Electronic Supplementary Information

A simple route towards the synthesis of 1,4,5-trisubstituted 1,2,3-triazoles from primary amines and 1,3-dicarbonyl compounds under metal free conditions

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1. General Remarks

All other reagents were purchased from TCI, Alfa Aesar, Accela and Adamas used without further purification. DCM were distilled from CaH_2 under nitrogen and stored under nitrogen. 1,4-Dioxane was distilled from sodium under nitrogen and stored under nitrogen. ^1H NMR (400 or 600 MHz) and ^{13}C NMR (101 or 151 MHz) were obtained on Bruker spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H NMR spectra as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of $CDCl_3$ (77.00 ppm) as the internal standard. The reported yields are the isolated yields.

2. General experimental procedures for the synthesis

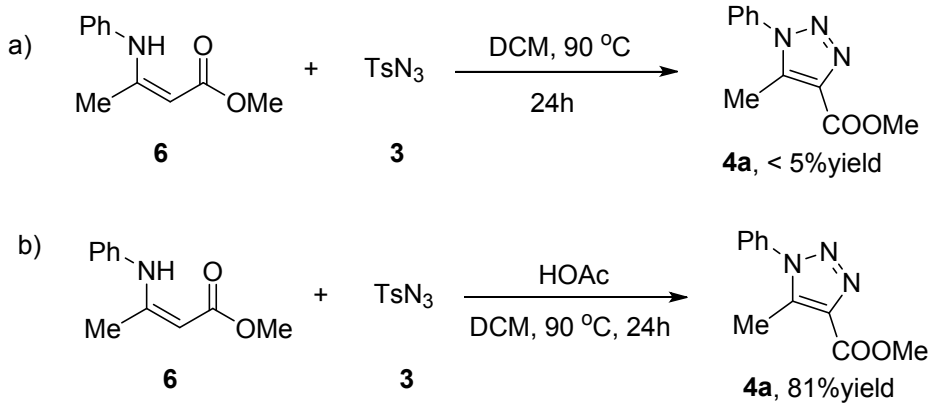
(1) The preparation of tosyl azide

To an oven-dried round bottom flask (100 mL) charged with a magnetic stir-bar was added sodium azide (30 mmol), water (10 mL). And then 4-methyl-benzenesulfonyl chloride (20 mmol) dissolved in acetone (15 mL) was added to the above solution. The mixture was stirred at room temperature for 12 h. The product (tosyl azide) was purified through column chromatography on 300-400 mesh silica gel with petroleum ether - ethyl acetate (100:10, v:v) as eluent to give the desired product (3.9328g, 96%).

(2) The procedure of the synthesis of 1,2,3-triazoles

Tosyl azide (0.3 mmol), primary amine (0.24 mmol), 1,3-dicarbonyl compound (0.2 mmol) and acetic acid (0.3 mmol) were successively added in a dried Schlenk tube (25 mL) by syringes. DCM (2 mL) was also added using a syringe. All the above of processes were done in the air. The mixture was stirred under an air atmosphere in a sealed Schlenk tube at 90 ^{o}C for 24 h. After cooling down, the solvent was removed in vacuo and the residue was purified by chromatography on silica gel (eluent: EtOAc/PE) to provide the corresponding product.

3. Mechanistic experiments

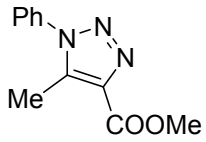


Aniline (2 mmol), methyl acetoacetate (2 mmol) and acetic acid (0.2 mmol) were added in dried a Schlenk tube (25 mL) by syringes. The process was done in the air. The mixture was stirred at 90 ℃ for 5 h. At the end of reaction, ethanol (5 mL) was added. The solution was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography with PE – EtOAc (100:1, v:v) as eluent to give the pure product **6** as a yellow oil (0.2712g, 73%).

The product **6** (0.2 mmol), tosyl azide (0.3 mmol) and acetic acid (0.3 mmol) were added in dried a Schlenk tube (25 mL) by syringes. The product **6** (0.2 mmol) and tosyl azide (0.3 mmol) were added in another dried Schlenk tube (25 mL) by syringes. DCM (2 mL) was also added using a syringe. All the above of processes were done in the air. The mixture was stirred under an air atmosphere in sealed Schlenk tubes at 90 °C for 24 h. After cooling down, the solvent was removed in vacuo and the residue was purified by chromatography on silica gel (eluent: EtOAc/PE) to provide the product **4a** as an off-white solid. The reaction with acetic acid could afford the desired product in 81% yield while the yield of the reaction without acetic acid was less than 5%.

4.Characterization of products

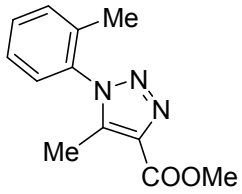
All the known compounds were in accordance with the data reported in the literatures.



Methyl 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate(4a)[1]

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-white solid (38.2mg, 88%).

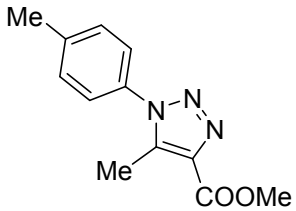
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 3H), 7.43 - 7.41(m, 2H), 3.95 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.13, 138.96, 136.49, 135.41, 130.09, 129.68, 125.32, 51.98, 9.93.



Methyl 5-methyl-1-(o-tolyl)-1H-1,2,3-triazole-4-carboxylate(4b)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (37.8mg, 82 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 1H), 7.42 – 7.33 (m, 2H), 7.22 (dd, J = 7.8, 1.1 Hz, 1H), 3.99 (s, 3H), 2.41 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.20, 139.85, 135.99, 135.49, 134.24, 131.46, 130.85, 52.03, 17.18, 9.33. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{14}N_3O_2$: 232.1081, found: 232.1077.

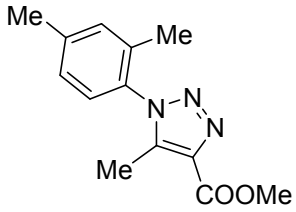


Methyl 5-methyl-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate(4c)[2]

The title compound was prepared according to the general experiment procedure

described above and purified by flash column chromatography with PE - EtOAc (100:15, v:v) as eluent. The title compound was isolated as an off-white solid (42.5mg, 92%).

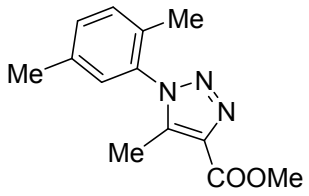
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 3.97 (s, 3H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.22, 140.39, 138.96, 136.40, 132.95, 130.20, 125.14, 51.95, 21.24, 9.90.



Methyl 1-(2,4-dimethylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4d)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:15, v:v) as eluent. The title compound was isolated as an off-white solid (47.0mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.26, 141.04, 139.91, 135.92, 135.07, 132.02, 131.74, 127.68, 126.90, 51.97, 21.23, 17.08, 9.31. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_2$: 246.1237, found: 246.1241.

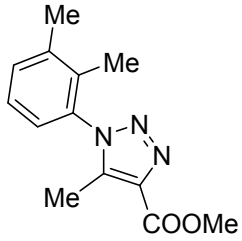


Methyl 1-(2,5-dimethylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4e)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:13, v:v) as eluent. The title compound was isolated as an off-colorless liquid (45.6mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 6.99 (s, 1H), 3.95 (d, J = 1.3 Hz, 3H),

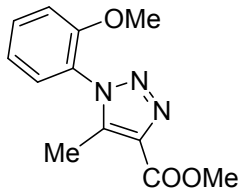
2.37 (d, J = 1.1 Hz, 3H), 2.34 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.19, 139.76, 137.13, 135.91, 134.04, 132.09, 131.54, 131.16, 127.53, 51.91, 20.66, 16.63, 9.30. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_2$: 246.1237, found: 246.1237.



Methyl 1-(2,3-dimethylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4f)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (39.7mg, 81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 3.97 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.26, 140.02, 139.04, 135.92, 134.25, 134.05, 132.14, 126.45, 124.78, 52.01, 20.26, 13.95, 9.33. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_2$: 246.1237, found: 246.1236.

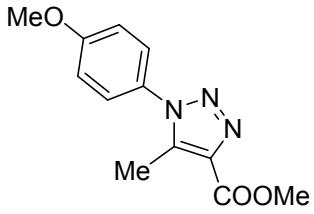


Methyl 1-(2-methoxyphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4g)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (40.5mg, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 1H), 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.16 – 7.04 (m, 2H), 3.97 (s, 3H), 3.79 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.37, 153.95, 141.08, 135.75, 132.13, 124.05, 121.08, 112.18, 55.86,

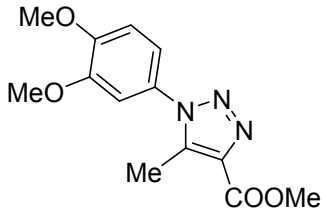
51.95, 9.37. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{14}N_3O_3$: 248.1030, found: 248.1034.



Methyl 1-(4-methoxyphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4h)[2]

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (41.0mg, 86%).

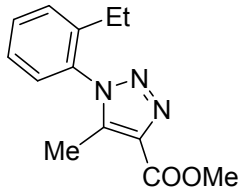
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.06 – 7.03 (m, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.25, 160.74, 139.14, 136.30, 128.20, 126.76, 114.78, 55.69, 52.03, 9.90.



Methyl 1-(3,4-dimethoxyphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4i)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (52.1mg, 94%).

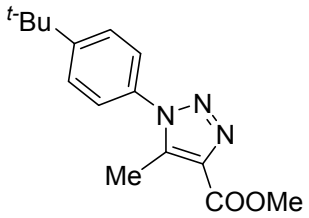
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 – 6.94 (m, 3H), 4.29 – 3.62 (m, 9H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.20, 150.38, 149.70, 139.17, 136.31, 128.27, 117.72, 111.01, 109.10, 56.26, 56.22, 52.00, 9.94. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_4$: 278.1135, found: 278.1140.



Methy 1-(2-enthylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4j)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:15, v:v) as eluent. The title compound was isolated as an off-colorless liquid (39.2mg, 80%).

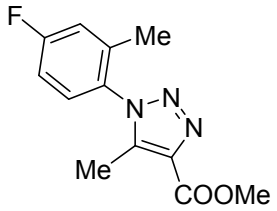
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 3.96 (d, *J* = 0.4 Hz, 3H), 2.38 (s, 3H), 2.28 (q, *J* = 7.6 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.18, 141.44, 139.96, 135.89, 133.67, 131.03, 129.89, 127.26, 126.99, 51.95, 23.90, 14.53, 9.41. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_2$: 246.1237, found: 246.1242.



Methyl 1-(4-(tert-butyl)phenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4k)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (46.6mg, 85%).

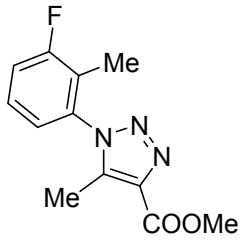
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.38 – 7.31 (m, 2H), 3.96 (d, *J* = 2.2 Hz, 3H), 2.57 (d, *J* = 1.6 Hz, 3H), 1.35 (d, *J* = 1.9 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.23, 153.51, 138.99, 136.38, 132.80, 126.61, 124.89, 52.00, 34.94, 31.23, 9.97. HRMS: m/z: $[M + H]^+$ calculated for $C_{15}H_{20}N_3O_2$: 274.1550, found: 274.1552.



Methyl 1-(4-fluoro-2-methylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4l)

The title compound was prepared according to the general experiment procedure described above (reaction temperature 70℃) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (37.3mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.09 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.07 – 7.01 (m, 1H), 3.92 (d, *J* = 2.1 Hz, 3H), 2.34 (d, *J* = 1.9 Hz, 3H), 1.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.29, 162.62, 162.06, 140.02, 138.40 (d, *J* = 9.0 Hz), 136.07, 130.25 (d, *J* = 3.0 Hz), 129.08 (d, *J* = 9.5 Hz), 118.19 (d, *J* = 22.8 Hz), 114.21 (d, *J* = 23.1 Hz), 52.06, 17.40 (d, *J* = 1.0 Hz), 9.30. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{13}FN_3O_2$: 250.0986, found: 250.0986.

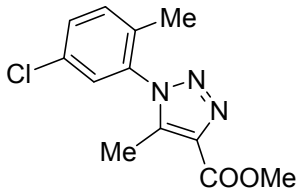


Methyl 1-(3-fluoro-2-methylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4m)

The title compound was prepared according to the general experiment procedure described above (reaction temperature 80℃) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (29.9mg, 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 4.00 (s, 3H), 2.42 (s, 3H), 1.95 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.32, 162.09, 139.97, 136.14, 127.65 (d, *J* = 9.4 Hz), 122.99 (d, *J* = 3.6 Hz), 117.72, 117.57, 52.12, 9.74 (d, J = 4.1 Hz), 9.33. HRMS: m/z: $[M + H]^+$

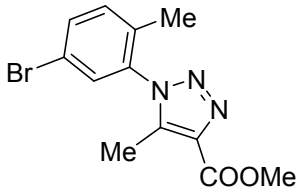
calculated for $C_{12}H_{13}FN_3O_2$: 250.0986, found: 250.0986.



Methyl 1-(5-chloro-2-methylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4n)

The title compound was prepared according to the general experiment procedure described above (reaction temperature 100℃) and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-white solid (33.5mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 3.98 (s, 3H), 2.41 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.01, 139.84, 136.13, 135.00, 134.15, 132.50, 132.45, 131.05, 127.33, 52.11, 16.80, 9.34. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{13}ClN_3O_2$: 266.0691, found: 266.0686.

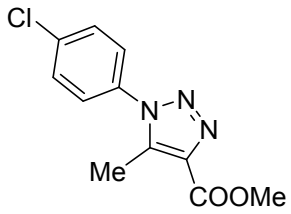


Methyl 1-(5-bromo-2-methylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4o)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-colorless liquid (27.9mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 2.41 (s, 3H), 1.96 (s, 3H).

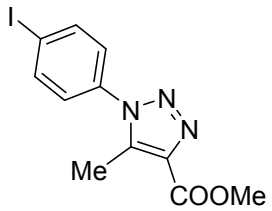
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.00, 139.86, 136.11, 135.22, 134.67, 133.98, 132.78, 130.15, 119.81, 52.12, 16.88, 9.35. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{13}BrN_3O_2$: 310.0186, found: 310.0184.



Methyl 1-(4-chlorophenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4p)[3]

The title compound was prepared according to the general experiment procedure described above (reaction time 48 h) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-white solid (25.7mg, 51%).

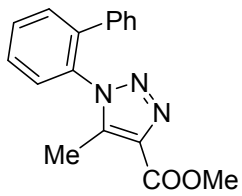
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 2H), 7.46 – 7.37 (m, 2H), 3.99 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.03, 138.97, 136.70, 136.33, 133.87, 129.99, 126.56, 52.12, 9.96.



Methyl 1-(4-iodophenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4q)

The title compound was prepared according to the general experiment procedure described above (reaction time 48 h) and purified by flash column chromatography with PE - EtOAc (100:6, v:v) as eluent. The title compound was isolated as an off-white solid (47.0mg, 50%).

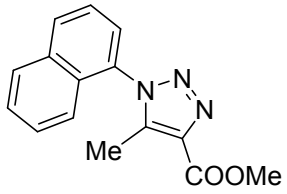
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.24 – 7.18 (m, 2H), 3.99 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 138.95, 138.86, 136.75, 135.08, 126.85, 95.84, 52.11, 9.97. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_{11}IN_3O_2$: 343.9890, found: 343.9892.



Methyl 1-([1,1'-biphenyl]-2-yl)-5-methyl-1H-1,2,3-triazole-4-carboxylate(4r)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:7, v:v) as eluent. The title compound was isolated as an off-colorless liquid (53.9mg, 92%).

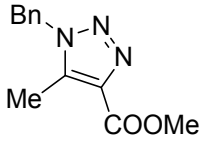
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.45 (m, 3H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 6.1 Hz, 3H), 6.99 (d, *J* = 5.5 Hz, 2H), 3.84 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.05, 140.28, 139.24, 136.81, 135.81, 132.86, 131.15, 131.03, 128.84, 128.68, 128.28, 128.22, 128.19, 51.94, 9.14. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{16}N_3O_2$: 294.1237, found: 294.1243.



Methyl 5-methyl-1-(naphthalen-1-yl)-1H-1,2,3-triazole-4-carboxylate(4s)[4]

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-white solid (49.7mg, 93%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.97 (s, 2H), 2.37 (s, 1H), 2.34 (s, 1H), 1.85 (s, 1H), 4.01 (s, 3H), 2.39 (s, 3H); ^{13}CNMR (151 MHz, $CDCl_3$) δ 162.24, 140.98, 136.10, 134.15, 131.45, 131.28, 129.37, 128.48, 128.27, 127.32, 125.32, 125.08, 121.80, 52.11, 9.47.

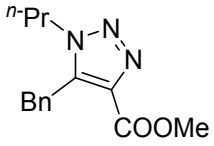


Methyl 1-benzyl-5-methyl-1H-1,2,3-triazole-4-carboxylate(4t)

The title compound was prepared according to the general experiment procedure described above (Reaction temperature 60 ^{o}C, react for 48 h) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (24.5mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.22 – 7.09 (m, 2H), 5.53 (s, 2H),

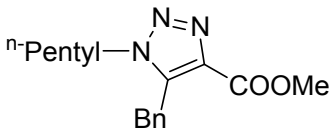
3.93 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.15, 138.45, 136.79, 133.91, 129.15, 128.63, 127.20, 52.01, 51.93, 29.70, 9.02. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{14}N_3O_2$: 232.1081, found: 232.1078.



Methyl 5-benzyl-1-propyl-1H-1,2,3-triazole-4-carboxylate(4u)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-colorless liquid (22.3mg, 43%).

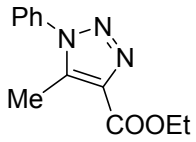
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 4.38 (s, 2H), 4.14 – 3.95 (m, 2H), 3.90 (s, 3H), 1.67 – 1.64 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.25, 140.01, 136.58, 135.60, 129.00, 128.10, 127.26, 52.04, 49.88, 28.60, 23.06, 10.95. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{18}N_3O_2$: 260.1394, found: 260.1394.



Methyl 5-benzyl-1-pentyl-1H-1,2,3-triazole-4-carboxylate(4v)

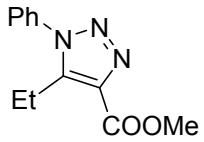
The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (25.8mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 4.37 (s, 2H), 4.06 (t, *J* = 7.5 Hz, 2H), 3.90 (s, 3H), 1.65 – 1.52 (m, 2H), 1.17 – 1.05 (m, 4H), 0.74 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.26, 139.94, 136.59, 135.61, 128.99, 128.11, 127.25, 52.03, 48.42, 29.31, 28.62, 28.54, 22.02, 13.77. HRMS: m/z: $[M + H]^+$ calculated for $C_{16}H_{22}N_3O_2$: 288.1707, found: 288.1789.



Ethyl 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate(5a)[1]

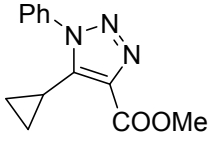
The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (37.4mg, 81%). HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{12}FN_3O_2$: 249.0914, found: . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.48 (m, 3H), 7.51 – 7.33 (m, 2H), 4.46 – 4.43 (m, 2H), 2.57 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.79, 138.87, 136.75, 135.46, 130.10, 129.70, 125.38, 61.10, 14.40, 10.01.



Methyl 5-ethyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate(5b)[5]

The title compound was prepared according to the general experiment procedure described above (reaction temperature 70℃) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent. The title compound was isolated as an off-colorless liquid (33.3mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.45 (m, 3H), 7.52 – 7.35 (m, 2H), 3.98 (s, 3H), 3.00 – 2.97 (m, 2H), 1.15 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.01, 144.68, 135.83, 135.50, 130.33, 129.73, 125.72, 52.05, 16.98, 13.20.

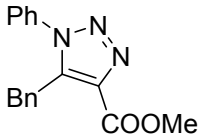


Methyl 5-cyclopropyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate(5c)

The title compound was prepared according to the general experiment procedure described above (tosyl azide 0.2mmol, aniline 0.3mmol, methyl 3-cyclopropyl-3-oxopropanoate 0.3mmol, $TsOH·H_2O$ 0.2mmol, DMSO 2mL) and purified by flash column chromatography with PE - EtOAc (100:7, v:v) as eluent. The title compound

was isolated as an off-white solid (11.7mg, 24%).

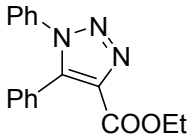
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.36 (m, 5H), 3.98 (s, 3H), 2.00 – 1.95 (m, 1H), 1.04 – 0.94 (m, 2H), 0.89 – 0.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.74, 143.38, 136.69, 136.00, 129.96, 129.42, 125.62, 52.10, 8.07, 5.60. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}N_3O_2$: 244.1081, found: 244.1084.



Eethyl 1,5-diphenyl-1H-1,2,3-triazole-4-carboxylate(5d)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:7, v:v) as eluent. The title compound was isolated as an off-Light yellow liquid (25.9mg, 44%).

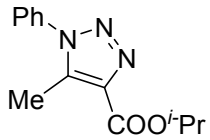
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 1H), 7.44 – 7.35 (m, 2H), 7.20 – 7.17 (m, 2H), 7.16 – 7.02 (m, 3H), 6.89 – 6.73 (m, 2H), 4.33 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.02, 140.33, 135.69, 134.96, 134.35, 129.34, 128.52, 127.67, 127.12, 125.97, 124.89, 51.16, 27.93. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{16}N_3O_2$: 294.1237, found: 294.1239.



Ethyl 1,5-diphenyl-1H-1,2,3-triazole-4-carboxylate(5e)[6]

The title compound was prepared according to the general experiment procedure described above (tosyl azide 0.2mmol, aniline 0.3mmol, ethyl benzoylacetate 0.3mmol, $TsOH·H_2O$ 0.2mmol, DMSO 2mL, react for 48 h) and purified by flash column chromatography with PE - EtOAc (100:5, v:v) as eluent. The title compound was isolated as an off-white solid (19.9mg, 34%).

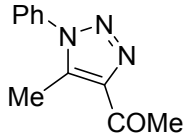
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 5H), 7.32 – 7.22 (m, 4H), 4.39 – 4.36 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.29, 129.95, 129.52, 129.34, 128.37, 125.26, 61.24, 14.19.



Isopropyl 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate(5f)

The title compound was prepared according to the general experiment procedure described above and purified by flash column chromatography with PE - EtOAc (100:8, v:v) as eluent. The title compound was isolated as an off-colorless liquid (34.3mg, 70%).

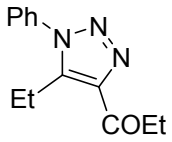
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 3H), 7.44 – 7.42 (m, 2H), 5.35 – 5.31 (m, 1H), 2.57 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.38, 138.72, 137.03, 135.51, 130.07, 129.69, 125.42, 68.75, 21.97, 10.06. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O_2$: 246.1237, found: 246.1233.



1-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)ethenone(5g)[6]

The title compound was prepared according to the general experiment procedure described above (reaction temperature 60℃) and purified by flash column chromatography with PE - EtOAc (100:10, v:v) as eluent**.** The title compound was isolated as an off-white solid (28.1mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 3H), 7.48 – 7.36 (m, 2H), 2.75 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.44, 143.68, 137.43, 135.33, 130.09, 129.71, 125.30, 27.88, 10.16.



1-(5-ethyl-1-phenyl-1H-1,2,3-triazol-4-yl)propan-1-one(5h)

The title compound was prepared according to the general experiment procedure described above (reaction temperature 60℃) and purified by flash column chromatography with PE - EtOAc (100:2, v:v) as eluent**.** The title compound was

isolated as an off-colorless liquid (38.9mg, 85%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 3H), 7.44 – 7.42 (m, 2H), 3.27 – 3.23 (m, 2H), 3.00 – 2.96 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.19, 143.06, 142.71, 135.53, 130.23, 129.71, 125.68, 33.30, 17.14, 12.94, 7.88. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O$: 230.1288, found: 230.1293.

References:

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[2] A. Pavani; T. Lakhshmi Viveka, *IOSR J. Applied Chem.*, 2013, **3**, 36.

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[4] W. Mitchell; G. C. Rees; *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999)*,1987, 0, 413.

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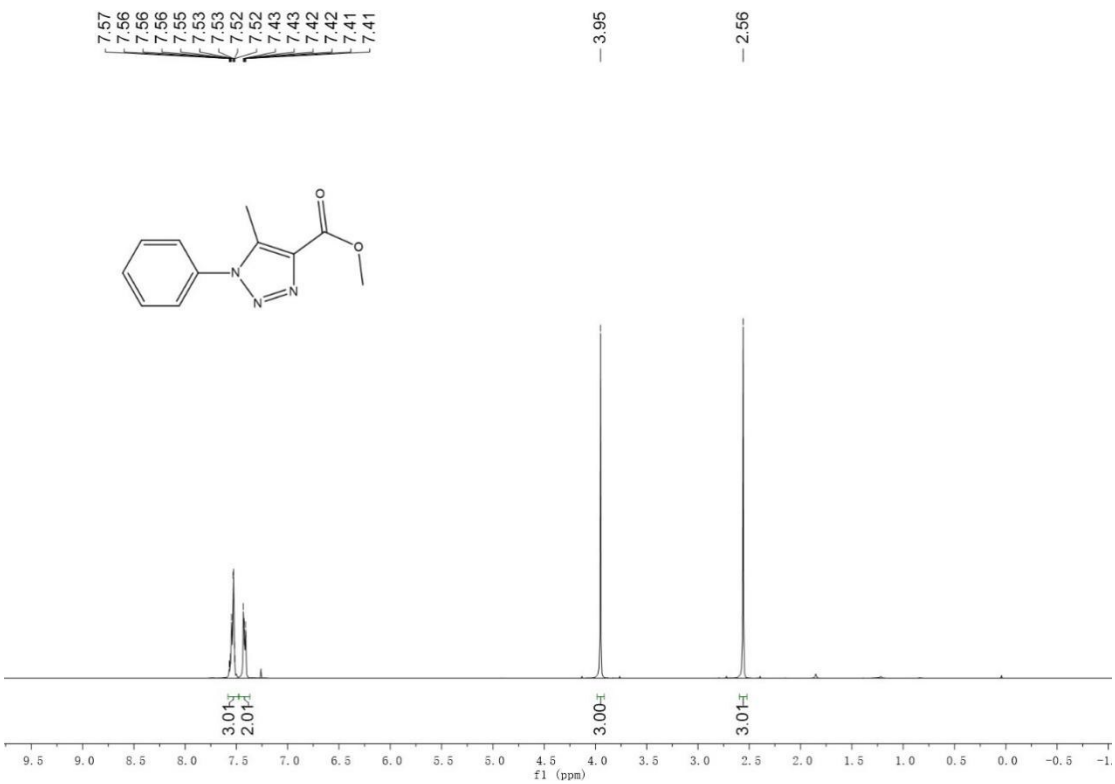
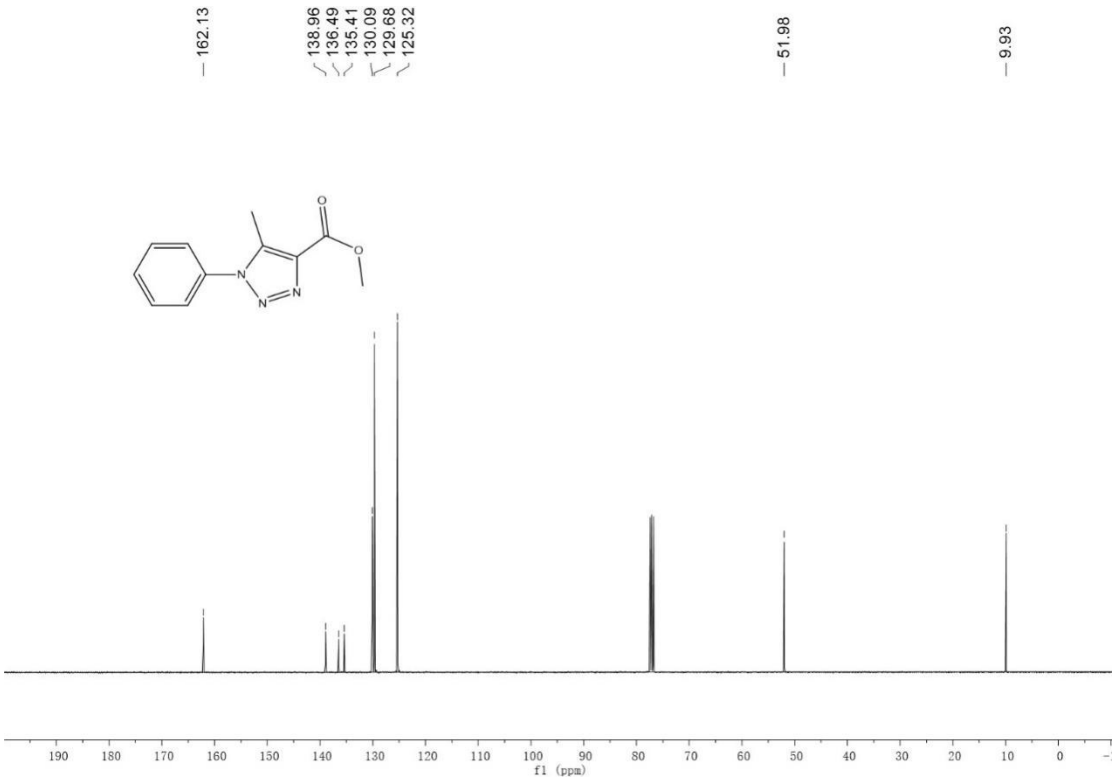
[6] L. J. T. Danence; Y. Gao; M. Li; Y. Huang; J. Wang, *Chem. – Eur. J.* 2011, **17**, 3584.

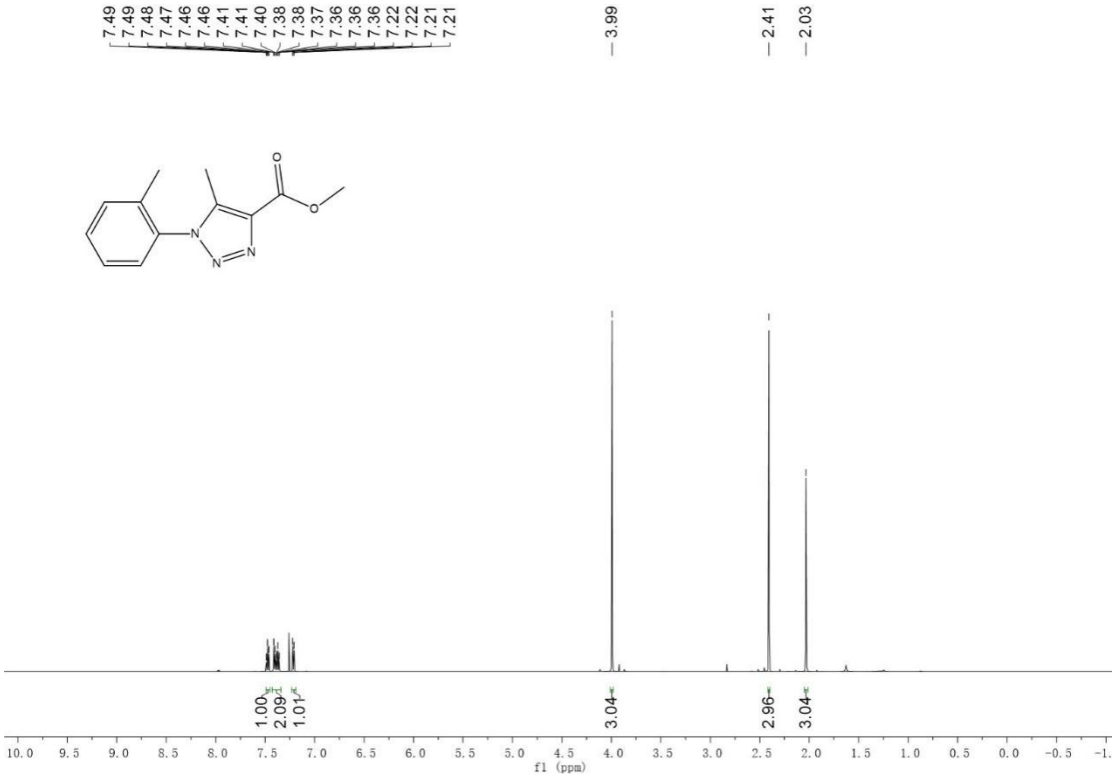
^{1}H NMR Spectra of **4a** ($CDCl_3$, 294.2 K)



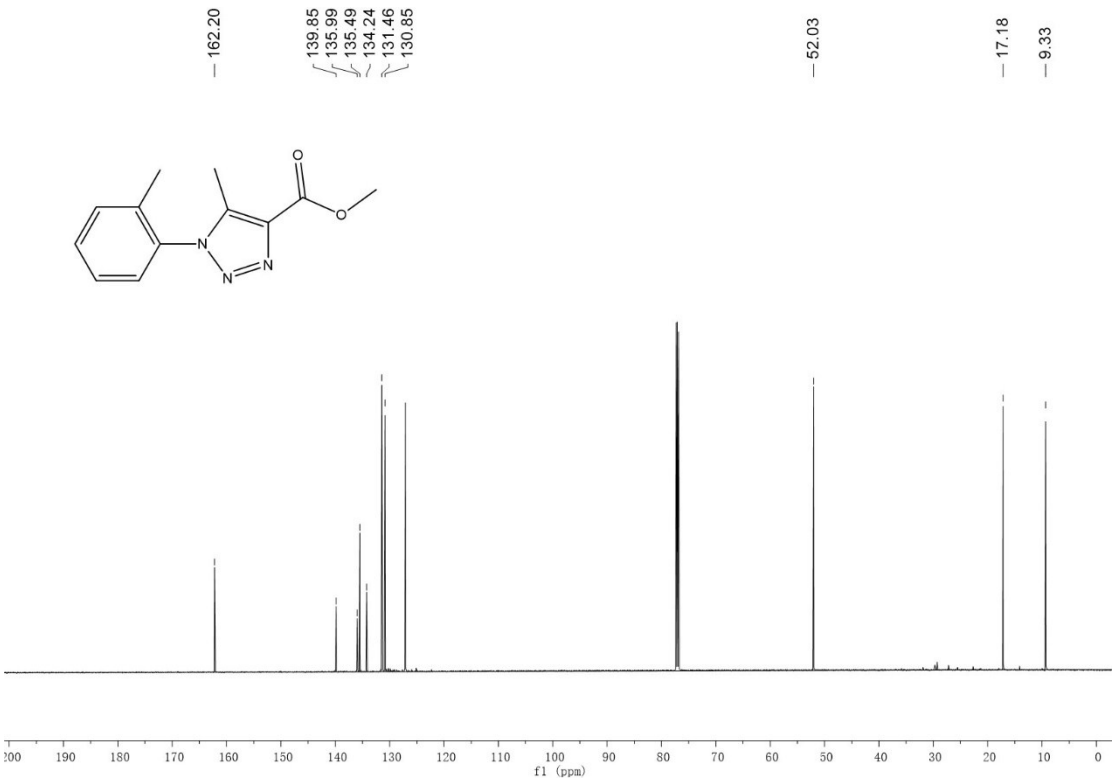
^{13}C NMR Spectra of **4a** ($CDCl_3$, 295.9 K)



^{1}H NMR Spectra of **4b** ($CDCl_3$, 298.0 K)

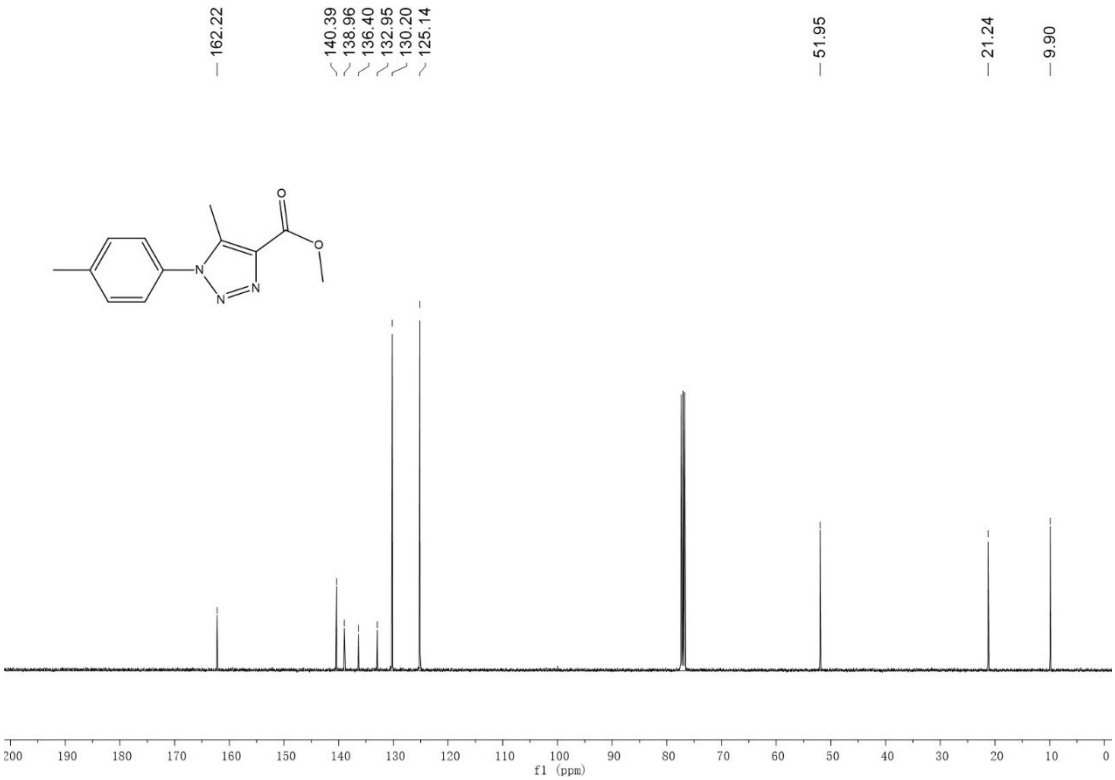


^{13}C NMR Spectra of **4b** ($CDCl_3$, 298.1 K)

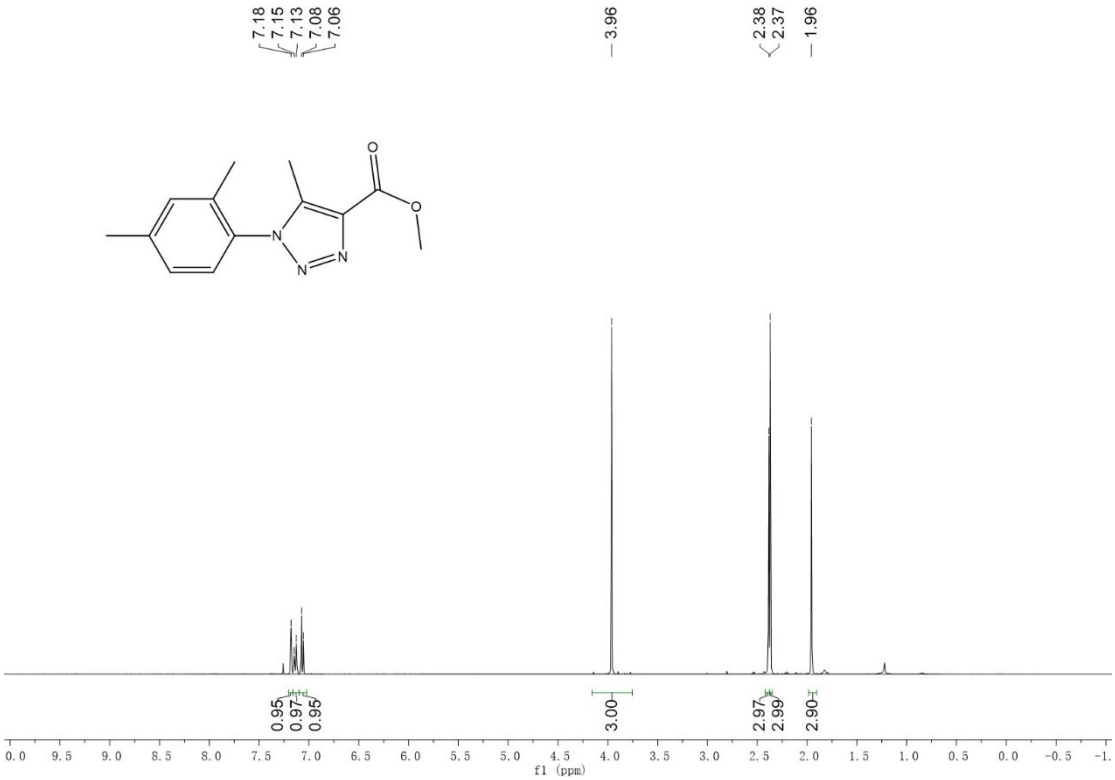


^{1}H NMR Spectra of **4c** ($CDCl_3$, 294.4 K)

^{13}C NMR Spectra of **4c** ($CDCl_3$, 296.5 K)

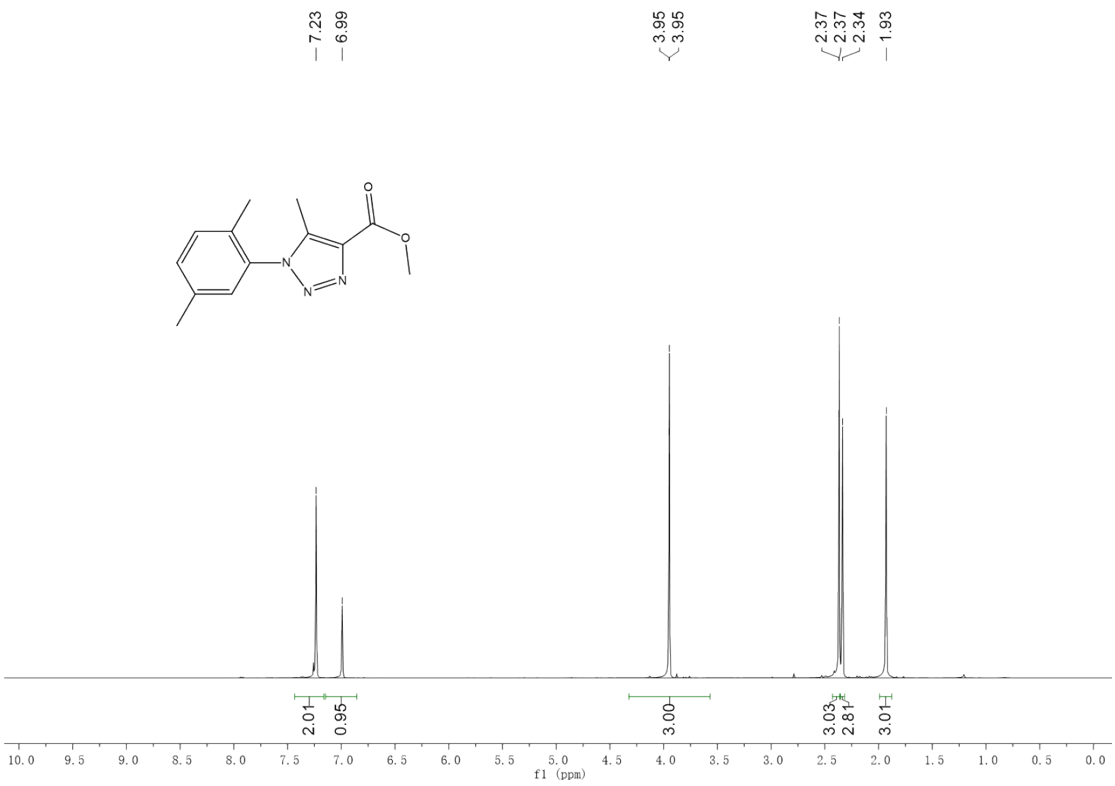


^{1}H NMR Spectra of **4d** ($CDCl_3$, 293.7 K)

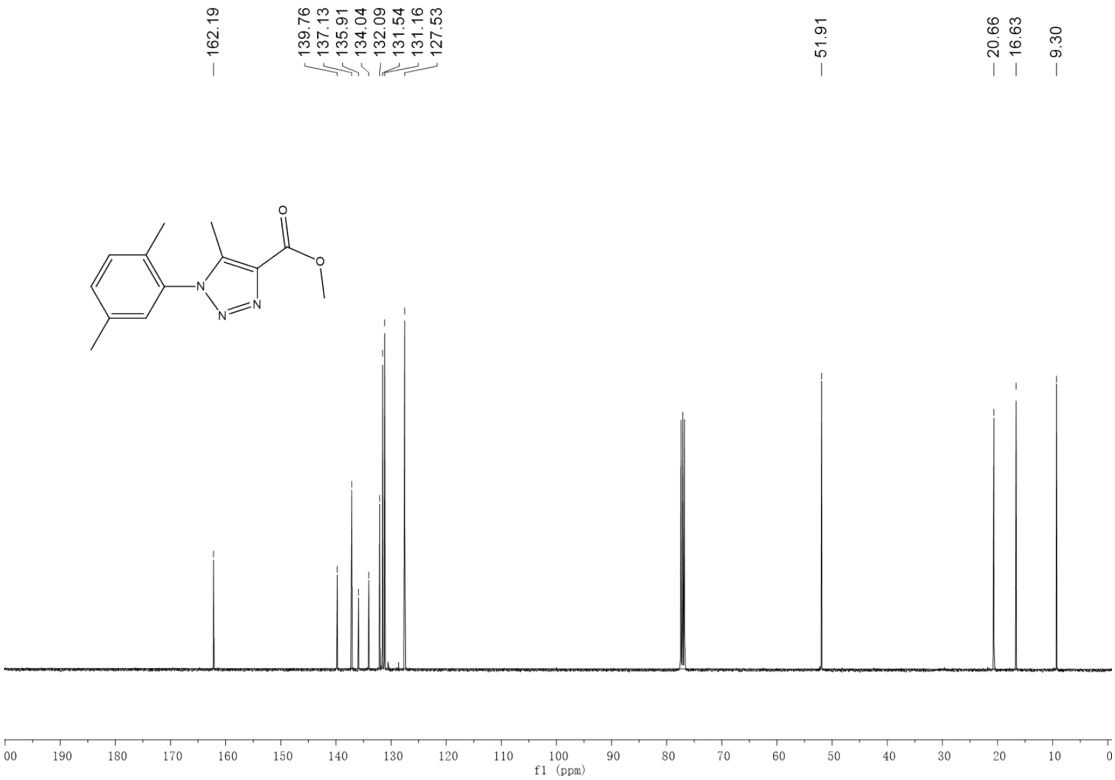


^{13}C NMR Spectra of **4d** ($CDCl_3$, 295.1 K)

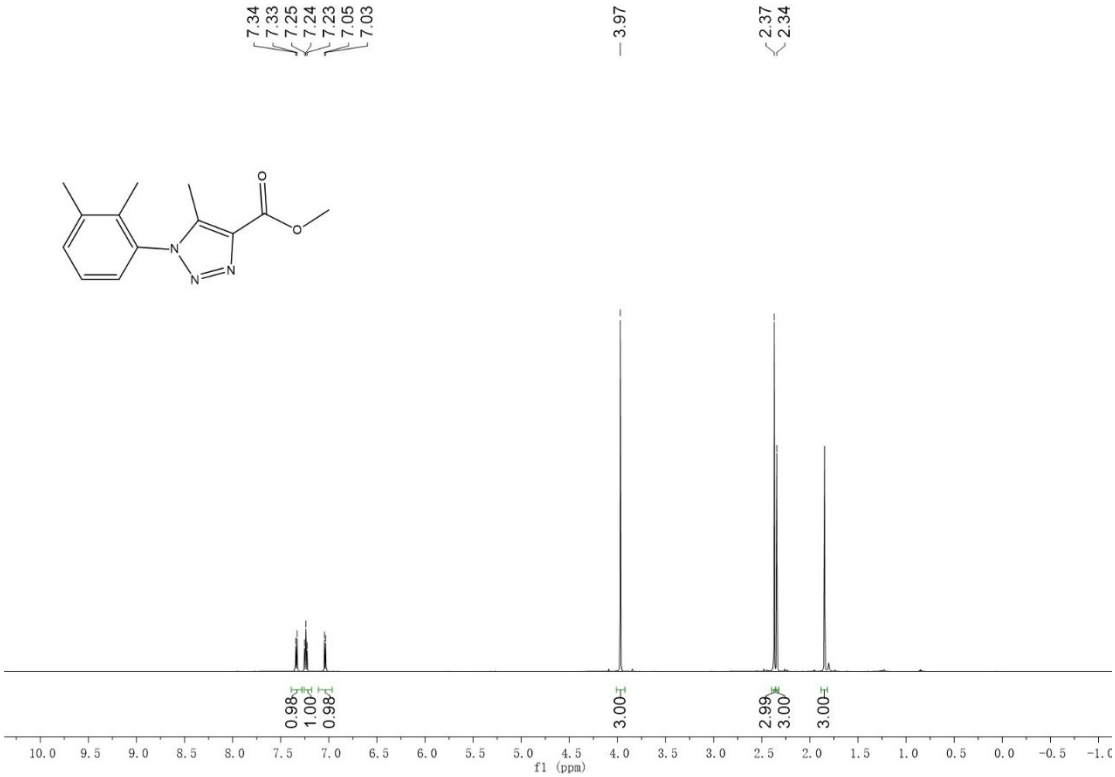
^{1}H NMR Spectra of **4e** ($CDCl_3$, 294.0 K)



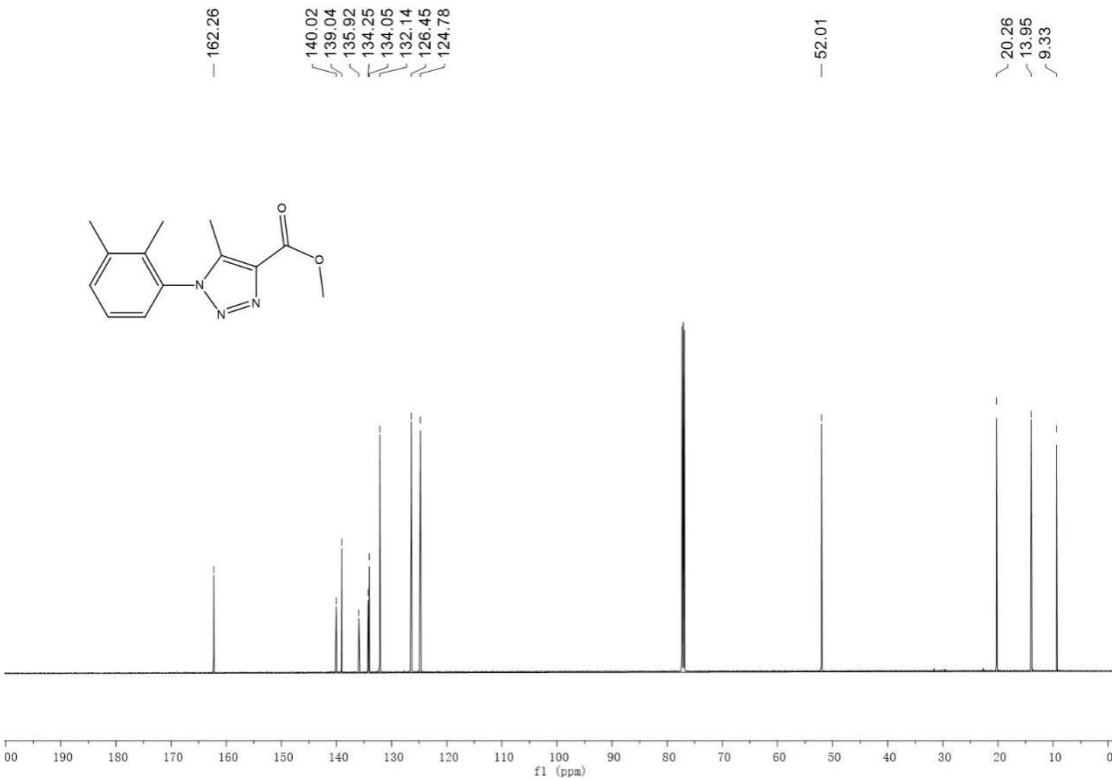
^{13}C NMR Spectra of **4e** ($CDCl_3$, 296.7 K)



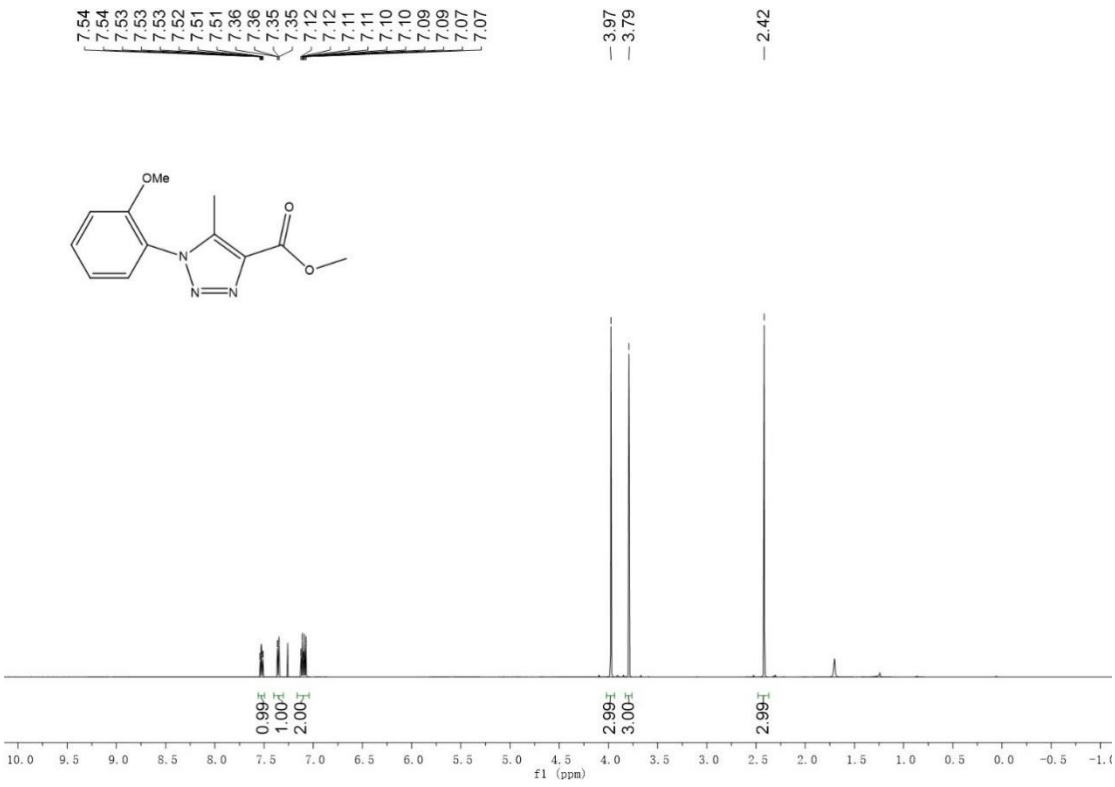
^{1}H NMR Spectra of **4f** ($CDCl_3$, 297.9 K)



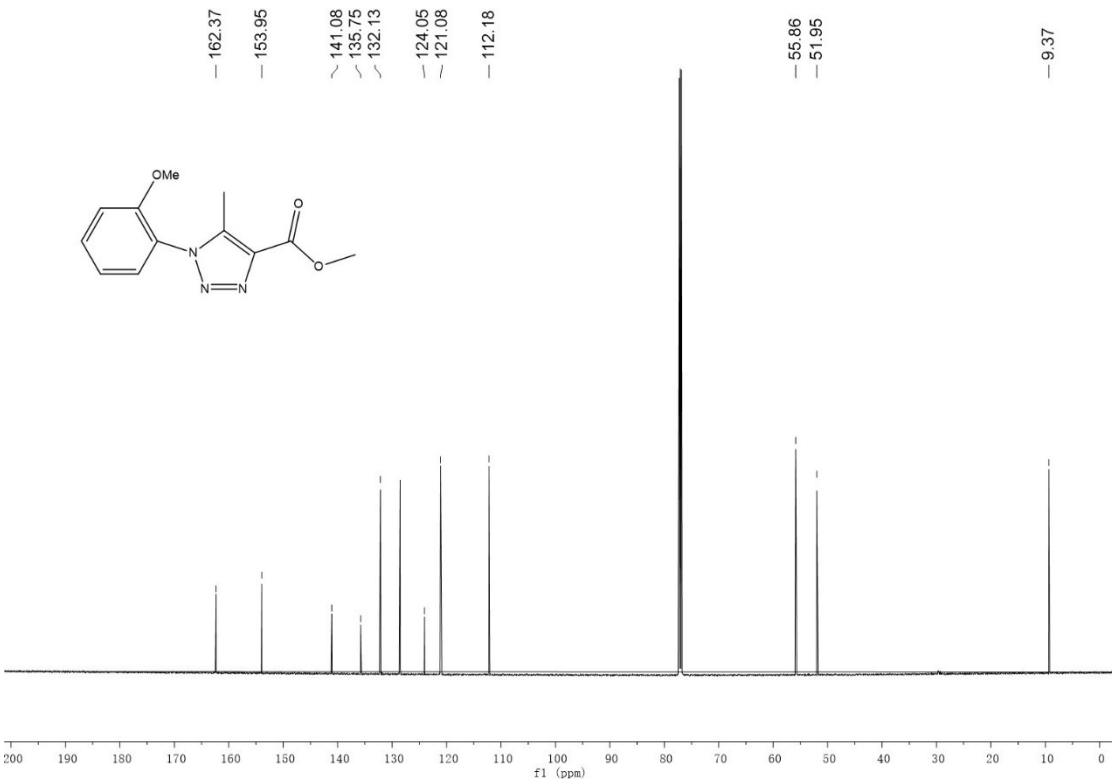
^{13}C NMR Spectra of **4f** ($CDCl_3$, 298.0 K)



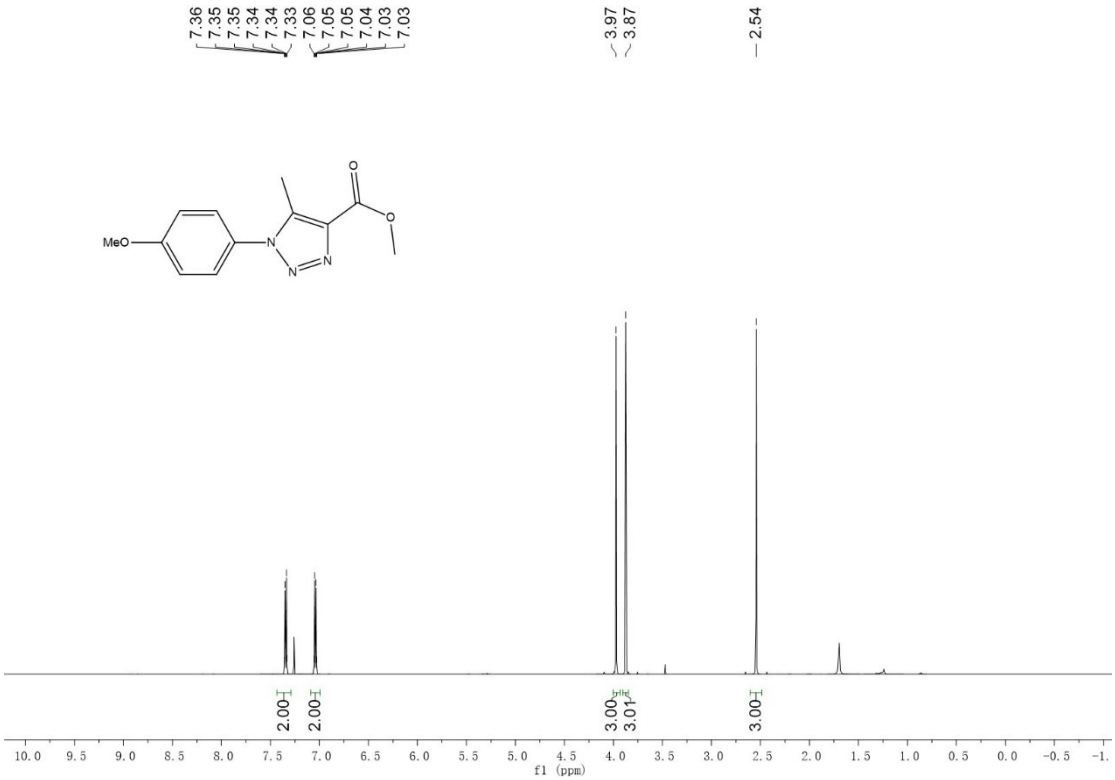
^{1}H NMR Spectra of **4g** ($CDCl_3$, 297.9 K)



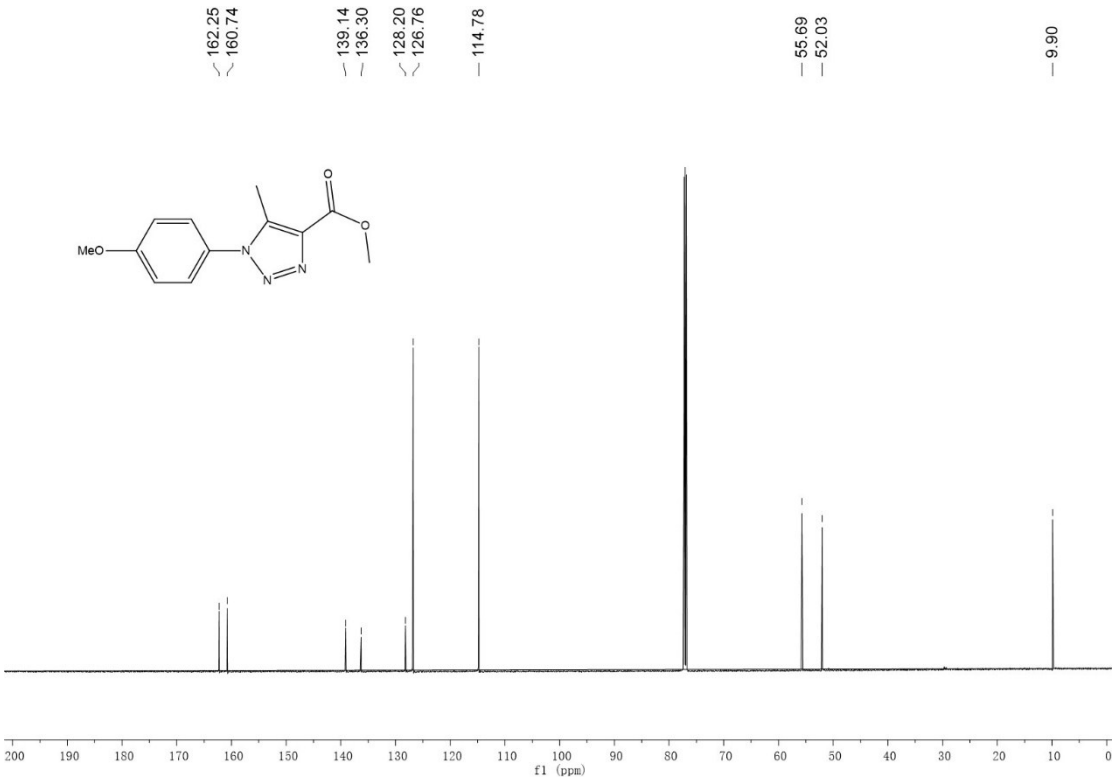
^{13}C NMR Spectra of **4g** ($CDCl_3$, 297.9 K)



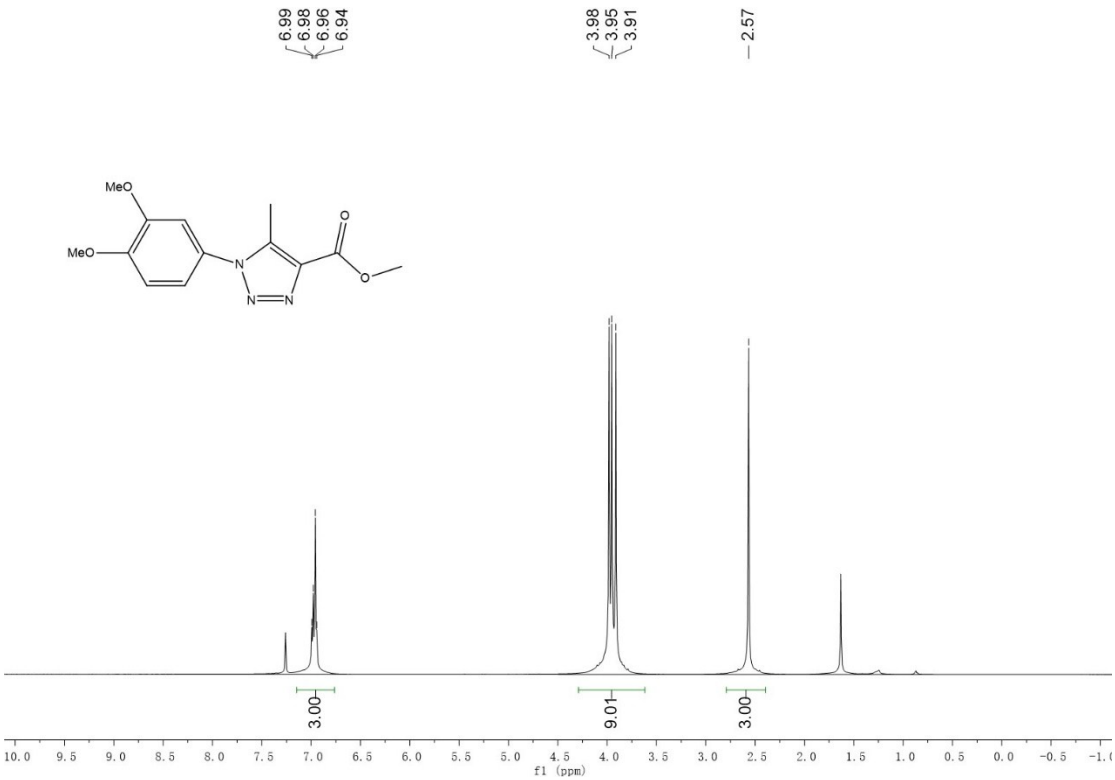
^{1}H NMR Spectra of **4h** ($CDCl_3$, 298.1 K)



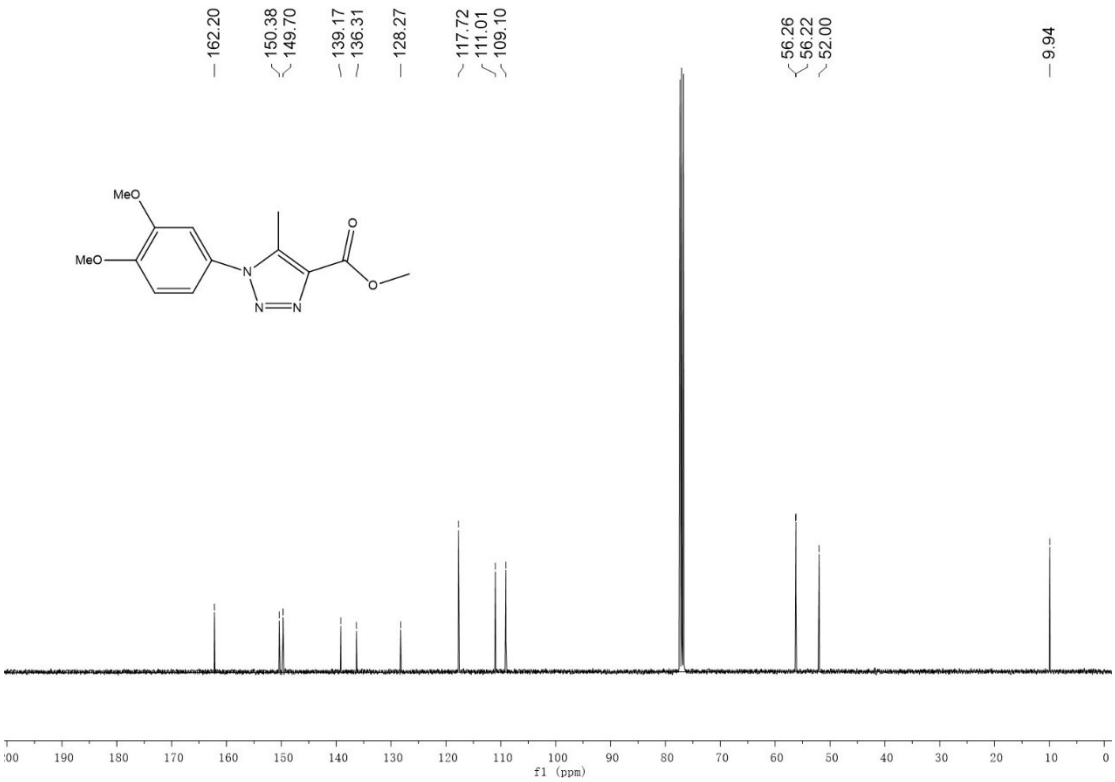
^{13}C NMR Spectra of **4h** ($CDCl_3$, 297.9 K)



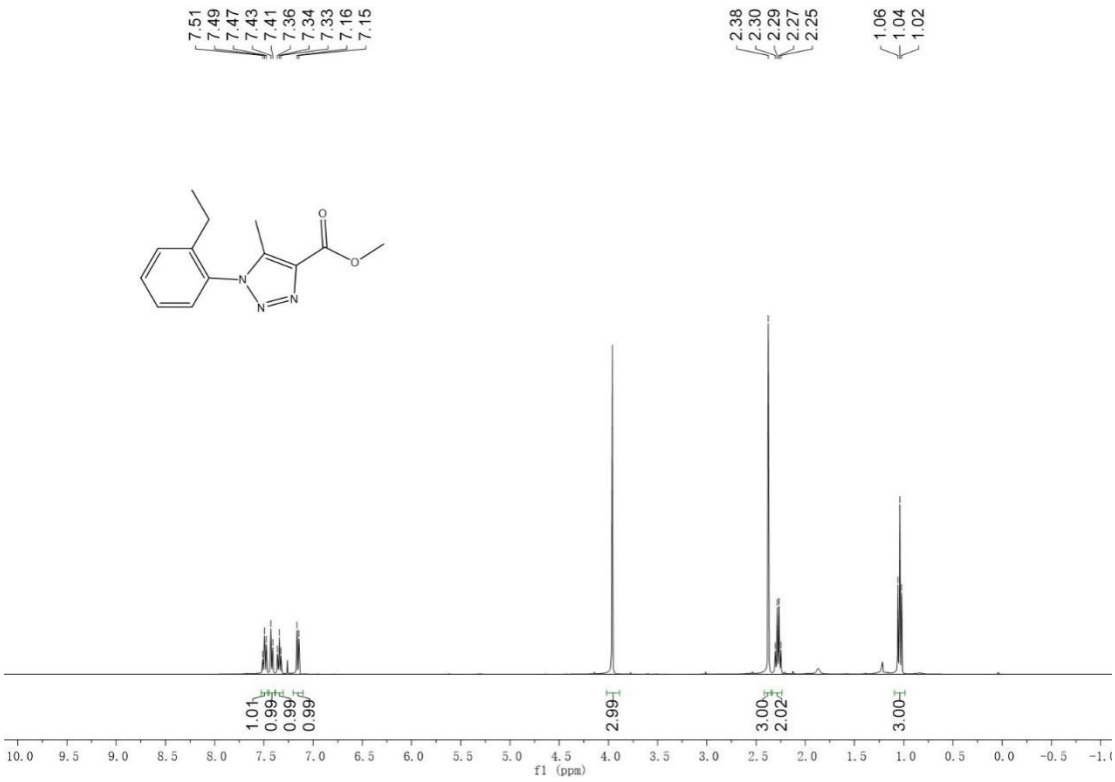
^{1}H NMR Spectra of **4i** ($CDCl_3$, 297.9 K))



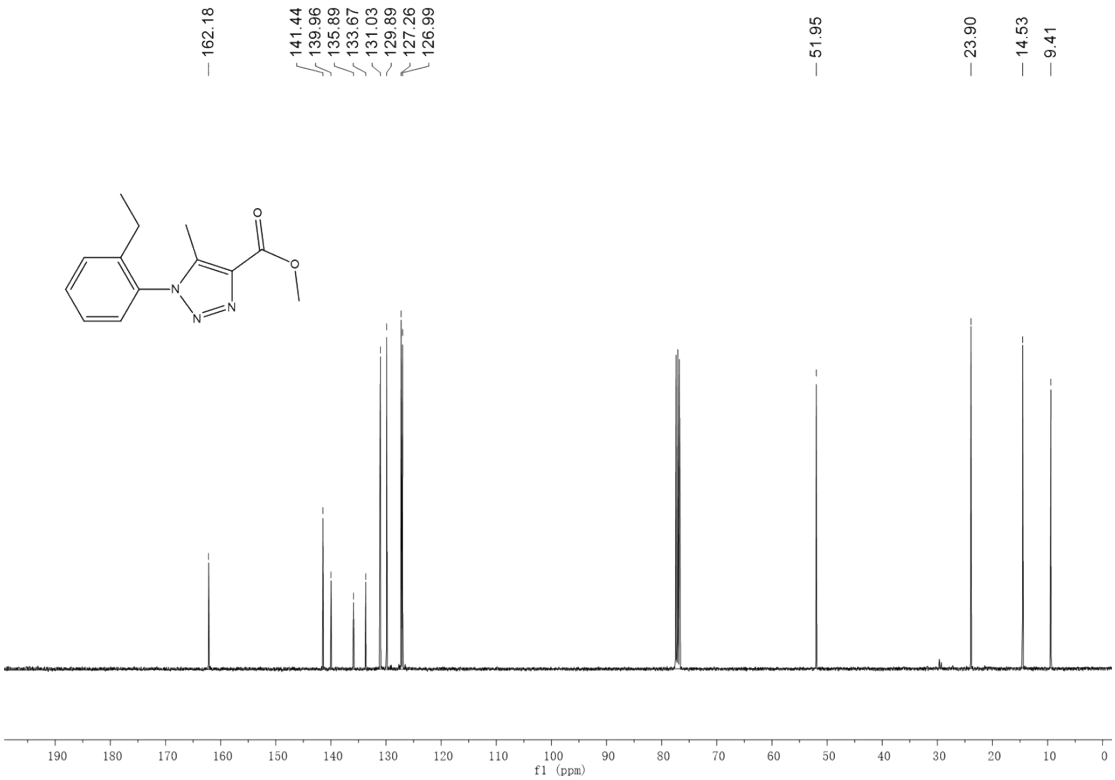
^{13}C NMR Spectra of **4i** ($CDCl_3$, 294.9 K)



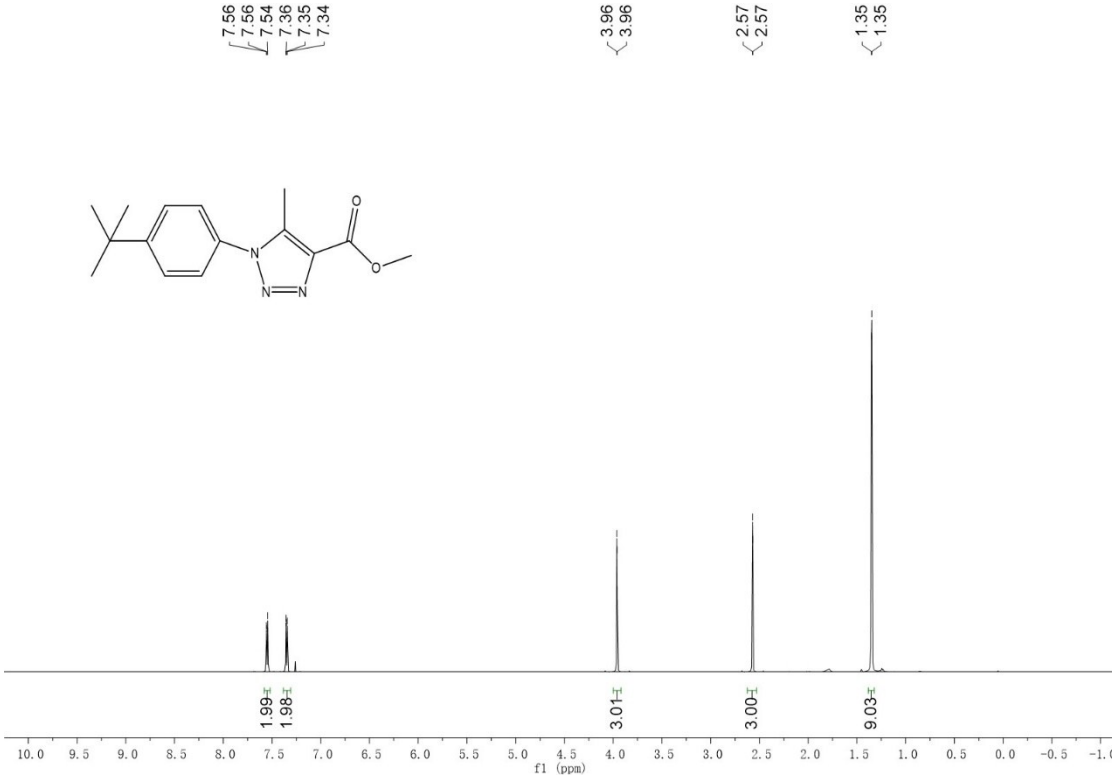
^{1}H NMR Spectra of **4j** ($CDCl_3$, 294.0 K)



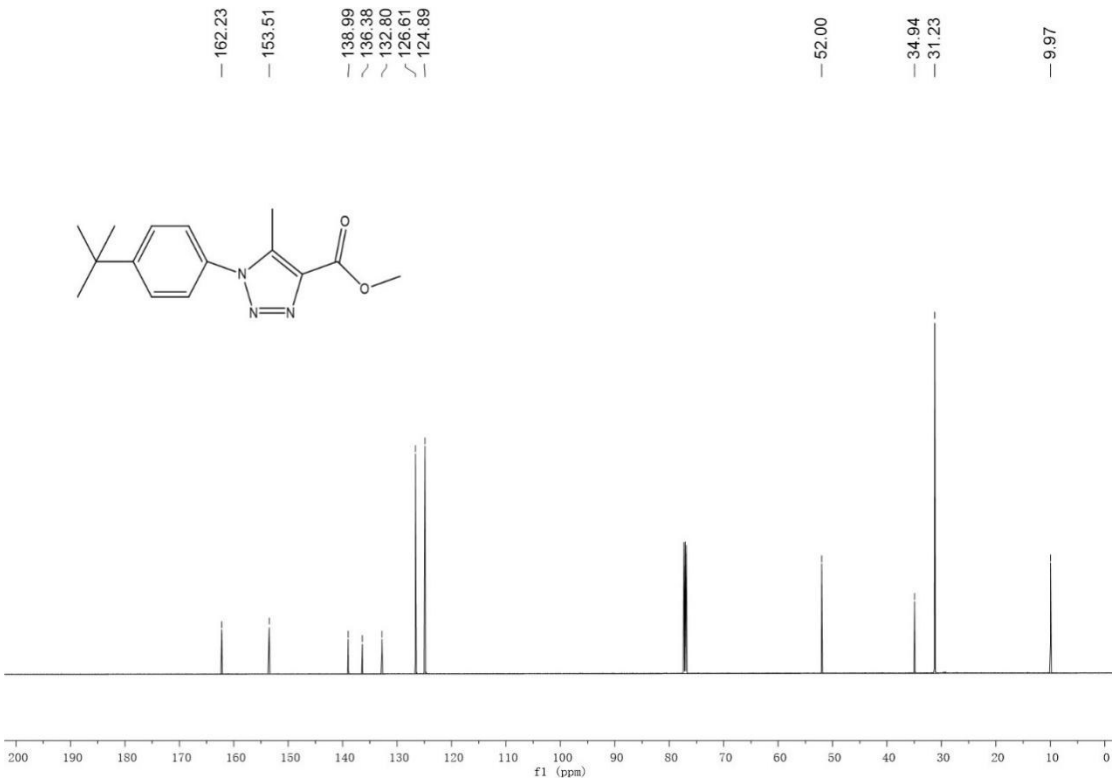
^{13}C NMR Spectra of **4j** ($CDCl_3$, 296.2 K)



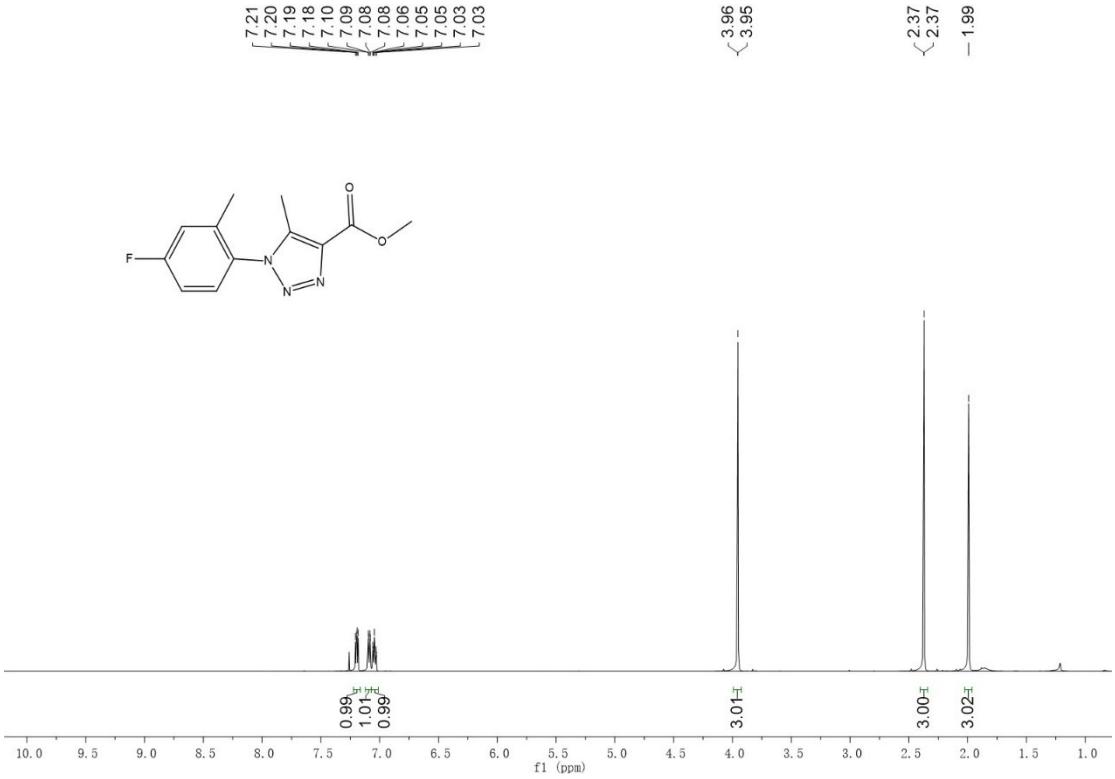
^{1}H NMR Spectra of **4k** ($CDCl_3$, 298.0 K)



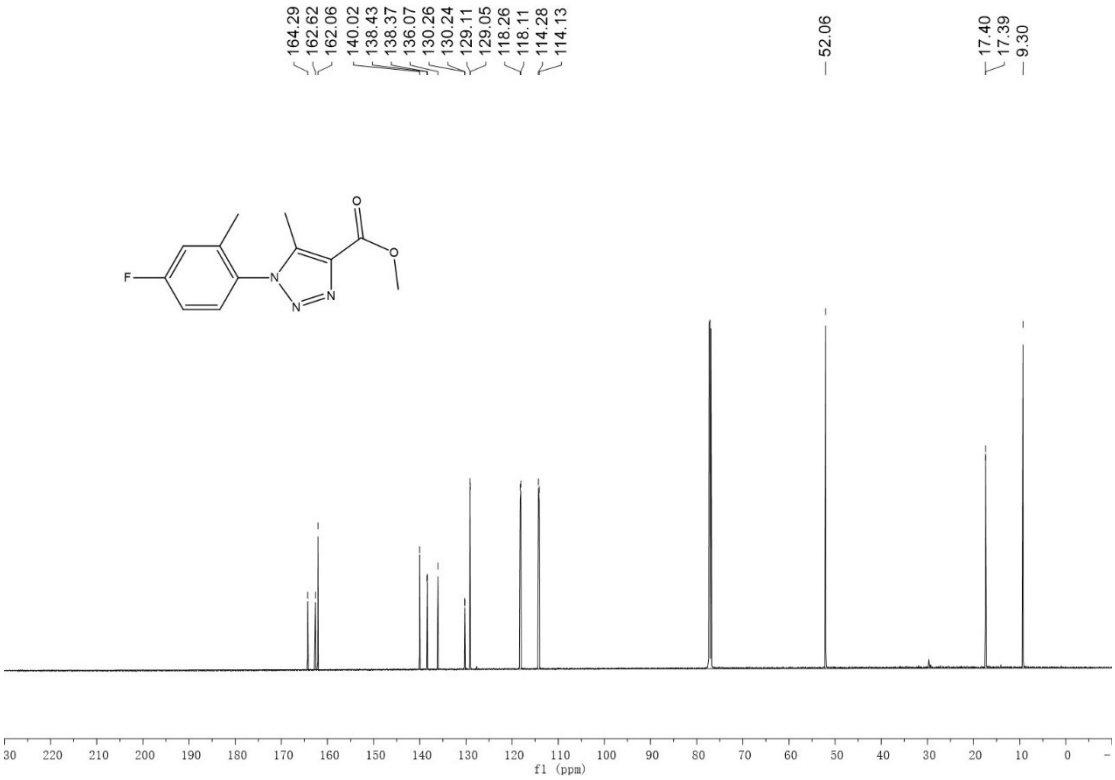
^{13}C NMR Spectra of **4k** ($CDCl_3$, 297.9 K)



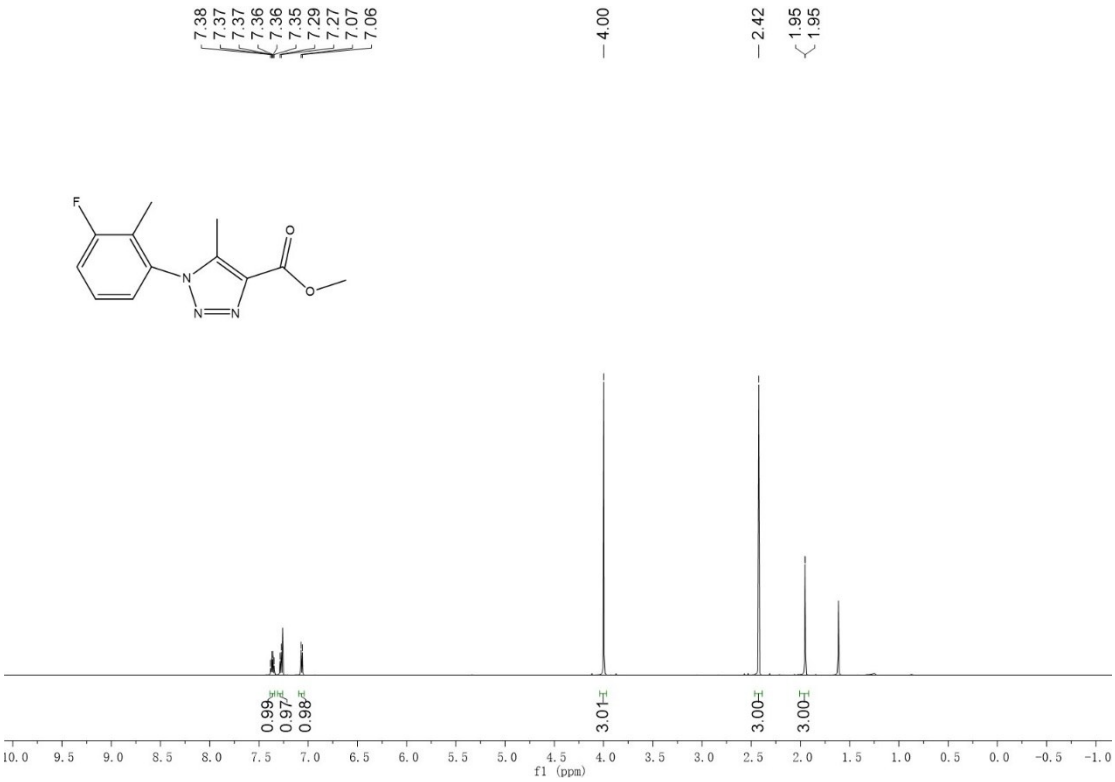
^{1}H NMR Spectra of **4l** ($CDCl_3$, 298.0 K)



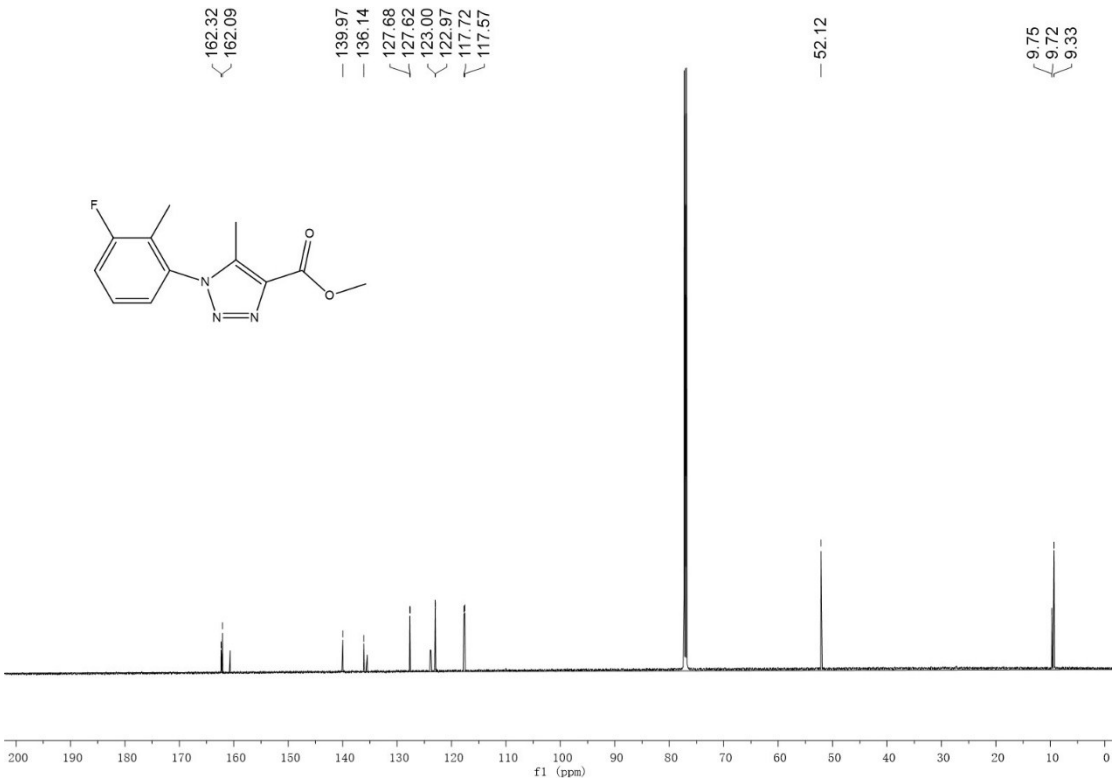
^{13}C NMR Spectra of **4l** ($CDCl_3$, 298.1 K)



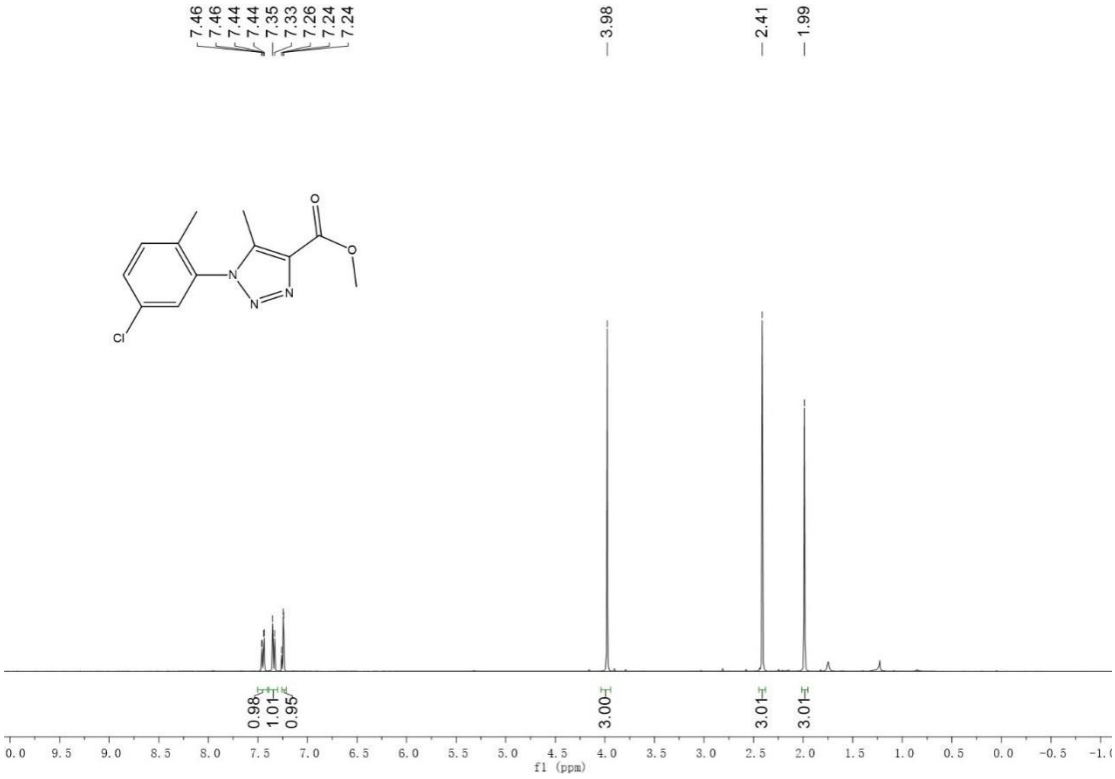
^{1}H NMR Spectra of **4m** ($CDCl_3$, 298.0 K)



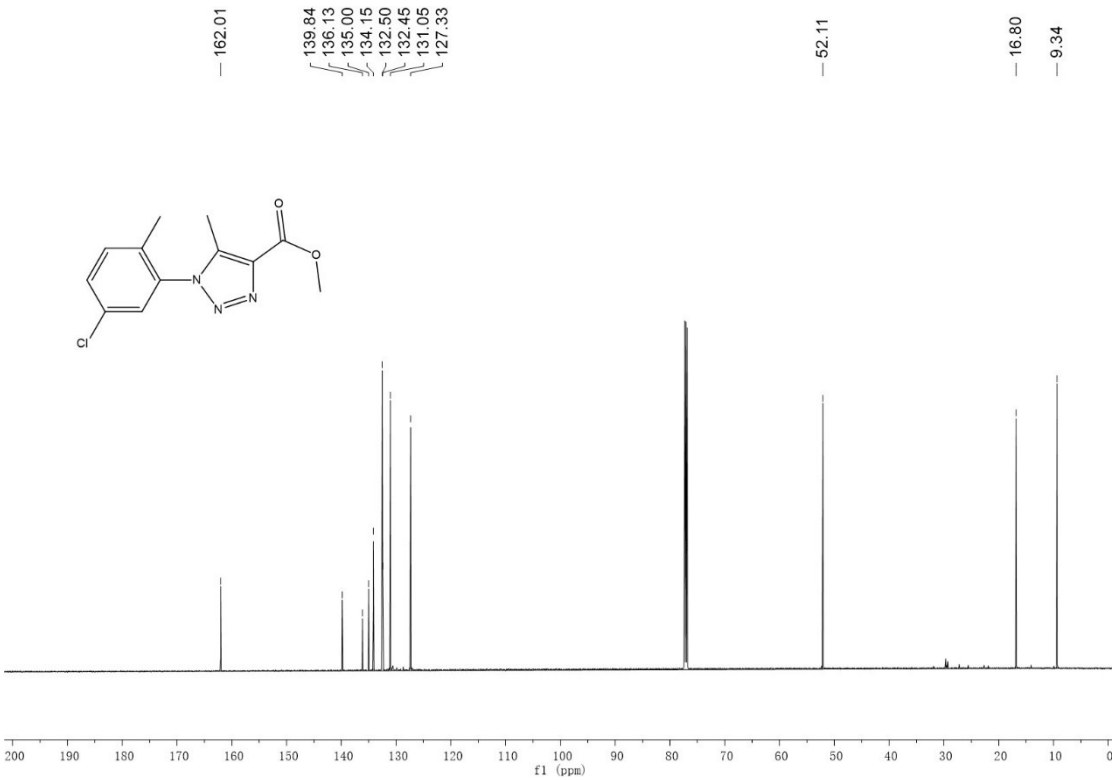
^{13}C NMR Spectra of **4m** ($CDCl_3$, 298.1 K)



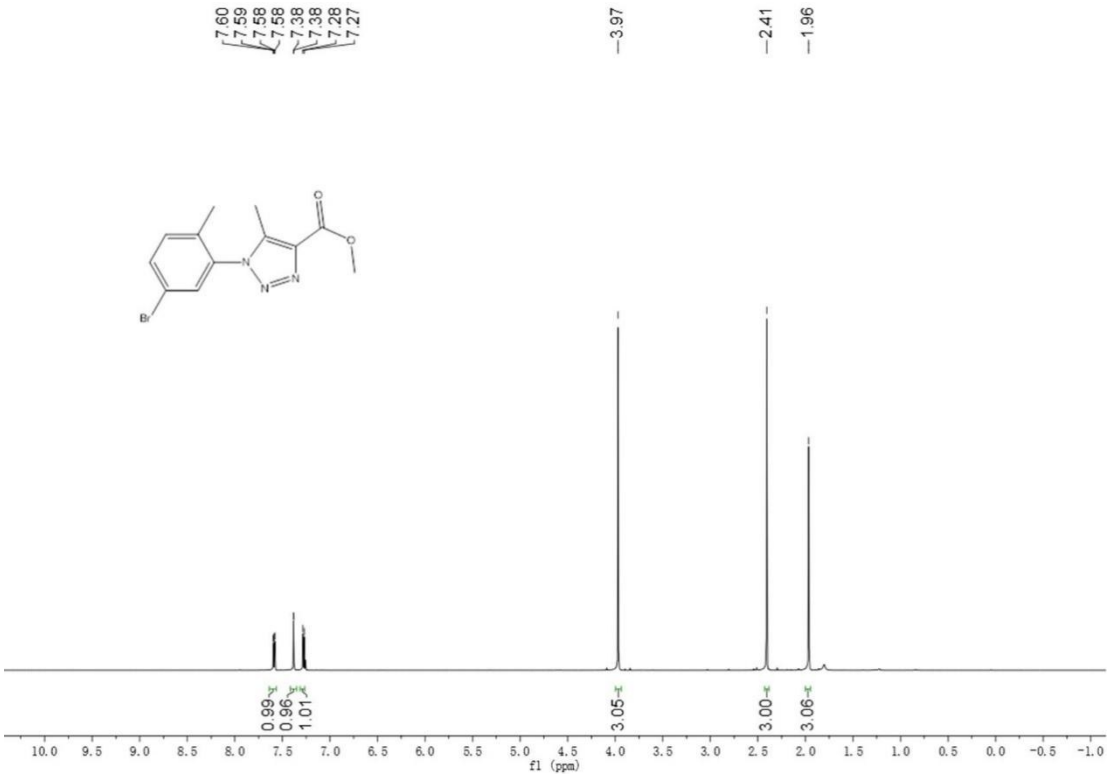
^{1}H NMR Spectra of **4n** ($CDCl_3$, 293.9 K)



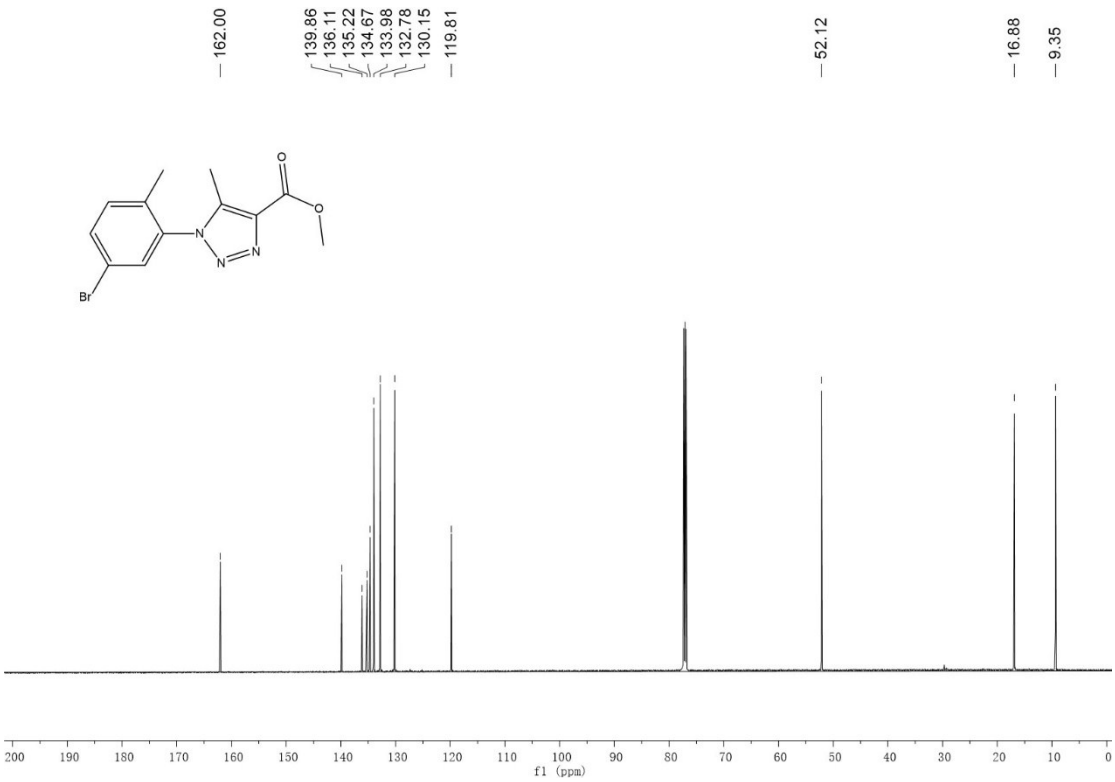
^{13}C NMR Spectra of **4n** ($CDCl_3$, 298.1 K)



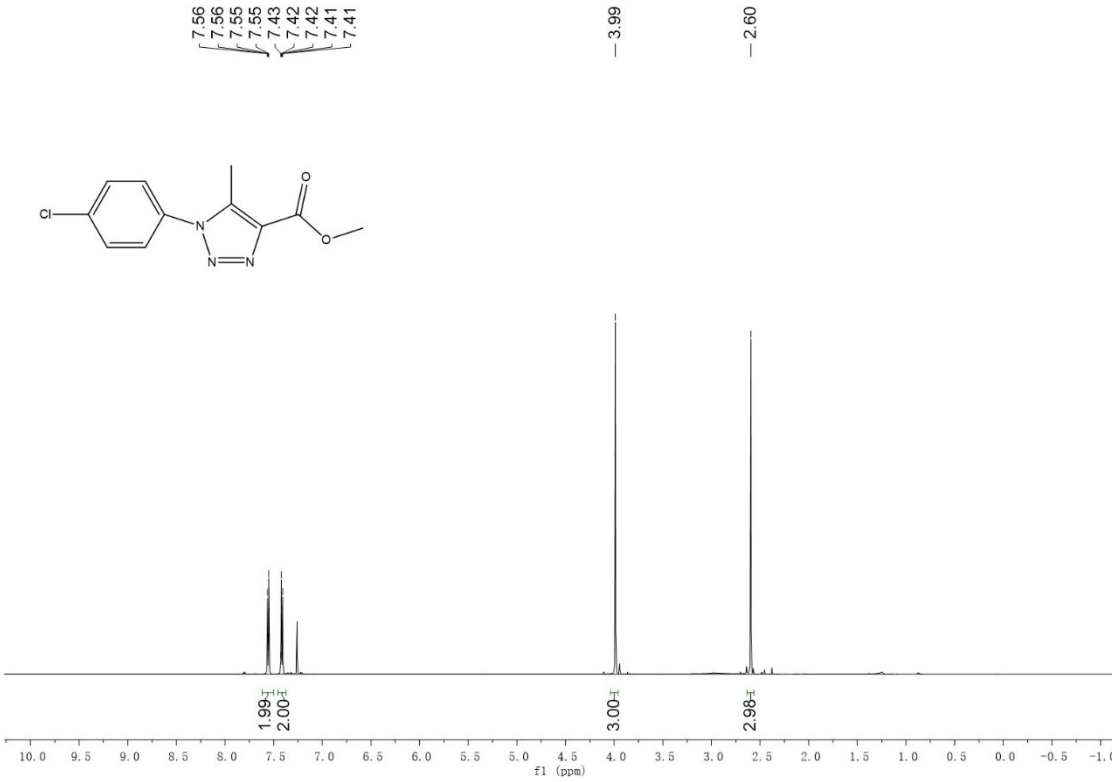
^{1}H NMR Spectra of **4o** ($CDCl_3$, 298.0 K)



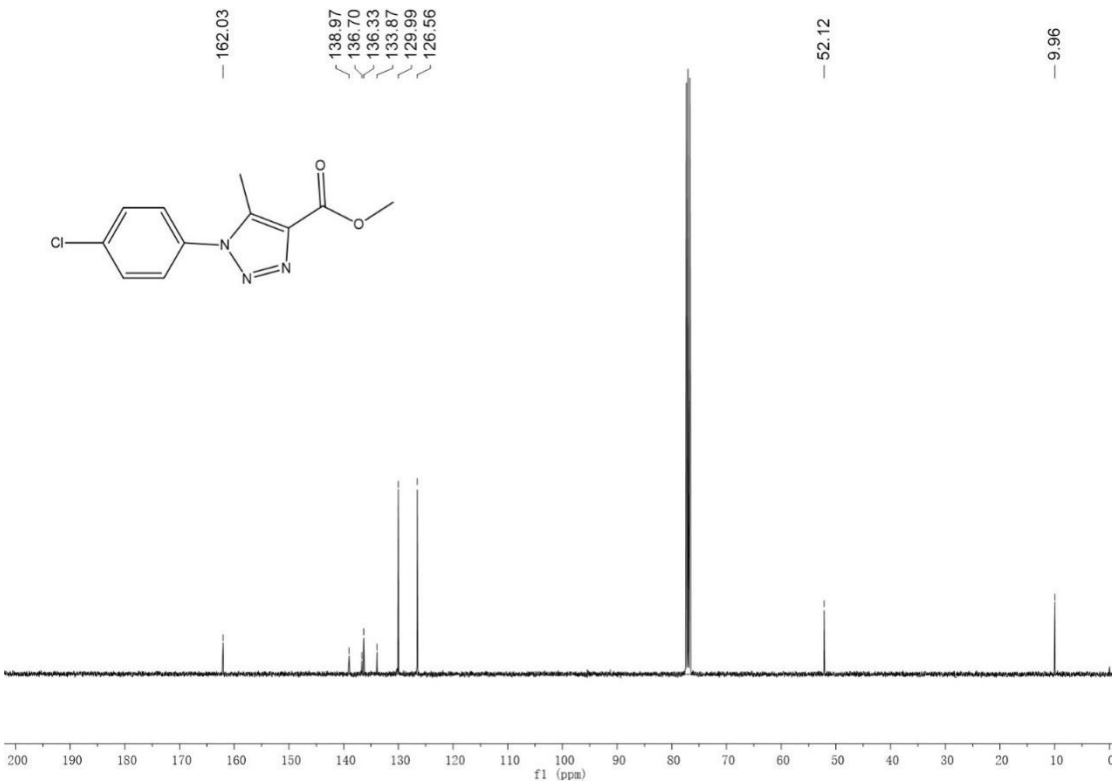
^{13}C NMR Spectra of **4o** ($CDCl_3$, 297.9 K)



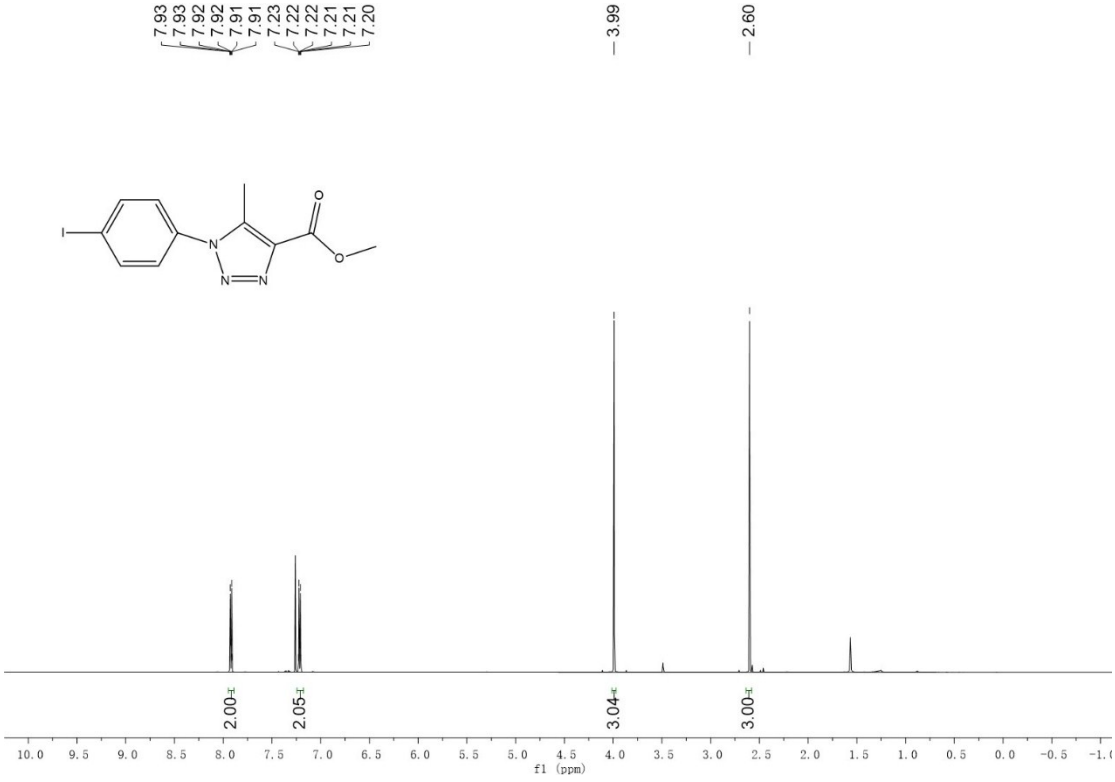
^{1}H NMR Spectra of **4p** ($CDCl_3$, 298.0 K)



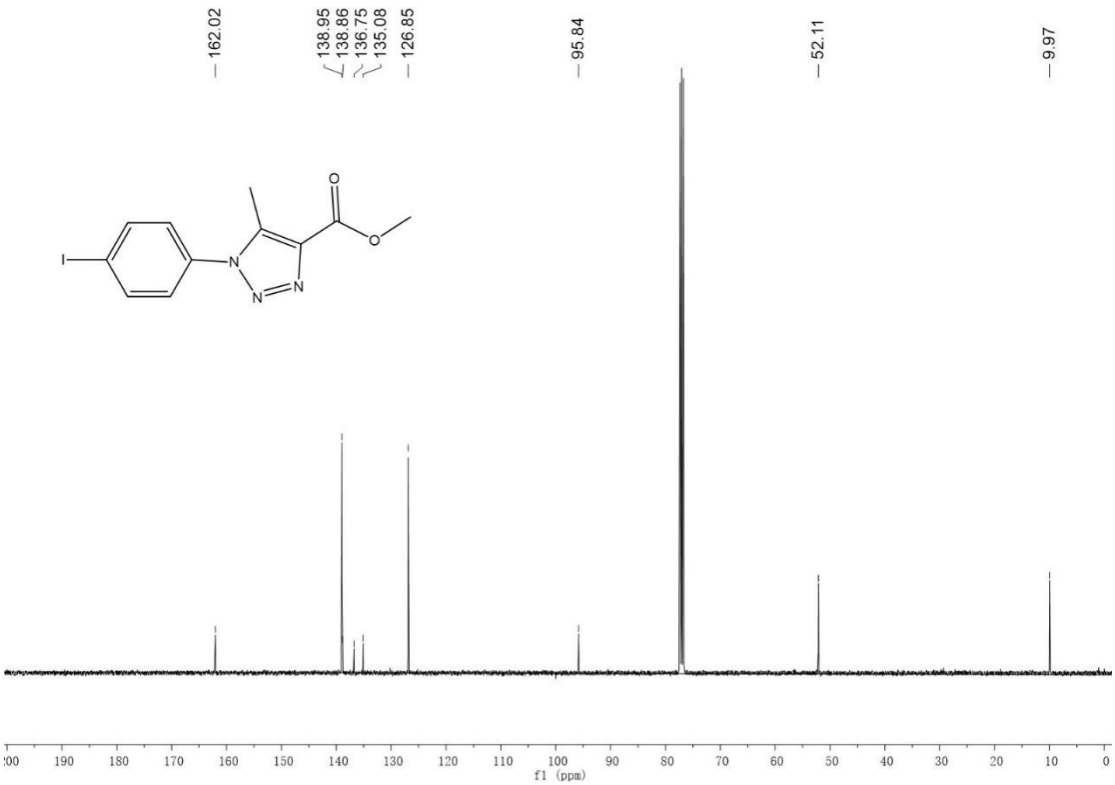
^{13}C NMR Spectra of **4p** ($CDCl_3$, 294.1 K)



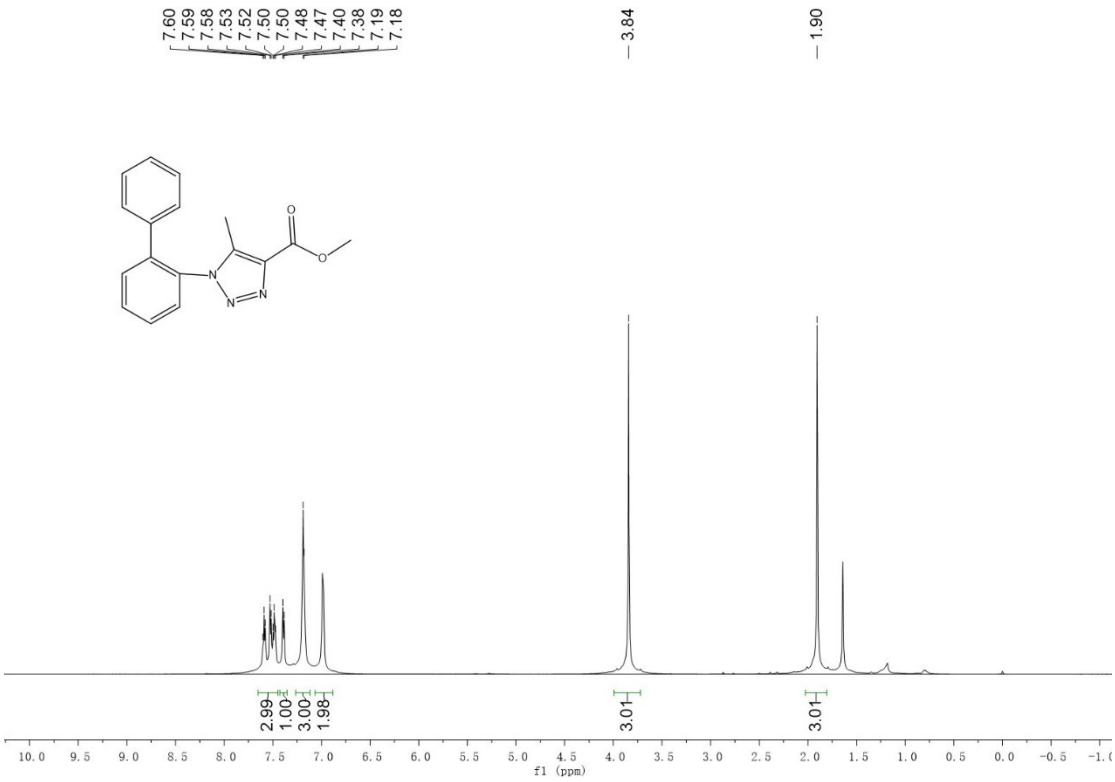
^{1}H NMR Spectra of **4q** ($CDCl_3$, 298.0 K)



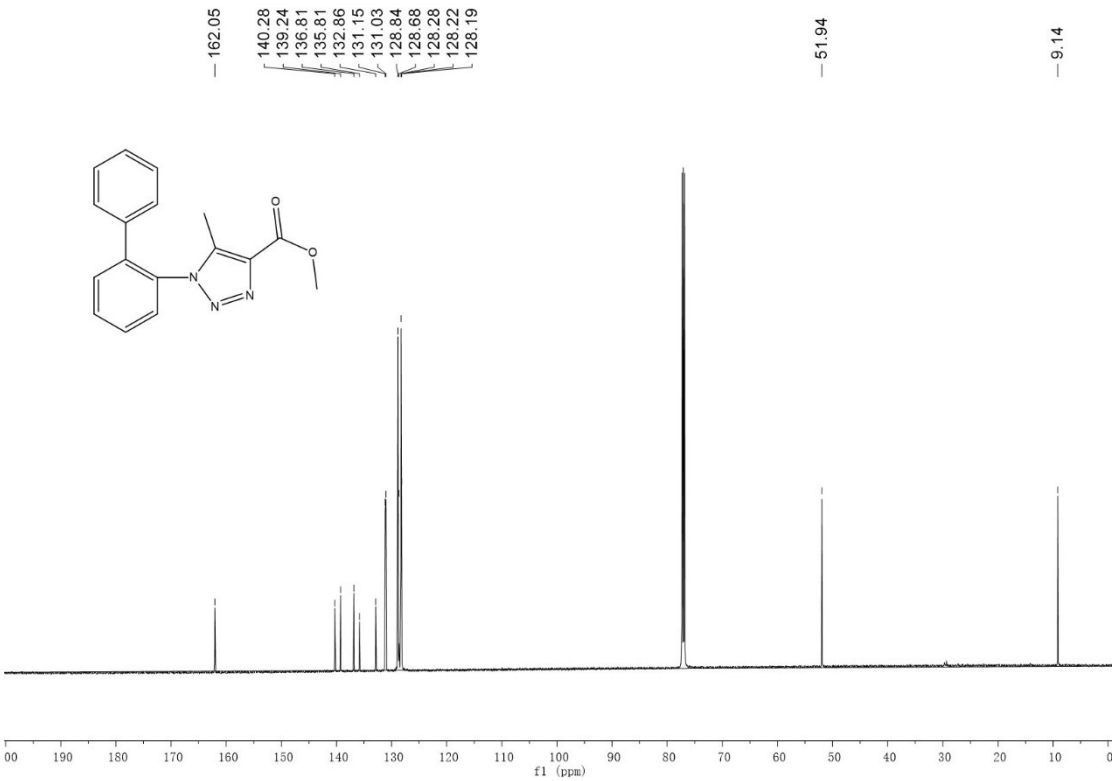
^{13}C NMR Spectra of **4q** ($CDCl_3$, 294.3 K)



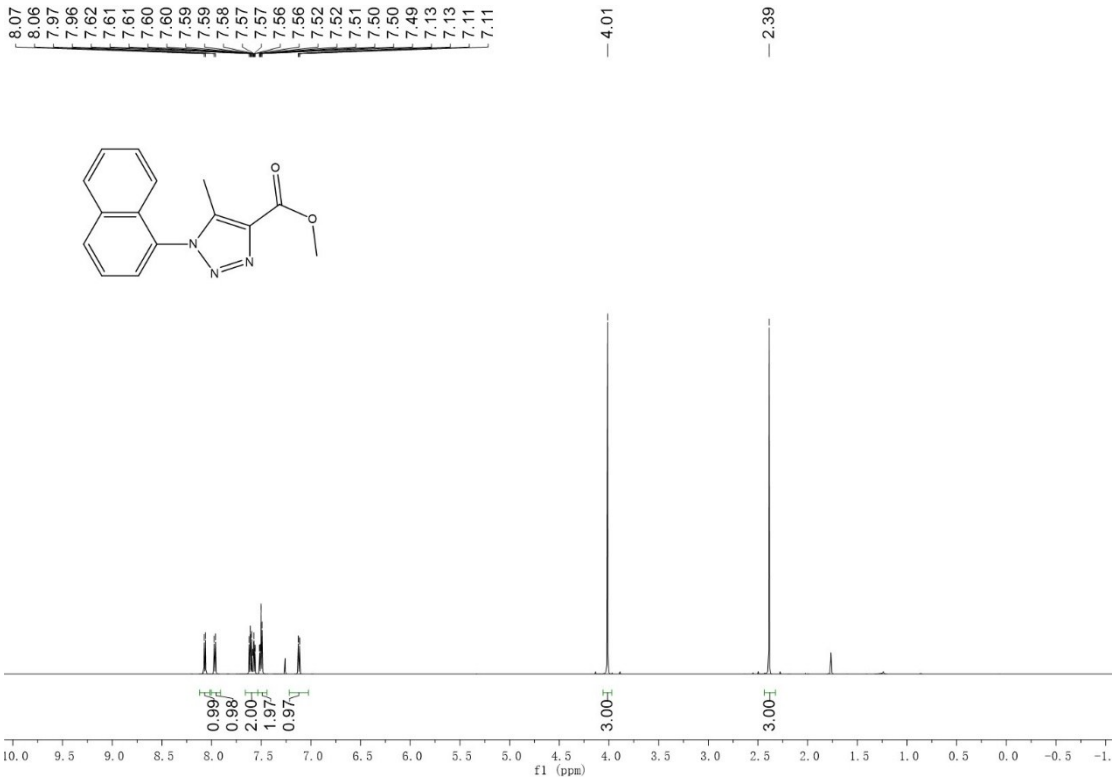
^{1}H NMR Spectra of **4r** ($CDCl_3$, 297.9 K)



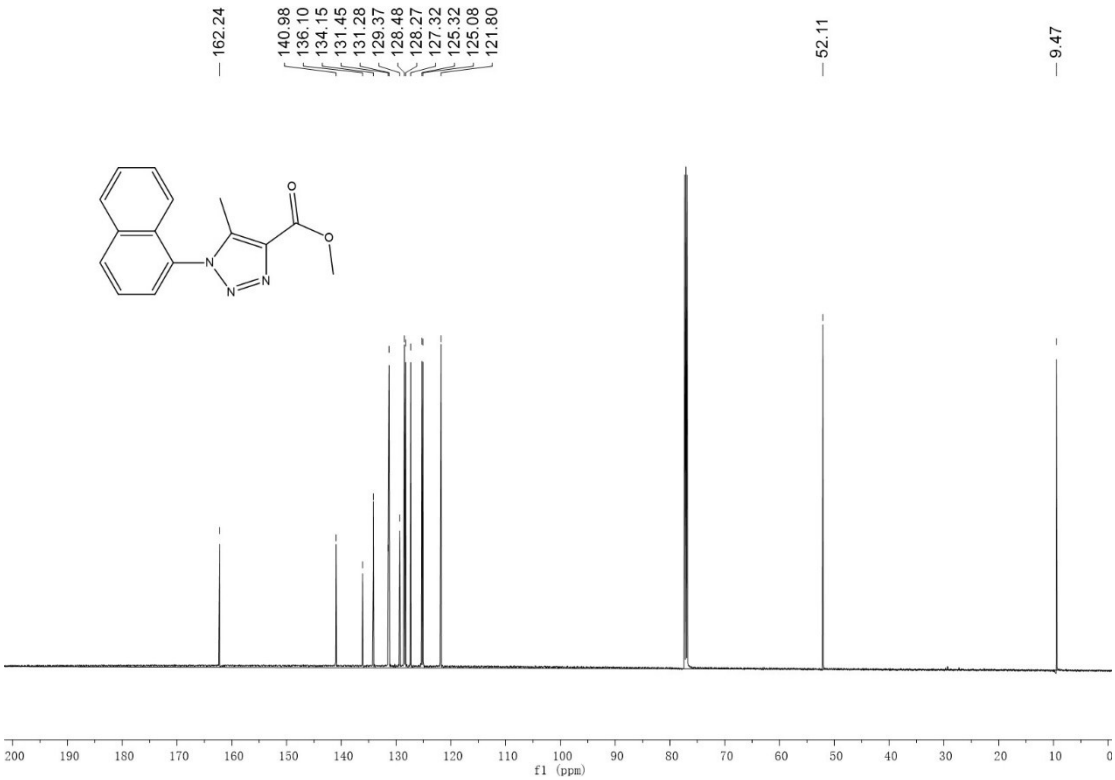
^{13}C NMR Spectra of **4r** ($CDCl_3$, 297.9 K)



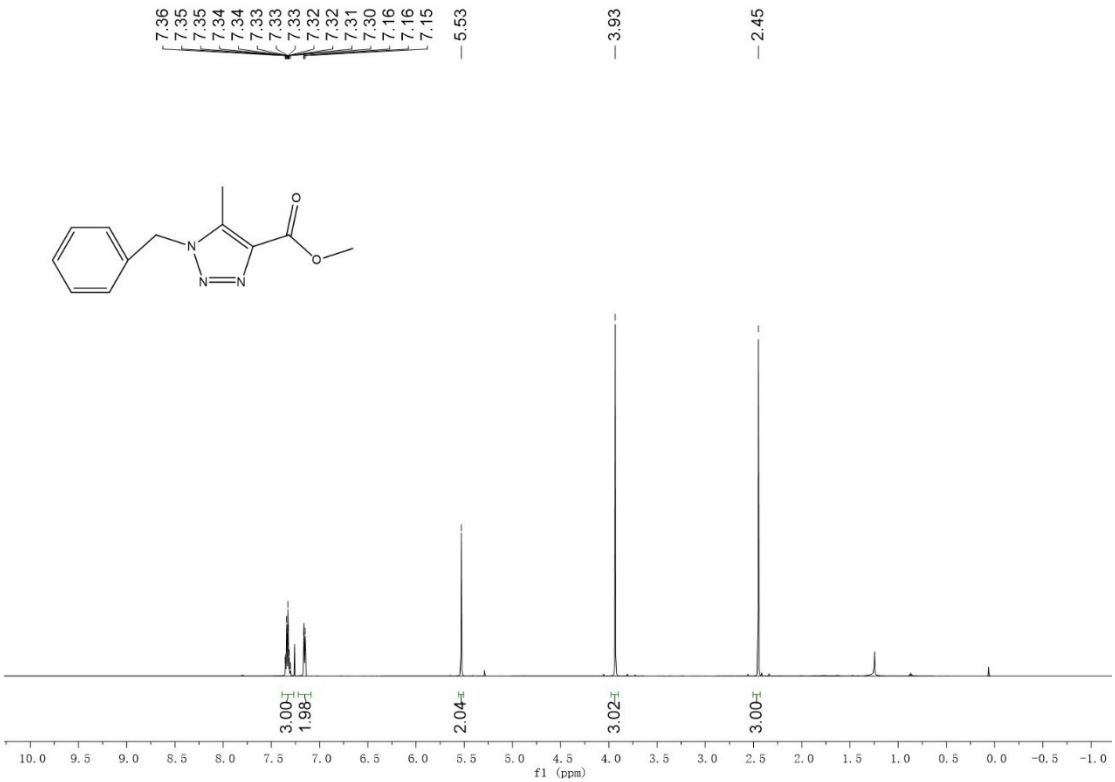
^{1}H NMR Spectra of **4s** ($CDCl_3$, 297.9 K)



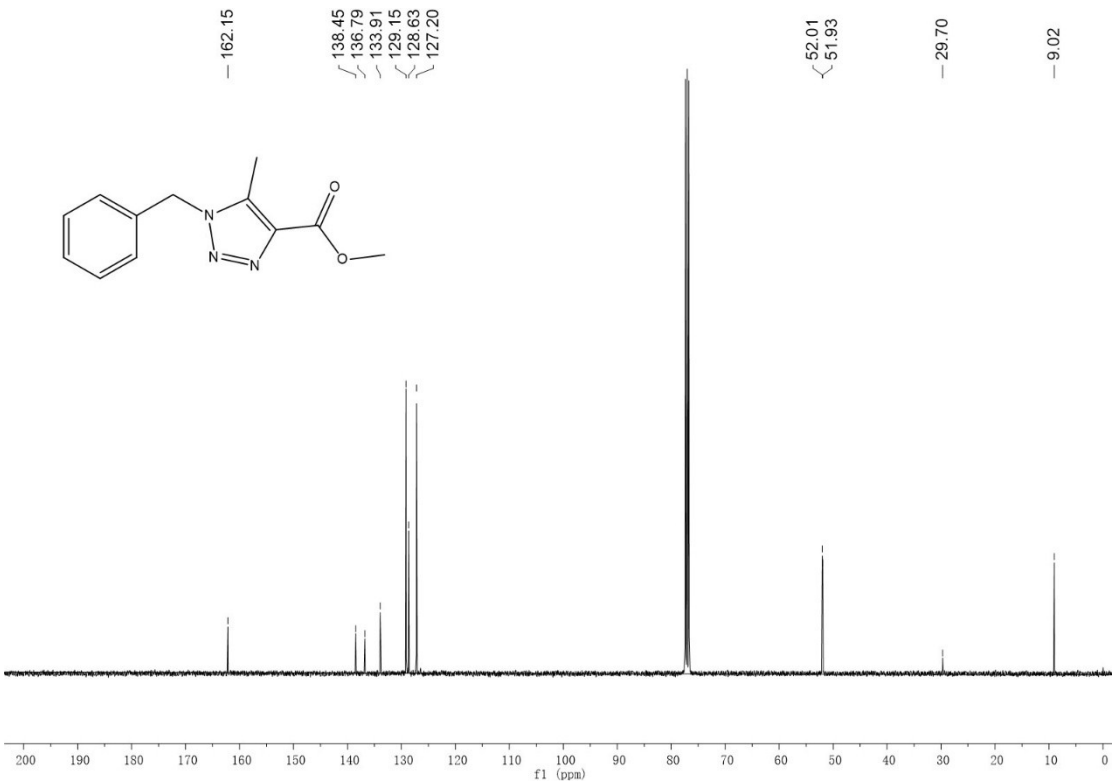
^{13}C NMR Spectra of **4s** ($CDCl_3$, 298.0 K)



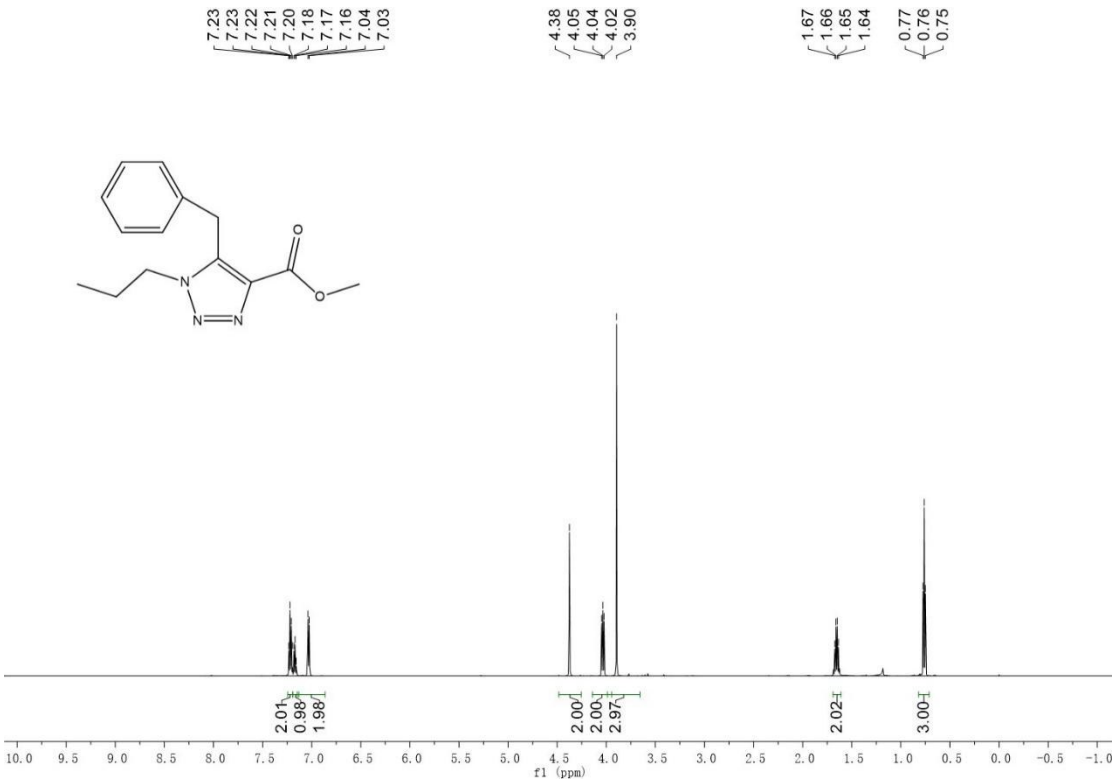
^{1}H NMR Spectra of **4t** ($CDCl_3$, 297.9 K)



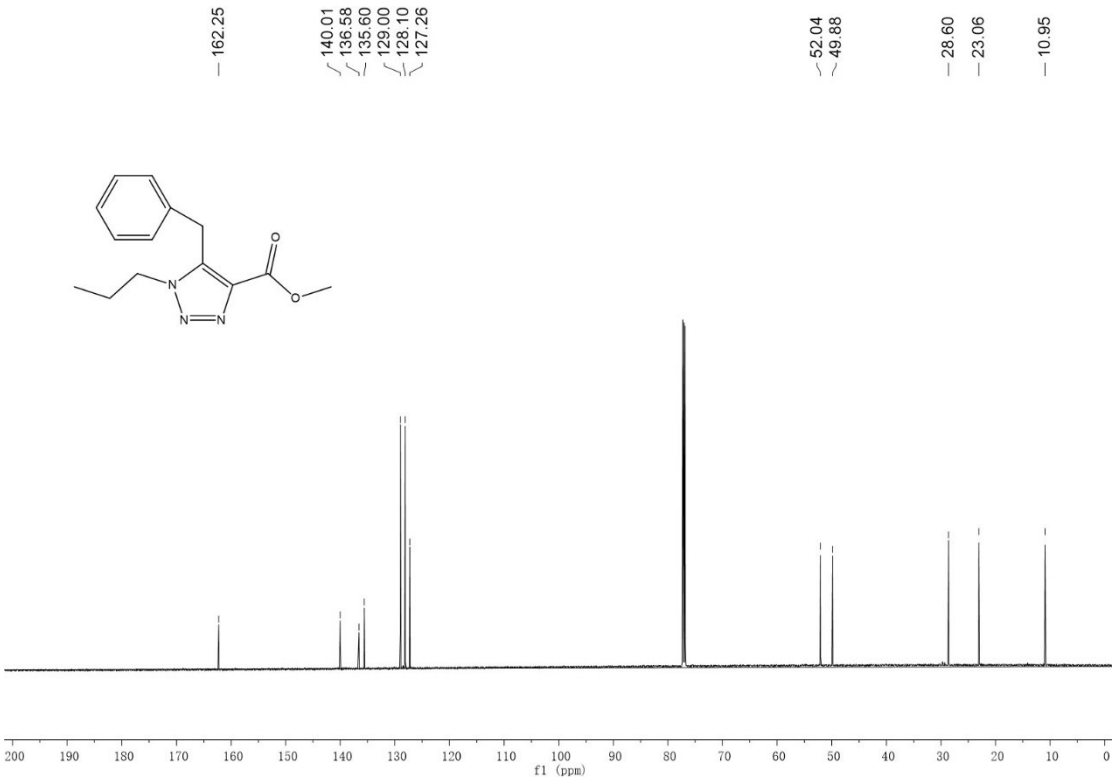
^{13}C NMR Spectra of **4t** ($CDCl_3$, 294.1 K)



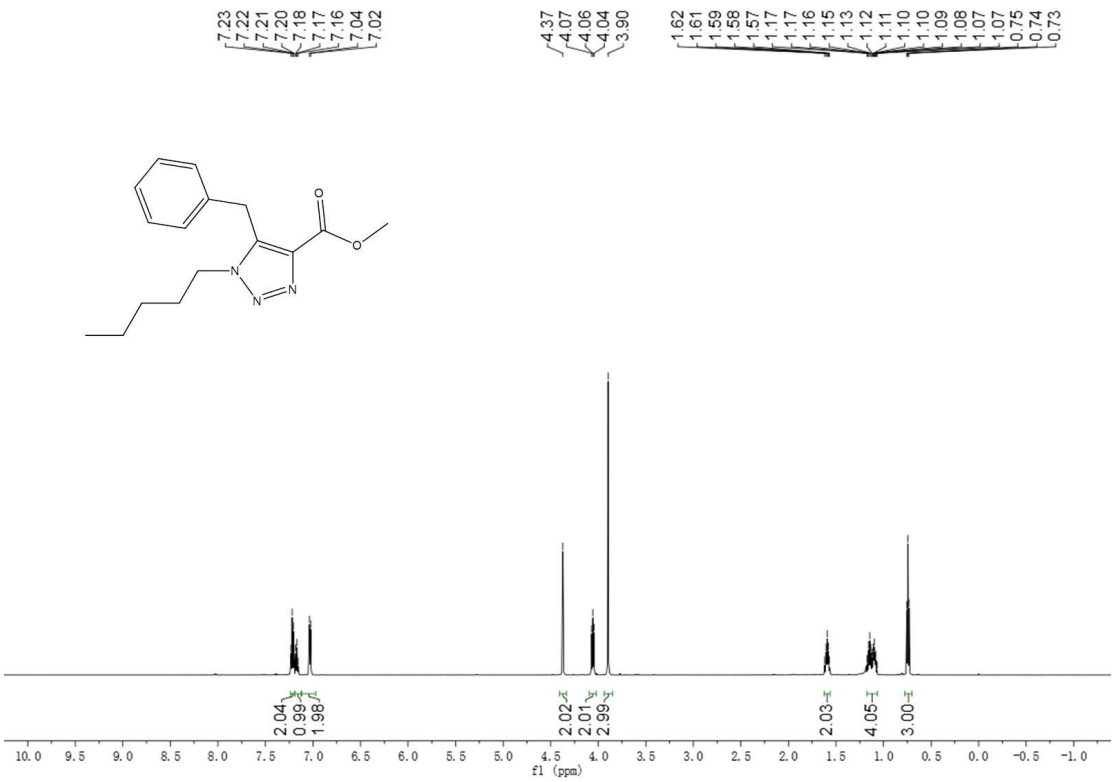
^{1}H NMR Spectra of **4u** ($CDCl_3$, 298.1 K)



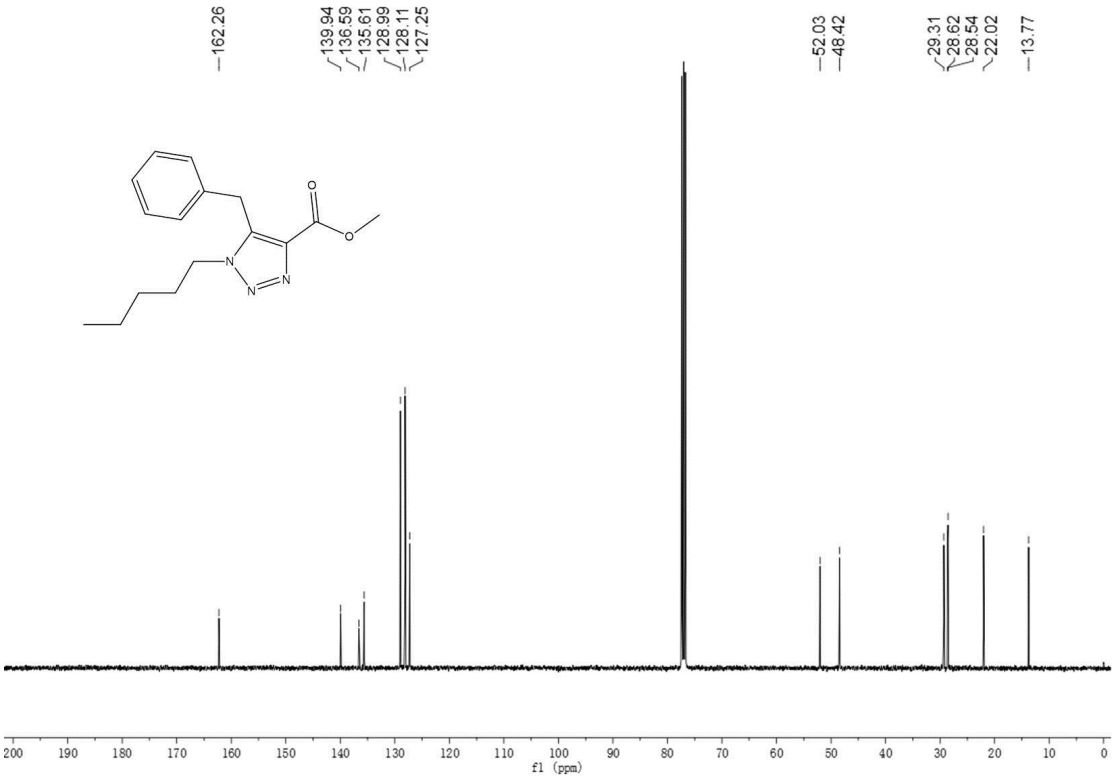
^{13}C NMR Spectra of **4u** ($CDCl_3$, 297.9 K)



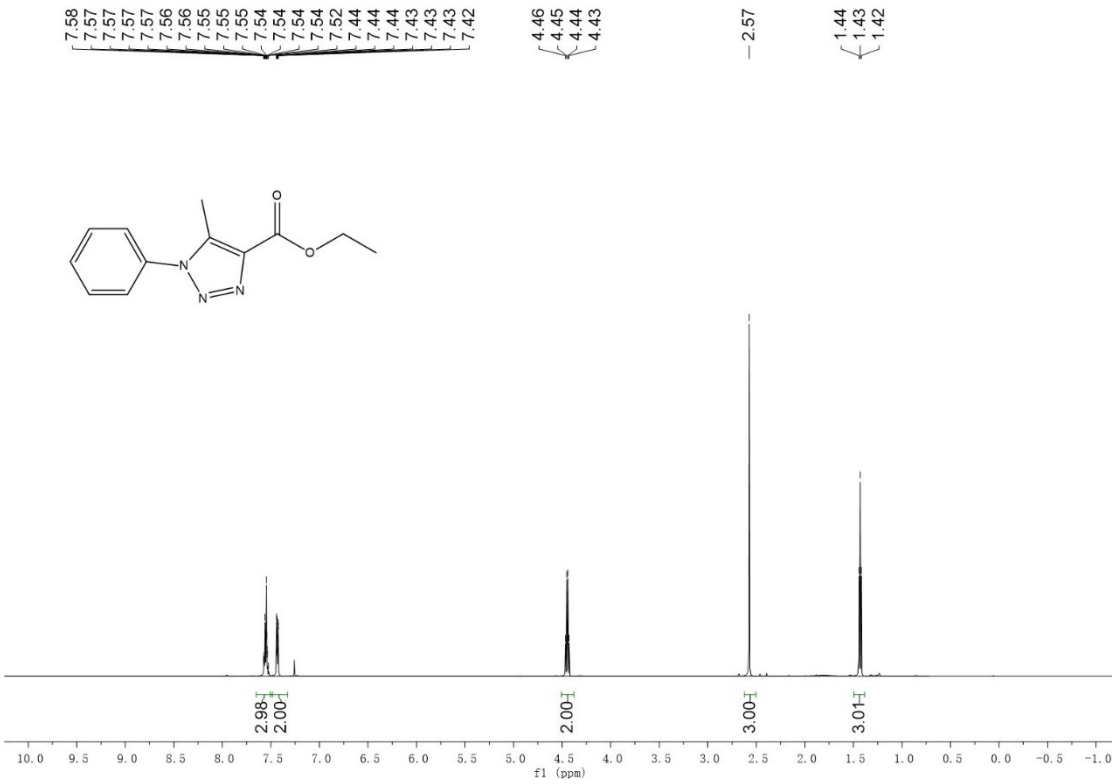
^{1}H NMR Spectra of **4v** ($CDCl_3$, 298.0 K)



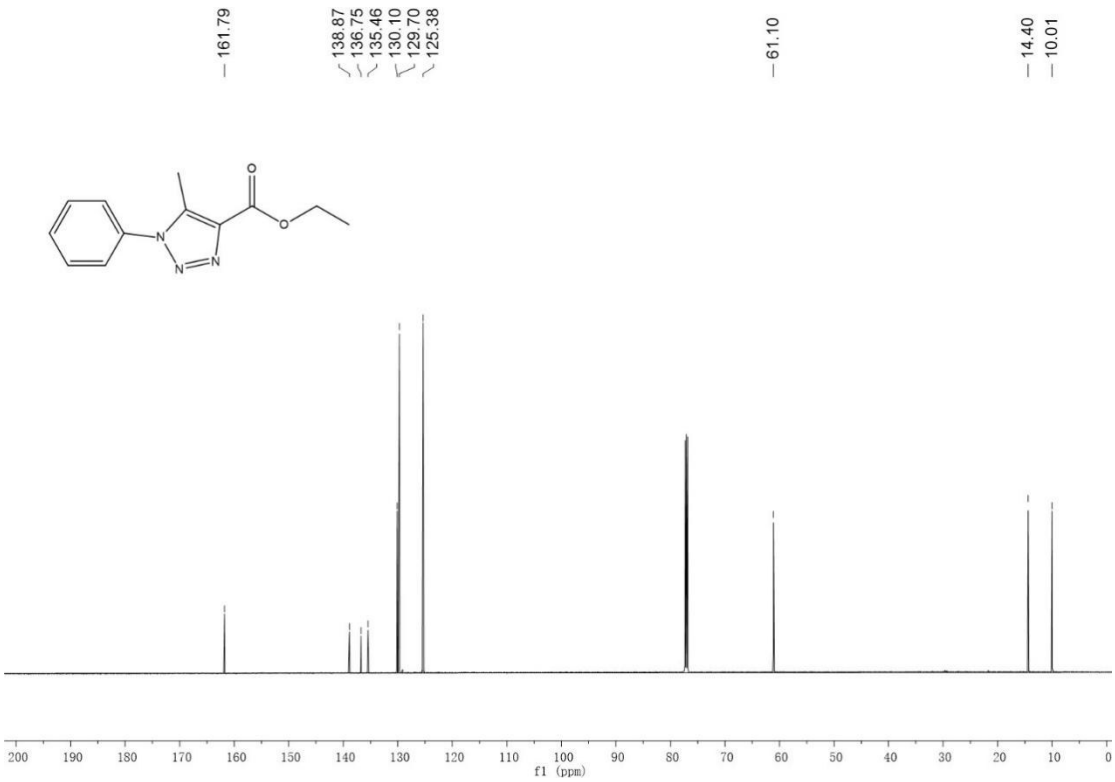
^{13}C NMR Spectra of **4v** ($CDCl_3$, 294.1 K)



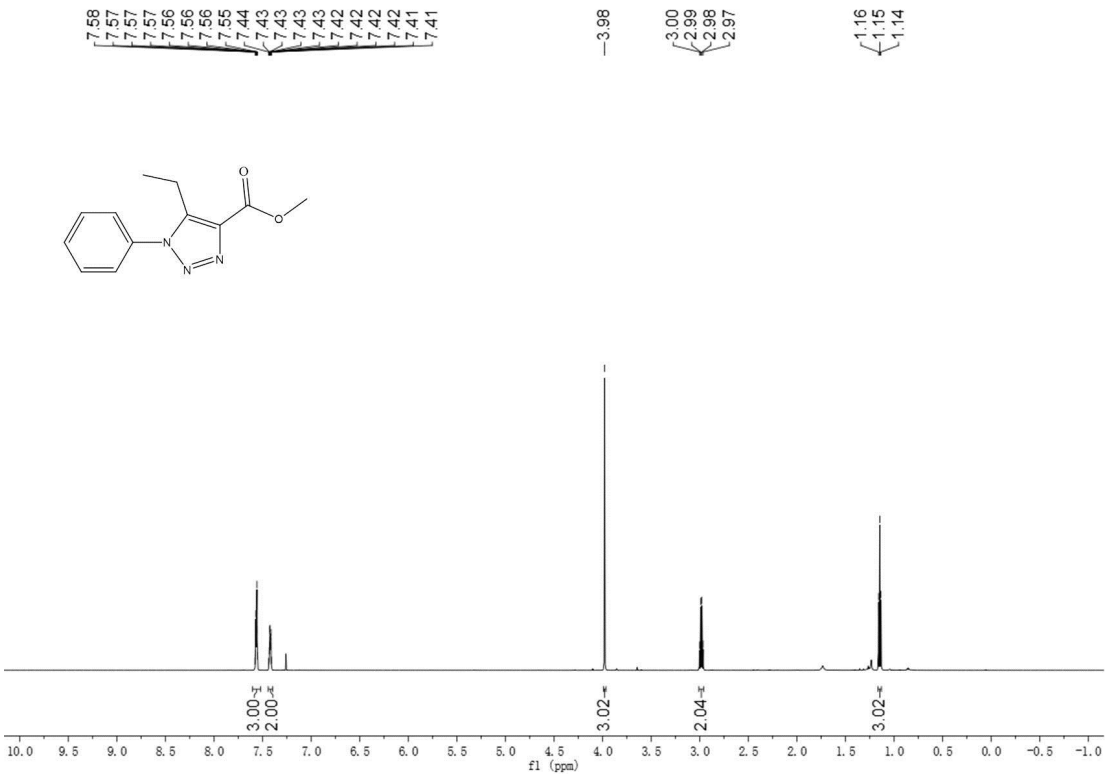
^{1}H NMR Spectra of **5a** ($CDCl_3$, 297.9 K)



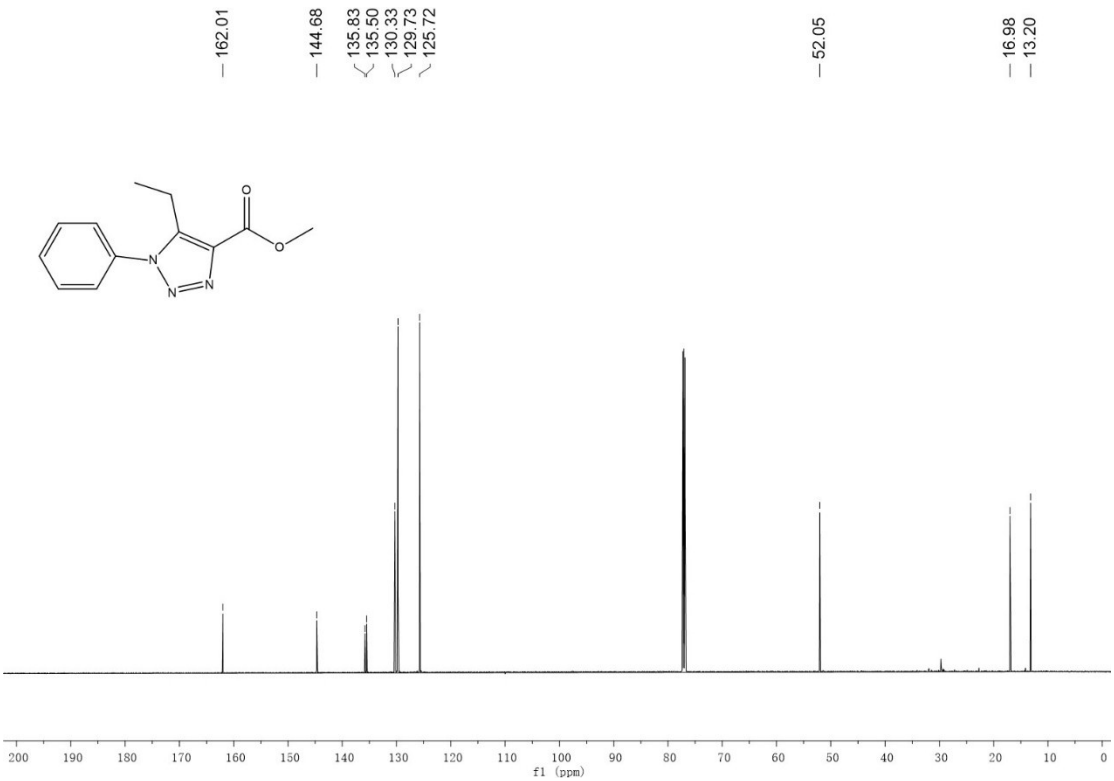
^{13}C NMR Spectra of **5a** ($CDCl_3$, 298.0 K)



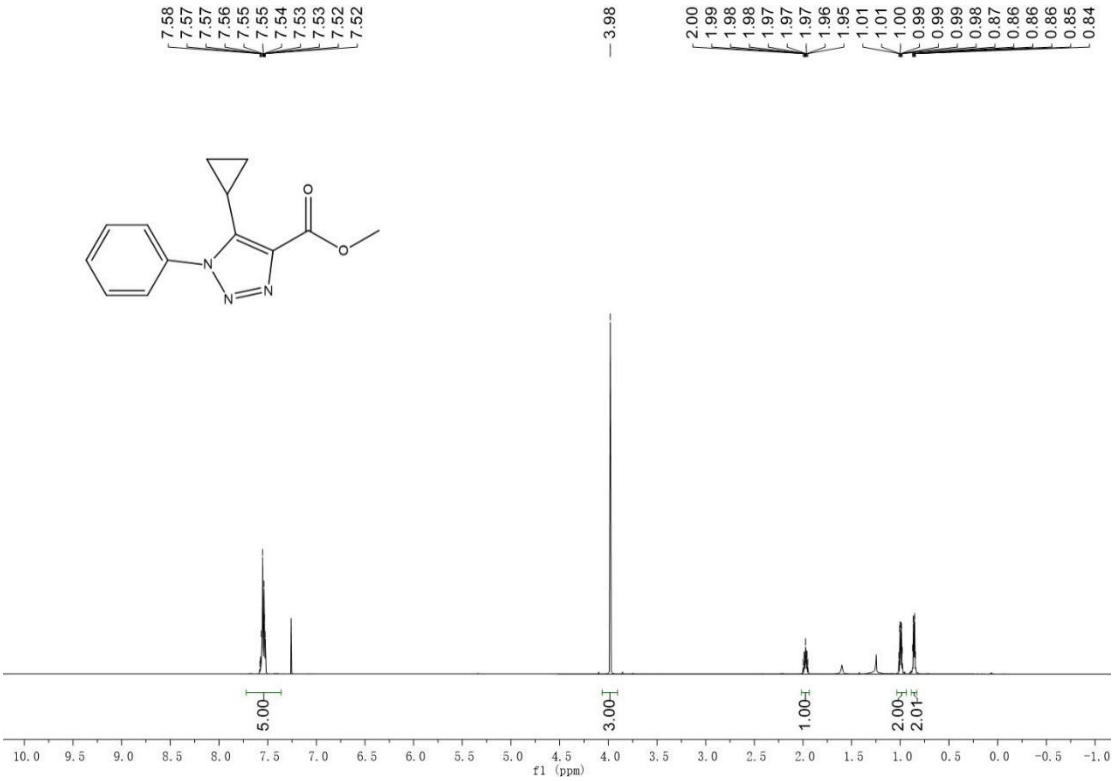
^{1}H NMR Spectra of **5b** ($CDCl_3$, 297.9 K)



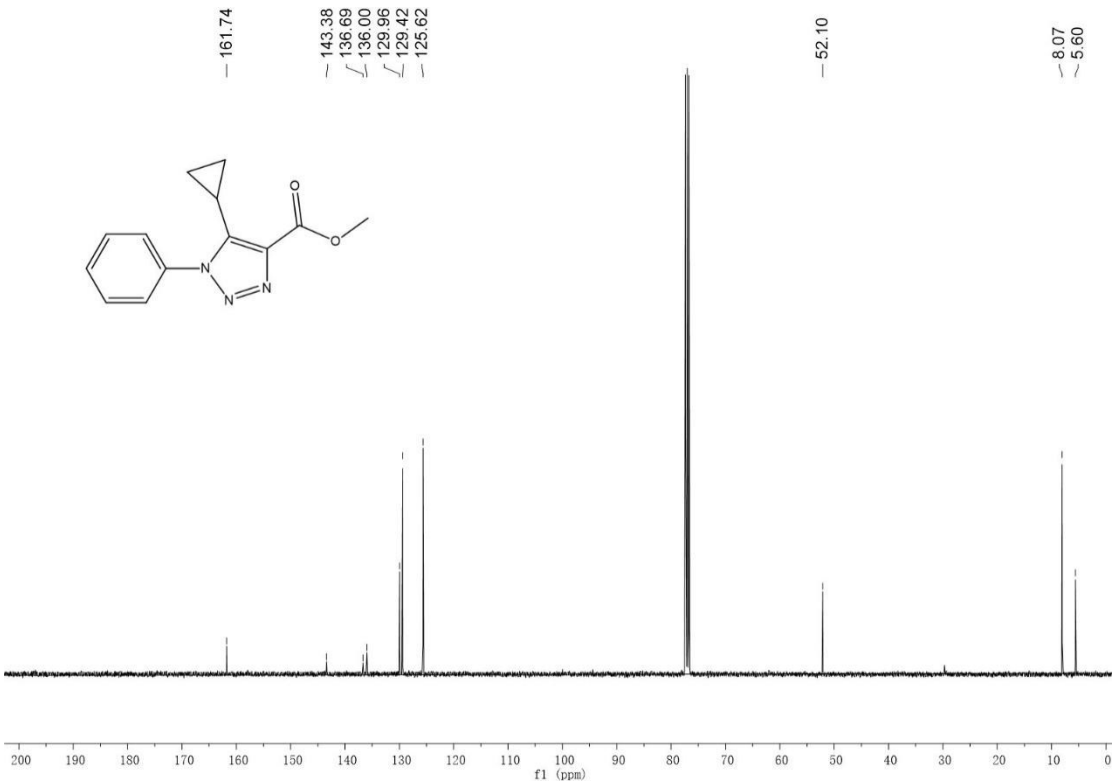
^{13}C NMR Spectra of **5b** ($CDCl_3$, 297.9 K)



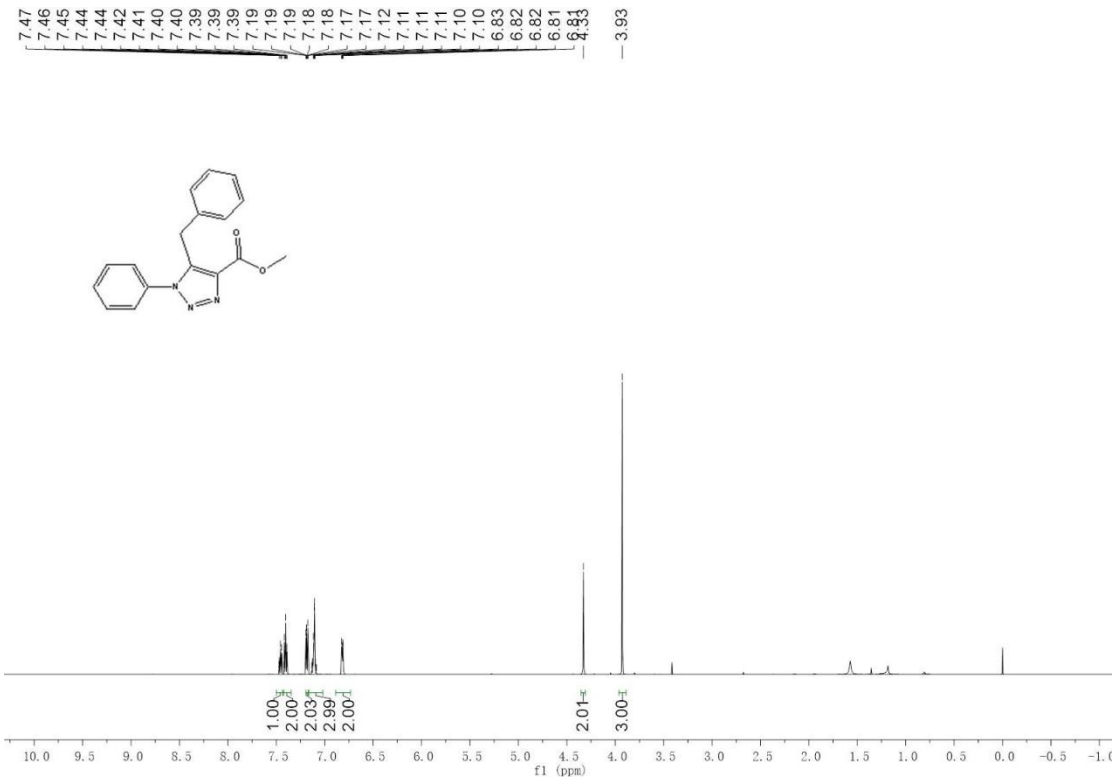
^{1}H NMR Spectra of **5c** ($CDCl_3$, 298.0 K)



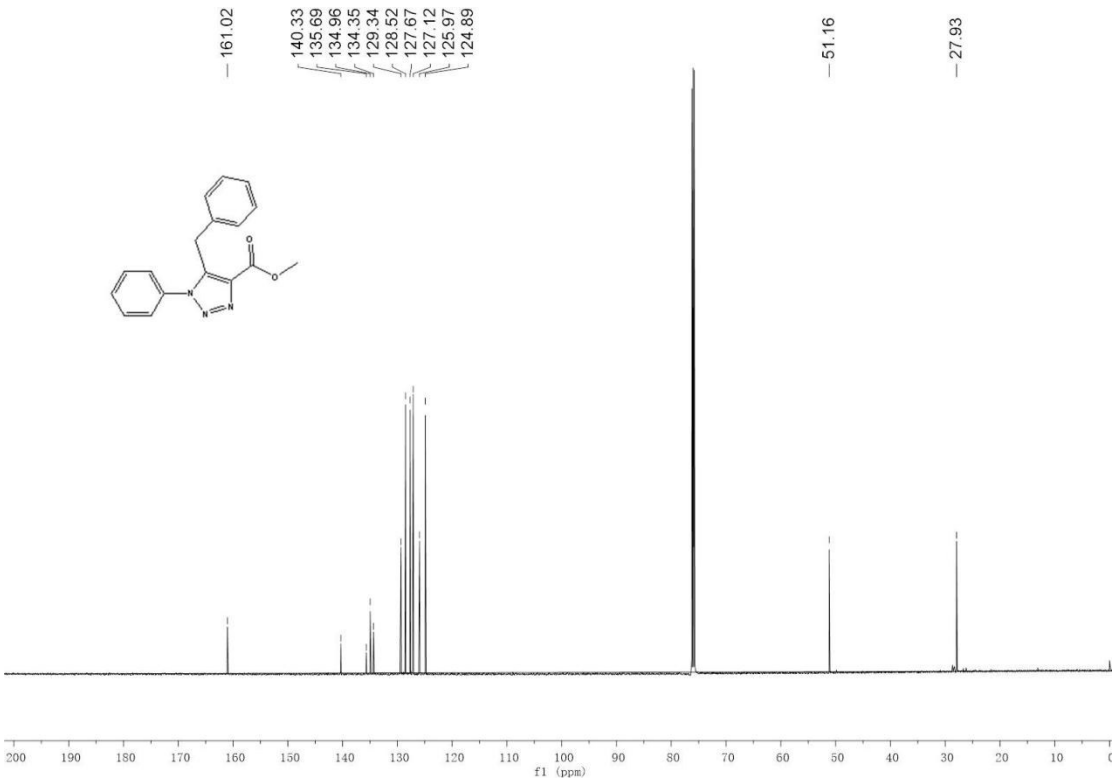
^{13}C NMR Spectra of **5c** ($CDCl_3$, 294.0 K)



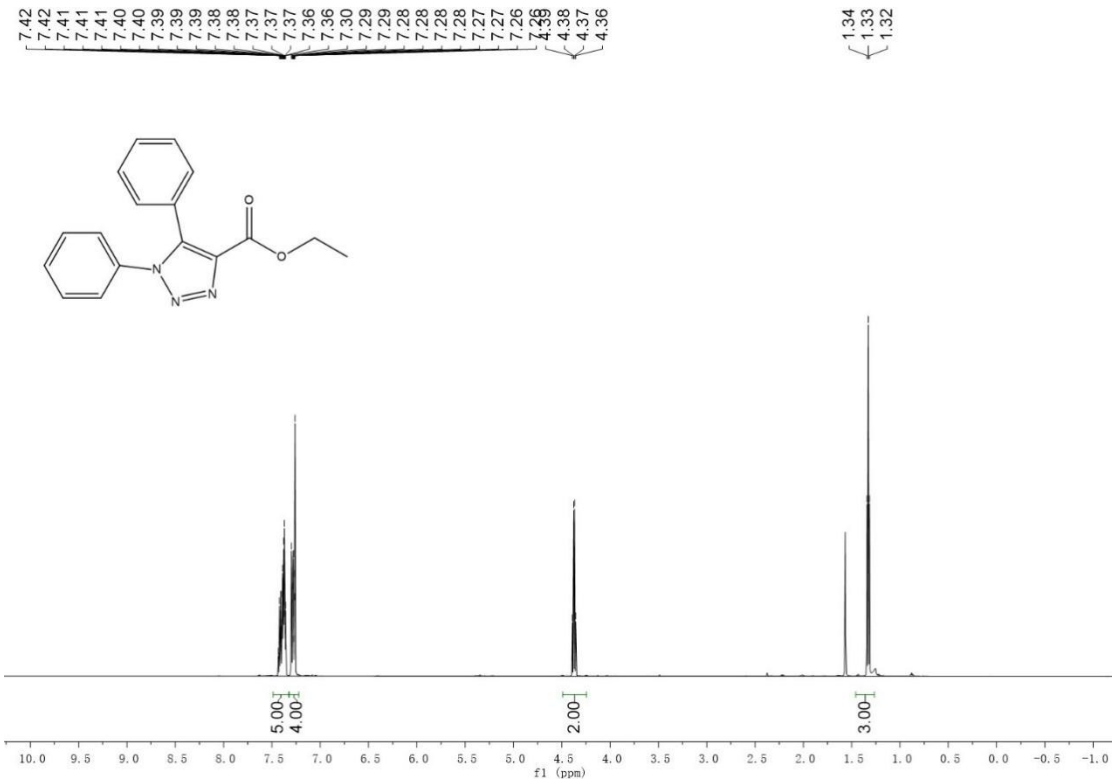
^{1}H NMR Spectra of **5d** ($CDCl_3$, 298.1 K)



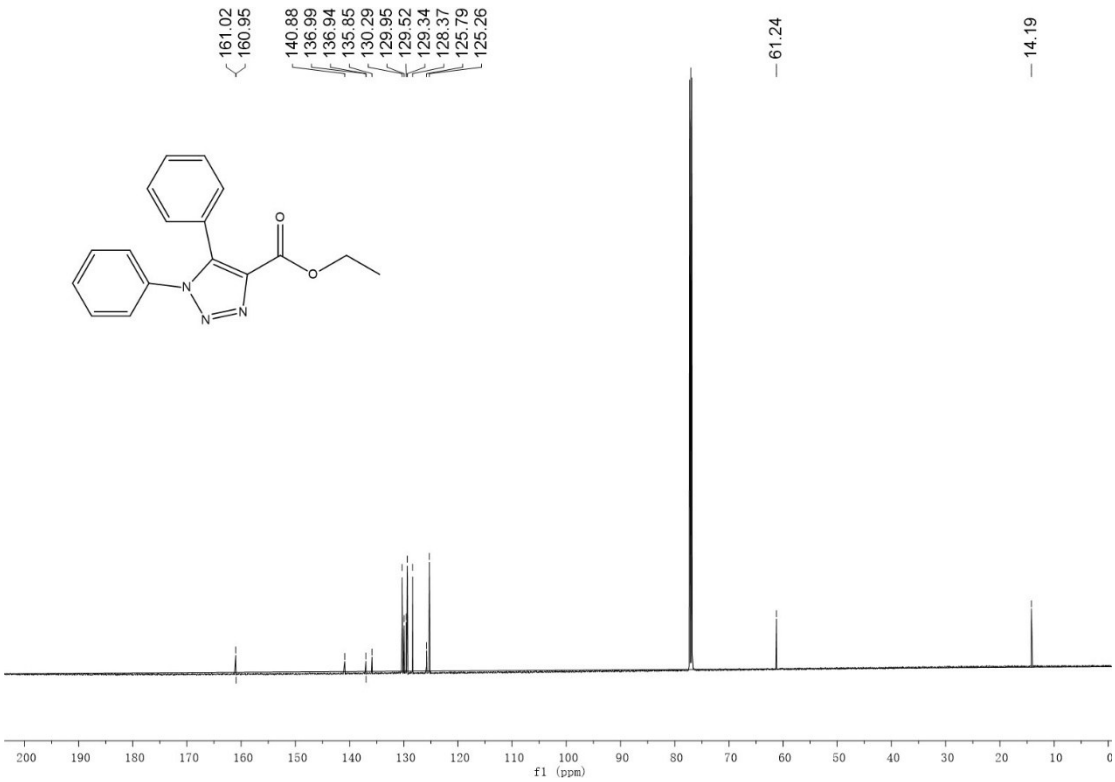
^{13}C NMR Spectra of **5d** ($CDCl_3$, 298.0 K)



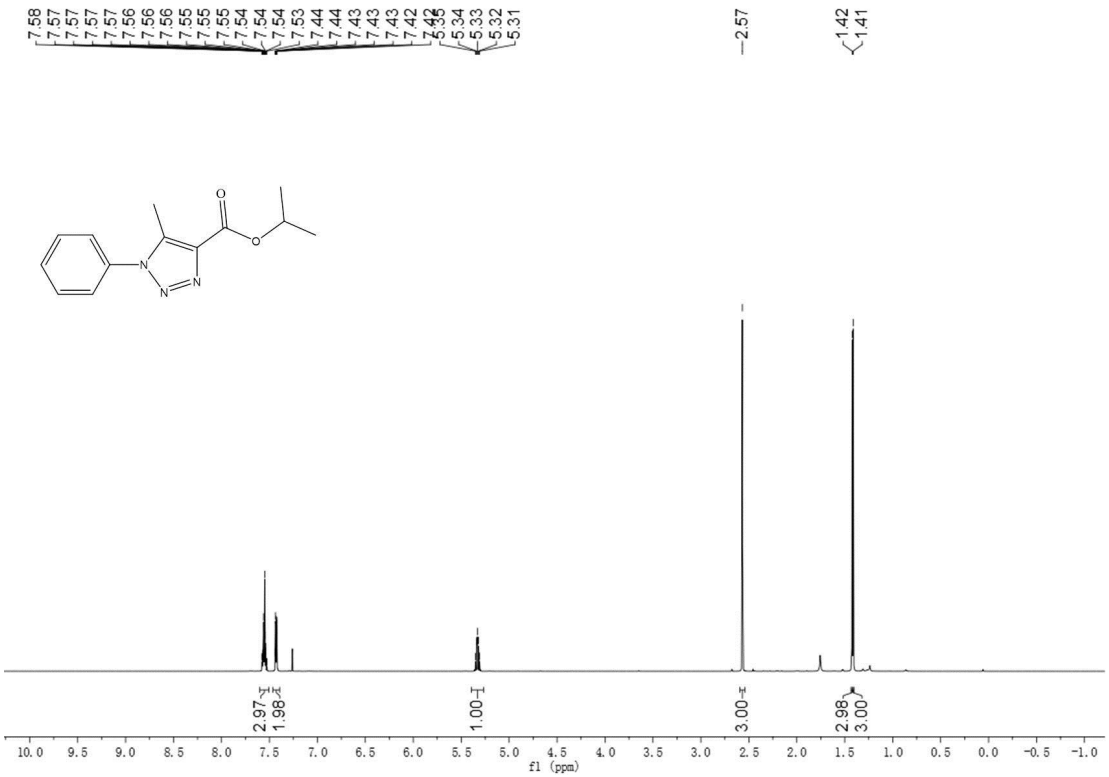
^{1}H NMR Spectra of **5e** ($CDCl_3$, 298.1 K)



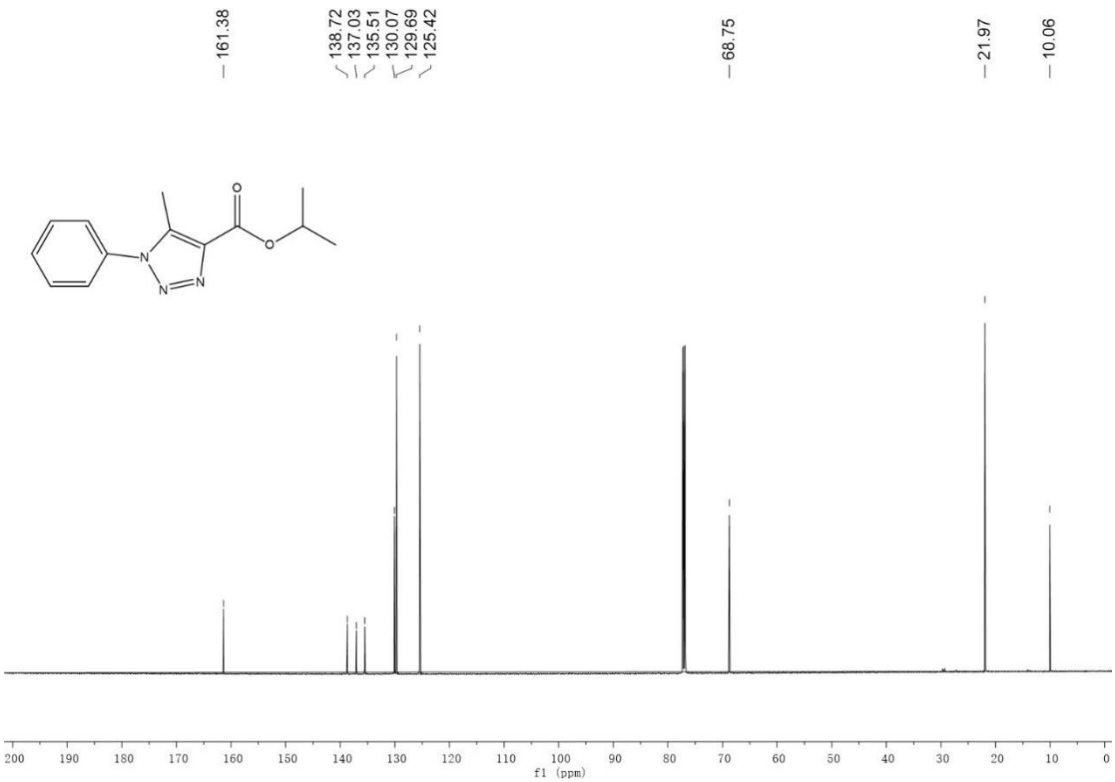
^{13}C NMR Spectra of **5e** ($CDCl_3$, 298.0 K)



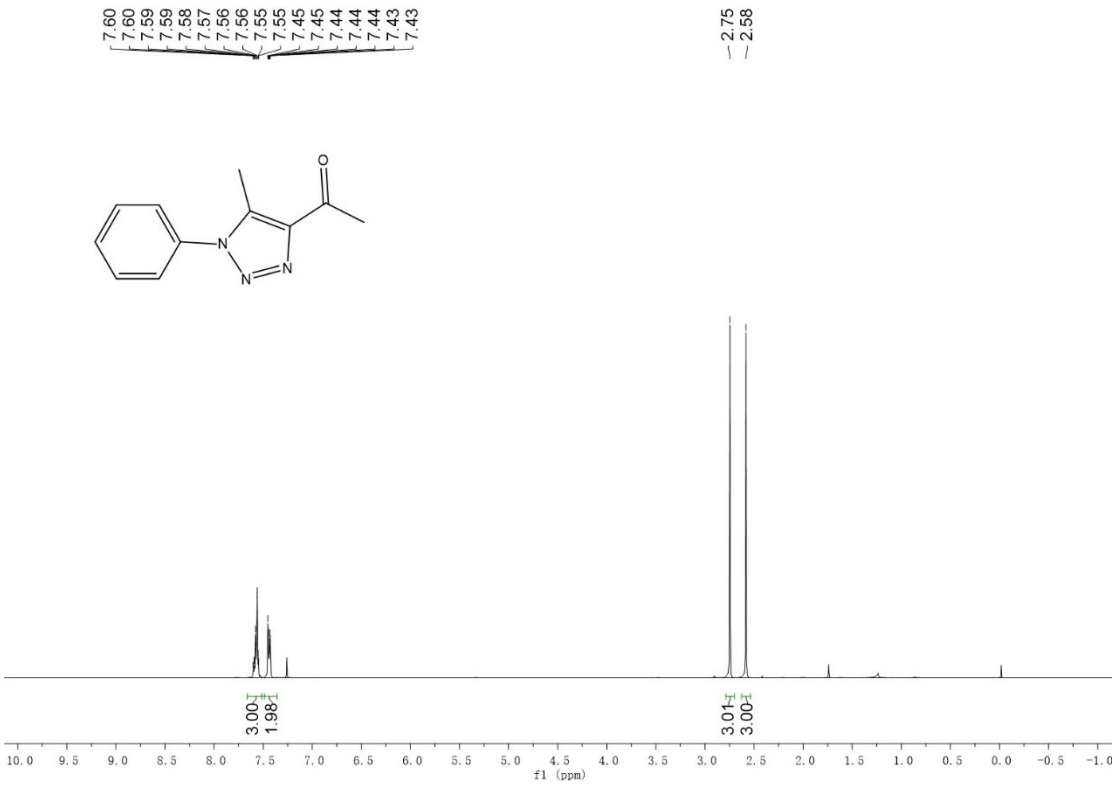
^{1}H NMR Spectra of **5f** ($CDCl_3$, 297.9 K)



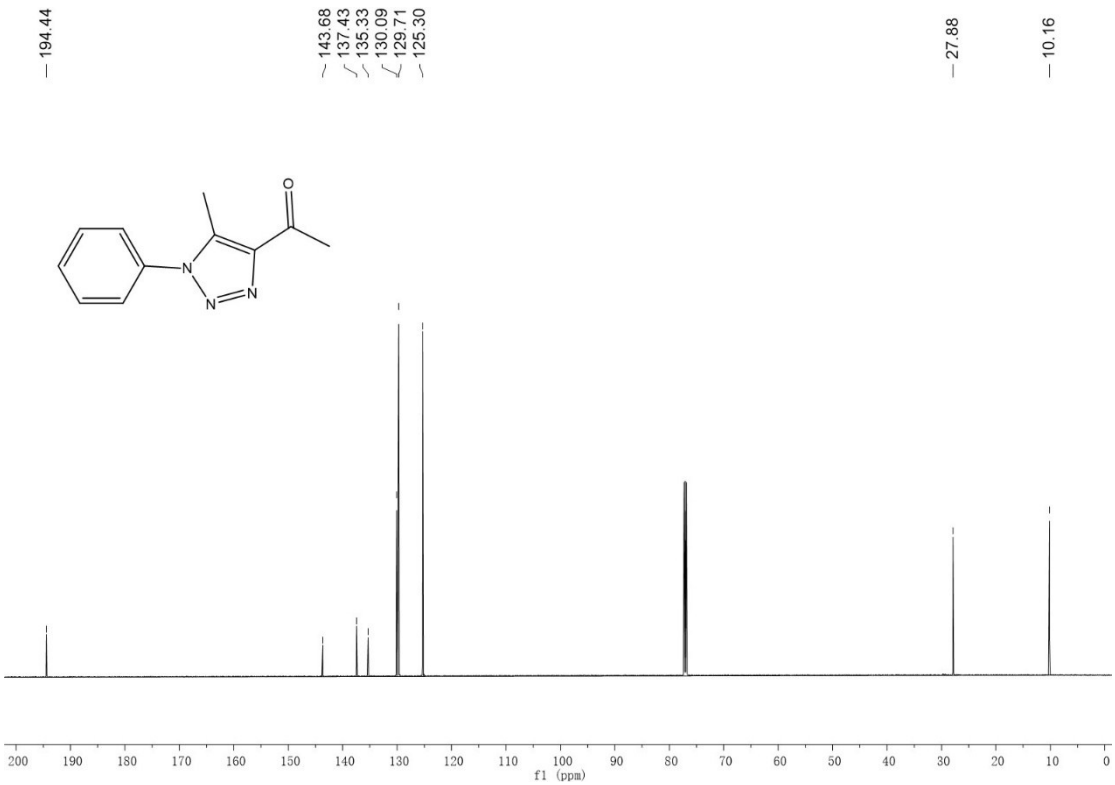
^{13}C NMR Spectra of **5f** ($CDCl_3$, 298.0 K)



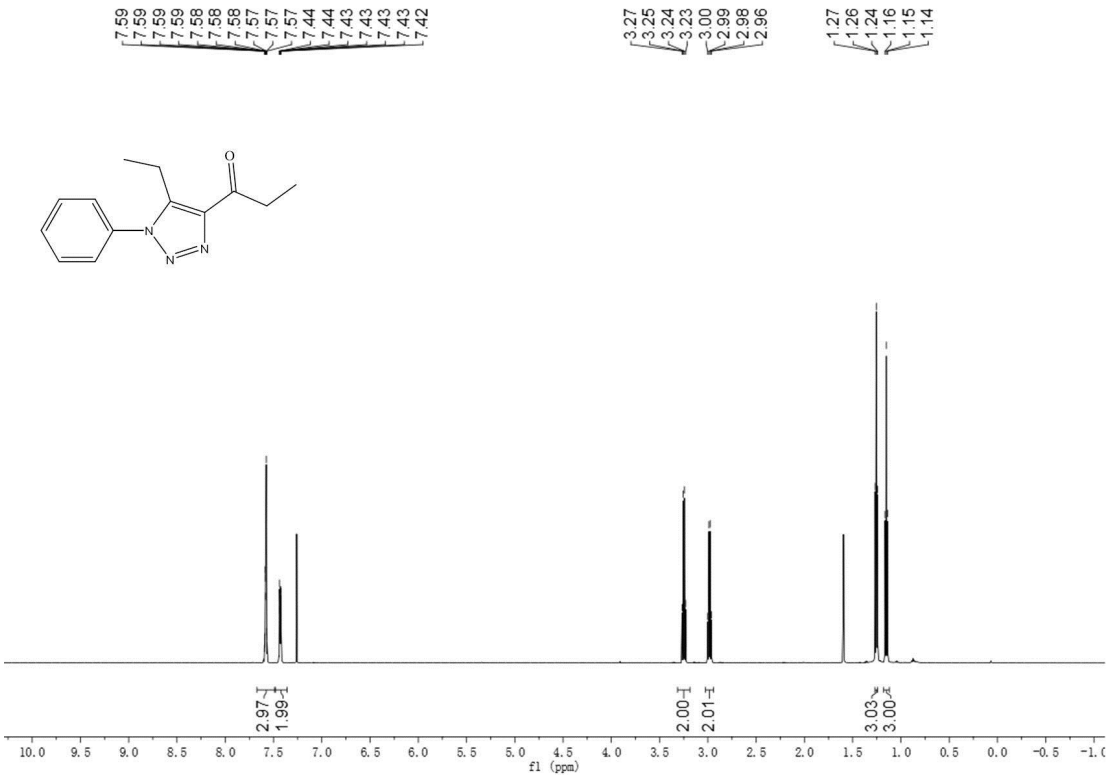
^{1}H NMR Spectra of **5g** ($CDCl_3$, 292.1 K)



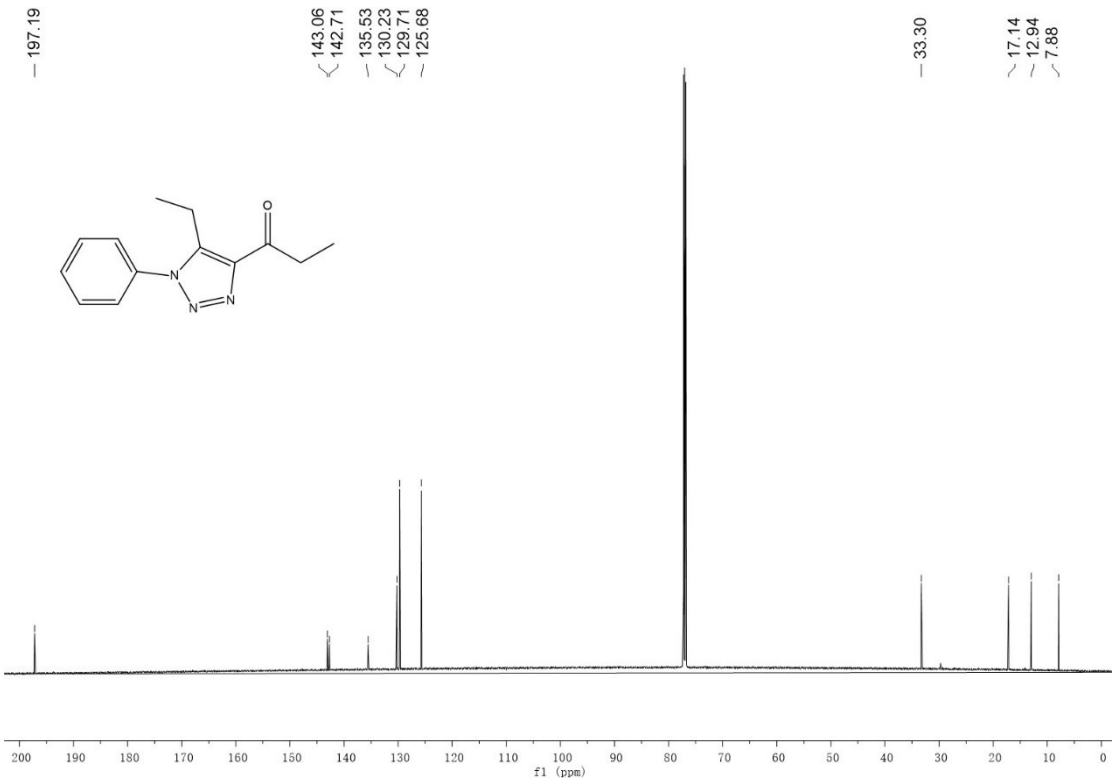
^{13}C NMR Spectra of **5g** ($CDCl_3$, 298.1 K)



^{1}H NMR Spectra of **5h** ($CDCl_3$, 297.9 K)



^{13}C NMR Spectra of **5h** ($CDCl_3$, 298.1 K)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f1 (ppm)