

## Base-promoted one-pot three-component desulphurization cross-coupling access to 4-cyanoimidazole

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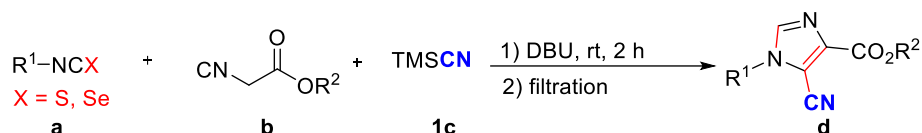
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### 1. General information

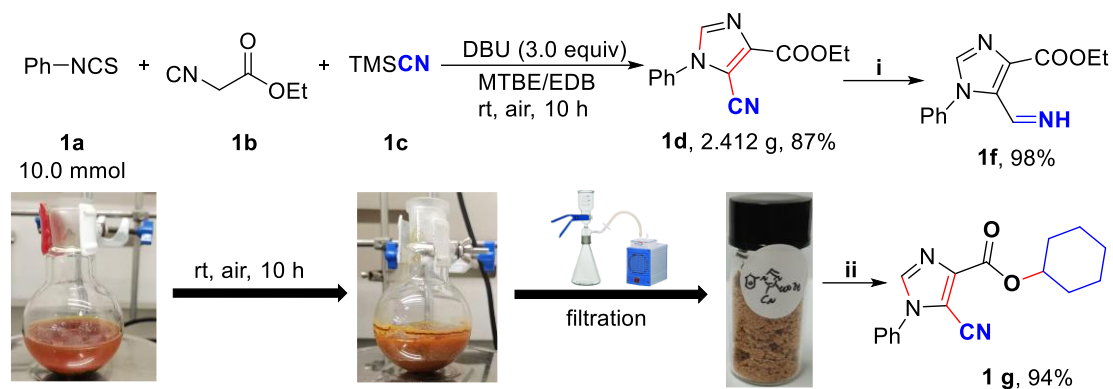
All glassware was oven-dried at 100 °C for 3 hours and cooled down under the atmospheric environment. All the reaction prepared using the solvent of methyl *tert*-butyl ether (AR), BrCH<sub>2</sub>Br (AR) was purchased from Adamas. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, CDCl<sub>3</sub>, 44.00 ppm, DMSO-*d*<sub>6</sub>).

### 2. General procedure for DBU-promoted one-pot three-component desulphurization cross-coupling access to 4-cyanoimidazole



In an oven-dried round-bottom flask (25 mL) equipped with a stir bar, **a** (2.0 mmol), alkyl 2-isocyanoacetates **b** (2.0 mmol), TMS-CN (2.0 mmol, 253 μL), MTBE/EDB (2.0 mL, *v* = 3 : 1) were combined and added, and then DBU (3.0 equiv, 896.4 μL) were added. The reaction mixture was stirred under room temperature for 2 h. When the reaction was finished, the desired product can be obtained by filtering the solid precipitate and washing with petroleum ether.

### 3. Large-scale synthesis of **1d** and application.

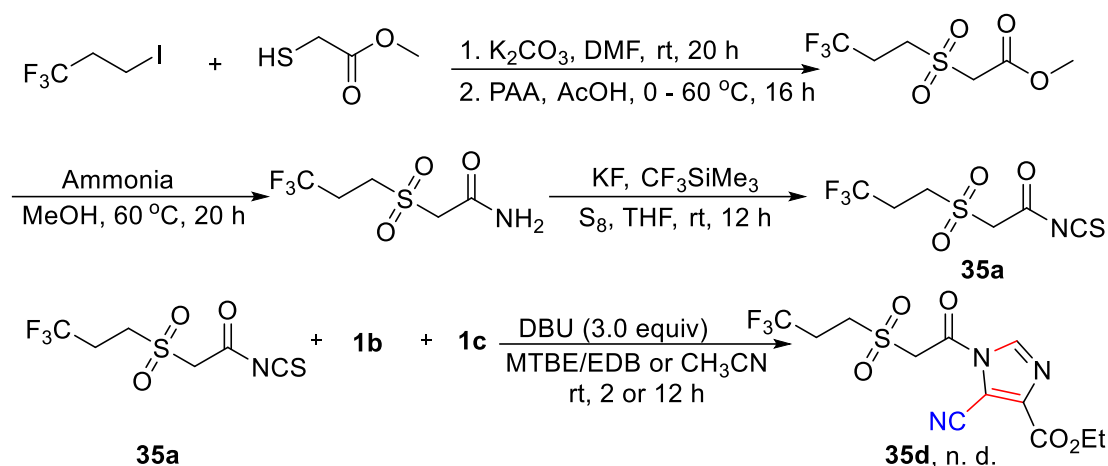


**Scheme S1. Large-scale synthesis of **1d** and application.** Reaction conditions of application. i: **1d** (0.2 mmol), EtOH, 0°C, H<sub>2</sub>O<sub>2</sub> (1.0 mL), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), 25 °C, 12 h. ii: **1d** (0.2 mmol), cyclohexylmagnesium bromide (3.0 equiv), THF (1.0 mL), N<sub>2</sub>, 3 h, then H<sub>2</sub>O (0.23 mL), H<sub>2</sub>SO<sub>4</sub> (10% aq., 0.43 mL), stir 30 min, NaOH (30% aq.), pH = 8.

**Large-scale synthesis of **1d**:** In an oven-dried round-bottom flask (50 mL) equipped with a stir bar, **1a** (10.0 mmol, 1.35 g), ethyl 2-isocyanoacetates **1b** (10.0 mmol, 1.13 g), TMSCN (10.0 mmol, 0.99 g), MTBE/EDB (10.0 mL, v = 3 : 1) were combined and added, and then DBU (3.0 equiv, 4.482 mL) were added. The reaction mixture was stirred under room temperature for 10 h. When the reaction was finished, the desired product can be obtained (2.412 g, 87%) by filtering the solid precipitate and washing with petroleum ether.

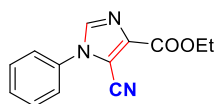
**1f:** In an oven-dried round-bottom flask (25 mL) equipped with a stir bar, **1d** (0.2 mmol) was dissolved in ethanol at 0 ° C, and then H<sub>2</sub>O<sub>2</sub> (1.0 mL) and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv) were added. The reaction was transferred to room temperature and stirred overnight. When the reaction was finished, the desired product **1f** can be obtained by column chromatography with a yield of 98%.

**1g:** In an oven-dried round-bottom flask (25 mL) equipped with a stir bar, **1d** (0.2 mmol) was dissolved in ethanol at 0 ° C, and then H<sub>2</sub>O<sub>2</sub> (1.0 mL) and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv) were added. The reaction was transferred to room temperature and stirred overnight. When the reaction was finished, the desired product **1g** can be obtained by column chromatography with a yield of 94%.

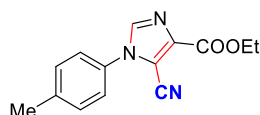


**Scheme S2.** The synthesis of pesticide derivatives **35d**.

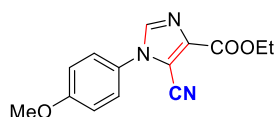
#### 4. Detail descriptions for products



**Ethyl 5-cyano-1-phenyl-1H-imidazole-4-carboxylate (1d):** yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 85% isolated yield (409.7 mg), filtrated yield: 82% (395.2 mg). m. p. = 101-103 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (s, 1H), 7.62 – 7.54 (m, 3H), 7.47 (dd, *J* = 7.8, 1.7 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.1, 142.1, 139.9, 133.8, 130.4, 130.3, 124.4, 109.7, 109.2, 61.9, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: 242.0925; found: 242.0925.

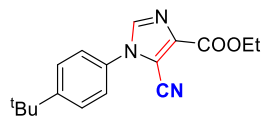


**Ethyl 5-cyano-1-(p-tolyl)-1H-imidazole-4-carboxylate (2d):** yellow solid was obtained with 81% filtrated yield (413.1 mg). m. p. = 123-125 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.2, 141.9, 140.8, 139.9, 131.3, 130.8, 124.2, 109.7, 109.3, 61.9, 21.2, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: 256.1081; found: 256.1081.

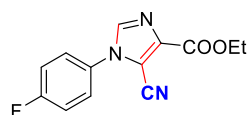


**Ethyl 5-cyano-1-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (3d):** yellow solid was obtained with 75% filtrated yield (405 mg). m. p. = 128-131 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (s, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.45 (t, *J* = 7.1

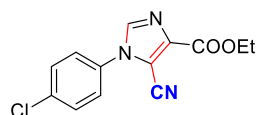
Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 160.2, 141.7, 140.1, 126.5, 125.9, 115.3, 109.8, 109.6, 61.9, 55.7, 14.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3$ : 272.1030; found: 272.1029.



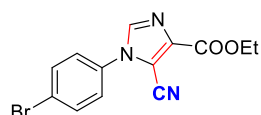
**Ethyl 1-(4-(tert-butyl)phenyl)-5-cyano-1H-imidazole-4-carboxylate (4d)**: yellow solid was obtained with 84% filtrated yield (498.9 mg). m. p. = 90-92 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (s, 1H), 7.58 (d,  $J$  = 8.6 Hz, 2H), 7.39 (d,  $J$  = 8.6 Hz, 2H), 4.47 (q,  $J$  = 7.1 Hz, 2H), 1.44 (t,  $J$  = 7.1 Hz, 3H), 1.36 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 153.9, 142.0, 139.9, 131.2, 127.2, 123.9, 109.8, 109.2, 61.9, 34.9, 31.1, 14.2. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_2$ : 298.1551; found: 298.1551.



**Ethyl 5-cyano-1-(4-fluorophenyl)-1H-imidazole-4-carboxylate (5d)**: yellow solid was obtained with 78% filtrated yield (404 mg). m. p. = 140-142 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (s, 1H), 7.47 (m, 2H), 7.22 (dd,  $J$  = 11.3, 5.4 Hz, 2H), 4.40 (q,  $J$  = 7.1 Hz, 2H), 1.37 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.33 (d,  $J$  = 252.1 Hz), 160.0, 142.0, 140.0, 129.85 (d,  $J$  = 3.2 Hz), 126.72 (d,  $J$  = 9.0 Hz), 117.44 (d,  $J$  = 23.5 Hz), 109.5, 109.4, 62.0, 14.1.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{FN}_3\text{O}_2$ : 260.0830; found: 260.0830.



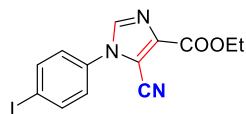
**Ethyl 1-(4-chlorophenyl)-5-cyano-1H-imidazole-4-carboxylate (6d)**: yellow solid was obtained with 75% filtrated yield (412.5 mg). m. p. = 141-143 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.51 (d,  $J$  = 8.7 Hz, 2H), 7.38 (d,  $J$  = 8.7 Hz, 2H), 4.40 (q,  $J$  = 7.1 Hz, 2H), 1.37 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 142.2, 139.8, 136.6, 132.2, 130.5, 125.8, 109.5, 109.2, 62.0, 14.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{ClN}_3\text{O}_2$ : 276.0534; found: 276.0534.



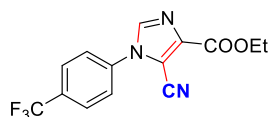
**Ethyl 1-(4-bromophenyl)-5-cyano-1H-imidazole-4-carboxylate (7d)**: yellow solid was obtained with 72% filtrated yield (459.4 mg). m. p. = 143-145 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (s, 1H), 7.71 (d,  $J$  = 8.3 Hz, 2H), 7.37 (d,  $J$  = 8.7 Hz, 2H), 4.44 (dd,  $J$  = 13.8, 6.8 Hz, 2H), 1.41 (t,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 142.2, 139.8, 133.5, 132.7, 126.0, 124.6, 109.5, 109.1, 62.0, 14.1.

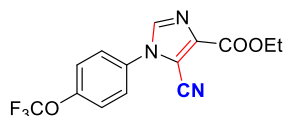
HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$ : 320.0029; found: 320.0021.



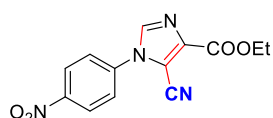
**Ethyl 5-cyano-1-(4-iodophenyl)-1H-imidazole-4-carboxylate (8d)**: yellow solid was obtained with 61% filtrated yield (447.7 mg). m. p. = 170-172 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J$  = 8.7 Hz, 2H), 7.84 (s, 1H), 7.23 (d,  $J$  = 8.7 Hz, 2H), 4.45 (q,  $J$  = 7.1 Hz, 2H), 1.42 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 142.3, 139.7, 139.5, 133.4, 126.0, 109.5, 109.0, 96.1, 62.0, 14.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{IN}_3\text{O}_2$ : 367.9890; found: 367.9886.



**Ethyl 5-cyano-1-(4-(trifluoromethyl)phenyl)-1H-imidazole-4-carboxylate (9d)**: yellow solid was obtained with 81% filtrated yield (500.5 mg). m. p. = 150-152 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 1H), 7.89 (d,  $J$  = 8.4 Hz, 2H), 7.66 (d,  $J$  = 8.5 Hz, 2H), 4.48 (q,  $J$  = 7.1 Hz, 2H), 1.44 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 142.6, 139.8, 136.5, 132.5 (q,  $J$  = 33.6 Hz), 127.6 (q,  $J$  = 3.6 Hz), 124.9, 123.5 (q,  $J$  = 273.2 Hz), 109.4, 108.9, 62.1, 14.1.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_3\text{O}_2$ : 310.0798; found: 310.0796.

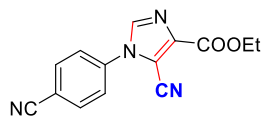


**Ethyl 5-cyano-1-(4-(trifluoromethoxy)phenyl)-1H-imidazole-4-carboxylate (10d)**: yellow solid was obtained with 85% filtrated yield (552.5 mg). m. p. = 132-134 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (s, 1H), 7.51 (d,  $J$  = 8.9 Hz, 2H), 7.38 (d,  $J$  = 8.6 Hz, 2H), 4.39 (q,  $J$  = 7.1 Hz, 2H), 1.36 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 150.2, 142.2, 140.0, 132.0, 126.3, 122.5, 120.7 (q,  $J$  = 262.6 Hz), 109.5, 109.2, 62.0, 14.0.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_3\text{O}_3$ : 326.0747; found: 326.0747.

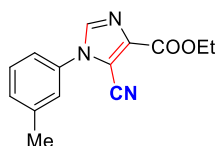


**Ethyl 5-cyano-1-(4-nitrophenyl)-1H-imidazole-4-carboxylate (11d)**: yellow solid was obtained with 62% filtrated yield (354.6 mg). m. p. = 178-180 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J$  = 8.9 Hz, 2H), 7.98 (s, 1H), 7.76 (d,  $J$  = 8.9 Hz, 2H), 4.50 (q,  $J$  = 7.1 Hz, 2H), 1.46 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR

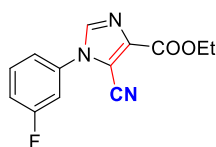
(126 MHz, CDCl<sub>3</sub>)  $\delta$  159.7, 148.5, 143.0, 139.6, 138.4, 125.9, 125.3, 109.3, 108.8, 62.3, 14.1. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>: 287.0775; found: 287.0773.



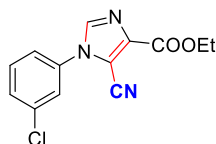
**Ethyl 5-cyano-1-(4-cyanophenyl)-1H-imidazole-4-carboxylate, hydrogen salt (12d):** yellow solid was obtained with 50% filtrated yield (266 mg). m. p. = 150-152 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d,  $J$  = 2.7 Hz, 1H), 7.93 (s, 1H), 7.69 (d,  $J$  = 8.6 Hz, 2H), 4.50 (q,  $J$  = 7.1 Hz, 2H), 1.45 (t,  $J$  = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 142.8, 139.6, 137.0, 134.3, 125.1, 117.0, 114.6, 109.3, 108.8, 62.2, 14.1. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>: 267.0877; found: 267.0877.



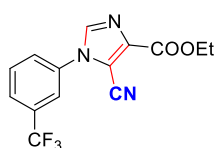
**Ethyl 5-cyano-1-(m-tolyl)-1H-imidazole-4-carboxylate (13d):** yellow solid was obtained with 64% filtrated yield (326.4 mg). m. p. = 104-106 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (s, 1H), 7.49 (m, 1H), 7.38 (d,  $J$  = 7.7 Hz, 1H), 7.27 (t,  $J$  = 2.2 Hz, 2H), 4.49 (q,  $J$  = 7.1 Hz, 2H), 2.47 (s, 3H), 1.45 (t,  $J$  = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 142.0, 140.7, 139.9, 133.7, 131.1, 130.0, 124.9, 121.5, 109.7, 109.2, 61.9, 21.3, 14.2. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: 256.1081; found: 256.1081.



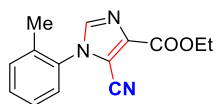
**Ethyl 5-cyano-1-(3-fluorophenyl)-1H-imidazole-4-carboxylate (14d):** yellow solid was obtained with 58% filtrated yield (300.4 mg). m. p. = 150-152 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (s, 1H), 7.53 (d,  $J$  = 5.9 Hz, 1H), 7.25 (dd,  $J$  = 10.5, 2.2 Hz, 2H), 7.18 (d,  $J$  = 8.5 Hz, 1H), 4.41 (q,  $J$  = 7.1 Hz, 2H), 1.38 (t,  $J$  = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.96 (d,  $J$  = 251.6 Hz), 159.9, 142.3, 139.8, 134.8 (d,  $J$  = 9.7 Hz), 131.8 (d,  $J$  = 8.9 Hz), 120.3 (d,  $J$  = 3.4 Hz), 117.6 (d,  $J$  = 21.0 Hz), 112.3 (d,  $J$  = 25.0 Hz), 109.4, 109.1, 62.0, 14.1. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -108.1. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>3</sub>O<sub>2</sub>: 260.0830; found: 260.0830.



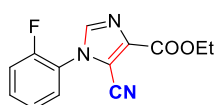
**Ethyl 1-(3-chlorophenyl)-5-cyano-1H-imidazole-4-carboxylate (15d):** yellow solid was obtained with 60% filtrated yield (330 mg). m. p. = 130-132 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 1H), 7.56 (dd, *J* = 12.7, 4.8 Hz, 2H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.42 (dt, *J* = 6.9, 1.9 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.9, 142.3, 139.8, 136.1, 134.6, 131.4, 130.7, 124.8, 122.7, 109.4, 109.1, 62.1, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>ClN<sub>3</sub>O<sub>2</sub>: 276.0534; found: 276.0533.



**Ethyl 5-cyano-1-(3-(trifluoromethyl)phenyl)-1H-imidazole-4-carboxylate (16d):** yellow solid was obtained with 72% filtrated yield (444.9 mg). m. p. = 133-135 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.77 (dt, *J* = 22.5, 8.0 Hz, 3H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.9, 142.4, 139.9, 134.2, 133.0 (q, *J* = 33.8 Hz), 131.2, 127.9, 127.2 (q, *J* = 3.6 Hz), 122.3 (q, *J* = 273.4 Hz), 121.6 (q, *J* = 3.8 Hz), 109.3, 109.1, 62.1, 14.1. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub>: 310.0798; found: 310.0797.

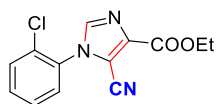


**Ethyl 5-cyano-1-(o-tolyl)-1H-imidazole-4-carboxylate (17d):** yellow solid was obtained with 70% filtrated yield (357 mg). m. p. = 101-103 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (s, 1H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.42 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.2, 141.3, 140.7, 134.7, 132.7, 131.8, 131.1, 127.5, 127.1, 110.4, 109.4, 61.9, 17.2, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: 256.1081; found: 256.1081.

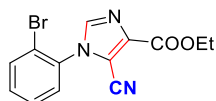


**Ethyl 5-cyano-1-(2-fluorophenyl)-1H-imidazole-4-carboxylate (18d):** yellow solid was obtained

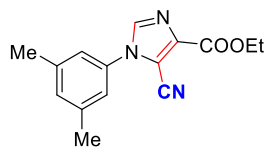
with 62% filtrated yield (321.1 mg). m. p. = 70-72 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 1.3 Hz, 1H), 7.60 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.51 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.39 (dd, *J* = 12.7, 5.4 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.0, 156.0 (d, *J* = 254.0 Hz), 141.7, 140.8 (d, *J* = 2.1 Hz), 132.5 (d, *J* = 7.8 Hz), 127.4, 125.5 (d, *J* = 4.1 Hz), 121.6 (d, *J* = 12.5 Hz), 117.5 (d, *J* = 19.2 Hz), 110.1, 109.2, 62.0, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>3</sub>O<sub>2</sub>: 260.0830; found: 260.0830.



**Ethyl 1-(2-chlorophenyl)-5-cyano-1H-imidazole-4-carboxylate (19d):** yellow solid was obtained with 62% filtrated yield (341 mg). m. p. = 78-80 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.66 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.60 (m, 1H), 7.54 (m, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.0, 141.4, 140.9, 132.3, 131.3, 131.2, 131.2, 128.6, 128.3, 110.4, 109.1, 62.0, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>ClN<sub>3</sub>O<sub>2</sub>: 276.0534; found: 276.0534.

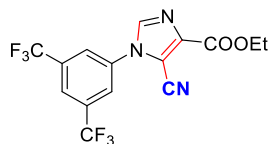


**Ethyl 1-(2-bromophenyl)-5-cyano-1H-imidazole-4-carboxylate (20d):** yellow solid was obtained with 59% filtrated yield (376.4 mg). m. p. = 90-92 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.51 (m, 1H), 7.45 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.0, 141.3, 140.8, 134.3, 132.9, 132.5, 129.0, 128.7, 121.0, 110.4, 109.1, 62.0, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>BrN<sub>3</sub>O<sub>2</sub>: 320.0029; found: 320.0026.

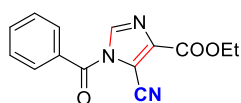


**Ethyl 5-cyano-1-(3,5-dimethylphenyl)-1H-imidazole-4-carboxylate (21d):** yellow solid was obtained with 68% filtrated yield (365.8 mg). m. p. = 136-138 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.15 (s, 1H), 7.04 (s, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.2, 141.8, 140.3, 140.0, 133.6, 131.9, 122.0, 109.7, 109.2, 61.8, 21.1, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: 270.1237; found: 270.1237.

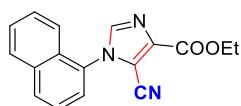




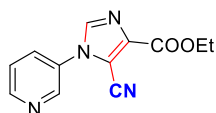
**Ethyl 1-(3,5-bis(trifluoromethyl)phenyl)-5-cyano-1H-imidazole-4-carboxylate (22d):** yellow solid substance was obtained with 63% filtrated yield (475.0 mg). m. p. = 112-114 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 7.95 (s, 2H), 7.93 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.6, 142.8, 139.9, 135.0, 134.2 (q, *J* = 34.8 Hz), 125.1, 124.2 (q, *J* = 3.6 Hz), 123.4 (q, *J* = 274.0 Hz), 109.1, 109.0, 62.3, 14.0. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.7, 62.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>: 378.0672; found: 378.0668.



**Ethyl 1-benzoyl-5-cyano-1H-imidazole-4-carboxylate (23d):** yellow oil was obtained with 57% isolated yield (306.6 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.92 (s, 1H), 7.48 (dd, *J* = 5.0, 2.5 Hz, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.9, 155.5, 149.0, 130.4, 128.5, 128.4, 126.7, 126.6, 110.2, 61.4, 14.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: 270.0873; found: 270.0873.



**Ethyl 5-cyano-1-(naphthalen-1-yl)-1H-imidazole-4-carboxylate (24d):** yellow solid was obtained with 65% filtrated yield (378.3 mg). m. p. = 115-117 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.91 (t, 1H), 7.79 (s, 1H), 7.56 (m, 4H), 7.24 (d, *J* = 8.2 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.2, 141.7, 141.4, 134.2, 131.5, 129.8, 129.0, 128.7, 128.6, 127.6, 125.1, 125.1, 121.0, 111.3, 109.3, 61.9, 14.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: 292.1081; found: 292.1076.

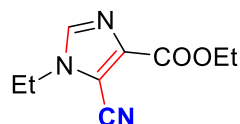


**Ethyl 5-cyano-1-(pyridin-3-yl)-1H-imidazole-4-carboxylate (25d):** yellow solid was obtained with 51% filtrated yield (246.8 mg). m. p. = 135-137 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.83 (dd, *J* = 4.8, 1.0 Hz, 1H), 8.79 (d, *J* = 2.5 Hz, 1H), 7.93 (m, 2H), 7.58 (dd, *J* = 8.2, 4.8 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.8, 151.6, 145.3, 142.6, 139.8, 132.1,

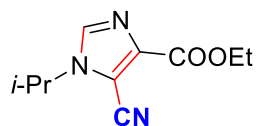
130.7, 124.6, 109.3, 62.1, 14.1. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{12}H_{10}N_4O_2$ : 243.0877; found: 243.0877.



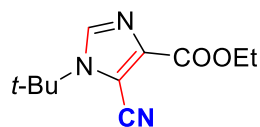
**Ethyl 5-cyano-1-methyl-1H-imidazole-4-carboxylate (26d)**: yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 71% isolated yield (254.2 mg). m. p. = 83-85 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.59 (s, 1H), 4.37 (q,  $J = 7.1$  Hz, 2H), 3.81 (s, 3H), 1.35 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.1, 141.2, 140.8, 109.7, 109.6, 61.7, 33.4, 14.1. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_8H_{10}N_3O_2$ : 180.0768; found: 180.0765.



**Ethyl 5-cyano-1-ethyl-1H-imidazole-4-carboxylate (27d)**: yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 73% isolated yield (281.8 mg). m. p. = 76-78 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.69 (s, 1H), 4.45 (q,  $J = 7.1$  Hz, 2H), 4.22 (q,  $J = 7.4$  Hz, 2H), 1.58 (t,  $J = 7.4$  Hz, 3H), 1.43 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.2, 141.4, 139.6, 109.7, 108.6, 61.7, 42.5, 15.9, 14.1. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_9H_{12}N_3O_2$ : 194.0924; found: 194.0922.

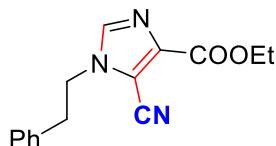


**Ethyl 5-cyano-1-isopropyl-1H-imidazole-4-carboxylate (28d)**: yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 67% isolated yield (277.4 mg).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.75 (s, 1H), 4.65 – 4.55 (m, 1H), 4.45 (q,  $J = 7.1$  Hz, 2H), 1.64 (d,  $J = 6.8$  Hz, 6H), 1.43 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.3, 141.3, 137.7, 109.9, 108.1, 61.8, 51.2, 22.9, 14.1. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{10}H_{14}N_3O_2$ : 208.1081; found: 208.1080.

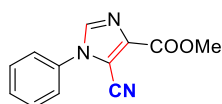


**Ethyl 1-(tert-butyl)-5-cyano-1H-imidazole-4-carboxylate (29d)**: yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 45% isolated yield (198.9 mg). m.

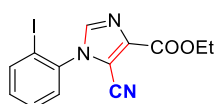
p. = 74-76 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.77 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.4, 143.6, 137.7, 111.4, 106.9, 61.7, 59.6, 29.6, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>: 222.1237; found: 222.1233.



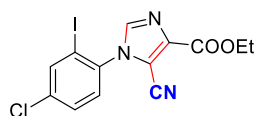
**Ethyl 5-cyano-1-phenethyl-1H-imidazole-4-carboxylate (30d)**: yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 82% isolated yield (441.2 mg). m. p. = 71-73 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.25 (m, 4H), 7.06 (d, *J* = 1.4 Hz, 1H), 7.04 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.37 (t, *J* = 6.9 Hz, 2H), 3.14 (t, *J* = 6.9 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.2, 141.2, 140.4, 135.6, 129.1, 128.5, 127.6, 109.7, 108.6, 61.8, 48.9, 36.8, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>: 270.1237; found: 270.1235.



**Methyl 5-cyano-1-phenyl-1H-imidazole-4-carboxylate (31d)**: yellow solid was obtained with 66% filtrated yield (299.6 mg). m. p. = 139-141 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.56 (m, 3H), 7.45 (m, 2H), 3.94 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.6, 141.8, 140.0, 133.7, 130.4, 130.3, 124.4, 109.6, 109.2, 52.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: 228.0768; found: 228.0766.

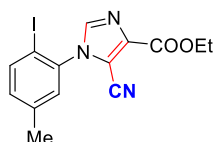


**Ethyl 5-cyano-1-(2-iodophenyl)-1H-imidazole-4-carboxylate (32d)**: yellow solid was obtained with 51% isolated yield (373.3 mg). m. p. = 95-97 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.69 (s, 1H), 7.50 (td, *J* = 7.7, 1.2 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.26 (td, *J* = 7.8, 1.5 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.1, 141.4, 140.7, 140.6, 136.5, 132.6, 129.8, 128.2, 109.1, 96.1, 62.0, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>IN<sub>3</sub>O<sub>2</sub>: 367.9891; found: 367.9891.

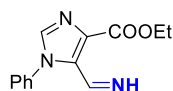


**Ethyl 1-(4-chloro-2-iodophenyl)-5-cyano-1H-imidazole-4-carboxylate (33d)**: yellow oil was

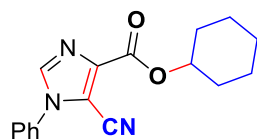
obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 38% isolated yield (304.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 2.2 Hz, 1H), 7.68 (s, 1H), 7.49 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.9, 141.5, 140.6, 140.0, 138.1, 135.1, 130.1, 128.7, 110.3, 108.9, 96.6, 62.1, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>9</sub>ClIN<sub>3</sub>O<sub>2</sub>: 401.9501; found: 401.9501.



**Ethyl 5-cyano-1-(2-iodo-5-methylphenyl)-1H-imidazole-4-carboxylate (34d):** yellow solid was obtained with 35% filtrated yield (266.7 mg). m. p. = 108-110 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.15 (d, *J* = 1.4 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.1, 141.3, 140.7, 140.6, 140.1, 136.3, 133.5, 128.8, 110.3, 109.1, 91.7, 62.0, 20.8, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>IN<sub>3</sub>O<sub>2</sub>: 382.0047; found: 382.0043.



**Ethyl 5-(iminomethyl)-1-phenyl-1H-imidazole-4-carboxylate (1f):** white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 98% isolated yield (47.6 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.53 (s, 1H), 7.65 (s, 1H), 7.53 (m, 3H), 7.32 (m, 2H), 5.83 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 164.7, 159.5, 140.2, 137.0, 133.0, 130.5, 129.0, 129.0, 125.8, 62.2, 14.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>: 244.1081; found: 244.1080.



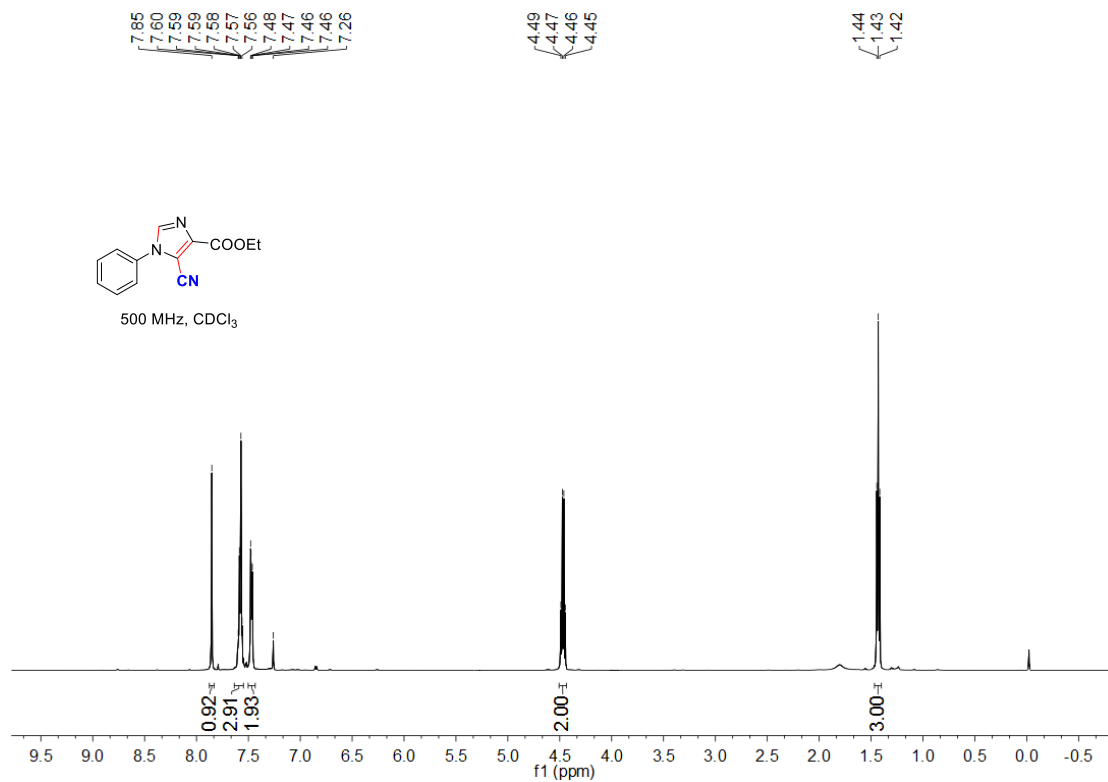
**Cyclohexyl 5-cyano-1-phenyl-1H-imidazole-4-carboxylate (1g):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 94% isolated yield (55.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (s, 1H), 7.64 – 7.55 (m, 3H), 7.50 – 7.44 (m, 2H), 5.24 – 4.98 (m, 1H), 2.04 – 1.91 (m, 2H), 1.87 – 1.77 (m, 2H), 1.72 – 1.61 (m, 2H), 1.60 – 1.52 (m, 1H), 1.49 – 1.38 (m, 2H), 1.38 – 1.31 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.6, 142.5, 139.9, 133.9, 130.3, 130.3,

124.4, 109.8, 109.0, 74.6, 31.4, 25.3, 23.5. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{17}H_{18}N_3O_2$ :  
296.1394; found: 296.1392.

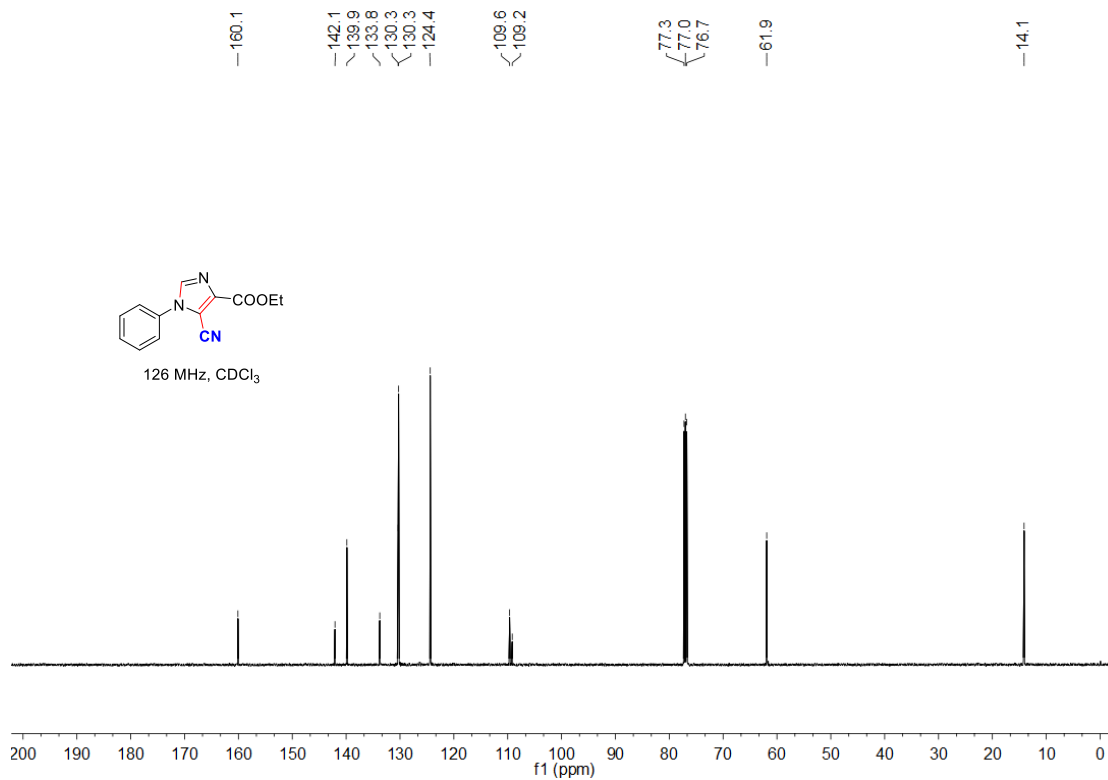
## 5. Copies of product NMR Spectra

**1d**

**<sup>1</sup>H NMR**

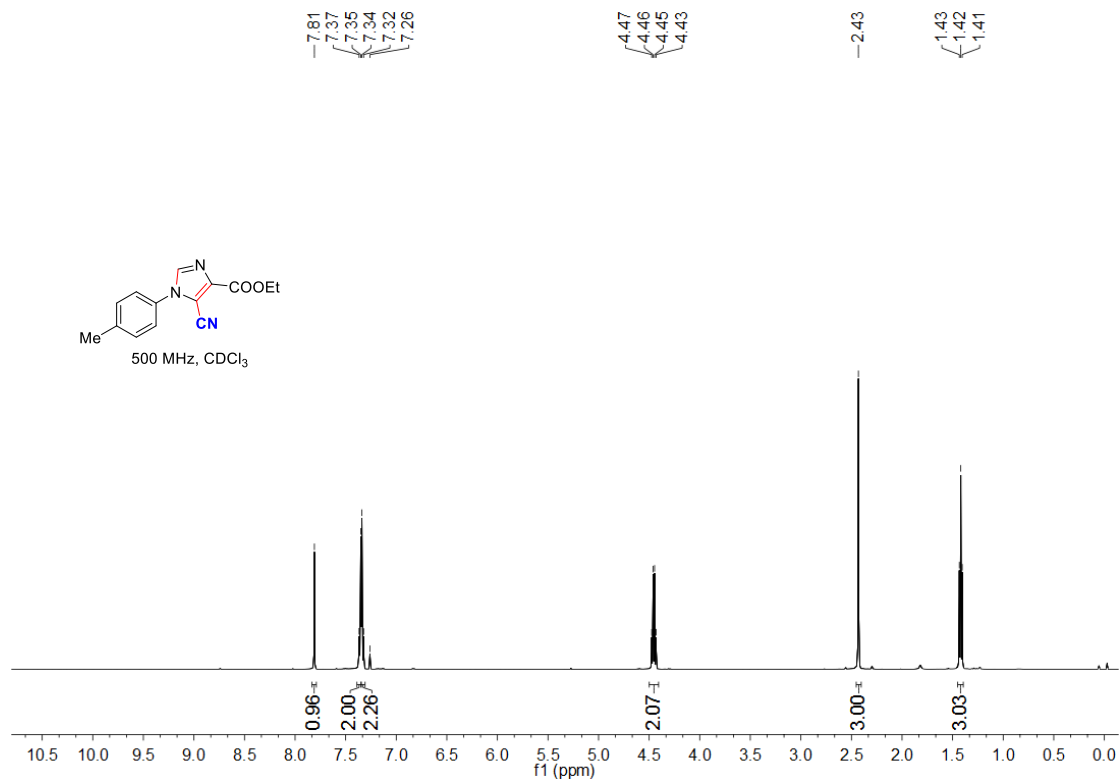


**<sup>13</sup>C NMR**

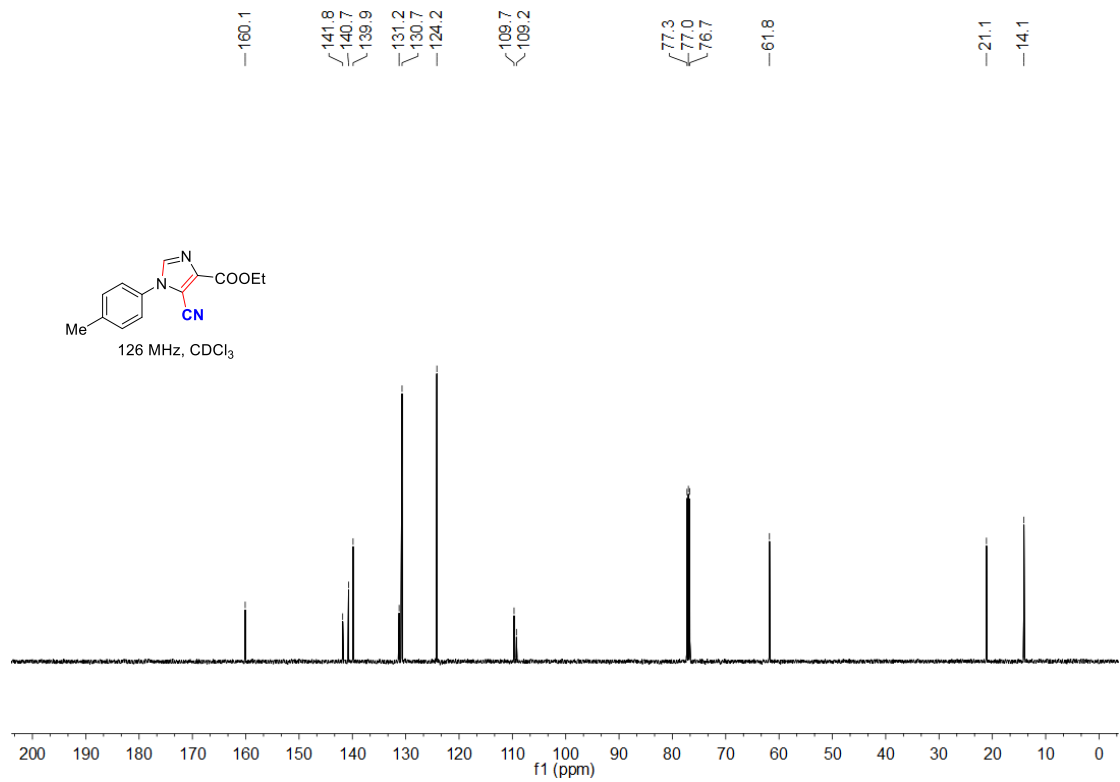


## 2d

### <sup>1</sup>H NMR

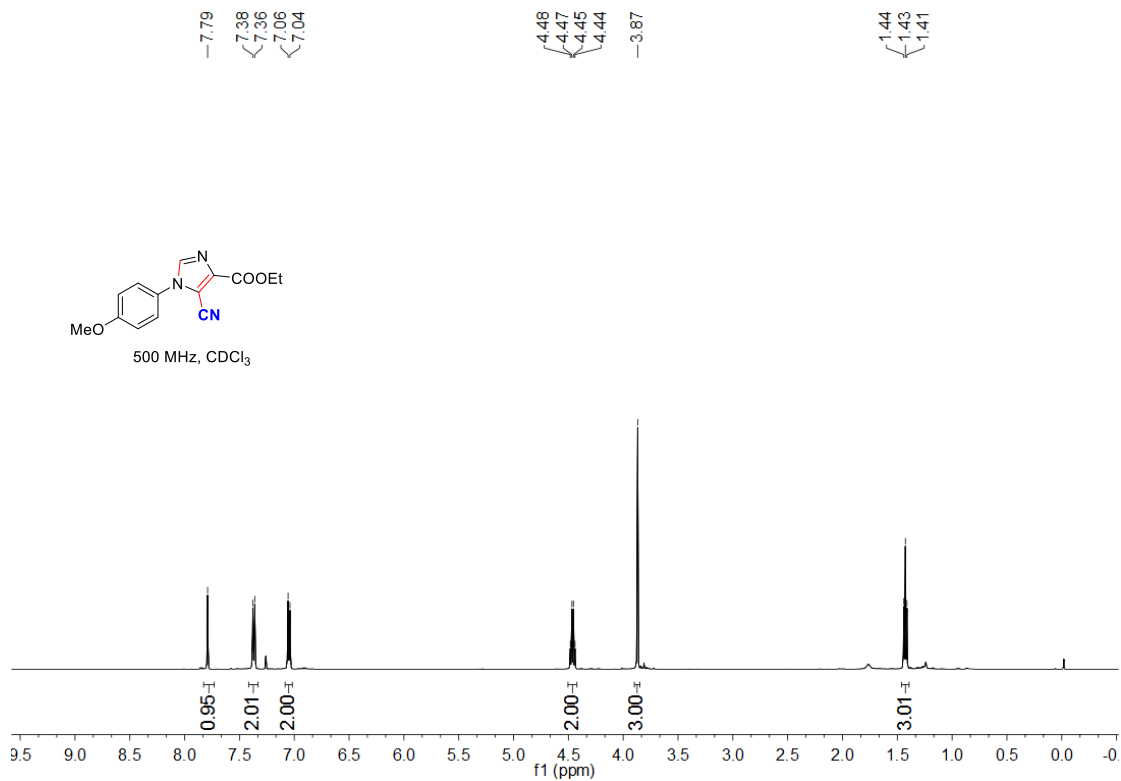


### <sup>13</sup>C NMR

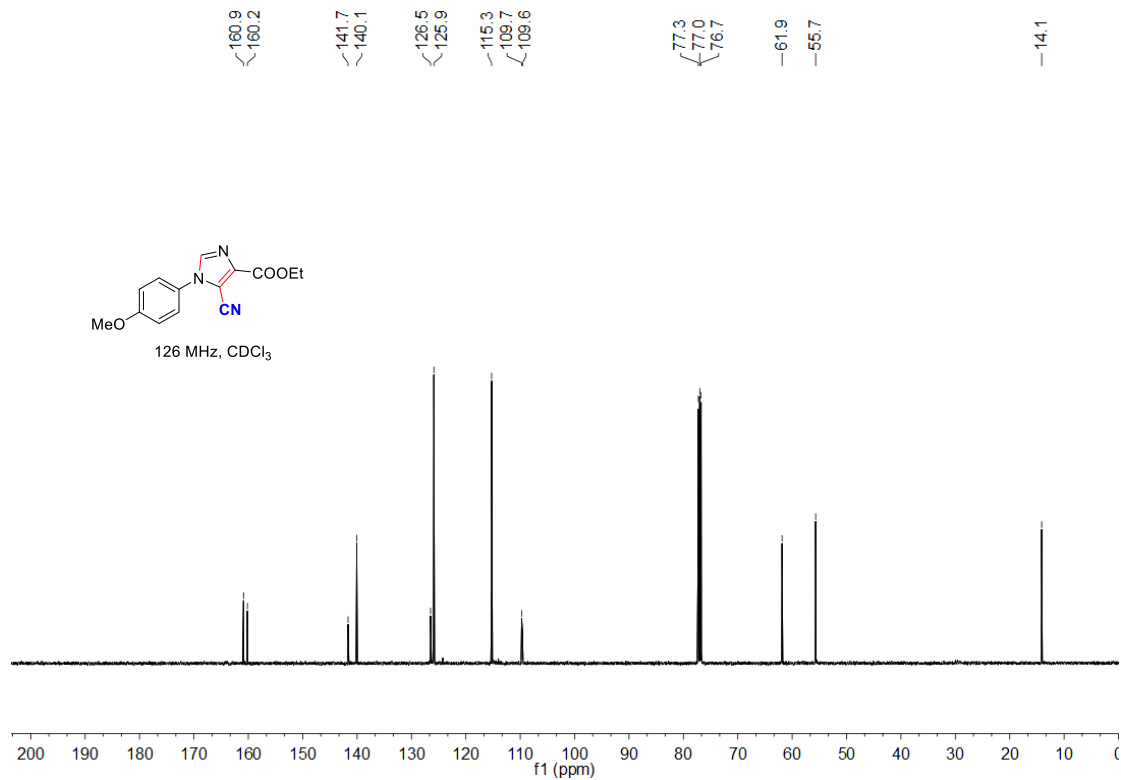


### 3d

#### <sup>1</sup>H NMR



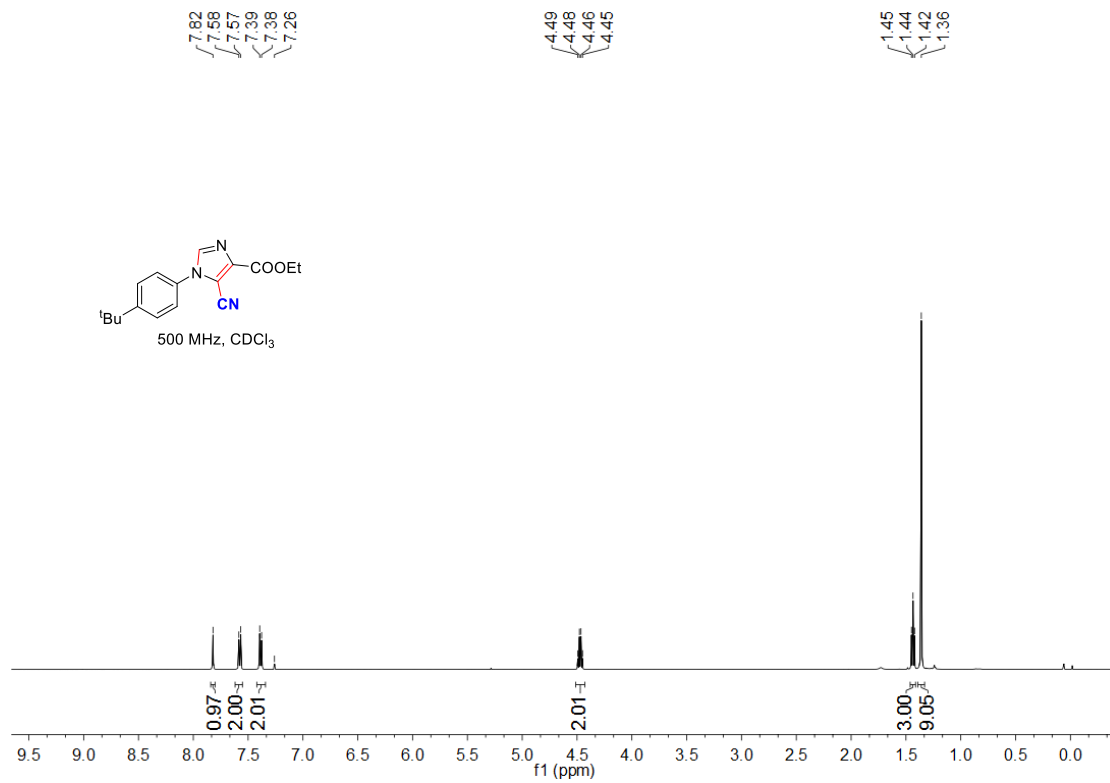
#### <sup>13</sup>C NMR



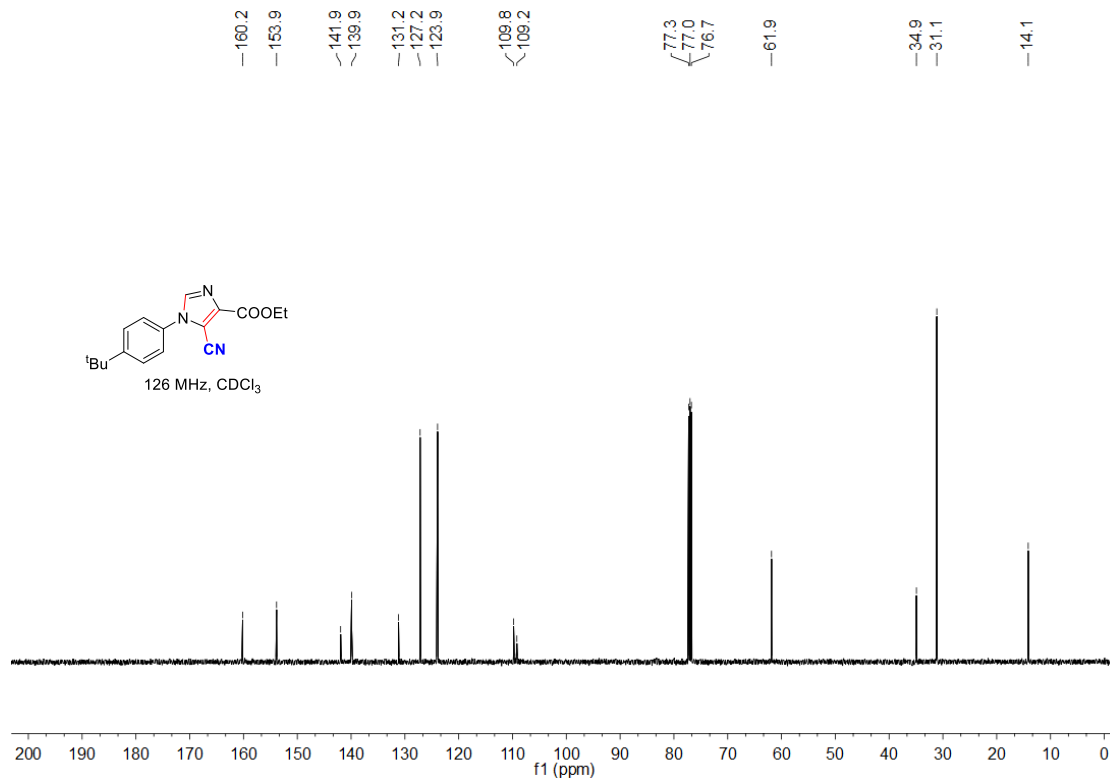


### 4d

### <sup>1</sup>H NMR



### <sup>13</sup>C NMR



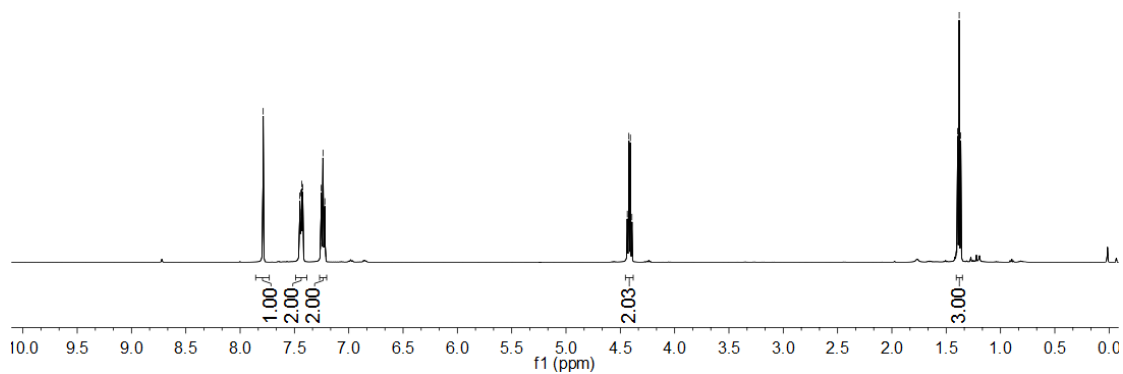
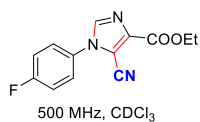
# 5d

## <sup>1</sup>H NMR

7.79  
7.45  
7.44  
7.44  
7.43  
7.42  
7.26  
7.25  
7.24  
7.23  
7.22

4.44  
4.42  
4.41  
4.39

1.39  
1.38  
1.37



## <sup>13</sup>C NMR

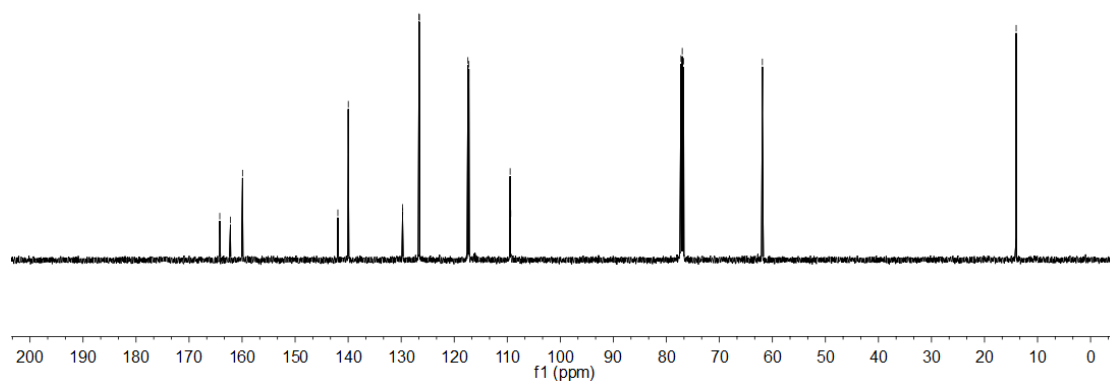
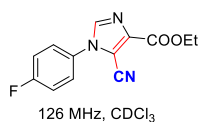
164.2  
162.2  
159.9

141.9  
140.0  
129.7  
129.7  
126.6  
126.6  
117.4  
117.2  
109.5  
109.3

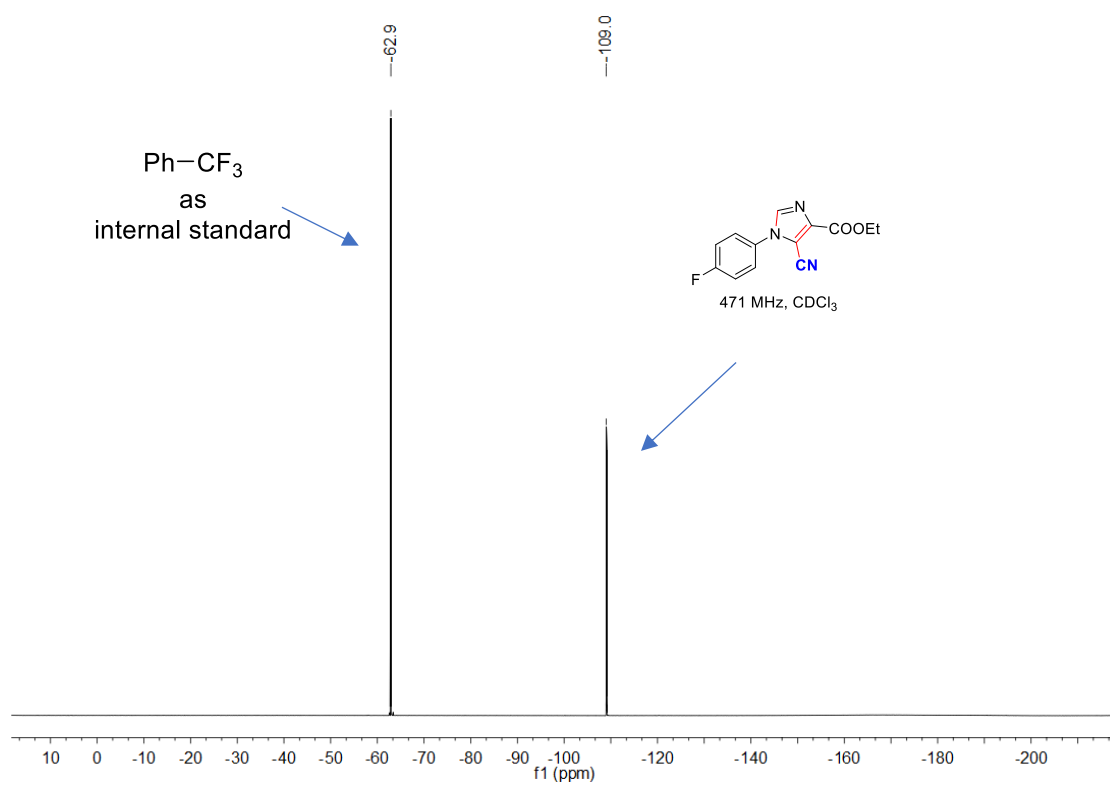
77.3  
77.0  
76.7

61.9

14.0



# <sup>19</sup>F NMR



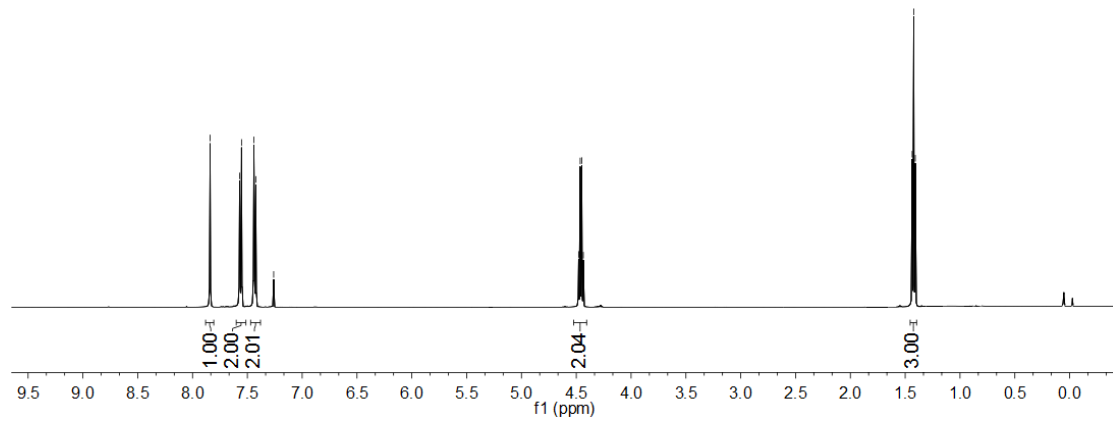
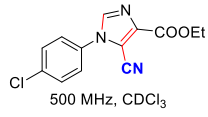
# 6d

## <sup>1</sup>H NMR

7.64  
7.57  
7.55  
7.44  
7.42  
7.26

4.48  
4.46  
4.45  
4.44

1.44  
1.42  
1.41



## <sup>13</sup>C NMR

159.9

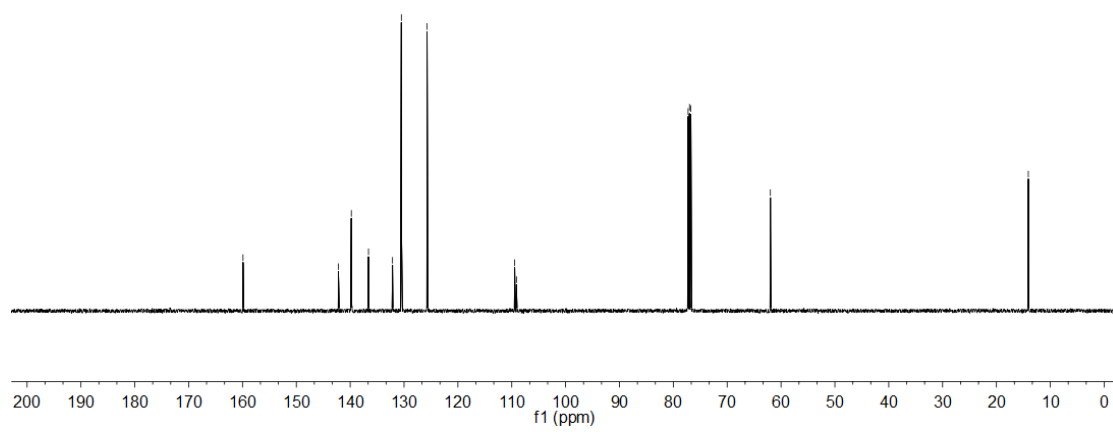
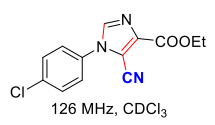
142.2  
139.8  
136.6  
132.1  
130.5  
125.7

109.5  
109.1

77.3  
77.0  
76.7

62.0

14.1



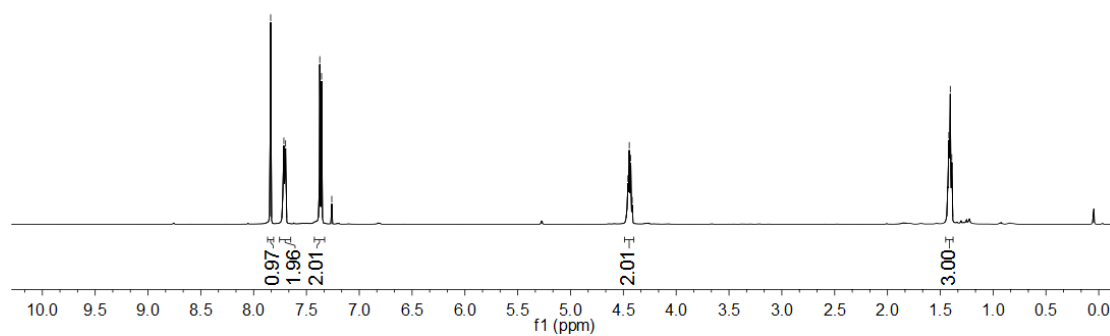
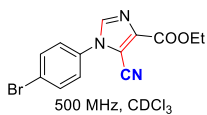
# 7d

## <sup>1</sup>H NMR

7.8387  
7.7137  
7.6972  
7.3739  
7.3586  
7.2602

4.4570  
4.4440  
4.4300  
4.4159

1.4181  
1.4053  
1.3912



## <sup>13</sup>C NMR

159.8

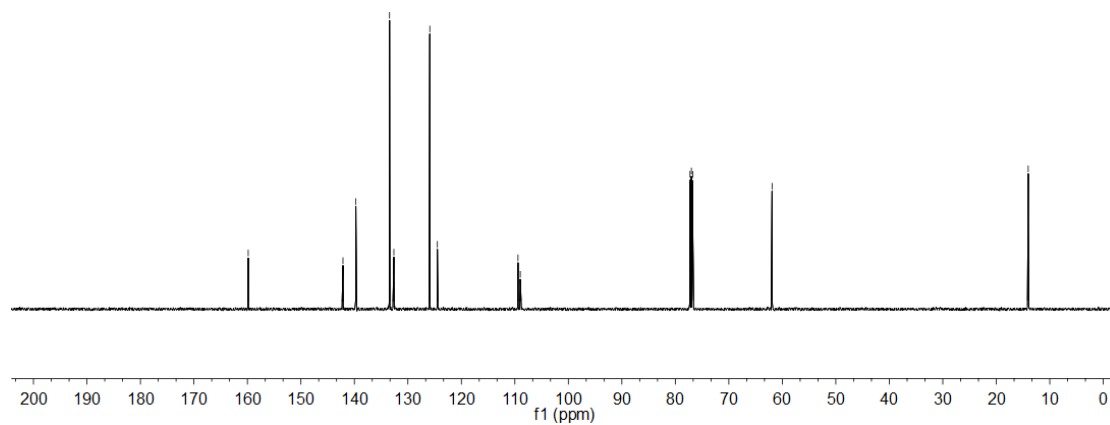
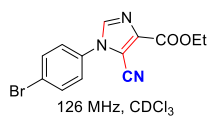
142.1  
139.7  
133.4  
132.6  
125.9  
124.5

109.4  
109.0

77.3  
77.0  
76.7

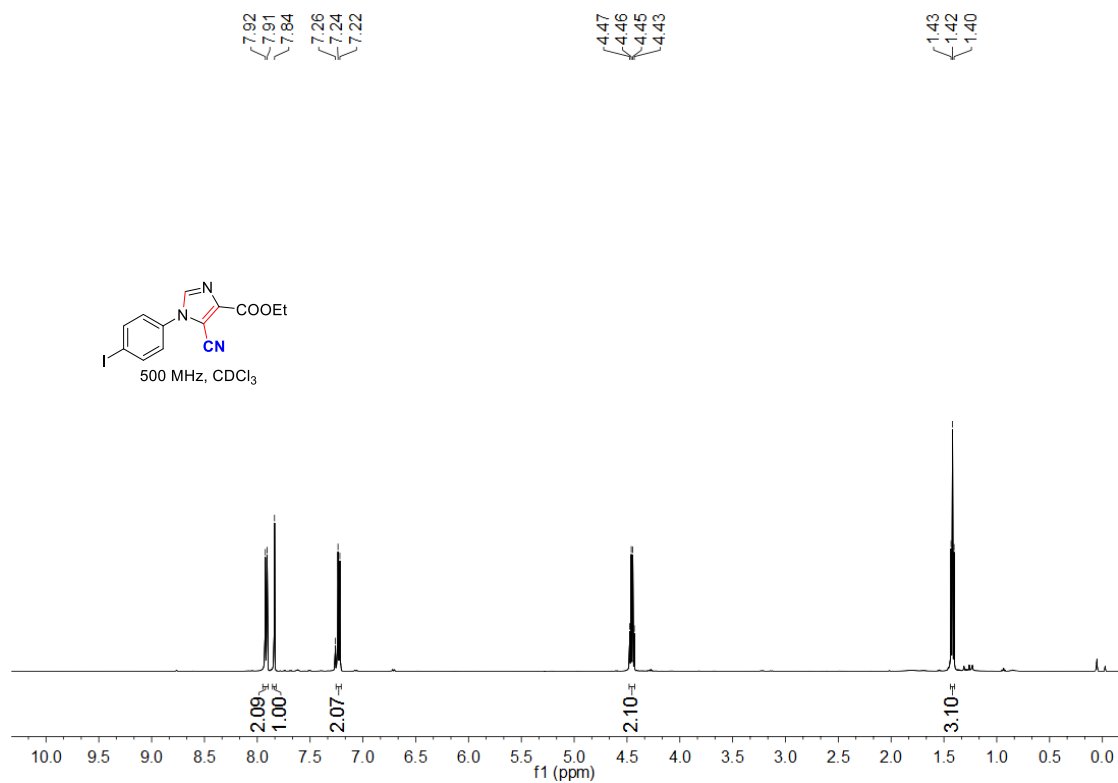
61.9

14.0

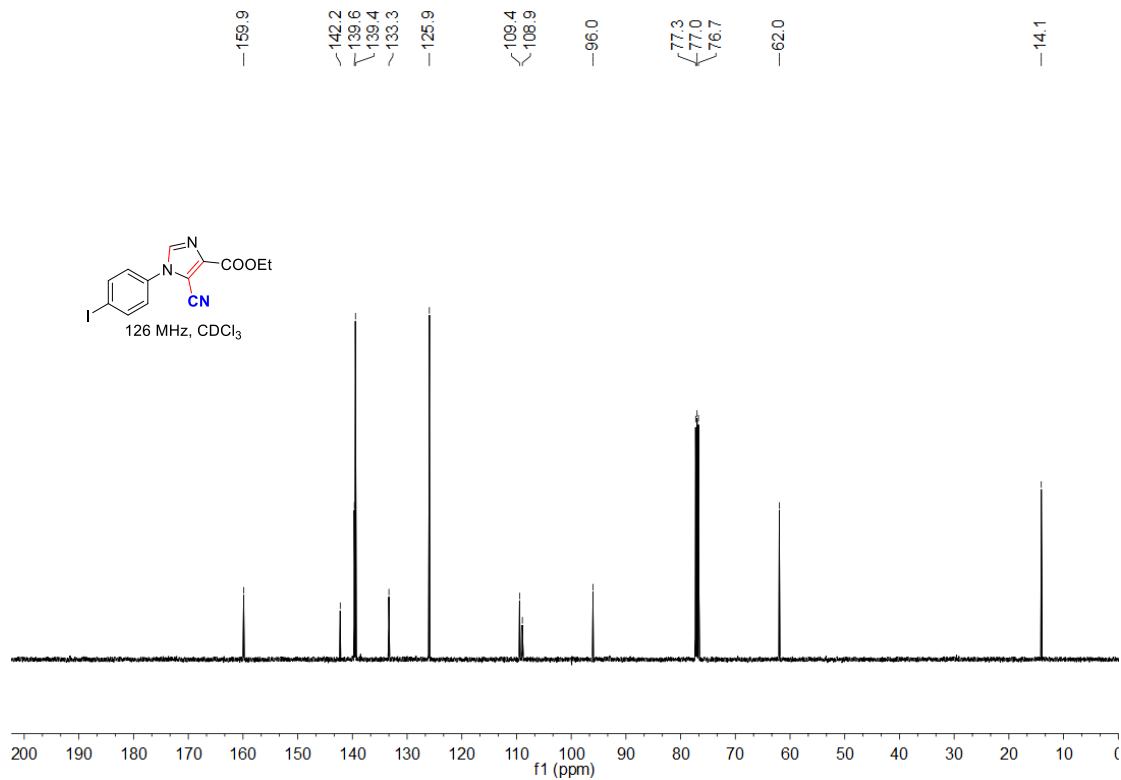


# 8d

## <sup>1</sup>H NMR

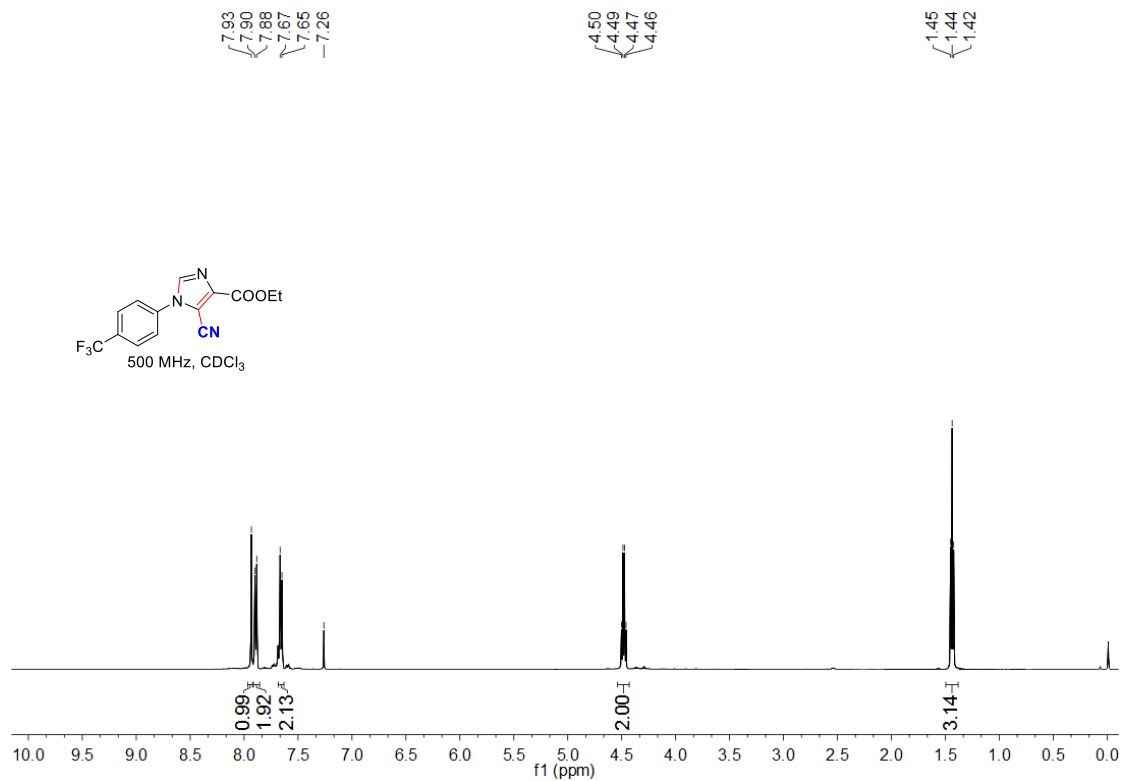


## <sup>13</sup>C NMR

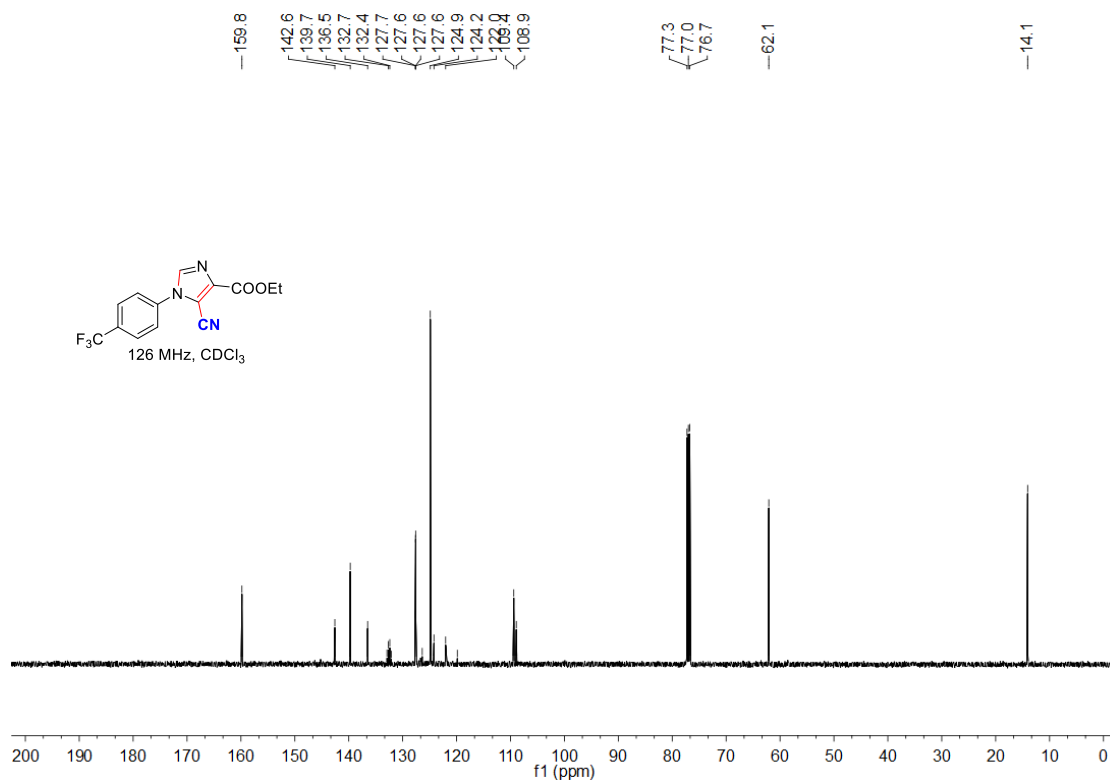


# 9d

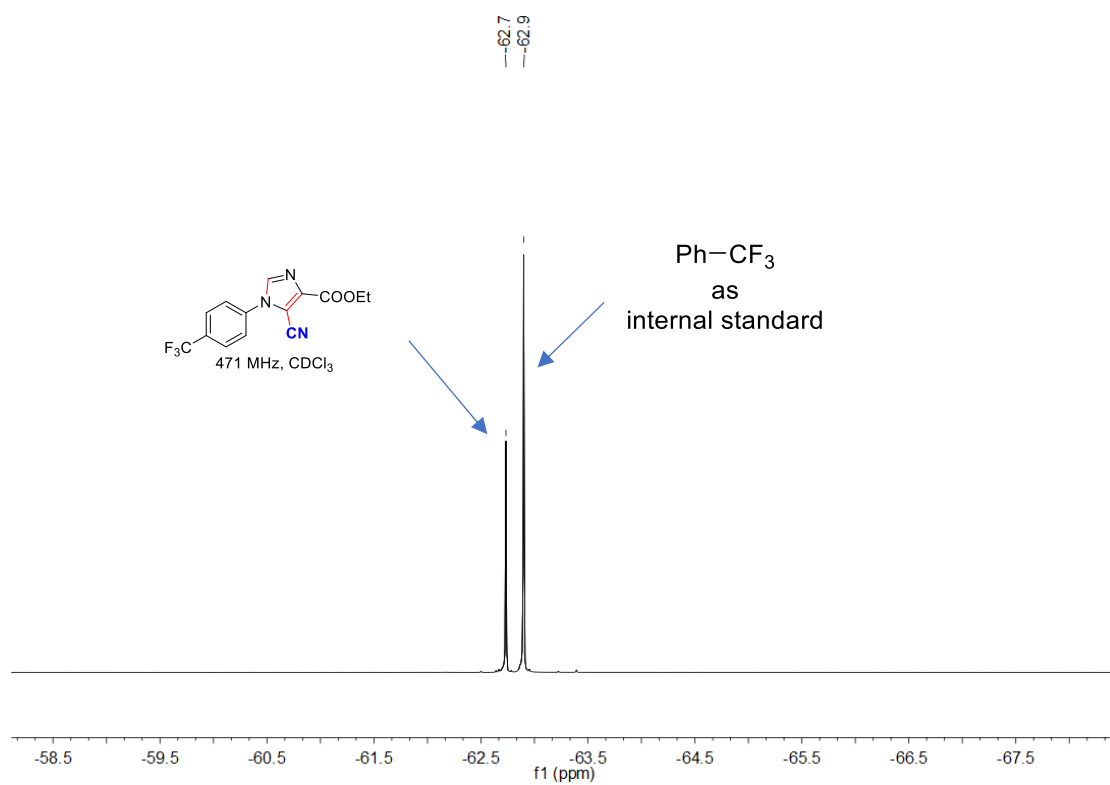
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR



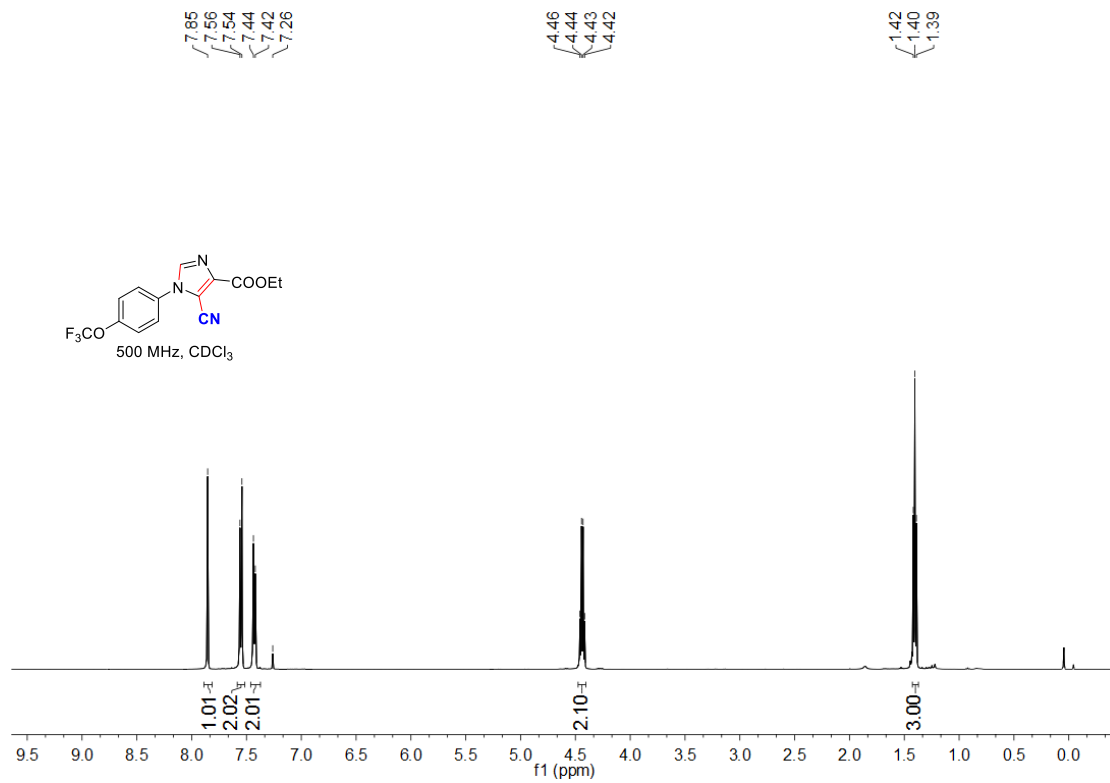
**<sup>19</sup>F NMR**



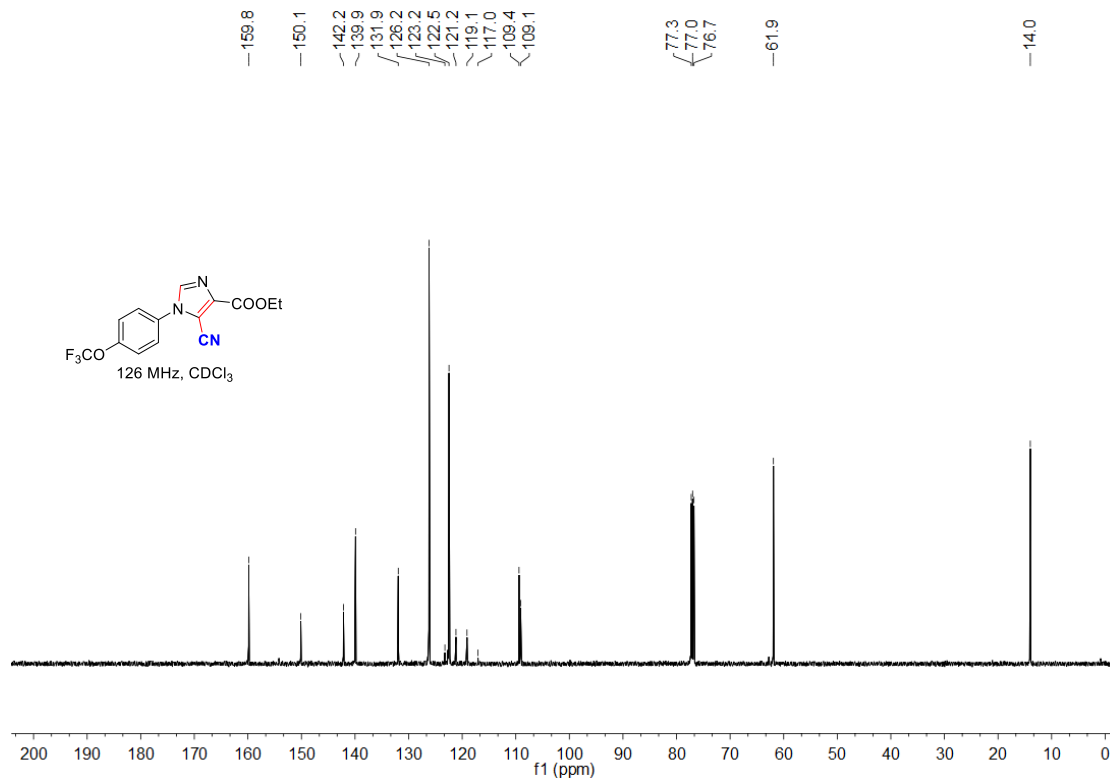


# 10d

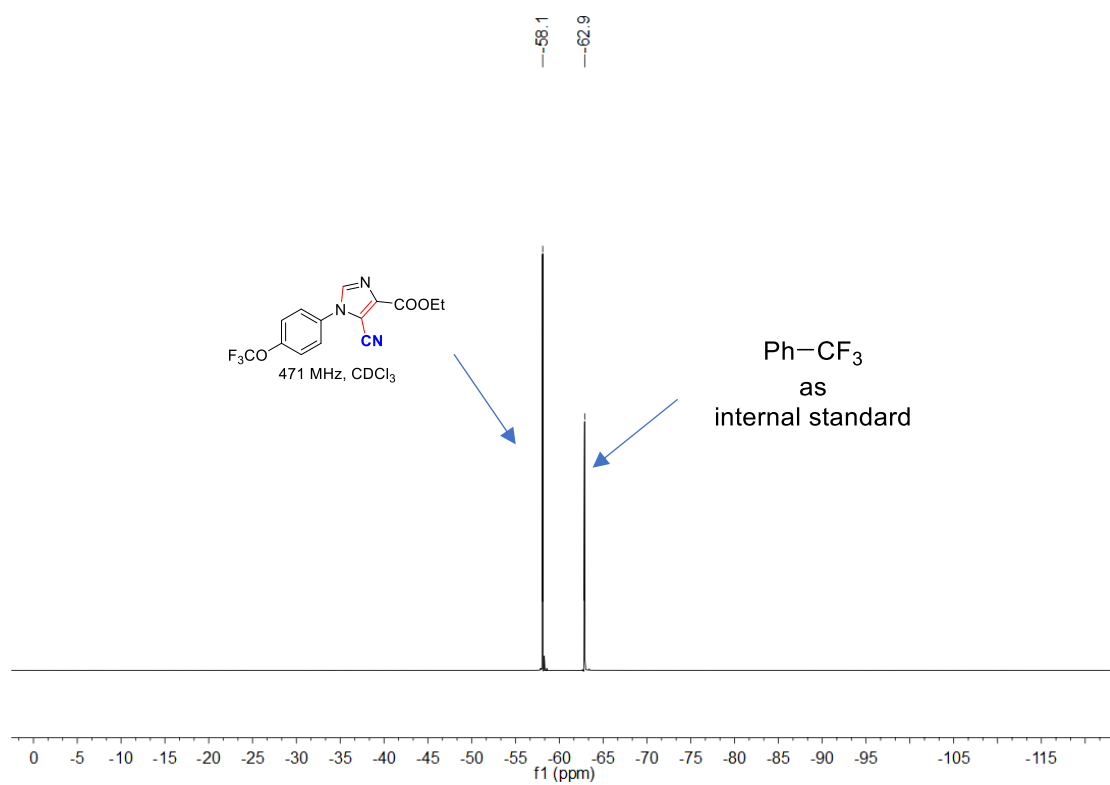
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR

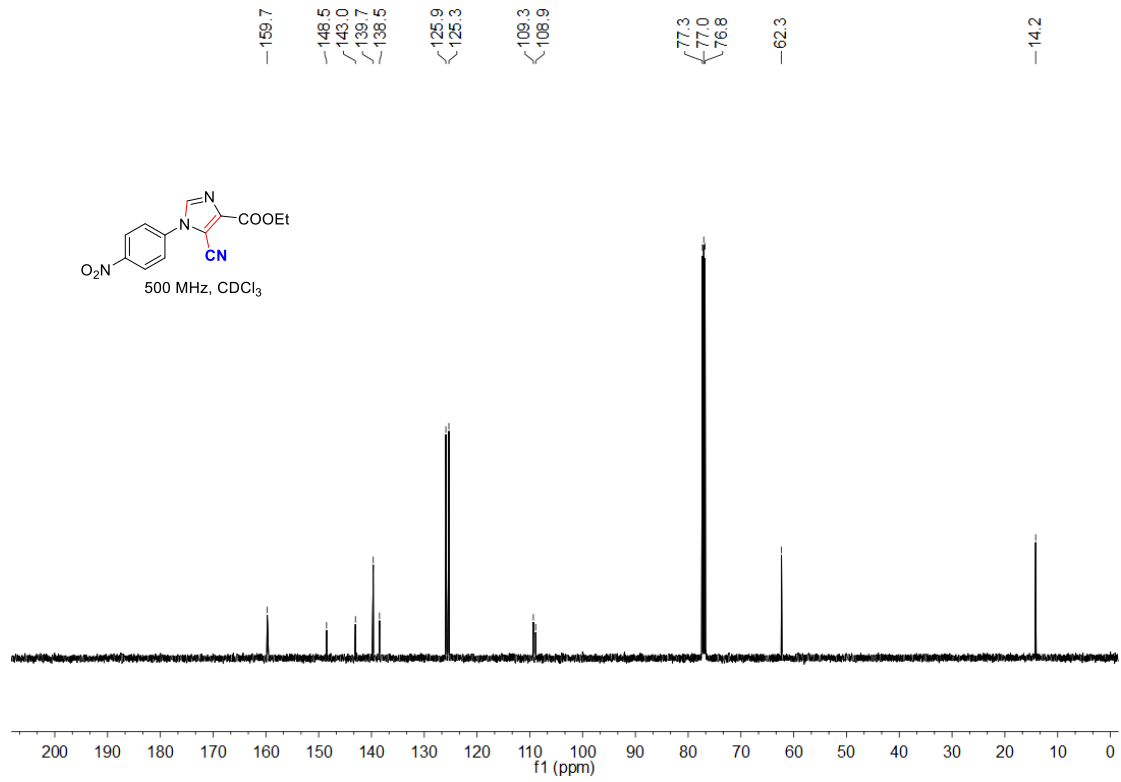


**<sup>19</sup>F NMR**

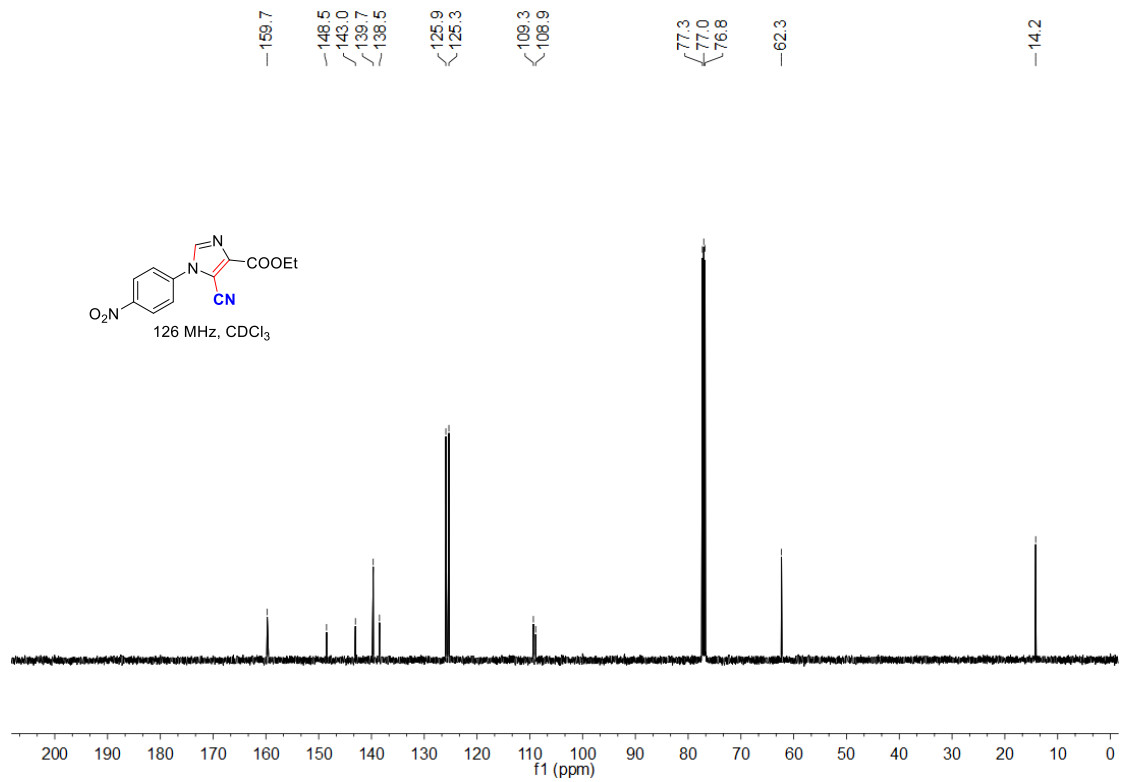


# 11d

## <sup>1</sup>H NMR

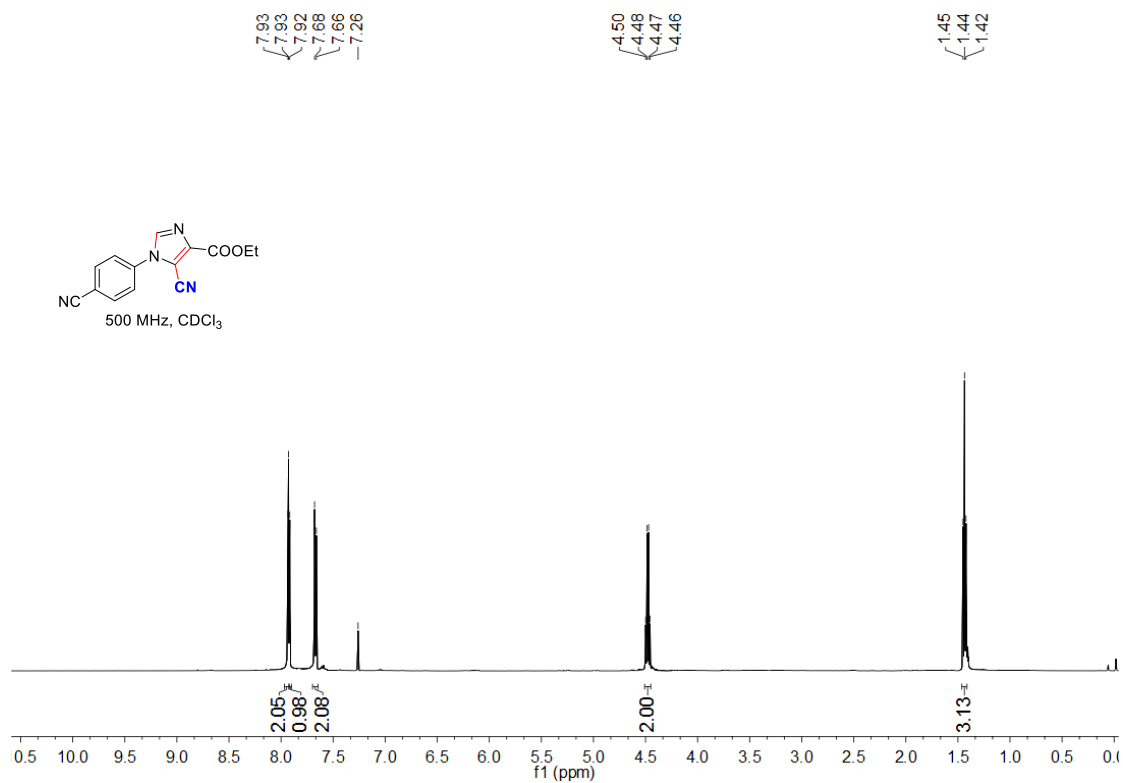


## <sup>13</sup>C NMR

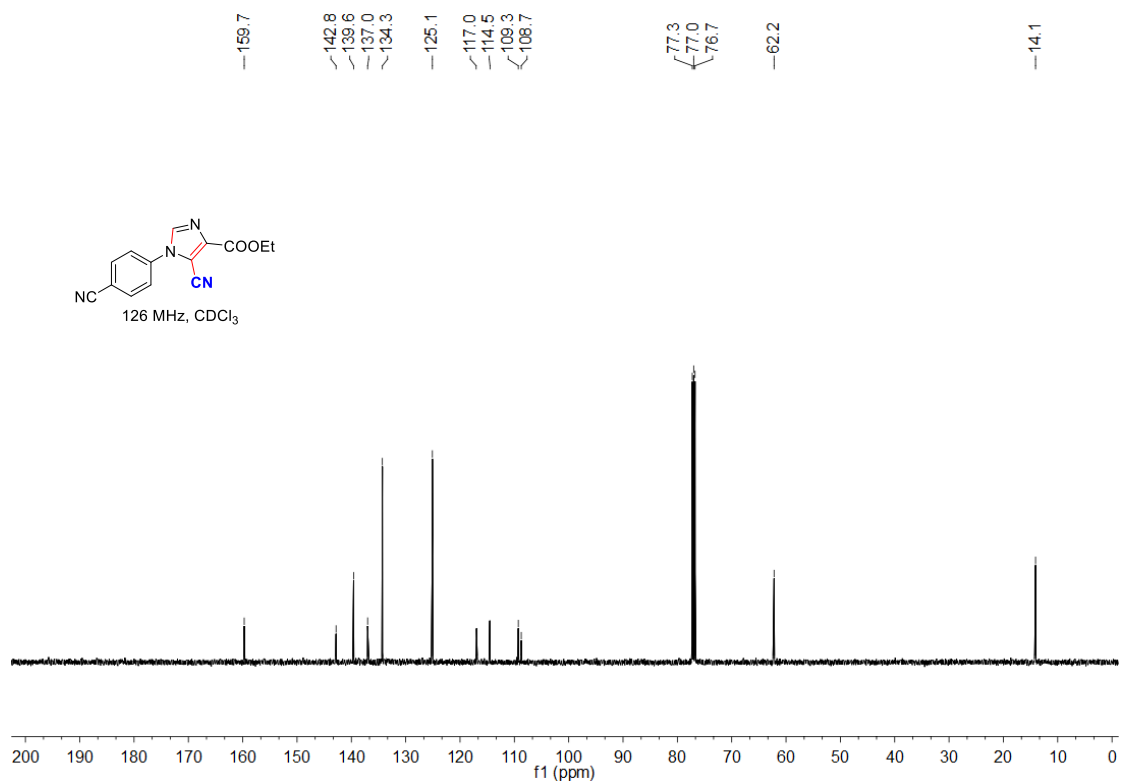


# 12d

## <sup>1</sup>H NMR

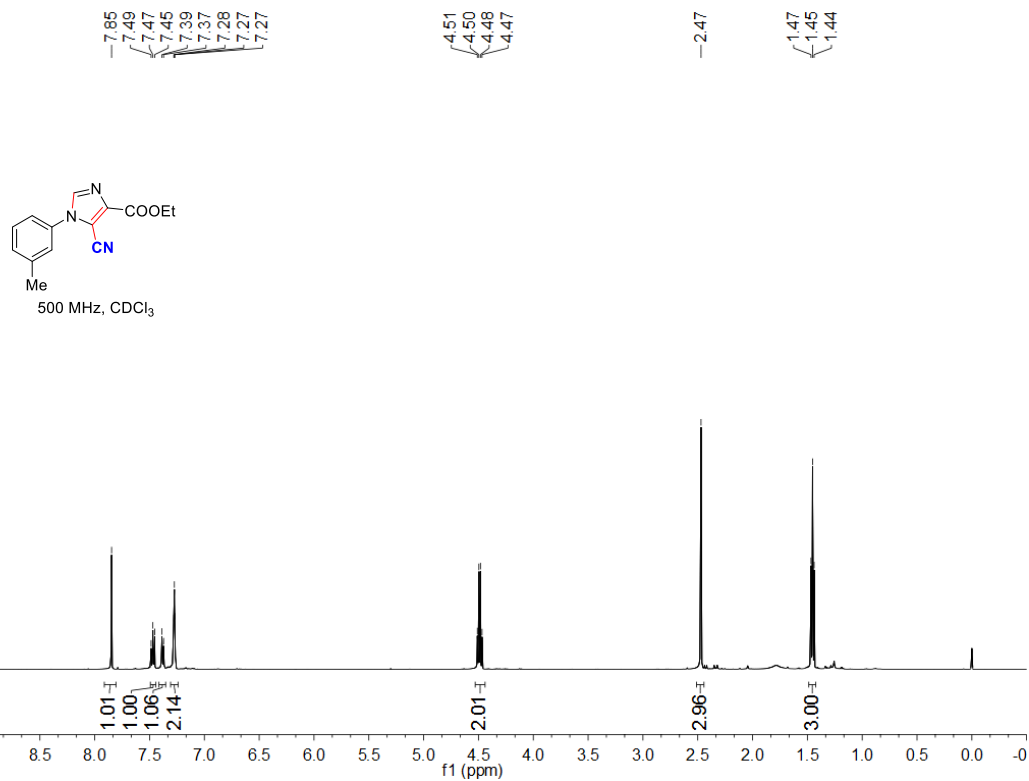


## <sup>13</sup>C NMR

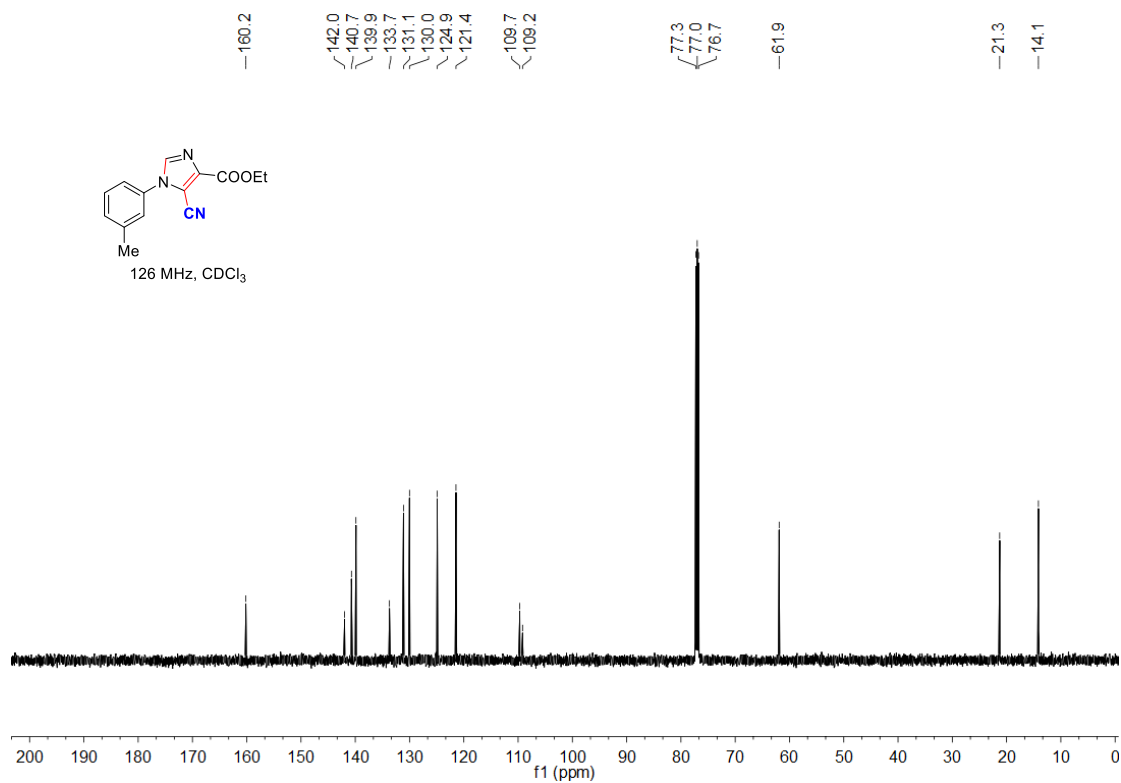


# 13d

## <sup>1</sup>H NMR

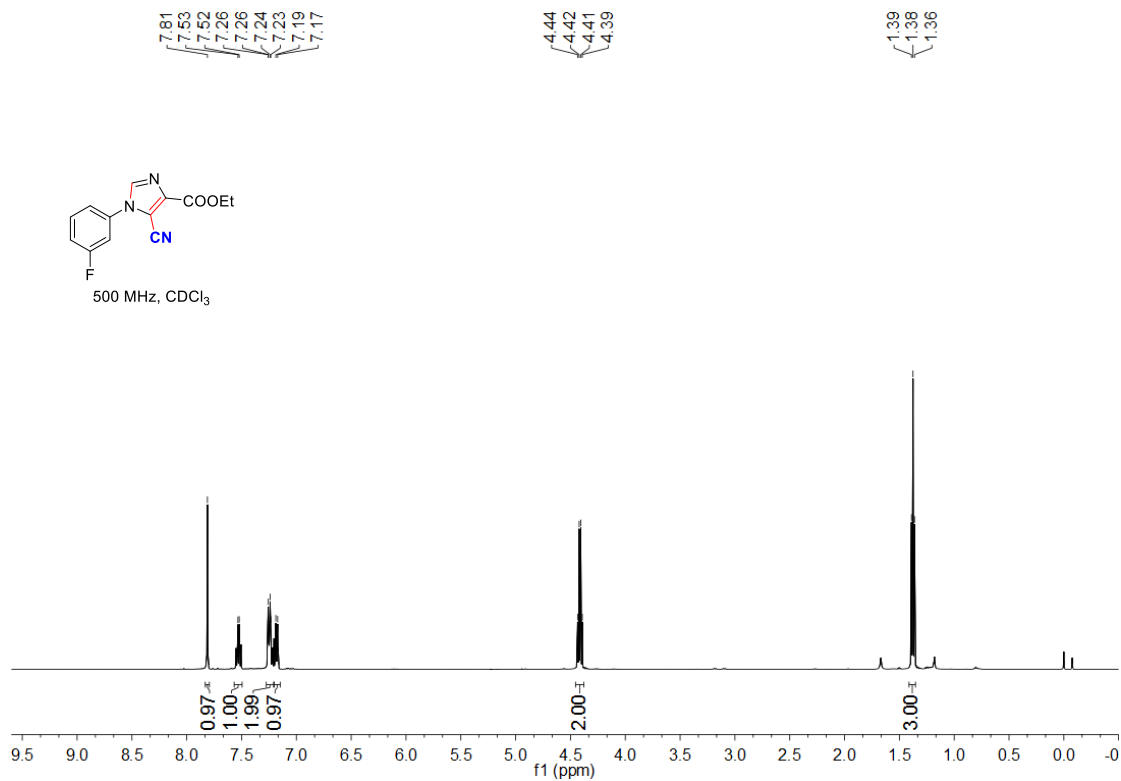


## <sup>13</sup>C NMR

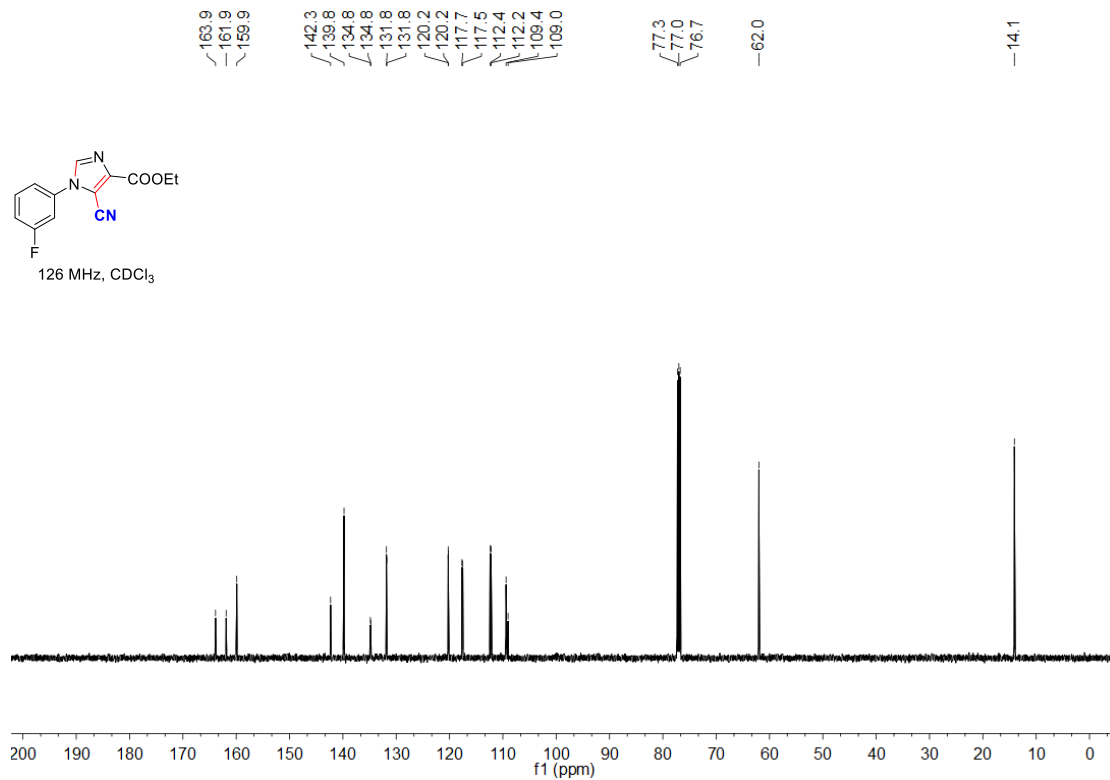


# 14d

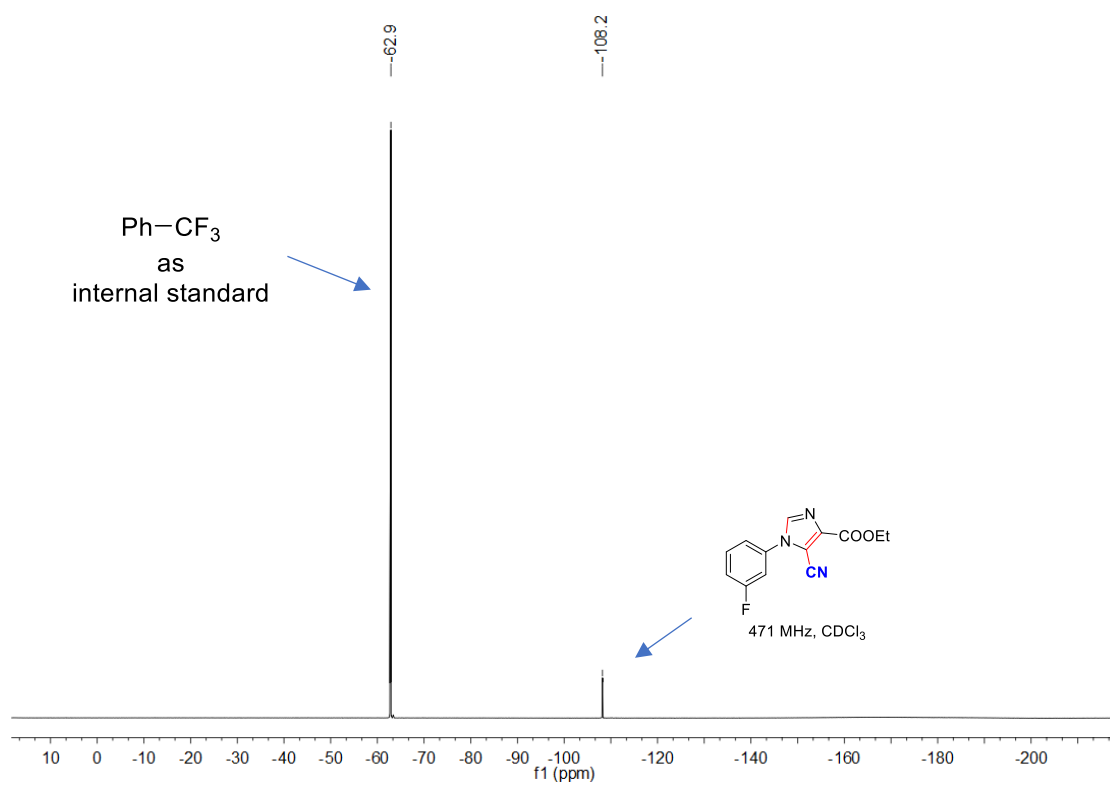
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR



# $^{19}\text{F}$ NMR



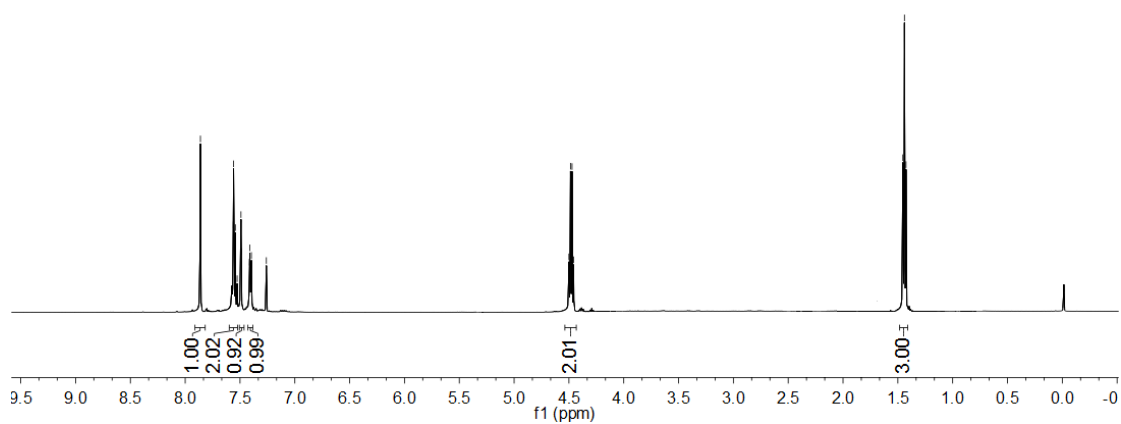
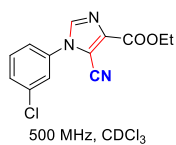
# 15d

## <sup>1</sup>H NMR

7.86  
7.56  
7.56  
7.54  
7.53  
7.49  
7.49  
7.41  
7.41  
7.40  
7.40  
7.39  
7.26

4.50  
4.49  
4.47  
4.46

1.45  
1.44  
1.43



## <sup>13</sup>C NMR

159.9

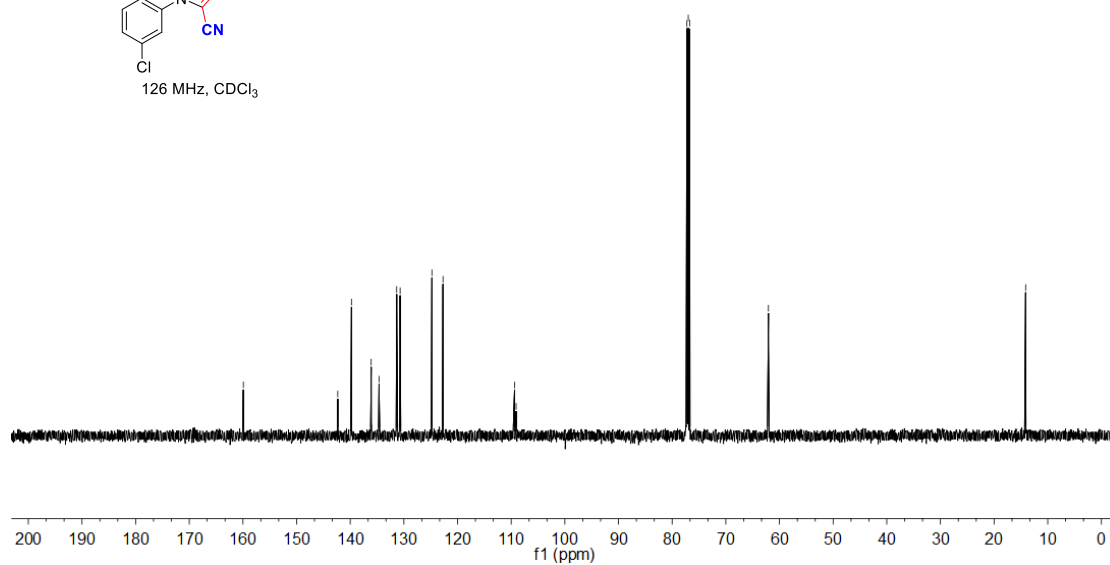
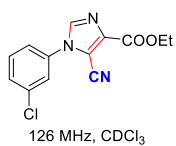
142.3  
139.8  
136.1  
134.6  
131.3  
130.7  
124.8  
122.7

109.4  
109.1

77.3  
77.0  
76.7

62.1

14.1





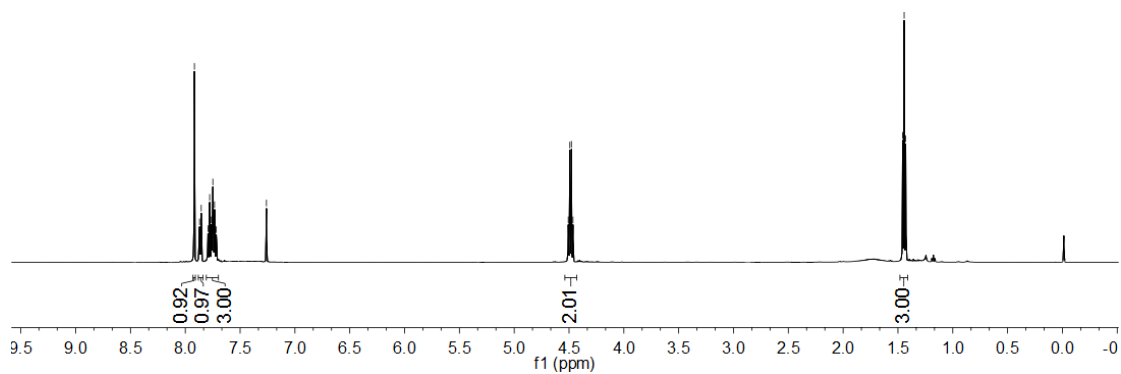
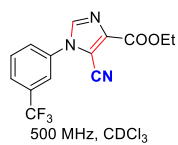
# 16d

## <sup>1</sup>H NMR

7.92  
7.87  
7.85  
7.79  
7.78  
7.76  
7.75  
7.73  
7.72  
7.26

4.51  
4.49  
4.48  
4.46

1.46  
1.44  
1.43



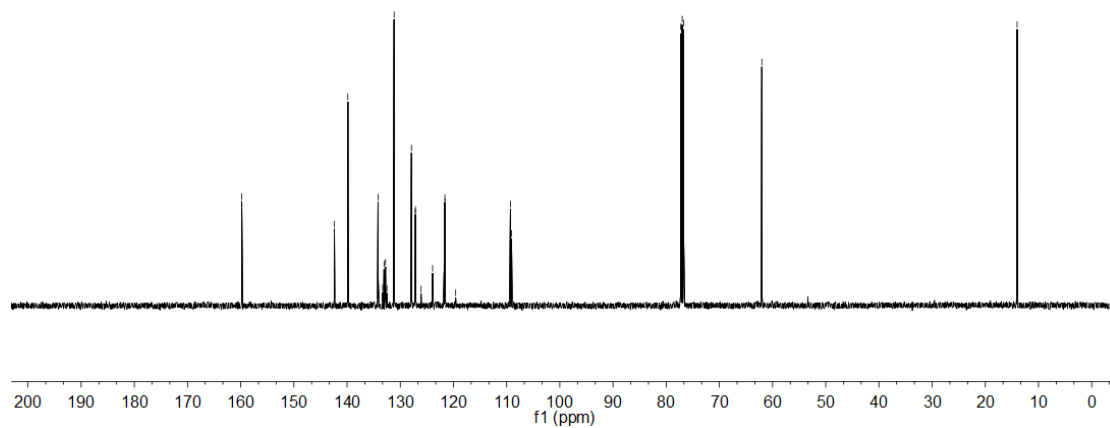
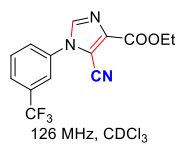
## <sup>13</sup>C NMR

159.8  
142.4  
139.9  
134.2  
133.0  
132.8  
131.2  
127.9  
127.2  
127.1  
121.6  
121.6  
109.5  
109.1

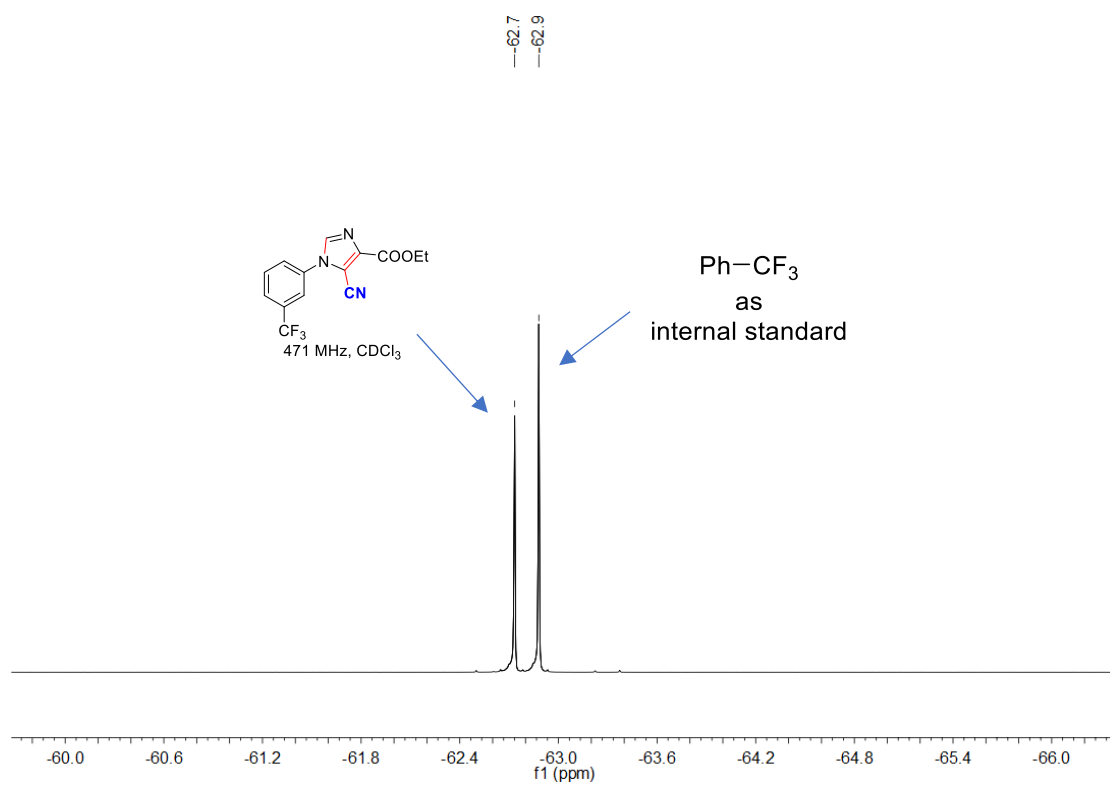
77.3  
77.0  
76.7

62.0

14.0



**<sup>19</sup>F NMR**



# 17d

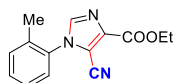
## <sup>1</sup>H NMR

7.70  
7.49  
7.47  
7.46  
7.41  
7.39  
7.38  
7.36  
7.35  
7.27  
7.26  
7.25

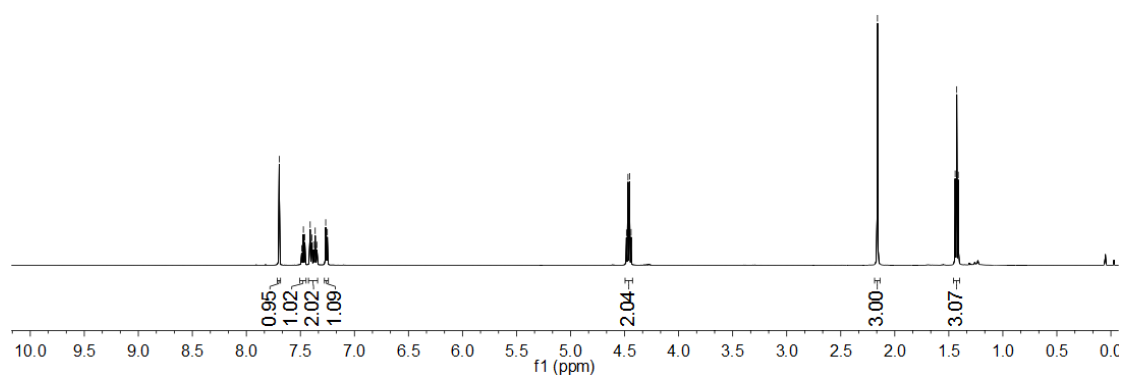
4.48  
4.47  
4.45  
4.44

-2.16

1.44  
1.43  
1.41



500 MHz, CDCl<sub>3</sub>



## <sup>13</sup>C NMR

-160.1

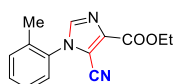
141.3  
140.6  
134.7  
132.6  
131.7  
131.0  
127.4  
127.0

110.4  
109.3

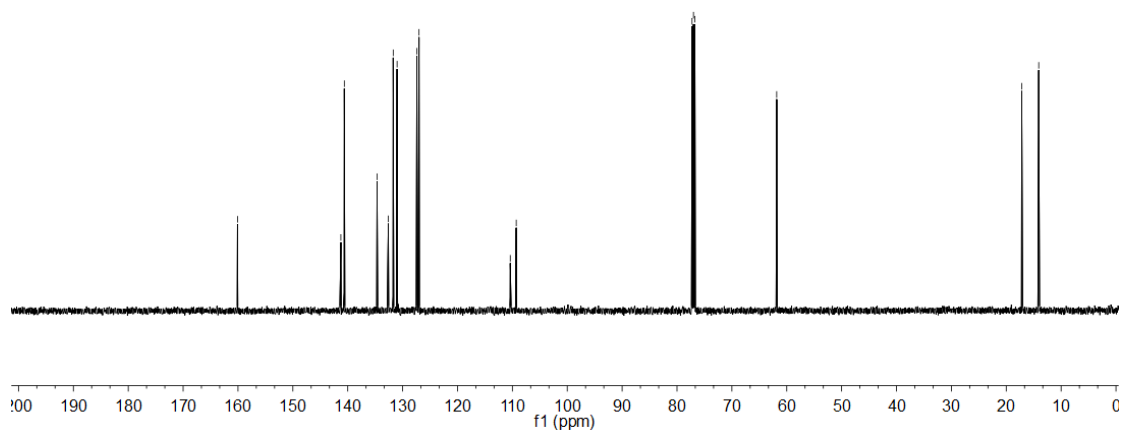
77.3  
77.0  
76.7

-61.8

-17.2  
-14.1

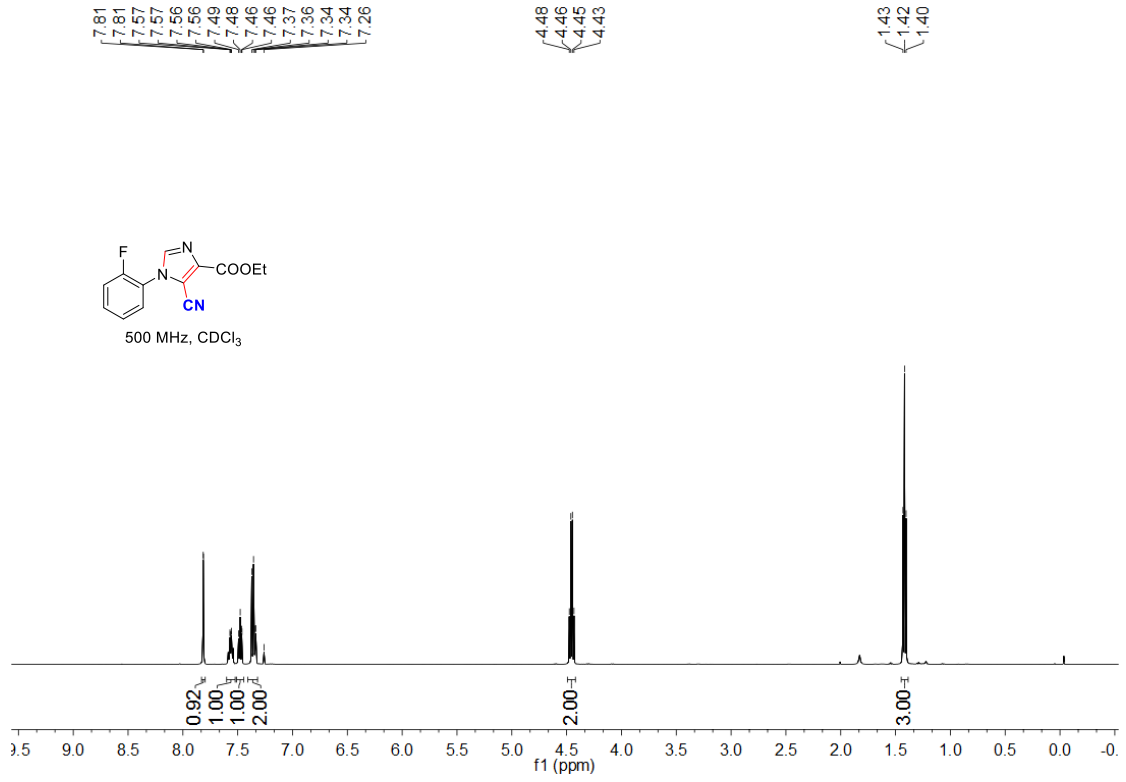


126 MHz, CDCl<sub>3</sub>

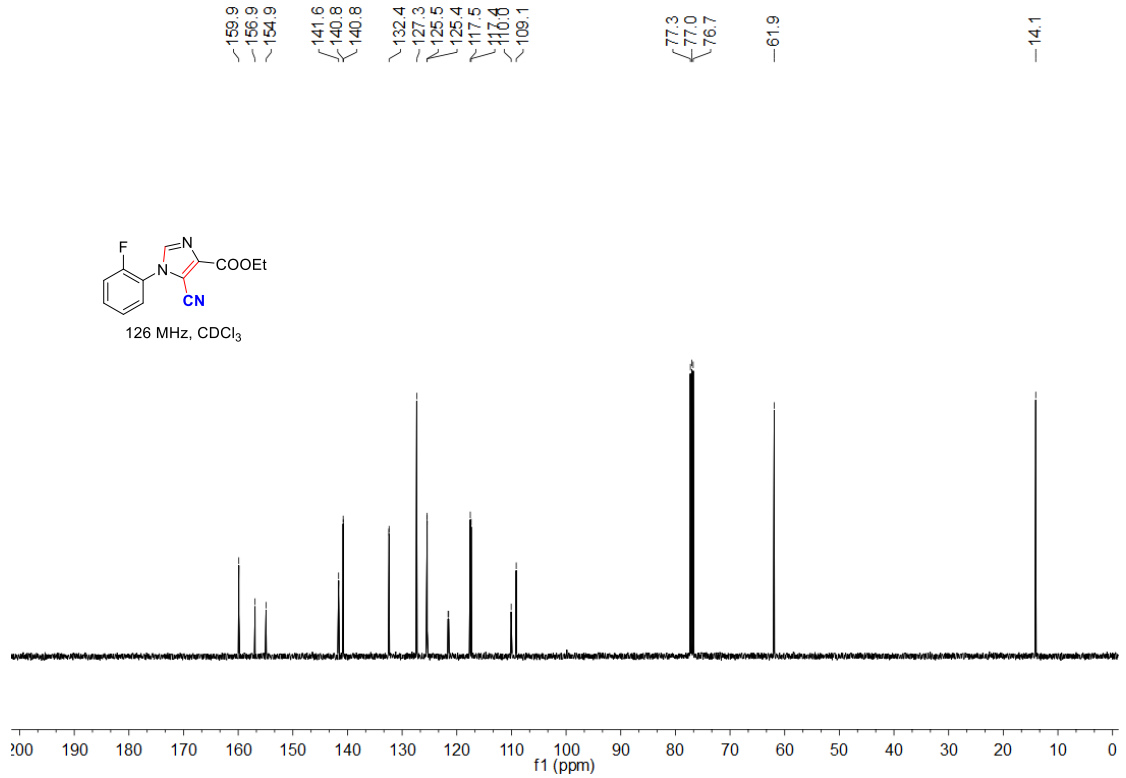


# 18d

## <sup>1</sup>H NMR

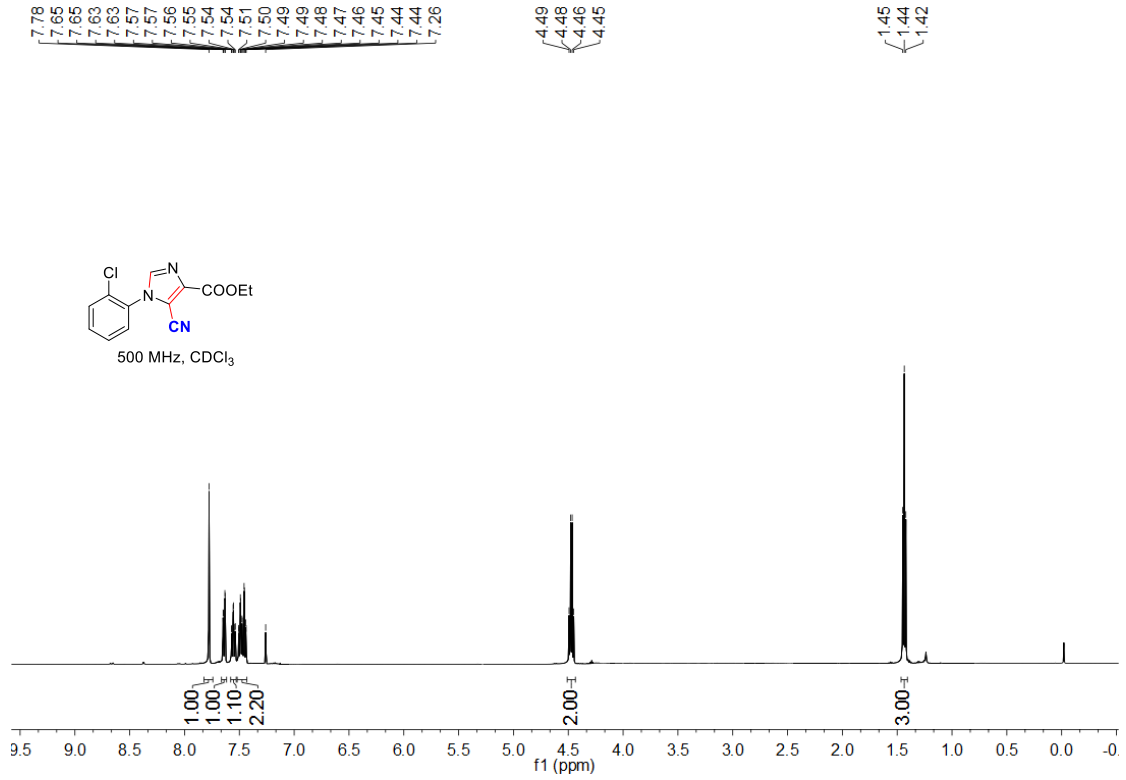


## <sup>13</sup>C NMR

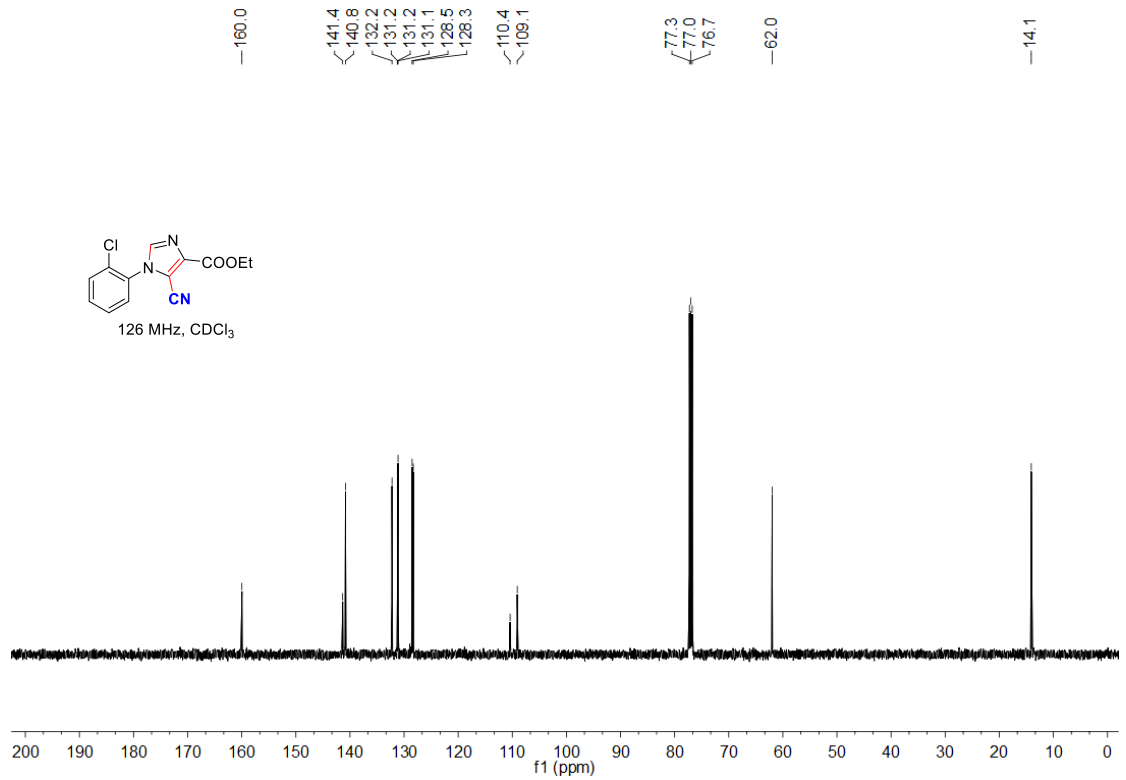


# 19d

## <sup>1</sup>H NMR

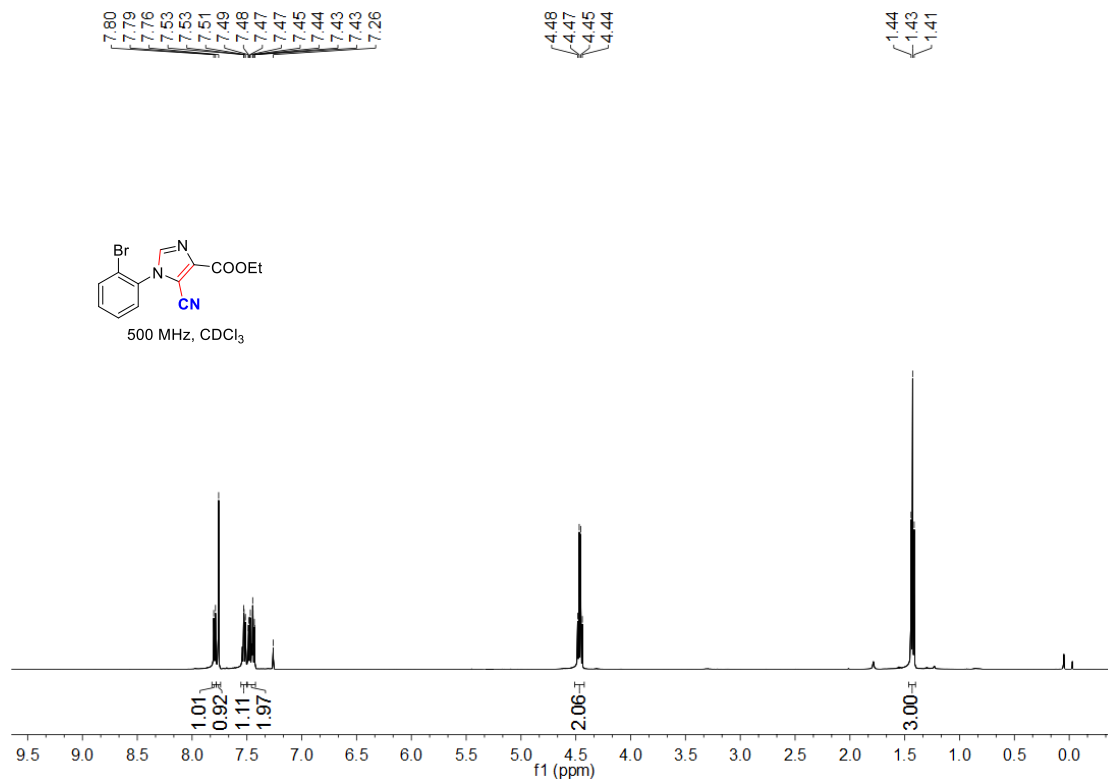


## <sup>13</sup>C NMR

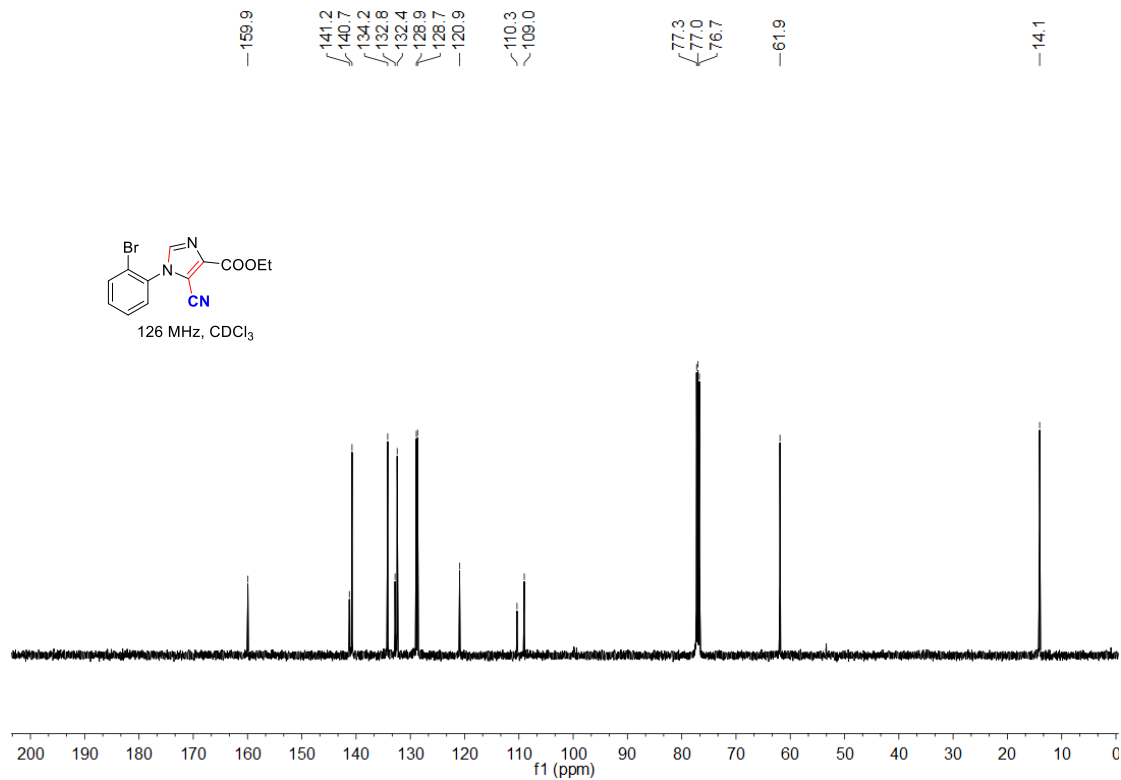


## 20d

### <sup>1</sup>H NMR

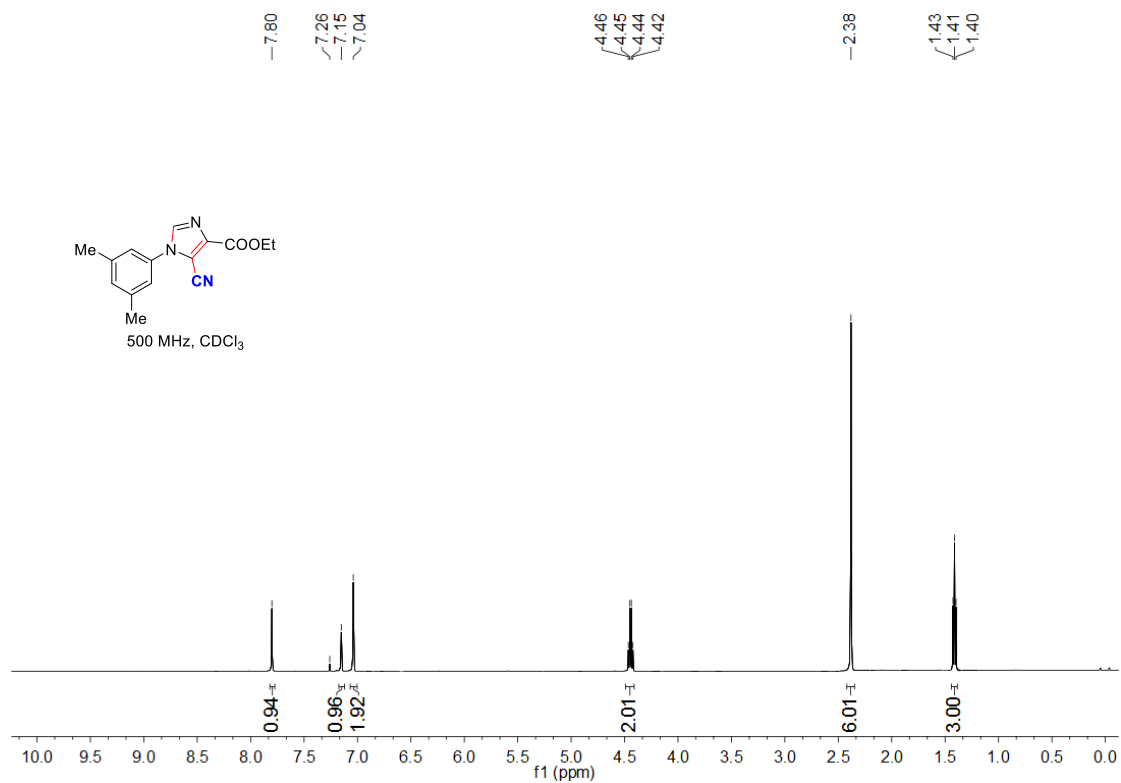


### <sup>13</sup>C NMR

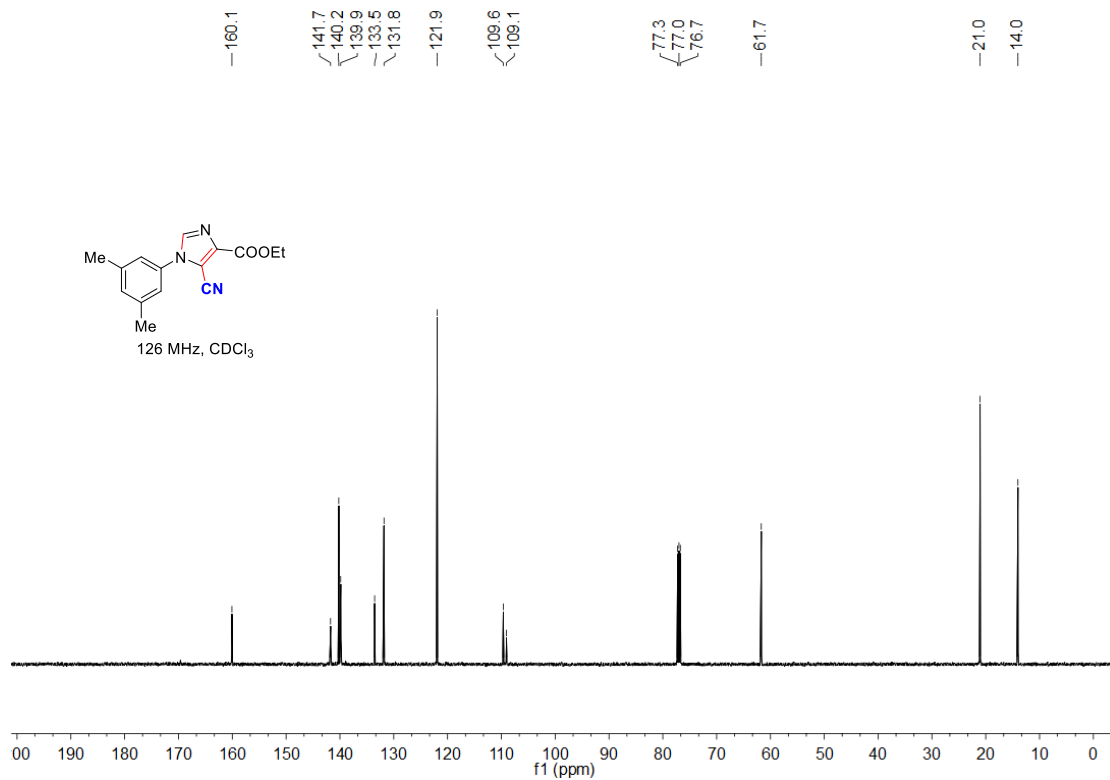


# 21d

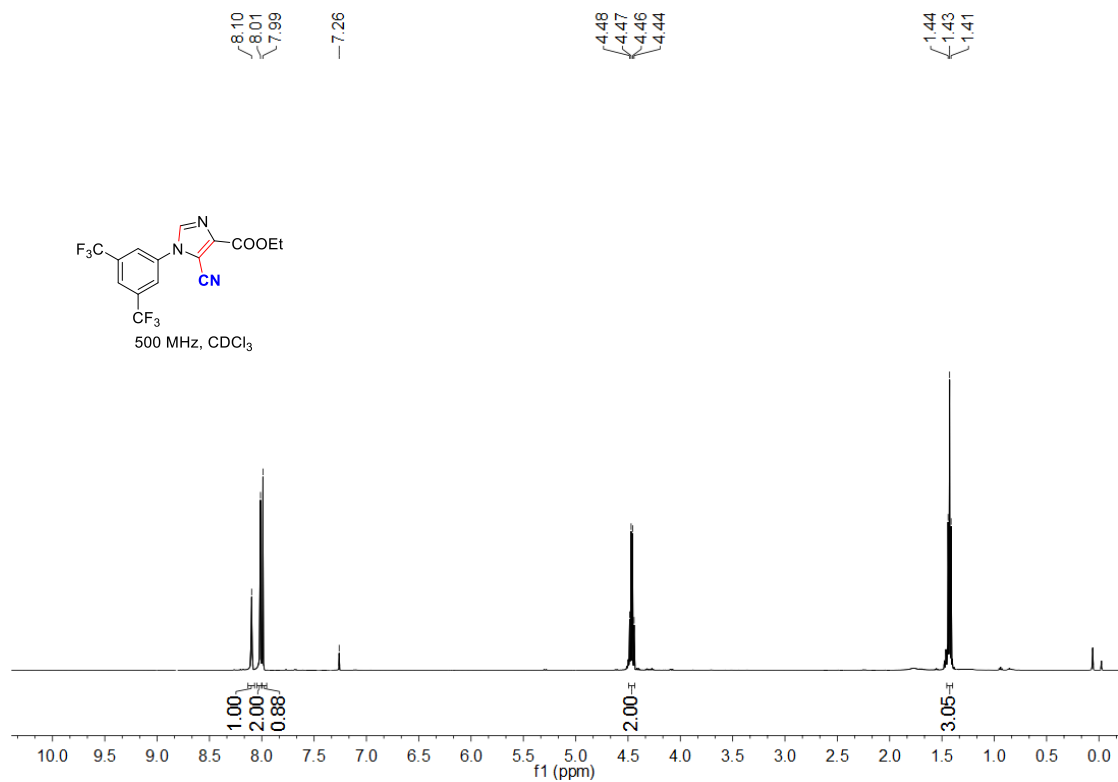
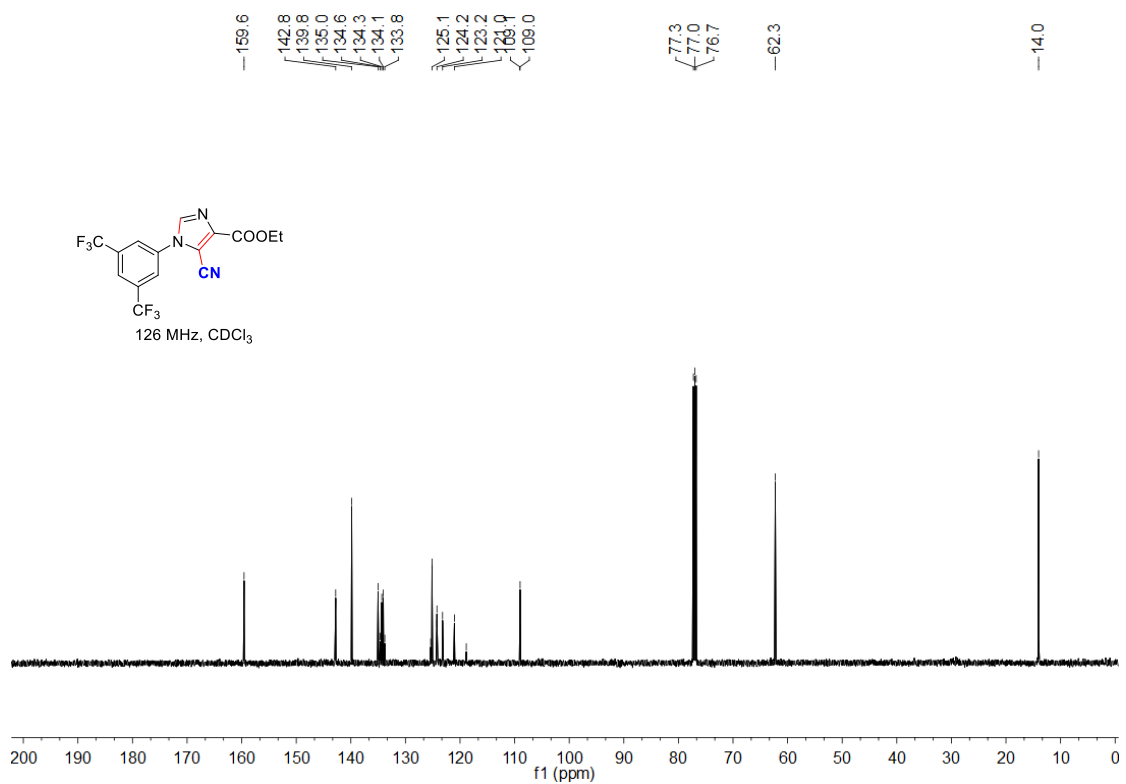
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR

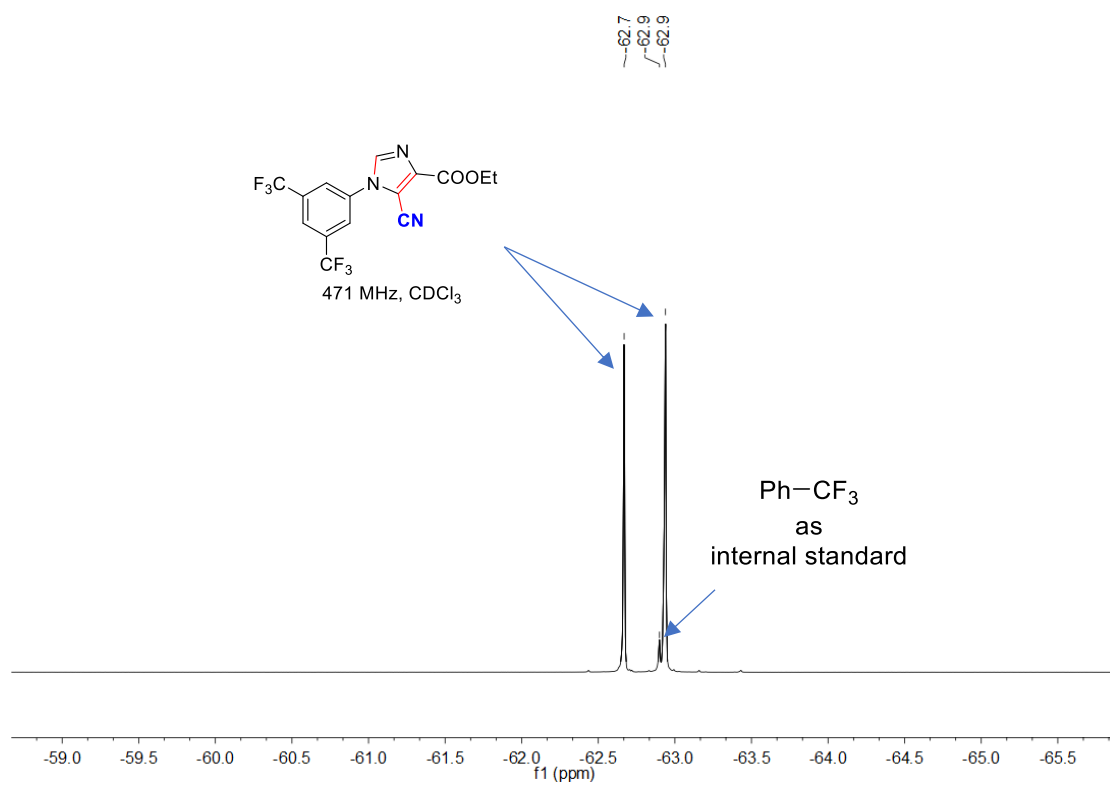


## 22d

 $^1\text{H}$  NMR $^{13}\text{C}$  NMR



**<sup>19</sup>F NMR**



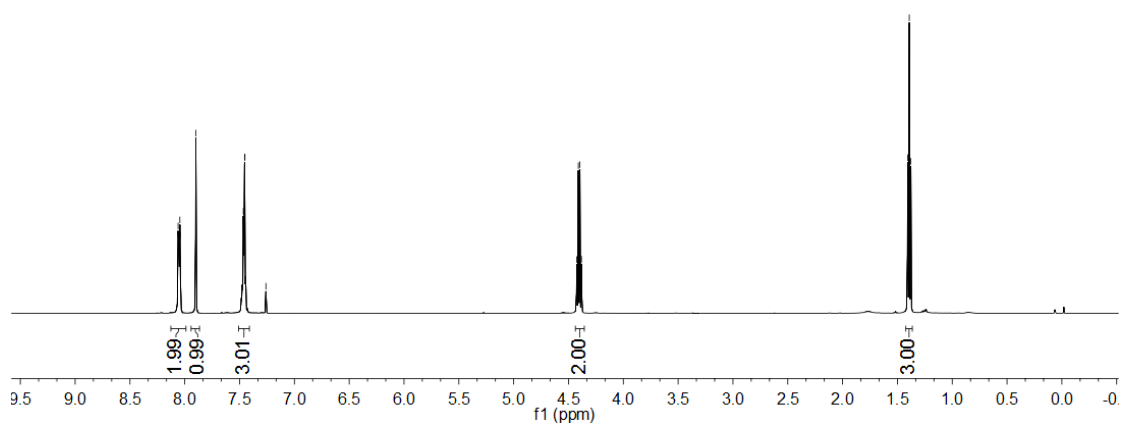
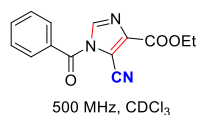
## 23d

 $^1\text{H NMR}$ 

8.06  
8.06  
8.04  
8.04  
7.90  
7.47  
7.46  
7.45  
7.26

4.42  
4.41  
4.40  
4.38

1.41  
1.39  
1.38

 $^{13}\text{C NMR}$ 

161.9  
155.4  
148.9

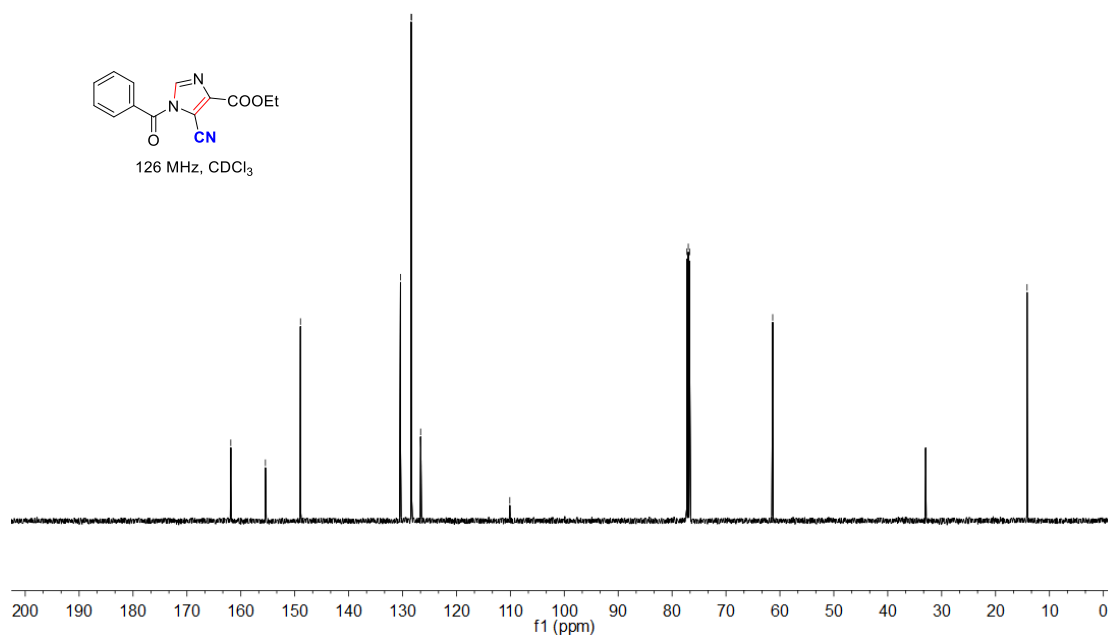
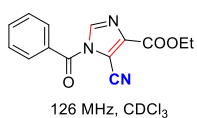
130.4  
128.4  
128.3  
126.6

110.1

77.3  
77.0  
76.7

61.3

14.2



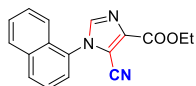
## 24d

<sup>1</sup>H NMR

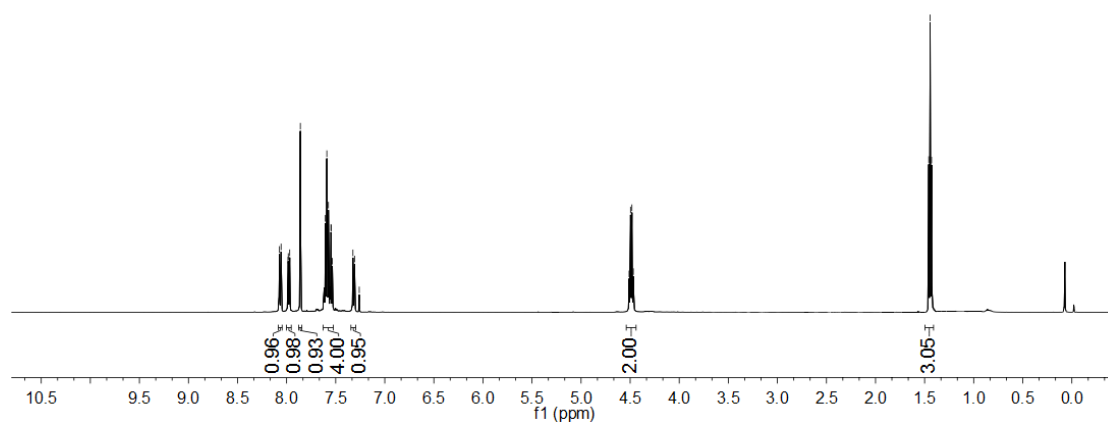
8.07  
8.06  
7.99  
7.98  
7.97  
7.86  
7.61  
7.59  
7.57  
7.55  
7.53  
7.32  
7.31  
7.26

4.51  
4.50  
4.48  
4.47

1.46  
1.44  
1.43



500 MHz, CDCl<sub>3</sub>

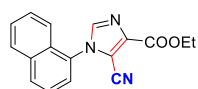
<sup>13</sup>C NMR

160.0  
141.5  
141.2  
131.4  
128.6  
128.5  
127.4  
125.0  
124.9  
111.2  
109.1

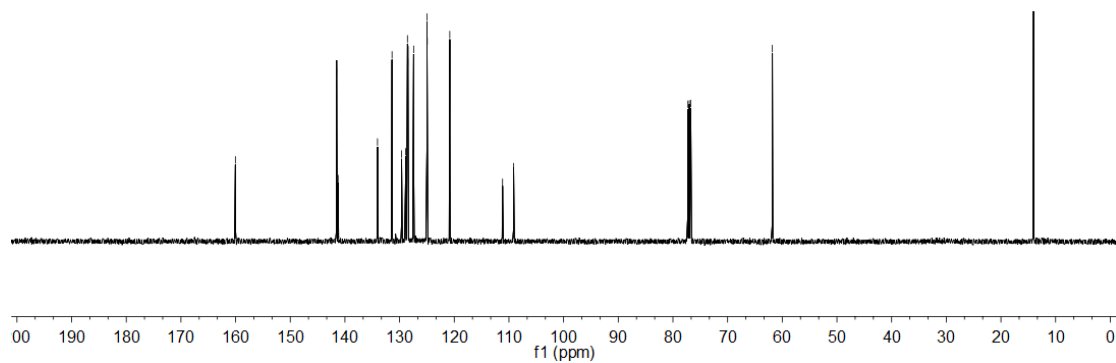
77.3  
77.0  
76.7

61.8

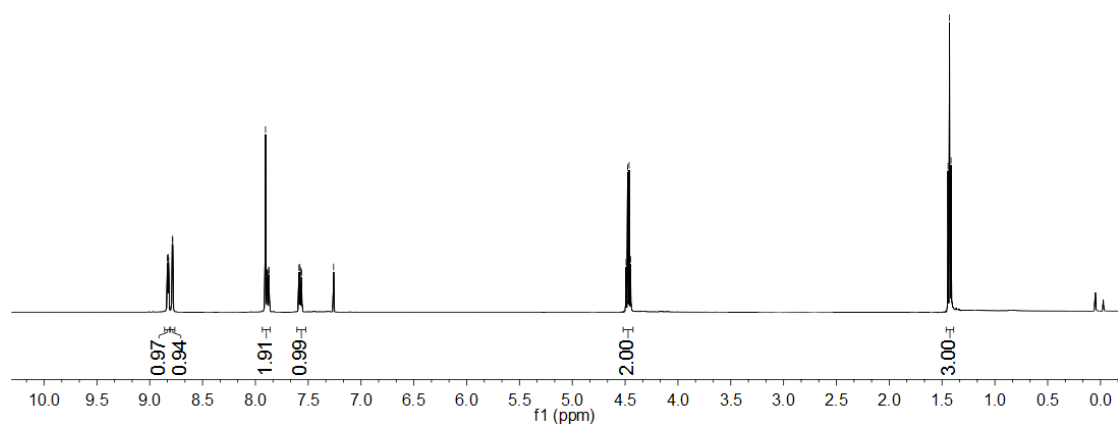
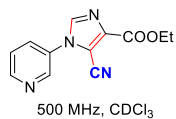
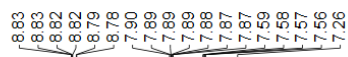
14.0



126 MHz, CDCl<sub>3</sub>



## 25d

 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

159.8

151.6

145.2

142.6

139.8

132.1

130.7

124.5

109.2

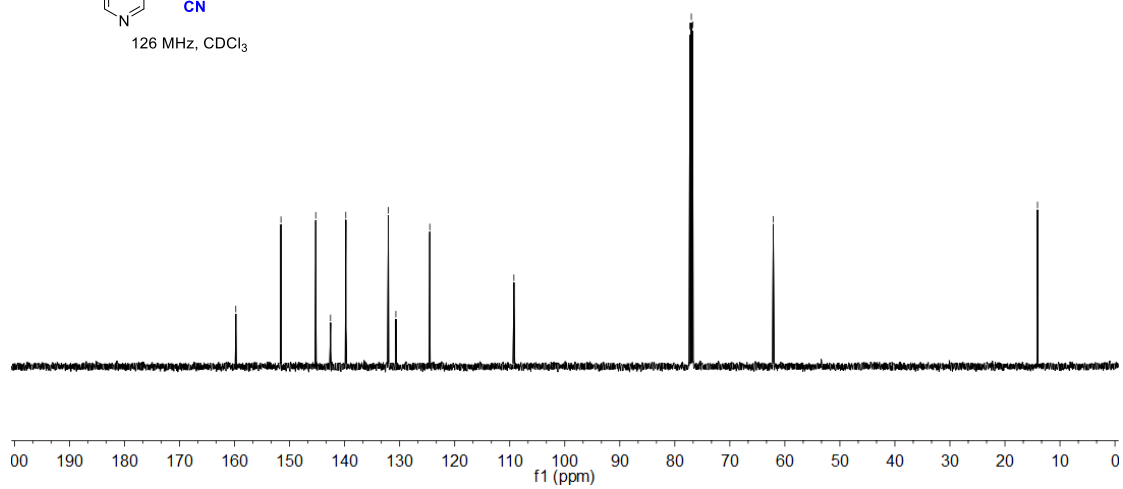
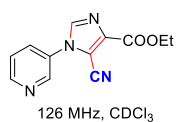
77.3

77.0

76.7

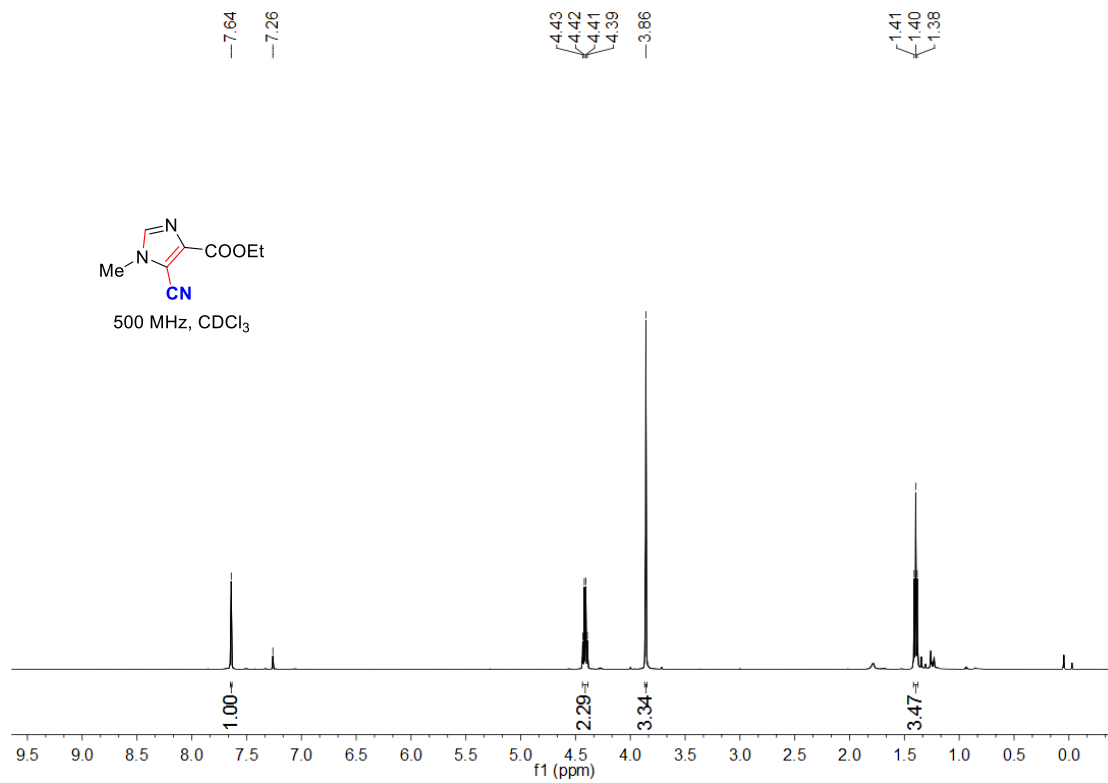
62.1

14.1

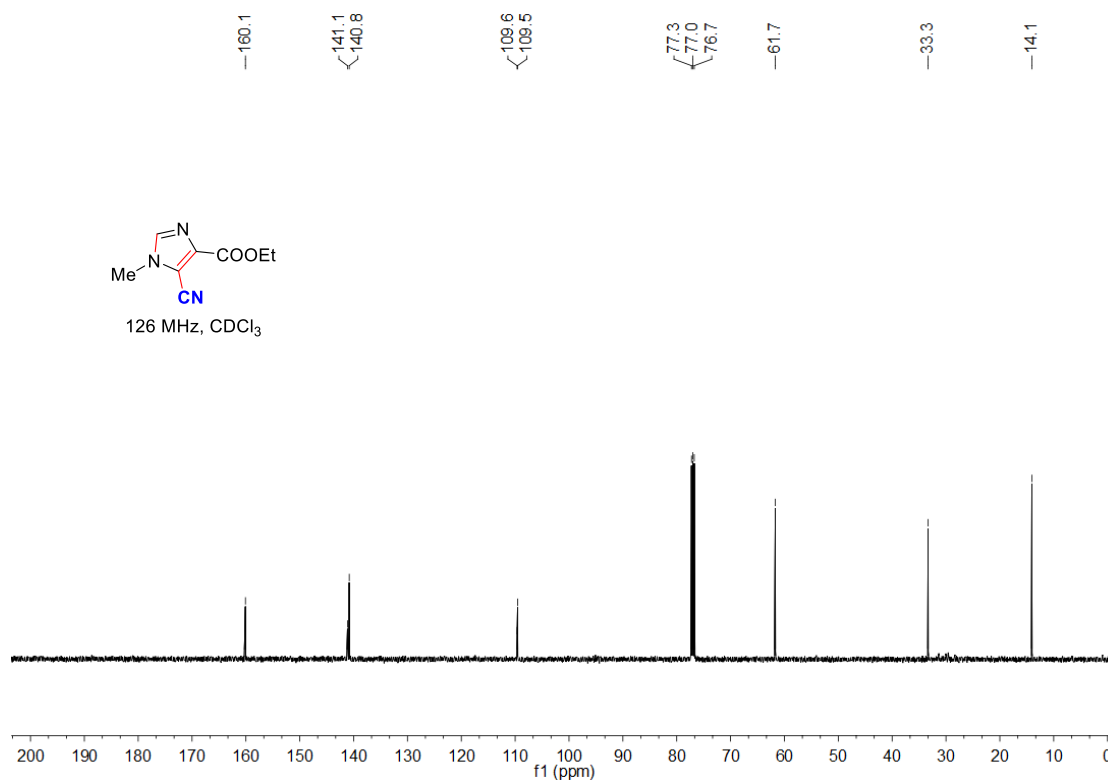


## 26d

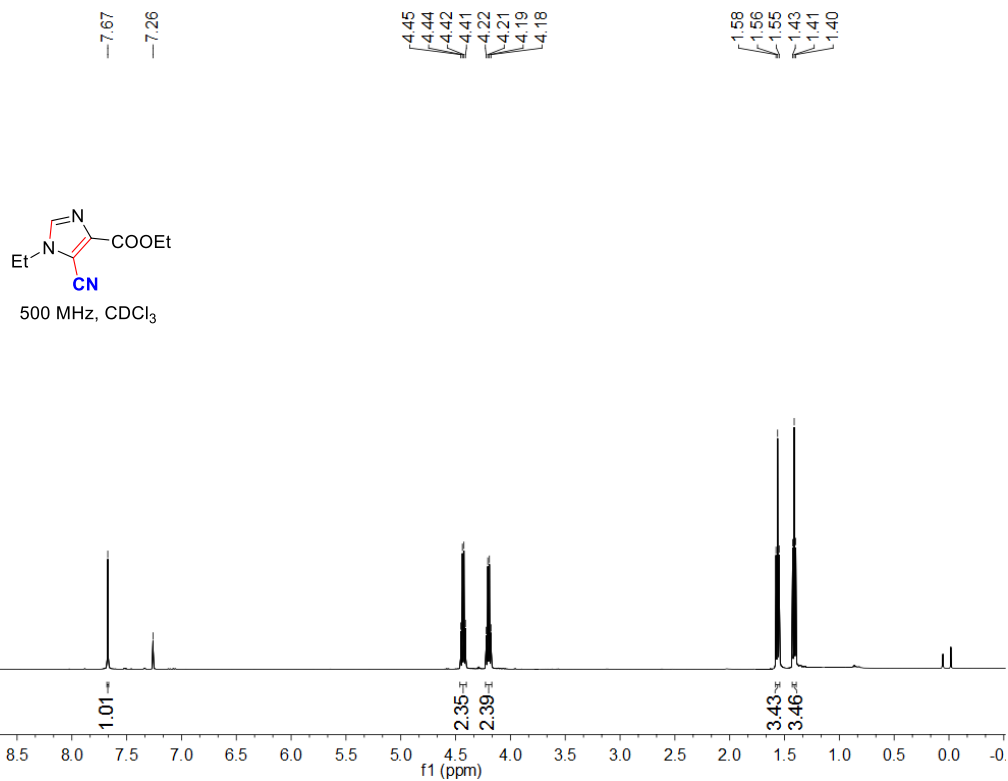
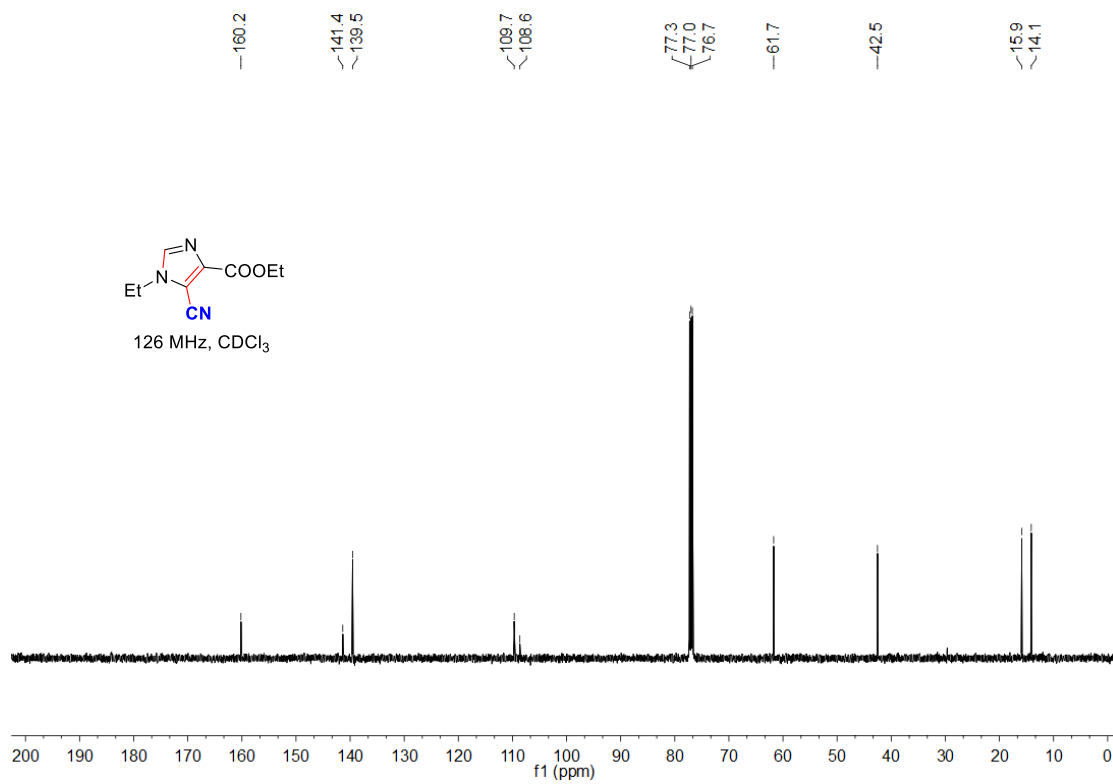
### <sup>1</sup>H NMR



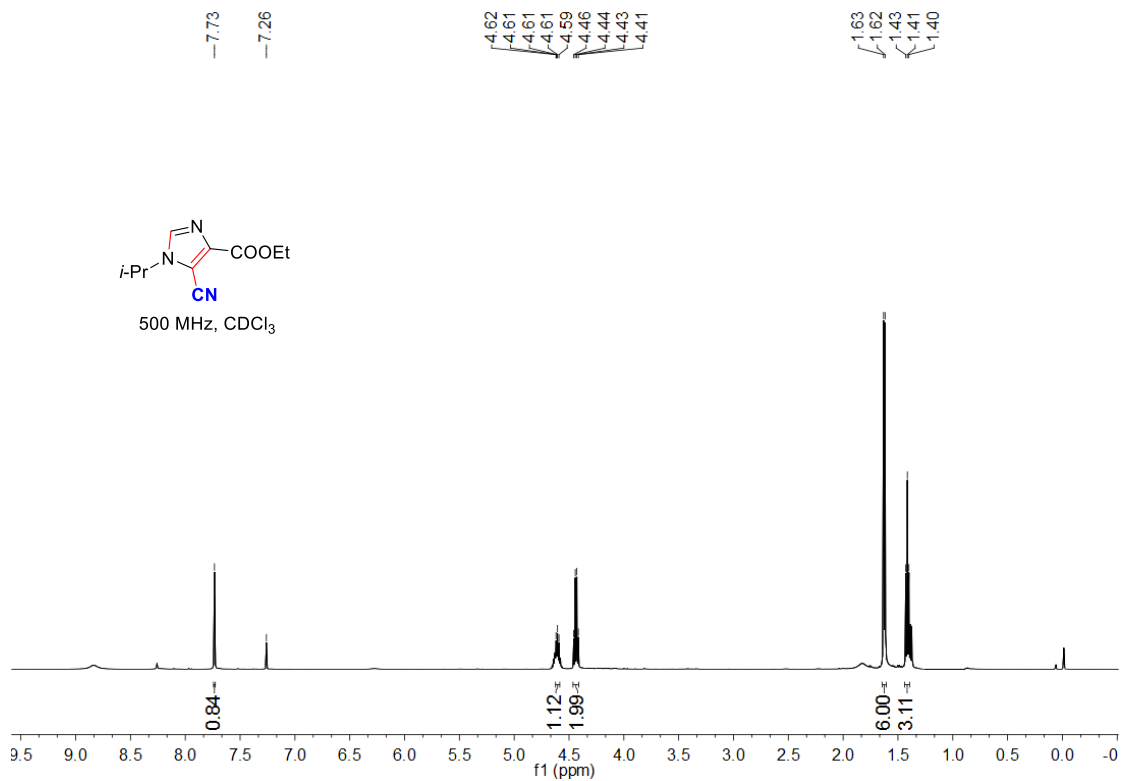
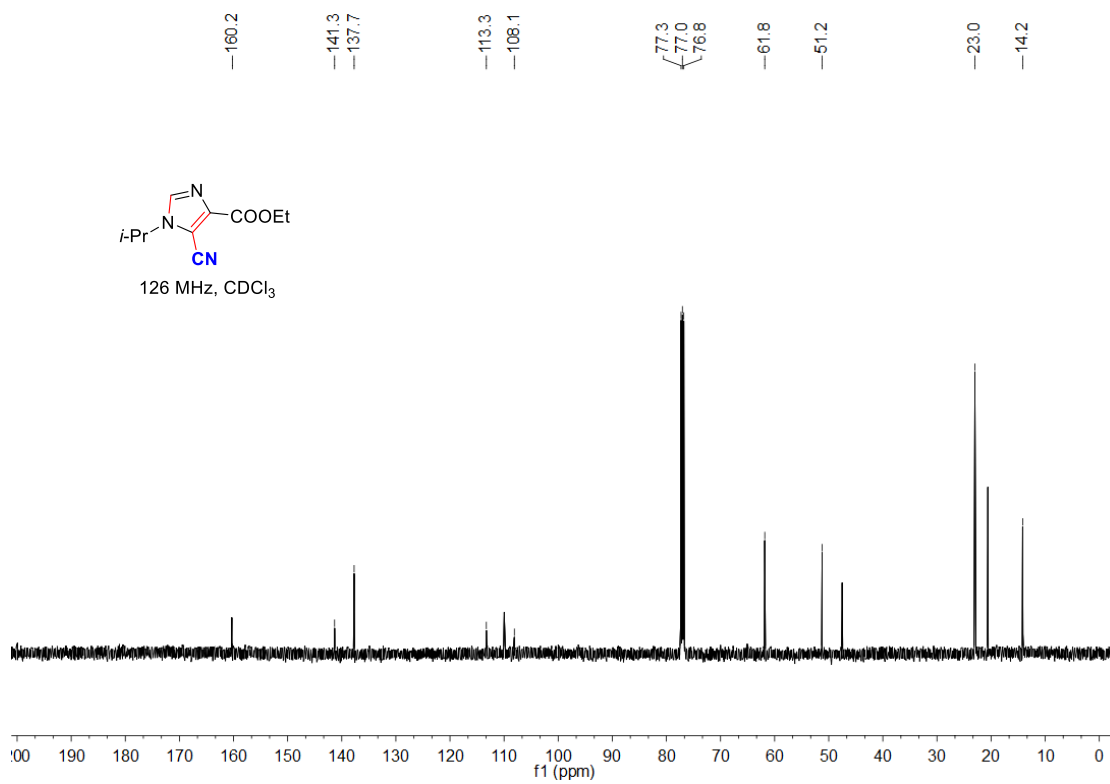
### <sup>13</sup>C NMR



## 27d

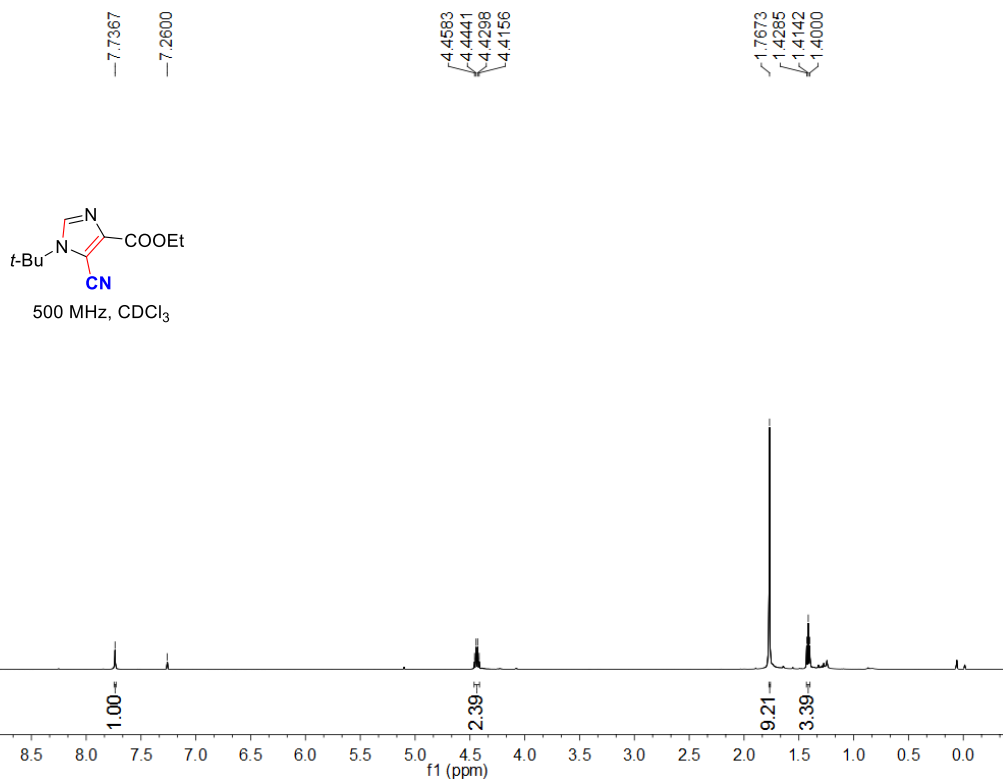
 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

## 28d

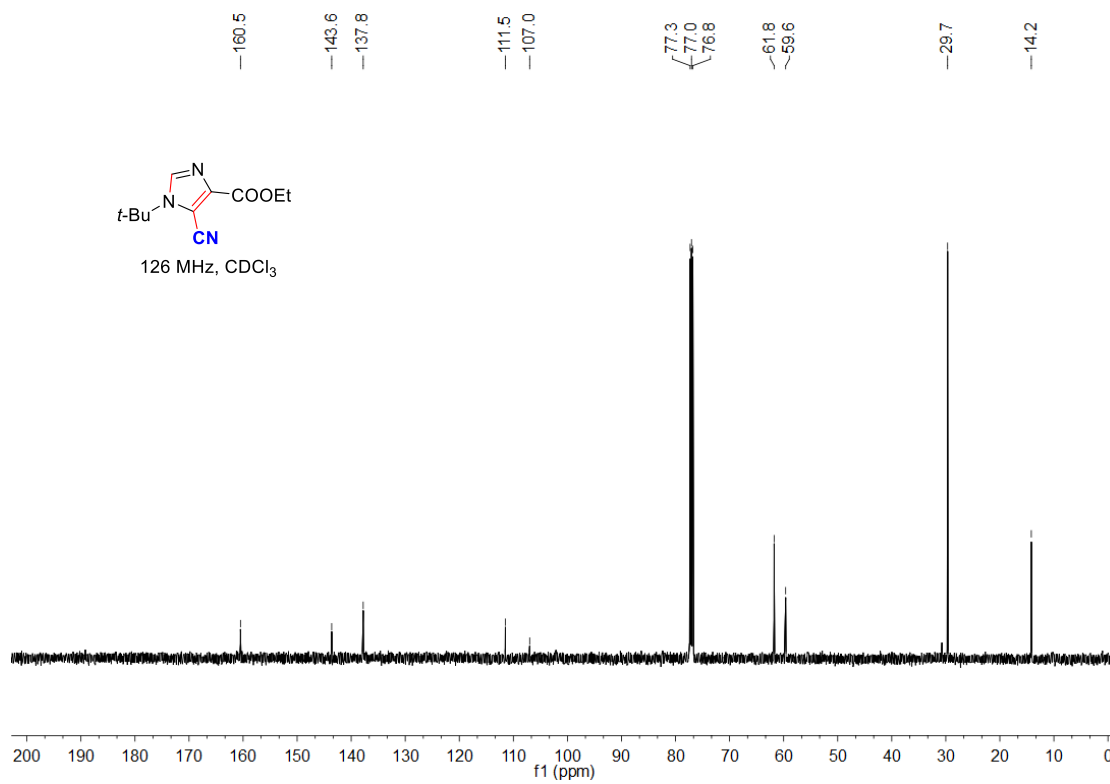
 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

# 29d

## <sup>1</sup>H NMR

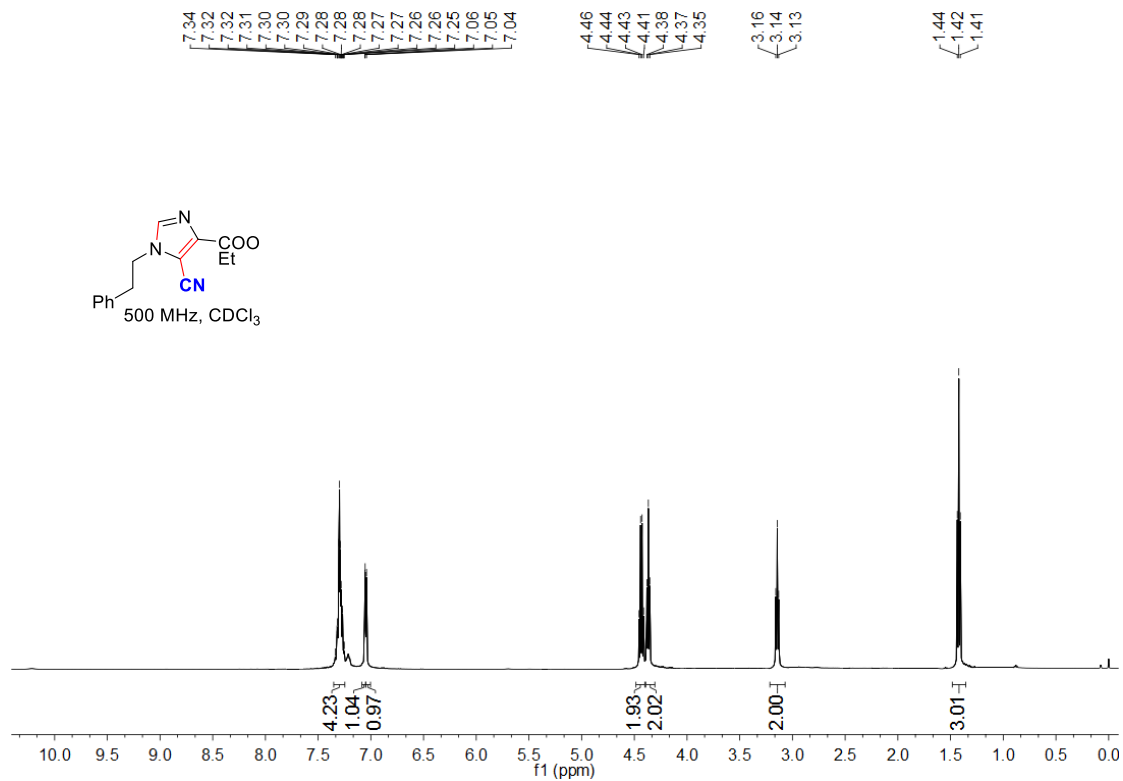
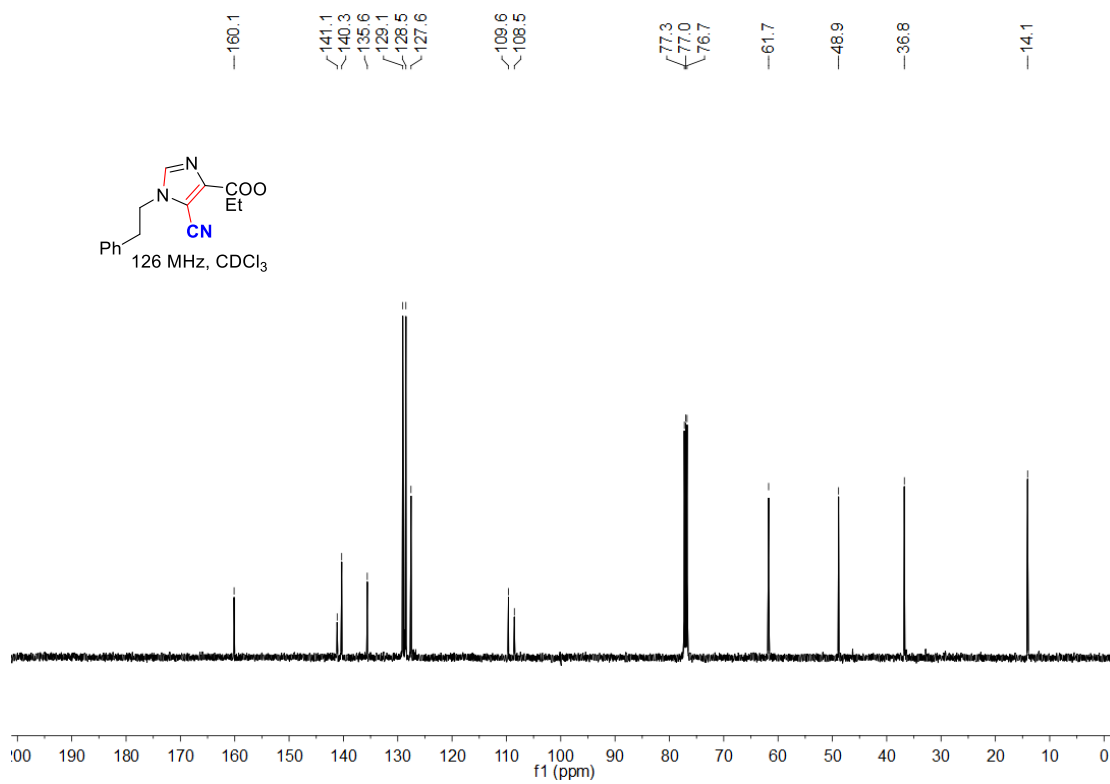


## <sup>13</sup>C NMR



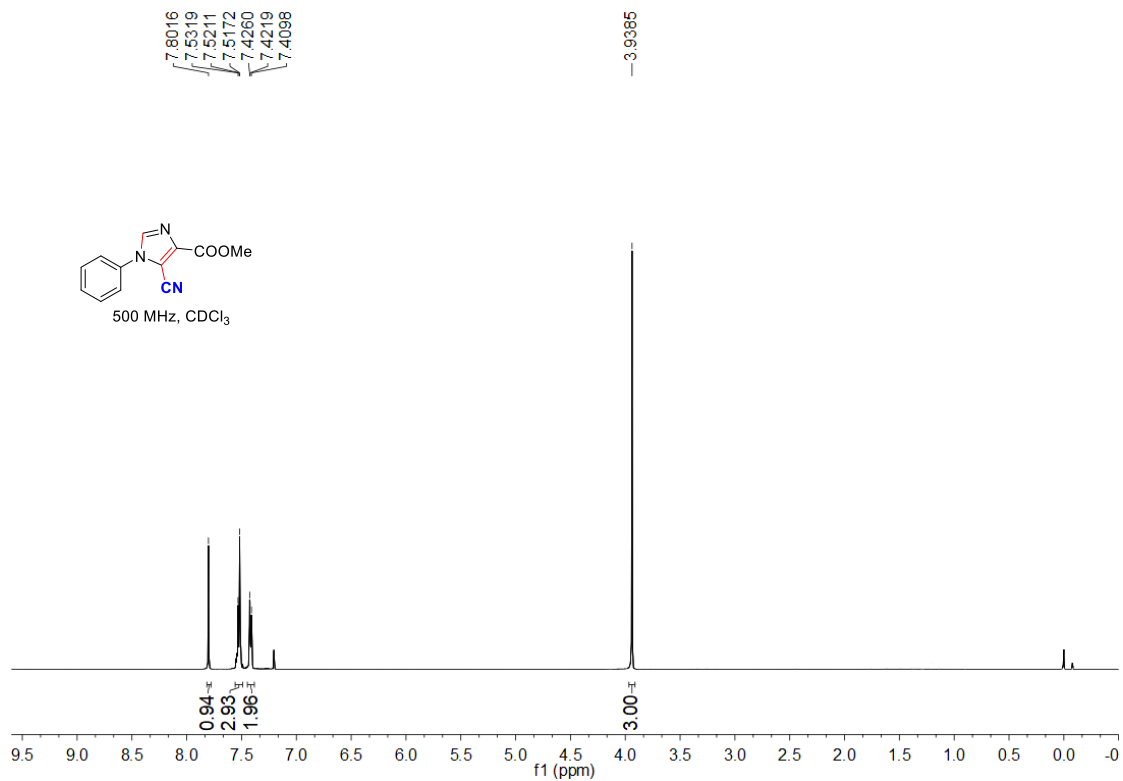


## 30d

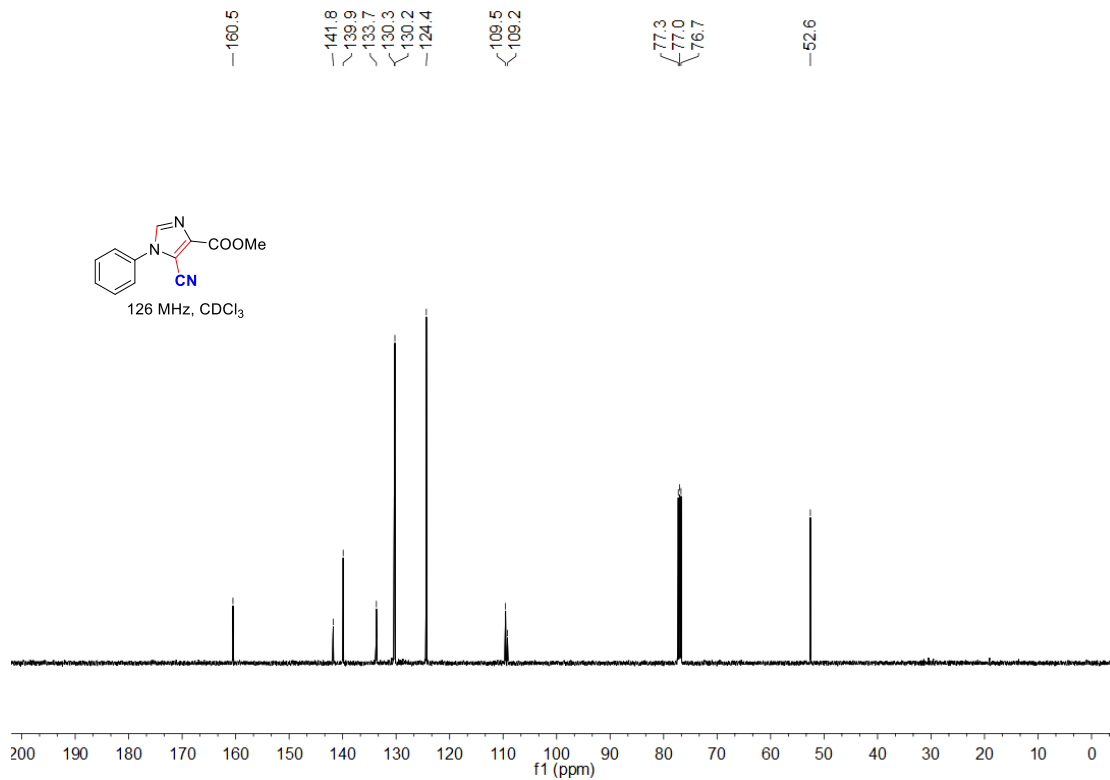
 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

### 31d

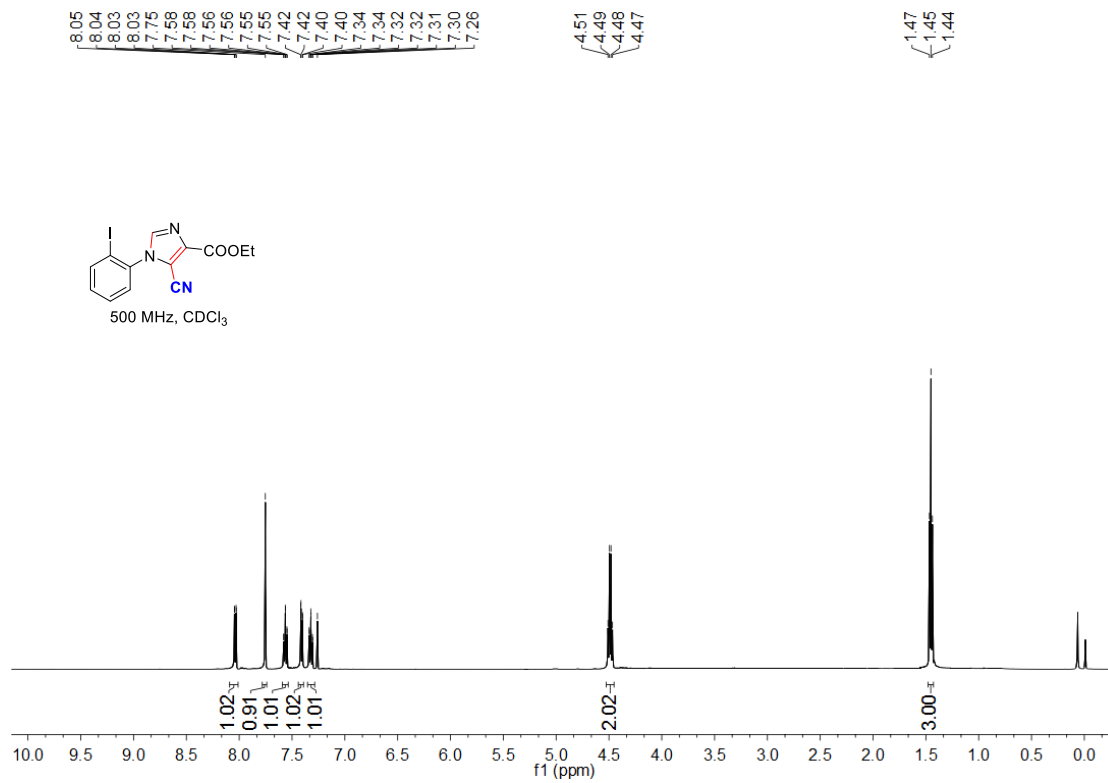
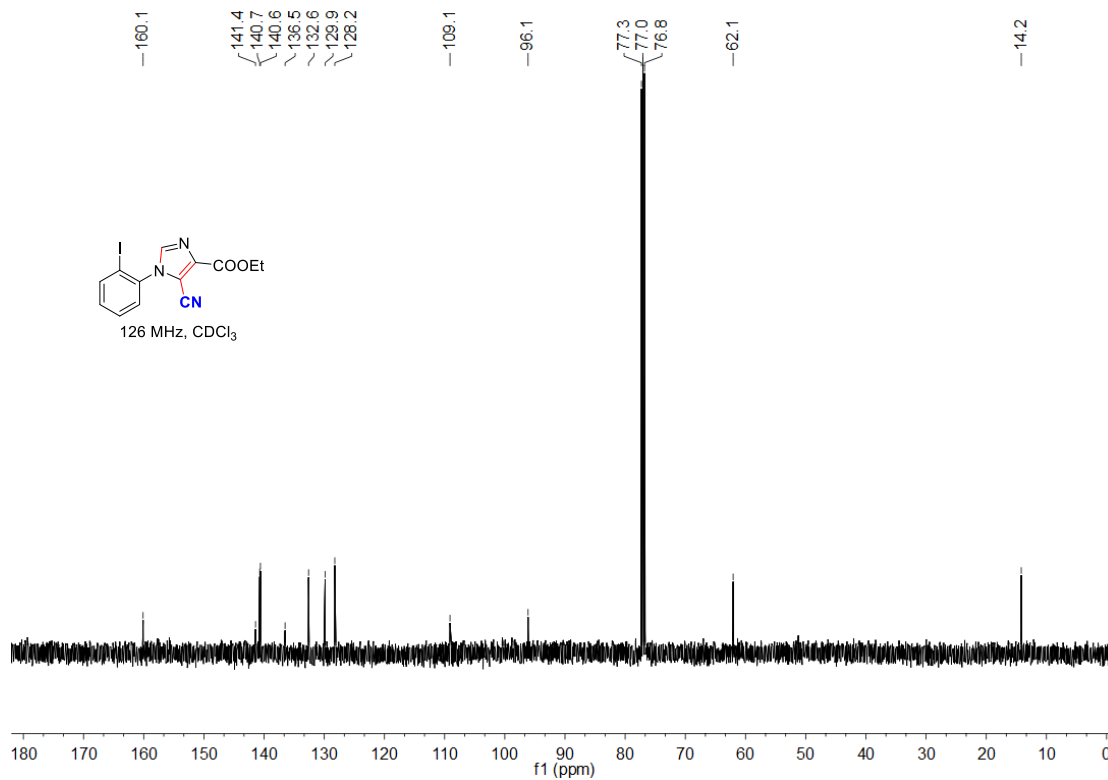
#### <sup>1</sup>H NMR



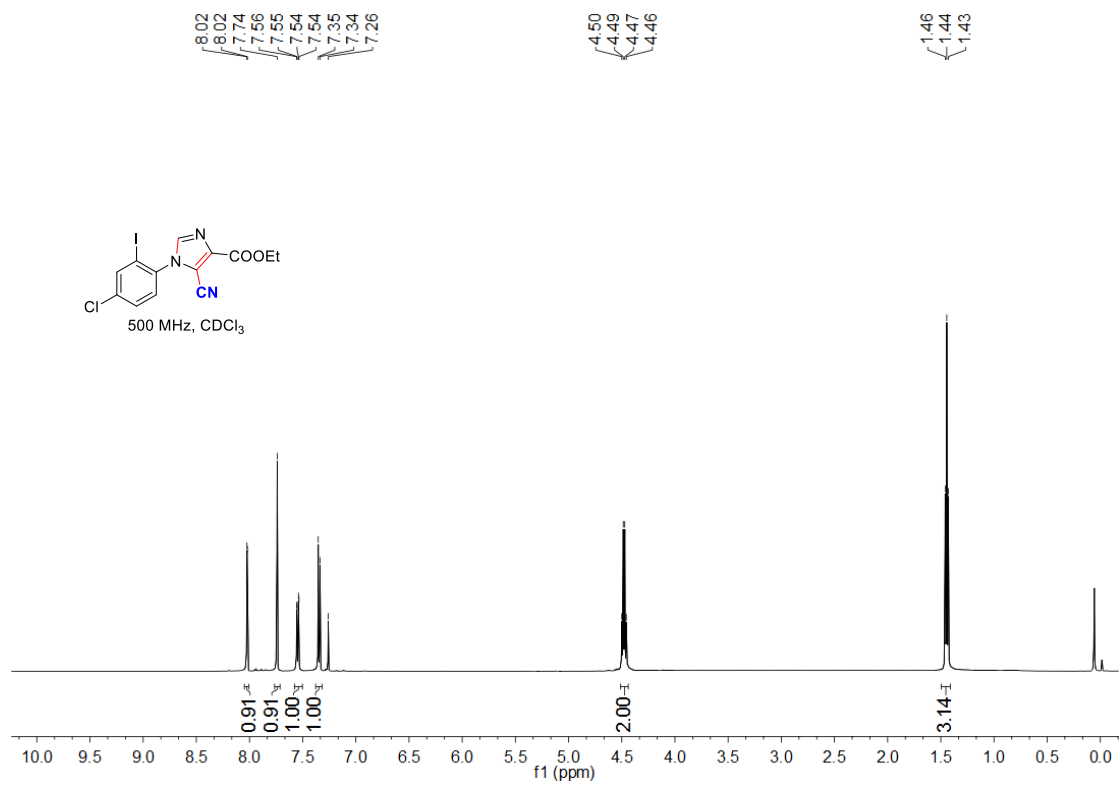
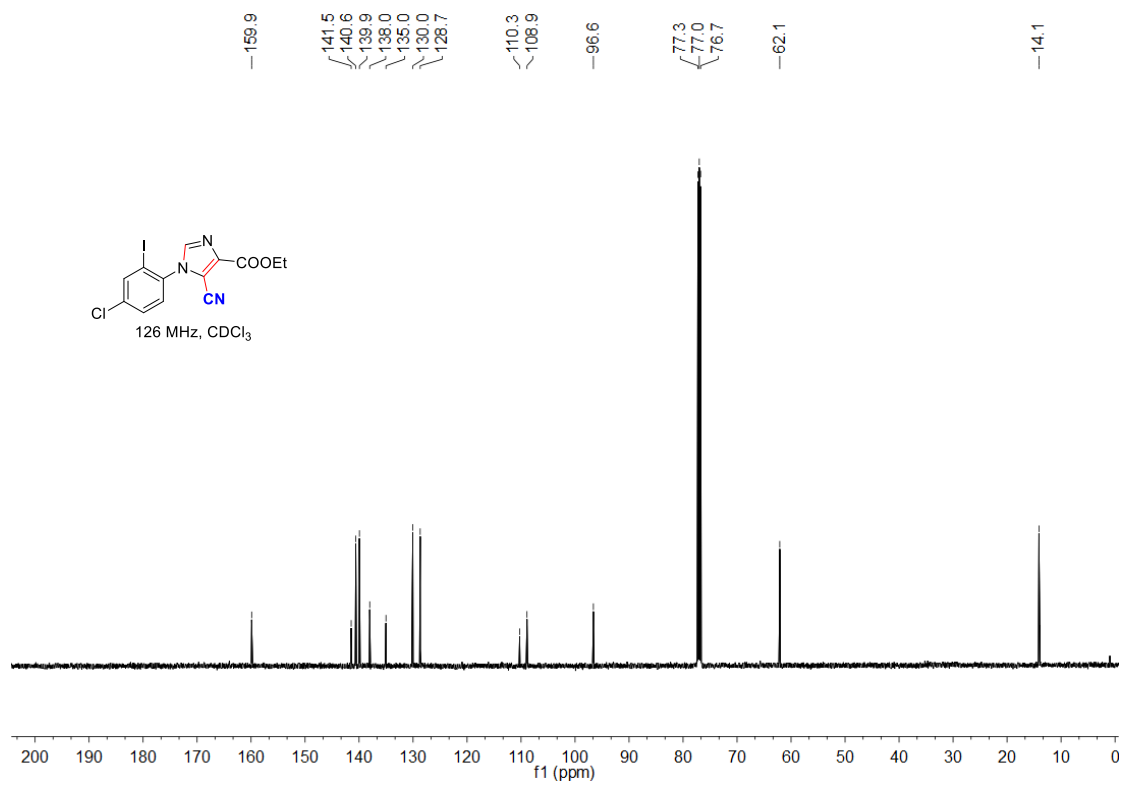
#### <sup>13</sup>C NMR



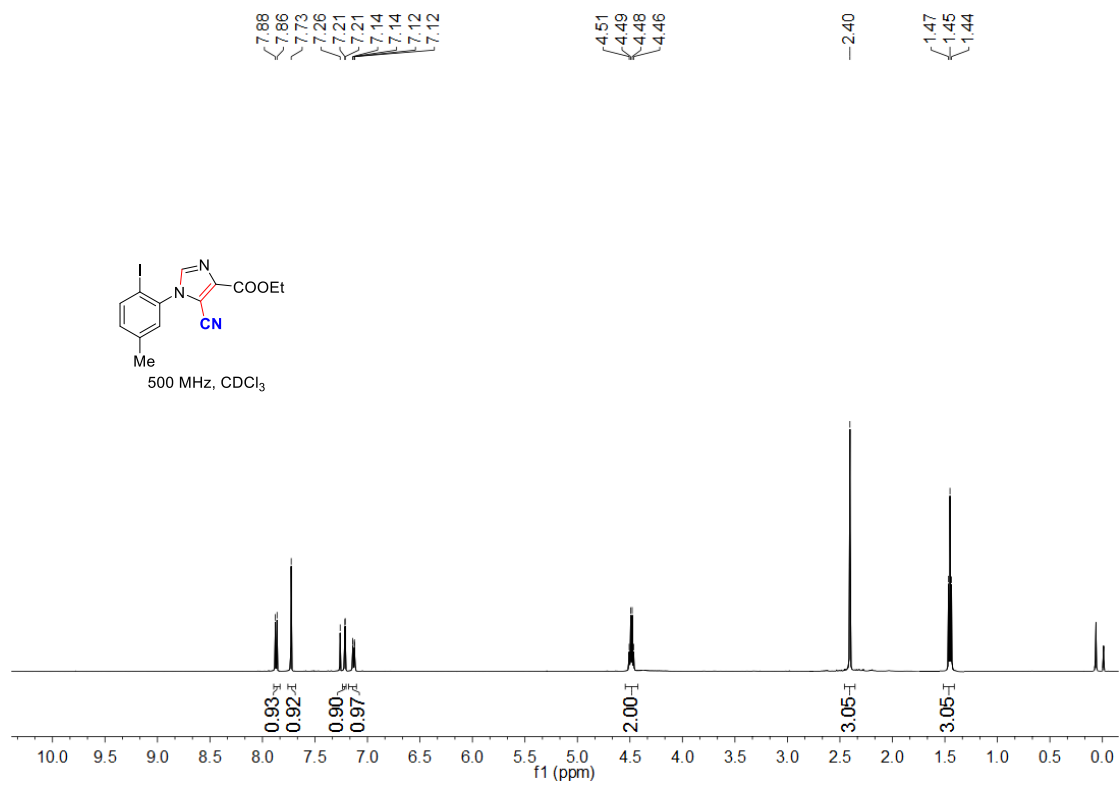
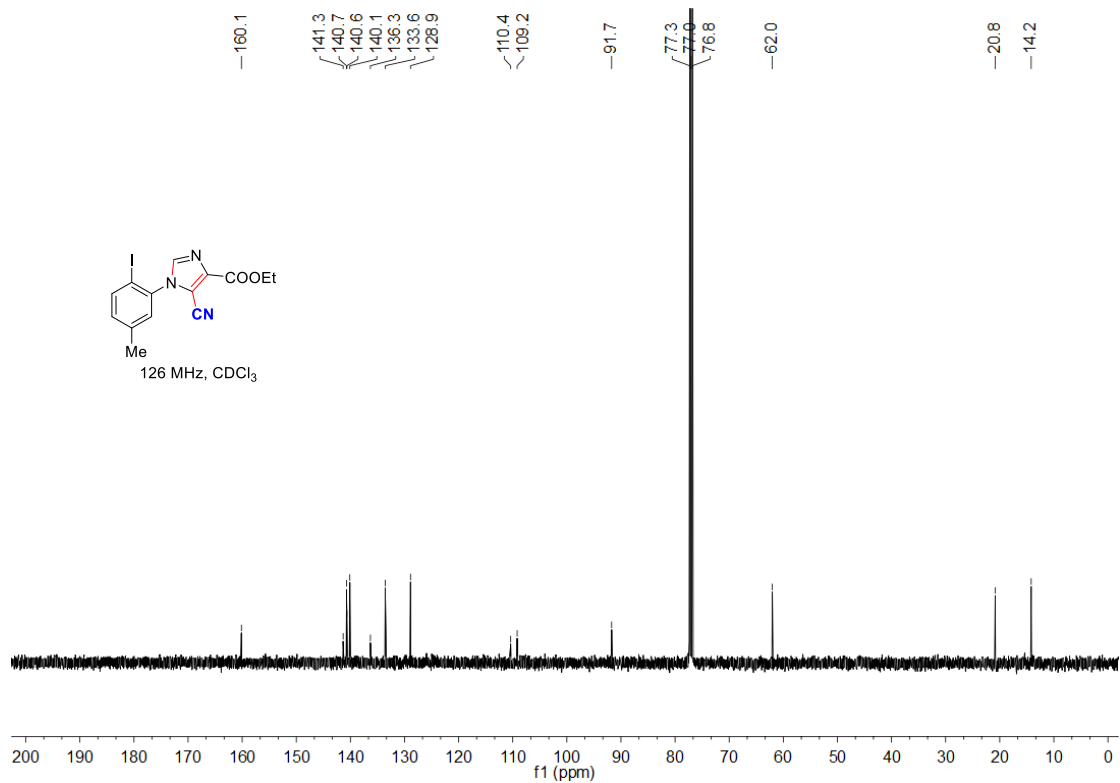
## 32d

 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

## 33d

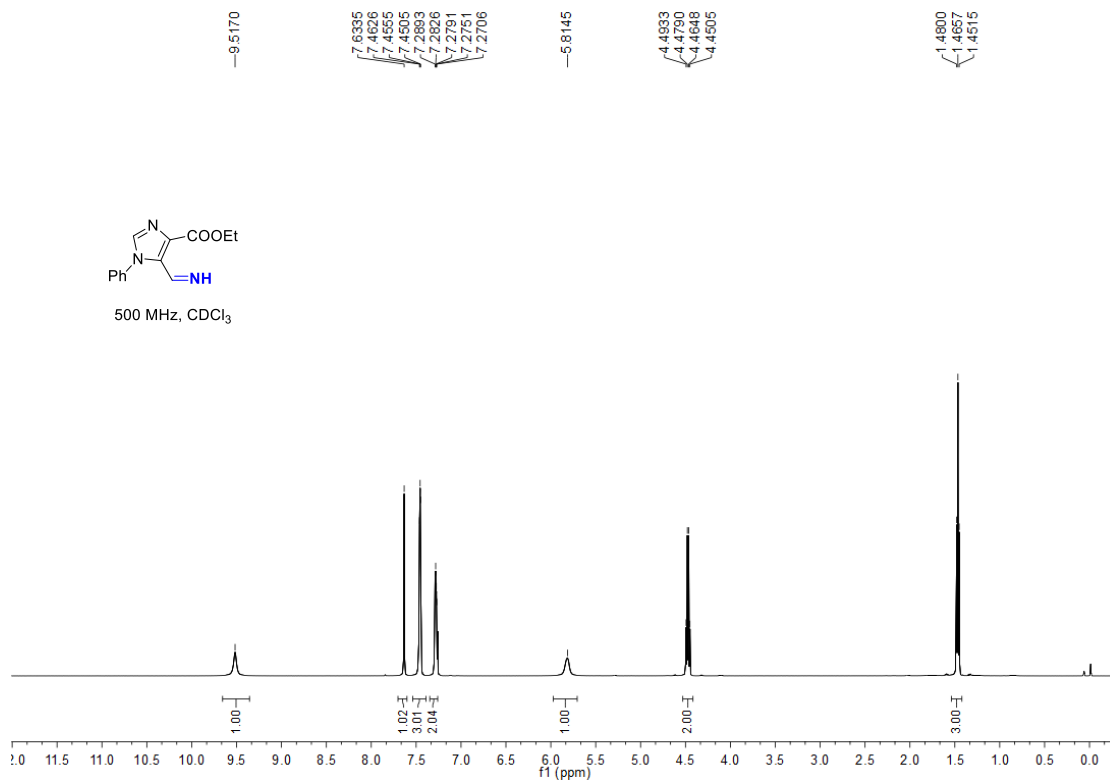
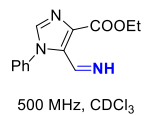
 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

## 34d

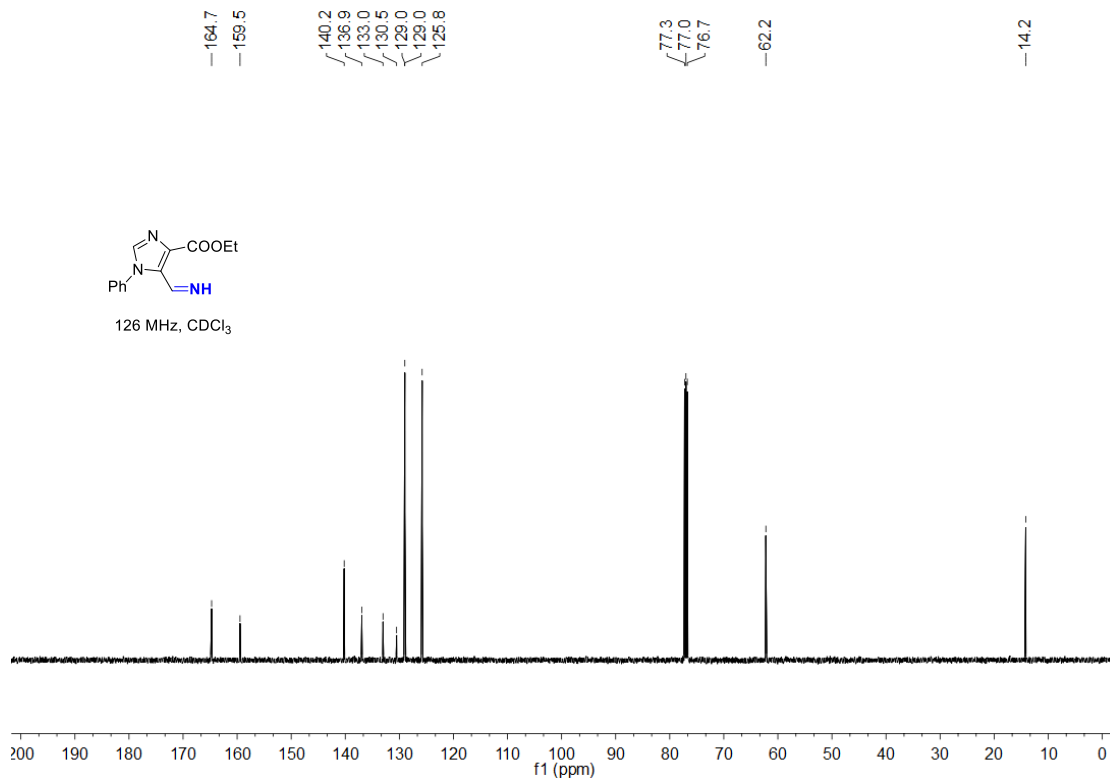
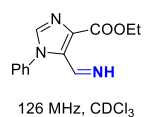
 $^1\text{H NMR}$  $^{13}\text{C NMR}$ 

# 1f

## <sup>1</sup>H NMR

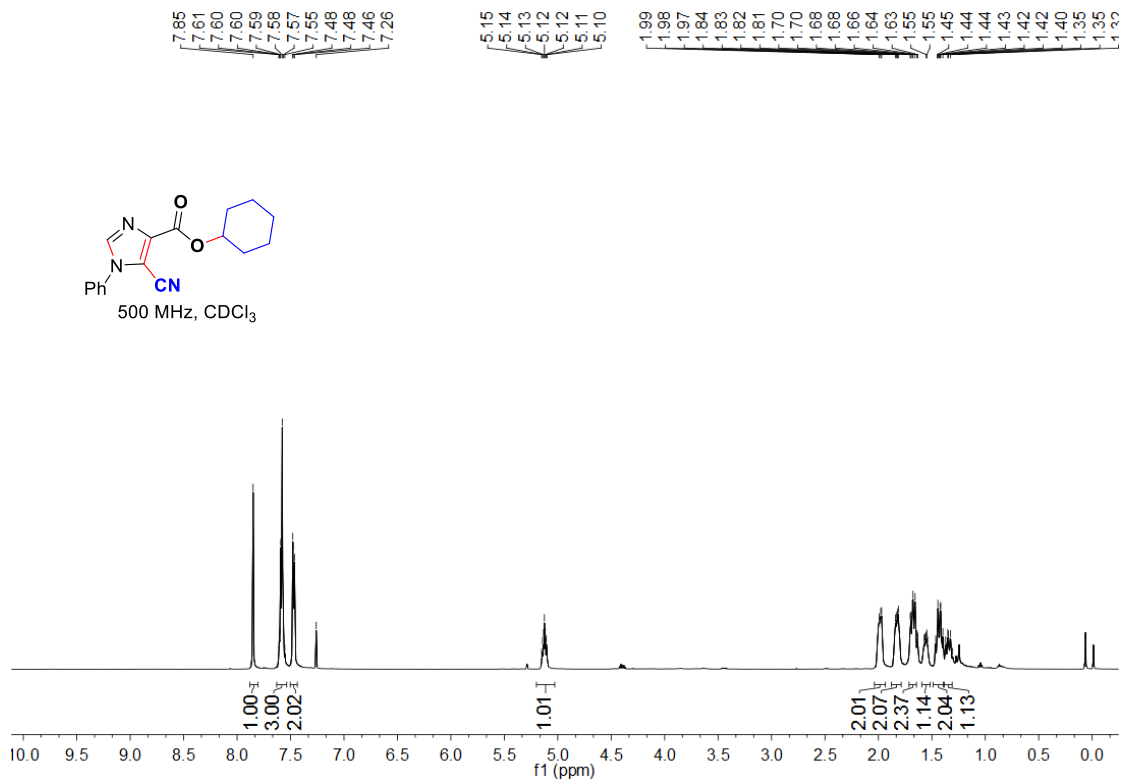


## <sup>13</sup>C NMR



# 1g

## <sup>1</sup>H NMR



## <sup>13</sup>C NMR

