Supporting Information

Cu-Enabled [3+2] Annulation of *In Situ* Formed Nitrile Ylides with Aryldiazonium Salts: Access to 5-Cyano-1,2,4-Triazoles

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General Information

Nuclear magnetic resonance (NMR) spectroscopies were recorded at 400 or 600 MHz for ^{1}H NMR spectroscopy, 100 or 150 MHz for ^{13}C NMR spectroscopy (decoupled), and 376 or 565 MHz for ^{19}F NMR spectroscopy (decoupled), respectively. Chemical shifts were reported in ppm using tetramethylsilane (TMS) and the residual solvent signals as the internal standards for ^{1}H and ^{13}C NMR spectroscopies (TMS: 0.00 ppm for ^{1}H NMR; $CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.20 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), p (pentet) and m (multiplet). Chemical shifts were reported in ppm using $CFCl_3$ (0.00 ppm) as the external standard for ^{19}F NMR spectroscopy. Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a microTOFQII or Waters Micromass GCT Premier Instrument. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected. Optical rotations were determined using an Autopol IV automatic polarimeter.

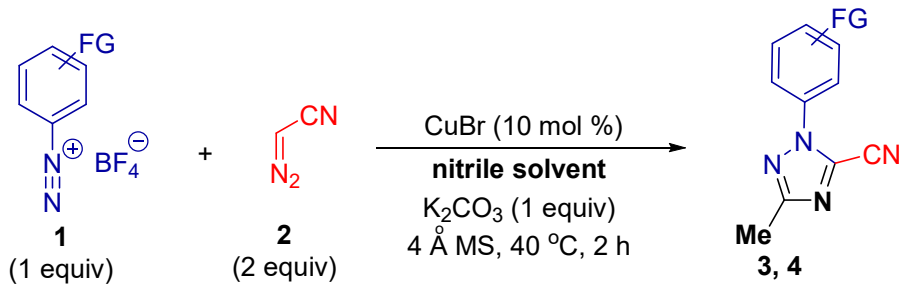
Materials: Without otherwise specified, the purchased reagents and reagents were used without prior purification. Aryldiazonium salts all known compounds and they were prepared according to the literature methods.[1-3] CH_3CN was distilled from P_2O_5. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash column chromatography.

Caution: 2-Diazoacetonitrile (N_2CHCN) is potentially explosive! Although no accident occurred in the course of this study, stringent safety precautions are necessary for all reactions of N_2CHCN.

Experimental Section

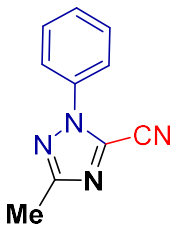
General procedure for the preparation of N_2CHCN.[4] 2-Aminoacetonitrile hydrochloride (4.63 g, 50 mmol) was dissolved in water (10 mL) in a 50 mL round-bottomed flask immersed in an ice-water bath, and then CH_2Cl_2 (20 mL) was added. The mixture was stirred vigorously, and $NaNO_2$ (3.45 g, 50 mmol) was added over 5 min. After stirring for another 15 min, the mixture was extracted with CH_2Cl_2 (50 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and then dried over anhydrous Na_2SO_4. The organic solution was dried at 0 °C under vacuum to afford N_2CHCN as a yellow liquid.

General procedure for the preparation of *N*[1]-aryl 5-cyano-1,2,4-triazoles via Cu-enabled [3+2] annulation of *in-situ* formed nitrile ylides with aryldiazonium salts.



An oven-dried rubber-capped Schlenk tube equipped with a magnetic stir bar was charged with aryldiazonium salt **1** (0.4 mmol, 1 equiv), CuBr (5.74 mg, 0.04 mmol,

0.1 equiv), 4 Å molecular sieve (100 mg) and K_2CO_3 (55.28 mg, 0.4 mmol, 1 equiv). Nitrile solvent (2 mL) followed by 2-diazoacetonitrile **2** (53.64 mg, 0.8 mmol, 2.0 equiv) were added into the reaction mixture via a syringe. The resulting mixture was stirred under air atmosphere at 40 °C for 2 h. At this point, the reaction mixture was diluted with ethyl acetate (10 mL) and the resulting mixture was filtered to remove the residue. The residue was rinsed with ethyl acetate (5 mL x 2), and the filtrate was concentrated under vacuum. The residue was purified by a silica gel column chromatography to obtain the *N*[1]-aryl 5-cyano-1,2,4-triazoles **3** and **4**.

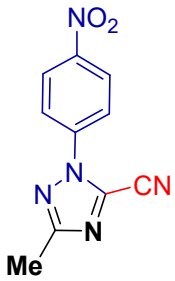


3a

3-methyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (3a)

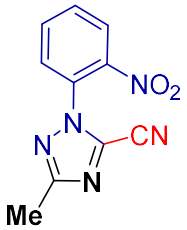
(i) Based on 0.4 mmol 3a. Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3a** (62 mg; 84% yield); yellow solid; m.p.: 54 – 55 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.69 (m, 2H), 7.58 – 7.50 (m, 3H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 136.0, 130.2, 130.1, 128.7, 122.9, 109.7, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_9N_4^+$ 185.0827, Found 185.0828.

(ii) Based on 7.8 mmol 3a. Based on **2a** (7.8 mmol, 1.50 g), **3a** was purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to be obtained in 1.36 g and in 86% yield. The spectral data are in agreements with that of the identical compound above.



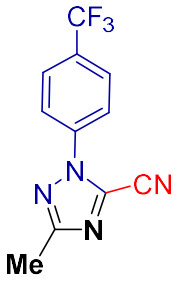
3b

Purified by silica gel chromatography (hexane to hexane/EtOAc = 2/1) to obtain **3-methyl-1-(4-nitrophenyl)-1H-1,2,4-triazole-5-carbonitrile 3b** (74 mg; 80% yield), white solid; m.p.: 91 – 92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.44 (m, 2H), 8.02 – 8.00 (m, 2H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 147.9, 140.1, 128.6, 125.5, 122.8, 109.2, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for 230.0678, Found: 230.0677.



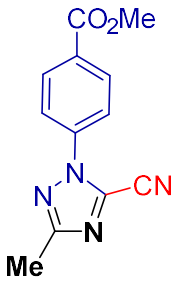
3c

Purified by silica gel chromatography (hexane to hexane/EtOAc = 2/1) to obtain **3-methyl-1-(2-nitrophenyl)-1H-1,2,4-triazole-5-carbonitrile 3c** (54.5 mg; 59% yield), brown solid; m.p.: 87 – 88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.9 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.64 (m, 1H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 144.7, 134.7, 132.4, 131.3, 128.9, 126.5, 108.5, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for 230.0678, Found: 230.0672.



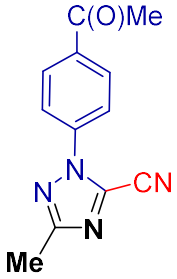
3d

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **3-methyl-1-(4-(trifluoromethyl)phenyl)-1H-1,2,4-triazole-5-carbonitrile 3d** (65 mg; 64% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 138.6, 132.2 (q, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 128.7, 127.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.5 (q, $^{1}J_{C\text{-}F}$ = 271.6 Hz), 122.9, 109.5, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.84. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_8N_4F_3^+$ 253.0701, Found: 253.0696.



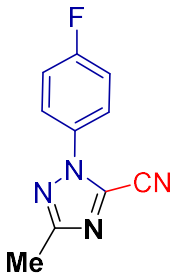
3e

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **methyl 4-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)benzoate 3e** (73 mg; 75% yield), white solid; m.p.: 124 – 125 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 3.97 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 163.4, 139.2, 131.6, 131.5, 128.6, 122.3, 109.6, 52.8, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4O_2^+$ 243.0882, Found: 243.0875.



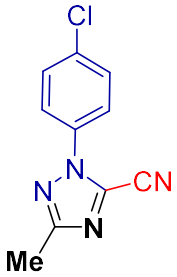
3f

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1-(4-acetylphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3f** (55 mg; 60% yield), white solid; m.p.: 111 – 112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H), 2.65 (s, 3H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 163.4, 139.1, 138.0, 130.2, 128.6, 122.5, 109.6, 26.9, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4O^+$ 227.0933, Found: 227.0939.



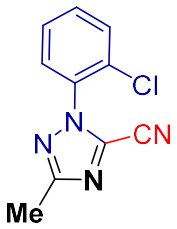
3g

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-fluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3g** (60 mg; 74% yield), white solid; m.p.: 71 – 72 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.29 – 7.25 (m, 2H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2 (d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 163.1, 132.1 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 128.8, 125.0 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 117.2 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 109.5, 14.0. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -109.38. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4F^+$ 203.0733, Found: 203.0734.



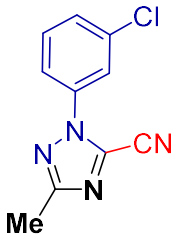
3h

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3h** (56 mg; 64% yield), white solid; m.p.: 89 – 90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) 7.67 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 136.3, 134.4, 130.4, 128.6, 124.0, 109.6, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4Cl^+$ 219.0437, Found: 219.0430.



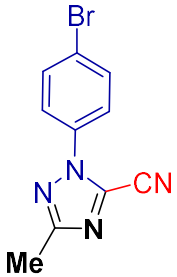
3i

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(2-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3i** (57 mg; 65% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 (d, *J* = 4.2 Hz, 2H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 133.4, 132.6, 131.8, 131.3, 131.2, 128.8, 128.3, 108.7, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4Cl^+$ 219.0437, Found: 219.0434.



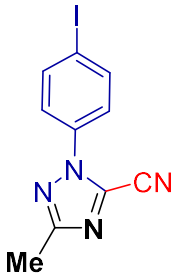
3j

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(3-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3j** (60 mg; 68% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.65 – 7.61 (m, 1H), 7.52 – 7.49 (m, 2H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 136.8, 136.0, 131.1, 130.3, 128.6, 123.3, 120.6, 109.4, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4Cl^+$ 219.0437, Found: 219.0437.



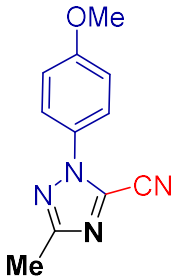
3k

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-bromophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3k** (71 mg; 67% yield), white solid; m.p.: 99 – 100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.61 – 7.58 (m, 2H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 135.0, 133.3, 128.6, 124.2, 109.6, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4Br^+$ 262.9932, Found: 262.9927.



3l

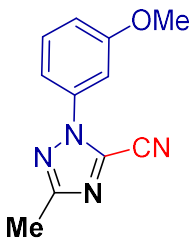
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-iodophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3l** (82 mg; 66% yield), white solid; m.p.: 90 – 91 °C; **3l** was recrystallized by dissolving into ethyl acetate (1 mL) followed by slow evaporation upon addition of hexane (15 mL) at room temperature. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 139.2, 135.6, 128.5, 124.2 109.5, 95.7, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4I^+$ 310.9794, Found: 310.9796.



3m

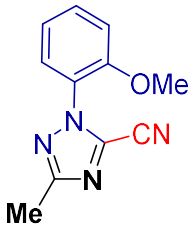
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1-(4-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3m** (60 mg; 70% yield), yellow solid; m.p.: 113 – 114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 162.7, 160.9, 129.0, 128.6, 124.5, 115.1, 109.7, 55.9, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_4O^+$ 215.0933, Found: 215.0931.



3n

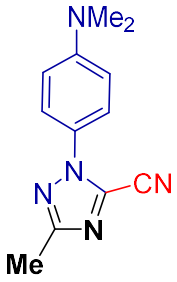
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1-(3-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3n** (46 mg; 54% yield), white solid; m.p.: 82 – 83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.2 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.26 (t, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.92 (s, 3H), 2.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 160.8, 136.9, 130.9, 128.7, 116.4, 114.8, 109.7, 108.5, 55.9, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_4O^+$ 215.0933, Found: 215.0940.



3o

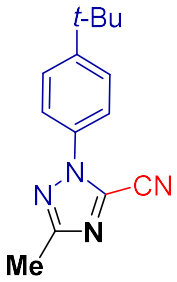
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1-(2-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3o** (53 mg; 62% yield), yellow solid; m.p.: 83 – 84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 1H), 7.41 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.10 – 7.07 (m, 2H), 3.88 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 153.2, 132.2, 131.8, 127.4, 124.7, 121.3, 112.6, 109.3, 55.9, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_4O^+$ 215.0933, Found: 215.0938.



3p

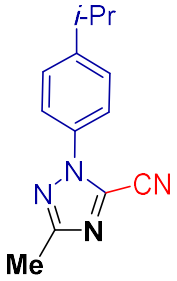
Purified by silica gel chromatography (hexane to hexane/EtOAc = 5/1) to obtain **1-(4-(dimethylamino)phenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3p** (37 mg; 40% yield; yellow solid; m.p.: 90 – 91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 9.1 Hz, 2H), 6.75 (d, J = 9.1 Hz, 2H), 3.03 (s, 6H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 151.2, 128.2, 124.7, 124.0, 123.9, 112.1, 112.0, 109.8, 40.3, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}N_5^+$ 228.1249, Found: 228.1244.



3q

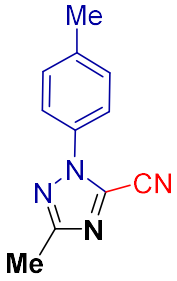
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-(tert-butyl)phenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3q** (59 mg; 61% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.57 – 7.54

(m, 2H), 2.51 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 153.8, 133.5, 128.6, 127.0, 122.5, 109.8, 35.2, 31.4, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}N_4^+$ 241.1453, Found: 241.1453.



3r

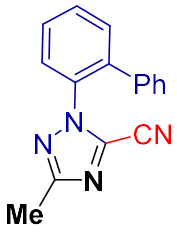
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-isopropylphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3r** (49 mg; 54% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 3.00 (q, J = 13.8, 6.9 Hz, 1H), 2.51 (s, 3H), 1.29 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 151.4, 133.8, 128.1, 122.9, 109.8, 34.1, 24.0, 14.1. **HRMS** (ESI): m/z calculated for $C_{13}H_{15}N_4^+$ ($[M + H]^+$) : 227.1297, Found: 227.1290.



3s

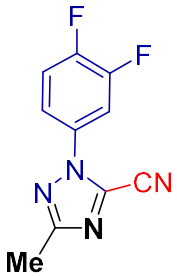
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-methyl-1-(p-tolyl)-1H-1,2,4-triazole-5-carbonitrile 3s** (56 mg; 71% yield), brown

solid; m.p.: 45 – 46 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.51 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 140.7, 133.7, 130.6, 128.7, 122.8, 109.8, 21.4, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_4^+$ 199.0984, Found: 199.0989.



3t

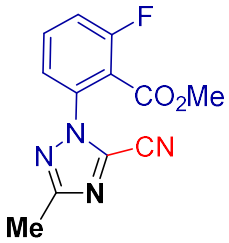
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1-([1,1'-biphenyl]-2-yl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3t** (65 mg; 62% yield), yellow solid; m.p.: 79 – 80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 1H), 7.59 – 7.48 (m, 3H), 7.33 – 7.31 (m, 3H), 7.13 – 7.11 (m, 2H), 2.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 139.4, 136.7, 133.4, 131.6, 131.52, 131.47, 129.0, 128.9, 128.7,128.5, 127.5, 108.6, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_4^+$ 261.1140, Found: 261.1148.



3u

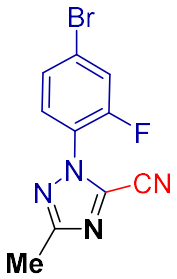
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(3,4-difluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3u** (55 mg; 63%

yield), pink solid; m.p.: 49 – 50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 1H), 7.53 – 7.49 (m, 1H), 7.36 (dd, J = 17.5, 9.0 Hz, 1H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 151.2 (dd, $^{1}J_{C\text{-}F}$ = 252.0, 13.0 Hz), 150.7 (dd, $^{1}J_{C\text{-}F}$ = 251.5, 13.0 Hz), 132.1 (dd, $^{3}J_{C\text{-}F}$ = 7.5 Hz, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 128.7, 119.0 (dd, $^{3}J_{C\text{-}F}$ = 7.0 Hz, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 118.7 (d, $^{2}J_{C\text{-}F}$ = 19.0 Hz), 113.1 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 109.4, 13.9. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -132.36 (d, J = 17.7 Hz), -133.67 (d, J = 23.5 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_7N_4F_2^+$ 221.0639, Found: 221.0636.



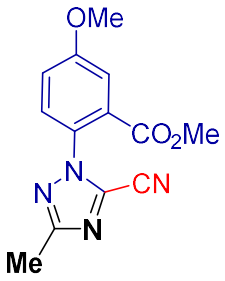
3v

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-fluorobenzoate 3v** (62 mg; 59% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.41 – 7.37 (m, 2H), 3.78 (s, 3H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 162.2, 160.7 (d, $^{1}J_{C\text{-}F}$ = 257.0 Hz), 134.6, 132.9 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 130.6, 121.7 (d, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 119.1 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 118.6 (d, $^{2}J_{C\text{-}F}$ = 17.0 Hz), 108.6, 53.1, 13.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.62. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{10}N_4O_2F^+$ 261.0788, Found: 261.0788.



3w

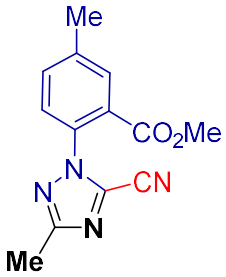
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-(4-bromo-2-fluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile 3w** (78 mg; 70% yield), yellow solid; m.p.: 104 – 105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.42 (t, J = 8.0 Hz, 1H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 155.5 (d, $^{1}J_{C\text{-}F}$ = 258.0 Hz), 131.4, 129.0 (d, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 128.5, 125.6 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 123.0 (d, $^{2}J_{C\text{-}F}$ = 12.1 Hz), 121.4 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 108.5, 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.51. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_7N_4FBr^+$ 280.9838, Found: 280.9842.



3x

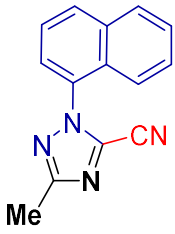
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-methoxybenzoate 3x** (55 mg; 51% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 2.9 Hz, 1H), 7.39 (d, J = 8.7 Hz, 1H), 7.19 (dd, J = 8.7, 2.9 Hz, 1H), 3.91 (s, 3H), 3.76 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 162.3, 161.2, 131.8, 129.5, 128.4,

127.4, 118.8, 116.7, 108.9, 56.0, 52.8, 13.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}N_4O_3^+$ 273.0988, Found: 273.0992.



3y

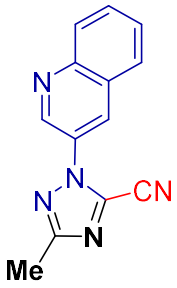
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-methylbenzoate 3y** (64 mg; 62% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.50 (d, *J* = 6.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 162.6, 142.1, 134.2, 132.7, 123.6, 131.8, 128.1, 127.0, 109.1, 52.9, 21.5, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}N_4O_2^+$ 257.1039, Found: 257.1039.



3z

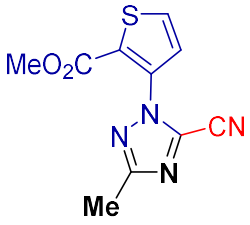
Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **3-methyl-1-(naphthalen-1-yl)-1H-1,2,4-triazole-5-carbonitrile 3z** (47 mg; 50% yield), brown solid; m.p.: 115 – 116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 1H), 8.00 – 7.98 (m, 1H), 7.64 – 7.58 (m, 4H), 7.52 – 7.49 (m, 1H), 2.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 134.5, 131.9, 131.8, 128.9, 128.7, 128.6, 127.7, 125.1, 124.8, 122.0, 108.9, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_4^+$ 235.0984, found: 235.0989.



3aa

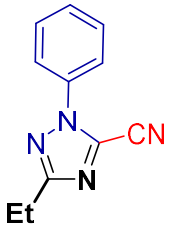
Purified by silica gel chromatography (hexane to hexane/EtOAc = 5/1) to obtain **3-methyl-1-(quinolin-3-yl)-1H-1,2,4-triazole-5-carbonitrile 3aa** (38 mg; 40% yield), white solid; m.p.: 131 – 132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 2.6 Hz, 1H), 8.51 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.73 – 7.69 (m, 1H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 148.3, 144.6, 131.6, 130.0, 129.5, 129.3, 128.9, 128.8, 128.6, 127.0, 109.5, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}N_5^+$ 236.0936, Found: 236.0932.



3ab

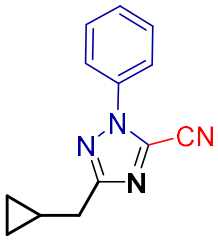
Purified by silica gel chromatography (hexane to hexane/EtOAc = 5/1) to obtain **methyl 3-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)thiophene-2-carboxylate 3ab**

(58mg; 58% yield), brown solid; m.p.: 117 – 118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 5.3 Hz, 1H), 7.24 (d, *J* = 5.3 Hz, 1H), 3.86 (s, 3H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 160.2, 135.9, 132.4, 131.7, 127.5, 127.0, 109.0, 53.0, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_9N_4O_2S^+$ 249.0446, Found: 249.0450.



4a

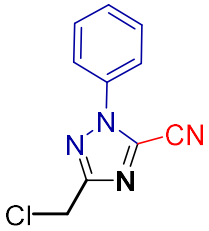
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-ethyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4a** (42 mg; 53% yield); yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.56 – 7.49 (m, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.8, 136.0, 130.2, 130.1, 128.6, 109.8, 21.9, 12.4. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_4^+$ 199.0984, found: 199.0980.



4b

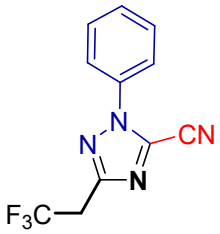
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-(cyclopropylmethyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4b** (33 mg; 36%

yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.60 – 7.53 (m, 3H), 2.75 (d, *J* = 7.1 Hz, 2H), 1.23 – 1.16 (m, 1H), 0.59 (q, *J* = 5.8 Hz, 2H), 0.30 (q, *J* = 4.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 136.1, 131.6, 130.3, 130.2, 130.1, 128.7, 123.0, 120.5, 109.8, 33.2, 9.8, 5.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}N_4^+$ 225.1140, found: 225.1134.



4c

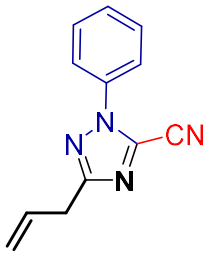
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-(chloromethyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4c** (27 mg; 30% yield), brown solid; m.p.: 74 – 75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.62 – 7.54 (m, 3H), 4.71 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 135.7, 130.8, 130.3, 129.6, 123.1, 109.2, 36.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_4Cl^+$ 219.0437, found: 219.0434.



4d

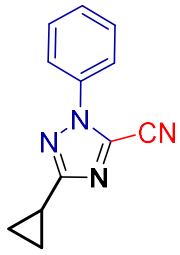
Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **1-phenyl-3-(2,2,2-trifluoroethyl)-1H-1,2,4-triazole-5-carbonitrile 4d** (36 mg; 35%

yield), yellow solid; m.p.: 71 – 72 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.60 – 7.58 (m, 3H), 3.71 (p, J = 9.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.8, 135.5, 130.7, 130.1, 129.4, 124.3 (q, $^{1}J_{C\text{-}F}$ = 276.3 Hz), 122.9, 109.2, 34.1 (q, $^{2}J_{C\text{-}F}$ = 22.0 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.44. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_8N_4F_3^+$ 253.0701, Found: 253.0708.



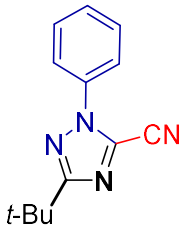
4e

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **3-allyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4e** (45 mg; 53% yield); yellow solid; m.p.: 39 – 40 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 2H), 7.58 – 7.50 (m, 3H), 6.12 – 6.02 (m, 1H), 5.29 – 5.20 (m, 2H), 3.63 (d, J = 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 135.9, 132.7, 130.3, 130.1, 128.9, 123.0, 118.4, 109.6, 32.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4^+$ 211.0984, Found: 211.0986.



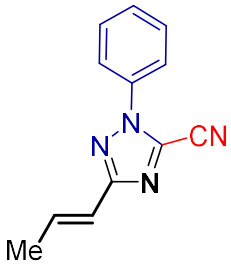
4f

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-cyclopropyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4f** (61 mg; 72% yield), yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 2H), 7.56 – 7.47 (m, 3H), 2.19 – 2.12 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 136.0, 130.1, 130.0, 128.3, 122.8, 109.7, 9.0, 8.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4^+$ 211.0984, Found: 211.0976.



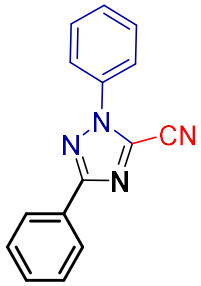
4g

Purified by silica gel chromatography (hexane to hexane/EtOAc = 20/1) to obtain **3-(tert-butyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile 4g** (64 mg; 70% yield), yellow solid; m.p.: 40 – 41 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.58 – 7.48 (m, 3H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 136.2, 130.1, 130.0, 128.4, 123.0, 109.9, 33.5, 29.5. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}N_4^+$ 227.1297, Found: 227.1298.



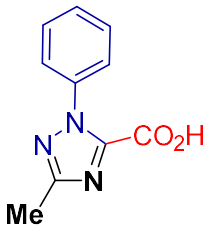
4h

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **(E)-1-phenyl-3-(prop-1-en-1-yl)-1H-1,2,4-triazole-5-carbonitrile 4h** (57 mg; 67% yield), yellow solid; m.p.: 45 – 46 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.60 – 7.53 (m, 3H), 6.93 (dd, *J* = 15.8, 6.8 Hz, 1H), 6.46 (dd, *J* = 15.8, 1.8 Hz, 1H), 1.97 (dd, *J* = 6.9, 1.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 136.0, 130.3, 130.2, 122.9, 119.3, 109.8, 18.7. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4^+$ 211.0984, Found: 211.0990.



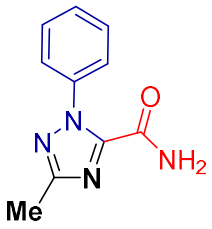
4i

Purified by silica gel chromatography (hexane to hexane/EtOAc = 10/1) to obtain **1,3-diphenyl-1H-1,2,4-triazole-5-carbonitrile 4i** (55 mg; 55% yield), white solid; m.p.: 94 – 95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 7.83 – 7.79 (m, 2H), 7.64 – 7.56 (m, 3H), 7.51 – 7.48 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 136.2, 130.8, 130.5, 130.2, 129.4, 129.2, 129.1, 127.1, 123.1, 109.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}N_4^+$ 247.0984, Found: 247.0980.



5a

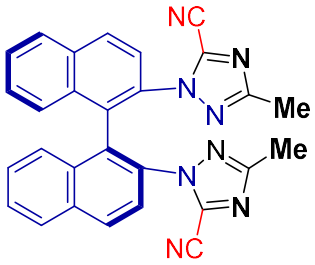
3-methyl-1-phenyl-1H-1,2,4-triazole-5-carboxylic acid (5a). A round-bottom flask equipped with a reflux condenser and magnetic stir bar was added with **3a** (0.54 mmol, 100 mg). A 15% aqueous solution of NaOH was added and the resulting mixture was heated under reflux with stirring in a preheated oil bath for 8 h. After the reaction, the mixture was cooled to room temperature, and 1M HCl aqueous solution was added until pH of 1 was reached. The reaction mixture was extracted with Et_2O (4 × 5 mL) and the combined fraction was concentrated in vacuo to provide **5a** (85 mg, 0.42 mmol, in 77% yield) as a yellow solid; m.p.: 83 – 84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.60 (d, J = 7.7 Hz, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 141.1, 137.2, 129.8, 127.9, 119.9, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{10}N_3O_2^+$ 204.0773, Found: 204.0769.



5b

3-methyl-1-phenyl-1H-1,2,4-triazole-5-carboxamide (5b). A flame-dried round bottom flask equipped with a magnetic stir bar was charged with **3a** (100 mg, 0.54

mmol, 1.0 equiv), KO^{t}Bu (182 mg, 1.63 mmol, 3.0 equiv), and dry toluene (4 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere overnight, and the progress of the reaction was monitored by TLC analysis. Upon reaction completion, the reaction mixture was quenched with water (10 mL). The precipitated amide product solid was filtered, washed with water, and dried under vacuum to afford **5a** (82 mg, 0.4 mmol, 75%) as a yellow solid. 75% yield; yellow solid; m.p.: 201 – 202 °C; **^{1}H NMR** (400 MHz, DMSO) δ 8.25 (s, 1H), 7.90 (s, 1H), 7.51 – 7.44 (m, 5H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 159.1, 158.8, 147.9, 137.9, 128.7, 124.9, 13.4. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}N_4O^+$ 203.0933, Found: 203.0929.



1,1'-([1,1'-binaphthalene]-2,2'-diyl)bis(3-methyl-1H-1,2,4-triazole-5-carbonitrile) (6). An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with the bis-naphthalene arenediazonium salt[2] (144.60 mg, 0.3 mmol), CuBr (8.61 mg, 0.06 mmol), K_2CO_3 (82.92 mg, 0.6 mmol) and 4Å molecular sieve (100 mg). Nitrile solvent (2 mL) followed by 2-diazoacetonitrile (80.47 mg, 1.2 mmol, 4.0 equiv) were added into the reaction mixture. The resulting mixture was stirred at 40 °C for 2 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (hexane to

hexane/EtOAc = 5/1 to obtain the desired product. 85 mg; 60% yield, brown liquid; $[\alpha]_D^{20}$ = -74 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.46 (t, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 2.12 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 133.9, 133.6, 132.3, 131.1, 131.0, 130.1, 128.52, 128.47, 128.3, 127.6, 122.7, 109.4, 13.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{19}N_8^+$ 467.1733, found: 467.1724.

References

(1) Chen, Z.; Fan, S.-Q.; Zheng, Y.; Ma, J.-A. Silver-catalyzed regioselective [3+2] cycloaddition of arenediazonium salts with 2,2,2-trifluorodiazoethane (CF_3CHN_2): a facile access to 2-aryl-5-trifluoromethyltetrazoles. *Chem. Commun.* **2015**, *51*, 16545−16548.

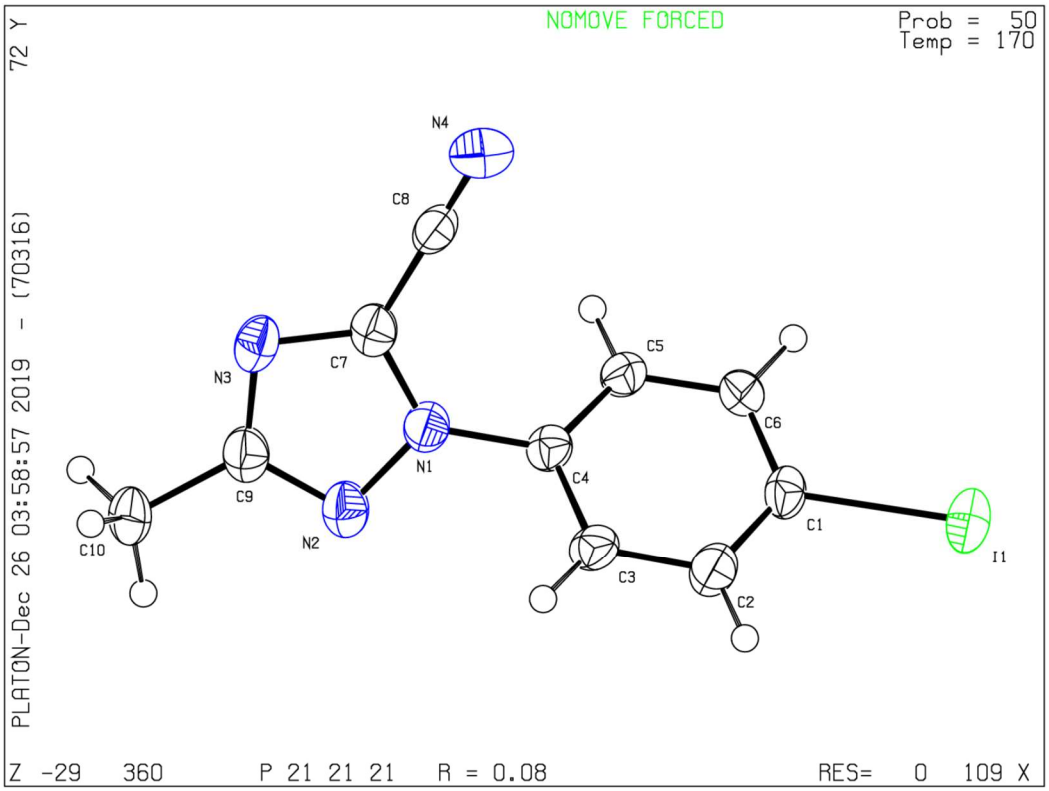
(2) Jimoh, A.-A.; Hosseyni, S.; Ye, X.-H.; Wojtas, L.; Hu, Y.; Shi, X.-D. Gold redox catalysis for cyclization/arylation of allylic oximes: synthesis of isoxazoline derivatives. *Chem. Commun.* **2019**, *55*, 8150−8153.

(3) Feng, F.-F.; Li, J.-K.; Liu, X.-Y.; Zhang, F.-G.; Cheung, C. W.; Ma, J.-A. General Synthesis of Tri-Carbo-Substituted N^2-Aryl-1,2,3-triazoles via Cu-Catalyzed Annulation of Azirines with Aryldiazonium Salts. *J. Org. Chem.* **2020**, *85*, 10872−10883.

(4) Chen, Z.; Zhang, Y.; Nie, J.; Ma, J.-A. Transition-Metal-Free [3+2] Cycloaddition of Nitroolefins and Diazoacetonitrile: A Facile Access to Multisubstituted Cyanopyrazoles. *Org. Lett.* **2018**, *20*, 2120–2124.

X-Ray Crystallographic Data

The following single crystals were grown by solvent diffusion method in 10 mL test tube. About 100 mg of the corresponding sample was dissolved in 1 mL ethyl acetate at the bottom of the tube, and then 15 mL of n-hexane was added to the upper part of the liquid surface. The test tube was sealed with plastic film. We pricked several holes on the plastic film to let the solvent slowly evaporated at room temperature. The single crystal of the target compound was obatined after several days and subjected to X-ray analysis. The X-ray crystallographic structure for **3l** (ORTEP representation with 50% probability thermal ellipsoids) has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1985560. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc. cam.ac.uk/data_request/cif.



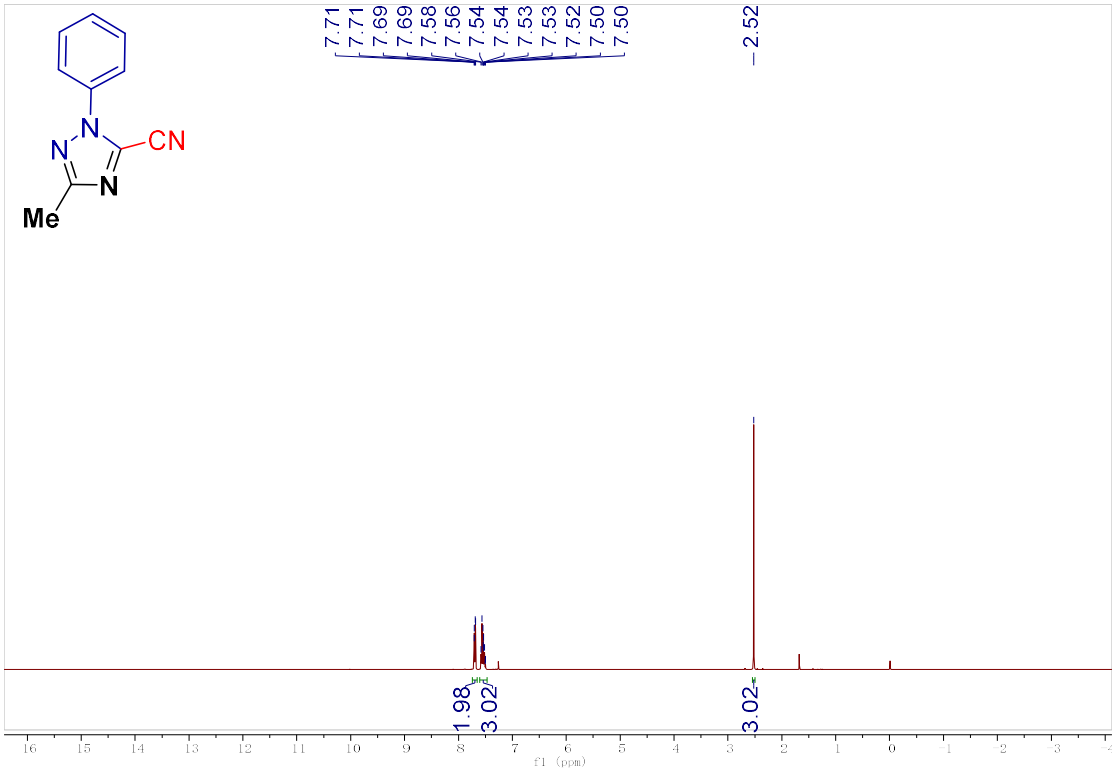
Crystal data and structure refinement for 360.

Identification code	360
Empirical formula	$C_{10}H_7IN_4$
Formula weight	310.10
Temperature/K	170.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.0475(4)
b/Å	12.3243(13)
c/Å	21.549(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1074.9(2)
Z	4
ρ_{calc}g/cm^3	1.916
μ/mm^{-1}	2.950
F(000)	592.0
Crystal size/mm^3	0.19 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.022 to 52.756
Index ranges	$-5 \leq h \leq 0$, $-15 \leq k \leq 15$, $0 \leq l \leq 26$
Reflections collected	2451
Independent reflections	2172 [R_{int} = 0.0829, R_{sigma} = 0.1011]
Data/restraints/parameters	2172/111/138
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0774, wR_2 = 0.1461

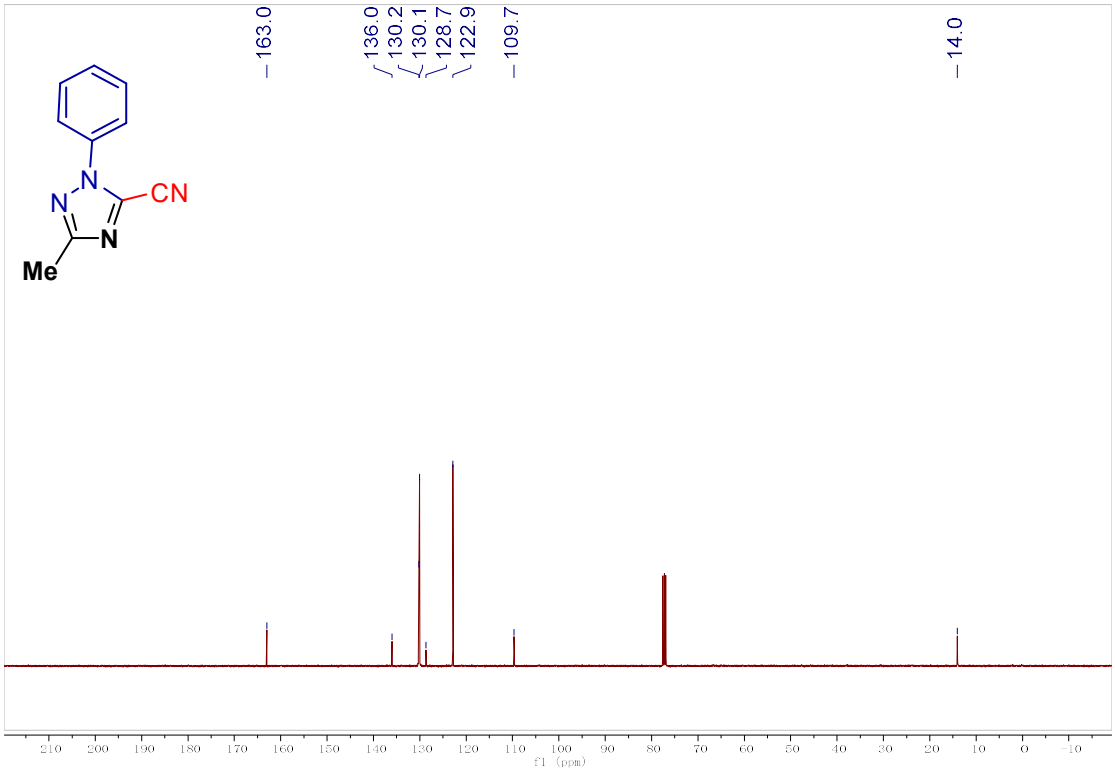
Final R indexes [all data]	$R_1 = 0.1255$, $wR_2 = 0.1627$
Largest diff. peak/hole / e $Å^{-3}$	1.40/-1.07
Flack parameter	0.47(12)

NMR Spectra

3-methyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (3a)

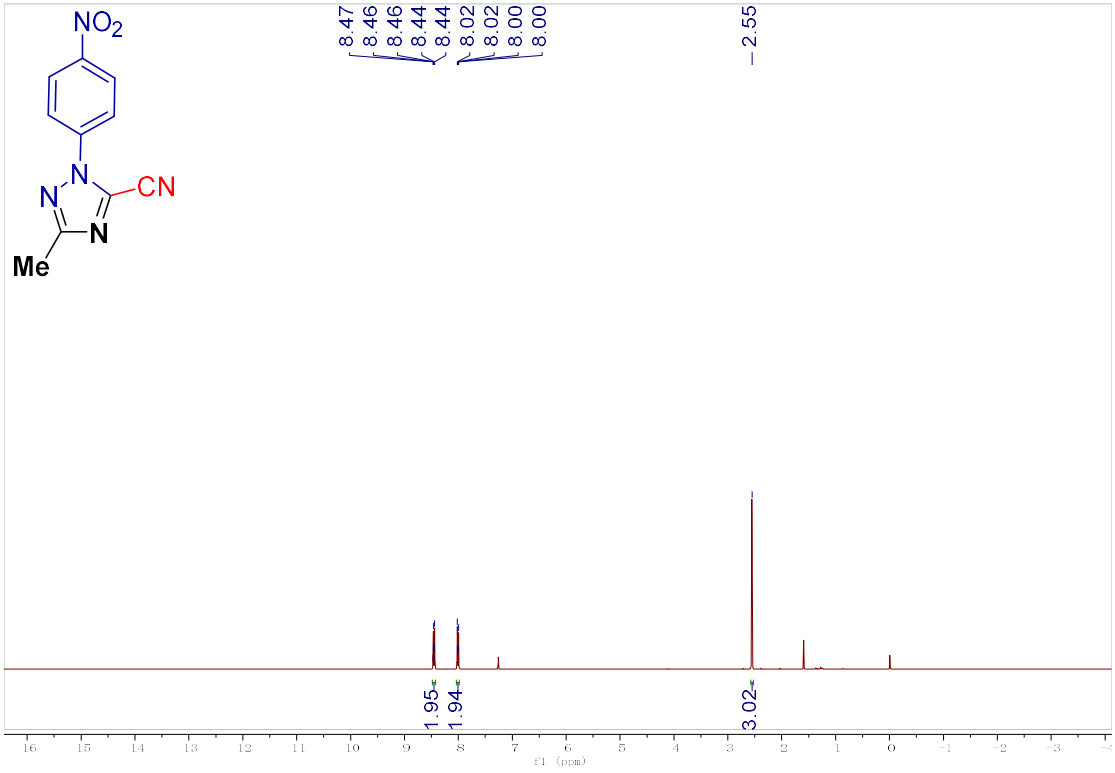


^{1}H NMR (400 MHz, $CDCl_3$) of **3a**

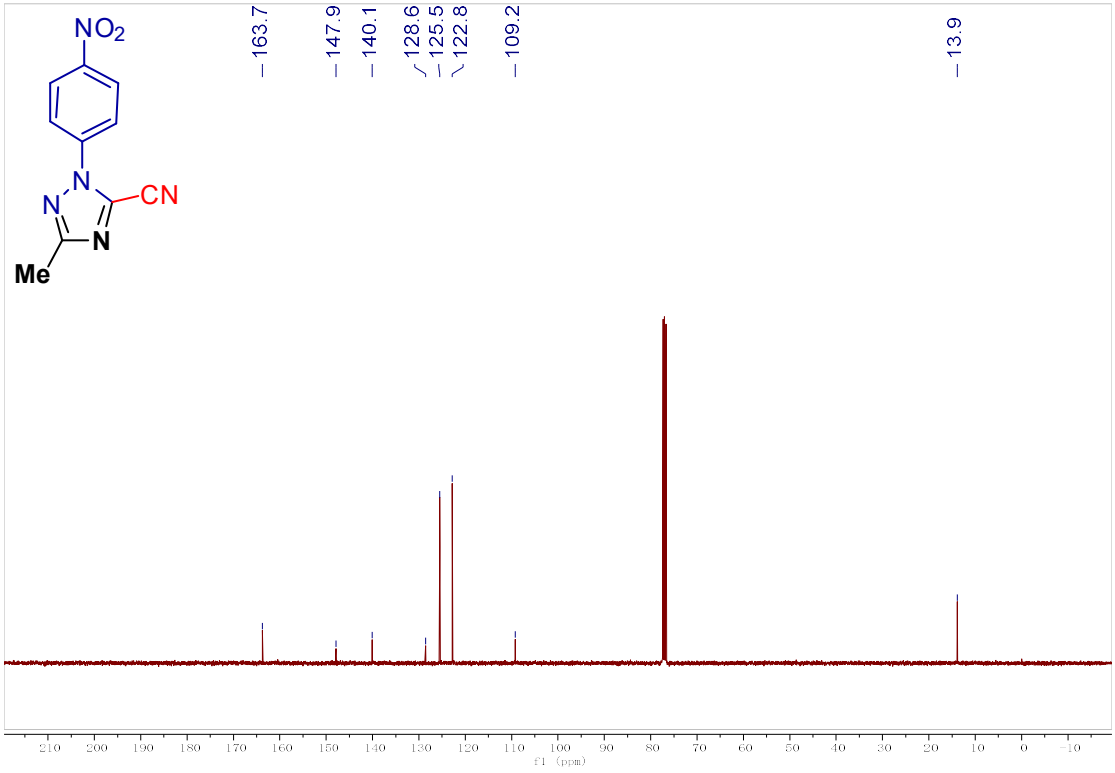


^{13}C NMR (100 MHz, $CDCl_3$) of **3a**

3-methyl-1-(4-nitrophenyl)-1H-1,2,4-triazole-5-carbonitrile (3b)

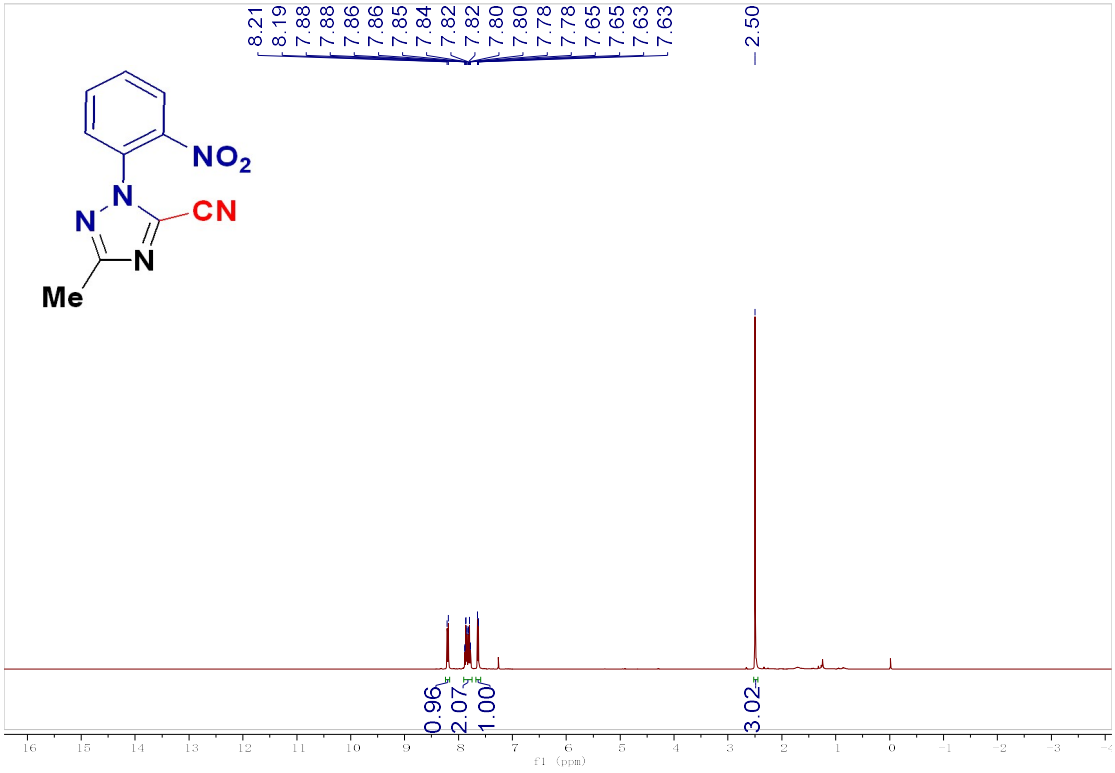


^{1}H NMR (400 MHz, $CDCl_3$) of **3b**

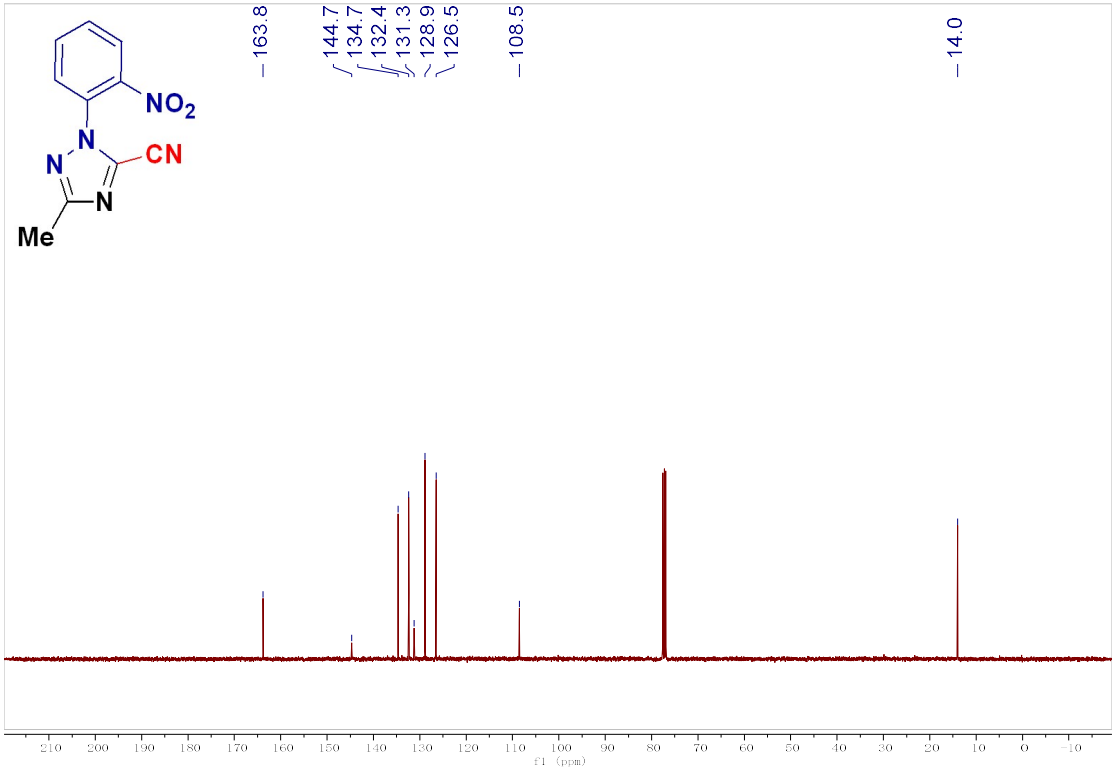


^{13}C NMR (100 MHz, $CDCl_3$) of **3b**

3-methyl-1-(2-nitrophenyl)-1H-1,2,4-triazole-5-carbonitrile (3c)

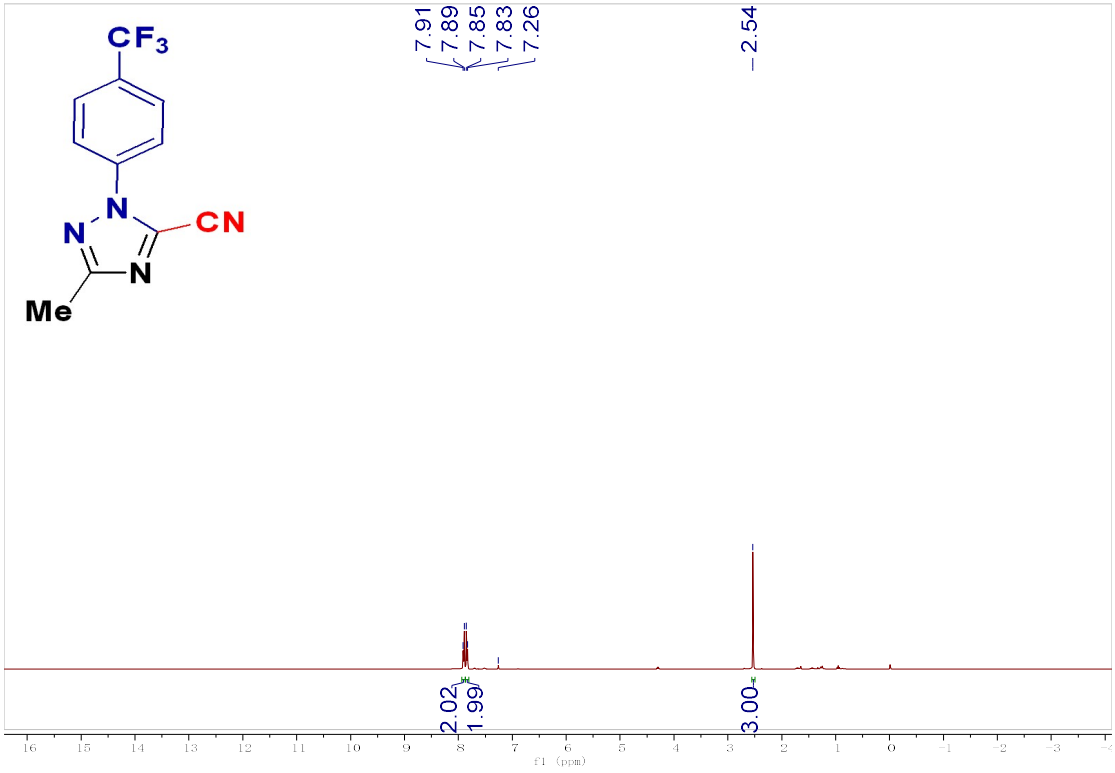


^{1}H NMR (400 MHz, $CDCl_3$) of **3c**

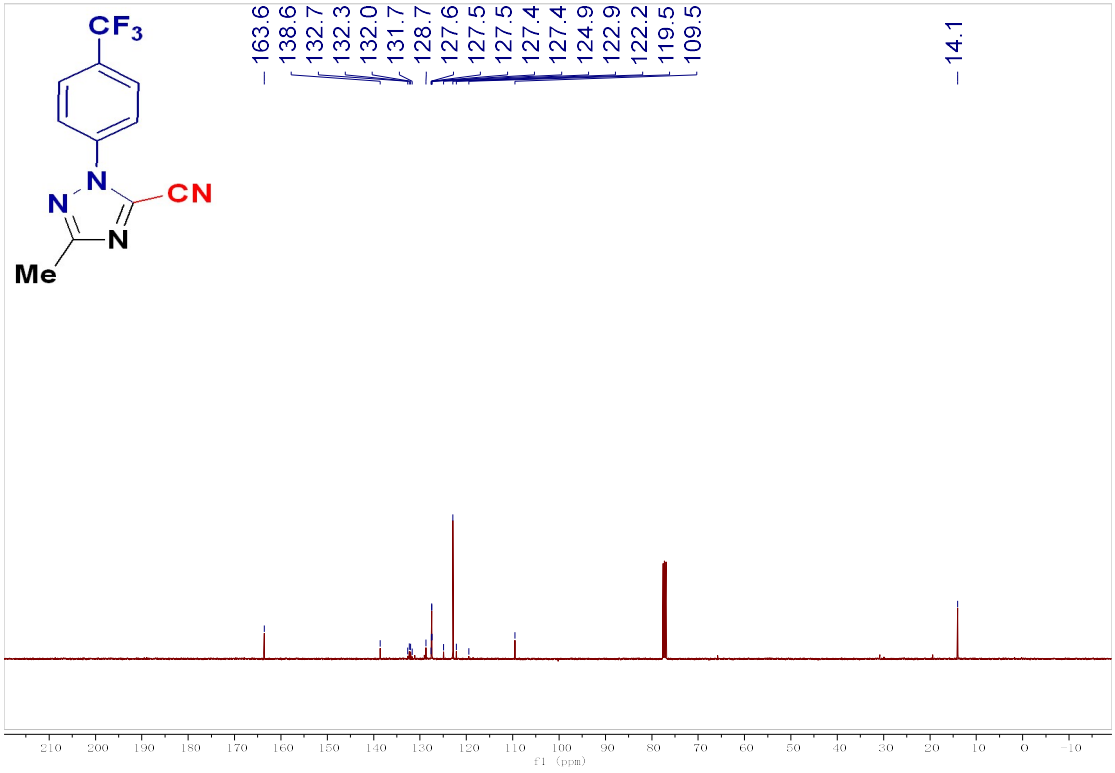


^{13}C NMR (100 MHz, $CDCl_3$) of **3c**

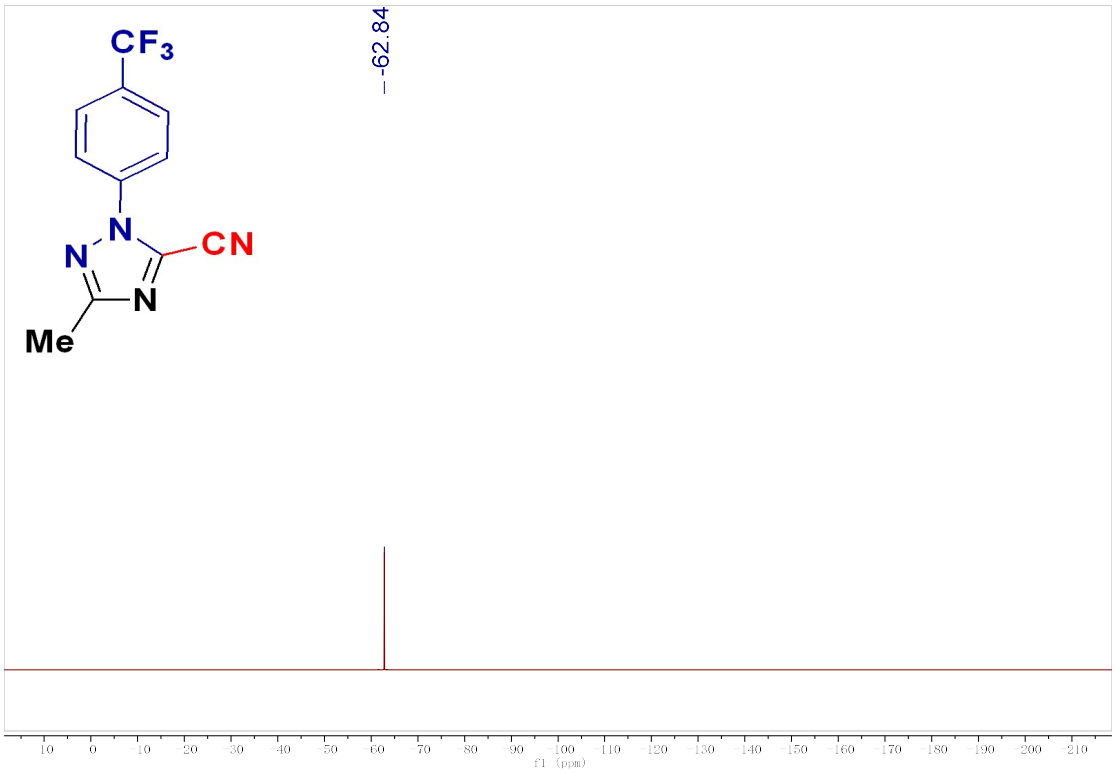
3-methyl-1-(4-(trifluoromethyl)phenyl)-1H-1,2,4-triazole-5-carbonitrile (3d)



^{1}H NMR (400 MHz, $CDCl_3$) of **3d**

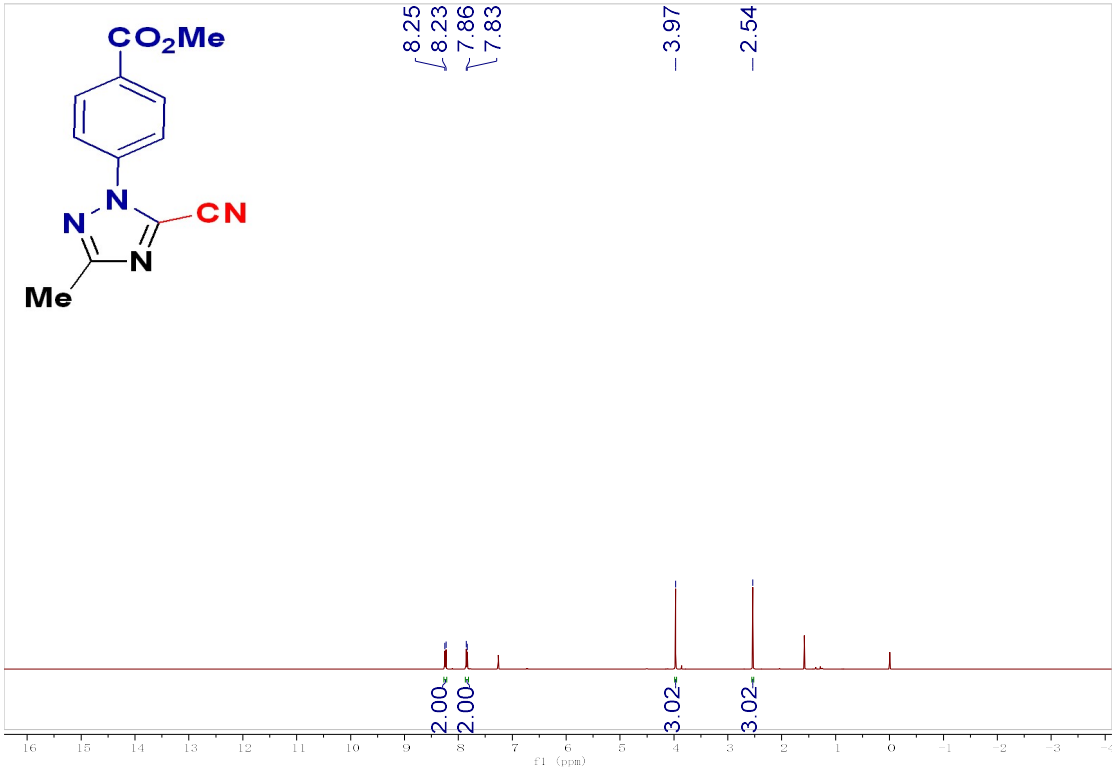


^{13}C NMR (100 MHz, $CDCl_3$) of **3d**

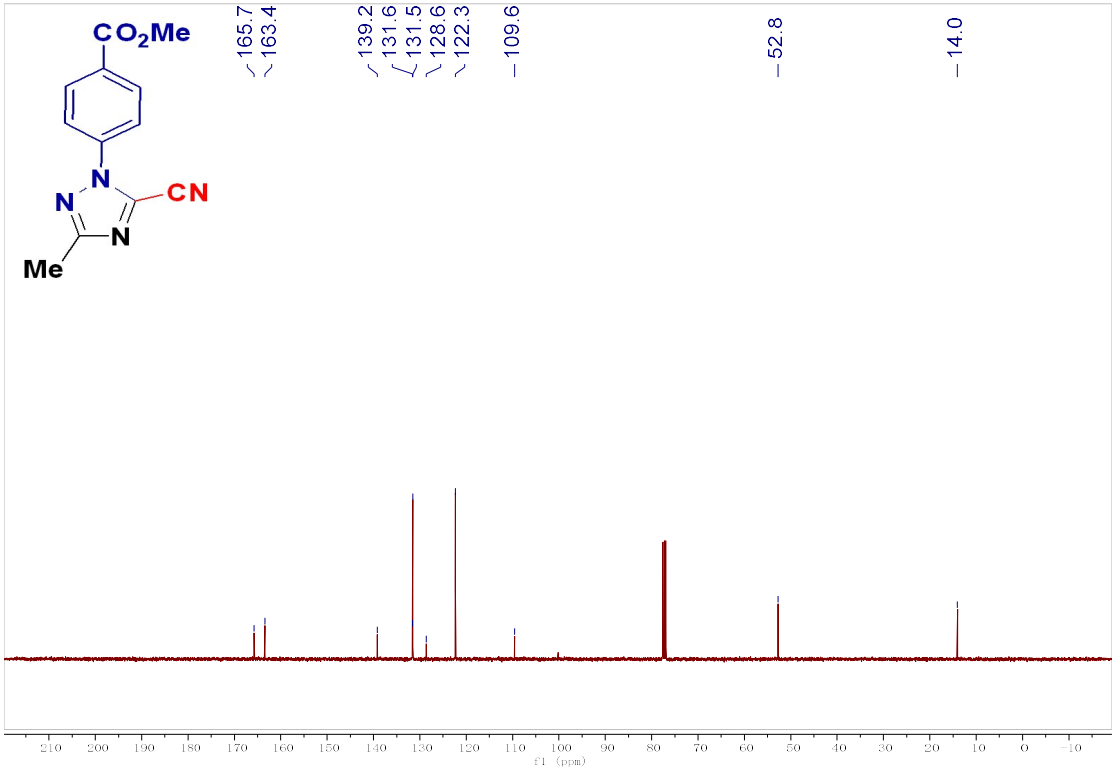


^{19}F NMR (376 MHz, $CDCl_3$) of **3d**

methyl 4-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)benzoate (3e)

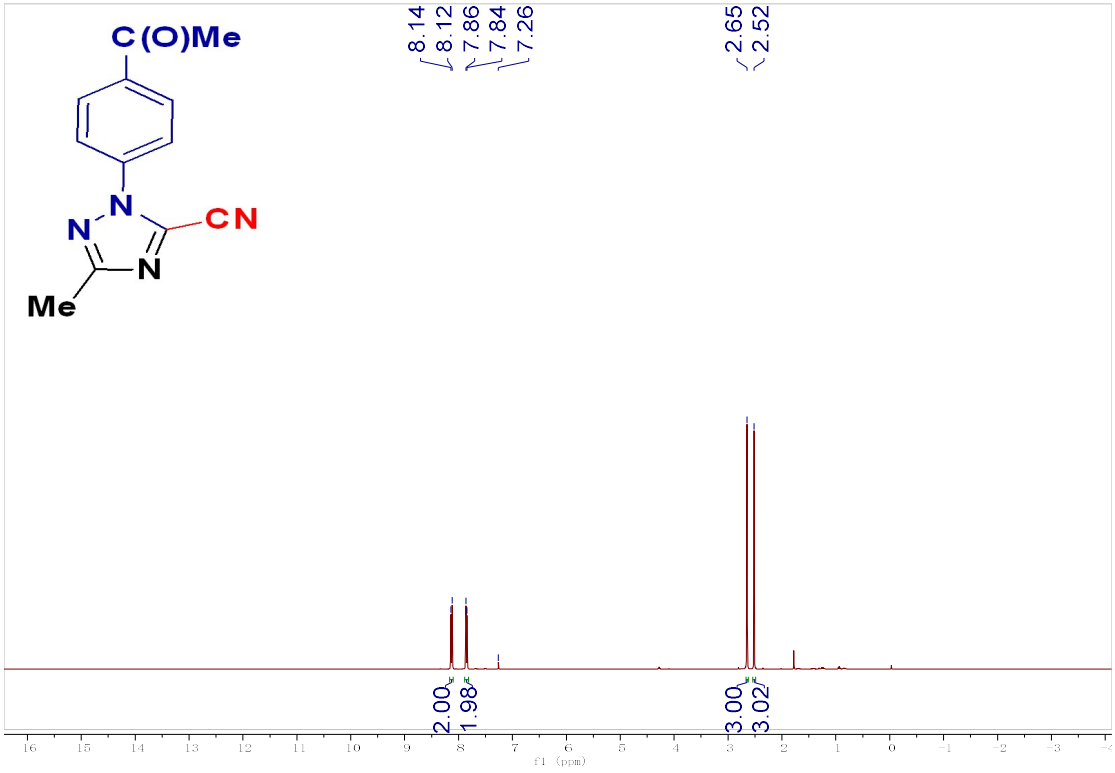


^{1}H NMR (400 MHz, $CDCl_3$) of **3e**

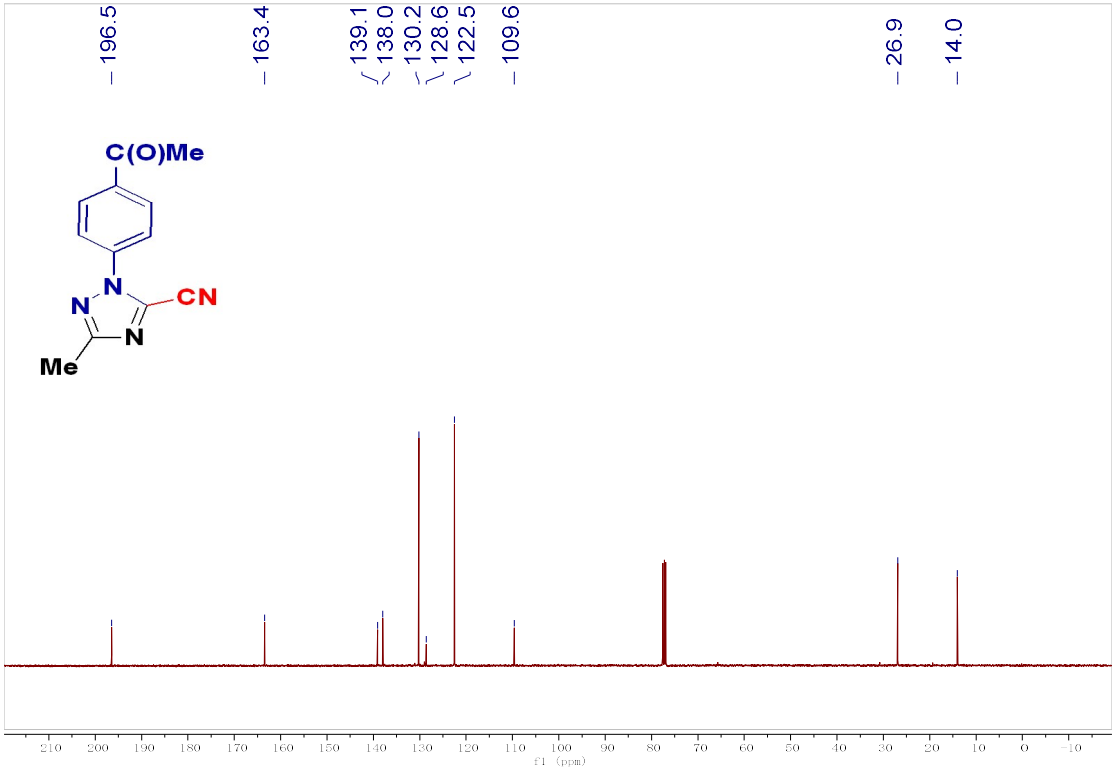


^{13}C NMR (100 MHz, $CDCl_3$) of **3e**

1-(4-acetylphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3f)

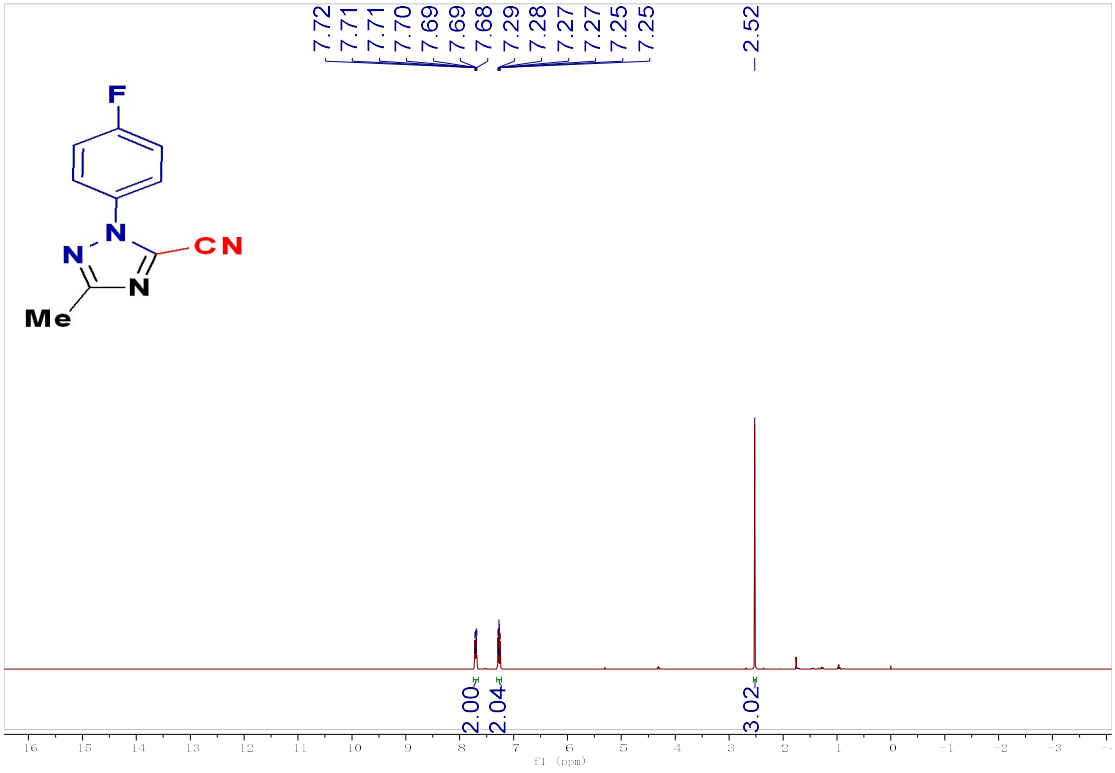


^{1}H NMR (400 MHz, $CDCl_3$) of **3f**

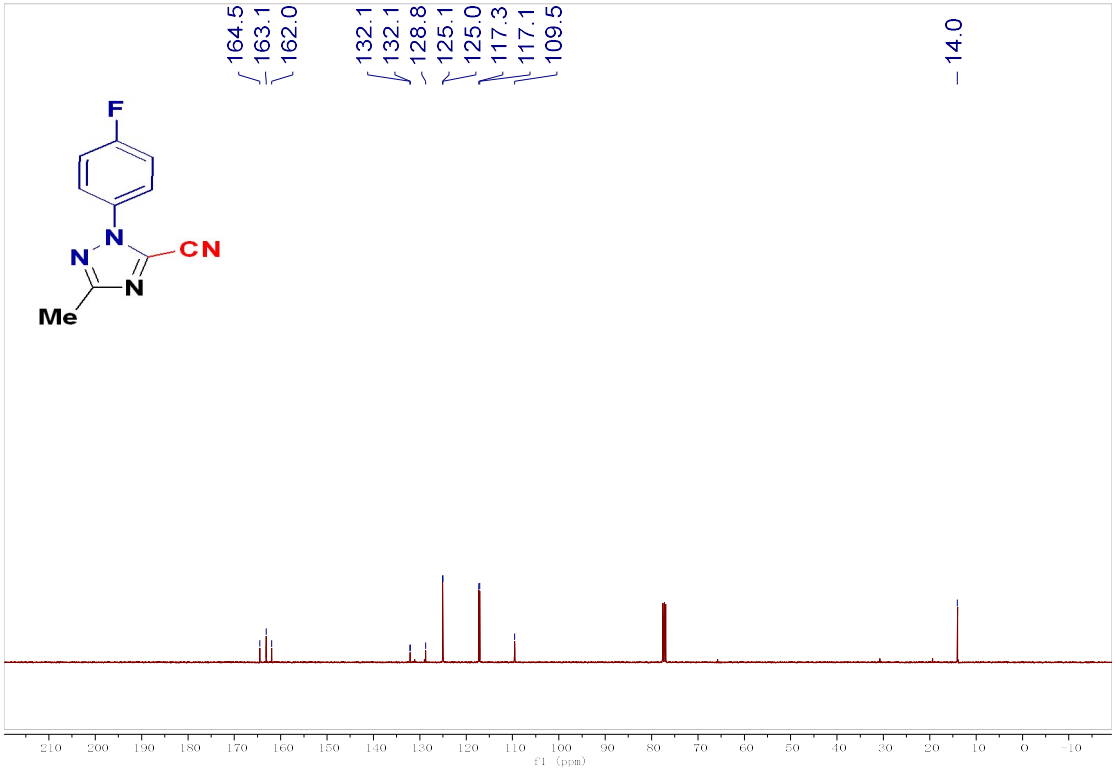


^{13}C NMR (100 MHz, $CDCl_3$) of **3f**

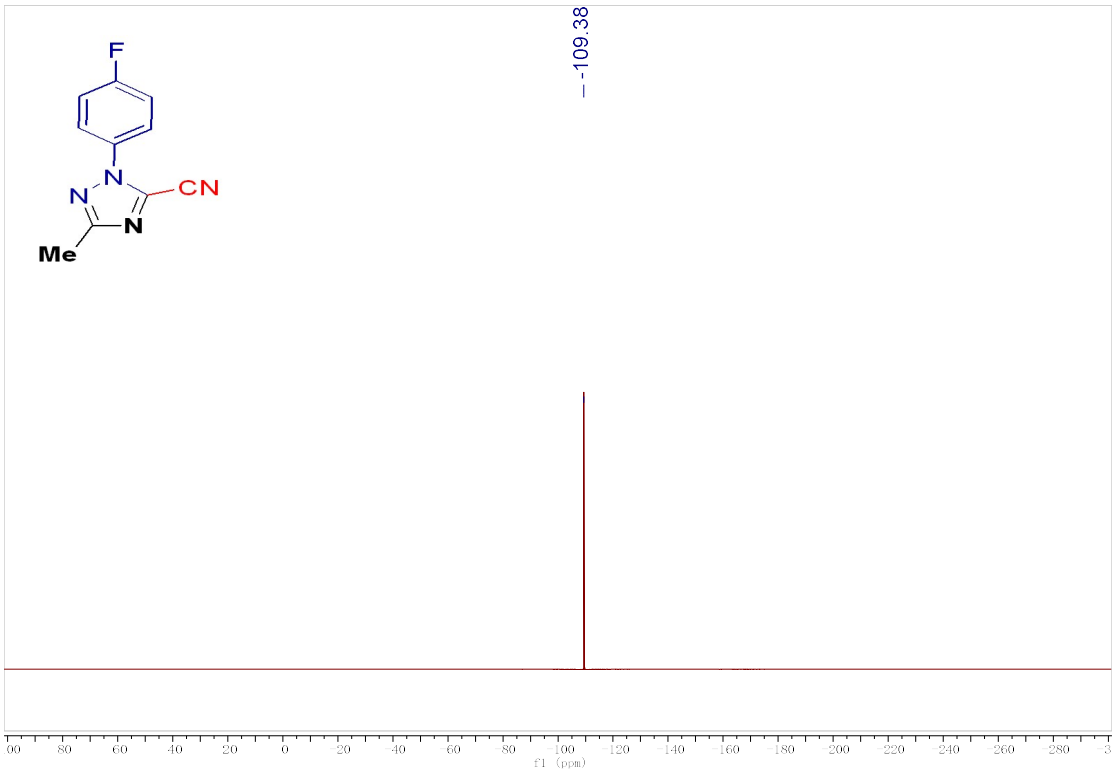
1-(4-fluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3g)



^{1}H NMR (400 MHz, $CDCl_3$) of **3g**

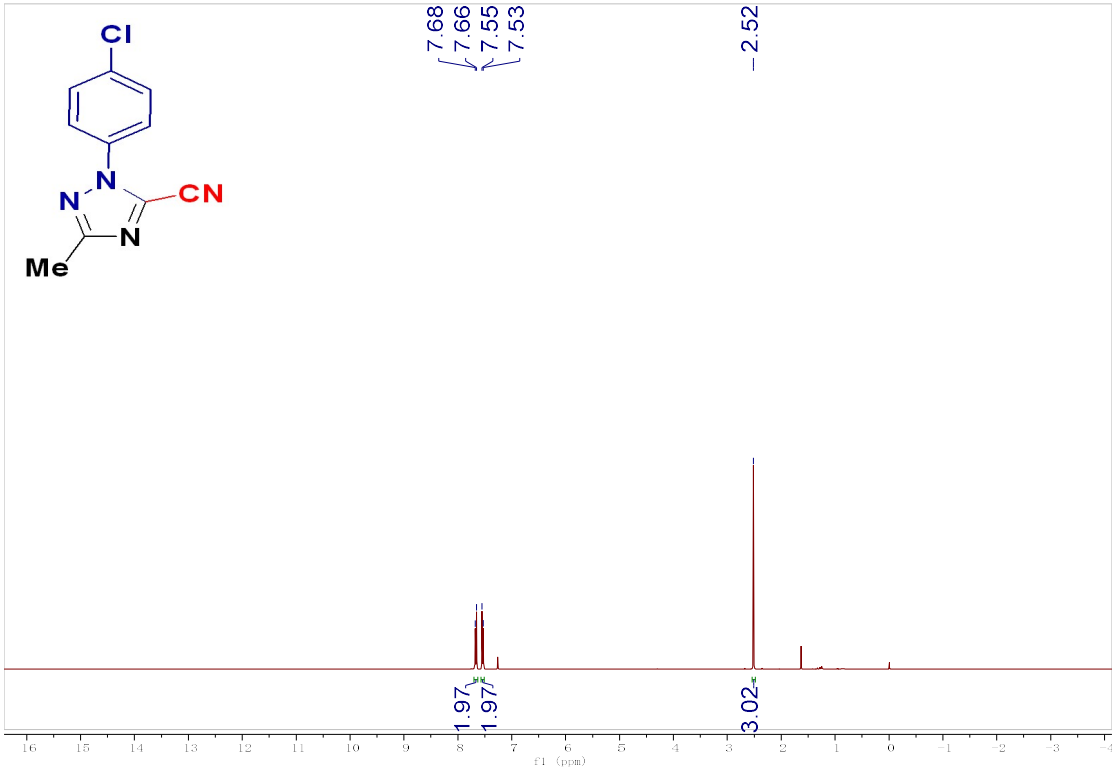


^{13}C NMR (100 MHz, $CDCl_3$) of **3g**

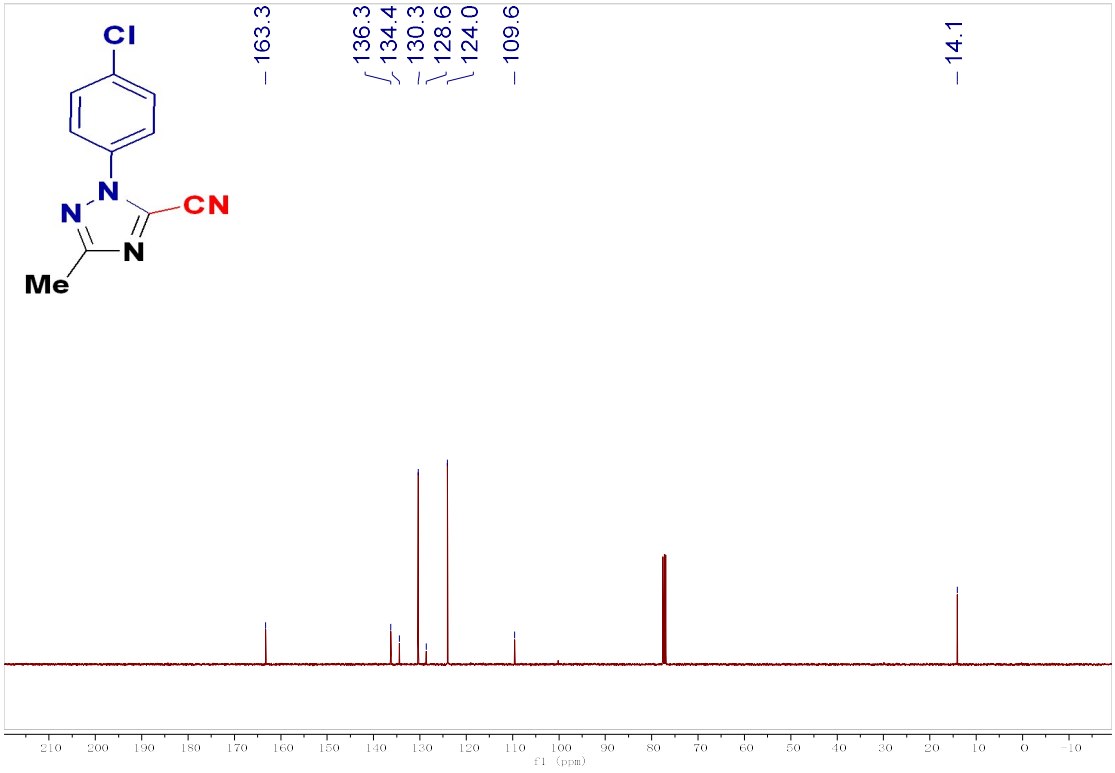


^{19}F NMR (565 MHz, $CDCl_3$) of **3g**

1-(4-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3h)

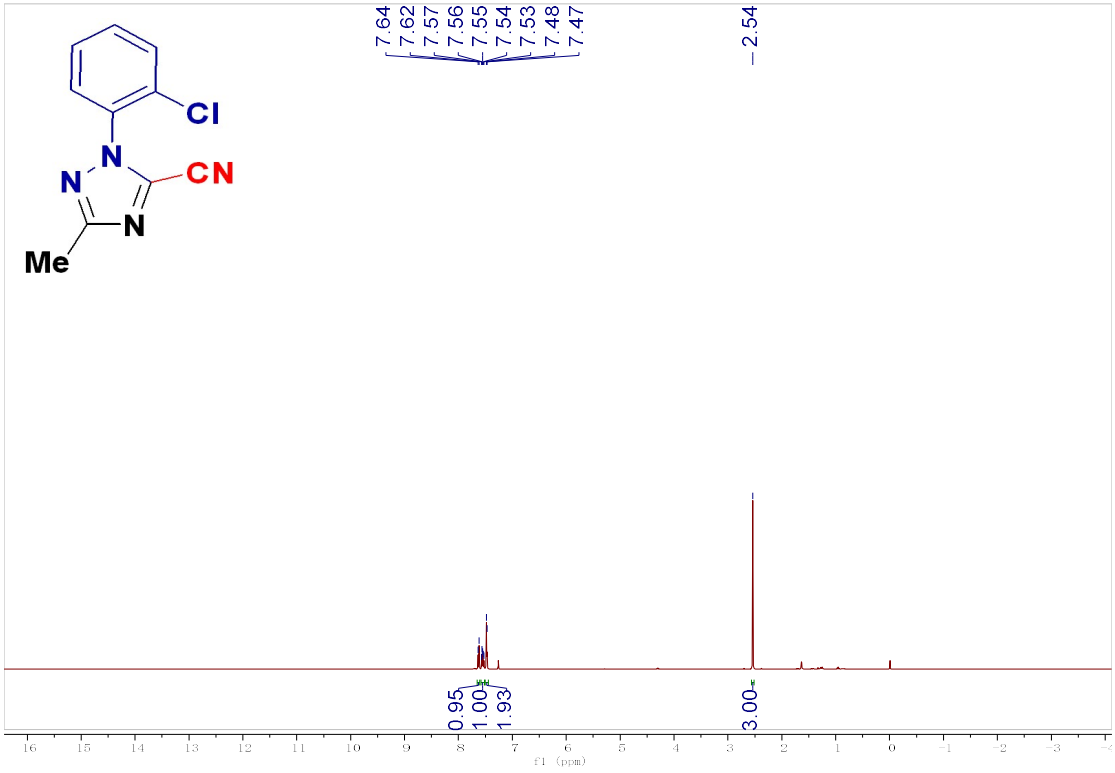


^{1}H NMR (400 MHz, $CDCl_3$) of **3h**

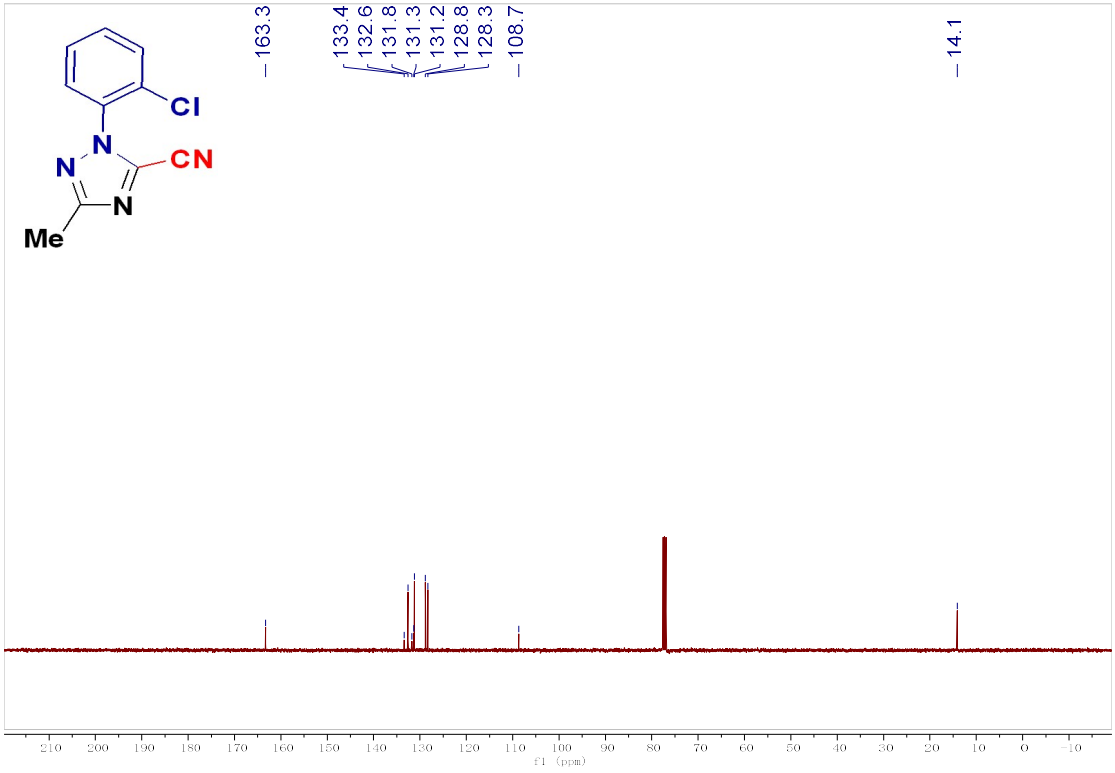


^{13}C NMR (100 MHz, $CDCl_3$) of **3h**

1-(2-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3i)

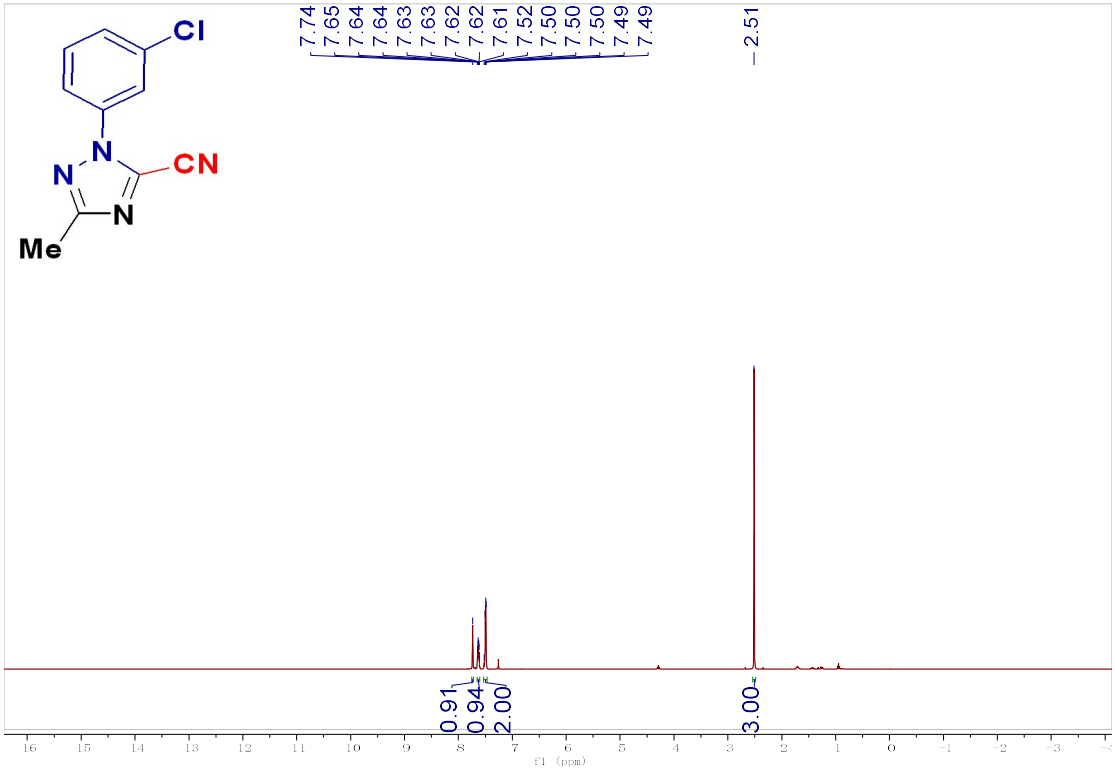


^{1}H NMR (400 MHz, $CDCl_3$) of **3i**

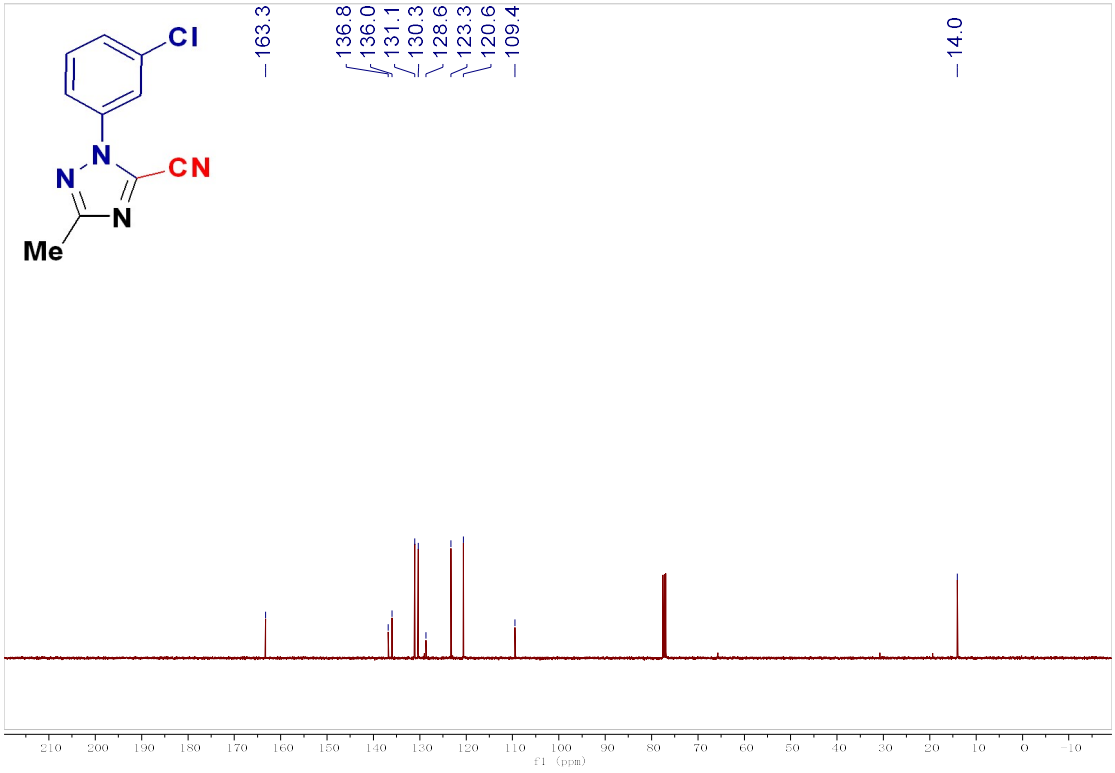


^{13}C NMR (100 MHz, $CDCl_3$) of **3i**

1-(3-chlorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3j)

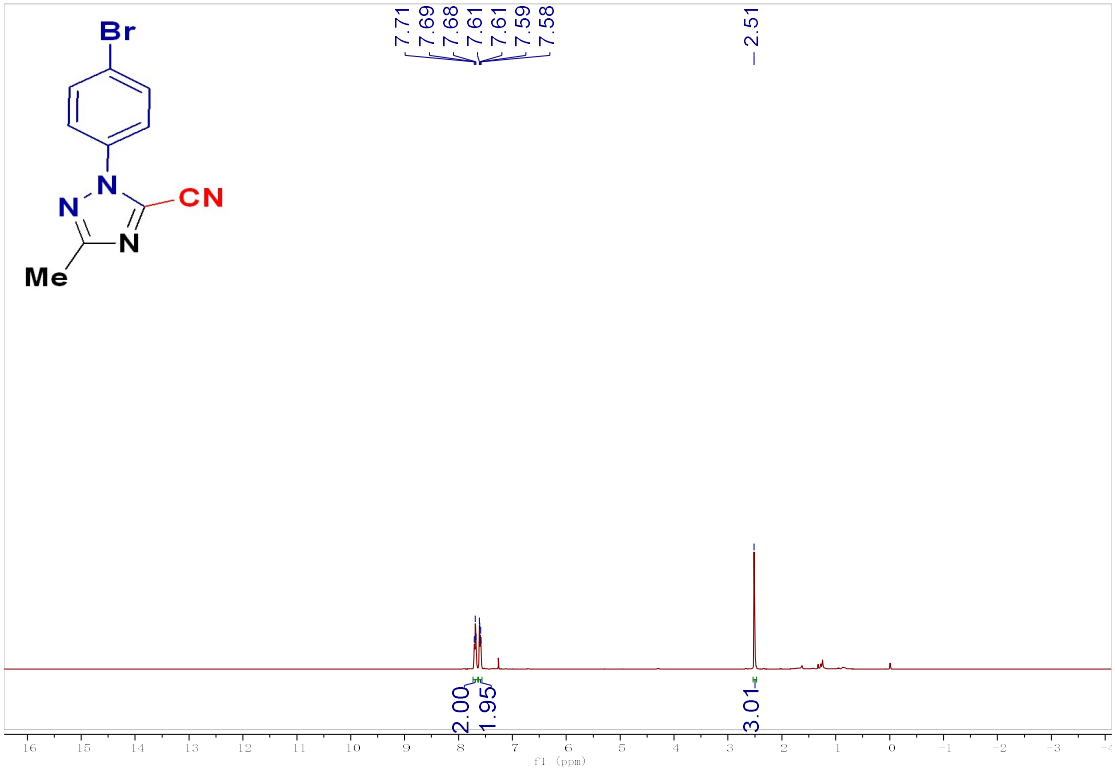


^{1}H NMR (400 MHz, $CDCl_3$) of **3j**

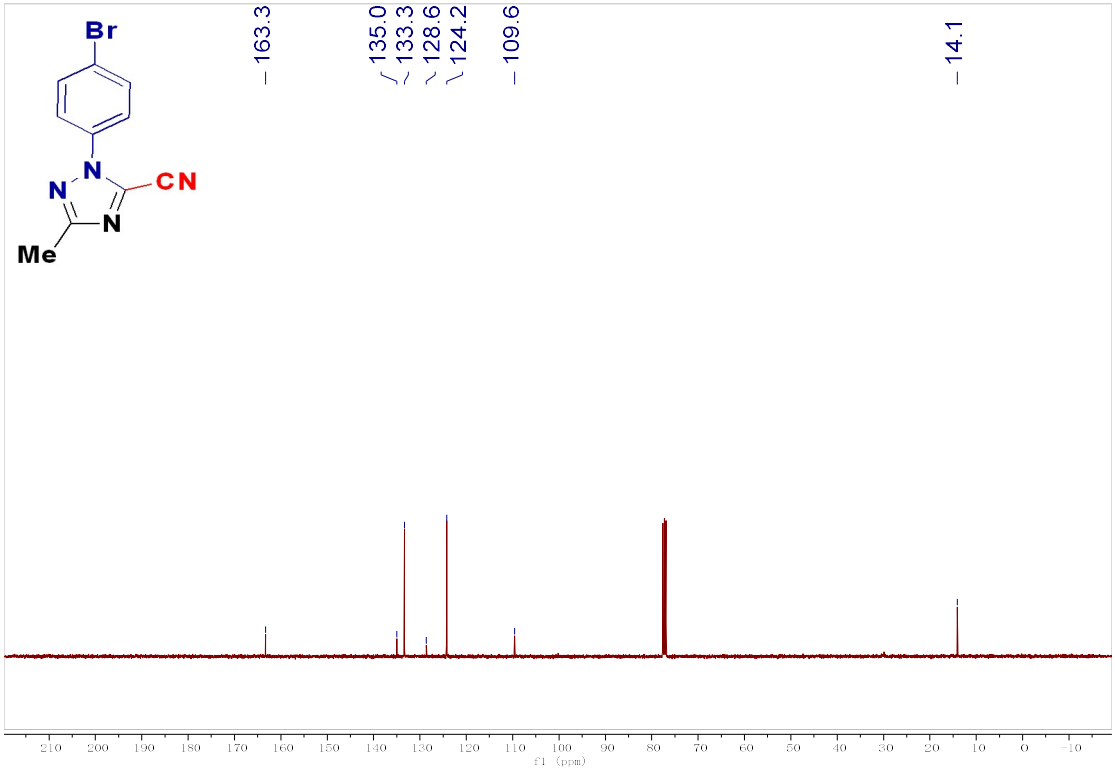


^{13}C NMR (100 MHz, $CDCl_3$) of **3j**

1-(4-bromophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3k)

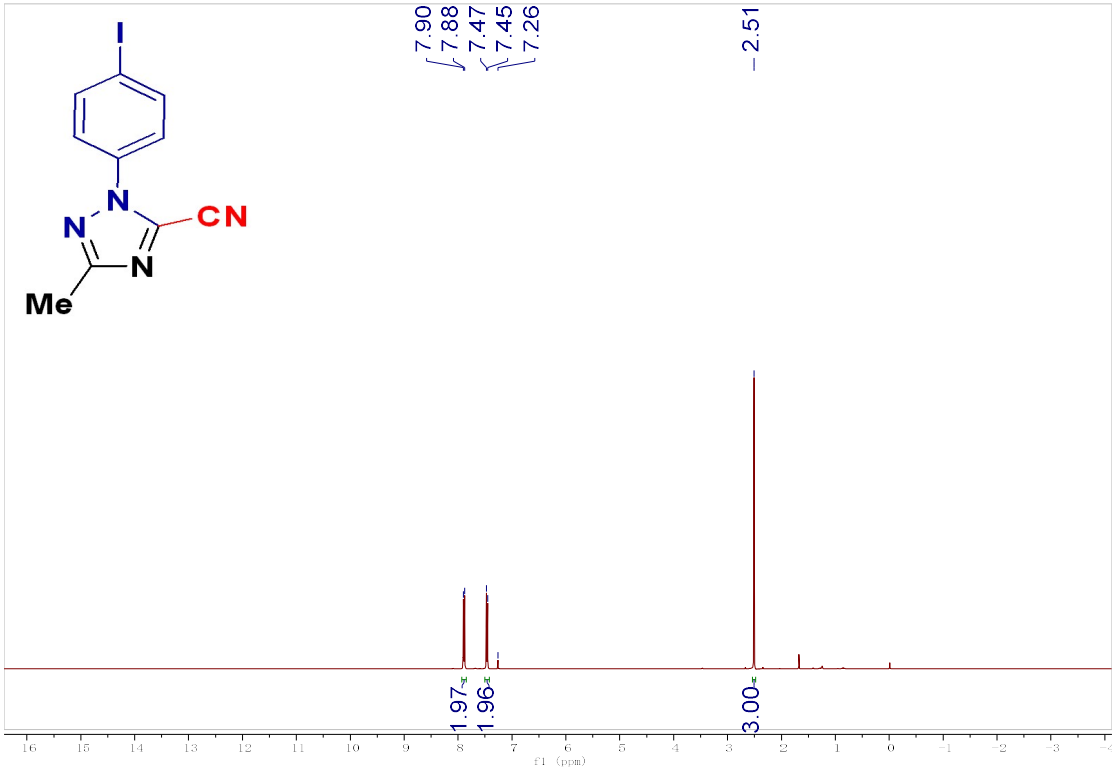


^{1}H NMR (400 MHz, $CDCl_3$) of **3k**

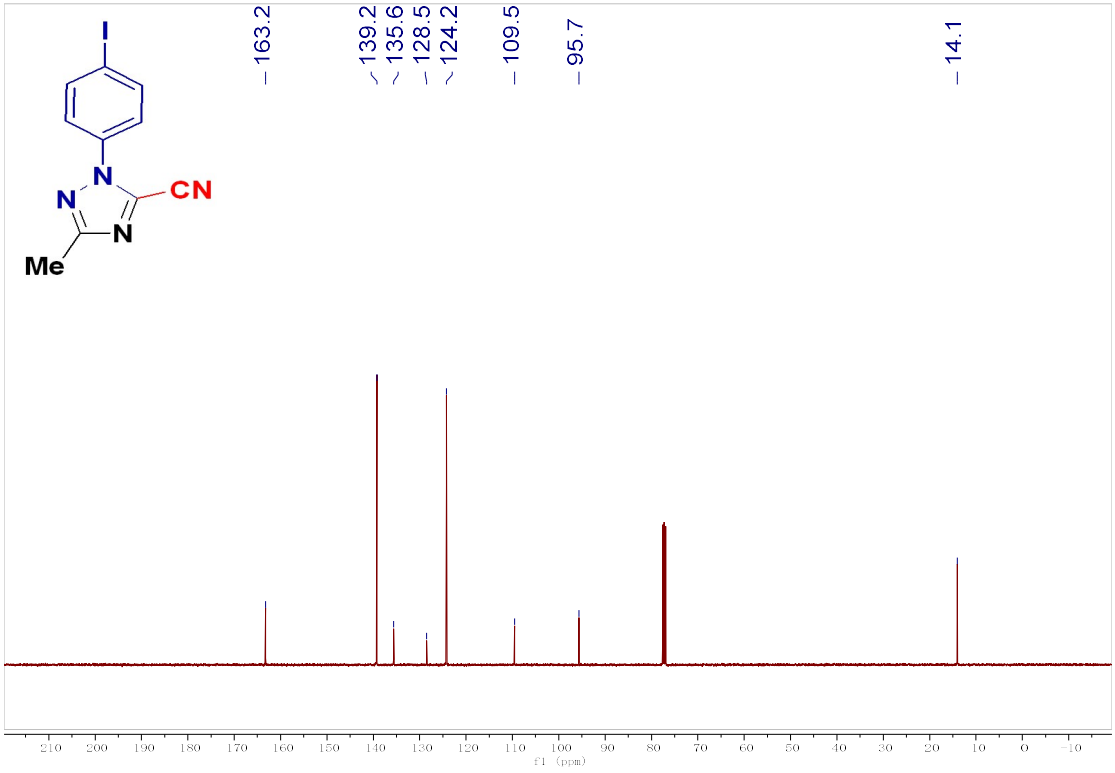


^{13}C NMR (100 MHz, $CDCl_3$) of **3k**

1-(4-iodophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3l)

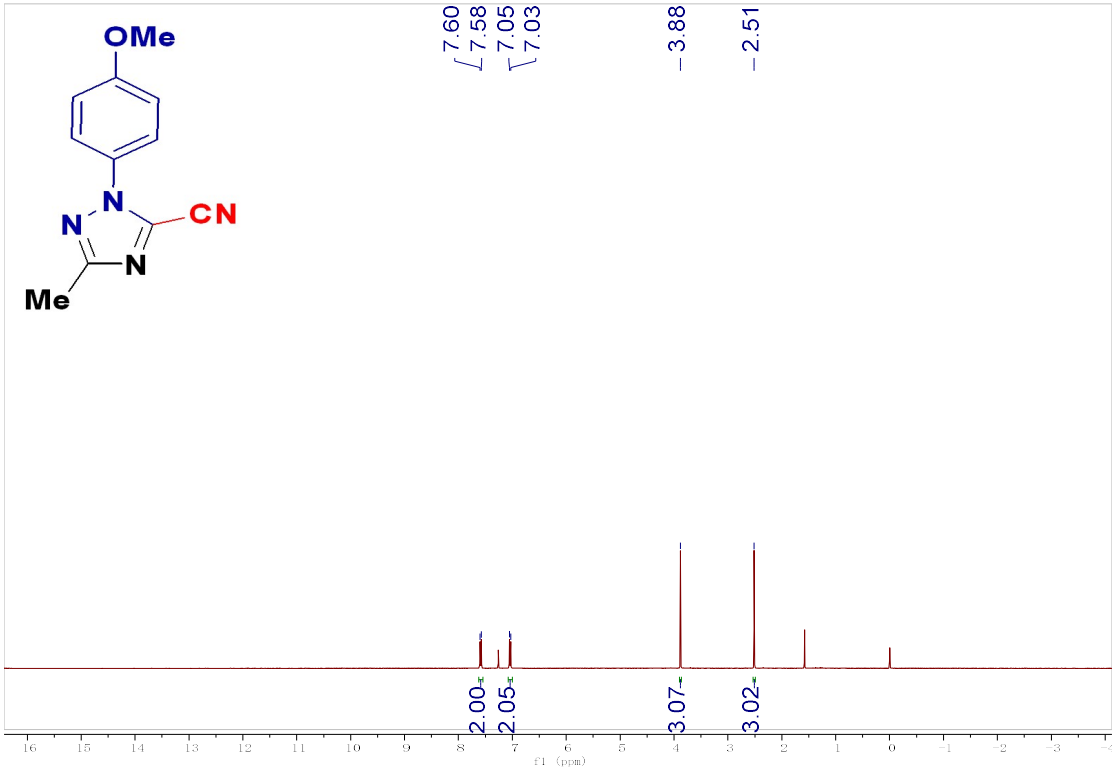


^{1}H NMR (400 MHz, $CDCl_3$) of **3l**

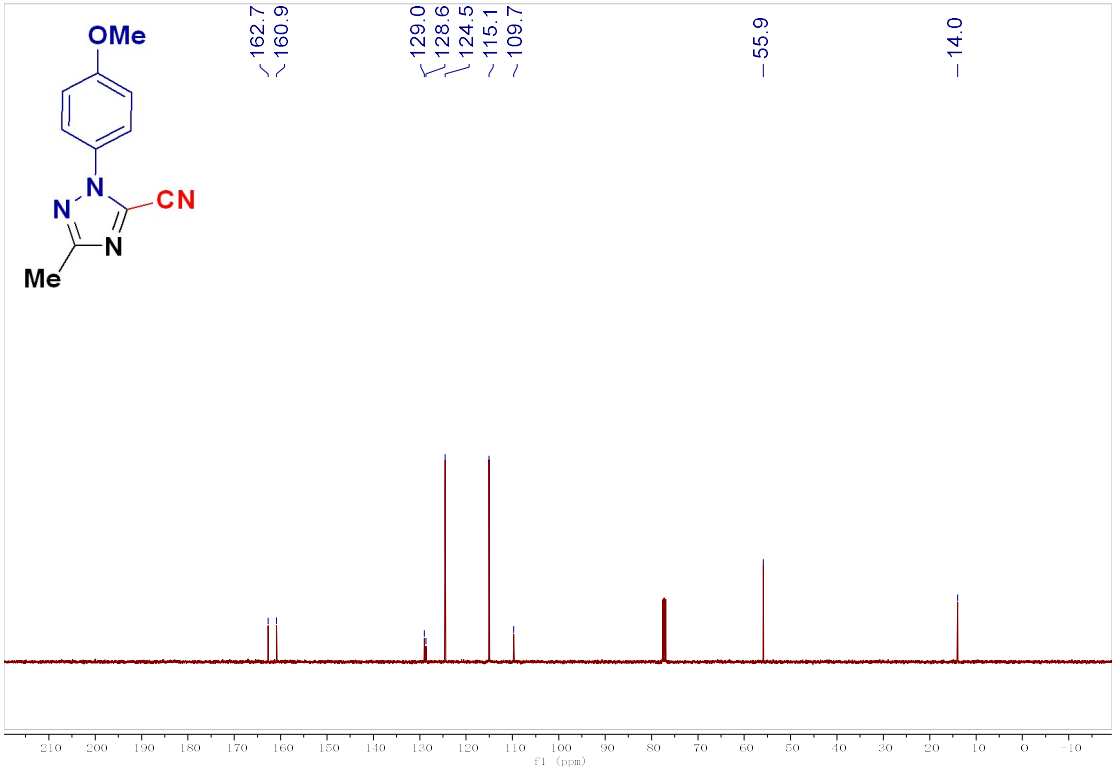


^{13}C NMR (100 MHz, $CDCl_3$) of **3l**

1-(4-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3m)

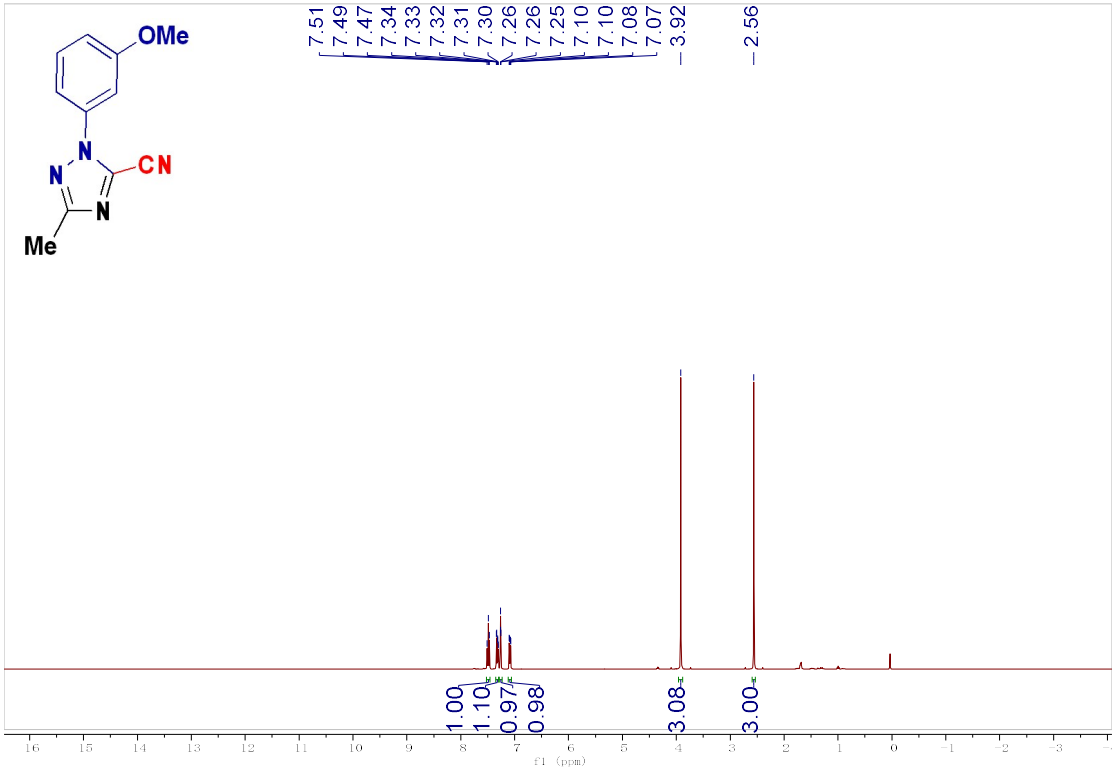


^{1}H NMR (400 MHz, $CDCl_3$) of **3m**

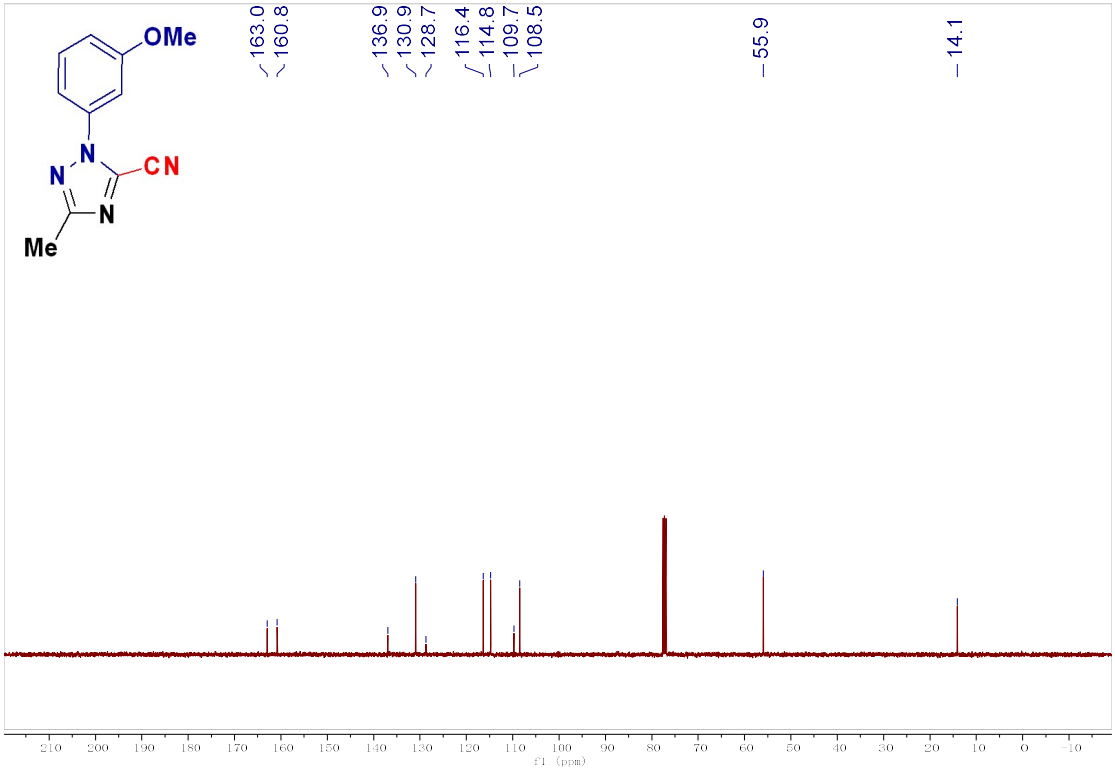


^{13}C NMR (100 MHz, $CDCl_3$) of **3m**

1-(3-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3n)

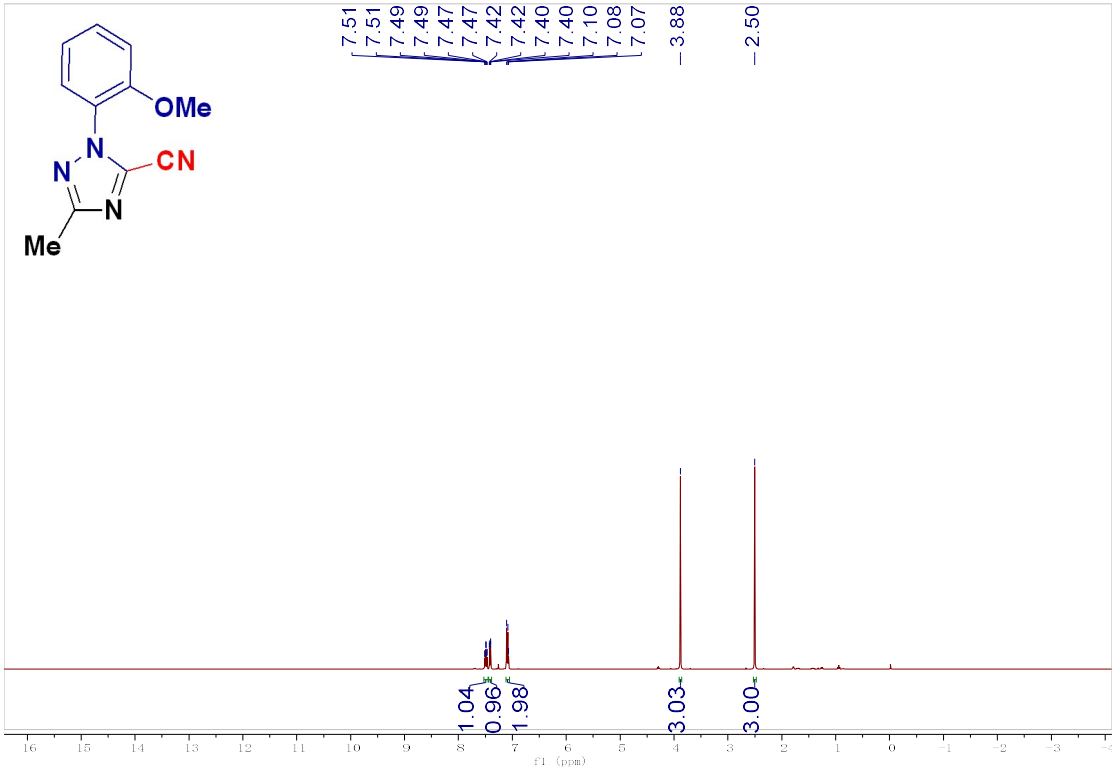


^{1}H NMR (400 MHz, $CDCl_3$) of **3n**

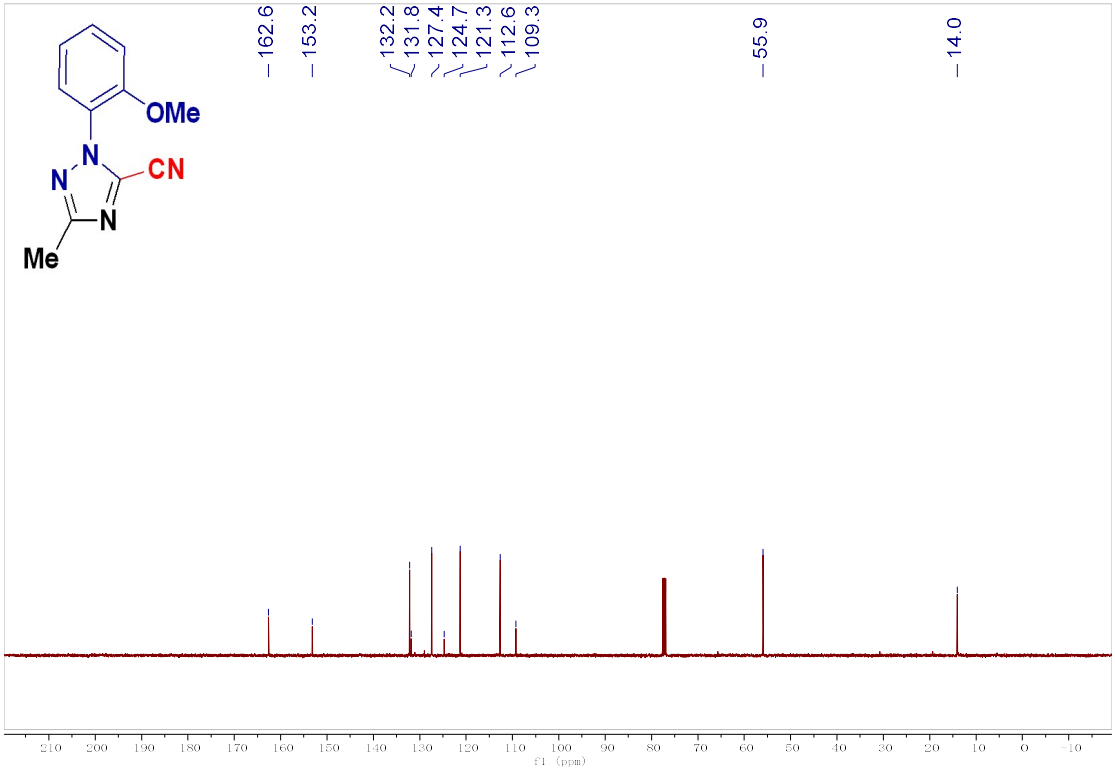


^{13}C NMR (100 MHz, $CDCl_3$) of **3n**

1-(2-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3o)

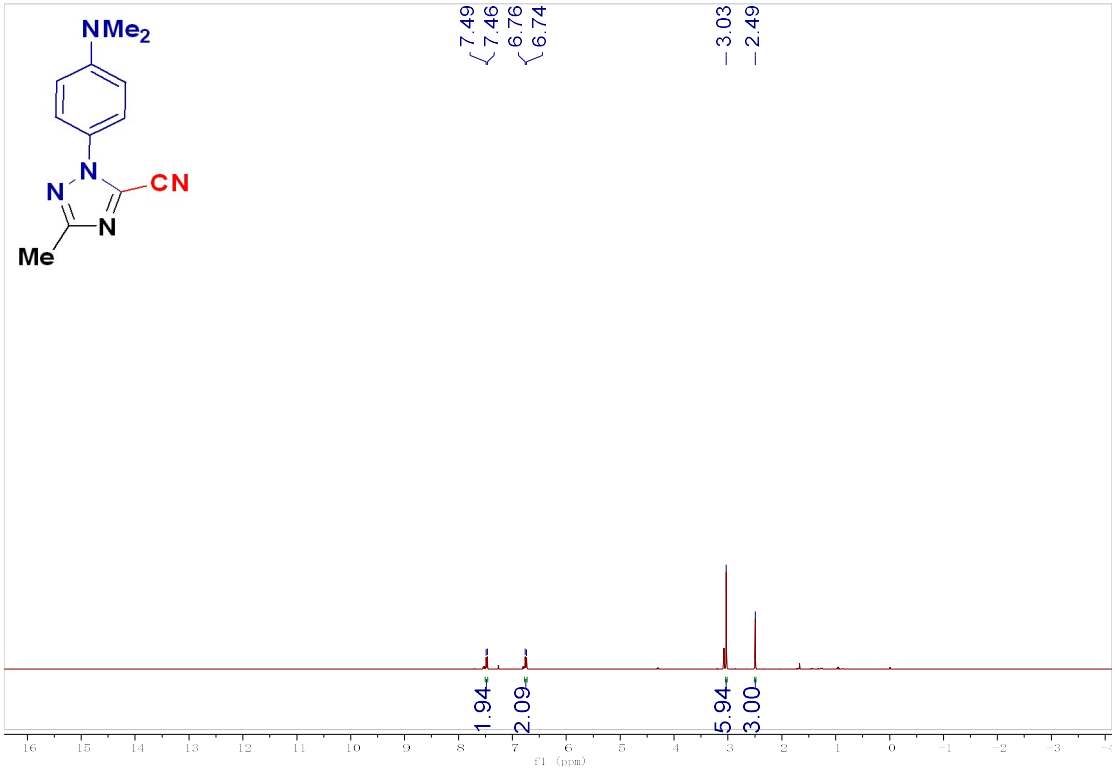


^{1}H NMR (400 MHz, $CDCl_3$) of **3o**

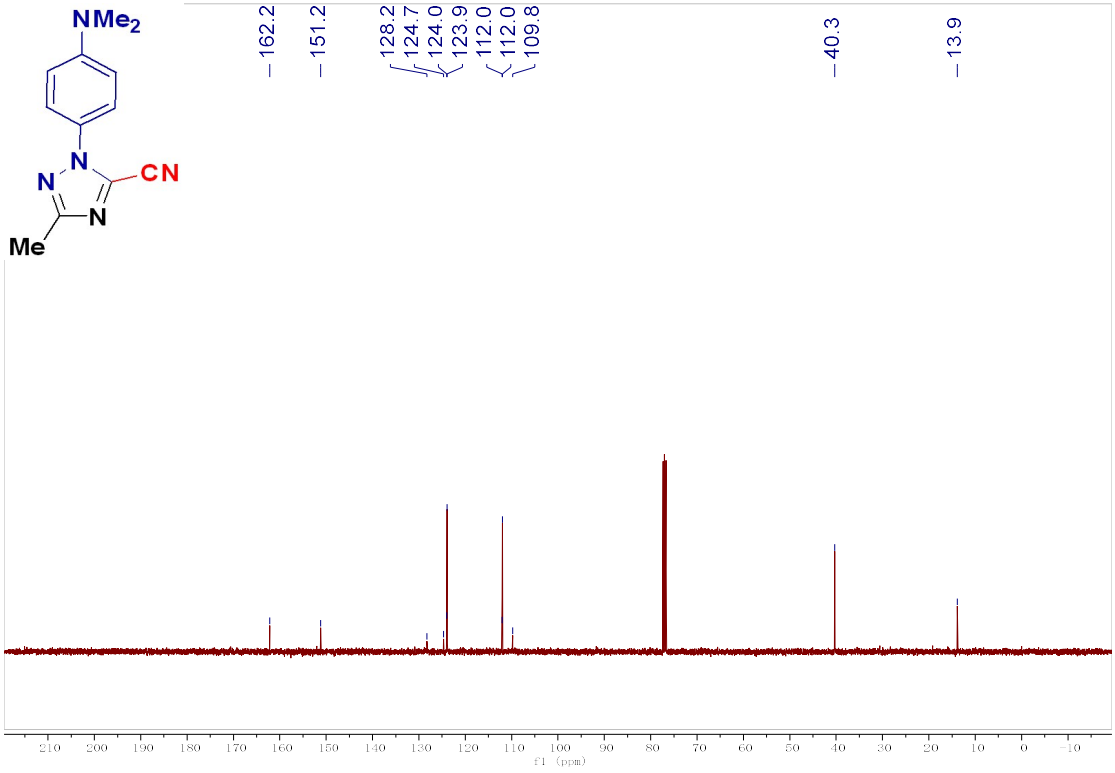


^{13}C NMR (100 MHz, $CDCl_3$) of **3o**

1-(4-(dimethylamino)phenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile(3p)

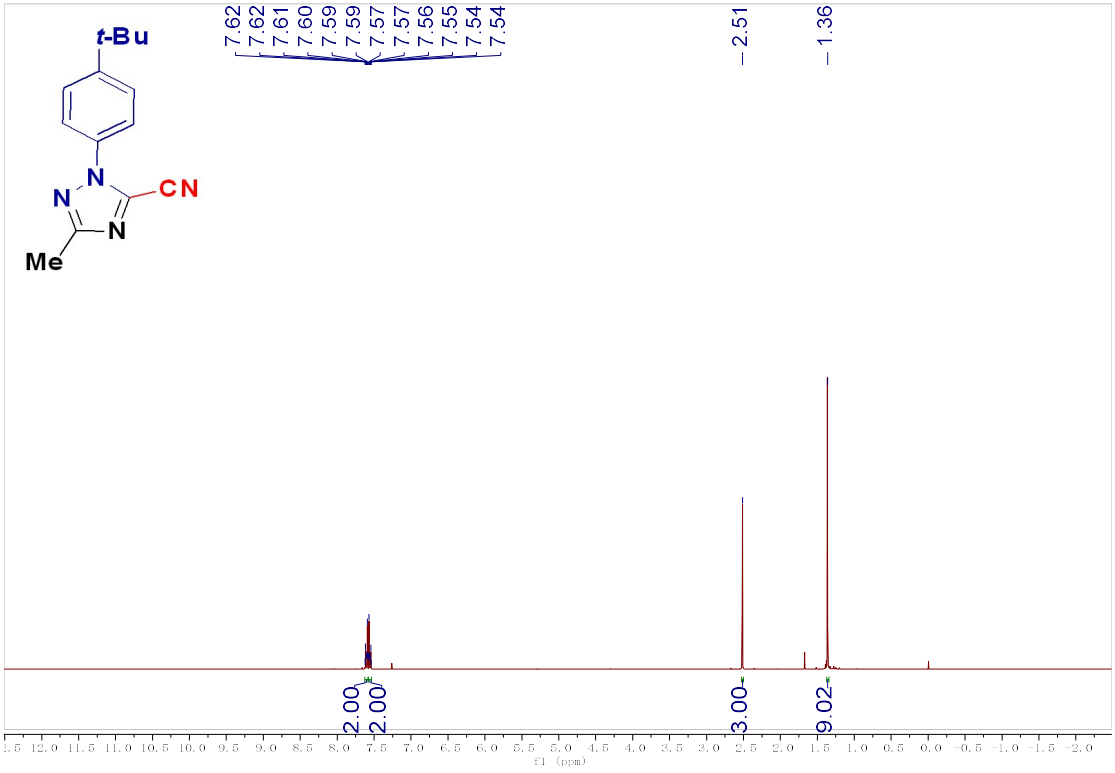


^{1}H NMR (400 MHz, $CDCl_3$) of **3p**

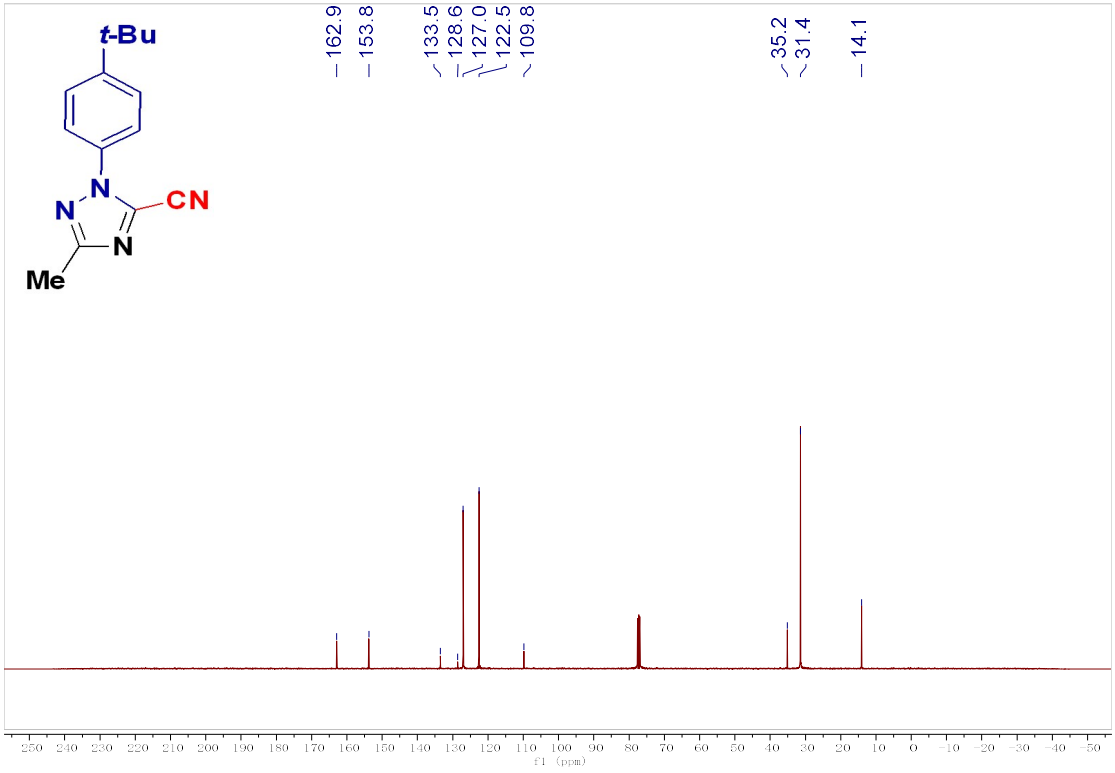


^{13}C NMR (100 MHz, $CDCl_3$) of **3p**

1-(4-(tert-butyl)phenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3q)

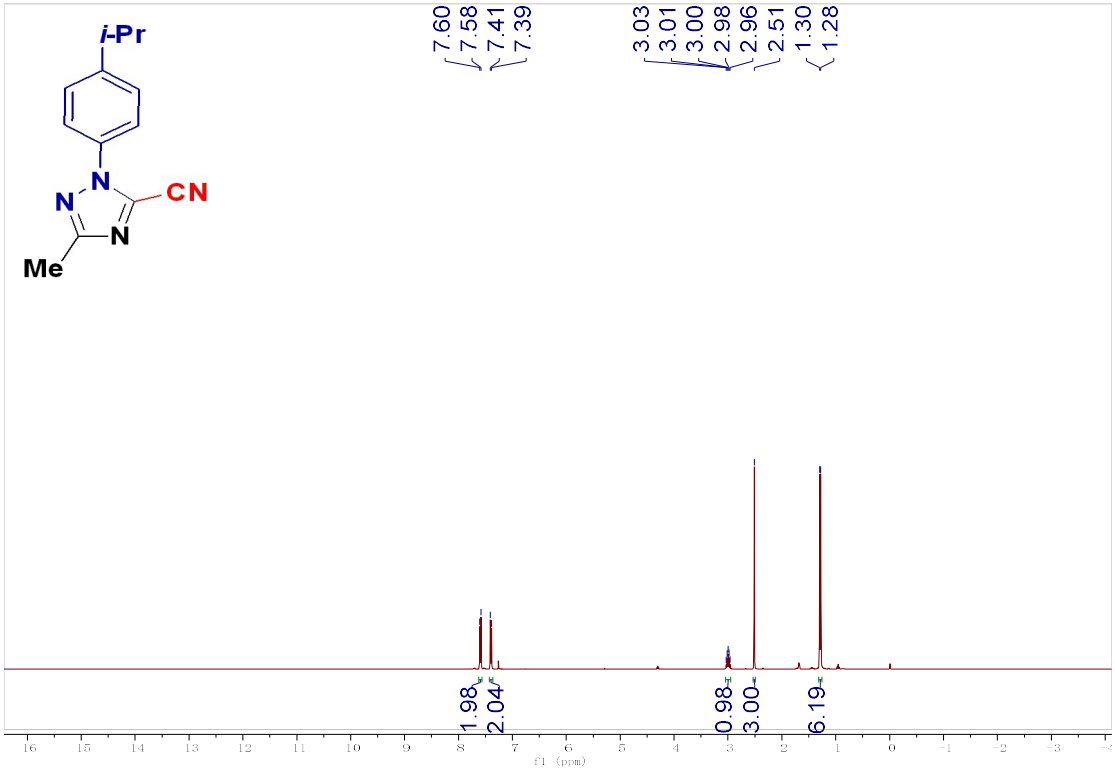


^{1}H NMR (400 MHz, $CDCl_3$) of **3q**

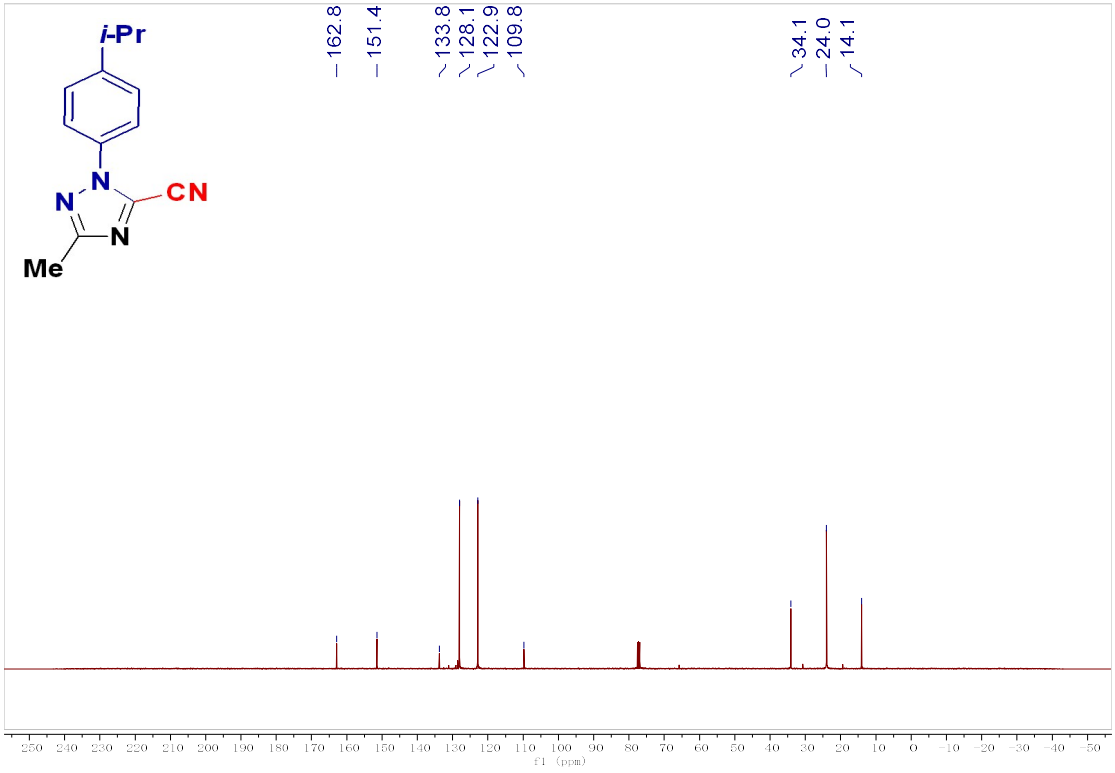


^{13}C NMR (100 MHz, $CDCl_3$) of **3q**

1-(4-isopropylphenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile(3r)

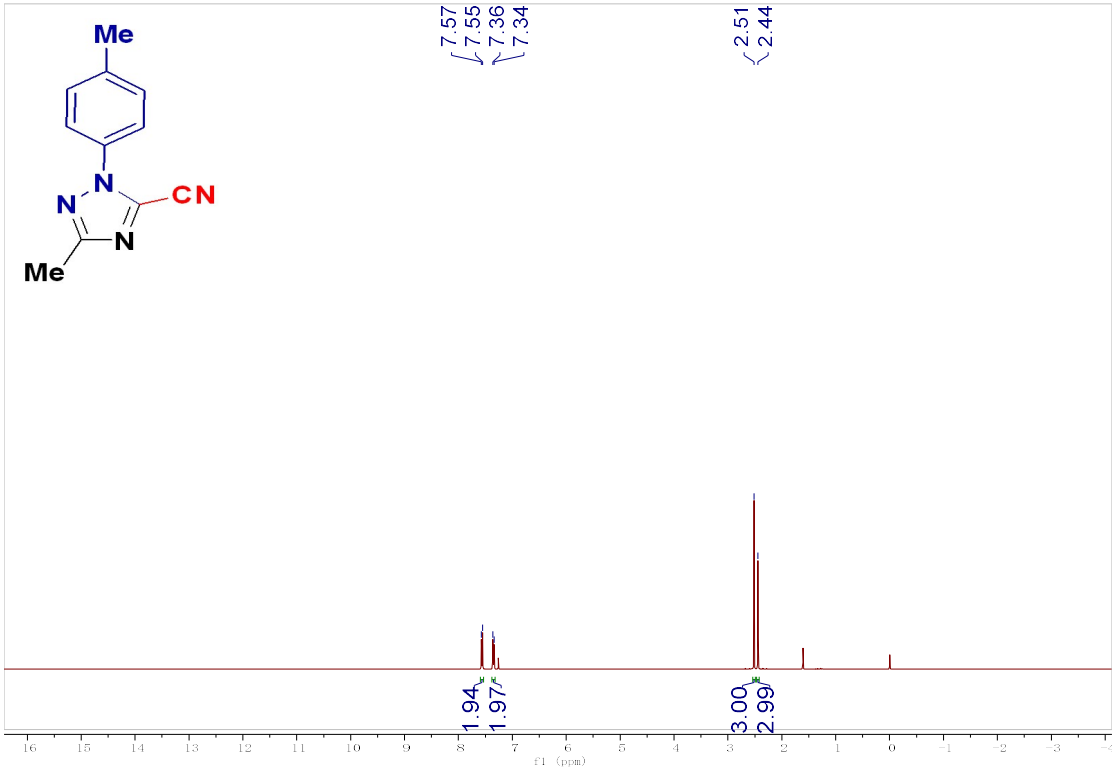


^{1}H NMR (400 MHz, $CDCl_3$) of **3r**

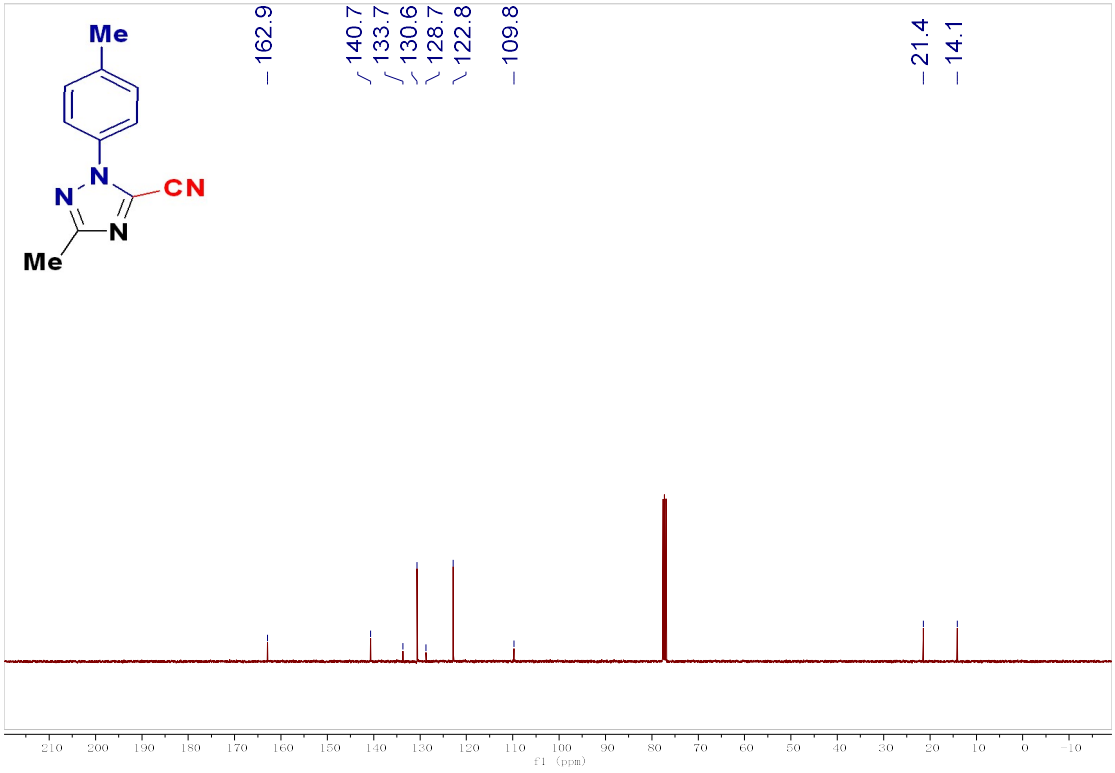


^{13}C NMR (100 MHz, $CDCl_3$) of **3r**

3-methyl-1-(p-tolyl)-1H-1,2,4-triazole-5-carbonitrile (3s)

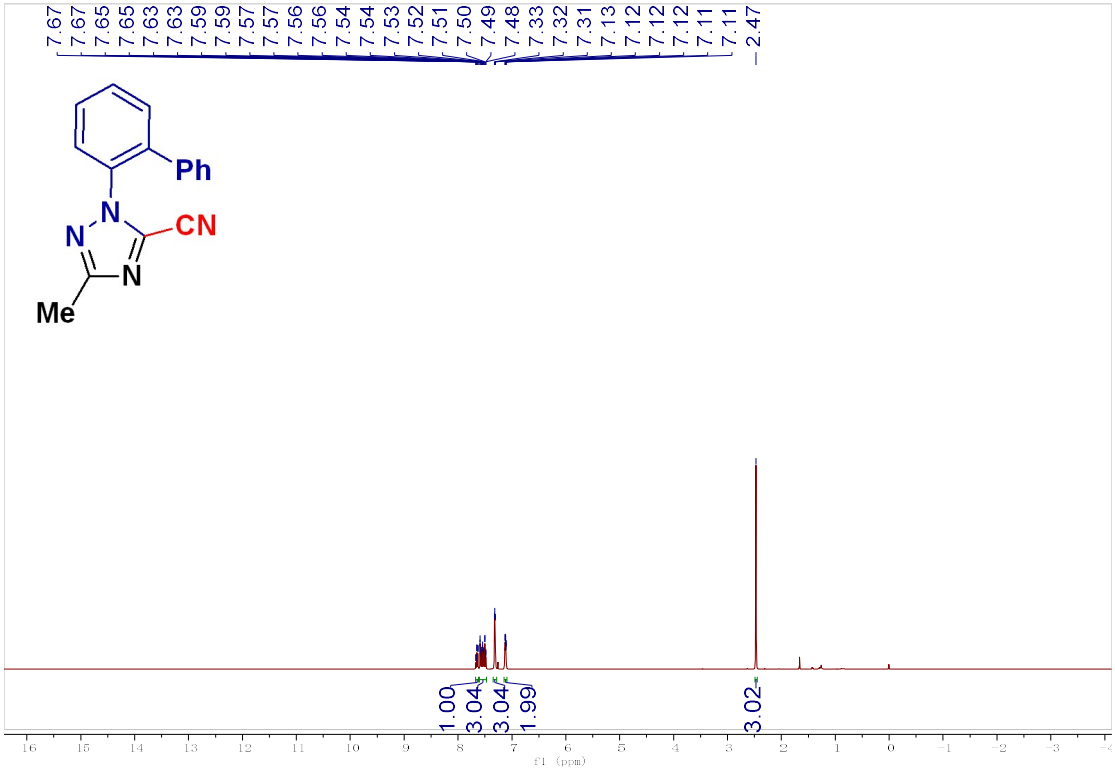


^{1}H NMR (400 MHz, $CDCl_3$) of **3s**

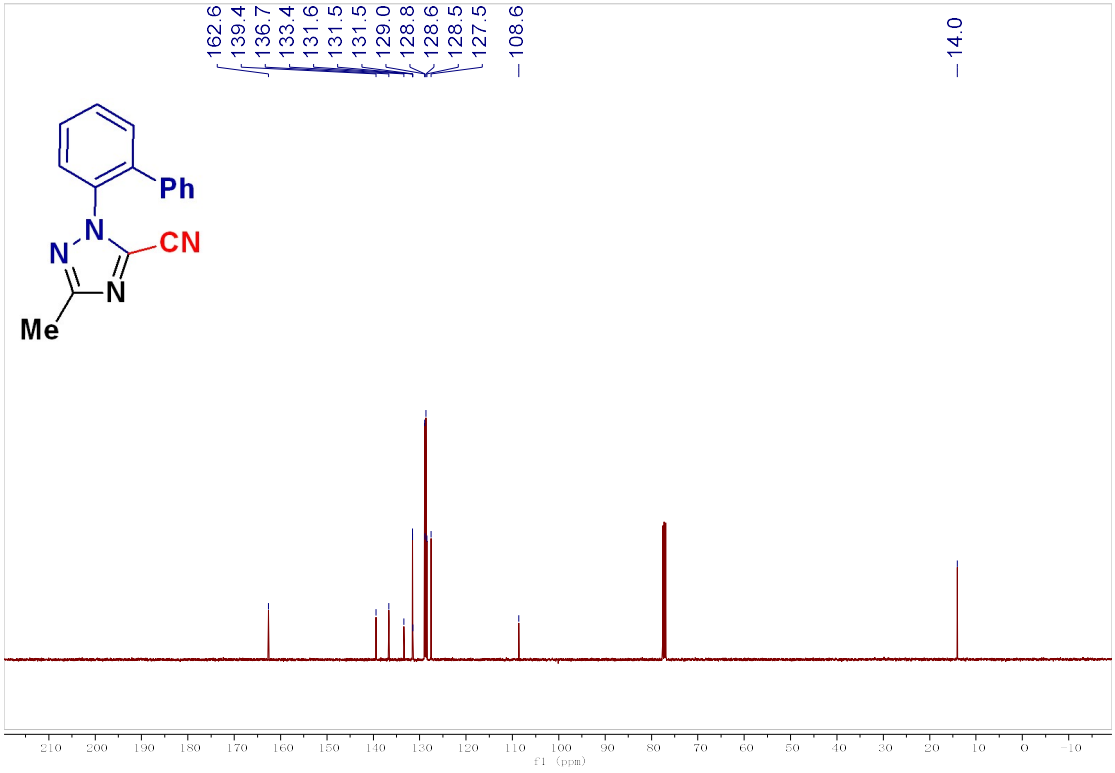


^{13}C NMR (100 MHz, $CDCl_3$) of **3s**

1-([1,1'-biphenyl]-2-yl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3t)

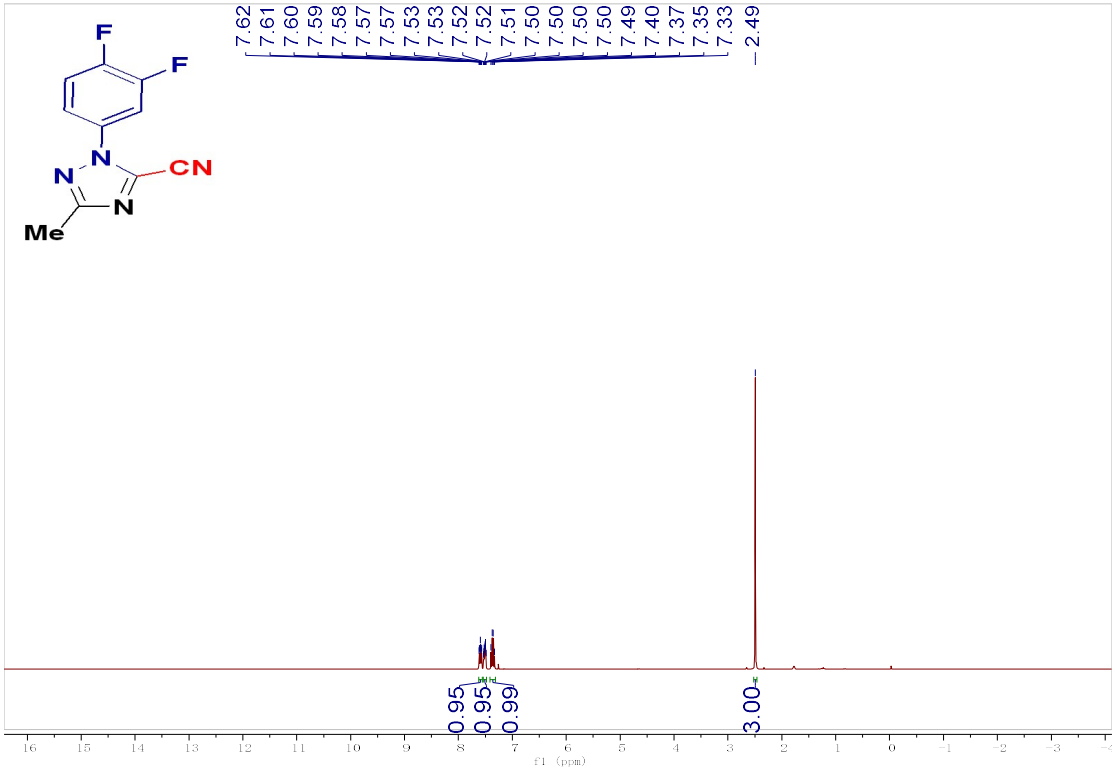


^{1}H NMR (400 MHz, $CDCl_3$) of **3t**

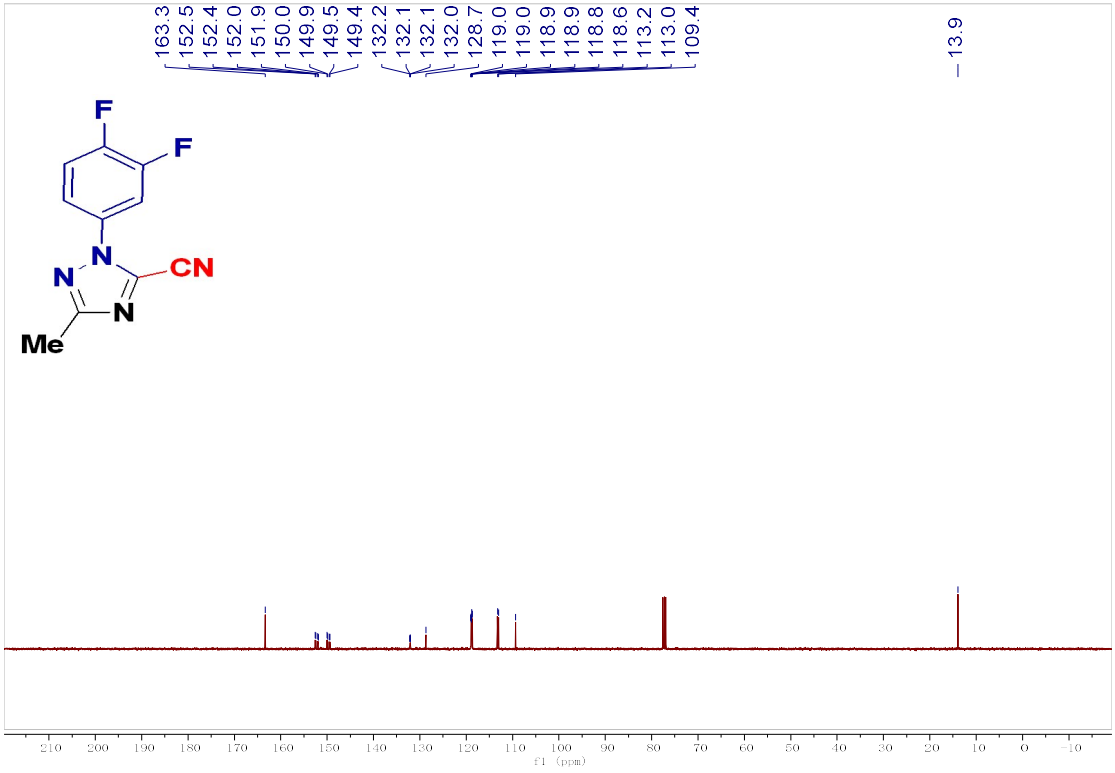


^{13}C NMR (100 MHz, $CDCl_3$) of **3t**

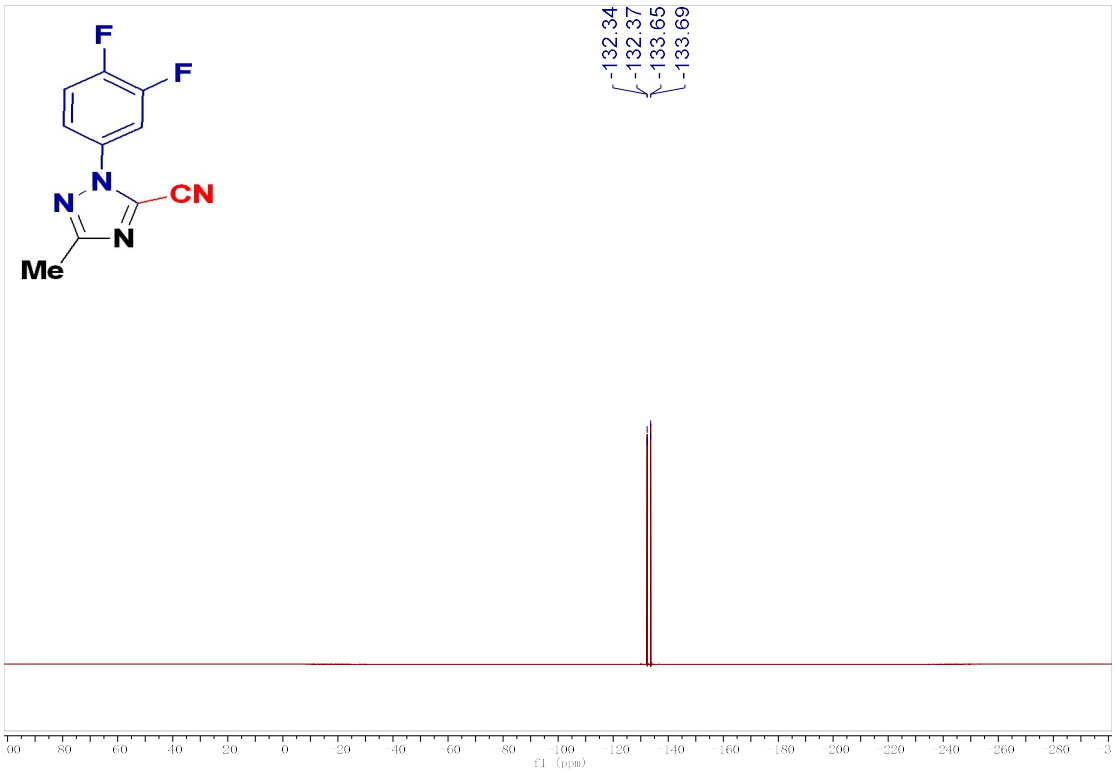
1-(3,4-difluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3u)



^{1}H NMR (400 MHz, $CDCl_3$) of **3u**

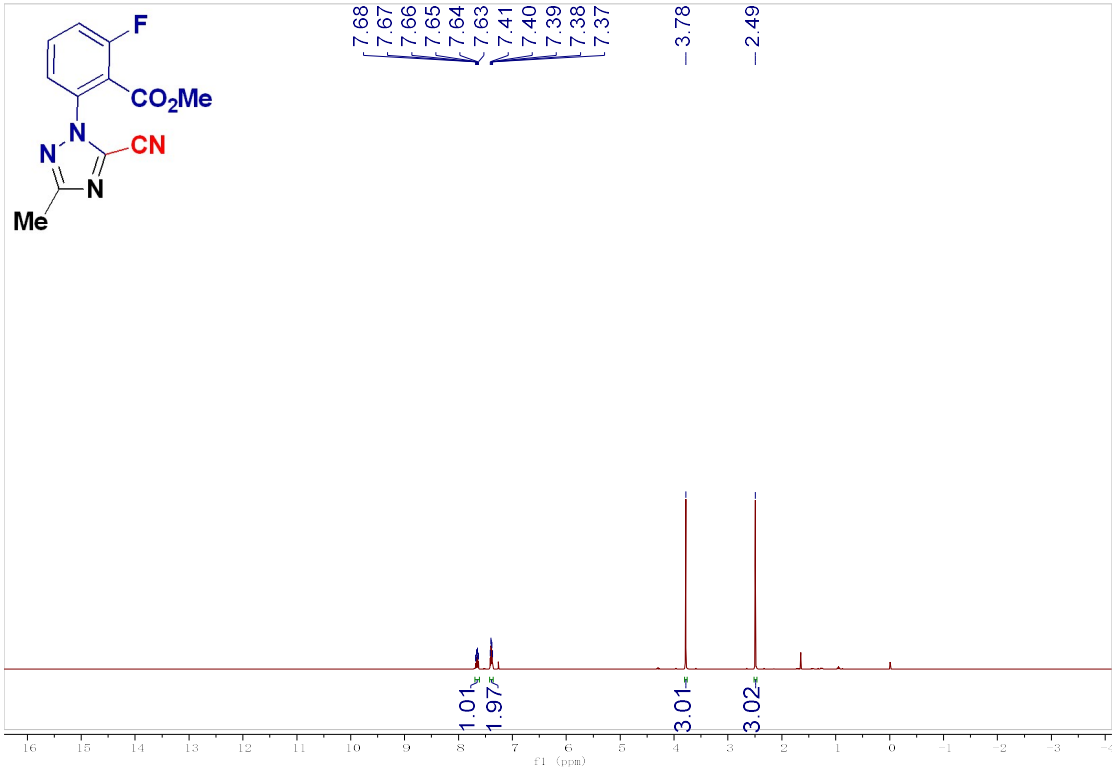


^{13}C NMR (100 MHz, $CDCl_3$) of **3u**

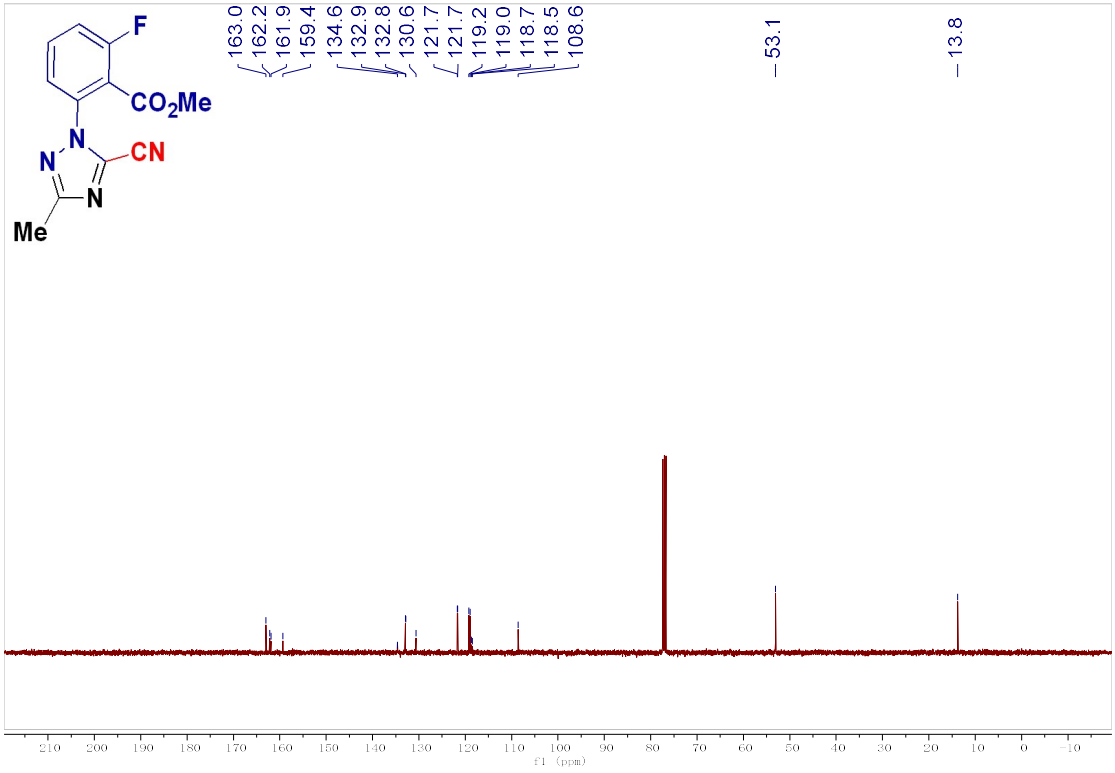


^{19}F NMR (565 MHz, $CDCl_3$) of **3u**

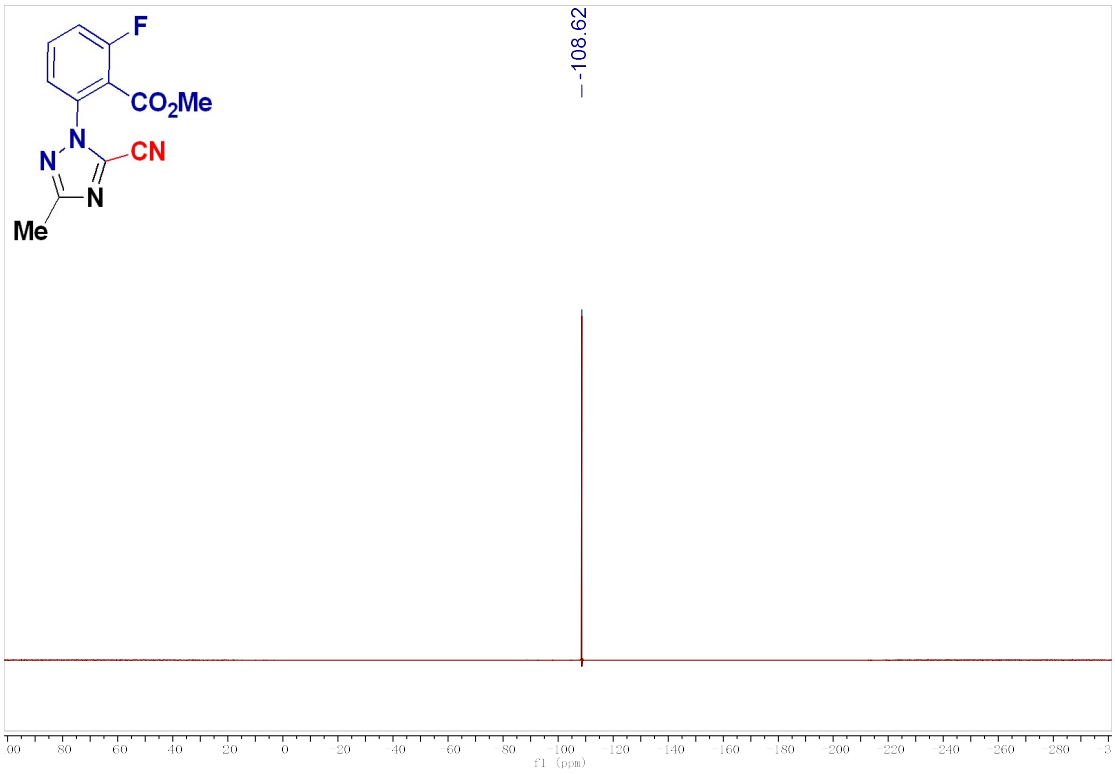
methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-fluorobenzoate (3v)



^{1}H NMR (400 MHz, $CDCl_3$) of **3v**

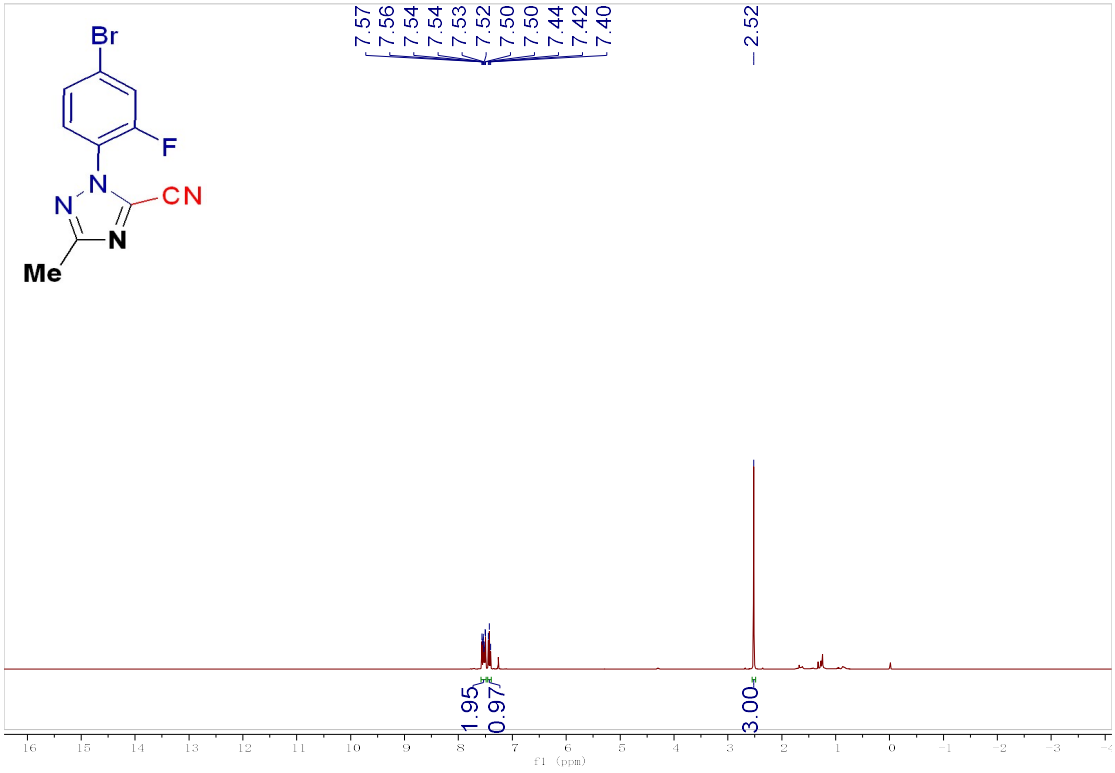


^{13}C NMR (100 MHz, $CDCl_3$) of **3v**

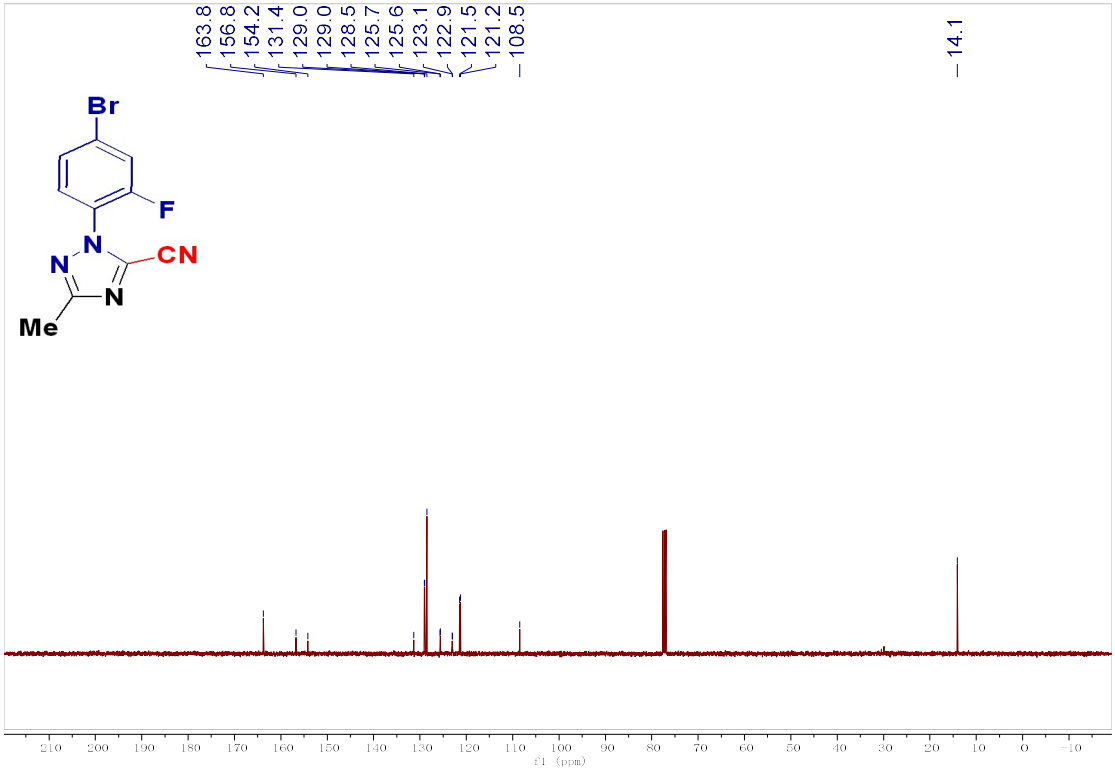


^{19}F NMR (565 MHz, $CDCl_3$) of **3v**

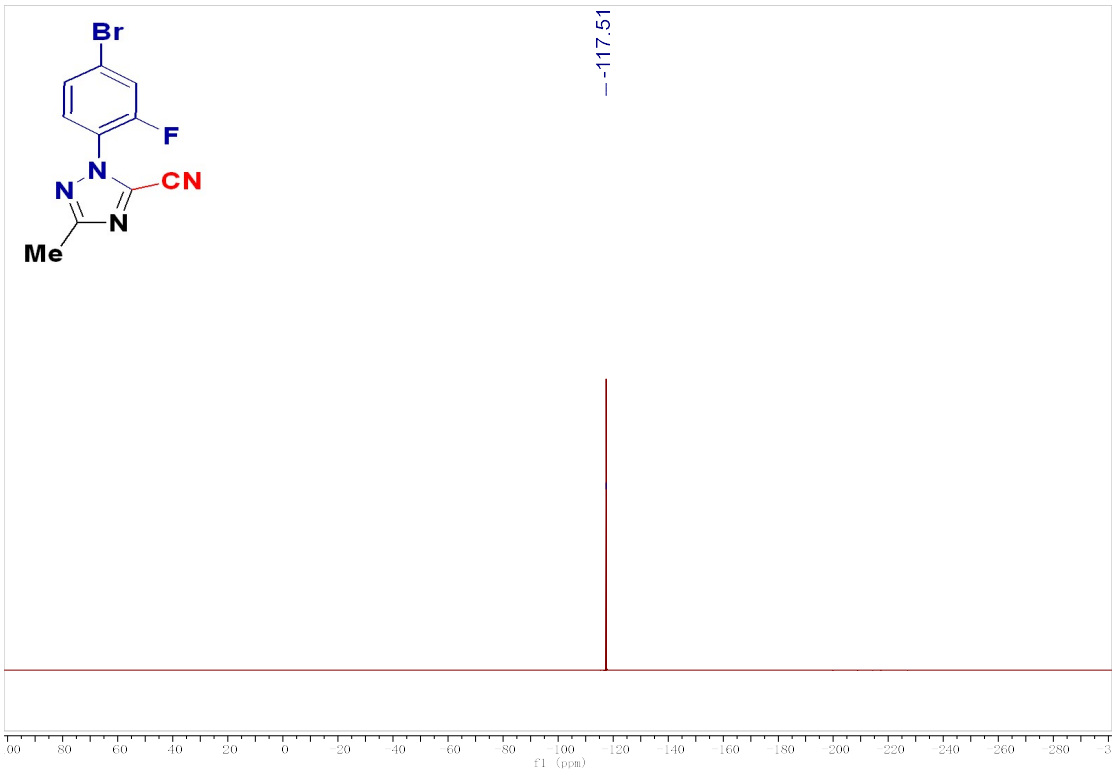
1-(4-bromo-2-fluorophenyl)-3-methyl-1H-1,2,4-triazole-5-carbonitrile (3w)



^{1}H NMR (400 MHz, $CDCl_3$) of **3w**

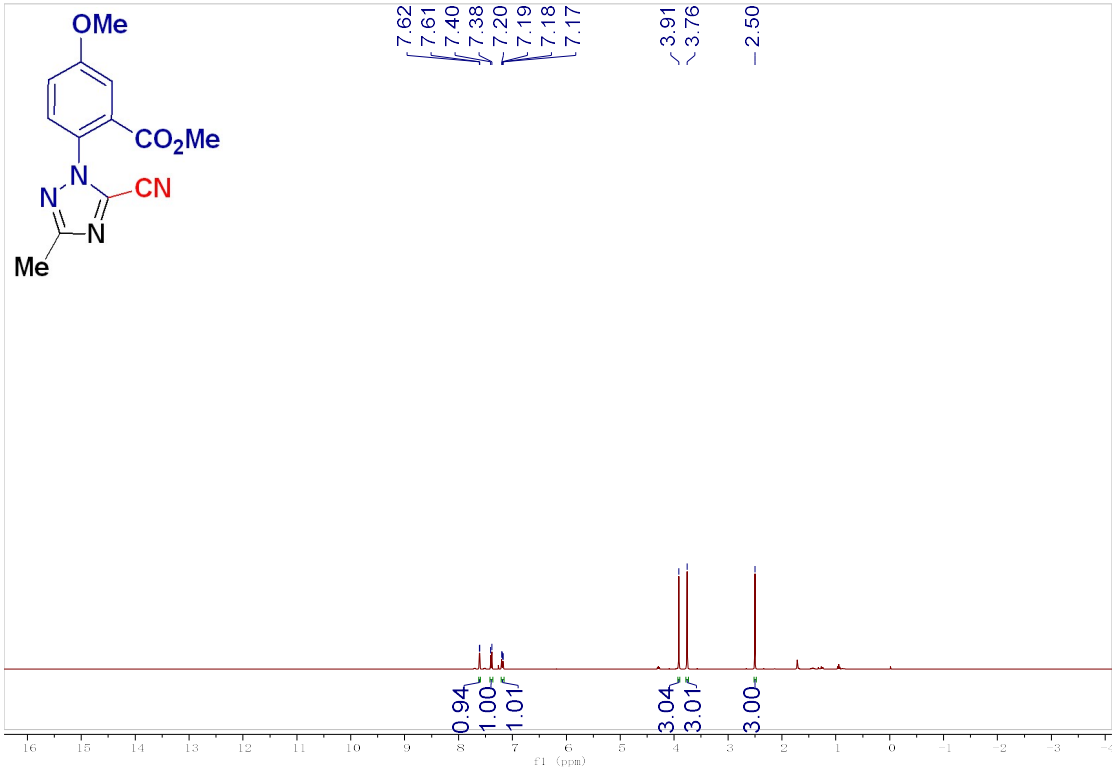


^{13}C NMR (100 MHz, $CDCl_3$) of **3w**

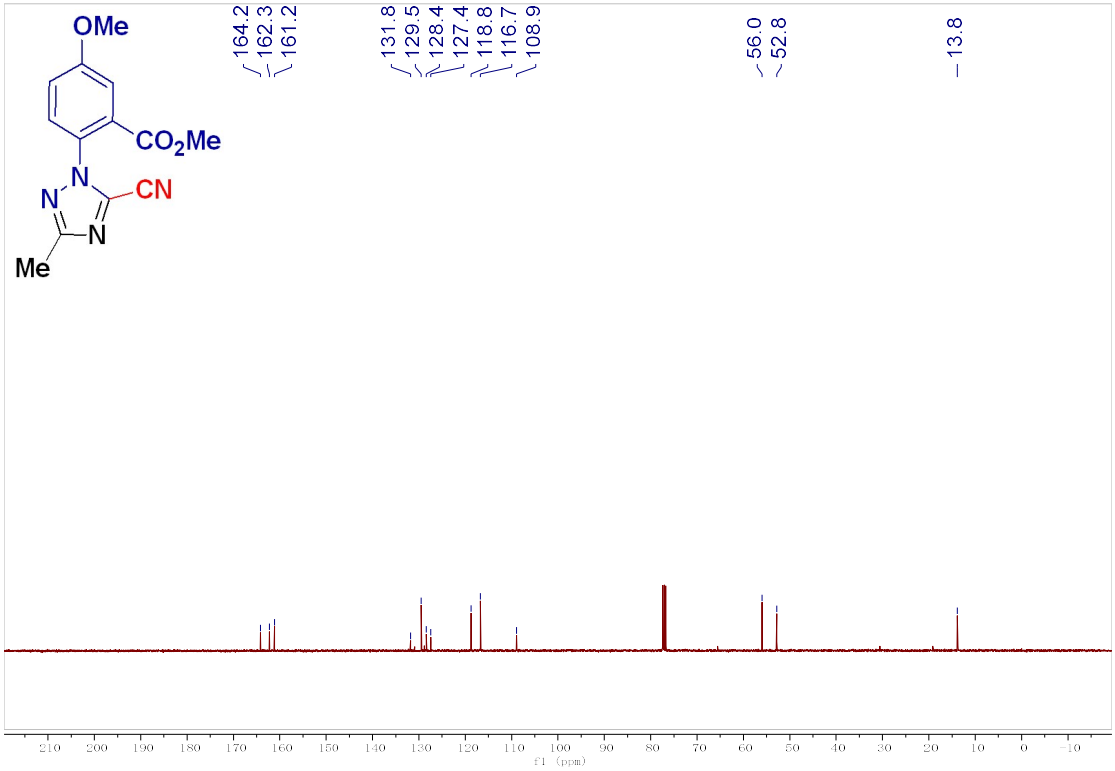


^{19}F NMR (565 MHz, $CDCl_3$) of **3w**

methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-methoxybenzoate (3x)

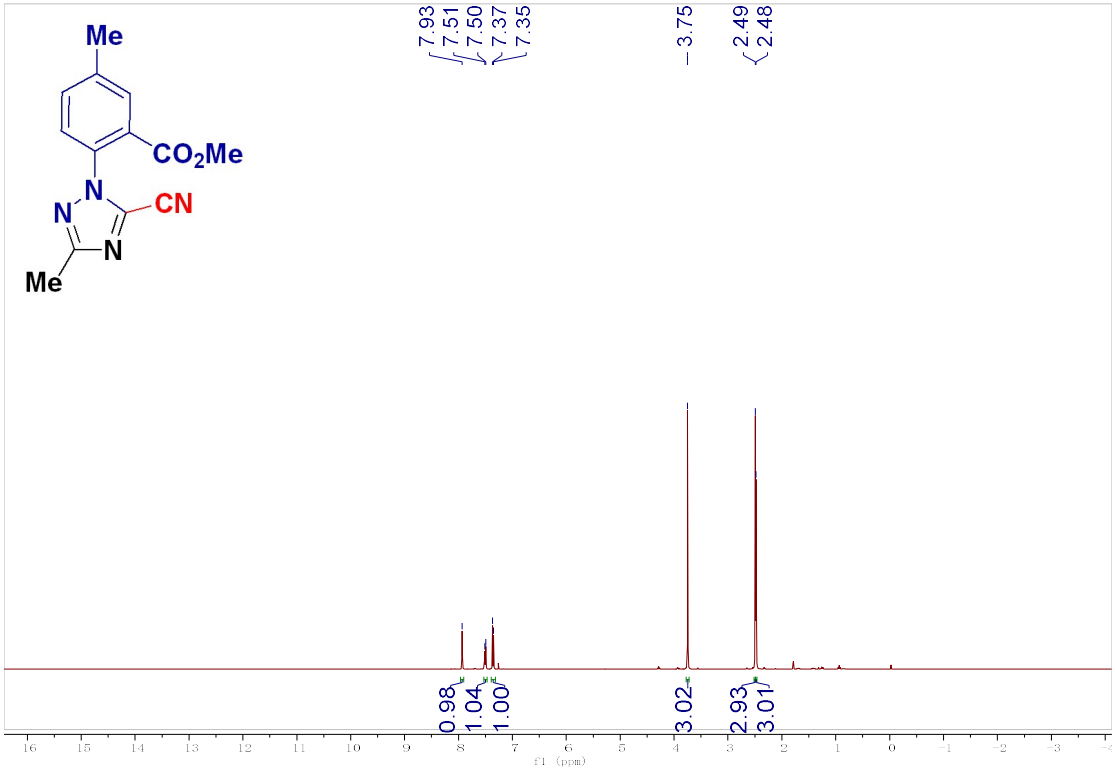


^{1}H NMR (400 MHz, $CDCl_3$) of **3x**

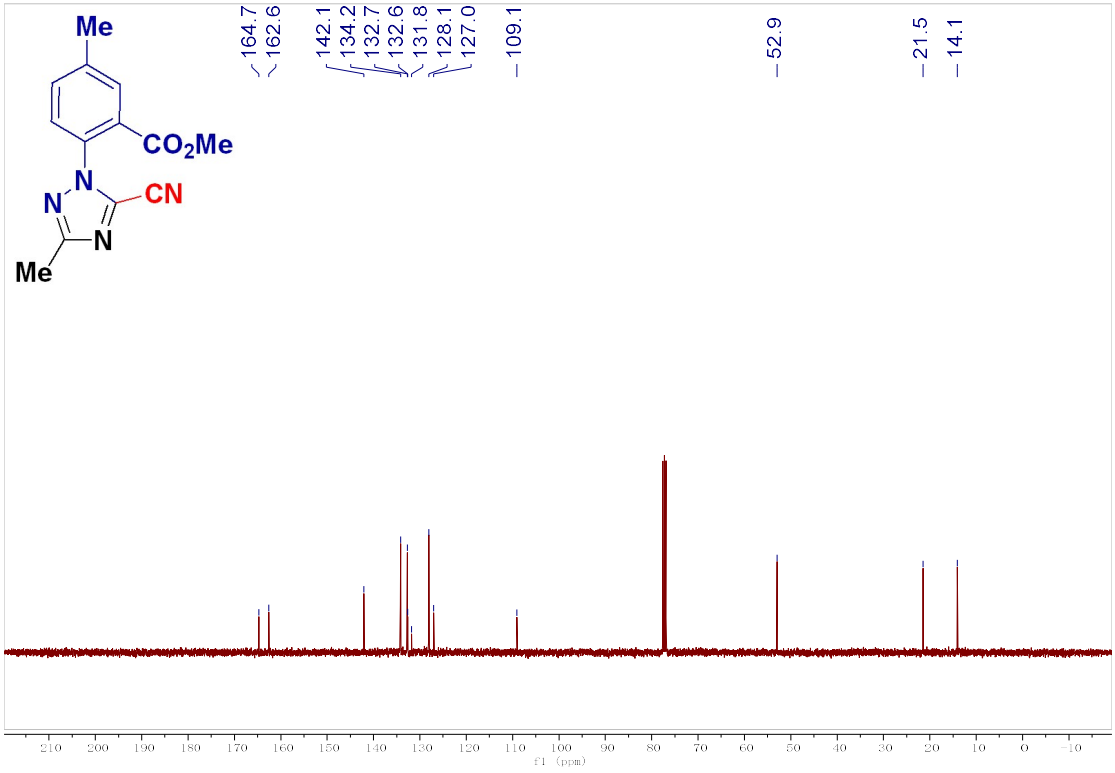


^{13}C NMR (100 MHz, $CDCl_3$) of **3x**

methyl 5-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)-2-methylbenzoate (3y)

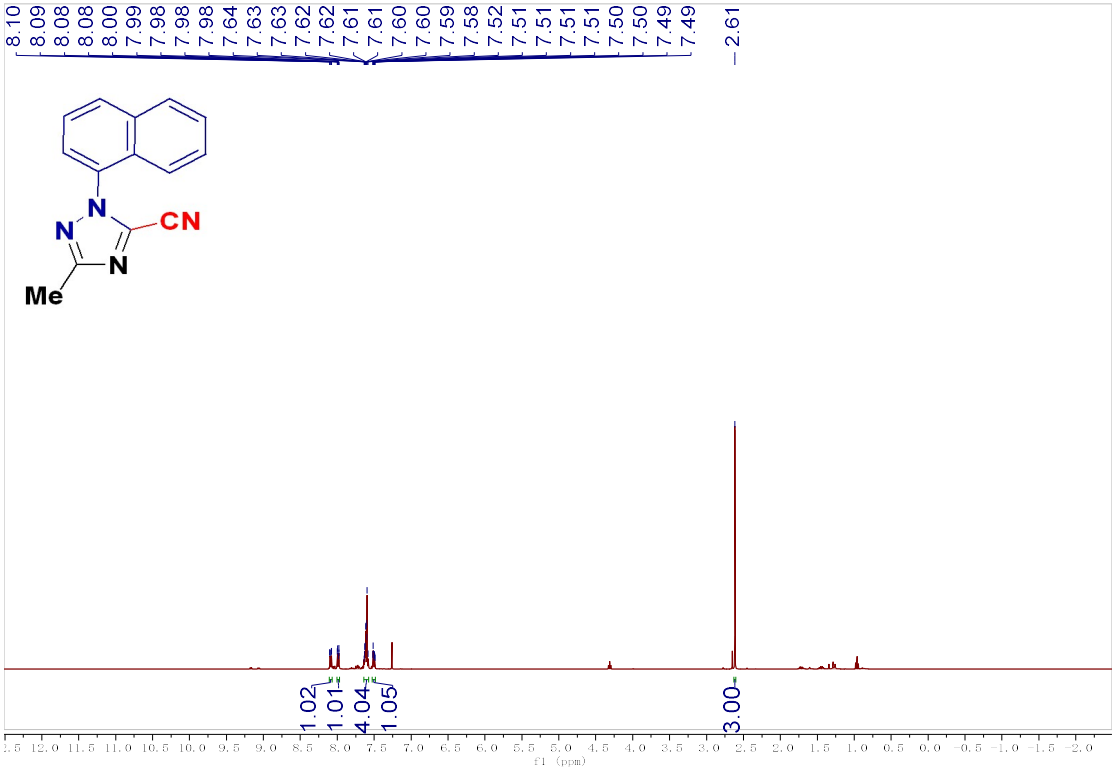


^{1}H NMR (400 MHz, $CDCl_3$) of **3y**

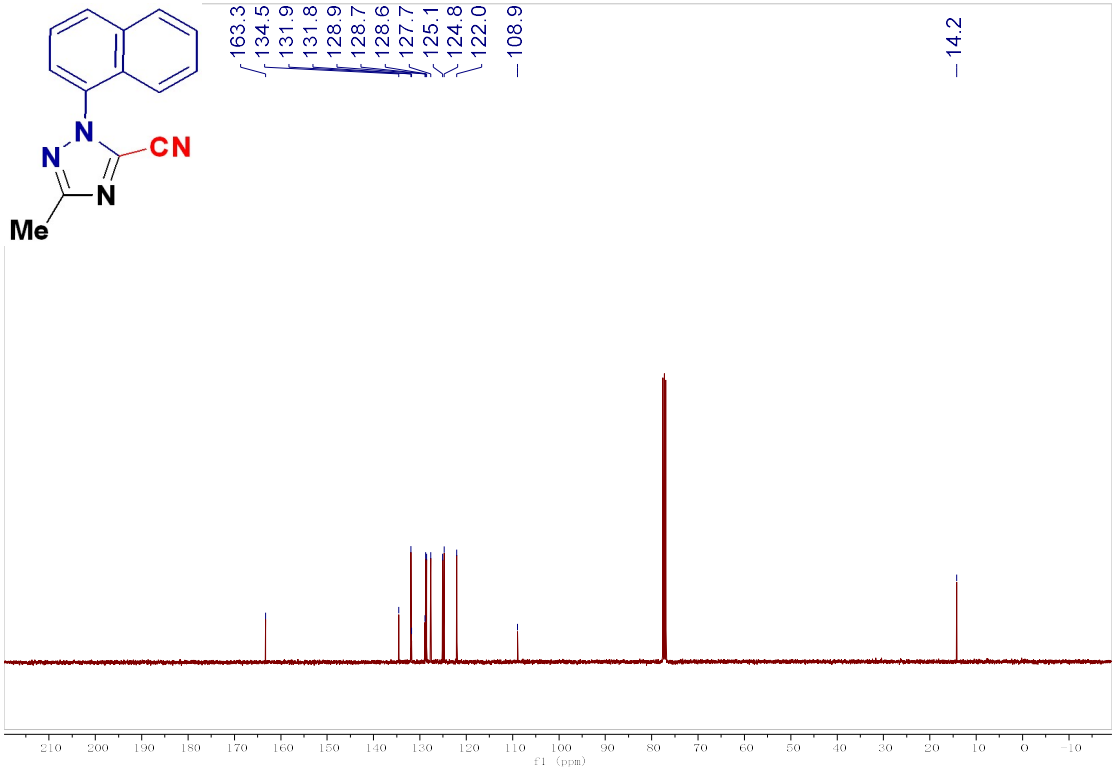


^{13}C NMR (100 MHz, $CDCl_3$) of **3y**

3-methyl-1-(naphthalen-1-yl)-1H-1,2,4-triazole-5-carbonitrile (3z)

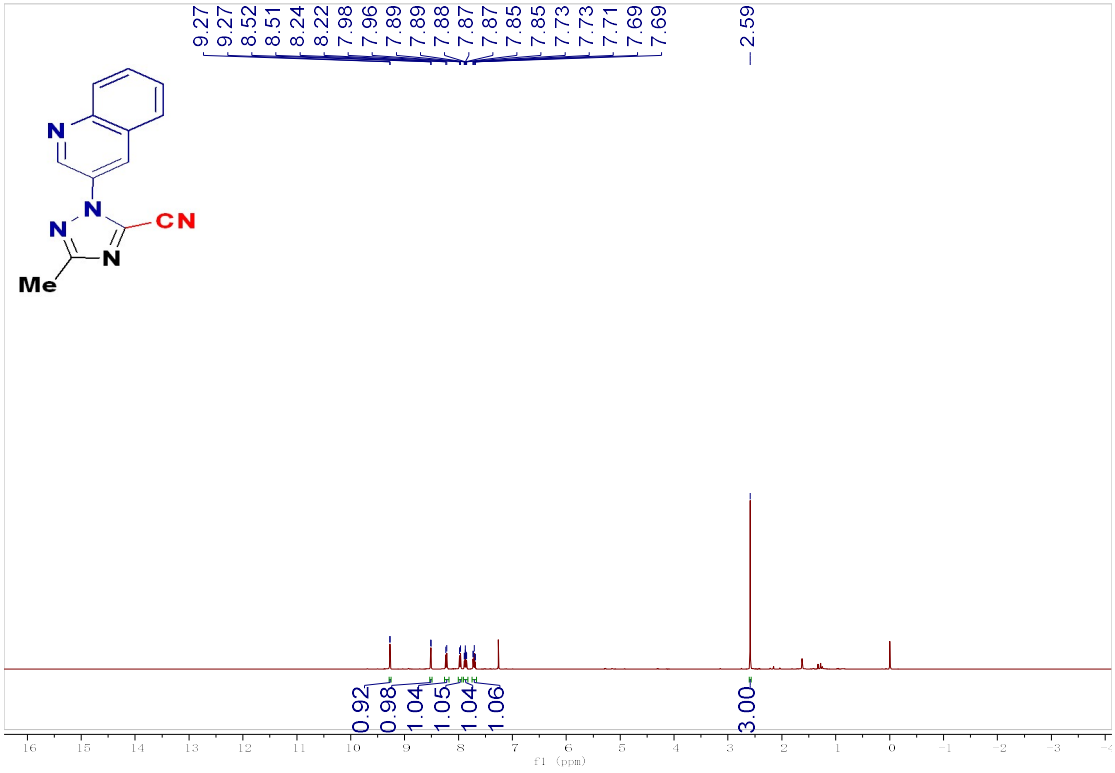


^{1}H NMR (400 MHz, $CDCl_3$) of **3z**

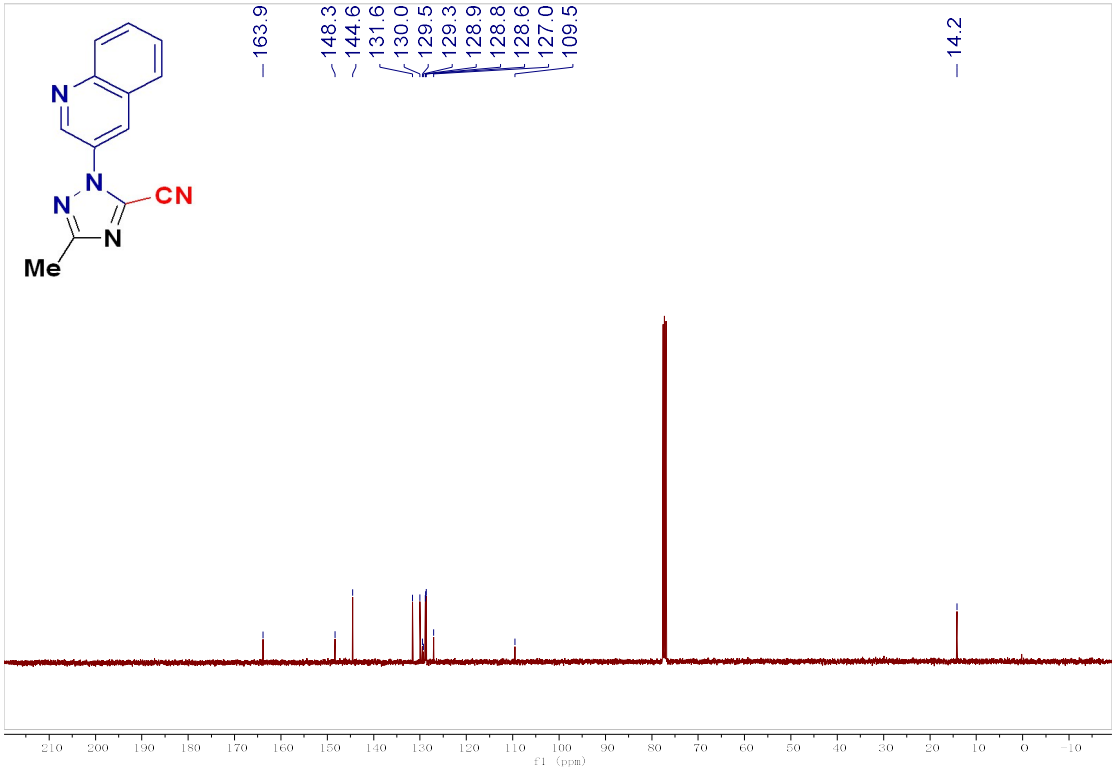


^{13}C NMR (100 MHz, $CDCl_3$) of **3z**

3-methyl-1-(quinolin-3-yl)-1H-1,2,4-triazole-5-carbonitrile (3aa)

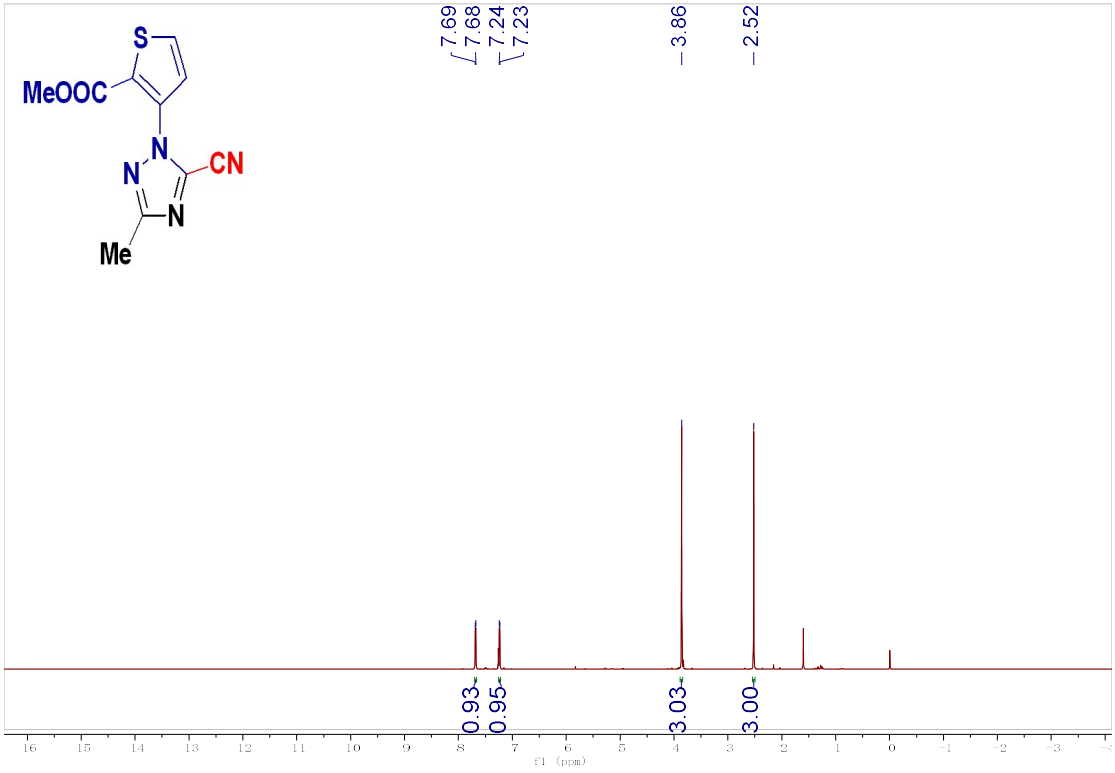


^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**

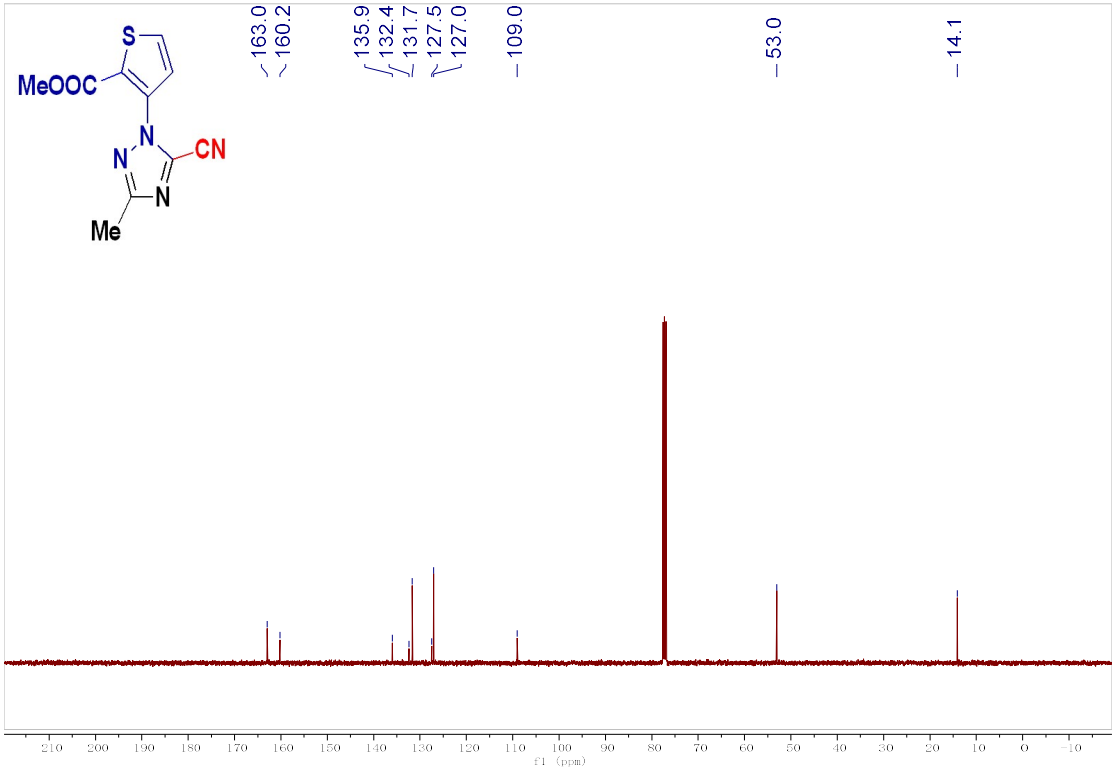


^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**

methyl 3-(5-cyano-3-methyl-1H-1,2,4-triazol-1-yl)thiophene-2-carboxylate (3ab)

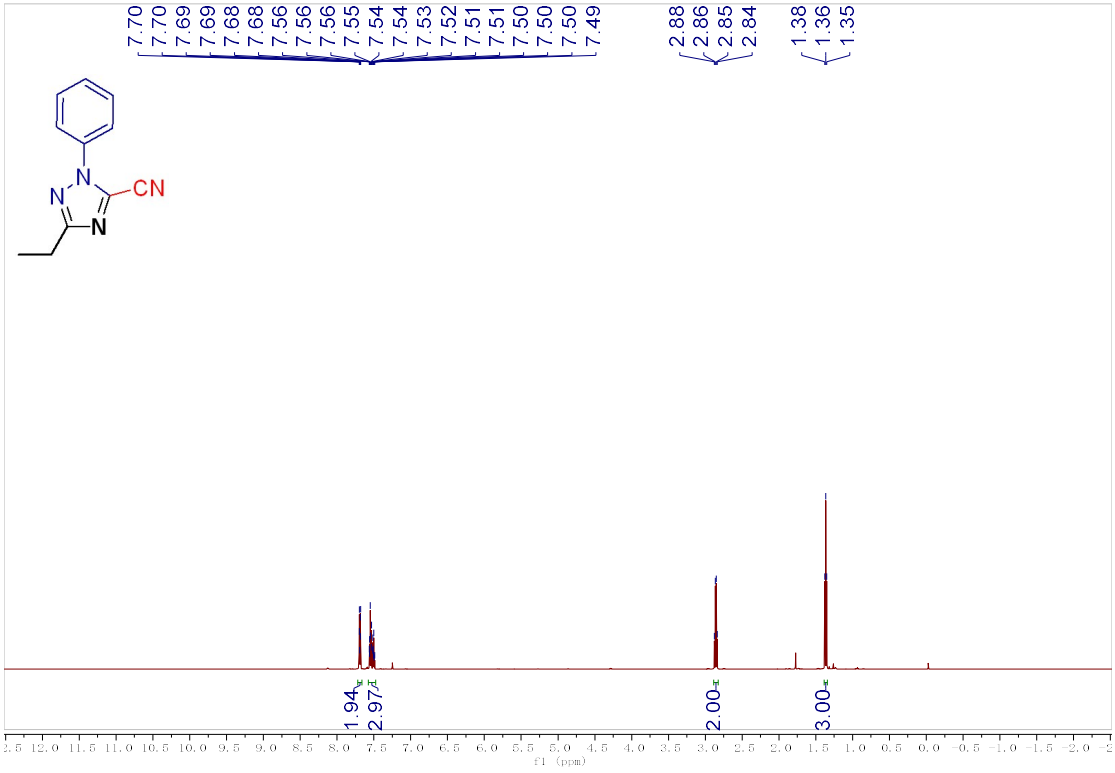


^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**

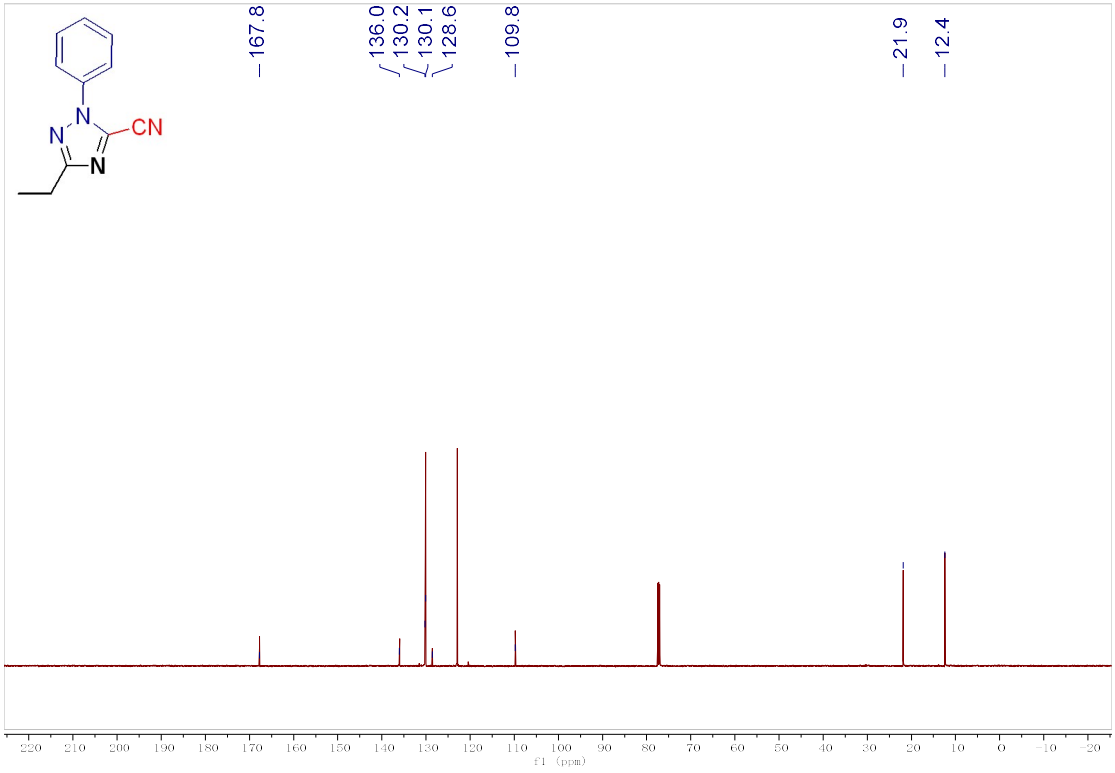


^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**

3-ethyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile(4a)

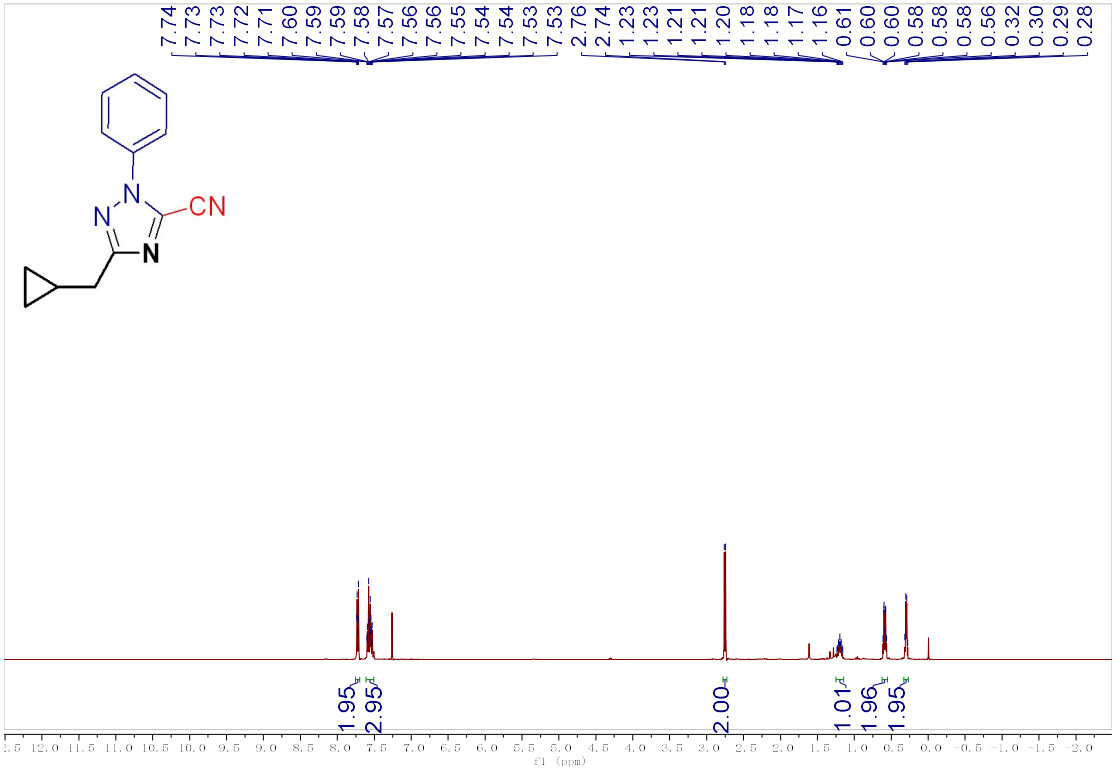


^{1}H NMR (600 MHz, $CDCl_3$) of **4a**

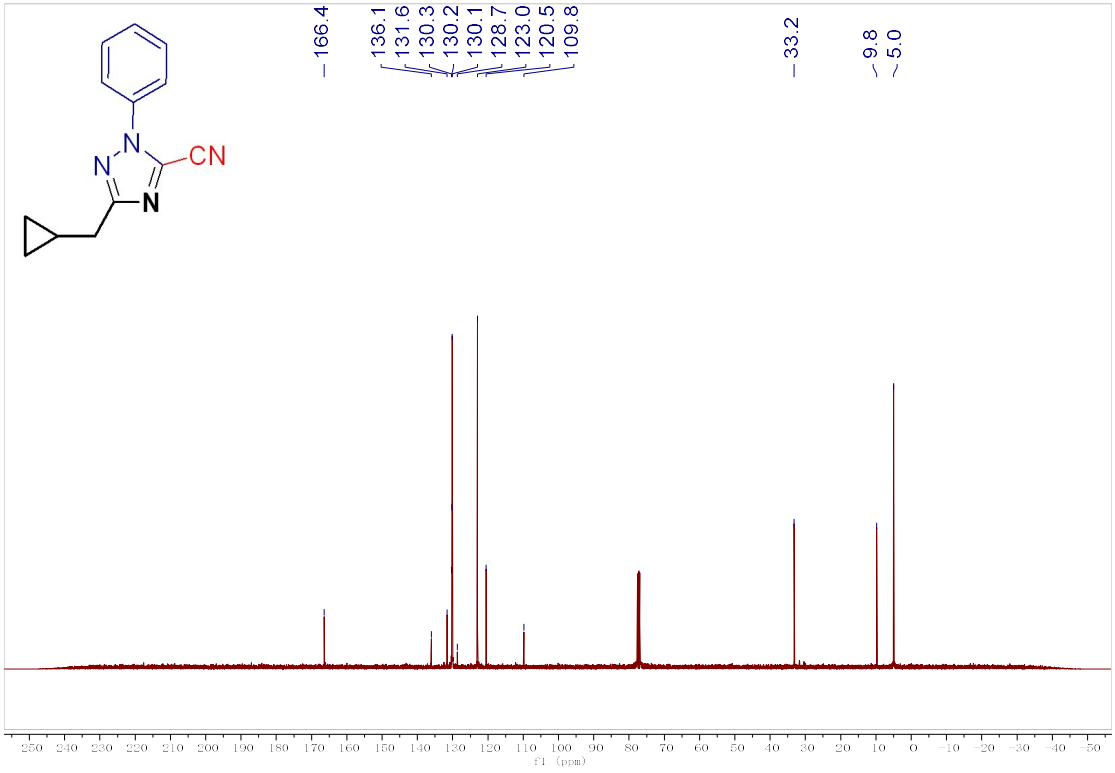


^{13}C NMR (150 MHz, $CDCl_3$) of **4a**

3-(cyclopropylmethyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (4b)

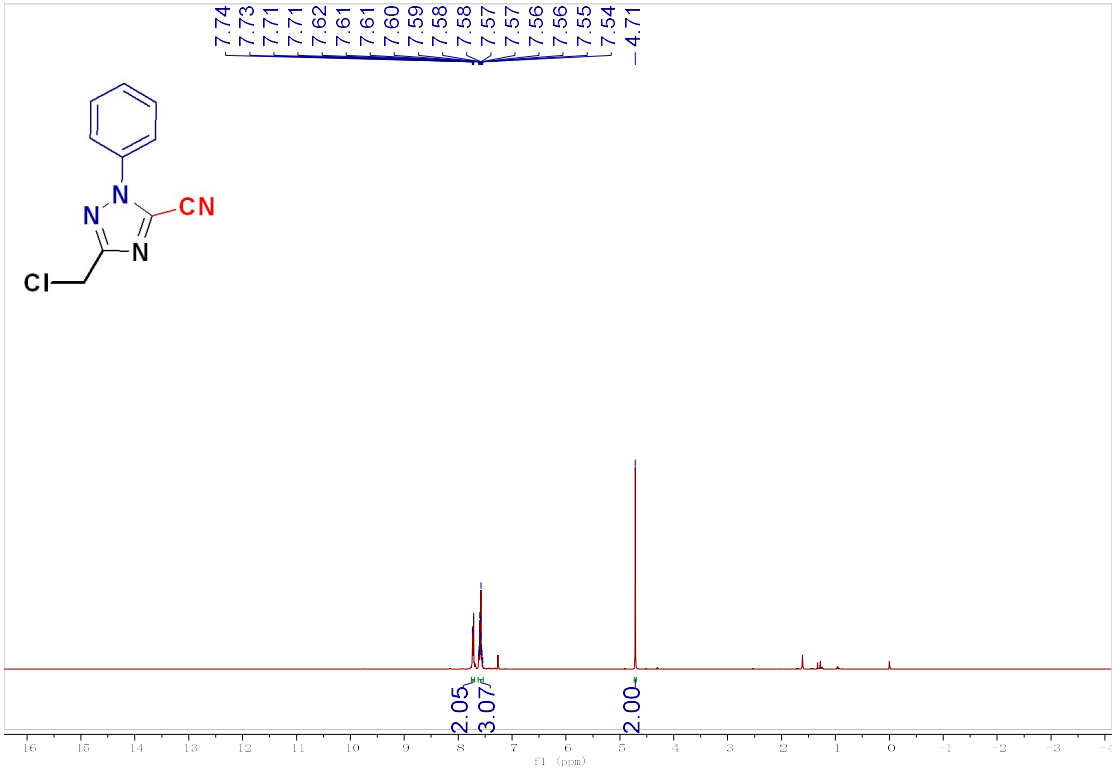


^{1}H NMR (400 MHz, $CDCl_3$) of **4b**

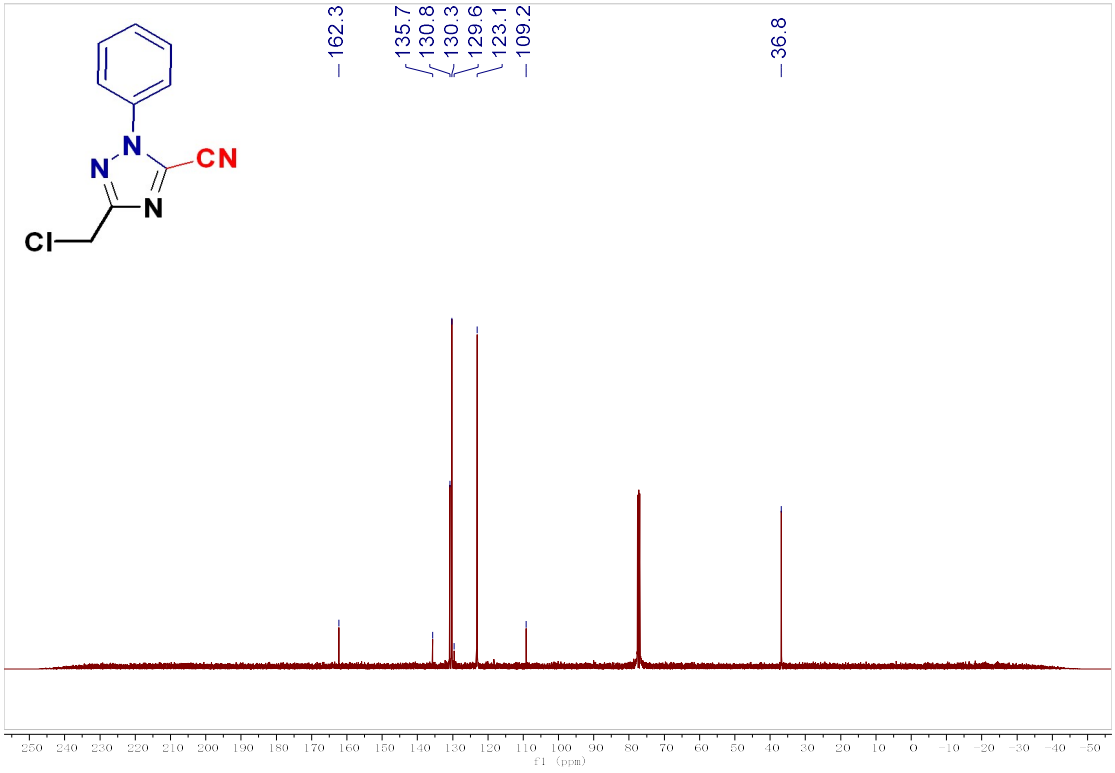


^{13}C NMR (100 MHz, $CDCl_3$) of **4b**

3-(chloromethyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (4c)

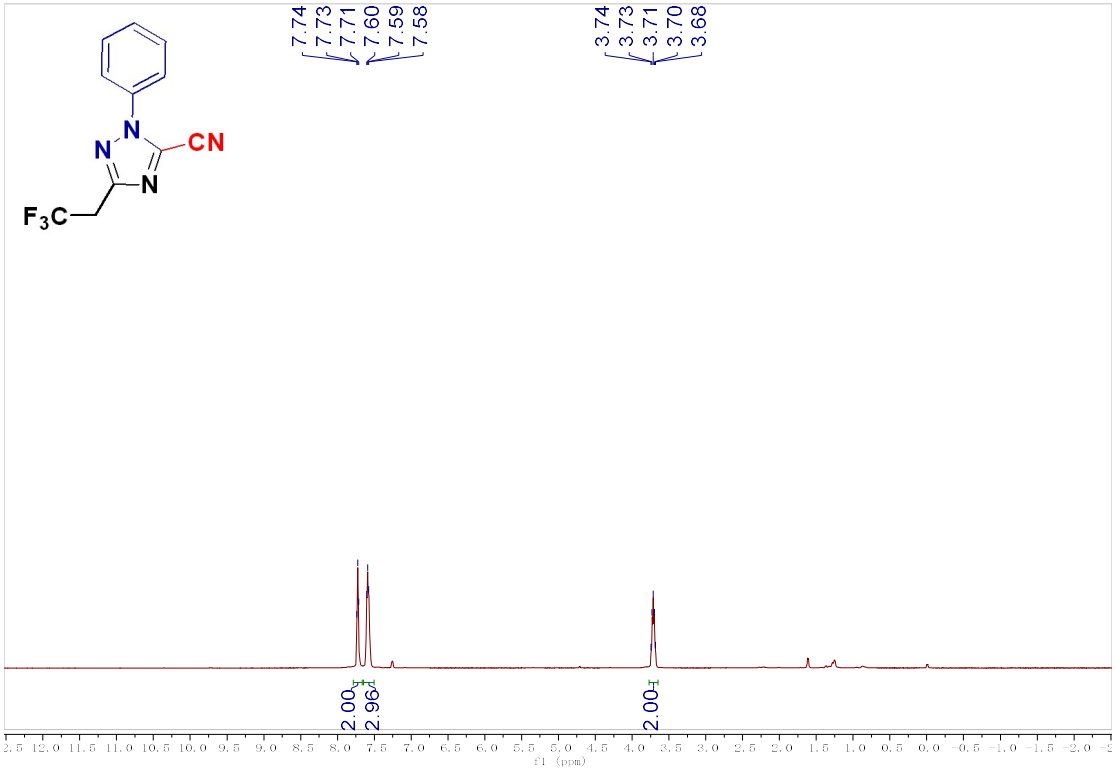


^{1}H NMR (400 MHz, $CDCl_3$) of **4c**

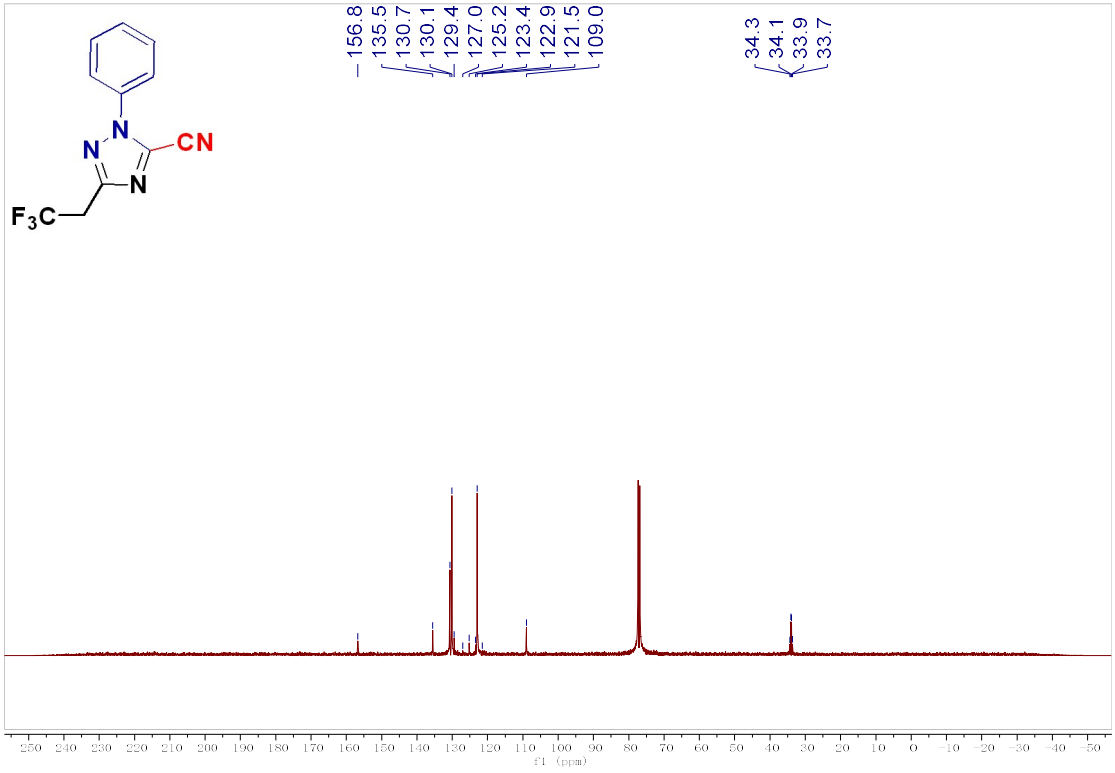


^{13}C NMR (100 MHz, $CDCl_3$) of **4c**

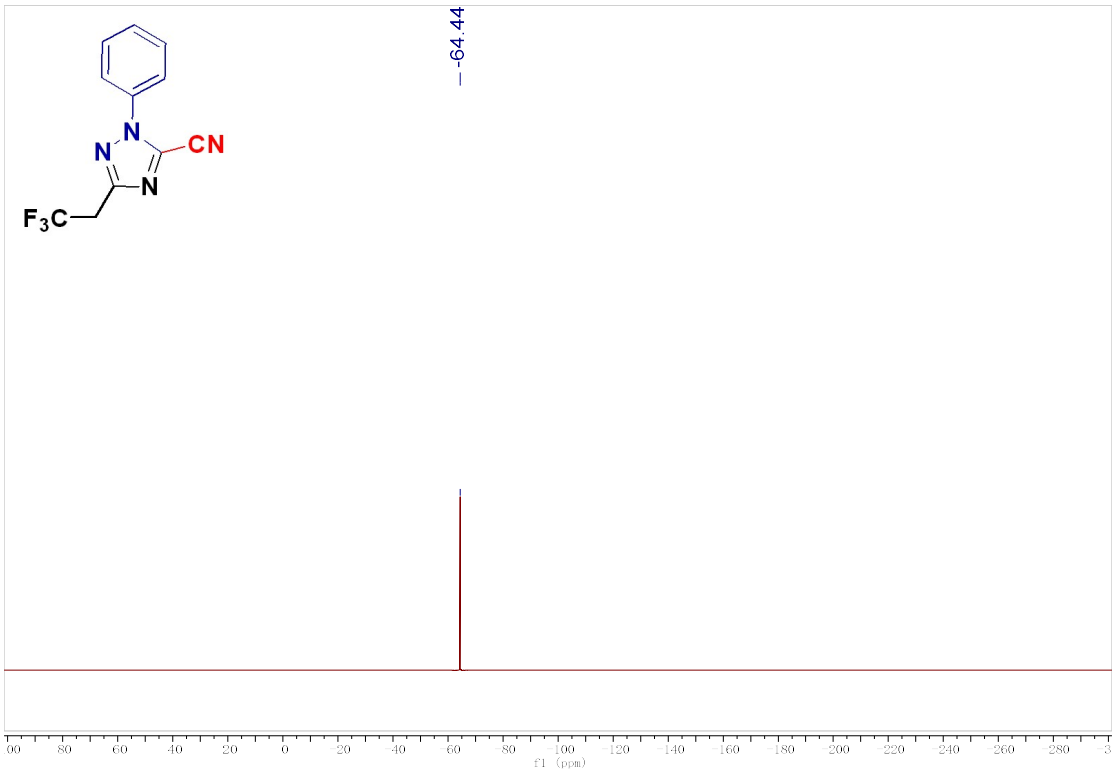
1-phenyl-3-(2,2,2-trifluoroethyl)-1H-1,2,4-triazole-5-carbonitrile(4d)



^{1}H NMR (600 MHz, $CDCl_3$) of **4d**

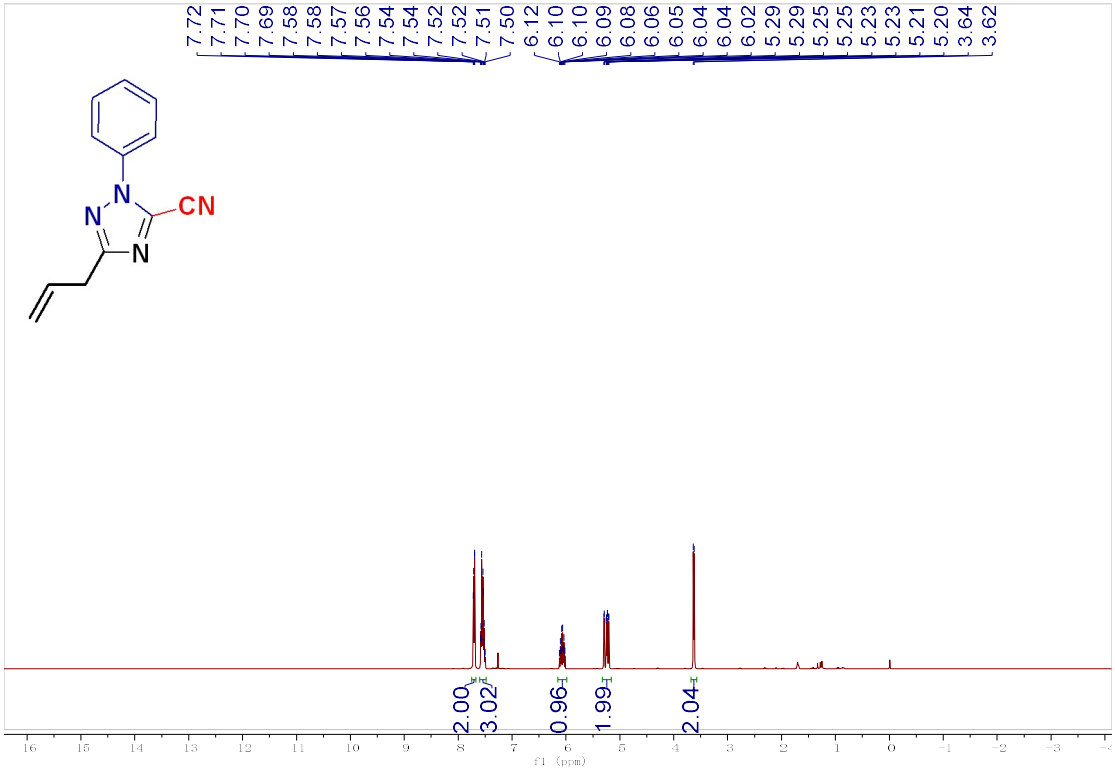


^{13}C NMR (150 MHz, $CDCl_3$) of **4d**

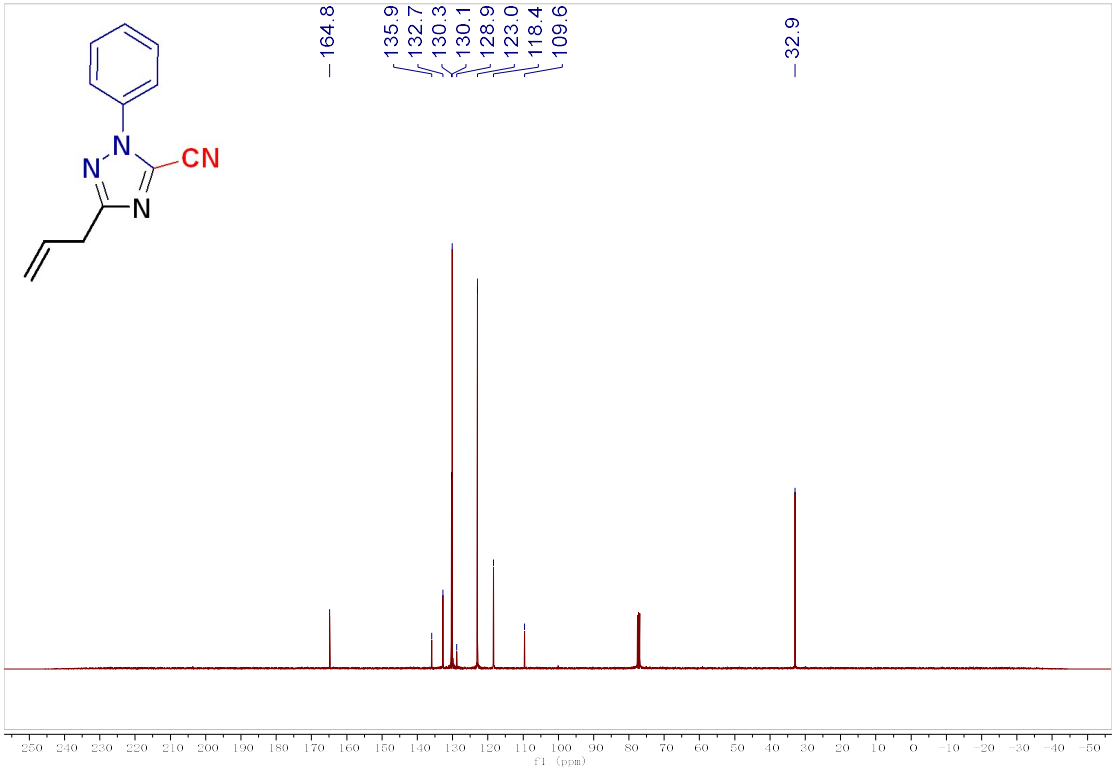


^{19}F NMR (565 MHz, $CDCl_3$) of **4d**

3-allyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (4e)

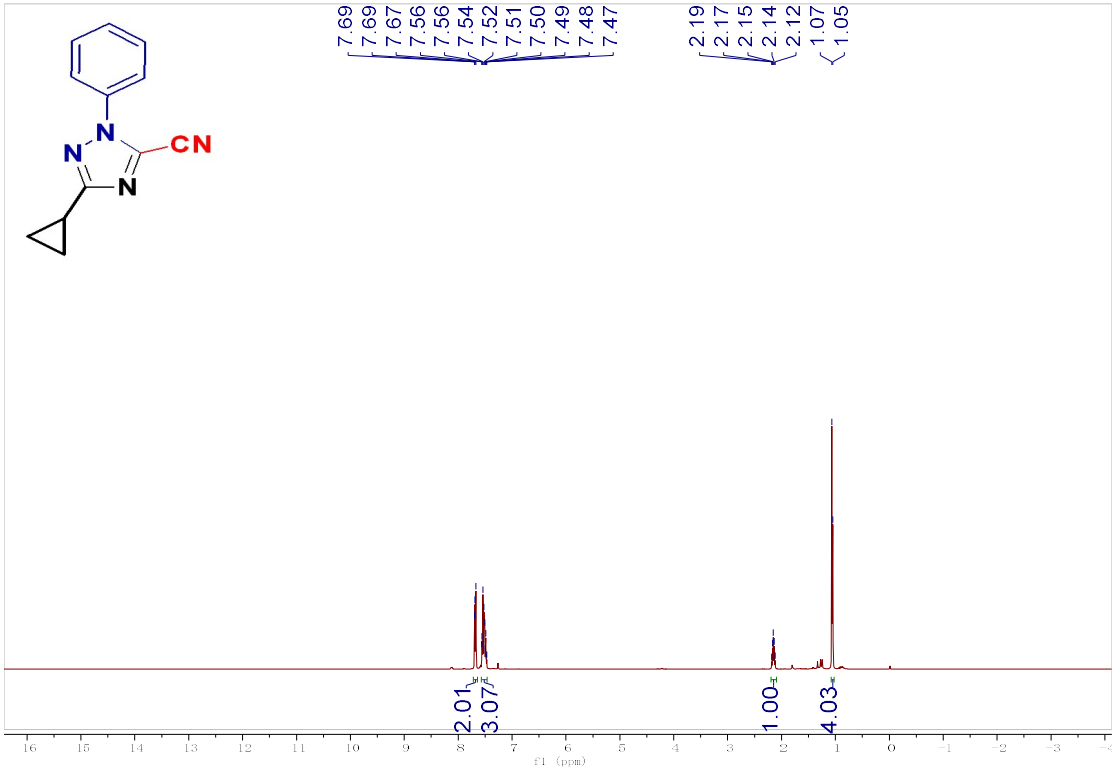


^{1}H NMR (400 MHz, $CDCl_3$) of **4e**

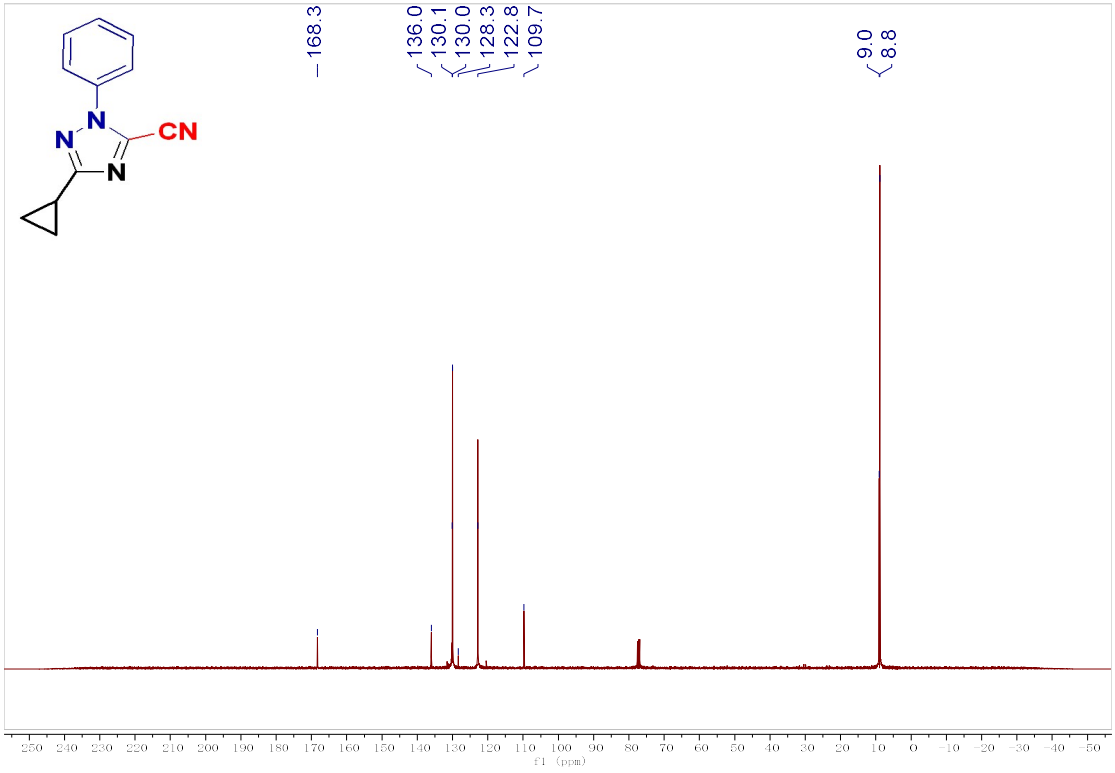


^{13}C NMR (100 MHz, $CDCl_3$) of **4e**

3-cyclopropyl-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (4f)

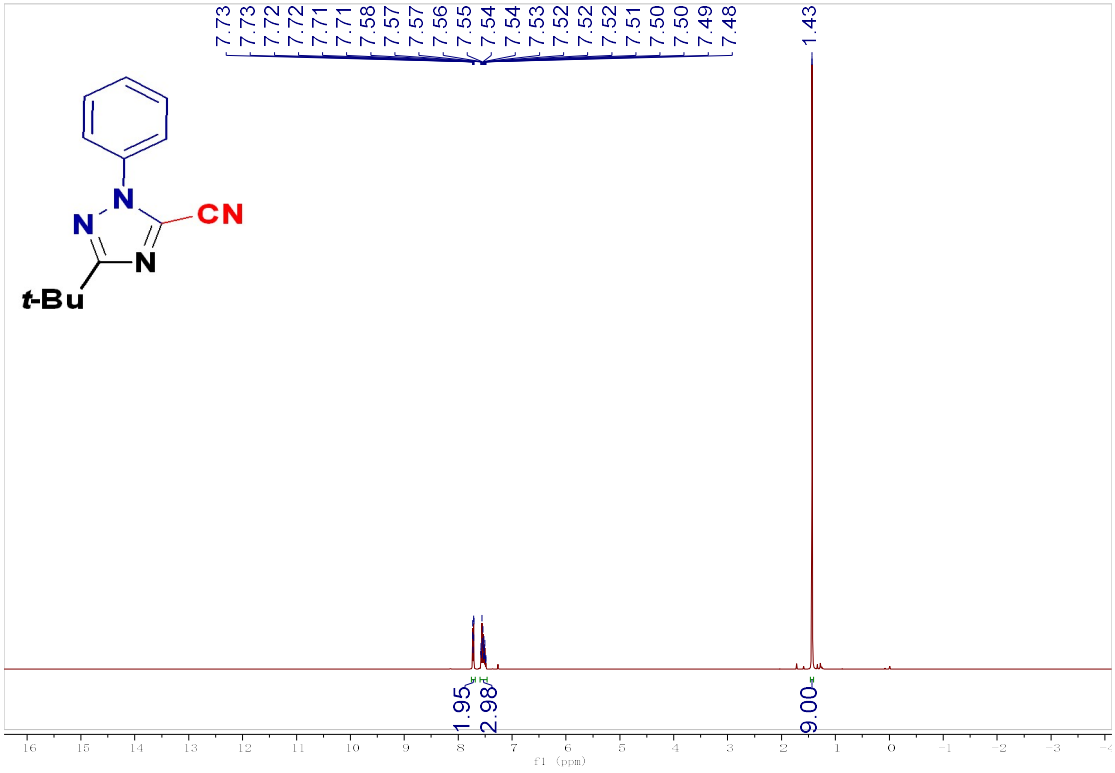


^{1}H NMR (400 MHz, $CDCl_3$) of **4f**

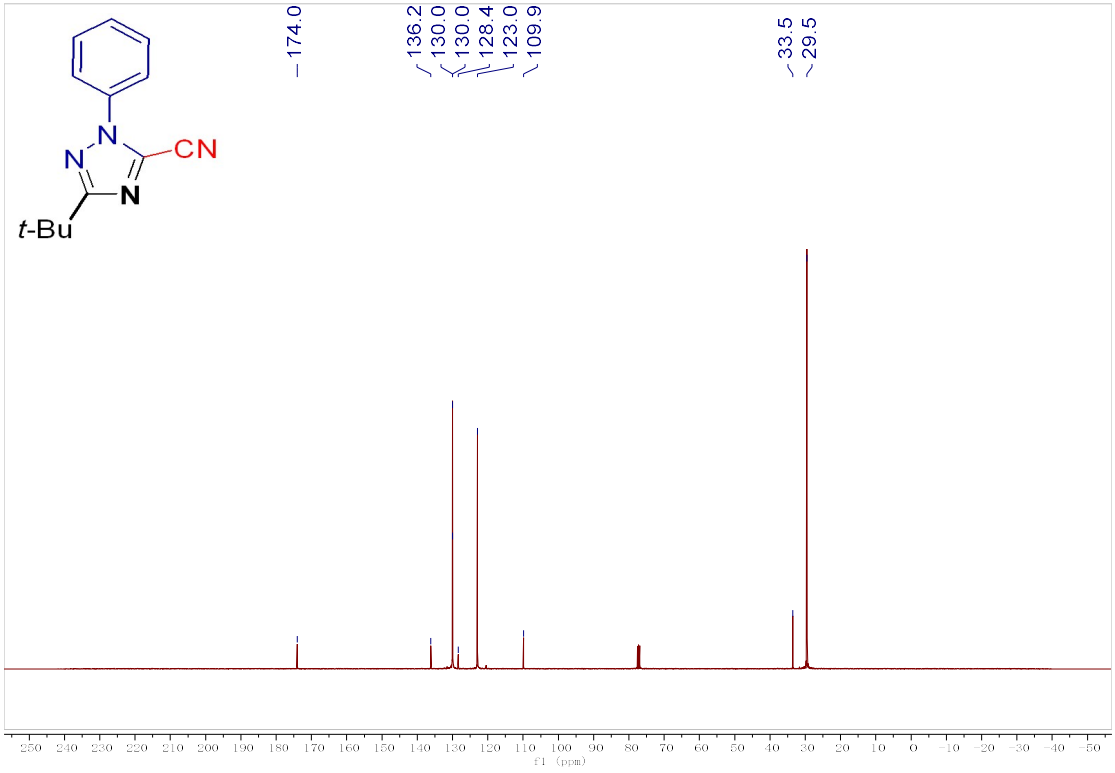


^{13}C NMR (100 MHz, $CDCl_3$) of **4f**

3-(tert-butyl)-1-phenyl-1H-1,2,4-triazole-5-carbonitrile (4g)

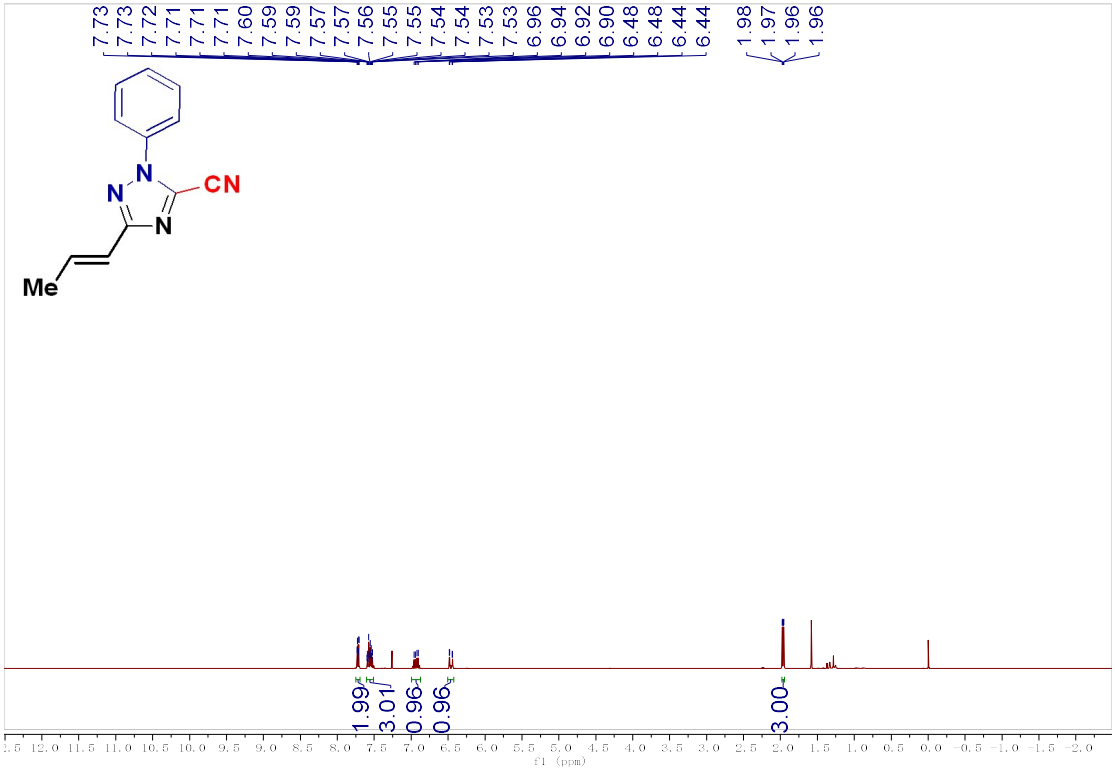


^{1}H NMR (400 MHz, $CDCl_3$) of **4g**

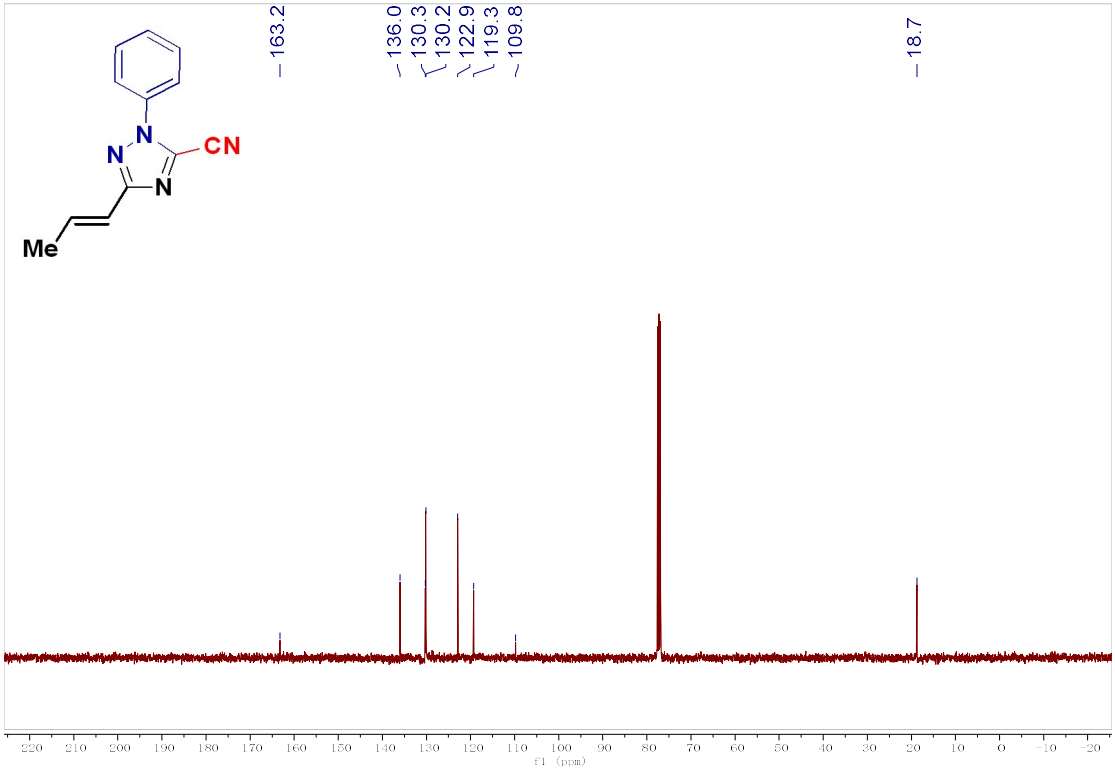


^{13}C NMR (100 MHz, $CDCl_3$) of **4g**

(E)-1-phenyl-3-(prop-1-en-1-yl)-1H-1,2,4-triazole-5-carbonitrile (4h)

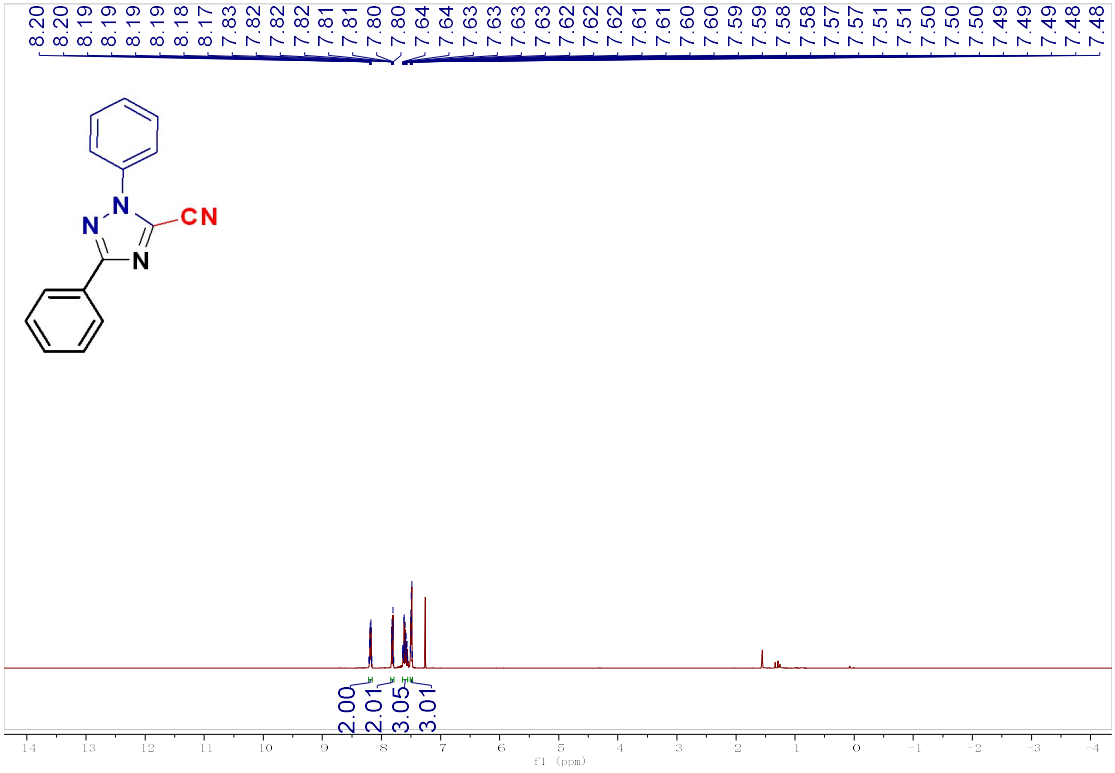


^{1}H NMR (400 MHz, $CDCl_3$) of **4h**

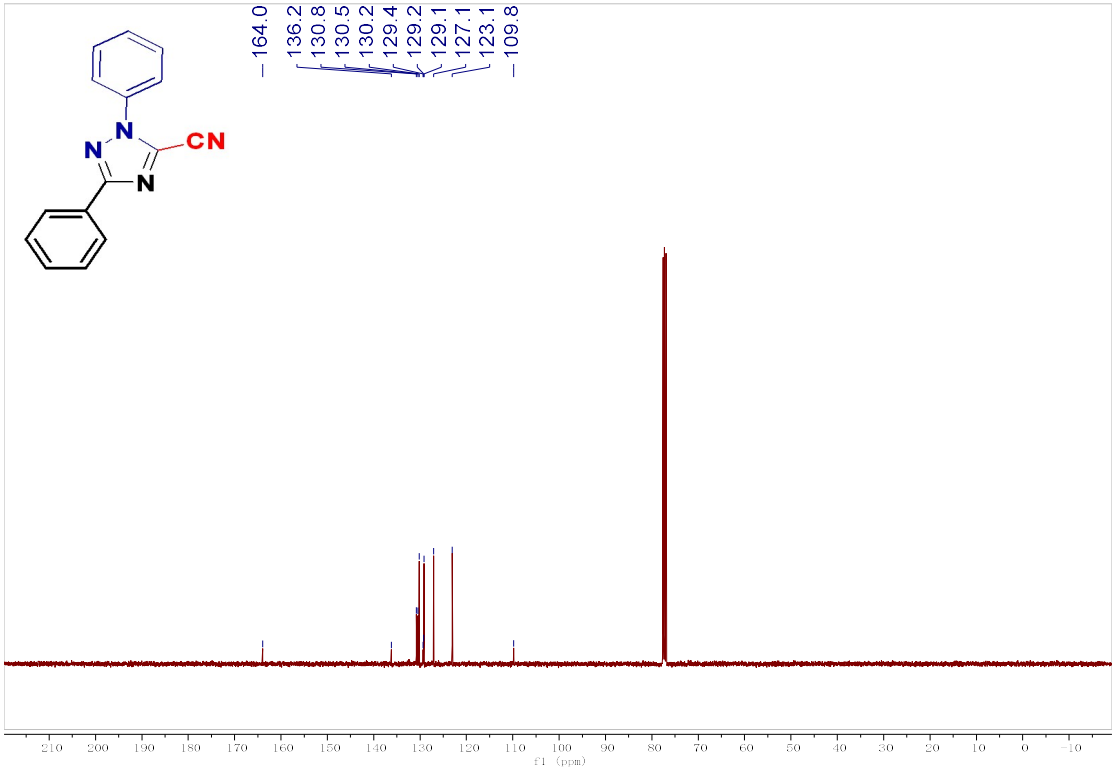


^{13}C NMR (100 MHz, $CDCl_3$) of **4h**

1,3-diphenyl-1H-1,2,4-triazole-5-carbonitrile (4i)

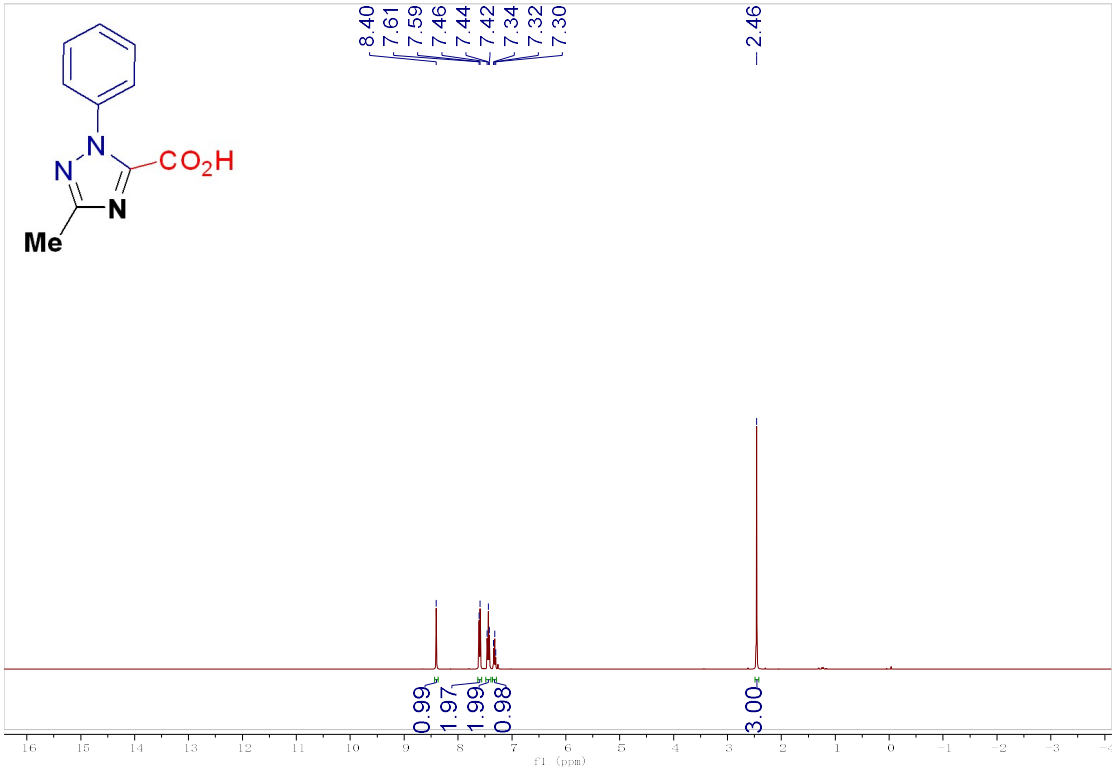


^{1}H NMR (400 MHz, $CDCl_3$) of **4i**

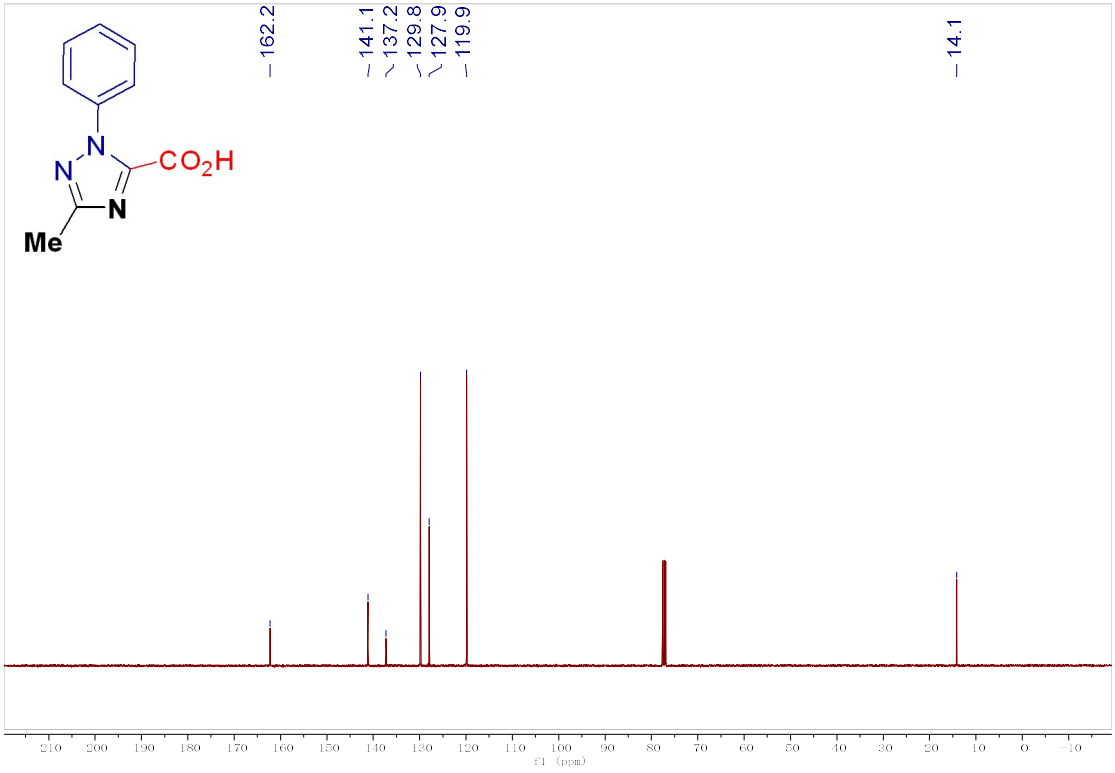


^{13}C NMR (100 MHz, $CDCl_3$) of **4i**

3-methyl-1-phenyl-1H-1,2,4-triazole-5-carboxylic acid (5a)

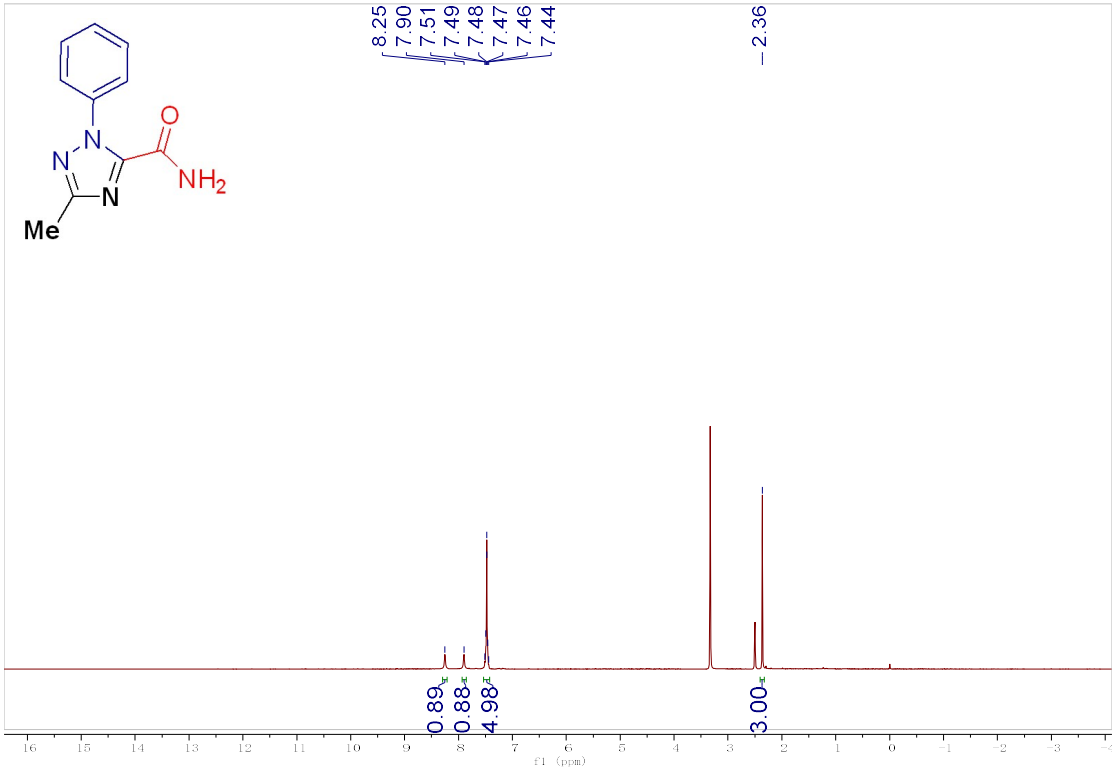


^{1}H NMR (400 MHz, $CDCl_3$) of **5a**

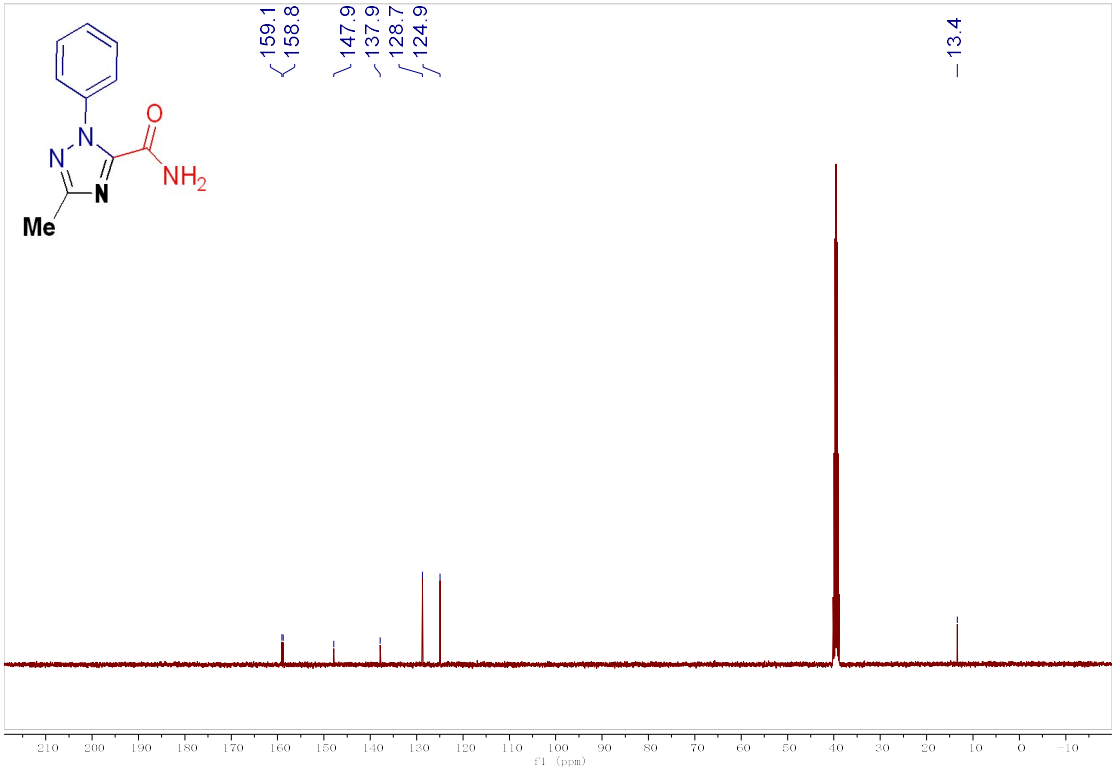


^{13}C NMR (100 MHz, $CDCl_3$) of **5a**

3-methyl-1-phenyl-1H-1,2,4-triazole-5-carboxamide (5b)

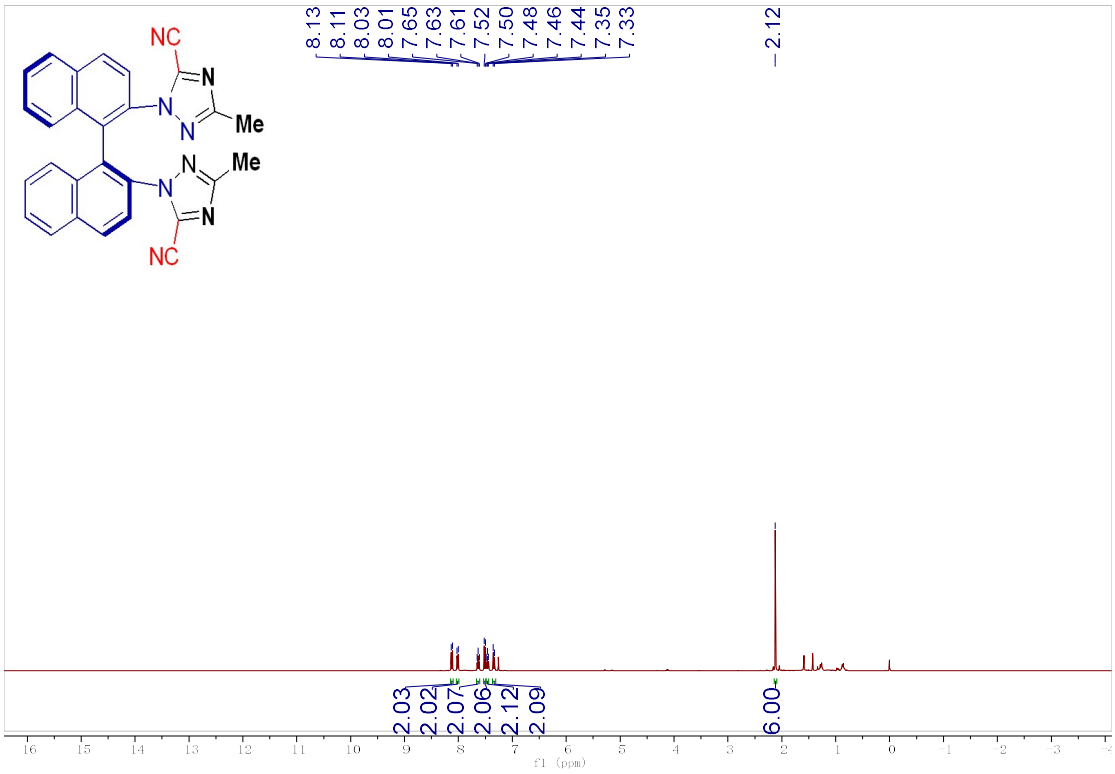


^{1}H NMR (400 MHz, DMSO) of **5b**

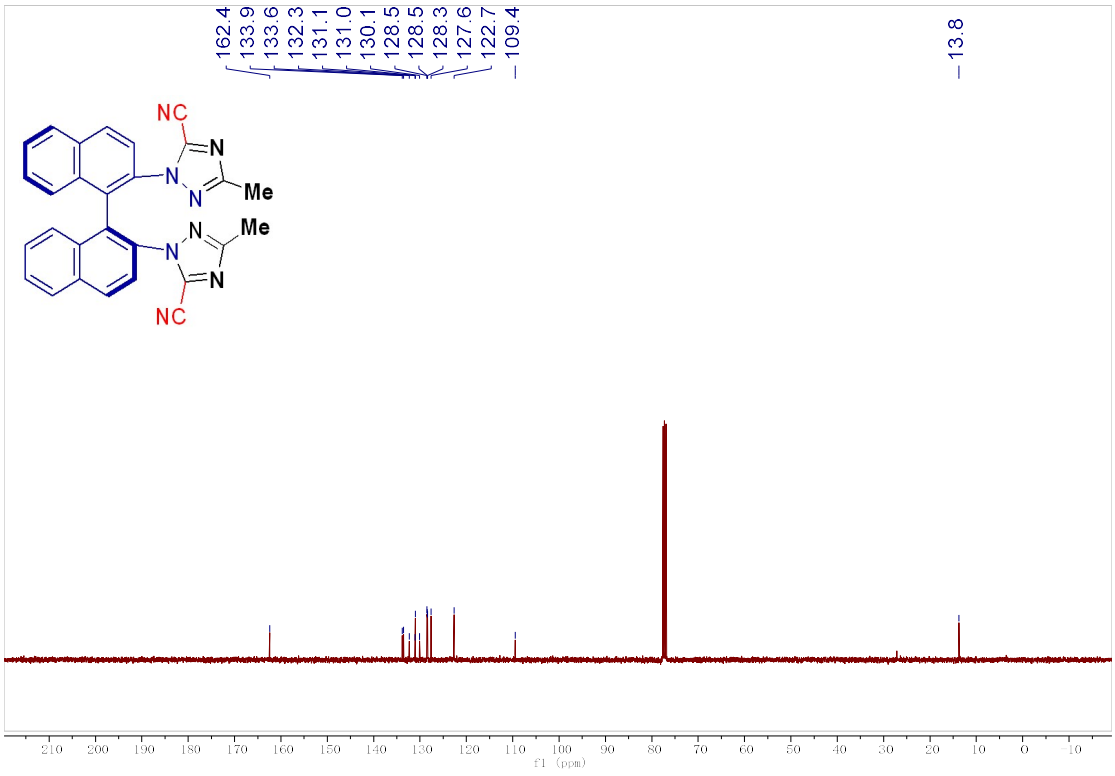


^{13}C NMR (100 MHz, DMSO) of **5b**

1,1'-([1,1'-binaphthalene]-2,2'-diyl)bis(3-methyl-1H-1,2,4-triazole-5-carbonitrile) (6)



^{1}H NMR (400 MHz, $CDCl_3$) of **6**



^{13}C NMR (100 MHz, $CDCl_3$) of **6**