

## Supporting Information

Access to C(sp<sup>3</sup>) borylated and silylated cyclic molecules: Hydrogenation of corresponding cycloarenes and heteroarenes

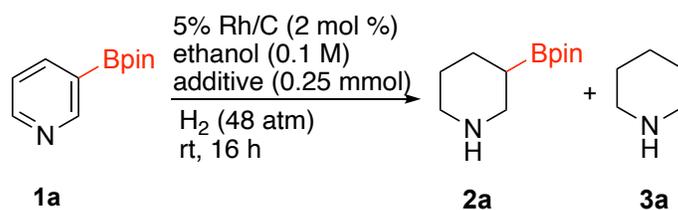
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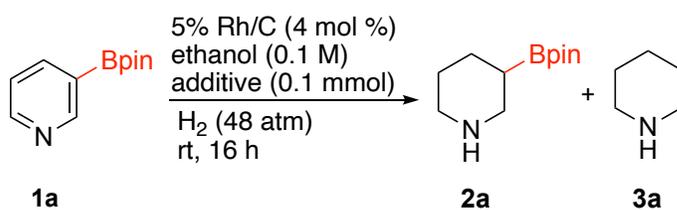
**Table S1 Additives for the hydrogenation of 1a by Rh/C<sup>a</sup>**



| Entry | Additive (1 equiv)             | Time (h) | 1a (%) | 2a (%) | 1a' (%) |
|-------|--------------------------------|----------|--------|--------|---------|
| 1     | HCl                            | 16       | 75     | 25     | 0       |
| 2     | HCl (dry)                      | 1        | 72     | 28     | 0       |
| 3     | HCl + 1 mL H <sub>2</sub> O    | 1        | 71     | 28     | 1       |
| 4     | MeSO <sub>3</sub> H            | 2        | 63     | 37     | 0       |
| 5     | NH <sub>4</sub> Cl             | 24       | 0      | 70     | 30      |
| 6     | H <sub>3</sub> PO <sub>4</sub> | 2        | 58     | 42     | 0       |
| 7     | 2,6-Dichloropyridine           | 36       | 38     | 62     | 0       |
| 8     | Sulfuric Acid                  | 2        | 39     | 61     | 0       |
| 9     | Triflic acid                   | 2        | 52     | 48     | 0       |

<sup>a</sup>Relative composition determined by <sup>1</sup>H-NMR (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.25 mmol), Additive (0.25 mmol), Hydrogen gas (48 atm), ethanol (2 mL), 5% Rh/C (10 mg), rt

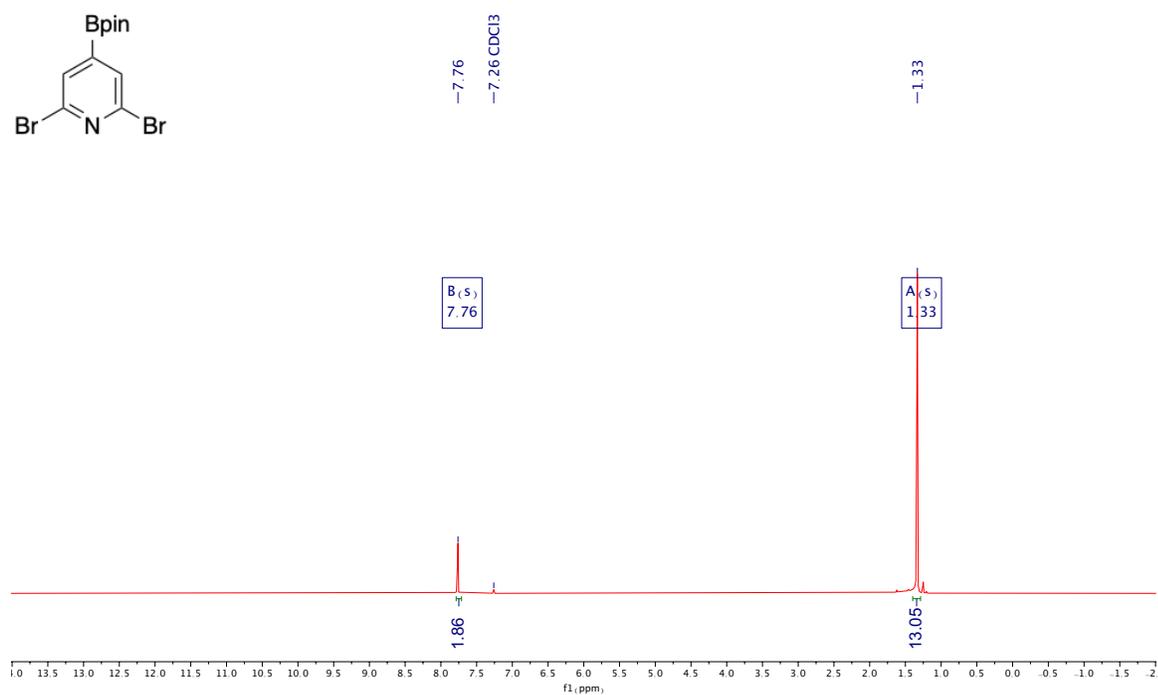
**Table S2 Additives for the hydrogenation of 1a by Rh/C<sup>a</sup>**



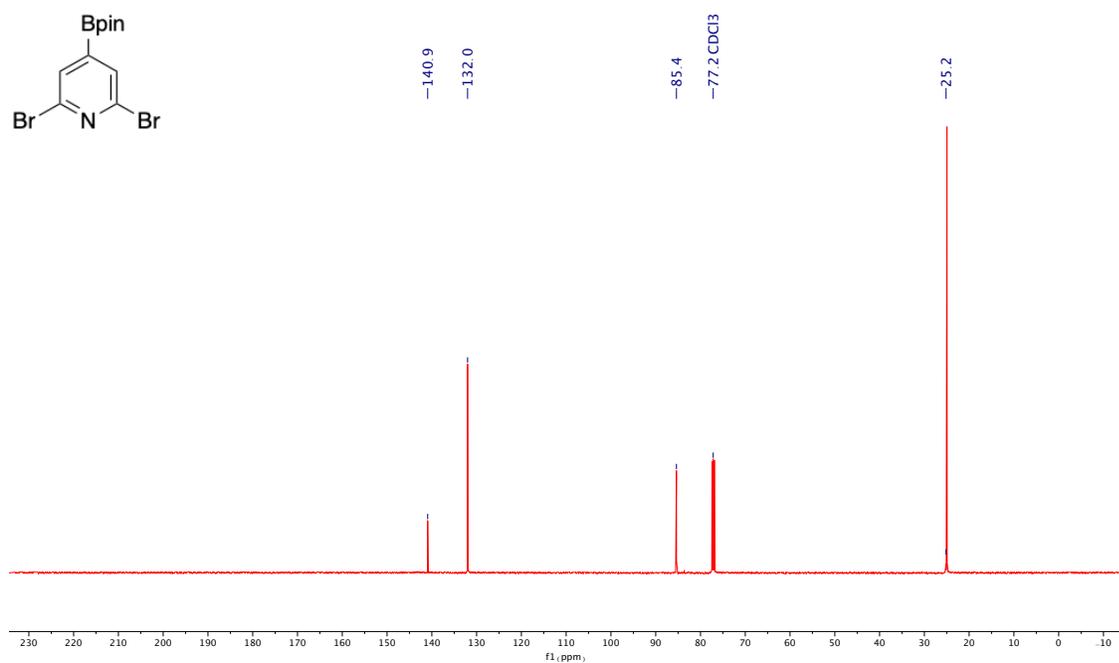
| Entry | Additive (1 equiv)    | <b>1a</b><br>(%) | <b>2a</b><br>(%) | <b>1a'</b> |
|-------|-----------------------|------------------|------------------|------------|
| 1     | Cerium (III) chloride | 0                | 100              | 0          |
| 2     | Magnesium chloride    | 0                | 30               | 70         |
| 3     | Copper sulfate        | 20               | 18               | 62         |
| 4     | Potassium Iodide      | 16               | 42               | 42         |
| 5     | Zinc chloride         | 0                | 15               | 85         |
| 6     | Iron powder (rusted)  | 0                | 15               | 85         |
| 7     | Magnesium sulfate     | 0                | 17               | 83         |
| 8     | Trimethyl borate      | 0                | 11               | 89         |
| 9     | 3Å molecular sieves   | 0                | 19               | 81         |

a) Conversion percentages determined by GCMS by comparing piperidine to starting material. 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.1 mmol), Additive (0.1 mmol), Hydrogen gas (700 psi), Ethanol (1 mL), 5% Rh/C (10 mg), rt.

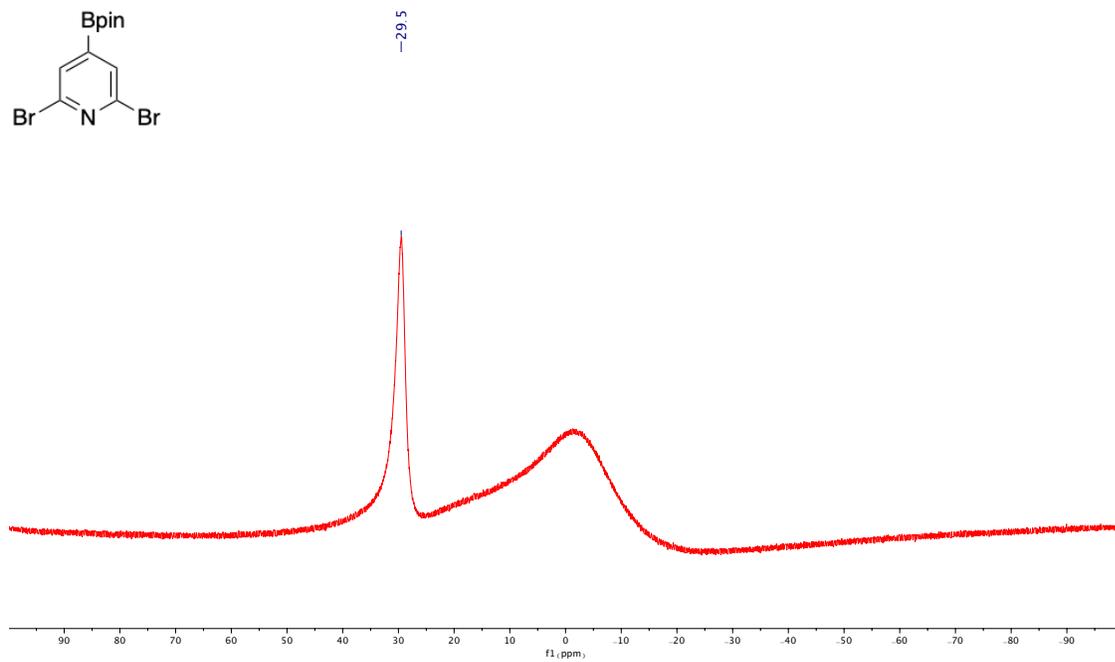
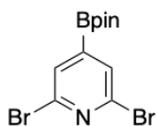
$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



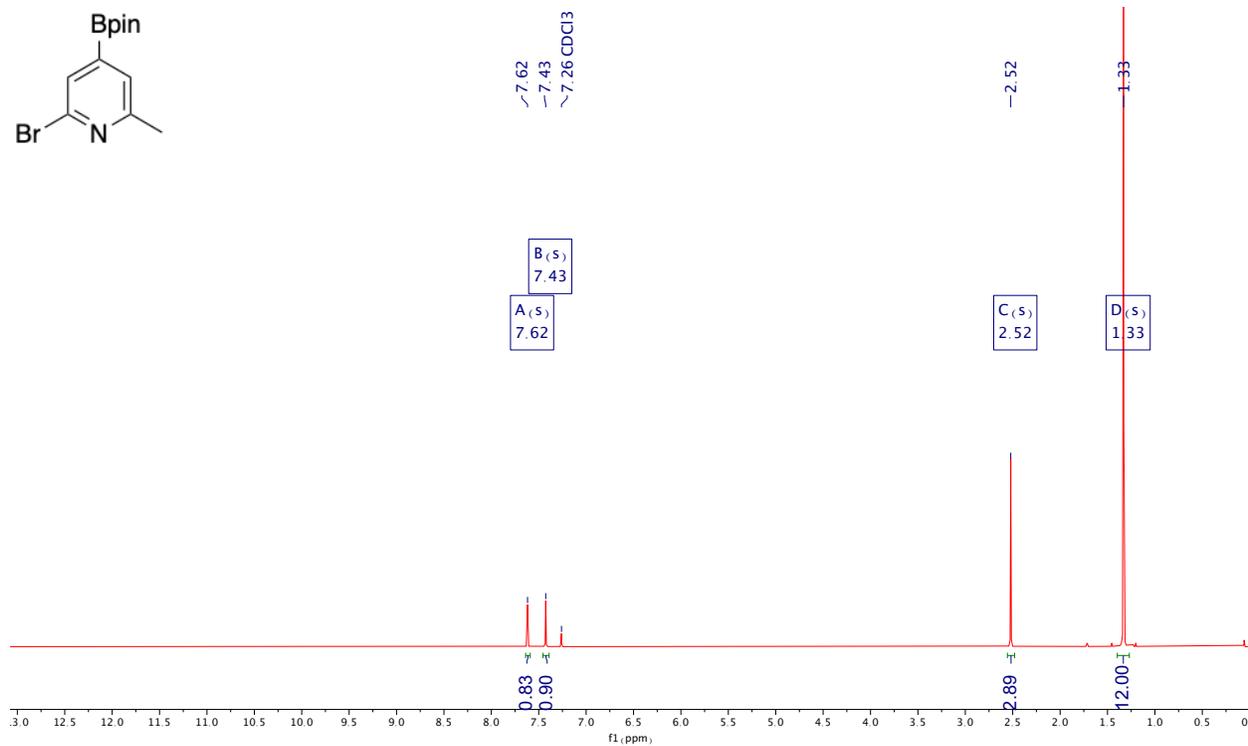
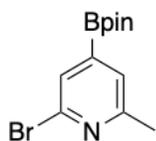
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



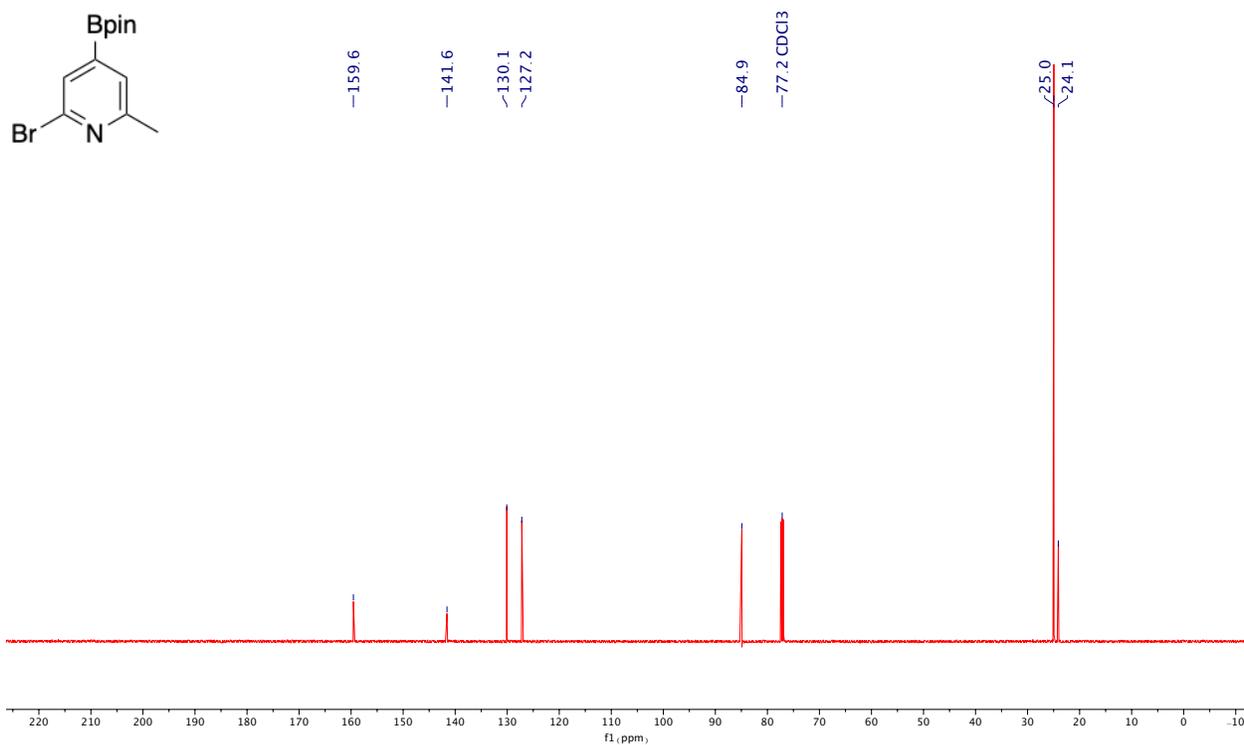
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



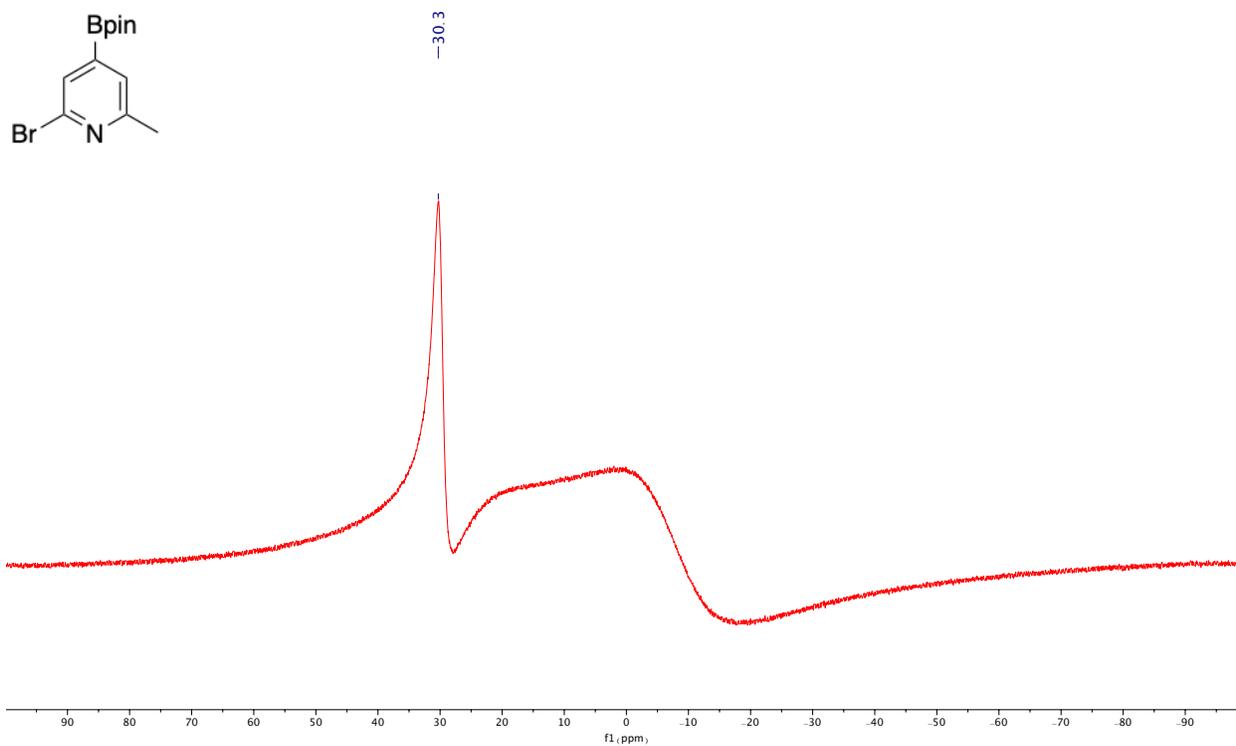
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1e)



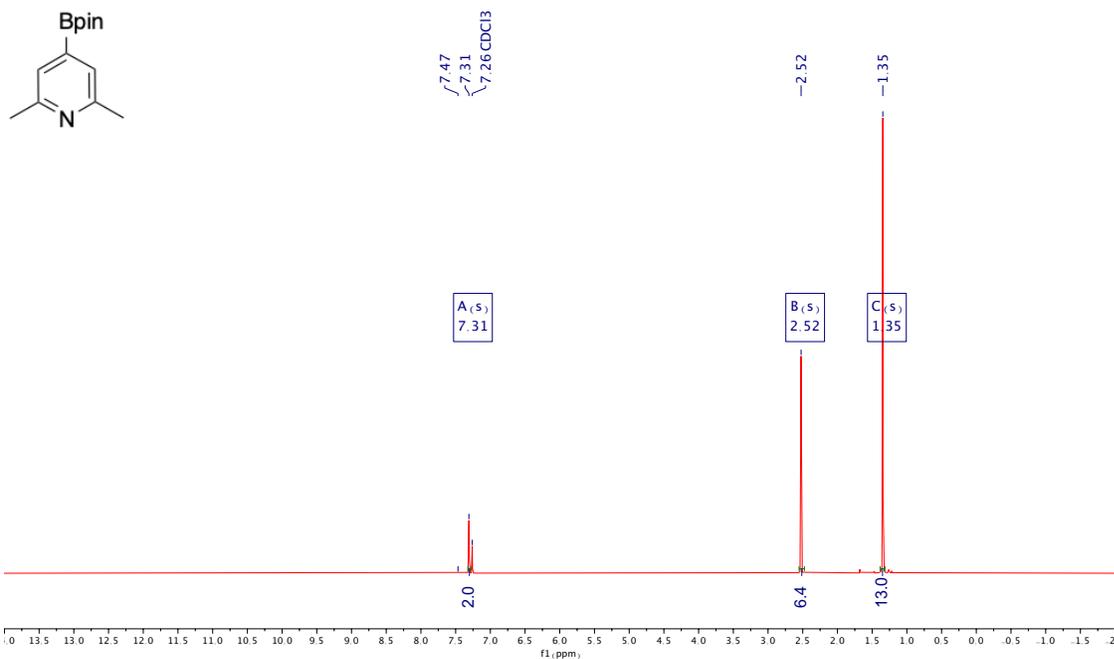
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1e)



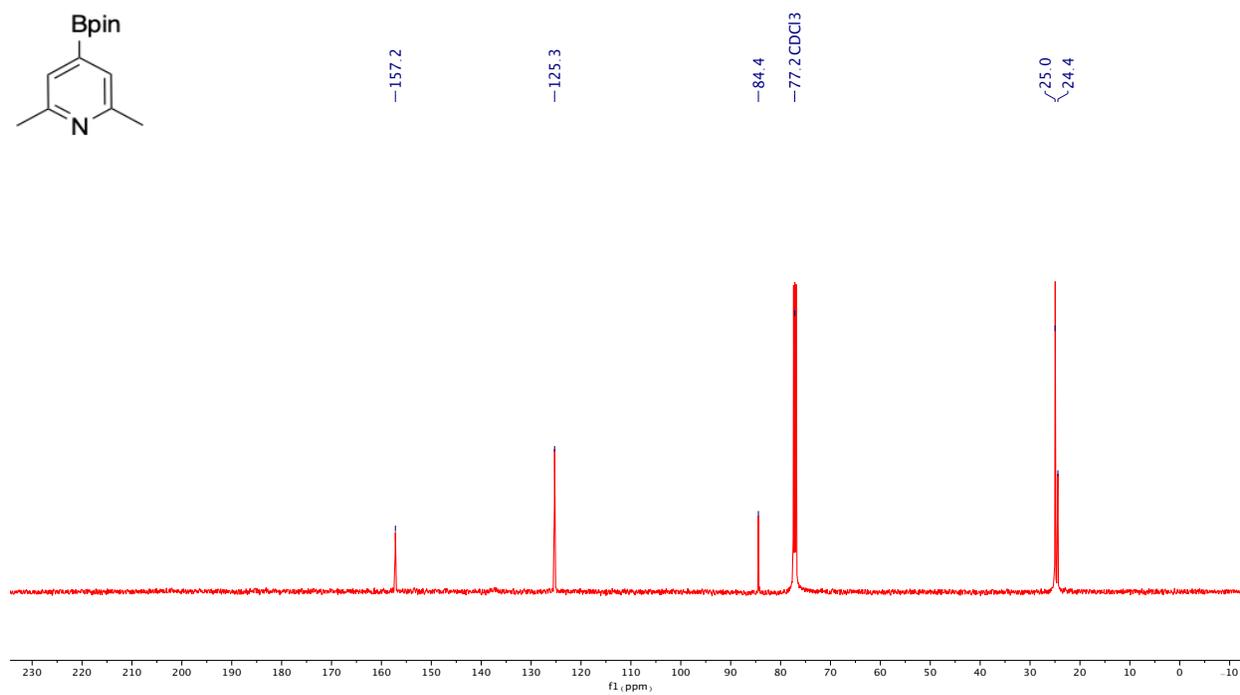
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1e)



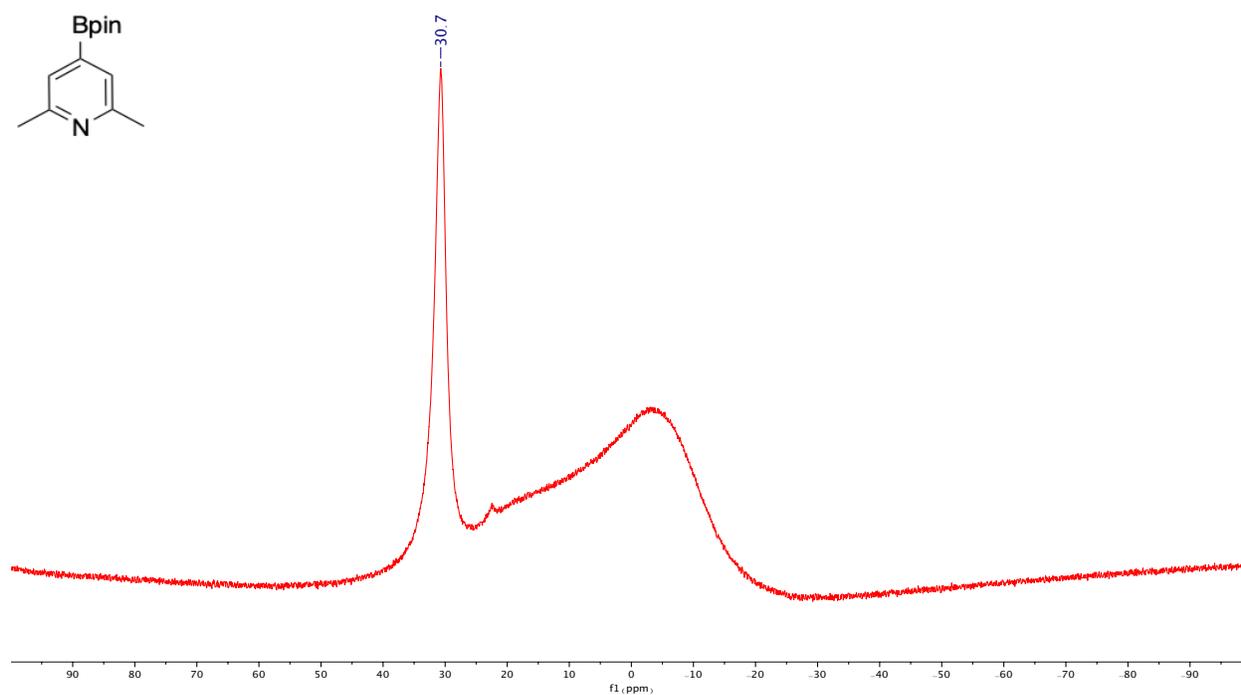
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)



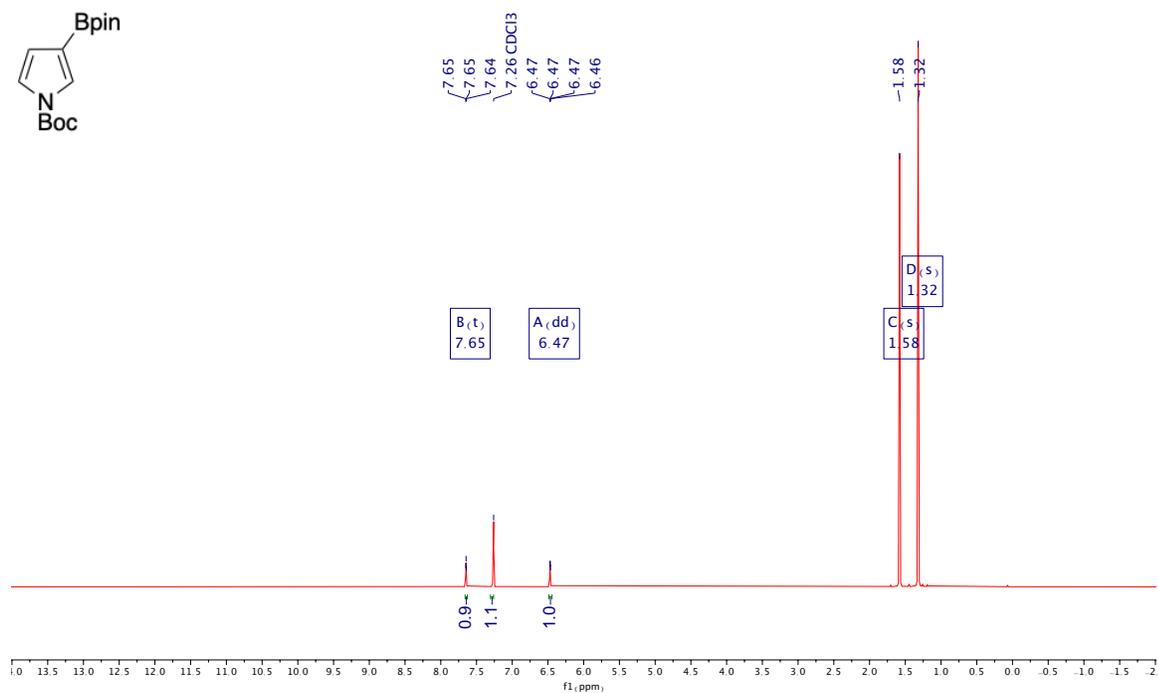
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)



$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)

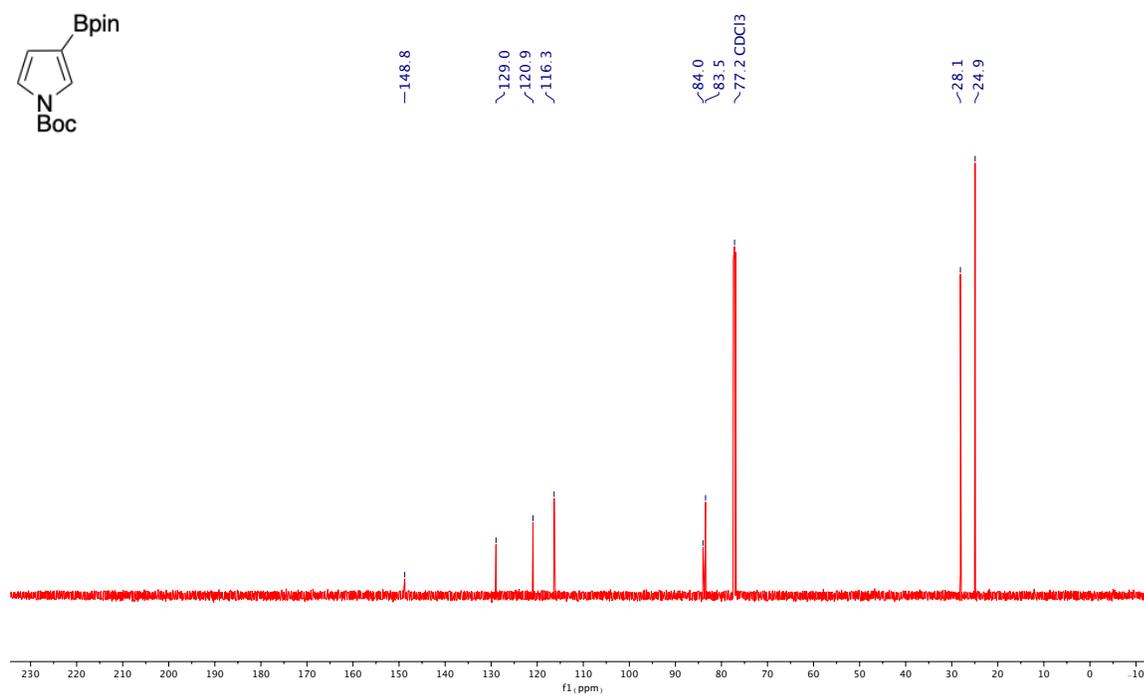


$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (1g)

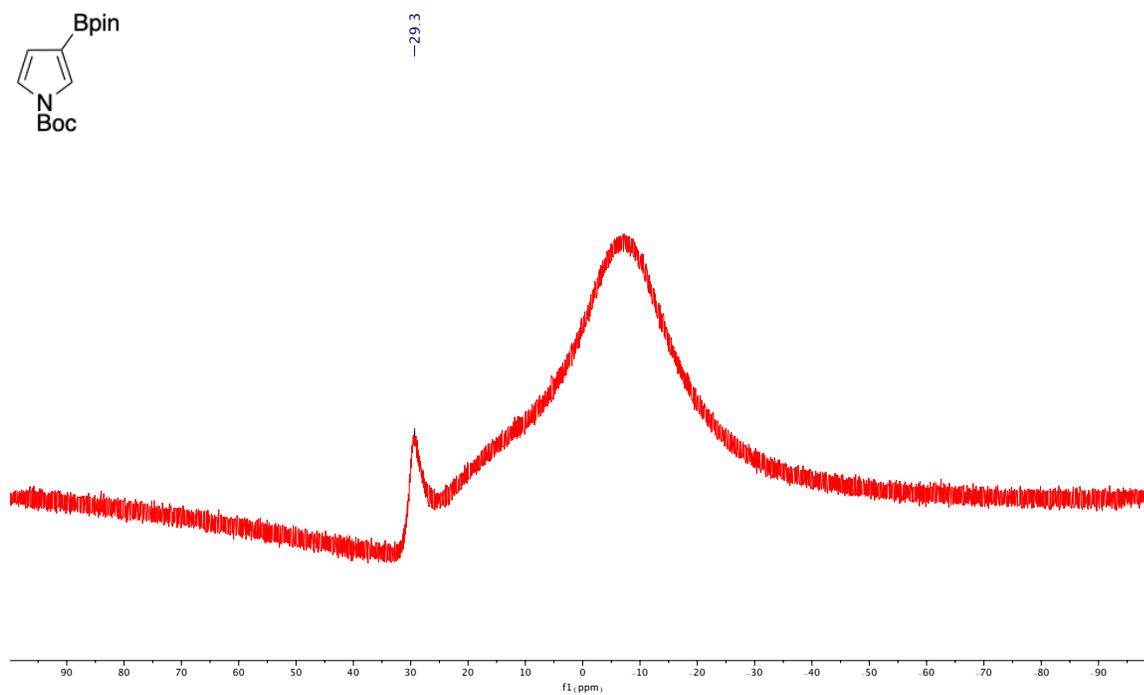


$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate

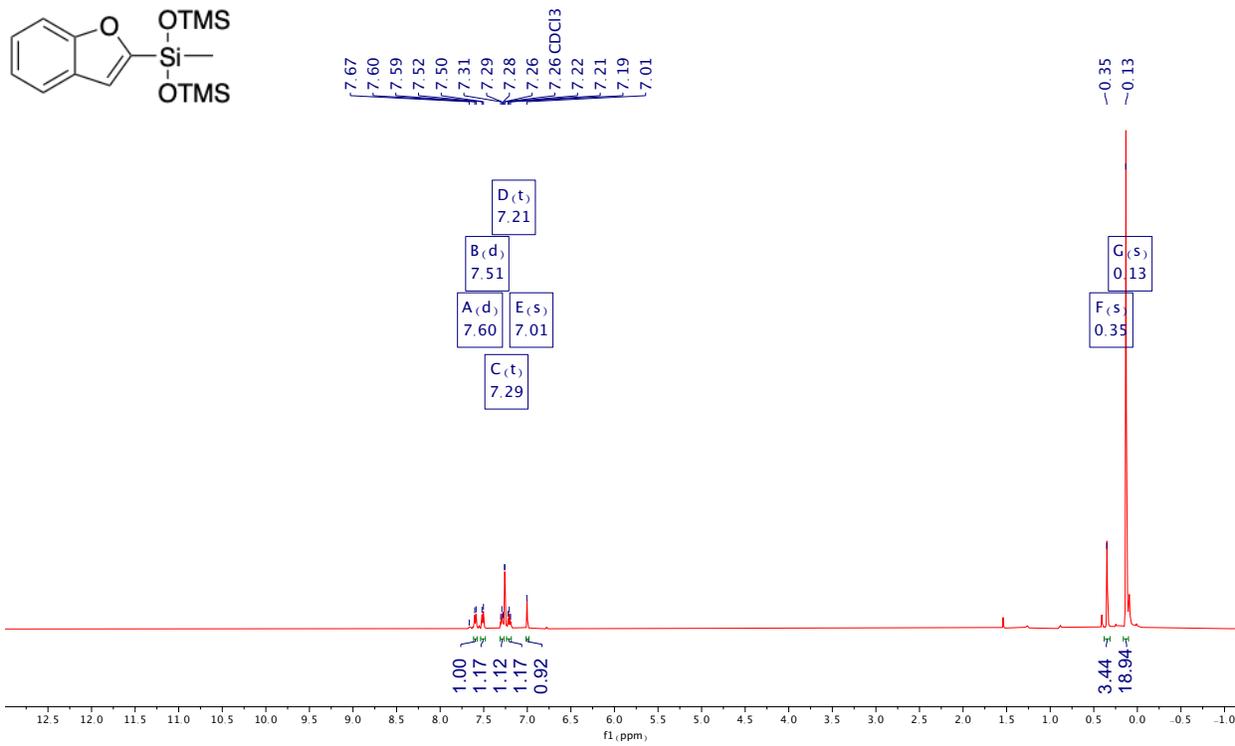
(1g)



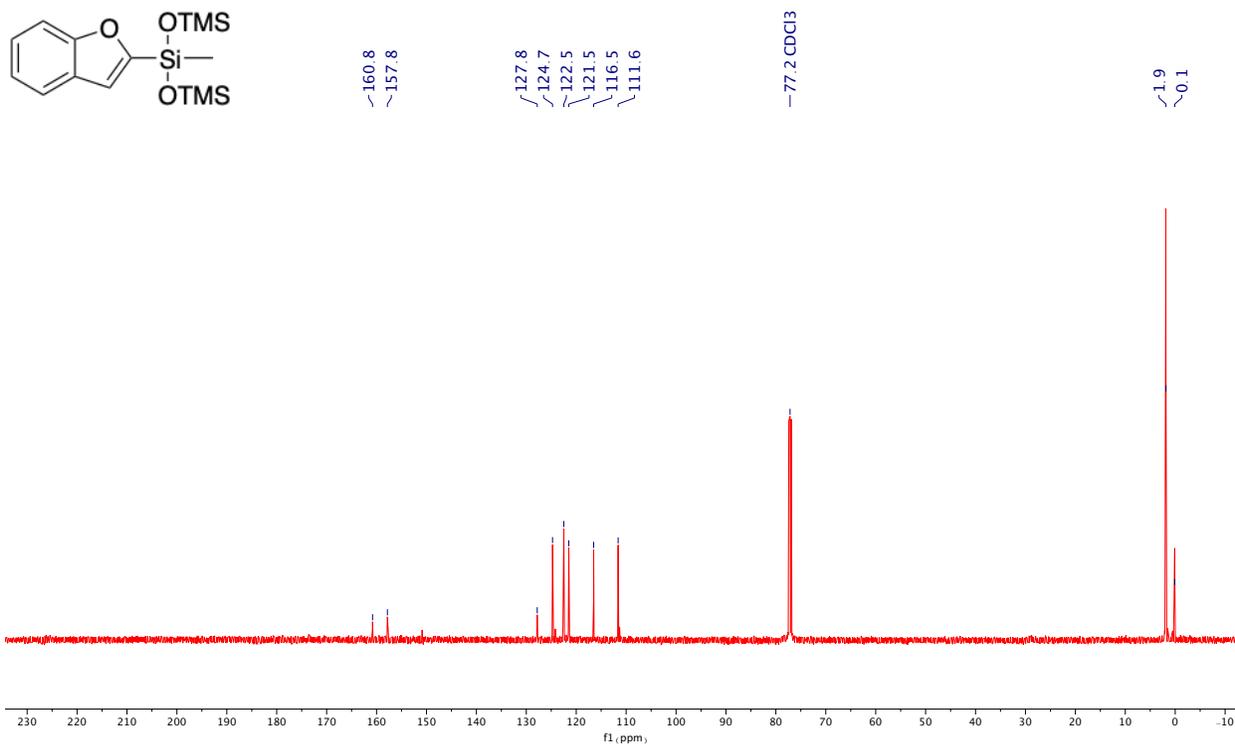
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (1g)



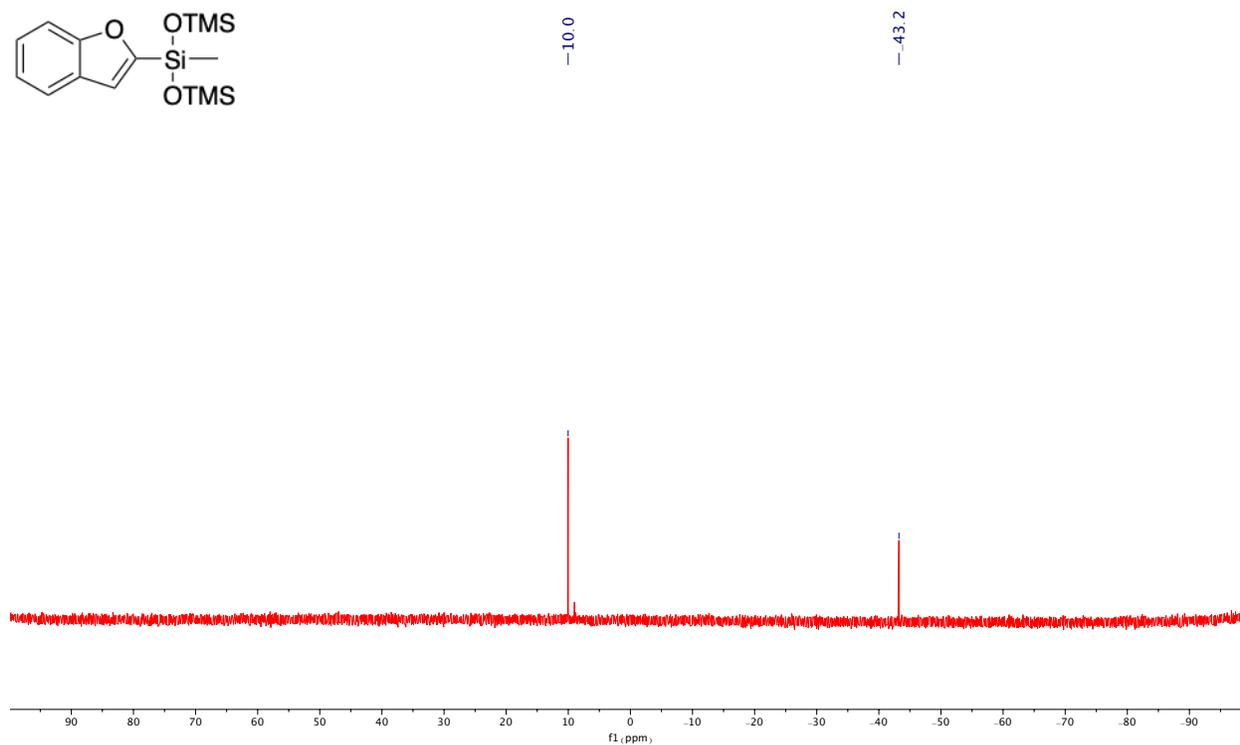
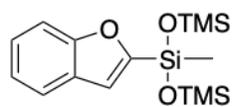
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptomethyltrisiloxane (1z)



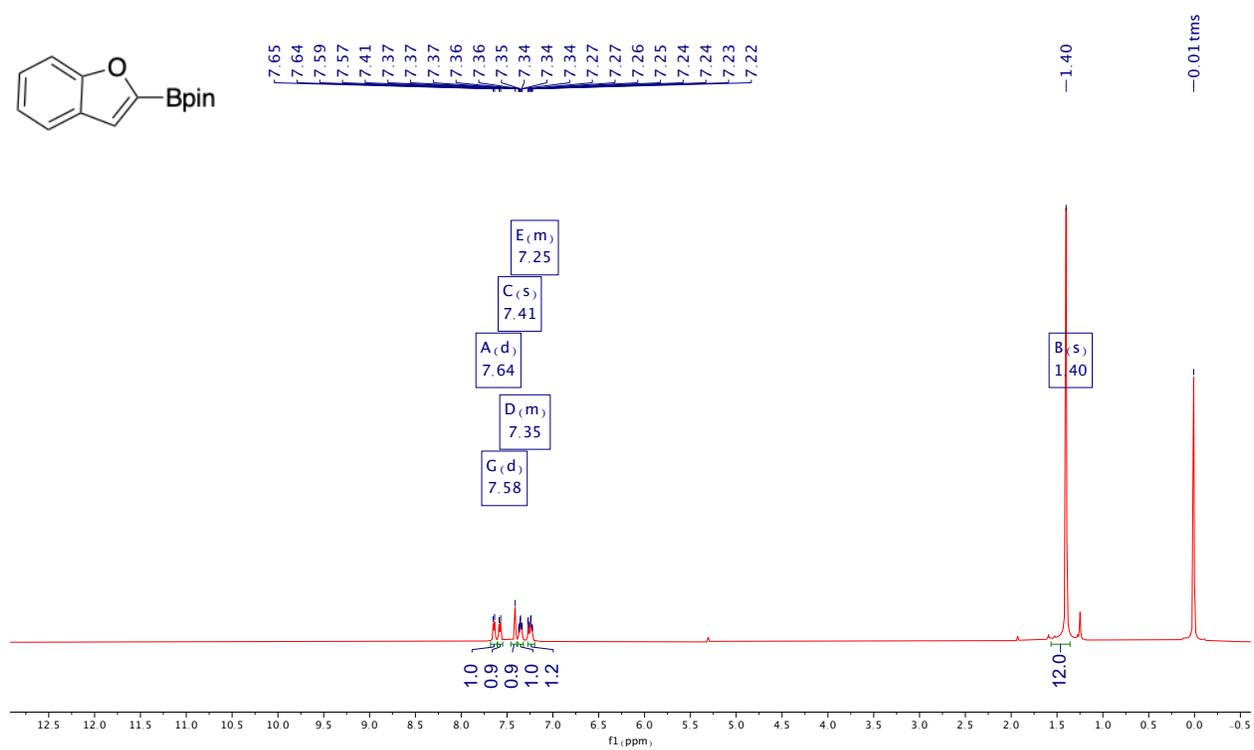
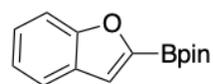
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptomethyltrisiloxane (1z)



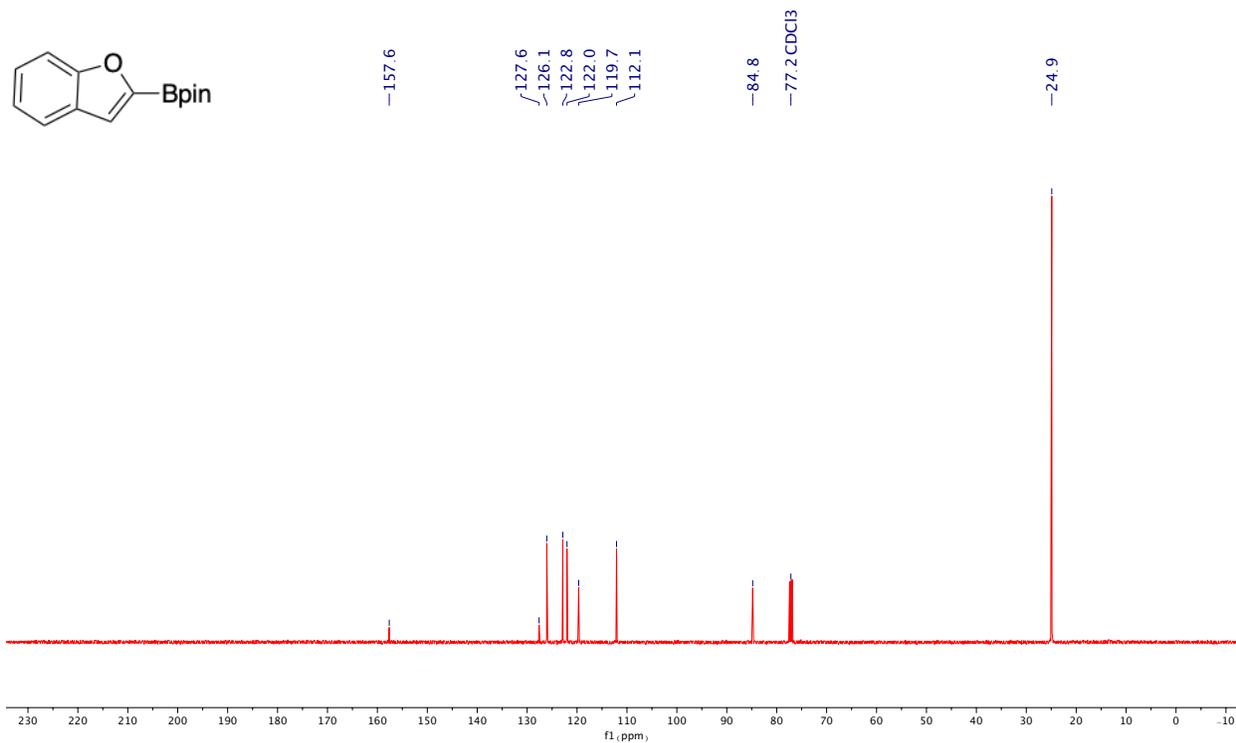
<sup>29</sup>Si NMR (99MHz, CDCl<sub>3</sub>) of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (1z)



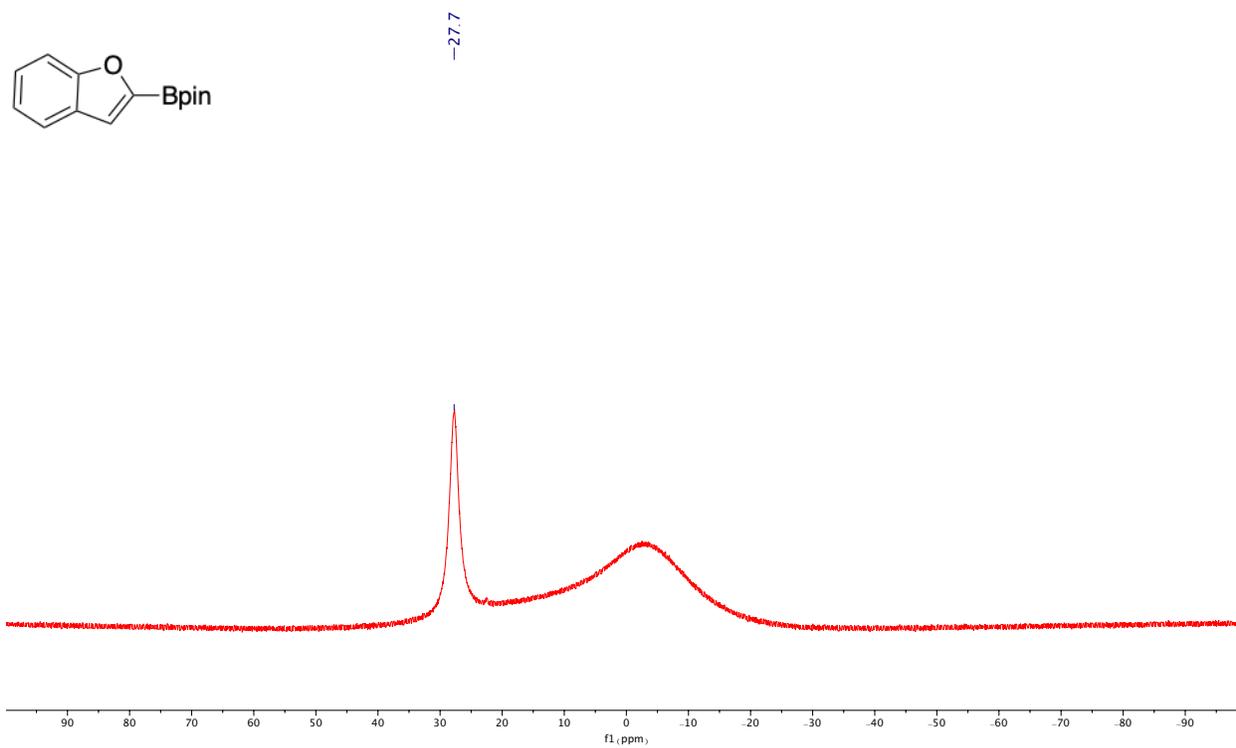
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



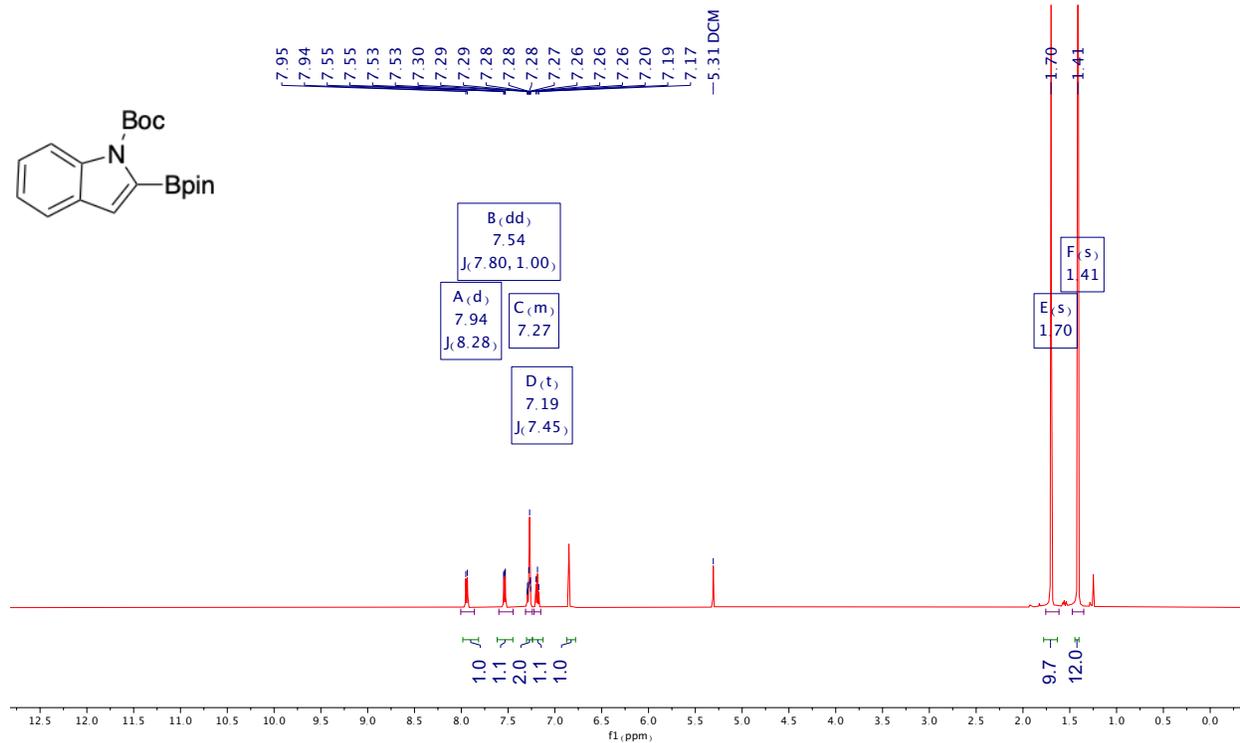
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



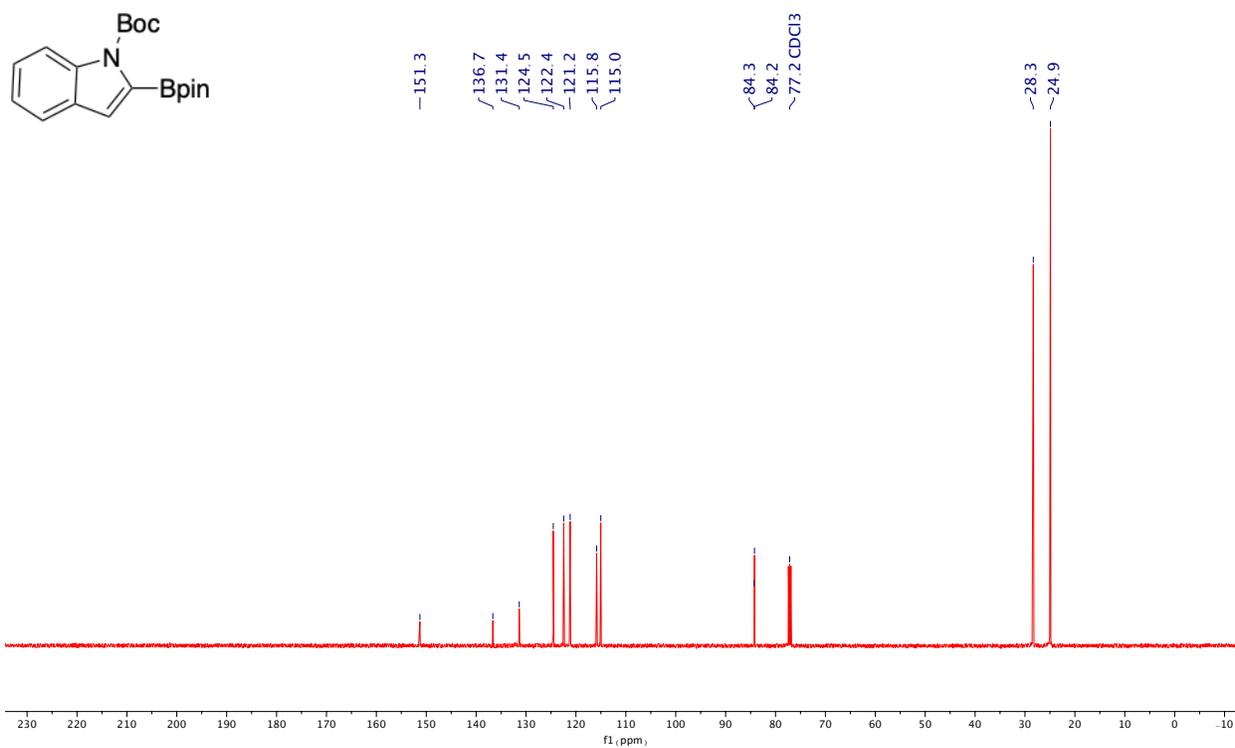
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



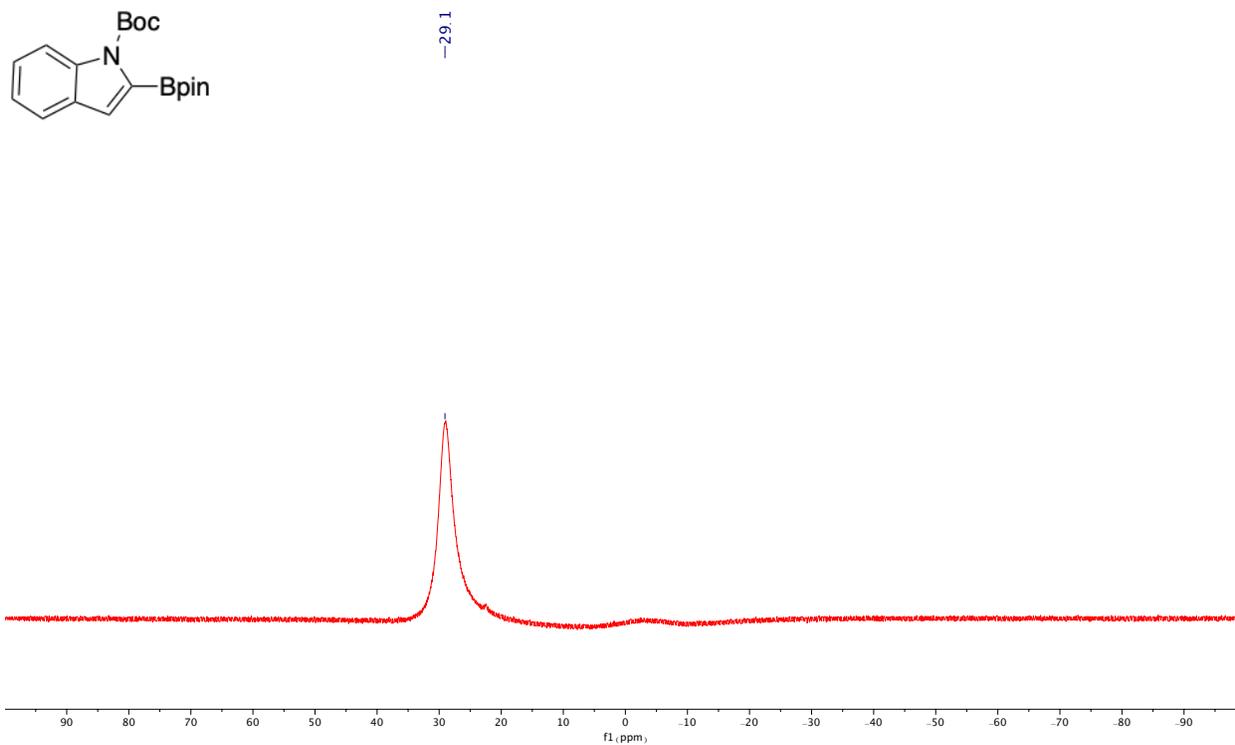
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of *Tert*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (11)



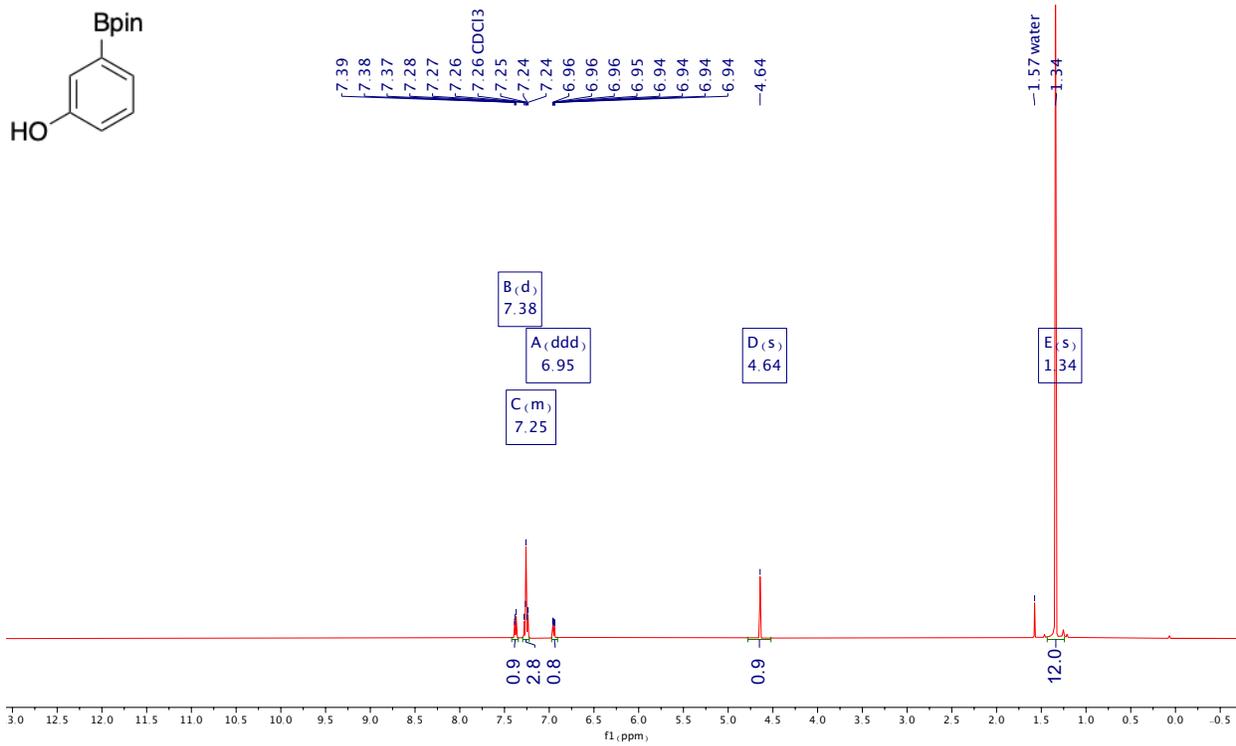
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of *Tert*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (11)



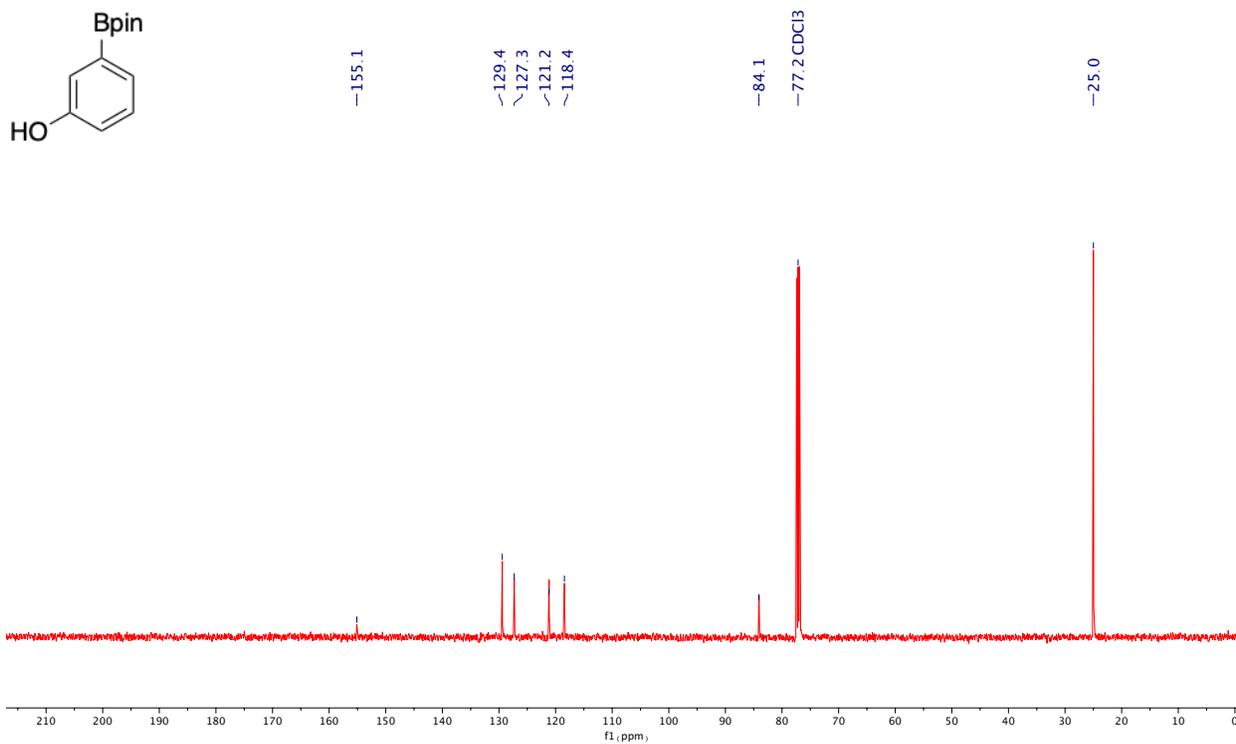
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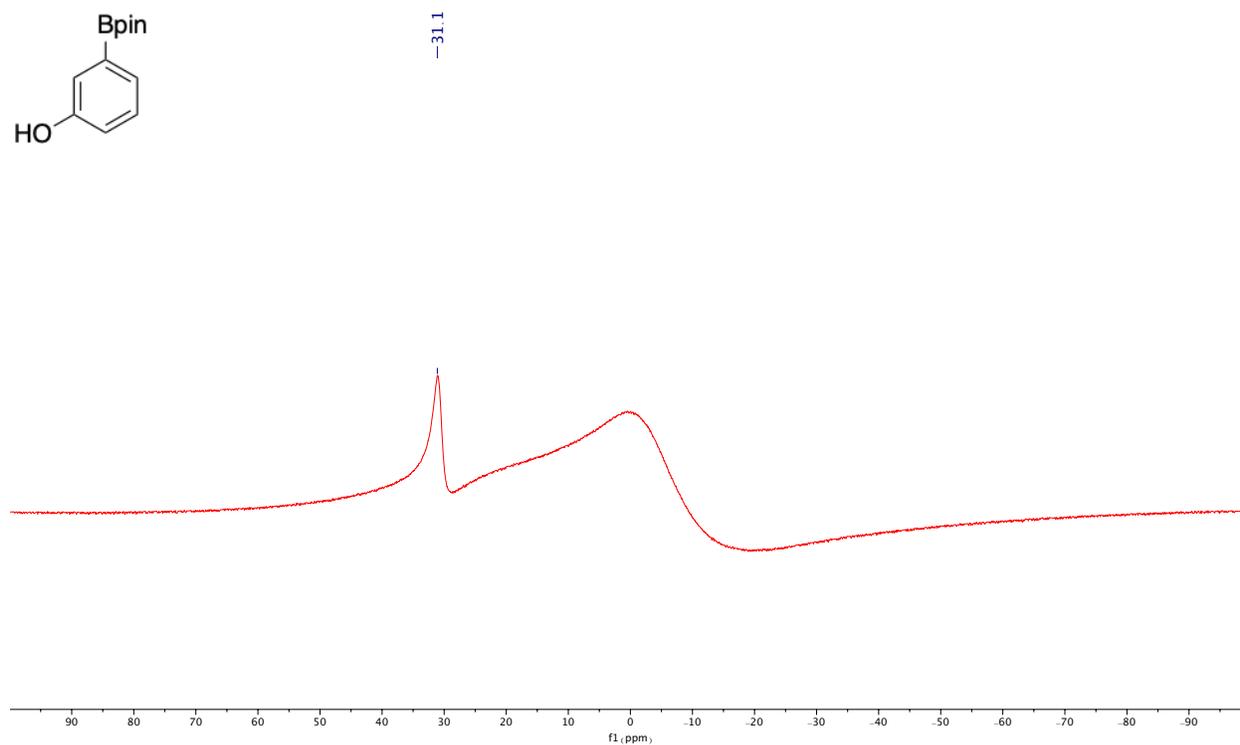
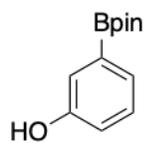
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)



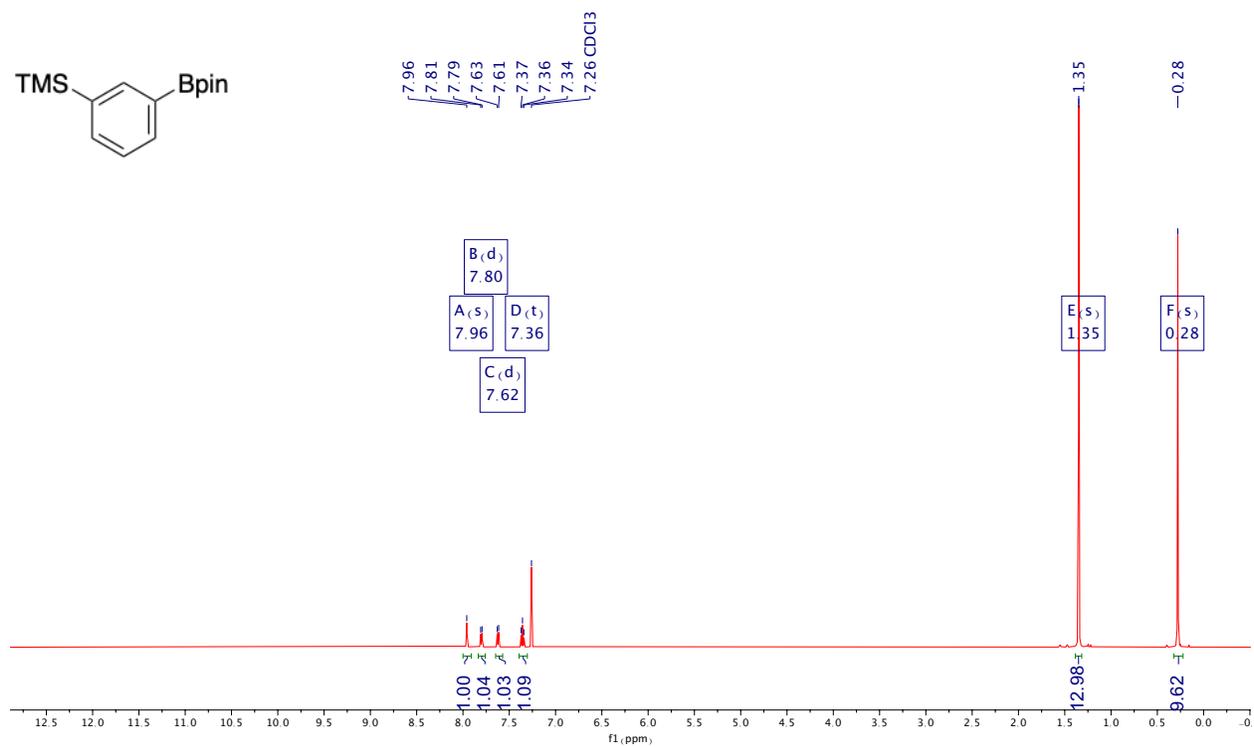
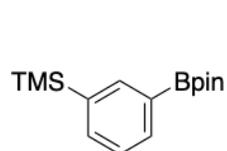
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)



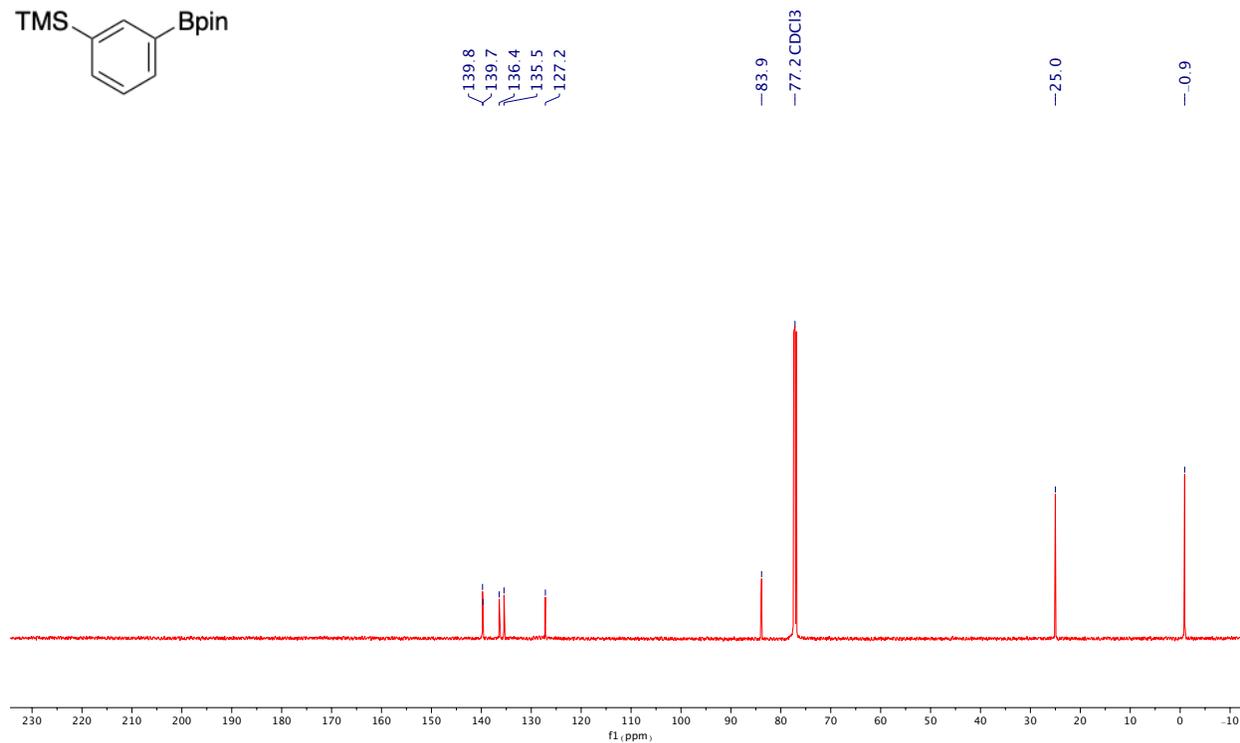
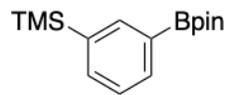
<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)



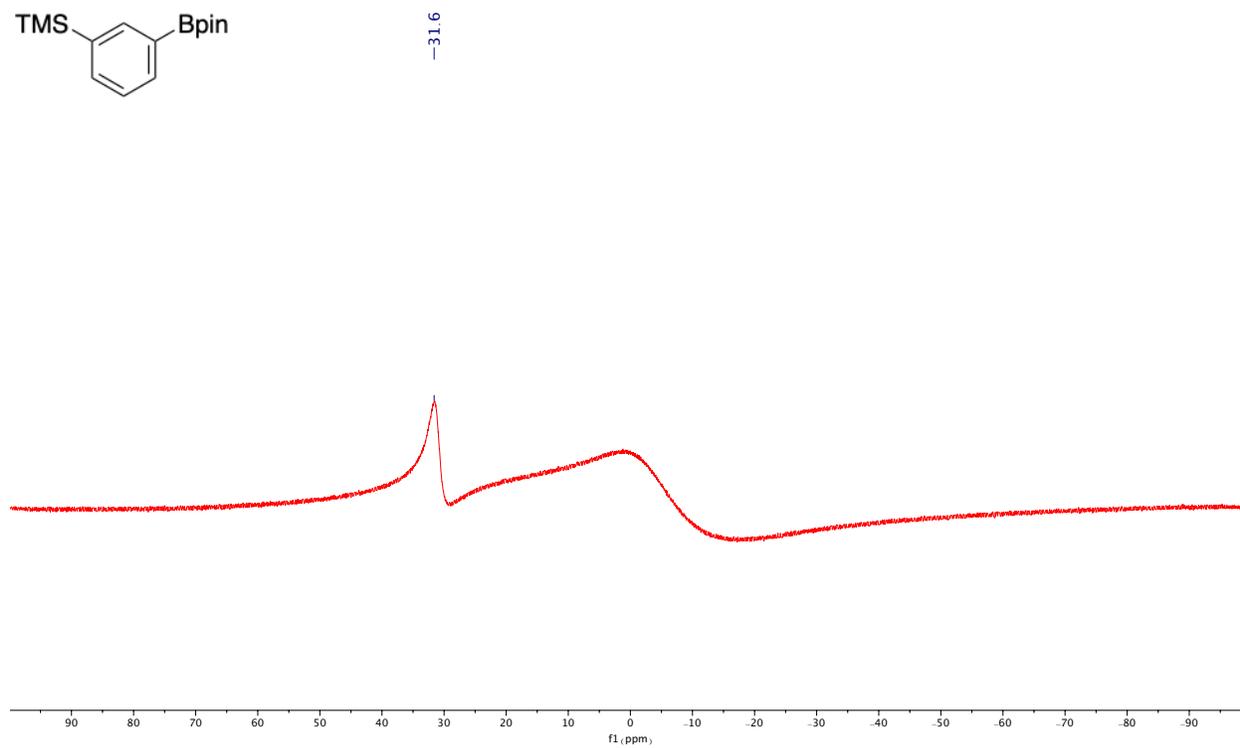
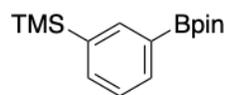
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



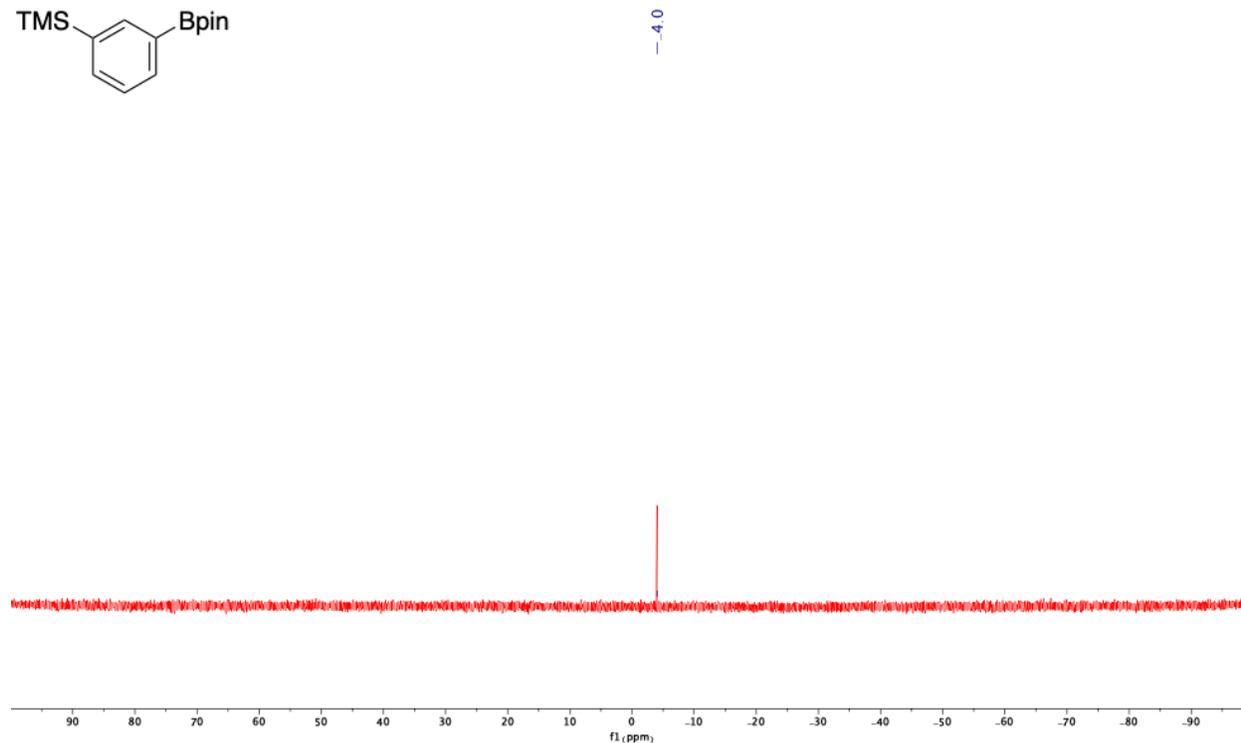
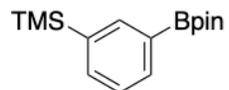
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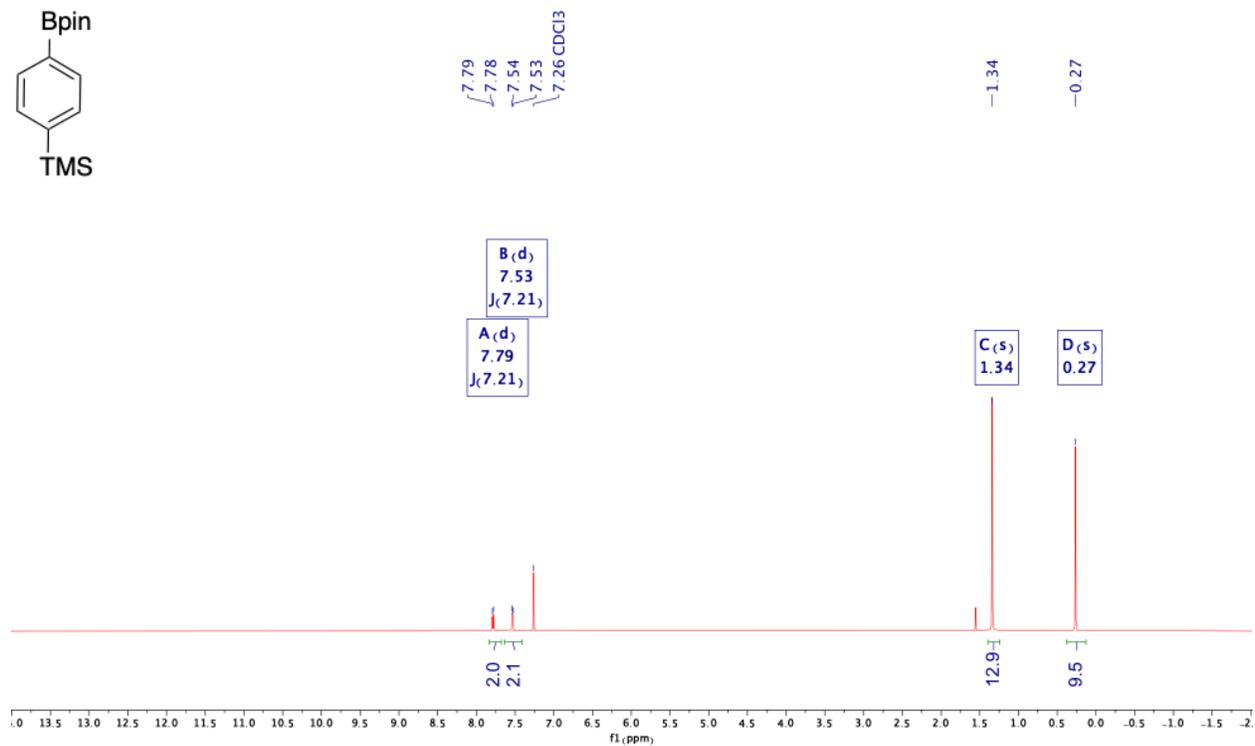
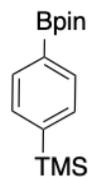
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



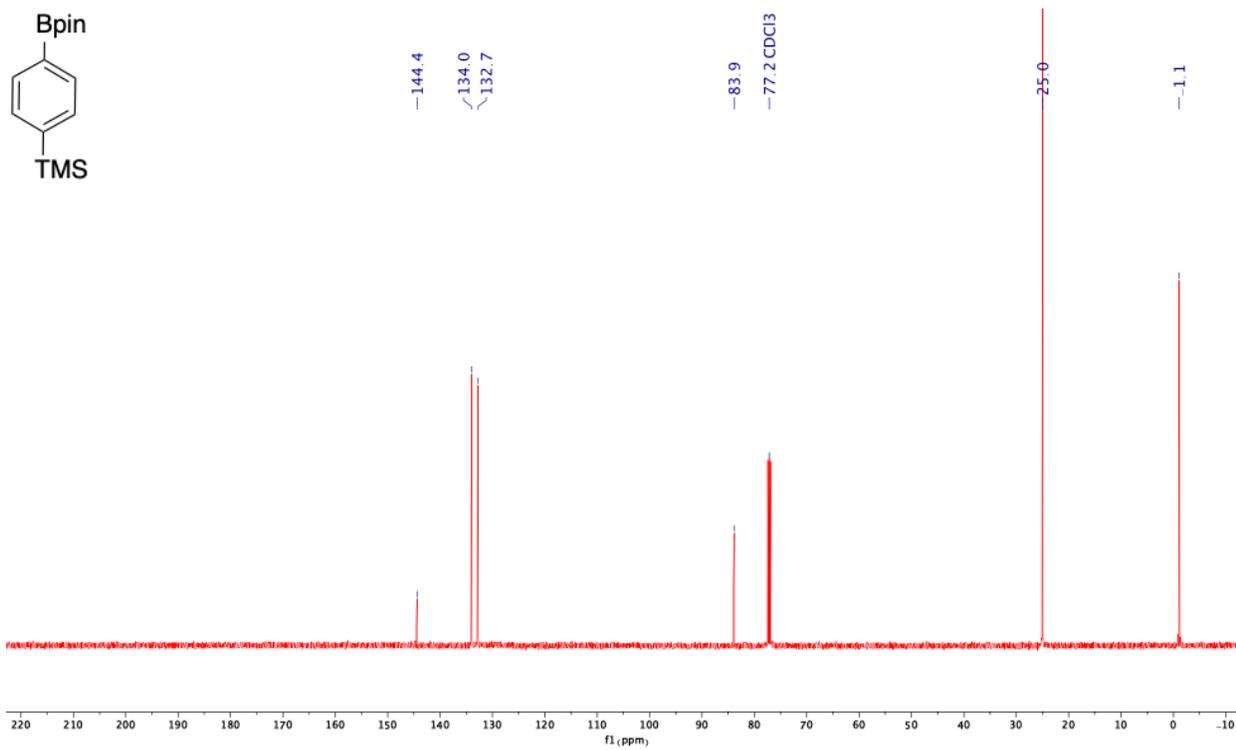
$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ ) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



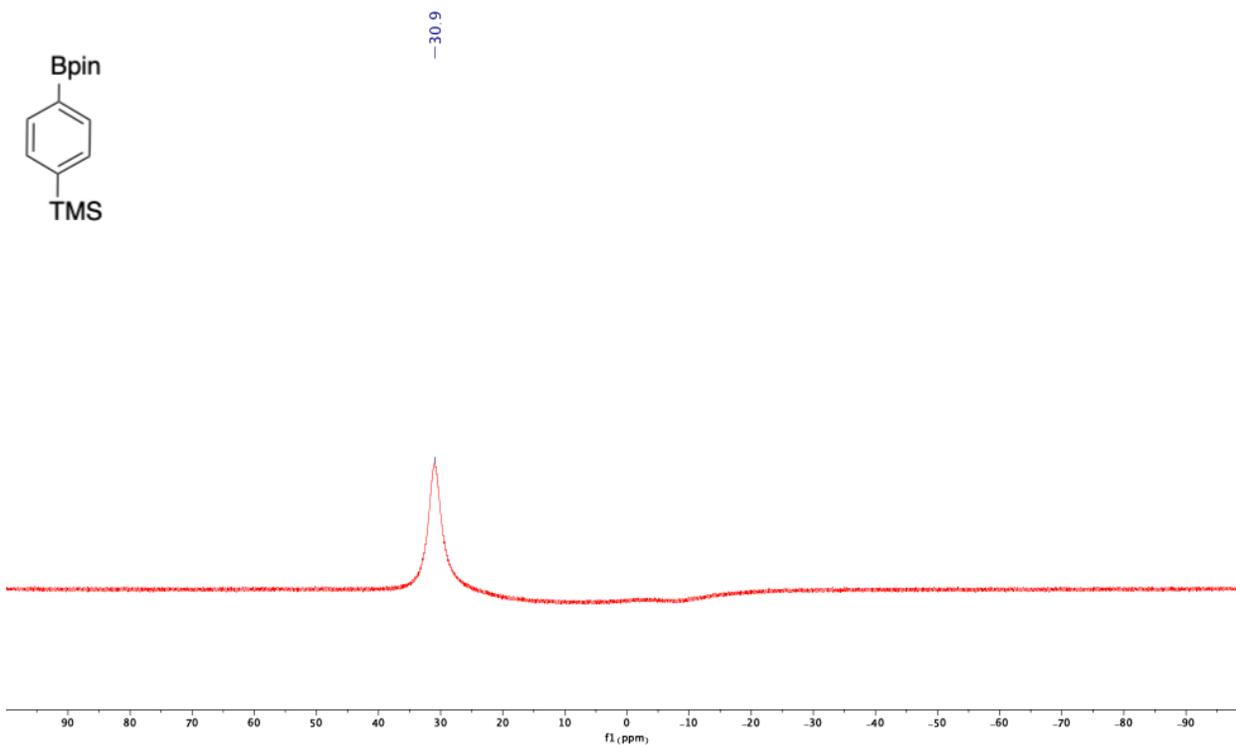
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1af)



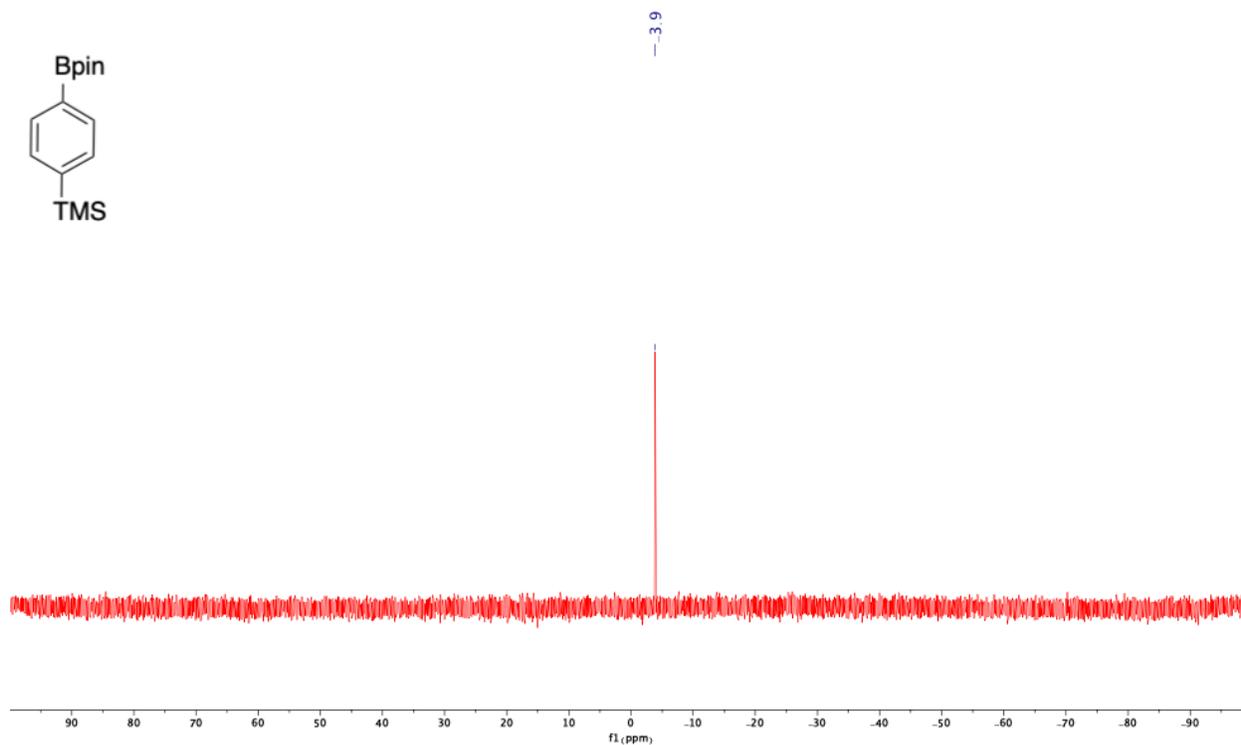
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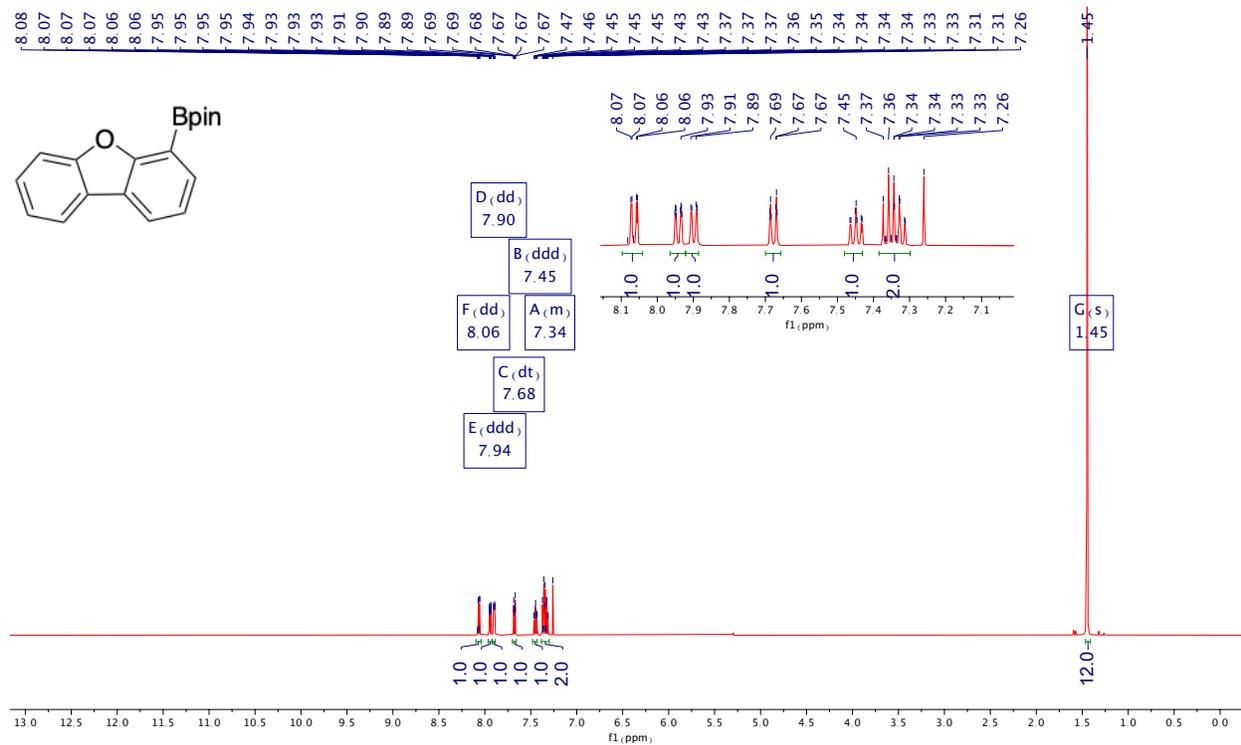
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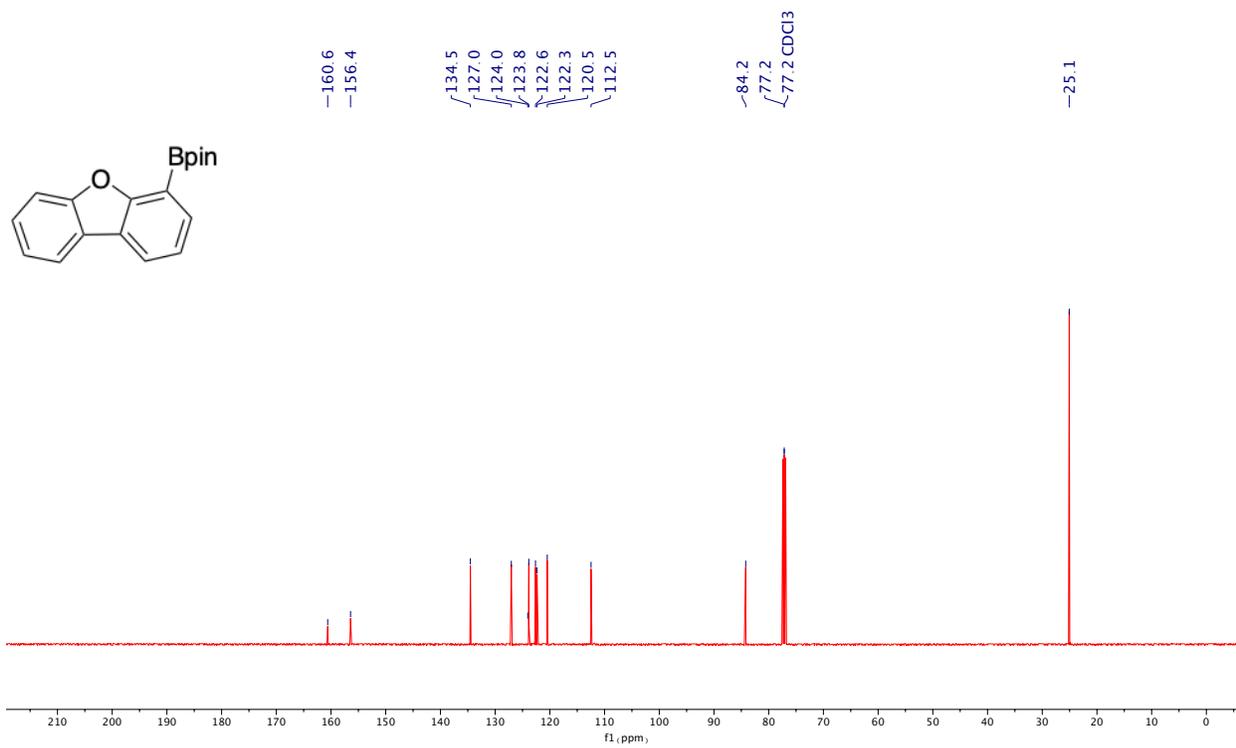
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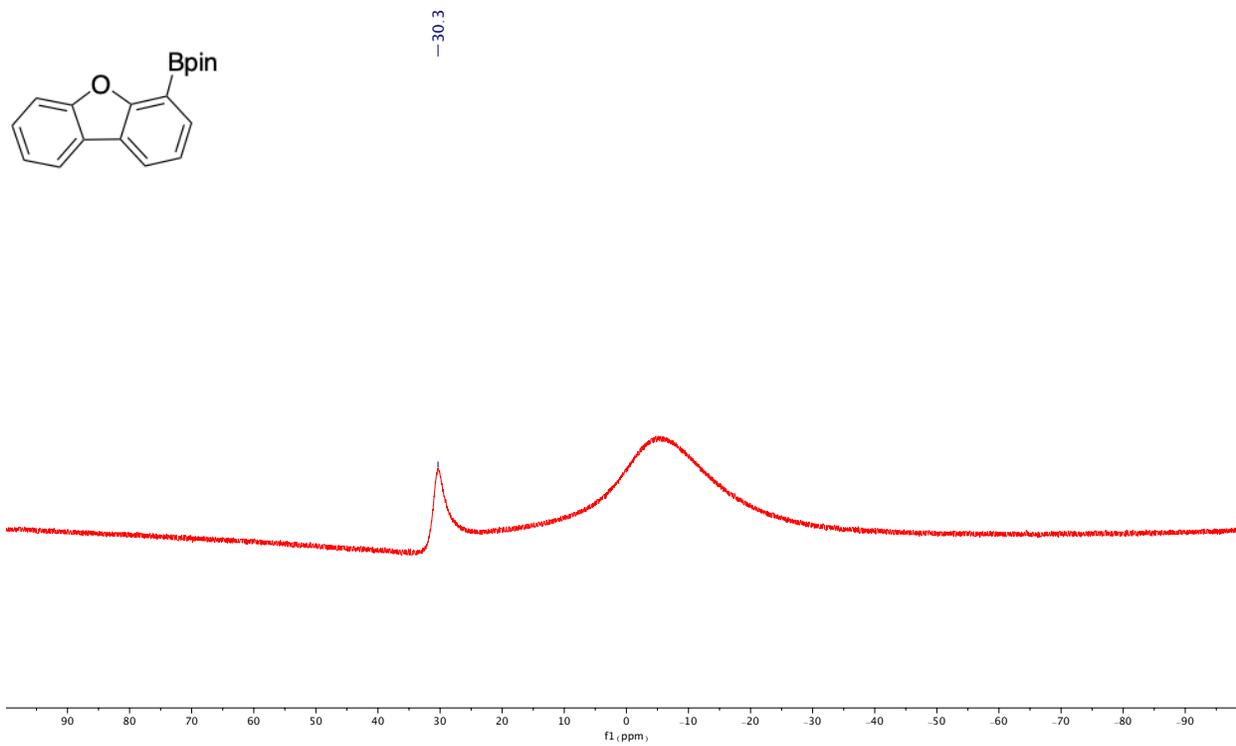
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2-(dibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k)



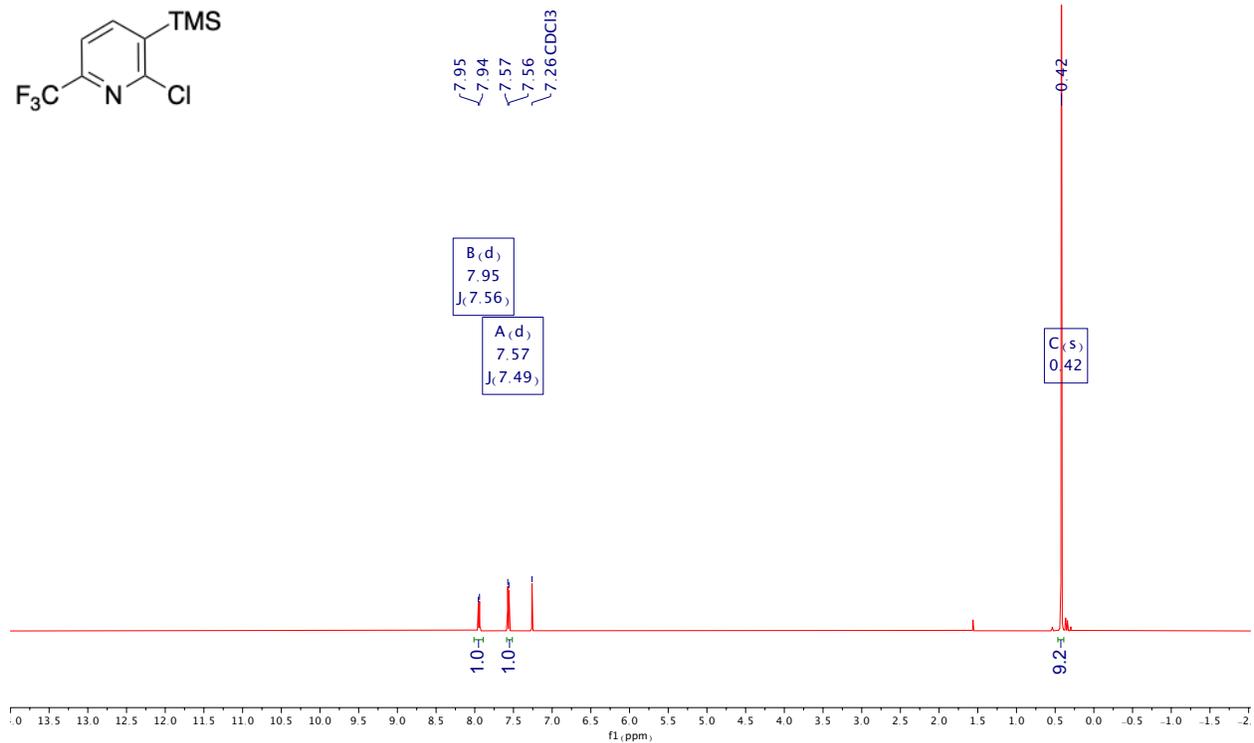
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 2-(dibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k)



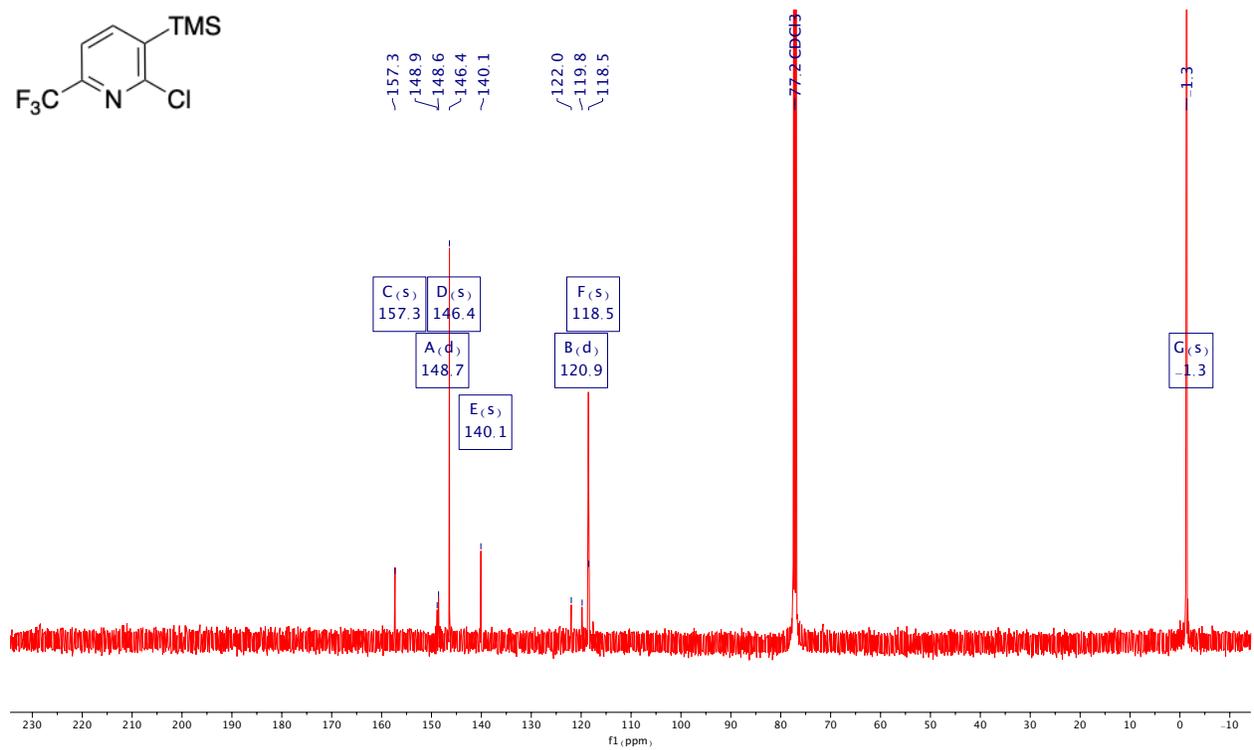
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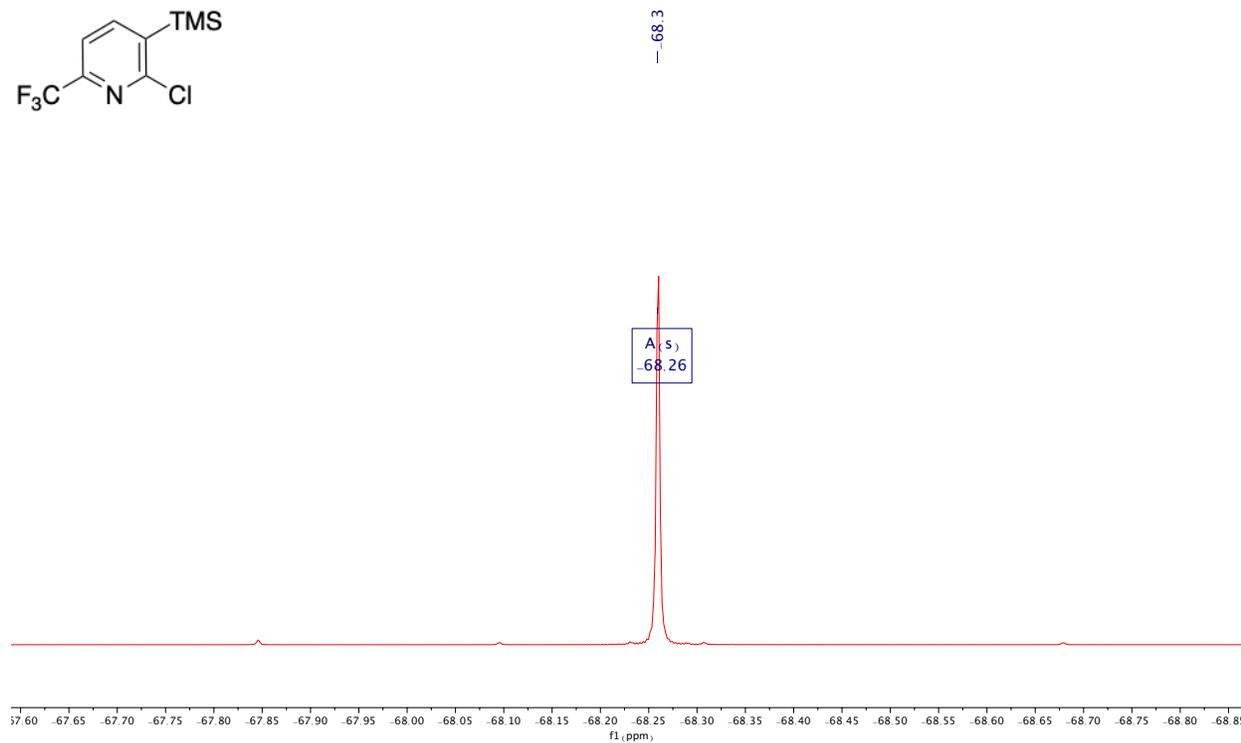
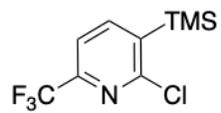
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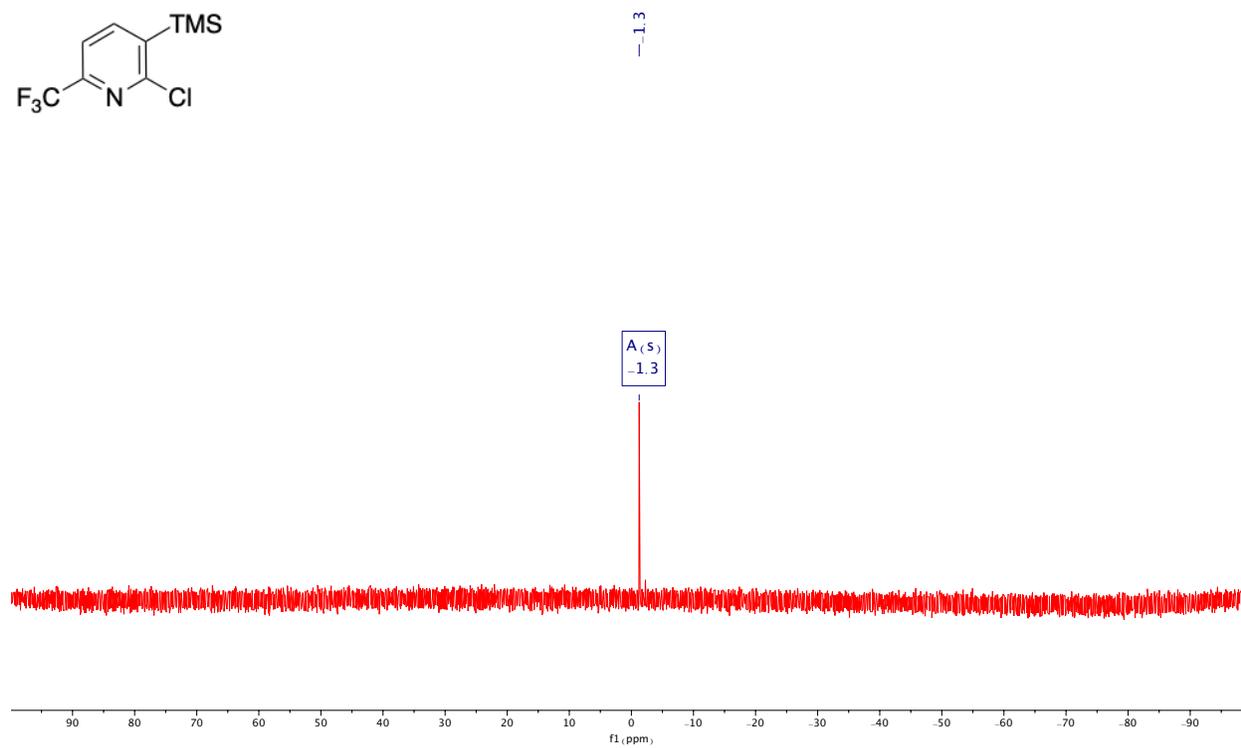
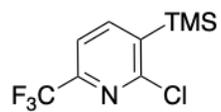
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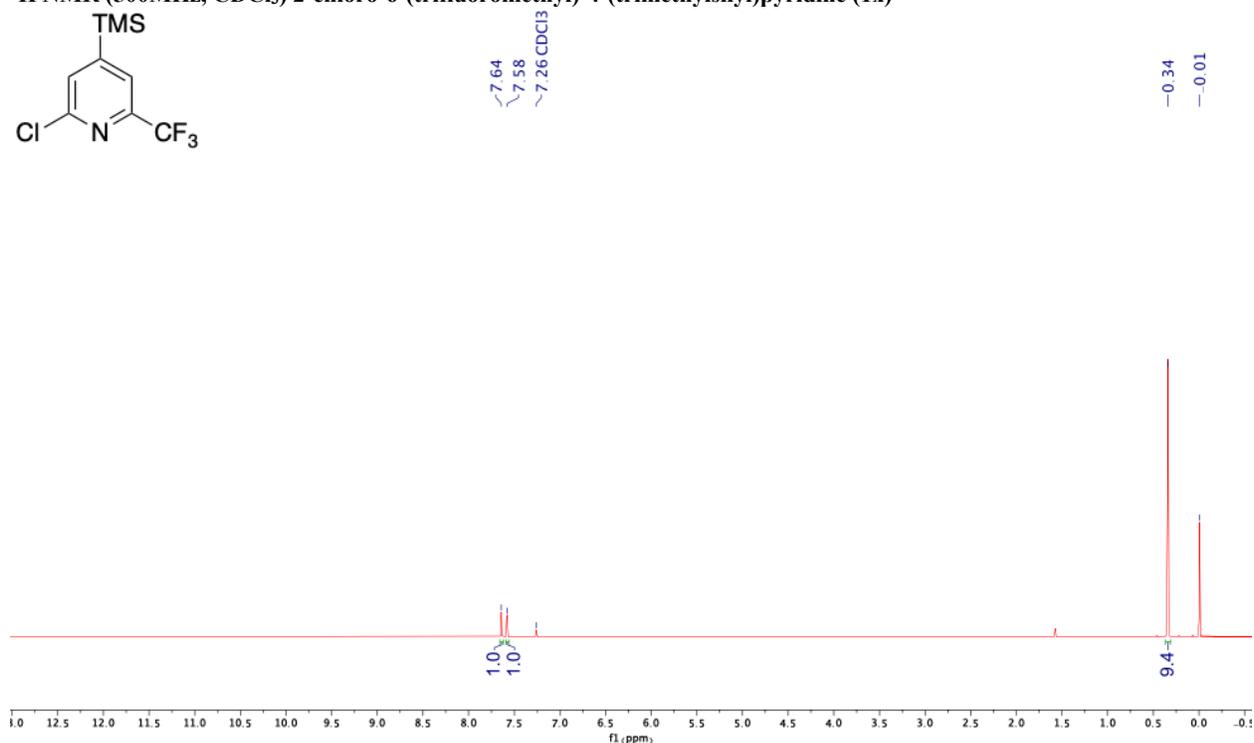
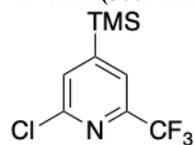
**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) of 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)**



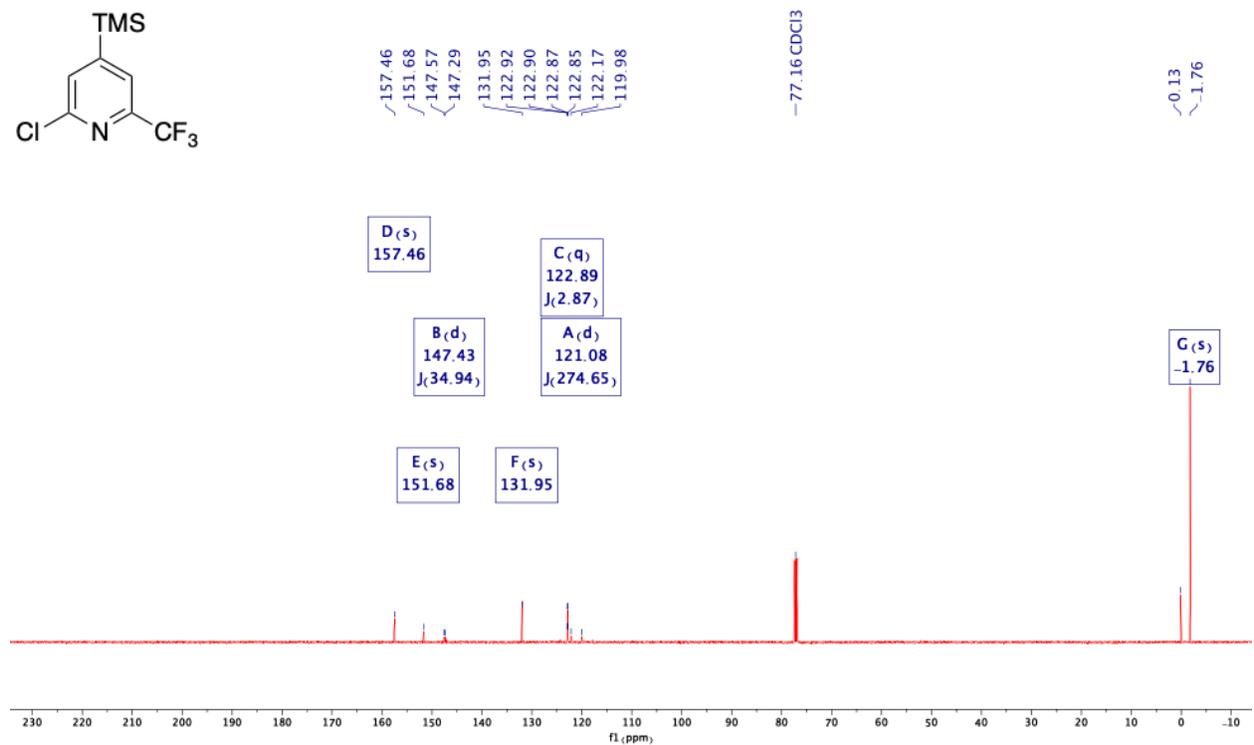
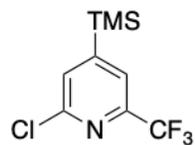
**$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ ) of 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)**



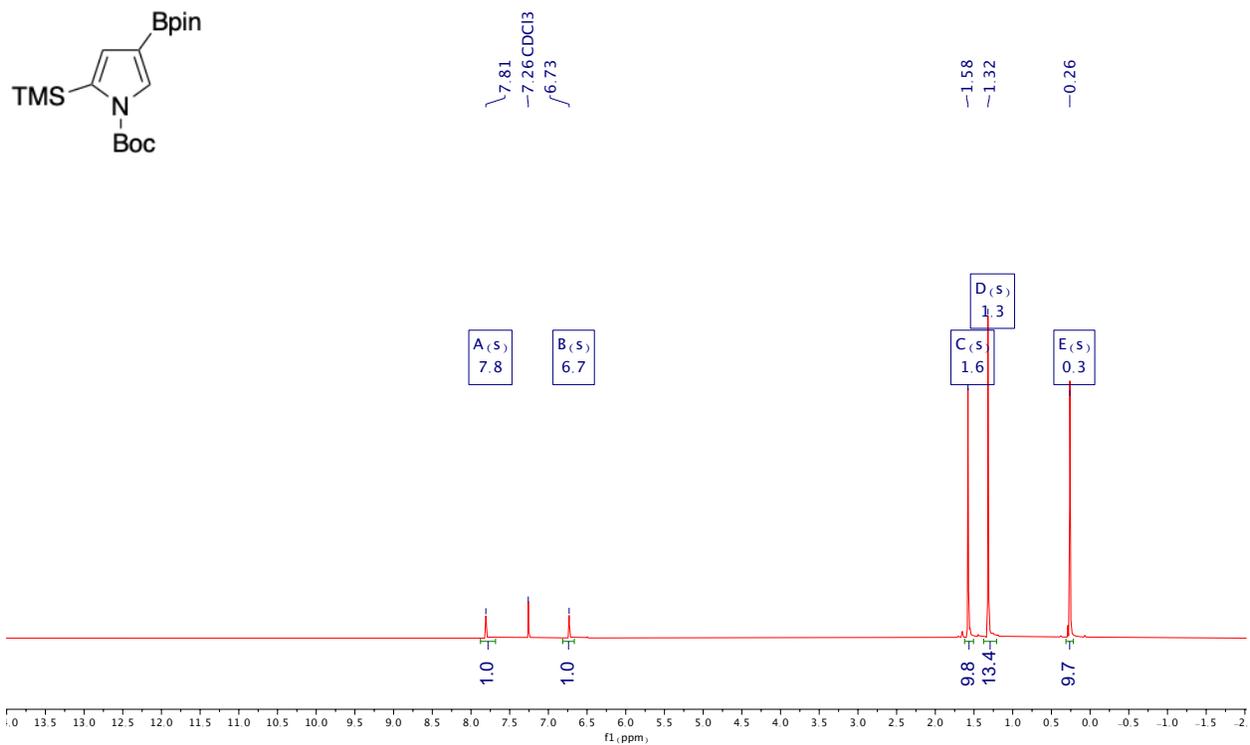
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) 2-chloro-6-(trifluoromethyl)-4-(trimethylsilyl)pyridine (1x)



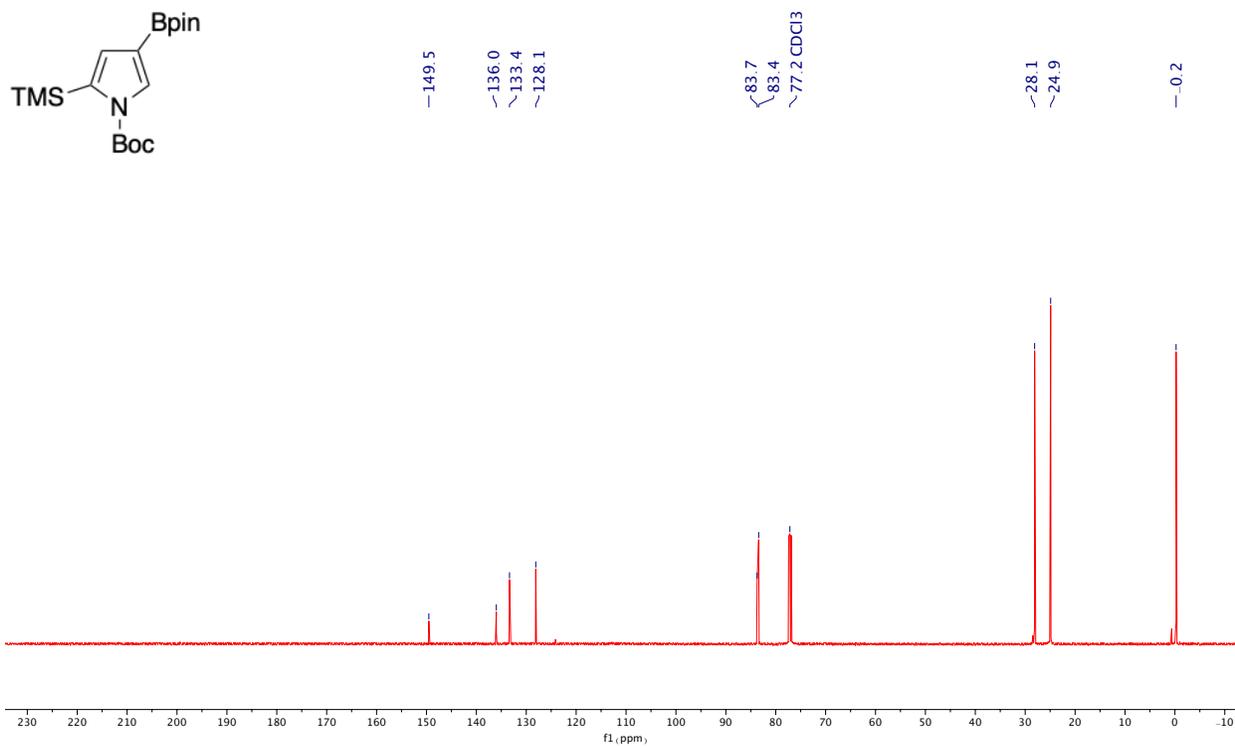
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2-chloro-6-(trifluoromethyl)-4-(trimethylsilyl)pyridine (1x)



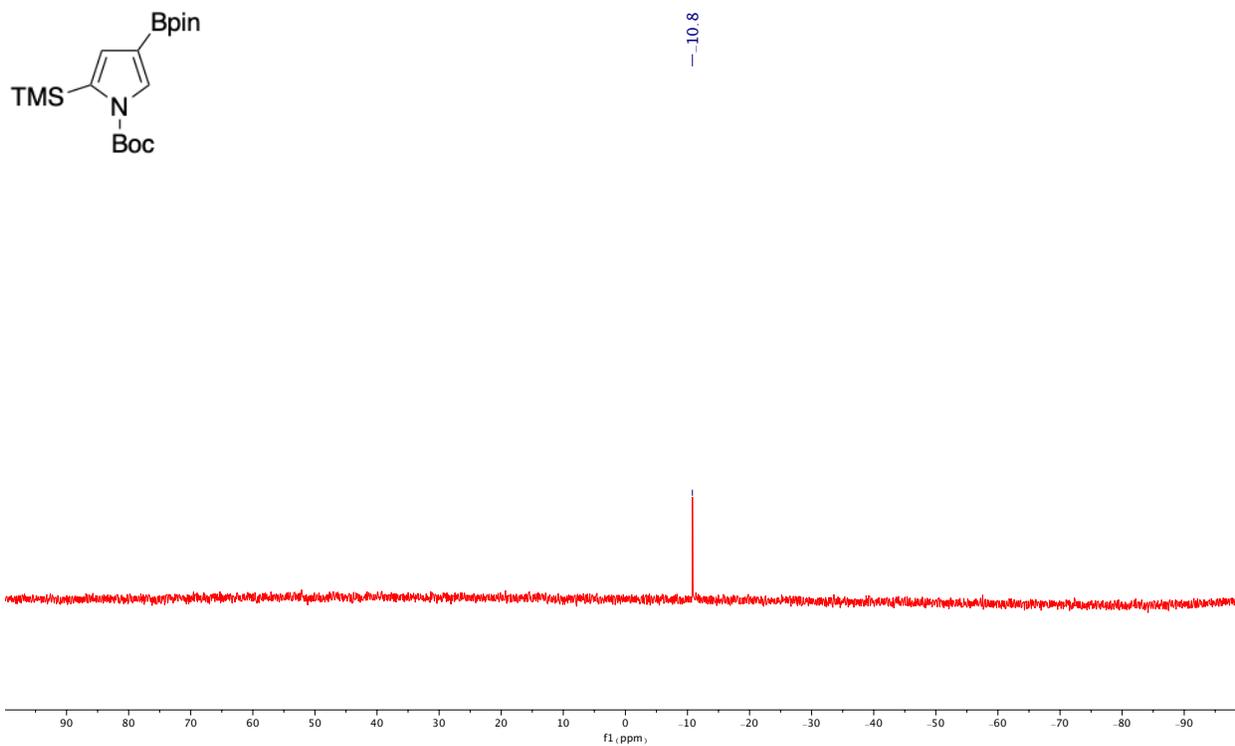
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1a)



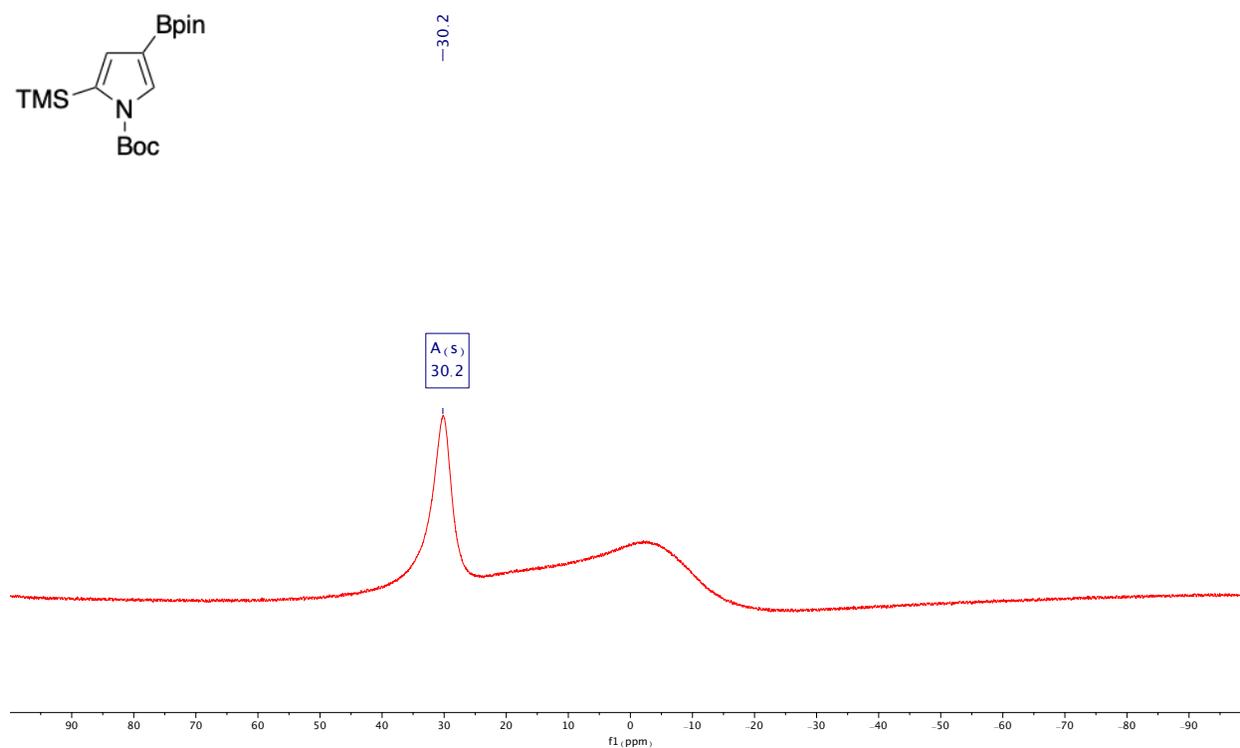
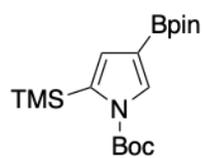
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1a)



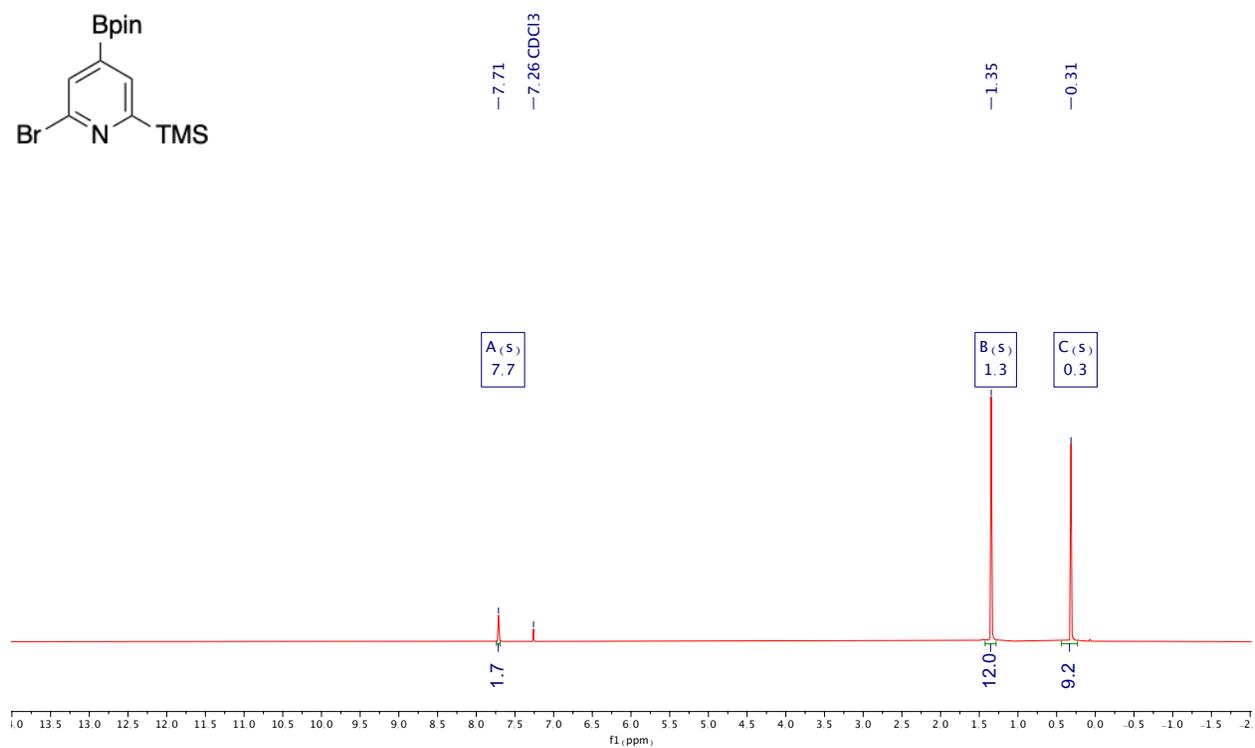
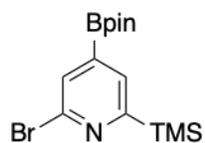
$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ ) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1ab)



<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (**1a**)

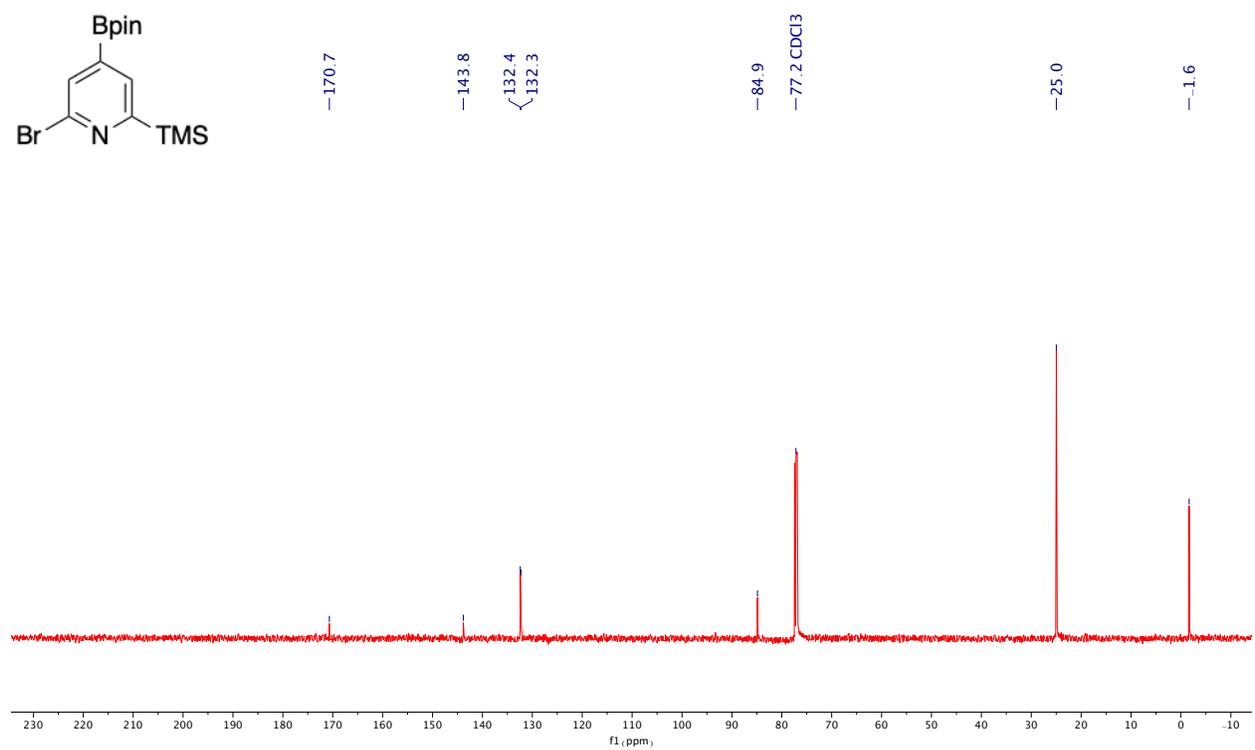
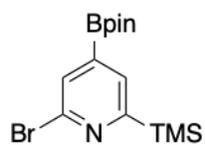


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (**1a**)

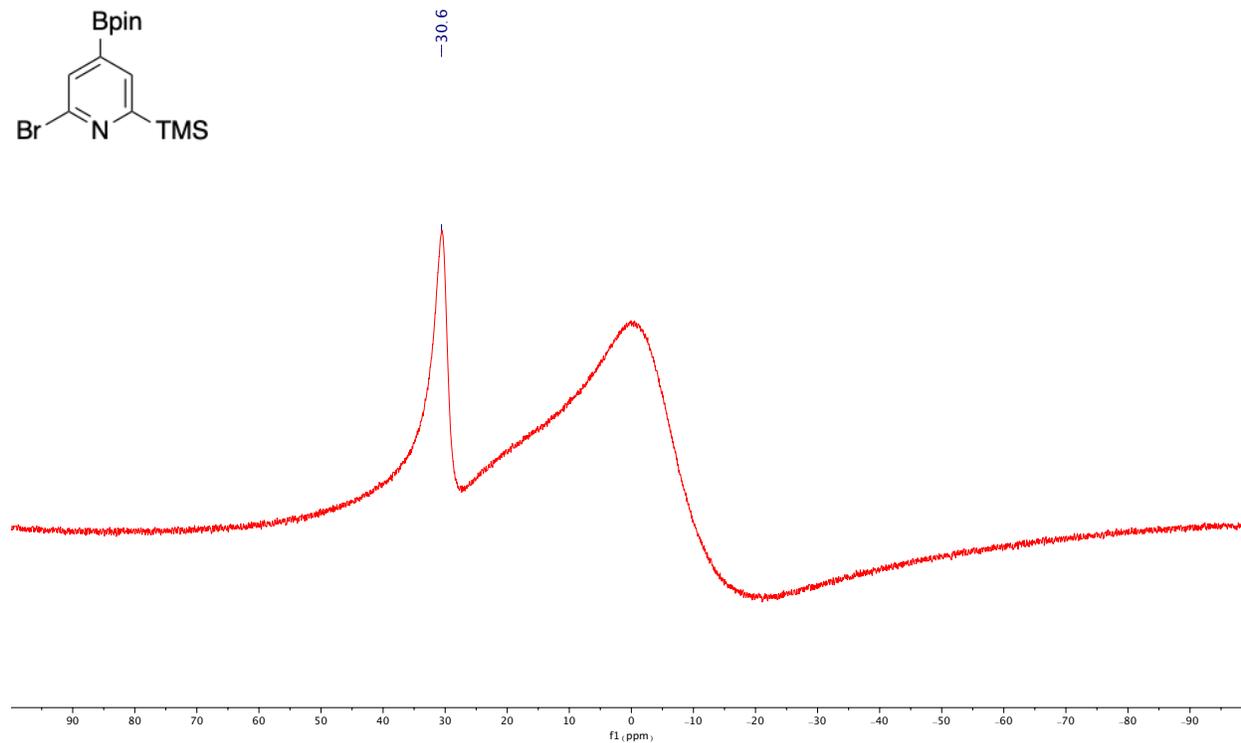
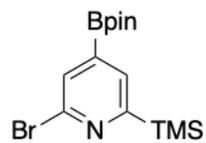


$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine

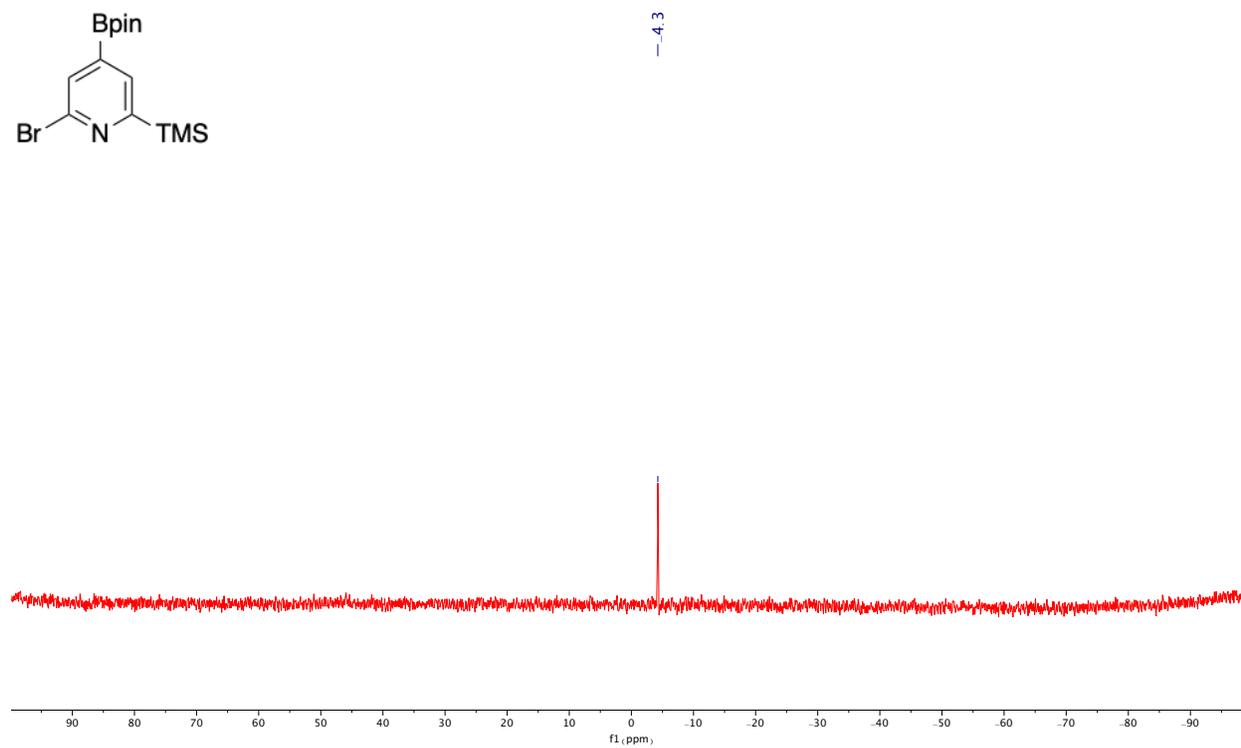
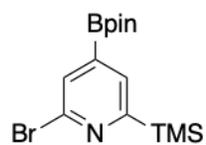
(1ac)



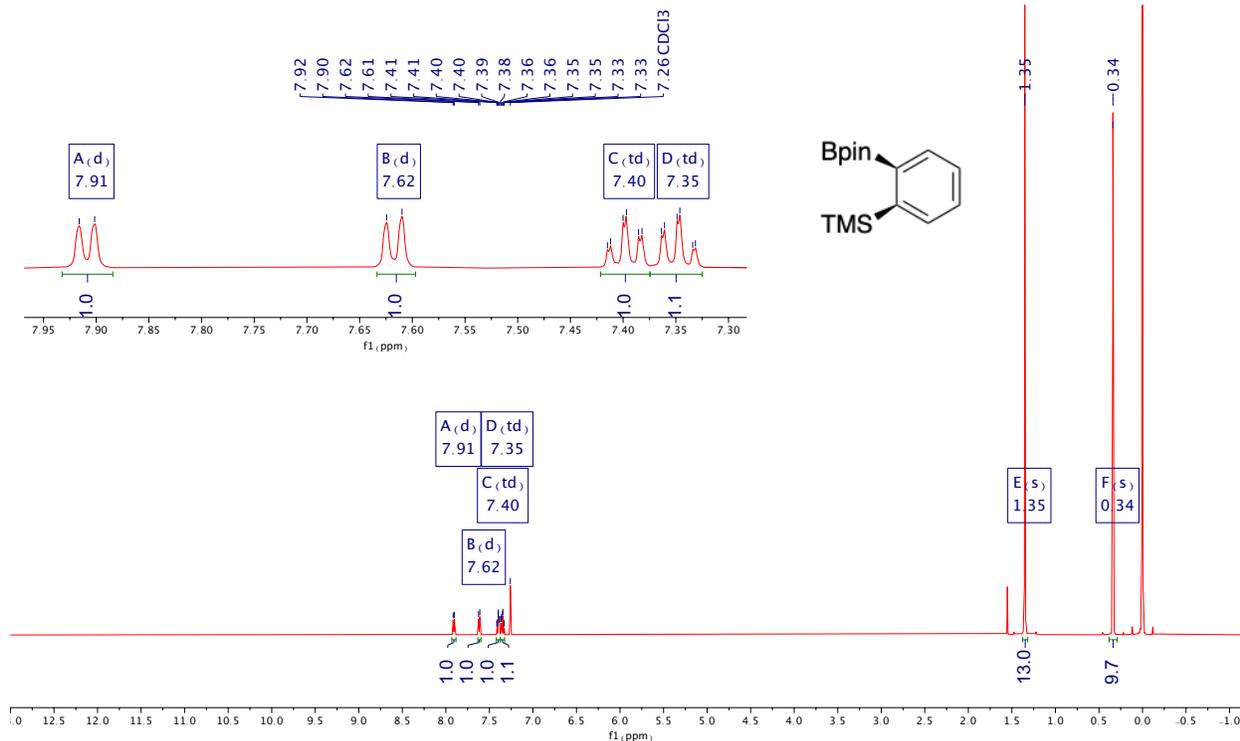
<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



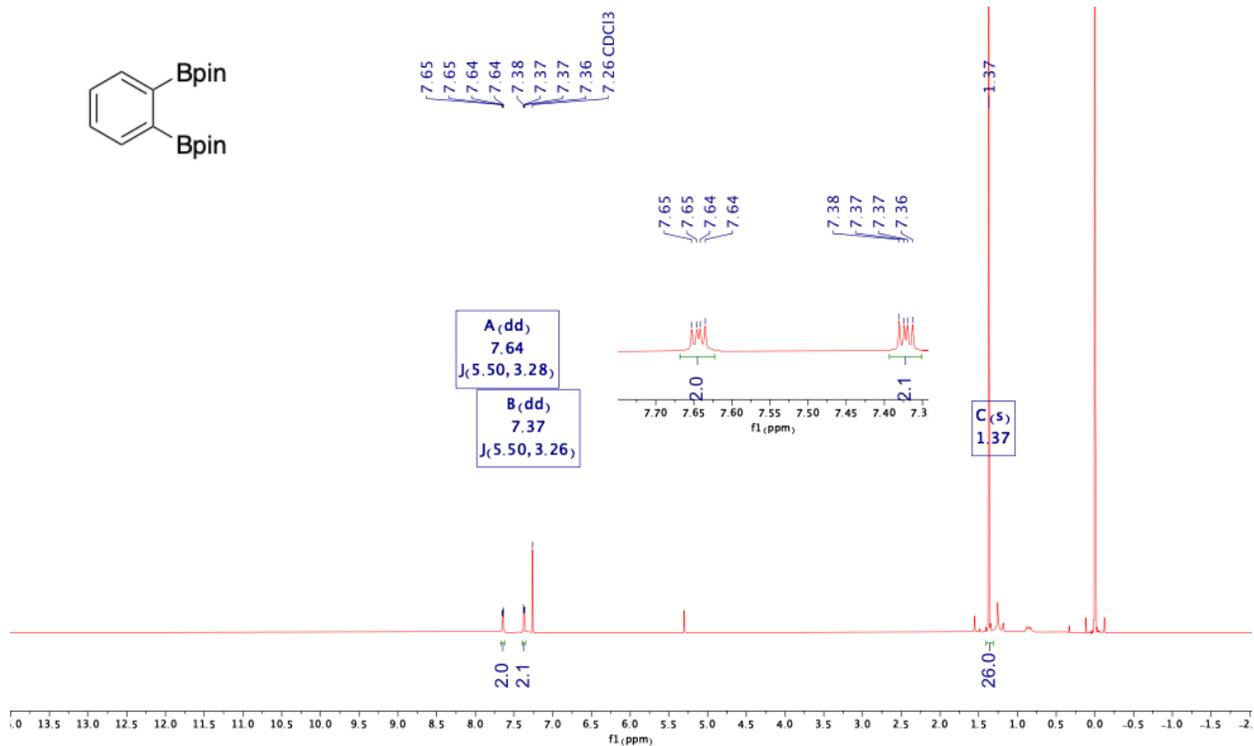
<sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



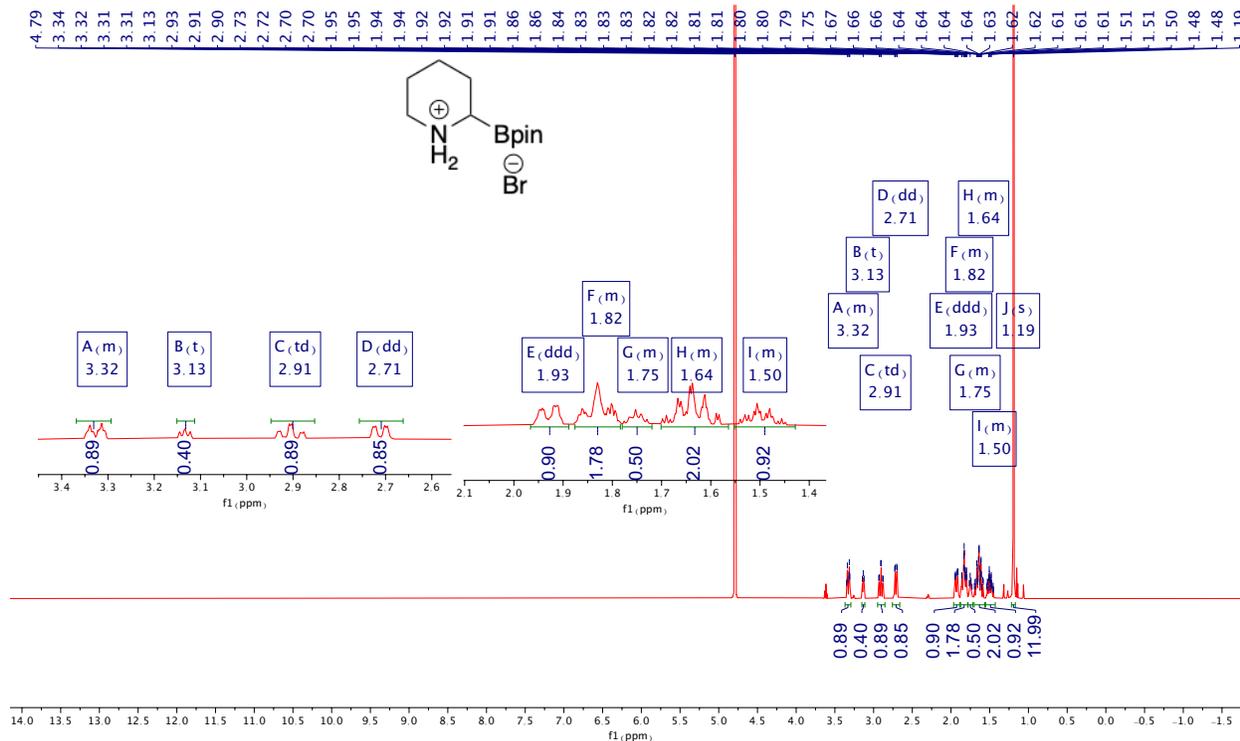
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ad)



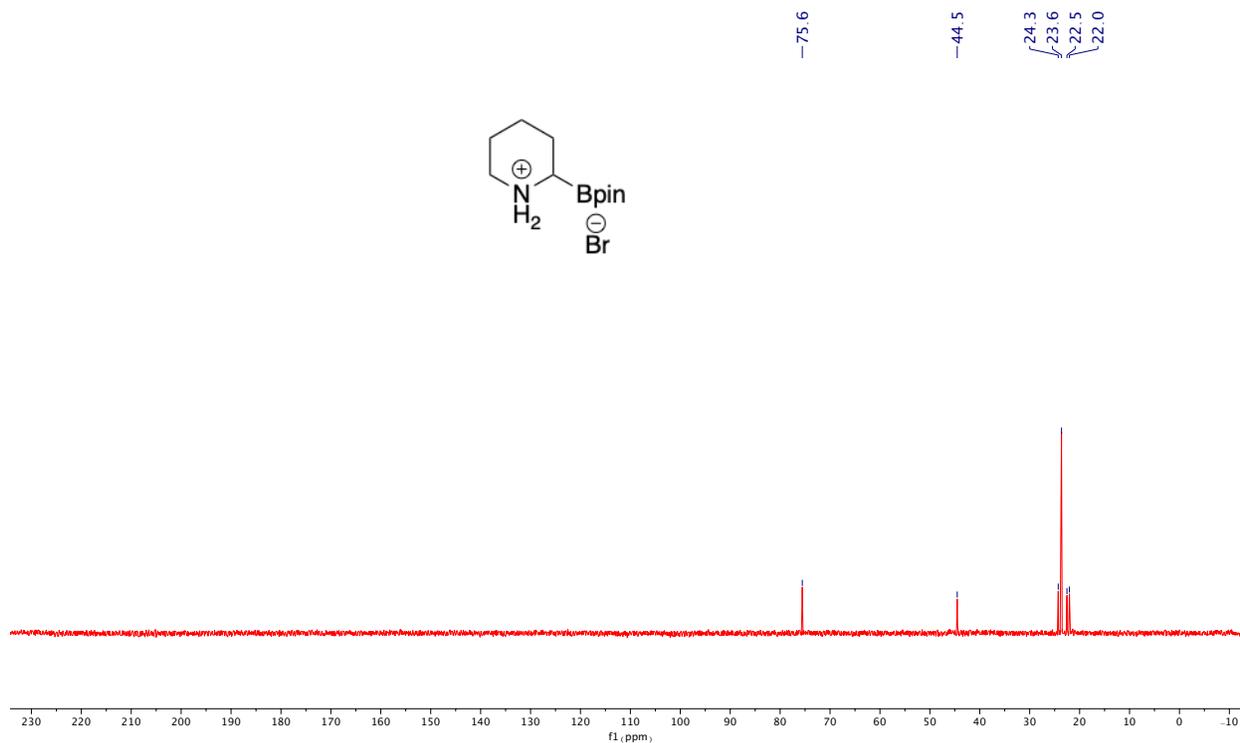
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1v)



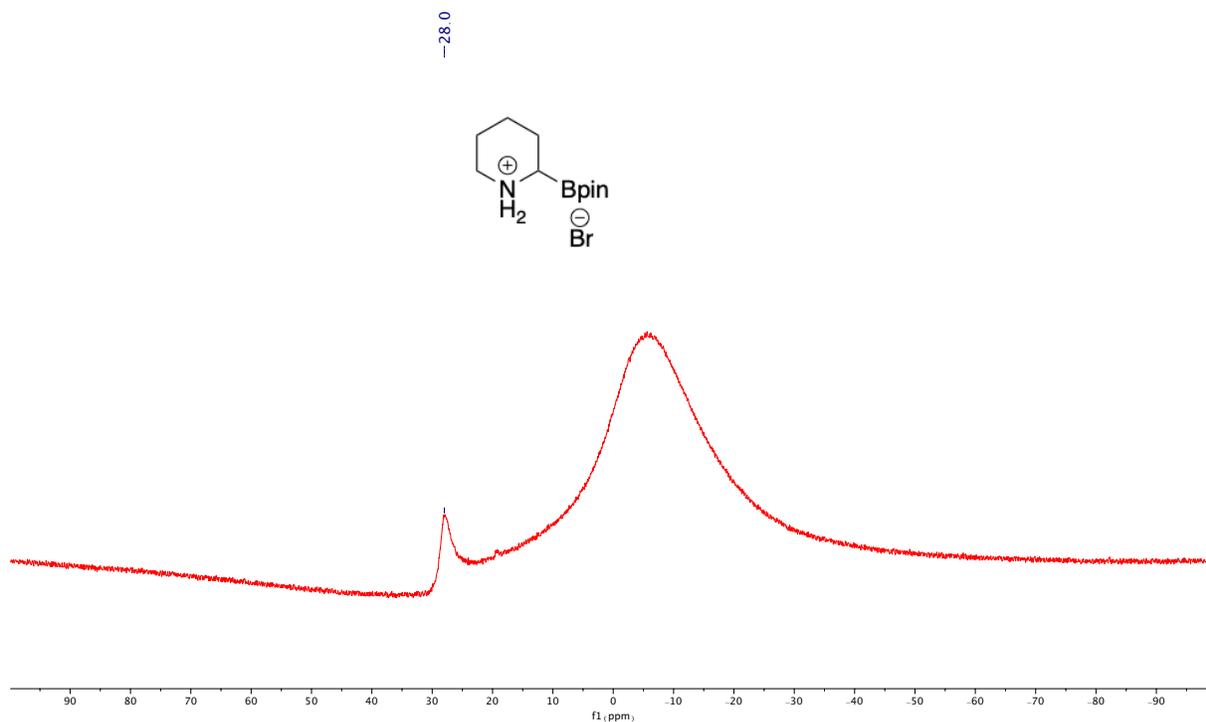
**<sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O) of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)**



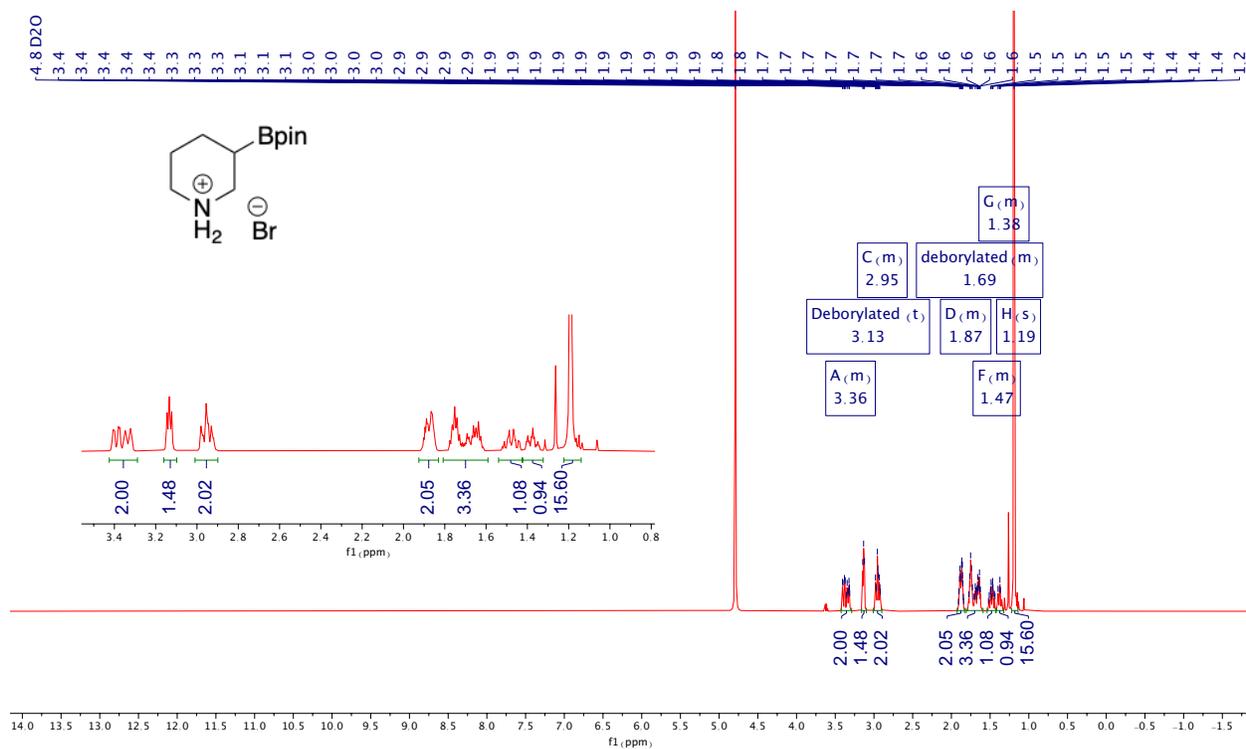
**<sup>13</sup>C{<sup>1</sup>H} (126 MHz, D<sub>2</sub>O) NMR of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)**



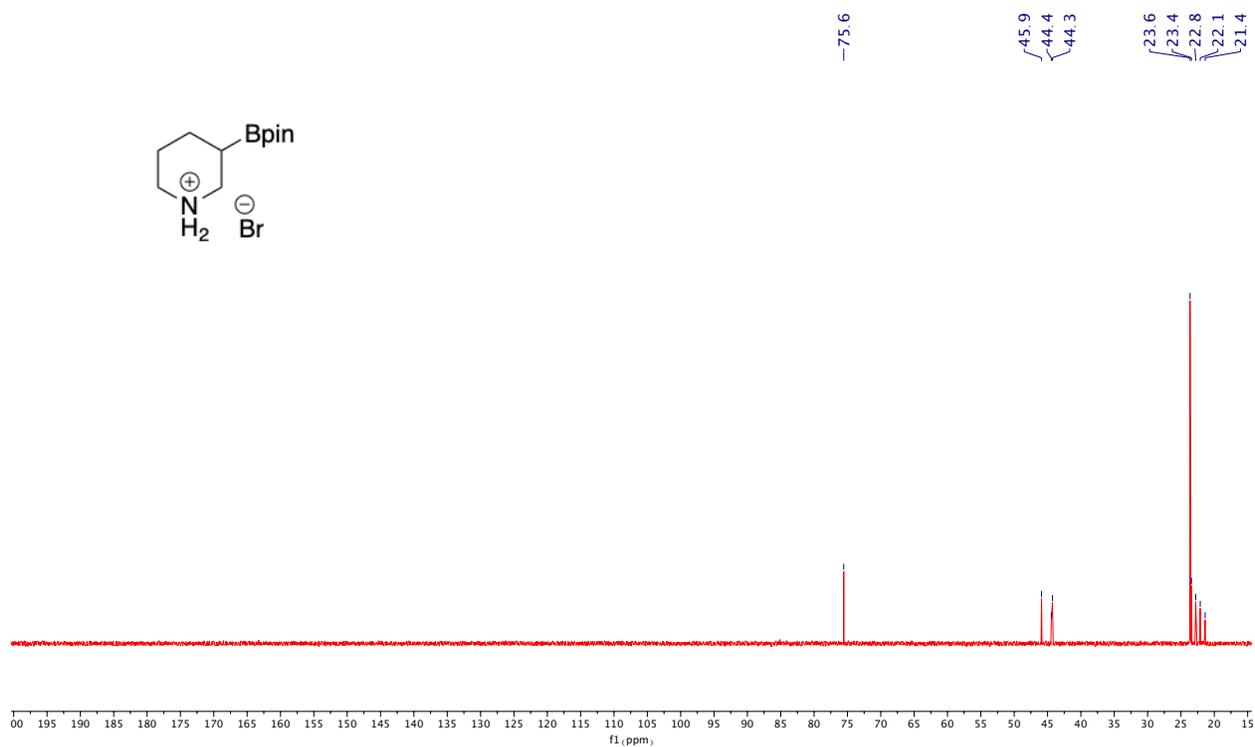
**$^{11}\text{B}$  NMR (160 MHz,  $\text{D}_2\text{O}$ ) of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)**



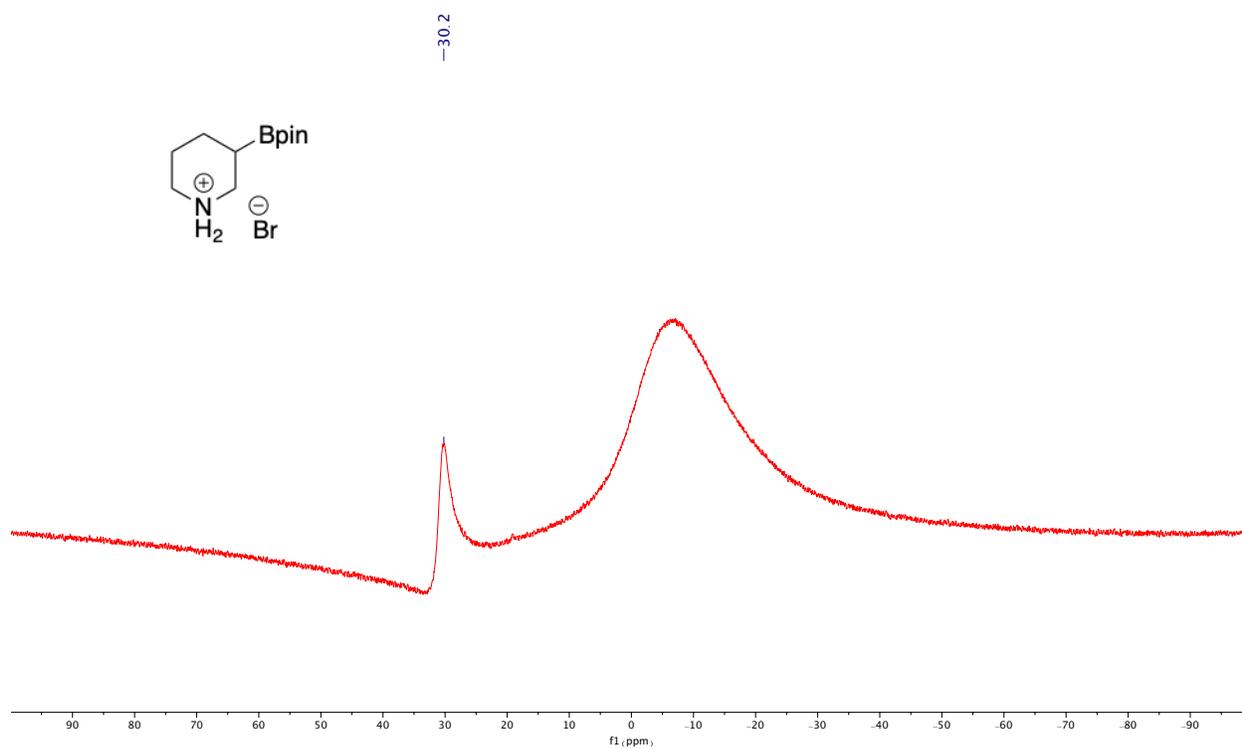
**$^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)**



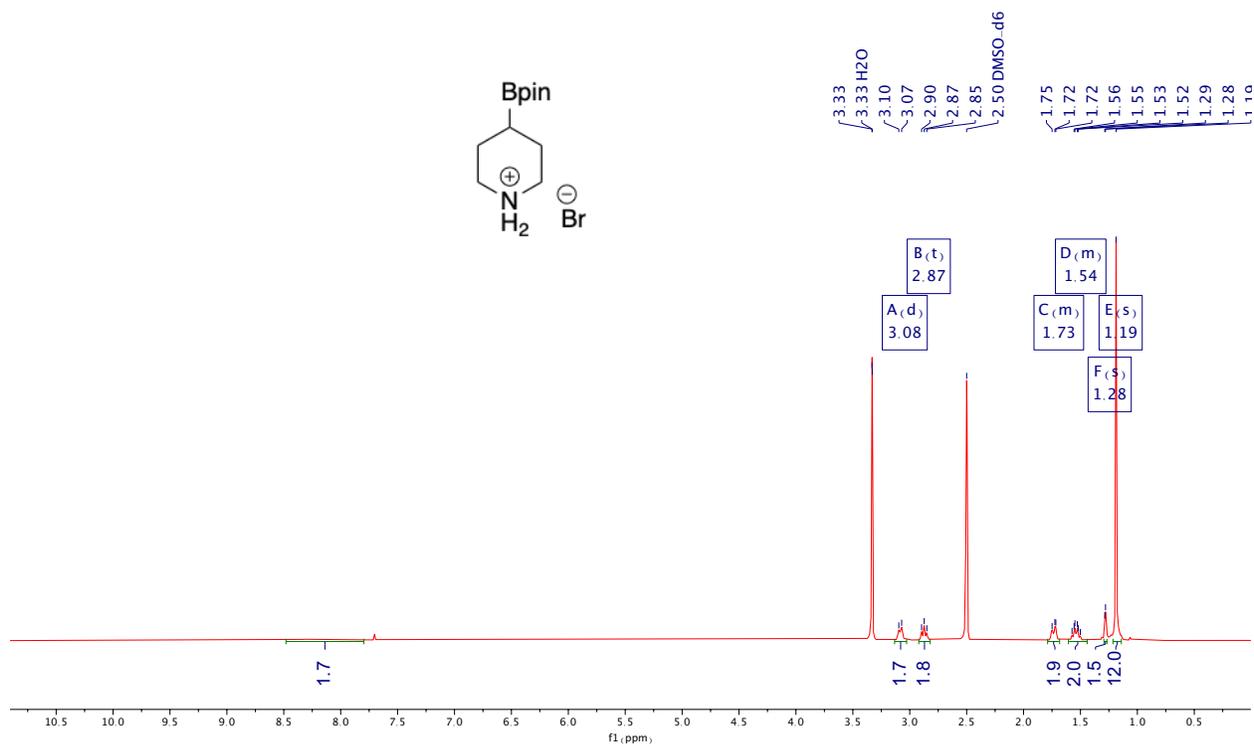
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{D}_2\text{O}$ ) NMR of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)



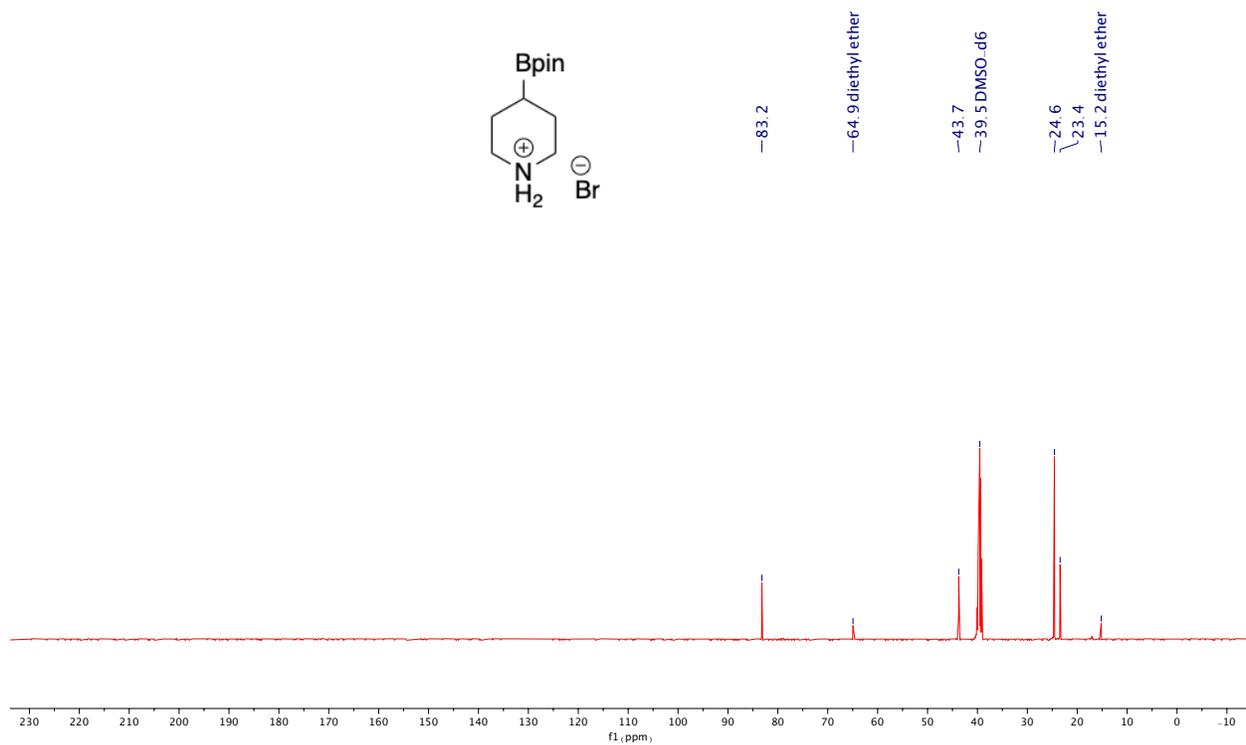
$^{11}\text{B}$  NMR (160 MHz,  $\text{D}_2\text{O}$ ) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)



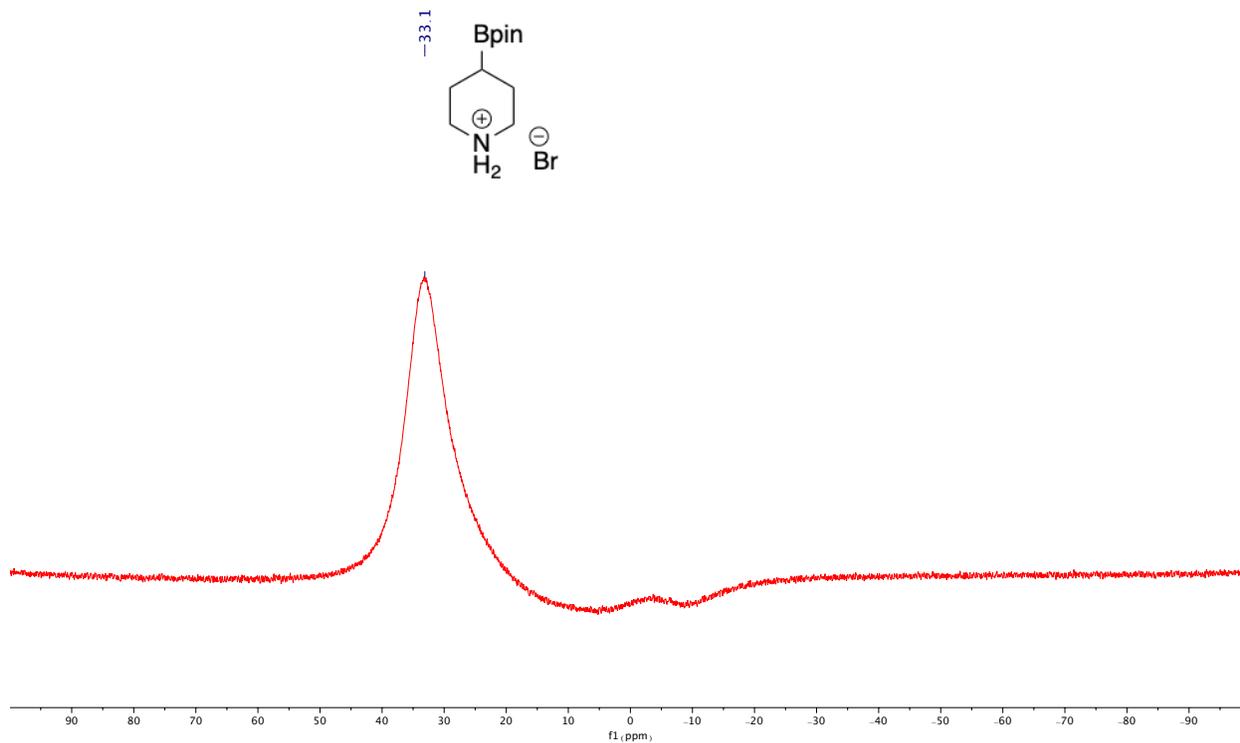
<sup>1</sup>H NMR (500 MHz, DMSO) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)



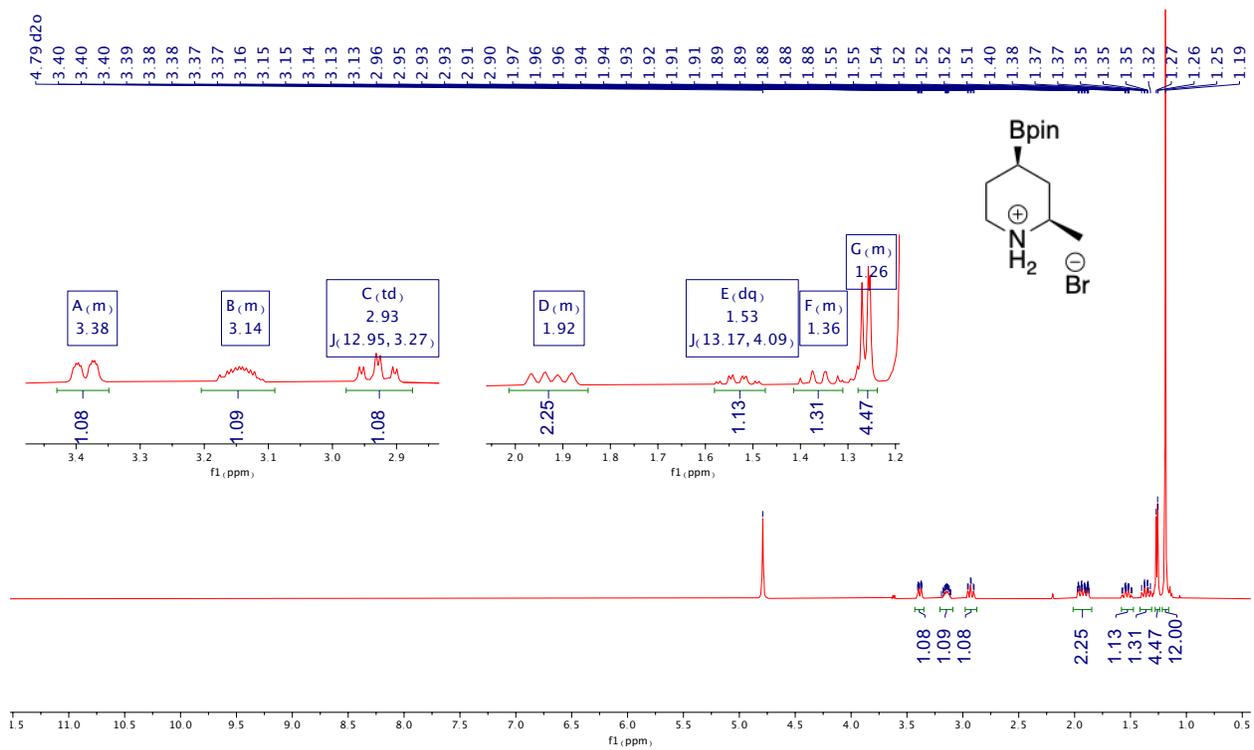
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, DMSO) NMR of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)



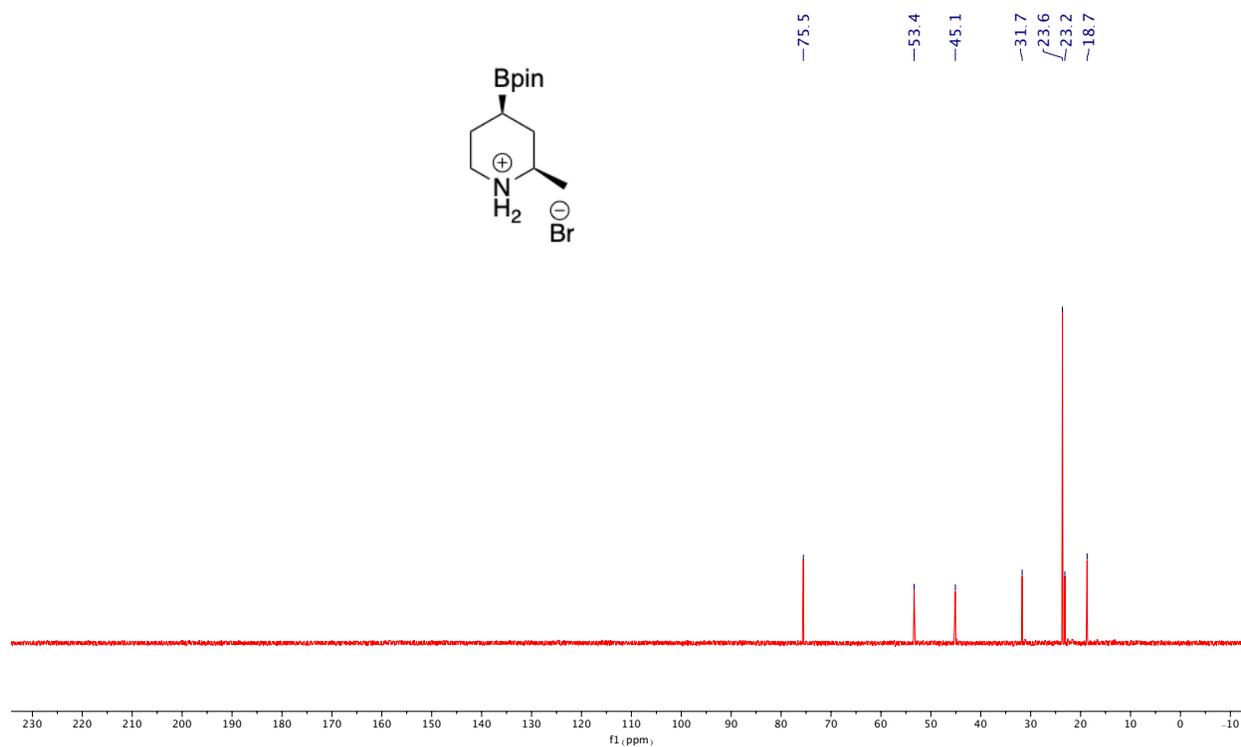
**$^{11}\text{B}$  NMR (160 MHz, DMSO) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)**



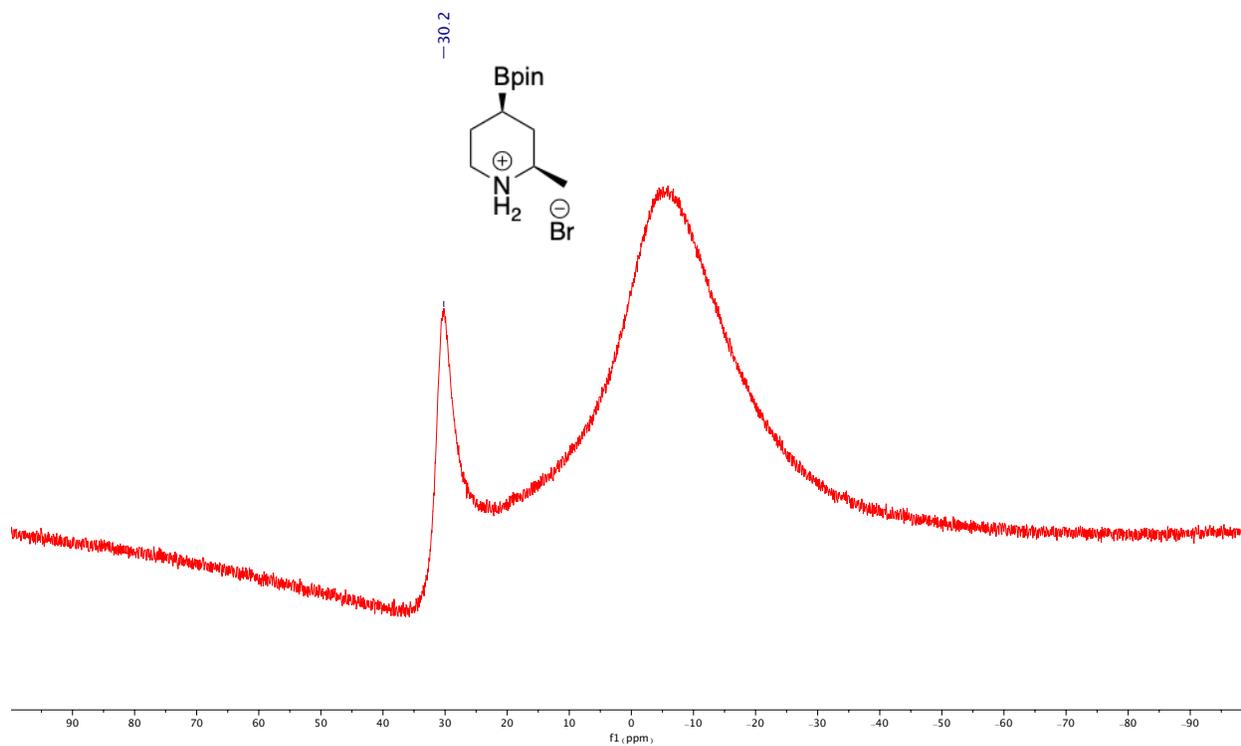
**$^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ) of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)**



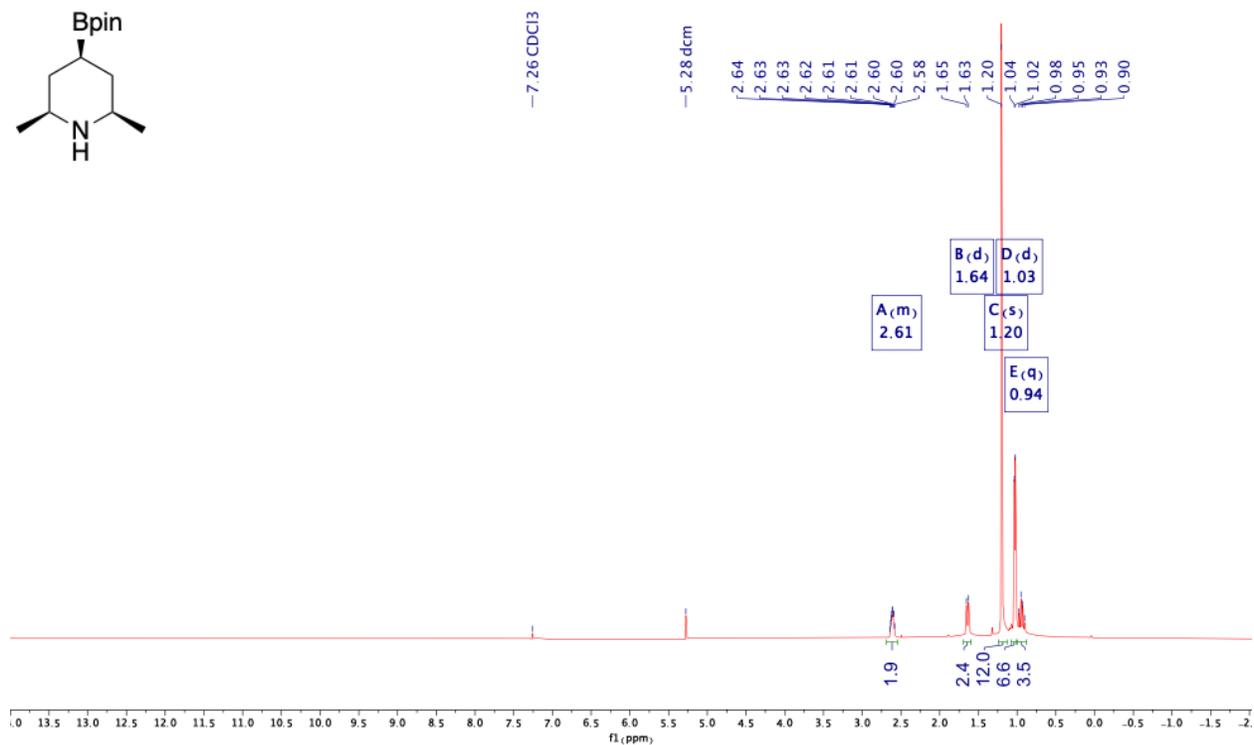
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{D}_2\text{O}$ ) NMR of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)



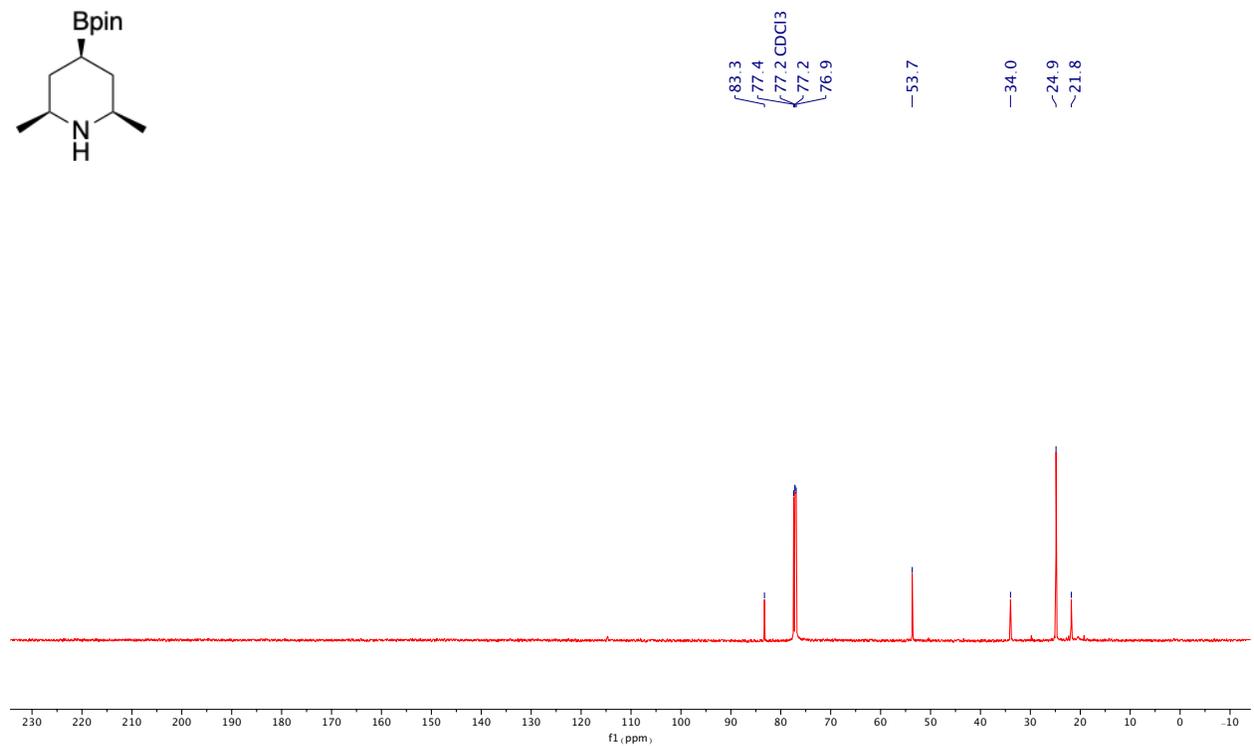
$^{11}\text{B}$  NMR (160 MHz,  $\text{D}_2\text{O}$ ) of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)



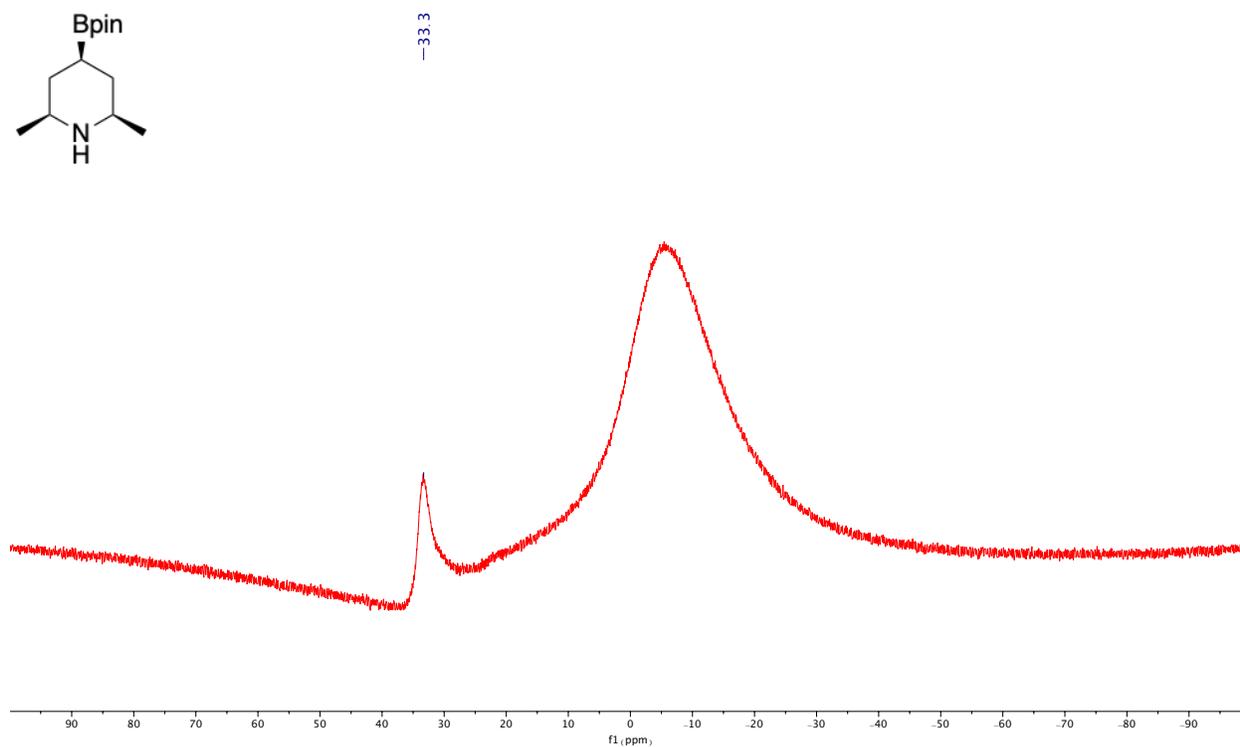
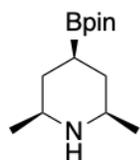
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



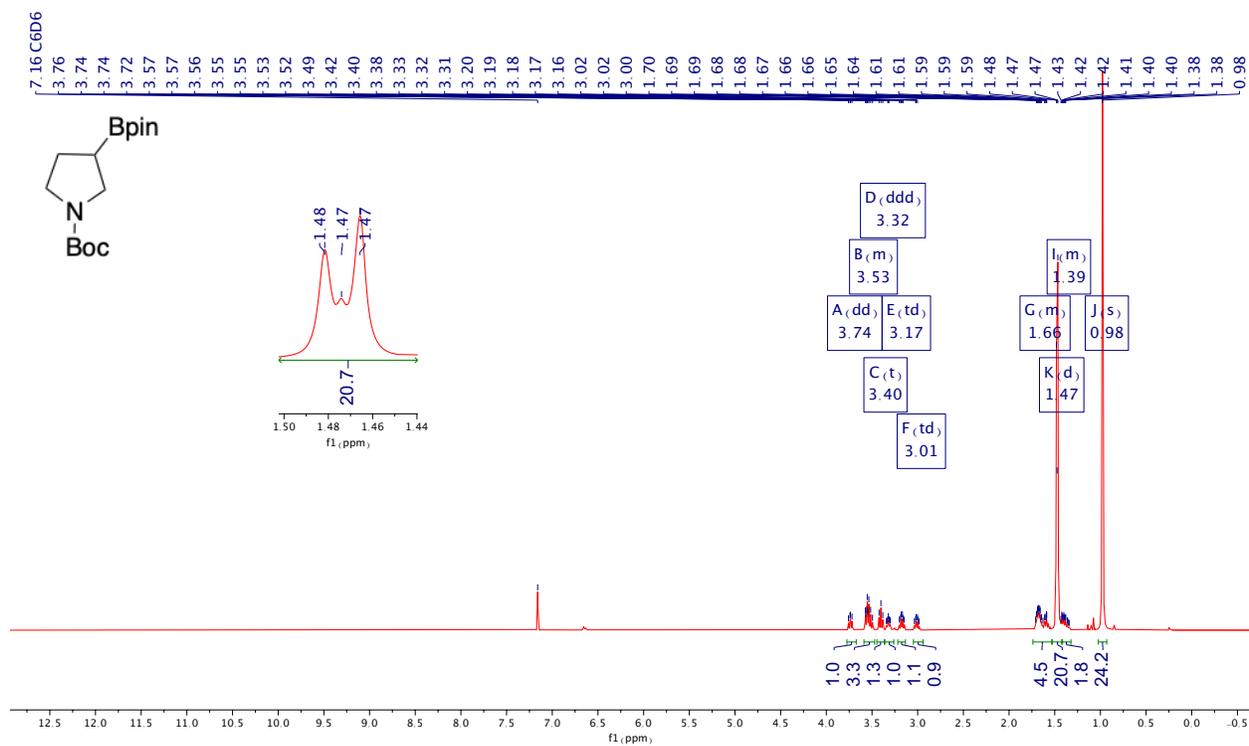
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



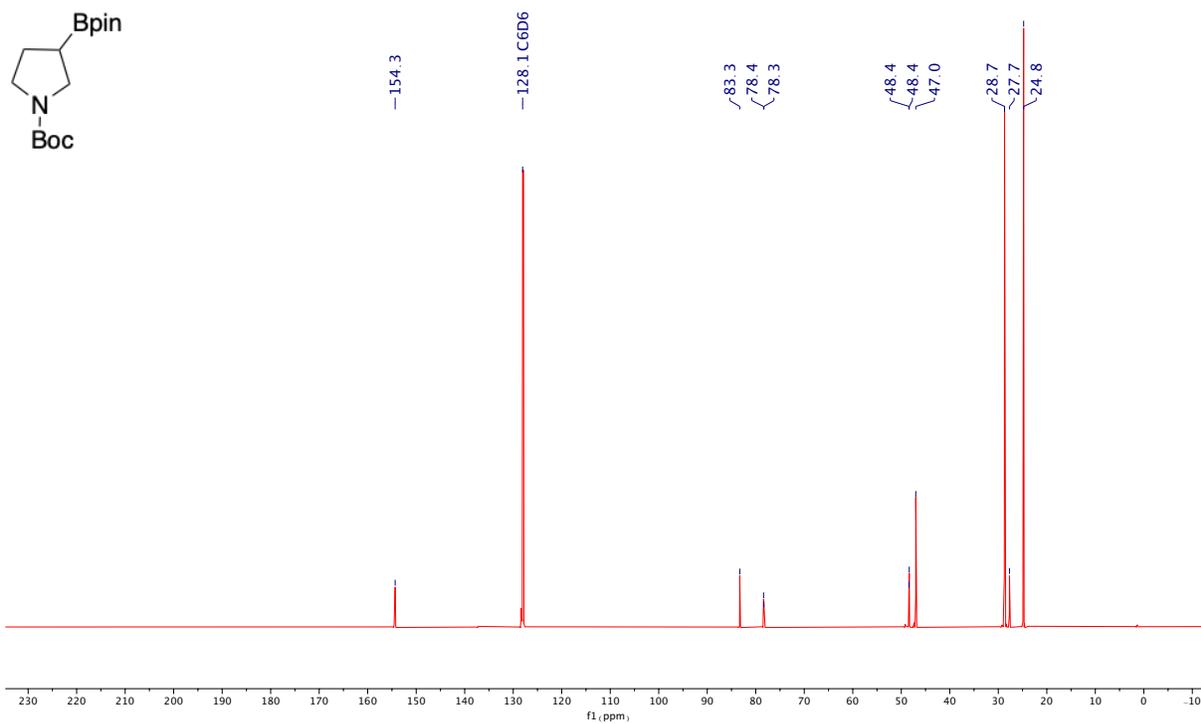
<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



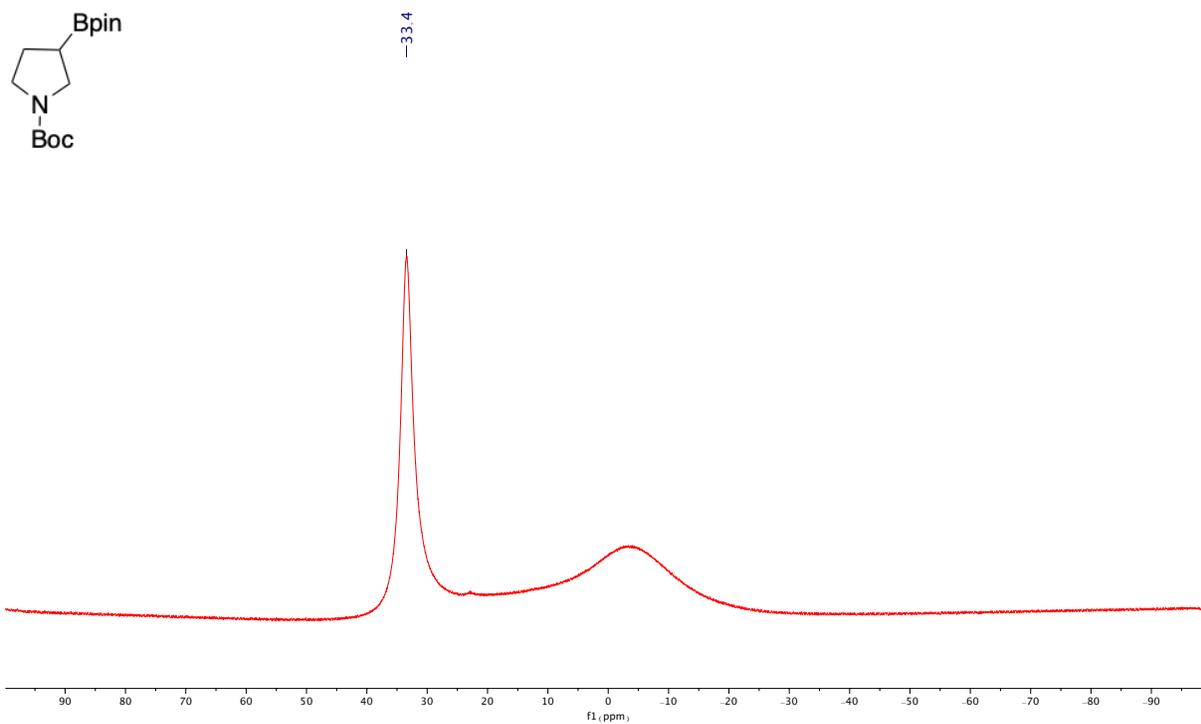
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) of *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



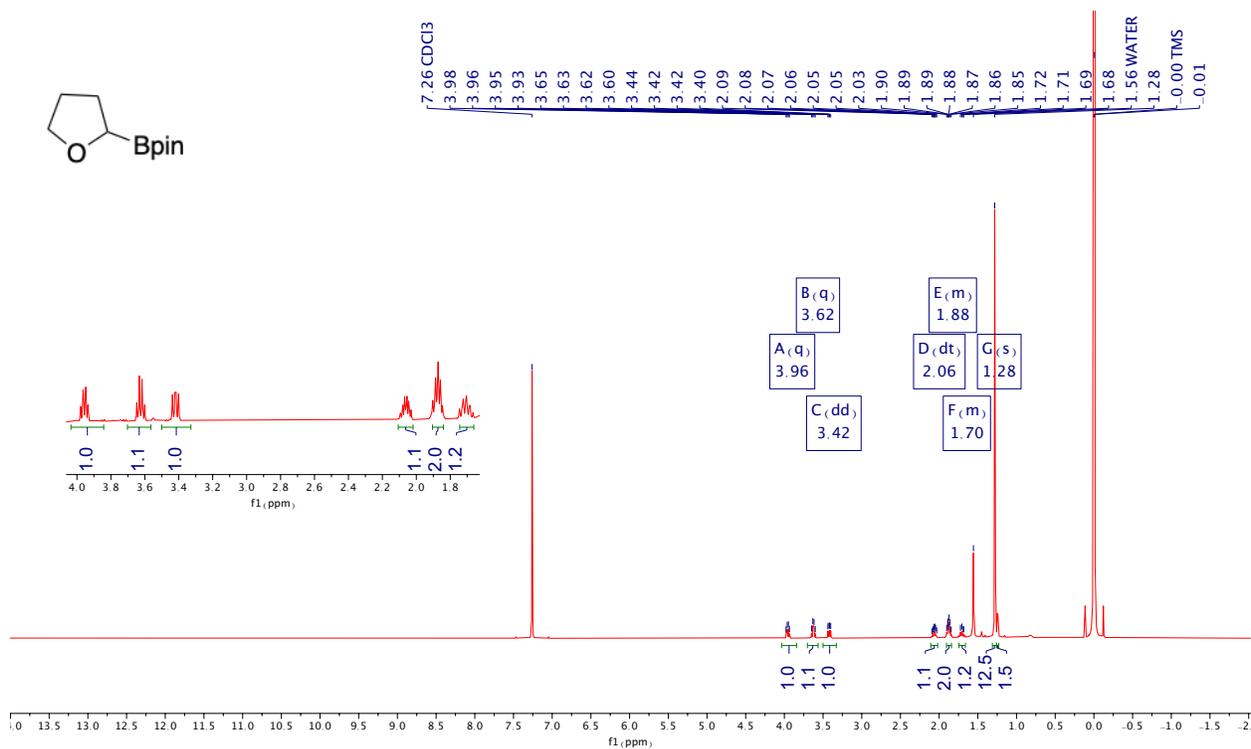
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) NMR of *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



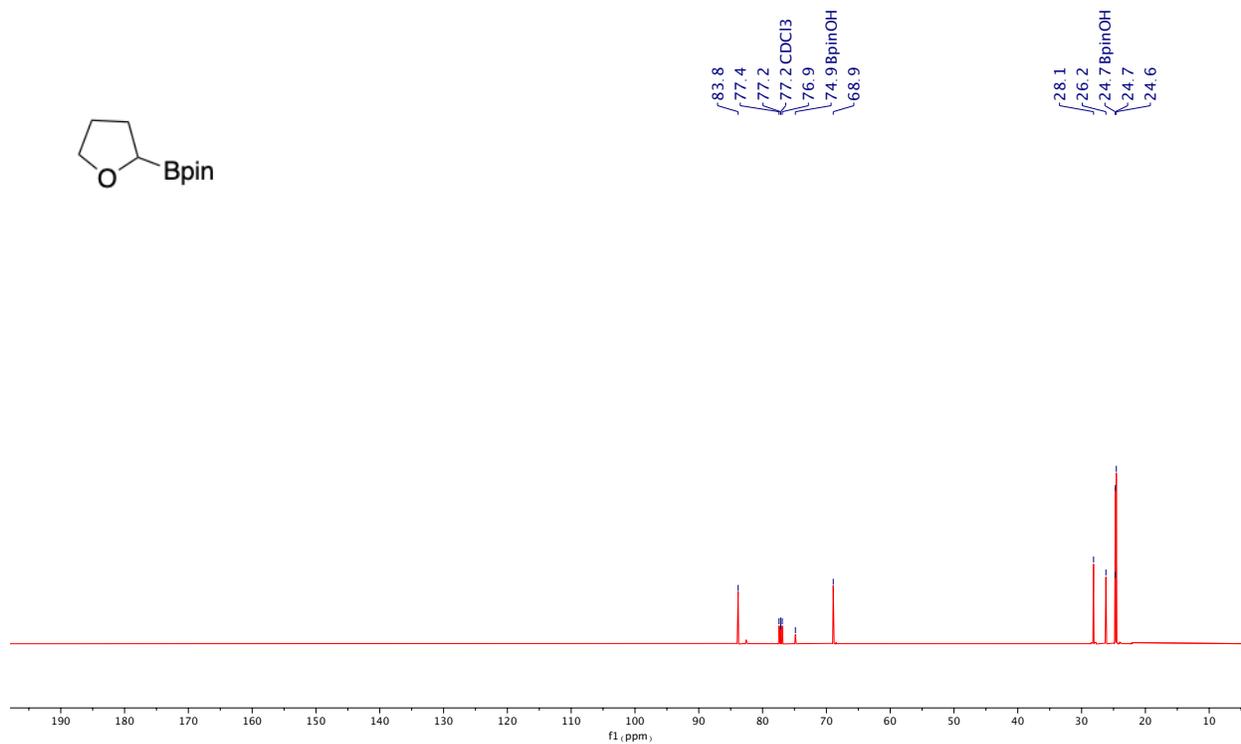
$^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ) of *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



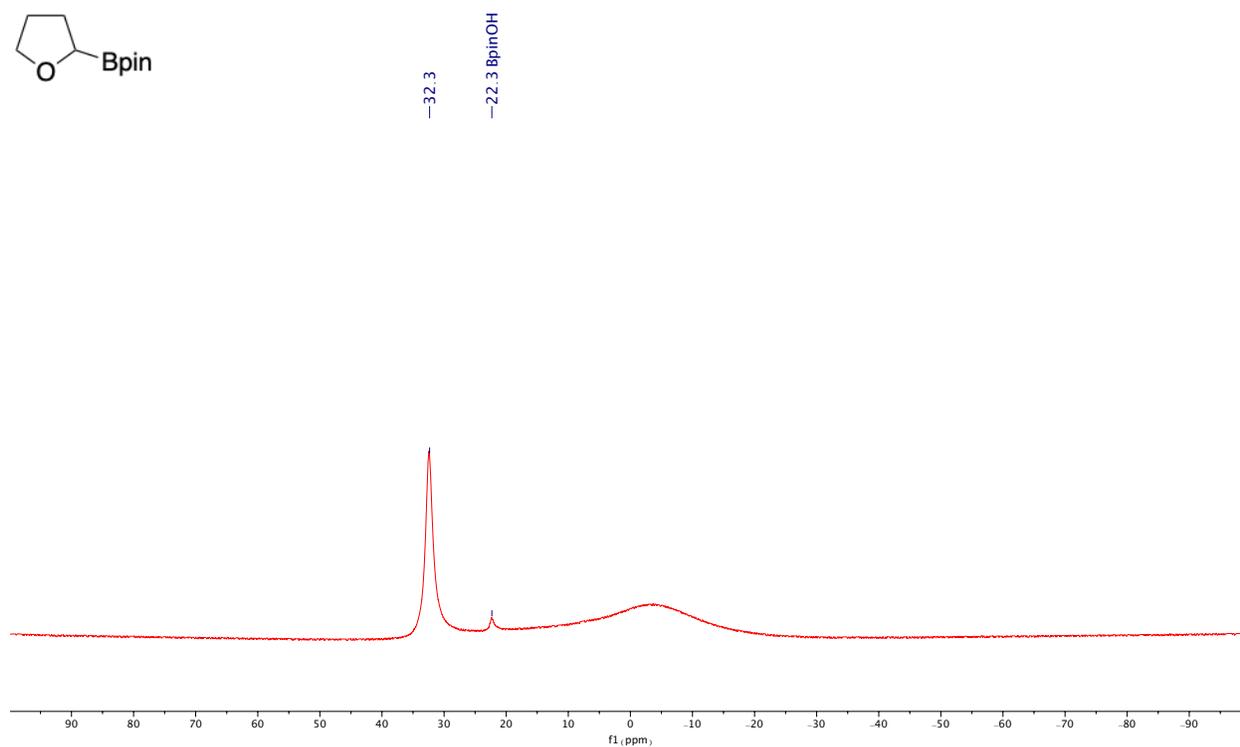
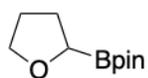
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



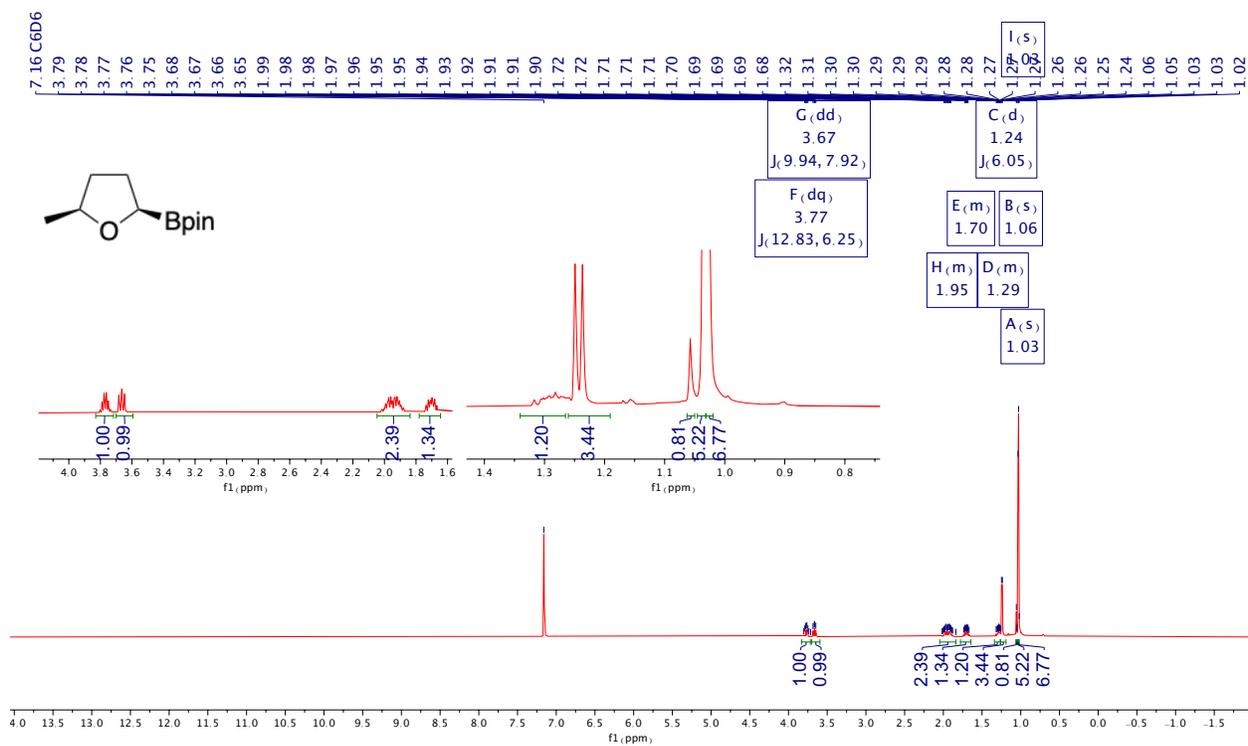
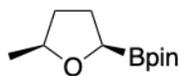
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



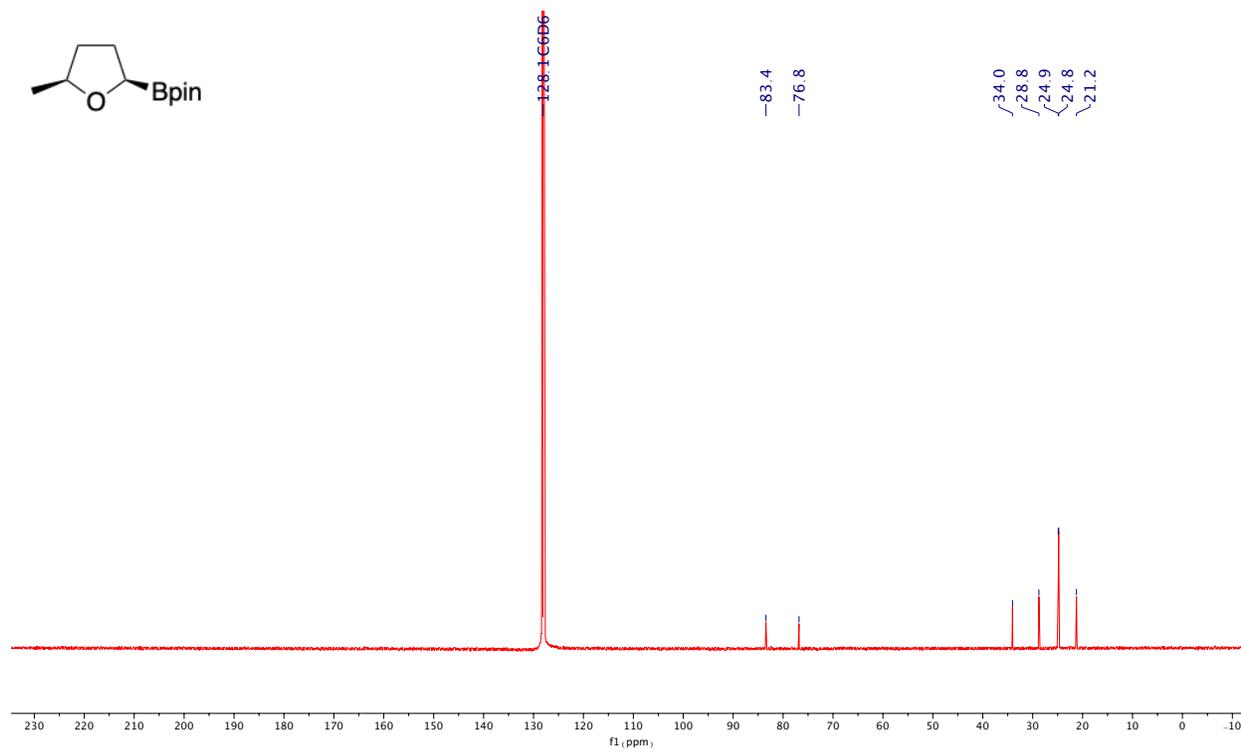
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



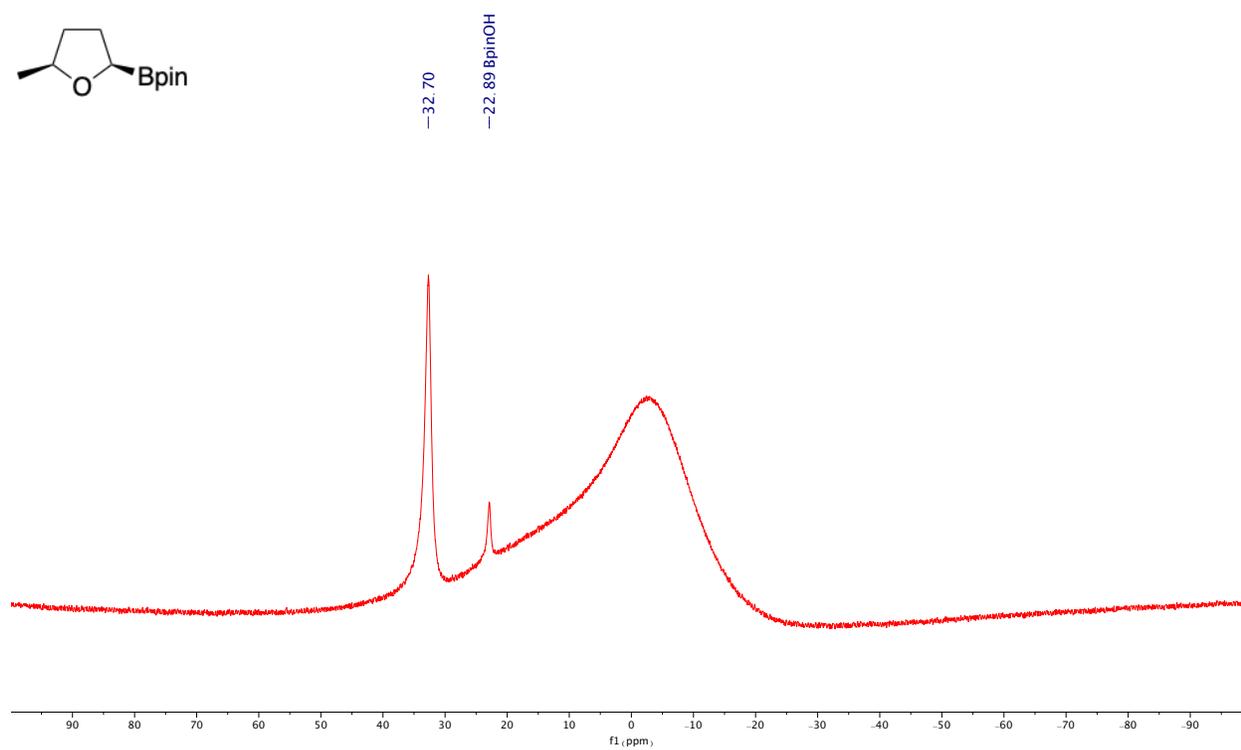
<sup>1</sup>H NMR (500MHz, C<sub>6</sub>D<sub>6</sub>) of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



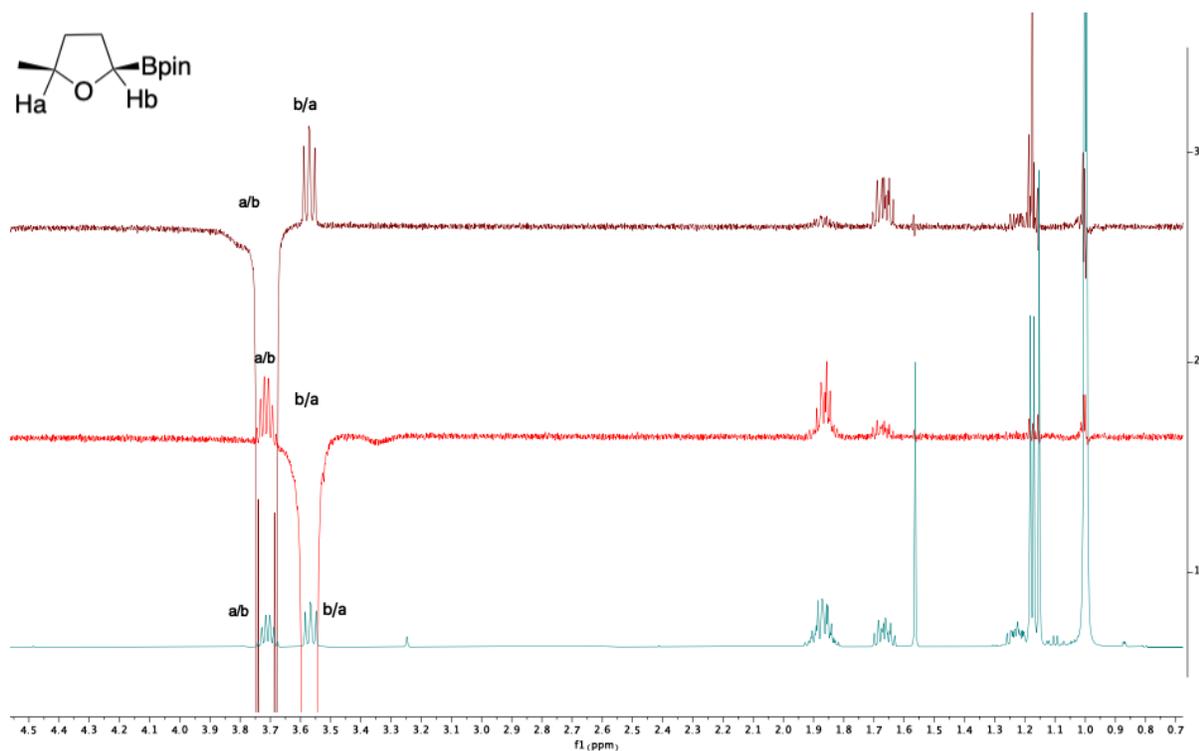
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) NMR of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



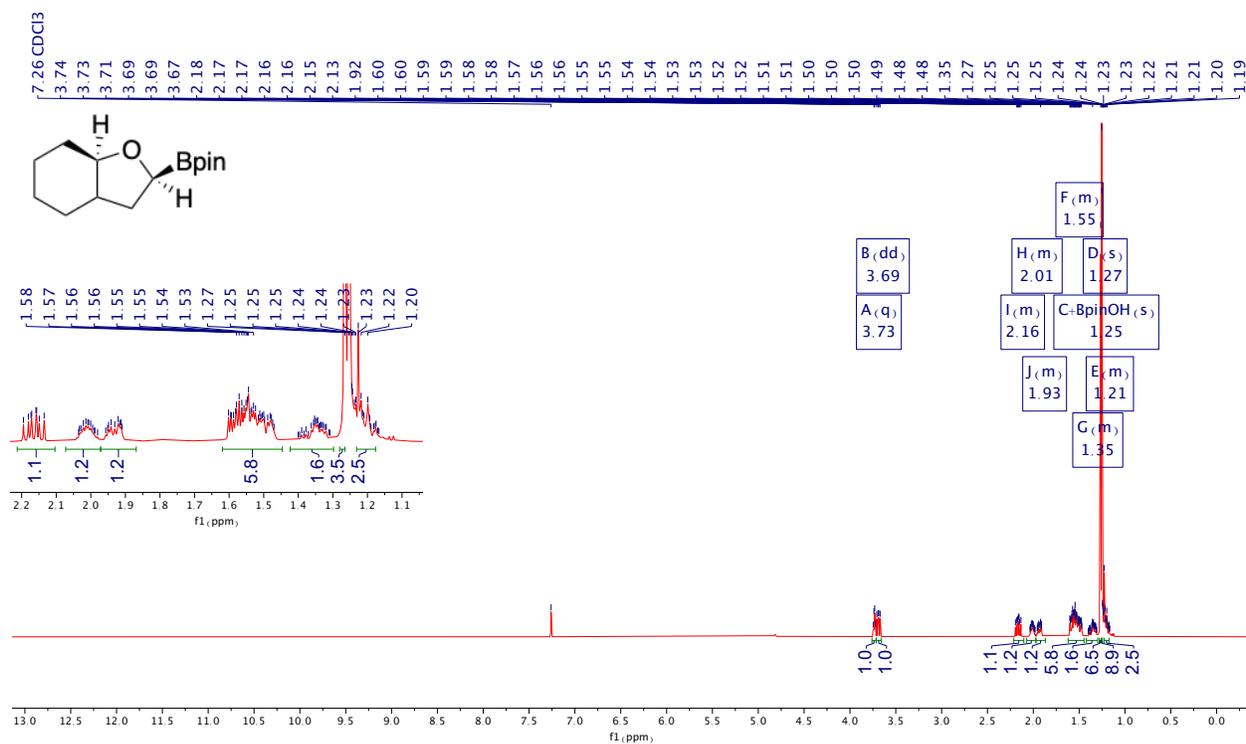
$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



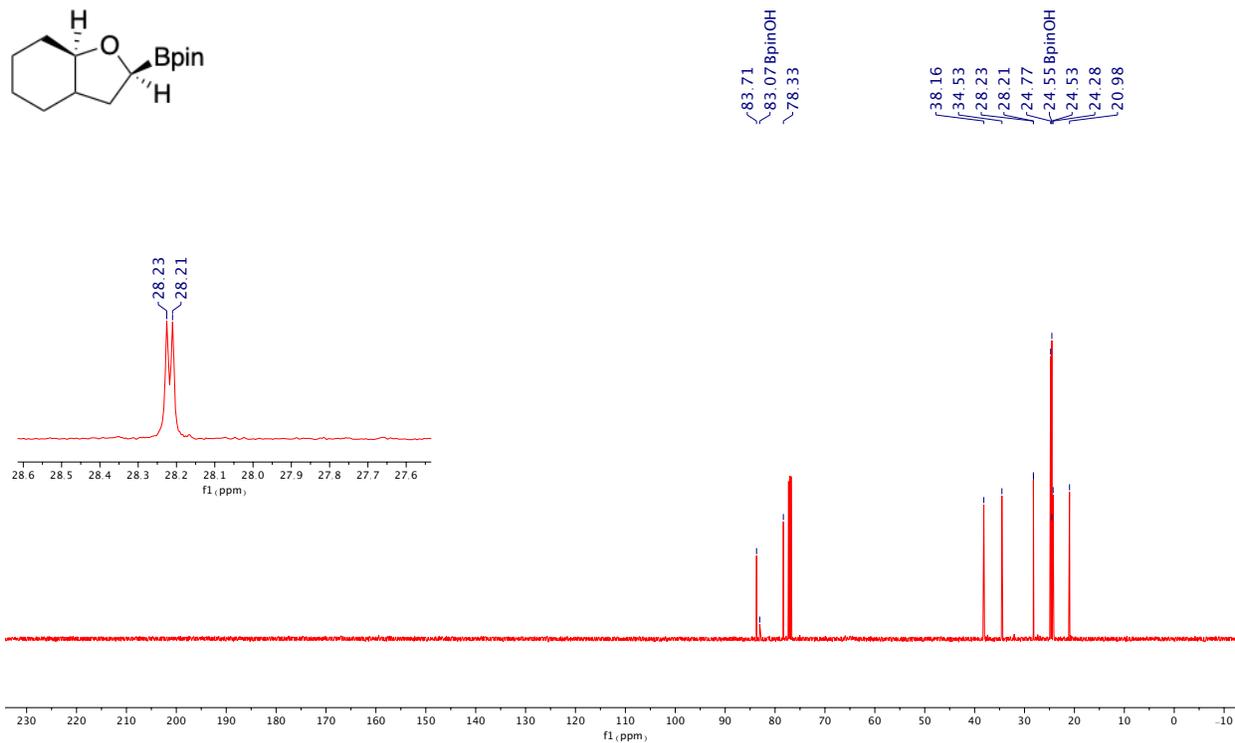
1D-NOE NMR of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



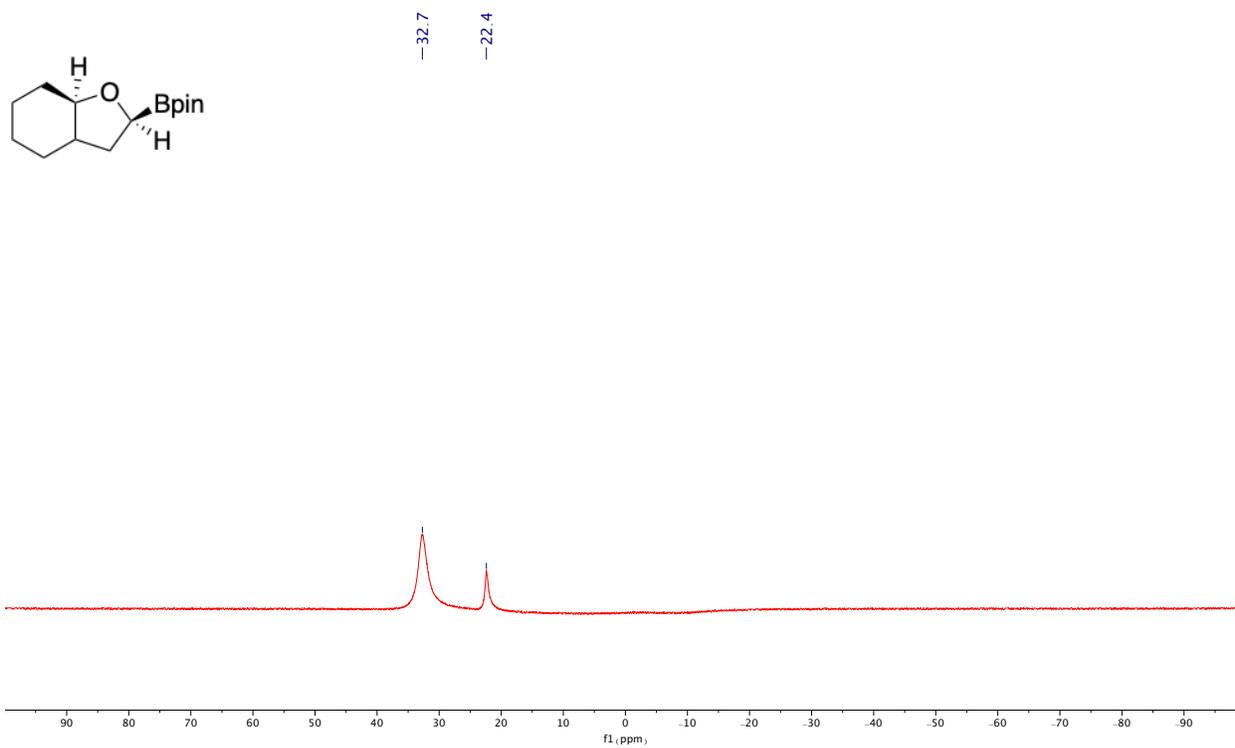
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



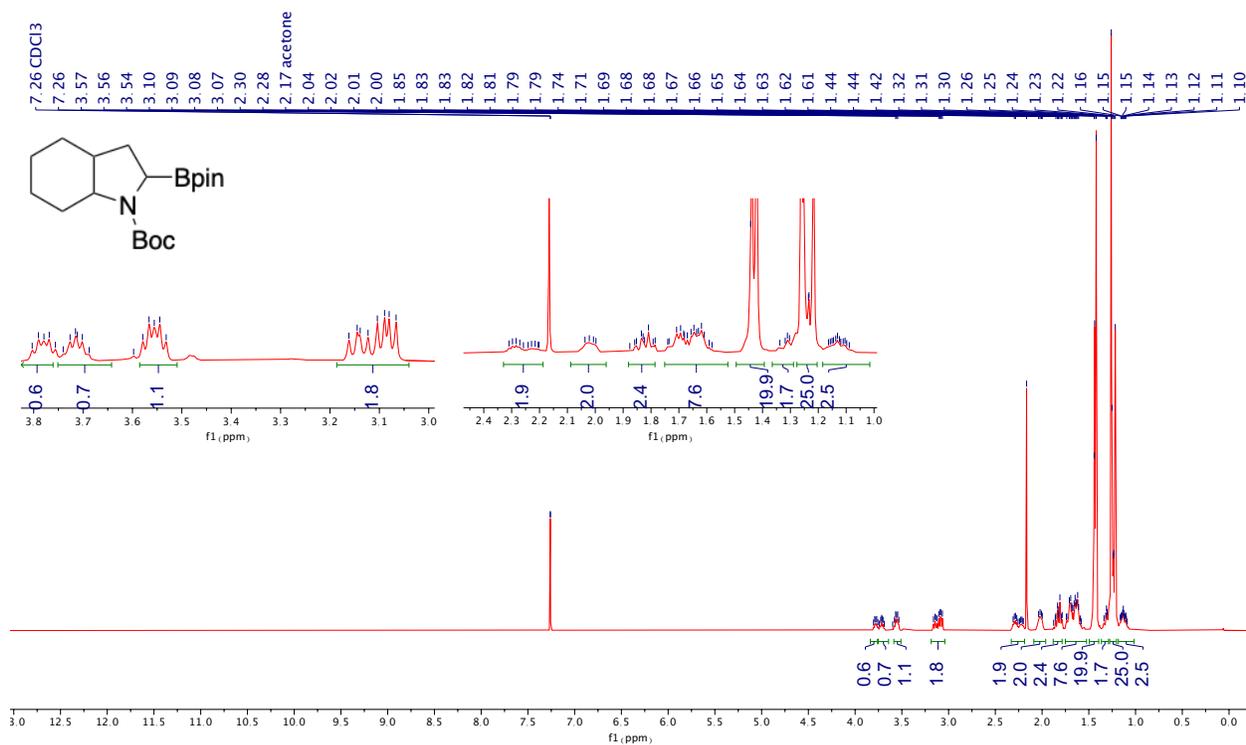
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



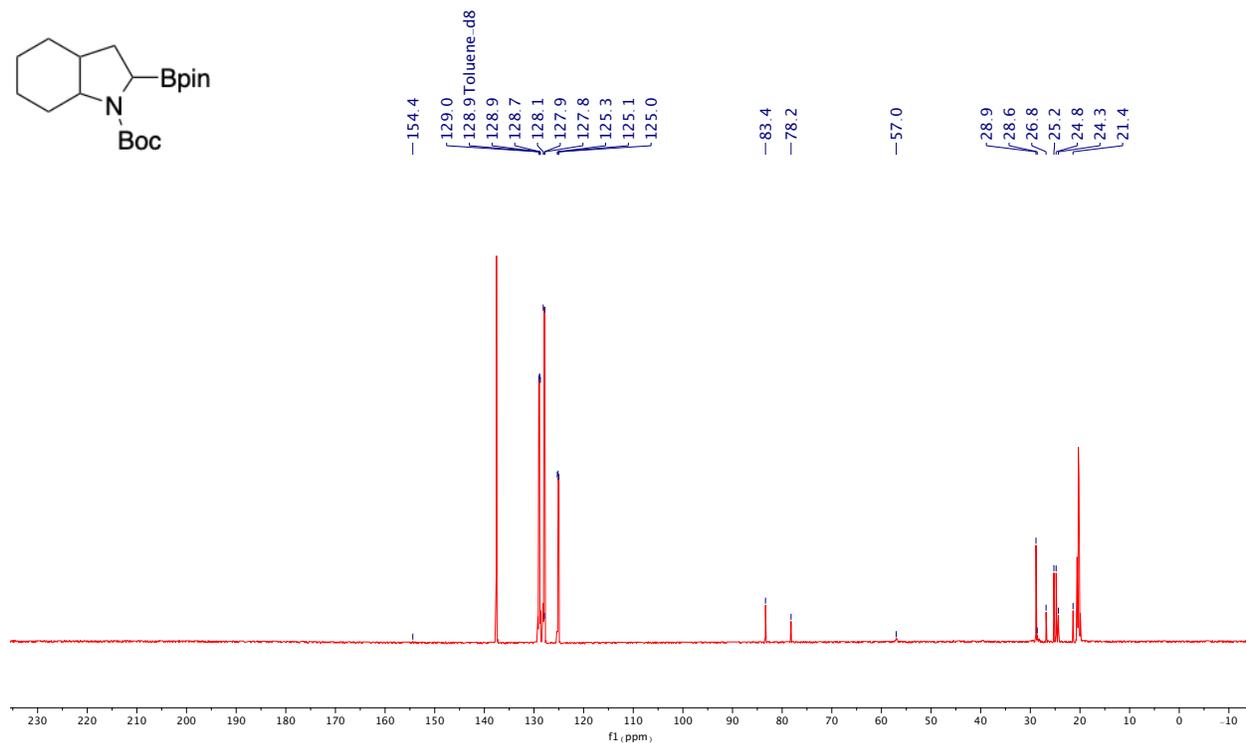
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



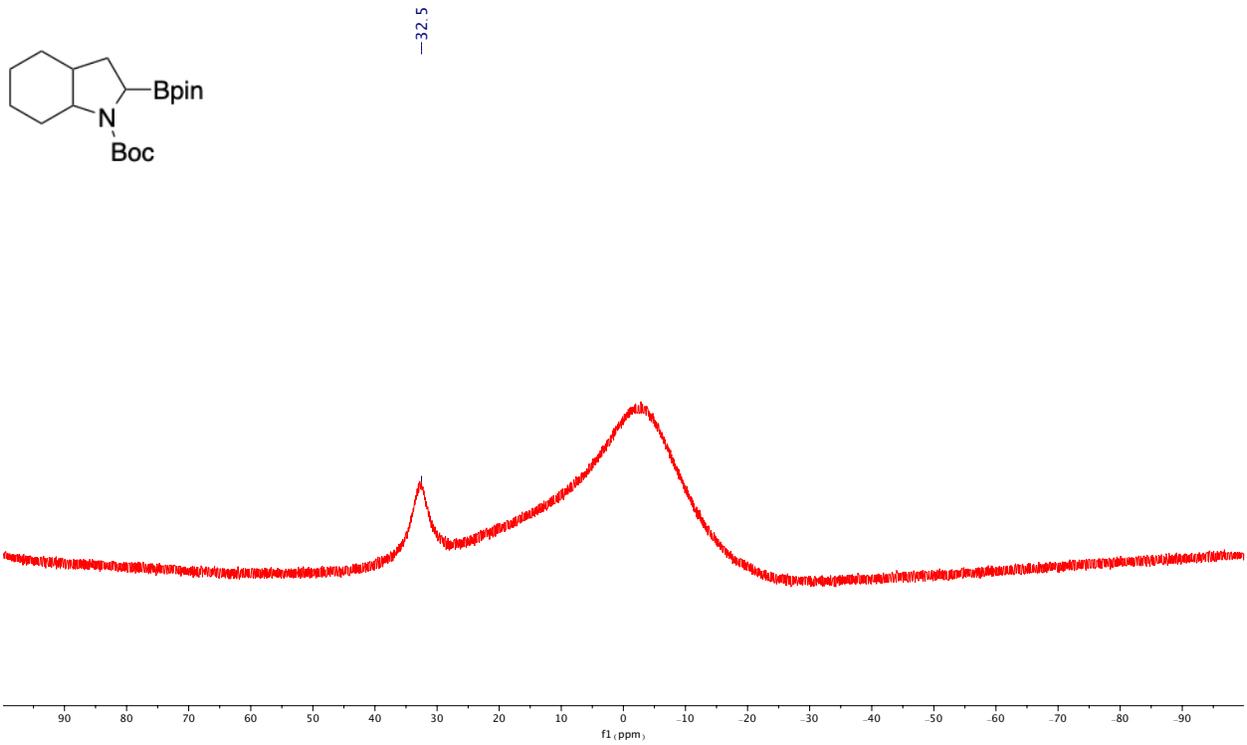
<sup>1</sup>H NMR(500MHz, CDCl<sub>3</sub>) of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



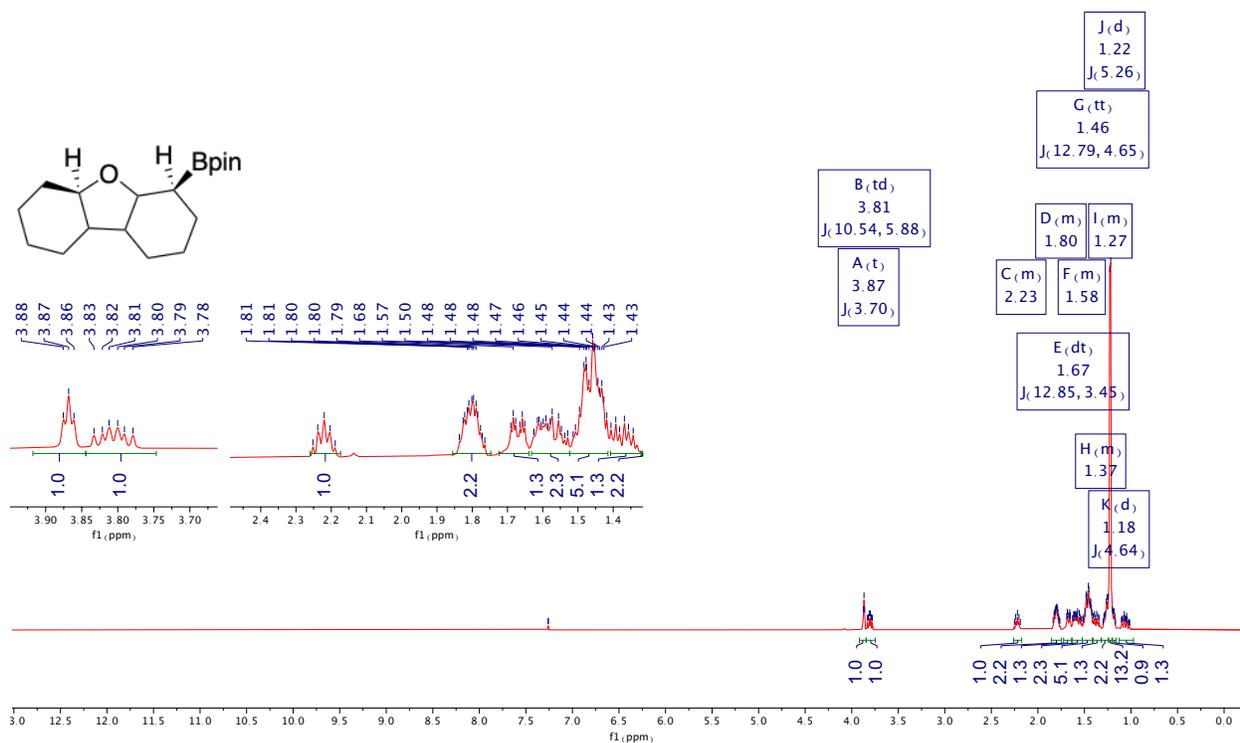
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, Toluene) NMR of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



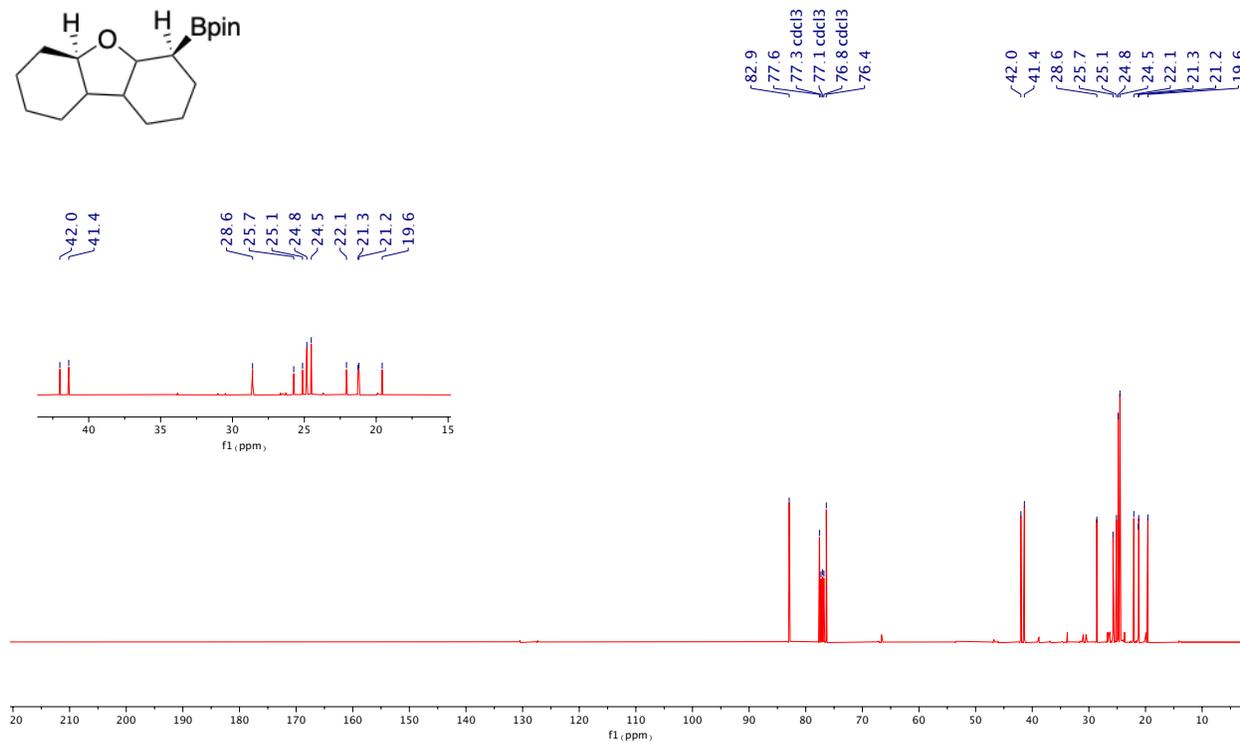
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



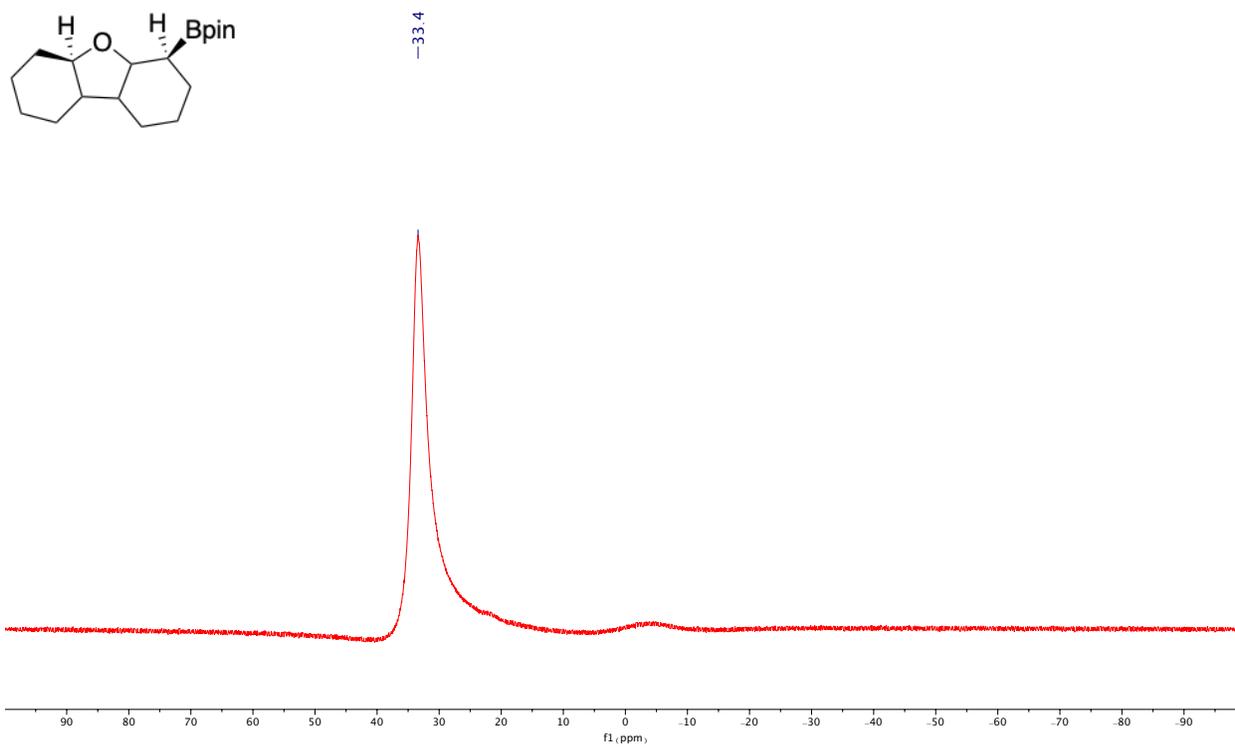
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2-(dodecahydrodibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



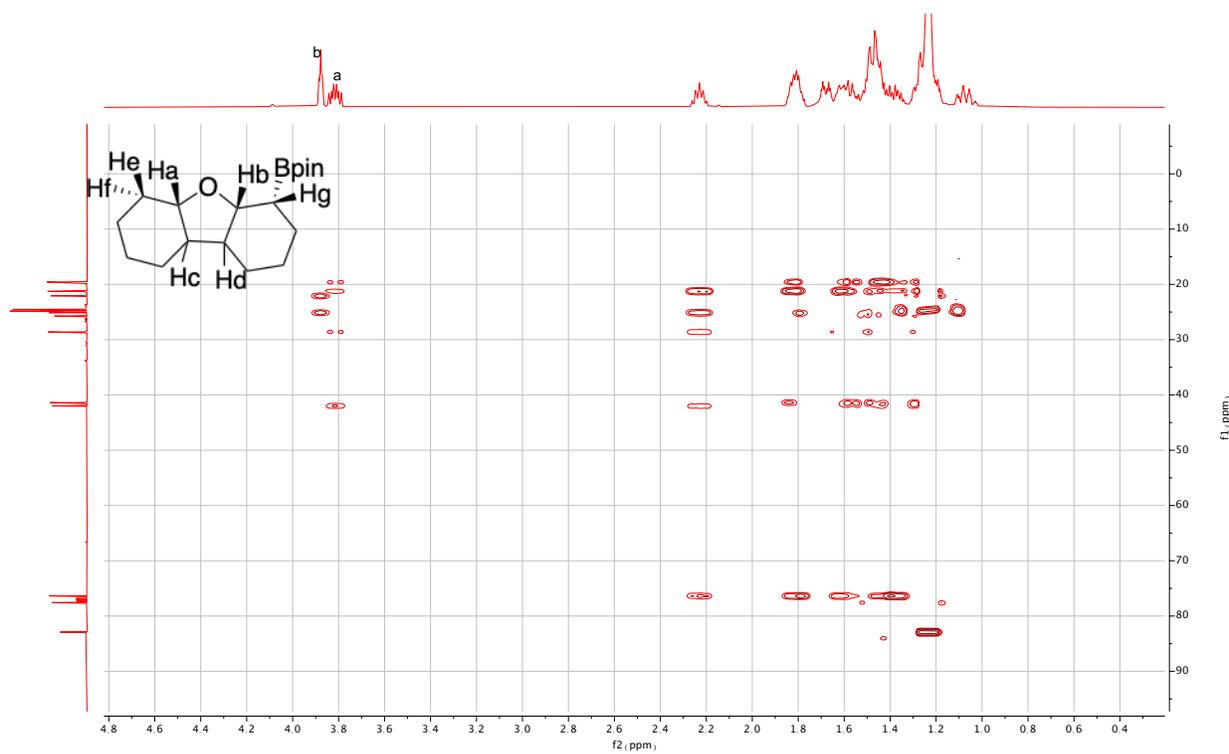
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2-(dodecahydrodibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



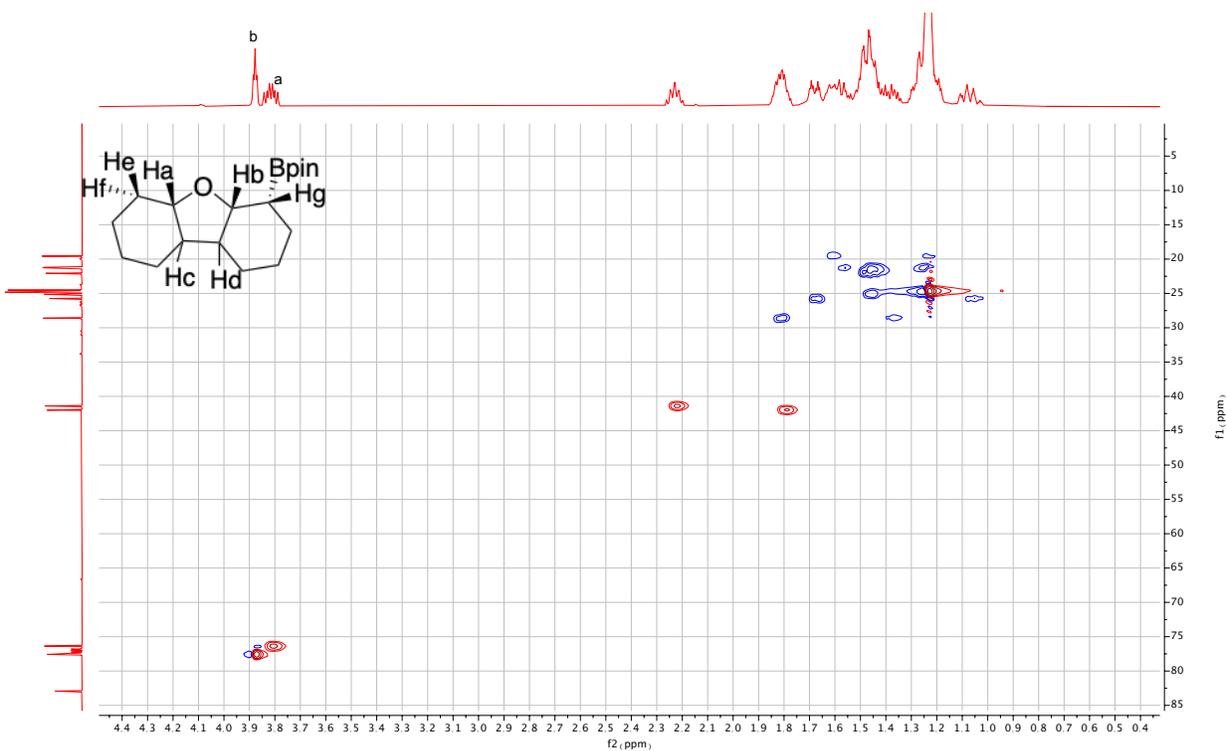
$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 2-(dodecahydrodibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



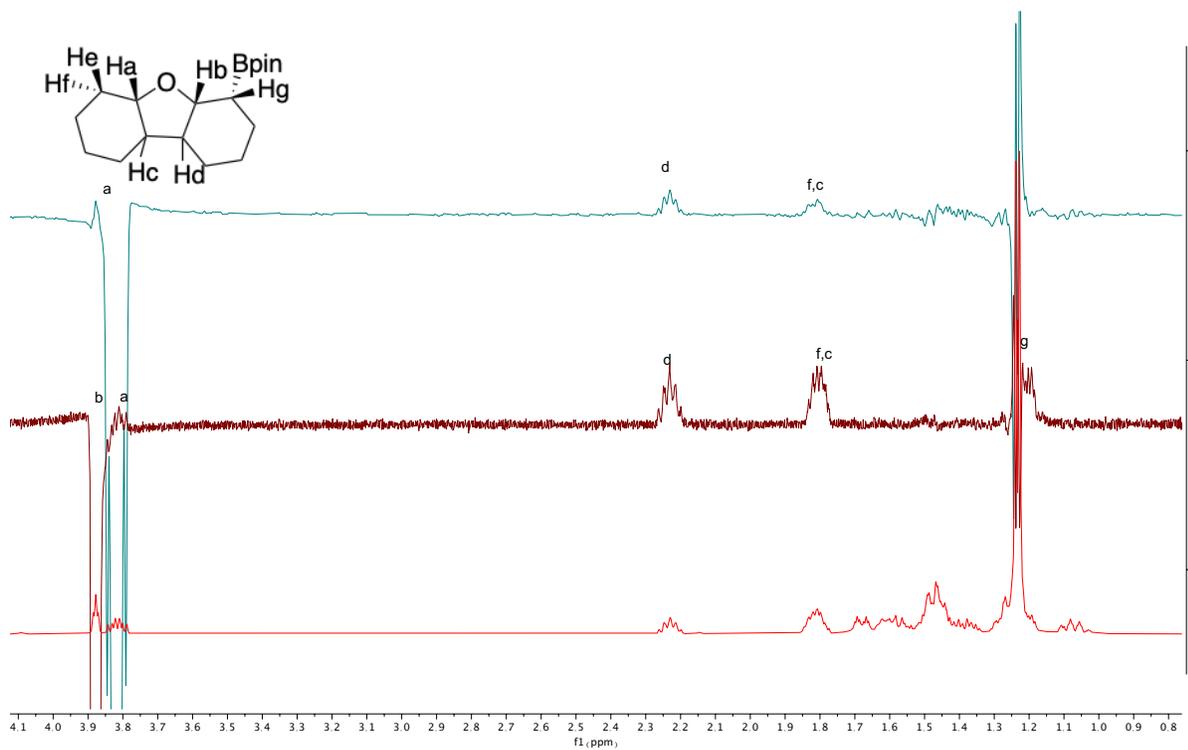
HMBC of 2-(dodecahydrodibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



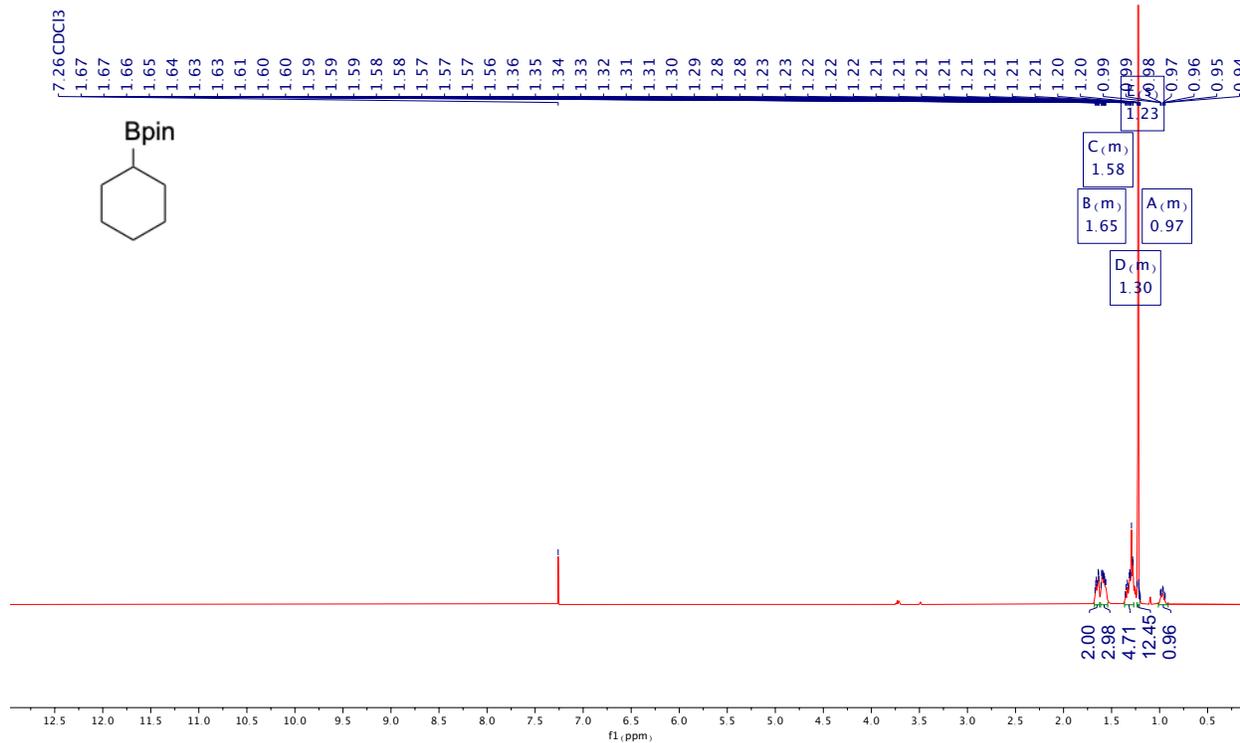
HSQC of 2-(dodecahydridibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



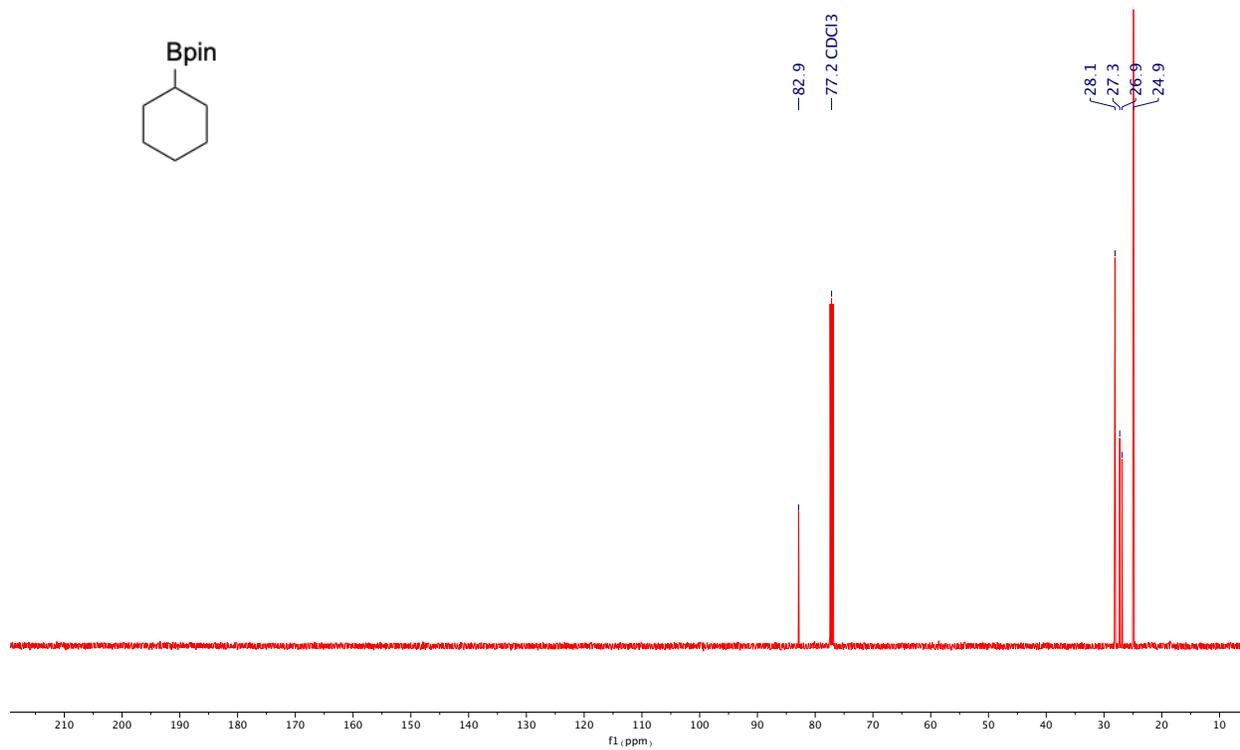
NOE of 2-(dodecahydridibenzo[*b,d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



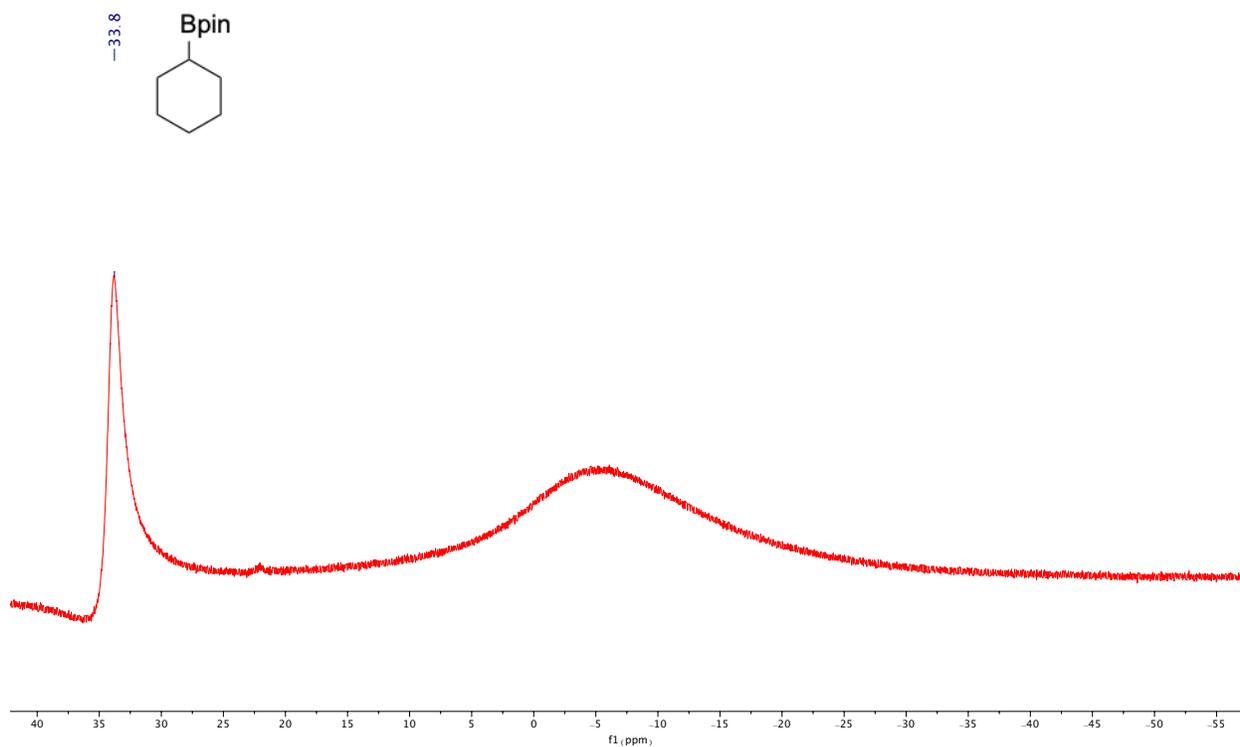
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



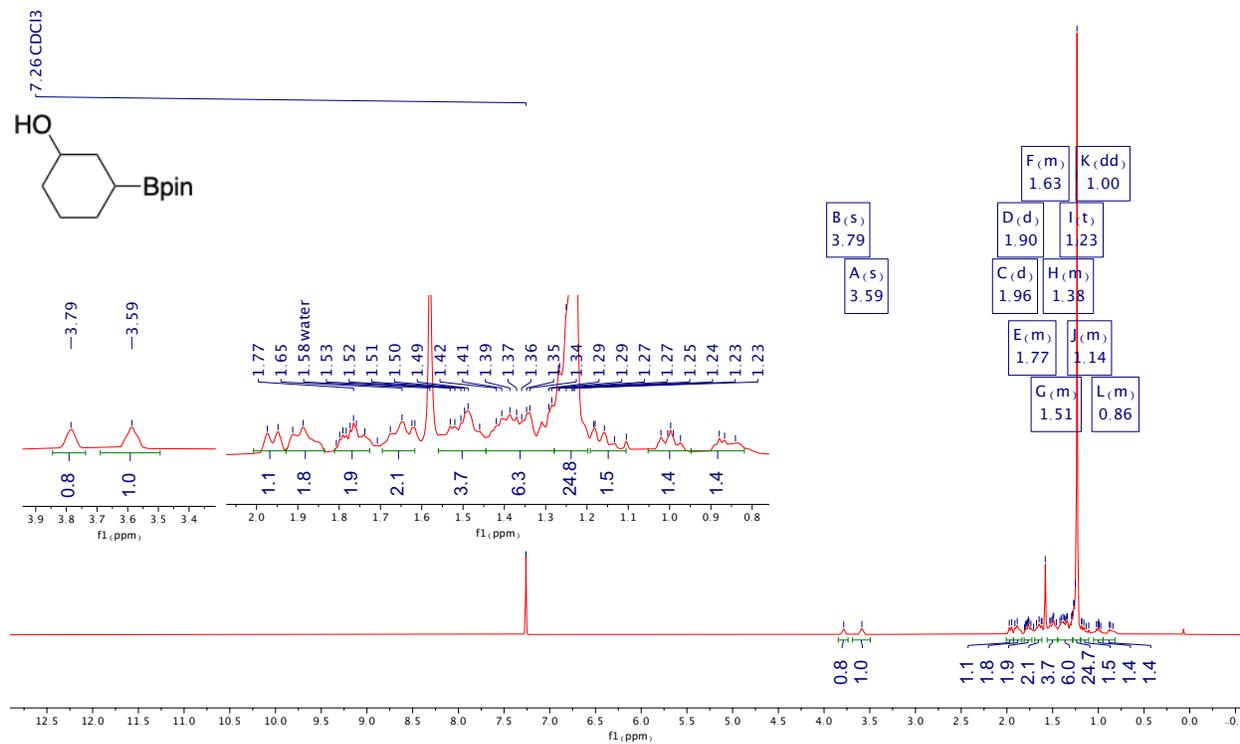
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



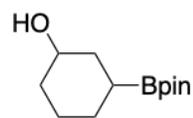
**$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)**



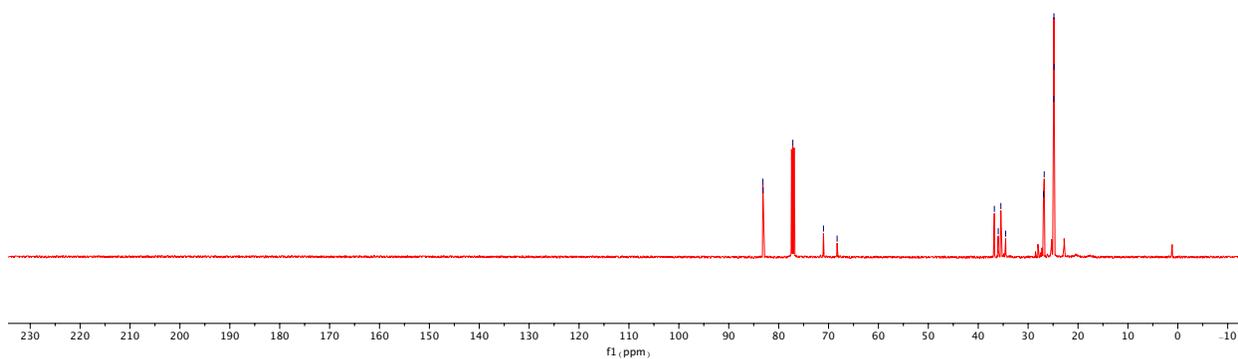
**$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)**



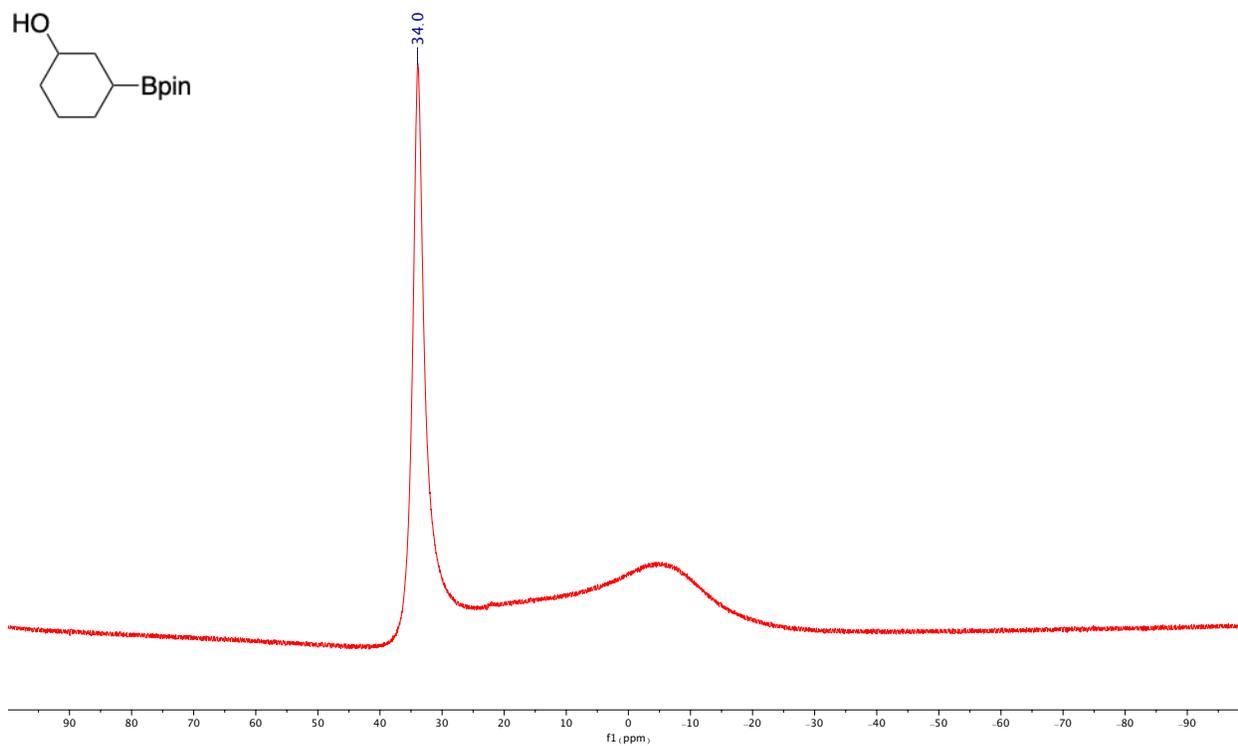
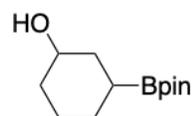
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)



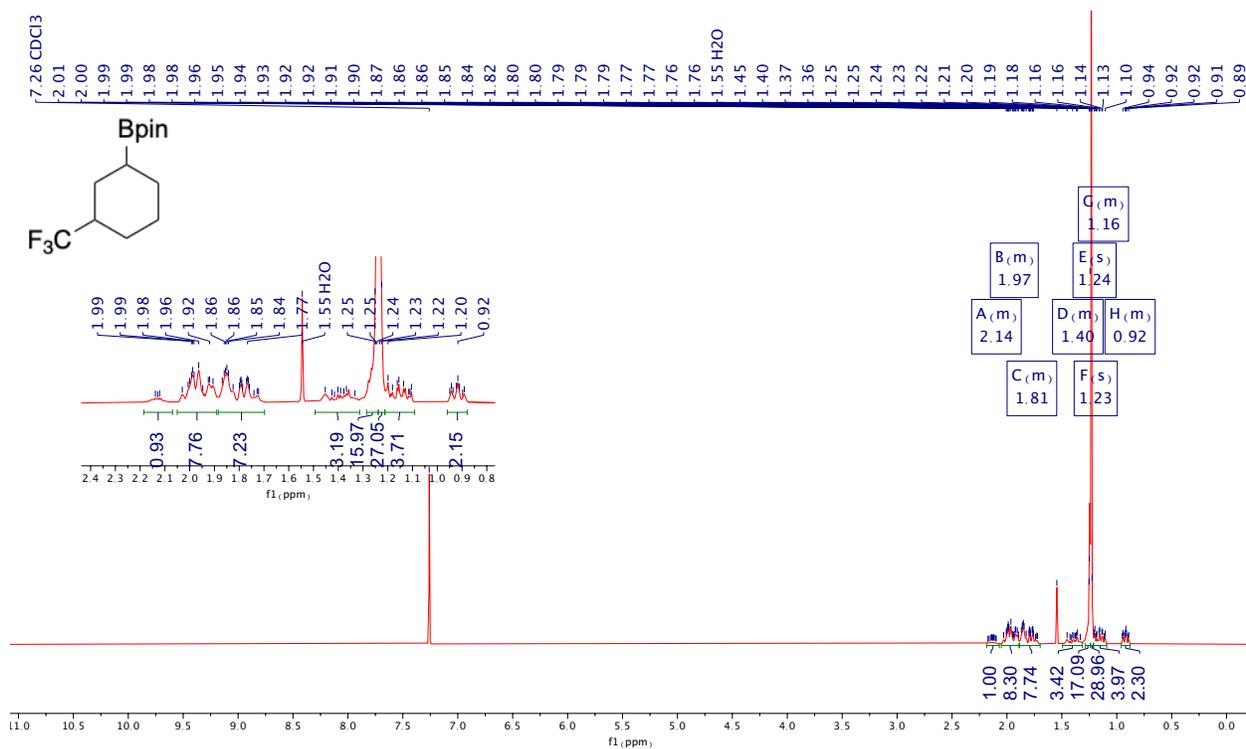
83.16  
83.13  
77.16  $\text{CDCl}_3$   
71.01  
68.29  
36.77  
35.99  
35.46  
34.50  
26.92  
26.78  
24.87  
24.83  
24.80



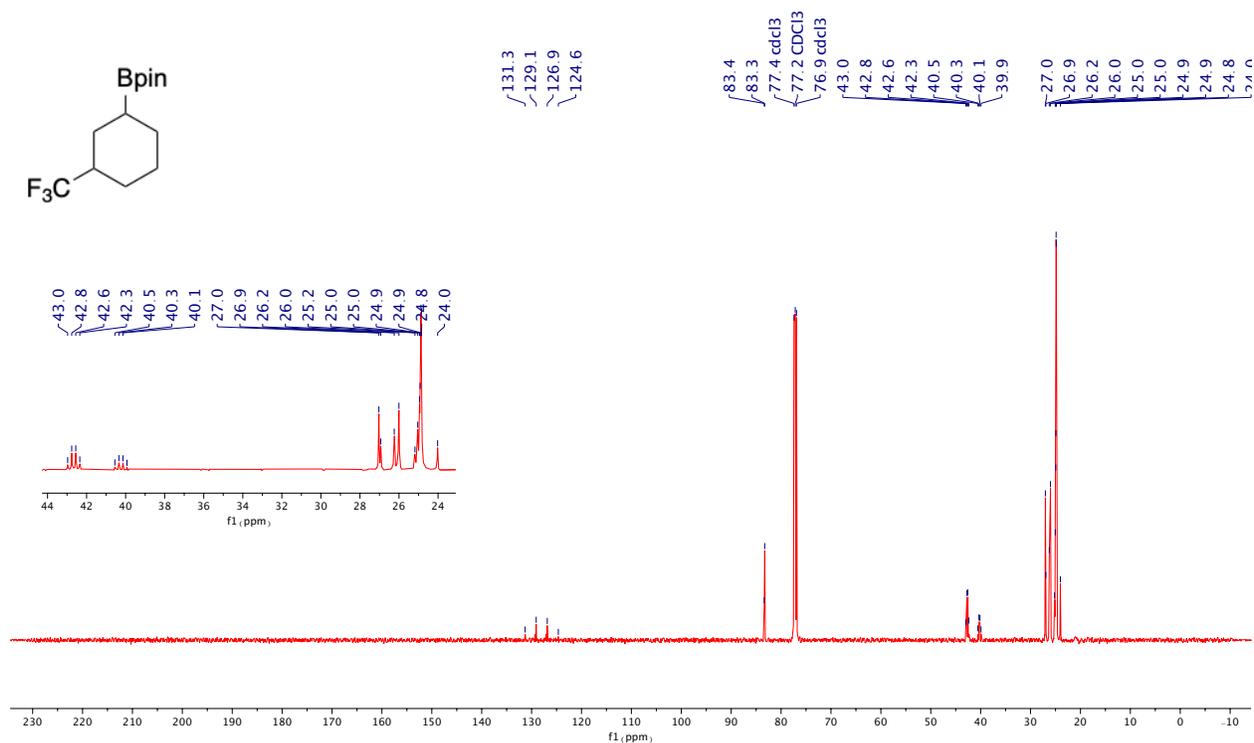
$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)



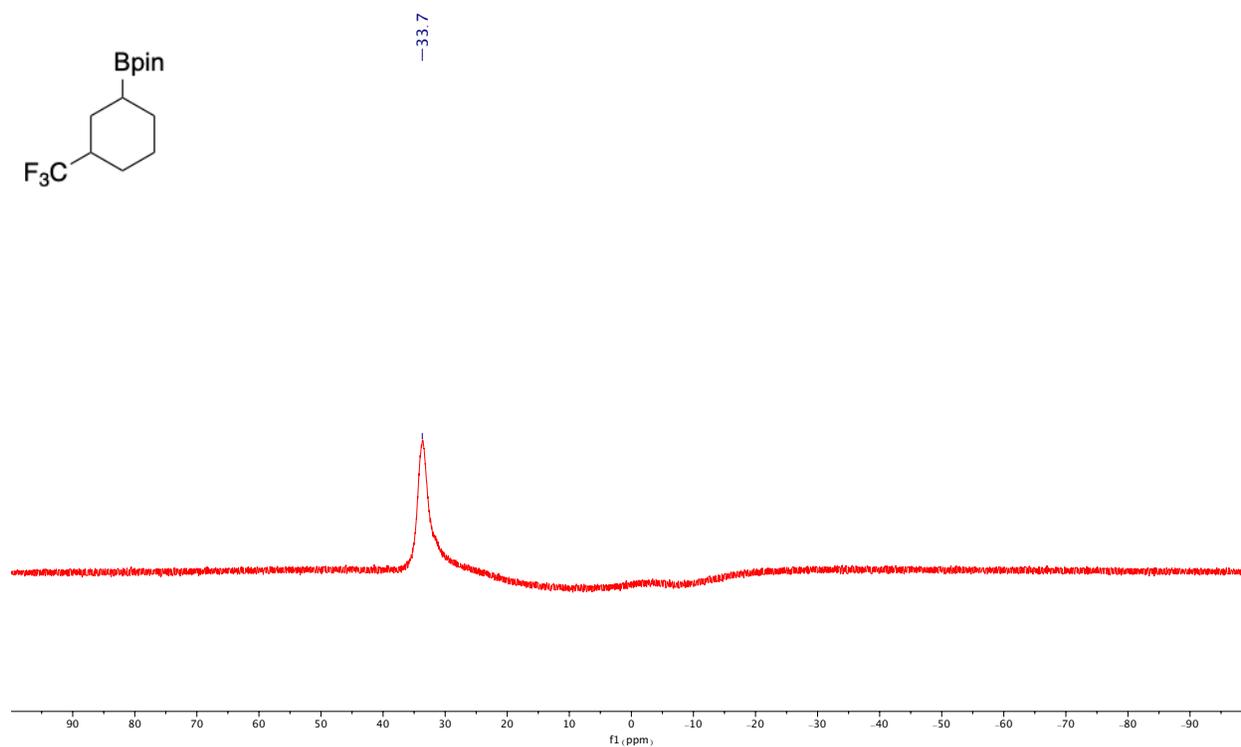
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



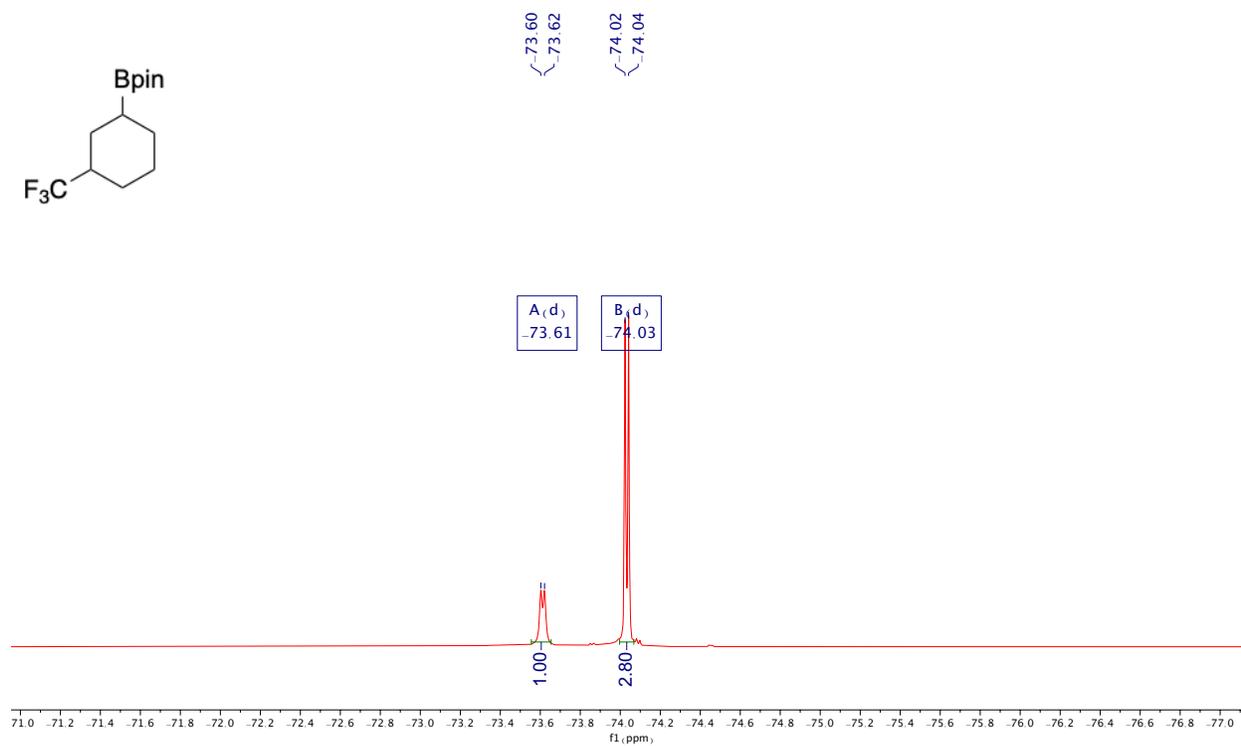
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



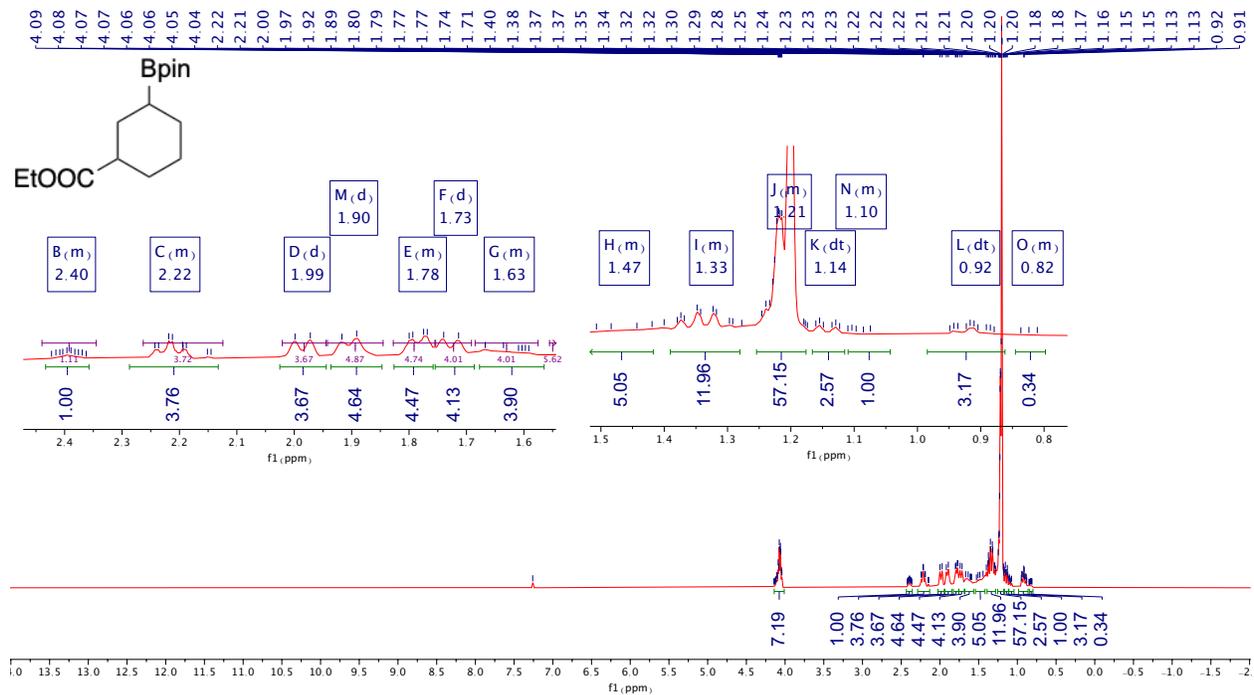
**$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)**



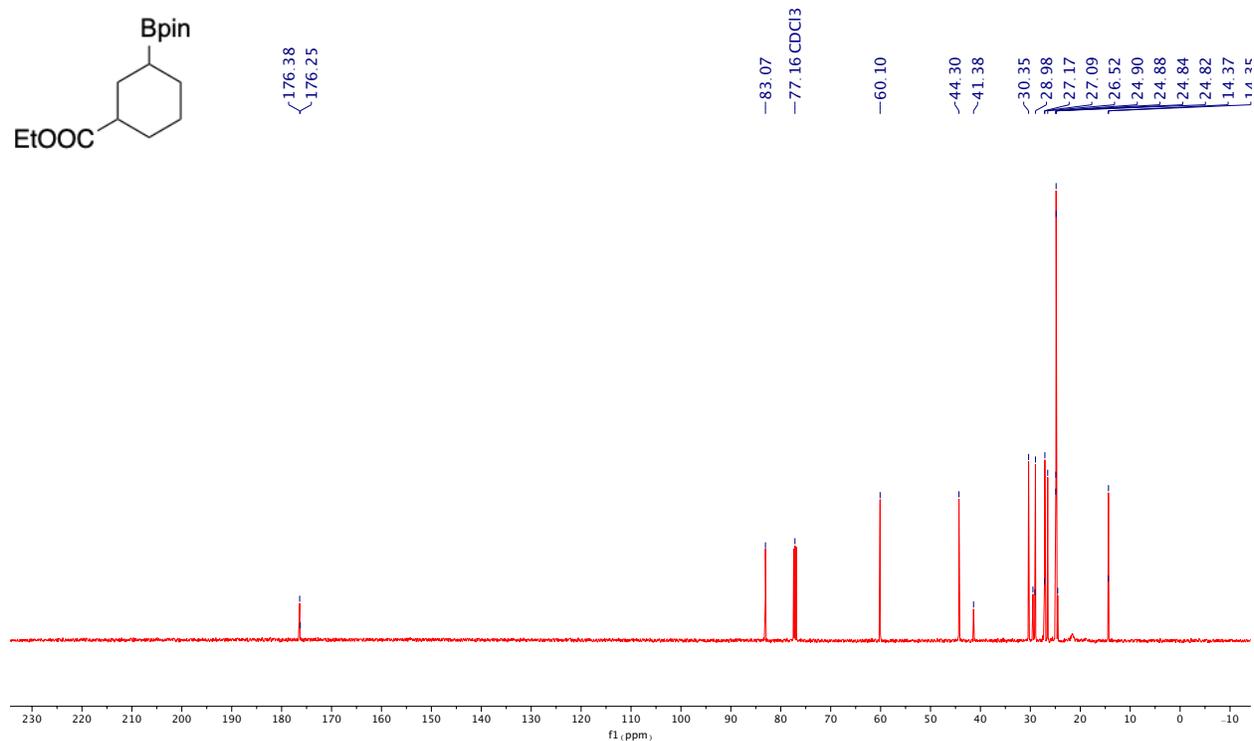
**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)**



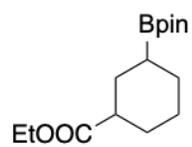
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



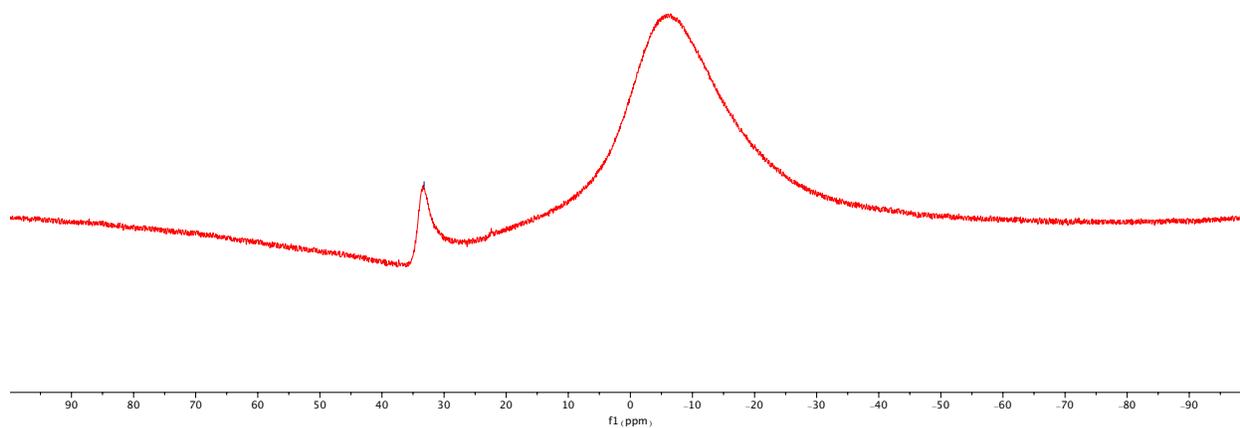
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



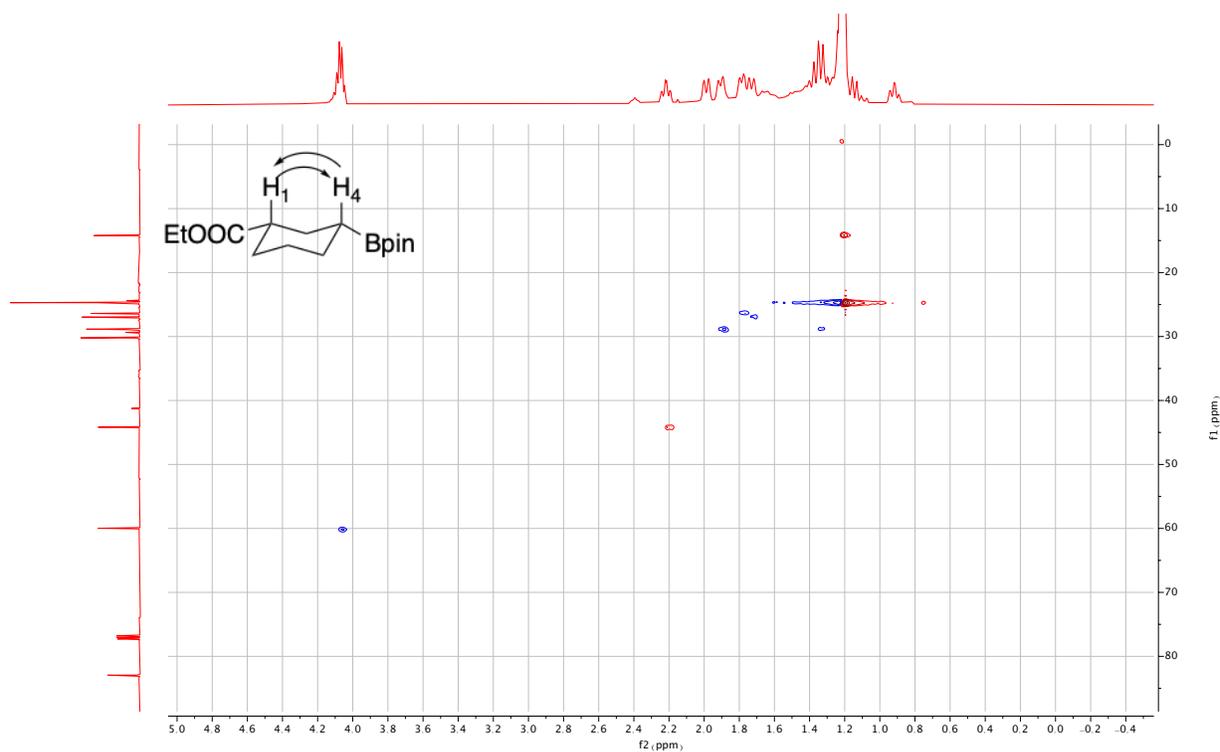
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



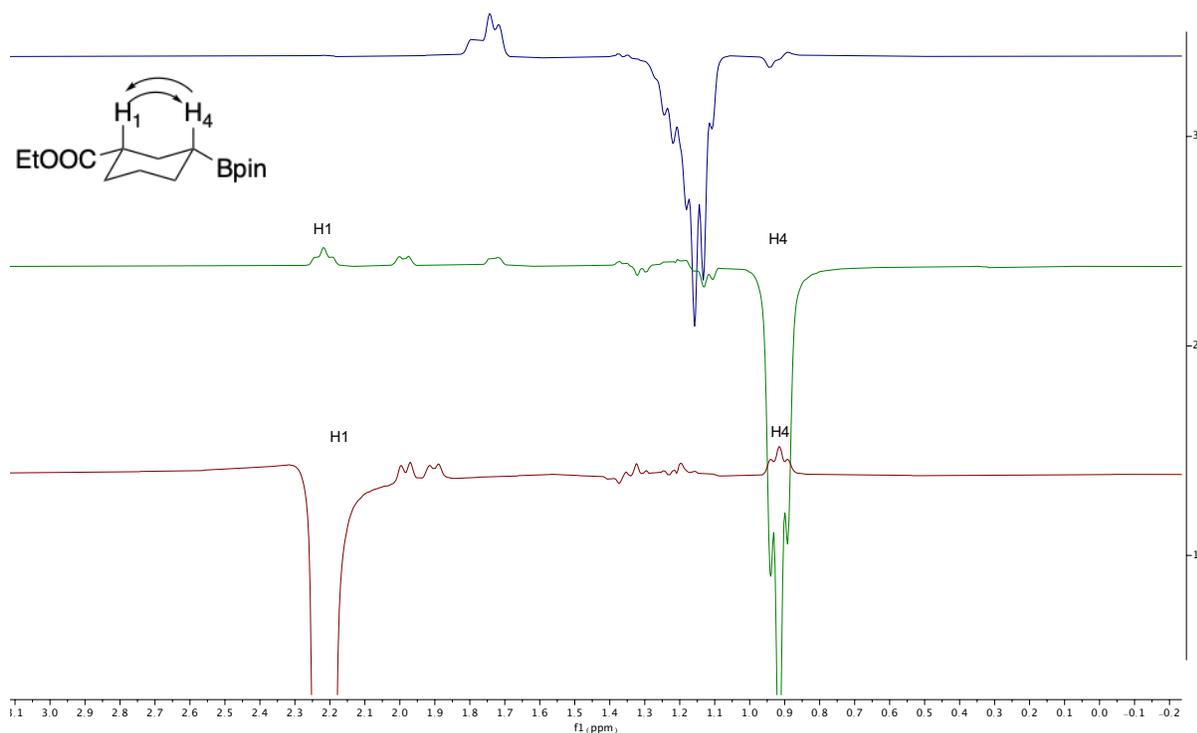
-33.2



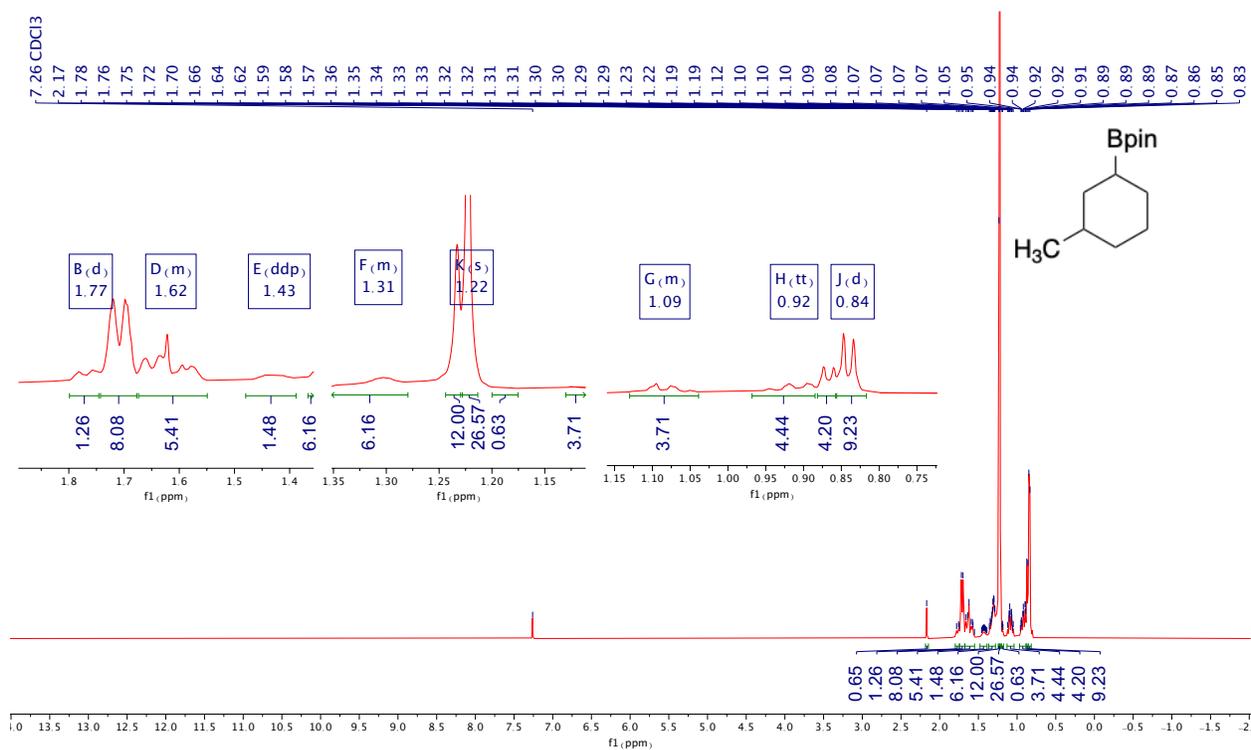
HSQC of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



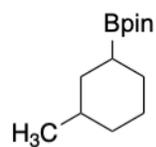
NOE of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)

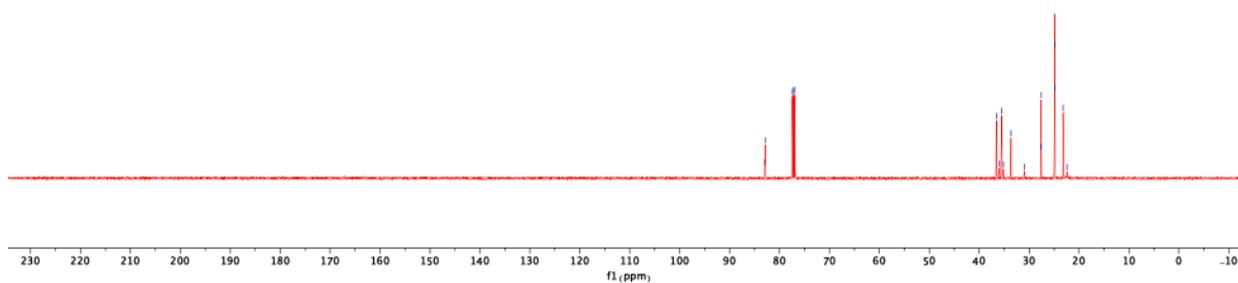


$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) NMR of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)

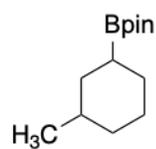


82.93  
82.87  
77.42 cdc13  
77.16 CDC13  
76.91 cdc13

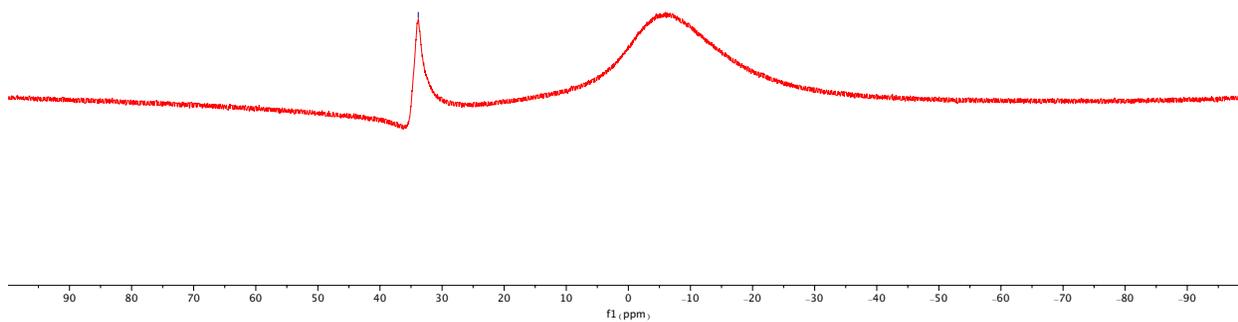
36.59  
36.06  
35.47  
35.14  
33.64  
30.98  
27.60  
27.58  
24.93  
24.87  
23.22  
22.46



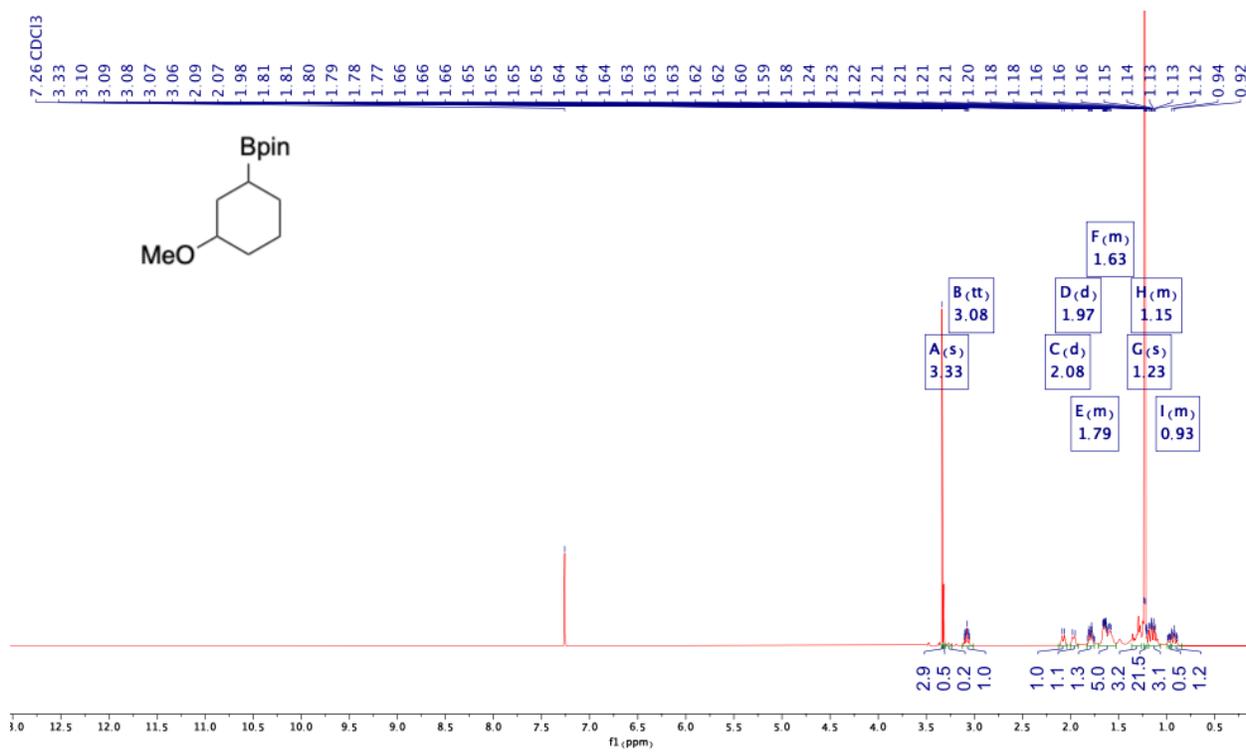
$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)



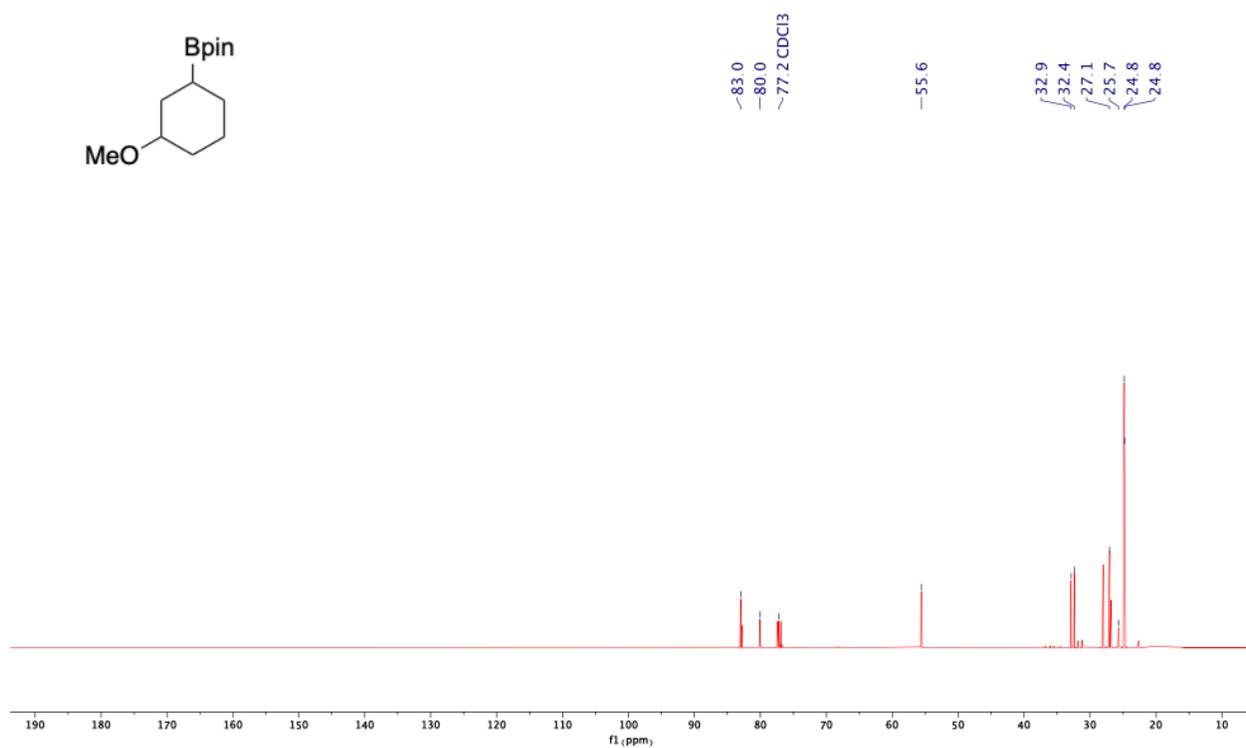
-33.8



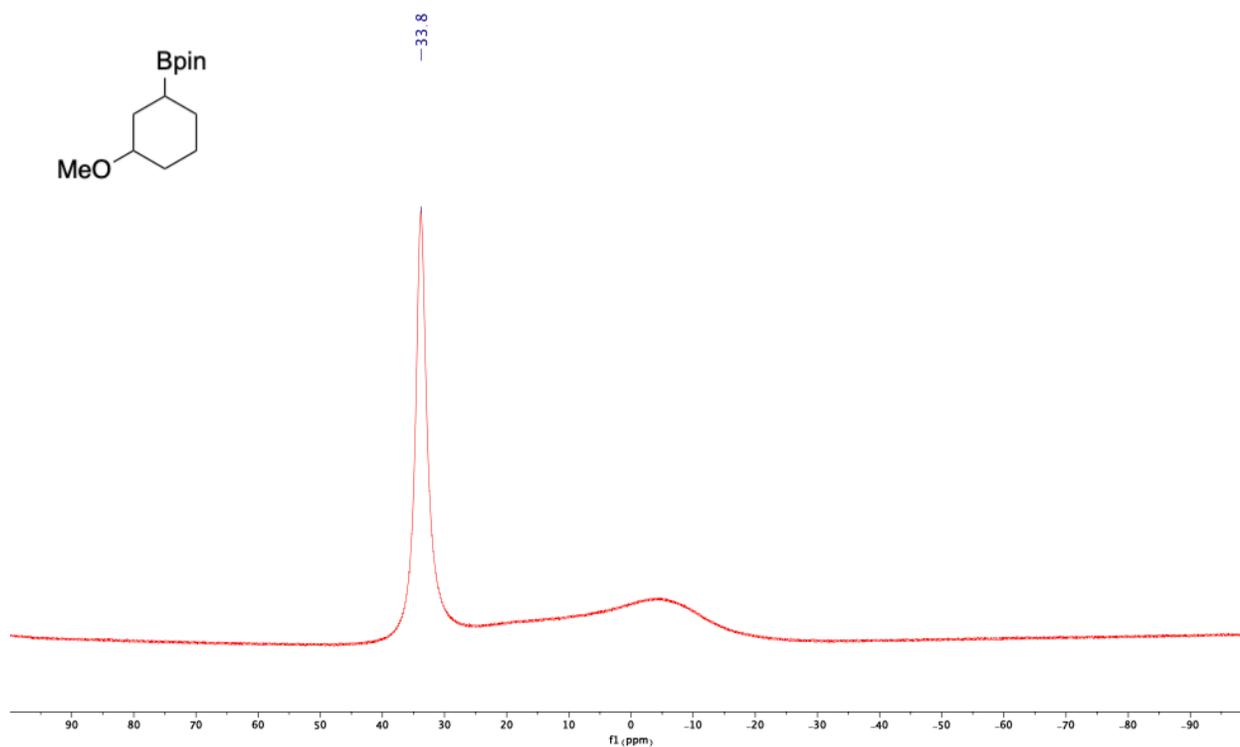
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2-(3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



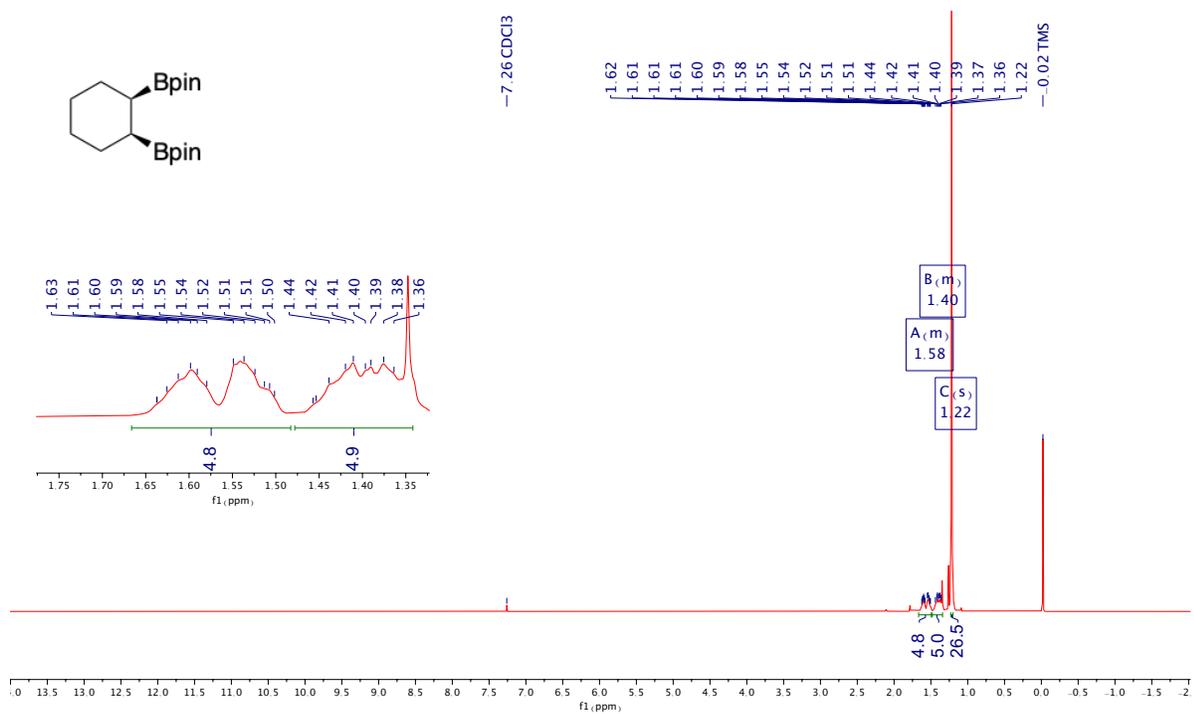
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of 2-(3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



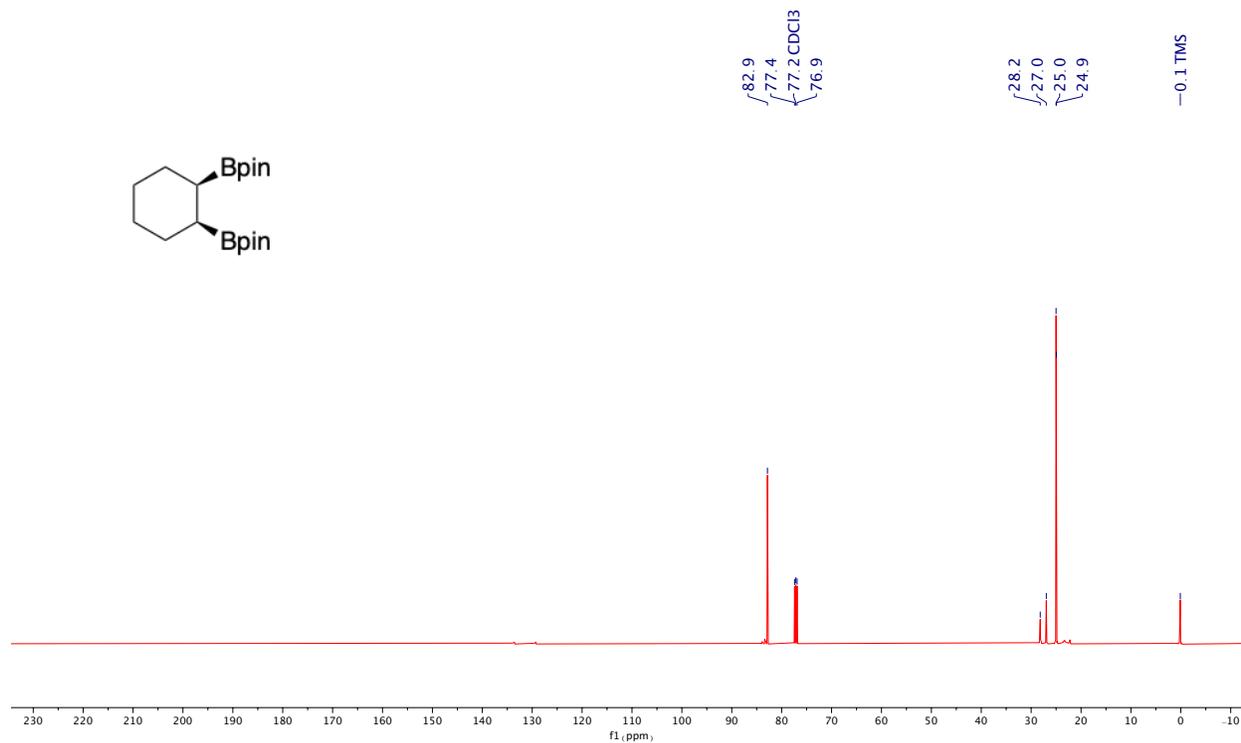
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of 2-(3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



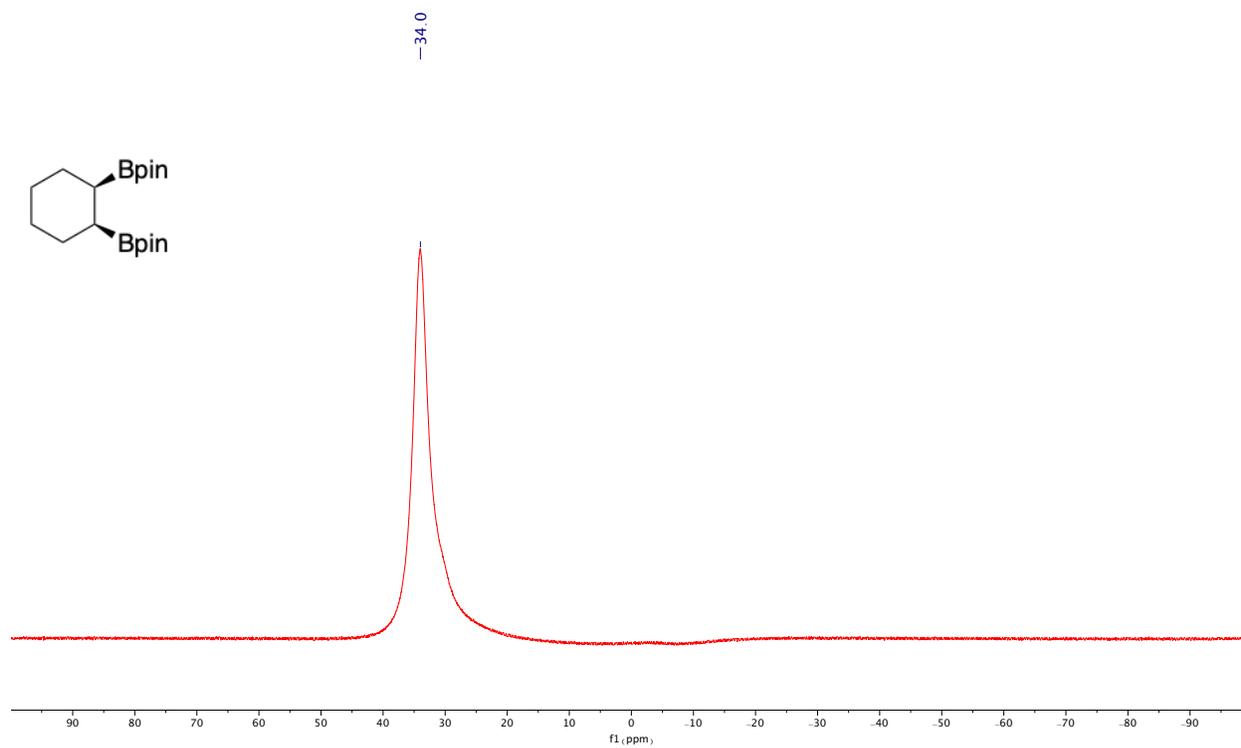
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of cis-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



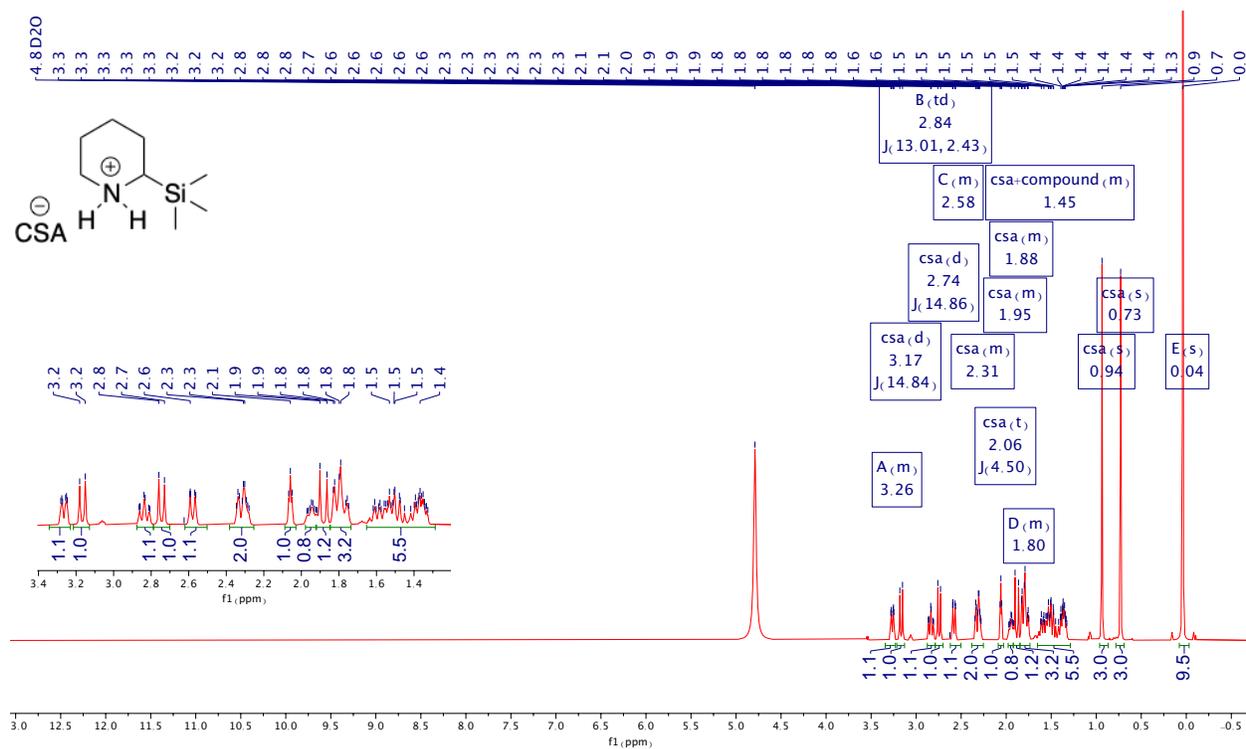
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) of cis-1,2-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



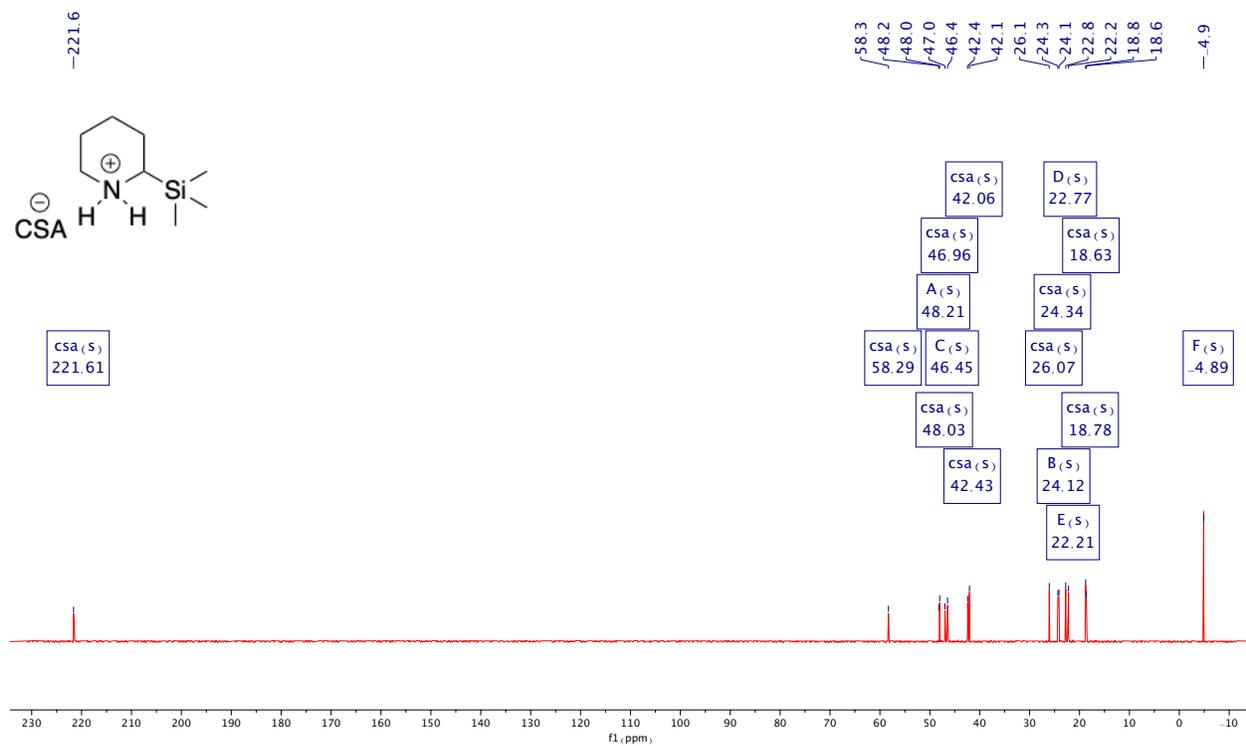
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of cis-1,2-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



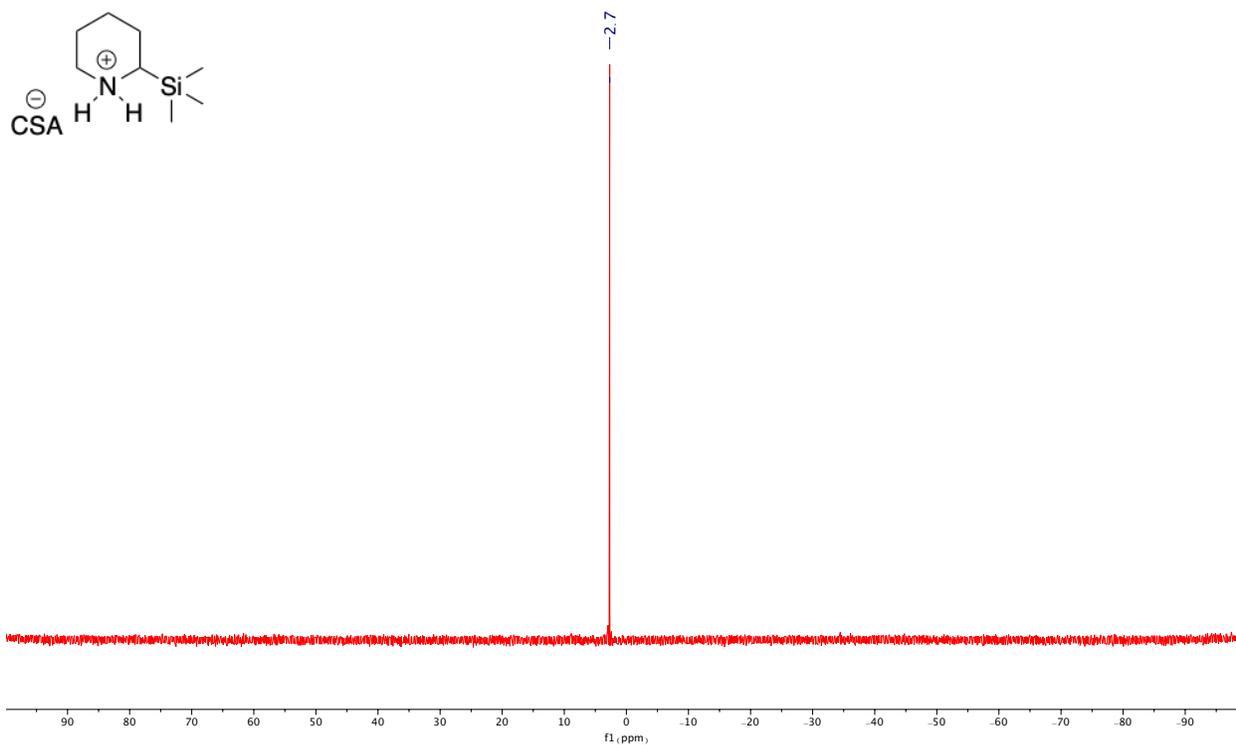
<sup>1</sup>H NMR (500MHz, D<sub>2</sub>O) of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



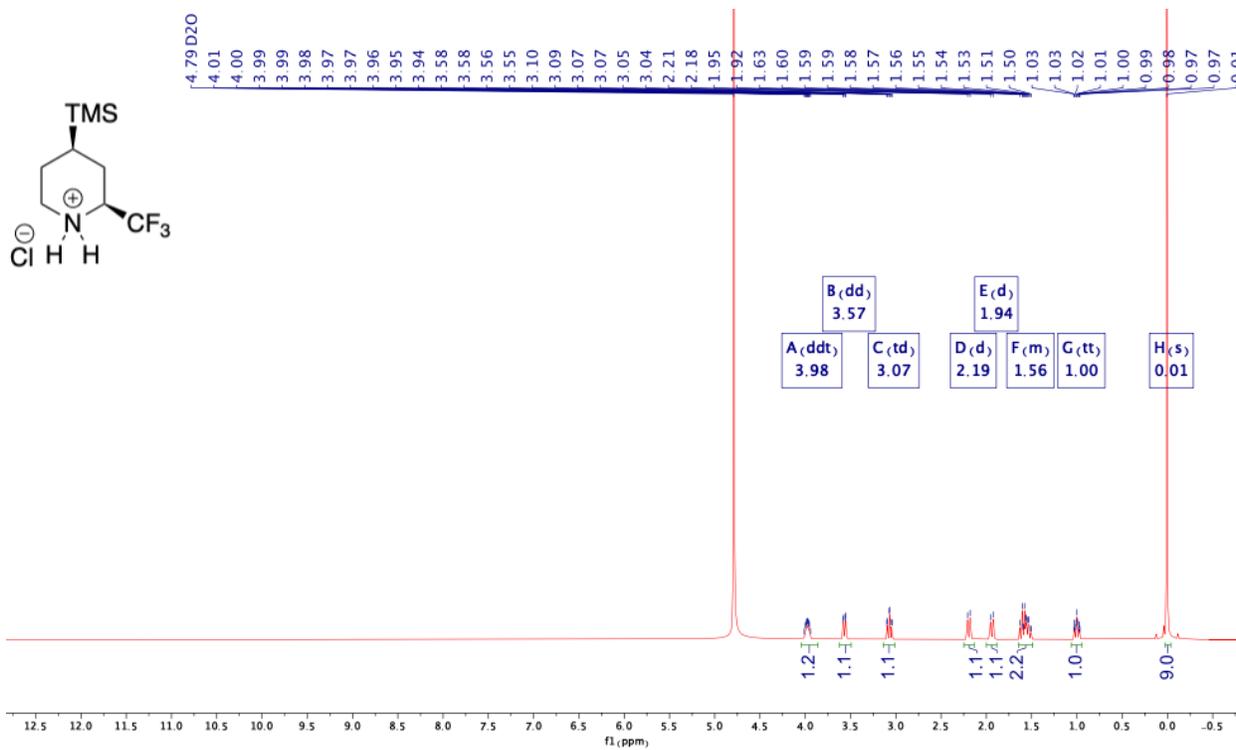
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, D<sub>2</sub>O) NMR of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



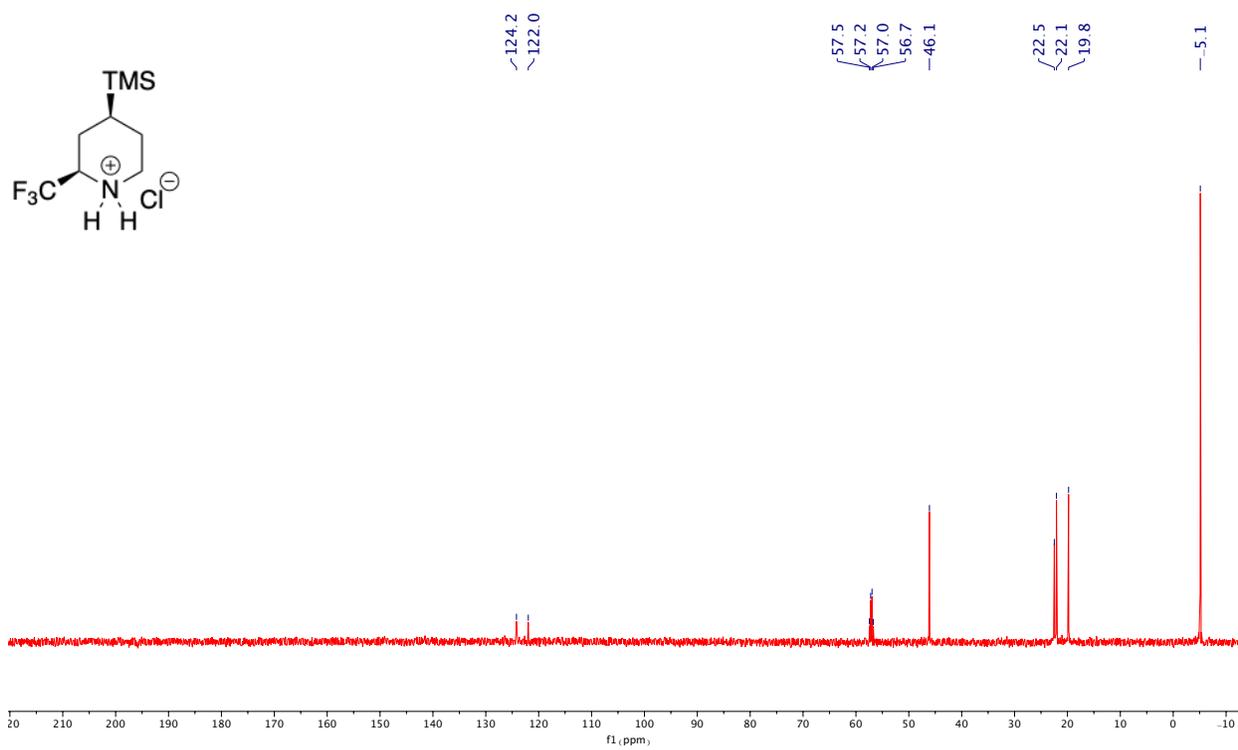
<sup>29</sup>Si NMR (99MHz, D<sub>2</sub>O) of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



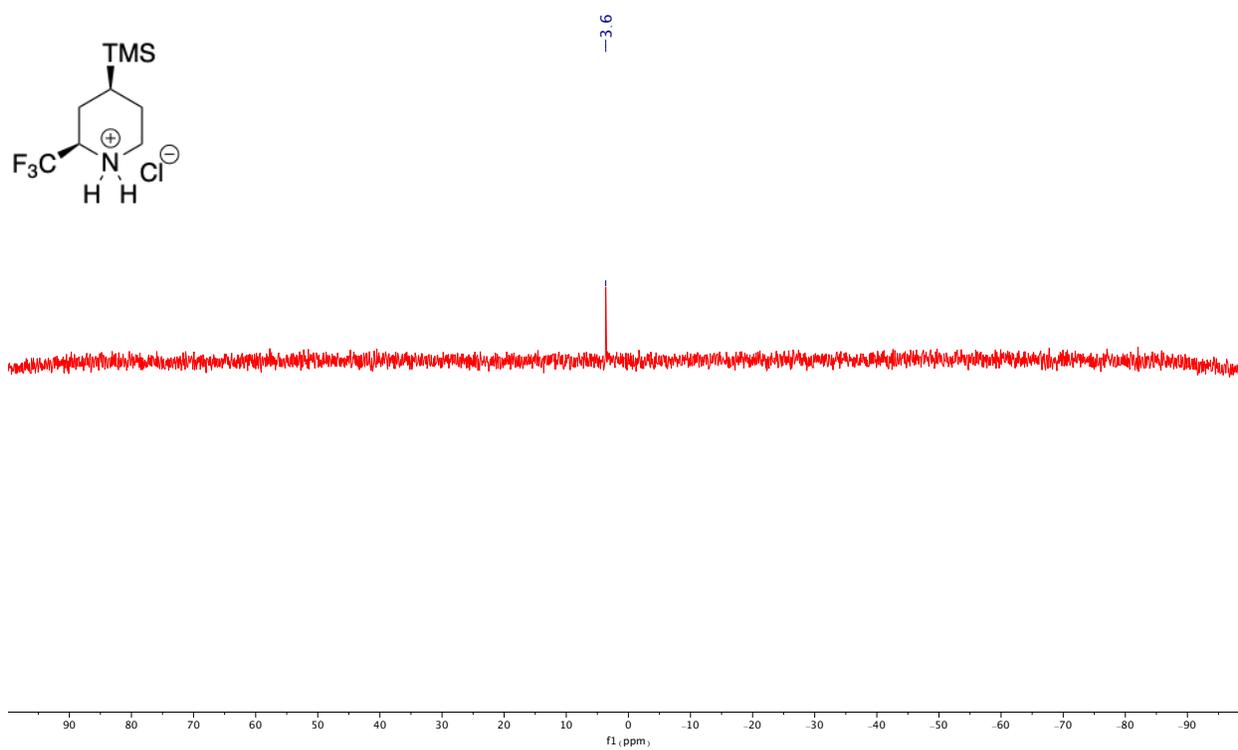
<sup>1</sup>H NMR (500MHz, D<sub>2</sub>O) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



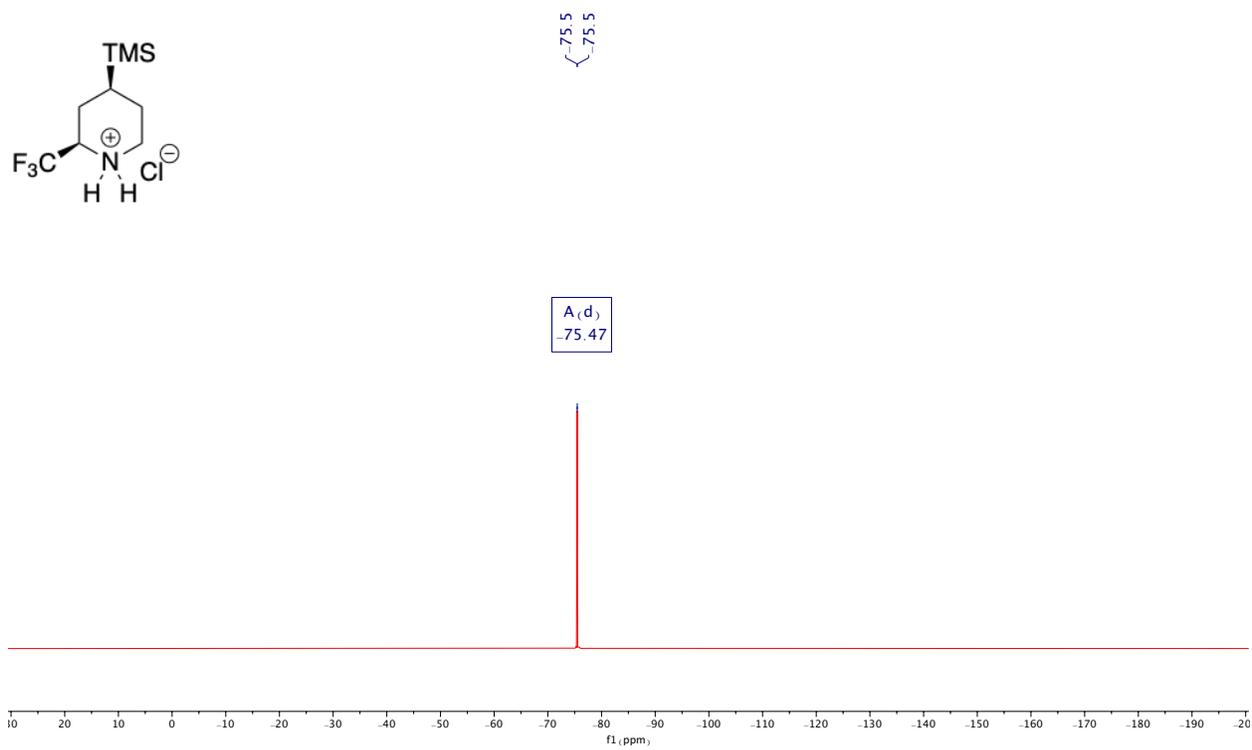
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{D}_2\text{O}$ ) NMR of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



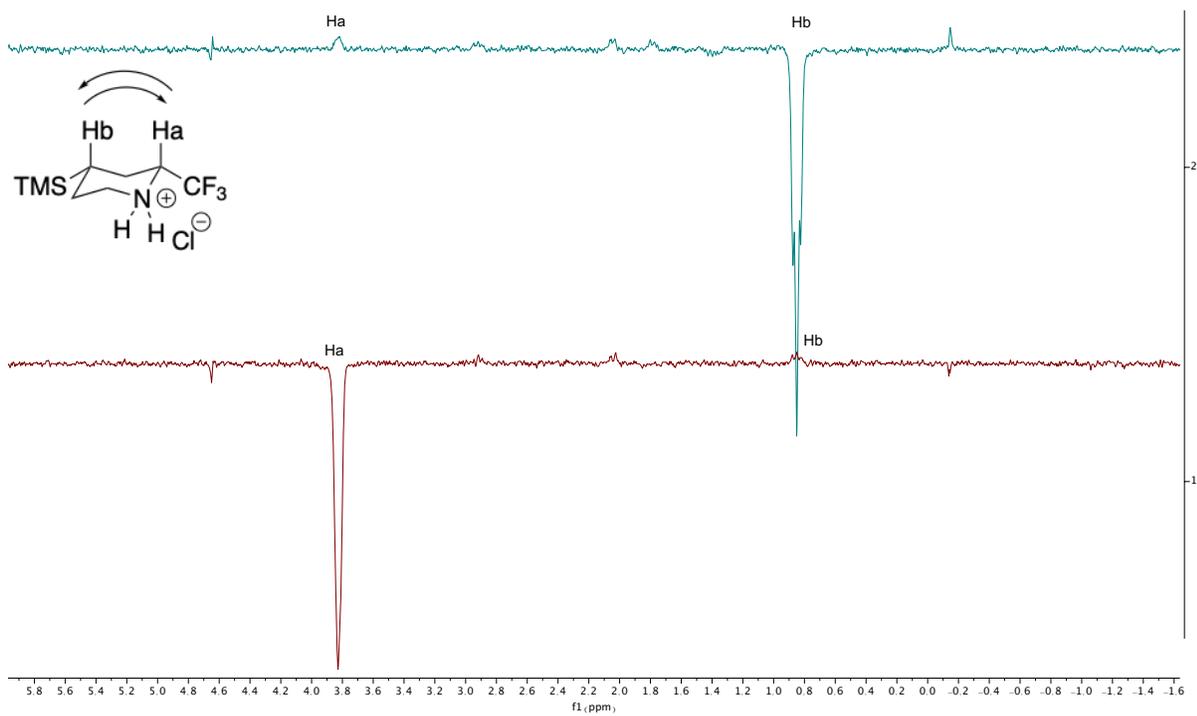
$^{29}\text{Si}$  NMR (99 MHz,  $\text{D}_2\text{O}$ ) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



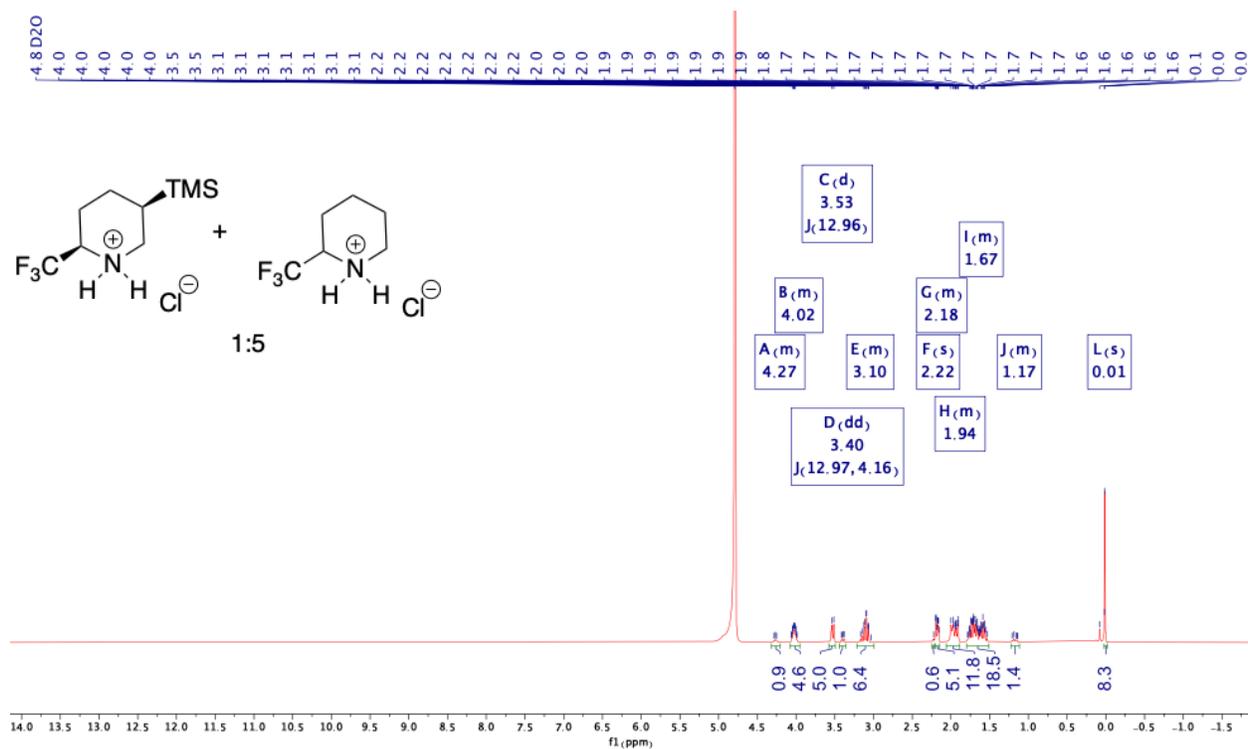
**<sup>19</sup>F NMR (470 MHz, D<sub>2</sub>O) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)**



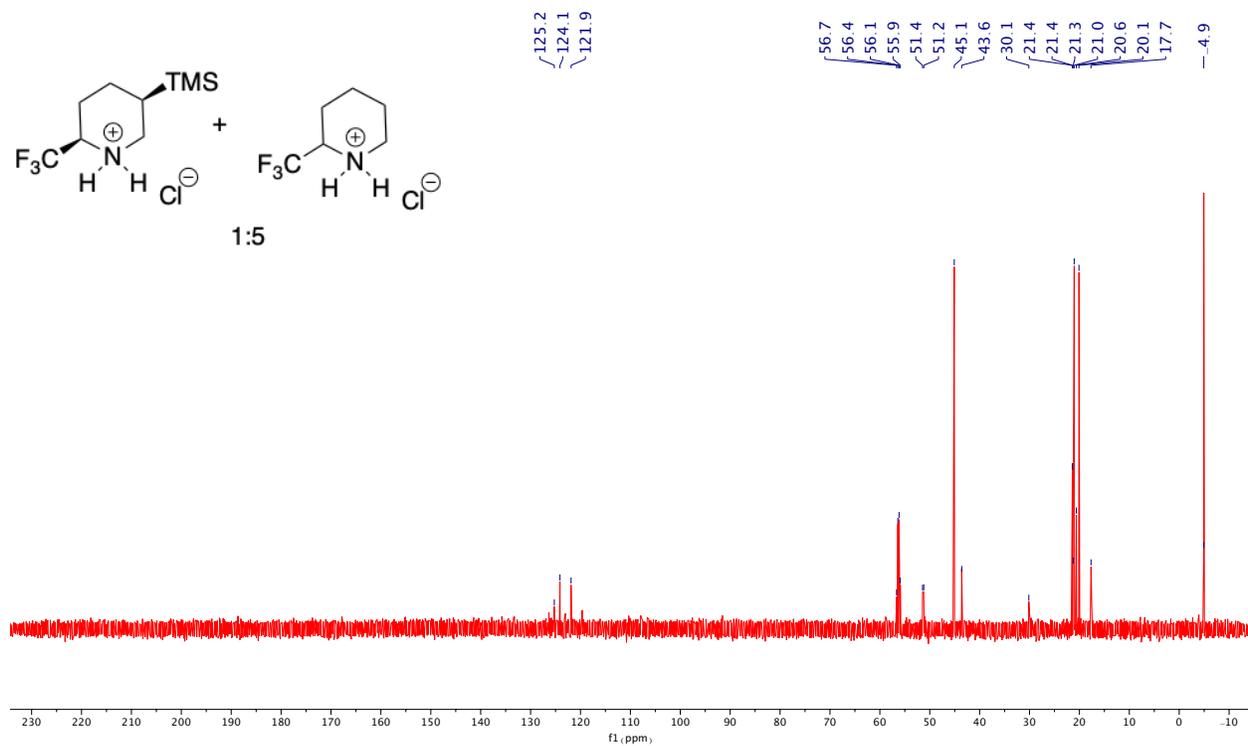
**NOE of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)**



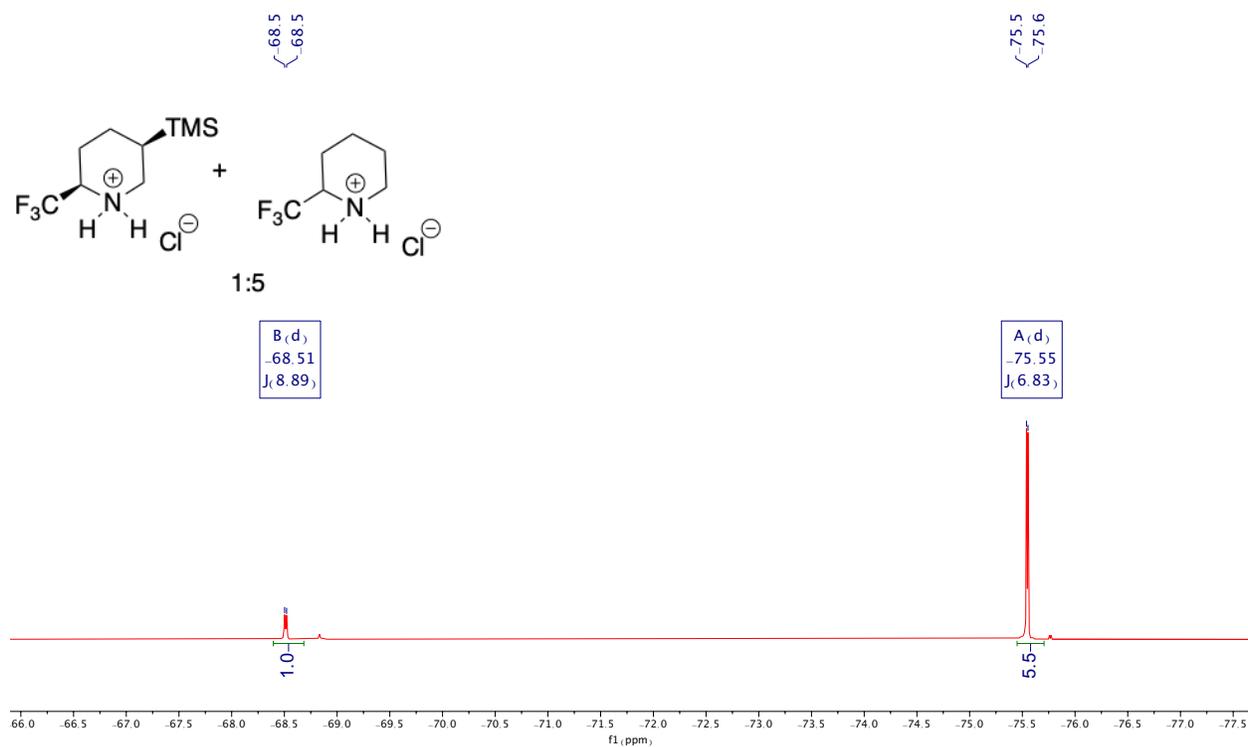
<sup>1</sup>H NMR (500MHz, D<sub>2</sub>O) of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)



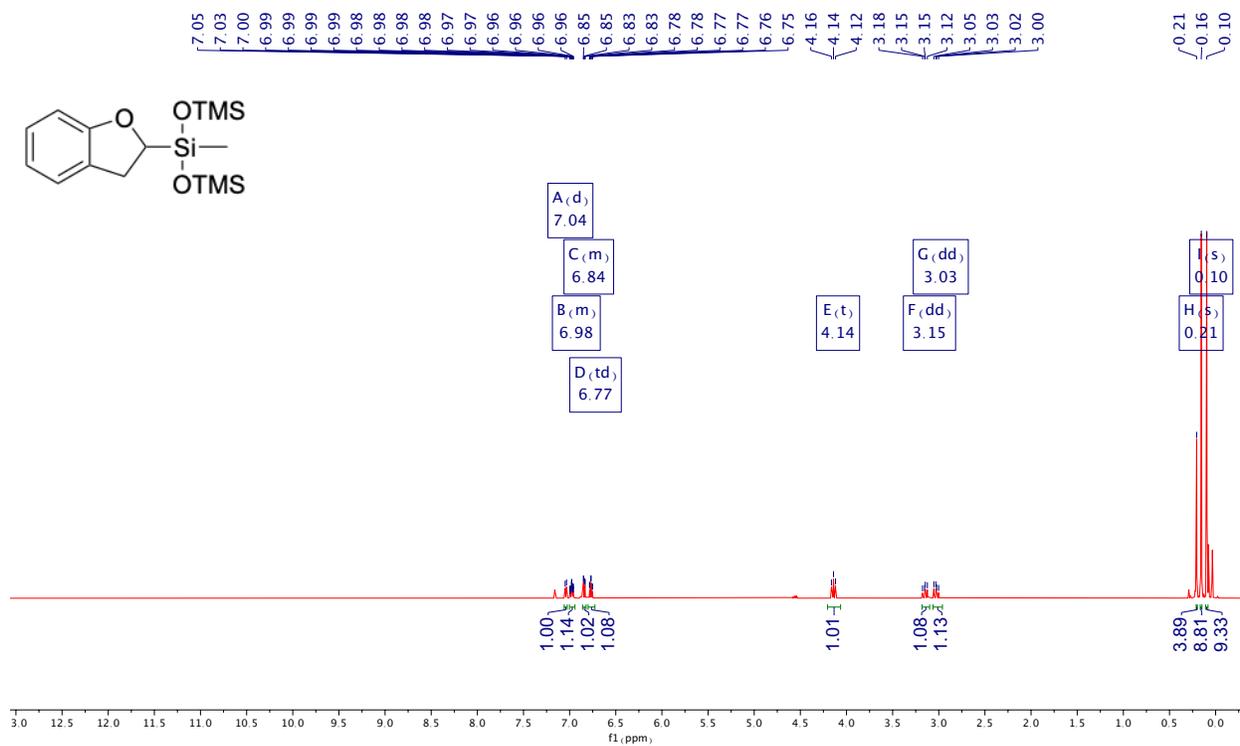
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, D<sub>2</sub>O) NMR of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)



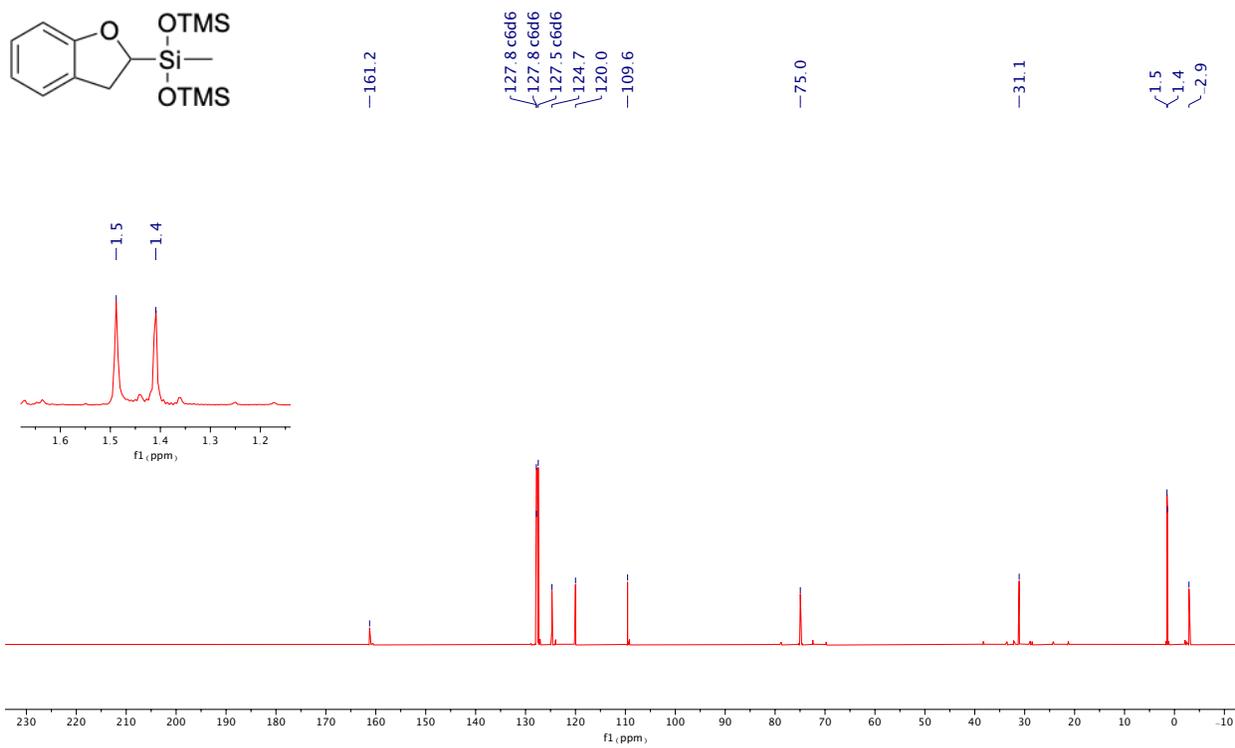
**$^{19}\text{F}$  NMR (470 MHz,  $\text{D}_2\text{O}$ ) of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)**



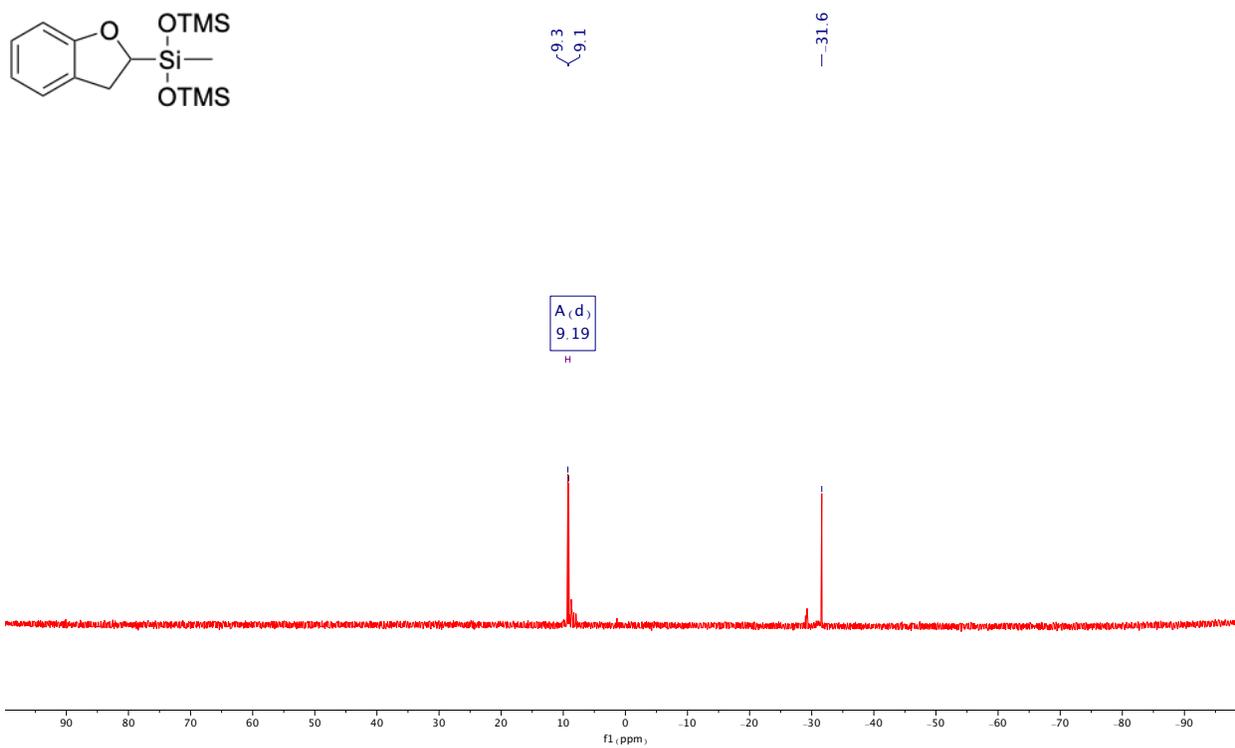
**$^1\text{H}$  NMR (500MHz,  $\text{C}_6\text{D}_6$ ) of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptomethyltrisiloxane (2z)**



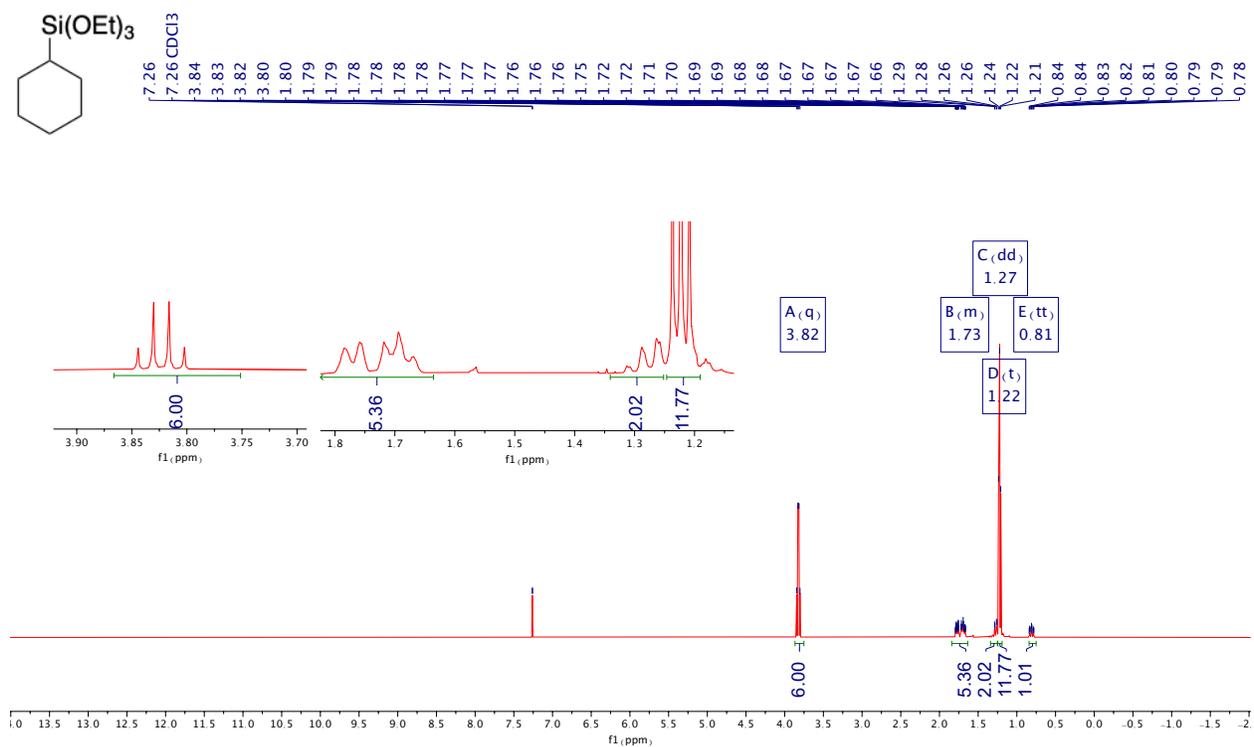
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz  $\text{C}_6\text{D}_6$ ) NMR of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (2z)



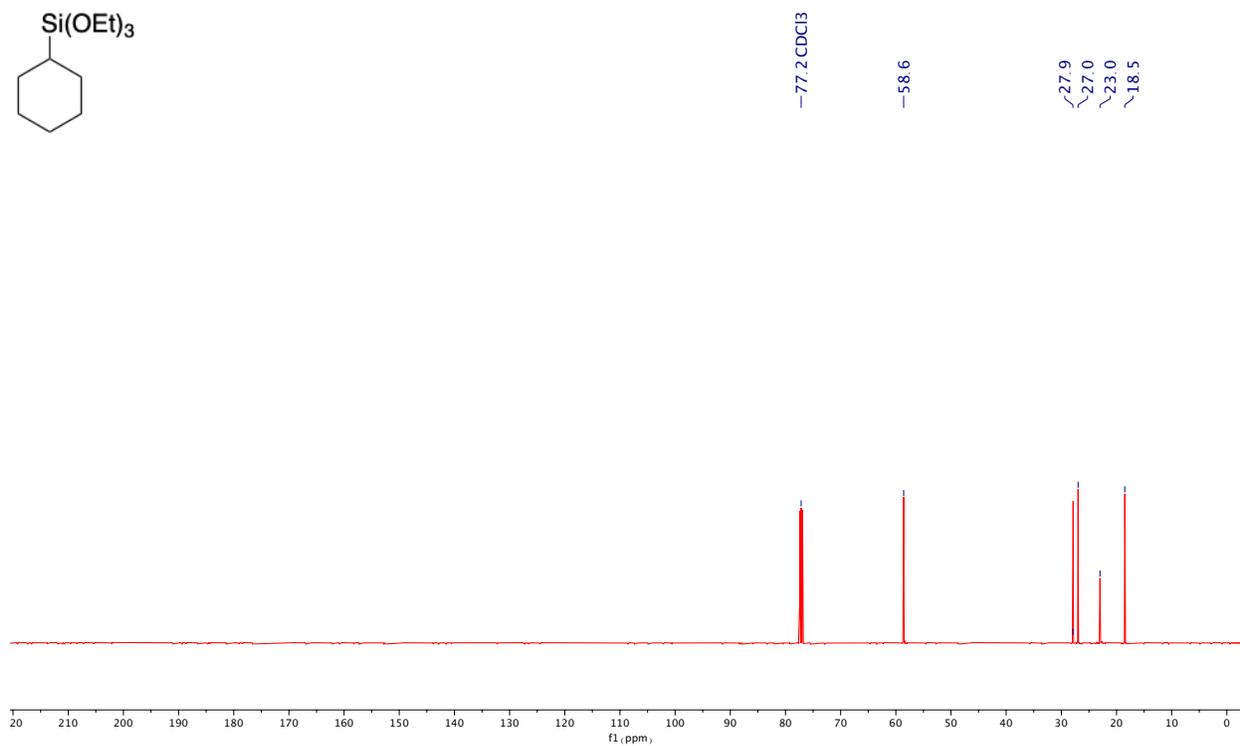
$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ ) of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (2z)



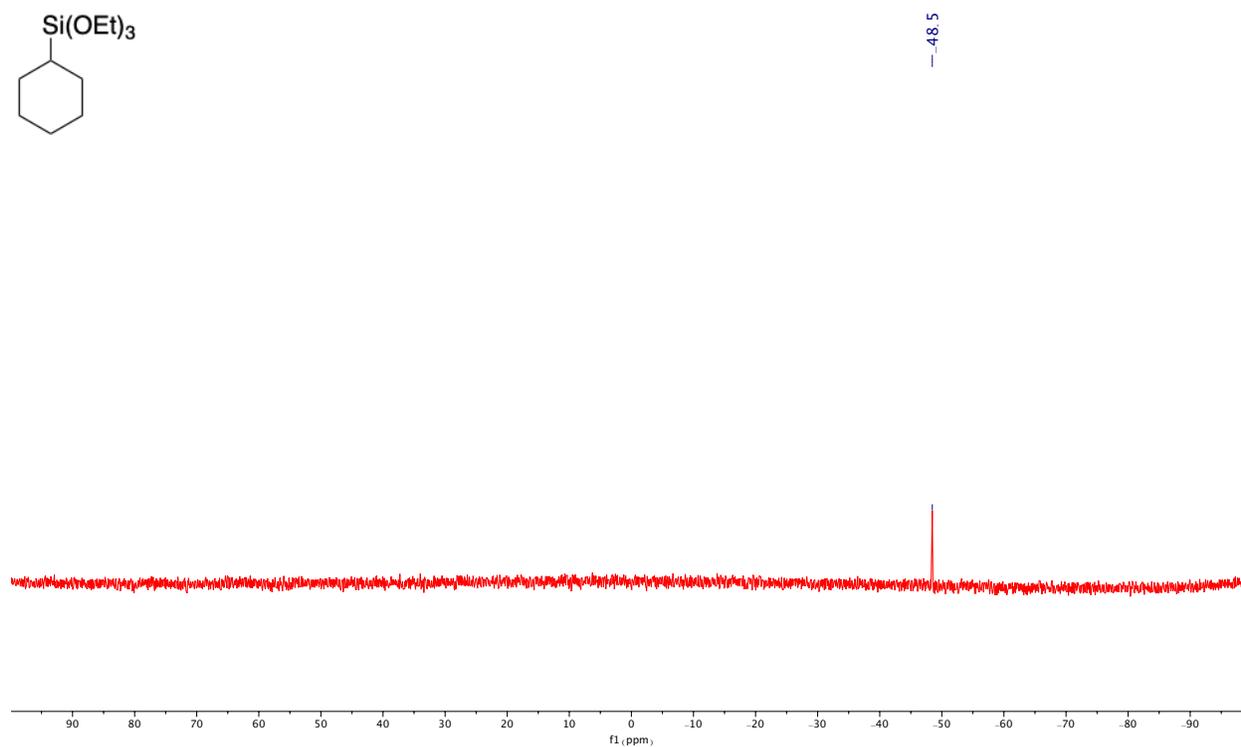
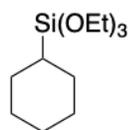
**<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of Cyclohexyltriethoxysilane (2aa)**



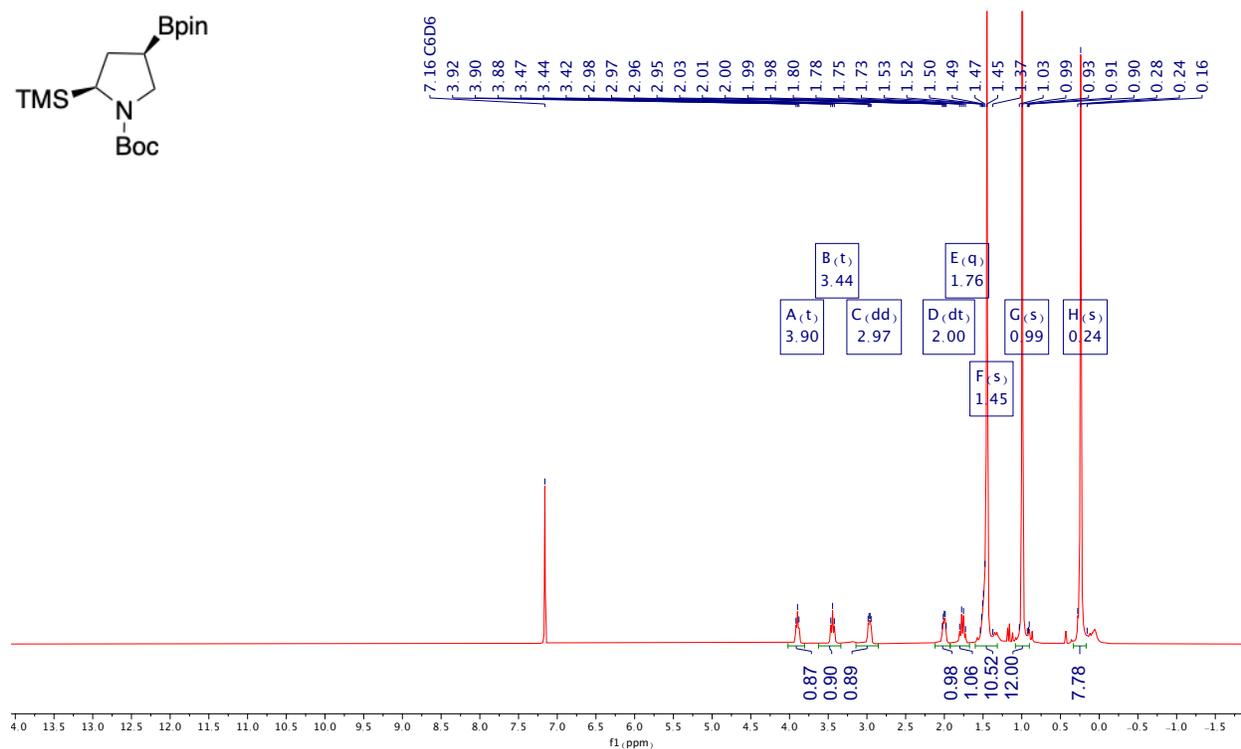
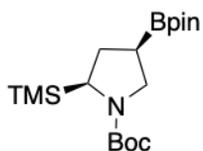
**<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of Cyclohexyltriethoxysilane (2aa)**



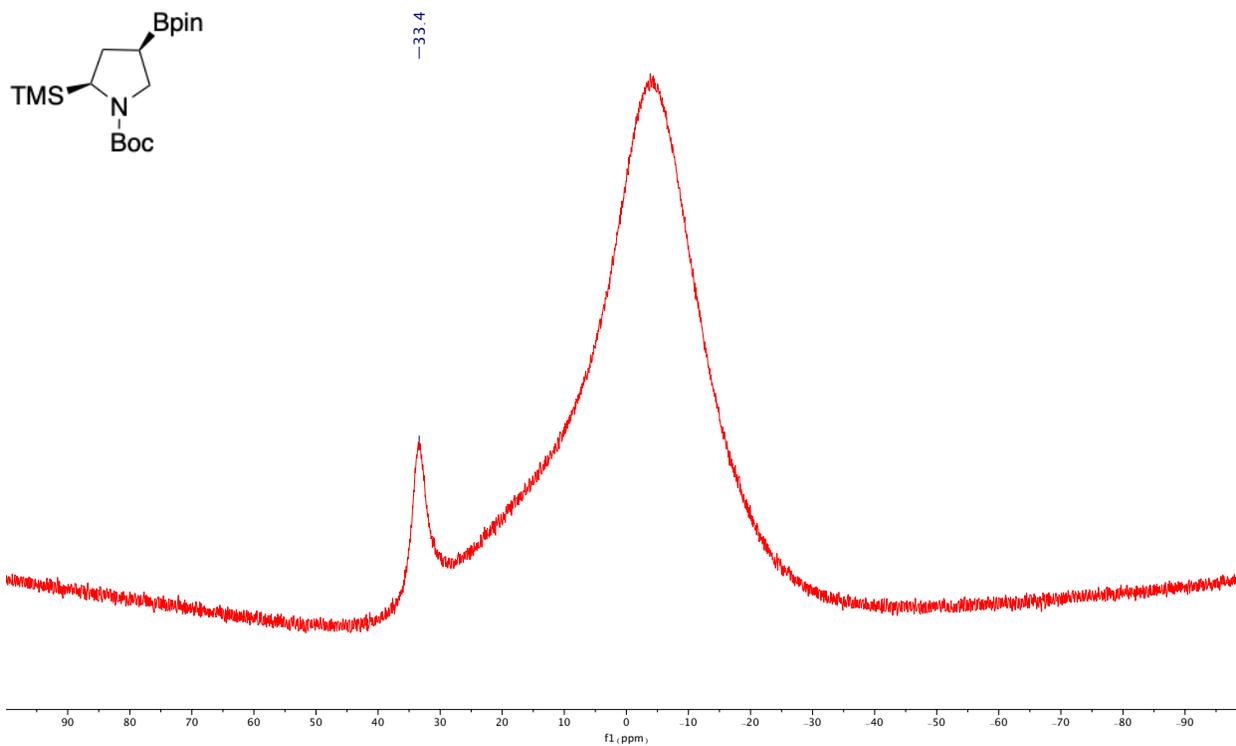
<sup>29</sup>Si NMR (99MHz, CDCl<sub>3</sub>) of Cyclohexyltriethoxysilane (2aa)



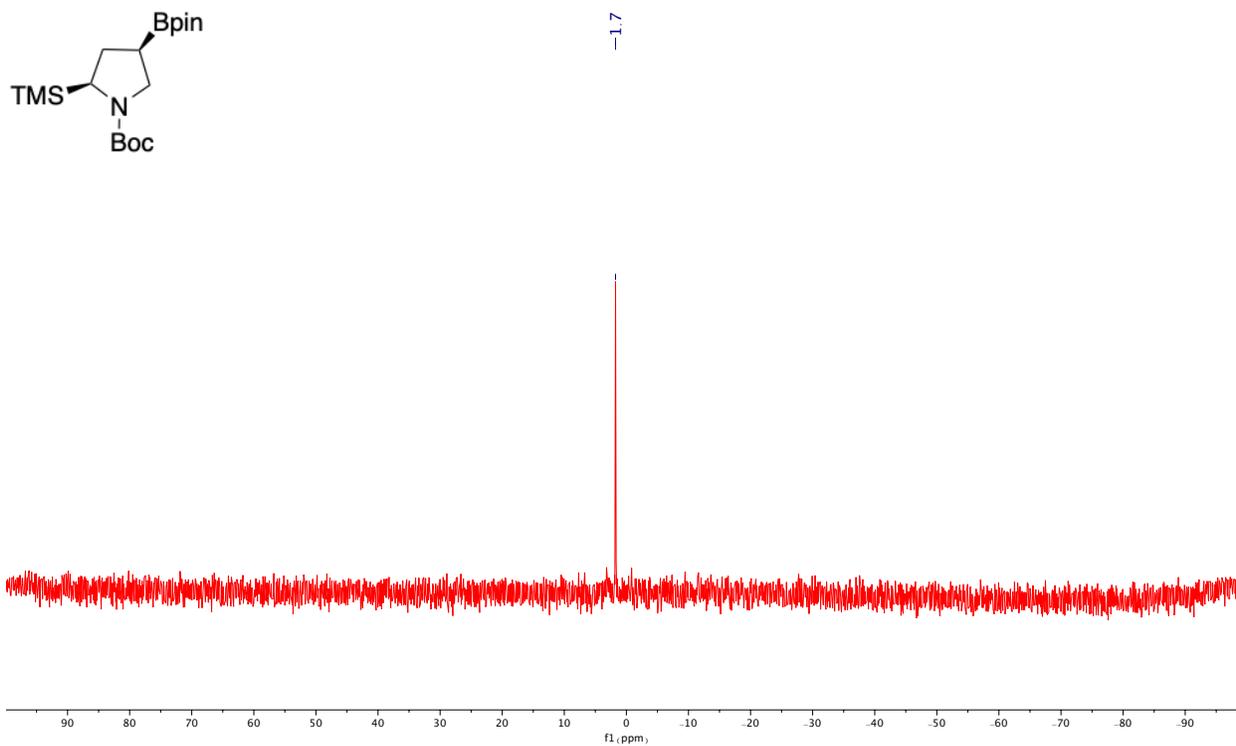
<sup>1</sup>H NMR (500MHz, C<sub>6</sub>D<sub>6</sub>) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



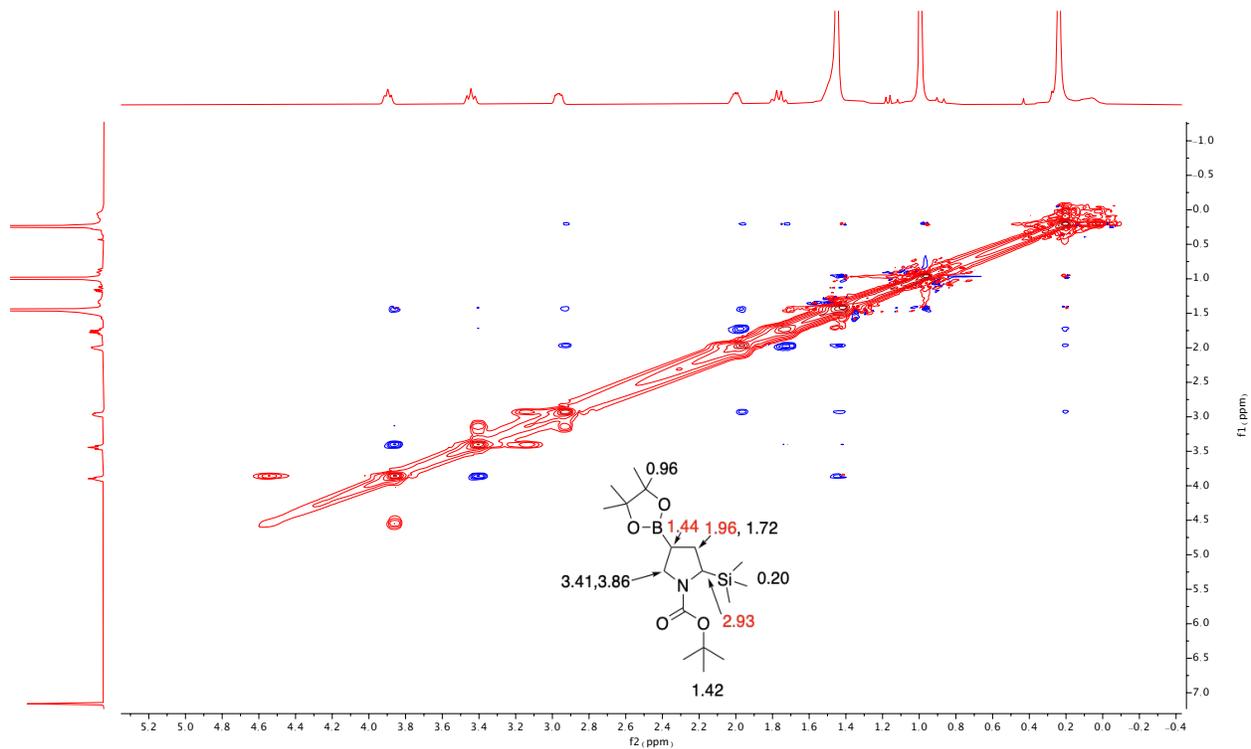




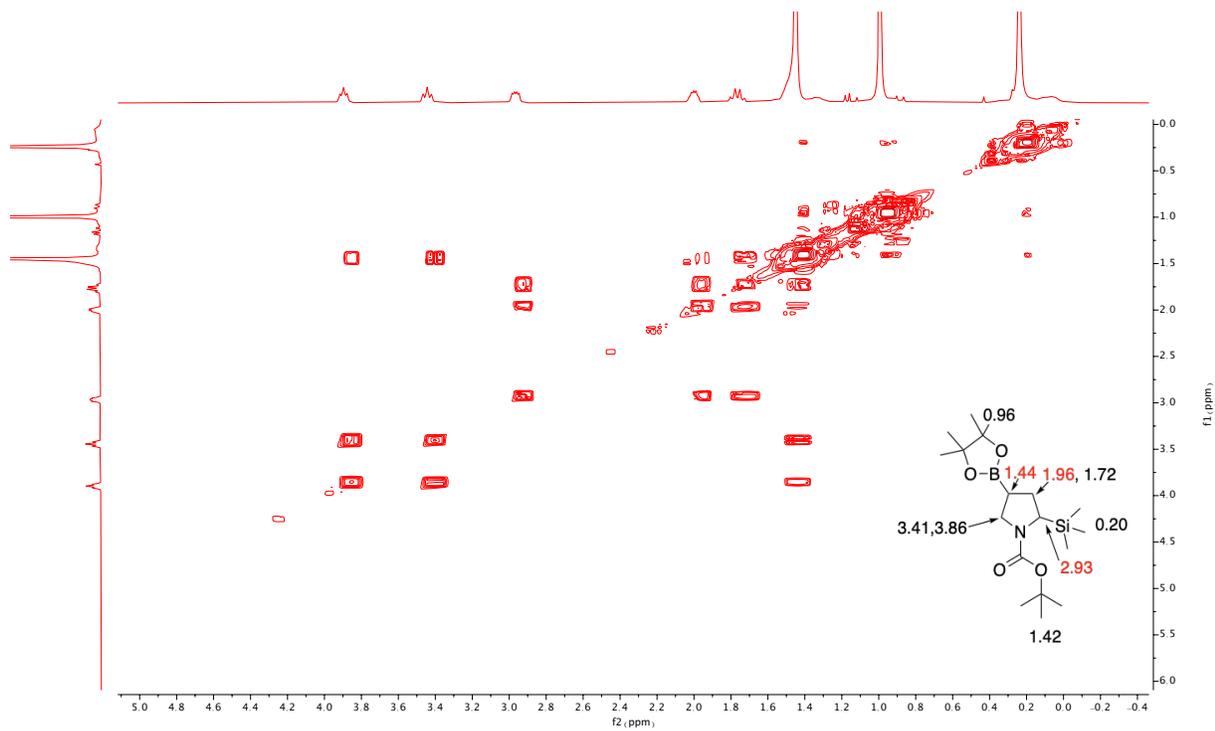
**<sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-trimethylsilylpyrrolidine-1-carboxylate (2ab)**



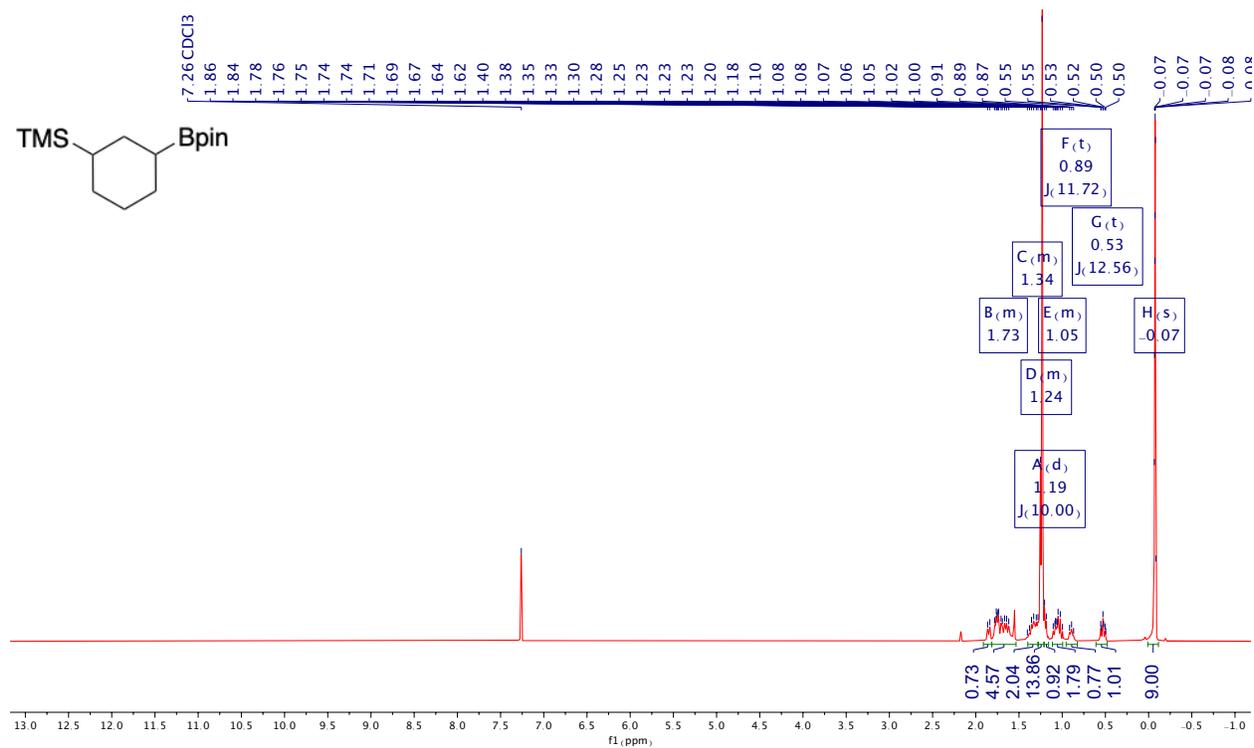
2D-NOE of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



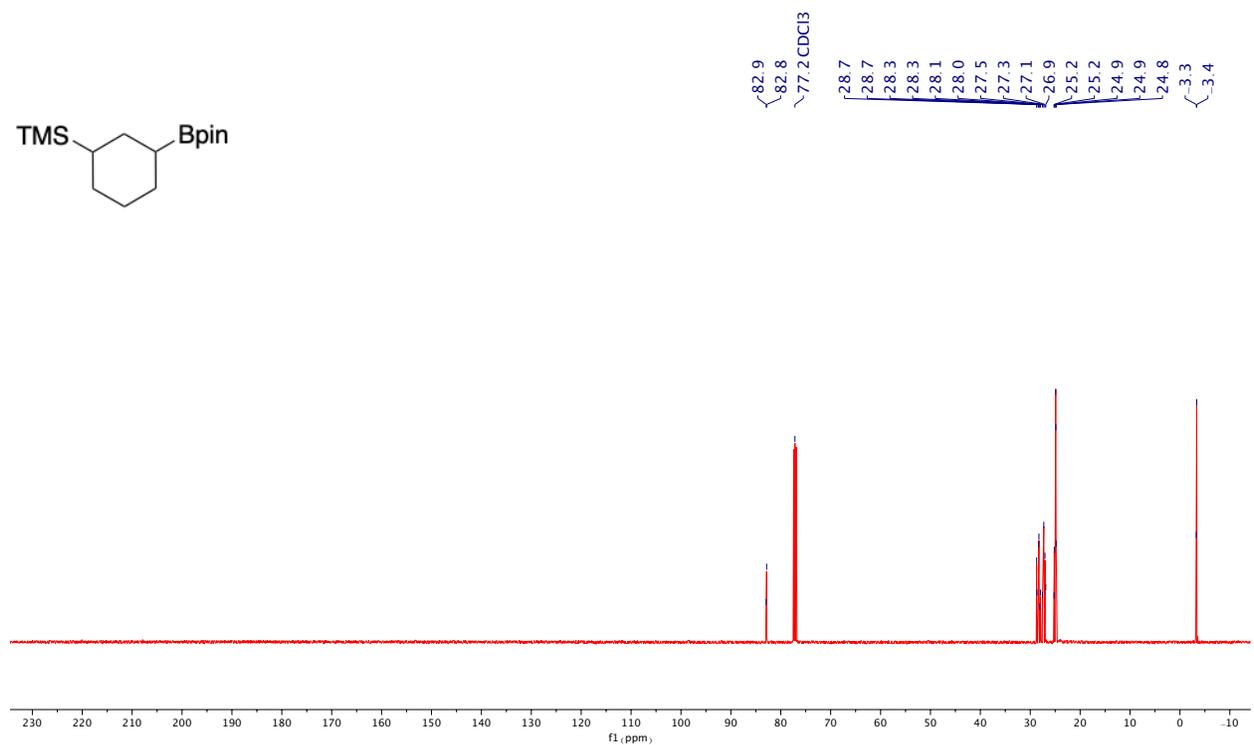
COSY of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



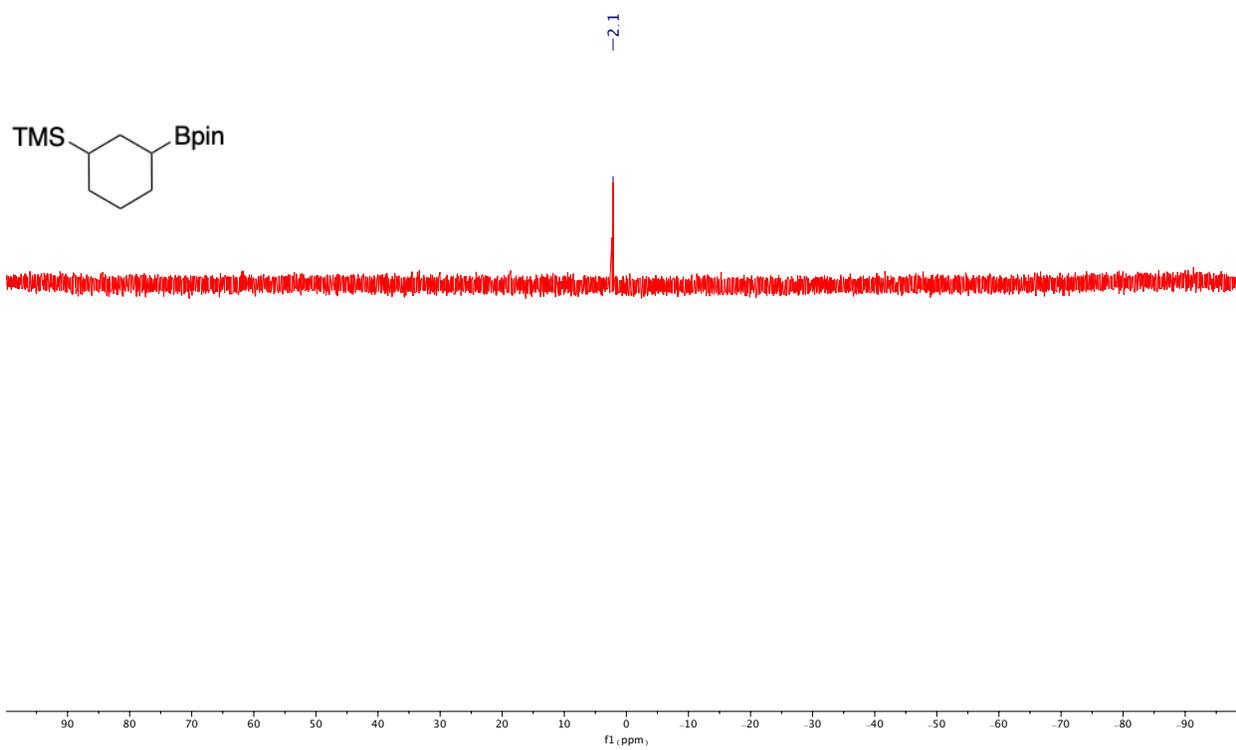
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



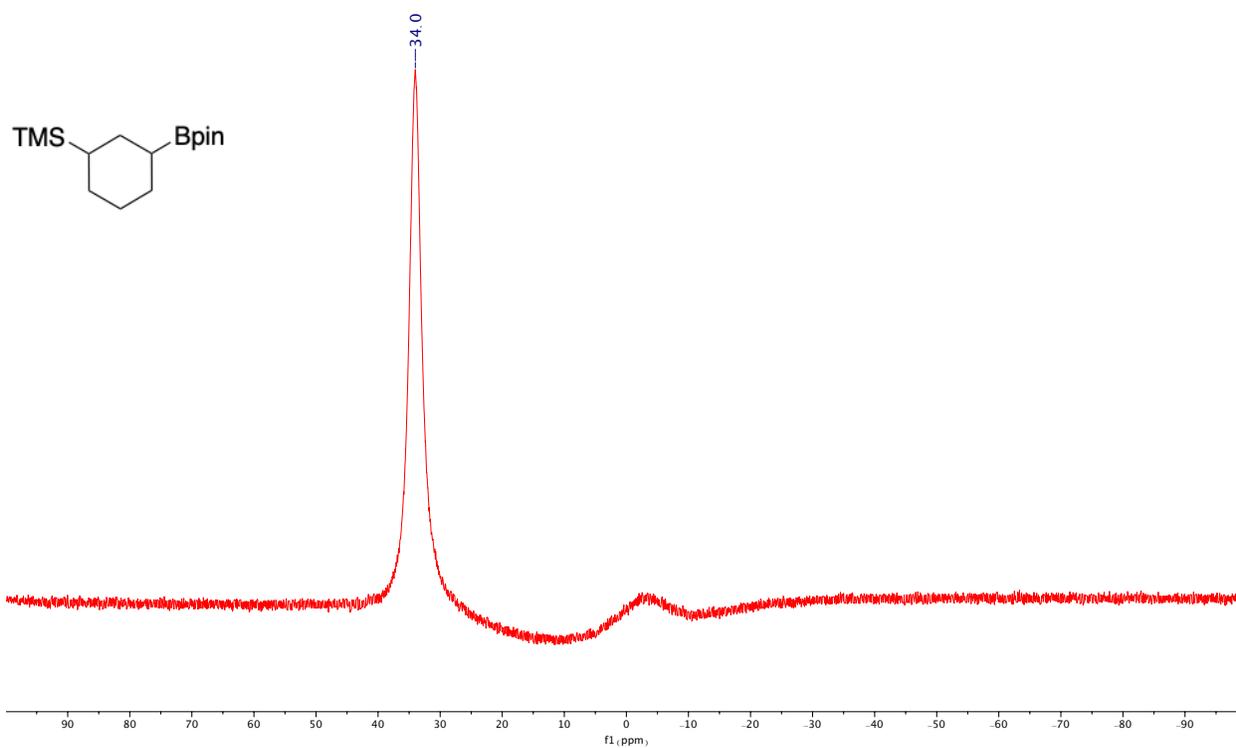
<sup>13</sup>C{<sup>1</sup>H} (126 MHz, CDCl<sub>3</sub>) NMR of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



<sup>29</sup>Si NMR (99MHz, CDCl<sub>3</sub>) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



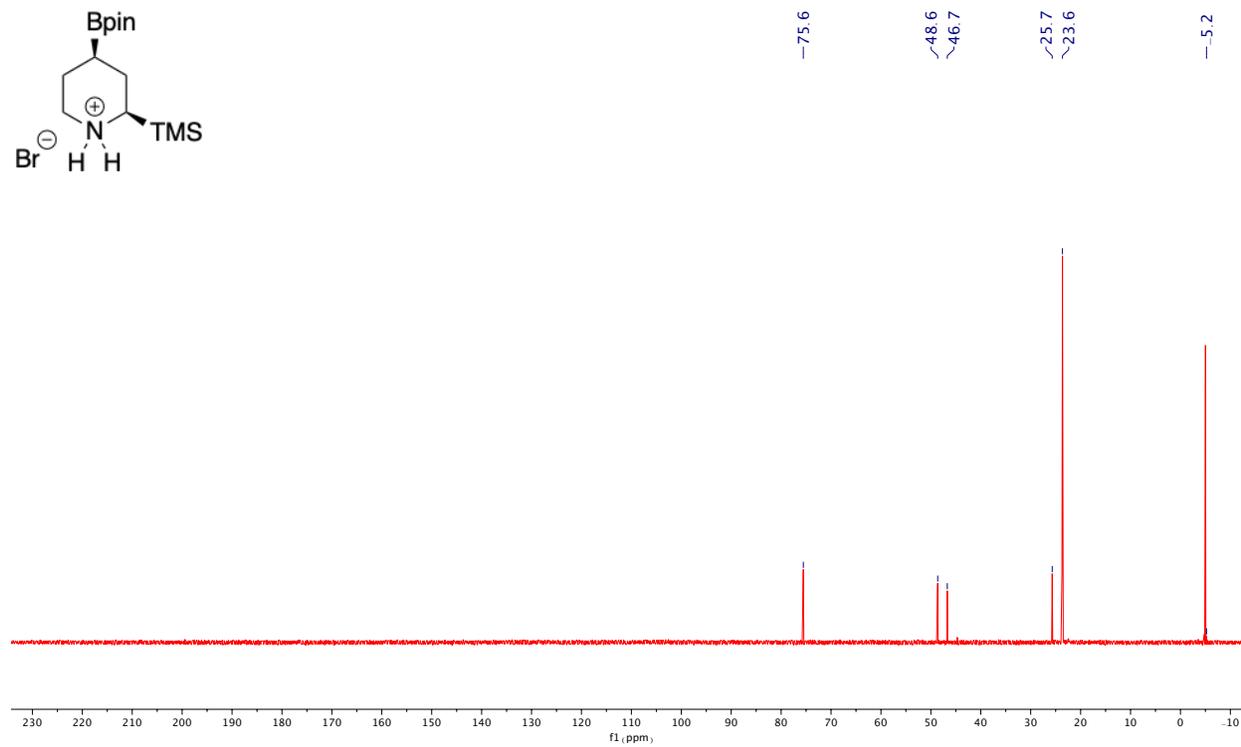
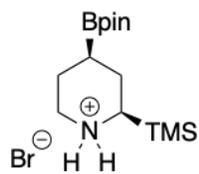
<sup>11</sup>B NMR (160MHz, CDCl<sub>3</sub>) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)





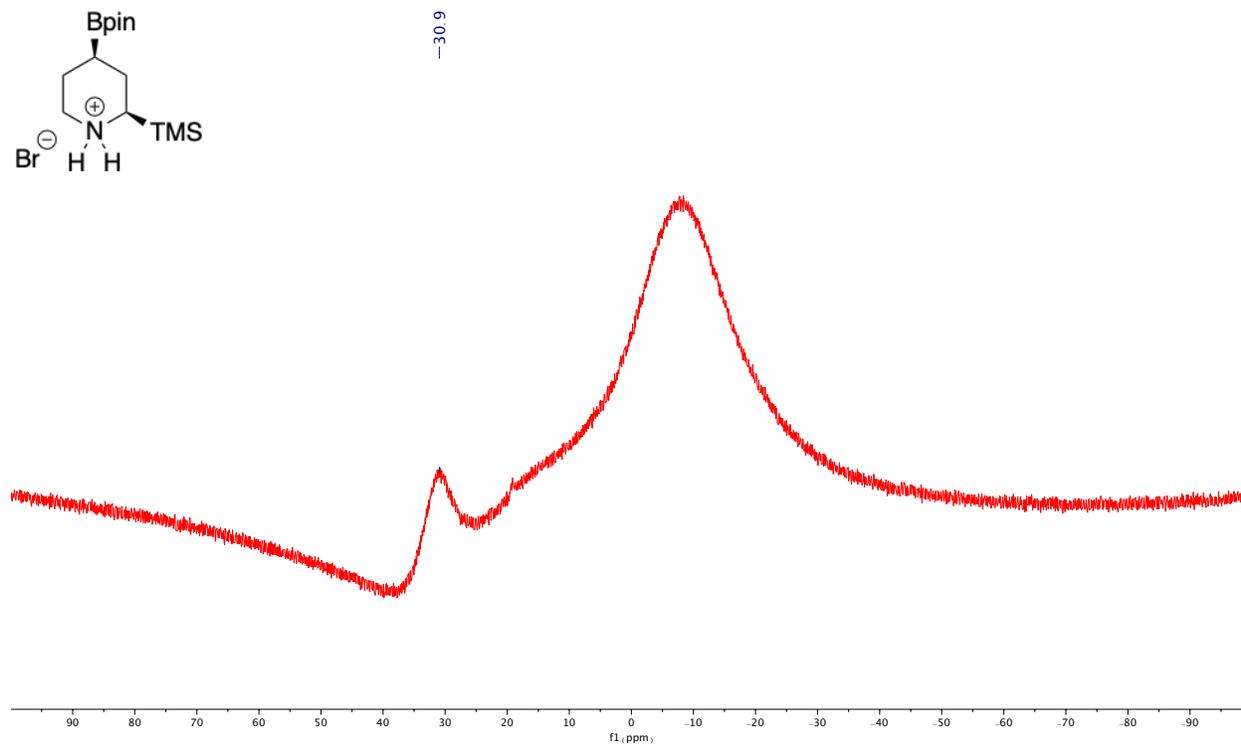
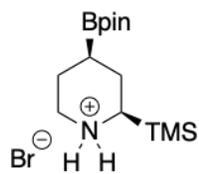
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{D}_2\text{O}$ ) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide

(2ac)



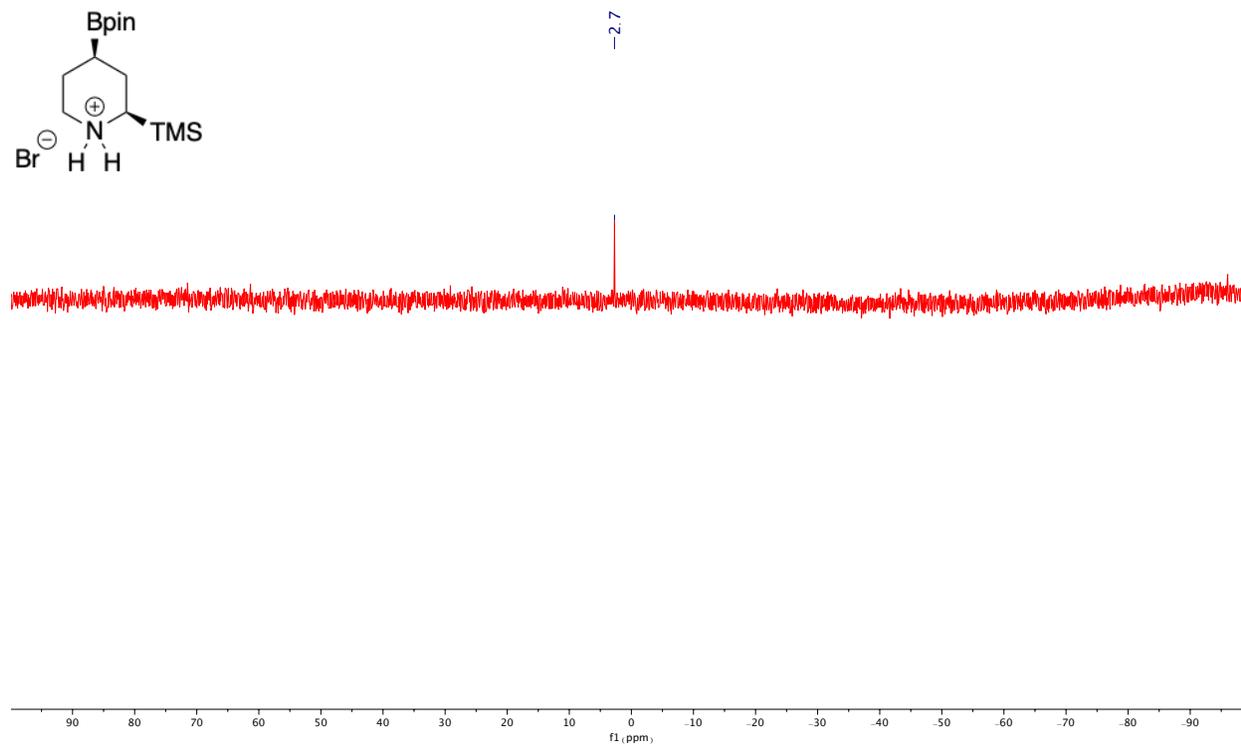
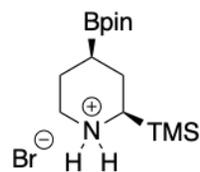
**$^{11}\text{B}$  NMR (160MHz,  $\text{D}_2\text{O}$ ) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide**

(2ac)

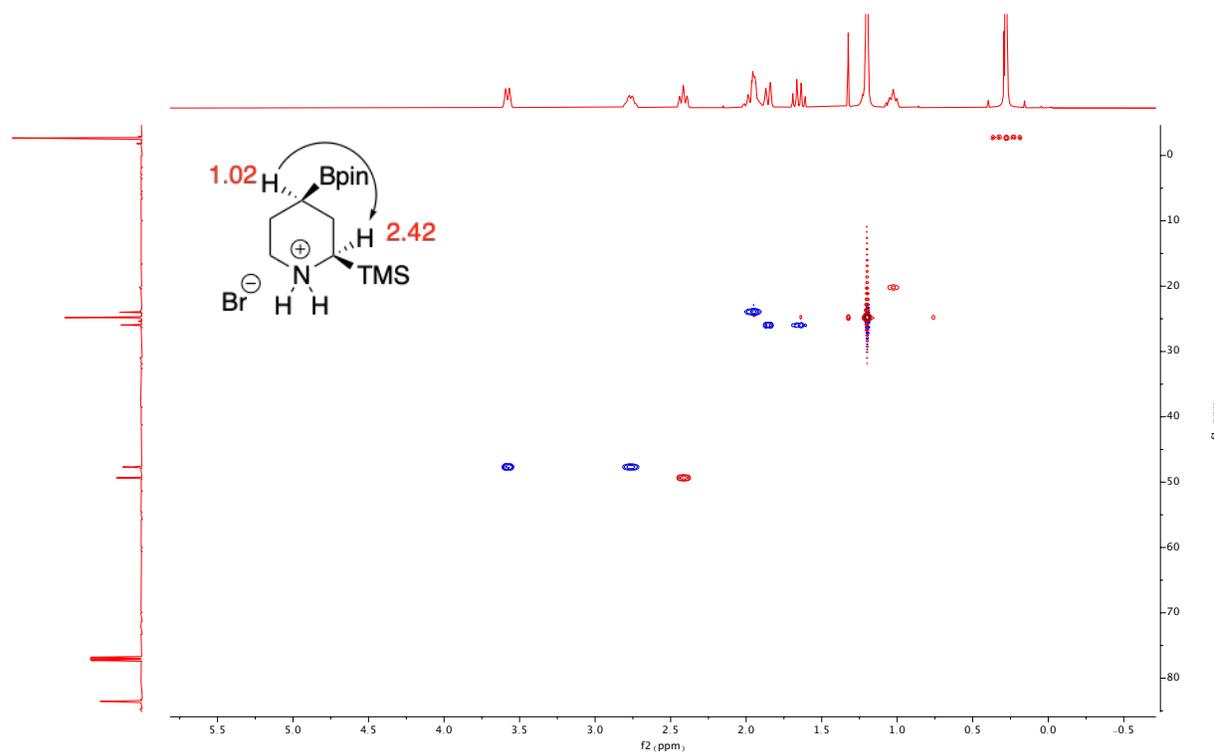


$^{29}\text{Si}$  NMR (99MHz,  $\text{CDCl}_3$ ) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide

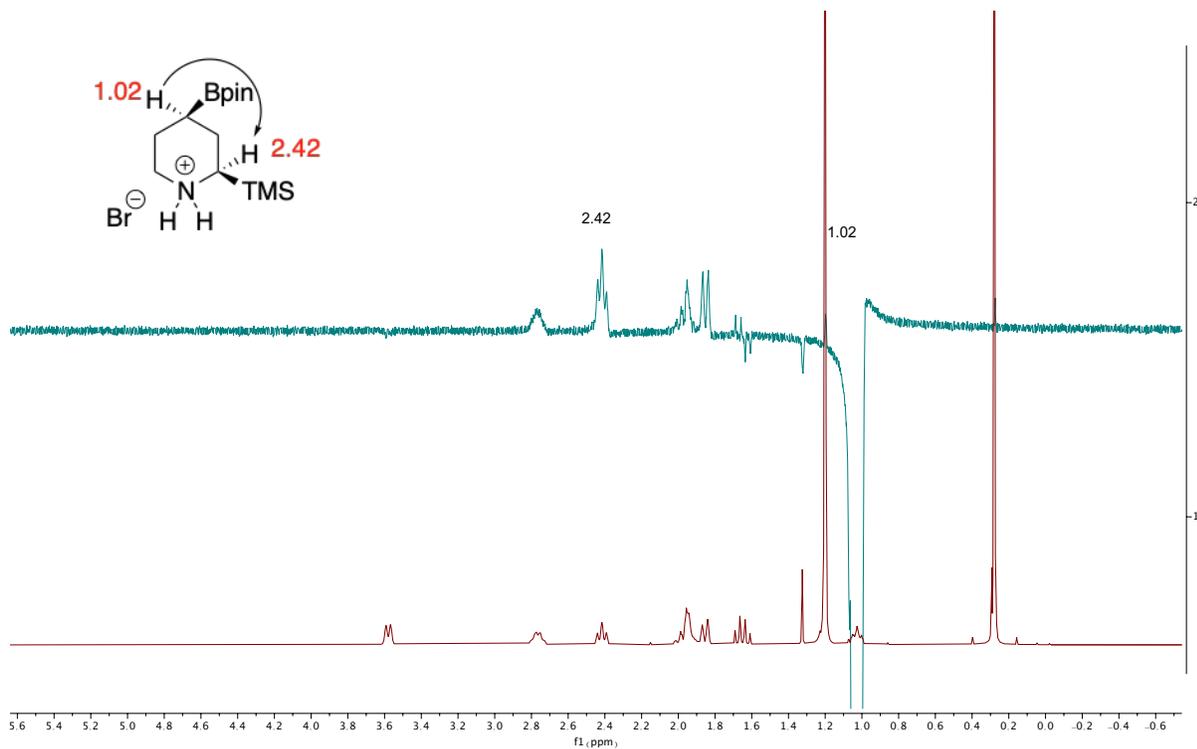
(2ac)



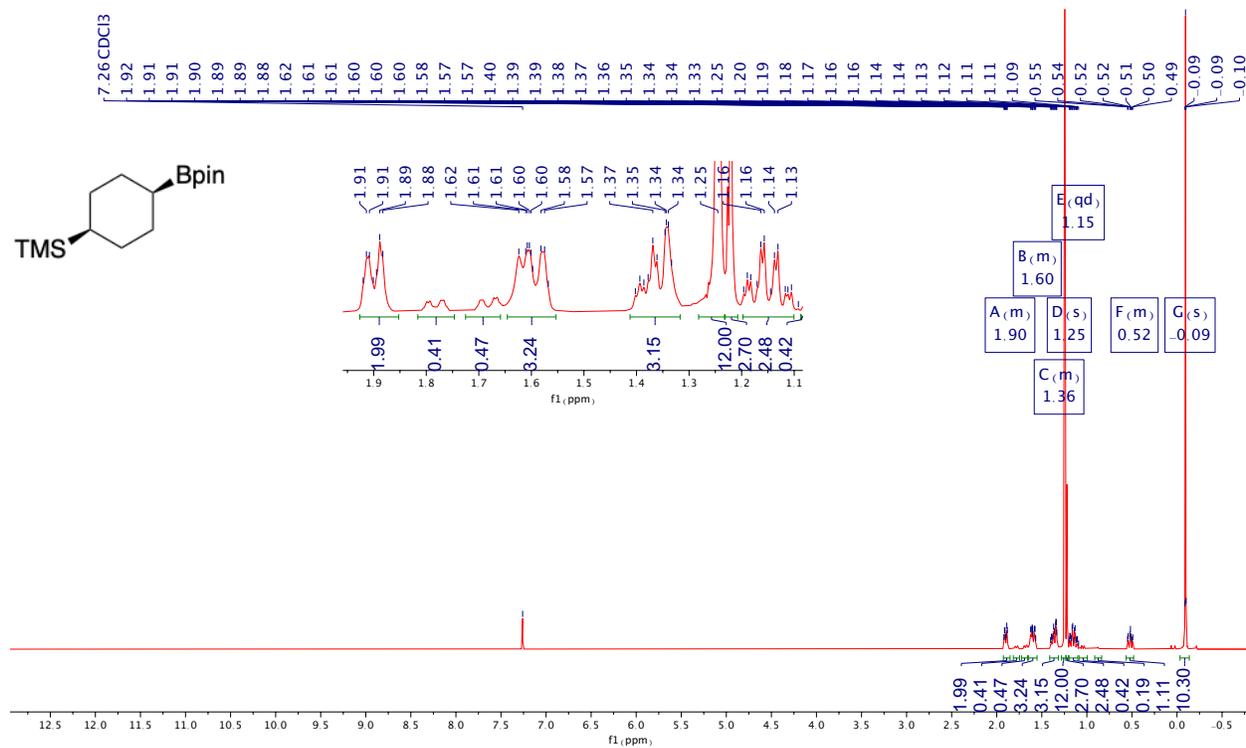
HSQC 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



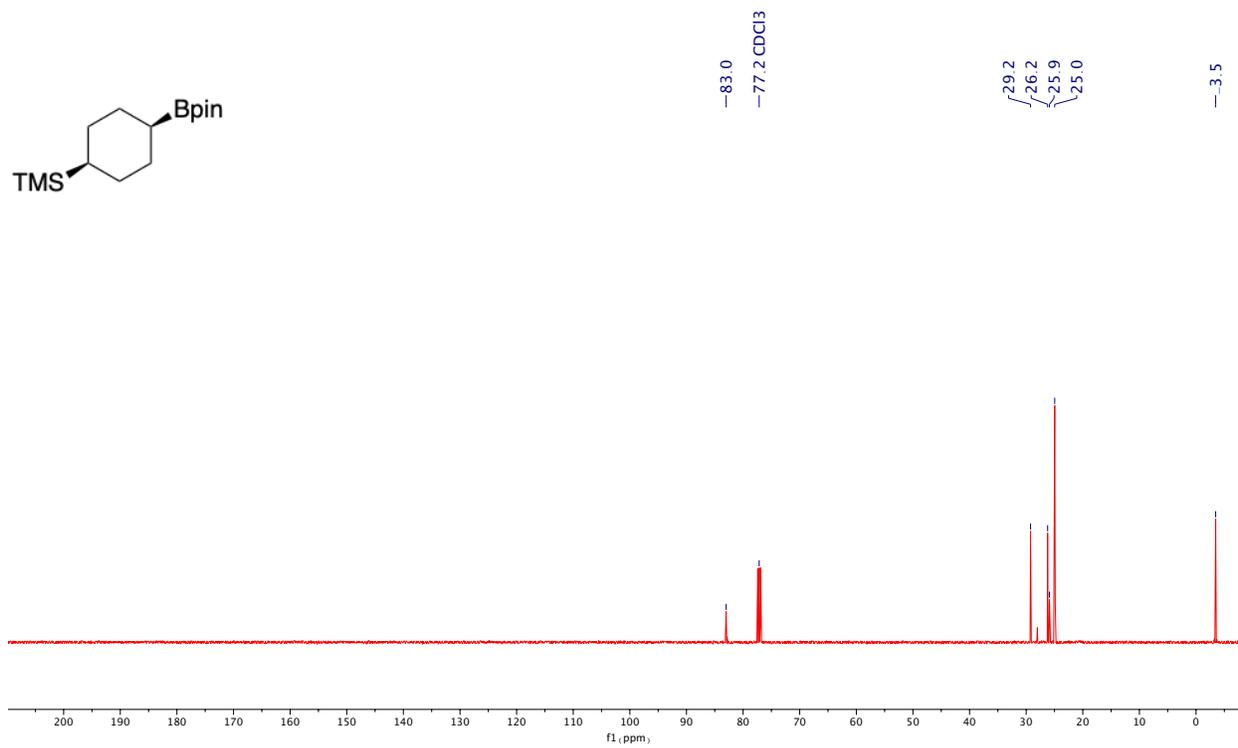
NOE of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



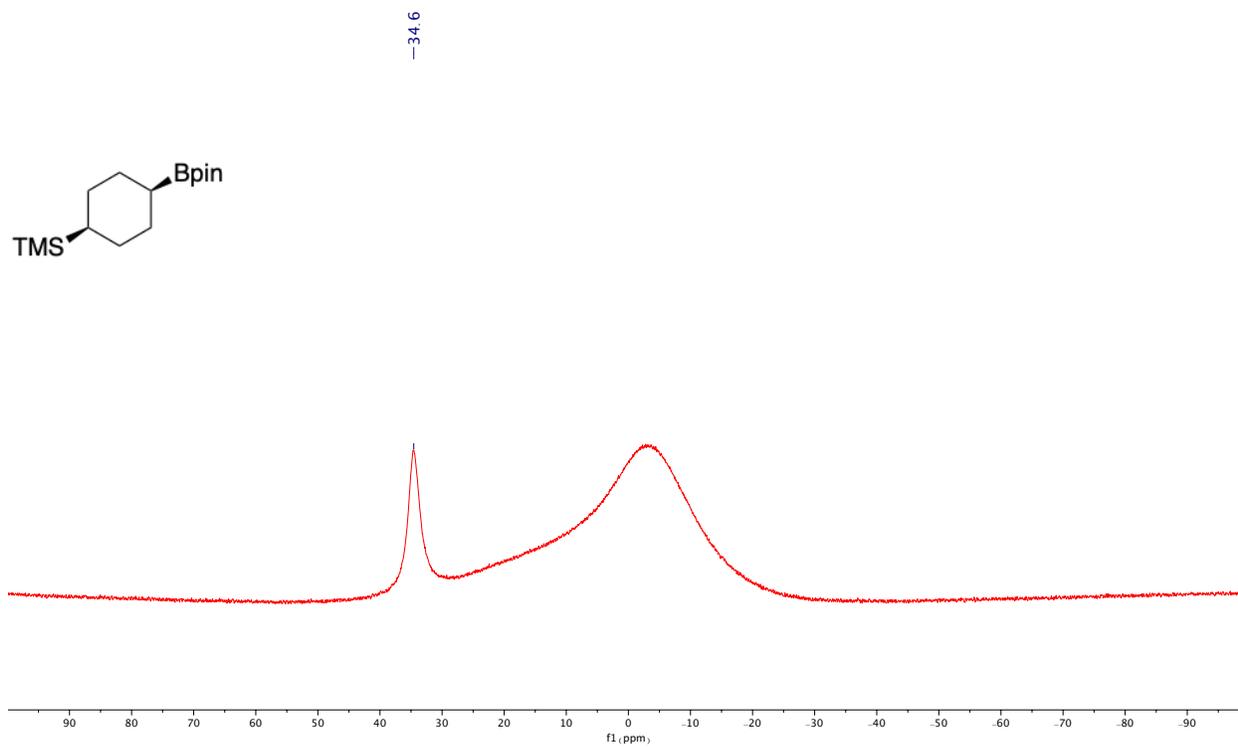
$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



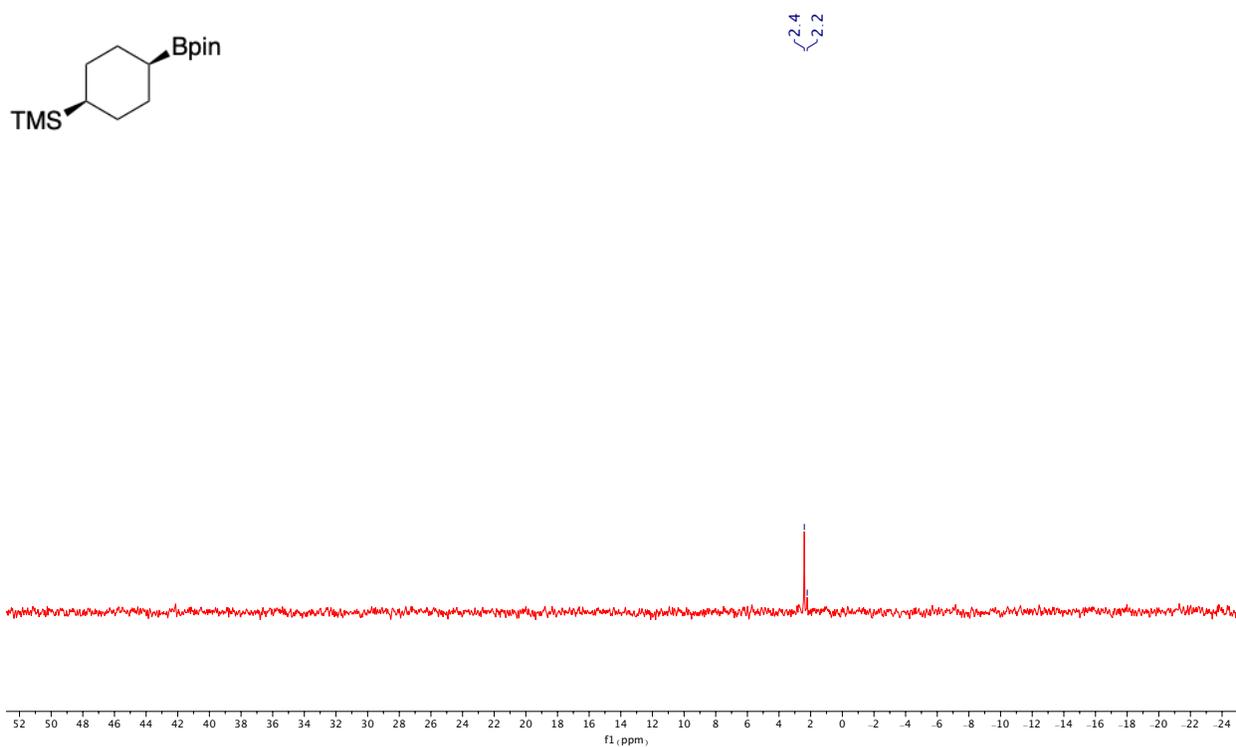
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexylsilane (2af)



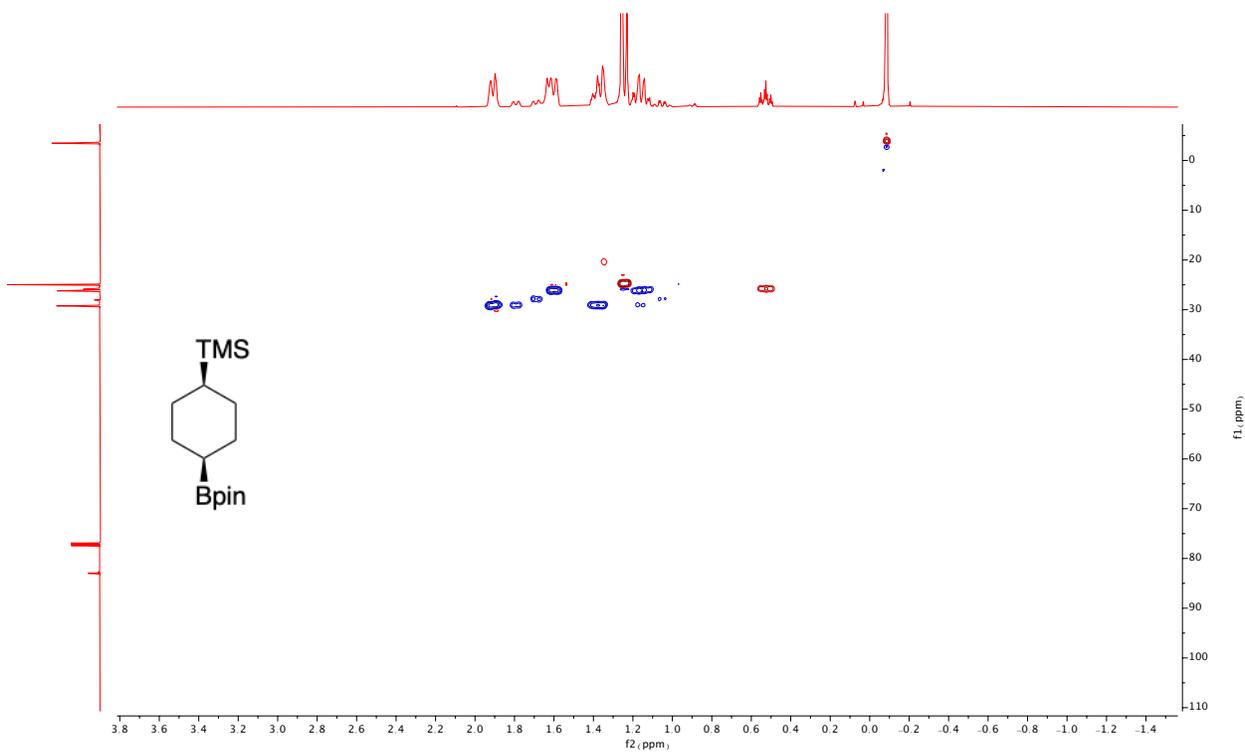
$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexylsilane (2af)



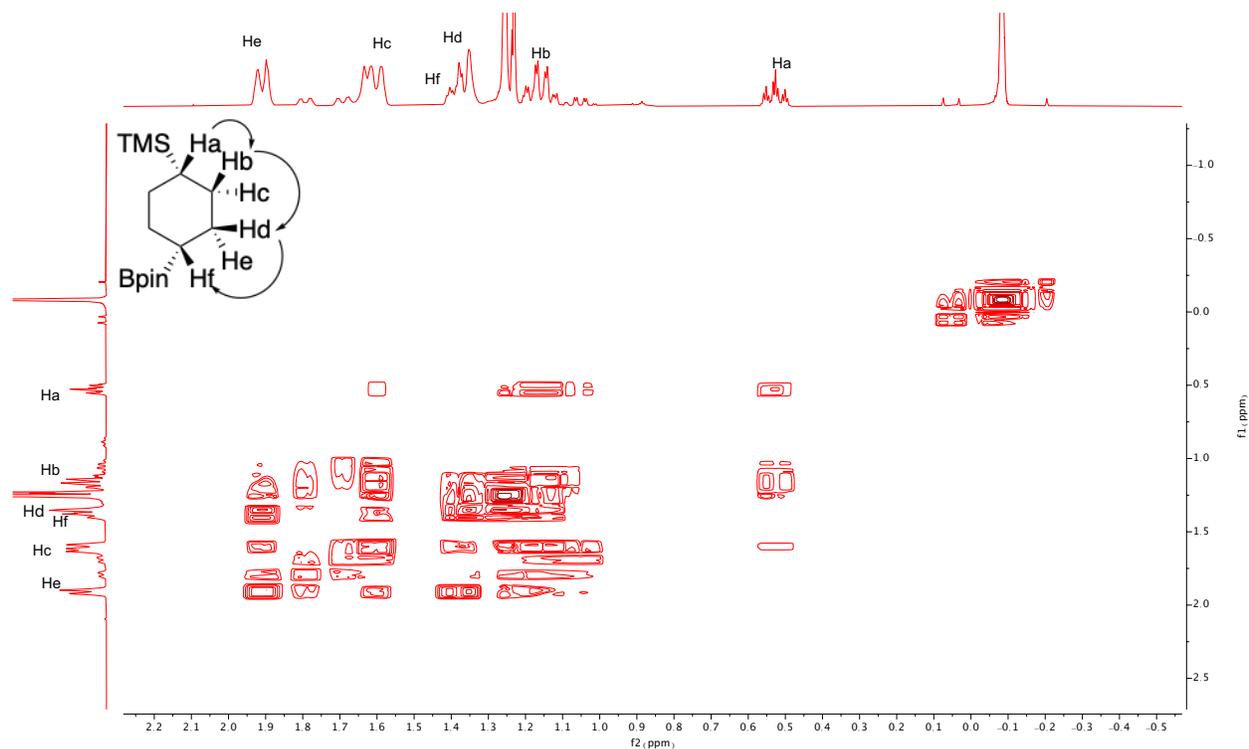
<sup>29</sup>Si NMR (99MHz, CDCl<sub>3</sub>) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexylsilane (2af)



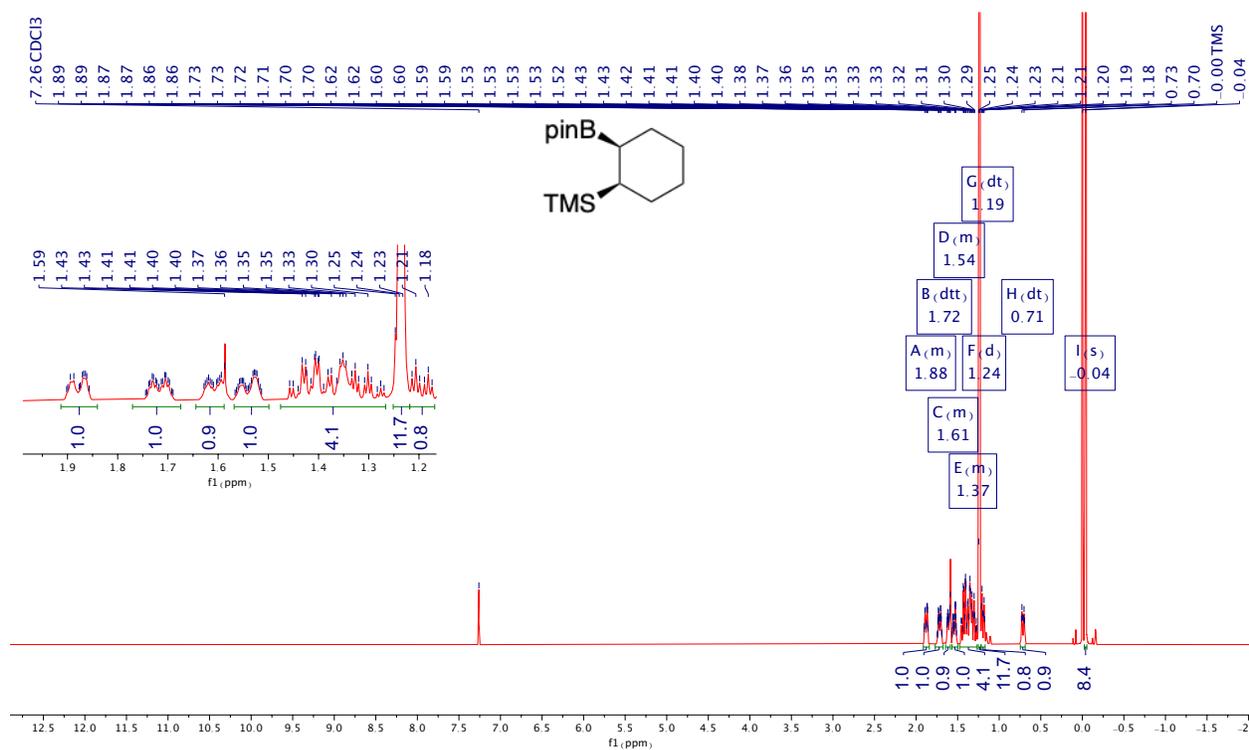
HSQC NMR Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexylsilane (2af)



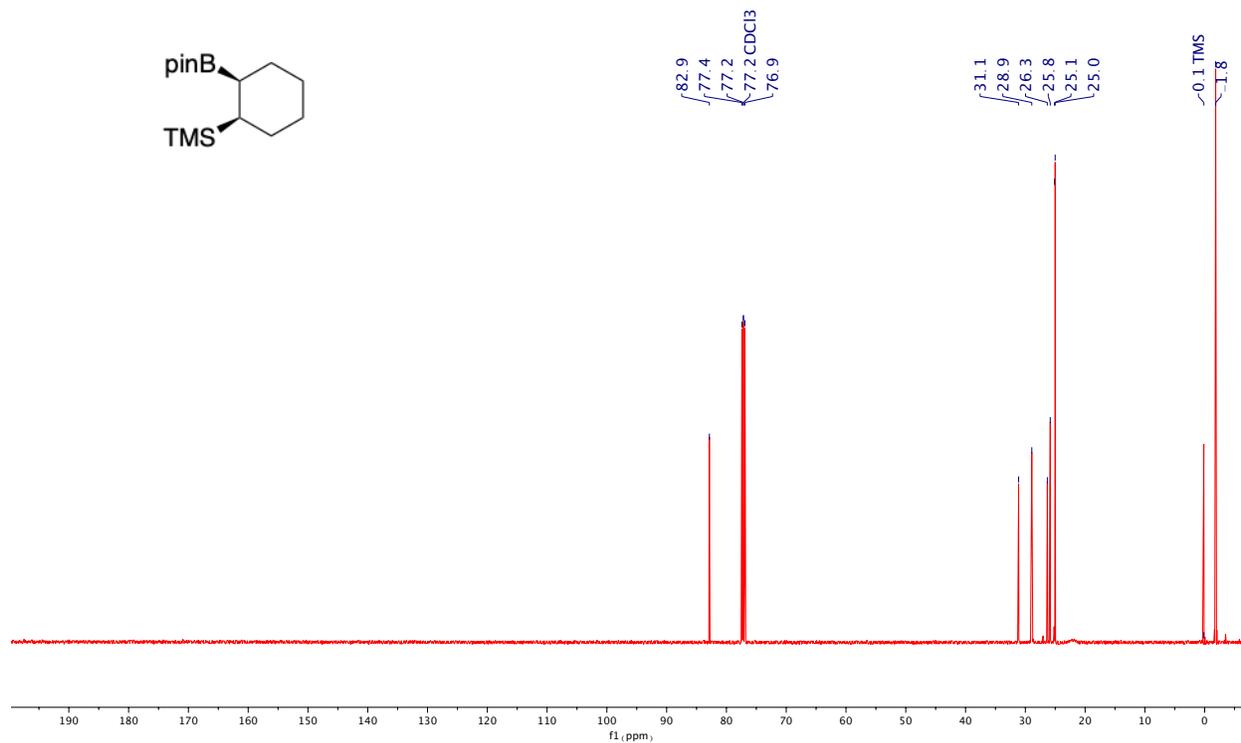
COSY NMR Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



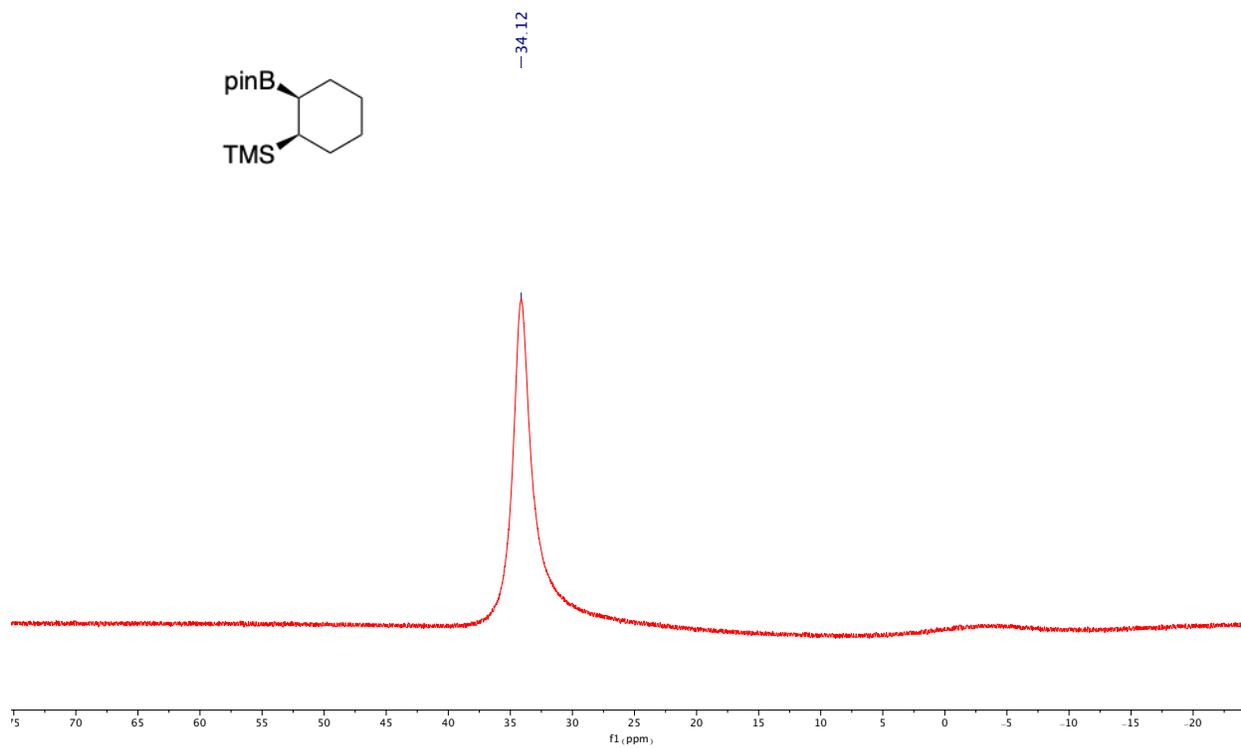
<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



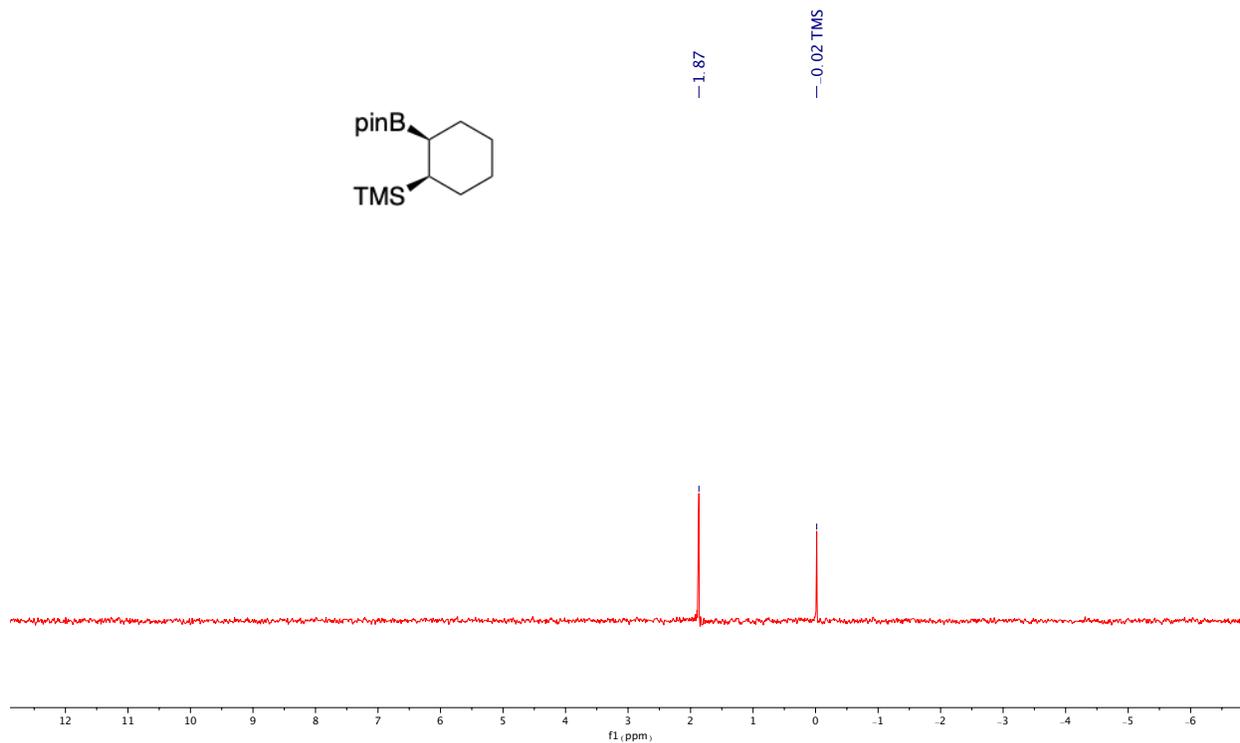
$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CDCl}_3$ ) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



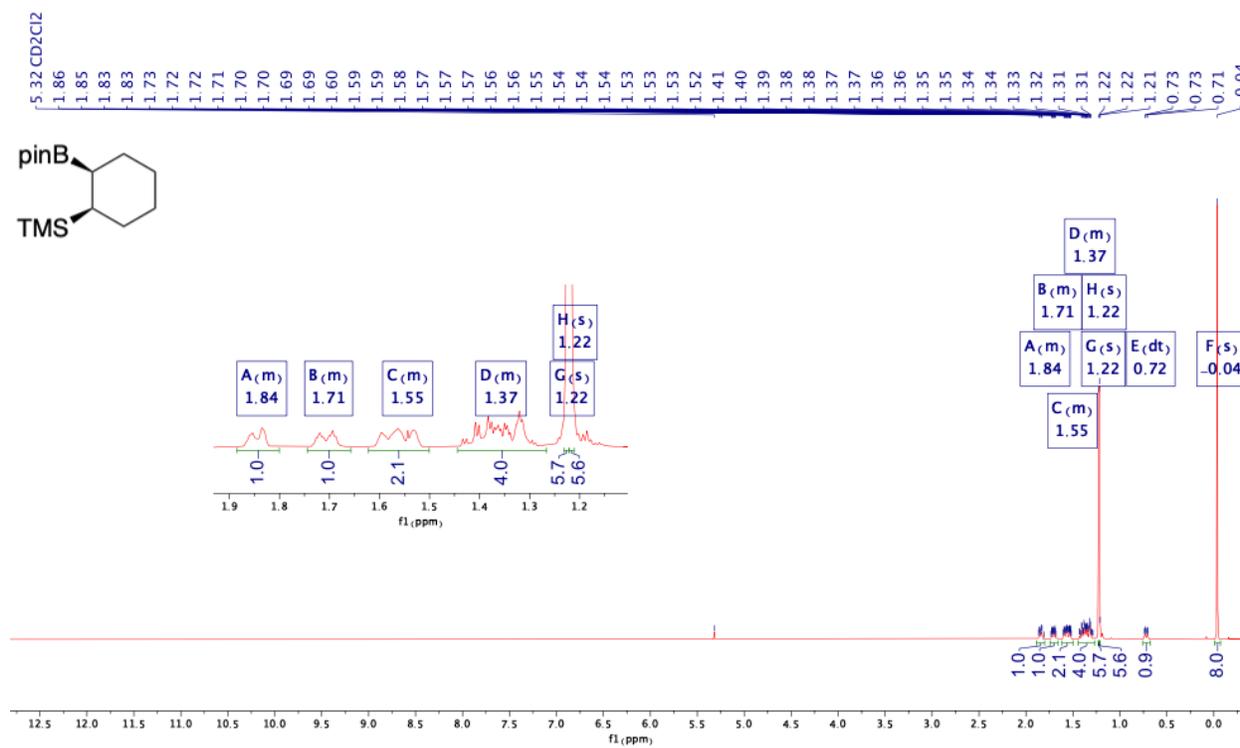
$^{11}\text{B}$  NMR (160MHz,  $\text{CDCl}_3$ ) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



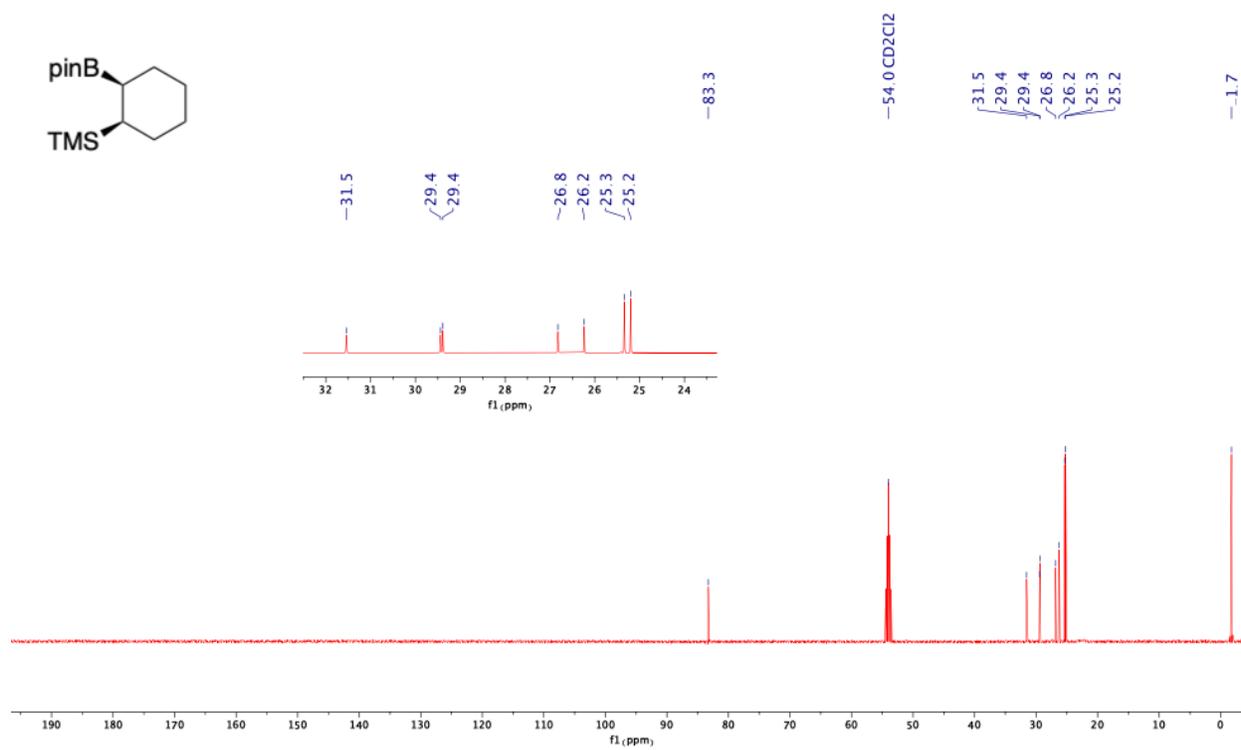
<sup>29</sup>Si NMR (99MHz, CDCl<sub>3</sub>) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



$^{13}\text{C}\{^1\text{H}\}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



$^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ ) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)

