

# Regioselective synthesis of new 2,4-(het)aryl-3H-pyrido[1',2':1,5]pyrazolo[4,3-*d*]pyrimidine involving palladium-catalyzed cross-coupling reactions

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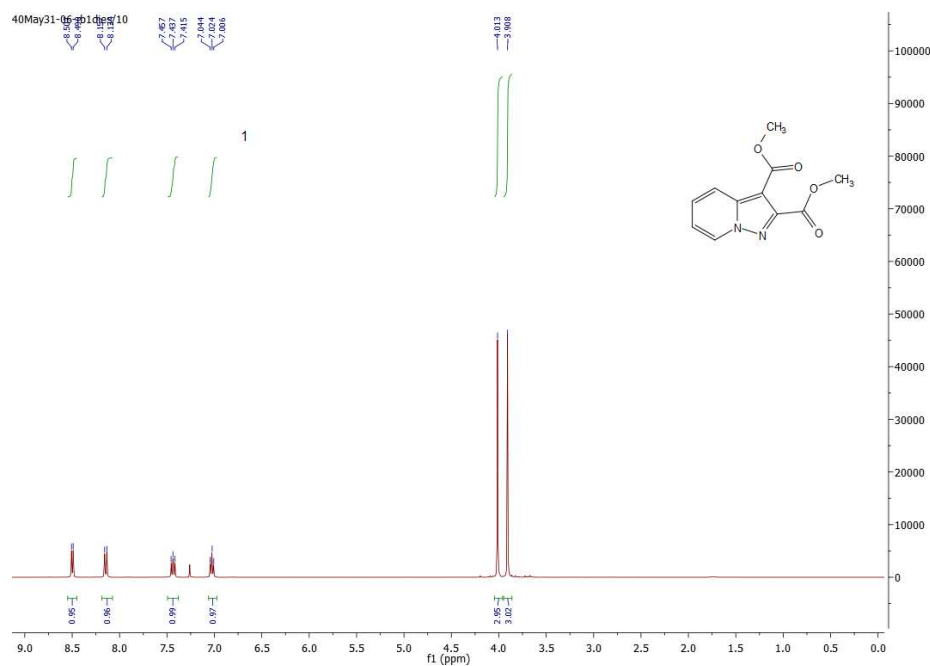
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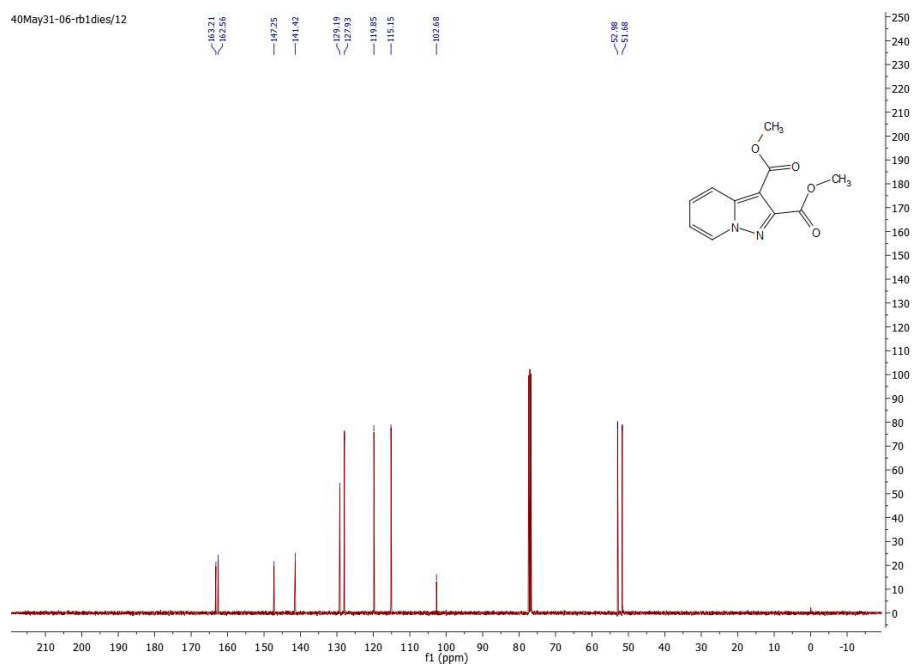
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*Dimethyl Pyrazolo[1,5-a]pyridine-2,3 dicarboxylate (2)*

$^1\text{H}$ NMR (400 MHz, Chloroform-*d*).

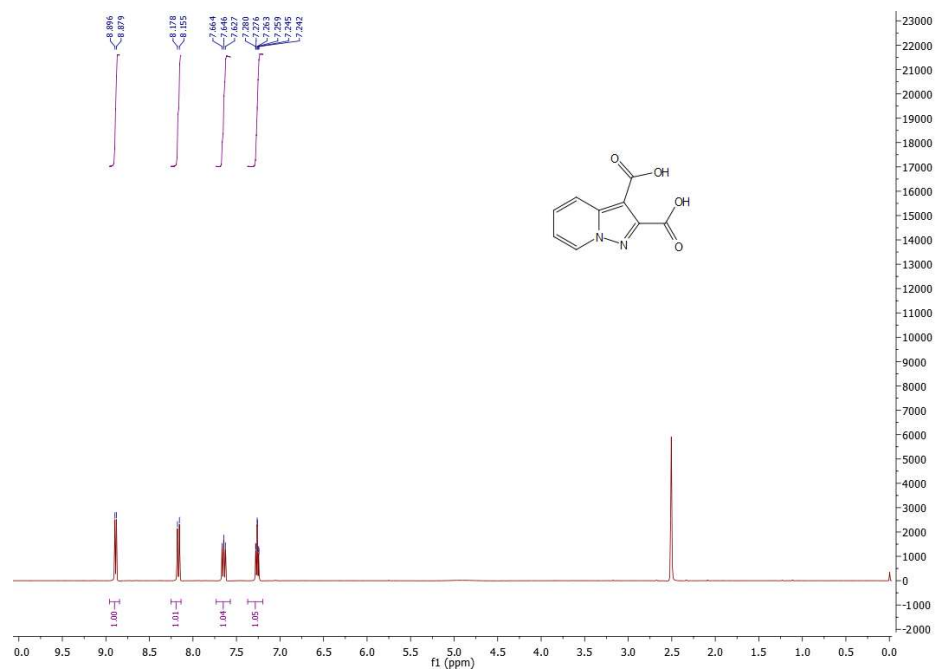


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).

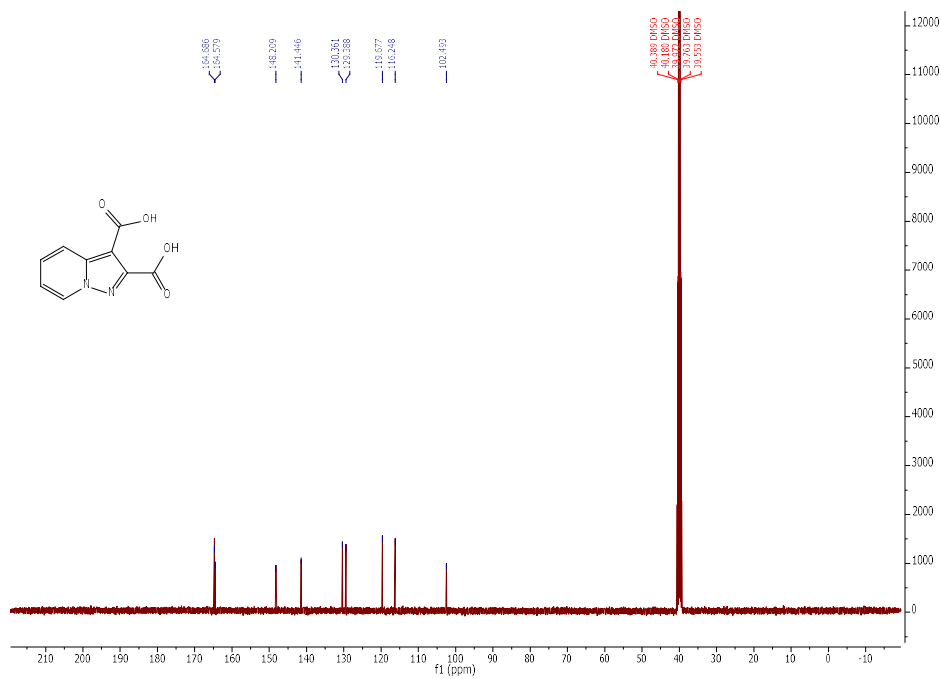


*Pyrazolo [1, 5-a] pyridine-2-Dicarboxylic Acid (3)*

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

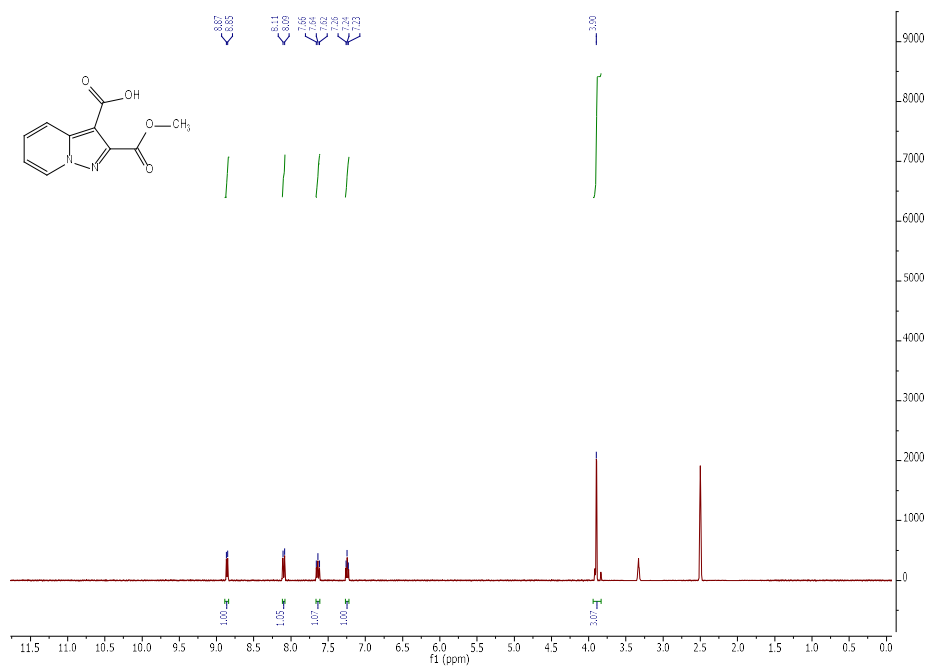


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )

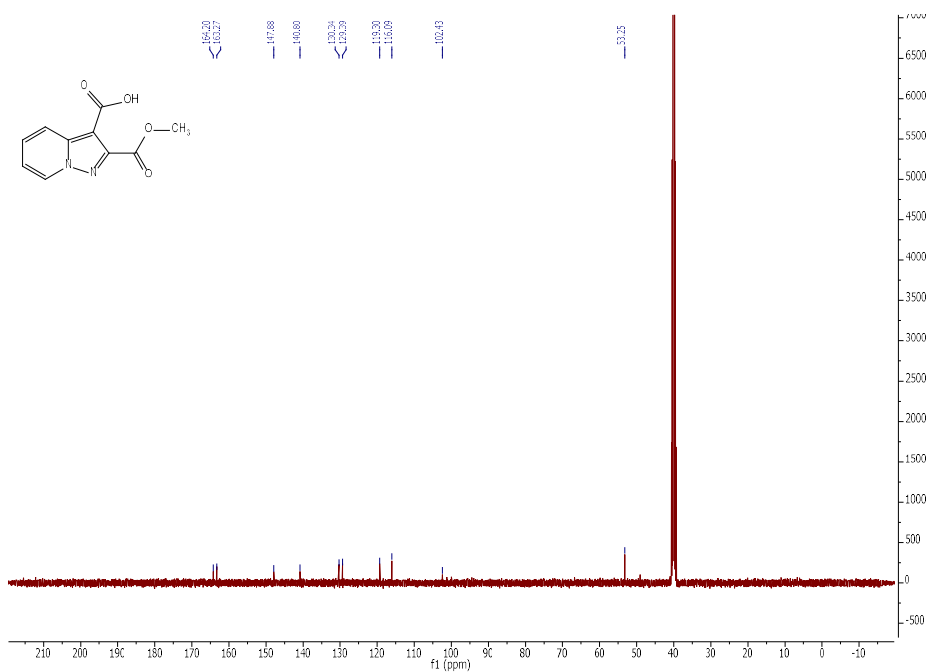


2-(Methoxycarbonyl)pyrazolo[1,5-a]pyridine-3-carboxylic Acid (**4**)

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

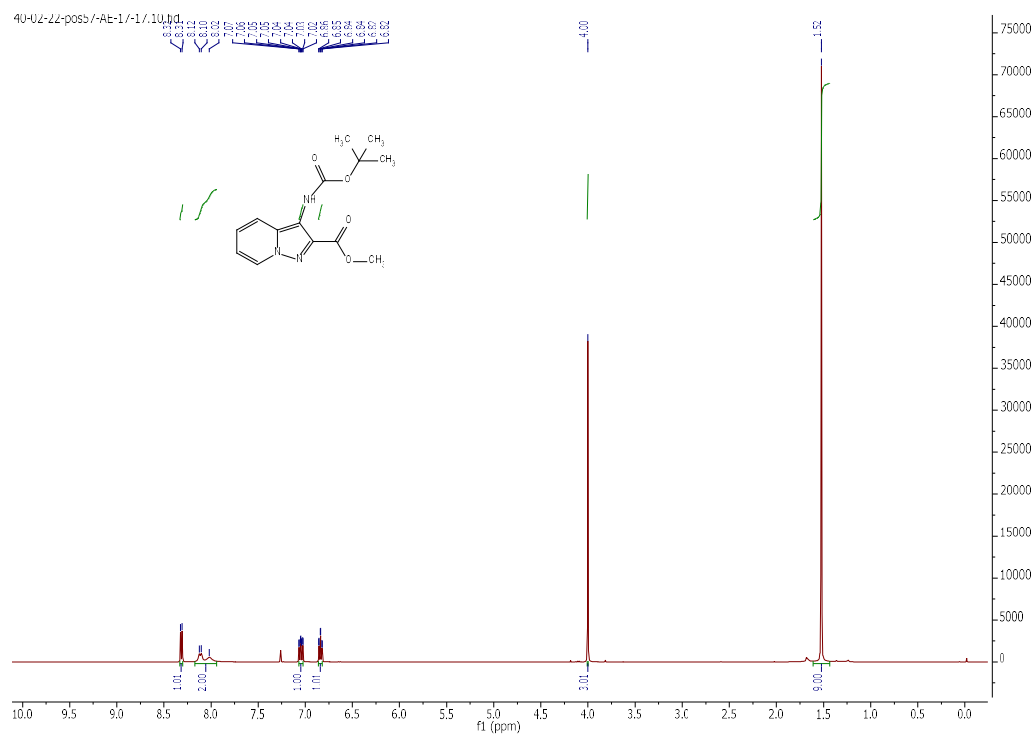


$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )

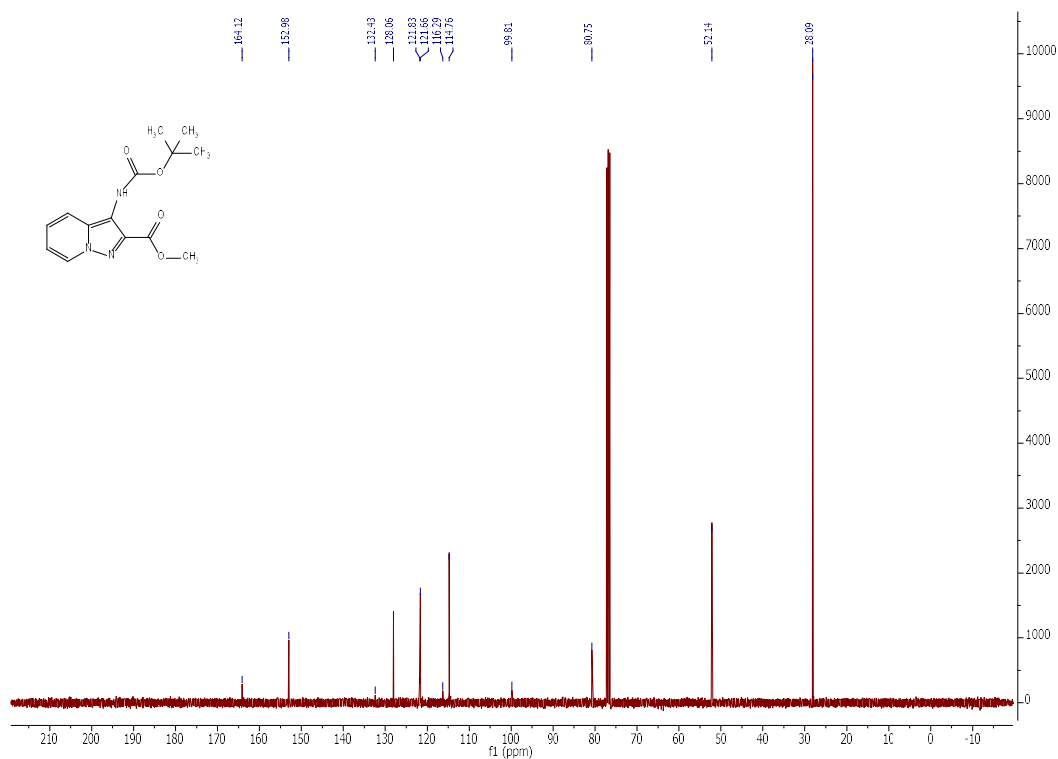


*Methyl 3-(tert-Butoxycarbonylamino)pyrazolo[1,5-a]pyridine-2-carboxylate (5)*

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)



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

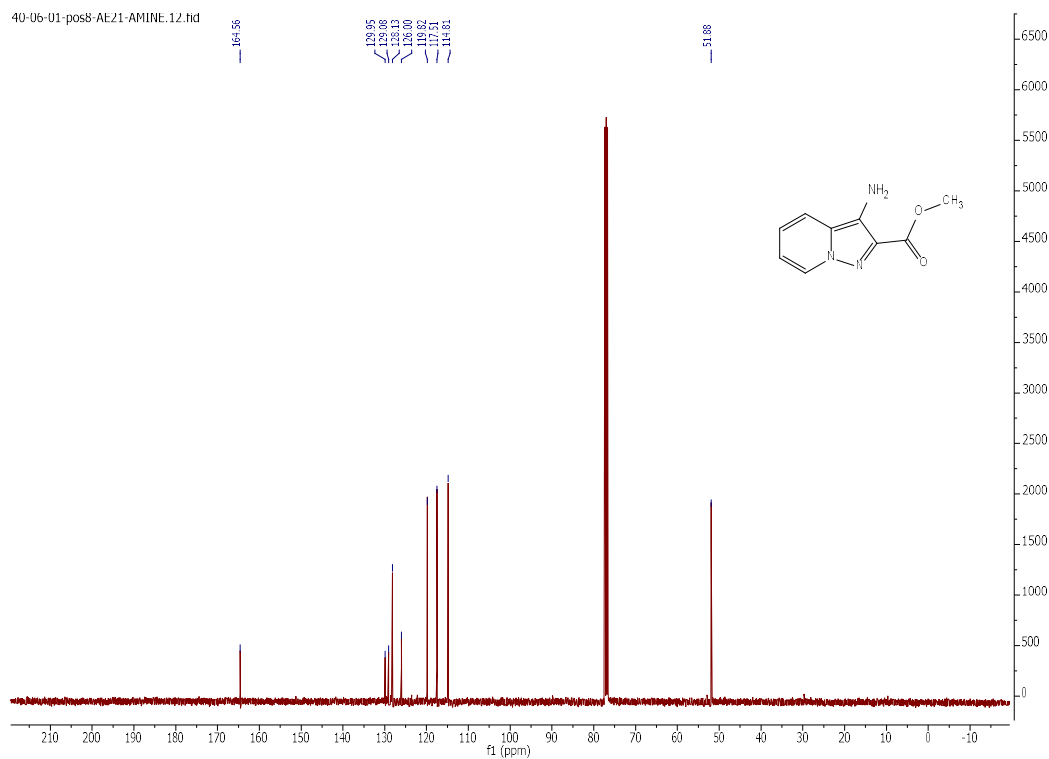


*Methyl 3-aminopyrazolo [1, 5-a] pyridine-2-carboxylate (6)*

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)

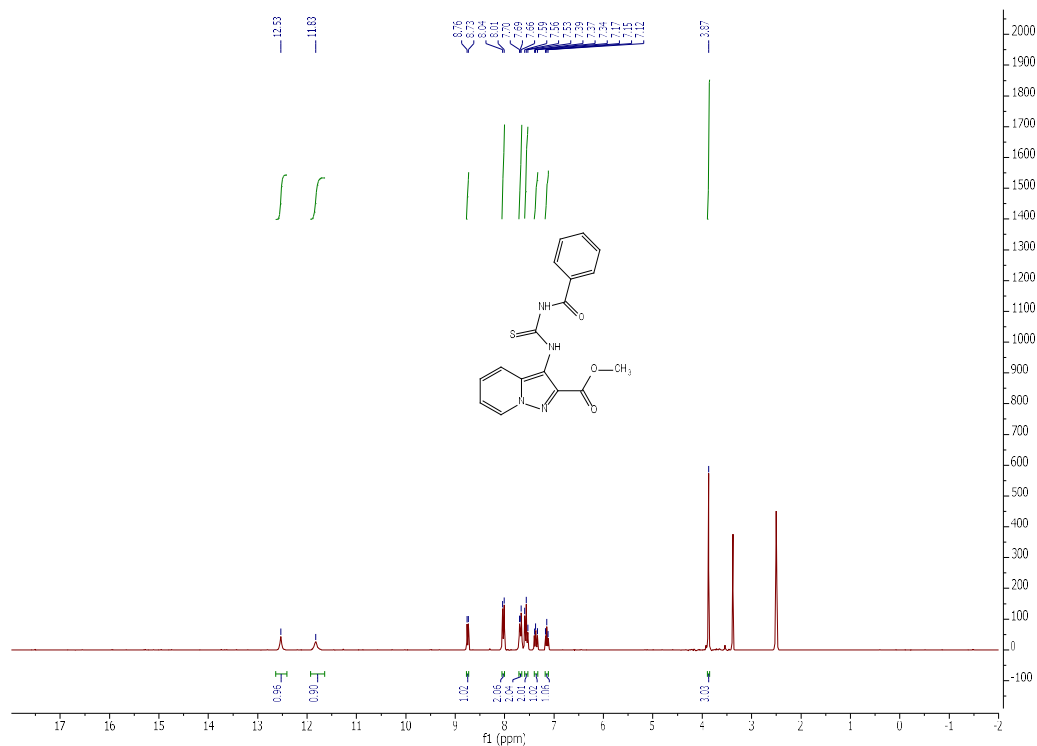


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ).

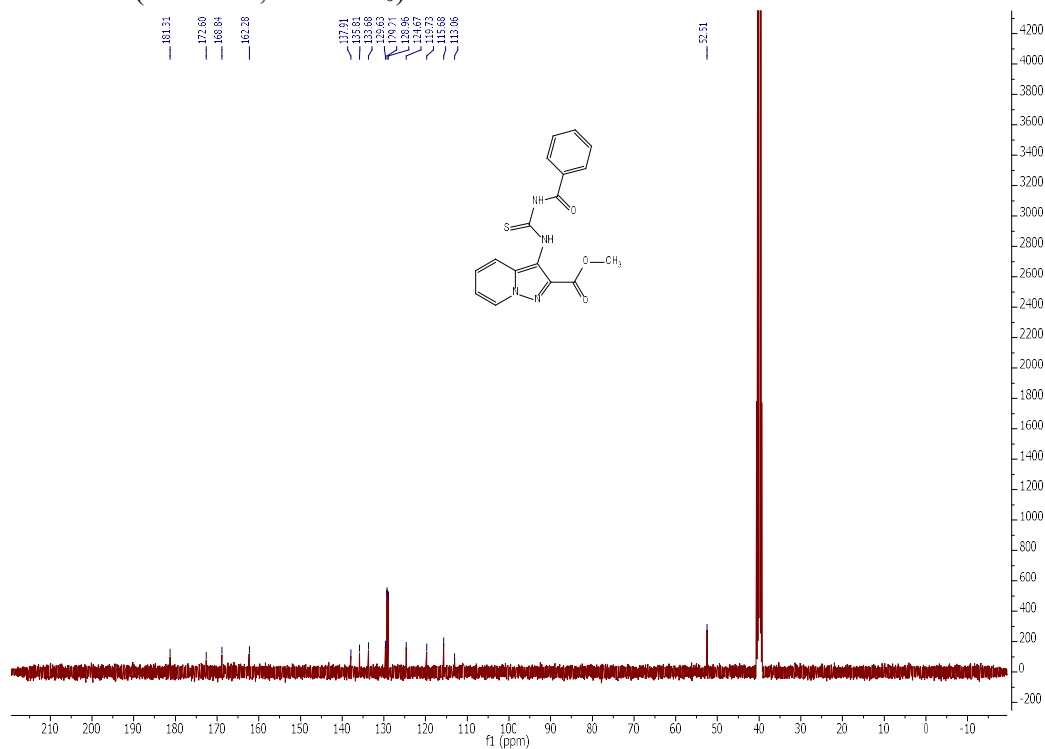


Methyl 3-[(3-oxo-3-phenyl-propanethioyl) amino] pyrazolo [1, 5-a] pyridine-2-carboxylate  
(7)

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

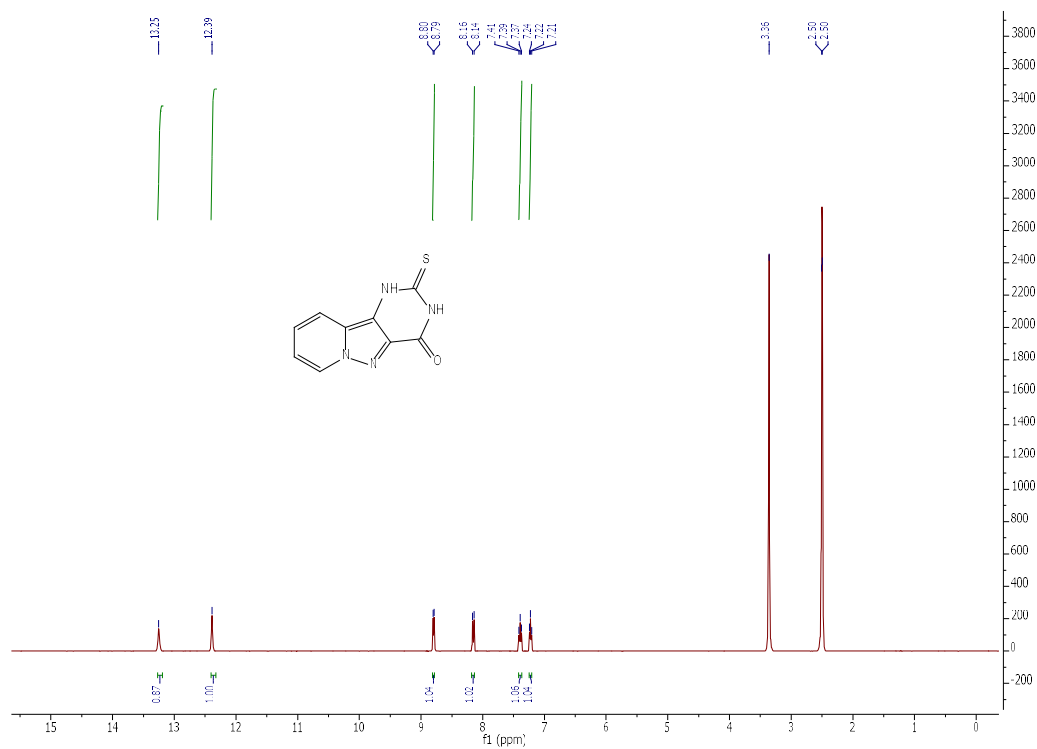


$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )

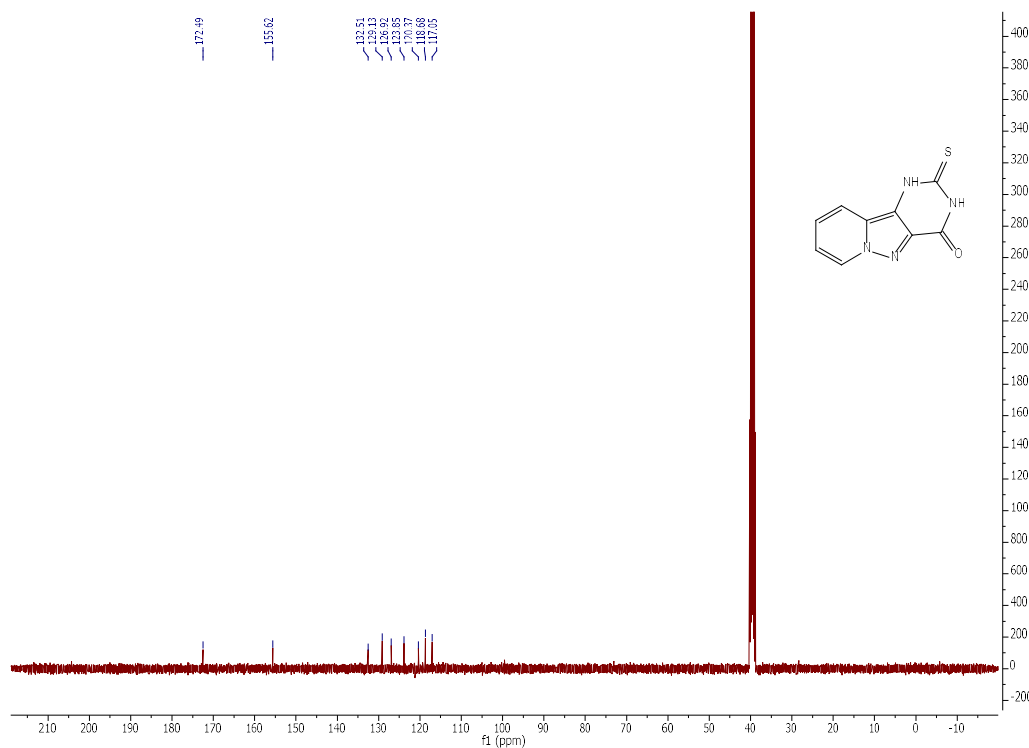


2-Thioxo-1H-pyrido [3, 4]pyrazolo[1,3-b]pyrimidin-4-one (**8**)

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

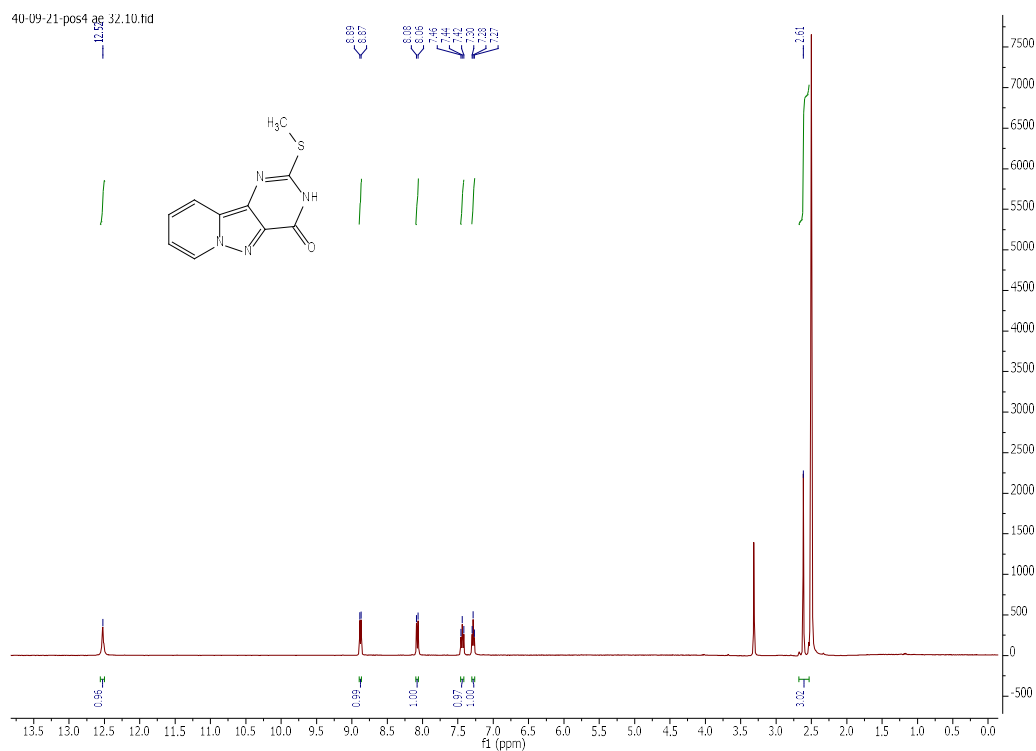


$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )

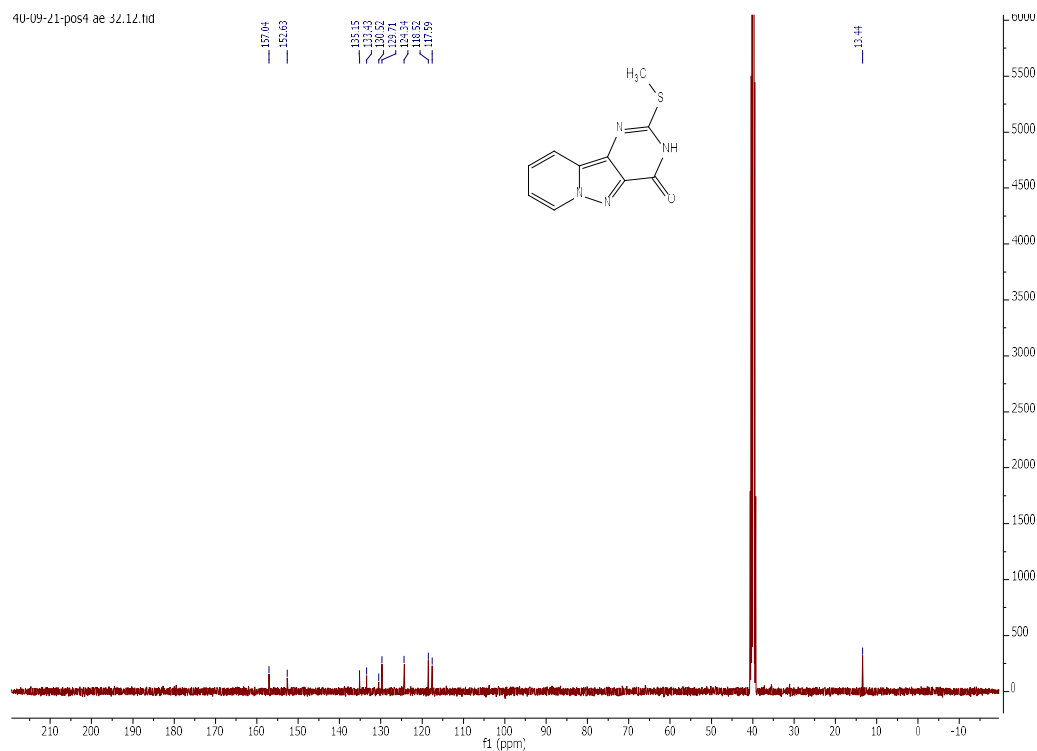


**2-methylsulfanyl-3H-pyrido[3,4]pyrazolo[1,3-b]pyrimidin-4-one (9)**

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

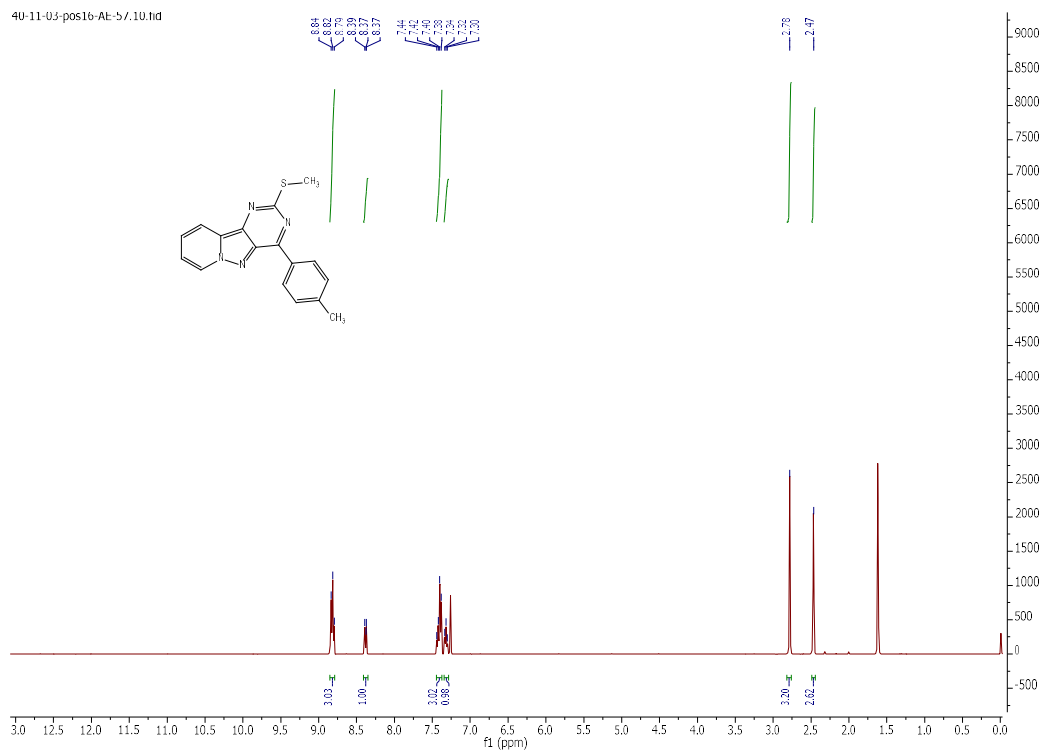


<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)

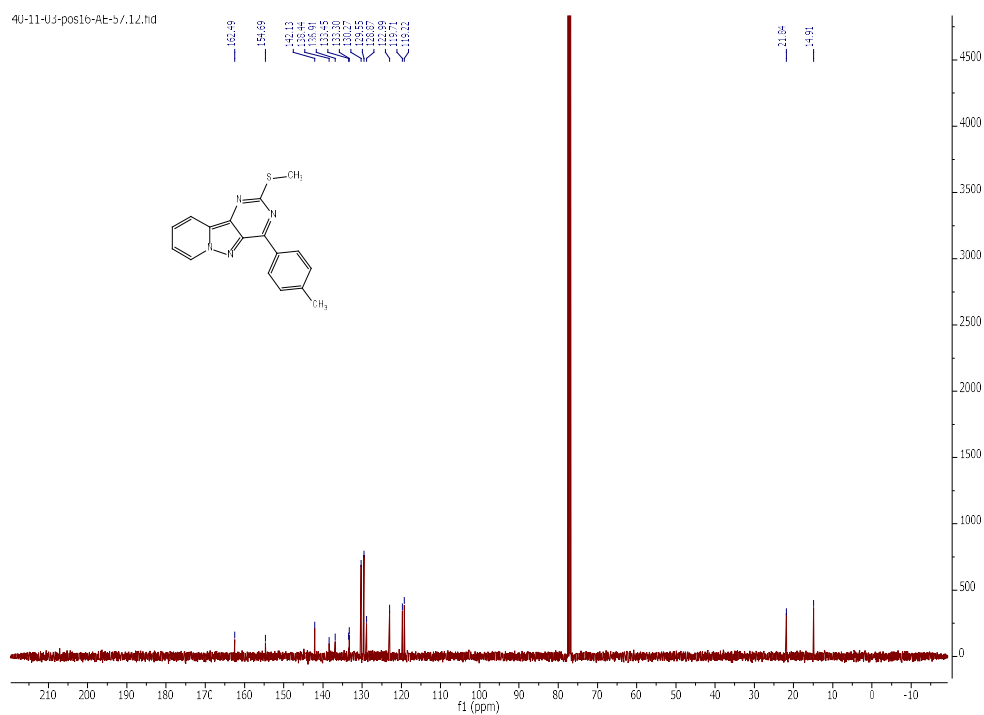


*2-methylsulfanyl-4-(p-tolyl)pyrido[3,4]pyrazolo[1,3-b]pyrimidine (10)*

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)

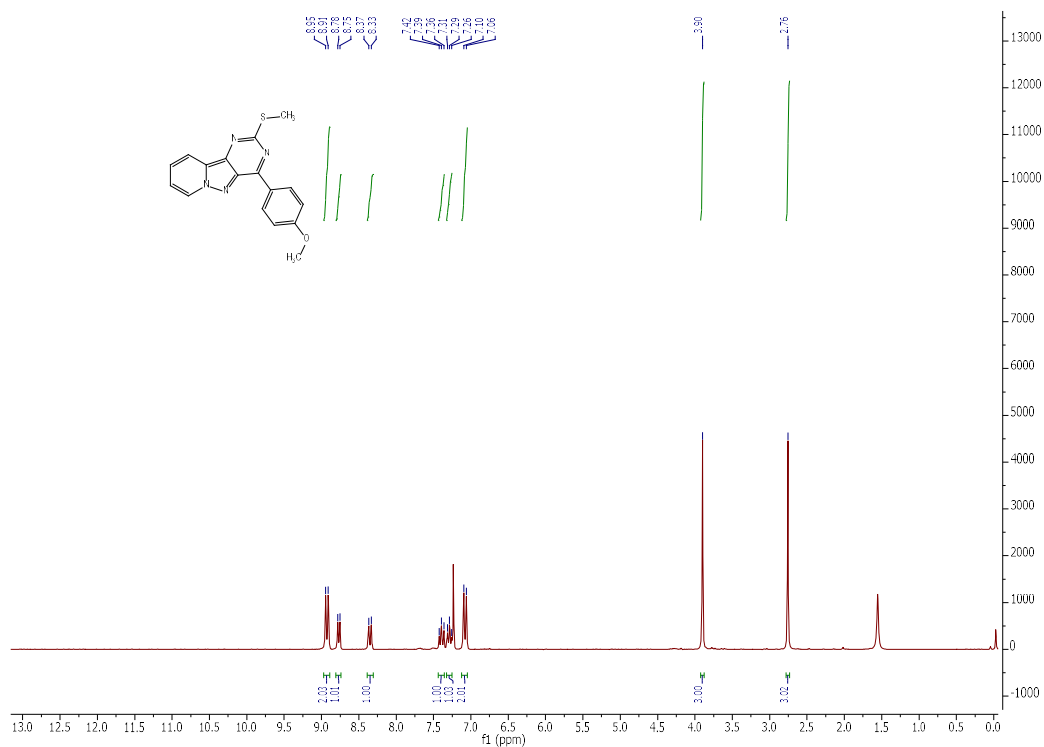


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

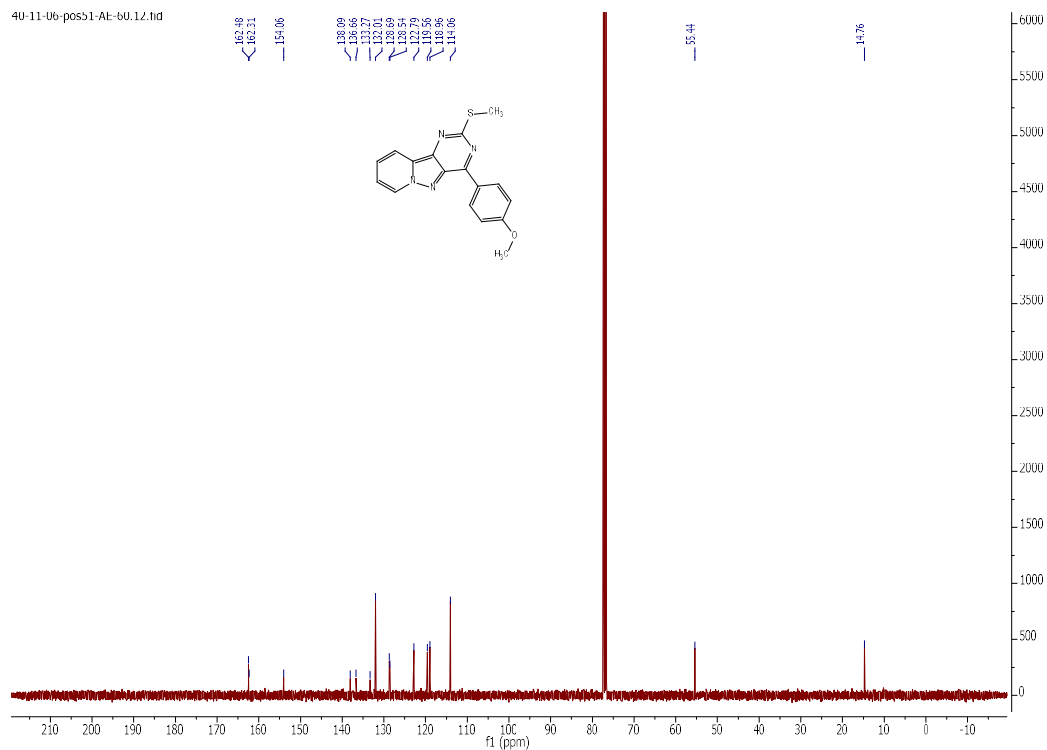


4-(4-methoxyphenyl)-2-methylsulfanyl-pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**11**)

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )

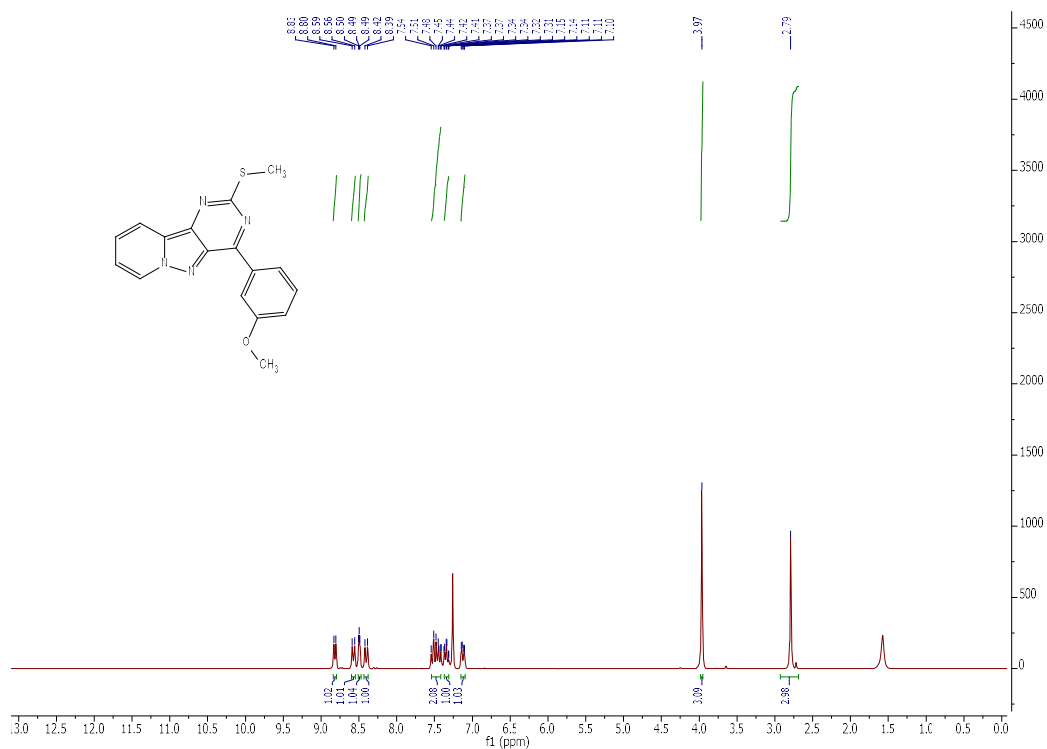


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

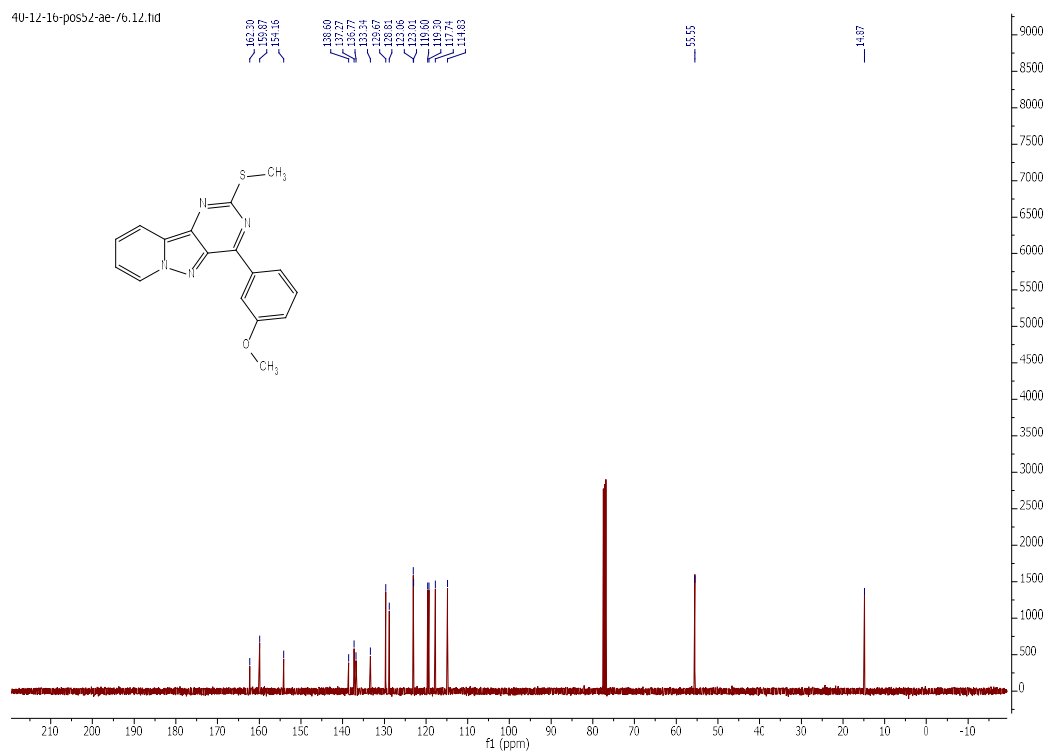


4-(3-methoxyphenyl)-2-methylsulfanyl-pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**12**)

$^1\text{H}$  NMR (250 MHz, Chloroform-*d*)

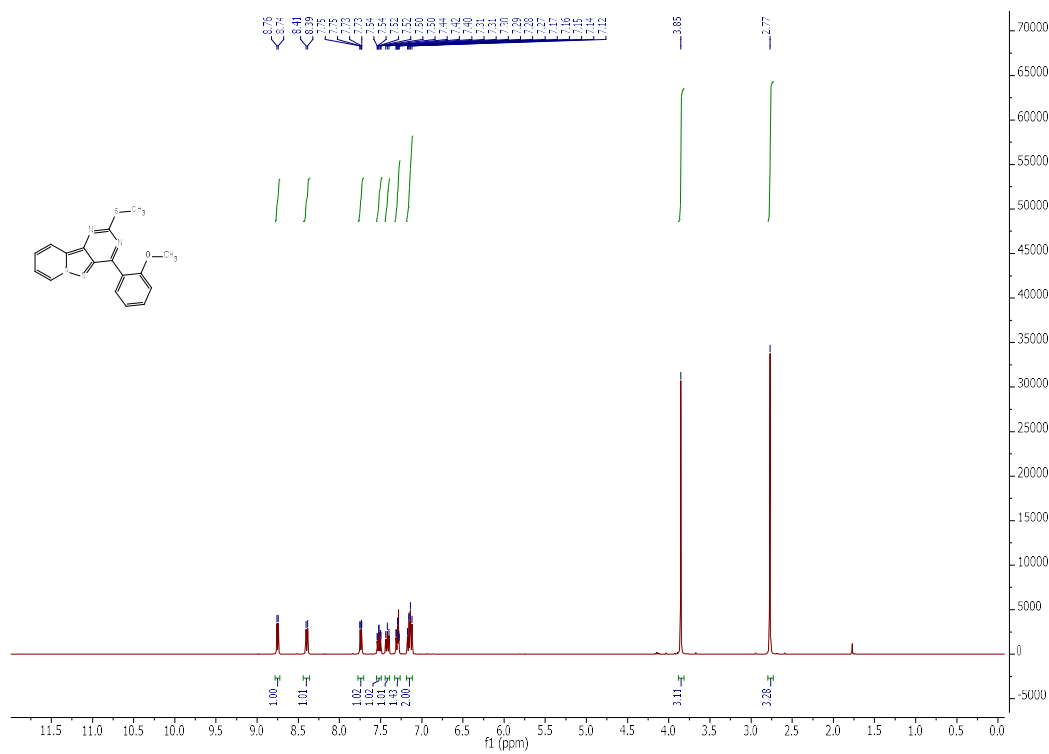


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

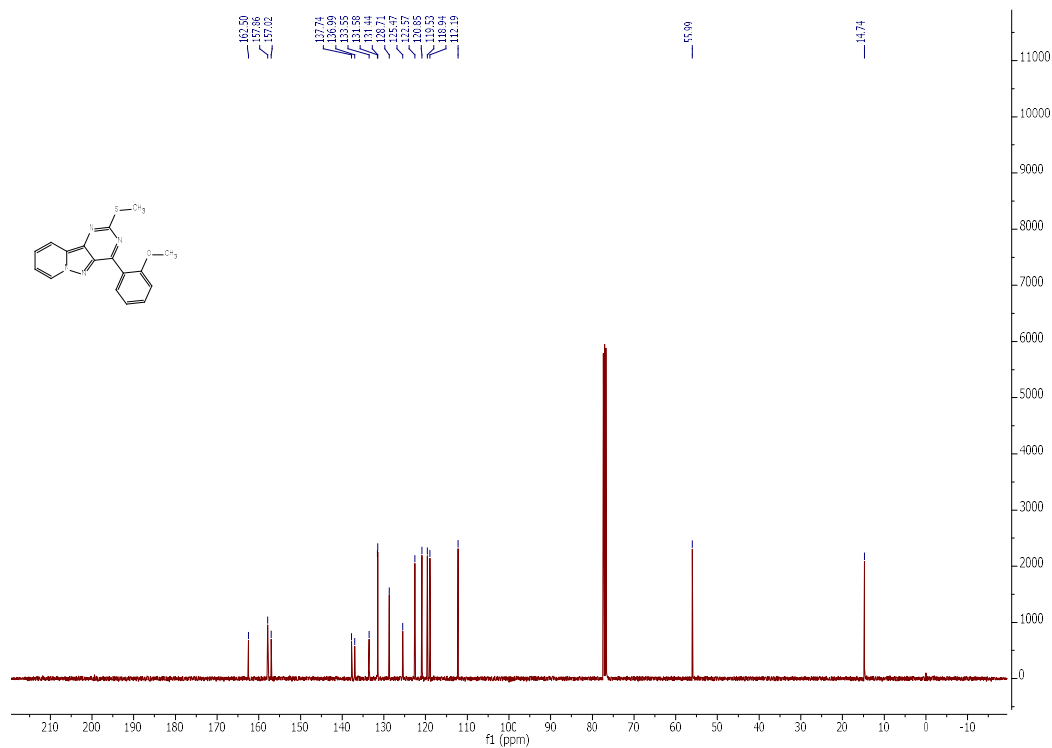


**4-(2-methoxyphenyl)-2-methylsulfanyl-pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**13**)**

<sup>1</sup>H NMR (250 MHz, Chloroform-*d*)



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

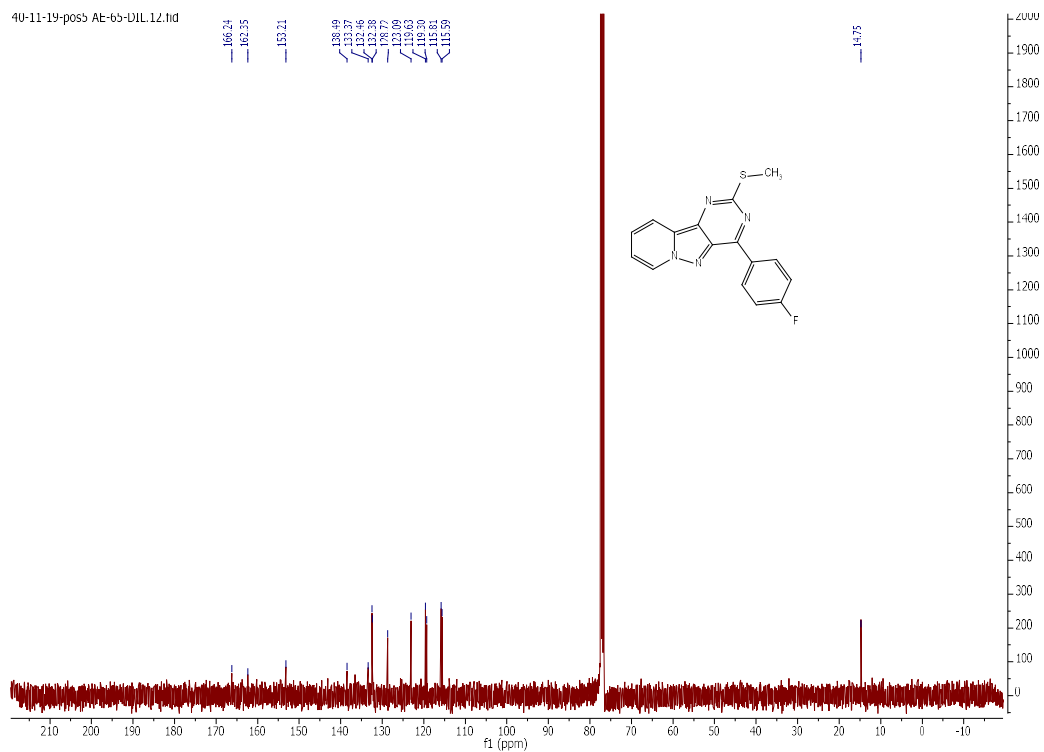


4-(4-fluorophenyl)-2-methylsulfanyl-pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**14**)

$^1\text{H}$  NMR (250 MHz, Chloroform-*d*)

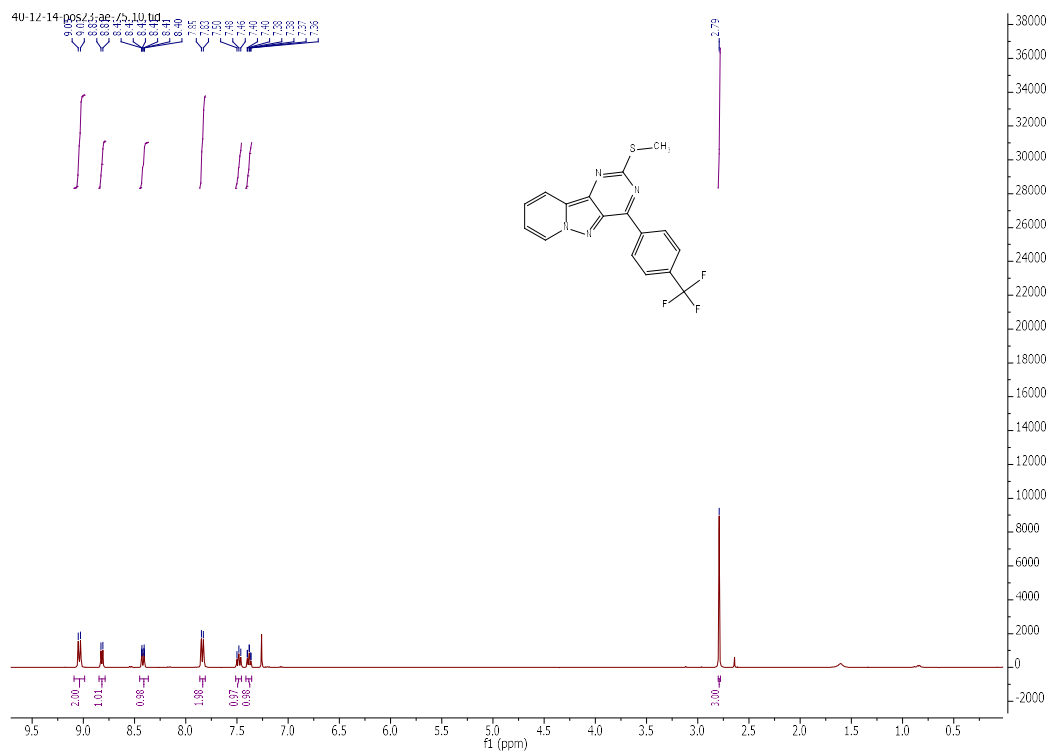


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

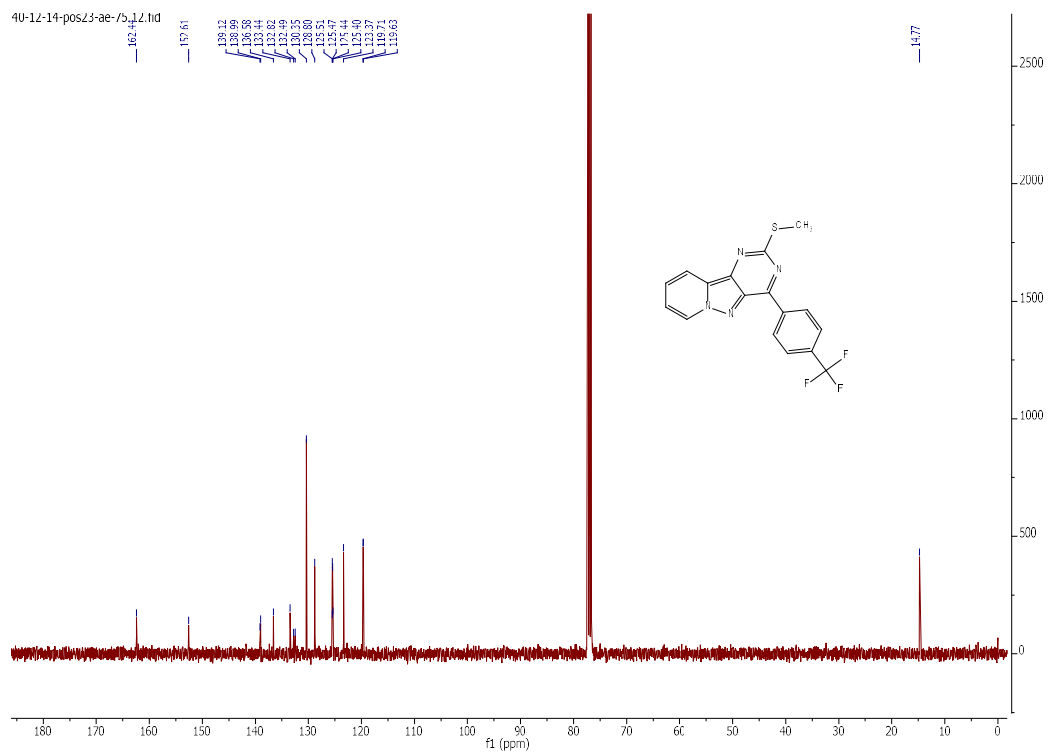


2-methylsulfanyl-4-[4-(trifluoromethyl)phenyl]pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**15**)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)

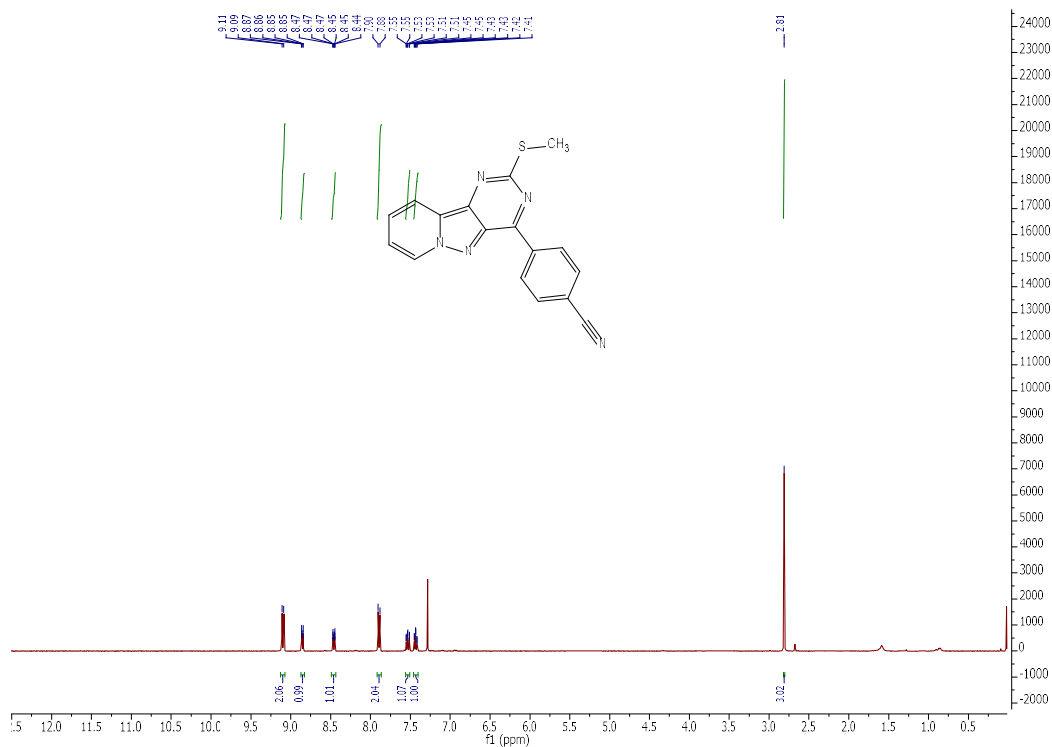


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

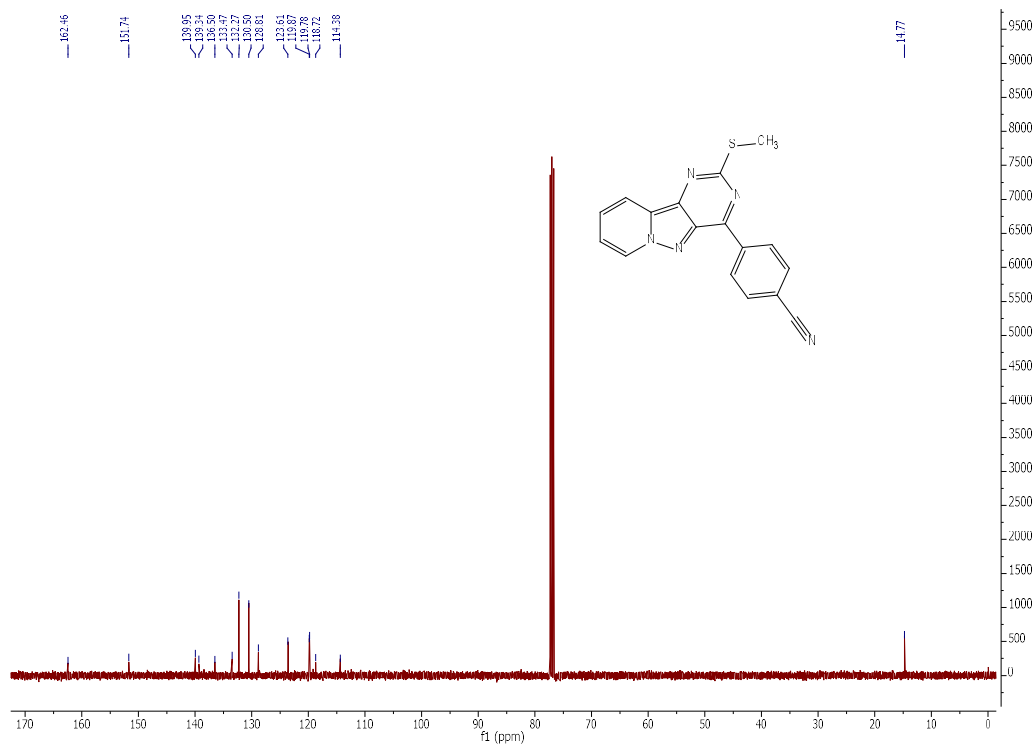


4-(2-methylsulfanylprido[3,4]pyrazolo[1,3-b]pyrimidin-4-yl)benzonitrile (**16**)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)



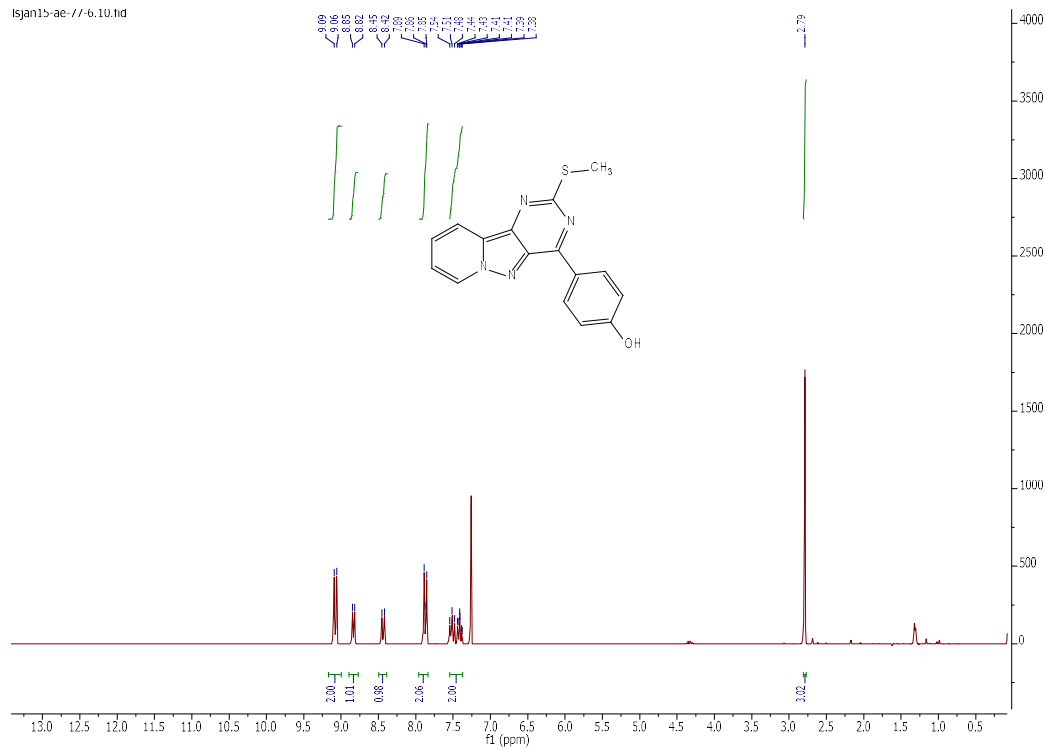
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



**4-(2-methylsulfanylpyrido[3,4]pyrazolo[1,3-b]pyrimidin-4-yl)phenol (**17**)**

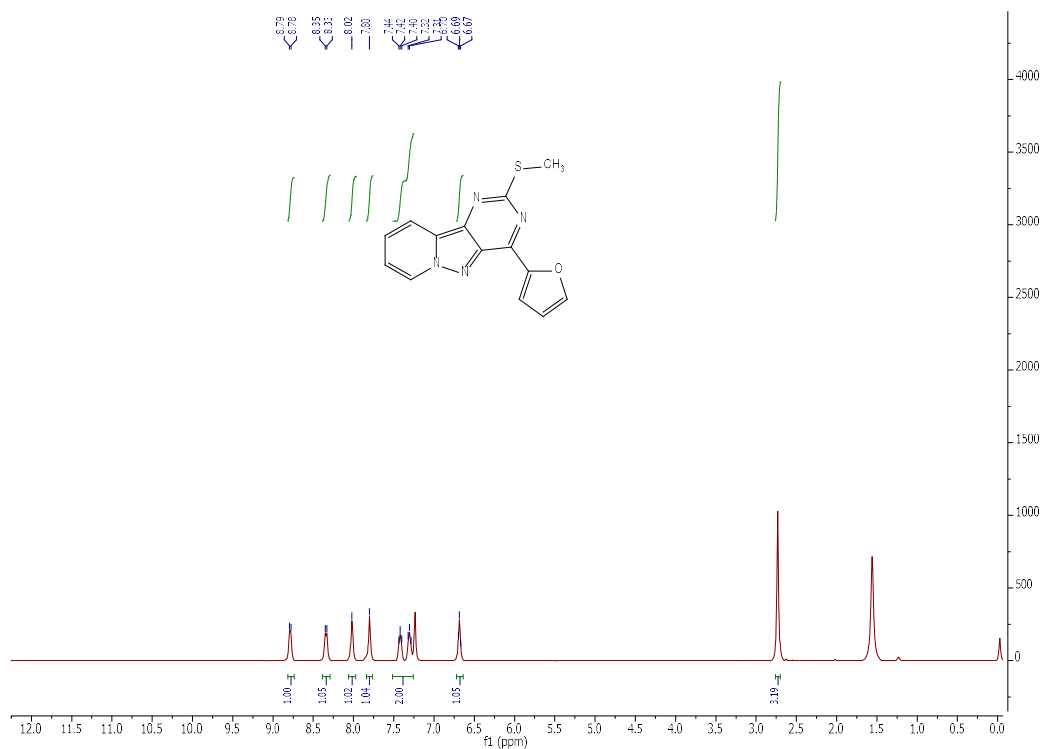
<sup>1</sup>H NMR (250 MHz, Chloroform-*d*)

lsjan15-ae-77-6.10.1d

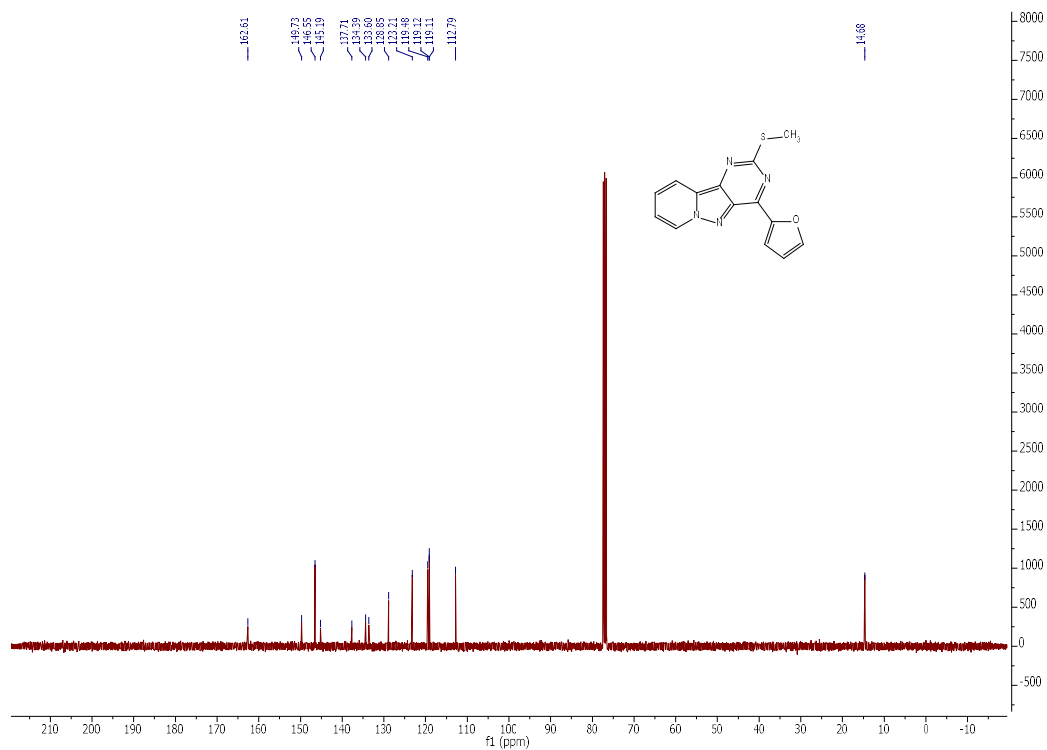


4-(2-furyl)-2-methylsulfonyl-pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**18**)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)

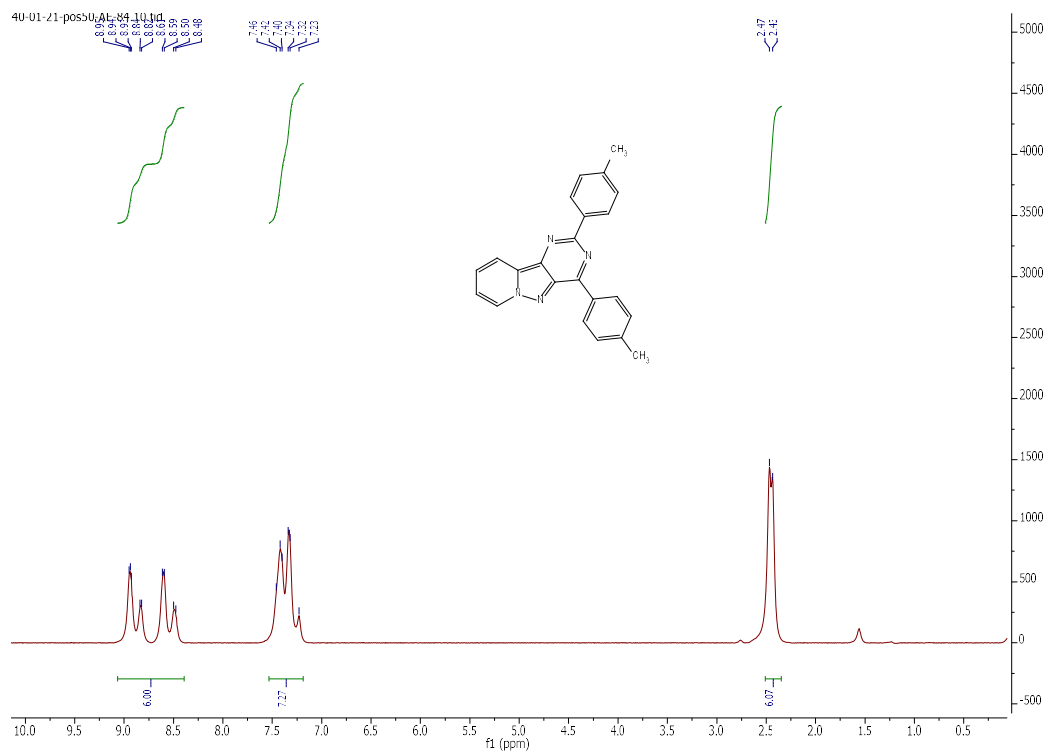


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

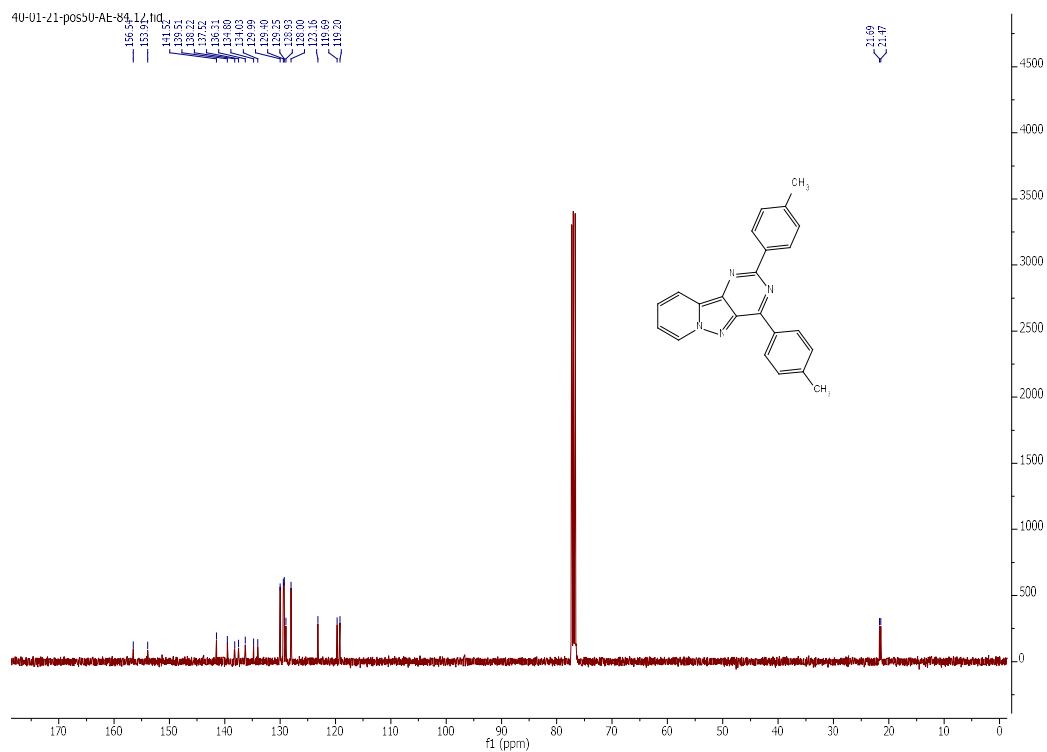


2,4-bis(*p*-tolyl)pyrido[3,4]pyrazolo[1,3-*b*]pyrimidine (**20**)

<sup>1</sup>H NMR 400 MHz, Chloroform-*d*)



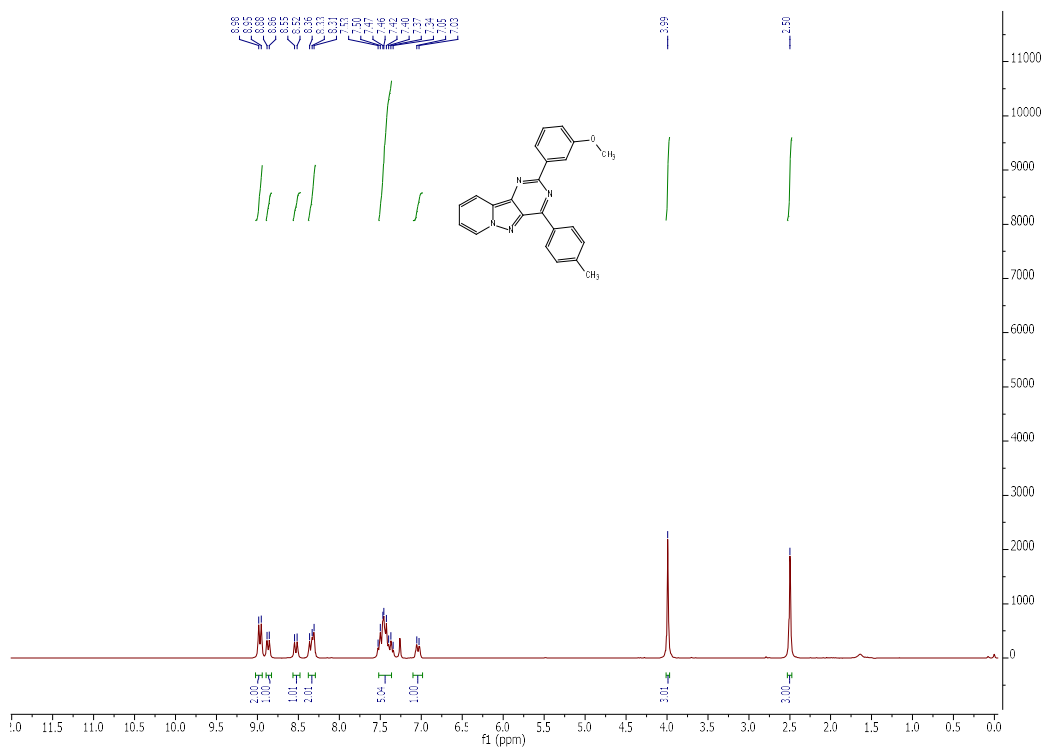
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



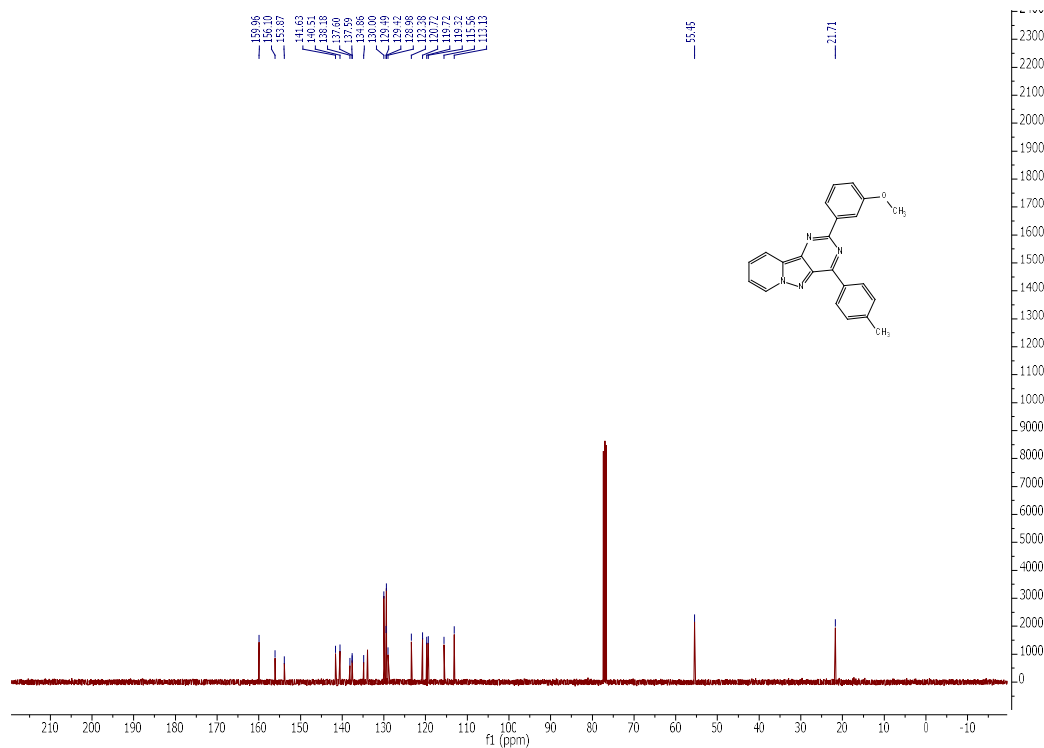


2-(3-methoxyphenyl)-4-(*p*-tolyl)pyrido[3,4]pyrazolo[1,3-*b*]pyrimidine (**22**)

$^1\text{H}$  NMR (250 MHz, Chloroform-*d*)

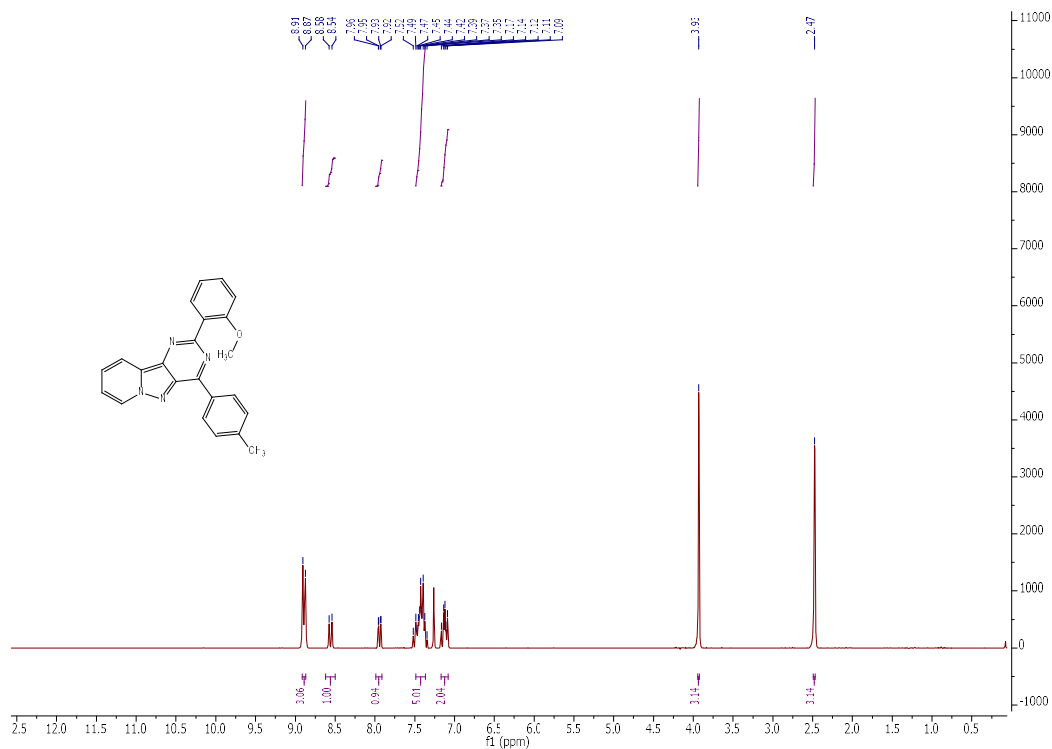


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

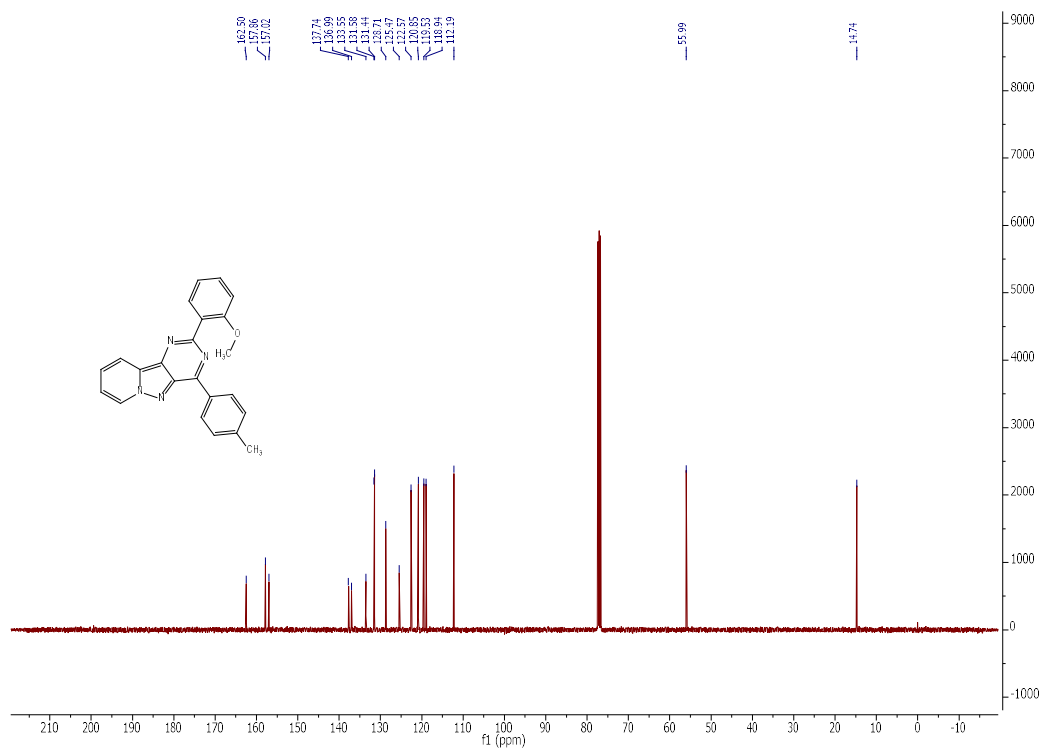


2-(2-methoxyphenyl)-4-(*p*-tolyl)pyrido[3,4]pyrazolo[1,3-*b*]pyrimidine (**23**)

$^1\text{H}$  NMR (250 MHz, Chloroform-*d*)

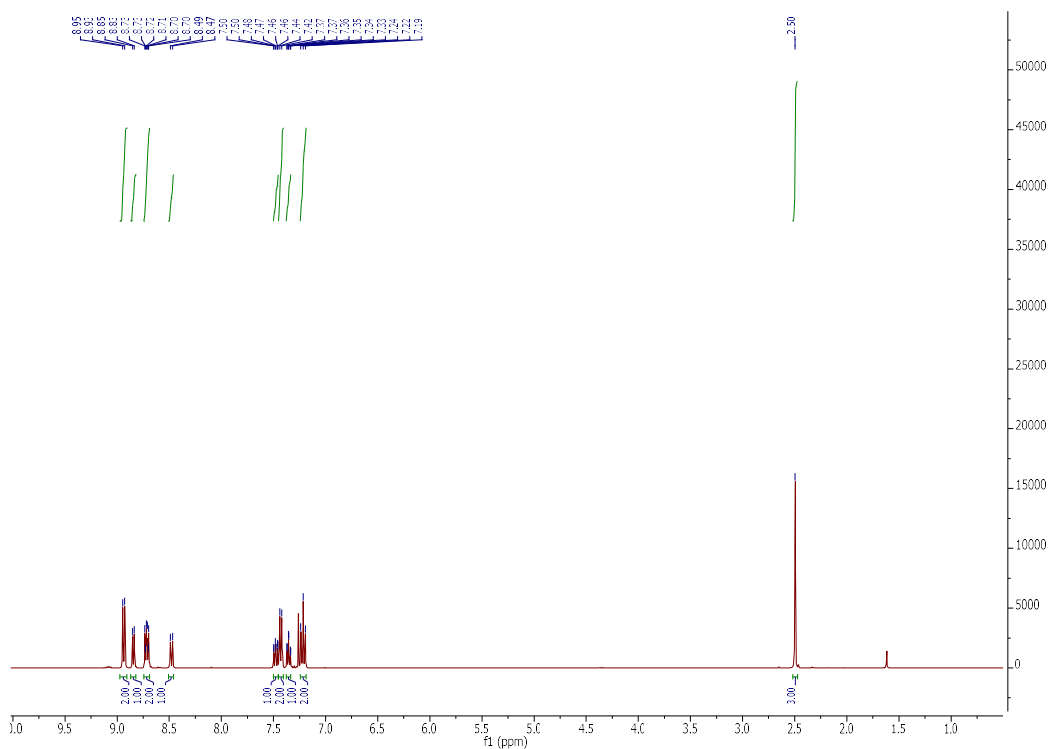


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

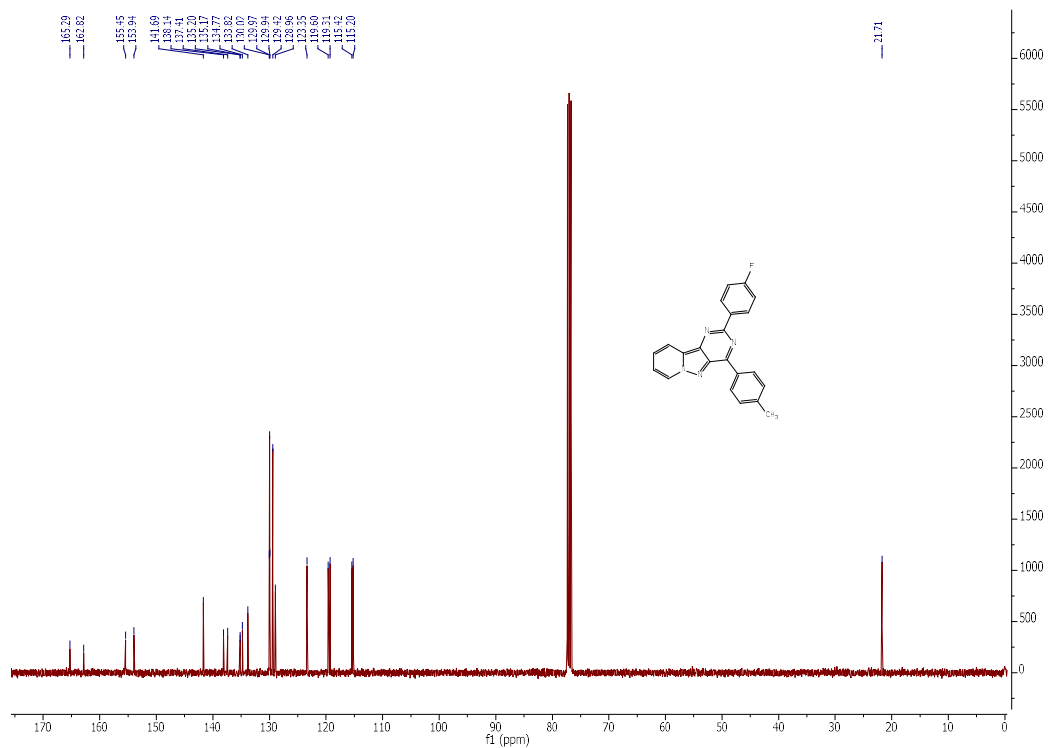


2-(4-fluorophenyl)-4-(*p*-tolyl)pyrido[3,4]pyrazolo[1,3-*b*]pyrimidine (**24**)

$^1\text{H}$  NMR (250 MHz, Chloroform-*d*)

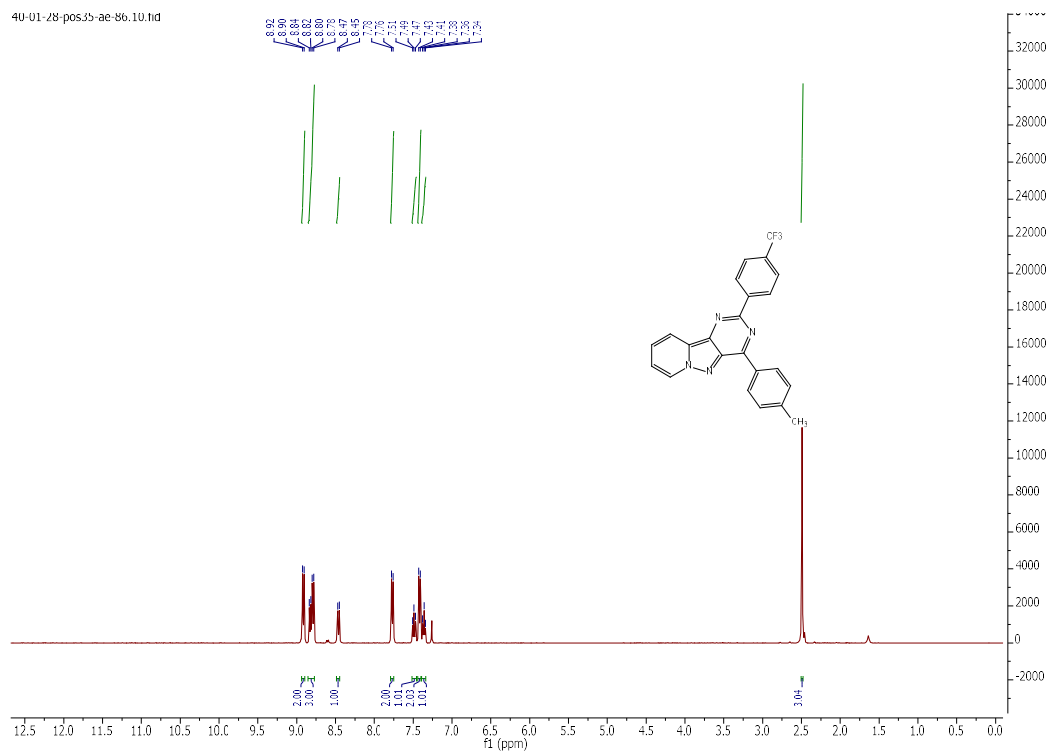


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

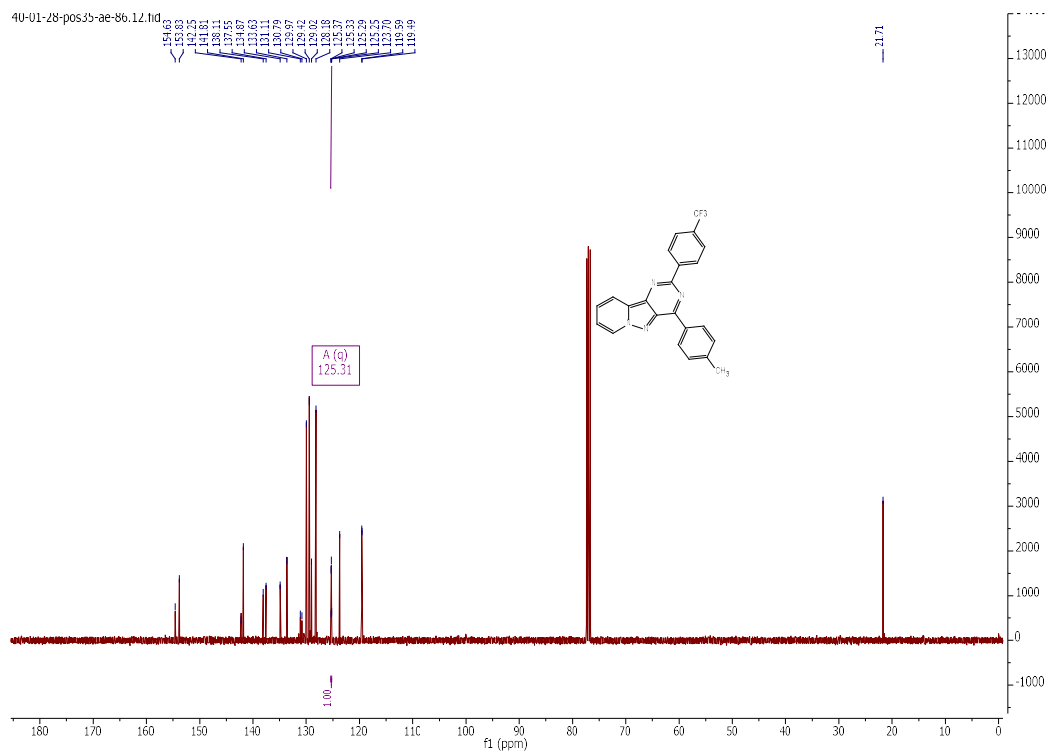


4-(*p*-tolyl)-2-[4-(trifluoromethyl)phenyl]pyrido[3,4]pyrazolo[1,3-*b*]pyrimidine (**25**)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)



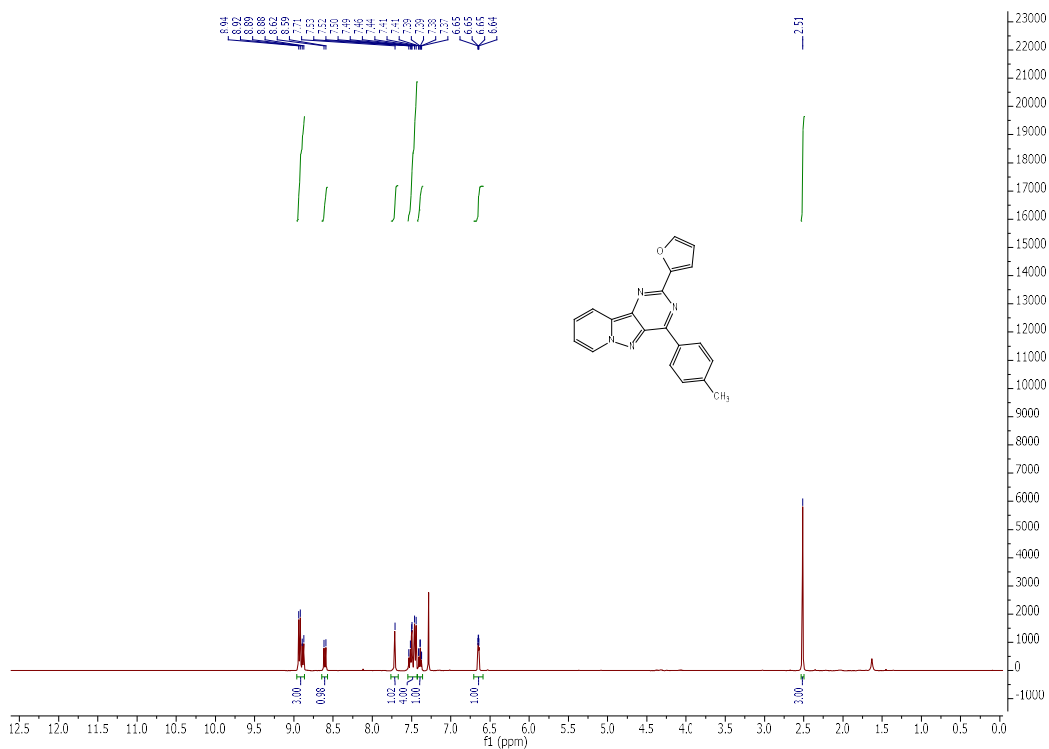
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



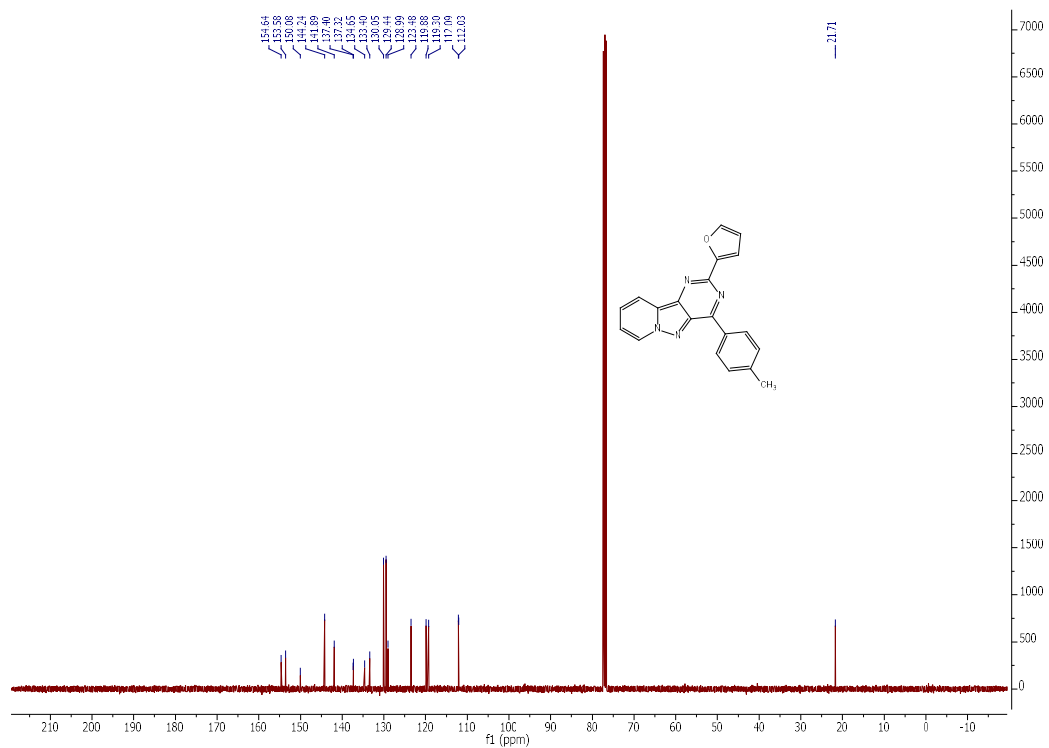


2-(2-furyl)-4-(p-tolyl)pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**27**)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)

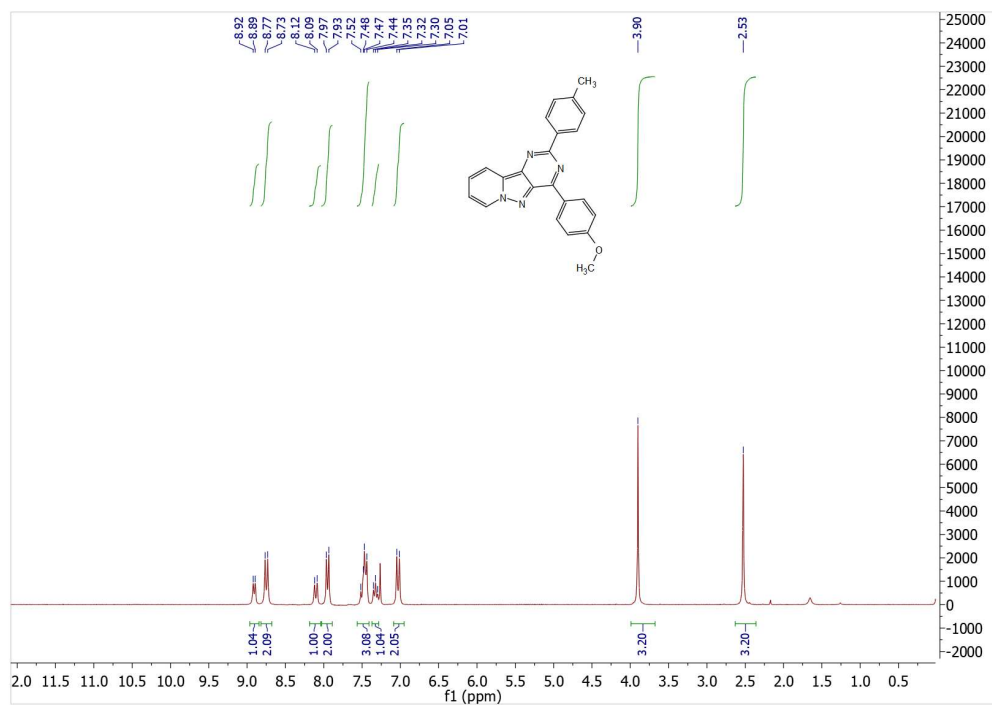


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

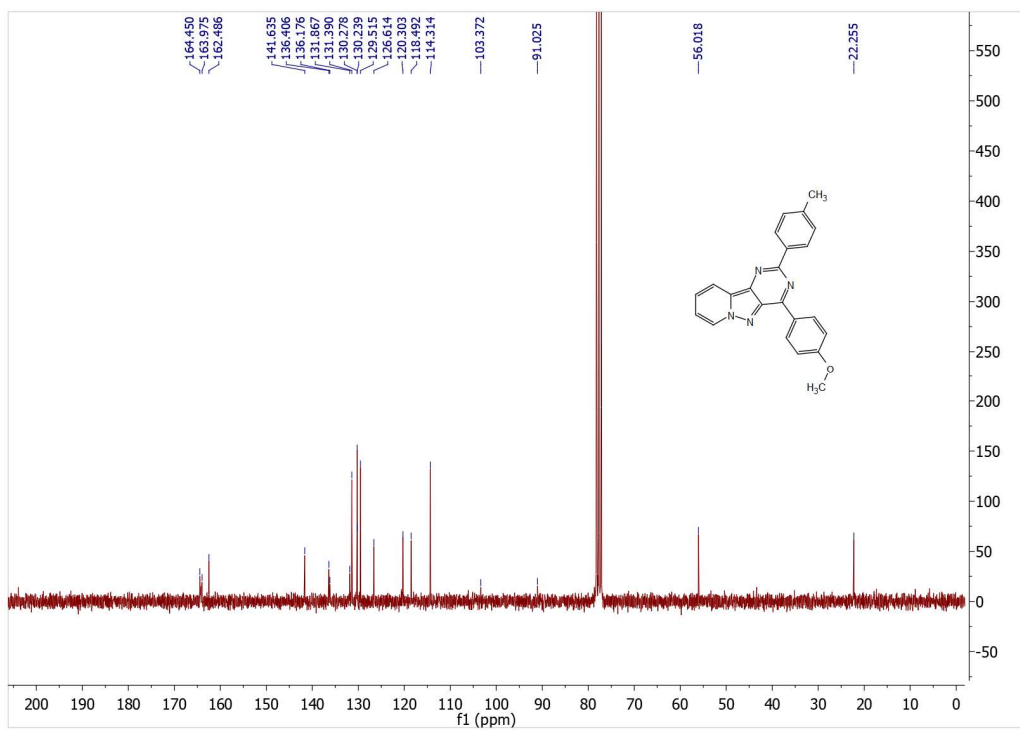


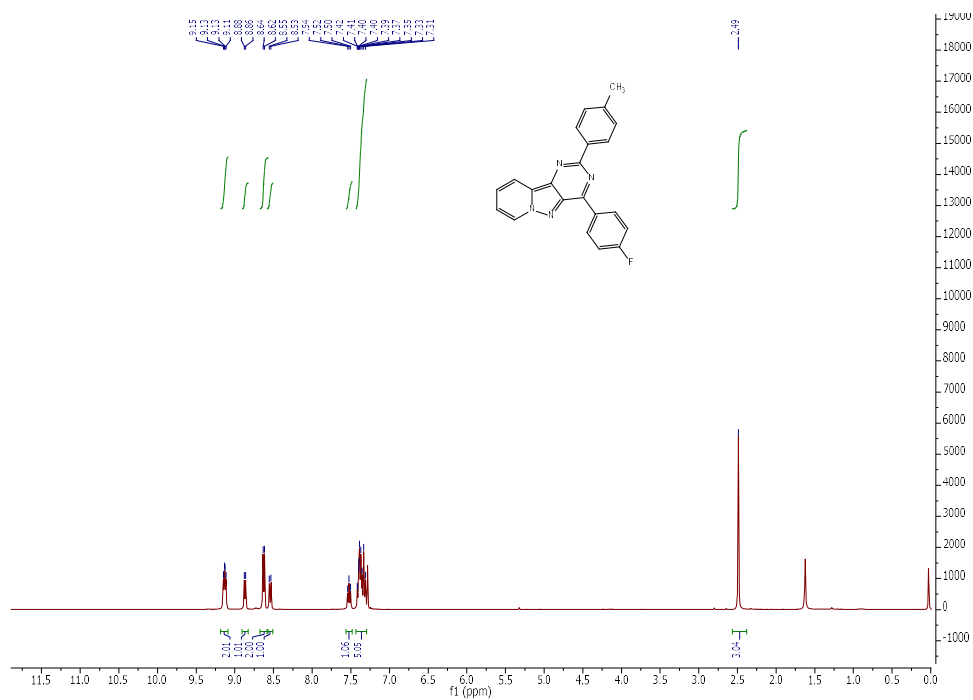
2-(2-tolyl)-4-(p-methoxyphenyl)pyrido[3,4]pyrazolo[1,3-b]pyrimidine (**29**)

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )



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



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)

Chemical structure: Cc1ccc(cc1)-c2nc3ccccc3nc2-c4nc5ccccc5nc4-c6ccc(F)cc6

<sup>13</sup>C NMR peaks (ppm): 156.06, 155.56, 156.47, 152.55, 138.67, 138.41, 137.47, 137.00, 136.84, 132.93, 132.90, 132.86, 132.78, 129.29, 129.26, 128.32, 127.77, 127.52, 127.39, 119.76, 119.44, 118.46, 118.26, 115.95, 21.46 (solvent).