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# *Synthesis and reactions of new N-heteroaryl boronic acids*

Kate Mary Clapham

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## APPENDIX 2 – NMR SPECTRA

$^1\text{H}$  and  $^{13}\text{C}$  NMR data for all new compounds are given herein. Some 2D NMR has been included where necessary, for discussion related in the main thesis. NMR spectra for literature reported compounds are not given.

### A2.1 NMR spectra of compounds from Chapter 2

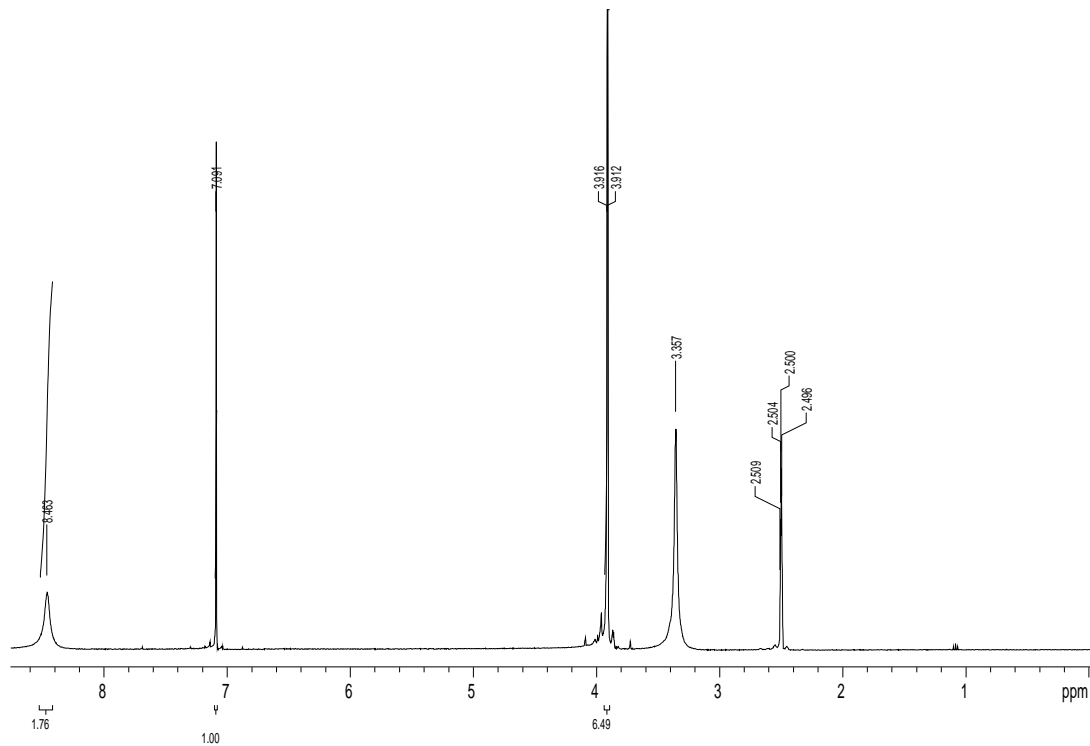
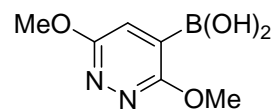
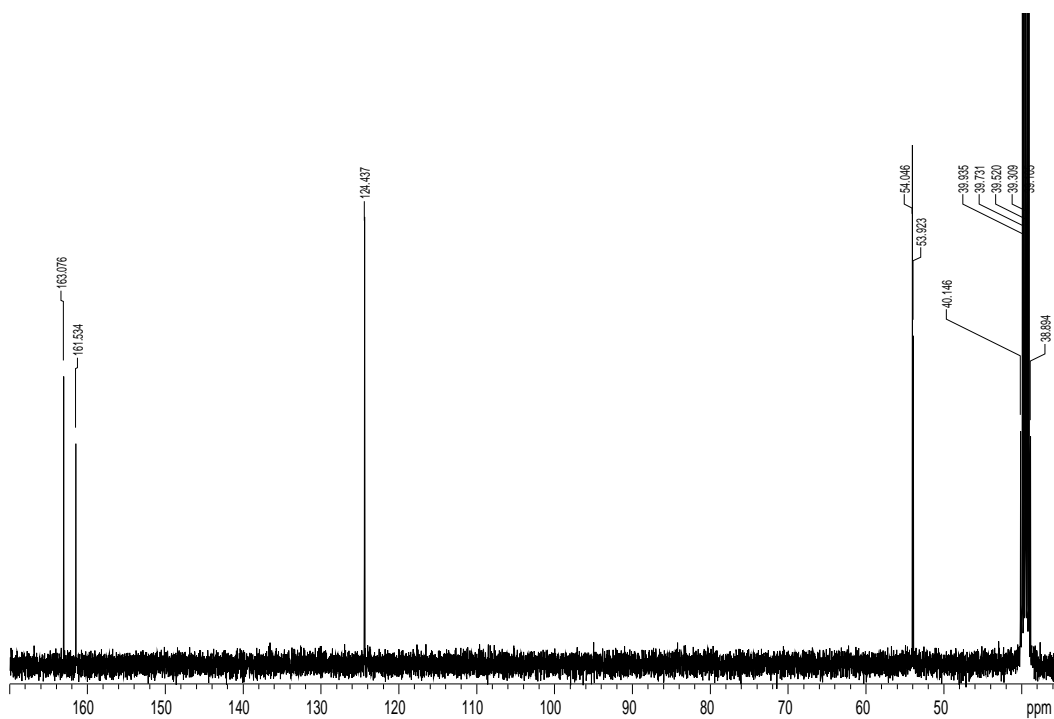
|  |                   |
|--|-------------------|
| NMR spectra of compound <b>59</b>                    | page A2.2         |
| NMR spectra of compounds <b>63-73</b>                | pages A2.3-A2.9   |
| NMR spectra of compounds <b>75c, d, 76a-d, 77a-d</b> | pages A2.10-A2.19 |
| NMR spectra of compounds <b>79, 80, 82-92</b>        | pages A2.11-A2.32 |

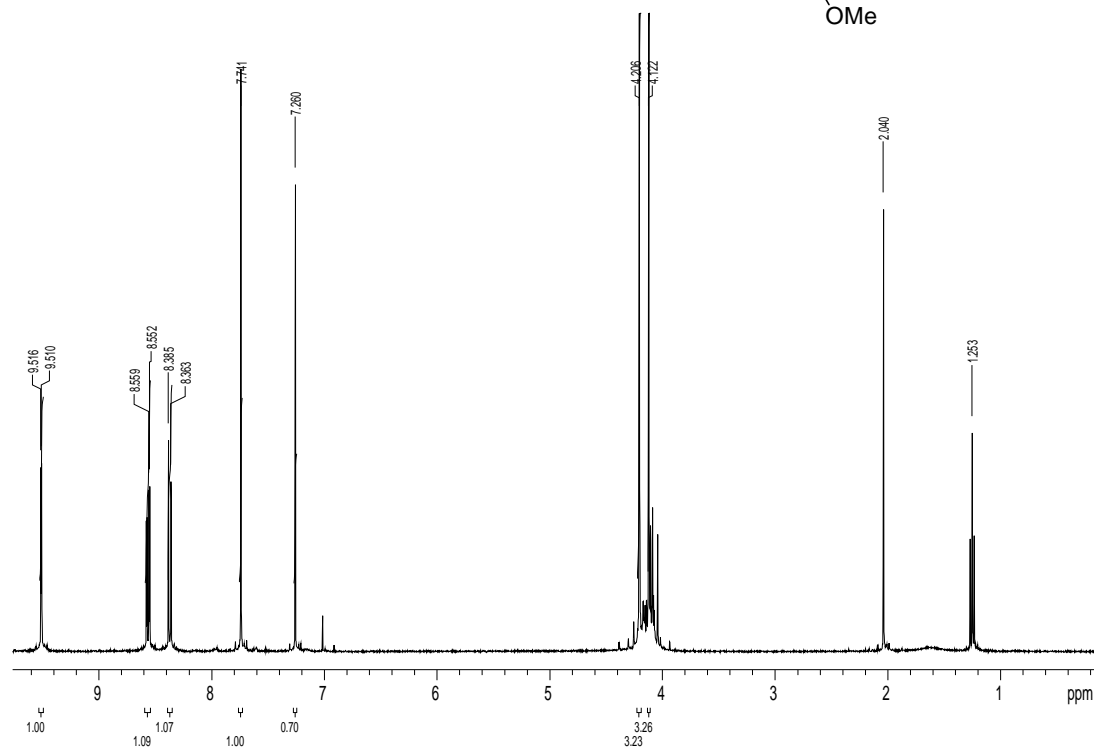
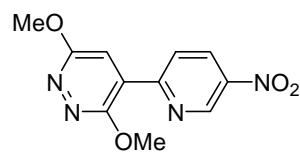
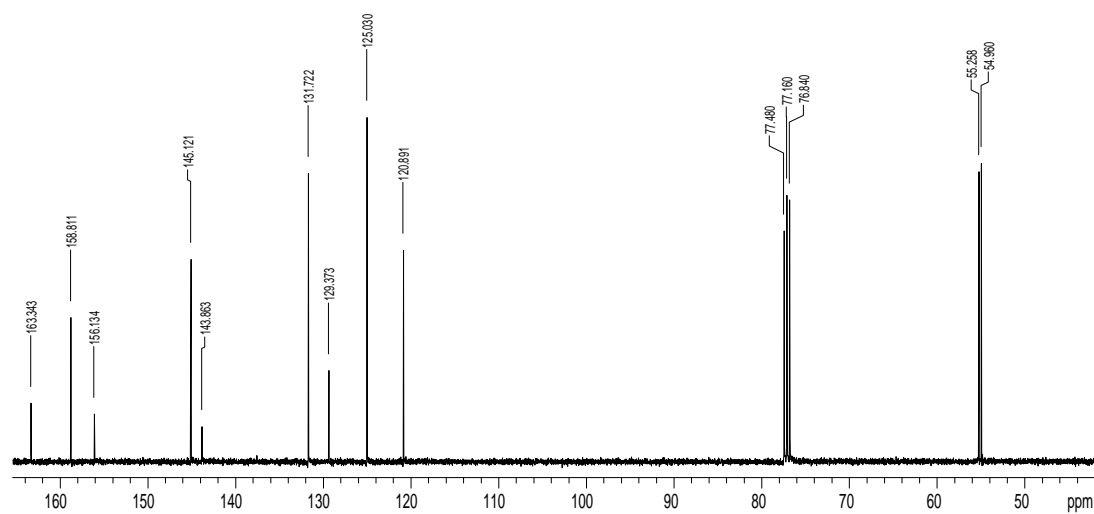
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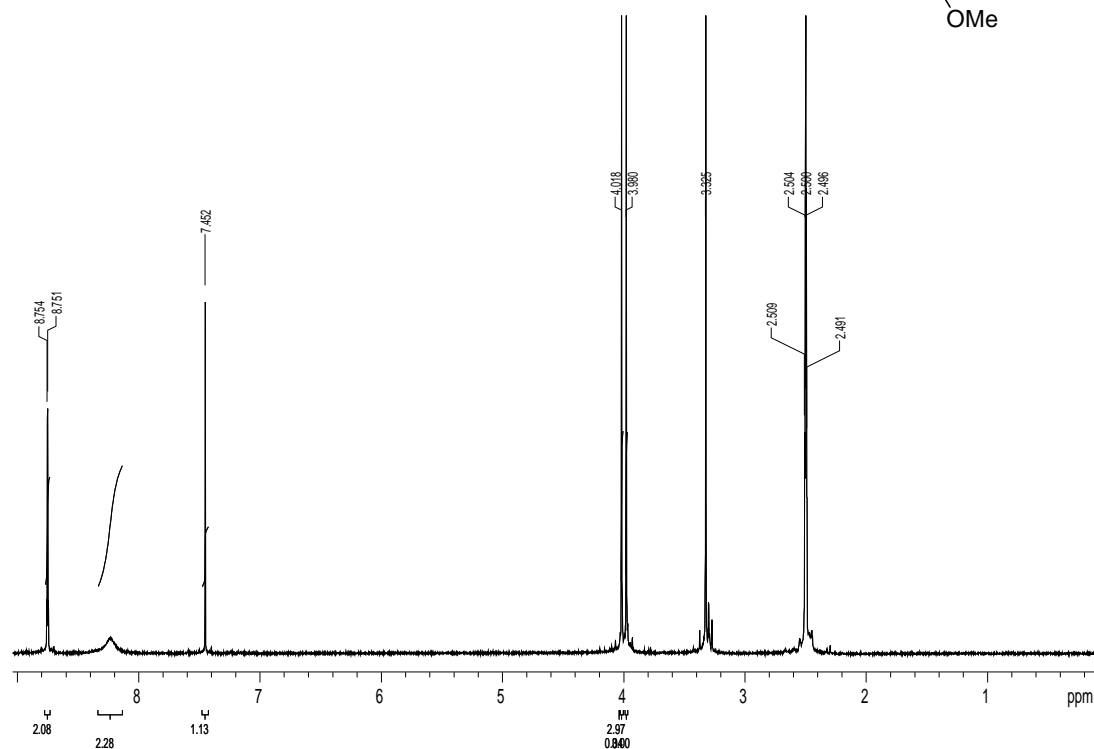
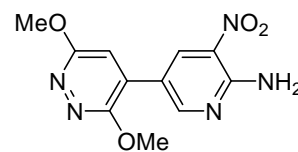
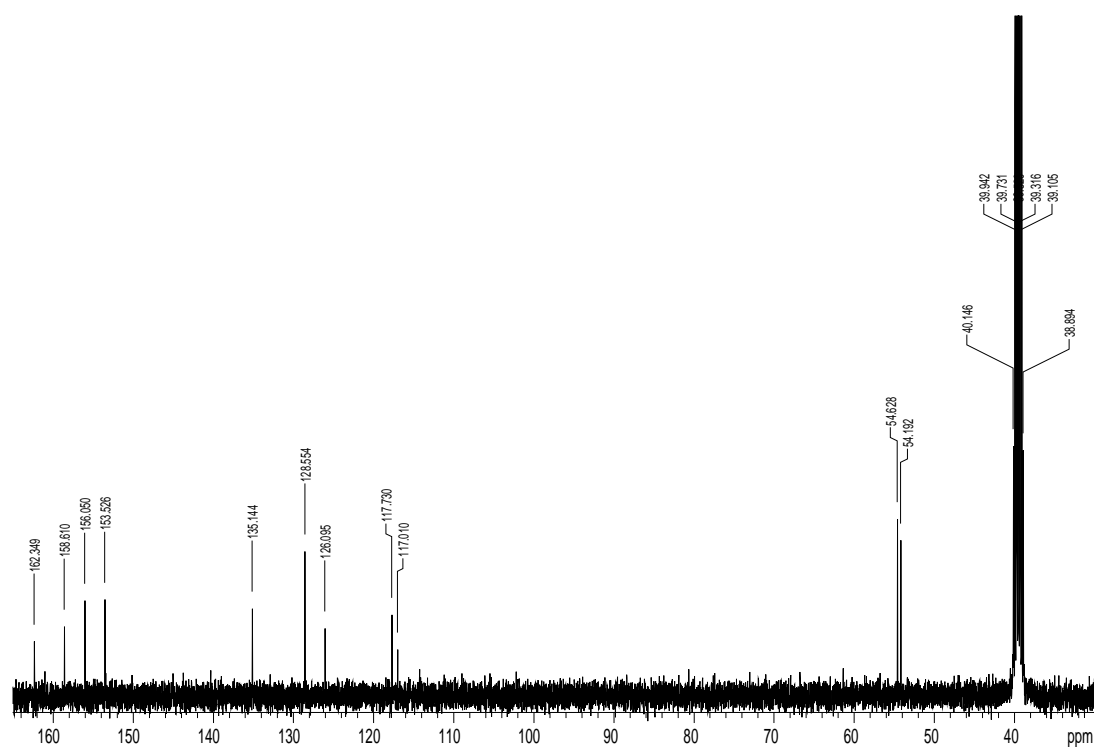
|   |                   |
|---|-------------------|
| NMR spectra of compounds <b>99, 103-106</b> | pages A2.33-A2.37 |
| NMR spectra of compounds <b>112-117</b>     | pages A2.38-A2.43 |
| NMR spectra of compounds <b>118-121</b>     | pages A2.44-A2.49 |

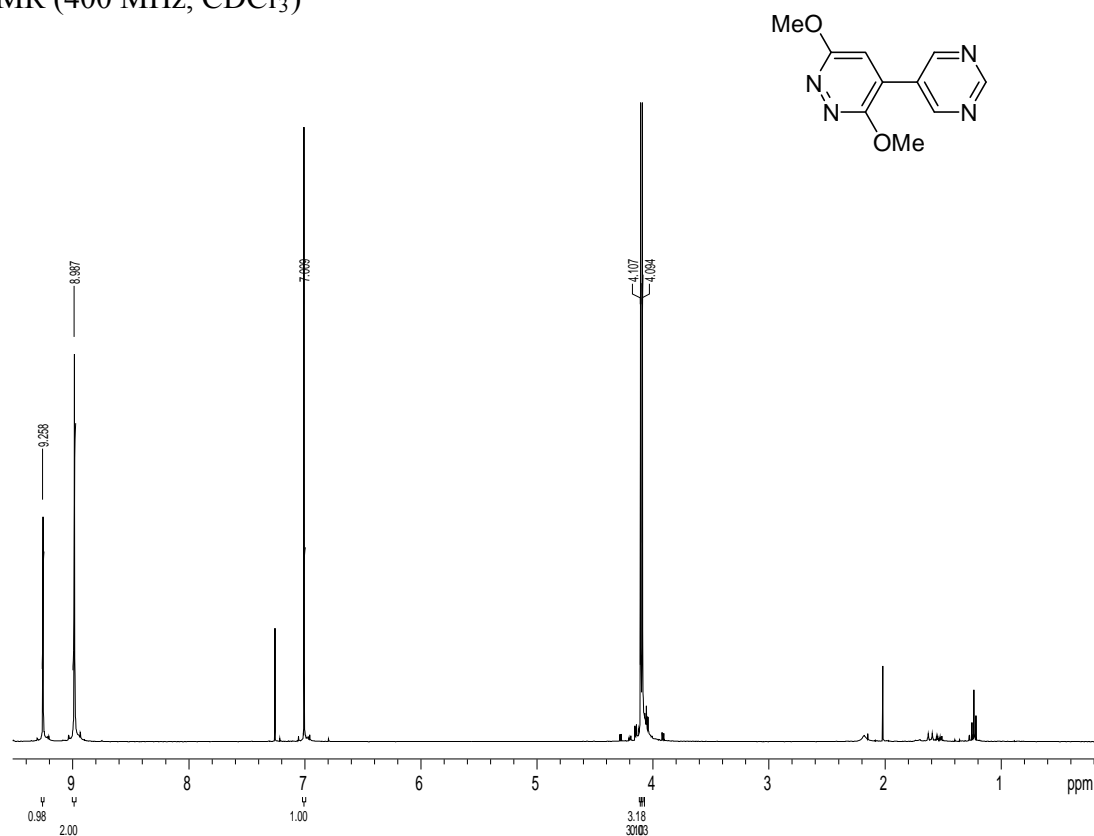
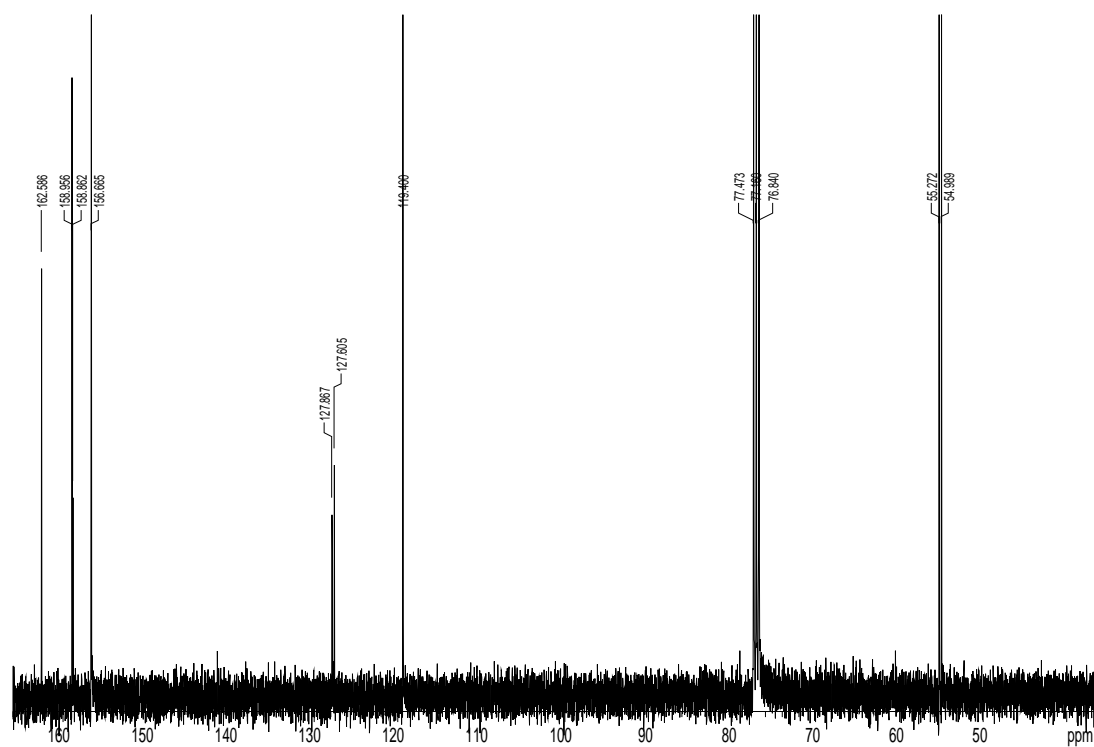
### A2.3 NMR spectra of compounds from Chapter 4

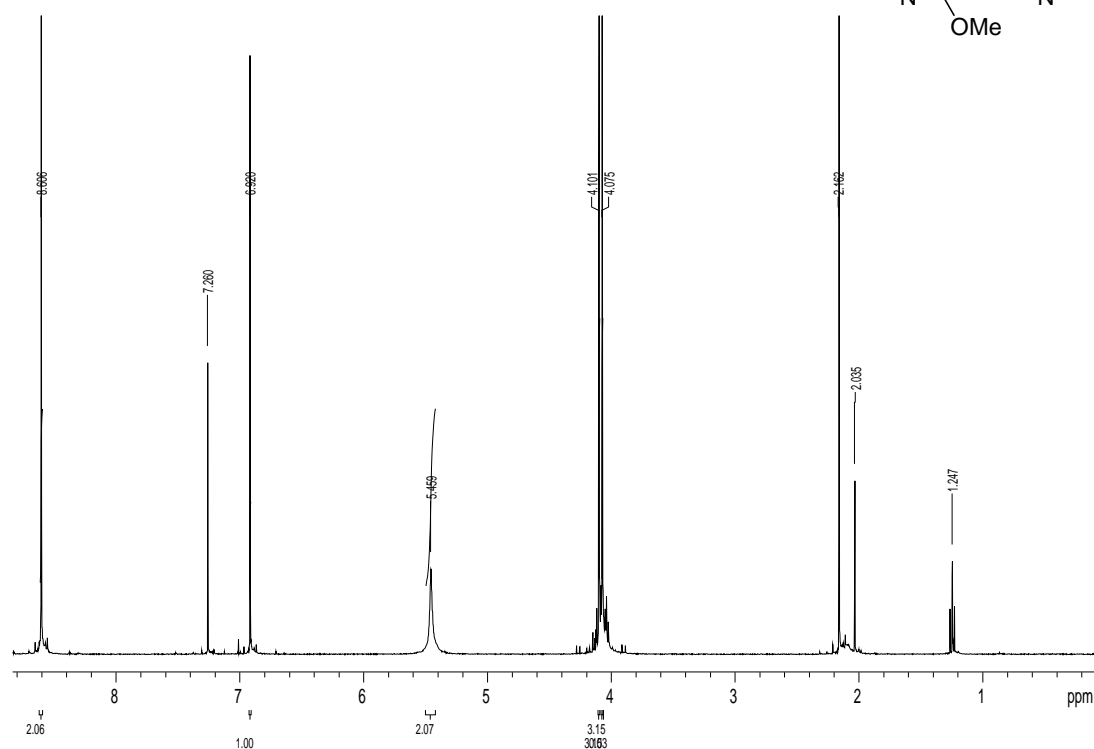
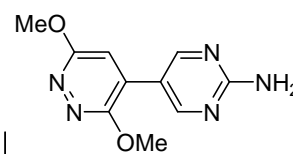
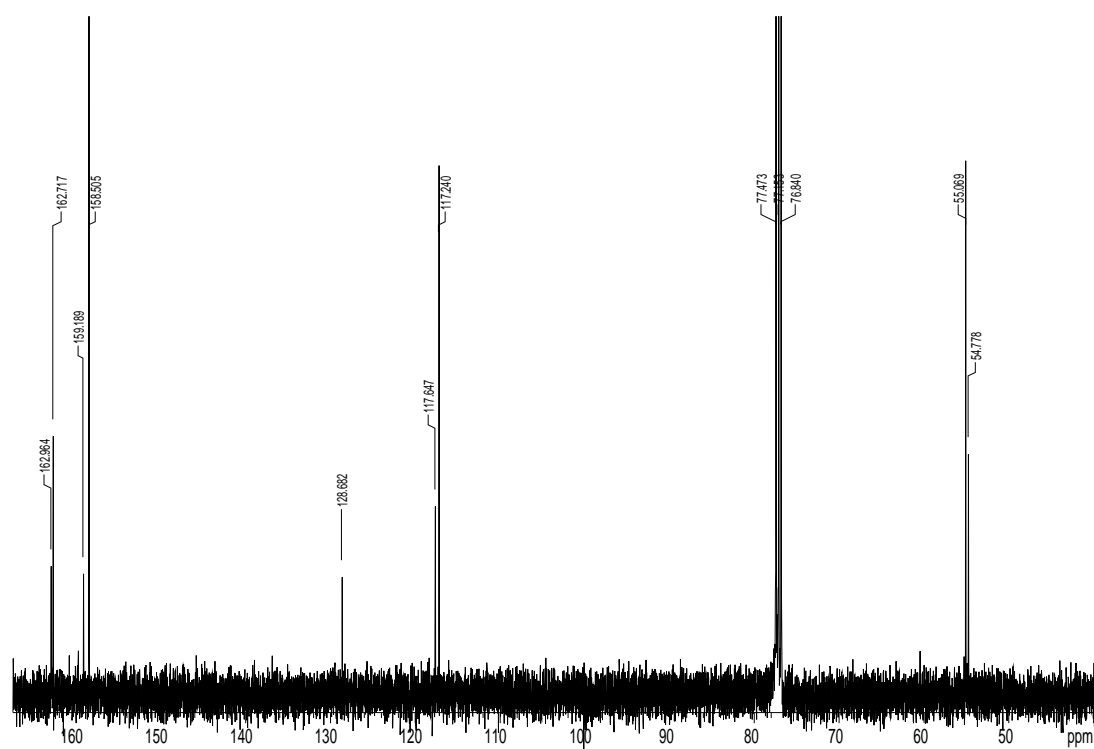
|   |                   |
|---|-------------------|
| NMR spectra of compounds <b>136, 137</b>          | pages A2.50-A2.51 |
| NMR spectra of compounds <b>143-155</b>           | pages A2.52-A2.65 |
| NMR spectra of compounds <b>157, 158</b>          | pages A2.66-A2.67 |
| NMR spectra of compounds <b>159b, c, 160a-c</b>   | pages A2.68-A2.72 |
| NMR spectra of compounds <b>162-175</b>           | pages A2.73-A2.86 |
| NMR spectra of compounds <b>177, 179, 181-189</b> | pages A2.87-A2.96 |

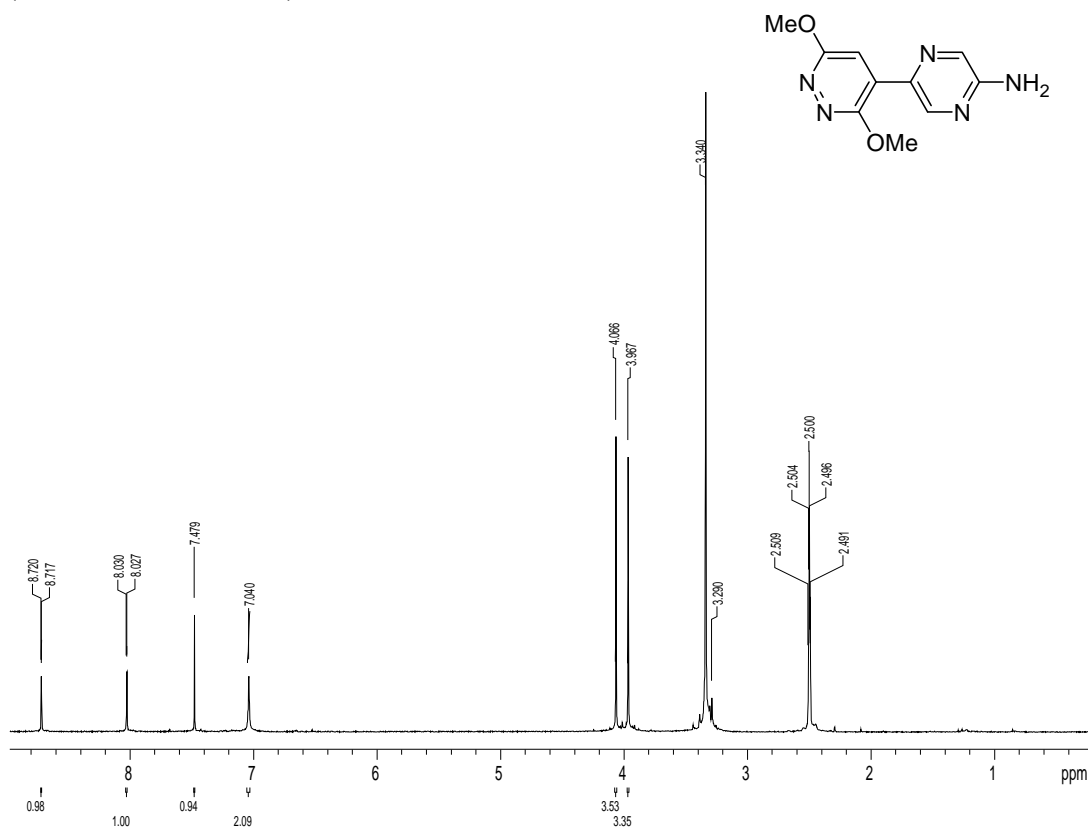
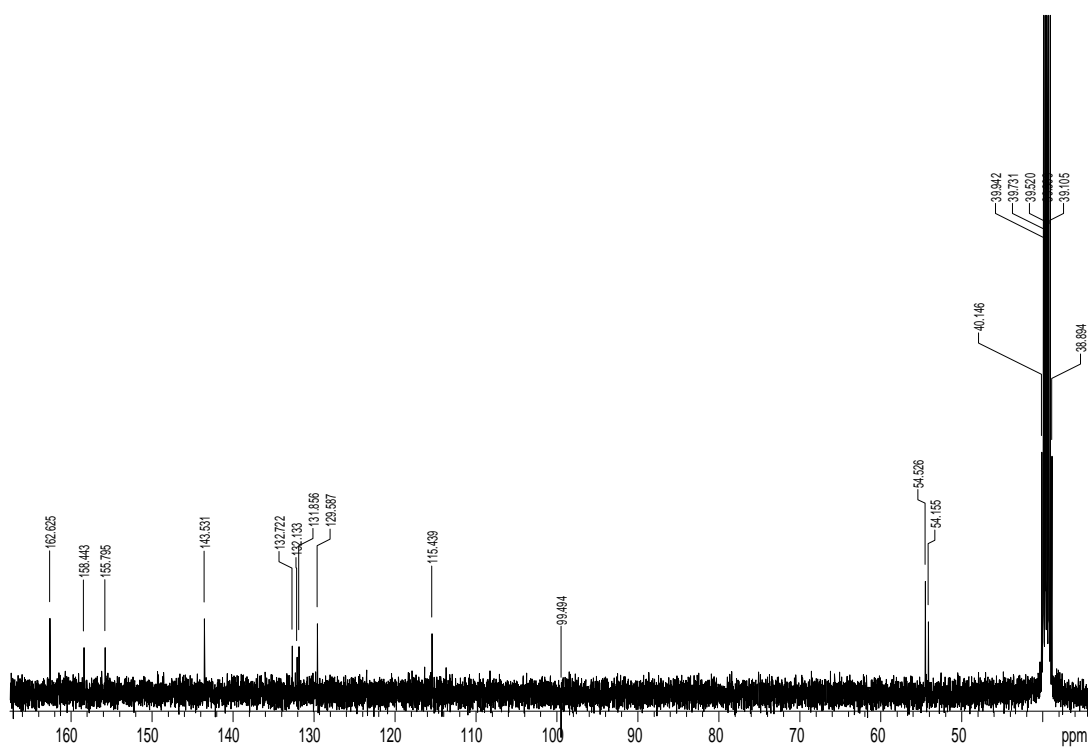
**A2.1 NMR spectra of compounds from Chapter 2****3,6-Dimethoxy-4-pyridazinylboronic acid (59)** $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )

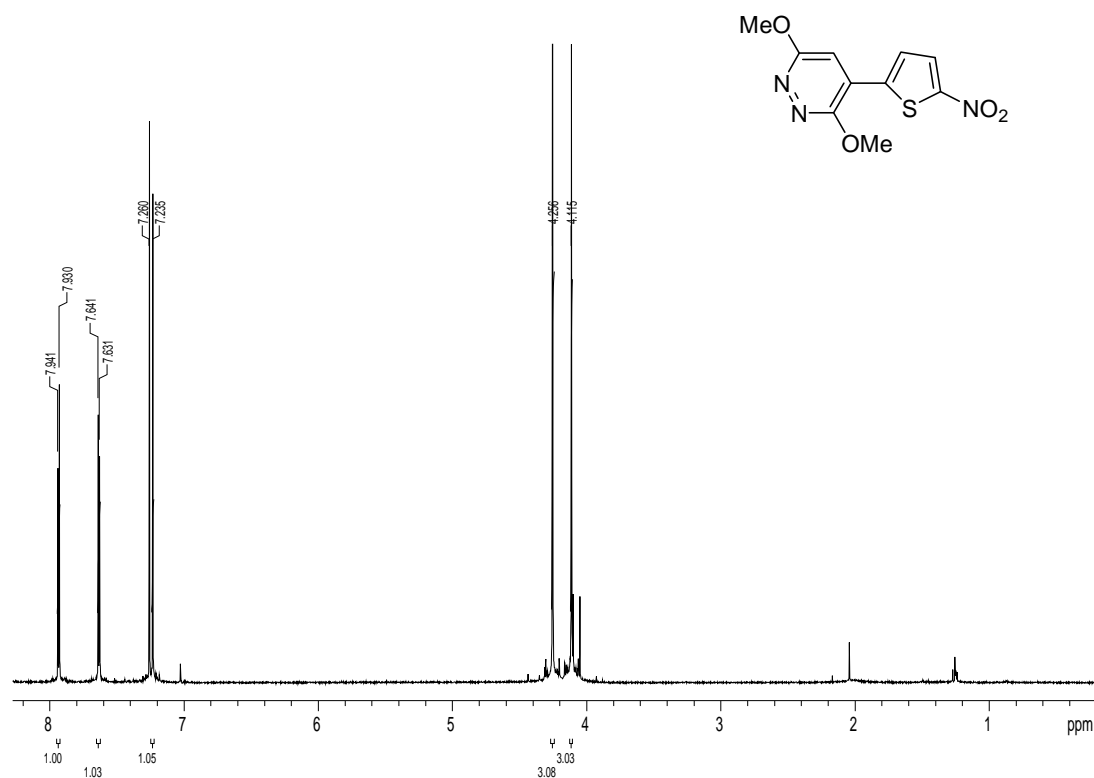
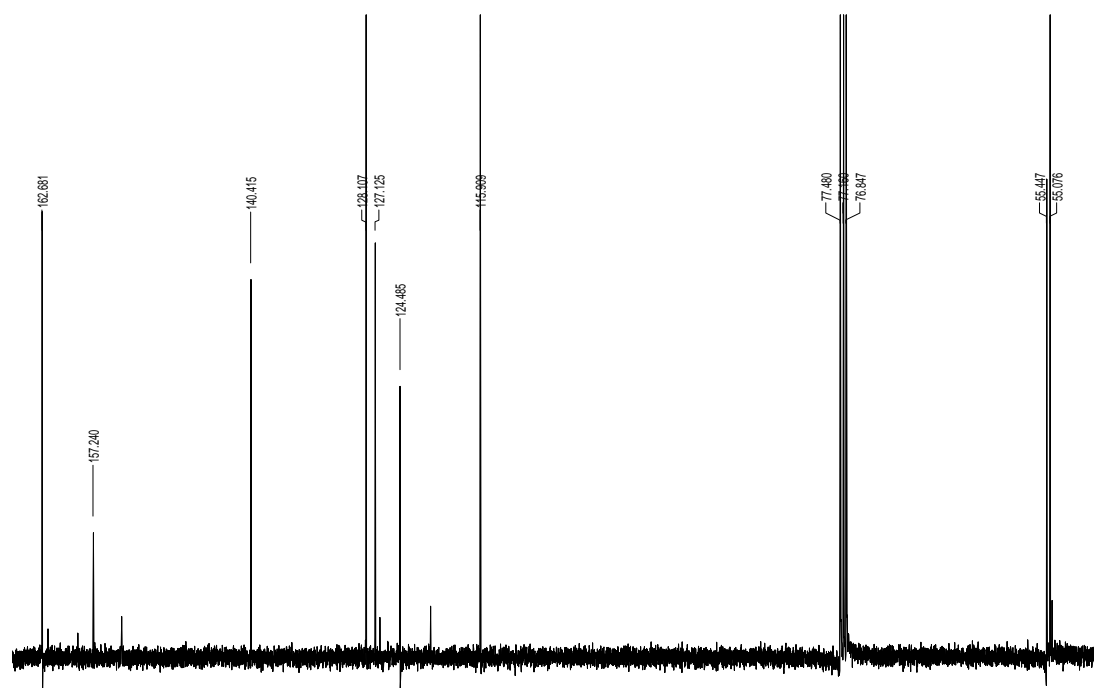
**2-(3,6-Dimethoxypyridazin-4-yl)-5-nitropyridine (67)** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

**2-Amino-3-nitro-5-(3,6-dimethoxypyridazin-4-yl)-pyridine (68)** $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )

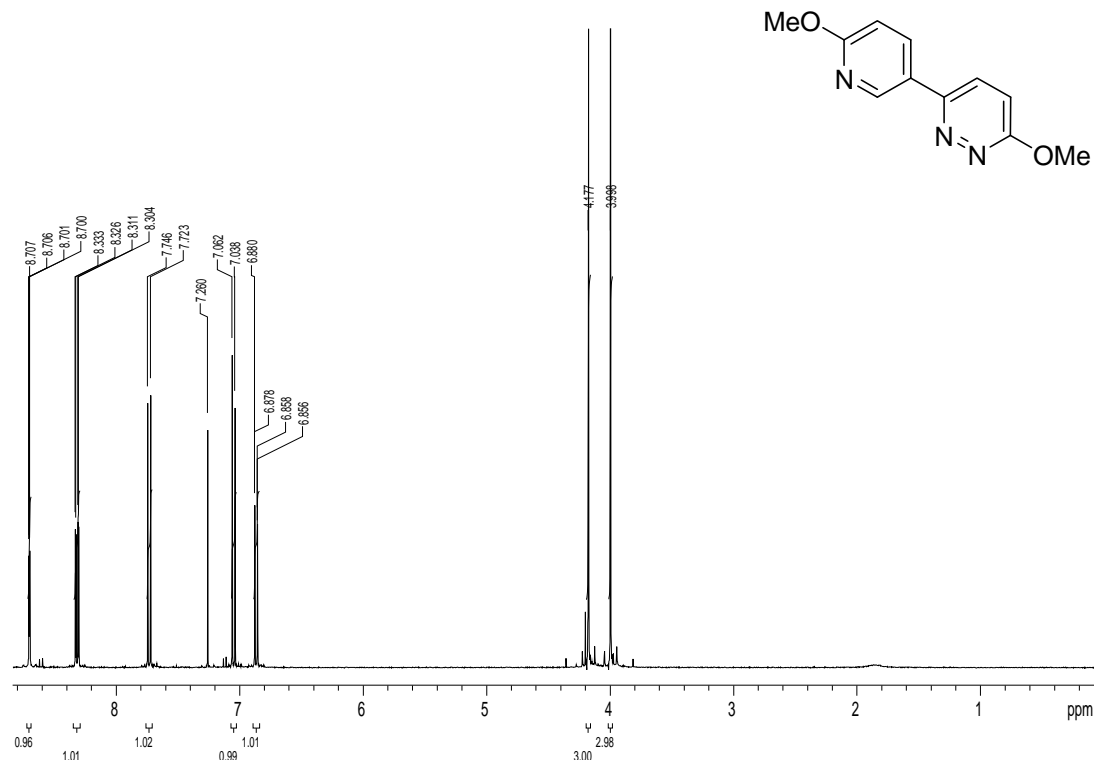
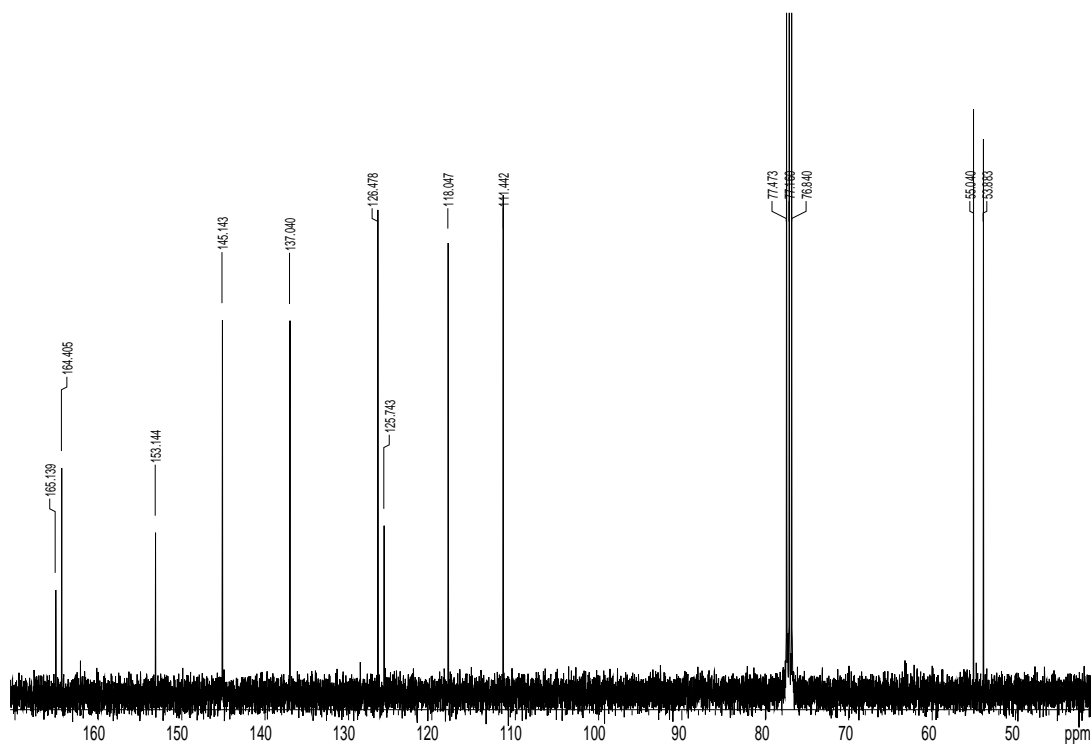
**5-(3,6-Dimethoxypyridazin-4-yl)-pyrimidine (69)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

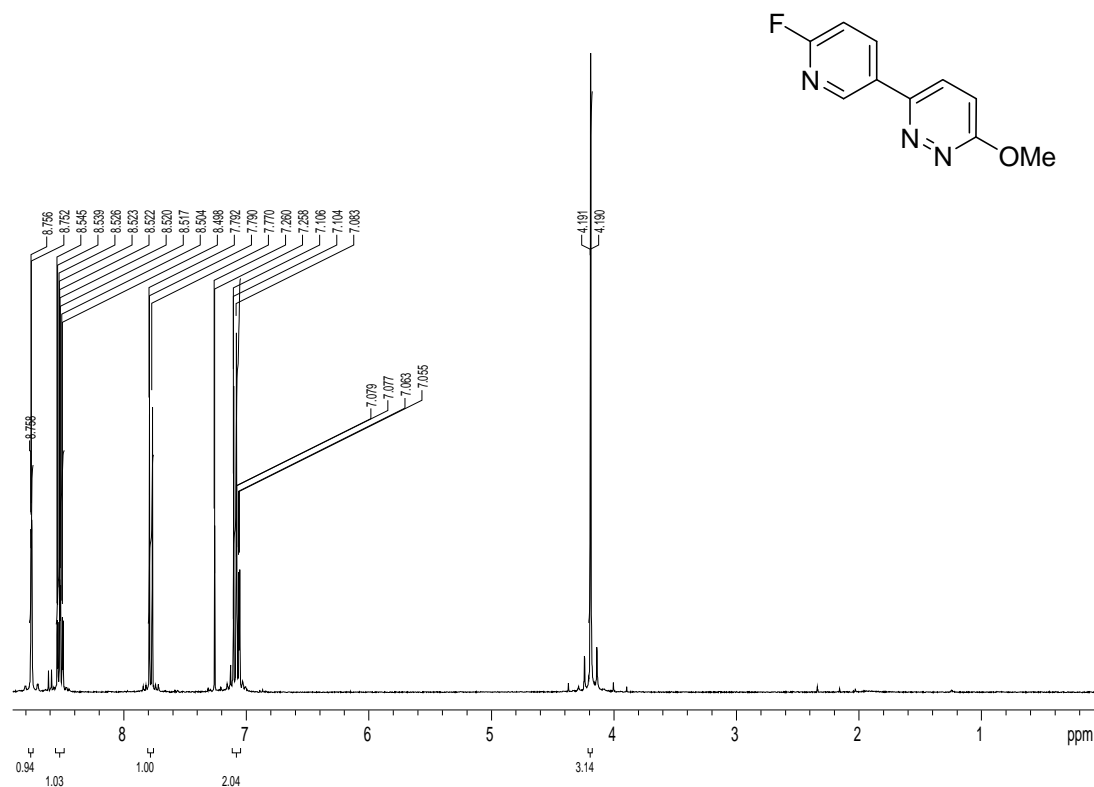
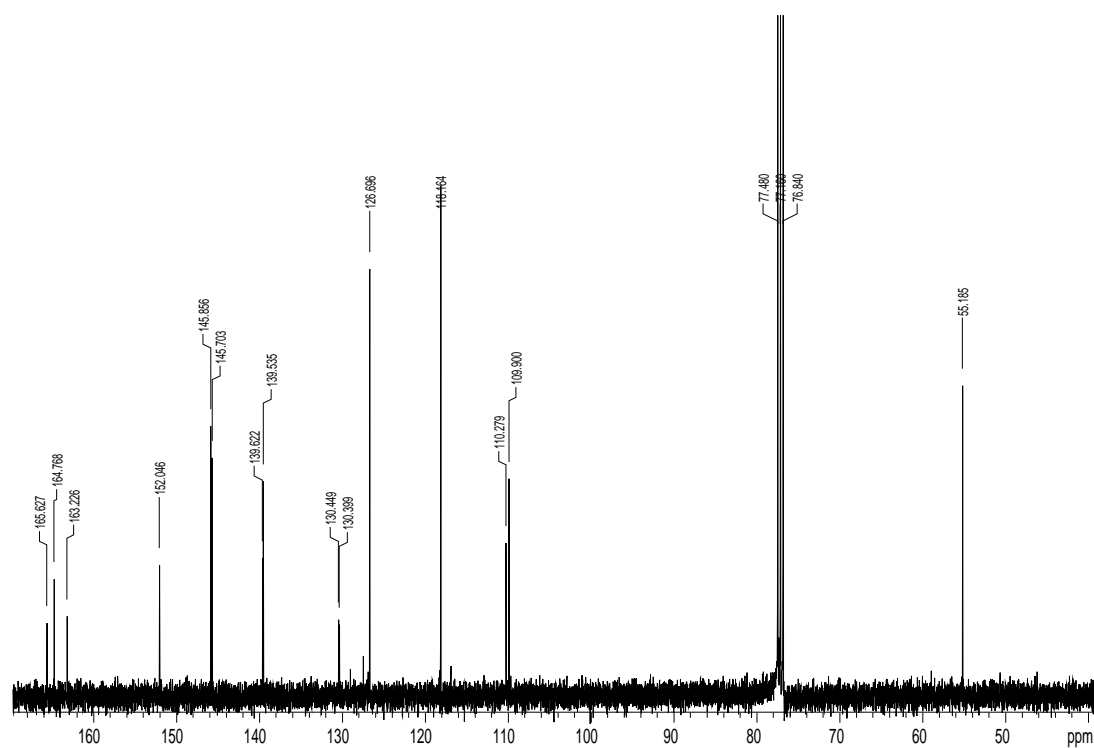
**2-Amino-5-(3,6-dimethoxypyridazin-4-yl)-pyrimidine (70)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

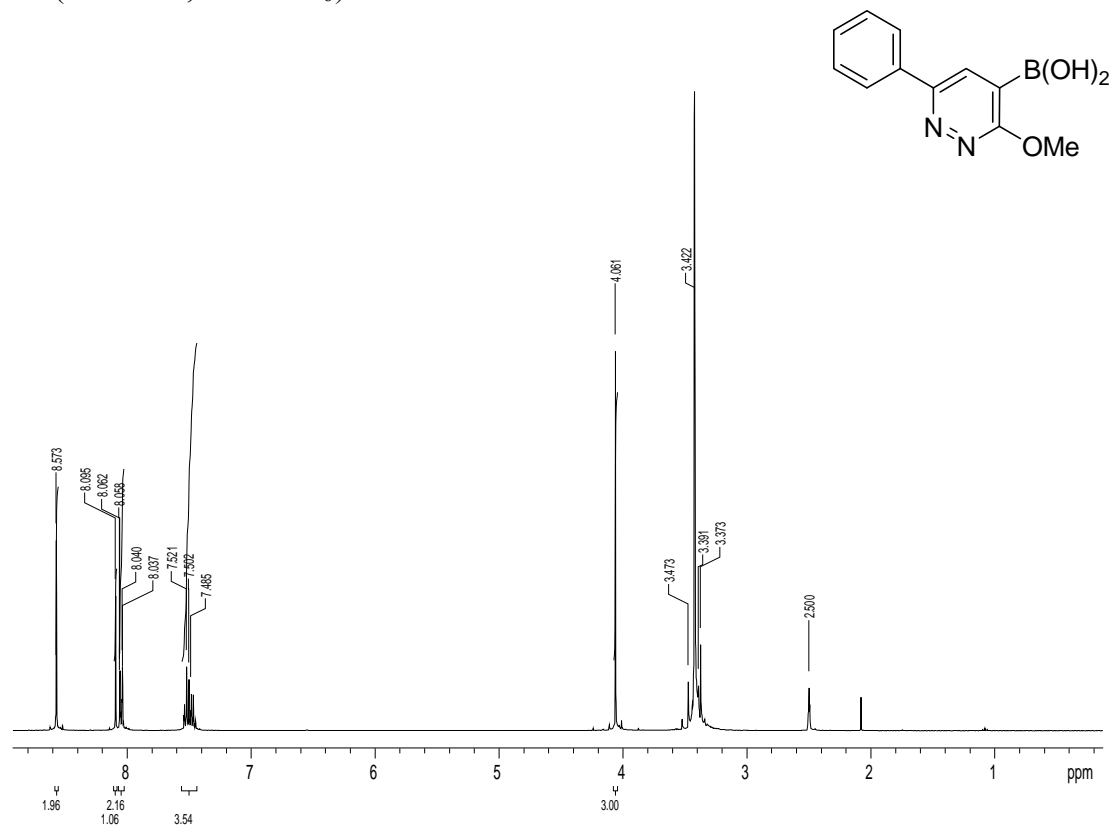
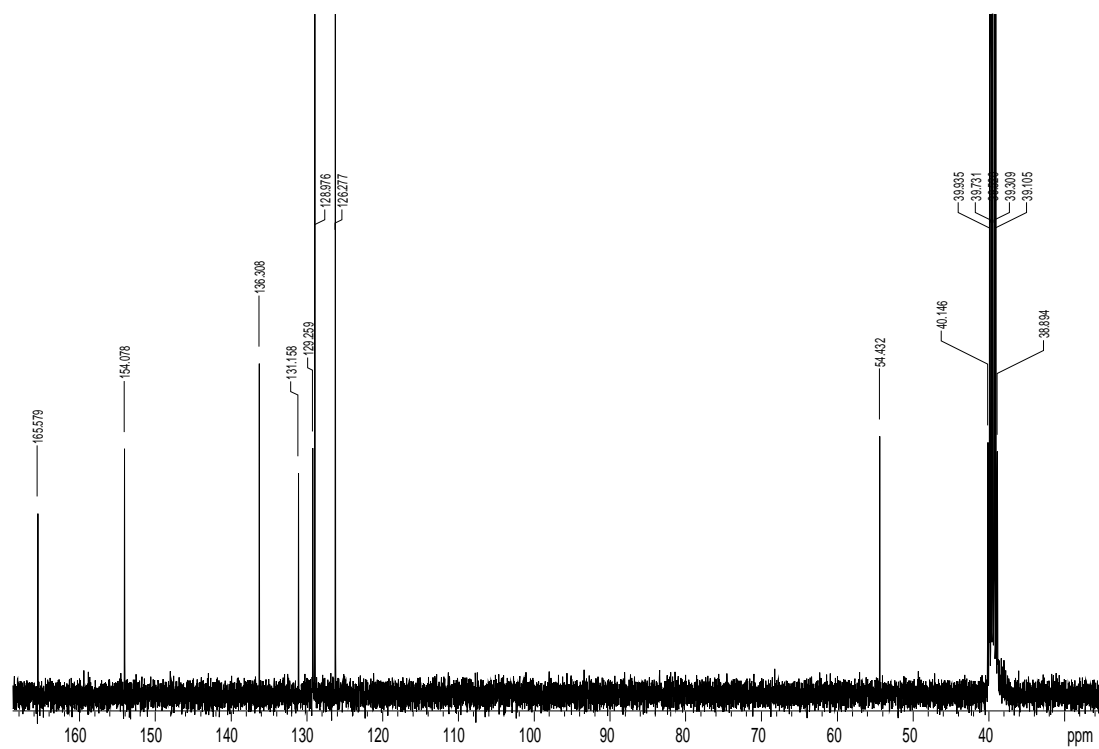
**2-Amino-5-(3,6-dimethoxypyridazin-4-yl)-pyrazine (71)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

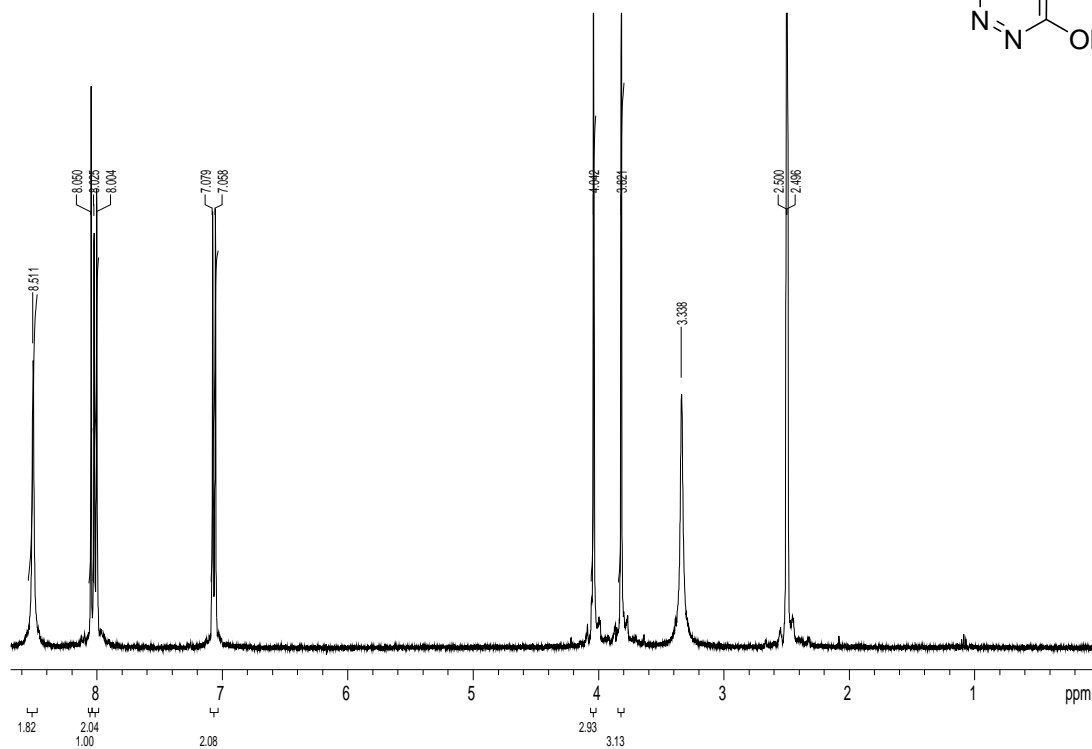
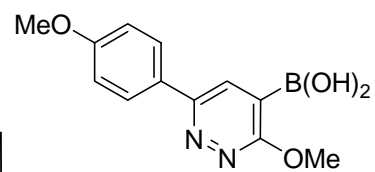
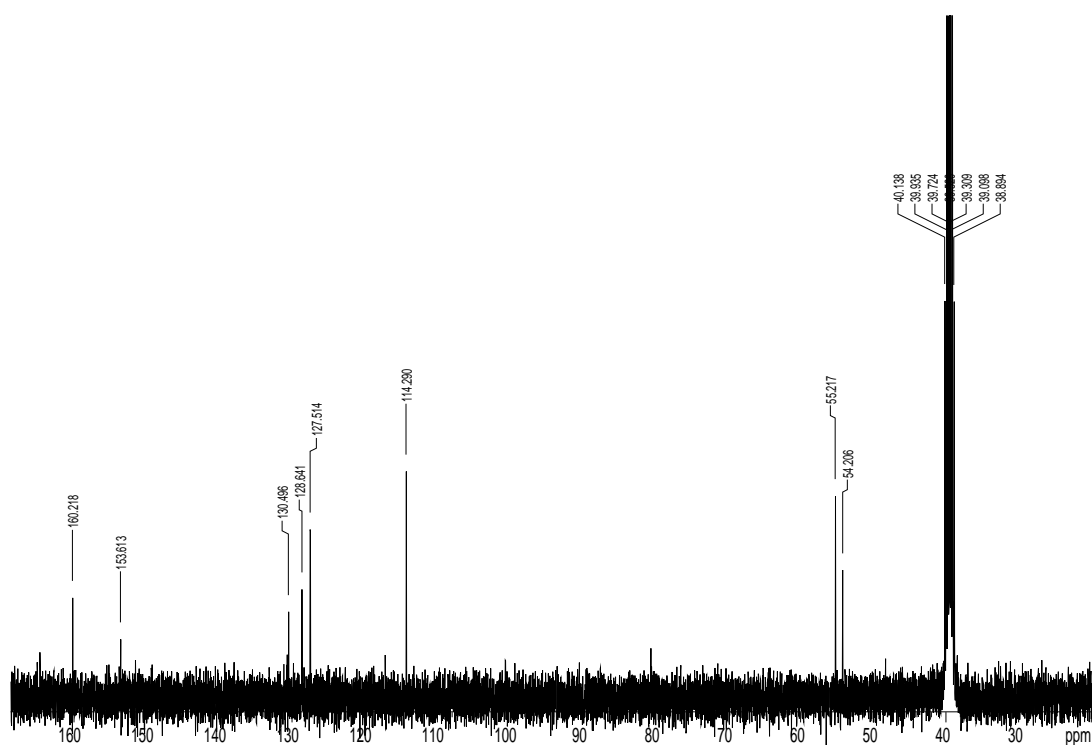
**2-Nitro-5-(3,6-dimethoxy-pyridazin-4-yl)-thiophene (72)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

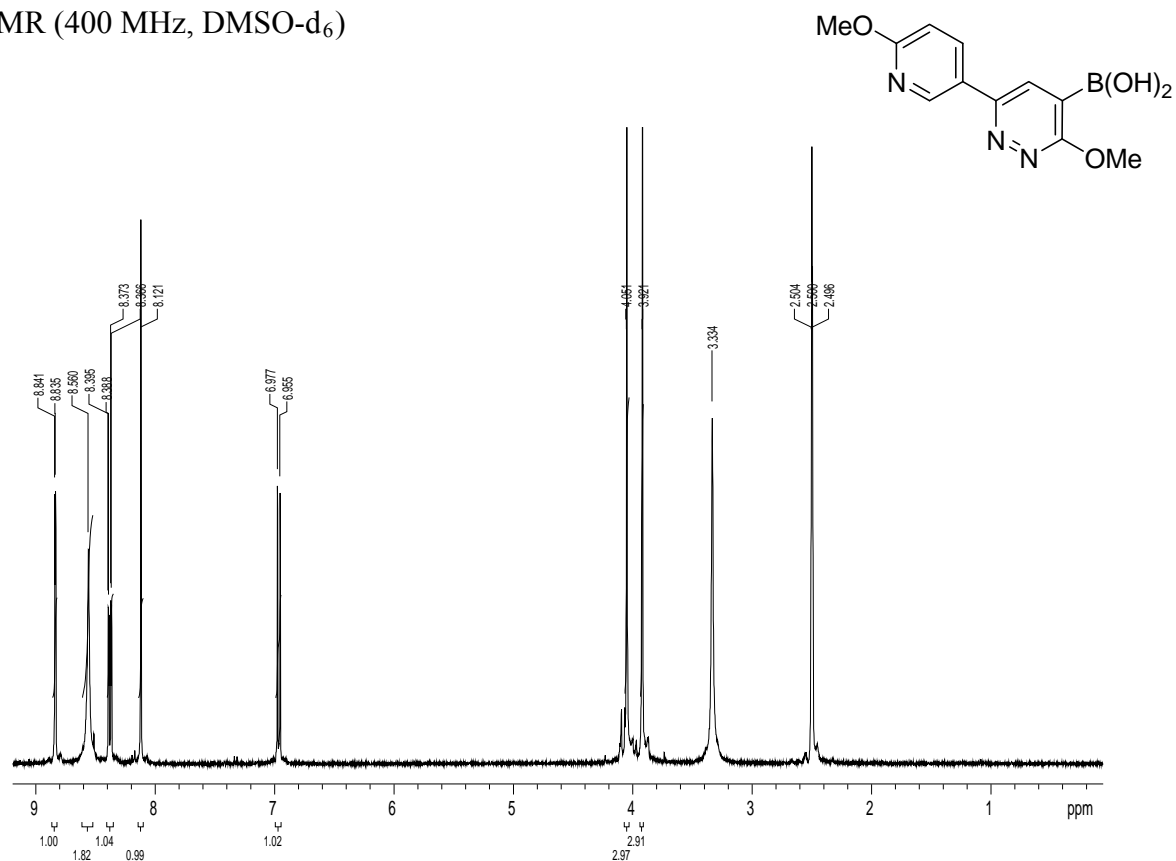
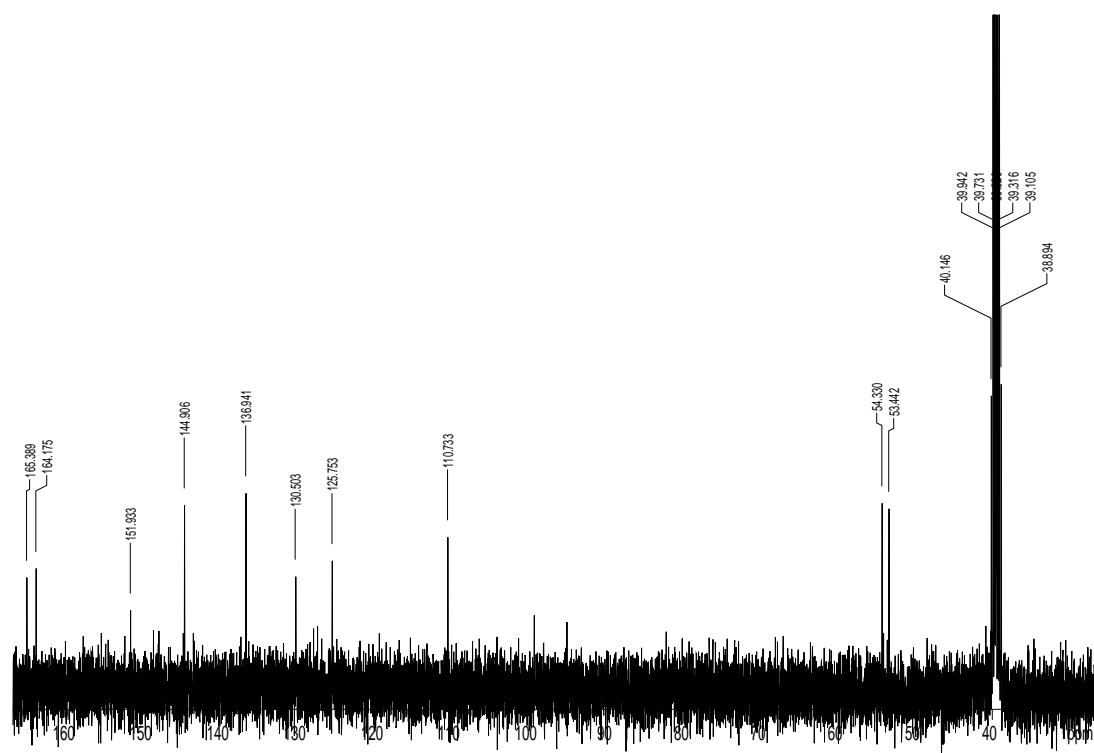


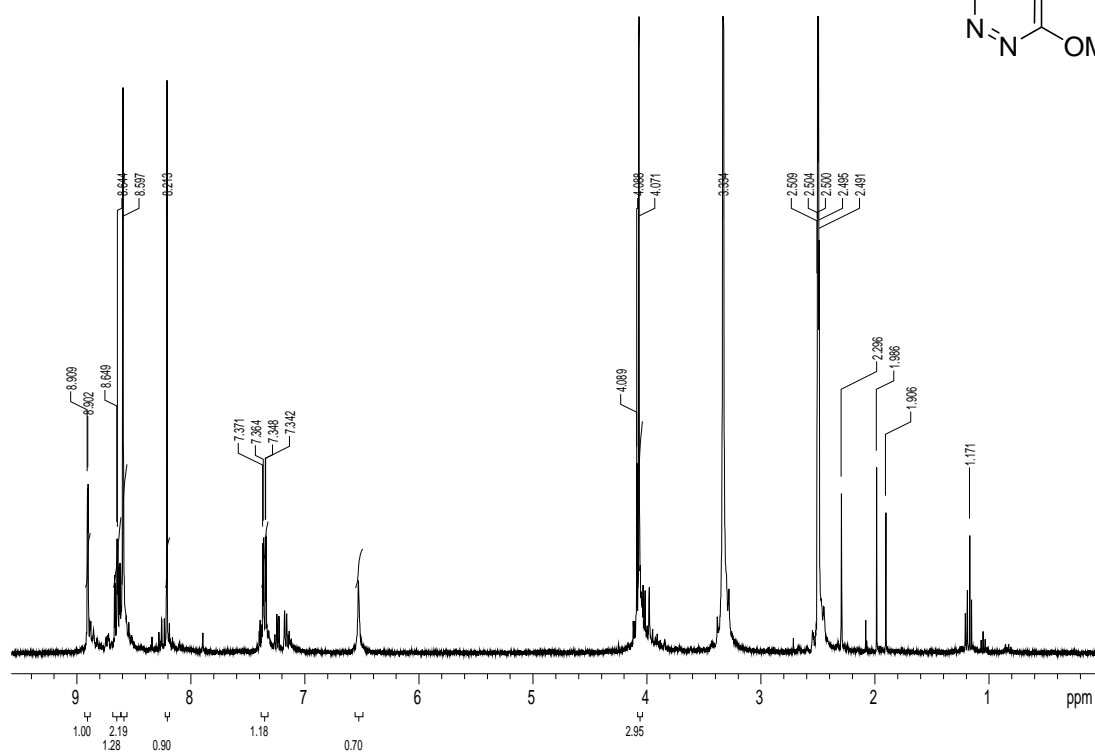
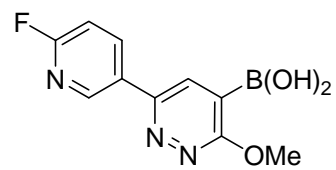
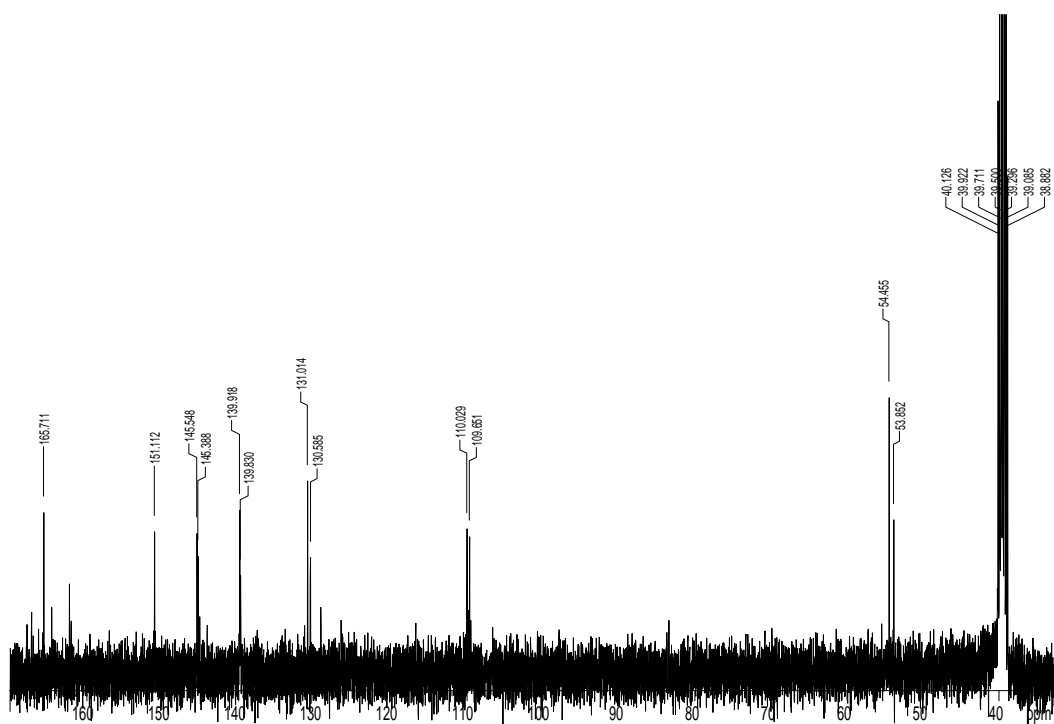
**3-Methoxy-6-(2-methoxypyridin-5-yl)-pyridazine (75c)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

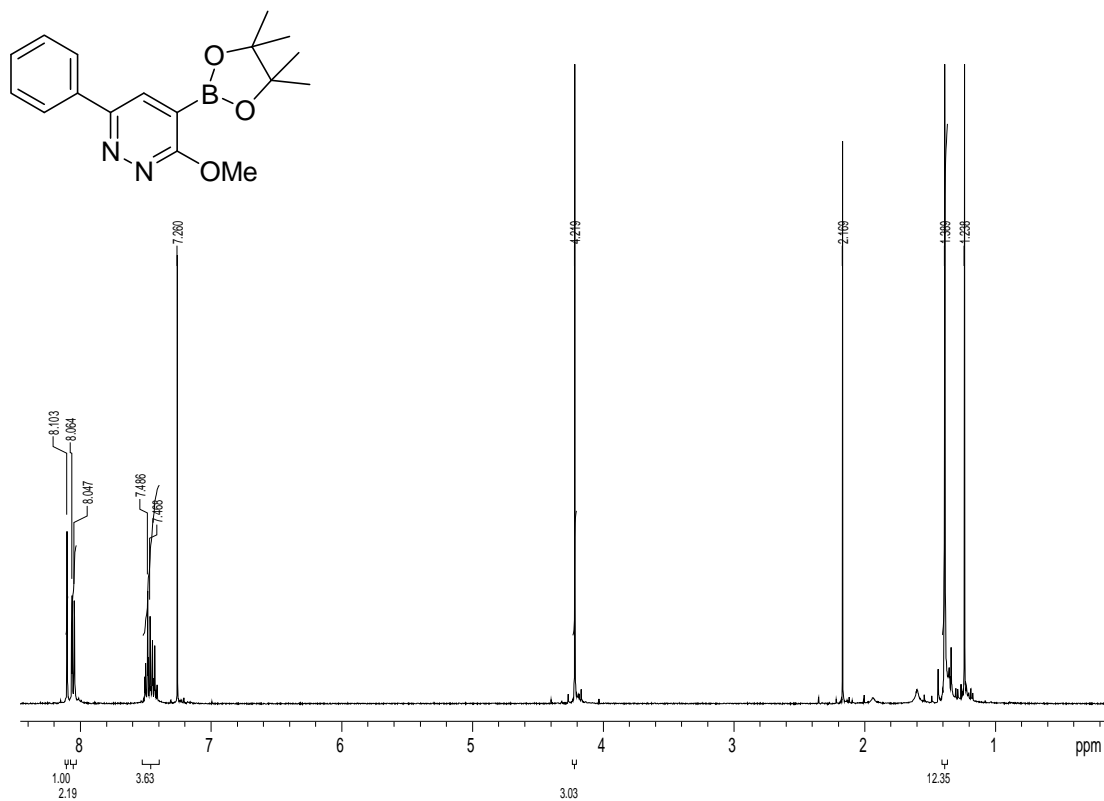
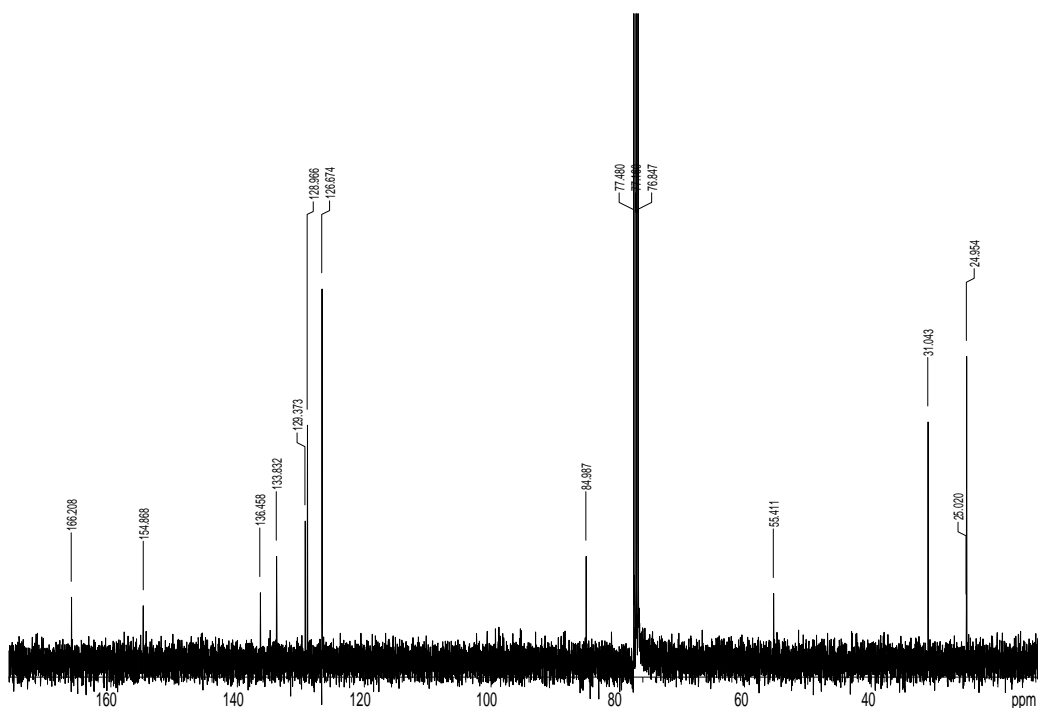
**3-Methoxy-6-(2-fluoropyridin-5-yl)-pyridazine (75d)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

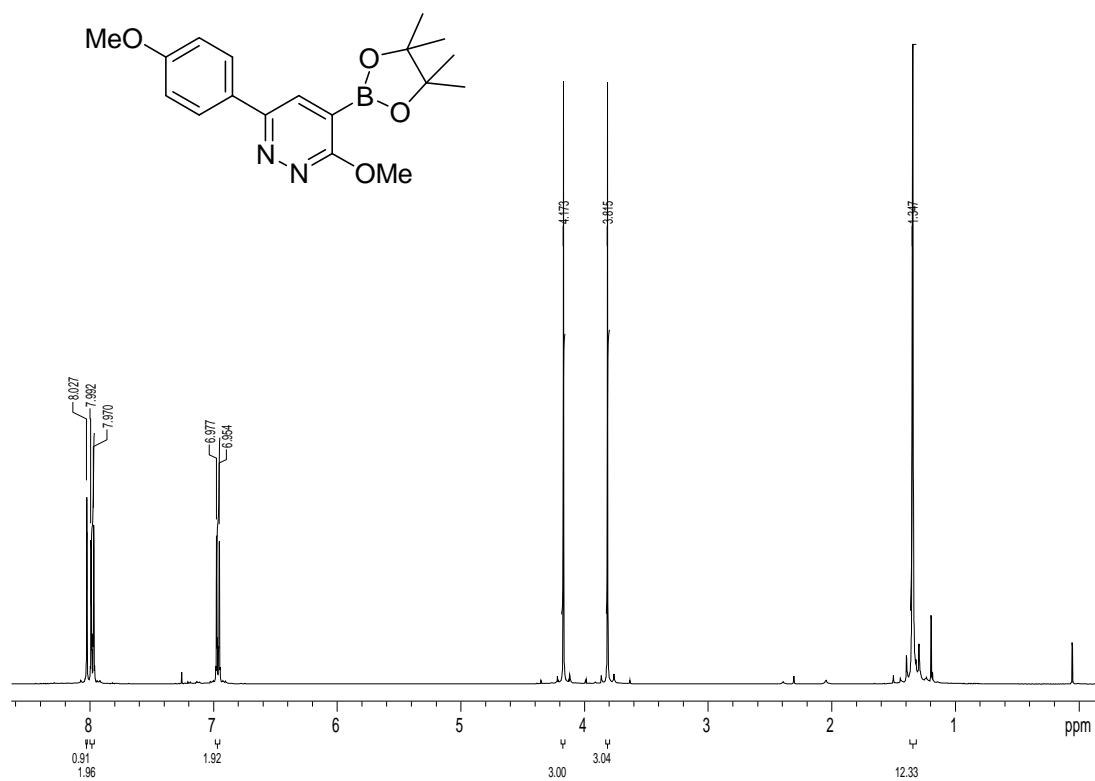
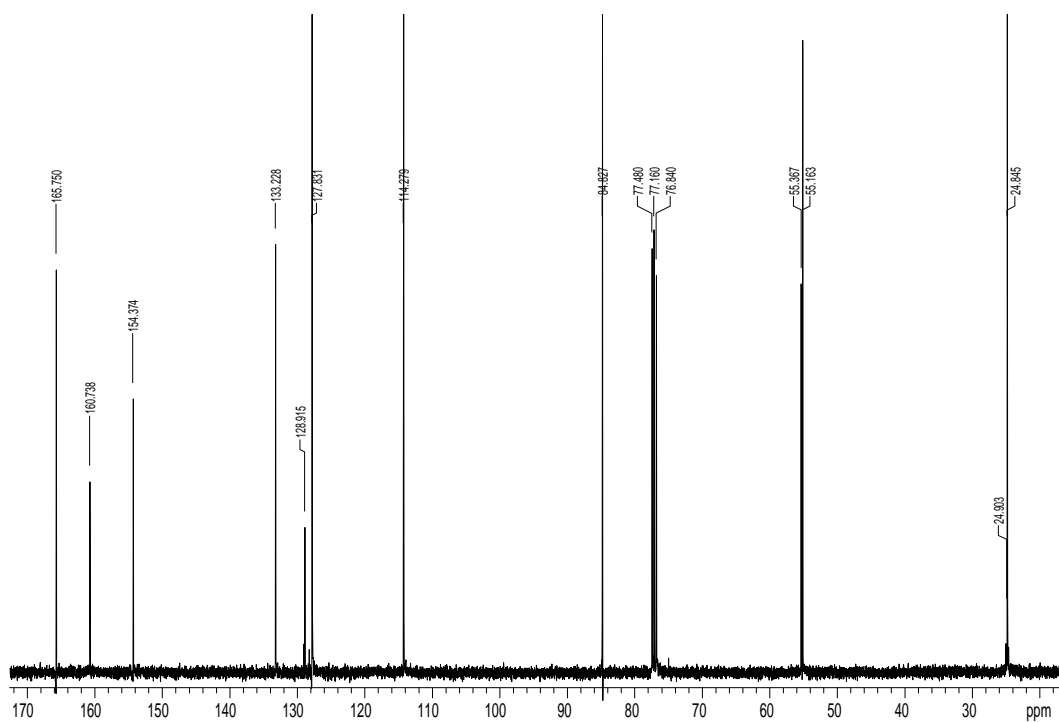
**3-Methoxy-6-phenyl-4-pyridazinylboronic acid (76a)** $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )

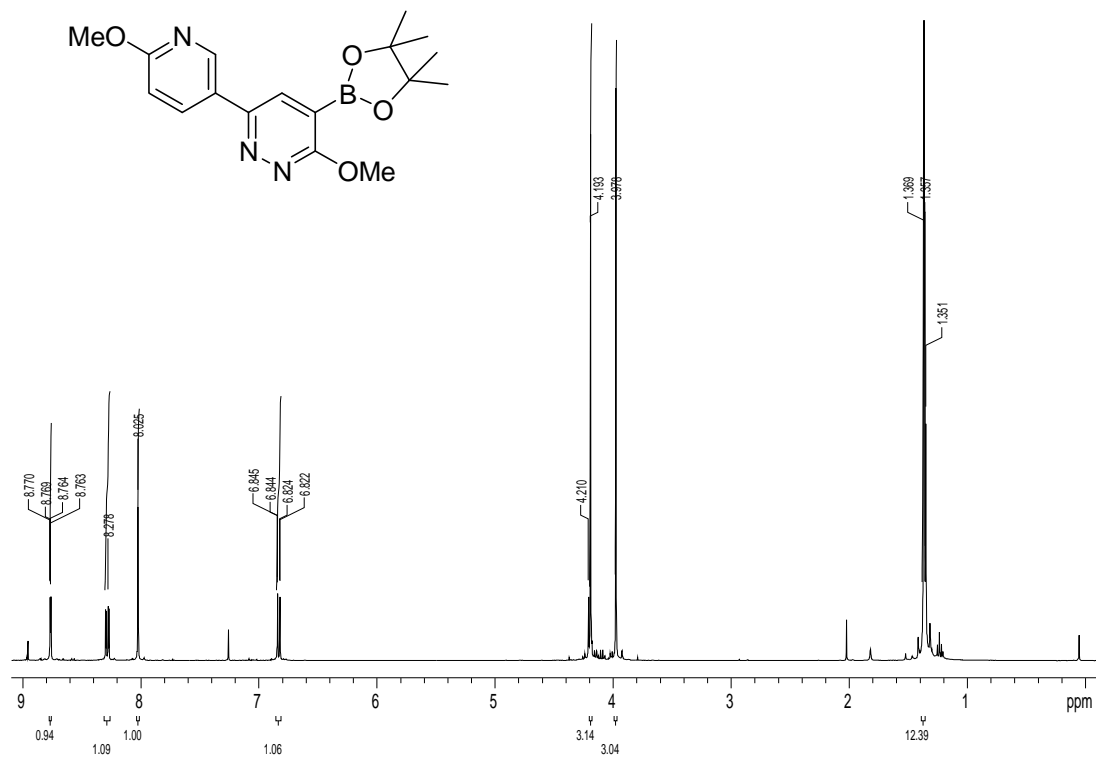
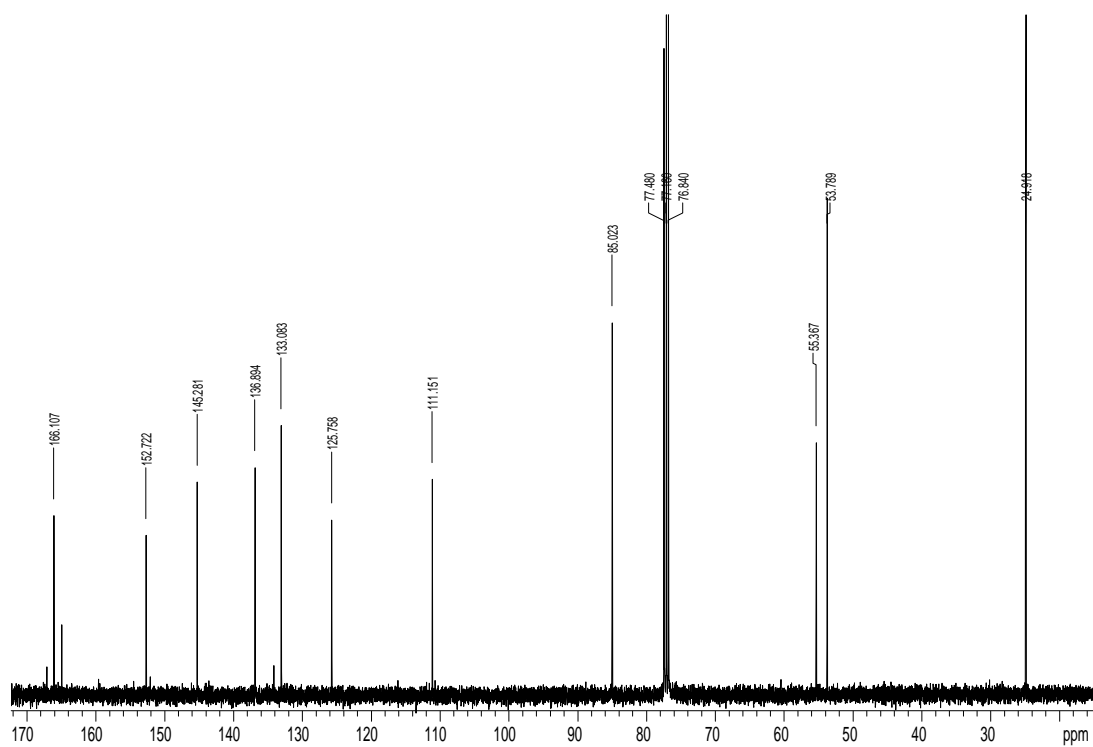
**3-Methoxy-6-(4-methoxyphenyl)-4-pyridazinylboronic acid (76b)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

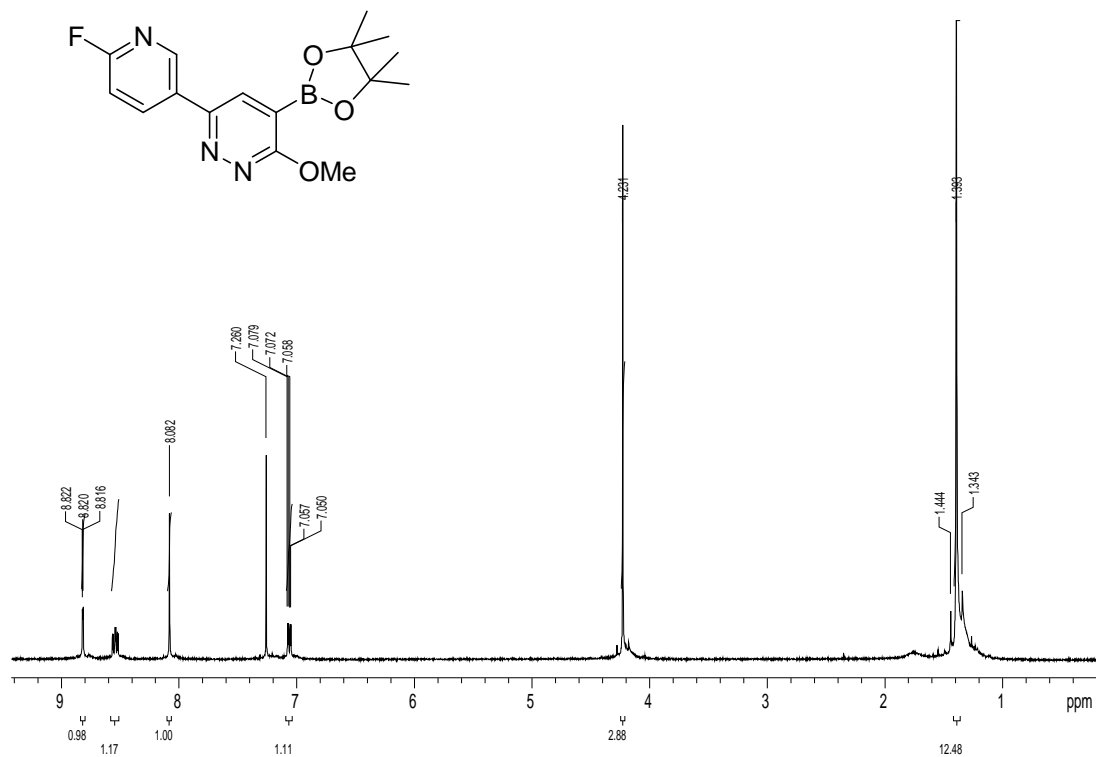
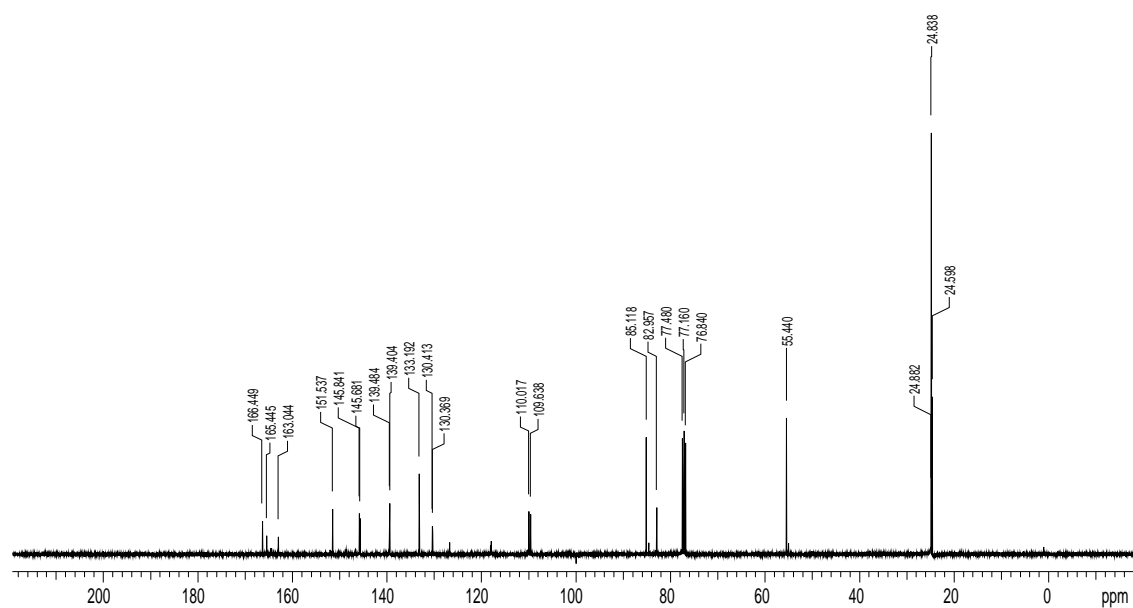
**3-Methoxy-6-(2-methoxypyridin-5-yl)-4-pyridazinylboronic acid (76c)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

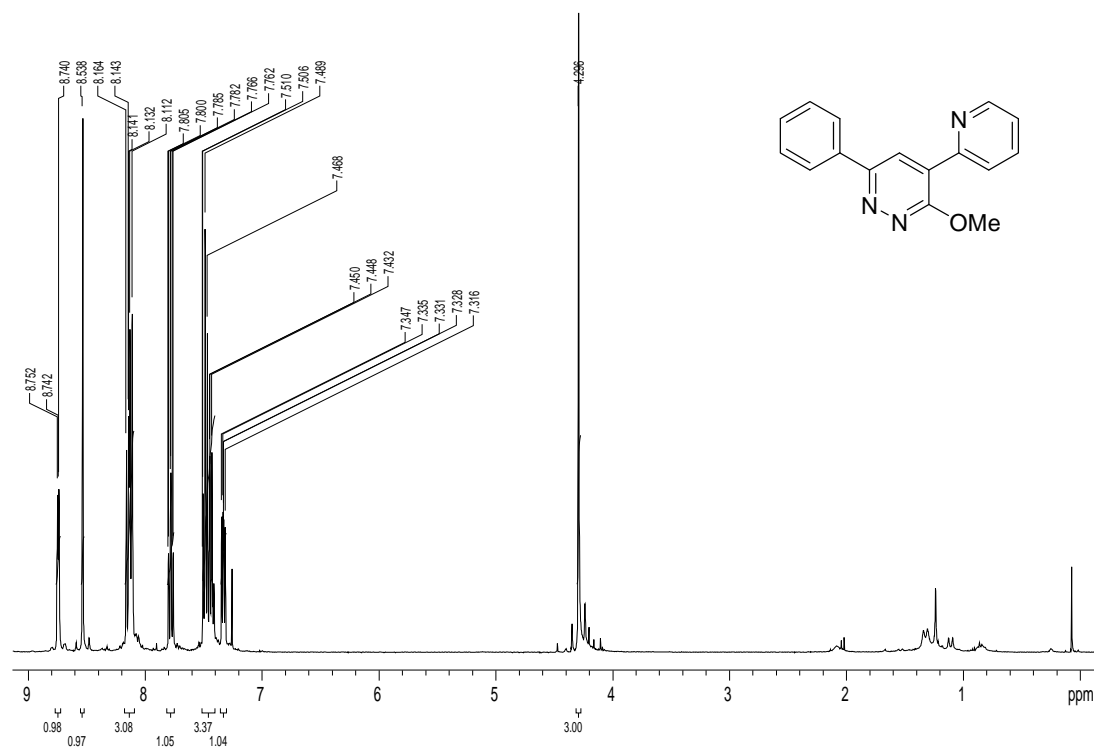
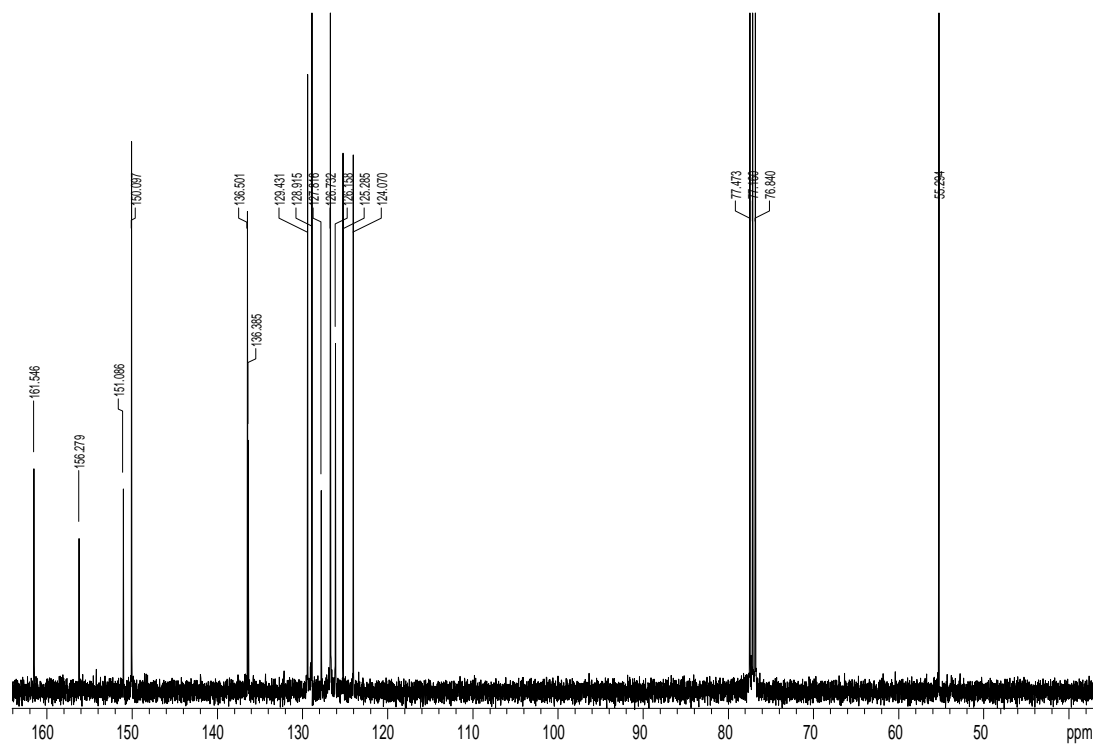
**3-Methoxy-6-(2-fluoropyridin-5-yl)-4-pyridazinylboronic acid (76d)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

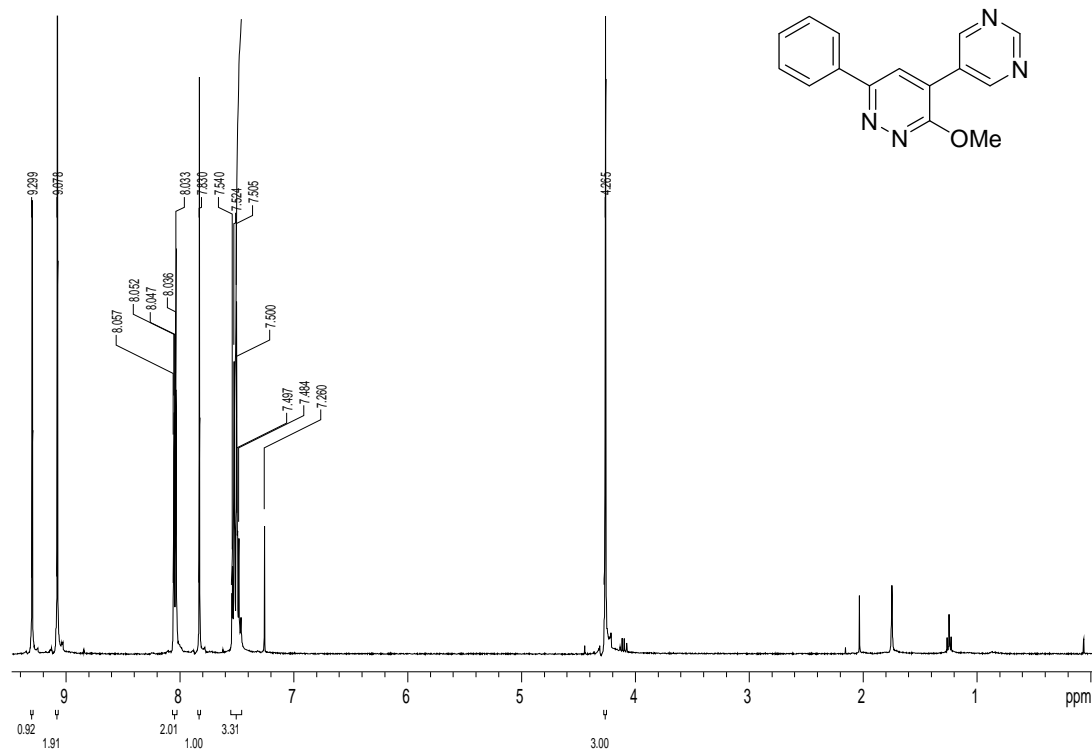
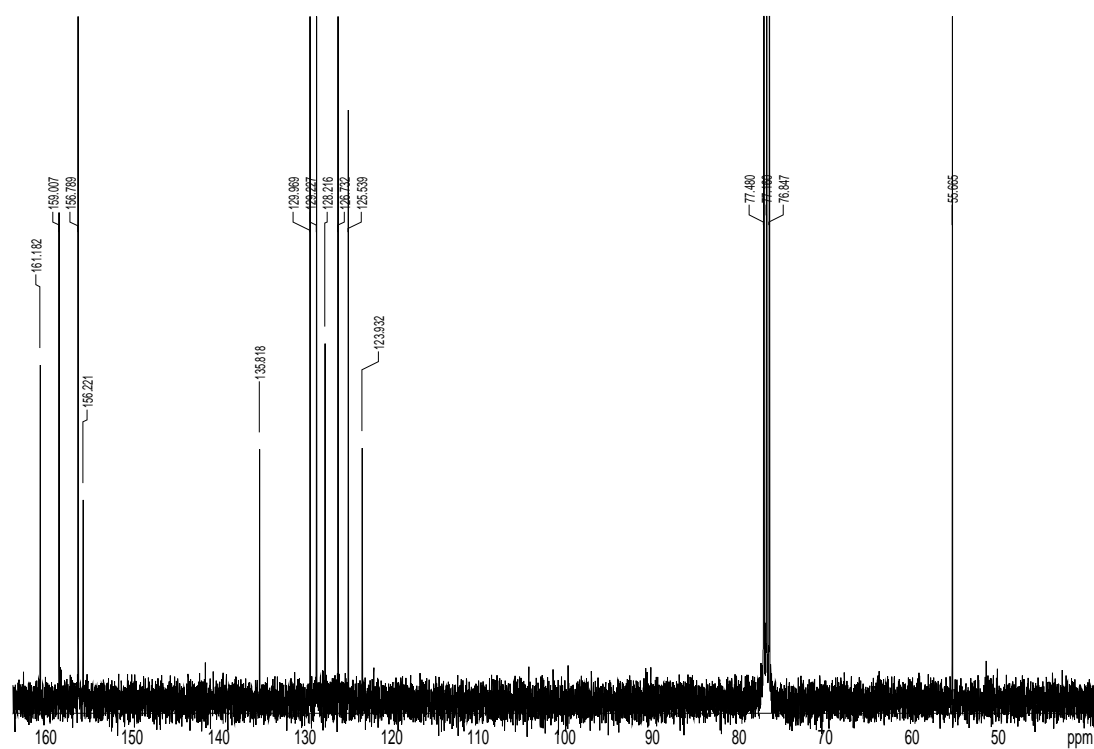
**3-Methoxy-6-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine****(77a)** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

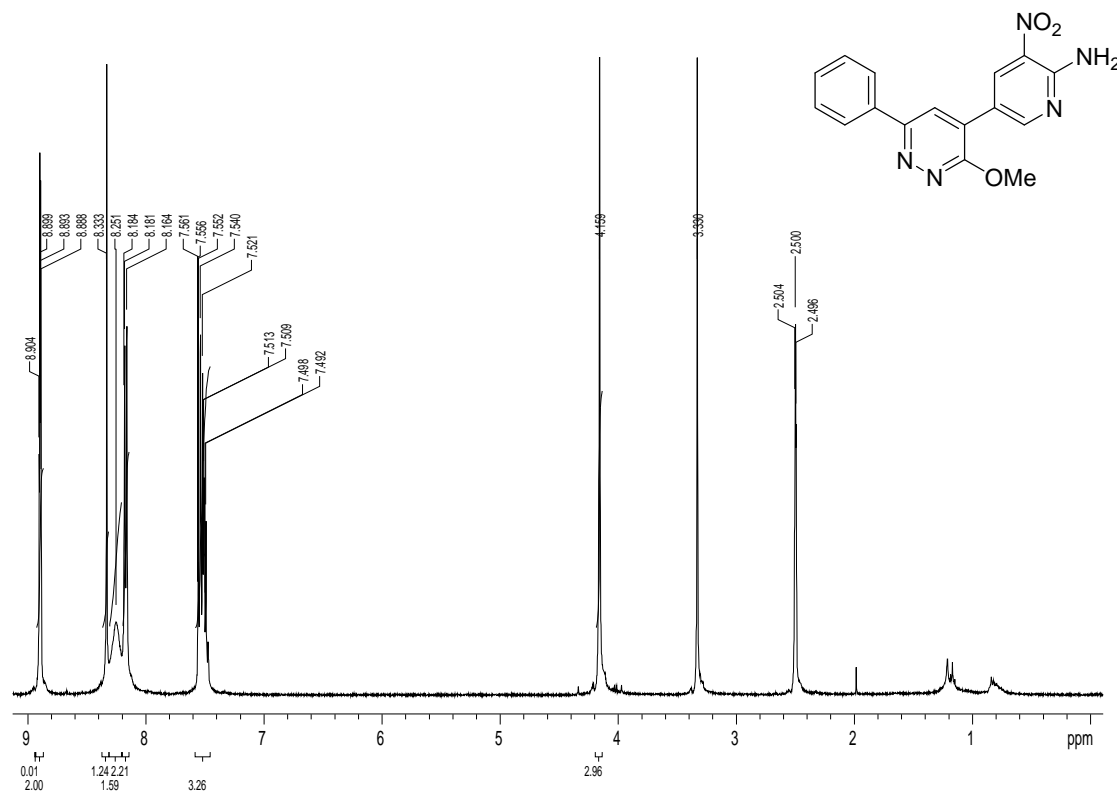
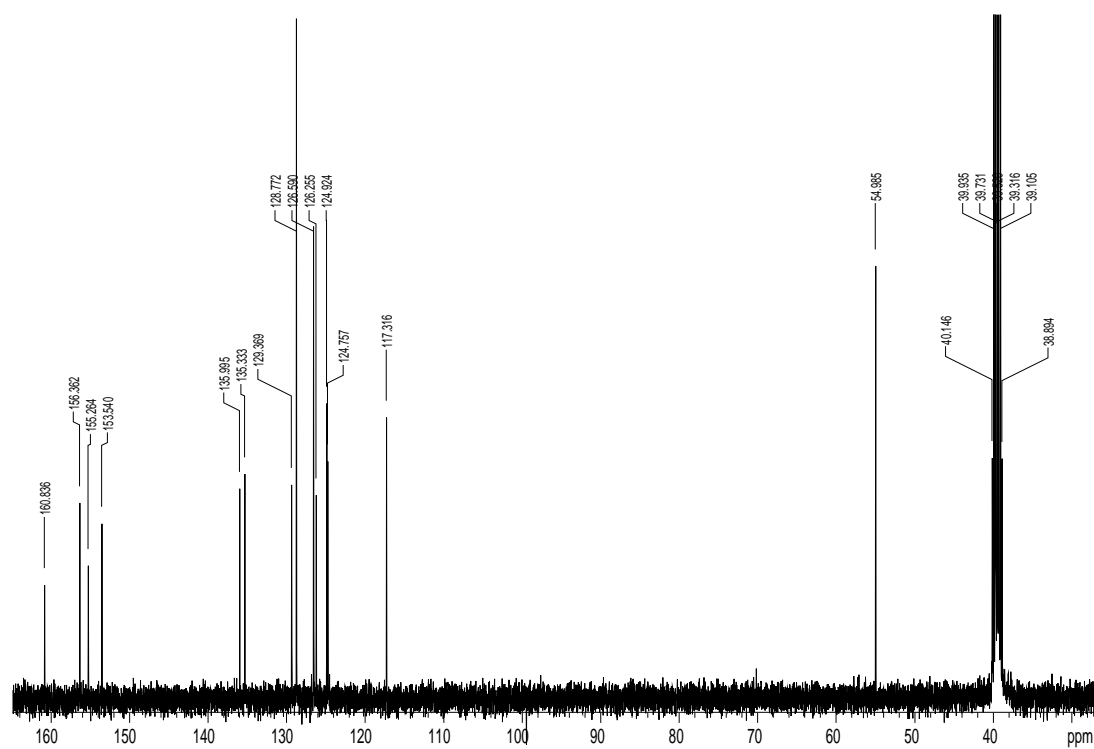
**3-Methoxy-6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (77b)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

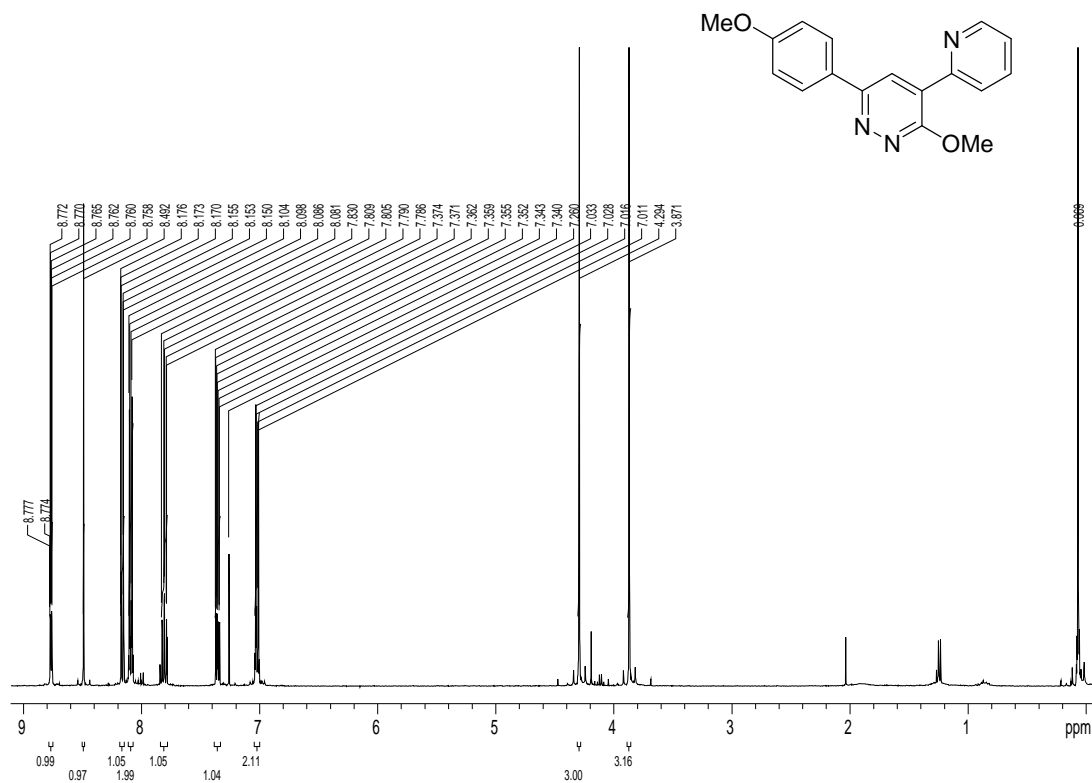
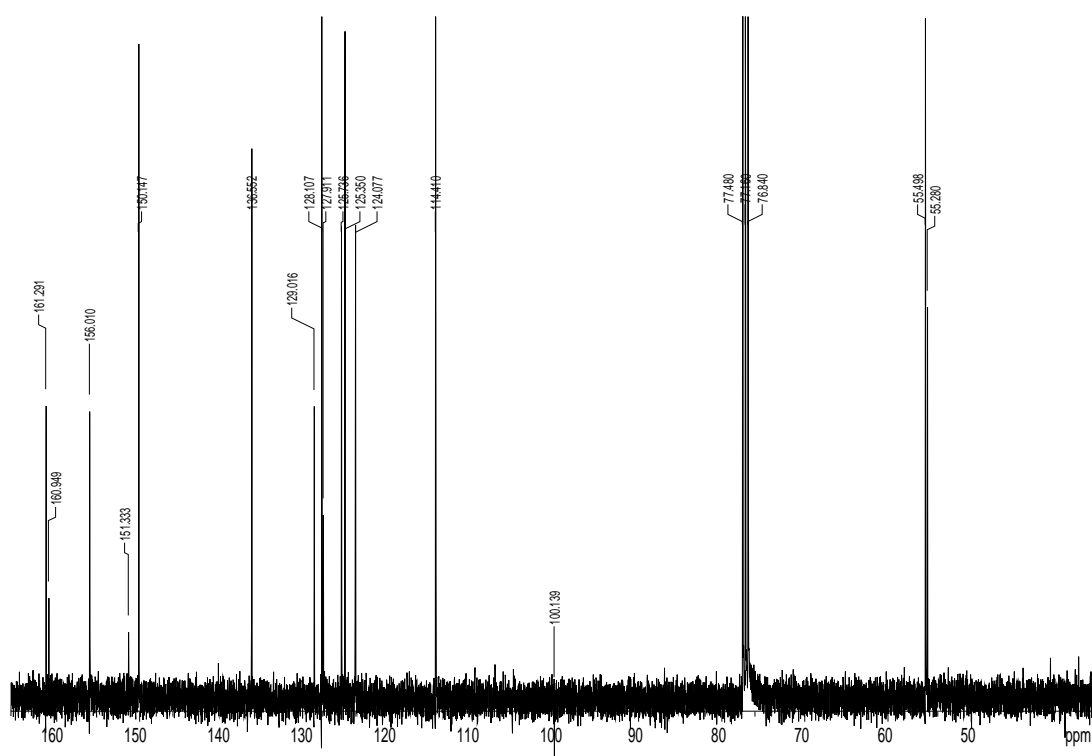
**3-Methoxy-6-(2-methoxypyridin-5-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (77c)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

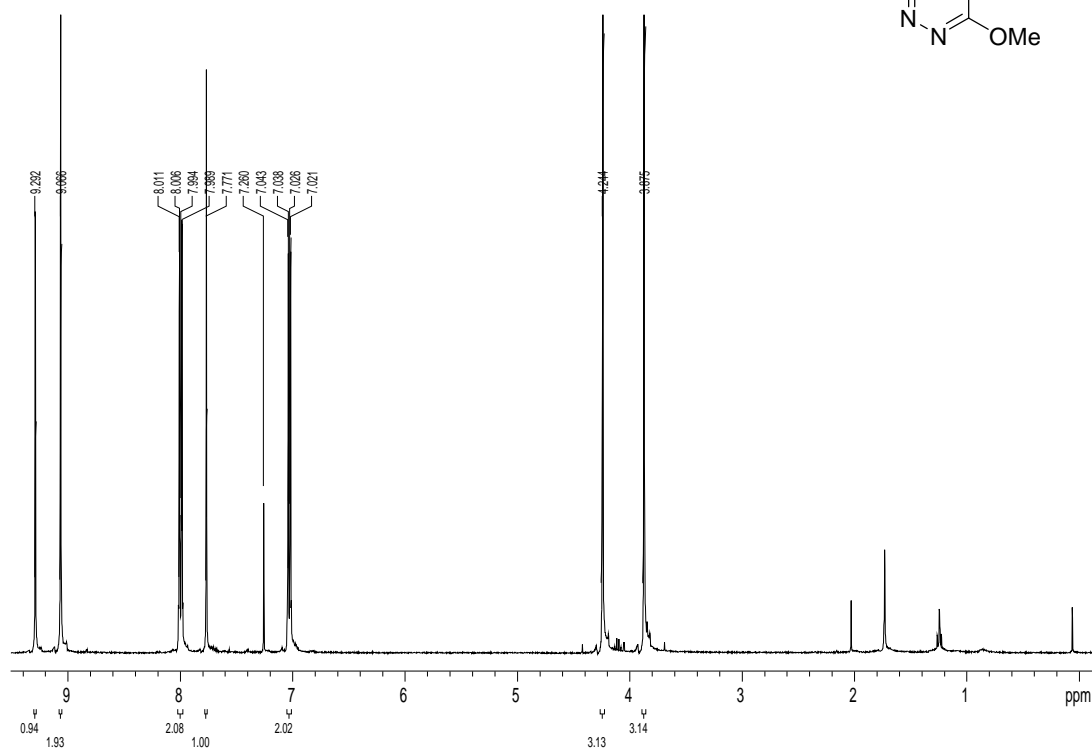
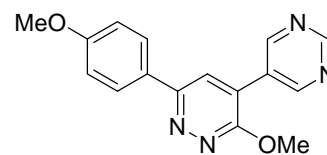
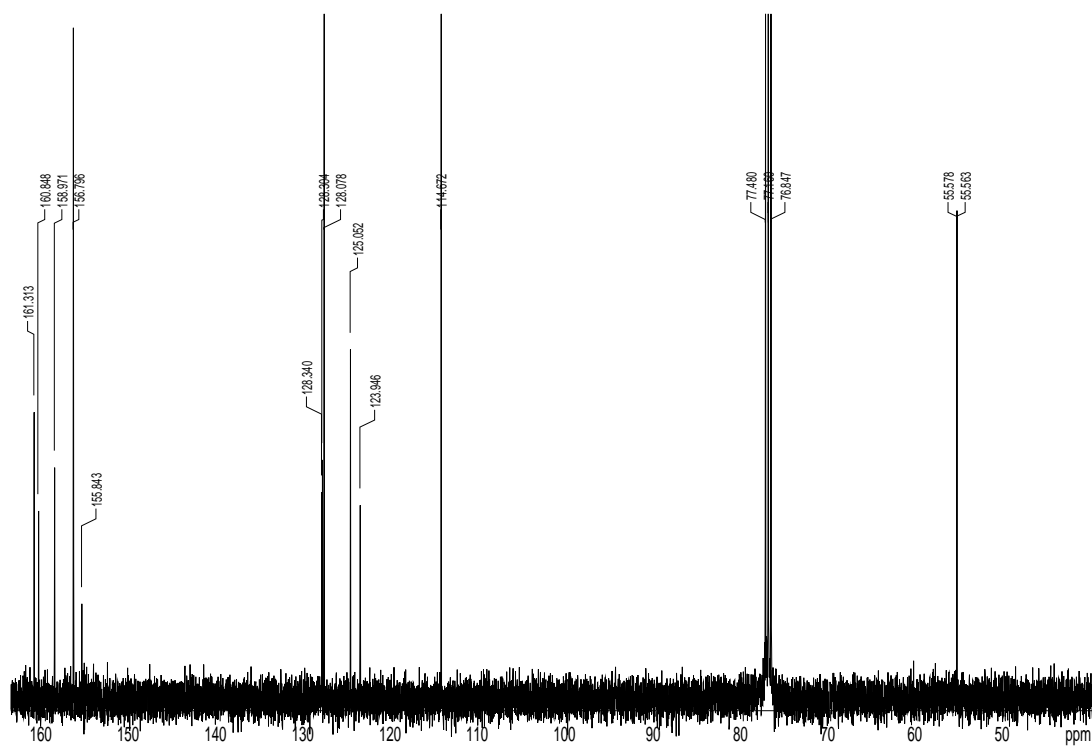
**3-Methoxy-6-(2-fluoropyridin-5-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (77d)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

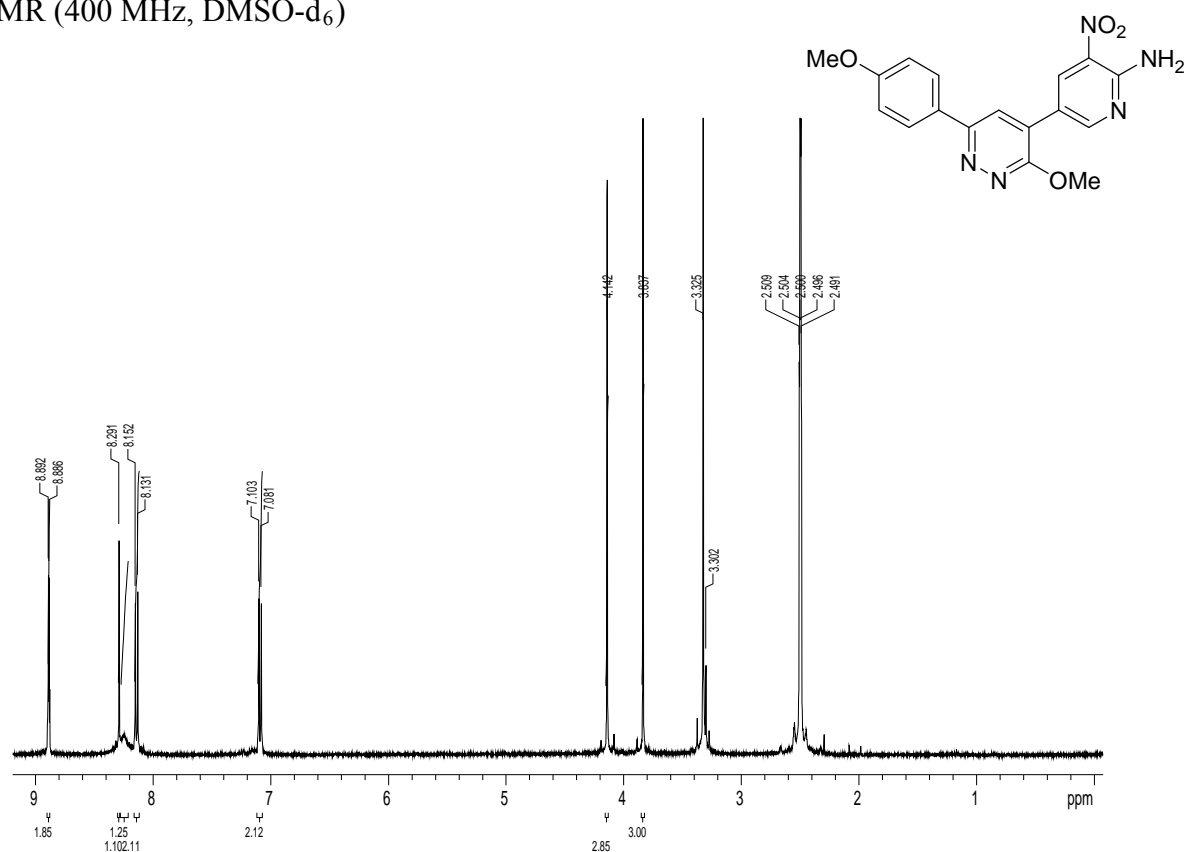
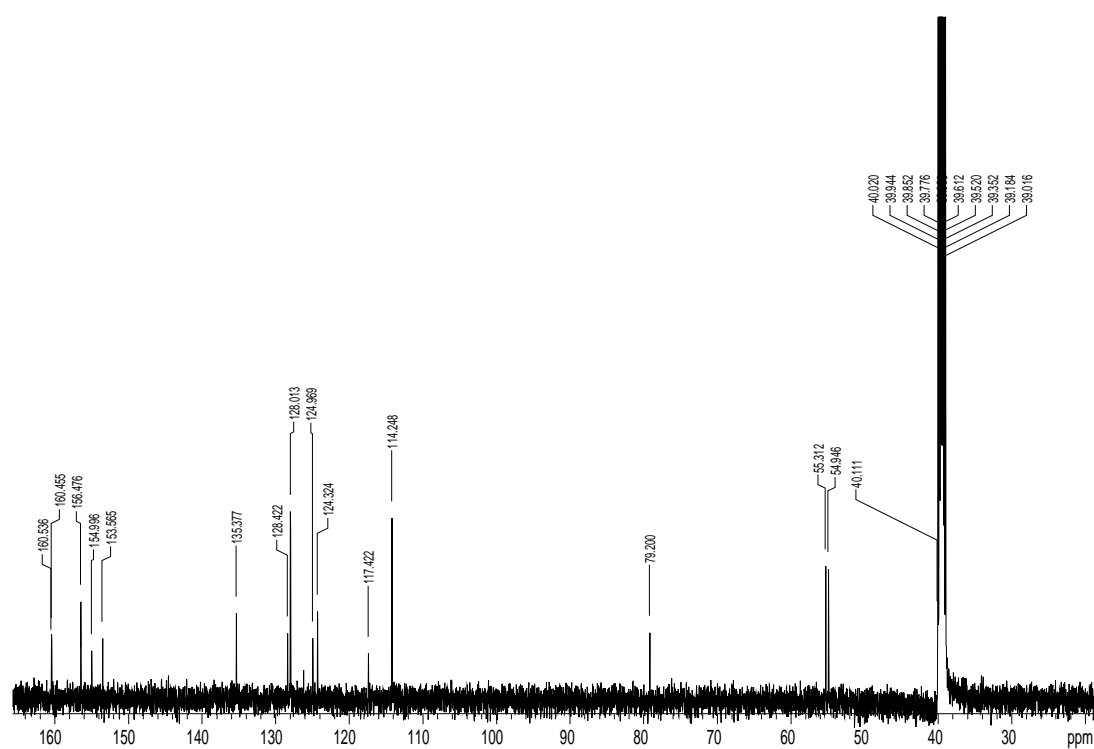
**3-Methoxy-6-phenyl-4-(pyridin-2-yl)pyridazine (79)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

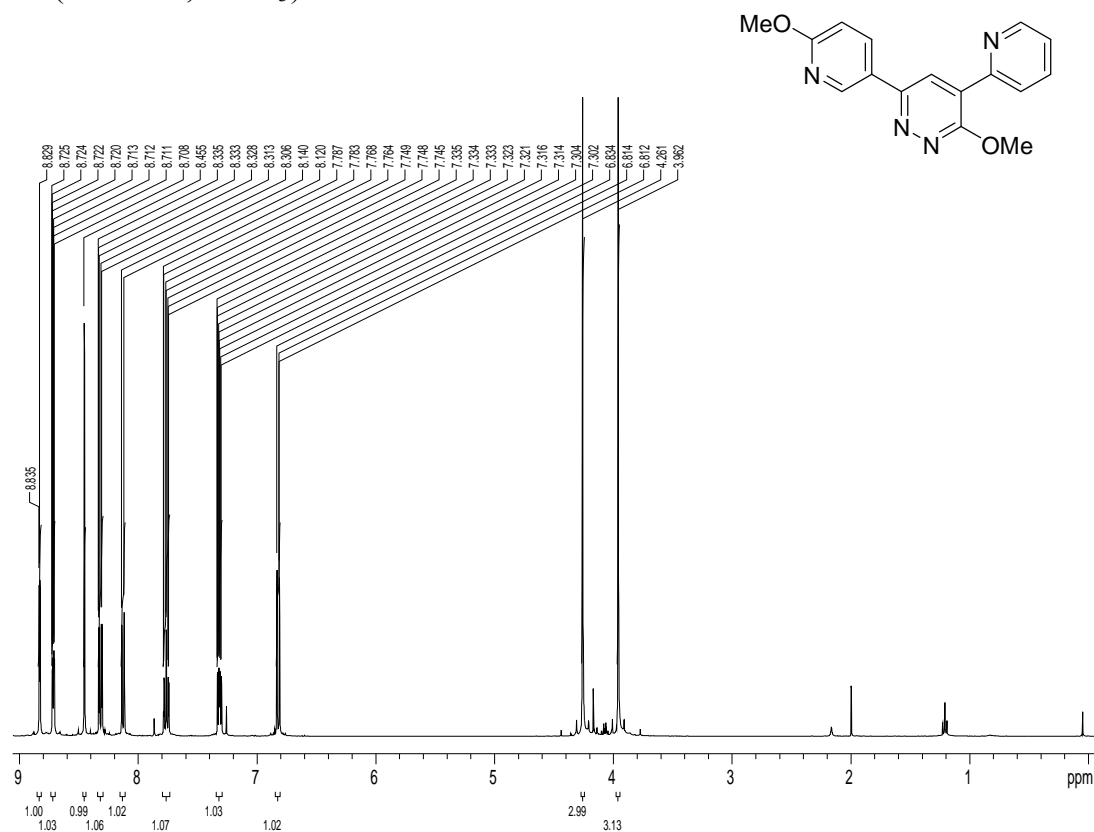
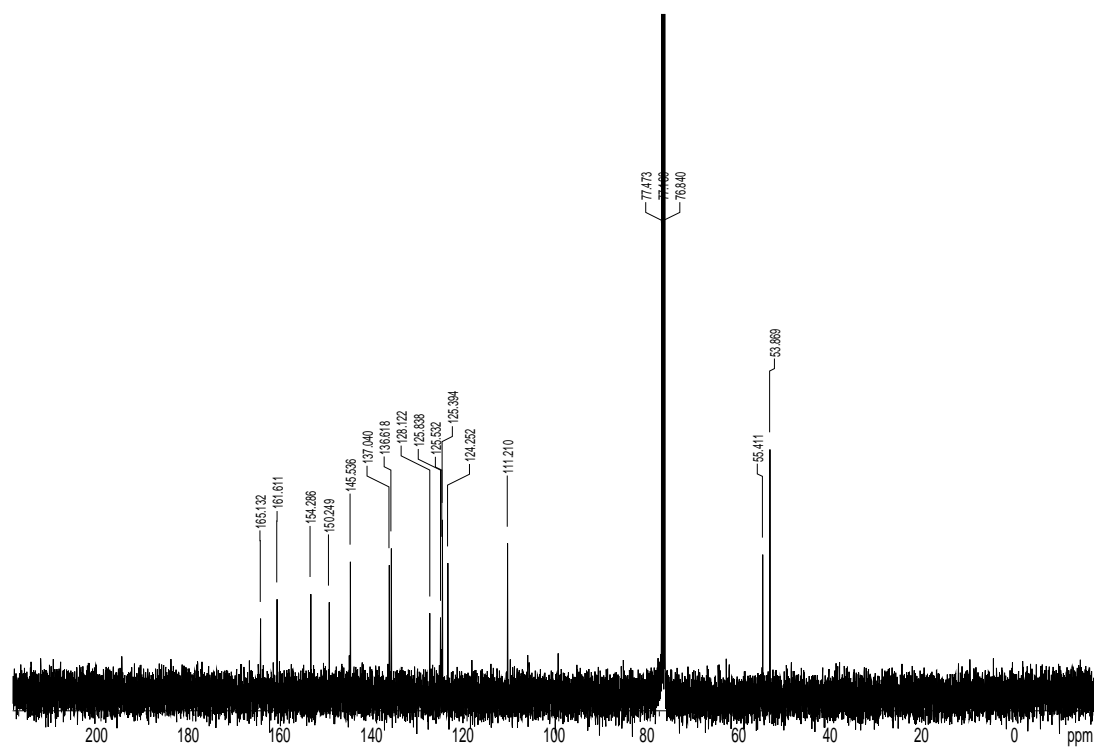
**3-Methoxy-6-phenyl-4-(pyrimidin-5-yl)pyridazine (80)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

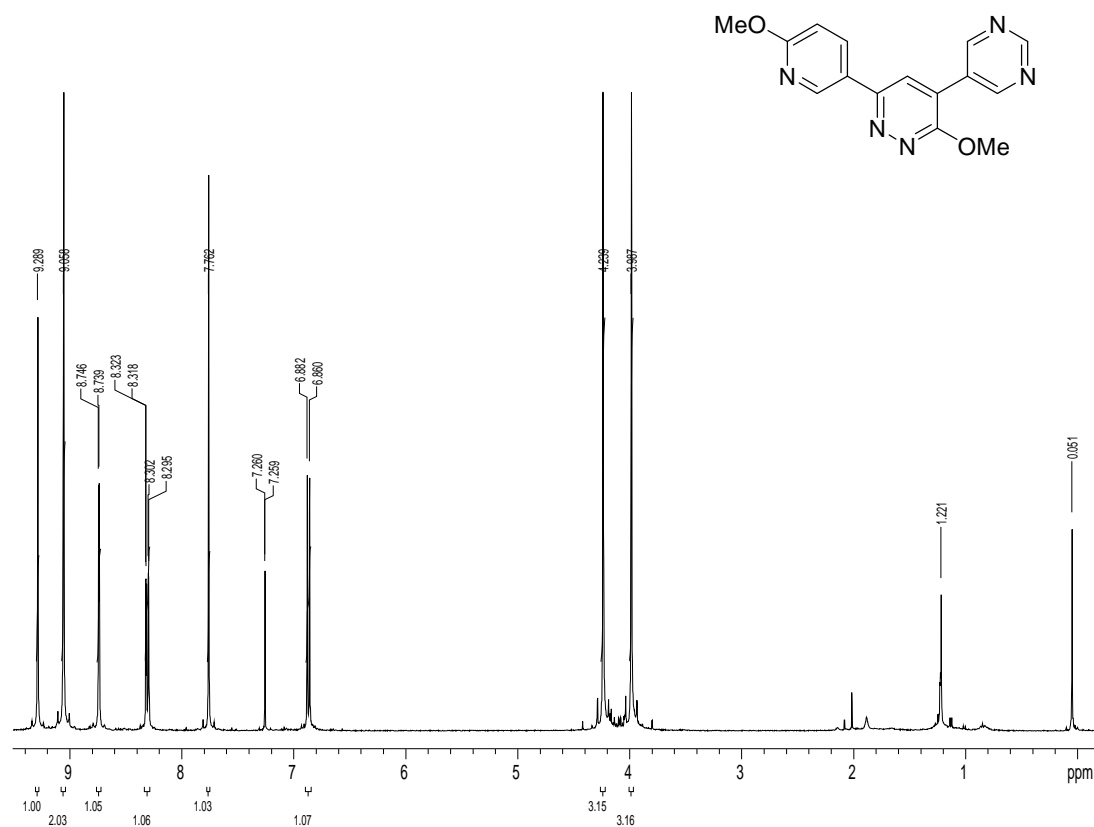
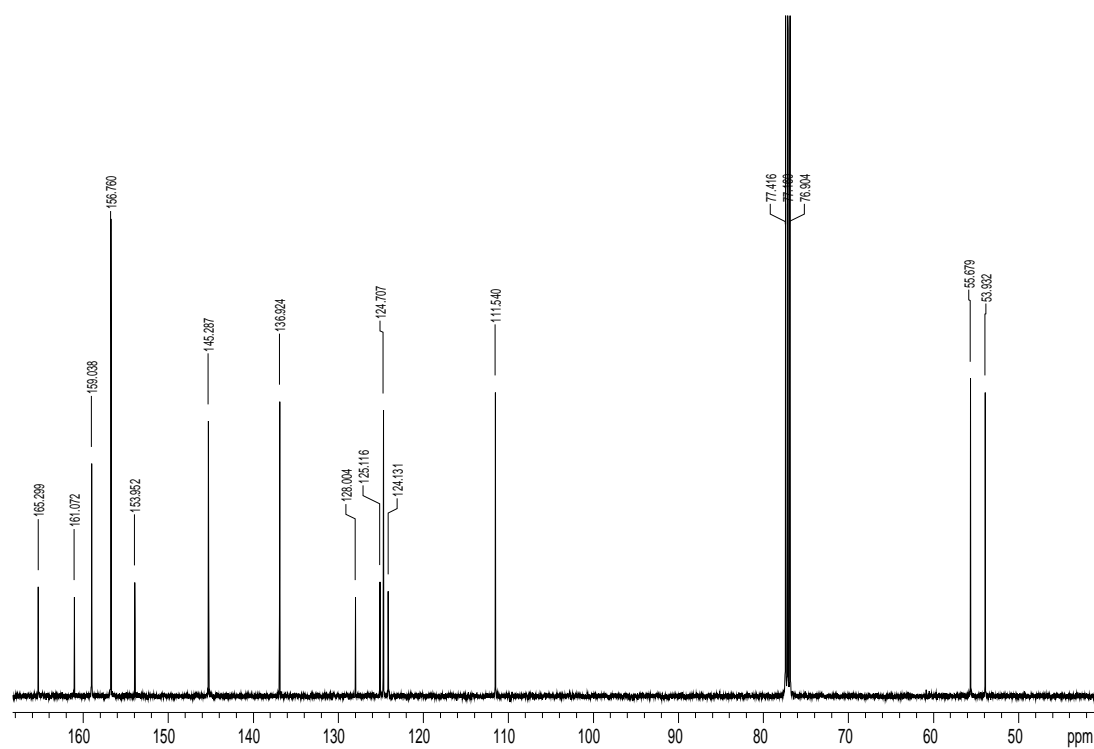
**2-Amino-3-nitro-5-(3-methoxy-6-phenylpyridazin-4-yl)-pyridine (82)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

**3-Methoxy-6-(4-methoxyphenyl)-4-(pyridin-2-yl)pyridazine (83)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**3-Methoxy-6-(4-methoxyphenyl)-4-(pyrimidin-5-yl)pyridazine (84)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

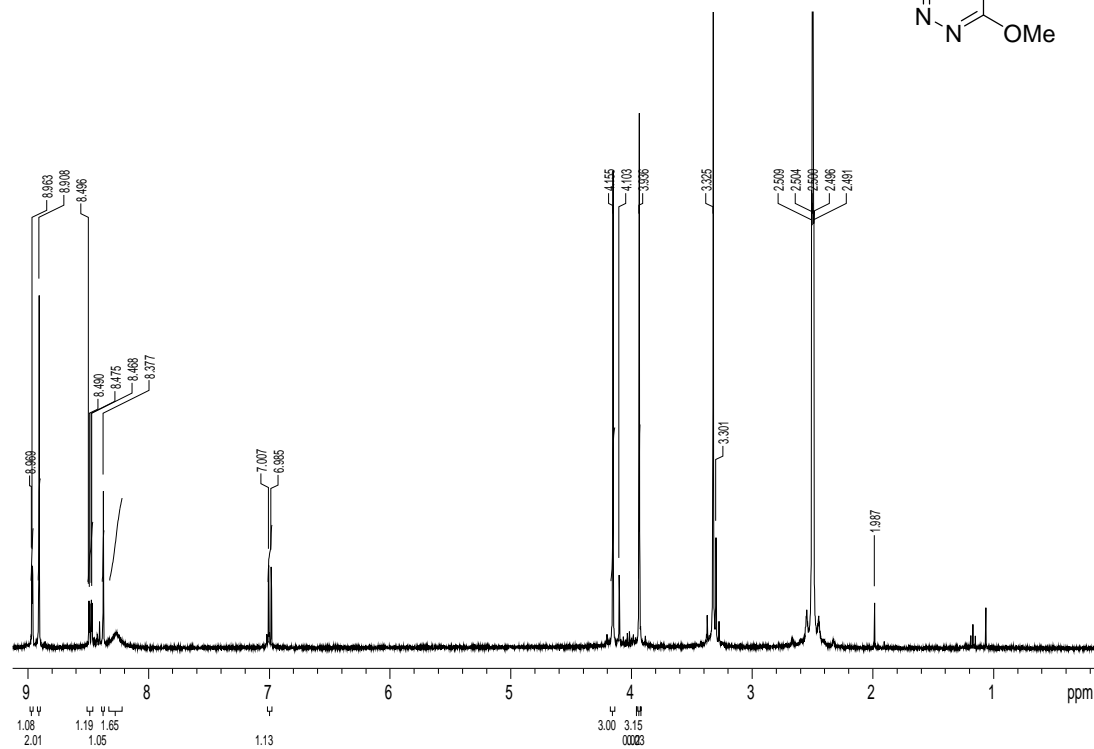
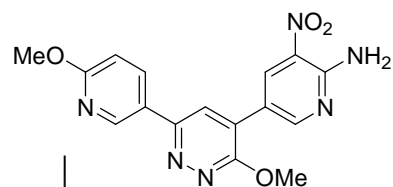
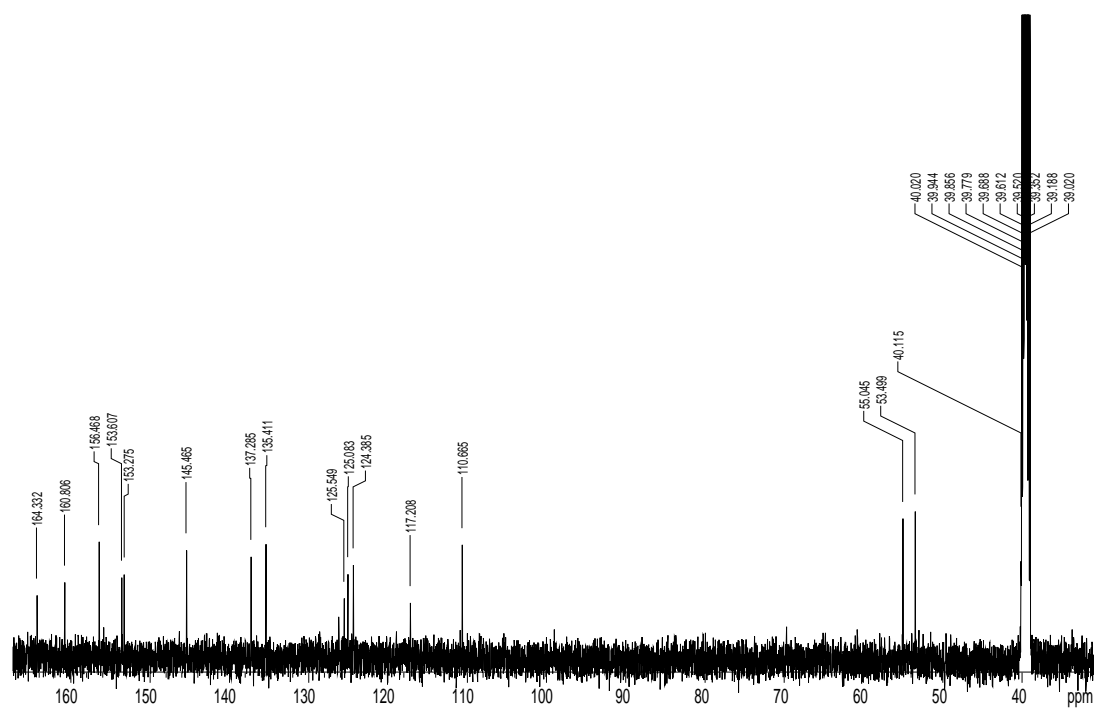
**5-(3-Methoxy-6-(4-methoxyphenyl)pyridazin-4-yl)-3-nitropyridin-2-amine (85)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)

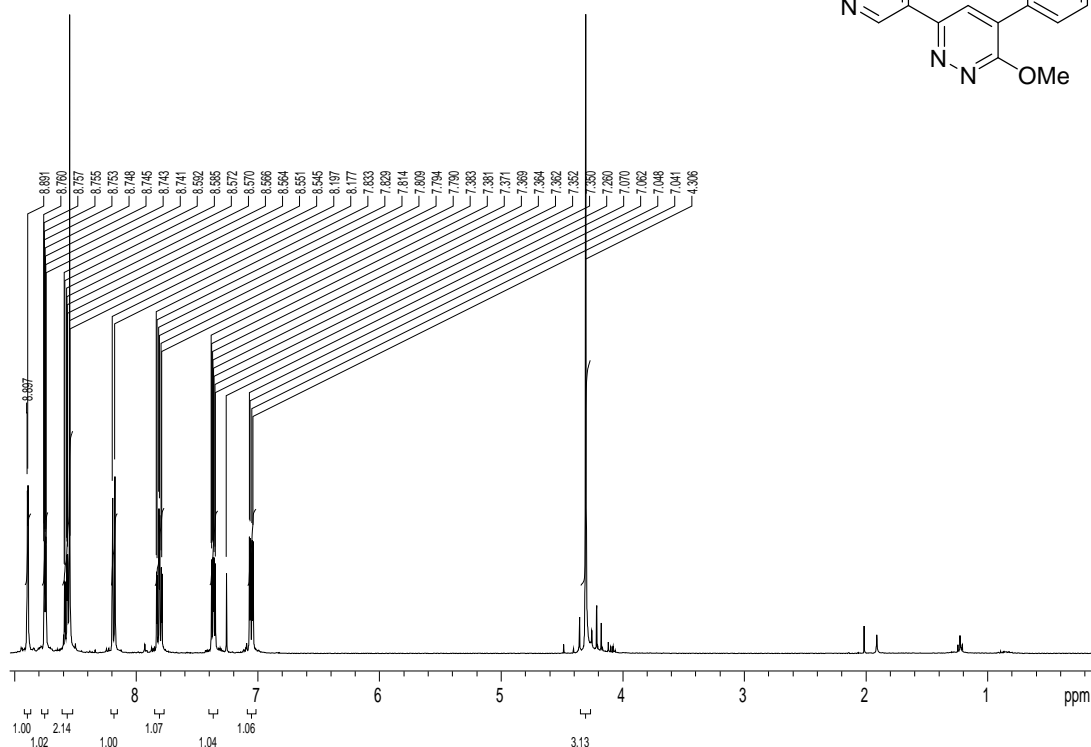
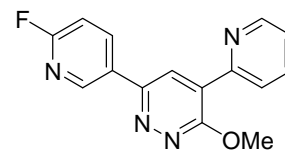
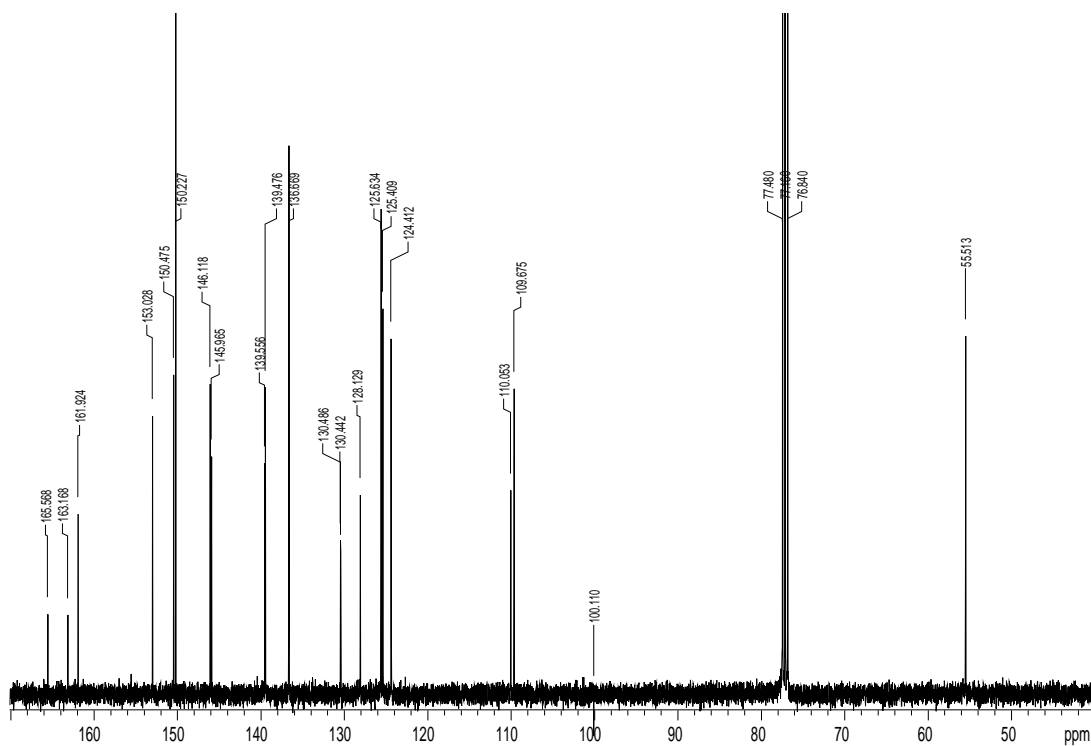
**3-Methoxy-6-(2-methoxypyridin-5-yl)-4-(pyridin-2-yl)pyridazine (86)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

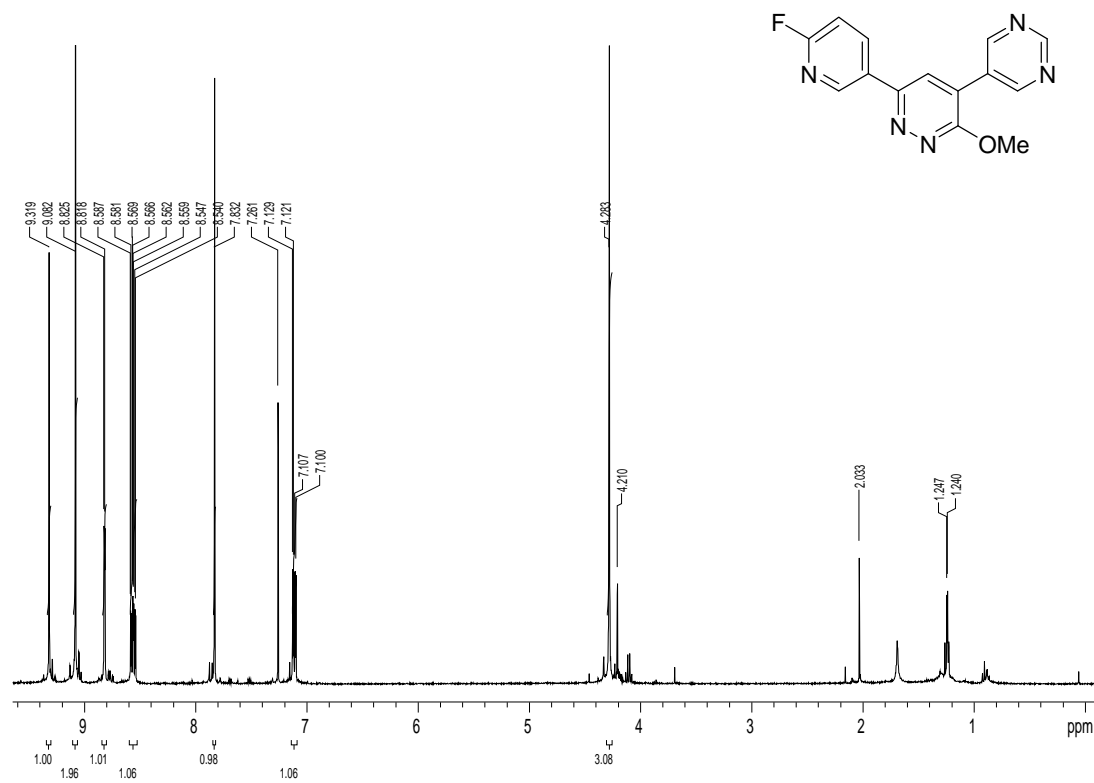
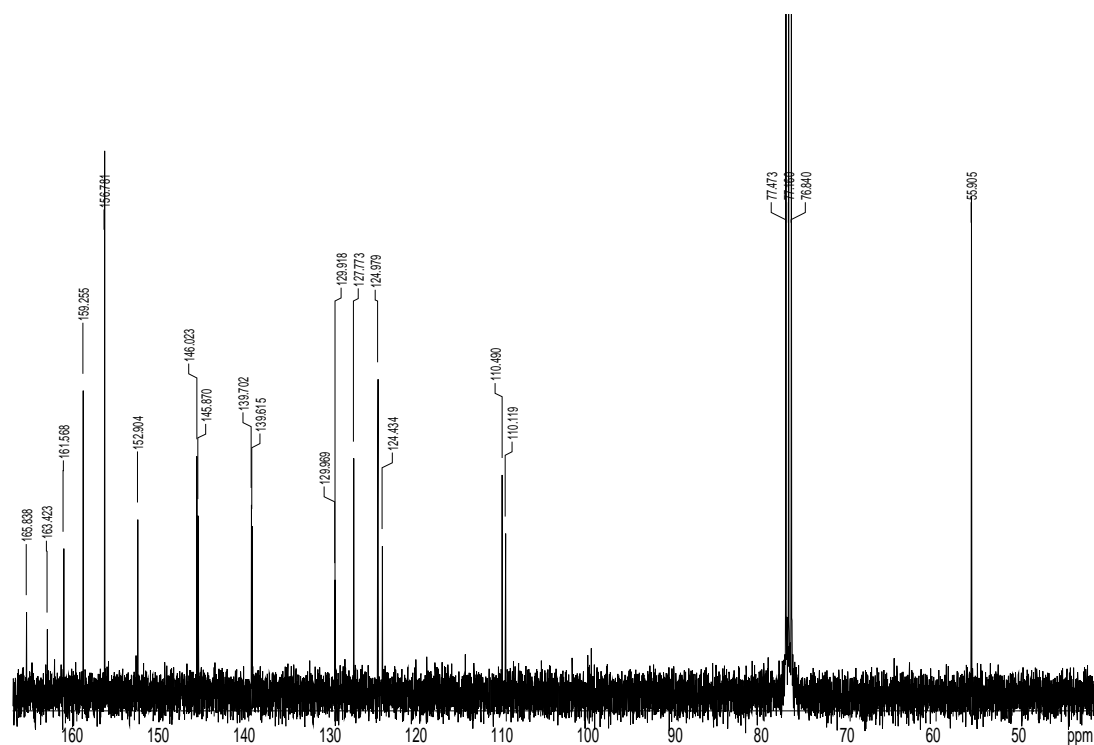
**3-Methoxy-6-(2-methoxypyridin-5-yl)-4-(pyrimidin-5-yl)pyridazine (87)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

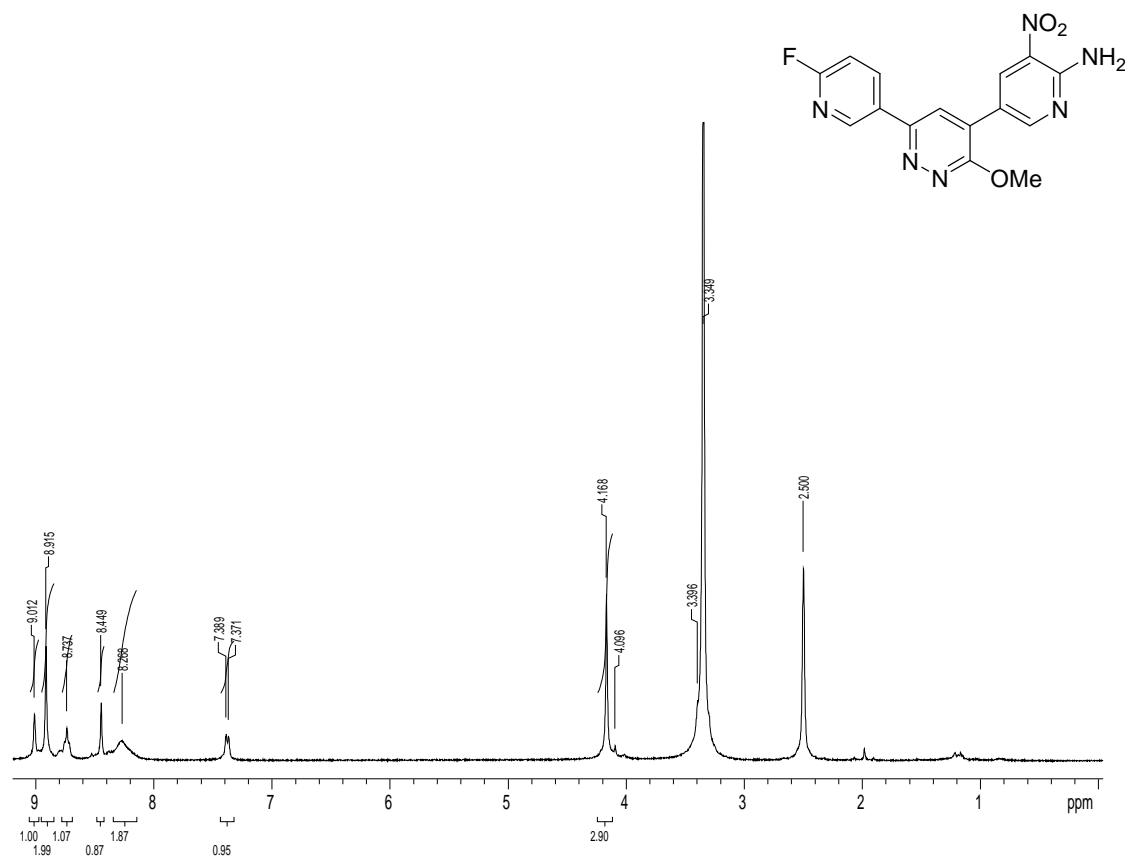
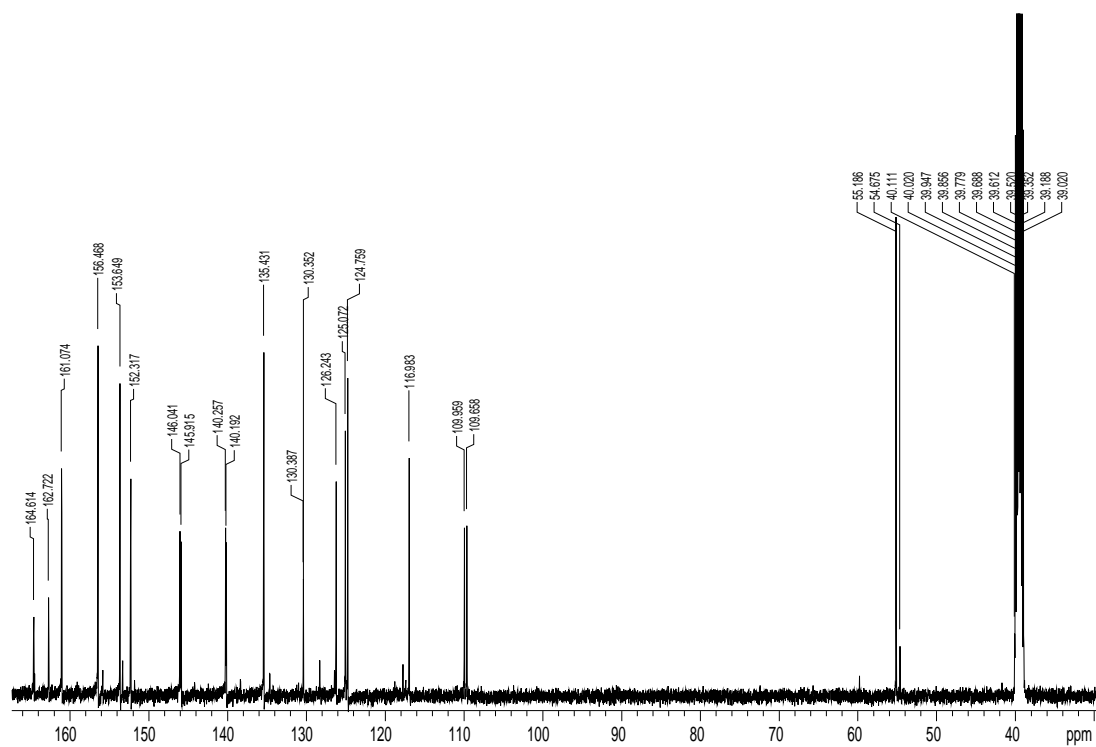
## 5-(3-Methoxy-6-(2-methoxypyridin-5-yl)-pyridazin-4-yl)-3-nitropyridin-2-amine

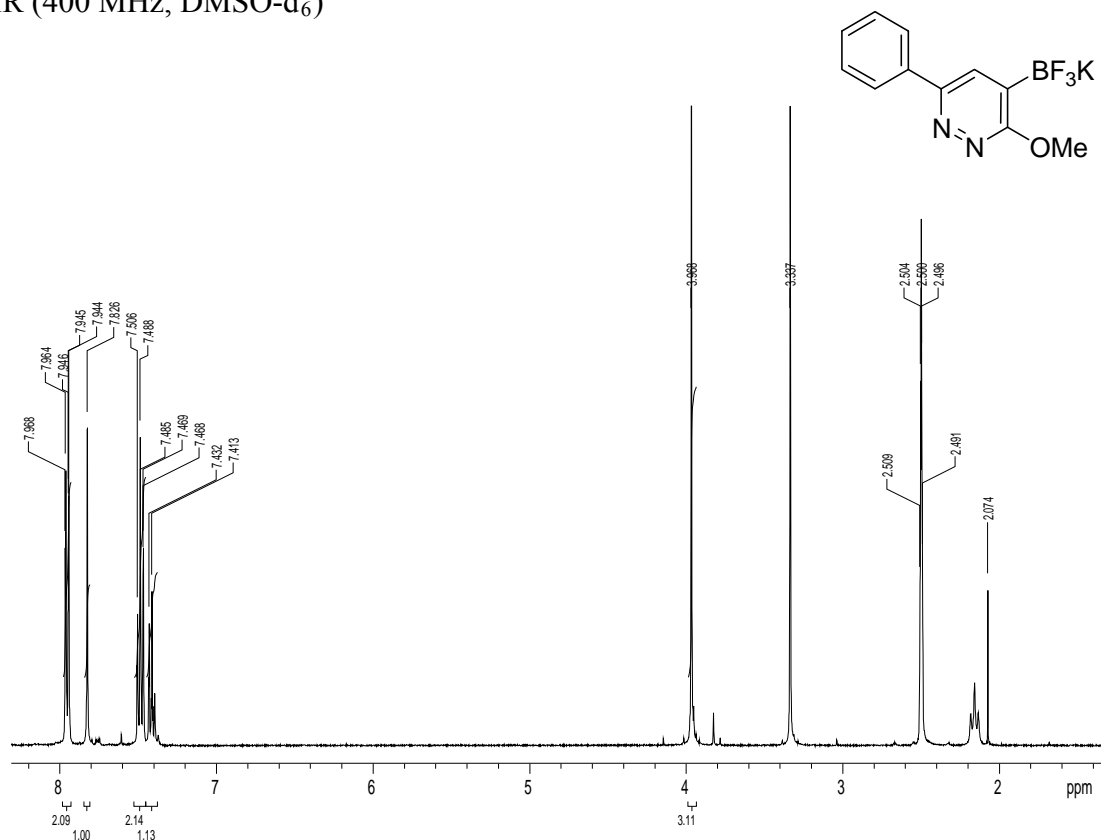
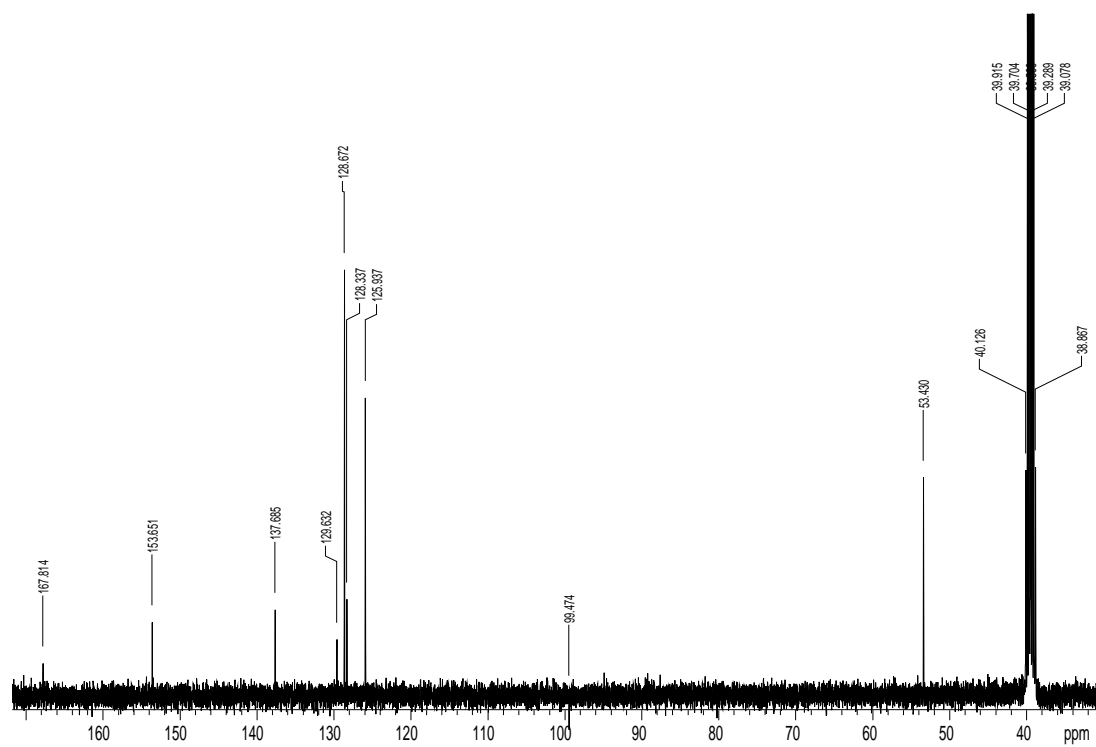
(88)

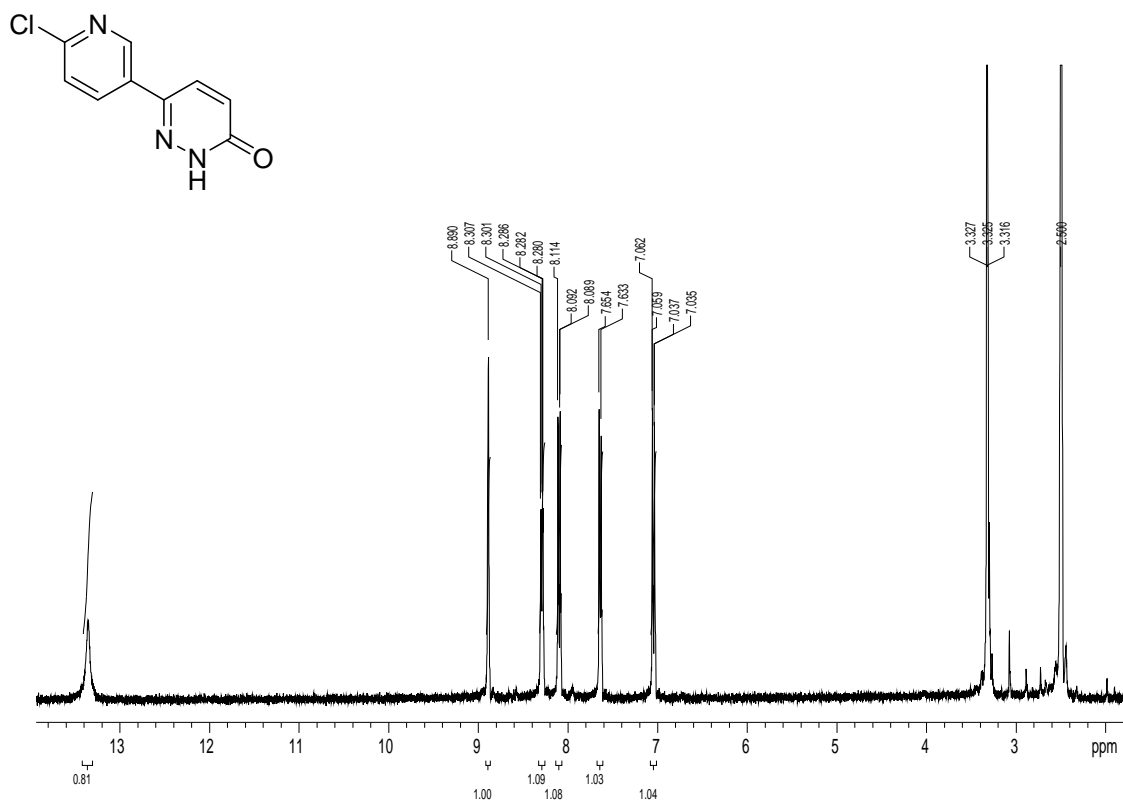
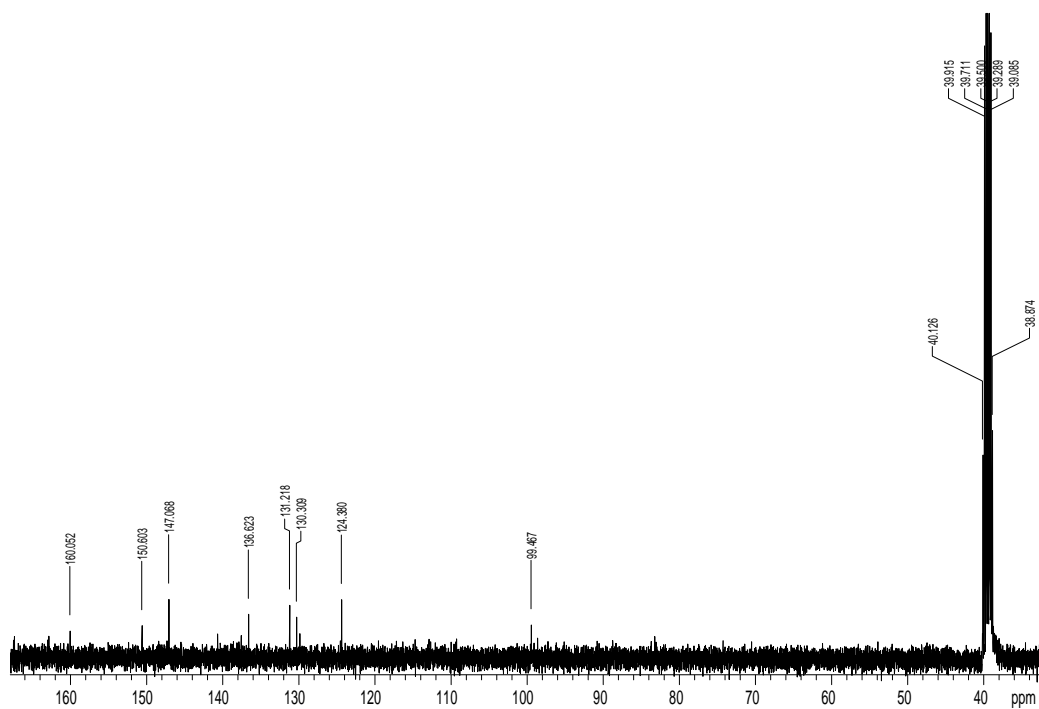
 $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )

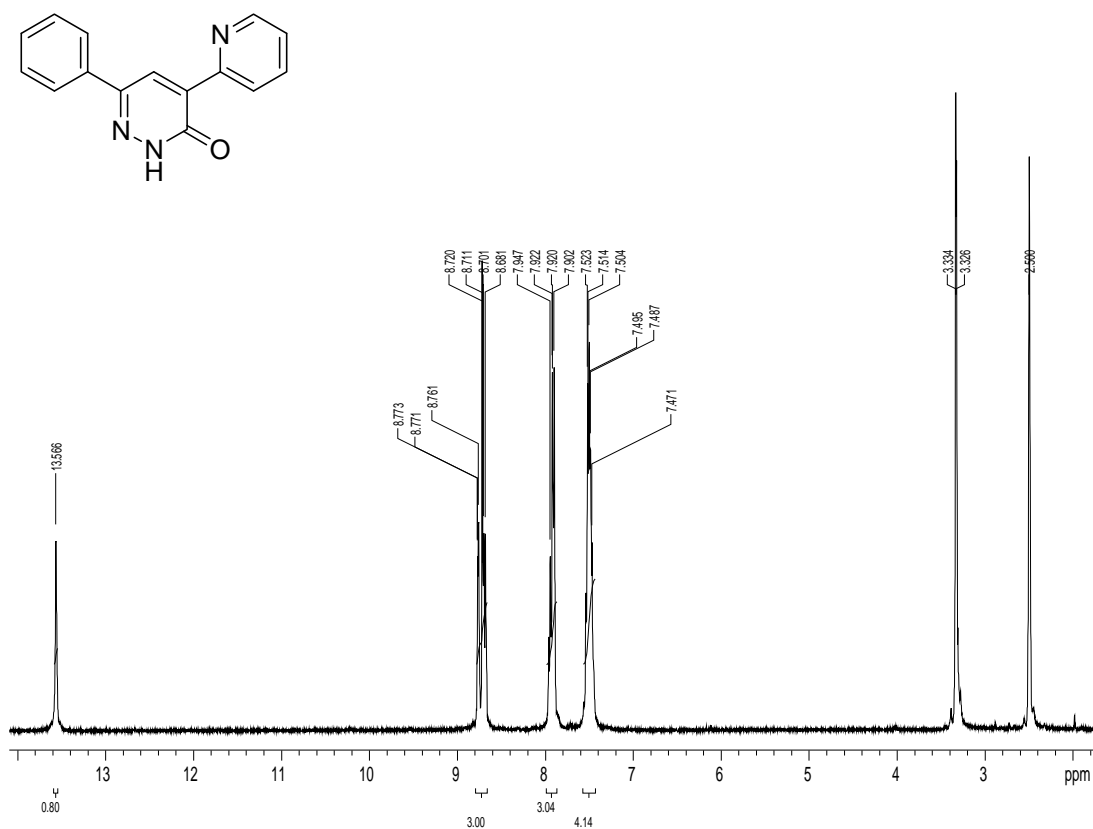
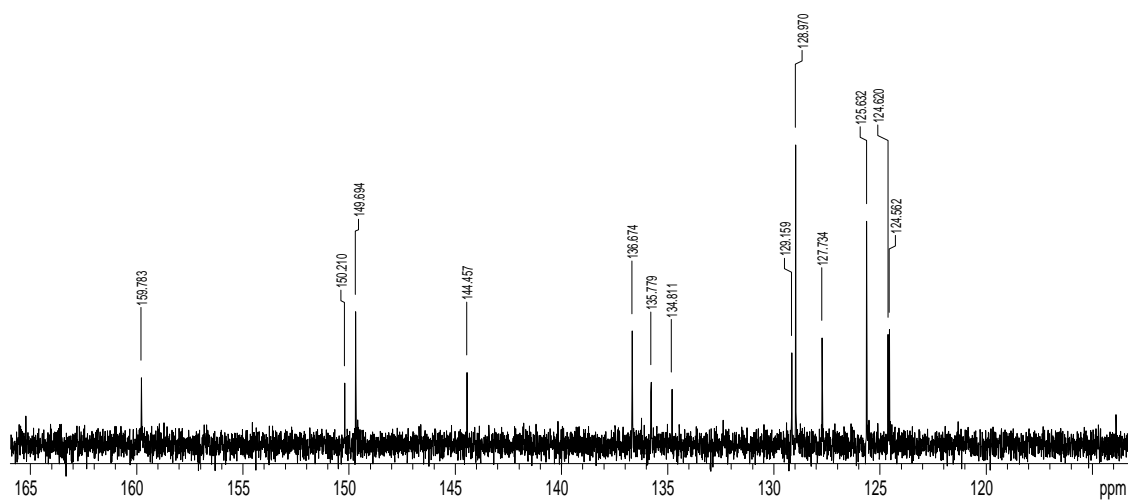
**3-Methoxy-6-(2-fluoropyridin-5-yl)-4-(pyridin-2-yl)pyridazine (89)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

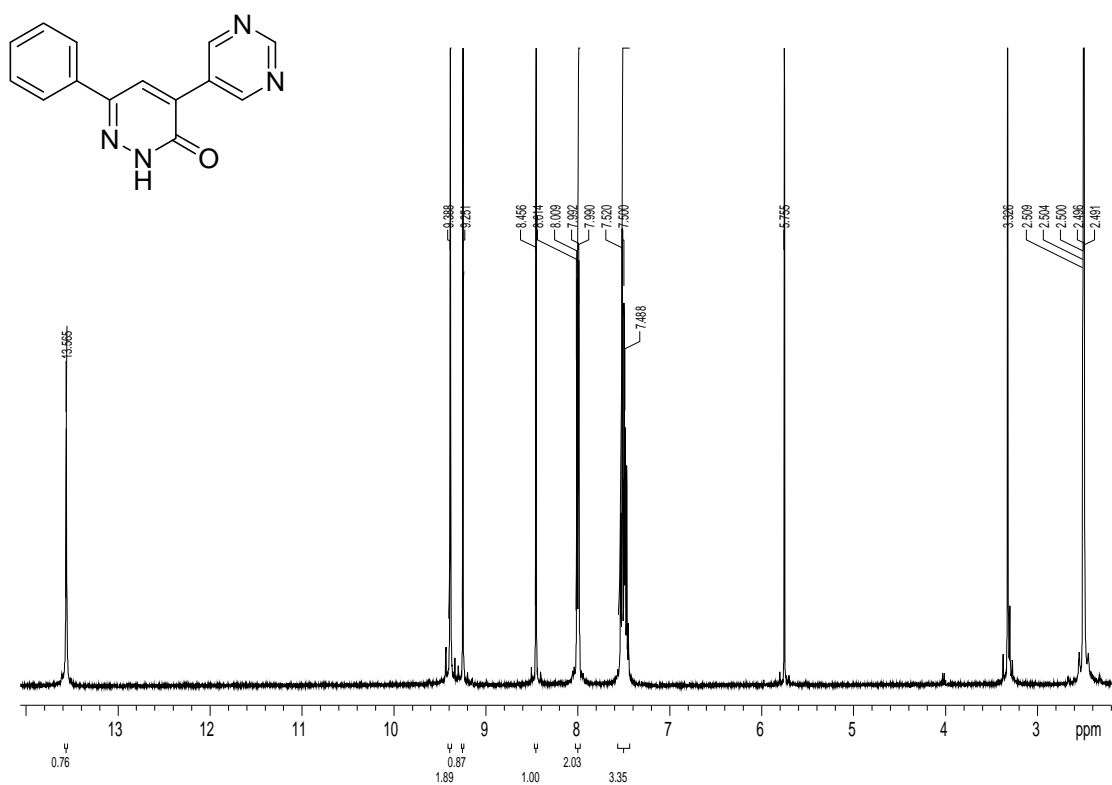
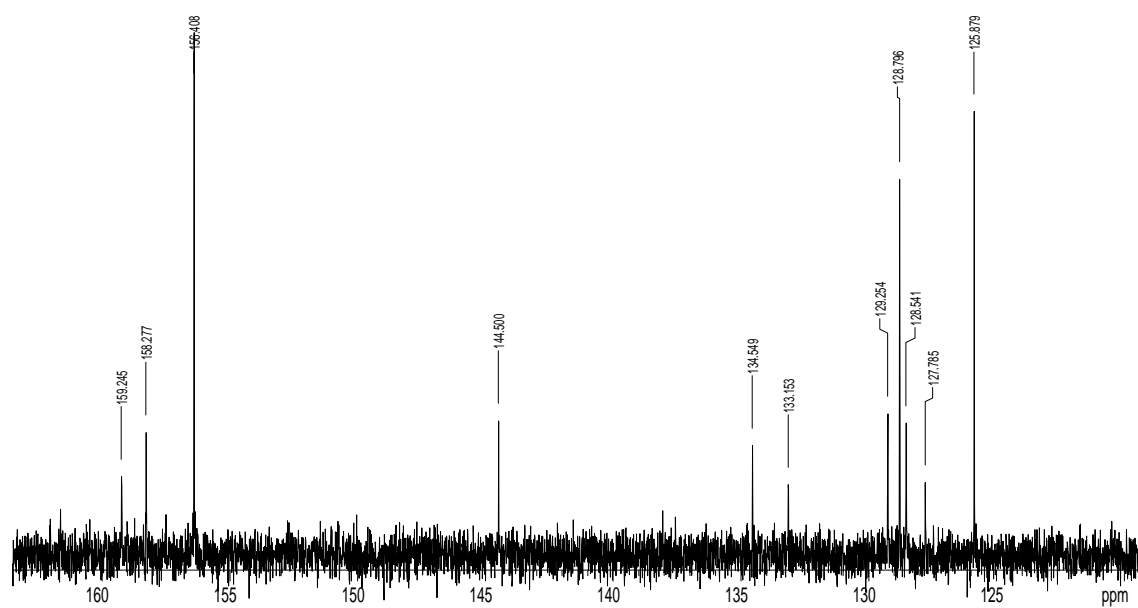
**3-Methoxy-6-(2-fluoropyridin-5-yl)-4-(pyrimidin-5-yl)pyridazine (90)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**5-(6-(2-Fluoropyridin-5-yl)-3-methoxypyridazin-4-yl)-3-nitropyridin-2-amine (91)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)

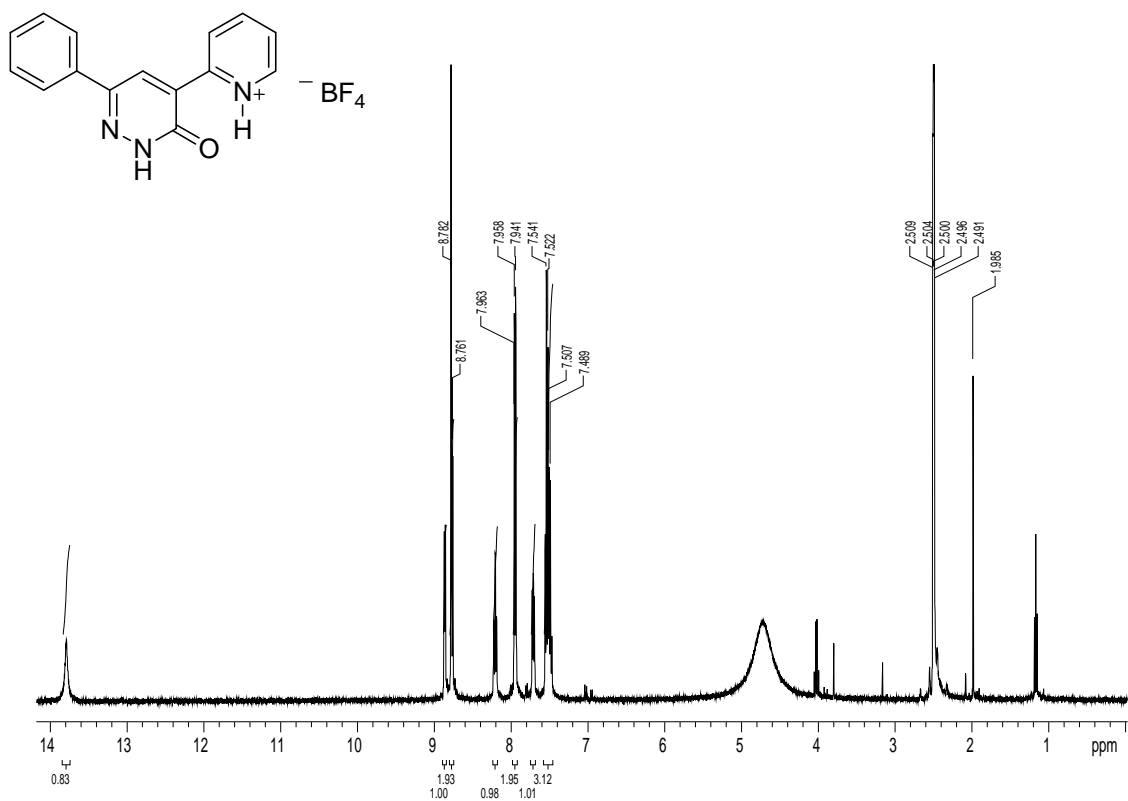
**Potassium 3-methoxy-6-phenyl-4-pyridazinyltrifluoroborate salt (92)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

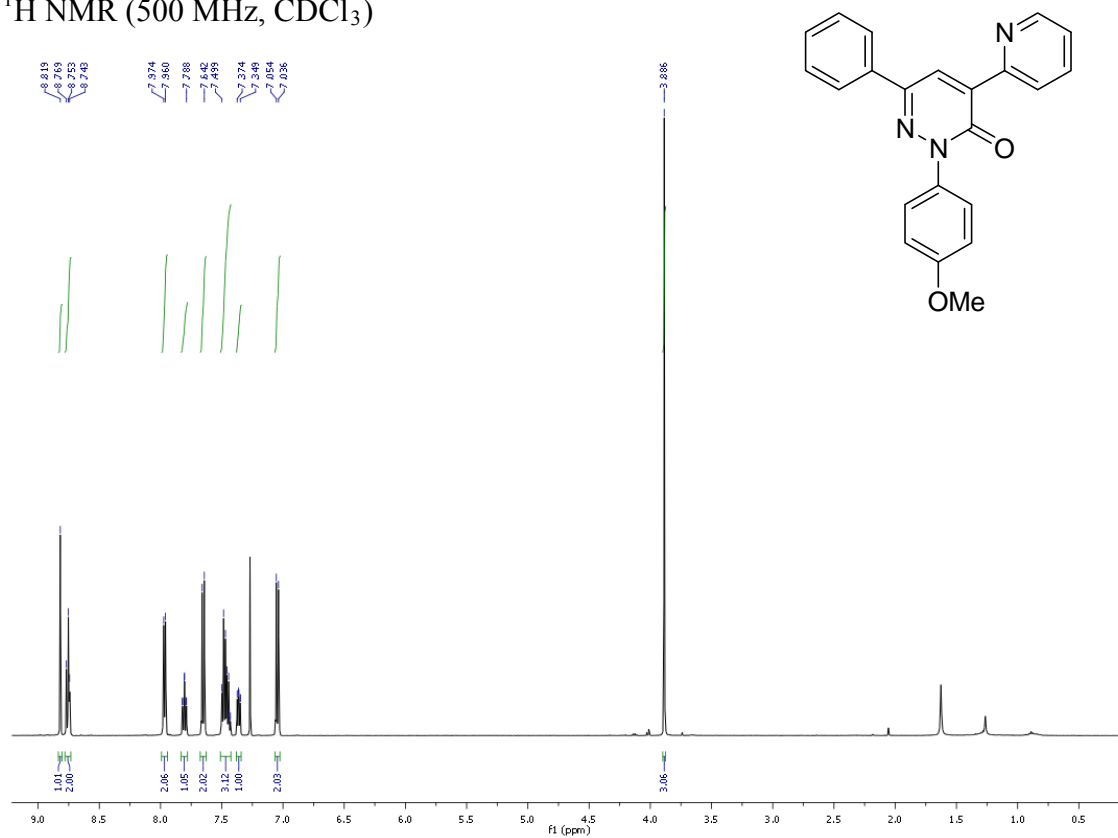
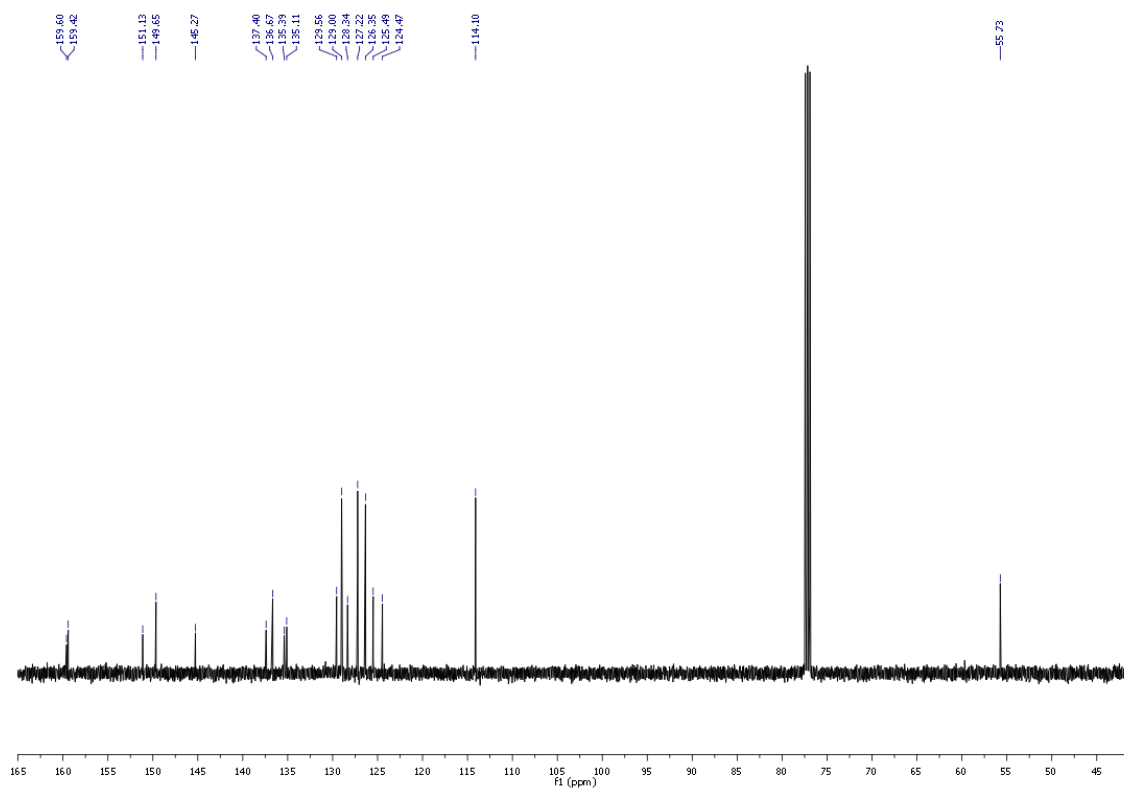
**A2.2 NMR spectra of compounds from Chapter 3****6-(6-Chloropyridin-3-yl)pyridazin-3(2H)-one (99)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

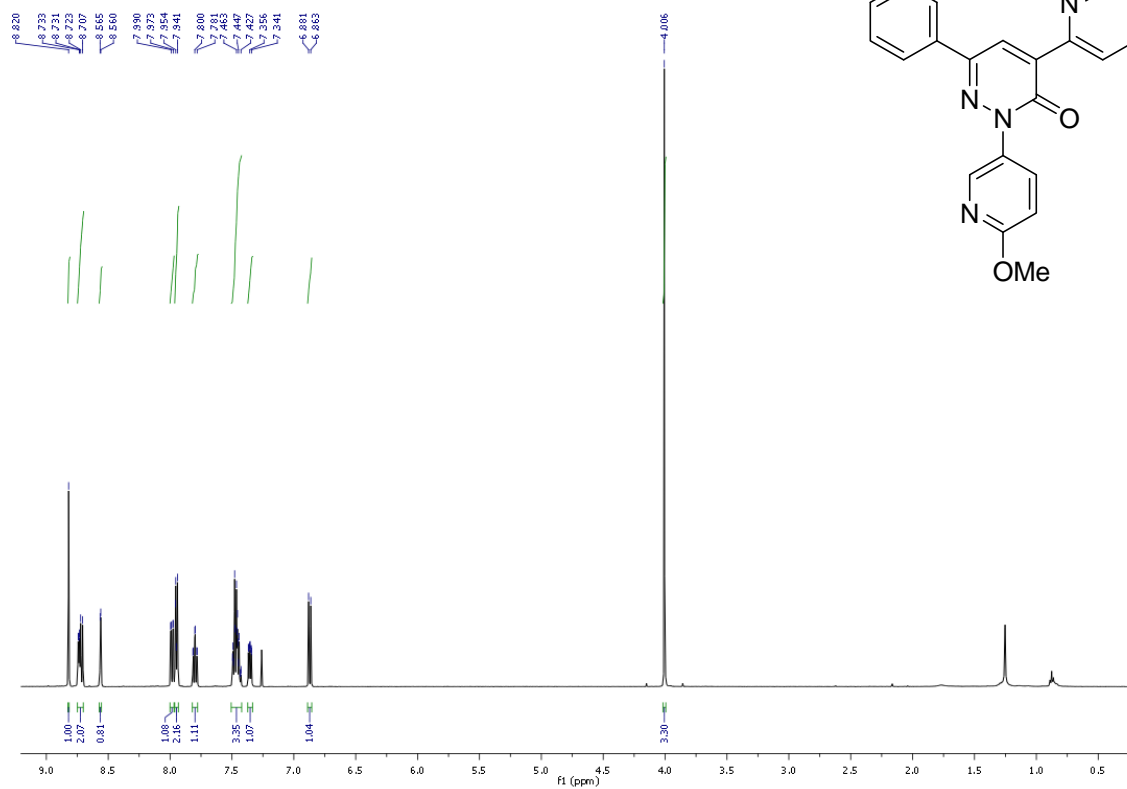
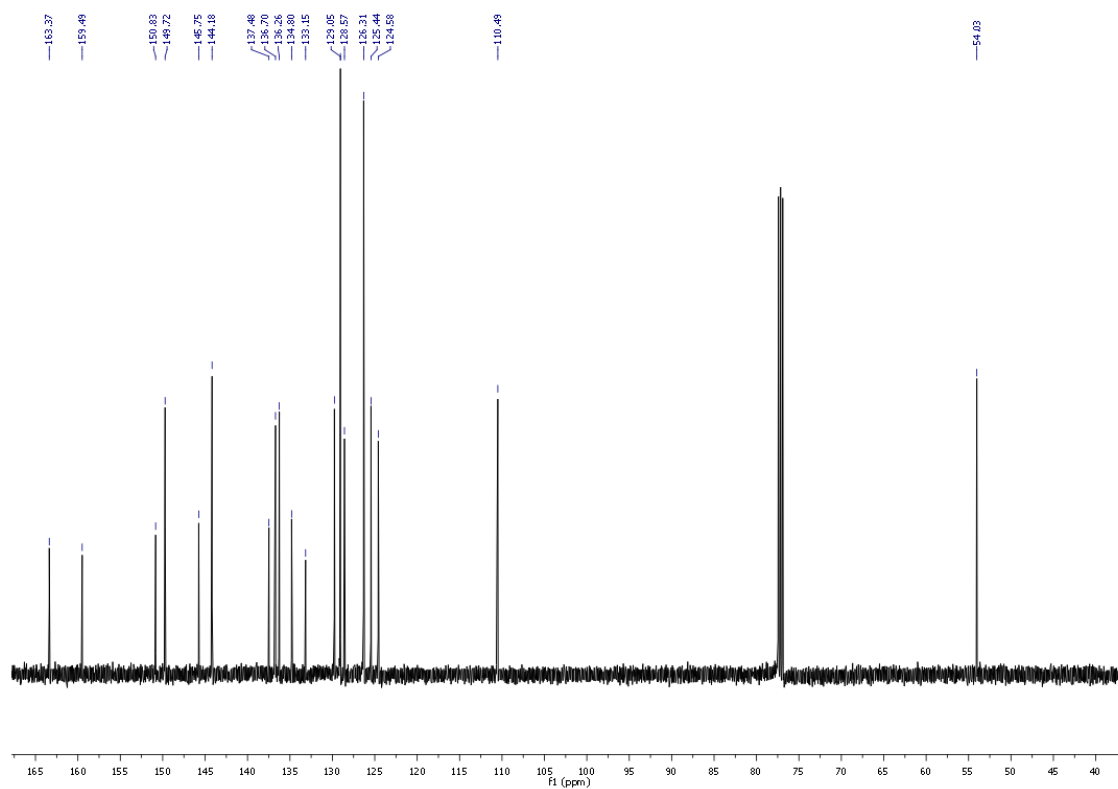
**6-Phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one (103)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

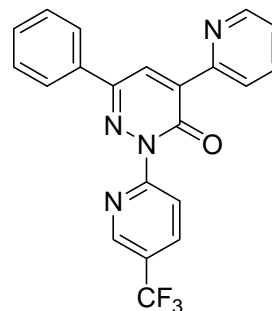
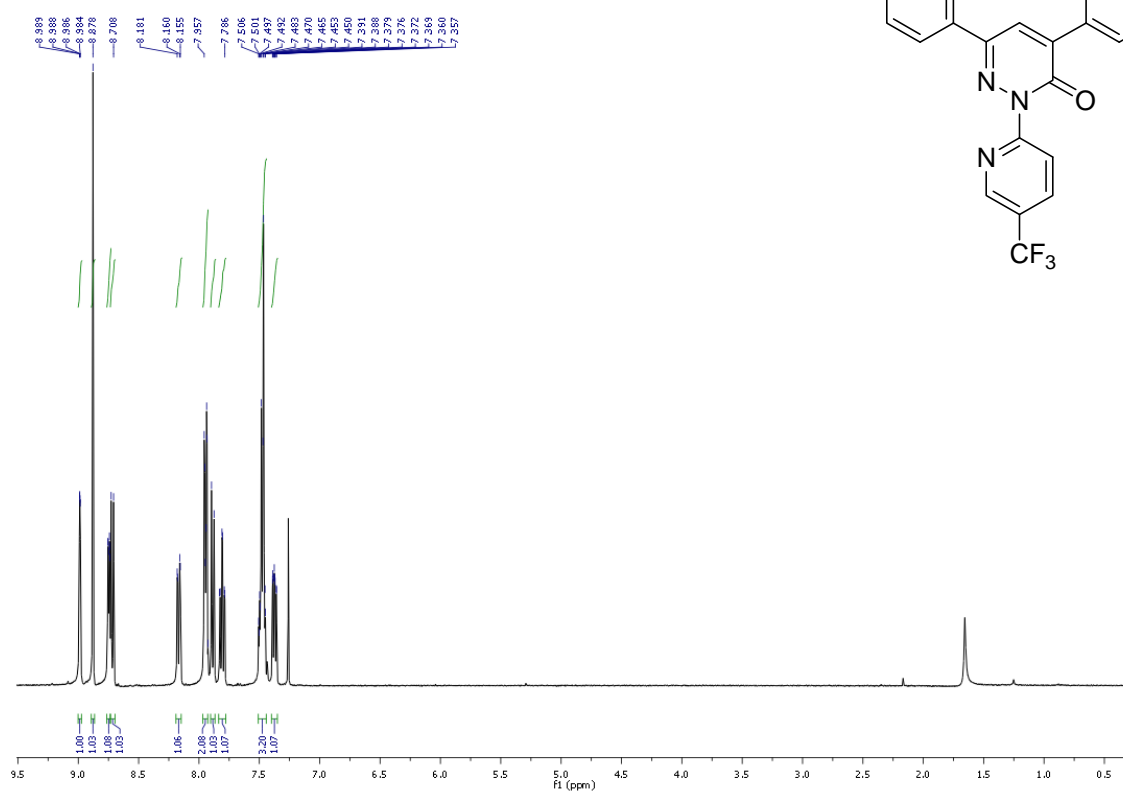
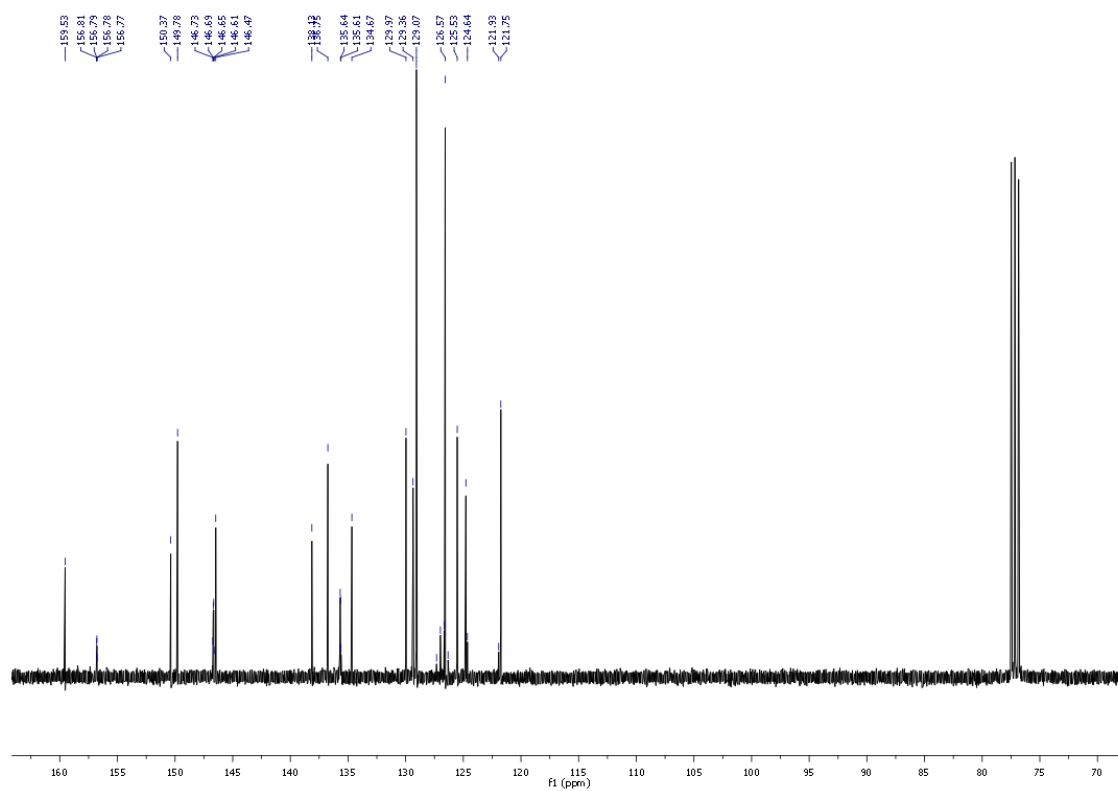
**6-Phenyl-4-(pyrimidin-5-yl)pyridazin-3(2H)-one (104)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

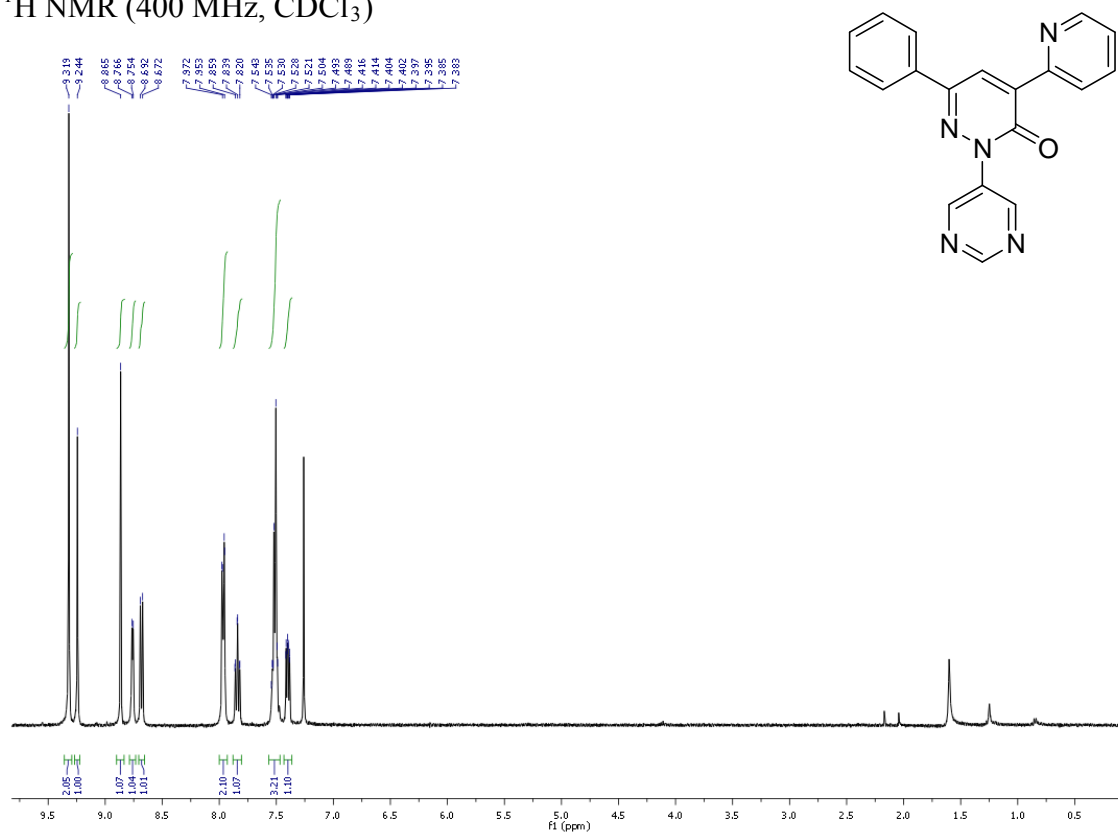
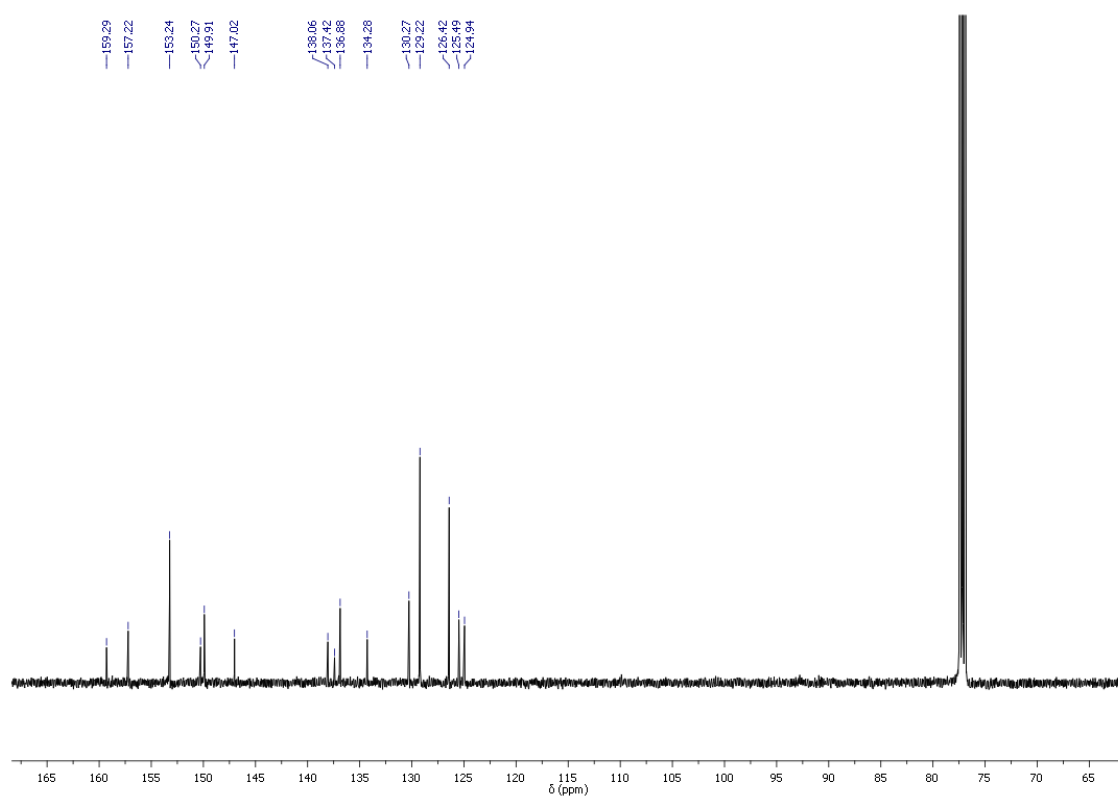


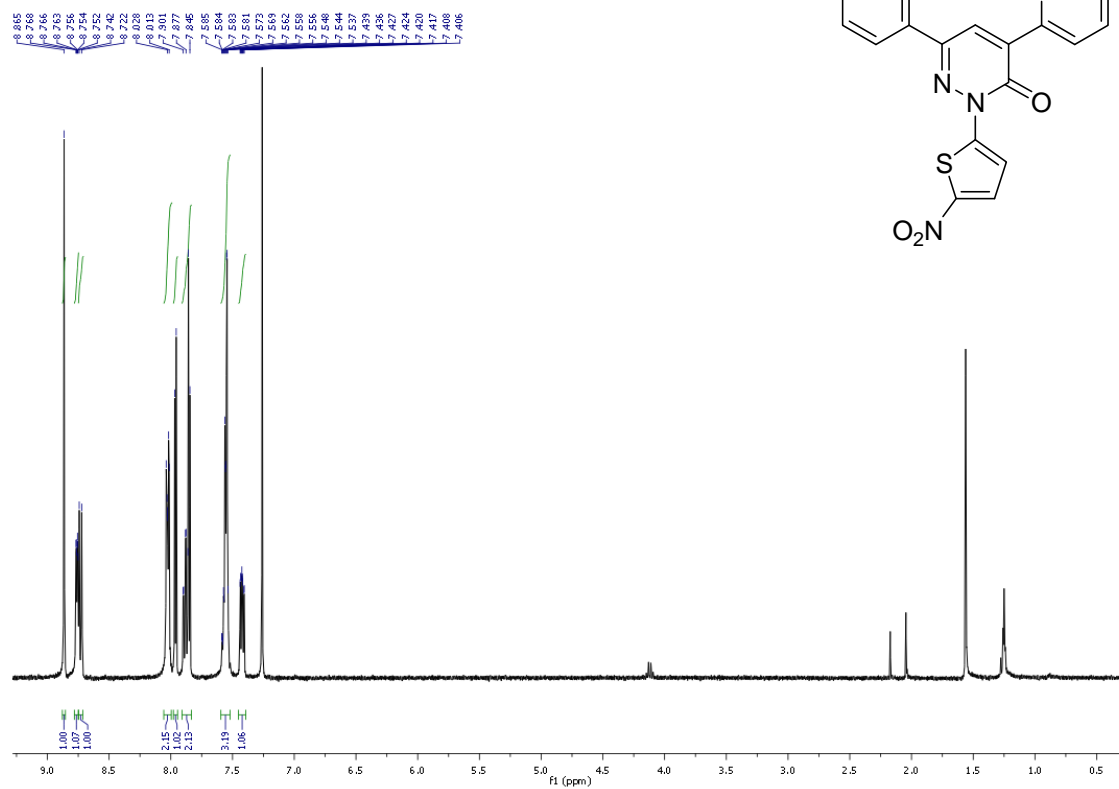
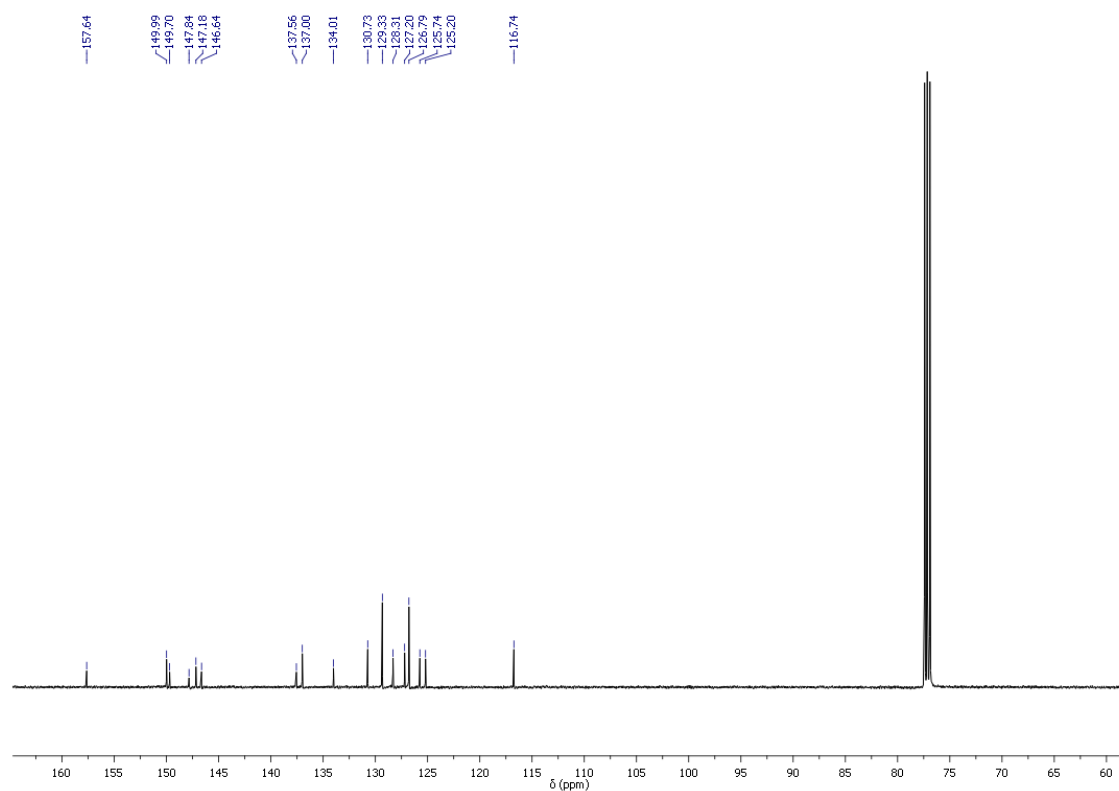
**Pyridinium salt 106** $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )

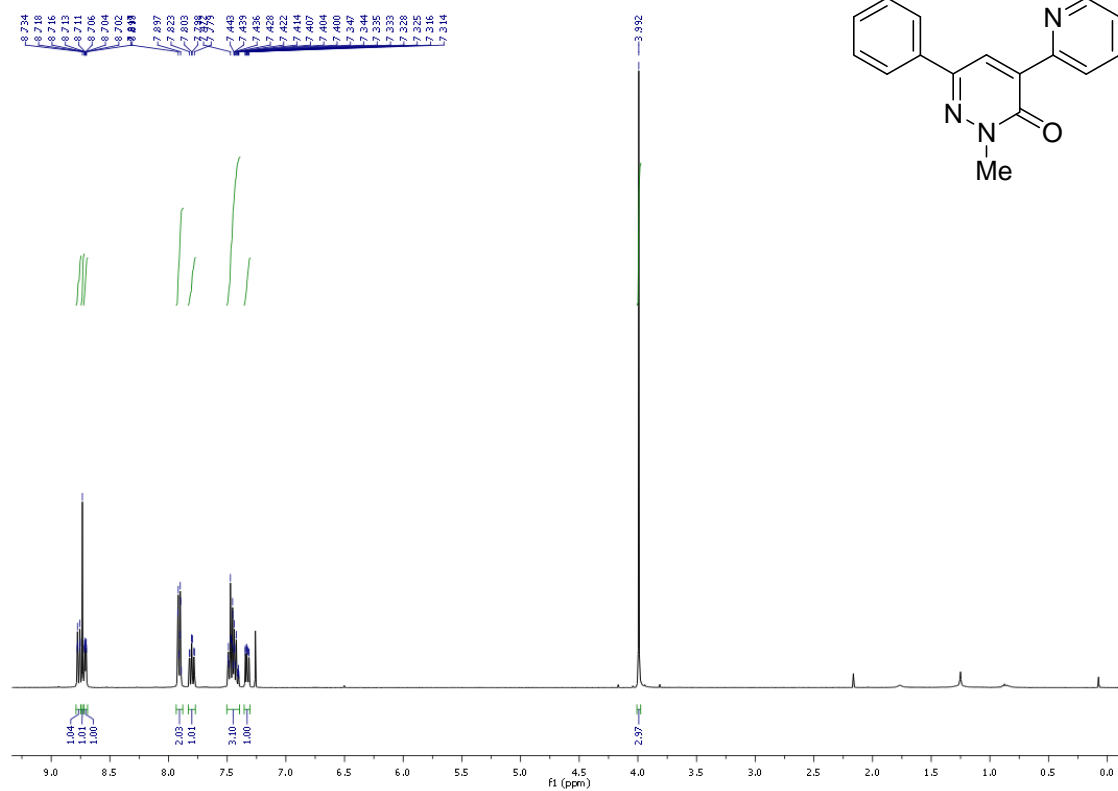
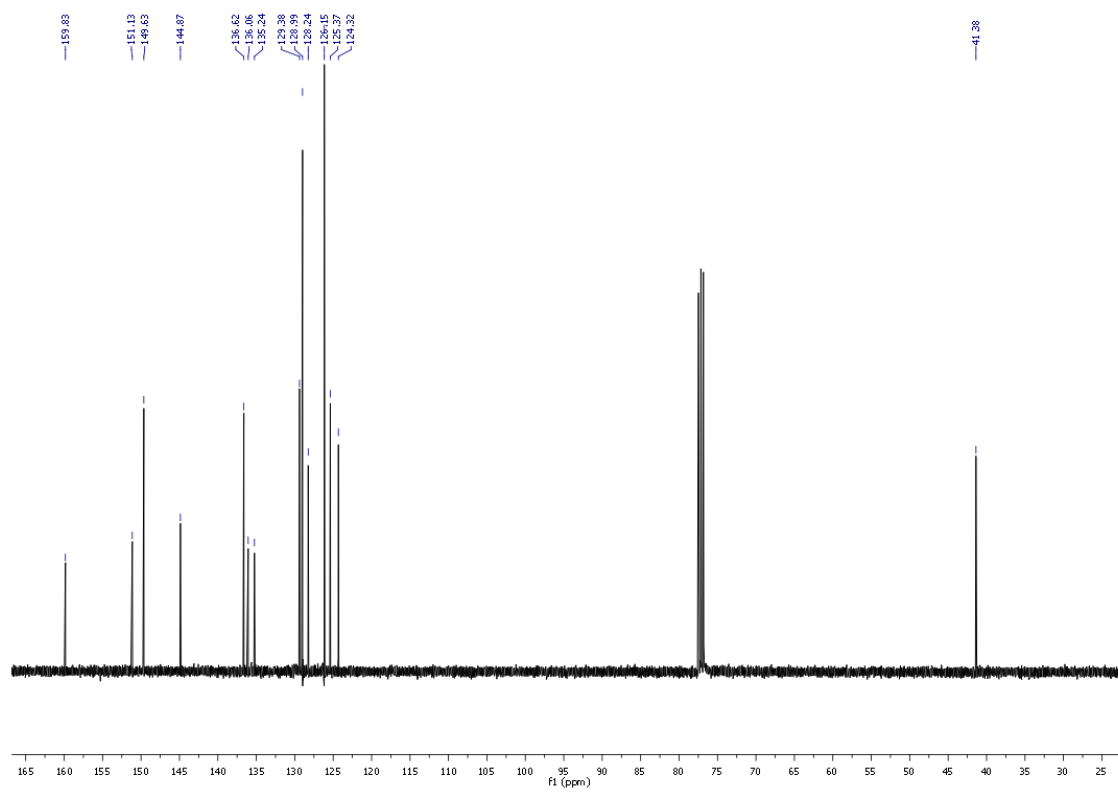
**2-(4-Methoxyphenyl)-6-phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one (112)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

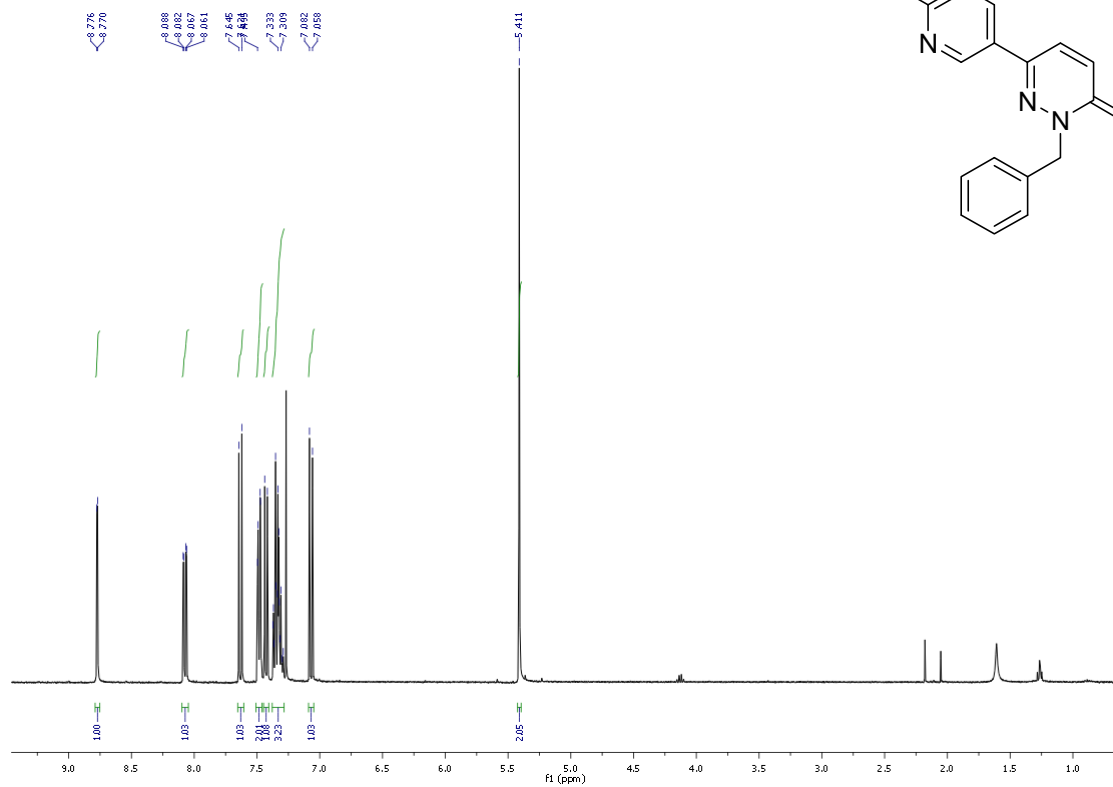
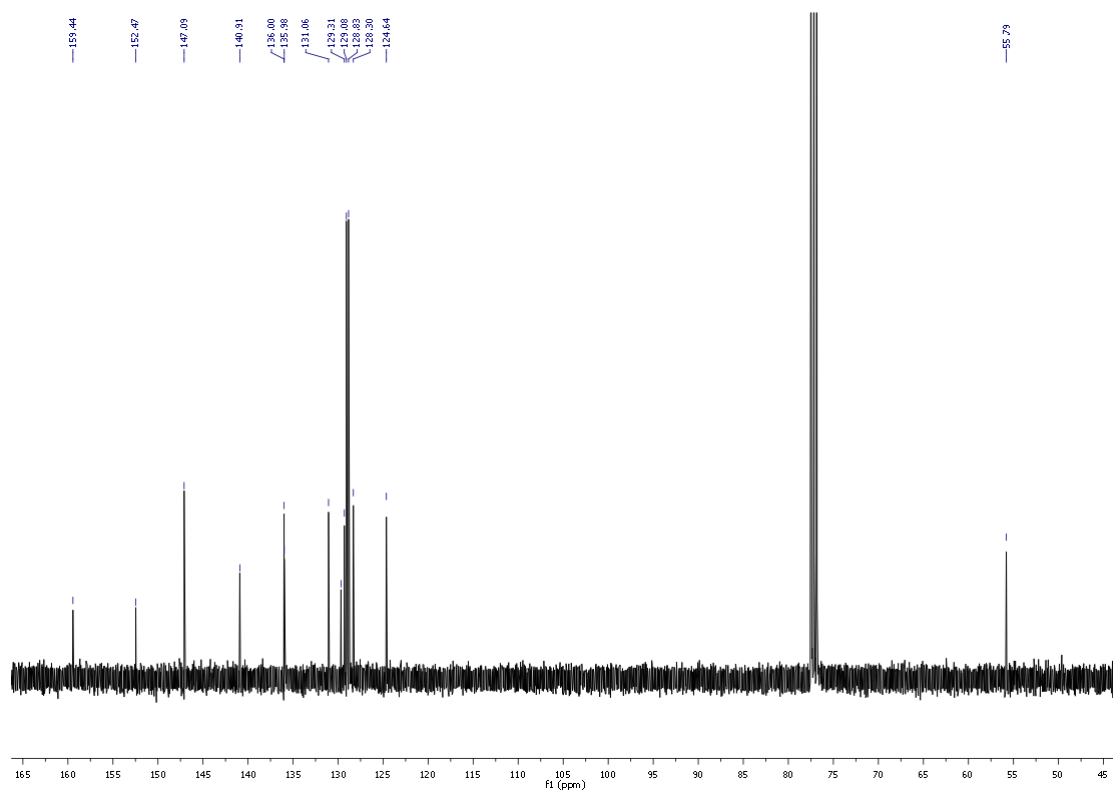
**2-(6-Methoxypyridin-3-yl)-6-phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one (113)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

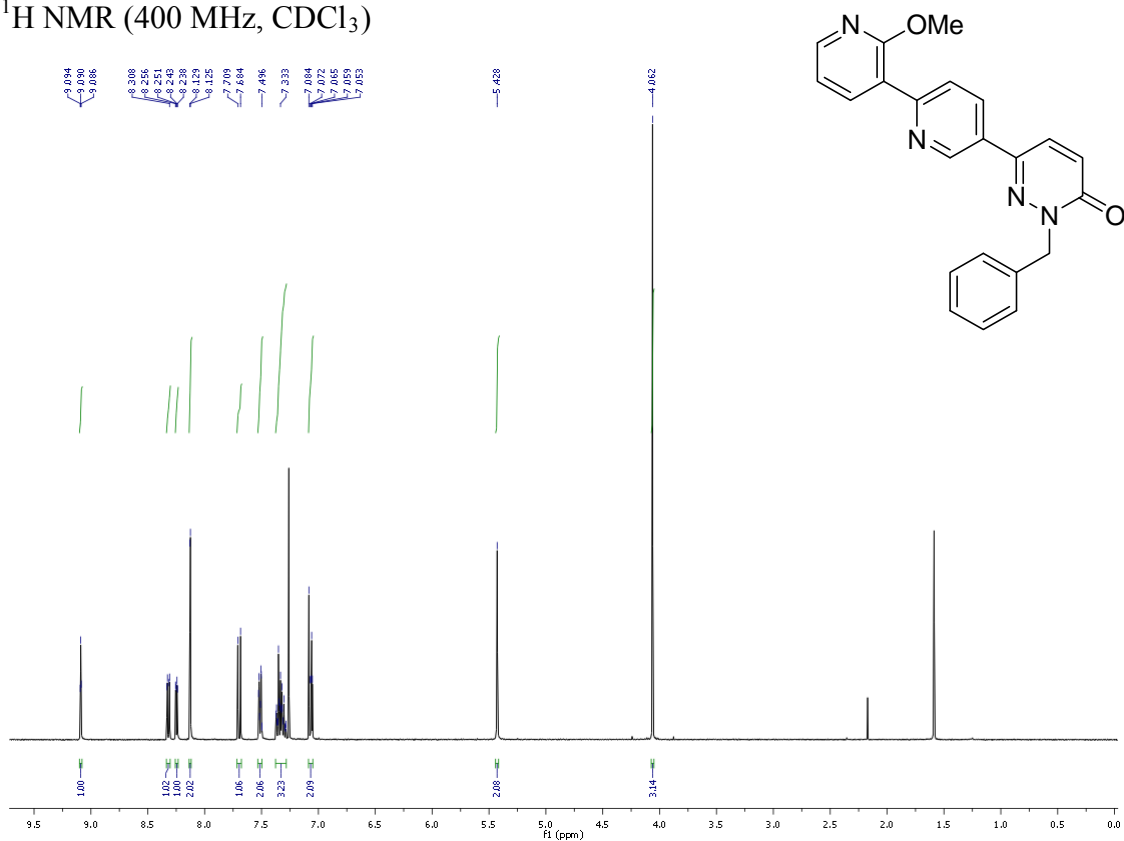
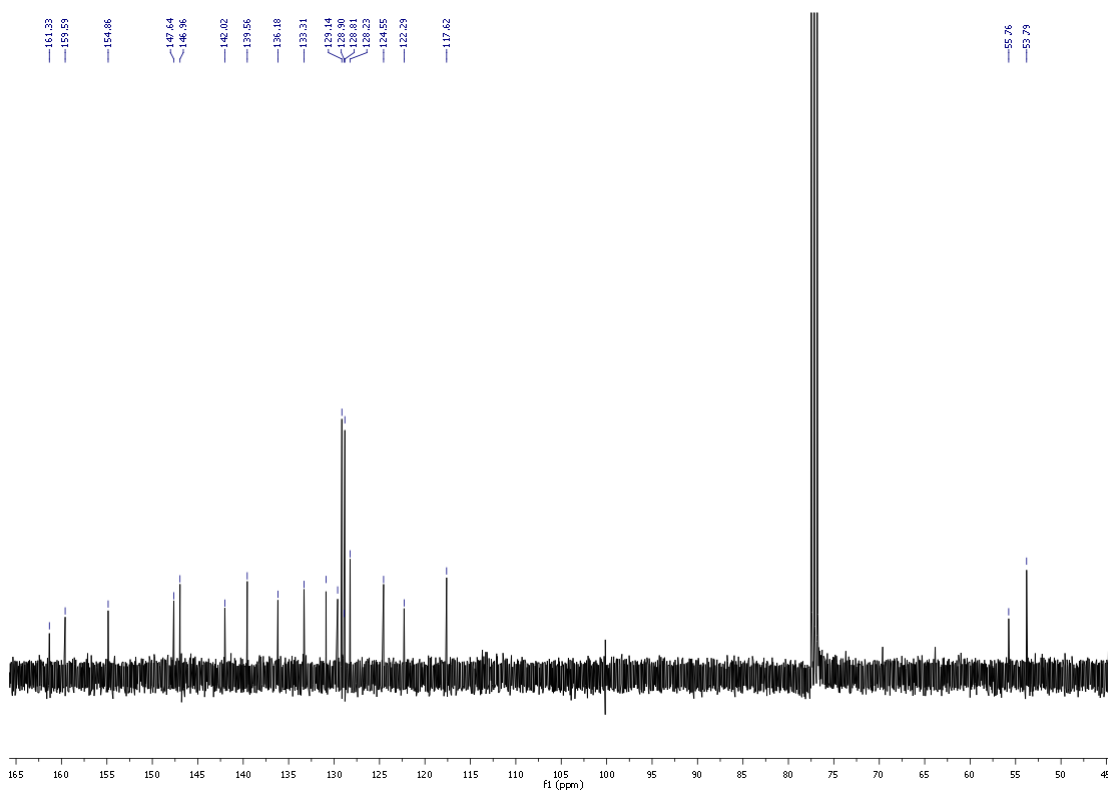
**2-(5-(Trifluoromethyl)pyridin-2-yl)-6-phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one  
(114)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

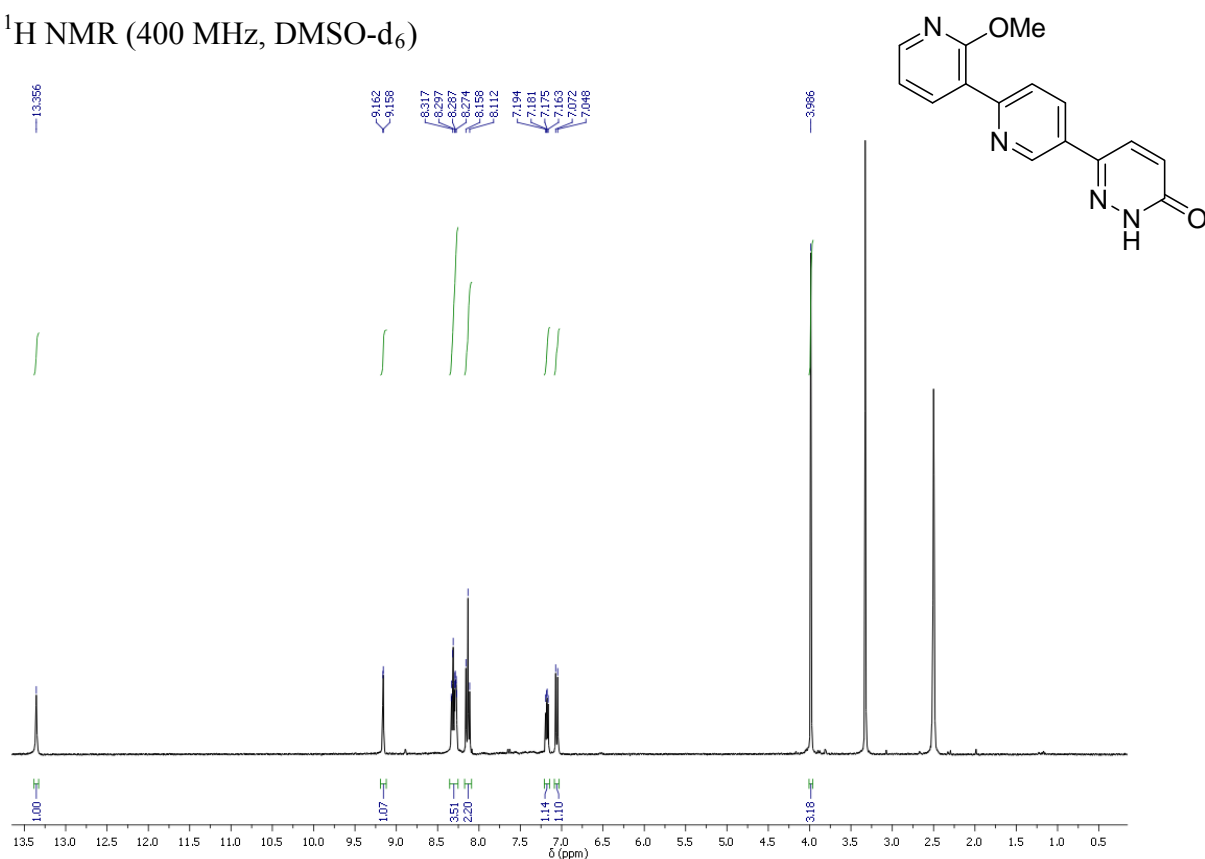
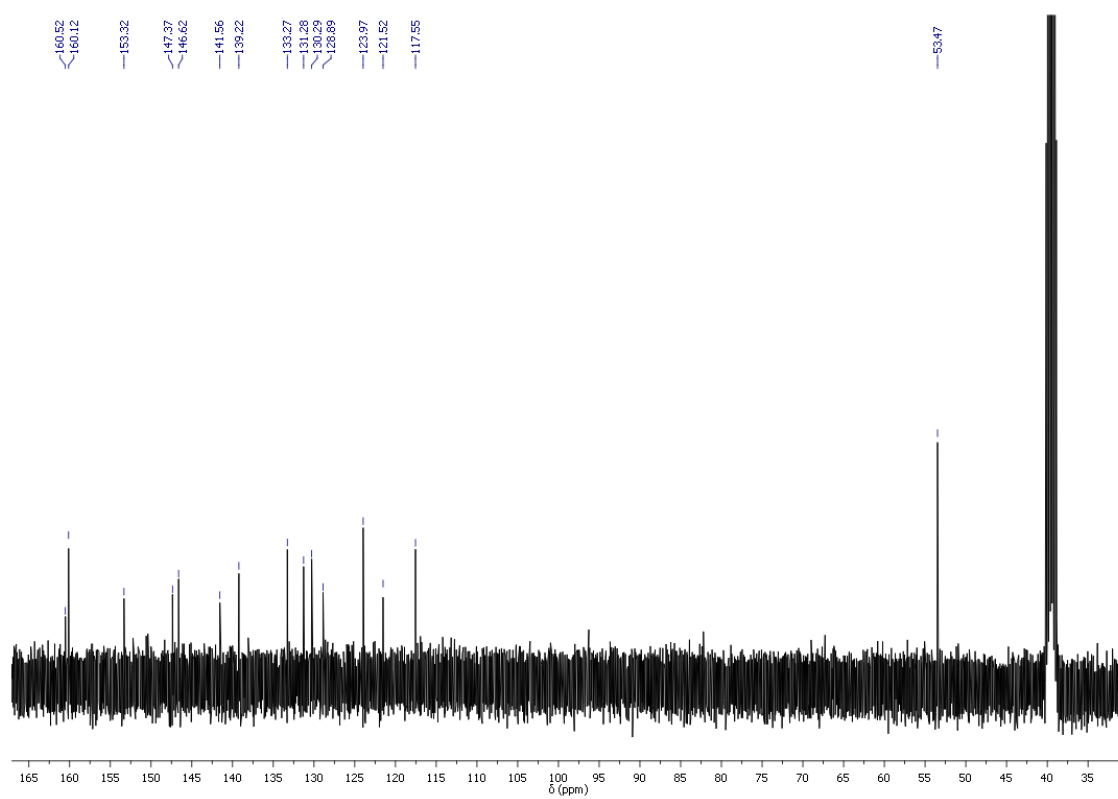
**6-Phenyl-4-(pyridin-2-yl)-2-(pyrimidin-5-yl)pyridazin-3(2H)-one (115)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

**2-(5-Nitrothiophen-2-yl)-6-phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one (116)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

**2-Methyl-6-phenyl-4-(pyridin-2-yl)pyridazin-3(2H)-one (117)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

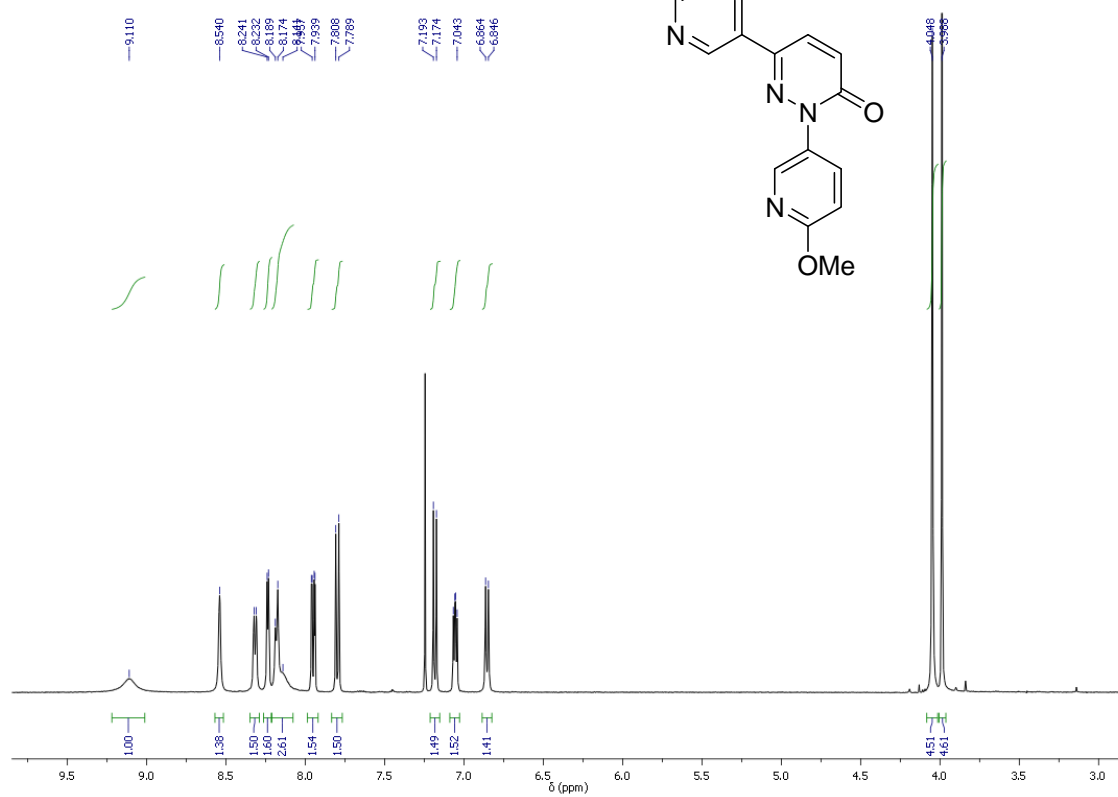
**2-Benzyl-6-(6-chloropyridin-3-yl)pyridazin-3(2H)-one (118)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**2-Benzyl-6-(6-(2-methoxypyridin-3-yl)pyridin-3-yl)pyridazin-3(2H)-one (119)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

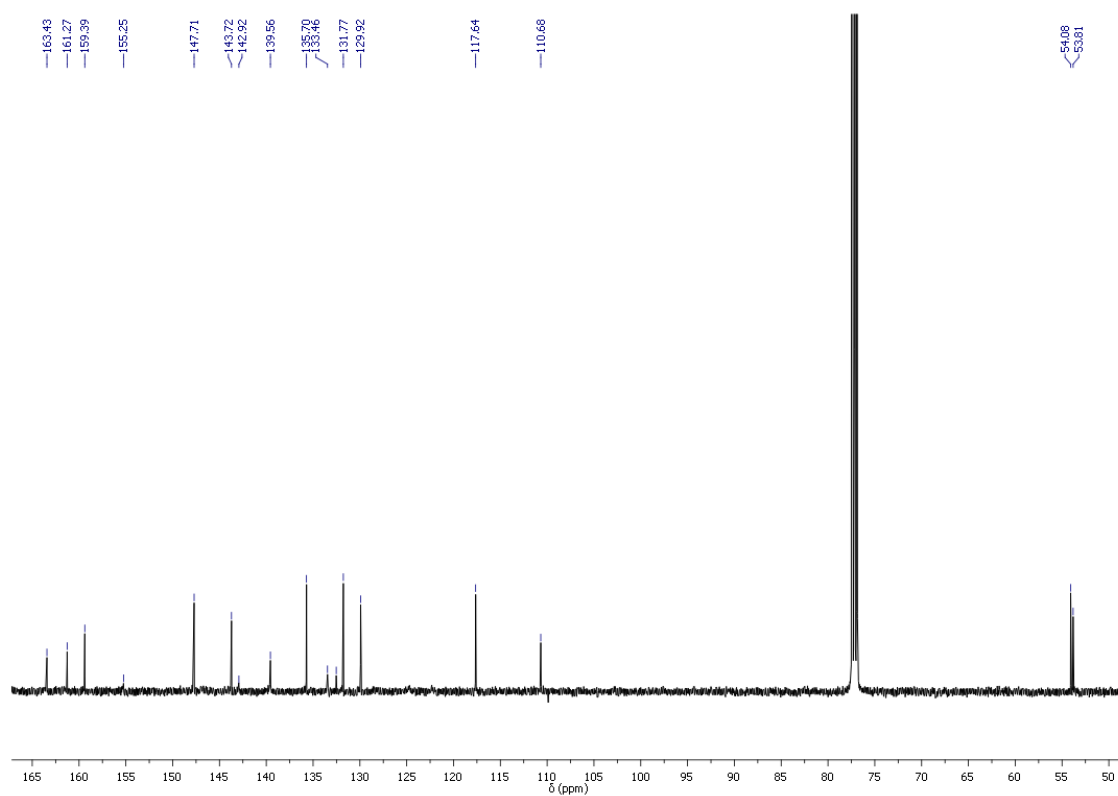
**6-(6-(2-Methoxypyridin-3-yl)pyridin-3-yl)pyridazin-3(2H)-one (120)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)

**2-(6-Methoxypyridin-3-yl)-6-(6-(2-methoxypyridin-3-yl)pyridin-3-yl)pyridazin-3(2H)-one (121)**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



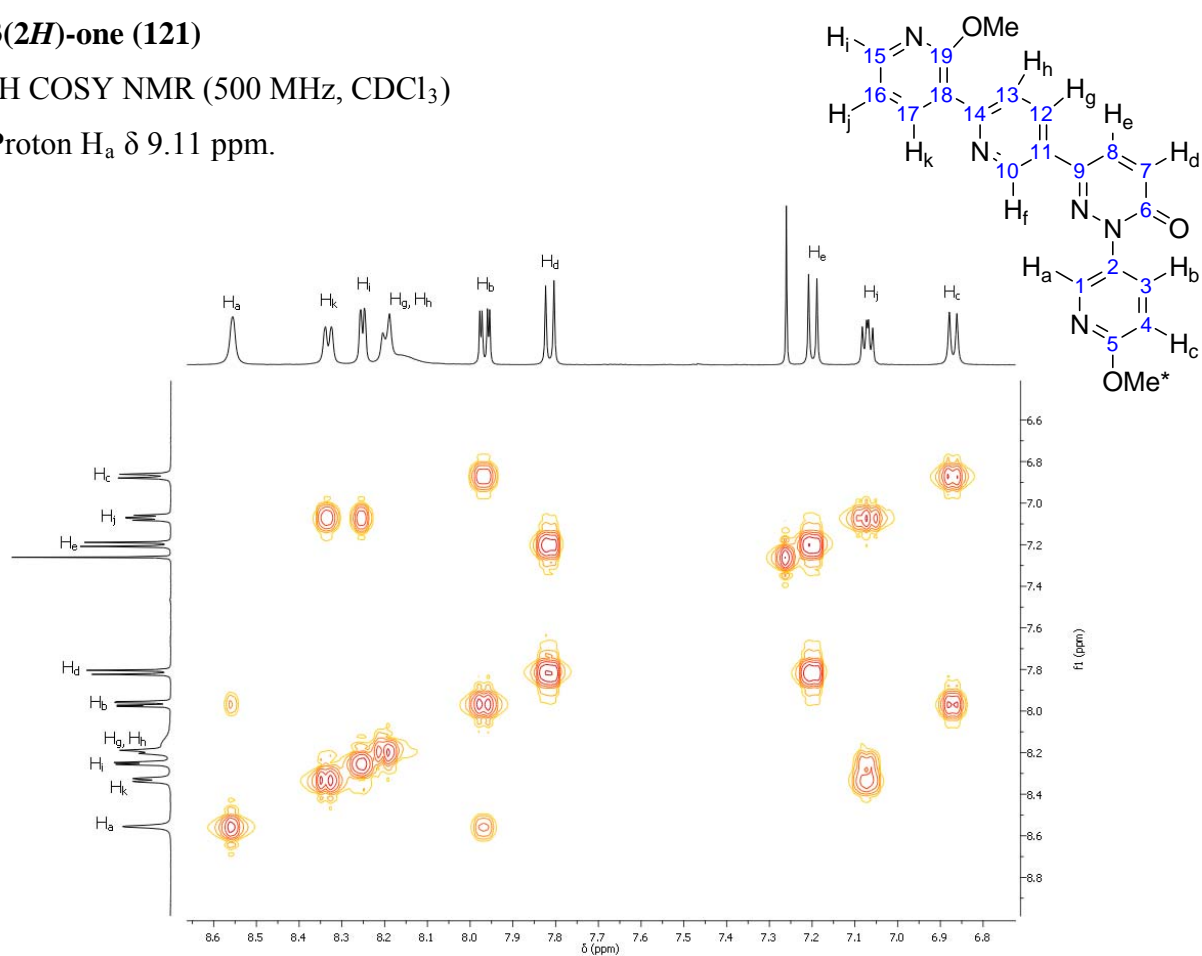
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )



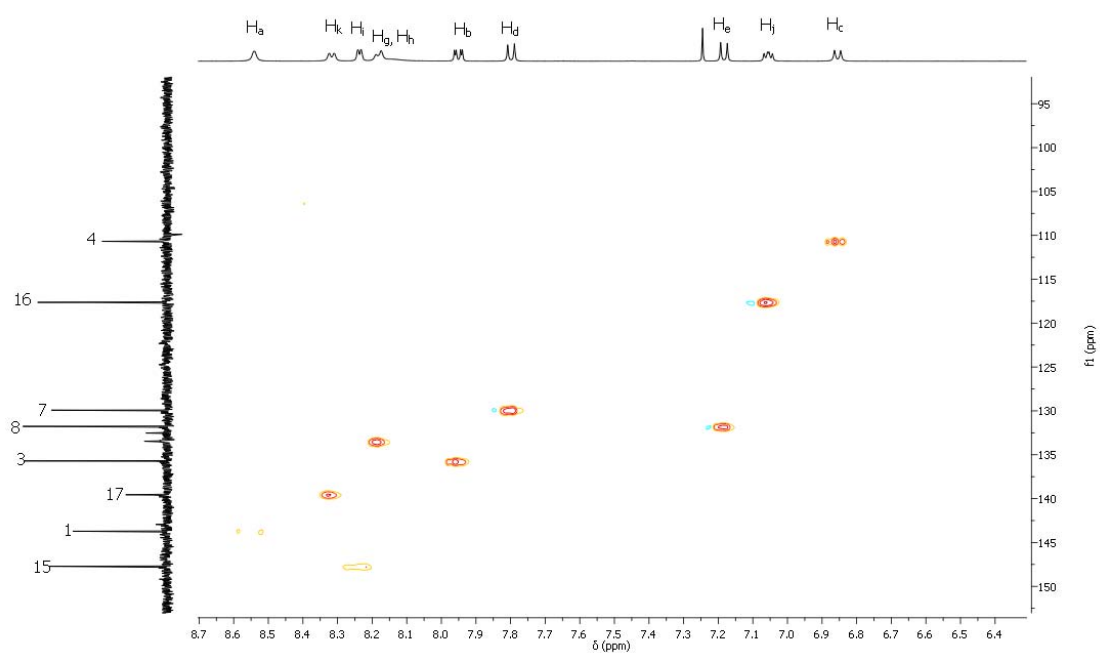
**2-(6-Methoxypyridin-3-yl)-6-(6-(2-methoxypyridin-3-yl)pyridin-3-yl)pyridazin-3(2H)-one (121)**

$^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ )

Proton  $\text{H}_a$   $\delta$  9.11 ppm.

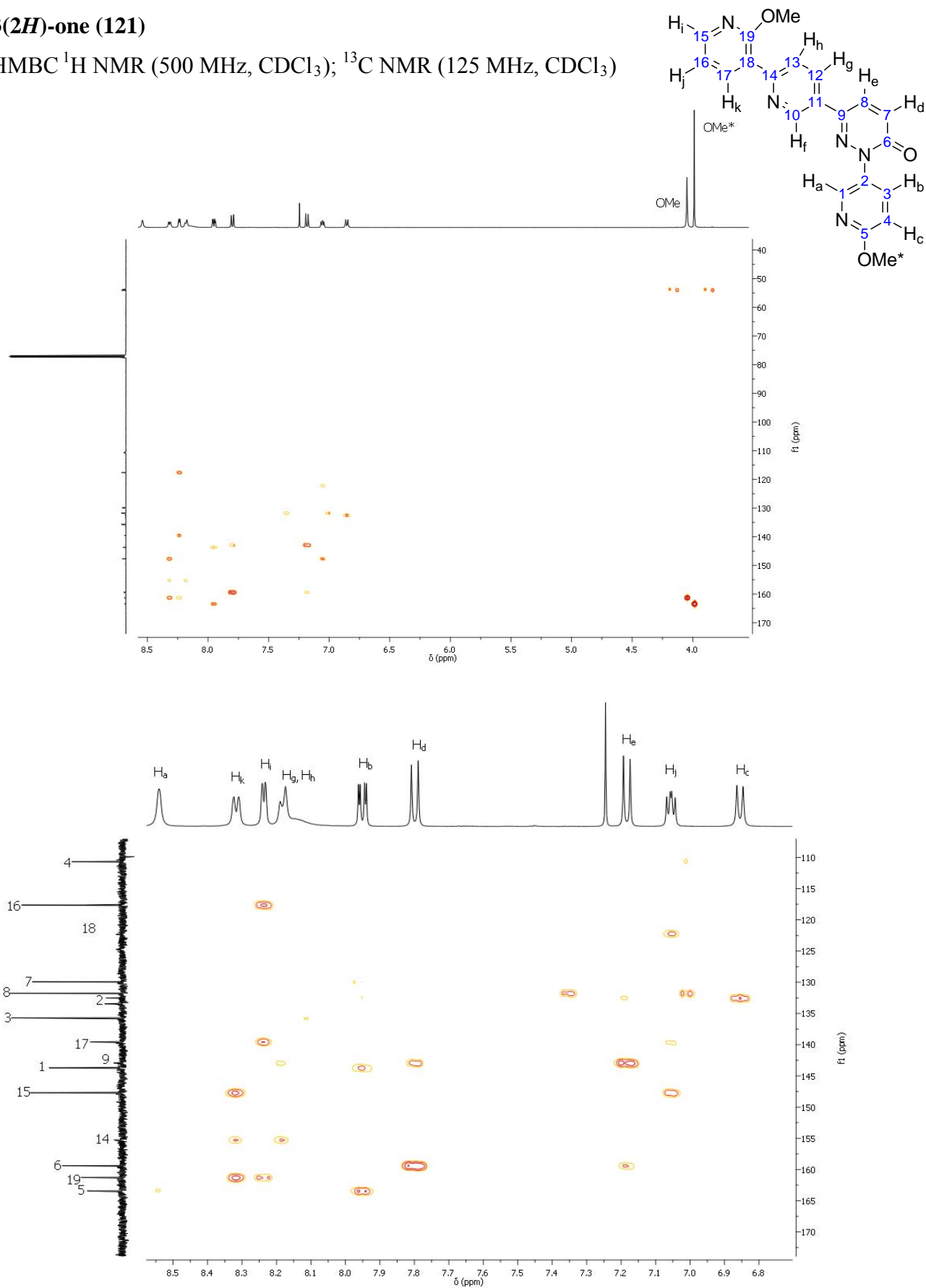


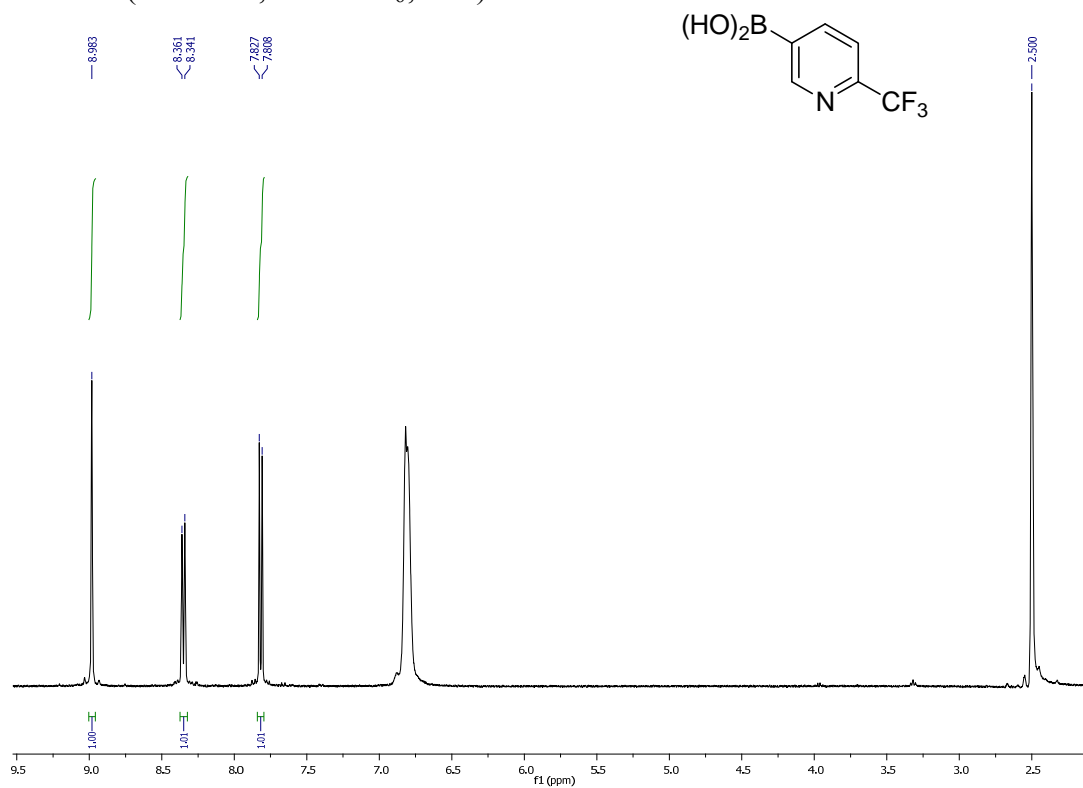
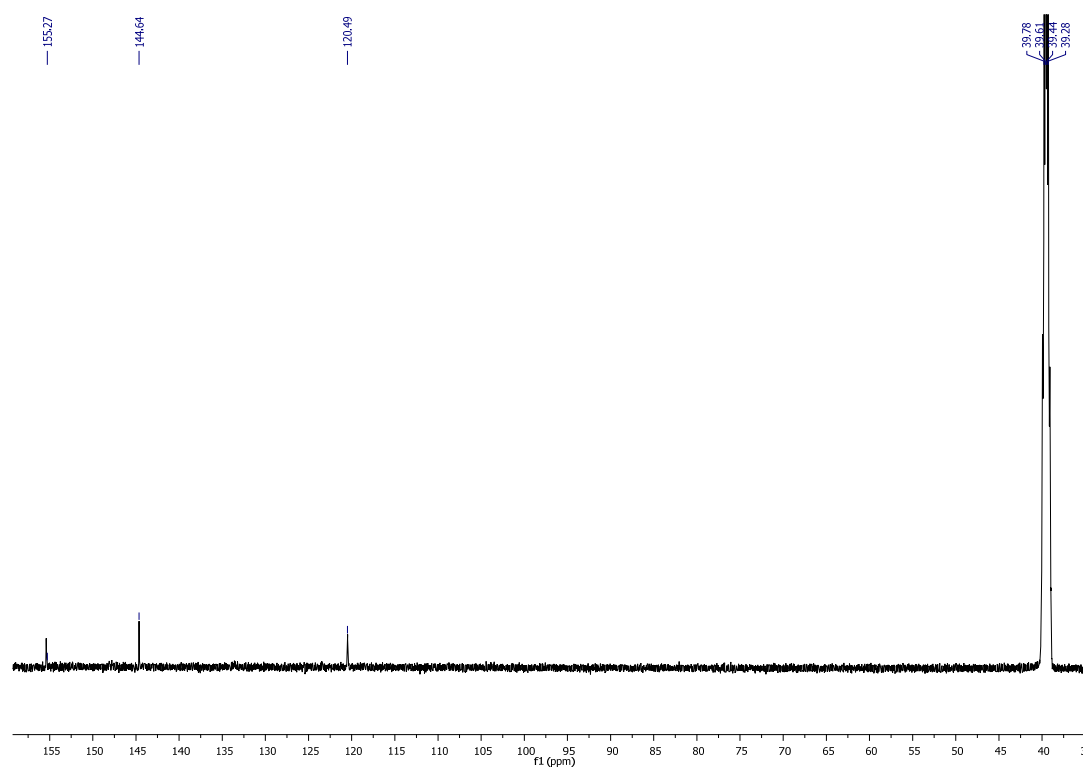
HSQC  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

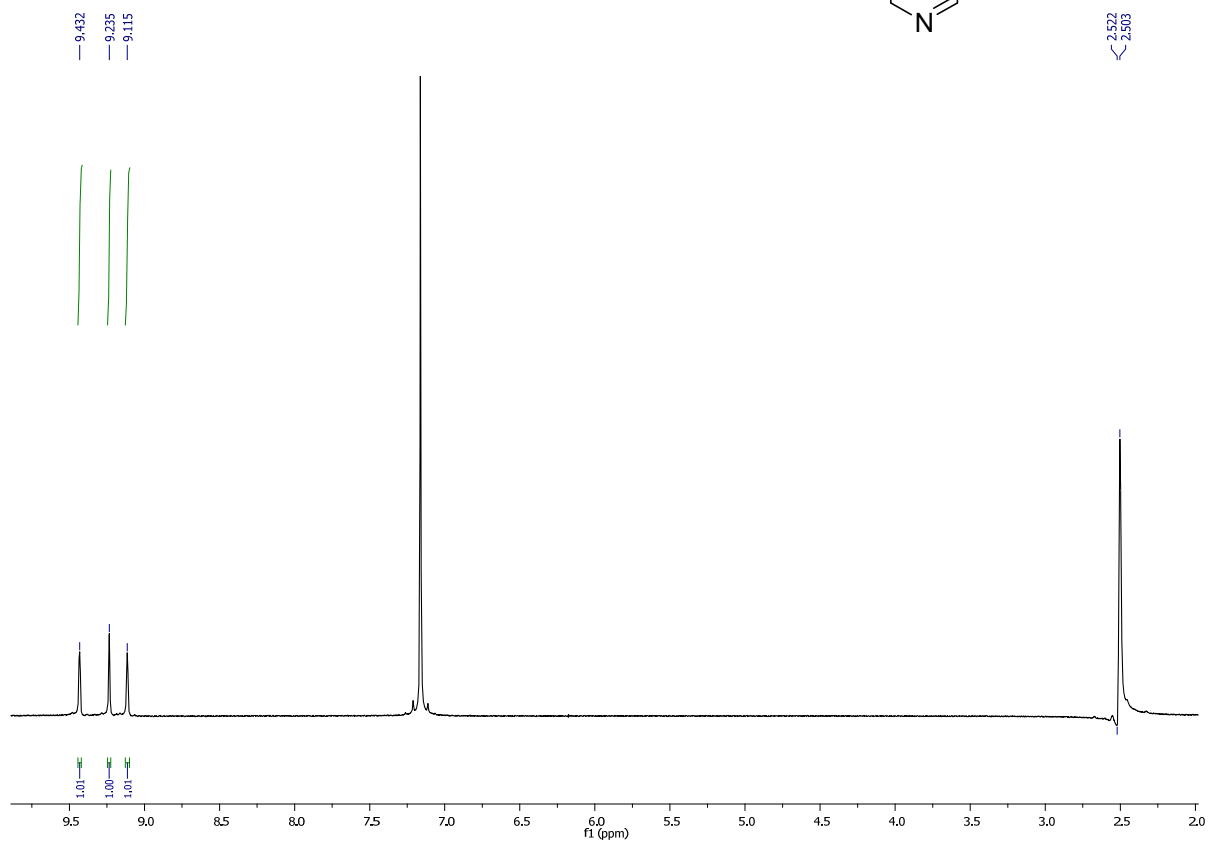
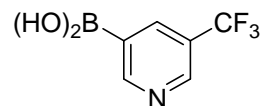
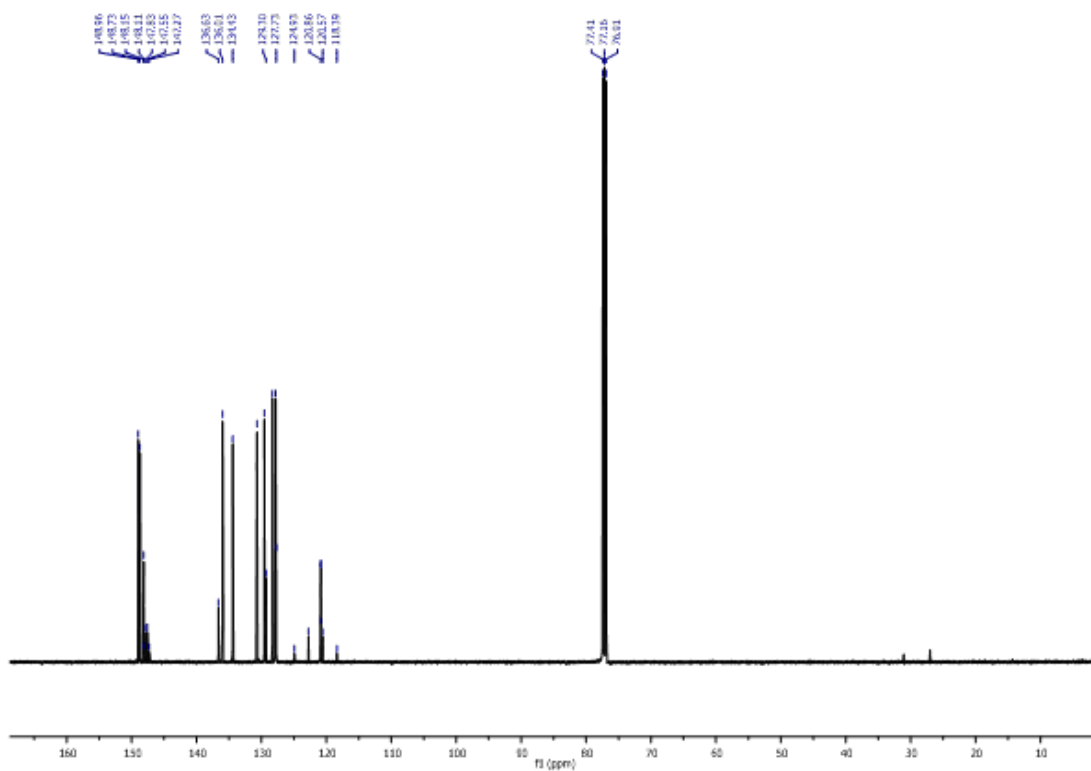


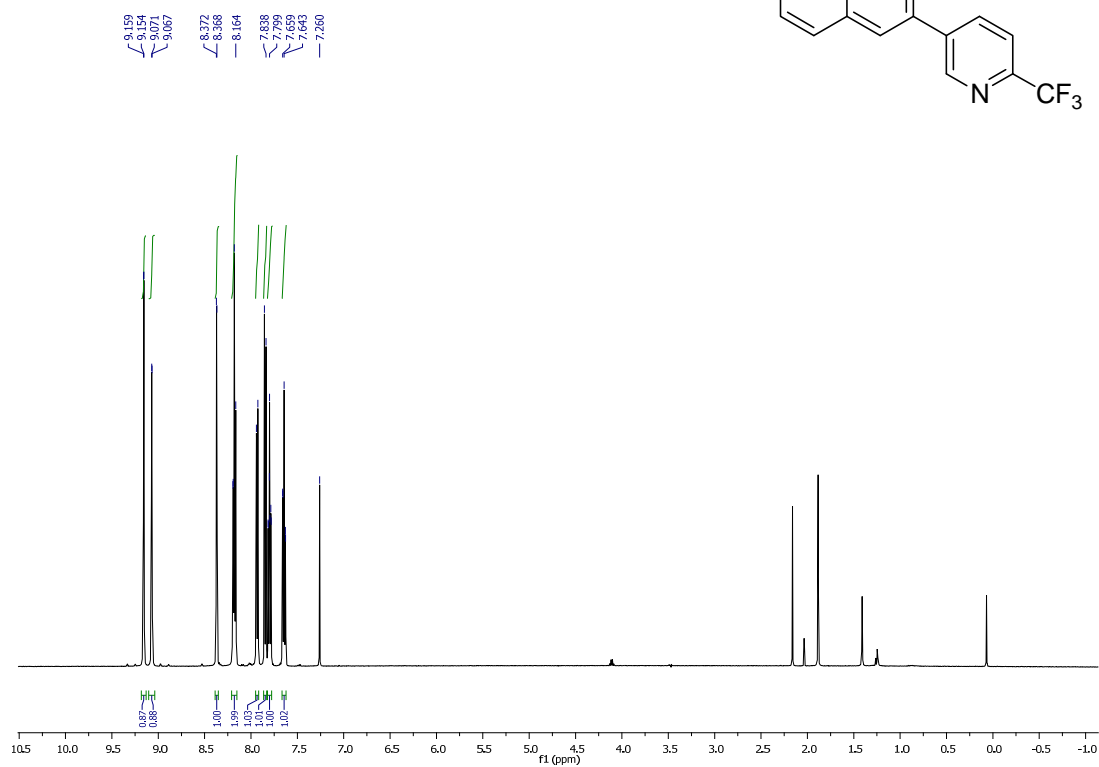
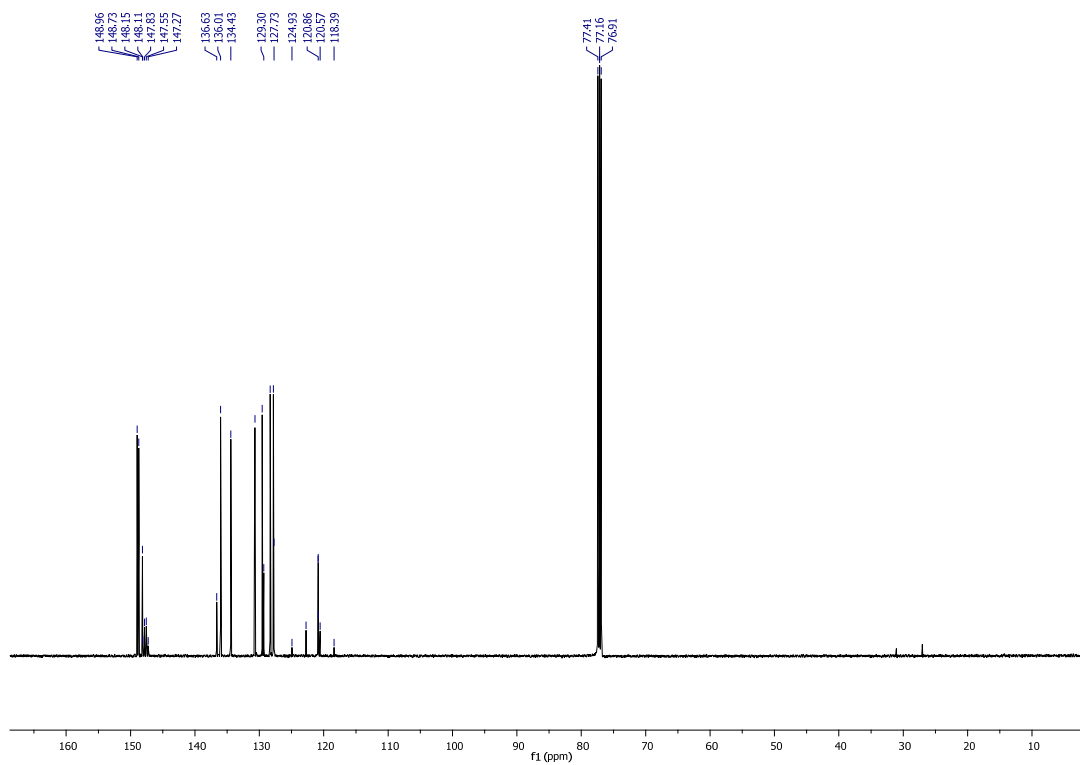
**2-(6-Methoxypyridin-3-yl)-6-(6-(2-methoxypyridin-3-yl)pyridin-3-yl)pyridazin-3(2H)-one (121)**

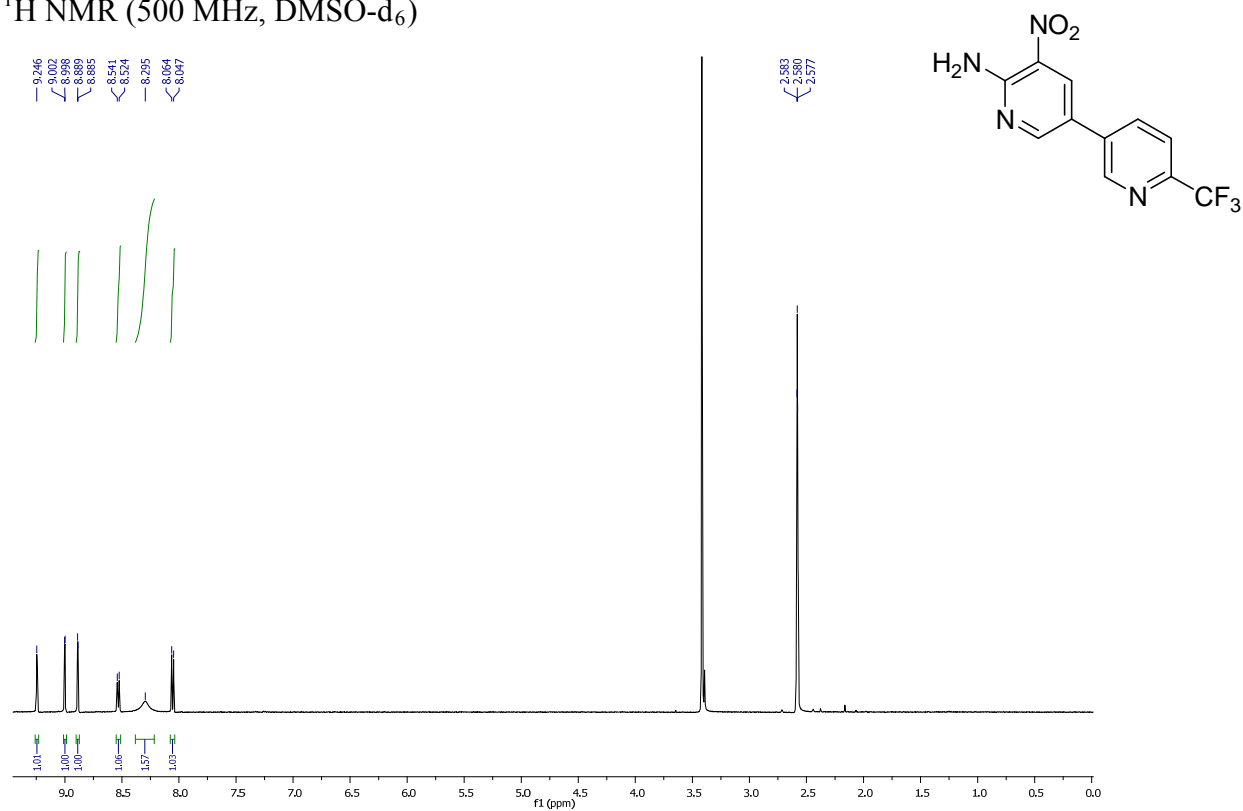
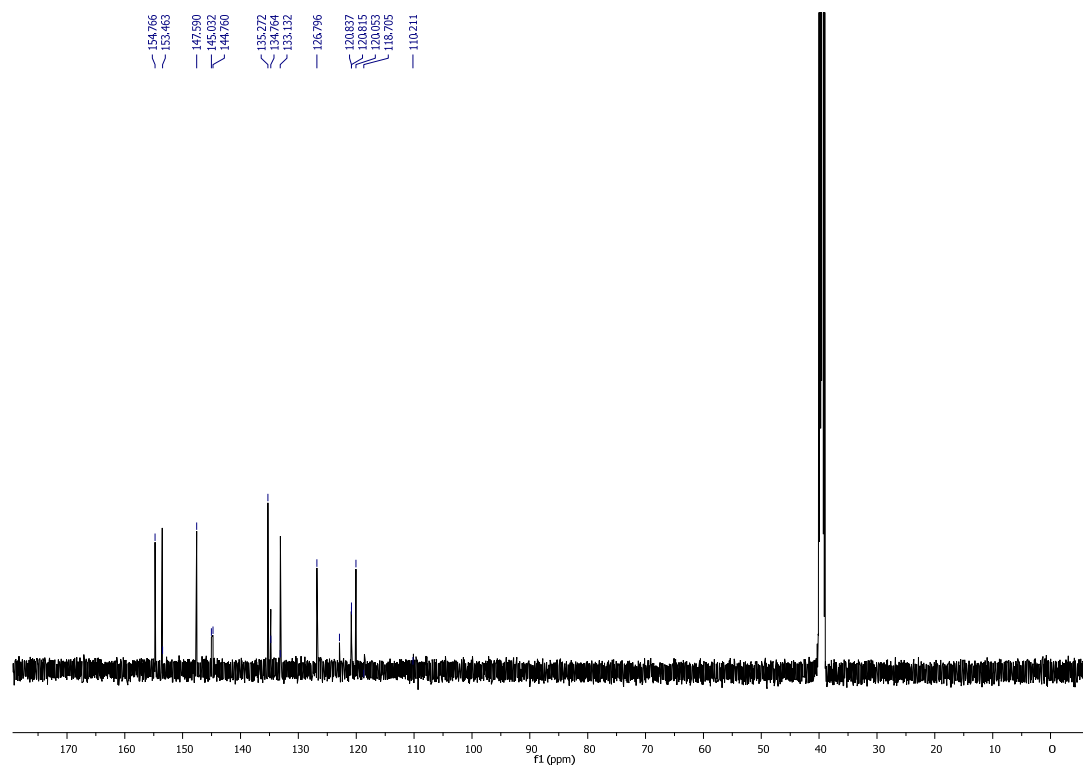
HMBC  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

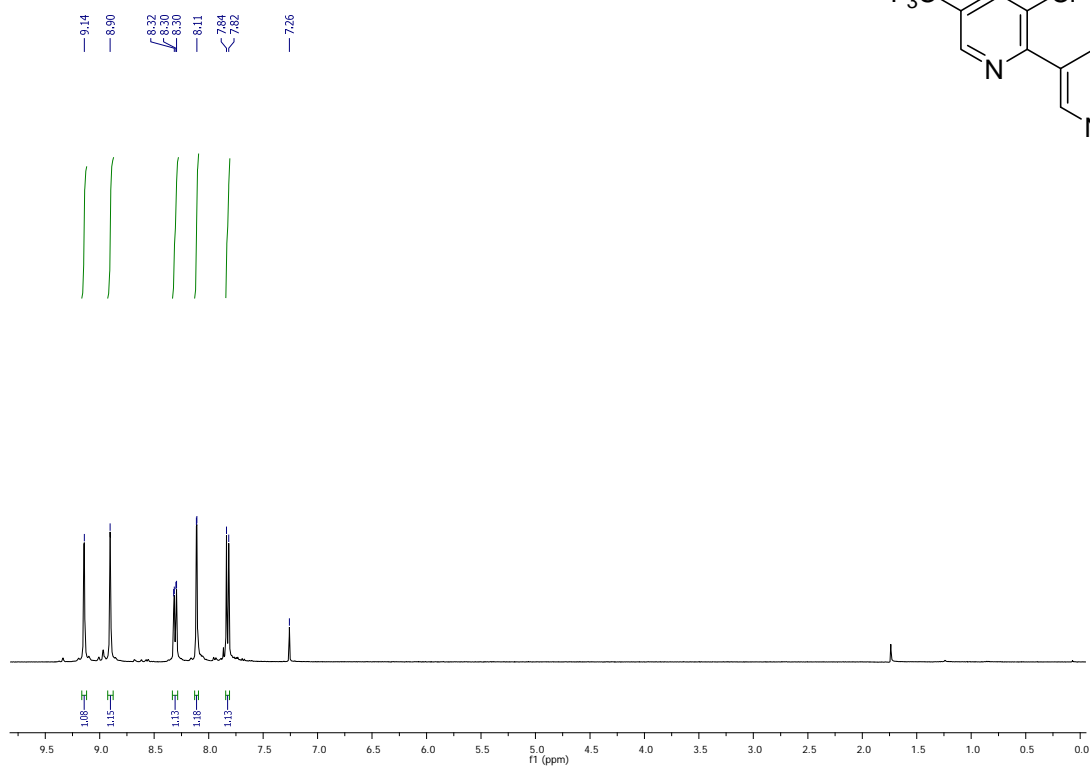
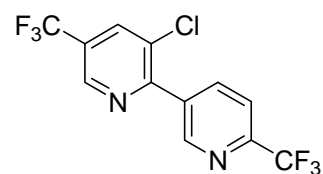
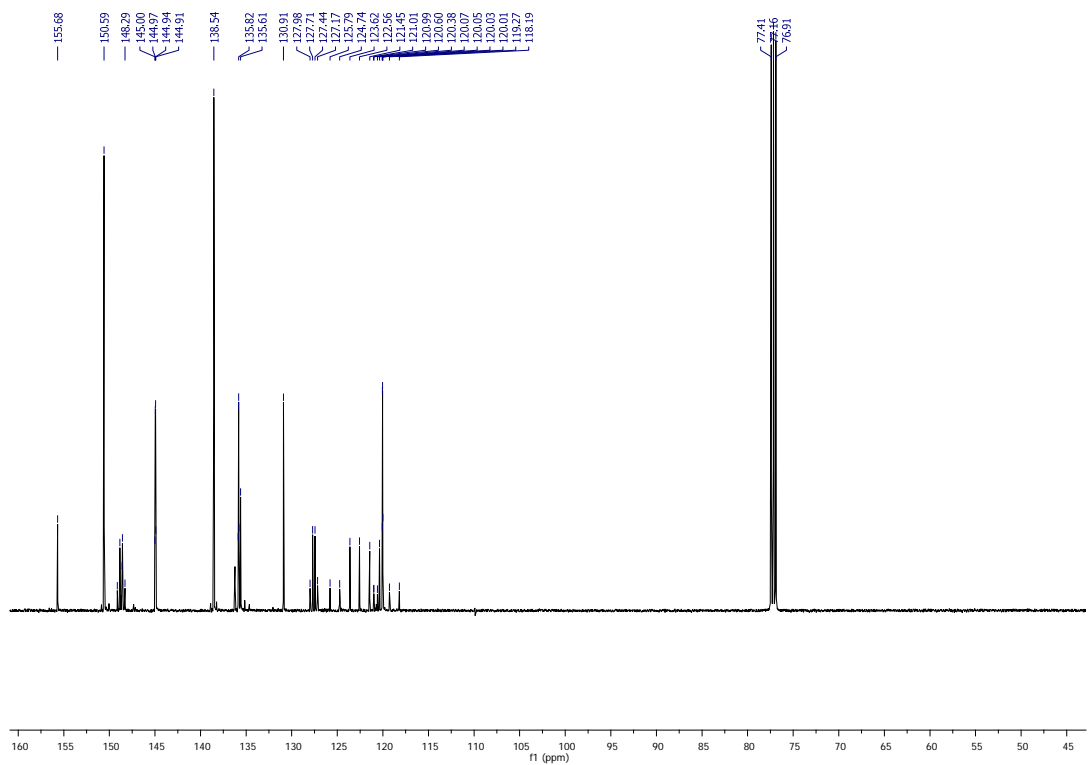


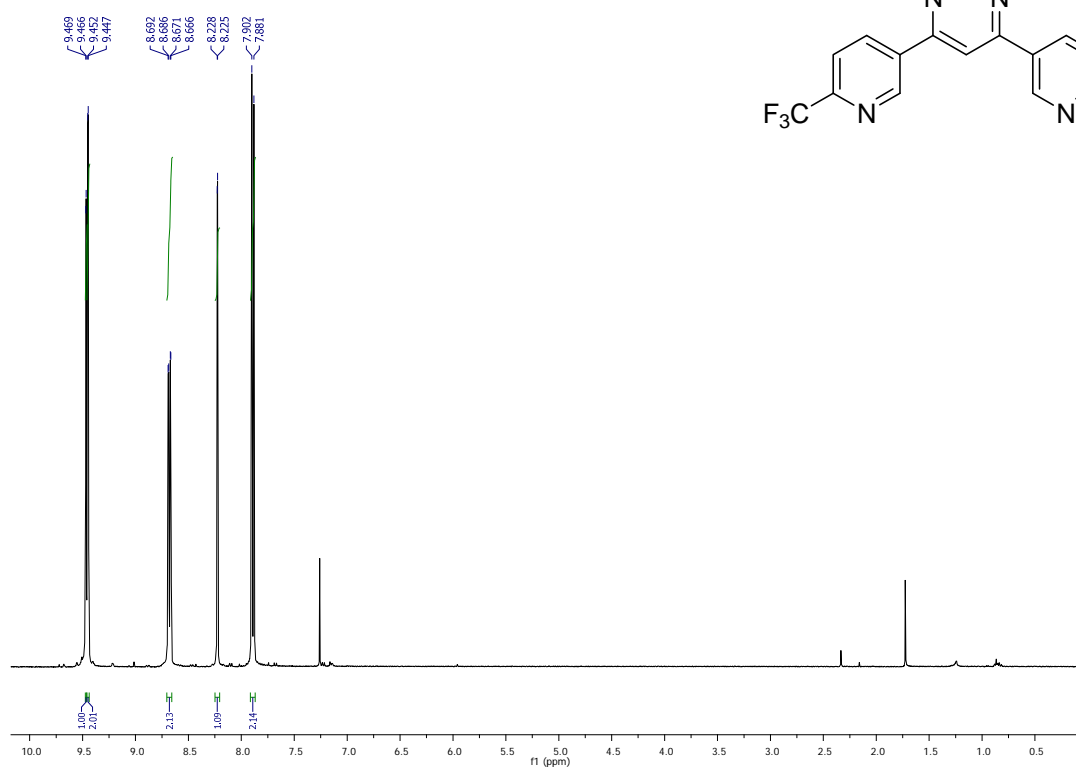
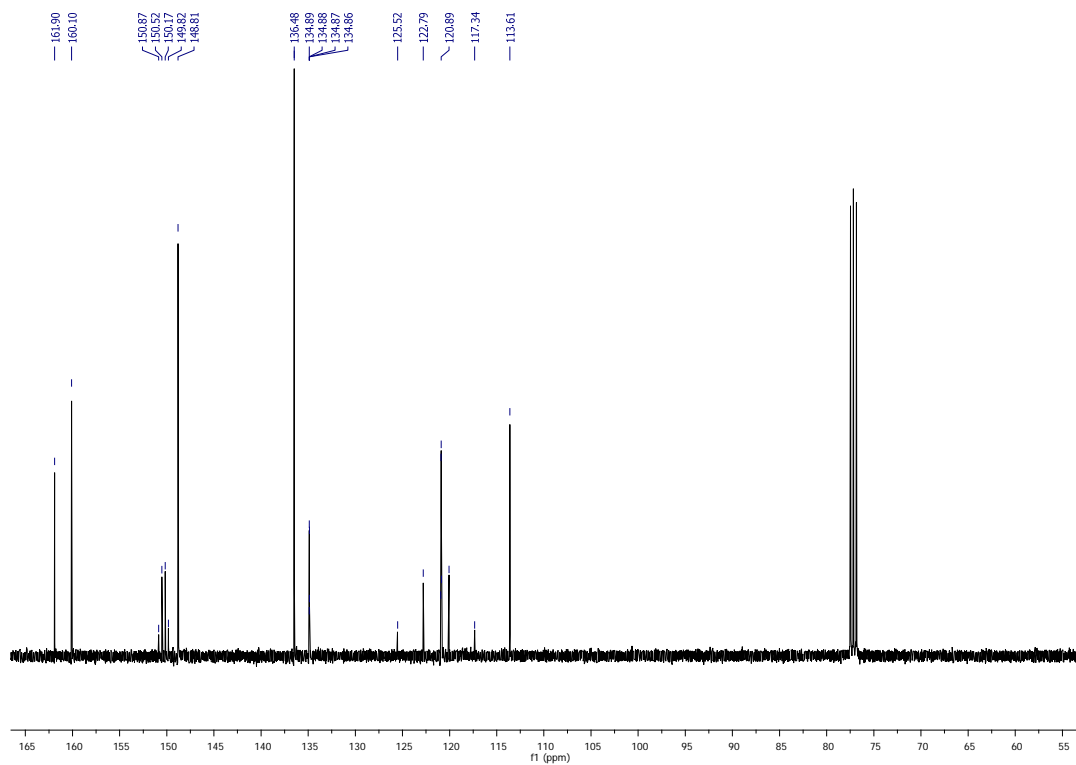
**A2.3 NMR spectra of compounds from Chapter 4****6-(Trifluoromethyl)-3-pyridylboronic acid (136)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, DCI)<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, DCI)

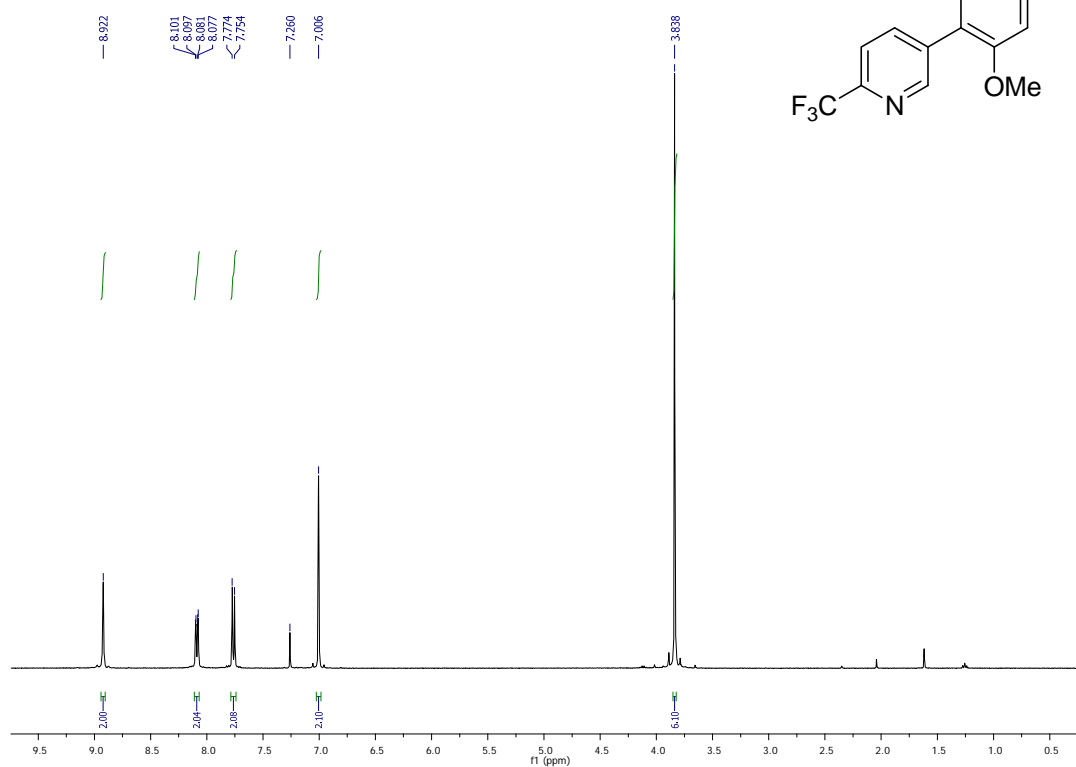
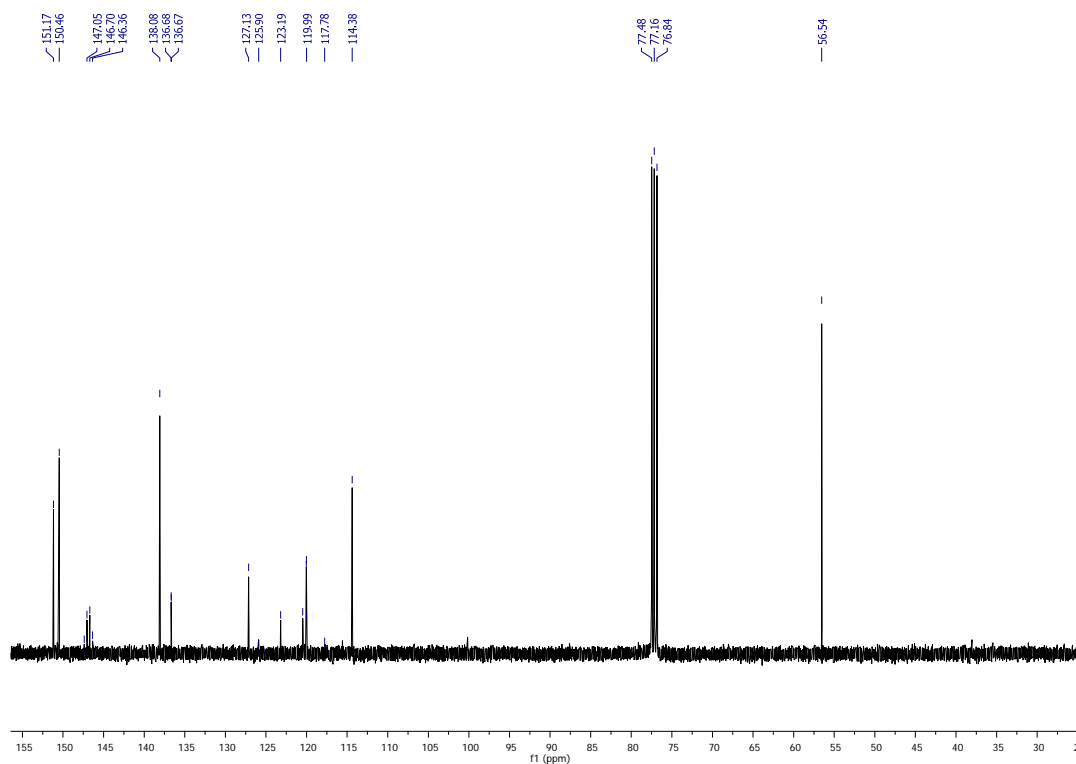
**5-(Trifluoromethyl)-3-pyridylboronic acid (137)** $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , DCl) $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ , DCl)

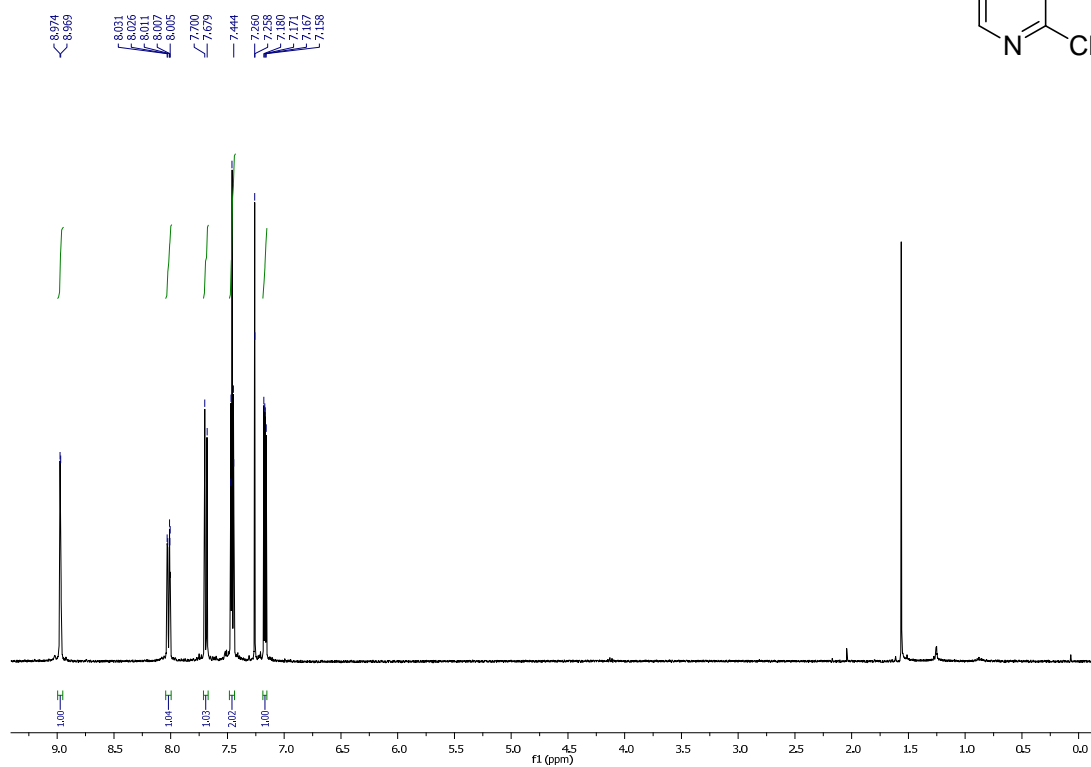
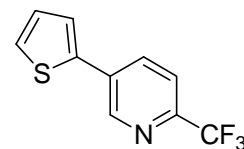
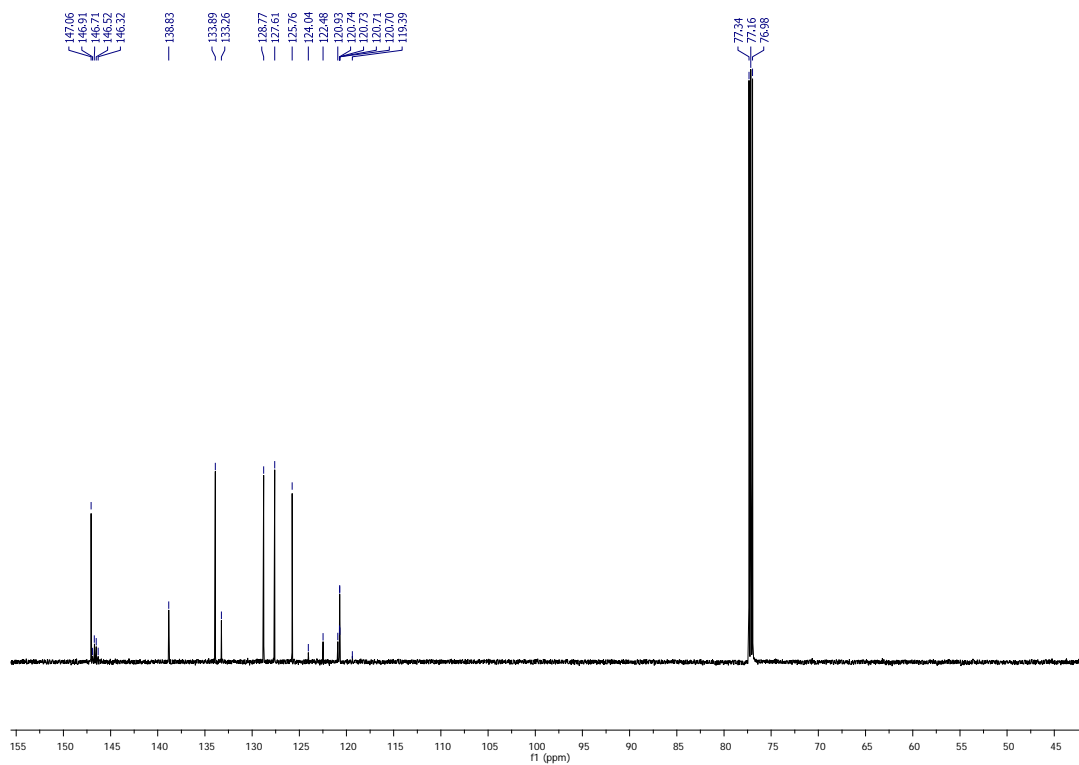
**3-[6-(Trifluoromethyl)pyridin-3-yl]quinoline (143)** $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

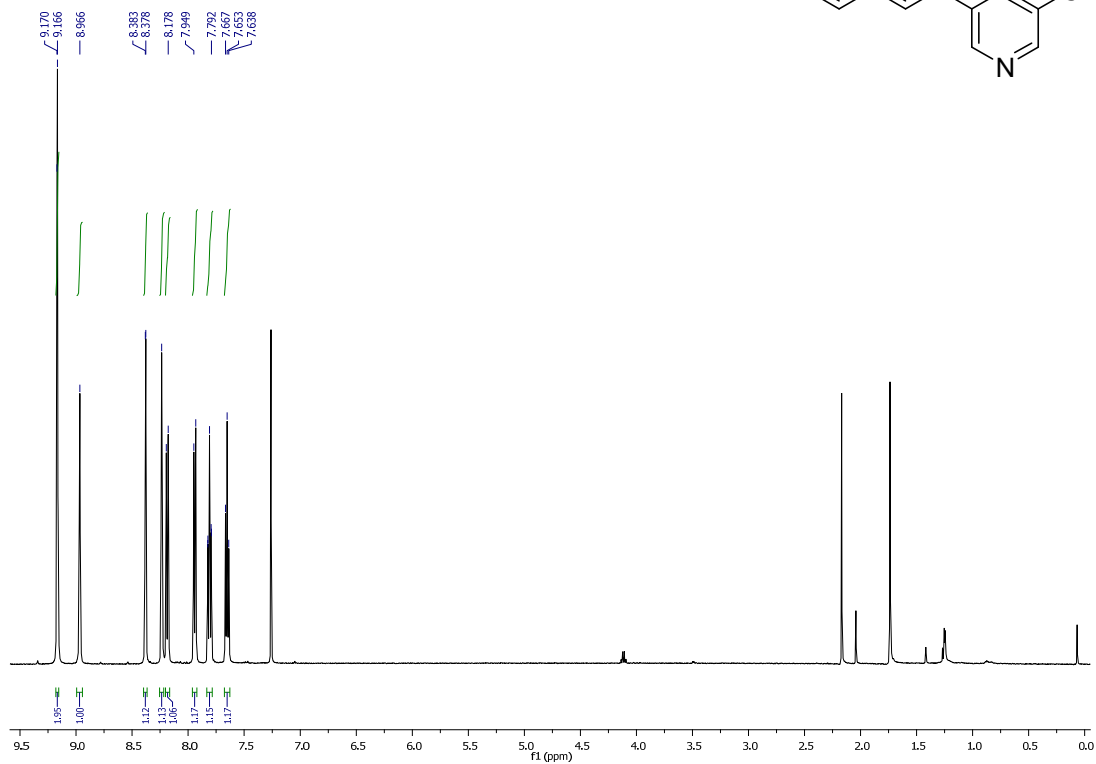
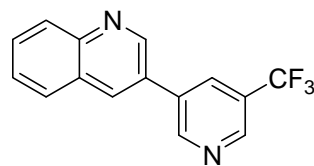
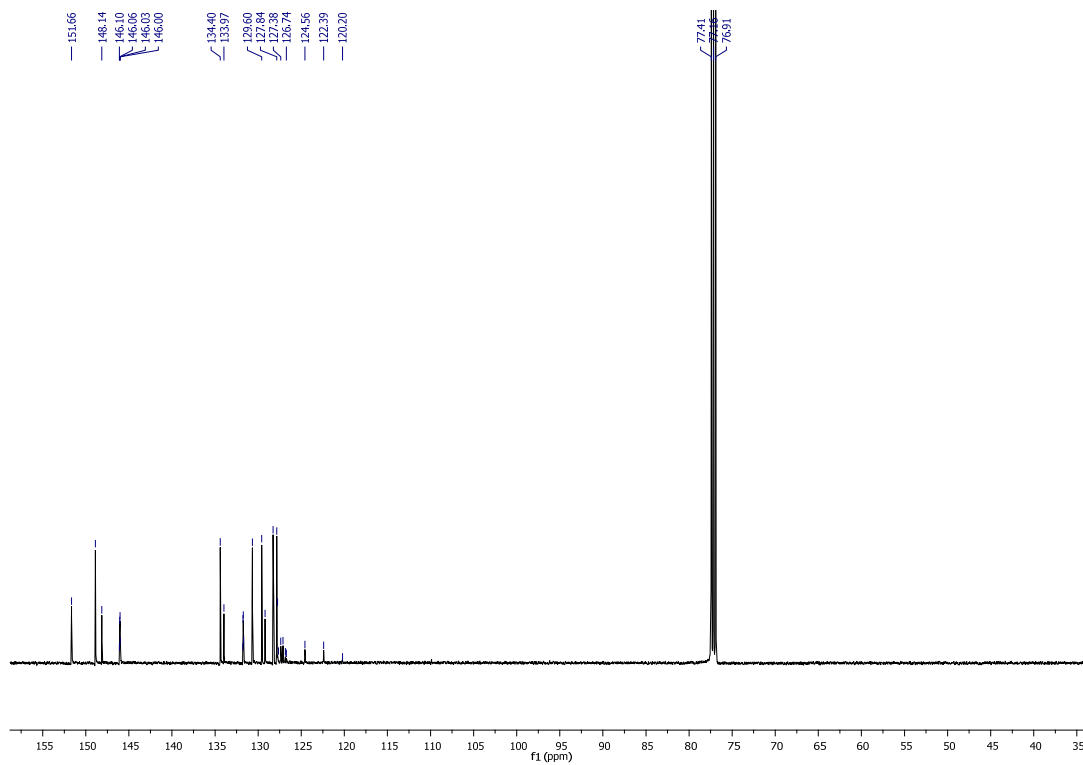
**5-[6-(Trifluoromethyl)pyridin-3-yl]-2-amino-3-nitropyridine (144)**<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)

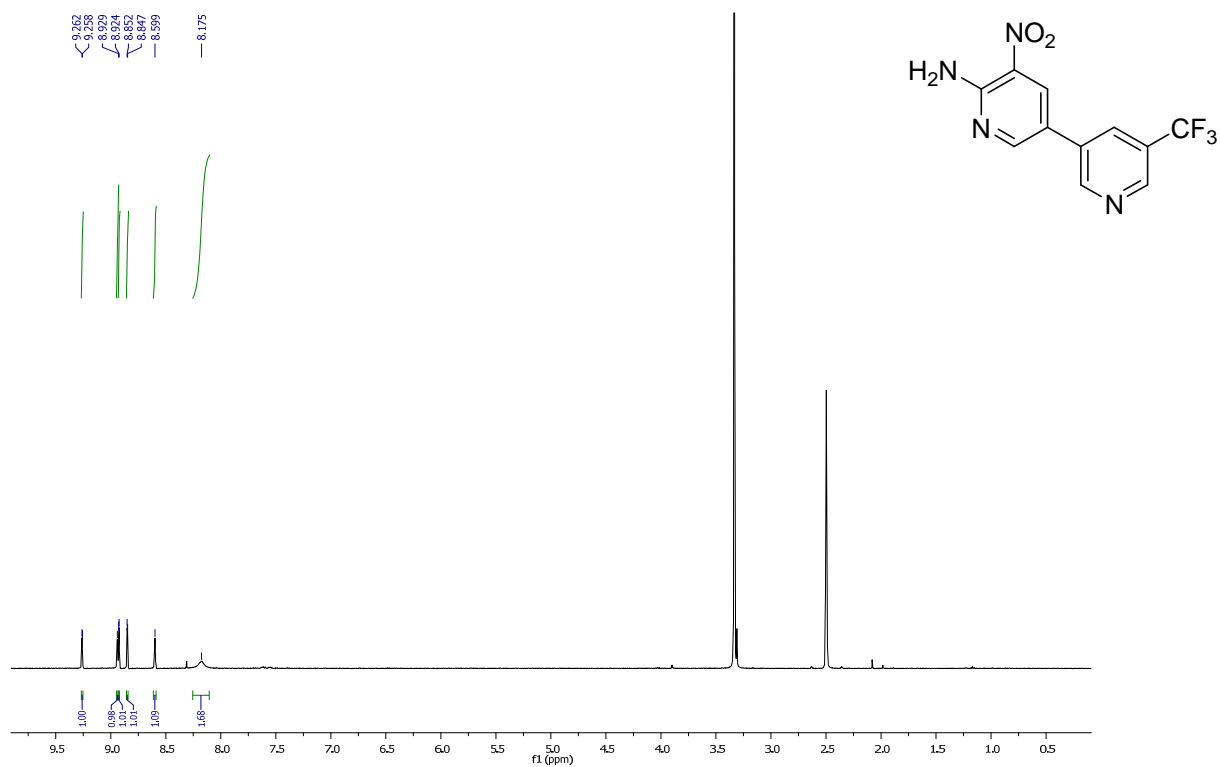
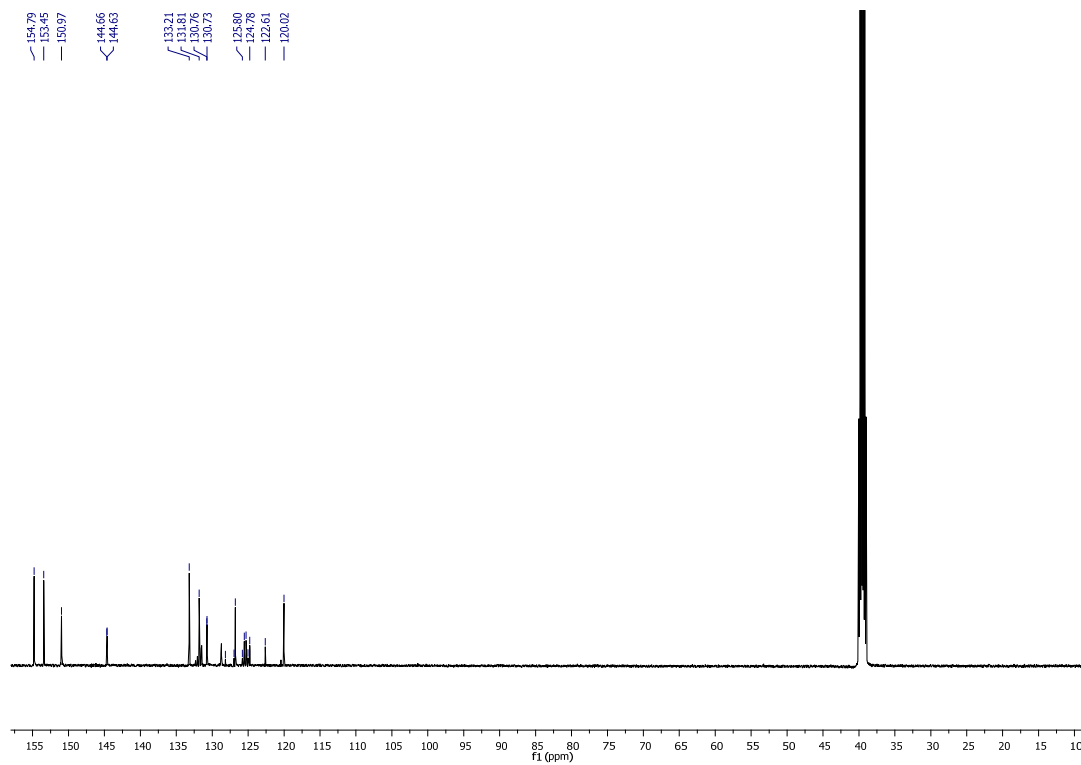
**3-Chloro-5-(trifluoromethyl)-2-[6-(trifluoromethyl)pyridin-3-yl]pyridine (145)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

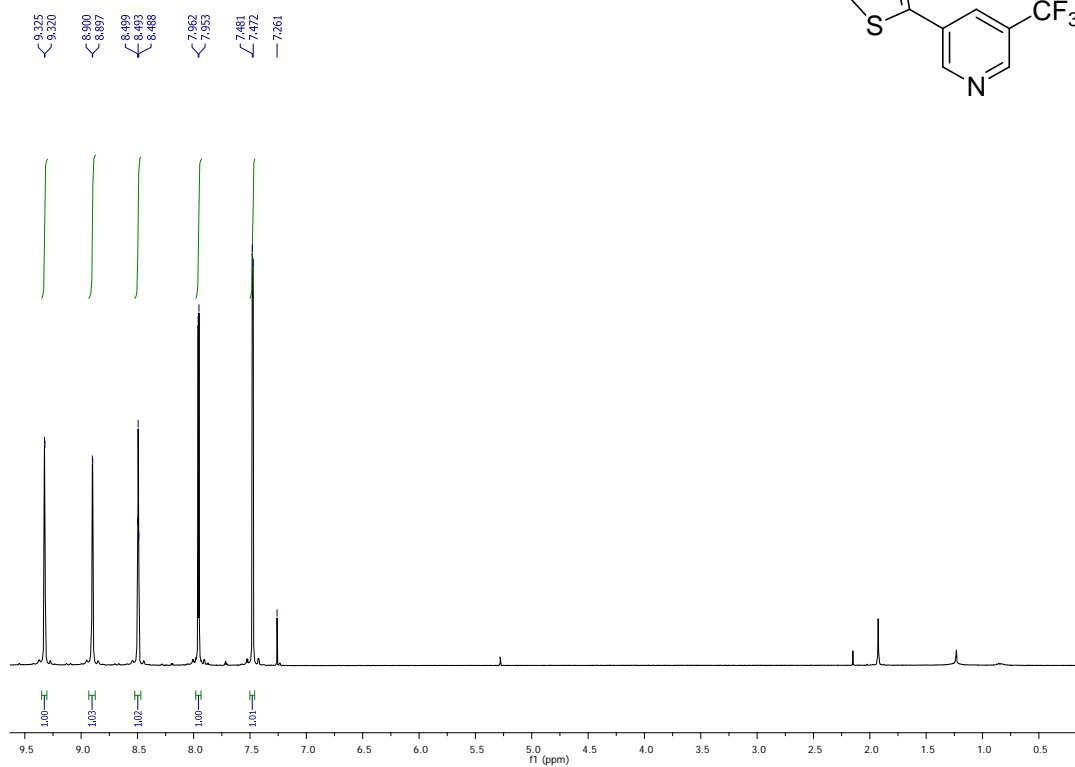
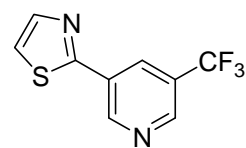
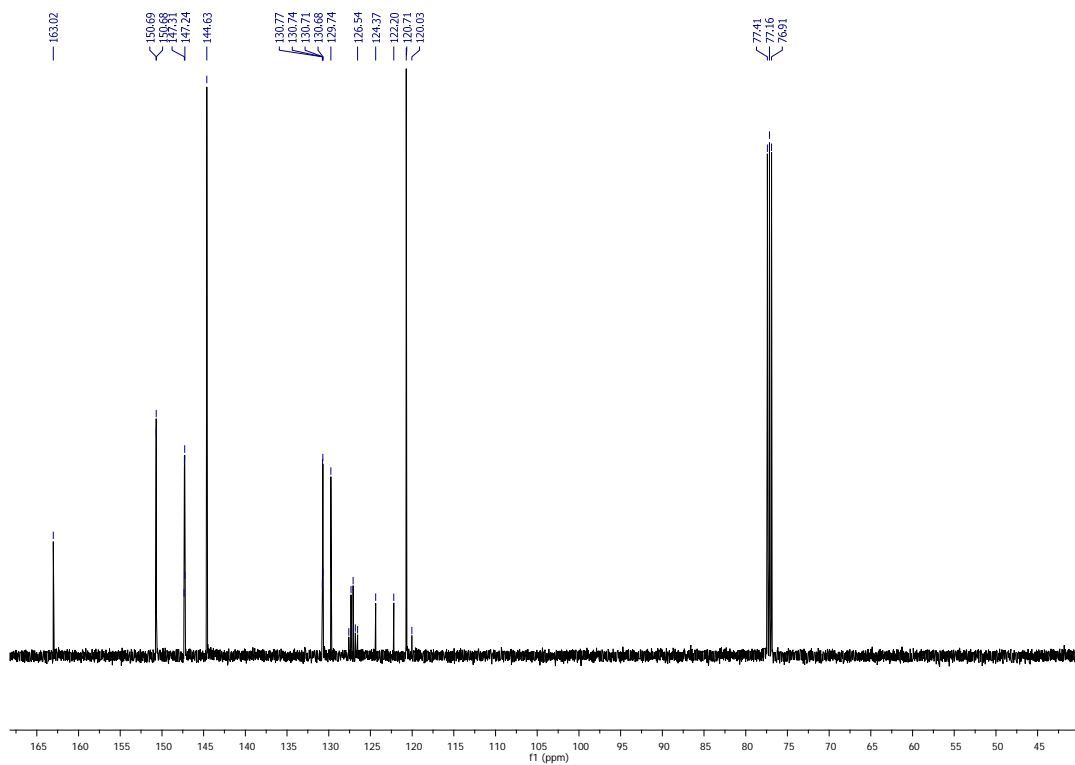
**4,6-Bis[6-(trifluoromethyl)pyridin-3-yl]pyrimidine (146)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

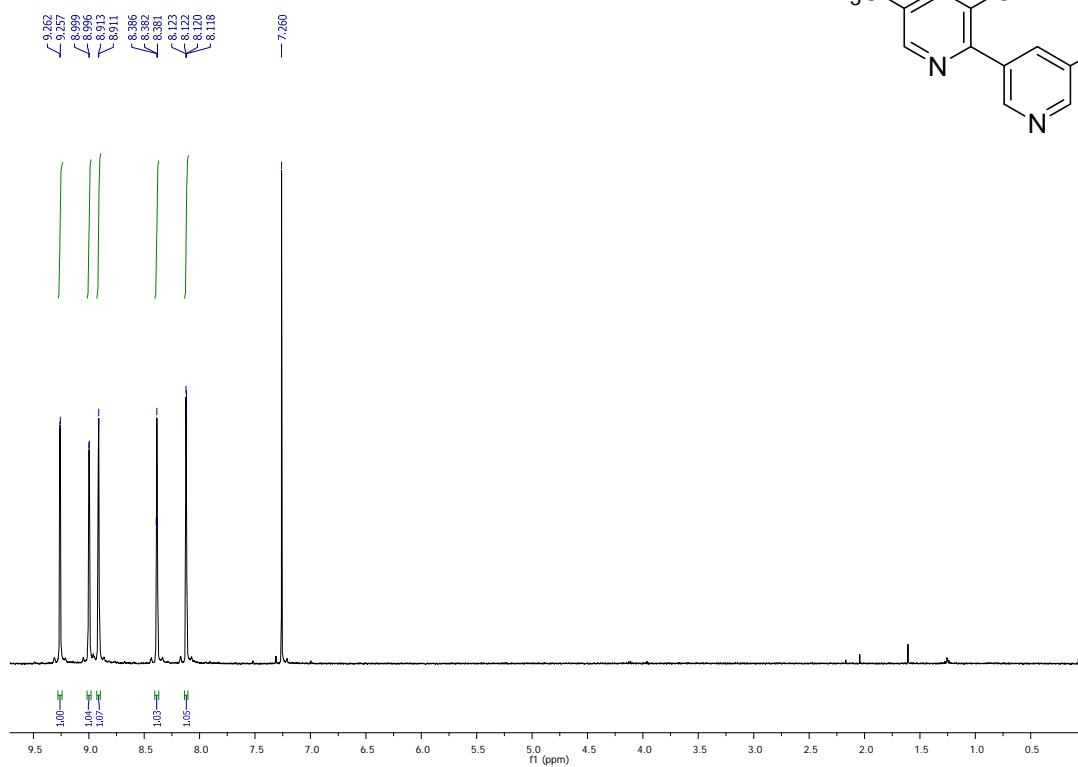
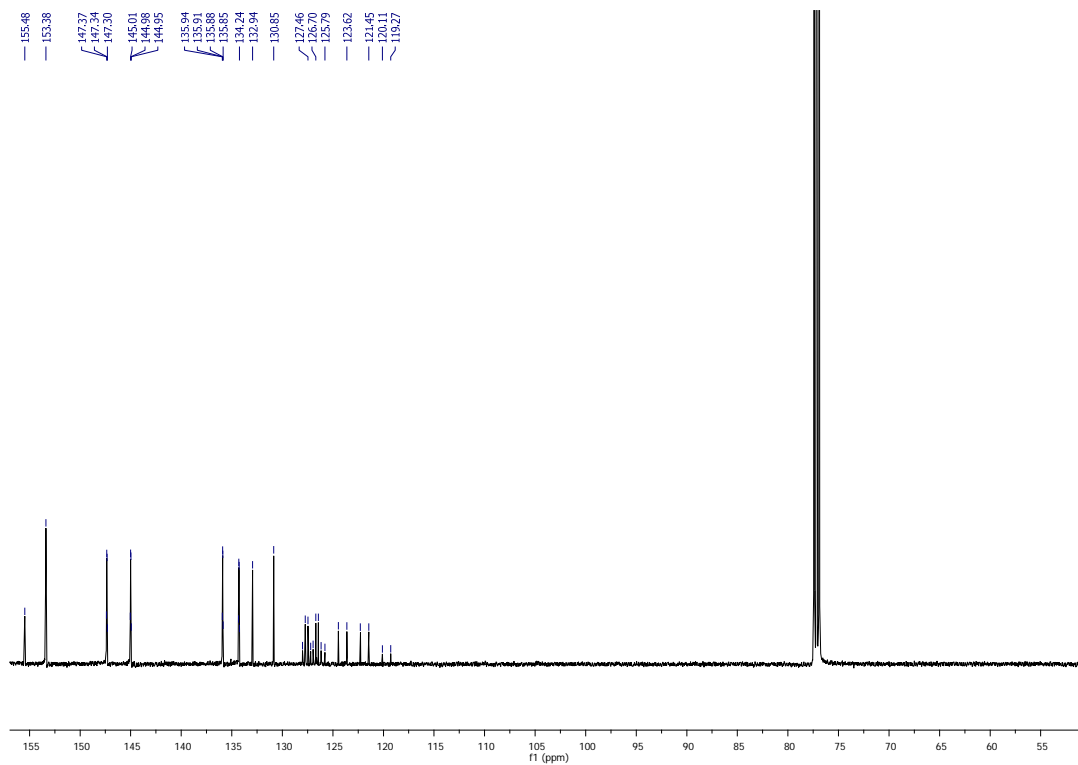
**2-(Trifluoromethyl)-5-[4-(6-(trifluoromethyl)pyridin-3-yl)-2,5-dimethoxyphenyl]pyridine (147)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

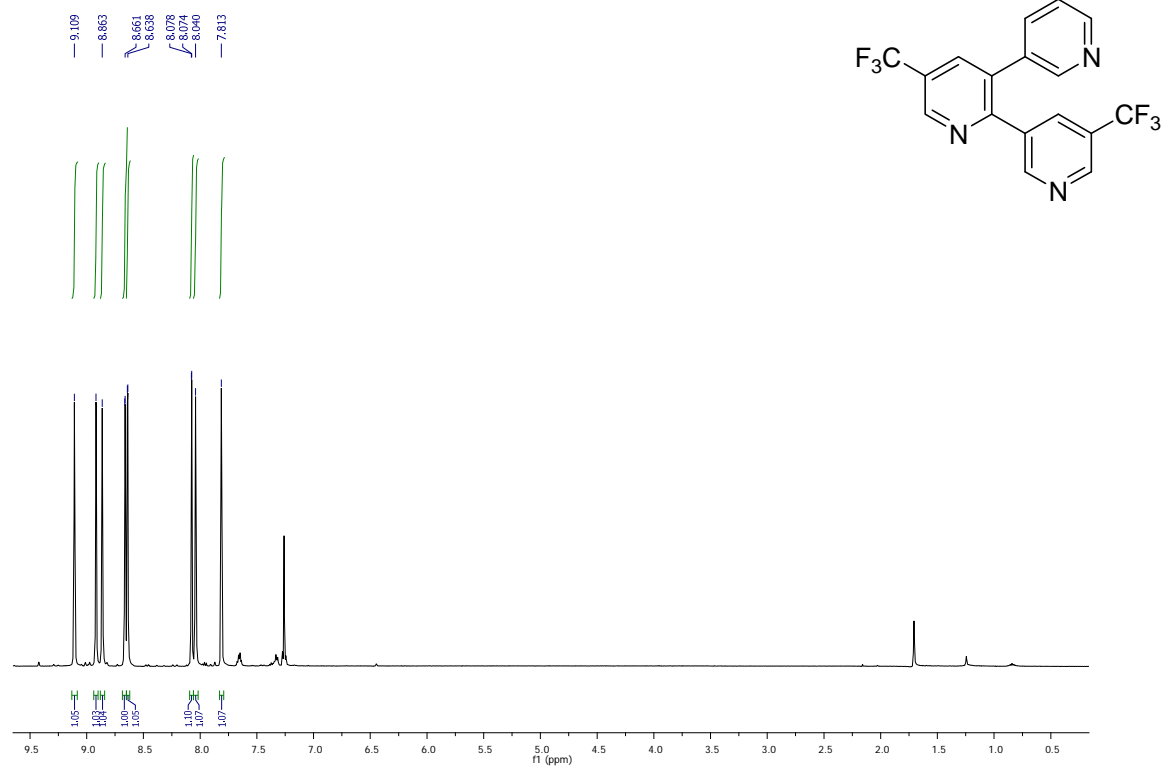
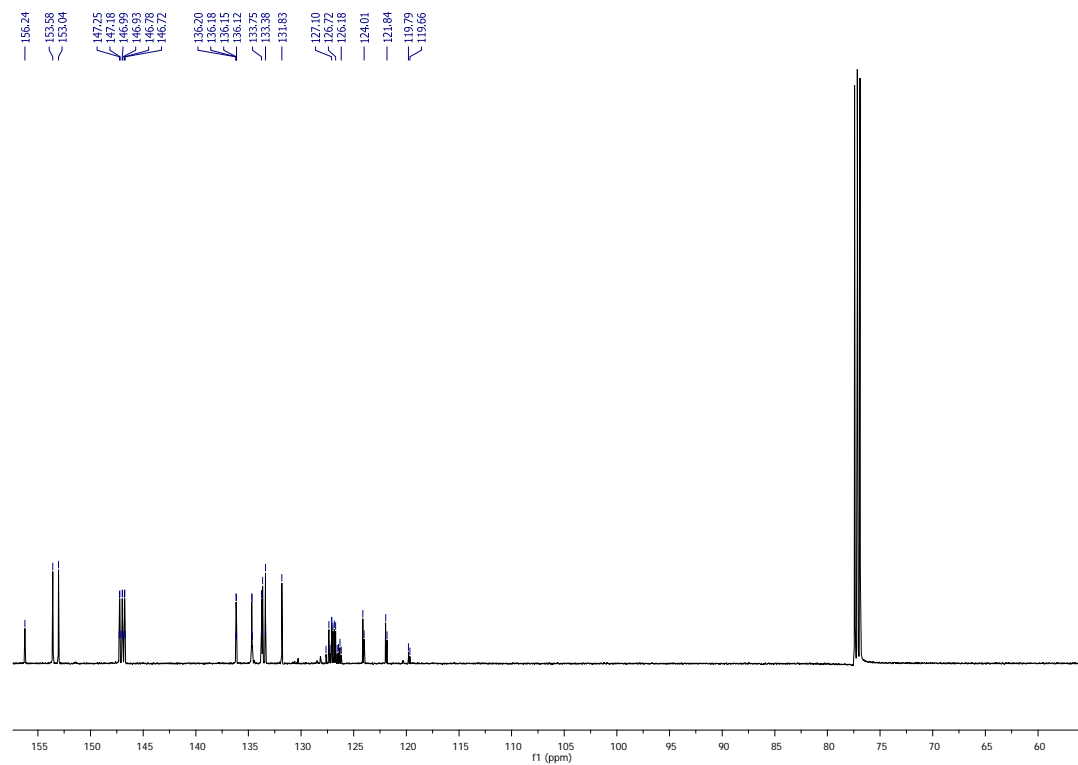
**2-(Trifluoromethyl)-5-(thiophen-2-yl)pyridine (148)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>)

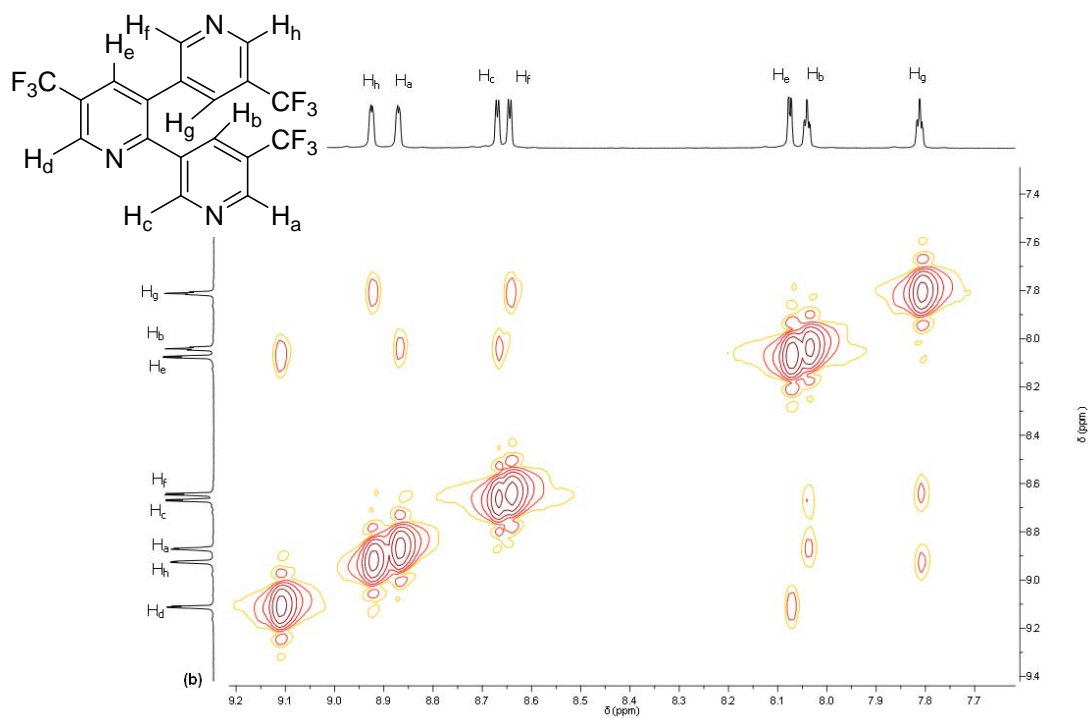
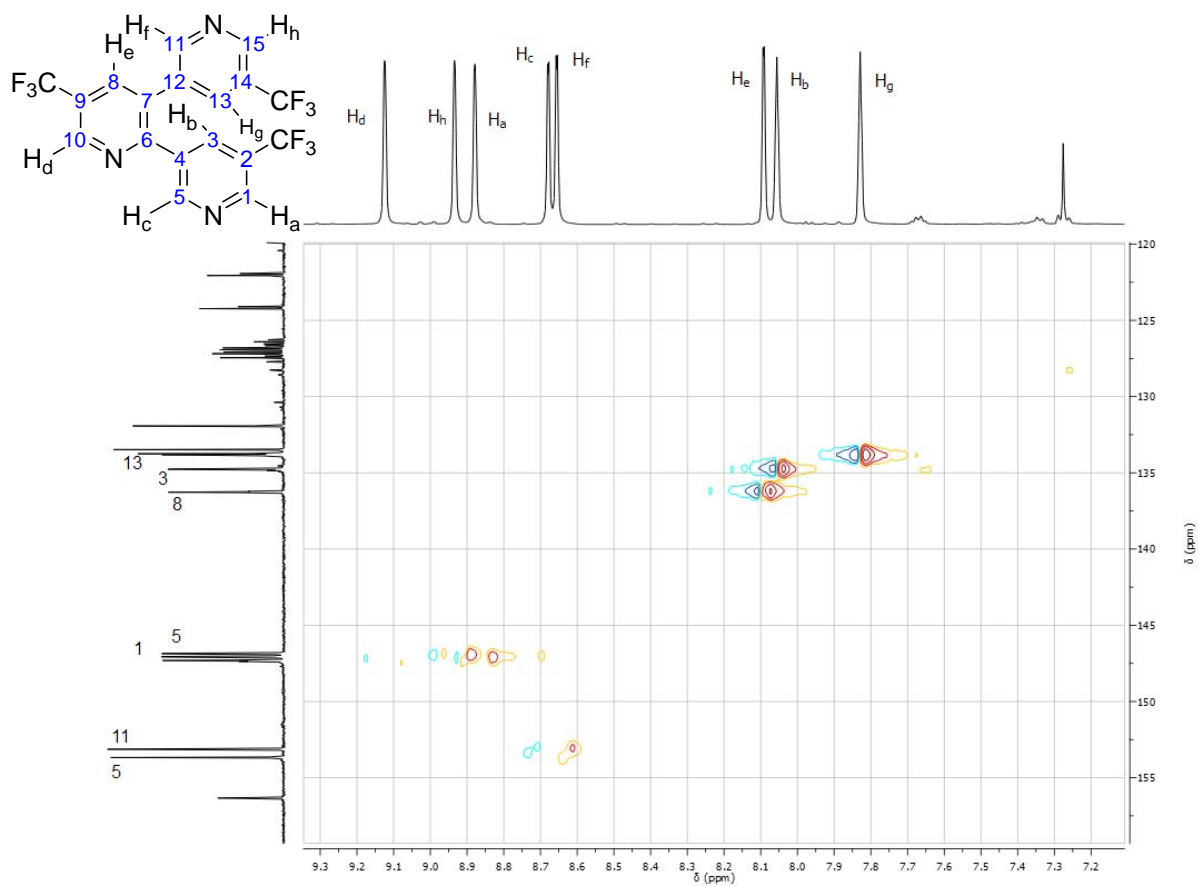
**3-[5-(Trifluoromethyl)pyridin-3-yl]quinoline (149)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

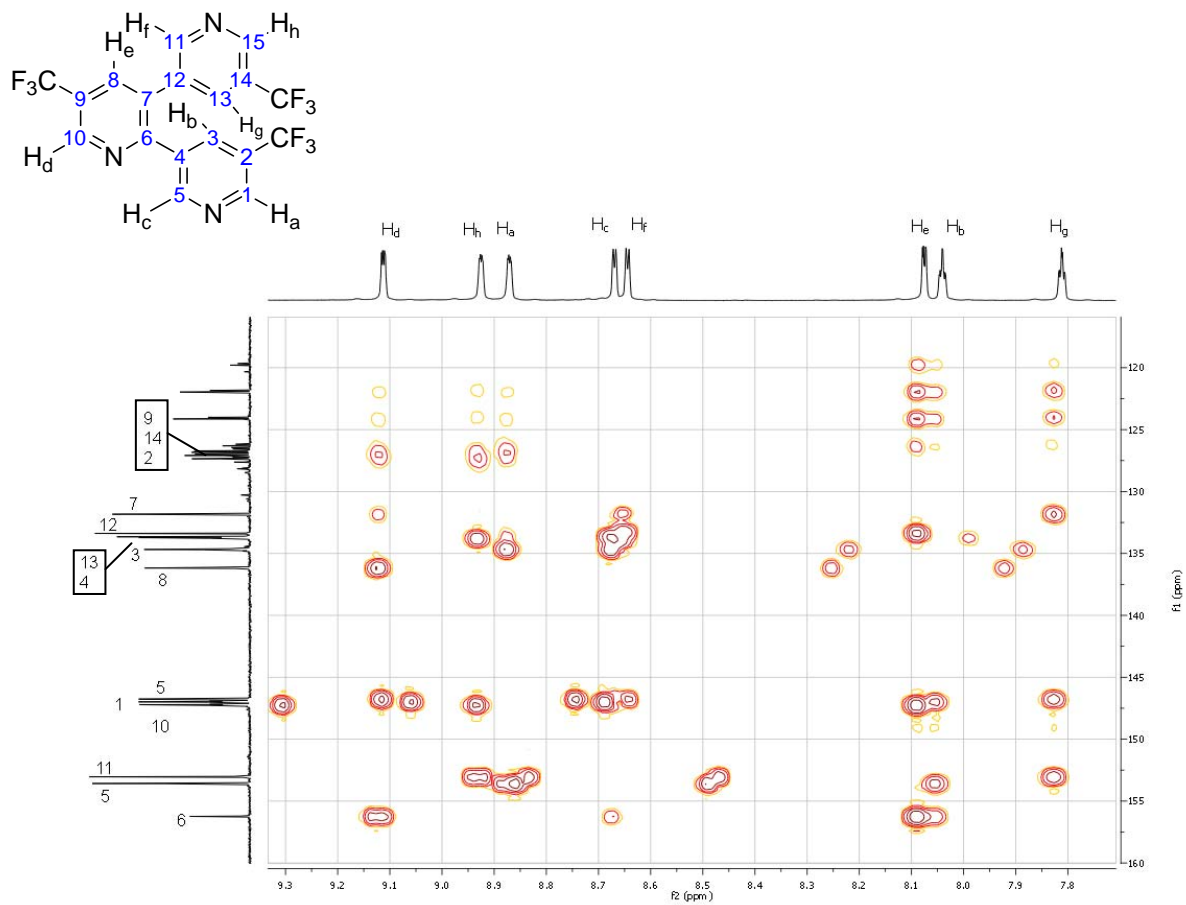
**5-[5-(Trifluoromethyl)pyridin-3-yl]-2-amino-3-nitropyridine (150)**<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)

**3-(Trifluoromethyl)-5-(thiazol-2-yl)pyridine (151)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

**3-Chloro-5-(trifluoromethyl)-2-[5-(trifluoromethyl)pyridin-3-yl]pyridine (152)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

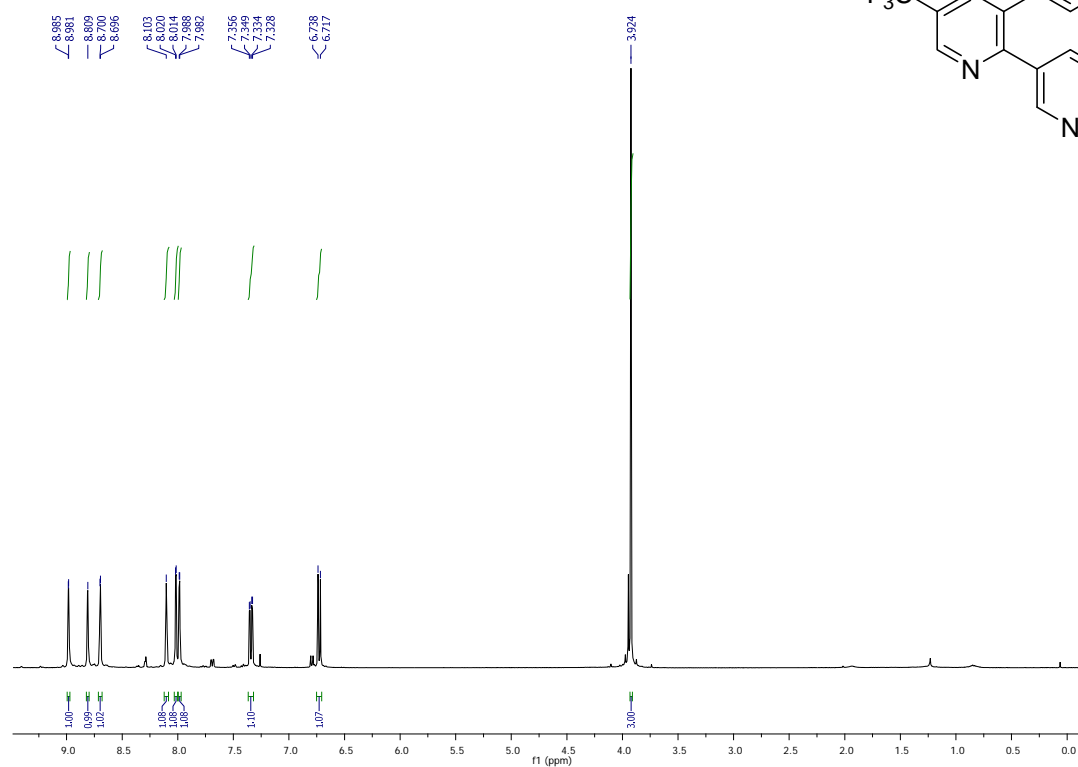
**5-(Trifluoromethyl)-2,3-bis[5-(trifluoromethyl)pyridin-3-yl]pyridine (153)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

**5-(Trifluoromethyl)-2,3-bis[5-(trifluoromethyl)pyridin-3-yl]pyridine (153)**<sup>1</sup>H COSY NMR (400 MHz, CDCl<sub>3</sub>)HSQC spectrum <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

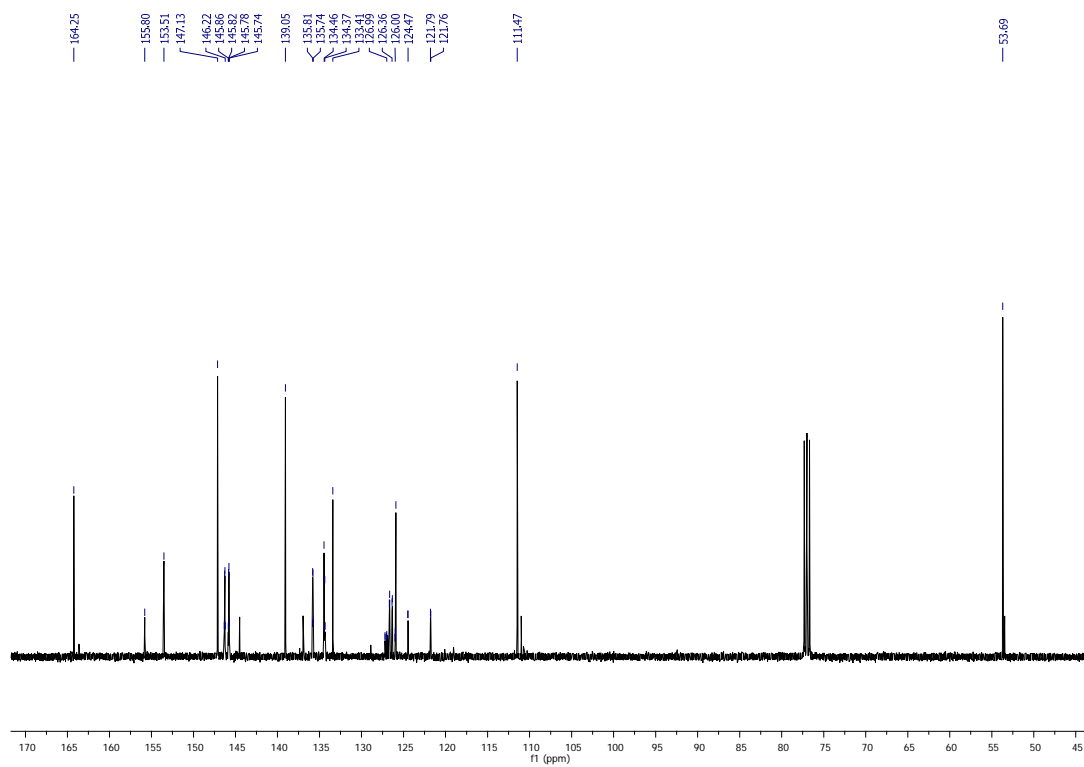
**5-(Trifluoromethyl)-2,3-bis[5-(trifluoromethyl)pyridin-3-yl]pyridine (153)**HMBC spectrum  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

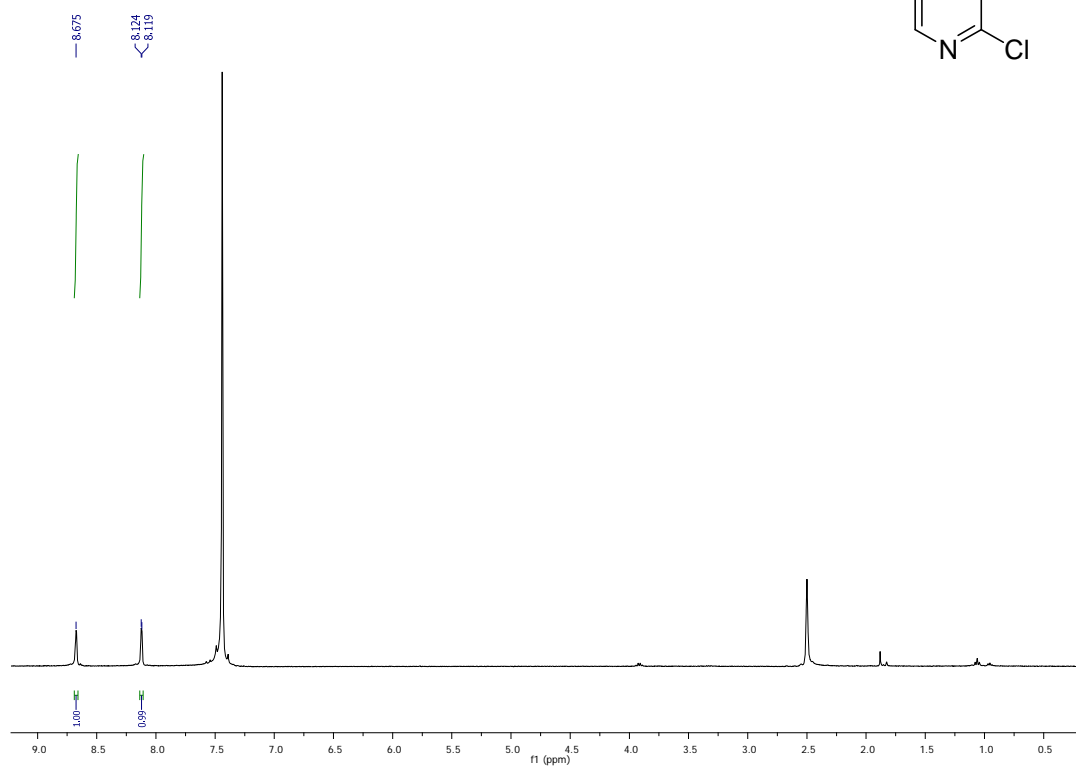
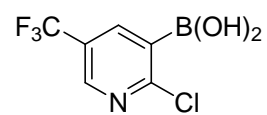
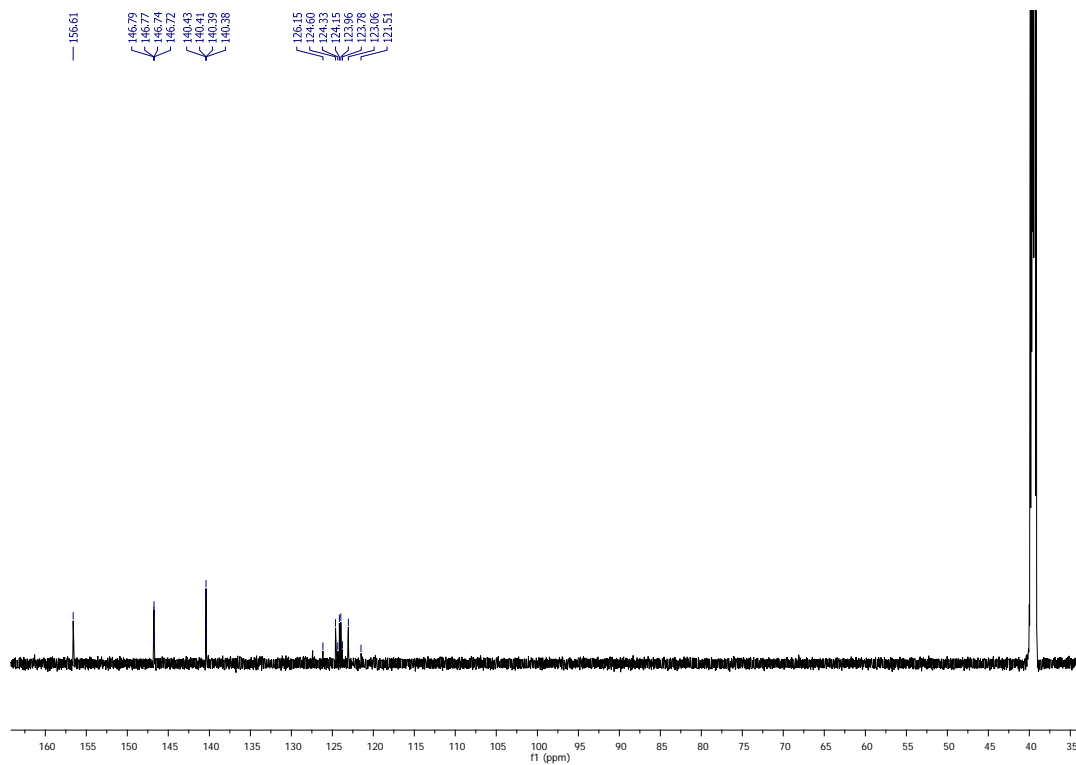
**5-(Trifluoromethyl)-2-[5-(trifluoromethyl)pyridin-3-yl]-3-(6-methoxypyridin-3-yl)pyridine (155)**

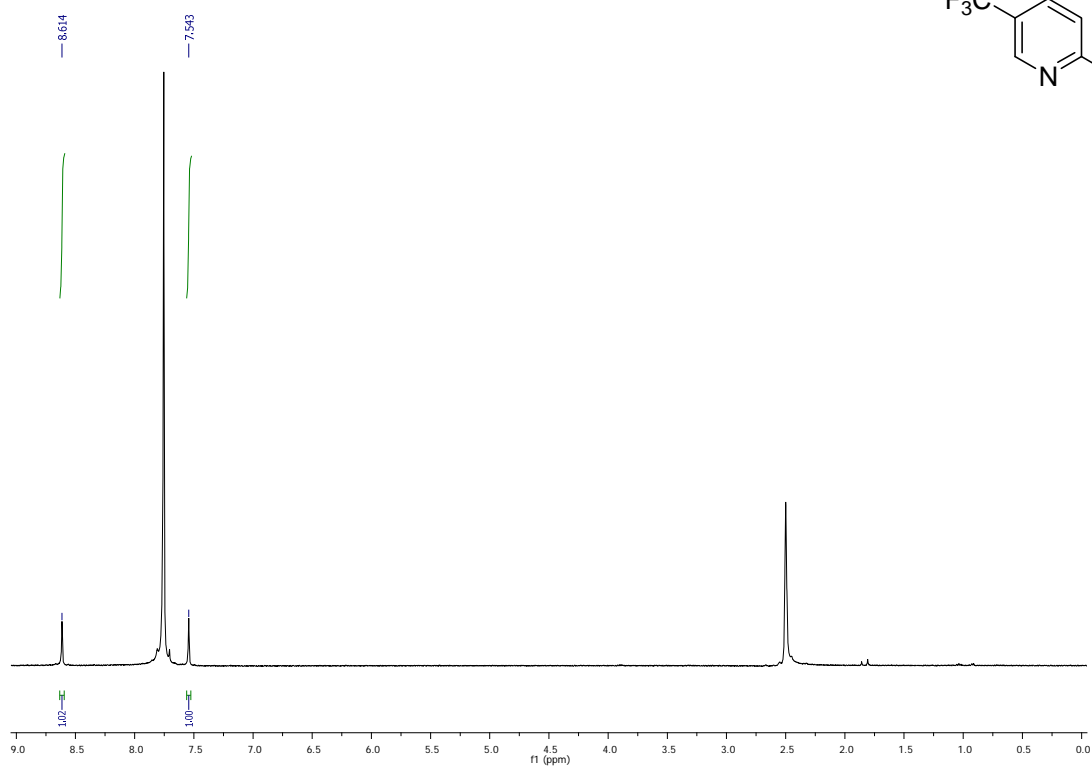
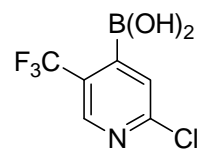
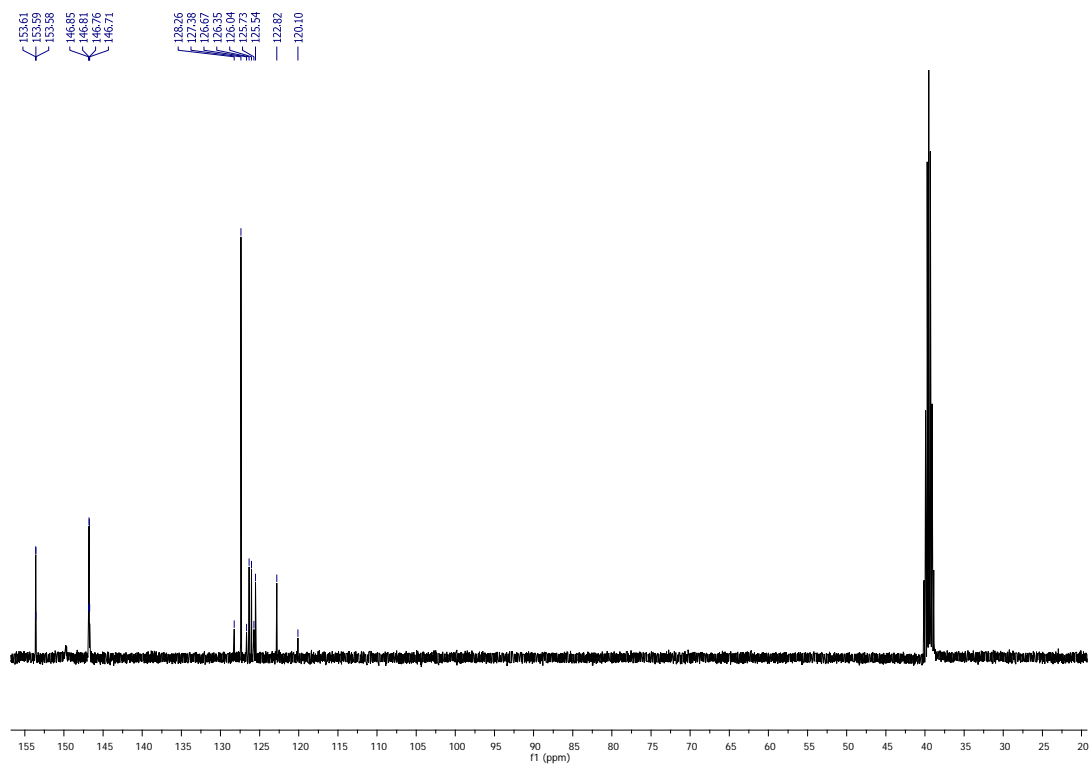
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

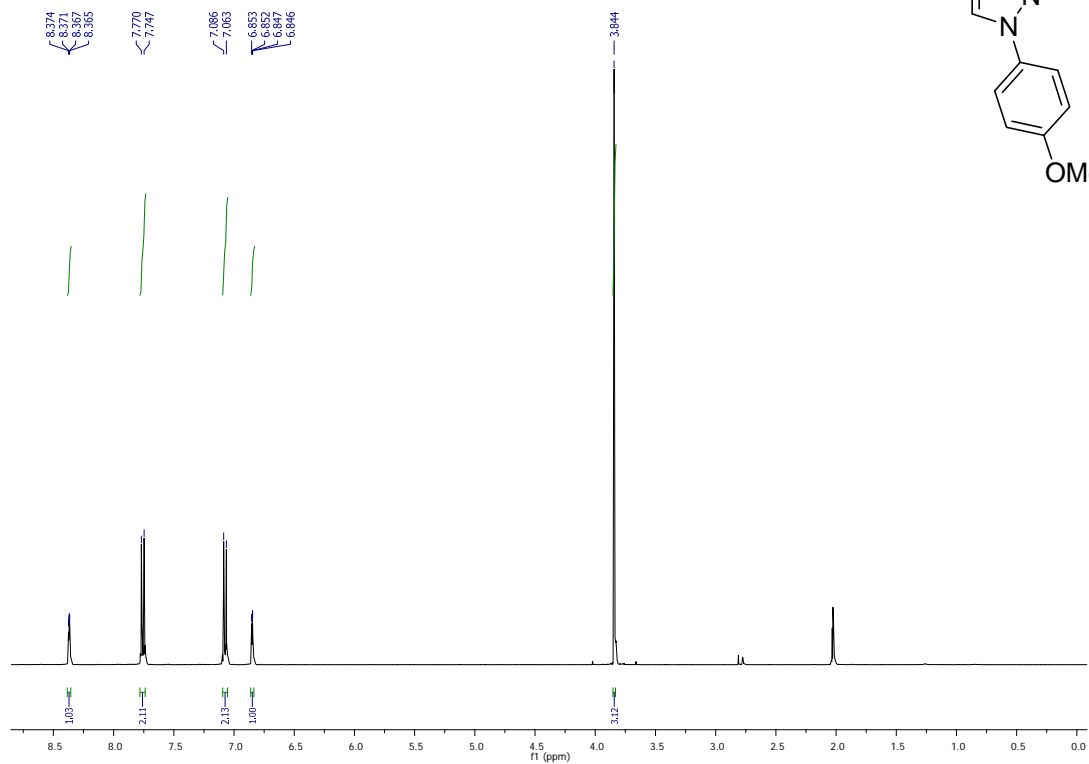
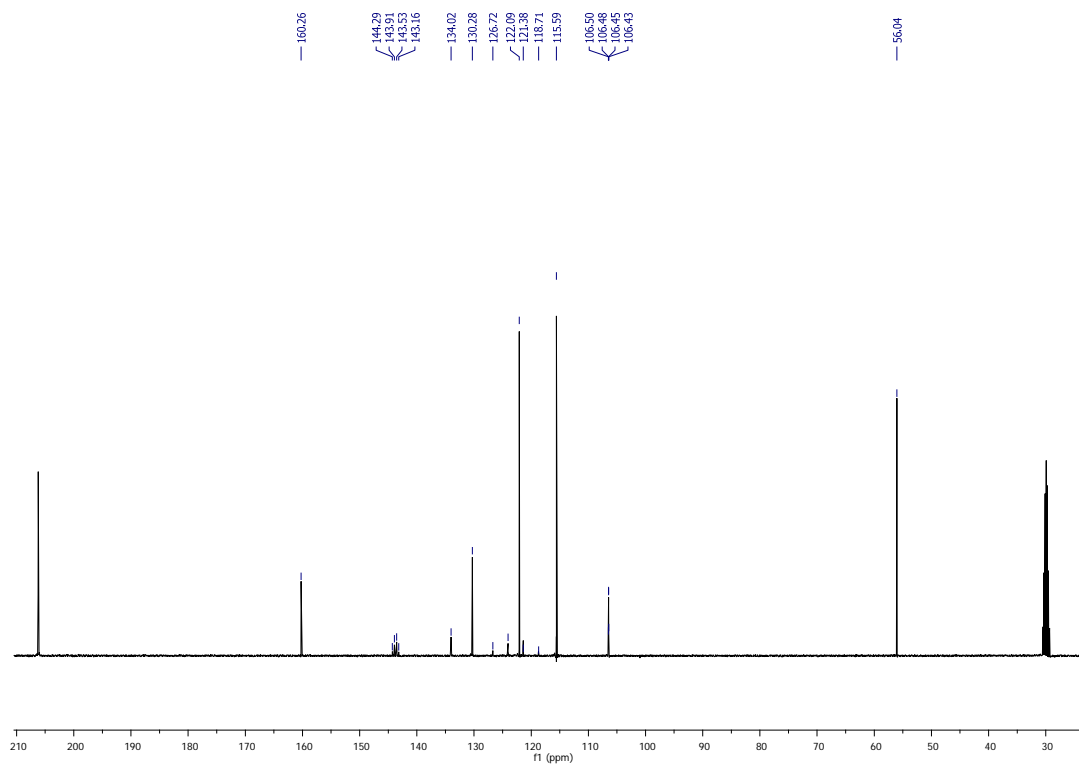


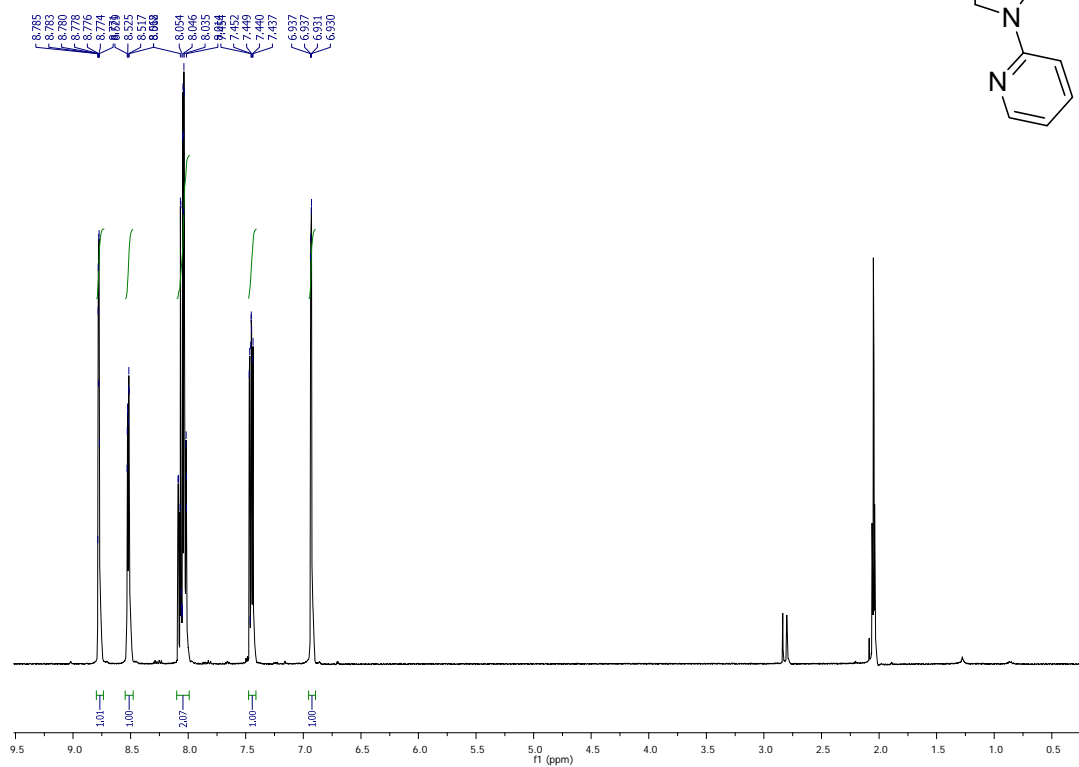
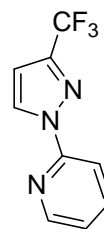
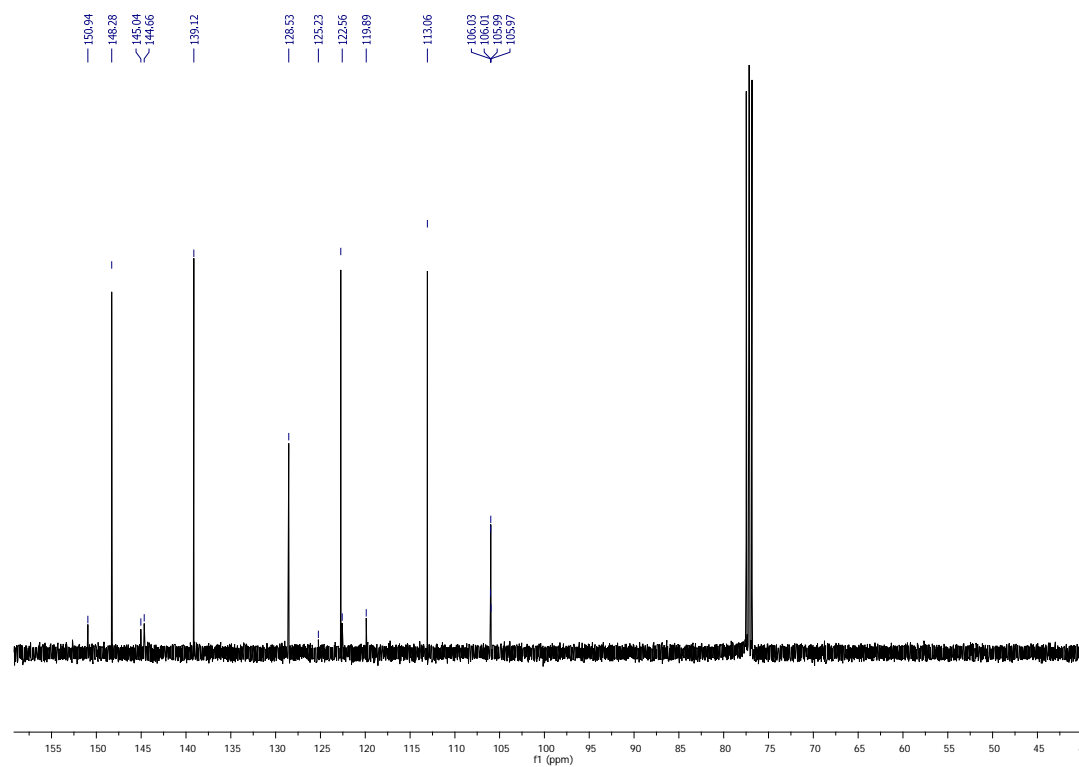
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

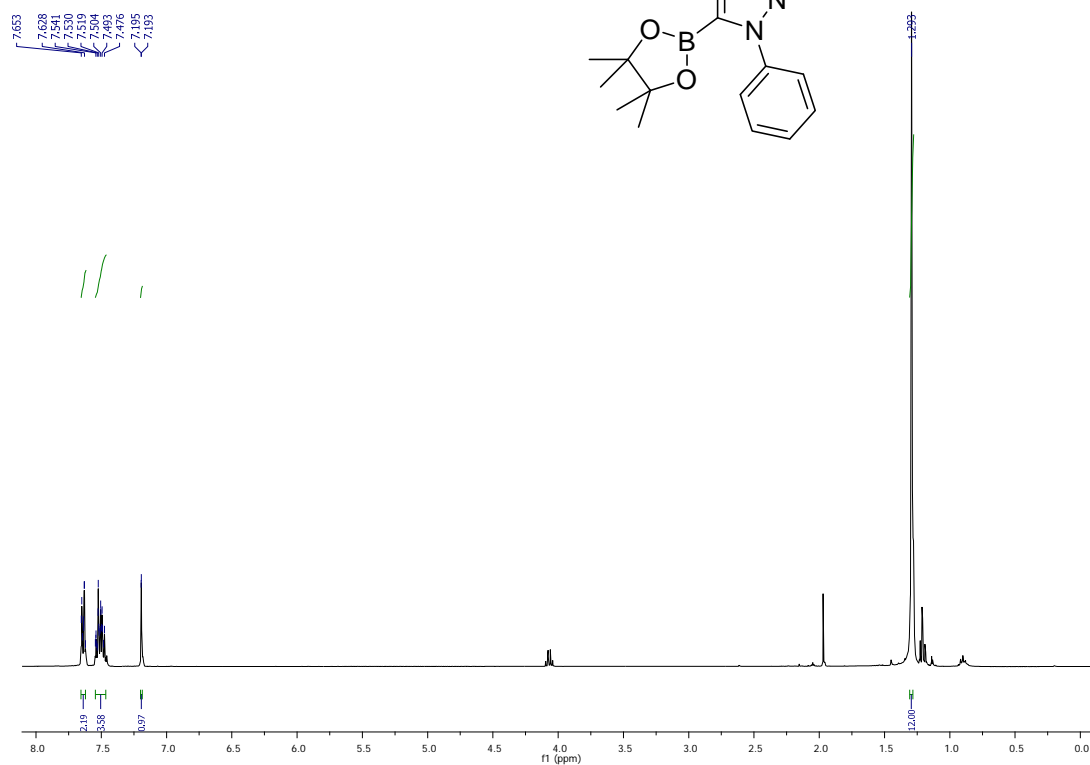
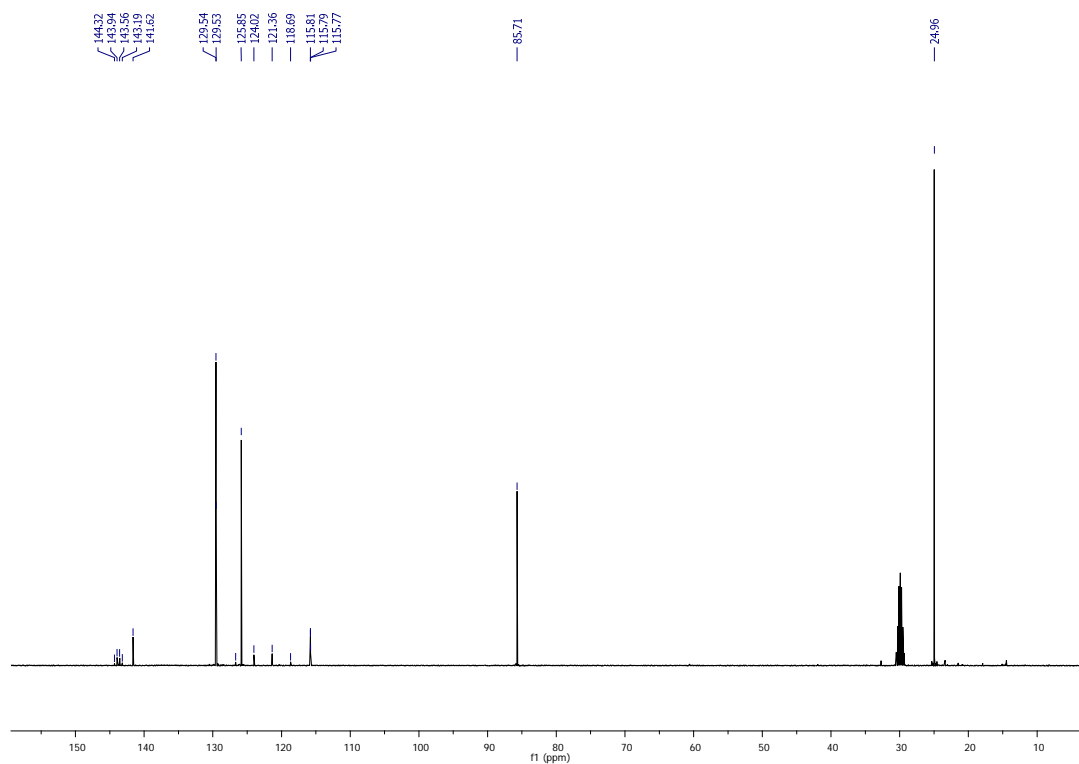


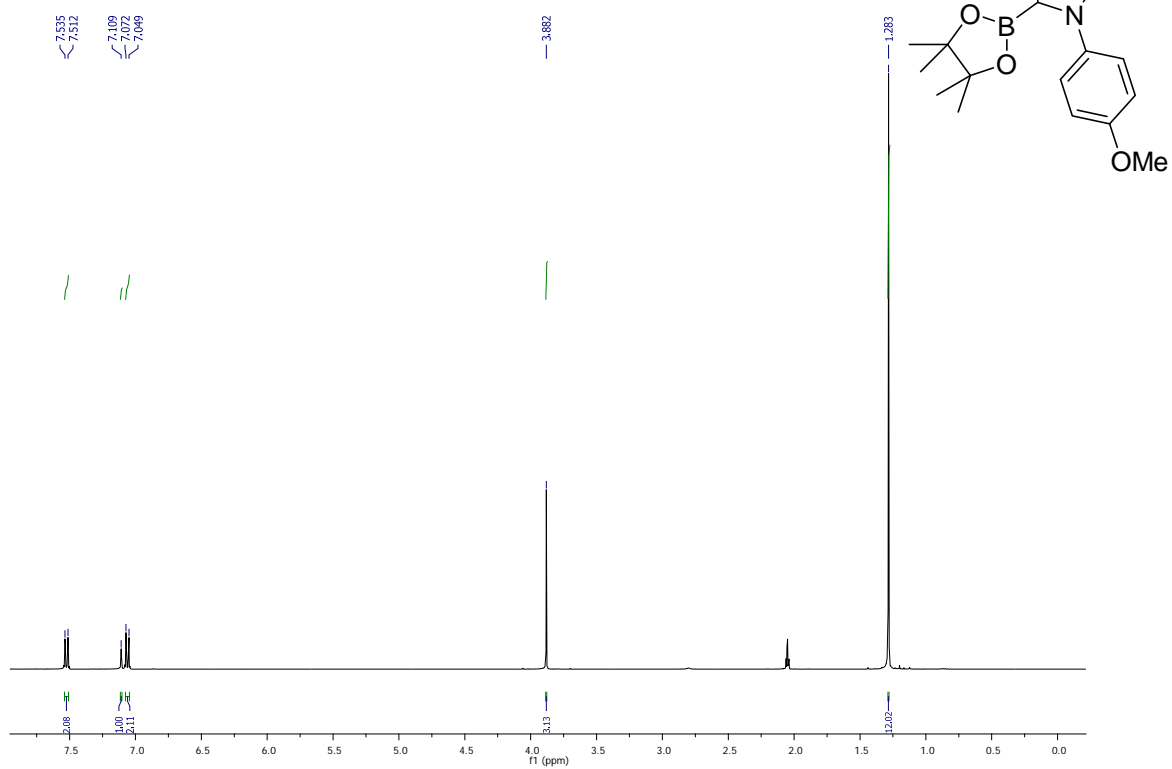
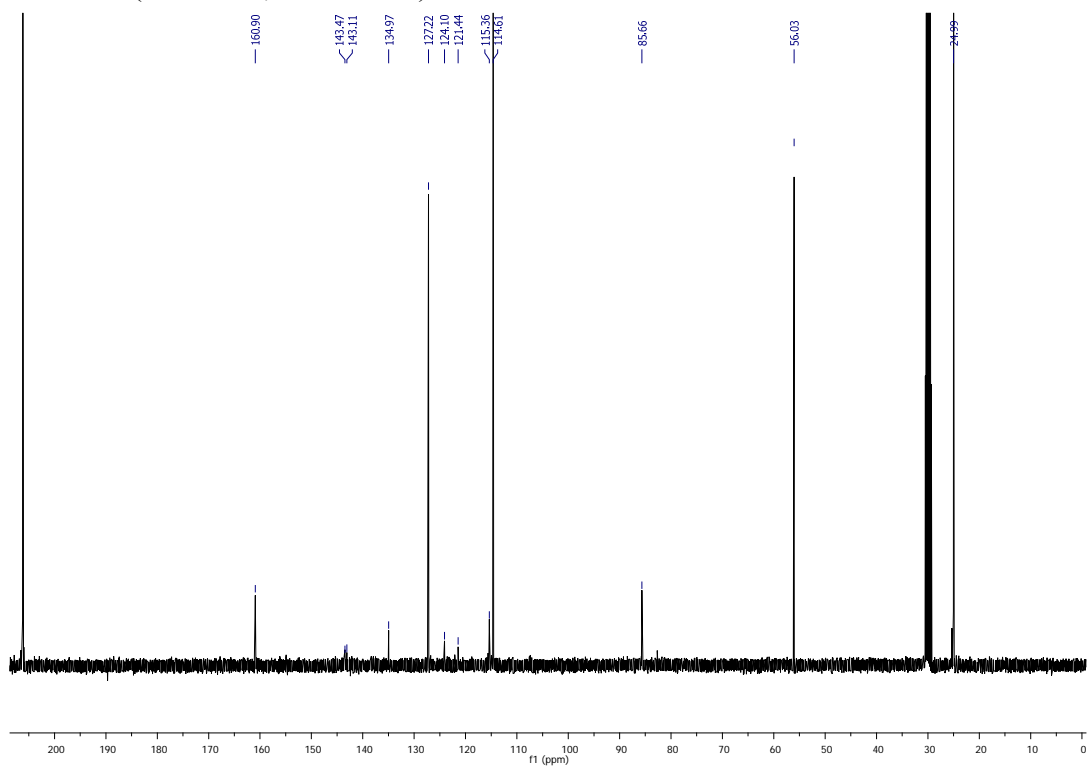
**2-Chloro-5-(trifluoromethyl)-3-pyridylboronic acid (157)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, DCl)<sup>13</sup>C NMR (175 MHz, DMSO-d<sub>6</sub>, DCl)

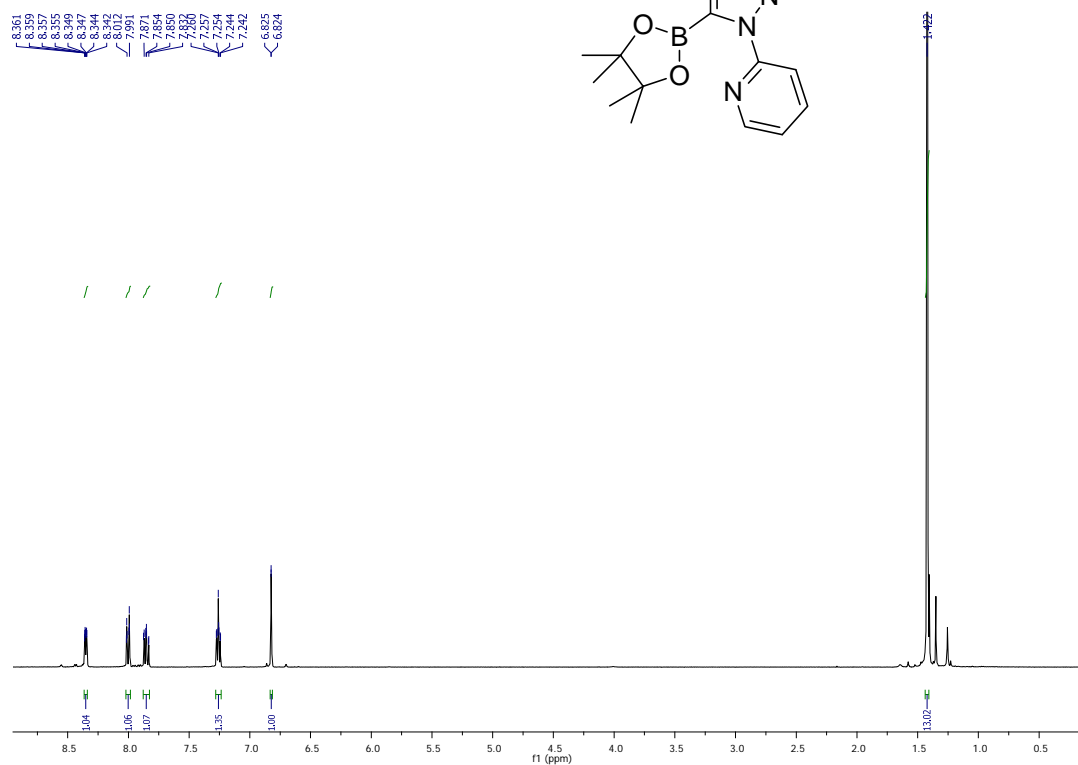
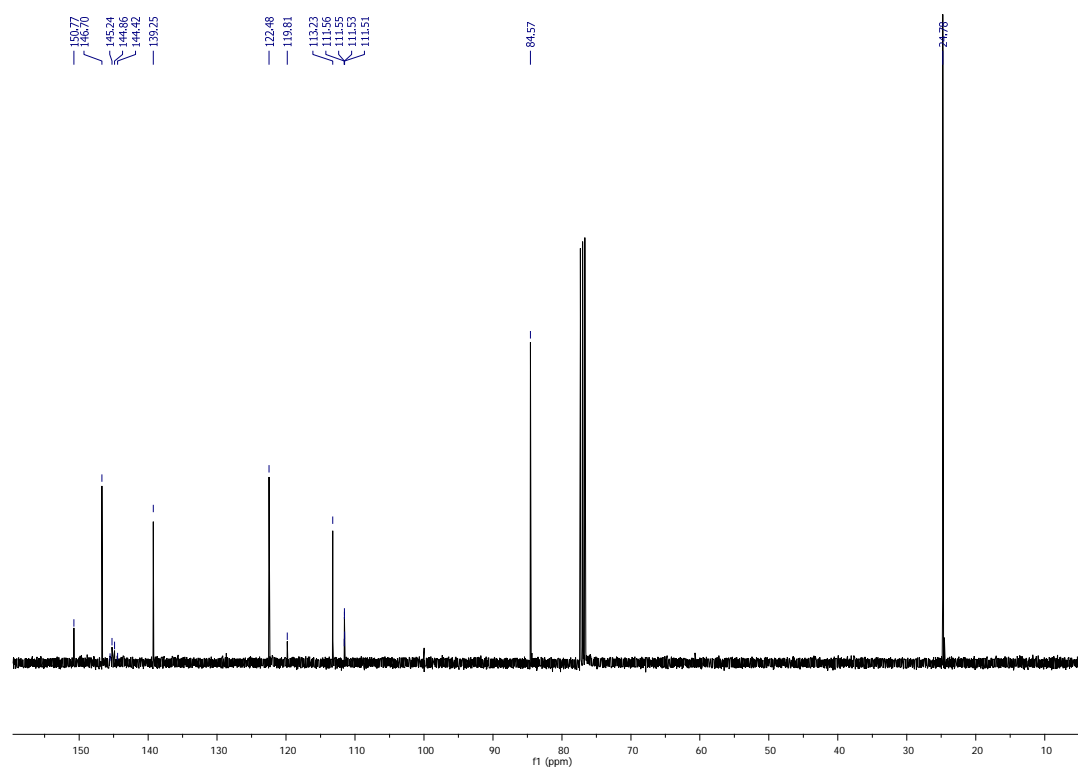
**2-Chloro-5-(trifluoromethyl)-4-pyridylboronic acid (158)**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, DCl)<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, DCl)

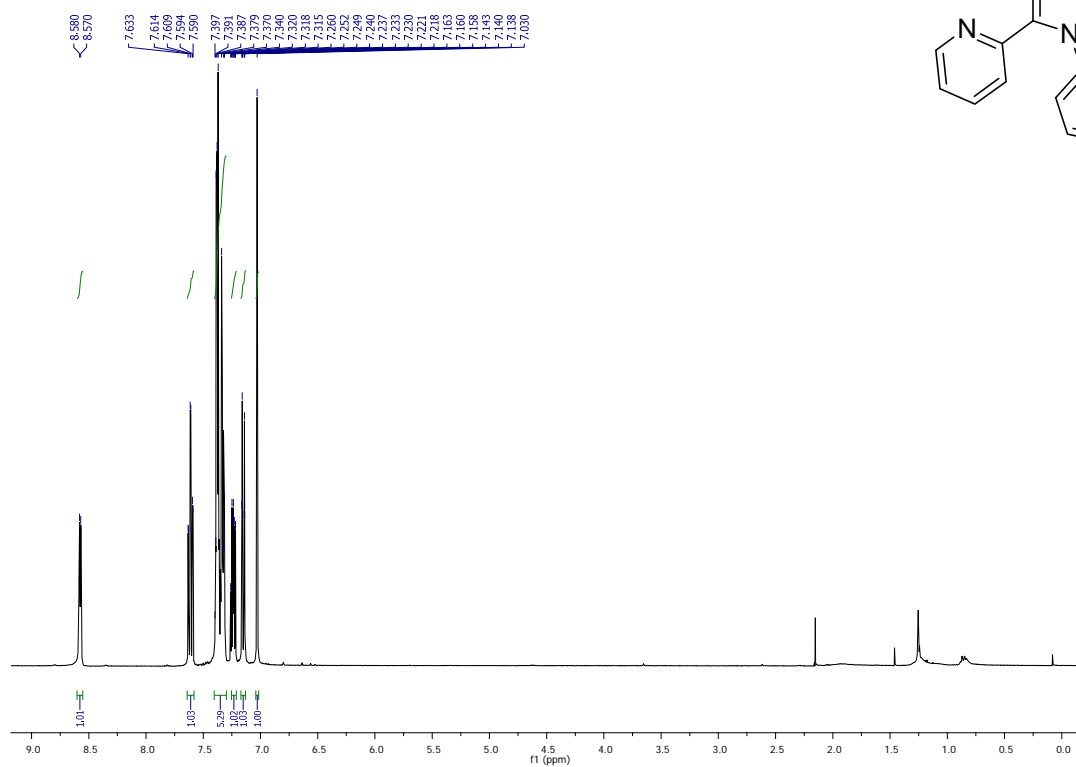
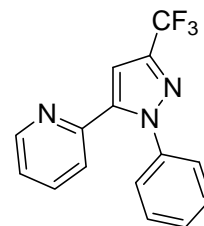
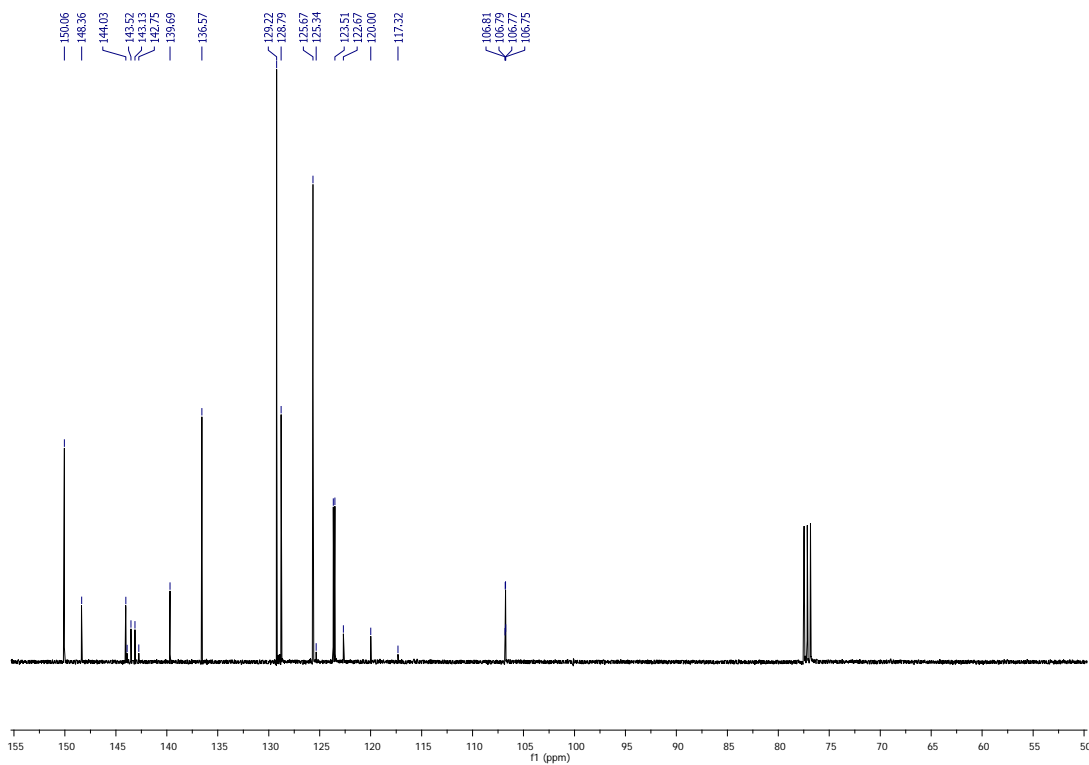
**3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazole (159b)**<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)

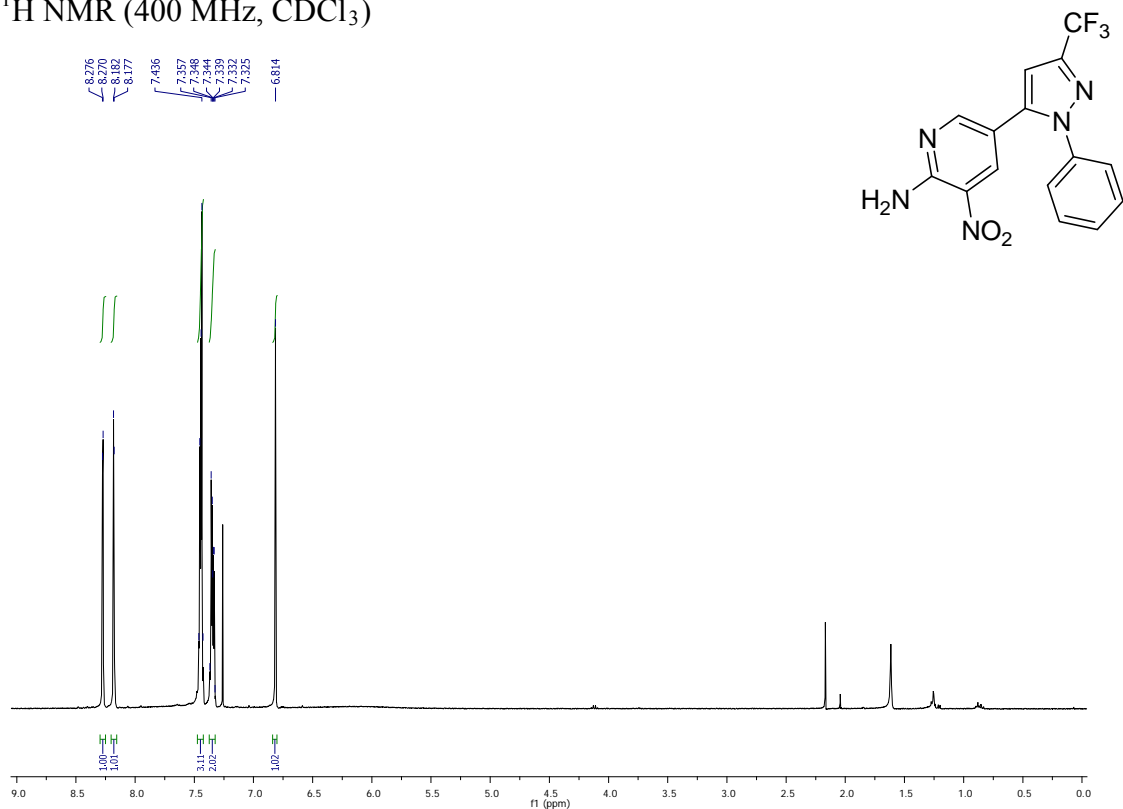
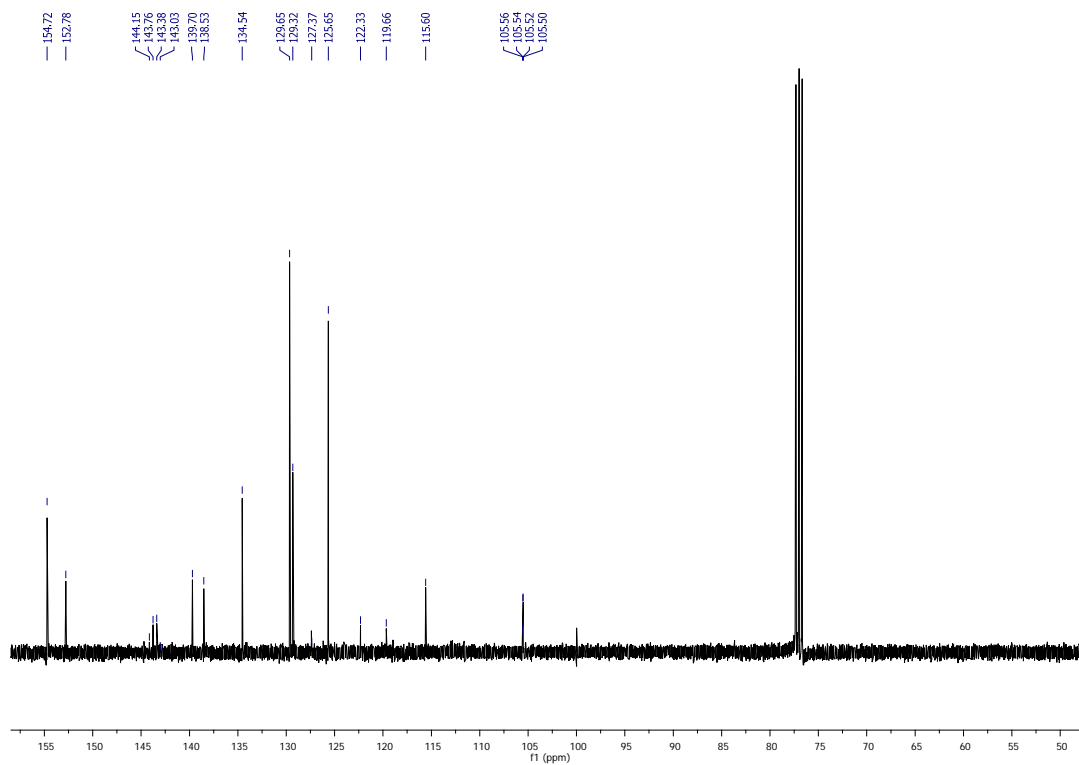
**3-(Trifluoromethyl)-1-(pyridin-2-yl)-1H-pyrazole (159c)**<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

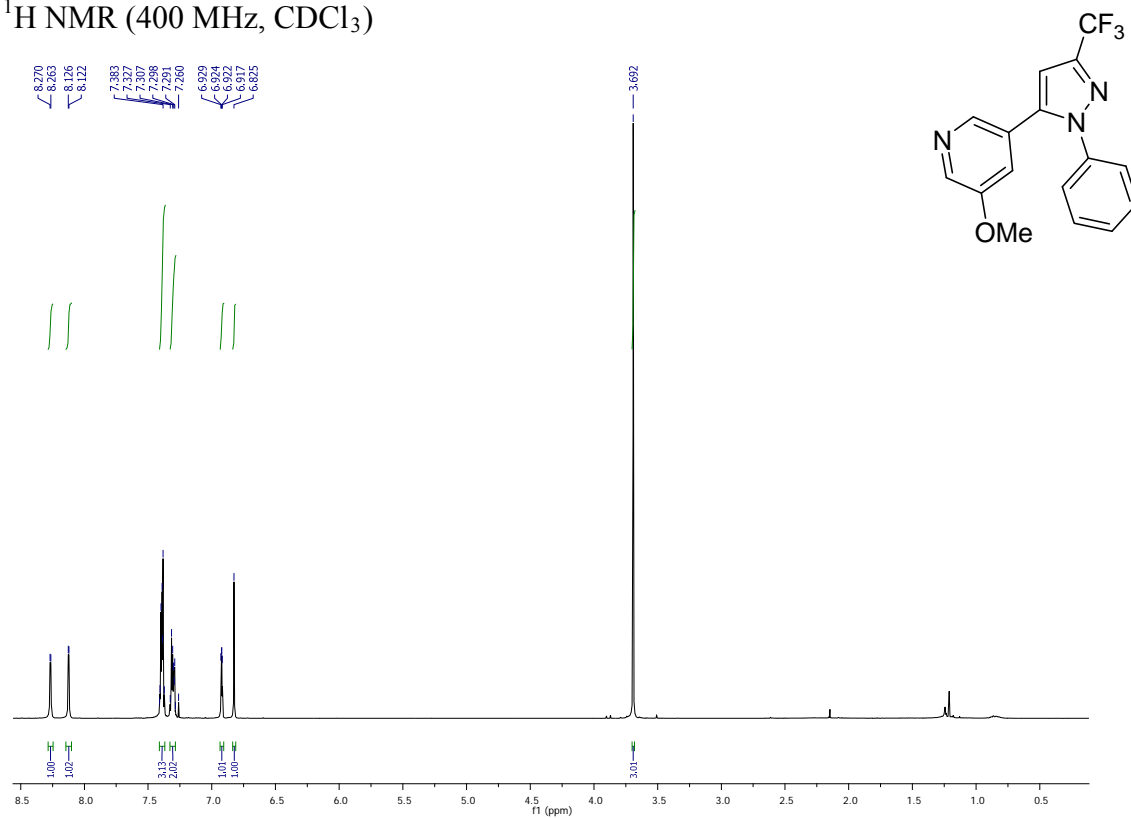
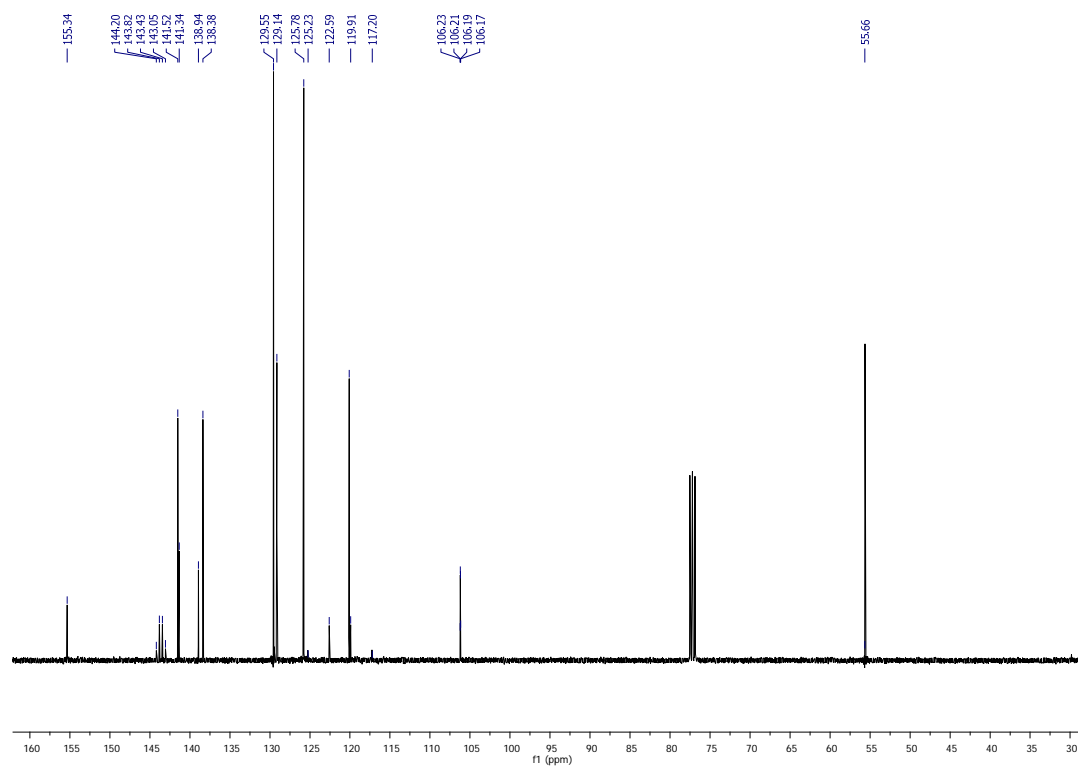
**3-(Trifluoromethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-1H-pyrazole (160a)**<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)

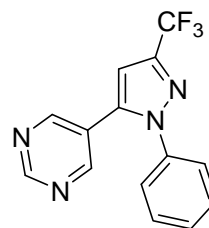
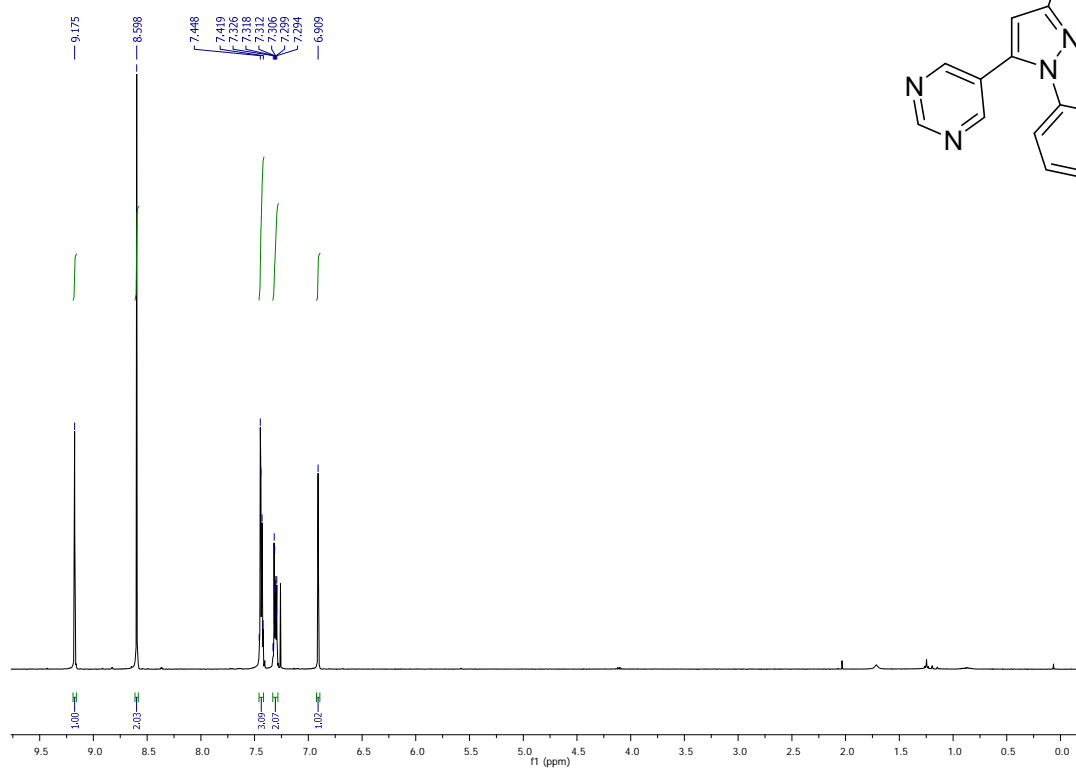
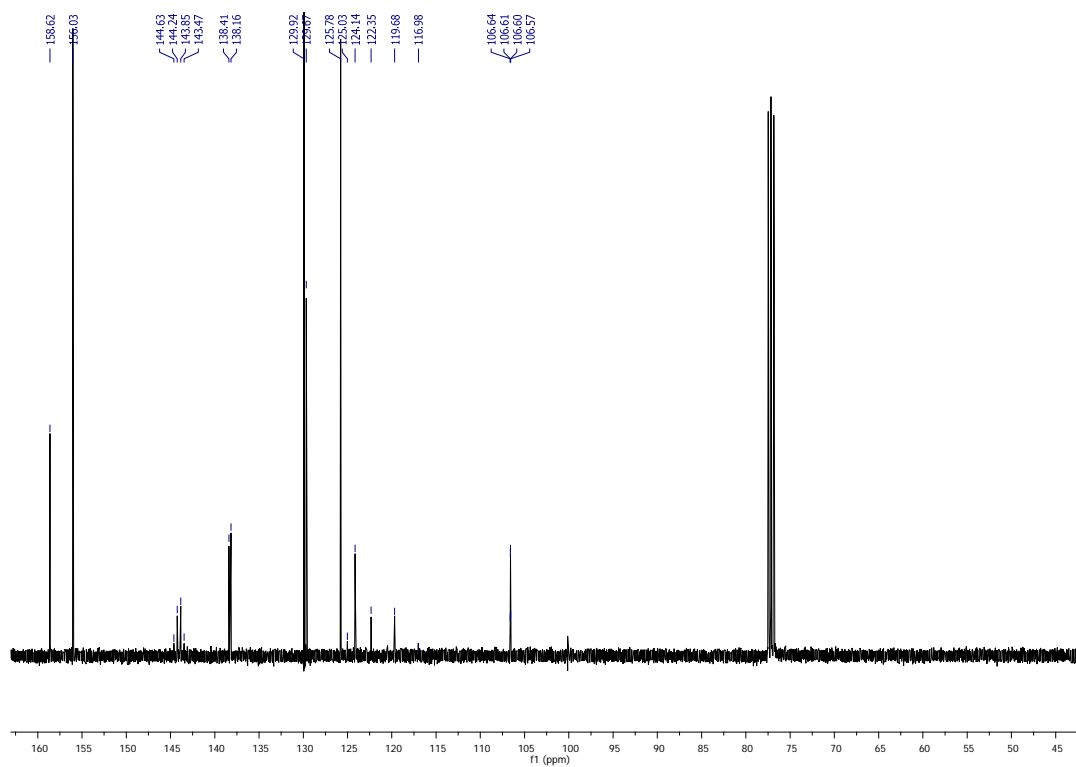
**3-(Trifluoromethyl)-1-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (160b)**<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)<sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>)

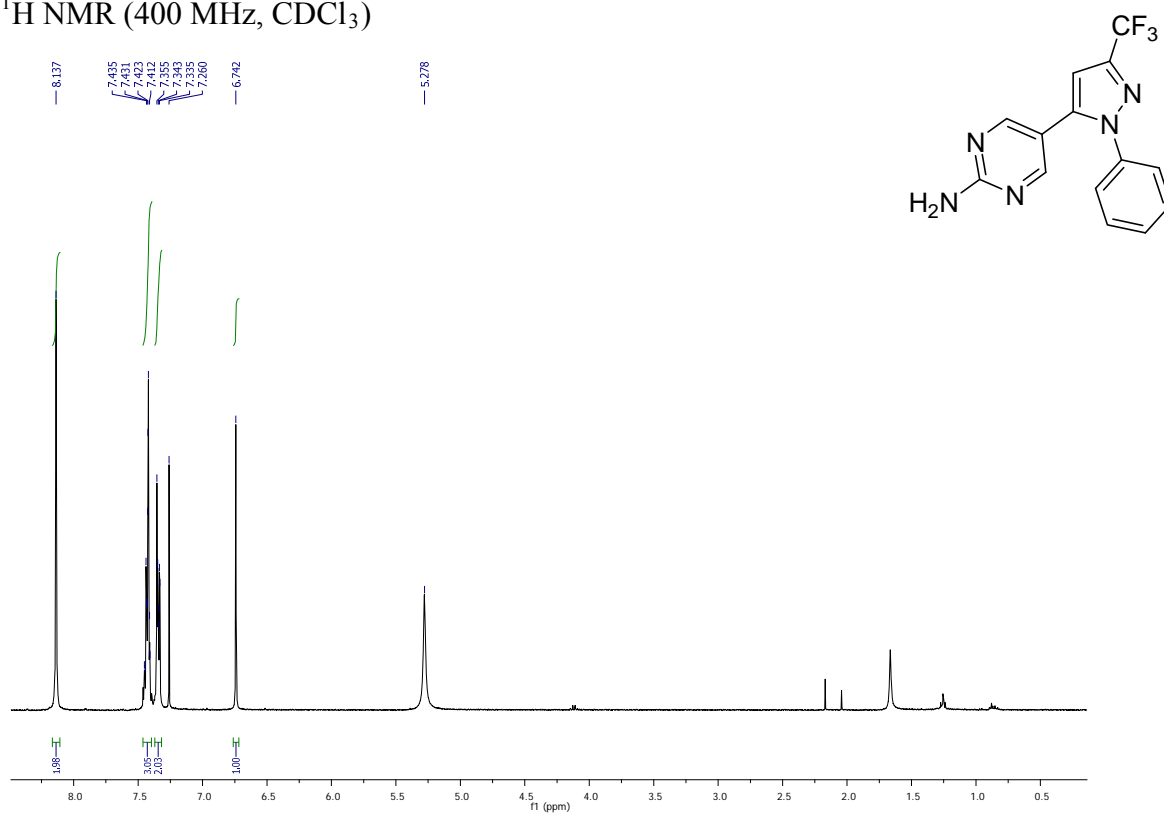
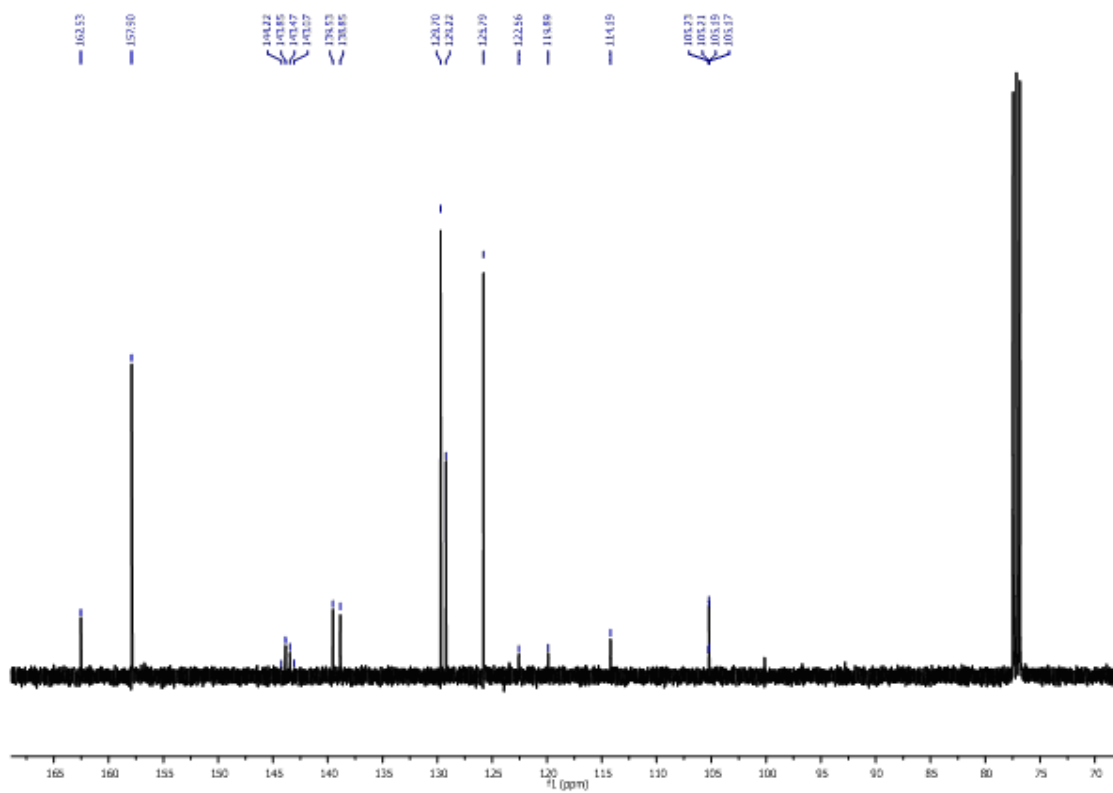
**3-(Trifluoromethyl)-1-(pyridin-2yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (160c)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

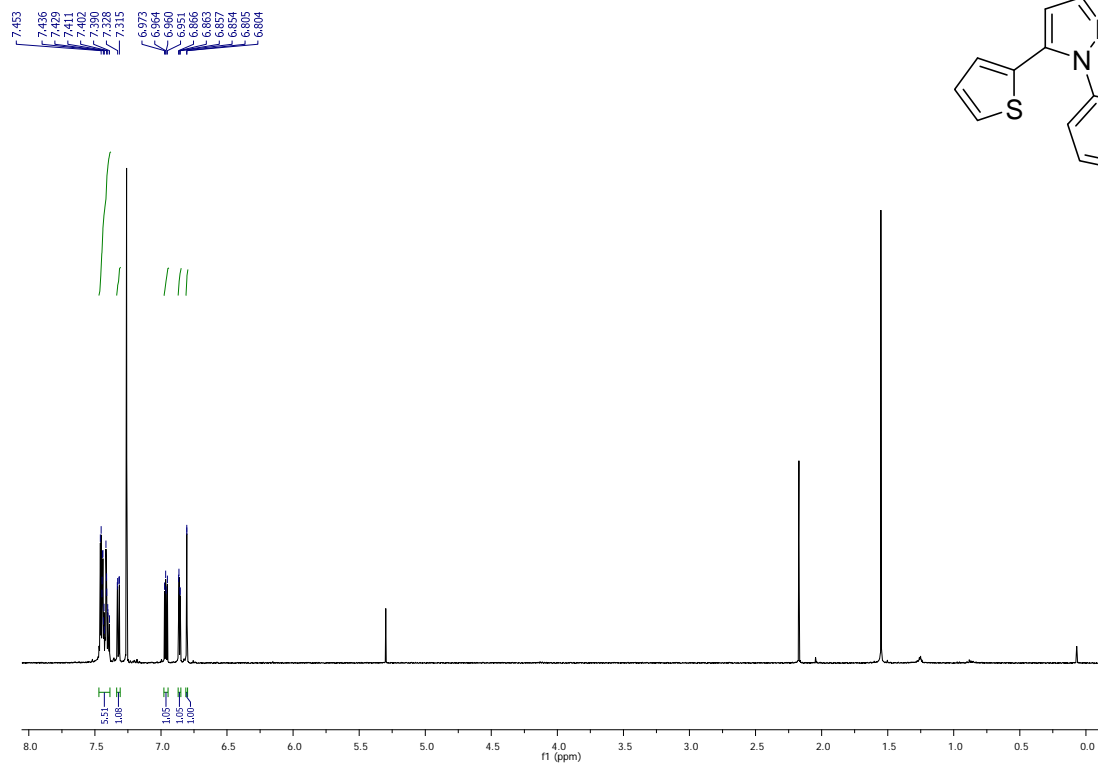
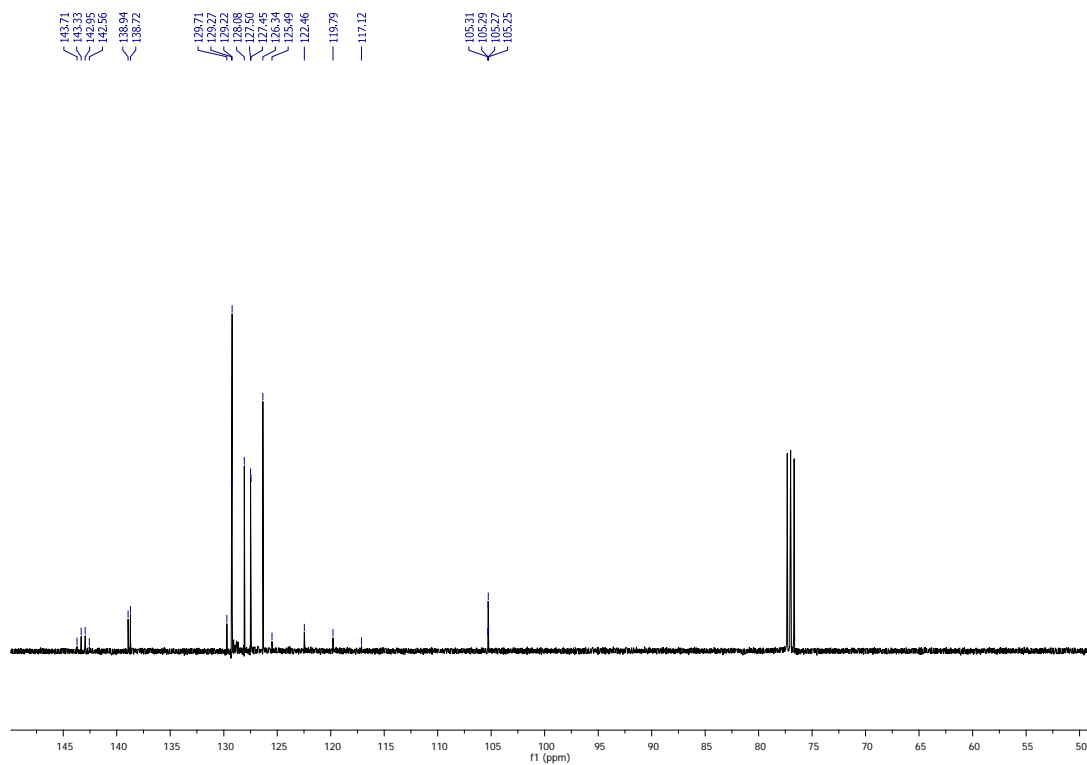
**2-[3-(Trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]pyridine (162)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**5-[3-(Trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]-3-nitropyridin-2-amine (163)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

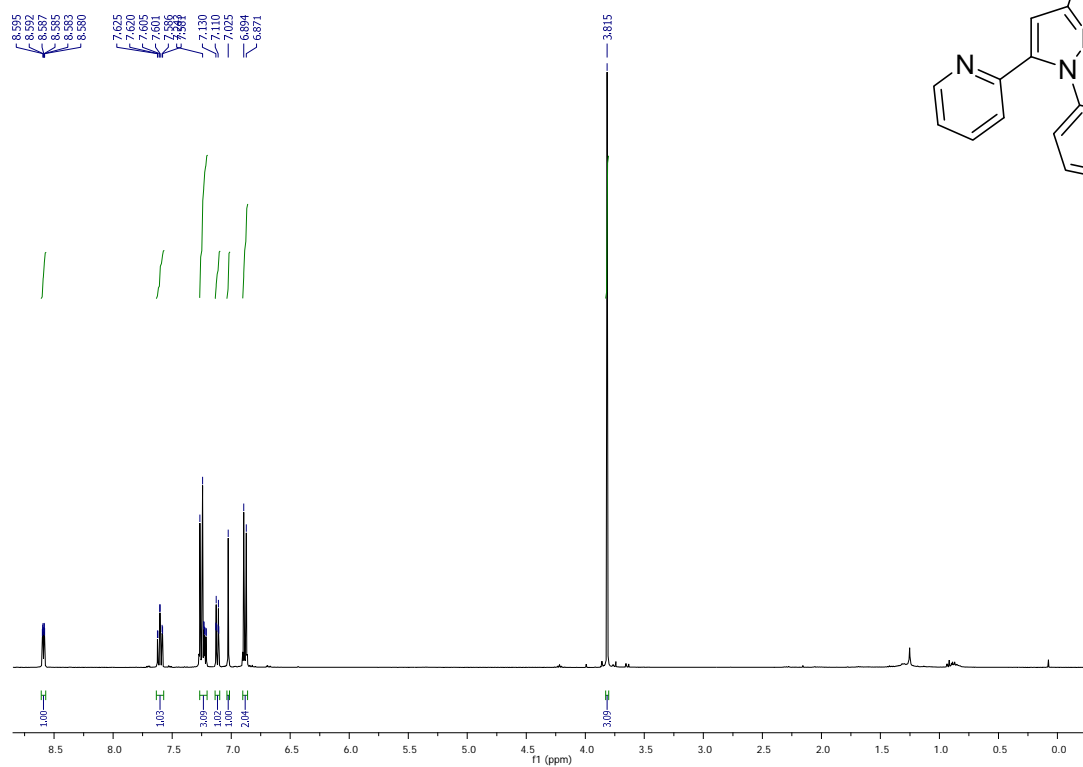
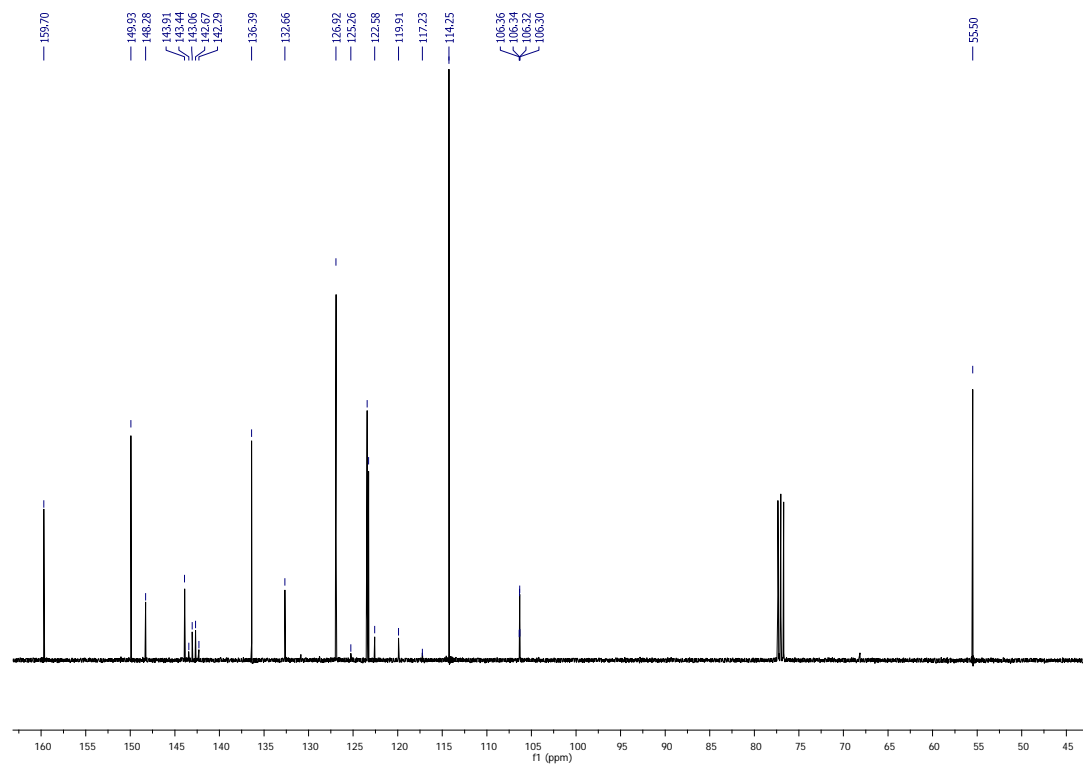
**3-[3-(Trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]-5-methoxypyridine (164)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

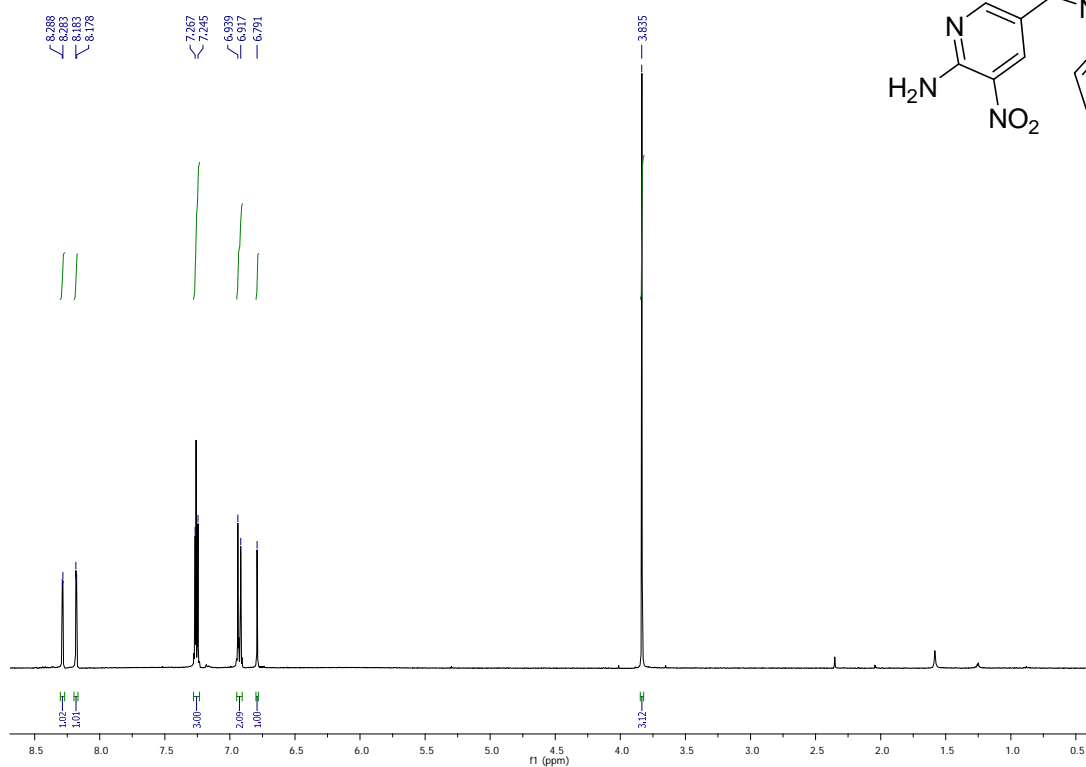
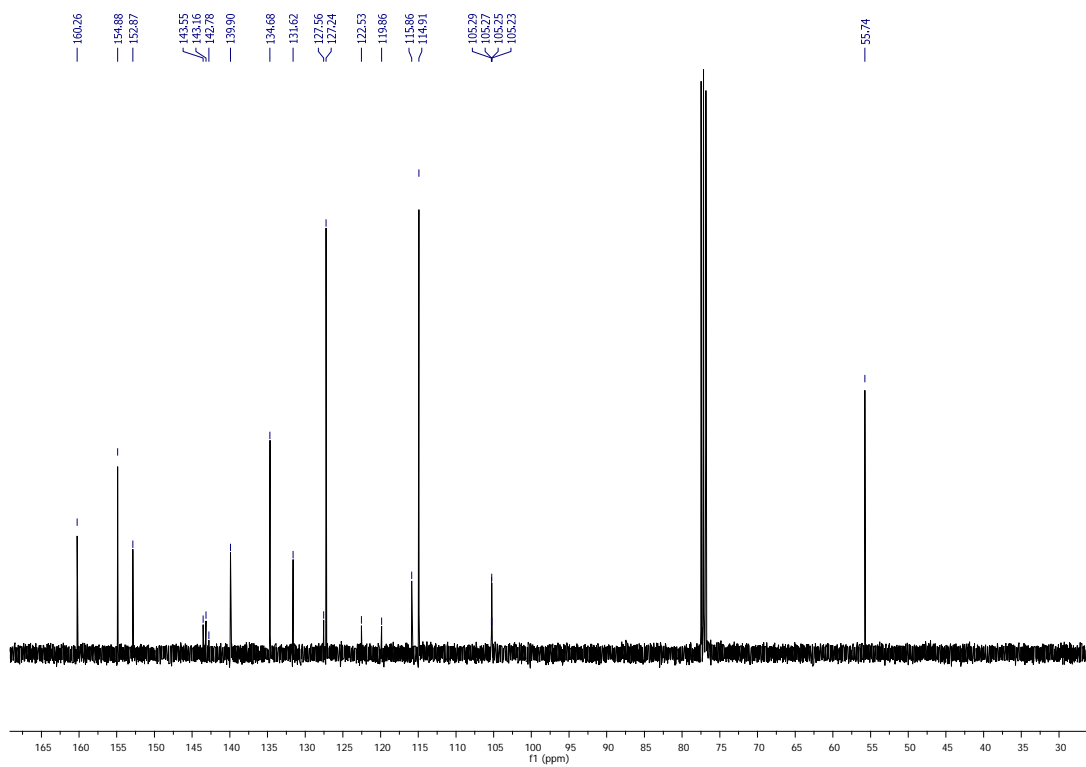
**5-[3-(Trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]pyrimidine (165)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

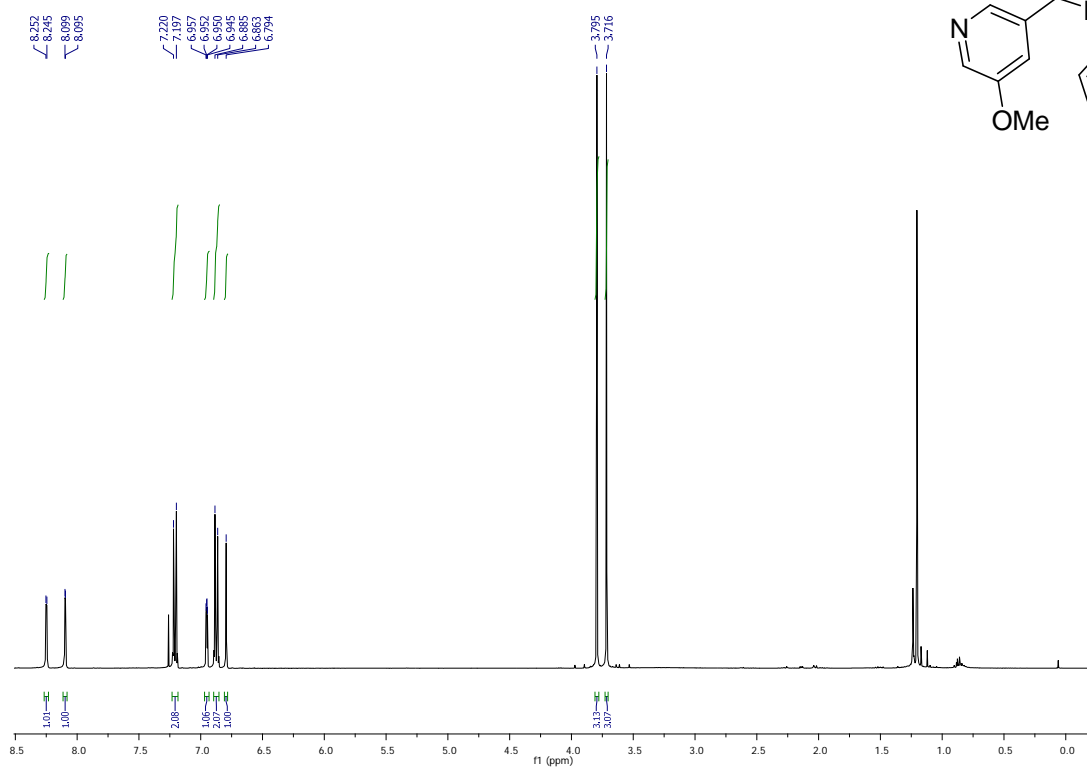
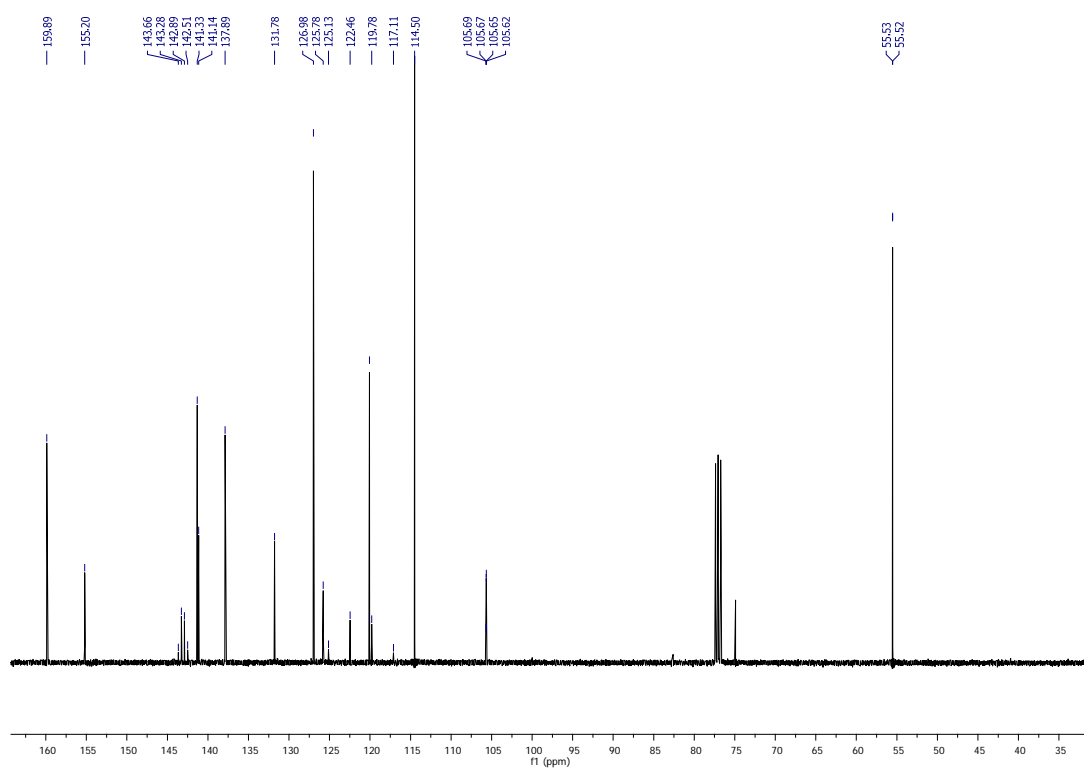
**5-(3-(Trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl)pyrimidin-2-amine (166)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

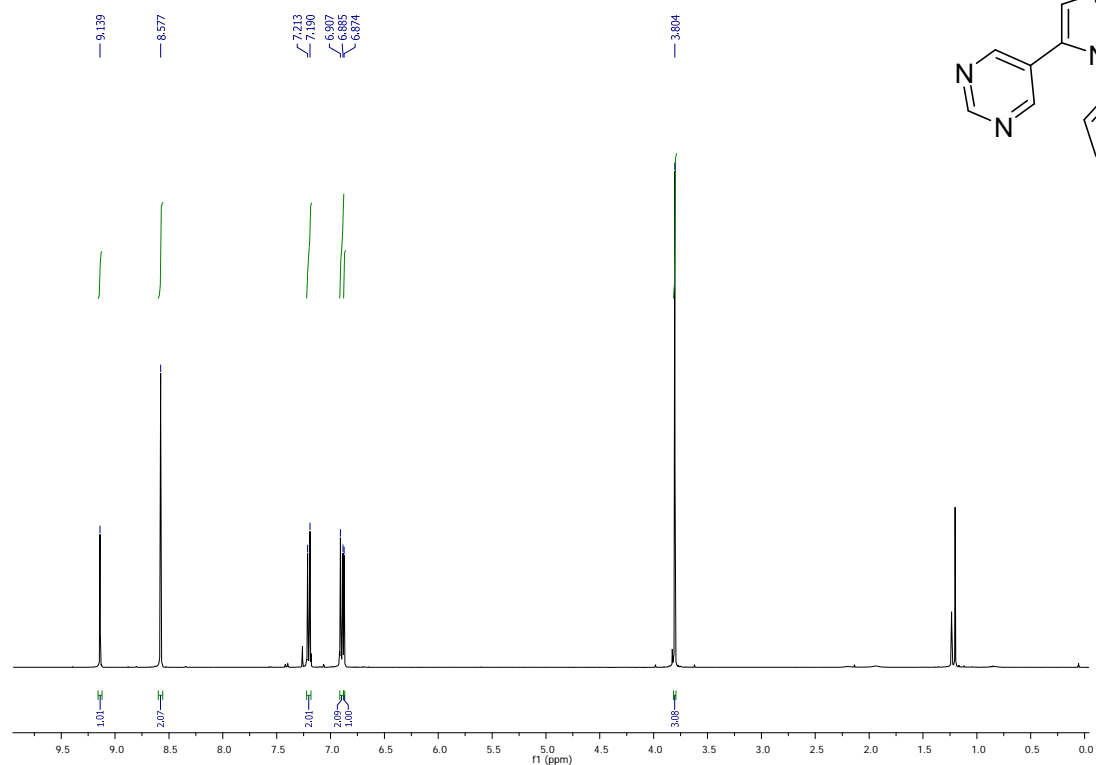
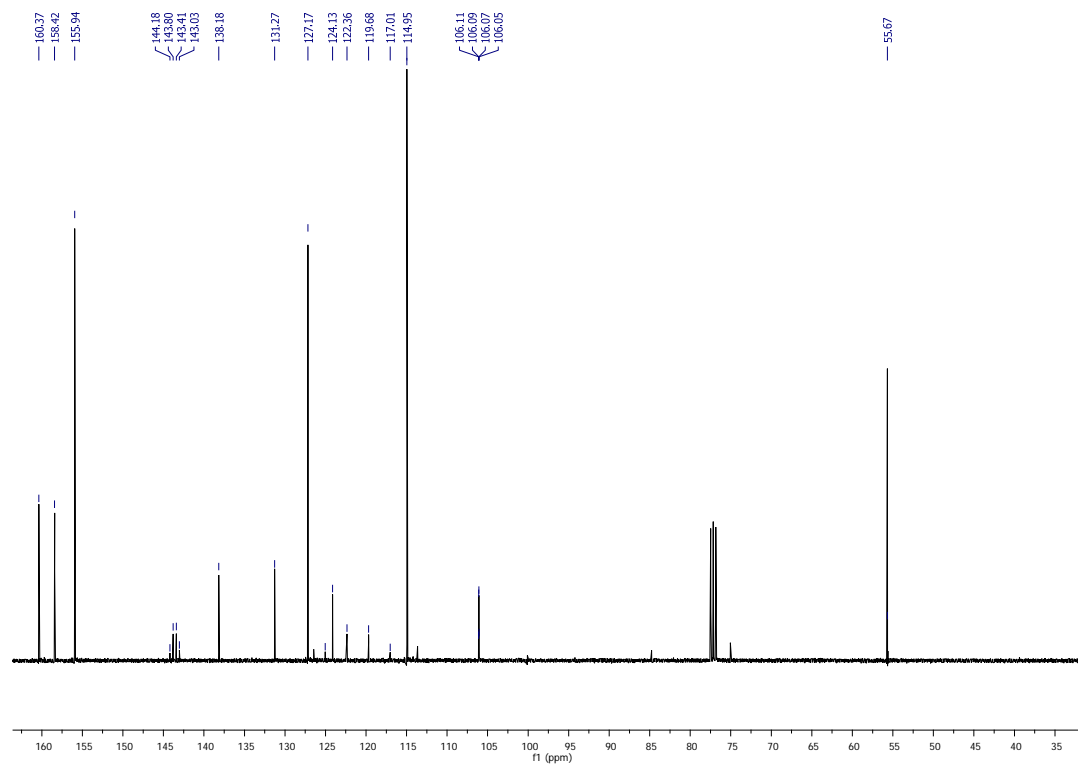
**3-(Trifluoromethyl)-1-phenyl-5-(thiophen-2-yl)-1H-pyrazole (167)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

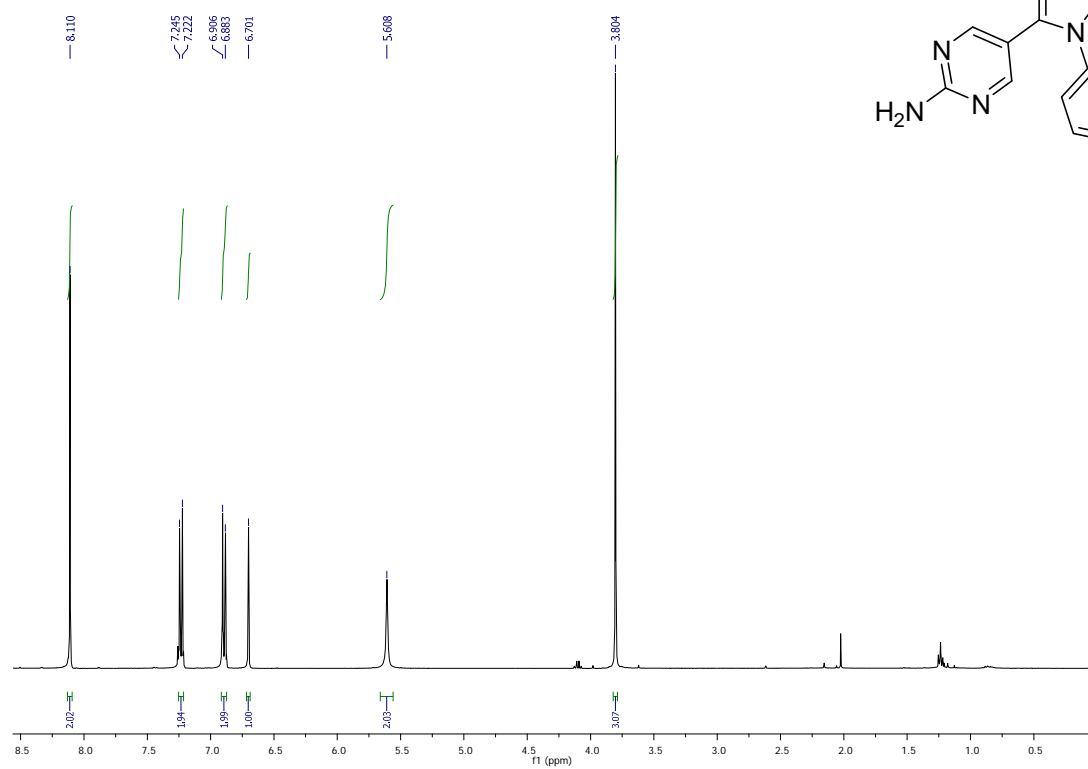
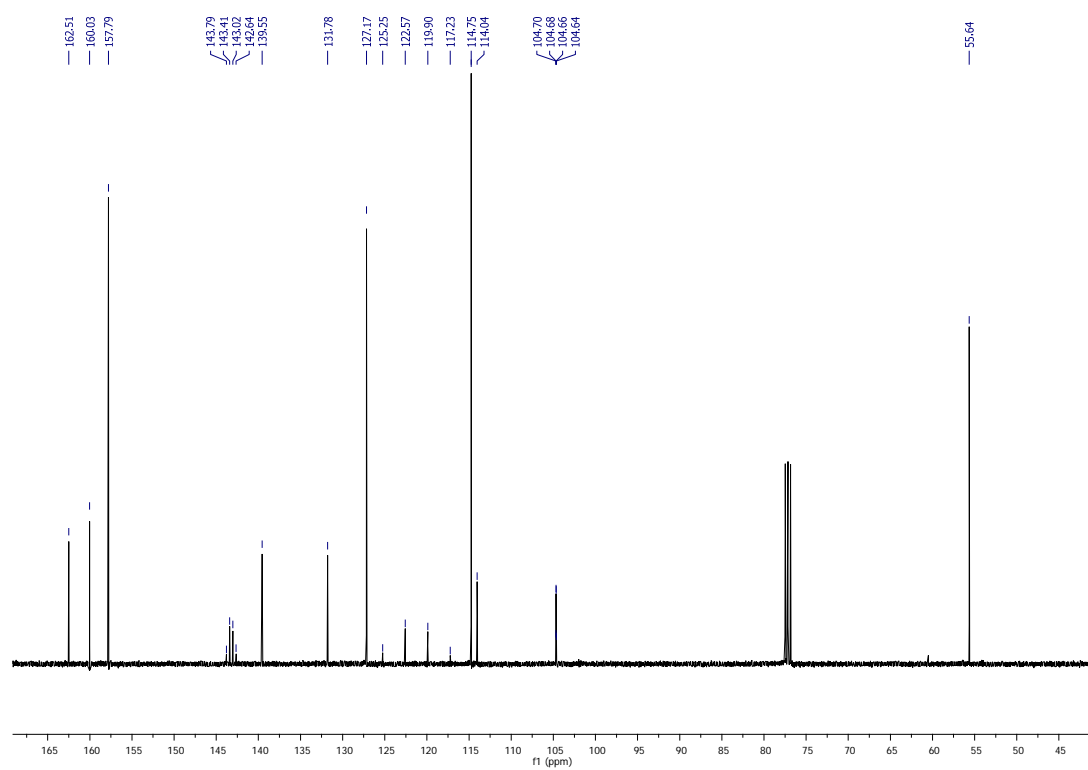
## 2-[3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazol-5-yl]pyridine (168)

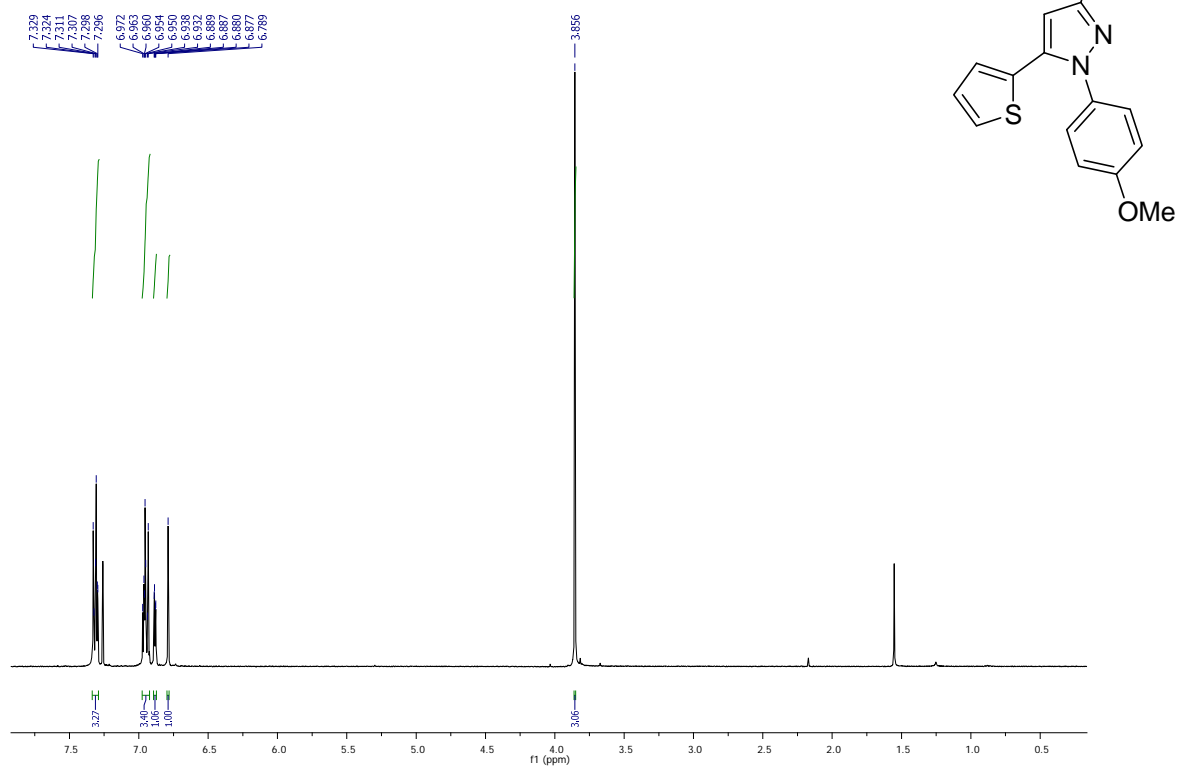
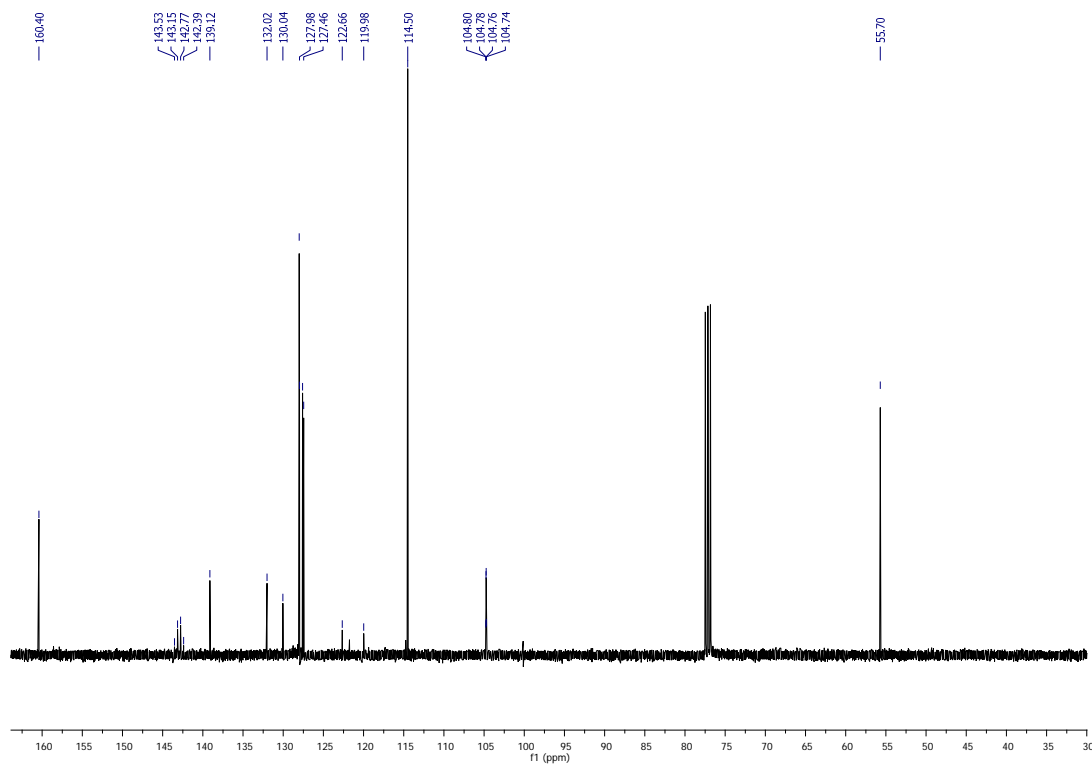
 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

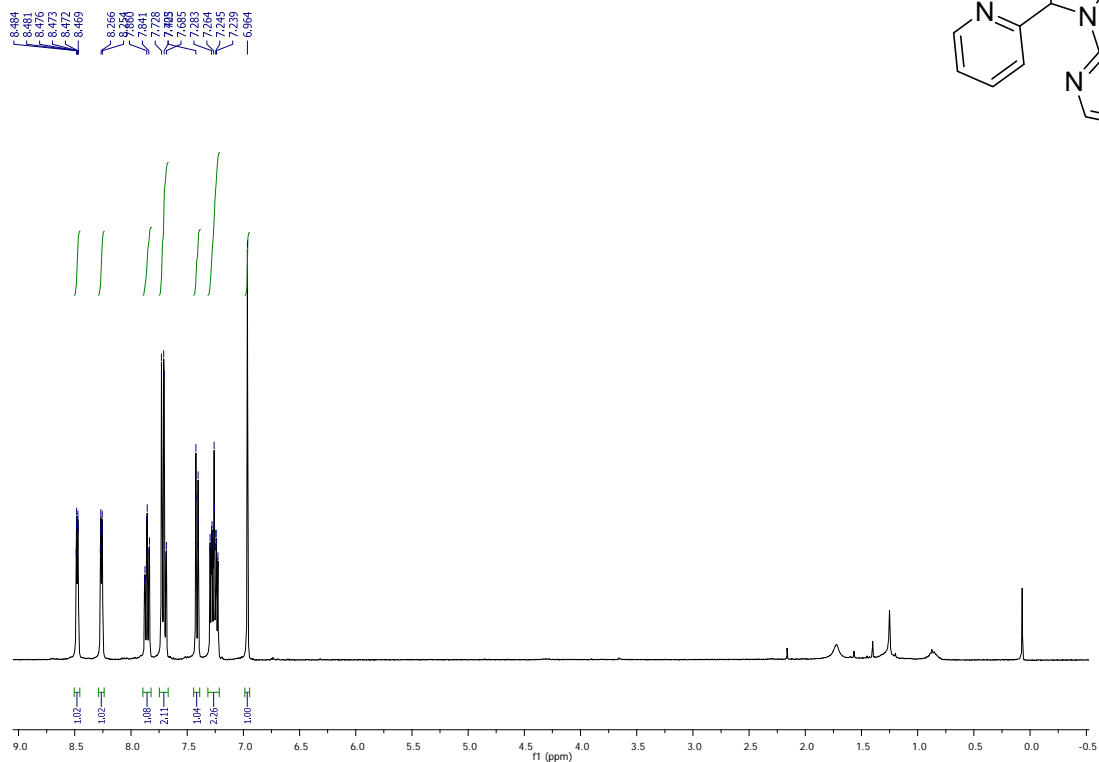
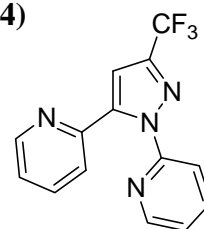
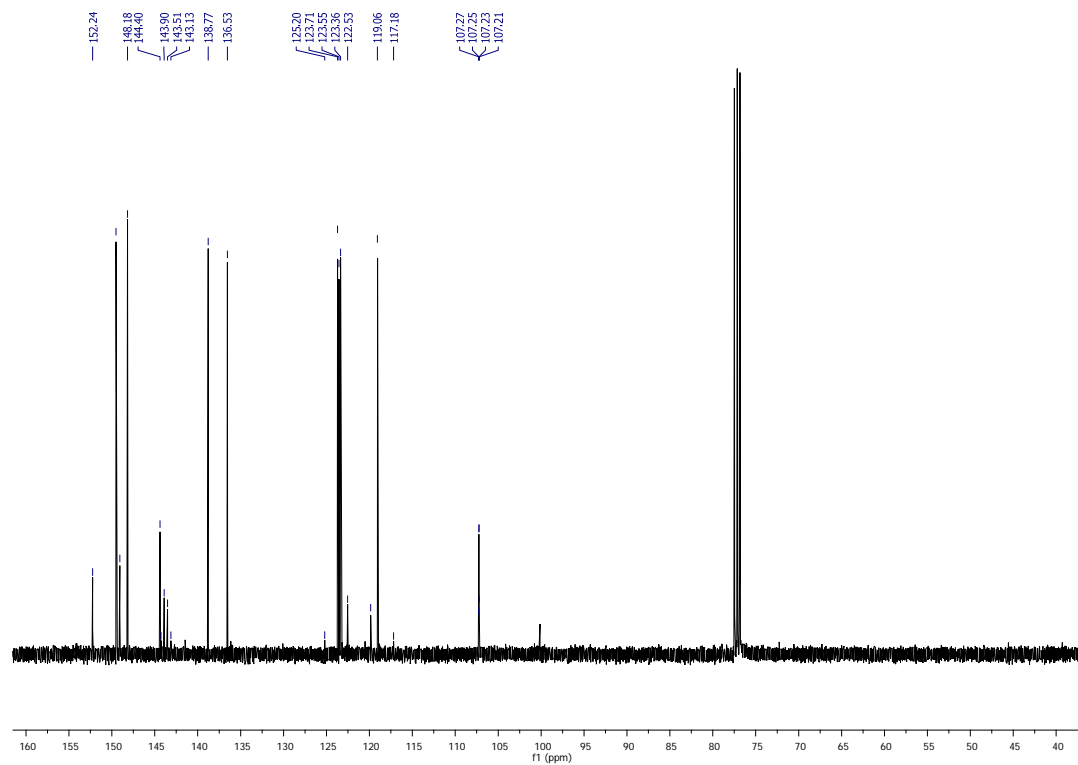
**5-[3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazol-5-yl]-3-nitropyridin-2-amine (169)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

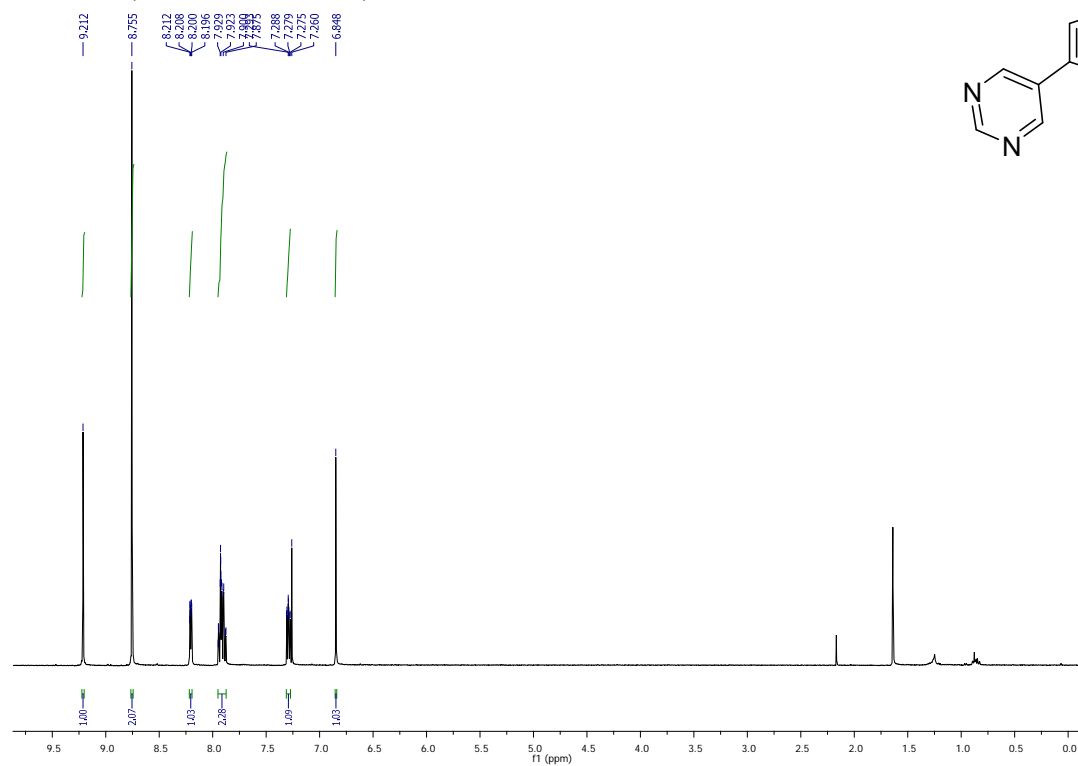
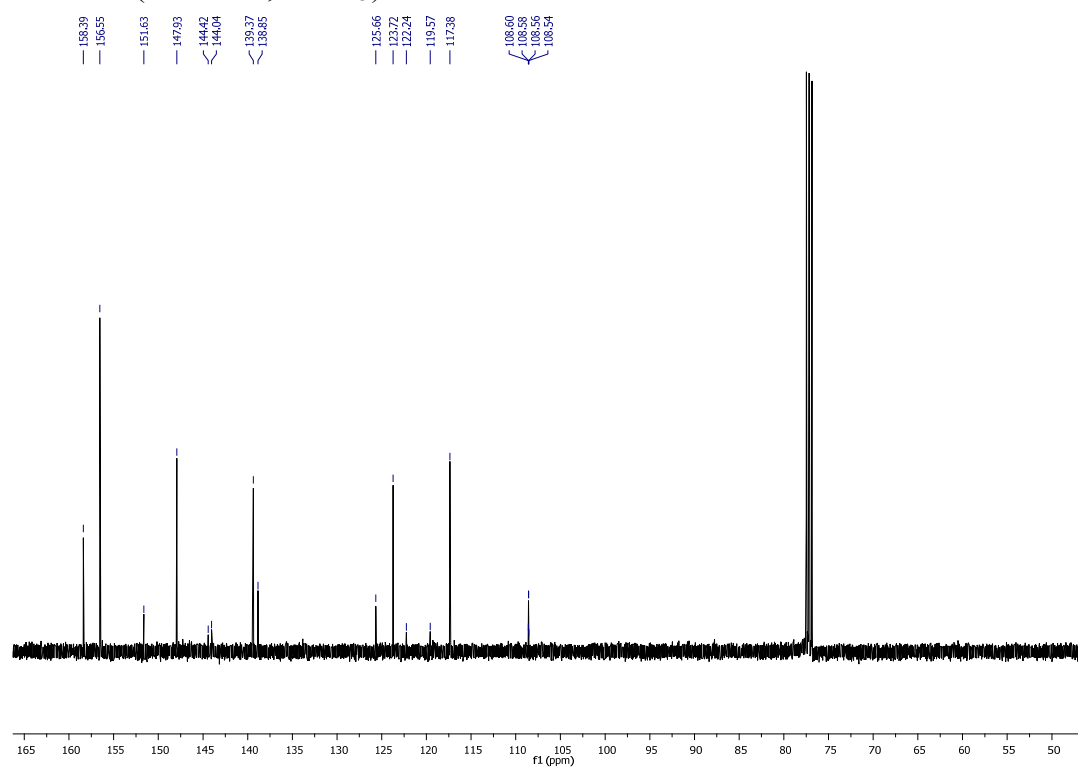
**3-[3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazol-5-yl]-5-methoxypyridine****(170)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

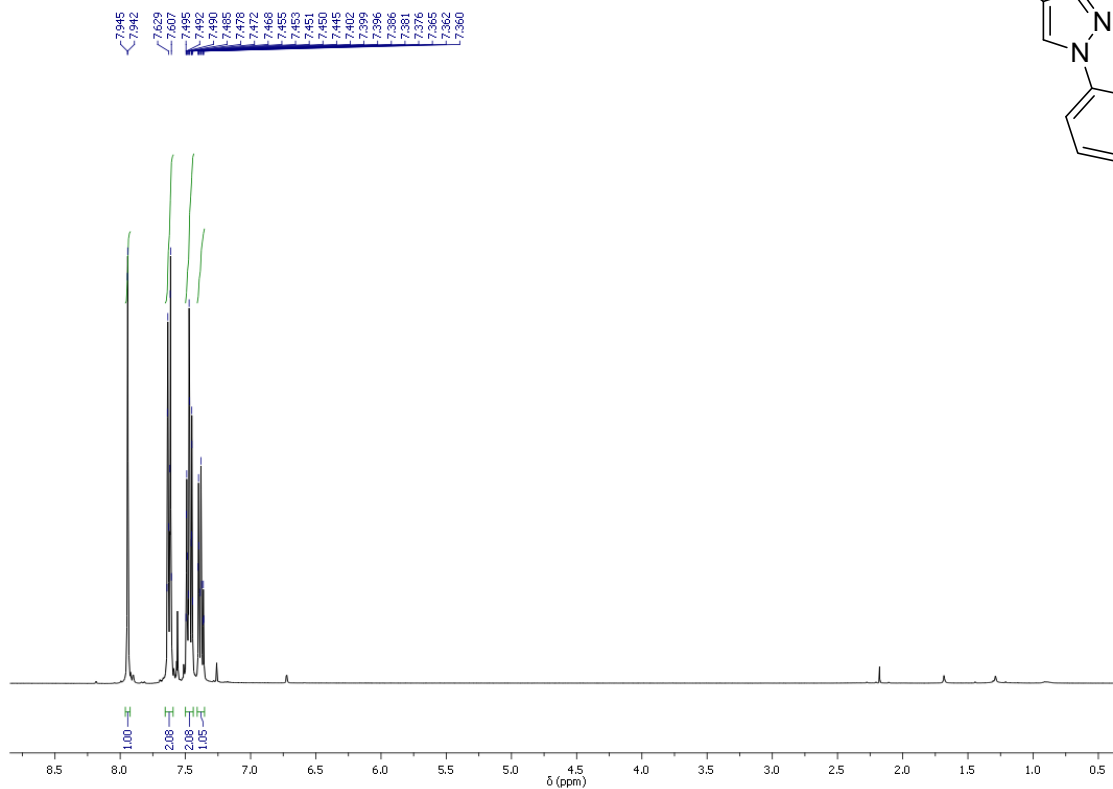
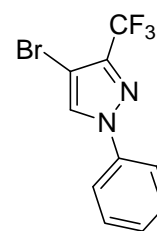
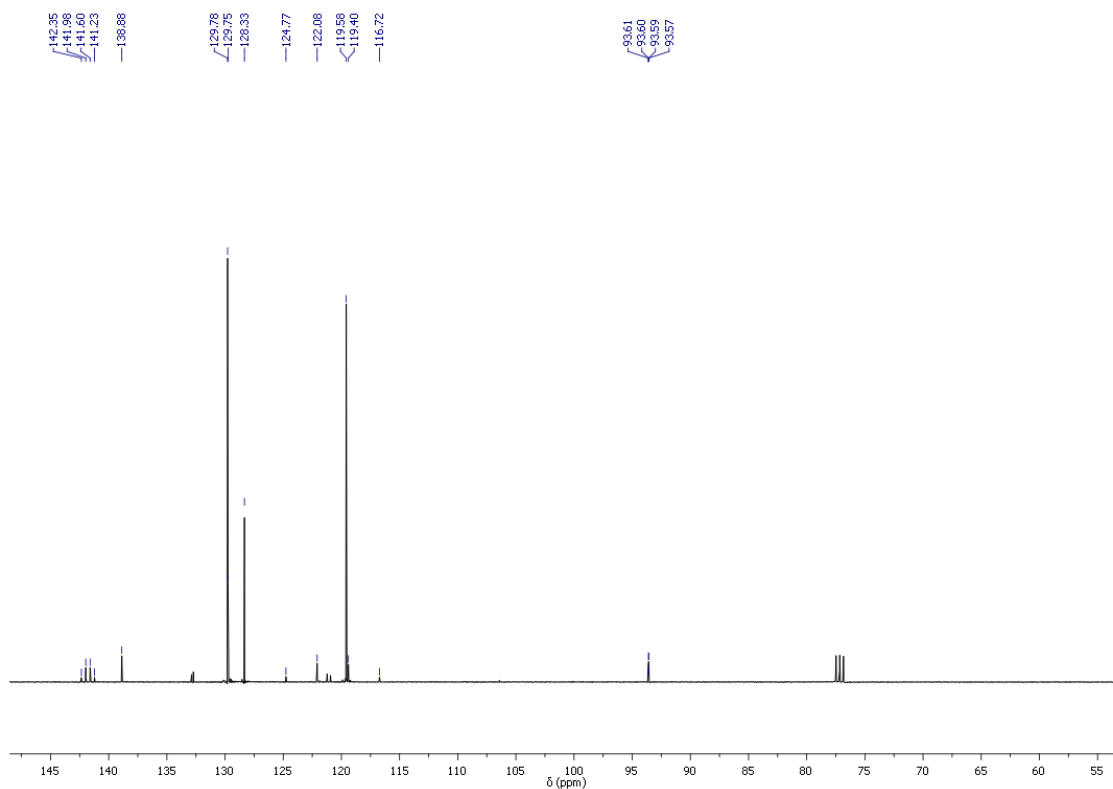
**5-[3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazol-5-yl]pyrimidine (171)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

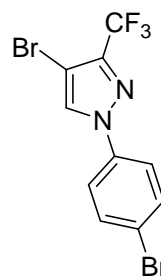
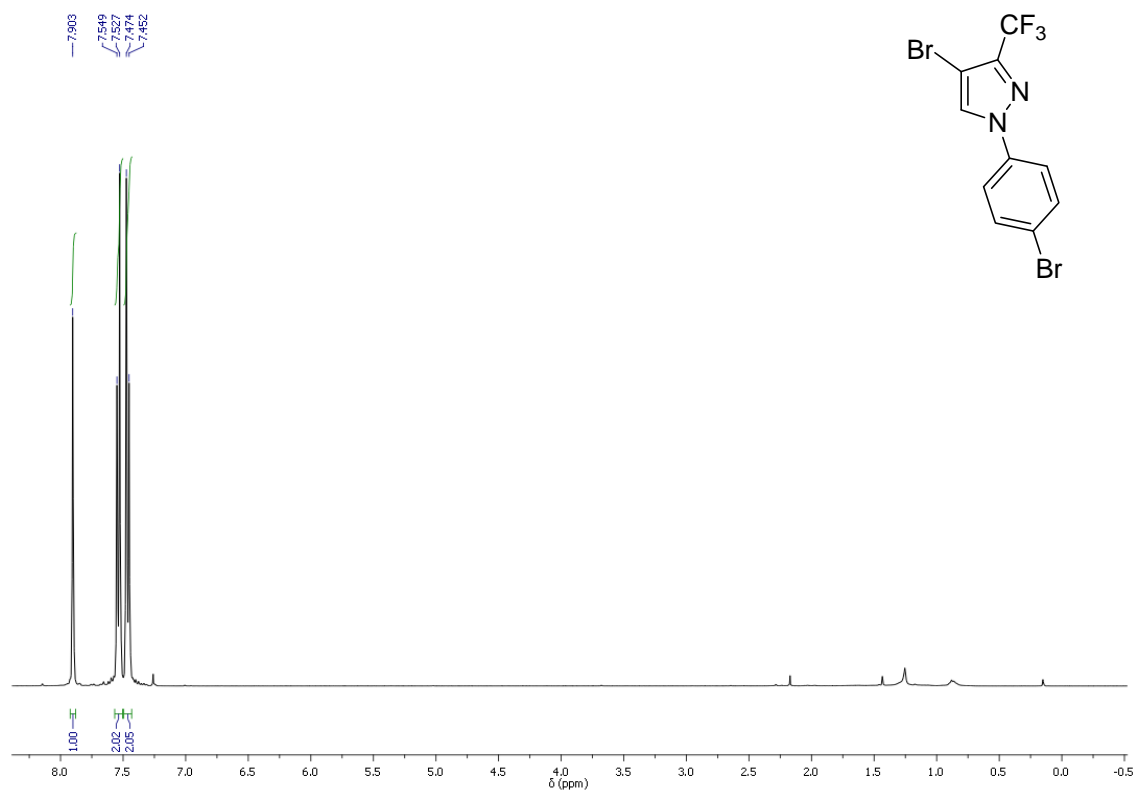
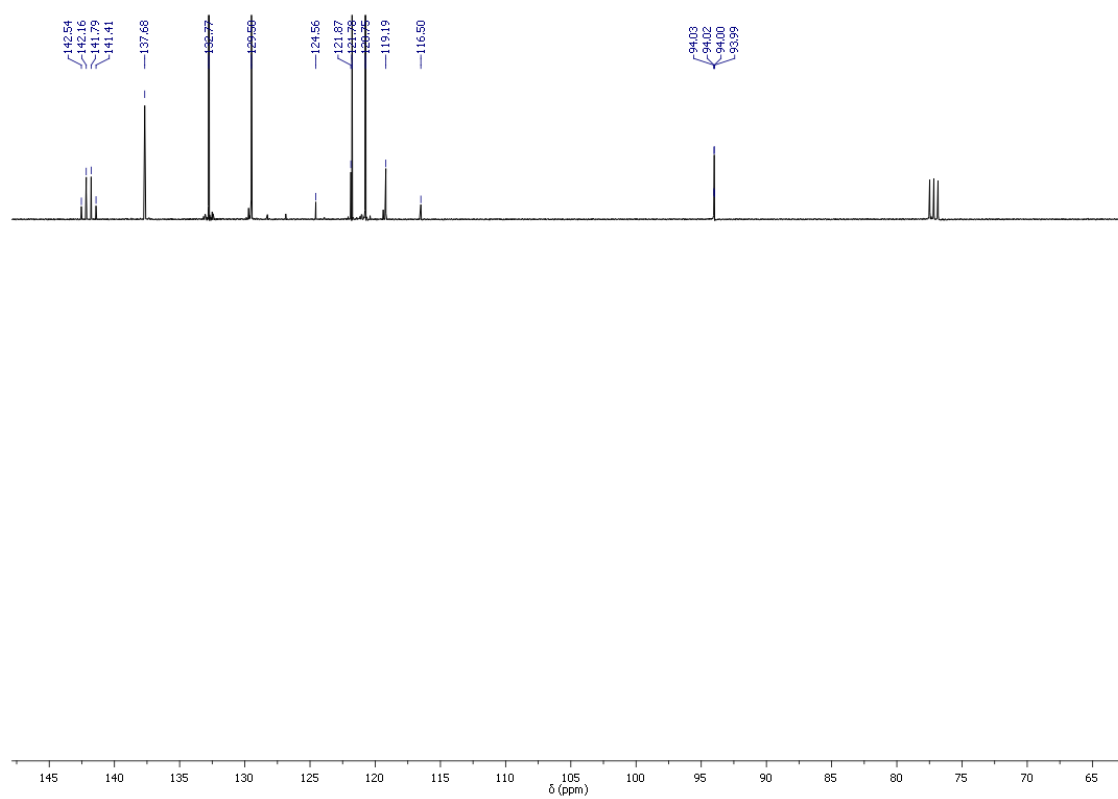
**5-[3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazol-5-yl]pyrimidin-2-amine****(172)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

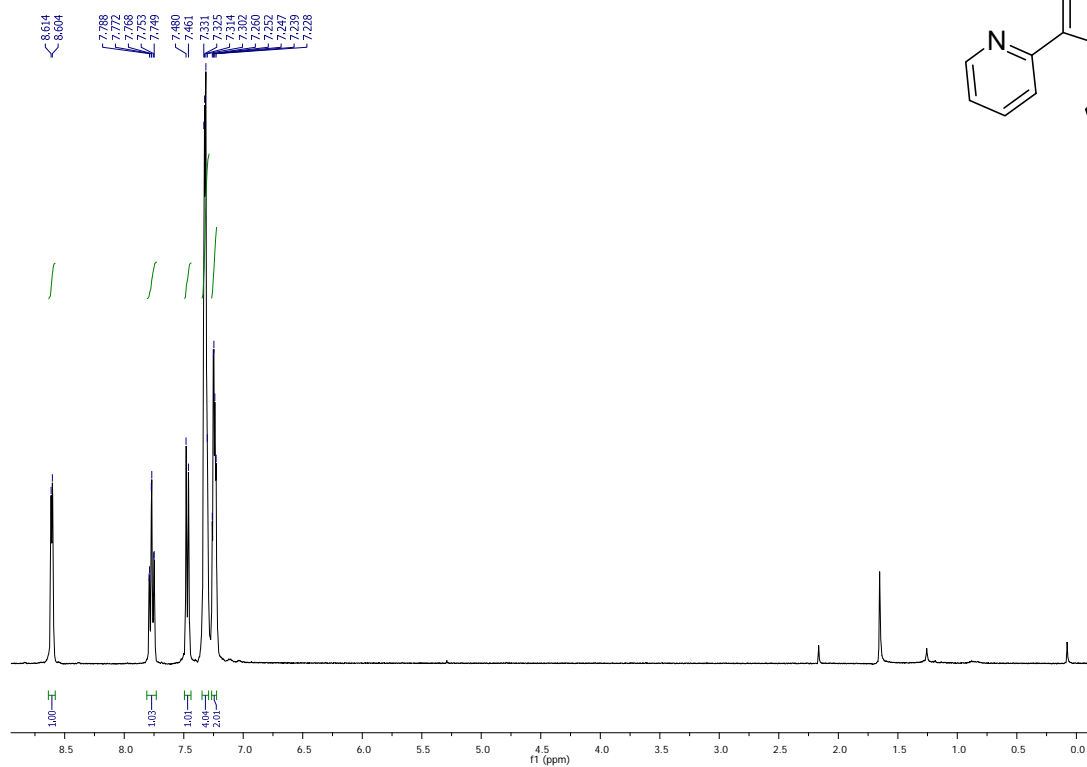
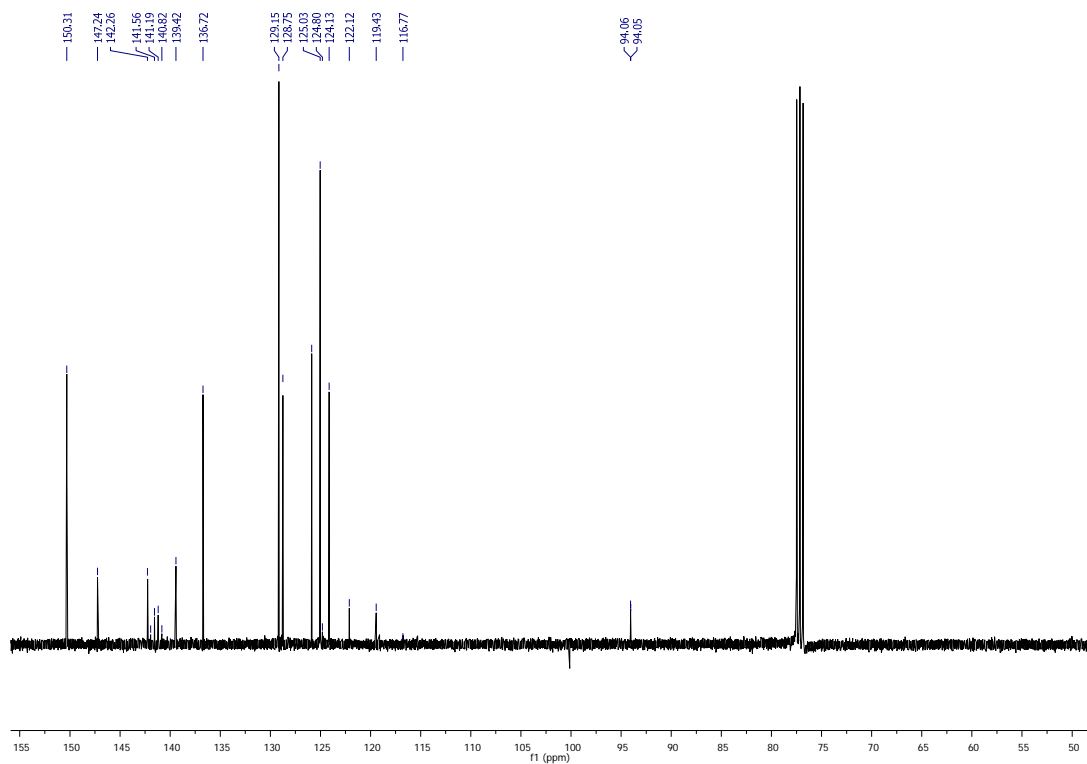
**3-(Trifluoromethyl)-1-(4-methoxyphenyl)-5-(thiophen-2-yl)-1H-pyrazole (173)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**2-(3-[Trifluoromethyl]-1-(pyridin-2-yl)-1H-pyrazol-5-yl)pyridine (174)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**5-[3-(Trifluoromethyl)-1-(pyridin-2-yl)-1H-pyrazol-5-yl]pyrimidine (175)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

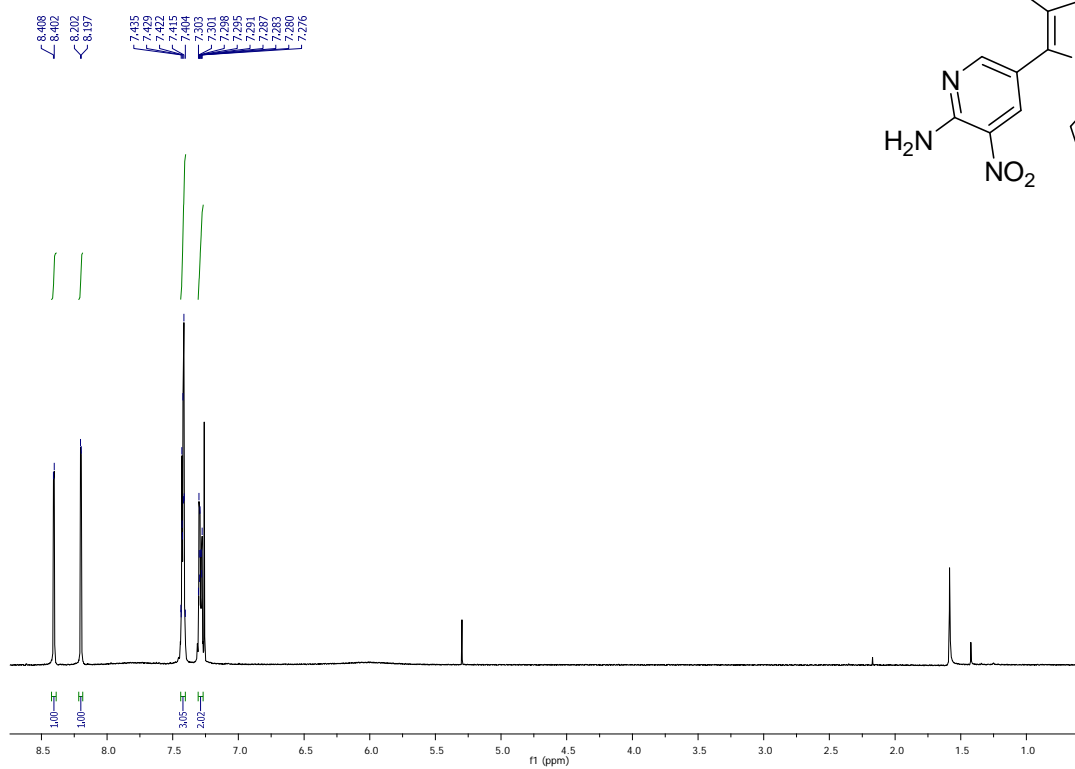
**4-Bromo-3-(trifluoromethyl)-1-phenyl-1H-pyrazole (177)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**4-Bromo-1-(4-bromophenyl)-3-(trifluoromethyl)-1H-pyrazole (179)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

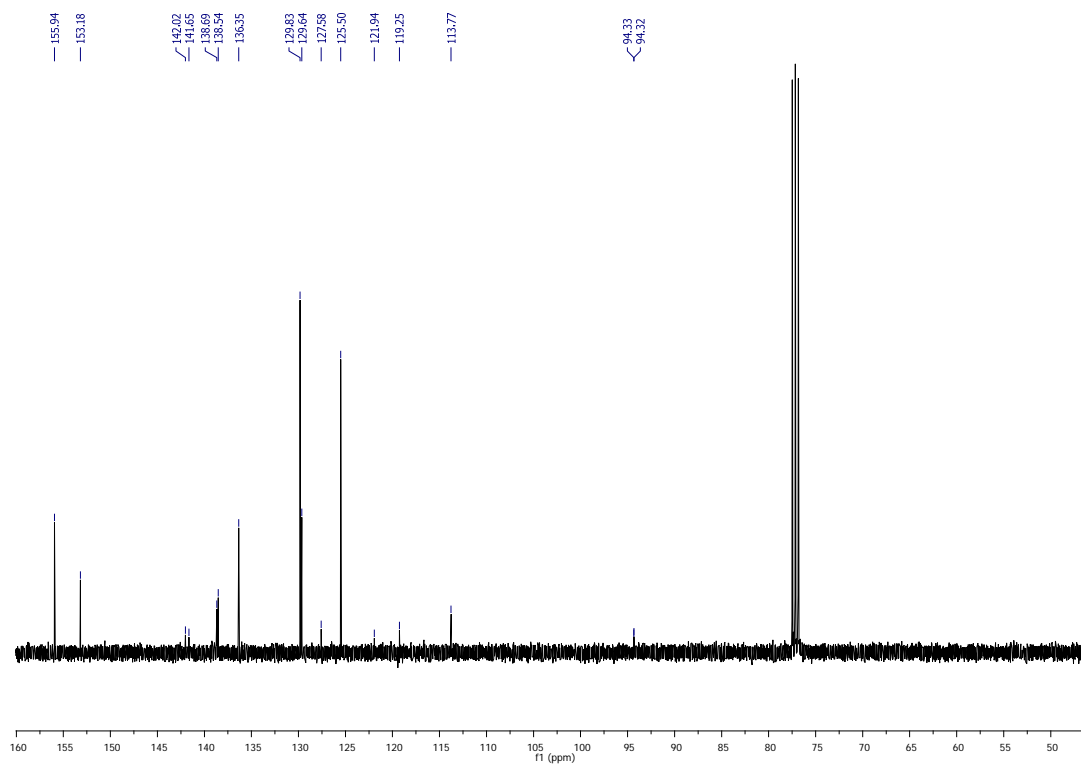
**2-[4-Bromo-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]pyridine (181)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

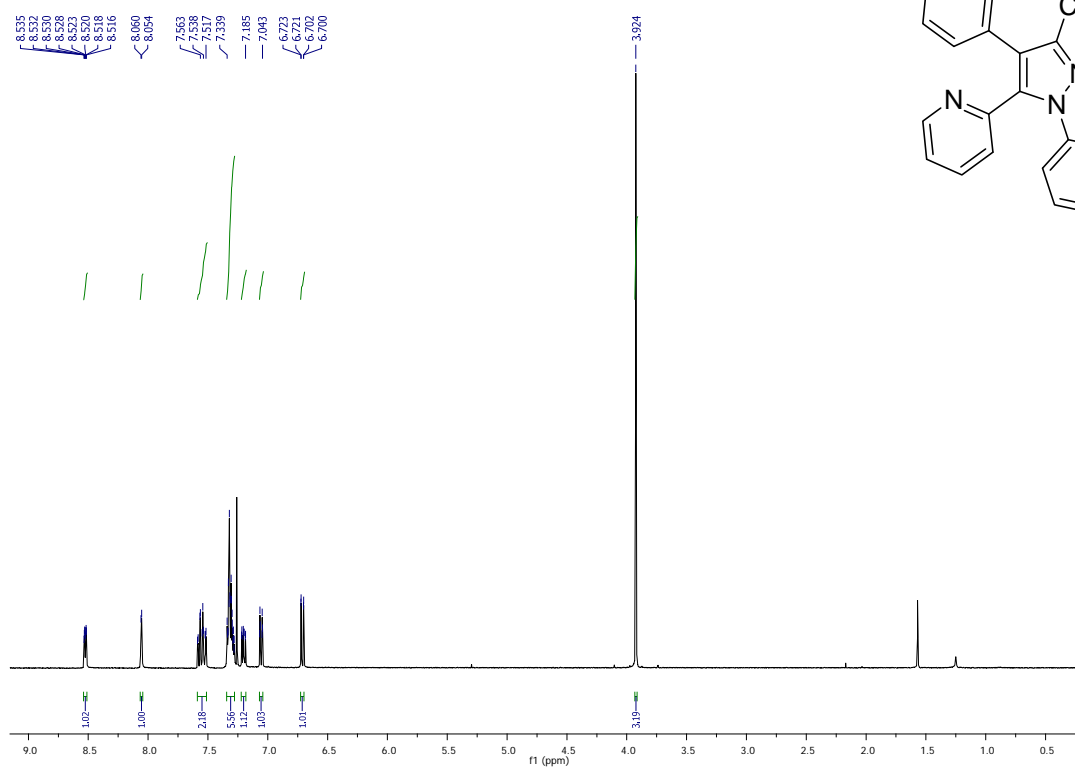
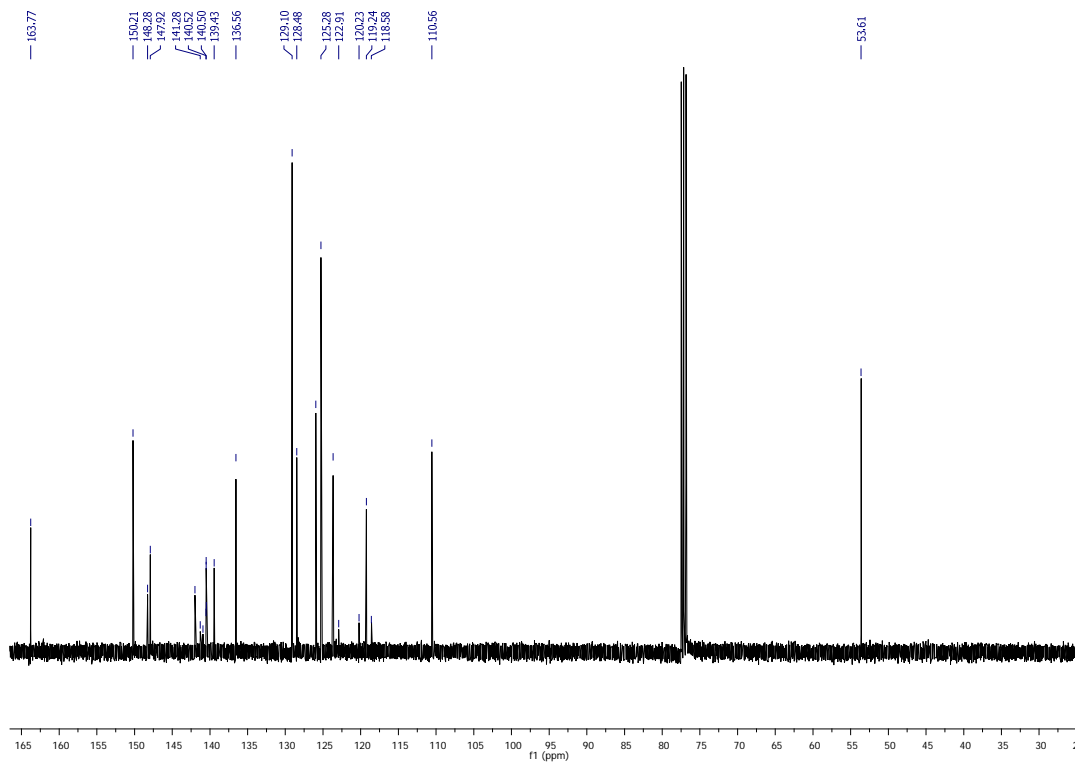
**5-[4-Bromo-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-yl]-3-nitropyridin-2-amine  
(182)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

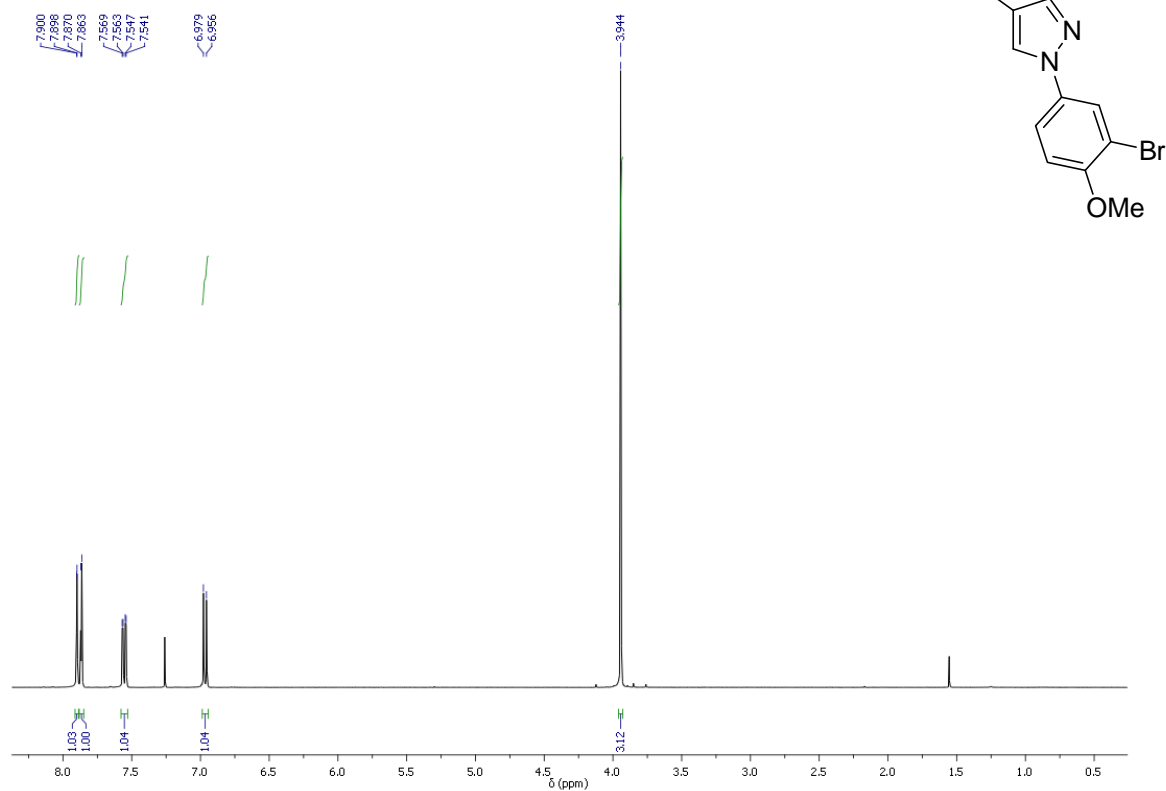
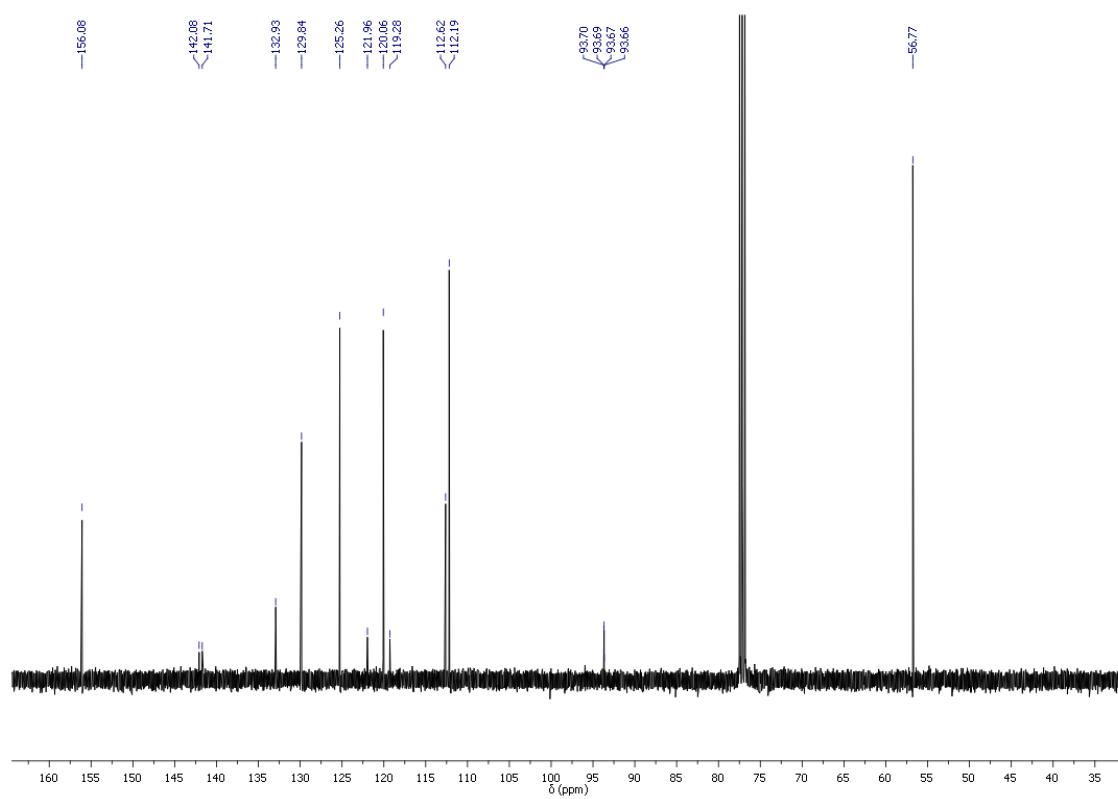


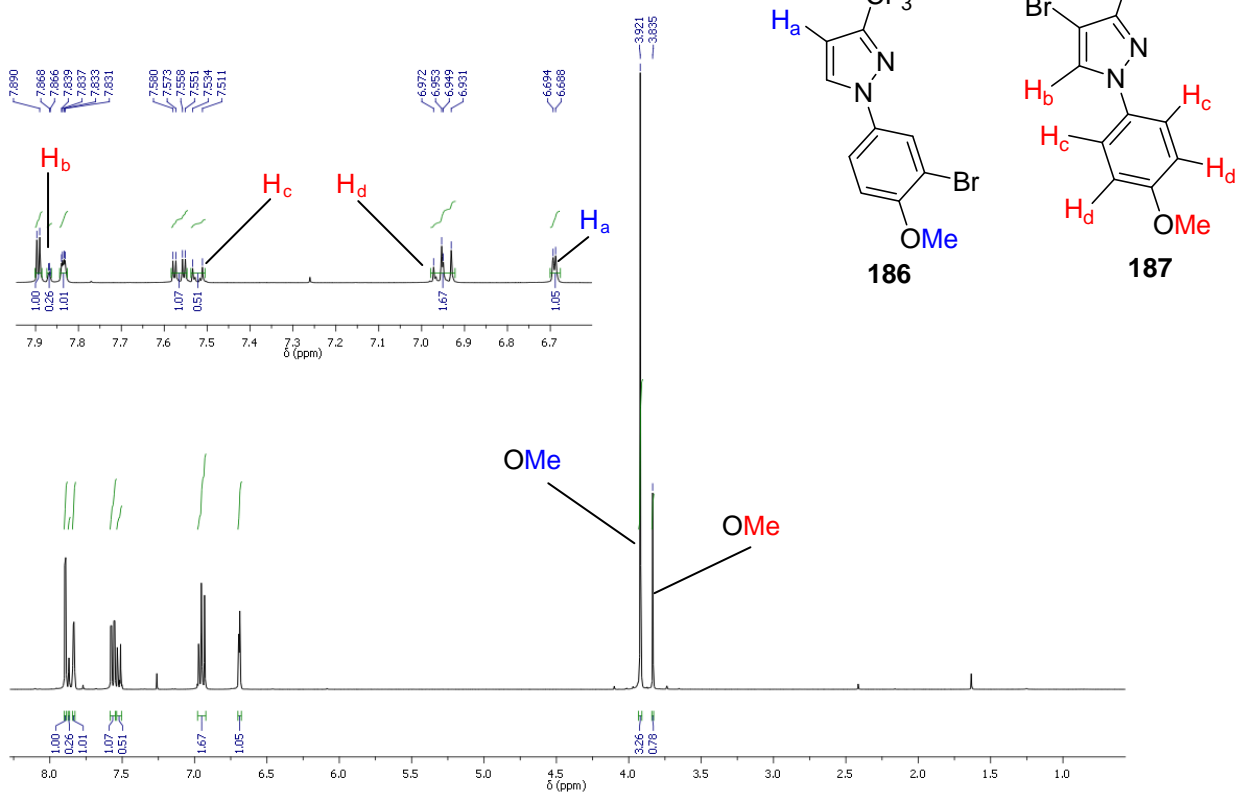
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

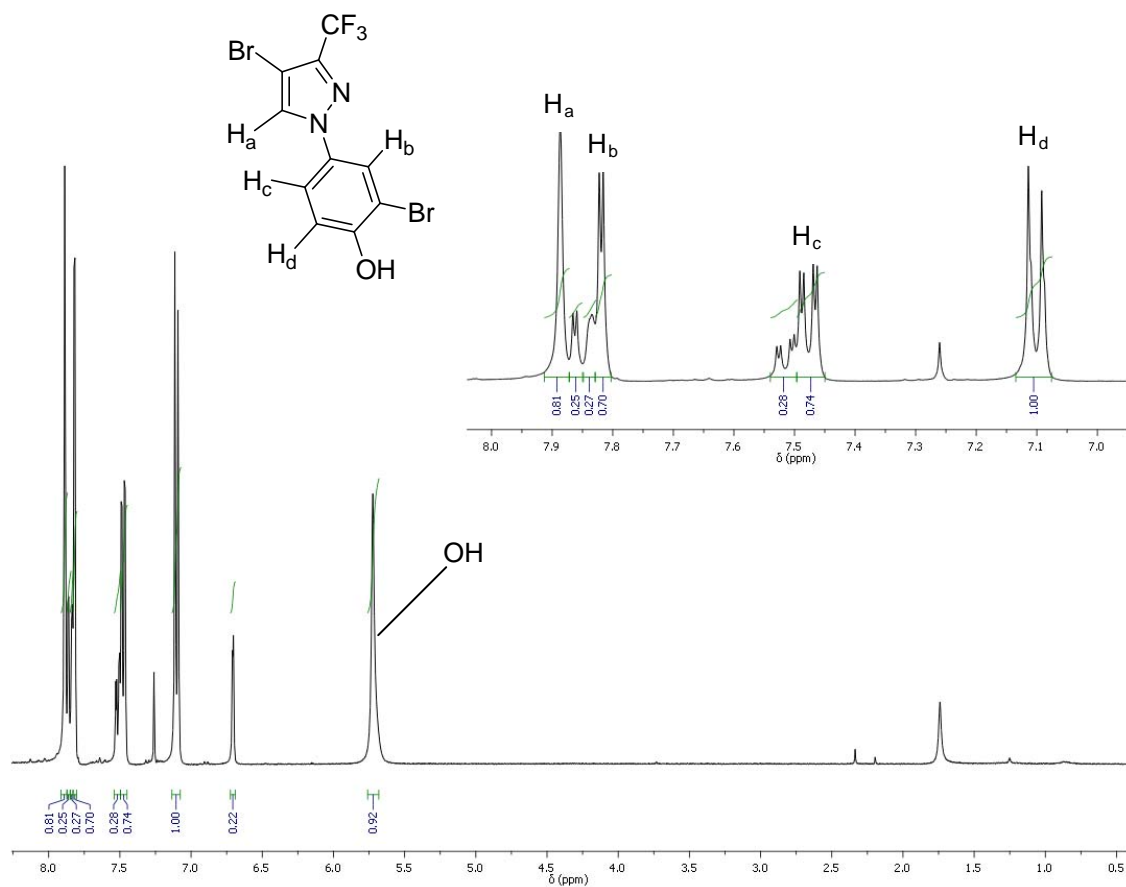


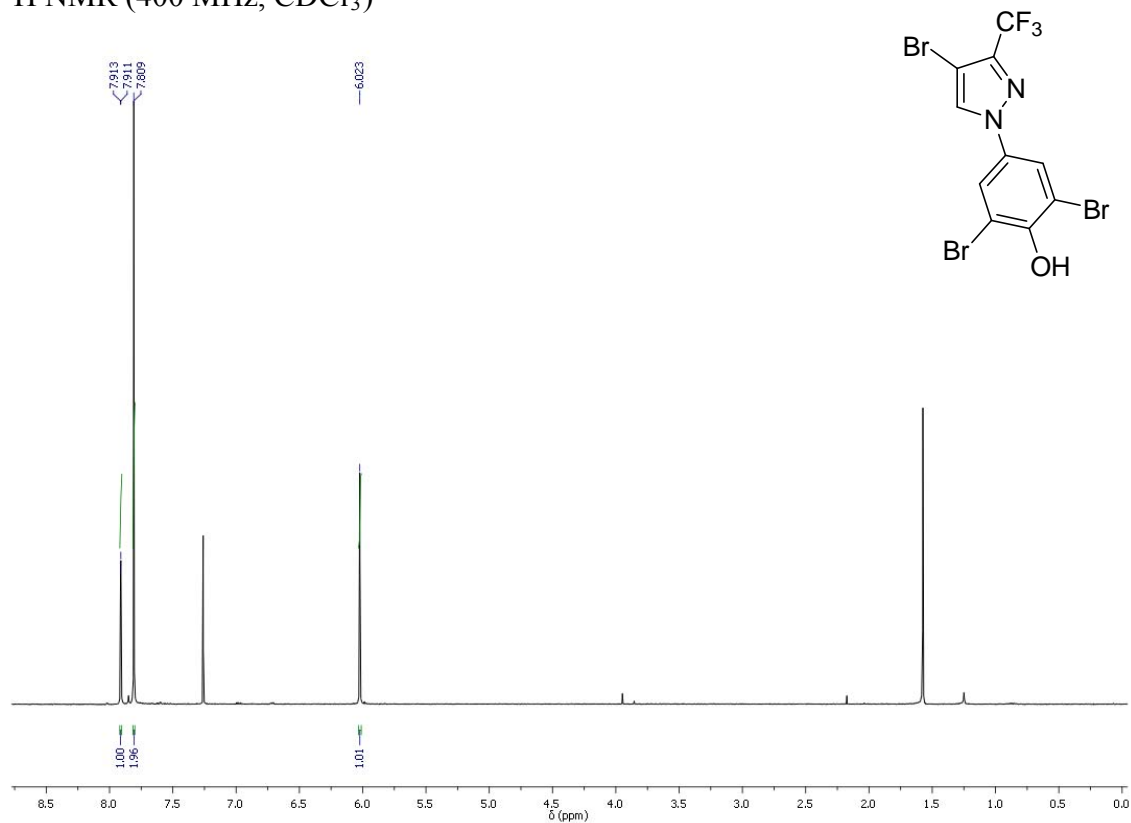
**2-[3-(Trifluoromethyl)-4-(6-methoxypyridin-3-yl)-1-phenyl-1H-pyrazol-5-yl]pyridine (183)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



**4-Bromo-1-(3-bromo-4-methoxyphenyl)-3-(trifluoromethyl)-1H-pyrazole (185)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**1-(3-bromo-4-methoxyphenyl)-3-(trifluoromethyl)-1H-pyrazole (186)****4-bromo-3-(trifluoromethyl)-1-(4-methoxyphenyl)-1H-pyrazole (187)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

**2-Bromo-4-(4-bromo-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenol (188)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

**2,6-Dibromo-4-(4-bromo-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenol (189)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)