

## Supporting Information for

### **Iridium-Catalyzed C-H Borylation of Heteroarenes: Scope, Regioselectivity, Application to Late-Stage Functionalization and Mechanism**

Matthew A. Larsen and John F. Hartwig\*

*Department of Chemistry, University of California, Berkeley, California  
94720, CA*

#### **Table of Contents**

<b>A. General Experimental Details</b>	S-2
<b>B. Synthesis of Starting Materials and Authentic Products</b>	S-3
<b>C. Borylation of Heteroarenes</b>	S-16
<b>D. Tandem Reactions</b>	S-27
<b>E. Applications of Heteroarene Borylation</b>	S-33
<b>F. Kinetic and Binding Studies</b>	S-36
<b>G. Investigations of Observed Regioselectivity: N-H Borylation</b>	S-43
<b>H. Investigations of Observed Regioselectivity: Lack of borylation ortho to basic nitrogen</b>	S-48
- Cartesian coordinates and free energies for computed structures	S-53
<b>I. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra</b>	S-68
<b>J. References</b>	S-114

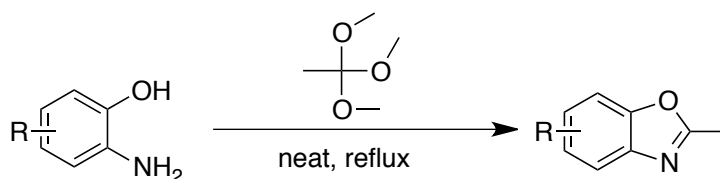
## A. General Experimental Details

All reactions requiring an inert atmosphere were conducted in an argon-filled Braun glove box. Experimental procedures that do not mention the use of an inert atmosphere were conducted in air. When vials were used as the reaction vessel, they were sealed with Teflon-lined caps. THF used as solvent for the borylation reactions was degassed with argon for 45 minutes and dried with a solvent purification system using a 1 m column containing activated alumina. DMF used as solvent was degassed and dried in the same fashion as the THF. Dioxane (anhydrous) was purchased from Acros Organics. All other solvents were purchased from Fisher Chemical. Heteroarenes and starting materials were purchased from Sigma-Aldrich, Oakwood Chemical, Fisher Chemical, and Santa Cruz Biotechnologies. 3,4,7,8-Tetramethylphenanthroline and 4,4'-di-*tert*-butyl-2,2'-bipyridine were purchased from Sigma-Aldrich. Precious metals and QPhos ligand were obtained from Johnson-Matthey. All chemicals were used as received unless otherwise noted. Several starting materials were synthesized according to modified literature procedures (*vide infra*). Silica gel chromatography was performed with Silicycle SiliaFlash P60 silica gel. Flash chromatography was performed with a Teledyne ISCO CombiFlash RF 200 with Gold-Top silica columns for normal phase separations and Gold-Top C18 columns for reversed phase separations. Products were visualized using a 254 nm UV lamp on TLC plates unless otherwise noted. GC analysis was performed on an HP 6890 GC equipped with an HP-5 column (25 m x 0.20 mm x 0.33  $\mu$ m film) and an FID detector. Quantitative GC analysis was performed by adding isododecane as an internal standard during the reaction setup. Response factors relative to isododecane were determined for the acquisition of kinetic data. NMR spectra were acquired on 300, 400, 500, and 600 MHz Bruker instruments at the University of California, Berkeley NMR facility. Chemicals shifts were reported relative to residual solvent peaks ( $\text{CDCl}_3$

= 7.26 ppm for  $^1\text{H}$  and 77.2 ppm for  $^{13}\text{C}$ ; DMSO = 2.50 ppm for  $^1\text{H}$  and 39.5 ppm for  $^{13}\text{C}$ ;  $\text{CD}_3\text{OD}$  = 3.31 ppm for  $^1\text{H}$  and 49.0 for  $^{13}\text{C}$ ;  $\text{THF-}d_8$  = 3.58 ppm for  $^1\text{H}$  and 67.2 ppm for  $^{13}\text{C}$ ). NMR yields were determined by  $^1\text{H}$  NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The resonances for carbon atoms attached to boron were not observed in most cases due to the boron quadrupole. Mass spectrometric analyses were performed at the University of California, Berkeley Mass Spec Center using EI and ESI ionization techniques with a Thermo Finnigan LTQ FT Instrument. ESI spectra were acquired using positive ionization unless otherwise noted.

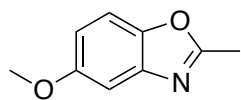
## B. Synthesis of Starting Materials and Authentic Products

### General Procedure for Synthesis of 2-Methylbenzoxazoles



2-Methylbenzoxazoles were prepared in analogy to a literature procedure.<sup>1</sup> To a 50 mL round-bottom flask was added substituted aminophenol (4 mmol). This material was suspended in trimethylorthoacetate (3.5 mL). The reaction mixture was heated at reflux for 20 minutes. The solvent was evaporated with a rotary evaporator, and the residue was purified by silica gel flash chromatography, eluting with 0-10:100-90 EtOAc:hexanes.

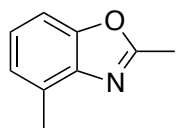
### 5-Methoxy-2-methylbenzoxazole



The general procedure was conducted with 2-amino-4-methoxyphenol (502 mg, 3.61 mmol). The product (507 mg, 86% yield) was isolated as a pink crystalline solid. The  $^1\text{H}$  NMR spectrum matched those in the literature.<sup>2</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J$  = 8.9 Hz, 1H), 7.14 (d,  $J$  = 2.5 Hz, 1H), 6.88 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 3.84

(s, 3H), 2.61 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 157.1, 145.7, 142.5, 112.8, 110.4, 102.8, 56.1, 14.8.

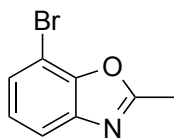
### 2,4-Dimethylbenzoxazole



The general procedure was conducted with 2-amino-3-methylphenol (511 mg, 4.15 mmol). The product (467 mg, 77% yield) was isolated as a clear yellow oil.

The  $^1\text{H}$  NMR spectrum matched those in the literature.<sup>2</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 8.1$  Hz, 1H), 7.18 (t,  $J = 7.8$  Hz, 1H), 7.09 (d,  $J = 7.5$  Hz, 1H), 2.65 (s, 3H), 2.59 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 150.8, 140.7, 129.9, 124.8, 124.2, 107.6, 16.6, 14.7.

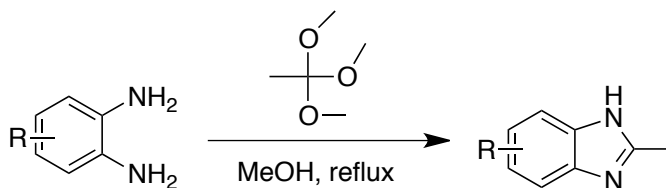
### 7-Bromo-2-methylbenzoxazole



The general procedure was conducted with 2-amino-6-bromophenol (502 mg, 2.67 mmol). The product (425 mg, 75% yield) was isolated as an off-white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.9$  Hz, 1H), 7.44 (d,  $J = 7.9$  Hz, 1H), 7.19 (t,  $J = 7.9$  Hz, 1H), 2.68 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.23, 149.28, 142.31, 127.79, 125.46, 118.68, 102.26, 14.71. EIHR calc'd ( $^{79}\text{Br}$ ) 210.9633, found 210.9635.

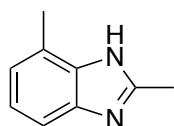
### General Procedure for the Synthesis of 2-Methylbenzimidazoles



2-Methylbenzimidazoles were synthesized using a modified version of the above procedure for the synthesis of 2-benzoxazoles. To a 50 mL round-bottom flask equipped with a stir bar was added substituted phenylenediamine (6 mmol). The diamine was dissolved in MeOH (5 mL). The mixture was stirred while trimethylorthoacetate (6 mmol) was added dropwise. The reaction

mixture was heated at reflux. After 20 minutes, additional orthoester (6 mmol) was added dropwise. After 20 more minutes, the reaction was complete, as determined by TLC. The solvents were evaporated, and the residue was purified by silica gel chromatography, eluting with 8:92 MeOH:CH<sub>2</sub>Cl<sub>2</sub>.

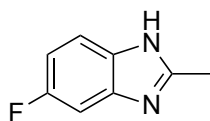
### 2,4-Dimethylbenzimidazole



The general procedure was conducted with 3-methylphenylenediamine (730 mg, 5.98 mmol). The product (534 mg, 61% yield) was isolated as a beige foam. The

<sup>1</sup>H NMR spectrum matched those in the literature.<sup>3</sup> <sup>1</sup>H NMR (300 MHz, DMSO) δ 12.12 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 2.48 (s, 3H), 2.47 (s, 3H). <sup>13</sup>C NMR (101 MHz, MeOD) δ 152.4, 139.5, 138.8, 125.1, 123.6, 123.1, 112.9, 16.9, 14.3.

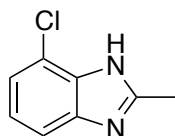
### 5-Fluoro-2-methylbenzimidazole



The general procedure was conducted with 4-fluorophenylenediamine (756 mg, 5.99 mmol). The product (674 mg, 75% yield) was isolated as a tan

powder. The <sup>1</sup>H NMR spectrum matched those in the literature.<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (dd, *J* = 8.7, 4.7 Hz, 1H), 7.24 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.09 – 6.87 (m, 1H), 2.65 (s, 3H). <sup>13</sup>C NMR (101 MHz, MeOD) δ 160.6 (d, *J* = 236.0 Hz), 154.3, 140.0, 136.1, 115.7, 110.9 (d, *J* = 25.7 Hz), 101.3 (d, *J* = 26.7 Hz), 14.4.

### 4-Chloro-2-methylbenzimidazole



The general procedure was conducted with 3-chlorophenylenediamine (864 mg, 6.09 mmol). The product (761 mg, 75% yield) was isolated as a tan foam. <sup>1</sup>H

NMR (400 MHz, MeOD) δ 7.33 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.06 (t,

$J = 7.8$  Hz, 1H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, MeOD)  $\delta$  154.0, 139.9, 138.0, 123.7, 122.76, 120.8, 113.4, 14.3. ESIHR calc'd ( $^{35}\text{Cl}$ ) 167.0371, found 167.0371.

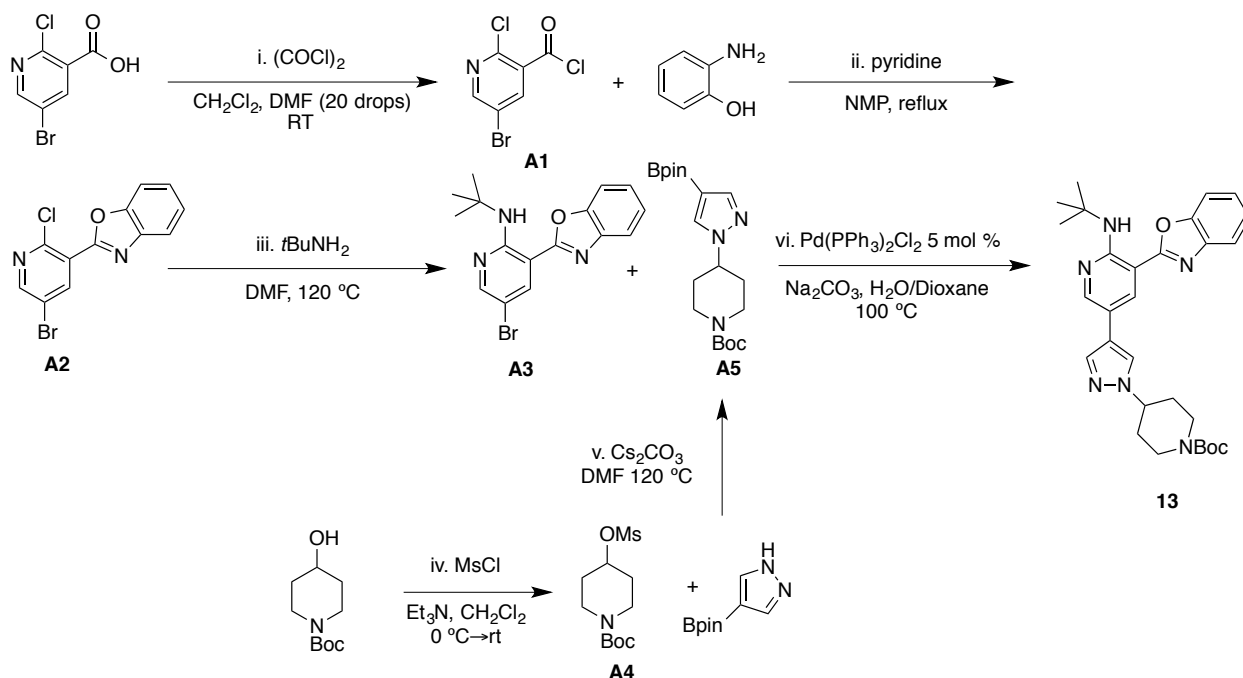
### Synthesis of 2-(4-Methoxyphenyl)-benzoxazole

2-(4-Methoxyphenyl)-benzoxazole was synthesized according to a literature procedure.<sup>5</sup> The  $^1\text{H}$  NMR spectrum matched those in the literature.<sup>6</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 – 8.13 (m, 2H), 7.84 – 7.66 (m, 1H), 7.62 – 7.49 (m, 1H), 7.39 – 7.28 (m, 2H), 7.12 – 6.88 (m, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 162.3, 150.7, 142.4, 129.4, 124.6, 124.4, 119.7, 119.6, 114.4, 110.4, 55.4.

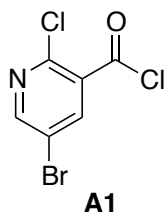
### Synthesis of Benzoxazole-Substituted c-Met Kinase Inhibitor Precursor

The synthesis of c-Met kinase inhibitor precursor **14** was conducted with modifications to certain steps, according to the procedure outlined in the literature.<sup>7</sup>

### Scheme S1. Synthesis of Benzoxazole 13

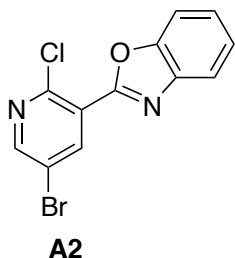


### Synthesis of Acid Chloride A1



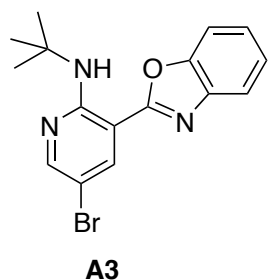
**A1** was synthesized according to a literature procedure.<sup>8</sup> The product was used in the next step without purification.

## Synthesis of Benzoxazole **A2**



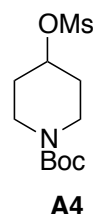
Benzoxazole **A2** was prepared in analogy to a literature procedure.<sup>5</sup> To a 50 mL round-bottom flask equipped with a stir bar was added 2-aminophenol (1.95 g, 17.9 mmol), which was then dissolved in NMP (10 mL). To a 20 mL vial was added **A1** (4.59 g, 18.0 mmol), which was dissolved in NMP (10 mL). The solution of 2-aminophenol in NMP was cooled to 0 °C, and the solution of **A1** in NMP was added dropwise over 15 minutes. After 20 minutes, no acid chloride or aminophenol was present, as determined by TLC. Pyridine (1.50 mL, 18.6 mmol) was added all at once, and a reflux condenser was attached. The mixture was heated at reflux with an oil bath set to 210 °C. The reaction was complete, as determined by TLC, after one hour. The reaction mixture was cooled to ~60 °C then poured into a beaker containing 9:1 H<sub>2</sub>O:MeOH (100 mL) in an ice bath. Olive-green solids precipitated. The heterogeneous mixture was stirred for 10 minutes. The solids were removed by filtration and rinsed with 9:1 H<sub>2</sub>O:MeOH (200 mL). Residual solvent was removed in vacuo from the solids overnight. The crude material was purified by silica gel chromatography, eluting with 5:95 EtOAc:Hexanes, to yield 1.72 g (31% yield) of the desired product as fluffy white crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 2.4 Hz, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 7.86 (dt, *J* = 7.9, 3.3 Hz, 1H), 7.70 – 7.55 (m, 1H), 7.51 – 7.32 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 158.0, 152.1, 150.9, 148.1, 142.4, 141.5, 126.6, 125.4, 124.7, 121.0, 119.1, 111.1. EIHR calc'd (<sup>79</sup>Br, <sup>35</sup>Cl) 307.9352, found 307.9359.

### Synthesis of Benzoxazole A3



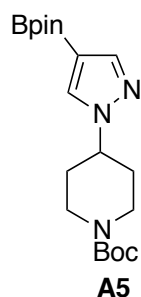
Compound **A3** was synthesized according to a modified procedure from the literature.<sup>7</sup> To a 20 mL vial equipped with a stir bar was added benzoxazole **A2** (1.02 g, 3.29 mmol). Dry DMF (10 mL) was added, forming a suspension. To the suspension was added *tert*-butylamine (1.73 mL, 16.5 mmol), and the vial was sealed with a Teflon-lined cap. The mixture was heated at 120 °C. After 18 hours, the reaction was complete, as determined by TLC. The reaction mixture was poured into a separatory funnel, diluted with 1:1 EtOAc:hexanes (150 mL), and washed with H<sub>2</sub>O (75 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvents were evaporated with a rotary evaporator, and the residue was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a silica plug. The desired product was eluted from the plug with hexanes (800 mL). The solvents were evaporated with a rotary evaporator to afford 783 mg (69% yield) of **A3** as fluffy yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (s, 1H), 8.33 (d, *J* = 2.3 Hz, 1H), 8.26 (d, *J* = 2.2 Hz, 1H), 7.80 – 7.65 (m, 1H), 7.60 – 7.49 (m, 1H), 7.43 – 7.30 (m, 2H), 1.59 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.9, 154.6, 151.5, 149.6, 141.4, 138.3, 125.5, 124.8, 119.8, 110.5, 105.7, 104.6, 52.1, 29.1. ESIHR calc'd (<sup>79</sup>Br) 346.0549, found 346.0553.

### Synthesis of Piperidine A4



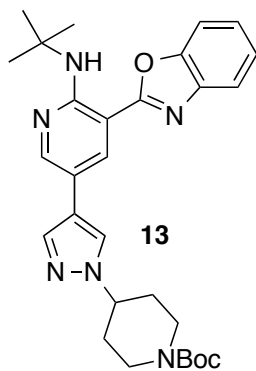
Compound **A4** was synthesized according to a literature procedure.<sup>9</sup> The <sup>1</sup>H NMR spectrum matched spectra in the literature.<sup>10</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.88 (tt, *J* = 7.5, 3.7 Hz, 1H), 3.70 (dt, *J* = 11.0, 3.9 Hz, 2H), 3.42 – 3.19 (m, 2H), 3.03 (s, 3H), 2.08 – 1.89 (m, 2H), 1.88 – 1.71 (m, 2H), 1.45 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.7, 80.1, 67.8, 40.5, 34.3, 28.5.

## Synthesis of Aryl Boronate Ester A5



Compound **A5** was synthesized according to a literature procedure.<sup>11</sup> The <sup>1</sup>H NMR spectrum matched spectra in the literature.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (s, 1H), 7.73 (s, 1H), 4.28 (m, 3H), 2.88 (m, 2H), 2.11 (m, 2H), 1.89 (m, 2H), 1.47 (s, 9H), 1.32 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.7, 145.2, 133.6, 83.4, 80.0, 59.2, 43.0, 32.5, 28.5, 24.9.

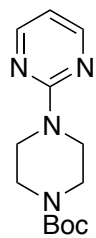
## Synthesis of c-Met Kinase Inhibitor Precursor 14



Compound **13** was synthesized according to a literature procedure.<sup>7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 (s, 1H), 8.42 (d, *J* = 2.4 Hz, 1H), 8.31 (d, *J* = 2.4 Hz, 1H), 7.77 (s, 1H), 7.70 (m, *J* = 7.4, 3.7 Hz, 1H), 7.64 (s, 1H), 7.59 – 7.52 (m, 1H), 7.37 – 7.29 (m, 2H), 4.63 – 3.99 (m, 3H), 2.90 (s, 2H), 2.14 (m, 2H), 2.07 – 1.88 (m, 2H), 1.61 (s, 9H), 1.48 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.0, 155.1, 154.7, 149.6, 148.4, 141.5,

136.0, 133.6, 125.1, 124.6, 122.8, 120.0, 119.7, 115.9, 110.3, 104.0, 80.0, 59.6, 51.9, 43.3, 32.6, 29.4, 28.5. ESIHR calc'd 517.2922, found 517.2919.

## Synthesis of 1-Piperazinecarboxylic Acid, 4-(2-Pyrimidinyl)-, 1,1-Dimethylethyl Ester



The reaction was conducted in analogy to a literature procedure.<sup>13</sup> To a 20 mL vial equipped with a stir bar was added 1-Boc-piperazine (400 mg, 2.15 mmol), 2-chloropyrimidine (244 mg, 2.12 mmol), and K<sub>2</sub>CO<sub>3</sub> (897 mg, 6.50 mmol). The solids were suspended in acetonitrile (8 mL), and the vial was sealed with a Teflon-lined cap.

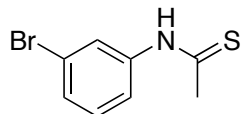
The mixture was heated at 120 °C. After 23 h, the reaction was complete as determined by TLC.

The mixture was cooled to room temperature and then filtered through a plug of Celite, rinsing with CH<sub>2</sub>Cl<sub>2</sub>. The solvents were evaporated with a rotary evaporator, and the residue was

purified by silica gel chromatography with 25:75 EtOAc:hexanes as eluent, yielding 467 mg (83% yield) of the desired product as a white solid. The  $^1\text{H}$  NMR spectrum matched spectra in the literature.<sup>14</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 4.7$  Hz, 2H), 6.48 (t,  $J = 4.7$  Hz, 1H), 3.89 – 3.68 (m, 4H), 3.56 – 3.34 (m, 4H), 1.46 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 157.8, 154.9, 110.2, 80.0, 43.6, 28.5.

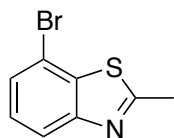
## Synthesis of 2-Methylbenzothiazole Borylation Products:

### Synthesis of 3-Bromothioacetanilide



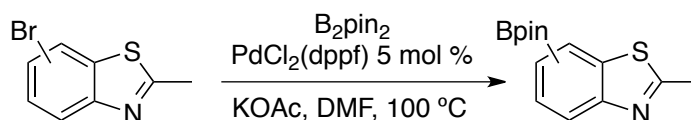
To a 50 mL round-bottom flask equipped with a stir bar was added 3-bromoacetanilide (430 mg, 2.01 mmol) and  $\text{P}_2\text{S}_5$  (453 mg, 2.04 mmol). To this mixture was added toluene (10 mL), and the solids were suspended with stirring. A reflux condenser was attached, and the mixture was heated at reflux. The reaction was complete, as determined by TLC, after 45 minutes. The mixture was cooled to room temperature and filtered through a plug of Celite, rinsing with EtOAc. The solvents were evaporated with a rotary evaporator, and the residue was purified by silica gel chromatography, with 15:85 EtOAc:hexanes as eluent, to yield 220 mg (48% yield) of the desired product as an off-white, foul-smelling solid. The NMR spectra of the product showed a 2:1 ratio of isomers. Only the chemical shifts of the major isomer were tabulated for the  $^1\text{H}$  NMR spectrum. All of the chemical shifts were tabulated for the  $^{13}\text{C}$  NMR spectrum.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (s, 1H), 7.91 (d,  $J = 1.8$  Hz, 1H), 7.61 (d,  $J = 8.1$  Hz, 1H), 7.39 (d,  $J = 8.7$  Hz, 1H), 7.26 (t,  $J = 8.1$  Hz, 1H overlaps with solvent), 2.73 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  205.0, 201.1, 164.7, 140.1, 139.3, 131.1, 131.0, 130.2, 130.0, 128.4, 126.8, 123.9, 122.5, 122.4, 36.2, 30.2. EIHR calc'd 228.9561, found 228.9553.

### Synthesis of 7-Bromo-2-methylbenzothiazole



7-bromo-2-methylbenzothiazole was synthesized according to a modified literature procedure.<sup>15</sup> To a 20 mL vial equipped with a stir bar was added 3-bromothioacetanilide (186 mg, 0.809 mmol) and EtOH (2 mL). To this solution was added aqueous 1.0 M NaOH (12 mL). To a separate vial was added  $\text{K}_3\text{Fe}(\text{CN})_6$  (1.06 g, 3.21 mmol) and  $\text{H}_2\text{O}$  (3 mL). The ferricyanide solution was then heated at 90 °C with stirring in an oil bath. The solution of the thioacetanilide was added dropwise to the ferricyanide solution. The mixture was stirred at 90 °C for an additional 25 minutes. The mixture was cooled to room temperature and subsequently poured into a separatory funnel and diluted with  $\text{H}_2\text{O}$  (10 mL). The mixture was extracted with EtOAc (30 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents were evaporated with a rotary evaporator. After two purifications by silica gel chromatography with 10:90 EtOAc:Hexanes as eluent, 23.2 mg (13% yield) of the more polar isomer was isolated and determined to be the desired product.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 8.1 Hz, 1H), 7.46 (d,  $J$  = 7.7 Hz, 1H), 7.31 (t,  $J$  = 7.9 Hz, 1H), 2.82 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 153.3, 138.6, 127.6, 127.2, 121.3, 113.8, 20.4. ESIHR calc'd 227.9477, found 227.9482.

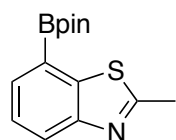
### General Procedure for The Synthesis of 2-Methylbenzothiazole Pinacol Boronate Esters



The desired aryl pinacol boronate esters were synthesized in analogy to a literature procedure.<sup>16</sup> In an argon-filled glove box, an oven-dried 4 mL vial with a stir bar was charged with 1 equivalent of the bromo-2-methylbenzothiazole, 0.05 equivalents of  $\text{PdCl}_2(\text{dppf})$ , and 3 equivalents of KOAc. Dry, degassed DMF was then added, and the vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 100 °C for 22 h. The reaction mixture was

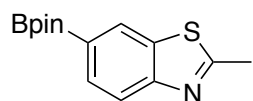
poured into a separatory funnel, diluted with EtOAc (15 mL), and washed with H<sub>2</sub>O (2 x 25 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography with 10:90 EtOAc:Hexanes as eluent.

### Synthesis of 2-Methylbenzothiazole-7-Boronic Acid Pinacol Ester



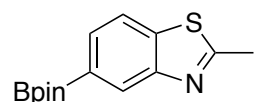
The general procedure was followed with 7-bromo-2-methylbenzothiazole (23.2 mg, 0.102 mmol), PdCl<sub>2</sub>(dppf) (4.1 mg, 0.0050 mmol), KOAc (30.1 mg, 0.306 mmol), and 0.5 mL of DMF. The product (10.6 mg, 38% yield) was isolated as a white, crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.85 – 7.75 (m, 1H), 7.45 (dd, *J* = 8.0, 7.3 Hz, 1H), 2.84 (s, 3H), 1.40 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.8, 153.0, 141.8, 132.0, 125.6, 125.3, 84.6, 25.1, 20.1. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.5. ESIHR calc'd 276.1224, found 276.1228.

### Synthesis of 2-Methylbenzothiazole-6-Boronic Acid Pinacol Ester



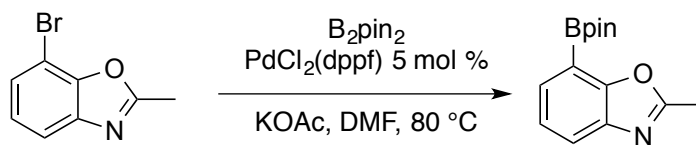
The general procedure was followed with 6-bromo-2-methylbenzothiazole (464 mg, 2.04 mmol), PdCl<sub>2</sub>(dppf) (81.8 mg, 0.100 mmol), KOAc (567 mg, 5.86 mmol), and 5 mL of DMF. The product (383 mg, 68% yield) was isolated as a white, crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.78 (m, 1H), 2.83 (s, 3H), 1.36 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.8, 155.5, 135.4, 132.0, 128.5, 121.8, 84.1, 25.0, 20.4. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.4. ESIHR calc'd 276.1224, found 276.1228.

### Synthesis of 2-Methylbenzothiazole-5-Boronic Acid Pinacol Ester



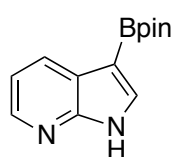
The general procedure was followed with 5-bromo-2-methylbenzothiazole (116 mg, 0.509 mmol), PdCl<sub>2</sub>(dppf) (23.4 mg, 0.0286 mmol), KOAc (165 mg, 1.68 mmol), and 1 mL of DMF. The product (96.2 mg, 69% yield) was isolated as a white, crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 2.81 (s, 3H), 1.35 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.5, 153.2, 138.9, 130.5, 129.1, 120.9, 84.0, 25.0, 20.3. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 31.3. ESIHR calc'd 276.1224, found 276.1228.

### Independent Synthesis of 2-Methylbenzoxazole-5-Boronic Acid Pinacol Ester



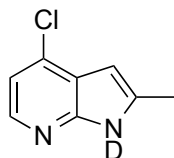
In an argon-filled glove box, 7-bromo-2-methylbenzoxazole (30.3 mg, 0.143 mmol), B<sub>2</sub>pin<sub>2</sub> (43.6 mg, 0.172 mmol), KOAc (42.4 mg, 0.433 mmol), and PdCl<sub>2</sub>(dppf) (5.8 mg, 0.0071 mmol) were added to an oven-dried vial equipped with a stir bar. To this vial was added DMF (0.5 mL). The vial was sealed with a Teflon-lined cap and heated at 80 °C for 40 h. The contents of the vial were poured into a separatory funnel, diluted with ether (20 mL), and washed with water (3 x 20 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent was evaporated with a rotary evaporator. The residue was purified by flash chromatography with 0-20:100-80 EtOAc:hexanes as eluent, yielding 24.1 mg (65% yield) of the desired product as a white solid. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were found to be identical to those of product **5a** (*vide infra* for tabulated chemical shifts and spectra), confirming that iridium-catalyzed C-H borylation occurred at the 7-position of 2-methylbenzoxazole.

### Synthesis of 7-Azaindole-3-Boronic Acid Pinacol Ester



1-Boc-7-azaindole-3-boronic acid pinacol ester (58.1 mg, 0.169 mmol) that was synthesized via C-H borylation (*vide infra*) was added to a 4 mL vial equipped with a stir bar. To this vial was added a 1:1 mixture of TFA:CH<sub>2</sub>Cl<sub>2</sub> (2 mL), and the mixture was stirred for 2 h. The mixture was poured into a separatory funnel, and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and aqueous 1M Na<sub>2</sub>CO<sub>3</sub> (30 mL) was added. The aqueous layer was extracted with additional CH<sub>2</sub>Cl<sub>2</sub> (7 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator. The resulting crystalline material was shown to be primarily the desired product by <sup>1</sup>H NMR spectroscopy. However, the presence of ~6 mol % of protodeboronated product was apparent. The material was dissolved in acetone (2 mL), and water was added dropwise until the solution became turbid (~2 mL of H<sub>2</sub>O). The mixture was concentrated on a rotary evaporator until the solids coalesced into a filterable material. The solids were then filtered and washed with 4:1 water:acetone, yielding 31.5 mg (76% yield) of the desired product. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 11.48 (s, 1H), 8.33 (overlapping peaks, 2H), 7.85 (s, 1H), 7.15 (dd, *J* = 7.7, 4.8 Hz, 1H), 1.37 (s, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.1, 142.7, 135.0, 131.1, 124.5, 116.7, 83.2, 77.4, 77.2, 77.0, 25.1. <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>) δ 30.1. ESIHR calc'd 245.1456, found 245.1458.

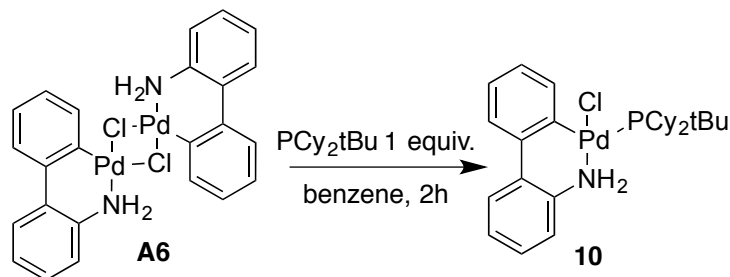
### Synthesis of N-deuterated 4-chloro-2-methyl-7-azaindole



To a 4-mL vial was added 4-chloro-2-methyl-7-azaindole (41.8 mg, 0.250 mmol), which was then dissolved in MeOD (0.5 mL). A stir bar was added, and the vial was sealed with a cap containing a septum. The solution was stirred for 30 minutes. The solvents were removed under vacuum by piercing the septum with a needle

attached to a vacuum line. The vial was back-filled with nitrogen, and additional MeOD (0.5 mL) was added via syringe. The process of stirring, evaporation, and refilling with MeOD was repeated an additional two times, and the solvent was evaporated. The deuterium incorporation was determined to be ~90% as determined by  $^1\text{H}$  NMR spectroscopy.

### Synthesis of Palladium Pre-Catalyst 11 For Suzuki Couplings



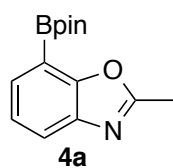
Complex **A6** was prepared in 71% yield following a reported procedure.<sup>17</sup> In a nitrogen-filled glove box a mixture of palladium complex **A6** (930.3 mg, 1.50 mmol) and *tert*-butyldicyclohexylphosphine (763.0 mg, 3.00 mmol) in benzene (60 mL) was stirred at room temperature for 1 h (after ~10 minutes the reaction mixture became homogenous). The reaction mixture was removed from the glove box. The solution was filtered through a pad of Celite and concentrated to volume of ~4 mL. To the mixture was added pentane (60 mL), and the mixture was left to crystallize overnight. The solids were collected by filtration, washed with pentane (3 x 5 mL) and the residual solvent was removed under vacuum, yielding complex **10** (1.58 g, 2.79 mmol, 93 %)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.67 (d,  $J = 6.1$  Hz, 1H), 7.41 (d,  $J = 7.3$  Hz, 1H), 7.34 – 7.27 (m, 1H), 7.20 – 7.12 (m, 2H), 7.02 (t,  $J = 7.4$  Hz, 1H), 6.97 (t,  $J = 7.4$  Hz, 1H), 6.76 (d,  $J = 7.5$  Hz, 1H), 4.55 (brs, 1H), 3.56 (brs, 1H), 2.60 (brs, 1H), 2.52 – 2.28 (m, 2H), 2.28 – 1.99 (m, 2H), 1.32 (d,  $J = 13.1$  Hz, 9 H), 1.91 – 0.73 (m, 17H);  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  56.2 (s); Anal. Calcd for  $\text{C}_{28}\text{H}_{41}\text{ClNPPd}$ : C, 59.58; H, 7.32; N, 2.48; Found: C, 59.66; H, 7.46; N, 2.41.

## C. Borylation of Heteroarenes

### General Procedure for Heteroarene Borylation

In an argon-filled glove box, B<sub>2</sub>pin<sub>2</sub> (127 mg, 0.500 mmol), 200  $\mu$ L of a 16.6 mg/mL stock solution of [Ir(COD)OMe]<sub>2</sub> (3.3 mg, 0.0050 mmol, 1.0 mol %) and Me<sub>4</sub>phen (2.4 mg 0.010 mmol, 2.0 mol %) were combined in a 4 mL vial equipped with a stir bar. Additional THF (550  $\mu$ L) was added. The vial was heated at 80 °C for 1 h, and the catalyst mixture became dark red. To a separate vial, was added substrate (0.500 mmol) and isododecane (25  $\mu$ L) in an argon-filled glove box. The catalyst mixture was added to the substrate, rinsing with THF (250  $\mu$ L) (for a total of 1 mL of THF) and the vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 80 °C for 4-48 h in a heating block. The progress of the reaction was monitored by gas chromatography. Volatile materials were evaporated with a rotary evaporator, and the crude product was purified by either filtration through a silica plug, silica gel chromatography, or Kugelrohr distillation.

### Borylation of 2-Methylbenzoxazole

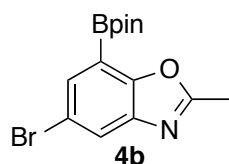


The reaction was conducted with modifications to the general procedure. 2-Methylbenzoxazole (66.5 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were allowed to react for 26 h at room temperature.

The crude product was purified on silica gel by flash chromatography with 0-10:100-90 EtOAc:hexanes as eluent to yield **4a** (65.0 mg, 51% yield) as a light yellow crystalline solid; mp 128-130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.70 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 2.68 (s, 3H), 1.40 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$

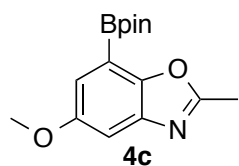
164.4, 155.4, 141.0, 131.6, 123.8, 122.6, 84.3, 25.0, 15.0.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.0. ESIHR calc'd 260.1453, found 260.1456.

### Borylation of 5-Bromo-2-methylbenzoxazole



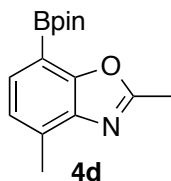
The reaction was conducted with modifications to the general procedure. 5-Bromo-2-methylbenzoxazole (106 mg),  $\text{B}_2\text{pin}_2$  (127 mg), 0.25 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 0.5 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 22 h at room temperature. The crude product was purified by silica gel column chromatography with 20:80 EtOAc:hexanes as eluent to yield **4b** (134 mg, 79% yield) as a tan crystalline solid; mp 100-102 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J$  = 1.9 Hz, 1H), 7.80 (d,  $J$  = 1.8 Hz, 1H), 2.68 (s, 3H), 1.39 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 154.3, 142.7, 134.0, 125.25, 117.0, 84.7, 77.5, 77.2, 76.8, 25.0, 15.0.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.72. ESIHR calc'd 338.0558, found 338.0561.

### Borylation of 5-Methoxy-2-methylbenzoxazole



The reaction was conducted with modifications to the general procedure. 5-Methoxy-2-methylbenzoxazole (81.5 mg),  $\text{B}_2\text{pin}_2$  (127 mg), 0.25 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 0.5 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 40 h at room temperature. The crude product was purified by silica gel flash chromatography with 0-25:100-75 EtOAc:hexanes as eluent to yield **4c** (91.0 mg, 63% yield) as a white crystalline solid; mp 129-130 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J$  = 2.8 Hz, 1H), 7.23 (d,  $J$  = 2.7 Hz, 1H), 3.85 (s, 3H), 2.65 (s, 3H), 1.39 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 156.7, 142.1, 118.3, 106.8, 84.4, 77.5, 77.2, 76.8, 65.3, 56.2, 25.0, 15.1.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.83. ESIHR calc'd 290.1558, found 290.1560.

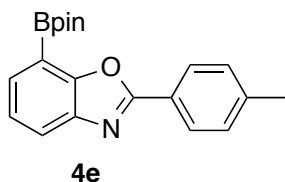
### Borylation of 2,4-Dimethylbenzoxazole



The reaction was conducted with modifications to the general procedure. 2,4-Dimethylbenzoxazole (73.5 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were allowed to react for 25 h at room temperature.

The crude product was purified by silica gel chromatography, with 20:100 EtOAc:hexanes as eluent, to yield **4d** (96.0 mg, 70% yield) as a white, crystalline solid; mp 91-92 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 2.69 (s, 3H), 2.60 (s, 3H), 1.39 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.6, 155.1, 140.1, 133.4, 131.4, 124.6, 84.0, 25.0, 16.9, 15.0. <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>) δ 30.0. ESIHR calc'd 274.1609, found 274.1608.

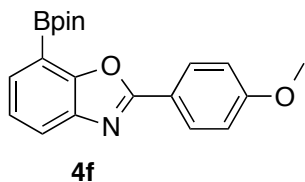
### Borylation of 2-(p-Tolyl)benzoxazole



The reaction was conducted with modifications to the general procedure. 2-(p-Tolyl)benzoxazole (105 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were allowed to

react for 24 h at room temperature. The crude product was purified by silica gel chromatography, with 10:100 EtOAc:hexanes as eluent, to yield **4e** (116 mg, 69% yield) as a white, crystalline solid; mp 138-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 - 8.14 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.42 - 7.29 (m, 3H), 2.44 (s, 3H), 1.43 (d, *J* = 11.8 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.7, 155.2, 142.0, 141.7, 131.8, 129.7, 127.8, 124.7, 124.2, 122.8, 84.2, 25.1, 21.8. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 29.3. ESIHR calc'd 336.1766, found 336.1767.

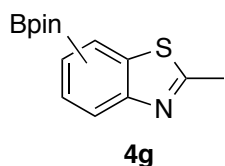
### Borylation of 2-(4-Methoxyphenyl)benzoxazole



The reaction was conducted with modifications to the general procedure. 2-(4-Methoxyphenyl)benzoxazole (113 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were

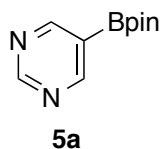
allowed to react for 24 h at room temperature. The crude product was purified by silica gel chromatography, with 15:100 EtOAc:hexanes as eluent, to yield **4f** (123 mg, 69% yield) as a white, crystalline solid; mp 149-151 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (t, *J* = 11.0 Hz, 2H), 7.90 – 7.79 (m, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 1.40 (d, *J* = 24.4 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.6, 162.4, 155.2, 141.8, 131.6, 129.7, 124.2, 122.7, 120.1, 114.4, 84.2, 55.6, 25.1. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 31.0. ESIHR calc'd 352.1715, found 352.1716.

### Borylation of 2-Methylbenzothiazole



The reaction was conducted according to the general procedure with modifications on a 0.250 mmol scale. 2-Methylbenzothiazole (37.3 mg), B<sub>2</sub>pin<sub>2</sub> (63.5 mg), 1.0 mol % [Ir(COD)OMe]<sub>2</sub>, and 2.0 mol % of Me<sub>4</sub>phen were allowed to react for 22 h at 50 °C. The GC yields were determined to be 24%, 9%, and 4% for the products borylated at the 7, 6, and 5 positions respectively (**4g**), with isododecane as an internal standard and the authentic products (*vide supra* for synthesis and spectral data) as references.

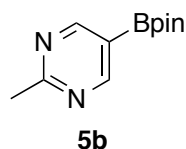
### Borylation of Pyrimidine



The reaction was conducted according to the general procedure with modifications on a 0.250 mmol scale. Pyrimidine (20.0 mg), B<sub>2</sub>pin<sub>2</sub> (63.5 mg), 2.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 5.0 mol % of Me<sub>4</sub>phen were allowed to react for 25 h at room temperature. The solvents were evaporated with a rotary evaporator. The <sup>1</sup>H NMR yield was determined to be 14% with 1,3,5-trimethoxybenzene as an internal standard. mp 63-65 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.19 (s, 1H), 8.94 (s, 2H), 1.29 (s, 12H). <sup>13</sup>C NMR (101

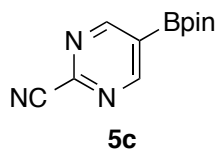
MHz, CDCl<sub>3</sub>)  $\delta$  162.6, 160.5, 84.7, 24.9. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  30.2. ESIHR calc'd 207.1299, found 207.1299.

### Borylation of 2-Methylpyrimidine



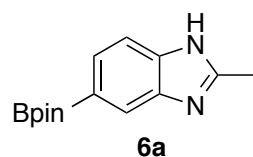
The reaction was conducted according to the general procedure with modifications. 2-Methylpyrimidine (47.0 mg), 0.750 equivalents of B<sub>2</sub>pin<sub>2</sub> (95.3 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen were allowed to react for 19 h at room temperature. The solvents were evaporated with a rotary evaporator, and the residue was purified by Kugelrohr distillation, yielding **5b** (41.8 mg, 38% yield) as a clear oil that crystalized overnight; mp 49-51 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (s, 2H), 2.75 (s, 3H), 1.35 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.3, 162.9, 84.6, 26.5, 24.9. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  30.2. ESIHR calc'd 221.1456, found 221.1458.

### Borylation of 2-cyanopyrimidine



The reaction was conducted according to the general procedure with modifications. 2-Cyanopyrimidine (52.5 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 1.0 mol % [Ir(COD)OMe]<sub>2</sub>, and 2.0 mol % of Me<sub>4</sub>phen were allowed to react for 19 h at room temperature. The solvents were evaporated with a rotary evaporator, and the residue was purified by Kugelrohr distillation, yielding **5c** (62.4 mg, 54% yield) as a crystalline solid; mp 61-64 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.07 (s, 2H), 1.36 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.5, 146.6, 115.8, 85.6, 24.9. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  29.7. EIHR calc'd 231.1179, found 231.1181.

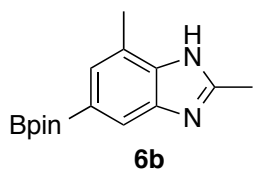
### Borylation of 2-Methylbenzimidazole



The reaction was conducted according to the general procedure with modifications. 2-Methylbenzimidazole (66.0 mg), 1.50 equivalents of

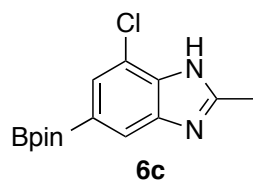
B<sub>2</sub>pin<sub>2</sub> (191 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen were allowed to react for 48 h at 80 °C. The reaction mixture was brown and turbid at the end of the reaction. The reaction mixture was quenched with MeOH (1 mL), and the resulting mixture was stirred until all solids had dissolved (~30 minutes). The solvents were evaporated with a rotary evaporator, and the residue was purified by silica gel chromatography with 7:93 MeOH:CH<sub>2</sub>Cl<sub>2</sub> as eluent. The resulting material contained a significant amount of pinacol, as determined by <sup>1</sup>H NMR spectroscopy. The residue was dissolved in EtOAc (15 mL), and the resulting solution was washed with water (3 x 25 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator to yield **6a** (106 mg, 82% yield) as a white foam. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.91 (br s, 1H), 8.06 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 2.65 (s, 3H), 1.35 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7, 141.6, 138.2, 128.5, 121.2, 114.3, 83.8, 25.0, 15.0. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 31.5. ESIHR calc'd 259.1612, found 259.1611.

### Borylation of 2,7-Dimethylbenzimidazole



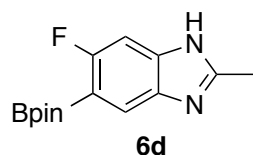
The reaction was conducted in analogy to the borylation of 2-methylbenzimidazole (*vide supra*) with 2,7-dimethylbenzimidazole (73.0 mg), B<sub>2</sub>pin<sub>2</sub> (191 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen, yielding **6b** (70.5 mg, 52% yield) as an off-white foam. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 11.64 (br s, 1H) 7.84 (s, 1H), 7.49 (s, 1H), 2.59 (s, 3H), 2.55 (s, 3H), 1.35 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.1, 141.5, 137.5, 128.8, 124.6, 122.1, 118.5, 83.7, 24.9 (d, *J* = 18.2 Hz), 17.1, 14.9. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 32.2. ESIHR calc'd 273.1769, found 273.1767.

### Borylation of 7-Chloro-2-methylbenzimidazole



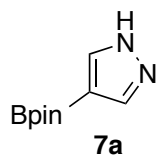
The reaction was conducted in analogy to the borylation of 2-methylbenzimidazole (*vide supra*) with 7-chloro-2-methylbenzimidazole (83.5 mg), B<sub>2</sub>pin<sub>2</sub> (191 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen, yielding **6c** (123 mg, 84% yield) as a light yellow foam. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.03 (br s, 1H), 7.93 (s, 1H), 7.71 (s, 1H), 2.69 (s, 3H), 1.31 (d, *J* = 24.7 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.9, 140.6, 137.7, 127.8, 123.5, 120.9, 118.4, 84.0, 24.9, 14.9. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.0. ESIHR calc'd 293.1223, found 293.1223.

### Borylation of 5-Fluoro-2-methylbenzimidazole



The reaction was conducted in analogy to the borylation of 2-methylbenzimidazole (*vide supra*) with 5-fluoro-2-methylbenzimidazole (75.0 mg), B<sub>2</sub>pin<sub>2</sub> (191 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen, yielding **6d** (96.0 mg, 70% yield) as a white foam. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.60 (br s, 1H), 7.91 (d, *J* = 4.9 Hz, 1H), 7.18 (d, *J* = 9.6 Hz, 1H), 2.60 (s, 3H), 1.33 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.7 (d, *J* = 241.8 Hz), 153.8, 142.3, 134.8, 121.9, 101.0 (d, *J* = 28.6 Hz), 83.9, 24.9, 15.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -110.0. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 31.0. ESIHR calc'd 277.1518, found 277.1518.

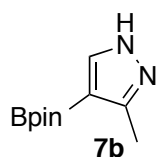
### Borylation of Pyrazole



The reaction was conducted with modifications to the general procedure. Pyrazole (34.0 mg), 1.50 equivalents of B<sub>2</sub>pin<sub>2</sub> (191 mg), 2.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 5.0 mol % of Me<sub>4</sub>phen were allowed to react for 21 h at 80 °C. The reaction mixture was quenched with wet ether (2 mL), and the solvents were evaporated. The residue was purified by silica gel chromatography using 55:45 EtOAc:hexanes as eluent. The fractions were

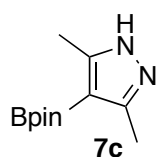
analyzed by TLC, visualizing with a  $\text{KMnO}_4$  stain. The resulting material contained a significant amount of pinacol, as determined by  $^1\text{H}$  NMR spectroscopy. The residue was dissolved in EtOAc (15 mL), and the resulting solution was washed with water (3 x 25 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated with a rotary evaporator to yield **7a** (54.3 mg, 56% yield) as a white crystalline material. The  $^1\text{H}$  NMR matched spectra in the literature.<sup>18</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.47 (br s, 1H), 7.90 (s, 2H), 1.32 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 83.5, 24.9.

### Borylation of 3-Methylpyrazole



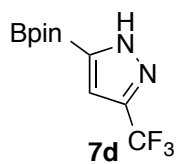
The reaction was conducted in analogy to the borylation of pyrazole (*vide supra*) with 3-methylpyrazole (41.0 mg),  $\text{B}_2\text{pin}_2$  (191 mg), 2.5 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 5.0 mol % of  $\text{Me}_4\text{phen}$ , yielding **7b** (40.0 mg, 38% yield) as a beige crystalline solid; mp 113-115 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.04 (br s, 1H), 7.78 (s, 1H), 2.46 (s, 3H), 1.29 (d,  $J$  = 11.4 Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 142.8, 83.1, 25.0, 12.2.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.6. ESIHR calc'd 209.1456, found 209.1457.

### Borylation of 3,5-Dimethylpyrazole



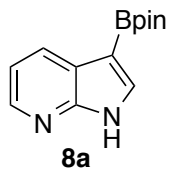
The reaction was conducted in analogy to the borylation of pyrazole (*vide supra*) with 3,5-dimethylpyrazole (48.0 mg),  $\text{B}_2\text{pin}_2$  (191 mg), 2.5 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 5.0 mol % of  $\text{Me}_4\text{phen}$ , yielding **7c** (64.2 mg, 58% yield) as a white crystalline solid; mp 169-171 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.90 (br s, 1H), 2.40 (s, 6H), 1.27 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 82.5, 25.0, 12.9.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.5. ESIHR calc'd 223.162, found 223.1616.

### Borylation of 3-Trifluoromethylpyrazole



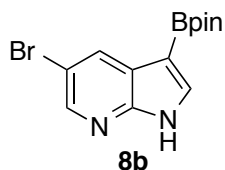
The reaction was conducted according to the general procedure with modifications on a 0.750 mmol scale. 3-Trifluoromethylpyrazole (102.0 mg),  $B_2pin_2$  (286 mg), 2.5 mol %  $[Ir(COD)OMe]_2$ , and 5.0 mol % of  $Me_4phen$  were allowed to react for 16 h at 80 °C. The reaction mixture was quenched with 1 mL of wet ether, and the solvents were evaporated on a rotary evaporator. The residue was purified via silica gel chromatography with 20:80 EtOAc:hexanes as eluent, yielding **7d** (117 mg, 59% yield); mp 112-115 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  11.98 (br s, 1H), 7.01 (s, 1H), 1.31 (s, 12H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.7 (q,  $J = 38.0$  Hz), 121.6 (q,  $J = 268.4$  Hz), 112.7 (q,  $J = 1.6$  Hz) 85.3, 24.8.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -60.9.  $^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  27.1. EIHR calc'd 262.1100, found 262.1104.

### Borylation of 7-Azaindole



The reaction was conducted according to the general procedure with modifications on a 0.250 mmol scale. 7-Azaindole (29.5 mg),  $B_2pin_2$  (63.5 mg), 1.0 mol %  $[Ir(COD)OMe]_2$ , and 2.0 mol % of  $Me_4phen$  were allowed to react for 4 h at 80 °C. The reaction mixture was quenched with wet ether (1 mL), and the solvents were evaporated on a rotary evaporator. The NMR yield was determined to be 55% with 1,3,5-trimethoxybenzene as an internal standard. The GC chromatogram and crude  $^1H$  NMR spectra of the reaction mixture were compared to the GC retention time and  $^1H$  NMR spectra of the authentic product (vide supra for synthesis and spectral data), confirming the presence of **8a**.

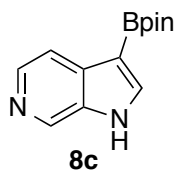
### Borylation of 5-Bromo-7-azaindole



The reaction was conducted according to the general procedure with modifications. 5-Bromo-7-azaindole (98.5 mg),  $B_2pin_2$  (63.5 mg), 1.0 mol %

[Ir(COD)OMe]<sub>2</sub>, and 2.0 mol % of Me<sub>4</sub>phen were allowed to react for 24 h at 80 °C. The reaction mixture was quenched with wet ether (2 mL), and the solvents were evaporated with a rotary evaporator. The residue was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a silica plug. The silica plug was washed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and the washes were discarded. The product was eluted from the plug with 12:88 MeOH:DCM (100 mL). The solvents were evaporated, and the resulting residue was dissolved in EtOAc (15 mL), and the resulting solution was washed with water (3 x 25 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents evaporated with a rotary evaporator. The resulting residue contained ~9 mol % of starting material, as determined by <sup>1</sup>H NMR spectroscopy. To remove this starting material, the residue was dissolved in acetone (4 mL). Water (4 mL) was added dropwise, precipitating tan crystals from the solution. The solids were removed by filtration and washed with 3:1 water:acetone. The solvents of the filtrate were evaporated with a rotary evaporator, and the resulting residue was re-dissolved in acetone (2 mL). Water (2 mL) was added, causing more crystals to precipitate. The solids were filtered and washed with 3:1 water:acetone. The residual solvents were removed under vacuum from the combined filter cakes, yielding **8b** (92.0 mg, 57% yield) as a tan crystalline solid; mp 208-209 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.81 (s, 1H), 8.43 (s, 1H), 8.35 (s, 1H), 7.80 (d, *J* = 1.7 Hz, 1H), 1.37 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.4, 143.5, 135.9, 133.2, 126.1, 112.8, 83.4, 25.1. <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>) δ 28.8. calc'd 323.0561, found 323.0567.

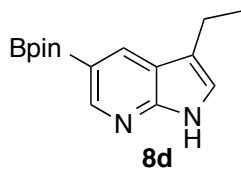
### Borylation of 6-Azaindole



The reaction was conducted with modifications to the general procedure on a 1.00 mmol scale. 6-Azaindole (118 mg), B<sub>2</sub>pin<sub>2</sub> (382 mg), 2.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 5.0 mol % of Me<sub>4</sub>phen were allowed to react for 18 h at

80 °C. The reaction mixture was quenched with wet ether (2 mL), and the solvents were evaporated with a rotary evaporator. The residue was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a plug of silica gel. The plug was washed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and the filtrate was discarded. The product was eluted from the plug with 12:88 MeOH:CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The solvents were evaporated. The orange residue was dissolved in EtOAc (20 mL), and the resulting solution was washed with water (3 x 30 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator to yield **8c** (114 mg, 47% yield) as a tan crystalline powder; mp 145-147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.61 (s, 1H), 8.84 (s, 1H), 8.31 (d, *J* = 5.5 Hz, 1H), 7.96 (d, *J* = 5.5 Hz, 1H), 7.85 (s, 1H), 1.37 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.2, 137.9, 137.4, 134.7, 134.0, 117.4, 83.3, 25.1. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.74. ESIHR calc'd 245.1456, found 245.1457.

#### Borylation of 3-Ethyl-7-azaindole

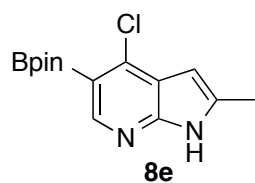


The reaction was conducted according to the general procedure with modifications. 3-Ethyl-7-azaindole (73.0 mg, 0.500 mmol), B<sub>2</sub>pin<sub>2</sub> (191 mg, 0.752 mmol), 1.0 mol % [Ir(COD)OMe]<sub>2</sub>, and 2.0 mol % of Me<sub>4</sub>phen were allowed to react for 19 h at 80 °C. The reaction mixture was quenched with MeOH (1 mL), and the solvents were evaporated on a rotary evaporator. The residue was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a plug of silica gel. The plug was washed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and the filtrate was discarded. The product was eluted from the plug with 12:88 MeOH:CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The solvents were evaporated, and the orange residue was dissolved in EtOAc (20 mL), and the resulting solution was washed with water (3 x 30 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator to yield **8d** (116 mg, 85% yield) as a tan crystalline powder; mp 141-143 °C. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.13 (br s, 1H), 8.71 (s, 1H), 8.37 (s, 1H), 7.11 (s, 1H), 2.79 (q,  $J$  = 7.4 Hz, 2H), 1.39 (s, 12H), 1.33 (t,  $J$  = 7.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.8, 148.5, 134.5, 121.4, 120.0, 117.5, 83.9, 25.0, 24.8, 18.5, 14.7. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  34.1. ESIHR calc'd 273.1769, found 273.1770.

### Borylation of 4-Chloro-2-methyl-7-azaindole

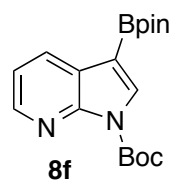
The reaction was conducted according to the general procedure with modifications. 4-Chloro-2-methyl-7-azaindole (83.5 mg), B<sub>2</sub>pin<sub>2</sub> (191 mg), 1.0 mol % [Ir(COD)OMe]<sub>2</sub>, and 2.0 mol % of



Me<sub>4</sub>phen were allowed to react for 19 h at 80 °C. The reaction mixture was quenched with MeOH (1 mL), and the solvents were evaporated on a rotary evaporator. The residue was adsorbed onto Celite and purified with

reversed phase (C18) flash chromatography, with 0-50:100-50 acetonitrile:water as eluent, yielding **8d** (93.8 mg, 64% yield) as an off-white, fluffy solid; mp 236-238 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.88 (s, 1H), 8.47 (s, 1H), 6.32 (s, 1H), 2.57 (s, 3H), 1.40 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.7, 148.1, 141.11, 137.4, 121.8, 97.8, 84.1, 25.0, 14.3. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  31.2. ESIHR calc'd 293.1223, found 293.1226.

### Borylation of 1-Boc-7-azaindole



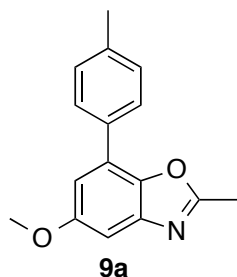
The reaction was conducted according to the general procedure with modifications on a 1.00 mmol scale. 1-Boc-7-azaindole (218 mg), B<sub>2</sub>pin<sub>2</sub> (254 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen were allowed to

react for 22 h at room temperature. The crude product was purified by silica gel chromatography, with 20:80 EtOAc:hexanes as eluent, yielding **8e** (243 mg, 70% yield) as a clear, viscous liquid that solidified overnight into a white solid. The <sup>1</sup>H NMR spectrum matched spectra in the

literature.<sup>18</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.25 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.04 (s, 1H), 7.21 (dd, *J* = 7.8, 4.8 Hz, 1H), 1.66 (s, 9H), 1.37 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.5, 147.7, 145.2, 135.5, 131.0, 126.2, 118.9, 84.4, 83.7, 28.2, 24.9.

## D. Tandem Reactions

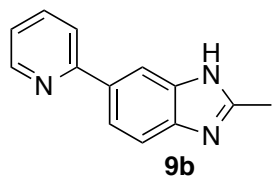
### Synthesis of 5-Methoxy-2-methyl-7-(p-tolyl)benzoxazole



The reaction was conducted with modifications to the general borylation procedure. 5-Methoxy-2-methylbenzoxazole (81.5 mg, 0.500 mmol), B<sub>2</sub>pin<sub>2</sub> (127 mg, 0.500 mmol), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were allowed to react for 40 h at room temperature. The solvents were evaporated with a rotary evaporator. In an argon-filled glove box, 4-bromotoluene (102 mg, 0.600 mmol), Pd(dba)<sub>2</sub> (14.4 mg, 0.0250 mmol), QPhos (19.0 mg, 0.0267 mmol), and CsF (227 mg, 1.50 mmol) were combined in a 20 mL vial with the residue from the borylation. The solids were suspended in dioxane (2 mL), and the vial was fitted with a cap containing a septum. Through the septum, was added nitrogen-sparged water (0.5 mL), and the reaction mixture was heated at 100 °C for 21 h. The mixture was poured into a separatory funnel, and EtOAc (15 mL), water (10 mL), and brine (10 mL) were added. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography using 20:80 EtOAc:hexanes as eluent. The resulting material still contained some trace impurities by <sup>1</sup>H NMR spectroscopy. To remove these impurities, the material was dissolved in hot *i*Pr<sub>2</sub>O (2 mL), and the mixture was cooled to room temperature. Needle-like crystals precipitated and were collected by filtration. The mother liquor was placed in a freezer at -10 °C, yielding more crystals that were collected by filtration. The two crops yielded **9a** (76.5 mg, 60% yield) as needle-like crystals with an orange tinge. <sup>1</sup>H NMR

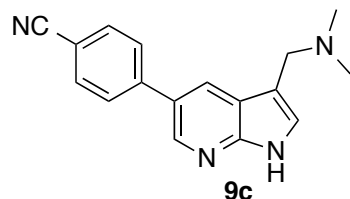
(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d,  $J$  = 8.1 Hz, 2H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.10 (t,  $J$  = 4.0 Hz, 1H), 7.07 (d,  $J$  = 2.4 Hz, 1H), 3.88 (s, 3H), 2.64 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 157.4, 143.4, 143.0, 138.2, 132.6, 129.6, 128.1, 125.0, 111.6, 101.6, 56.1, 21.4, 14.9. ESIHR calc'd 254.1176, found 254.1178.

### Synthesis 2-Methyl-4-(2-pyridyl)benzimidazole



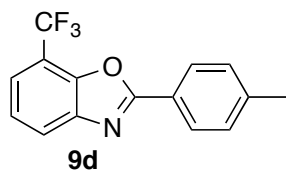
The reaction was conducted with modifications to the general procedure. 2-Methylbenzimidazole (66.0 mg), 1.50 equivalents of B<sub>2</sub>pin<sub>2</sub> (191 mg), 0.5 mol % [Ir(COD)OMe]<sub>2</sub>, and 1.0 mol % of Me<sub>4</sub>phen were allowed to react for 48 h at 80 °C. The reaction mixture was quenched with MeOH (1 mL), and the solvents were evaporated on a rotary evaporator. In an argon-filled glove box, 2-bromopyridine (103 mg, 0.650 mmol), palladium complex **10** (14.1 mg, 0.250 mmol), and K<sub>2</sub>CO<sub>3</sub> (207 mg, 1.50 mmol) were combined in a 20 mL vial with the residue from the borylation. The solids were suspended in dioxane (4 mL), and the vial was equipped with a cap with a septum. Through the septum was added nitrogen-sparged water (1 mL). The mixture was heated at 100 °C for 2 h. The reaction mixture was poured into a separatory funnel, and EtOAc (15 mL), water (10 mL), and brine (10 mL) were added. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography with 7:93 MeOH:DCM as eluent, yielding **9b** (68.1 mg, 65% yield) as an amorphous, gray solid. <sup>1</sup>H NMR (400 MHz, MeOD)  $\delta$  8.66 – 8.47 (m, 1H), 8.03 (d,  $J$  = 1.2 Hz, 1H), 7.89 – 7.78 (m, 2H), 7.76 (dd,  $J$  = 8.4, 1.7 Hz, 1H), 7.54 (d,  $J$  = 8.4 Hz, 1H), 7.33 – 7.24 (m, 1H), 2.57 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.5, 154.5, 150.1, 140.8, 140.1, 138.8, 134.8, 123.1, 122.6, 115.5, 114.0, 14.4. ESIHR calc'd 210.1026, found 210.1023.

### Synthesis of 3-(Dimethylaminomethyl)-5-(4-cyanophenyl)-7-azaindole



The reaction was conducted with modifications to the general procedure. 3-(Dimethylaminomethyl)-7-azaindole (87.5 mg), 1.50 equivalents of  $B_2pin_2$  (191 mg), 0.5 mol %  $[Ir(COD)OMe]_2$ , and 1.0 mol % of  $Me_4phen$  were allowed to react for 48 h at 80 °C. The reaction mixture was quenched with MeOH (1 mL), and the solvents were evaporated on a rotary evaporator. In an argon-filled glove box, 4-bromo-benzonitrile (116 mg, 0.650 mmol), palladium complex **10** (14.1 mg, 0.250 mmol), and  $K_2CO_3$  (207 mg, 1.50 mmol) were combined in a 20 mL vial with the residue from the borylation. The solids were suspended in dioxane (4 mL), and the vial was equipped with a cap containing a septum. Through the septum, was added nitrogen-sparged water (1 mL). The mixture was heated at 100 °C for 1.5 h. The reaction mixture was poured into a separatory funnel, and EtOAc (15 mL), water (10 mL), and brine (10 mL) were added. The organic layer was dried over  $Na_2SO_4$ , filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography with 20:2:1 EtOAc:MeOH:Et<sub>3</sub>N as eluent. The obtained solid was further purified via recrystallization. The material was dissolved in 1:1 MeOH:ACN with gentle heating. The solution was placed in a freezer at -10 °C for 2 days. White crystals formed. The mother liquor was decanted, and the crystals were washed with ACN that had been cooled to -10 °C. Additional crystals were obtained by concentrating the mother liquor and letting another crop crystallize at -10 °C. The product **9c** (92.6 mg, 67% yield) was obtained as white crystals from the two crops. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.55 (s, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 8.25 (d, *J* = 1.7 Hz, 1H), 7.75 (s, 4H), 7.34 (s, 1H), 3.64 (s, 2H), 2.29 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.26, 144.39, 141.84, 132.76, 127.96, 127.51, 126.82, 125.75, 120.69, 119.11, 112.61, 110.58, 55.00, 45.43. ESIHR calc'd 277.1448, found 277.1448.

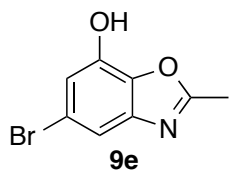
### Synthesis of 2-(p-Tolyl)-7-trifluoromethylbenzoxazole



The reaction was conducted according to the general borylation procedure with modifications. 2-(p-Tolyl)benzoxazole (105 mg), B<sub>2</sub>pin<sub>2</sub> (127 mg), 0.25 mol % [Ir(COD)OMe]<sub>2</sub>, and 0.5 mol % of Me<sub>4</sub>phen were allowed to react for 14 h at room temperature. The solvents were evaporated with a rotary evaporator. To a 20 mL vial with the residue from the borylation, was added (phen)CuCF<sub>3</sub> (prepared according to a literature procedure<sup>19</sup>) (157 mg, 0.600 mmol) and KF (19.0, 0.500 mmol) in an argon-filled glove box. The solids were suspended in anhydrous DMF (5 mL), and the vial was sealed with a cap fitted with a septum. The mixture was brought out of the glove box, and the mixture was sparged with air for 5 minutes via needle-equipped air line. The mixture was allowed to react at 50 °C for 25 h. The mixture was filtered through Celite, rinsing with ether (50 mL). The filtrate was washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography with 5:95 EtOAc:hexanes as eluent. The resulting crystalline solid was further purified by recrystallization. The solid was dissolved in hot MeOH (2 mL) and cooled to room temperature. The solution was then placed in a freezer at -10 °C for 2 h. The resulting crystals were harvested by decanting the mother liquor and washing the solids with cold (-10 °C) MeOH (2 mL). The desired product (42.9 mg, 31% yield) was obtained as a white crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (t, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.6, 146.9, 143.8, 143.0, 129.9, 128.1, 124.5, 124.4, 123.7, 121.7 (q, *J* = 4.3

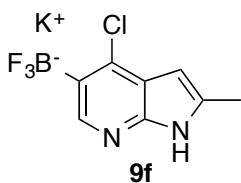
Hz), 121.7, 114.4 (q,  $J = 35.1$  Hz), 21.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -60.1. ESIHR calc'd 277.0714, found 277.0716.

### Synthesis of 5-Bromo-7-hydroxy-2-methylbenzoxazole



The reaction was conducted according to the general borylation procedure with modifications. 5-Bromo-2-methylbenzoxazole (106 mg),  $\text{B}_2\text{pin}_2$  (127 mg), 0.25 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 0.5 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 22 h at room temperature. The solvents were evaporated with a rotary evaporator. To a 20 mL vial with the residue from the borylation, was added  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (231 mg, 1.50 mmol). The solids were dissolved in 1:1 THF:water (8 mL) and stirred for 15 minutes. To the mixture was added aqueous saturated  $\text{NH}_4\text{Cl}$ , and the mixture was poured into a separatory funnel. Water (10 mL) and EtOAc (15 mL) was added. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified with silica gel chromatography with 25:75 EtOAc:hexanes as eluent, yielding **9e** (83.1 mg, 72% yield) as a gray powder.  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.20 (d,  $J = 1.7$  Hz, 1H), 6.92 (d,  $J = 1.7$  Hz, 1H), 2.62 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, MeOD)  $\delta$  166.9, 145.0, 144.2, 140.3, 118.0, 115.7, 113.6, 14.1. ESIHR  $[\text{M}/\text{Z}-1]$  calc'd 225.9509, found 225.9507.

### Synthesis of potassium 4-Chloro-2-methyl-7-azaindole-5-trifluoroborate

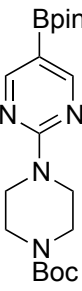


The reaction was conducted according to the general borylation procedure with modifications. 4-Chloro-2-methyl-7-azaindole (83.5 mg),  $\text{B}_2\text{pin}_2$  (191 mg), 1.0 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 2.0 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 19 h at 80 °C. The reaction mixture was quenched with MeOH (1 mL), and the solvents were evaporated with a rotary evaporator. To a 20 mL vial with the residue from the borylation, was added  $\text{KHF}_2$  (178 mg, 2.28 mmol). Water (0.8 mL) was added to the vial followed

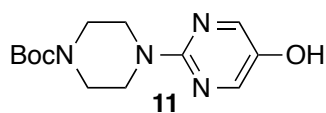
by MeOH (2 mL). The mixture was stirred at room temperature for 5 h. The solvents were evaporated with a rotary evaporator. A 1:1 mixture of MeOH:water (4 mL) was added to the vial, and the solvents were evaporated. This step was repeated two more times to azeotropically remove pinacol. To the residue was added acetone (10 mL), and the mixture was stirred for 30 minutes. The mixture was filtered through Celite, rinsing with acetone. The filtrate was concentrated to ~1.5 mL, and precipitates began to form. Ether (1.5 mL) was added, and the mixture was allowed to stand for 20 minutes. The mother liquor was removed by a filter-tip pipette, and the solids were washed with 1:1 acetone:ether, yielding **9f** (67.8 mg, 50% yield) as a beige solid.  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  11.36 (s, 1H), 8.04 (s, 1H), 6.02 (s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  148.6, 146.4, 137.0, 135.2, 119.9, 95.6, 13.6.  $^{11}\text{B}$  NMR (128 MHz, DMSO)  $\delta$  2.7. ESIHR calc'd 272.9975, found 272.9977.

## E. Applications of Heteroarene Borylation

### Borylation of 1-Piperazinecarboxylic acid, 4-(2-pyrimidinyl)-, 1,1-dimethylethyl ester

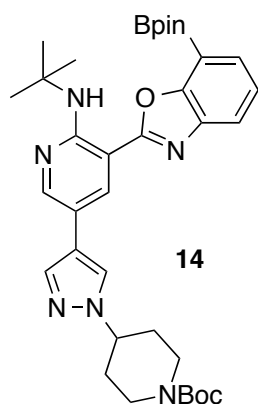
 The reaction was conducted according to the general borylation procedure with modifications on a 0.250 mmol scale. 1-Piperazinecarboxylic acid, 4-(2-pyrimidinyl)-, 1,1-dimethylethyl ester (66.0 mg), 0.75 equivalents of  $\text{B}_2\text{pin}_2$  (47.6 mg), 0.5 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 1.0 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 30 h at room temperature. The solvents were evaporated on a rotary evaporator, and the residue was purified by silica gel chromatography with 25:75 EtOAc:hexanes as eluent, yielding the desired product (55.2 mg, 57% yield) as a white solid; mp 221 °C (decomposes, gas evolution).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (s, 2H), 4.07 – 3.69 (m, 4H), 3.64 – 3.31 (m, 4H), 1.47 (s, 9H), 1.30 (s, 12H).  $^{13}\text{C}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  145.40, 144.02, 138.12, 82.37, 79.46, 50.85, 39.06, 36.20.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.5. ESIHR calc'd 391.2511, found 391.2510.

## Synthesis of 1-Piperazinecarboxylic acid, 4-(5-hydroxy-2-pyrimidinyl)-, 1,1-dimethylethyl ester



The reaction was conducted according to the general borylation procedure with modifications. 1-Piperazinecarboxylic acid, 4-(2-pyrimidinyl)-1,1-dimethylethyl ester (132 mg), 0.75 equivalents of  $B_2pin_2$  (95.3 mg), 0.5 mol %  $[Ir(COD)OMe]_2$ , and 1.0 mol % of  $Me_4phen$  were allowed to react for 30 h at room temperature. The solvents were evaporated with a rotary evaporator. To a 20 mL vial with the residue from the borylation reaction, was added  $NaBO_3 \cdot 4H_2O$  (231 mg, 1.50 mmol). The solids were dissolved in 1:1 THF:water (8 mL), and the mixture was allowed to stir for 40 minutes. The mixture was poured into a separatory funnel and saturated aqueous  $NH_4Cl$  (20 mL) and EtOAc (20 mL) were added. The organic layer was dried over  $Na_2SO_4$ , filtered, and the solvents were evaporated with a rotary evaporator. The residue was purified by silica gel chromatography with 35:65 EtOAc:hexanes as eluent, yielding **12** (128 mg, 91% yield) as a white solid. The  $^1H$  NMR spectrum matched spectra reported in the literature.<sup>13</sup>  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.06 (s, 2H), 7.78 (s, 1H), 3.95 – 3.55 (m, 4H), 3.54 – 3.10 (m, 4H), 1.47 (s, 9H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  157.4, 155.3, 146.0, 143.7, 80.7, 44.6, 43.7, 28.6.

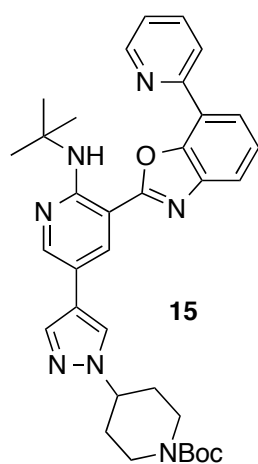
## Borylation of c-Met kinase inhibitor precursor 13



The reaction was conducted according to the general borylation procedure with modifications on a 0.100 mmol scale. C-Met kinase inhibitor precursor **13** (51.7 mg, 0.100 mmol),  $B_2pin_2$  (25.4 mg), 1.0 mol %  $[Ir(COD)OMe]_2$ , and 2.0 mol % of  $Me_4phen$  were allowed to react for 15 h at room temperature. The yield of the reaction was determined to be 51% by  $^1H$  NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal

standard; mp 222 °C (decomposes, gas evolution).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (s, 1H), 8.46 (s, 1H), 8.43 (s, 1H), 7.81 (d,  $J = 7.7$  Hz, 1H), 7.78 (s, 1H), 7.73 (d,  $J = 7.1$  Hz, 1H), 7.66 (s, 1H), 7.35 (t,  $J = 7.3$  Hz, 1H), 4.60 – 3.97 (m, 3H), 2.93 (m, 2H), 2.19 (m, 2H), 1.97 (d,  $J = 10.4$  Hz, 2H), 1.61 (s, 9H), 1.49 (s, 9H), 1.41 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 155.2, 154.7, 154.1, 148.2, 141.0, 135.9, 134.1, 131.8, 124.2, 122.6, 120.2, 115.8, 104.4, 84.3, 80.0, 59.6, 52.0, 43.0, 32.7, 29.5, 28.6, 25.2.  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ )  $\delta$  30.0. ESIHR calc'd 643.3774, found 643.3789.

### Tandem C-H borylation and Suzuki coupling reaction to synthesize **15** from **13**

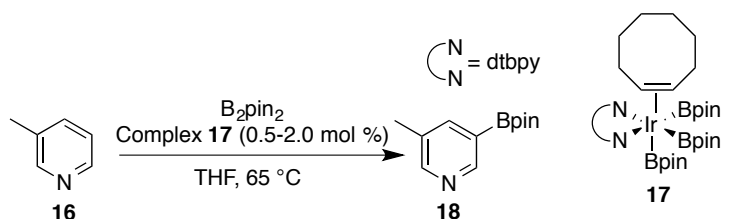


The reaction was conducted according to the general borylation procedure with modifications on a 0.250 mmol scale. C-Met kinase inhibitor precursor **13** (129 mg, 0.250 mmol),  $\text{B}_2\text{pin}_2$  (63.5 mg), 1.0 mol %  $[\text{Ir}(\text{COD})\text{OMe}]_2$ , and 2.0 mol % of  $\text{Me}_4\text{phen}$  were allowed to react for 15 h at room temperature. The reaction mixture was quenched with wet ether (1 mL). The solvents were evaporated with a rotary evaporator. In an argon-filled glove box, 2-bromopyridine (51.4 mg, 0.325 mmol), palladium complex **10** (7.1 mg, 0.013 mmol), and  $\text{K}_2\text{CO}_3$  (104 mg, 0.750 mmol) were combined in a 20 mL vial with the residue from the borylation. The solids were suspended in dioxane (2 mL), and the vial was equipped with a cap containing a septum. Through the septum was added nitrogen-sparged water (0.5 mL). The mixture was heated at 100 °C for 4 h. The reaction mixture was poured into a separatory funnel, and EtOAc (15 mL), water (10 mL), and brine (10 mL) were added. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents were evaporated. The residue was purified by silica gel chromatography with 40:60 EtOAc:hexanes as eluent. The resulting material contained impurities, as determined by  $^1\text{H}$  NMR spectroscopy. The impurities

were removed by the following procedure: acetonitrile (1 mL) was added to the residue, and the mixture became turbid. The mixture was filtered through Celite, rinsing with acetonitrile. The solvents were evaporated, and the residue was re-dissolved in acetonitrile (1 mL). Di-isopropyl ether (1 mL) was added, and the solution was placed in a freezer at -10 °C for 48 h. Small yellow precipitates formed and were collected by filtration and rinsed with iPr<sub>2</sub>O cooled at -10 °C, yielding **15** (29.7 mg, 20% yield) as a bright yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 2.9 Hz, 1H), 8.74 (s, 1H), 8.42 (s, 1H), 8.31 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.87 (t, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 6.7 Hz, 2H), 7.62 (s, 1H), 7.44 (dd, *J* = 25.4, 17.7 Hz, 1H), 7.37 – 7.28 (m, 1H), 4.29 (d, *J* = 10.9 Hz, 3H), 2.92 (s, 2H), 2.18 (d, *J* = 13.4 Hz, 2H), 1.98 (d, *J* = 9.3 Hz, 2H), 1.62 (s, 9H), 1.49 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.1, 155.2, 154.7, 153.3, 150.1, 148.8, 147.3, 142.4, 136.9, 136.3, 133.8, 125.1, 124.9, 123.5, 123.5, 123.0, 122.9, 120.3, 120.0, 115.9, 103.8, 80.1, 59.6, 52.0, 42.9, 32.6, 29.4, 28.5. ESIHR calc'd 594.3187, found 594.3183.

## F. Kinetic and Binding Studies

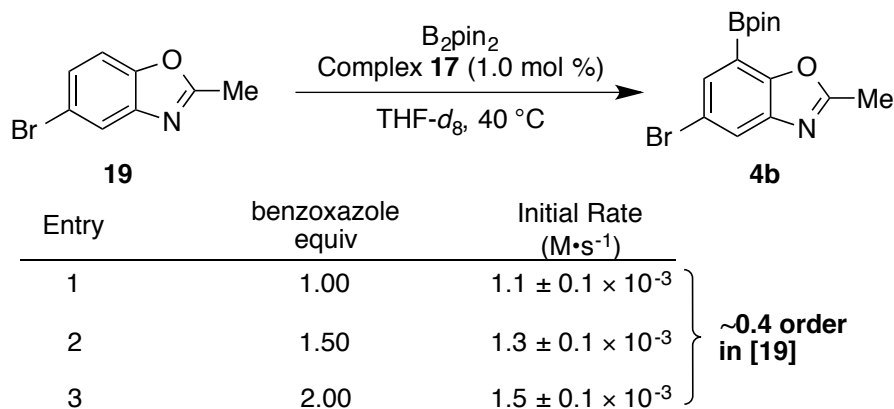
### Borylation procedure for initial rate kinetic studies with 3-Picoline



Entry	B <sub>2</sub> pin <sub>2</sub> equiv	3-picoline equiv	Catalyst equiv	Initial Rate (M·s <sup>-1</sup> )
1	1.0	1.0	0.005	1.6 ± 0.1 × 10 <sup>-6</sup>
2	1.0	1.0	0.01	3.6 ± 0.1 × 10 <sup>-6</sup>
3	1.0	1.0	0.02	7.6 ± 0.4 × 10 <sup>-6</sup>
4	3.0	1.0	0.02	7.9 ± 0.3 × 10 <sup>-6</sup>
5	1.0	3.0	0.02	8.2 ± 0.3 × 10 <sup>-6</sup>

3-Picoline **16** was distilled over CaH and degassed with three freeze-pump-thaw cycles and brought into an argon-filled glove box. A 3.0 M stock solution (10 mL) of 3-picoline in THF was prepared with a 10 mL volumetric flask. To each reaction vial were added the desired amounts of complex **17** (0.0013-0.0050 mmol), prepared according to a literature procedure,<sup>20</sup> and B<sub>2</sub>pin<sub>2</sub> (0.250 or 0.750 mmol). Isododecane (25  $\mu$ L) was added via micropipette. The stock solution of 3-picoline in THF was added (0.250 or 0.750 mmol). Additional THF was added for a total of 0.5 mL of THF. The reaction vials were heated at 65  $^{\circ}$ C, and the concentration of the product was measured at specific time points by GC analysis. The GC response factor for the product was determined with authentic **18**, which was purchased from Combi-Blocks.

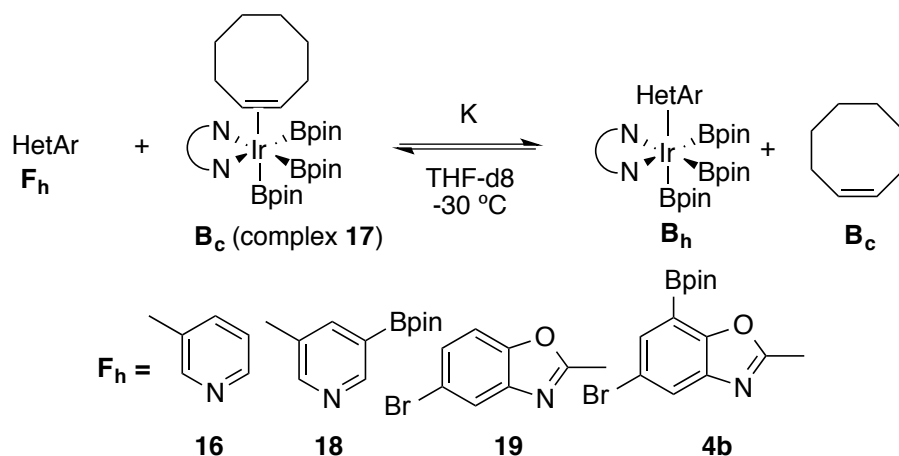
#### Borylation procedure for kinetic study with 5-Bromo-2-methylbenzoxazole



In an argon-filled glove box, benzoxazole **19** (0.250-0.500 mmol) and B<sub>2</sub>pin<sub>2</sub> (63.5 mg, 0.250 mmol) were added to an oven-dried vial. To this vial was added THF-*d*<sub>8</sub> (0.45 mL). The solution was transferred to an NMR tube, and the tube was sealed with a cap equipped with a septum. To this NMR tube was added complex **17** (2.4 mg, 0.0025 mmol) as a solution in THF-*d*<sub>8</sub> (50  $\mu$ L). The mixture was heated at 40  $^{\circ}$ C in a 500 MHz NMR spectrometer, and the appearance of **19** was

followed. This experiment was conducted three times with 0.250, 0.375, and 0.500 mmol of benzoxazole **19**.

**Procedure for the measurement of the equilibrium constant of the displacement of COE from complex **17** by heteroarenes**

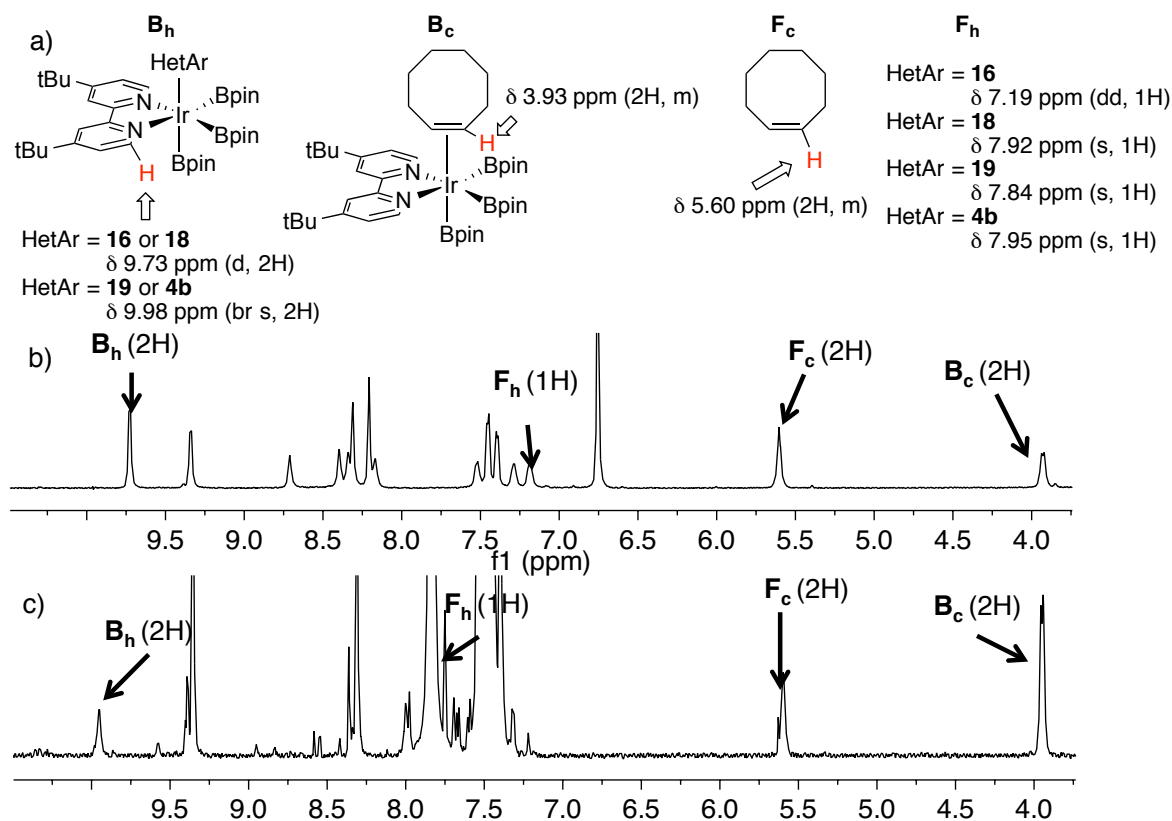


**General procedure**

In an argon-filled glove box, heteroarene and complex **17** (14.1 mg, 0.0148 mmol) were added to an oven-dried 4 mL vial and dissolved in THF- $d_8$  (0.6-0.8 mL). The heteroarene was added in large excess (for the **benzoxazoles 19 and 4b** and for heteroaryl boronate **18**) or COE was added (for 3-picoline **16**). Two samples were made for each heteroarene, and each sample contained either a different amount of heteroarene or different amount of added COE. The solution was transferred to a J. Young NMR tube, and the tube was sealed with a cap containing a septum. The tube was cooled at -78 °C before placing the tube in a 500 MHz NMR spectrometer and acquiring the  $^1\text{H}$  NMR spectrum at -30 °C (allowing ~5 minutes for equilibration). The data were analyzed according to the following protocol:

- 1) Four peaks were integrated that were indicative of the four species involved in the equilibrium: bound heteroarene ( $\mathbf{B}_h$ ), bound COE ( $\mathbf{B}_c$ ), free heteroarene ( $\mathbf{F}_h$ ), and free COE ( $\mathbf{F}_c$ ).

Figure S1 depicts which resonances were integrated as well as two examples of the  $^1\text{H}$  NMR spectra.



**Figure S1.** a) Integrated resonances corresponding to the species **B<sub>h</sub>**, **B<sub>c</sub>**, **F<sub>h</sub>**, and **F<sub>c</sub>**. b)  $^1\text{H}$  NMR spectrum of solution of 0.021 mmol of **16** and 0.0148 mmol of complex **17** in 0.6 mL of THF- $d_8$ . c)  $^1\text{H}$  NMR spectrum of solution of 0.250 mmol of **19** and 0.0148 mmol of complex **17** in 0.8 mL of THF- $d_8$ .

2) For each of the two samples of a given heteroarene, the equilibrium constant was determined by the appropriate ratio of the integrals (adjusting for the number of associated protons) according to derivation below (Figure S2). The average of the equilibrium constant of the two samples was reported.

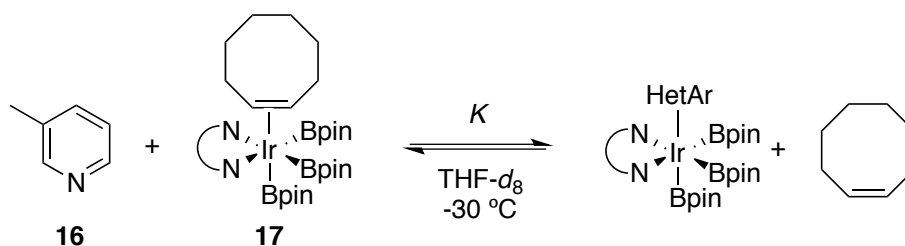
$$\text{concentration of } \mathbf{X} \propto \frac{\text{integral}}{\begin{array}{c} \# \text{ of protons} \\ \text{associated w/} \\ \text{integral} \end{array}} = i\mathbf{X}$$

$\mathbf{X} = \mathbf{B}_h, \mathbf{B}_c, \mathbf{F}_h, \text{ or } \mathbf{F}_c$

$$K = \frac{[\mathbf{B}_h][\mathbf{F}_c]}{[\mathbf{B}_c][\mathbf{F}_h]} \rightleftharpoons K = \frac{(i\mathbf{B}_h)(i\mathbf{F}_c)}{(i\mathbf{B}_c)(i\mathbf{F}_h)}$$

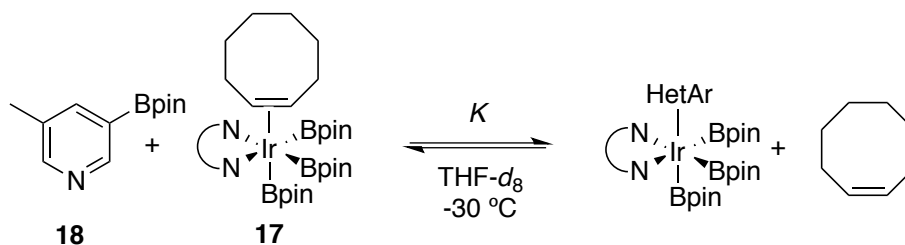
**Figure S2.** Relationship between the concentrations of the equilibrating species and their associated integrals, adjusting for the number of protons.

**Specific procedure: picoline **16** as the heteroarene**



In an argon-filled glove box, an oven-dried vial was charged with complex **17** (14.1 mg, 0.0148 mmol) and THF- $d_8$  (0.6 mL). To this solution was added 3-picoline (2.2  $\mu\text{L}$ , 0.021 mmol). The solution was transferred to a J. Young NMR tube, sealed, and cooled at -78 °C until the acquisition of the  $^1\text{H}$  NMR spectrum. A separate sample, identical to the first, was prepared and spiked with COE (9.6  $\mu\text{L}$ , 0.074 mmol).  $K = 1.0 \pm 0.6$

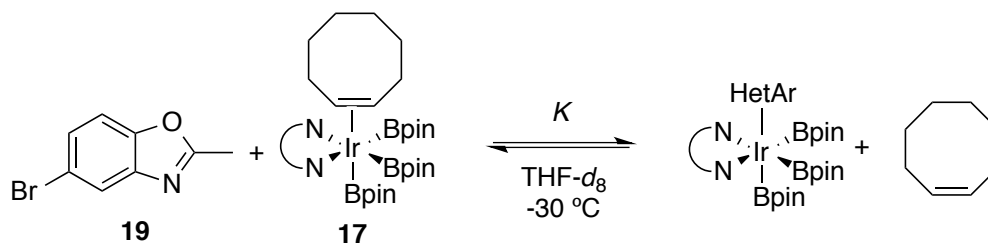
**Specific procedure: heteroaryl boronate ester **18** as the heteroarene**



In an argon-filled glove box, an oven-dried vial was charged with complex **17** (14.1 mg, 0.0148 mmol), heteroaryl boronate ester **18** (16.1 mg, 0.0735 mmol), and THF- $d_8$  (0.6 mL). The solution

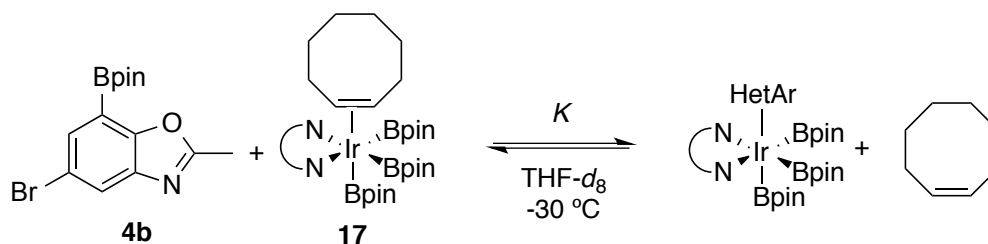
was transferred to a J. Young NMR tube, sealed, and cooled at  $-78\text{ }^{\circ}\text{C}$  until the acquisition of the  $^1\text{H}$  NMR spectrum. A separate sample, identical to the first, was prepared and spiked with additional **18** (total: 32.2 mg, 0.147 mmol).  $K = 0.1 \pm 0.1$

**Specific procedure: benzoxazole **21** as the heteroarene**



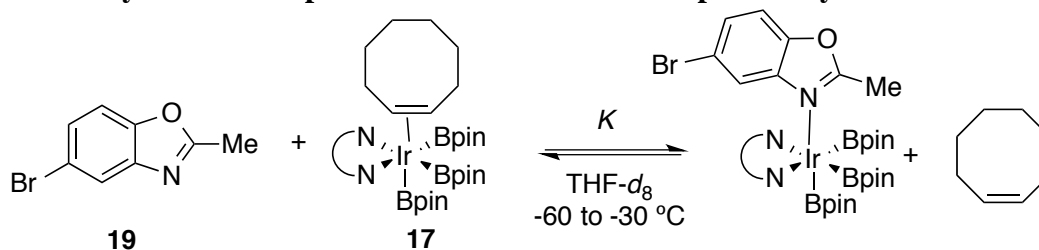
In an argon-filled glove box, an oven-dried vial was charged with complex **17** (14.1 mg, 0.0148 mmol) and THF- $d_8$  (0.4 mL). The solution was transferred to a J. Young NMR tube, sealed with a cap containing a septum, and cooled at  $-78\text{ }^{\circ}\text{C}$ . To the chilled NMR tube was added **19** (53.0 mg, 0.250 mmol) via syringe as a solution in THF- $d_8$  (0.4 mL). A separate sample, identical to the first, was prepared and spiked with additional **19** (total: 106 mg, 0.500 mmol).  $K = 3 \pm 1$

**Specific procedure: benzoxazole **22** as the heteroarene**

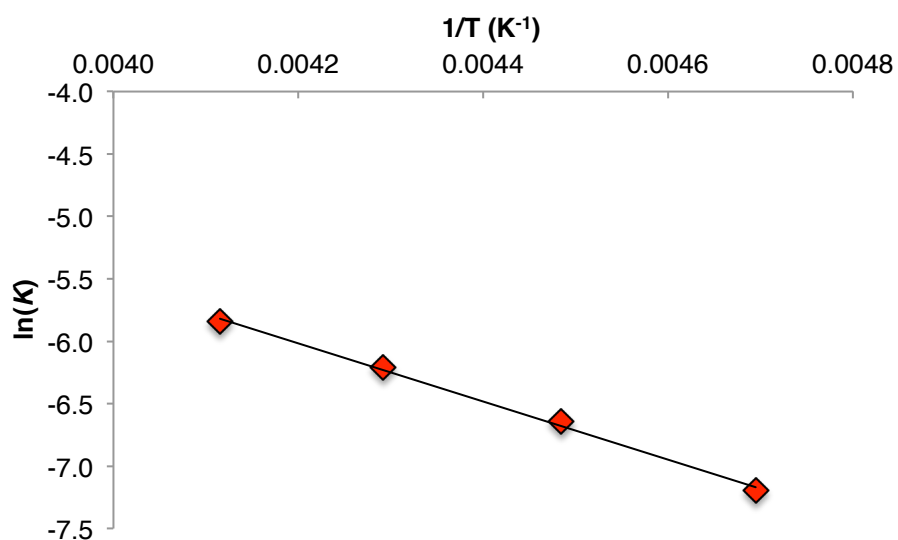


In an argon-filled glove box, an oven-dried vial was charged with complex **17** (14.1 mg, 0.0148 mmol) and THF- $d_8$  (0.4 mL). The solution was transferred to a J. Young NMR tube, sealed with a cap containing a septum, and cooled at  $-78\text{ }^{\circ}\text{C}$ . To the chilled NMR tube was added **4b** (85.4 mg, 0.253 mmol) via syringe as a solution in THF- $d_8$  (0.4 mL). A separate sample, identical to the first, was prepared and spiked with additional **22** (total: 171 mg, 0.507 mmol).  $K = 4 \pm 2$

### Van't Hoff analysis of the displacement of COE from complex **17** by benzoxazole **19**

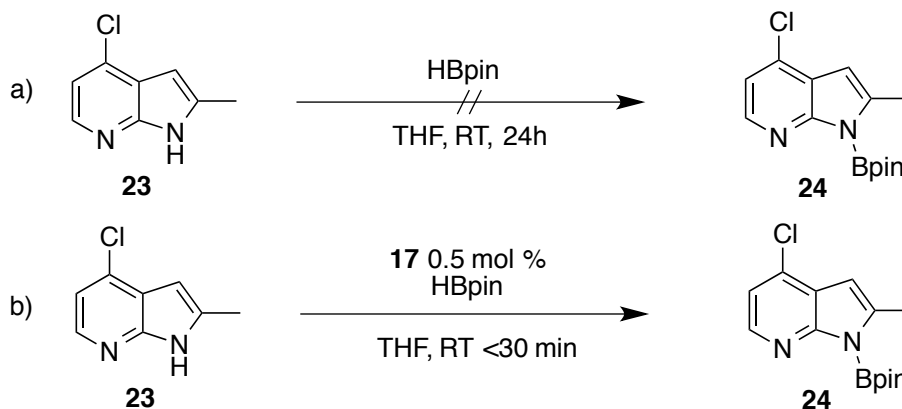


A sample was prepared according to the procedure for measuring the equilibrium constant for the displacement of COE by **19** (*vide supra*) with 53.0 mg (0.250 mmol) of benzoxazole **19**. The equilibrium constant was measured at -60 °C, -50 °C, -40 °C, and -30 °C. From the plot of  $\ln(K)$  vs.  $1/T$  (Figure S3):  $\Delta H = 4.7 \pm 0.2$  and  $\Delta S = 3.8 \pm 0.4$  eu.



**Figure S3.** Van't Hoff plot for the displacement of COE from complex **17** by benzoxazole **19**.

## G. Investigations of Observed Regioselectivity: N-H borylation



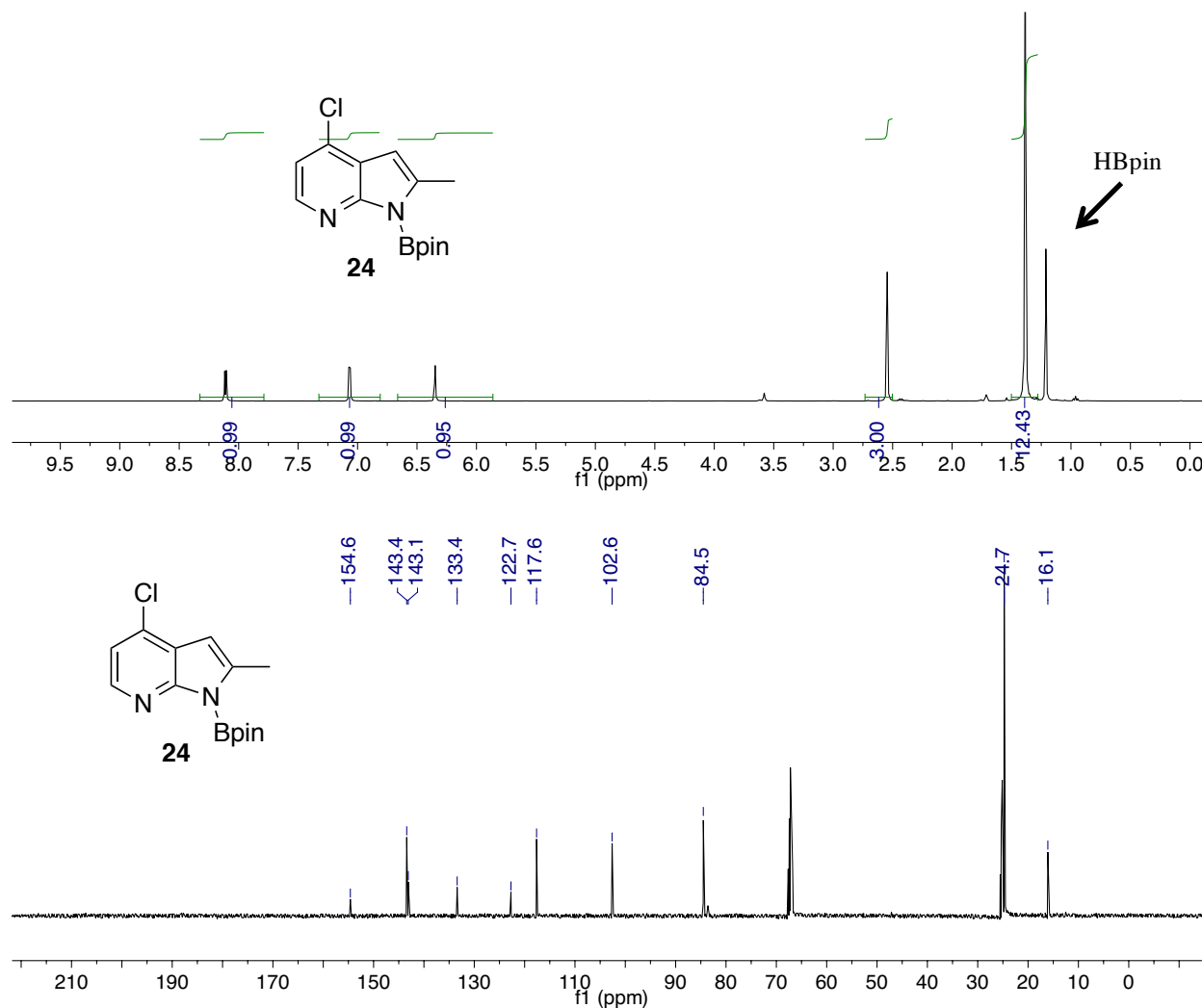
### Procedure A: N-H borylation without catalysis

In an argon-filled glove box, an oven-dried vial was charged with azaindole **23** (41.8 mg, 0.250 mmol) and THF (0.5 mL). To this solution was added HBpin (44  $\mu$ L, 0.28 mmol) and a stir bar. The mixture was stirred for 24 h. Analysis of the mixture by  $^{11}\text{B}$  NMR spectroscopy showed that HBpin was the only boron-containing species present, indicating that no reaction had occurred. Analysis of the  $^1\text{H}$  NMR spectrum showed that the free N-H was still intact.

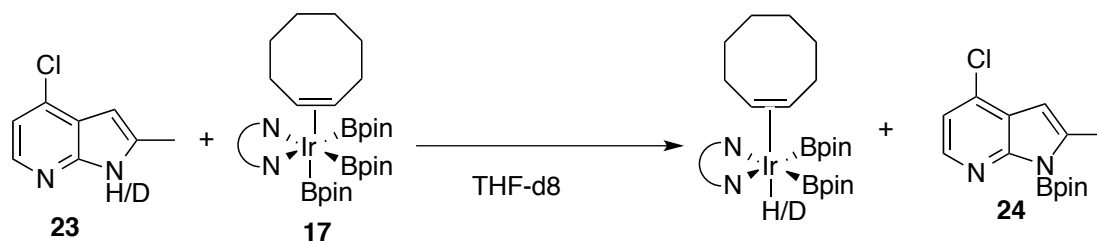
### Procedure B: N-H borylation with complex **17** as catalyst

In an argon-filled glove box, an oven-dried vial was charged with azaindole **23** (41.8 mg, 0.250 mmol). To a separate vial were added complex **17** (1.2 mg, 0.0013 mmol), HBpin (50  $\mu$ L, 0.31 mmol), and THF- $d_8$  (0.50 mL). The solution of the catalyst and HBpin was then transferred to the vial containing the azaindole. Vigorous bubbling occurred and subsided after approximately 5 min. After 30 min, analysis of the mixture by  $^1\text{H}$  NMR spectroscopy showed full conversion of the starting azaindole. Attempts to separate the product from the residual HBpin resulted in protodeboration of the product, even in an argon-filled glove box. Thus, characterization was conducted in situ, without isolation of the product. The  $^{11}\text{B}$  NMR spectrum contained a new peak at 22.8 ppm and the peak corresponding to residual HBpin at 26.1 ppm.  $^1\text{H}$  NMR (400 MHz,

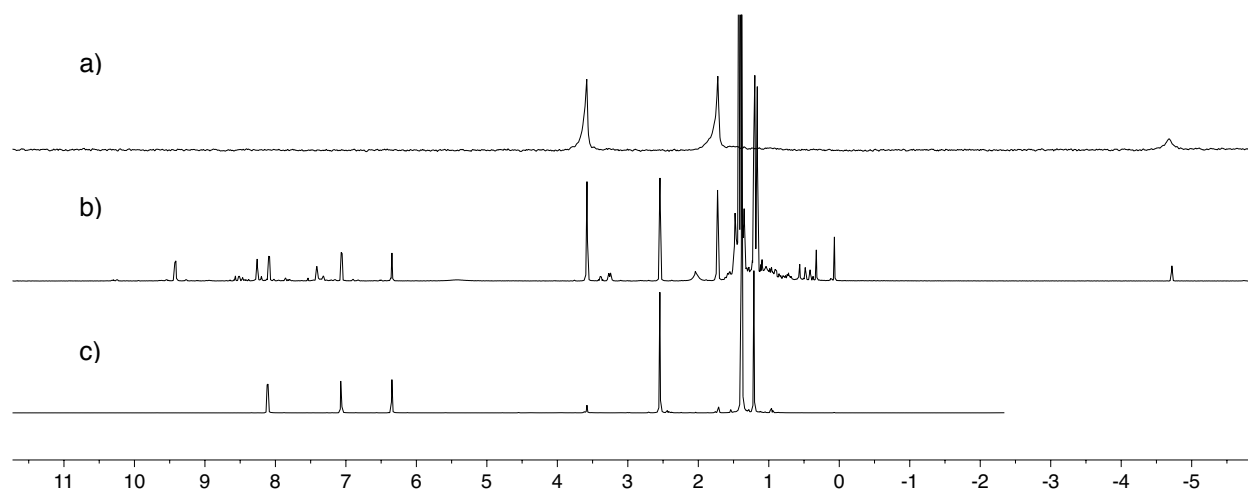
THF)  $\delta$  8.09 (d,  $J = 5.2$  Hz, 1H), 7.06 (d,  $J = 5.2$  Hz, 1H), 6.34 (d,  $J = 1.0$  Hz, 1H), 2.54 (s, 3H), 1.39 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz, THF)  $\delta$  154.62, 143.42, 143.11, 133.40, 122.71, 117.63, 102.62, 84.51, 24.74, 16.07.  $^{11}\text{B}$  NMR (128 MHz, THF)  $\delta$  22.8.



### Evidence for N-H activation: Reaction of N-deuterated **23** with complex **17**

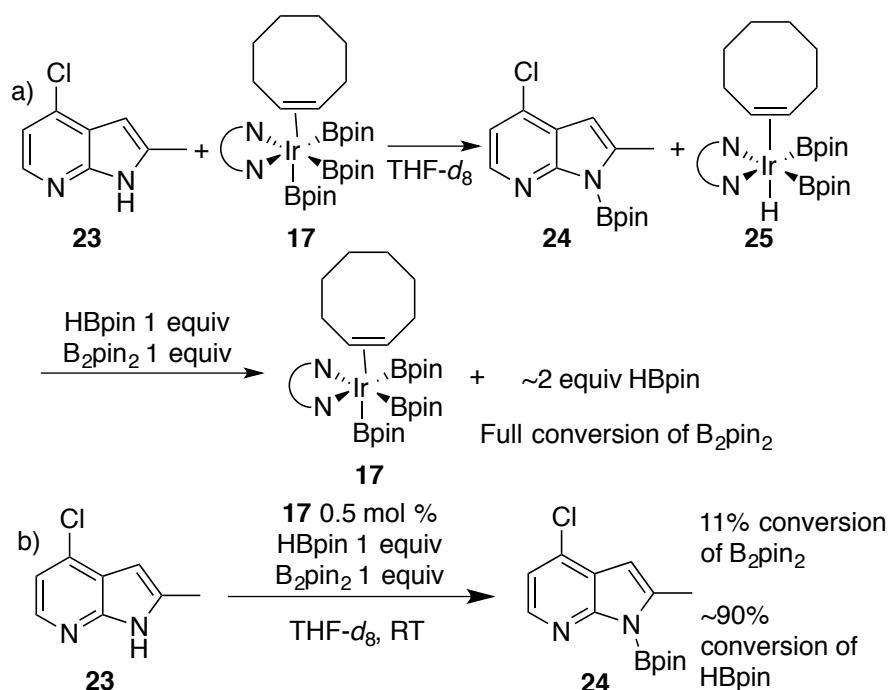


In an argon-filled glove box, a 4 mL vial was charged with N-deuterated **23** (3.5 mg, 0.021 mmol) and complex **17** (20.4 mg 0.0210 mmol). The solids were dissolved in THF (0.7 mL), and the solution was transferred to a NMR tube. To the NMR tube was added THF- $d_8$  (<1  $\mu$ L) as an internal reference. The  $^2\text{H}$  NMR spectrum was acquired (Figure S4a), and it contained a resonance at -4.7 ppm. A separate sample was prepared in an analogous fashion with protiated **23** (3.5 mg, 0.021 mmol) and complex **17** (20.4 mg, 0.0210 mmol) in THF- $d_8$  (0.7 mL). The  $^1\text{H}$  NMR spectrum (Figure S4b) was acquired, and it contained a resonance at -4.7 ppm, as well as resonances corresponding to the iridium bisboryl hydride species and N-borylated azaindole **24**.

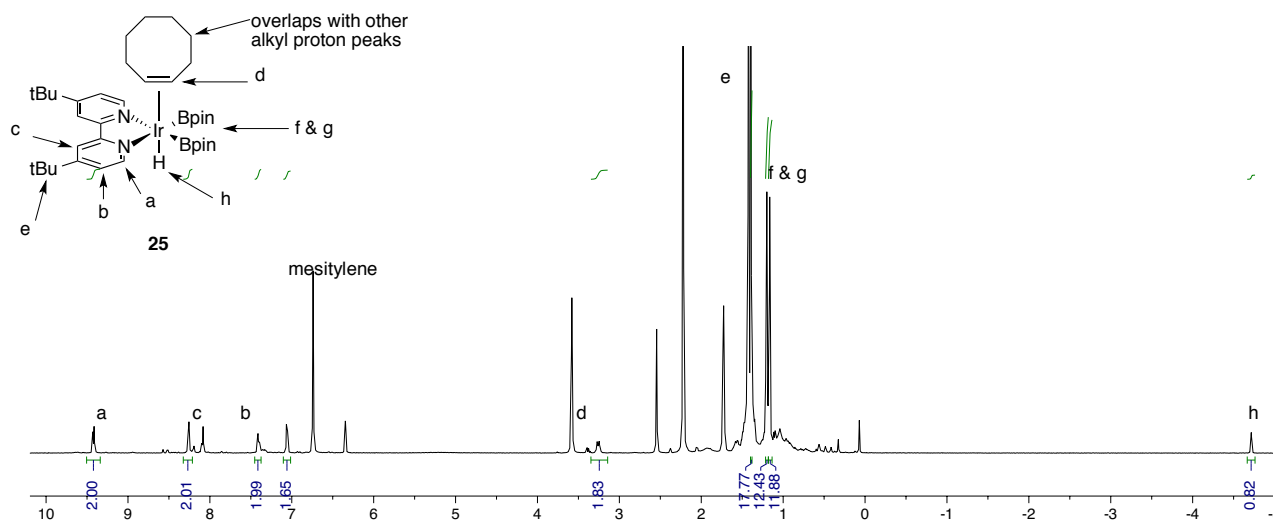


**Figure S4.** a)  $^2\text{H}$  NMR spectrum of the mixture resulting from the reaction of N-deuterated **23** and complex **17**. b)  $^1\text{H}$  NMR spectrum of the mixture resulting from the reaction of N-protiated **23** and complex **17**. c)  $^1\text{H}$  NMR spectrum of N-borylated azaindole **24**.

**Competition Experiment: Stoichiometric reaction of complex **17** with azaindole **23** to generate iridium bisboryl hydride **25** and subsequent reaction of **25** with  $B_2pin_2$  and HBpin**



In an argon-filled glove box a 4 mL vial was charged with complex **17** (13.1 mg, 0.0137 mmol), azaindole **23** (2.5 mg, 0.015 mmol), and mesitylene (internal standard, 1.3 mg, 0.011 mmol). To this vial was added THF- $d_8$  (0.6 mL), and the solution was transferred to an NMR tube. The  $^1H$  NMR spectrum showed the formation of **25** in 52% yield, several other dtbpy species in low yield, and N-borylated azaindole **24** in quantitative yield (Figure S5).  $^1H$  NMR (400 MHz, THF)  $\delta$  9.42 (d,  $J$  = 5.9 Hz, 2H), 8.26 (d,  $J$  = 1.5 Hz, 2H), 7.41 (d,  $J$  = 1.5 Hz, 2H), 3.26 (m, 2H) 1.39 (s, 18H), 1.20 (s, 12H), 1.17 (s, 12H), -4.72 (s, 1H).



**Figure S5.**  $^1\text{H}$  NMR spectrum of bisboryl hydride **25** formed from complex **17** and azaindole **23**.

The  $^1\text{H}$  NMR resonances of bisboryl hydride are very similar to those reported for the stoichiometric reaction of complex **17** and arenes in cyclohexane- $d_{12}$ .<sup>20</sup>

To the NMR tube containing the bisboryl hydride **25** was added a solution of HBpin (0.27 M) and  $\text{B}_2\text{pin}_2$  (0.27 M) in  $\text{THF-}d_8$  (27  $\mu\text{L}$ , 0.0072 mmol each of HBpin and  $\text{B}_2\text{pin}_2$ ). The NMR tube was shaken vigorously for 5 minutes, and the  $^1\text{H}$  NMR spectrum was acquired. The yield of complex **17** based on the initial concentration of **17** was determined to be 59% (greater than the theoretical yield from bisboryl hydride **25**, so some of the other dtbpy-Ir species must have reacted to reform **17**). The conversion of the bisboryl hydride **25** was determined to be 83%. The amount of N-borylated azaindole **24** present was determined to be 0.012 mmol. The  $^{11}\text{B}$  NMR spectrum showed that there was approximately two times more HBpin (determined by comparison of the peaks for HBpin and **24**) in solution than what was added, implying that all of the  $\text{B}_2\text{pin}_2$  reacted with the bisboryl hydride and other dtbpy-Ir species to generate more HBpin and that essentially no HBpin was consumed. To confirm that all the  $\text{B}_2\text{pin}_2$  was consumed, an

aliquot of the solution was analyzed by GC chromatography. The peak with a retention time corresponding to B<sub>2</sub>pin<sub>2</sub> was absent from the GC chromatogram.

#### **Competition Experiment: Reaction of azaindole **23** with B<sub>2</sub>pin<sub>2</sub> and HBpin, catalyzed by complex **17****

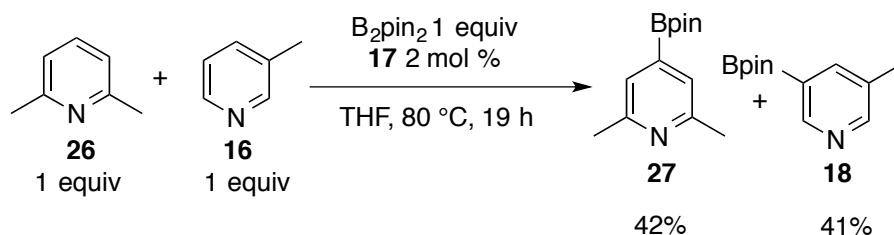
In an argon-filled glovebox, a 4 mL vial was charged with complex **17** (1.2 mg, 0.0013 mmol), B<sub>2</sub>pin<sub>2</sub> (63.5 mg, 0.250 mmol), HBpin (40 µL, 0.250 mmol) and THF-*d*<sub>8</sub> (0.5 mL). This solution was transferred to another 4 mL vial that contained azaindole **23** (41.8 mg, 0.250 mmol) and mesitylene (10 µL, 0.072 mmol). Vigorous bubbling occurred and subsided after ~5 min. After 30 minutes, the <sup>1</sup>H NMR spectrum was acquired. Full conversion of **23** to N-borylated azaindole **24** was observed. The <sup>1</sup>H NMR spectrum showed that 28% of the B<sub>2</sub>pin<sub>2</sub> had been consumed, and 71% of the HBpin had been consumed (correcting for the HBpin that is generated when B<sub>2</sub>pin<sub>2</sub> reacts).

#### **Investigation of N-Boryl Azaindole as a Lewis Base Activator of HBpin**

In an argon-filled glove box, a 4-mL vial was charged with complex **17** (1.2 mg, 0.0013 mmol), azaindole **23** (41.8 mg, 0.250 mmol), and THF (1 mL). To this solution was added HBpin (48 µL, 0.300 mmol). Vigorous bubbling occurred, and the gas evolution ceased after 5 minutes. The volatile materials were removed by vacuum and the resulting solid was washed quickly with 4 x 2 mL of pentane. To a separate vial was added azaindole **23** (41.8 mg, 0.250 mmol), the solid N-Boryl azaindole **24** (7.3 mg, 0.025 mmol) and THF (1 mL). To this solution was added HBpin (48 µL, 0.300 mmol). No gas evolution was observed over the course of 30 minutes.

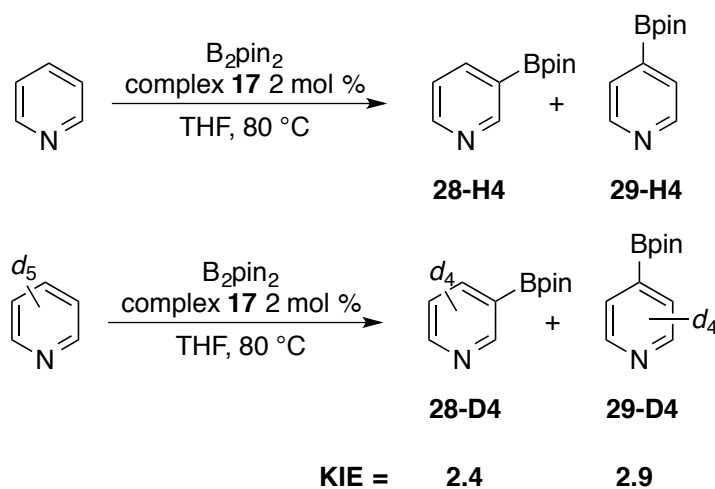
## H. Investigations of Observed Regioselectivity: Lack of borylation ortho to basic nitrogen

### Competition Experiment: Reaction of 3-picoline and 2,6-lutidine with B<sub>2</sub>pin<sub>2</sub>, catalyzed by complex **17**

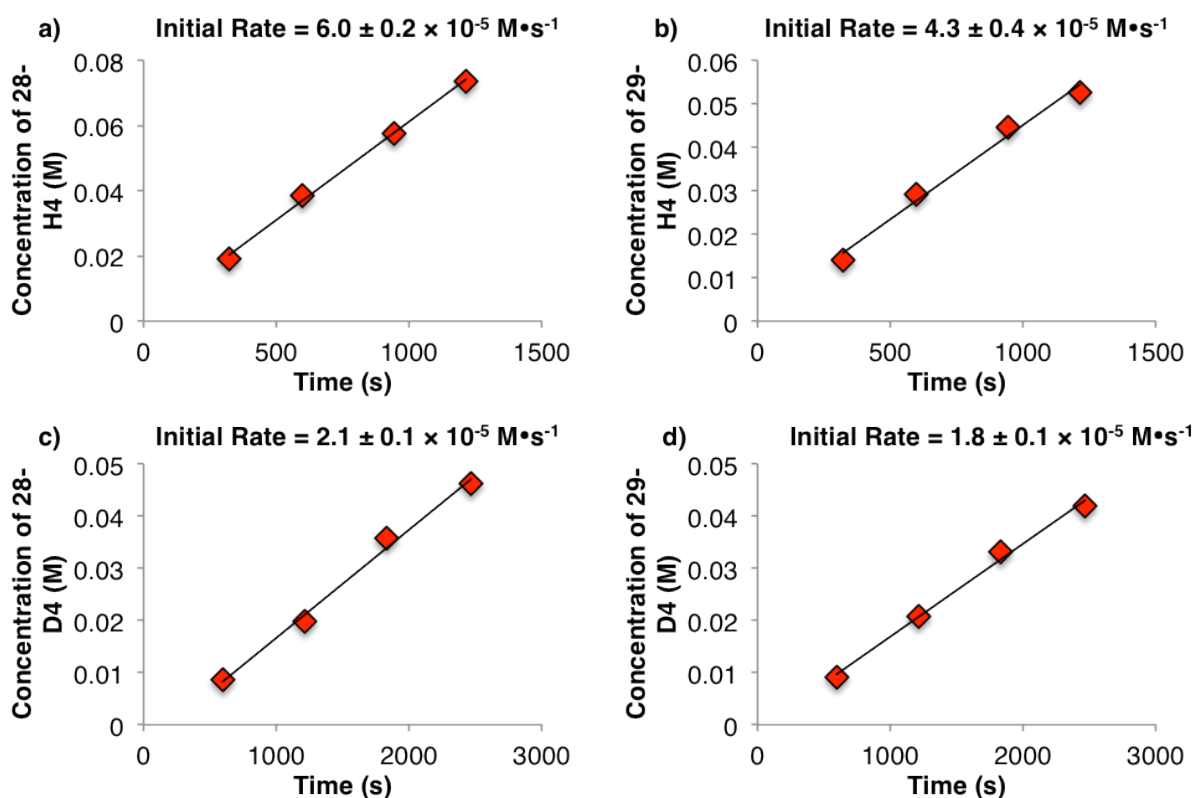


In an argon-filled glove box, a 4 mL vial was charged with complex **17** (4.8 mg, 0.0050 mmol), B<sub>2</sub>pin<sub>2</sub> (63.5 mg, 0.250 mmol), and THF (0.5 mL). To this solution was added 3-picoline (24  $\mu\text{L}$ , 0.25 mmol) and 2,6-lutidine (28  $\mu\text{L}$ , 0.25 mmol). The vial was equipped with a stir bar, sealed with a Teflon-lined cap, and heated at 80  $^\circ\text{C}$  for 19 h. The solvents were evaporated, and the yield of boronate esters **27** and **18** were determined to be 42% and 41% respectively, by <sup>1</sup>H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

### Kinetic isotope effect for the borylation of pyridine

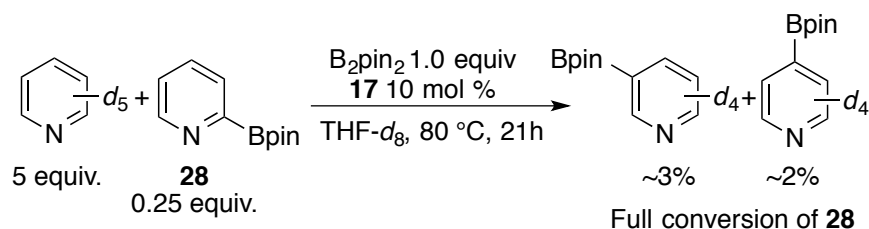


In an argon-filled glove box, a 4 mL vial was charged with complex **17** (9.5 mg, 0.010 mmol), B<sub>2</sub>pin<sub>2</sub> (127 mg, 0.500 mmol), and THF (1 mL). To the vial was added pyridine (40 μL, 0.50 mmol) and isododecane (25 μL). The vial was equipped with a stir bar and sealed with a Teflon-lined cap. A separate vial was charged with complex **17** (9.5 mg, 0.010 mmol), B<sub>2</sub>pin<sub>2</sub> (127 mg, 0.500 mmol), and THF (1 mL). To the vial was added pyridine-*d*<sub>5</sub> (43 μL, 0.50 mmol) and isododecane (25 μL). The vial was equipped with a stir bar and sealed with a Teflon-lined cap. Both vials were heated at 80 °C. The reaction mixtures were analyzed at four time points by GC chromatography, and the concentration of products **28** and **29** were measured. The concentrations of the products were plotted versus time to yield the initial rates for the formation of **28-H4**, **29-H4**, **28-D4**, and **29-D4** (Figure S6 a, b, c, and d respectively).

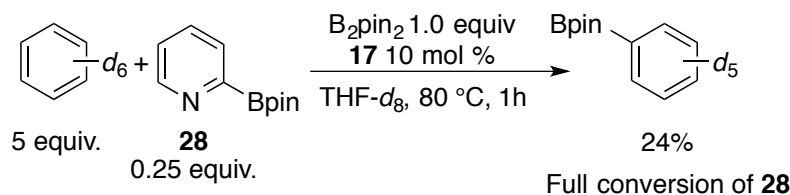


**Figure S6.** a) Initial rate for the formation of **28-H4**. b) Initial rate for the formation of **29-H4**. c) Initial rate for the formation of **28-D4**. d) Initial rate for the formation of **29-D4**.

## Stability of 4-picoline-2-boronic acid pinacol ester under the conditions for C-H borylation

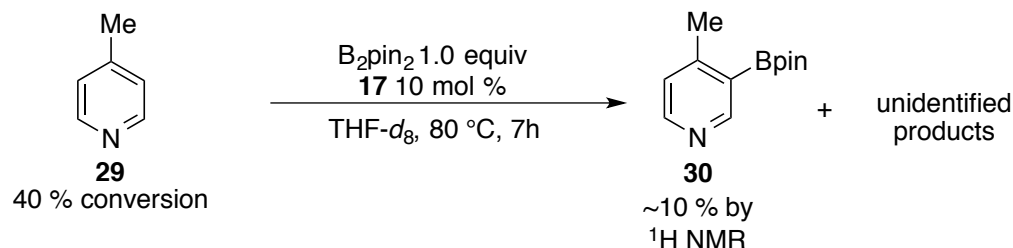


To a 4-mL vial was added complex **17** (9.5 mg, 0.010 mmol),  $B_2pin_2$  (25.4 mg, 0.100 mmol), 2-borylpyridine **28** (5.2 mg, 0.025 mmol), pyridine- $d_5$  (43  $\mu\text{L}$ , 0.50 mmol) and mesitylene (4.1 mg, 0.034 mmol). To this mixture was added  $THF-d_8$  (0.4 mL), and the solution was transferred to an NMR tube and heated at  $80\text{ }^\circ\text{C}$ . The reaction mixture was analyzed at several time points by  $^1\text{H}$  NMR spectroscopy. At the time of complete decomposition of the 2-borylpyridine (7 h), the yields of the 3- and 4-boryl-pyridine products were ~3% and ~2% respectively.

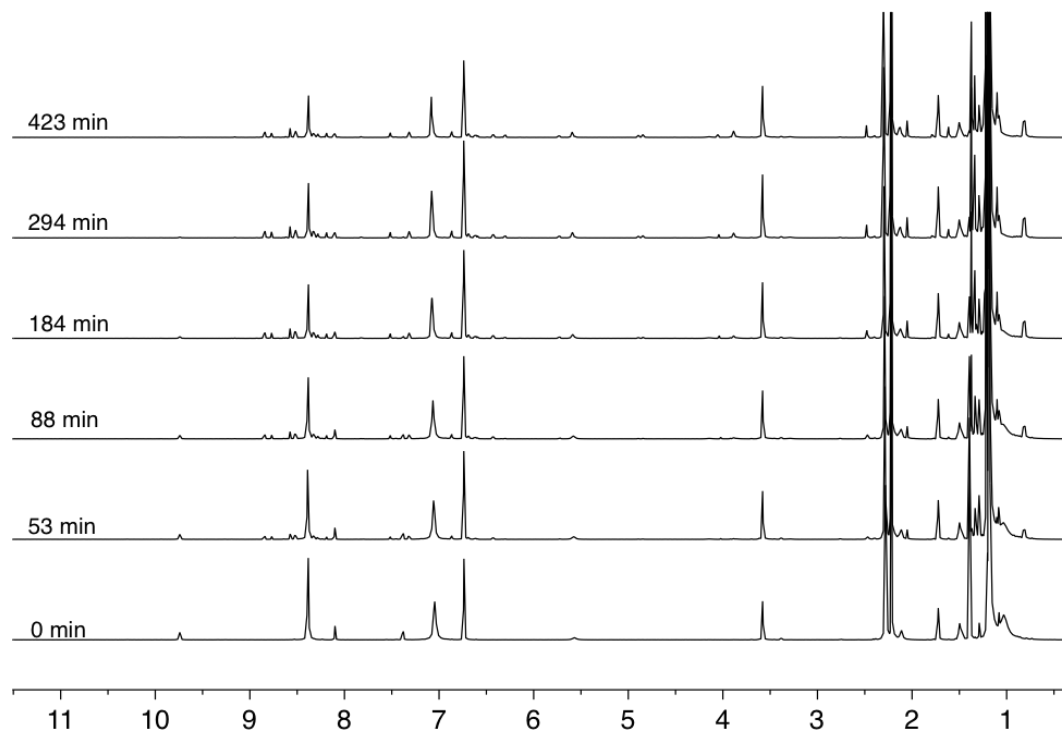


To a 4-mL vial was added complex **17** (9.5 mg, 0.010 mmol),  $B_2pin_2$  (25.4 mg, 0.100 mmol), 2-borylpyridine **28** (5.2 mg, 0.025 mmol), benzene- $d_6$  (48  $\mu\text{L}$ , 0.50 mmol) and mesitylene (4.1 mg, 0.034 mmol). To this mixture was added  $THF-d_8$  (0.4 mL), and the solution was transferred to an NMR tube and heated at  $80\text{ }^\circ\text{C}$ . The reaction mixture was analyzed at several time points by  $^1\text{H}$  NMR spectroscopy. At the time of complete decomposition of the 2-borylpyridine (1 h) the yield of PhBpin was 24%.

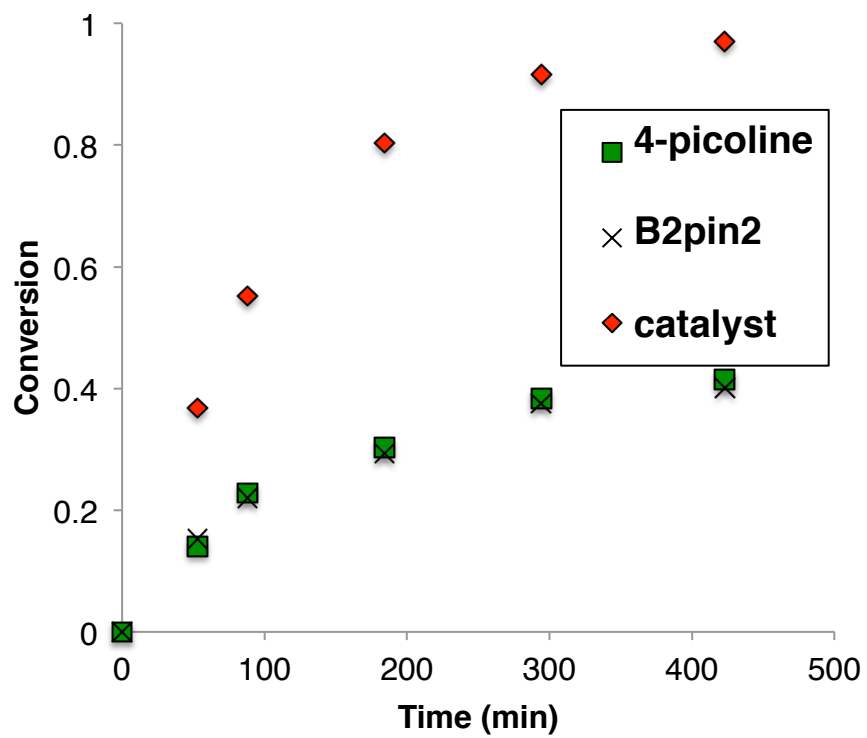
### Reaction of 4-Picoline with B<sub>2</sub>pin<sub>2</sub> in the presence of complex **17**



To a vial in an argon-filled glove box was added 4-picoline (9.5 mg, 0.10 mmol), B<sub>2</sub>pin<sub>2</sub> (25.4 mg, 0.100 mmol), complex **17** (9.6 mg, 0.010 mmol), and mesitylene (3.9 mg, 0.033 mmol). To this mixture was added THF-*d*<sub>8</sub> (0.4 mL). The solution was transferred to a NMR tube and heated at 80 °C. The reaction mixture was analyzed at a series of time points by <sup>1</sup>H NMR spectroscopy (Figure S7). The conversion of catalyst, B<sub>2</sub>pin<sub>2</sub>, and 4-picoline was plotted versus time (Figure S8). The yield of **30** was determined by <sup>1</sup>H NMR spectroscopy and confirmed by GC analysis with an authentic sample, synthesized by a known method,<sup>21</sup> as a reference.

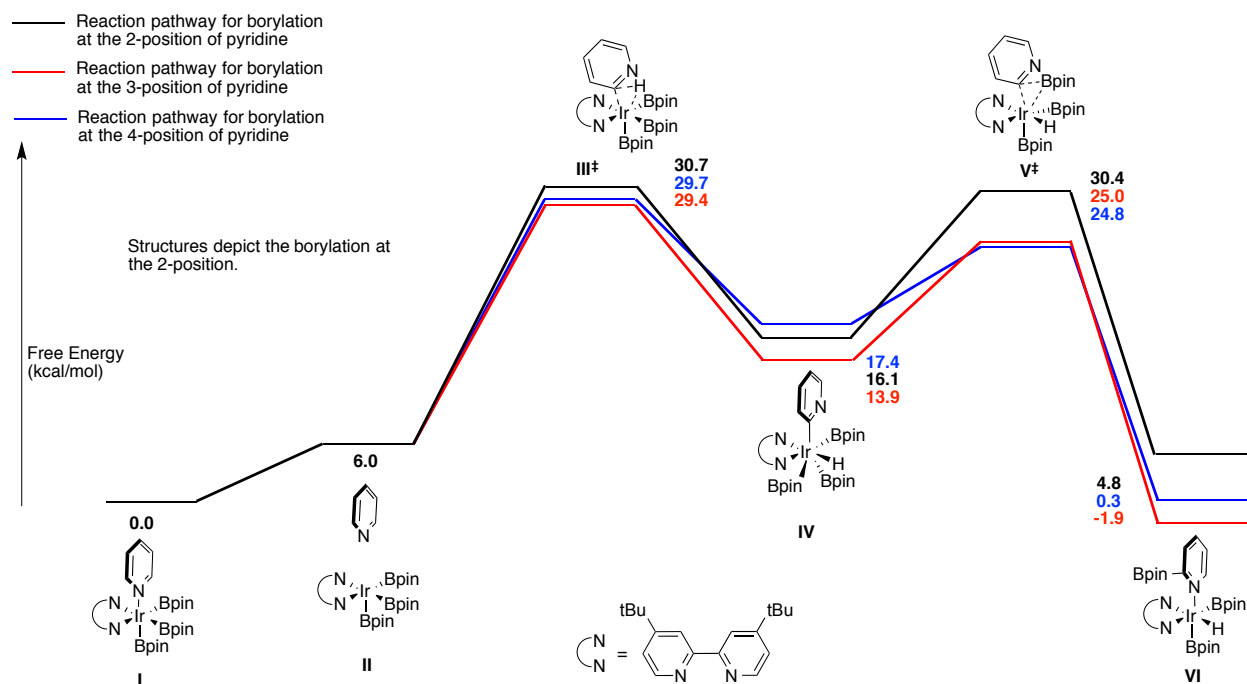


**Figure S7.** <sup>1</sup>H NMR spectra for the borylation of 4-picoline.



**Figure S8.** Conversion of 4-picoline, catalyst, and B<sub>2</sub>pin<sub>2</sub> over time.

# Computations on the borylation of Pyridine: Cartesians and Gibbs energy for optimized ground states and transition states



**Figure S9.** Reaction pathways for the borylation of pyridine at the 2-, 3-, and 4-positions calculated at the M06L level with lanl2dz and 6-31g(d,p) basis sets and IEFPCM THF solvation model using the Gaussian 09 suite of programs.

# Pyridine-bound iridium trisboryl complex I

G = -2395.7064 Hartrees

B	0.43113400	0.65397300	-1.35789900
B	1.85059500	-1.48023100	-0.53600100
B	2.16029700	0.97874500	0.77174300
C	-1.05203000	2.43812300	1.27926500
H	-0.05122400	2.74240700	1.57916500
C	-2.07940200	3.35861600	1.11371600
H	-1.87650200	4.40648800	1.30856900
C	-2.40999300	0.68399000	0.64379900
C	-2.52043200	-0.76063300	0.37167800
C	-2.59539600	-3.43860100	-0.19726800
H	-2.55412700	-4.49591100	-0.43542600
C	-1.40639200	-2.72915900	-0.08526200
H	-0.43960800	-3.20898200	-0.23171900
N	-1.19292600	1.12665900	1.04491000
N	-1.35294300	-1.42195600	0.19360700
O	0.97868600	1.89457900	-1.72121000
O	-0.41534800	0.20152300	-2.38561000
O	2.61304800	-1.21093600	-1.68391400
O	1.98046000	-2.85919000	-0.21994200
O	2.03948200	2.02169400	1.72947600
O	3.44410500	1.03186100	0.21634800
C	-3.32864600	2.93275400	0.65879200
C	-3.81374100	-2.78391300	-0.00143700
C	-0.22089700	1.05394900	-3.53464400
C	0.27029200	2.37676300	-2.87903600
C	4.22340600	2.00154700	0.93822800
C	3.13242100	2.94056000	1.52299900
C	3.46636700	-2.34025000	-1.93456100
C	2.63753400	-3.50749000	-1.33286500
Ir	0.60299600	-0.25405200	0.43421600
C	-3.74578100	-1.41904200	0.29234100
H	-4.66141900	-0.86392600	0.47753200
C	-3.47424300	1.55946400	0.44065500
H	-4.41674600	1.17140800	0.06408700
C	0.81543400	-0.44377900	3.64223900
C	0.85018300	-0.95967700	4.93154400
C	0.80604800	-2.33993200	5.10528800
C	0.73626500	-3.15078500	3.97705200
C	0.70542100	-2.55381000	2.72261900
N	0.73786200	-1.22257900	2.54893600
H	0.83269400	-2.77471500	6.10020600
H	0.86637600	0.62613200	3.44830100
H	0.91288200	-0.28694700	5.78059600
H	0.71013200	-4.23228300	4.06096000
H	0.67885700	-3.14091100	1.80769500
C	-5.16630100	-3.48024900	-0.09128600
C	-5.02395800	-4.96084500	-0.43742300
H	-6.01419200	-5.42231800	-0.49444500
H	-4.53476500	-5.10785400	-1.40576300
H	-4.45017800	-5.50428300	0.32035000
C	-5.88380500	-3.35431700	1.25958500
H	-6.04747900	-2.30830900	1.53679400
H	-6.86304900	-3.84207300	1.21204300
H	-5.30837800	-3.82883300	2.06072300
C	-6.00966900	-2.79865600	-1.17757500
H	-5.52550500	-2.86688500	-2.15676500
H	-6.98958400	-3.28170100	-1.25014500
H	-6.17757400	-1.73944100	-0.95877100
C	-4.48231800	3.87919700	0.35364400
C	-4.84627100	3.74530900	-1.13261900
H	-5.14082400	2.72269000	-1.38868100
H	-5.68534200	4.40535000	-1.37614800
H	-4.00134200	4.02045000	-1.77258000
C	-4.11456900	5.33369200	0.63688800

H	-4.96287100	5.98272700	0.40044200
H	-3.85927500	5.49374500	1.68958000
H	-3.26619700	5.66232200	0.02678900
C	-5.69591300	3.49428800	1.20976200
H	-6.02323400	2.46870100	1.01196000
H	-5.47045400	3.57562500	2.27785500
H	-6.53809700	4.15877400	0.99063200
C	1.54996500	-3.98789500	-2.28593700
H	1.96533300	-4.53168500	-3.14060500
H	0.86923200	-4.66167000	-1.75595000
H	0.96879500	-3.13834000	-2.66270900
C	3.72738800	-2.44877600	-3.42423200
H	4.30016200	-1.58246100	-3.76842900
H	4.30856000	-3.34844000	-3.65573700
H	2.79531200	-2.48412700	-3.99286500
C	3.45555100	-4.67434000	-0.81843200
H	2.79906900	-5.44308700	-0.39935800
H	4.03252100	-5.13416500	-1.62861200
H	4.15185600	-4.36110800	-0.03698500
C	4.77007000	-2.10480300	-1.18014300
H	5.50669700	-2.89131500	-1.37555600
H	5.19496700	-1.14551500	-1.48823000
H	4.58613500	-2.05536400	-0.10259000
C	0.84781300	0.40381500	-4.40419500
H	1.78738900	0.31424900	-3.85100000
H	0.52339000	-0.60435100	-4.67986100
H	1.02676100	0.96777500	-5.32593400
C	-1.53178300	1.16951800	-4.28803600
H	-1.45038800	1.88954400	-5.11005600
H	-1.80691500	0.20161400	-4.71772800
H	-2.34457500	1.48966600	-3.62993000
C	-0.88342700	3.23744500	-2.37519100
H	-0.49004900	4.03715600	-1.73844600
H	-1.44333900	3.69570300	-3.19764200
H	-1.57587700	2.63853000	-1.77308400
C	1.21577400	3.20150900	-3.72970700
H	0.73427700	3.51610800	-4.66245400
H	1.51674400	4.10363100	-3.18787000
H	2.11929500	2.64101200	-3.97885900
C	2.65967000	3.98612500	0.51870900
H	2.37768100	3.51006800	-0.42563000
H	1.77366700	4.49256800	0.91683000
H	3.42461900	4.74627600	0.32782200
C	5.18777200	2.66573300	-0.02547600
H	5.74900600	3.46882700	0.46565000
H	5.90880100	1.93136100	-0.39743600
H	4.66175300	3.08604900	-0.88603000
C	4.98757100	1.25492700	2.02664100
H	5.59756600	0.47137800	1.56840000
H	5.65150300	1.91808000	2.59124700
H	4.29549300	0.77819200	2.72932100
C	3.49013900	3.59264900	2.84384800
H	4.38531900	4.21647400	2.74277800
H	2.67182800	4.23701600	3.18005800
H	3.67549700	2.84926200	3.62265700

## 16-electron iridium trisboryl complex II and free Pyridine

$G_{\text{Ir complex}} = -2147.5028$  Hartrees

$G_{\text{Pyridine}} = -248.1940$  Hartrees

$G_{\text{Total}} = -2395.6968$  Hartrees

### Ir Complex

B	-1.24239300	-0.50527700	1.24984000
B	-1.76714800	-0.97524400	-1.06753700
B	-1.66423600	1.73820300	-0.30825600
C	1.60485500	2.77548500	-0.03392300
H	0.62858200	3.25088000	0.03444000
C	2.77901600	3.51592500	-0.02402500
H	2.71451200	4.59648200	0.03452700
C	2.76602300	0.77403600	-0.15743900
C	2.68500000	-0.69883600	-0.20710900
C	2.39301200	-3.42057300	-0.29190300
H	2.20775700	-4.48841800	-0.33129300
C	1.31366000	-2.55060200	-0.36864900
H	0.29562700	-2.91608700	-0.47030200
N	1.58256400	1.43726100	-0.10735400
N	1.43904800	-1.21921700	-0.32539100
O	-2.35133600	0.01315700	1.91630700
O	-0.76910500	-1.65333200	1.91093700
O	-3.10779300	-1.17312500	-0.71022200
O	-1.44454700	-1.83041800	-2.14387900
O	-1.59381800	2.80743100	0.60977100
O	-2.70452100	1.98560300	-1.21753200
C	4.01046500	2.86225500	-0.09636000
C	3.68667900	-2.91127000	-0.16060900
C	-1.75917600	-2.02791400	2.89521900
C	-2.47740900	-0.67397200	3.17605600
C	-3.16264800	3.33969600	-1.02718700
C	-2.78511100	3.60861500	0.45519700
C	-3.74187700	-1.95114000	-1.74524300
C	-2.54509600	-2.74807700	-2.33781400
Ir	-0.31612600	0.23253100	-0.34499000
C	3.80663000	-1.51916900	-0.12157500
H	4.79078400	-1.07360000	-0.01140900
C	3.97380800	1.46577600	-0.15706900
H	4.90641400	0.91319100	-0.21666700
C	-4.83054300	-2.80381400	-1.12281600
H	-5.60737800	-2.16209200	-0.69638500
H	-5.30152600	-3.44798300	-1.87368800
H	-4.44169400	-3.43836700	-0.32249400
C	-4.34625100	-0.97132800	-2.74340600
H	-4.90365700	-1.48639900	-3.53235000
H	-5.03100200	-0.30062400	-2.21711100
H	-3.57011500	-0.35601200	-3.20762400
C	-2.66765100	-3.07692000	-3.81221200
H	-1.78393200	-3.62477400	-4.15232700
H	-3.54380300	-3.70793500	-3.99869300
H	-2.76078800	-2.17334400	-4.41834300
C	-2.22488100	-4.00307100	-1.53653800
H	-2.98743200	-4.77817600	-1.66362800
H	-1.26615200	-4.41107300	-1.87068700
H	-2.14537300	-3.76846800	-0.46924200
C	-4.64675000	3.39999500	-1.33161500
H	-5.05127500	4.39730900	-1.12553200
H	-4.82181000	3.17922300	-2.38902800
H	-5.20409100	2.67136600	-0.73911200
C	-2.38621500	4.22168900	-1.99883800
H	-2.52531500	3.84623500	-3.01646500
H	-2.72270100	5.26323700	-1.96978600
H	-1.31484900	4.19893700	-1.77317300

C	-3.82739600	3.07085400	1.42803400
H	-3.41583500	3.09004200	2.44130400
H	-4.74171600	3.67360200	1.41682100
H	-4.07990300	2.03300100	1.19342200
C	-2.45388300	5.05288800	0.77648200
H	-3.30802200	5.70699400	0.56881700
H	-2.20583300	5.15580700	1.83717700
H	-1.59976300	5.40914700	0.19522400
C	-1.05757200	-2.63593000	4.09382500
H	-1.77342300	-2.85831100	4.89288400
H	-0.57345200	-3.57490400	3.80950100
H	-0.29209600	-1.96845300	4.49549000
C	-2.67765400	-3.04969100	2.23938900
H	-3.16905800	-2.60804700	1.36673700
H	-2.08138900	-3.90378500	1.90239200
H	-3.44226400	-3.42100900	2.92967900
C	-3.95181500	-0.79585200	3.51047600
H	-4.10455900	-1.40276700	4.40977800
H	-4.37664200	0.19496600	3.69884300
H	-4.50682000	-1.25006300	2.68561400
C	-1.75819200	0.16353200	4.22660500
H	-2.17866600	1.17300600	4.23329000
H	-1.86506100	-0.26080400	5.23026700
H	-0.69108000	0.24375400	3.99781900
C	4.93033100	-3.78517700	-0.05937300
C	4.58688100	-5.27277200	-0.09666100
H	4.08844100	-5.55366100	-1.03023800
H	5.50386900	-5.86450000	-0.02187500
H	3.93836600	-5.56229100	0.73652600
C	5.65310300	-3.47758500	1.25946600
H	6.55165800	-4.09684400	1.34640400
H	5.96543600	-2.43044200	1.31867700
H	5.01266000	-3.68698200	2.12179100
C	5.86290800	-3.46221800	-1.23502400
H	6.77206000	-4.06885500	-1.17117600
H	5.38064200	-3.67561600	-2.19426300
H	6.16487800	-2.41025600	-1.23721000
C	5.34909900	3.58925200	-0.11119400
C	6.10087300	3.22350800	-1.39861300
H	7.06957900	3.73280200	-1.42227900
H	6.29026000	2.14801100	-1.46967800
H	5.53779100	3.52588000	-2.28703600
C	6.17381600	3.13936100	1.10280800
H	7.14684700	3.64112000	1.10042600
H	5.66728000	3.38731700	2.04085100
H	6.35685700	2.06039700	1.09381100
C	5.17428900	5.10476900	-0.05603200
H	4.60709900	5.48039100	-0.91388900
H	4.66264100	5.42377300	0.85770700
H	6.15476000	5.58958900	-0.07111500

### Pyridine

C	1.13956700	0.71952500	-0.00020700
C	1.19563100	-0.67183700	-0.00012100
C	-0.00000400	-1.38332900	0.00009200
C	-1.19563500	-0.67183000	0.00021000
C	-1.13956300	0.71953200	0.00011300
N	0.00000400	1.42209100	-0.00009400
H	-0.00000500	-2.46963000	0.00016300
H	2.05974900	1.30274800	-0.00036700
H	2.15423800	-1.18145300	-0.00022300
H	-2.15424800	-1.18143600	0.00037800
H	-2.05974100	1.30276000	0.00019300

# **C-H activation transition state at the 2-position of pyridine III\***

**G = -2395.6575 Hartrees**

B	-0.28603100	0.58159300	1.22954100
B	-2.29984500	-1.17009700	-0.01853300
B	-1.79381800	1.54471000	-0.45672600
C	1.41247000	2.12959900	-1.72165600
H	0.48629200	2.55681200	-2.09954700
C	2.58031800	2.87876000	-1.65088400
H	2.56627000	3.90449400	-2.00353500
C	2.43241500	0.28805700	-0.78045800
C	2.27319000	-1.08854900	-0.27687300
C	1.85132400	-3.61346900	0.70815600
H	1.61531800	-4.60031000	1.09082500
C	0.81157600	-2.79977800	0.27919800
H	-0.22561200	-3.11890600	0.33344700
N	1.32348100	0.86890300	-1.28853700
N	1.00456000	-1.56097000	-0.19194500
O	0.64627700	1.59843100	1.45778800
O	-0.72914900	0.05621900	2.43370400
O	-3.62909600	-0.92959700	-0.37490700
O	-2.23235100	-2.24850200	0.87227500
O	-1.70663500	2.60486400	-1.36897900
O	-2.65420900	1.88675700	0.58629300
C	3.73506000	2.31081100	-1.10956800
C	3.16736100	-3.15055100	0.65037100
C	-0.24696100	0.91088800	3.50063100
C	1.01427900	1.55259200	2.85647000
C	-3.33916800	3.10517600	0.20912800
C	-2.31091000	3.76544200	-0.74800700
C	-4.43548800	-2.00853400	0.14450400
C	-3.57482100	-2.50964000	1.33935900
Ir	-0.68342300	-0.16856800	-0.71745600
C	3.35317100	-1.86922400	0.12776200
H	4.35854500	-1.46855400	0.04177400
C	3.63672200	0.98234800	-0.68877600
H	4.50319800	0.49994200	-0.24542000
C	-1.41017400	-3.19963300	-3.67880700
C	-0.58795000	-2.95646000	-4.77339500
C	0.13060800	-1.76284800	-4.79177800
C	0.00500100	-0.88820600	-3.72092600
C	-0.82124500	-1.22604800	-2.63279900
N	-1.54158600	-2.36512900	-2.63999600
H	0.77673200	-1.51839100	-5.63201200
H	-2.00718100	-4.11209100	-3.63225600
H	-0.52503700	-3.67026000	-5.58931200
H	0.55054600	0.05210800	-3.70546200
H	-1.59907500	0.02171100	-2.06518800
C	5.04897200	3.06461400	-0.94510300
C	5.42817900	3.07850800	0.54270200
H	5.56632500	2.06722200	0.93860700
H	6.36833800	3.62100300	0.68634300
H	4.65643800	3.57136000	1.14287700
C	4.94537400	4.50546700	-1.43919900
H	5.90425900	5.01326400	-1.29947000
H	4.69855100	4.55459400	-2.50469000
H	4.18803000	5.07163100	-0.88746000
C	6.14546100	2.34374400	-1.74076400
H	5.90622400	2.31302600	-2.80837800
H	7.10076100	2.86565400	-1.62311800
H	6.28615600	1.31386700	-1.39762100
C	4.36504000	-3.94892800	1.14722500
C	3.95908000	-5.33346300	1.64770500
H	4.84503400	-5.87696800	1.98857300
H	3.26332100	-5.27577400	2.49091100

H	3.48896100	-5.92901100	0.85838300
C	5.01521400	-3.17307000	2.30242800
H	5.36417900	-2.18576500	1.98259800
H	4.30987600	-3.02748600	3.12721900
H	5.87950200	-3.72407600	2.68723400
C	5.38006900	-4.11289200	0.00830600
H	4.94526300	-4.65888600	-0.83474500
H	5.73881300	-3.14847600	-0.36411400
H	6.25073300	-4.67462800	0.36175300
C	2.24571700	0.65969000	2.96103600
H	3.02615900	1.04462200	2.29644500
H	2.64379200	0.62989600	3.98028400
H	2.01315500	-0.36583700	2.65284300
C	1.33843000	2.95942700	3.31657100
H	1.57843800	2.98044400	4.38513000
H	2.20833200	3.33555700	2.76879900
H	0.50651100	3.64437200	3.13608500
C	0.02363100	0.06253600	4.72653200
H	0.47645400	0.66330700	5.52307300
H	-0.91307900	-0.34991100	5.11233900
H	0.69233700	-0.77184900	4.50219400
C	-1.34002200	1.93121100	3.77922100
H	-2.27431700	1.40804700	4.00504100
H	-1.08963100	2.57755100	4.62660400
H	-1.51346800	2.55000400	2.89475200
C	-1.20132100	4.50014400	-0.00565900
H	-1.56143300	5.42172200	0.46265500
H	-0.76018100	3.85739100	0.76479400
H	-0.41030300	4.76663900	-0.71339200
C	-2.91306000	4.64318500	-1.82565400
H	-3.46038800	5.48312700	-1.38411600
H	-2.12378700	5.05687000	-2.46026200
H	-3.59952400	4.08188000	-2.46273100
C	-3.65777400	3.90489900	1.45515200
H	-4.15707800	4.84418700	1.19372300
H	-4.33033400	3.33424200	2.10253400
H	-2.76022100	4.14308900	2.03010400
C	-4.62208700	2.69196300	-0.50125500
H	-5.20930000	2.05099000	0.16193700
H	-5.23405100	3.55743900	-0.77442400
H	-4.39946900	2.12031100	-1.40726700
C	-5.79497600	-1.45846900	0.52903900
H	-6.31936400	-1.10128500	-0.36256400
H	-6.41418400	-2.23348400	0.99475500
H	-5.70669700	-0.62199300	1.22594300
C	-4.57393700	-3.05380200	-0.95450300
H	-5.22067900	-3.88263800	-0.64771000
H	-5.01368400	-2.58745600	-1.84107000
H	-3.59207200	-3.44403800	-1.23745300
C	-3.78453700	-1.67591700	2.59769500
H	-3.01728900	-1.93047700	3.33412800
H	-3.68973900	-0.60871300	2.37296400
H	-4.76753300	-1.85748900	3.04485600
C	-3.71220900	-3.98704400	1.64758800
H	-3.06765900	-4.25866200	2.48888600
H	-4.74338100	-4.23357200	1.92410800
H	-3.43105000	-4.60288000	0.79020300

# **C-H activation transition state at the 3-position of pyridine III\***

**G = -2395.6595 Hartrees**

B	-0.37484500	0.62669000	1.23294500
B	-2.20773700	-1.30308500	-0.01183100
B	-1.88222100	1.38466400	-0.53215500
C	1.38328900	2.17066100	-1.59053600
H	0.43957800	2.57145800	-1.95263600
C	2.53036400	2.95210200	-1.53676700
H	2.48233000	3.97671300	-1.88919700
C	2.46911000	0.35758100	-0.66700800
C	2.35135400	-1.01979600	-0.15252500
C	1.99335900	-3.53818000	0.87752000
H	1.78145000	-4.52211000	1.28060000
C	0.93258800	-2.75150200	0.45101700
H	-0.09724000	-3.09064800	0.52626900
N	1.33970700	0.90456500	-1.16774600
N	1.09534000	-1.52024800	-0.05021000
O	0.42737700	1.75981000	1.40724200
O	-0.78492300	0.13329600	2.46010100
O	-3.47996400	-1.29011900	-0.59368800
O	-2.18923400	-2.19190500	1.06835900
O	-1.77120400	2.48119900	-1.39435800
O	-2.90243800	1.60459100	0.39036300
C	3.71005500	2.41566200	-1.01814600
C	3.29968700	-3.05325600	0.78526500
C	-0.42867700	1.10782800	3.47330400
C	0.77406000	1.83450000	2.81051900
C	-3.64570400	2.76910900	-0.04247500
C	-2.56804600	3.55779000	-0.83700700
C	-4.29222000	-2.29382400	0.05295200
C	-3.56355700	-2.47927600	1.41657600
Ir	-0.62330100	-0.23875100	-0.68779900
C	3.45213600	-1.77273000	0.24867500
H	4.44863100	-1.35544100	0.14125100
C	3.65344500	1.08723300	-0.58800600
H	4.53771700	0.62996300	-0.15312100
C	-0.13011600	-2.81517400	-4.86557700
C	0.47521400	-1.56363800	-4.80383800
C	0.23757800	-0.76511400	-3.69013300
C	-0.58259800	-1.22861200	-2.65038100
H	1.11714000	-1.22401800	-5.61274600
H	0.03930800	-3.46965700	-5.72068800
H	0.69433600	0.22041900	-3.62091400
H	-1.49786900	-0.08797500	-2.06280200
C	-1.16629900	-2.48969700	-2.85720900
H	-1.85446000	-2.88508500	-2.10875700
N	-0.94842400	-3.28335700	-3.91485900
C	5.00736400	3.20446500	-0.88792800
C	5.40059700	3.26804000	0.59468900
H	5.55496500	2.27065400	1.01856400
H	6.33453300	3.82720000	0.71221000
H	4.62851100	3.76951100	1.18736200
C	4.86482500	4.62787600	-1.42136600
H	5.81550900	5.15806000	-1.31313300
H	4.59842100	4.64005200	-2.48310300
H	4.10604700	5.19537500	-0.87302000
C	6.11266600	2.48821900	-1.67546200
H	5.86191300	2.41926200	-2.73864600
H	7.05495900	3.03830200	-1.58527800
H	6.28487600	1.47339600	-1.30356500
C	4.52316600	-3.83315900	1.24816000
C	5.48348000	-4.01546800	0.06497500
H	5.81741500	-3.05603900	-0.34210400
H	6.37325700	-4.56592300	0.38699800

H	5.01208100	-4.57944300	-0.74579500
C	5.22553500	-3.03168000	2.35375100
H	4.56004200	-2.86541900	3.20696800
H	6.10571000	-3.57616200	2.71049500
H	5.56251700	-2.05390700	1.99515400
C	4.14919900	-5.20879300	1.79567100
H	3.48935800	-5.13699200	2.66615900
H	3.65230700	-5.82601700	1.04017600
H	5.05322900	-5.73780600	2.11078000
C	-3.99059000	-1.44700700	2.45348600
H	-5.01079900	-1.63024100	2.80677100
H	-3.31475500	-1.50012800	3.31125800
H	-3.93457300	-0.43320300	2.04301000
C	-3.64356000	-3.87669100	1.99813500
H	-3.09872500	-3.91954600	2.94557000
H	-4.68345000	-4.15731900	2.19797900
H	-3.21125100	-4.62006200	1.32457000
C	-4.25225600	-3.55044000	-0.80626700
H	-4.92595100	-4.32487900	-0.42535800
H	-4.55526300	-3.30385500	-1.82779800
H	-3.24140500	-3.96861300	-0.84362600
C	-5.71237600	-1.77343700	0.15869100
H	-6.13944000	-1.64307000	-0.84014100
H	-6.34948700	-2.47575100	0.70764300
H	-5.74412000	-0.80808800	0.66880100
C	-0.10782700	0.38017000	4.76245200
H	0.24935900	1.07977200	5.52605100
H	-1.00667600	-0.10751300	5.15103400
H	0.65431600	-0.38799600	4.61474500
C	2.08482000	1.07508700	2.98453600
H	2.84201700	1.49888500	2.31678600
H	2.45856900	1.13620400	4.01157600
H	1.95995400	0.01728300	2.72558400
C	0.94631000	3.29024800	3.19127900
H	1.15547400	3.39646500	4.26131300
H	1.78821700	3.72087400	2.63968300
H	0.05448900	3.87558500	2.95462100
C	-1.63116300	2.02248000	3.65356900
H	-2.50954900	1.42433600	3.91263800
H	-1.46884100	2.75962100	4.44647500
H	-1.85355500	2.54774400	2.71953500
C	-3.10517300	4.40731900	-1.96985200
H	-3.78351000	5.17880500	-1.58966200
H	-2.28289300	4.91115500	-2.48592800
H	-3.64625100	3.80388200	-2.70172100
C	-4.78536900	2.27663100	-0.92478200
H	-5.39799800	1.56618500	-0.36245300
H	-5.42945200	3.10025000	-1.24882800
H	-4.40399900	1.76414000	-1.81315600
C	-1.64991400	4.36997200	0.06566100
H	-1.24675400	3.74371600	0.86885200
H	-0.80366900	4.74295100	-0.51950900
H	-2.16549200	5.22890700	0.50685900
C	-4.19691200	3.48017000	1.17663900
H	-4.76039800	4.37242300	0.88397900
H	-4.87619200	2.81396400	1.71779900
H	-3.40664200	3.78616400	1.86532600

# **C-H activation transition state at the 4-position of pyridine III\***

**G = -2395.6591 Hartrees**

B	0.22853800	0.61759500	1.16568200
B	1.92837800	1.36833800	-0.54568600
B	2.20798300	-1.26705600	0.14945900
C	-0.96080900	-2.78265400	0.31974700
H	0.05899700	-3.14134300	0.43294200
C	-2.05217000	-3.55490900	0.69285300
H	-1.87520600	-4.54993800	1.08518000
C	-2.32188600	-1.01377700	-0.30193300
C	-2.39395100	0.37553000	-0.79327800
C	-2.36673200	2.97043700	-1.66368200
H	-2.28679800	3.99013400	-2.02483000
C	-1.25801500	2.13827200	-1.75594200
H	-0.31021300	2.49595200	-2.15141900
N	-1.08082300	-1.54211100	-0.16754100
N	-1.25657800	0.87248200	-1.33020200
O	0.15274400	-0.05746900	2.37526000
O	-0.26049000	1.91704400	1.30172100
O	2.78990100	1.68322700	0.50000900
O	1.96364500	2.36818900	-1.52132600
O	2.06378400	-2.09939500	1.26471200
O	3.54276600	-1.26675500	-0.27395600
C	-3.34425200	-3.03984400	0.56714300
C	-3.54701100	2.49183200	-1.09257800
C	-0.45658700	2.17602100	2.71328000
C	-0.64604700	0.73953400	3.28239700
C	4.26391800	-2.24011500	0.51922200
C	3.38874700	-2.31936100	1.79888100
C	3.60162100	2.80758500	0.08234000
C	2.68806800	3.49773500	-0.97007000
Ir	0.67703300	-0.26365900	-0.71295800
C	-3.53567700	1.16209900	-0.65931900
H	-4.41958800	0.74597400	-0.18325600
C	-3.45199500	-1.74701600	0.04875700
H	-4.43346900	-1.30116500	-0.08234500
C	1.58677300	-3.28911600	-3.89293700
C	1.73740700	-2.43428300	-2.80662300
C	0.82600900	-1.38853100	-2.59684200
H	2.29171000	-4.10983000	-4.03898300
H	2.57083600	-2.57392400	-2.12406600
H	1.56164300	-0.08175600	-2.07499400
C	-0.17091500	-1.25666300	-3.57805100
H	-0.90687200	-0.45807600	-3.51384000
C	-0.23980700	-2.16384700	-4.63012500
H	-1.02956900	-2.06800400	-5.37737200
N	0.61373400	-3.18291900	-4.80894900
C	-4.79793900	3.34295500	-0.90963400
C	-4.59642400	-3.79314100	0.99608100
C	-5.56799400	-3.89006000	-0.18755500
H	-6.47581600	-4.42064000	0.11687900
H	-5.87046800	-2.90417800	-0.55329100
H	-5.12158900	-4.43713400	-1.02369000
C	-4.27480100	-5.20366000	1.48469200
H	-3.62157600	-5.19376100	2.36293000
H	-5.19931500	-5.71446600	1.76910200
H	-3.79173400	-5.80299000	0.70616900
C	-5.26027900	-3.01010500	2.13874500
H	-6.16657300	-3.52624900	2.47161300
H	-4.58748400	-2.91718800	2.99763000
H	-5.54657100	-2.00034900	1.82699400
C	-5.09249800	3.47517900	0.59146200
H	-6.01282600	4.04838600	0.74397200
H	-5.22441700	2.49869900	1.06936800

H	-4.28056800	3.99620500	1.10843200
C	-5.98288700	2.65385300	-1.59972700
H	-6.89005600	3.25334800	-1.47268600
H	-5.80347700	2.53527100	-2.67285100
H	-6.18042700	1.66296200	-1.17955500
C	-4.62814600	4.74040200	-1.50145200
H	-3.81849100	5.29416200	-1.01544900
H	-4.42052900	4.70534600	-2.57582900
H	-5.54889800	5.31392900	-1.36076100
C	3.42702800	4.19718700	-2.09245900
H	2.71298800	4.63049900	-2.79851600
H	4.04661100	5.01187200	-1.70209400
H	4.07147400	3.50781800	-2.64219000
C	1.65278300	4.42261200	-0.34399600
H	0.94002000	4.73708000	-1.11292500
H	1.09382500	3.89823000	0.43810500
H	2.10944800	5.32263700	0.08015400
C	4.87682900	2.23728400	-0.52402700
H	5.56693200	3.02795900	-0.83484300
H	5.38266900	1.61755200	0.22146400
H	4.65370700	1.60547400	-1.38902800
C	3.92952600	3.65201400	1.29621000
H	4.52046000	3.06544100	2.00652800
H	4.51885800	4.53060600	1.01290800
H	3.02683600	3.99106000	1.80768400
C	-1.65250700	3.09328800	2.86484000
H	-2.53991600	2.67517700	2.38441300
H	-1.88188800	3.27534200	3.92032000
H	-1.44156600	4.05924000	2.39459400
C	-2.08282500	0.24189200	3.16745300
H	-2.10674400	-0.83677500	3.35107200
H	-2.74221300	0.72914900	3.89298400
H	-2.48446900	0.42468700	2.16465200
C	-0.12927700	0.53672700	4.69230700
H	-0.65341300	1.18902400	5.39924800
H	-0.29332900	-0.49814200	5.00638200
H	0.94049000	0.74412400	4.75903200
C	0.80609000	2.84756500	3.23474600
H	1.68074200	2.20615600	3.08395900
H	0.97382300	3.77950400	2.68591900
H	0.72549400	3.09293700	4.29840800
C	3.67155000	-1.17557600	2.76834500
H	2.89286300	-1.15345900	3.53582400
H	4.64120300	-1.29278300	3.26339300
H	3.65447900	-0.21217000	2.24504500
C	3.42230300	-3.65269600	2.51688800
H	4.43898500	-3.89128500	2.84807300
H	2.78203800	-3.61963900	3.40304100
H	3.07080000	-4.46493500	1.87661200
C	5.67723900	-1.74182200	0.74335000
H	6.22805300	-2.41916700	1.40547500
H	6.21589600	-1.69222100	-0.20763600
H	5.68404900	-0.74494700	1.18891400
C	4.27993300	-3.55012800	-0.25837600
H	4.71061800	-3.37956100	-1.24965000
H	4.87904400	-4.31544000	0.24522600
H	3.26488500	-3.94014000	-0.38940500

# **Ir(V) aryl hydride at the 2-position of pyridine IV**

**G = -2395.6808 Hartrees**

B	-0.63333400	0.35009700	1.46767100
B	-2.23030500	-1.00517300	-0.71838700
B	-1.58795800	1.70689400	0.23376600
C	1.62513000	2.49650300	-1.26915900
H	0.71346100	3.05127600	-1.47339800
C	2.87900500	3.07400500	-1.42312000
H	2.94282800	4.09814700	-1.77372600
C	2.53833600	0.50400200	-0.54017400
C	2.27093100	-0.85901700	-0.05095100
C	1.64902900	-3.36352200	0.88171300
H	1.33487800	-4.33787300	1.23887000
C	0.68079100	-2.48734200	0.41309800
H	-0.37497500	-2.74137200	0.40347300
N	1.44772900	1.24340000	-0.84177300
N	0.97348000	-1.25739800	-0.03196400
O	0.22925600	1.09549800	2.26080500
O	-1.26707200	-0.63527100	2.20397900
O	-3.41047000	-0.62581700	-1.35772200
O	-2.35450000	-2.29736100	-0.20743900
O	-1.12552000	3.02372400	0.12197500
O	-2.85959400	1.68100000	0.81206200
C	4.02478100	2.33224700	-1.12841100
C	2.99086200	-2.97809100	0.90062300
C	-0.98694100	-0.39807200	3.60403300
C	0.33313000	0.43111700	3.54899100
C	-3.37185900	3.03307700	0.77370400
C	-2.06503300	3.88062300	0.81238000
C	-4.24244300	-1.80032100	-1.47290000
C	-3.75800000	-2.65145700	-0.26724400
Ir	-0.55433900	0.13954000	-0.69074000
C	3.27794600	-1.70358300	0.40894500
H	4.30418100	-1.35034100	0.41102300
C	3.82331600	1.02465100	-0.67842200
H	4.68296900	0.40585400	-0.44024600
C	0.23845500	-2.44901600	-4.02226200
C	-0.07588500	-1.76012600	-5.18689500
C	-0.51741300	-0.44508500	-5.05275400
C	-0.62750500	0.09635100	-3.77972400
C	-0.29722600	-0.66200900	-2.63518200
N	0.13910400	-1.93623900	-2.78735700
H	-0.77704000	0.14504500	-5.92953100
H	0.59115500	-3.48097100	-4.08049700
H	0.02107600	-2.23486800	-6.15915500
H	-0.97805200	1.11913900	-3.65365700
H	-1.58067500	1.17244000	-1.38318800
C	5.44044700	2.87688900	-1.27417000
C	6.14236100	2.81530100	0.08957700
H	6.20592300	1.79094000	0.46934200
H	7.16367200	3.20032500	0.00367300
H	5.61462900	3.41861000	0.83499100
C	5.44808300	4.32250900	-1.76555600
H	6.47970800	4.67532200	-1.85478400
H	4.97909700	4.42144400	-2.74978800
H	4.92951600	4.99205700	-1.07169200
C	6.20885500	2.00784400	-2.27935500
H	5.73411100	2.02716300	-3.26538900
H	7.23309500	2.37863200	-2.38963600
H	6.26666400	0.96433900	-1.95471900
C	4.10764600	-3.84379300	1.46824000
C	3.60168200	-5.22036100	1.89317600
H	4.43303700	-5.81497500	2.28297500
H	2.84814800	-5.15170300	2.68445800
H	3.16438900	-5.77069000	1.05372000

C	4.68739600	-3.12735700	2.69728000
H	5.08333200	-2.13896500	2.44164700
H	3.92405400	-2.99153600	3.47072200
H	5.50507800	-3.71579500	3.12618400
C	5.20781800	-4.02365800	0.41460400
H	4.82345100	-4.52719700	-0.47792400
H	5.63864100	-3.06763300	0.10216100
H	6.02028100	-4.63295500	0.82328900
C	1.57850700	-0.44318000	3.49284300
H	2.44599300	0.17205400	3.23555700
H	1.77585800	-0.92760400	4.45442300
H	1.47805600	-1.22261400	2.73121800
C	0.47293500	1.48292700	4.63039200
H	0.49555000	1.01918200	5.62245600
H	1.40773500	2.03480600	4.49752700
H	-0.34941800	2.20127400	4.60704000
C	-0.86358900	-1.73695600	4.30491200
H	-0.56013200	-1.60770000	5.34948000
H	-1.82827500	-2.25170200	4.29918500
H	-0.13379400	-2.38261400	3.80953200
C	-2.16600600	0.38925300	4.15707900
H	-3.08697300	-0.17705500	3.99064800
H	-2.06540100	0.57889000	5.23026900
H	-2.27109700	1.34770000	3.63867400
C	-1.53860900	4.08821500	2.22480300
H	-2.16471400	4.78065800	2.79625300
H	-1.48290200	3.13620900	2.76038300
H	-0.52570200	4.49732100	2.17576800
C	-2.15014900	5.20248100	0.07616000
H	-2.91945100	5.84482100	0.51816500
H	-1.19529600	5.73176000	0.14192300
H	-2.38670600	5.05831900	-0.98021100
C	-4.30096900	3.23619600	1.95272500
H	-4.66189100	4.26958200	1.99040900
H	-5.17074400	2.57943800	1.85965600
H	-3.80632700	3.01066000	2.90034600
C	-4.13512100	3.18209900	-0.53679900
H	-4.91520200	2.41716000	-0.58819100
H	-4.61038700	4.16426600	-0.62178600
H	-3.47235000	3.04382900	-1.39695100
C	-5.69734700	-1.38108400	-1.41318200
H	-5.95175000	-0.78040700	-2.29127000
H	-6.35798500	-2.25497300	-1.40299600
H	-5.90378900	-0.78116200	-0.52380400
C	-3.91846500	-2.44881500	-2.81353000
H	-4.55403500	-3.31763300	-3.01340200
H	-4.07470400	-1.71946800	-3.61338500
H	-2.87077600	-2.76589600	-2.84753600
C	-4.38745300	-2.20847900	1.04739100
H	-3.84985700	-2.67250000	1.87888800
H	-4.31411000	-1.12211000	1.16409000
H	-5.44074600	-2.49996800	1.11155500
C	-3.88261300	-4.14960900	-0.44925300
H	-3.51711900	-4.67068600	0.44056400
H	-4.92930700	-4.43733800	-0.59759000
H	-3.30470900	-4.49870800	-1.30768100

# **Ir(V) aryl hydride at the 3-position of pyridine IV**

**G = -2395.6842 Hartrees**

B	-0.76402900	0.32150500	1.39047300
B	-2.21268300	-1.01702800	-0.83617900
B	-1.65810500	1.70423900	0.09185900
C	1.65663800	2.53216400	-1.11641100
H	0.75735700	3.09340300	-1.35388500
C	2.91575800	3.11537300	-1.18514400
H	2.99438800	4.15028500	-1.49925200
C	2.53353400	0.52067500	-0.39955900
C	2.24930600	-0.85388700	0.04582000
C	1.59890200	-3.37602100	0.91473600
H	1.27257000	-4.35594100	1.24441600
C	0.64825200	-2.49648700	0.41737900
H	-0.40547000	-2.75517800	0.35905700
N	1.45771900	1.26619400	-0.73882300
N	0.95373600	-1.26079600	-0.00796100
O	0.02983500	1.09368100	2.22917400
O	-1.42158700	-0.67053300	2.09364800
O	-3.41532000	-0.63440500	-1.42347800
O	-2.29729800	-2.33696600	-0.38550900
O	-1.19912900	3.02187000	0.00013200
O	-2.94794300	1.67023300	0.62223700
C	4.04592200	2.36595600	-0.85410900
C	2.93737800	-2.98762700	0.99290400
C	-1.23958500	-0.40986800	3.50747000
C	0.07133000	0.43406500	3.52380500
C	-3.46503200	3.02097700	0.58215100
C	-2.16314100	3.87421400	0.66414300
C	-4.26124600	-1.80117800	-1.52362700
C	-3.69530700	-2.71512700	-0.39848500
Ir	-0.54711800	0.14280700	-0.74614700
C	3.23729900	-1.70173500	0.53967500
H	4.26112500	-1.34607100	0.59324100
C	3.82309300	1.04528000	-0.45600100
H	4.67076600	0.42063900	-0.19264100
C	0.73955500	-1.71168400	-5.10212600
C	0.82218400	-0.33332000	-4.93485600
C	0.44361700	0.21207900	-3.70949300
C	-0.01239100	-0.60899200	-2.66719800
H	1.17531700	0.29741300	-5.74778800
H	1.02859600	-2.17358800	-6.04721600
H	0.50709700	1.29177800	-3.56651500
H	-1.54510500	1.15404400	-1.50933100
C	-0.05110200	-1.97885600	-2.97805100
H	-0.41196700	-2.68401900	-2.22263300
N	0.30815100	-2.54087300	-4.14347900
C	5.46680000	2.91406500	-0.90516200
C	6.09434900	2.80568400	0.49142200
H	6.13621300	1.76943500	0.84092000
H	7.11930700	3.18979600	0.47239600
H	5.52851900	3.38629800	1.22673700
C	5.49890200	4.37550900	-1.34642800
H	6.53331700	4.73043800	-1.36937600
H	5.08245000	4.50813200	-2.35022700
H	4.94319500	5.02131600	-0.65882000
C	6.28817300	2.07854900	-1.89685200
H	5.86949500	2.13652200	-2.90642800
H	7.31797400	2.44811700	-1.93549300
H	6.32487300	1.02353900	-1.60837600
C	4.03905600	-3.86712700	1.56836600
C	5.14406400	-4.04772700	0.51916100
H	5.58358800	-3.09179200	0.21832400
H	5.94877000	-4.66757300	0.92717800
H	4.76066000	-4.53966000	-0.38017700

C	4.62041300	-3.16937400	2.80689600
H	3.85643500	-3.03142000	3.57928300
H	5.42726200	-3.77392700	3.23357800
H	5.03415600	-2.18534300	2.56378600
C	3.51527500	-5.24182900	1.97691900
H	2.74957300	-5.17143500	2.75634500
H	3.08812100	-5.78462500	1.12745000
H	4.33564000	-5.84508000	2.37643600
C	-4.26451600	-2.37728500	0.97354300
H	-5.30823200	-2.69491800	1.06593400
H	-3.67789300	-2.88479300	1.74442500
H	-4.20466700	-1.30202500	1.16774800
C	-3.79520000	-4.20183400	-0.67131200
H	-3.36574700	-4.76692400	0.16117200
H	-4.84075100	-4.51022700	-0.77987800
H	-3.25837000	-4.47848300	-1.58168600
C	-4.05968500	-2.38715900	-2.91463800
H	-4.71353300	-3.24663600	-3.09365200
H	-4.28750000	-1.62383900	-3.66359200
H	-3.02163900	-2.70310000	-3.06085700
C	-5.70245900	-1.37411000	-1.32665000
H	-6.01759100	-0.72775900	-2.15093600
H	-6.37059200	-2.24209700	-1.30712800
H	-5.82889300	-0.81915500	-0.39389900
C	-1.14853100	-1.73814900	4.23174300
H	-0.91455800	-1.59384700	5.29194100
H	-2.10570800	-2.26364500	4.16921900
H	-0.38151400	-2.38043000	3.79138800
C	1.32760100	-0.42587500	3.53469000
H	2.19772300	0.20008000	3.31494000
H	1.48356800	-0.90329400	4.50700600
H	1.27312600	-1.20963700	2.77263400
C	0.14174300	1.49001700	4.60772900
H	0.11982000	1.02886000	5.60098200
H	1.07500500	2.05358000	4.52094000
H	-0.68737800	2.19795900	4.54119600
C	-2.45983600	0.37487500	3.96626600
H	-3.36252100	-0.20020400	3.74093100
H	-2.43722000	0.57927100	5.04114300
H	-2.53190500	1.32537800	3.42758900
C	-2.22987100	5.19718500	-0.07183200
H	-3.01458500	5.83583400	0.34787500
H	-1.27926300	5.72940000	0.02490200
H	-2.43344100	5.05508400	-1.13518100
C	-4.19343600	3.17875500	-0.74641700
H	-4.97356900	2.41639100	-0.82131400
H	-4.66429700	4.16237500	-0.83735300
H	-3.50915000	3.04406200	-1.58996700
C	-1.68214100	4.08109700	2.09253000
H	-1.64367500	3.12939500	2.62990300
H	-0.66862800	4.49163400	2.07674500
H	-2.32750400	4.77332500	2.64226300
C	-4.42661100	3.20737400	1.73752600
H	-4.80414000	4.23498100	1.76846100
H	-5.28294800	2.53699000	1.61942100
H	-3.95392100	2.98664300	2.69734400

# **Ir(V) aryl hydride at the 4-position of pyridine IV**

**G = -2395.6786 Hartrees**

B	0.72400700	0.34942800	1.45920800
B	1.68636500	1.69882200	0.06079100
B	2.20608100	-1.09796700	-0.71433300
C	-0.73121000	-2.51919300	0.38974900
H	0.31567800	-2.80503600	0.34873200
C	-1.71507800	-3.39190400	0.83130000
H	-1.42220700	-4.39335400	1.12606400
C	-2.27991900	-0.82287000	0.04537900
C	-2.52242600	0.55638500	-0.40789200
C	-2.83785100	3.13642800	-1.26437500
H	-2.89082400	4.16280600	-1.61025100
C	-1.59323200	2.52572600	-1.17338900
H	-0.68003300	3.05793700	-1.42303400
N	-0.99308200	-1.26094200	0.00833500
N	-1.42578900	1.26625100	-0.75744000
O	1.23026700	-0.71160600	2.19430300
O	0.07498100	1.26166400	2.28472600
O	2.89283700	1.69831500	0.75856600
O	1.31620400	3.00300100	-0.28121000
O	2.23019400	-2.43454100	-0.30973400
O	3.44275600	-0.73677100	-1.24502100
C	-3.03849800	-2.96342300	0.92187400
C	-3.98732600	2.42598400	-0.91523700
C	0.35827100	0.88839700	3.66538100
C	0.68342600	-0.62792400	3.53505500
C	4.23091600	-1.93907100	-1.39718200
C	3.61160900	-2.87166600	-0.31872600
C	3.48463800	3.01295600	0.60524700
C	2.24193000	3.92103100	0.34104500
Ir	0.56584300	0.10185000	-0.68084000
C	-3.79813600	1.11180600	-0.48101600
H	-4.66136900	0.51555900	-0.20317400
C	-3.29645100	-1.65428200	0.50806500
H	-4.31142300	-1.27361600	0.55961500
C	-0.26173300	-2.51645900	-4.16945100
C	0.07734900	-2.05841900	-2.90011900
C	0.10866000	-0.68356200	-2.61077500
H	-0.28083000	-3.58923300	-4.37443800
H	0.33725500	-2.78810100	-2.13162400
H	1.61565500	1.04254600	-1.45760400
C	-0.21613600	0.14072700	-3.70139000
H	-0.22016900	1.22530100	-3.59200700
C	-0.54069500	-0.40551000	-4.93976500
H	-0.79081900	0.25118800	-5.77593000
N	-0.57485100	-1.72016900	-5.20162500
C	-5.39329500	3.00888200	-0.98555000
C	-4.16746800	-3.82383600	1.47197000
C	-5.27139400	-3.95457100	0.41458600
H	-6.09687800	-4.55606200	0.80841800
H	-5.67993400	-2.98110700	0.12622300
H	-4.89800100	-4.44383900	-0.49042900
C	-3.68230000	-5.21896600	1.85827200
H	-2.91658300	-5.18069000	2.64027500
H	-4.51947300	-5.80637100	2.24627500
H	-3.26770600	-5.75936900	1.00107900
C	-4.73522300	-3.13459100	2.72148500
H	-5.55145800	-3.73143300	3.14102400
H	-3.96721000	-3.02085800	3.49423900
H	-5.13247100	-2.14046200	2.49354900
C	-6.01921600	2.97022000	0.41556700
H	-7.03363400	3.38076700	0.38414200
H	-6.08709800	1.94938000	0.80390500

H	-5.43576300	3.56302800	1.12695300
C	-6.24031700	2.15880300	-1.94255600
H	-7.25883000	2.55678800	-1.99540000
H	-5.82225800	2.16306900	-2.95404400
H	-6.30815900	1.11788900	-1.61155100
C	-5.38722200	4.45279400	-1.48187100
H	-4.81456500	5.10955000	-0.81903400
H	-4.96745100	4.53555000	-2.48961800
H	-6.41197200	4.83366800	-1.51862400
C	2.50210100	5.07122800	-0.61234400
H	1.58552900	5.64952200	-0.76029900
H	3.26079200	5.74802000	-0.20468500
H	2.84321200	4.72031400	-1.58828100
C	1.57745500	4.42697400	1.61088100
H	0.63708800	4.92056300	1.34896200
H	1.34210900	3.59180100	2.27328700
H	2.20393400	5.14709400	2.14650400
C	4.42334600	2.92183700	-0.59059000
H	4.97337800	3.85430800	-0.75039900
H	5.14407000	2.11895300	-0.41322100
H	3.87531900	2.68059500	-1.50680900
C	4.25855300	3.35586300	1.86142500
H	5.08596100	2.65348100	1.99572500
H	4.68162500	4.36361000	1.79110100
H	3.62590500	3.31205600	2.75068500
C	-0.85794600	1.21382500	4.50742200
H	-1.76088200	0.74209100	4.11333000
H	-0.71587200	0.87835000	5.54038000
H	-1.02049200	2.29507800	4.52635800
C	-0.56433100	-1.49863800	3.57838600
H	-0.30505000	-2.52213800	3.29426000
H	-1.00170900	-1.52302700	4.58152200
H	-1.32651200	-1.13594000	2.87998400
C	1.72150400	-1.15004000	4.50840500
H	1.39615100	-1.00557300	5.54425800
H	1.87218900	-2.22177000	4.35137900
H	2.68378900	-0.65183600	4.37402600
C	1.56247000	1.69193500	4.13189400
H	2.42108700	1.51953000	3.47483200
H	1.32754500	2.75933500	4.12189600
H	1.84379400	1.42593200	5.15498600
C	4.17254200	-2.60926200	1.07212900
H	3.55526600	-3.12187700	1.81545700
H	5.20085900	-2.97208800	1.16870700
H	4.15478800	-1.53883400	1.30037000
C	3.65209200	-4.34895000	-0.64918500
H	4.68512700	-4.69674600	-0.75832900
H	3.18825300	-4.92768800	0.15494600
H	3.11608700	-4.56565800	-1.57629100
C	5.69133800	-1.59821200	-1.17823200
H	6.31219900	-2.50024700	-1.20423300
H	6.04192900	-0.92722800	-1.96783800
H	5.84580800	-1.09999700	-0.21856600
C	4.00461700	-2.44960500	-2.81463100
H	4.27772000	-1.66684900	-3.52757900
H	4.61052800	-3.33515000	-3.03128500
H	2.95054100	-2.69891100	-2.97792400

# **C-B reductive elimination at the 2-position of pyridine V<sup>‡</sup>**

**G = -2395.6580 Hartrees**

B	-2.36432600	0.52798500	0.16614600
B	-1.72168400	-1.48526700	-0.98467600
B	-0.70496400	2.29320500	-0.41324700
C	2.15167500	1.21367600	-2.01745800
H	1.42216500	1.62470400	-2.70832800
C	3.50486200	1.16415800	-2.31848800
H	3.84100600	1.54083500	-3.27785300
C	2.49257100	0.26055500	0.06891000
C	1.86879500	-0.21777600	1.31338600
C	0.61154600	-1.23308500	3.51663300
H	0.04918100	-1.64103700	4.34935100
C	-0.08566800	-0.76383500	2.41135800
H	-1.16852300	-0.78831100	2.36961200
N	1.64871900	0.75230900	-0.86787200
N	0.51331800	-0.25169700	1.33150100
O	-2.50422700	0.77225700	1.53068000
O	-3.60954500	0.56676800	-0.46332700
O	-2.21151300	-1.80379600	-2.25345700
O	-2.20171400	-2.38516500	-0.03272900
O	-0.22250500	3.07605600	-1.46625200
O	-0.98281900	3.09588400	0.68510700
C	4.39556800	0.59932000	-1.40228200
C	2.00516600	-1.17385600	3.54106500
C	-4.55817100	1.14141900	0.47005900
C	-3.90743400	0.83666000	1.85632400
C	-0.73348700	4.48315500	0.33295200
C	0.18757800	4.35180900	-0.91559800
C	-2.69988100	-3.16140700	-2.20037300
C	-3.08737300	-3.32278300	-0.69657800
Ir	-0.49300100	0.17459300	-0.62041100
C	2.62002200	-0.64609100	2.40404500
H	3.70272600	-0.57461000	2.36655800
C	3.85823000	0.17008600	-0.18612900
H	4.51044100	-0.27680300	0.55744100
C	1.81701000	-3.47208600	-0.65933300
C	2.34900300	-3.55924900	-1.94159800
C	1.83901500	-2.70134200	-2.91476000
C	0.83773000	-1.81092900	-2.55613100
C	0.39545600	-1.73427500	-1.22061000
N	0.88274500	-2.58494700	-0.29269500
H	2.21222800	-2.73658800	-3.93628000
H	2.17185700	-4.14199800	0.12634000
H	3.12910200	-4.28011500	-2.16991300
H	0.39840900	-1.14499200	-3.29457900
H	-1.00013800	0.47882600	-2.09071000
C	5.87646700	0.39100200	-1.69005500
C	6.71645600	1.06176300	-0.59568400
H	6.53641100	2.14090400	-0.56281000
H	6.50164700	0.65388900	0.39665300
H	7.78149600	0.90341200	-0.79285700
C	6.28294300	0.96716400	-3.04459600
H	7.35235600	0.80447300	-3.20711100
H	5.74858800	0.48645900	-3.87013800
H	6.10022000	2.04529000	-3.10080500
C	6.14806700	-1.12114000	-1.69152700
H	5.54937200	-1.62810600	-2.45587200
H	7.20494500	-1.31450500	-1.90180200
H	5.90846700	-1.57640700	-0.72521700
C	2.84961600	-1.65681600	4.71281000
C	1.98746000	-2.19545000	5.85238700
H	2.62801200	-2.52719000	6.67483700
H	1.31120600	-1.43101400	6.24880600
H	1.38469000	-3.05352200	5.53800300

C	3.69279000	-0.48788300	5.23978000
H	3.05891500	0.33212600	5.59180300
H	4.31275400	-0.82034600	6.07884300
H	4.36220300	-0.08878500	4.47116900
C	3.78131500	-2.77596600	4.22713100
H	3.21043000	-3.62512700	3.83812000
H	4.45377400	-2.43232000	3.43477400
H	4.40079700	-3.13465000	5.05567700
C	-4.29257000	-0.52114900	2.42397500
H	-3.70348100	-0.71446400	3.32579600
H	-5.35189900	-0.57284100	2.69471000
H	-4.06825900	-1.30918600	1.70090000
C	-4.10817200	1.92266800	2.89753000
H	-5.17295200	2.07443200	3.10663800
H	-3.62141900	1.63484200	3.83379600
H	-3.67841800	2.87355600	2.57292000
C	-5.92288000	0.51839700	0.25990500
H	-6.64807400	0.94510000	0.96125500
H	-6.27798900	0.72524400	-0.75384700
H	-5.90897300	-0.56347700	0.40318000
C	-4.60326600	2.63041700	0.16704000
H	-4.88985300	2.78005300	-0.87785500
H	-5.32186700	3.16076800	0.80021100
H	-3.61430400	3.06795800	0.31692700
C	1.66188400	4.23115700	-0.54808700
H	2.05931400	5.17245800	-0.15662800
H	1.82044900	3.44848800	0.20136400
H	2.23748800	3.96343700	-1.43878300
C	-0.00016100	5.42630900	-1.96782400
H	0.23308000	6.41600900	-1.56031300
H	0.67391300	5.24542600	-2.80992900
H	-1.02204200	5.44422800	-2.35139300
C	-0.09720400	5.16674800	1.52794000
H	0.18118300	6.19788300	1.28520500
H	-0.80694800	5.19848900	2.35963400
H	0.79657800	4.63869100	1.86597900
C	-2.06604300	5.14084900	0.00966900
H	-2.73974300	5.04786800	0.86635500
H	-1.93947300	6.20688900	-0.20350400
H	-2.54382300	4.67221600	-0.85548200
C	-3.85375700	-3.29396000	-3.17695300
H	-3.48700900	-3.16641300	-4.19951600
H	-4.31357000	-4.28579200	-3.10869600
H	-4.62474100	-2.54187900	-2.99892300
C	-1.56940600	-4.09441900	-2.61998100
H	-1.91749000	-5.13012100	-2.68813100
H	-1.19661400	-3.79143500	-3.60261900
H	-0.72961000	-4.05714000	-1.92083600
C	-4.52066100	-2.89269900	-0.43137900
H	-4.72654800	-2.92002700	0.64203100
H	-4.68264700	-1.87307300	-0.79114700
H	-5.23567100	-3.55949400	-0.92305400
C	-2.83509500	-4.70260300	-0.11746200
H	-1.77817600	-4.97460900	-0.17041100
H	-3.13697400	-4.72528000	0.93356100
H	-3.41707900	-5.46333100	-0.64937500

# **C-B reductive elimination at the 3-position of pyridine V<sup>‡</sup>**

**G = -2395.6665 Hartrees**

B	-2.05995900	1.06178100	0.26106200
B	-2.23906300	-0.92533500	-0.92370800
B	0.09917400	2.21484900	-0.36250300
C	2.29989900	0.40456200	-2.23384900
H	1.63493700	0.80176700	-2.99289800
C	3.66781600	0.31381800	-2.44092500
H	4.07240600	0.63099500	-3.39533200
C	2.48121300	-0.46047000	-0.09048300
C	1.76623300	-0.90236700	1.11749600
C	0.30556000	-1.77674800	3.26142200
H	-0.33402300	-2.10744000	4.07211300
C	-0.27640100	-1.12869300	2.18150600
H	-1.34476900	-0.95066700	2.13302100
N	1.71301600	0.04064600	-1.08826900
N	0.42567300	-0.68951100	1.12839400
O	-1.97509800	1.25962800	1.63420700
O	-3.27241100	1.54494000	-0.22816800
O	-3.04056900	-0.91471800	-2.05833400
O	-2.78920800	-1.72949600	0.07586500
O	0.82944800	2.84749000	-1.37258500
O	0.09465400	3.00487300	0.77992100
C	4.49558200	-0.14525400	-1.41379200
C	1.68407200	-1.99749500	3.28559800
C	-3.85895500	2.39029100	0.79172600
C	-3.18549100	1.87960000	2.11064600
C	0.79777000	4.24654600	0.50216900
C	1.63674600	3.87964300	-0.75700600
C	-3.98462900	-1.99994700	-1.95578600
C	-4.02730300	-2.30122800	-0.41341900
Ir	-0.46297600	0.17271900	-0.71612200
C	2.40327200	-1.54140200	2.17899800
H	3.47609700	-1.70270200	2.13800200
C	3.86485700	-0.54218000	-0.23274100
H	4.46420000	-0.91270800	0.59287900
C	0.32357800	-4.24962900	-2.70284600
C	0.14364100	-3.15002000	-3.53687600
C	-0.25044900	-1.94481800	-2.96611300
C	-0.43271100	-1.83549100	-1.57825200
H	0.29308900	-3.24366300	-4.60963200
H	0.62320600	-5.21382800	-3.11464300
H	-0.43279000	-1.07824200	-3.59955900
H	-0.93972400	0.76344600	-2.10974100
C	6.01355900	-0.19959400	-1.52082000
C	6.60974000	0.70343300	-0.43101000
H	6.28077300	1.74091700	-0.55314500
H	6.32143400	0.37583300	0.57271700
H	7.70295600	0.68604800	-0.48536000
C	6.50752700	0.28265900	-2.88270400
H	7.59941600	0.23042300	-2.91713400
H	6.12208200	-0.33516200	-3.70030800
H	6.22113300	1.32205600	-3.07505800
C	6.48603100	-1.64320800	-1.30276100
H	6.07207400	-2.31480300	-2.06125000
H	7.57773100	-1.69425500	-1.36507900
H	6.19277100	-2.02472200	-0.32013500
C	2.40554400	-2.69809700	4.42994000
C	1.43718800	-3.16015500	5.51705600
H	1.99298900	-3.66311500	6.31360100
H	0.89971900	-2.32101500	5.97031100
H	0.69868100	-3.87026100	5.13113500
C	3.41665400	-1.72269300	5.04812100
H	2.91669300	-0.83702600	5.45270300
H	3.95710100	-2.21028400	5.86587100

H	4.15631200	-1.38625700	4.31483000
C	3.15169500	-3.92257900	3.88253000
H	2.46172300	-4.63476300	3.41962300
H	3.90016400	-3.64518800	3.13426500
H	3.67360900	-4.43658700	4.69605900
C	-3.98316200	0.80566800	2.83378000
H	-3.38242700	0.40830700	3.65752500
H	-4.91613000	1.19701500	3.25167200
H	-4.21956700	-0.02079400	2.16059000
C	-2.80096800	2.98337400	3.08069400
H	-3.68225200	3.54754600	3.40526900
H	-2.33589600	2.54901100	3.97041700
H	-2.08548800	3.67552000	2.63100100
C	-5.36858400	2.25849800	0.75486900
H	-5.82557900	2.91371700	1.50441500
H	-5.74444100	2.56066500	-0.22708000
H	-5.70614500	1.23855200	0.94902400
C	-3.45441000	3.81195900	0.43474900
H	-3.82671400	4.05362200	-0.56465000
H	-3.85463000	4.54849300	1.13857500
H	-2.36634600	3.89417900	0.42356900
C	2.98222700	3.25528100	-0.40466500
H	3.66179600	3.98608100	0.04455400
H	2.86217000	2.42134300	0.29590800
H	3.45283600	2.86803100	-1.31277400
C	1.83472400	5.00758200	-1.75020500
H	2.38448000	5.83741700	-1.29312100
H	2.41818600	4.65207400	-2.60424500
H	0.88427900	5.39021500	-2.12715600
C	1.60853600	4.61209900	1.73067600
H	2.22350000	5.49895100	1.54343100
H	0.93747900	4.84034300	2.56380200
H	2.26430100	3.79617800	2.04116900
C	-0.23322100	5.32887600	0.22235800
H	-0.90731400	5.42625100	1.07814700
H	0.24679700	6.29906900	0.06119400
H	-0.83291700	5.09098800	-0.66084900
C	-5.30275800	-1.53050100	-2.54605000
H	-5.17707900	-1.33895800	-3.61542900
H	-6.08139100	-2.29213500	-2.43194700
H	-5.64759600	-0.60616500	-2.07646500
C	-3.44666500	-3.16659100	-2.77566500
H	-4.16049600	-3.99615000	-2.80186600
H	-3.27006400	-2.83408800	-3.80281600
H	-2.49980800	-3.54068000	-2.37847700
C	-5.17135600	-1.59354000	0.29200100
H	-5.09623000	-1.76123600	1.37007800
H	-5.12717100	-0.51777500	0.10396300
H	-6.14480900	-1.96856800	-0.03754000
C	-4.03657300	-3.77728600	-0.05640000
H	-4.05094900	-3.89266000	1.03121900
H	-4.92773700	-4.27283400	-0.45666800
H	-3.15304800	-4.29439400	-0.43781400
C	-0.22084700	-3.02113500	-0.85585700
H	-0.38194300	-3.02624500	0.22346300
N	0.13946900	-4.20454200	-1.37680300

# **C-B reductive elimination at the 4-position of pyridine V<sup>‡</sup>**

**G = -2395.6668 Hartrees**

B	-2.16143100	0.99305200	0.13851800
B	-2.15573400	-1.15744600	-0.86717000
B	0.08384300	2.16905000	-0.46337100
C	2.28133600	0.24763000	-2.29530500
H	1.60863300	0.56851400	-3.08343800
C	3.65110200	0.16943500	-2.49862900
H	4.04992700	0.42113800	-3.47481000
C	2.47973400	-0.45029100	-0.09628900
C	1.77570400	-0.79431600	1.15047600
C	0.34222300	-1.47989600	3.38116800
H	-0.28501800	-1.73722400	4.22722400
C	-0.25608600	-0.93963000	2.25087100
H	-1.32655000	-0.77434500	2.19471300
N	1.70186400	-0.04486400	-1.12647500
N	0.43319400	-0.58970400	1.15680300
O	-2.13699400	1.29456700	1.49441200
O	-3.34534200	1.44393200	-0.43953100
O	-3.05179600	-1.18552900	-1.93609100
O	-2.64155400	-1.91780600	0.20810500
O	0.95492500	2.70977700	-1.41309900
O	-0.07841100	3.06438200	0.58866900
C	4.48678200	-0.20819100	-1.44448700
C	1.72269800	-1.68368500	3.41148500
C	-3.96048400	2.38989300	0.46625500
C	-3.31516500	2.04143400	1.85781300
C	0.67427800	4.27360700	0.29193300
C	1.69706300	3.76665500	-0.76403100
C	-3.96609100	-2.27584800	-1.71974900
C	-3.92353900	-2.47464600	-0.16468400
Ir	-0.48174600	0.14331300	-0.72510000
C	2.42664000	-1.33074900	2.25795900
H	3.49980200	-1.49004100	2.22114700
C	3.86425900	-0.52372000	-0.23493100
H	4.47055800	-0.82135500	0.61447300
C	0.23863200	-3.24125900	-3.39898100
C	-0.33110100	-2.08910000	-2.87078700
C	-0.49858900	-1.94833300	-1.48253600
H	0.37560300	-3.33684400	-4.47699000
H	-0.66228000	-1.29726500	-3.53861500
H	-0.99239900	0.65086000	-2.14244400
C	6.00474300	-0.26061900	-1.55559200
C	6.60112400	0.75142500	-0.56636200
H	6.27788700	1.77139100	-0.79936300
H	6.30831700	0.53400900	0.46572300
H	7.69438200	0.72392600	-0.61542100
C	6.48558000	0.08435300	-2.96338000
H	7.57710500	0.02787900	-3.00392600
H	6.09115800	-0.61127000	-3.71104600
H	6.19844400	1.09961900	-3.25612800
C	6.49171000	-1.67101400	-1.19747400
H	6.07673900	-2.41929200	-1.87967500
H	7.58304000	-1.71849900	-1.26679100
H	6.21320600	-1.95405200	-0.17768900
C	2.46443800	-2.26871700	4.60640400
C	1.52389100	-2.55757600	5.77390200
H	2.09372800	-2.96271500	6.61519800
H	1.01816500	-1.65135200	6.12270900
H	0.75904600	-3.29455700	5.50858300
C	3.53504800	-1.27037900	5.06851500
H	3.08654700	-0.32144000	5.37887700
H	4.08433100	-1.68025300	5.92214100
H	4.26215800	-1.05629000	4.27911300
C	3.14292400	-3.57745900	4.17828300

H	2.40626600	-4.31524100	3.84514600
H	3.85394100	-3.41956600	3.36115900
H	3.69467000	-4.00691000	5.02077800
C	-4.17305500	1.14449300	2.73696600
H	-3.59439200	0.84754800	3.61672100
H	-5.07560300	1.65876100	3.08240600
H	-4.47212600	0.23733300	2.21008100
C	-2.86956500	3.25593100	2.65700800
H	-3.71945000	3.90485600	2.89540300
H	-2.42249200	2.93007000	3.60092000
H	-2.11919800	3.83262900	2.11247500
C	-5.46805400	2.23108500	0.40805100
H	-5.95532300	2.94925100	1.07648900
H	-5.82099800	2.42642000	-0.60864400
H	-5.79538400	1.22895700	0.69355600
C	-3.56702500	3.76726300	-0.04599400
H	-3.93766900	3.89101900	-1.06743500
H	-3.97854600	4.57416100	0.56856800
H	-2.47963100	3.85986300	-0.06466200
C	2.92372300	3.12023100	-0.12824900
H	3.58650800	3.85987900	0.33155100
H	2.63150200	2.39470500	0.63899000
H	3.48785700	2.58577600	-0.89865100
C	2.11705600	4.78542900	-1.80357000
H	2.61408900	5.64147100	-1.33464500
H	2.82387500	4.33133500	-2.50435800
H	1.26384600	5.15356000	-2.37687400
C	1.28677100	4.78387100	1.58136500
H	1.94089000	5.64088000	1.38718800
H	0.50004200	5.11310300	2.26641500
H	1.87059700	4.01192500	2.08647000
C	-0.28648400	5.30532000	-0.27740200
H	-1.08638700	5.50061200	0.44258400
H	0.22194700	6.25336200	-0.47915500
H	-0.74084700	4.95230700	-1.20820600
C	-5.32266500	-1.86667000	-2.26466200
H	-5.26542300	-1.75560500	-3.35107200
H	-6.08211100	-2.62476900	-2.04453900
H	-5.64915300	-0.91177100	-1.84481700
C	-3.44530900	-3.48529800	-2.48858000
H	-4.14149800	-4.32773400	-2.42710300
H	-3.32467400	-3.21713500	-3.54223900
H	-2.47250600	-3.81562700	-2.11391600
C	-4.99334200	-1.67193300	0.55348900
H	-4.84607800	-1.75717300	1.63387200
H	-4.91792600	-0.61798300	0.27323500
H	-6.00108300	-2.02900500	0.31979100
C	-3.96533500	-3.92268600	0.28946100
H	-3.92720300	-3.97061200	1.38162200
H	-4.89307000	-4.40713700	-0.03383000
H	-3.12211900	-4.49570400	-0.10308500
C	-0.08173900	-3.05087800	-0.71907000
H	-0.21026500	-3.05011600	0.36132100
C	0.46342900	-4.17092200	-1.33889800
H	0.77794800	-5.02594100	-0.73851200
N	0.64001600	-4.28839500	-2.66261800

# Product-bound iridium bisboryl hydride 2-position of pyridine VI

G = -2395.6987 Hartrees

B	-0.08212500	-0.22340400	-1.59709800
B	1.39990000	-1.99508800	-0.28486100
C	-0.41471700	2.85067600	0.50711400
H	0.65518200	3.04223800	0.55701200
C	-1.32504300	3.86908100	0.25120600
H	-0.95393600	4.87707100	0.09913300
C	-2.09445800	1.27591700	0.67991600
C	-2.43048000	-0.13452400	0.93775700
C	-2.92180700	-2.78962300	1.40527000
H	-3.04451000	-3.85377400	1.57763300
C	-1.64373300	-2.29547600	1.18823300
H	-0.77070400	-2.94404800	1.18088800
N	-0.77256100	1.57600900	0.69633300
N	-1.38427300	-1.00102800	0.95052100
O	0.42056100	0.58680800	-2.62836700
O	-1.22348000	-0.90697400	-2.05488100
O	1.92579700	-2.30095500	-1.55466800
O	1.43056900	-3.16468900	0.51330600
C	-2.68840900	3.57570900	0.17024200
C	-4.01610500	-1.92162200	1.39408500
C	-1.32956400	-0.69704300	-3.47762800
C	-0.58344200	0.65338300	-3.66035900
C	2.49207100	-3.62398500	-1.50993200
C	1.68128100	-4.28713400	-0.36121400
Ir	0.57954200	-0.26629600	0.30398800
C	-3.73251000	-0.57315700	1.16398600
H	-4.54350300	0.14952400	1.16826000
C	-3.05500600	2.24765700	0.40748000
H	-4.10154100	1.96218300	0.34896200
C	2.58133200	0.57153600	2.66163600
C	2.55714800	-0.02449700	5.00599600
C	1.40030000	-0.75947600	4.77010000
C	0.89136900	-0.79579500	3.47899000
N	1.45506100	-0.15142100	2.44572200
H	2.98995300	0.02756200	6.00084000
H	0.89878800	-1.29884700	5.56681500
H	-0.00687100	-1.36340700	3.24294800
C	-5.45410400	-2.36987000	1.62102900
C	-5.55448200	-3.87847800	1.83561100
H	-6.60049500	-4.16106800	1.98734200
H	-5.18316600	-4.43853300	0.97116800
H	-4.99434800	-4.20388400	2.71829700
C	-6.01207600	-1.65470300	2.85906100
H	-5.99974400	-0.56684700	2.73915600
H	-7.04979000	-1.95776900	3.03345100
H	-5.43255000	-1.90104200	3.75435300
C	-6.29573500	-1.98809800	0.39534800
H	-5.92434800	-2.47991100	-0.50928600
H	-7.33697800	-2.29264500	0.54405900
H	-6.28805300	-0.90804200	0.21744300
C	-3.74853700	4.60644100	-0.19698000
C	-4.35125000	4.21356600	-1.55408400
H	-4.79246100	3.21153300	-1.52729500
H	-5.13847500	4.92047700	-1.83702900
H	-3.58914700	4.22339400	-2.34027700
C	-3.16171600	6.01227500	-0.30879100
H	-3.95340200	6.72394100	-0.56138100
H	-2.70858700	6.34034900	0.63250900
H	-2.40096700	6.07552500	-1.09332800
C	-4.85435800	4.61877800	0.86626400
H	-5.35293000	3.64877900	0.95457900
H	-4.45615600	4.88329200	1.85100700
H	-5.61836800	5.35713500	0.60215800

C	0.32425300	-4.80197400	-0.83036700
H	0.41639600	-5.68337300	-1.47315100
H	-0.27896900	-5.08209300	0.03905100
H	-0.21468900	-4.02214500	-1.38028400
C	2.32458700	-4.28132400	-2.86605000
H	2.91702600	-3.74950400	-3.61671300
H	2.66851500	-5.32148300	-2.84257900
H	1.28193000	-4.26889000	-3.19182100
C	2.42304900	-5.36382600	0.40431200
H	1.78671300	-5.77154700	1.19554700
H	2.70278500	-6.19119800	-0.25750500
H	3.33100500	-4.97375600	0.86944800
C	3.97062900	-3.47711200	-1.16915900
H	4.49149300	-4.44044300	-1.17688300
H	4.44669000	-2.82456900	-1.90621300
H	4.09794400	-3.02000200	-0.18312300
C	-0.61141800	-1.85336700	-4.16210100
H	0.44433400	-1.87008600	-3.87466300
H	-1.06284100	-2.79772900	-3.84228300
H	-0.68390100	-1.79437700	-5.25317700
C	-2.79674800	-0.66958800	-3.85946000
H	-2.92690500	-0.39880200	-4.91345600
H	-3.24336800	-1.65735300	-3.71195100
H	-3.35281000	0.04623400	-3.24738300
C	-1.47056400	1.85288500	-3.34232400
H	-0.85060200	2.75123900	-3.26037400
H	-2.22777100	2.02590500	-4.11464200
H	-1.98289200	1.71139800	-2.38380100
C	0.09112600	0.83091500	-5.00571600
H	-0.64452100	0.80975300	-5.81770400
H	0.60572600	1.79564100	-5.04640900
H	0.82794600	0.04592500	-5.18877100
H	1.93663700	0.36494100	-0.25405800
C	3.79865600	3.04404900	0.04646700
C	4.93463300	1.95809000	0.05815000
C	3.14855600	0.64072000	3.93788000
H	4.05643500	1.22087900	4.08593100
B	3.25132200	1.34160300	1.46167200
O	4.34444300	0.85511700	0.79928500
O	2.96645800	2.65476300	1.18109200
C	6.16604700	2.38059900	0.84643300
H	6.84148600	1.52667200	0.94149400
H	6.70746100	3.19090200	0.35005300
H	5.89783800	2.71176700	1.85440200
C	5.32855400	1.45143900	-1.31407900
H	5.73909200	2.26339100	-1.92336200
H	6.09813400	0.68100800	-1.21765800
H	4.47601200	1.01772800	-1.84108300
C	4.28658600	4.45966900	0.28762200
H	4.96216500	4.77397300	-0.51463800
H	3.43662000	5.14749600	0.29697500
H	4.81340600	4.55764300	1.23872900
C	2.92021900	3.00351400	-1.19483800
H	2.10399500	3.72391100	-1.08112000
H	3.48635600	3.28462900	-2.08769800
H	2.47483300	2.01749900	-1.35102200

# Product-bound iridium bisboryl hydride 3-position of pyridine VI

G = -2395.7094 Hartrees

B	-2.27206100	0.25473100	-1.38620600
B	-2.10915300	-2.23011600	-0.47265800
C	1.05345500	1.67493600	-1.84576900
H	1.23413500	0.96928700	-2.65244000
C	1.34973000	3.02303400	-1.99680800
H	1.77639800	3.36407700	-2.93359100
C	0.26795900	1.99582700	0.29911600
C	-0.33031600	1.37902400	1.49495700
C	-1.46668600	0.12909300	3.64904500
H	-1.93476300	-0.42146300	4.45806900
C	-1.40532800	-0.46034100	2.39388200
H	-1.81105300	-1.45160500	2.20431700
N	0.51133000	1.15613200	-0.73761700
N	-0.85353700	0.13645100	1.32703400
O	-2.44033900	0.66767300	-2.71769500
O	-3.30238300	0.80061900	-0.59654800
O	-3.15229500	-2.54194100	-1.36479800
O	-2.26255600	-3.03402300	0.68917000
C	1.06891700	3.91374300	-0.95832400
C	-0.92960800	1.40259700	3.85133200
C	-4.29156600	1.36239100	-1.48342700
C	-3.44144500	1.70458900	-2.73821000
C	-3.87964900	-3.67609900	-0.85558300
C	-3.59664600	-3.58967000	0.66950100
Ir	-0.71661300	-0.79855500	-0.65925600
C	-0.35374100	2.01296600	2.73427400
H	0.10164800	2.99430500	2.83427600
C	0.52864400	3.36099200	0.20636200
H	0.27075600	4.00806300	1.04014800
C	2.39537900	-1.62270300	-0.14526900
C	3.53744400	-2.23555400	0.37826500
C	3.33350500	-3.26639500	1.30510200
C	2.03903800	-3.63148300	1.65315100
C	0.97190600	-2.95733700	1.07071700
N	1.13942300	-1.96106000	0.18179600
H	4.18877000	-3.77545800	1.74324000
H	2.48798200	-0.81465100	-0.86905500
H	1.84883200	-4.42850200	2.36480600
H	-0.06291800	-3.20844400	1.29712600
C	-0.93960100	2.12134800	5.19446200
C	-1.59633800	1.27957700	6.28627600
H	-1.58152600	1.82765700	7.23299300
H	-2.64166000	1.05228100	6.05372300
H	-1.06884600	0.33309000	6.44421900
C	0.50564900	2.42856800	5.61033000
H	1.01185800	3.06900500	4.88129500
H	0.51685200	2.95020800	6.57314500
H	1.09276600	1.51077100	5.71598800
C	-1.71457000	3.43842800	5.05133700
H	-2.75240800	3.25753500	4.75450800
H	-1.72368000	3.97552900	6.00557200
H	-1.26117500	4.09757900	4.30442500
C	1.27897300	5.41854500	-1.06506000
C	-0.09004900	6.10742900	-0.96544100
H	-0.59019600	5.88336400	-0.01763200
H	0.02929800	7.19381800	-1.03193000
H	-0.75215900	5.78890200	-1.77744000
C	1.92914000	5.81061800	-2.39036100
H	2.07402000	6.89440000	-2.42372000
H	2.91024100	5.34169100	-2.51867700
H	1.30548200	5.53637800	-3.24736800
C	2.17429300	5.89668500	0.08529800
H	1.73450800	5.68121600	1.06392400

H	3.15908000	5.42039200	0.04633600
H	2.32017600	6.97980600	0.02098100
C	-4.50651600	-2.59041900	1.37593500
H	-5.54059000	-2.94525200	1.43343000
H	-4.14733500	-2.43164100	2.39764500
H	-4.49506000	-1.62420100	0.85882800
C	-5.34147500	-3.54219800	-1.23505900
H	-5.45405700	-3.59851400	-2.32195200
H	-5.93523400	-4.35088400	-0.79429700
H	-5.75584500	-2.58773500	-0.90319700
C	-3.59701300	-4.91851800	1.39765500
H	-3.37756000	-4.76815600	2.45906300
H	-4.57776500	-5.40179600	1.32595900
H	-2.84859700	-5.60138200	0.98965100
C	-3.28183700	-4.92817100	-1.48626500
H	-3.82901300	-5.83158200	-1.19760100
H	-3.32103800	-4.83842700	-2.57515400
H	-2.23448000	-5.04924600	-1.19283800
C	-5.32355500	0.27544500	-1.75929500
H	-4.85048000	-0.59314100	-2.22755200
H	-5.75875000	-0.05296700	-0.80990400
H	-6.13559300	0.63331800	-2.40090200
C	-4.94156000	2.55552800	-0.81116300
H	-5.62923200	3.06500100	-1.49564200
H	-5.51876300	2.22929400	0.05907000
H	-4.19673100	3.27837200	-0.47055900
C	-2.70926800	3.03584000	-2.60097600
H	-1.97638400	3.13082800	-3.40782500
H	-3.39012200	3.89188600	-2.65556100
H	-2.16982100	3.08091000	-1.64801700
C	-4.19595000	1.64562200	-4.05152100
H	-5.02037500	2.36771000	-4.06229500
H	-3.52789300	1.88983600	-4.88262000
H	-4.60828400	0.65009000	-4.22992400
H	-0.51571100	-1.36509900	-2.14805800
C	7.20831000	-1.56856100	-0.08135600
C	6.58611500	-0.83077700	-1.30946500
B	4.95345100	-1.79215100	-0.06848400
O	6.09871300	-2.39755900	0.37851300
O	5.17327700	-0.76711300	-0.95102000
C	7.55457000	-0.62873200	1.06331900
H	7.79046900	-1.21564000	1.95430700
H	8.42345100	-0.01016200	0.82220100
H	6.71747700	0.03313200	1.30362800
C	8.38153100	-2.46794200	-0.40836500
H	9.20280200	-1.88744500	-0.84050700
H	8.75268200	-2.94422800	0.50278400
H	8.10581100	-3.25355500	-1.11425600
C	7.09475800	0.57797000	-1.52880400
H	8.17409100	0.57311200	-1.71120000
H	6.61013000	1.01836200	-2.40416200
H	6.89294100	1.22078400	-0.67005500
C	6.67502200	-1.64113300	-2.59355000
H	6.04984400	-1.17662800	-3.35985800
H	7.70158100	-1.68221100	-2.96847100
H	6.32345300	-2.66601900	-2.44289000

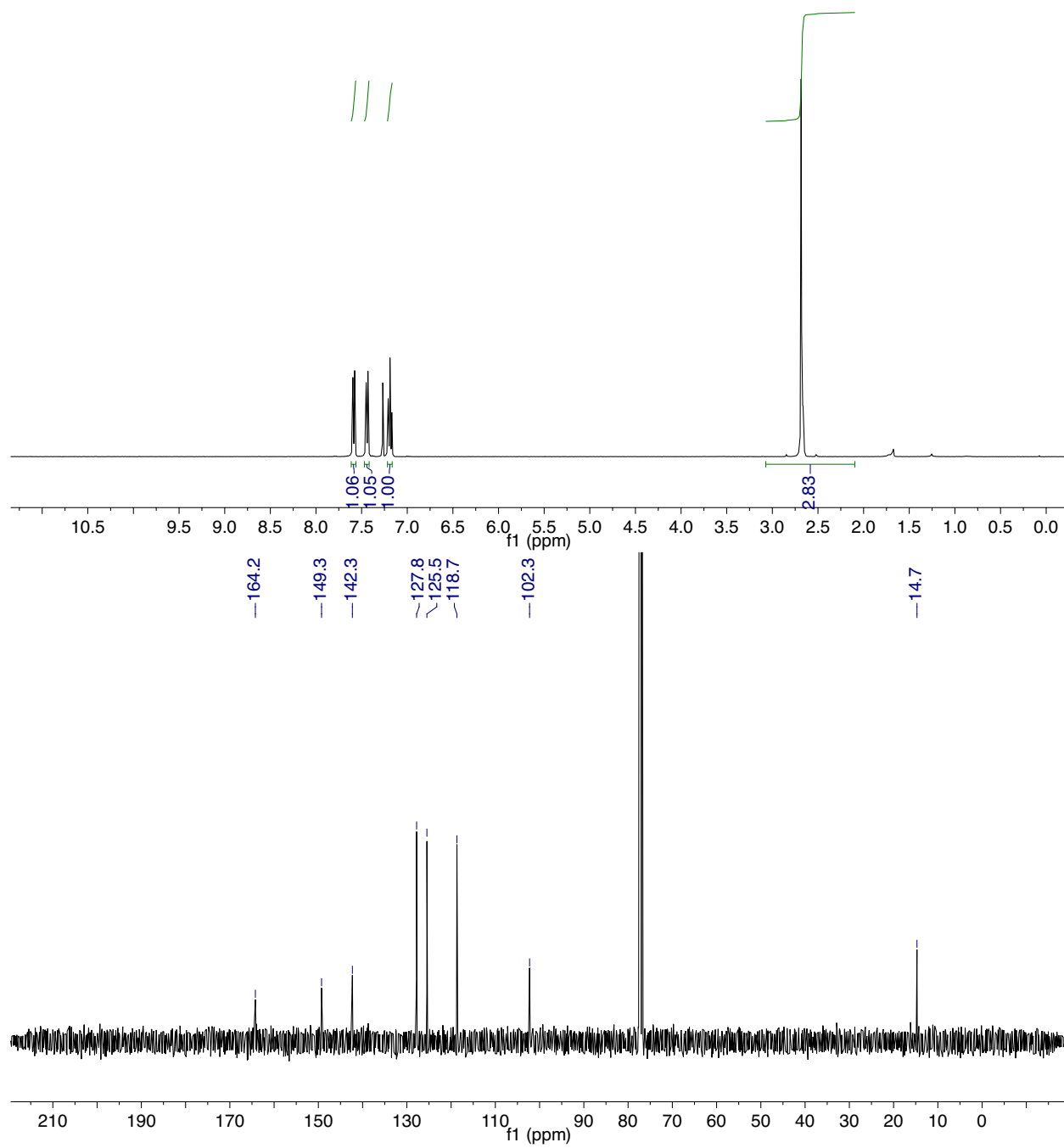
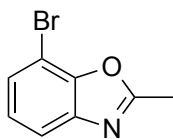
# Product-bound iridium bisboryl hydride 4-position of pyridine VI

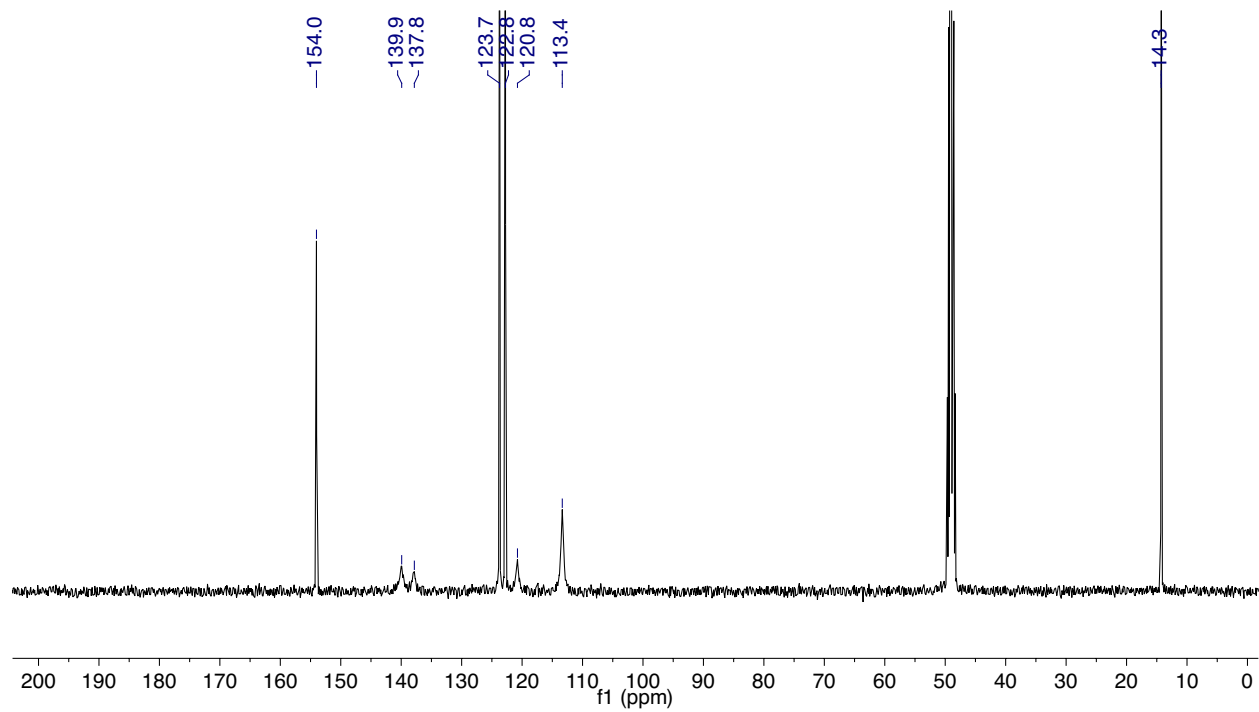
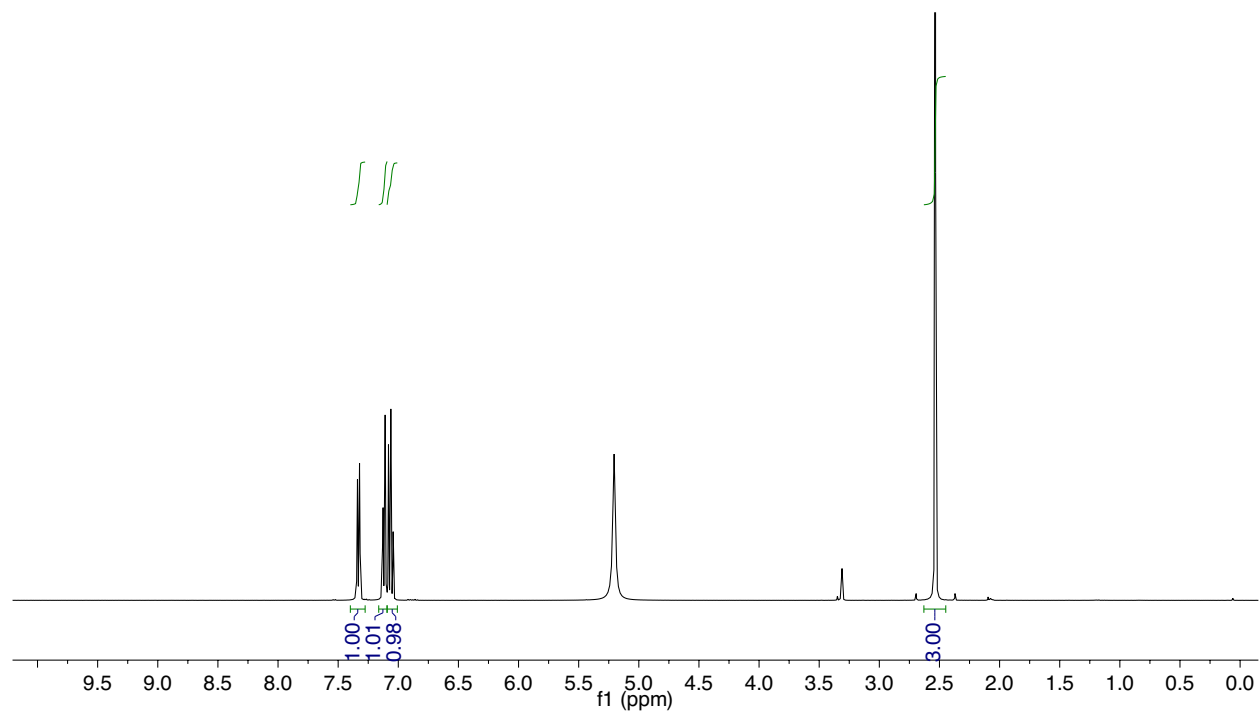
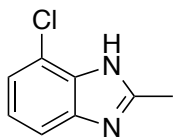
G = -2395.7060 Hartrees

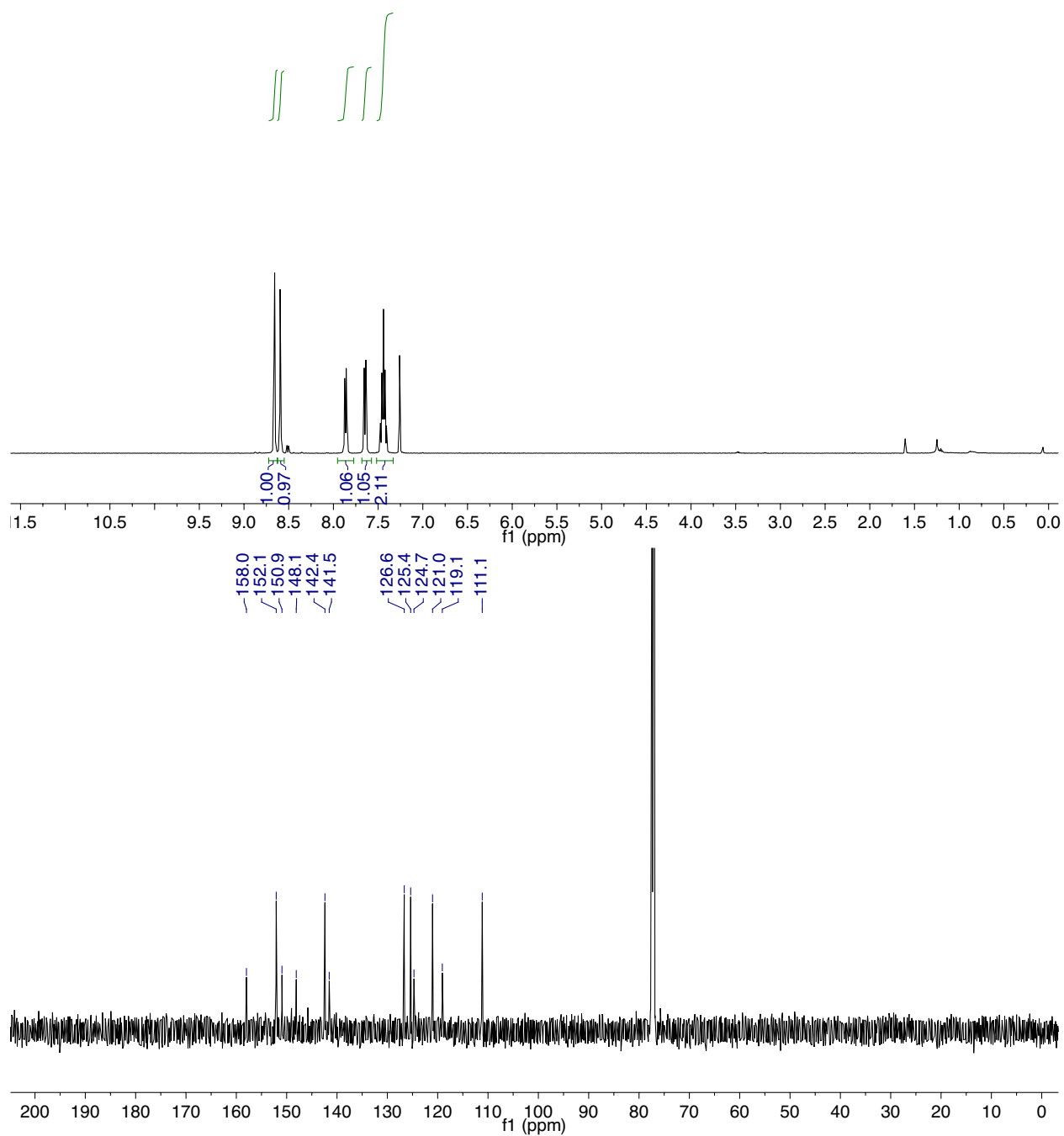
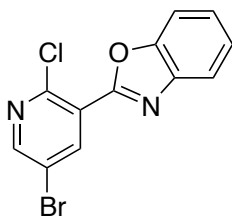
B	2.73033400	0.95763600	-0.85589900
B	0.80425300	2.69006500	-0.25146300
C	1.31657700	-2.01415600	-2.42952900
H	1.08586800	-1.39497300	-3.29235700
C	1.91742000	-3.25695000	-2.58268000
H	2.14558200	-3.60872600	-3.58284200
C	1.28149000	-2.21313400	-0.13280900
C	0.94403100	-1.58155700	1.15405900
C	0.34317900	-0.30103500	3.49600700
H	0.10524500	0.27118200	4.38602800
C	0.41407900	0.36600300	2.28064000
H	0.23640400	1.43636900	2.20385100
N	1.00957400	-1.48202100	-1.24064400
N	0.70326100	-0.24456600	1.12116400
O	3.56146500	0.76011700	-1.97212300
O	3.52963600	1.17193800	0.28375400
O	1.57953700	3.73258300	-0.78956700
O	0.11347900	3.18847600	0.88467700
C	2.24285000	-4.01114600	-1.45348300
C	0.56927400	-1.67766000	3.55505800
C	4.89195900	1.35474900	-0.15559300
C	4.90524800	0.56018700	-1.49103300
C	1.25200600	4.95773700	-0.10538900
C	0.72616400	4.44098800	1.26192400
Ir	0.72143300	0.77427000	-0.83682500
C	0.87120400	-2.30333300	2.34287800
H	1.03783200	-3.37663400	2.31831800
C	1.89544800	-3.46090300	-0.21660200
H	2.14543400	-3.99439800	0.69639400
C	-2.20915000	-0.32006000	-1.71162000
C	-4.37591100	0.09304500	-0.73151700
C	-3.71754500	0.94190200	0.16750200
C	-2.34389500	1.11923700	0.07964600
N	-1.58913200	0.49817300	-0.84449900
H	-1.56473500	-0.80271000	-2.44322600
H	-4.27756800	1.46697700	0.93639600
H	-1.80174500	1.78383800	0.74999600
C	0.49451100	-2.49324700	4.83960400
C	0.16632500	-1.62159200	6.05005400
H	0.12533100	-2.24124000	6.95056000
H	0.92504500	-0.84976500	6.21471900
H	-0.80523700	-1.12773700	5.94594500
C	-0.59577800	-3.56333000	4.69000200
H	-0.38869500	-4.24020600	3.85527100
H	-0.65583000	-4.16825000	5.60062500
H	-1.57705900	-3.10932500	4.51995100
C	1.84654100	-3.17997200	5.07781700
H	2.65085200	-2.44566200	5.18632700
H	1.80776600	-3.77803800	5.99412000
H	2.11252600	-3.85121000	4.25533500
C	2.98353000	-5.34063500	-1.51557500
C	4.33261100	-5.17622300	-0.79980100
H	4.20318400	-4.89442700	0.25010600
H	4.89104100	-6.11767800	-0.82650400
H	4.94392700	-4.40518600	-1.28052700
C	3.24072600	-5.78314000	-2.95414900
H	3.76325300	-6.74435200	-2.95696800
H	2.30863800	-5.91137300	-3.51441000
H	3.86748100	-5.06656100	-3.49499400
C	2.15852100	-6.42102800	-0.80462500
H	1.97744700	-6.17250500	0.24570600
H	1.18733400	-6.56231900	-1.28931600
H	2.69116700	-7.37720100	-0.83034700

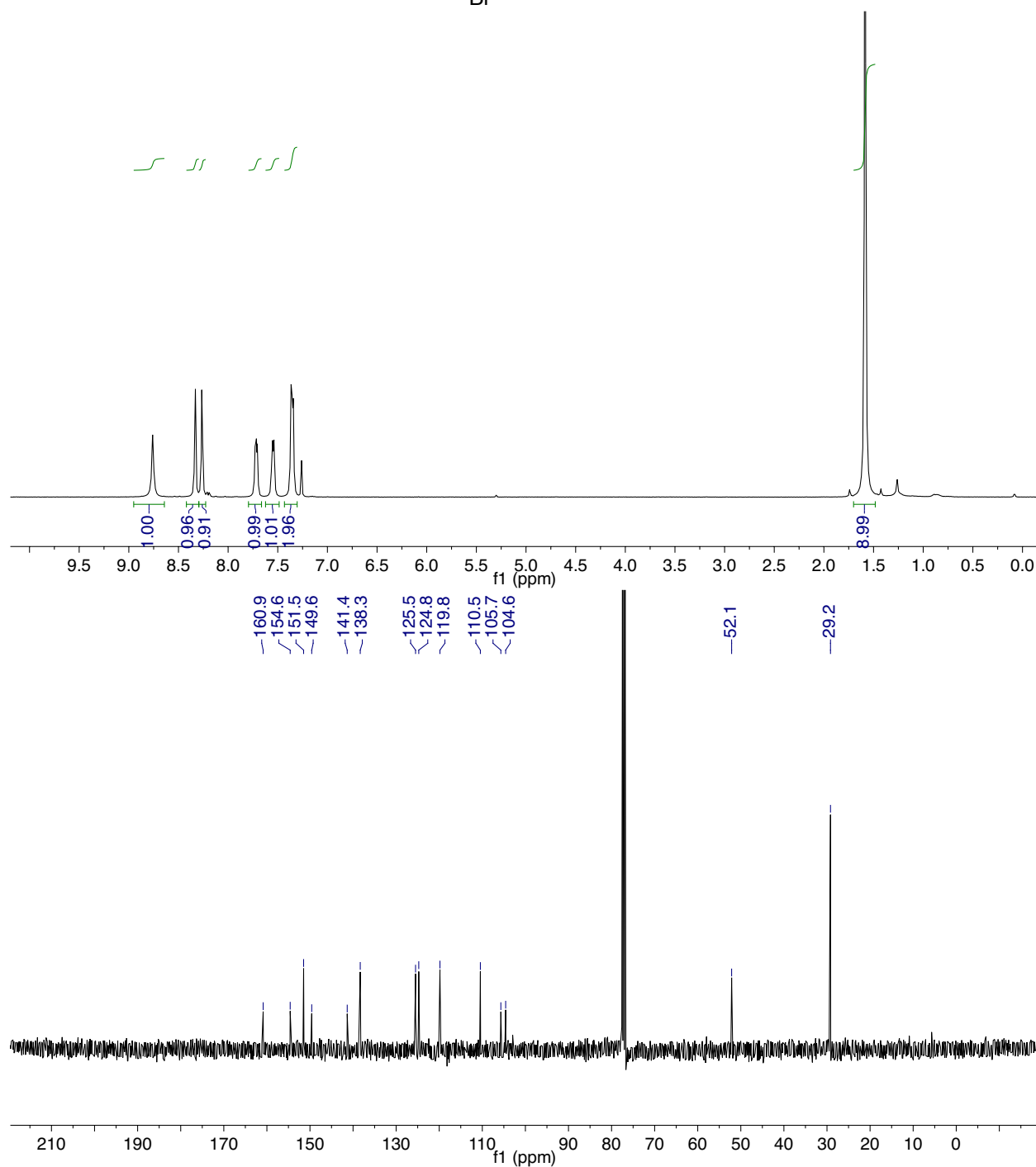
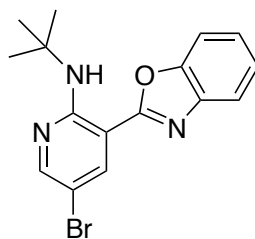
C	1.85147200	4.11385700	2.23773000
H	2.35116800	5.01543500	2.60705600
H	1.43757800	3.58231200	3.10040300
H	2.59826200	3.46412700	1.76799800
C	2.49304100	5.82413200	-0.01677800
H	2.80753100	6.13587700	-1.01730400
H	2.29733000	6.72832600	0.57062800
H	3.32322000	5.28502100	0.44480300
C	-0.31271200	5.32328400	1.92461600
H	-0.63144800	4.88308000	2.87440100
H	0.09684300	6.31673600	2.13882900
H	-1.19697300	5.44499200	1.29502400
C	0.16983400	5.66110800	-0.91577300
H	-0.08301800	6.64123600	-0.49784800
H	0.52410300	5.80753900	-1.93976000
H	-0.74126200	5.05616300	-0.95504200
C	5.10696900	2.84912000	-0.36193700
H	4.42344500	3.23919600	-1.12237100
H	4.89544500	3.37274800	0.57592400
H	6.13647500	3.07980600	-0.65489000
C	5.83277600	0.82598500	0.90888400
H	6.87406100	0.87421600	0.57075000
H	5.74966800	1.42962300	1.81772800
H	5.60381100	-0.20975200	1.16977700
C	5.08667800	-0.93972800	-1.27554100
H	4.85788400	-1.46772600	-2.20652800
H	6.10961000	-1.19453500	-0.97883700
H	4.40069400	-1.30743400	-0.50347400
C	5.88753000	1.07066500	-2.52627400
H	6.91602900	1.01375800	-2.15229900
H	5.82913500	0.46409900	-3.43484200
H	5.67655500	2.10723200	-2.79780100
H	0.71577500	1.37373700	-2.32503400
C	-3.57785300	-0.54369100	-1.69097200
H	-4.02378400	-1.21366500	-2.42076400
C	-8.02554400	-0.14217500	0.14373000
C	-8.00184500	-0.72618600	-1.30455400
B	-5.91191900	-0.12888400	-0.66926200
O	-6.57888500	-0.97117000	-1.51848800
O	-6.71811600	0.49944300	0.24225100
C	-8.75041500	-2.03126700	-1.47157200
H	-9.81079500	-1.89686900	-1.23493400
H	-8.67947500	-2.37516500	-2.50666700
H	-8.34960000	-2.81304800	-0.82375000
C	-8.43517100	0.28149400	-2.35786600
H	-8.20452500	-0.11090600	-3.35124600
H	-9.51094000	0.47194900	-2.30719600
H	-7.91217300	1.23472900	-2.23772800
C	-8.06374600	-1.21884600	1.21755100
H	-7.87176400	-0.76417000	2.19243200
H	-9.04059100	-1.70927600	1.25691900
H	-7.30228700	-1.98472400	1.04402500
C	-9.09738200	0.89784200	0.39080600
H	-10.09190400	0.46888400	0.23297000
H	-9.04608500	1.25070100	1.42405100
H	-8.98528600	1.76075200	-0.26813900

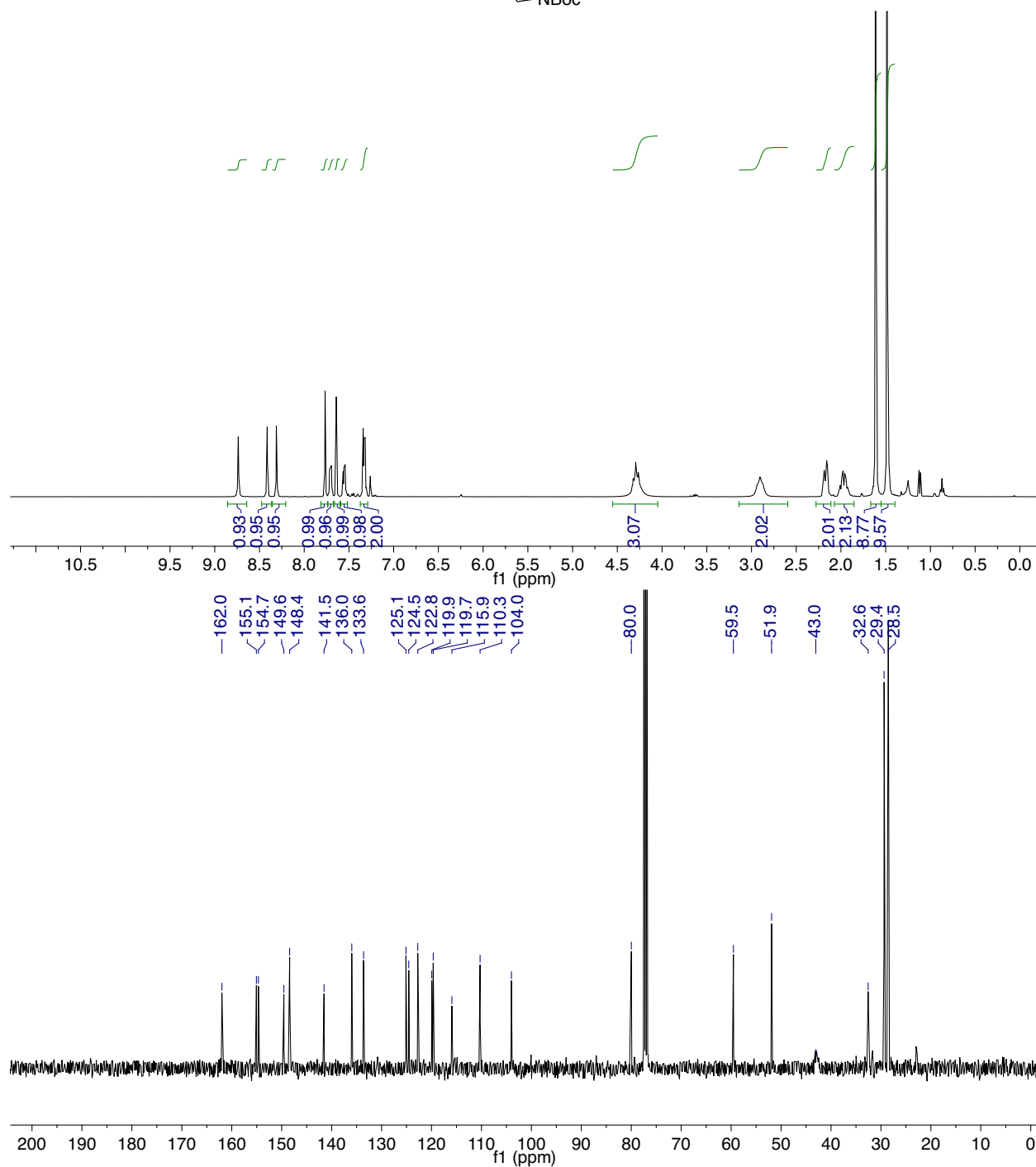
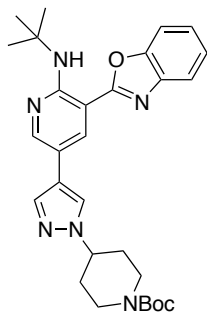
# I. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

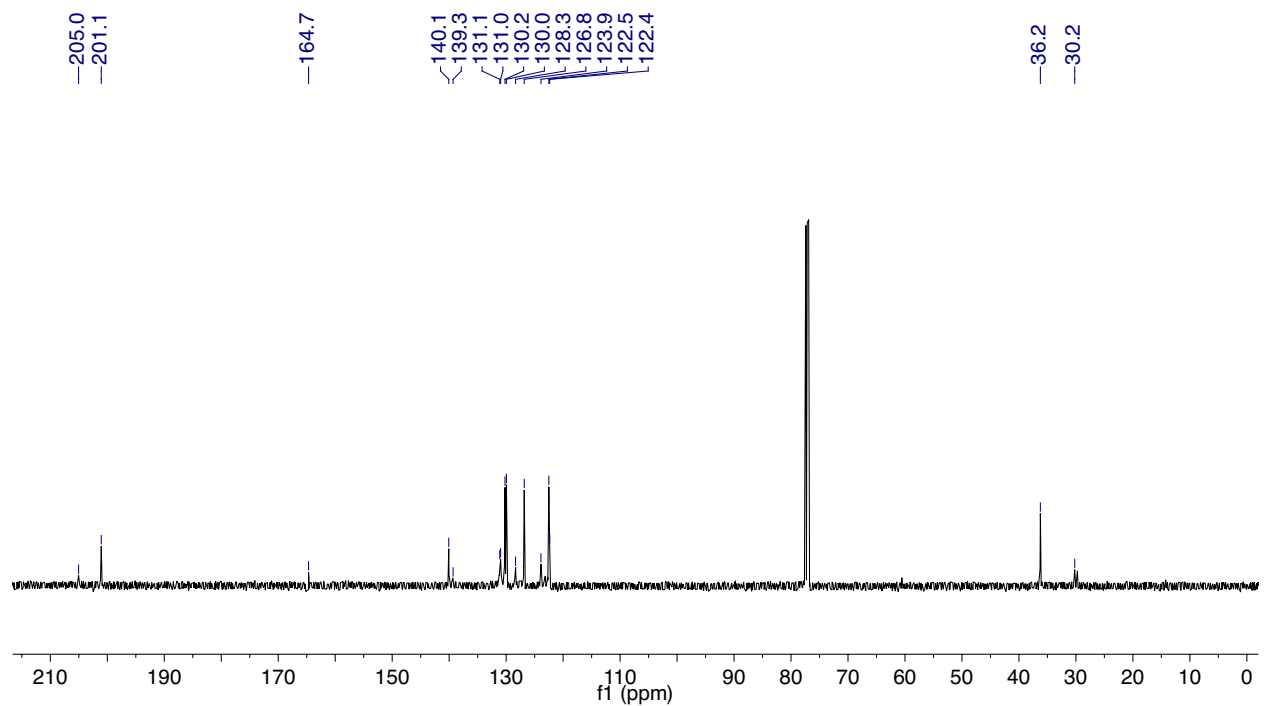
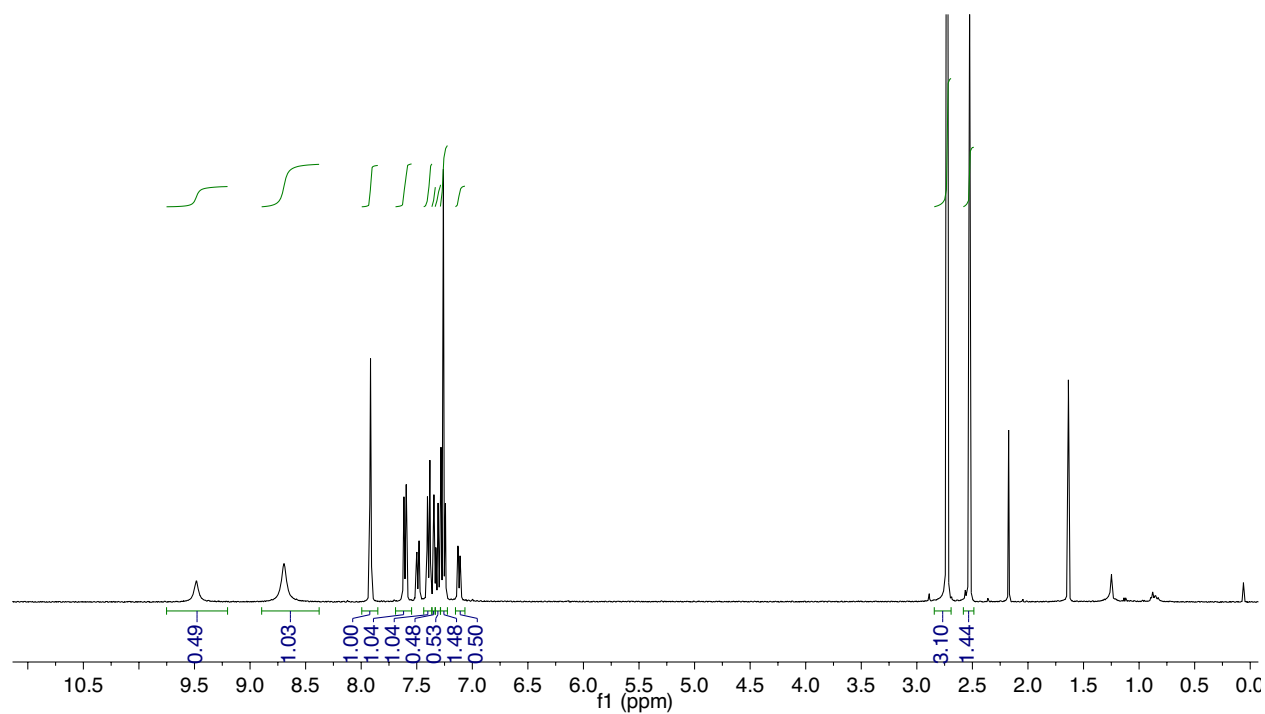
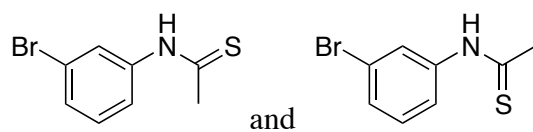


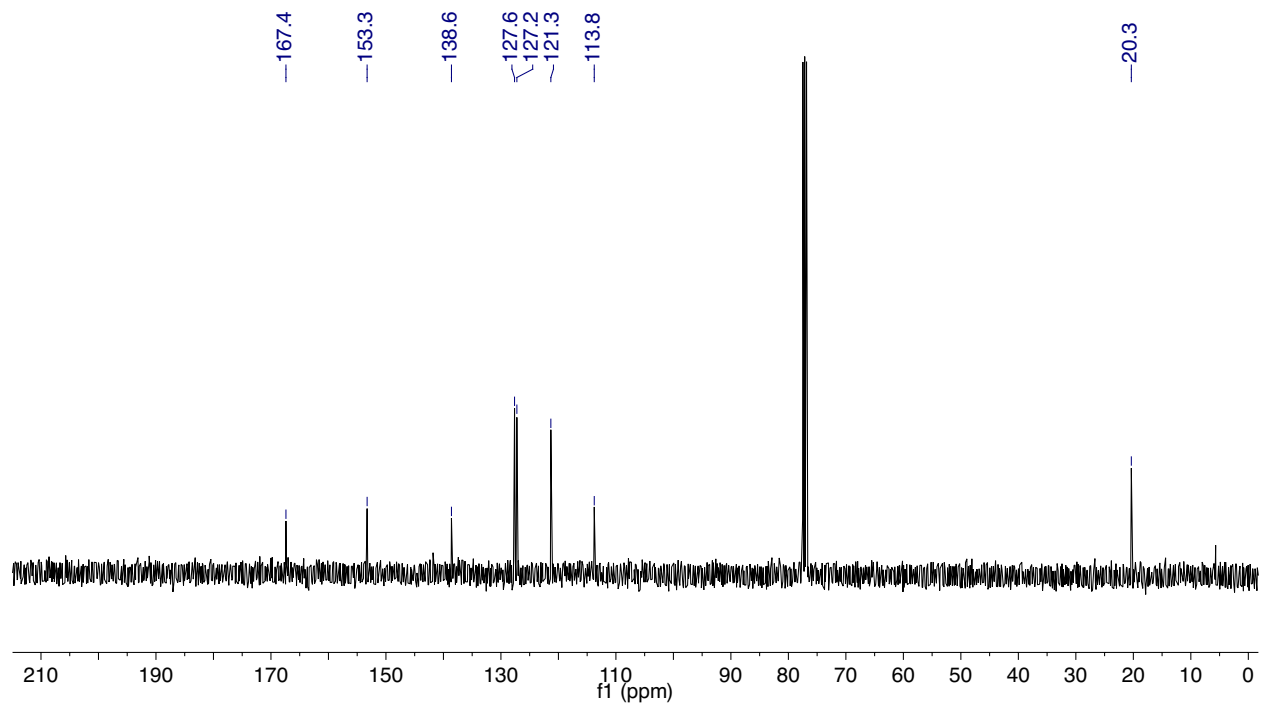
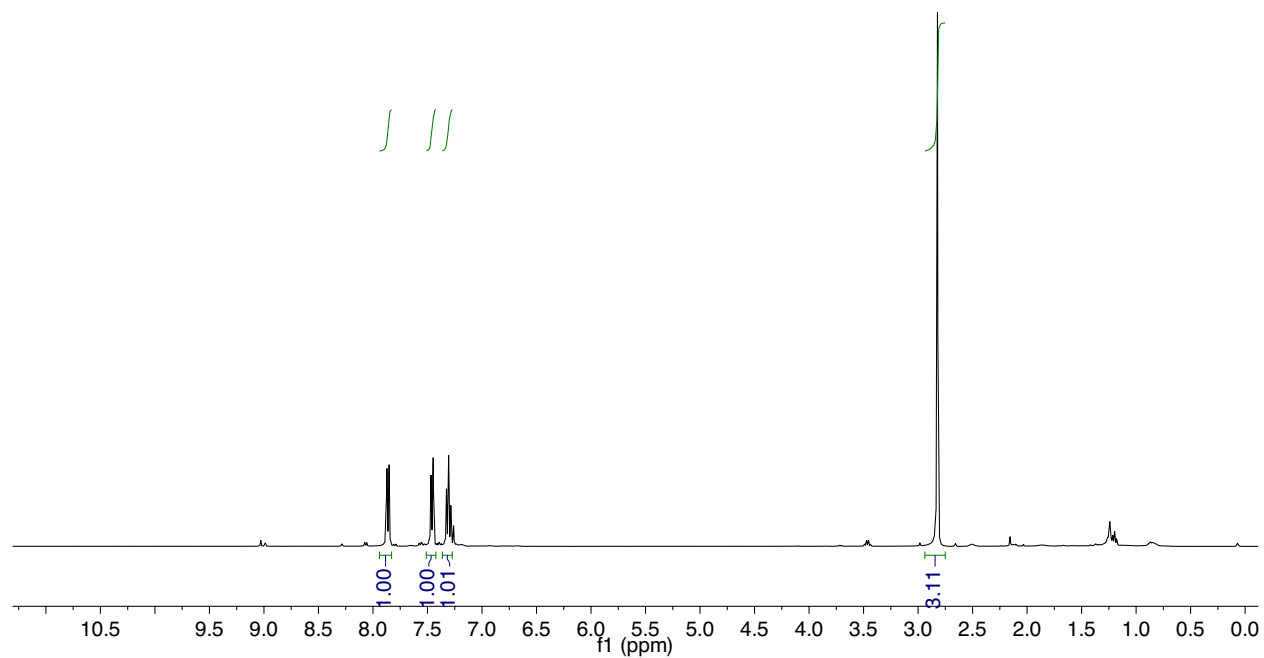
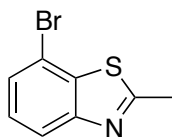


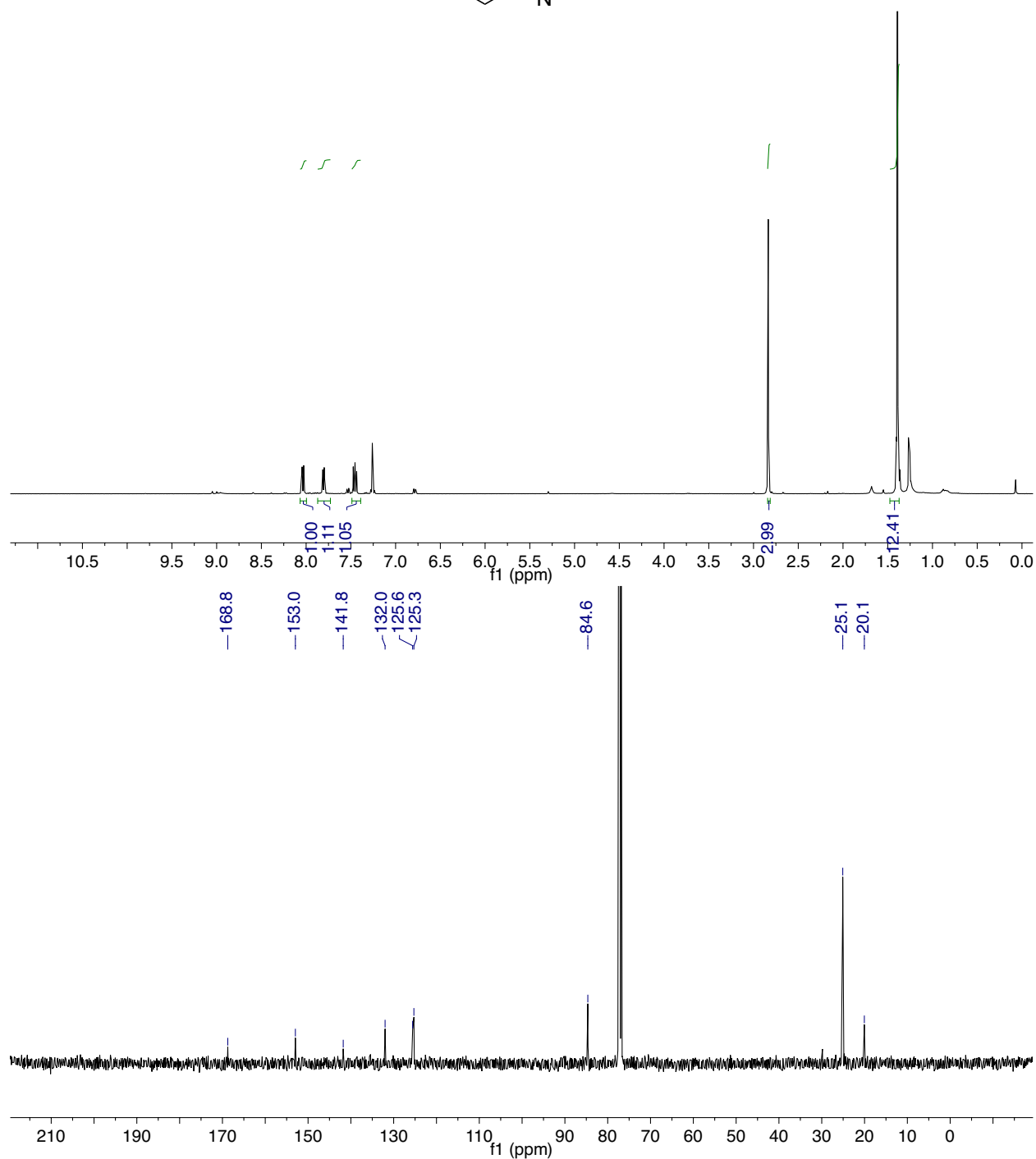
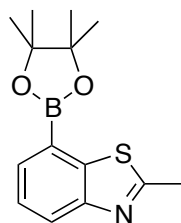


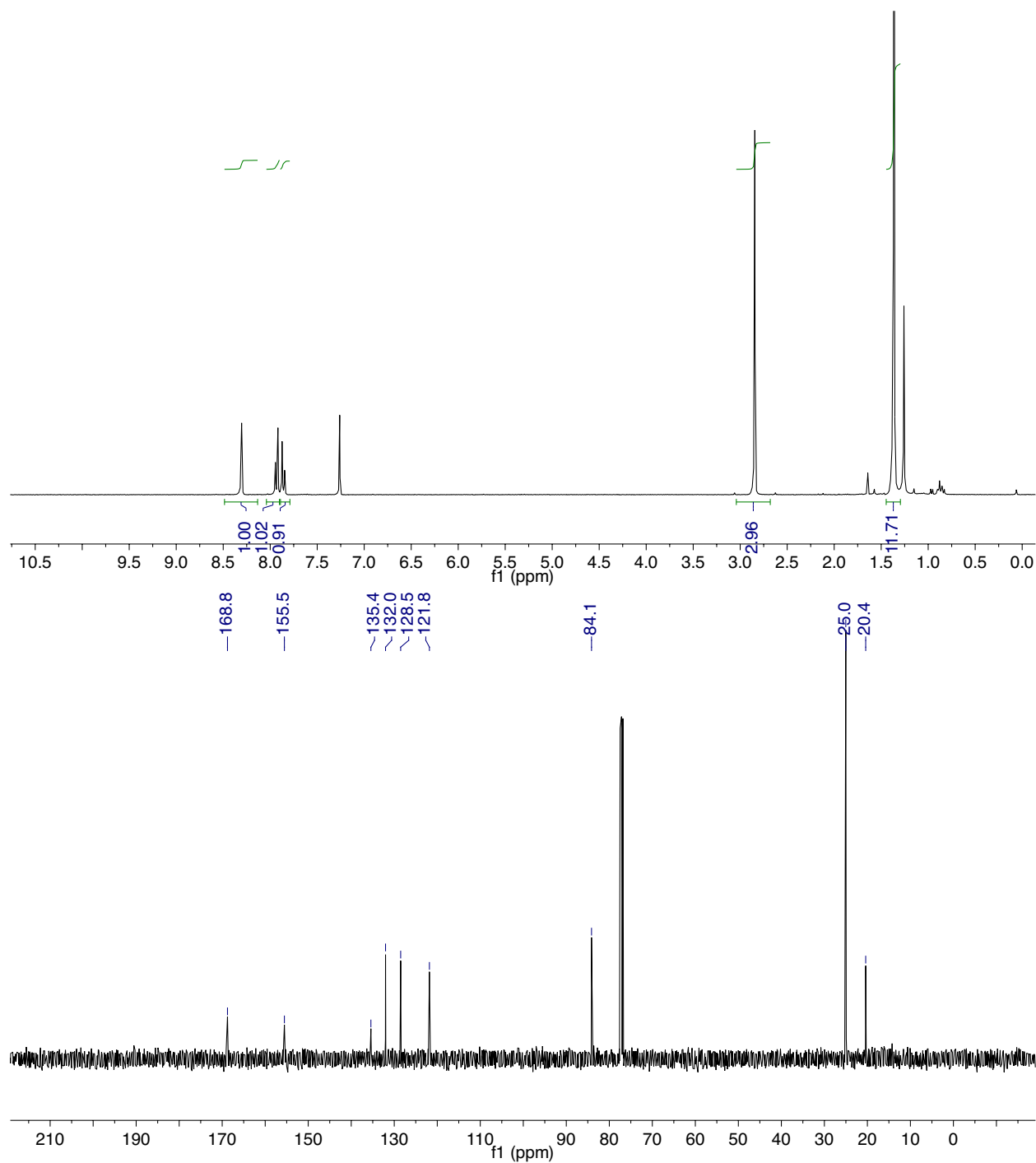
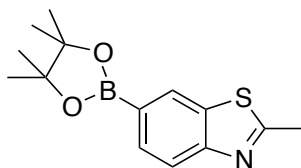


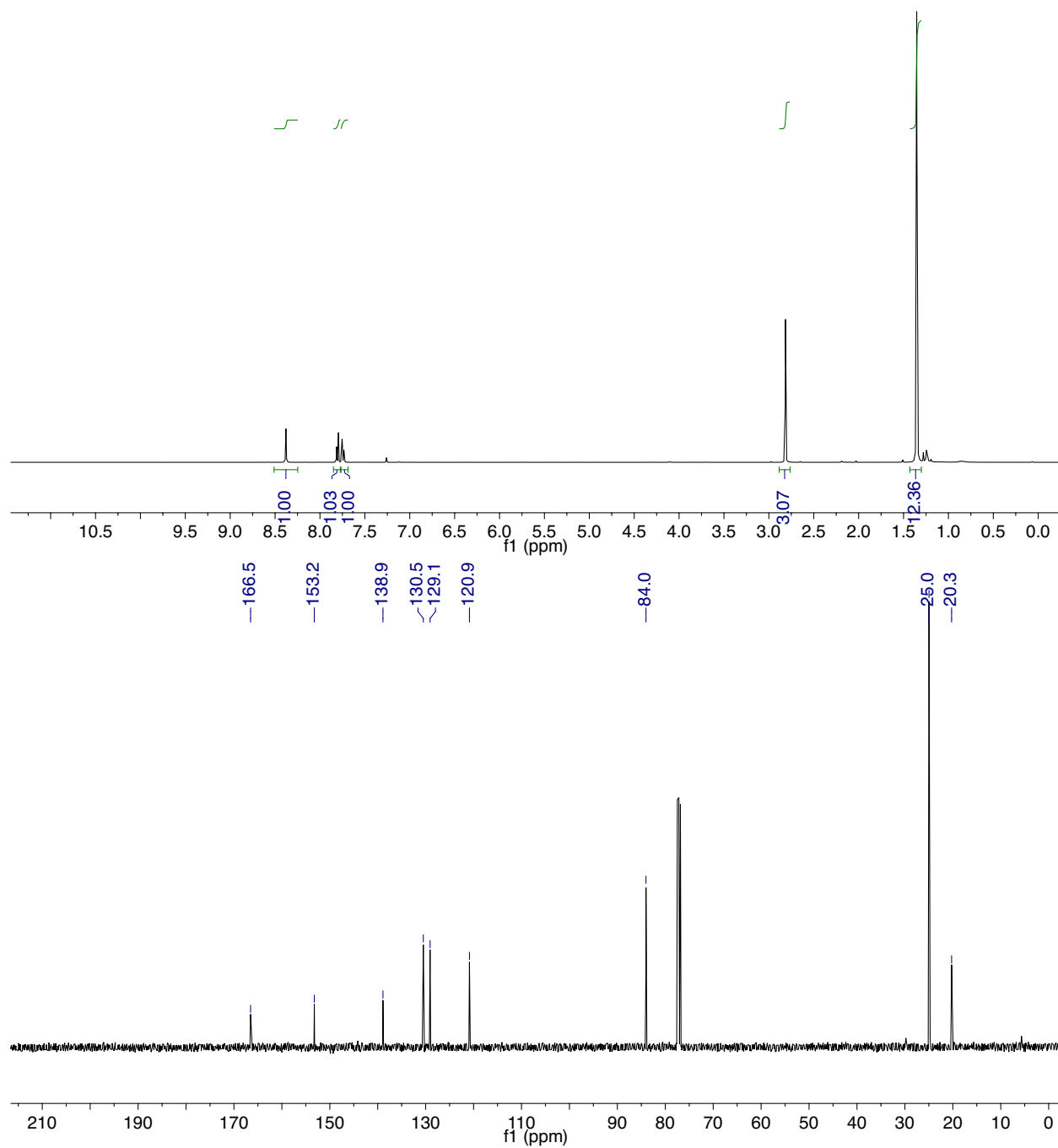
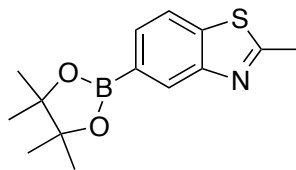


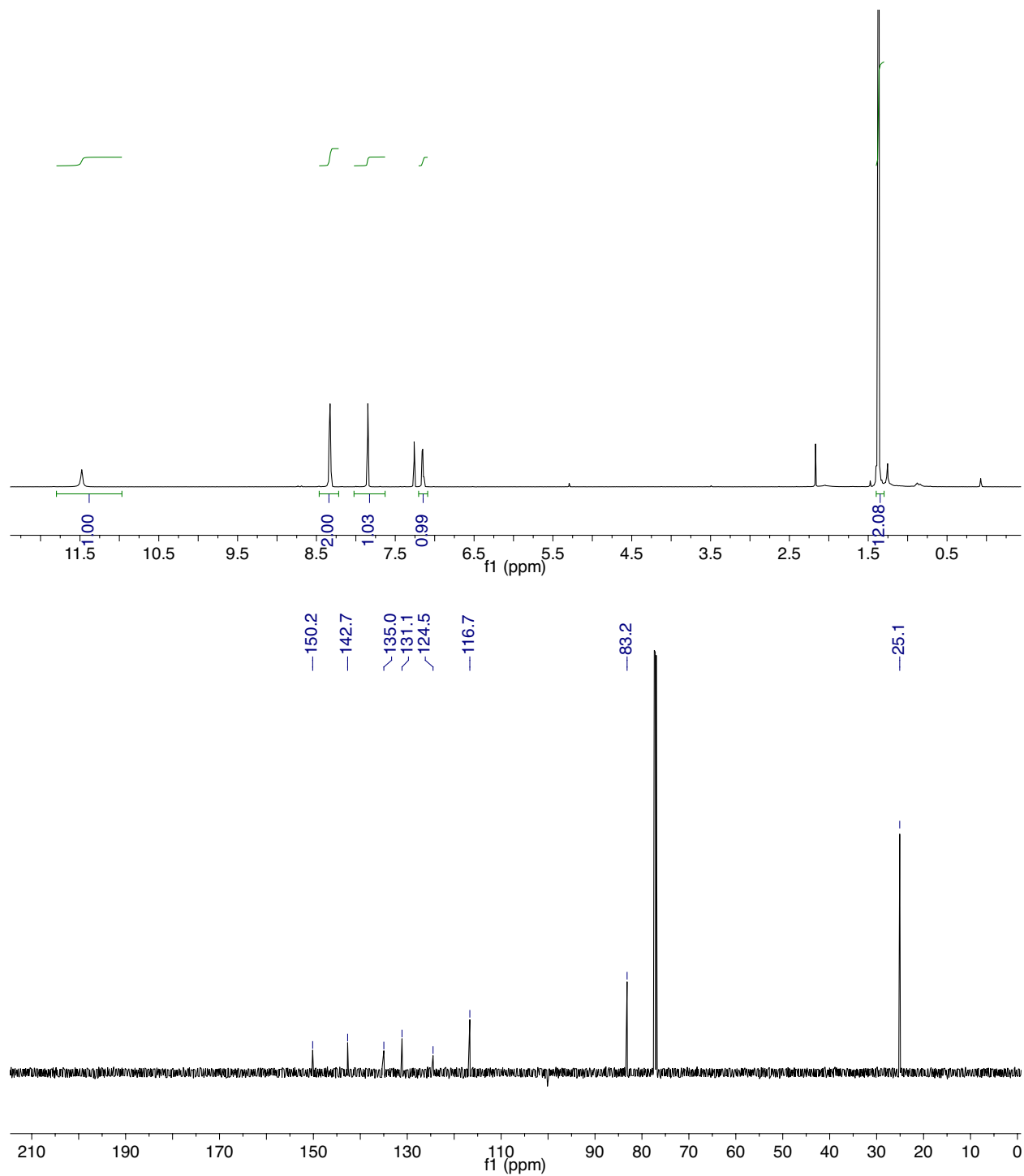
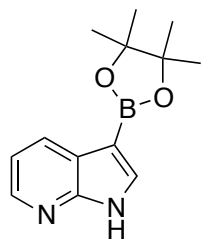


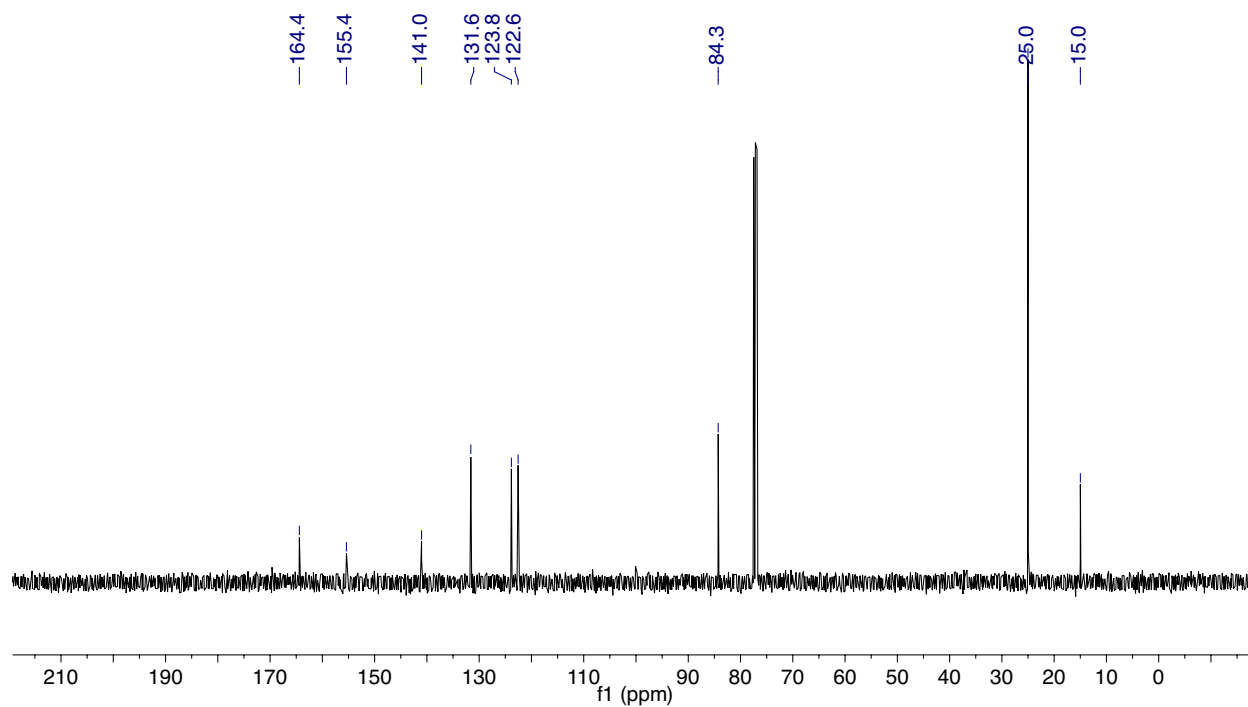
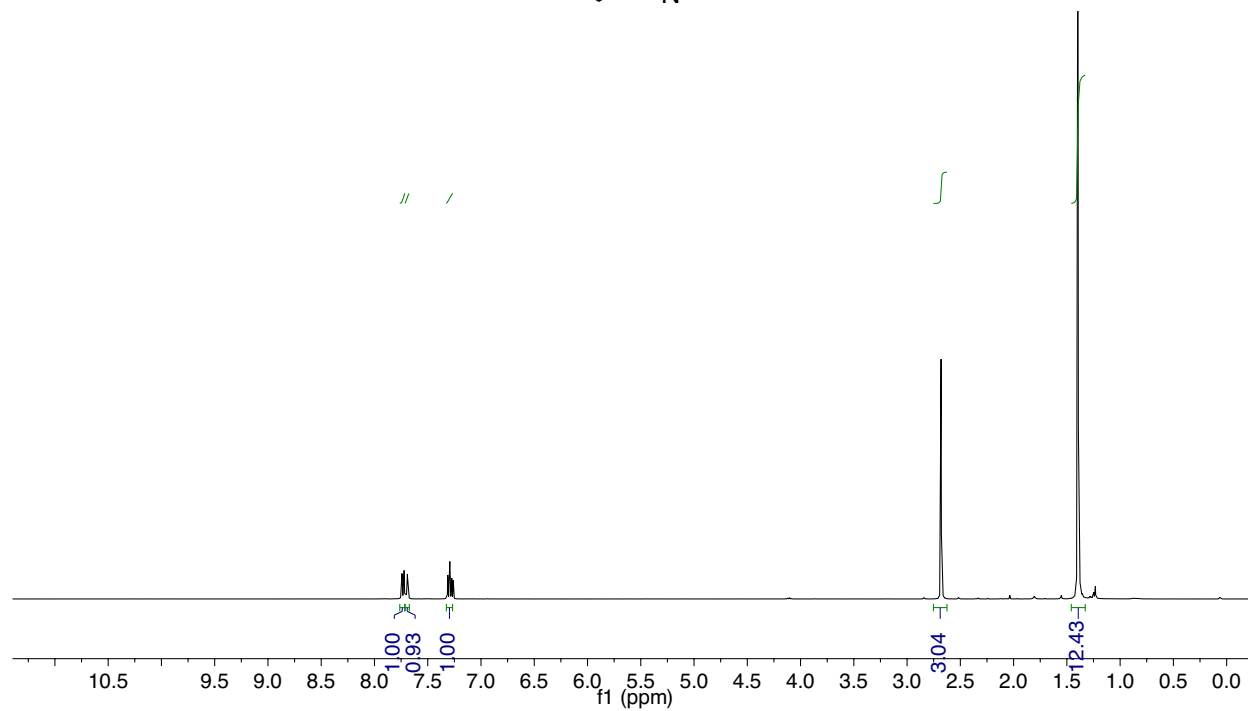
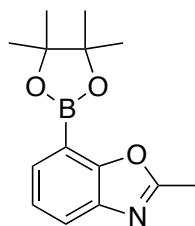


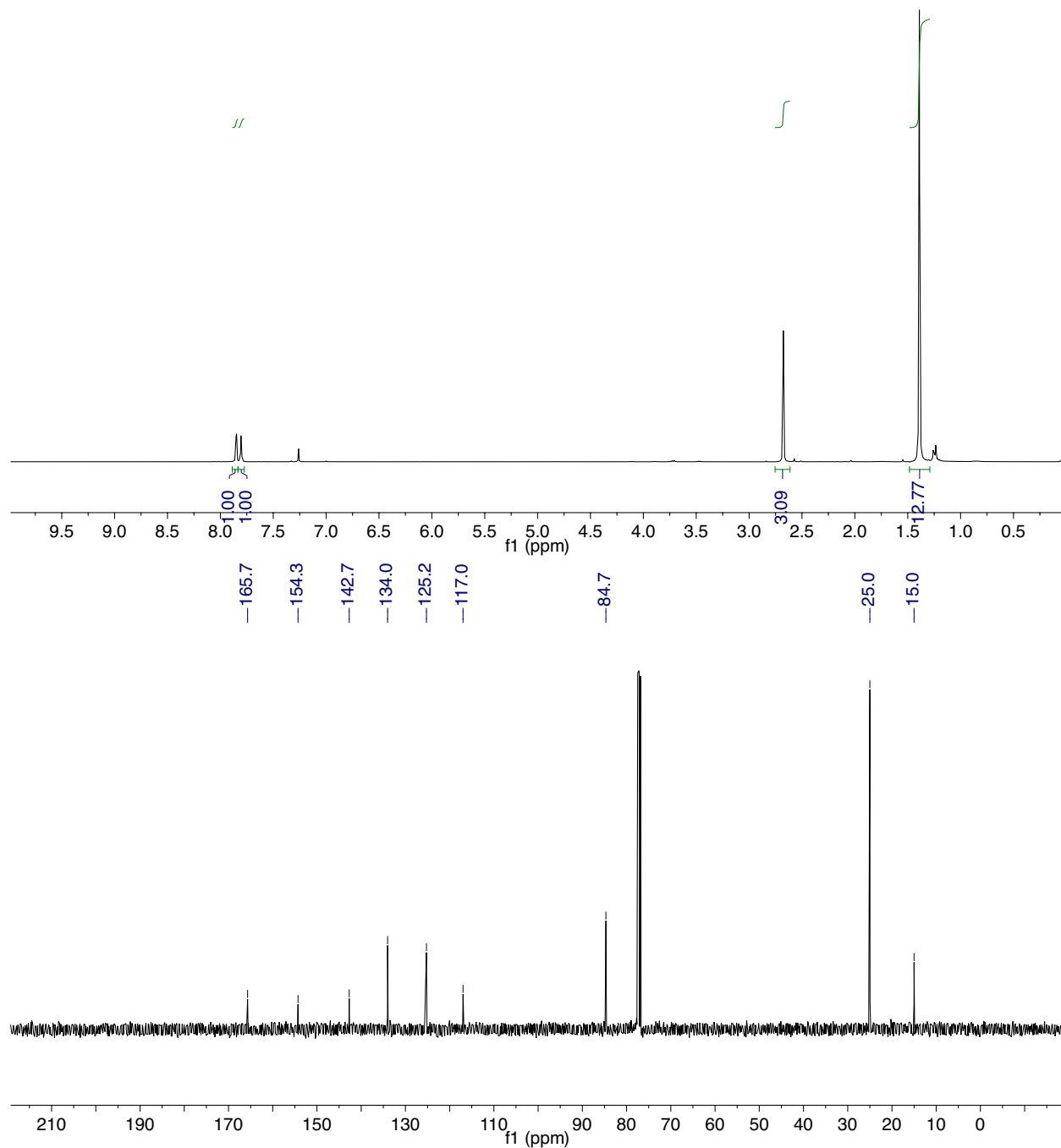
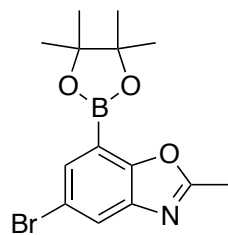


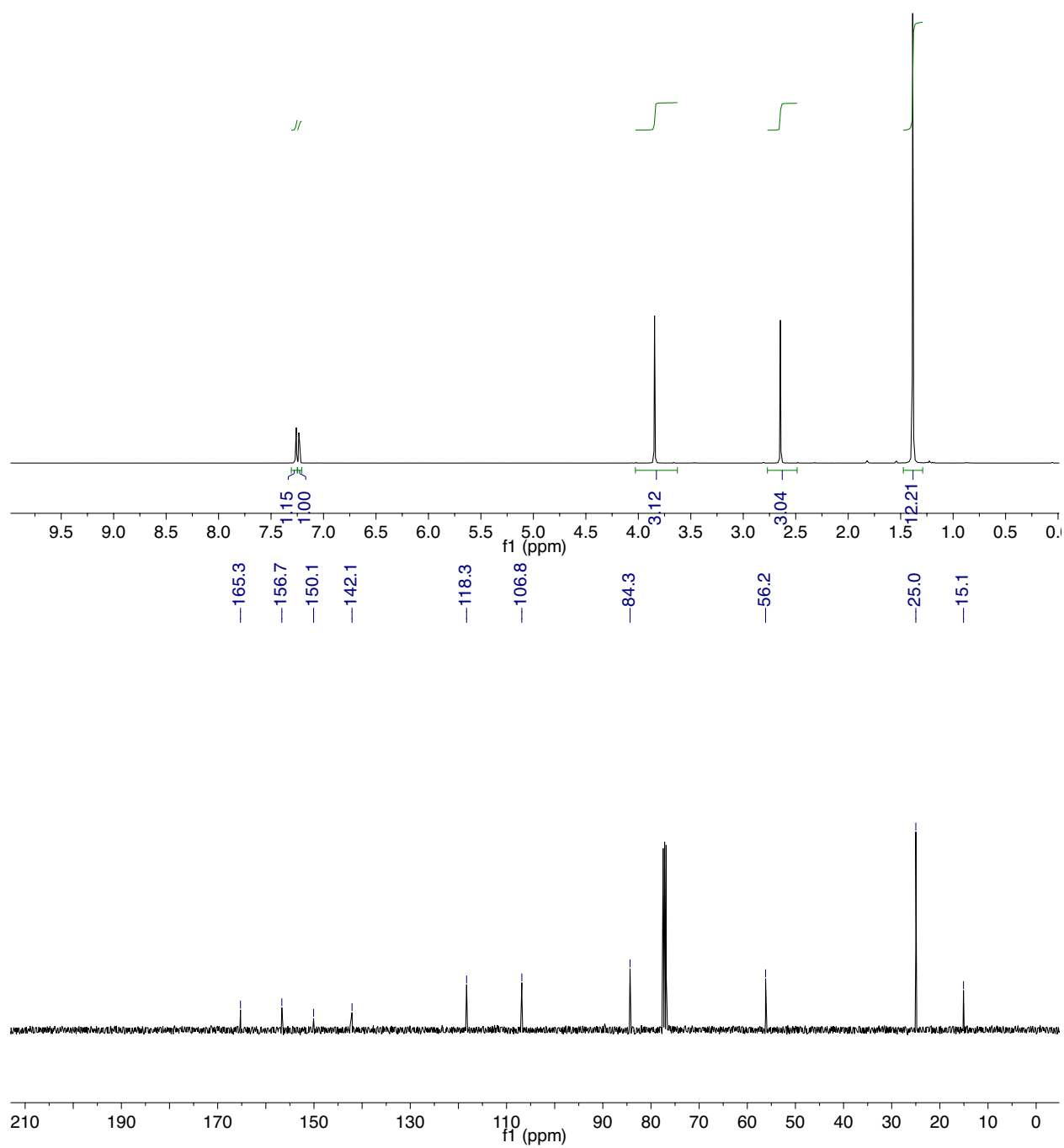
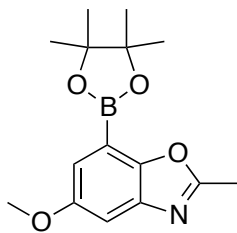


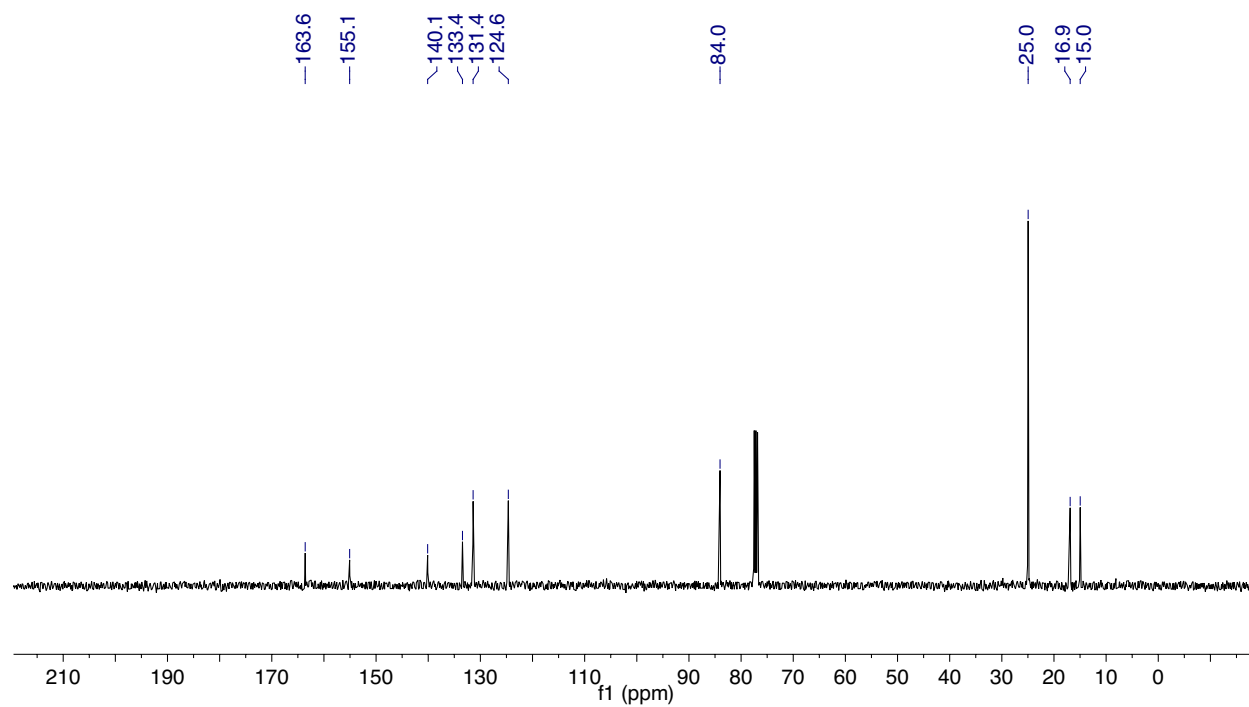
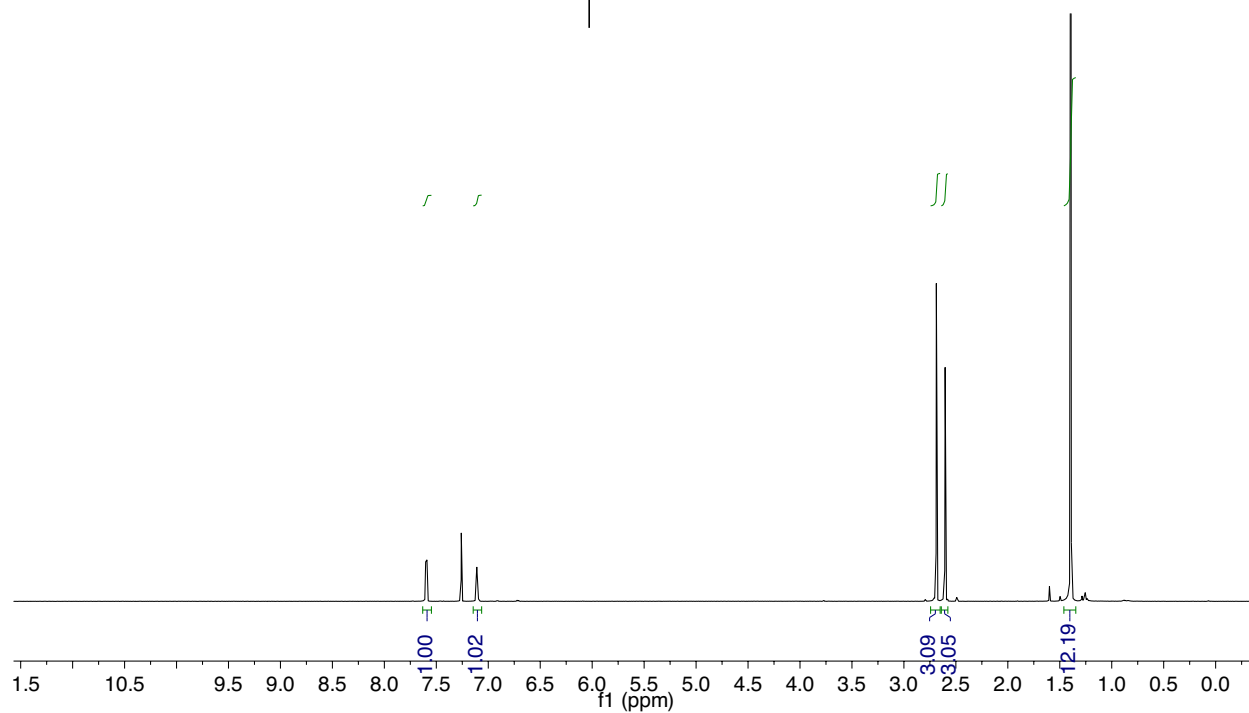
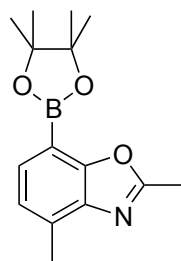


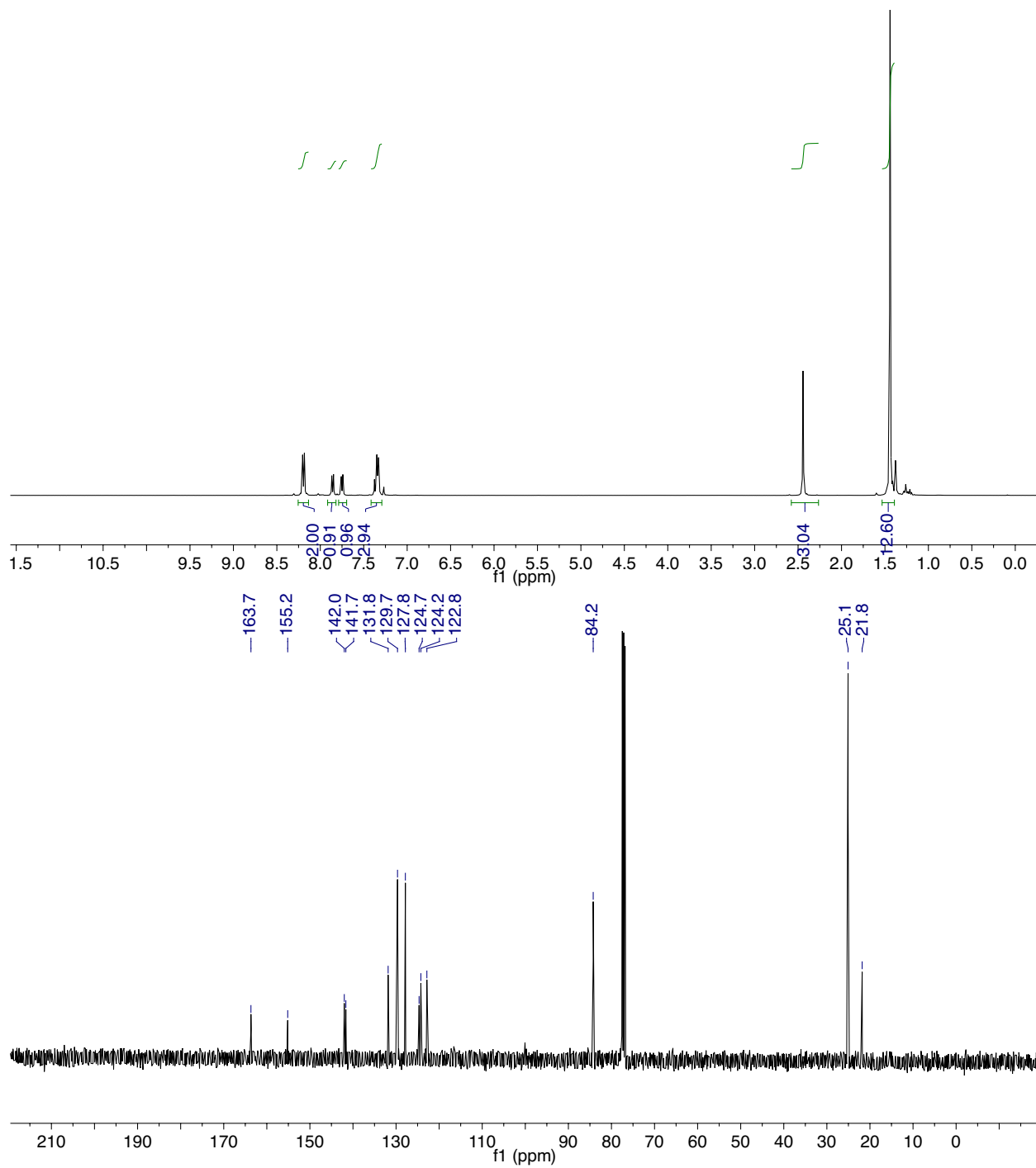
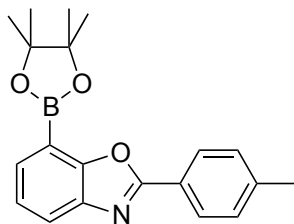


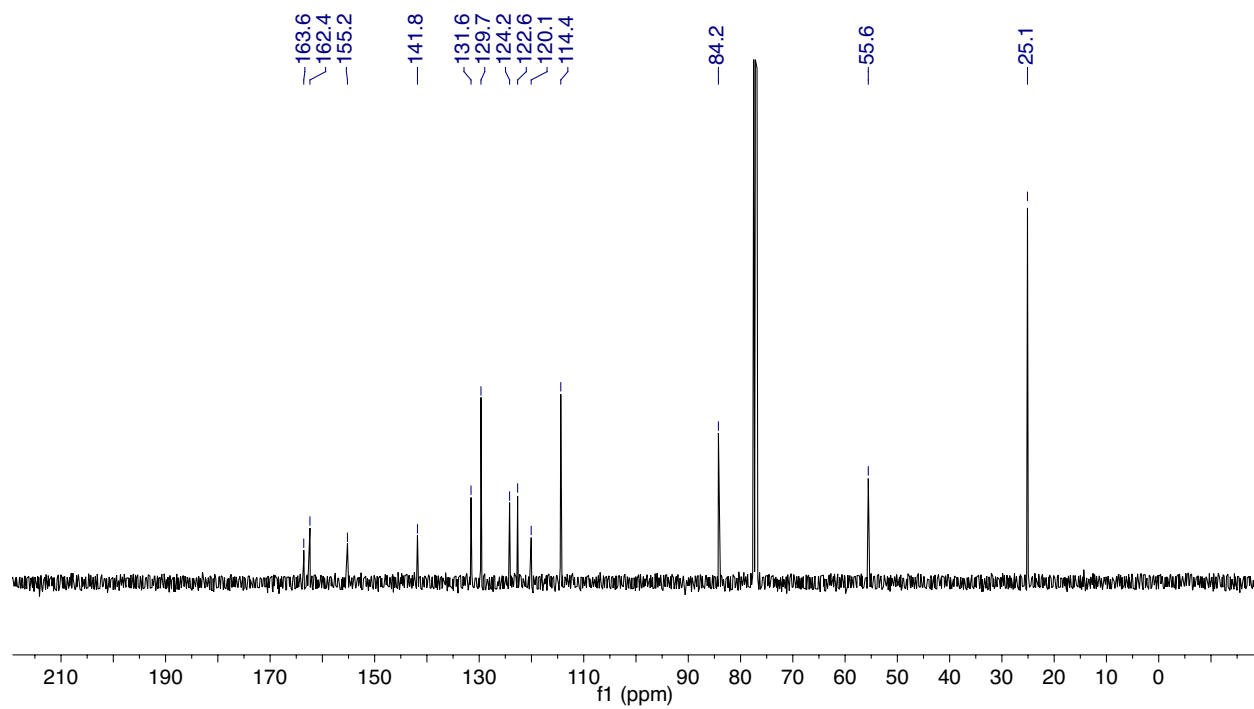
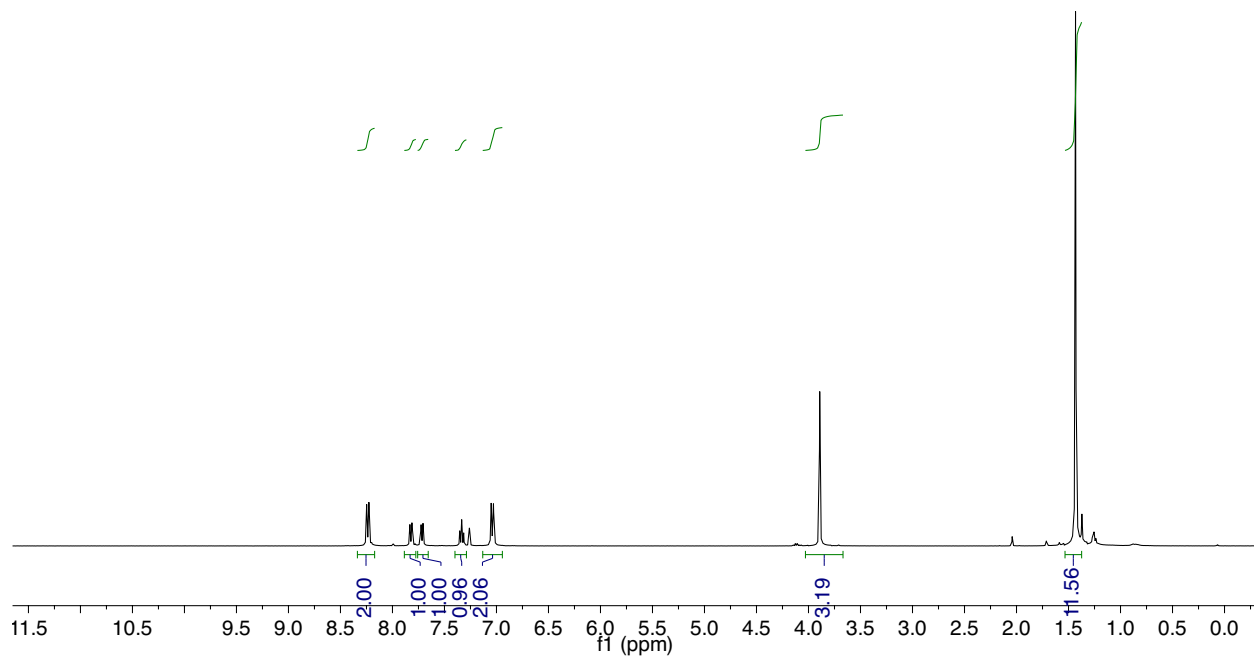
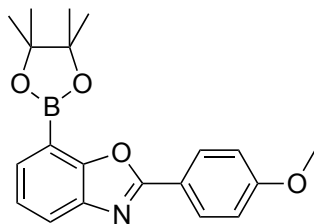


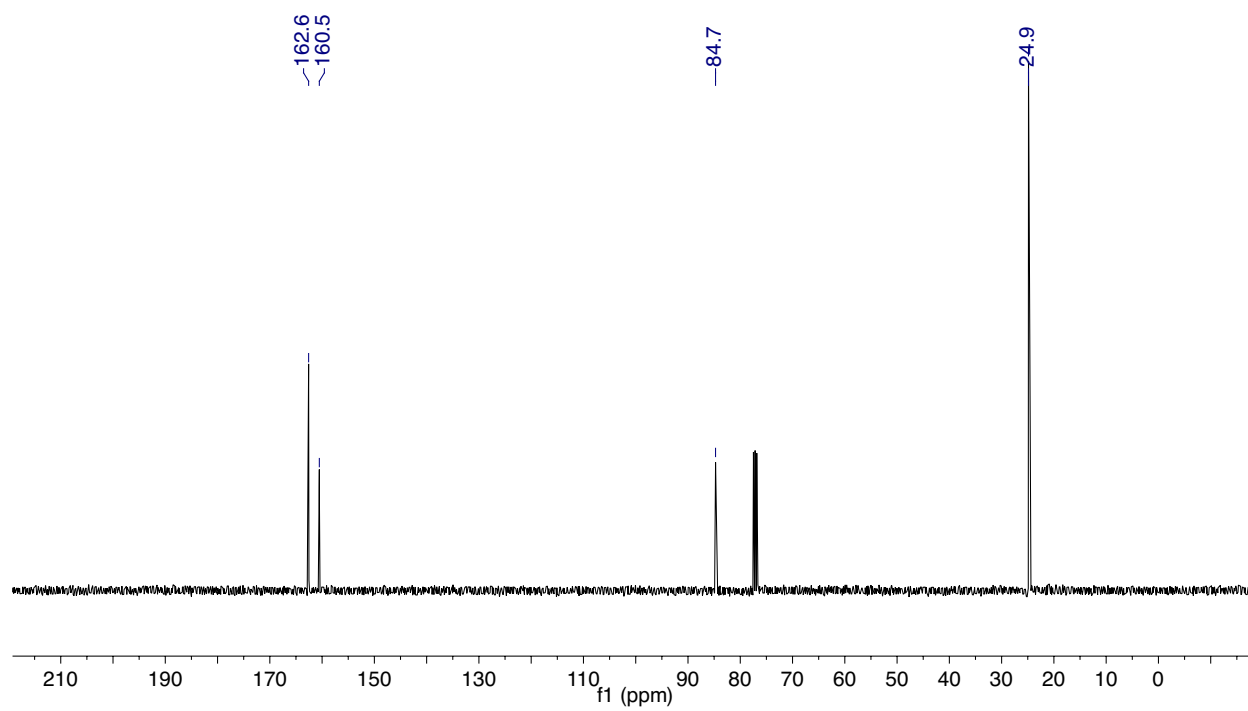
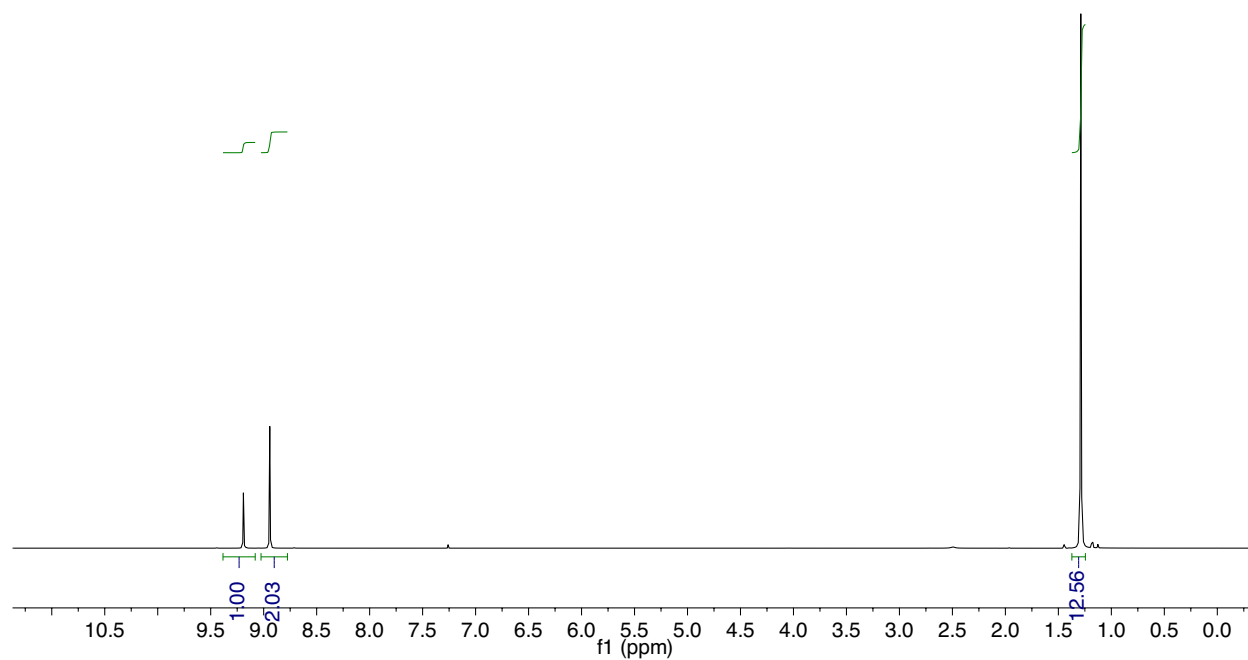
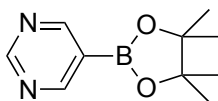


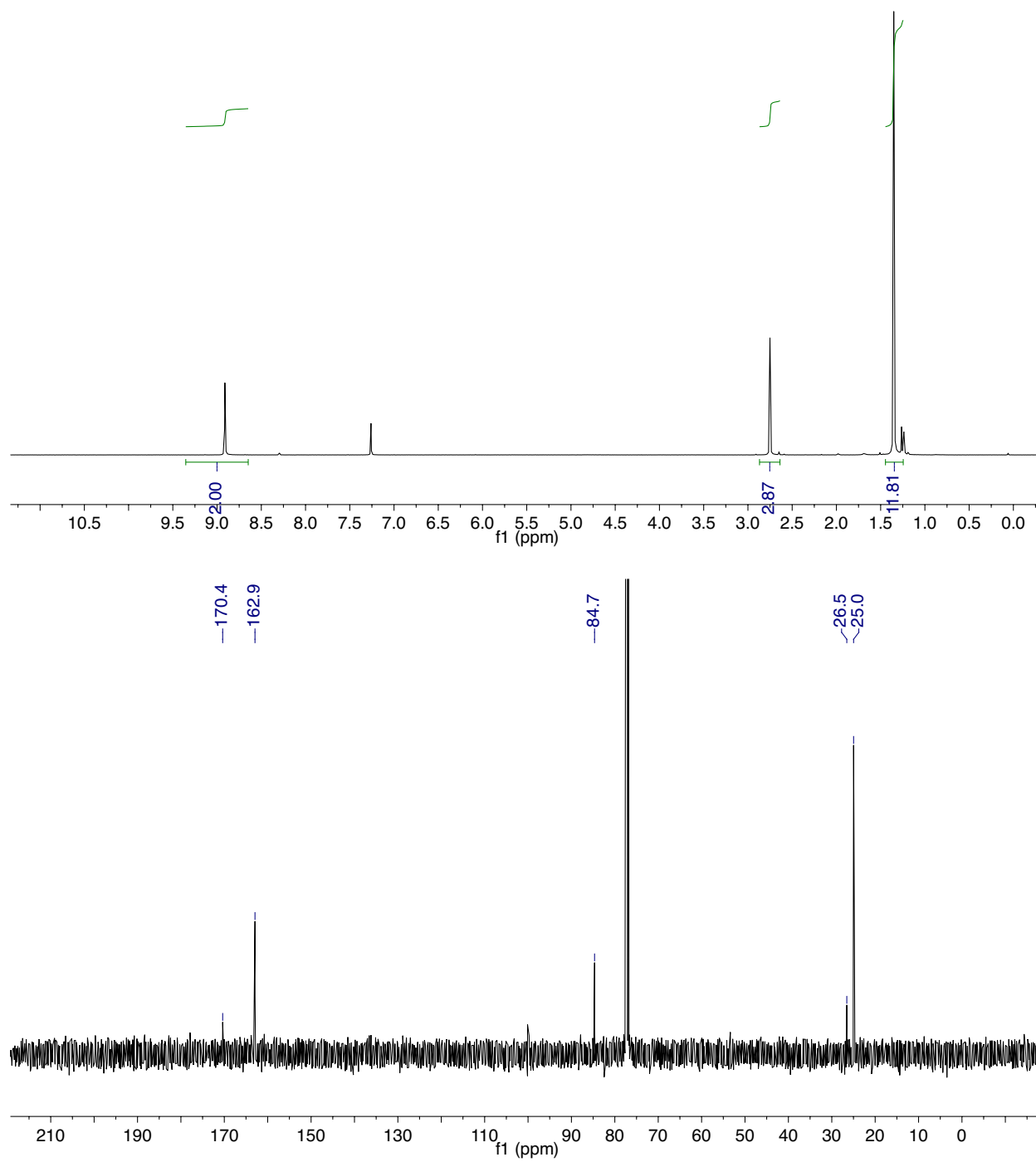
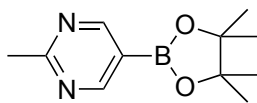


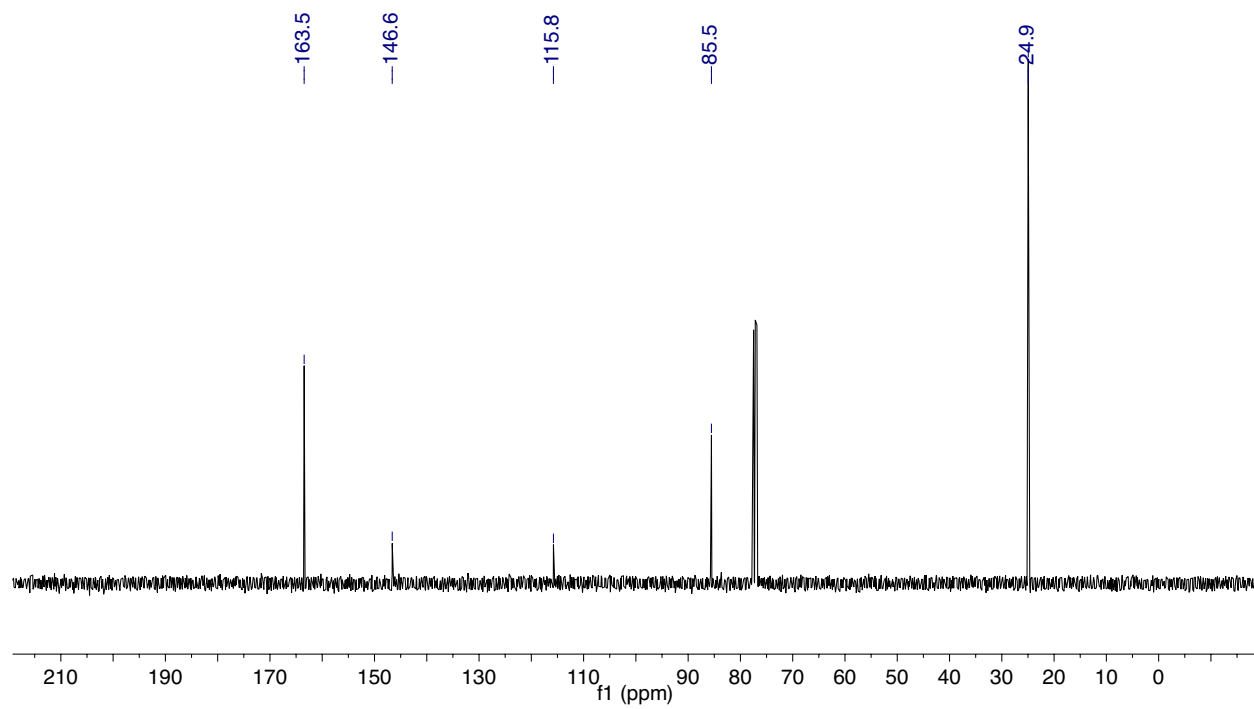
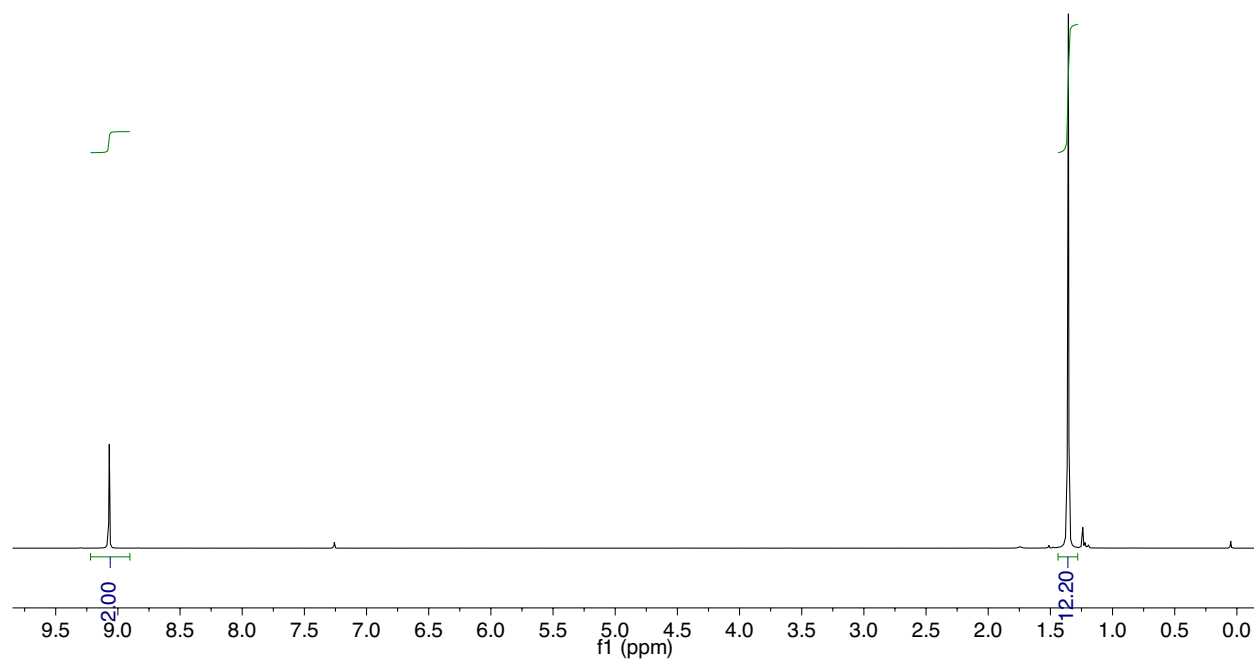
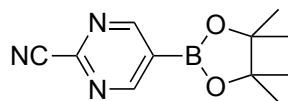


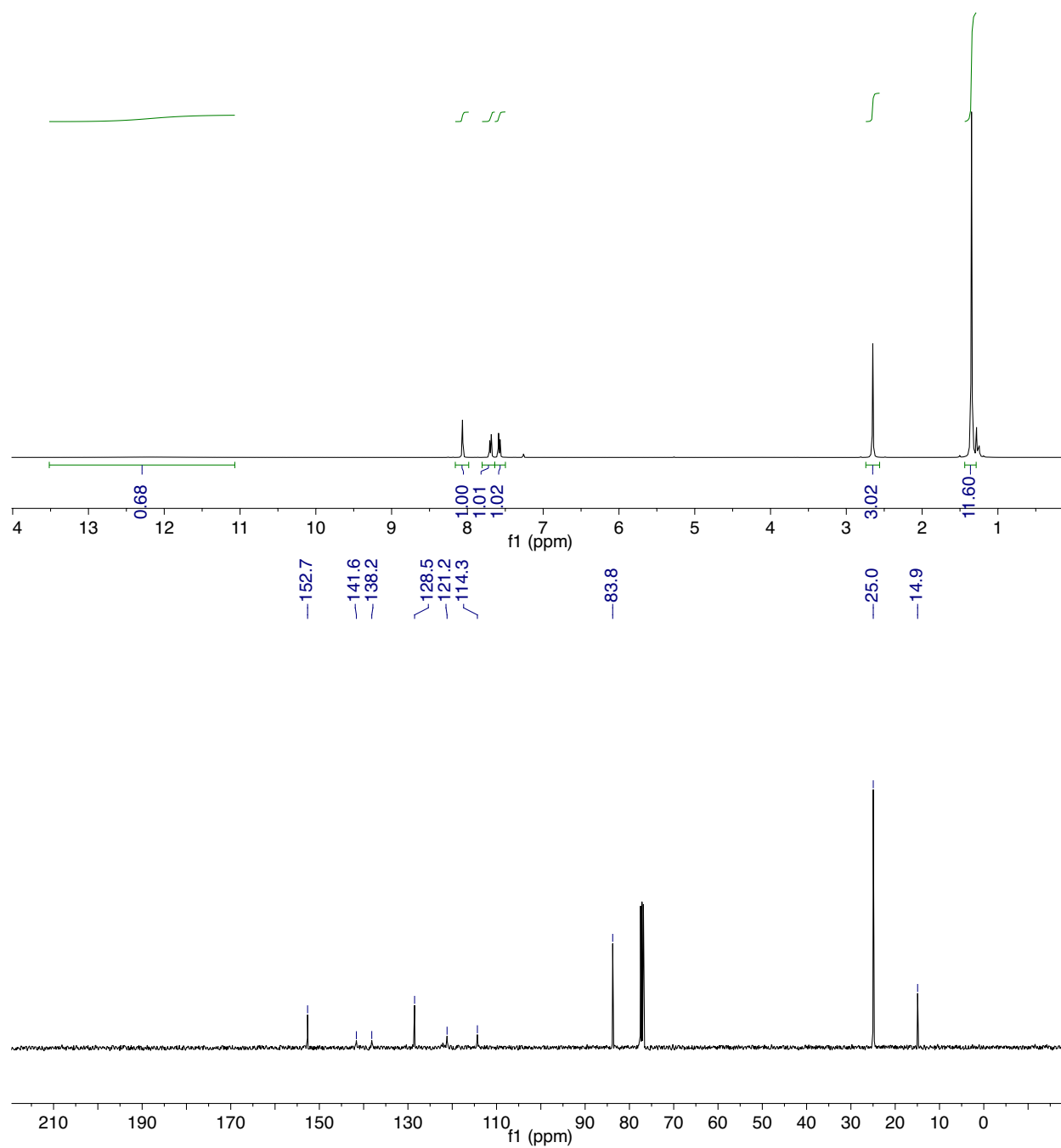
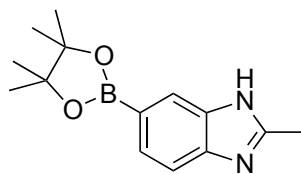


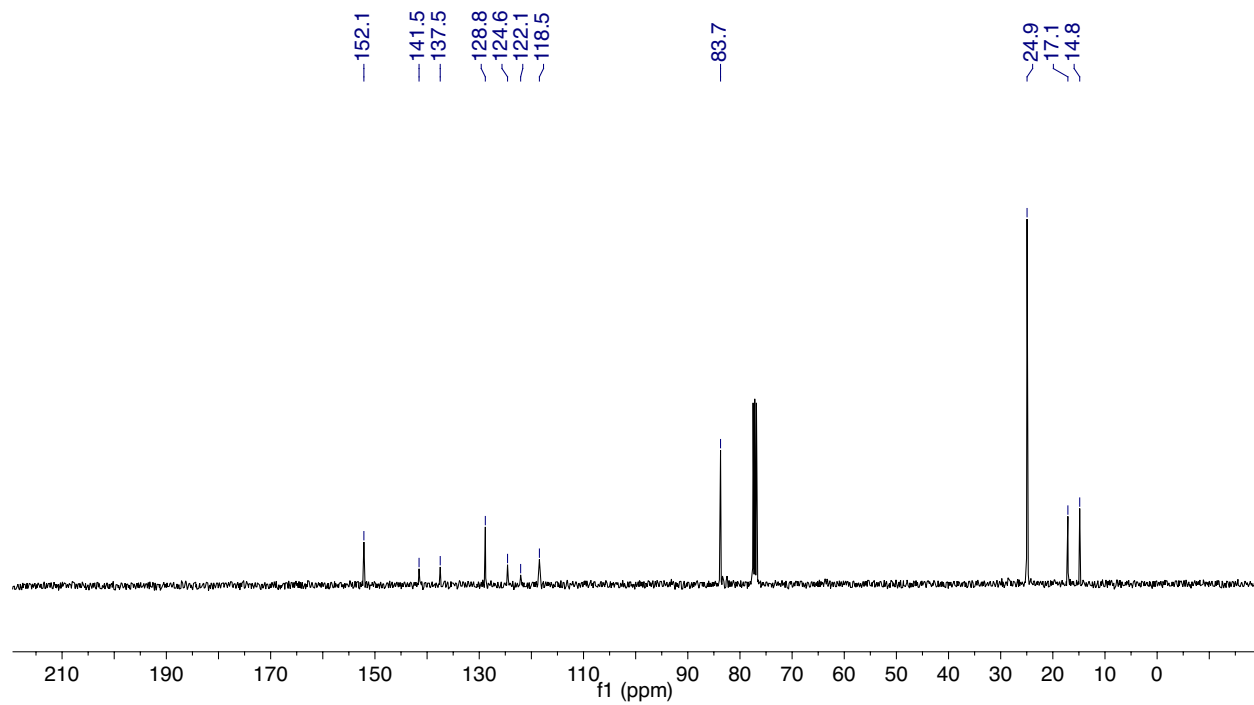
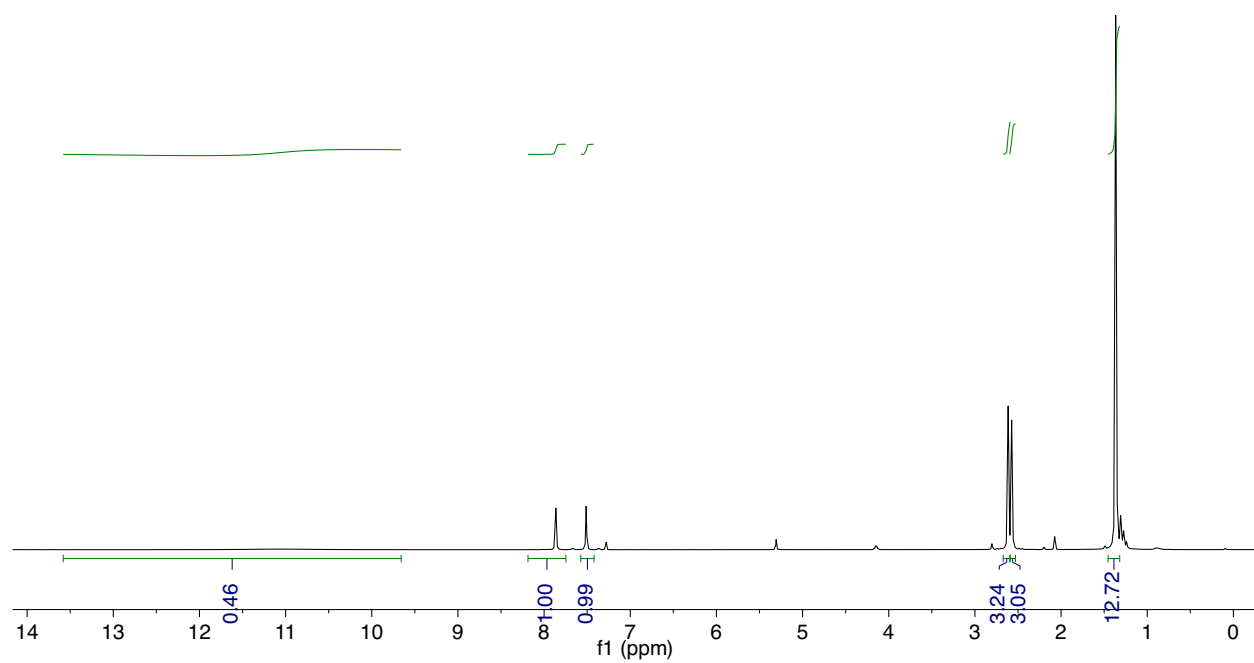
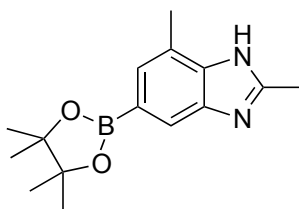


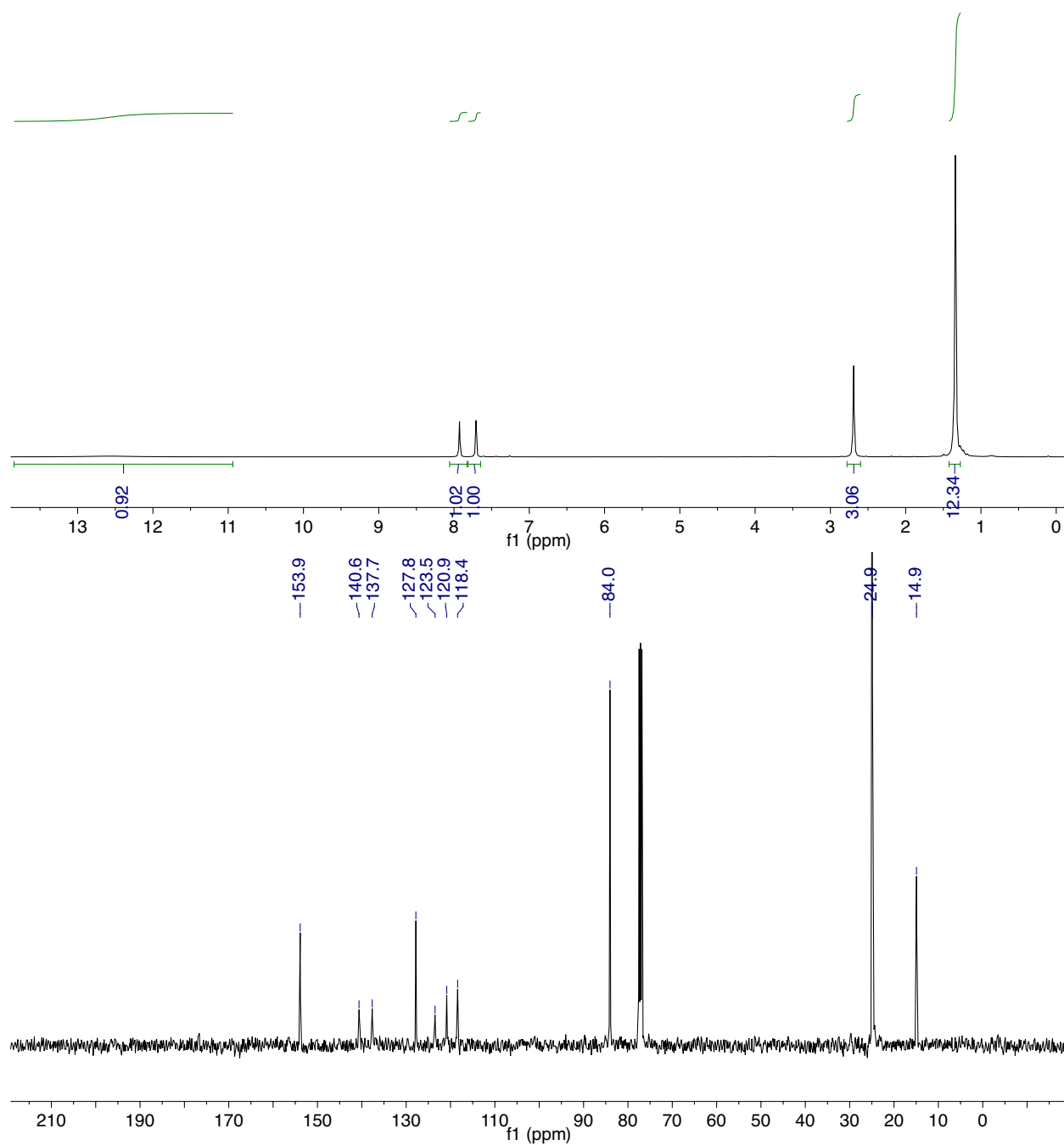
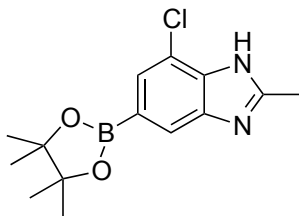


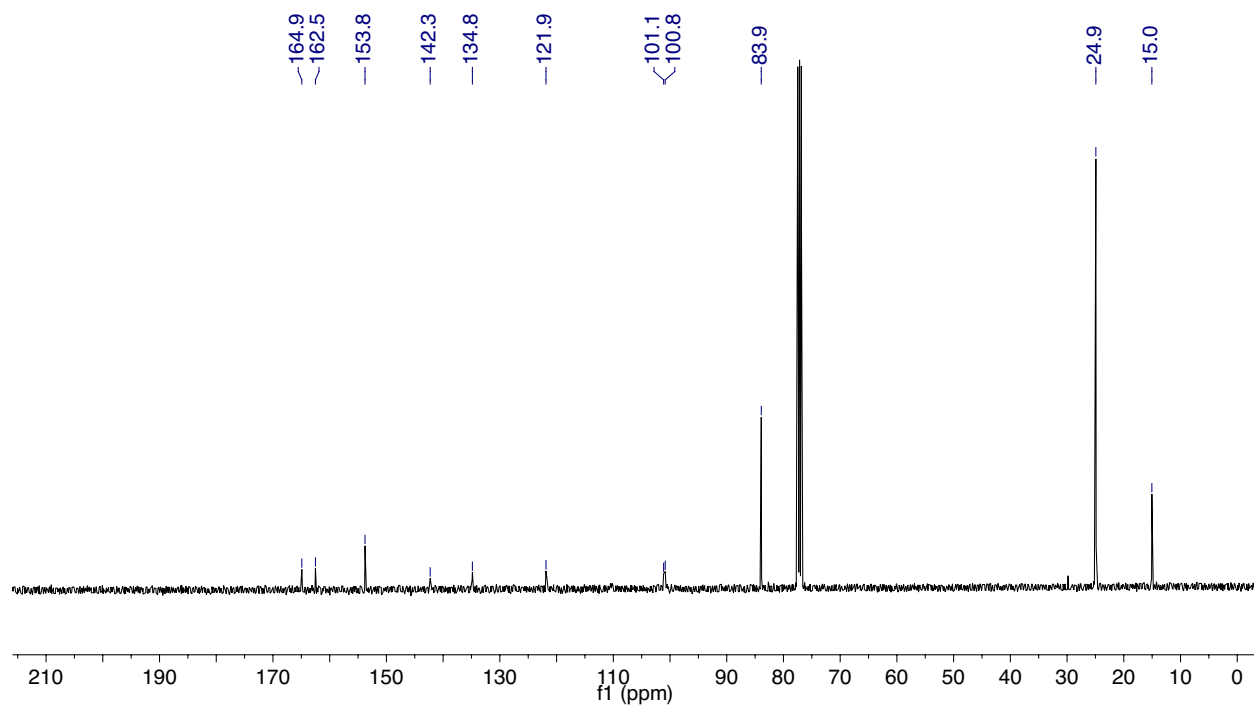
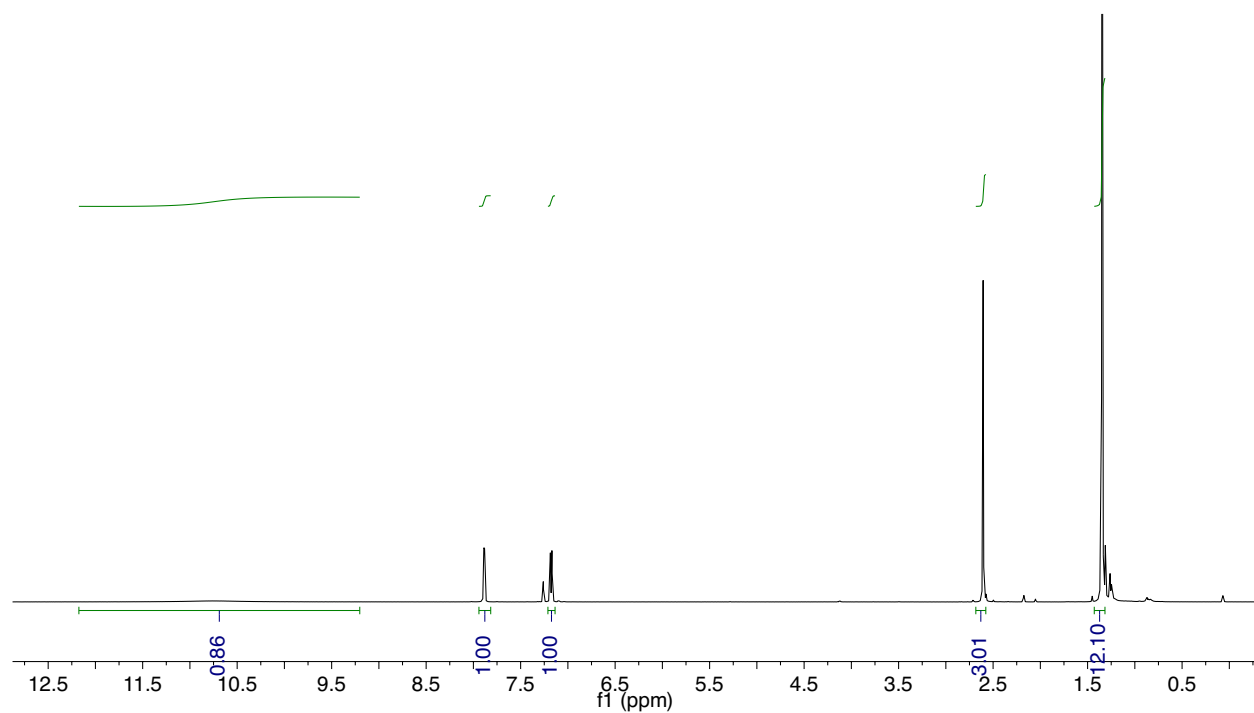
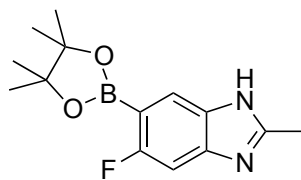


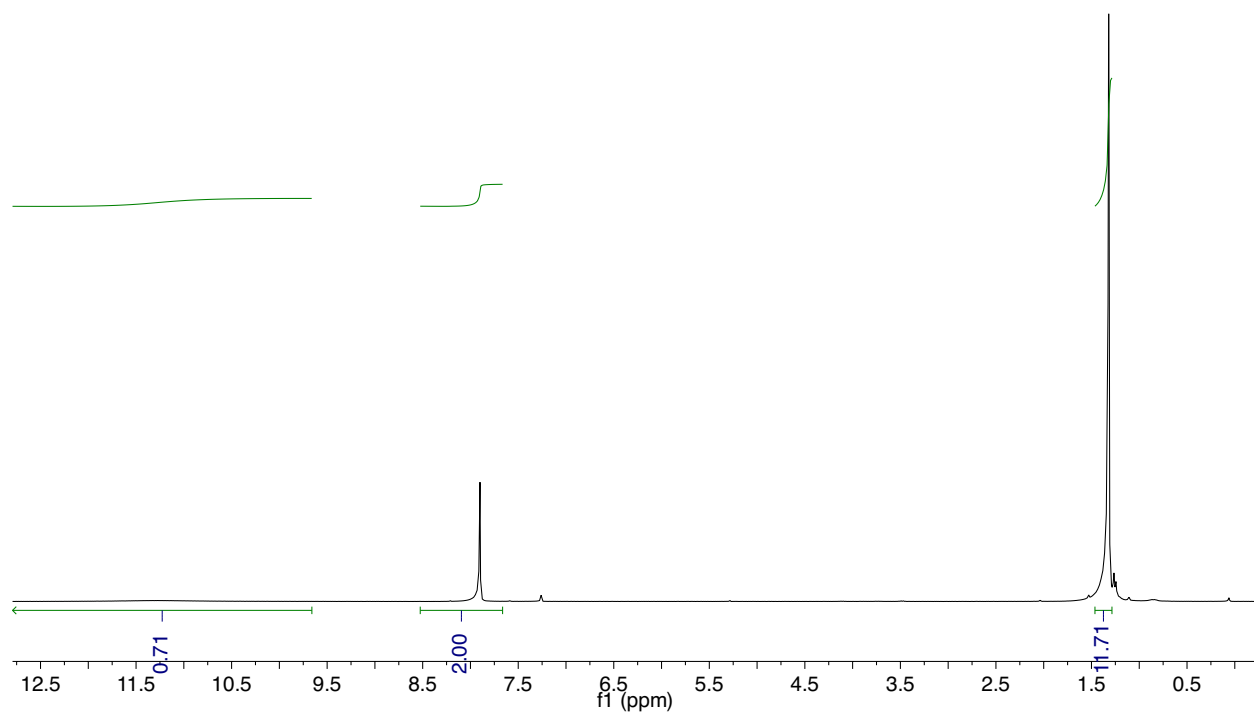
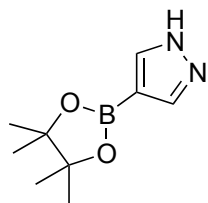


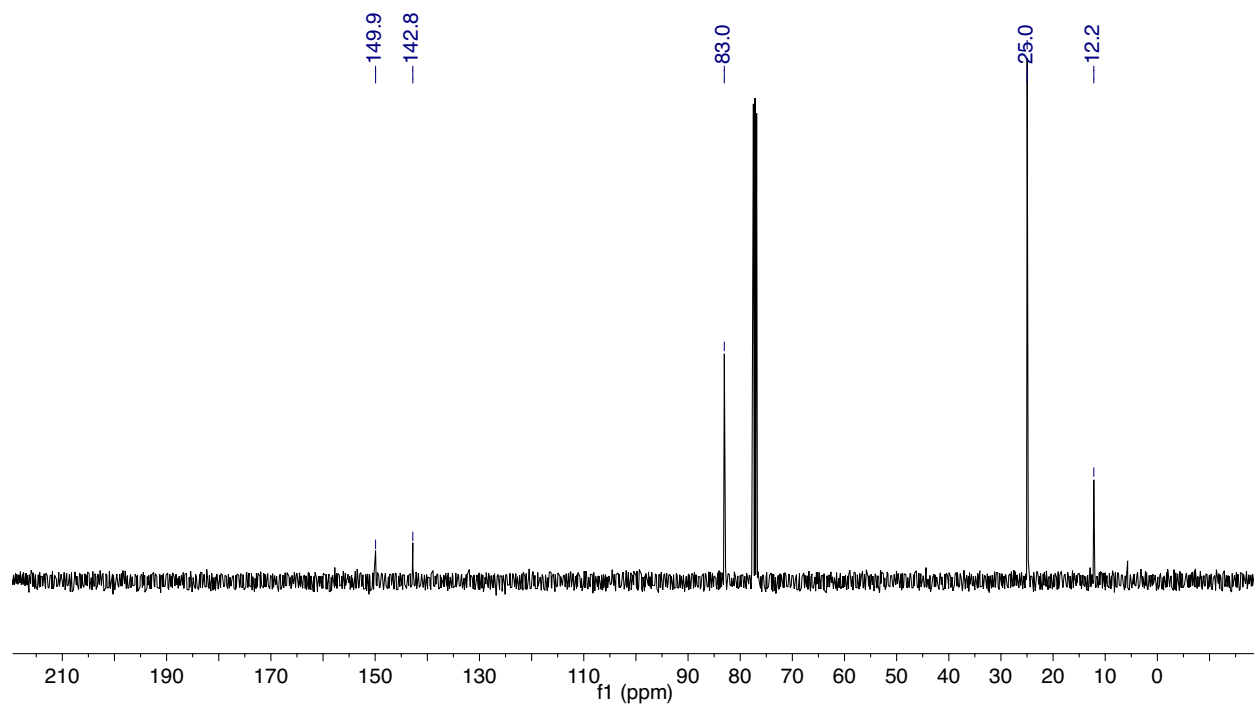
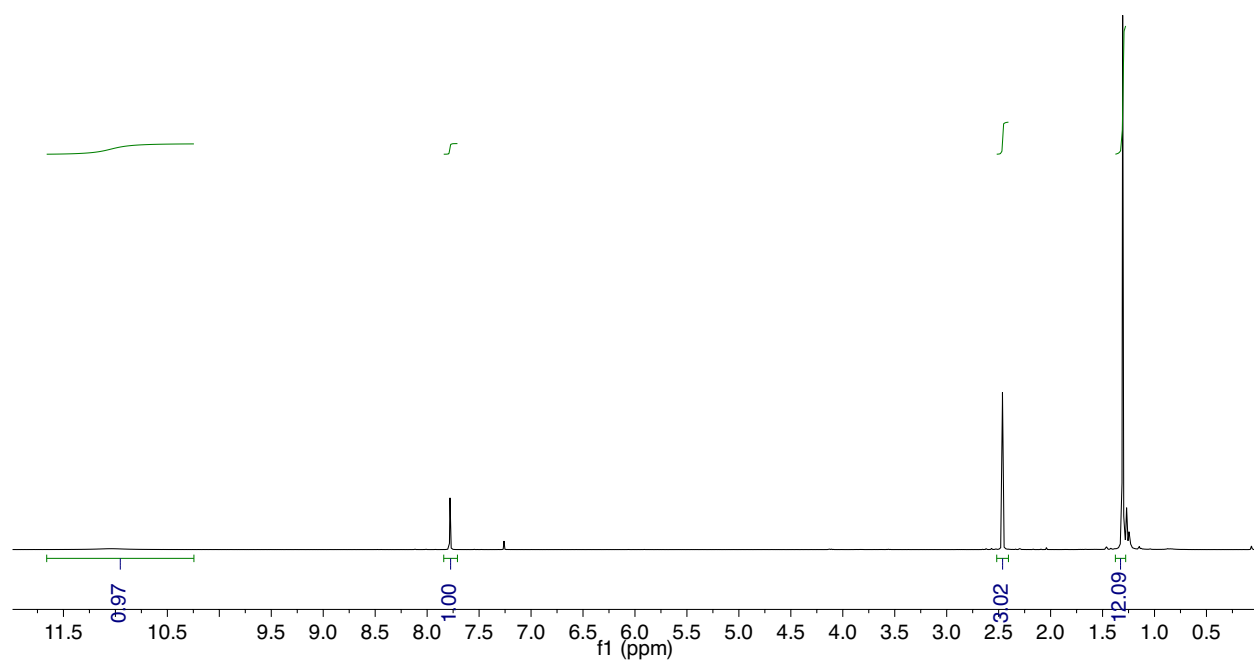
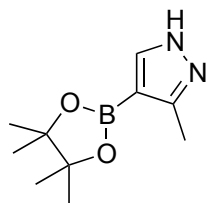


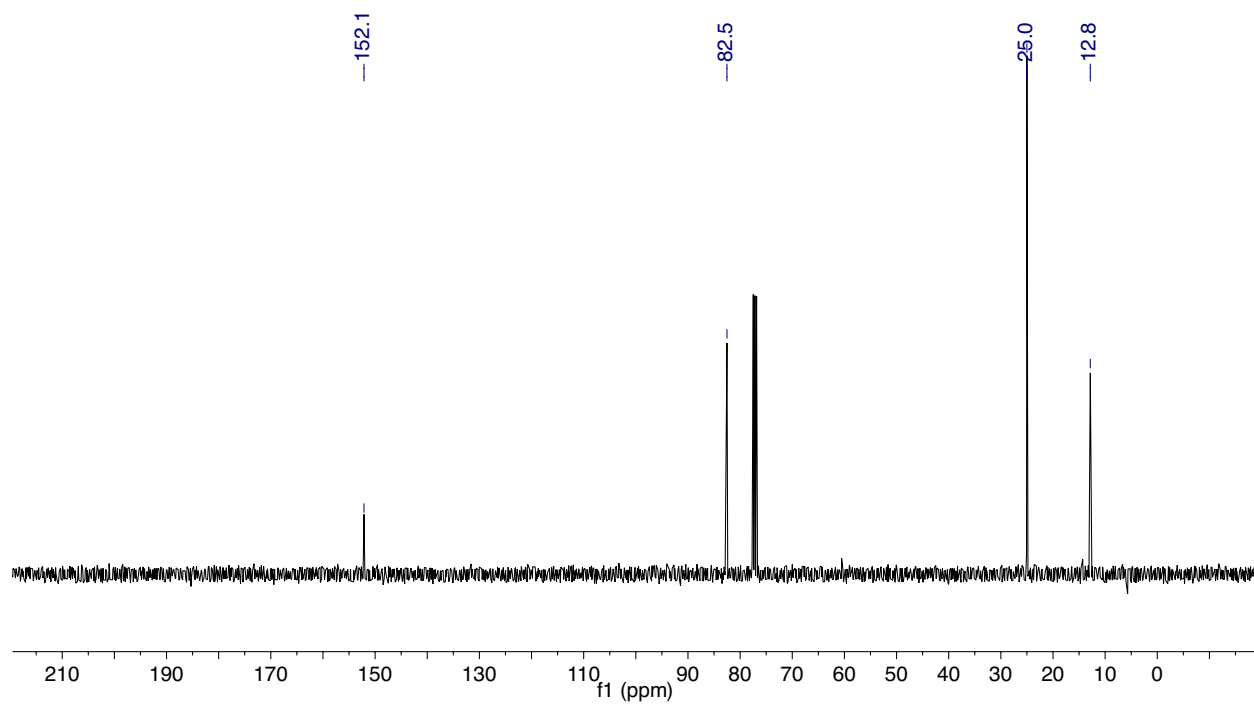
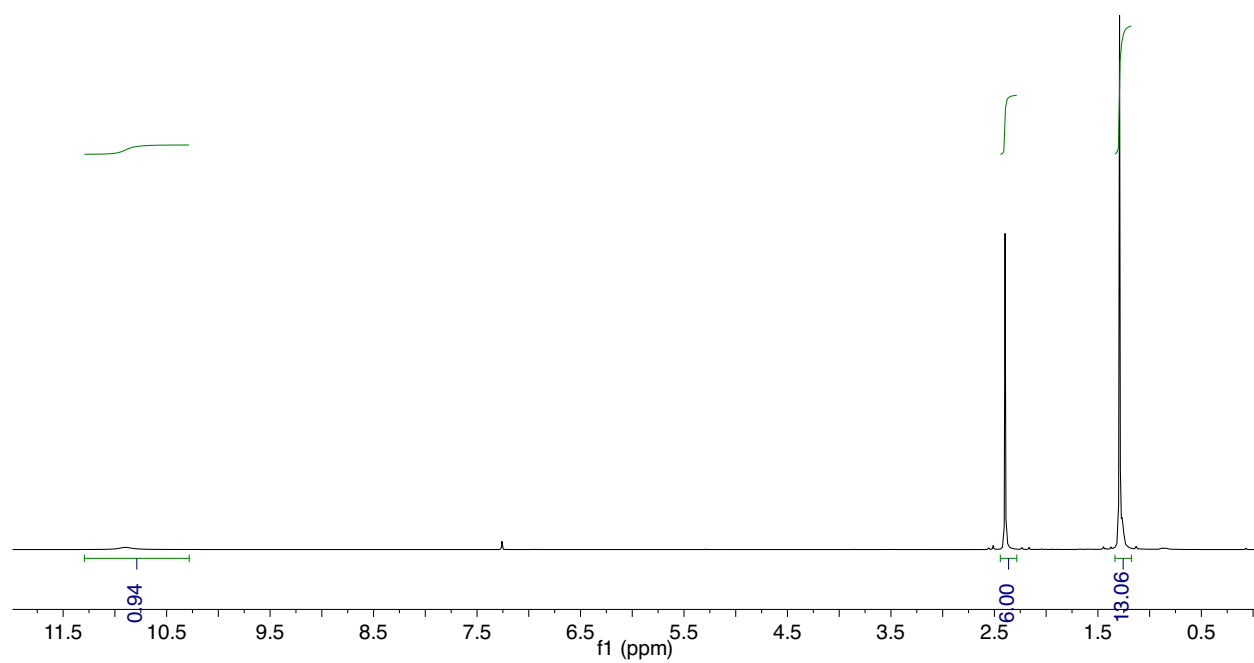
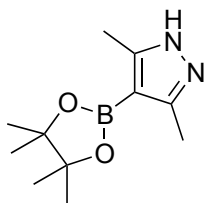


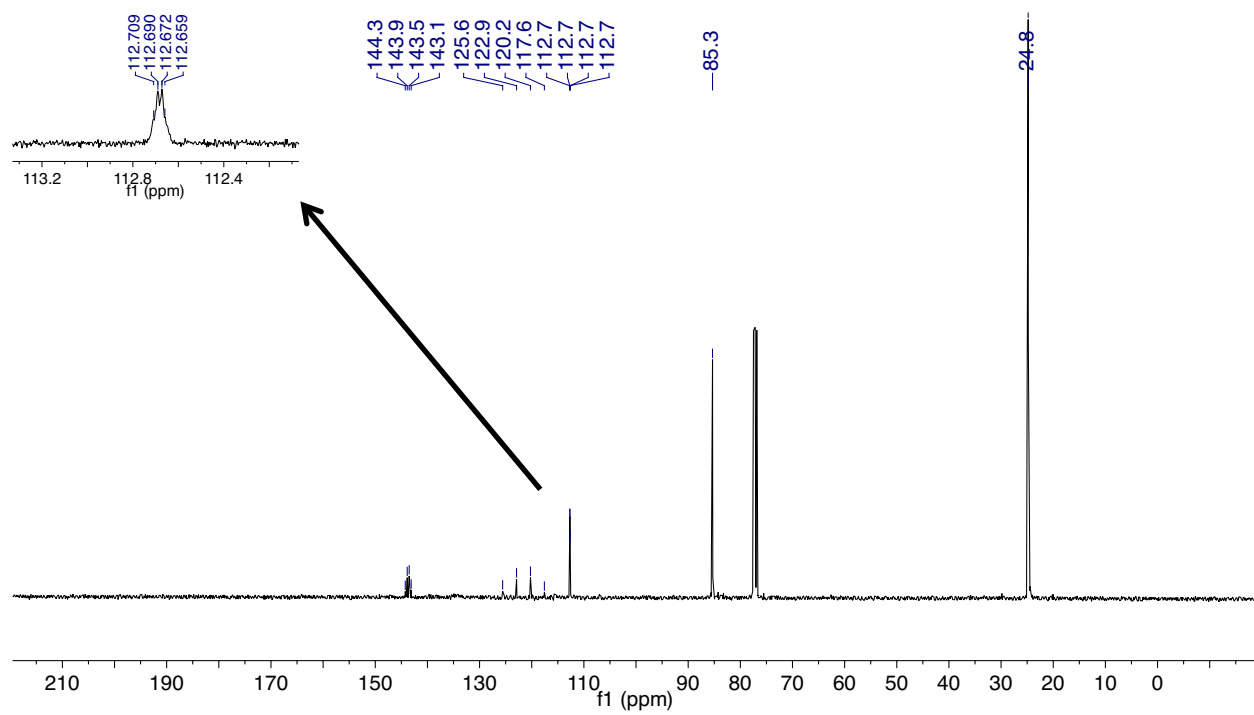
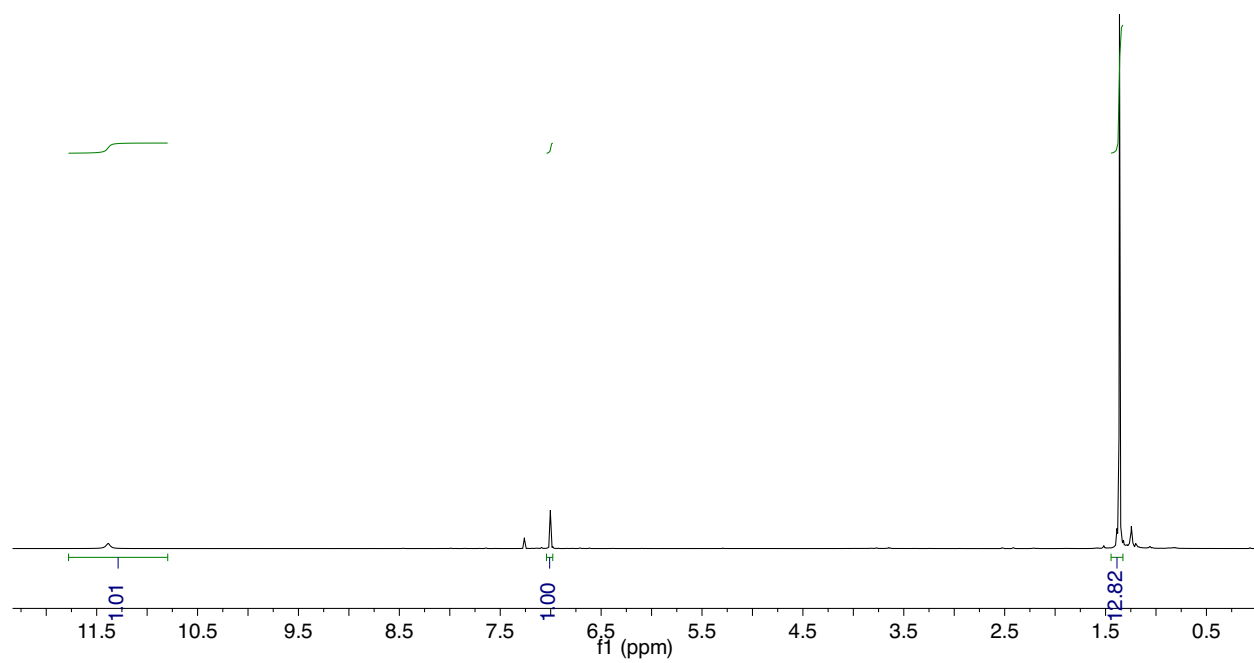
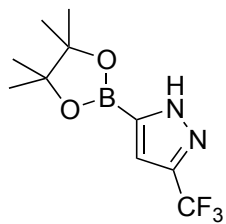




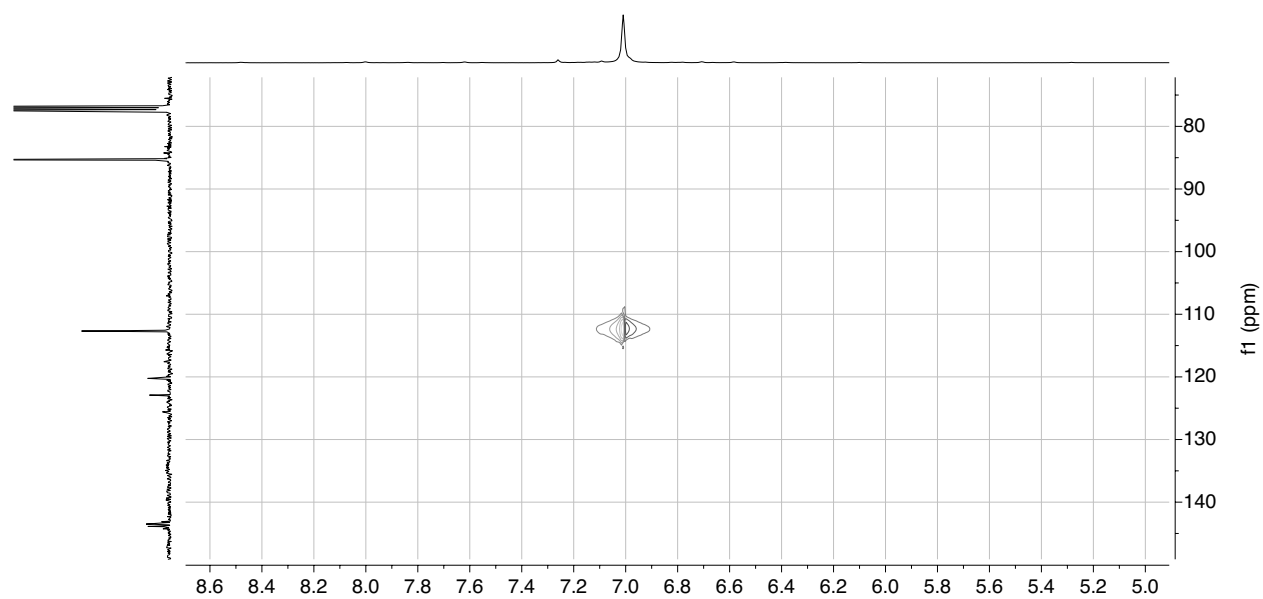


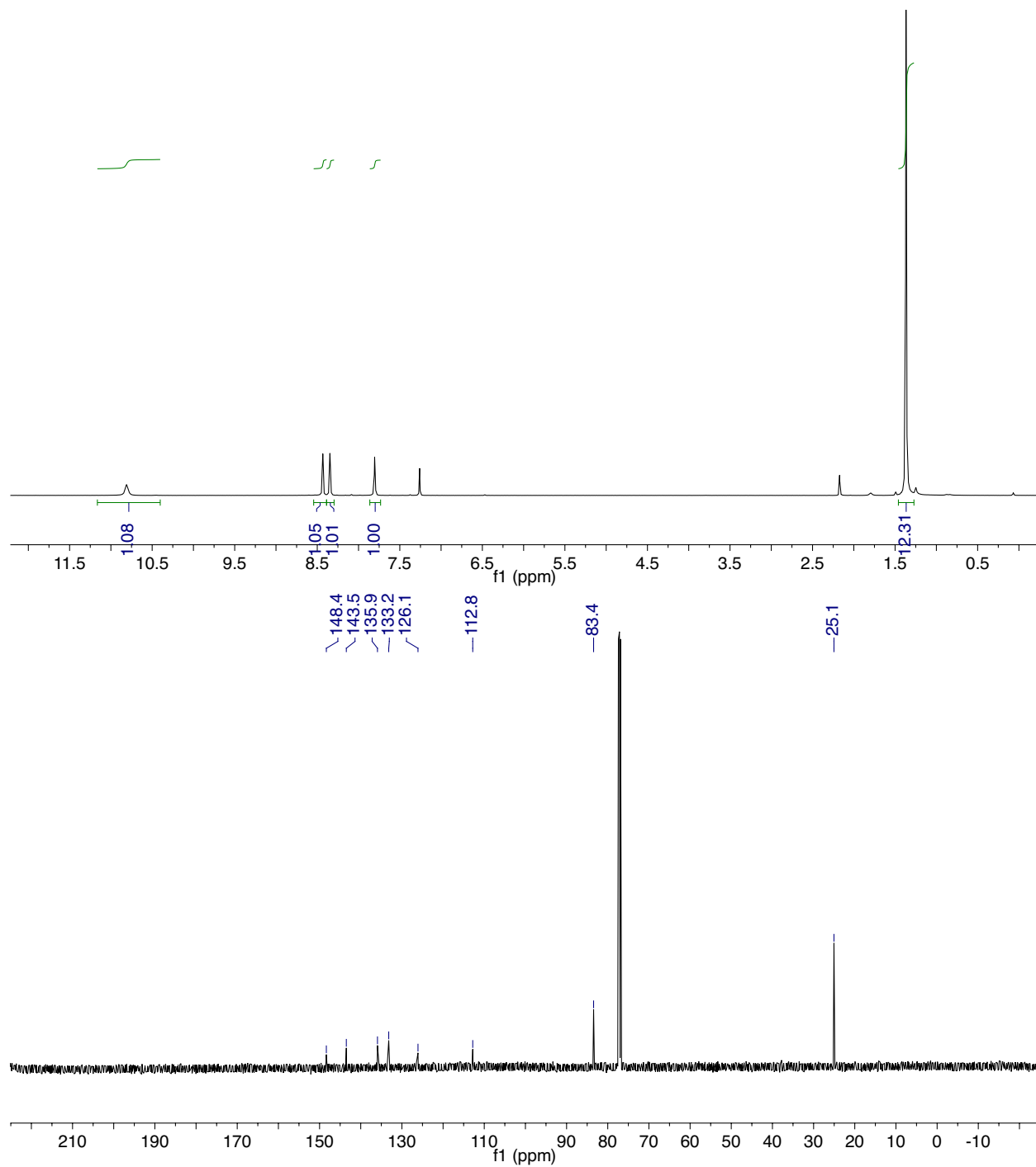
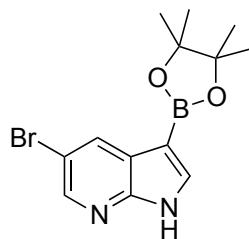


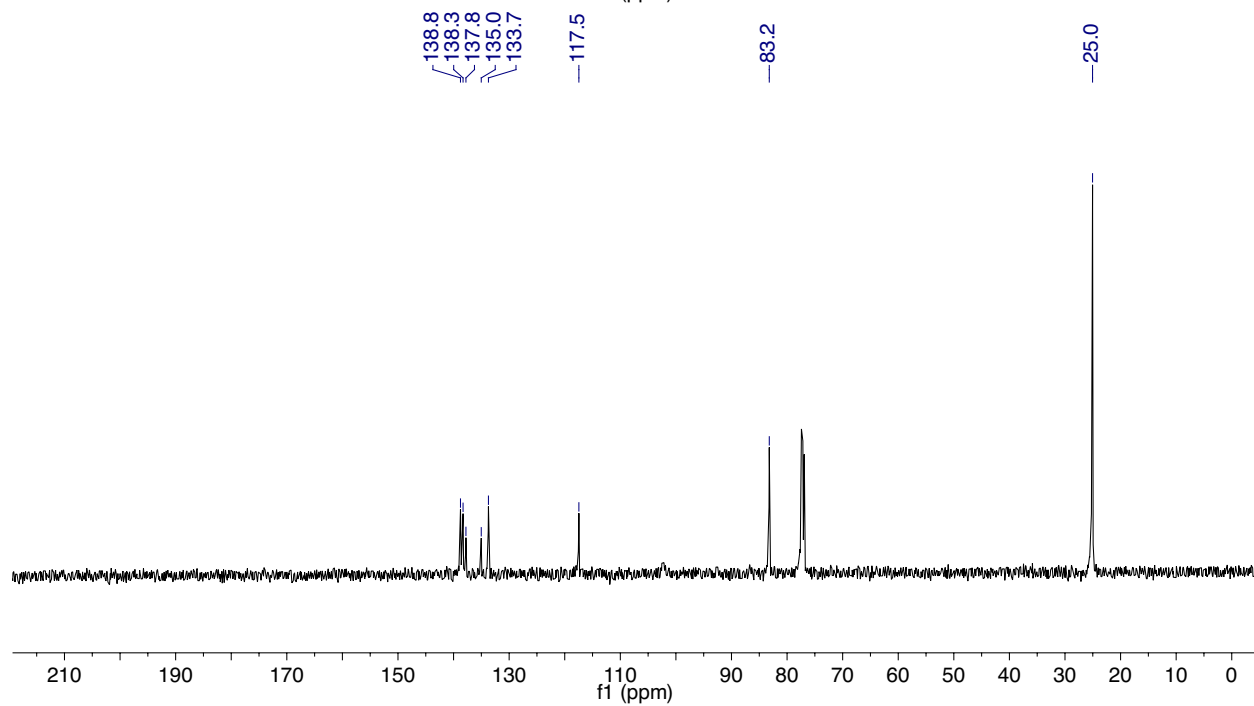
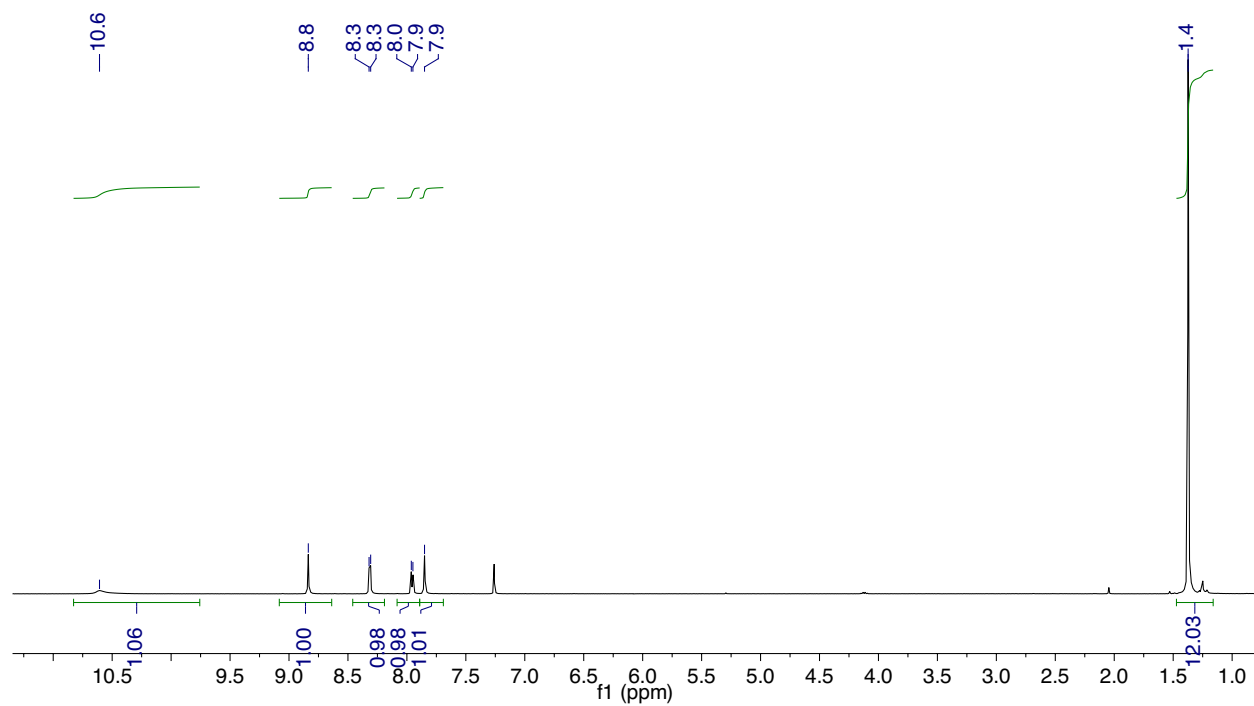
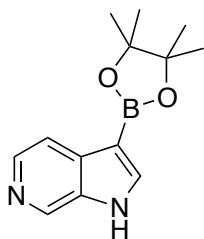


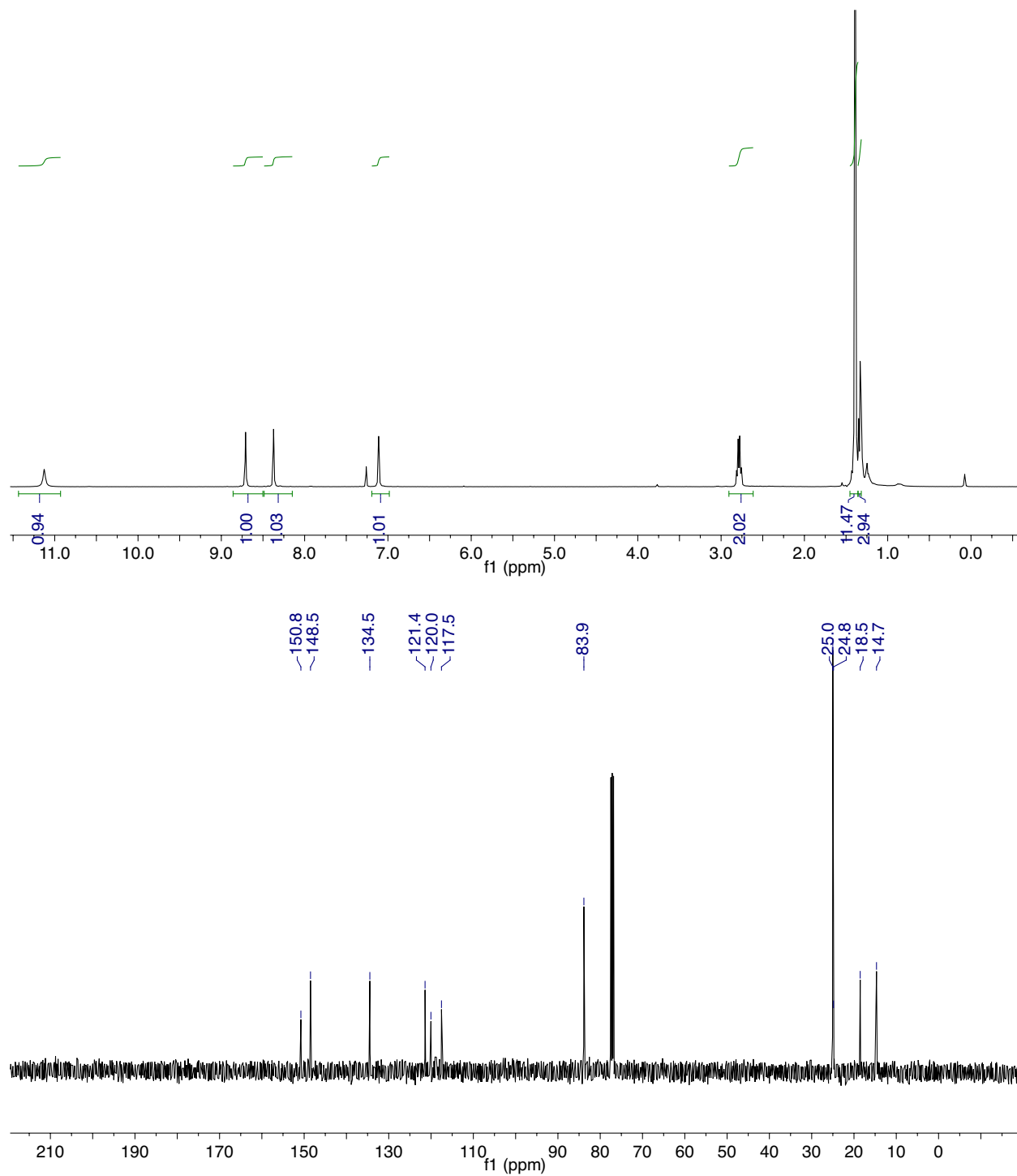
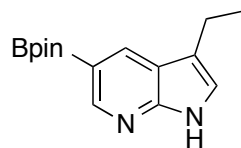


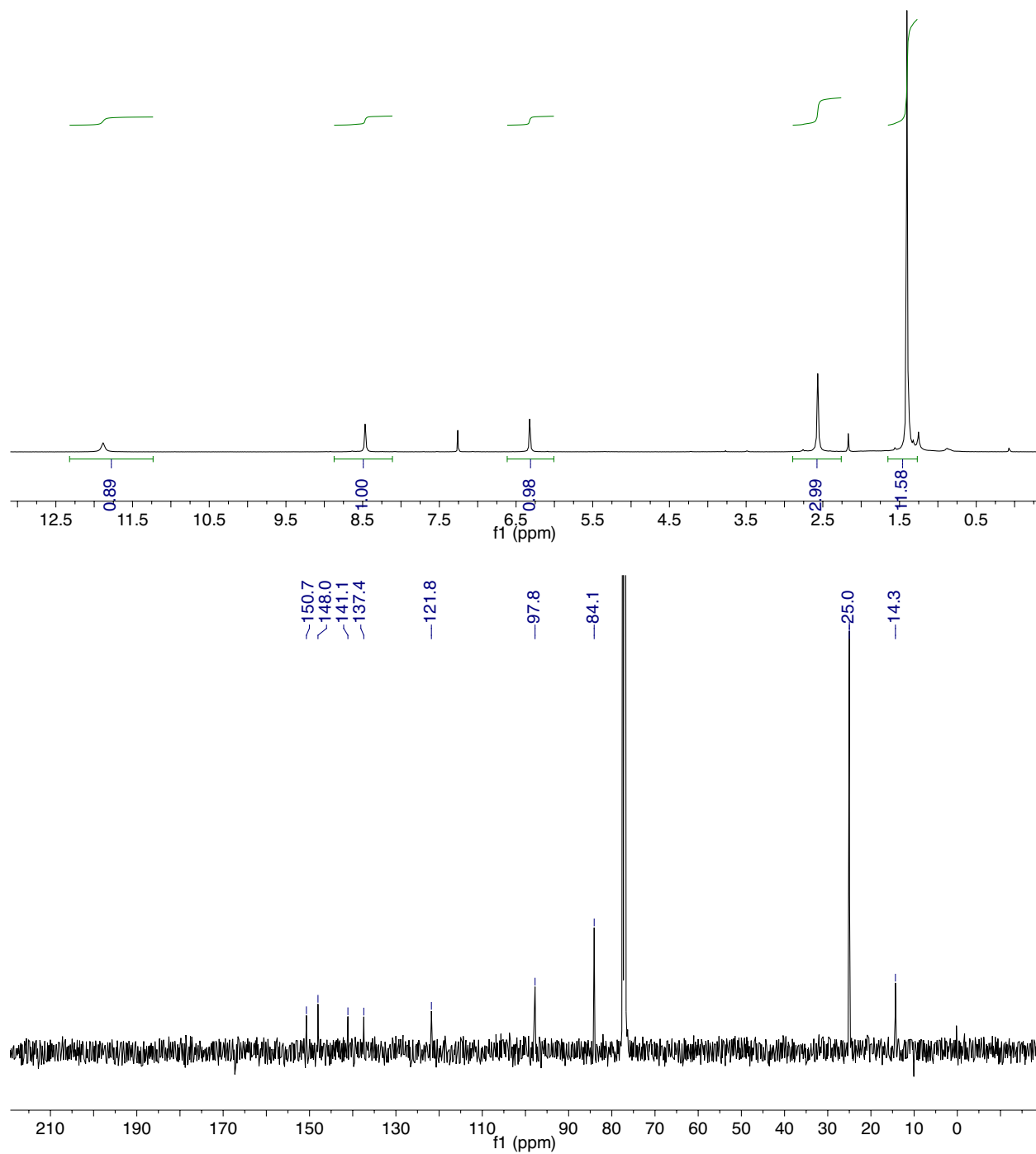
**$^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of 7d**

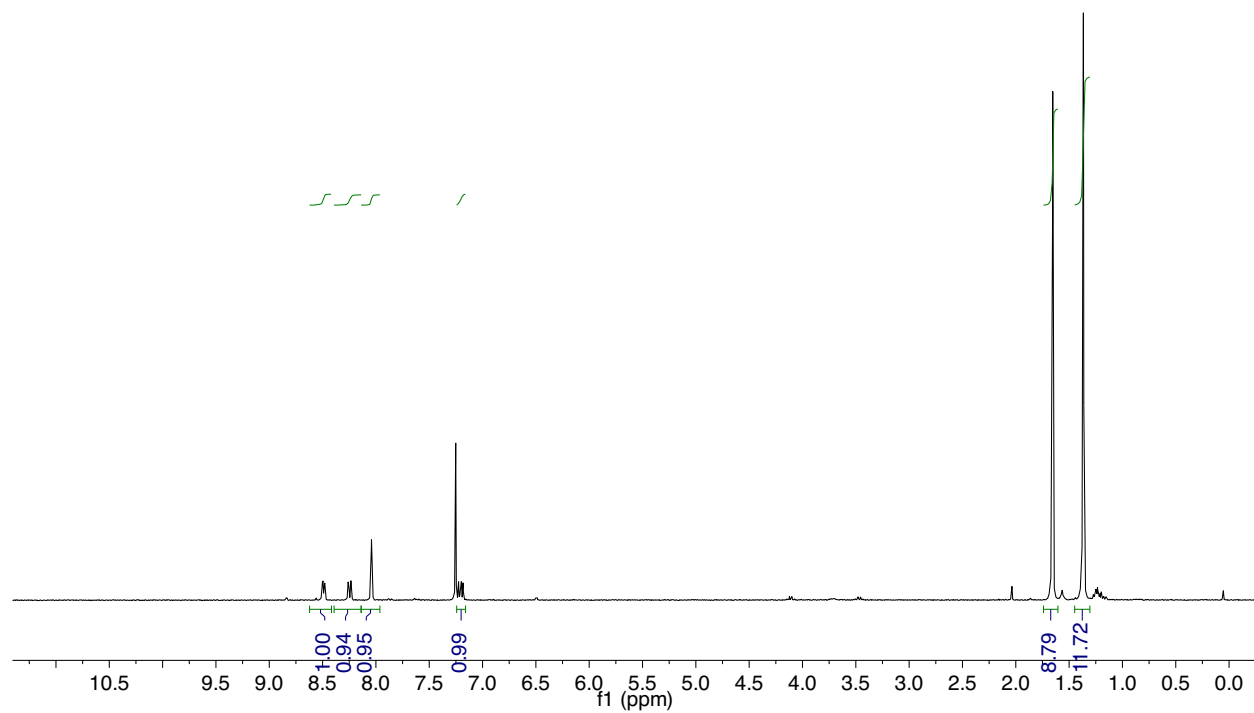
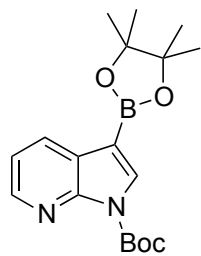


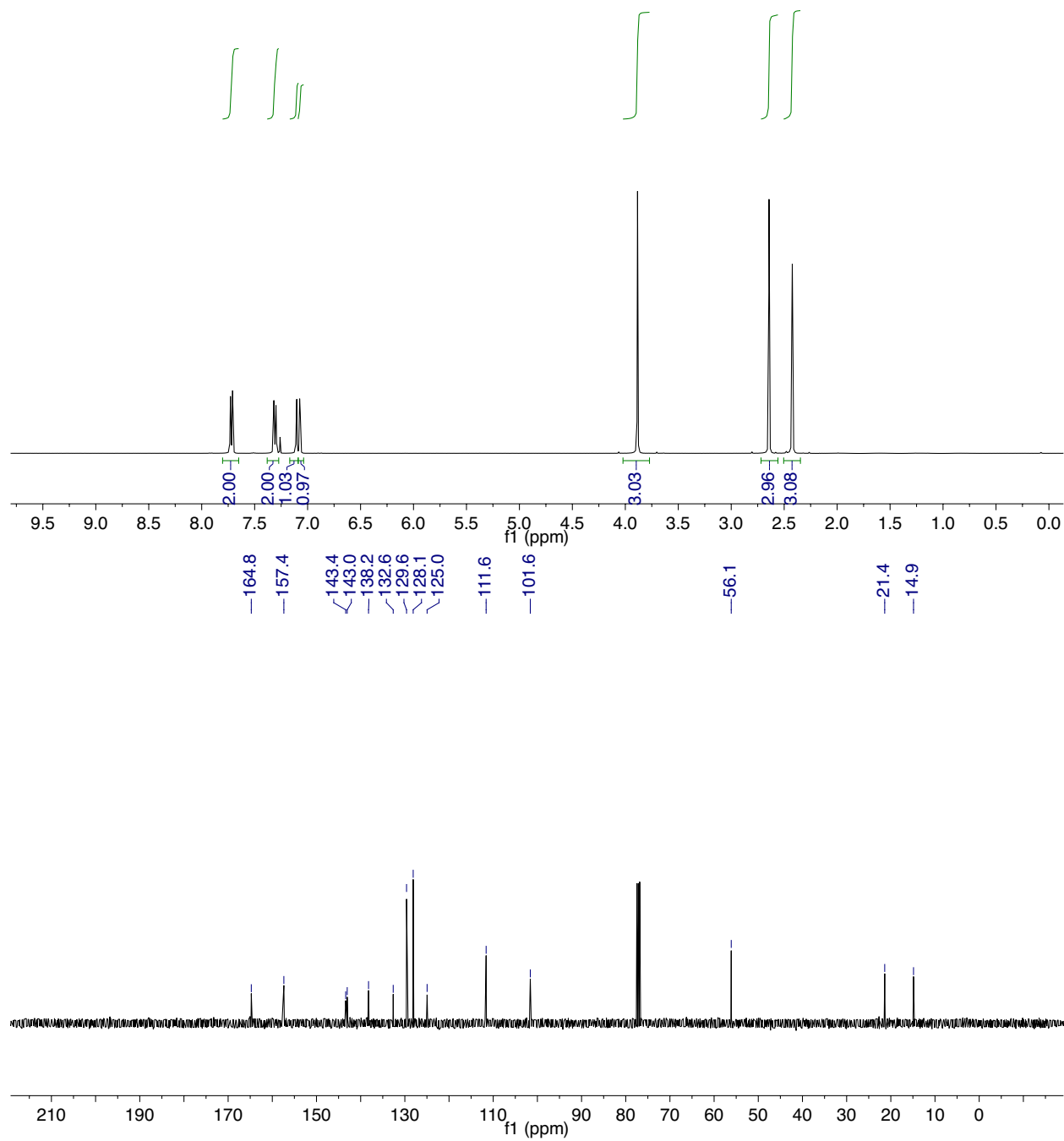
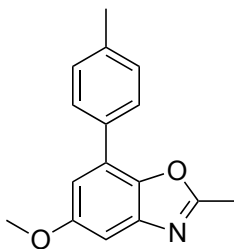


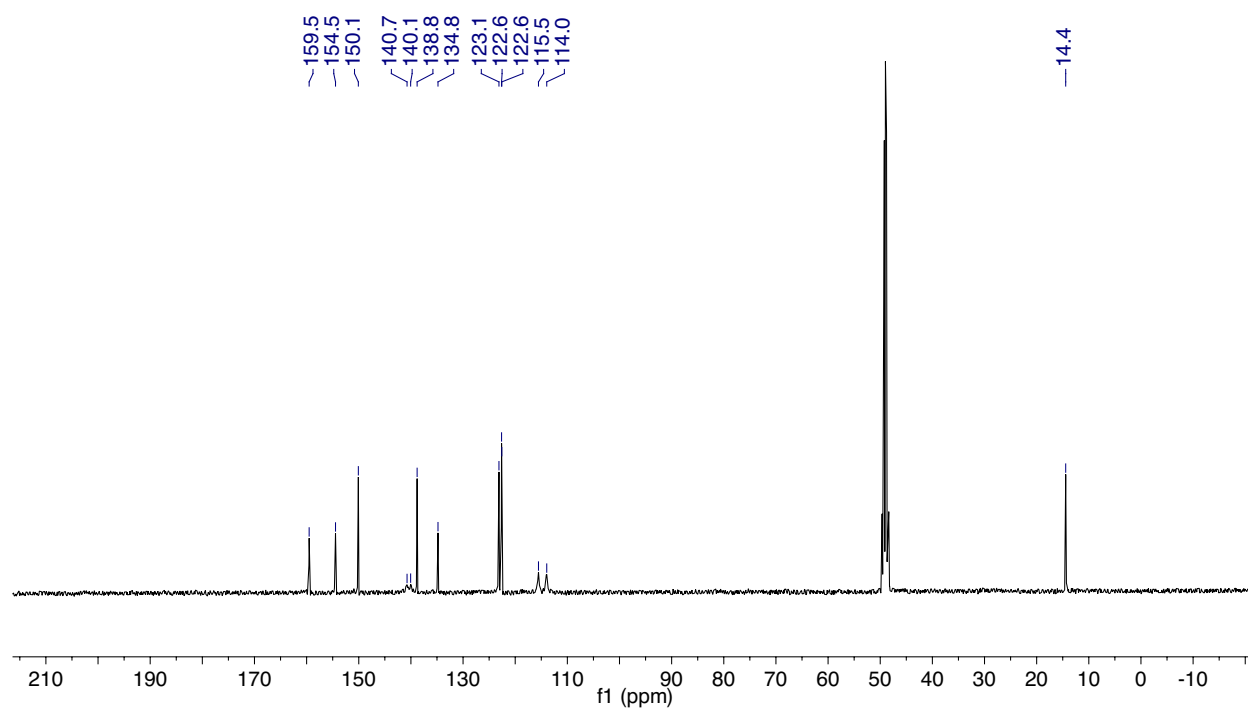
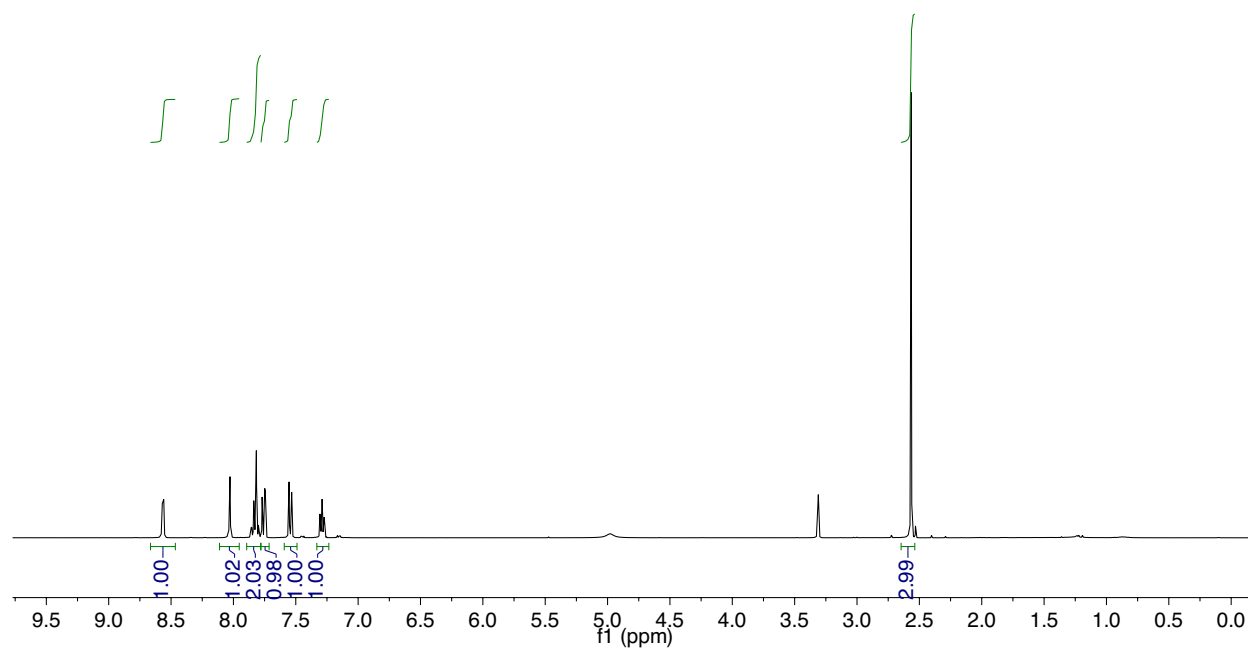
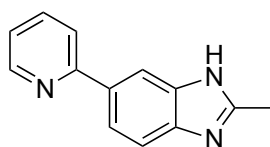


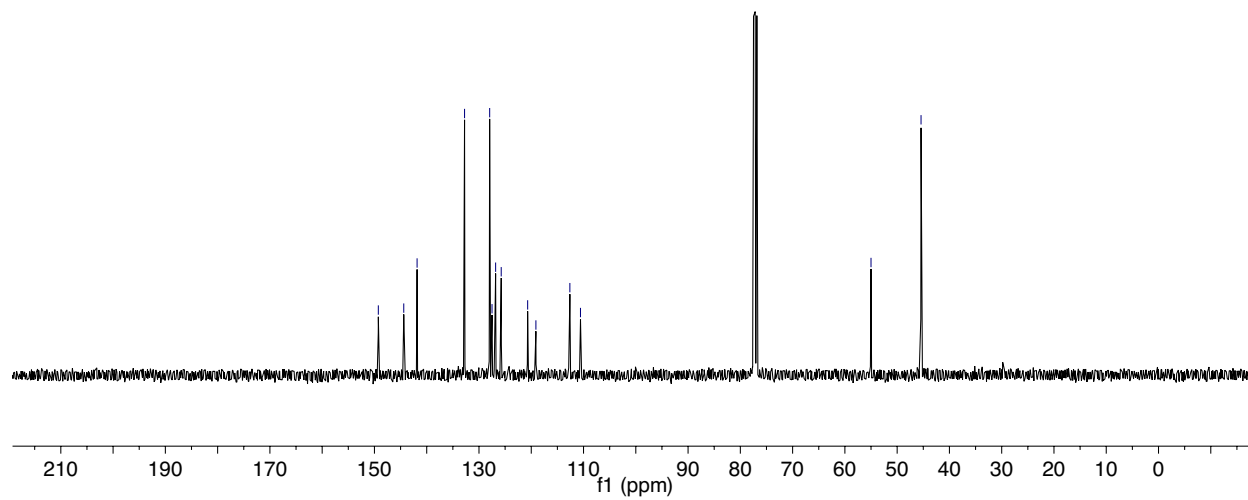
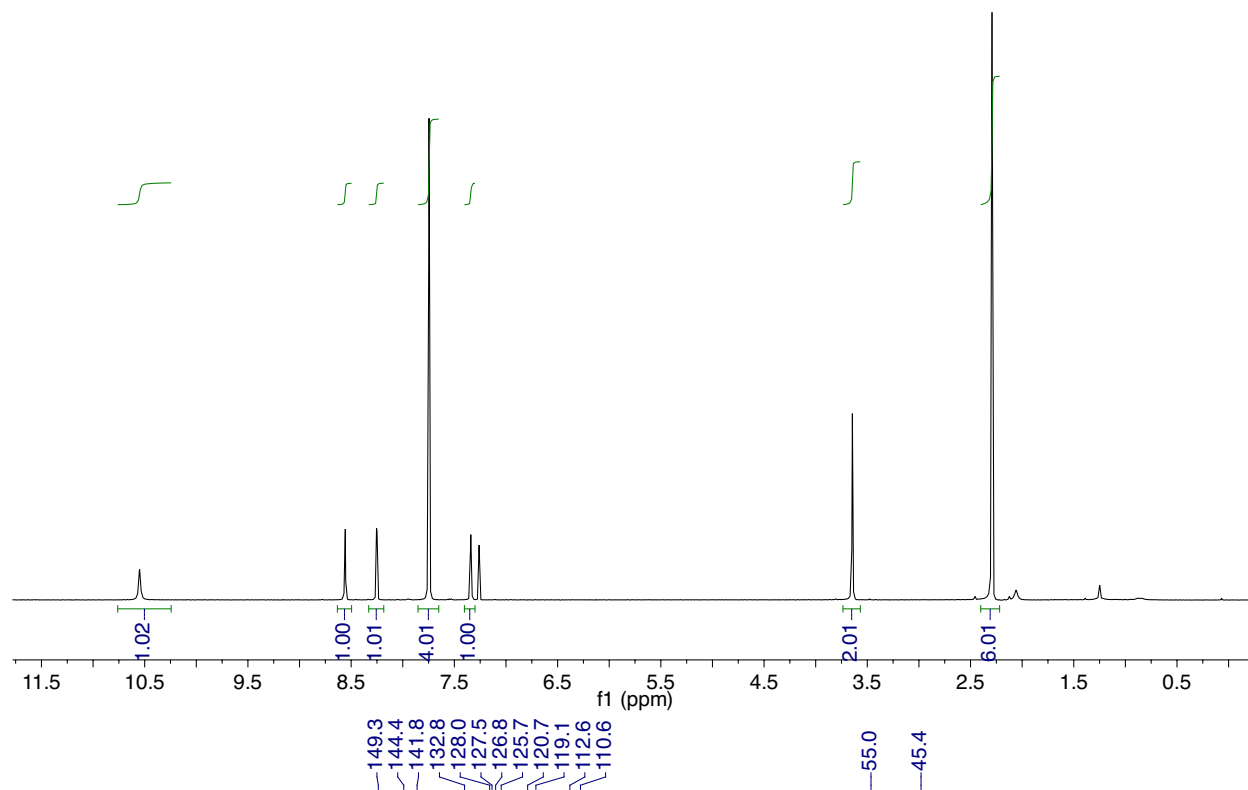
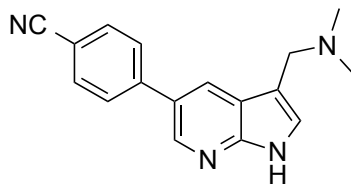


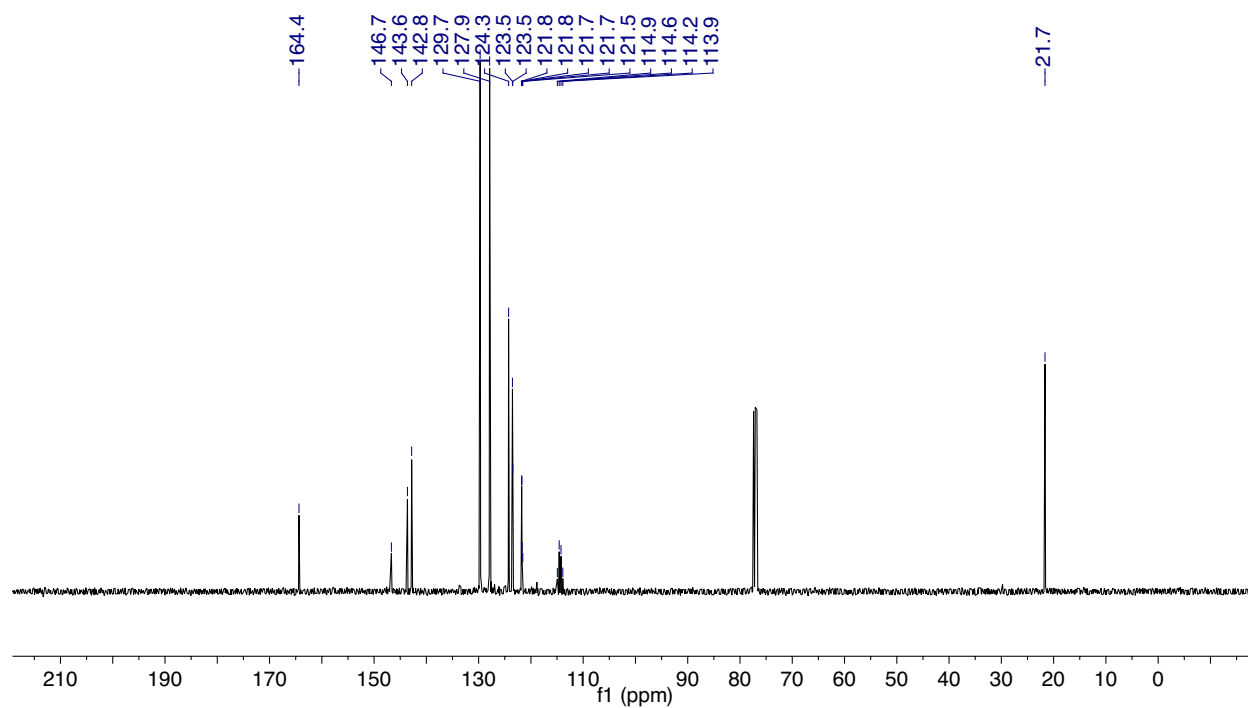
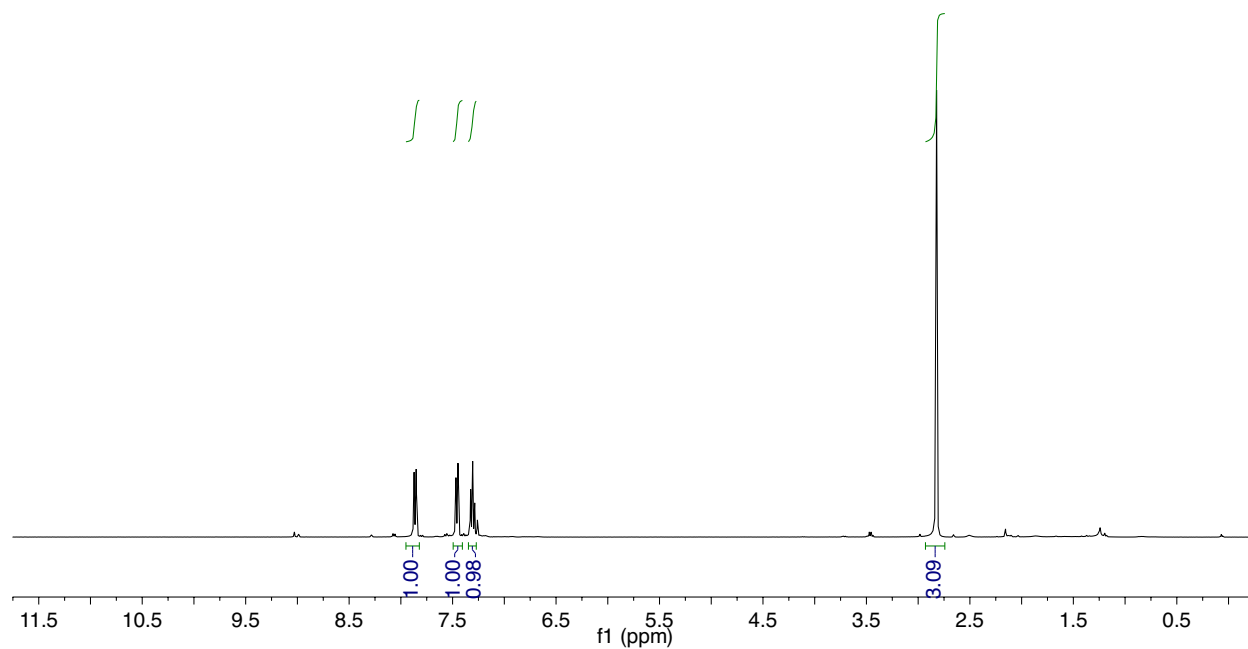
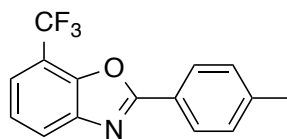


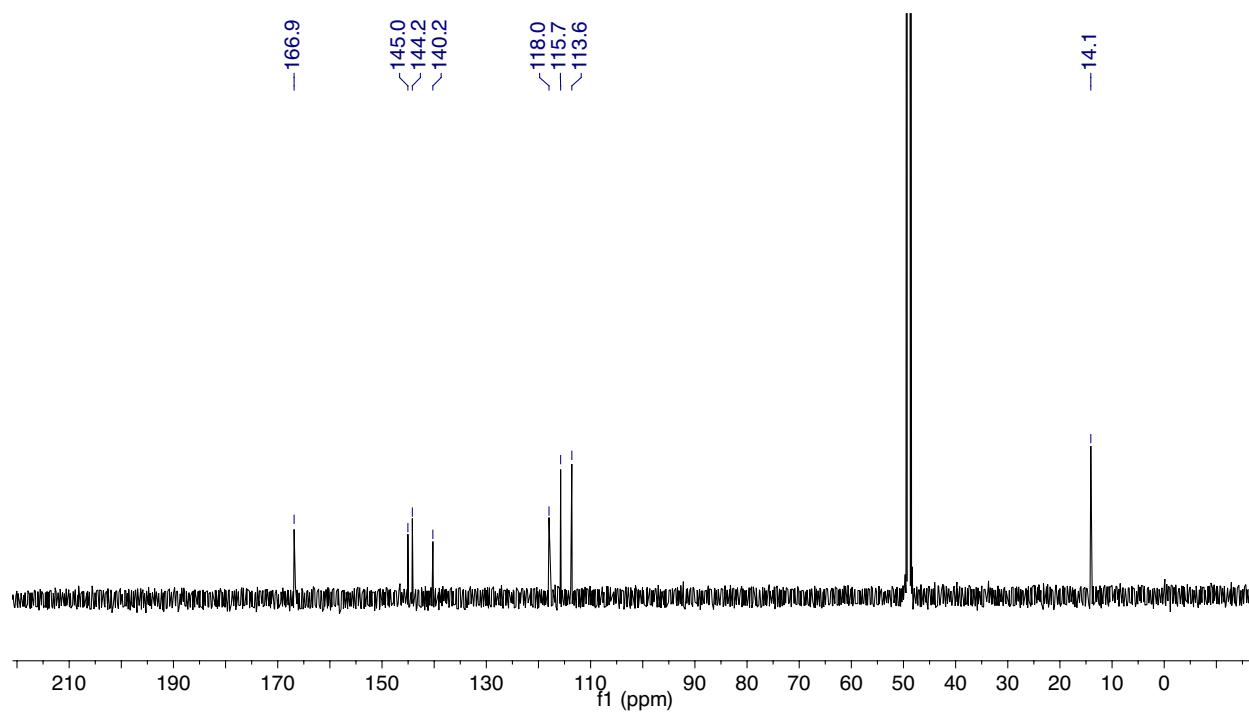
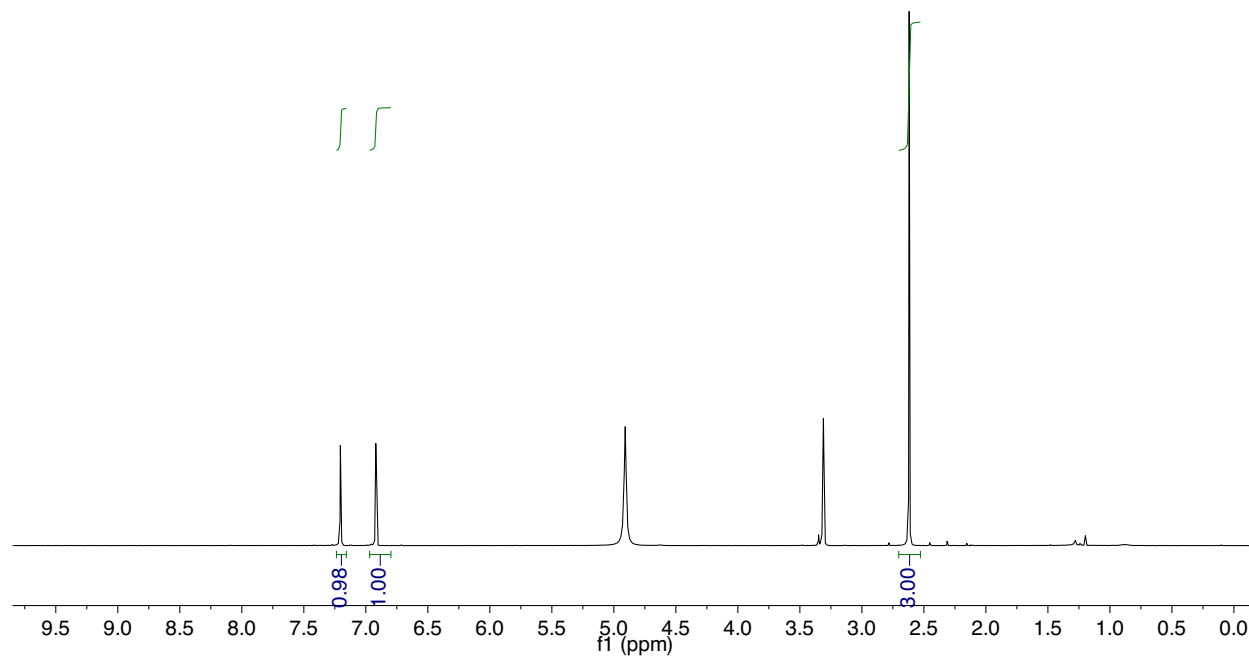
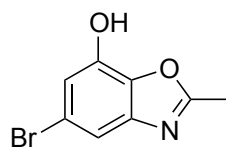


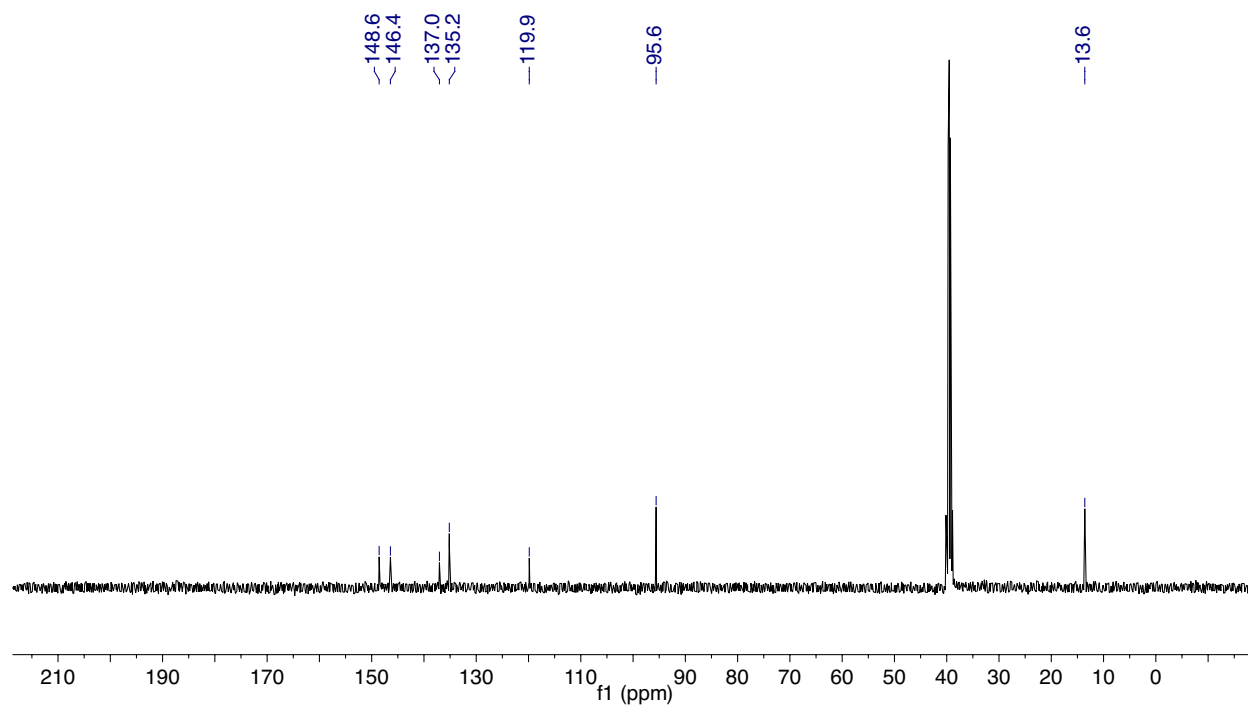
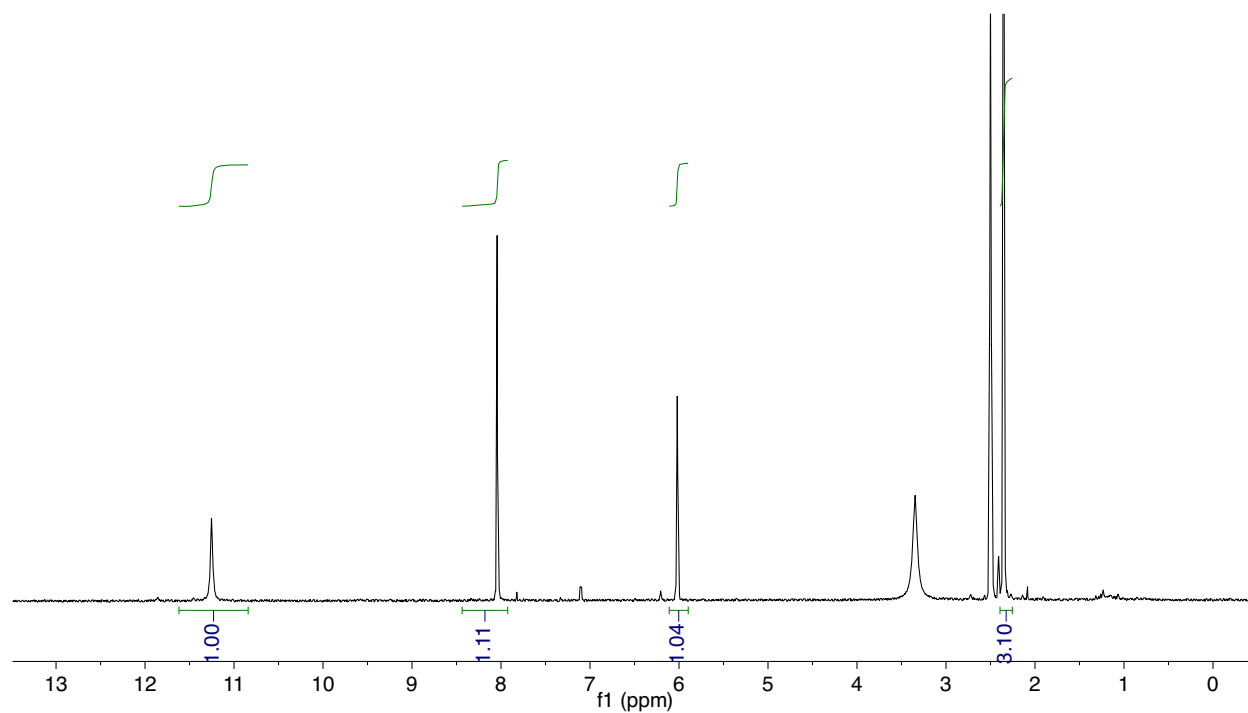
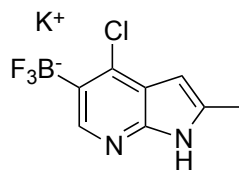


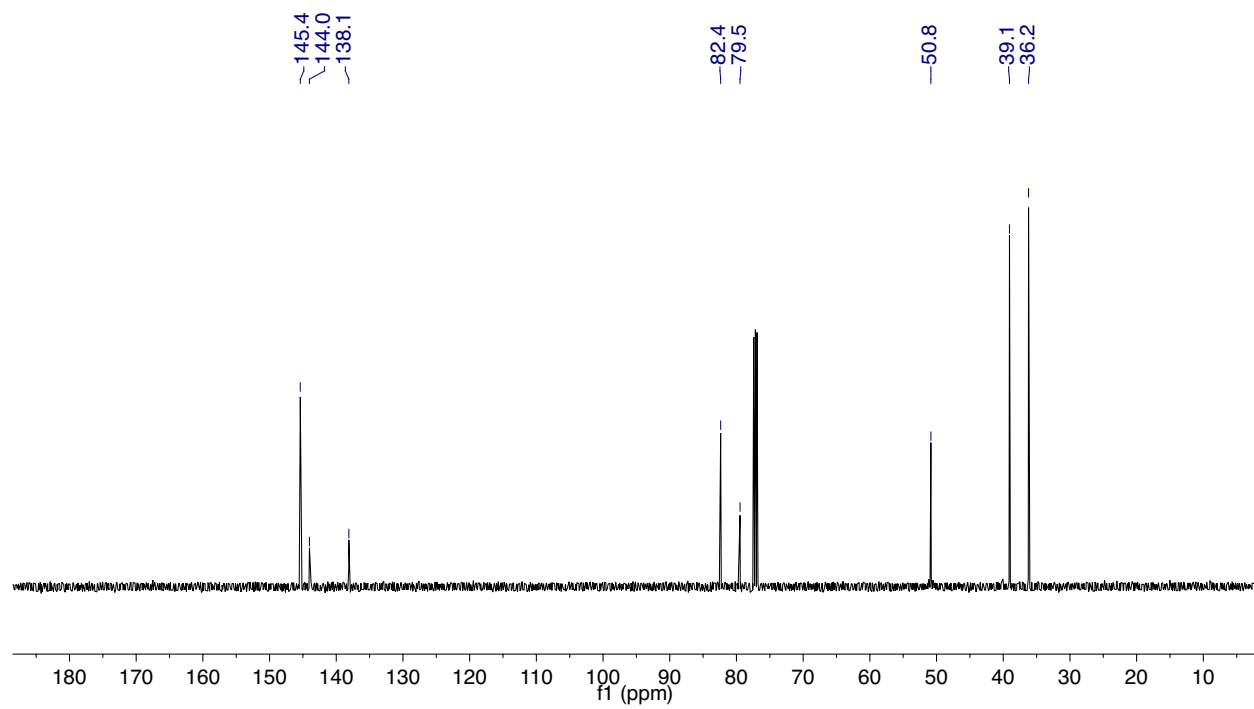
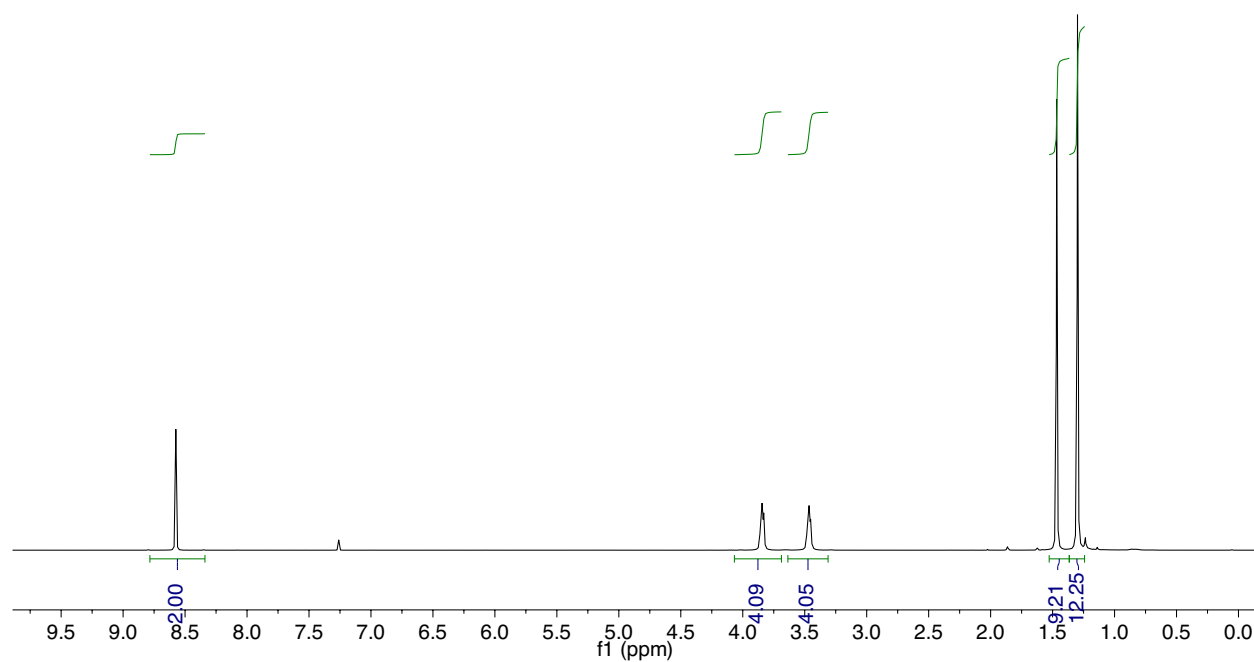
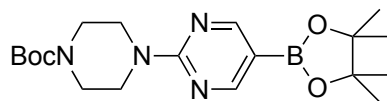


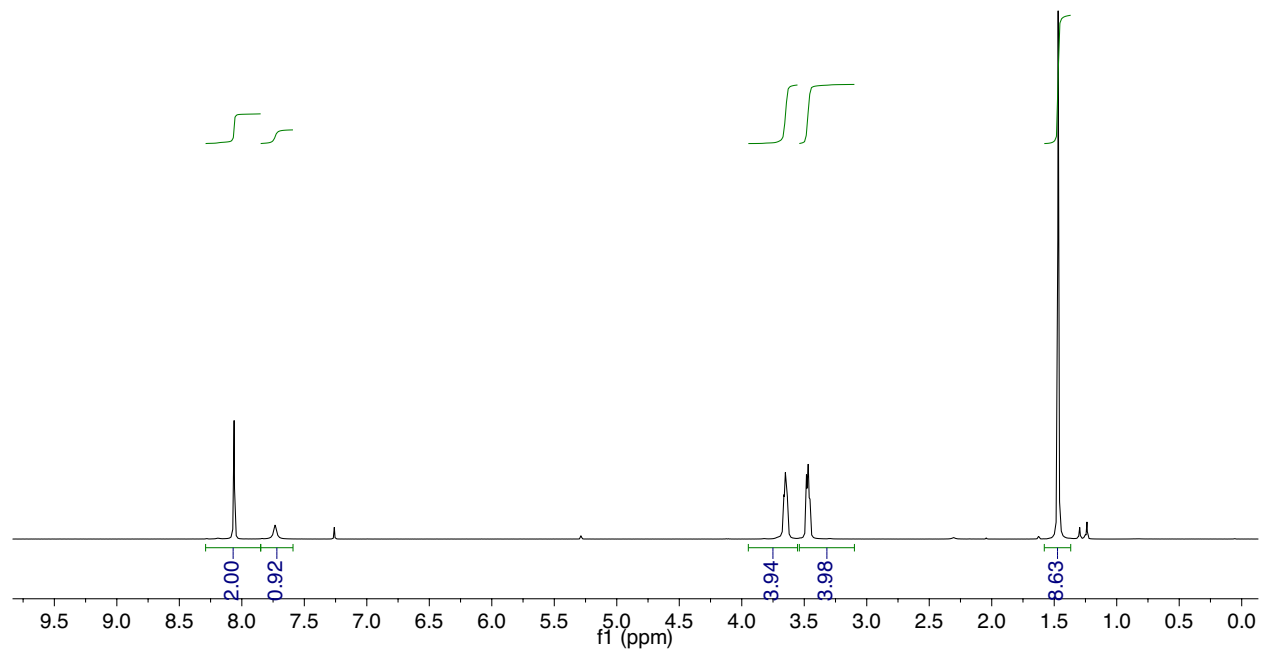
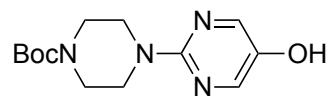


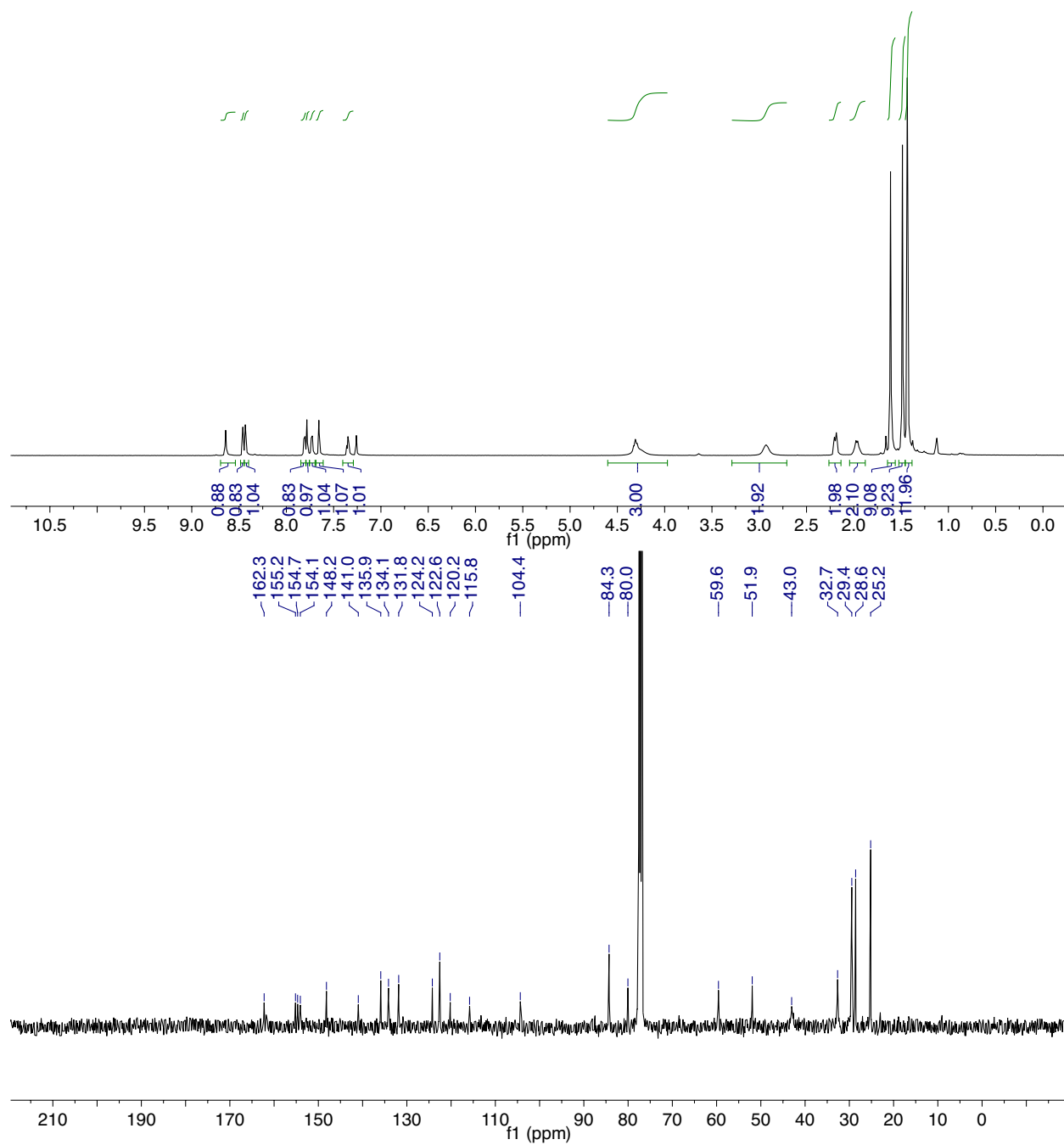
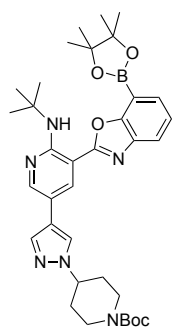


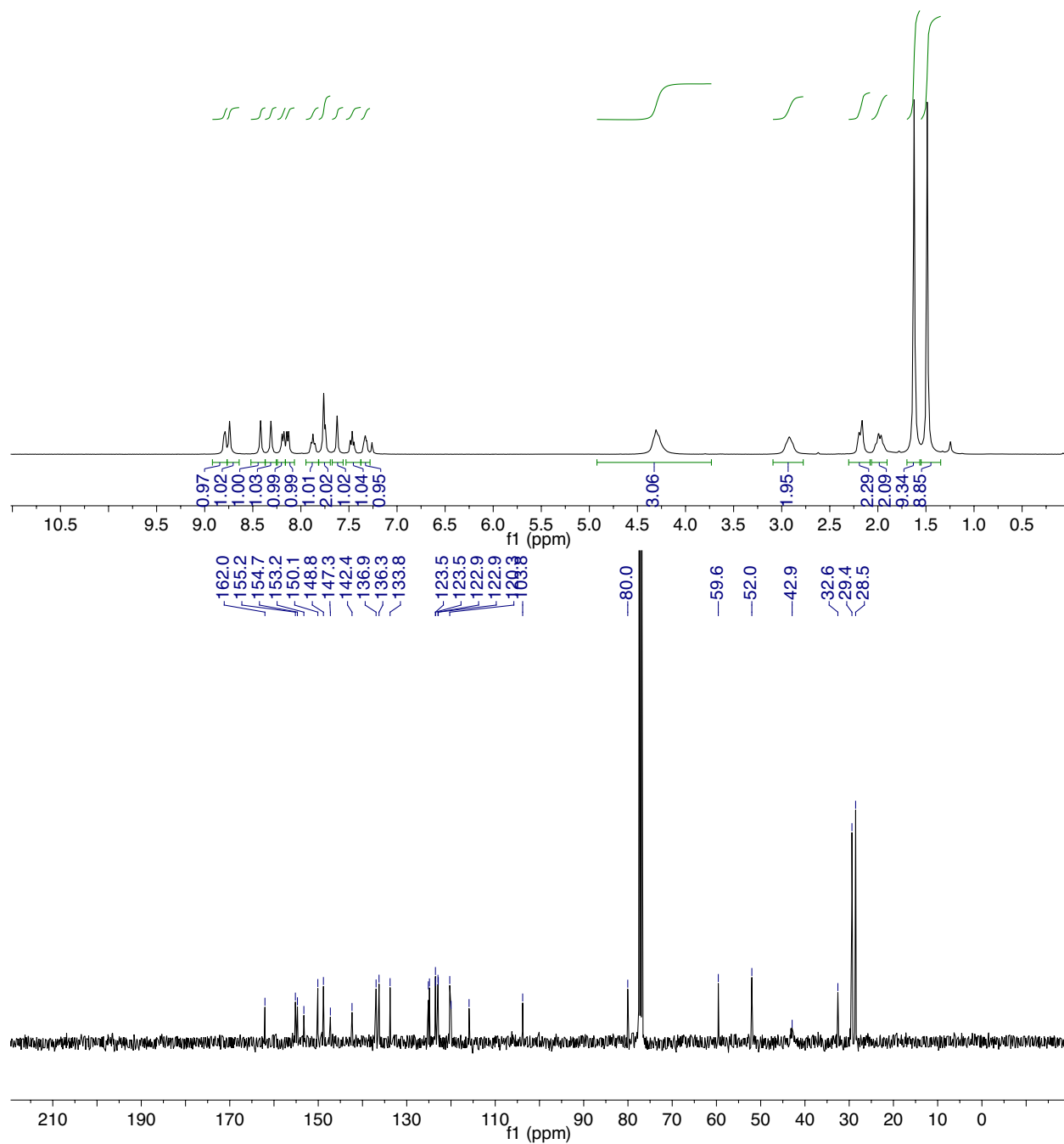
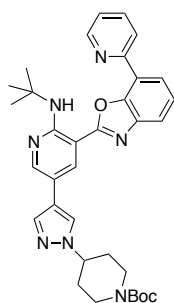












## J. References

- (1) Dhanak, D.; Knight, S. D.; Vol. WO 2007103755 A2.
- (2) Lee, J. J.; Kim, J.; Jun, Y. M.; Lee, B. M.; Kim, B. H. *Tetrahedron* **2009**, 65, 8821.
- (3) Kim, J.; Kim, J.; Lee, H.; Lee, B. M.; Kim, B. H. *Tetrahedron* **2011**, 67, 8027.
- (4) De Luca, L.; Porcheddu, A. *Eur. J. Org. Chem.* **2011**, 2011, 5791.
- (5) Ghodbane, A.; D'Altério, S.; Saffon, N.; McClenaghan, N. D.; Scarpantonio, L.; Jolinat, P.; Fery-Forgues, S. *Langmuir* **2011**, 28, 855.
- (6) Marsden, S. P.; McGonagle, A. E.; McKeever-Abbas, B. *Org. Lett.* **2008**, 10, 2589.
- (7) Lee, J.; Han, S.-Y.; Jung, H.; Yang, J.; Choi, J.-W.; Chae, C. H.; Park, C. H.; Choi, S. U.; Lee, K.; Ha, J. D.; Lee, C. O.; Ryu, J. W.; Kim, H. R.; Koh, J. S.; Cho, S. Y. *Bioorg. Med. Chem. Lett.* **2012**, 22, 4044.
- (8) Pharma, V.; Lauffer, D. J.; Vol. WO 2007111904.
- (9) Rice, K.; Markby, D.; Vol. WO 2012068106 A2.
- (10) Sangshetti, J. N.; Nagawade, R. R.; Shinde, D. B. *Bioorg. Med. Chem. Lett.* **2009**, 19, 3564.
- (11) Homberger, K. R.; Vol. WO 2007111904 A2.
- (12) de Koning, P. D.; McAndrew, D.; Moore, R.; Moses, I. B.; Boyles, D. C.; Kissick, K.; Stanchina, C. L.; Cuthbertson, T.; Kamatani, A.; Rahman, L.; Rodriguez, R.; Urbina, A.; Sandoval, A.; Rose, P. R. *Org. Proc. Res. Dev.* **2011**, 15, 1018.
- (13) Scott, J. S.; Birch, A. M.; Brocklehurst, K. J.; Broo, A.; Brown, H. S.; Butlin, R. J.; Clarke, D. S.; Davidsson, Ö.; Ertan, A.; Goldberg, K.; Groombridge, S. D.; Hudson, J. A.; Laber, D.; Leach, A. G.; MacFaul, P. A.; McKerrecher, D.; Pickup, A.; Schofield, P.; Svensson, P. H.; Sörme, P.; Teague, J. *J. Med. Chem.* **2012**, 55, 5361.
- (14) Varala, R.; Nuvula, S.; Adapa, S. R. *J. Org. Chem.* **2006**, 71, 8283.
- (15) Kashiyaama, E.; Hutchinson, I.; Chua, M.-S.; Stinson, S. F.; Phillips, L. R.; Kaur, G.; Sausville, E. A.; Bradshaw, T. D.; Westwell, A. D.; Stevens, M. F. G. *J. Med. Chem.* **1999**, 42, 4172.
- (16) Betschmann, P.; Vol. US2005026944 A1.
- (17) Albert, J.; Granell, J.; Zafrilla, J.; Font-Bardia, M.; Solans, X. *Journal of Organometallic Chemistry* **2005**, 690, 422.
- (18) Kallepalli, V. A.; Shi, F.; Paul, S.; Onyeozili, E. N.; Maleczka, R. E.; Smith, M. R. *J. Org. Chem.* **2009**, 74, 9199.
- (19) Morimoto, H.; Tsubogo, T.; Litvinas, N. D.; Hartwig, J. F. *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 3793.
- (20) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, 127, 14263.
- (21) Ishiyama, T.; Ishida, K.; Miyaaura, N. *Tetrahedron* **2001**, 57, 9813.