

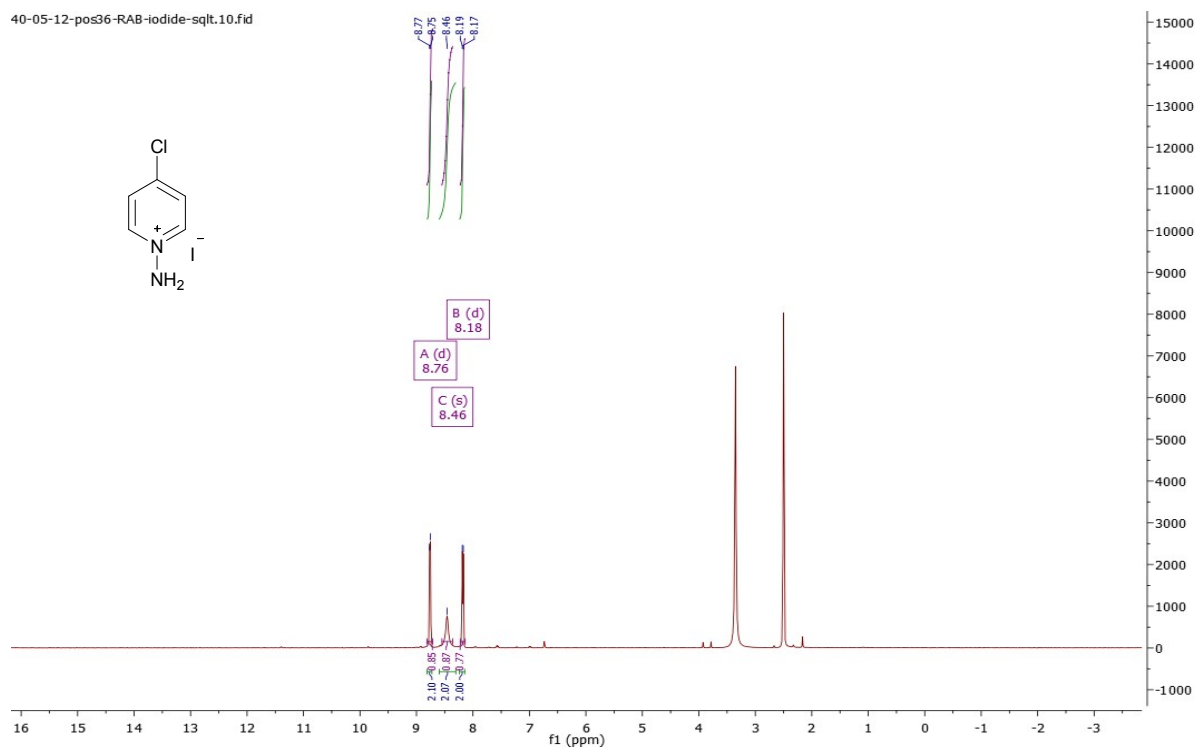
## Supporting Information

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

## 1-Amino-4-chloro-pyridinium iodide 1

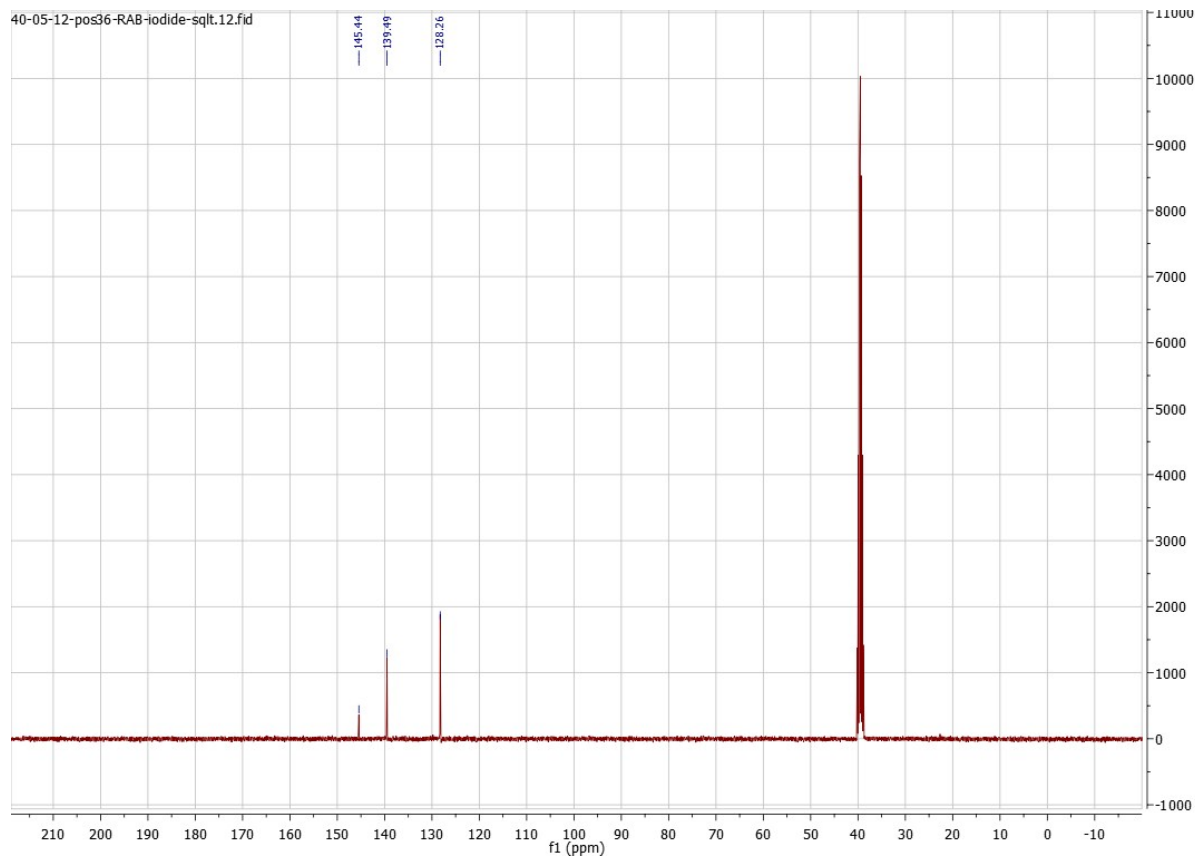
$^1\text{H}$  NMR (250 MHz,  $\text{DMSO-}d_6$ )

40-05-12-pos36-RAB-iodide-sqlt.10.fid



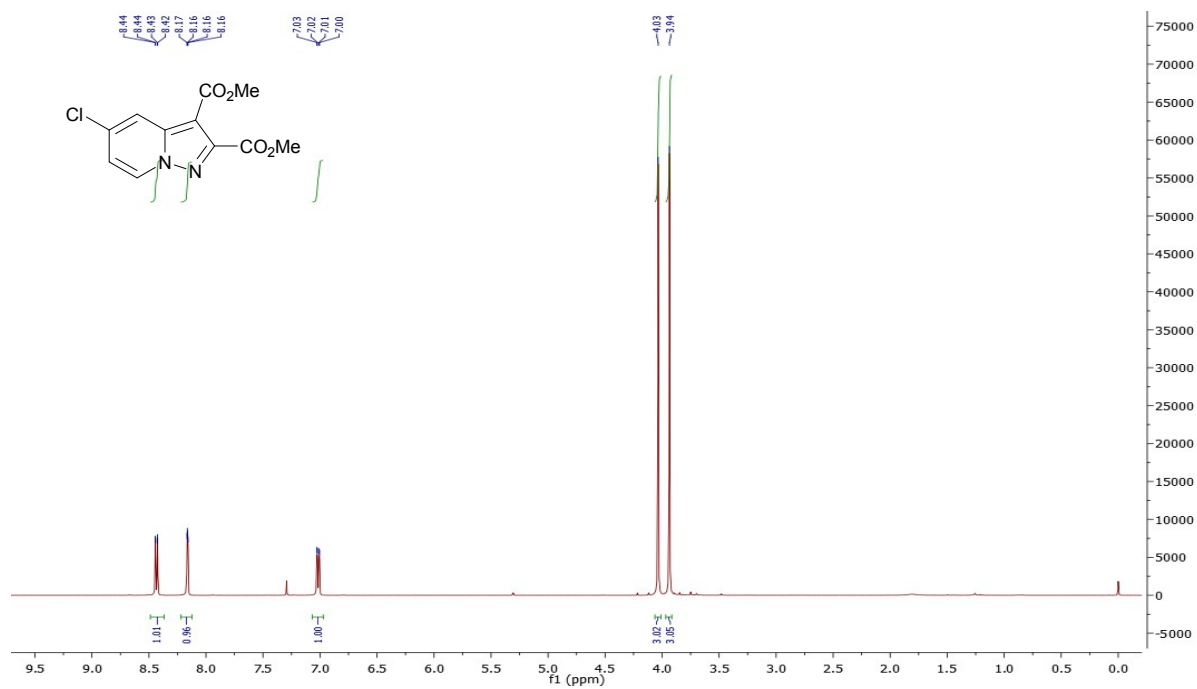
$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )

40-05-12-pos36-RAB-iodide-sqlt.12.fid

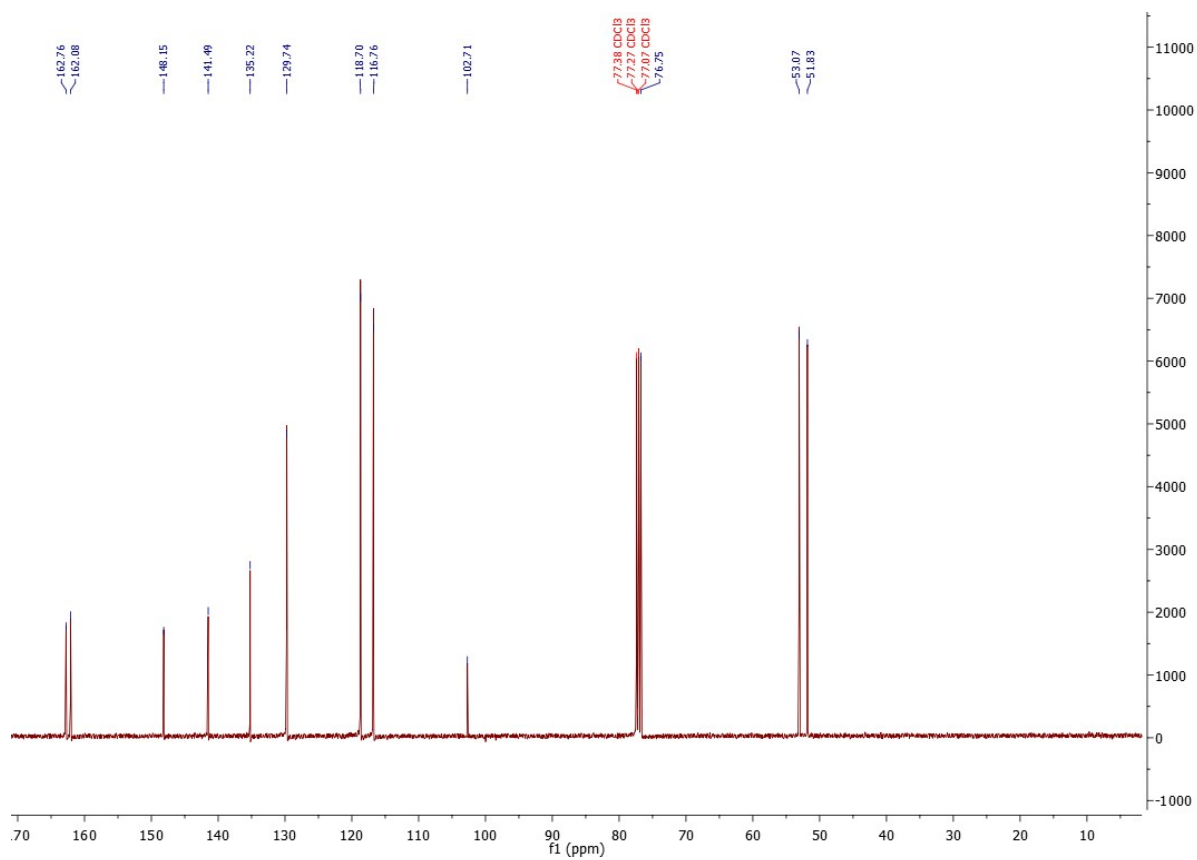


## Dimethyl 5-chloropyrazolo[1,5- $\alpha$ ]pyridine-2,3-dicarboxylate 2

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

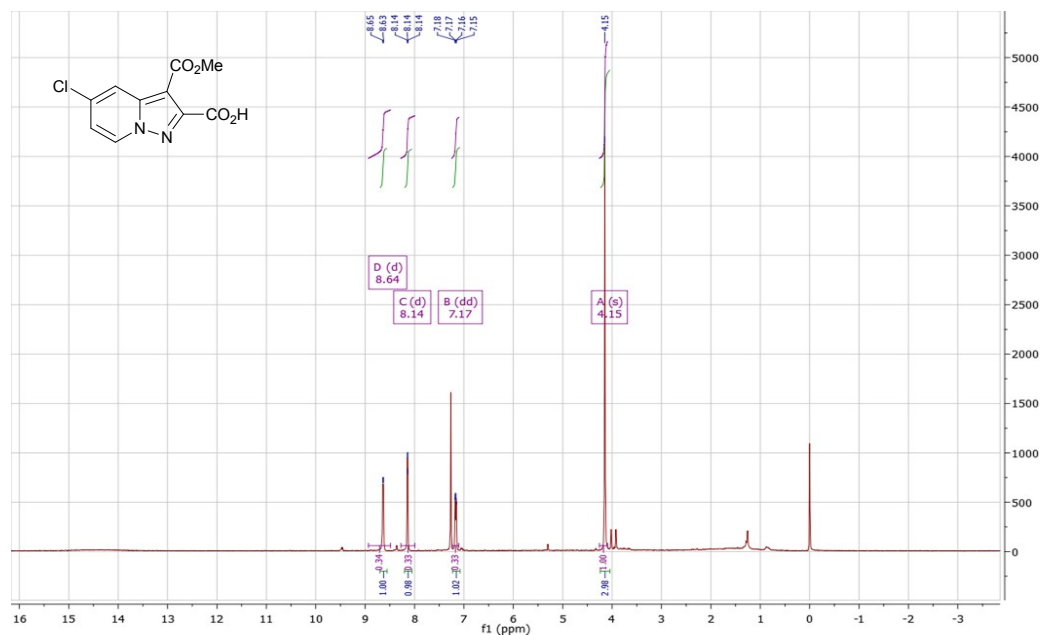


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

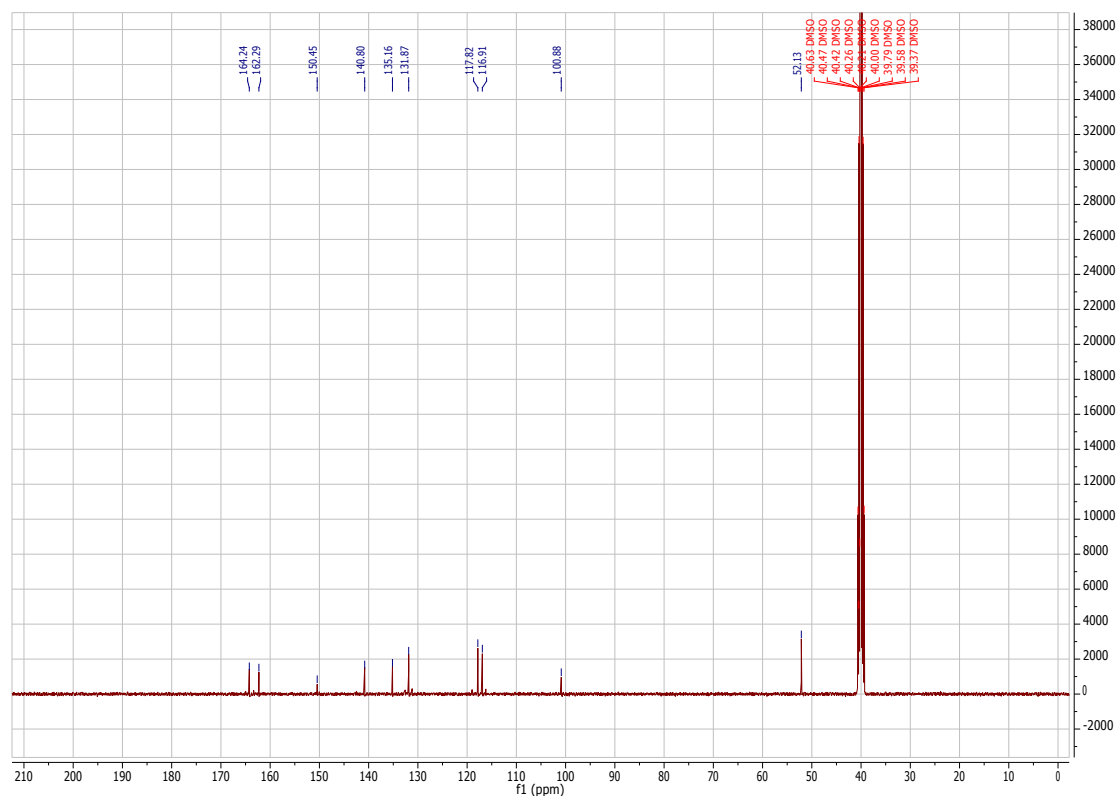


# 5-Chloro-3-(methoxycarbonyl)pyrazolo[1,5-*a*]pyridine-2-carboxylic acid **3**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

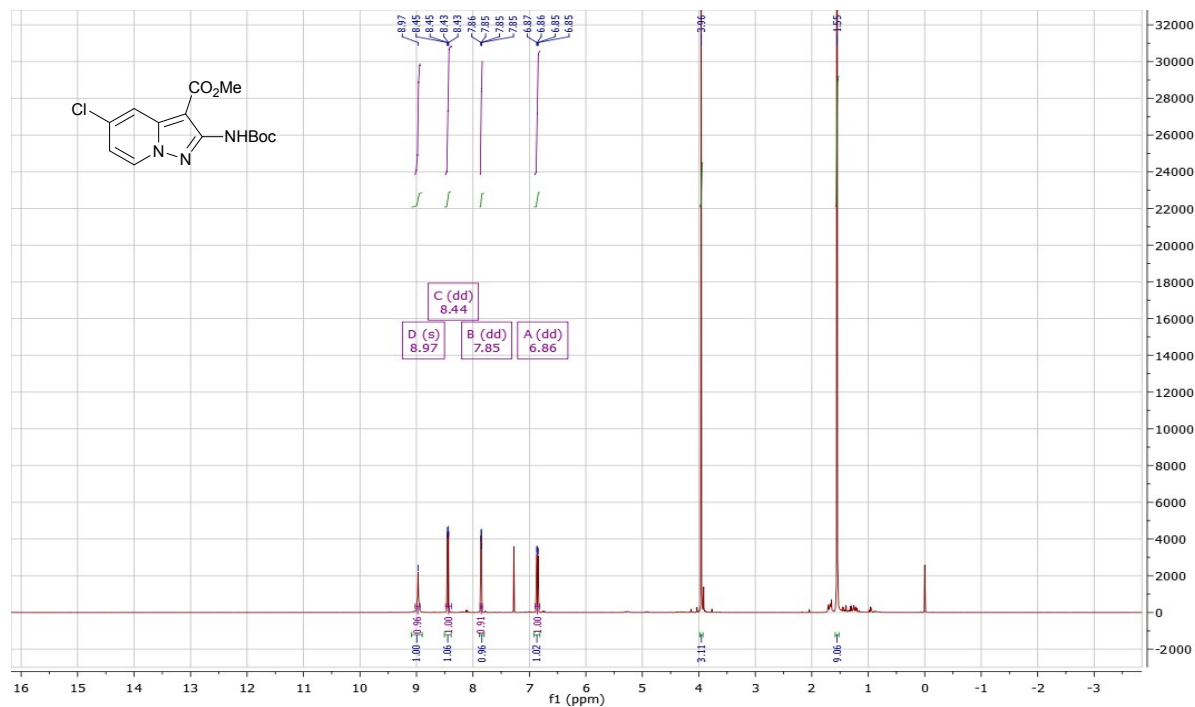


<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).

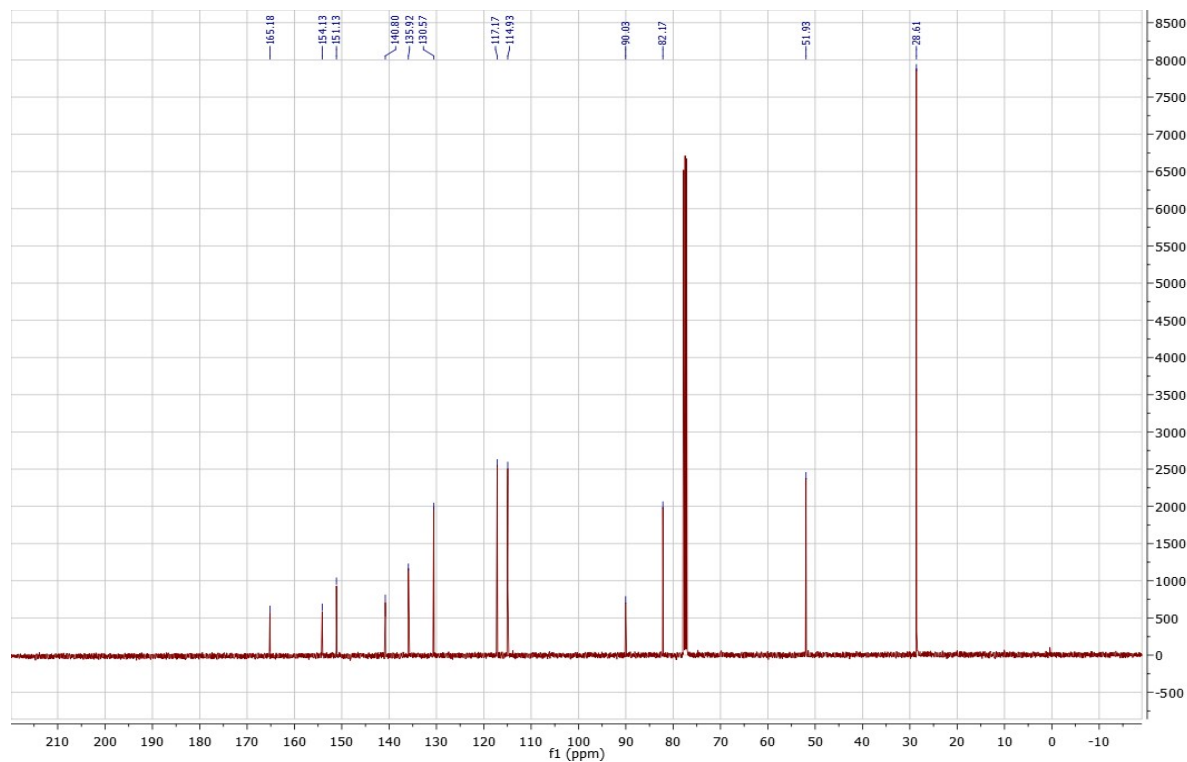


**Methyl 2-((*tert*-butoxycarbonyl)amino)-5-chloropyrazolo[1,5-*a*]pyridine-3-carboxylate 4**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

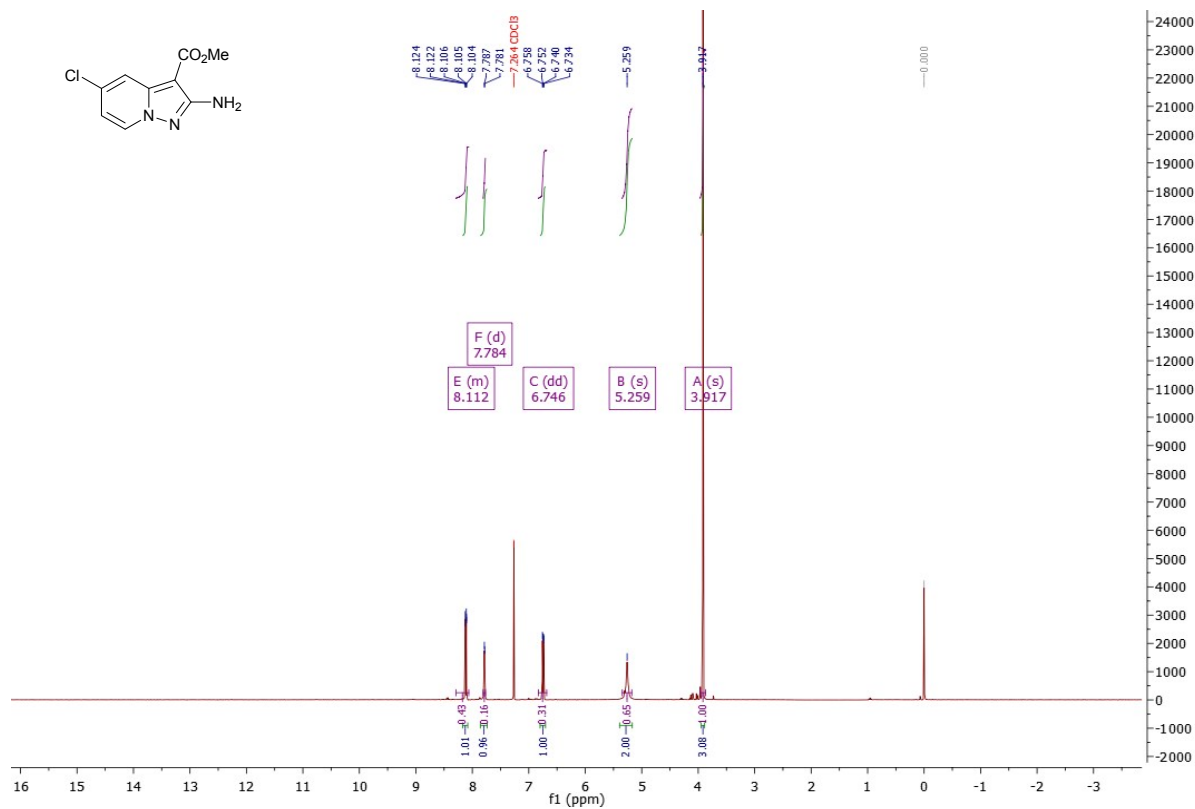


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).

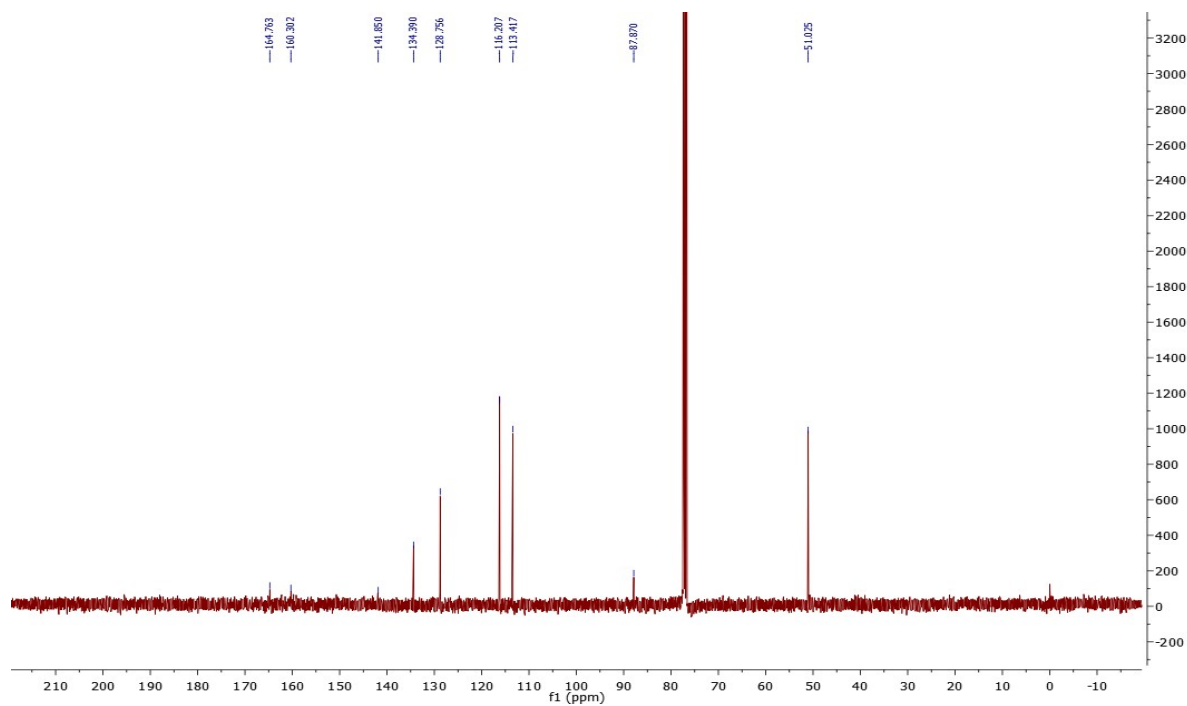


Methyl 2-amino-5-chloropyrazolo[1,5-a]pyridine-3-carboxylate 5

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

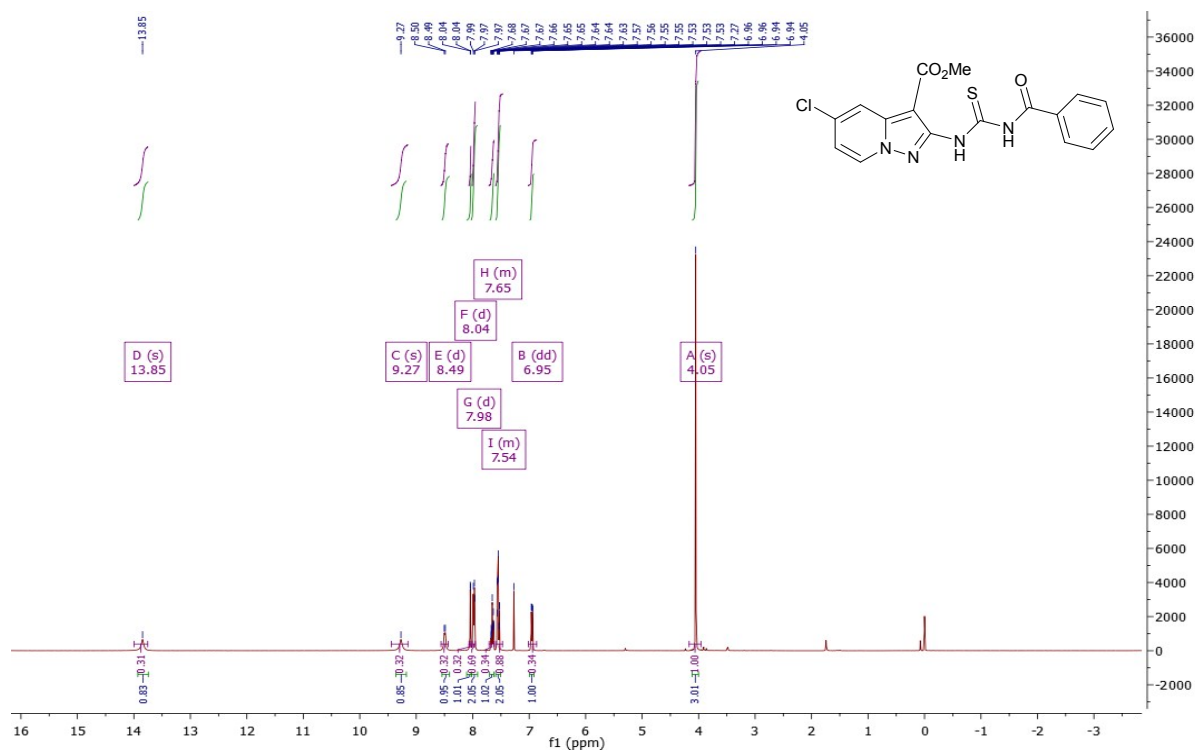


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).

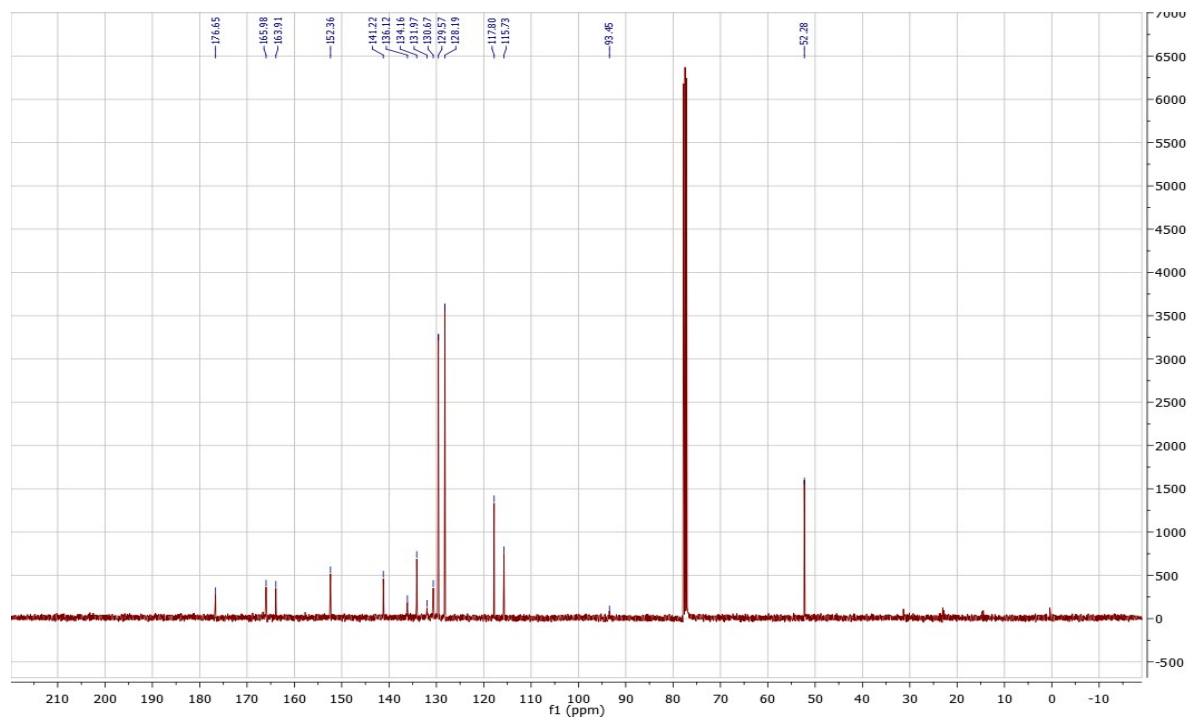


# Methyl 2-(3-benzoylthioureido)-5-chloropyrazolo[1,5-a]pyridine-3-carboxylate 6

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

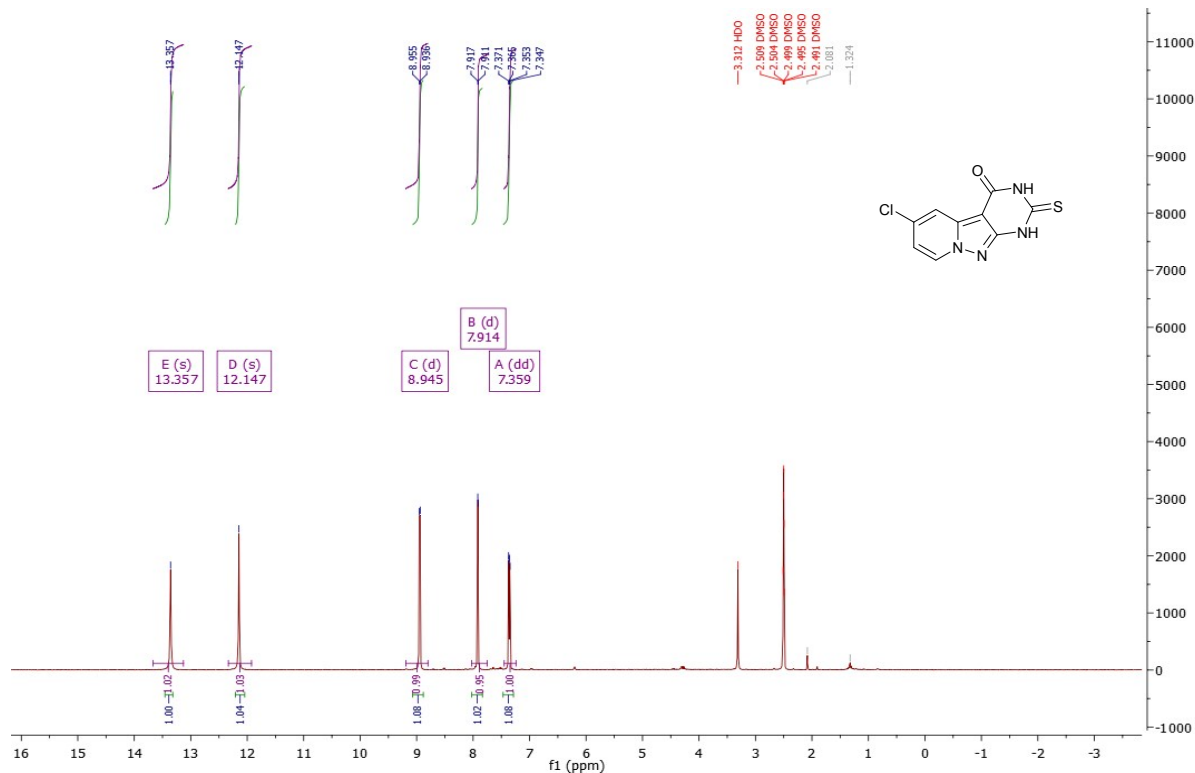


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).

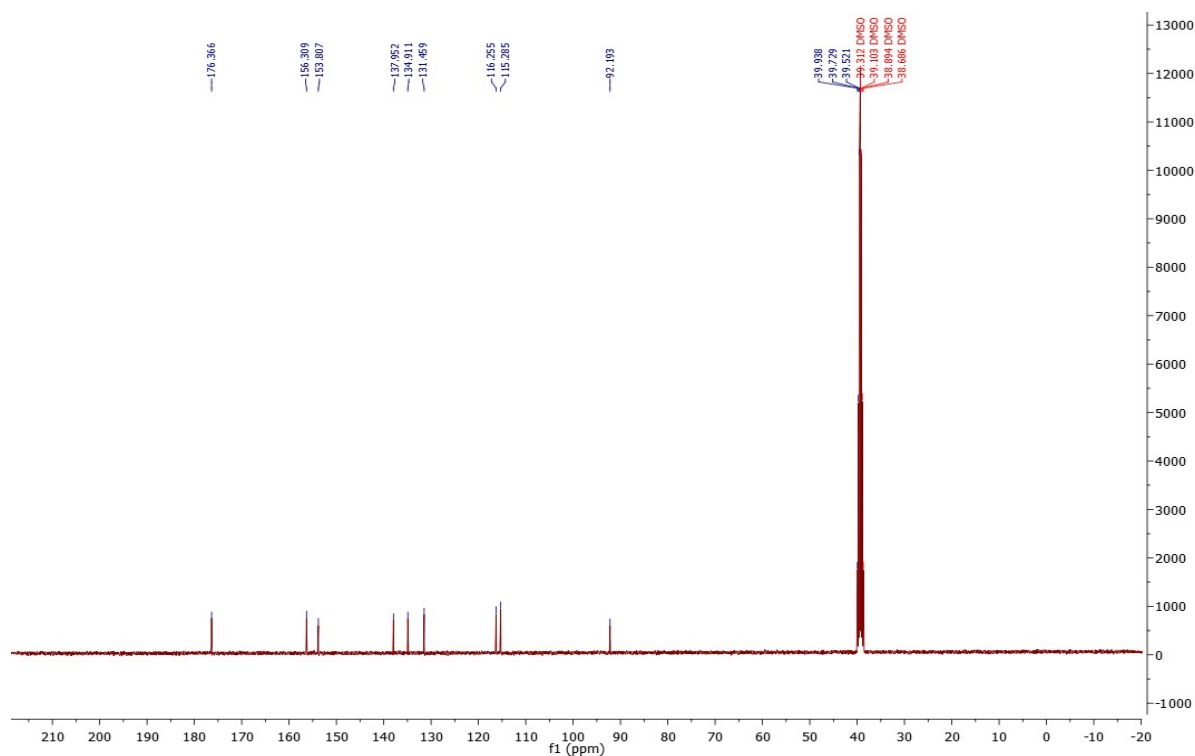


6-Chloro-2-thioxo-2,3-dihydropyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidin-4(1*H*)-one 7

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



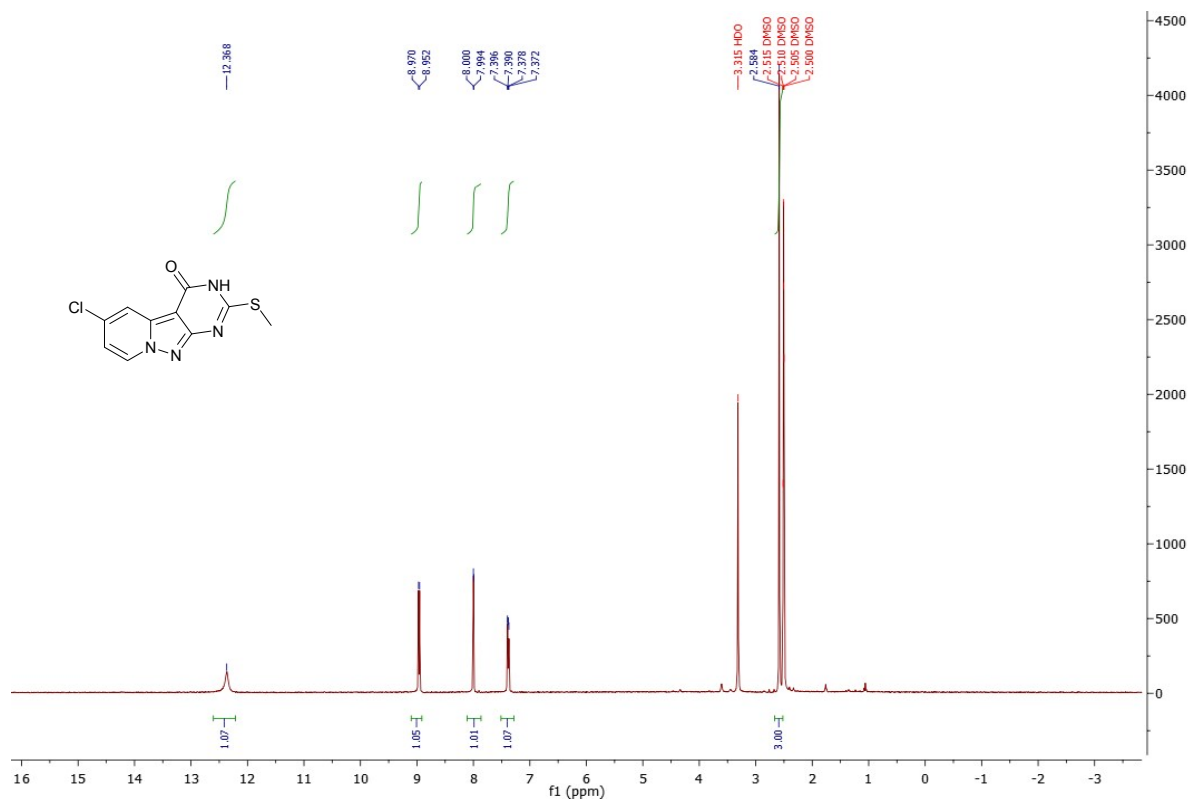
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).



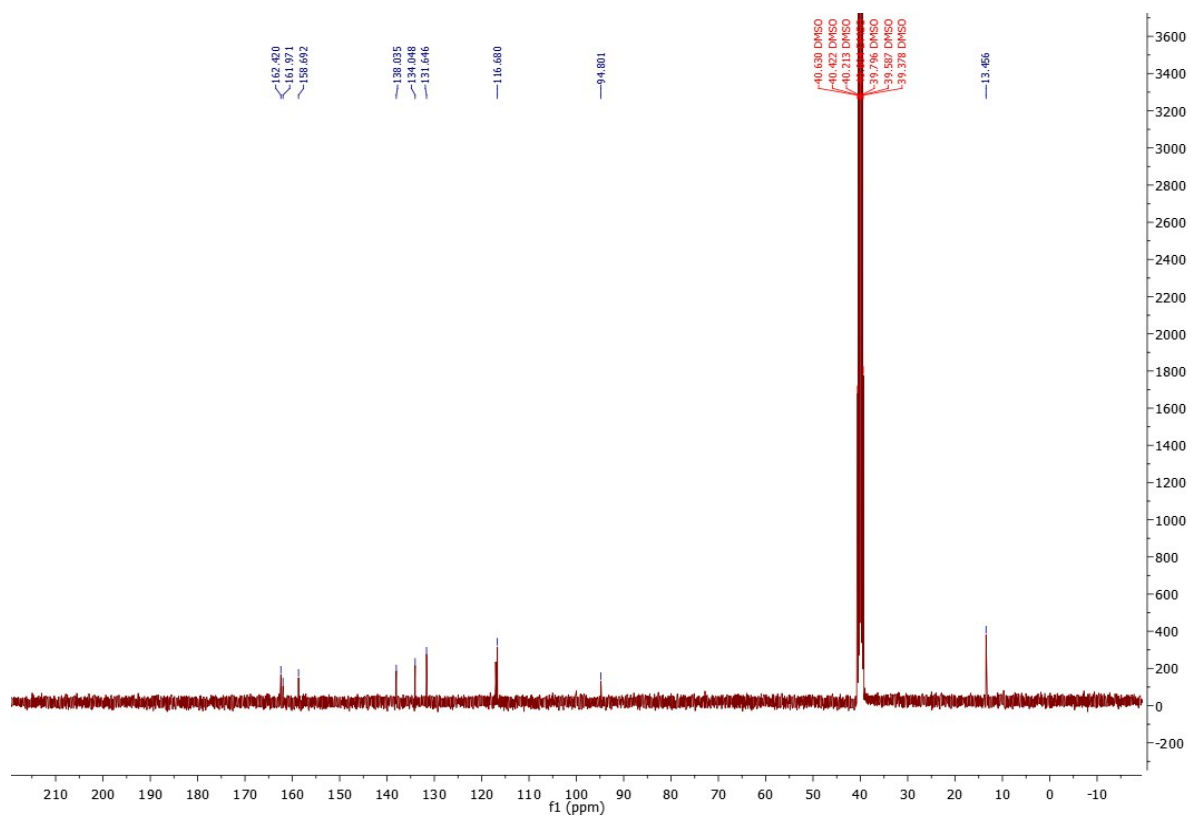


6-Chloro-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4(3H)-one 8

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

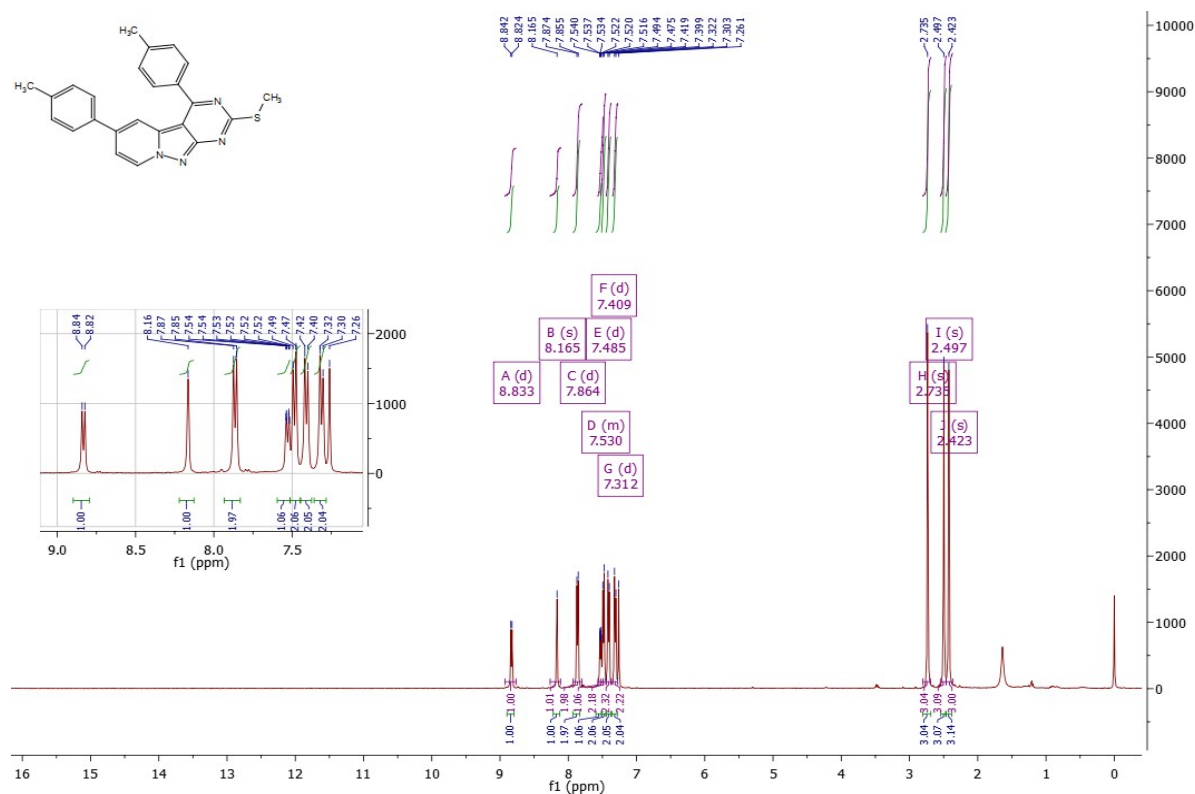


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ).

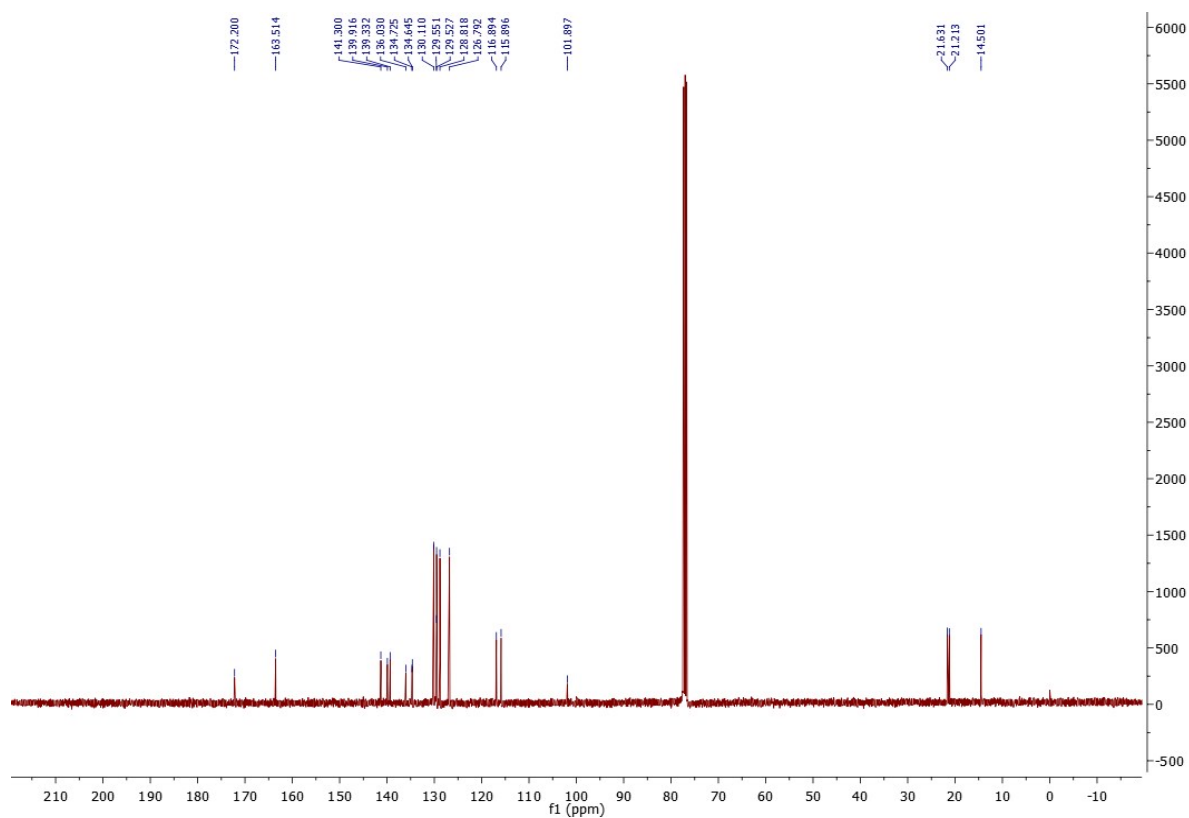


**2-(Methylthio)-4,6-di-*p*-tolylpyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 9**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).

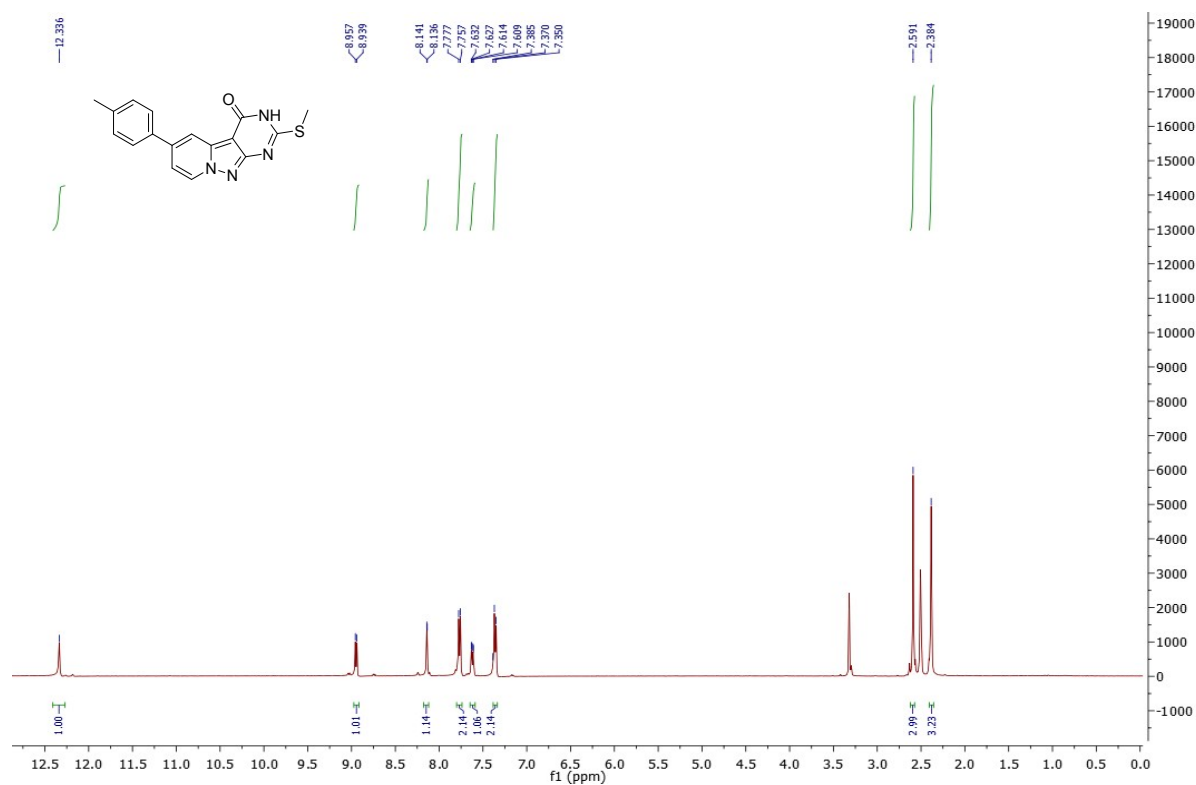


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).

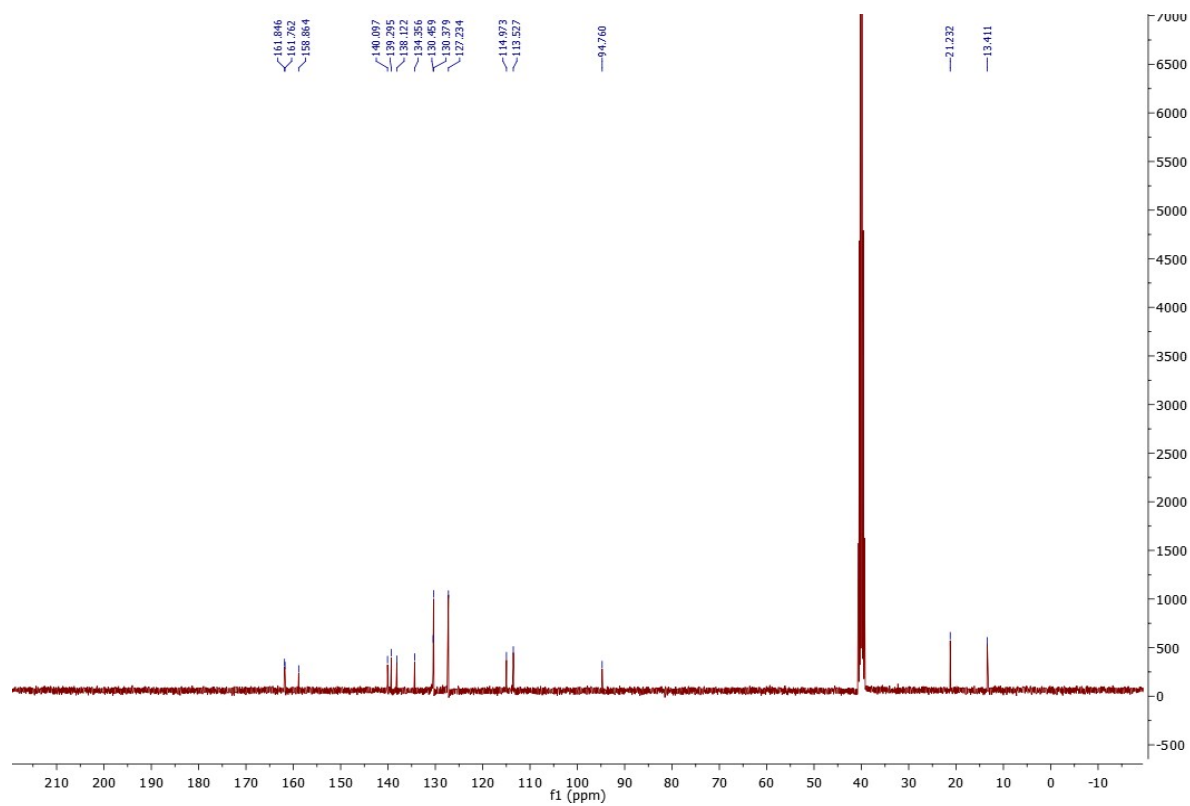


2-(Methylthio)-6-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidin-4(3*H*)-one 10

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

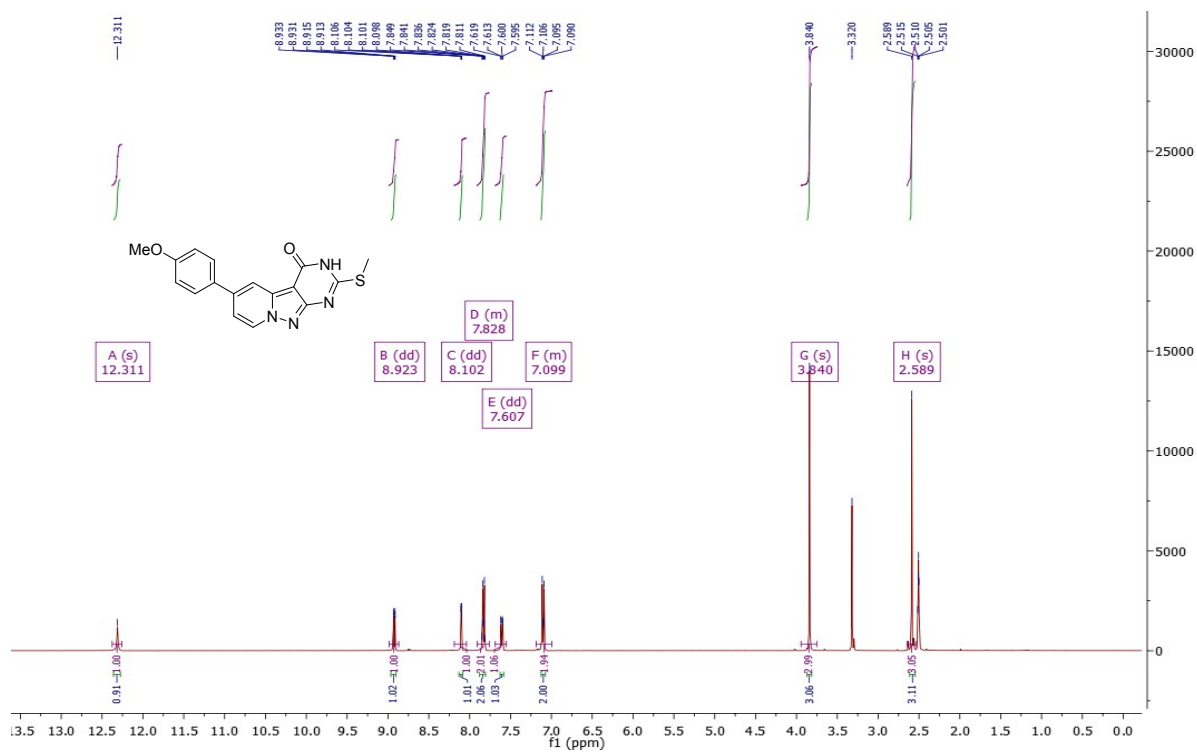


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ).

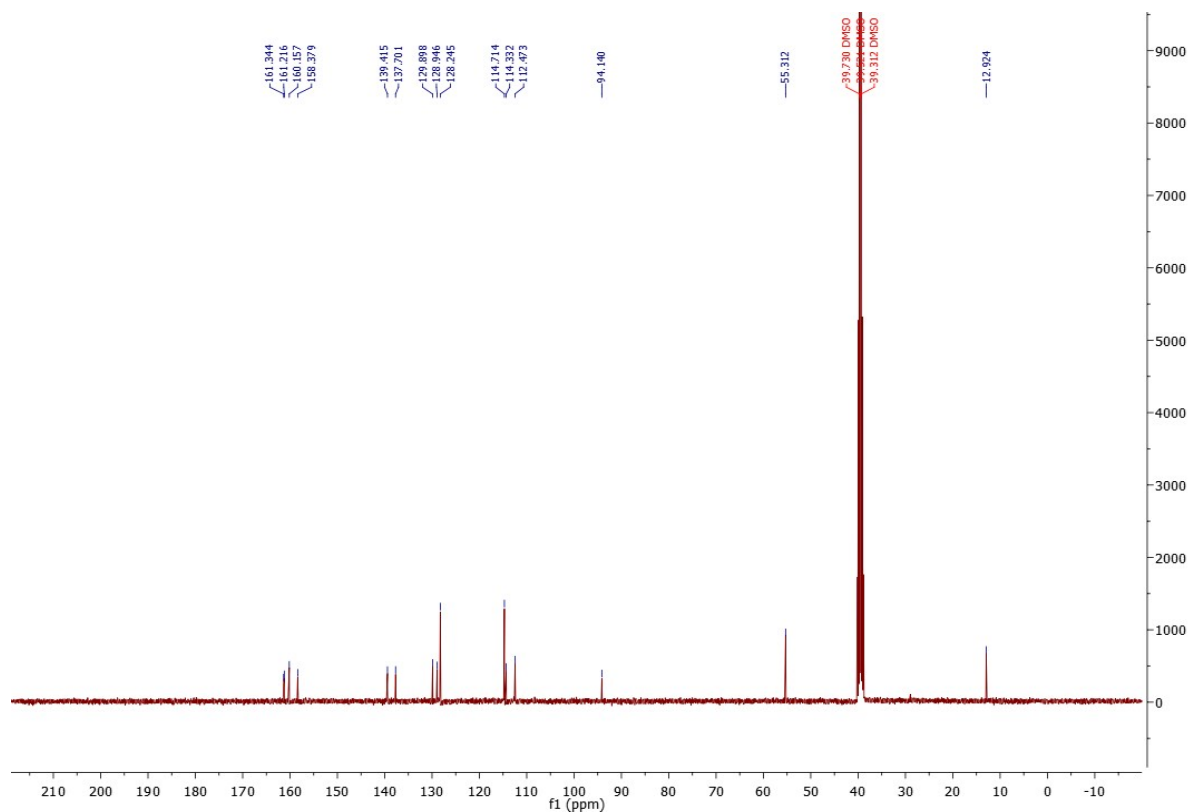


6-(4-Methoxyphenyl)-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4(3H)-one 11

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

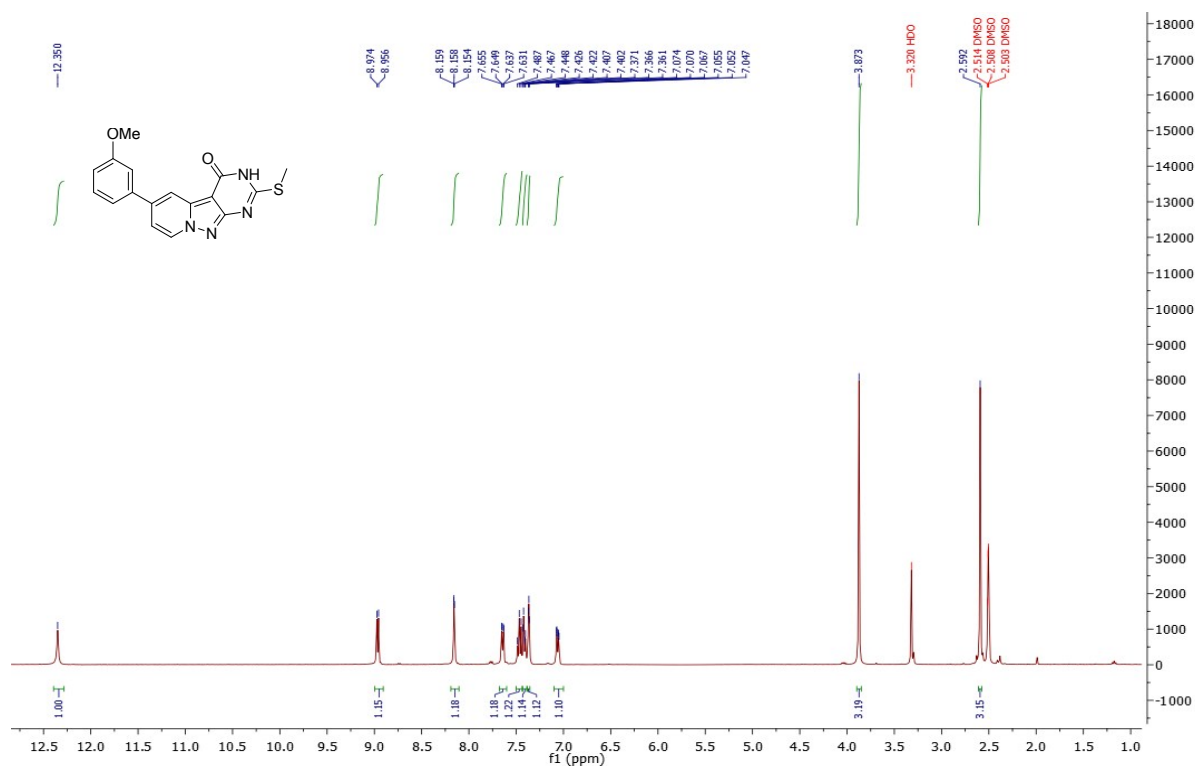


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ).

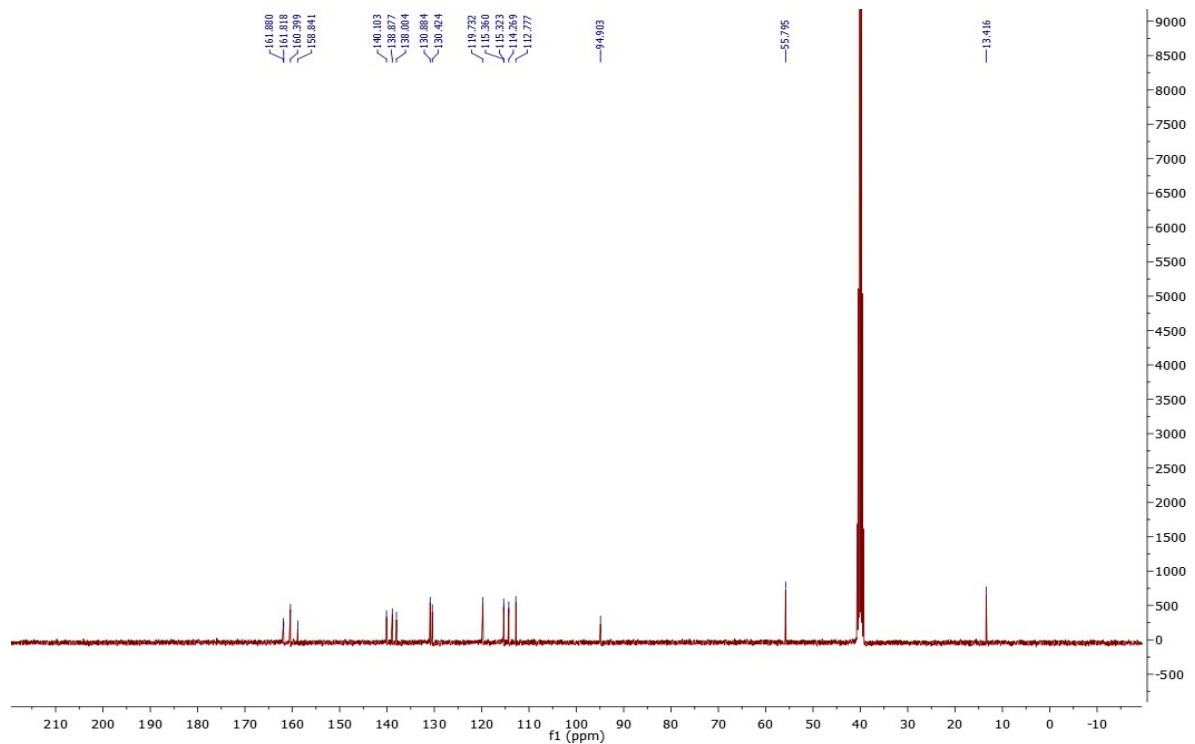


6-(3-Methoxyphenyl)-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidin-4(3*H*)-one 12

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>).

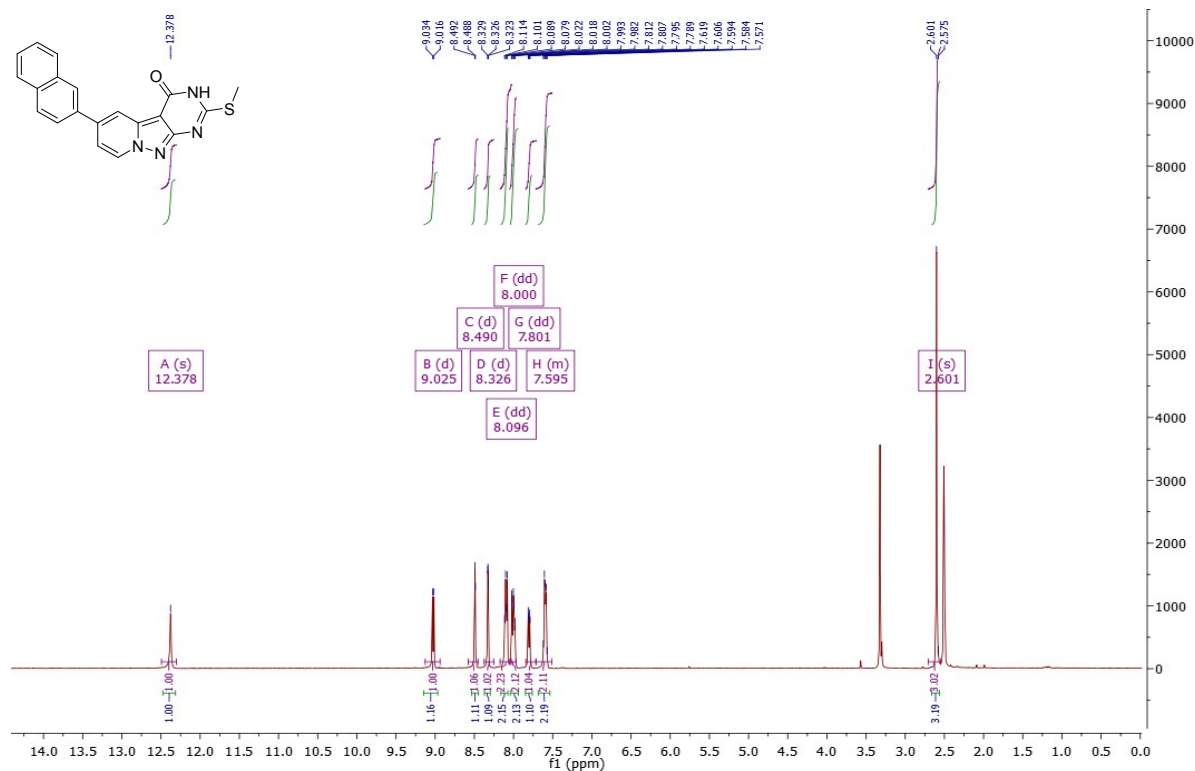


<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).

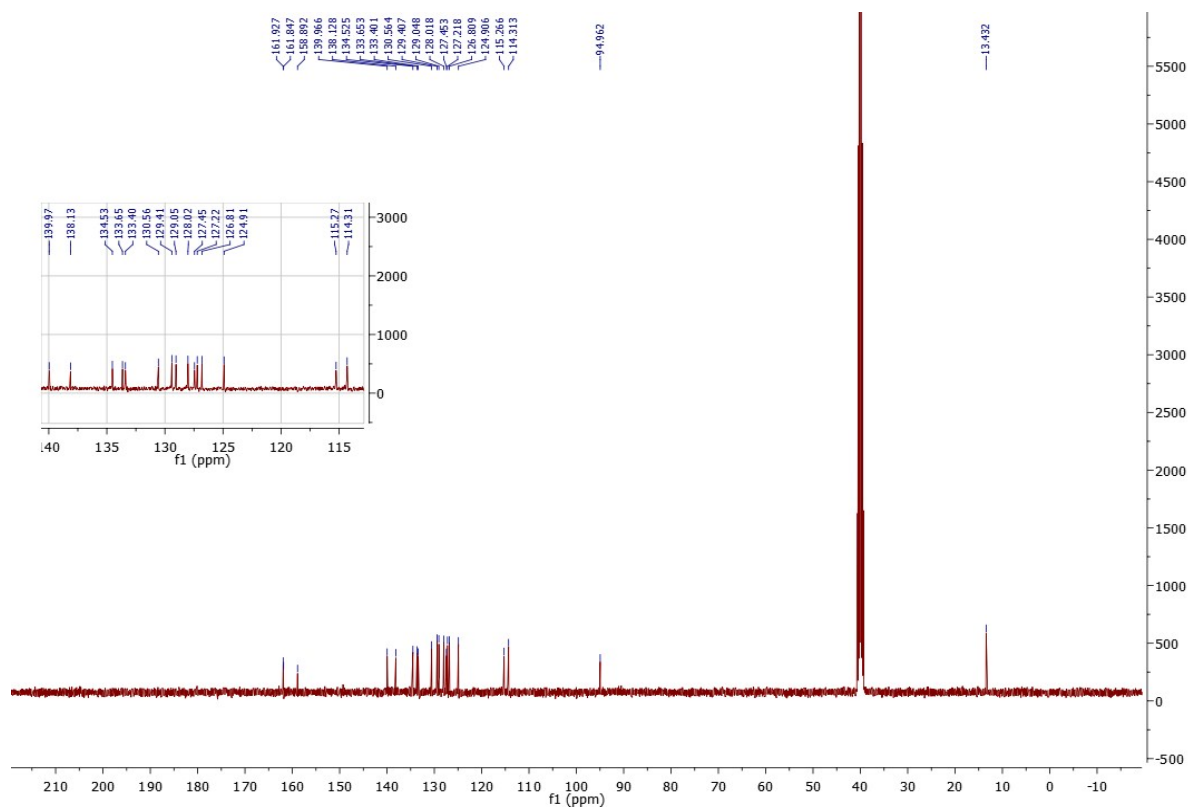


**2-(Methylthio)-6-(naphthalen-2-yl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4(3H)-one 13**

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>).**

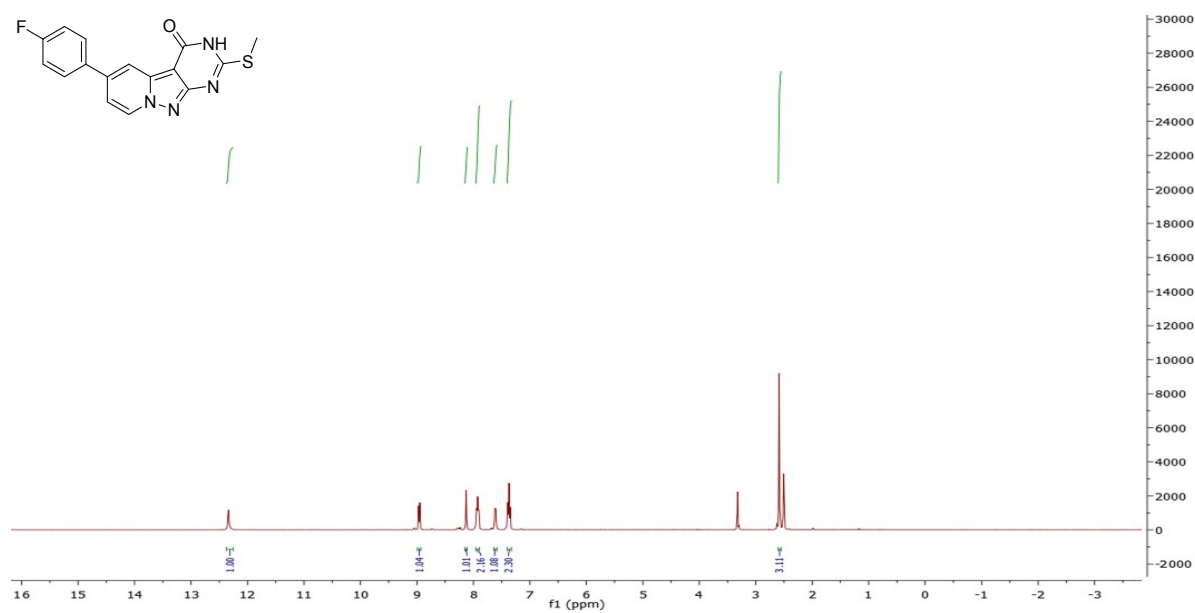


**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).**

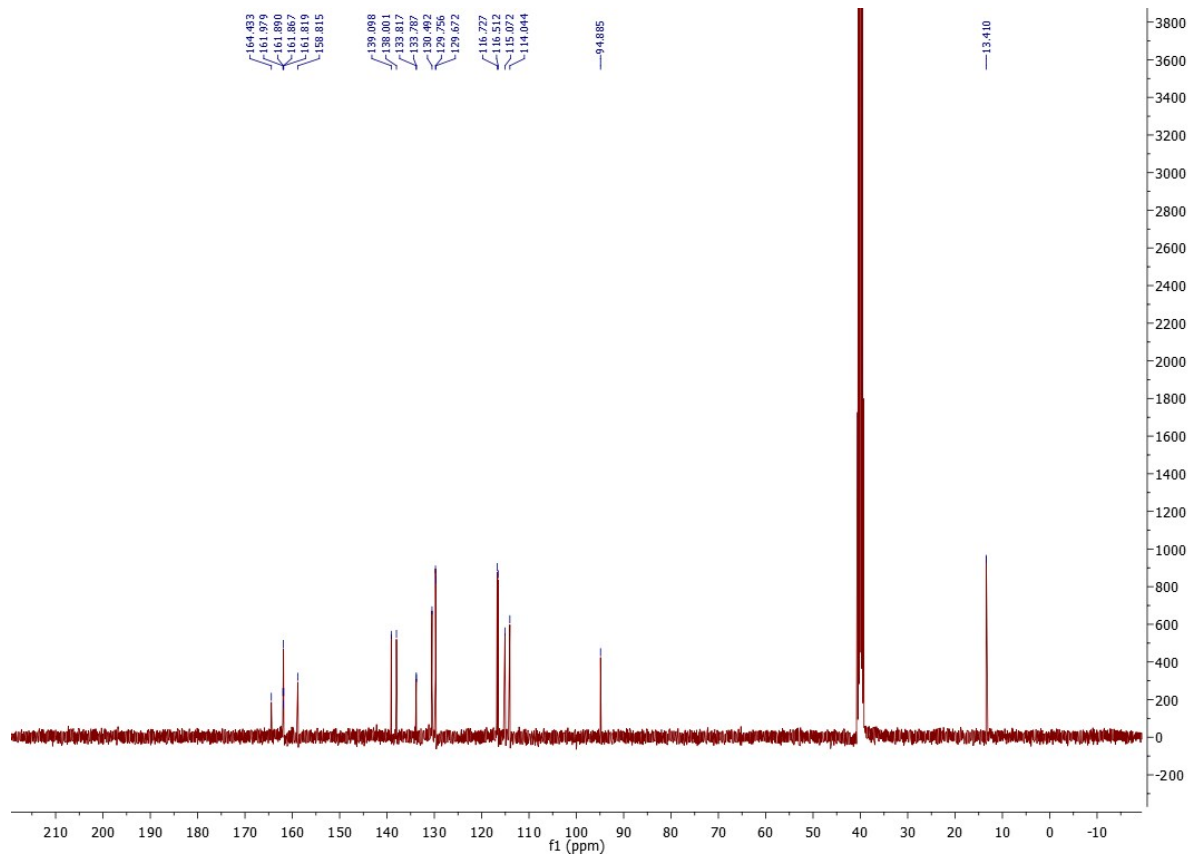


6-(4-Fluorophenyl)-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4(3H)-one 14

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

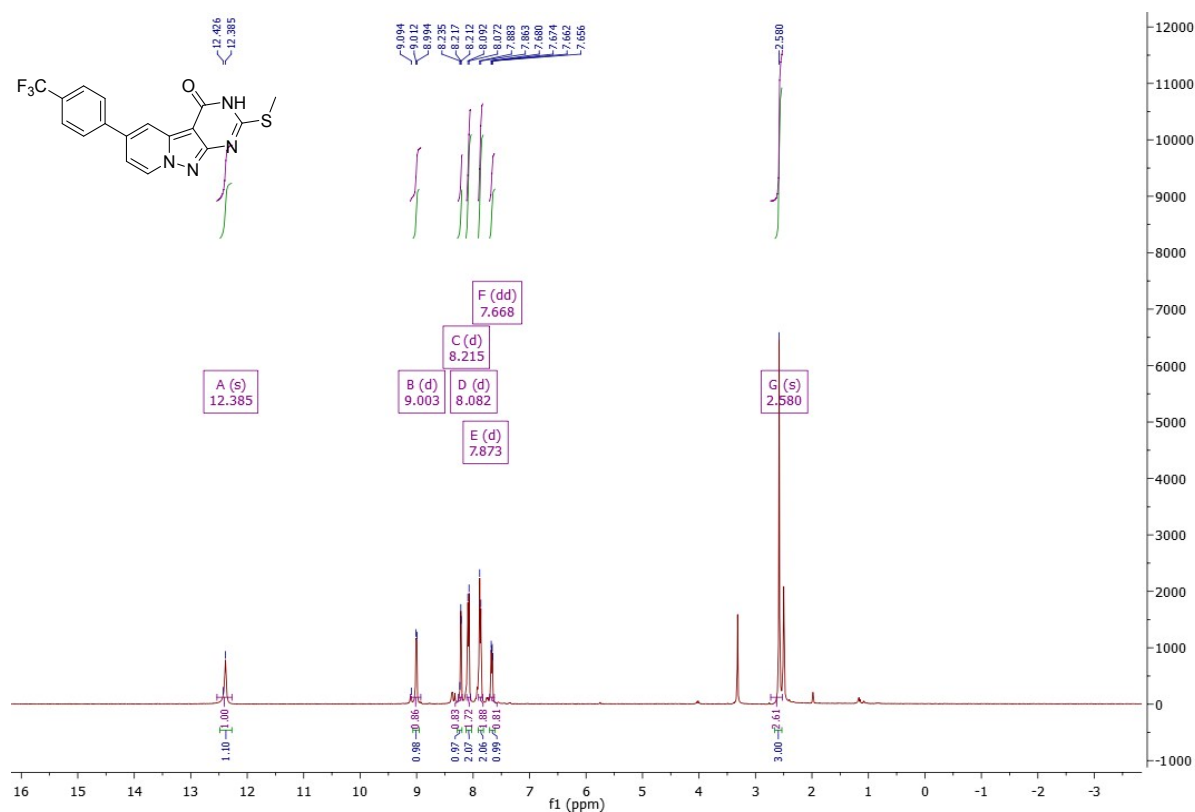


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ).

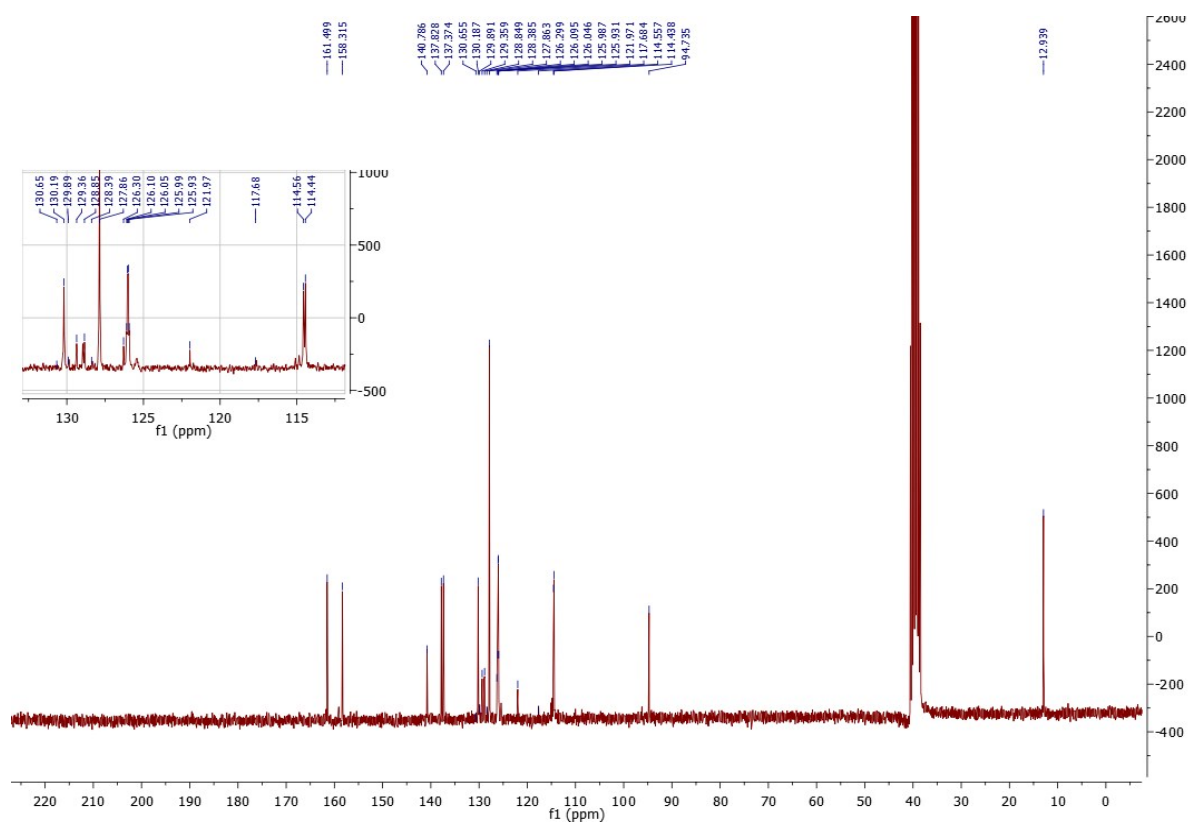


**2-(Methylthio)-6-(4-(trifluoromethyl)phenyl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4(3H)-one 15**

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>).



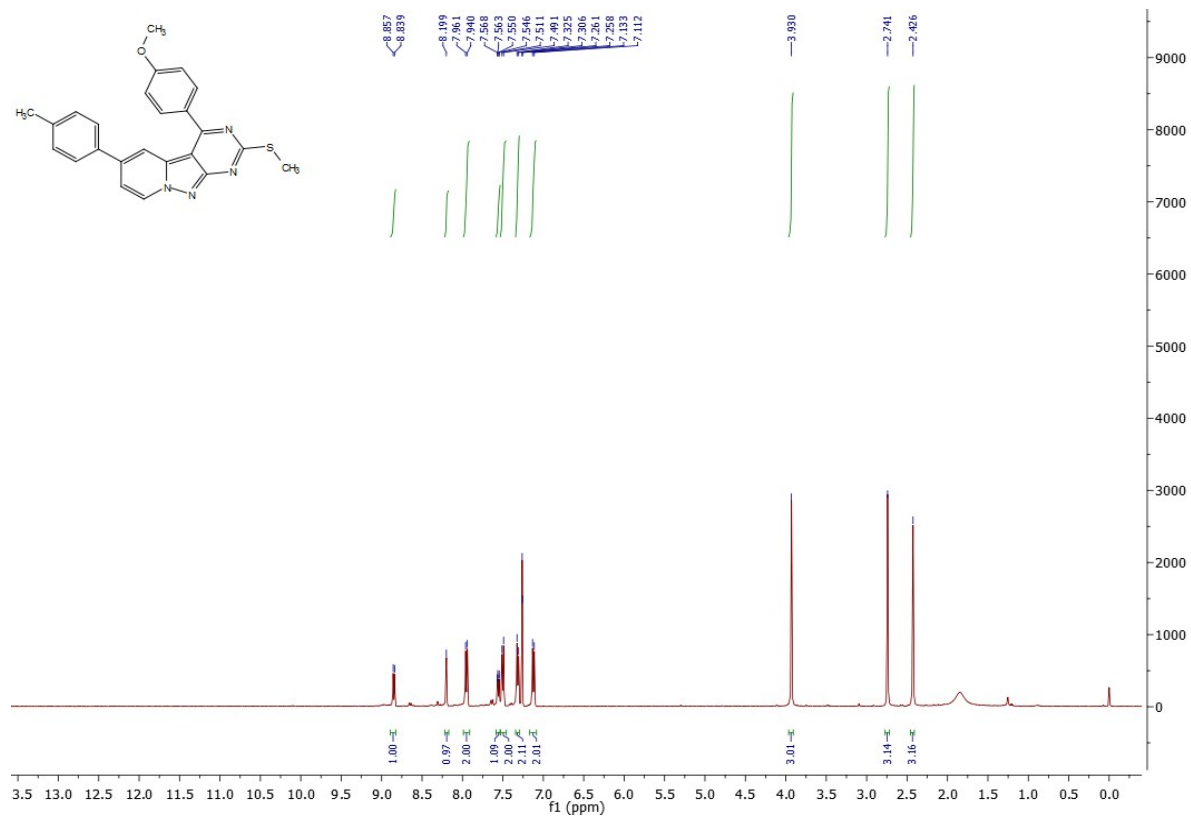
<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).



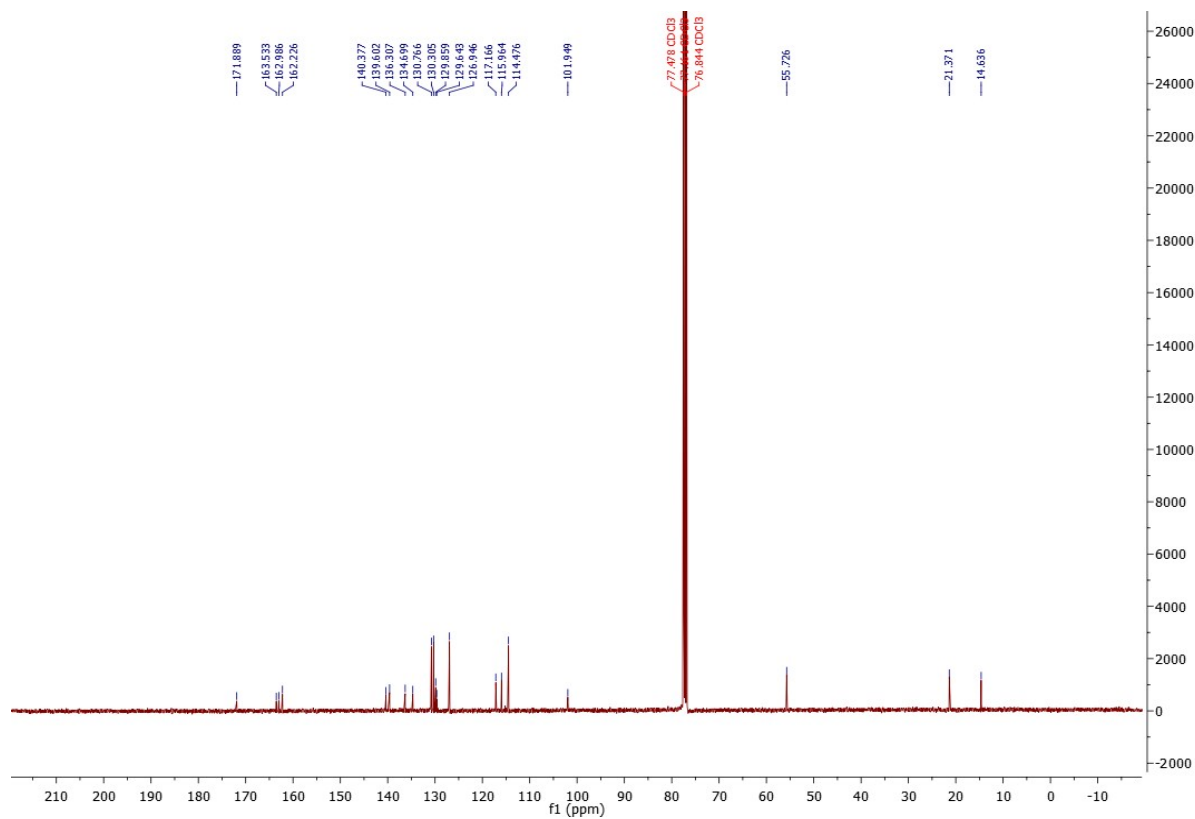


**4-(4-Methoxyphenyl)-2-(methylthio)-6-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 16**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

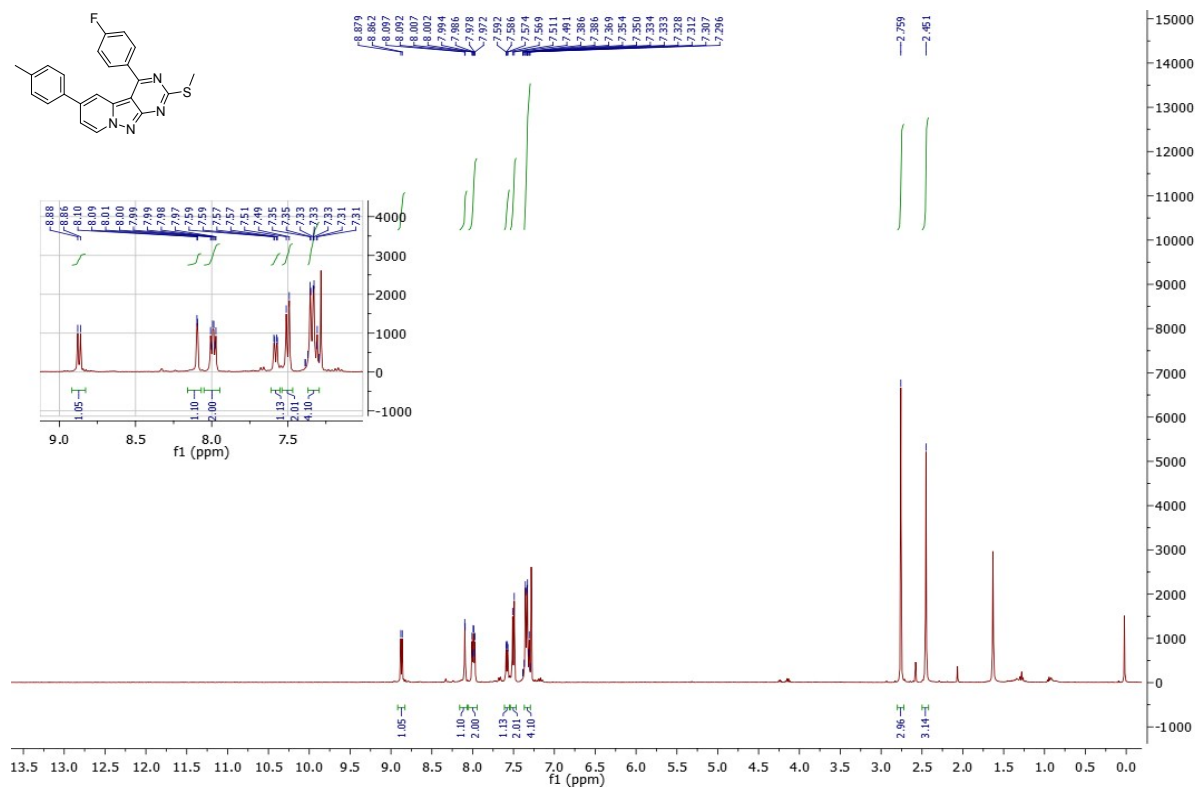


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

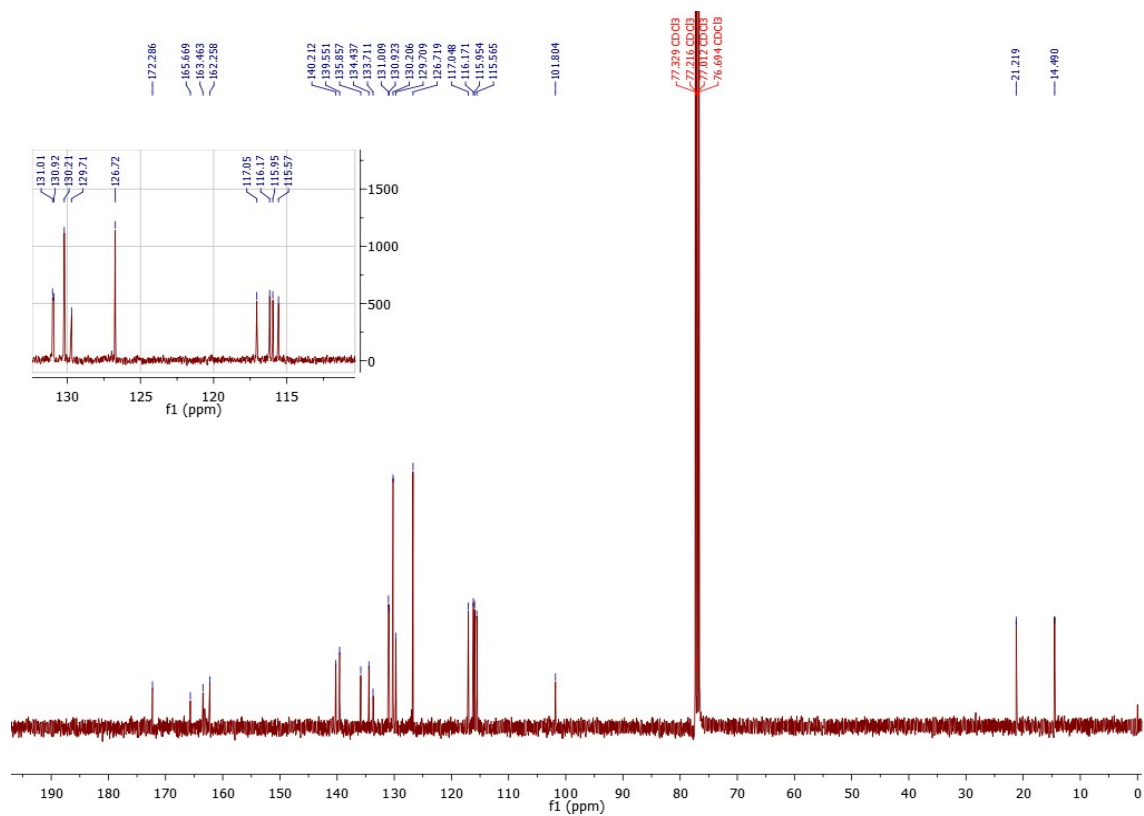


**4-(4-Fluorophenyl)-2-(methylthio)-6-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 17**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

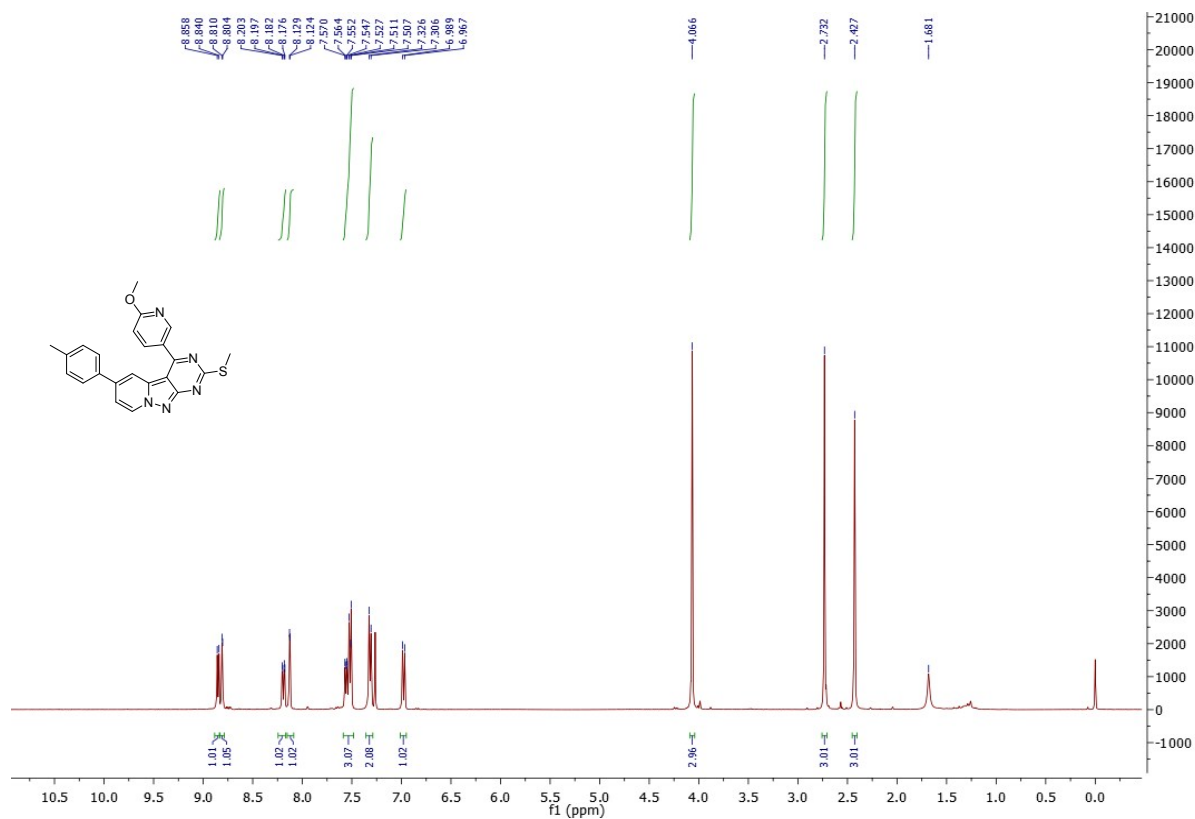


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

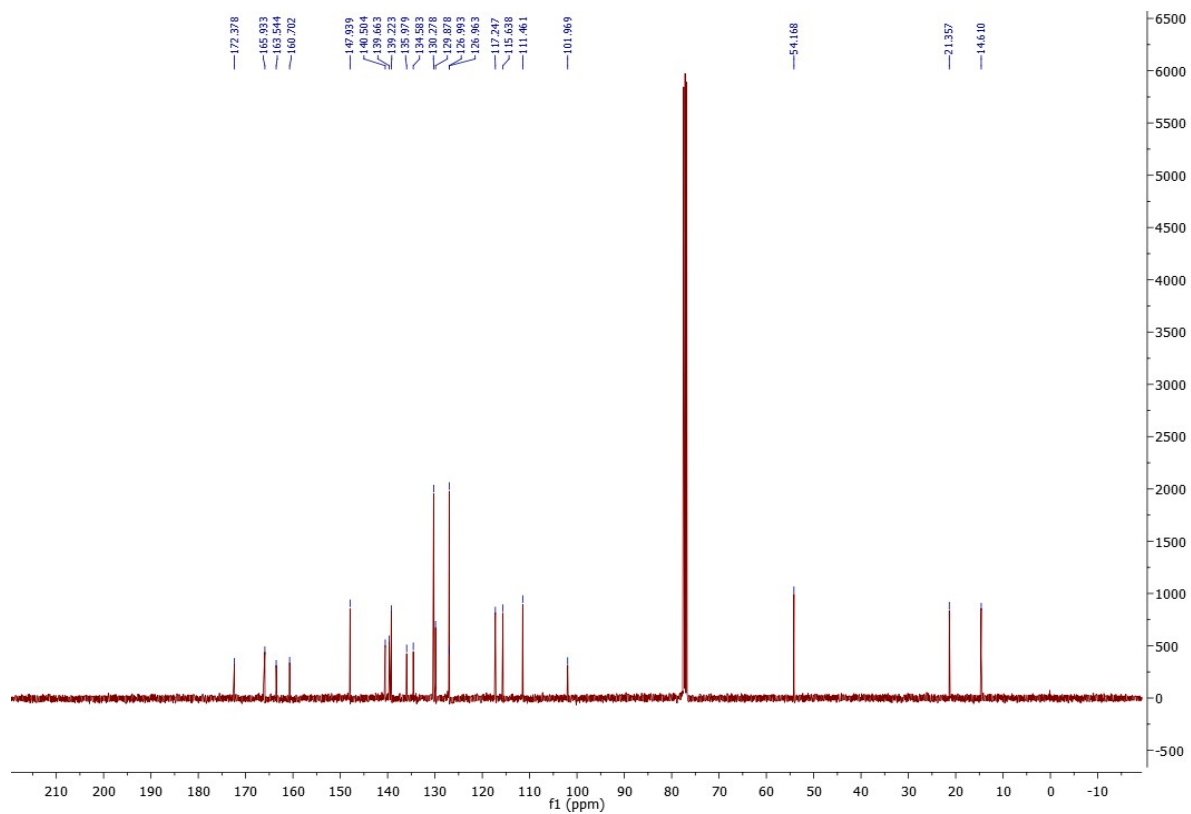


**4-(6-Methoxypyridin-3-yl)-2-(methylthio)-6-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 18**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

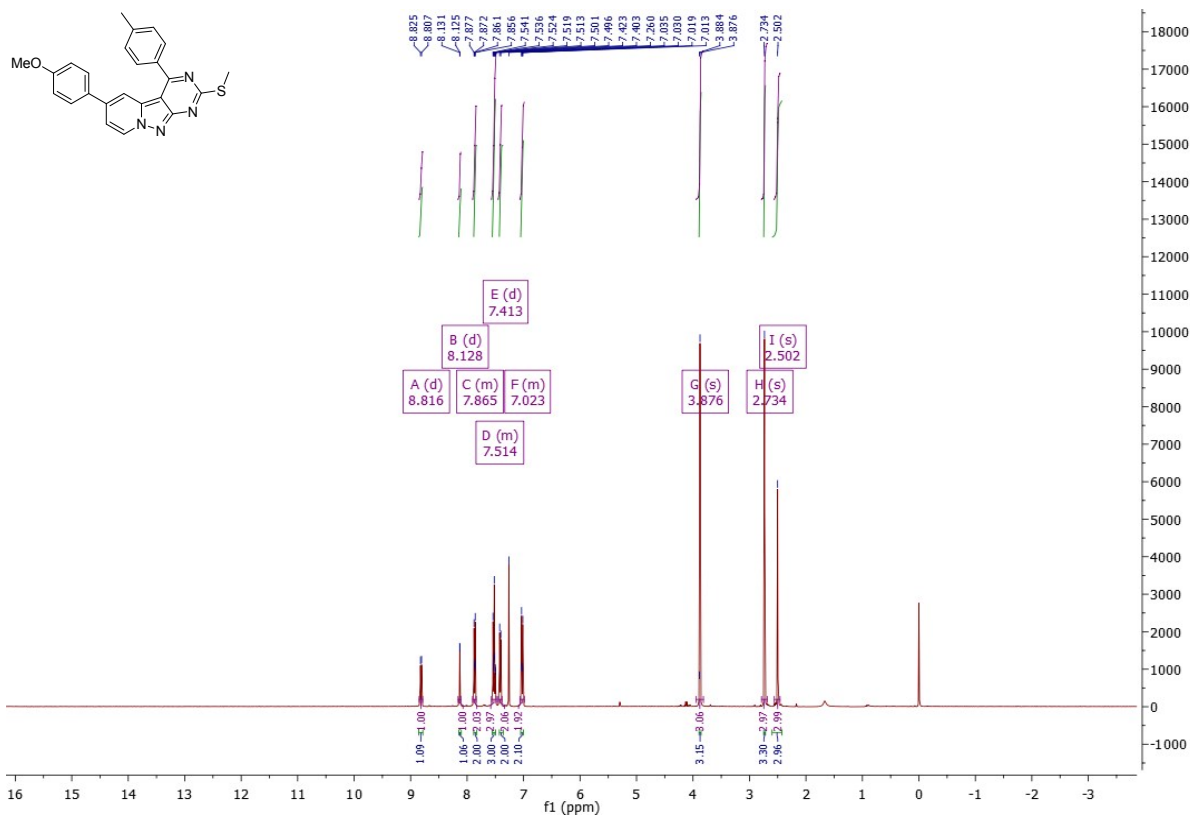


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

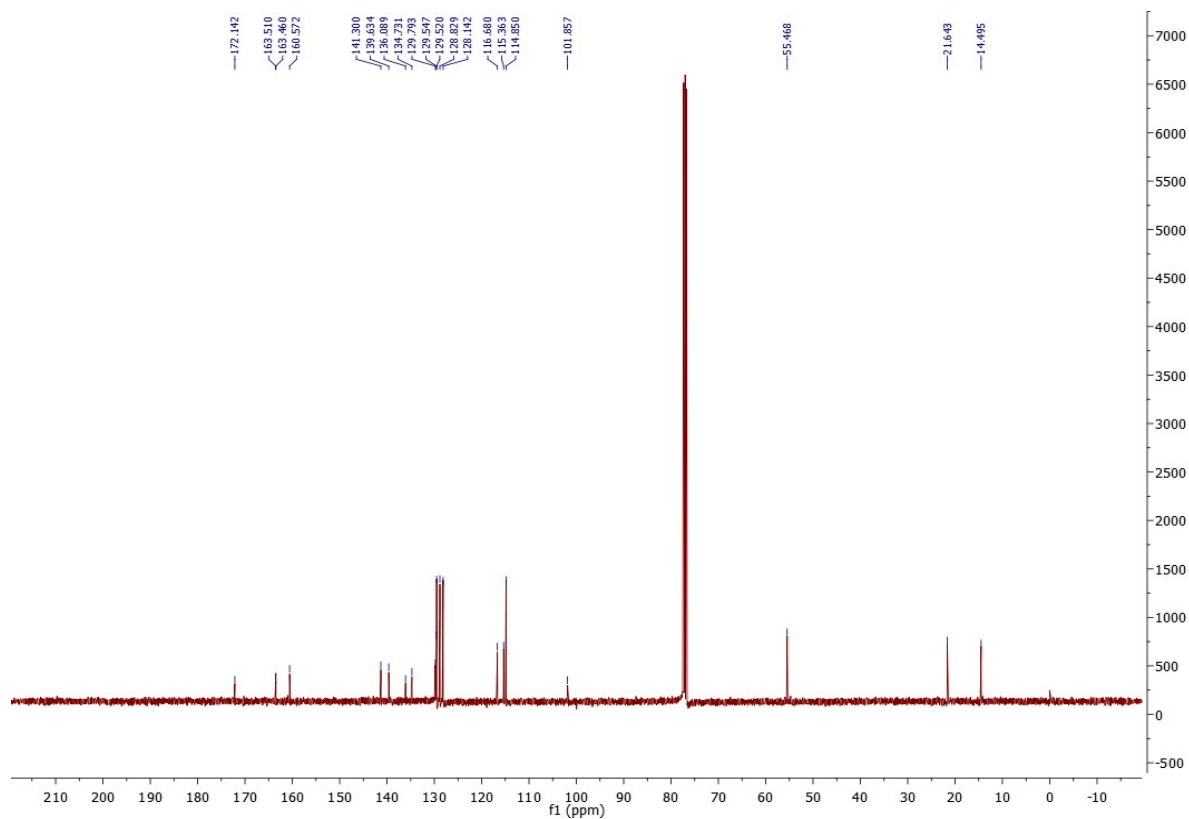


6-(4-Methoxyphenyl)-2-(methylthio)-4-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 19

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

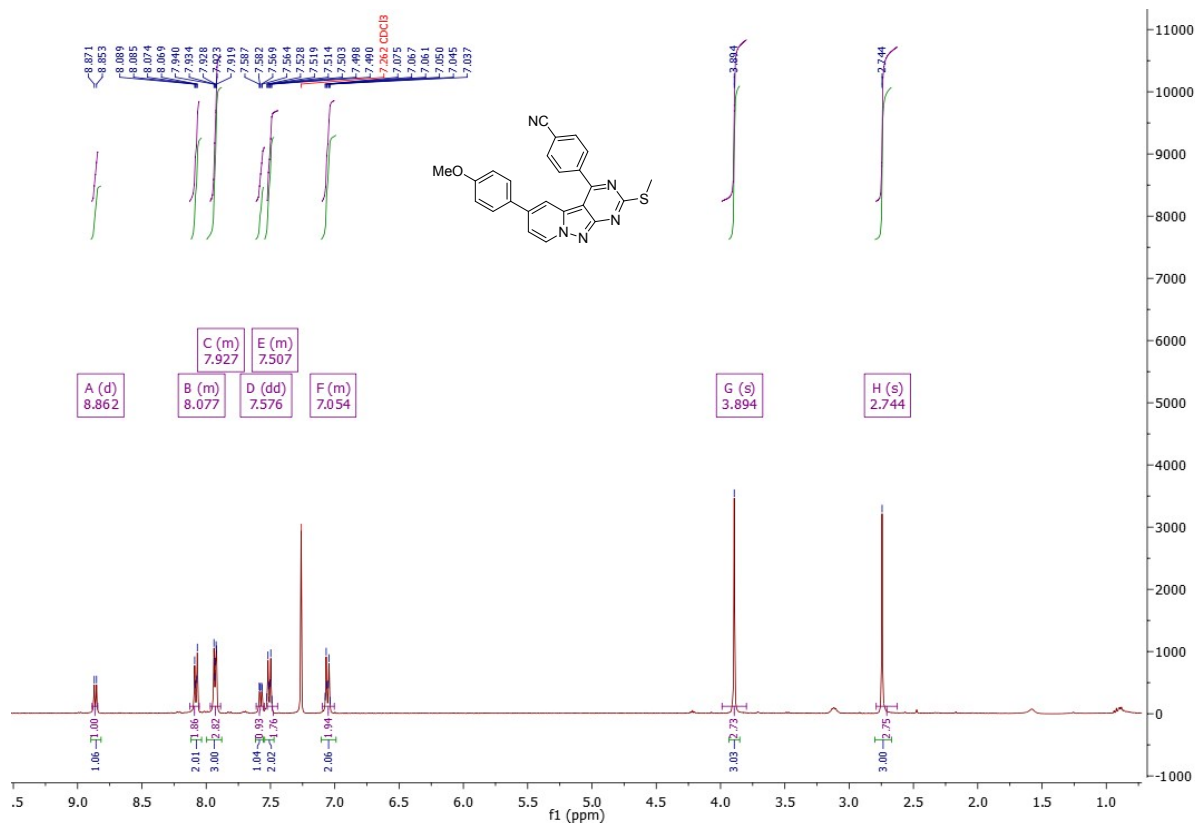


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).

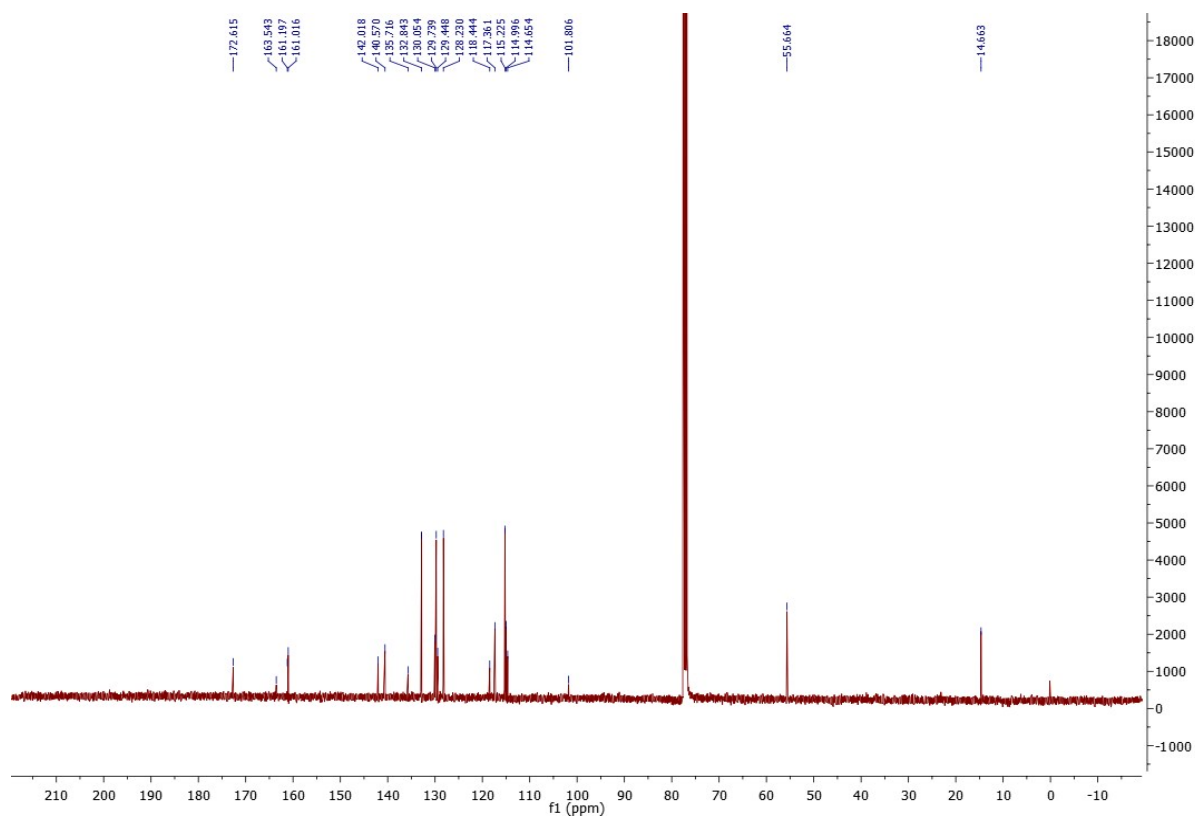


**4-(6-(4-Methoxyphenyl)-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4-yl)benzonitrile 20**

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>).

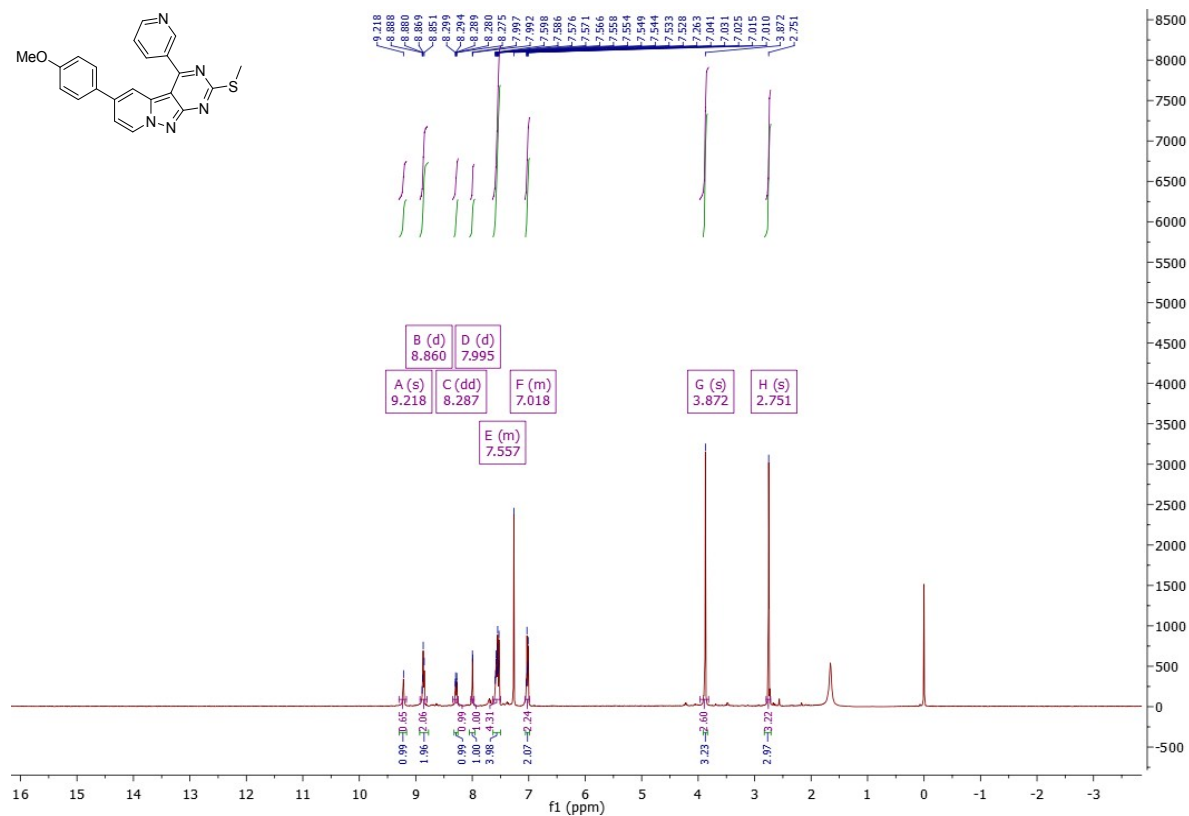


<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>).

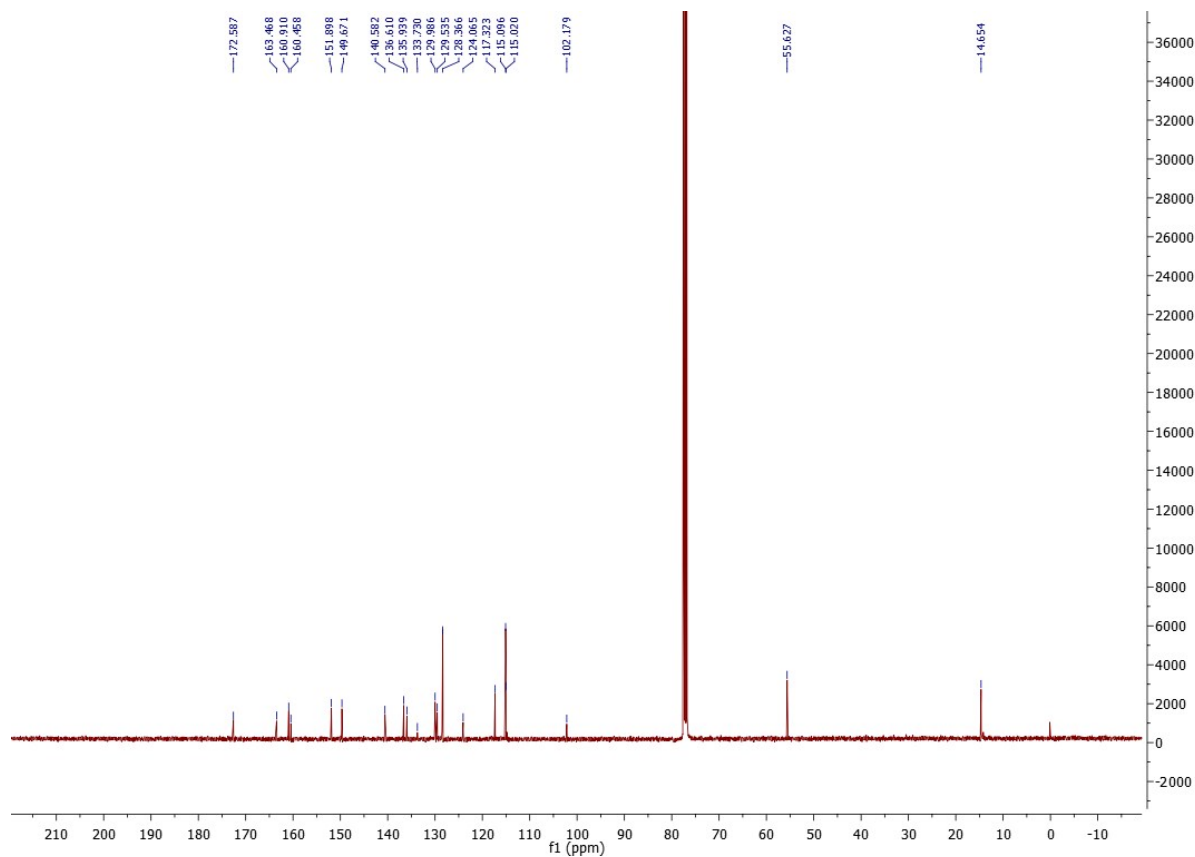


**6-(4-Methoxyphenyl)-2-(methylthio)-4-(pyridin-3-yl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidine 21**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).**

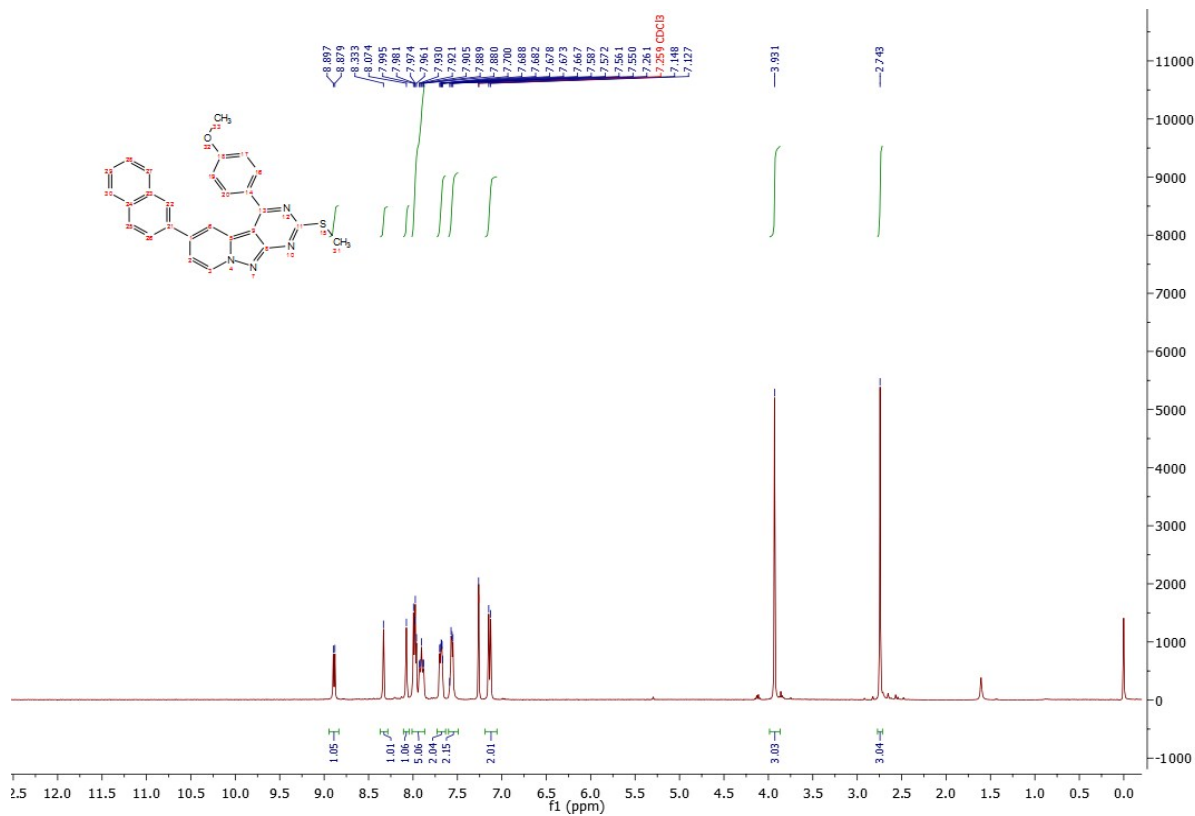


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

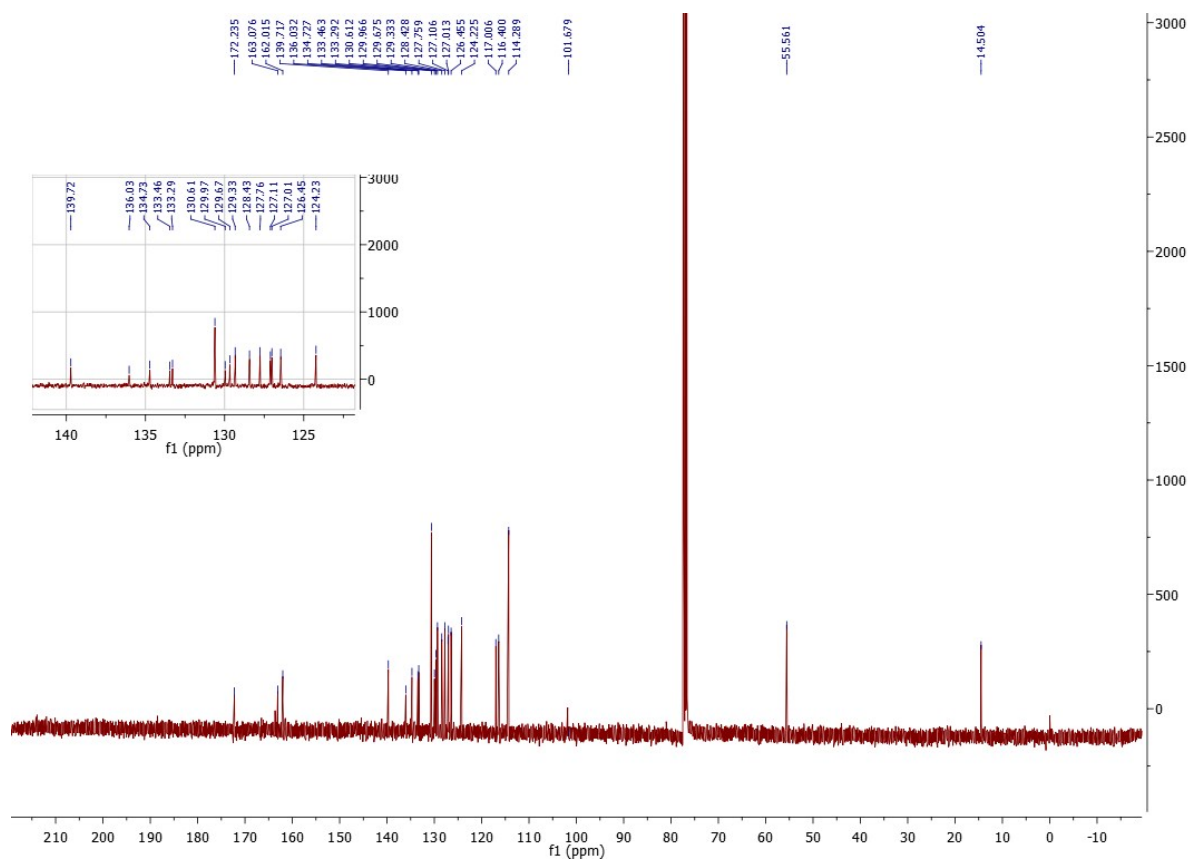


**4-(4-Methoxyphenyl)-2-(methylthio)-6-(naphthalen-2-yl)-3,4-dihydropyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidine 22**

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

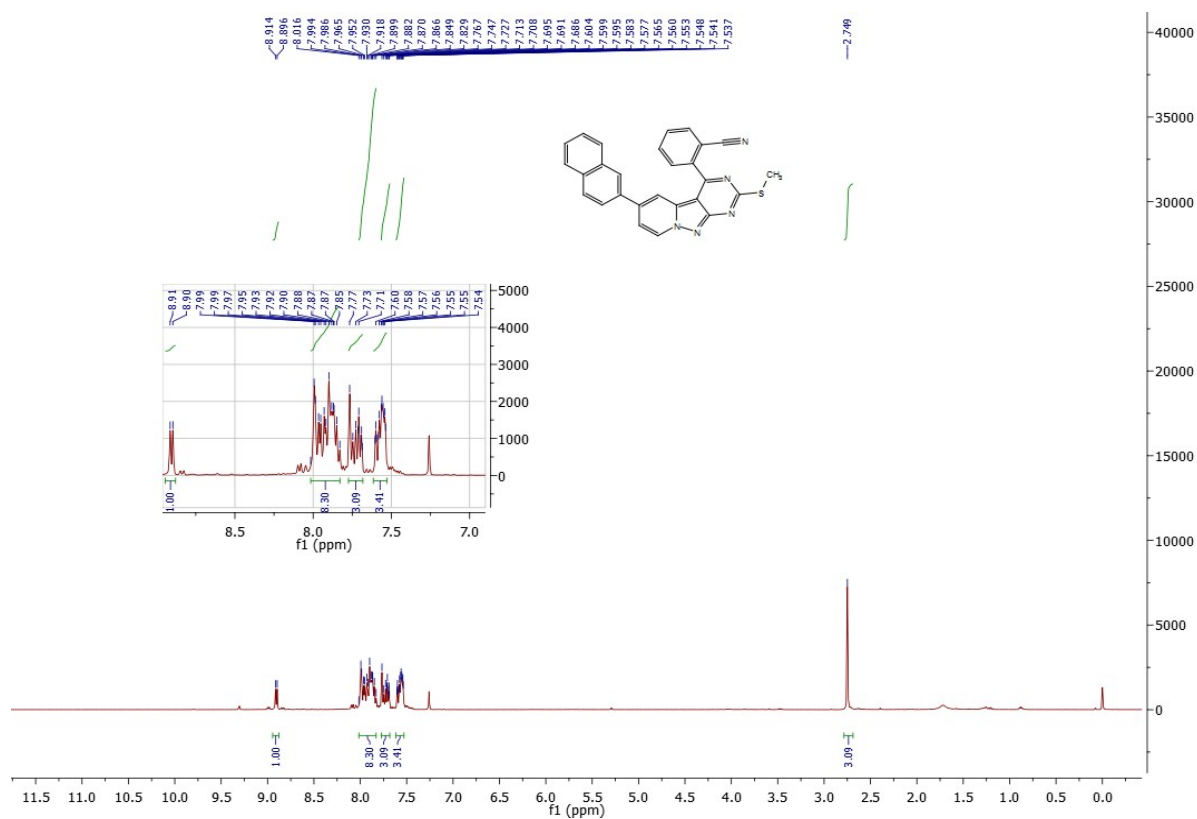


**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).**

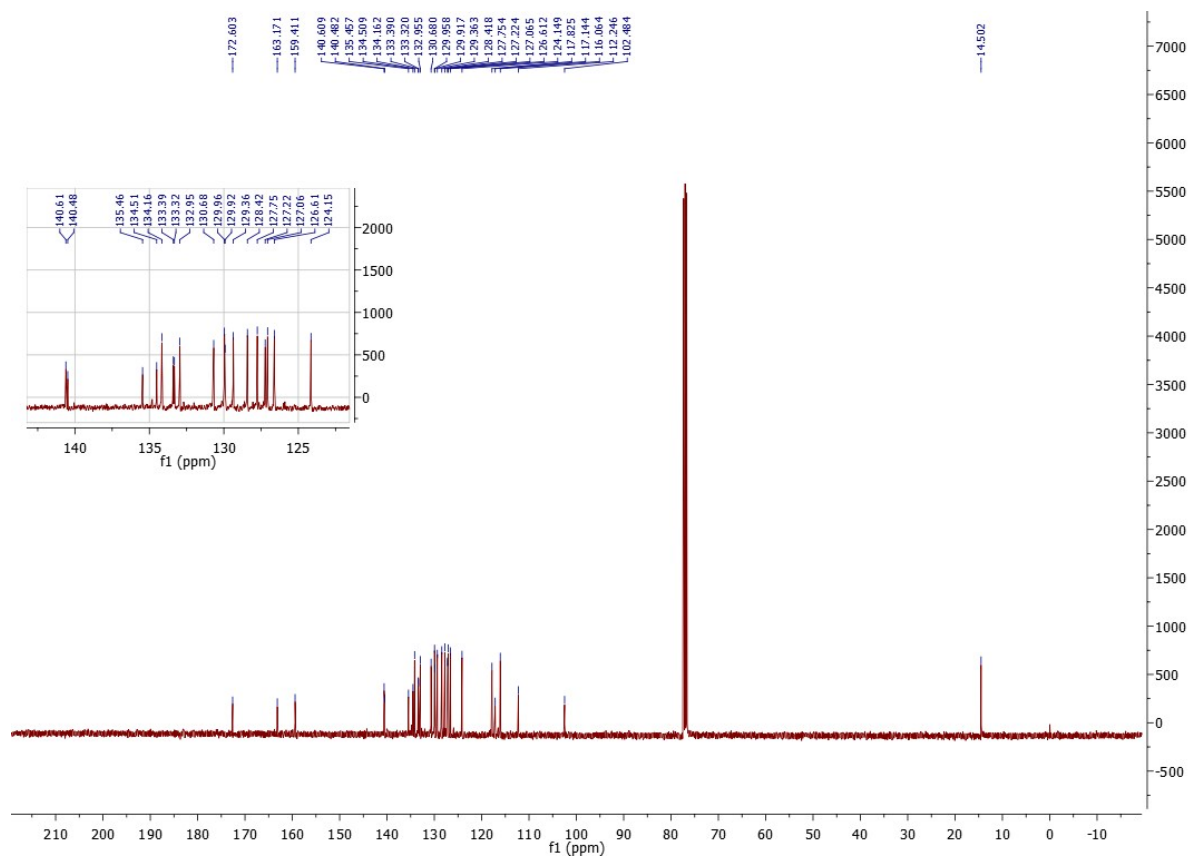


**2-(2-(methylthio)-6-(naphthalen-2-yl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4-yl)benzonitrile 23**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).**



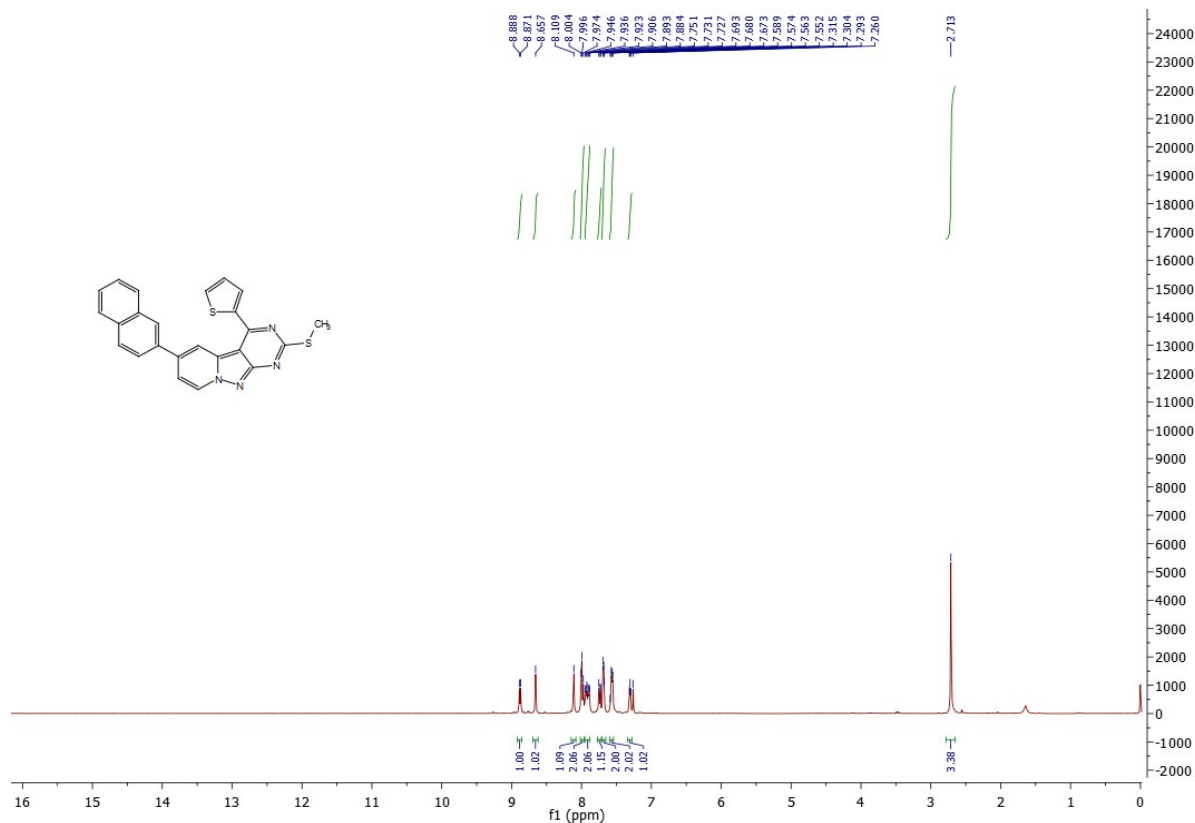
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**



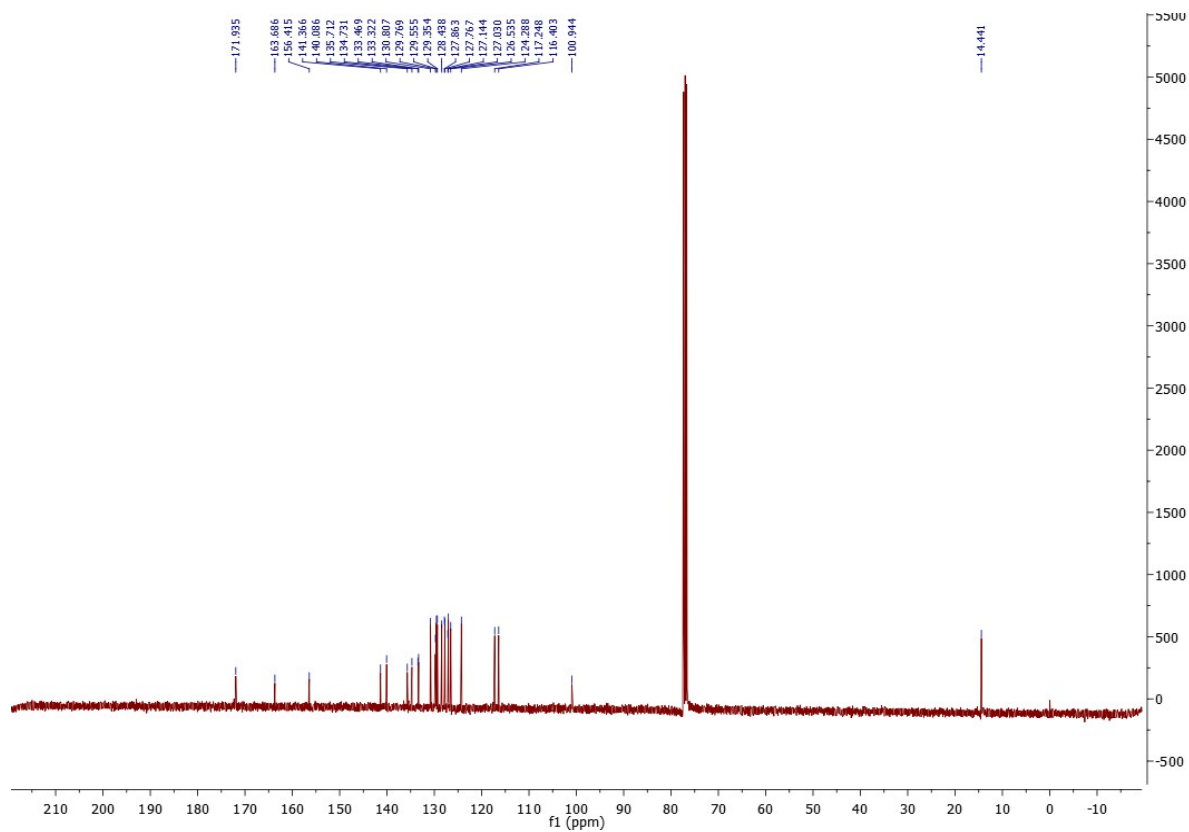


**2-(Methylthio)-6-(naphthalen-2-yl)-4-(thiophen-2-yl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 24**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).**

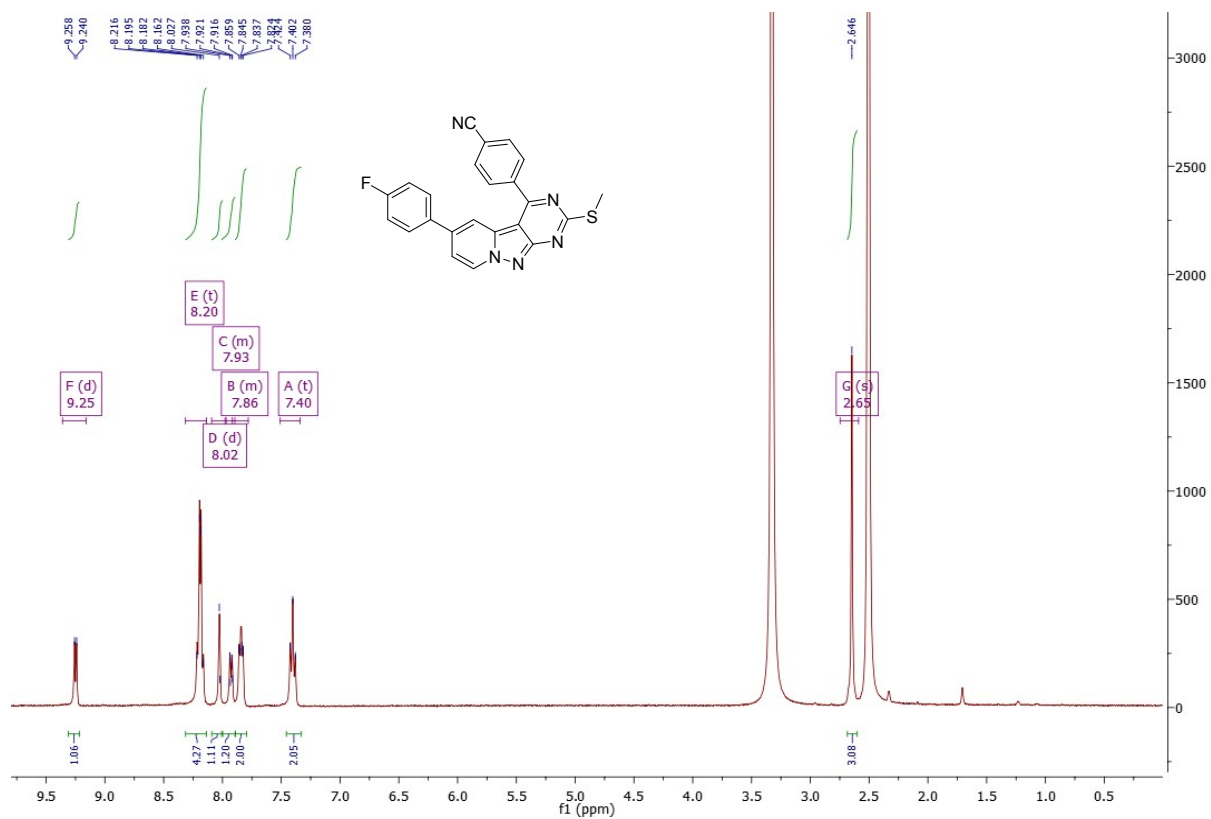


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**

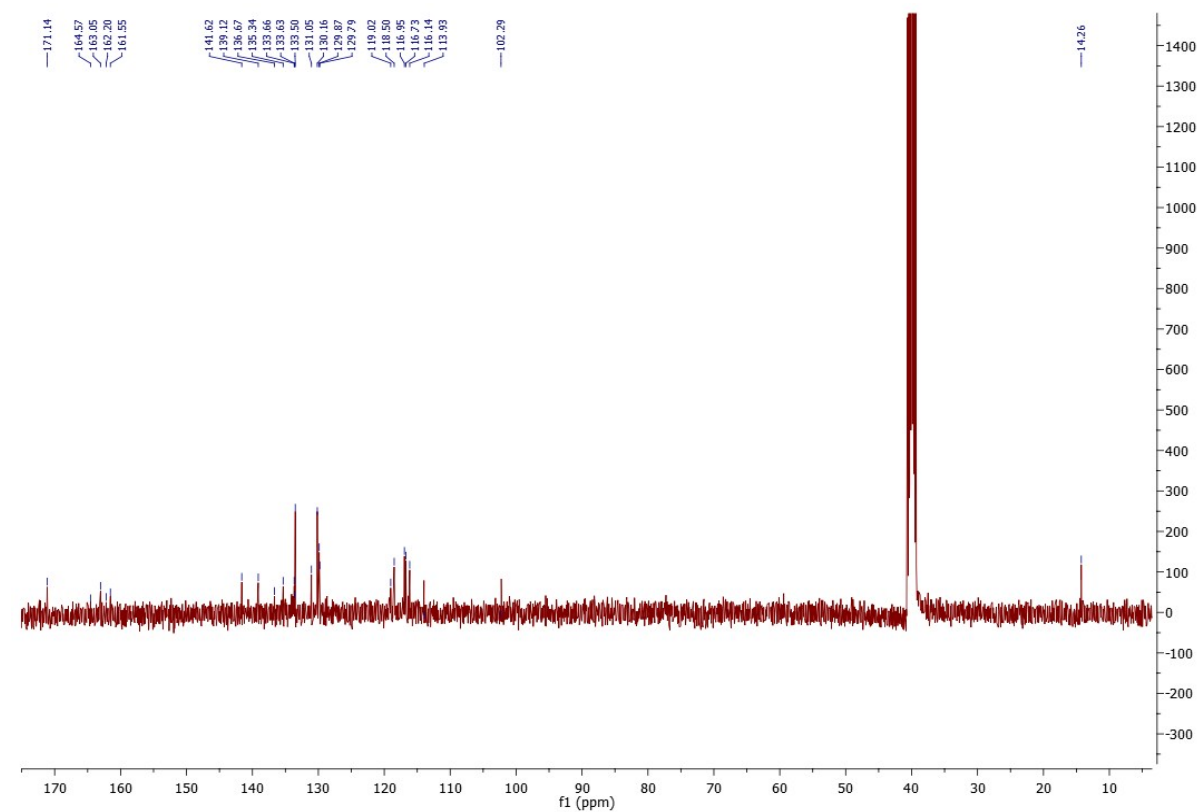


**4-(6-(4-fluorophenyl)-2-(methylthio)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-4-yl)benzonitrile 25**

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>).**

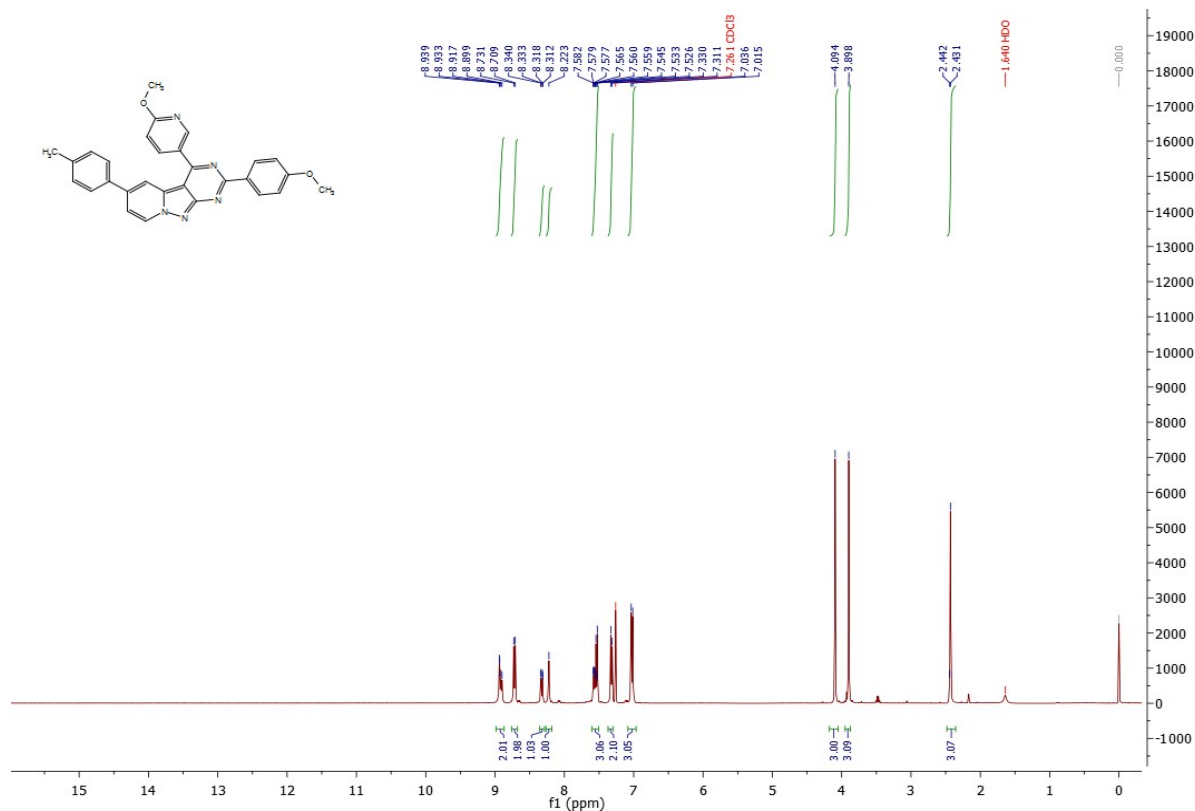


**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).**

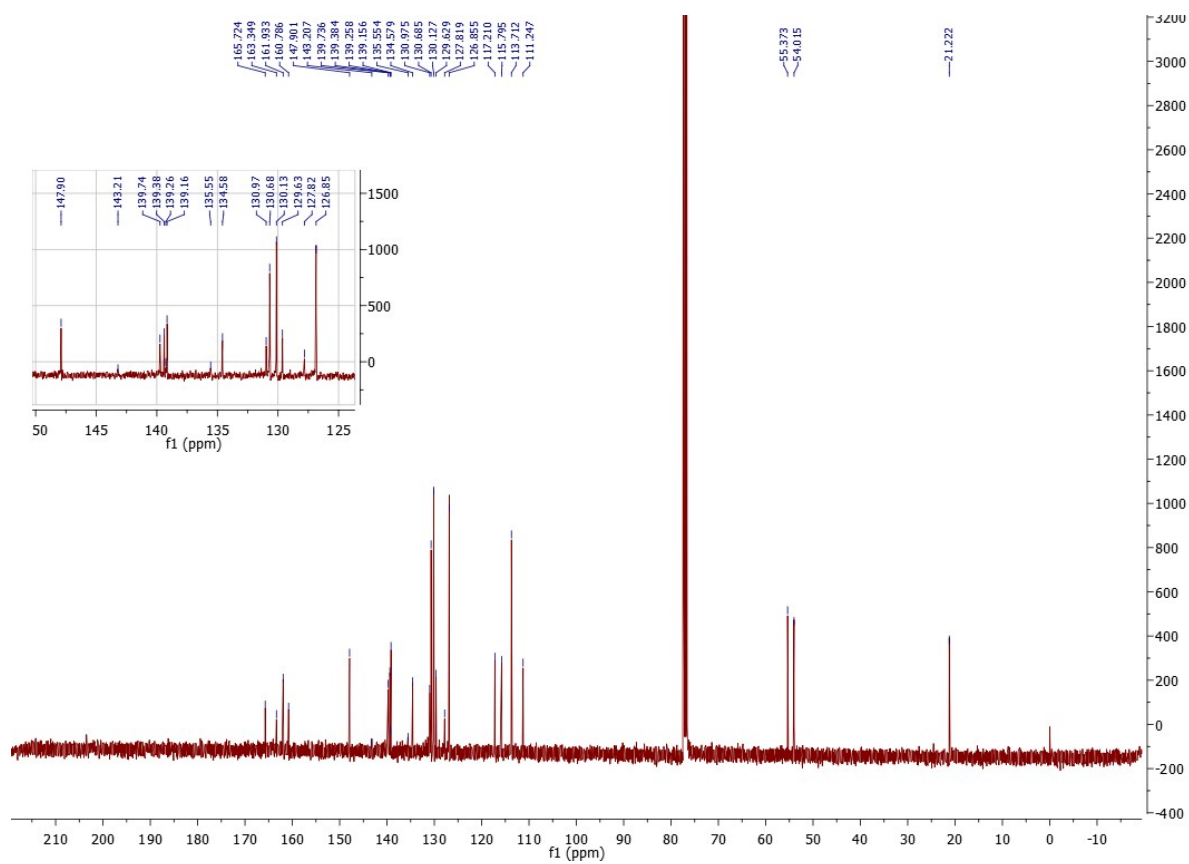


**2-(4-methoxyphenyl)-4-(6-methoxypyridin-3-yl)-6-(*p*-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-*d*]pyrimidine 26**

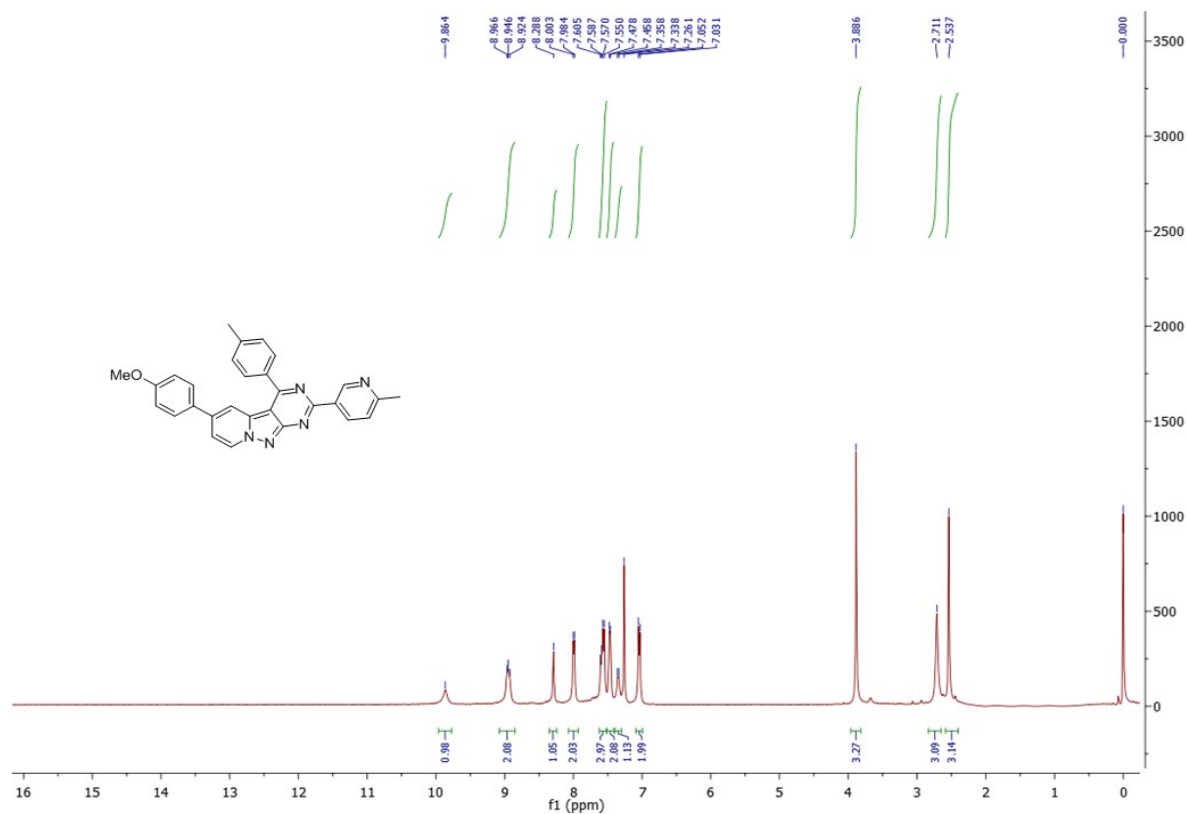
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).**



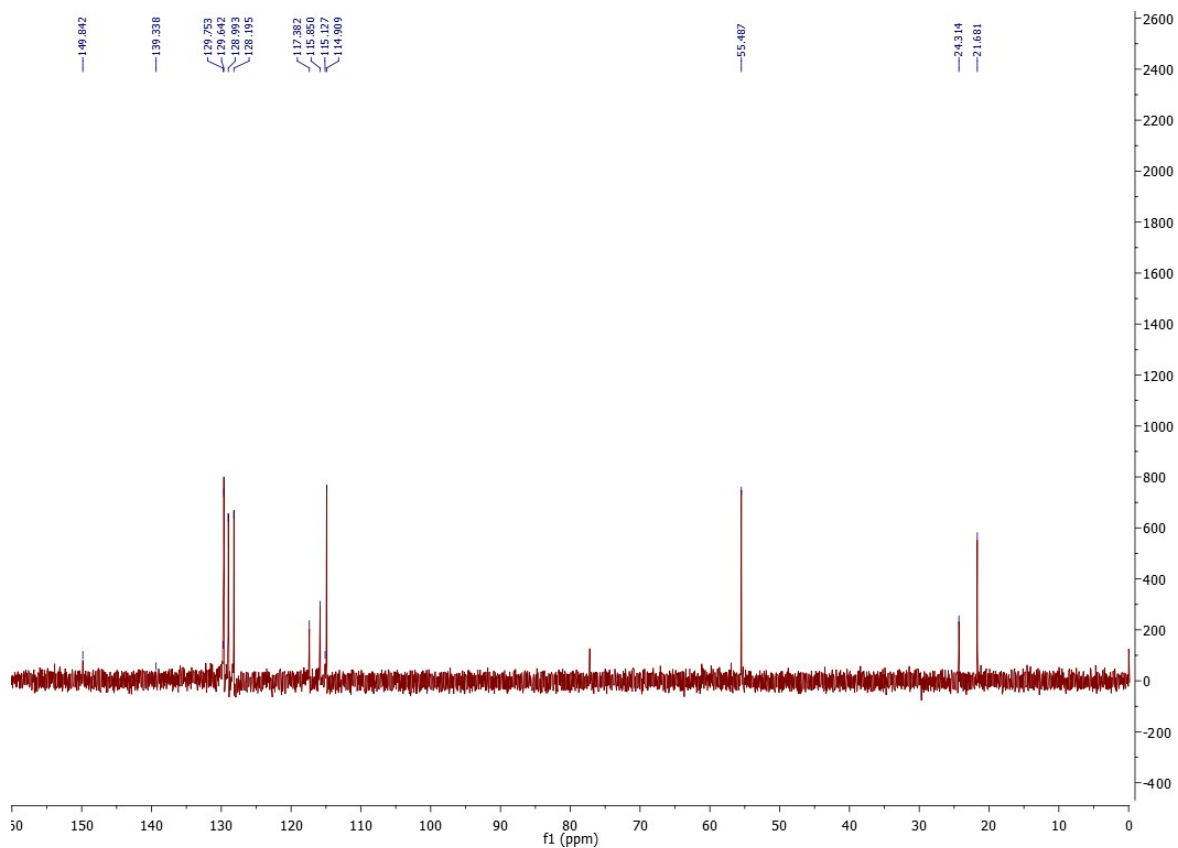
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>).**



**6-(4-Methoxyphenyl)-2-(6-methylpyridin-3-yl)-4-(p-tolyl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidine 27**  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>).



<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>).



**4-(4-(4-Methoxyphenyl)-6-(naphthalen-2-yl)pyrido[1',2':1,5]pyrazolo[3,4-d]pyrimidin-2-yl)benzonitrile 28.**

<sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>).

