

## Supporting Information

### **A convenient synthesis of *N*-(hetero)arylamides by oxidative coupling of methylheteroarenes with amines**

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## I. General Information:

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR Spectra were recorded on a JEOL ECZ 500R FT NMR spectrometer ( $^1\text{H}$  NMR at 500 MHz,  $^{13}\text{C}$  NMR at 126 MHz, &  $^{19}\text{F}$  NMR at 471 MHz). Chemical shifts for protons and carbons are reported in parts per million downfield from tetramethylsilane, and are referenced to the residual deuterium in the solvent ( $^1\text{H}$  NMR  $\text{CDCl}_3$  at 7.26 ppm) and carbon of the solvent peak ( $^{13}\text{C}$  NMR  $\text{CDCl}_3$  at 77.160 ppm) respectively. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, brs = broad singlet and m = multiplet), coupling constant ( $J$ ) (Hz), and integration. Mass spectra were recorded on a Sciex X500R QTOF mass spectrometer. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 GF 254 plates (thickness 0.25 mm). Visualization of TLC was performed with a 254 nm UV lamp, and by staining in  $\text{I}_2$  chamber. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the crude products was done by column chromatography using silica gel 100-200 mesh. All the reactions were carried out in oven-dried open glass vessels. Yield refers to the isolated analytically pure material.

## II. Materials:

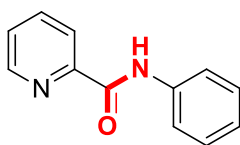
All the reagents and solvents were purchased from Sigma-Aldrich, Merck and TCI Chemicals. The chemicals were used as such without any further purification, whereas the solvents were purified by standard methods.

## III. General Experimental Procedure:

A mixture of methyltetarene (**1**, 1.5 mmol), amine (**2**, 1.0 mmol), elemental sulfur (2.0 mmol),  $\text{Cu}(\text{OAc})_2$  (20 mol %) and DMSO (2 mL) was stirred in an open air glass vessel at 110 °C for 15 h. After completion of the reaction (monitored through TLC), a cold brine solution (10 mL) was added to the mixture, and then extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated using rotary vacuum evaporator. The residue was purified by column chromatography using ethyl acetate/n-hexane as eluent to afford the pure product **3**.

## IV. Physical and Spectral Data:

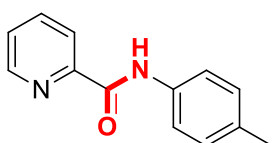
### *N*-Phenylpicolinamide (3a)<sup>1</sup>:



3a

Brownish yellow solid (76%, 150 mg); mp: 78-79 °C (lit. 76-77 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.13 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 6.5 Hz, 1H) 7.78 (d, *J* = 8.0 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 4.0 Hz, 2H), 10.03 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 115.1, 119.7, 122.4, 124.4, 126.5, 129.1, 137.7, 148.0, 149.9, 162.0.

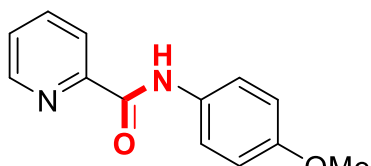
### *N*-(*p*-Tolyl)picolinamide (3b)<sup>1</sup>:



3b

Yellow solid (77 %, 163 mg); mp: 106-108 °C (lit. 105-107 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 2.34 (s, 3H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.45-7.47 (m, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.87 (dt, *J* = 7.5 Hz, 2.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 4.5 Hz, 1H), 9.96 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 21.0, 119.7, 122.4, 126.4, 129.6, 134.0, 135.3, 137.7, 148.0, 150.0, 161.9.

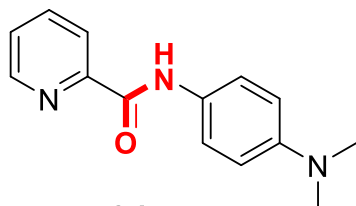
### *N*-(4-Methoxyphenyl)picolinamide (3c)<sup>1</sup>:



3c

Yellow solid (79%, 180 mg); mp: 91-93 °C (lit. 94-95 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 3.78 (s, 3H), 6.80-6.91 (m, 2H), 7.41-7.44 (m, 1H), 7.67-7.70 (m, 2H), 7.84 (t, *J* = 7.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.56 (d, *J* = 4.5 Hz, 1H), 9.91 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 55.5, 114.2, 121.2, 122.3, 126.3, 131.0, 137.6, 147.9, 149.9, 156.4, 161.7.

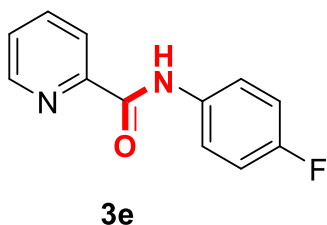
### *N*-(4-(Dimethylamino)phenyl)picolinamide (3d)<sup>3</sup>:



3d

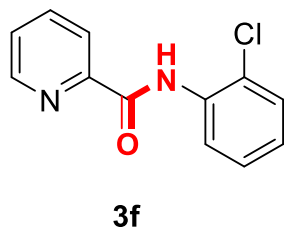
Brownish yellow solid (57%, 142 mg); mp: 129-130 °C (lit. 131-132 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 2.95 (s, 6H), 6.76 (d, *J* = 8.5 Hz, 2H), 7.44-7.46 (m, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 6.5 Hz, 1H), 8.59 (d, *J* = 4.5 Hz, 1H), 9.84 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 41.0, 113.2, 114.7, 121.2, 122.3, 123.9, 126.1, 136.9, 137.6, 147.9, 161.5.

### *N*-(4-Fluorophenyl)picolinamide (**3e**)<sup>2</sup>:



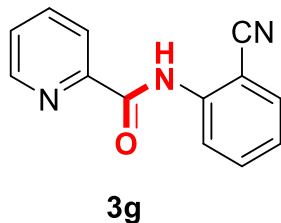
Brown solid (78%, 168 mg); mp: 103-105 °C (lit. 104-105 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.05-7.10 (m, 2H), 7.47-7.49 (m, 1H), 7.72-7.76 (m, 2H), 7.89 (t, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 4.5 Hz, 1H), 10.0 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 115.7 (d, *J* = 22.1 Hz, 2C), 121.4 (d, *J* = 7.5 Hz, 2C), 122.5, 126.6, 133.9, 137.8, 148.1, 149.7, 158.5 (d, *J* = 244.3 Hz, 2C), 162.0. <sup>19</sup>F (470 MHz, CDCl<sub>3</sub>) δ<sub>F</sub> = -117.72.

### *N*-(2-Chlorophenyl)picolinamide (**3f**):



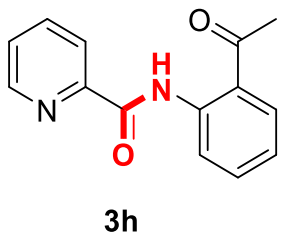
Light yellow sticky solid (78%, 181 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.05-7.09 (m, 1H), 7.31-7.34 (m, 1H), 7.41-7.43 (m, 1H), 7.48-7.50 (m, 1H), 7.89 (dt, *J* = 7.5 Hz, 2.0 Hz, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.64-8.67 (m, 2H), 10.71 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 121.2, 122.5, 123.6, 124.7, 126.7, 127.8, 129.3, 134.8, 137.7, 148.4, 149.8, 162.3; HRMS: (M+H)<sup>+</sup> calcd. for C<sub>12</sub>H<sub>10</sub>ClN<sub>2</sub>O: 233.0482; found: 233.0504.

### *N*-(2-Cyanophenyl)picolinamide (**3g**)<sup>4</sup>:



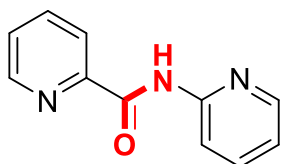
Yellow sticky solid (72%, 160 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.47-7.54 (m, 2H), 7.78 (quint, *J* = 7.0 Hz, 2H), 7.90-7.94 (m, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 4.5 Hz, 1H), 10.97 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 122.0, 122.5, 126.3, 126.8, 127.4, 128.1, 134.6, 137.6, 148.4, 148.8, 149.0, 149.2, 161.5.

### *N*-(2-Acetylphenyl)picolinamide (**3h**)<sup>5</sup>:



Brownish yellow solid (69%, 166 mg); mp: 106-108 °C (lit. 109-112 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 2.72 (s, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.46-7.49 (m, 1H), 7.60-7.63 (m, 1H), 7.87 (td, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.95-7.96 (m, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 4.5 Hz, 1H), 9.01 (d, *J* = 8.0 Hz, 1H), 13.54 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 28.7, 121.2, 122.9, 123.3, 126.5, 131.8, 135.0, 137.5, 138.4, 140.3, 148.8, 150.6, 164.1, 202.3.

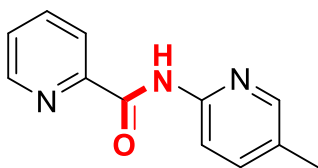
***N*-(Pyridin-2-yl)picolinamide (3i)<sup>6</sup>:**



**3i**

White solid (80%, 159 mg); mp: 145-147 °C (lit.142-145 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.06 (dd, *J* = 6.5 Hz, 5.5 Hz, 1H), 7.48 (t, *J* = 6.0 Hz, 1H), 7.74 (t, *J* = 7.0 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.36 (d, *J* = 4.0 Hz, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 4.5 Hz, 1H), 10.55 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 114.0, 120.0, 122.5, 126.8, 137.7, 138.4, 148.3, 148.4, 149.4, 151.3, 162.7.

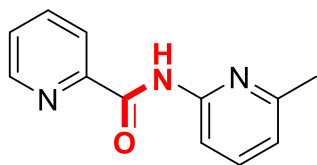
***N*-(5-Methylpyridin-2-yl)picolinamide (3j):**



**3j**

Yellow solid (83%, 176 mg); mp: 125-127 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 2.32 (s, 3H), 7.47 (dd, *J* = 7.5 Hz, 4.5 Hz, 1H), 7.56 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.88-7.92 (m, 1H), 8.18 (s, 1H), 8.27 (m, 2H), 8.62 (d, *J* = 9.0 Hz, 1H), 10.49 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 18.0, 113.5, 122.5, 126.7, 129.3, 137.6, 138.9, 148.2, 148.3, 149.1, 149.5, 162.5; HRMS: (M+H)<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O: 214.0980; found: 214.0995.

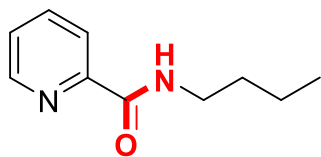
***N*-(6-Methylpyridin-2-yl)picolinamide (3k):**



**3k**

Yellow solid (80%, 170 mg); mp: 90-92 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 2.50 (s, 3H), 6.92 (d, *J* = 7.5 Hz, 1H), 7.46-7.48 (m, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.88 (t, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.62 (d, *J* = 4.0 Hz, 1H), 10.47 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 24.2, 110.8, 119.4, 122.5, 126.7, 137.6, 138.6, 148.3, 149.5, 150.5, 157.3, 162.6; HRMS: (M+H)<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O: 214.0980; found: 214.0996.

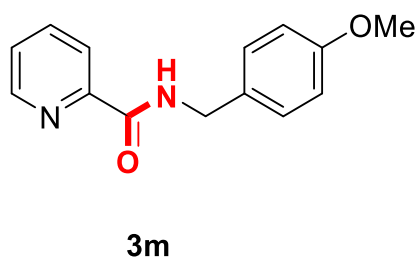
***N*-Butylpicolinamide (3l)<sup>13</sup>:**



**3l**

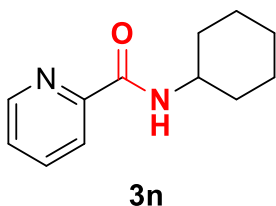
Brown sticky solid (59%, 105 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 0.93 (t, *J* = 7.5 Hz, 3H), 1.39-1.45 (m, 2H), 1.58-1.64 (m, 2H), 3.44 (q, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 6.0 Hz, 1H), 7.80 (t, *J* = 8.5 Hz, 1H), 8.03 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 4.5, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 13.9, 20.3, 31.6, 39.2, 122.3, 126.1, 137.4, 148.1, 150.1 164.3.

***N*-(4-Methoxybenzyl)picolinamide (3m)<sup>14</sup>:**



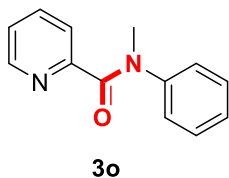
Brownish yellow solid (64%, 155 mg); mp: 54-56 °C (lit. 58-60 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 3.77 (s, 3H), 4.58 (d, *J* = 5.5 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 7.24-7.25 (m, 2H), 7.38 (qd, *J* = 5.4 Hz, 4.5 Hz, 1H), 7.82-7.85 (m, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.31 (s, 1H), 8.49 (d, *J* = 4.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 43.3, 55.3, 114.1, 122.5, 126.2, 129.3, 130.3, 137.5, 148.0, 149.8, 159.1, 164.1.

***N*-Cyclohexylpicolinamide (3n)<sup>13</sup>:**



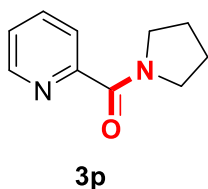
Brownish yellow solid (72%, 147 mg); mp: 51-53 °C (lit. 54-56 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 1.17-1.40 (m, 5H), 1.58-1.61 (m, 1H), 1.70-1.74 (m, 2H), 1.95-1.98 (m, 2H), 3.88-3.96 (m, 1H), 7.35 (dd, *J* = 5.0 Hz, 2.5 Hz, 1H), 7.77 (td, *J* = 6.0 Hz, 1.5 Hz, 1H), 7.93 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 8.48 (d, *J* = 4.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 24.9, 25.6, 33.0, 48.2, 122.2, 126.0, 137.4, 147.9, 150.2, 163.2.

***N*-Methyl-*N*-phenylpicolinamide (3o)<sup>11</sup>:**



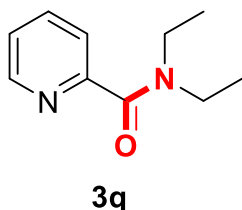
Brownish yellow sticky solid (71%, 150 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 3.51 (s, 3H), 7.04-7.19 (m, 6H), 7.42 (s, 1H), 7.58 (s, 1H), 8.33 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 38.1, 123.7, 124.0, 126.6, 126.7, 129.1, 136.3, 144.4, 148.6, 154.4, 168.9.

**Pyridin-2-yl(pyrrolidin-1-yl)methanone (3p)<sup>12</sup>:**



Yellow sticky solid (56%, 101 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 1.96-2.08 (m, 4H), 3.61 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 7.0 Hz, 2H), 7.26 (t, *J* = 5.5 Hz, 1H), 7.70-7.77 (m, 2H), 8.49 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 24.4, 26.7, 53.4, 53.8, 124.1, 124.3, 138.7, 146.2, 158.0, 166.6.

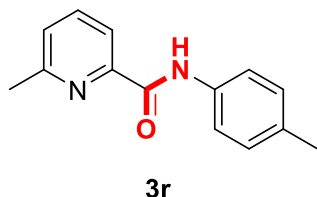
***N,N*-Diethylpicolinamide (3q)<sup>12</sup>:**



Brown sticky solid (58%, 103 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 1.11 (t, *J* = 6.5 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 3.33 (q, *J* = 7.0 Hz, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 6.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 4.0 Hz, 1H);

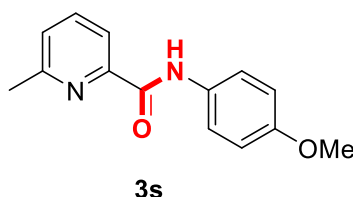
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  = 12.9, 14.3, 40.2, 43.3, 123.1, 124.2, 137.3, 148.2, 155.0, 168.4.

**6-Methyl-*N*-(*p*-tolyl)picolinamide (3r)<sup>7</sup>:**



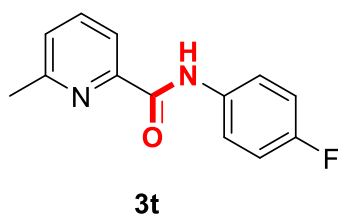
Brownish yellow solid (78%, 176 mg); mp 114-116 °C (lit.117-118 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 2.34 (s, 3H), 2.63 (s, 3H), 7.18 (d,  $J$  = 8.0 Hz, 2H), 7.30 (d,  $J$  = 7.5 Hz, 1H), 7.66 (d,  $J$  = 7.5 Hz, 2H), 7.75 (t,  $J$  = 7.5 Hz, 1H), 8.09 (d,  $J$  = 7.5 Hz, 1H), 10.02 (s, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  = 21.0, 24.4, 119.5, 119.8, 126.2, 129.6, 133.9, 135.4, 137.8, 149.3, 157.2, 162.2.

***N*-(4-Methoxyphenyl)-6-methylpicolinamide (3s):**



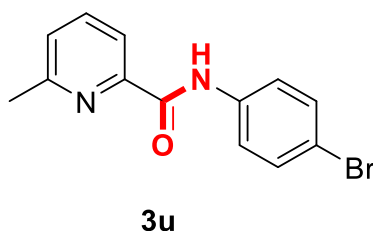
Brownish yellow sticky solid (80%, 193 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 2.61 (s, 3H), 3.80 (s, 3H), 6.90 (d,  $J$  = 9.0 Hz, 2H), 7.28 (d,  $J$  = 7.5 Hz, 1H), 7.68-7.70 (m, 2H), 7.73 (t,  $J$  = 7.5 Hz, 1H), 8.07 (d,  $J$  = 7.5 Hz, 1H), 9.96 (s, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  = 24.3, 55.5, 114.2, 119.4, 121.3, 126.1, 131.1, 137.8, 149.3, 156.4, 157.2, 162.0; HRMS: (M+H)<sup>+</sup> calcd. for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ : 243.1134; found: 243.1141.

***N*-(4-Fluorophenyl)-6-methylpicolinamide (3t)<sup>8</sup>:**



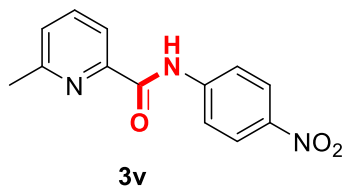
Brown sticky solid (80%, 184 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 2.63 (s, 3H), 7.06 (t,  $J$  = 9.0 Hz, 2H), 7.32 (d,  $J$  = 7.5 Hz, 1H), 7.73-7.80 (m, 3H), 8.09 (d,  $J$  = 8.0 Hz, 1H), 10.05 (s, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  = 24.3, 115.6 (d,  $J$  = 22.5 Hz, 2C), 119.6, 121.4 (d,  $J$  = 8.0 Hz, 2C), 126.4, 134.0, 137.9, 149.0, 157.3, 158.4 (d,  $J$  = 244.1 Hz, 2C), 162.2.  $^{19}\text{F}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  = - 117.90.

***N*-(4-Bromophenyl)-6-methylpicolinamide (3u)<sup>7</sup>:**



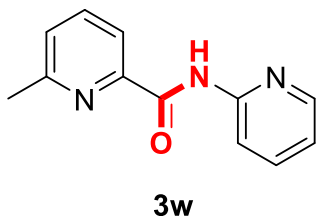
Light yellow sticky solid (85%, 247 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 2.59 (s, 3H), 7.29 (d,  $J$  = 8.0 Hz, 1H), 7.44 (d,  $J$  = 9.0 Hz, 2H), 7.66 (d,  $J$  = 9.0 Hz, 2H), 7.72 (t,  $J$  = 8.0 Hz, 1H), 8.04 (d,  $J$  = 7.5 Hz, 1H), 10.06 (s, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  = 24.3, 116.7, 119.5, 121.2, 126.4, 132.0, 136.9, 137.8, 148.8, 157.3, 162.2.

### 6-Methyl-*N*-(4-nitrophenyl)picolinamide (3v):



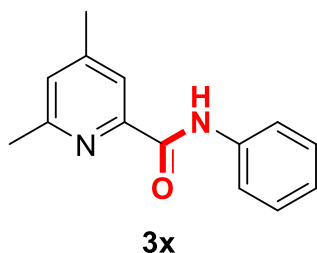
Light yellow solid (78%, 200 mg); mp: 196-198 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.65$  (s, 3H), 7.37 (d,  $J = 7.5$  Hz, 1H), 7.80 (t,  $J = 8.0$  Hz, 1H), 7.95 (d,  $J = 9.5$  Hz, 2H), 8.10 (d,  $J = 8.0$  Hz, 1H), 8.26 (d,  $J = 9.5$  Hz, 2H), 10.43 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 24.3, 116.7, 119.5, 121.2, 126.4, 132.0, 136.9, 137.8, 148.8, 157.3, 162.2$ ; **HRMS:** (M+H) $^+$  calcd. For  $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_3$ : 258.0879; found: 258.0910.

### 6-Methyl-*N*-(pyridin-2-yl)picolinamide (3w):



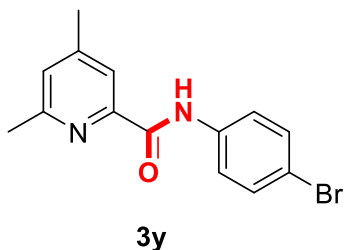
Light yellow solid (83%, 176 mg); mp: 70-72 °C ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.61$  (s, 3H), 7.05 (dd,  $J = 6.5$  Hz, 5.0 Hz, 1H), 7.31 (d,  $J = 7.5$  Hz, 1H), 7.74 (quint,  $J = 7.5$  Hz, 2H), 8.07 (d,  $J = 8.0$  Hz, 1H), 8.36 (d,  $J = 4.0$  Hz, 1H), 8.42 (d,  $J = 8.5$  Hz, 1H), 10.59 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 24.3, 114.0, 119.6, 119.9, 126.6, 137.8, 138.4, 148.2, 148.7, 151.3, 157.6, 162.9$ ; **HRMS:** (M+H) $^+$  calcd. for  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}$ : 214.0980; found: 214.0994.

### 4,6-Dimethyl-*N*-phenylpicolinamide (3x):



Light yellow solid (68%, 153 mg); mp: 122-125 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.40$  (s, 3H), 2.57 (s, 3H), 7.12 (t,  $J = 8.0$  Hz, 2H), 7.36 (t,  $J = 8.0$  Hz, 2H), 7.77 (d,  $J = 8.5$  Hz, 2H), 7.93 (s, 1H), 10.09 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 21.1, 24.2, 119.8, 120.6, 124.2, 125.1, 127.0, 138.0, 149.0, 149.2, 157.0, 162.6$ ; **HRMS:** (M+H) $^+$  calcd. for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}$ : 227.1184; found: 227.1164.

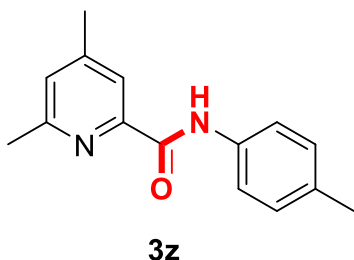
### *N*-(4-Bromophenyl)-4,6-dimethylpicolinamide (3y):



Yellow sticky solid (72%, 224 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.40$  (s, 3H), 2.57 (s, 3H), 7.14 (s, 1H), 7.47 (d,  $J = 8.5$  Hz, 2H), 7.68 (d,  $J = 8.5$  Hz, 2H), 7.91 (s, 1H), 10.10 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 21.1, 24.1, 116.8, 120.6, 121.3, 127.2, 132.1, 137.1, 148.8, 149.4, 157.1, 162.6$ ; **HRMS:** (M+H) $^+$  calcd. for  $\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}$ : 305.0290; found: 305.0319.

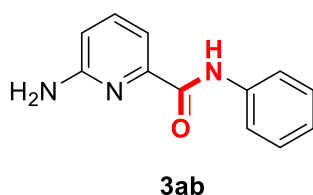


#### 4,6-Dimethyl-*N*-(*p*-tolyl)picolinamide (**3z**):



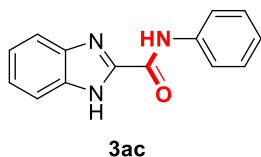
Light yellow sticky solid (74%, 177 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.33$  (s, 3H), 2.38 (s, 3H), 2.56 (s, 3H), 7.11 (s, 1H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.64 (d,  $J = 8.0$  Hz, 2H), 7.91 (s, 1H), 10.01 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 21.0, 21.1, 24.1, 119.7, 120.5, 126.9, 129.6, 133.7, 135.4, 149.1, 149.2, 156.9, 162.4$ ; **HRMS**: (M+H) $^+$  calcd. for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$ : 241.1341; found: 241.1291.

#### 6-Amino-*N*-phenylpicolinamide (**3ab**):



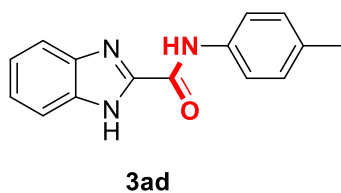
Yellow solid (70%, 149 mg); mp: 125-127 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 4.58$  (s, 2H), 6.66 (d,  $J = 8.0$  Hz, 1H), 7.11 (t,  $J = 7.5$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 2H), 7.60-7.67 (m, 2H), 7.74 (d,  $J = 8.0$  Hz, 2H), 9.83 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 112.1, 113.2, 119.7, 124.2, 129.1, 138.0, 139.2, 148.2, 157.0, 162.4$ ; **HRMS**: (M+H) $^+$  calcd. for  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}$ : 214.0980; found: 214.0998.

#### *N*-Phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide (**3ac**)<sup>9</sup>:



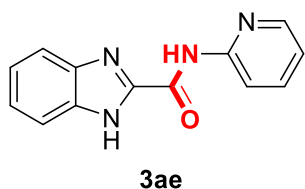
Yellow solid (81%, 192 mg); mp: 238-239 °C (lit.235-236 °C);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 7.21$  (t,  $J = 7.5$  Hz, 2H), 7.35-7.45 (m, 4H), 7.57 (d,  $J = 8.0$  Hz, 1H), 7.81-7.85 (m, 3H), 9.53 (s, 1H), 11.6 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 112.5, 120.2, 120.8, 123.8, 125.3, 125.5, 129.3, 134.5, 137.1, 142.9, 145.1, 157.2$ .

#### *N*-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole-2-carboxamide (**3ad**):



Light yellow solid (83%, 208 mg); mp: 235-240 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 2.38$  (s, 3H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.34 (quint,  $J = 7.5$  Hz, 2H), 7.57 (d,  $J = 7.5$  Hz, 1H), 7.71 (d,  $J = 8.0$  Hz, 2H), 7.82 (d,  $J = 7.5$  Hz, 1H), 9.57 (s, 1H), 12.11 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 21.1, 112.6, 120.3, 120.6, 123.7, 125.4, 129.8, 134.6, 134.7, 135.0, 142.9, 145.2, 157.3$ ; **HRMS**: (M+H) $^+$  calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$ : 252.1137; found: 252.1114.

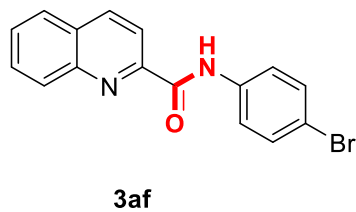
#### *N*-(Pyridin-2-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide (**3ae**):



Light yellow solid (85%, 202 mg); mp: 160-165 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}} = 7.02$  (t,  $J = 5.0$  Hz, 1H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.52 (d,  $J = 7.5$  Hz, 1H), 7.67 (t,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 7.5$  Hz, 1H), 8.29-8.32 (m, 2H), 9.95 (s, 1H), 12.51 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}} = 112.1, 114.2, 120.5, 121.3, 123.7, 125.6,$

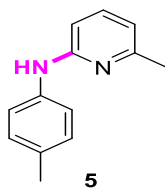
134.3, 138.3, 143.1, 144.5, 148.5, 150.6, 157.5; **HRMS:** (M+H)<sup>+</sup>  
calcd. for C<sub>13</sub>H<sub>11</sub>N<sub>4</sub>O : 239.0933; found: 239.0919.

***N*-(4-Bromophenyl)quinoline-2-carboxamide (3af)<sup>10</sup>:**



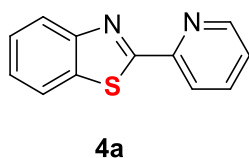
Yellow solid (85%, 278 mg); mp: 220-224 °C; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ<sub>H</sub> = 7.50 (d, *J* = 9.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.36-8.38 (m, 2H), 10.24 (s, 1H); **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ<sub>C</sub> = 117.0, 118.8, 121.4, 127.9, 128.4, 129.6, 129.7, 130.5, 132.2, 137.0, 138.1, 146.4, 149.4, 162.3.

**6-Methyl-*N*-(*p*-tolyl)pyridin-2-amine (5)<sup>15</sup>:**



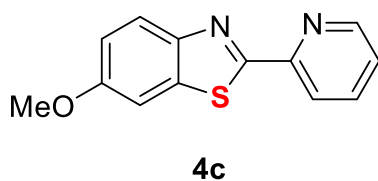
Yellow solid (70%, 138 mg); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ<sub>H</sub> = 2.23 (s, 3H), 2.33 (s, 3H), 6.47 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 7.03-7.09 (m, 5H), 7.25 (t, *J* = 8.0 Hz, 1H); **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ<sub>C</sub> = 20.9, 24.3, 104.3, 114.1, 121.2, 129.9, 132.7, 138.0, 138.1, 156.1, 157.3.

**2-(Pyridin-2-yl)benzo[*d*]thiazole (4a)<sup>16</sup>:**



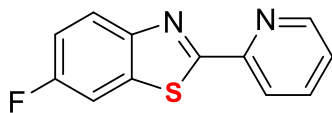
Brownish yellow solid (12%, 42 mg); mp: 135-136 °C (lit. 134-136 °C); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ<sub>H</sub> = 7.38-7.44 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 4.5 Hz, 1H); **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ<sub>C</sub> = 120.9, 122.1, 123.7, 125.4, 125.8, 126.4, 136.3, 137.1, 146.8, 150.0, 151.6, 169.5.

**6-Methoxy-2-(pyridin-2-yl)benzo[*d*]thiazole (4c)<sup>17</sup>:**



Brown solid (19%, 46 mg); mp: 134-135 °C (lit 136.5-137.5 °C); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ<sub>H</sub> = 3.89 (s, 3H), 7.10-7.14 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 8.28-8.33 (m, 1H), 8.83 (s, 1H); **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ<sub>C</sub> = 55.9, 104.1, 104.2, 115.4, 116.0, 120.5, 124.1, 124.2, 125.0, 129.7, 137.1, 151.6, 166.9.

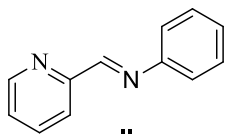
**6-Fluoro-2-(pyridin-2-yl)benzo[*d*]thiazole (4e)<sup>16</sup>:**



**4e**

White solid (20%, 51 mg); mp: 149-151 °C (lit.150-152 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.21-7.25 (m, 1H), 7.38-7.40 (m, 1H), 7.62-7.64 (m, 1H), 7.83-7.87 (m, 1H), 8.01 (q, *J* = 5.0 Hz, 1H), 8.32 (d, *J* = 7.5 Hz, 1H), 8.67 (d, *J* = 4.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 108.1, 108.4, 115.1, 115.3, 120.7, 124.6, 124.7, 125.4, 137.2, 149.8, 151.1, 151.2, 160.0, 161.9, 169.3; <sup>19</sup>F (470 MHz, CDCl<sub>3</sub>) δ<sub>F</sub> = -114.84.

**<sup>1</sup>H NMR of (*E*)-*N*-(Pyridin-2-ylmethylene)aniline intermediate (II)<sup>18</sup>:**



**II**

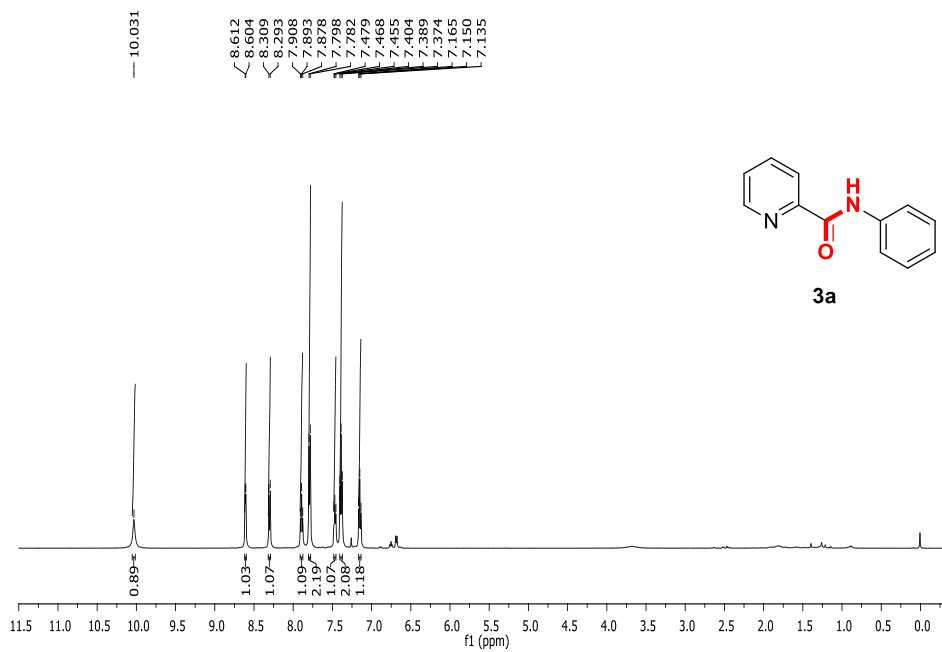
Brown viscous liquid (65%, 118 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 7.25-7.29 (m, 4H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.78 (t, *J* = 10 Hz, 1H), 8.19 (d, *J* = 5.0 Hz, 1H), 8.60 (s, 1H), 8.70 (d, *J* = 5.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 212.1, 121.9, 125.2, 126.8, 129.3, 136.7, 149.7, 151.0, 154.6, 160.7.

## V. References:

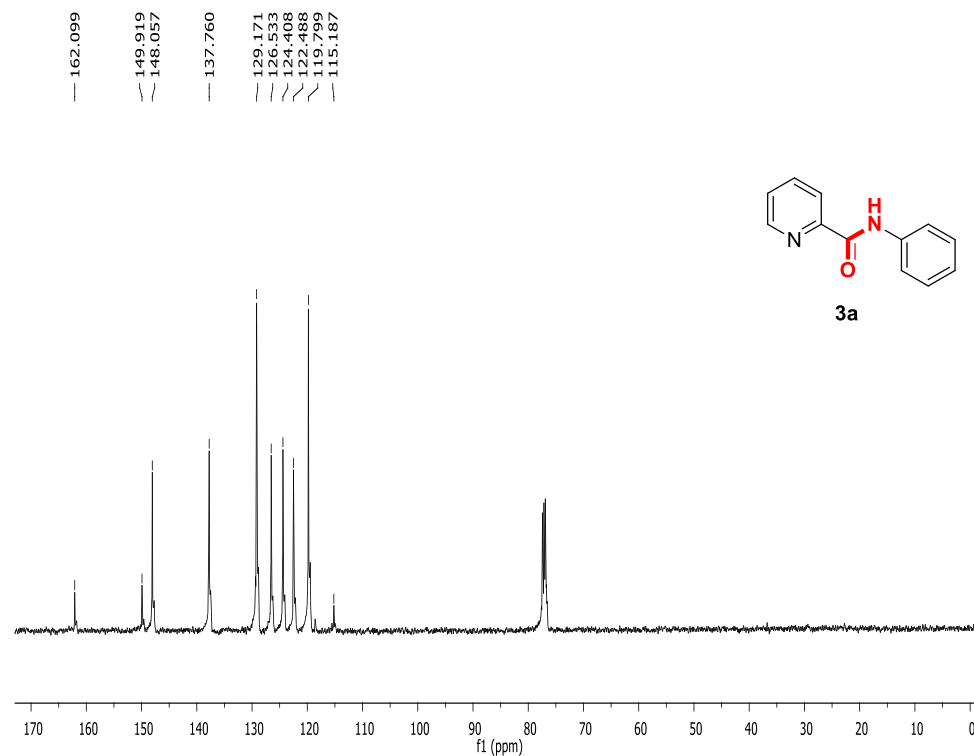
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## VI. Copies of $^1\text{H}$ , $^{13}\text{C}$ NMR and $^{19}\text{F}$ spectra of the products:

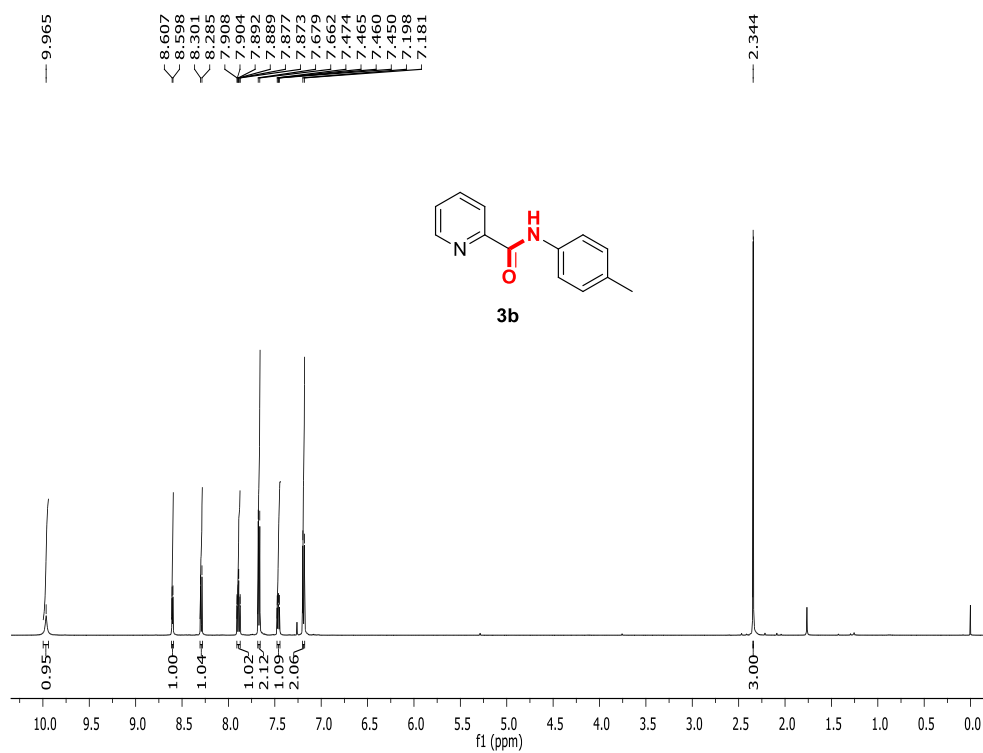
### $^1\text{H}$ NMR of *N*-Phenylpicolinamide (3a):



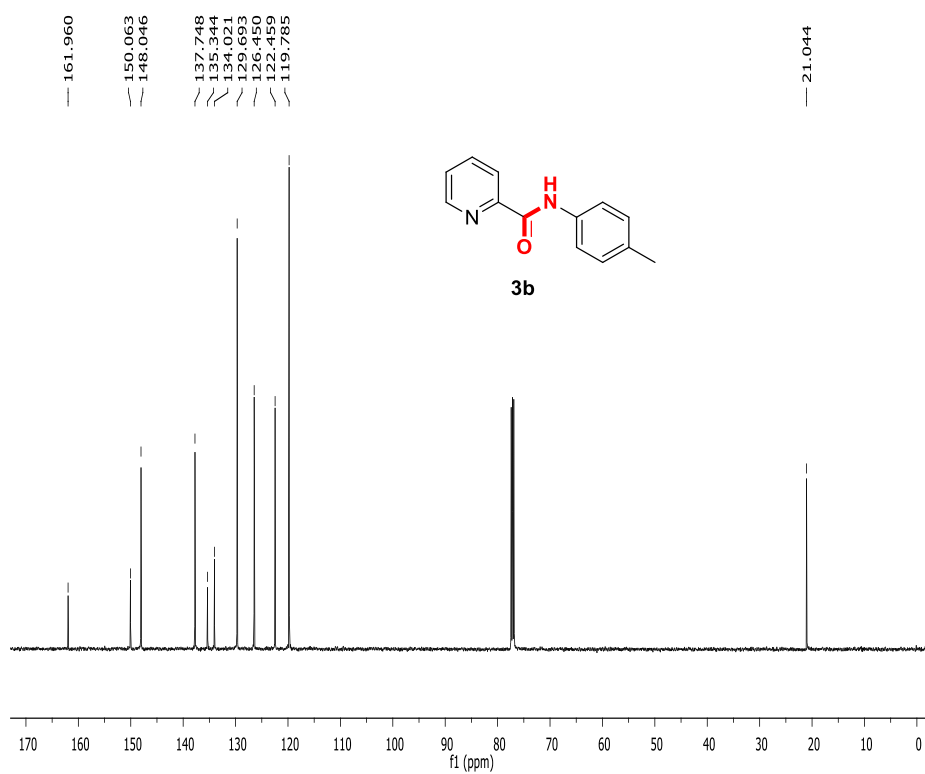
### $^{13}\text{C}$ NMR of *N*-Phenylpicolinamide (3a):



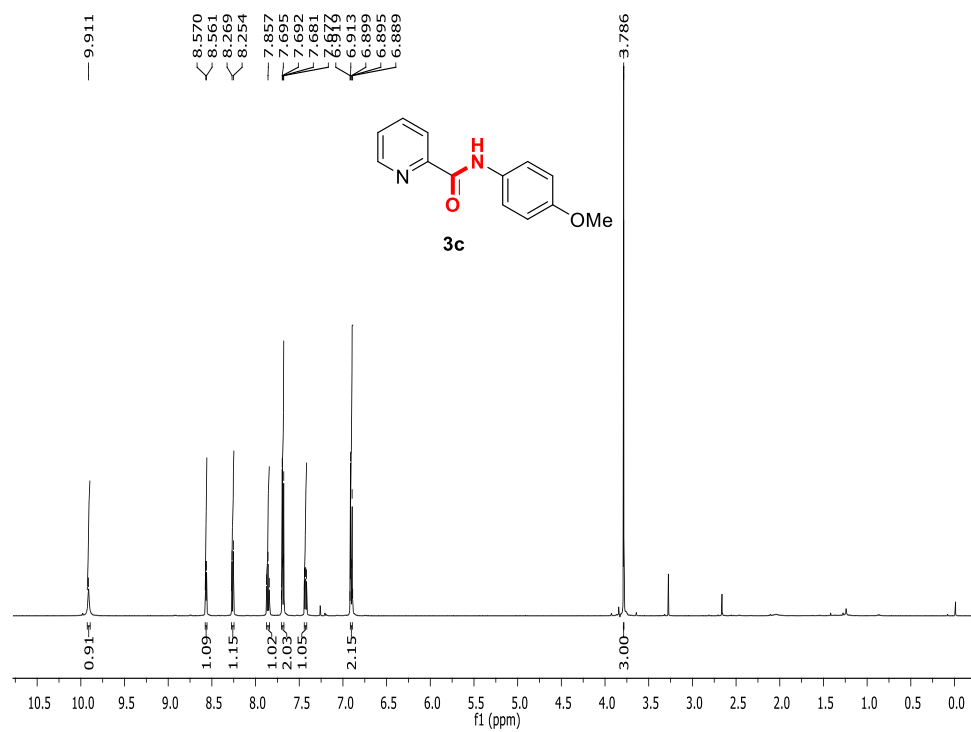
### <sup>1</sup>H NMR of *N*-(*p*-Tolyl)picolinamide (**3b**):



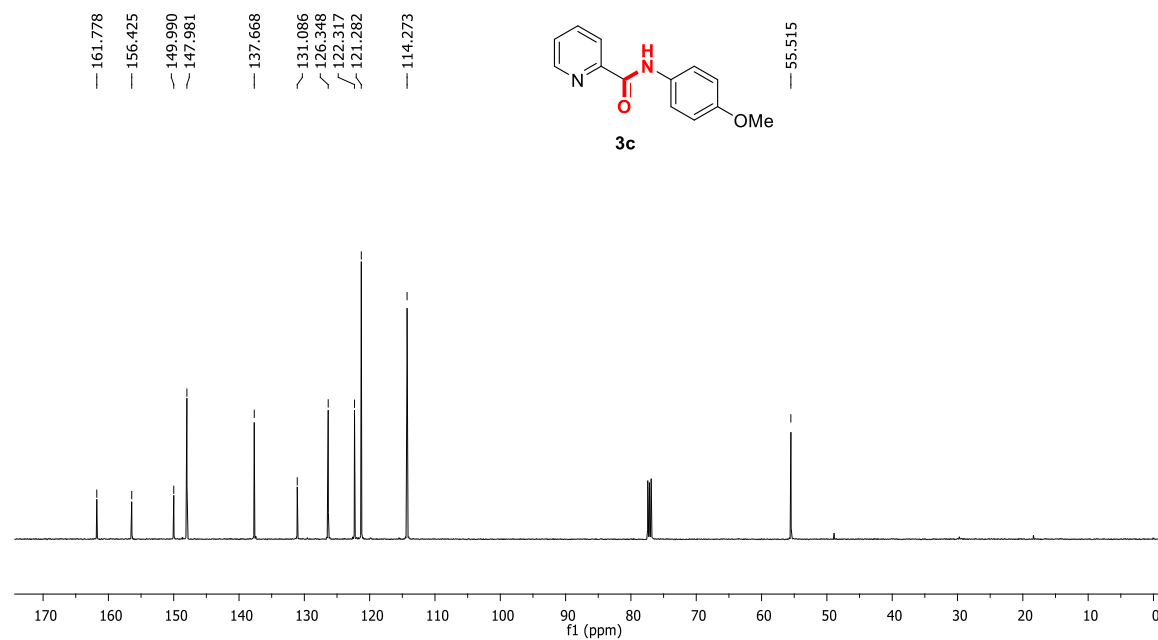
### <sup>13</sup>C NMR of *N*-(*p*-Tolyl)picolinamide (**3b**):



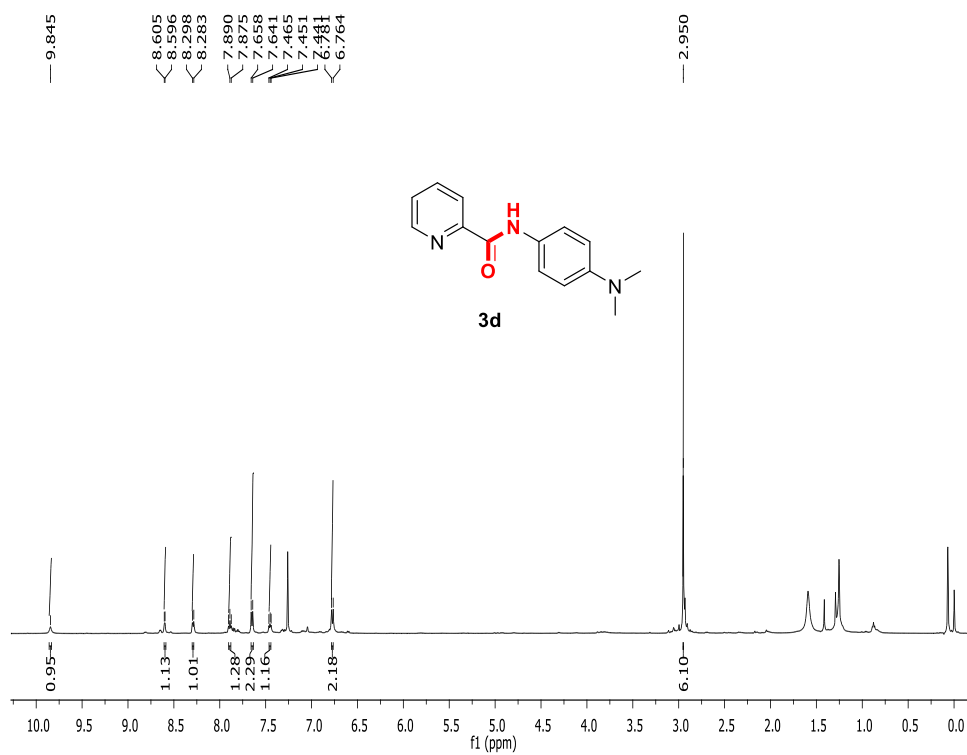
### <sup>1</sup>H NMR of *N*-(4-Methoxyphenyl)picolinamide (3c):



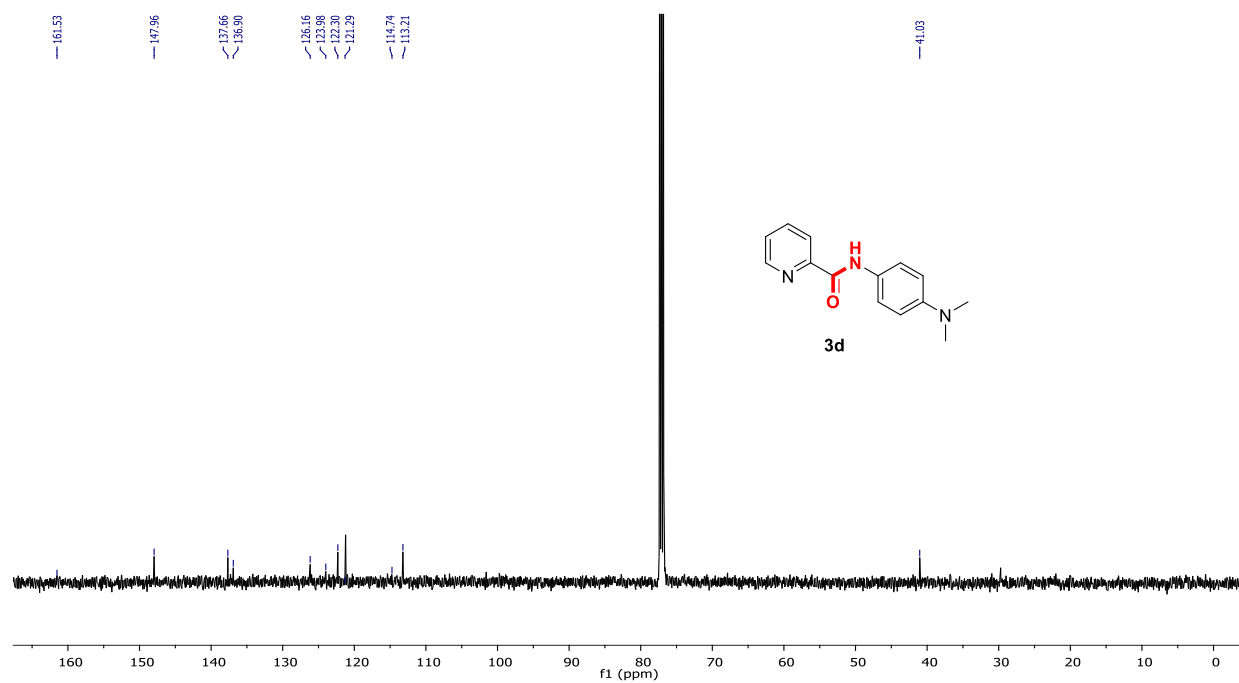
### <sup>13</sup>C NMR of *N*-(4-Methoxyphenyl)picolinamide (3c):



### <sup>1</sup>H NMR of *N*-(4-(Dimethylamino)phenyl)picolinamide (3d):

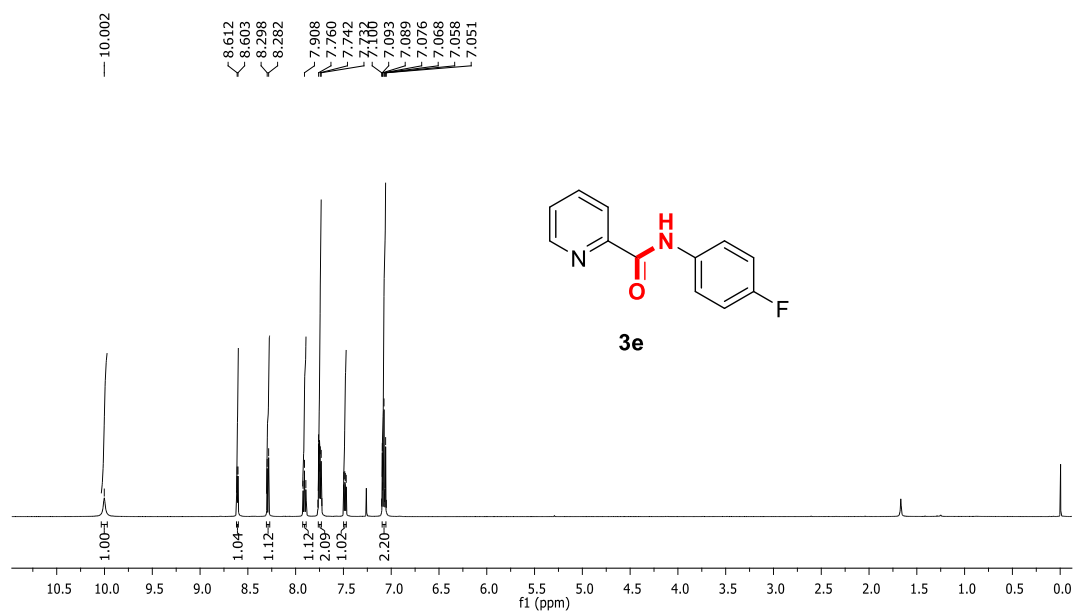


### <sup>13</sup>C NMR of *N*-(4-(Dimethylamino)phenyl)picolinamide (3d):

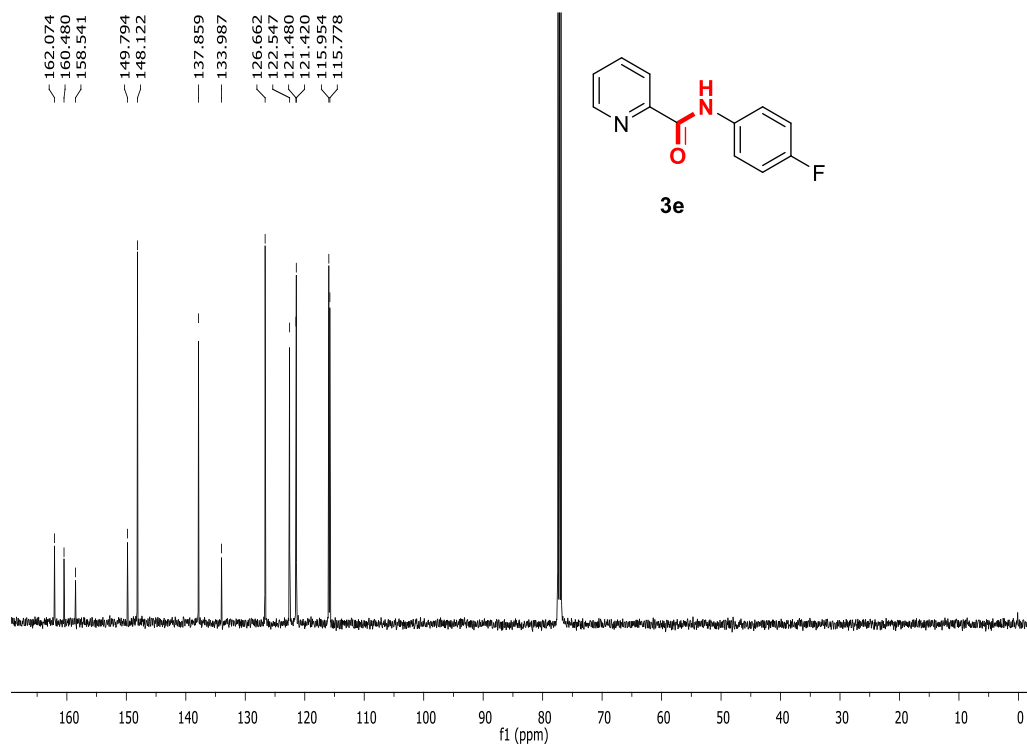




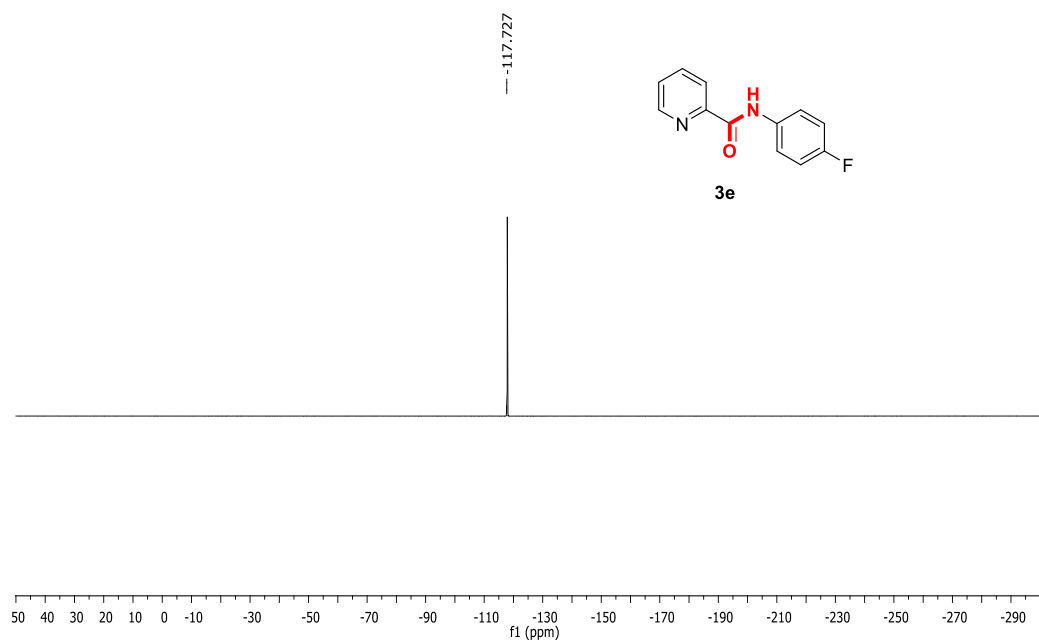
### <sup>1</sup>H NMR of *N*-(4-Fluorophenyl)picolinamide (3e):



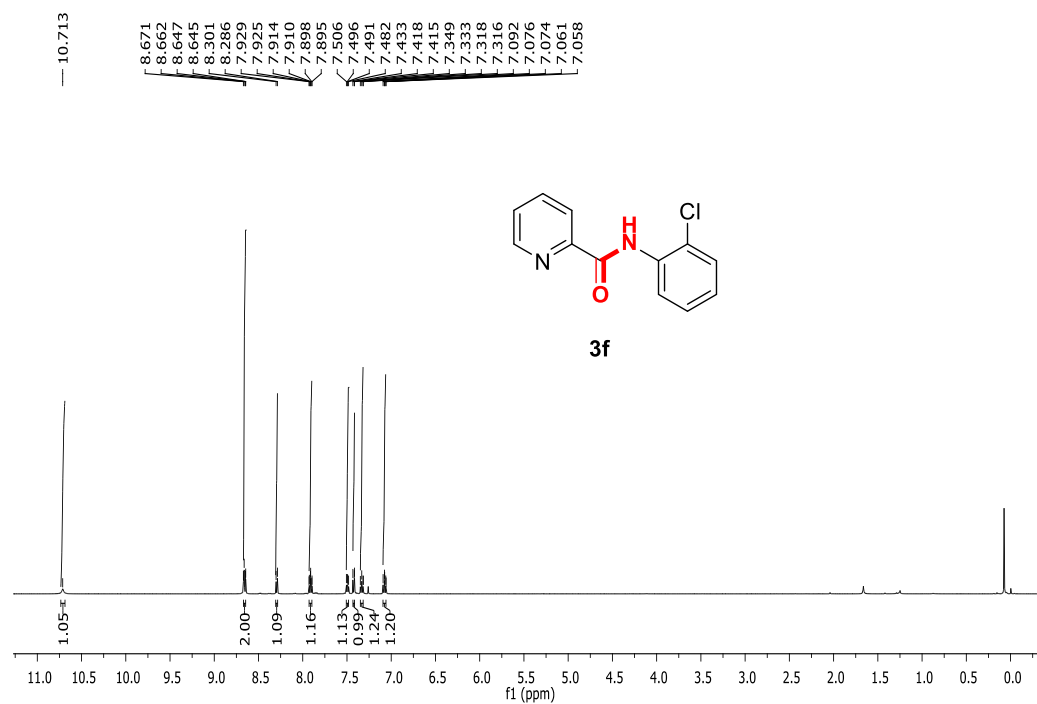
### <sup>13</sup>C NMR of *N*-(4-Fluorophenyl)picolinamide (3e):



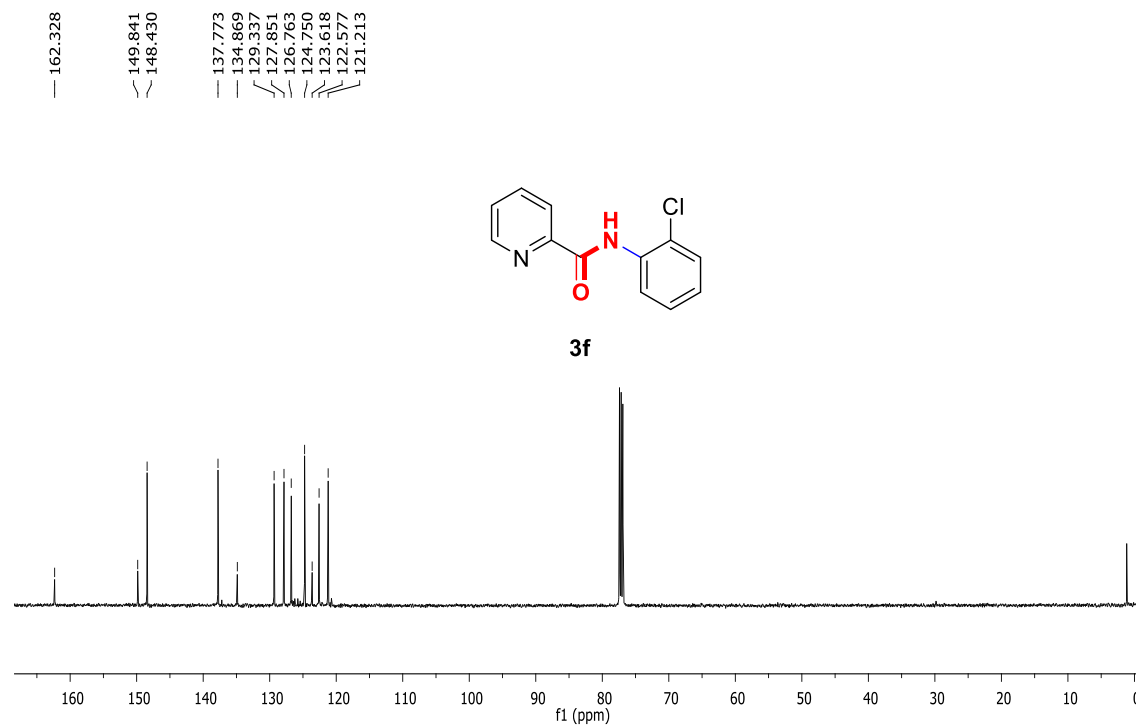
**$^{19}\text{F}$  NMR of *N*-(4-Fluorophenyl)picolinamide (3e):**



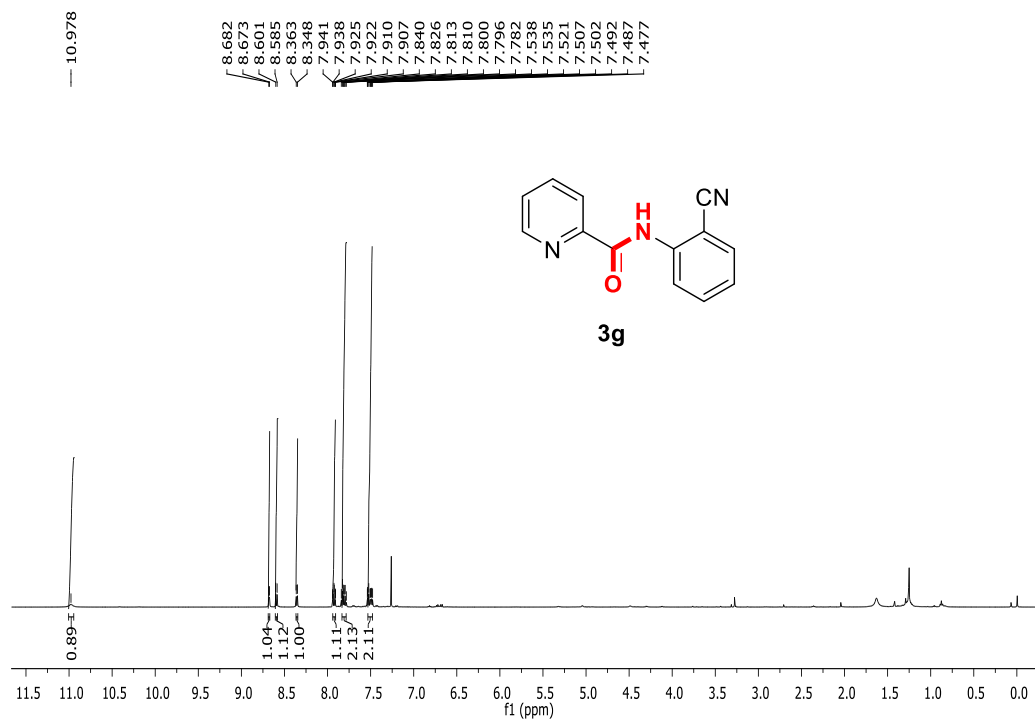
### <sup>1</sup>H NMR of *N*-(2-Chlorophenyl)picolinamide (3f):



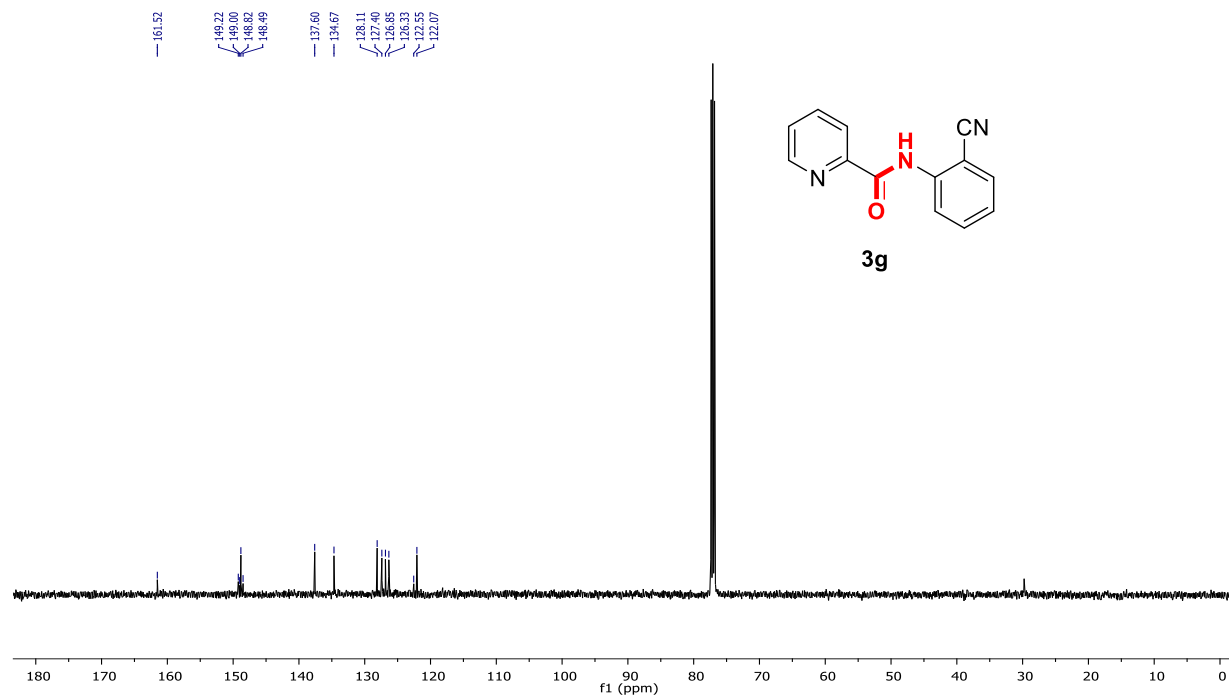
### <sup>13</sup>C NMR of *N*-(2-Chlorophenyl)picolinamide (3f):



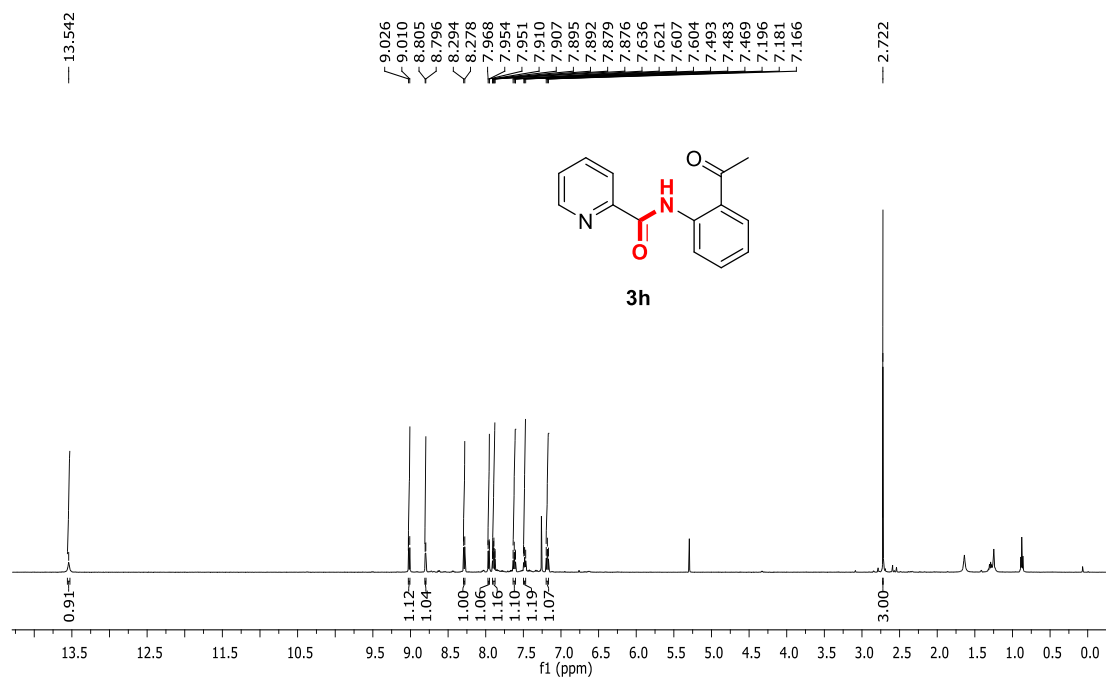
### $^1\text{H}$ NMR of *N*-(2-Cyanophenyl)picolinamide (**3g**):



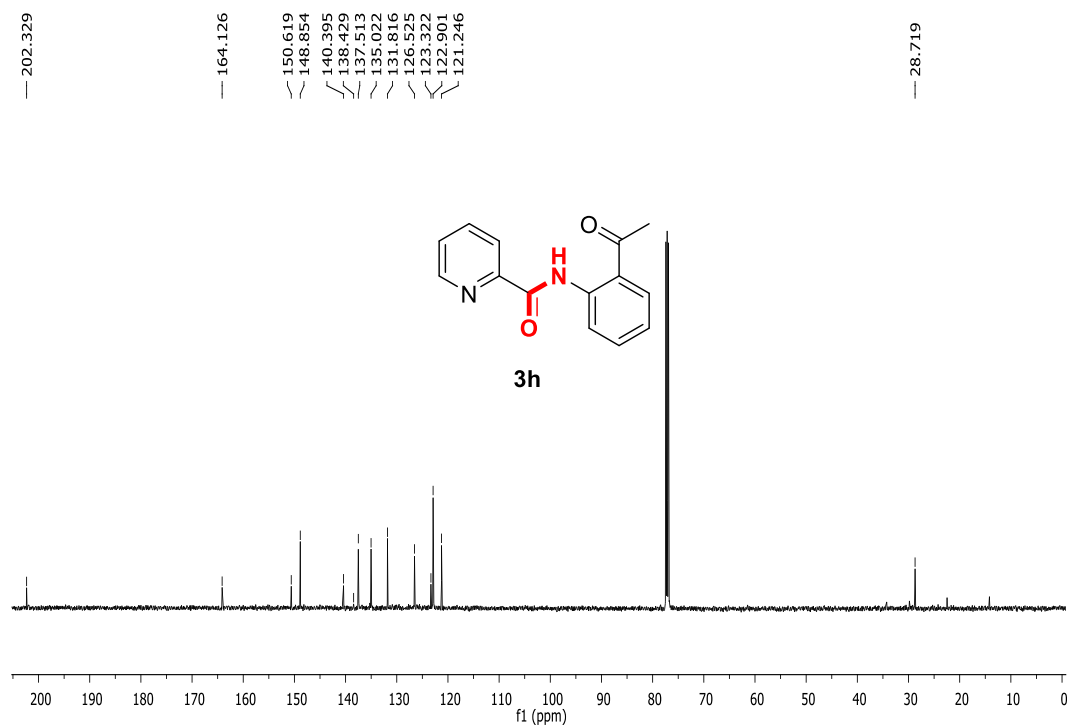
### $^{13}\text{C}$ NMR of *N*-(2-Cyanophenyl)picolinamide (**3g**):



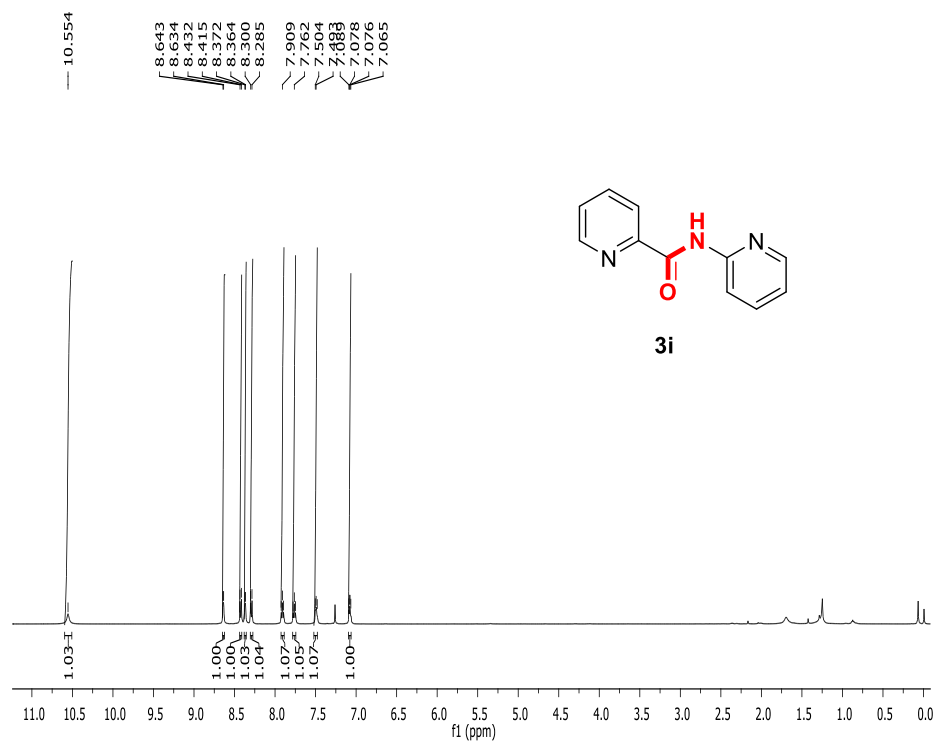
### <sup>1</sup>H NMR of *N*-(2-Acetylphenyl)picolinamide (3h):



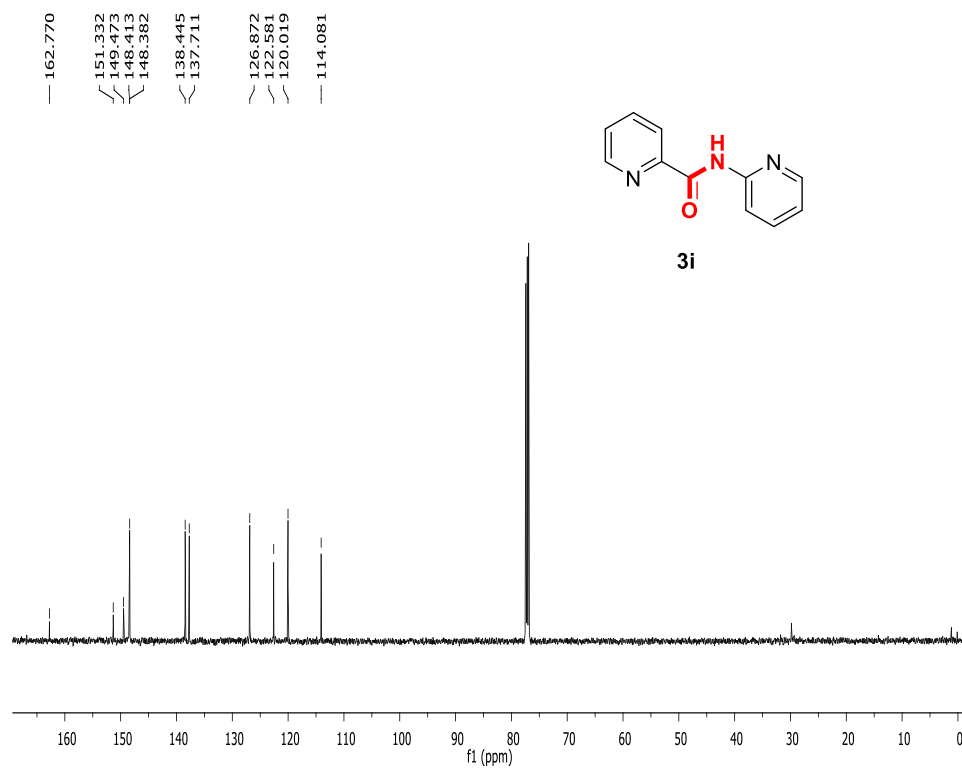
### <sup>13</sup>C NMR of *N*-(2-Acetylphenyl)picolinamide (3h):



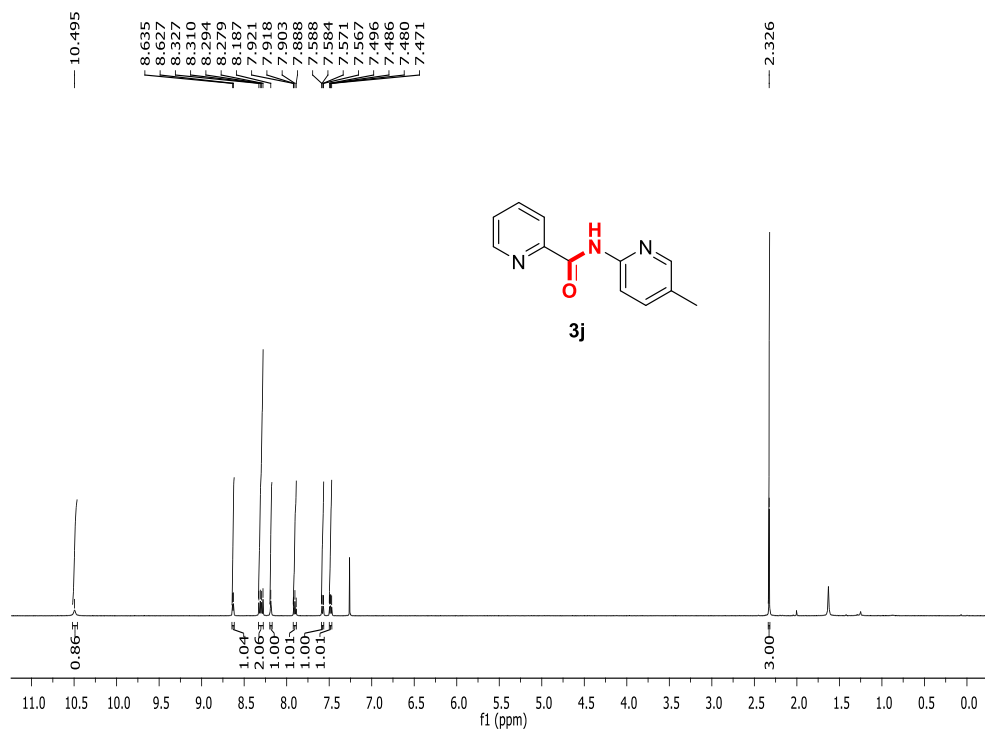
### <sup>1</sup>H NMR of *N*-(Pyridin-2-yl)picolinamide (3i):



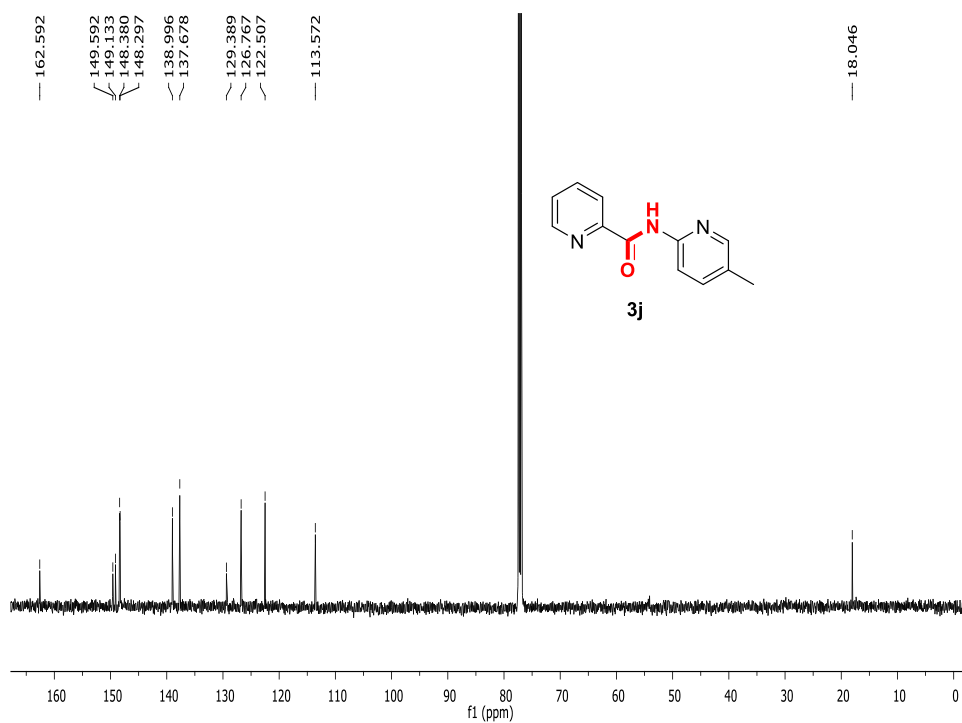
### <sup>13</sup>C NMR of *N*-(Pyridin-2-yl)picolinamide (3i):



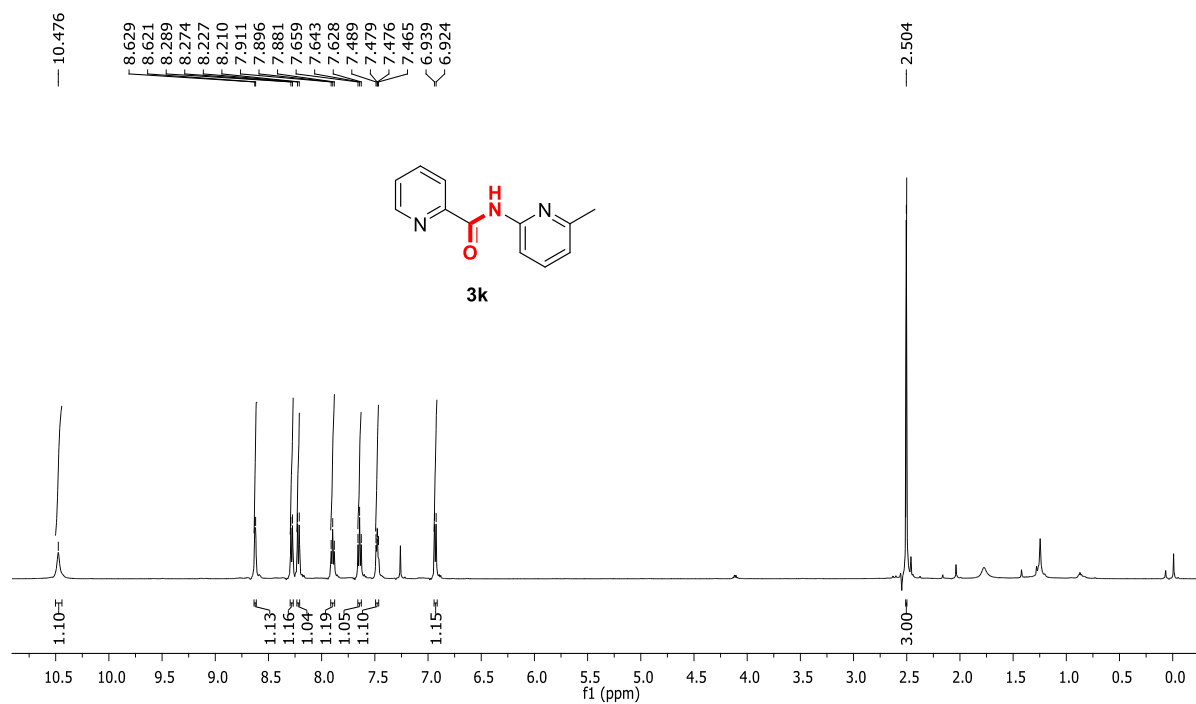
### <sup>1</sup>H NMR of *N*-(5-Methylpyridin-2-yl)picolinamide (**3j**):



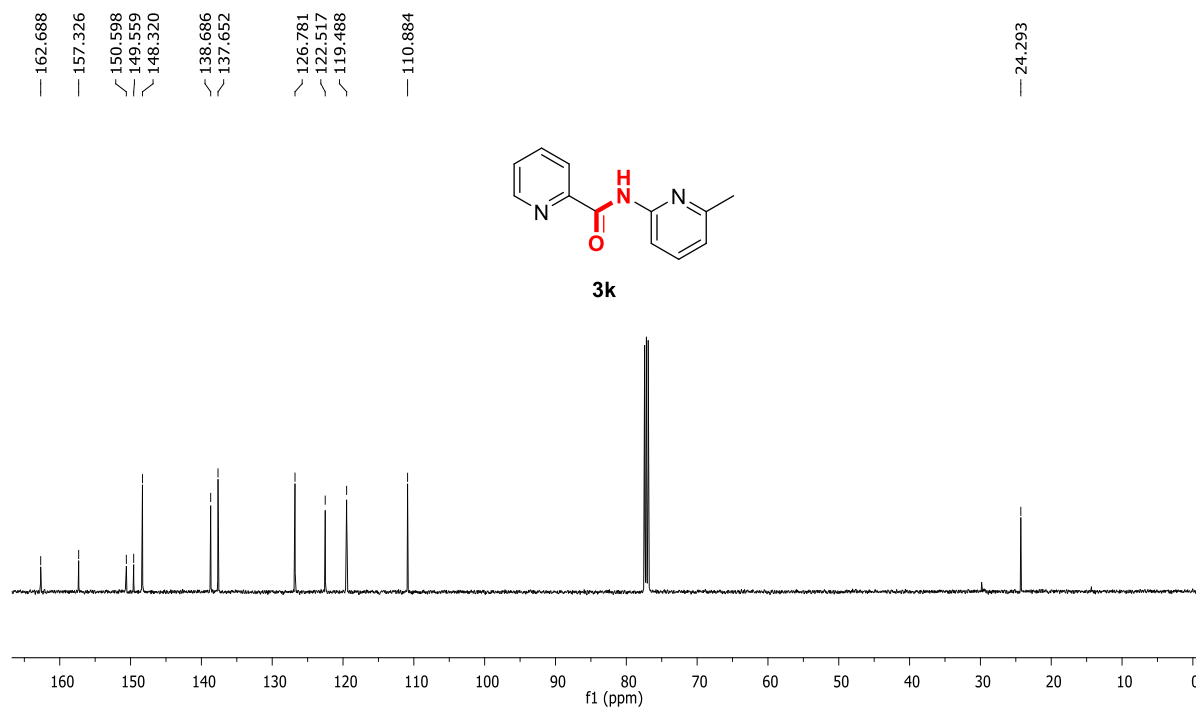
### <sup>13</sup>C NMR of *N*-(5-Methylpyridin-2-yl)picolinamide (**3j**):



### <sup>1</sup>H NMR of *N*-(6-Methylpyridin-2-yl)picolinamide (3k):

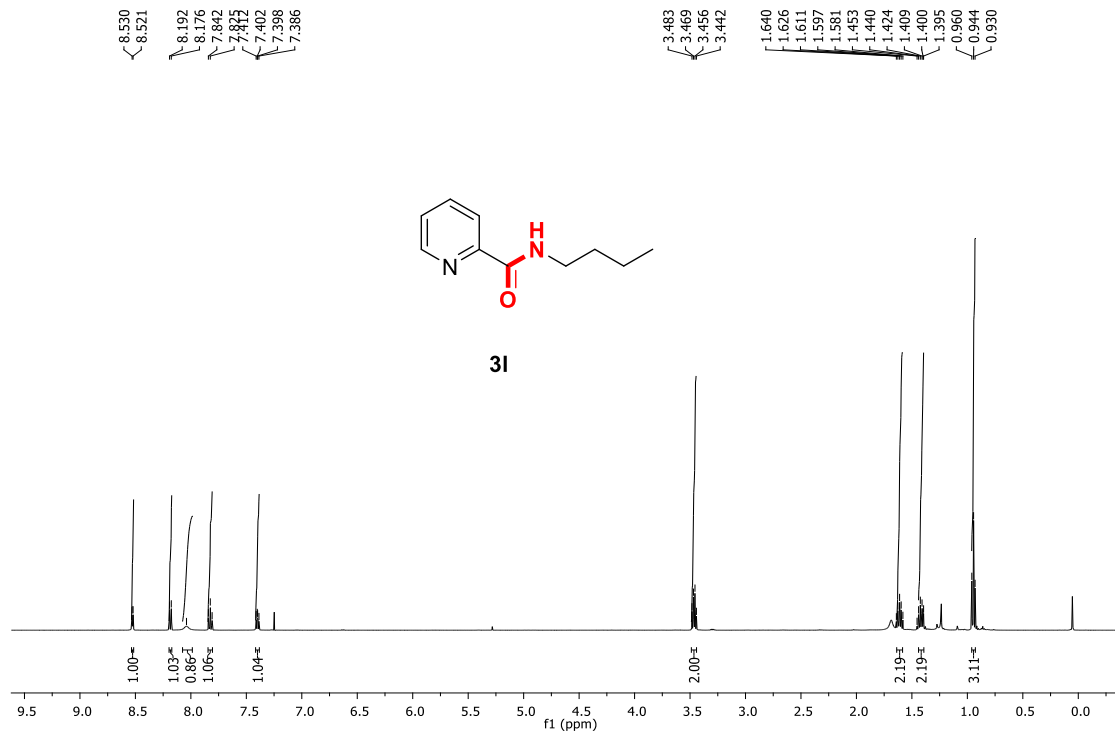


### <sup>13</sup>C NMR of *N*-(6-Methylpyridin-2-yl)picolinamide (3k):

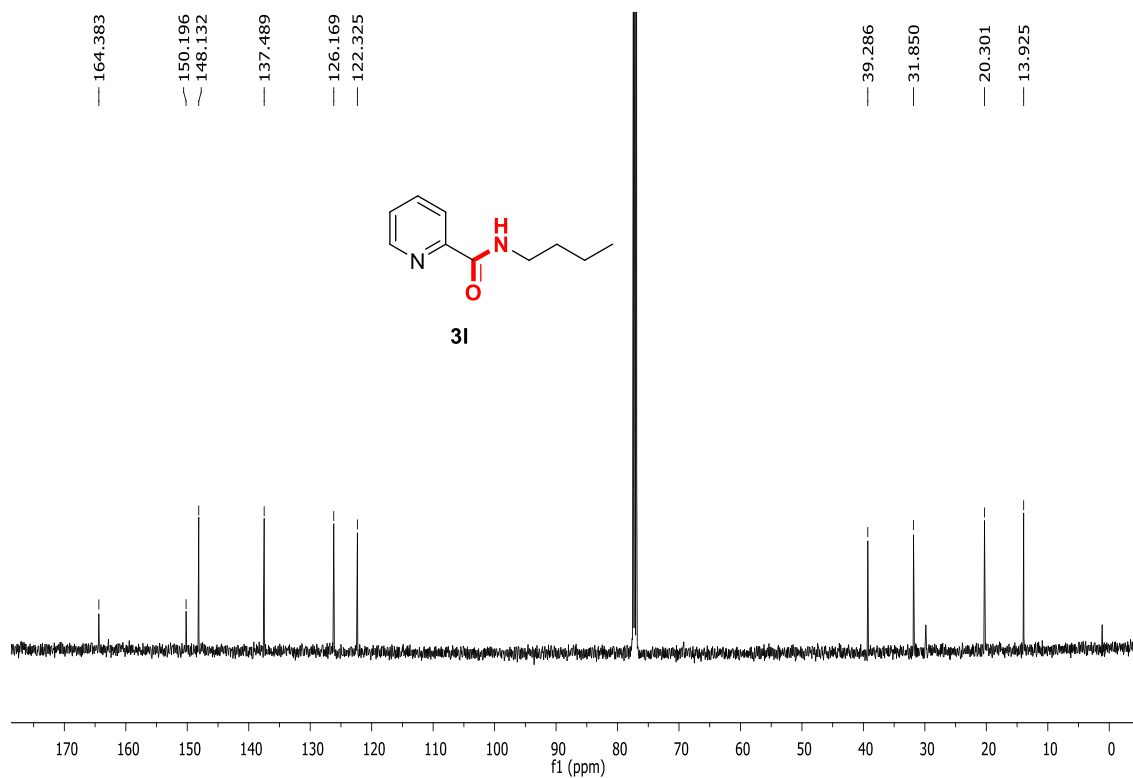




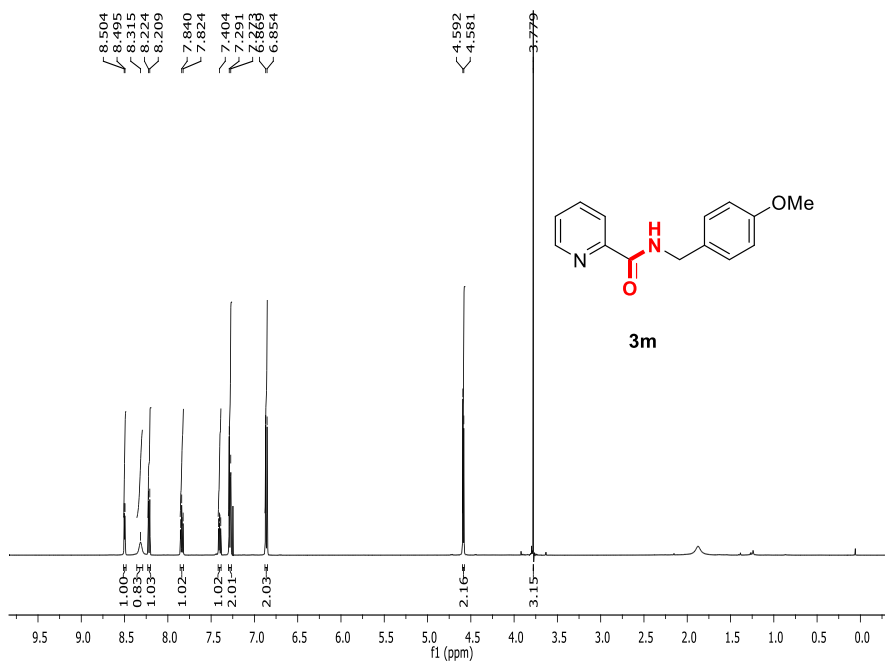
### <sup>1</sup>H NMR of *N*-Butylpicolinamide (31):



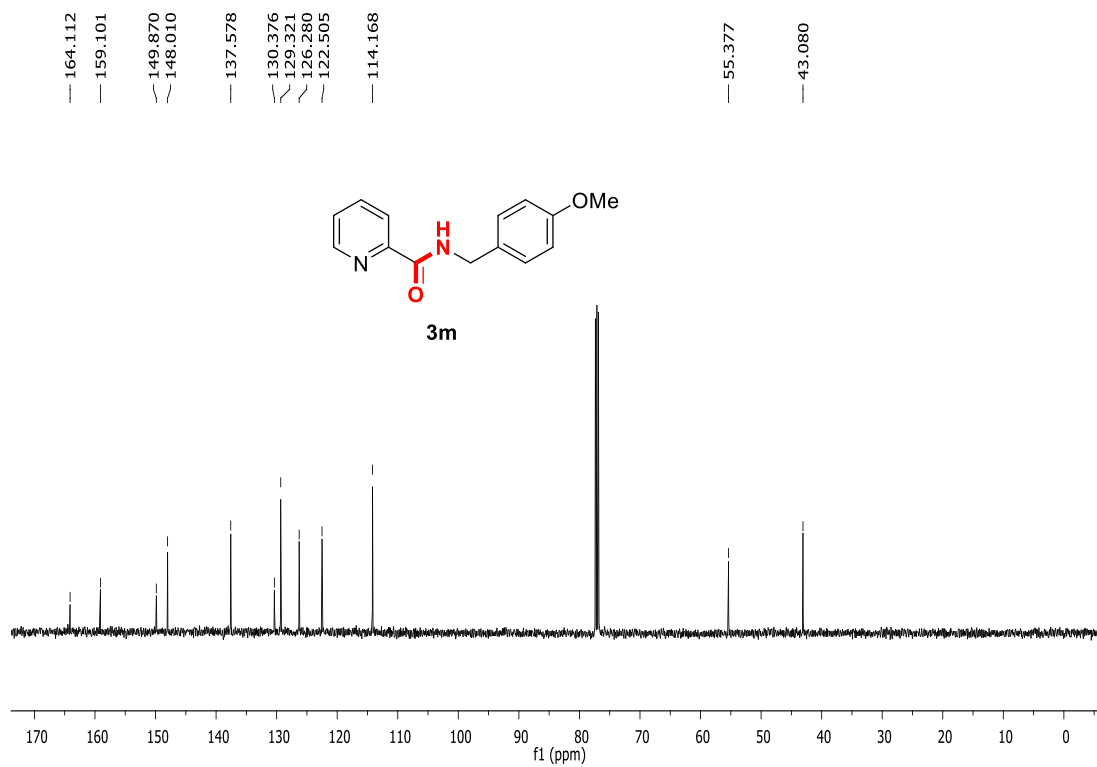
### <sup>13</sup>C NMR of *N*-Butylpicolinamide (31):



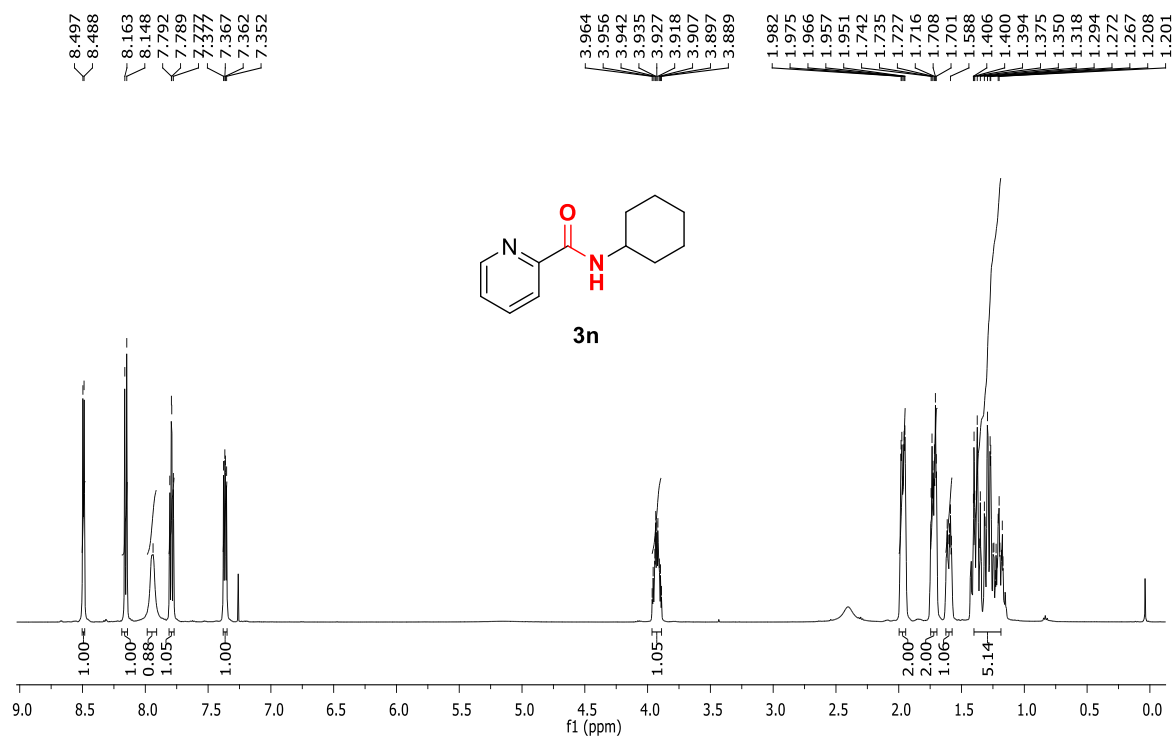
### <sup>1</sup>H NMR of *N*-(4-Methoxybenzyl)picolinamide (3m):



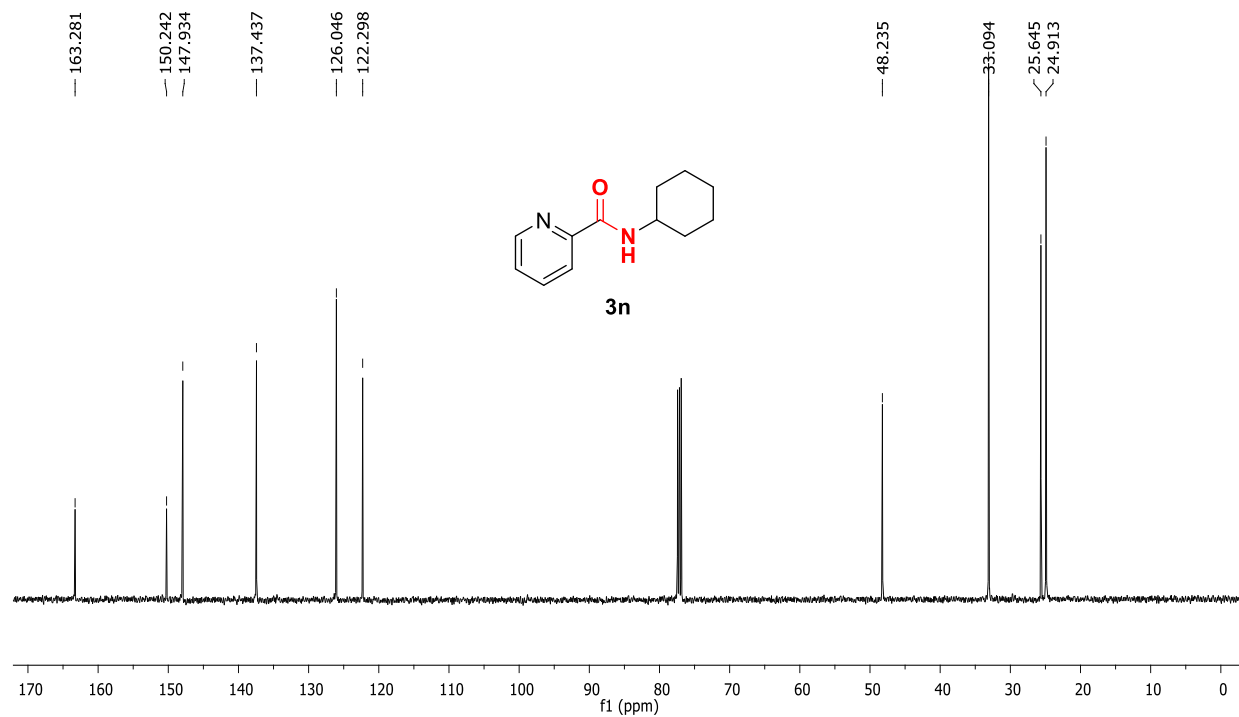
### <sup>13</sup>C NMR of *N*-(4-Methoxybenzyl)picolinamide (3m):



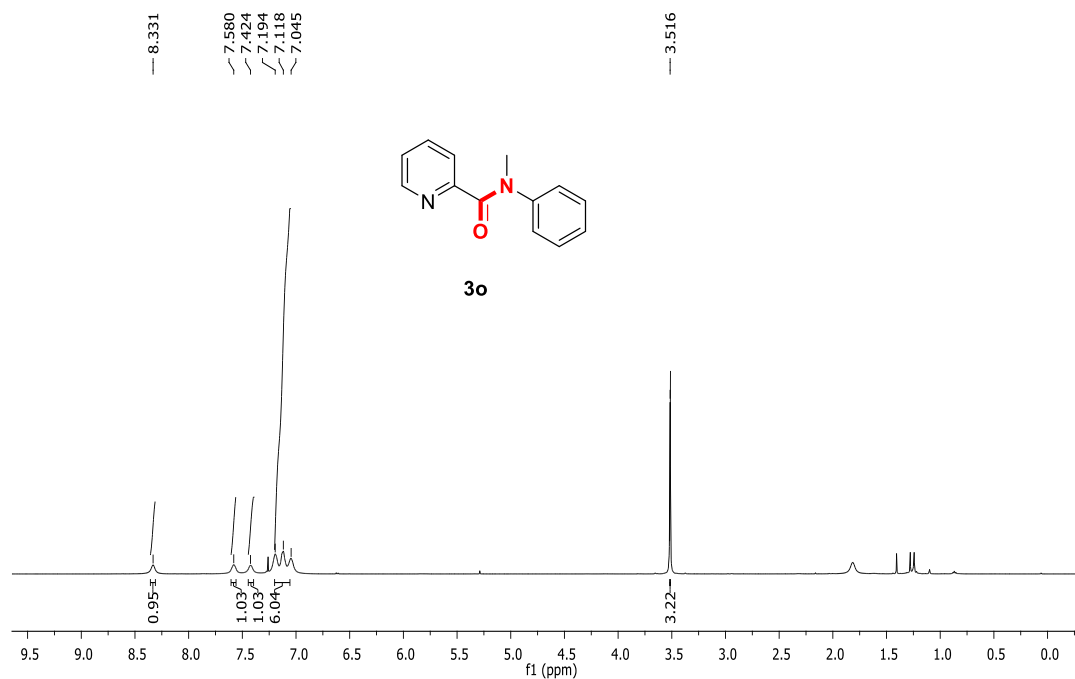
### <sup>1</sup>H NMR of *N*-Cyclohexylpicolinamide (3n):



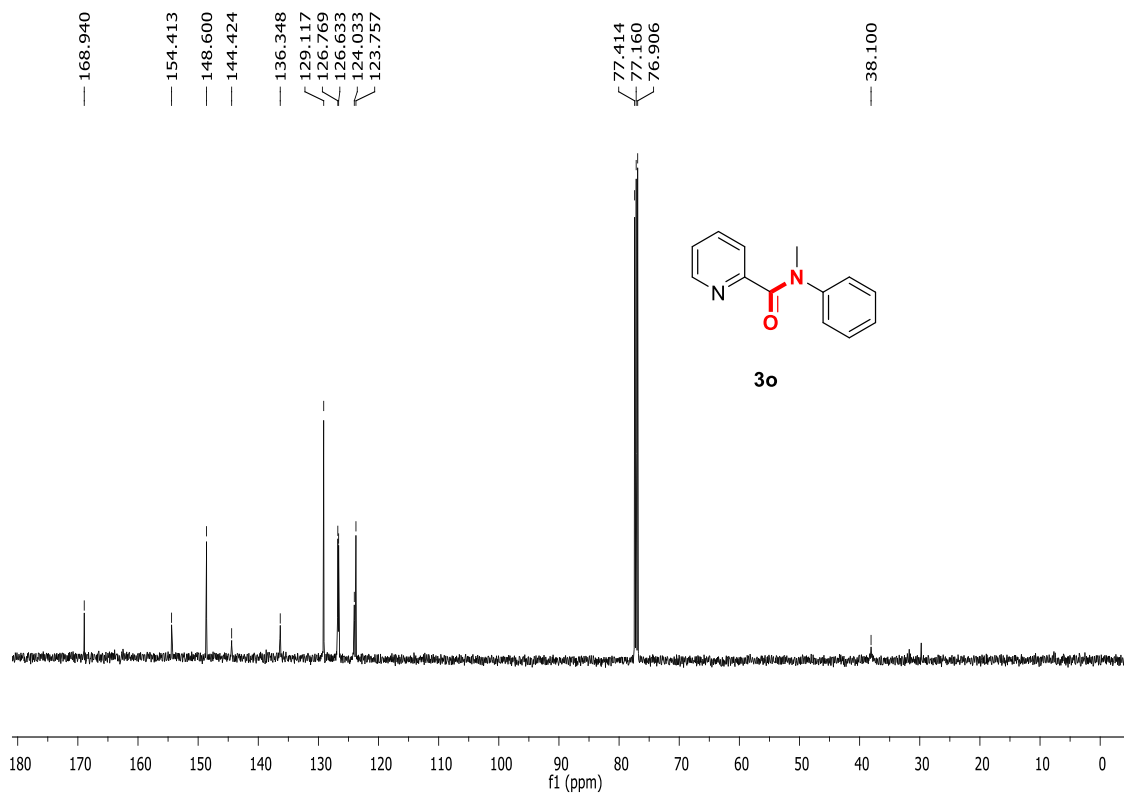
### <sup>13</sup>C NMR of *N*-Cyclohexylpicolinamide (3n):



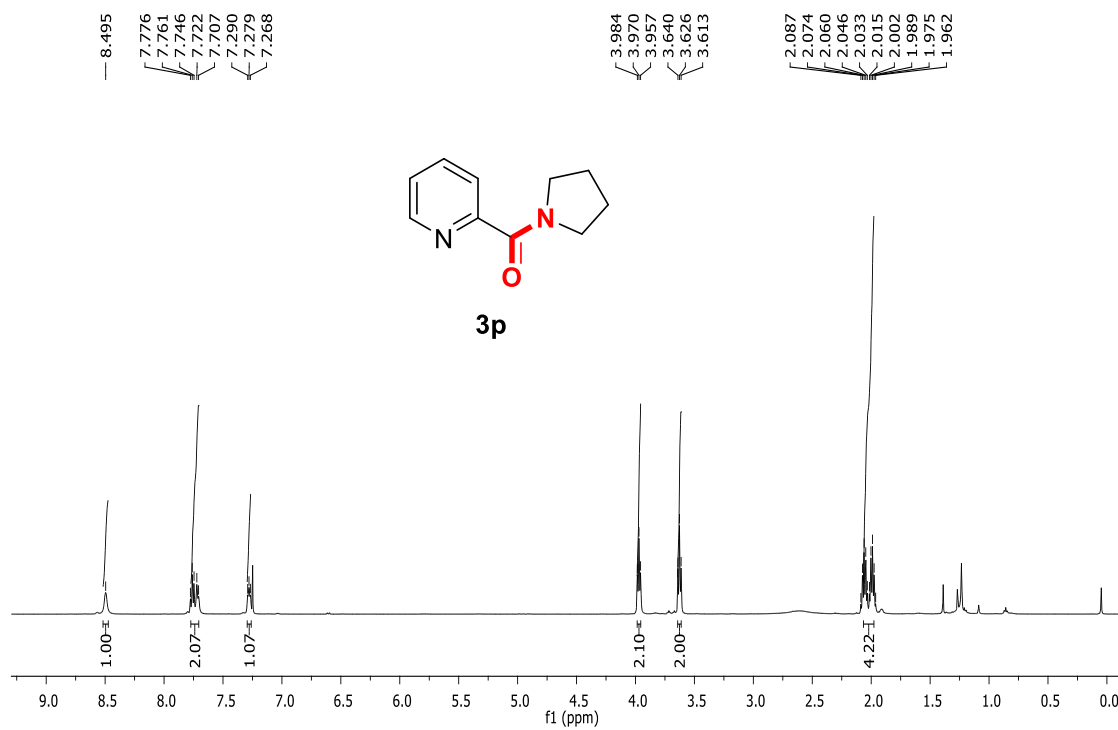
### <sup>1</sup>H NMR of *N*-Methyl-*N*-phenylpicolinamide (3o):



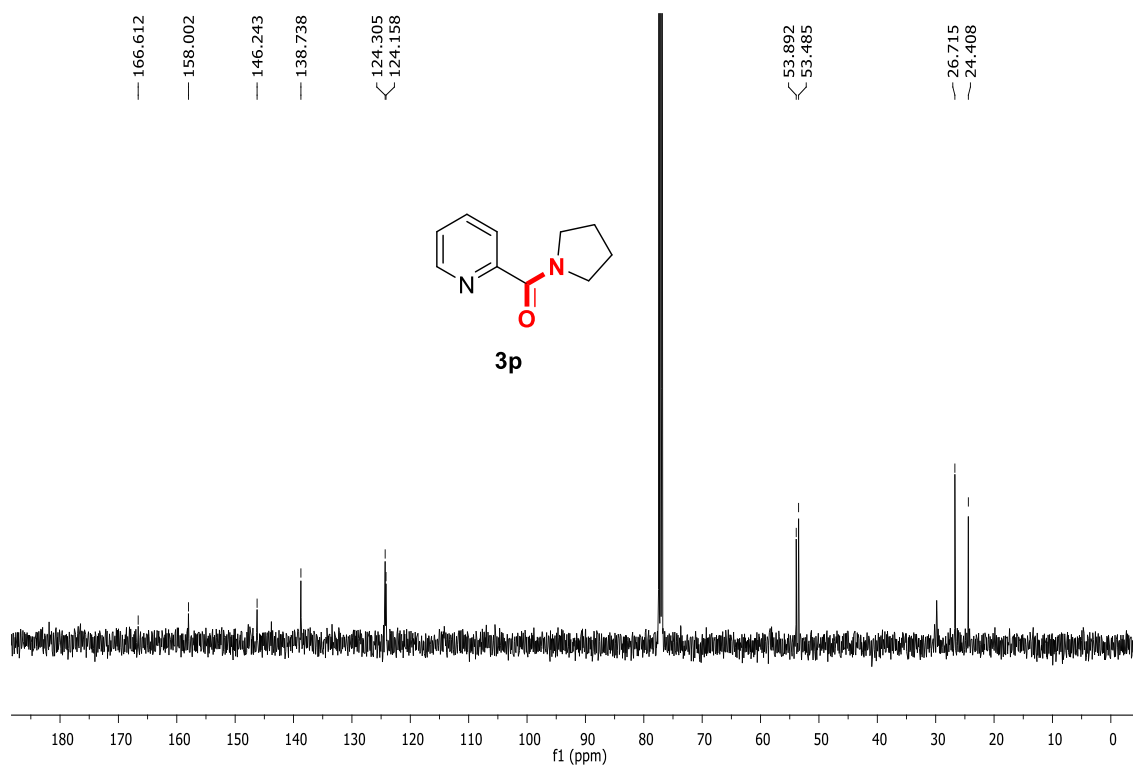
### <sup>13</sup>C NMR of *N*-Methyl-*N*-phenylpicolinamide (3o):



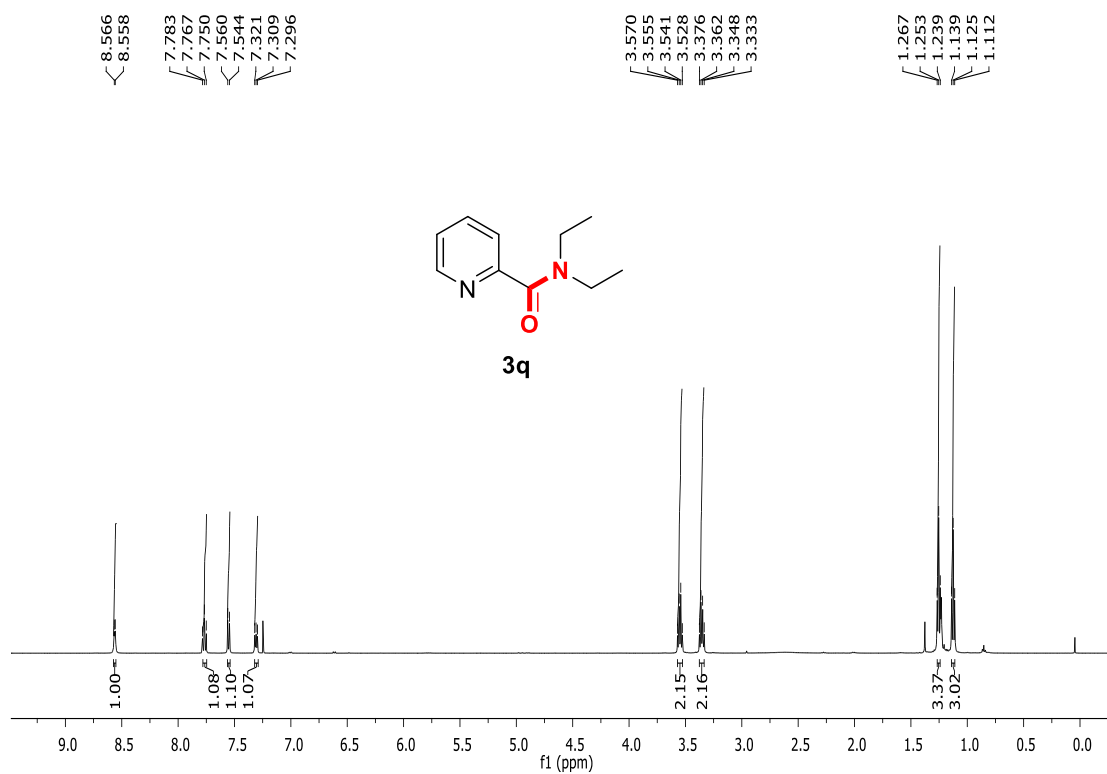
### <sup>1</sup>H NMR of Pyridin-2-yl(pyrrolidin-1-yl)methanone (3p):



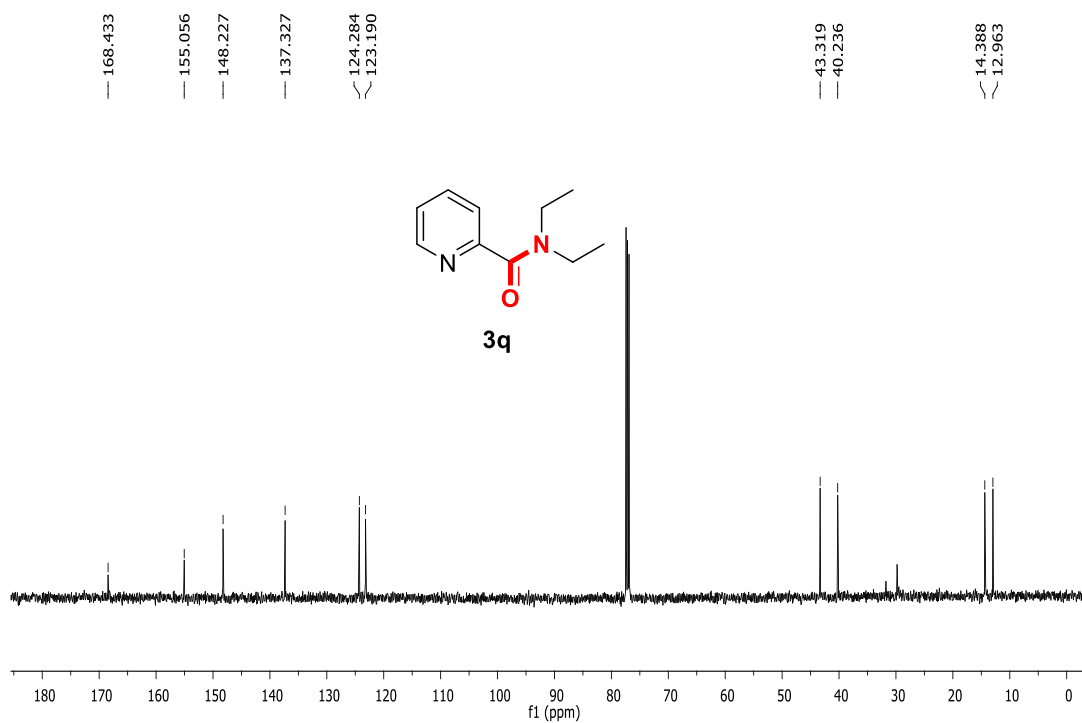
### <sup>13</sup>C NMR of Pyridin-2-yl(pyrrolidin-1-yl)methanone (3p):



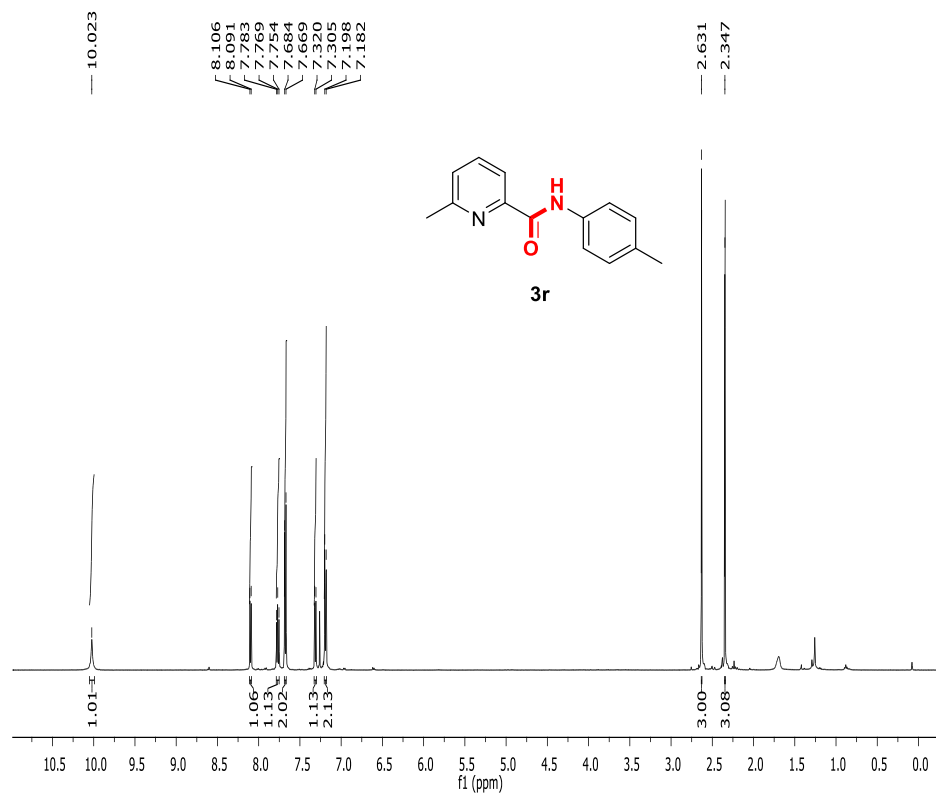
### <sup>1</sup>H NMR of *N,N*-Diethylpicolinamide (3q):



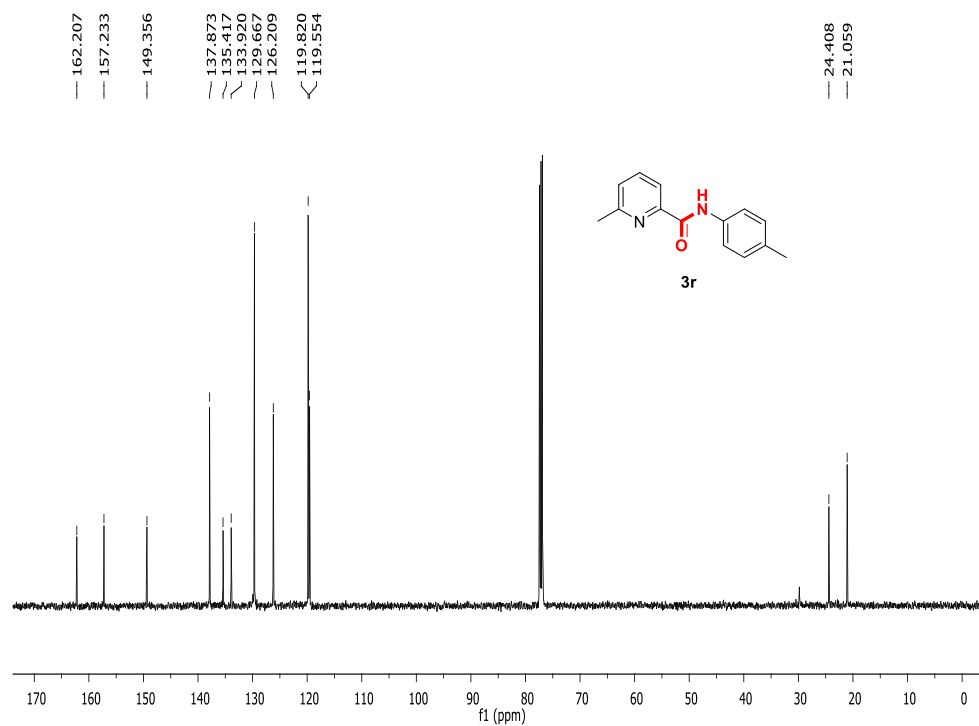
### <sup>13</sup>C NMR of *N,N*-Diethylpicolinamide (3q):



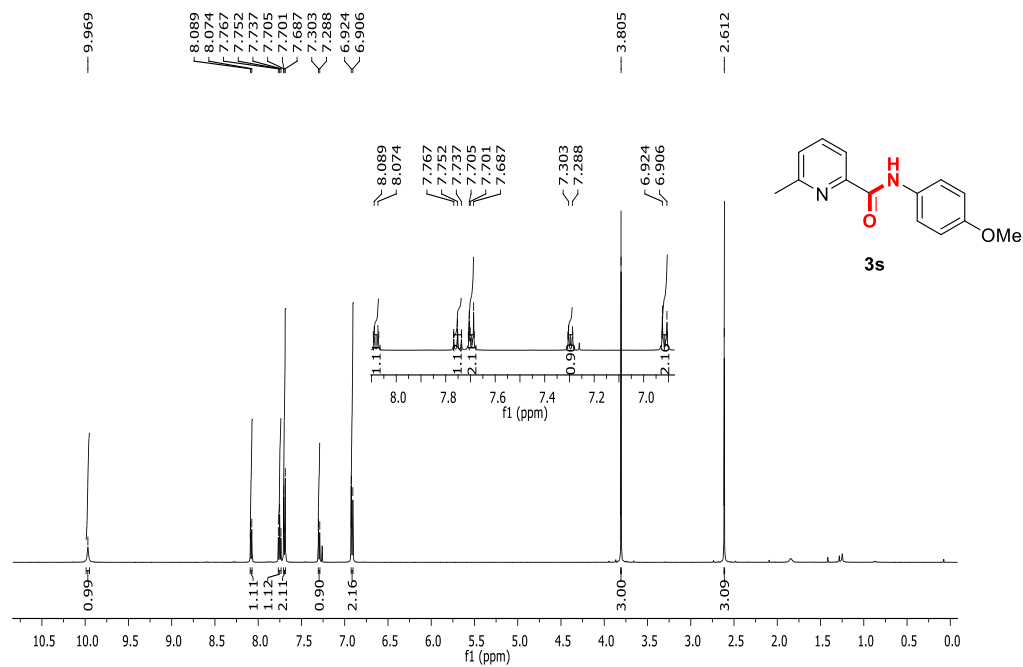
### <sup>1</sup>H NMR of 6-Methyl-N-(p-tolyl)picolinamide (3r):



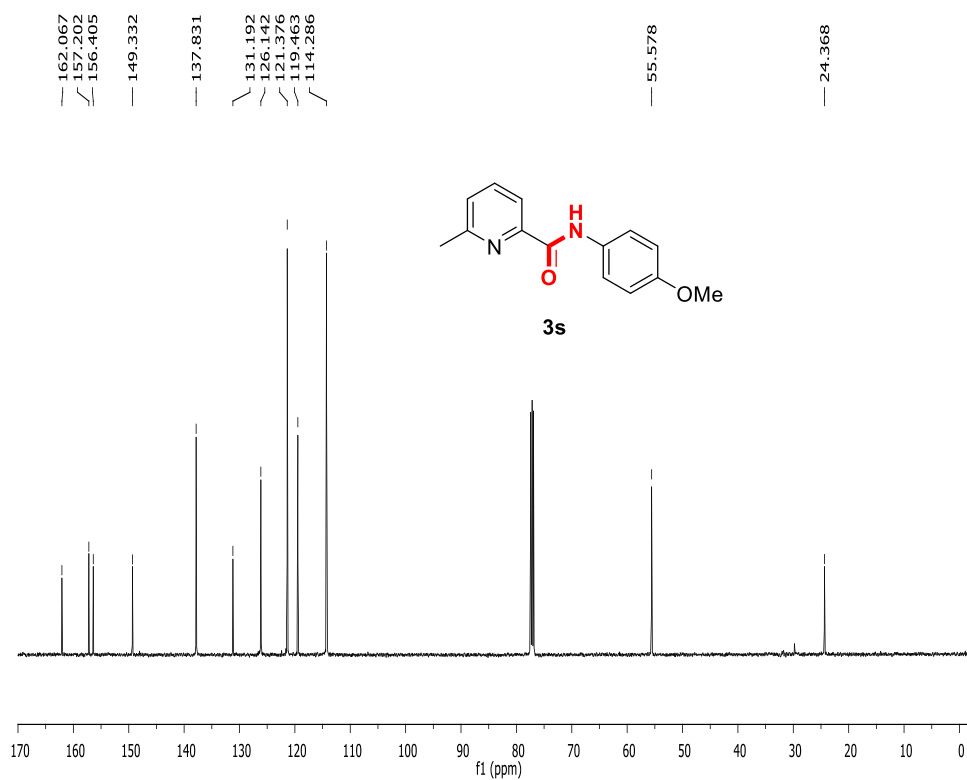
### <sup>13</sup>C NMR of 6-Methyl-N-(p-tolyl)picolinamide (3r):



### <sup>1</sup>H NMR of *N*-(4-Methoxyphenyl)-6-methylpicolinamide (3s):

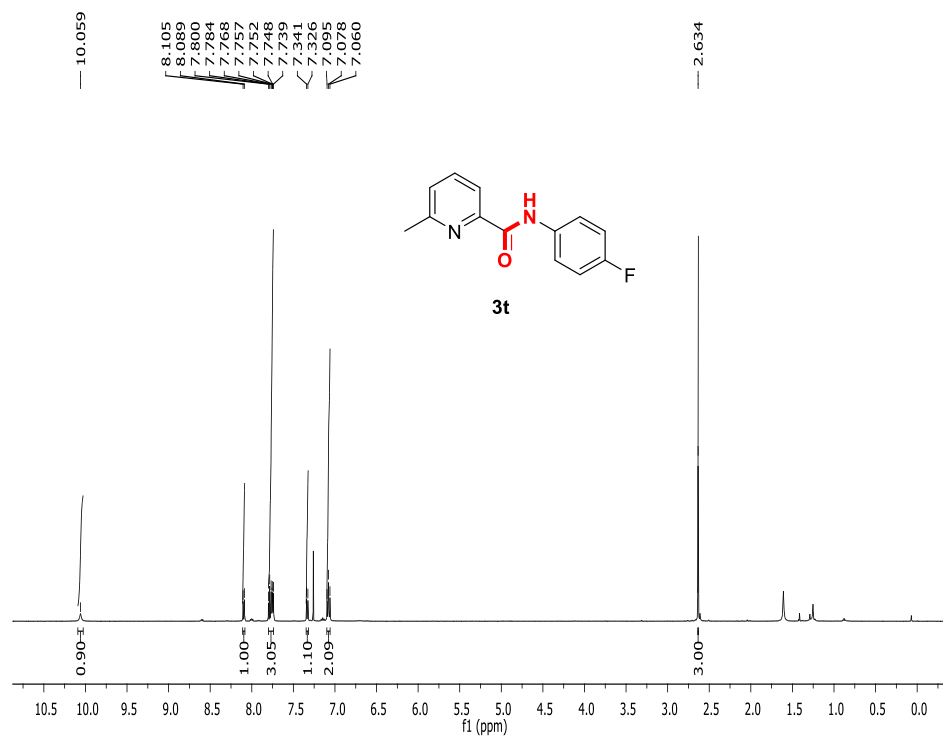


### <sup>13</sup>C NMR of *N*-(4-Methoxyphenyl)-6-methylpicolinamide (3s):

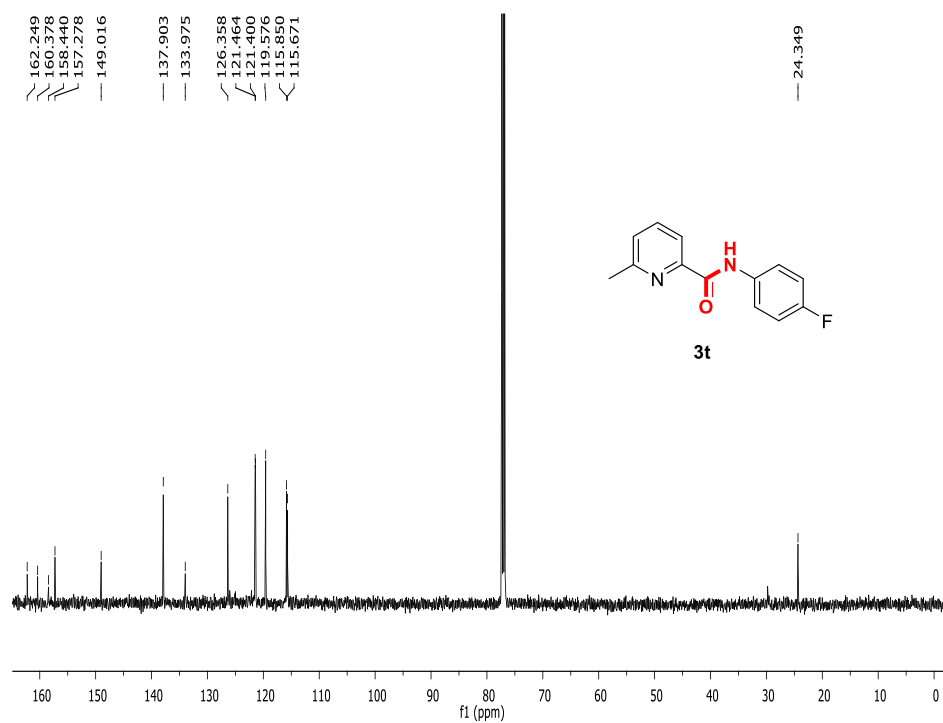




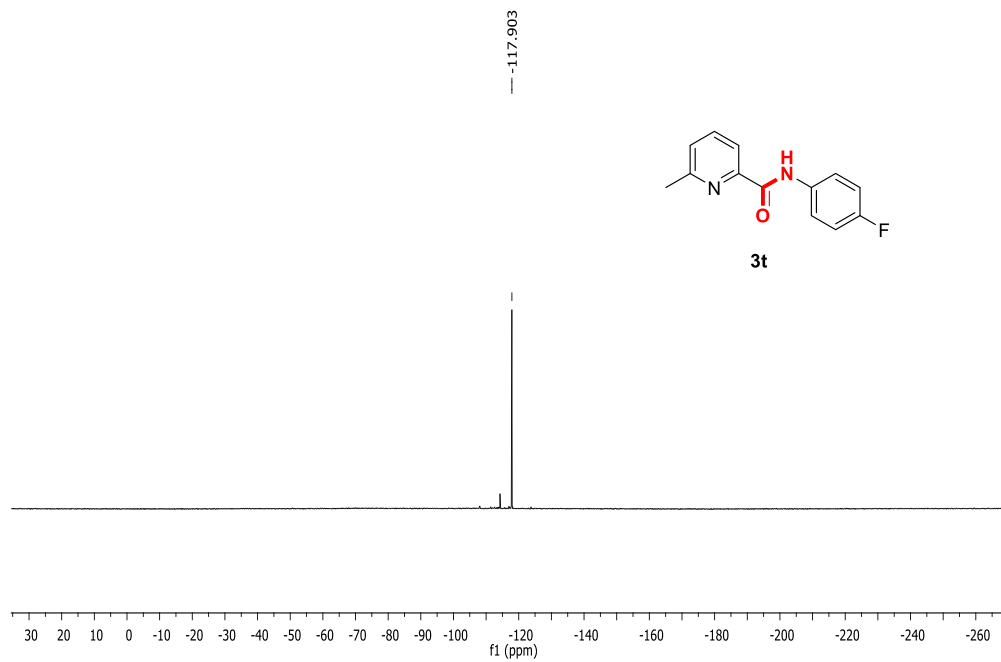
### <sup>1</sup>H NMR of *N*-(4-Fluorophenyl)-6-methylpicolinamide (3t):



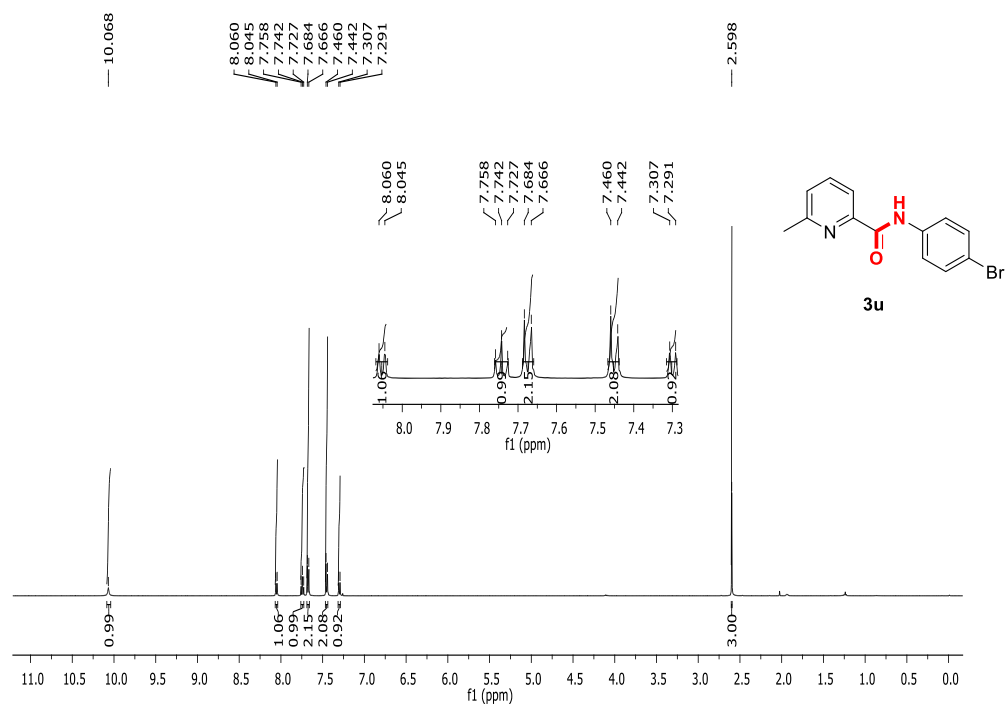
### <sup>13</sup>C NMR of *N*-(4-Fluorophenyl)-6-methylpicolinamide (3t):



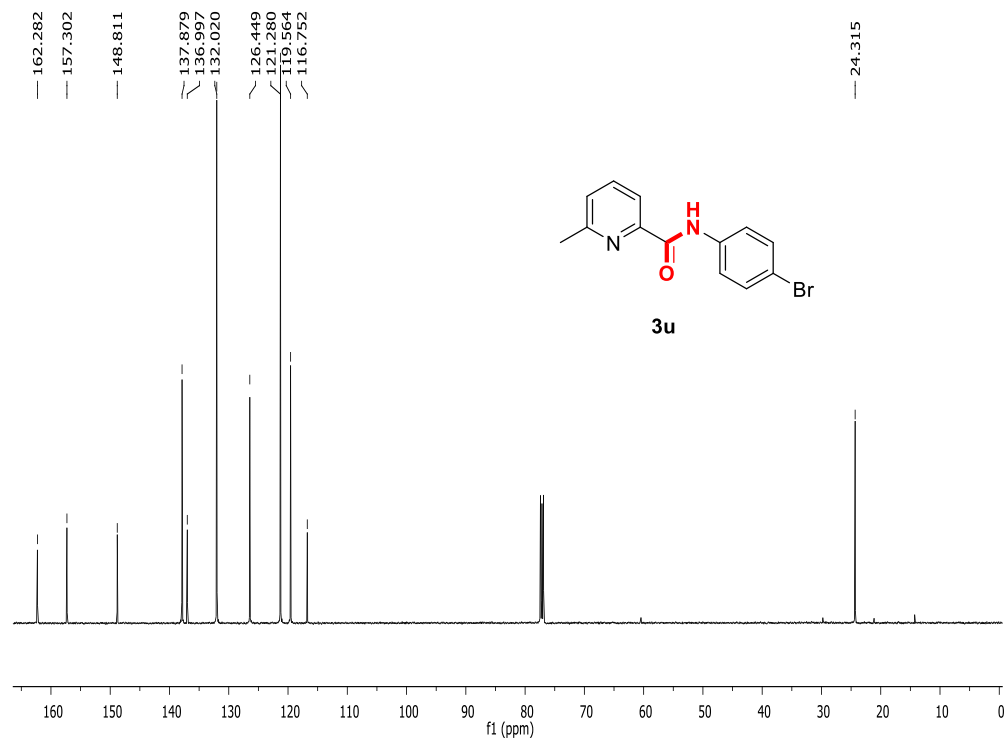
**<sup>19</sup>F NMR of *N*-(4-Fluorophenyl)-6-methylpicolinamide (3t):**



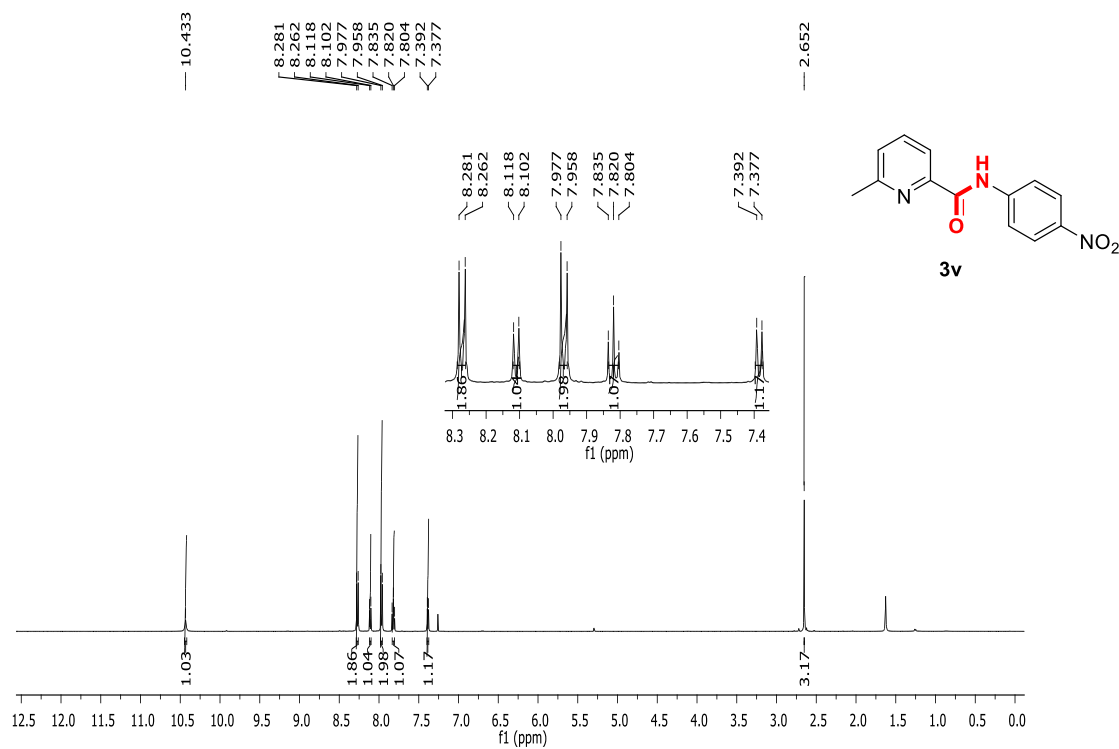
### <sup>1</sup>H NMR of *N*-(4-Bromophenyl)-6-methylpicolinamide (**3u**):



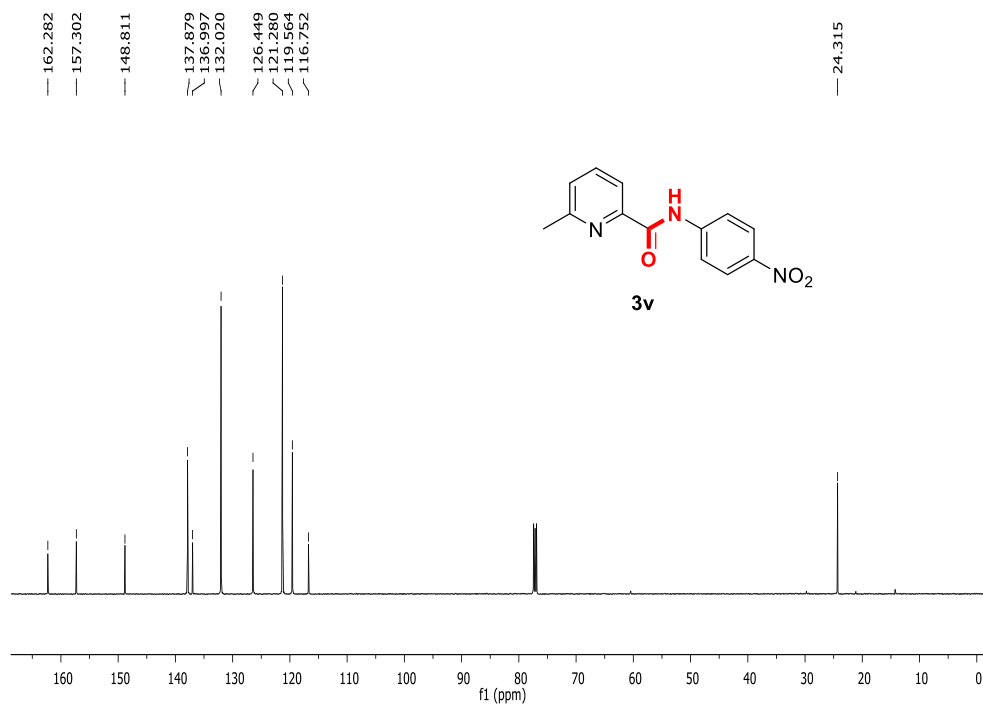
### <sup>13</sup>C NMR of *N*-(4-Bromophenyl)-6-methylpicolinamide (**3u**):



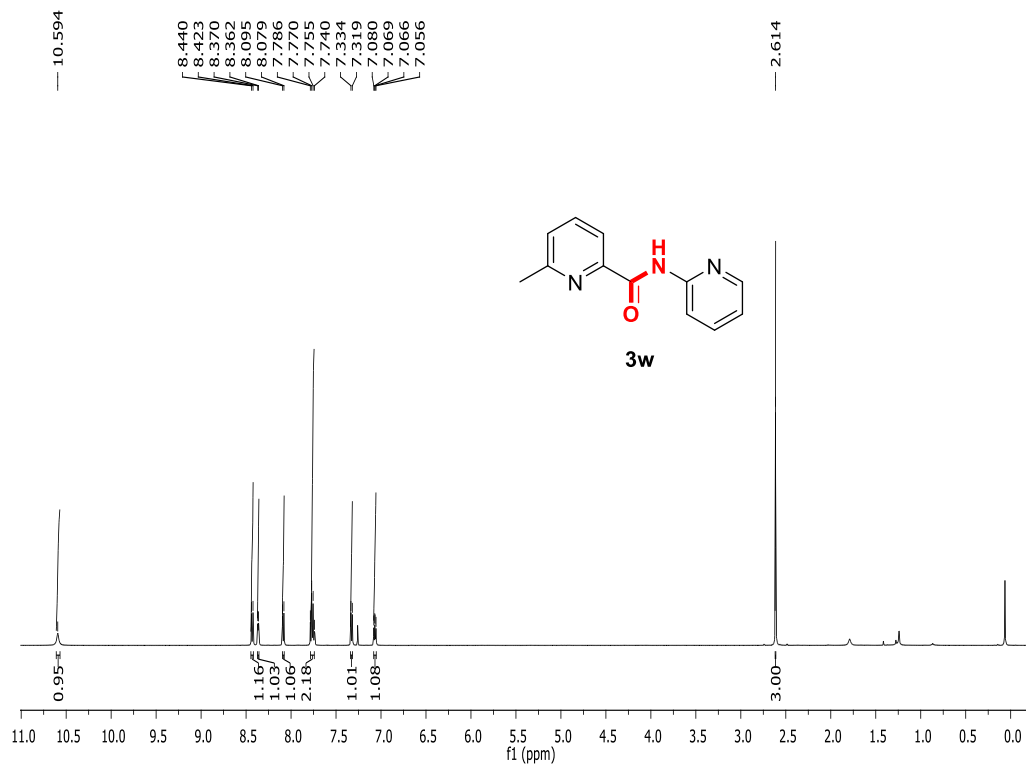
### <sup>1</sup>H NMR of 6-Methyl-N-(4-nitrophenyl)picolinamide (3v):



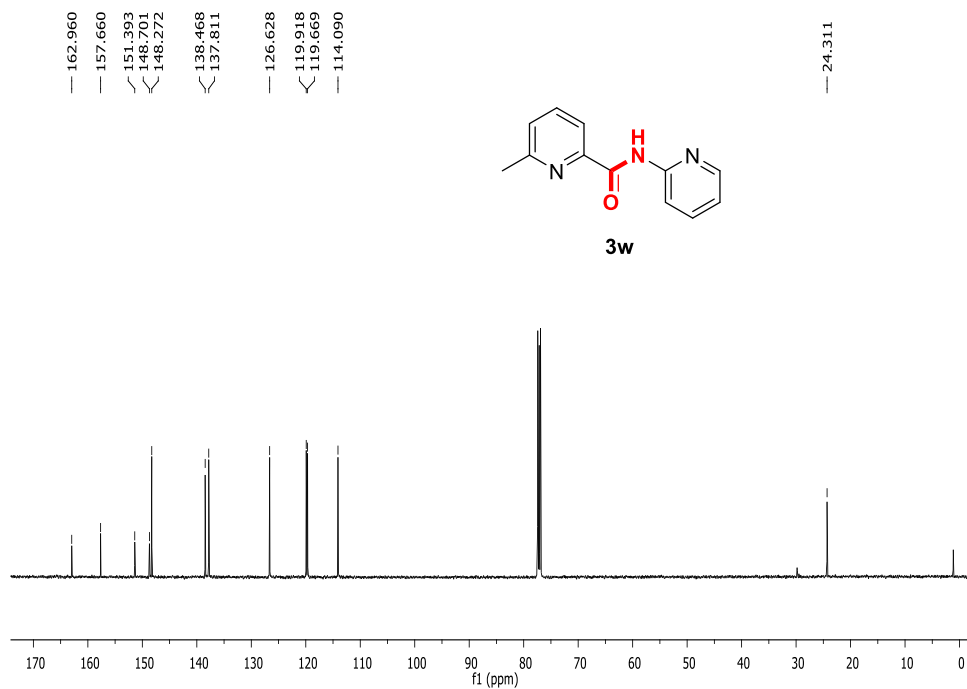
### <sup>13</sup>C NMR of 6-Methyl-N-(4-nitrophenyl)picolinamide (3v):



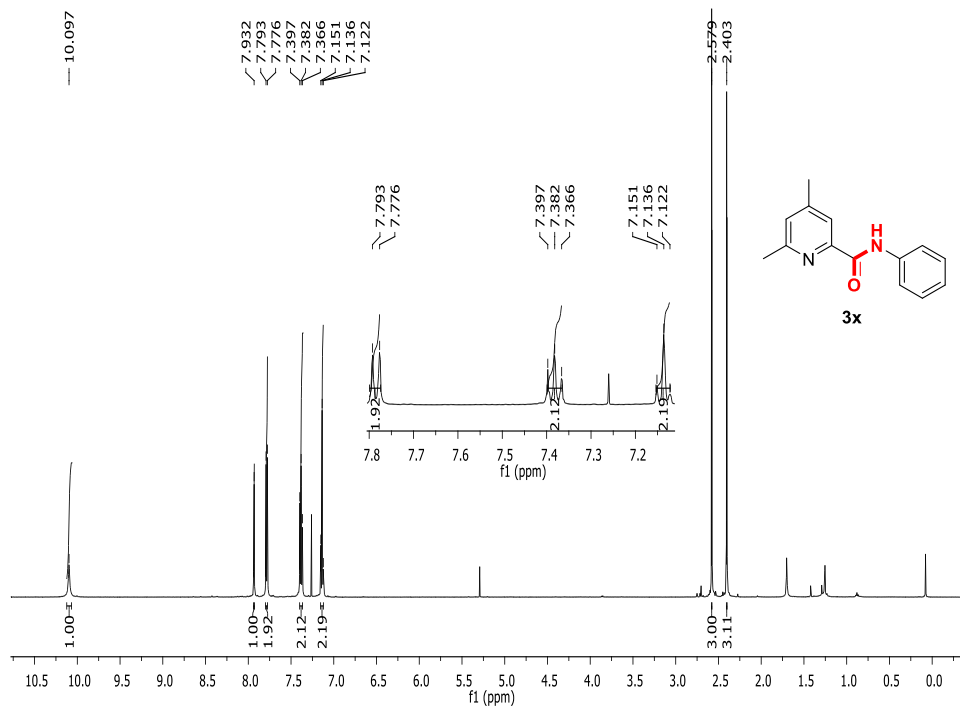
### <sup>1</sup>H NMR of 6-Methyl-N-(pyridin-2-yl)picolinamide (3w):



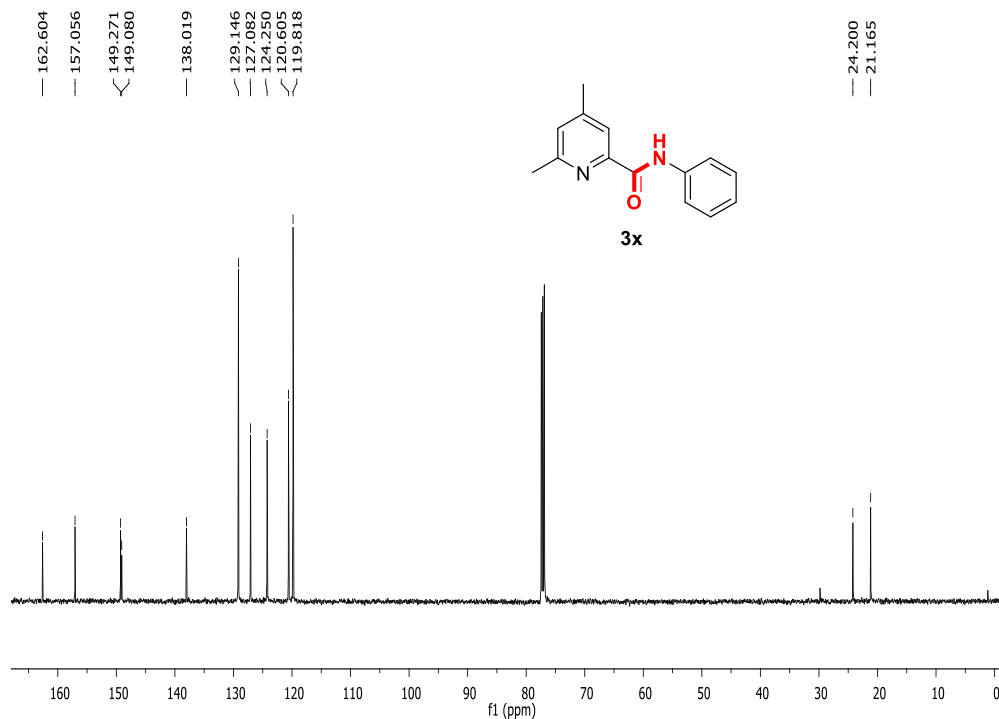
### <sup>13</sup>C NMR of 6-Methyl-N-(pyridin-2-yl)picolinamide (3w):



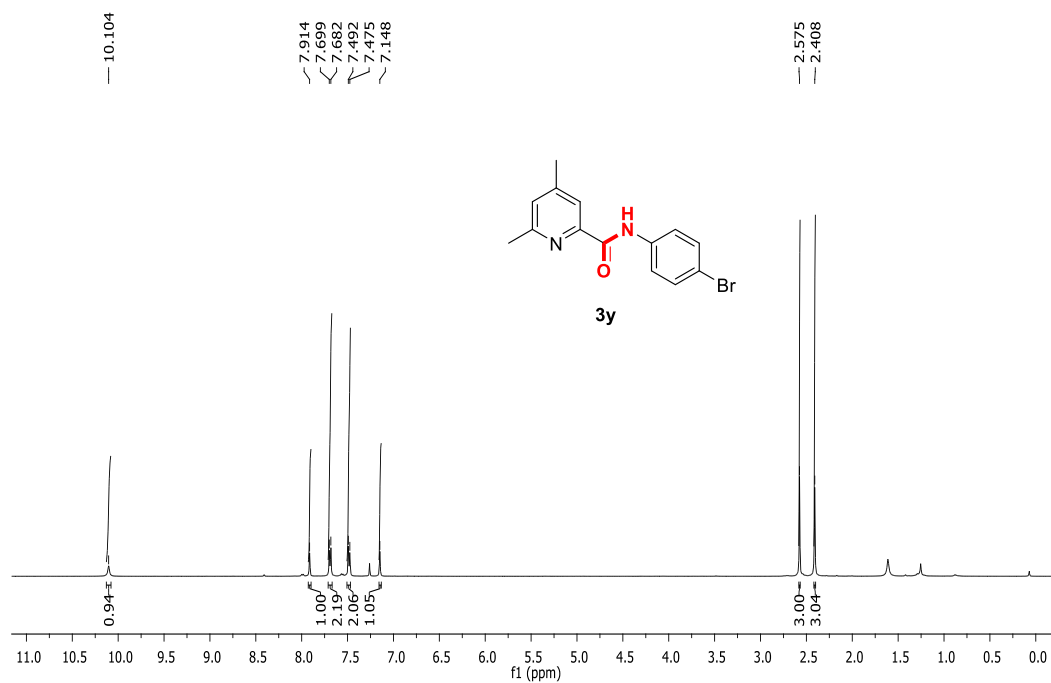
### <sup>1</sup>H NMR of 4,6-Dimethyl-N-phenylpicolinamide (3x):



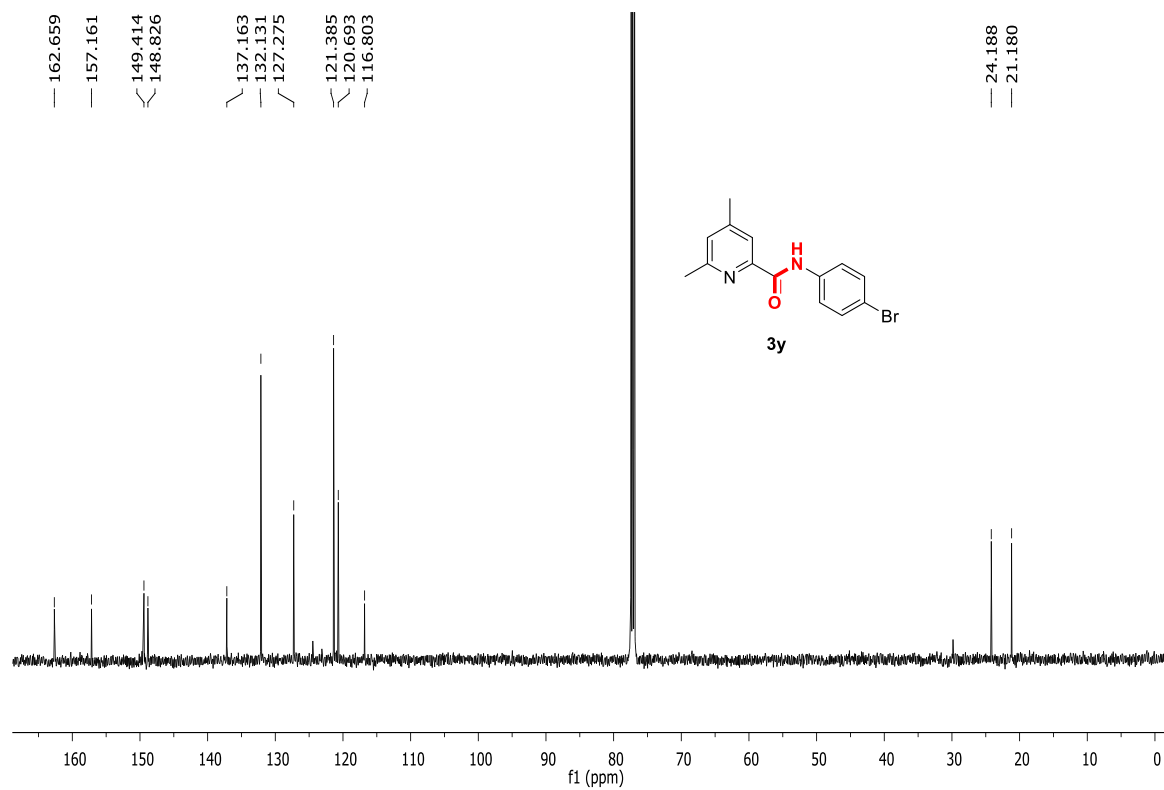
### <sup>13</sup>C NMR of 4,6-Dimethyl-N-phenylpicolinamide (3x):



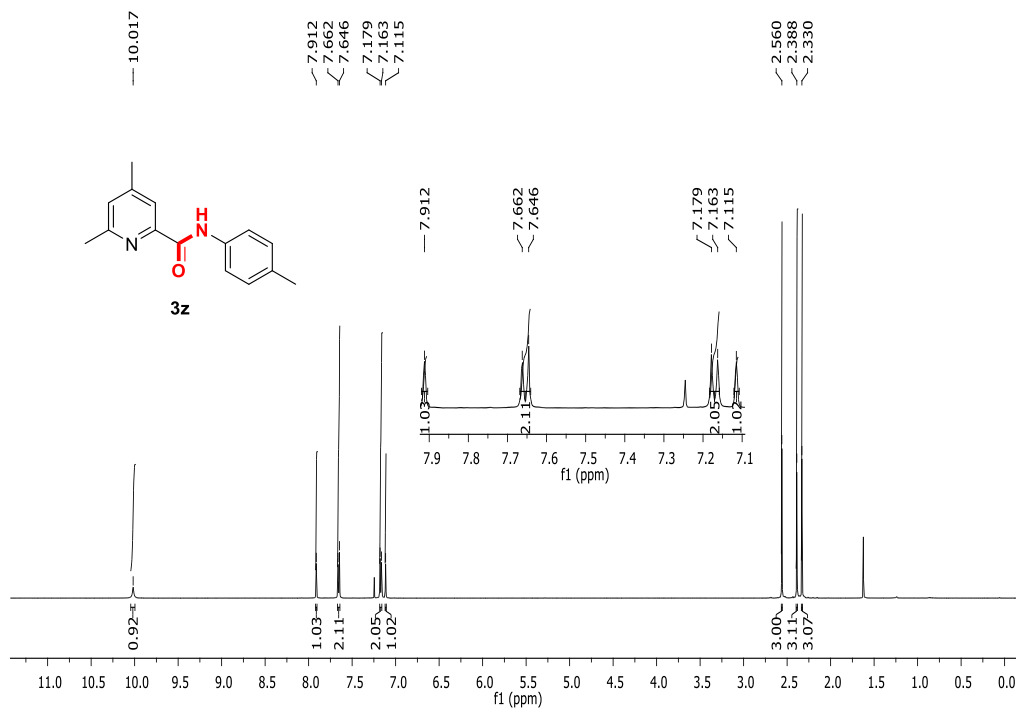
### <sup>1</sup>H NMR of *N*-(4-Bromophenyl)-4,6-dimethylpicolinamide (**3y**):



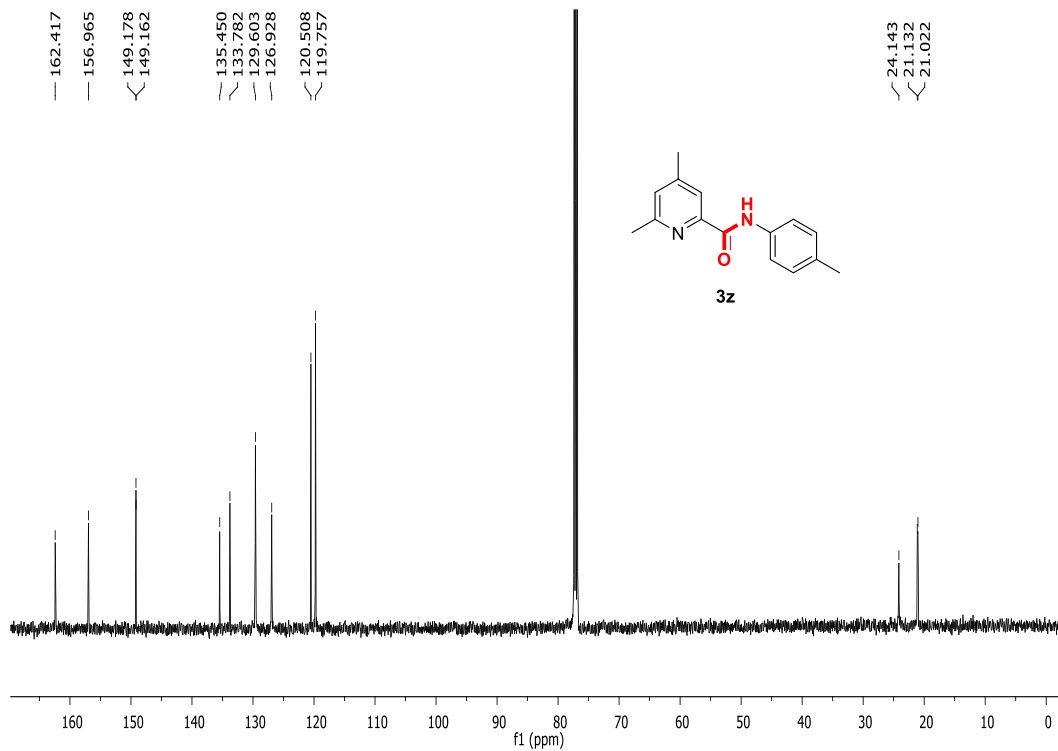
### <sup>13</sup>C NMR of *N*-(4-Bromophenyl)-4,6-dimethylpicolinamide (**3y**):



### <sup>1</sup>H NMR of 4,6-Dimethyl-N-(p-tolyl)picolinamide (3z):

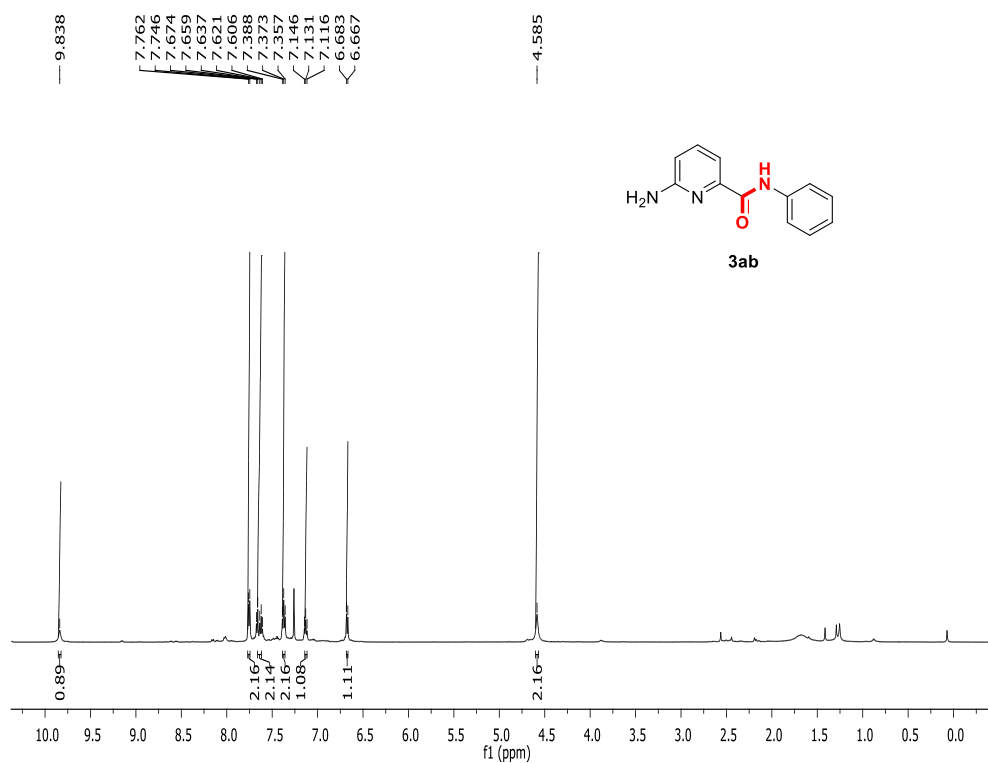


### <sup>13</sup>C NMR of 4,6-Dimethyl-N-(p-tolyl)picolinamide (3z):

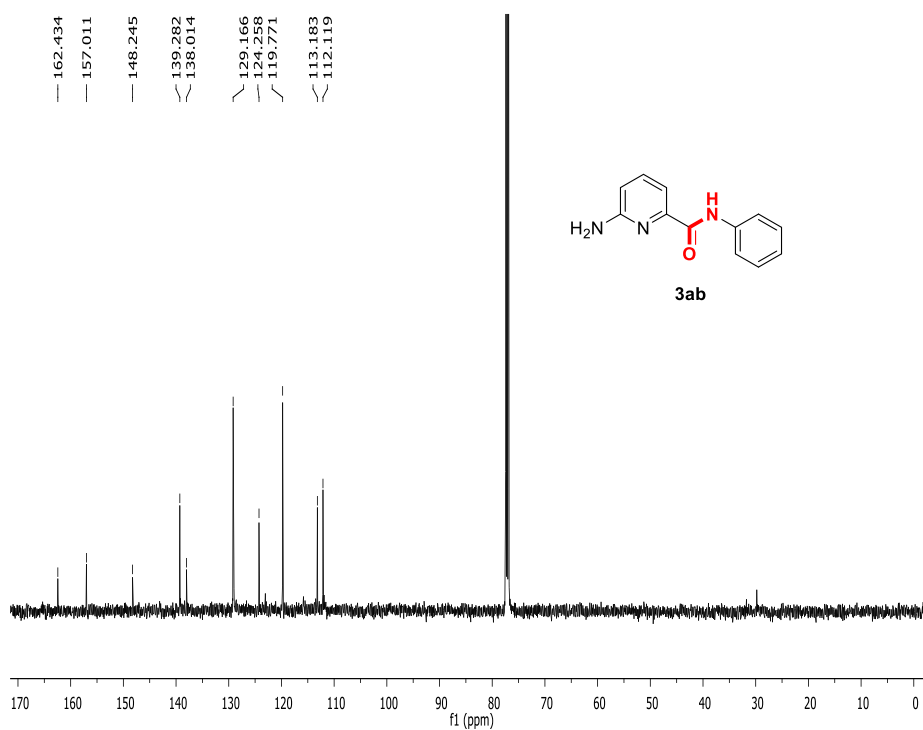




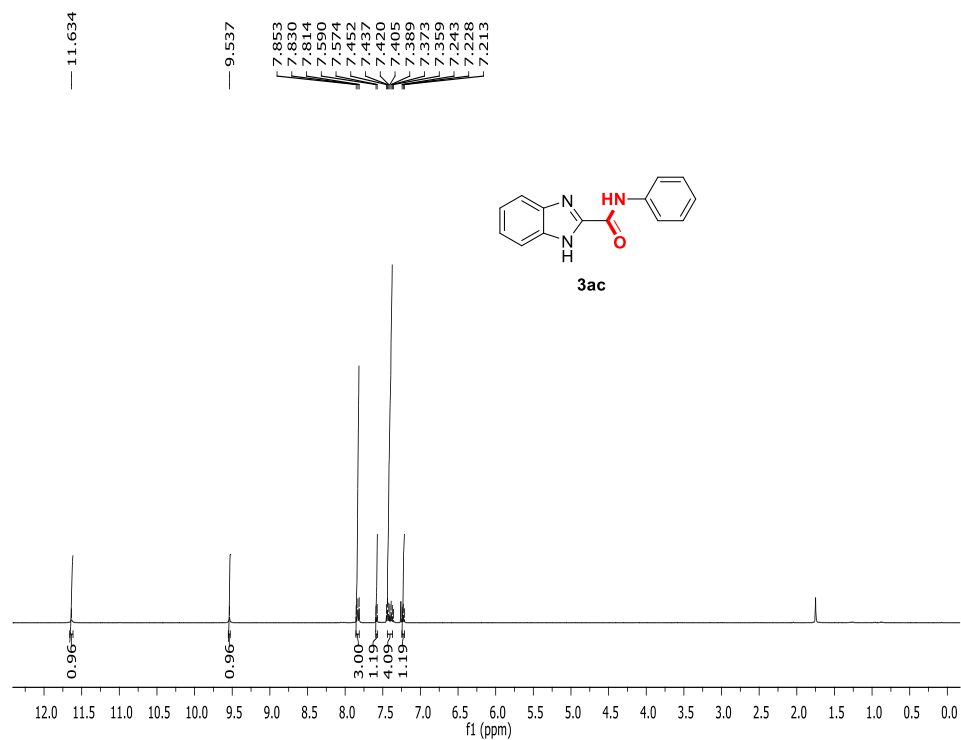
### <sup>1</sup>H NMR of 6-Amino-*N*-phenylpicolinamide (3ab):



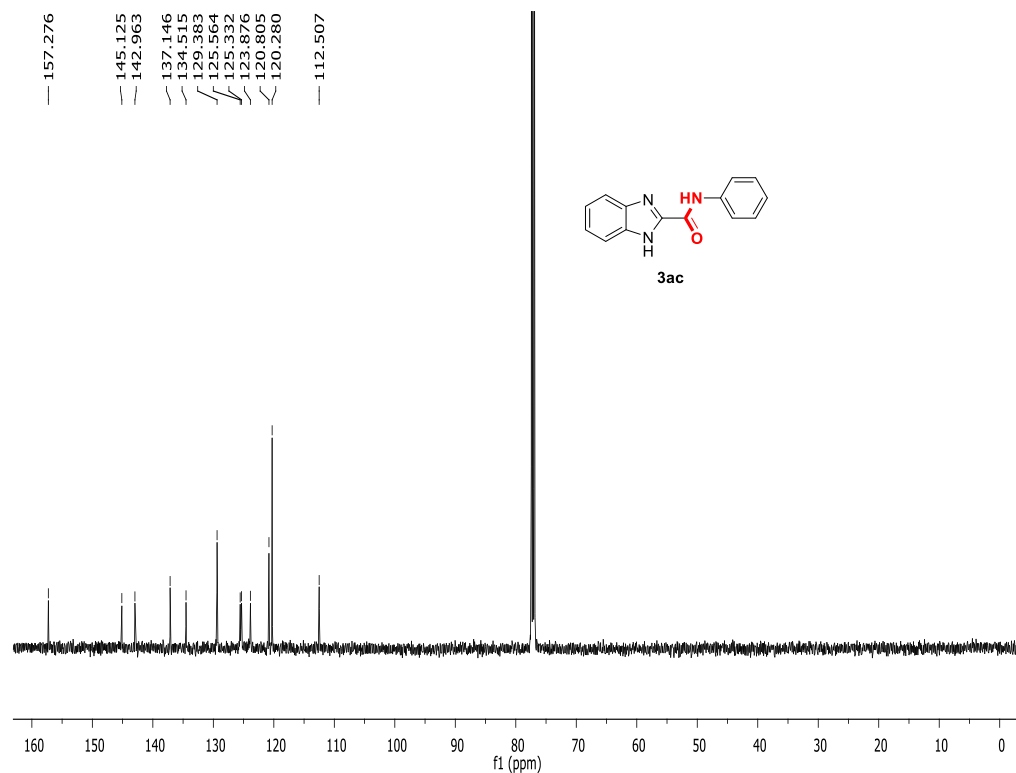
### <sup>13</sup>C NMR of 6-Amino-*N*-phenylpicolinamide (3ab):



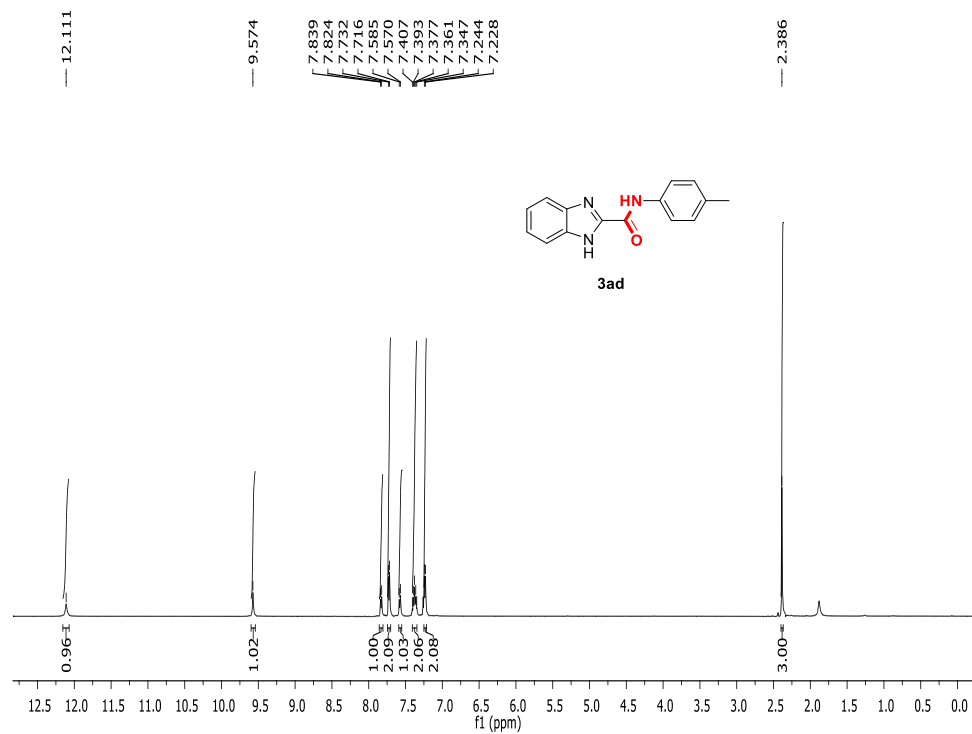
### <sup>1</sup>H NMR of *N*-Phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide (3ac):



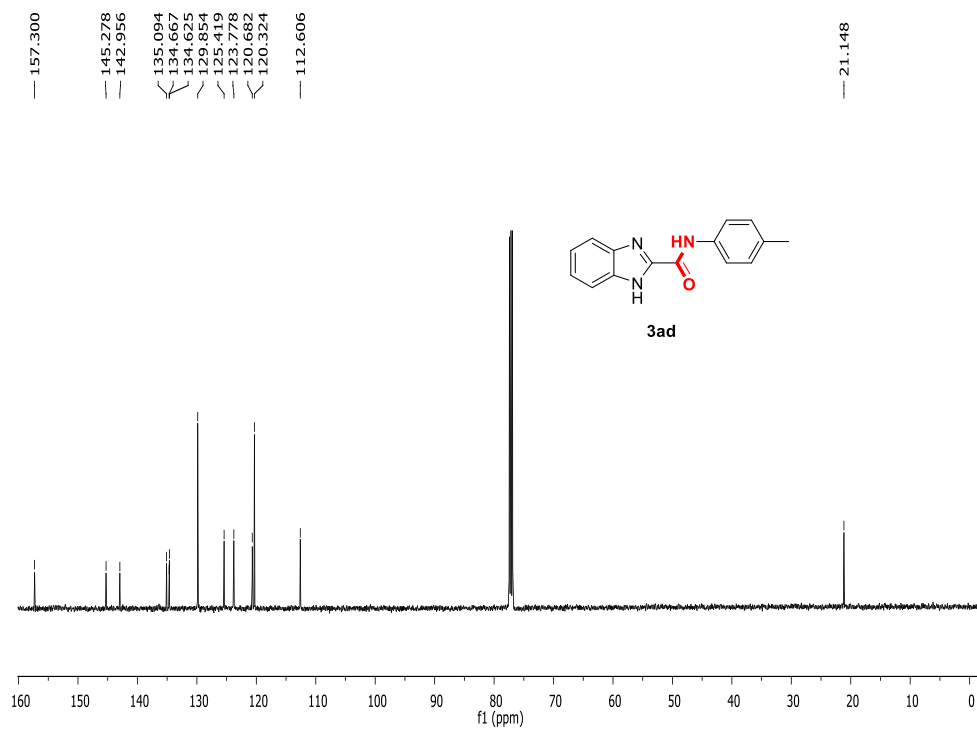
### <sup>13</sup>C NMR of *N*-Phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide (3ac):



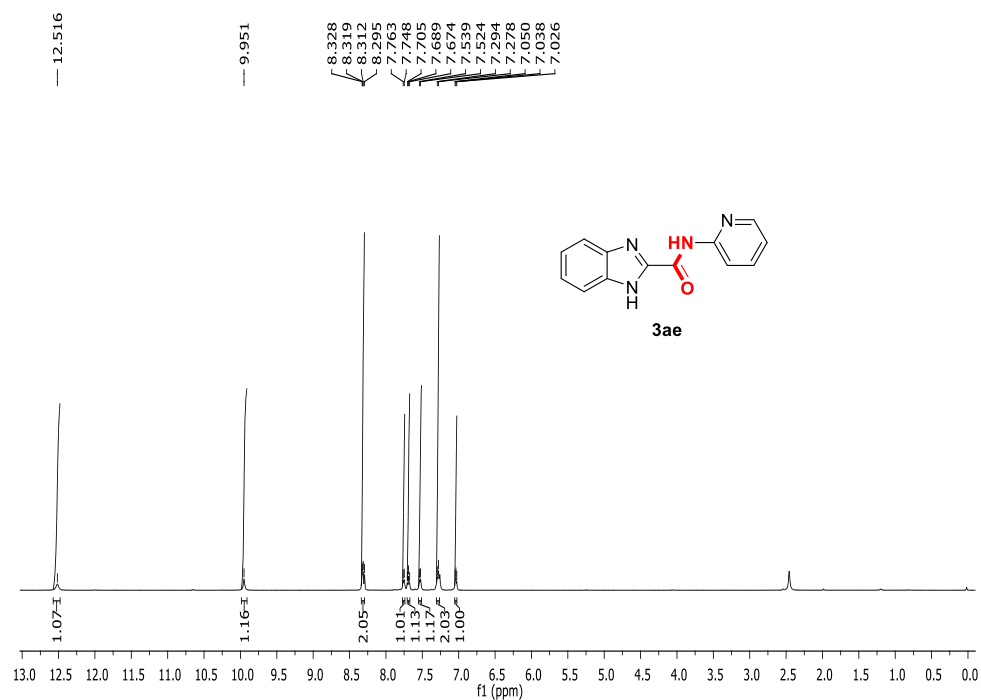
**<sup>1</sup>H NMR of *N*-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3ad):**



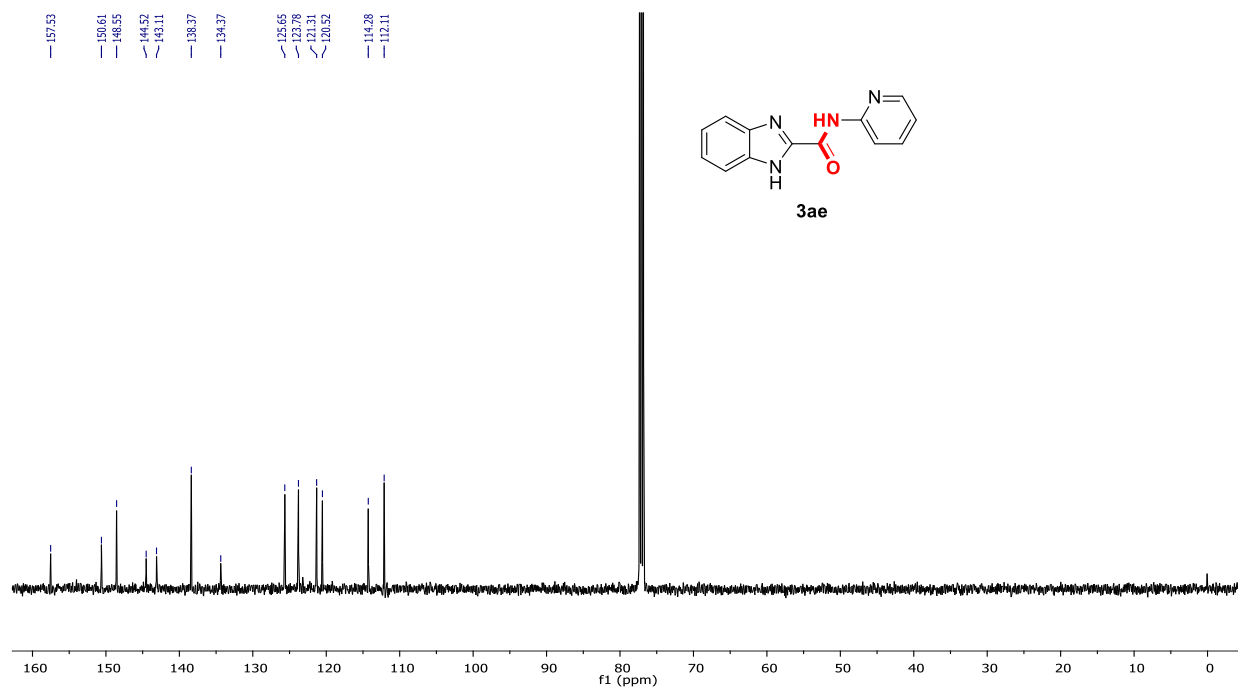
**<sup>13</sup>C NMR of *N*-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3ad):**



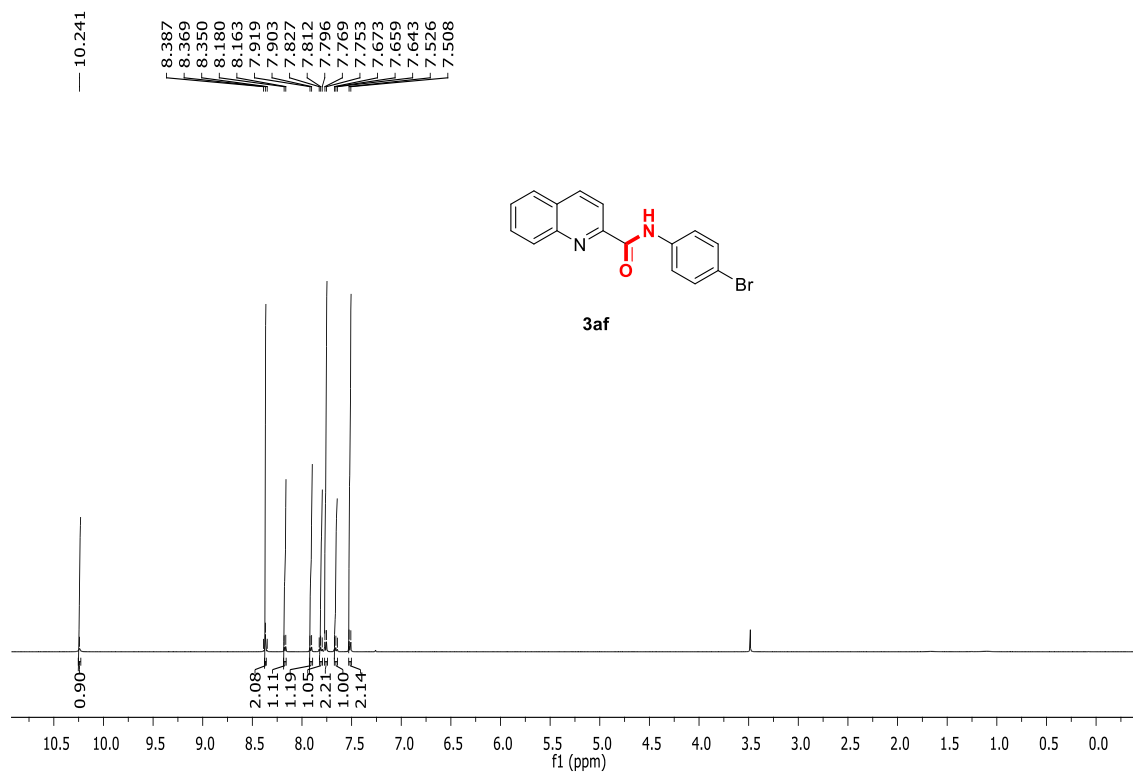
### <sup>1</sup>H NMR of *N*-(Pyridin-2-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3ae):



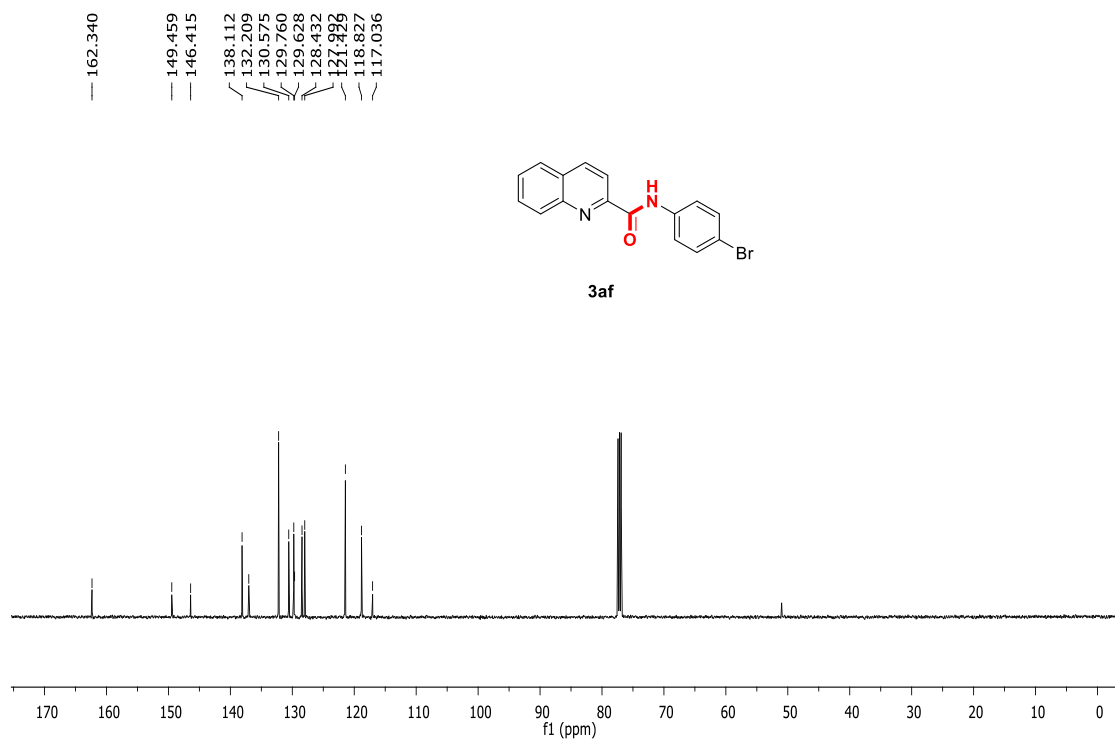
### <sup>13</sup>C NMR of *N*-(Pyridin-2-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3ae):



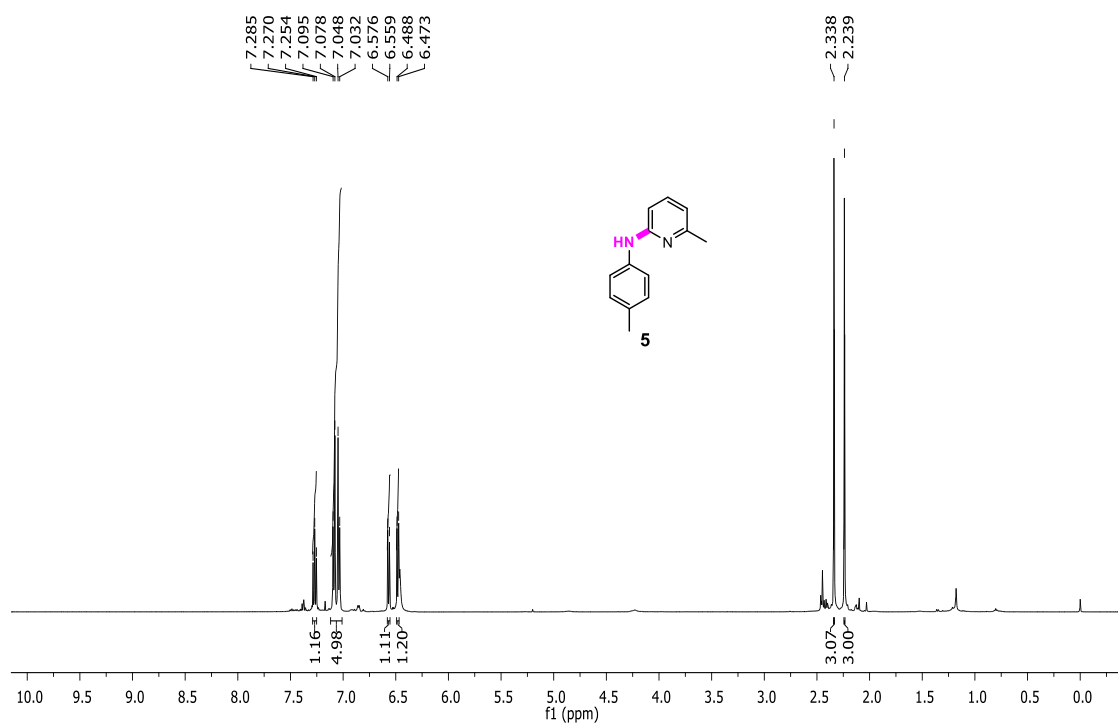
### <sup>1</sup>H NMR of *N*-(4-Bromophenyl)quinoline-2-carboxamide (3af):



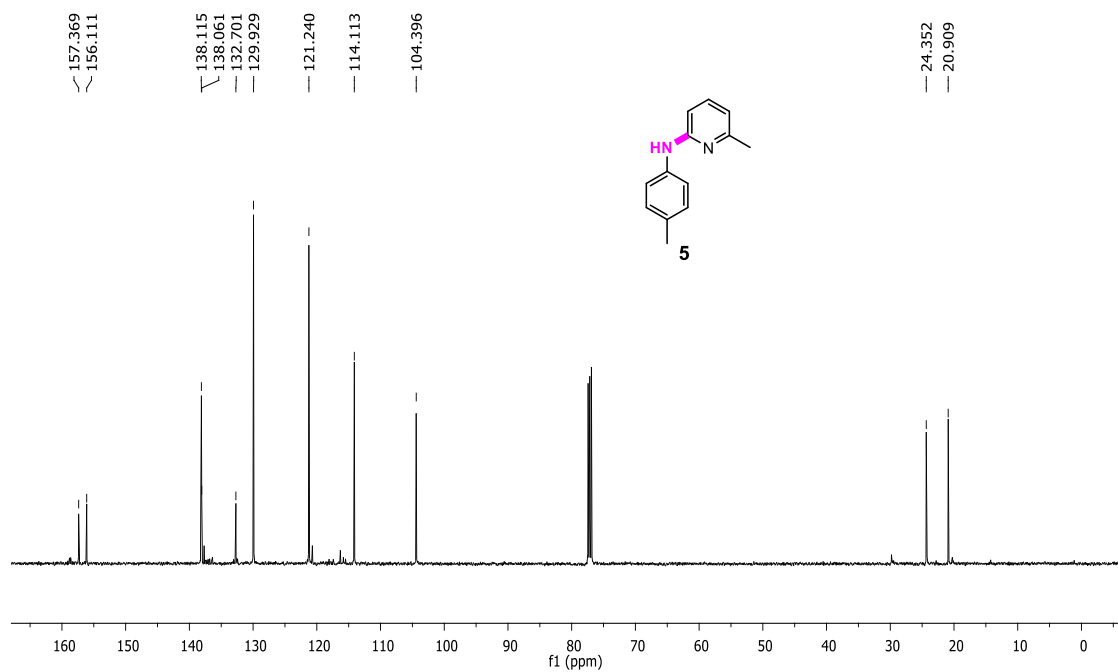
### <sup>13</sup>C NMR of *N*-(4-Bromophenyl)quinoline-2-carboxamide (3af):



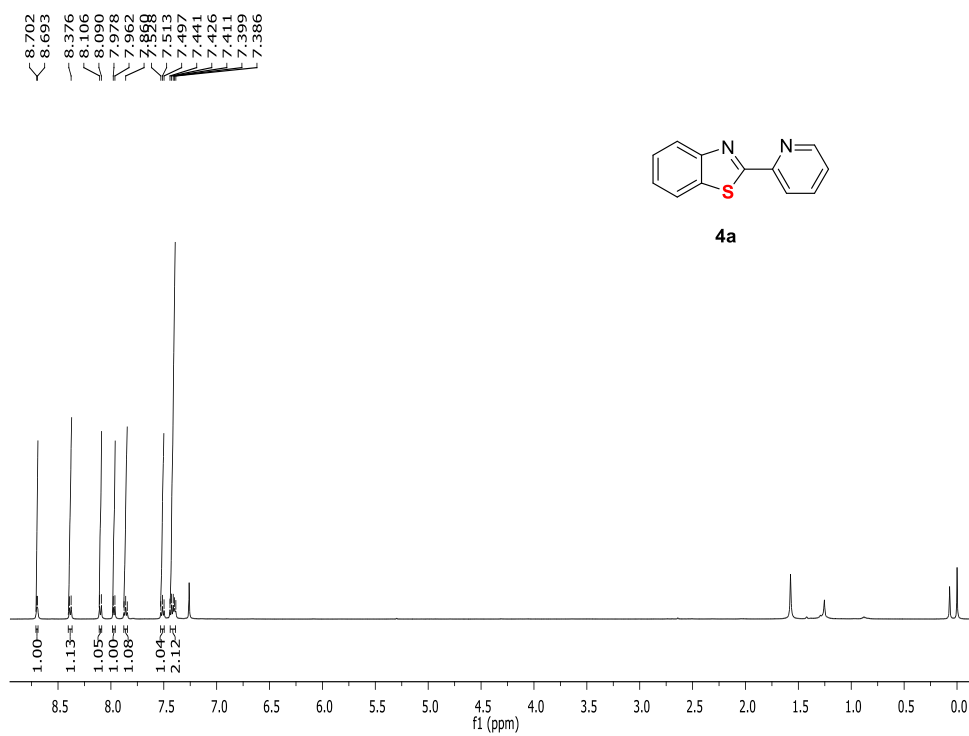
**<sup>1</sup>H NMR of 6-Methyl-N-(p-tolyl)pyridin-2-amine (5):**



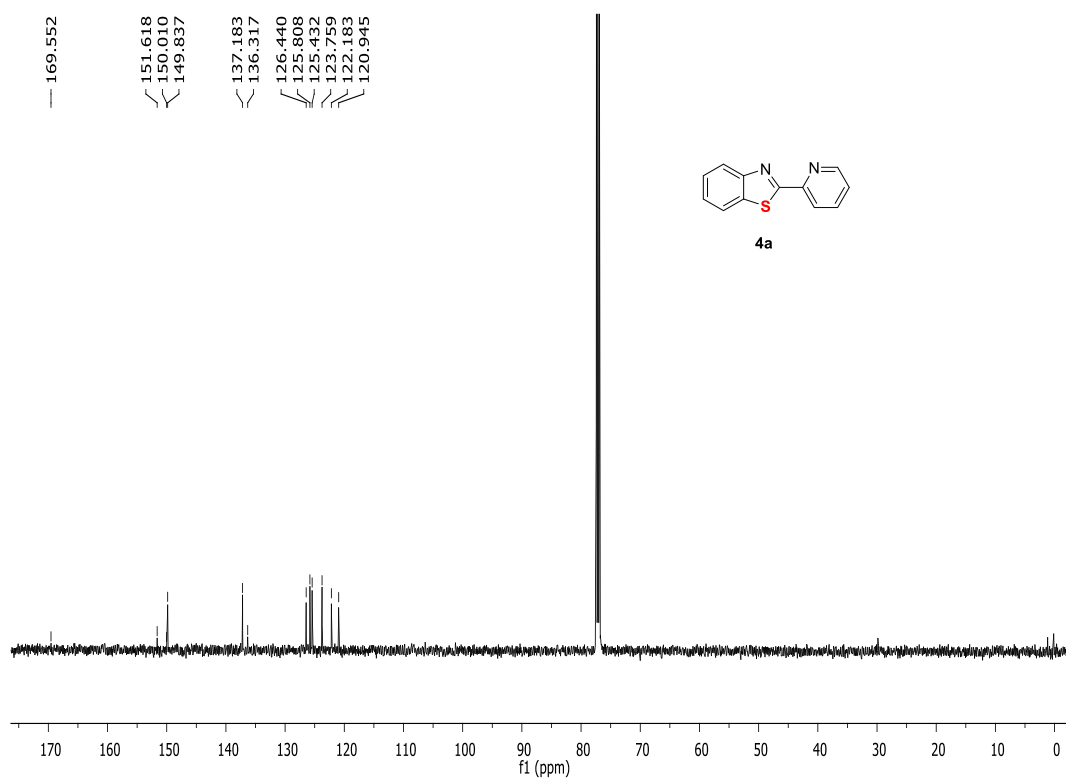
**<sup>13</sup>C NMR of 6-Methyl-N-(p-tolyl)pyridin-2-amine (5):**



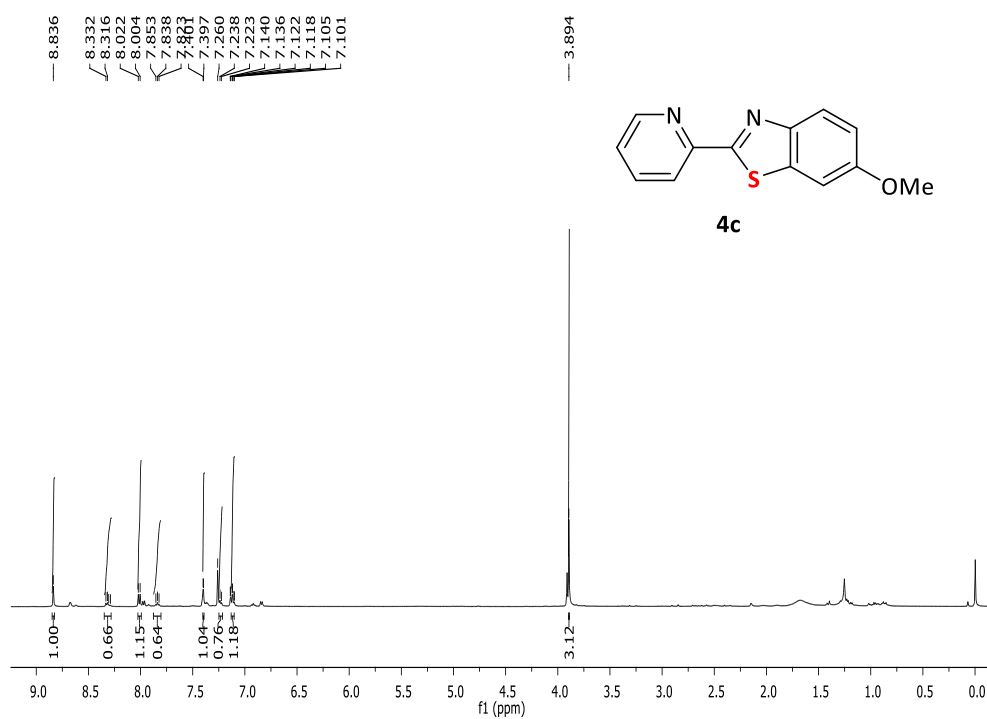
### <sup>1</sup>H NMR of 2-(Pyridin-2-yl)benzo[d]thiazole (4a):



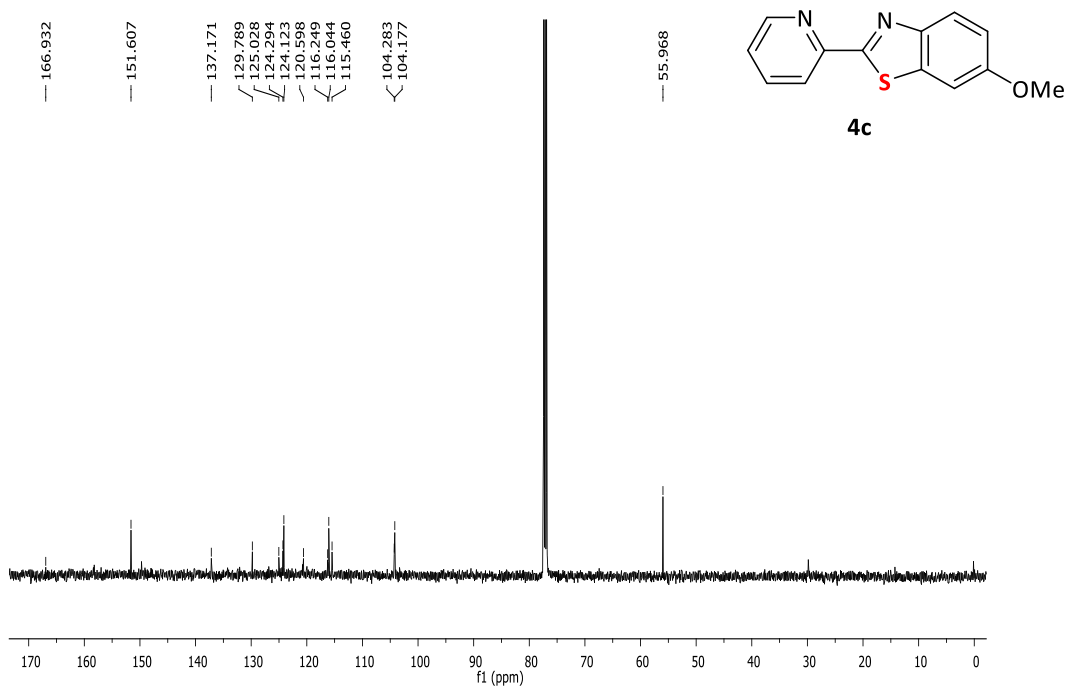
### <sup>13</sup>C NMR of 2-(Pyridin-2-yl)benzo[d]thiazole (4a):



### <sup>1</sup>H NMR of 6-methoxy-2-(pyridin-2-yl)benzo[d]thiazole (4c)

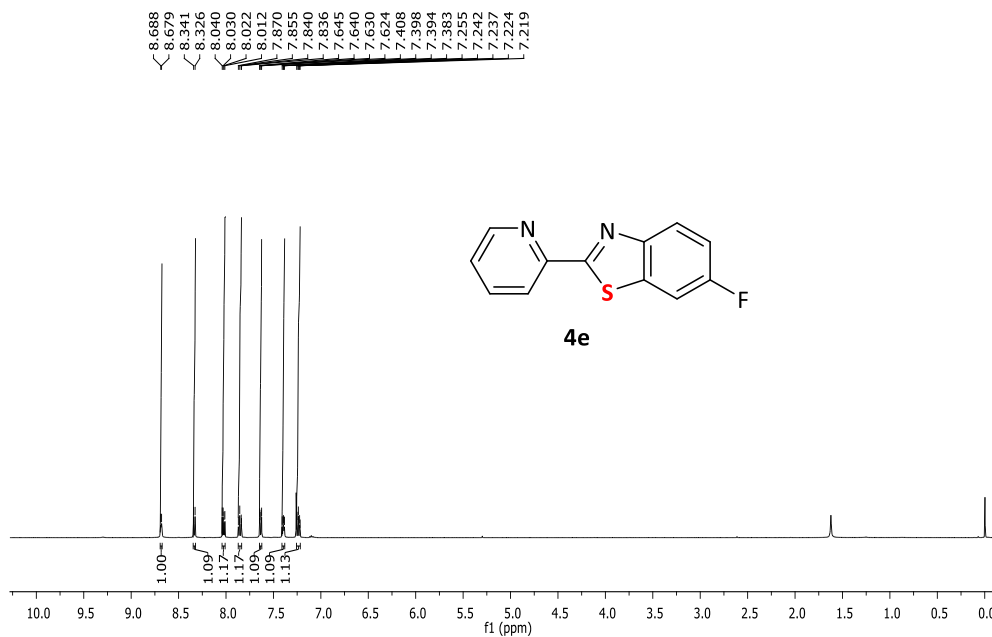


### <sup>13</sup>C NMR of 6-methoxy-2-(pyridin-2-yl)benzo[d]thiazole (4c)

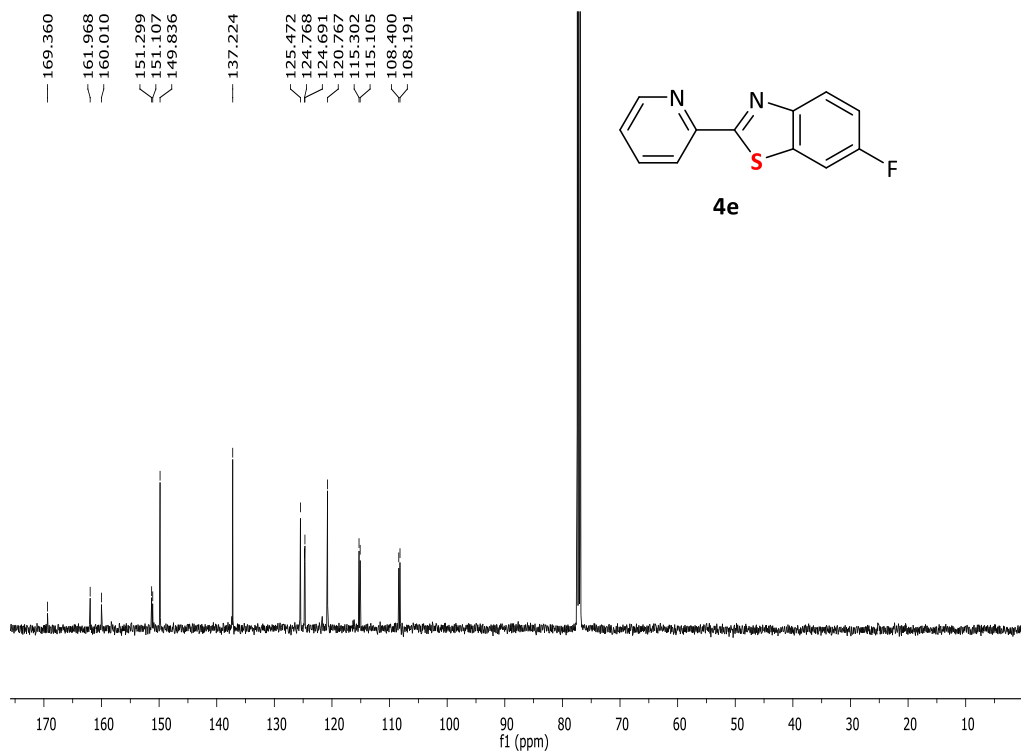




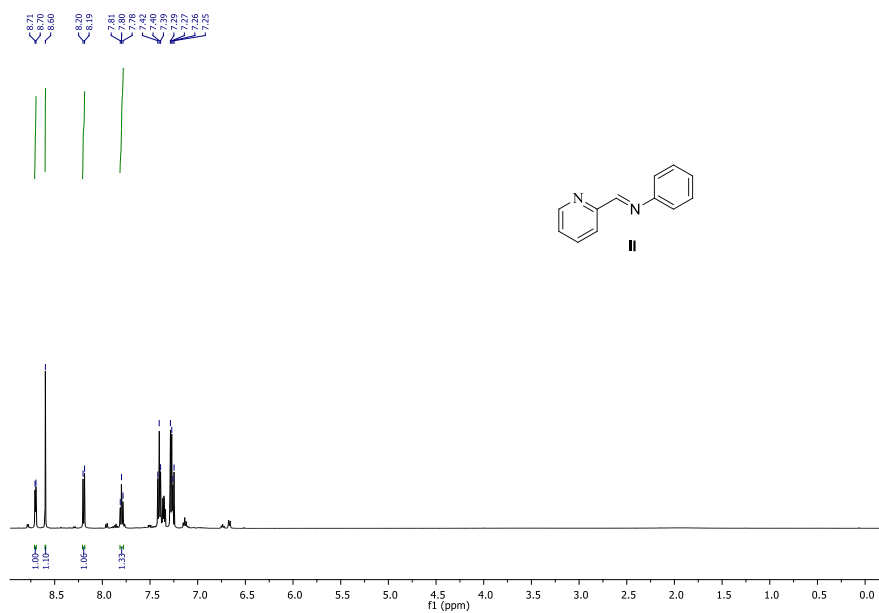
### <sup>1</sup>H NMR of 6-fluoro-2-(pyridin-2-yl)benzo[d]thiazole (4e)



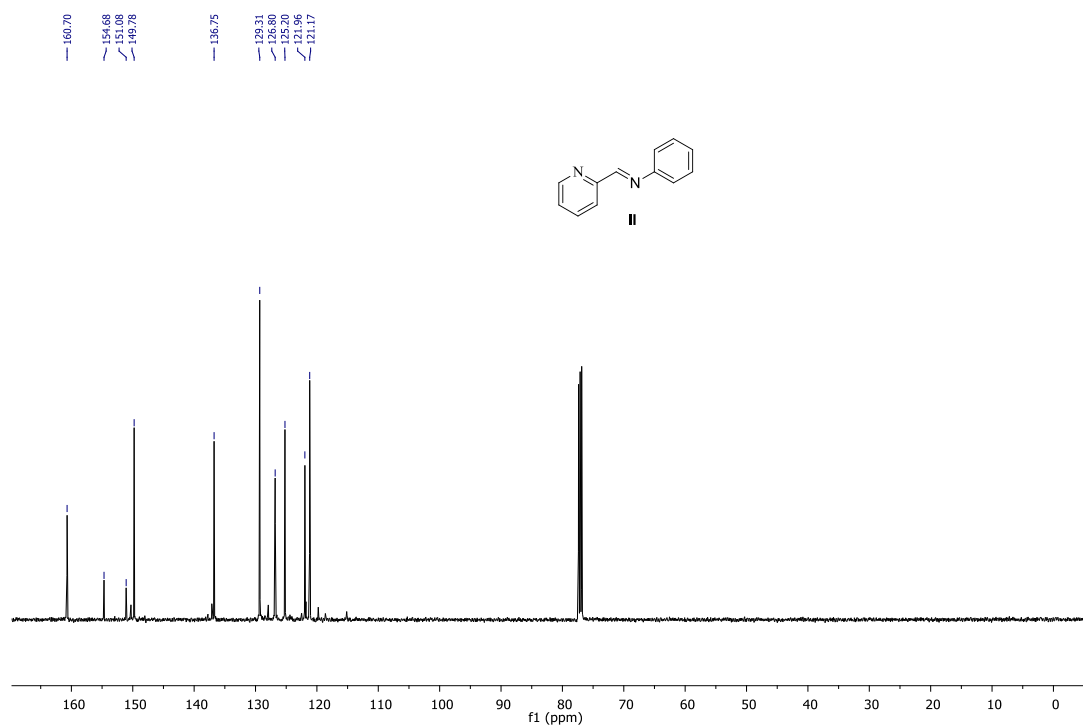
### <sup>13</sup>C NMR of 6-fluoro-2-(pyridin-2-yl)benzo[d]thiazole (4e)



### <sup>1</sup>H NMR of (*E*)-*N*-(Pyridin-2-ylmethylene)aniline Intermediate (II):

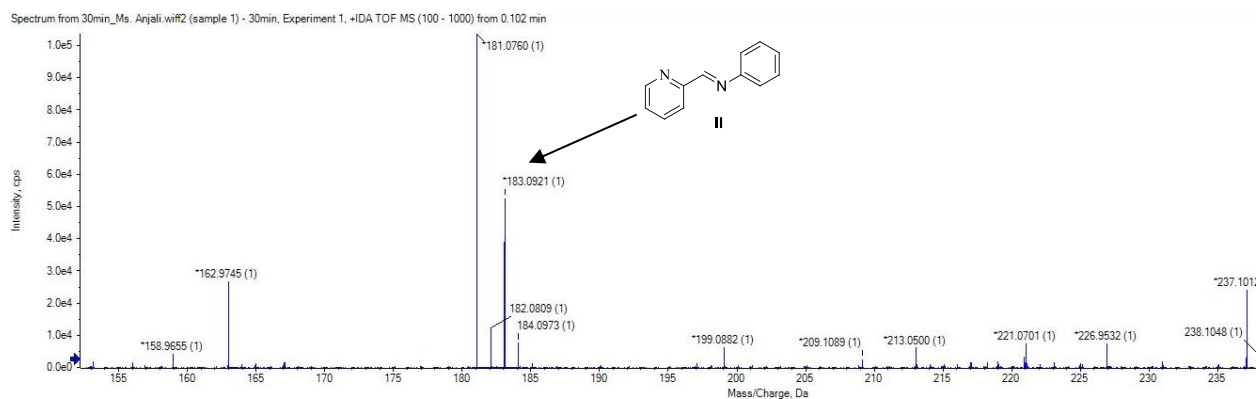


### <sup>13</sup>C NMR of (*E*)-*N*-(Pyridin-2-ylmethylene)aniline Intermediate (II):

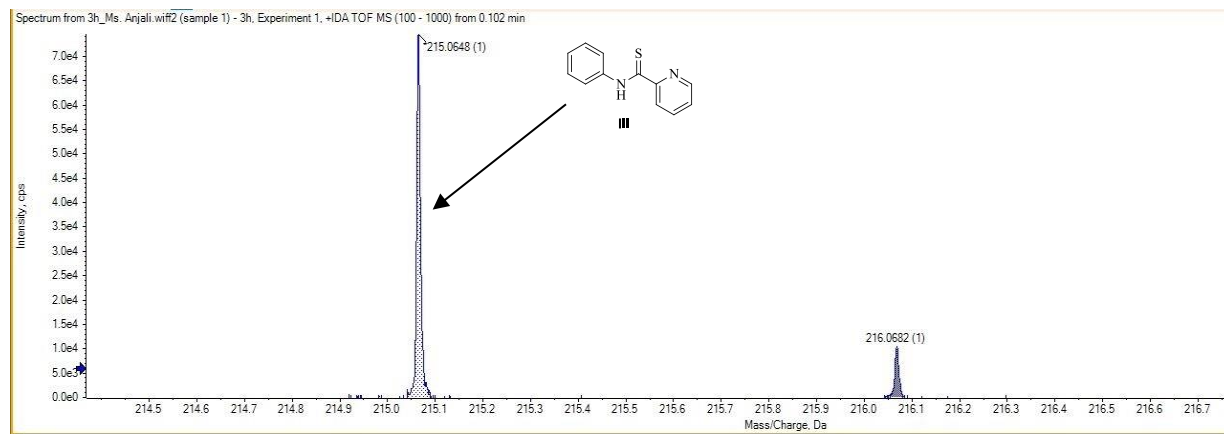


## I. HRMS of Intermediates:

### (E)-N-(Pyridin-2-ylmethylene)aniline Intermediate (II)



### N-Phenylpyridine-2-carbothioamide Intermediate (III)



### N-(pyridin-2-ylmethyl)aniline intermediate (I) (without S<sub>8</sub>)

