

Electronic Supplementary Information (ESI)

Nickel-catalyzed multicomponent reaction of dinitriles and hydrazine hydrochlorides with boronic acids: access to 1,3-diaryl-1*H*-pyrazol-5-amines and 4,5-dihydropyridazin-3(2*H*)-ones

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Supporting Information Placeholder

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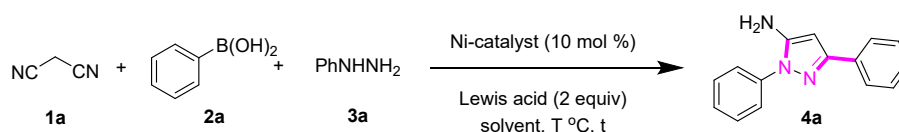
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1. General Information

All chemicals were obtained from commercial sources and were used as received without any purification. ^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz and 400 MHz Bruker spectrometer, using $\text{DMSO-}d_6$ or CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quarter (q), multiplet (m), and broad (br). High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) quadrupole time-of-flight mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh).

2. Experimental Section

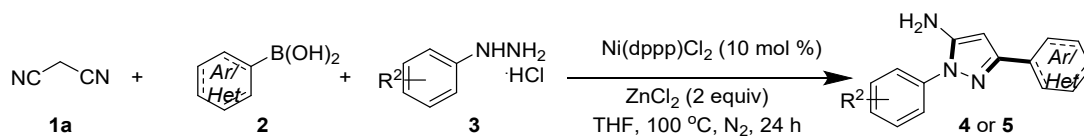
2.1. Table S1 Optimization of reaction conditions



entry	catalyst	additive	solvent	yield(%) ^b
1	Ni(dppe)Cl ₂	ZnCl ₂	THF	31
2	Ni(dppe)Cl ₂	ZnCl ₂	toluene	trace
3	Ni(dppe)Cl ₂	ZnCl ₂	DMSO	ND
4	Ni(PPh ₃) ₂ Cl ₂	ZnCl ₂	THF	ND
5	Ni(dppp)Cl ₂	ZnCl ₂	THF	60
6	NiCl ₂ /dppp	ZnCl ₂	THF	26
7	Ni(dppp)Cl ₂	Zn(OTf) ₂	THF	35
8	Ni(dppp)Cl ₂	CuCl ₂	THF	ND
9	Ni(dppp)Cl ₂	FeCl ₃	THF	ND
10 ^c	Ni(dppp)Cl ₂	ZnCl ₂	THF	65
11 ^{c,d}	Ni(dppp)Cl ₂	ZnCl ₂	THF	71
12 ^{c,e}	Ni(dppp)Cl ₂	ZnCl ₂	THF	57
13^{c,d,f}	Ni(dppp)Cl₂	ZnCl₂	THF	85
14 ^{c,d,g}	Ni(dppp)Cl ₂	ZnCl ₂	THF	66
15 ^{c,d,f}	--	ZnCl ₂	THF	ND
16 ^{c,d,f}	Ni(dppp)Cl ₂	--	THF	ND

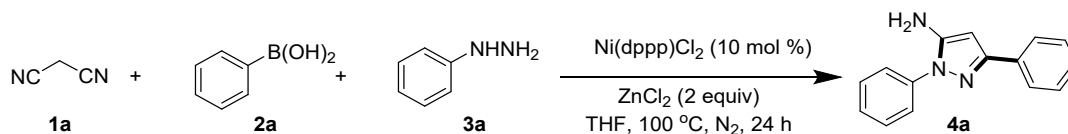
^aReaction conditions: **1a** (0.3 mmol), **2a** (0.8 mmol), **3a** (0.6 mmol), Ni-catalyst (10 mol %), Lewis acid (2 equiv), solvent (2 mL), 80 °C, 24 h, under air atmosphere. ^bIsolated yields. ^c**1a** (0.6 mmol), **2a** (0.8 mmol), **3a** (0.3 mmol) was used. ^dT = 100 °C. ^eT = 60 °C. ^funder N₂ atmosphere. ^gunder O₂ atmosphere. ND represents no detected.

2.2. General procedure for the synthesis of 1,3-diaryl-1*H*-pyrazol-5-amines



In a 10 mL Schlenk reaction tube, malononitrile (**1a**) (0.6 mmol, 2.0 equiv), organoboronic acid (**2**) (0.8 mmol, 2.6 equiv), phenylhydrazine or substituted phenylhydrazine hydrochloride (**3**) (0.3 mmol, 1.0 equiv), Ni(dppp)Cl₂ (0.03 mmol, 10 mol %, 16.3 mg), ZnCl₂ (0.6 mmol, 2.0 equiv, 81.8mg), were dissolved in tetrahydrofuran (2.0 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent to afford the desired products **4** or **5**.

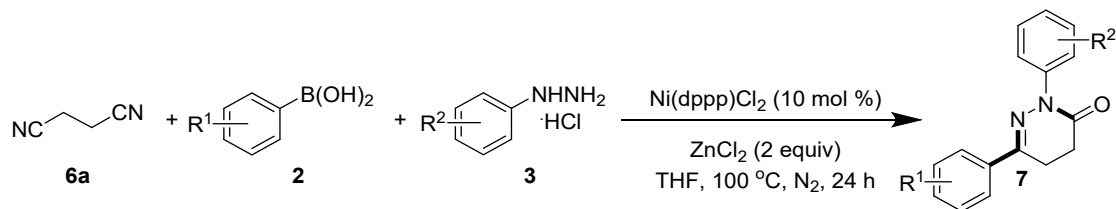
2.3. Scaled-up synthesis of 1,3-diphenyl-1*H*-pyrazol-5-amine



In a 100 mL Schlenk reaction tube, malononitrile (**1a**) (10 mmol, 0.66 g), phenylboronic acid (**2a**) (13.3 mmol, 1.63 g), phenylhydrazine (**3a**) (5 mmol, 0.54 g), Ni(dppp)Cl₂ (0.5 mmol, 10 mol %, 0.27 g), ZnCl₂ (10 mmol, 2.0 equiv, 1.36 g), were dissolved in tetrahydrofuran (33.3 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 50 mL) and then brine (1 × 50 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1)

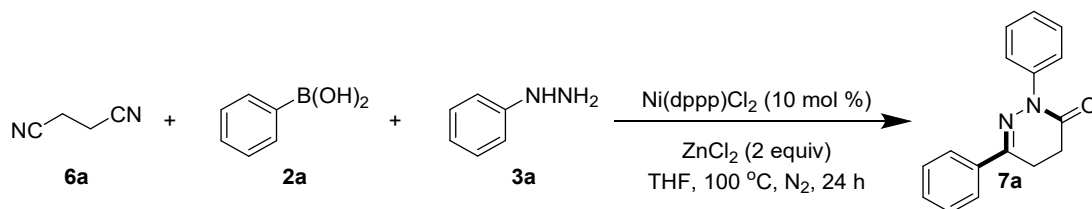
as the eluent to afford the desired product 1,3-diphenyl-1*H*-pyrazol-5-amine (**4a**, 80 %, 0.94 g).

2.4. General procedure for the synthesis of 4,5-dihydropyridazin-3(2*H*)-ones



In a 10 mL Schlenk reaction tube, succinonitrile (**6a**) (0.6 mmol, 2.0 equiv), phenylboronic acid (**2**) (0.8 mmol, 2.6 equiv), phenylhydrazine or substituted phenylhydrazine hydrochloride (**3**) (0.3 mmol, 1.0 equiv), Ni(dppp)Cl₂ (0.03 mmol, 10 mol %, 16.3 mg), ZnCl₂ (0.6 mmol, 2.0 equiv, 81.8mg), were dissolved in tetrahydrofuran (2.0 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (4:1) as the eluent to afford the desired products **7**.

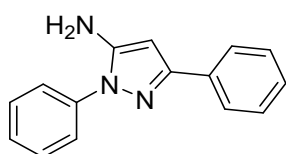
2.5. Scaled-up synthesis of 2,6-diphenyl-4,5-dihydropyridazin-3(2*H*)-one



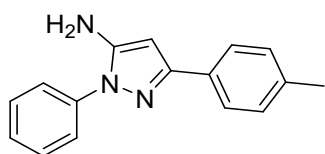
In a 100 mL Schlenk reaction tube, succinonitrile (**6a**) (10 mmol, 2.0 equiv, 0.80 g), phenylboronic acid (**2a**) (13.3 mmol, 2.6 equiv, 1.63 g), phenylhydrazine (**3a**) (5 mmol, 1.0 equiv, 0.54 g), Ni(dppp)Cl₂ (0.5 mmol, 10 mol %, 0.27 g), ZnCl₂ (10 mmol, 2.0 equiv, 1.36 g), were dissolved in tetrahydrofuran (33.3 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours.

After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 50 mL) and then brine (1 × 50 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (4:1) as the eluent to afford the desired product 2,6-diphenyl-4,5-dihydropyridazin-3(2H)-one (**7a**, 50 %, 0.63 g).

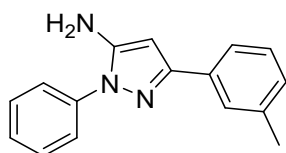
3. Analytical Data for All Products



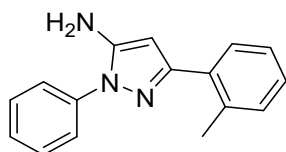
1,3-diphenyl-1H-pyrazol-5-amine (4a): pale brown solid (59.2 mg, 84%). mp: 129-130 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.41-7.35 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 5.95 (s, 1H), 3.84 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 151.5, 145.8, 138.8, 133.6, 129.5, 128.5, 127.8, 127.4, 125.7, 124.2, 88.2. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄N₃ 236.1182; Found 236.1179. Spectroscopic data for the title compound were consistent with those reported in the literature.¹



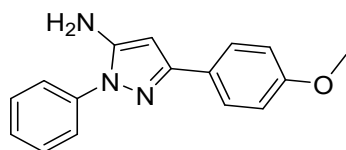
1-phenyl-3-(p-tolyl)-1H-pyrazol-5-amine (4b): pale brown solid (56.1 mg, 75%). mp: 169-170 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 5.92 (s, 1H), 3.78 (br, 2H), 2.37 (s, 3H). **¹³C NMR** (125MHz, CDCl₃) δ 151.6, 145.9, 138.6, 137.7, 130.5, 129.5, 129.2, 127.5, 125.6, 124.2, 88.1, 21.3. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆N₃ 250.1339; Found 250.1349. Spectroscopic data for the title compound were consistent with those reported in the literature.²



1-phenyl-3-(*m*-tolyl)-1*H*-pyrazol-5-amine (4c): pale brown solid (65.7 mg, 88%). mp: 128-129 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 5.95 (s, 1H), 3.78 (br, 2H), 2.39 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 151.6, 145.8, 138.5, 138.1, 133.2, 129.6, 128.7, 128.4, 127.6, 125.3, 124.3, 122.9, 88.2, 21.5. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆N₃ 250.1339; Found 250.1339.

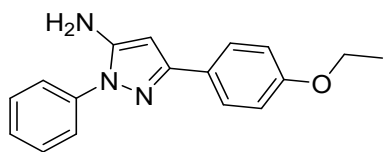


1-phenyl-3-(*o*-tolyl)-1*H*-pyrazol-5-amine (4d): Yellow Oil (20.2 mg, 27%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.60-7.59 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23-7.21 (m, 3H), 5.83 (s, 1H), 3.85 (br, 2H), 2.54 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.2, 144.8, 136.2, 133.4, 130.7, 129.4, 129.2, 127.6, 127.2, 125.7, 123.9, 91.5, 21.2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆N₃ 250.1339; Found 250.1342.

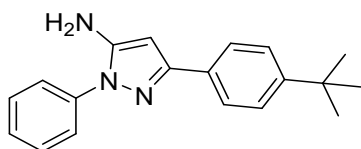


3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-5-amine (4e): White solid (37.4 mg, 47%). mp: 184-185 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.91 (s, 1H), 3.83 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 151.3, 145.8, 138.6, 129.5, 127.4, 127.0, 125.1, 124.2, 113.9, 87.9, 55.3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆N₃O 266.1288; Found 266.1282. Spectroscopic data for the title

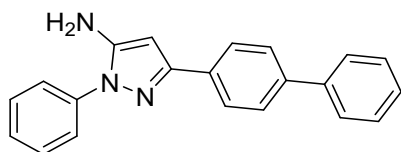
compound were consistent with those reported in the literature.²



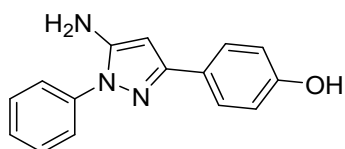
3-(4-ethoxyphenyl)-1-phenyl-1H-pyrazol-5-amine (4f): White solid (42.7 mg, 51%). mp: 186-188 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.67-7.64 (m, 4H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.84 (s, 1H), 5.40 (br, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 158.6, 150.4, 148.6, 139.9, 129.6, 125.8, 125.7, 125.5, 123.2, 114.8, 87.3, 63.5, 15.2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₈N₃O 280.1444; Found 280.1447.



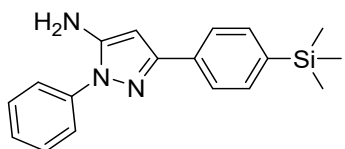
3-(4-(*tert*-butyl)phenyl)-1-phenyl-1H-pyrazol-5-amine (4g): White solid (41.0 mg, 47%). mp: 165-166 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 5.94 (s, 1H), 3.81 (br, 2H), 1.34 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 151.5, 151.0, 145.8, 138.6, 130.5, 129.5, 129.3, 127.5, 125.4, 124.2, 88.2, 34.6, 31.4. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₂N₃ 292.1808; Found 292.1804.



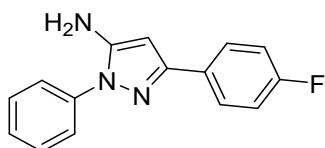
3-([1,1'-biphenyl]-4-yl)-1-phenyl-1H-pyrazol-5-amine (4h): White solid (60.7 mg, 65%). mp: 217-218 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 6H), 7.53-7.46 (m, 4H), 7.38-7.34 (m, 2H), 5.98 (s, 1H), 5.47 (br, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 149.6, 148.3, 139.8, 139.3, 139.1, 132.8, 129.1, 128.9, 127.4, 125.7, 125.4, 125.3, 125.6, 122.9, 87.3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₁₈N₃ 312.1495; Found 312.1483.



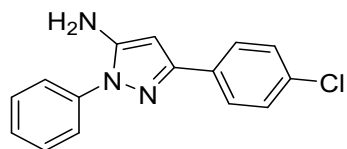
4-(5-amino-1-phenyl-1H-pyrazol-3-yl)phenol (4i): white solid (36.9 mg, 49%), mp: 189-192 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.45 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.79 (s, 1H), 5.36 (br, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.6, 150.8, 148.5, 140.0, 129.6, 125.9, 125.4, 125.3, 123.2, 115.7, 87.2. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄N₃O 252.1131; Found 252.1140.



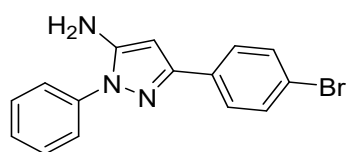
1-phenyl-3-(4-(trimethylsilyl)phenyl)-1H-pyrazol-5-amine (4j): White solid (35.9 mg, 39%). mp: 141-143 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.96 (s, 1H), 3.86 (br, 2H), 0.29 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 151.6, 145.8, 140.0, 138.7, 133.9, 133.6, 129.6, 127.5, 124.9, 124.2, 88.3, -1.0. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₈H₂₂N₃Si 308.1578; Found 308.1581.



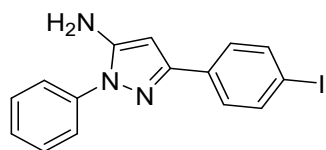
3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-5-amine (4k): White solid (59.2 mg, 78%). mp: 157-158 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.80-7.77 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 8.5 Hz, 2H), 5.92 (s, 1H), 3.87 (br, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 162.7 (C-F, ¹*J*_{C-F} = 245.0), 150.6, 146.0, 138.5, 129.6, 127.6, 127.4, 127.3, 124.2, 115.4 (C-F, ²*J*_{C-F} = 21.3), 88.0. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃FN₃ 254.1088; Found 254.1081. Spectroscopic data for the title compound were consistent with those reported in the literature.²



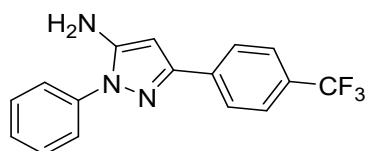
3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-5-amine (4l): White solid (65.4 mg, 81%). mp: 186-187 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.40-7.34 (m, 3H), 5.94 (s, 1H), 3.87 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 150.4, 146.0, 138.4, 133.6, 131.9, 129.6, 128.7, 127.7, 125.9, 124.2, 88.0. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃ClN₃ 270.0793; Found 270.0798.



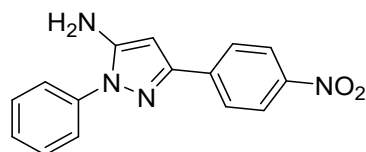
3-(4-bromophenyl)-1-phenyl-1H-pyrazol-5-amine (4m): White solid (70.4 mg, 75%). mp: 208-210 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 5.49 (br, 2H). **¹³C NMR** (125 MHz, DMSO-*d*₆) δ 148.9, 148.4, 139.1, 132.9, 131.4, 129.1, 127.0, 125.4, 123.0, 120.4, 87.2. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃BrN₃ 314.0287; Found 314.0281.



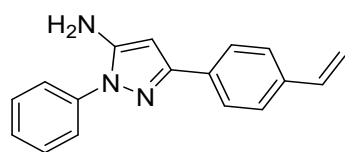
3-(4-iodophenyl)-1-phenyl-1H-pyrazol-5-amine (4n): White solid (66.1 mg, 61%). mp: 228-230 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 5.92 (s, 1H), 5.47 (br, 2H). **¹³C NMR** (125 MHz, DMSO-*d*₆) δ 149.0, 148.4, 139.1, 137.2, 133.2, 129.1, 127.1, 125.4, 123.0, 93.2, 87.1. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃IN₃ 362.0149; Found 362.0149.



1-phenyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-amine (4o): White solid (63.7 mg, 70%). mp: 208-210 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 6.02 (s, 1H), 5.54 (br, 2H). **¹³C NMR** (125 MHz, DMSO-*d*₆) δ 148.6, 148.5, 139.0, 137.6, 129.2, 127.6 (C-F, ²*J*_{C-F} = 32.5 Hz), 126.6, 125.4 (C-F, ³*J*_{C-F} = 3.8 Hz), 124.3(C-F, ¹*J*_{C-F} = 300.0 Hz), 123.3, 87.5. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₃F₃N₃ 304.1056; Found 304.1052.

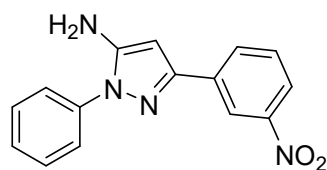


3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-5-amine (4p): Yellow solid (52.9 mg, 63%). mp: 178-179 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 6.04 (s, 1H), 3.91 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 149.1, 147.2, 146.4, 139.8, 138.2, 129.7, 128.1, 125.0, 124.3, 124.0, 88.6. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃N₄O₂ 281.1033; Found 281.1030.

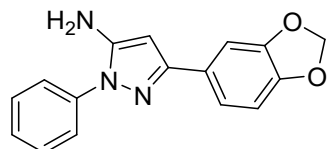


1-phenyl-3-(4-vinylphenyl)-1H-pyrazol-5-amine (4q): White solid (30.6mg, 39%). mp: 157-159 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.51-7.48 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38-7.35 (m, 1H), 6.74 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.96 (s, 1H), 5.78 (d, *J* = 17.5 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 3.86 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 151.2, 145.8, 138.7, 137.1, 136.7, 133.0,

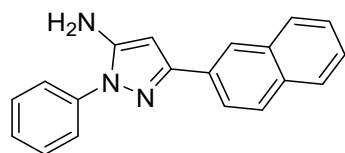
129.5, 127.5, 125.4, 125.7, 124.2, 113.6, 88.2. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{17}H_{16}N_3$ 262.1339; Found 262.1346.



3-(3-nitrophenyl)-1-phenyl-1H-pyrazol-5-amine (4r): Yellow solid (62.2 mg, 74%). mp: 140-141 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.17-8.13 (m, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.56-7.51 (m, 3H), 7.41 (t, $J = 7.5$ Hz, 1H), 6.03 (s, 1H), 3.93 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.2, 148.7, 146.3, 138.4, 135.5, 131.3, 129.6, 129.4, 127.9, 124.2, 122.3, 120.4, 88.2. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{15}H_{13}N_4O_2$ 281.1033; Found 281.1040.

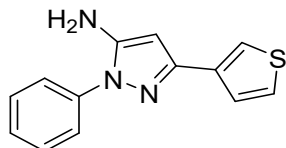


3-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-1H-pyrazol-5-amine (4s): White solid (74.5 mg, 89%). mp: 153-154 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.37-7.34 (m, 2H), 7.29 (d, $J = 8.0$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 2H), 5.87 (s, 1H), 3.85 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 147.9, 147.4, 145.8, 138.6, 129.5, 127.8, 127.4, 124.1, 119.4, 108.3, 106.3, 101.0, 88.0. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{16}H_{14}N_3O_2$ 280.1081; Found 280.1091.

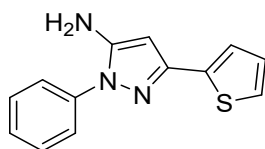


3-(naphthalen-2-yl)-1-phenyl-1H-pyrazol-5-amine (4t): White solid (52.2 mg, 61%). mp: 191-193 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.02-8.00 (m, 1H), 7.88-7.82 (m, 3H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.49-7.44 (m, 2H), 7.39 (t, $J = 7.5$ Hz, 1H), 6.11 (s, 1H), 3.89 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ

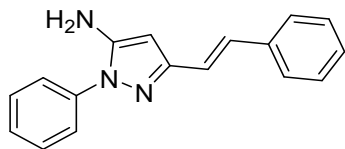
151.5, 146.0, 138.6, 133.6, 133.2, 130.8, 129.6, 128.3, 128.1, 127.7, 127.6, 125.1, 125.8, 124.3, 124.1, 88.4. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{19}H_{16}N_3$ 286.1339; Found 286.1326.



1-phenyl-3-(thiophen-3-yl)-1H-pyrazol-5-amine (4u): White solid (31.8 mg, 44%). mp: 158-160 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.58 (m, 3H), 7.49 (t, $J = 8.5$ Hz, 3H), 7.38-7.32 (m, 2H), 5.86 (s, 1H), 3.85 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 145.6, 138.6, 135.4, 129.5, 127.5, 125.1, 125.6, 124.3, 120.8, 88.5. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{13}H_{12}N_3S$ 242.0746; Found 242.0743.

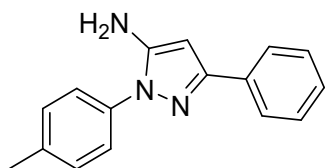


1-phenyl-3-(thiophen-2-yl)-1H-pyrazol-5-amine (4v): White solid (34.7 mg, 48%). mp: 117-118 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.37-7.33 (m, 2H), 7.24-7.23 (m, 1H), 7.05-7.03 (m, 1H), 5.86 (s, 1H), 3.82 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.9, 145.8, 138.4, 136.9, 129.5, 127.6, 127.3, 124.5, 124.3, 123.9, 88.2. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{13}H_{12}N_3S$ 242.0746; Found 242.0755.

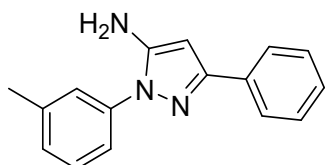


(E)-1-phenyl-3-styryl-1H-pyrazol-5-amine (4w): White solid (18.1 mg, 23%). mp: 120-123 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **1H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.50-7.47 (m, 4H), 7.38-7.32 (m, 3H), 7.25 (d, $J = 5.6$ Hz, 1H), 7.09 (d, $J = 16.4$ Hz, 1H), 7.03 (d, $J = 16.4$ Hz, 1H), 5.88 (s, 1H), 3.84 (br, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 145.7, 138.5, 137.3, 130.3, 129.6, 128.7, 127.6, 127.5, 125.5, 124.0, 121.2, 87.5.

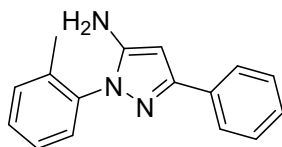
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}N_3$ 262.1339; Found 262.1343.



3-phenyl-1-(p-tolyl)-1H-pyrazol-5-amine (5a): White solid (54.5 mg, 73%). mp: 141-143 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.31-7.28 (m, 3H), 5.95 (s, 1H), 3.83 (br, 2H), 2.41 (s, 3H). **¹³C NMR** (125 MHz, $CDCl_3$) δ 151.3, 145.8, 137.5, 136.1, 133.6, 130.1, 128.5, 127.7, 125.6, 124.2, 87.9, 21.1. **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{16}H_{16}N_3$ 250.1339; Found 250.1340.

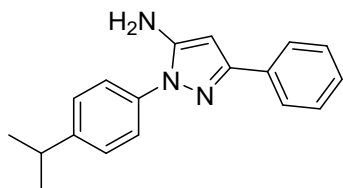


3-phenyl-1-(m-tolyl)-1H-pyrazol-5-amine (5b): White solid (48.6 mg, 65%). mp: 90-91 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.46 (s, 1H), 7.41-7.29 (m, 5H), 7.18 (d, $J = 7.2$ Hz, 1H), 5.93 (s, 1H), 3.86 (br, 2H), 2.42 (s, 3H). **¹³C NMR** (101 MHz, $CDCl_3$) δ 151.4, 145.9, 139.7, 138.5, 133.6, 129.2, 128.5, 128.3, 127.8, 125.7, 125.0, 121.1, 88.0, 21.4. **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{16}H_{16}N_3$ 250.1339; Found 250.1337.

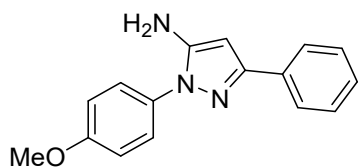


3-phenyl-1-(o-tolyl)-1H-pyrazol-5-amine (5c): Yellow oil (47.1 mg, 63%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.41-7.34 (m, 5H), 7.31-7.28 (m, 2H), 5.94 (s, 1H), 3.61 (br, 2H), 2.21 (s, 3H). **¹³C NMR** (125 MHz, $CDCl_3$) δ 151.3, 146.4, 137.0, 136.8, 133.8, 131.4, 129.4, 128.4, 128.1, 127.6, 125.9, 125.6, 86.5, 17.5. **HRMS**

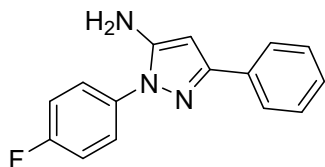
(ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₆N₃ 250.1339; Found 250.1346.



1-(4-isopropylphenyl)-3-phenyl-1H-pyrazol-5-amine (5d): White solid (51.6 mg, 62%). mp: 132-133 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35-7.29 (m, 3H), 5.93 (s, 1H), 3.84 (br, 2H), 3.01-2.93 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 151.2, 148.5, 145.8, 136.3, 133.6, 128.5, 127.7, 127.5, 125.6, 124.3, 87.9, 33.9, 24.0. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₈H₂₀N₃ 278.1652; Found 278.1620.

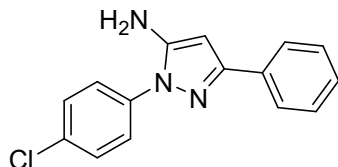


1-(4-methoxyphenyl)-3-phenyl-1H-pyrazol-5-amine (5e): White solid (38.2 mg, 48%). mp: 183-184 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.95 (s, 1H), 3.85 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 159.1, 151.2, 145.8, 133.6, 131.5, 128.4, 127.7, 125.1, 125.6, 114.7, 87.7, 55.6. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₆N₃O 266.1288; Found 266.1292.

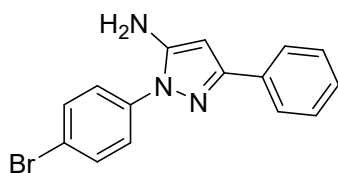


1-(4-fluorophenyl)-3-phenyl-1H-pyrazol-5-amine (5f): White solid (60.7 mg, 80%). mp: 134-136 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.61-7.58 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 5.93 (s, 1H), 3.80 (br, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 161.7 (C-F, ¹*J*_{C-F} = 246.3 Hz), 151.6,

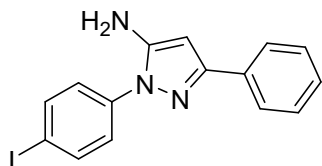
145.9, 134.8 (C-F, $^4J_{C-F} = 3.8$ Hz), 133.4, 128.5, 127.9, 125.2 (C-F, $^2J_{C-F} = 8.8$ Hz), 125.6, 116.3 (C-F, $^2J_{C-F} = 22.5$ Hz), 88.3. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{15}H_{13}FN_3$ 254.1088; Found 254.1084.



1-(4-chlorophenyl)-3-phenyl-1H-pyrazol-5-amine (5g): White solid (44.4 mg, 55%). mp: 141-143 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). 1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, $J = 7.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 5.97 (s, 1H), 3.82 (br, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 145.9, 137.3, 133.3, 133.0, 129.6, 128.6, 128.0, 125.6, 125.1, 88.7. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{15}H_{13}ClN_3$ 270.0793; Found 270.0791.

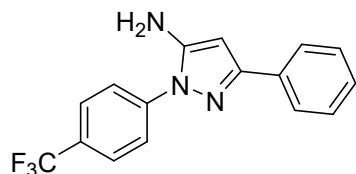


1-(4-bromophenyl)-3-phenyl-1H-pyrazol-5-amine (5h): White solid (60.1 mg, 64%). mp: 157-158 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). 1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, $J = 7.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 5.94 (s, 1H), 3.81 (br, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 145.8, 137.9, 133.3, 132.6, 128.5, 128.0, 125.7, 125.4, 120.8, 88.9. **HRMS (ESI)** m/z : $[M + H]^+$ Calcd for $C_{15}H_{13}BrN_3$ 314.0287; Found 314.0276.

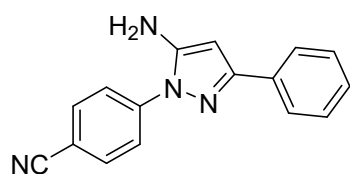


1-(4-iodophenyl)-3-phenyl-1H-pyrazol-5-amine (5i): White solid (58.5 mg, 54%). mp: 177-178 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). 1H NMR (500 MHz, $CDCl_3$) δ 7.81-7.79 (m, 4H), 7.44-7.38 (m, 4H), 7.31

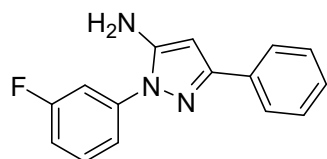
(t, $J = 7.5$ Hz, 1H), 5.96 (s, 1H), 3.81 (br, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 151.9, 145.8, 138.6, 133.2, 128.5, 128.0, 125.7, 125.5, 91.9, 88.9. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{IN}_3$ 362.0149; Found 362.0134.



3-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-amine (5j): White solid (54.5 mg, 60%). mp: 171-172 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ^1H NMR (500 MHz, CDCl_3) δ 7.85-7.81 (m, 4H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 5.98 (s, 1H), 3.88 (br, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.3, 146.0, 141.8, 133.1, 128.8 (C-F, $^2J_{\text{C-F}} = 33.8$ Hz), 128.6, 128.2, 125.6 (C-F, $^3J_{\text{C-F}} = 3.8$ Hz), 125.7, 123.9 (C-F, $^1J_{\text{C-F}} = 270.0$ Hz), 123.3, 89.5. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}_3$ 304.1056; Found 304.1057.

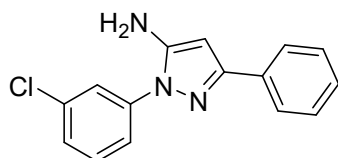


4-(5-amino-3-phenyl-1H-pyrazol-1-yl)benzotrile (5k): White solid (50.7 mg, 65%). mp: 168-170 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 9.0$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 6.02 (s, 1H), 3.91 (br, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.7, 146.1, 142.7, 133.4, 132.8, 128.6, 128.4, 125.7, 123.0, 118.4, 109.9, 90.4. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_4$ 261.1135; Found 261.1135.

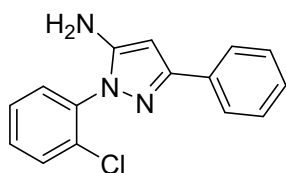


1-(3-fluorophenyl)-3-phenyl-1H-pyrazol-5-amine (5l): White solid (61.5 mg, 81%). mp: 98-99 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl

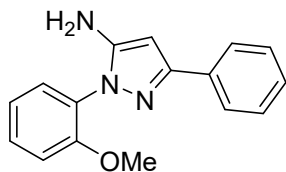
acetate, 5/1). **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.46-7.38 (m, 5H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 5.96 (s, 1H), 3.89 (br, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 163.1 (C-F, ¹*J*_{C-F} = 246.3 Hz), 151.9, 145.9, 140.2 (C-F, ³*J*_{C-F} = 10.0 Hz), 133.2, 130.7 (C-F, ³*J*_{C-F} = 10.0 Hz), 128.6, 128.1, 125.7, 119.0 (C-F, ⁴*J*_{C-F} = 3.8 Hz), 114.1 (C-F, ²*J*_{C-F} = 21.3 Hz), 111.3 (C-F, ²*J*_{C-F} = 25.0 Hz), 88.8. **HRMS (ESI)** m/z: [M + H]⁺ Calcd for C₁₅H₁₃FN₃ 254.1088; Found 254.1093.



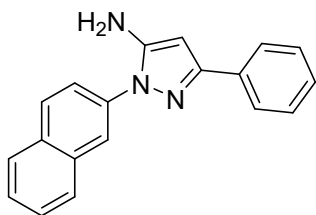
1-(3-chlorophenyl)-3-phenyl-1H-pyrazol-5-amine (5m): White solid (58.1 mg, 72%). mp: 135-137 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.72 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 3H), 7.33-7.32 (m, 2H), 5.95 (s, 1H), 3.87 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 152.0, 145.9, 139.9, 135.2, 133.2, 130.4, 128.5, 128.1, 127.3, 125.7, 124.1, 121.6, 88.9. **HRMS (ESI)** m/z: [M + H]⁺ Calcd for C₁₅H₁₃ClN₃ 270.0793; Found 270.0785.



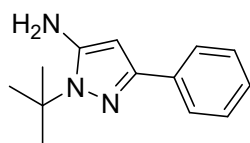
1-(2-chlorophenyl)-3-phenyl-1H-pyrazol-5-amine (5n): White solid (53.3 mg, 66%). mp: 103-105 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.55-7.53 (m, 2H), 7.42-7.37 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 5.96 (s, 1H), 3.70 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 152.2, 147.1, 135.9, 133.4, 132.3, 130.6, 130.5, 130.4, 128.5, 128.0, 127.9, 125.7, 87.7. **HRMS (ESI)** m/z: [M + H]⁺ Calcd for C₁₅H₁₃ClN₃ 270.0793; Found 270.0794. Spectroscopic data for the title compound were consistent with those reported in the literature.³



1-(2-methoxyphenyl)-3-phenyl-1H-pyrazol-5-amine (5o): White solid (39.8 mg, 50%). mp: 146-148 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.40-7.36 (m, 3H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 1H), 3.87 (br, 2H), 3.84 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 153.6, 152.0, 147.6, 133.9, 129.8, 129.3, 128.4, 128.0, 127.6, 125.7, 121.8, 112.8, 87.9, 56.4. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆N₃O 266.1288; Found 266.1290.

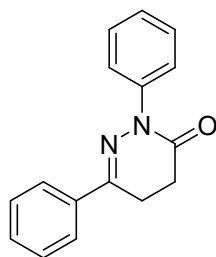


1-(naphthalen-2-yl)-3-phenyl-1H-pyrazol-5-amine (5p): White solid (60.7 mg, 71%). mp: 133-135 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.87-7.82 (m, 4H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.53-7.50 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 5.96 (s, 1H), 3.90 (br, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 146.2, 136.1, 133.5, 133.4, 132.2, 129.7, 128.6, 128.1, 127.9, 127.9, 125.9, 125.5, 125.7, 122.8, 121.7, 88.3. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₉H₁₆N₃ 286.1339; Found 286.1325.

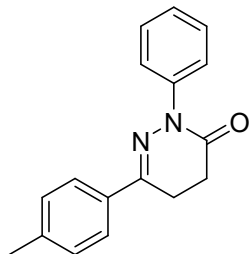


1-(tert-butyl)-3-phenyl-1H-pyrazol-5-amine (5q): White solid (17.4 mg, 27%). mp: 102-104 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 5.90 (s, 1H), 3.58 (br, 2H), 1.69 (s, 9H). ¹³C NMR

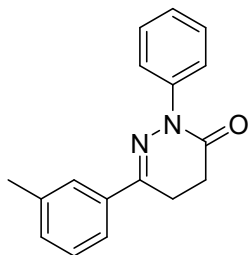
(125 MHz, CDCl₃) δ 147.6, 145.4, 134.3, 128.4, 127.1, 125.3, 91.4, 58.9, 29.4. **HRMS (ESI)** m/z : [M + H]⁺ Calcd for C₁₃H₁₈N₃ 216.1495; Found 216.1506.



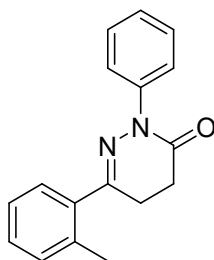
2,6-diphenyl-4,5-dihydropyridazin-3(2H)-one (7a): off white solid (41.3 mg, 55%). mp: 96-98 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (400 MHz, CDCl₃) δ 7.81-7.78 (m, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.43-7.39 (m, 5H), 7.27 (t, J = 7.6 Hz, 1H), 3.07 (t, J = 8.0 Hz, 2H), 2.77 (t, J = 8.0 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 165.4, 151.6, 141.3, 135.5, 130.1, 128.7, 128.6, 125.7, 125.1, 125.0, 28.1, 22.9. **HRMS (ESI)** m/z : [M + H]⁺ Calcd for C₁₆H₁₅N₂O 251.1179; Found 251.1170. Spectroscopic data for the title compound were consistent with those reported in the literature.⁴



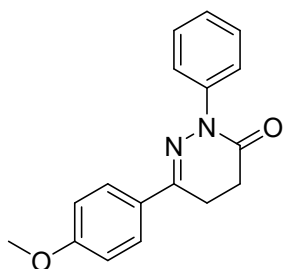
2-phenyl-6-(*p*-tolyl)-4,5-dihydropyridazin-3(2H)-one (7b): red oil (33.3 mg, 42%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.69 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.28-7.21 (m, 3H), 3.05 (t, J = 8.0 Hz, 2H), 2.75 (t, J = 8.0 Hz, 2H), 2.38 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.4, 151.7, 141.4, 140.3, 132.7, 129.4, 128.5, 125.5, 125.1, 124.9, 28.1, 22.9, 21.4. **HRMS (ESI)** m/z : [M + Na]⁺ Calcd for C₁₇H₁₆N₂NaO 287.1155; Found 287.1169. Spectroscopic data for the title compound were consistent with those reported in the literature.⁴



2-phenyl-6-(*m*-tolyl)-4,5-dihydropyridazin-3(2H)-one (7c): red oil (38.0 mg, 48%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.62-7.57 (m, 4H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.31-7.21 (m, 3H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.4, 151.9, 141.3, 138.4, 135.5, 130.8, 128.5, 125.7, 125.6, 125.0, 123.3, 28.1, 23.0, 21.5. **HRMS (ESI)** *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₆N₂NaO 287.1155; Found 287.1160.

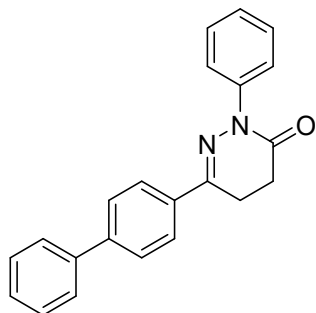


2-phenyl-6-(*o*-tolyl)-4,5-dihydropyridazin-3(2H)-one (7d): red oil (19.8 mg, 25%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.41-7.36 (m, 3H), 7.30-7.25 (m, 4H), 3.00 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.3, 155.2, 141.1, 136.5, 135.8, 131.3, 129.2, 128.5, 128.0, 125.6, 125.0, 124.9, 28.3, 26.6, 21.1. **HRMS (ESI)** *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₆N₂NaO 287.1155; Found 287.1157.

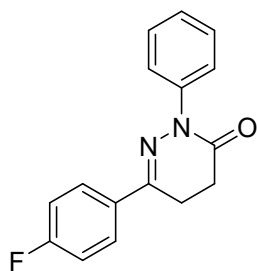


6-(4-methoxyphenyl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7e): red oil (26.1 mg, 31%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate,

4/1). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (d, $J = 9.0$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.26 (t, $J = 7.0$ Hz, 1H), 6.92 (d, $J = 9.0$ Hz, 2H), 3.83 (s, 3H), 3.04 (t, $J = 8.0$ Hz, 2H), 2.75 (t, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 165.4, 161.2, 151.4, 141.4, 128.5, 128.0, 127.7, 125.5, 124.9, 114.0, 55.4, 28.1, 22.8. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2$ 281.1285; Found 281.1279.

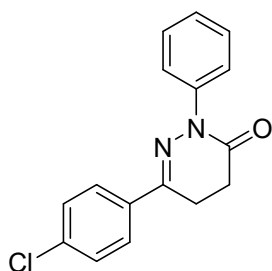


6-([1,1'-biphenyl]-4-yl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7f): light brown solid (58.7 mg, 60%). mp: 123-125 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.64-7.60 (m, 6H), 7.46-7.35 (m, 4H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 3.07 (t, $J = 8.0$ Hz, 2H), 2.77 (t, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 165.3, 151.2, 142.7, 141.3, 140.2, 134.4, 129.0, 128.6, 127.9, 127.3, 127.1, 125.6, 125.6, 124.9, 28.1, 22.9. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}$ 327.1492; Found 327.1501.

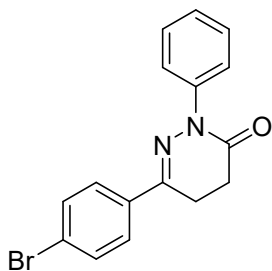


6-(4-fluorophenyl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7g): light green oil (41.8 mg, 52%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80-7.77 (m, 2H), 7.59-7.57 (m, 2H), 7.43-7.40 (m, 2H), 7.29-7.25 (m, 1H), 7.11-7.08 (m, 2H), 3.05 (t, $J = 8.0$ Hz, 2H), 2.77(t, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 165.1, 163.9 (C-F, $^1J_{\text{C-F}} = 248.8$ Hz), 150.5, 141.2, 131.7 (C-F, $^4J_{\text{C-F}} = 2.5$ Hz), 128.6, 128.1 (C-F, $^3J_{\text{C-F}} = 8.8$ Hz), 125.7, 124.9, 115.7 (C-F, $^2J_{\text{C-F}} = 21.2$ Hz), 28.0, 22.9. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for

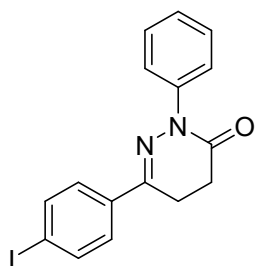
C₁₆H₁₄FN₂O 269.1085; Found 269.1092.



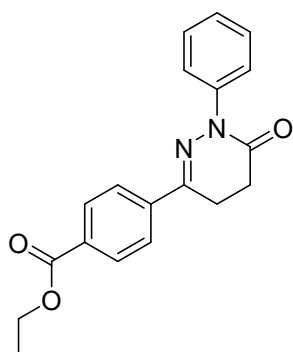
6-(4-chlorophenyl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7h): light yellow oil (56.2 mg, 66%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.44- 7.38 (m, 4H), 7.28 (t, *J* = 7.5 Hz, 1H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.1, 150.2, 141.1, 136.1, 133.9, 128.9, 128.6, 127.4, 125.7, 124.9, 27.9, 22.8. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄ClN₂O 285.0789; Found 285.0791. Spectroscopic data for the title compound were consistent with those reported in the literature.⁴



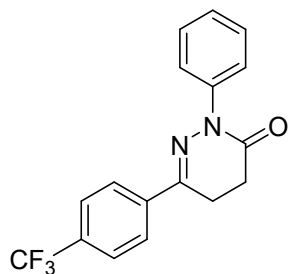
6-(4-bromophenyl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7i): light yellow oil (68.9 mg, 70%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.65 (d, *J* = 9.0 Hz, 2H), 7.57-7.52 (m, 4H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.1, 150.3, 141.2, 134.4, 131.8, 128.6, 127.6, 125.7, 124.9, 124.4, 27.9, 22.7. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄BrN₂O 329.0284; Found 329.0296.



6-(4-iodophenyl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7j): brown solid (67.7 mg, 60%). mp: 98-100 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.57-7.50 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 150.4, 141.2, 137.8, 135.0, 128.6, 127.7, 125.7, 124.9, 96.4, 27.9, 22.6. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄IN₂O 377.0145; Found 377.0133.

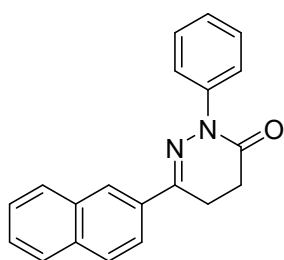


ethyl 4-(6-oxo-1-phenyl-1,4,5,6-tetrahydropyridazin-3-yl)benzoate (7k): light brown solid (73.4 mg, 76%). mp: 59-60 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 165.1, 150.2, 141.1, 139.4, 131.5, 129.8, 128.6, 125.8, 125.9, 124.9, 61.2, 27.9, 22.9, 14.3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₉N₂O₃ 323.1390; Found 323.1388.

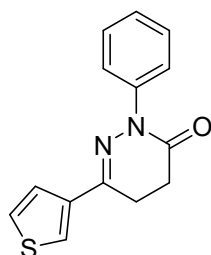


2-phenyl-6-(4-(trifluoromethyl)phenyl)-4,5-dihydropyridazin-3(2H)-one (7l): brown solid (72.5 mg, 76%). mp: 79-81 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5

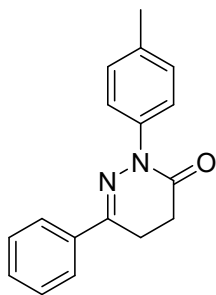
Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 1H), 3.12 (t, $J = 8.0$ Hz, 2H), 2.82 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.0, 149.7, 141.1, 138.8, 131.6 (C-F, $^2J_{\text{C-F}} = 32.8$ Hz), 128.6, 125.9, 125.4, 125.6 (C-F, $^3J_{\text{C-F}} = 3.8$ Hz), 124.9, 123.9 (C-F, $^1J_{\text{C-F}} = 272.2$ Hz), 27.8, 22.9. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ 319.1053; Found 319.1053.



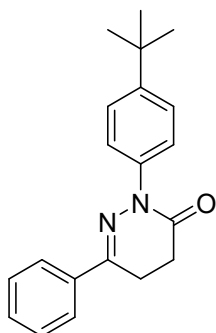
6-(naphthalen-2-yl)-2-phenyl-4,5-dihydropyridazin-3(2H)-one (7m): light yellow oil (28.8 mg, 32%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ^1H NMR (500 MHz, CDCl_3) δ 8.12-8.07 (m, 2H), 7.89-7.84 (m, 3H), 7.64 (d, $J = 7.5$ Hz, 2H), 7.53-7.43 (m, 4H), 7.29 (t, $J = 7.5$ Hz, 1H), 3.21 (t, $J = 8.0$ Hz, 2H), 2.83 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.4, 151.3, 141.3, 134.0, 133.0, 132.9, 128.6, 128.6, 128.4, 127.8, 127.2, 125.7, 125.2, 125.0, 123.2, 28.1, 22.8. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$ 301.1335; Found 301.1344.



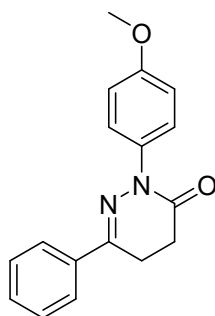
2-phenyl-6-(thiophen-3-yl)-4,5-dihydropyridazin-3(2H)-one (7n): red oil (23.1 mg, 30%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ^1H NMR (500 MHz, CDCl_3) δ 7.59-7.57 (m, 4H), 7.42 (t, $J = 8.0$ Hz, 2H), 7.35-7.34 (m, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 3.06 (t, $J = 8.0$ Hz, 2H), 2.78 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.2, 148.2, 141.2, 138.6, 128.5, 125.6, 125.6, 125.7, 125.0, 124.9, 28.1, 23.7. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OS}$ 257.0743; Found 257.0755.



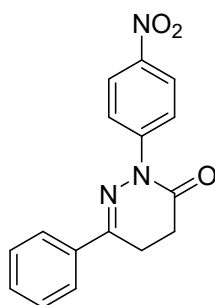
6-phenyl-2-(*p*-tolyl)-4,5-dihydropyridazin-3(2*H*)-one (7o): off white solid (22.2 mg, 28%). mp: 116-118 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.80-7.79 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.42-7.40 (m, 3H), 7.22 (d, *J* = 8.5 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.3, 151.3, 138.8, 136.5, 135.5, 129.9, 129.2, 128.6, 125.1, 124.9, 28.0, 22.9, 21.1. **HRMS (ESI)** *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₆N₂NaO 287.1155; Found 287.1159.



2-(4-(*tert*-butyl)phenyl)-6-phenyl-4,5-dihydropyridazin-3(2*H*)-one (7p): brown solid (20.2 mg, 22%), mp: 133-135 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). **¹H NMR** (500 MHz, CDCl₃) δ 7.81-7.79 (m, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.45-7.40 (m, 5H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 1.34 (s, 9H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.3, 151.4, 149.5, 138.7, 135.5, 129.9, 128.6, 125.1, 125.5, 124.5, 34.6, 31.4, 28.0, 22.9. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₂₀H₂₃N₂O 307.1805; Found 307.1801.



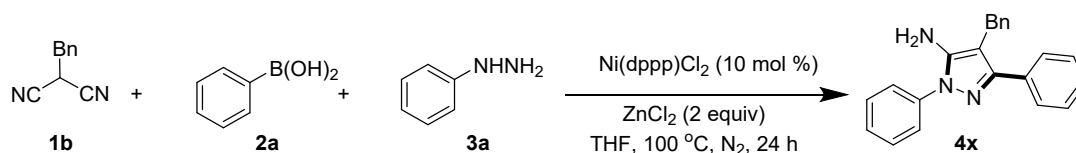
2-(4-methoxyphenyl)-6-phenyl-4,5-dihydropyridazin-3(2H)-one (7q): light brown solid (34.5 mg, 41%), mp: 125-128 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ¹H NMR (500 MHz, CDCl₃) δ 7.80-7.78 (m, 2H), 7.53-7.40 (m, 5H), 6.95-6.93 (m, 2H), 3.82 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 165.4, 158.2, 151.4, 135.5, 134.4, 130.0, 128.6, 125.4, 125.1, 113.9, 55.5, 27.9, 22.9. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₇H₁₇N₂O₂ 281.1285; Found 281.1275.



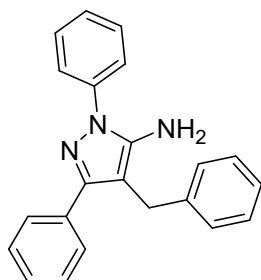
2-(4-nitrophenyl)-6-phenyl-4,5-dihydropyridazin-3(2H)-one (7r): yellow solid (23.1 mg, 26%), mp: 110-112 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 4/1). ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, *J* = 9.5 Hz, 2H), 7.95 (d, *J* = 9.5 Hz, 2H), 7.84-7.82 (m, 2H), 7.48-7.47 (m, 3H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.84 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 165.7, 153.3, 146.3, 144.9, 135.0, 130.6, 128.8, 125.2, 124.0, 123.8, 28.3, 22.9. **HRMS (ESI)** *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄N₃O₃ 296.1030; Found 296.1034. Spectroscopic data for the title compound were consistent with those reported in the literature.⁵

4.Synthetic Applications

4.1. Synthesis of tetra-substituted pyrazole

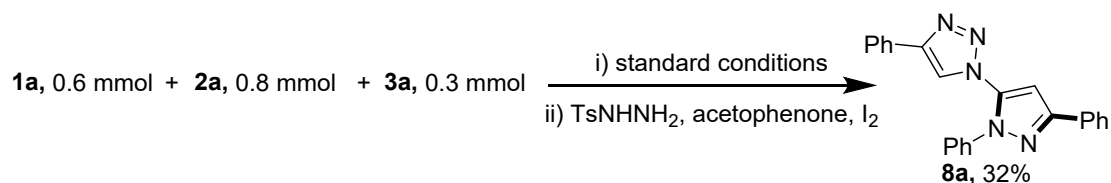


In a 10 mL Schlenk reaction tube, 2-benzylmalononitrile (**1b**) (0.6 mmol, 2.0 equiv, 93.6 mg), phenylboronic acid (**2a**) (0.8 mmol, 2.6 equiv, 97.6 mg), phenylhydrazine or substituted phenylhydrazine hydrochloride (**3a**) (0.3 mmol, 1.0 equiv, 32.4 mg), Ni(dppp)Cl₂ (0.03 mmol, 10 mol %, 16.3 mg), ZnCl₂ (0.6 mmol, 2.0 equiv, 81.8mg), were dissolved in tetrahydrofuran (2.0 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent to afford the desired products **4x** in 90% yield.

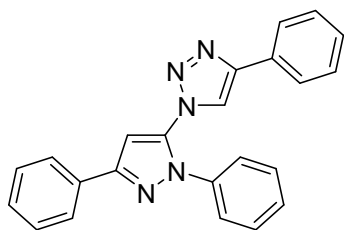


4-benzyl-1,3-diphenyl-1H-pyrazol-5-amine (4x): yellow oil (87.8 mg, 90%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.63 (t, *J* = 8.0 Hz, 4H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.37-7.29 (m, 8H), 7.21 (t, *J* = 7.0 Hz, 1H), 3.93 (s, 2H), 3.53 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 151.4, 143.6, 139.9, 138.8, 133.9, 129.5, 128.8, 128.4, 128.2, 128.0, 127.7, 127.3, 125.3, 124.0, 99.8, 29.4. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₀N₃ 326.1652; Found 326.1657

4.2. Synthesis of biologically active molecule in one pot



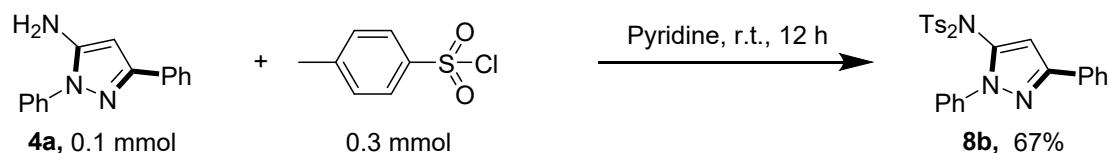
In a 10 mL Schlenk reaction tube, malononitrile (**1a**) (0.6 mmol, 2.0 equiv, 39.6 mg), phenylboronic acid (**2a**) (0.8 mmol, 2.6 equiv, 97.6 mg), phenylhydrazine or substituted phenylhydrazine hydrochloride (**3a**) (0.3 mmol, 1.0 equiv, 32.4 mg), Ni(dppp)Cl₂ (0.03 mmol, 10 mol %, 16.3 mg), ZnCl₂ (0.6 mmol, 2.0 equiv, 81.8 mg), were dissolved in tetrahydrofuran (2.0 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the mixture was cooled to room temperature, acetophenone (0.25 mmol, 1.0 equiv, 30.1 mg), 4-Methylbenzenesulfonhydrazide (0.375 mmol, 1.5 equiv, 69.8 mg), iodine (0.375 mmol, 1.5 equiv, 95.2 mg) was added to the mixture, The mixture was stirred at 100 °C under air for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and water (30 mL) was added to the mixture, which was then extracted with EtOAc (3 × 10 mL). The extract was washed with 10% w/w Na₂S₂O₃ (aq), dried over anhydrous Na₂SO₄, and the solvent was removed under vacuum to provide the crude product, which was purified by column chromatography on silica gel to afford the desired products **8a** in 32% yield.⁶



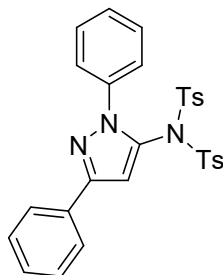
1-(1,3-diphenyl-1H-pyrazol-5-yl)-4-phenyl-1H-1,2,3-triazole (8a): light-yellow solid (34.9 mg, 32%), mp: 122-123 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.80-7.78 (m, 3H), 7.46-7.30 (m, 11H), 7.02 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 148.1, 137.7, 135.5, 132.1, 129.5, 129.0, 128.9, 128.8, 128.6, 126.0, 125.8, 123.8, 121.8, 102.3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₁₈N₅ 364.1557; Found

364.1577. Spectroscopic data for the title compound were consistent with those reported in the literature.³

4.3. The transformation of amino group



In a 10 mL Schlenk reaction tube, 4-tosyl chloride (0.3 mmol, 3.0 equiv, 57.2 mg) was added to a mixture of 1,3-diphenyl-1*H*-pyrazol-5-amine (**4a**) (0.1 mmol, 1.0 equiv, 23.5 mg) in pyridine (1 mL). The mixture was stirred at room temperature under air for 12 h. After completion of the reaction, water (10 mL) was added to the mixture, which was then extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (8:1) as the eluent to afford the desired products **8b** in 67% yield.



***N*-(1,3-diphenyl-1*H*-pyrazol-5-yl)-4-methyl-*N*-tosylbenzenesulfonamide (8b)**: off white solid (36.4 mg, 67%), mp: 205-207 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 8/1). ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.64-7.61 (m, 6H), 7.42-7.34 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 4H), 6.32 (s, 1H), 2.46 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 151.2, 145.7, 138.4, 135.1, 132.6, 132.5, 129.5, 129.3, 129.1, 128.7, 128.4, 128.2, 125.7, 125.6, 105.9, 21.8. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₉H₂₆N₃O₄S₂ 544.1359; Found 544.1348.

4.4. The late-stage oxidation of the obtained product⁷

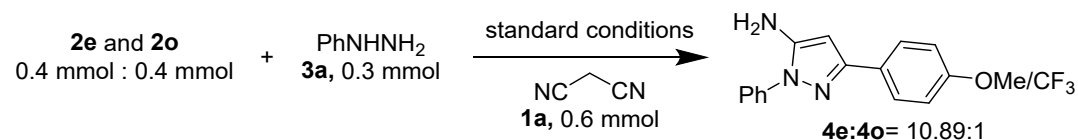


A mixture of 2,6-diphenyl-4,5-dihydropyridazin-3(2H)-one **7a** (0.2 mmol) and iodine (25 mol%) in DMSO was stirred for 8 h at 100 °C. The completion of reaction was monitored by TLC (acetone:hexane = 30:70). The brown-red coloured reaction mixture was poured into saturated solution of sodium thiosulphate. The separated solid product was filtered, dried and recrystallized from methanol. The 2,6-diphenylpyridazin-3(2H)-one **8c** was obtained in 85% yield.

2,6-diphenylpyridazin-3(2H)-one (8c): White solid, (42.2 mg, 85%). Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 2/1). ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 9.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.53-7.40 (m, 6H), 7.15 (d, *J* = 9.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 144.9, 141.8, 134.5, 131.5, 130.3, 129.7, 129.0, 128.8, 128.3, 126.1, 125.50.

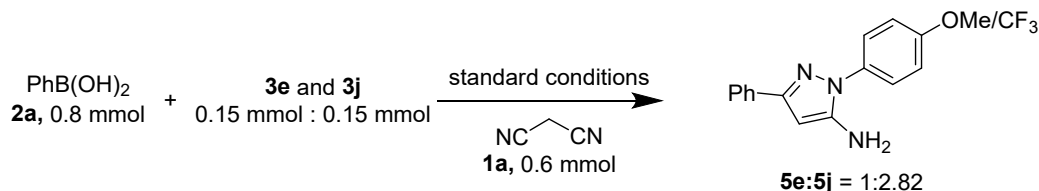
5. The Mechanistic Investigations

5.1. Competitive experiments



In a 10 mL Schlenk reaction tube, malononitrile (**1a**) (0.6 mmol, 2.0 equiv, 39.6 mg), 4-methoxyphenylboronic acid (**2e**) (0.4 mmol, 1.3 equiv, 60.8 mg), 4-trifluoromethylphenylboronic acid (**2o**) (0.4 mmol, 1.3 equiv, 76.0 mg), phenylhydrazine (**3a**) (0.3 mmol, 1.0 equiv, 32.4 mg), Ni(dppp)Cl₂ (0.03 mmol, 10 mol %, 16.3 mg), ZnCl₂ (0.6 mmol, 2.0 equiv, 81.8 mg), were dissolved in tetrahydrofuran (2.0 mL) under N₂ atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO₃ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate,

the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent to afford the desired product **4e** and **4o** separately, the ratio of **4e** and **4o** is 10.89.



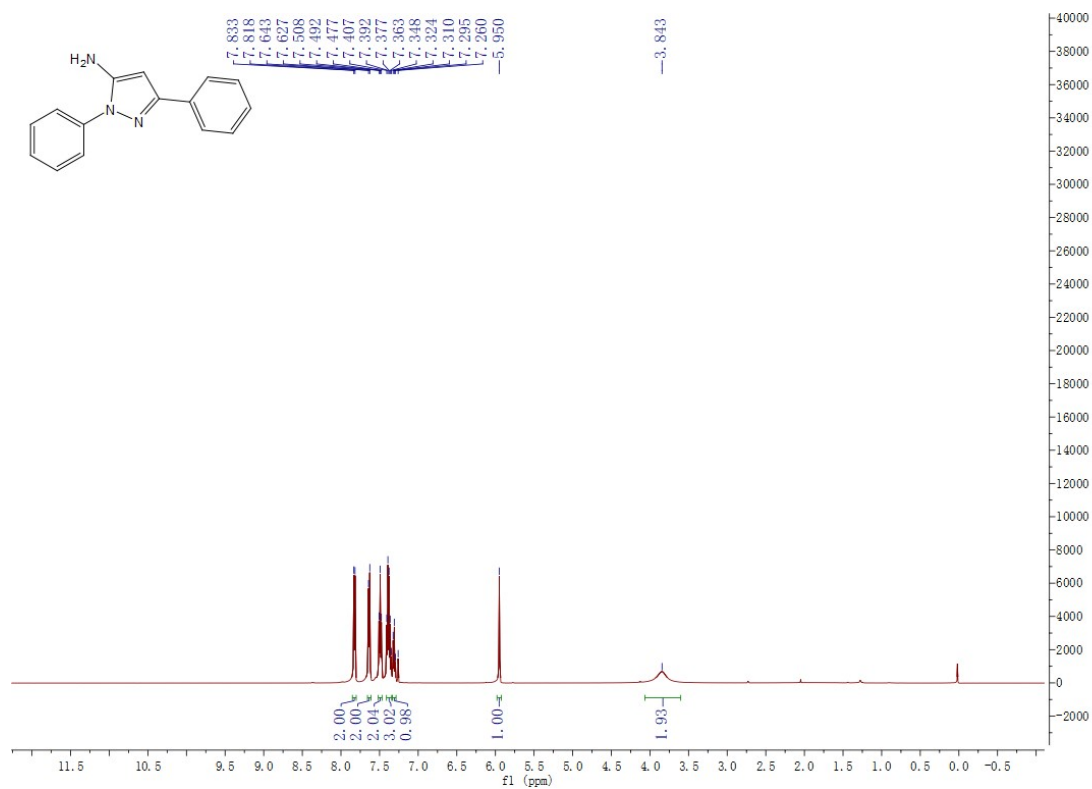
In a 10 mL Schlenk reaction tube, malononitrile (**1a**) (0.6 mmol, 2.0 equiv, 39.6 mg), phenylboronic acid (**2a**) (0.8 mmol, 2.6 equiv, 97.6mg), 4-methoxyphenylhydrazine hydrochloride (**3e**) (0.15 mmol, 1.0 equiv, 26.2mg), 4-(trifluoromethyl)phenylhydrazine hydrochloride (**3j**) (0.15 mmol, 1.0 equiv, 31.9 mg), Ni(dppp)Cl_2 (0.03 mmol, 10 mol %, 16.3 mg), ZnCl_2 (0.6 mmol, 2.0 equiv, 81.8mg), were dissolved in tetrahydrofuran (2.0 mL) under N_2 atmosphere. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated NaHCO_3 (2×10 mL) and then brine (1×10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent to afford the desired product **5e** and **5j** separately, the ratio of **5e** and **5j** is 1 to 2.82.

6. Reference

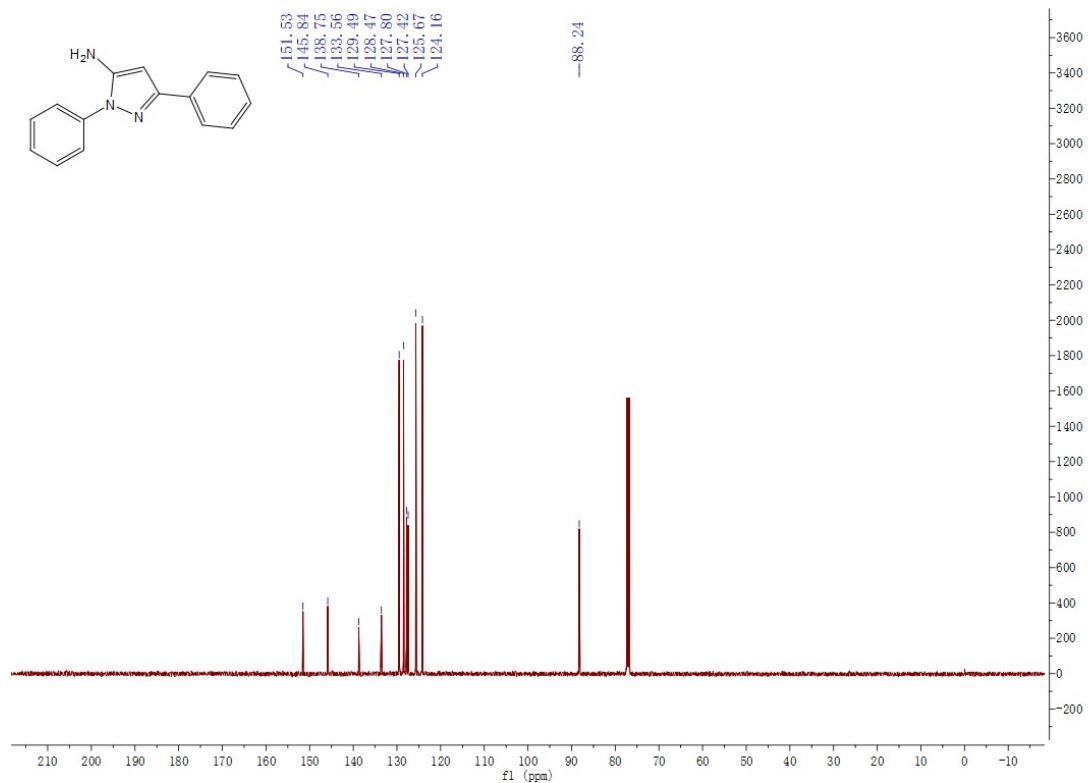
1. J. C. Antilla, J. M. Baskin, T. E. Barder and S. L. Buchwald, *J. Org. Chem.*, 2004, **69**, 5578–5587.
2. G. J. Reddy, D. Latha and K. Srinivasa Rao, *Org. Prep. Proced. Int.*, 2004, **36**, 494–498.
3. T. De Paulis, K. Hemstapat, Y. Chen, Y. Zhang, S. Saleh, D. Alagille, R. M. Baldwin, G. D. Tamagnan and P. J. Conn, *J. Med. Chem.* 2006, **49**, 3332–3344.
4. L. Zare, N.O. Mahmoodi, A. Yahyazadeh, M. Mamaghani and K. Tabatabaeian, *Chin. Chem. Lett.* 2010, **21**, 538–541.

5. G. Tsolomiti, K. Tsolomiti and A. Tsolomiti, *Heterocycl. Commun.* 2007, **13**, 161–164.
6. Z. Chen, Q. Yan, H. Yi, Z. Liu, A. Lei and Y. Zhang, *Chem. Eur. J.* 2014, **20**, 17635–17639.
7. V. T. Humne, S. G. Konda, K. Hasanzadeh, P. D. Lokhande, *Chinese Chemical Letters.* 2011, **20**, 1435–1438.

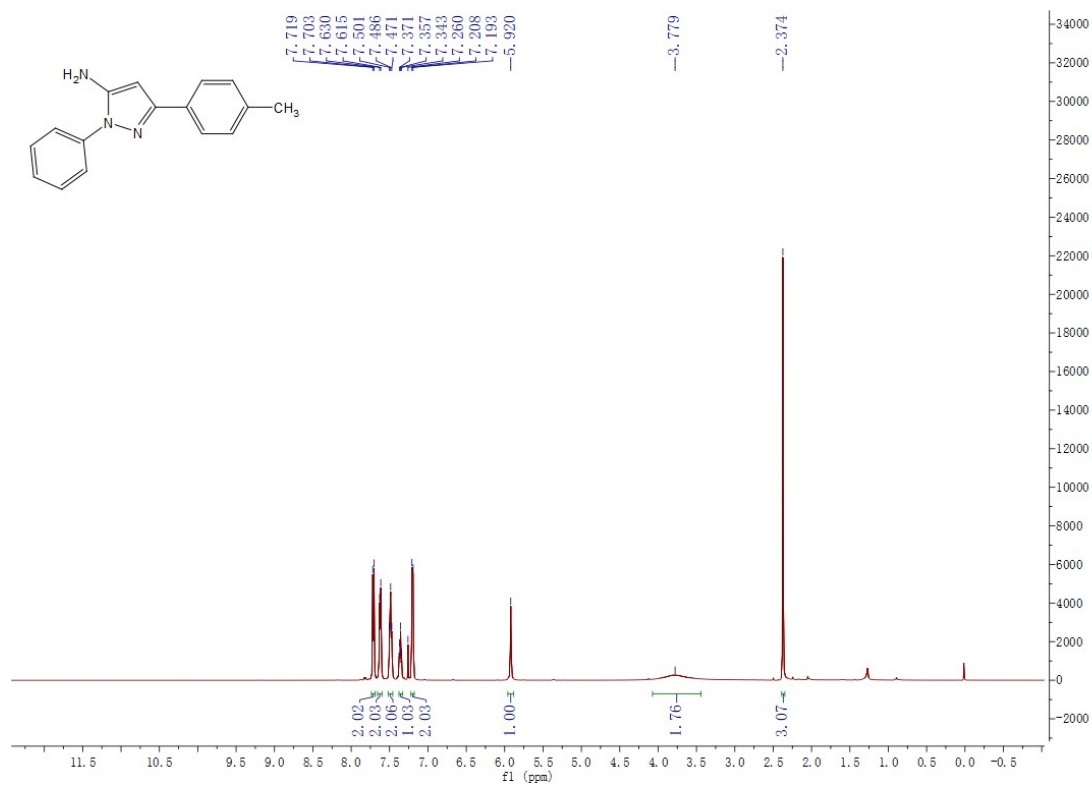
7. NMR Spectra for All Products



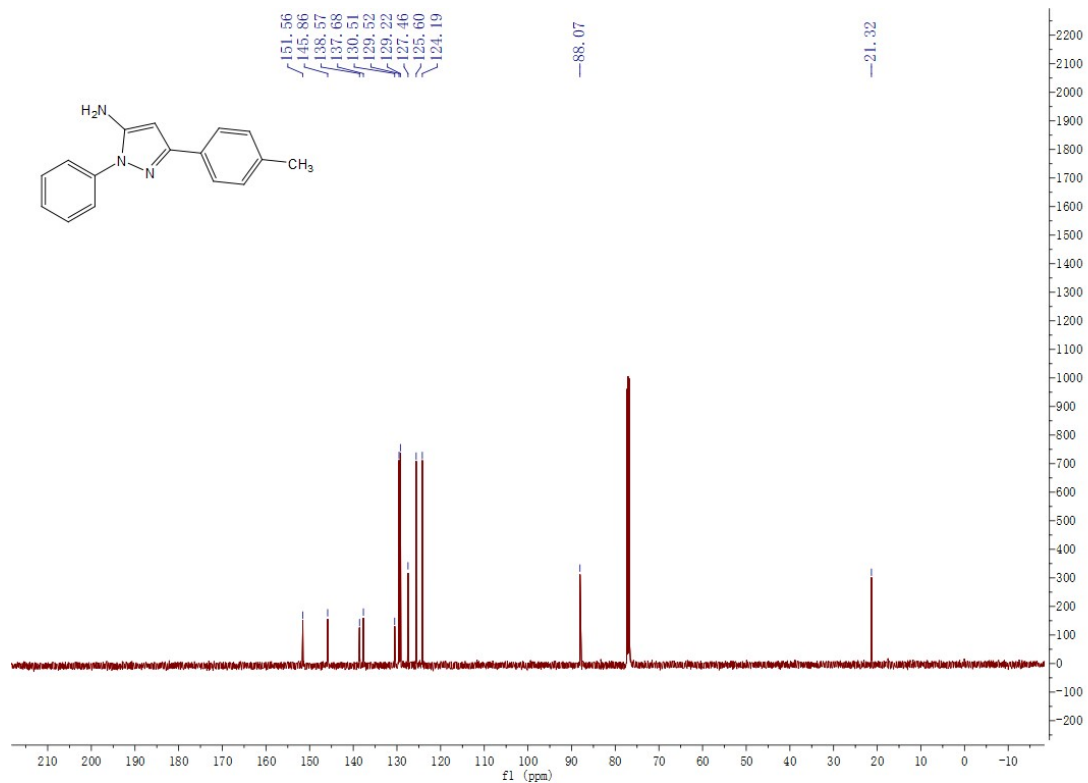
^1H NMR (500 MHz, CDCl_3) of compound **4a**



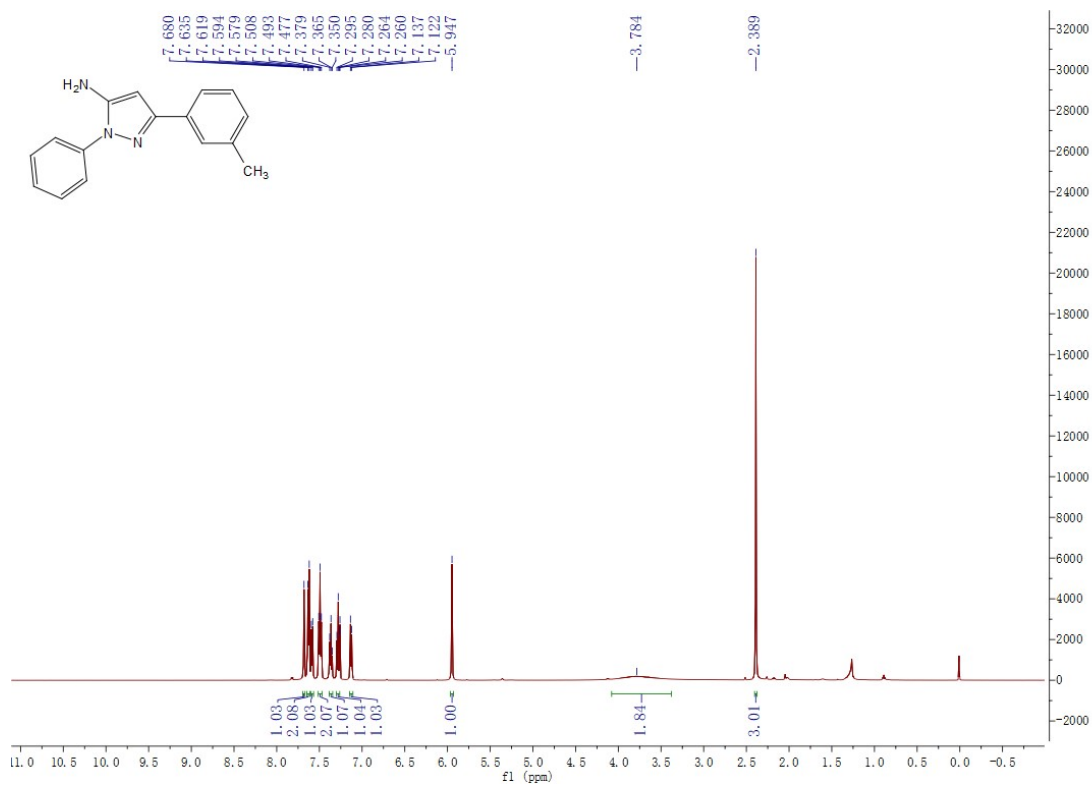
^{13}C NMR (125 MHz, CDCl_3) of compound **4a**



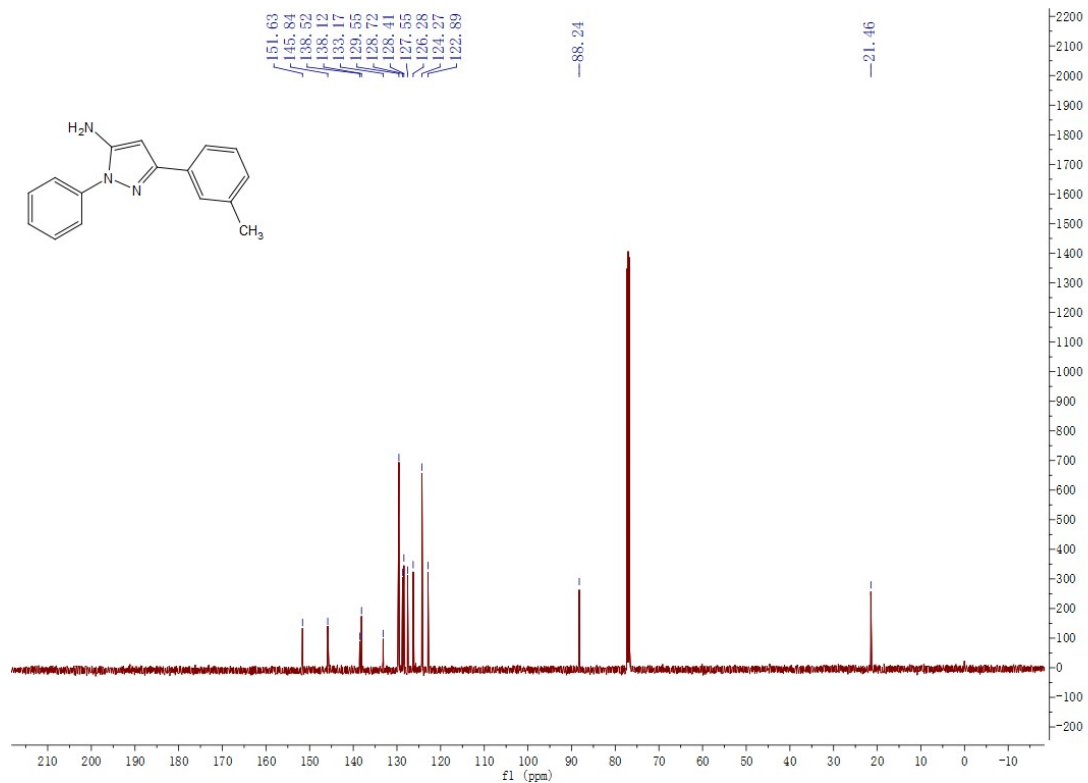
^1H NMR (500 MHz, CDCl_3) of compound **4b**



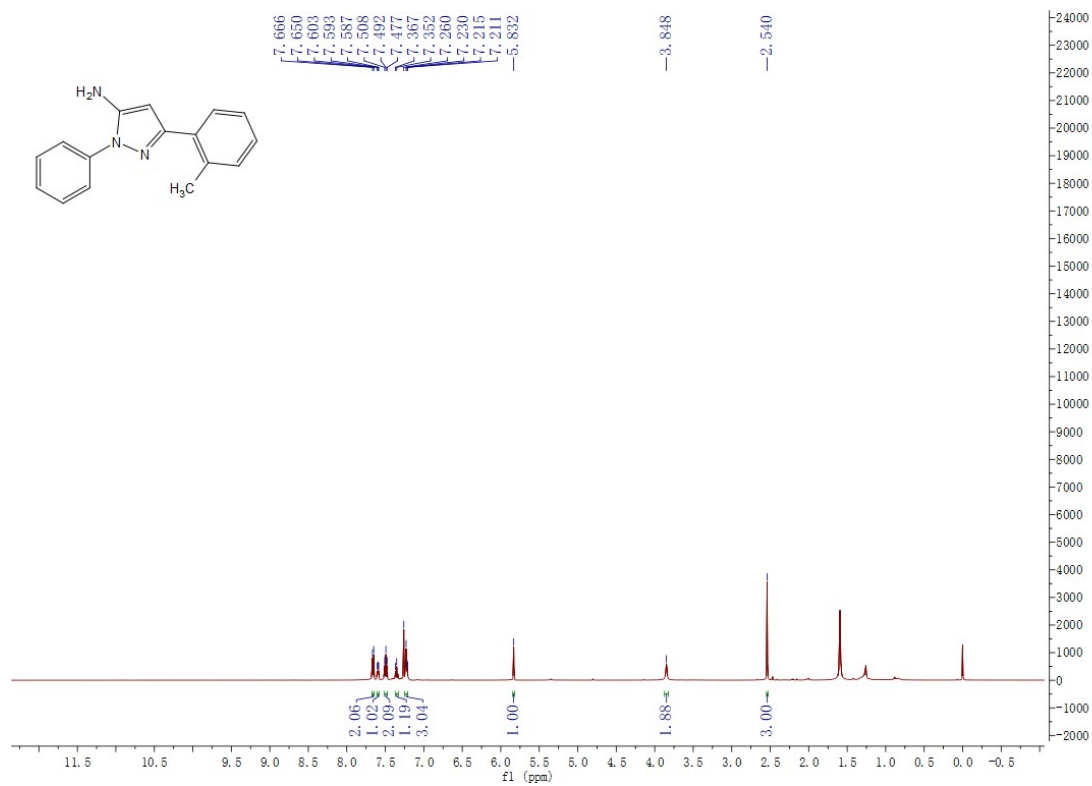
^{13}C NMR (125 MHz, CDCl_3) of compound **4b**



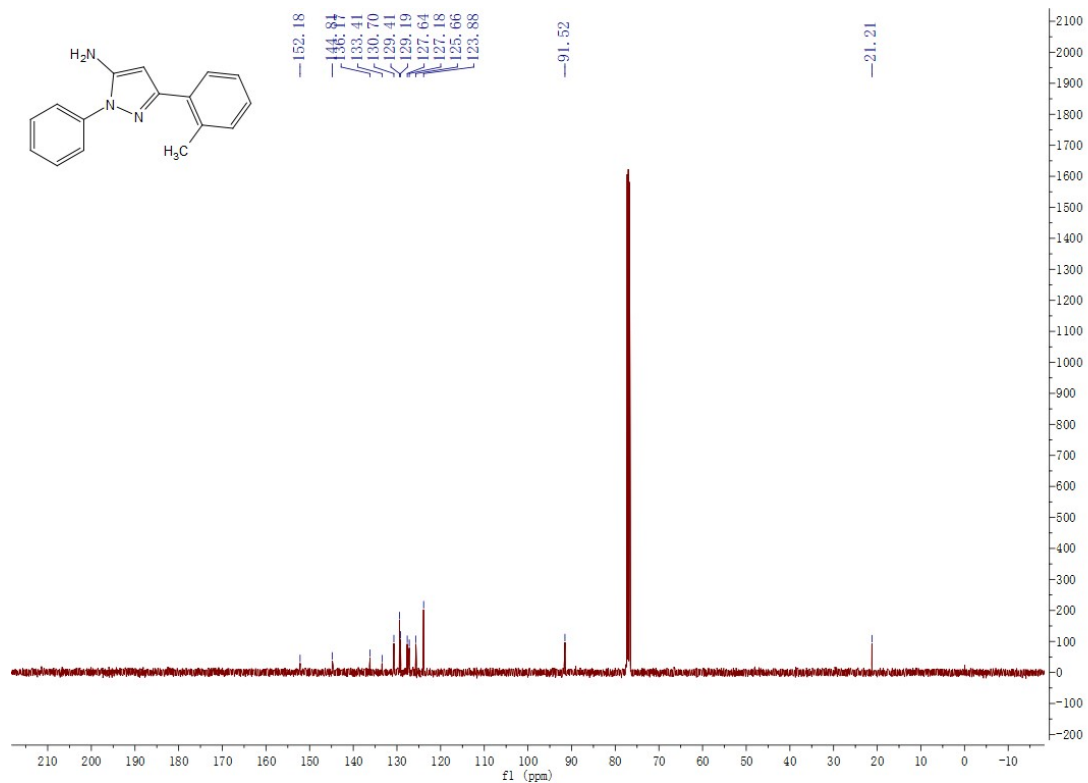
^1H NMR (500 MHz, CDCl_3) of compound **4c**



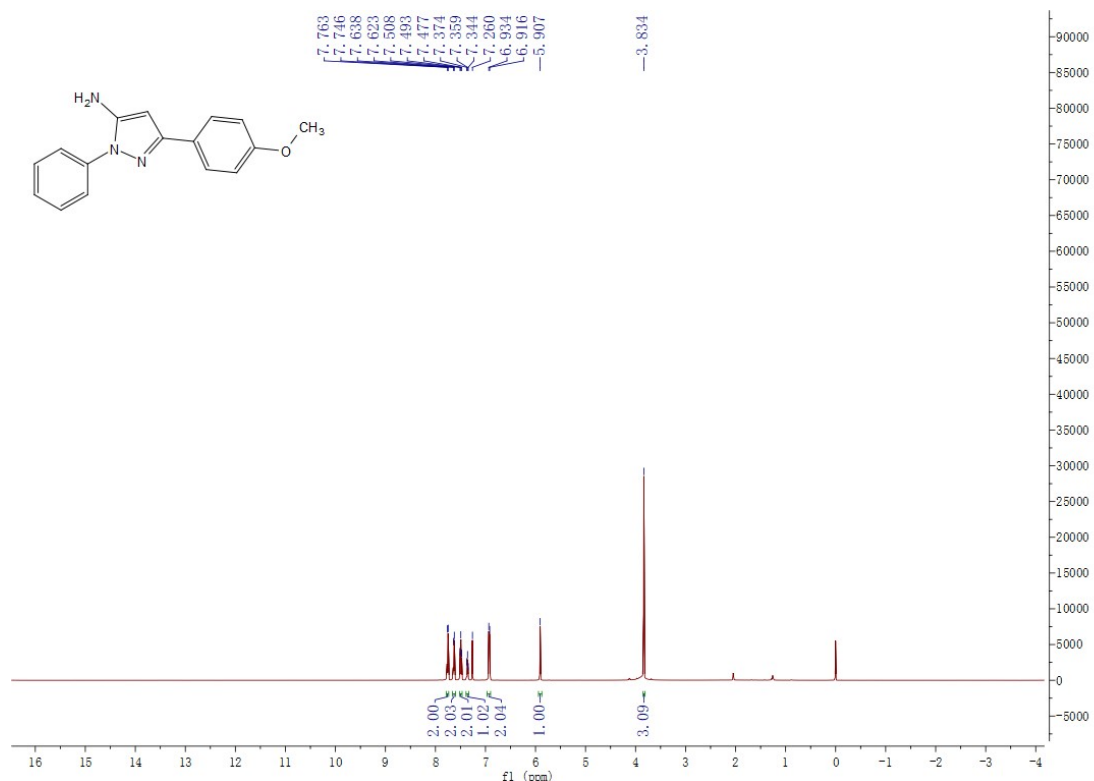
^{13}C NMR (125 MHz, CDCl_3) of compound 4c



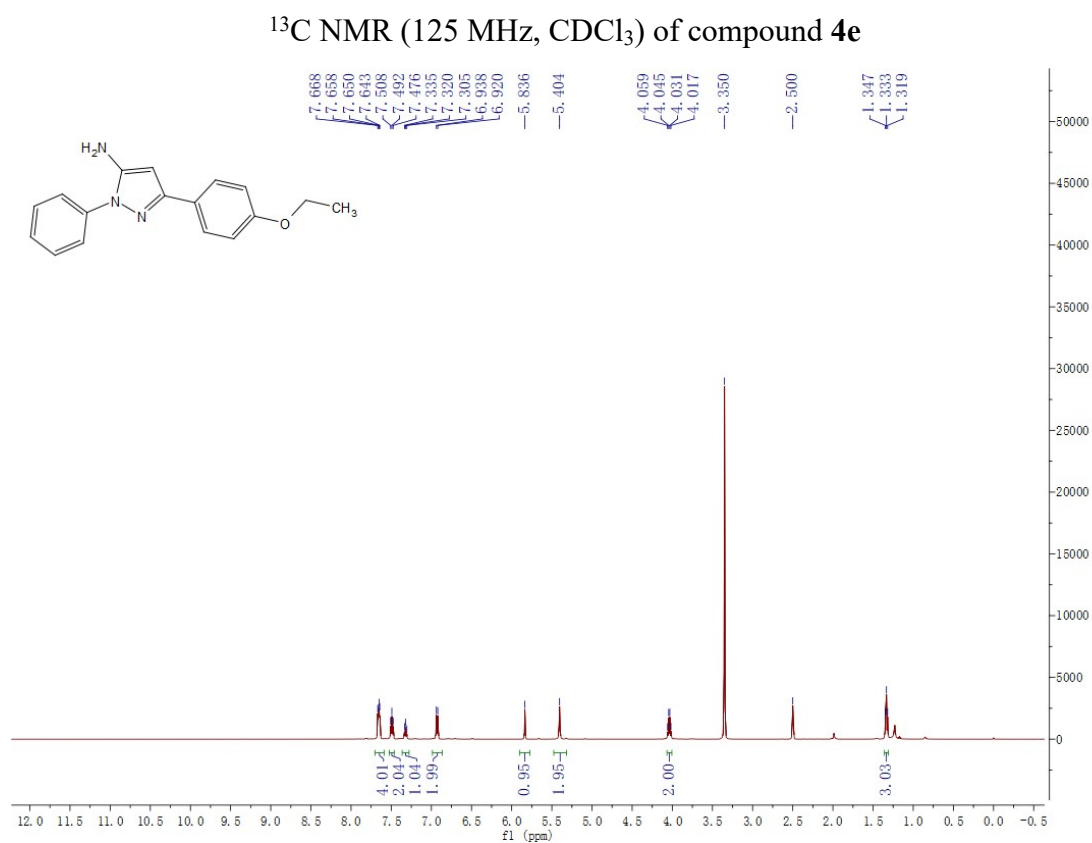
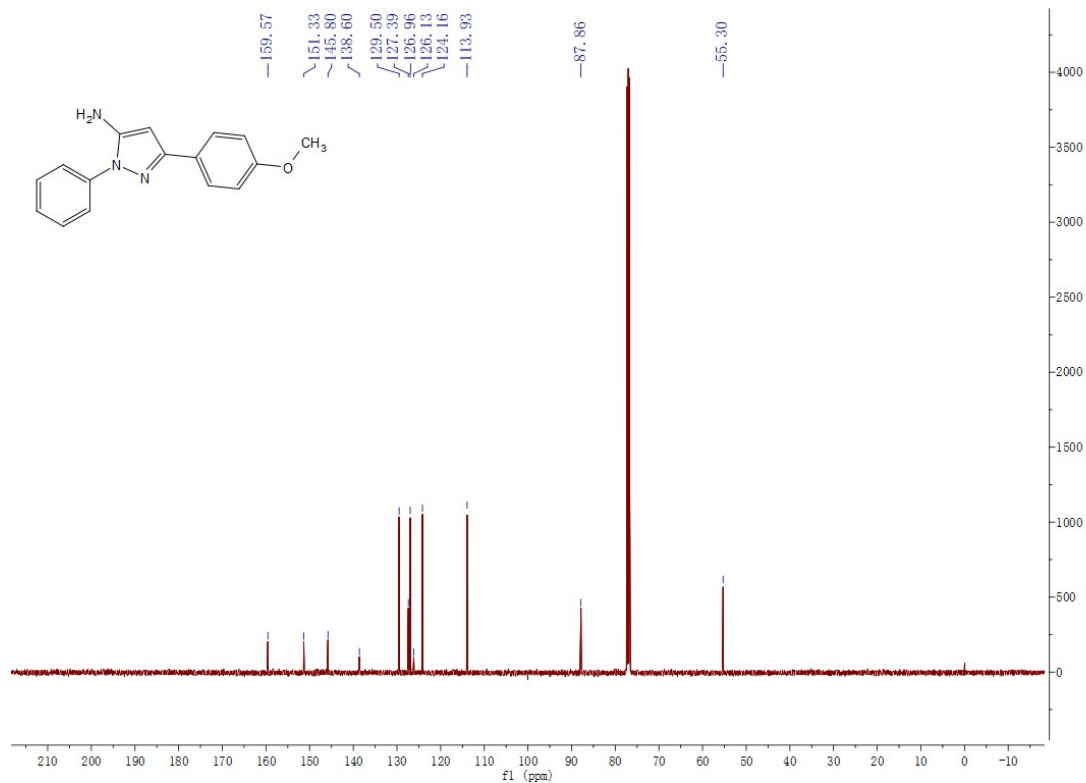
^1H NMR (500 MHz, CDCl_3) of compound 4d

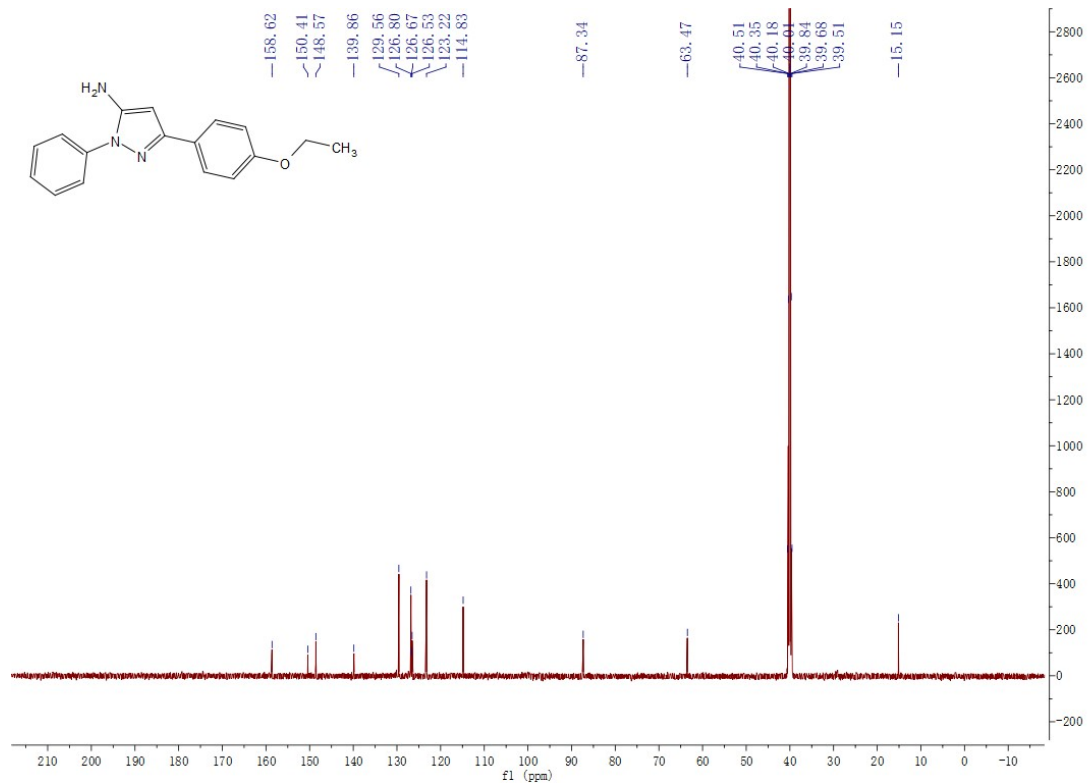


^{13}C NMR (125 MHz, CDCl_3) of compound **4d**

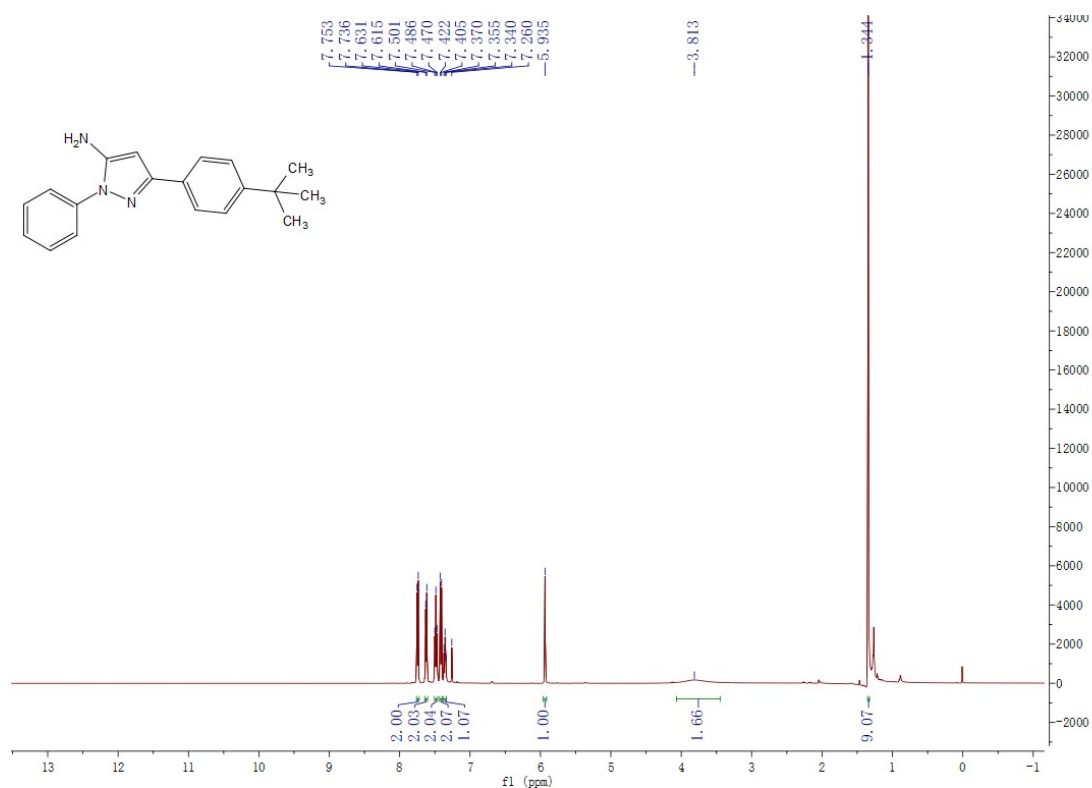


^1H NMR (500 MHz, CDCl_3) of compound **4e**

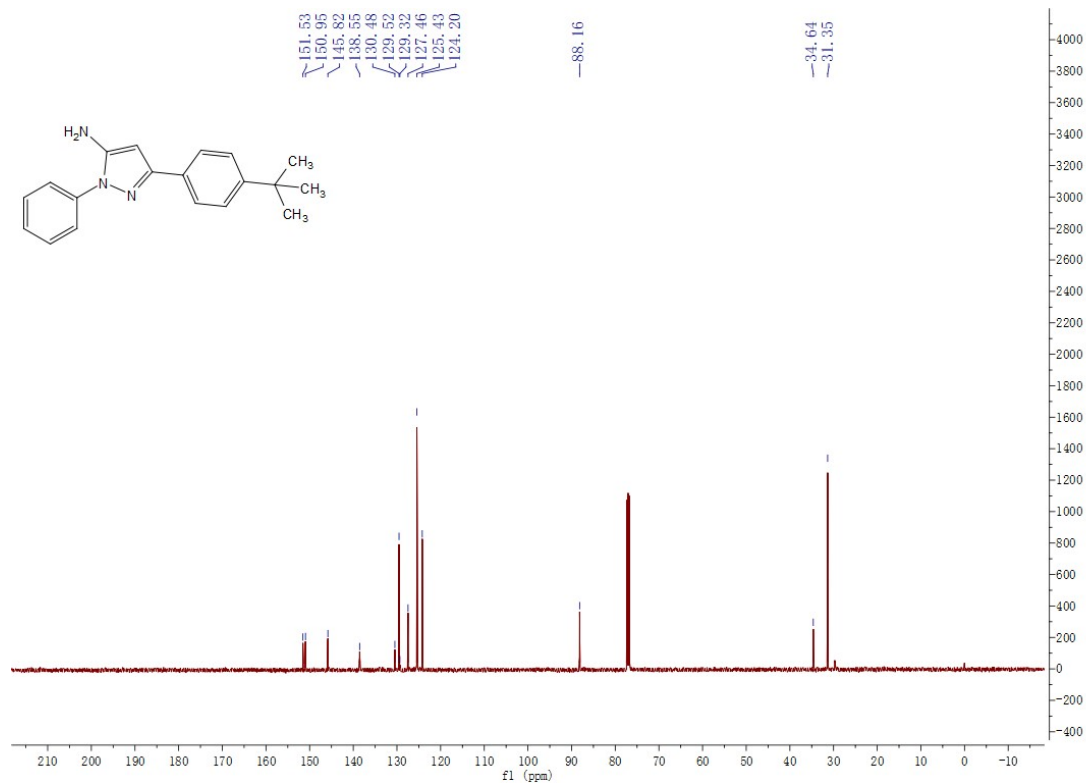




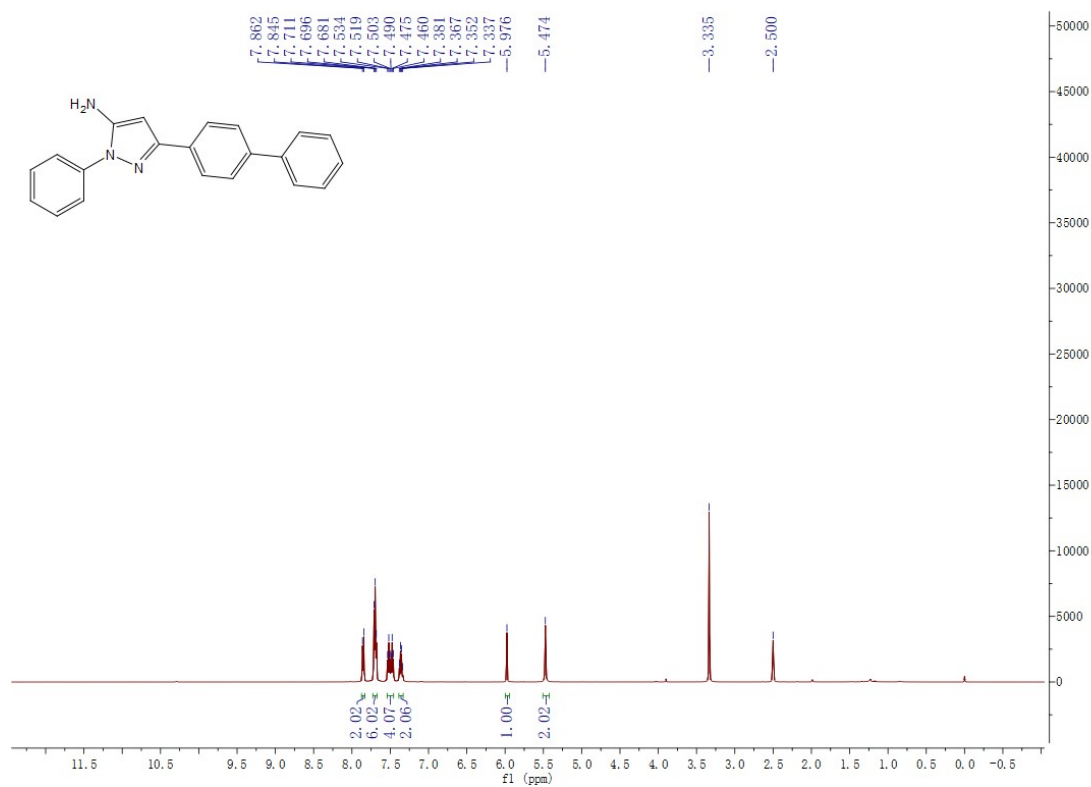
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of compound **4f**



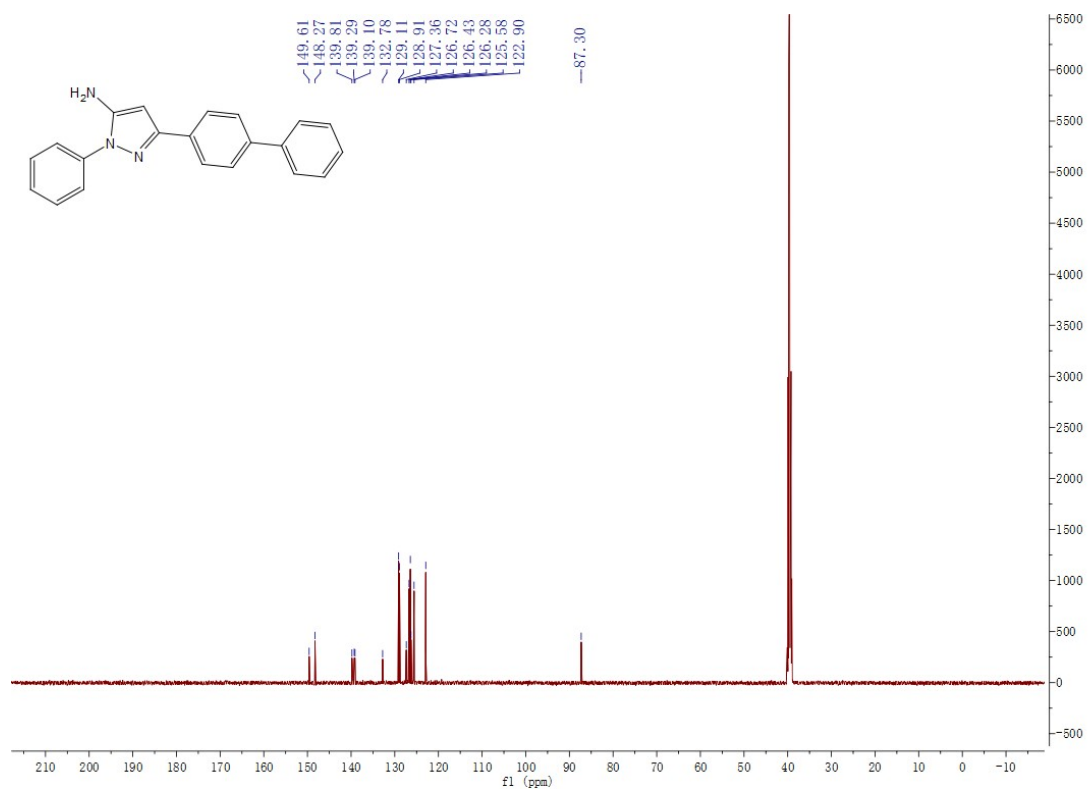
^1H NMR (500 MHz, CDCl_3) of compound **4g**



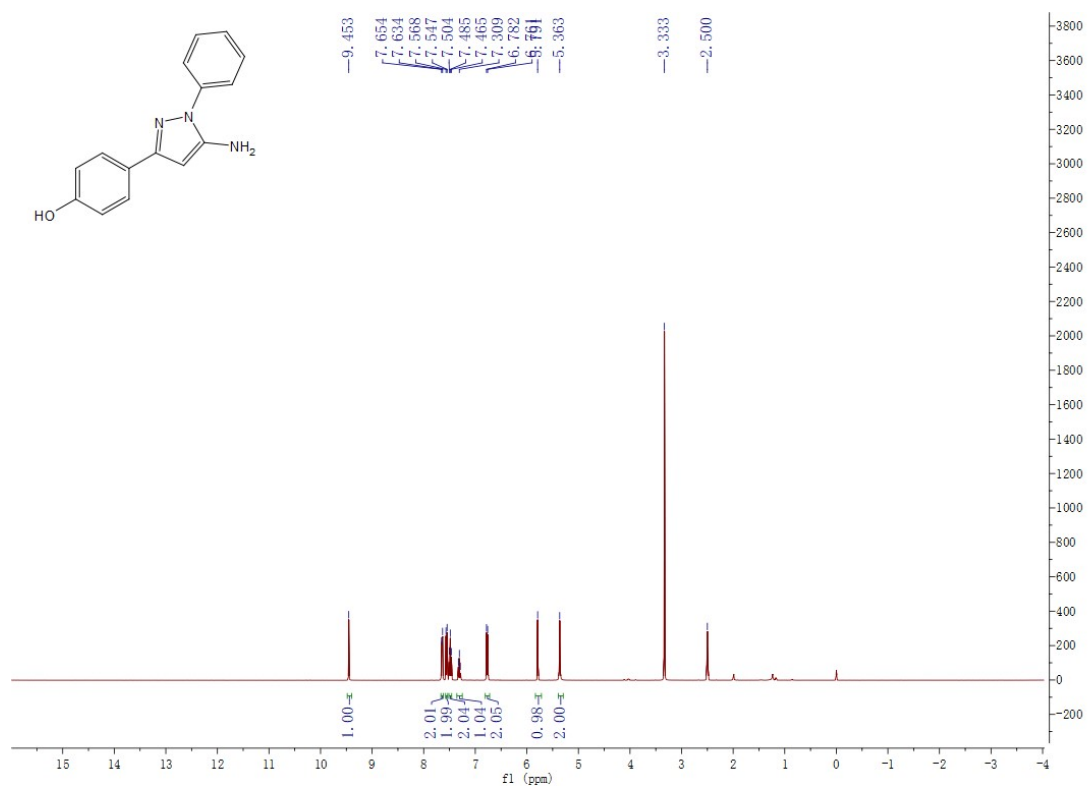
^{13}C NMR (125 MHz, CDCl_3) of compound **4g**



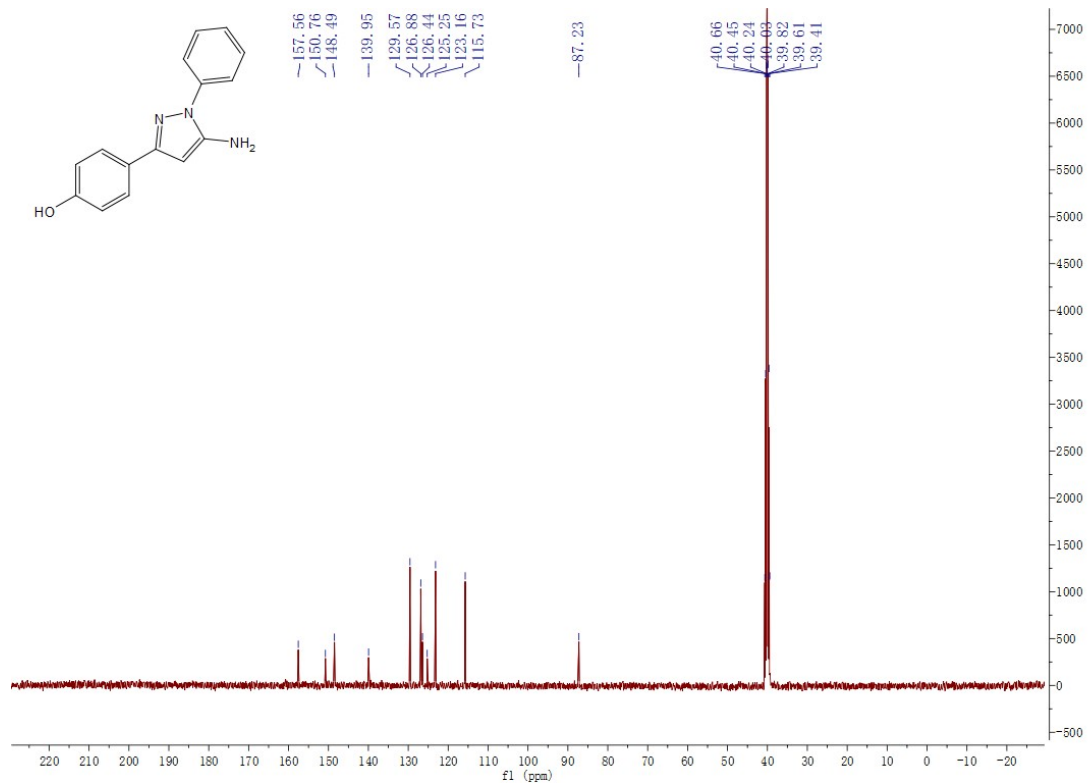
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of compound **4h**



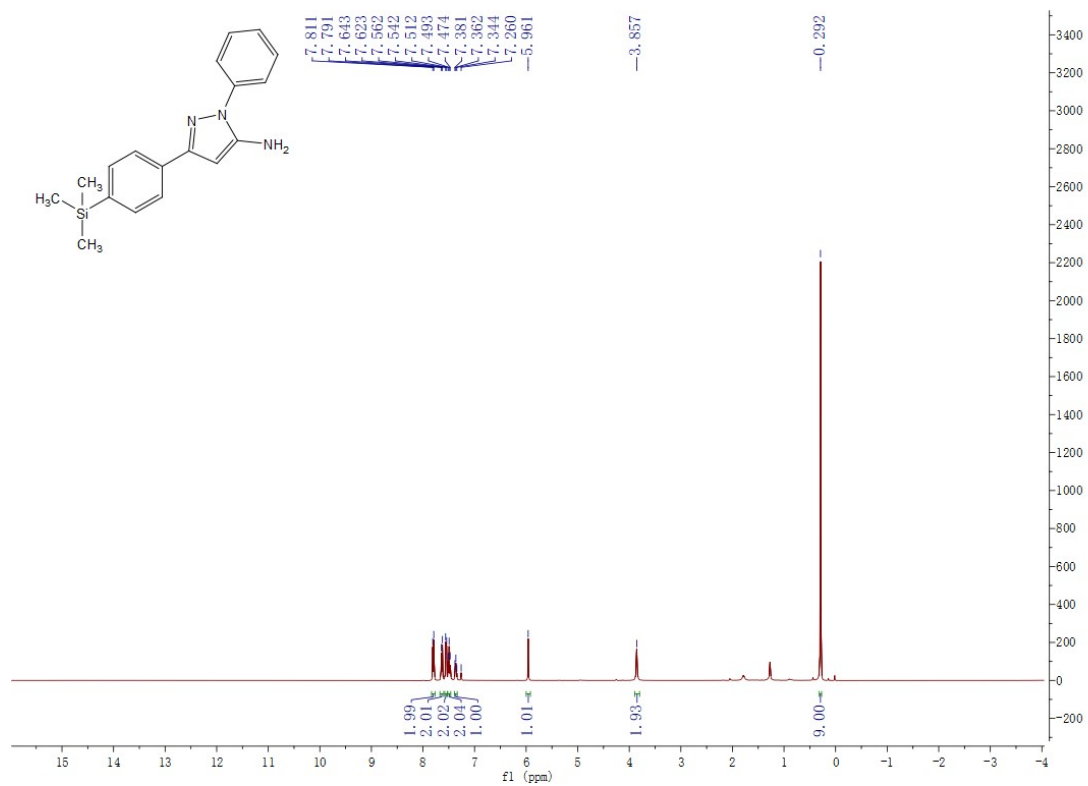
¹³C NMR (125 MHz, DMSO-*d*₆) of compound **4h**



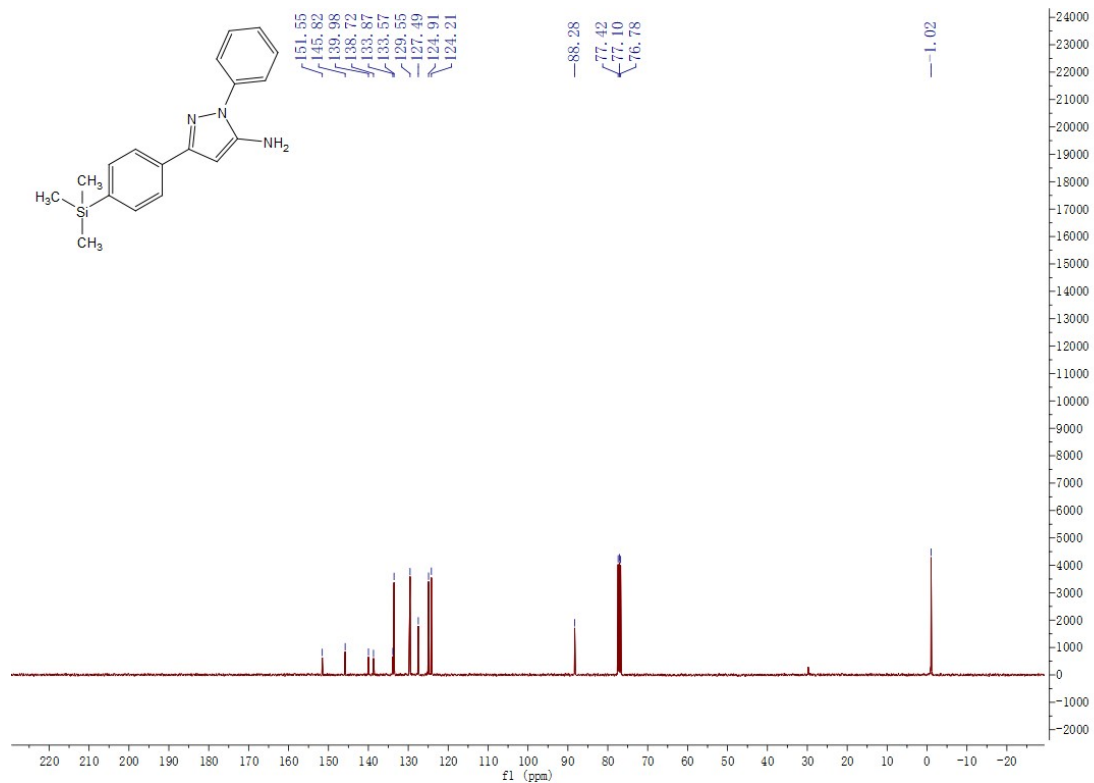
¹H NMR (400 MHz, DMSO-*d*₆) of compound **4i**



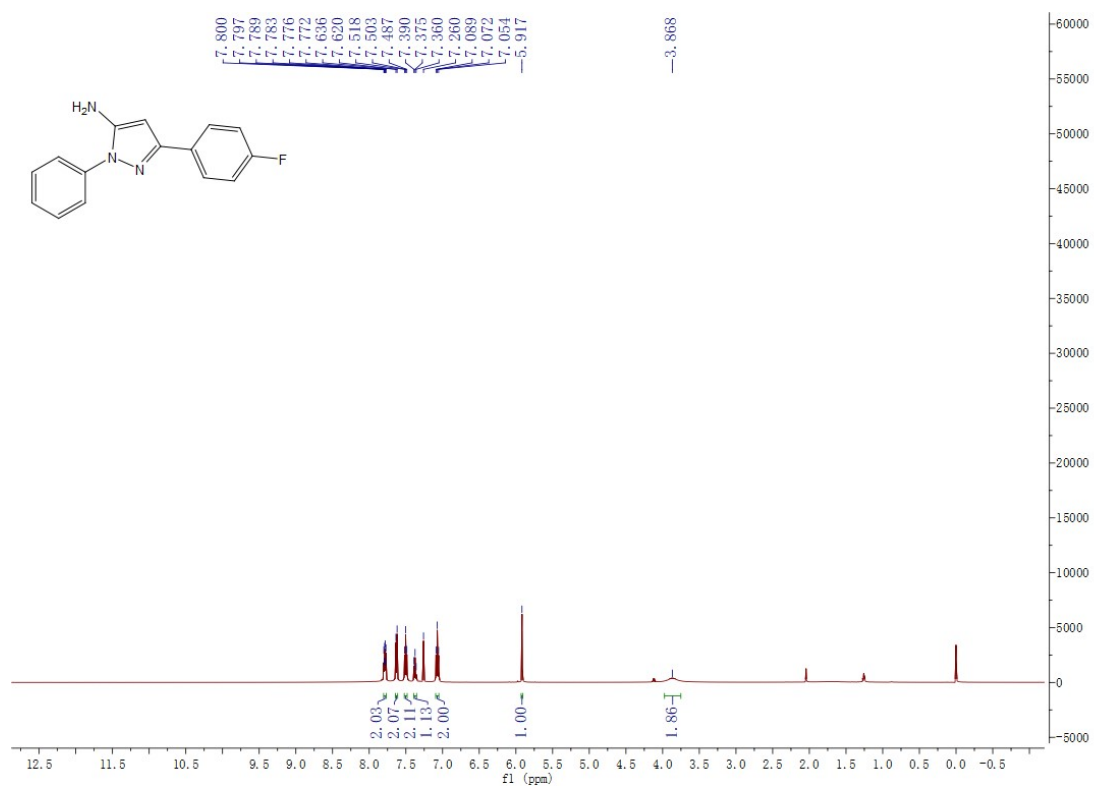
^{13}C NMR (101 MHz, DMSO- d_6) of compound **4i**



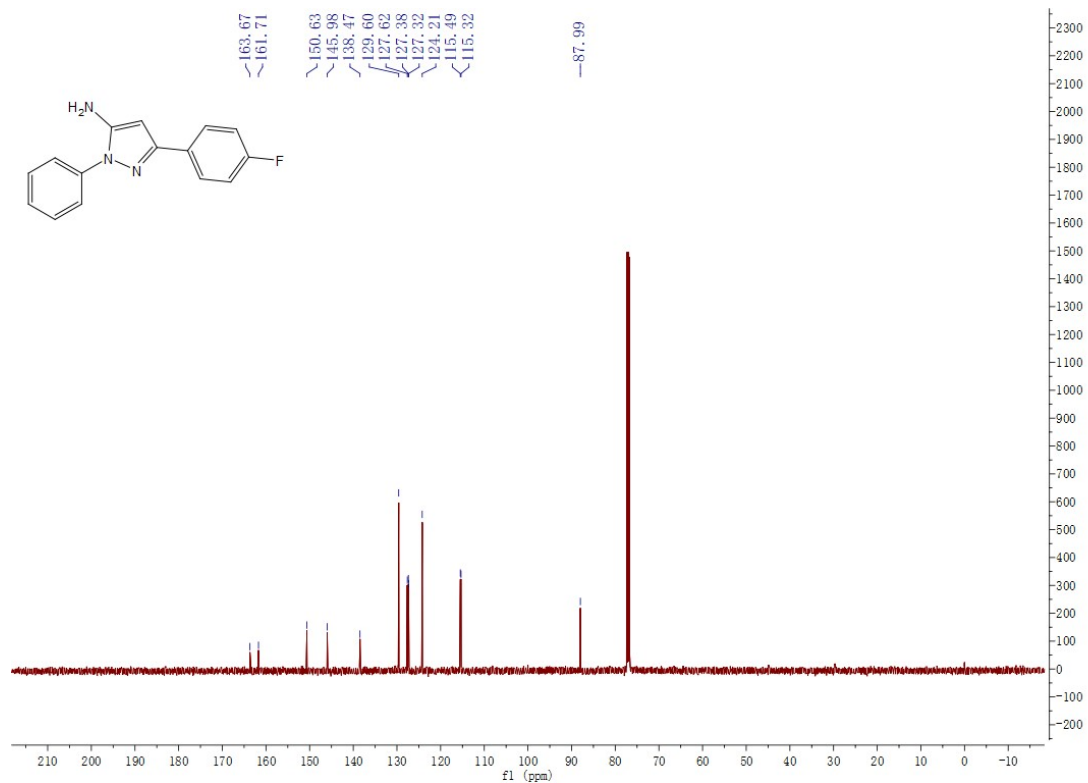
^1H NMR (400 MHz, CDCl_3) of compound **4j**



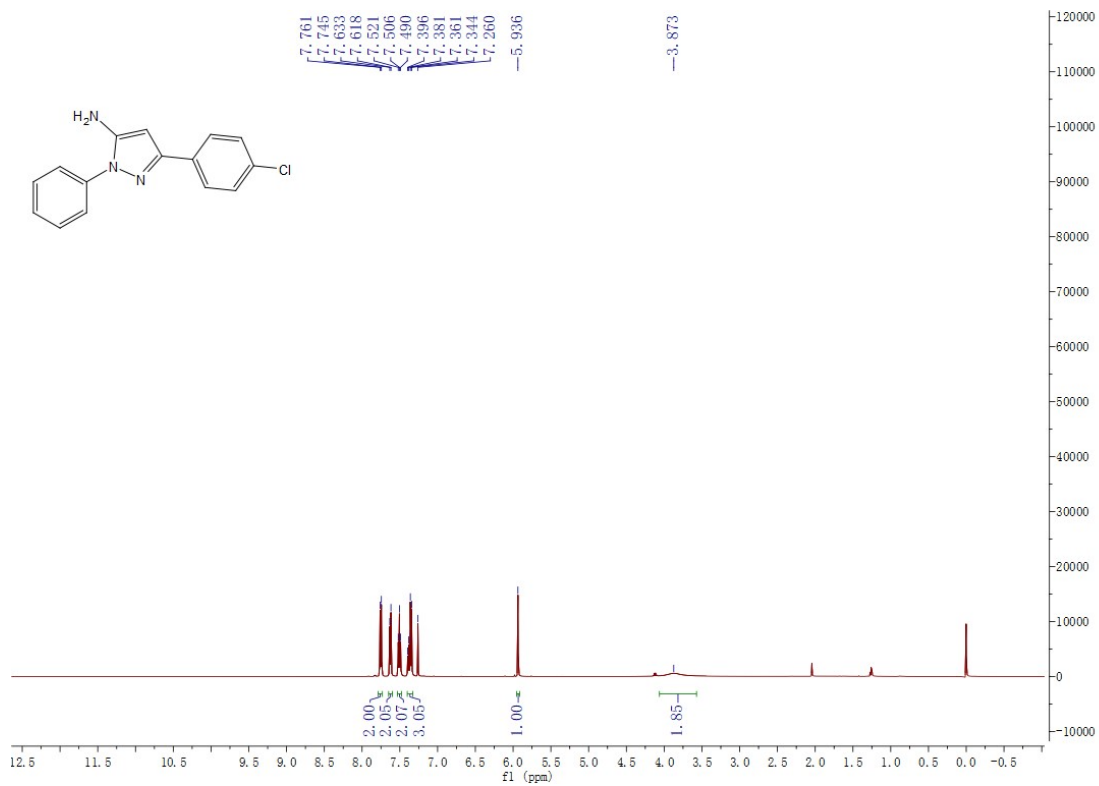
^{13}C NMR (101 MHz, CDCl_3) of compound **4j**



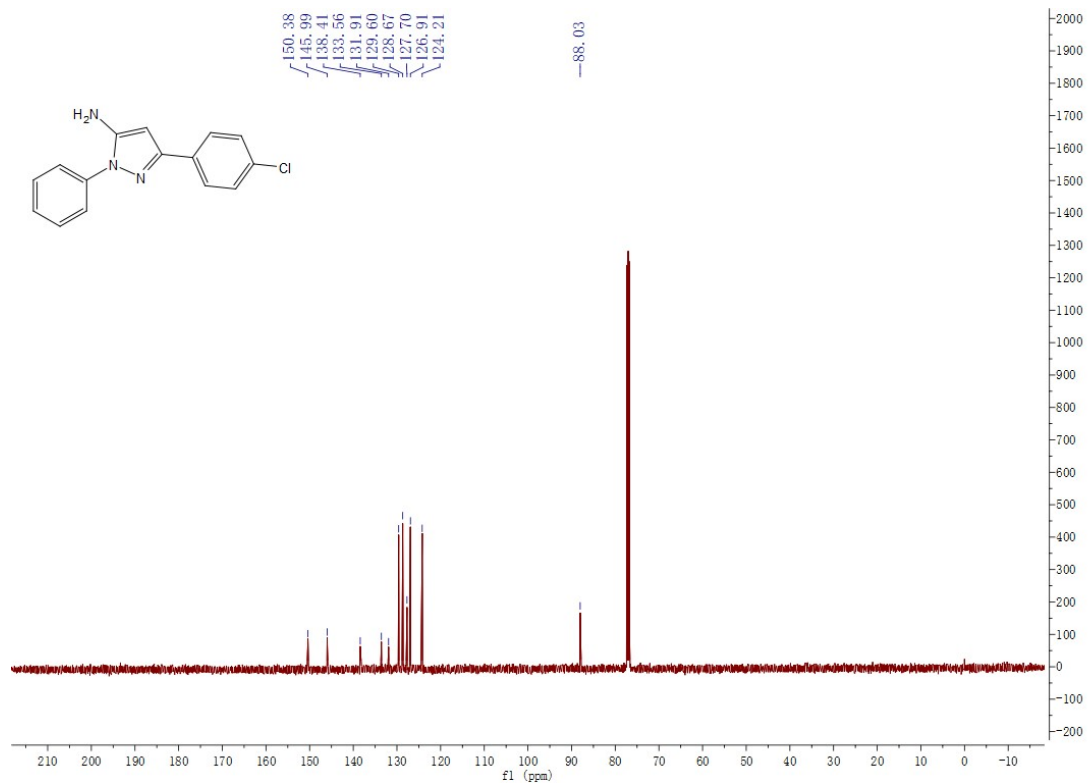
^1H NMR (500 MHz, CDCl_3) of compound **4k**



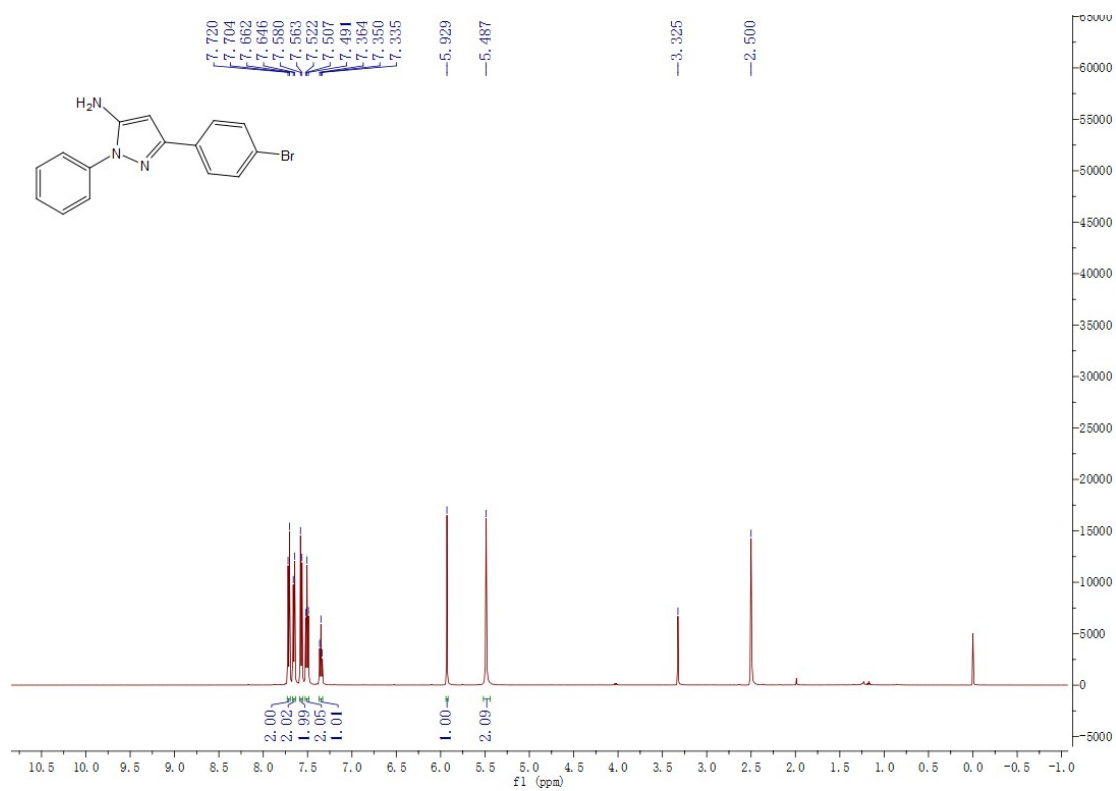
^{13}C NMR (125 MHz, CDCl_3) of compound 4k



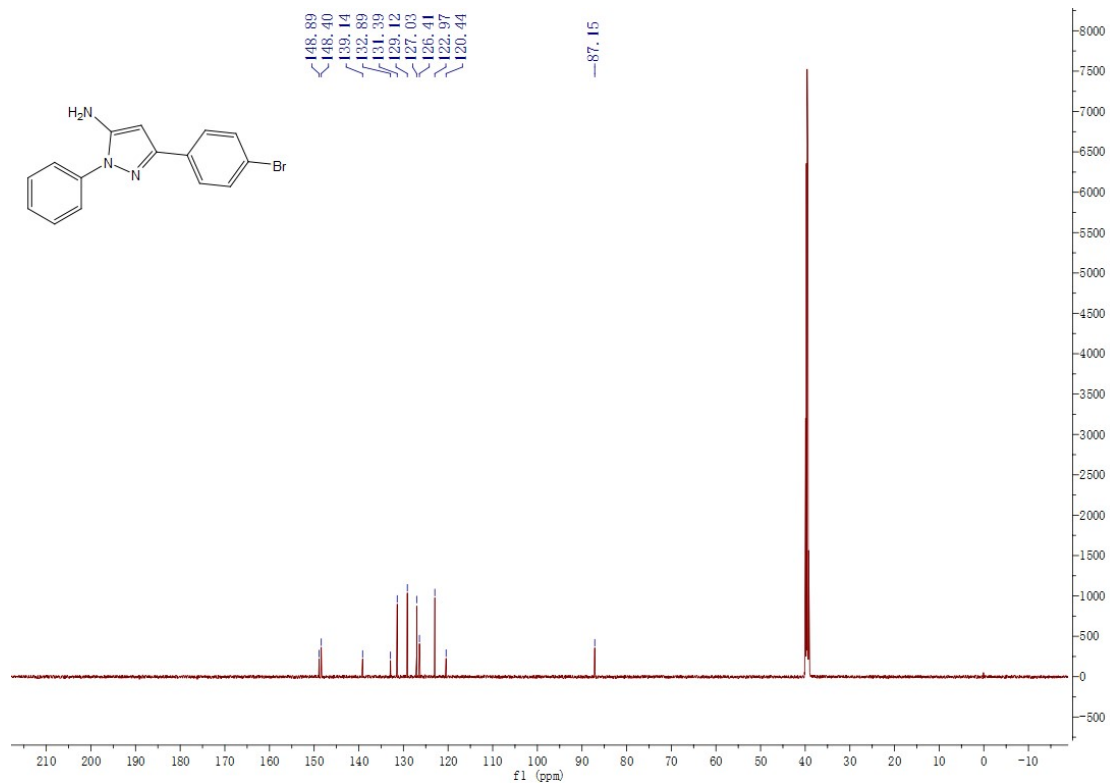
^1H NMR (500 MHz, CDCl_3) of compound 4l



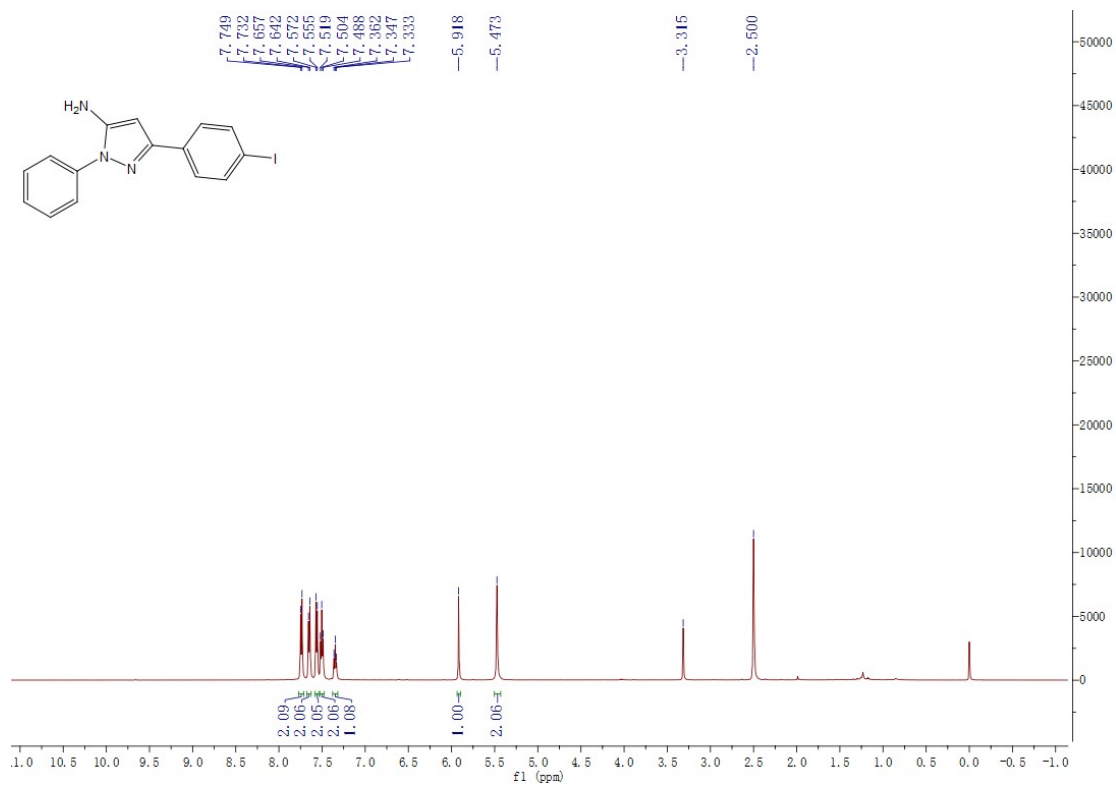
^{13}C NMR (125 MHz, CDCl_3) of compound **4l**



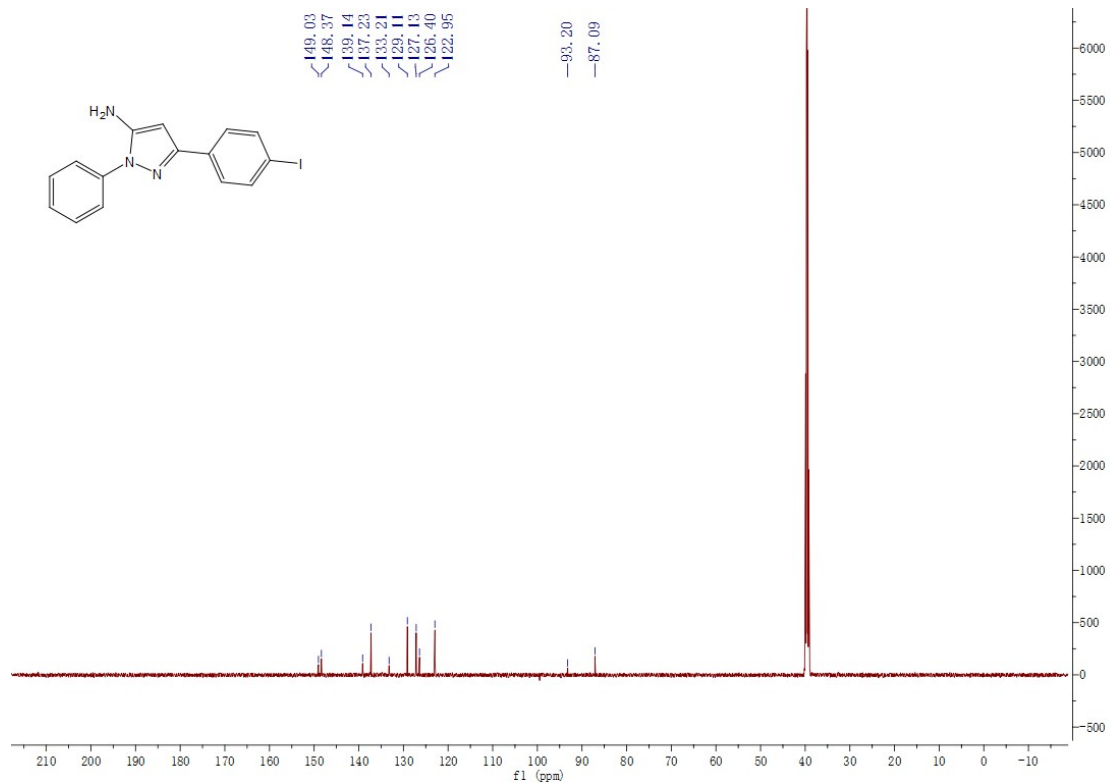
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of compound **4m**



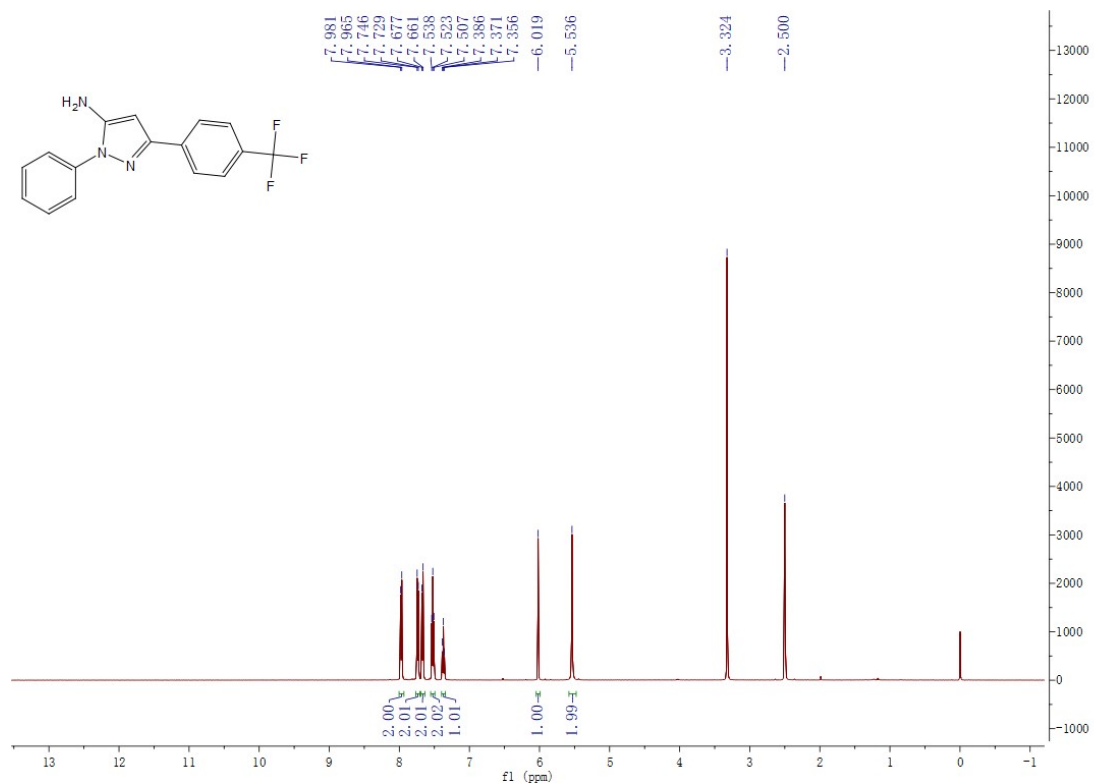
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of compound **4m**



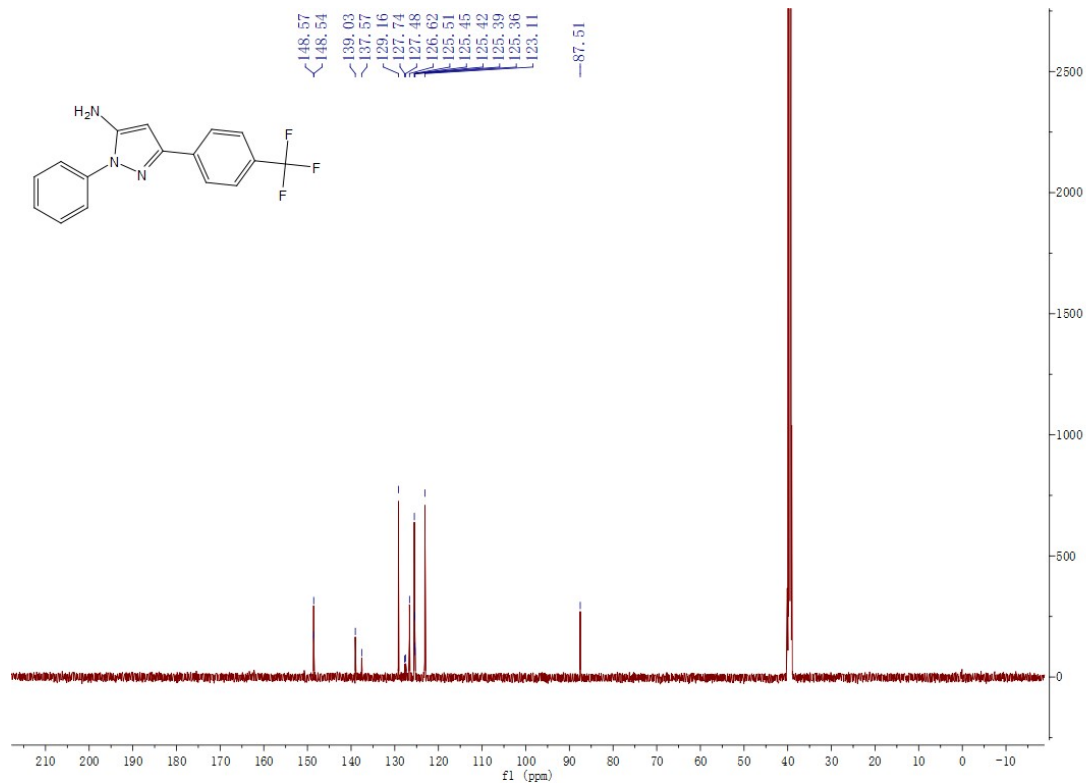
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **4n**



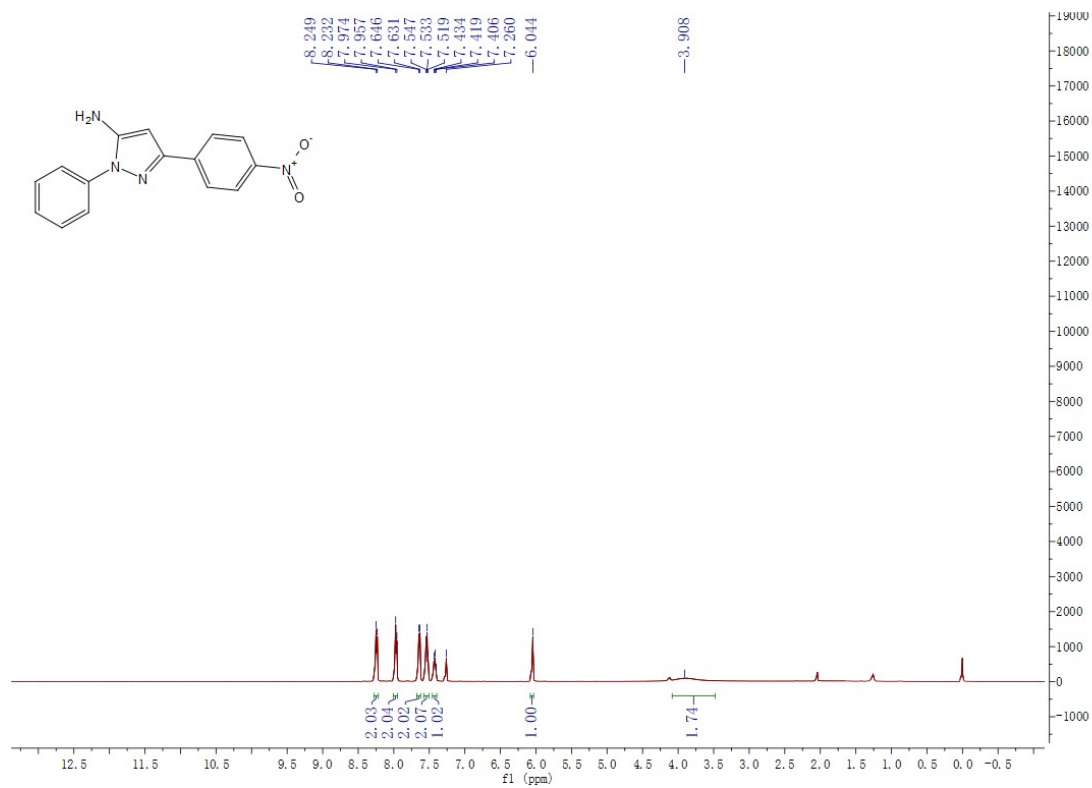
¹³C NMR (125 MHz, DMSO-*d*₆) of compound **4n**



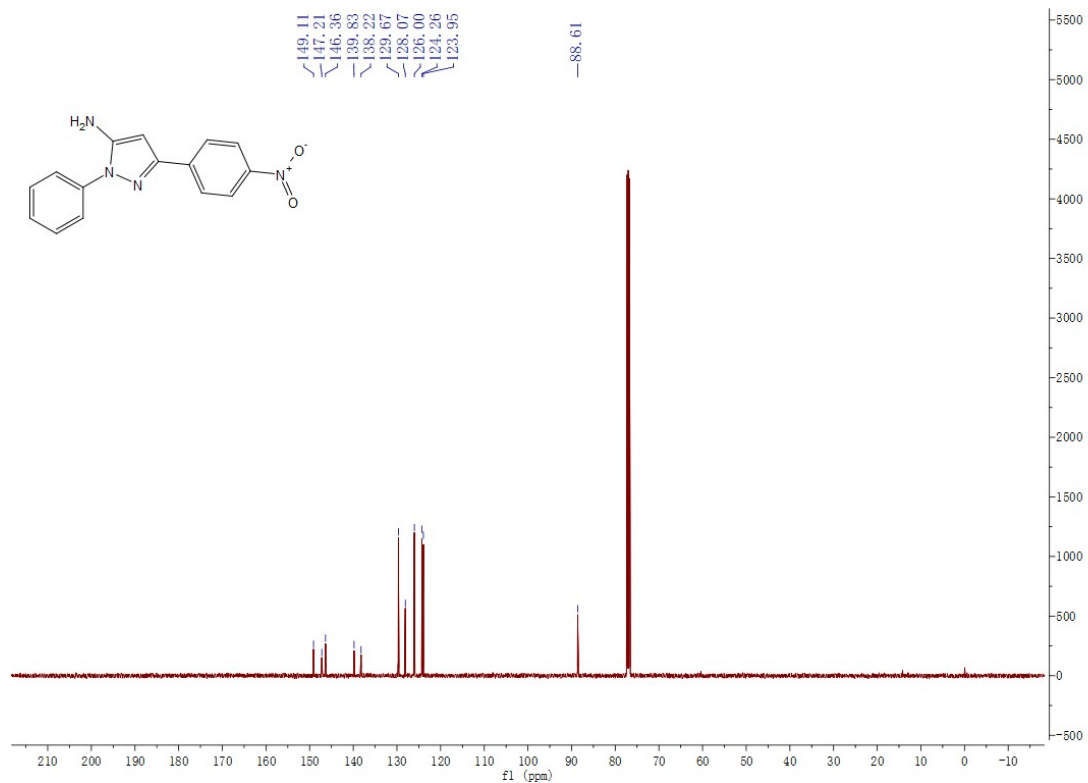
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4o**



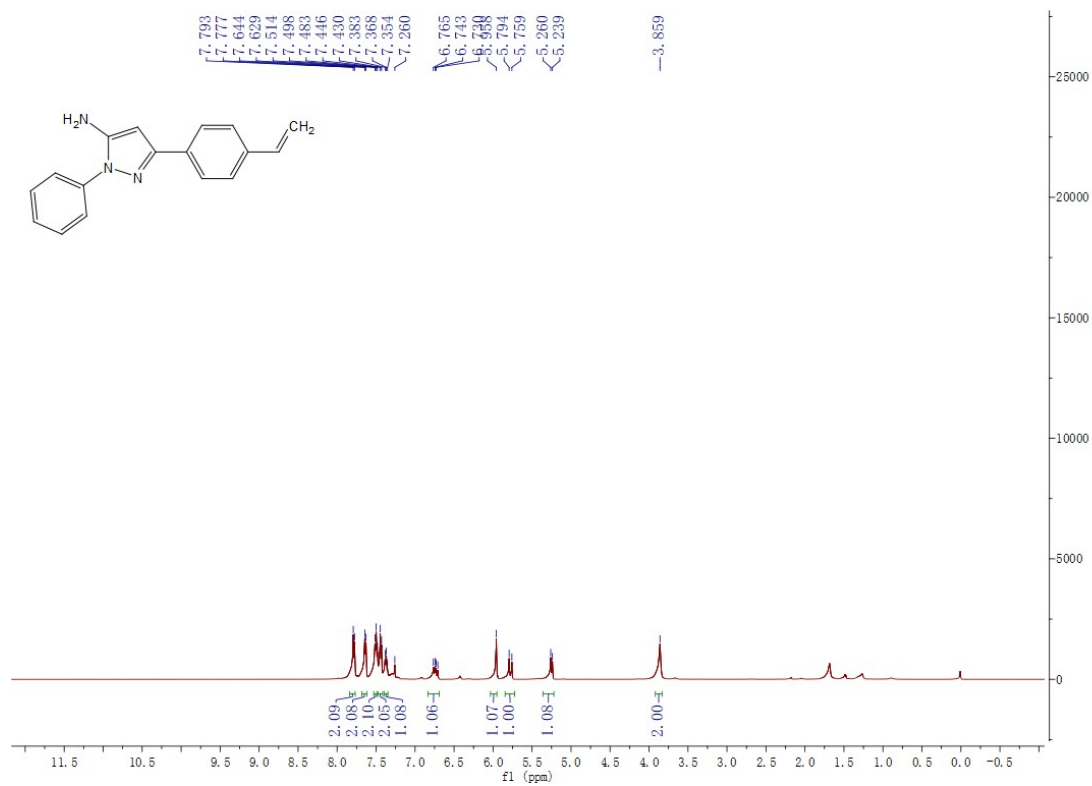
¹³C NMR (125 MHz, DMSO-*d*₆) of compound **4o**



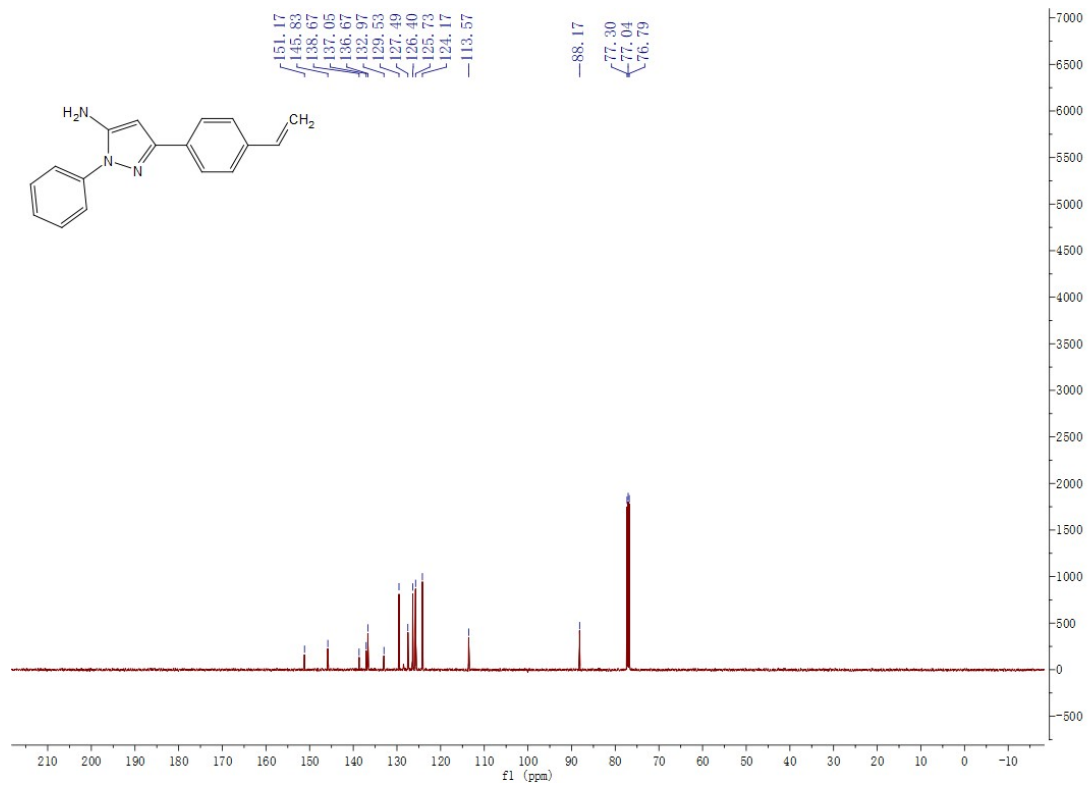
¹H NMR (500 MHz, CDCl₃) of compound **4p**



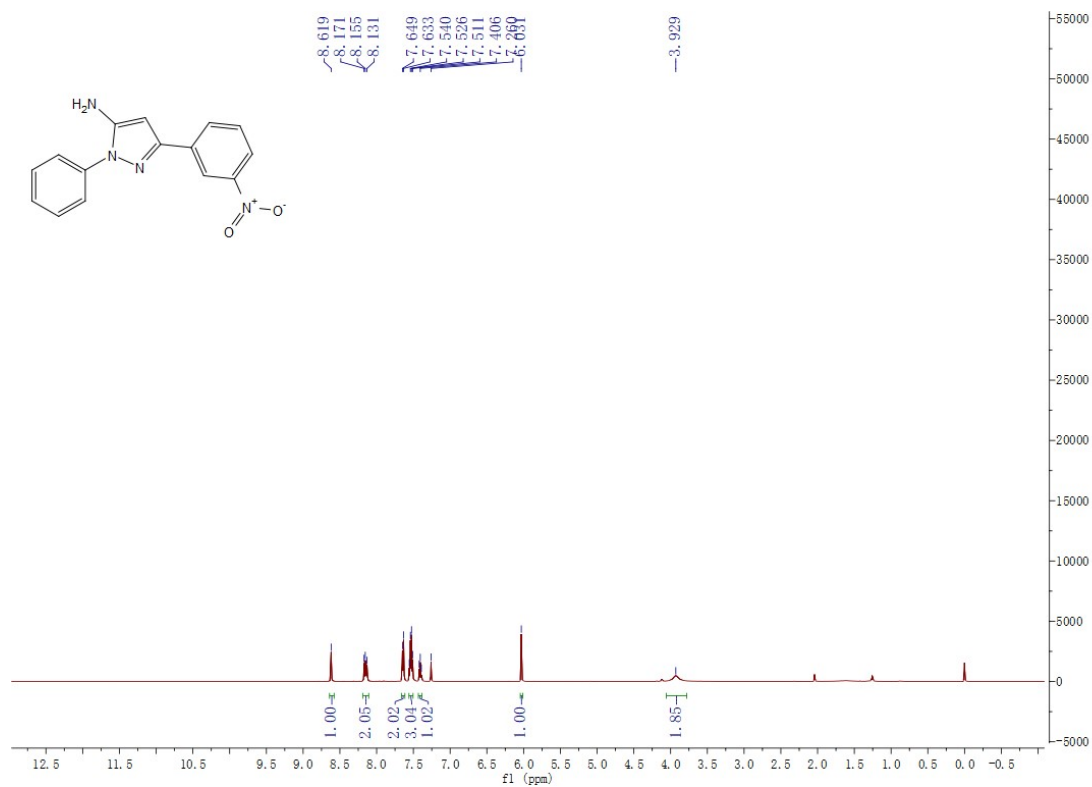
^{13}C NMR (125 MHz, CDCl_3) of compound **4p**



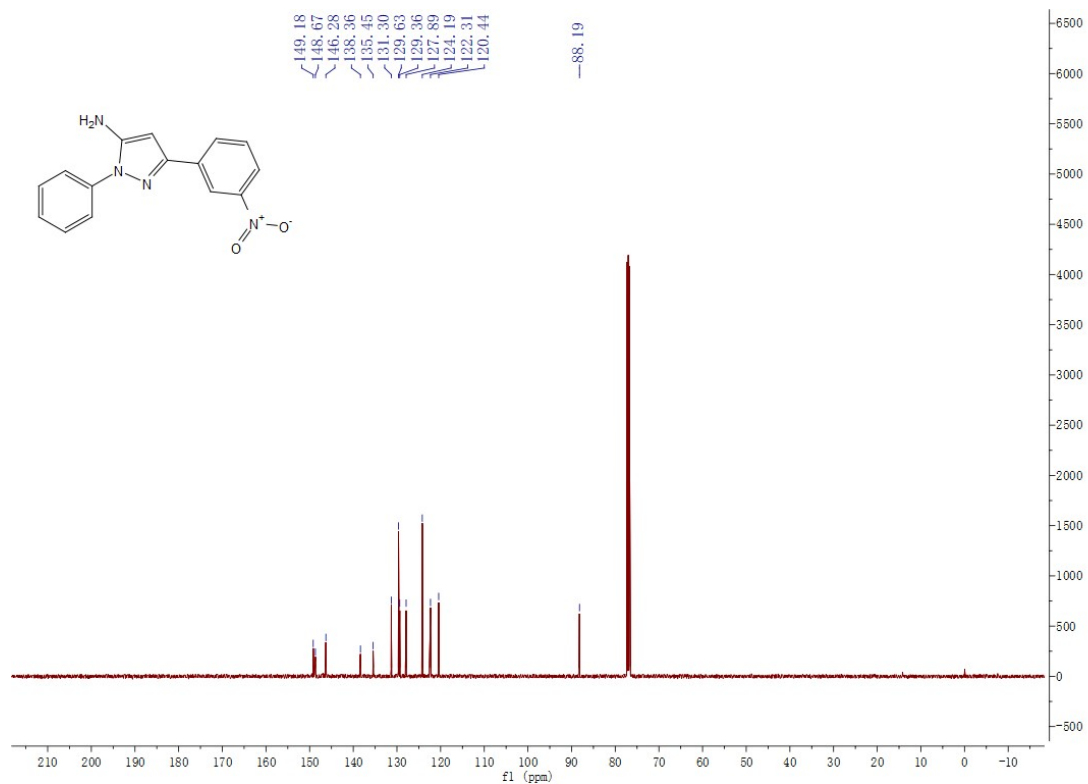
^1H NMR (500 MHz, CDCl_3) of compound **4q**



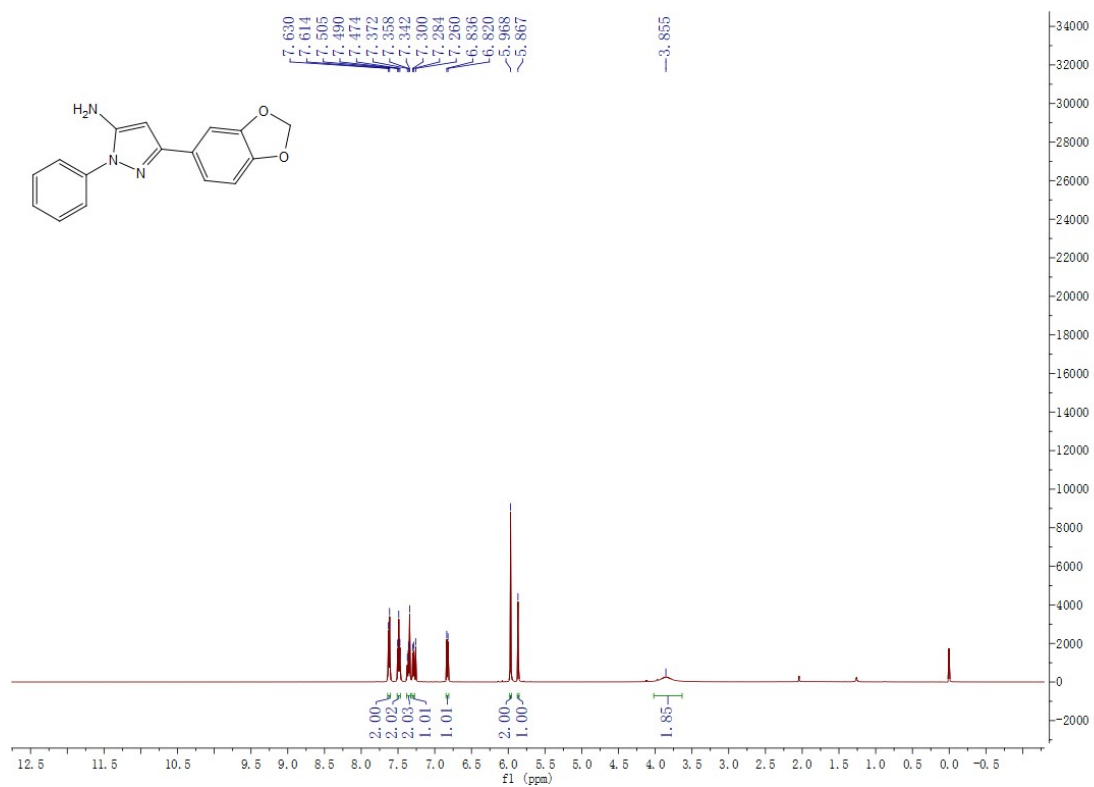
^{13}C NMR (125 MHz, CDCl_3) of compound **4q**



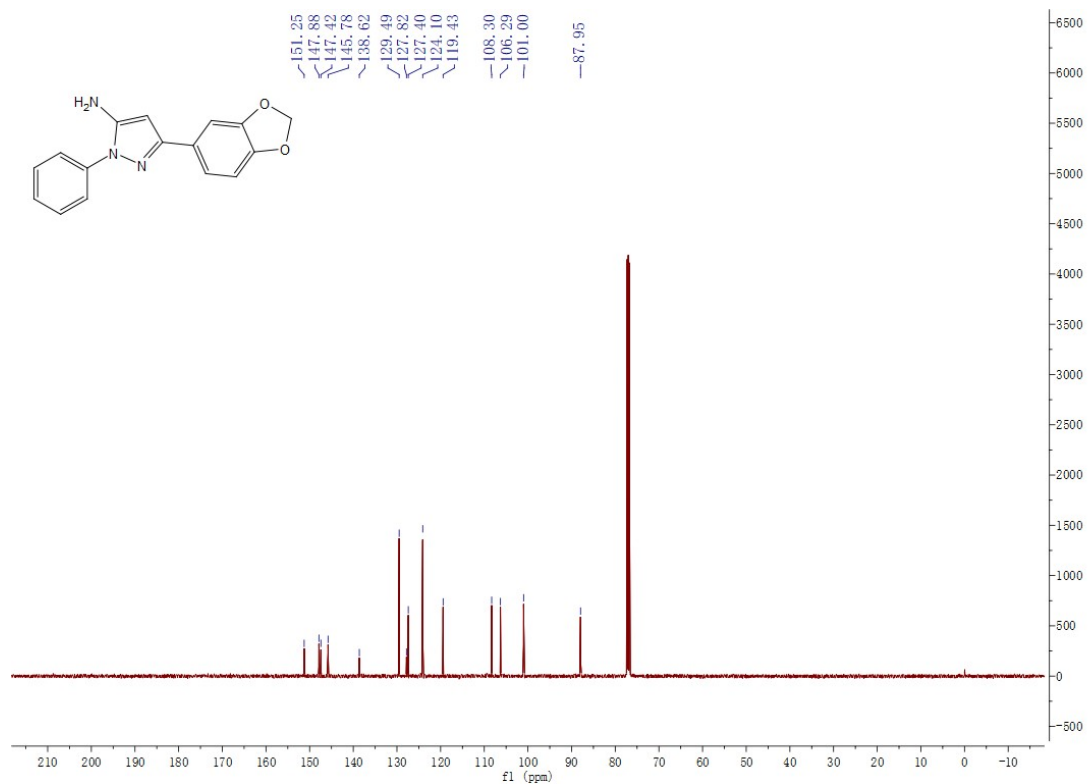
^1H NMR (500 MHz, CDCl_3) of compound **4r**



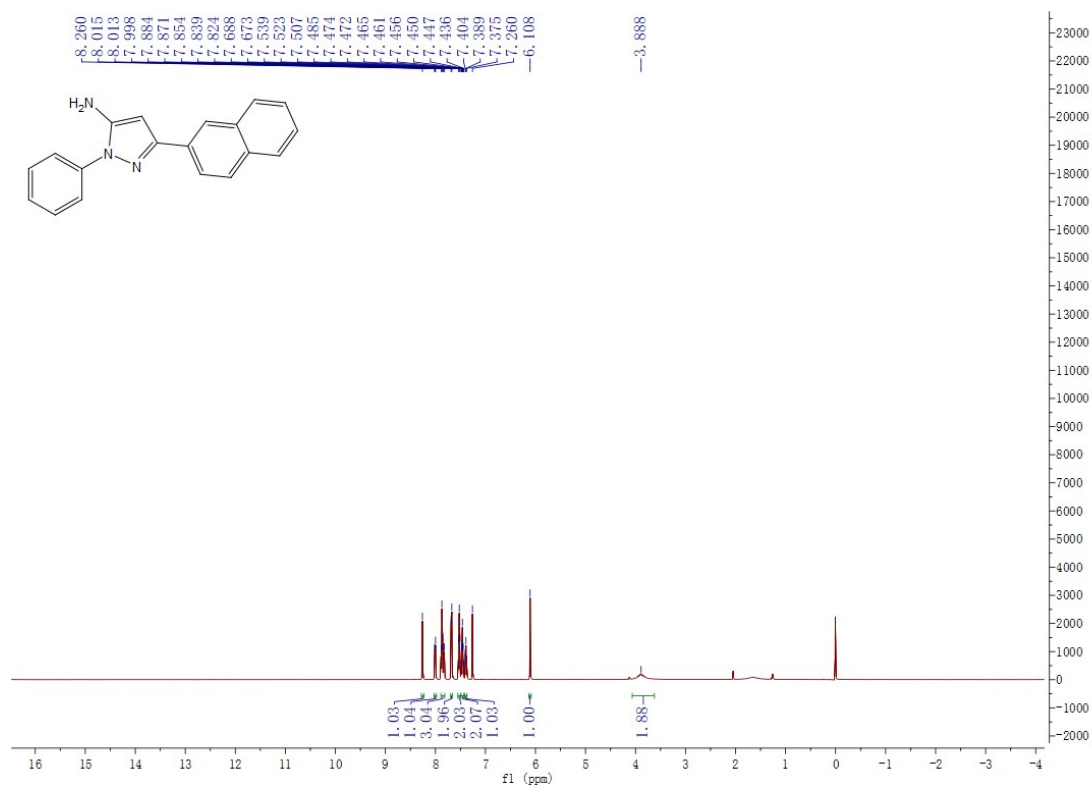
^{13}C NMR (125 MHz, CDCl_3) of compound **4r**



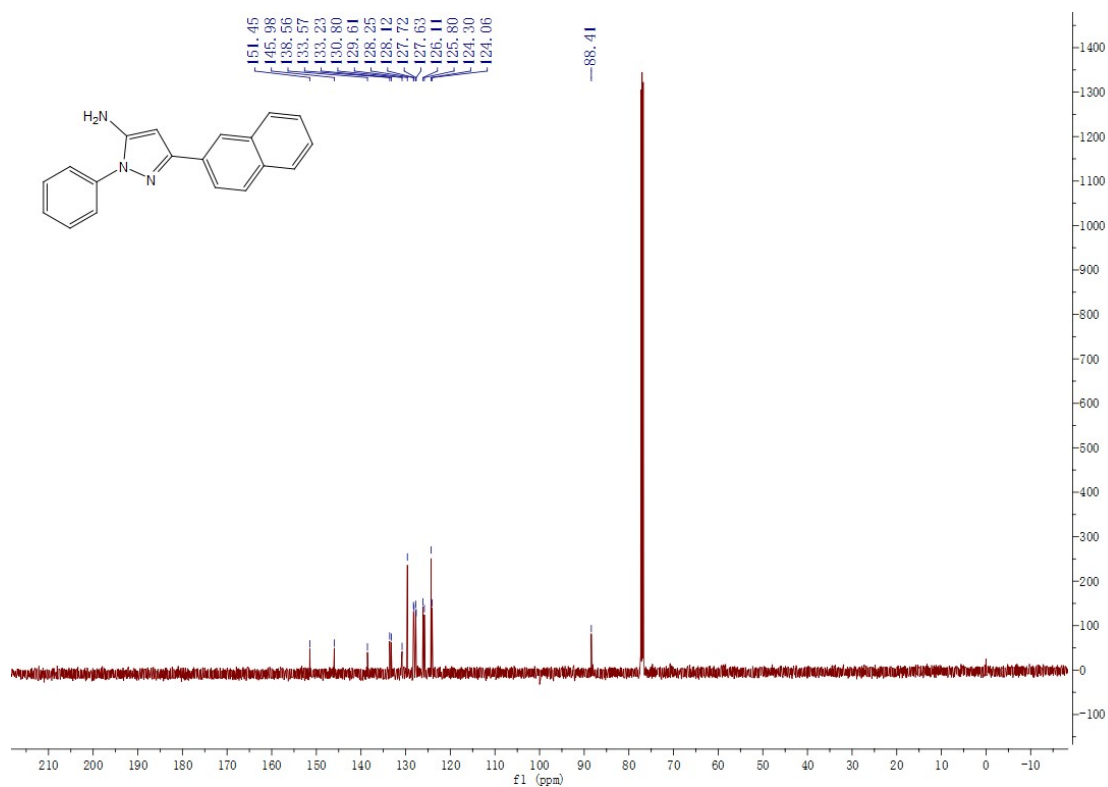
^1H NMR (500 MHz, CDCl_3) of compound **4s**



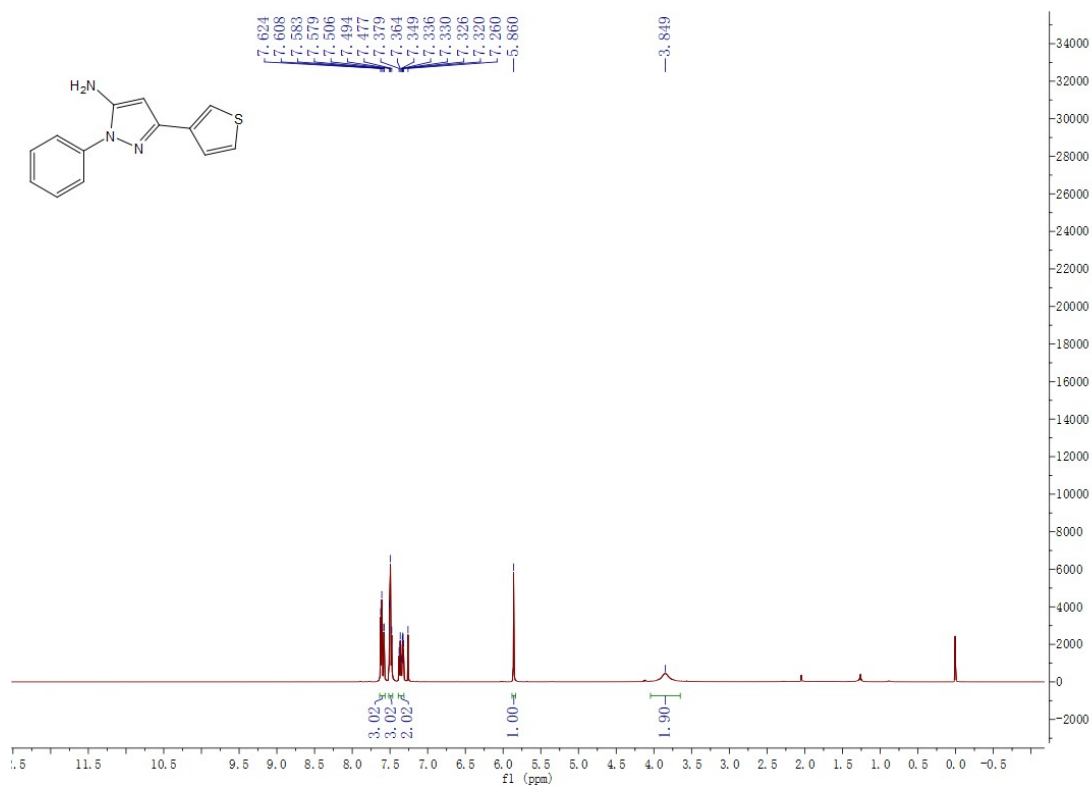
^{13}C NMR (125 MHz, CDCl_3) of compound 4s



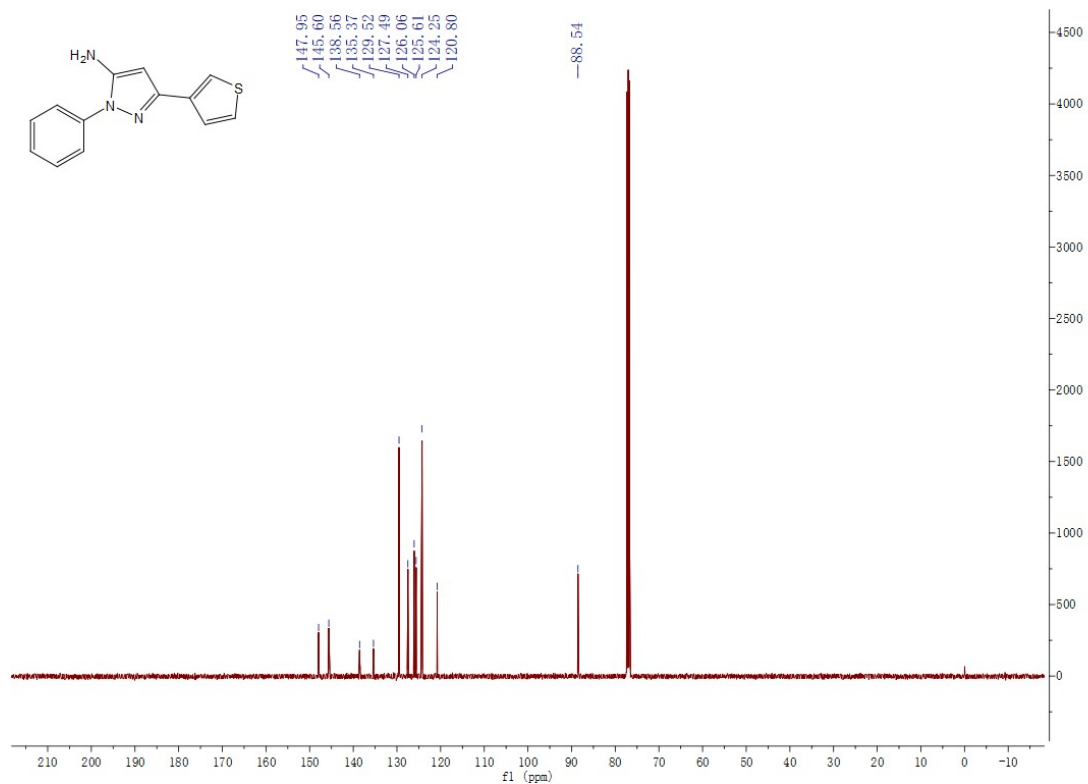
^1H NMR (500 MHz, CDCl_3) of compound 4t



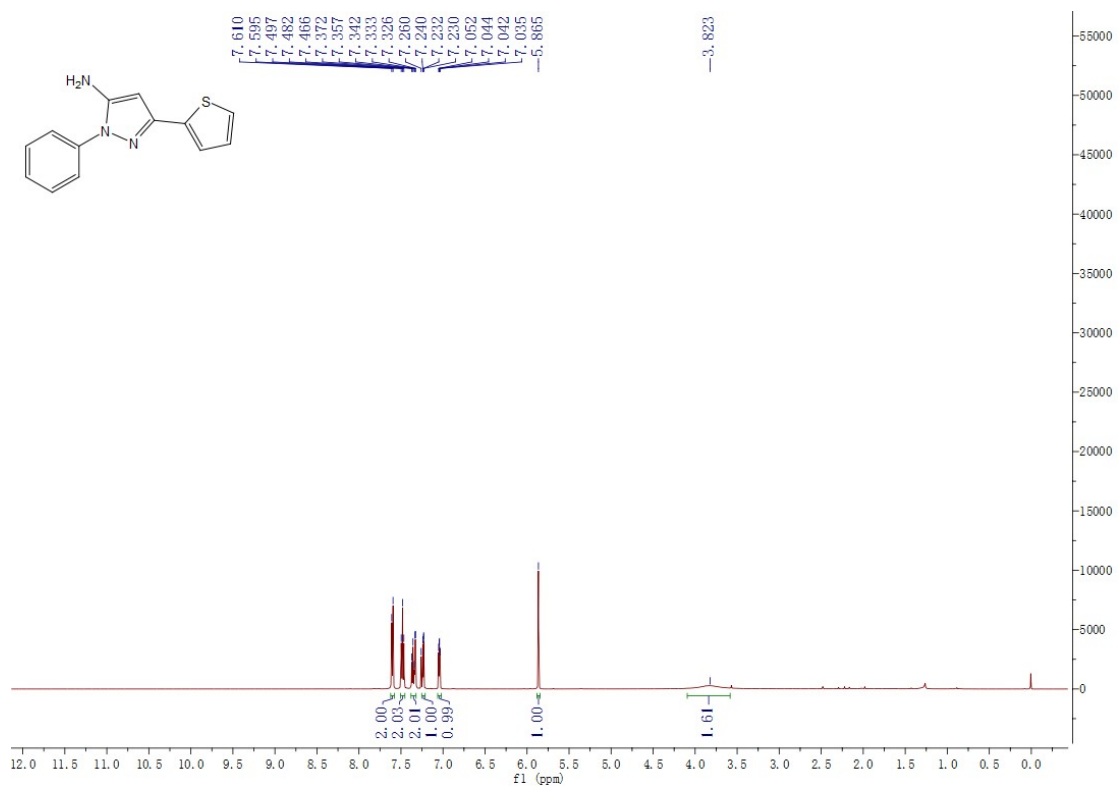
^{13}C NMR (125 MHz, CDCl_3) of compound **4t**



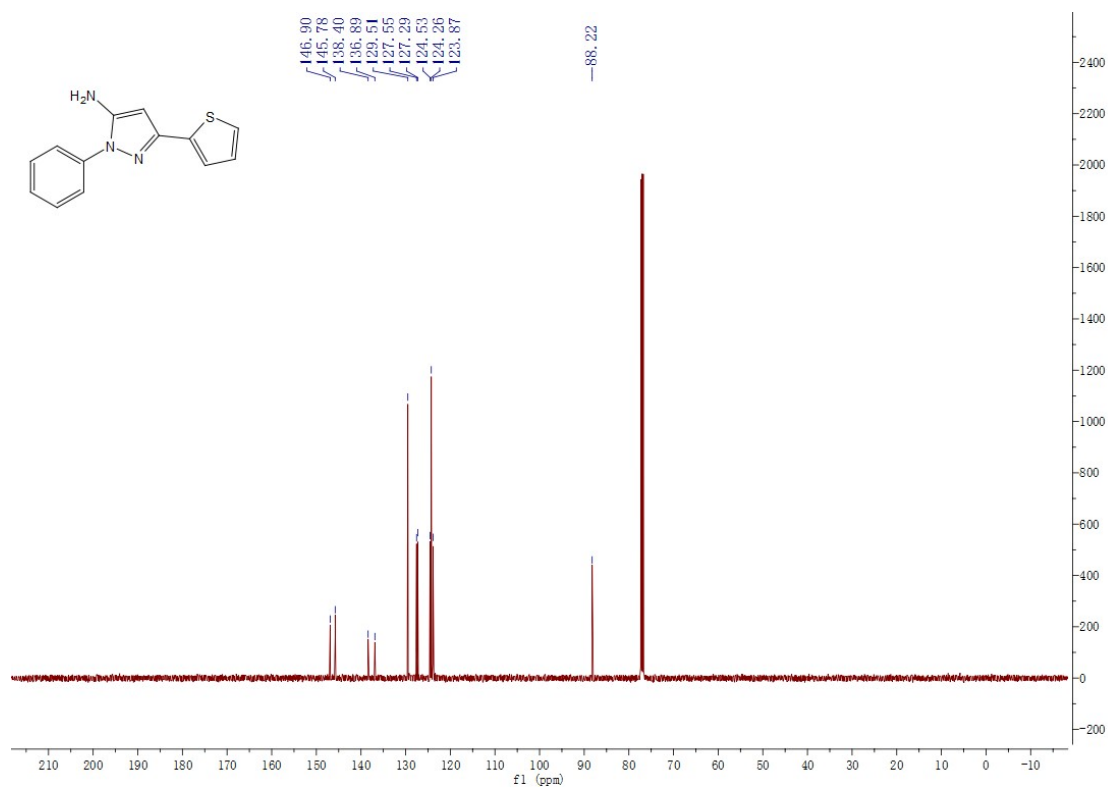
^1H NMR (500 MHz, CDCl_3) of compound **4u**



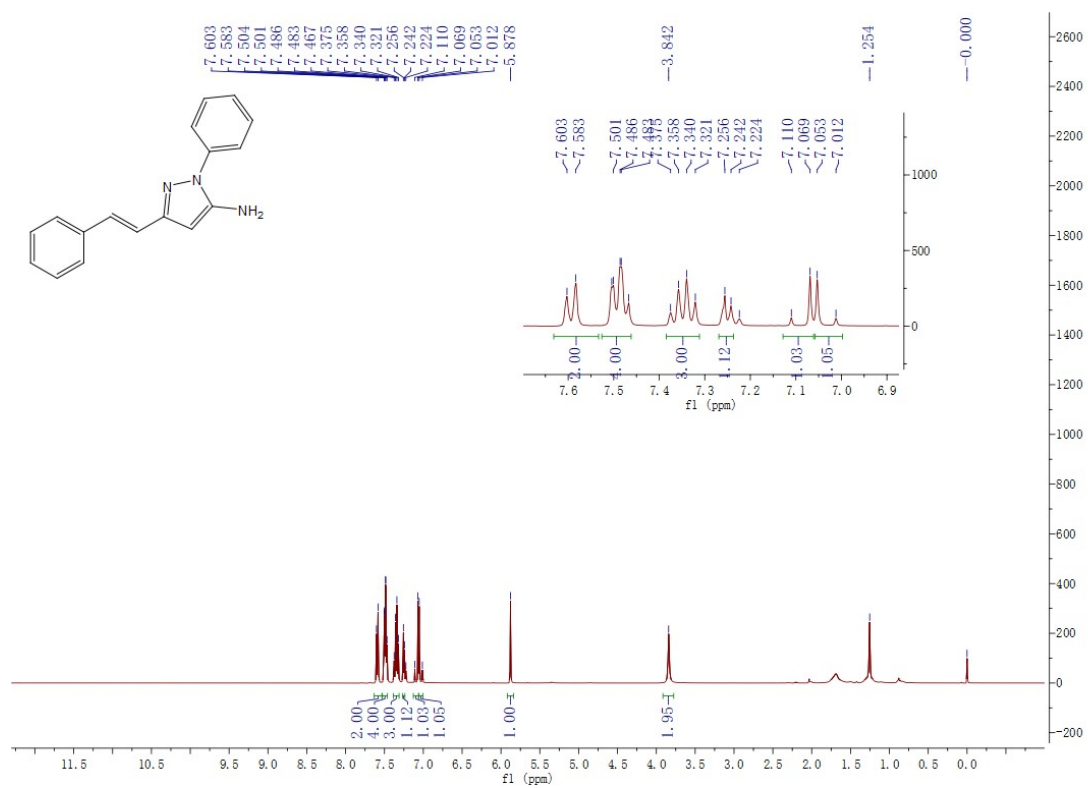
¹³C NMR (125 MHz, CDCl₃) of compound 4u



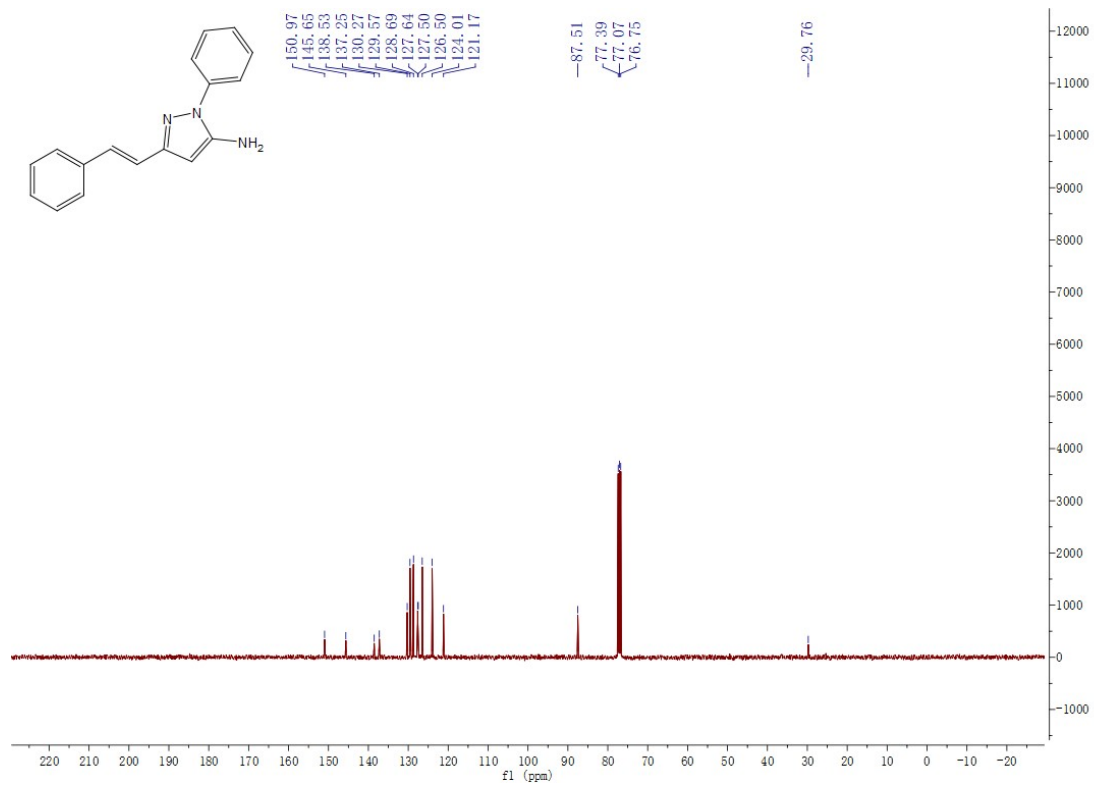
¹H NMR (500 MHz, CDCl₃) of compound 4v



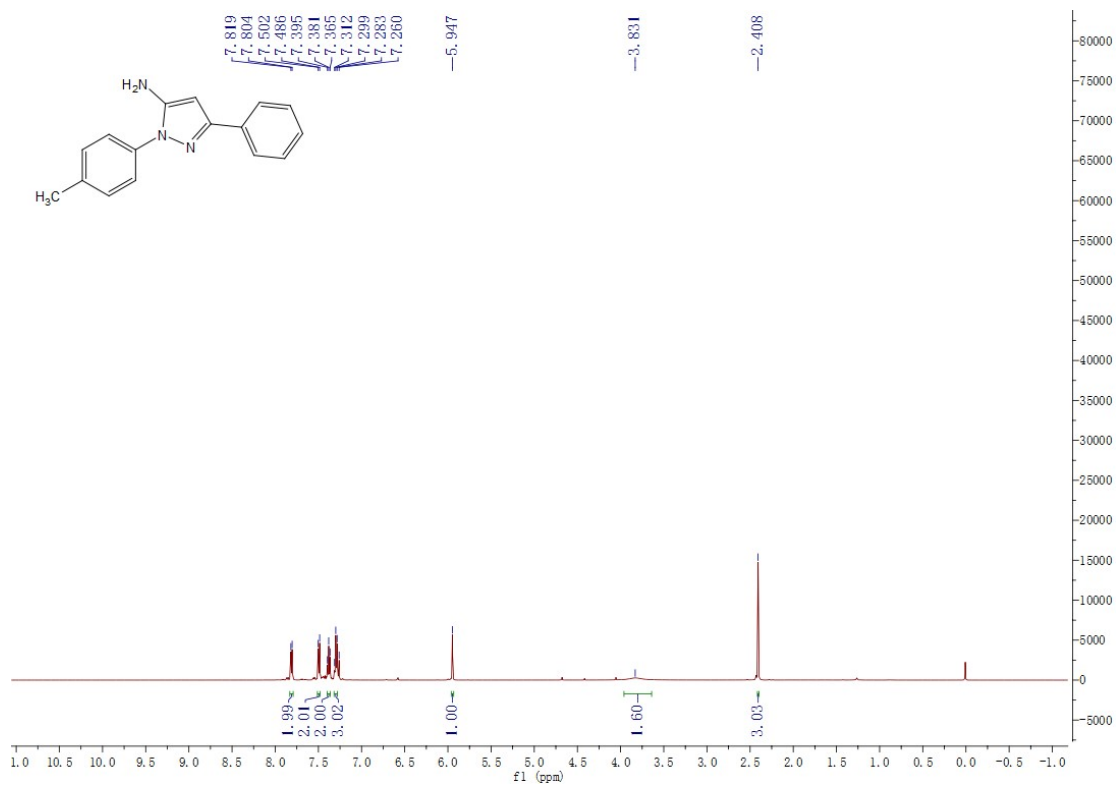
¹³C NMR (125 MHz, CDCl₃) of compound 4v



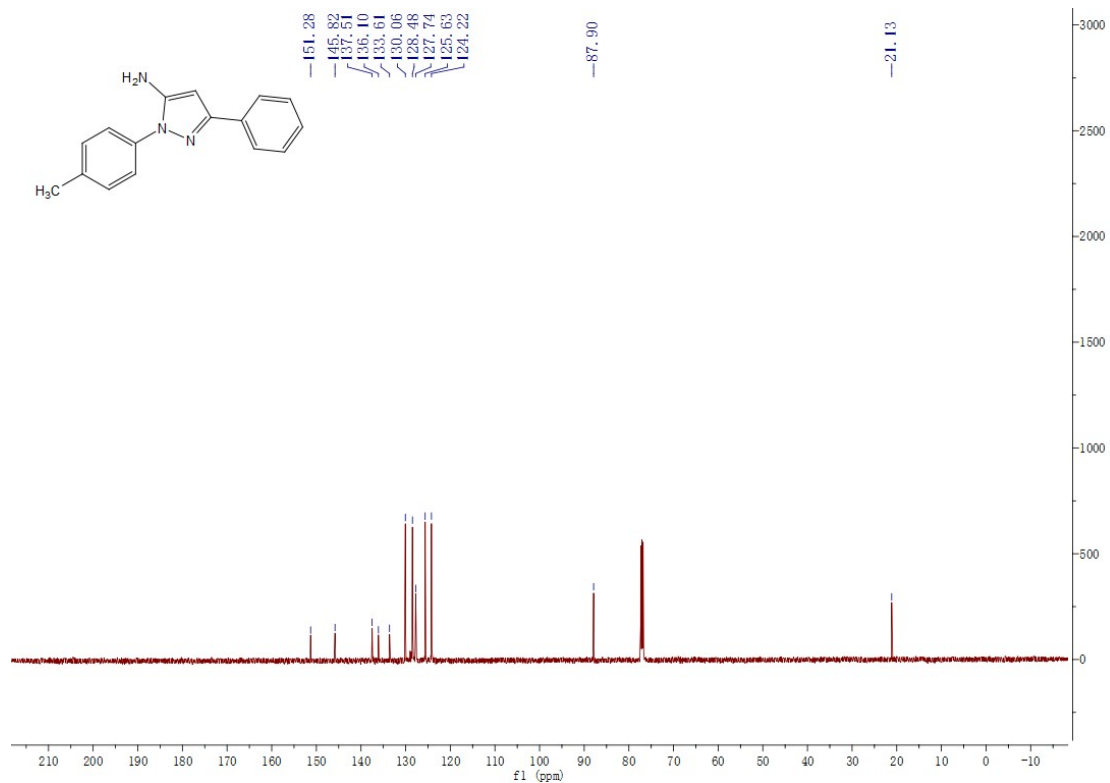
¹H NMR (400 MHz, CDCl₃) of compound 4w



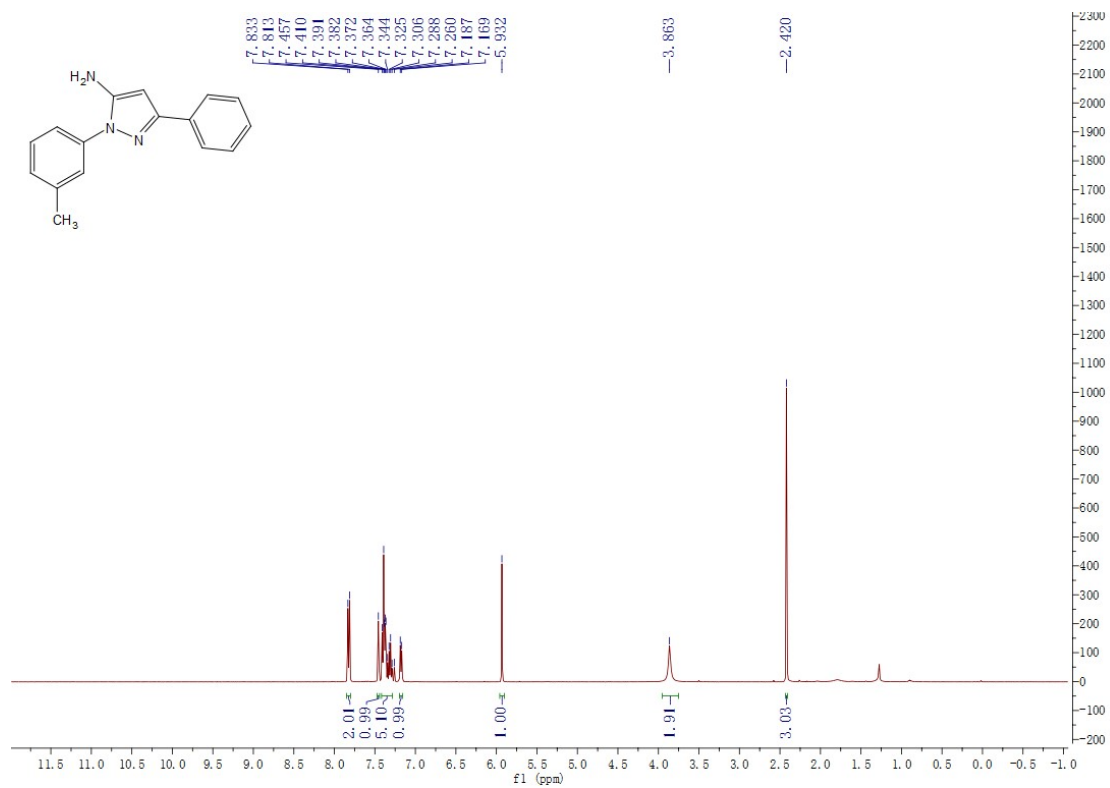
^{13}C NMR (101 MHz, CDCl_3) of compound **4w**



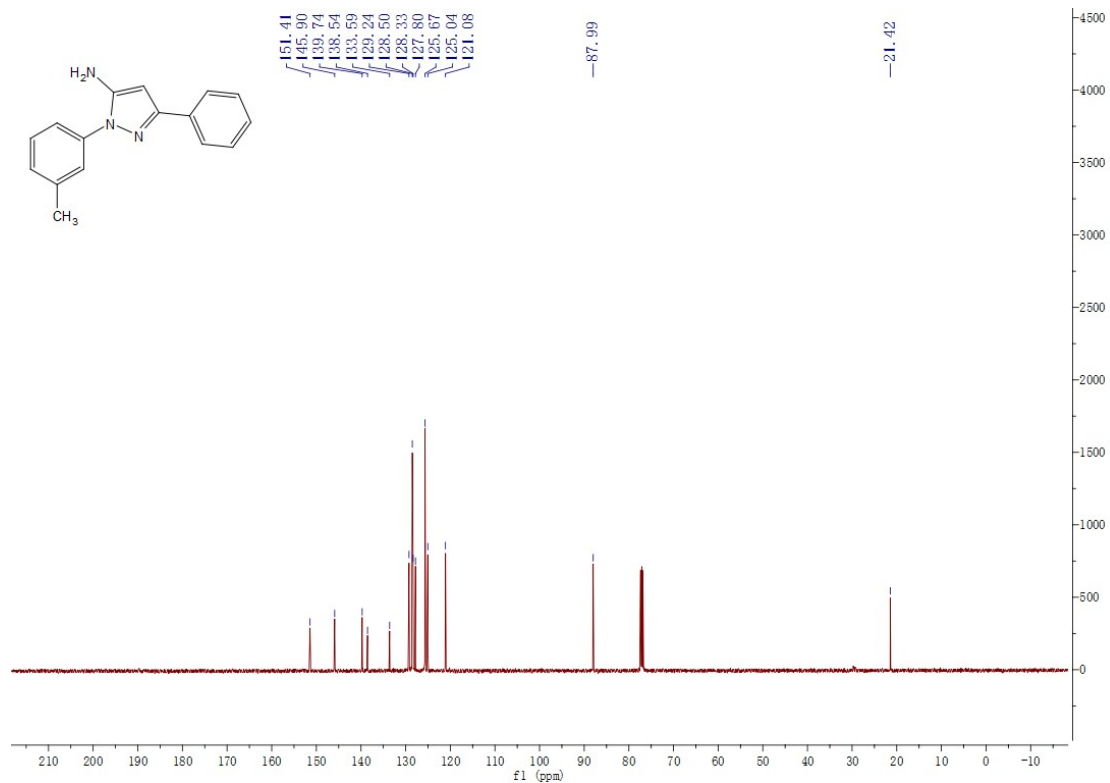
^1H NMR (500 MHz, CDCl_3) of compound **5a**



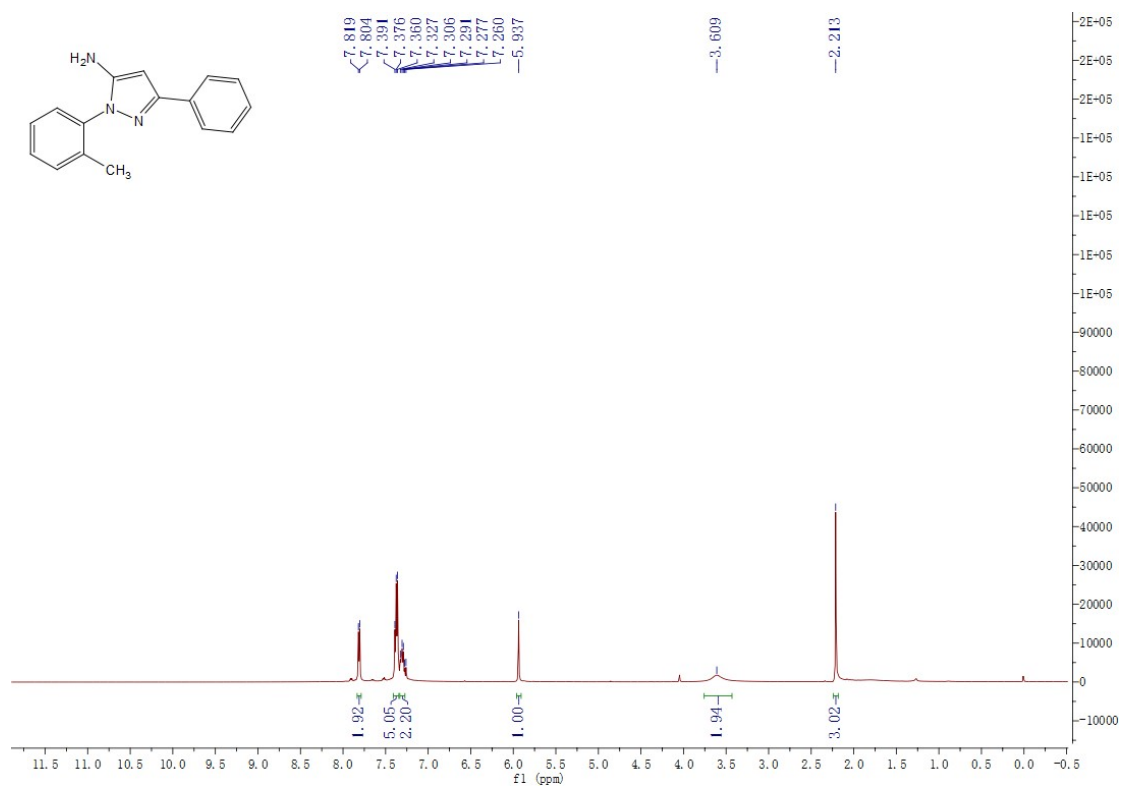
^{13}C NMR (125 MHz, CDCl_3) of compound **5a**



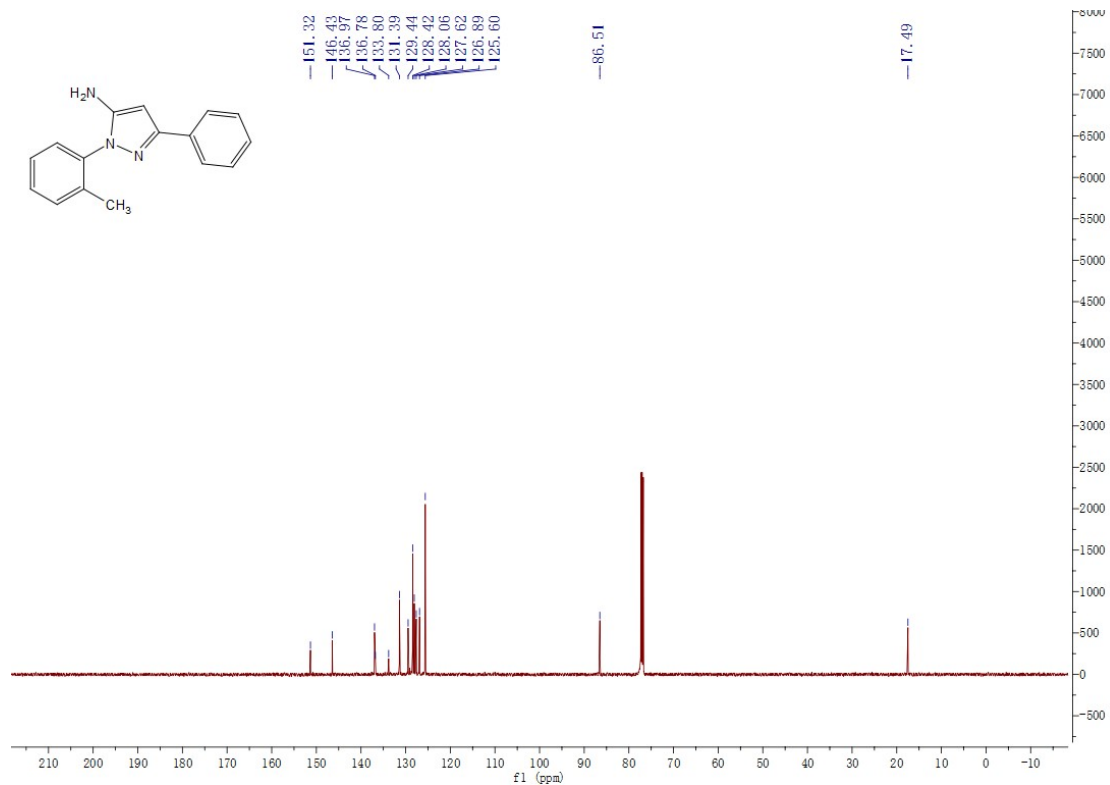
^1H NMR (400 MHz, CDCl_3) of compound **5b**



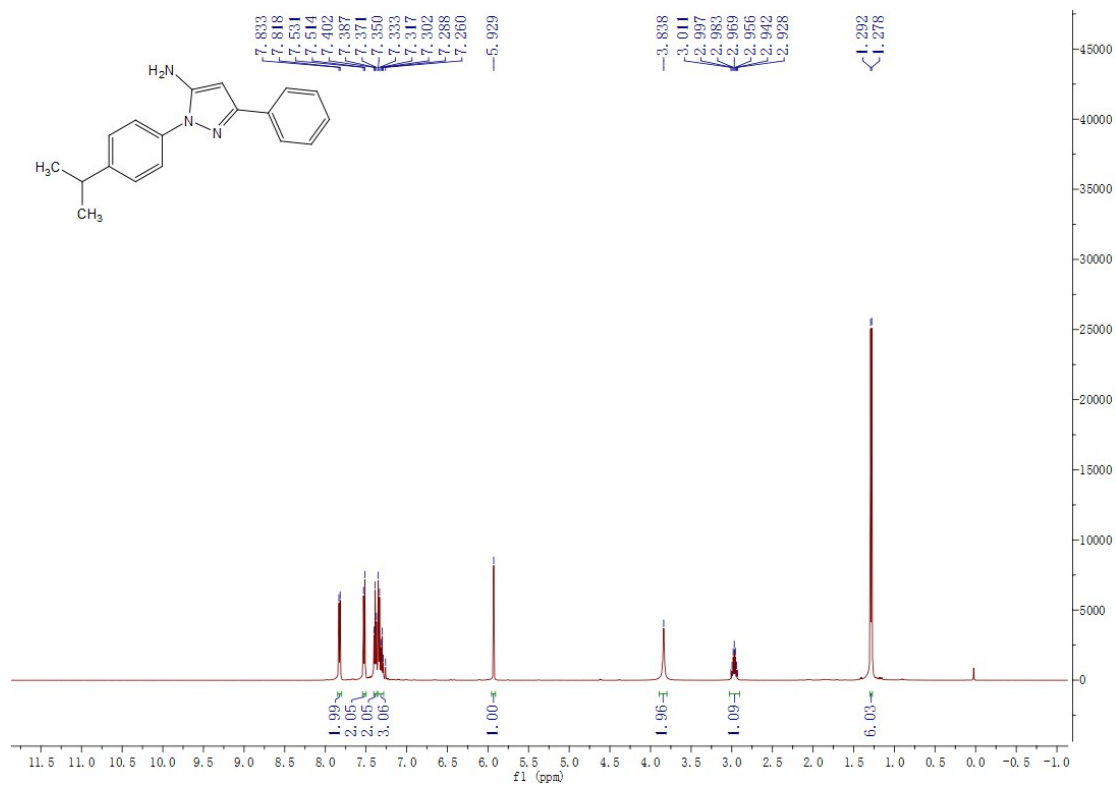
^{13}C NMR (101 MHz, CDCl_3) of compound **5b**



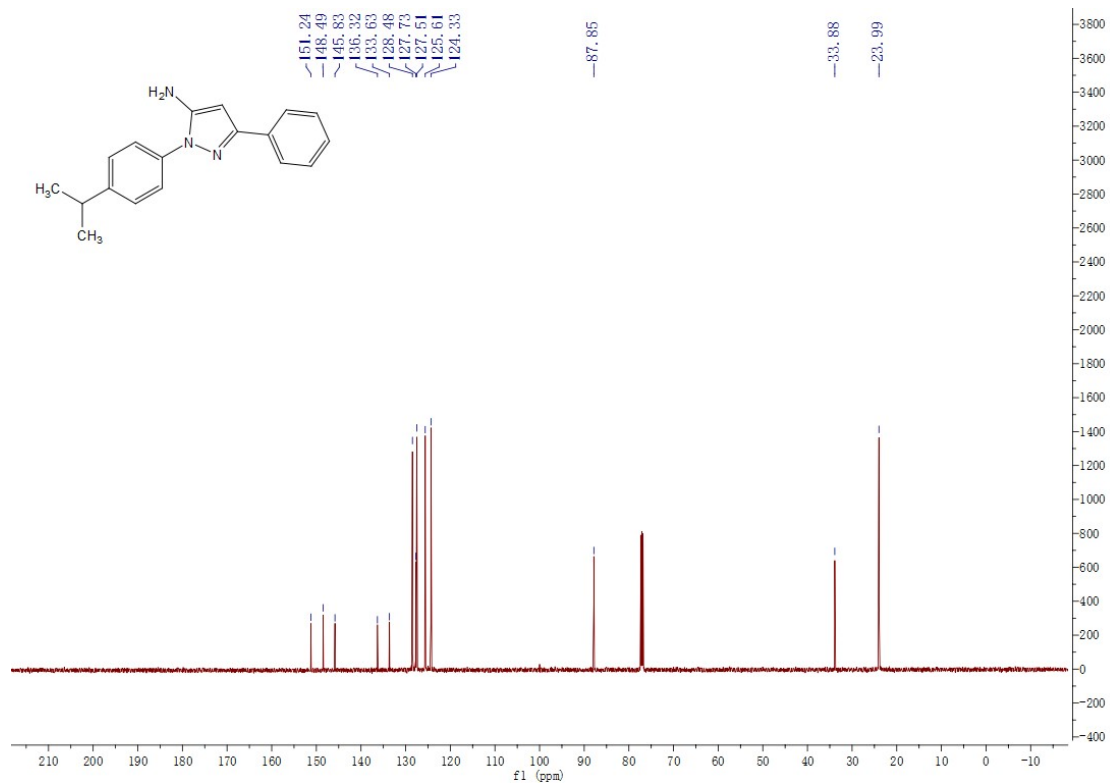
^1H NMR (500 MHz, CDCl_3) of compound **5c**



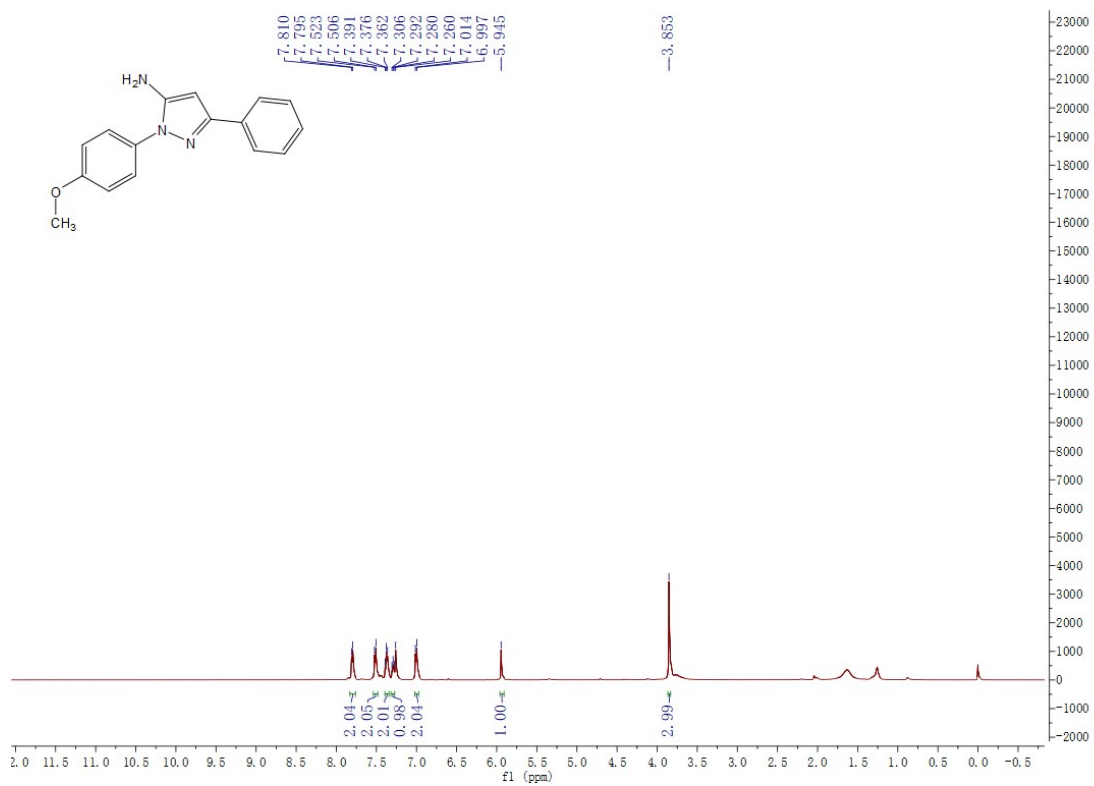
^{13}C NMR (125 MHz, CDCl_3) of compound **5c**



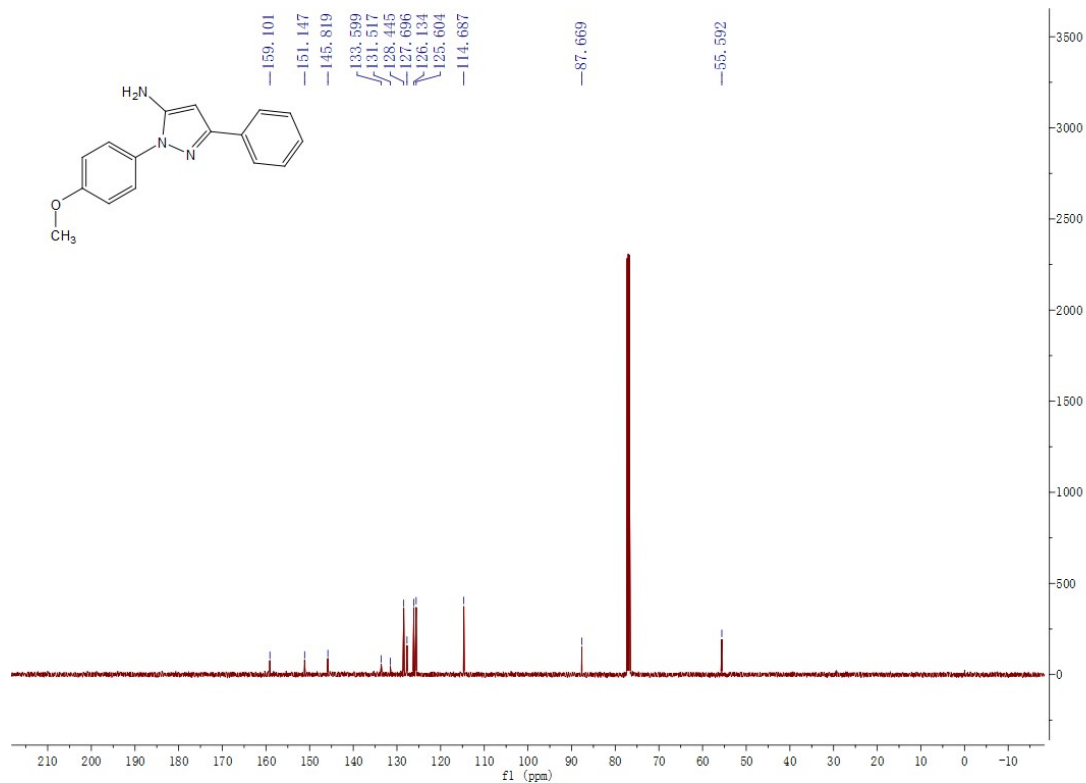
^1H NMR (500 MHz, CDCl_3) of compound **5d**



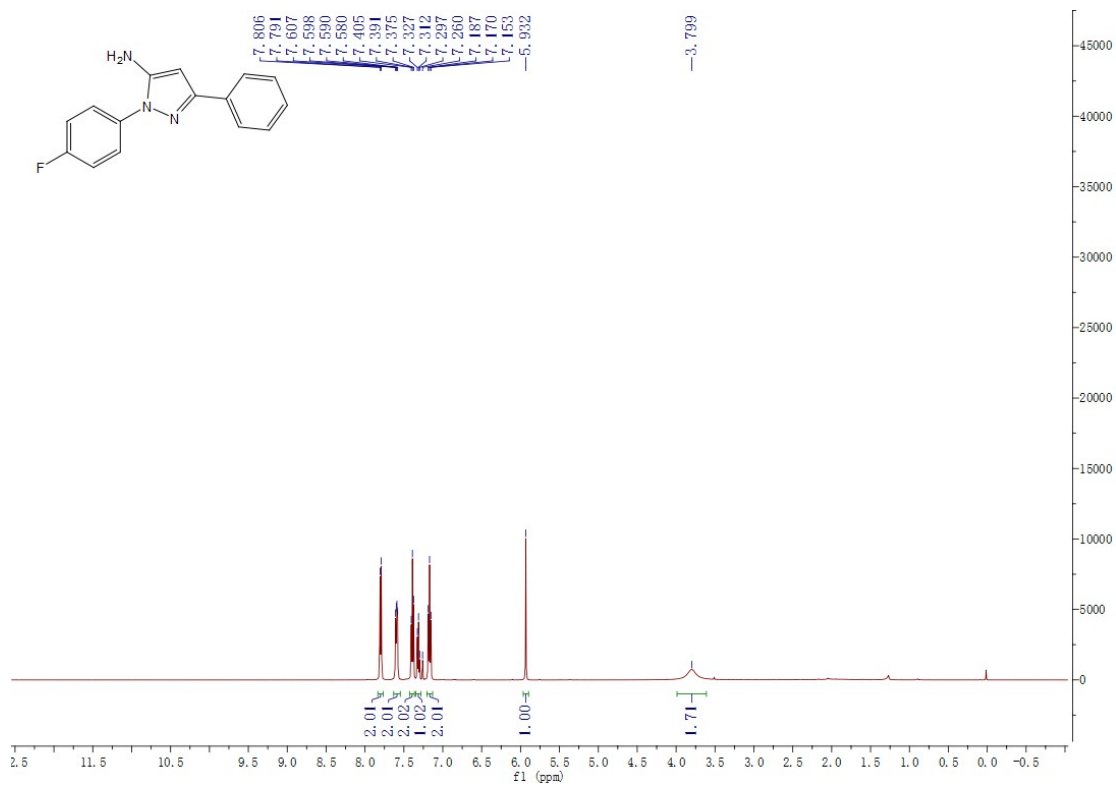
^{13}C NMR (125 MHz, CDCl_3) of compound **5d**



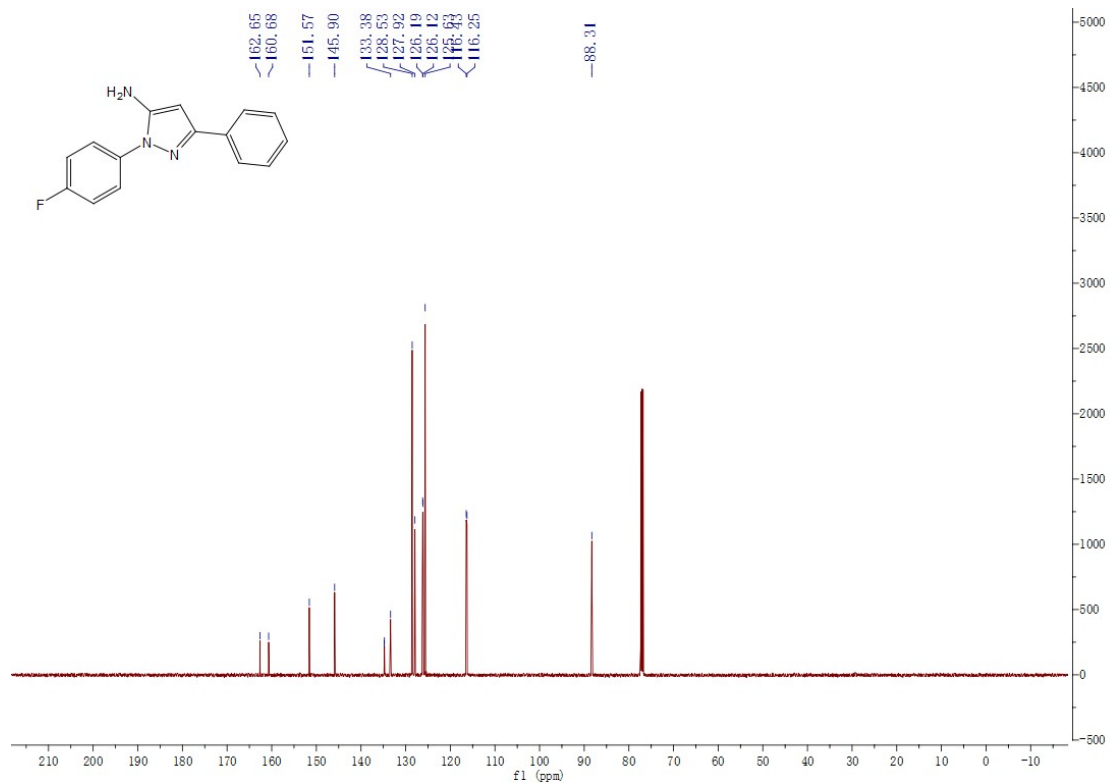
^1H NMR (500 MHz, CDCl_3) of compound **5e**



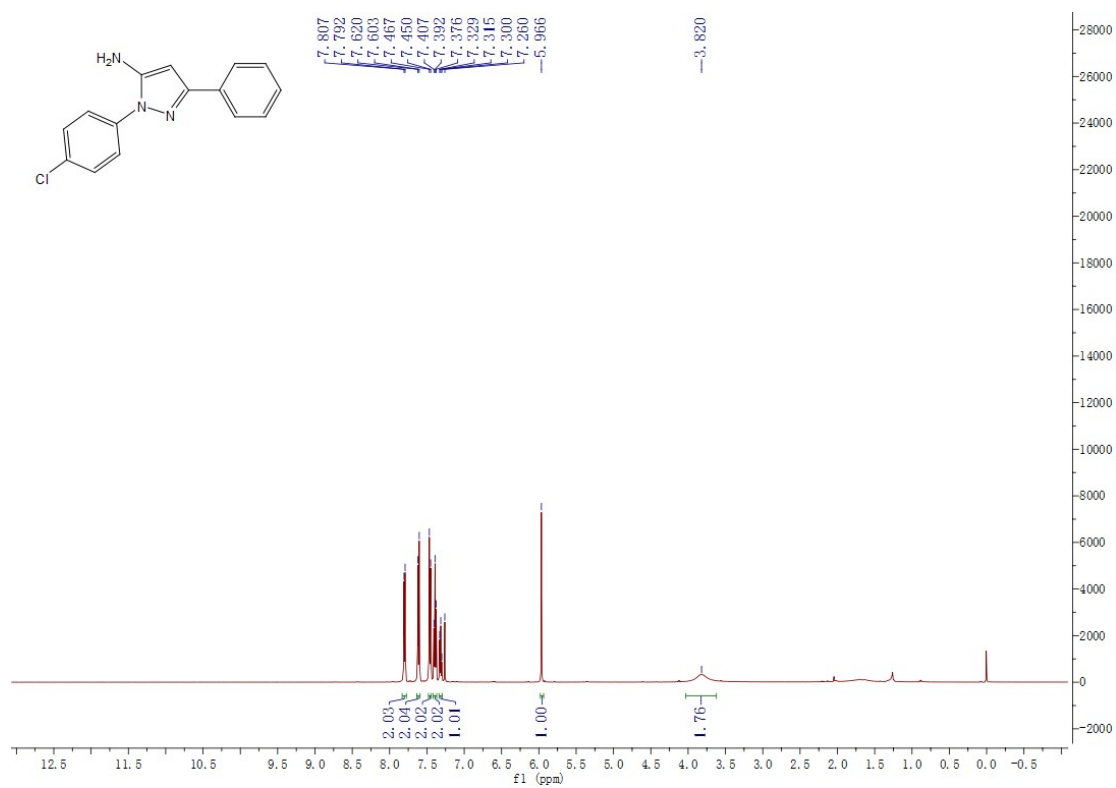
^{13}C NMR (125 MHz, CDCl_3) of compound **5e**



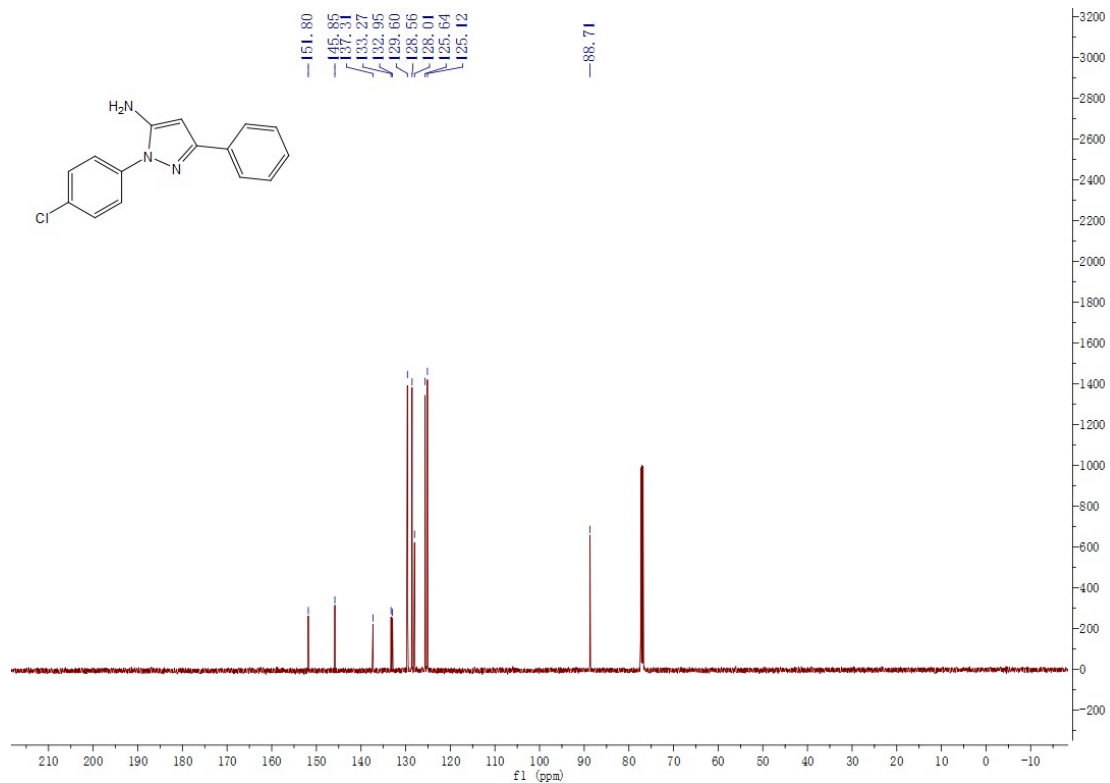
^1H NMR (500 MHz, CDCl_3) of compound **5f**



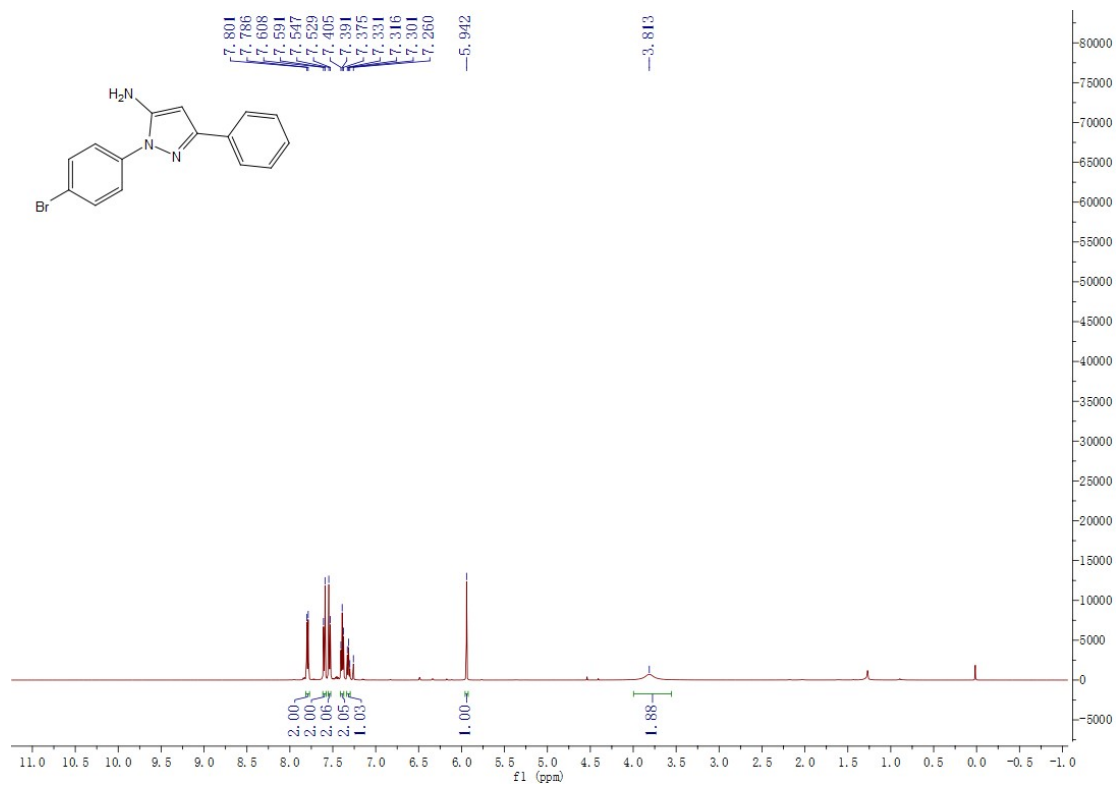
^{13}C NMR (125 MHz, CDCl_3) of compound **5f**



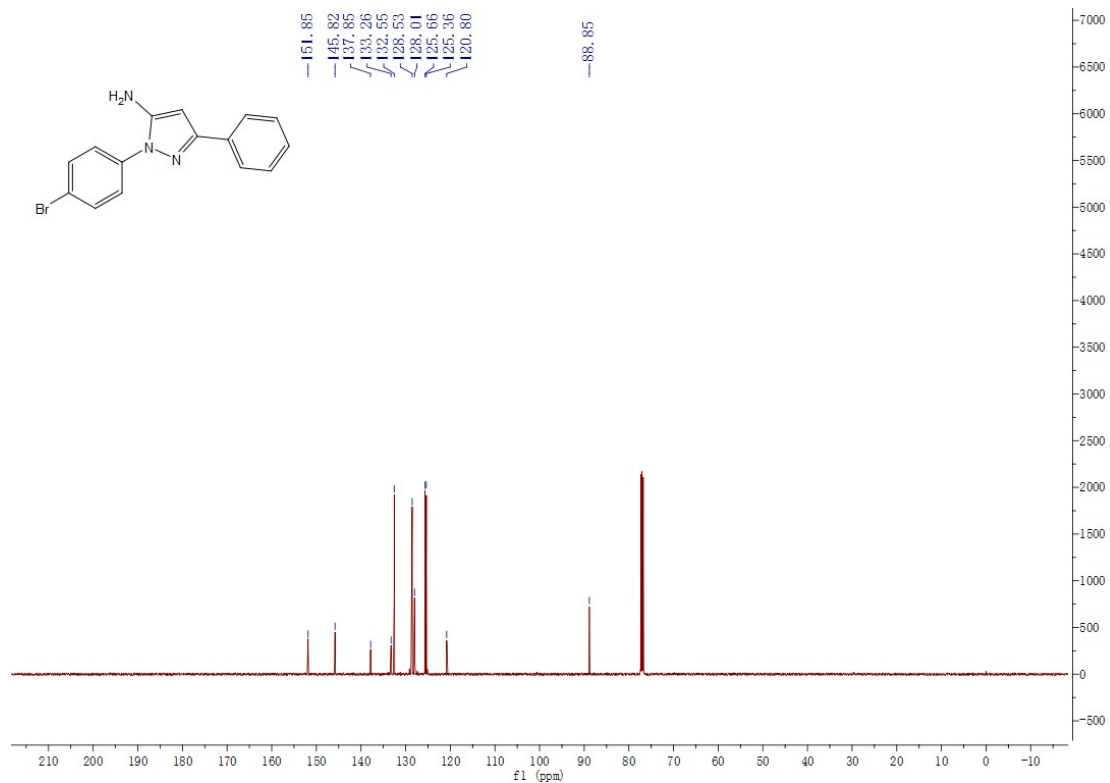
^1H NMR (500 MHz, CDCl_3) of compound **5g**



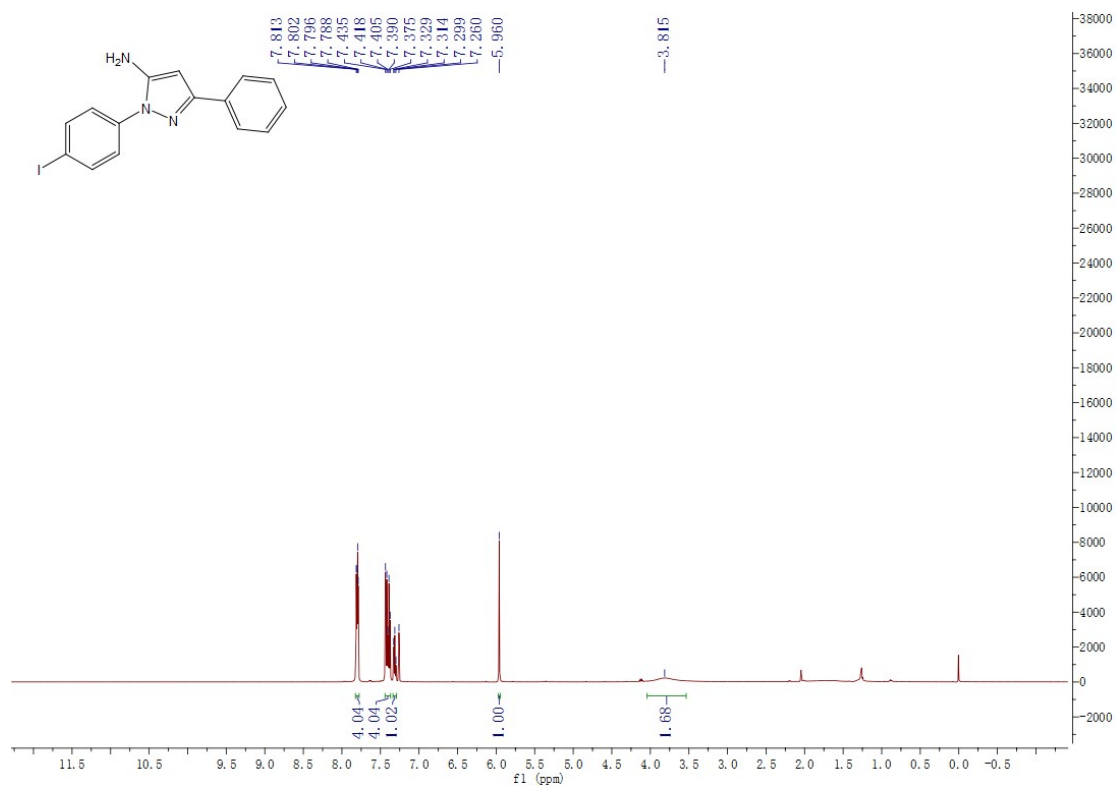
^{13}C NMR (125 MHz, CDCl_3) of compound **5g**



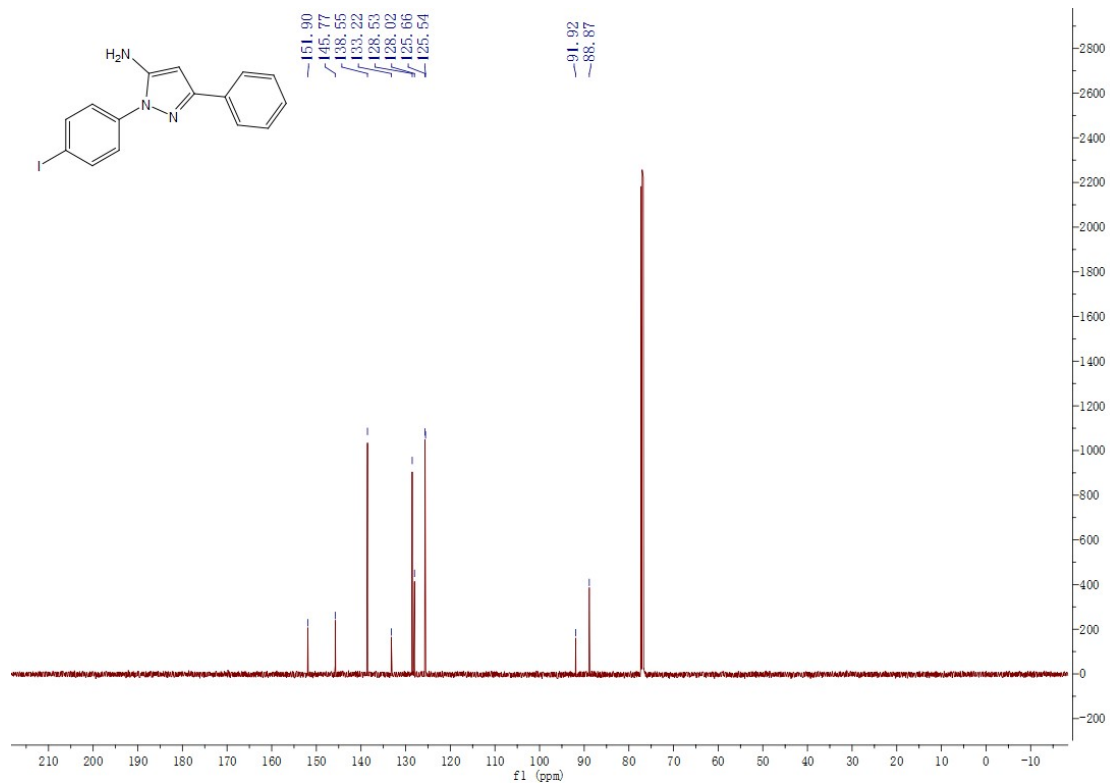
^1H NMR (500 MHz, CDCl_3) of compound **5h**



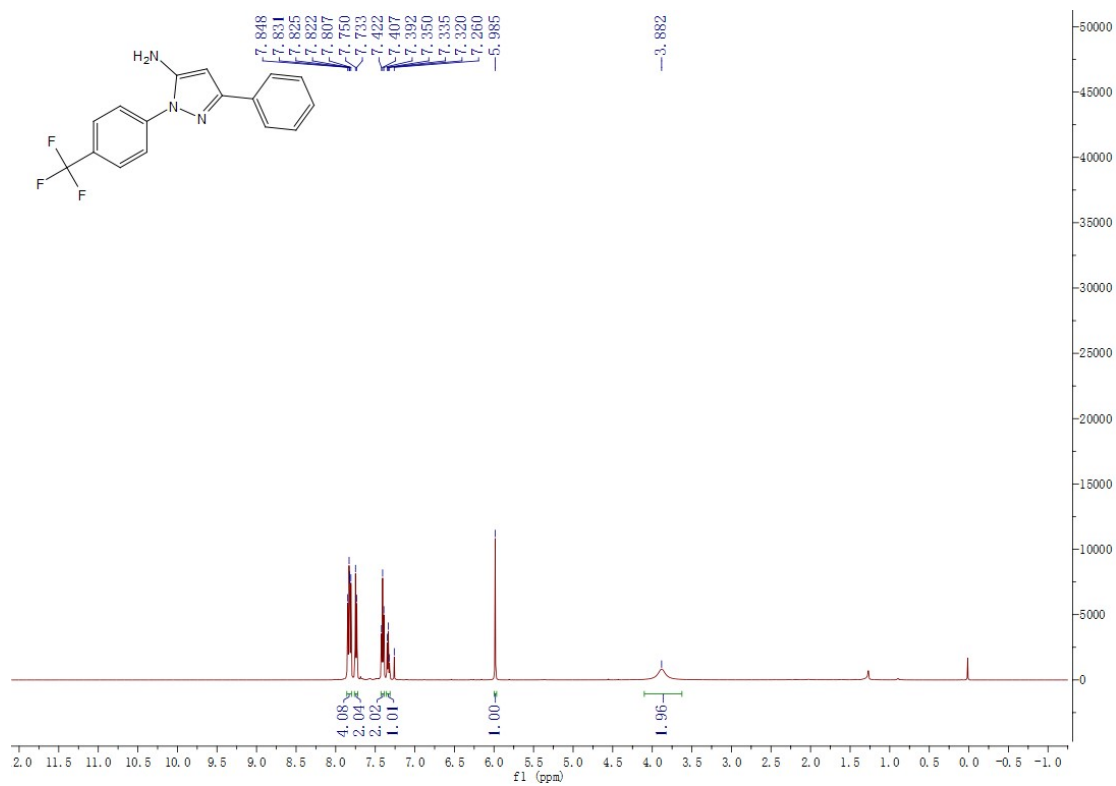
^{13}C NMR (125 MHz, CDCl_3) of compound **5h**



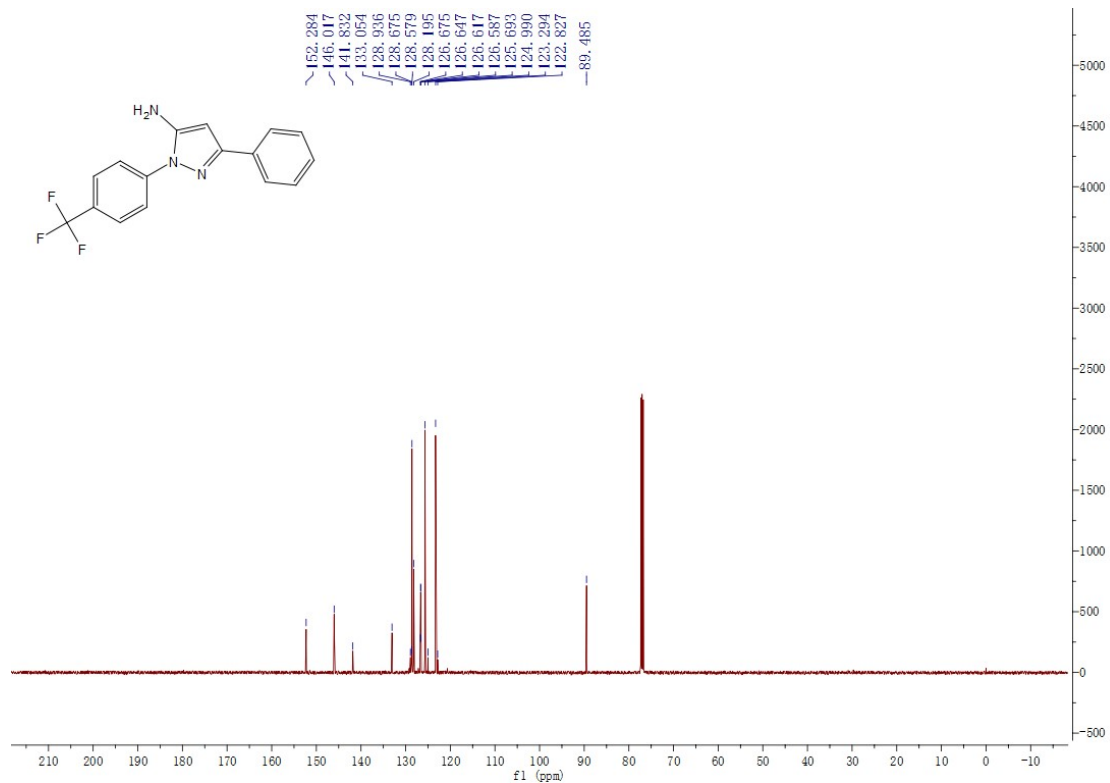
^1H NMR (500 MHz, CDCl_3) of compound **5i**



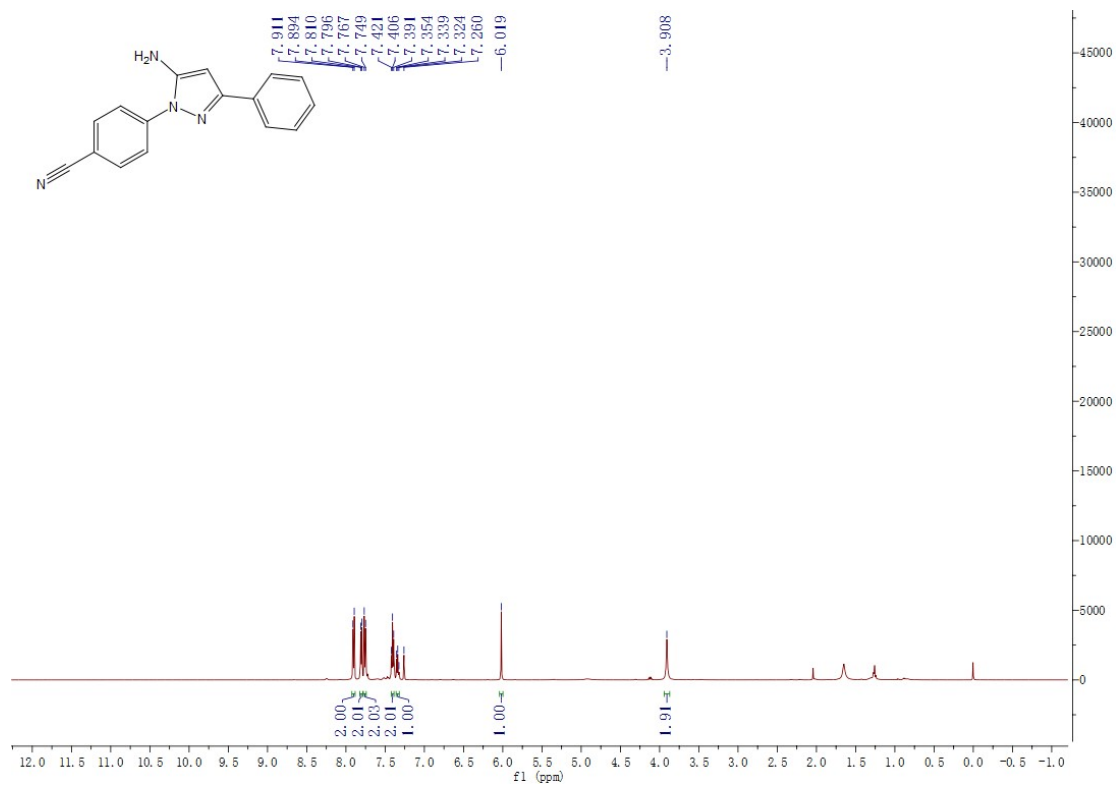
^{13}C NMR (125 MHz, CDCl_3) of compound **5i**



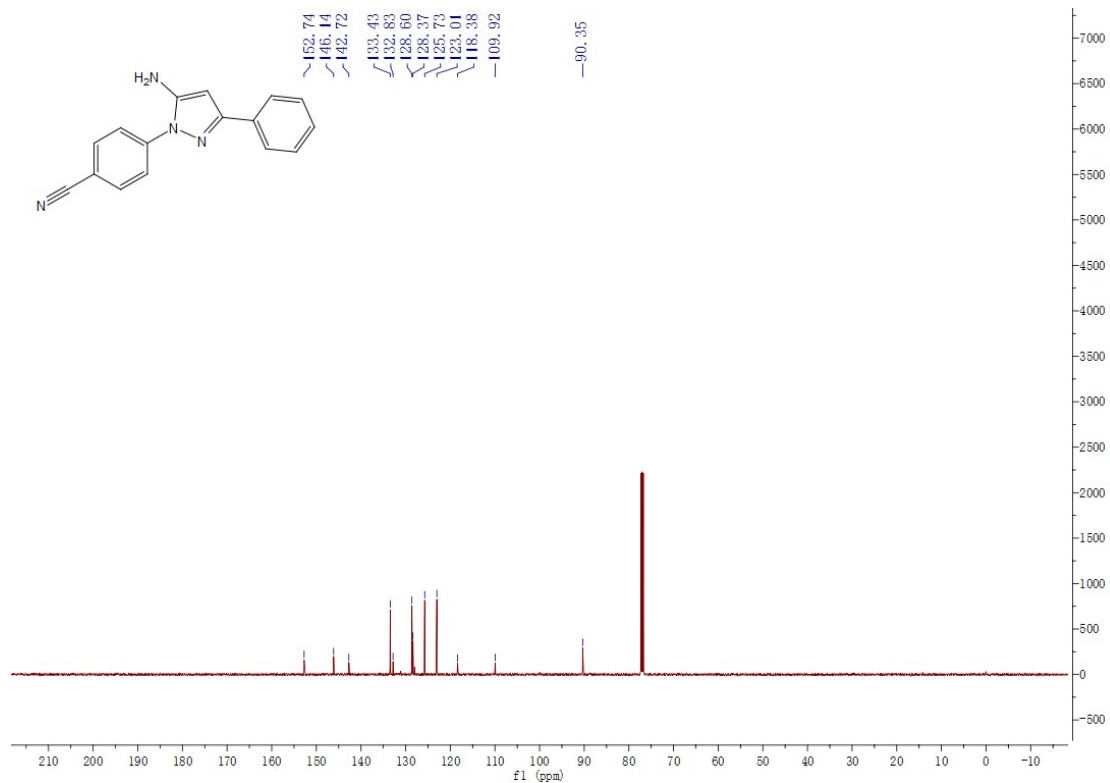
^1H NMR (500 MHz, CDCl_3) of compound **5j**



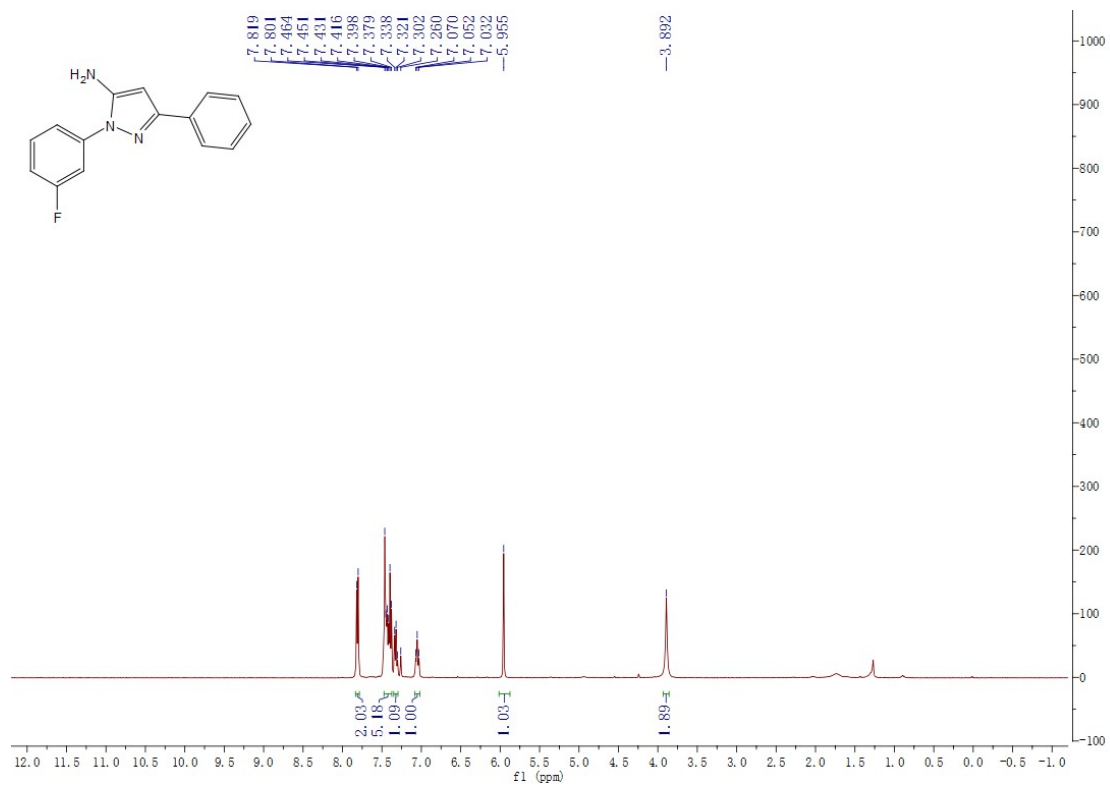
^{13}C NMR (125 MHz, CDCl_3) of compound **5j**



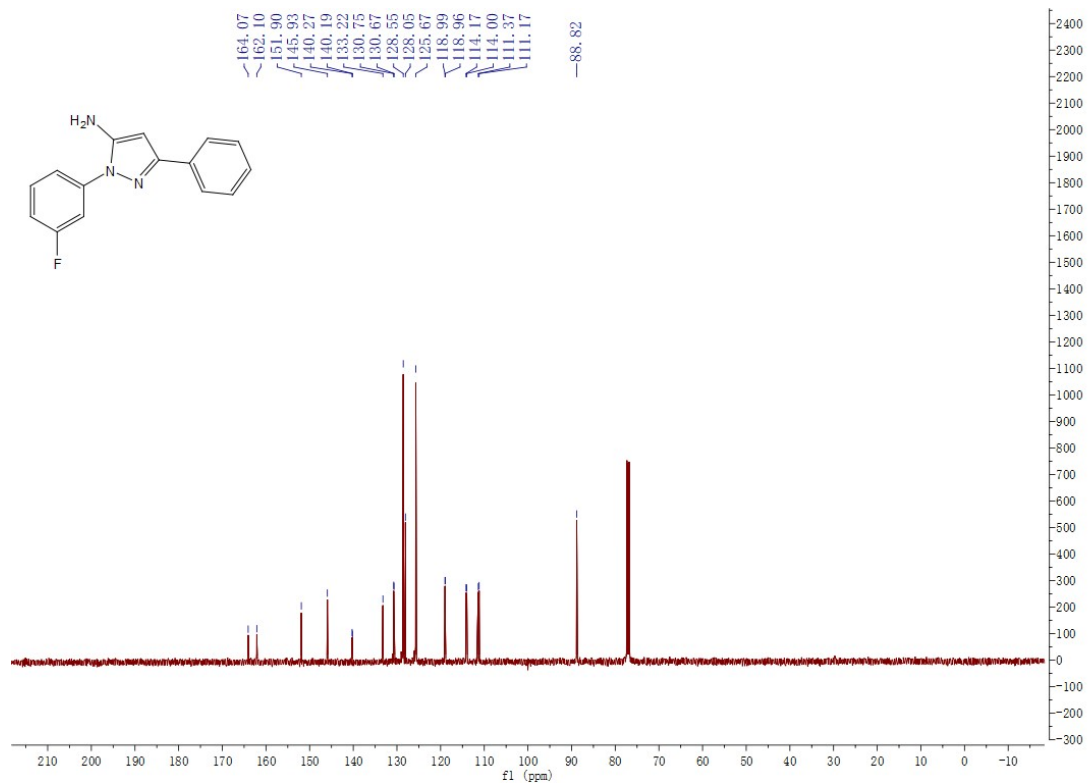
^1H NMR (500 MHz, CDCl_3) of compound **5k**



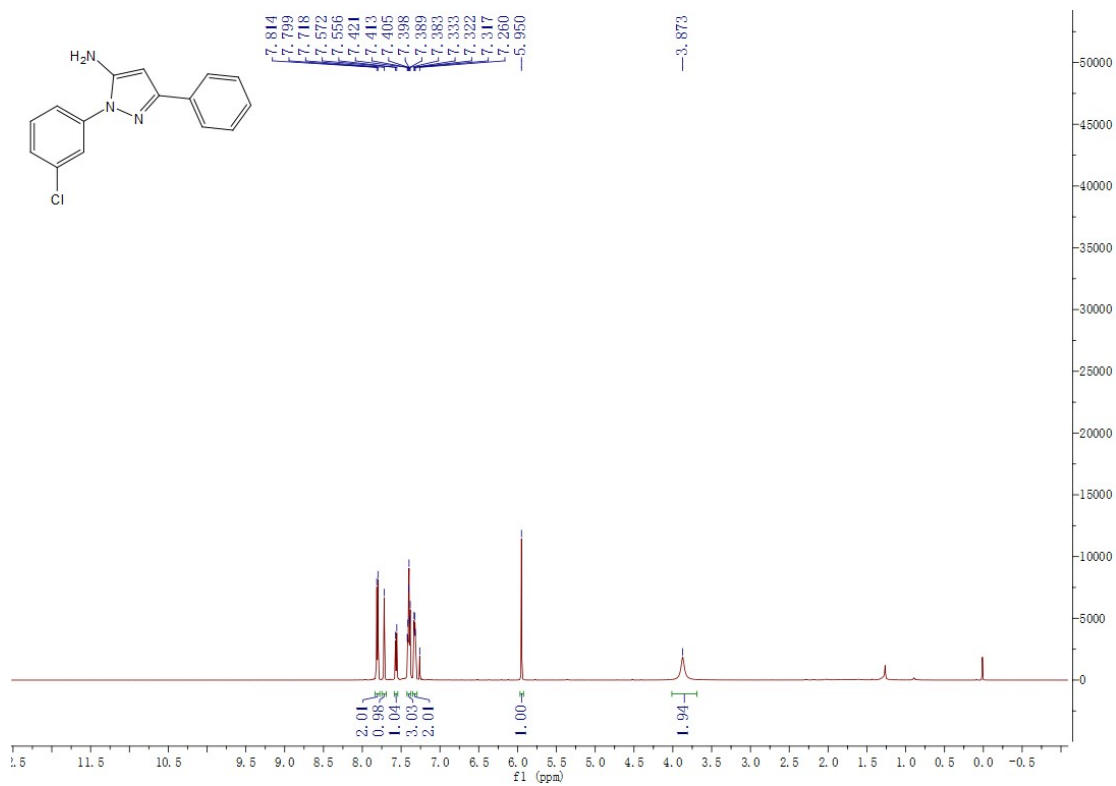
^{13}C NMR (125 MHz, CDCl_3) of compound **5k**



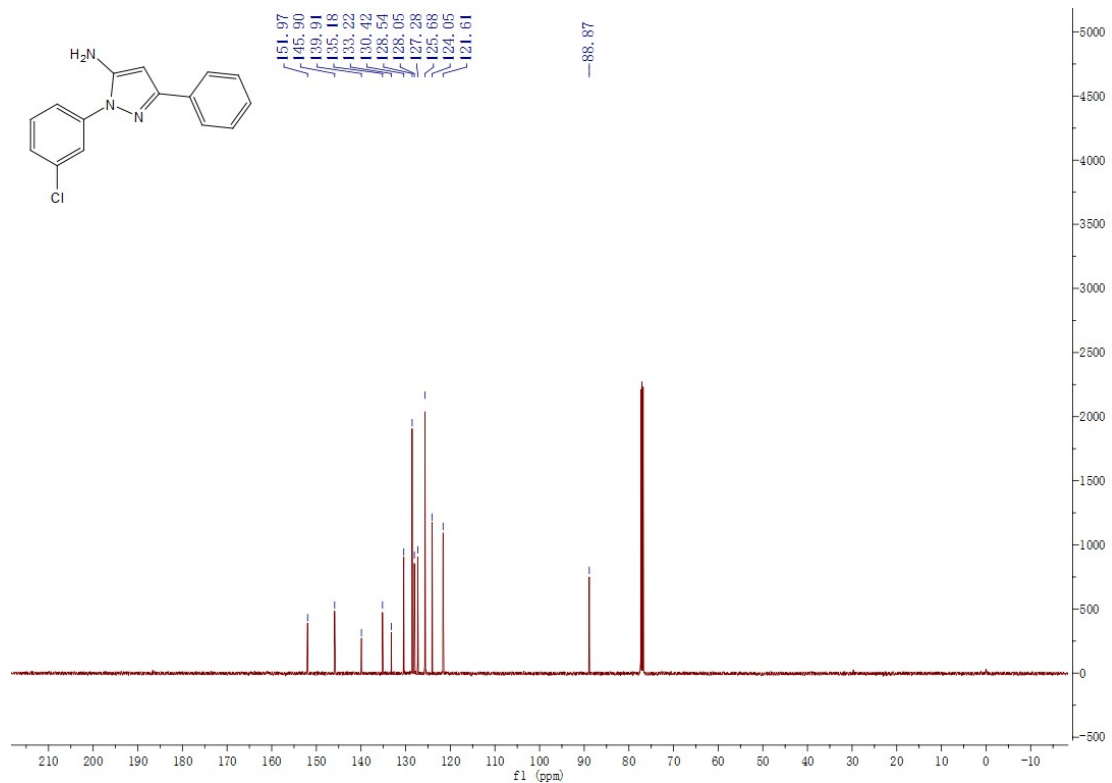
^1H NMR (400 MHz, CDCl_3) of compound **5l**



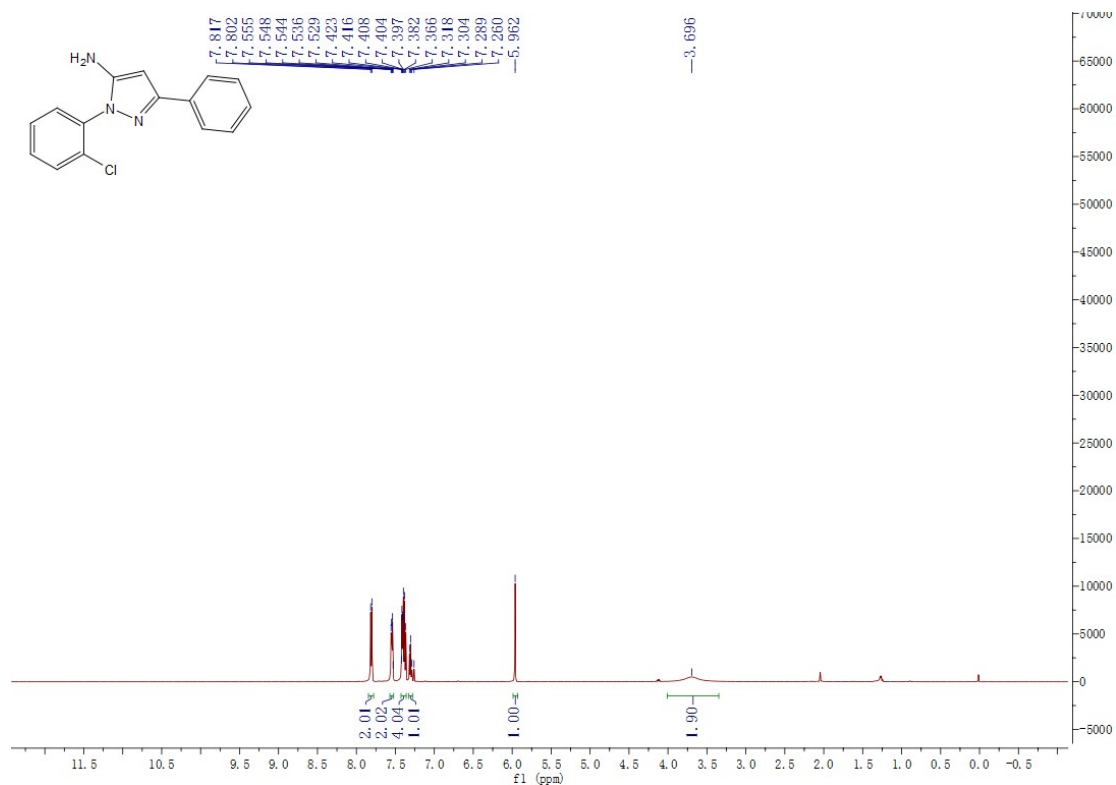
¹³C NMR (101 MHz, CDCl₃) of compound **5l**



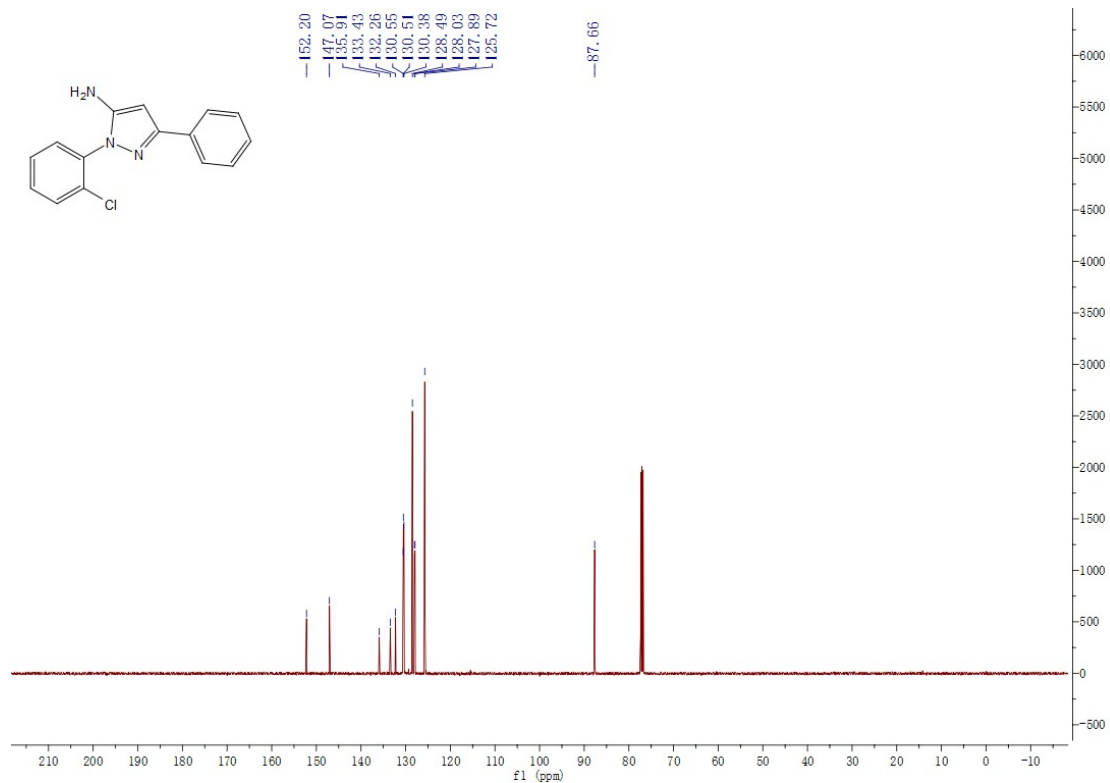
¹H NMR (500 MHz, CDCl₃) of compound **5m**



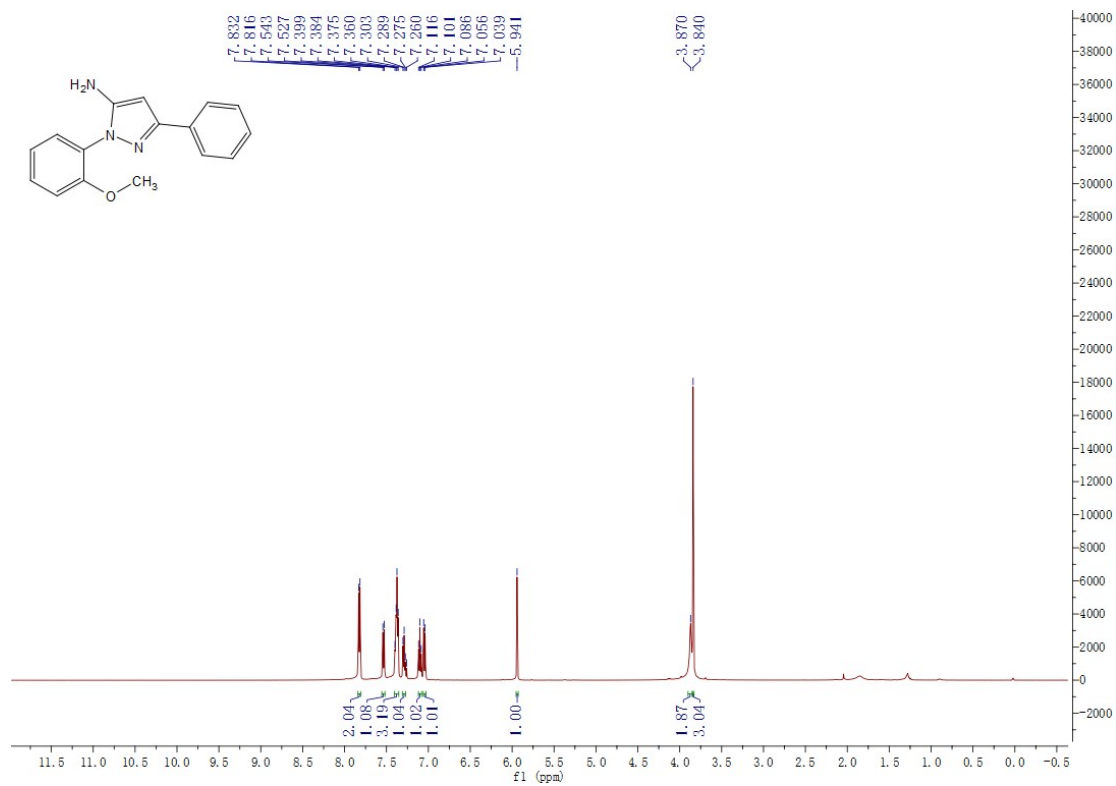
^{13}C NMR (125 MHz, CDCl_3) of compound **5m**



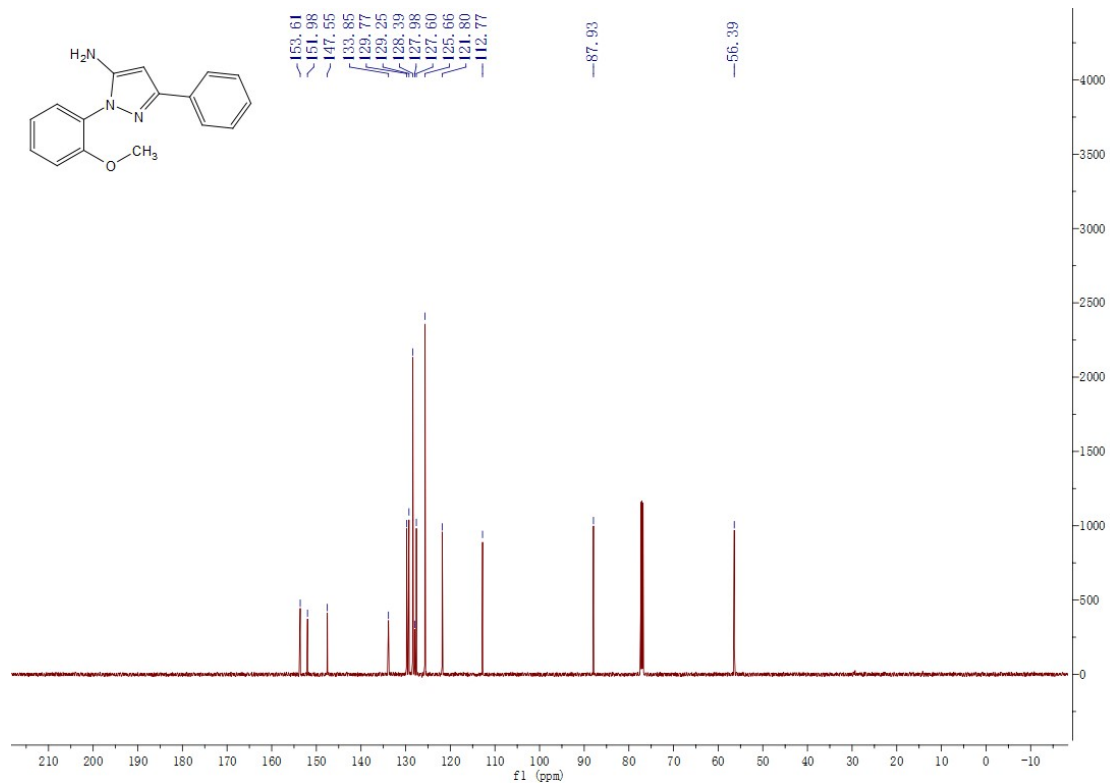
^1H NMR (500 MHz, CDCl_3) of compound **5n**



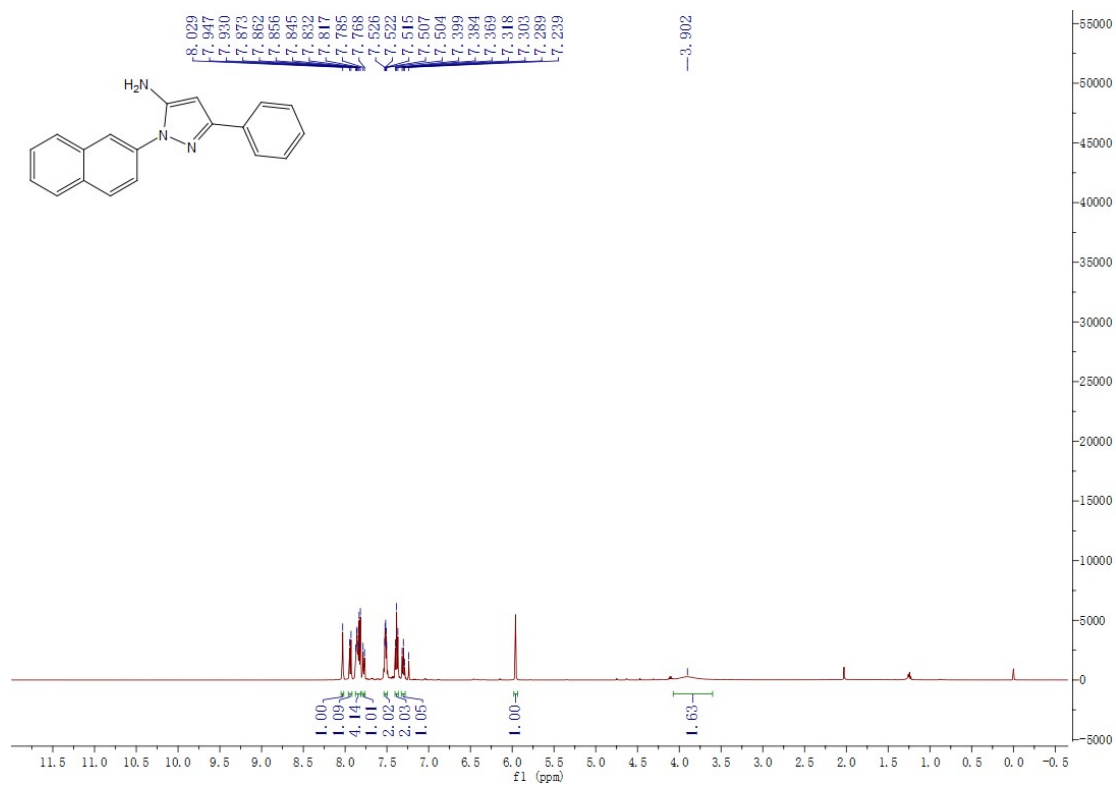
^{13}C NMR (125 MHz, CDCl_3) of compound **5n**



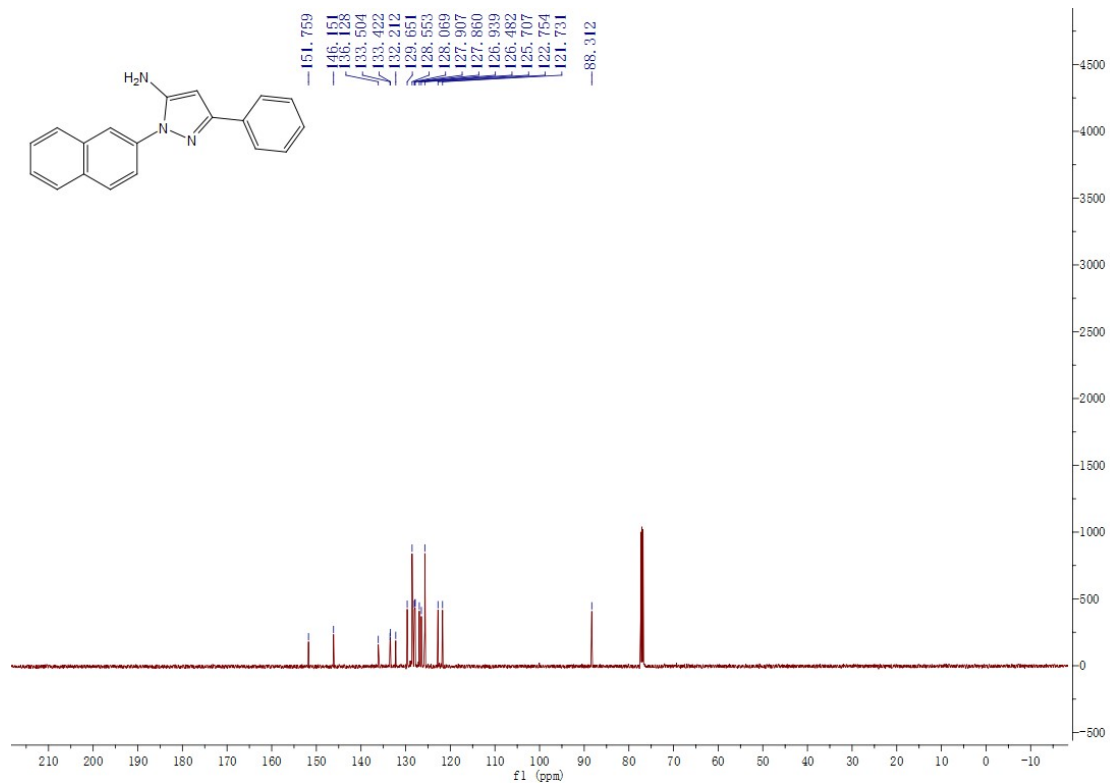
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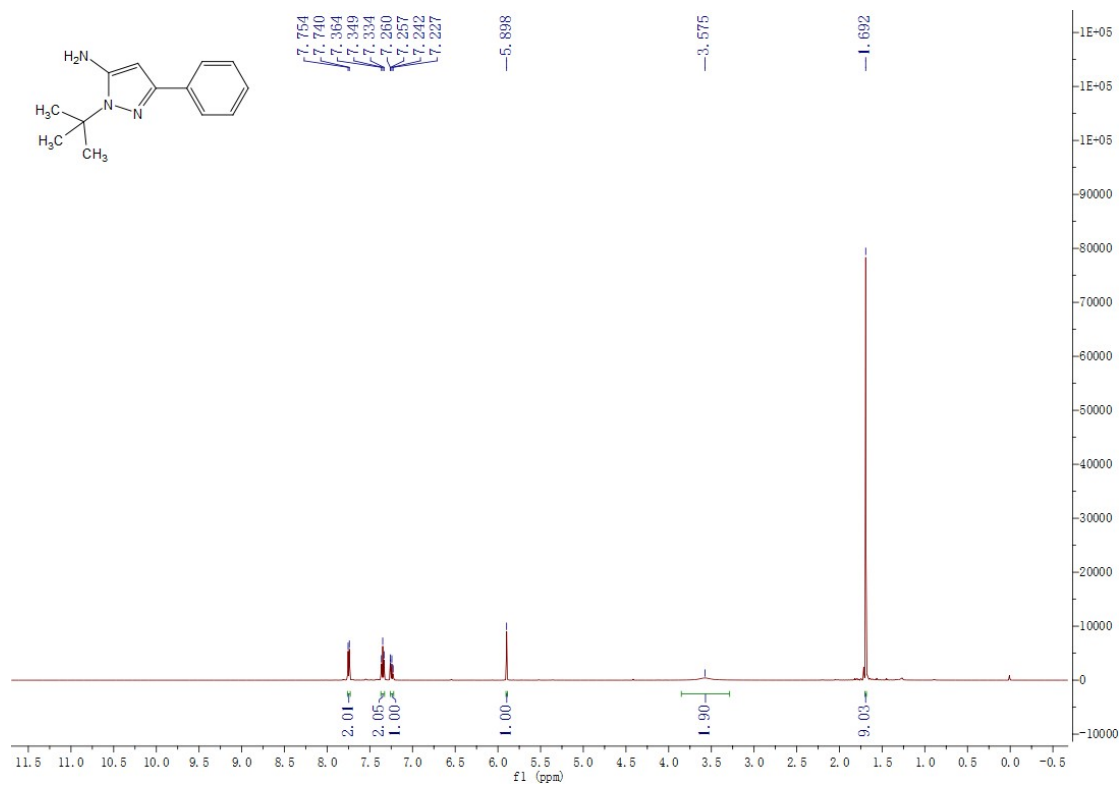
^{13}C NMR (125 MHz, CDCl_3) of compound **5o**



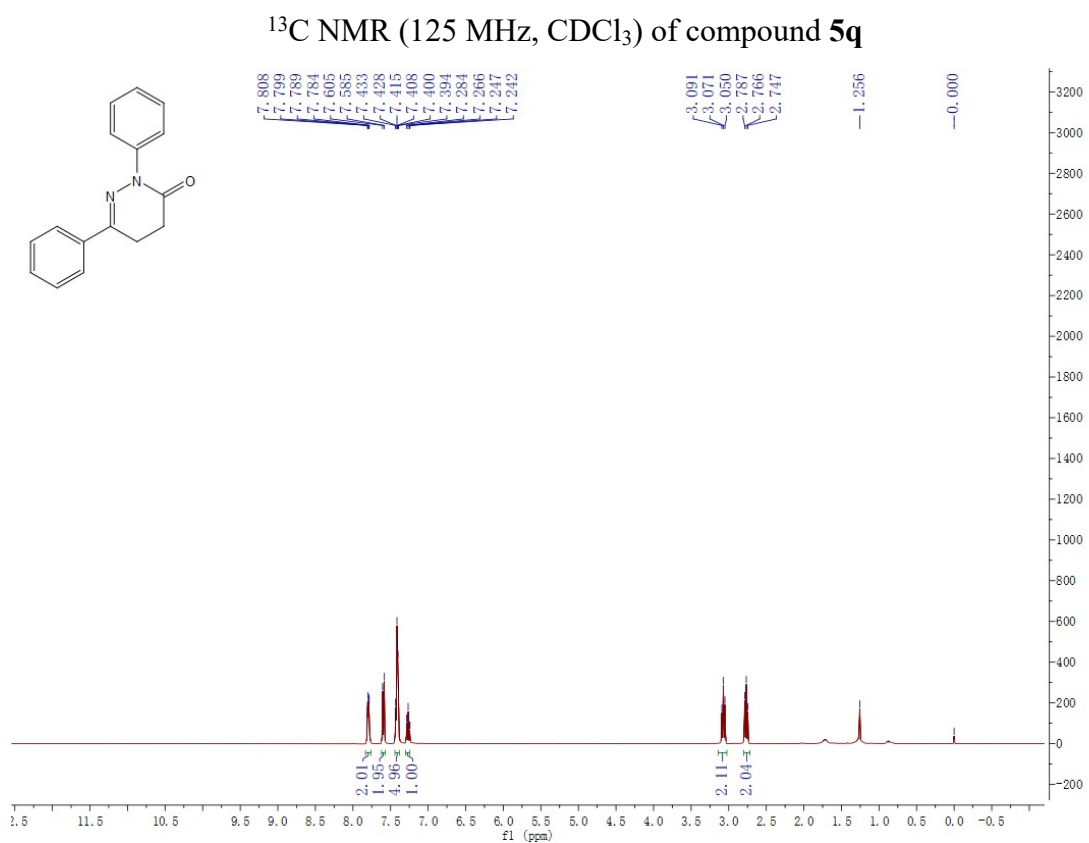
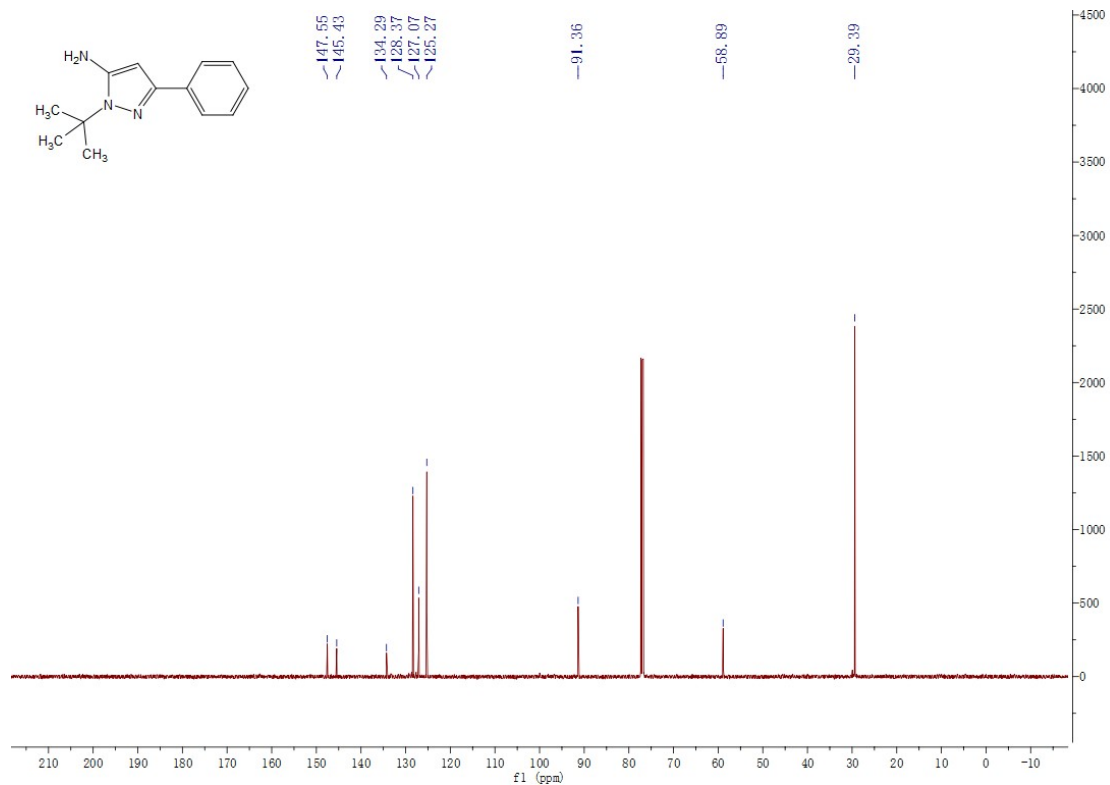
^1H NMR (500 MHz, CDCl_3) of compound **5p**

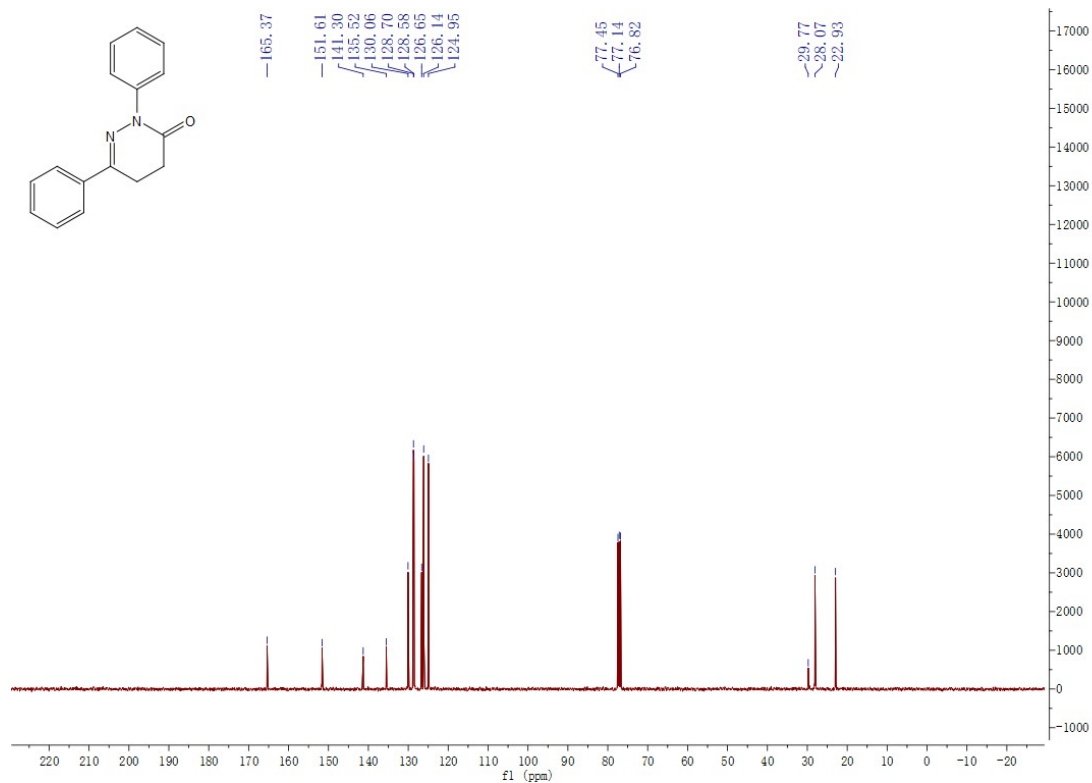


^{13}C NMR (125 MHz, CDCl_3) of compound **5p**

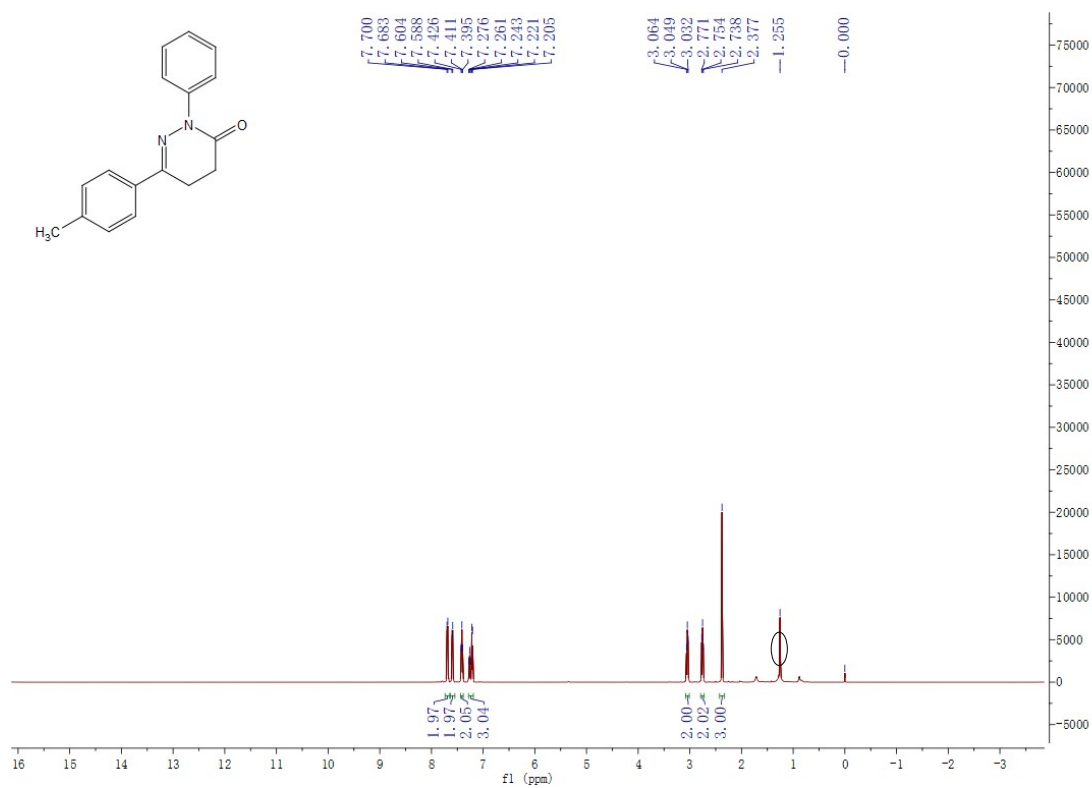


^1H NMR (500 MHz, CDCl_3) of compound **5q**



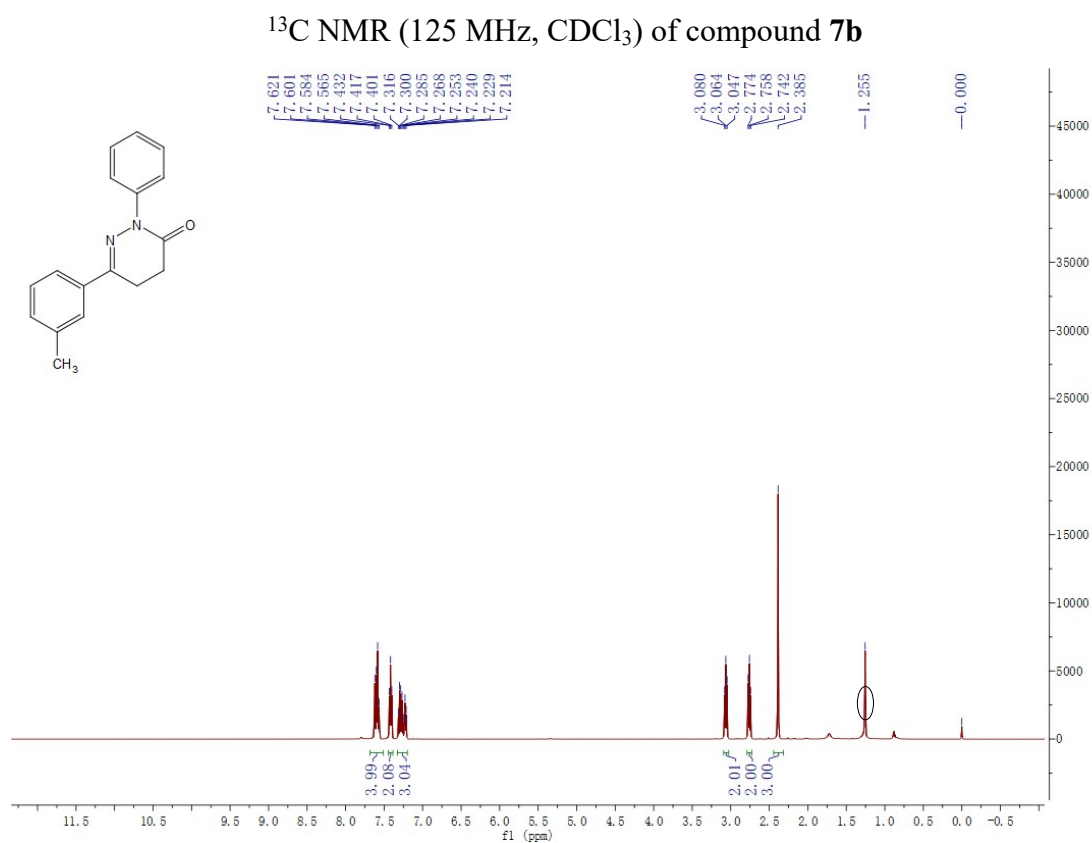
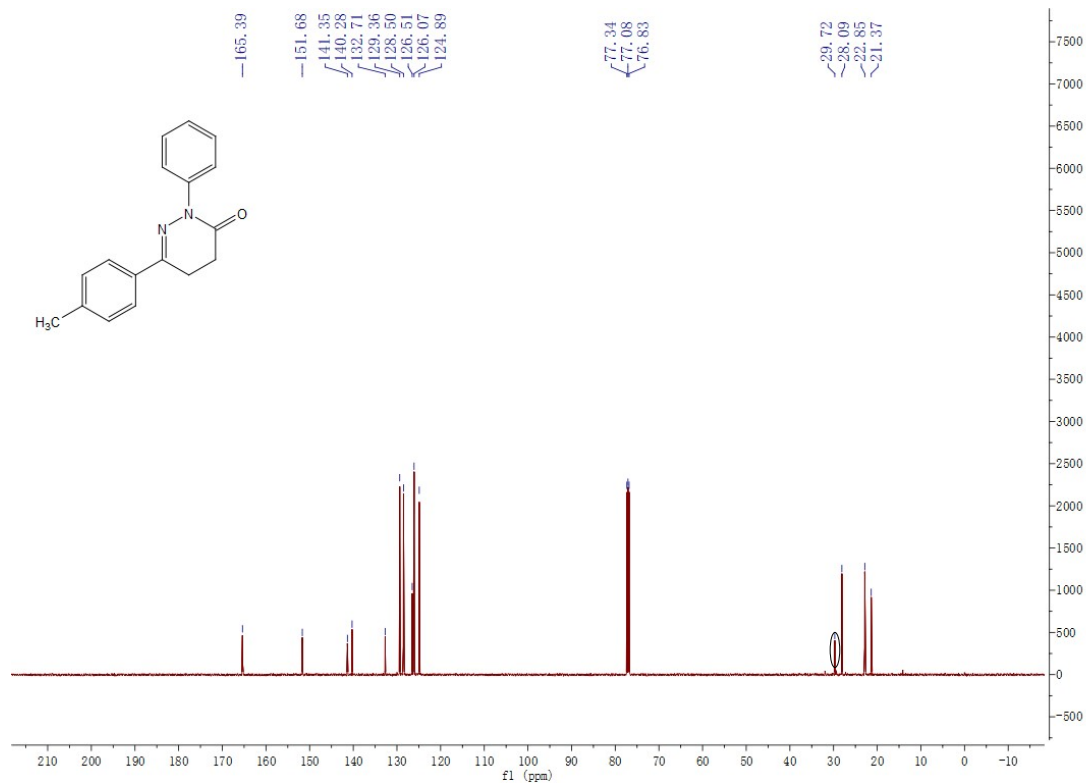


^{13}C NMR (125 MHz, CDCl_3) of compound **7a**

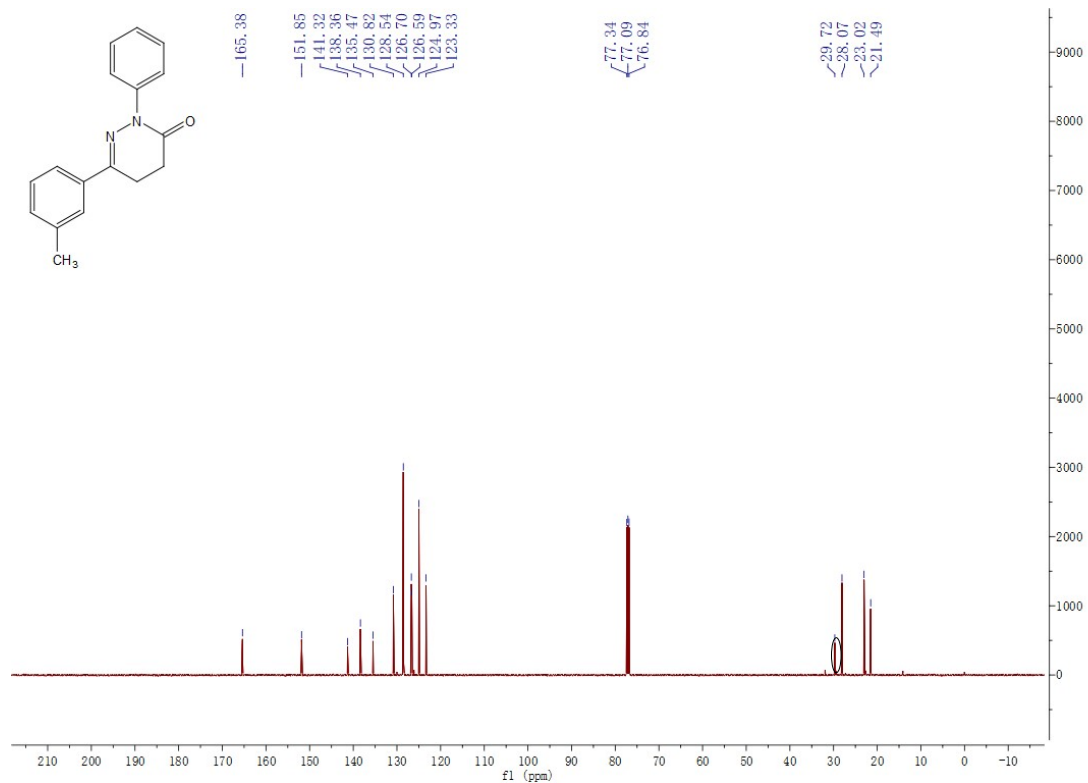


^1H NMR (500 MHz, CDCl_3) of compound **7b**

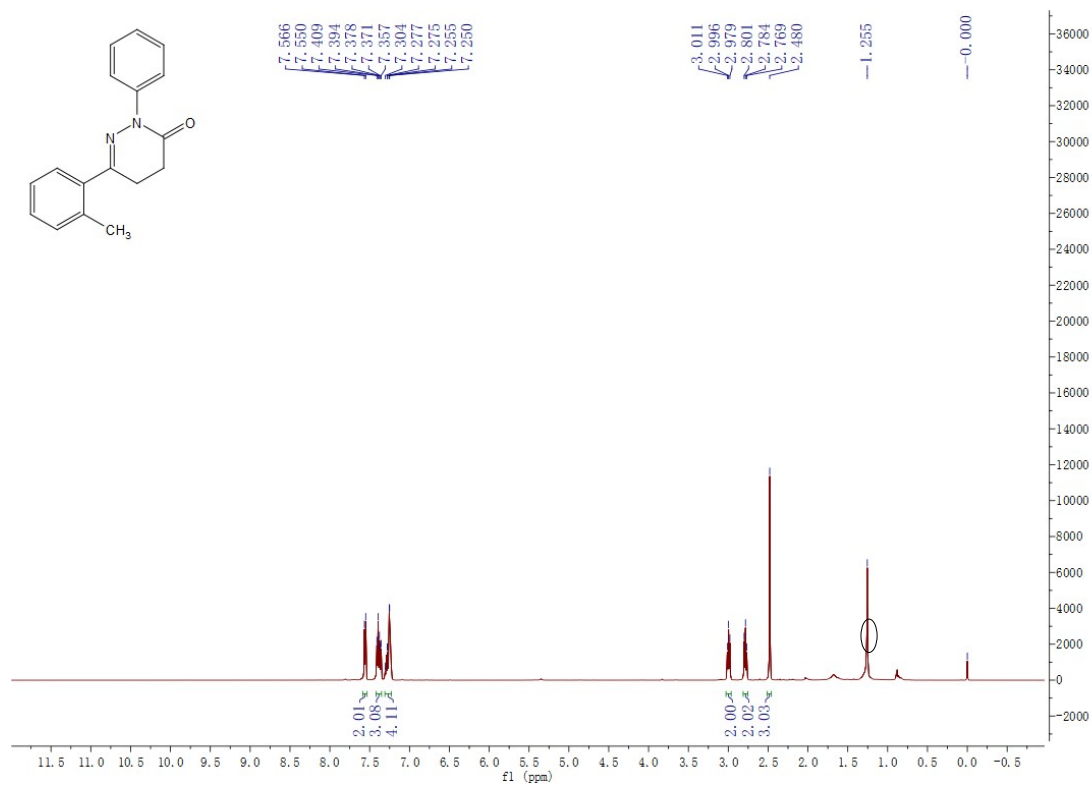
The peak in black oval is the signal of Apiezon grease.



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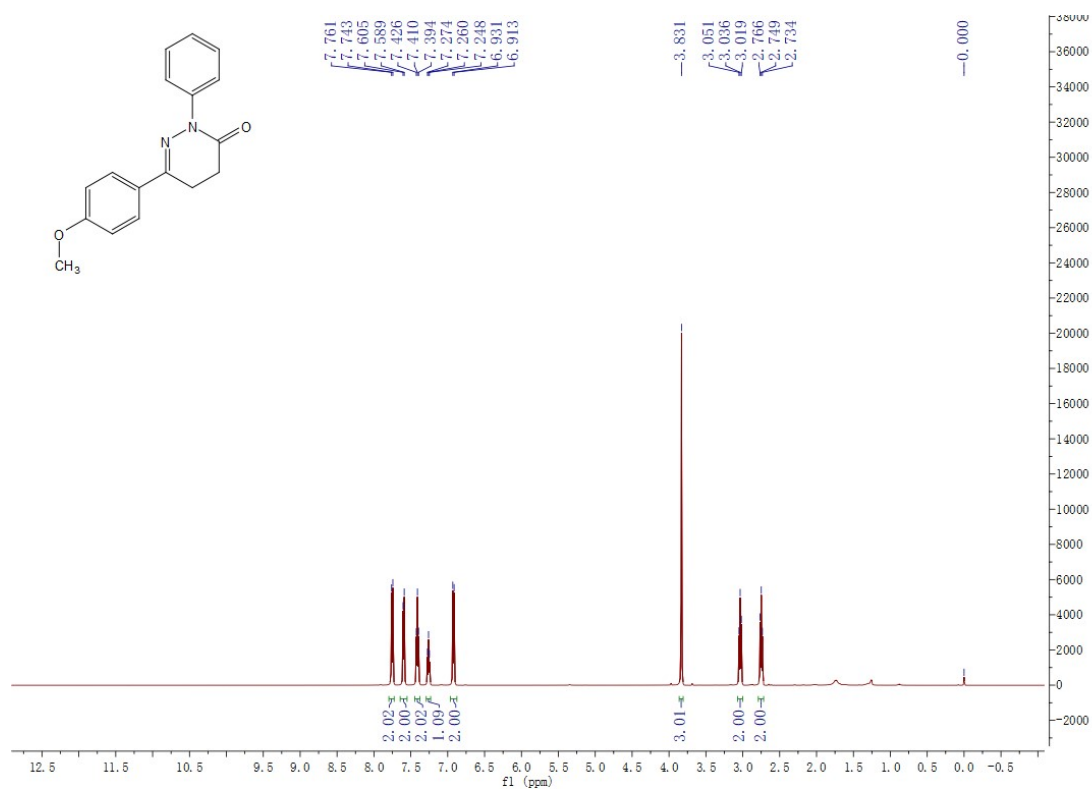
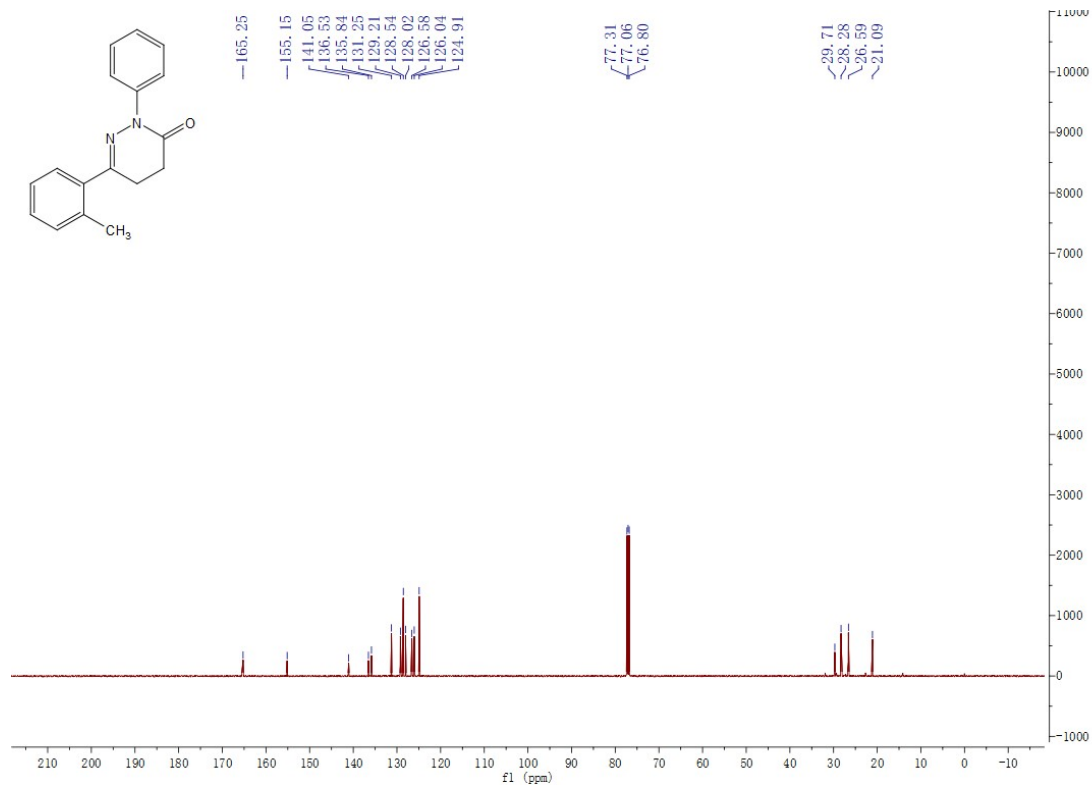


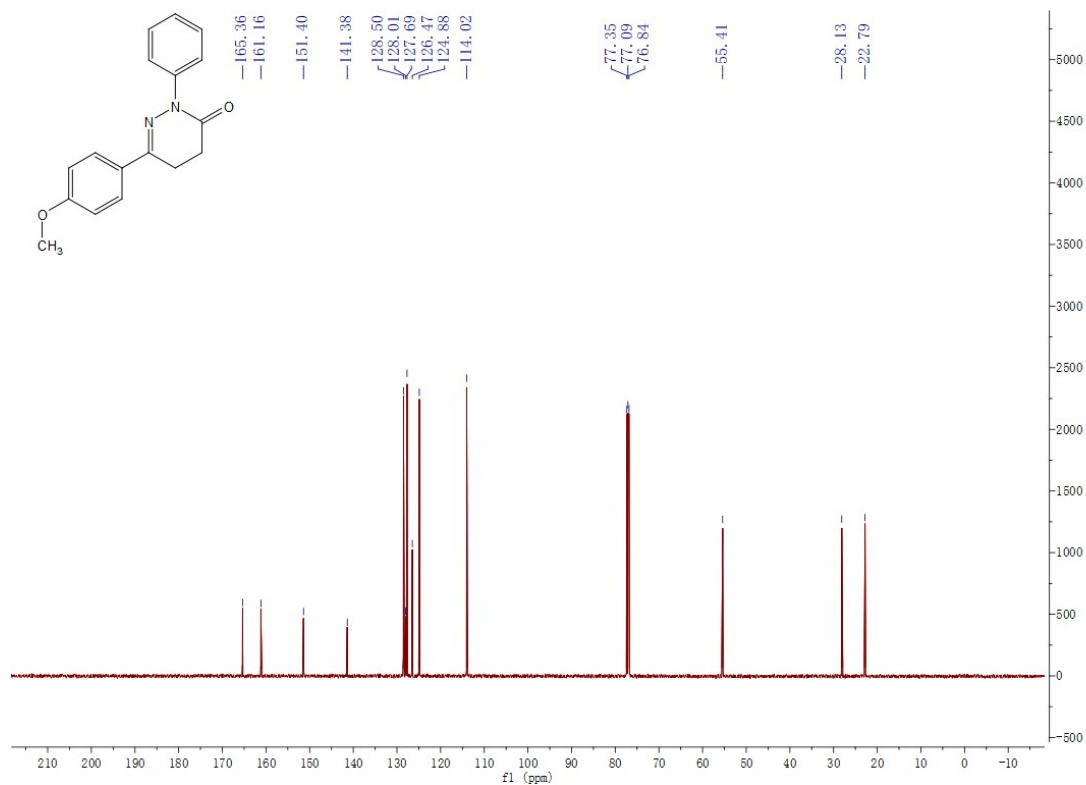
^{13}C NMR (125 MHz, CDCl_3) of compound **7c**



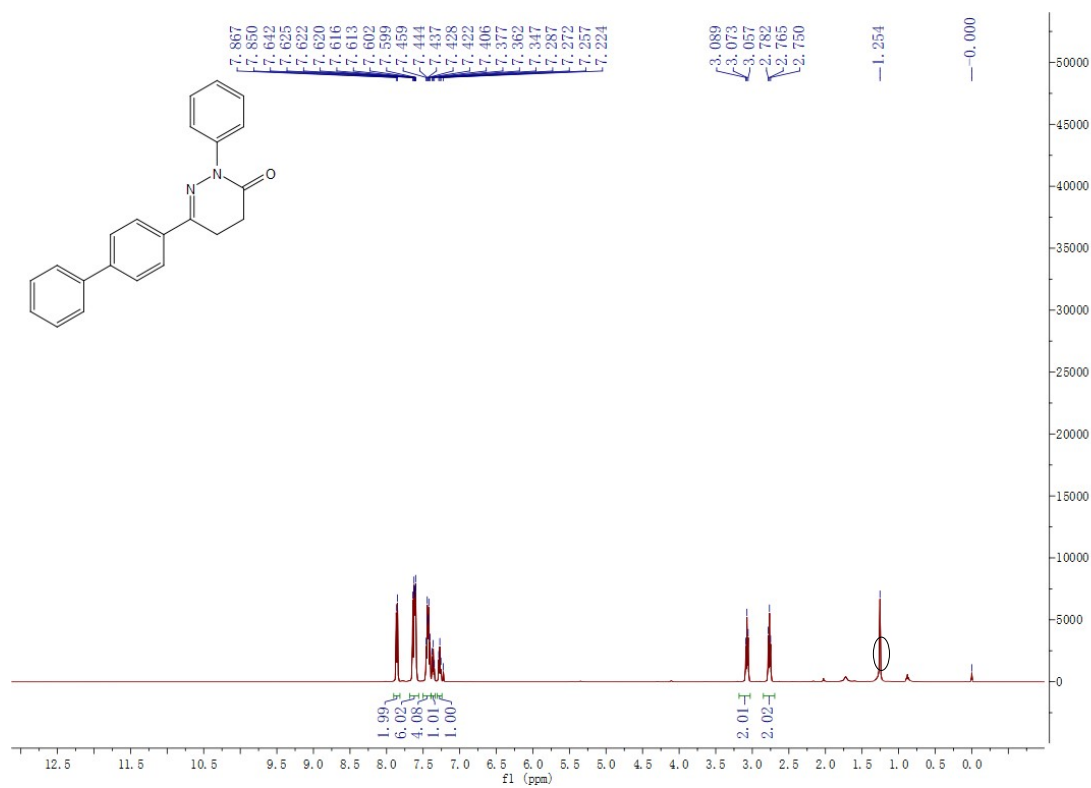
^1H NMR (500 MHz, CDCl_3) of compound **7d**

The peak in black oval is the signal of Apiezon grease.



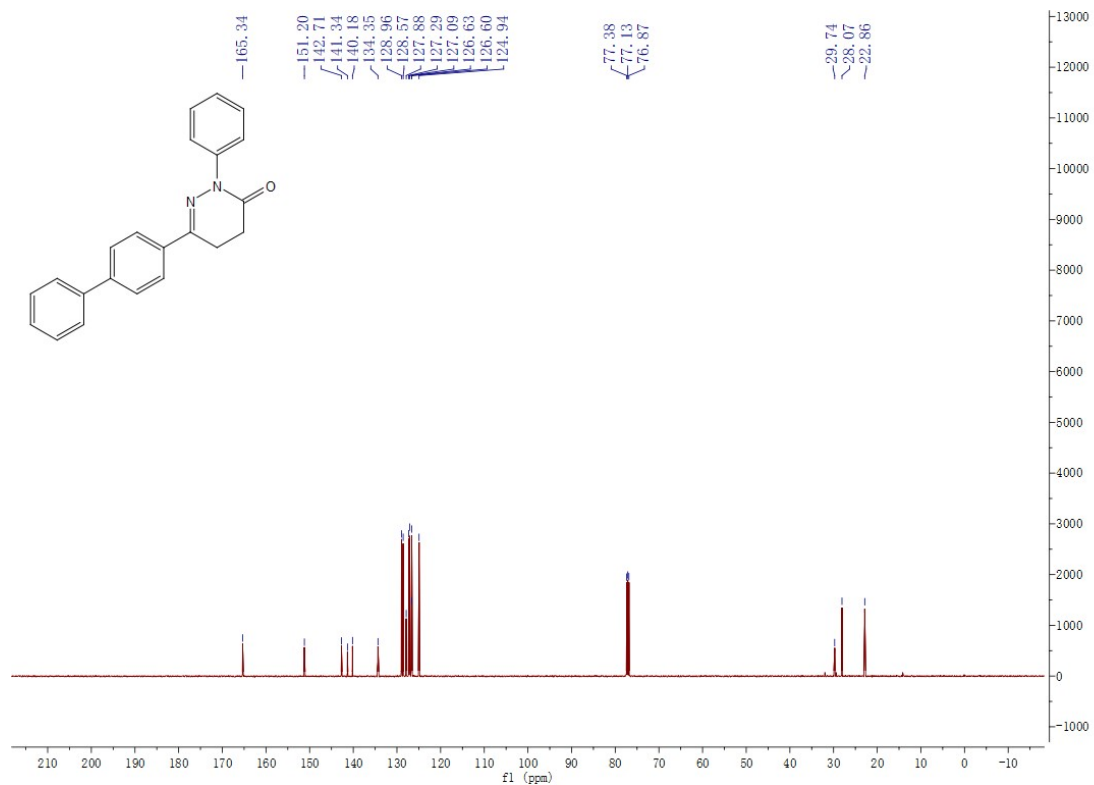


^{13}C NMR (125 MHz, CDCl_3) of compound **7e**

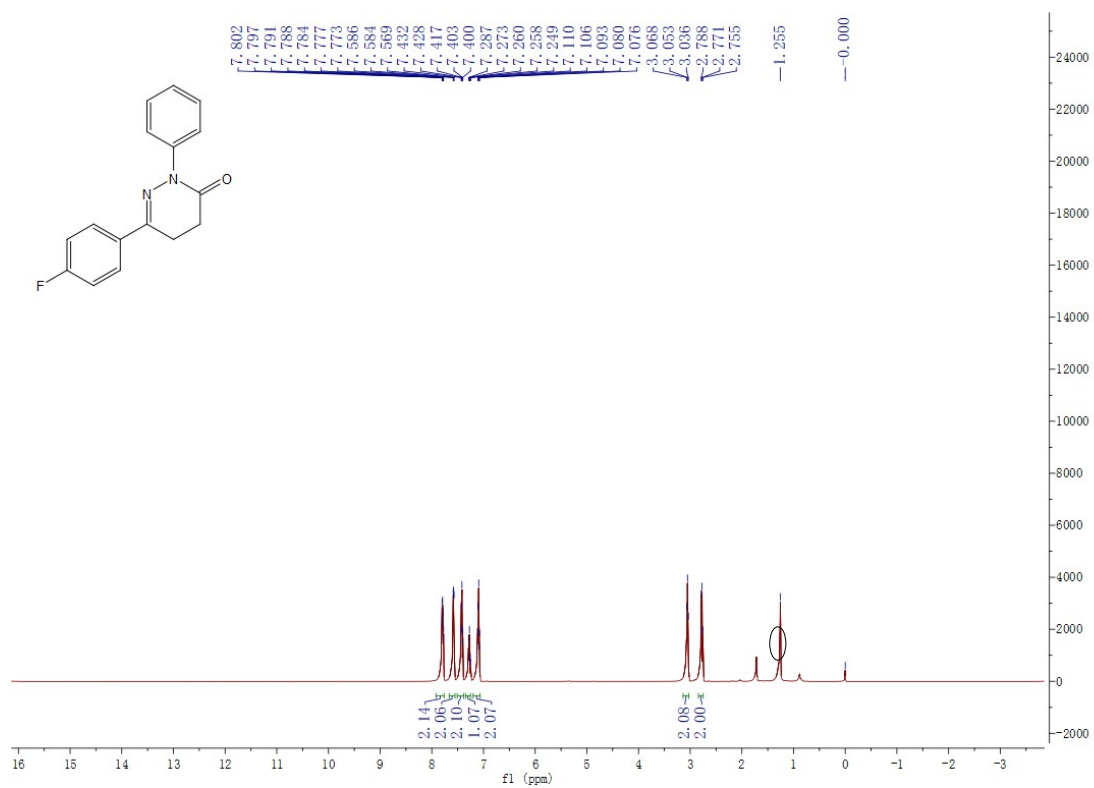


^1H NMR (500 MHz, CDCl_3) of compound **7f**

The peak in black oval is the signal of Apiezon grease.

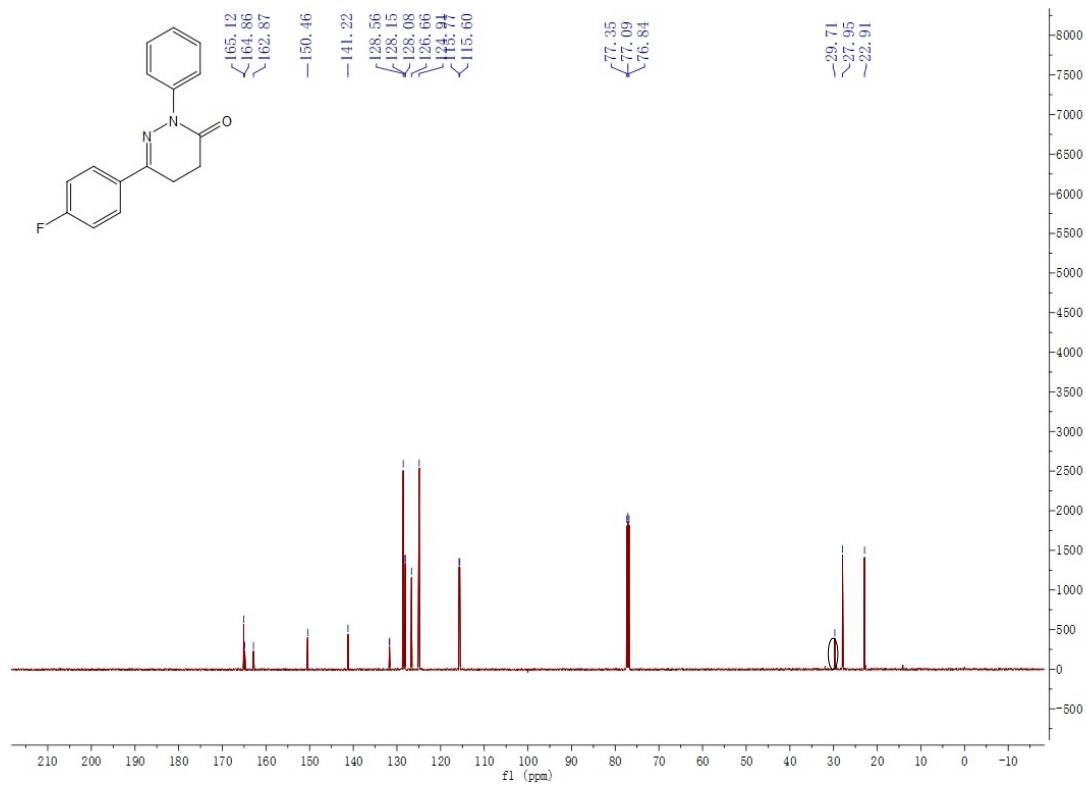


^{13}C NMR (125 MHz, CDCl_3) of compound **7f**

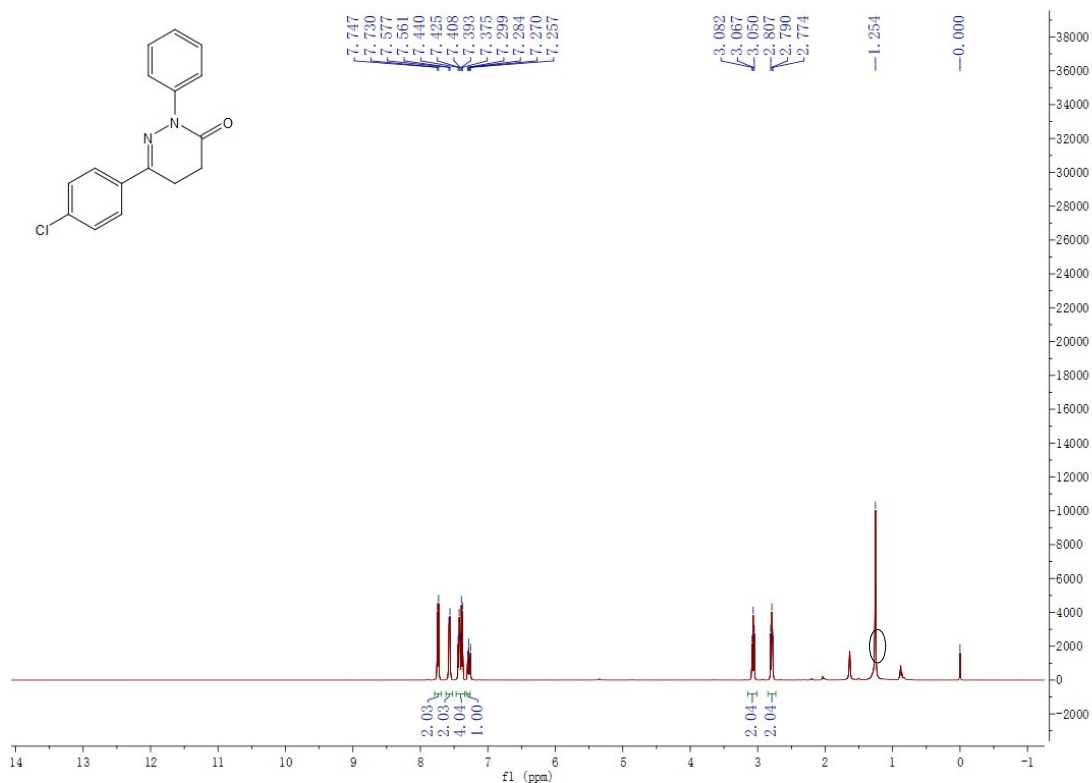


^1H NMR (500 MHz, CDCl_3) of compound **7g**

The peak in black oval is the signal of Apiezon grease.

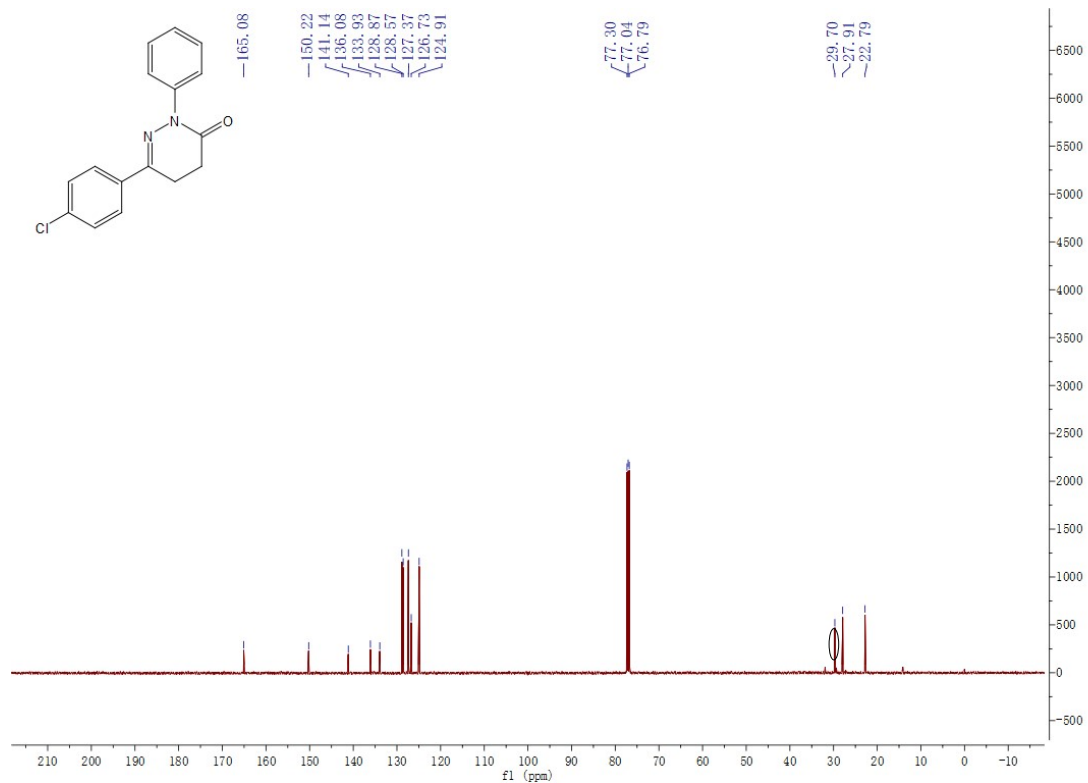


^{13}C NMR (125 MHz, CDCl_3) of compound **7g**

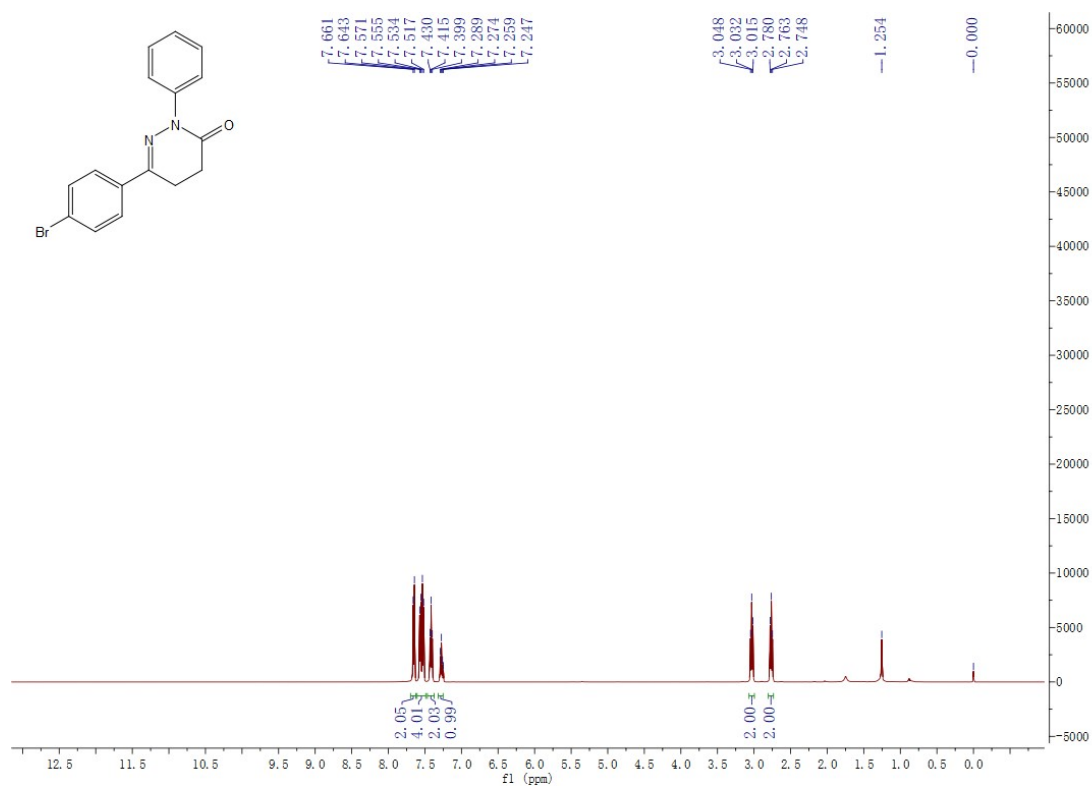


^1H NMR (500 MHz, CDCl_3) of compound **7h**

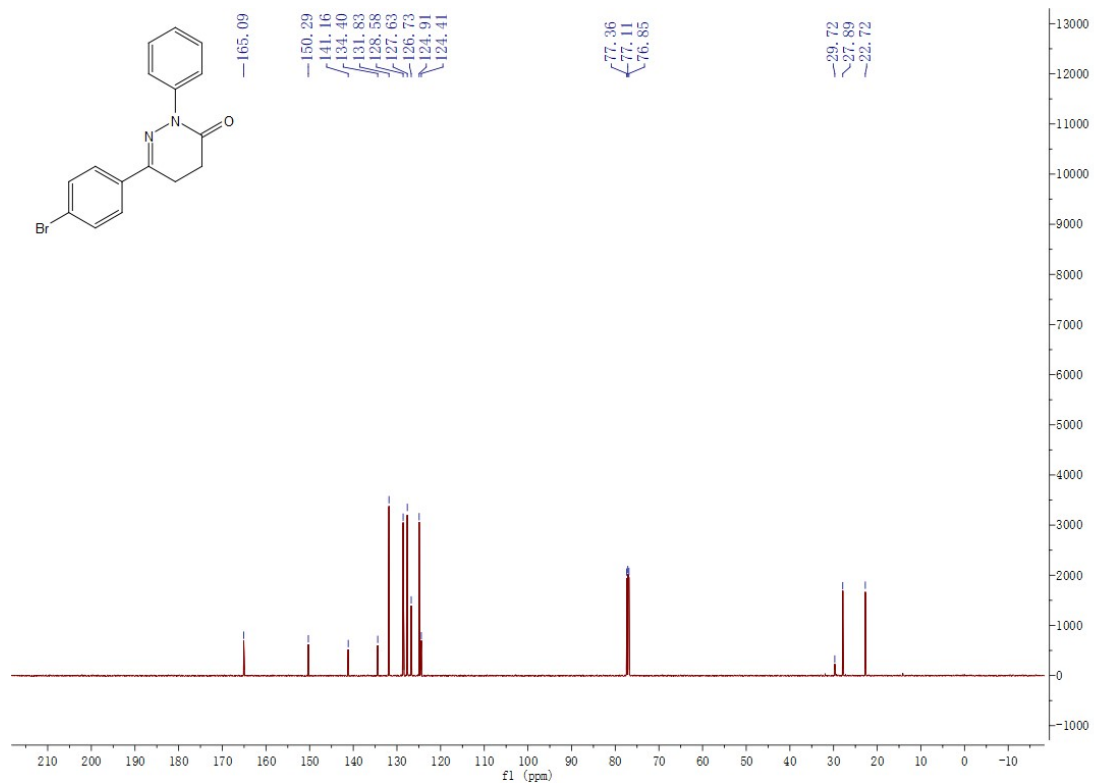
The peak in black oval is the signal of Apiezon grease.



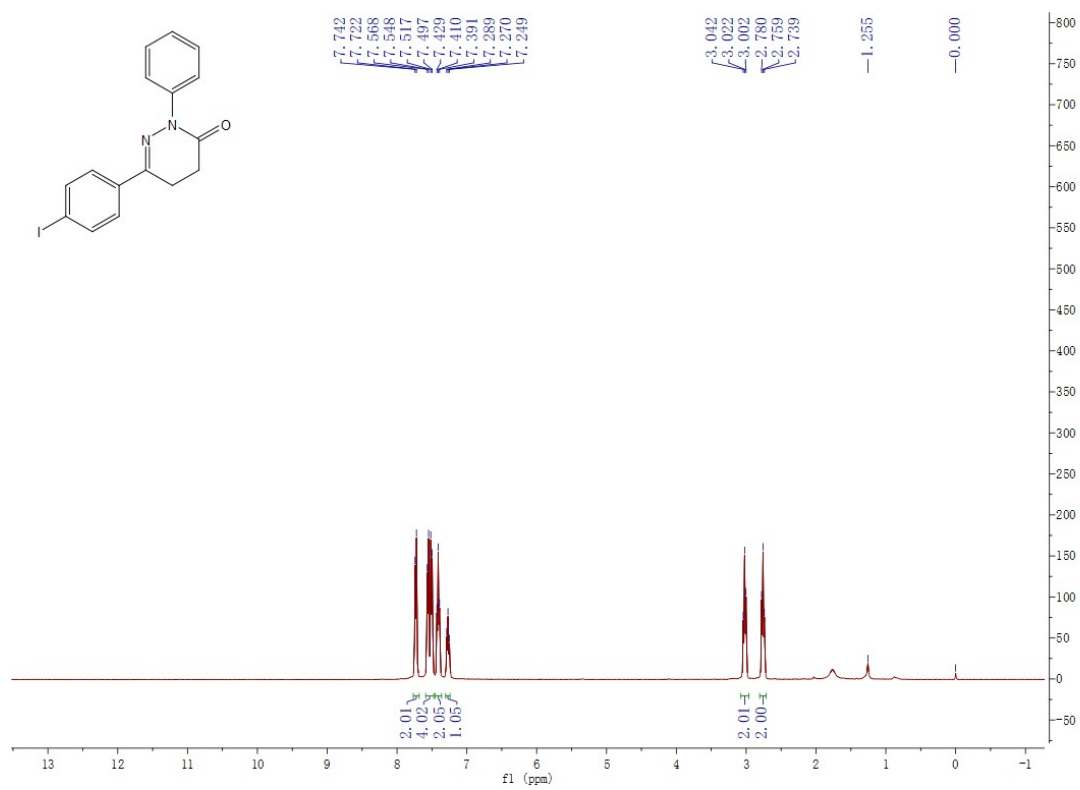
^{13}C NMR (125 MHz, CDCl_3) of compound **7h**



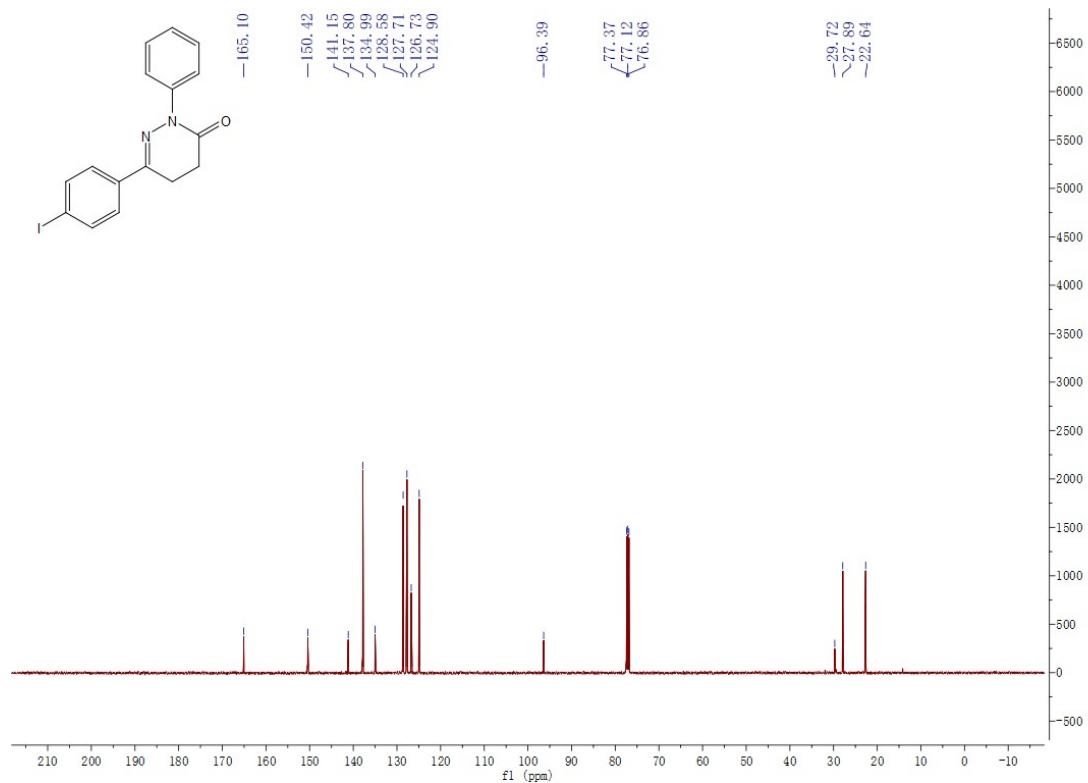
^1H NMR (500 MHz, CDCl_3) of compound **7i**



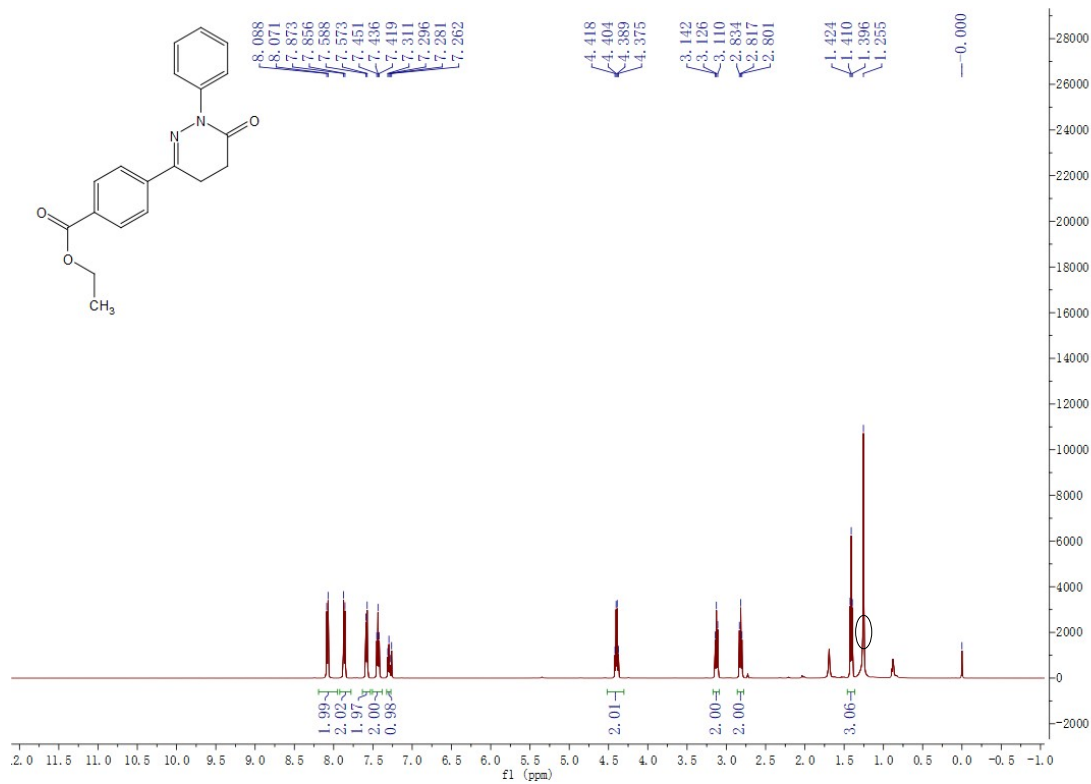
^{13}C NMR (125 MHz, CDCl_3) of compound **7i**



^1H NMR (400 MHz, CDCl_3) of compound **7j**

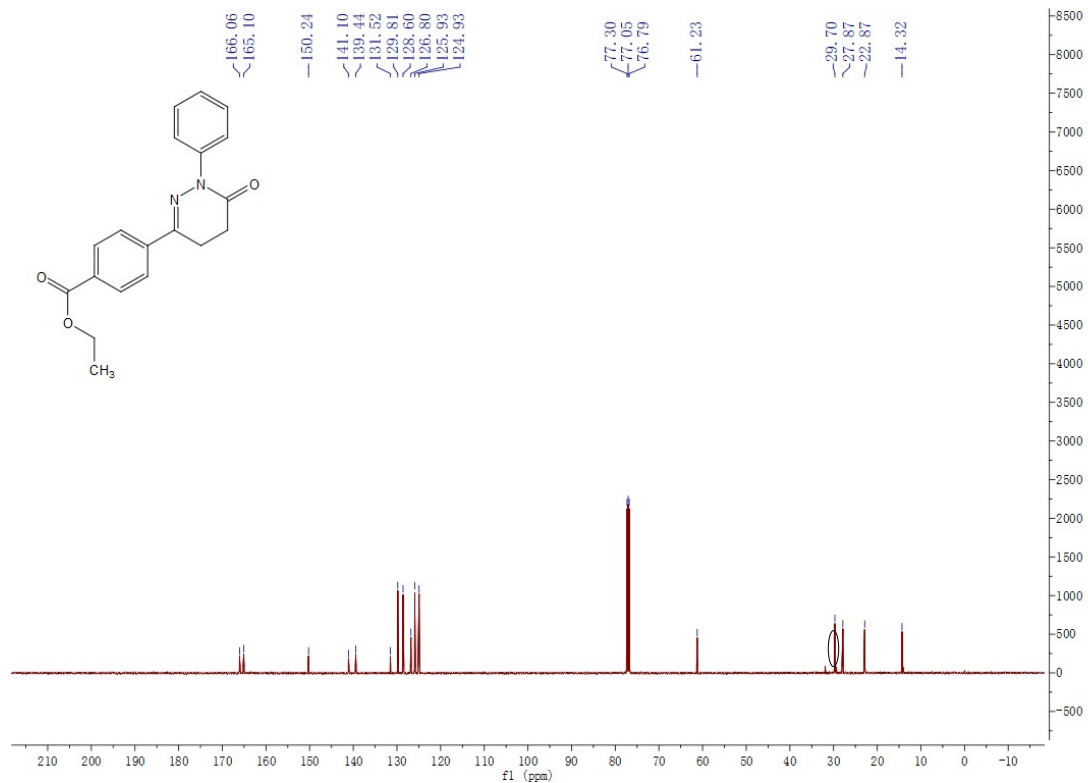


^{13}C NMR (101 MHz, CDCl_3) of compound **7j**

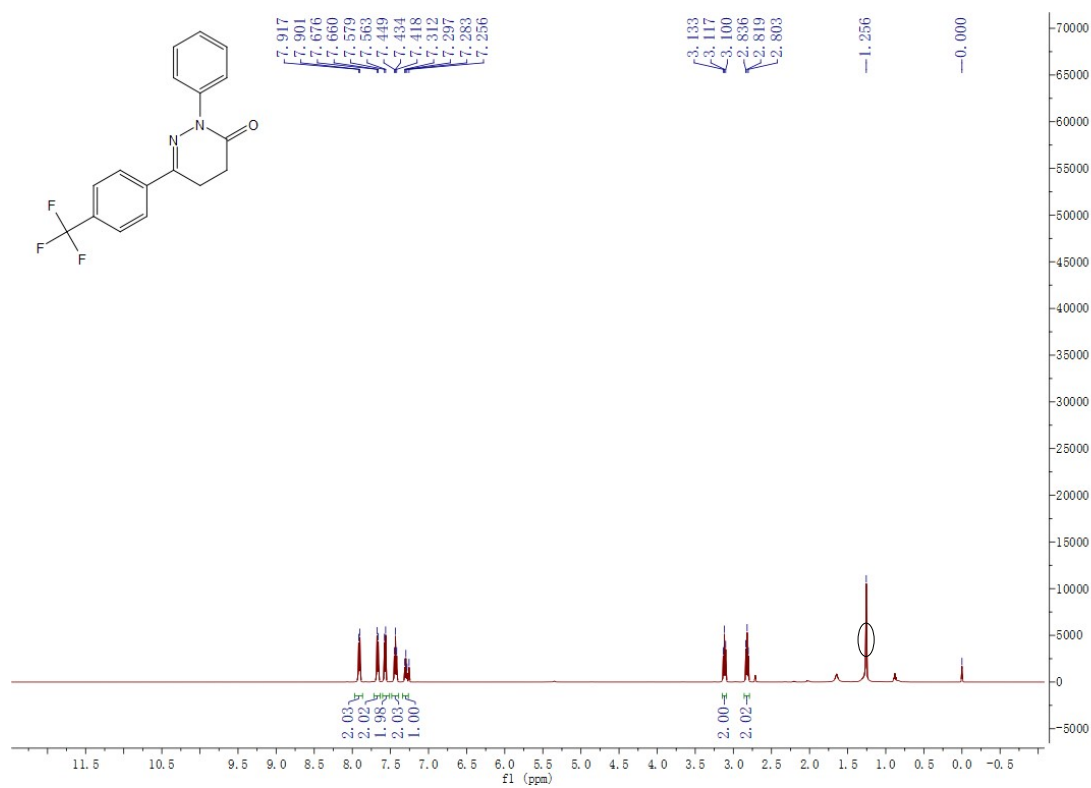


^1H NMR (500 MHz, CDCl_3) of compound **7k**

The peak in black oval is the signal of Apiezon grease.

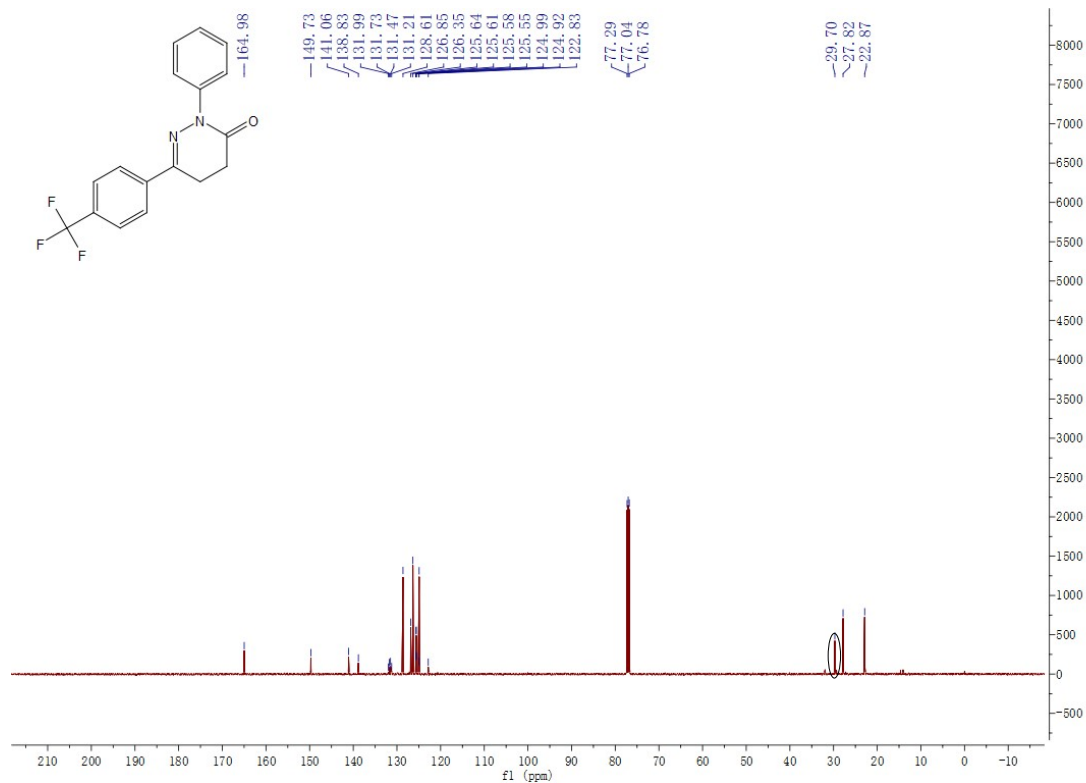


¹³C NMR (125 MHz, CDCl₃) of compound **7k**

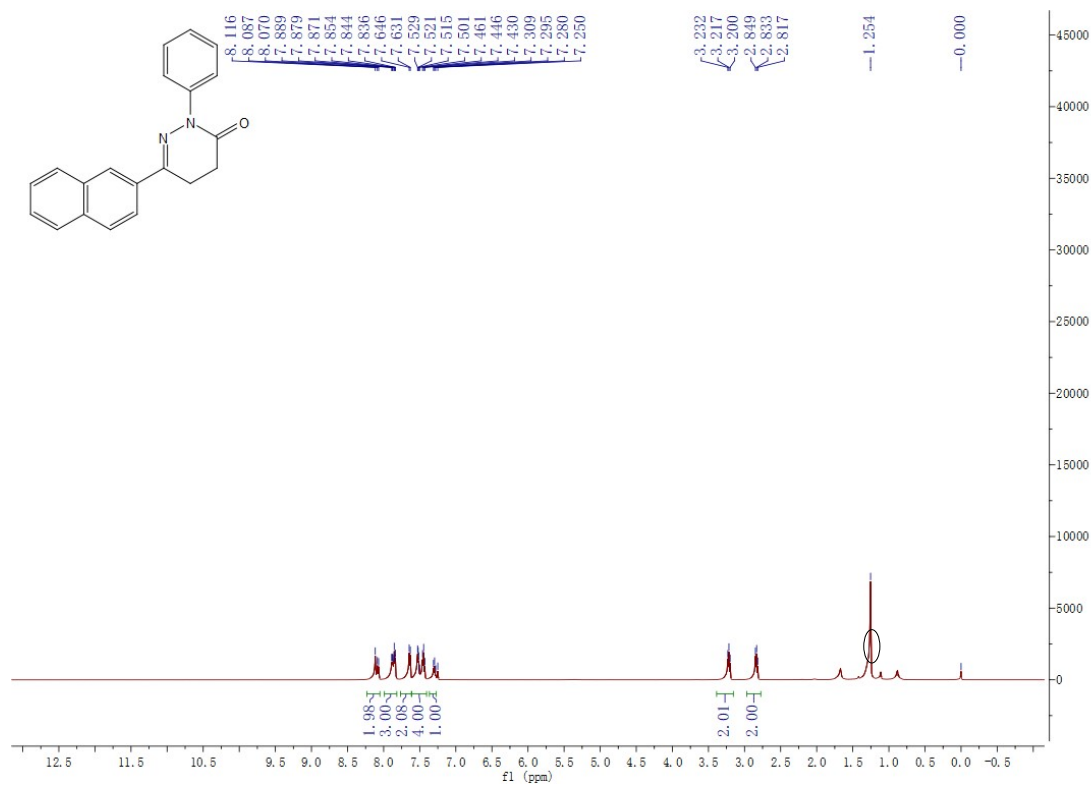


¹H NMR (500 MHz, CDCl₃) of compound **7l**

The peak in black oval is the signal of Apiezon grease.

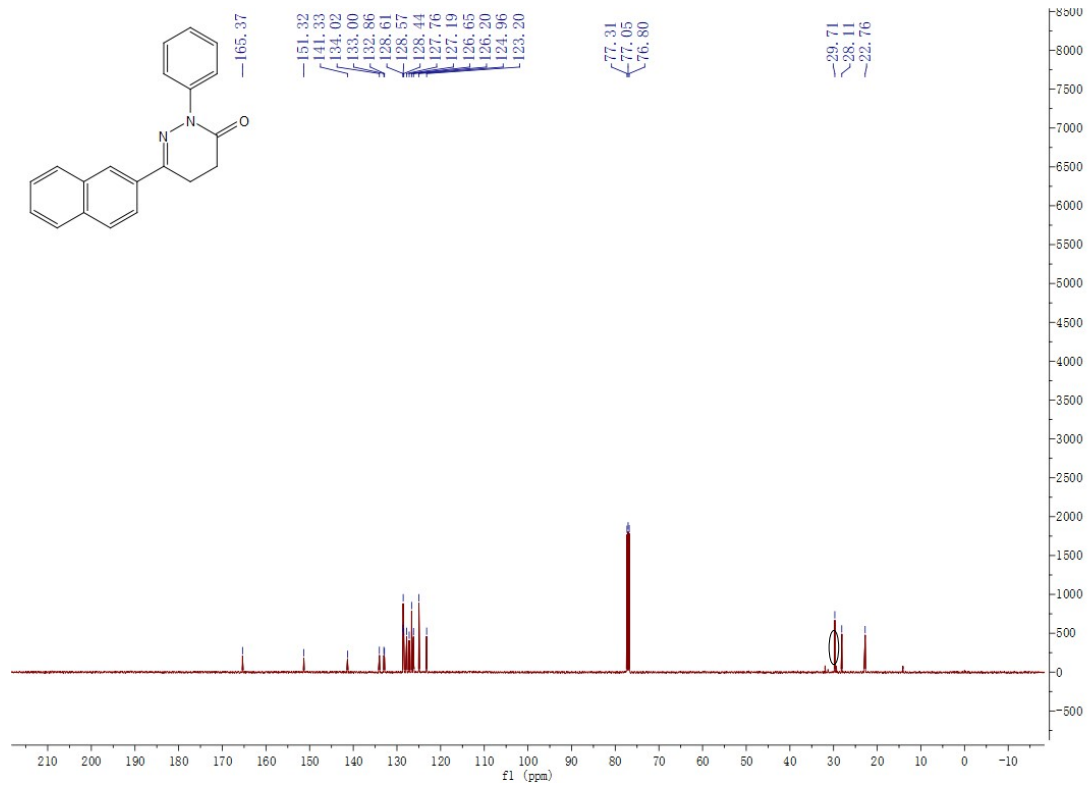


¹³C NMR (125 MHz, CDCl₃) of compound 7i

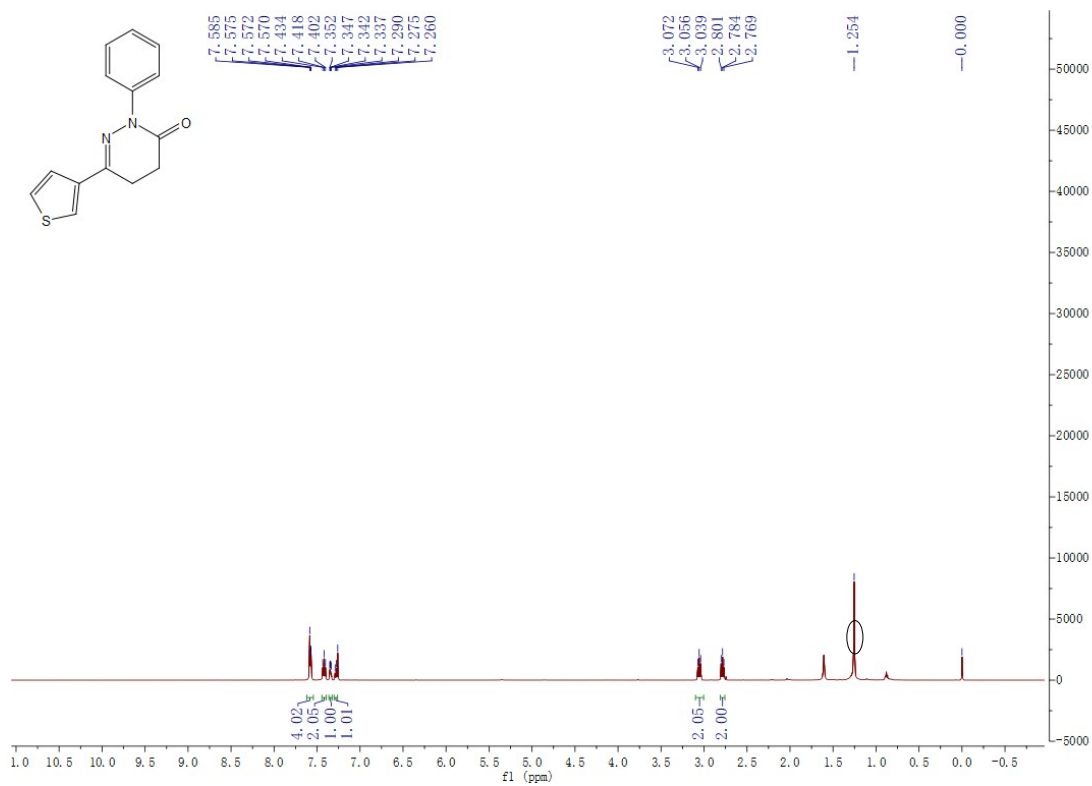


¹H NMR (500 MHz, CDCl₃) of compound 7m

The peak in black oval is the signal of Apiezon grease.

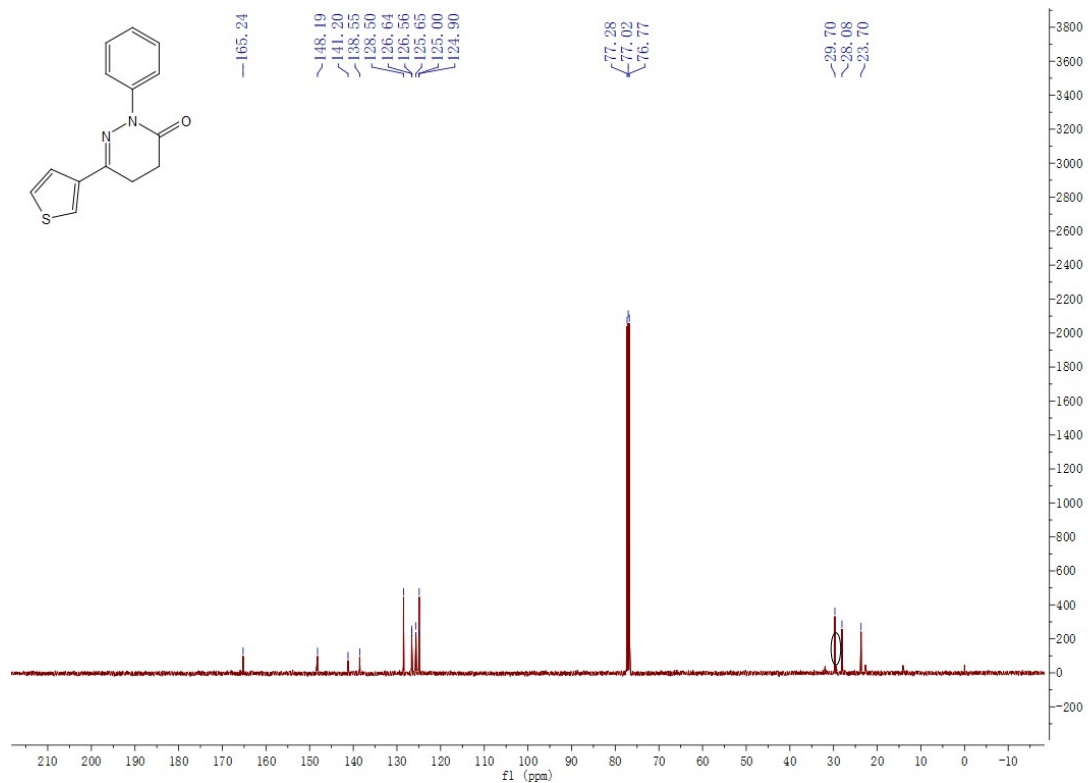


^{13}C NMR (125 MHz, CDCl_3) of compound **7m**

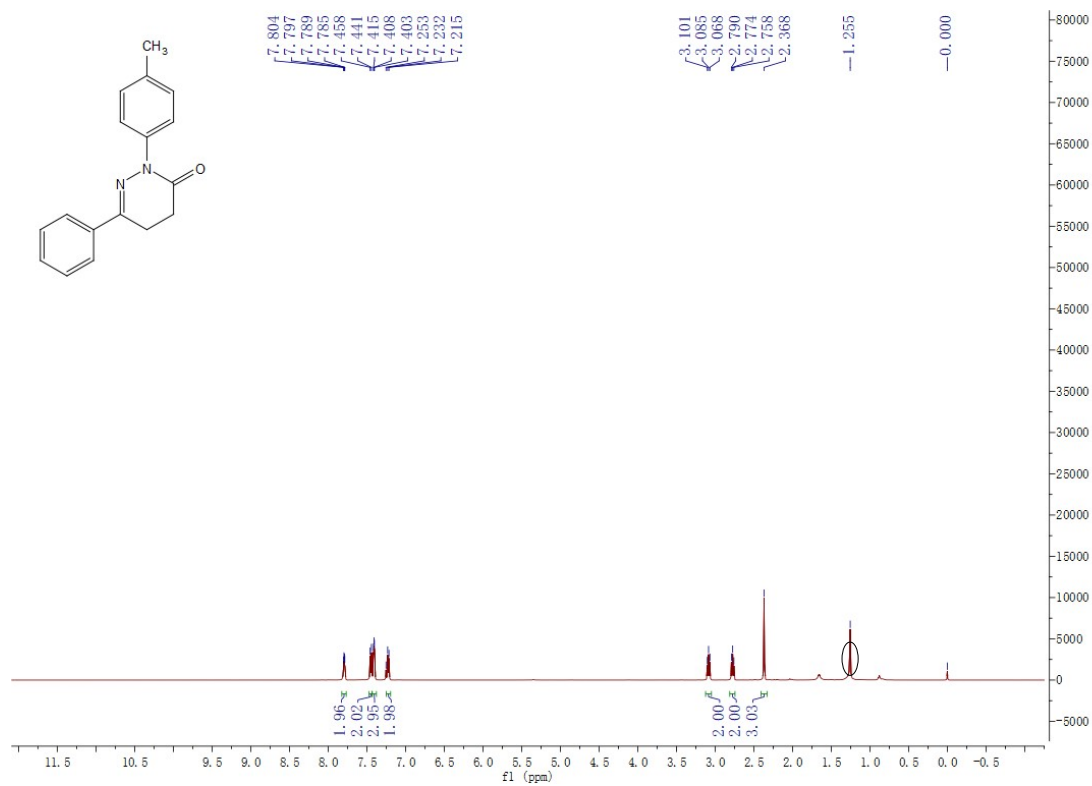


^1H NMR (500 MHz, CDCl_3) of compound **7n**

The peak in black oval is the signal of Apiezon grease.

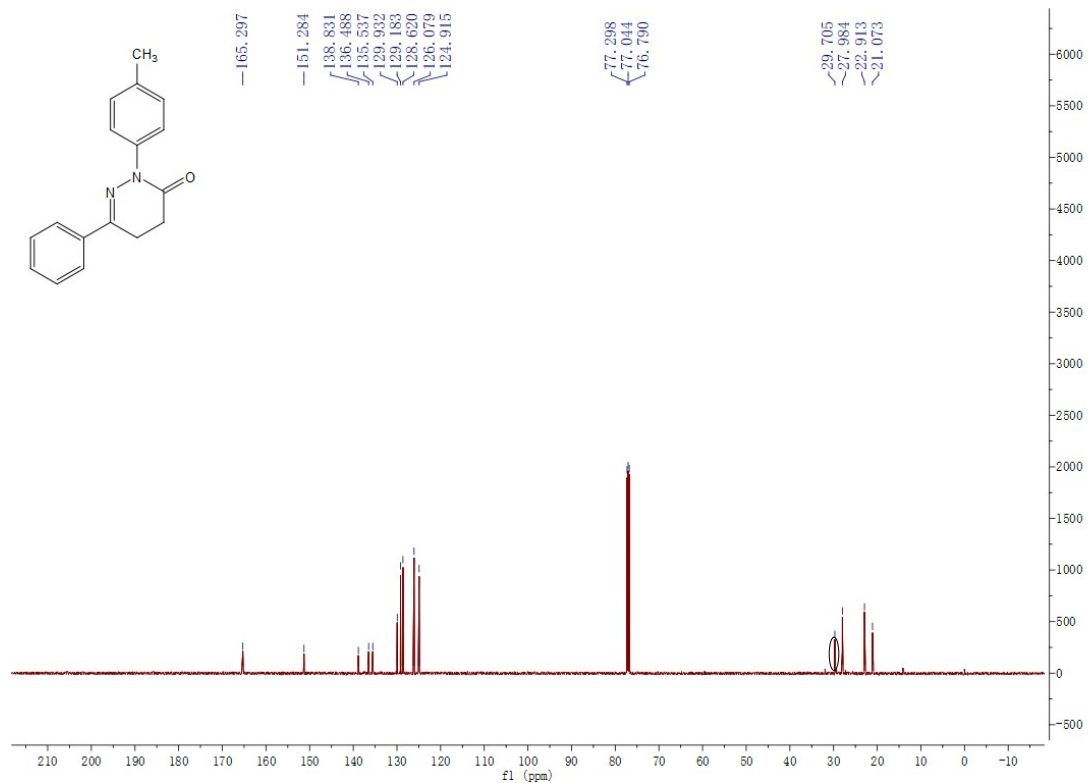


^{13}C NMR (125 MHz, CDCl_3) of compound **7n**

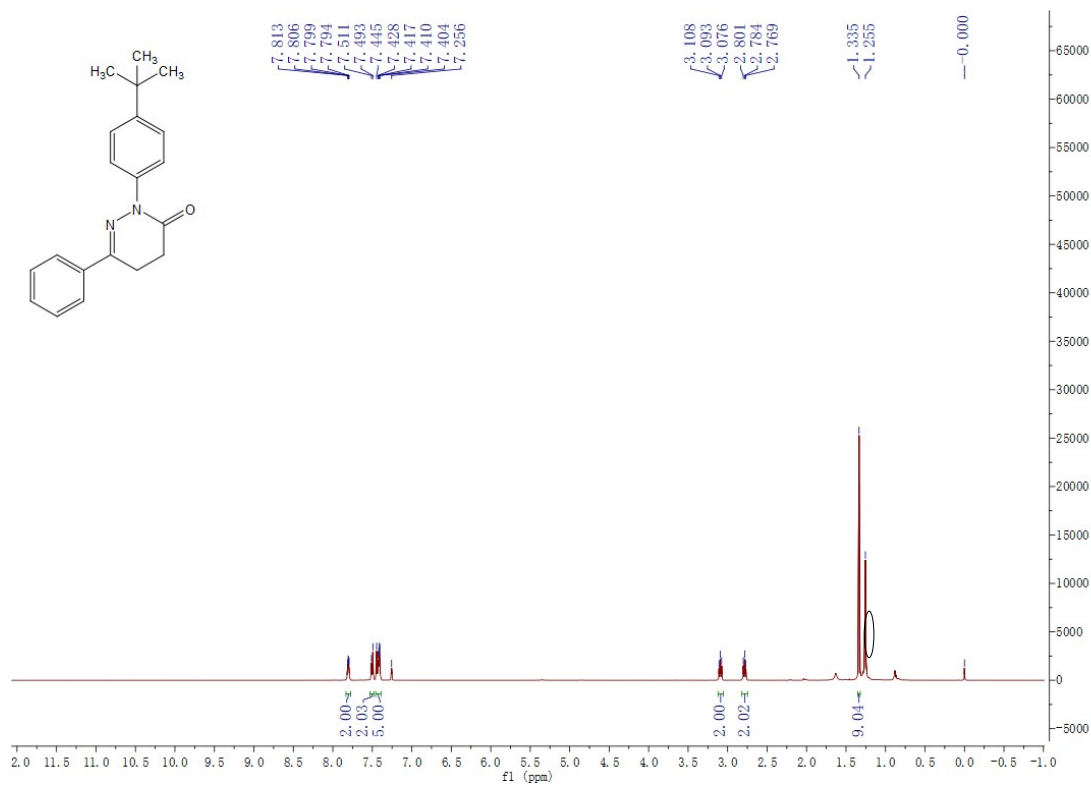


^1H NMR (500 MHz, CDCl_3) of compound **7o**

The peak in black oval is the signal of Apiezon grease.

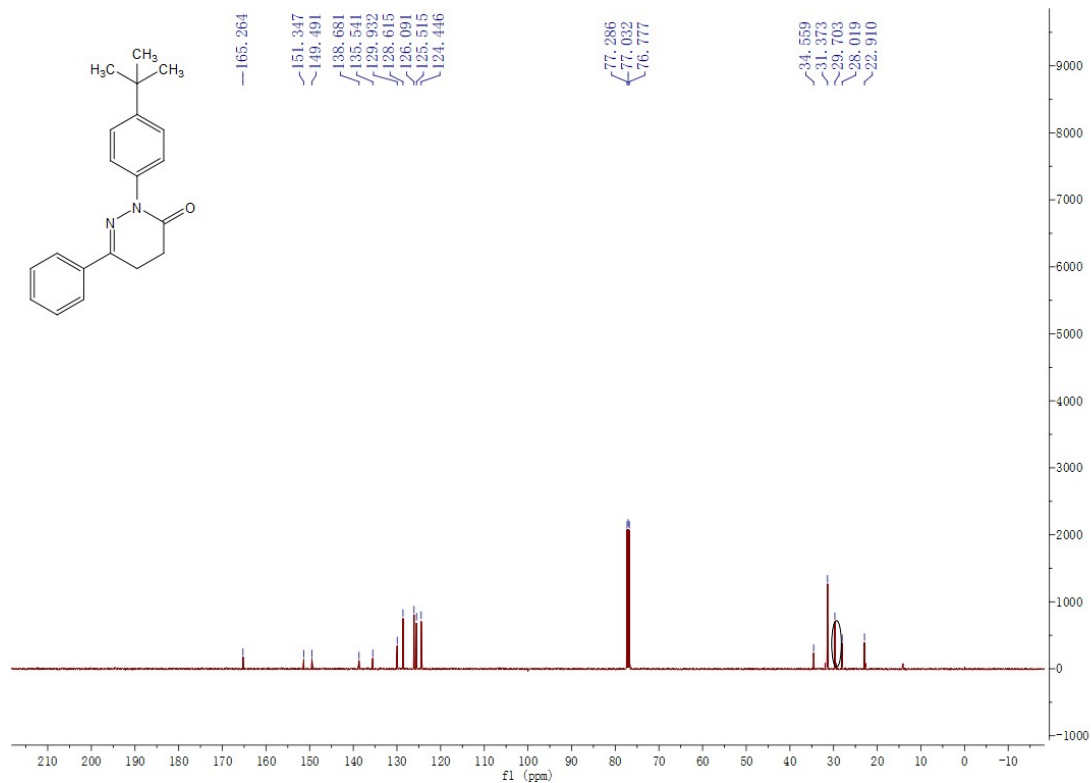


^{13}C NMR (125 MHz, CDCl_3) of compound **7o**

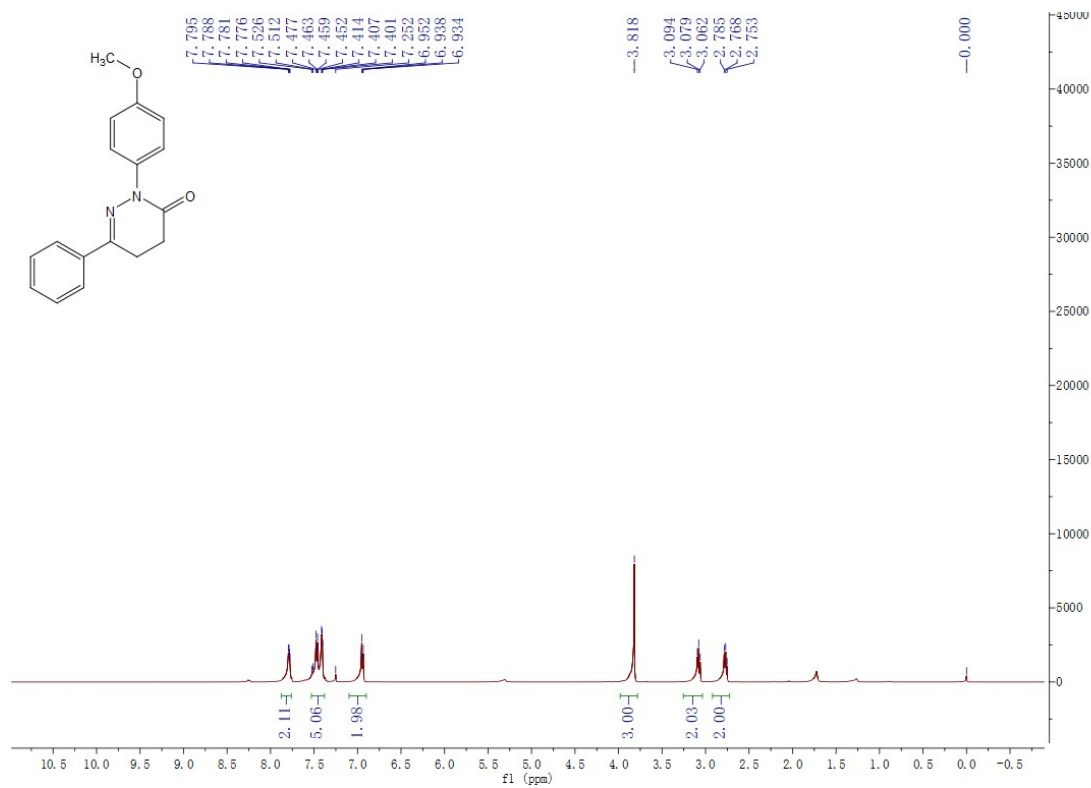


^1H NMR (500 MHz, CDCl_3) of compound **7p**

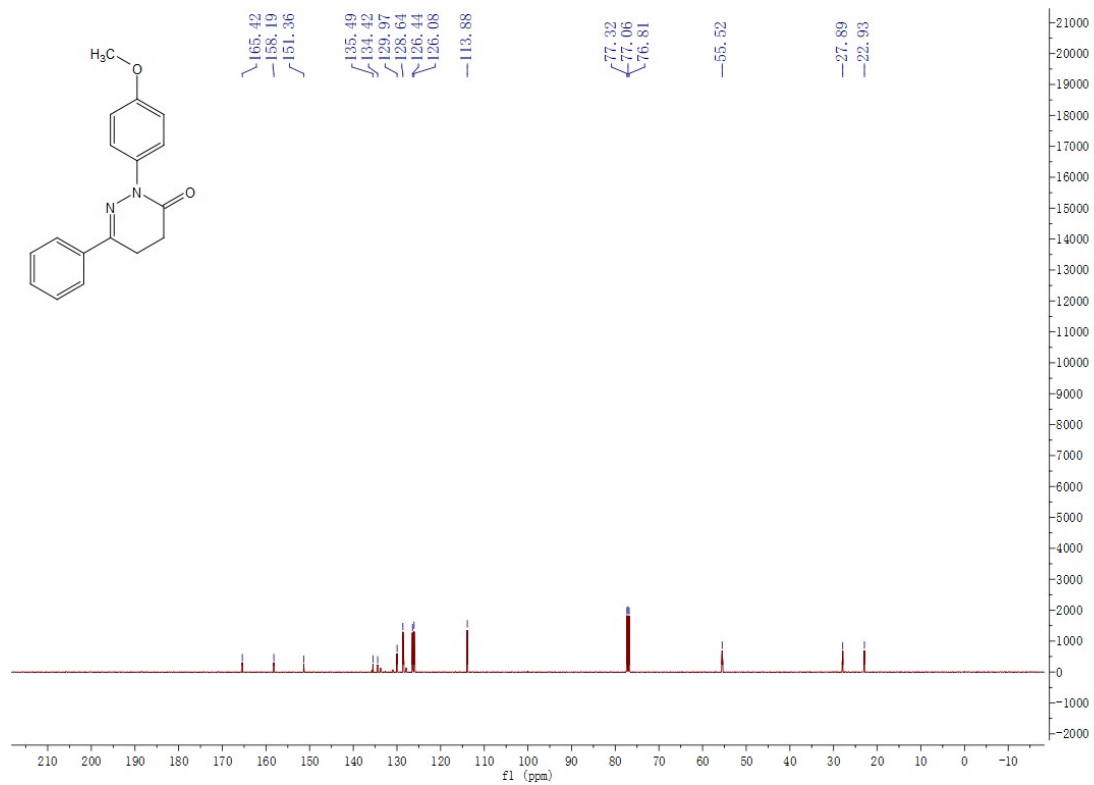
The peak in black oval is the signal of Apiezon grease.



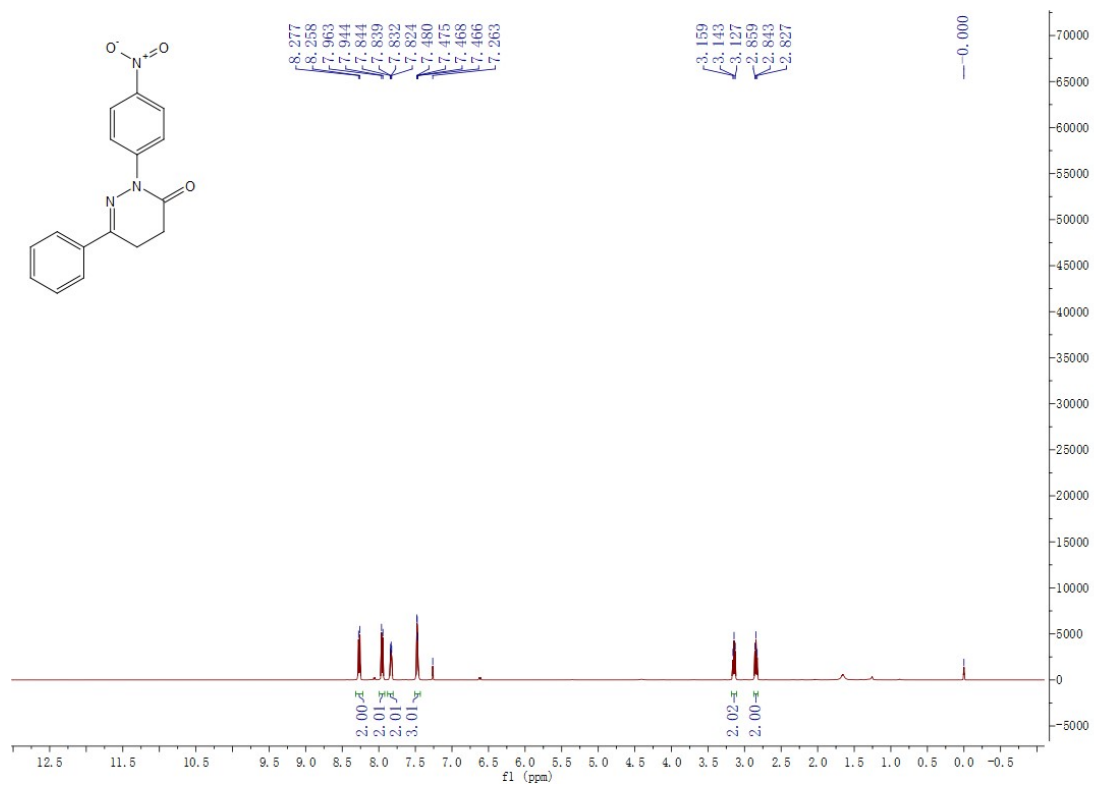
¹³C NMR (125 MHz, CDCl₃) of compound **7p**



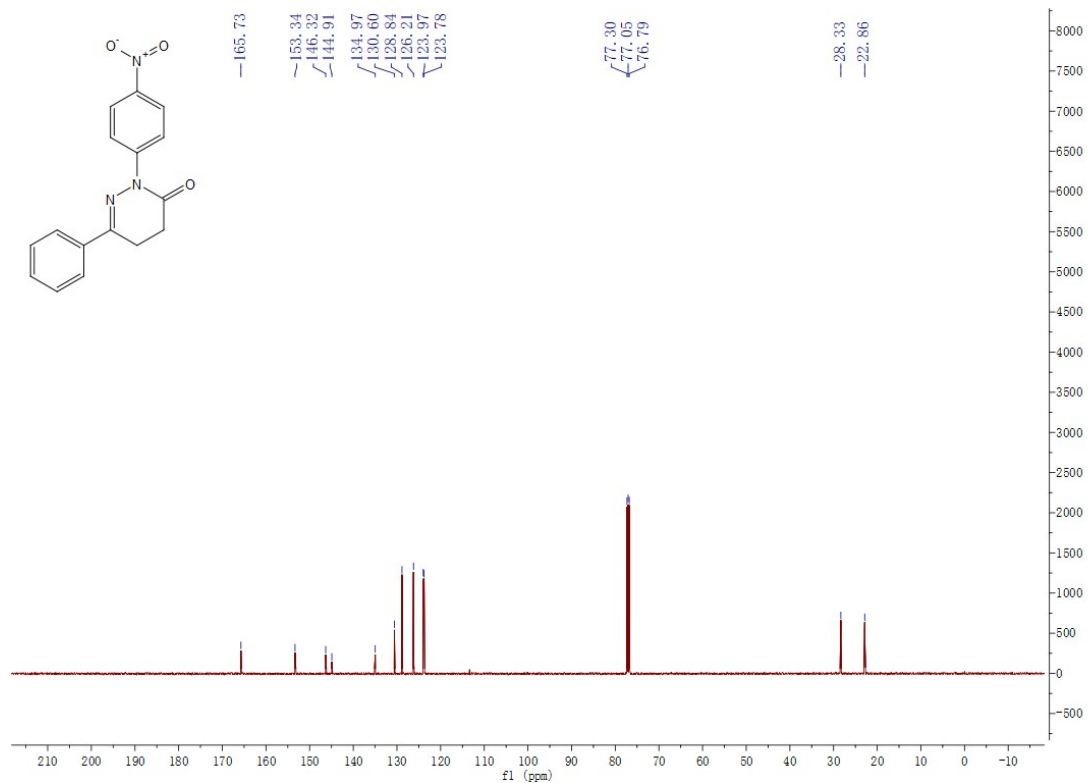
¹H NMR (500 MHz, CDCl₃) of compound **7q**



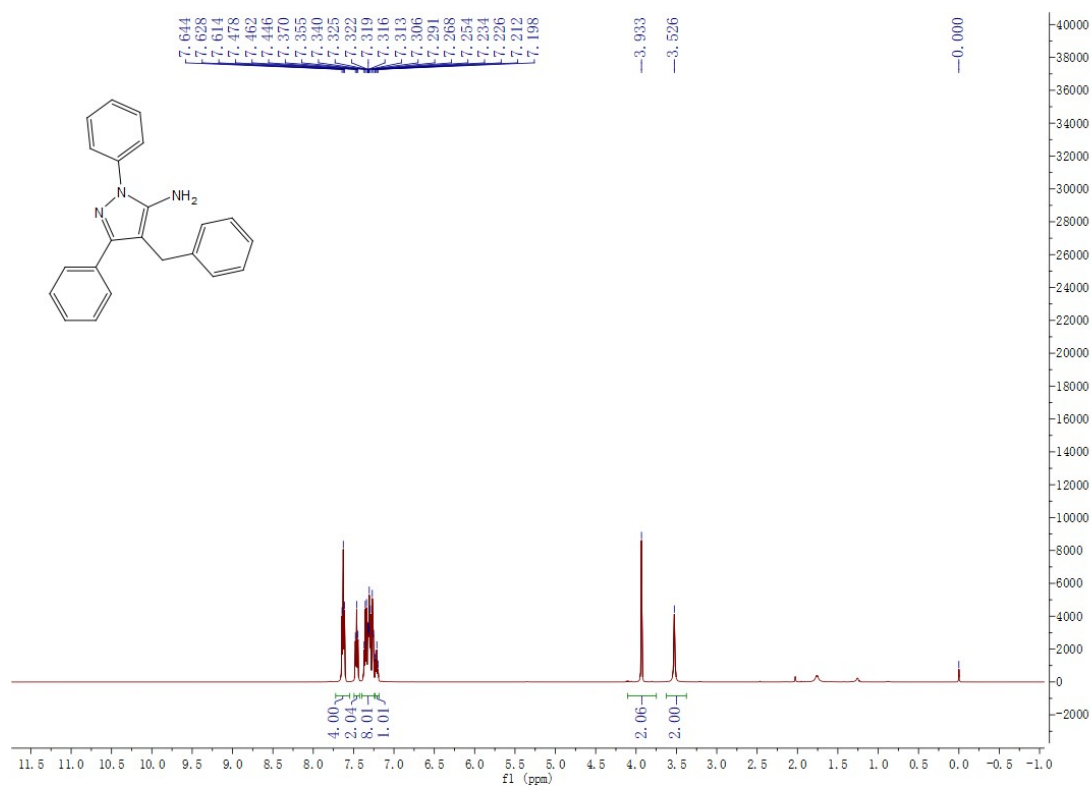
¹³C NMR (125 MHz, CDCl₃) of compound **7q**



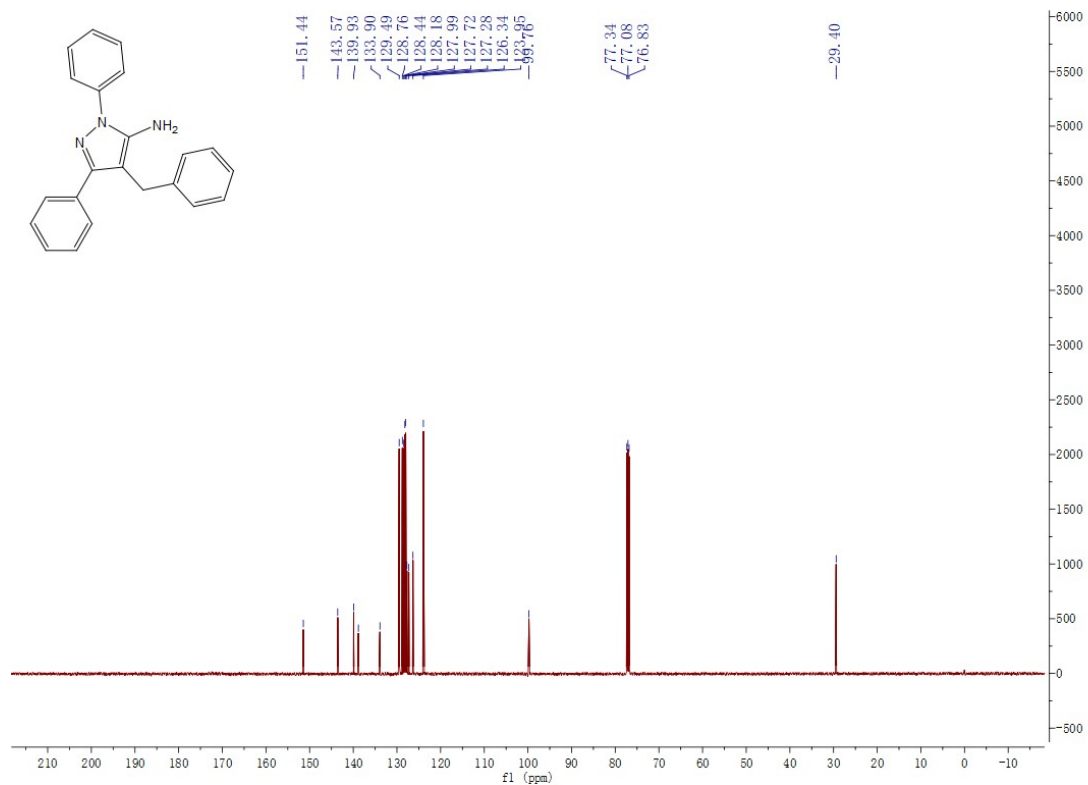
¹H NMR (500 MHz, CDCl₃) of compound **7r**



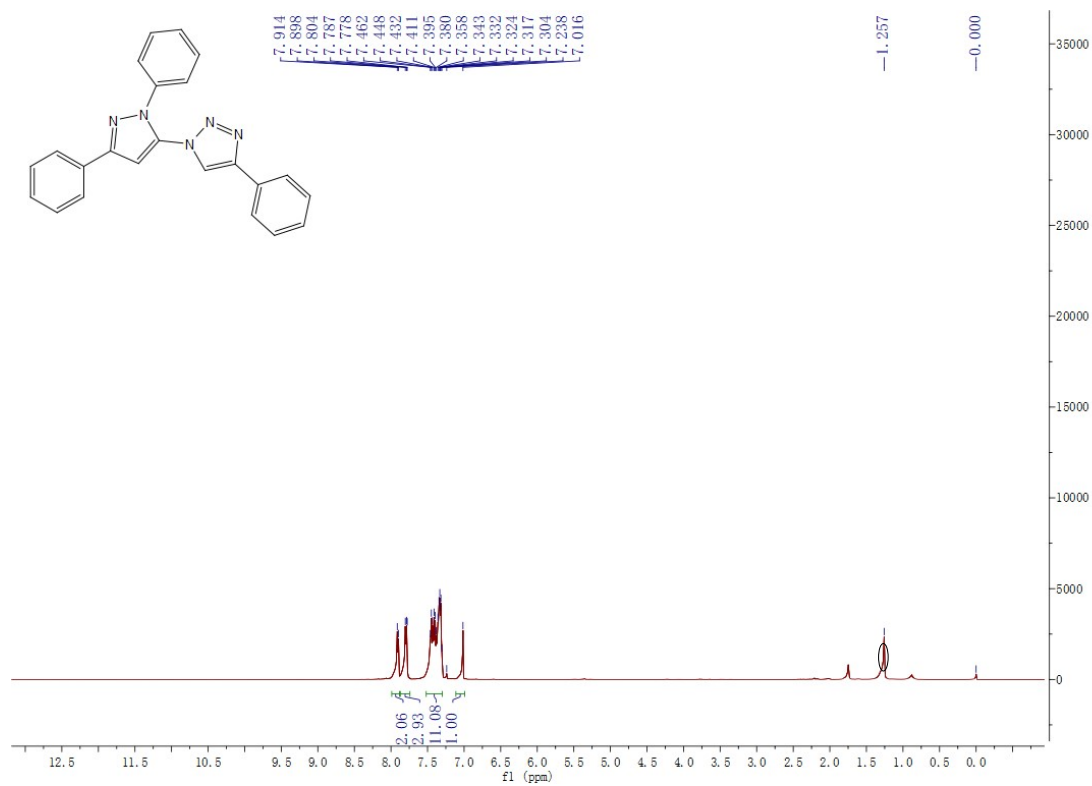
¹³C NMR (125 MHz, CDCl₃) of compound **7r**



¹H NMR (500 MHz, CDCl₃) of compound **4x**

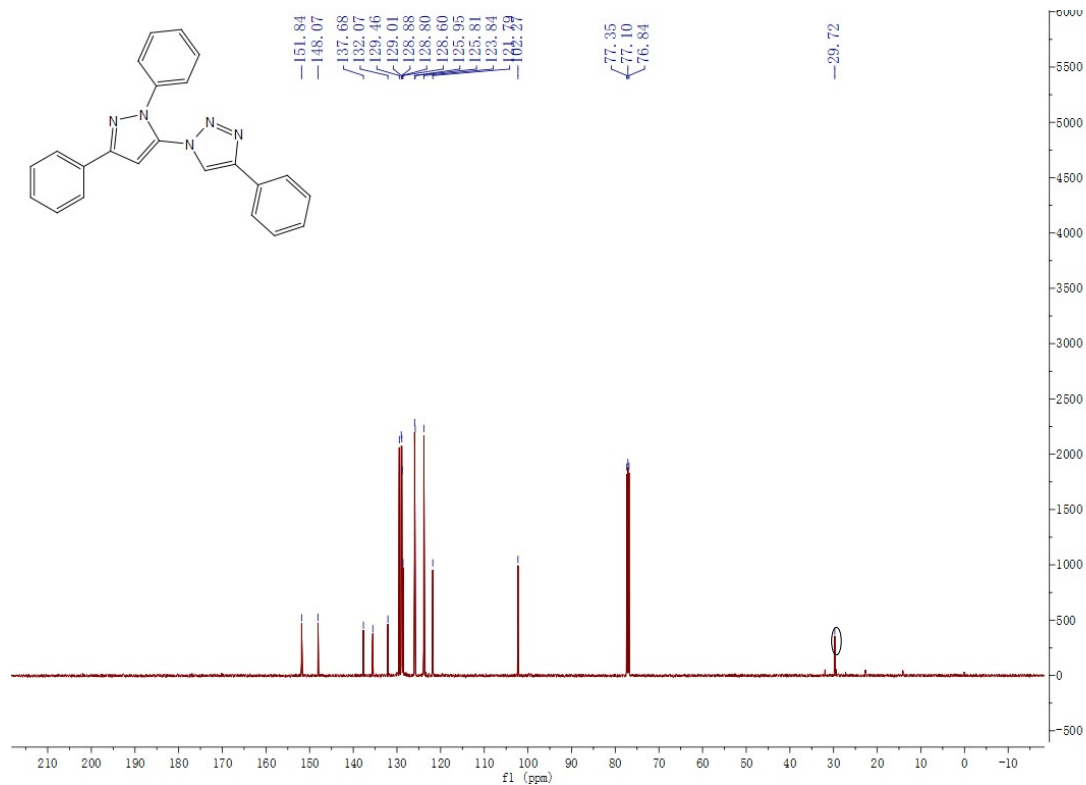


^{13}C NMR (125 MHz, CDCl_3) of compound **4x**

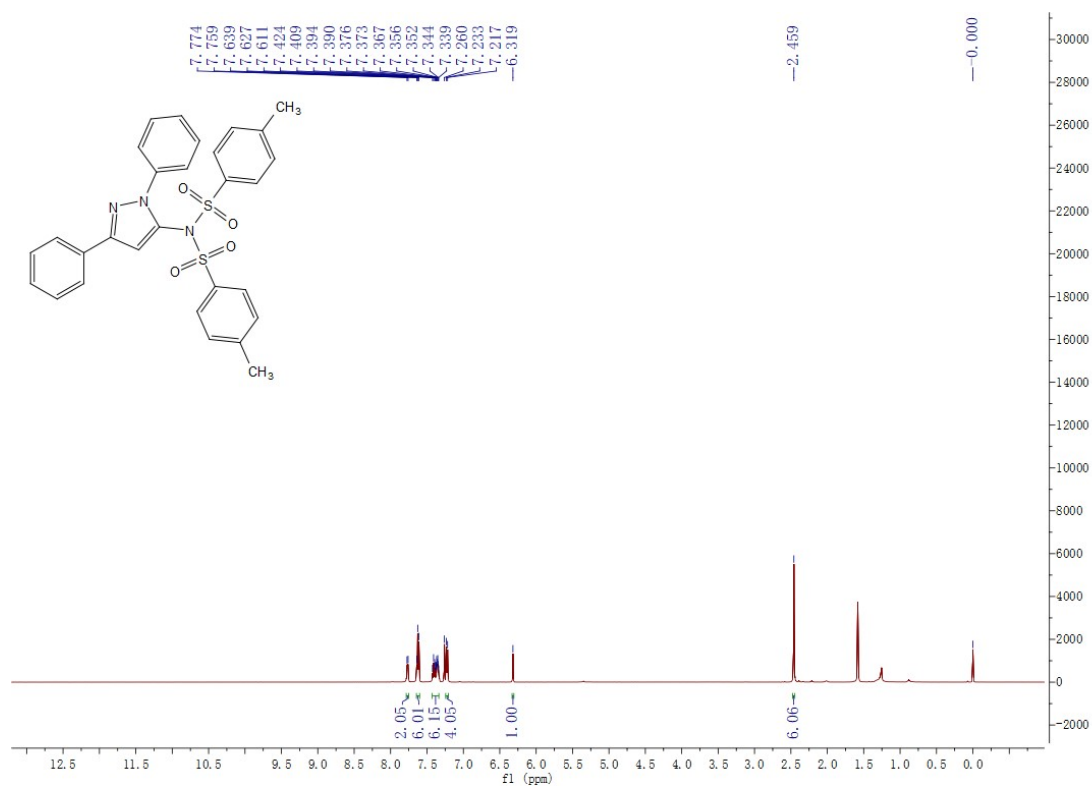


^1H NMR (500 MHz, CDCl_3) of compound **8a**

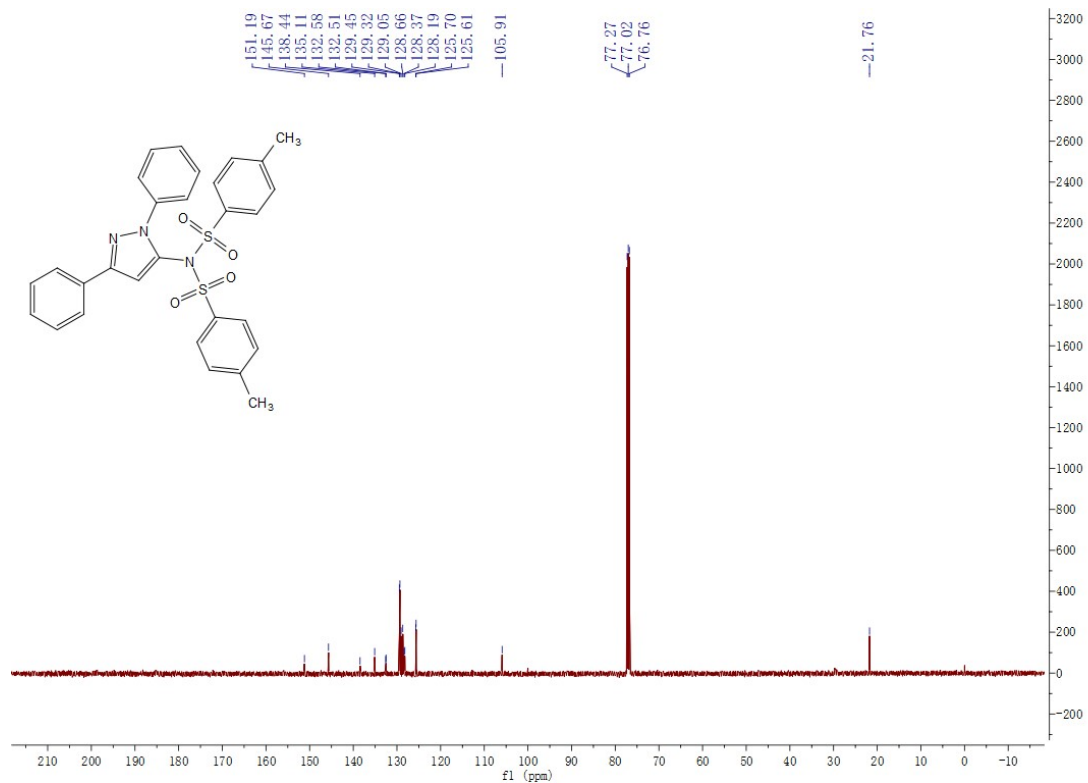
The peak in black oval is the signal of Apiezon grease.



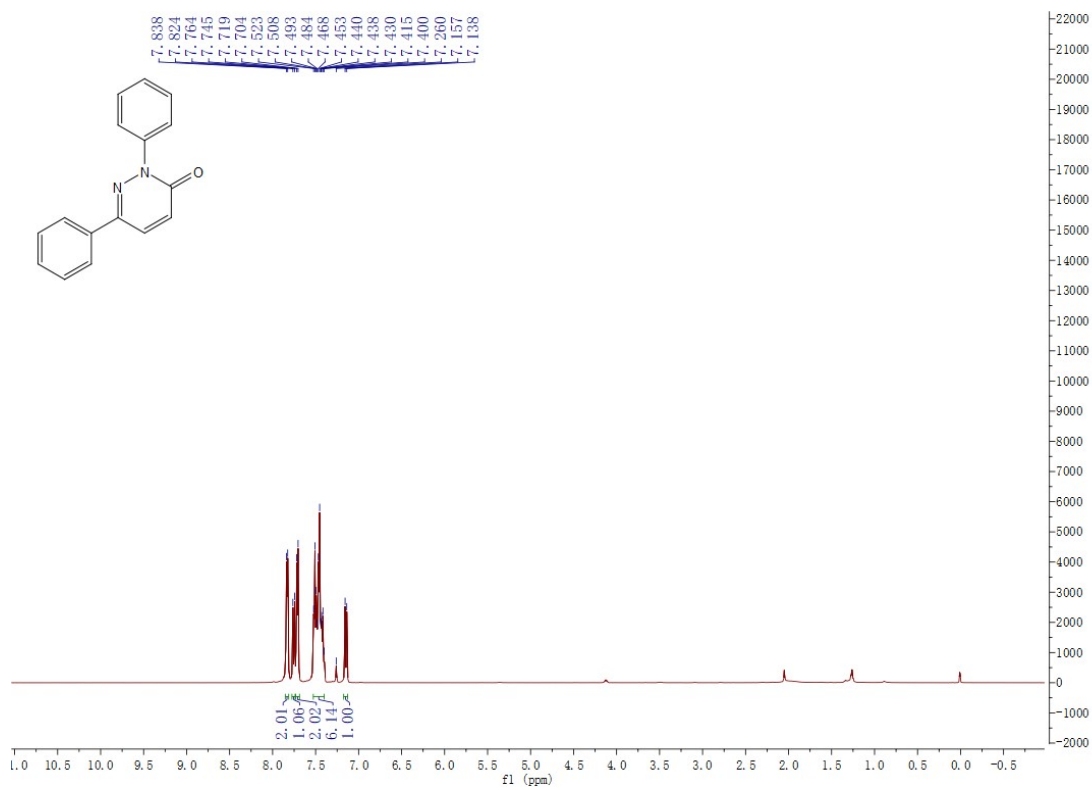
^{13}C NMR (125 MHz, CDCl_3) of compound **8a**



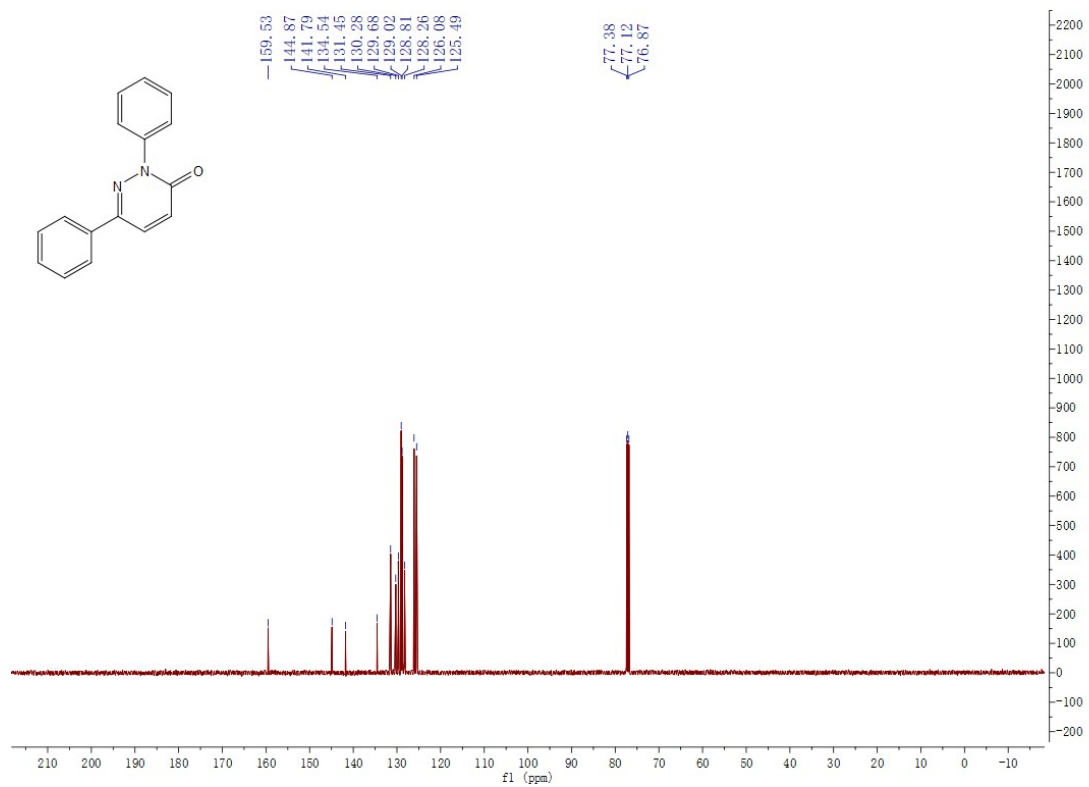
^1H NMR (500 MHz, CDCl_3) of compound **8b**



¹³C NMR (125 MHz, CDCl₃) of compound **8b**



¹H NMR (500 MHz, CDCl₃) of compound **8c**



^{13}C NMR (125 MHz, CDCl_3) of compound **8c**