

# Supporting Information

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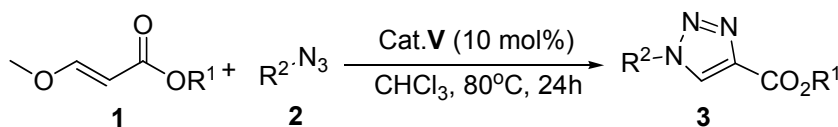
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## A: General Information and Starting Materials.

**General Information.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CDCl}_3$ :  $\delta$  7.26,  $\text{DMSO-}d_6$ :  $\delta$  2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.16,  $\text{DMSO-}d_6$ :  $\delta$  39.52). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

**Starting Materials.** All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. The azides were prepared following the literature procedures.<sup>(1)</sup>

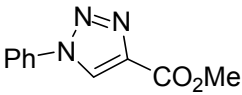
## B: General Procedure for 1,3-Dipolar Cycloadditions of $\alpha,\beta$ -Unsaturated Esters with Azides.



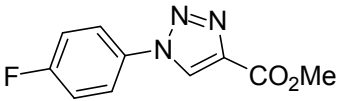
To a solution of  $\text{CHCl}_3$  (0.3 mL) were added  $\alpha,\beta$ -unsaturated esters **1** (0.10 mmol), azides **2** (0.20 mmol) and catalyst **V** (0.01 mmol). The reaction mixture was stirred at  $80^\circ\text{C}$  for 24h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

## C: Characterization Data.

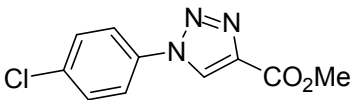
### Methyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (3aa)

 Yellow oil, 90% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.55 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.60-7.57 (m, 2H), 7.53-7.50 (m, 1H), 4.02 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 161.0, 140.5, 136.4, 129.9, 129.6, 125.6, 120.8, 52.3. HRMS (EI): exact mass calculated for M(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>) requires *m/z* 203.0695, found *m/z* 203.0692.

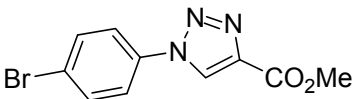
### Methyl 1-(4-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ab)

 Yellow solid, 87% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.50 (s, 1H), 7.78-7.75 (m, 2H), 7.30-7.28 (m, 2H), 4.02 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 162.9 (d, *J* = 1000.0 Hz), 160.9, 140.7, 132.6, 125.7, 122.9 (d, *J* = 36.0 Hz), 117.1 (d, *J* = 92.0 Hz), 52.4. HRMS (EI): exact mass calculated for M(C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>F) requires *m/z* 221.0601, found *m/z* 221.0603.

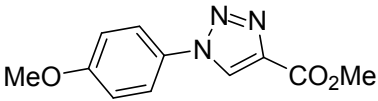
### Methyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ac)

 Yellow solid, 91% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.53 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 4.02 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 160.8, 140.7, 135.5, 134.8, 130.2, 125.4, 122.0, 52.4. HRMS (EI): exact mass calculated for M(C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>Cl) requires *m/z* 237.0305, found *m/z* 237.0303.

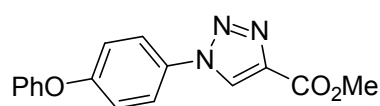
### Methyl 1-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (3ad)

 Yellow solid, 93% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.54 (s, 1H), 7.72-7.67 (m, 4H), 4.01 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 160.8, 140.8, 135.3, 133.1, 125.4, 123.4, 122.2, 52.4. HRMS (EI): exact mass calculated for M(C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>Br) requires *m/z* 280.9800, found *m/z* 280.9801.

### Methyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (3ae)

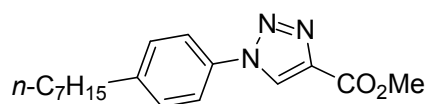
 Yellow solid, 89% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.45 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 4.00 (s, 3H), 3.89 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 161.1, 160.4, 140.3, 129.7, 125.6, 122.4, 114.9, 55.7, 52.3. HRMS (EI): exact mass calculated for M(C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>) requires *m/z* 233.0800, found *m/z* 233.0796.

### Methyl 1-(4-phenoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (3af)



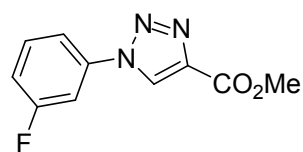
Yellow oil, 92% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.49 (s, 1H), 7.71 (d,  $J = 8.5$  Hz, 2H), 7.42 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.5$  Hz, 1H), 7.16 (d,  $J = 8.5$  Hz, 2H), 7.09 (d,  $J = 8.5$  Hz, 2H), 4.01 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 161.0, 158.6, 156.0, 140.5, 131.3, 130.1, 125.6, 124.4, 122.6, 119.6, 119.2, 52.3. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3)$  requires  $m/z$  295.0957, found  $m/z$  295.0959.

### Methyl 1-(4-heptylphenyl)-1H-1,2,3-triazole-4-carboxylate (3ag)



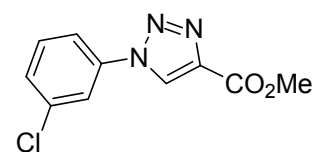
Yellow oil, 88% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.50 (s, 1H), 7.66 (d,  $J = 8.5$  Hz, 2H), 7.36 (d,  $J = 8.5$  Hz, 2H), 4.00 (s, 3H), 2.70-2.67 (m, 2H), 1.66-1.63 (m, 2H), 1.34-1.29 (m, 8H), 0.90-0.88 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 161.1, 144.8, 140.4, 134.1, 129.8, 125.5, 120.7, 52.3, 35.5, 31.7, 31.2, 29.1, 22.6, 14.0. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_2)$  requires  $m/z$  301.1790, found  $m/z$  301.1793.

### Methyl 1-(3-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ah)



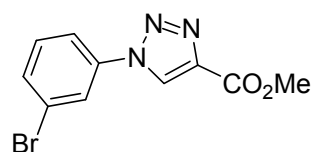
Yellow oil, 85% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.55 (s, 1H), 7.61-7.54 (m, 3H), 7.25-7.22 (m, 1H), 4.03 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 163.1 (d,  $J = 1000.0$  Hz), 160.8, 140.8, 131.5 (d,  $J = 35.5$  Hz), 125.5, 116.7, 116.5, 116.1 (d,  $J = 13.5$  Hz), 108.7 (d,  $J = 105.0$  Hz), 52.4. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2\text{F})$  requires  $m/z$  221.0601, found  $m/z$  221.0606.

### Methyl 1-(3-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ai)



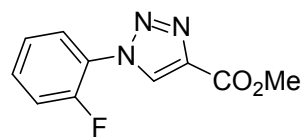
Yellow solid, 94% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.57 (s, 1H), 7.84 (s, 1H), 7.69-7.68 (m, 1H), 7.53-7.47 (m, 2H), 4.01 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.8, 140.7, 137.1, 135.8, 131.0, 129.6, 125.5, 121.1, 118.7, 52.4. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2\text{Cl})$  requires  $m/z$  237.0305, found  $m/z$  237.0303.

### Methyl 1-(3-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (3aj)



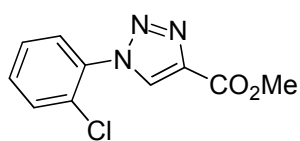
Yellow oil, 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.57 (s, 1H), 7.99 (s, 1H), 7.74 (d,  $J = 8.5$  Hz, 1H), 7.64 (d,  $J = 8.5$  Hz, 1H), 7.45 (t,  $J = 8.5$  Hz, 1H), 4.01 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.8, 140.7, 137.2, 132.6, 131.2, 125.5, 123.9, 123.5, 119.2, 52.4. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2\text{Br})$  requires  $m/z$  280.9800, found  $m/z$  280.9799.

### Methyl 1-(2-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ak)



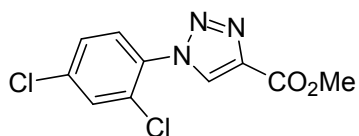
Yellow solid, 82% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.63 (s, 1H), 8.03-7.99 (m, 1H), 7.53-7.49 (m, 1H), 7.39-7.33 (m, 2H), 4.02 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.9, 153.3 (d,  $J = 1000.0$  Hz), 140.4, 131.0 (d,  $J = 36.5$  Hz), 128.6 (d,  $J = 34.0$  Hz), 125.4 (d,  $J = 14.5$  Hz), 124.9, 117.2 (d,  $J = 79.5$  Hz), 52.3. HRMS (EI): exact mass calculated for M ( $\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2\text{F}$ ) requires  $m/z$  221.0601, found  $m/z$  221.0609.

### Methyl 1-(2-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3al)



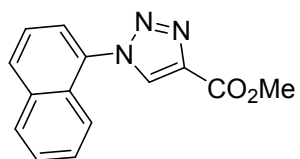
Yellow solid, 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.54 (s, 1H), 7.66-7.60 (m, 2H), 7.53-7.47 (m, 2H), 4.00 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.9, 139.8, 134.1, 131.4, 130.9, 129.5, 128.5, 128.1, 127.7, 52.3. HRMS (EI): exact mass calculated for M ( $\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2\text{Cl}$ ) requires  $m/z$  237.0305, found  $m/z$  237.0298.

### Methyl 1-(2,4-dichlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3am)



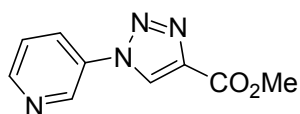
Yellow oil, 87% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.53 (s, 1H), 7.63-7.61 (m, 2H), 7.49-7.47 (m, 1H), 4.00 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.7, 140.0, 137.0, 132.7, 130.7, 129.4, 129.3, 128.5, 128.4, 52.4. HRMS (EI): exact mass calculated for M ( $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_2\text{Cl}_2$ ) requires  $m/z$  270.9915, found  $m/z$  270.9907.

### Methyl 1-(naphthalen-1-yl)-1H-1,2,3-triazole-4-carboxylate (3an)



Yellow solid, 85% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.49 (s, 1H), 8.10-8.08 (m, 1H), 8.02-8.00 (m, 1H), 7.65-7.61 (m, 3H), 7.60-7.58 (m, 2H), 4.06 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 161.1, 140.0, 134.1, 132.8, 131.0, 130.0, 128.4, 128.3, 127.3, 124.9, 123.7, 121.8, 52.4. HRMS (EI): exact mass calculated for M ( $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$ ) requires  $m/z$  253.0851, found  $m/z$  253.0846.

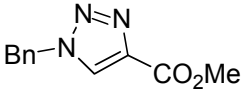
### Methyl 1-(pyridin-3-yl)-1H-1,2,3-triazole-4-carboxylate (3ao)



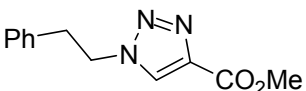
Yellow oil, 88% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 9.07-9.06 (m, 1H), 8.79-8.78 (m, 1H), 8.63 (s, 1H), 8.21-8.19 (m, 1H), 7.58-7.56 (m, 1H), 4.03 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 160.7, 150.8, 141.8, 141.1, 133.1, 128.5, 125.5,

124.4, 52.5. HRMS (EI): exact mass calculated for M (C<sub>9</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>) requires m/z 204.0647, found m/z 204.0650.

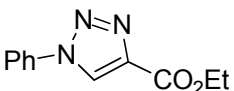
### Methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (3ap)

 Yellow solid, 87% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.01 (s, 1H), 7.39-7.38 (m, 3H), 7.30-7.28 (m, 2H), 5.58 (s, 2H), 3.91 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 161.1, 140.3, 133.7, 129.3, 129.1, 128.3, 127.4, 54.5, 52.2. HRMS (EI): exact mass calculated for M (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>) requires m/z 217.0851, found m/z 217.0846.

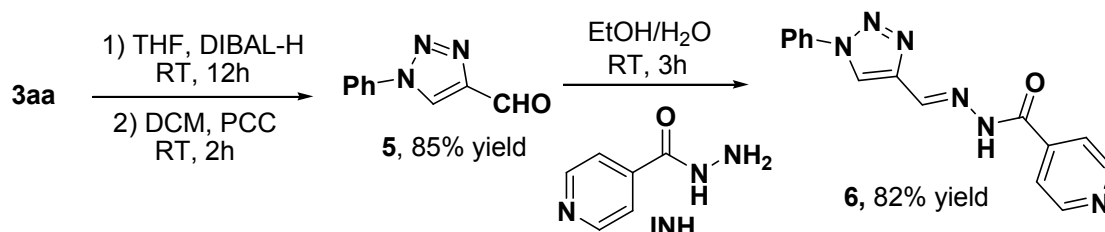
### Methyl 1-phenethyl-1H-1,2,3-triazole-4-carboxylate (3aq)

 Yellow solid, 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.80 (s, 1H), 7.33-7.28 (m, 3H), 7.11-7.09 (m, 2H), 4.67 (t, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 3.26 (t, *J* = 7.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 161.1, 139.7, 136.4, 128.9, 128.6, 127.7, 127.4, 52.1, 52.0, 36.5. HRMS (EI): exact mass calculated for M (C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>) requires m/z 231.1008, found m/z 231.1006.

### Ethyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ba)

 Yellow solid, 92% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.54 (s, 1H), 7.77-7.76 (m, 2H), 7.57-7.54 (m, 2H), 7.51-7.48 (m, 1H), 4.47 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 160.6, 140.8, 136.4, 129.9, 129.5, 125.5, 120.8, 61.5, 14.3. HRMS (EI): exact mass calculated for M (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>) requires m/z 217.0851, found m/z 217.0848.

## D: Synthetic Transformations.



**Scheme 1: Synthesis of Isonicotinoyl Hydrazide 6.**

To a solution of **3aa** (0.10 mmol) in dry THF was added DIBAL-H (0.2 mmol, 1.0 M in cyclohexane) in one portion. The reaction mixture was stirred at room temperature for 12h. Then the reaction was quenched by water (3.0 mL) and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x5.0 mL). The organic phase was dried with dry Na<sub>2</sub>SO<sub>4</sub> and reduced in vacuum to yield the alcohol intermediate. To a solution of alcohol intermediate in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was added PCC (1.5 eq.) in one portion. The reaction mixture was stirred at room temperature for 2h. Then the reaction solution was reduced in vacuum to yield a residue, which was purified by silica gel to yield the desired product **5** in 85% yield (two steps).

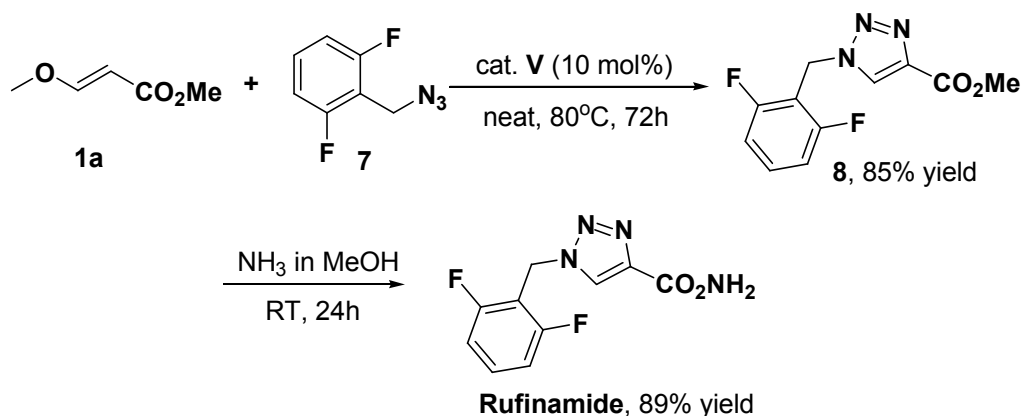
To a solution of **5** (0.10 mmol) in ethanol (1.0 mL) was added the solution of INH (0.10 mmol) in H<sub>2</sub>O (1.0 mL). After stirring for 3h at room temperature, the resulting mixture was concentrated under reduced pressure to give a residue, which was purified by washing with cold ethanol and ethyl ether to yield the desired product **6** in 82% yield.

### 1-Phenyl-1H-1,2,3-triazole-4-carbaldehyde (**5**)

Yellow oil, 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 10.26 (s, 1H), 8.55 (s, 1H), 7.81-7.79 (m, 2H), 7.63-7.60 (m, 2H), 7.57-7.54 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 185.1, 148.2, 136.2, 130.1, 129.8, 123.1, 120.9. HRMS (EI): exact mass calculated for M<sup>+</sup> (C<sub>9</sub>H<sub>8</sub>N<sub>3</sub>O) requires m/z 174.0667, found m/z 174.0659.

### (E)-N'-((1-phenyl-1H-1,2,3-triazol-4-yl)methylene)isonicotinohydrazide (**6**)

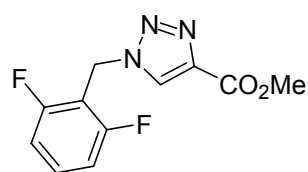
White solid, 82% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ (ppm) 12.17 (s, 1H), 9.35 (s, 1H), 8.82 (d, *J* = 5.0 Hz, 2H), 8.66 (s, 1H), 8.04-8.02 (m, 2H), 7.85 (d, *J* = 5.0 Hz, 2H), 7.65-7.62 (m, 2H), 7.55-7.52 (m, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): δ (ppm) 162.1, 150.8, 144.4, 141.4, 140.8, 136.8, 130.4, 129.5, 122.0, 120.8. HRMS (EI): exact mass calculated for M<sup>+</sup> (C<sub>15</sub>H<sub>11</sub>N<sub>6</sub>O) requires m/z 291.0994, found m/z 291.0996.



### Scheme 2: Synthesis of Rufinamide.

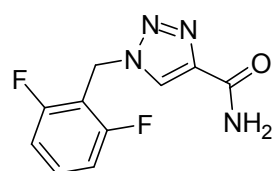
The reaction mixture of  $\alpha,\beta$ -unsaturated ester **1a** (0.10 mmol), azide **7** (0.20 mmol) and catalyst **V** (0.01 mmol) was stirred at 80 °C for 72h. Then the mixture was purified by silica gel chromatography to yield the desired product **8** in 85% yield. To a solution of methanolic  $\text{NH}_3$  (0.5 mL, 3.5 mmol, 7 M) was added **8** (0.10 mmol). The reaction was stirred at room temperature for 18h, then the solvent was removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product rufinamide in 89% yield.

#### Methyl 1-(2,6-difluorobenzyl)-1H-1,2,3-triazole-4-carboxylate (**8**)



White solid, 85% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.12 (s, 1H), 7.45-7.39 (m, 1H), 7.03-7.00 (m, 2H), 5.71 (s, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 161.3 (dd,  $^1J_{\text{CF}} = 1000.0$  Hz,  $^2J_{\text{CF}} = 26.0$  Hz), 161.1, 140.2, 131.9 (t,  $J = 41.0$  Hz), 127.5, 112.0 (dd,  $^1J_{\text{CF}} = 80.0$  Hz,  $^2J_{\text{CF}} = 18.5$  Hz), 110.0 (t,  $J = 73.5$  Hz), 52.2, 41.7. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{11}\text{H}_9\text{N}_3\text{O}_2\text{F}_2)$  requires  $m/z$  253.0663, found  $m/z$  253.0666.

#### Rufinamide

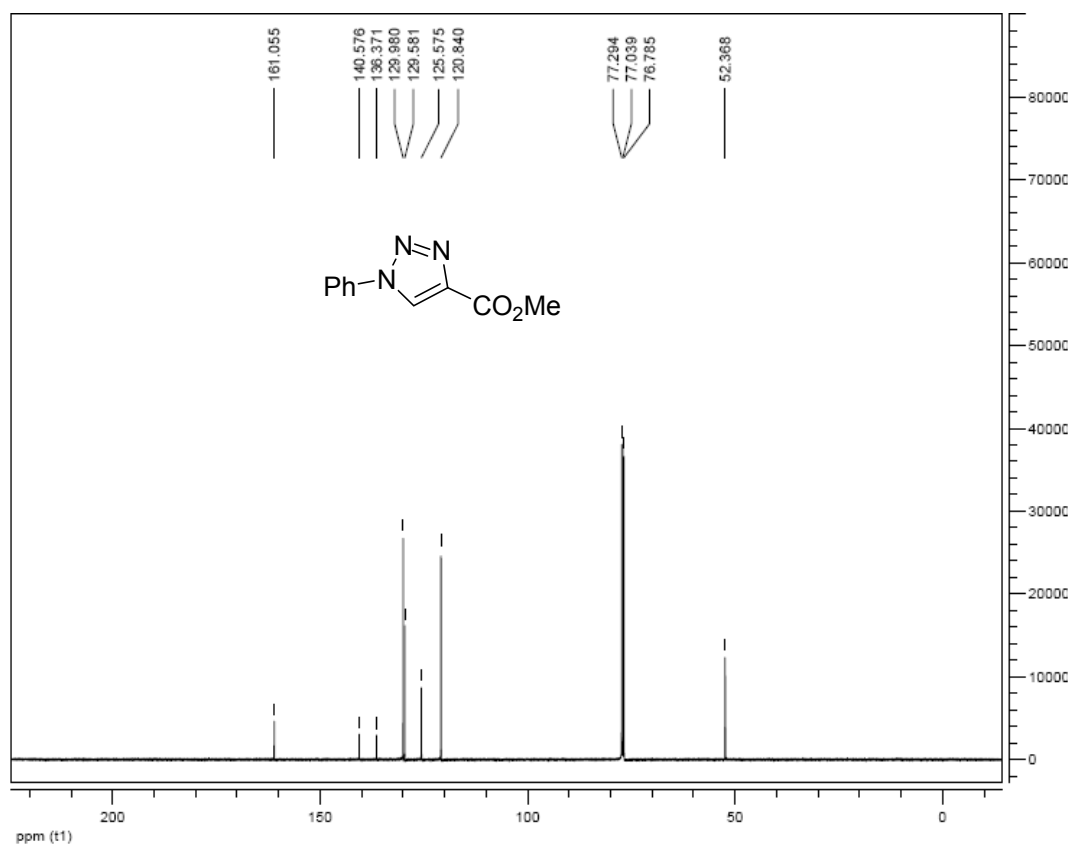
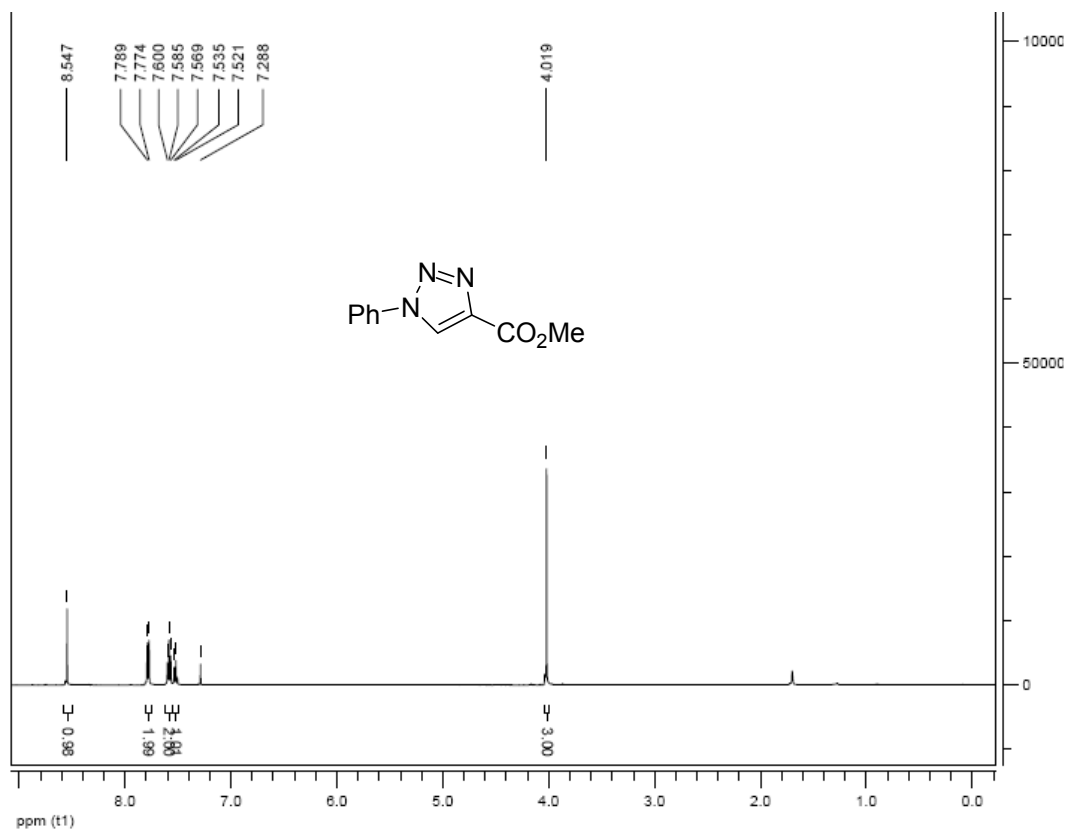


White solid, 89% yield.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz):  $\delta$  (ppm) 8.56 (s, 1H), 7.86 (s, 1H), 7.56-7.49 (m, 2H), 7.21-7.18 (m, 2H), 5.73 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 125 MHz):  $\delta$  (ppm) 161.3 (dd,  $^1J_{\text{CF}} = 991.0$  Hz,  $^2J_{\text{CF}} = 29.0$  Hz), 161.7, 143.3, 132.3 (t,  $J = 41.0$  Hz), 127.2, 112.4 (dd,  $^1J_{\text{CF}} = 80.0$  Hz,  $^2J_{\text{CF}} = 19.5$  Hz), 111.5 (t,  $J = 76.0$  Hz), 41.7. HRMS (EI): exact mass calculated for  $[\text{M}+\text{Na}]$  ( $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_2\text{F}_2\text{Na}$ ) requires  $m/z$  261.0564, found  $m/z$  261.0561.

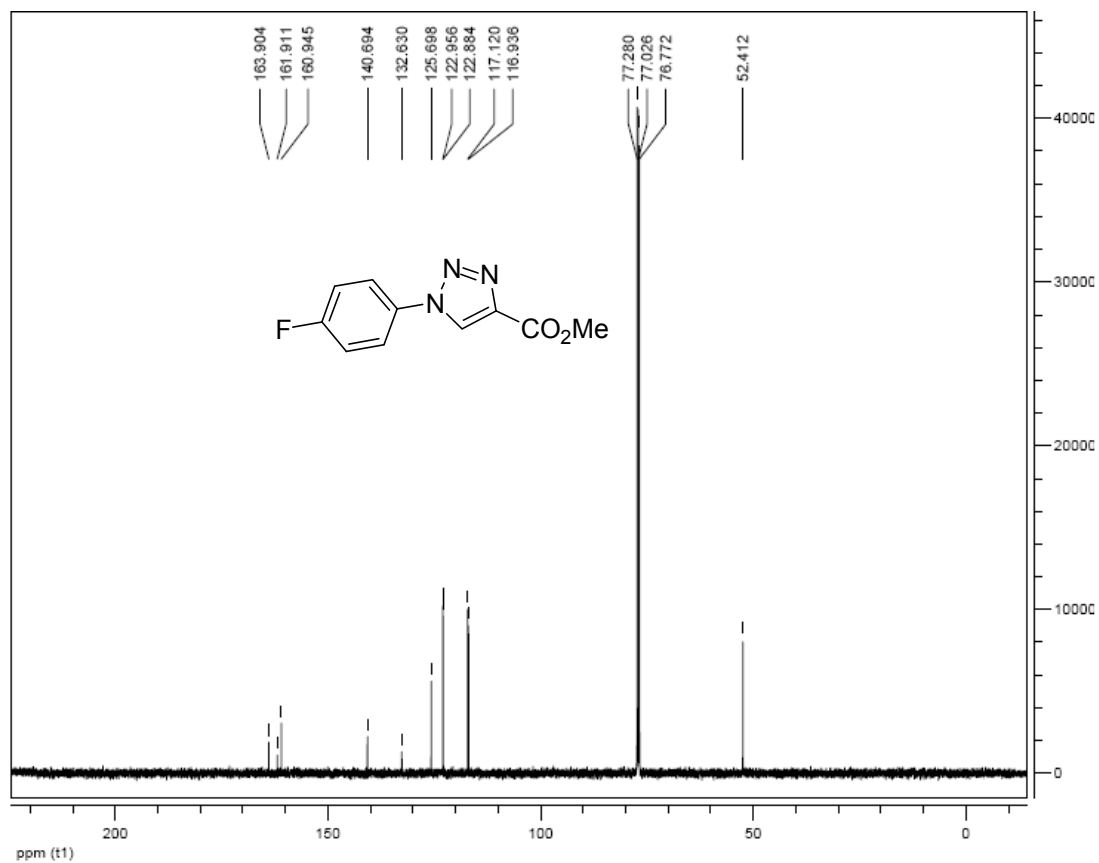
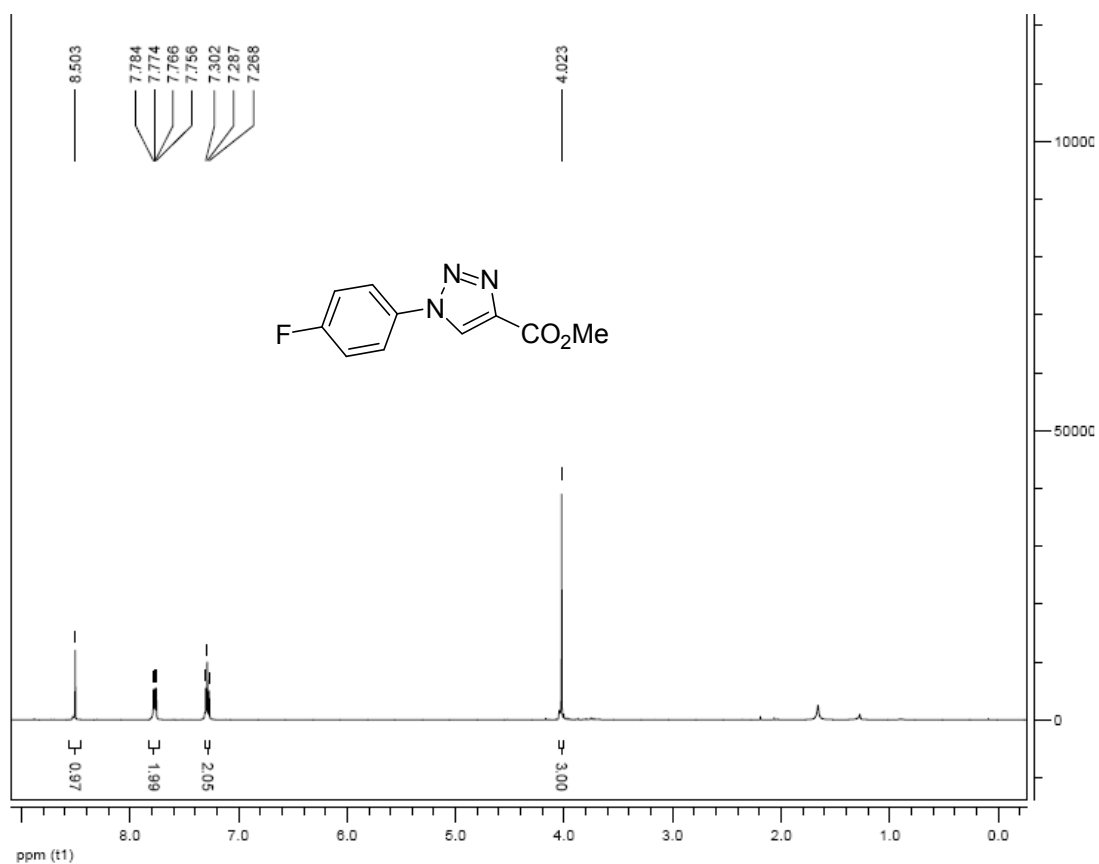


## E: NMR Spectra.

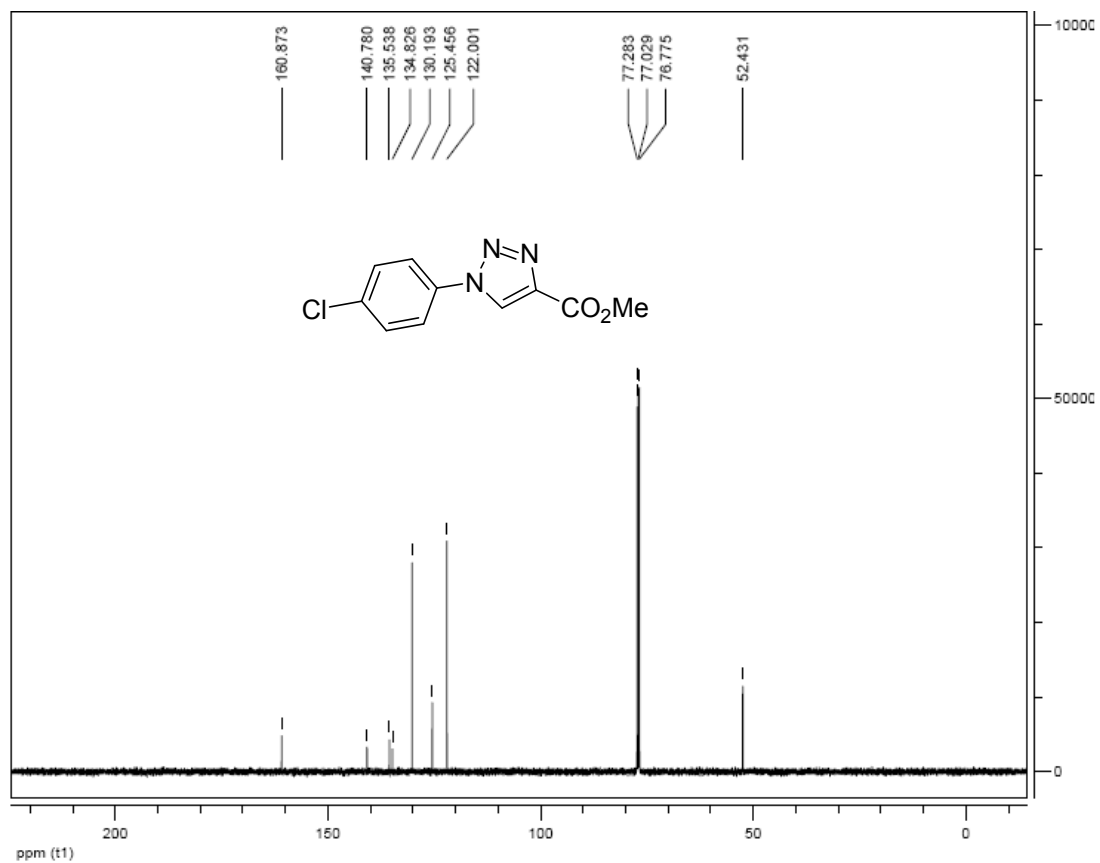
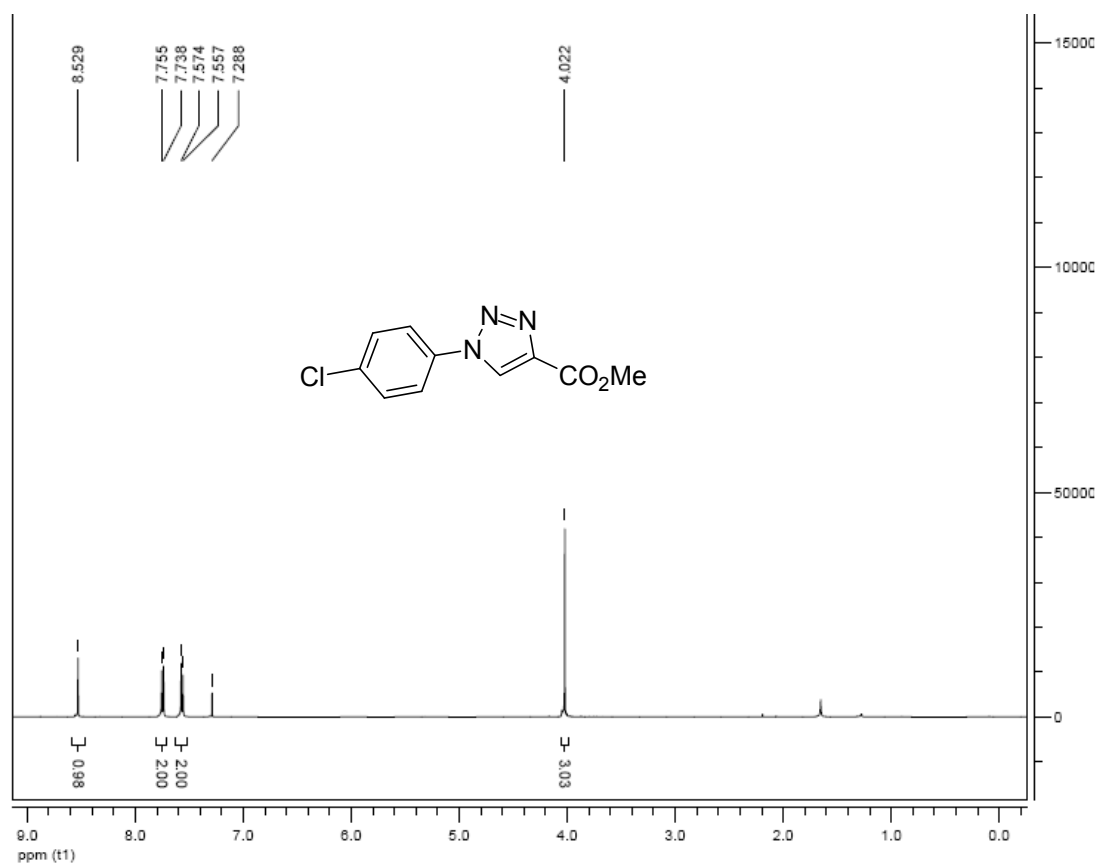
### Methyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (3aa)



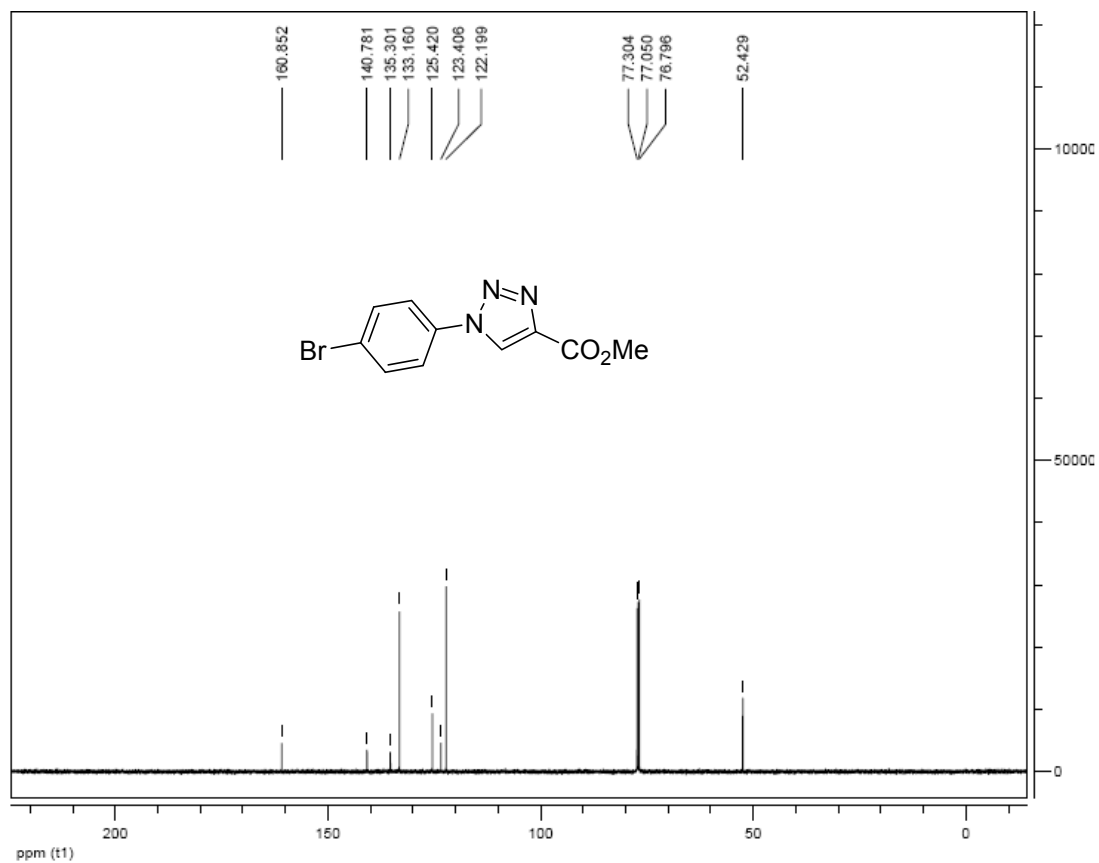
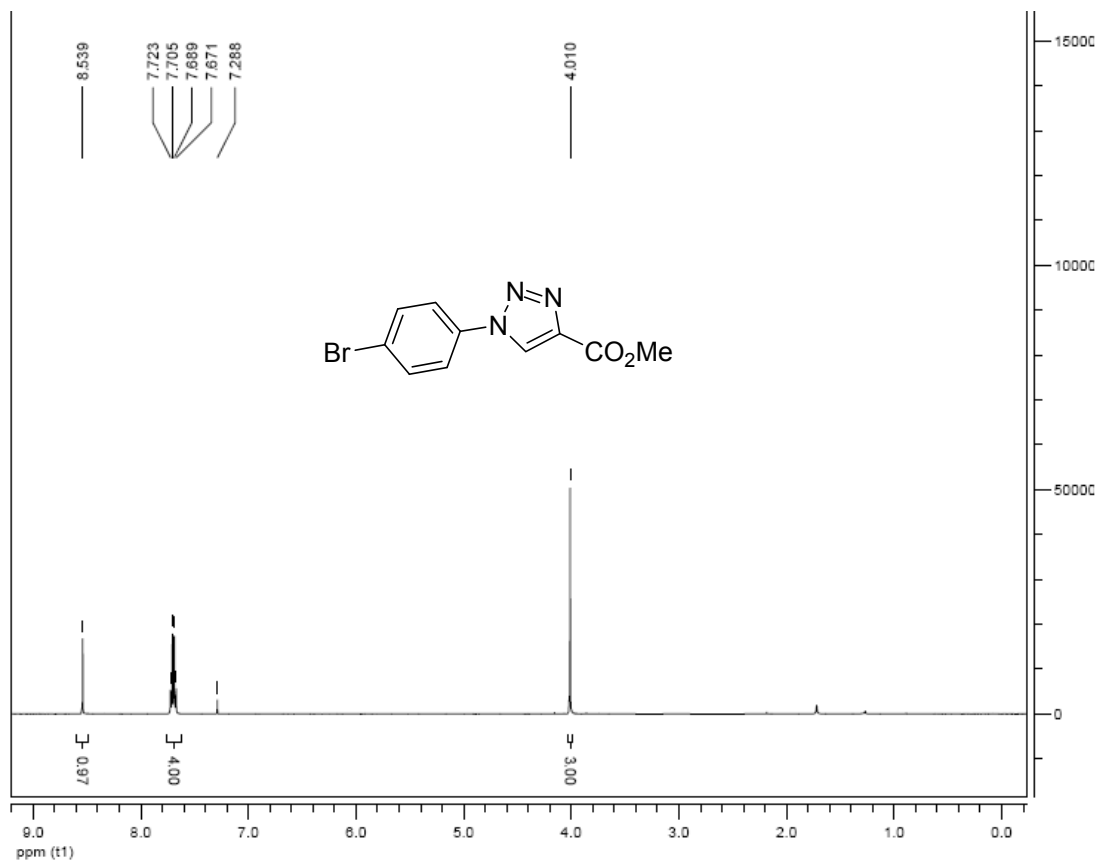
### Methyl 1-(4-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ab)



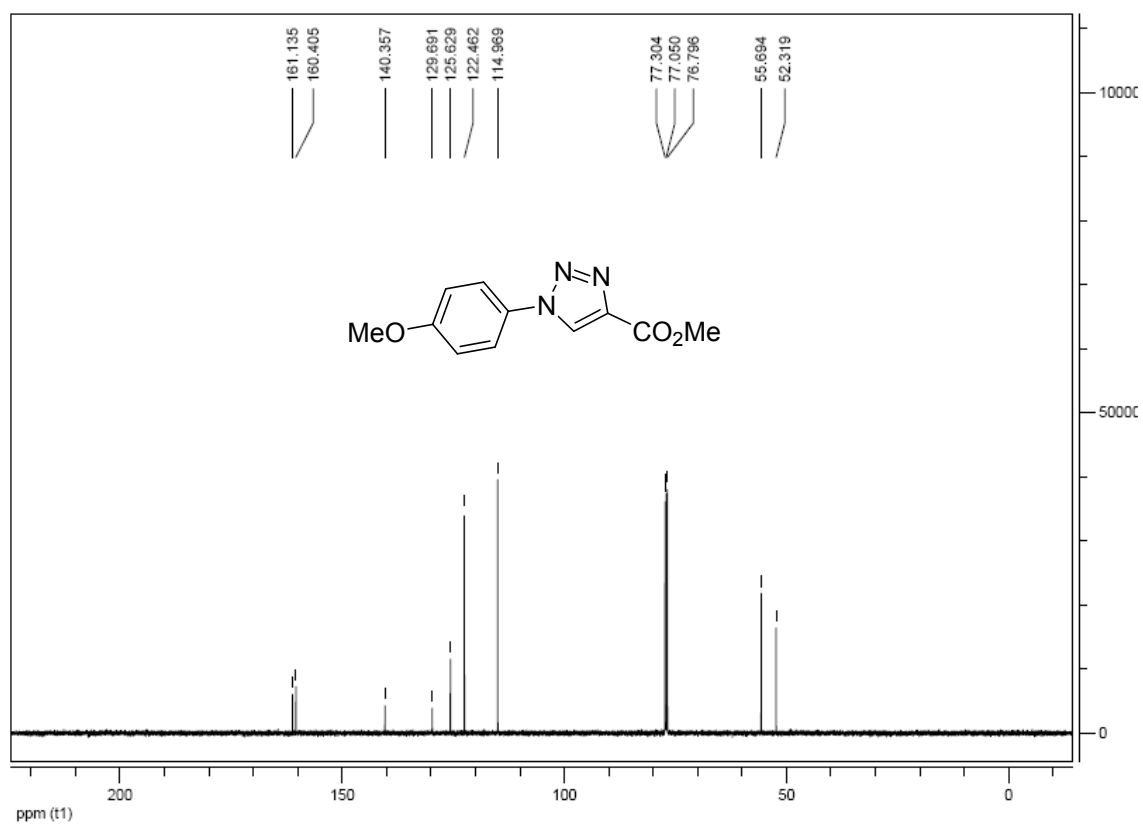
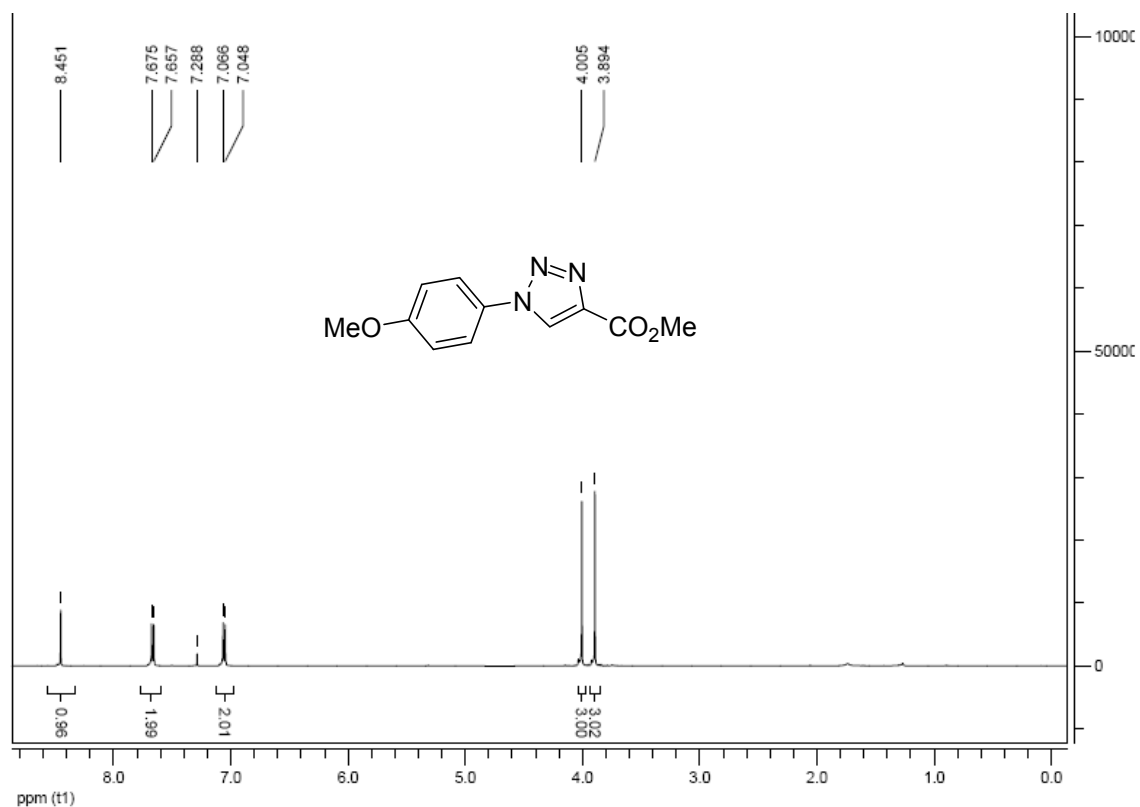
### Methyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ac)



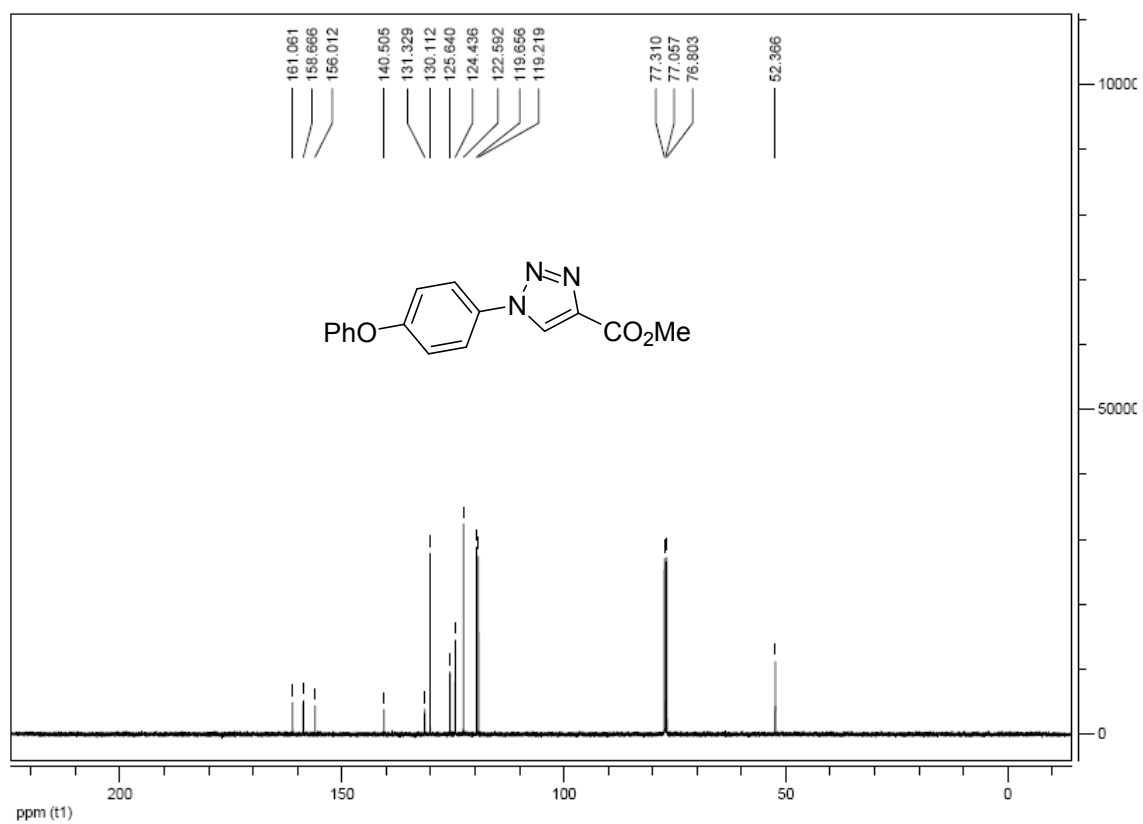
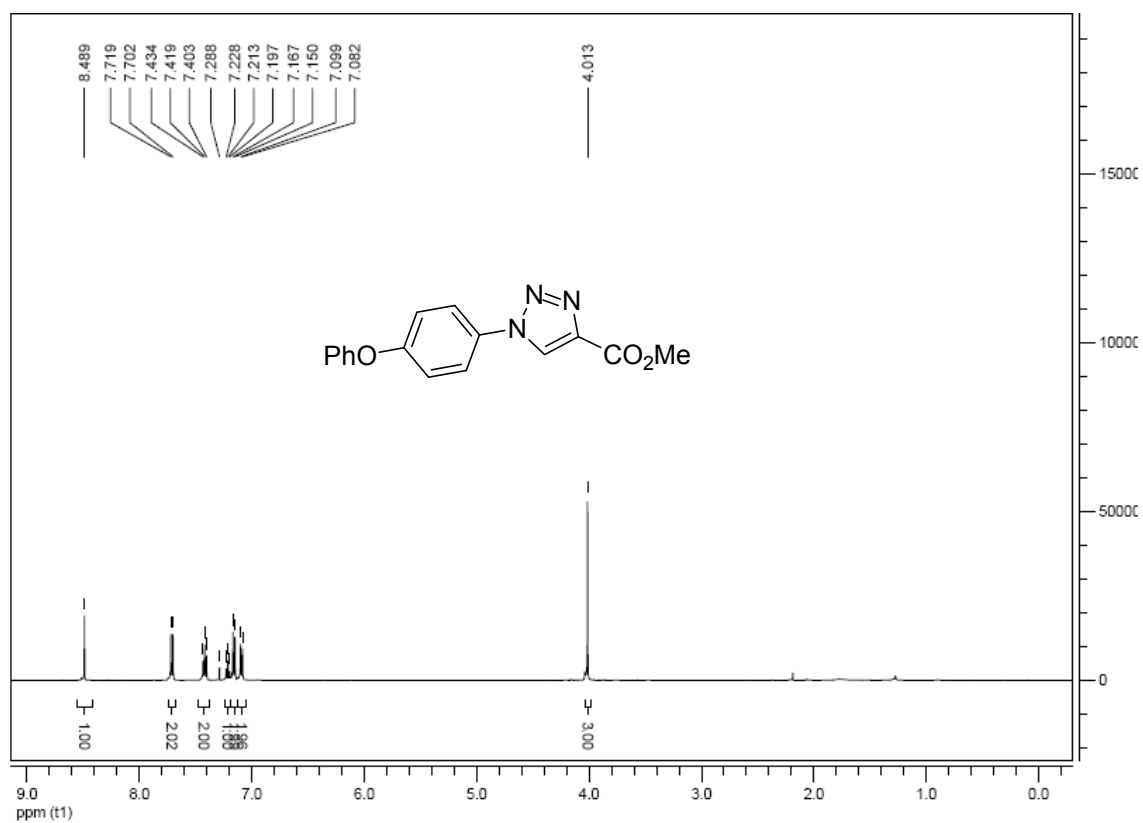
### Methyl 1-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (3ad)



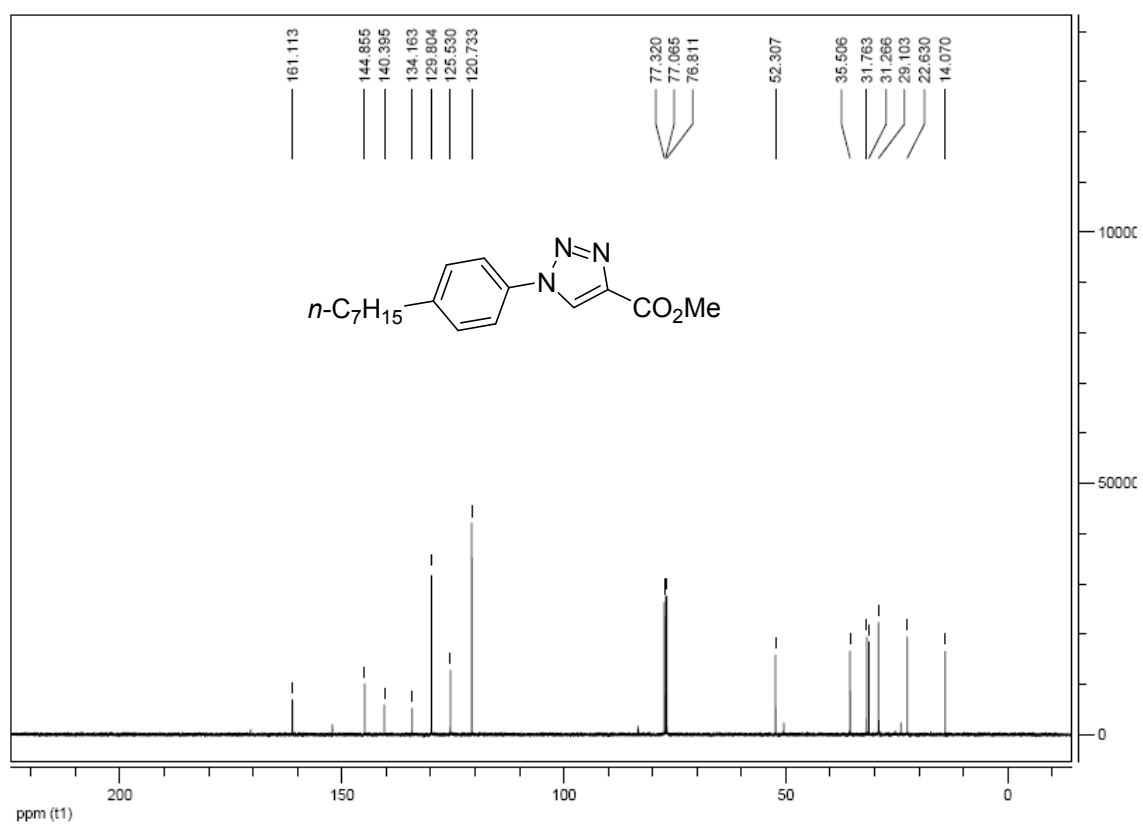
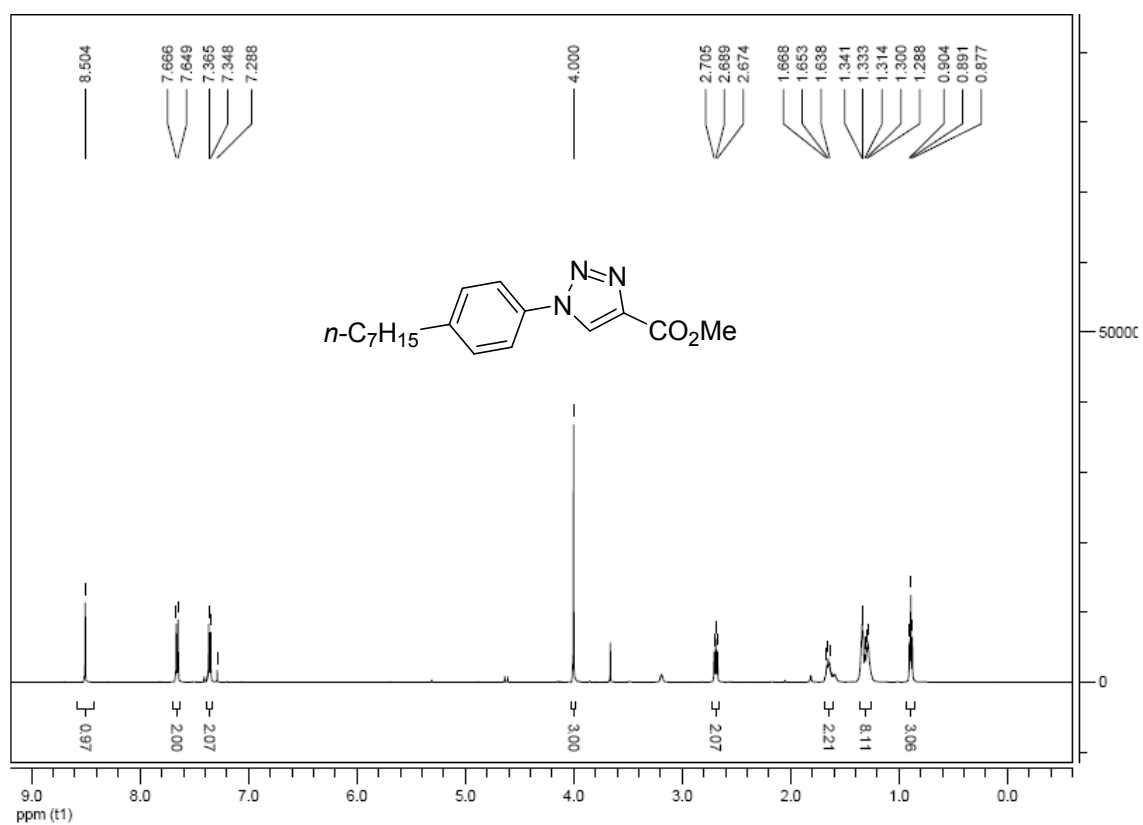
### Methyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (3ae)



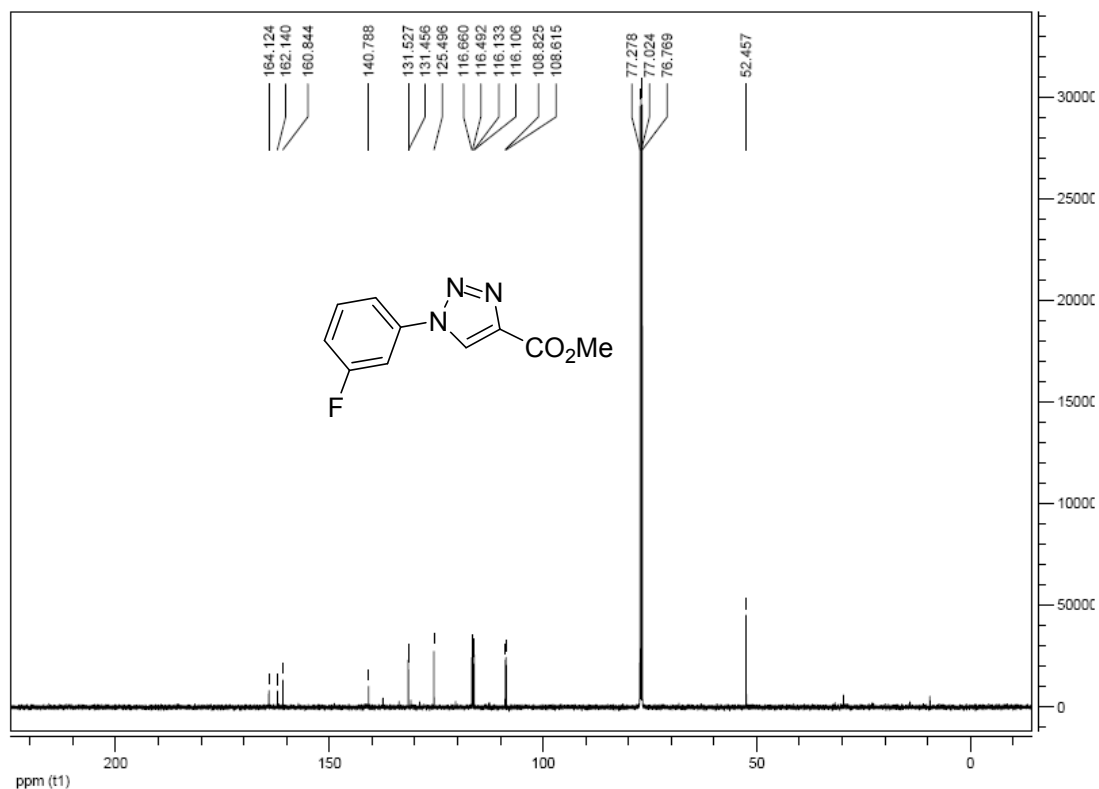
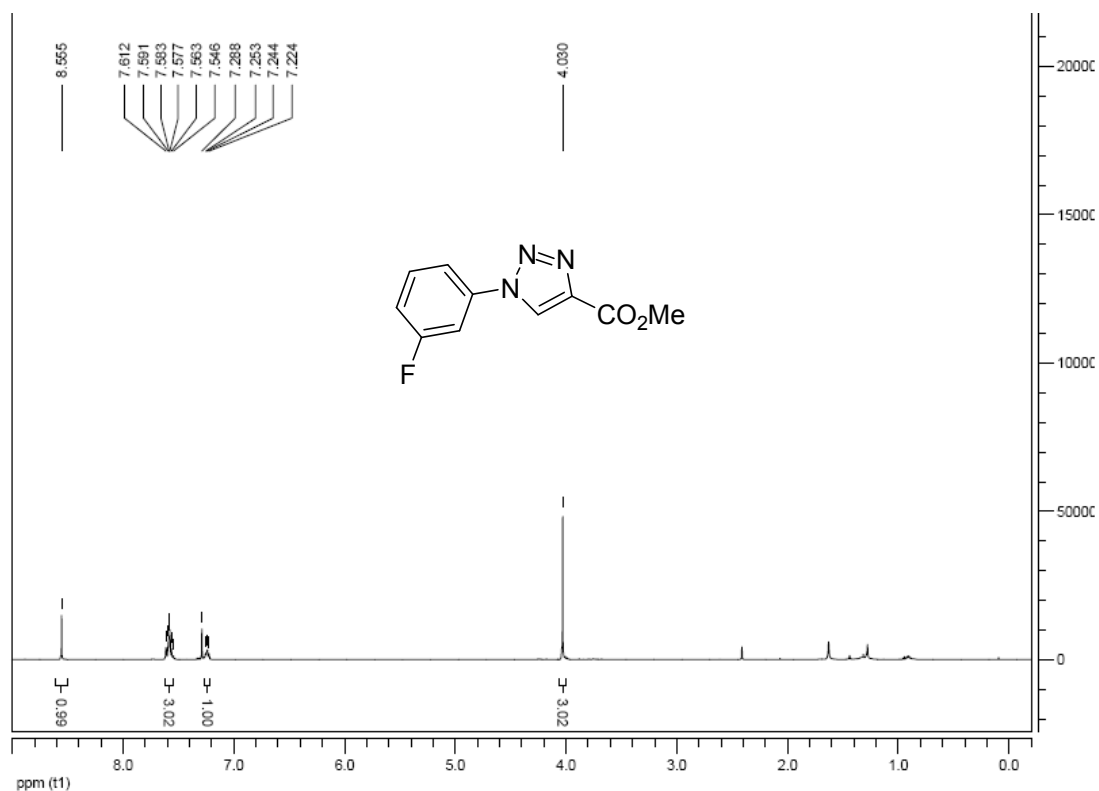
### Methyl 1-(4-phenoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (3af)



**Methyl 1-(4-heptylphenyl)-1H-1,2,3-triazole-4-carboxylate (3ag)**

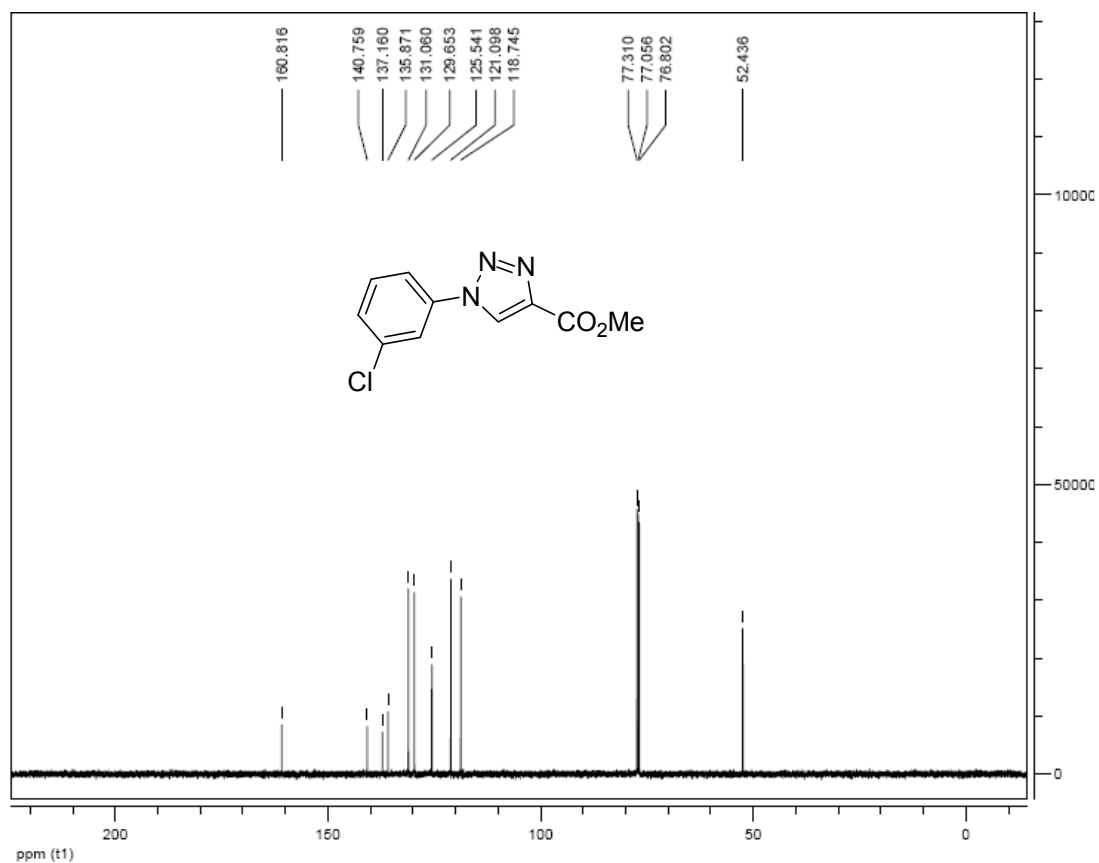
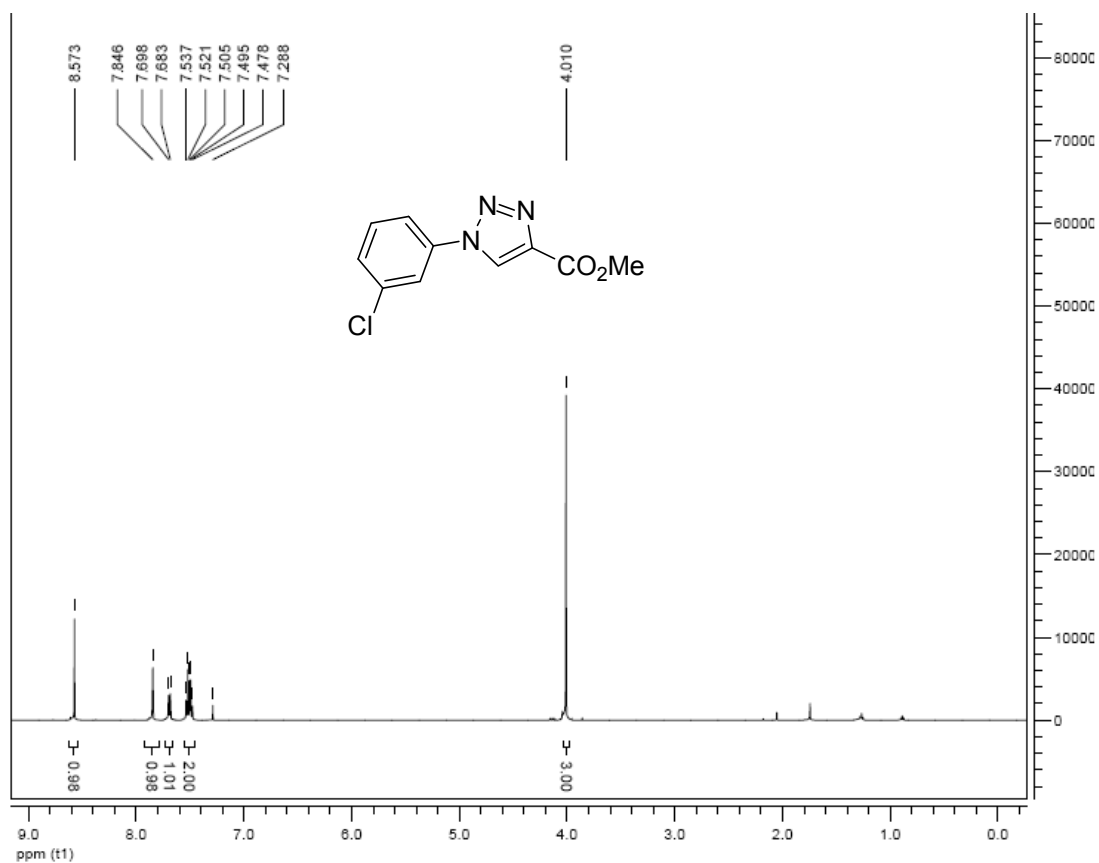


# Methyl 1-(3-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ah)

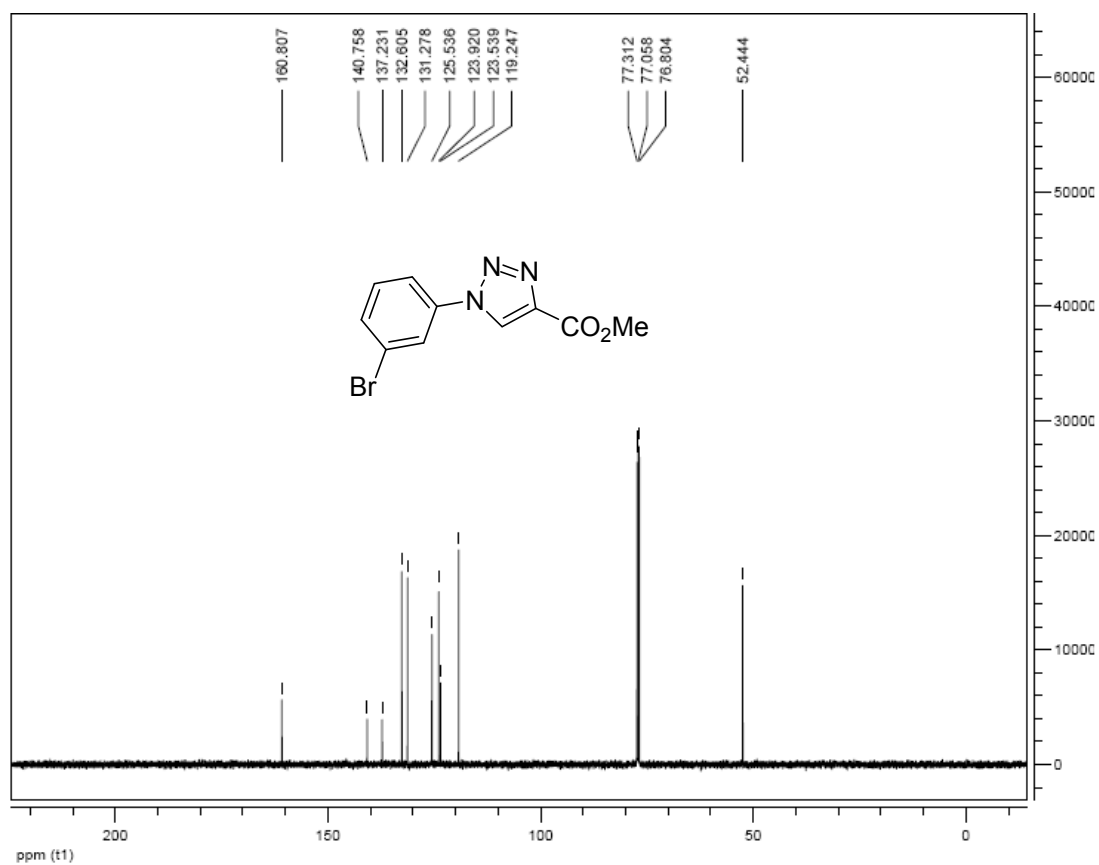
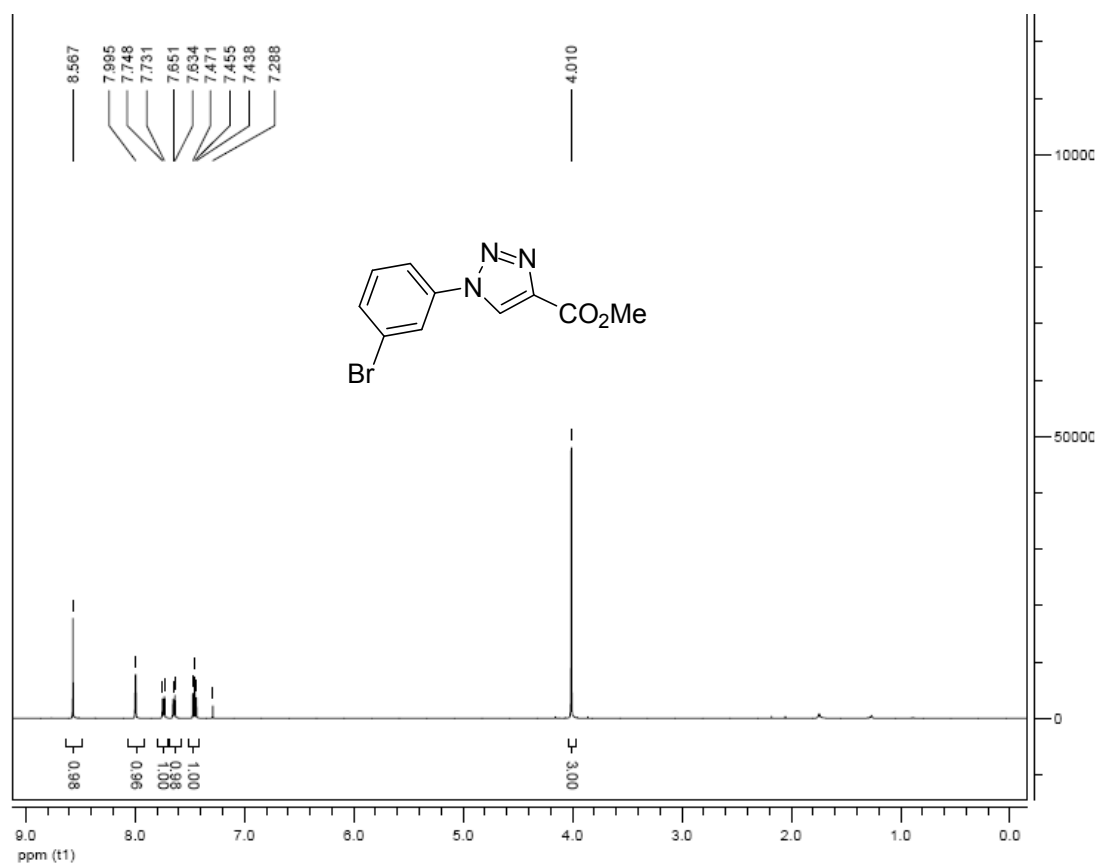




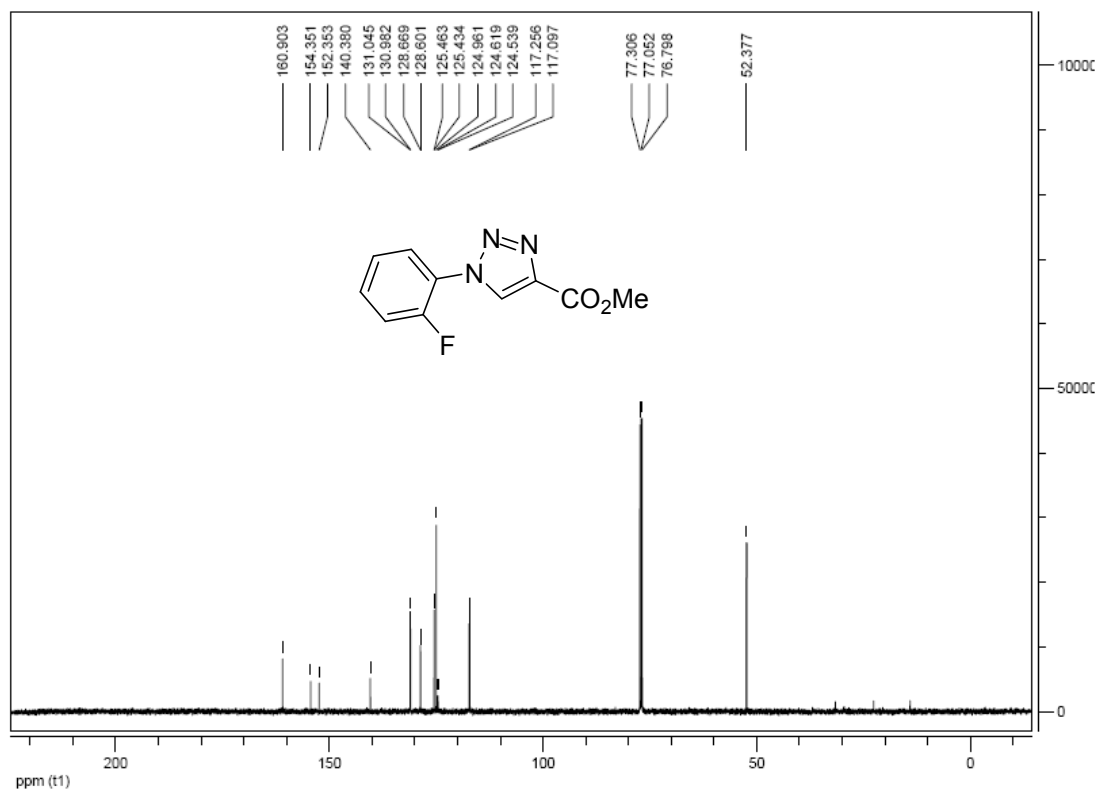
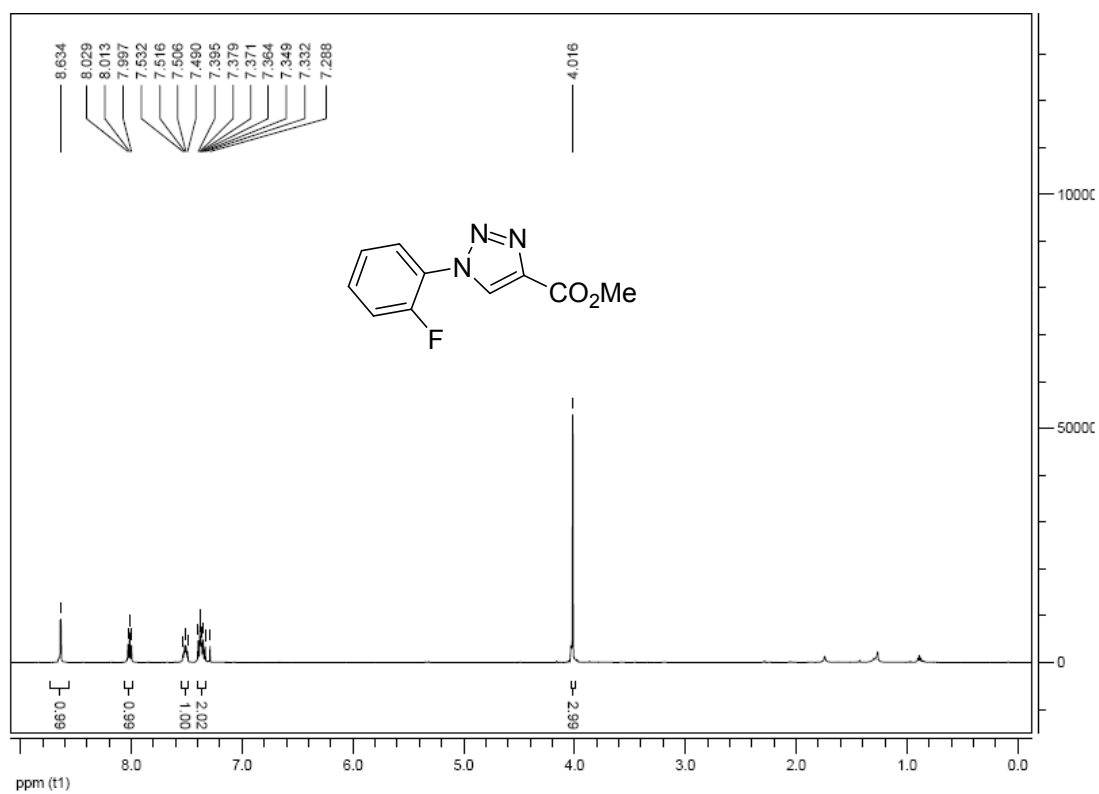
### Methyl 1-(3-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ai)



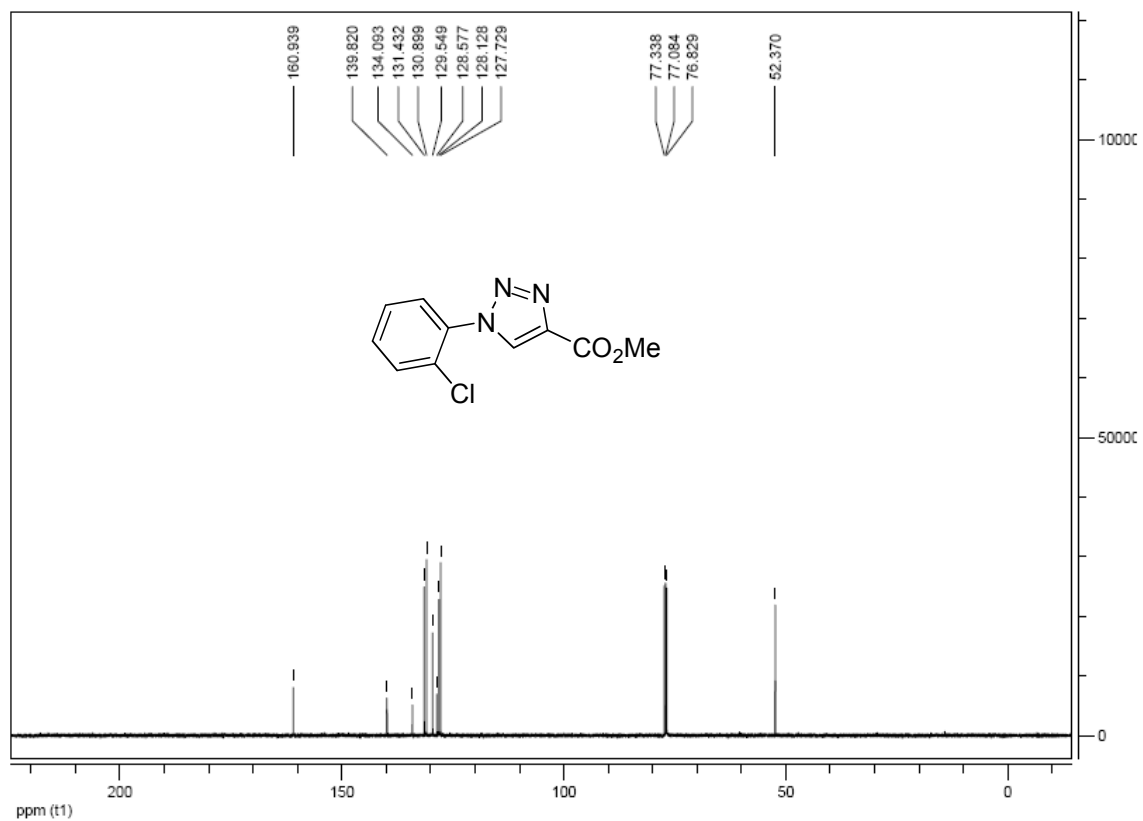
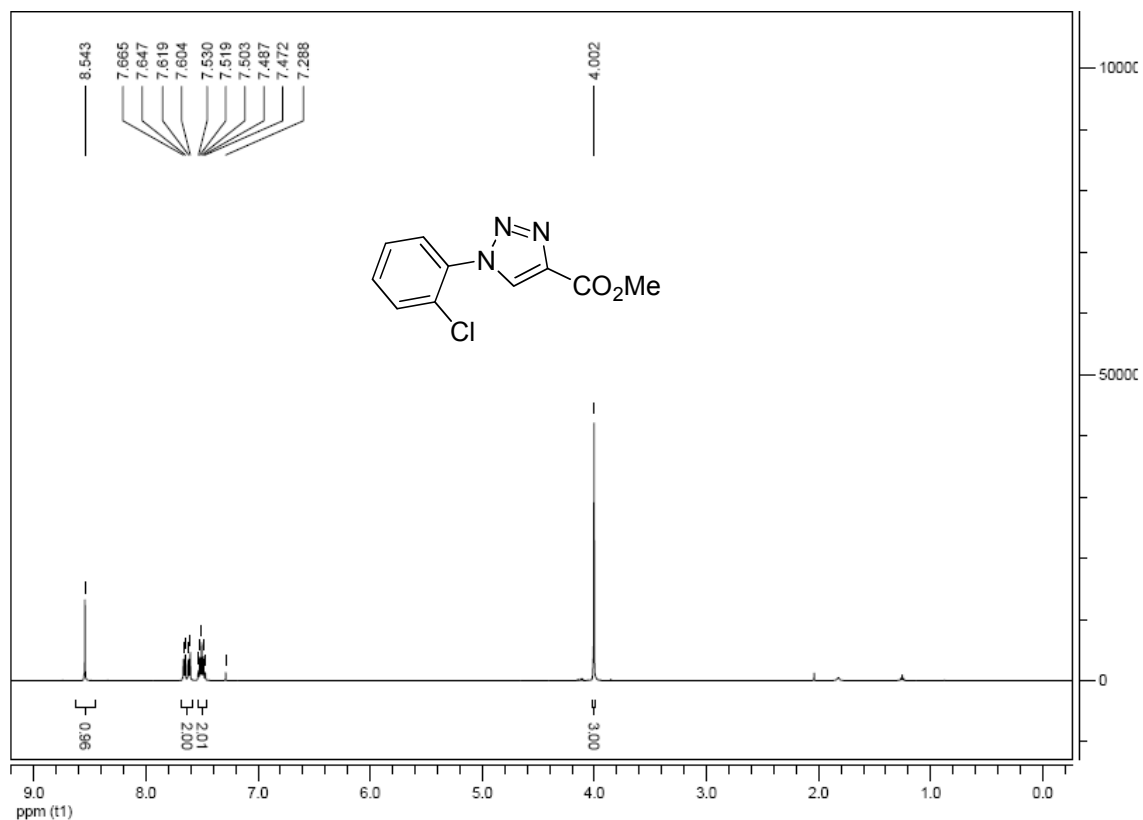
### Methyl 1-(3-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (3aj)



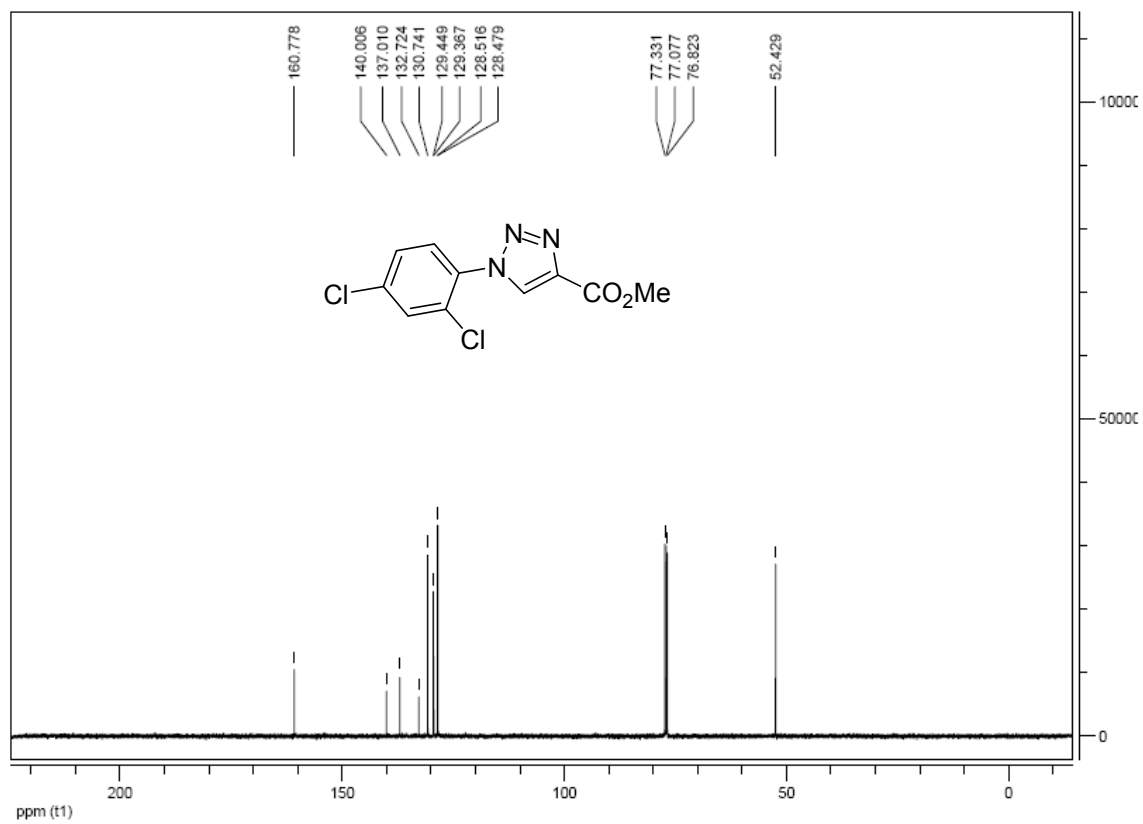
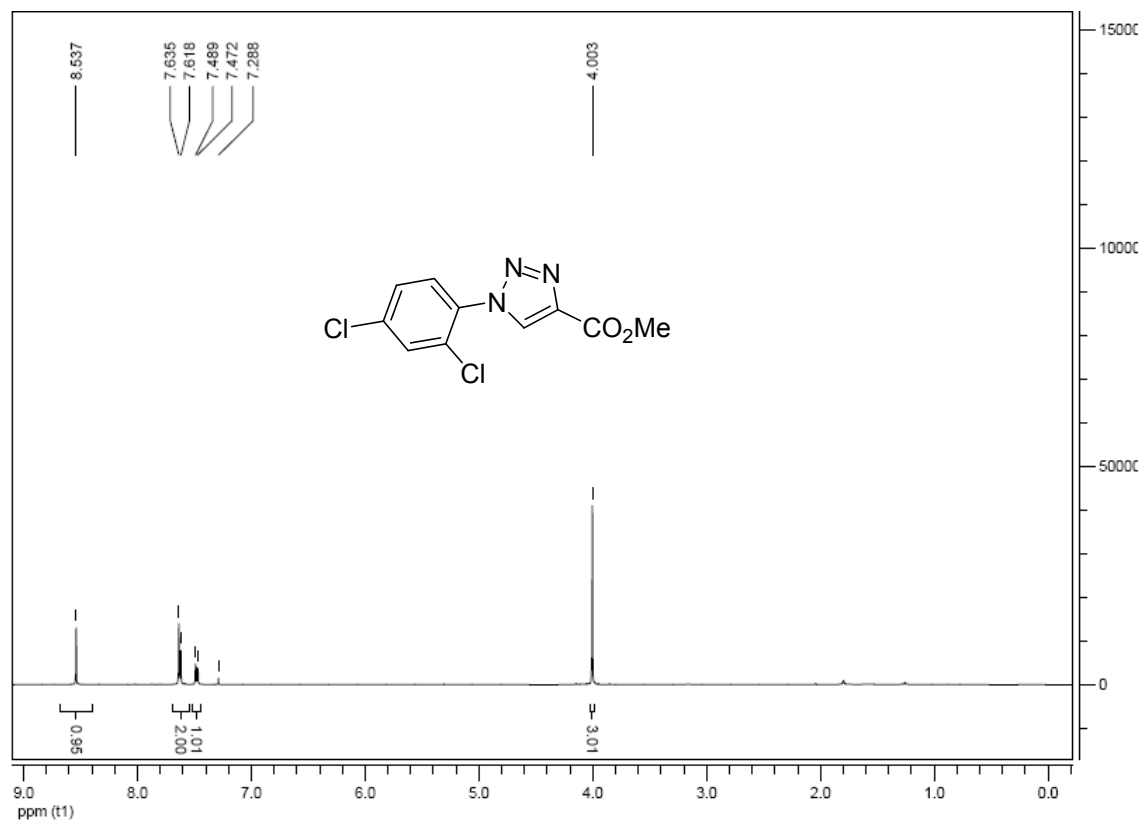
### Methyl 1-(2-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3ak)



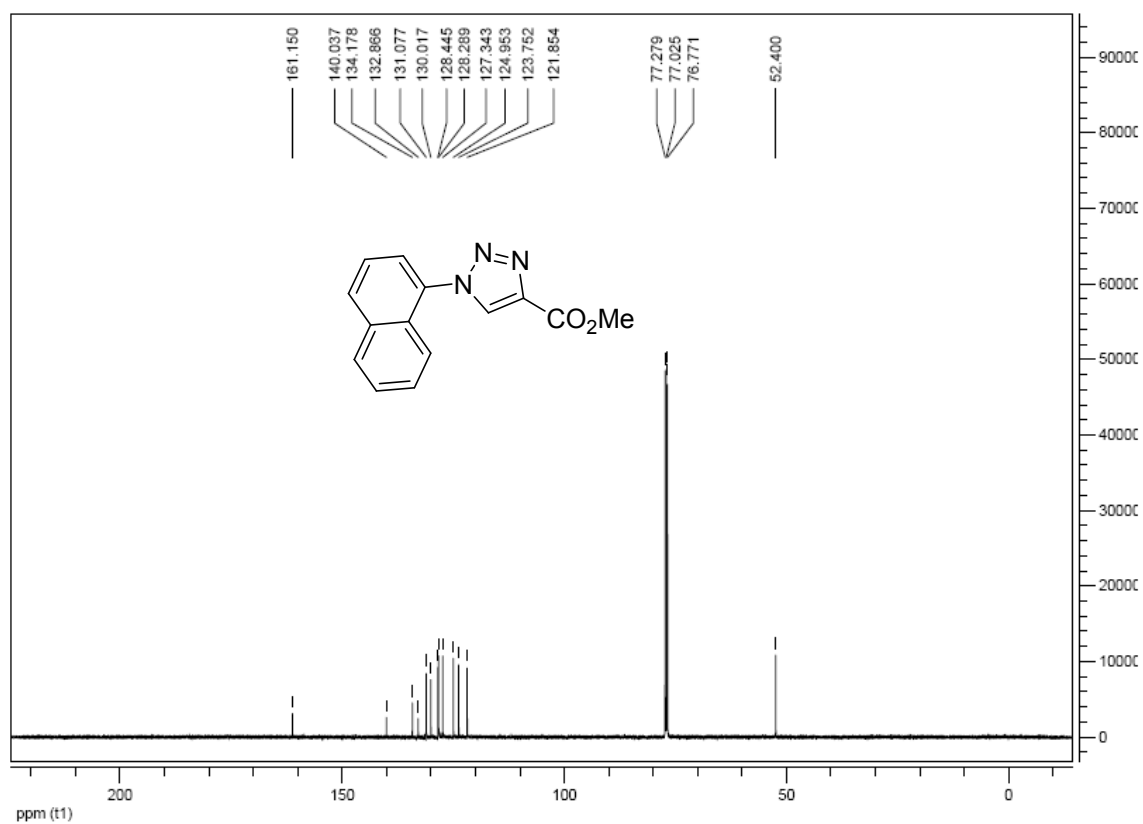
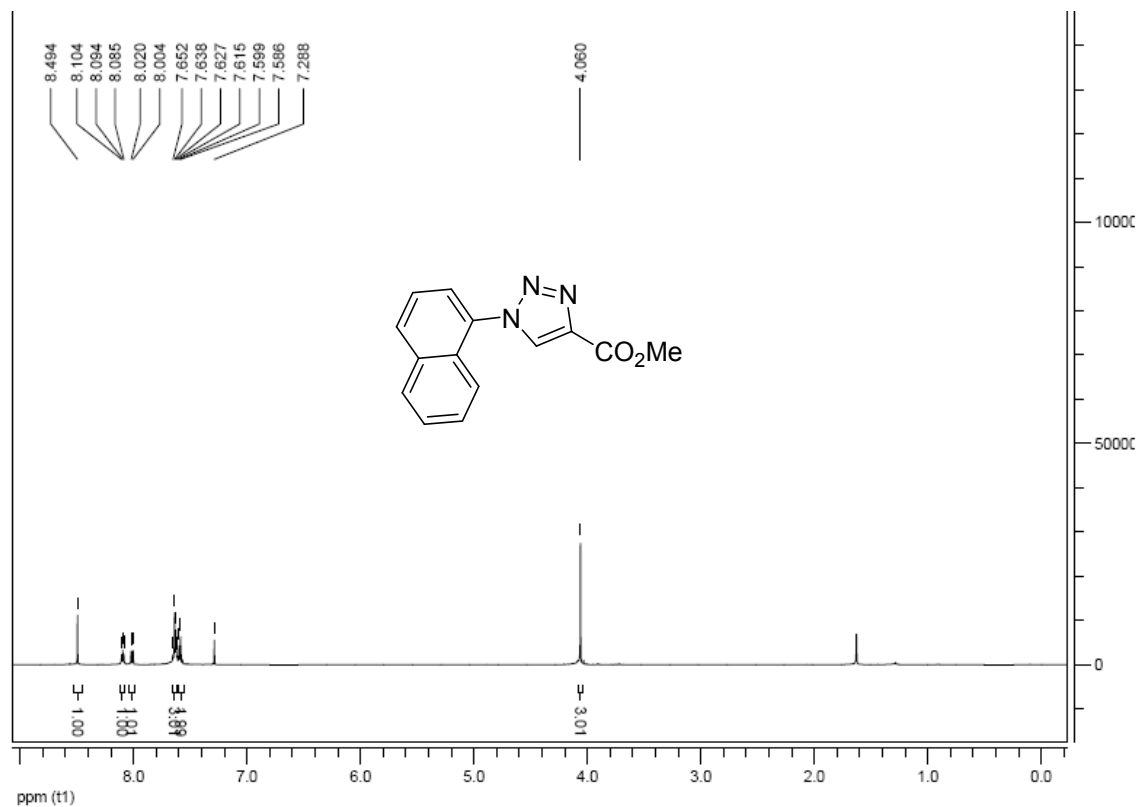
**Methyl 1-(2-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3a)**



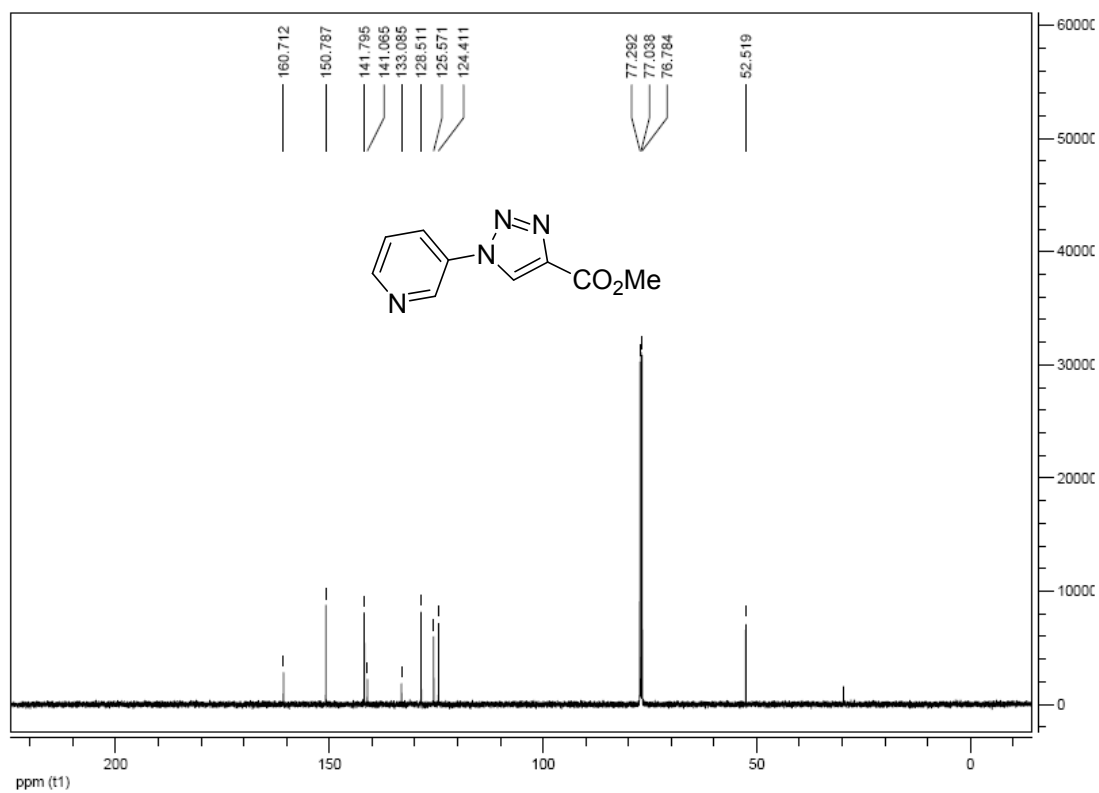
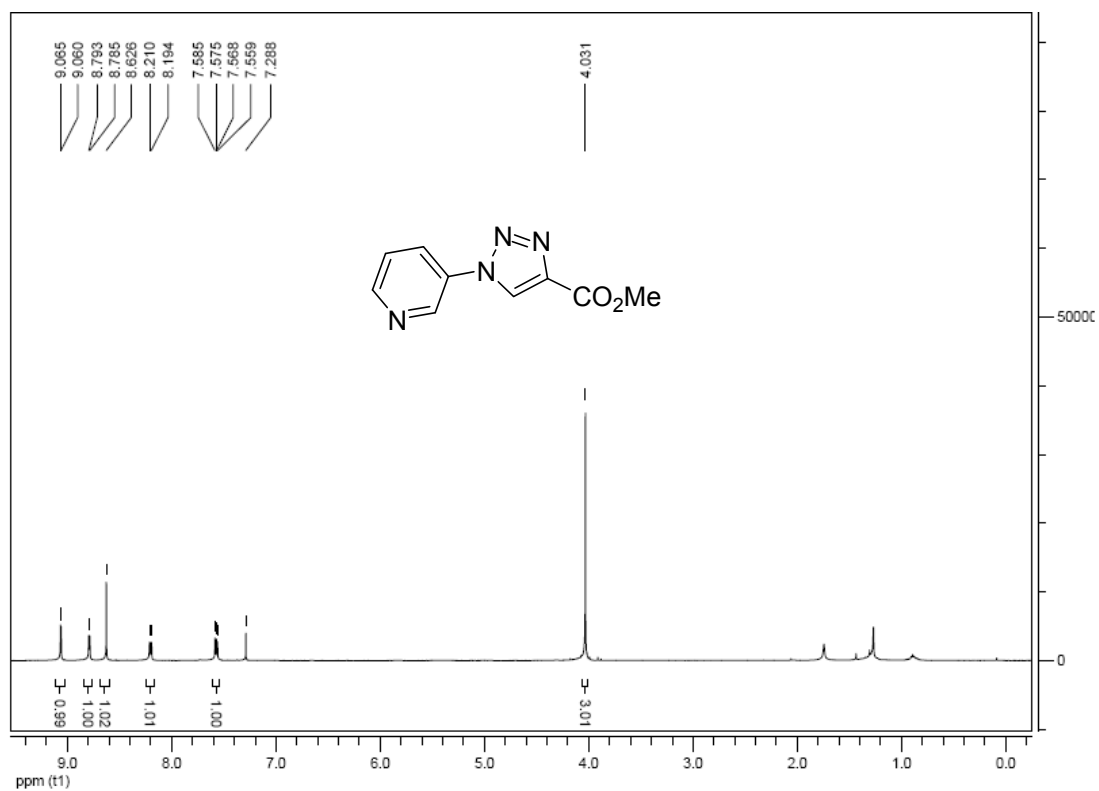
**Methyl 1-(2,4-dichlorophenyl)-1H-1,2,3-triazole-4-carboxylate (3am)**



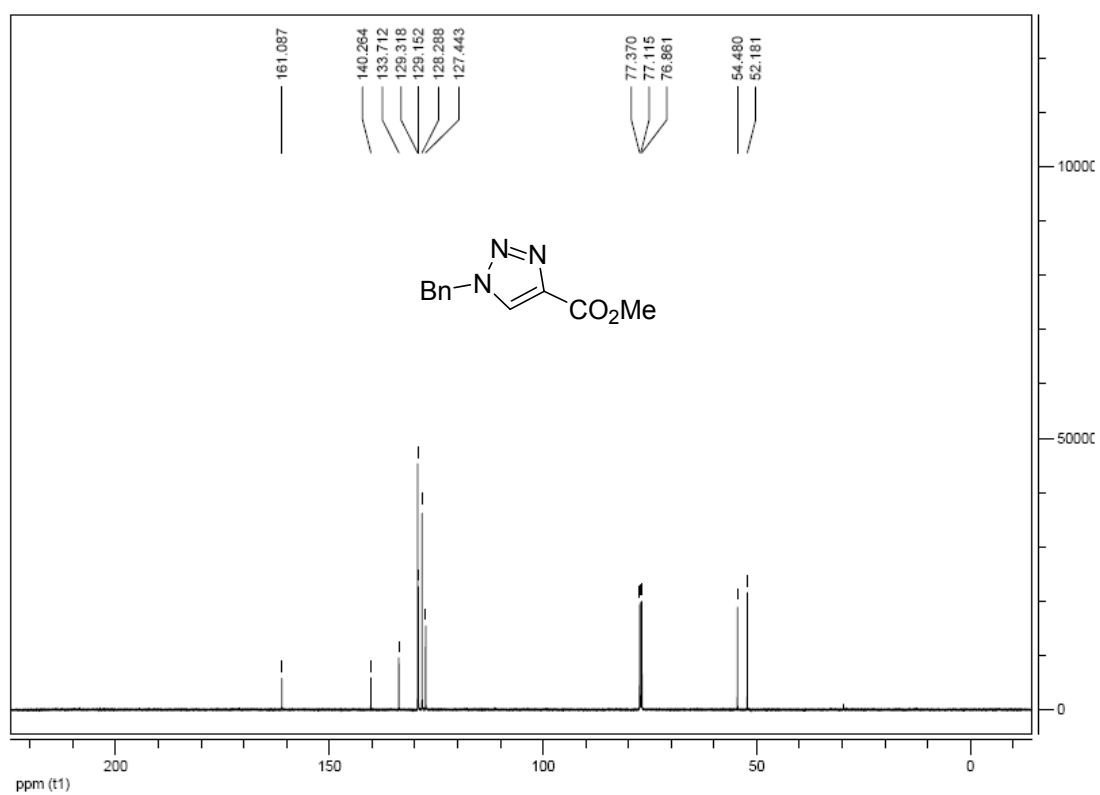
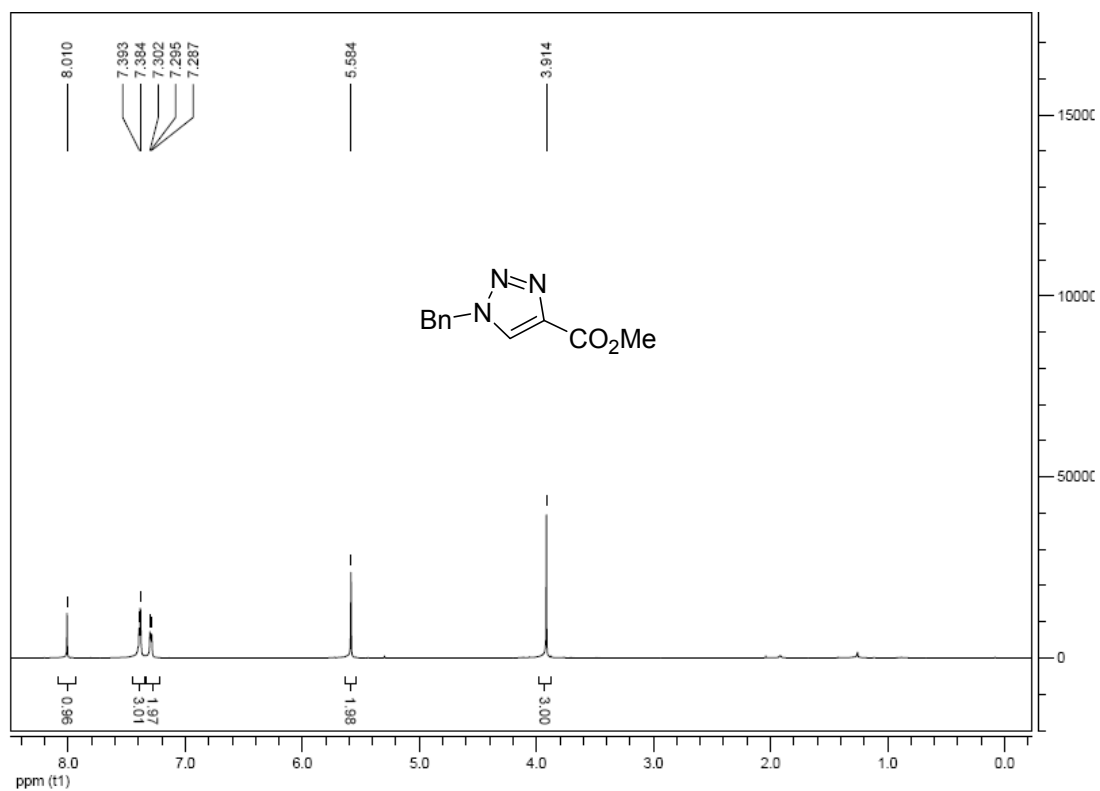
### Methyl 1-(naphthalen-1-yl)-1H-1,2,3-triazole-4-carboxylate (3an)



# Methyl 1-(pyridin-3-yl)-1H-1,2,3-triazole-4-carboxylate (3ao)

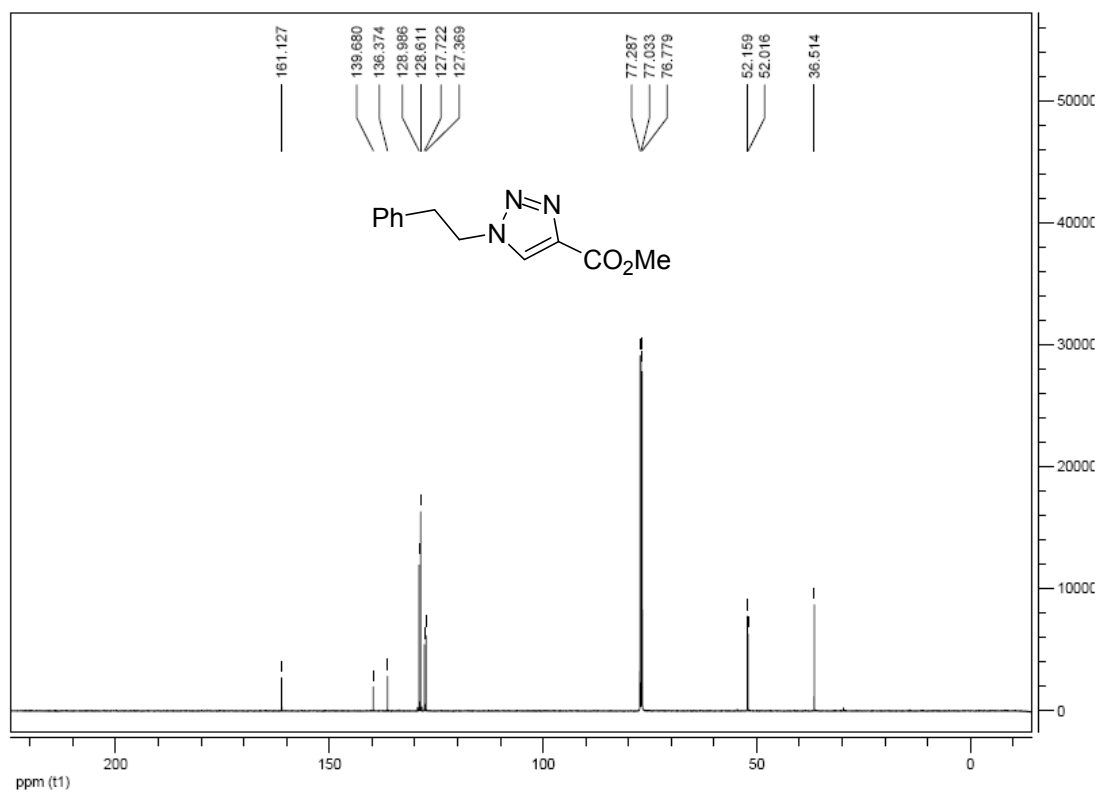
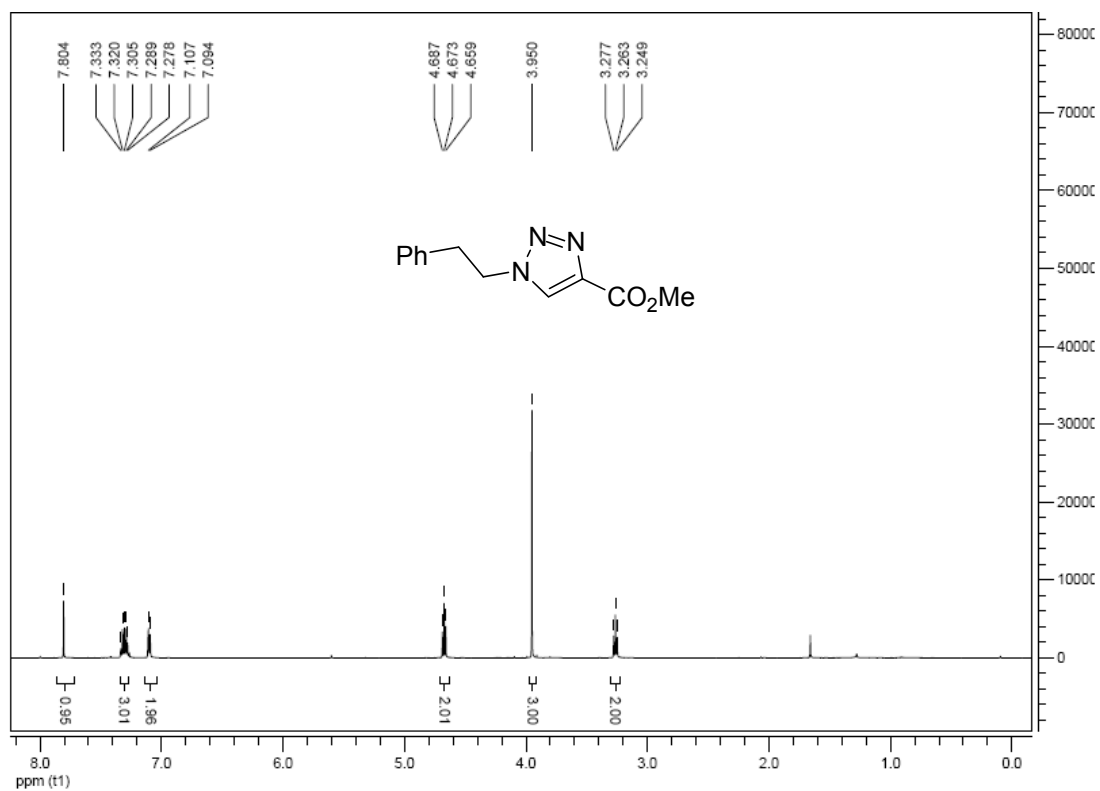


### Methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (3ap)

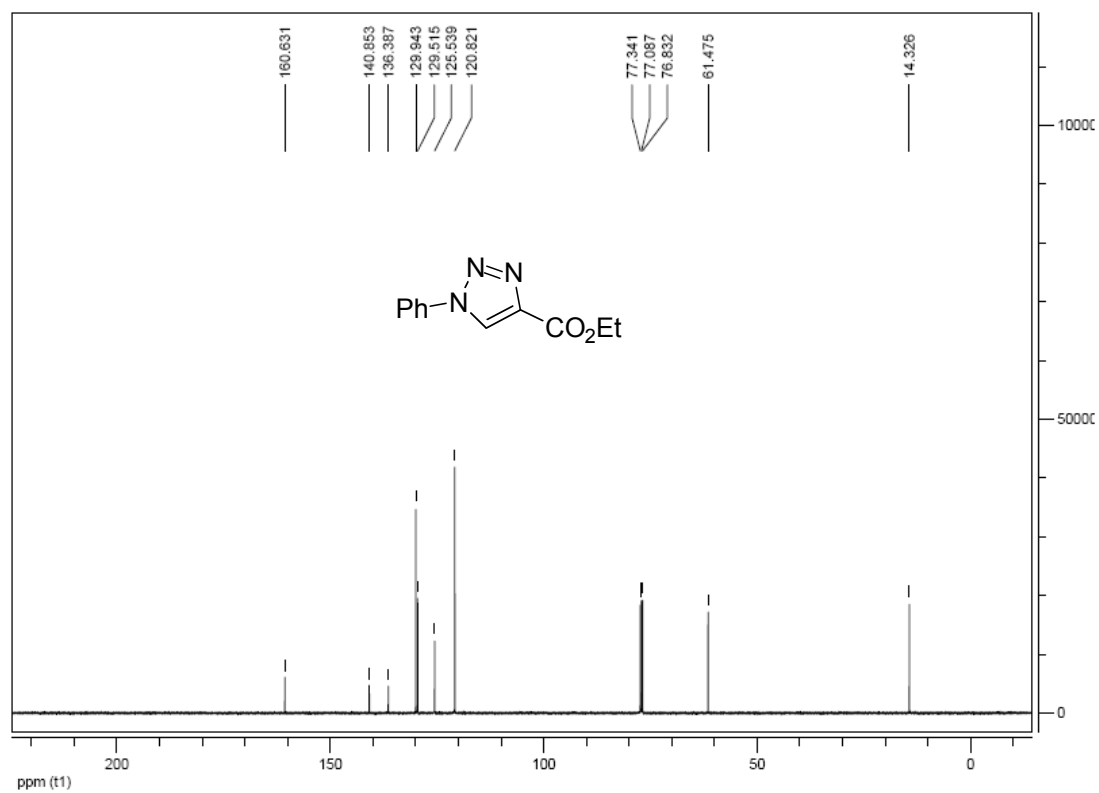
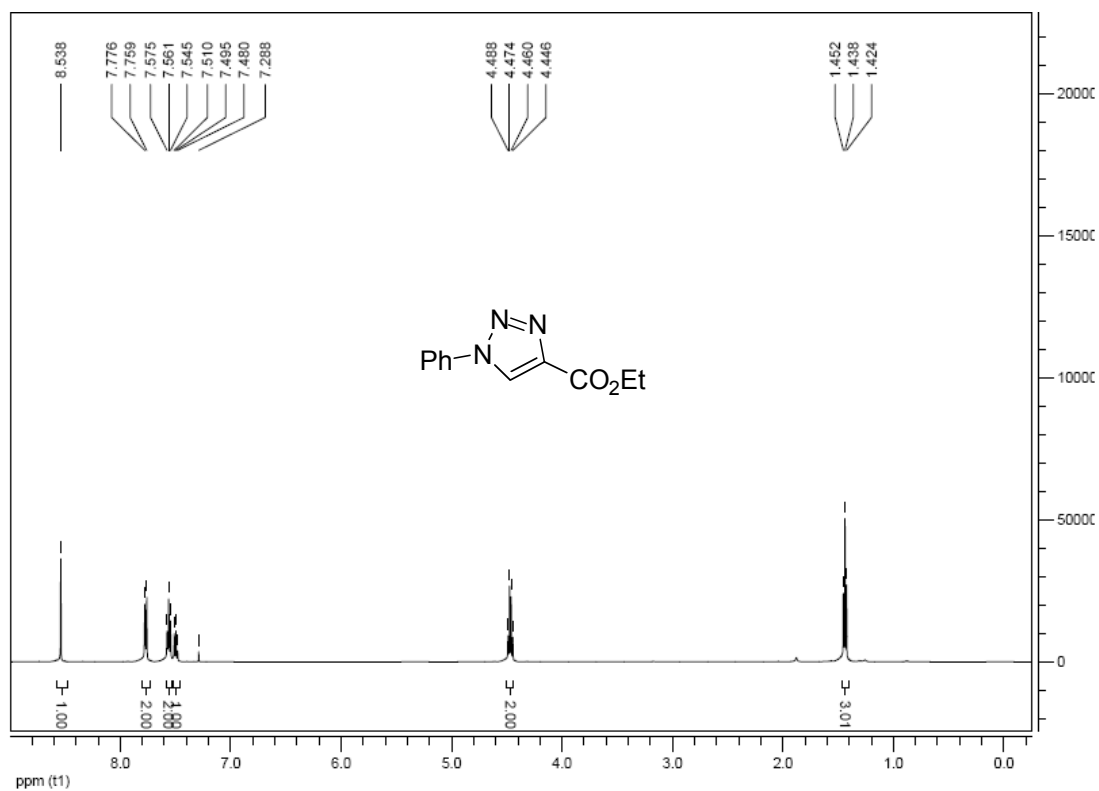




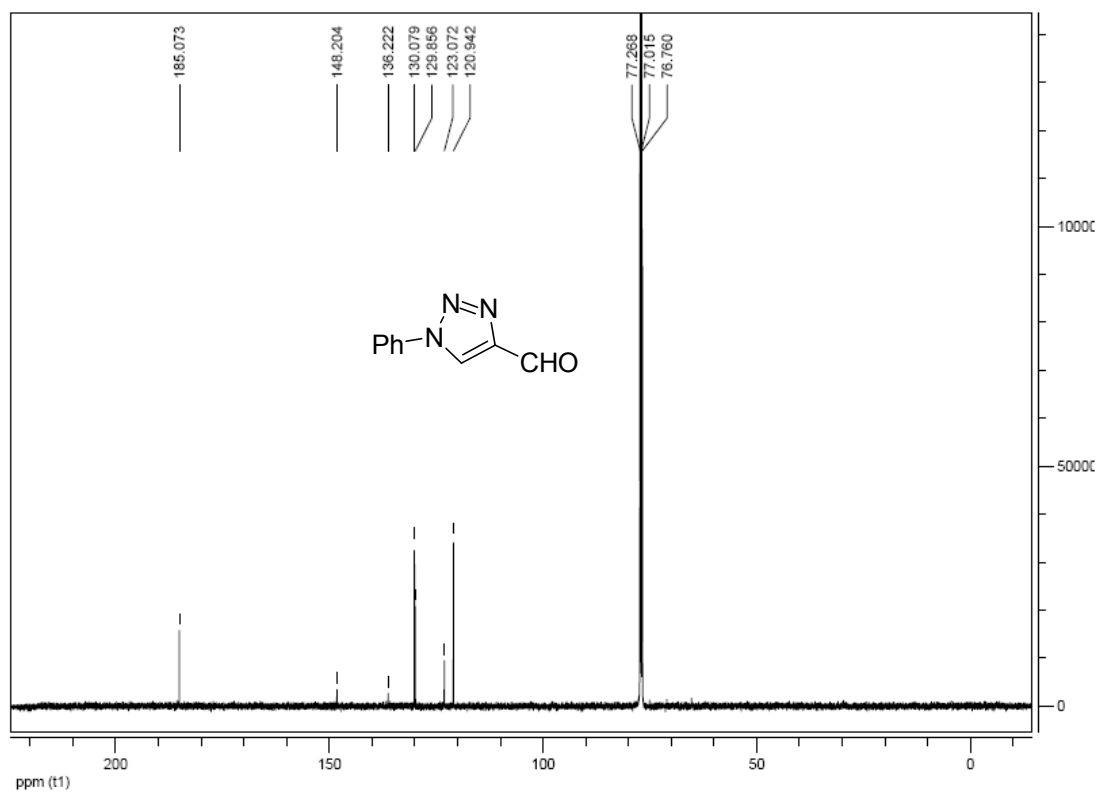
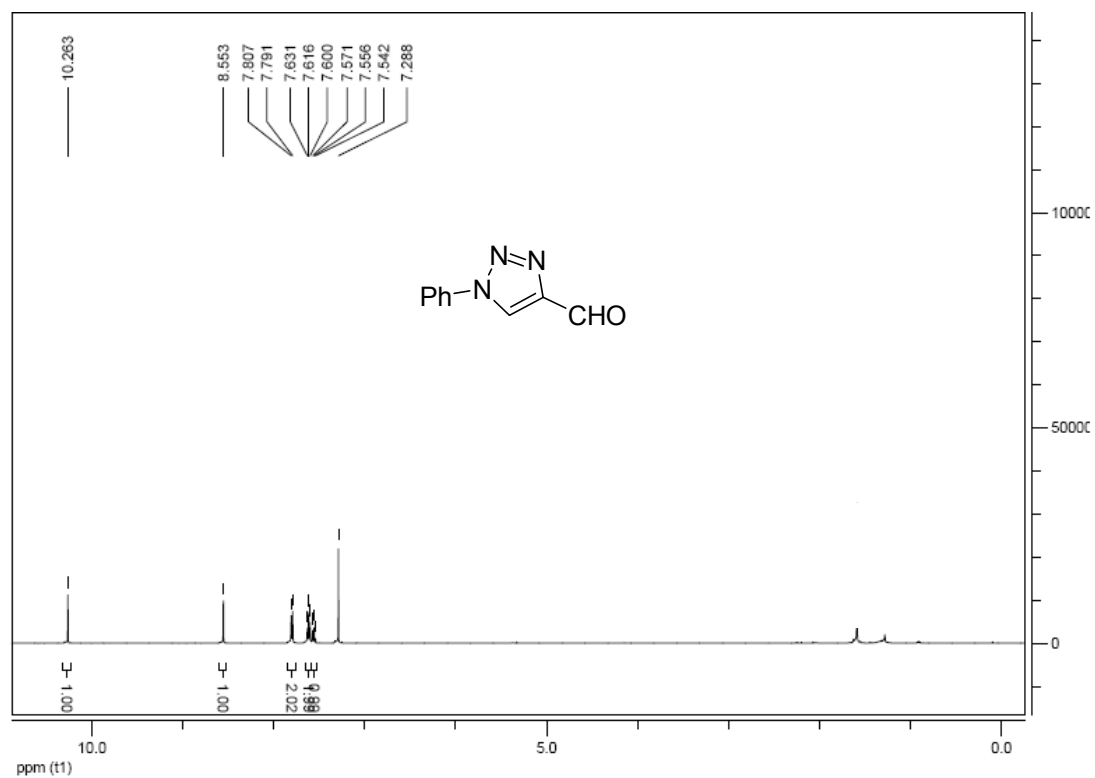
### Methyl 1-phenethyl-1H-1,2,3-triazole-4-carboxylate (3aq)



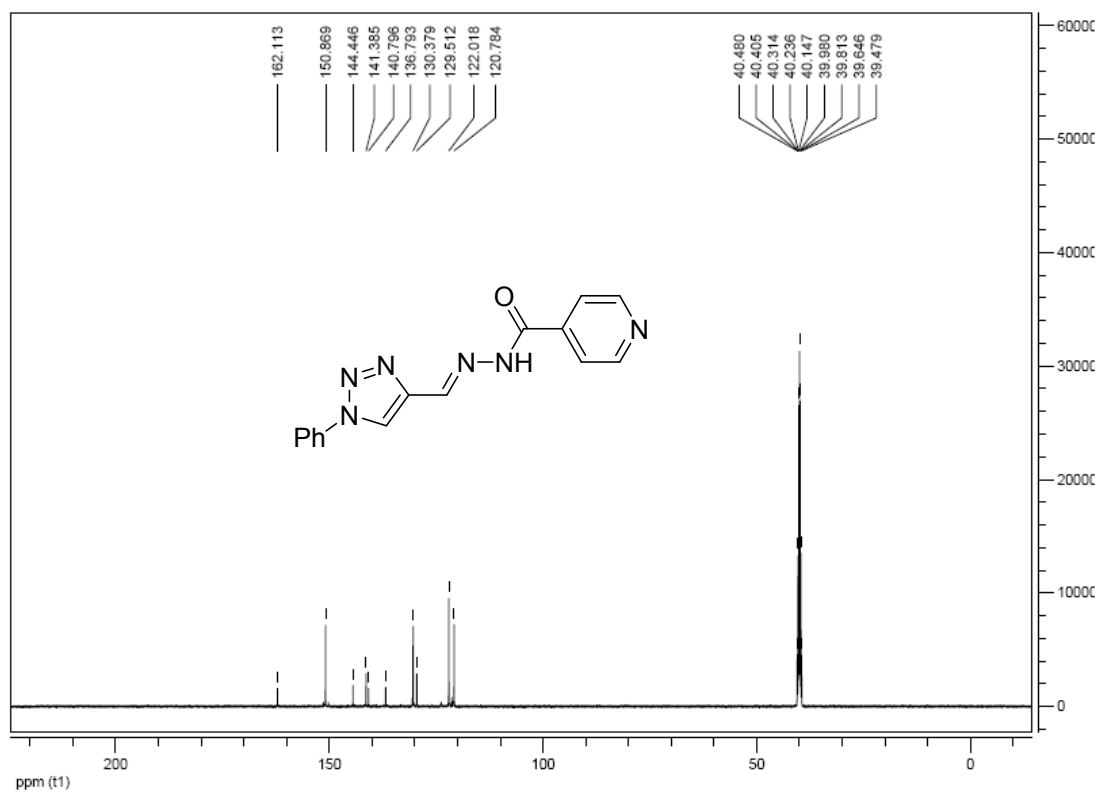
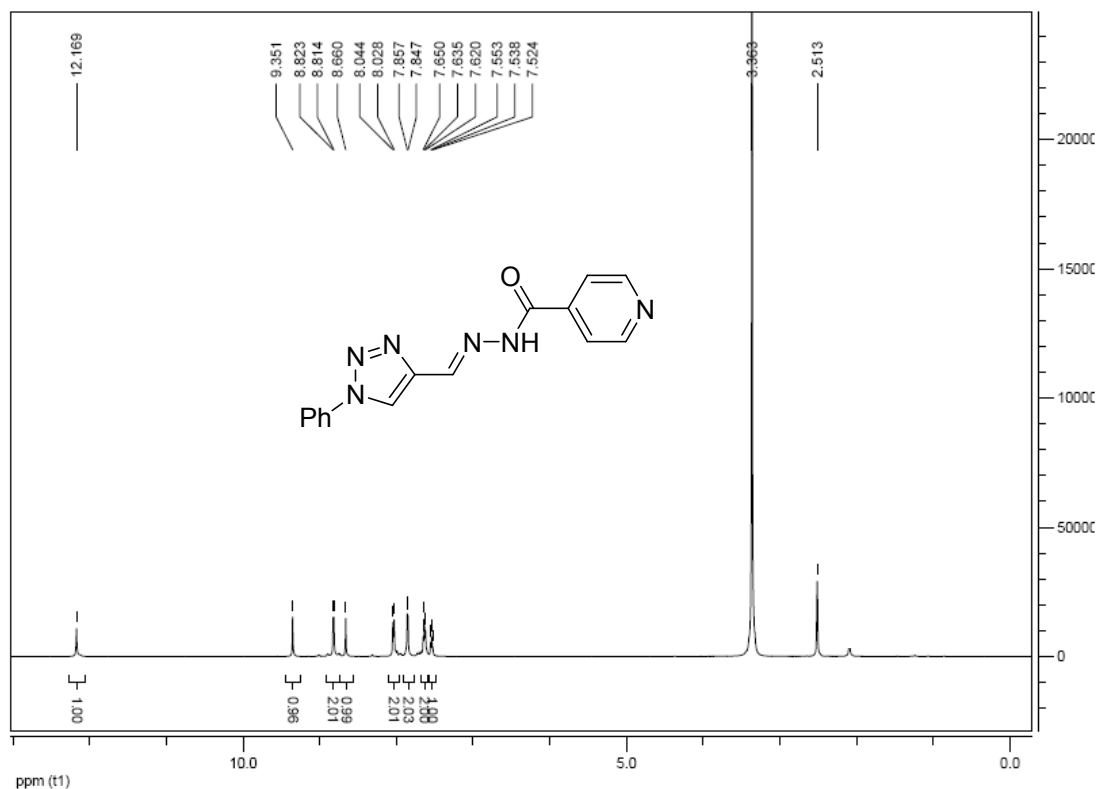
### Ethyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ba)



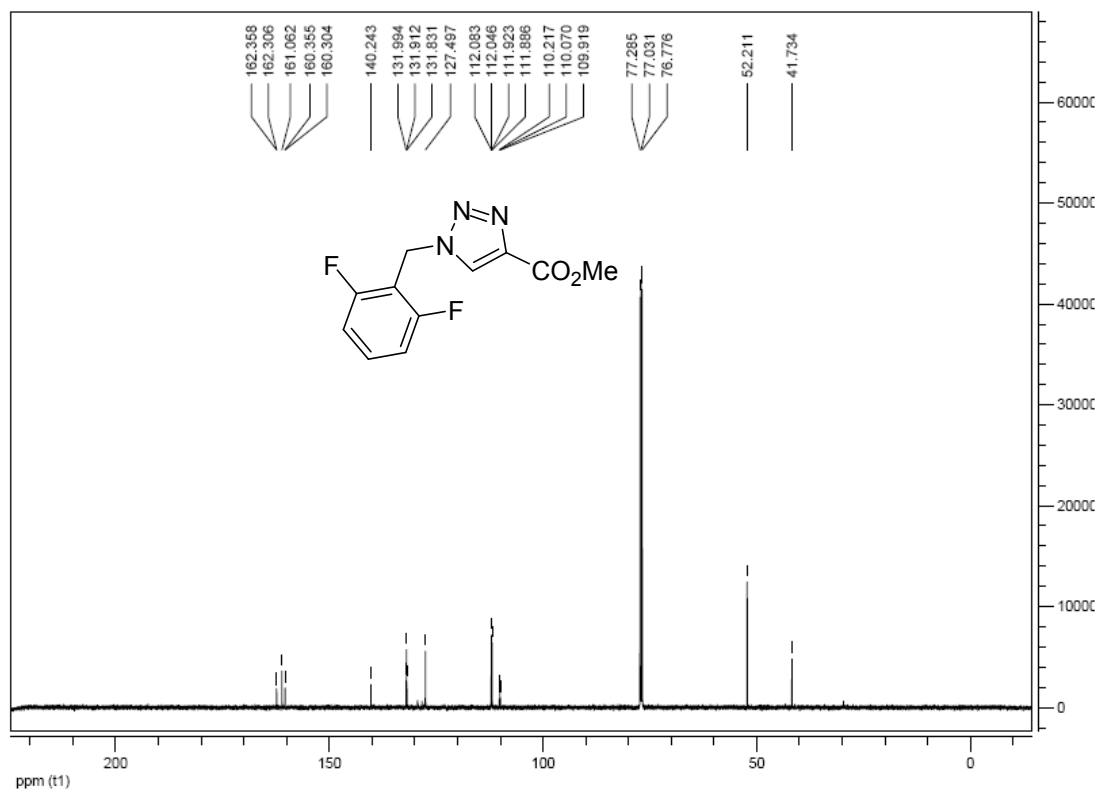
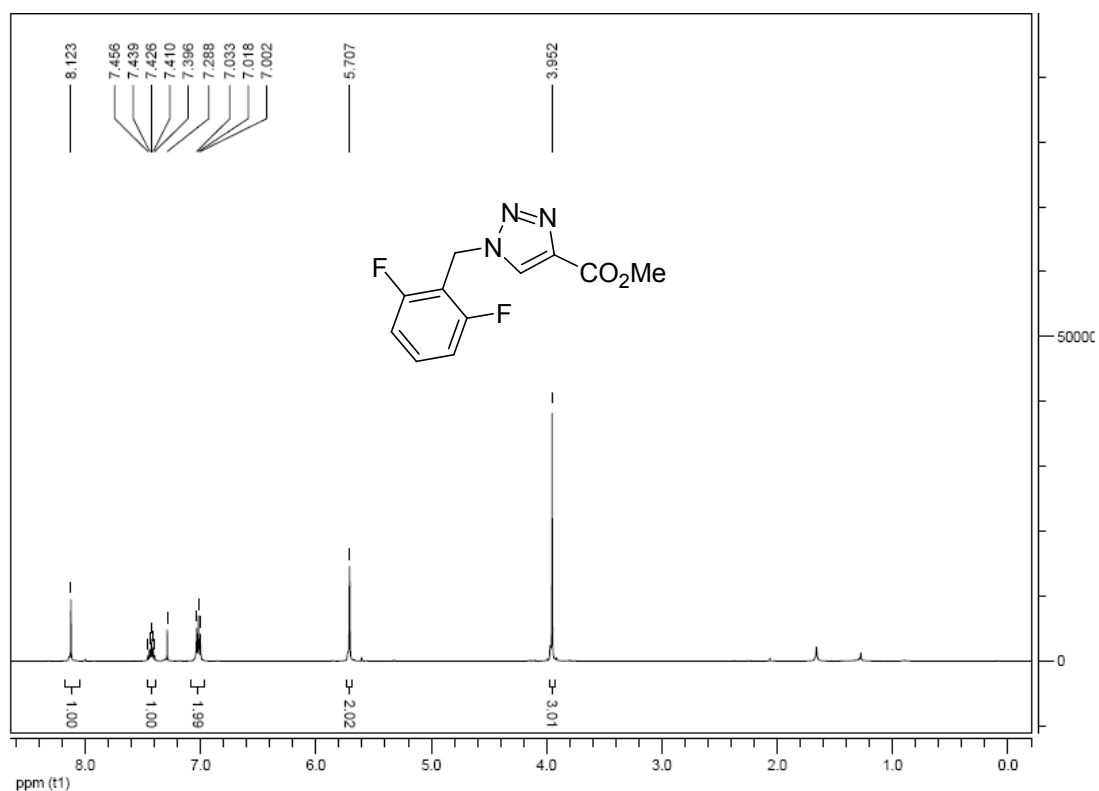
# 1-Phenyl-1H-1,2,3-triazole-4-carbaldehyde (5)



**(E)-N'-((1-phenyl-1H-1,2,3-triazol-4-yl)methylene)isonicotinohydrazide (6)**



### Methyl 1-(2,6-difluorobenzyl)-1H-1,2,3-triazole-4-carboxylate (8)





**F: Reference**

(1) Berger, O.; Kanthi, A.; Tran van Ba, C.; Vial, H.; Ward, S. A.; Biagini, G. A.; Gray, P. G.; O'Neil, P. M. *ChemMedChem* **2011**, *6*, 2094.