1,2,3-Triazole -Assisted C–H Amidation by Cobalt(III) Catalysis

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Supporting information

1. General information S-2

2. General Procedure for the Synthesis of **3** (**3a** as an example) S-2

3. Spectroscopic Characterization Data of Products S-2

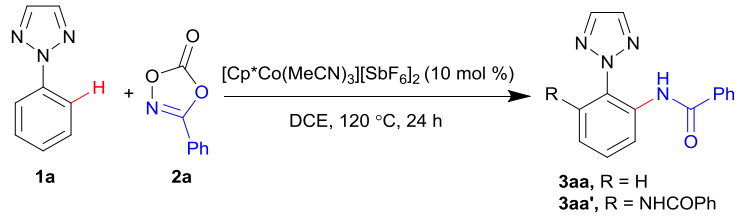
4. References S-10

5. ^{1}H NMR and ^{13}C NMR Spectra of Products S-10

1. General Information

The following starting materials were synthesized according to previously described procedures: 2-aryl-1,2,3-triazoles **1a-o**, [1] dioxazolones **2a-j**,[2] $[Cp^*Co(CO)I_2]$[3] and $[Cp^*Co(CH_3CN)_3][SbF_6]_2$[4]. Other materials were purchased from commercial suppliers and used without further purification. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2mm), while column chromatography characterization was performed with silica gel (100-200mesh). ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 MHz (Varian). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) or DMSO-d_6 (δ = 2.54 ppm) for ^{1}H NMR and chemical shifts for ^{13}C NMR spectra are reported in ppm relative to the central $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ = 39.6 ppm). Coupling constants are given in Hz. Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). High resolution mass spectroscopy data of the products were collected on a Waters Micromass GCT or a Bruker Apex IV FTMS instrument.

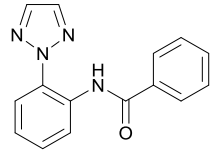
2. General Procedure for the Synthesis of 3(3a as an example)



A 15ml sealed tube were charged with 2-phenyl-2*H*-1,2,3-triazole **1a** (29.0 mg, 0.2 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (126.9 mg, 0.48 mmol), $[Cp^*Co(CH_3CN)_3][SbF_6]_2$ (15.8 mg, 0.02 mmol), and DCE (1ml). The mixture was stirred at 120 °C for 24 h, then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product **3aa** and **3aa'** were obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc). Both of them are white solids. 3aa (33.3 mg, 63% yield); 3aa' (23.8 mg, 31% yield).

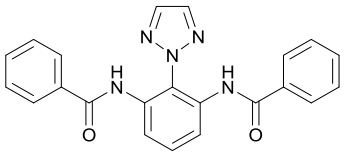
3. Spectroscopic Characterization Data of Products

***N*-(2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3aa)**



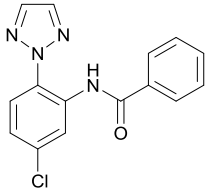
Yield 63%; white solid; m.p.138-139 °C; ^{1}H NMR (400MHz, DMSO-d_6) : δ 10.87 (s, 1H), 8.23 (s, 1H), 8.20 (s, 2H), 7.92 (t, *J* = 8.0 Hz, 3H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.55 (m, 3H), 7.40 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.0, 141.2, 141.2, 139.4, 137.1, 135.3, 133.9, 133.7, 132.5, 130.5, 130.1, 128.5; HRMS (ESI) Calcd. For $C_{15}H_{12}N_4O$: $[M+Na]^+$,287.0909, Found: *m/z* 287.0910.

***N,N'*-(2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3aa')**



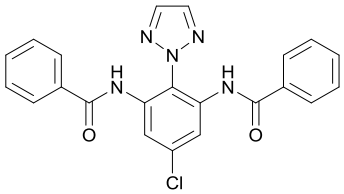
Yield 31%; white solid; m.p.206-208 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.98 (s, 1H), 8.07 (s, 2H), 7.74 (m, 6H), 7.60 (m, 8H), 7.48 (m, 4H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.2, 140.9, 139.1, 138.7, 136.9, 134.3, 133.6, 132.6, 132.0, 129.0; HRMS (ESI) Calcd. For $C_{22}H_{17}N_5O_2$: $[M+Na]^+$, 406.1280, Found: *m/z* 406.1279.

***N*-(5-chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ba)**



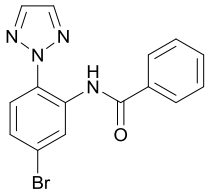
Yield 37%; white solid; m.p.157-158 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 11.13 (s, 1H), 8.42 (s, 1H), 8.24 (s, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.1, 141.4, 139.0, 137.5, 137.4, 136.3, 134.1, 134.0, 132.5, 130.0, 129.6, 128.5; HRMS (ESI) Calcd. For $C_{15}H_{11}ClN_4O$: $[M+Na]^+$, 321.0519, Found: *m/z* 321.0520.

***N,N'*-(5-chloro-2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3ba')**



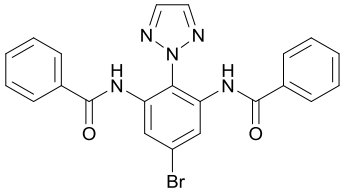
Yield 50%; white solid; m.p.235-236 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.11 (s, 1H), 8.13 (s, 2H), 7.88 (s, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.6, 136.7, 135.3, 135.2, 134.2, 133.3, 132.5, 129.0, 128.0, 123.2; HRMS (ESI) Calcd. For $C_{22}H_{16}ClN_5O_2$: $[M+Na]^+$, 440.0890, Found: *m/z* 440.0890.

***N*-(5-bromo-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ca)**



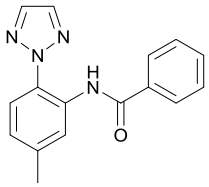
Yield 34%; white solid; m.p.140-142 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 11.12 (s, 1H), 8.42 (s, 1H), 8.26 (s, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.2, 141.5, 139.1, 137.6, 137.4, 136.4, 134.3, 134.0, 132.5, 130.1, 129.8, 128.7; HRMS (ESI) Calcd. For $C_{15}H_{11}BrN_4O$: $[M+Na]^+$, 365.0014, Found: *m/z* 365.0014.

***N,N'*-(5-bromo-2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3ca')**



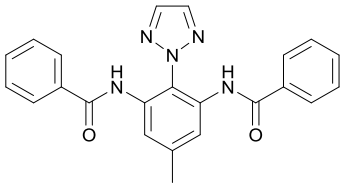
Yield 51%; white solid; m.p.231-232 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.10 (s, 1H), 8.13 (s, 2H), 7.89 (s, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.6, 136.6, 135.3, 135.2, 134.1, 133.3, 132.4, 129.0, 127.9, 123.2; HRMS (ESI) Calcd. For $C_{22}H_{16}BrN_5O_2$: $[M+Na]^+$, 484.0385, Found: *m/z* 484.0386.

***N*-(5-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3da)**



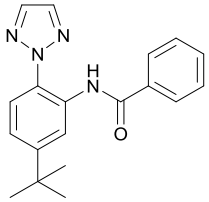
Yield 57%; white solid; m.p.121-123 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.83 (s, 1H), 8.17 (s, 2H), 8.07 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.2, 138.7, 136.2, 134.7, 132.3, 130.3, 129.2, 129.2, 127.7, 126.3, 125.3, 123.5, 21.3; HRMS (ESI) Calcd. For $C_{16}H_{14}N_4O$: $[M+Na]^+$, 301.1065, Found: *m/z* 301.1064.

***N,N'*-(5-methly-2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3da')**



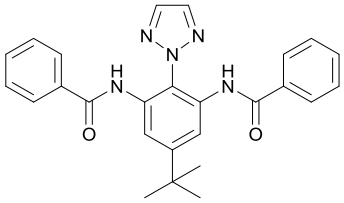
Yield 38%; white solid; m.p.212-214 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.92 (s, 1H), 8.06 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.56 (s, 2H), 7.46 (m, 5H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.4, 136.1, 134.5, 133.6, 132.1, 129.2, 128.9, 127.8, 124.6, 118.6, 21.4; HRMS (ESI) Calcd. For $C_{23}H_{19}N_5O_2$: $[M+Na]^+$, 420.1436, Found: *m/z* 420.1436.

***N*-(5-(*tert*-butyl)-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ea)**



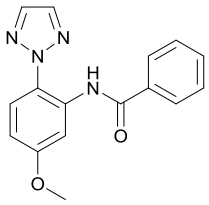
Yield 55%; white solid; m.p.78-80 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.87 (s, 1H), 8.27 (s, 1H), 8.16 (s, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.0, 156.4, 140.9, 139.5, 137.1, 134.9, 133.9, 133.9, 132.4, 128.1, 127.5, 126.7, 39.7, 36.1; HRMS (ESI) Calcd. For $C_{19}H_{20}N_4O$: $[M+Na]^+$, 343.1535, Found: *m/z* 343.1535.

***N,N'*-(5-(*tert*-butyl)-2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3ea')**



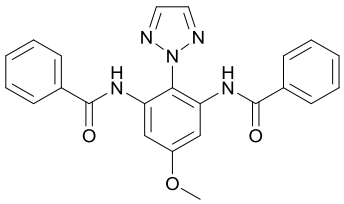
Yield 31%; white solid; m.p.169-170 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.00 (s, 2H), 8.03 (s, 2H), 7.76 (t, *J* = 8.0 Hz, 6H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 4H), 1.38 (s, 9H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.1, 157.0, 140.7, 139.2, 138.2, 136.9, 133.6, 132.6, 132.0, 125.9, 39.9, 36.0; HRMS (ESI) Calcd. For $C_{26}H_{25}N_5O_2$: $[M+Na]^+$, 462.1906, Found: *m/z* 462.1907.

***N*-(5-methoxy-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3fa)**



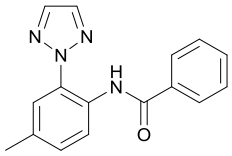
Yield 42%; white solid; m.p.149-151 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.96 (s, 1H), 8.16 (s, 2H), 7.93 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 4.0 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.1, 159.1, 135.8, 134.4, 132.3, 131.6, 129.0, 127.5, 124.6, 124.5, 110.7, 109.1, 55.8; HRMS (ESI) Calcd. For $C_{16}H_{14}N_4O_2$: $[M+Na]^+$, 317.1014, Found: *m/z* 317.1013.

***N,N'*-(5-methoxy-2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)dibenzamide (3fa')**



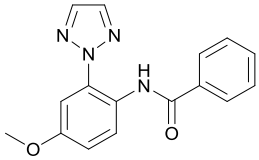
Yield 54%; white solid; m.p.219-220 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.94 (s, 1H), 8.08 (s, 2H), 7.75 (s, 4H), 7.40 (m, 8H), 3.88 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.2, 159.1, 135.9, 134.7, 134.2, 132.0, 128.7, 128.4, 127.6, 108.5, 56.0; HRMS (ESI) Calcd. For $C_{23}H_{19}N_5O_3$: $[M+Na]^+$, 436.1386, Found: *m/z* 436.1386.

***N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ga)**



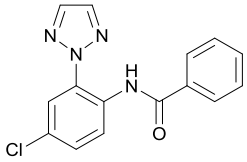
Yield 87%; white solid; m.p.104-106 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.73 (s, 1H), 8.17 (s, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (100MHz, DMSO-d_6): δ 169.9, 141.1, 140.2, 139.5, 137.0, 136.2, 134.2, 133.8, 132.8, 132.4, 130.2, 128.7, 25.5; HRMS (ESI) Calcd. For $C_{16}H_{14}N_4O$: $[M+Na]^+$, 301.1065, Found: *m/z* 301.1065.

***N*-(4-methoxy-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ha)**



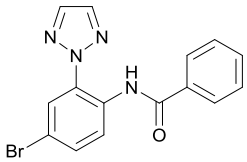
Yield 84%; white solid; m.p.104-105 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.35 (s, 1H), 8.16 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.1, 161.8, 141.2, 139.5, 137.9, 136.9, 133.8, 133.5, 132.5, 128.3, 119.6, 113.5, 60.8; HRMS (ESI) Calcd. For $C_{16}H_{14}N_4O_2$: $[M+Na]^+$,317.1014, Found: *m/z* 317.1014.

***N*-(4-chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ia)**



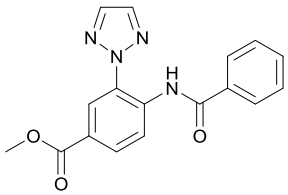
Yield 78%; white solid; m.p.102-104 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 11.00 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 2H), 8.02 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.63 (m, 4H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.1, 136.7, 134.2, 132.3, 131.6, 129.3, 129.0, 128.9, 128.5, 127.5, 126.5, 122.8; HRMS (ESI) Calcd. For $C_{15}H_{11}ClN_4O$: $[M+Na]^+$, 321.0519, Found: *m/z* 321.0519.

***N*-(4-bromo-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ja)**



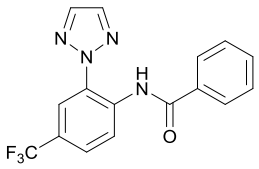
Yield 77%; white solid; m.p.104-105 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.95 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 2H), 7.97 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.57 (m, 4H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.1, 136.7, 134.2, 132.3, 131.7, 129.3, 129.0, 129.0, 128.5, 127.5, 126.5, 122.9; HRMS (ESI) Calcd. For $C_{15}H_{11}BrN_4O$: $[M+Na]^+$, 365.0014, Found: *m/z* 365.0014.

methyl 4-benzamido-3-(2*H*-1,2,3-triazol-2-yl)benzoate (3ka)



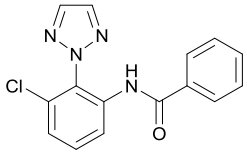
Yield 73%; white solid; m.p.124-126 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 11.44 (s, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.51 (s, 1H), 8.28 (s, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.57(t, *J* = 8.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.1, 170.1, 141.5, 139.1, 139.1, 137.5, 134.2, 134.1, 134.0, 132.5, 130.5, 128.5, 128.2, 57.6; HRMS (ESI) Calcd. For $C_{17}H_{14}N_4O_3$: $[M+Na]^+$, 345.0964, Found: *m/z* 345.0965.

***N*-(2-(2*H*-1,2,3-triazol-2-yl)-4-(trifluoromethyl)phenyl)benzamide (3la)**



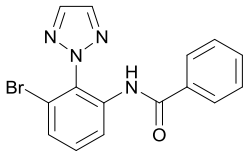
Yield 57%; white solid; m.p.124-126 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 11.34 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.30 (s, 2H), 8.25 (s, 1H),7.95 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 170.2, 141.8, 139.0, 138.6, 137.6, 134.8, 134.1,132.6, 133.8, 132.6, 130.4, 129.6, 124.8; HRMS (ESI) Calcd. For $C_{16}H_{11}F_3N_4O$: $[M+Na]^+$, 355.0783, Found: *m/z* 355.0783.

***N*-(3-chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ma)**



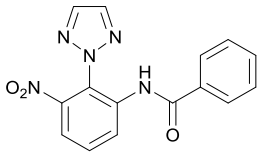
Yield 74%; white solid; m.p.109-110 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.79 (s, 1H), 8.11 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 4H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.7, 136.8, 136.3, 136.2, 133.8, 132.0, 131.4, 131.3, 128.6, 127.8, 127.7, 127.1; HRMS (ESI) Calcd. For $C_{15}H_{11}ClN_4O$: $[M+Na]^+$, 321.0519, Found: *m/z* 321.0520.

***N*-(3-bromo-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3na)**



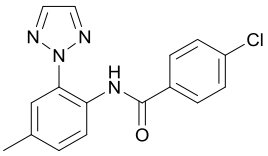
Yield 70%; white solid; m.p.104-106 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.79 (s, 1H), 8.12 (s, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 4H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.9, 137.0, 136.5, 136.4, 134.0, 132.2, 131.6, 131.5, 128.8, 128.0, 127.9, 127.3; HRMS (ESI) Calcd. For $C_{15}H_{11}BrN_4O$: $[M+Na]^+$, 365.0014, Found: *m/z* 365.0014.

***N*-(3-nitro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3oa)**



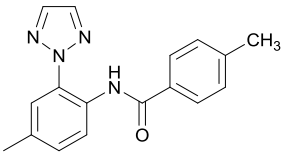
Yield 28%; white solid; m.p.138-139 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.26 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 2H), 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 165.7, 137.4, 134.8, 133.7, 132.3, 131.7, 130.5, 128.7, 127.8, 126.4, 121.9, 120.0; HRMS (ESI) Calcd. For $C_{15}H_{11}N_5O_3$: $[M+Na]^+$, 332.0760, Found: *m/z* 332.0759.

4-chloro-*N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3gb)



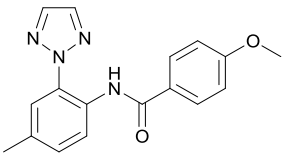
Yield 72%; white solid; m.p.138-140 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.70 (s, 1H), 8.14 (s, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 169.0, 141.7, 141.1, 140.5, 138.2, 136.7, 134.4, 134.2, 133.9, 132.6, 130.7, 128.9, 25.5; HRMS (ESI) Calcd. For $C_{16}H_{13}ClN_4O$: $[M+Na]^+$, 335.0676, Found: *m/z* 335.0677.

4-methyl-*N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3gc)



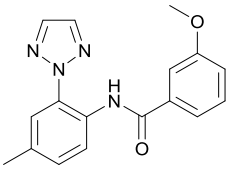
Yield 63%; white solid; m.p.113-114 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.73 (s, 1H), 8.18 (s, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.32 (t, *J* = 8.0 Hz, 3H),2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 169.8, 147.1, 141.0, 139.9, 136.7, 135.8, 134.4, 134.3, 132.8, 132.4, 129.8, 128.5, 26.1, 25.5; HRMS (ESI) Calcd. For $C_{17}H_{16}N_4O$: $[M+Na]^+$, 315.1222, Found: *m/z* 315.1222.

4-methoxy-*N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3gd)



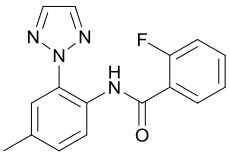
Yield 68%; white solid; m.p.118-120 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.67 (s, 1H), 8.18 (s, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 169.9, 167.2, 141.0, 139.7, 135.7, 134.3, 134.2, 132.9, 131.6, 129.8, 128.5, 119.1, 60.6, 25.5; HRMS (ESI) Calcd. For $C_{17}H_{16}N_4O_2$: $[M+Na]^+$, 331.1171, Found: *m/z* 331.1171.

3-methoxy-*N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3ge)



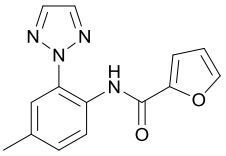
Yield 83%; white solid; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.86 (s, 1H), 8.20 (s, 2H), 7.94 (s, 1H), 7.46 (m, 4H), 7.17 (d, 2H), 3.83 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 164.9, 159.1, 136.2, 136.0, 131.2, 130.3, 130.1, 128.8, 125.5, 125.0, 123.6, 119.6, 118.1, 112.5, 55.5, 25.5; HRMS (ESI) Calcd. For $C_{17}H_{16}N_4O_2$: $[M+Na]^+$, 331.1171, Found: *m/z* 331.1171.

2-fluoro-*N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)benzamide (3gf)



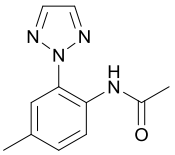
Yield 79%; white solid; m.p.100-101 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.64 (s, 1H), 8.18 (s, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 3H), 2.39 (s, 3H); HRMS (ESI) Calcd. For $C_{16}H_{13}FN_4O$: $[M+Na]^+$, 319.0971, Found: *m/z* 319.0972.

***N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)furan-2-carboxamide (3gg)**



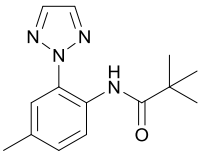
Yield 73%; white solid; m.p.99-100 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.93 (s, 1H), 8.22 (s, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.77 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 6.71 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 160.8, 152.4, 151.2, 141.2, 139.9, 134.9, 134.3, 131.9, 128.9, 128.4, 120.3, 117.7, 25.5; HRMS (ESI) Calcd. For $C_{14}H_{12}N_4O_2$: $[M+Na]^+$, 291.0858, Found: *m/z* 291.0858.

***N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)acetamide (3gh)**



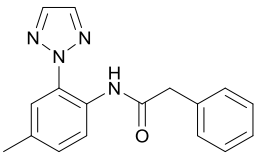
Yield 85%; white solid; m.p.64-65 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.79 (s, 1H), 8.13 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 2.35 (s, *3*H), 1.98 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ 168.6, 136.3, 135.0, 131.5, 129.6, 128.5, 125.5, 124.7, 34.2, 20.7; HRMS (ESI) Calcd. For $C_{11}H_{12}N_4O$: $[M+Na]^+$,239.0909, Found: *m/z* 239.0909.

***N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)pivalamide (3gi)**



Yield 77%; white solid; ^{1}H NMR (400MHz, DMSO-d_6): δ 10.32 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 2H), 7.93 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 1.20 (s, 9H) ; ^{13}C NMR (100MHz, DMSO-d_6): δ 181.4, 141.1, 135.4, 134.6, 133.6, 129.6, 128.6, 128.0, 44.6, 32.3, 25.4; HRMS (ESI) Calcd. For $C_{14}H_{18}N_4O$: $[M+Na]^+$, 281.1378, Found: *m/z* 281.1377.

***N*-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)-2-phenylacetamide (3gj)**



Yield 80%; white solid; m.p.77-79 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 9.93 (s, 1H), 8.02 (s, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.26 (t, *J* = 8.0 Hz, 1H), 3.66 (s, 2H), 2.33 (s, 3H); ^{13}C

NMR (100MHz, DMSO-d_6): δ 174.4, 140.9, 140.2, 139.6, 135.3, 134.7, 134.3, 133.6, 132.9, 132.0, 129.3, 128.9, 48.7, 25.4; HRMS (ESI) Calcd. For $C_{17}H_{16}N_4O$: $[M+Na]^+$, 315.1222, Found: *m/z* 315.1223.

4. References

[1] X. J. Wang, L. Zhang, H, Lee, N. Haddad, D. Krishnamurthy, C. H. Senanayake, *Org. Lett*., 2009, **11**, 5026.

[2] V, Bizet, L. Buglioni, C. Bolm, *Angew. Chem. Int.,* 2014, **53**, 5639.

[3] B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal*., 2014, **356**, 1491.

[4] D. G. Yu, T. Gensch, F. d. Azambuja, S. V. Céspedes, F. Glorius, *J. Am. Chem. Soc*., 2014, **136**, 17722.

5. ^{1}H NMR and ^{13}C NMR Spectra of Products

Figure 1. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3aa**.

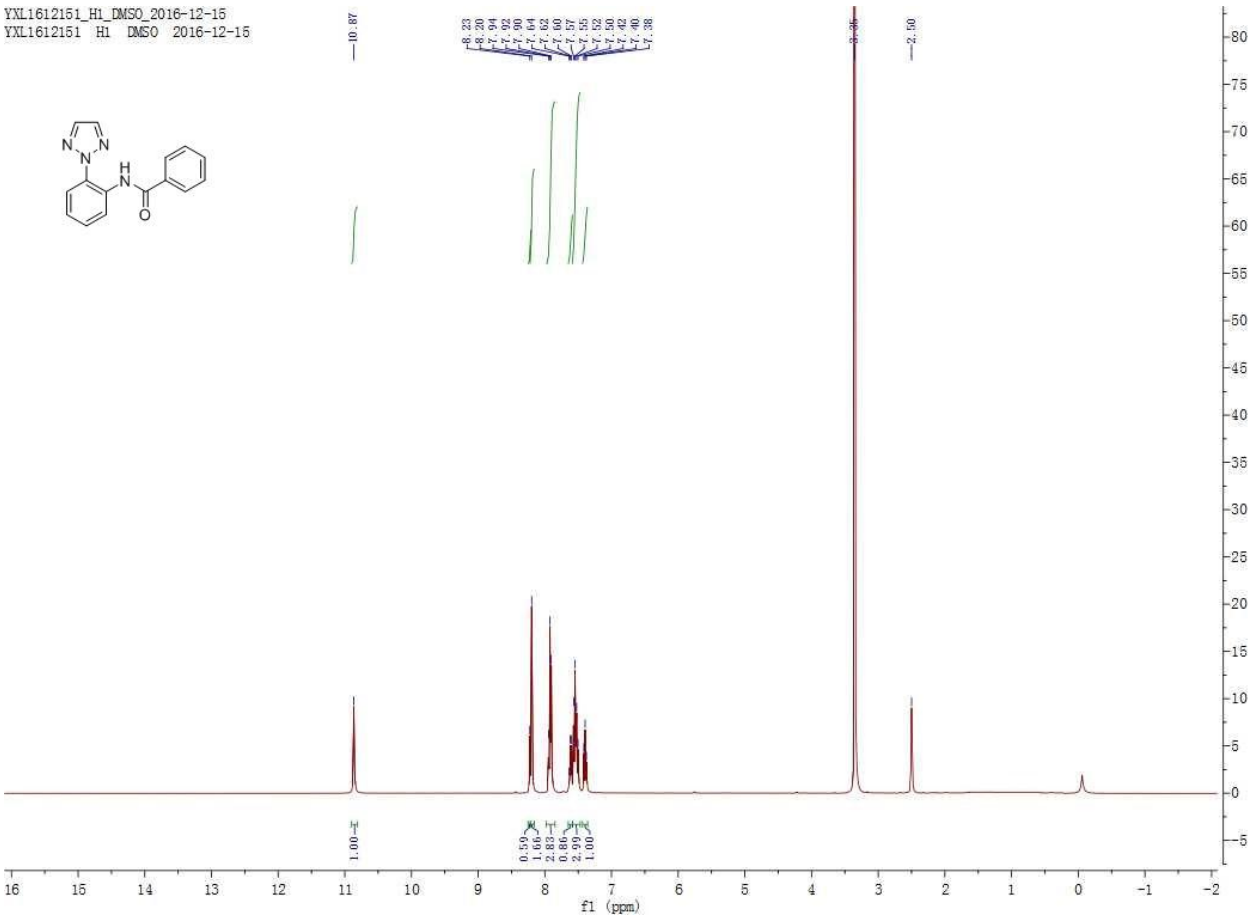


Figure 2. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3aa**.

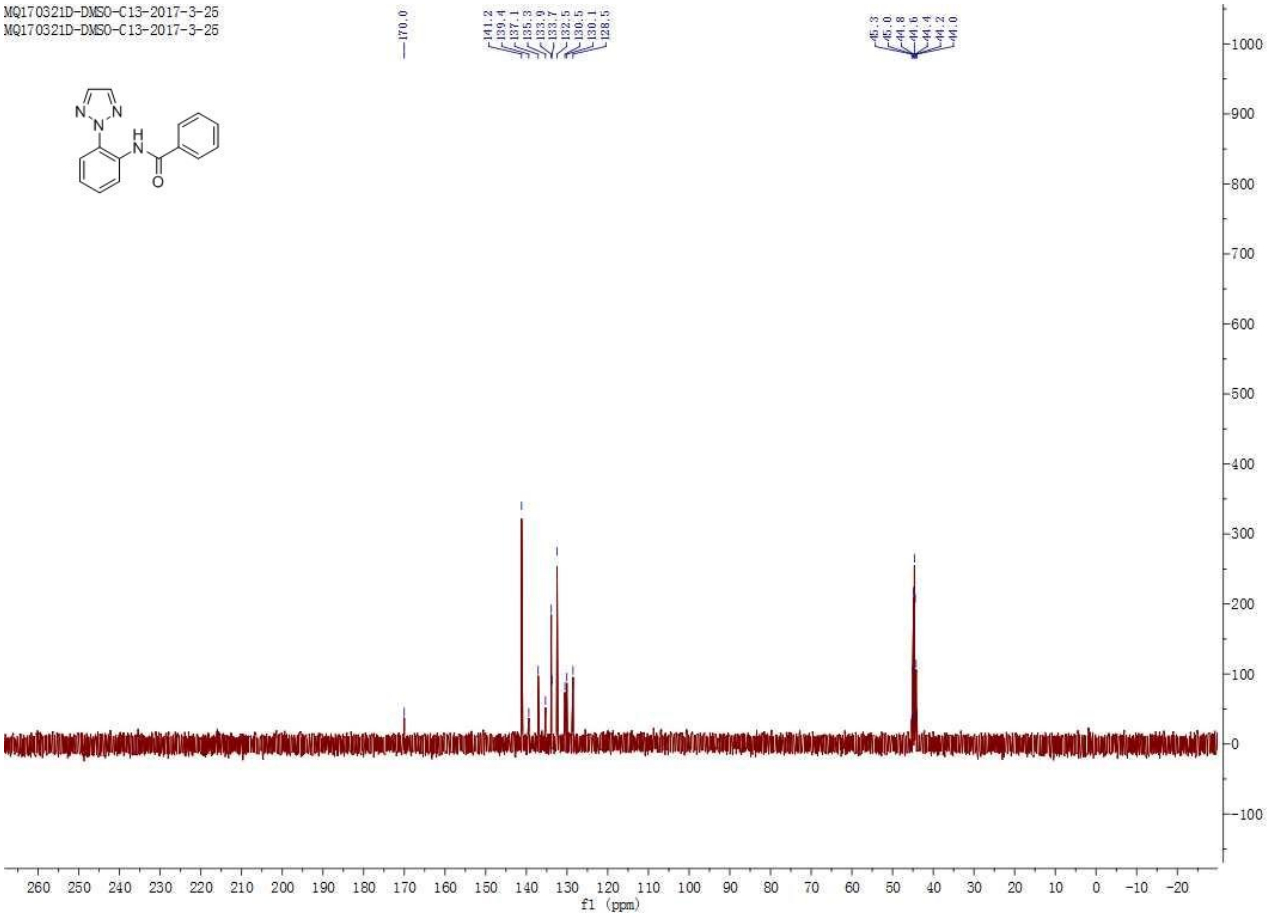


Figure 3. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3aa'**.

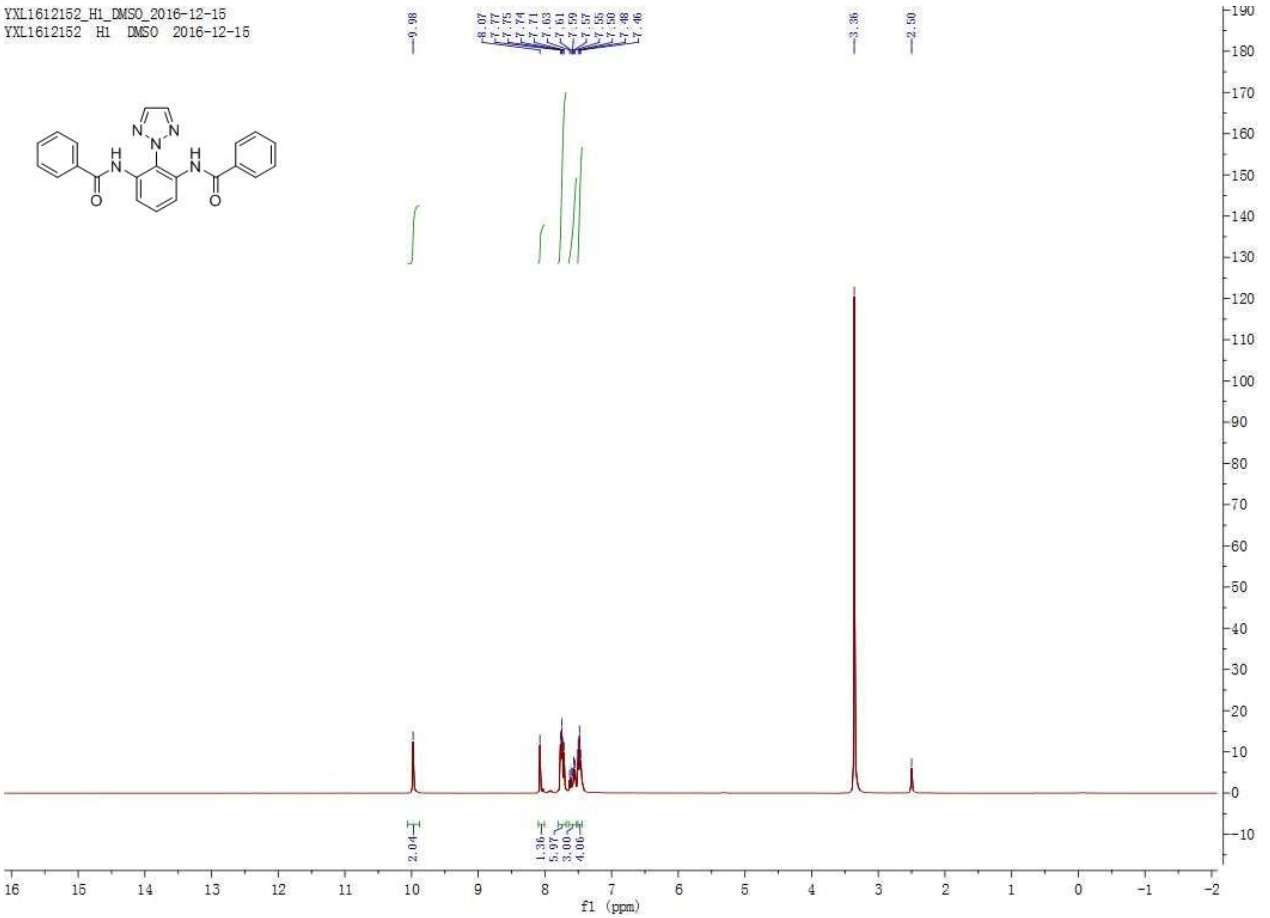


Figure 4. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3aa'**.

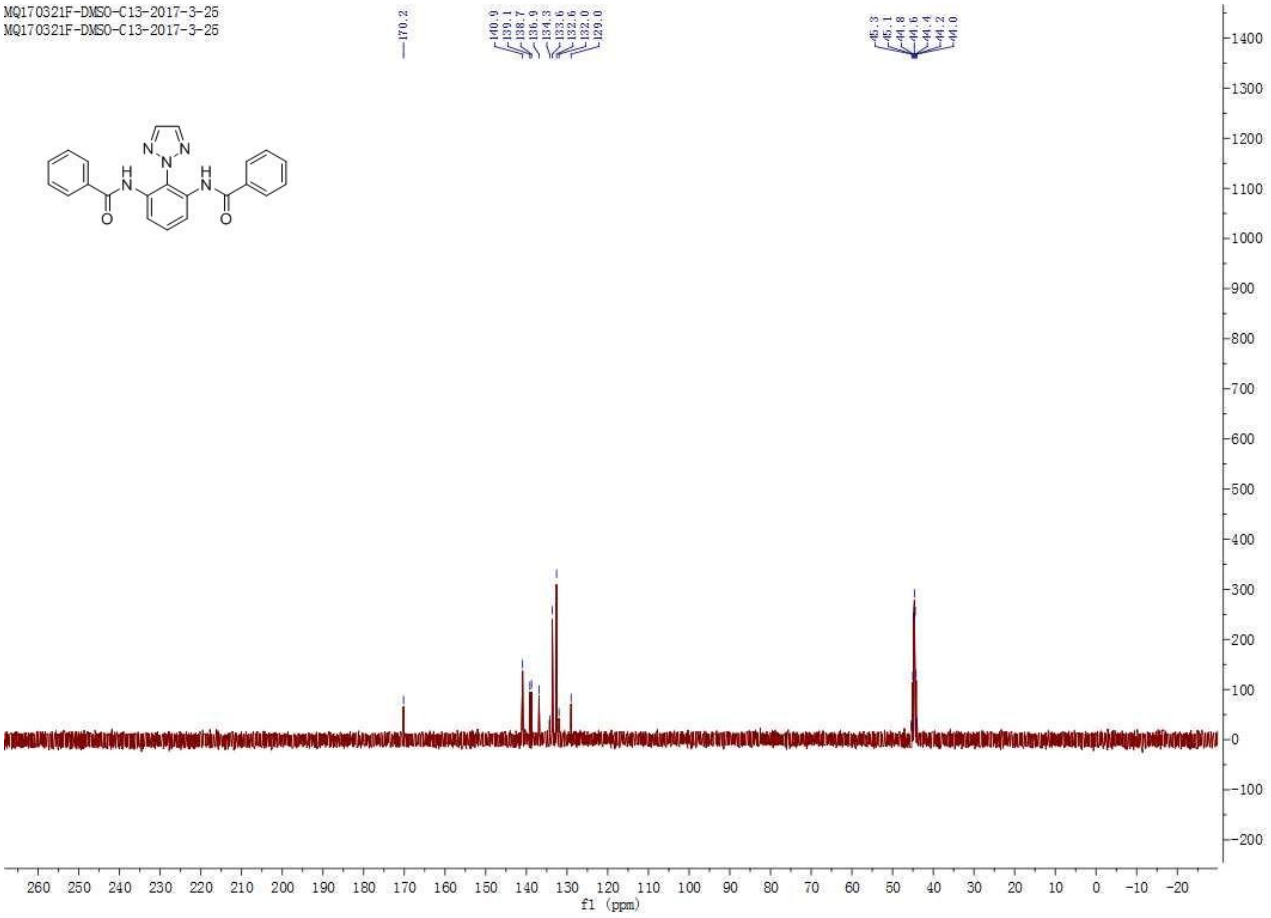


Figure 5. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ba**.

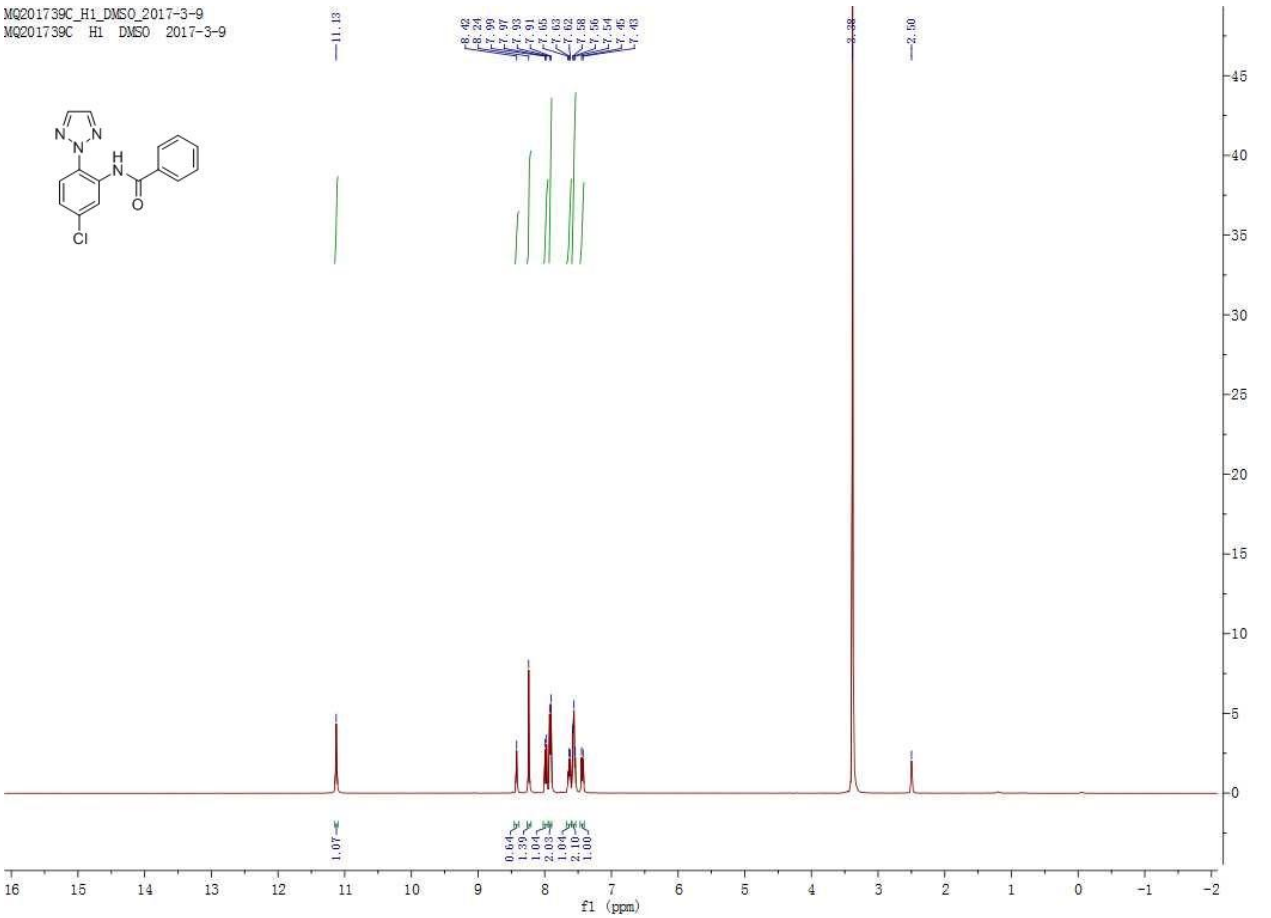


Figure 6. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ba**.

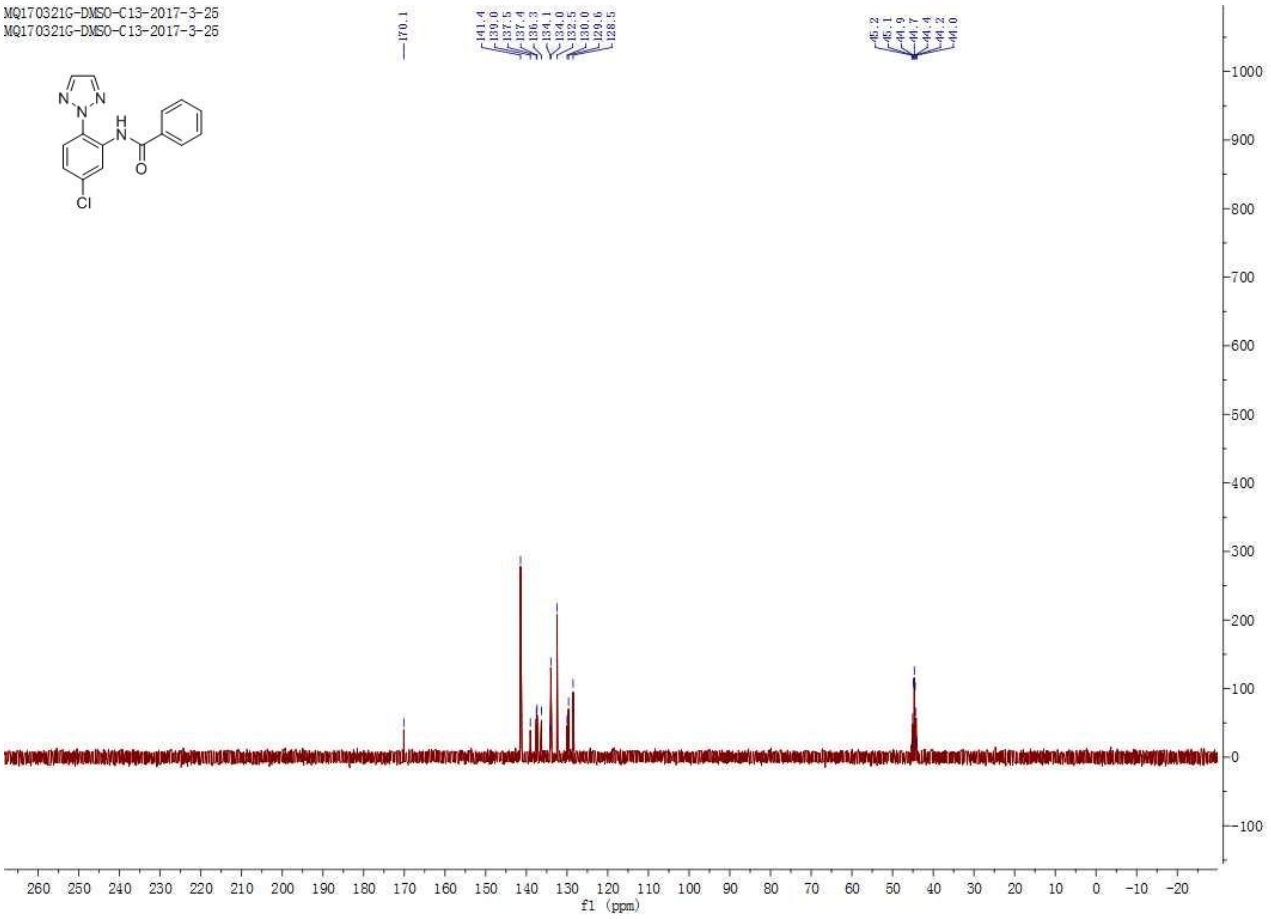


Figure 7. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ba'**.

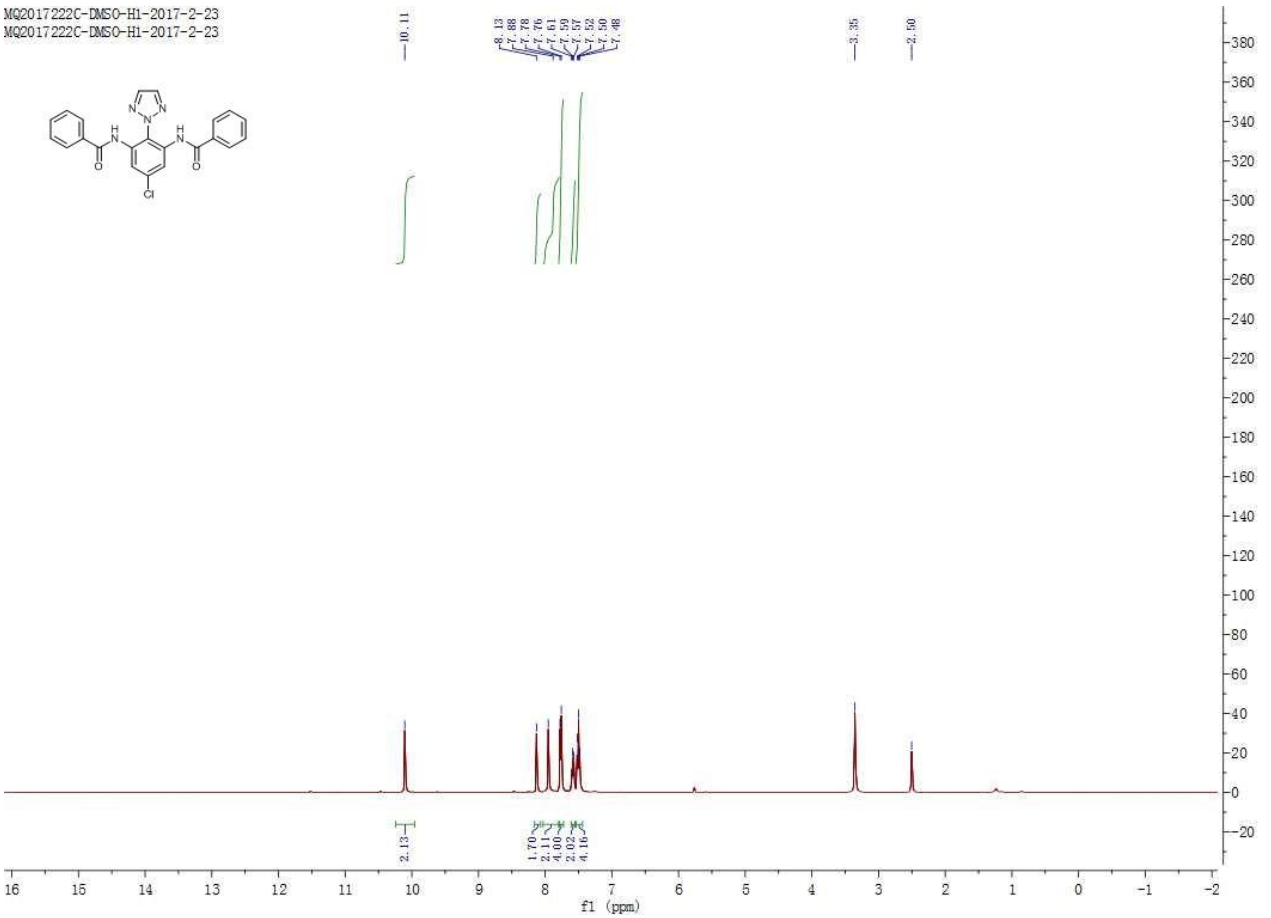


Figure 8. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ba'**.

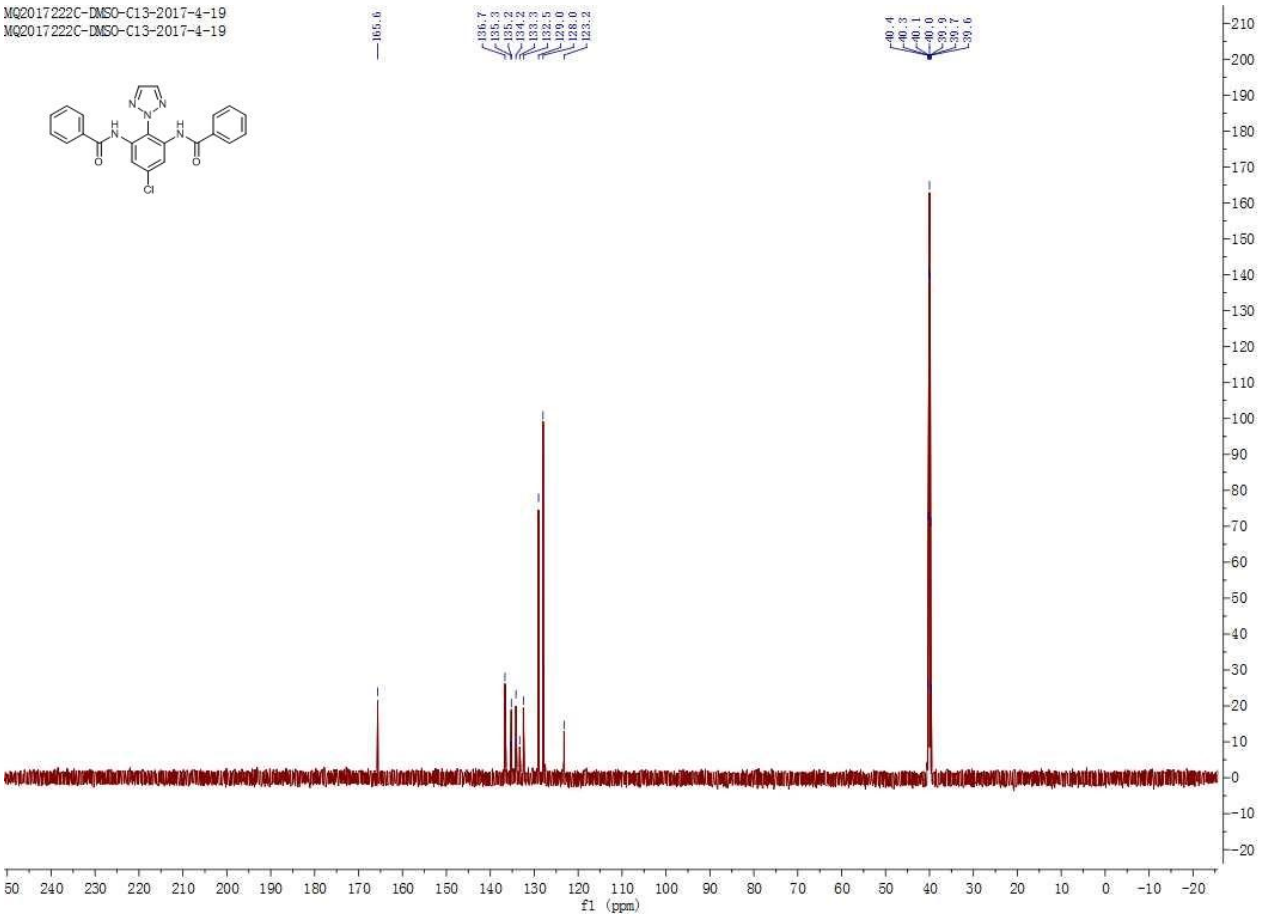


Figure 9. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ca**.

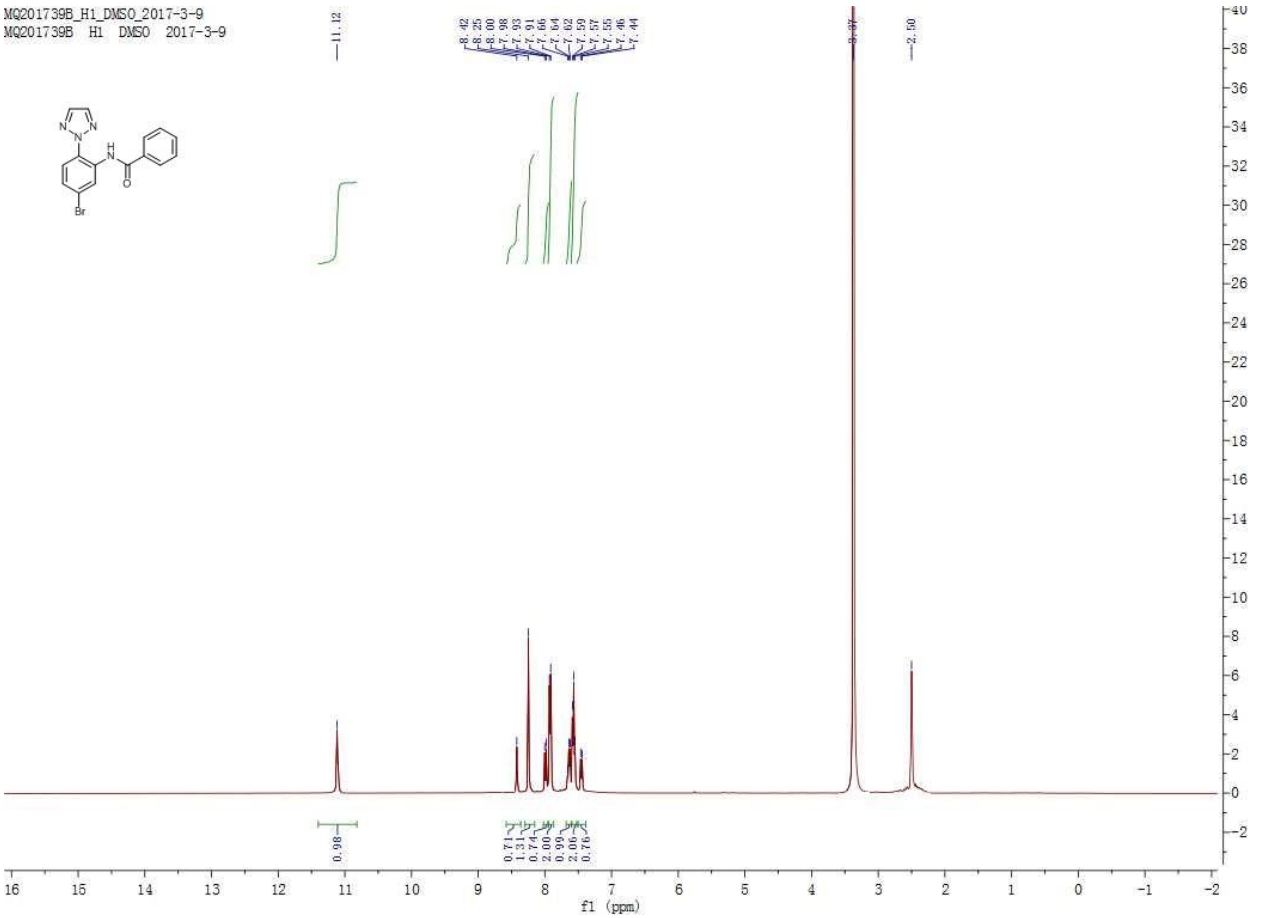


Figure 10. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ca**.

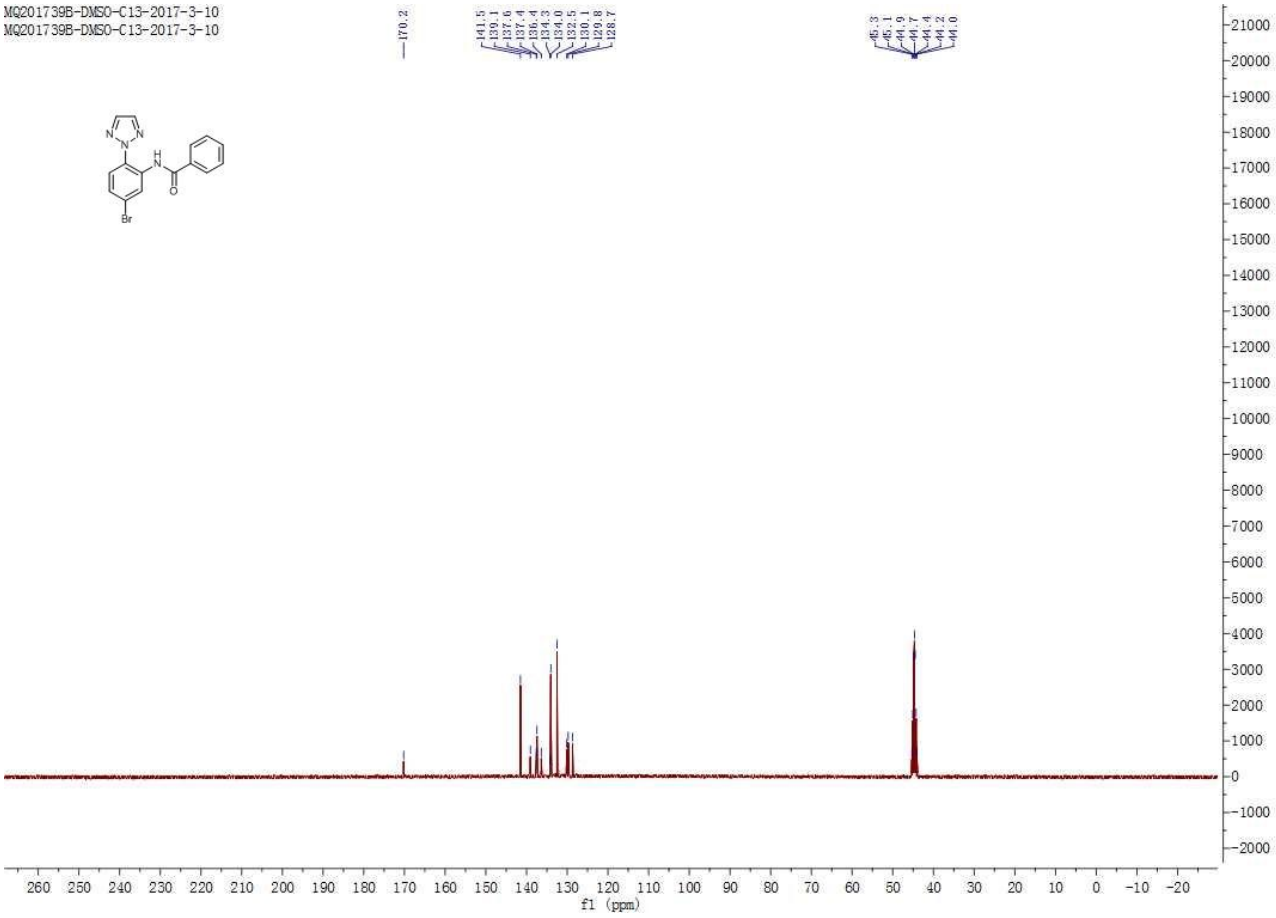


Figure 11. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ca'**.

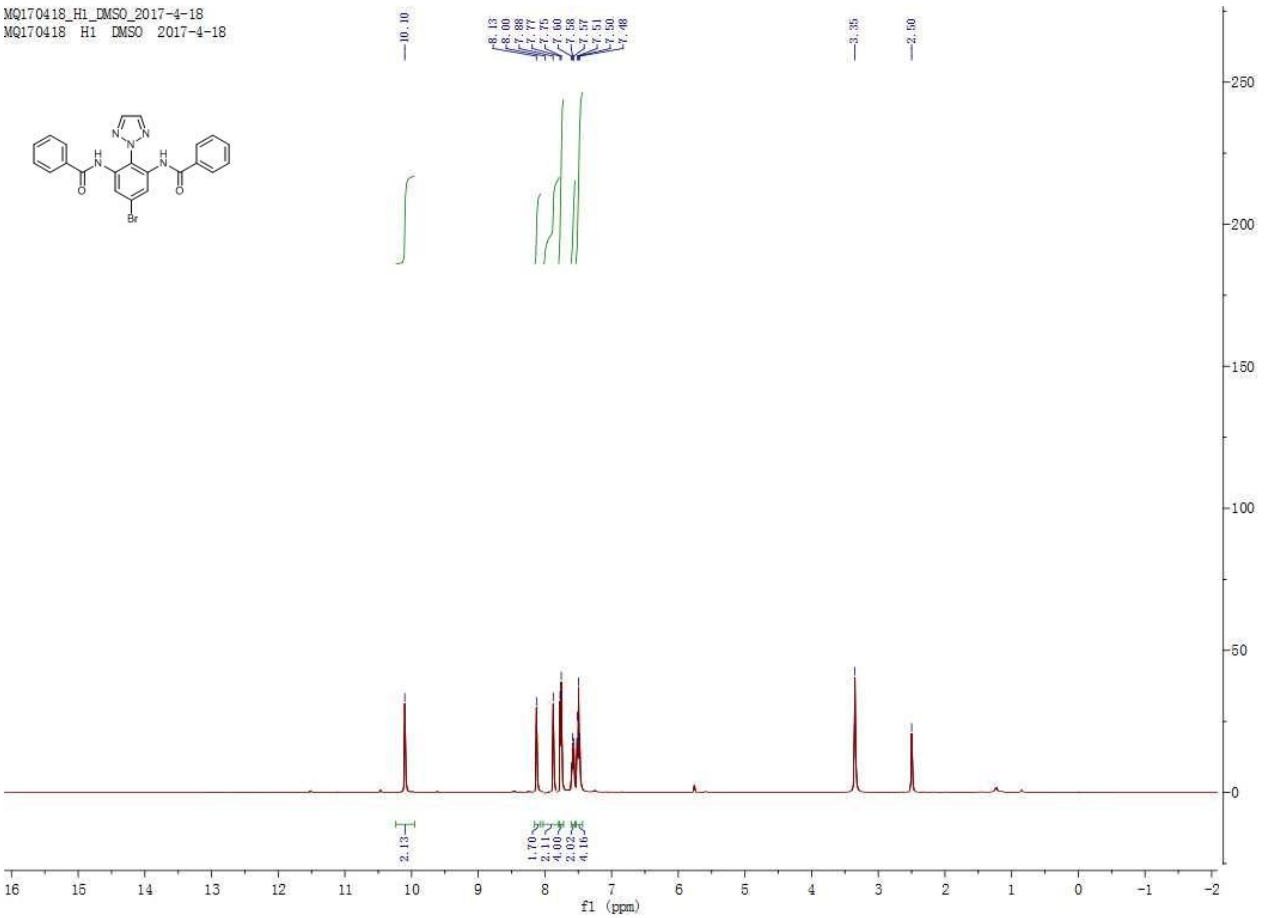


Figure 12. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ca'**.

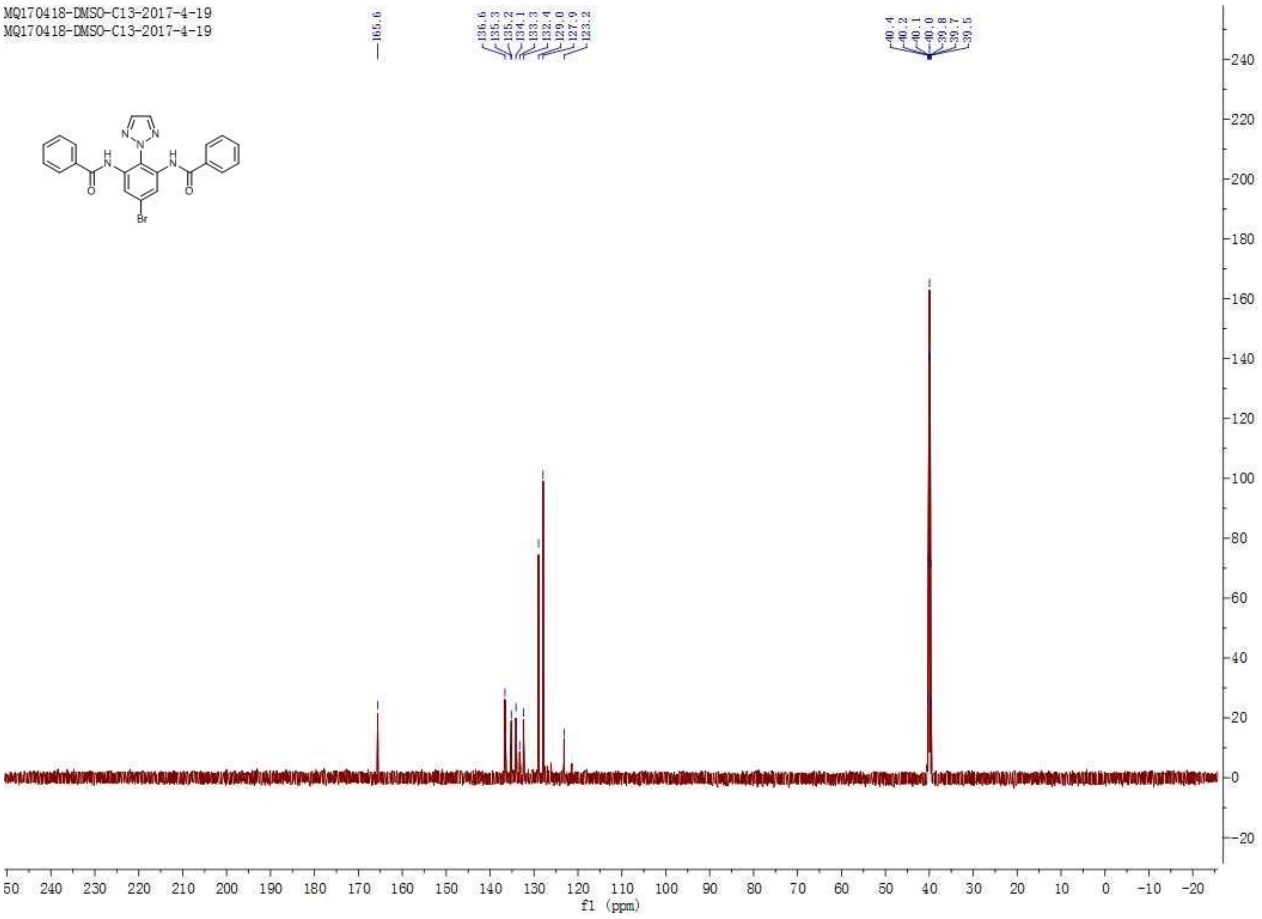


Figure 13. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3da**.

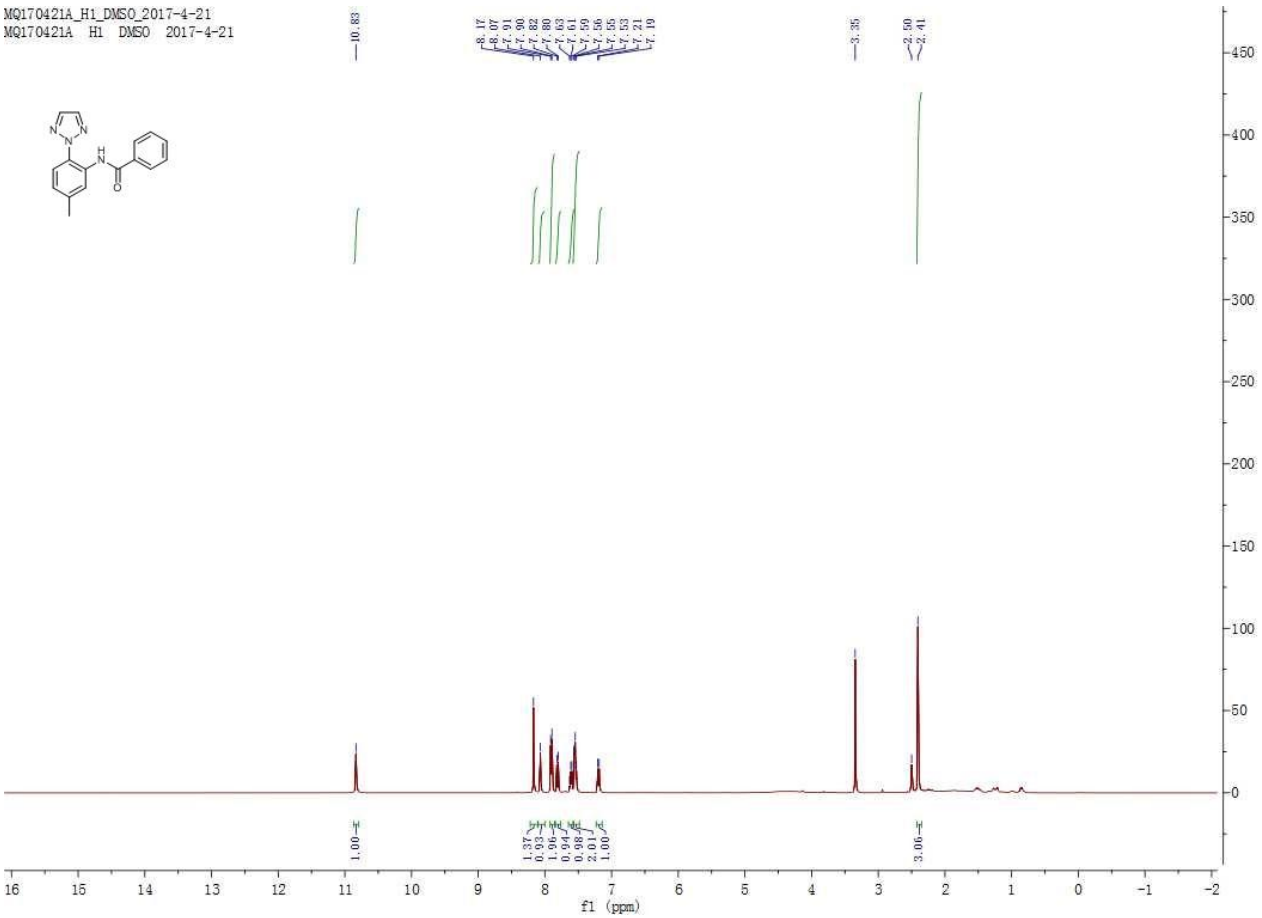


Figure 14. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3da**.

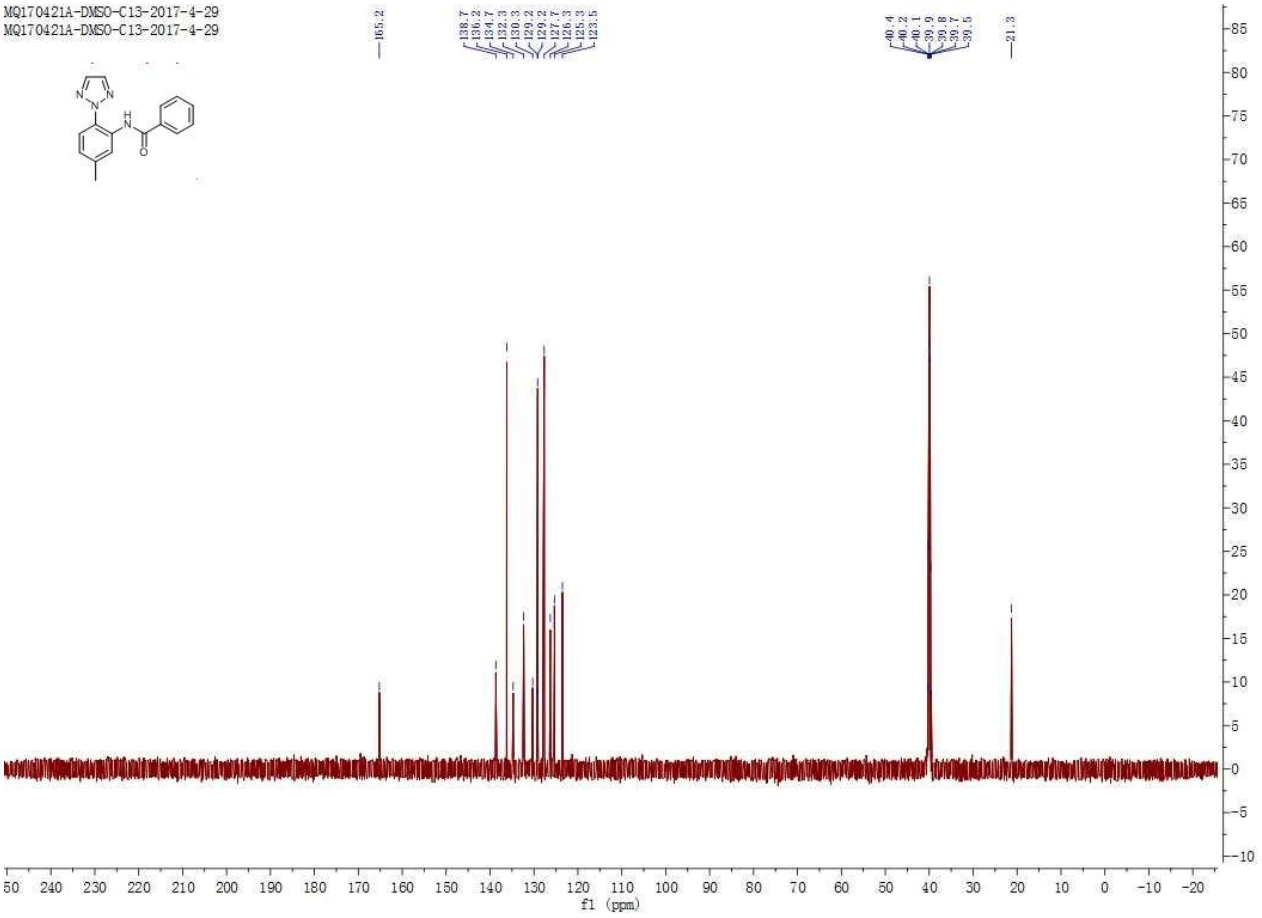


Figure 15. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3da'**.

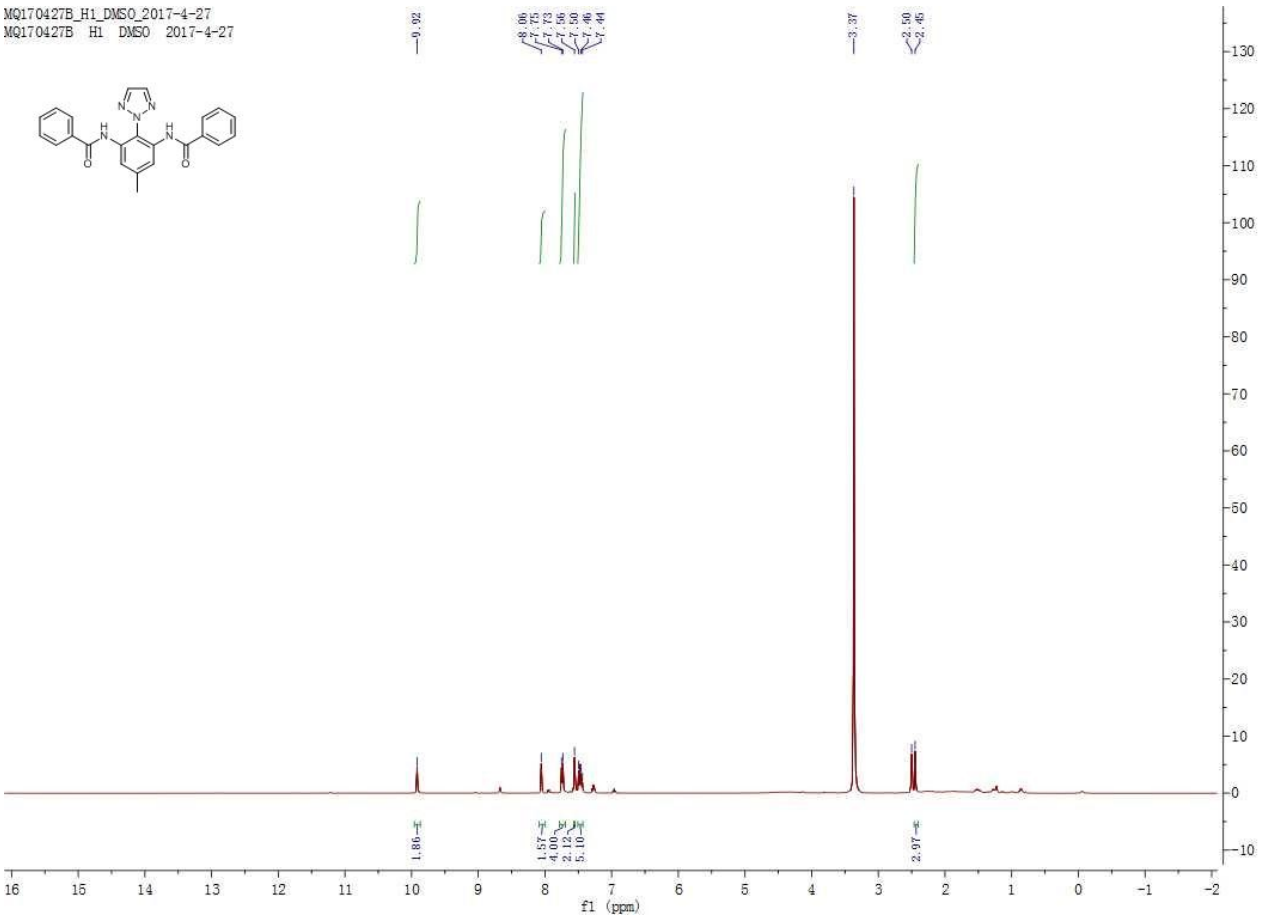


Figure 16. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3da'**.

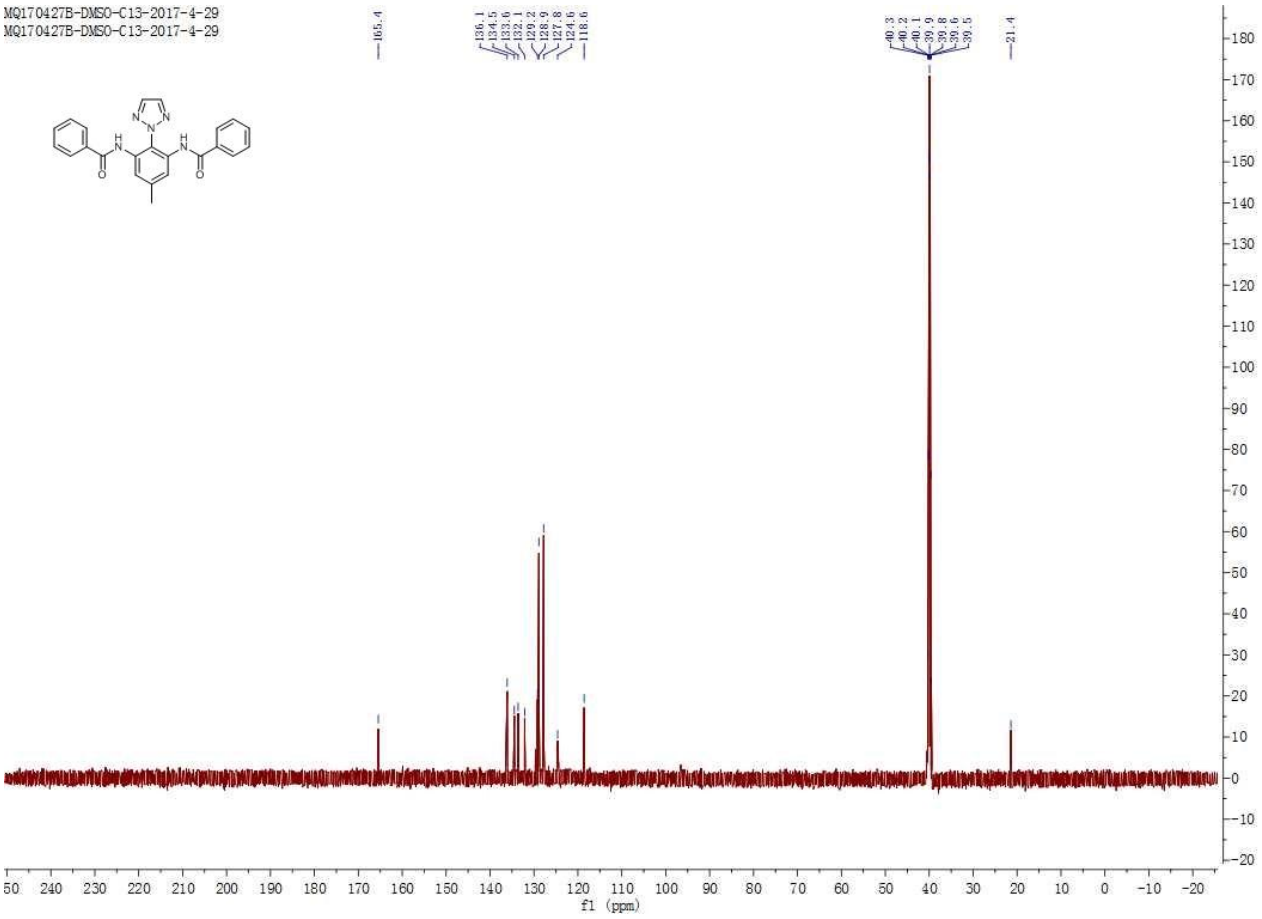


Figure 17. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ea**.

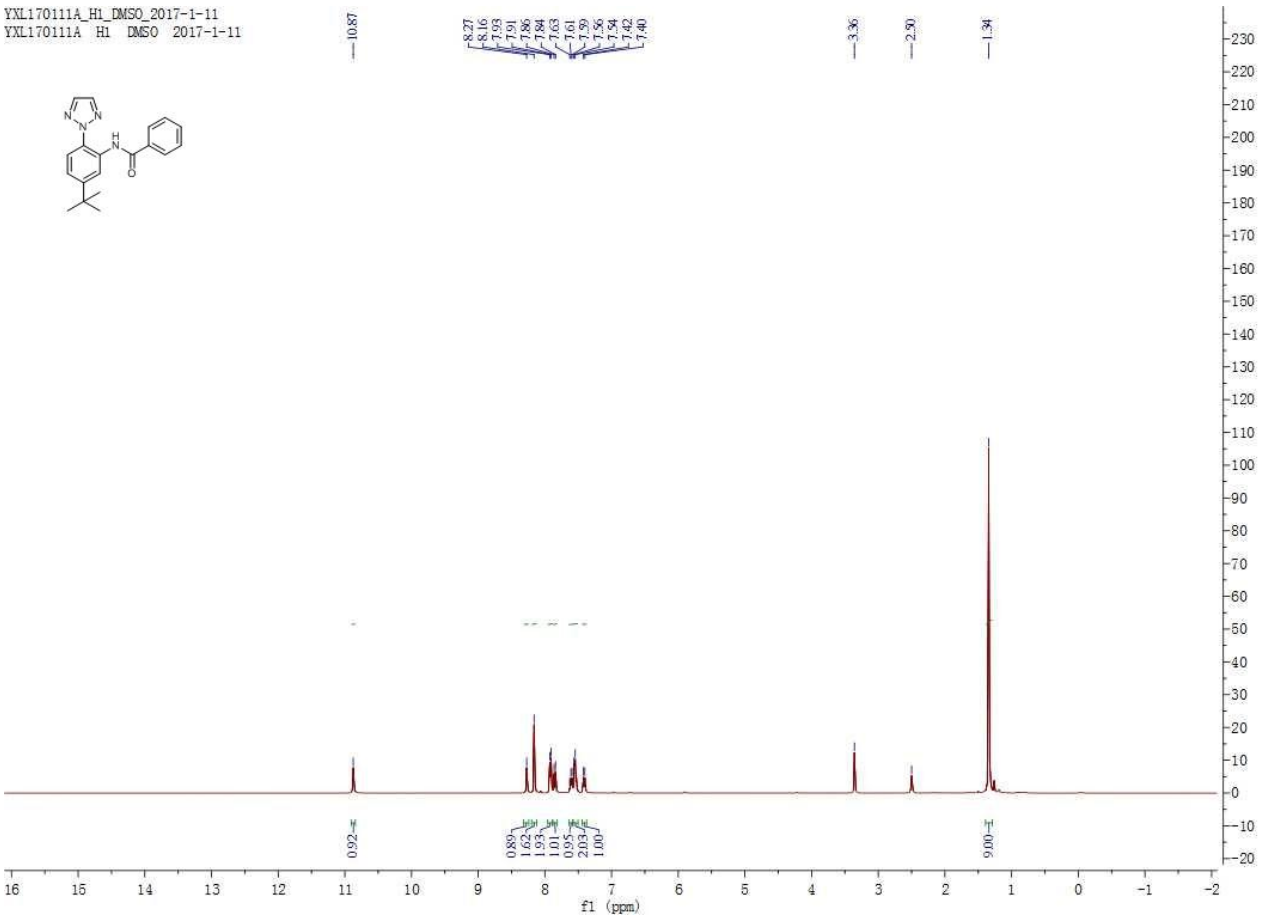


Figure 18. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ea**.

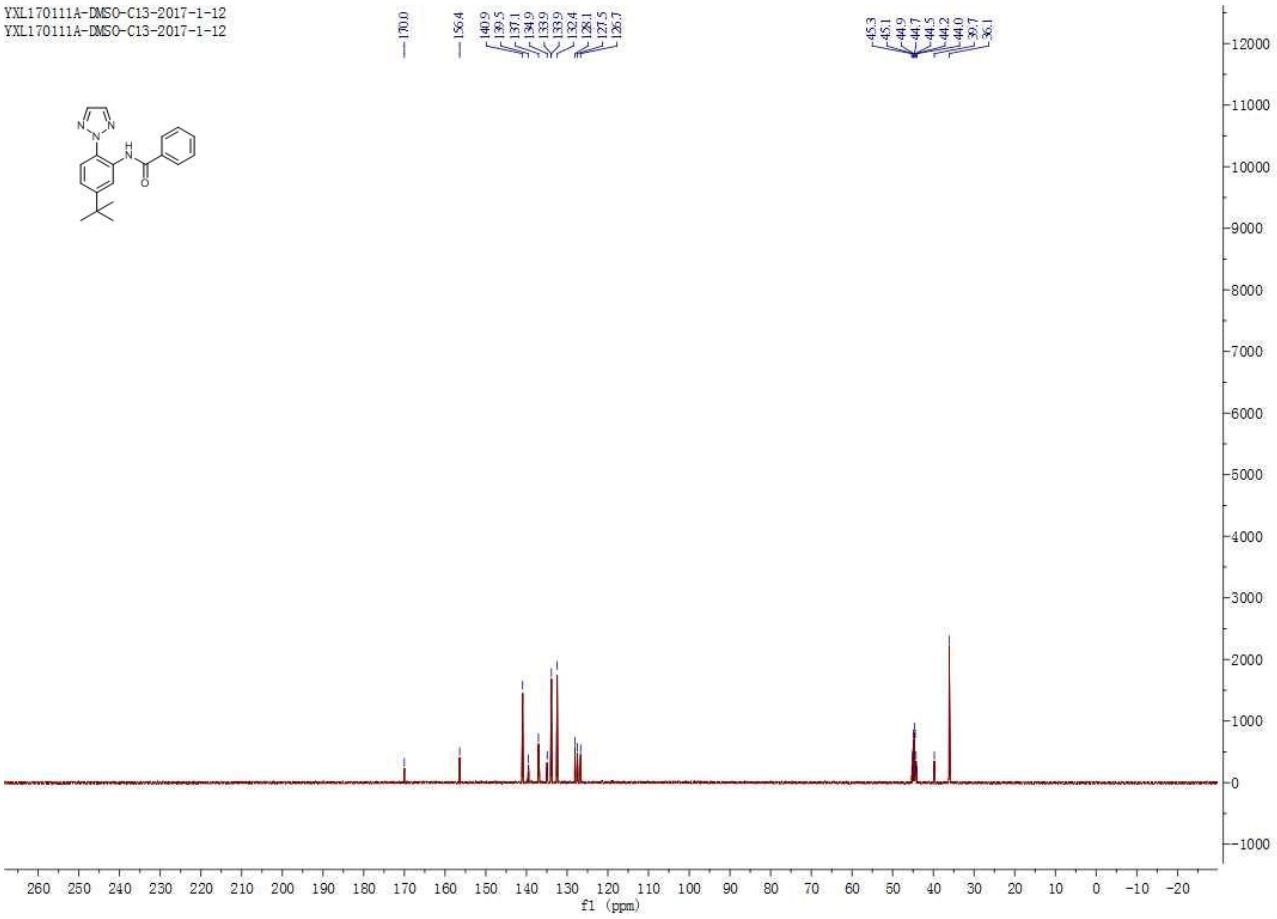


Figure 19. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ea'**.

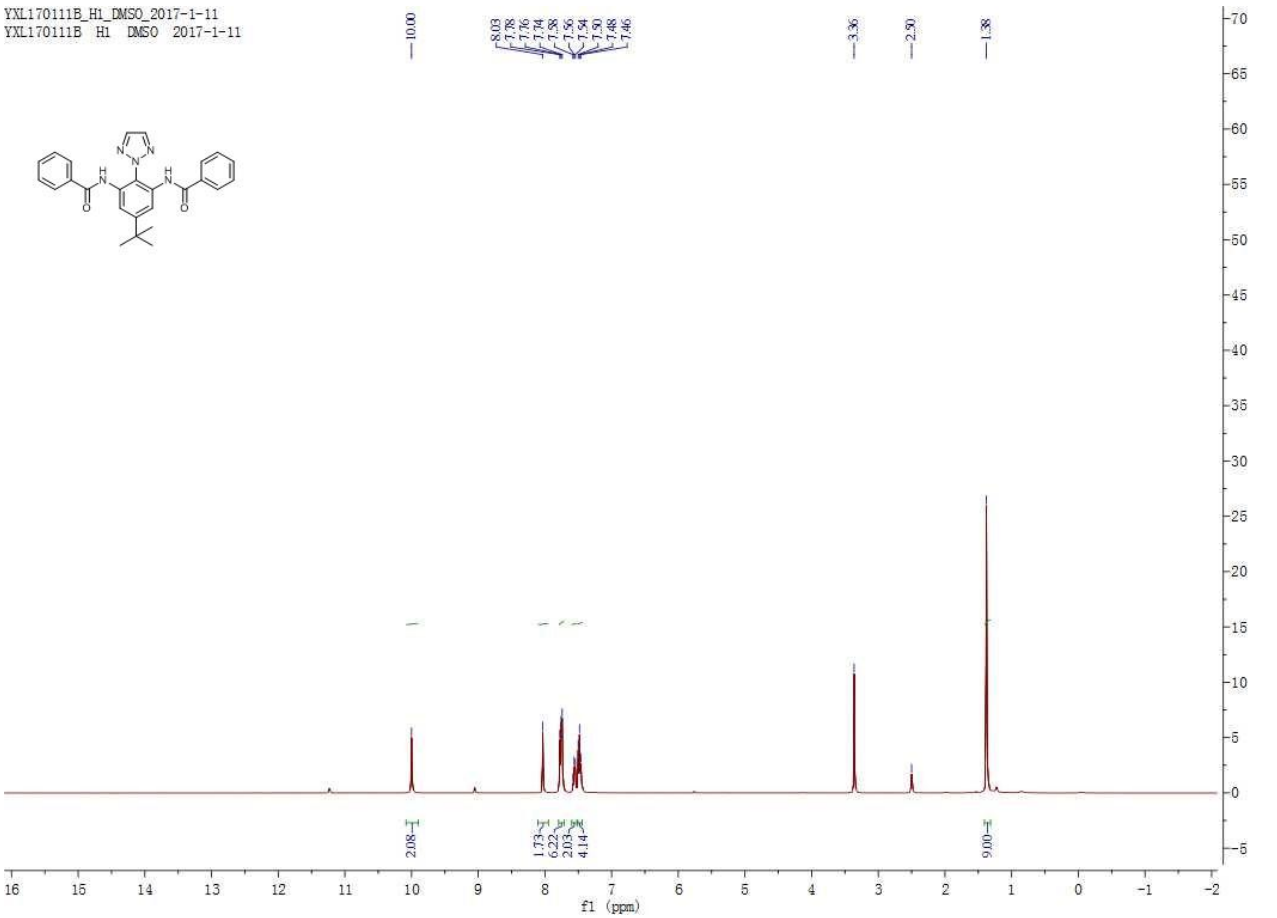


Figure 20. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ea'**.

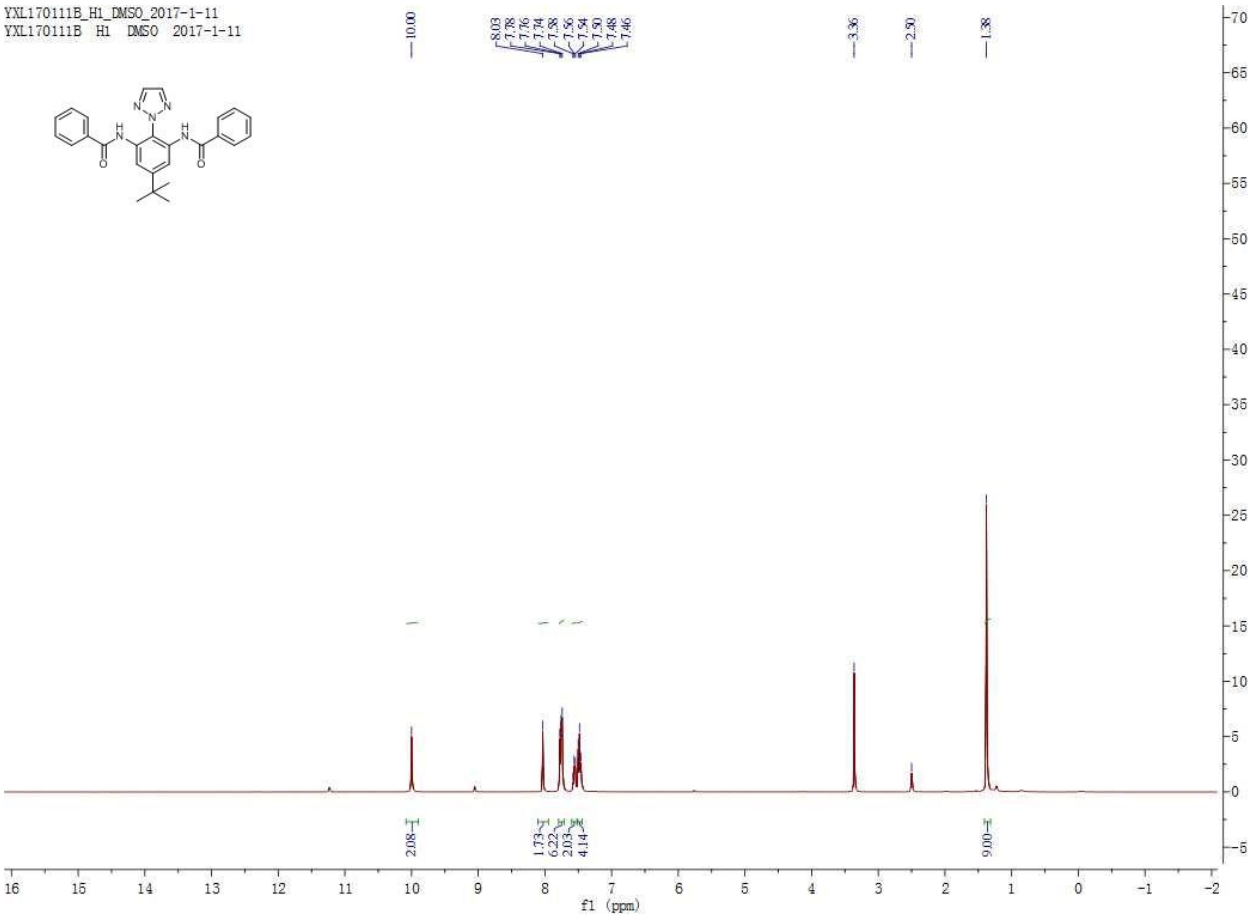


Figure 21. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3fa**.

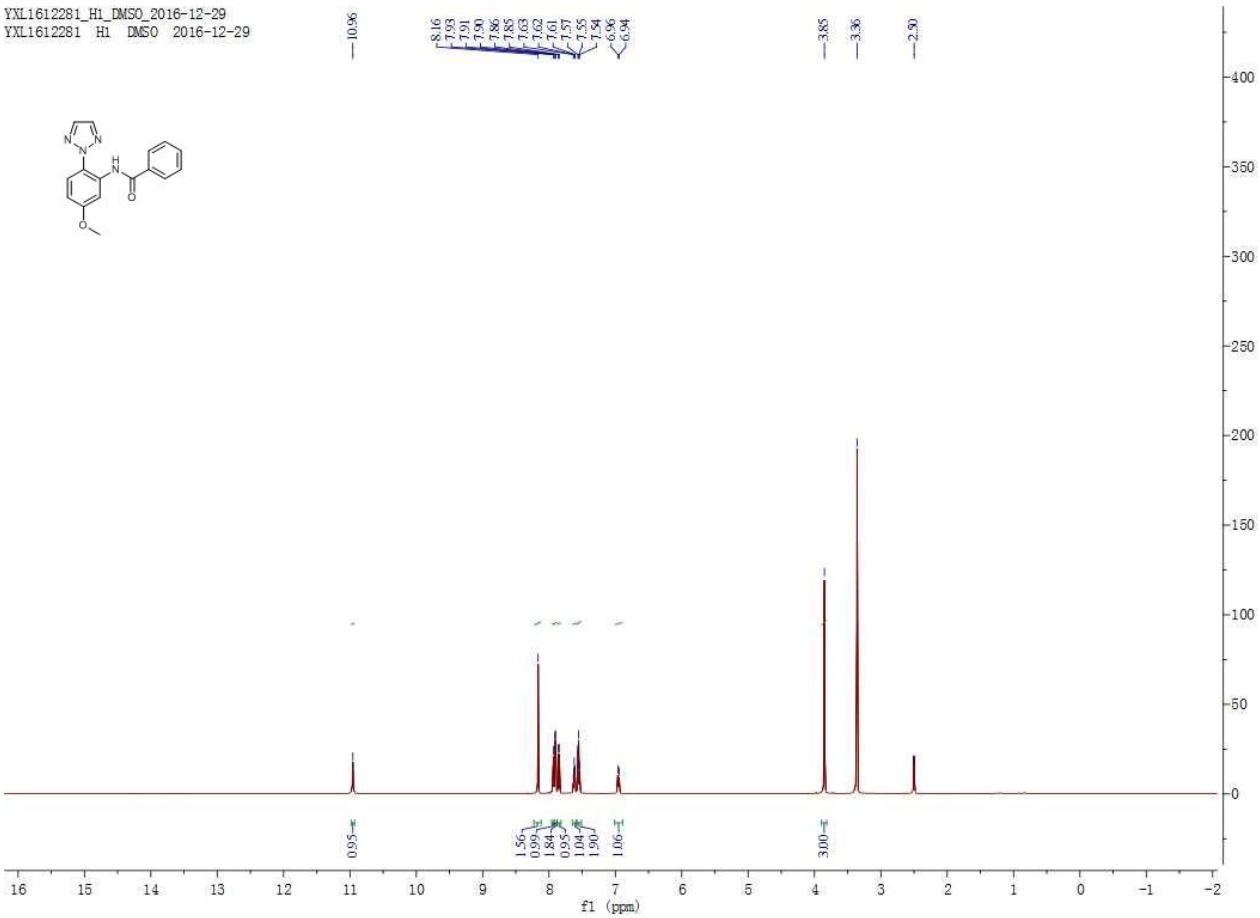


Figure 22. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3fa**.

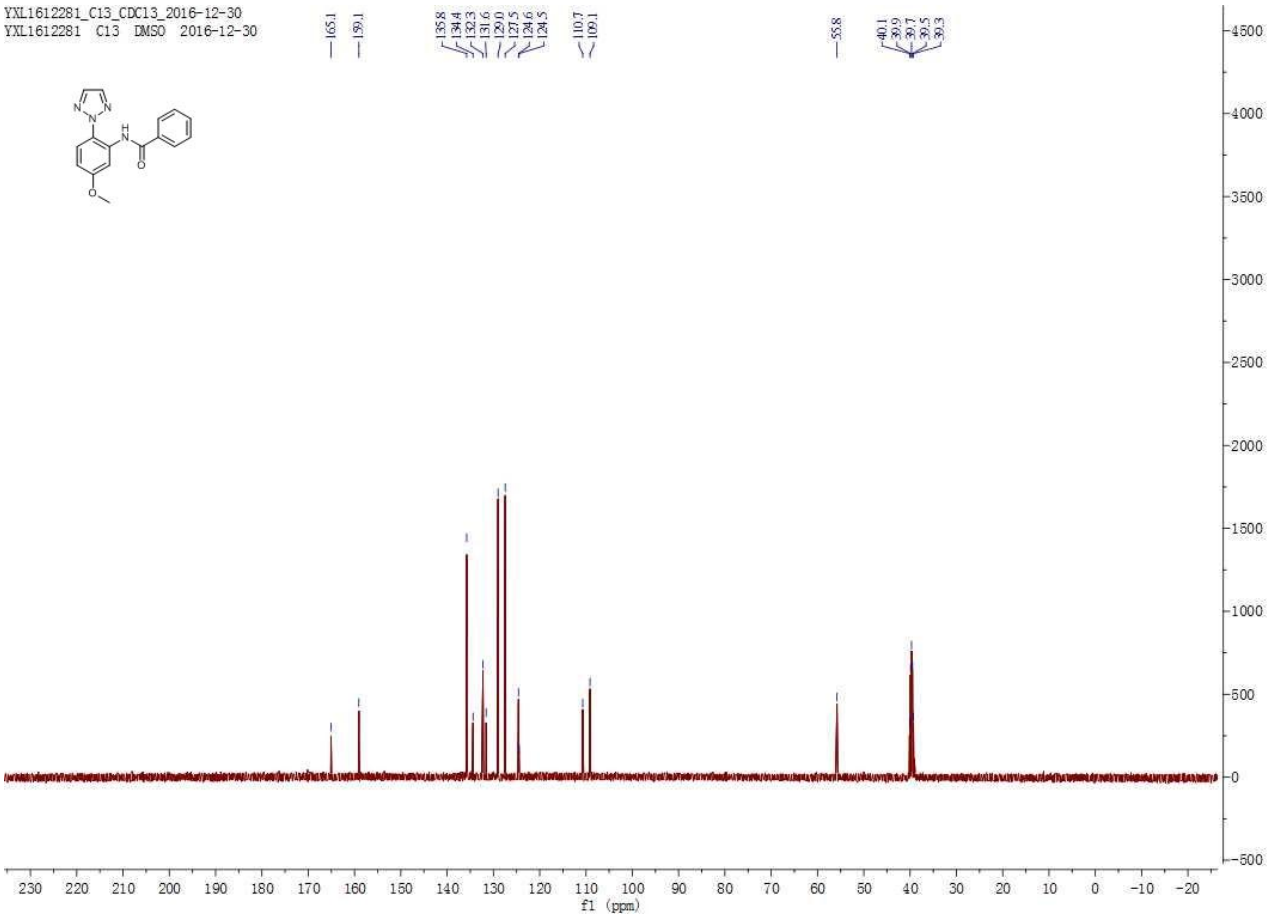


Figure 23. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3fa'**.

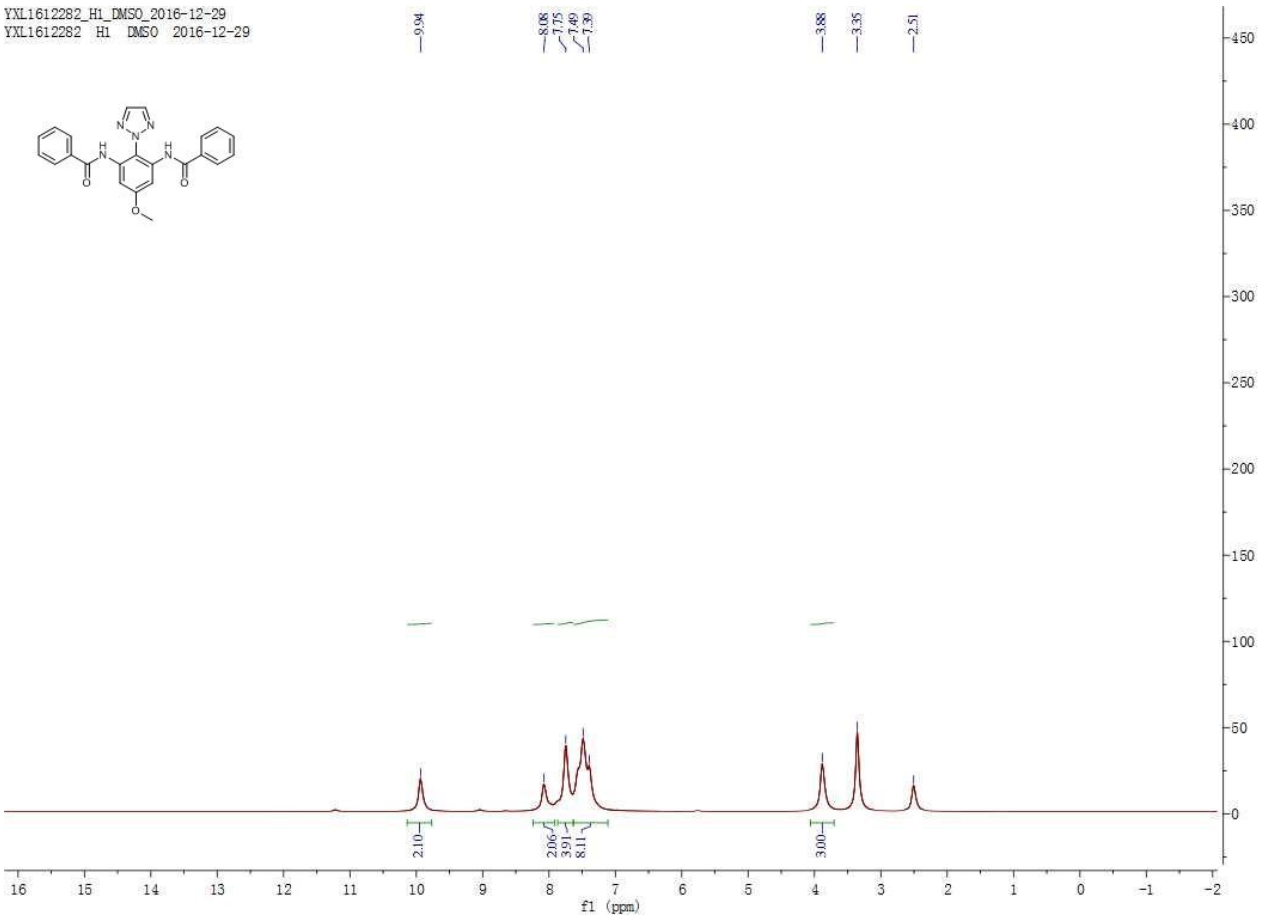


Figure 24. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3fa'**.

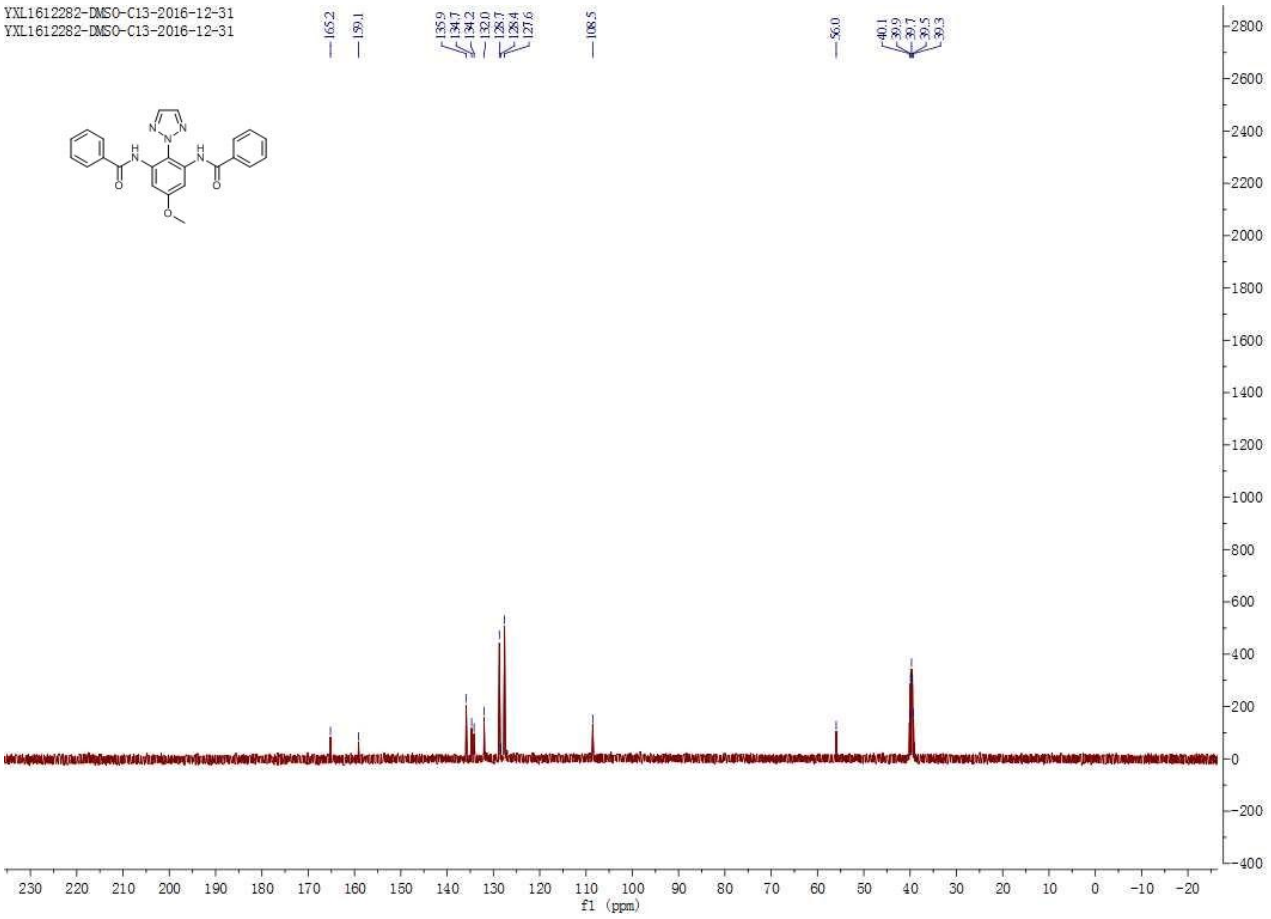


Figure 25. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ga**.

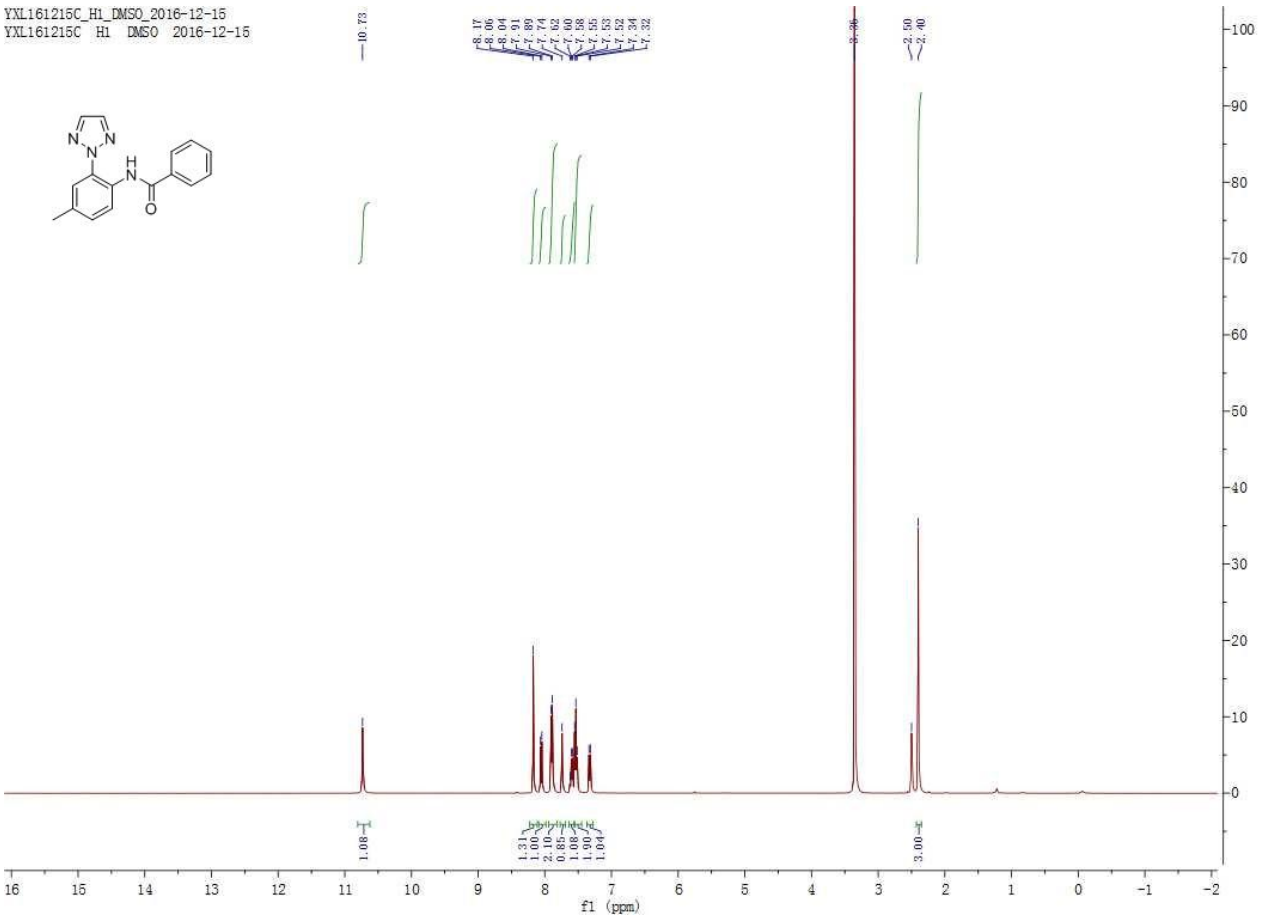


Figure 26. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ga**.

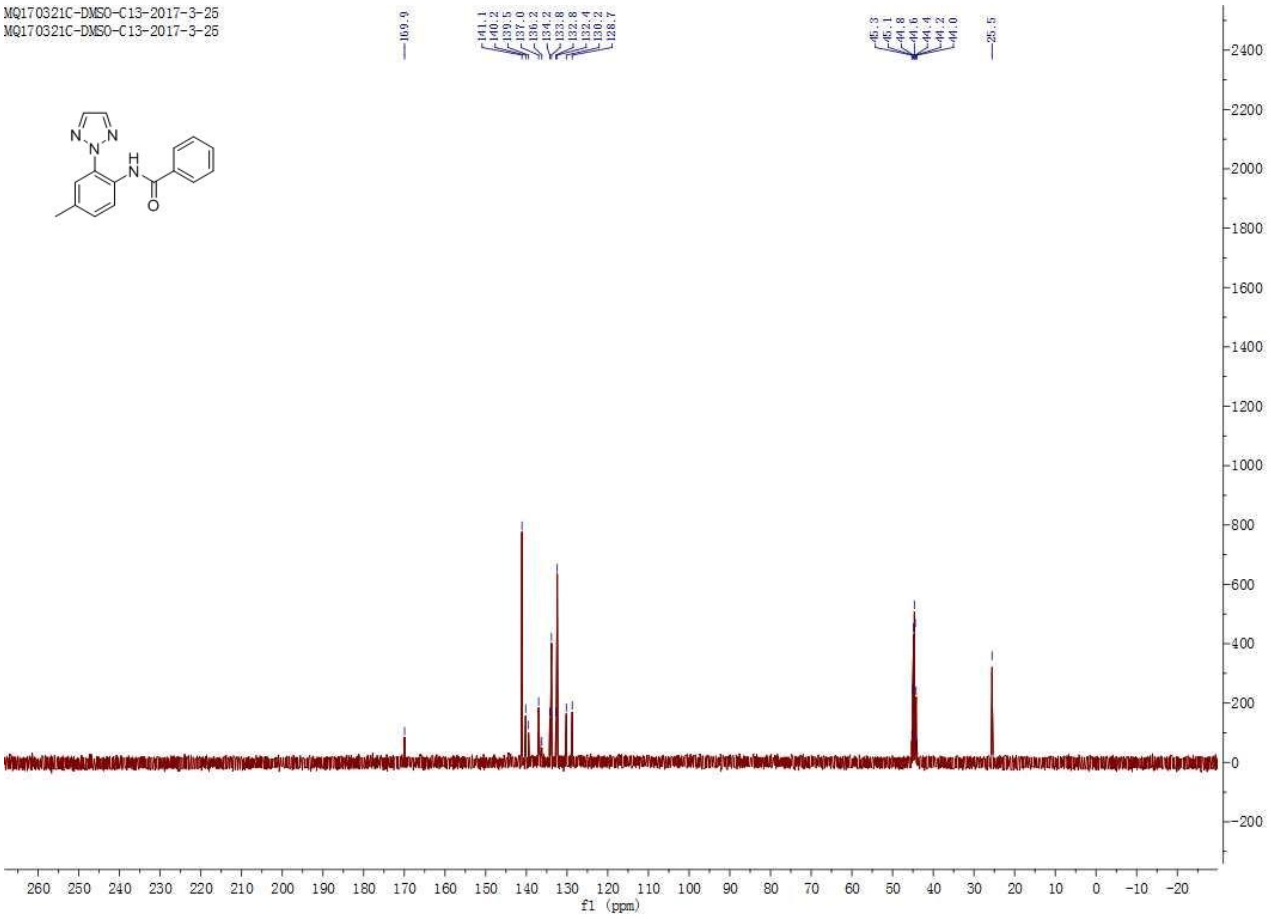


Figure 27. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ha**.

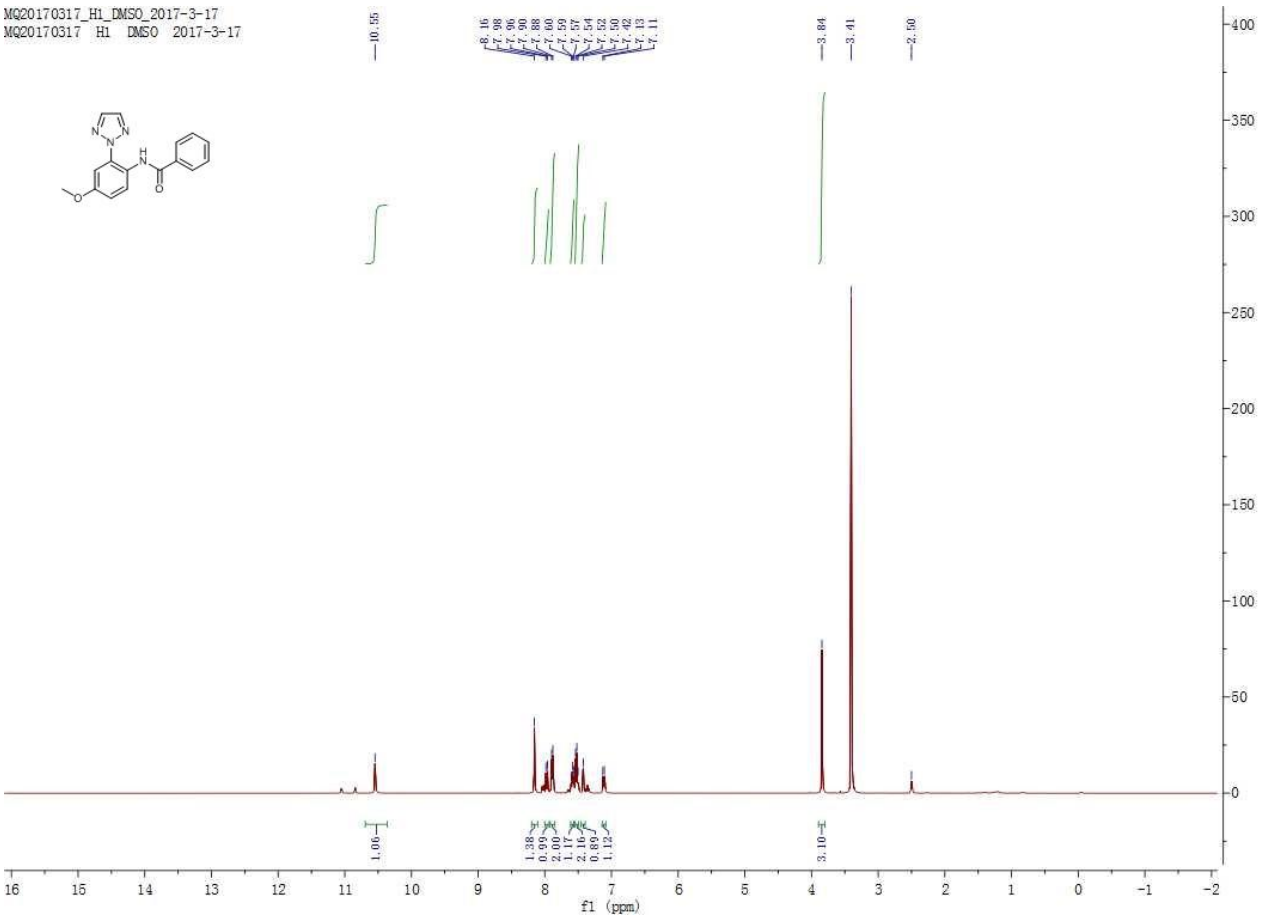


Figure 28. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ha**.

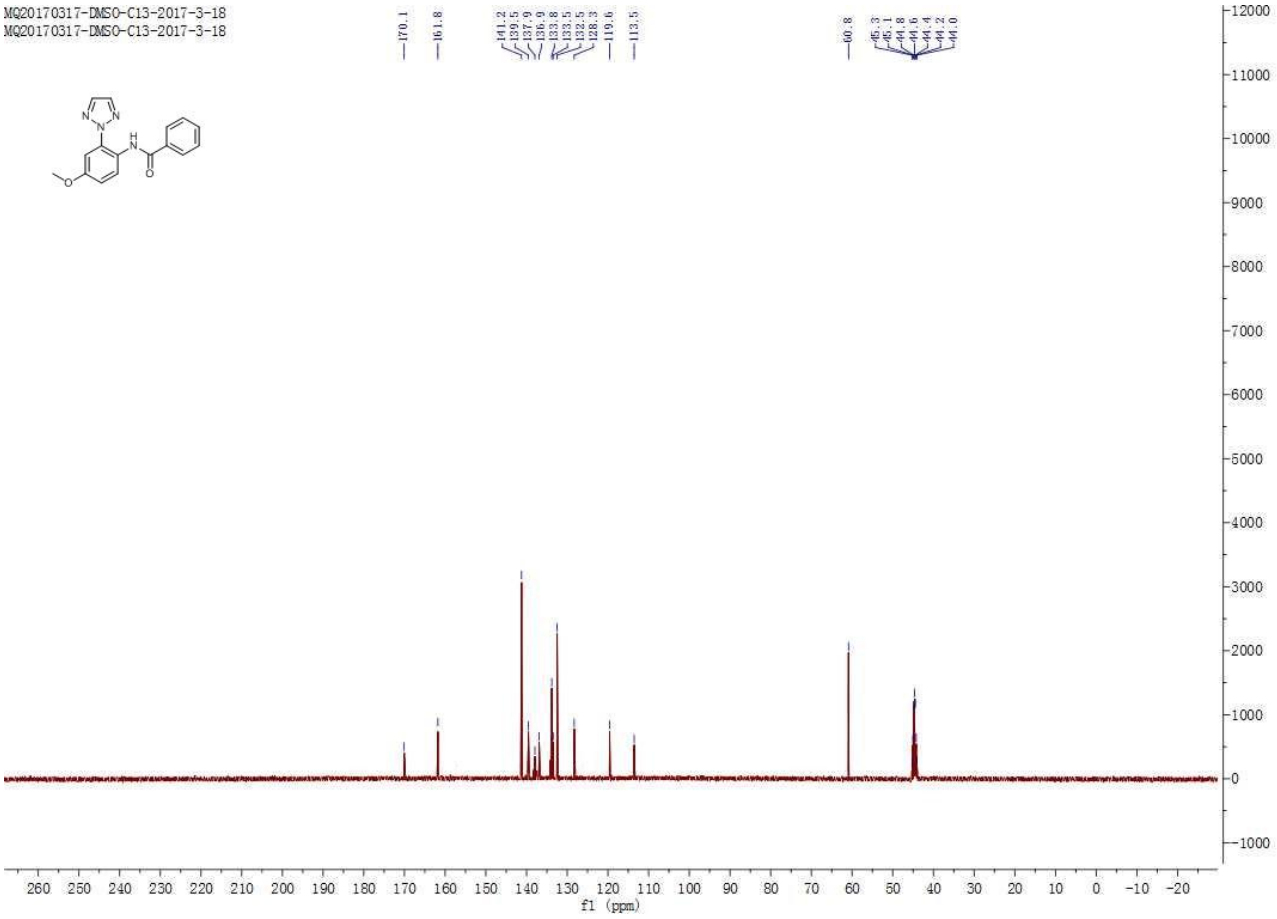


Figure 29. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ia**.

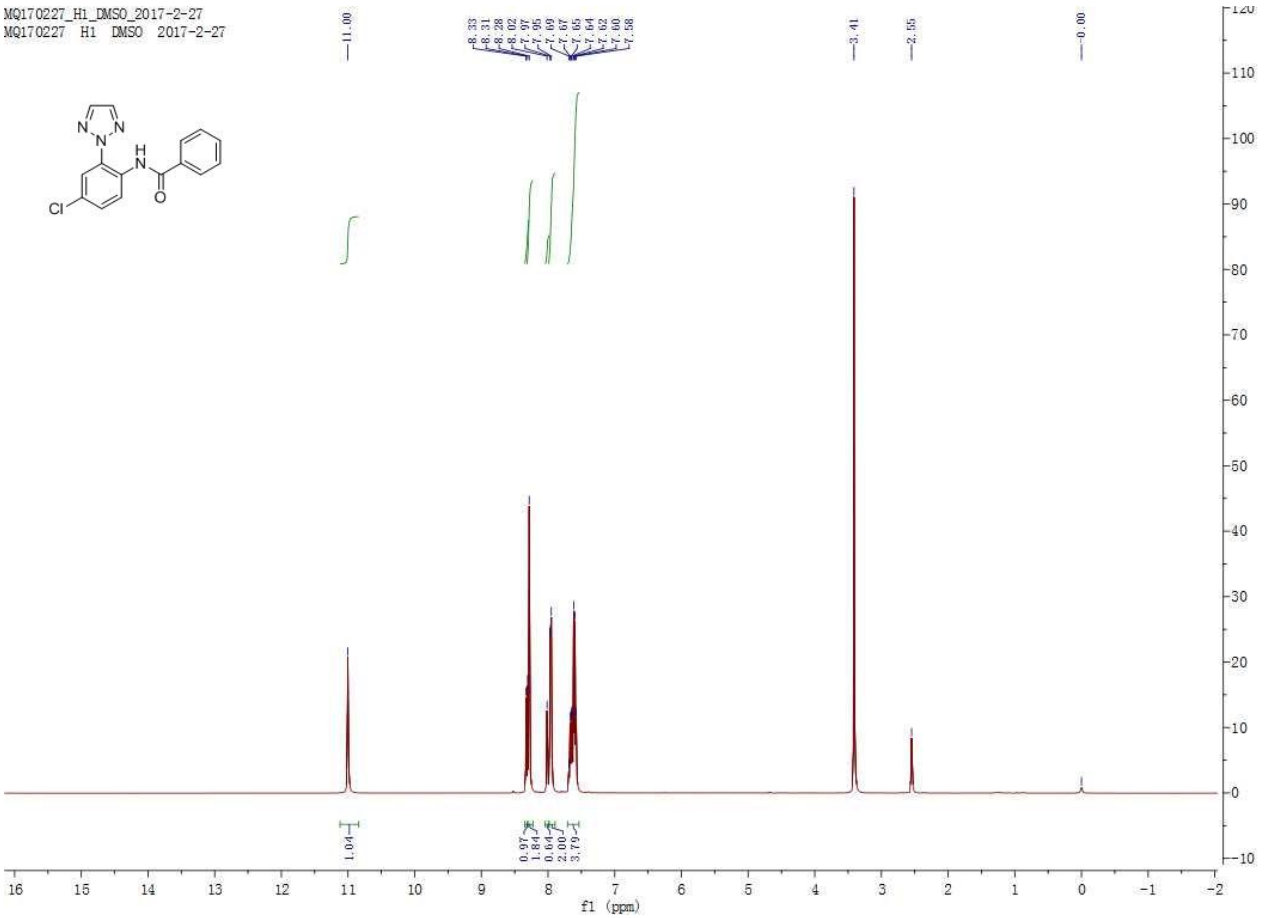


Figure 30. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ia**.

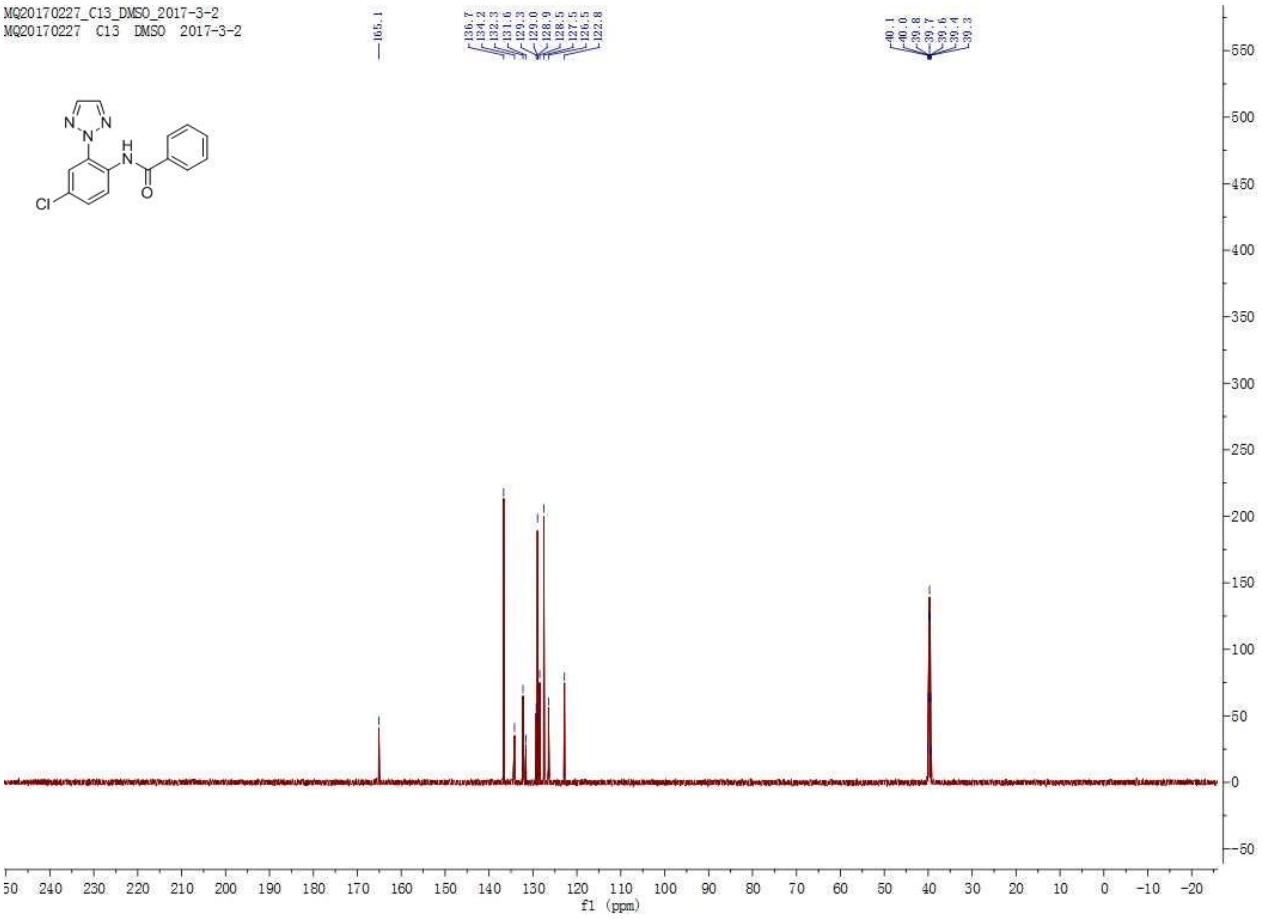


Figure 31. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ja**.

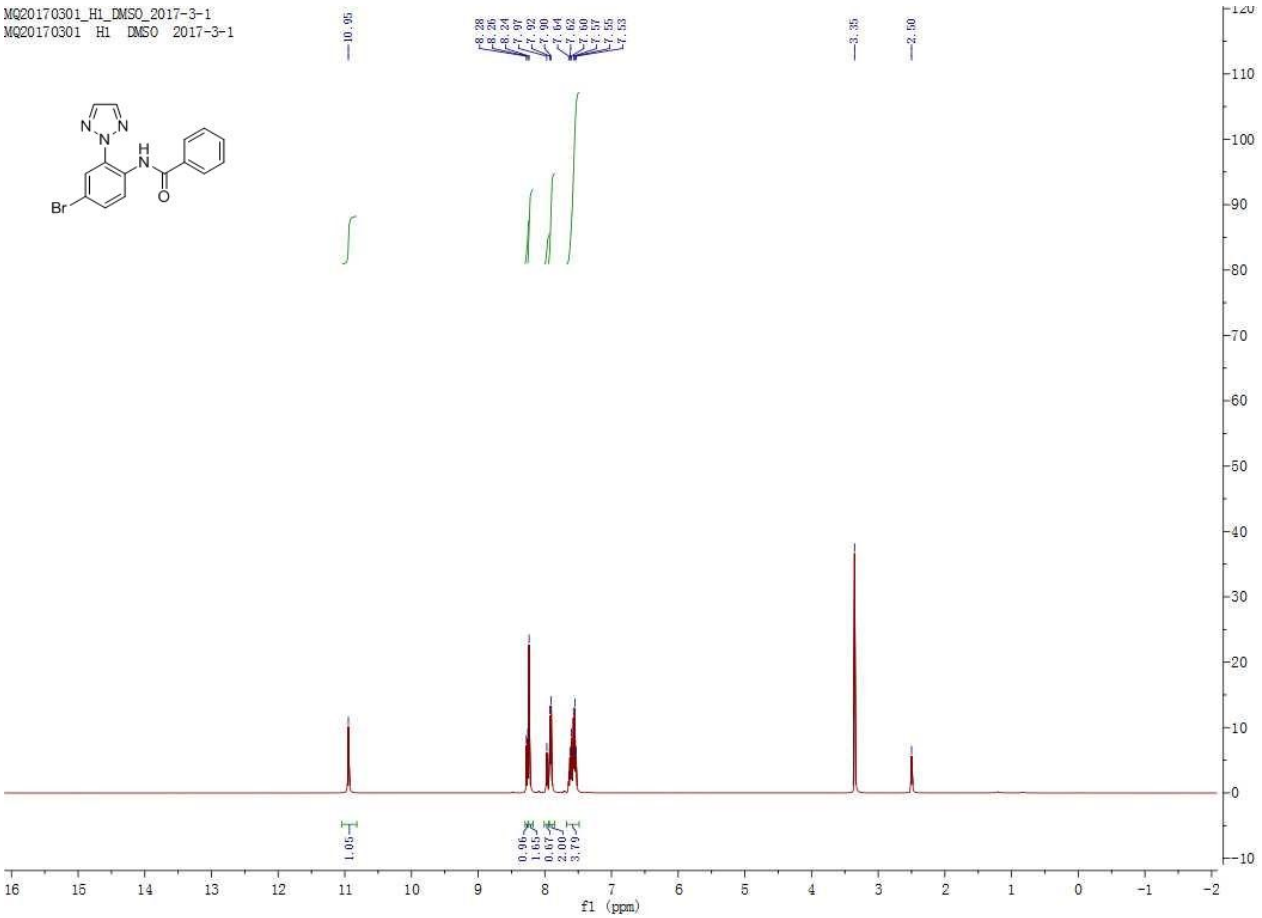


Figure 32. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ja**.

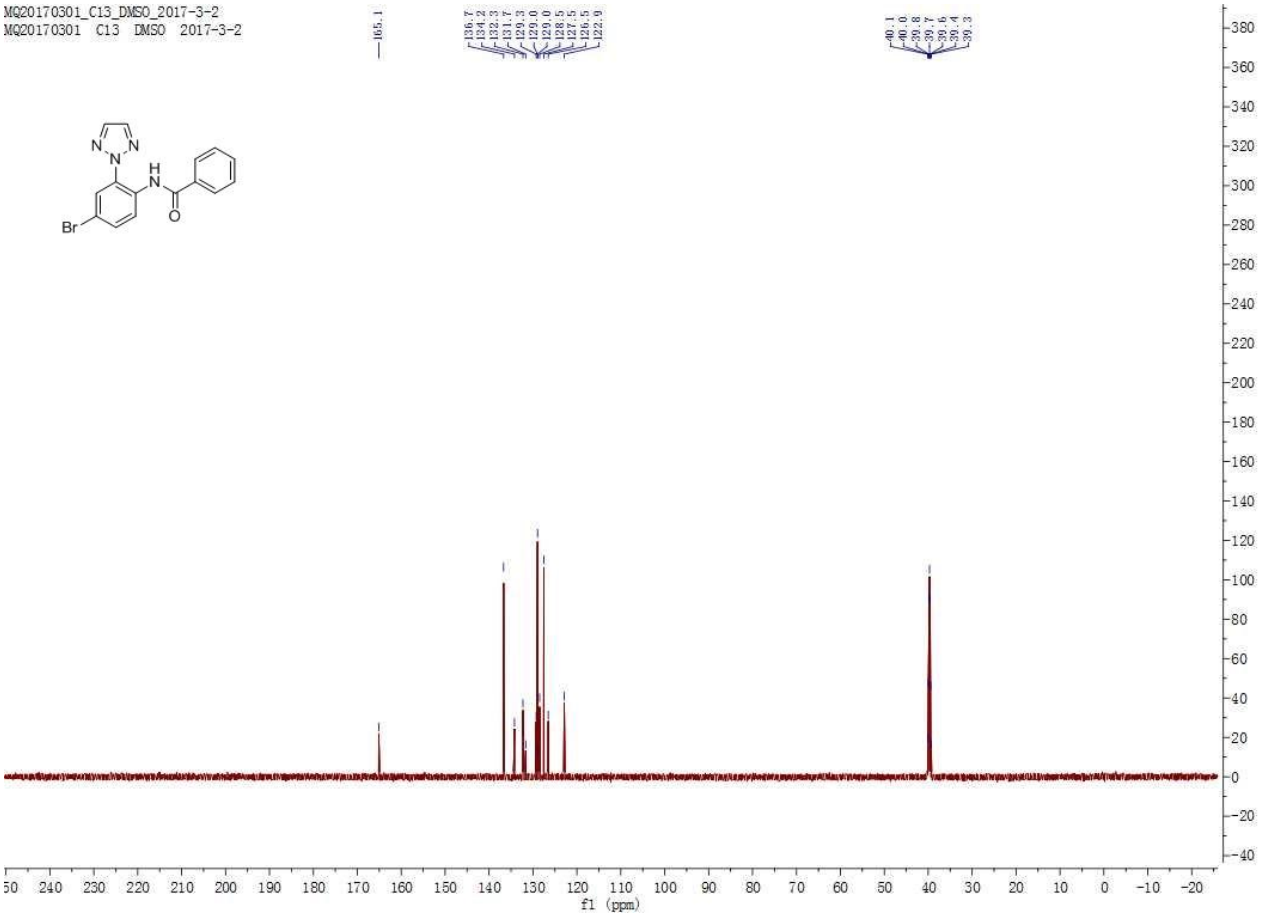


Figure 33. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ka**.

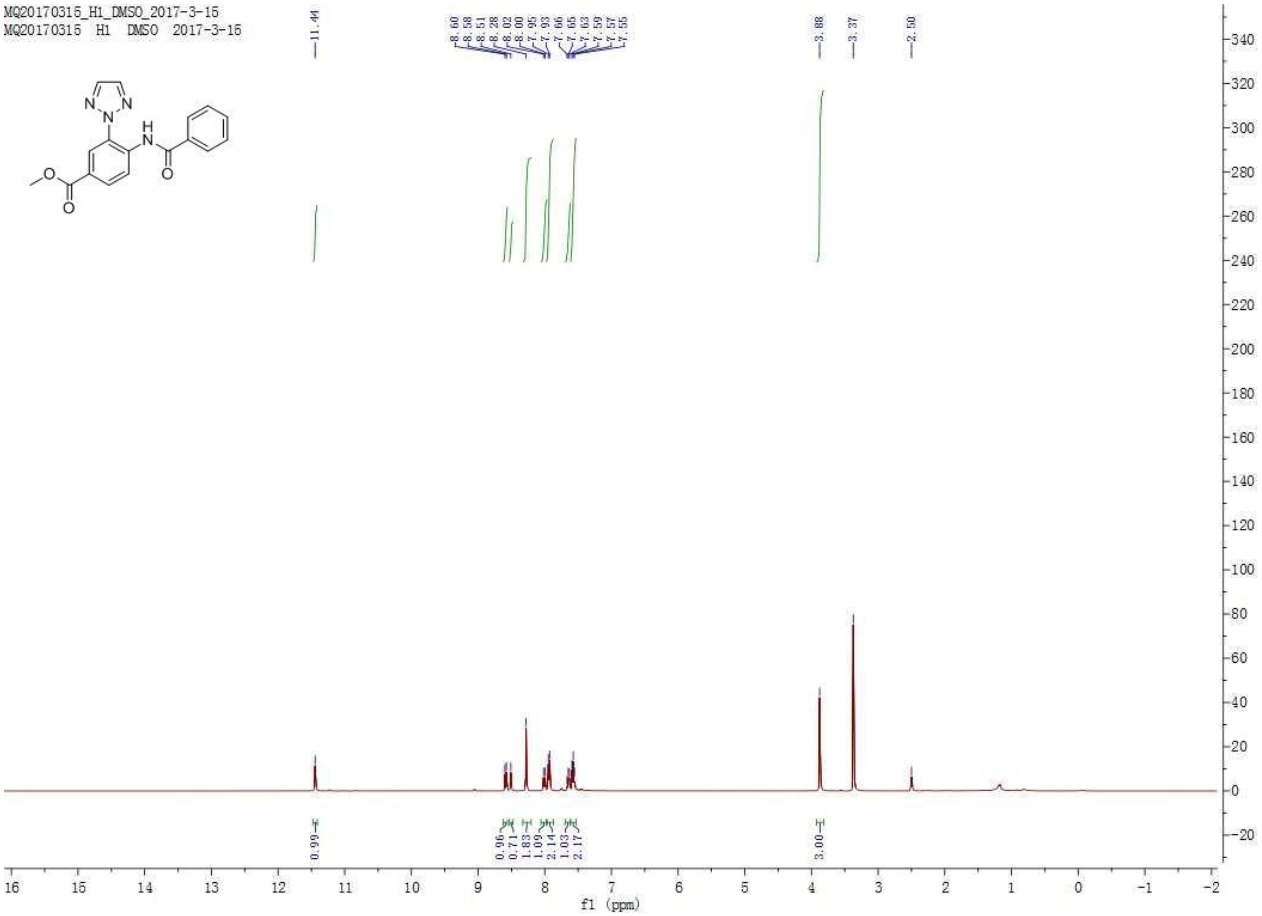


Figure 34. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ka**.

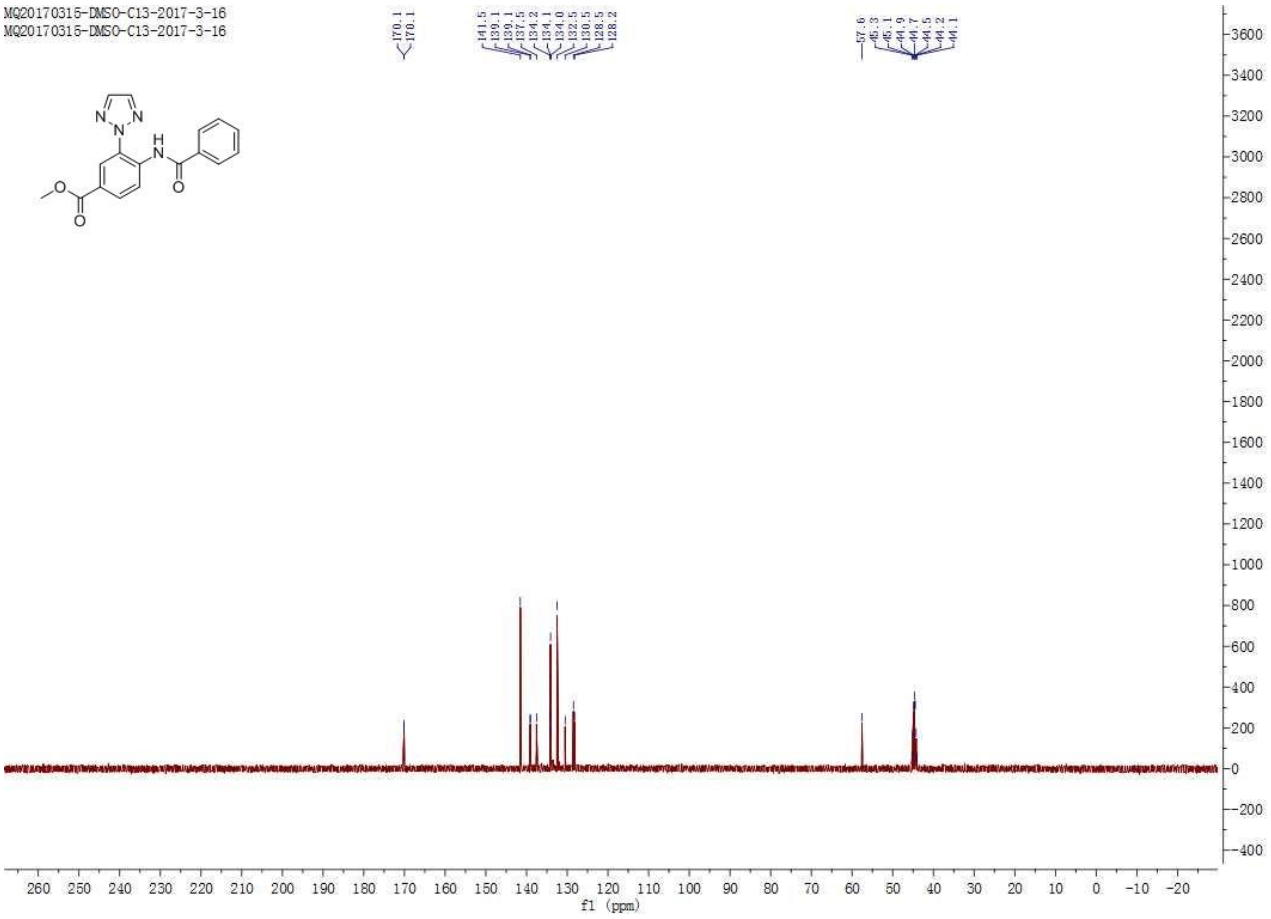


Figure 35. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3la**.

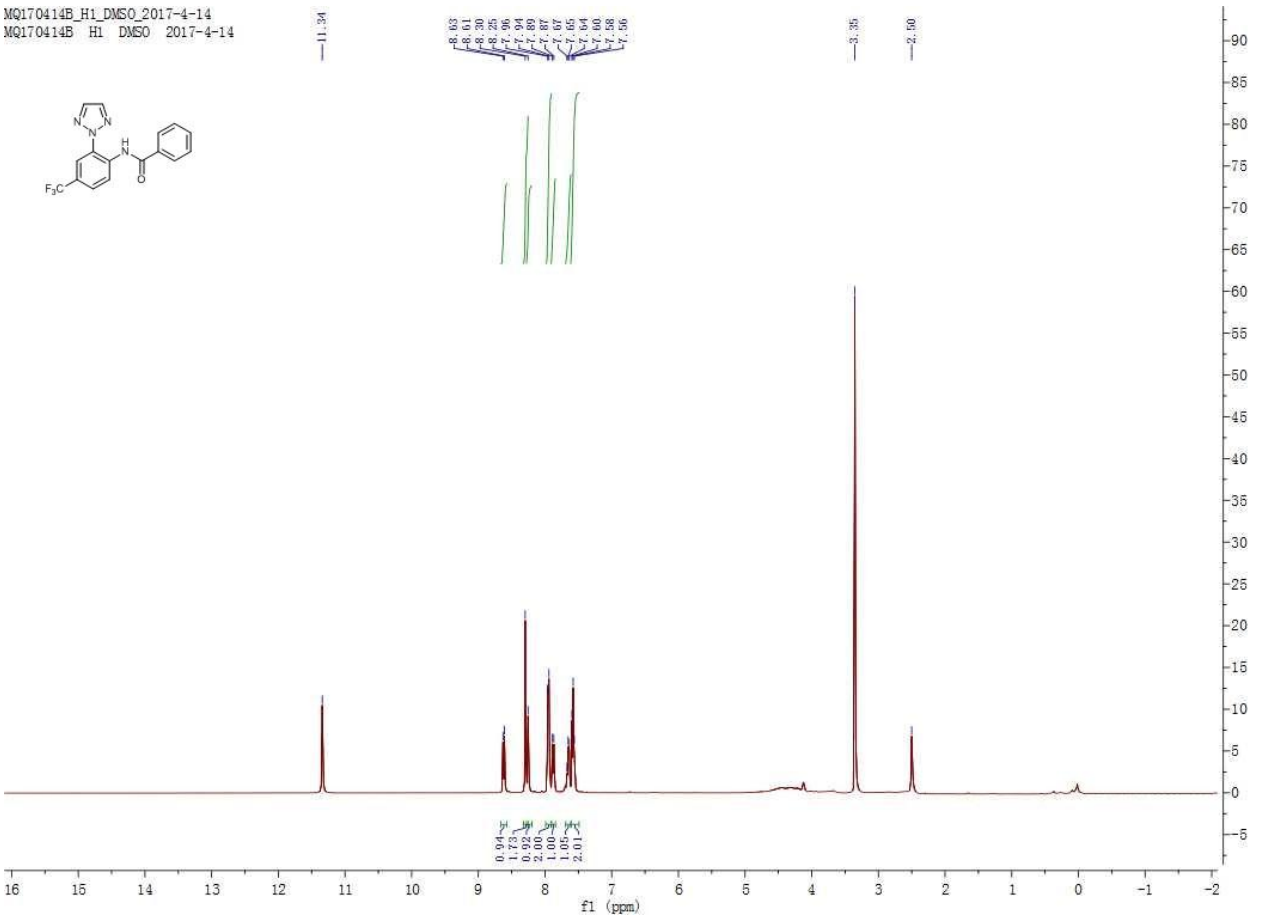


Figure 36. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3la**.

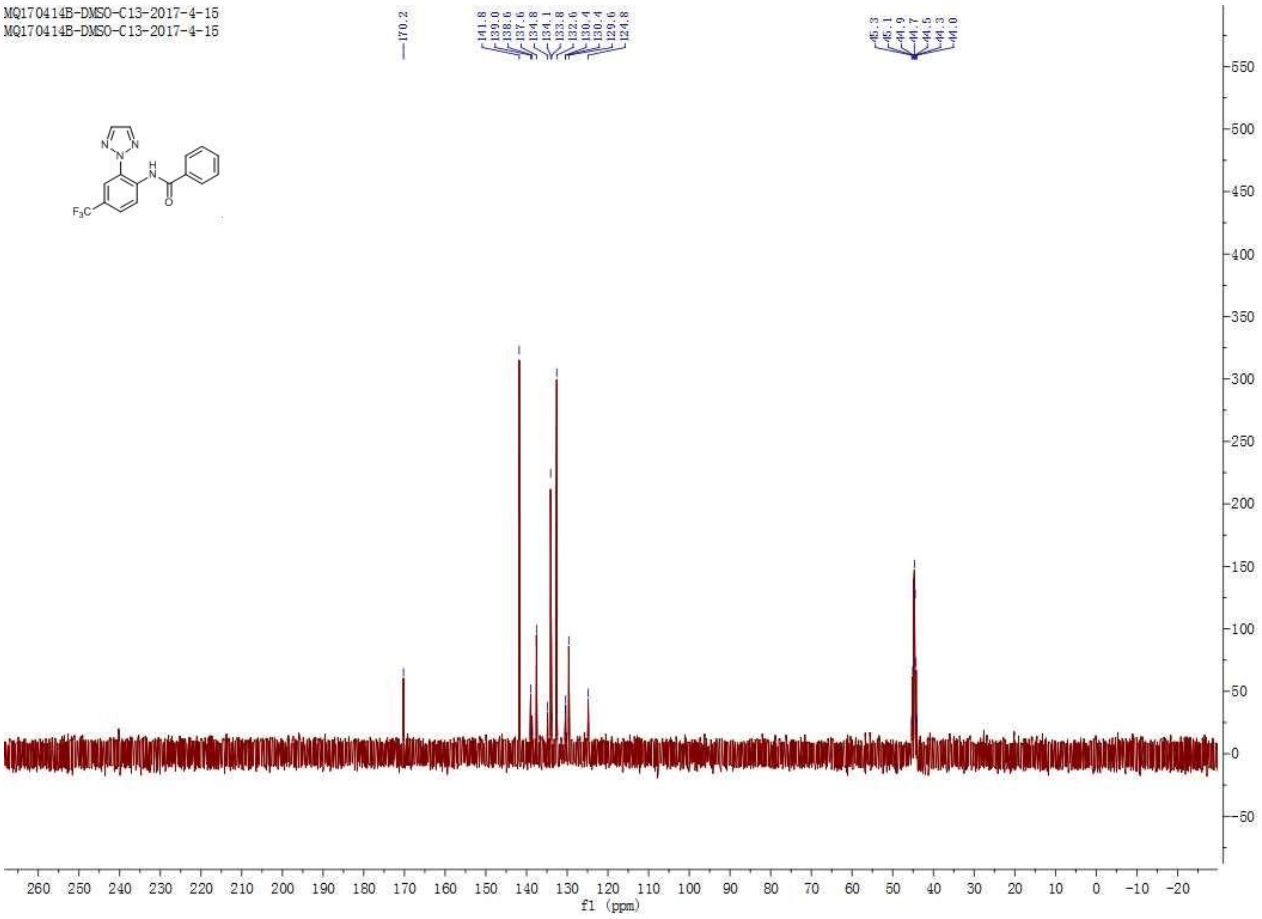


Figure 37. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ma**.

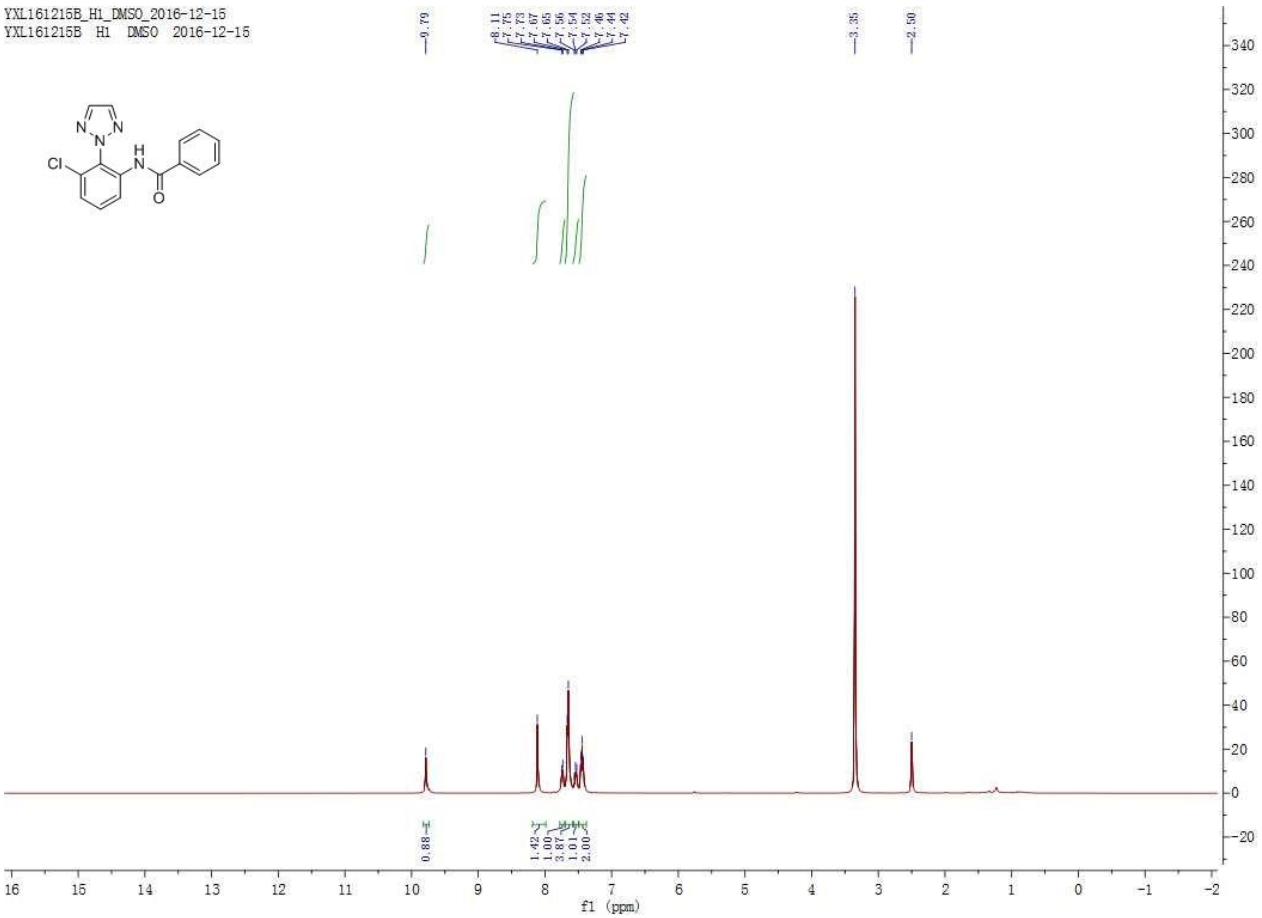


Figure 38. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ma**.

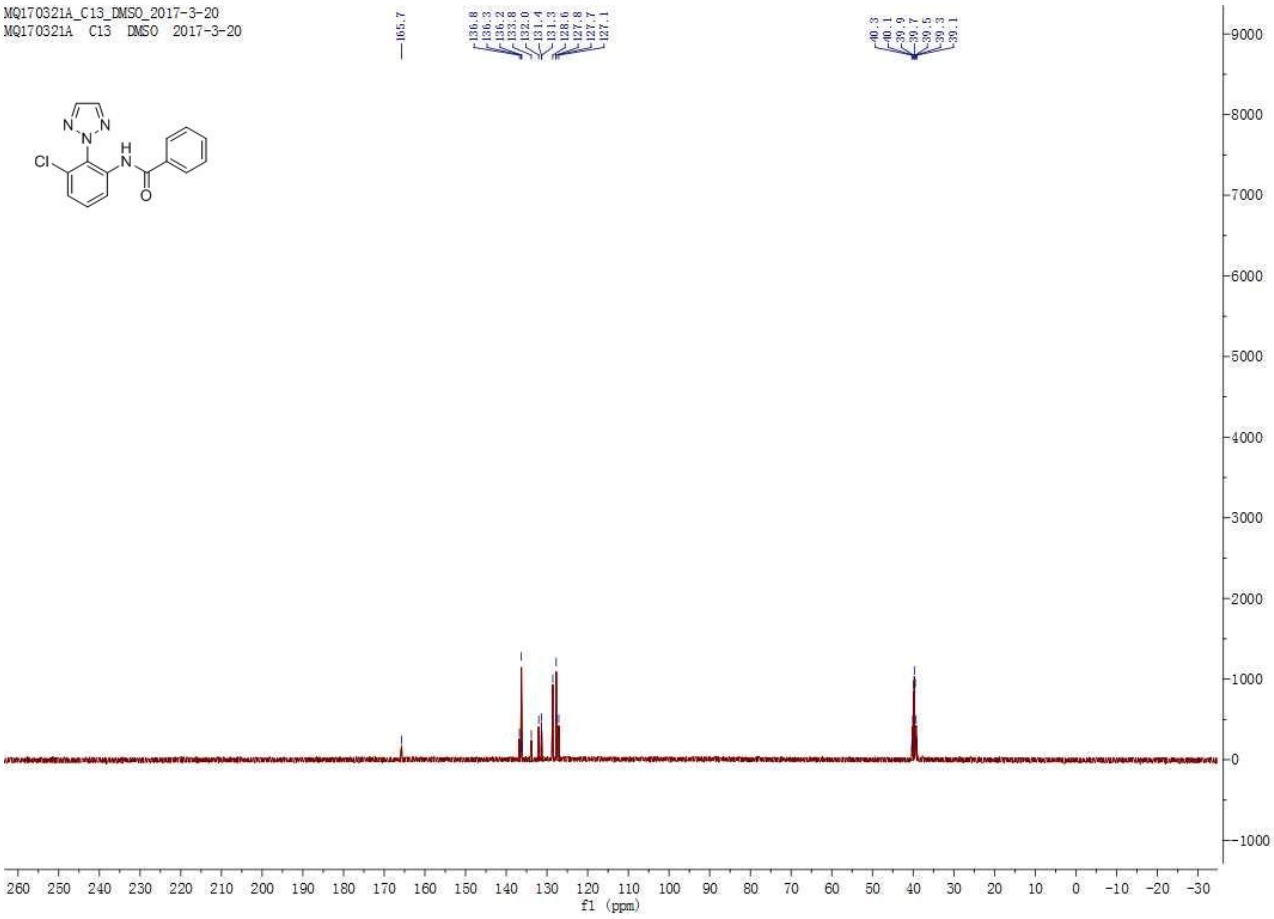


Figure 39. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3na**.

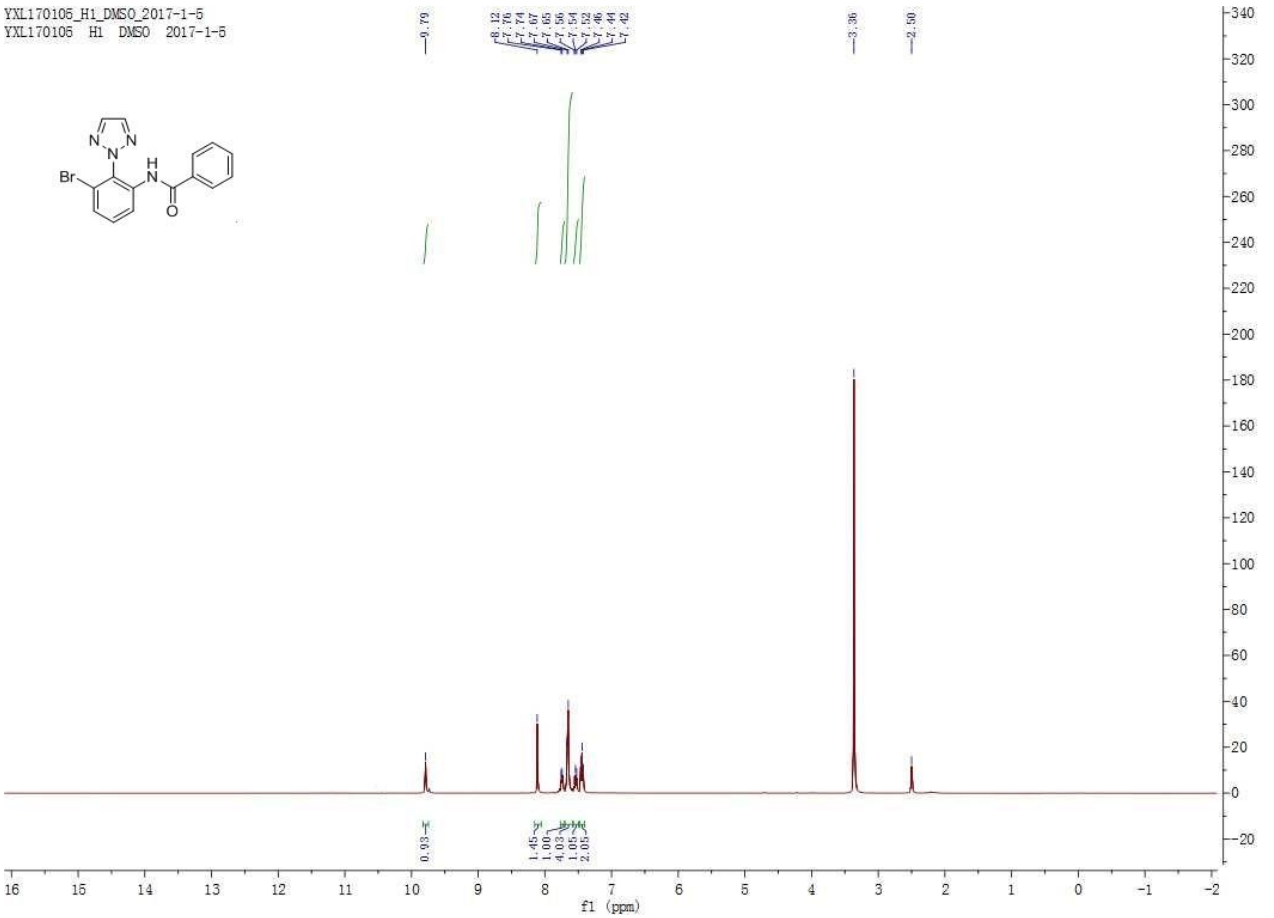


Figure 40. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3na**.

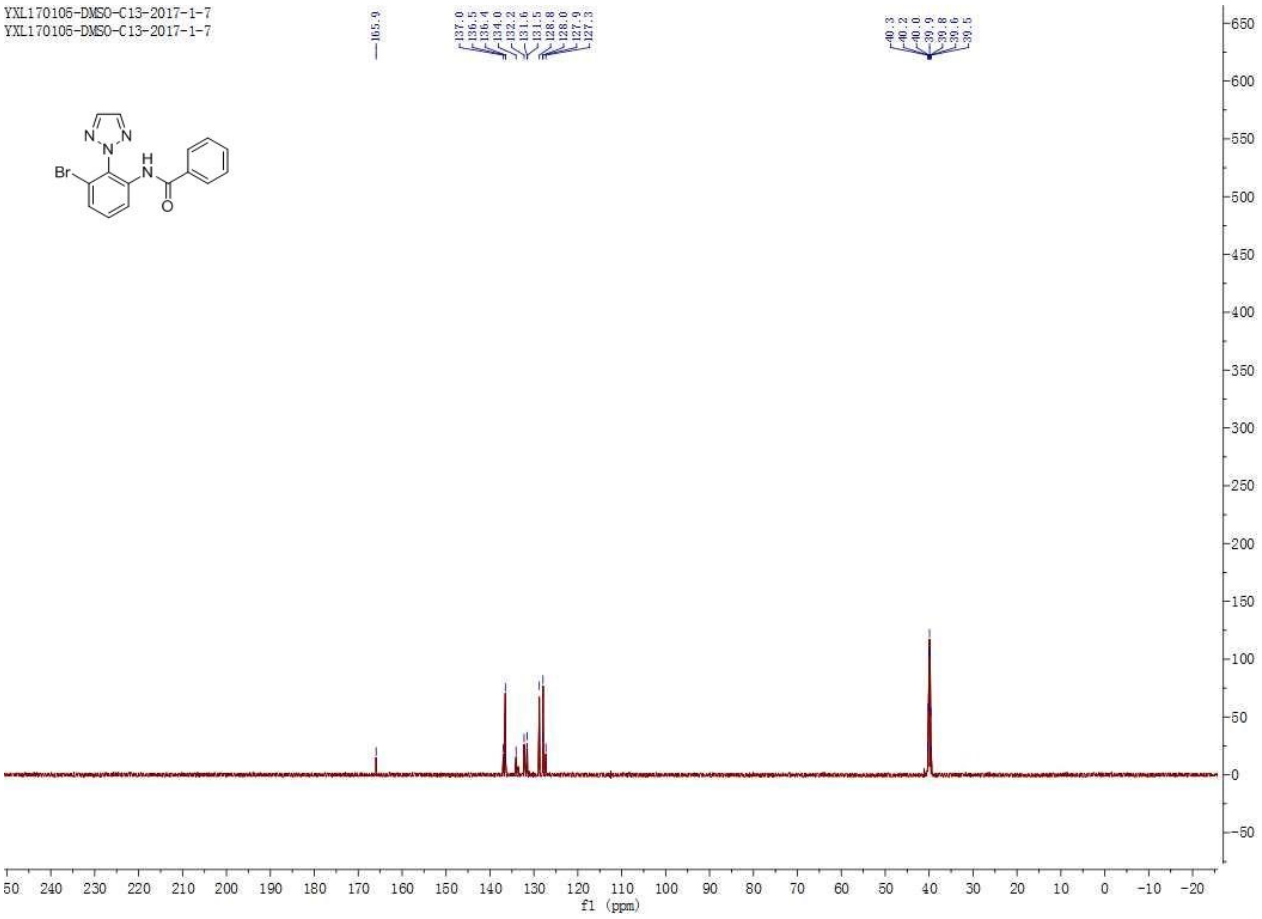


Figure 41. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3oa**.

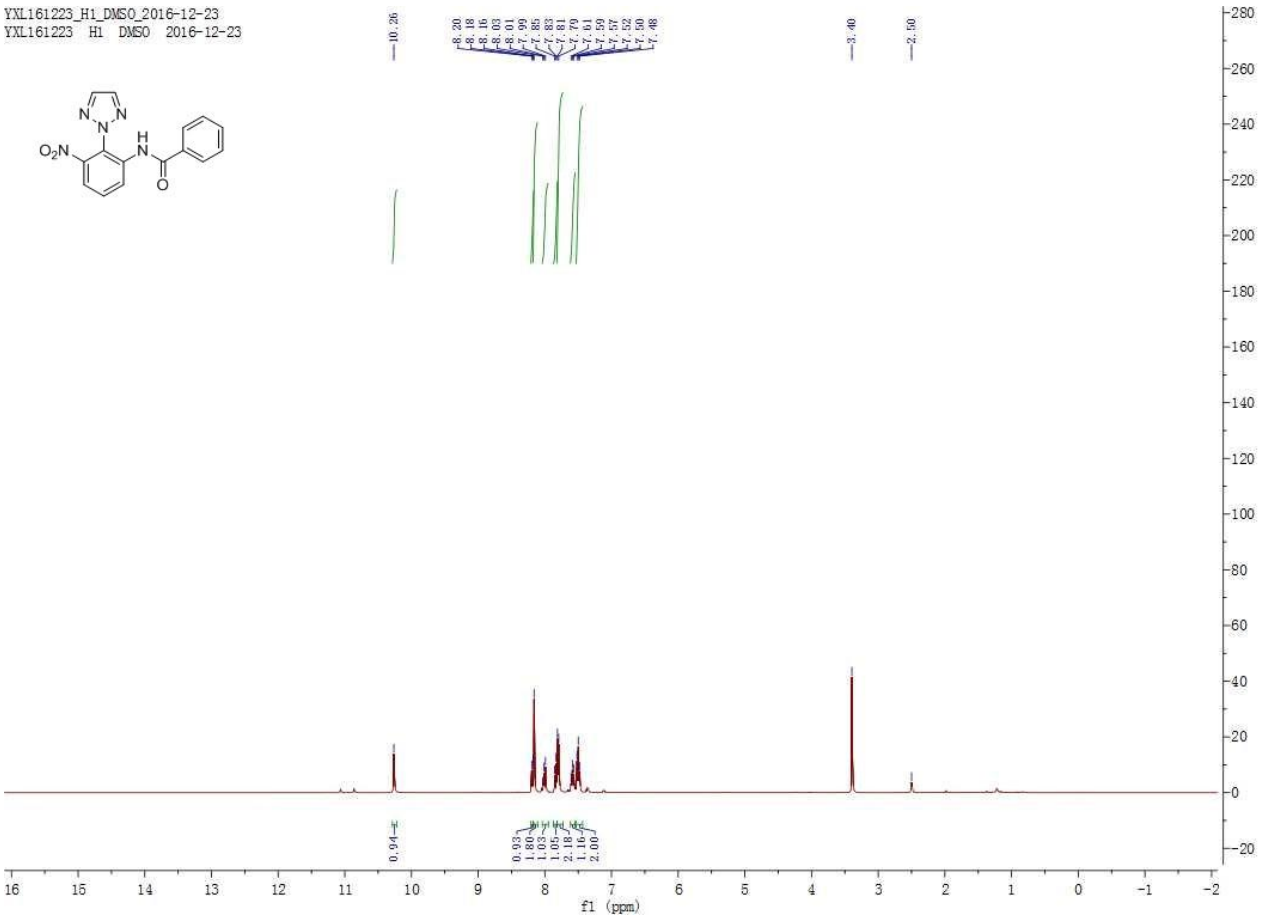


Figure 42. The ^{13}C NMR (100 MHz, $CDCl_3$) of **3oa**.

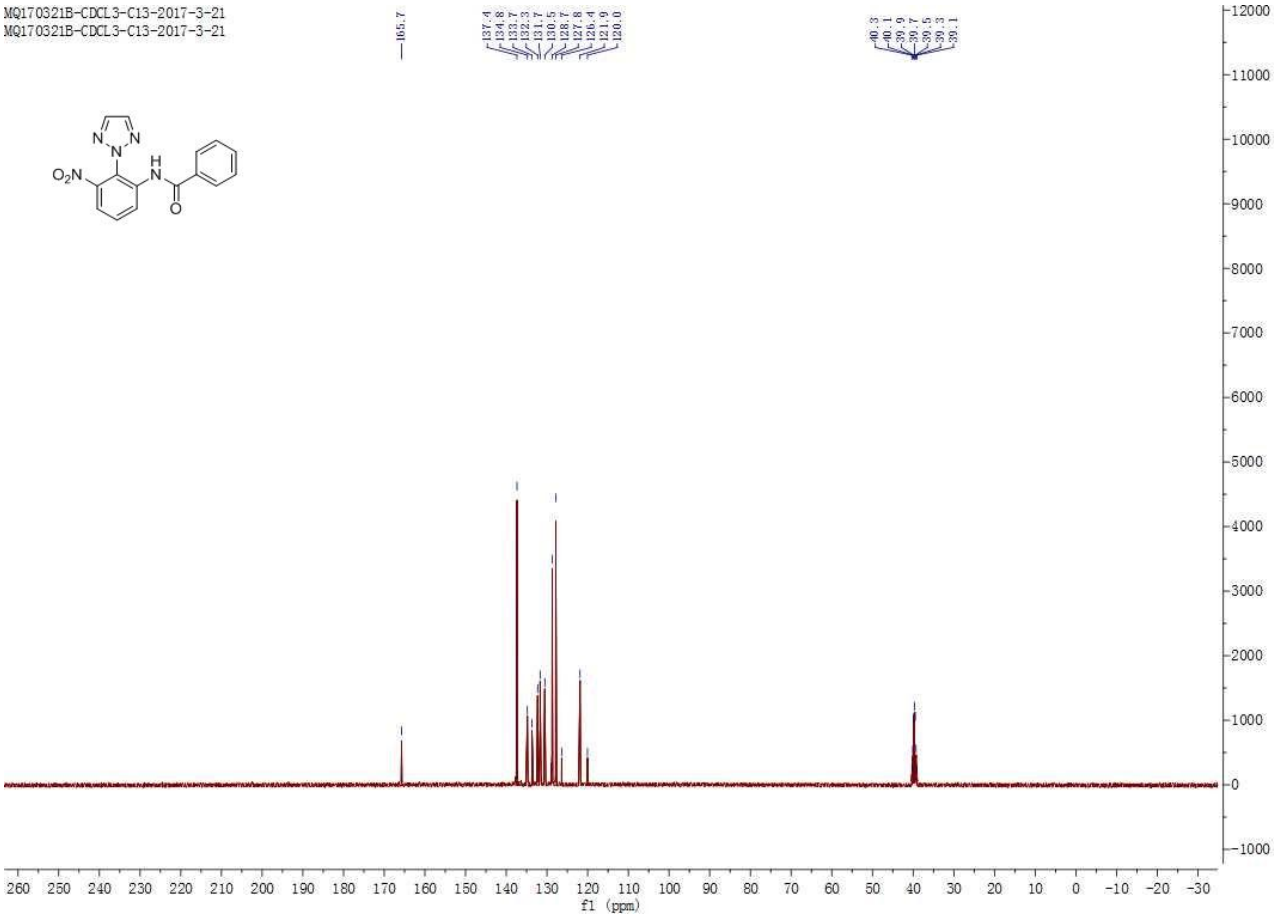


Figure 43. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gb**.

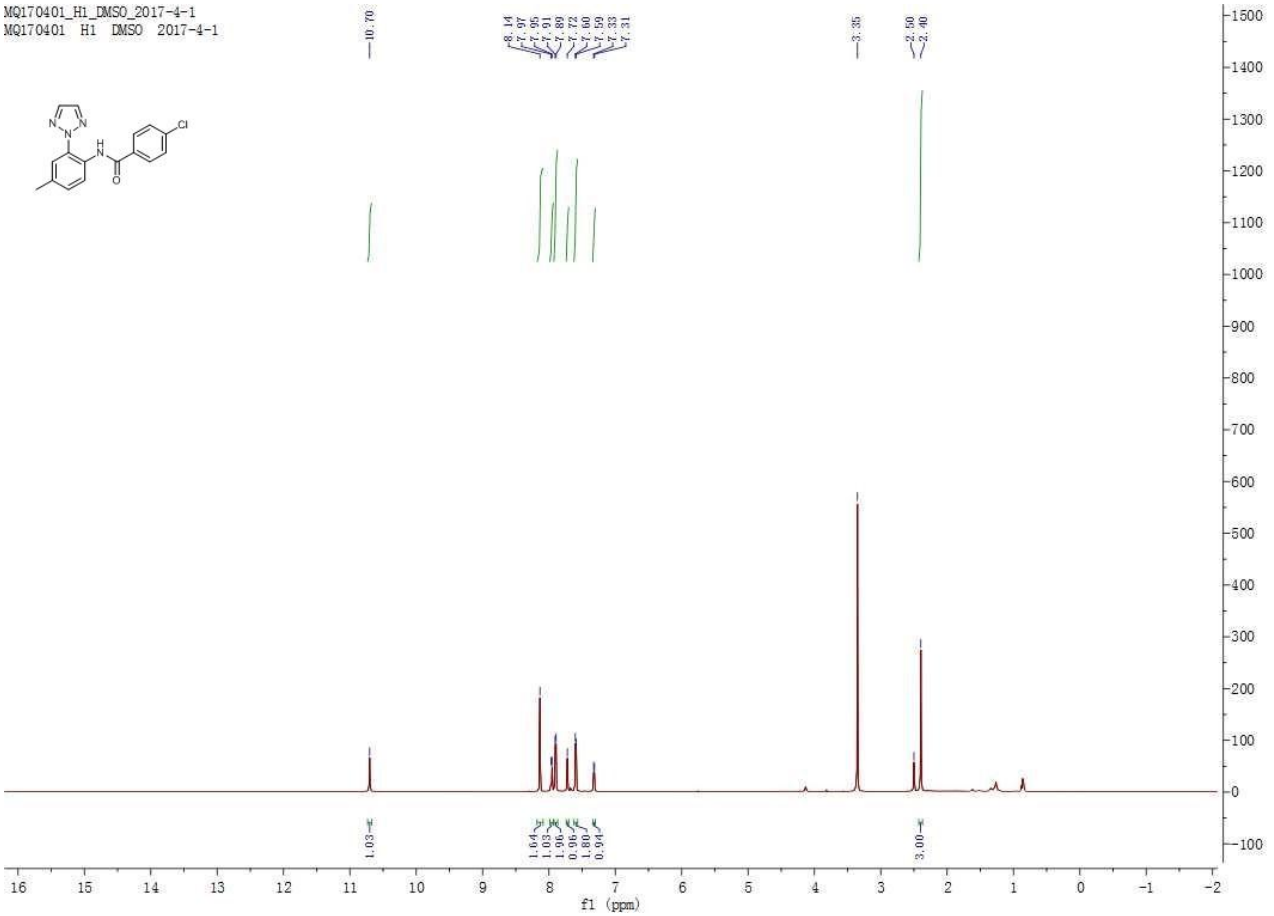


Figure 44. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gb**.

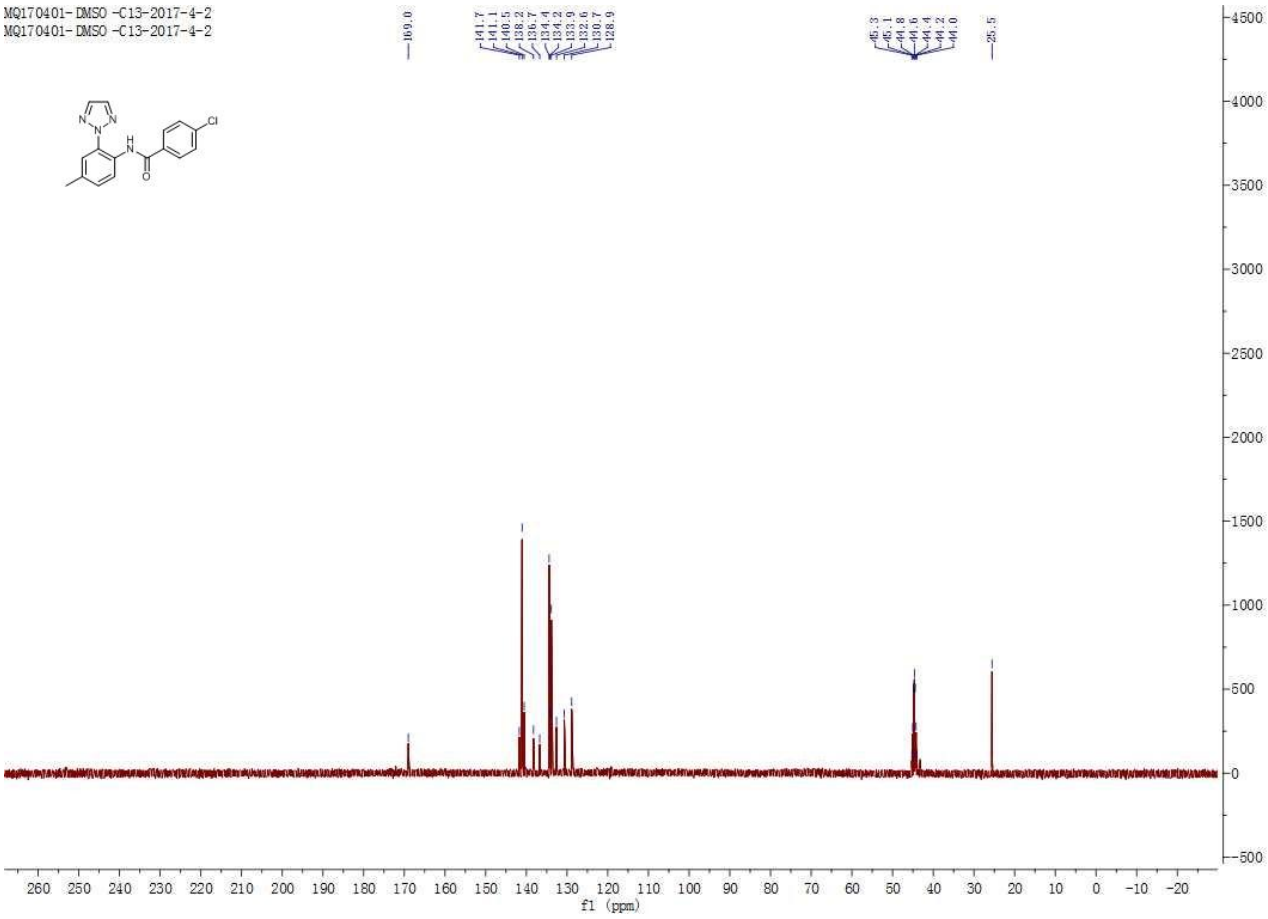


Figure 45. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gc**.

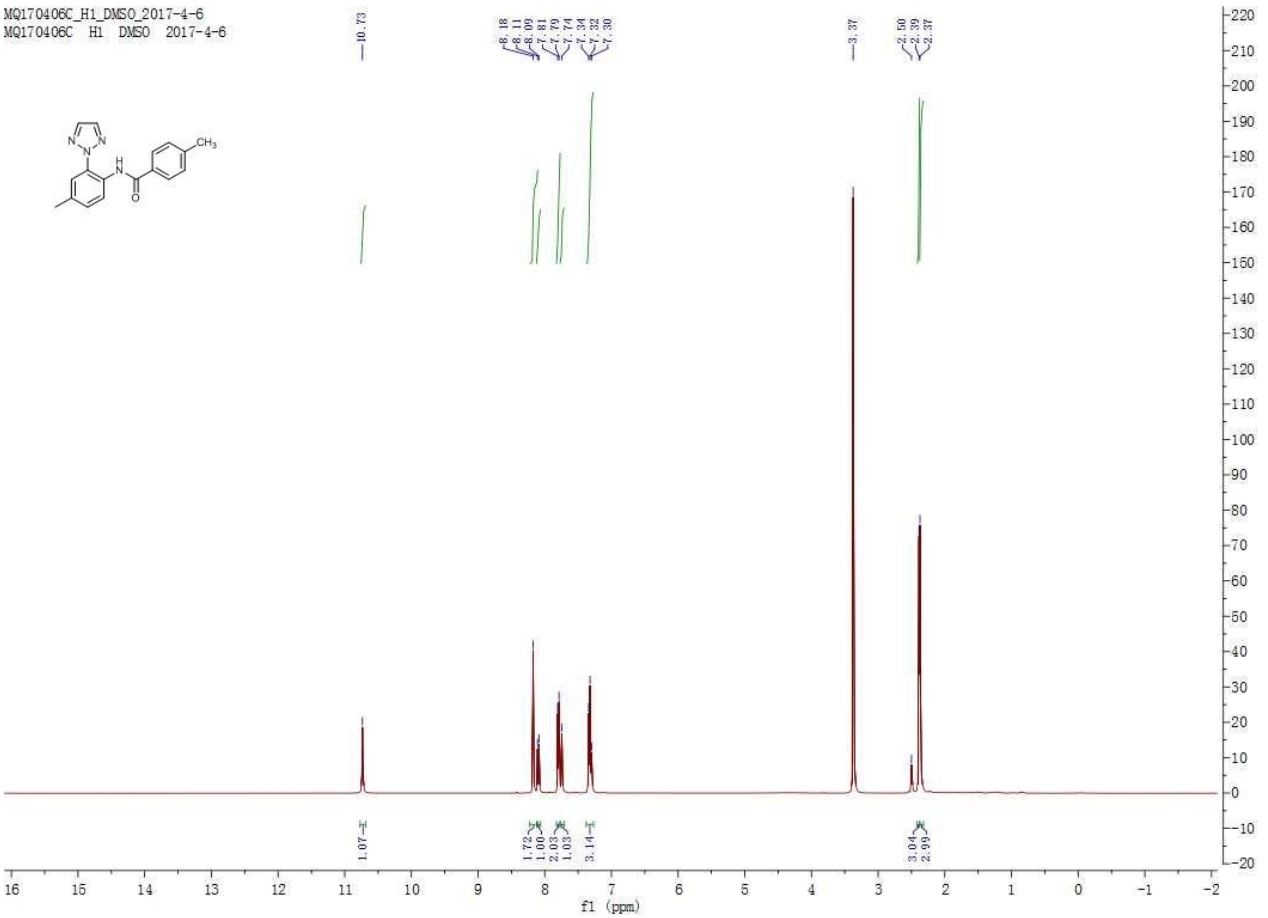


Figure 46. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gc**.

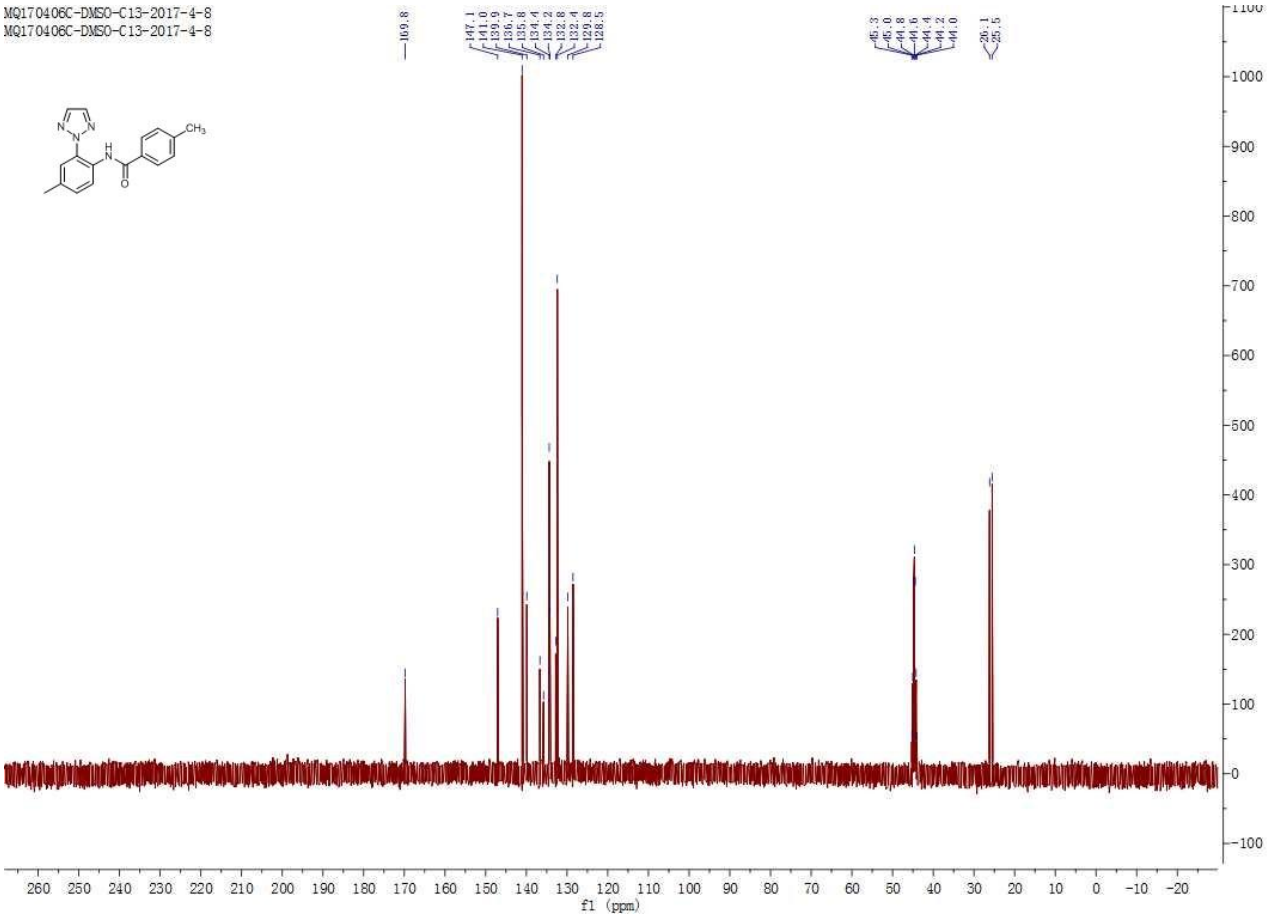


Figure 47. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gd**.

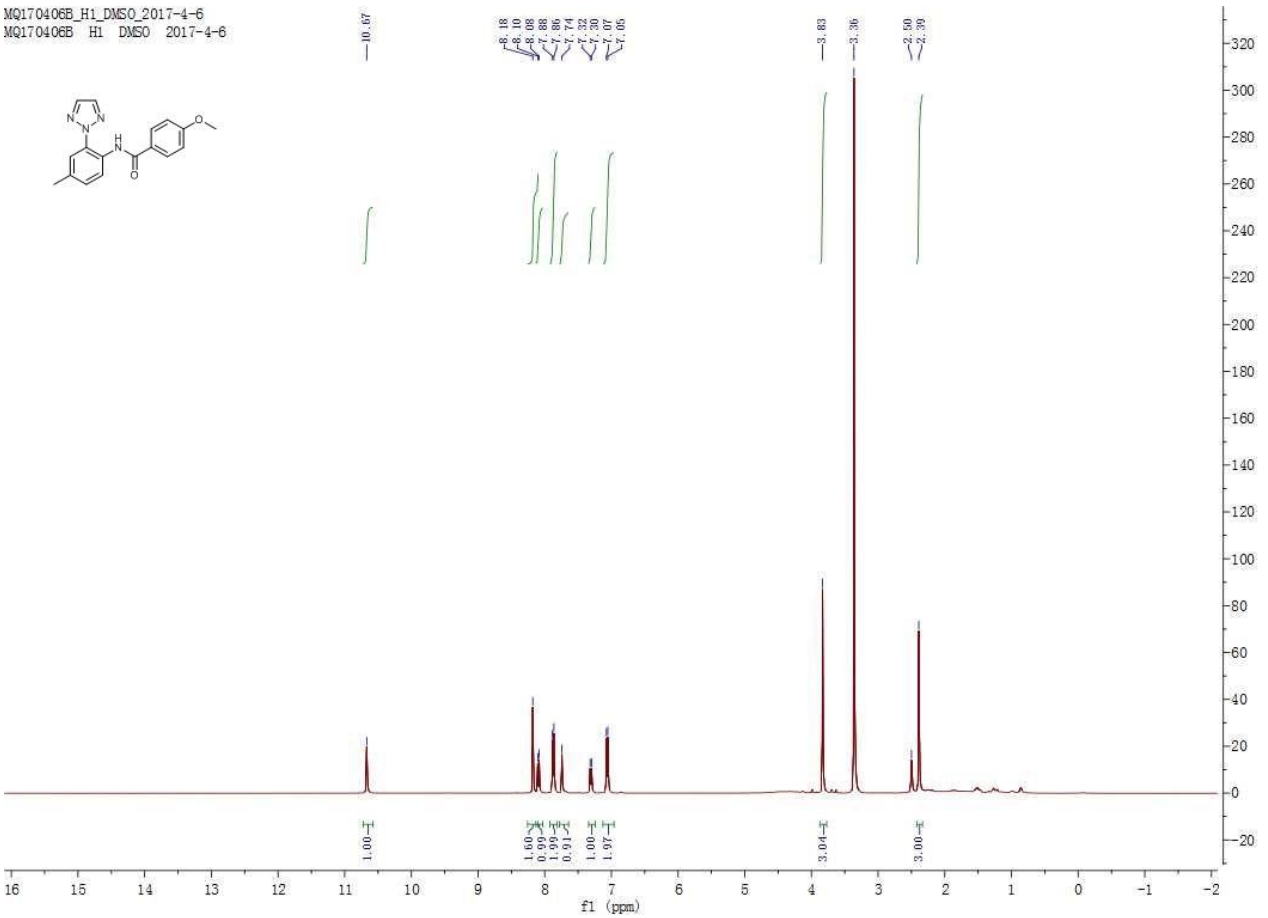


Figure 48. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gd**.

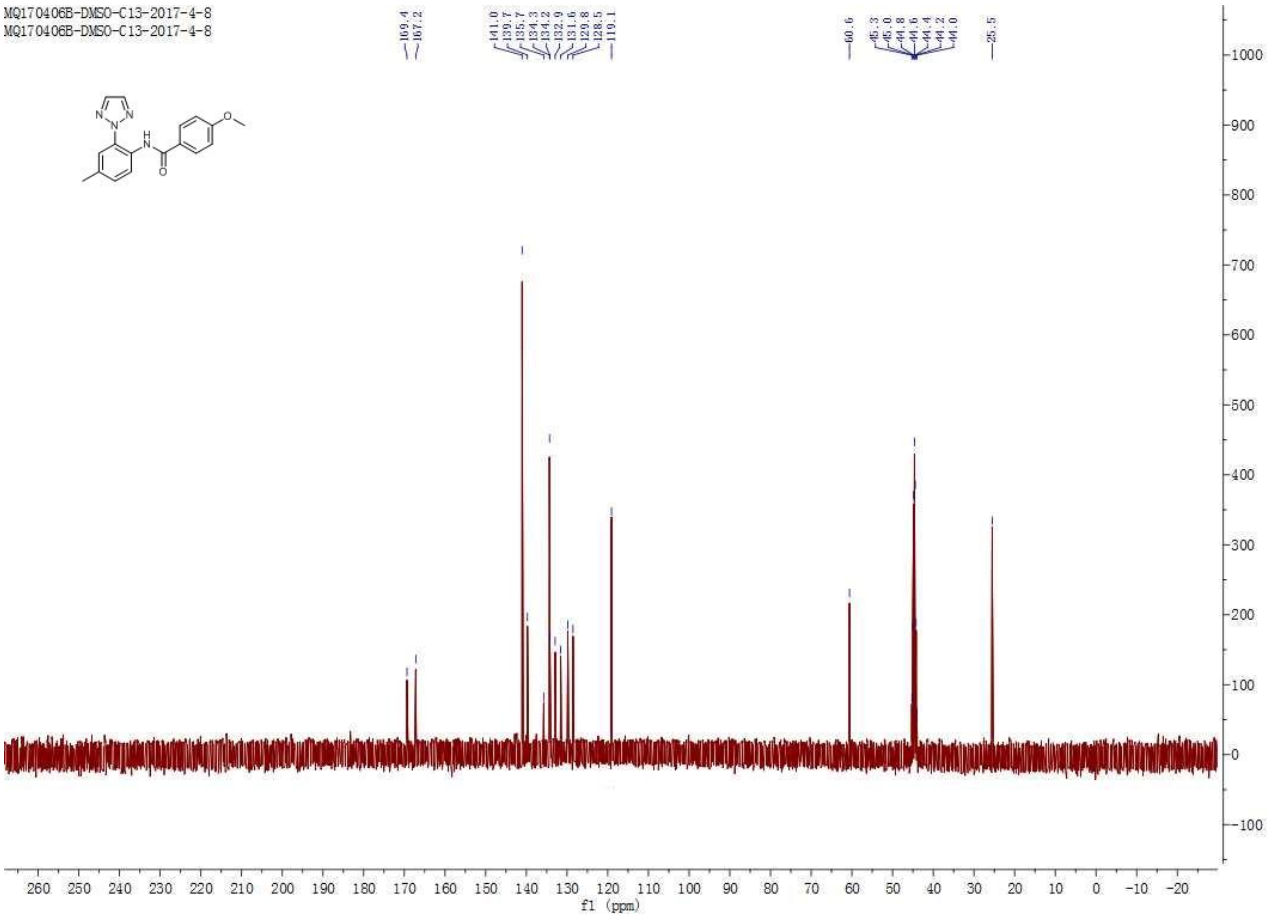


Figure 49. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3ge**.

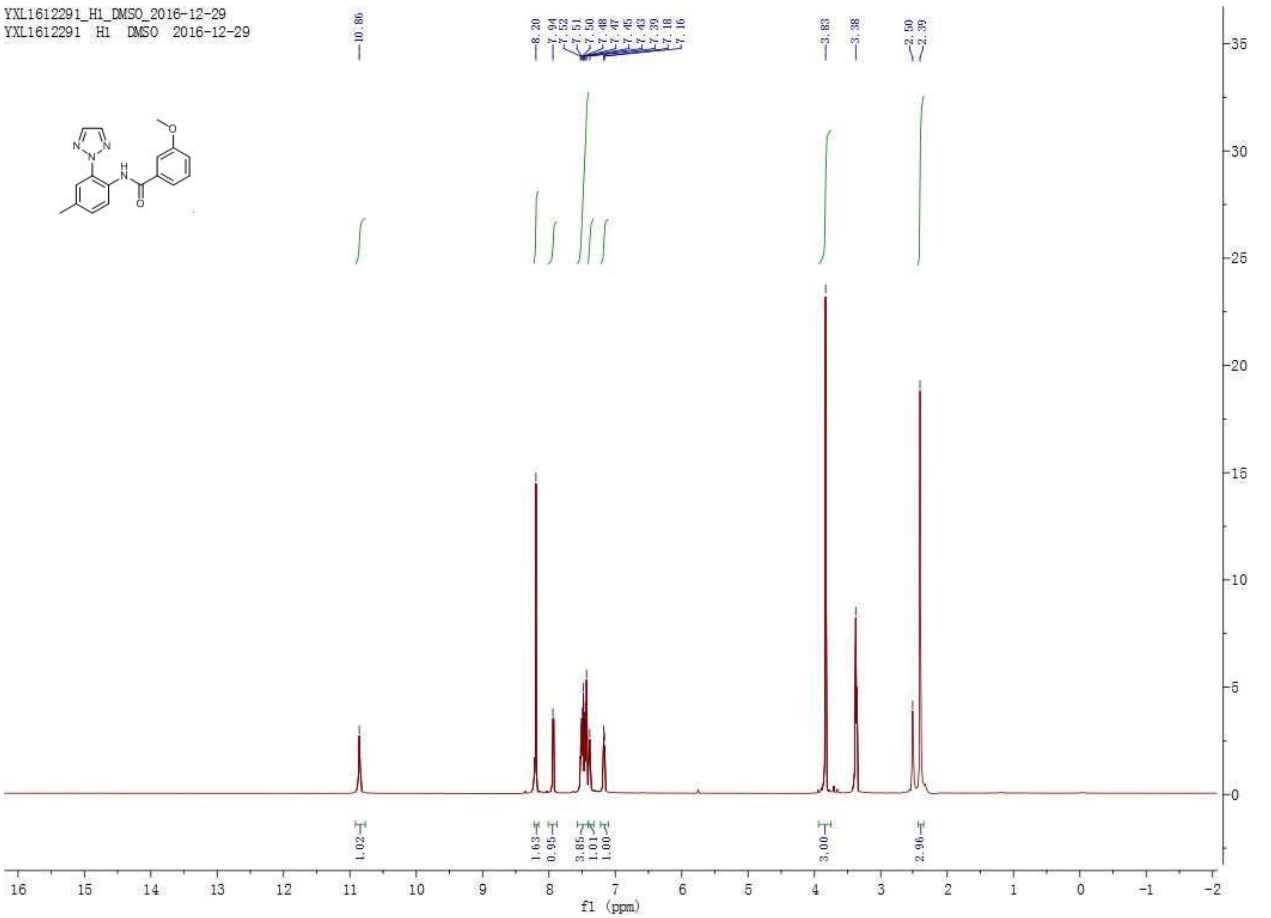


Figure 50. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3ge**.

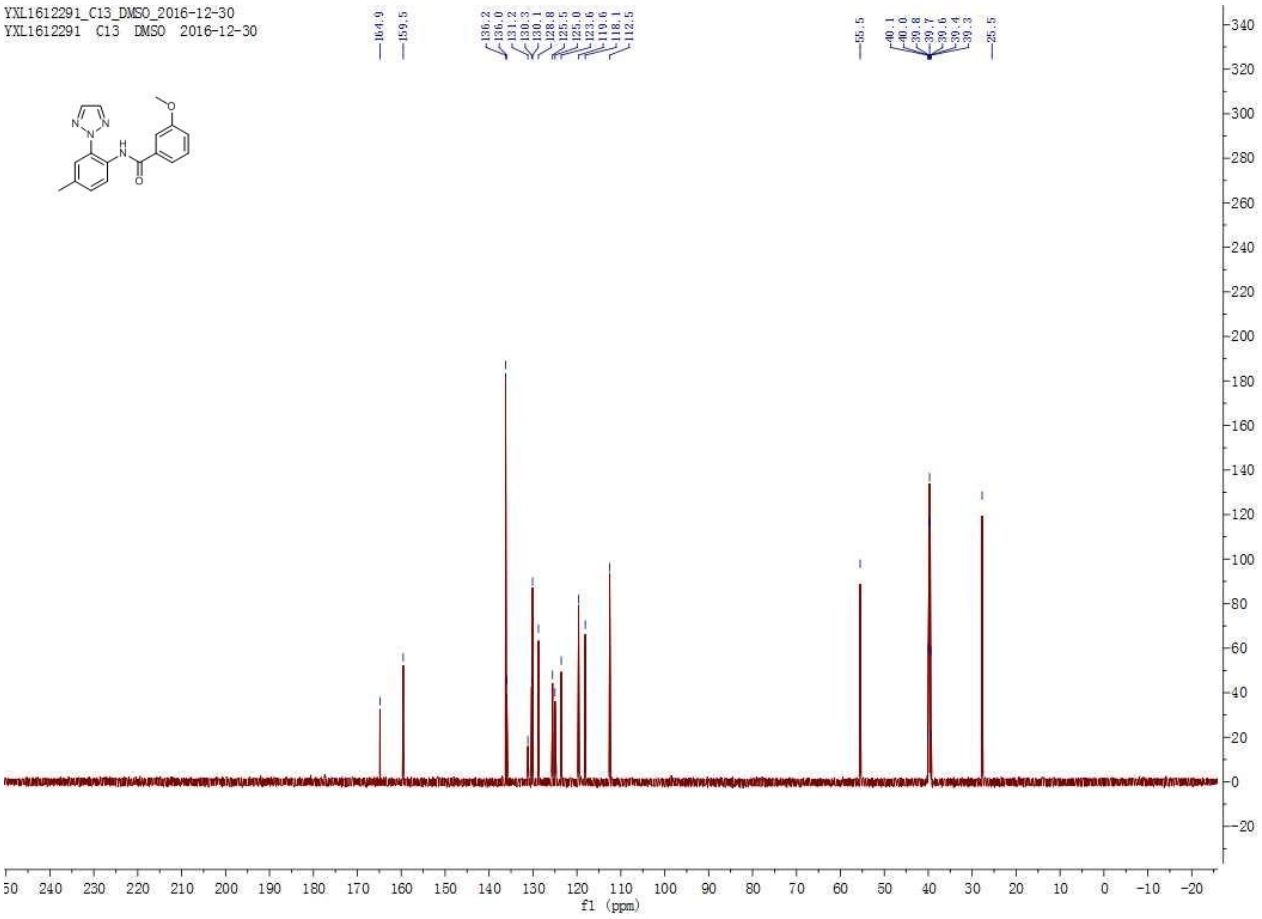


Figure 51. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gf**.

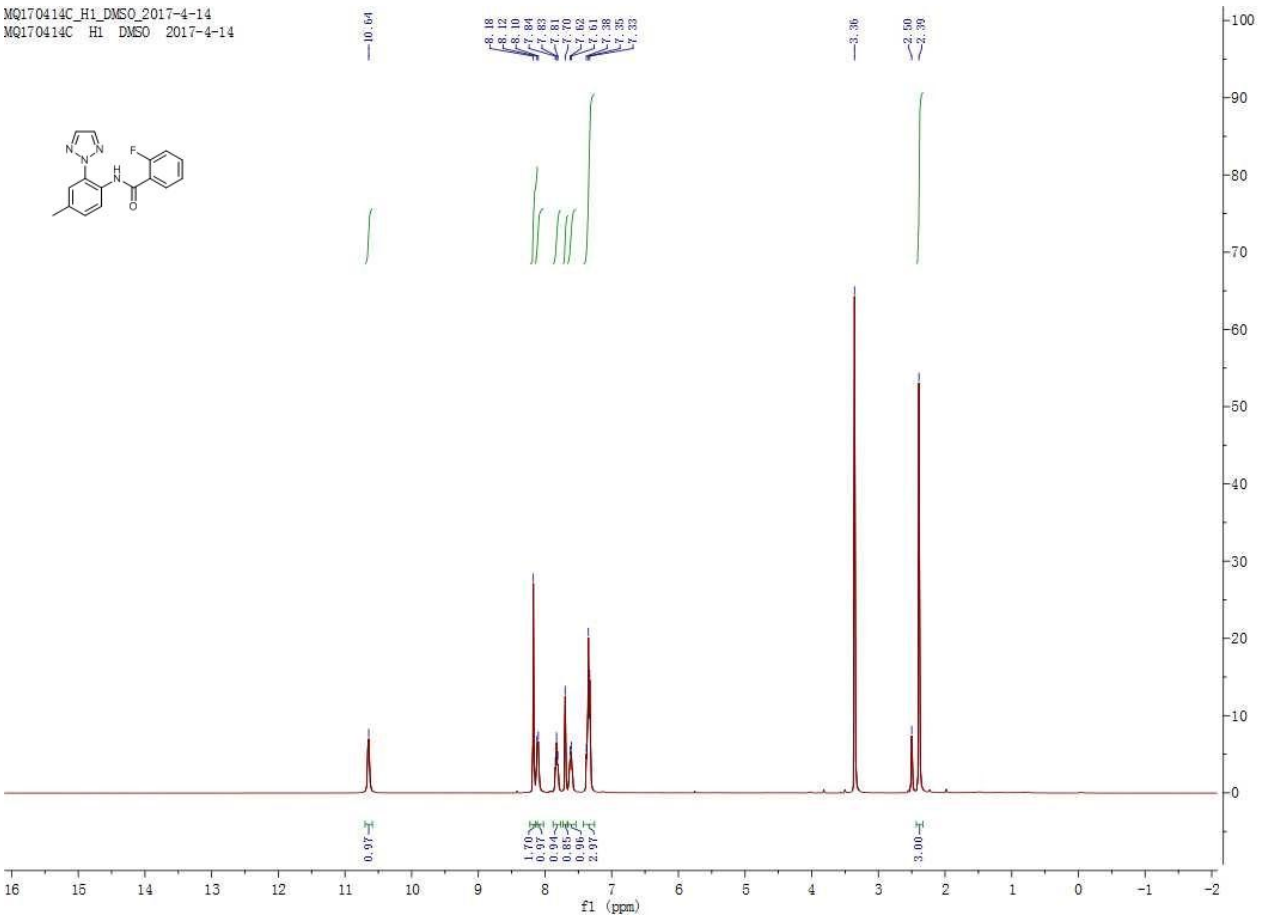


Figure 52. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gg**.

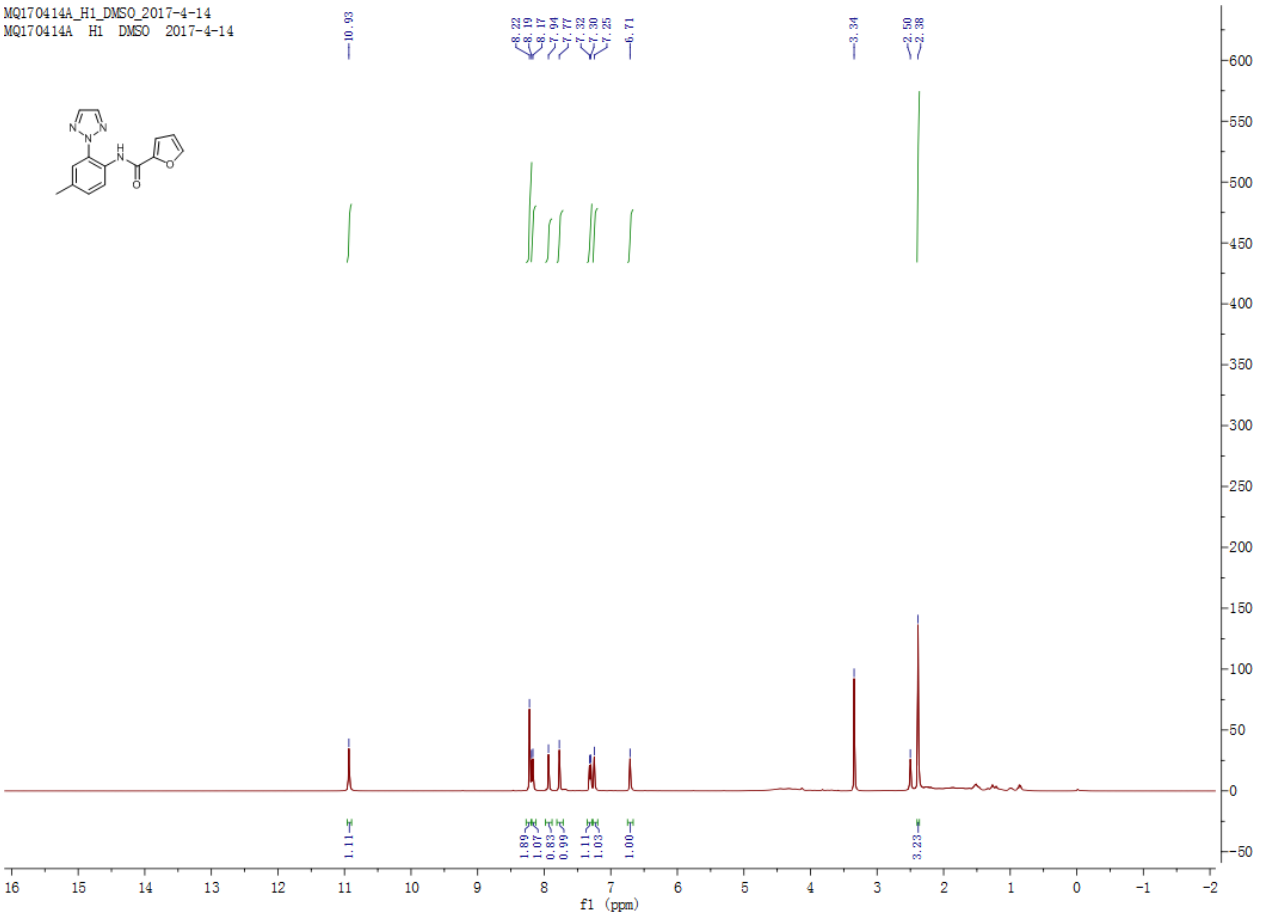


Figure 53. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gg**.

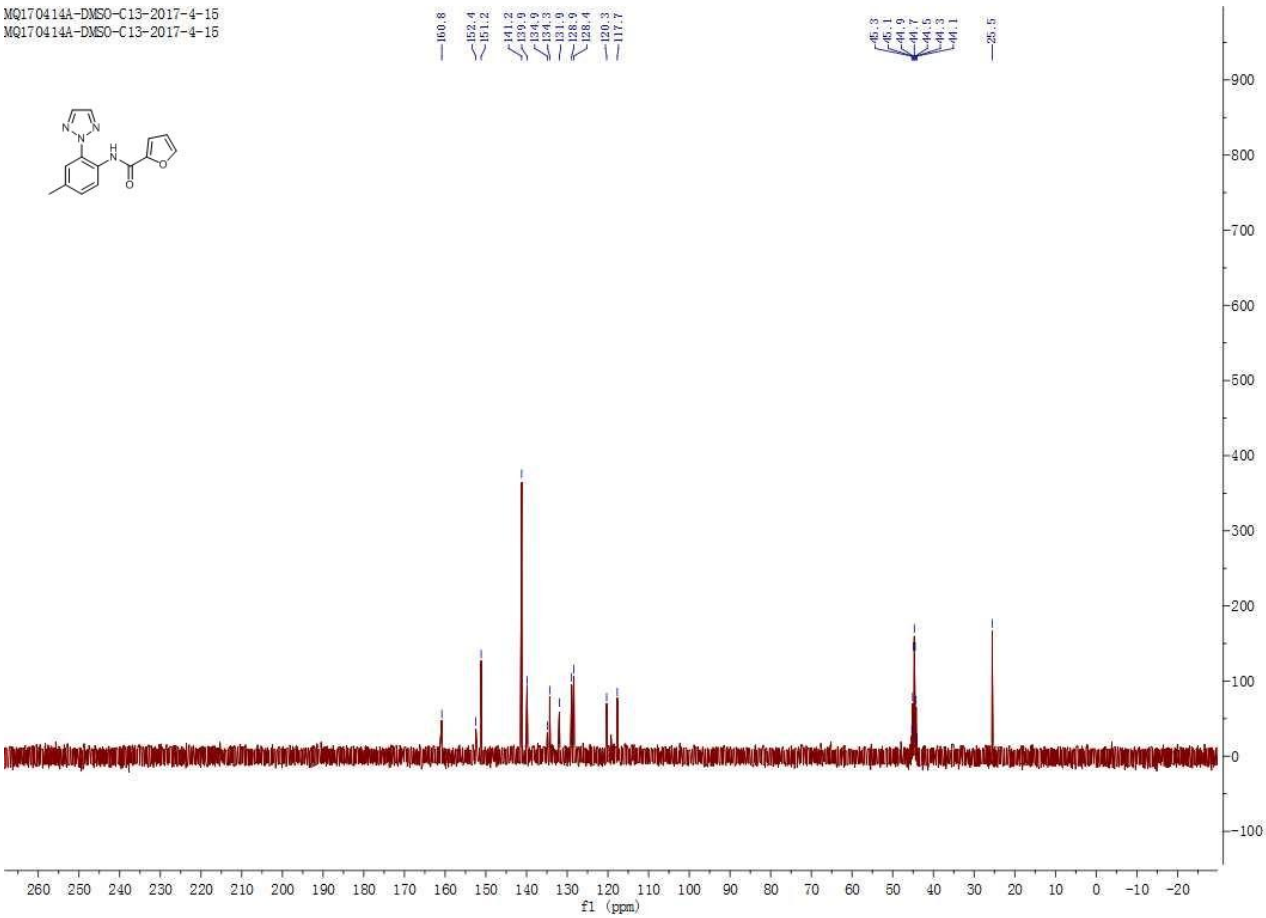


Figure 54. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gh**.

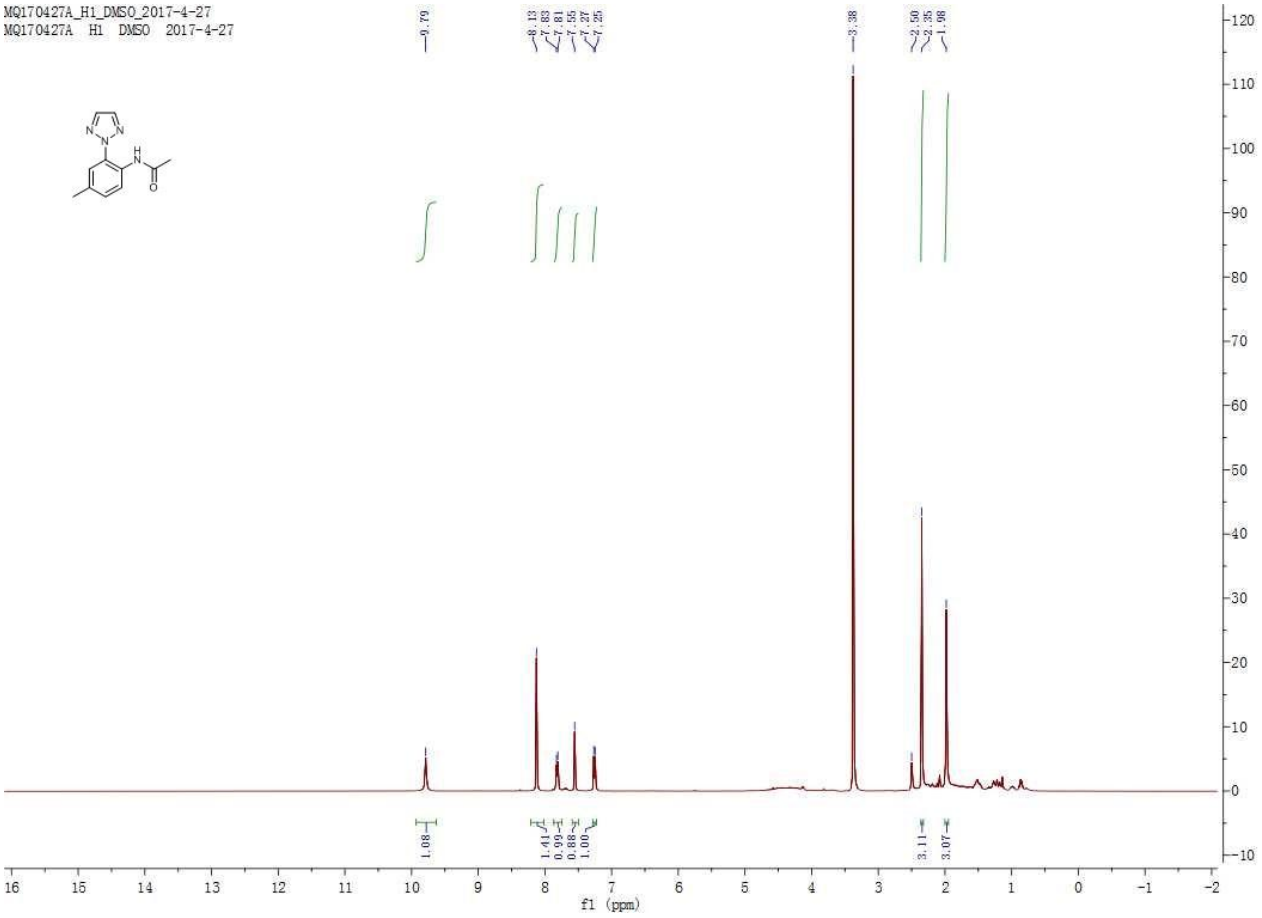


Figure 55. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gh**.

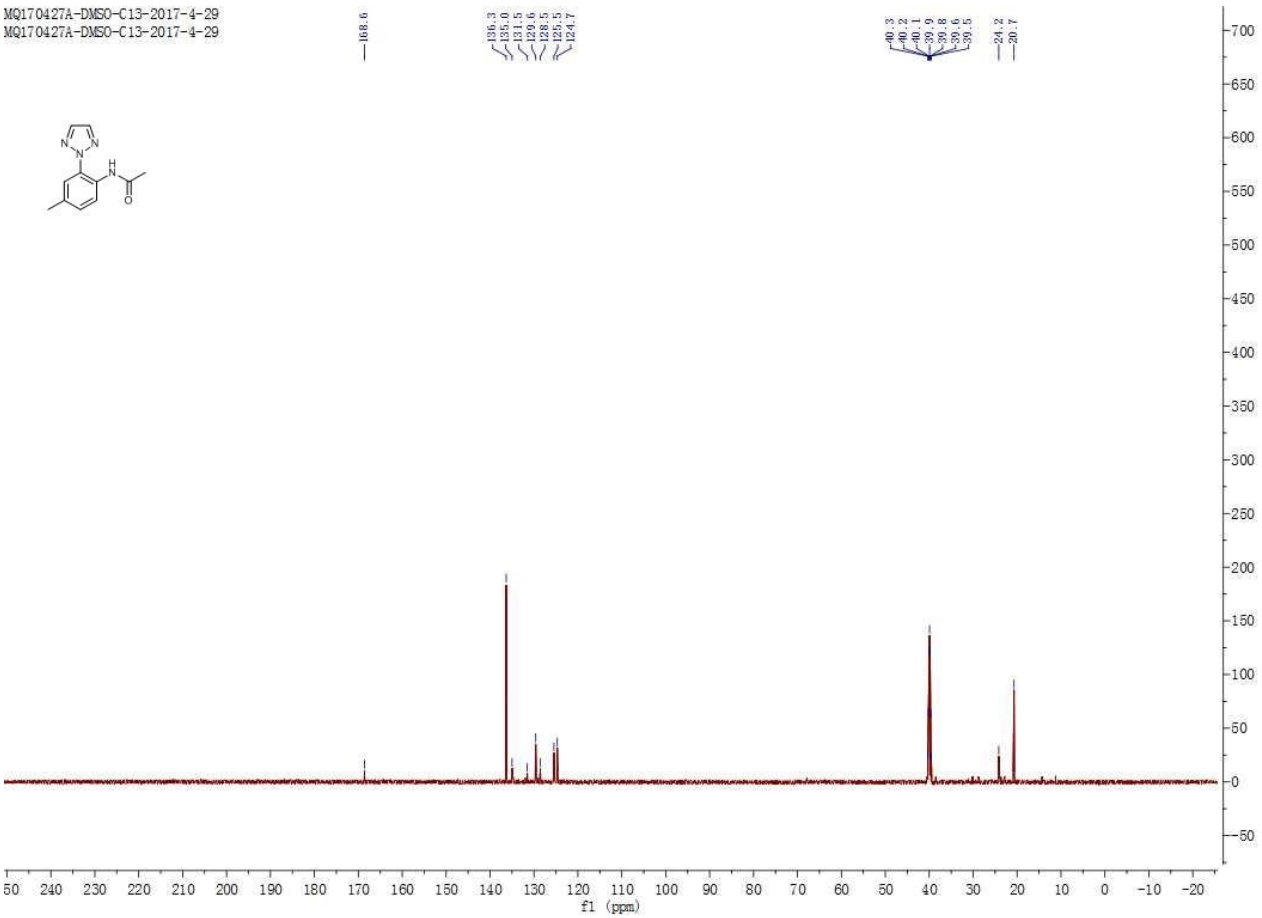


Figure 56. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gi**.

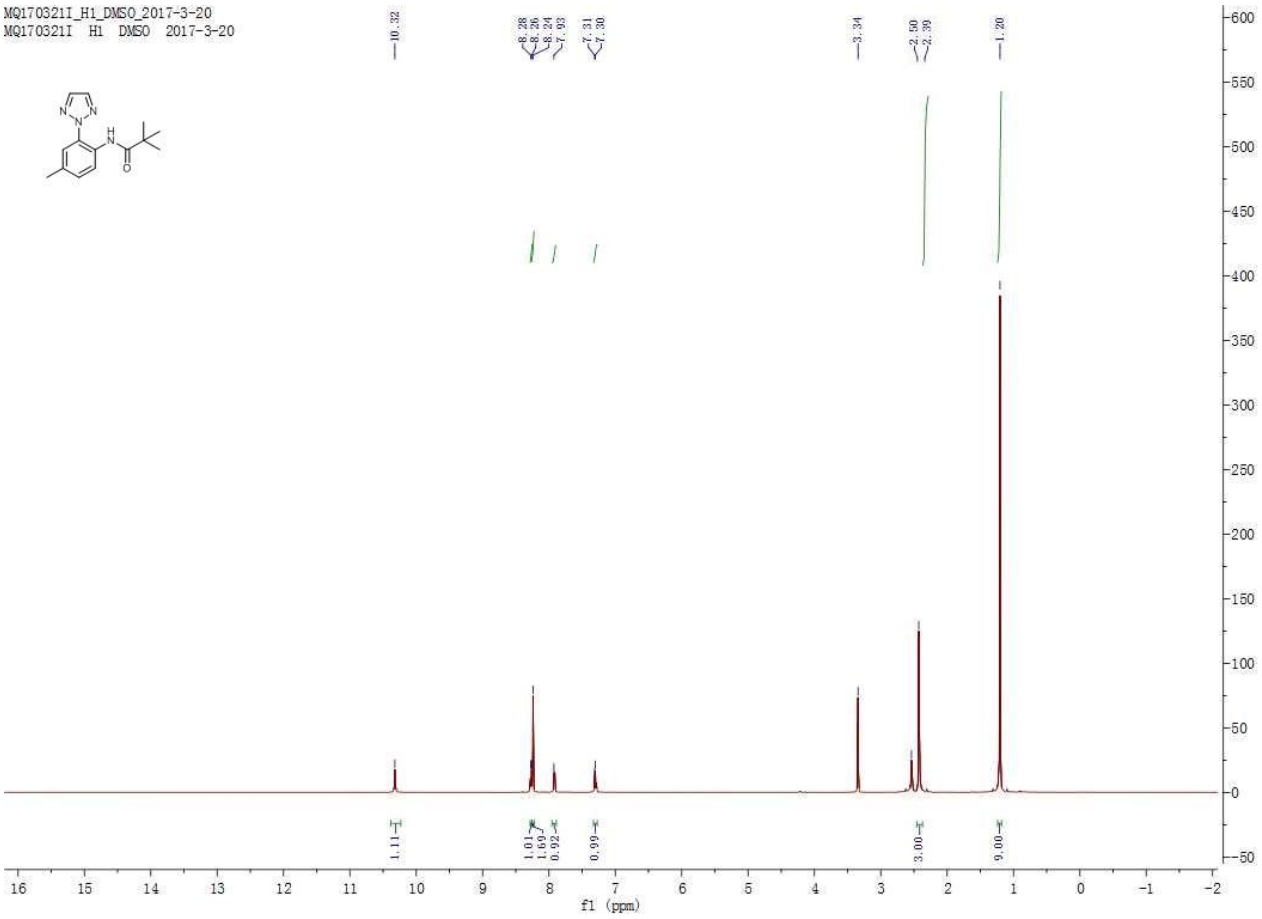


Figure 57. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gi**.

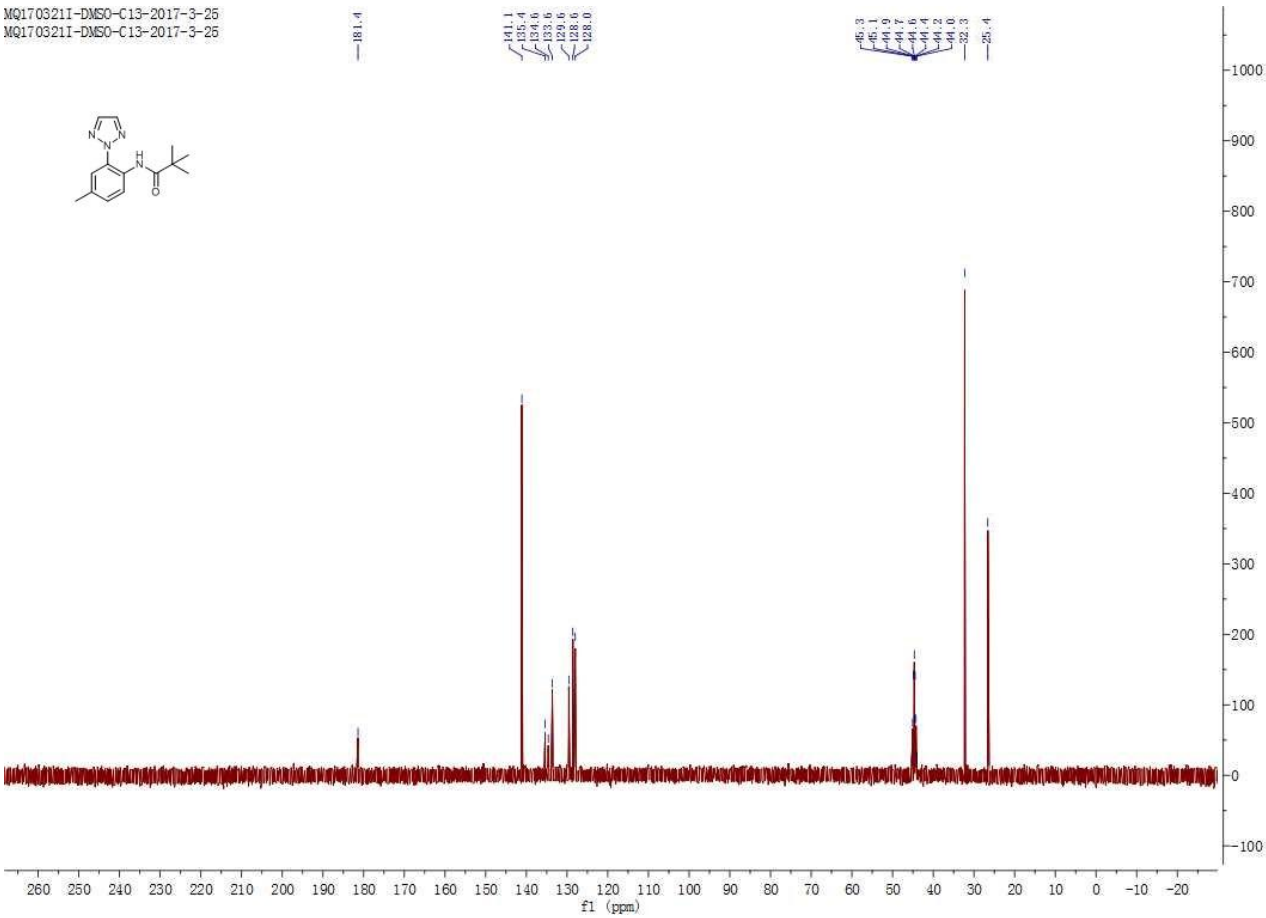


Figure 58. The ^{1}H NMR (400 MHz, DMSO-d_6) of **3gj**.

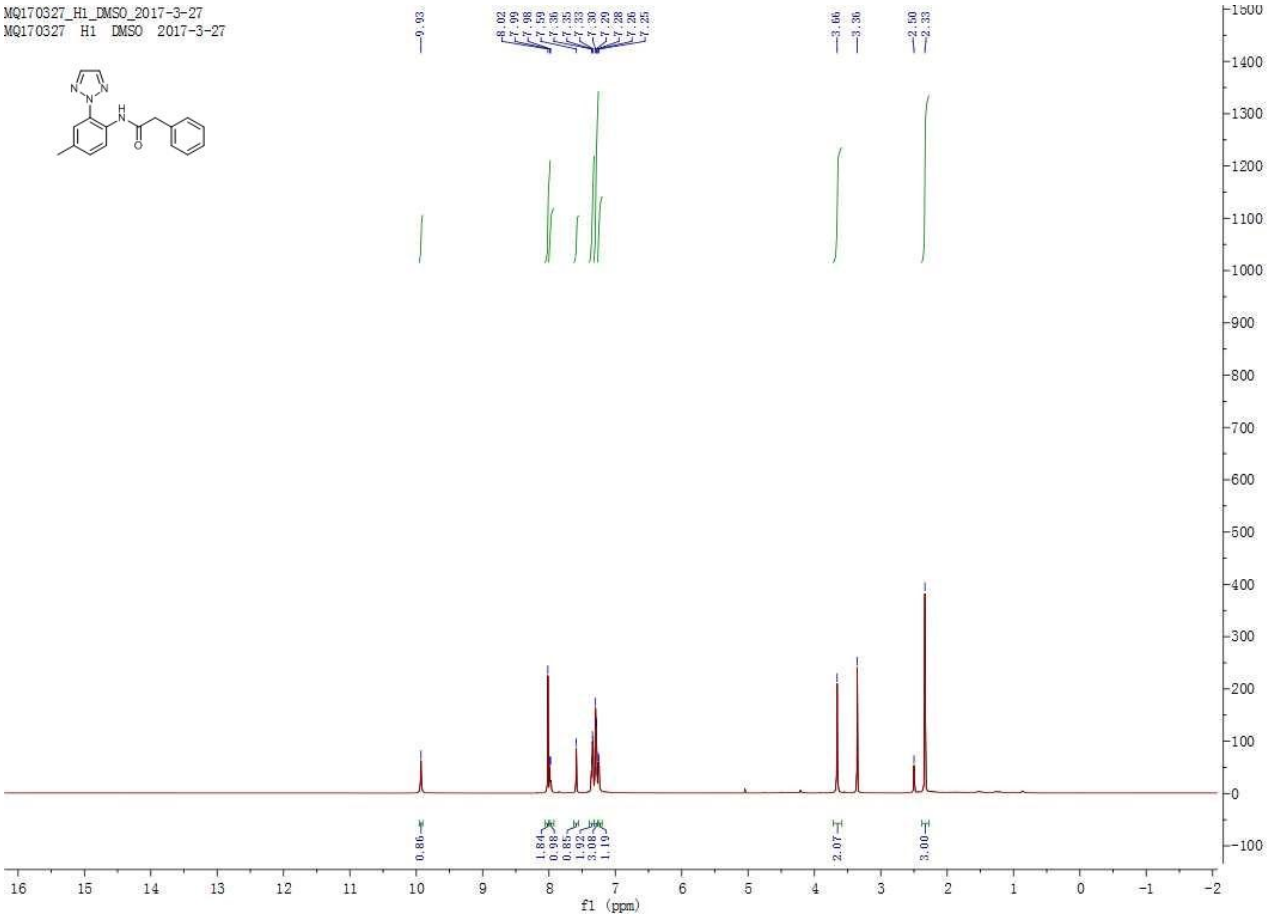


Figure 59. The ^{13}C NMR (100 MHz, DMSO-d_6) of **3gj**.