **34a**



<sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **34a**



$^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **34a**

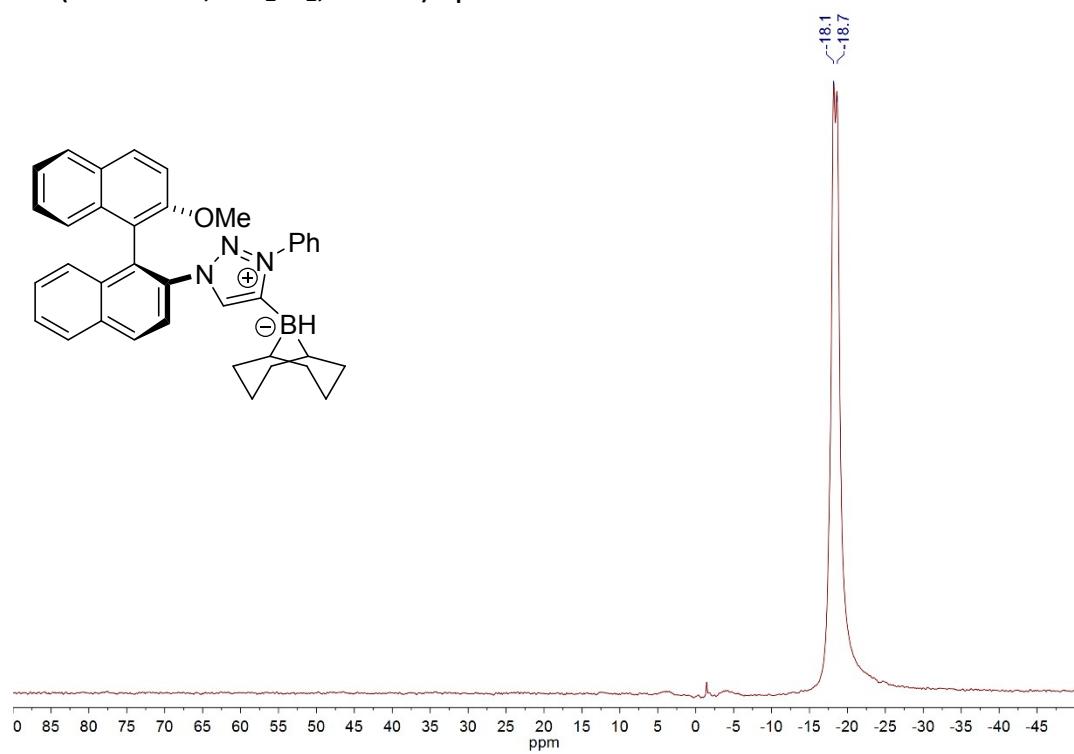
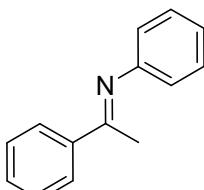
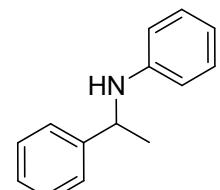
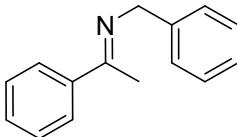
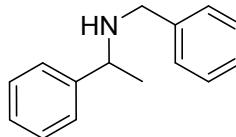
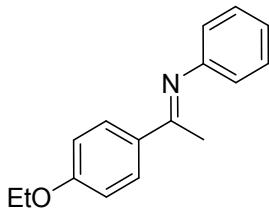
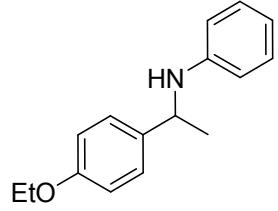
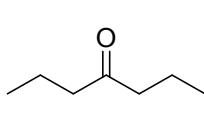
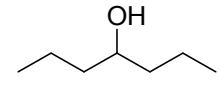
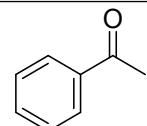
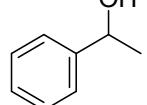


Table for catalytic hydrogenations of **20**, **21**, **23**, **24**, **25**, **26**, **27**, **28**, and **34**

Entry	Substrate	Precursor	5 mol% precursor + 5 mol% [Tritiy][BArF]			product	Yield (%)	e.e.
			t (h)	Temp.	DCM, 102 atm H <sub>2</sub>			
1		20	24	r.t.			100	7
2		20	6	r.t.			88	9
3		20	3	r.t.			50	12
4		20	12	0 °C			94	1
5		20	3	50 °C			71	8
6		21	24	r.t.			3	5
7		21	3	50 °C			6	7
8		23	24	r.t.			0	-
9		23	48	r.t.			0	-
10		24	4	r.t.			55	12
11		24	20	-30			5	20
12		24 <sup>a</sup>	24	25			0	-
13		24 <sup>b</sup>	24	25			12	15
14		25	24	-30			<5	8
15		26	4	25			47	13
16		26	24	25			5	13
17		27	20	-30			<5	-
18		28	4	25			0	-
19		28	20	-30			0	-
20		34	18	25			100	6
10		20	6	r.t.			0	-
11		20	6	r.t.			91	11
12		20 <sup>c</sup>	24	r.t.			0	-
13		20 <sup>c</sup>	24	70 °C			0	-
14		21 <sup>c</sup>	24	r.t.			0	-
15		21 <sup>c</sup>	24	70 °C			0	-
16		20	48	r.t.			0	-
17		23	48	r.t.			0	-

Carried out in <sup>a</sup> toluene, <sup>b</sup> chlorobenzene, <sup>c</sup> diethyl ether