Supporting Information

Electrochemical deoxygenative sulfenylation of aminopyrazoles with sodium sulfinates

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Table of Contents

General information:

All products were characterized by ^{1}H NMR and ^{13}C NMR, using TMS as an internal reference (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). HRMS (ESI) data were recorded on a Q-TOF Premier. Flash column chromatography (including Biotage Selekt) was performed using silica gel (200-300 mesh). All the compounds **1** and **2** were purchased from commercial supplies and used without purification. Electrolysis experiments were performed using a power supply (HY 3005MT), which is purchased from HYELEC. Platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) were purchased from Gaoss Union (Tianjin) as the anodic and cathodic electrodes (Distance: 6 mm). Cyclic voltammograms were obtained on a CHI760F potentiostat.

Experimental section

Representative procedures for the synthesis of 3 (Synthesis of 3aa as an example):

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), sodium *p*-methylbenzene sulfinate **2a** (0.9 mmol, 160.4 mg, 3.0 equiv), *n*-Bu_4NI (0.3 mmol, 110.8 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (5 mA) at 80 °C using a heating mantle. After the reaction was completed (about 6.6 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (73.1 mg, 83%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Photographic depiction of the electrolysis setup

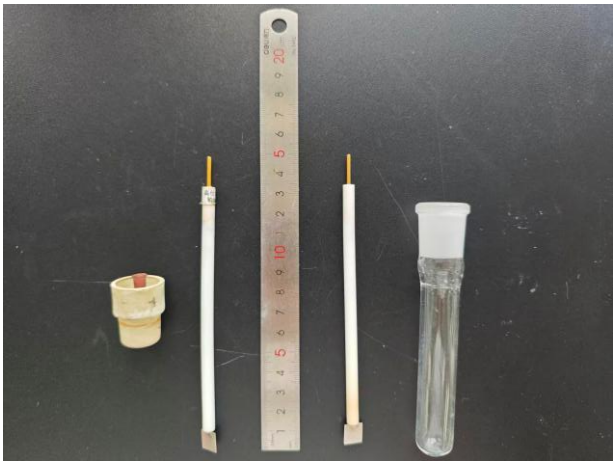


Figure S1 Electrodes (Platinum plates were purchased from Gaoss Union; Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm;) and electrolysis cell

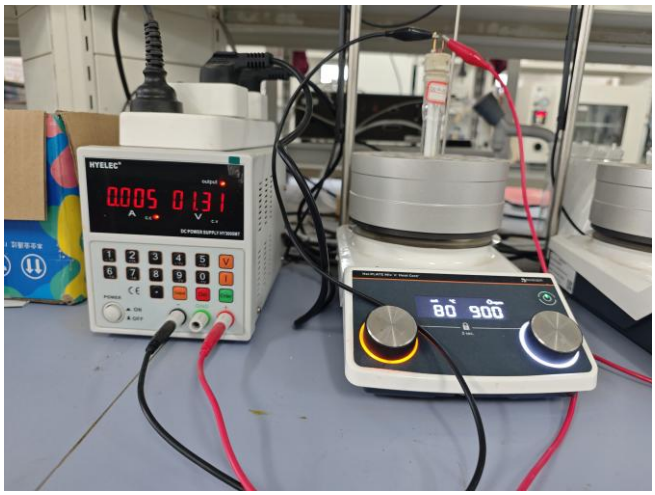
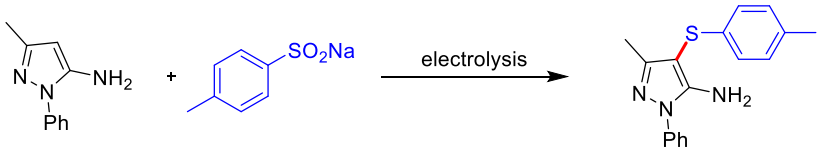


Figure S2 Electrolysis set-up (HY 3005MT)

Table S1 The optimization of reaction conditions[a]

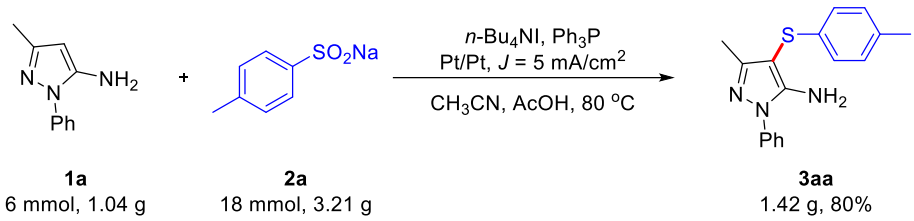


1a **2a** **3aa**

entry	electrolyte	solvent	T (°C)	Additive	I (mA)	yield[b] (%)
1	$^{n}Bu_4NI$	CH_3CN	80	AcOH	7	66
2	KI	CH_3CN	80	AcOH	7	56
3	Et_4NI	CH_3CN	80	AcOH	7	42
4	$^{n}Bu_4NBF_4$	CH_3CN	80	AcOH	7	n.d.
5	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	83
6	$^{n}Bu_4NI$	CH_3CN	80	AcOH	3	64
7	$^{n}Bu_4NI$	CH_3CN	80	AcOH	10	58
8	$^{n}Bu_4NI$	CH_3CN	70	AcOH	5	55
9	$^{n}Bu_4NI$	CH_3CN	30	AcOH	5	33
10	$^{n}Bu_4NI$	CH_3CN	85	AcOH	5	68
11	$^{n}Bu_4NI$	DMSO	80	AcOH	5	56
12	$^{n}Bu_4NI$	DMA	80	AcOH	5	37
13	$^{n}Bu_4NI$	CH_3CN	80	HCl	5	75
14	$^{n}Bu_4NI$	CH_3CN	80	TFA	5	76
15	$^{n}Bu_4NI$	CH_3CN	80	/	5	trace
16[c]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	71
17[d]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	50
18[e]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	61
19[f]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	45
20[g]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	66
21[h]	$^{n}Bu_4NI$	CH_3CN	80	AcOH	5	59
22	$^{n}Bu_4NI$	CH_3CN	80	AcOH	0	16

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $^{n}Bu_4NI$ (0.3 mmol), Ph_3P (0.6 mmol), AcOH (0.3 mmol), CH_3CN (3.0 mL), Pt/Pt (1.0 x 1.0 cm^2); the electrolysis was conducted at a constant current of 5 mA for 6.6 h (4.1 F/mol) in an undivided cell at 80 °C. [b]Yields of the isolated products. [c]Pt/C. [d]C/Pt. [e]C/C. [f]In the absence of Ph_3P. [g] $^{n}Bu_4NI$ (50 mol%). [g] $^{n}Bu_4NI$ (20 mol%).

A gram scale reaction for the synthesis of 3aa:



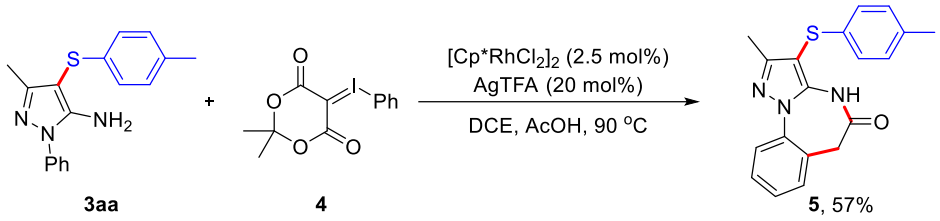
1a
6 mmol, 1.04 g

2a
18 mmol, 3.21 g

3aa
1.42 g, 80%

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (6 mmol, 1.04 g, 1.0 equiv), sodium *p*-methylbenzene sulfinate **2a** (18 mmol, 3.21 g, 3.0 equiv), *n*-Bu_4NI (6 mmol, 2.22 g, 1.0 equiv), Ph_3P (12 mmol, 3.15 g, 2.0 equiv), AcOH (18 mmol, 1.03 mL, 3.0 equiv), CH_3CN (60.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 15 mm; Width: 15 mm; Thickness: 0.3 mm; Immergence depth 20 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (11 mA) at 80 °C using a heating mantle. After the reaction was completed (about 60 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (1.42 g, 80%).

Synthetic utility of 3aa

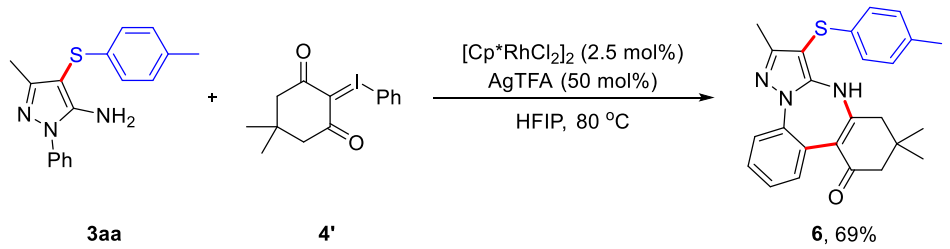


3aa

4

5, 57%

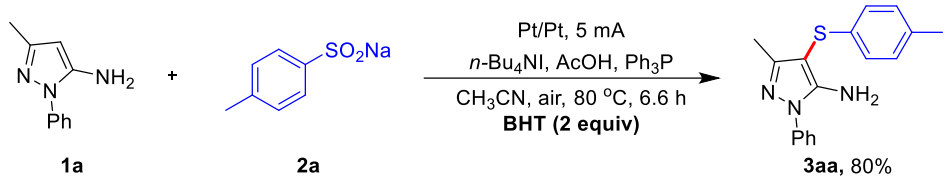
3-Methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-amine **3aa** (0.3 mmol, 1.0 equiv.), iodonium ylides **4** (0.36 mmol 1.2 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgTFA (20 mol%), AcOH (1.0 equiv.) and DCE (2 mL) were charged into a 15 mL Ace Glass pressure tubes, and the mixture was stirred at 90 °C using a heating mantle for 6 h until **3aa** were completely consumed (monitored by TLC). The mixture was cooled to room temperature, the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **5** (57.2 mg, 57%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.



3-Methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-amine **3aa** (0.3 mmol, 1.0 equiv.), iodonium ylides **4'** (0.36 mmol 1.2equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgTFA (50 mol%), and HFIP (1.5 mL) were charged into a 15 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C using a heating mantle for 6 h until **3aa** were completely consumed (monitored by TLC). The mixture was cooled to room temperature, the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **6** (85.4 mg, 69%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

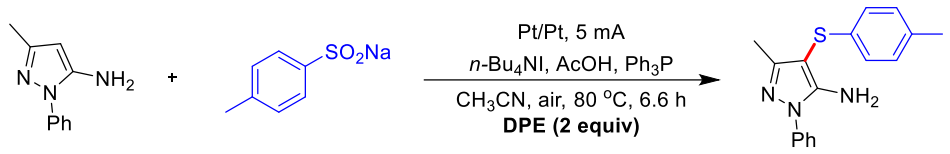
Preliminary mechanistic studies:

The addition of BHT in the model reaction system:



A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), sodium *p*-methylbenzene sulfinate **2a** (0.9 mmol, 160.4 mg, 3.0 equiv), *n*-Bu_4NI (0.3 mmol, 110.8 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), 2,6-*di*-tert-butyl-4-methylphenol (BHT, 0.60 mmol, 132.2 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (5 mA) at 80 °C using a heating mantle. After the reaction was completed (about 6.6 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (70.5 mg, 80%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

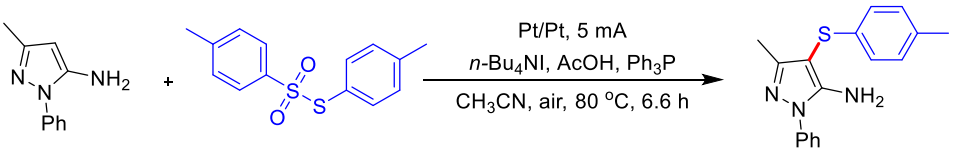
The addition of DPE in the model reaction system:



1a **2a** **3aa**, 77%

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), sodium *p*-methylbenzene sulfinate **2a** (0.9 mmol, 160.4 mg, 3.0 equiv), *n*-Bu_4NI (0.3 mmol, 110.8 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), 1,1-diphenylethylene (DPE, 0.60 mmol, 108.2 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (5 mA) at 80 °C using a heating mantle. After the reaction was completed (about 6.6 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (68.1 mg, 77%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

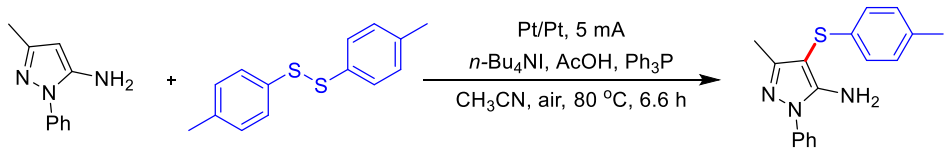
S-(p-tolyl) 4-methylbenzenesulfonothioate (2A) as an intermediate:



1a **2A** **3aa**, 85%

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), S-(p-tolyl) 4-methylbenzenesulfonothioate **2A** (0.45 mmol, 125.3 mg, 1.5 equiv), *n*-Bu_4NI (0.3 mmol, 110.8 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (5 mA) at 80 °C using a heating mantle. After the reaction was completed (about 6.6 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (74.9 mg, 85%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

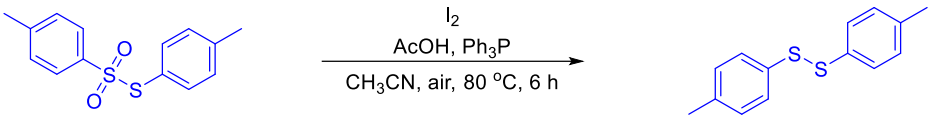
1,2-di-p-tolyldisulfane (2A') as an intermediate:



1a **2A'** **3aa**, 57%

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), 1,2-di-p-tolyldisulfane **2A'** (0.45 mmol, 110.9 mg, 1.5 equiv), *n*-Bu_4NI (0.3 mmol, 110.8 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Then, the electrolytic cell was equipped with a magnet stirrer, two platinum plates (Length: 10 mm; Width: 10 mm; Thickness: 0.3 mm; Immergence depth 15 mm) electrodes as the working electrode and counter electrode (Distance: 6 mm). Subsequently, the mixture was allowed to stir and electrolyze at a constant current condition (5 mA) at 80 °C using a heating mantle. After the reaction was completed (about 6.6 h, 4.1 F/mol), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (50.8 mg, 57%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

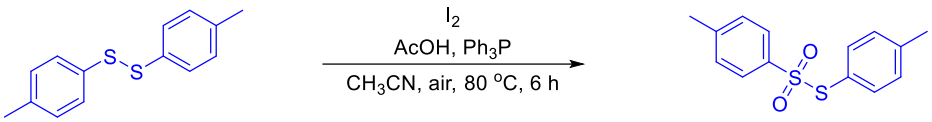
S-(p-tolyl) 4-methylbenzenesulfonothioate (2A) as a starting material:



2A **2A'**, 42%

A mixture of S-(p-tolyl) 4-methylbenzenesulfonothioate **2A** (0.45 mmol, 125.3 mg, 1.0 equiv), I_2 (0.45 mmol, 114.2 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 1.3 equiv), AcOH (0.9 mmol, 52 µL, 2.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Subsequently, the mixture was allowed to stir at 80 °C using a heating mantle without electrolysis for 6 h. The solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **2A'** (46.6 mg, 42%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

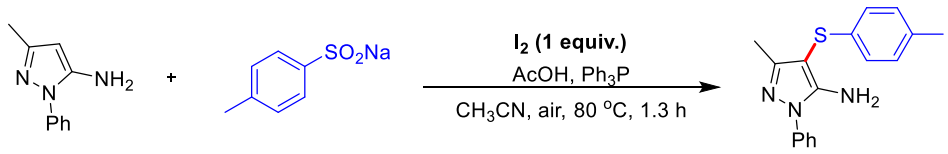
1,2-di-p-tolyldisulfane (2A') as a starting material:



2A' **2A**, n.d.

A mixture of 1,2-di-p-tolyldisulfane **2A'** (0.45 mmol, 110.9 mg, 1.0 equiv), I_2 (0.45 mmol, 114.2 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 1.3 equiv), AcOH (0.9 mmol, 52 µL, 2.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Subsequently, the mixture was allowed to stir at 80 °C using a heating mantle without electrolysis for 6 h, and no corresponding S-(p-tolyl) 4-methylbenzenesulfonothioate **2A** was detected.

I_2 as an oxidant:



1a **2a** **3aa**, 96%

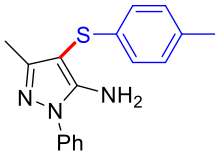
A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-amine **1a** (0.3 mmol, 52.0 mg, 1.0 equiv), sodium *p*-methylbenzene sulfinate **2a** (0.9 mmol, 160.4 mg, 3.0 equiv), I_2 (0.30 mmol, 76.1 mg, 1.0 equiv), Ph_3P (0.6 mmol, 157.4 mg, 2.0 equiv), AcOH (0.9 mmol, 52 µL, 3.0 equiv), CH_3CN (3.0 mL) were added in sequence in an undivided cell. Subsequently, the mixture was allowed to stir at 80 °C using a heating mantle without electrolysis for 80 min. The solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (85.1 mg, 96%).

Cyclic voltammetric (CV) studies:

CV plotting convention is IUPAC. The cyclic voltammetry was carried out with a CHI760F workstation. All cyclic voltammograms were measured at room temperature under air using a platinum disk electrode (3 mm-diameter) as the working electrode, a Pt wire as counter electrode, and a Ag/AgCl submerged in saturated aqueous KCl solution as the reference electrode. The platinum disk electrode was polished on an aluminum oxide powder (0.3 µm). All solutions were used without prior deoxygenation, and the experiment was conducted in CH_3CN at room temperature. The conditions of the experiments were as follows: (a) background (0.1 M *n*-Bu_4NPF_6 in CH_3CN), (b) *n*-Bu_4NI (5 mM) and *n*-Bu_4NPF_6 (0.1 M) in CH_3CN, (c) Ph_3P (5 mM) and *n*-Bu_4NPF_6 (0.1 M) in CH_3CN, (d) **1a** (5 mM) and *n*-Bu_4NPF_6 (0.1 M) in CH_3CN, (e) **2a** (5 mM) and *n*-Bu_4NPF_6 (0.1 M) in CH_3CN. The scan rate is 50 mV/s from 0 V to 2.0 V (starting from 0 V).

Detail descriptions for products

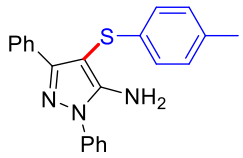
*3-Methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3aa**)*[1]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a brown oil in 83% yield (73.1 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.61 – 7.56 (m, 2H), 7.50 – 7.46 (m, 2H), 7.37 – 7.32 (m, 1H), 7.08 – 6.99

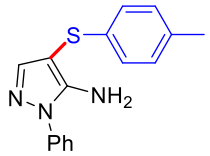
(m, 4H), 4.23 (s, 2H), 2.29 (s, 3H), 2.24 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.2, 148.5, 138.7, 134.9, 134.6, 129.8, 129.7, 127.5, 125.4, 123.4, 88.4, 21.0, 12.4.

*1,3-Diphenyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ba**)*[1]



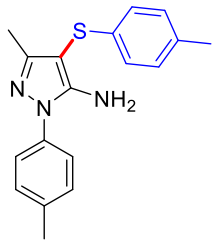
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 92% yield (99.0 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm)δ = 8.02 – 7.98 (m, 2H), 7.72 – 7.68 (m, 2H), 7.53 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.10 (d, *J* = 1.5 Hz, 4H), 4.34 (s, 2H), 2.31 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.4, 149.6, 138.6, 135.0, 134.6, 132.7, 129.9, 129.7, 128.4, 128.3, 127.8, 127.6, 125.4, 123.6, 86.8, 21.0.

*1-Phenyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ca**)*[1]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 54% yield (46.0 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.60 (d, *J* = 8.3 Hz, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.06 (s, 4H), 4.26 (s, 2H), 2.29 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 148.1, 145.3, 138.7, 135.2, 134.7, 129.8, 129.7, 127.8, 125.8, 123.5, 89.2, 21.0.

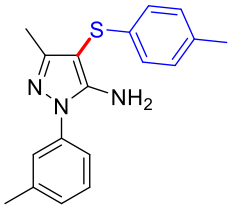
*3-Methyl-1-(p-tolyl)-4-(p-tolylthio)-1H-pyrazol-5-amine (**3da**)*[1]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 69% yield (63.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.44 – 7.41 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 7.00 –

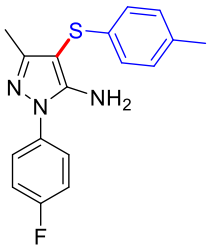
6.97 (m, 2H), 4.17 (s, 2H), 2.37 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 152.9, 148.4, 137.4, 136.1, 134.8, 134.7, 130.2, 129.8, 125.3, 123.4, 88.0, 21.2, 20.9, 12.4.

*3-Methyl-1-(m-tolyl)-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ea**)*[2]



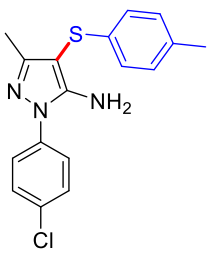
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 68% yield (63.5 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.42 (d, *J* = 2.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.18 – 7.14 (m, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.03 – 6.99 (m, 2H), 4.23 (s, 2H), 2.41 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.0, 148.4, 139.9, 138.6, 134.9, 134.7, 129.8, 129.4, 128.2, 125.3, 124.2, 120.2, 88.1, 21.5, 21.0, 12.4.

*1-(4-Fluorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3fa**)*[2]



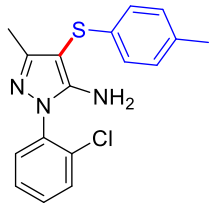
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 76% yield (71.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.57 – 7.51 (m, 2H), 7.18 – 7.12 (m, 2H), 7.08 – 6.97 (m, 4H), 4.21 (s, 2H), 2.29 (s, 3H), 2.22 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 161.5 (d, *J* = 246.0 Hz), 153.2, 148.5, 135.0, 134.8 (d, *J* = 2.0 Hz), 134.5, 129.8, 125.4, 125.4 (d, *J* = 8.0 Hz), 116.5, (d, *J* = 23.0 Hz) 88.5, 20.9, 12.3. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm) δ = -113.6.

*1-(4-Chlorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ga**)*[2]



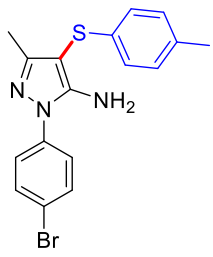
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 79% yield (77.9 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.59 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.96 (m, 2H), 4.20 (s, 2H), 2.29 (s, 3H), 2.23 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.6, 148.5, 137.3, 135.1, 134.4, 133.0, 129.9, 129.8, 125.5, 124.5, 89.1, 21.0, 12.4.

*1-(2-Chlorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ha**)*



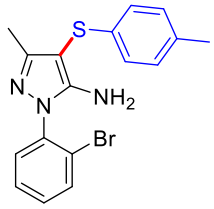
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 66% yield (65.2 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.57 – 7.48 (m, 2H), 7.43 – 7.38 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.97 (m, 2H), 4.06 (s, 2H), 2.29 (s, 3H), 2.23 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.6, 149.9, 135.7, 134.8, 134.7, 132.0, 130.7, 130.6, 130.1, 129.8, 128.2, 125.1, 87.4, 21.0, 12.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_3SCl$ 330.0835; Found: 330.0832.

*1-(4-Bromophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ia**)*[2]



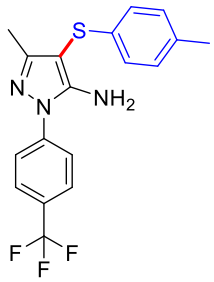
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 59% yield (65.7 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.64 – 7.55 (m, 2H), 7.53 – 7.45 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.97 (m, 2H), 4.22 (s, 2H), 2.29 (s, 3H), 2.22 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.6, 148.5, 137.8, 135.1, 134.4, 132.8, 129.9, 125.4, 124.6, 120.8, 89.2, 21.0, 12.4.

*1-(2-Bromophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3ja**)*[2]



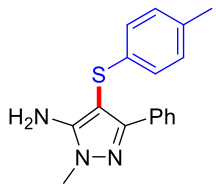
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 76% yield (85.1 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.71 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.34 (td, *J* = 7.6, 1.9 Hz, 1H), 7.03 (q, *J* = 8.4 Hz, 4H), 4.02 (s, 2H), 2.29 (s, 3H), 2.23 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.4, 149.6, 137.3, 134.7, 134.7, 133.7, 131.1, 130.3, 129.7, 128.8, 125.0, 122.1, 87.2, 20.9, 12.5.

*3-Methyl-4-(p-tolylthio)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-amine (**3ka**)*



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 85% yield (93.0 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm)δ = 7.84 – 7.75 (m, 4H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.02 (m, 2H), 4.37 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 154.0, 148.7, 141.7, 135.2, 134.1, 129.8, 128.7 (q, *J* = 32.0 Hz), 126.8 (q, *J* = 4.0 Hz), 126.4 (q, *J* = 240.0 Hz), 125.5, 122.5, 89.9, 20.9, 12.4.^{19}F NMR ($CDCl_3$, 376 MHz, ppm) δ = -62.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_3SF_3$ 364.1095; Found: 364.1098.

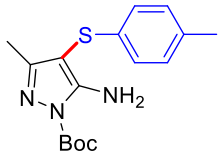
*1-Methyl-3-phenyl-4-(p-tolylthio)-1H-pyrazol-5-amine (**3la**)*[1]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 73% yield (64.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.89 – 7.84 (m, 2H), 7.36 – 7.28 (m, 3H), 7.06 – 6.99 (m, 4H), 3.72 (s, 3H),

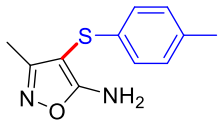
2.28 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 152.0, 149.6, 134.9, 134.8, 132.9, 129.8, 128.3, 128.1, 127.3, 125.2, 86.4, 35.2, 20.9.

*Tert-butyl 5-amino-3-methyl-4-(p-tolylthio)-1H-pyrazole-1-carboxylate (**3ma**)*[1]



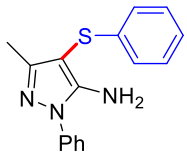
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 54% yield (51.3 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.02 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.88 (m, 2H), 5.72 (s, 2H), 2.27 (s, 3H), 2.17 (s, 3H), 1.67 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 156.5, 153.2, 150.2, 135.1, 133.6, 129.8, 127.9, 125.3, 87.2, 85.9, 28.1, 20.9, 12.8.

*3-Methyl-4-(p-tolylthio)isoxazol-5-amine (**3oa**)*



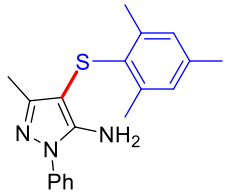
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a colorless oil in 43% yield (28.7 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.06 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.93 (m, 2H), 4.99 (s, 2H), 2.29 (s, 3H), 2.14 (d, *J* = 4.7 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 170.7, 164.0, 135.5, 133.3, 130.0, 125.5, 21.0, 10.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2OS$ 221.0749; Found: 221.0745.

*3-Methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5-amine (**3ab**)*[2]



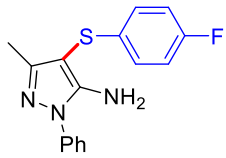
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 67% yield (56.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.64 – 7.57 (m, 2H), 7.50 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.30 – 7.22 (m, 2H), 7.15 – 7.08 (m, 3H), 4.25 (s, 2H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.2, 148.5, 138.7, 138.3, 129.7, 129.0, 127.5, 125.0, 123.4, 12.4.

*4-(Mesitylthio)-3-methyl-1-phenyl-1H-pyrazol-5-amine (**3ac**)*



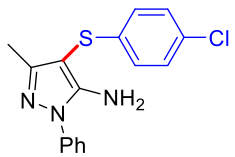
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 64% yield (62.1 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.61 (dt, *J* = 8.6, 1.9 Hz, 2H), 7.54 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.00 (s, 2H), 4.14 (s, 2H), 2.56 (s, 6H), 2.36 (s, 3H), 2.21 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 151.4, 146.2, 141.0, 138.7, 137.3, 129.5, 129.5, 129.4, 127.2, 123.3, 91.5, 22.0, 21.0, 12.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}N_3S$ 324.1534; Found: 324.1538.

*4-((4-Fluorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-amine (**3ad**)*[1]



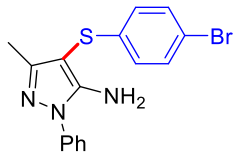
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 48% yield (43.5 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.58 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 4.25 (s, 2H), 2.23 (s, 3H).^{13}C NMR (CDCl3, 100 MHz, ppm) δ = 162.1 (d, *J* = 243.0 Hz), 159.9, 153.1, 148.5, 138.6, 133.3 (d, *J* = 3.0 Hz), 129.8, 127.62, 127.0 (d, *J* = 8.0 Hz), 123.5, 116.1 (d, *J* = 22.0 Hz), 88.3, 12.4. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm) δ = -118.0.

*4-((4-Chlorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-amine (**3ae**)*[1]



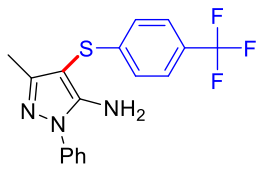
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 58% yield (54.5 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.59 – 7.55 (m, 2H), 7.51 – 7.45 (m, 2H), 7.38 – 7.32 (m, 1H), 7.21 – 7.17 (m, 2H), 7.03 – 6.99 (m, 2H), 4.25 (s, 2H), 2.21 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.0, 148.5, 138.5, 136.9, 130.8, 129.7, 129.1, 127.6, 126.3, 123.4, 87.3, 12.3.

*4-((4-Bromophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-amine (**3af**)*[1]



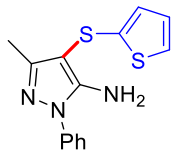
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 54% yield (58.3 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.57 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.35 (tt, *J* = 9.3, 2.1 Hz, 3H), 6.99 – 6.92 (m, 2H), 4.24 (s, 2H), 2.21 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.1, 148.6, 138.5, 137.7, 132.0, 129.8, 127.7, 126.7, 123.4, 118.6, 87.2, 12.4.

*3-Methyl-1-phenyl-4-((4-(trifluoromethyl)phenyl)thio)-1H-pyrazol-5-amine (**3ag**)*[1]



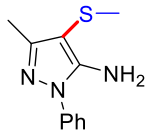
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a colorless oil in 83% yield (86.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.59 – 7.55 (m, 2H), 7.48 (dd, *J* = 8.8, 7.2 Hz, 4H), 7.38 – 7.33 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.27 (s, 2H), 2.21 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 153.1, 148.7, 143.7, 138.5, 129.7, 127.7, 127.2 (q, *J* = 32.0 Hz), 125.8 (q, *J* = 4.0 Hz), 124.8, 124.3 (q, *J* = 270.0 Hz), 123.4, 86.1, 12.3.^{19}F NMR ($CDCl_3$, 376 MHz, ppm) δ = -62.2.

*3-Methyl-1-phenyl-4-(thiophen-2-ylthio)-1H-pyrazol-5-amine (**3ah**)*[1]



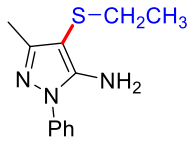
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 71% yield (60.7 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.53 – 7.50 (m, 2H), 7.44 (dd, *J* = 8.7, 7.0 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.18 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.01 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.90 (dd, *J* = 5.3, 3.5 Hz, 1H), 4.32 (s, 2H), 2.33 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 152.1, 147.8, 138.5, 137.9, 129.6, 128.7, 127.6, 127.4, 127.0, 91.8, 12.5.

*3-Methyl-4-(methylthio)-1-phenyl-1H-pyrazol-5-amine (**3ai**)*



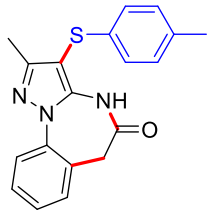
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 17% yield (11.1 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.56 – 7.52 (m, 2H), 7.48 – 7.43 (m, 2H), 7.34 – 7.30 (m, 1H), 4.20 (s, 2H), 2.30 (s, 3H), 2.16 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 152.3, 147.5, 138.8, 129.6, 127.2, 123.3, 93.0, 19.7, 12.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}N_3S$ 220.0908; Found: 220.0911.

*4-(Ethylthio)-3-methyl-1-phenyl-1H-pyrazol-5-amine (**3aj**)*



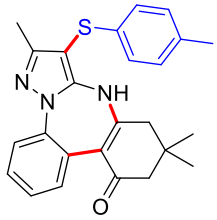
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 7:1) to give the product as a yellow oil in 41% yield (28.8 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.57 – 7.51 (m, 2H), 7.47 – 7.42 (m, 2H), 7.34 – 7.28 (m, 1H), 4.20 (s, 2H), 2.53 (q, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.21 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 152.9, 148.3, 138.9, 129.6, 127.2, 123.3, 91.1, 30.4, 15.3, 12.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}N_3S$ 234.1065; Found: 234.1067.

*2-Methyl-3-(p-tolylthio)-4H-benzo[f]pyrazolo[1,5-a][1,3]diazepin-5(6H)-one (**5**)*[3]



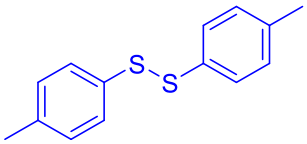
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pink solid substance in 57% yield (57.2 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.91 – 7.77 (m, 2H), 7.47 (ddd, *J* = 8.1, 6.9, 2.1 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 – 6.92 (m, 2H), 3.63 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 169.5, 154.4, 140.1, 137.4, 135.9, 132.9, 130.1, 129.9, 129.2, 128.2, 126.3, 124.9, 122.5, 96.2, 41.1, 21.0, 12.5.

*7,11,11-Ttrimethyl-8-(p-tolylthio)-11,12-dihydro-9H-dibenzo[d,f]pyrazolo[1,5-a][1,3]diazepin-13(10H)-one (**6**)*[4]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 5:1) to give the product as a yellow solid substance in 69% yield (85.4 mg);^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.72 – 7.69 (m, 1H), 7.35 – 7.33 (m, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 2.33 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H), 2.17 (s, 2H), 1.04 (s, 6H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.8, 161.4, 154.4, 150.2, 138.6, 135.9, 133.7, 132.2, 130.1, 128.3, 126.1, 126.0, 125.5, 122.4, 117.6, 94.5, 51.1, 45.3, 30.7, 28.0, 21.0, 12.6.

1,2-Di-p-tolyldisulfane (**2A'**) [5]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 20:1) to give the product as a yellow oil substance in 42% yield (46.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.39 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 2.33 (s, 6H).^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 137.6, 134.0, 129.9, 128.7, 21.2.

Reference

(1) W. B. Zhang, Q. Zou, Q. Wang, D. S. Jin, S. Jiang, P. Qian. *J. Org. Chem.* 2024, **89**, 5434–5441.

(2) K. Perumal, M. Shanthi, V. Hemamalini, R. Shanmugam, B. Shankar, S. Ramesh. *J. Heterocyclic. Chem*. 2025, **62**, 154–163.

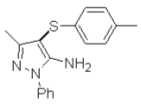
(3) L.-K. Chen, Y.-M. Yin, Q. Luo, J.-Q. Shao, C.-H. Zhang, S.-J. Yan. *J. Org. Chem.* 2025, **90**, 11344−11355.

(4) L. K. Chen, M. S. Zhang, M. C. Liu, Z. Y. Liu, Y. T. Qiu, Z. L. Zhang, F. C. Yu, J. Z. Huang. *Chem. Commun.* 2024, **60**, 432−435.

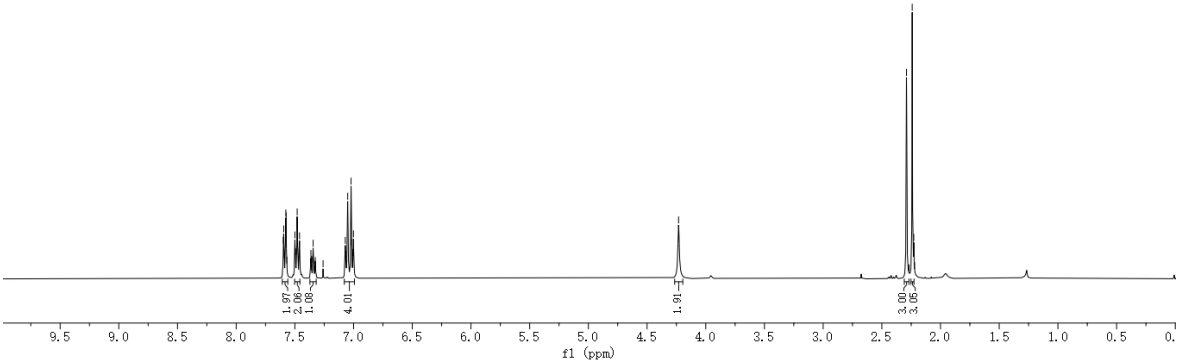
(5) W. J. Zhou, L. Y. Le, Y. W. Chen, W. X. Xie, Y. Chen, S.-F. Yin, R. H. Qiu. *J. Org. Chem*. 2025, **90**, 2927–2936.

NMR Spectra of products

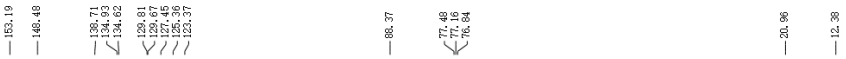
3aa-^{1}H NMR

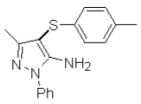


400 MHz，$CDCl_3$

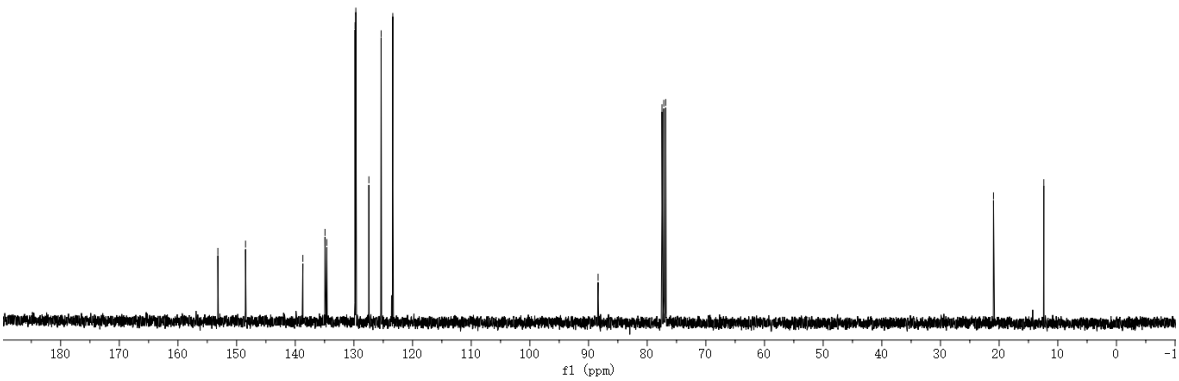


3aa-^{13}C NMR

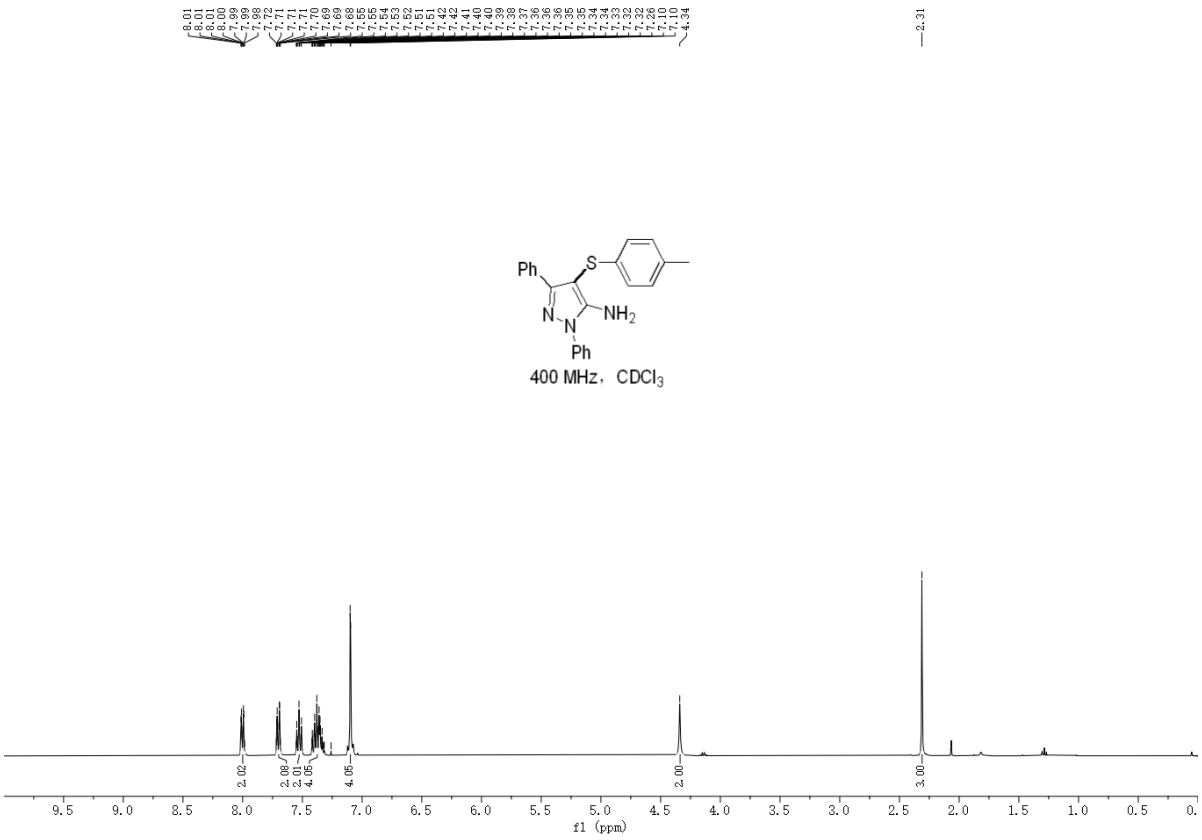




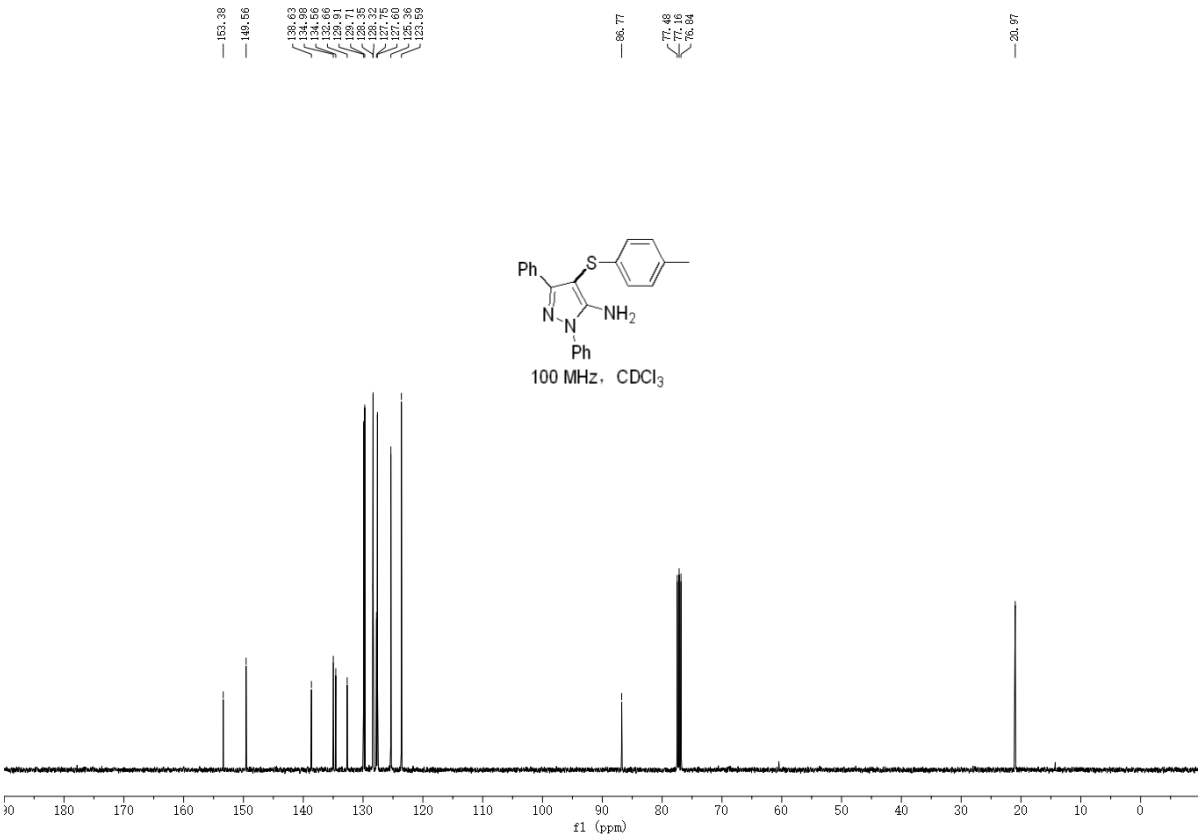
100 MHz，$CDCl_3$



3ba-^{13}C NMR



3ba-^{13}C NMR



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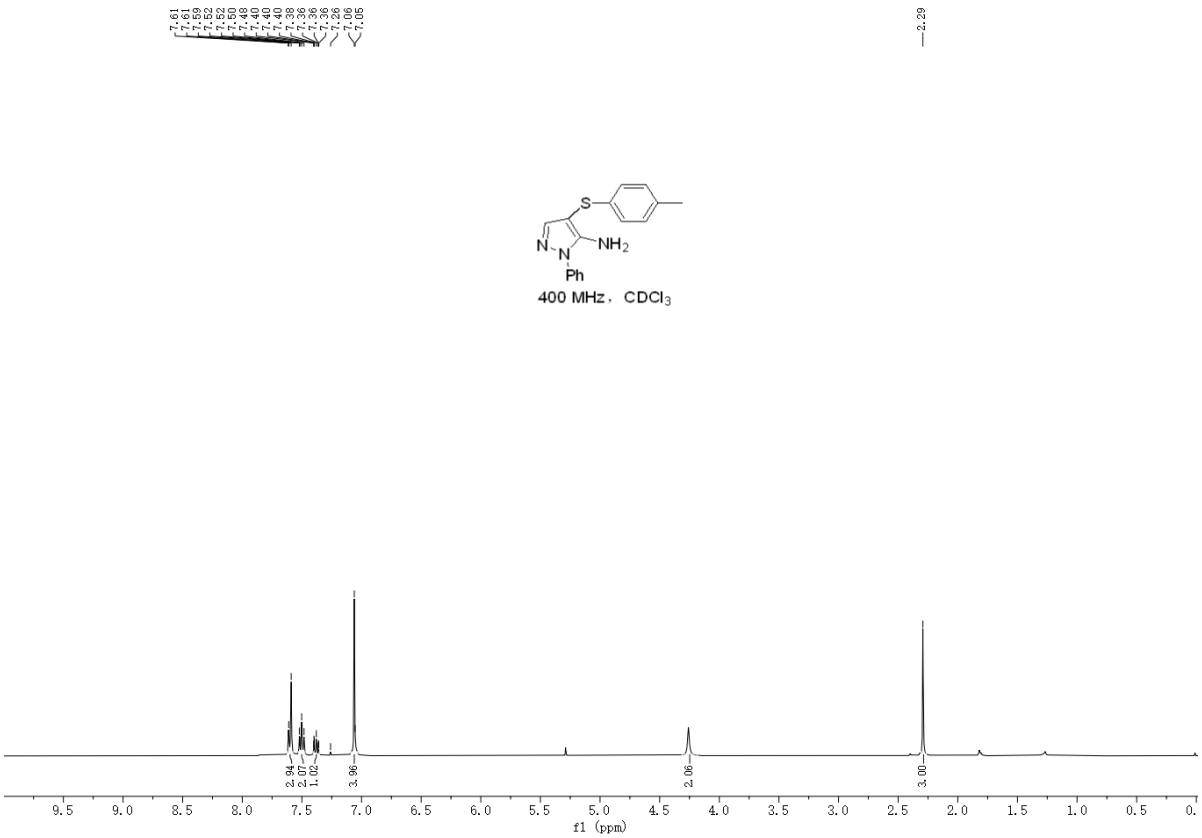
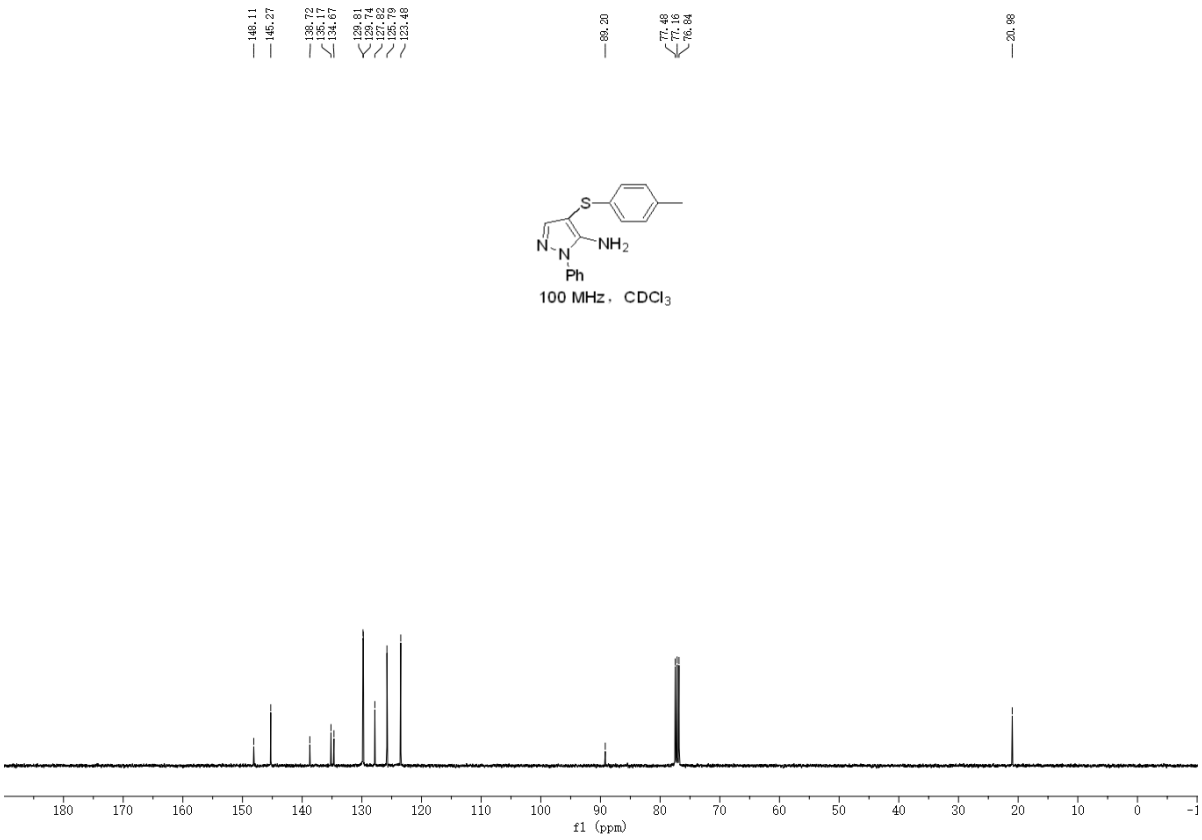
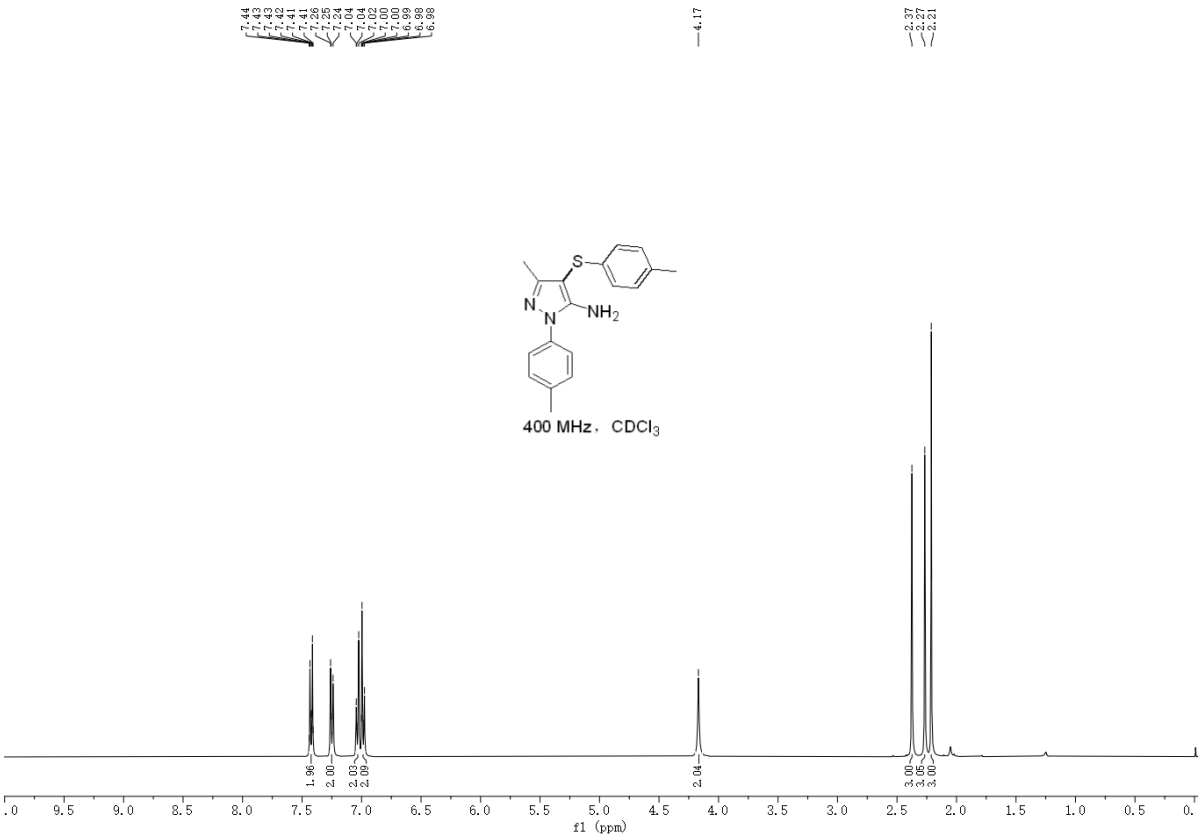


3ca-^{13}C NMR



3da-^{1}H NMR



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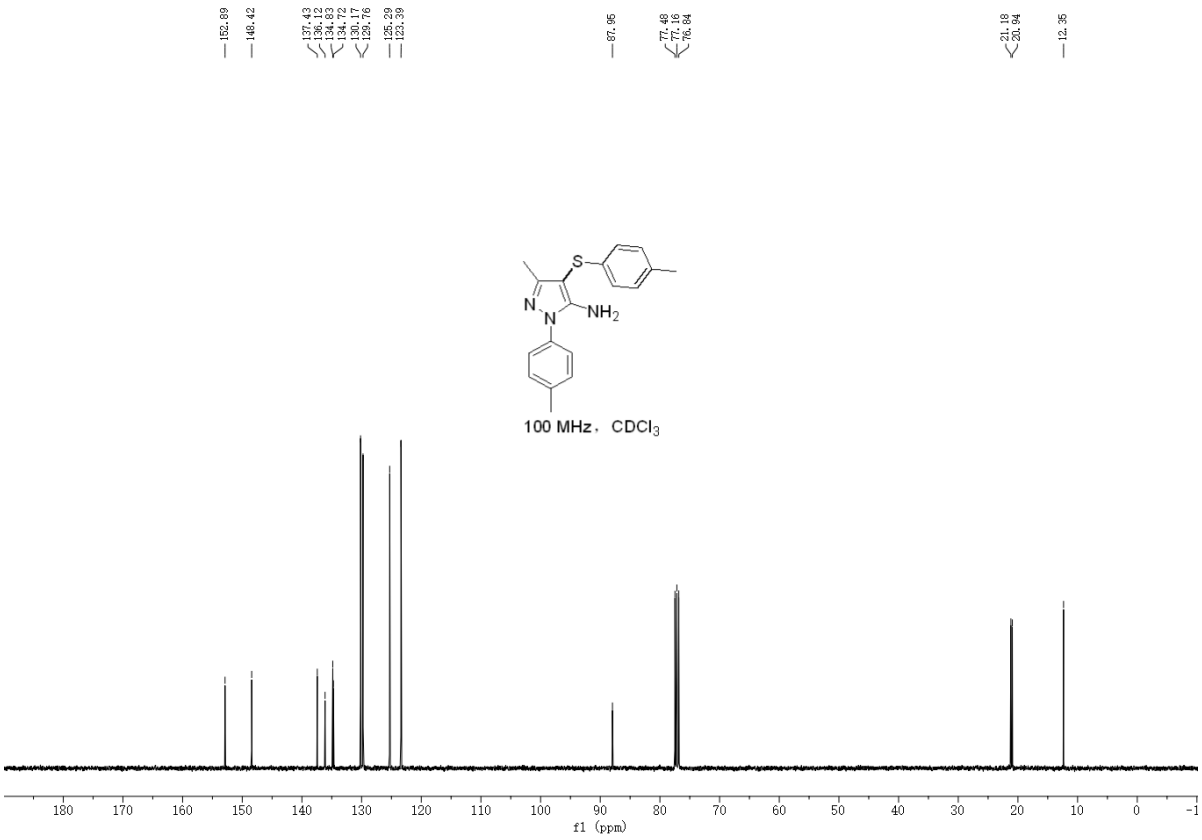
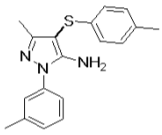
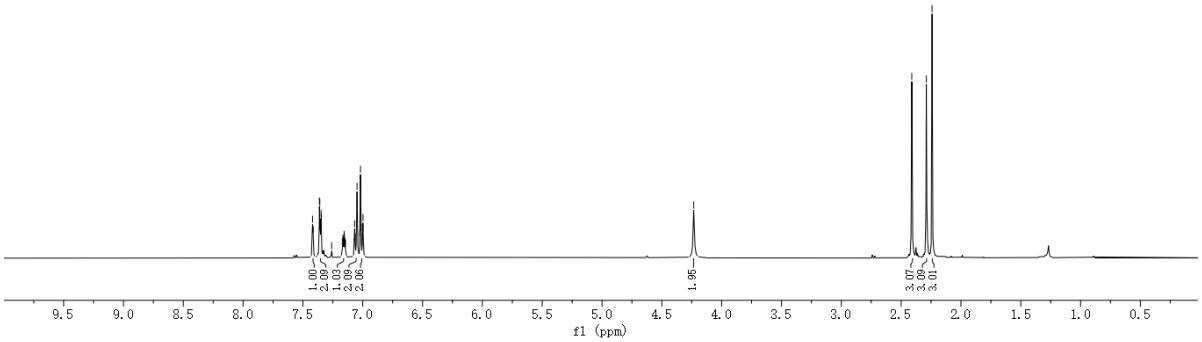


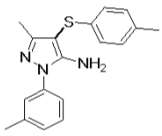
3ea-^{1}H NMR



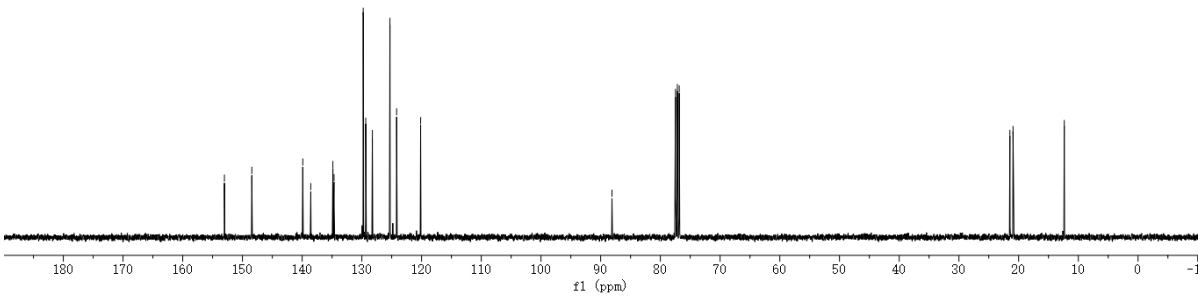
400 MHz，$CDCl_3$



3ea-^{13}C NMR



100 MHz，$CDCl_3$



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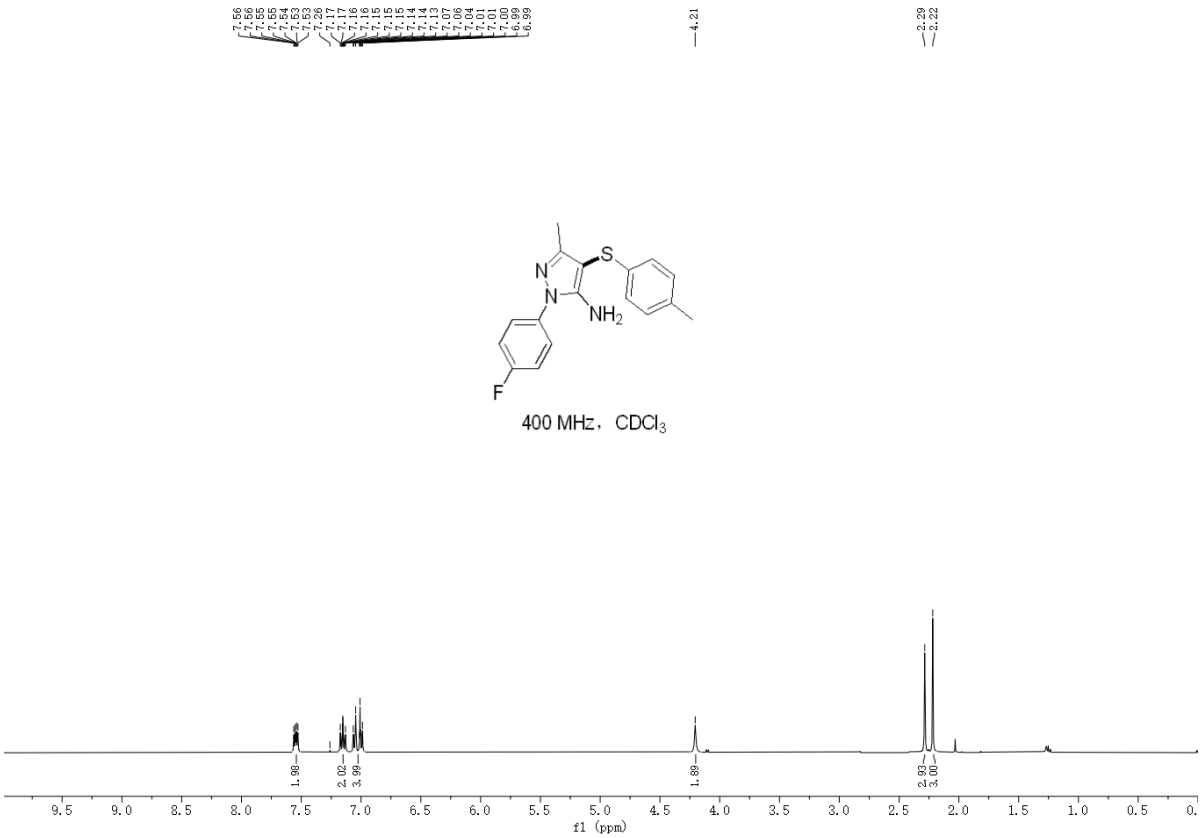
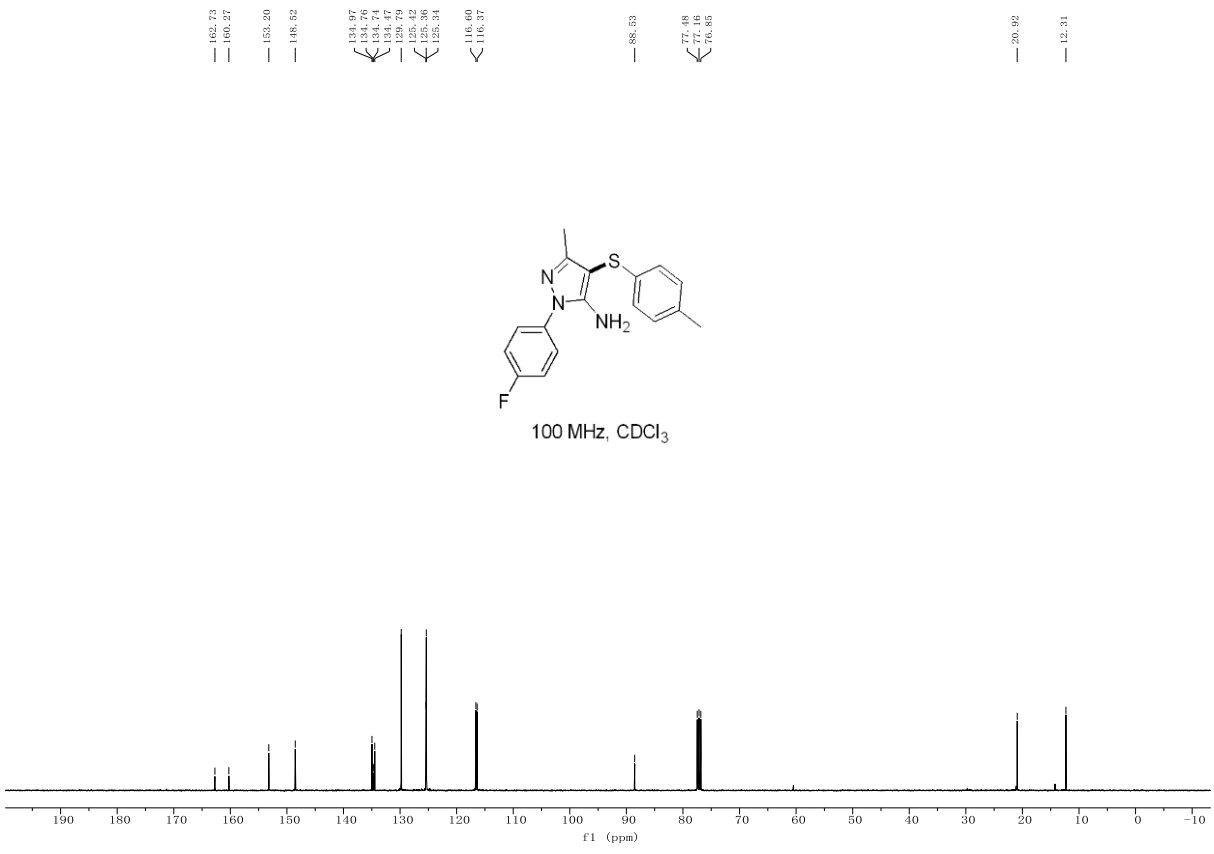


3fa-^{13}C NMR



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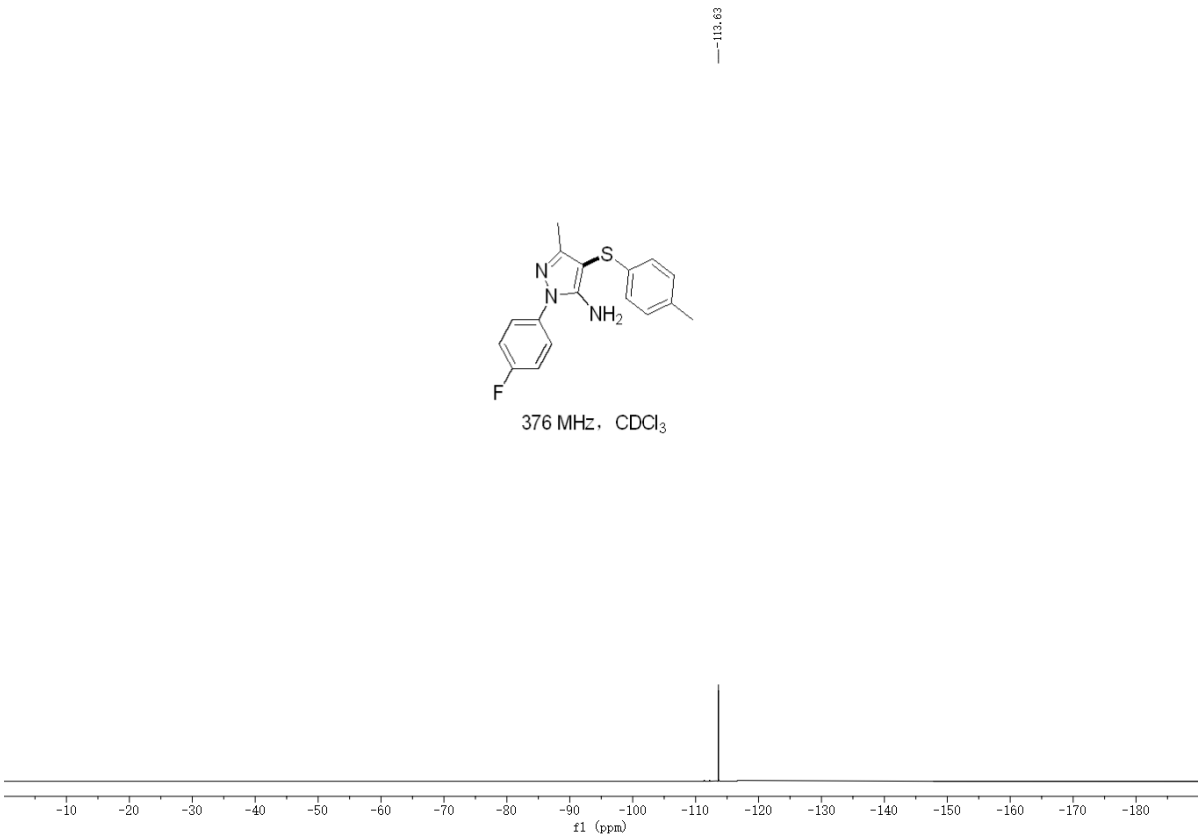
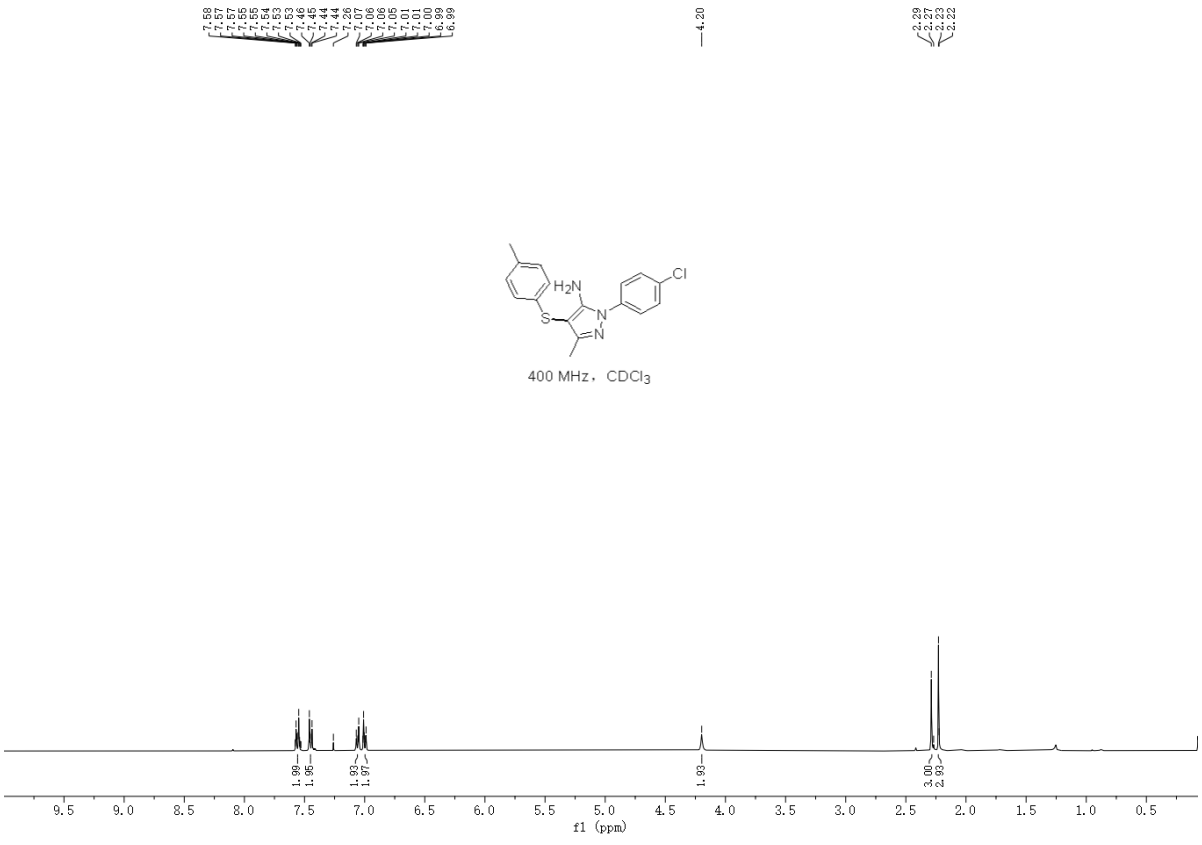
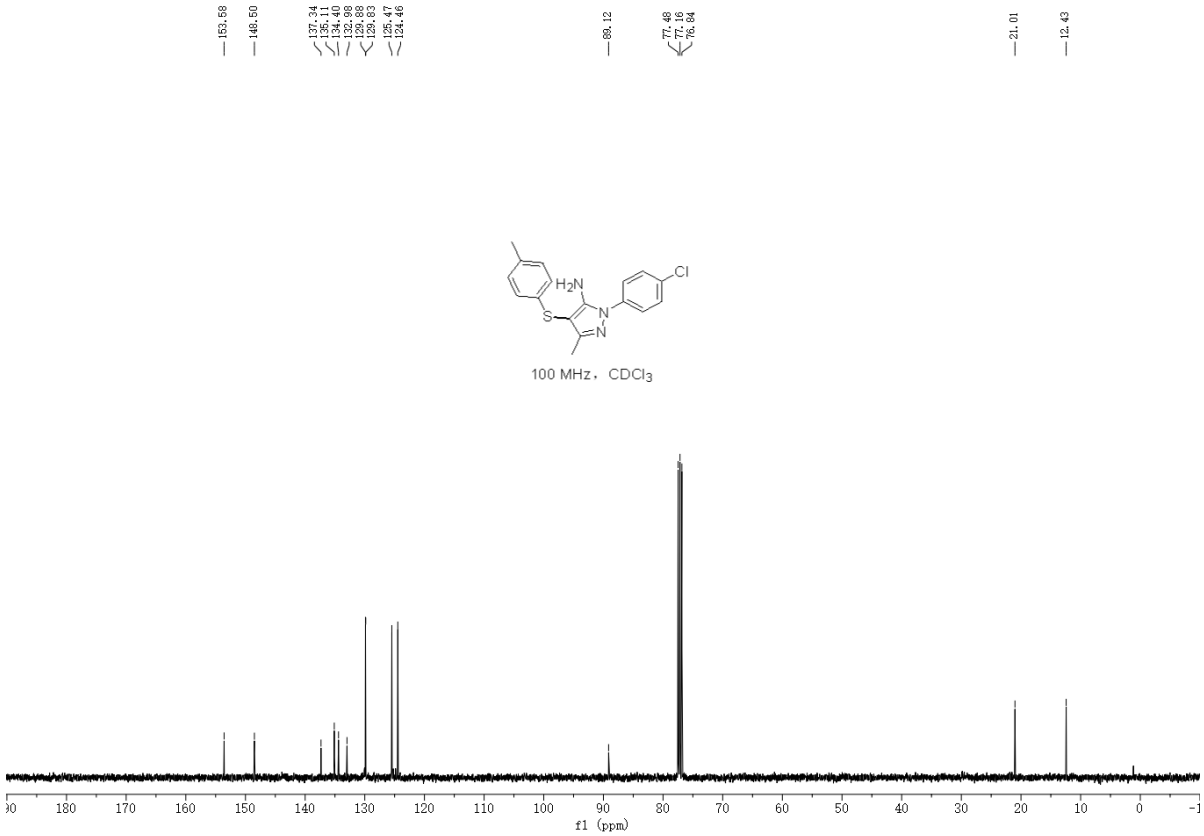


3ga-^{1}H NMR



3ga-^{13}C NMR



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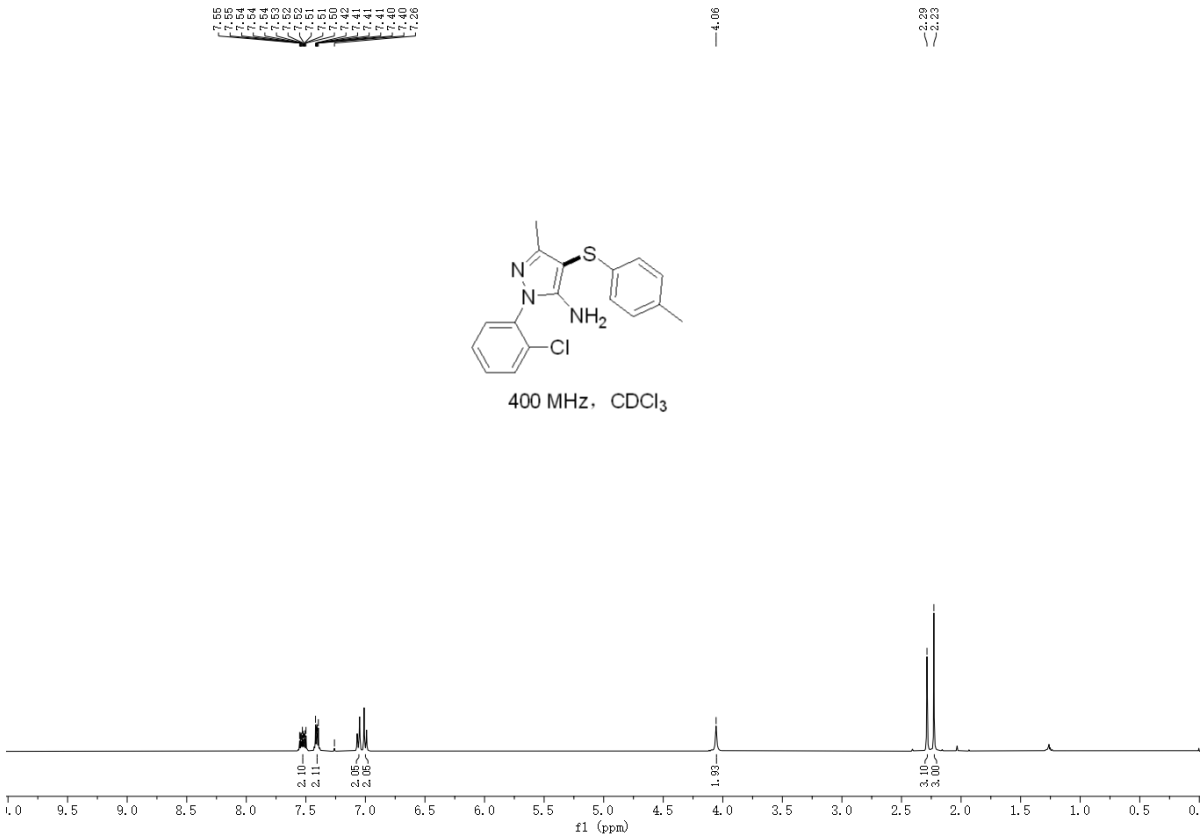

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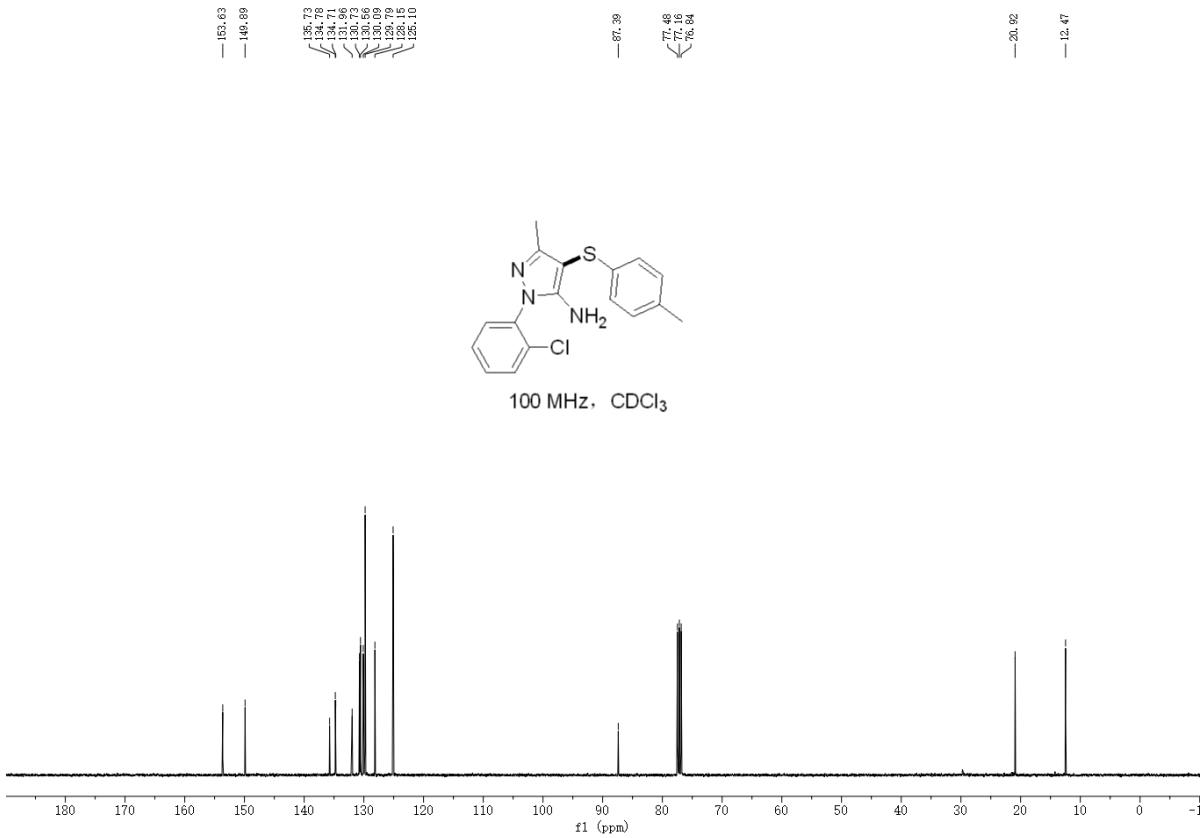
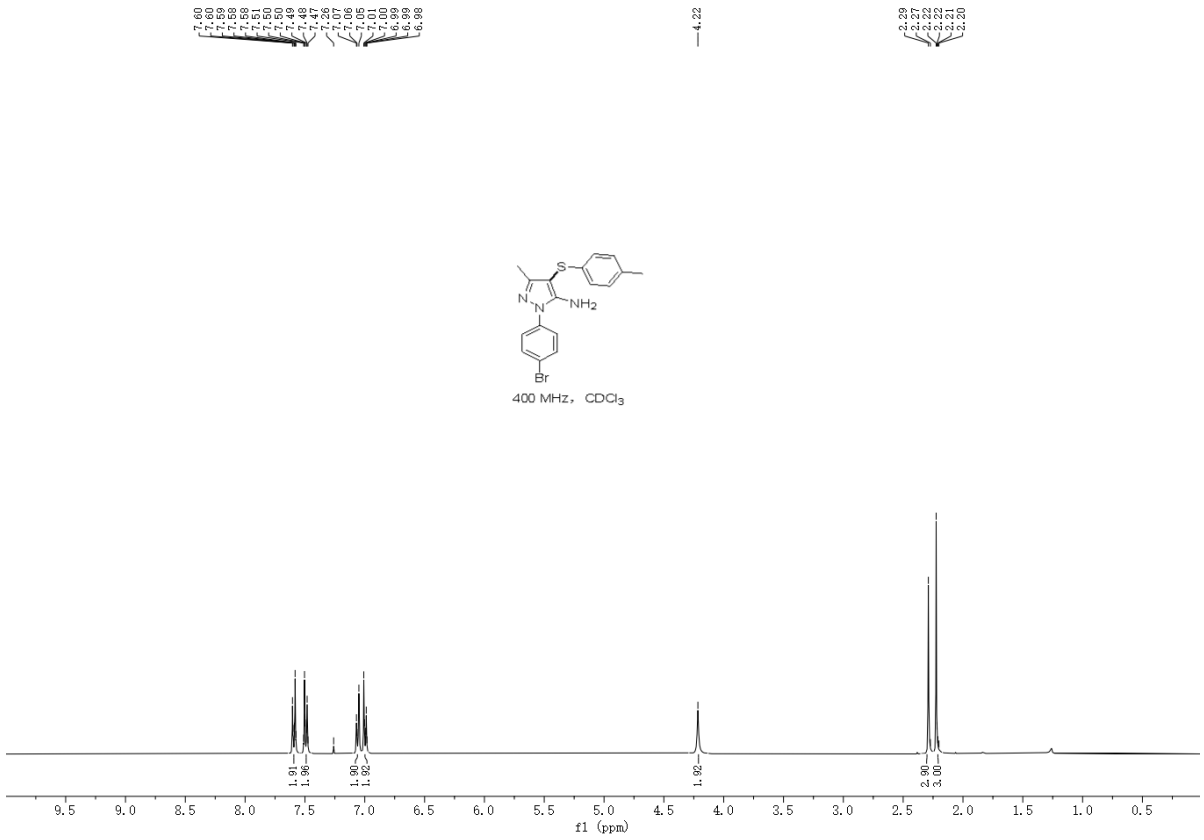


3ia-^{1}H NMR



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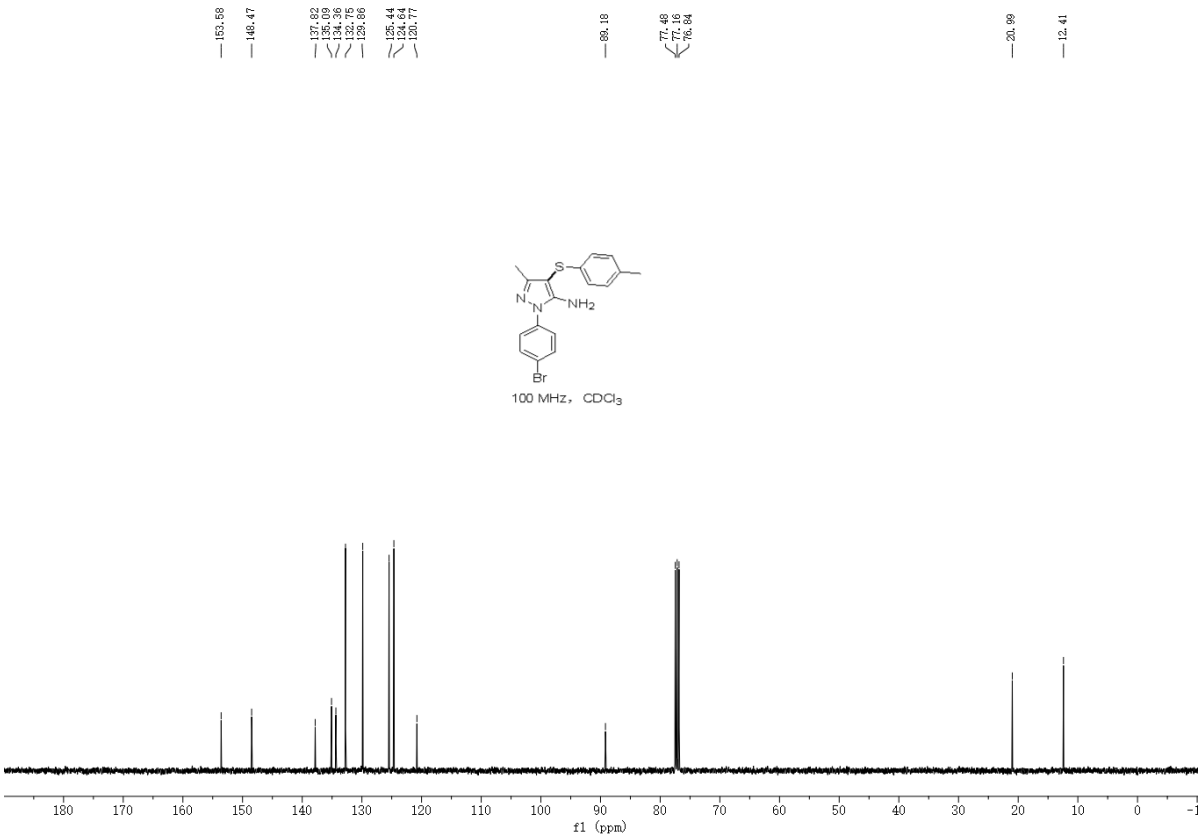

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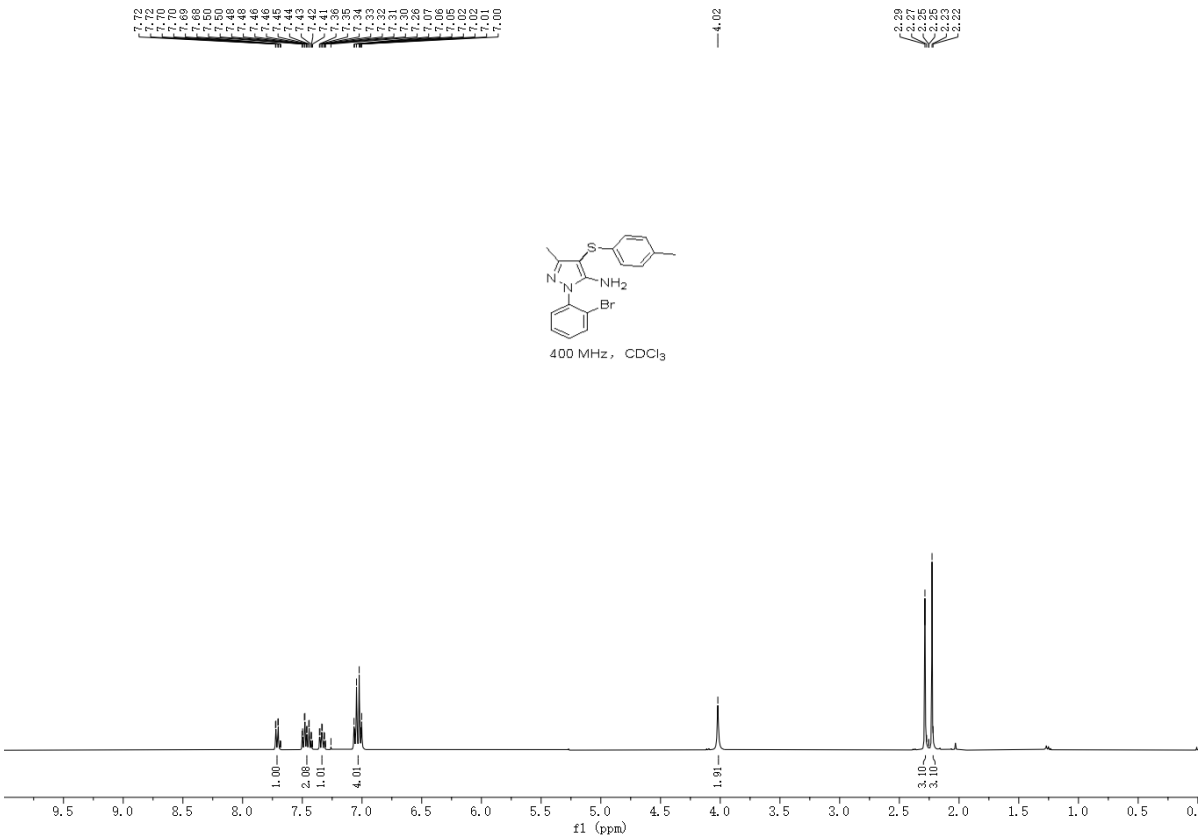

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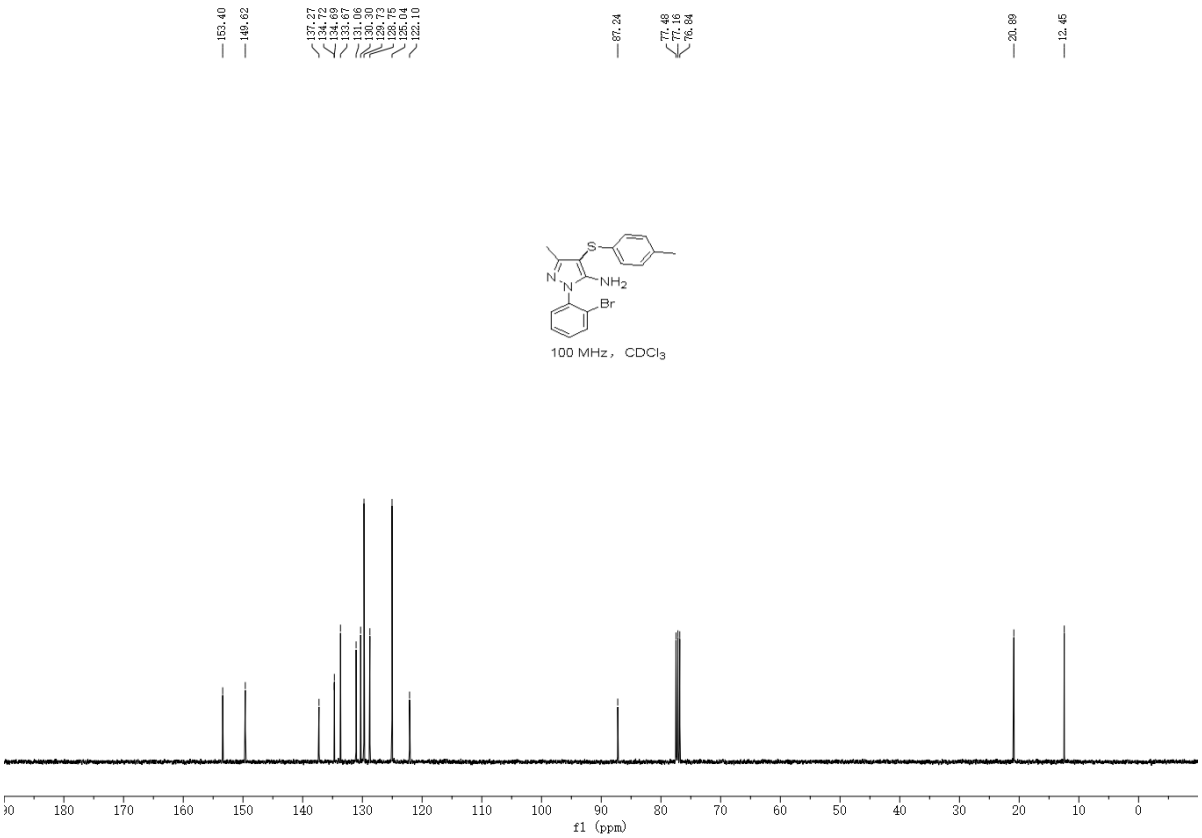
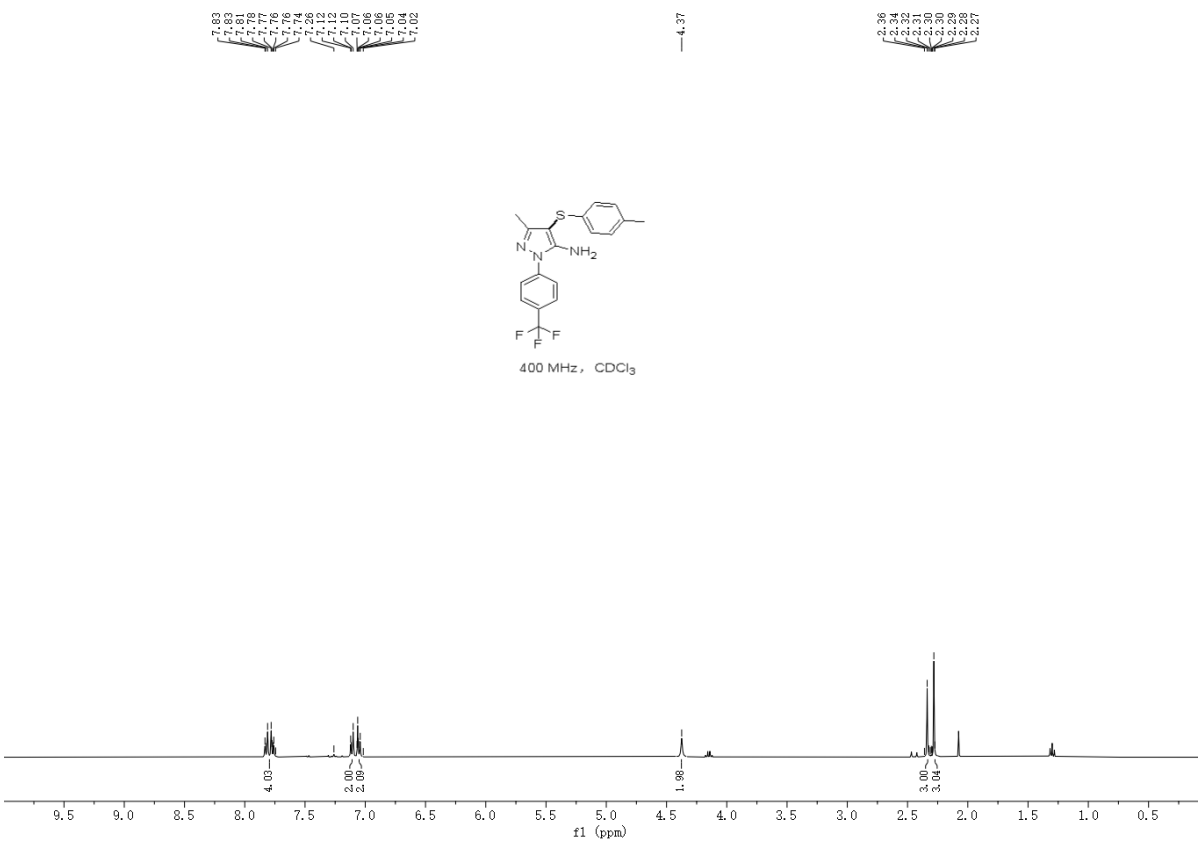
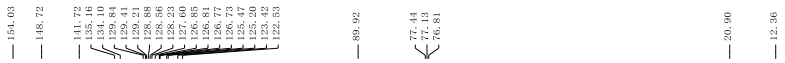
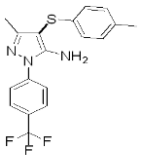


3ka-^{1}H NMR

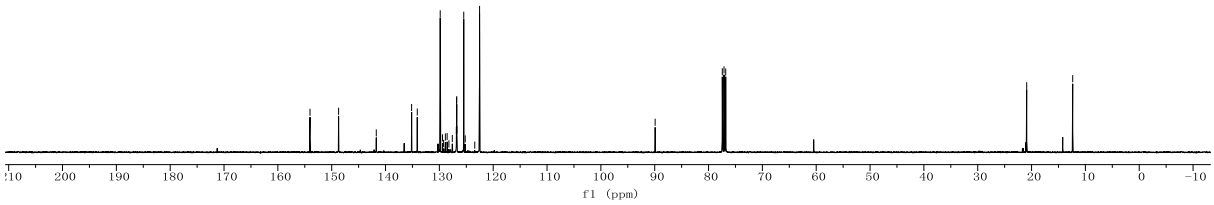


3ka-^{13}C NMR

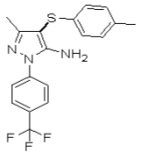




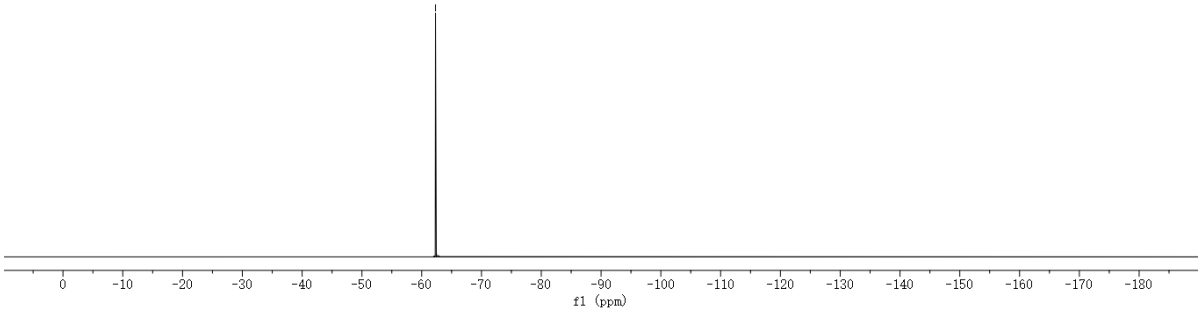
100 MHz，$CDCl_3$



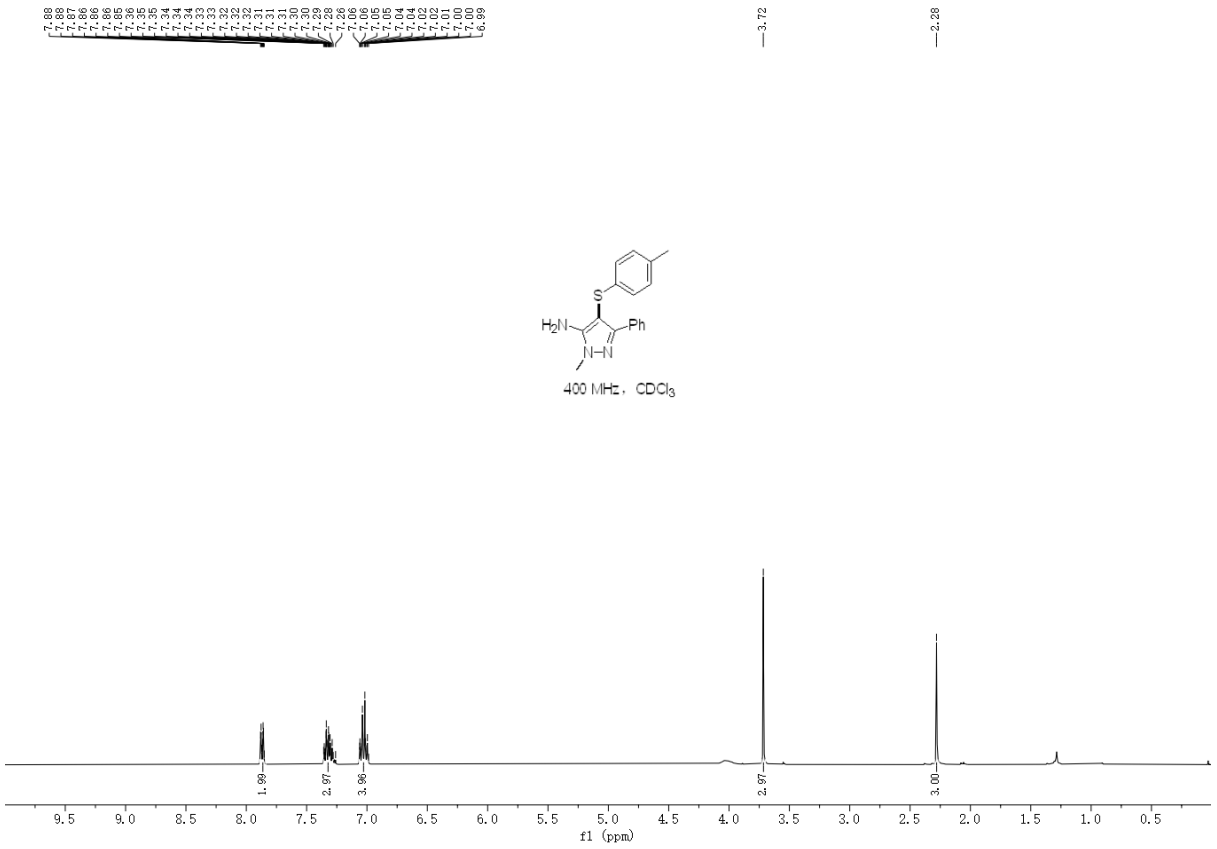
3ka-^{19}F NMR



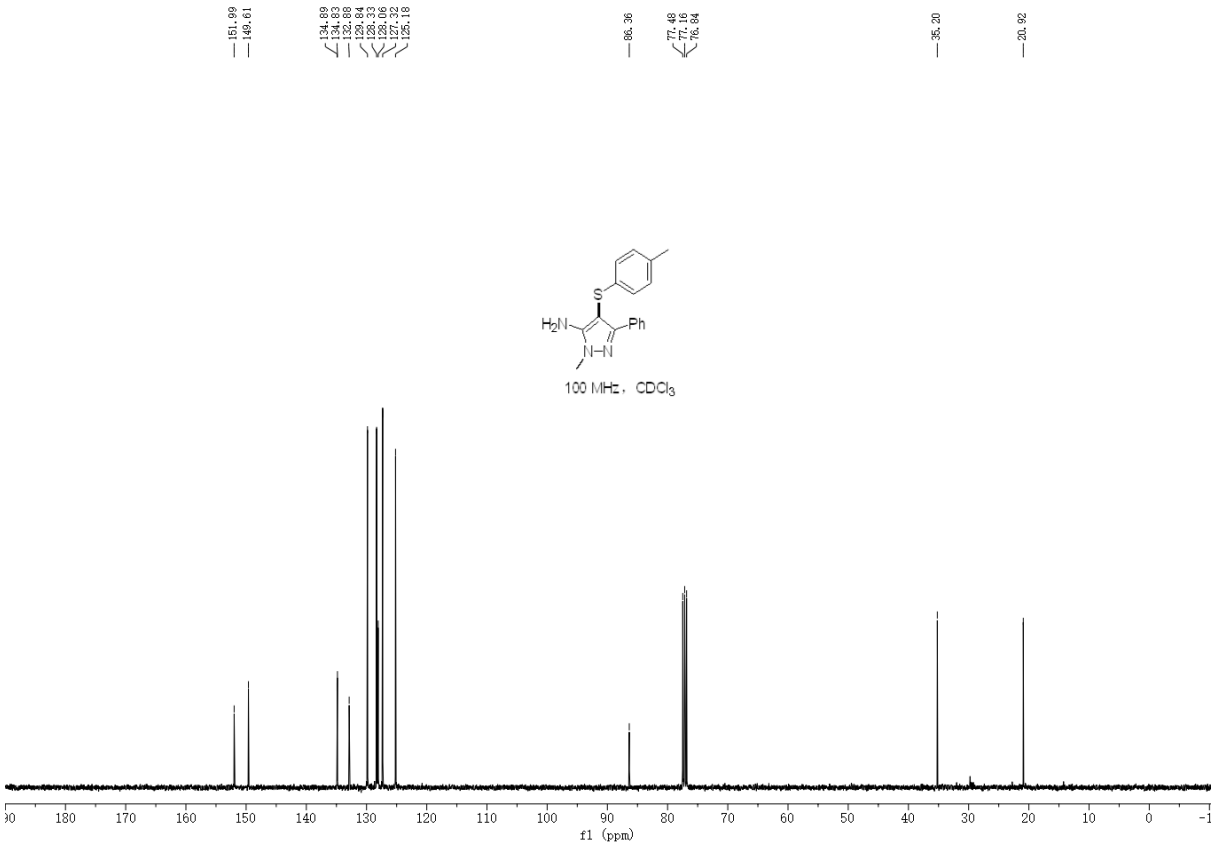
376 MHz，$CDCl_3$



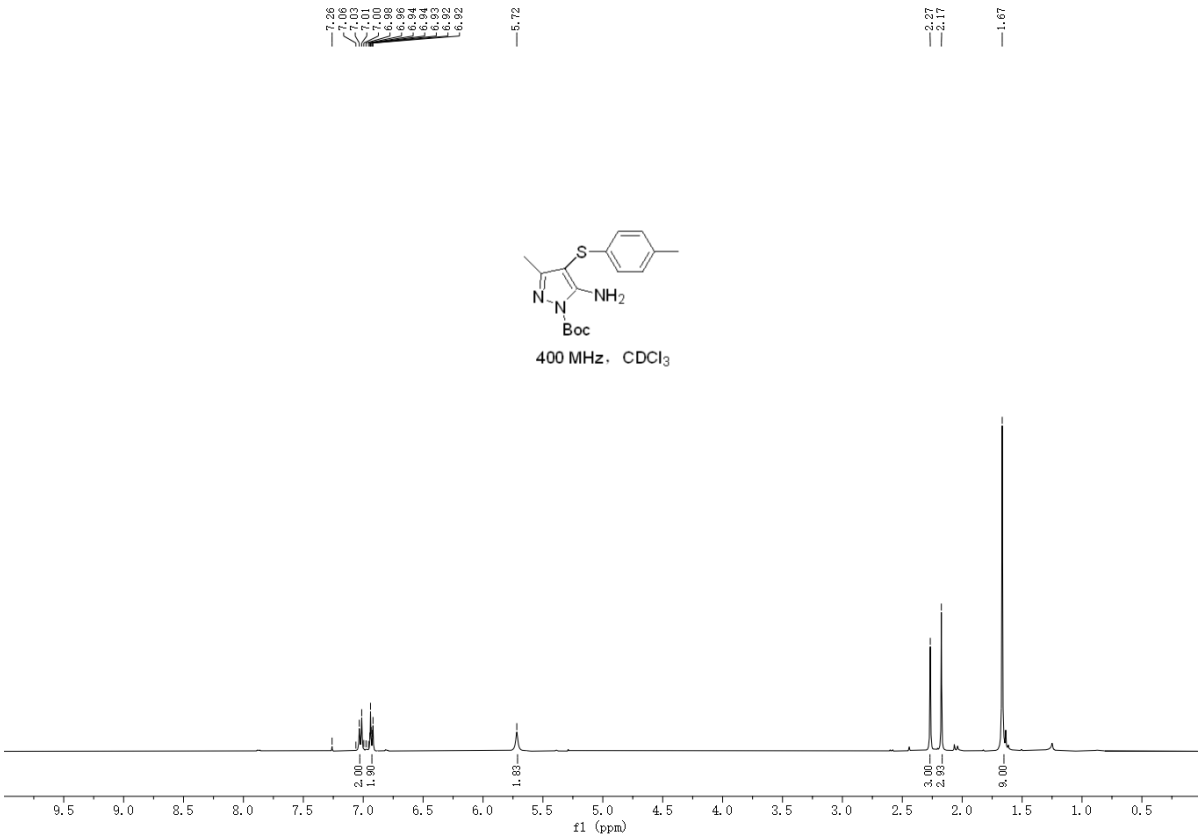
3la-^{1}H NMR



3la-^{13}C NMR



3ma-^{1}H NMR



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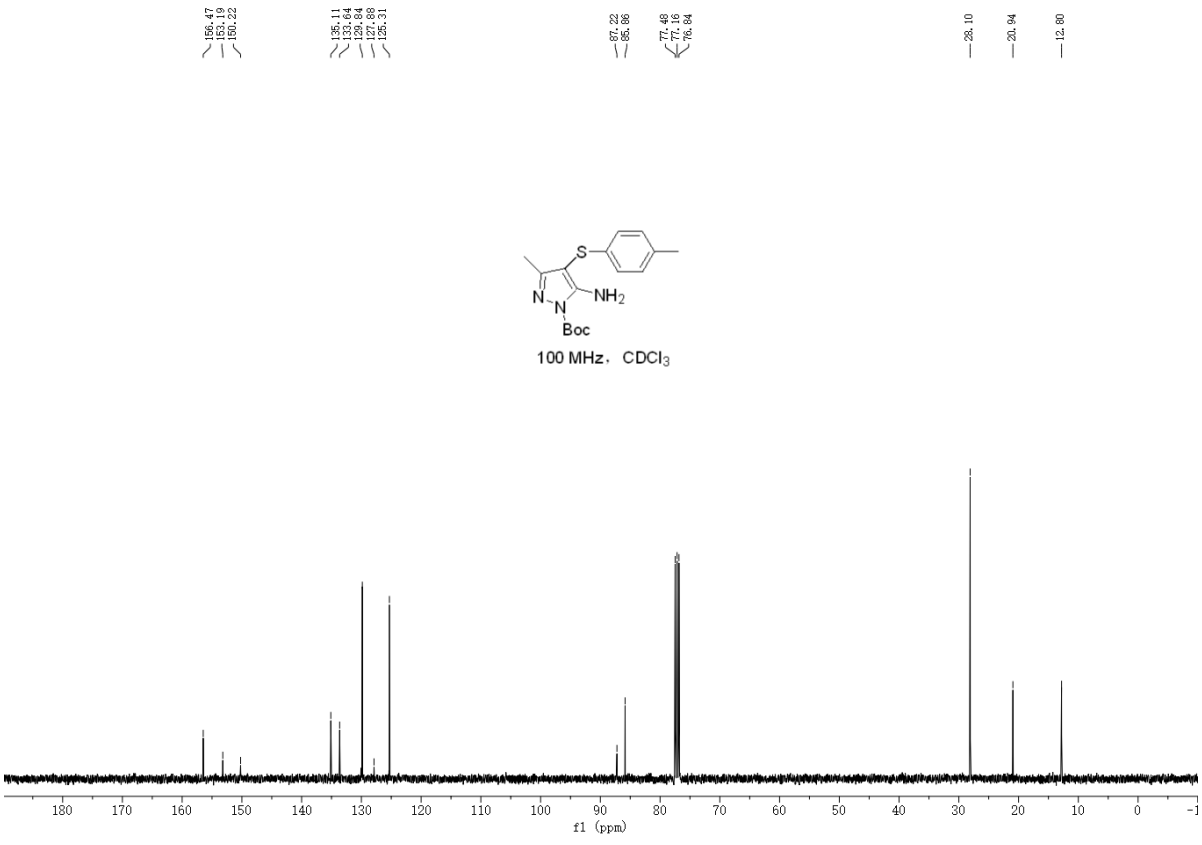
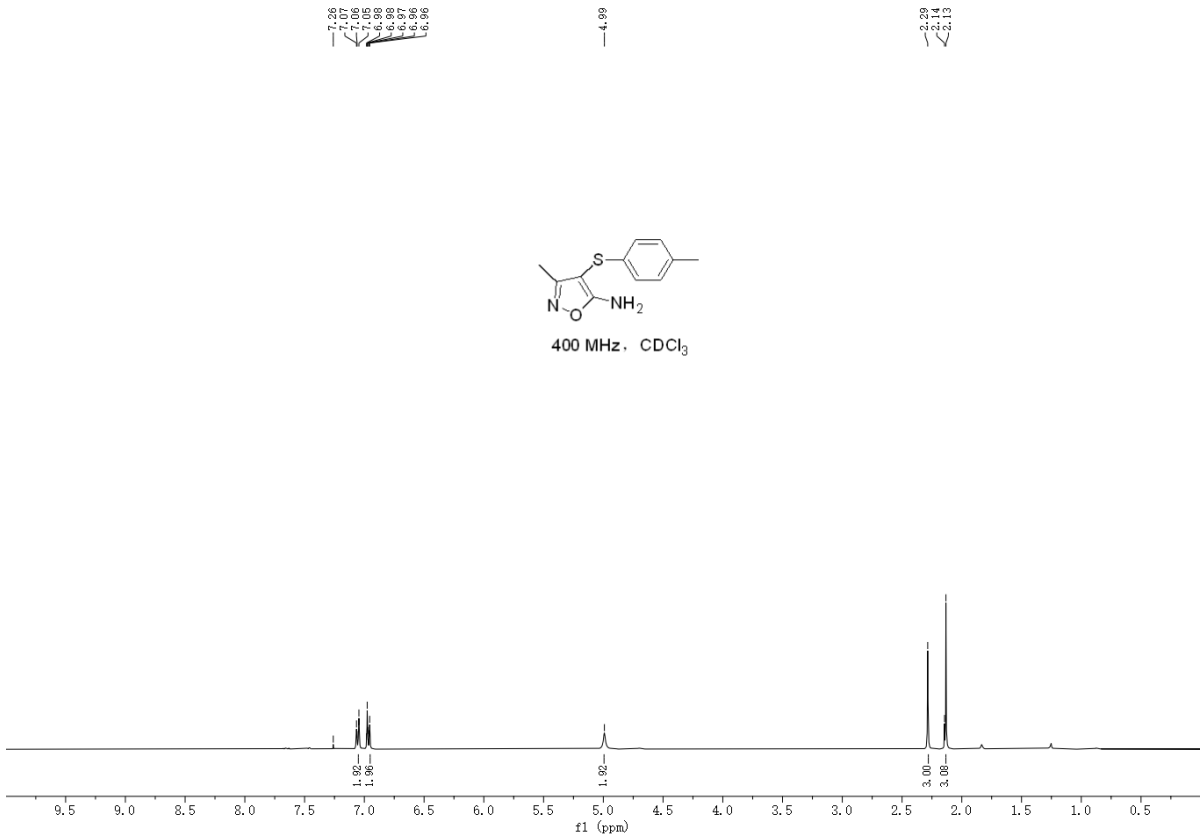
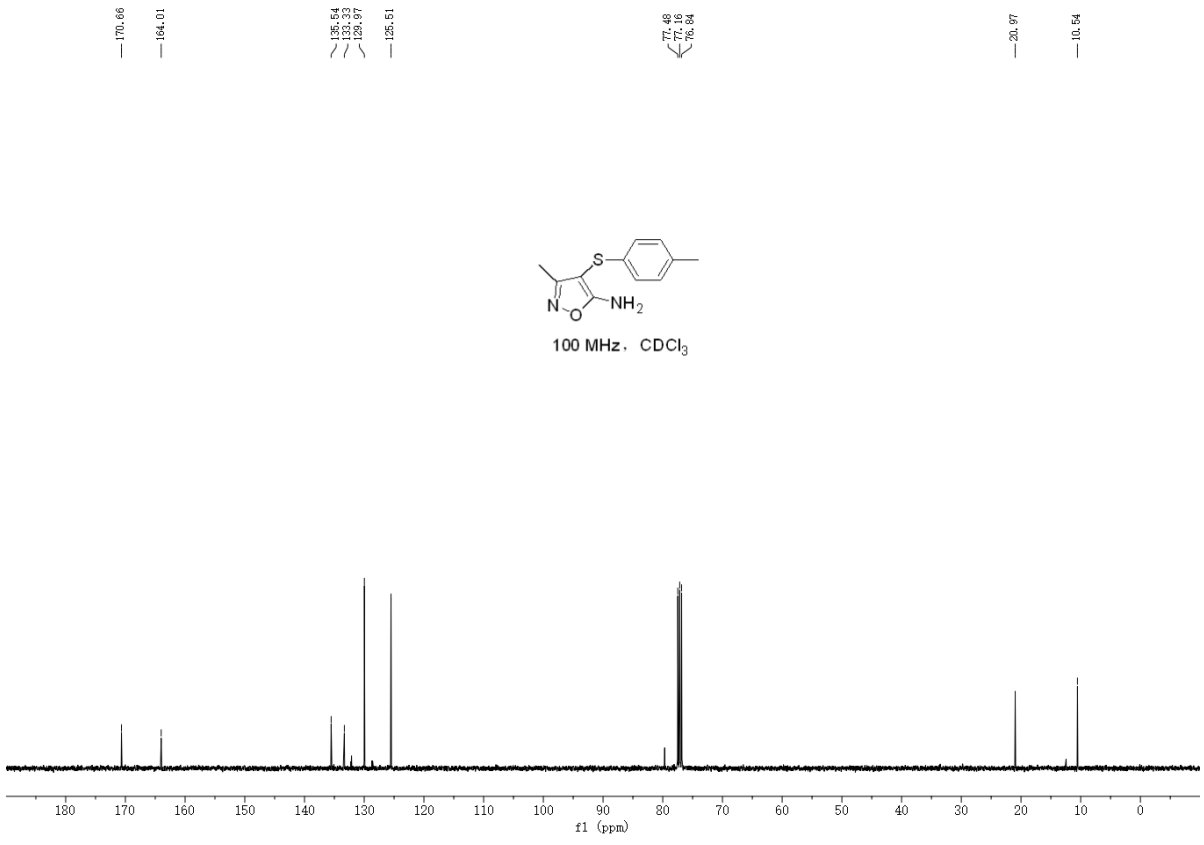


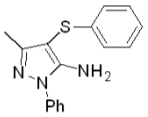
3oa-^{1}H NMR



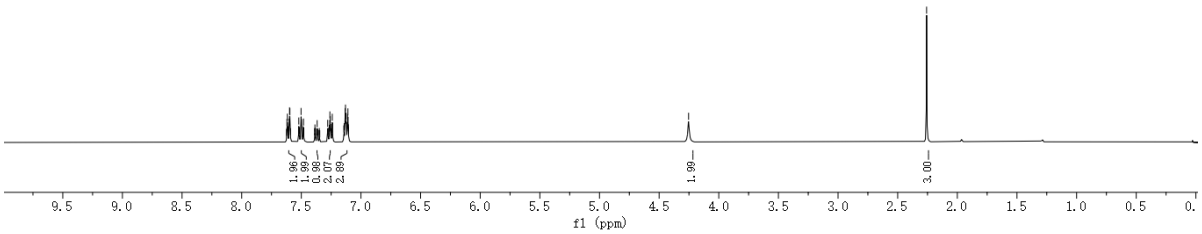
3oa-^{13}C NMR



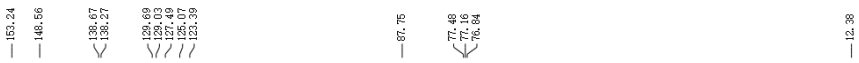
3ab-^{1}H NMR

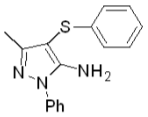


400 MHz，$CDCl_3$

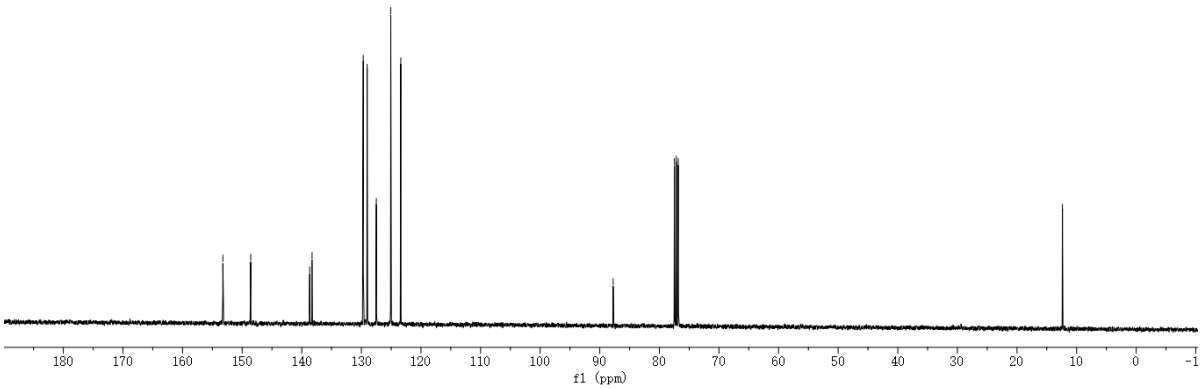


3ab-^{13}C NMR

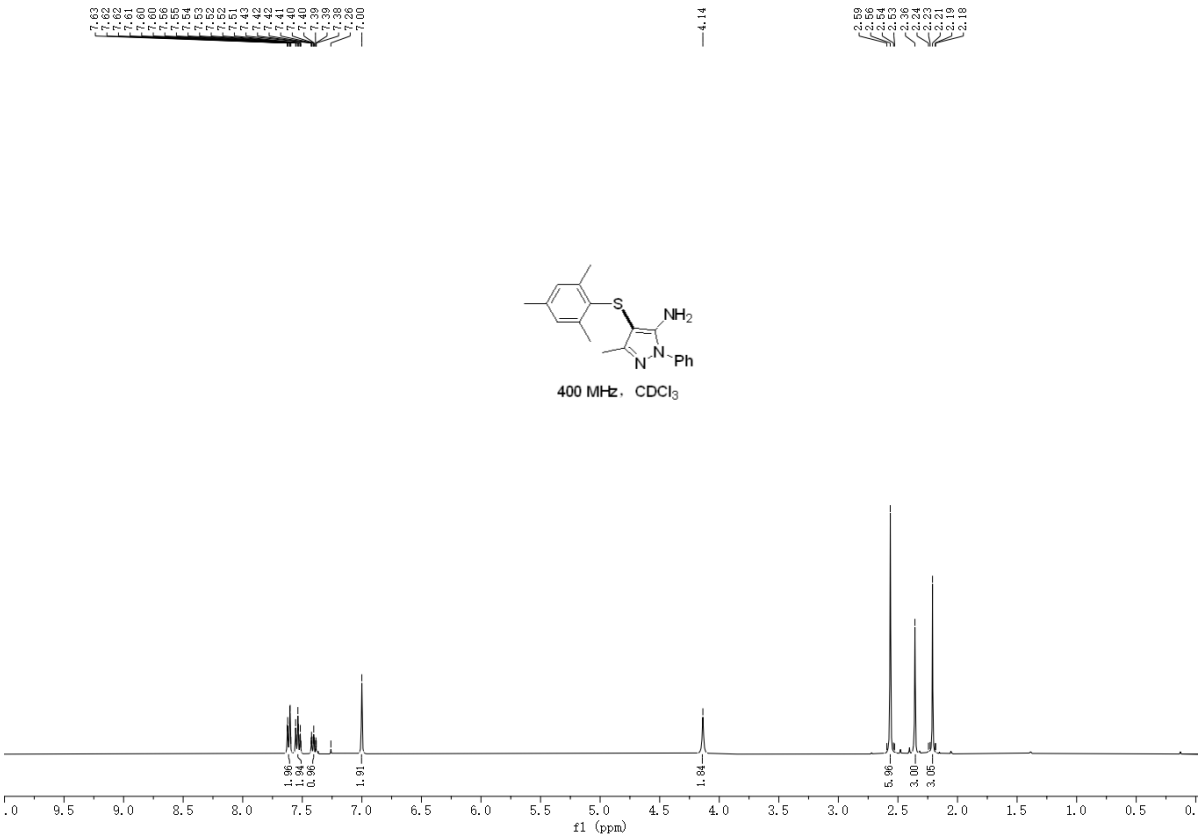




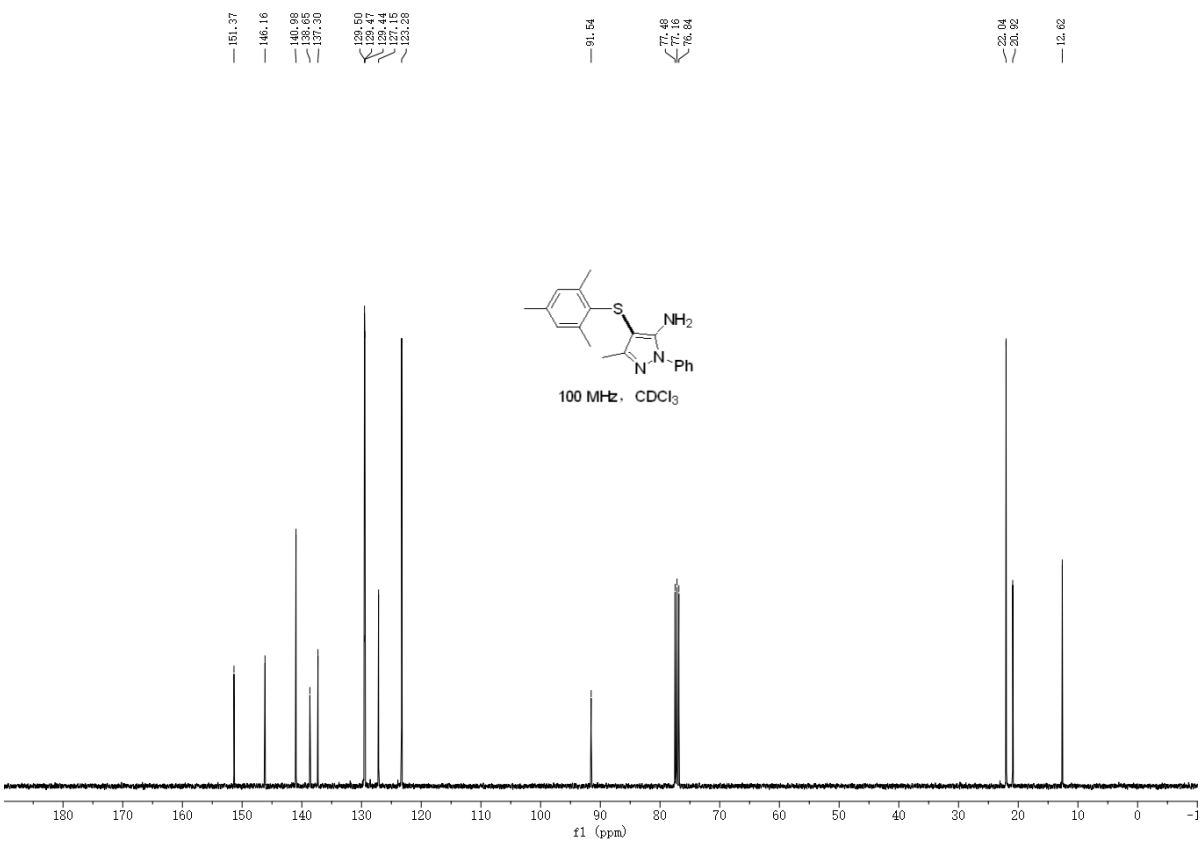
100 MHz，$CDCl_3$



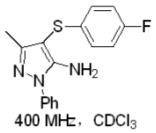
3ac-^{1}H NMR



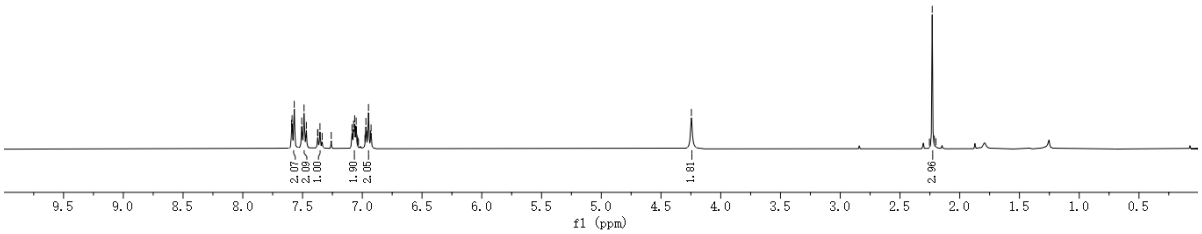
3ac-^{13}C NMR



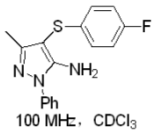
3ad-^{1}H NMR



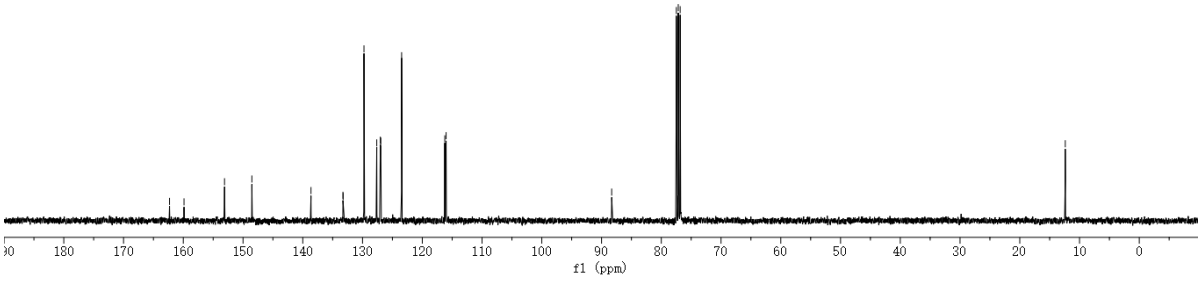
400 MHz，$CDCl_3$



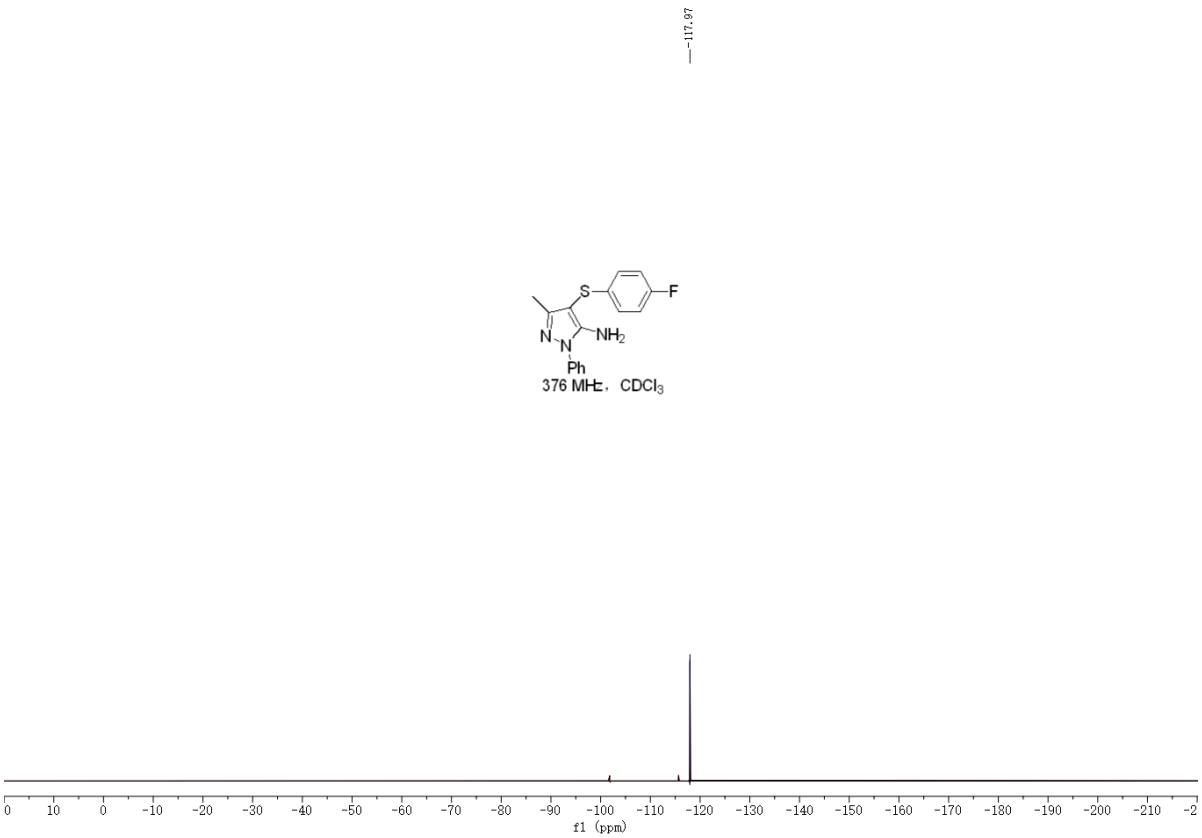
3ad-^{13}C NMR



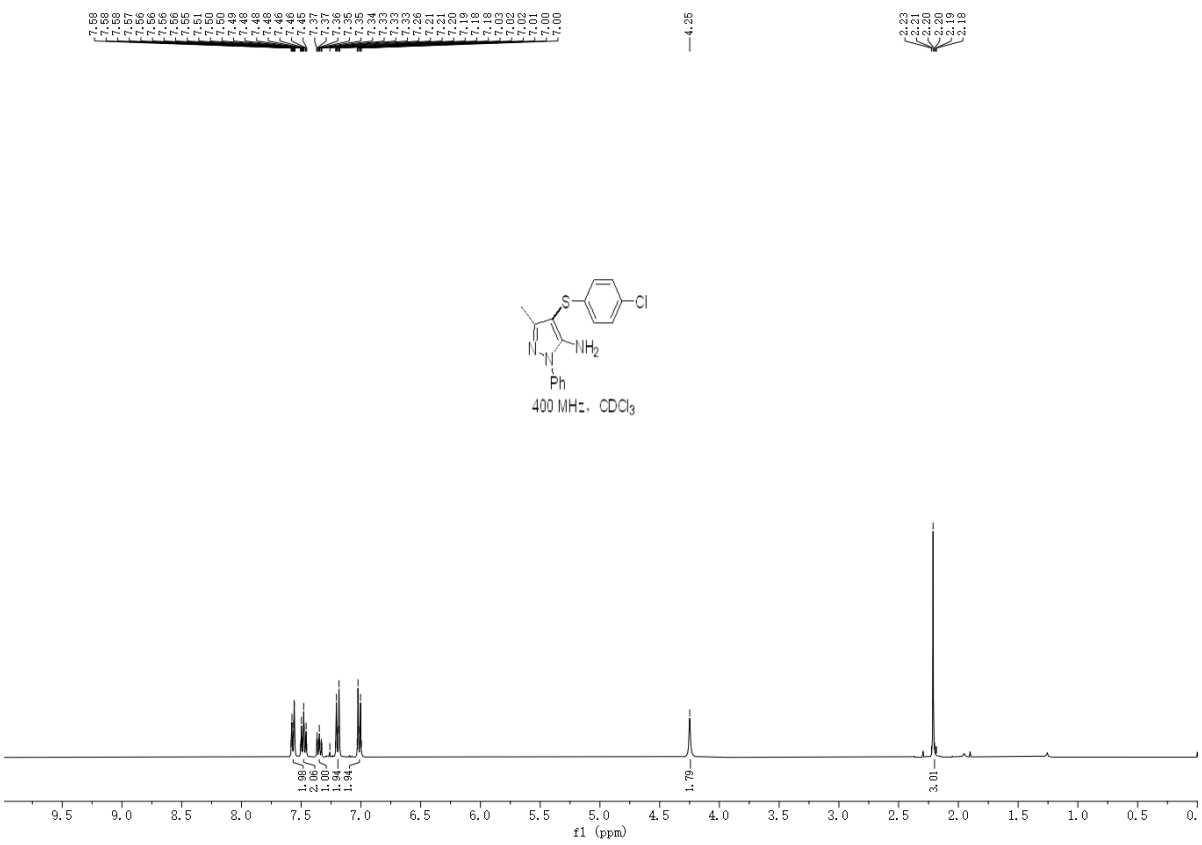
100 MHz，$CDCl_3$



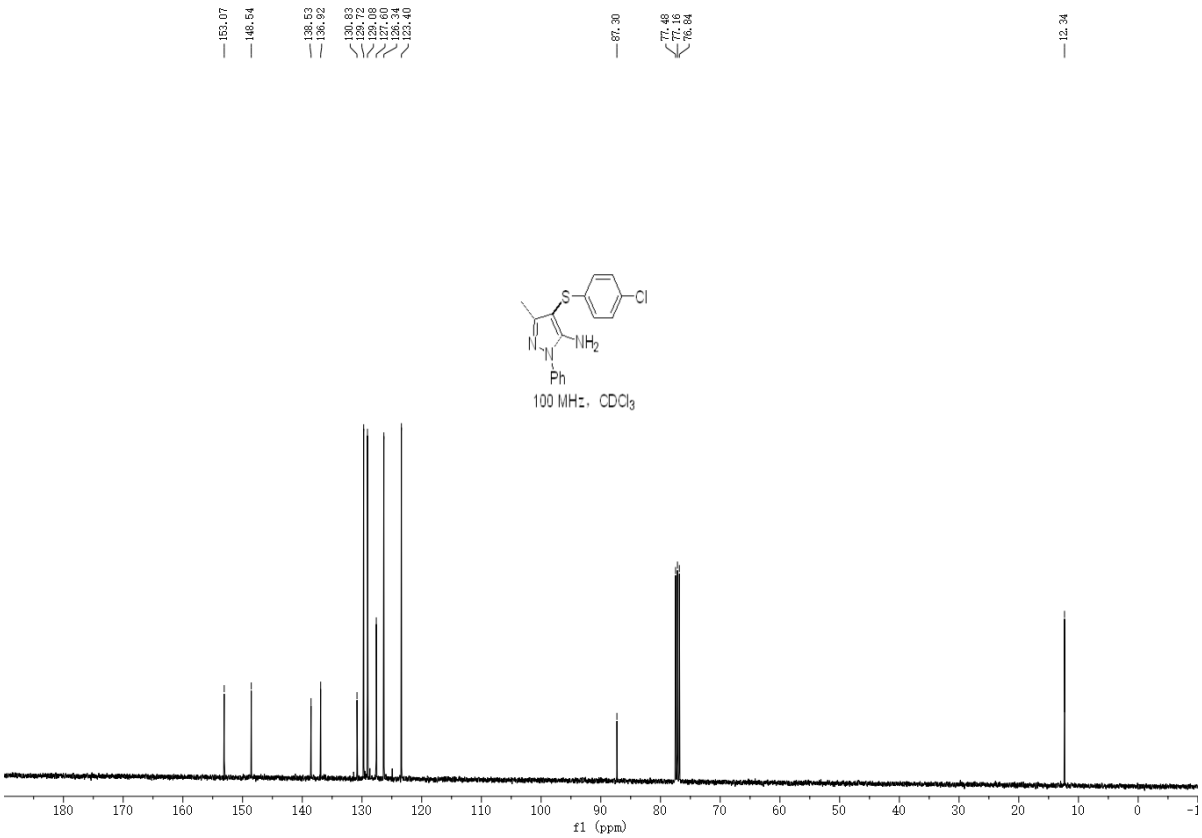
3ad-^{19}F NMR



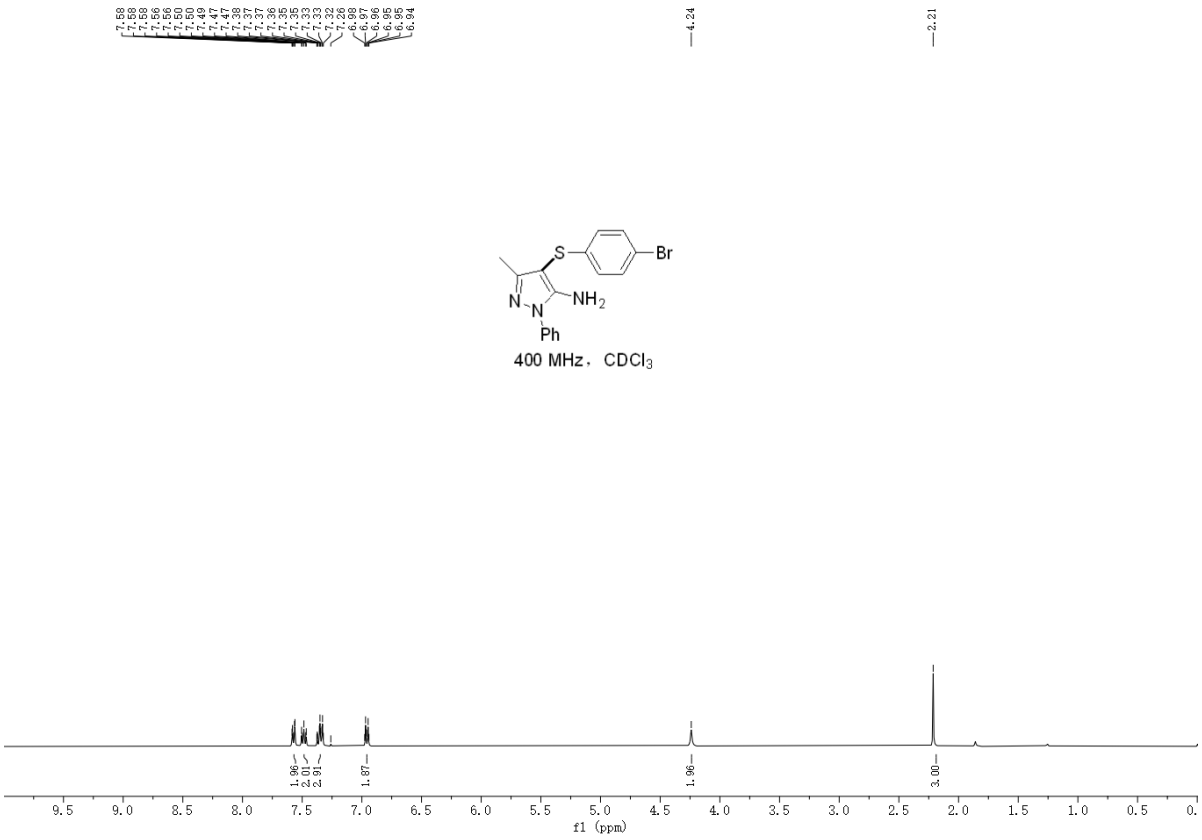
3ae-^{1}H NMR



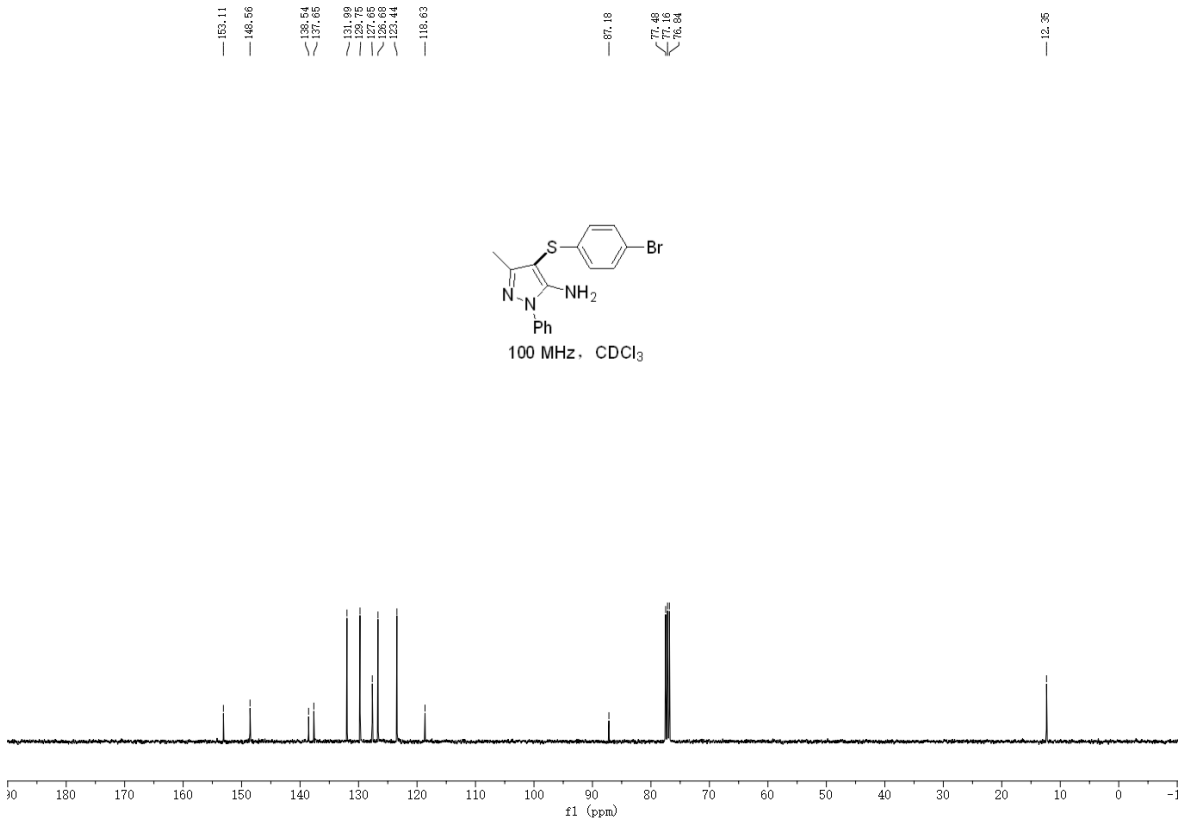
3ae-^{13}C NMR



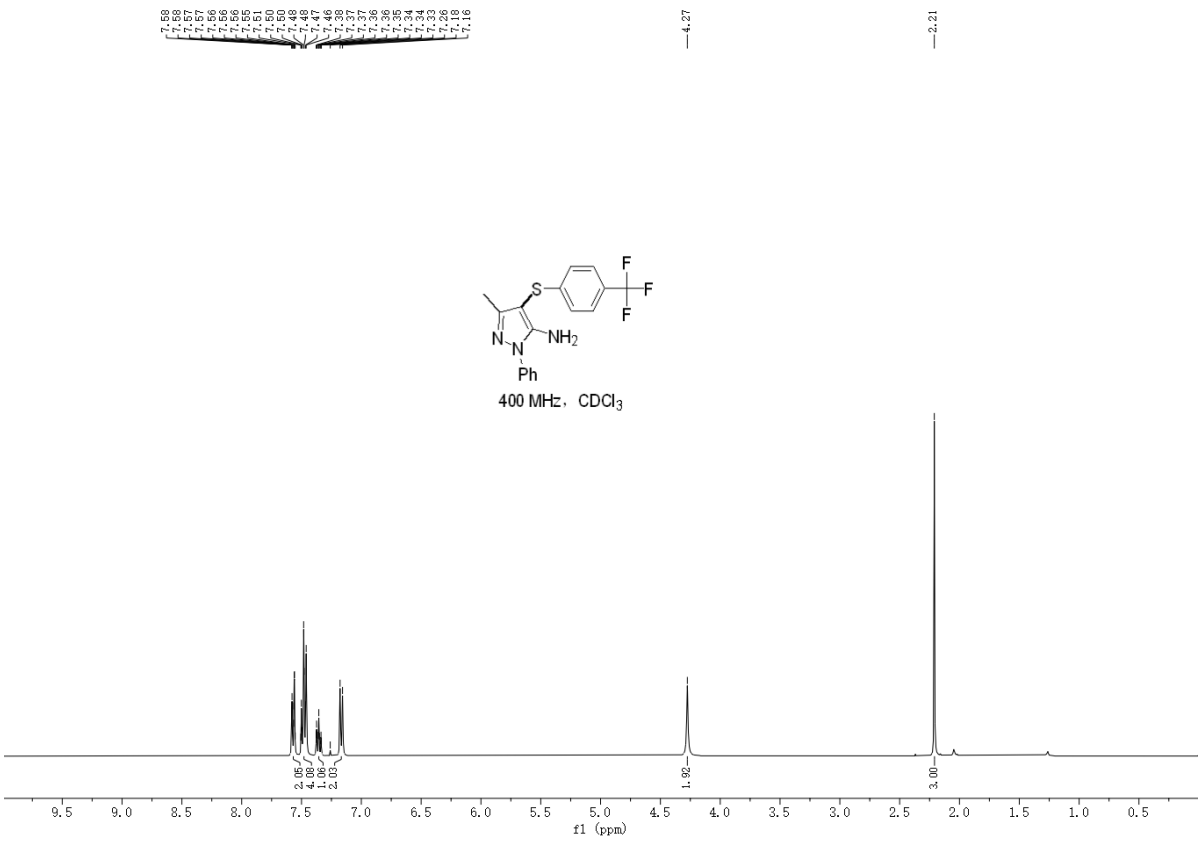
3af-^{1}H NMR



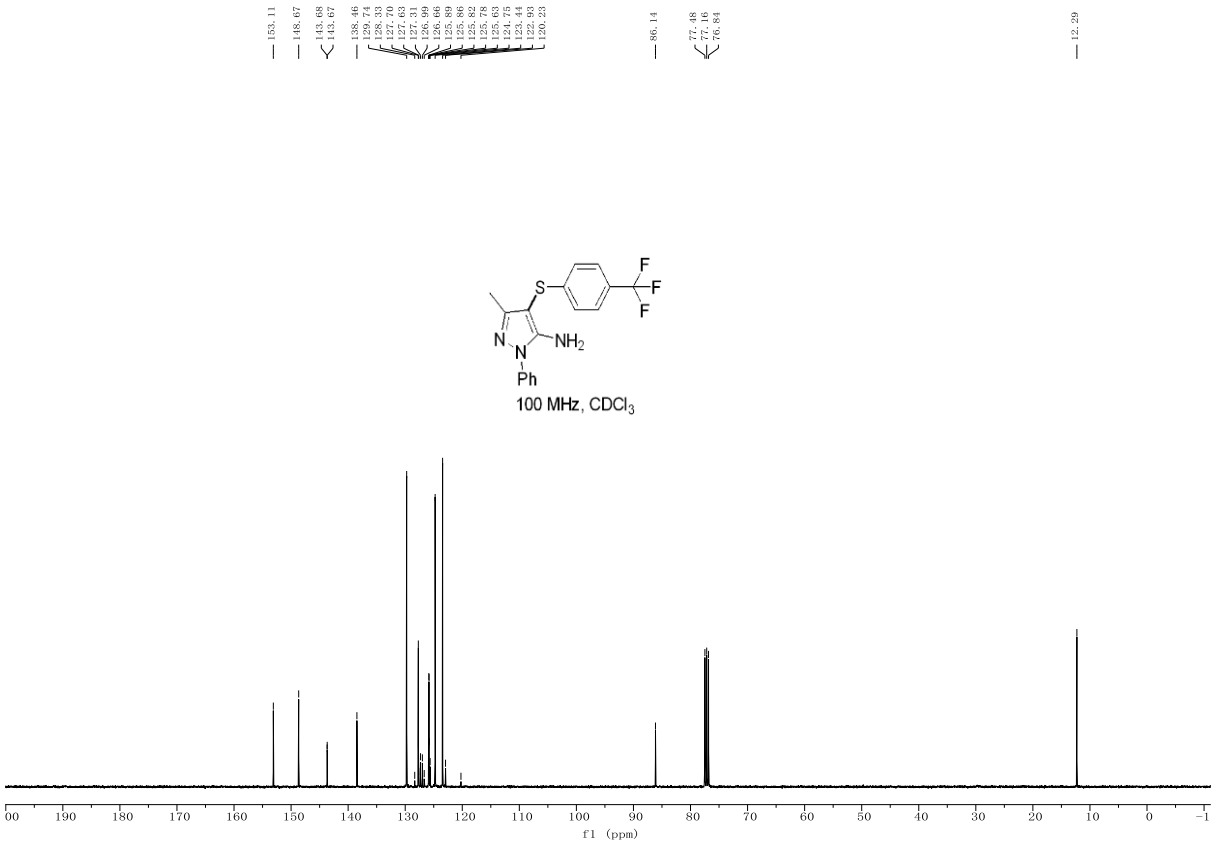
3af-^{13}C NMR



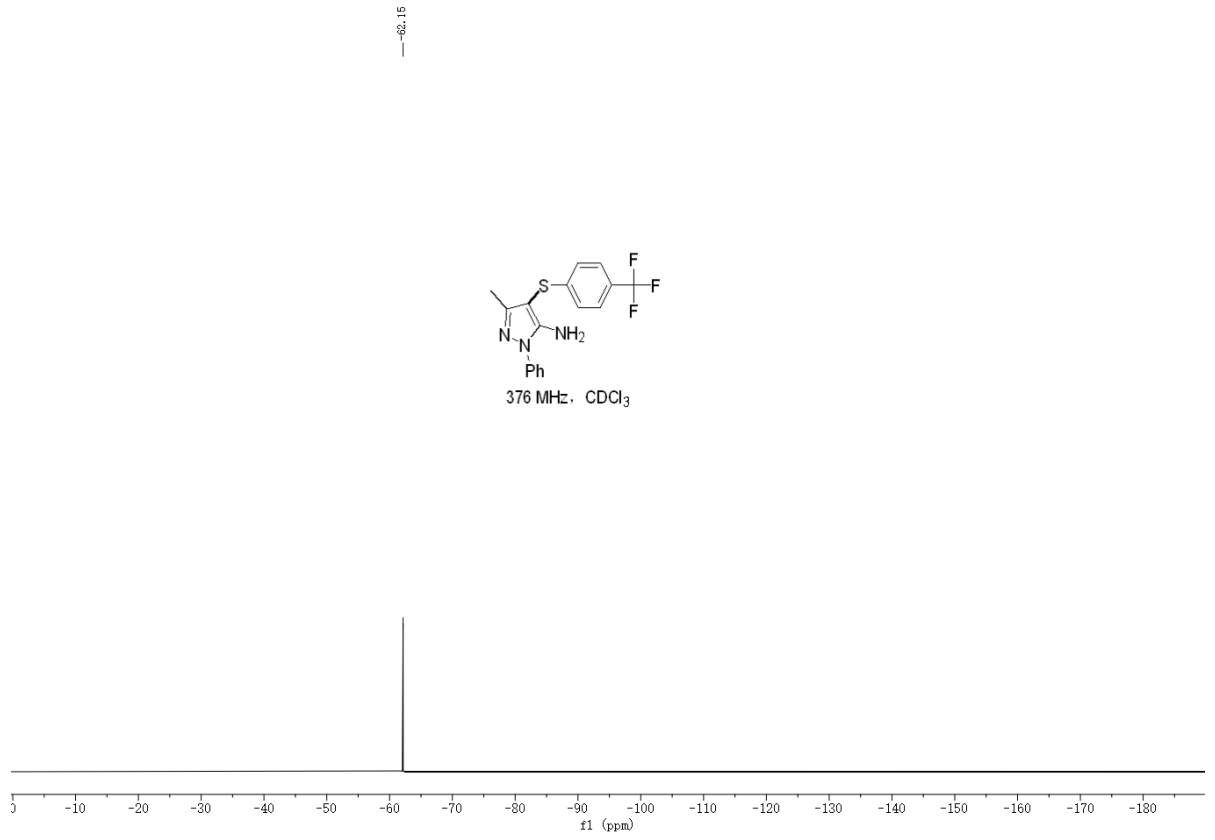
3ag-^{1}H NMR



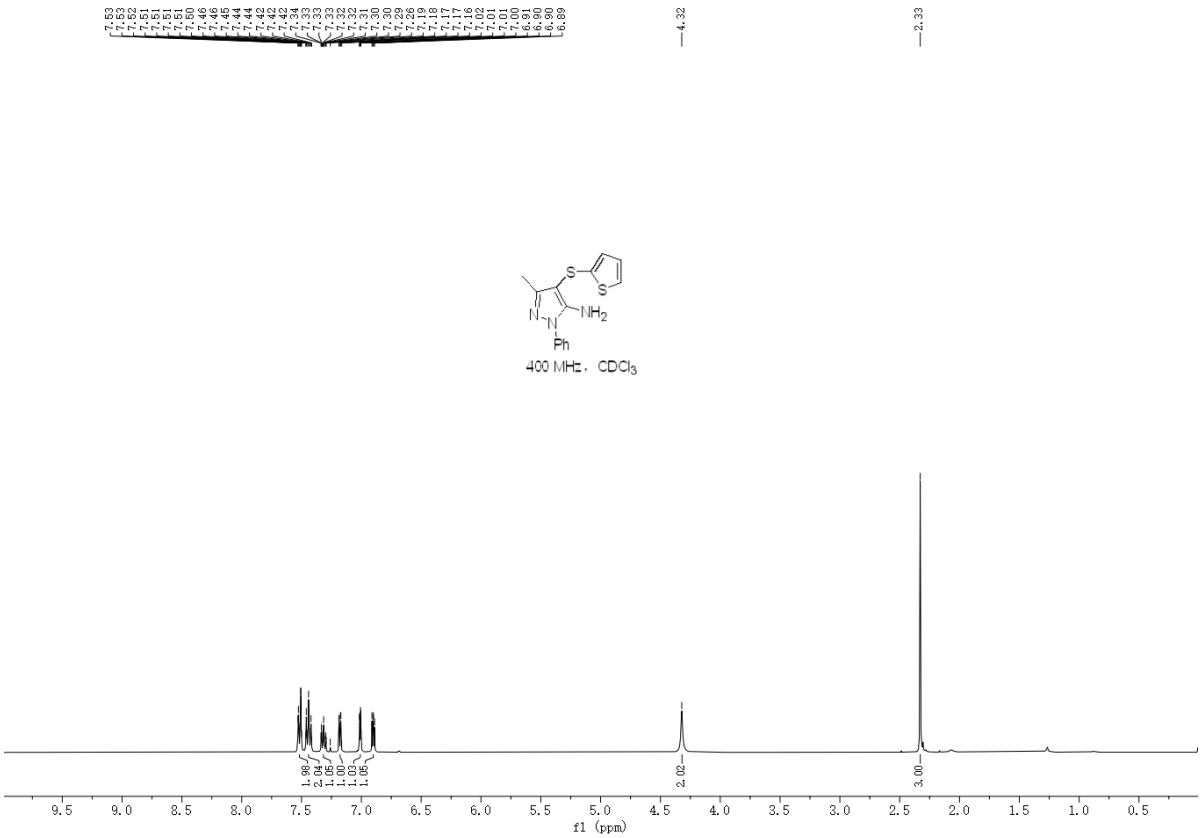
3ag-^{13}C NMR



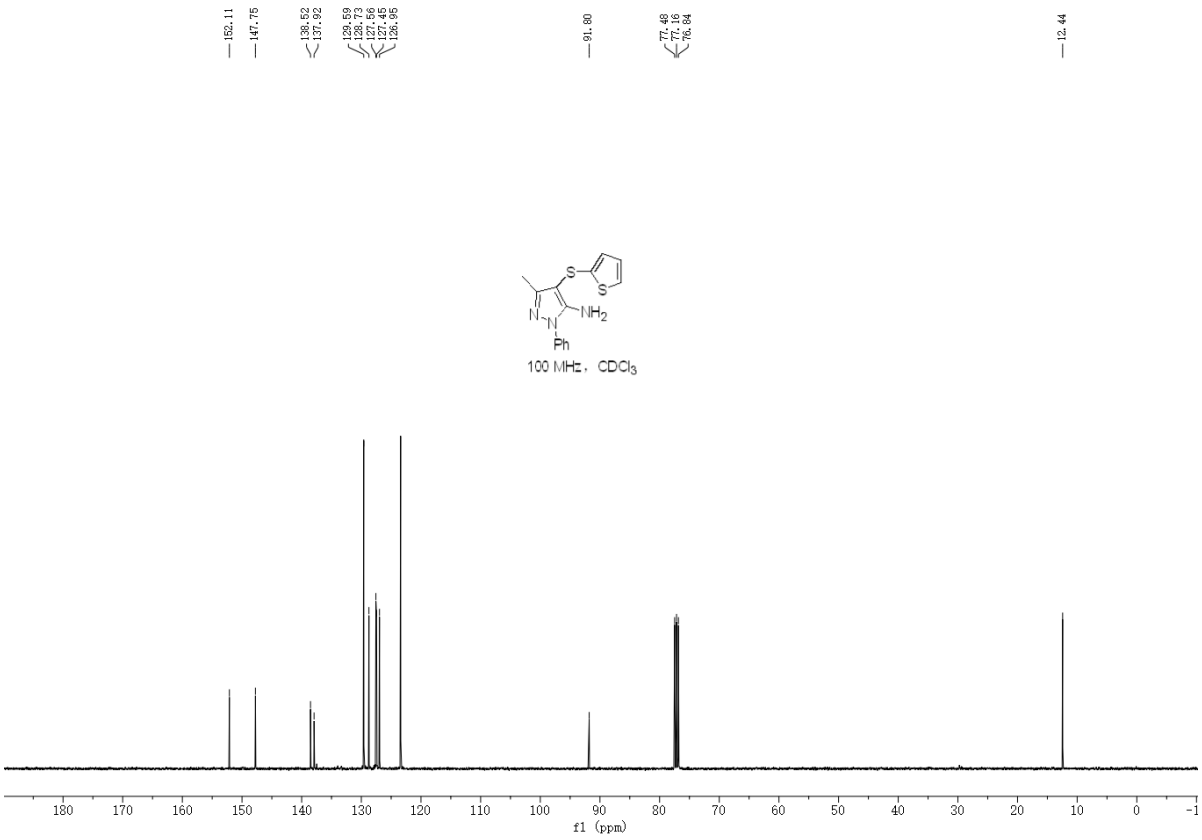
3ag-^{19}F NMR



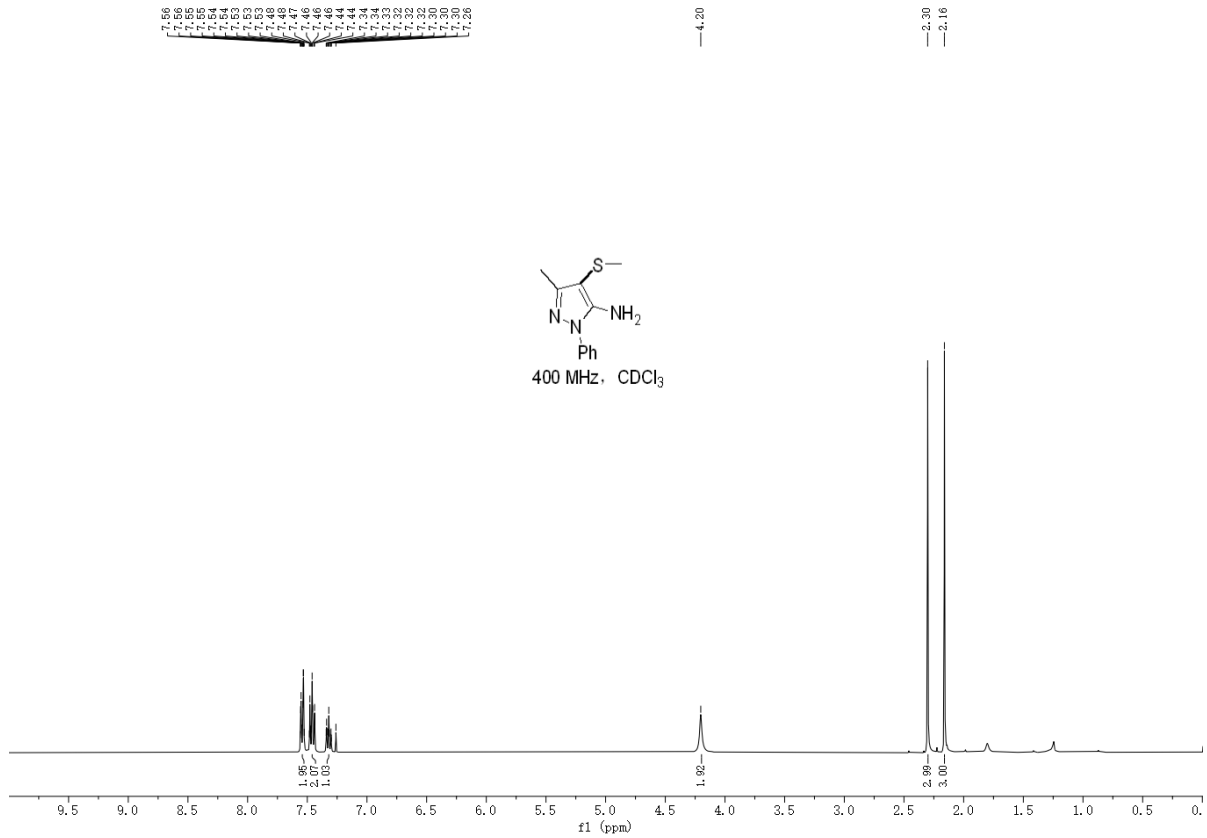
3ah-^{1}H NMR



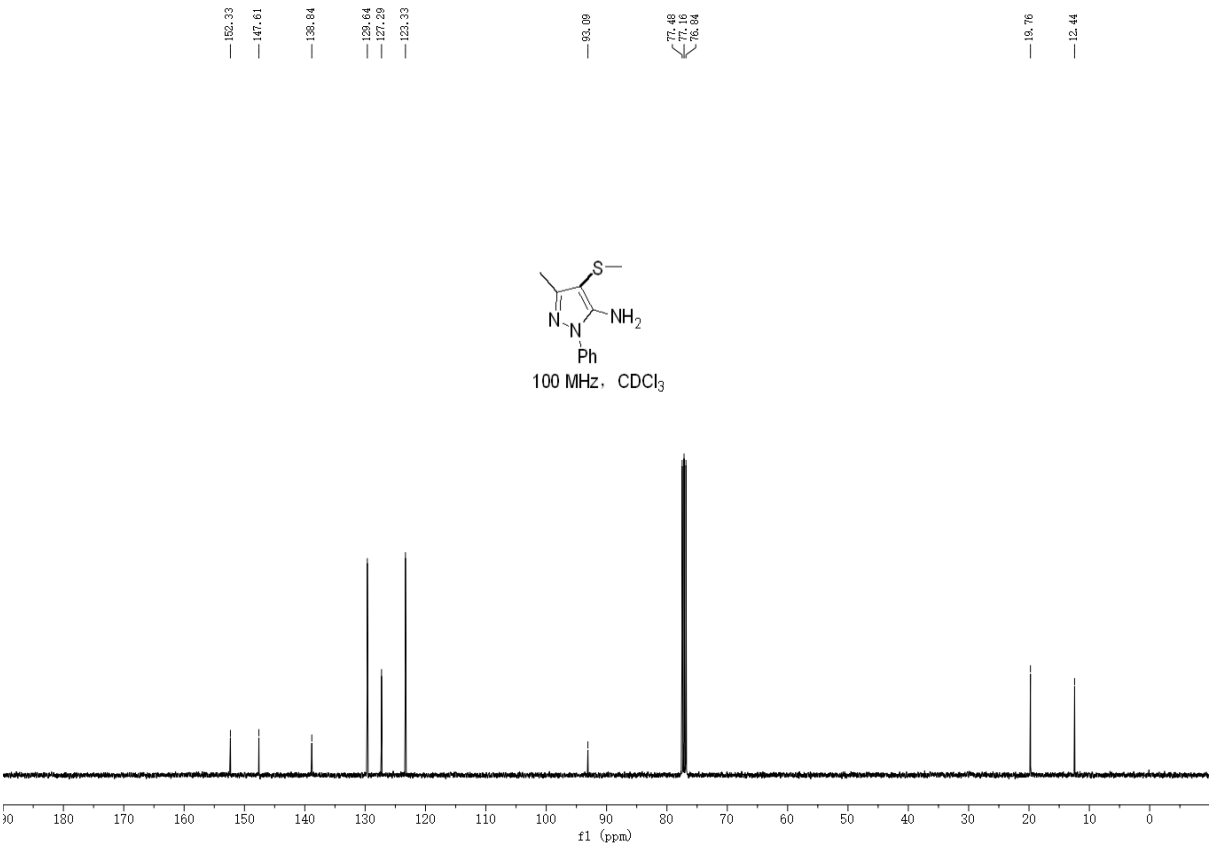
3ah-^{13}C NMR



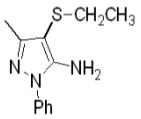
3ai-^{1}H NMR



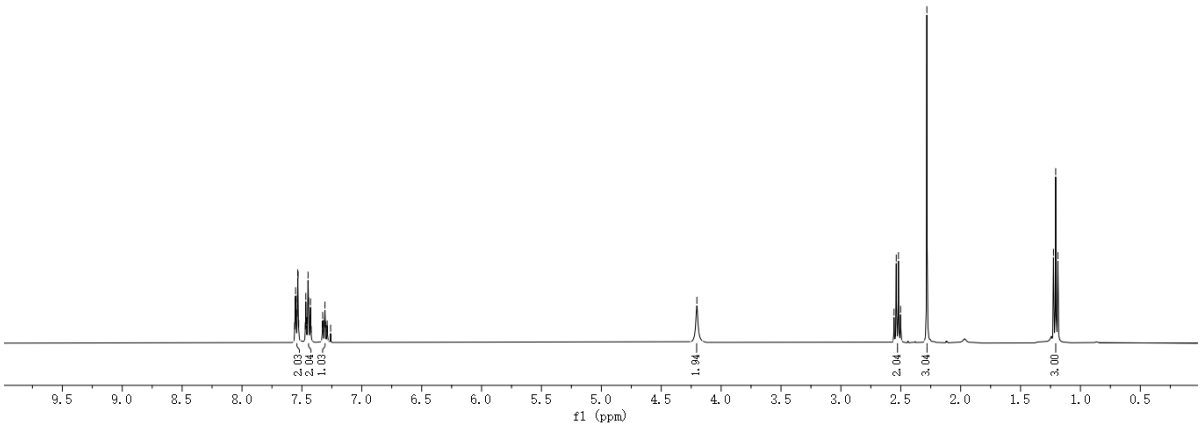
3ai-^{13}C NMR



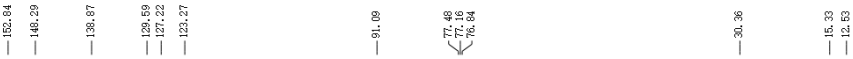
3aj-^{1}H NMR

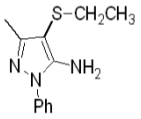


400 MHz，$CDCl_3$

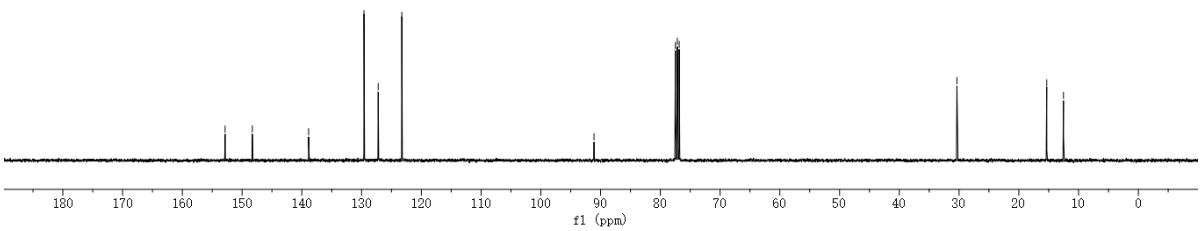


3aj-^{13}C NMR

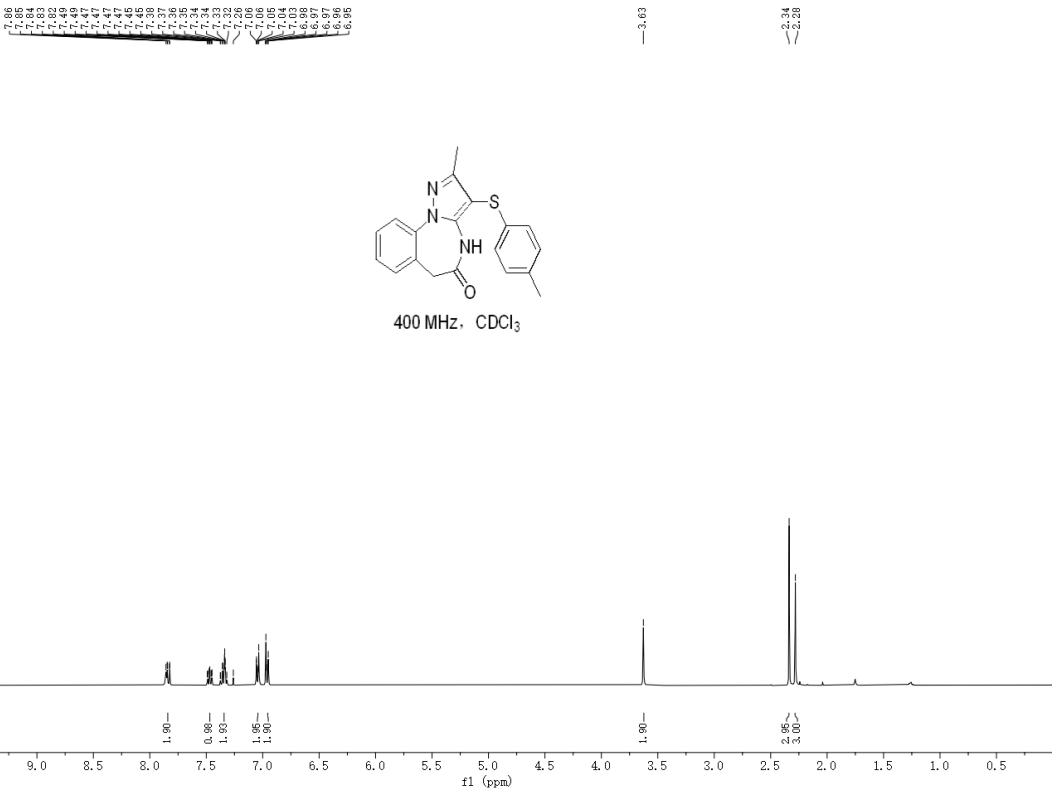




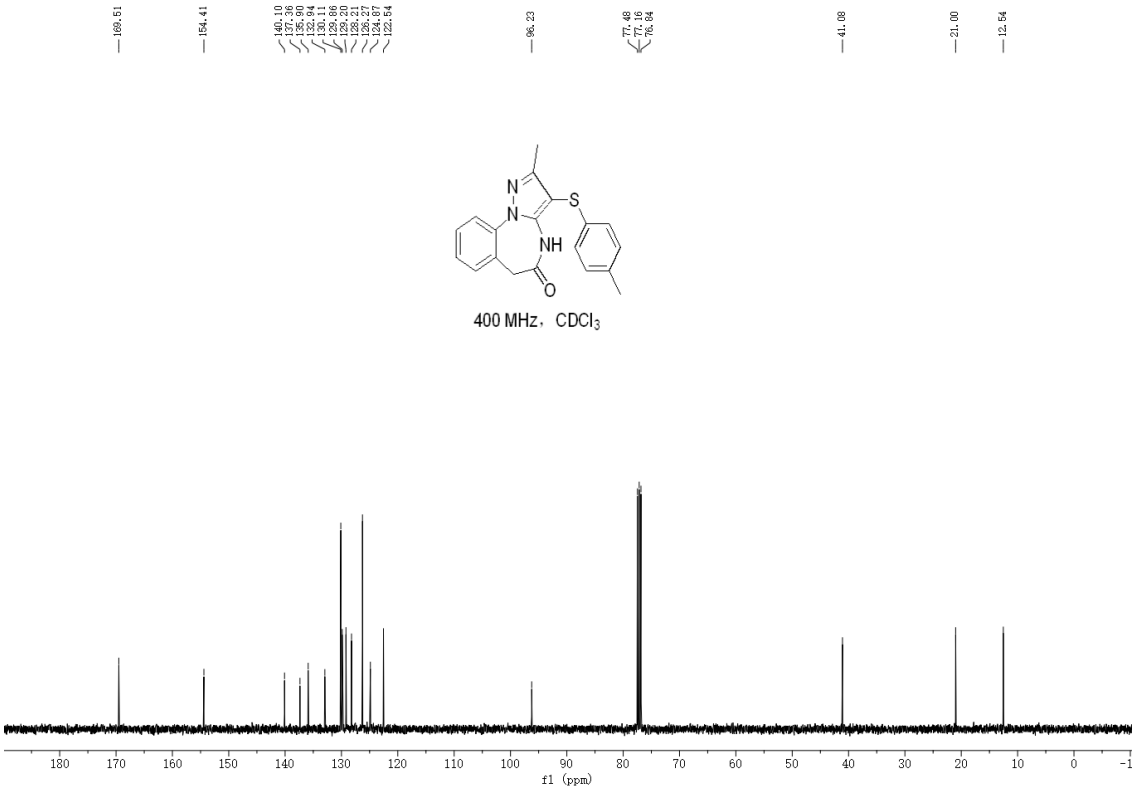
100 MHz，$CDCl_3$



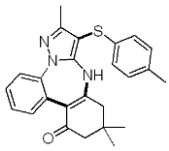
5-^{1}H NMR



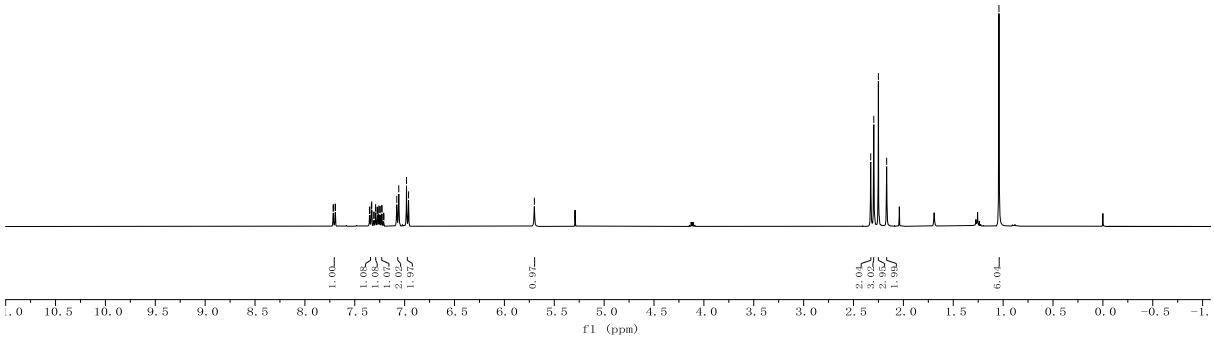
5-^{13}C NMR



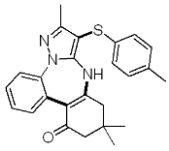
6-^{1}H NMR



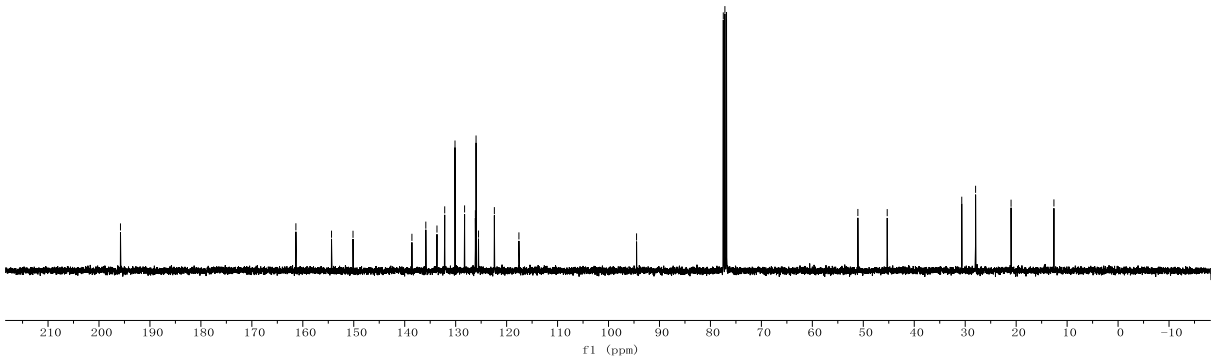
400 MHz, $CDCl_3$



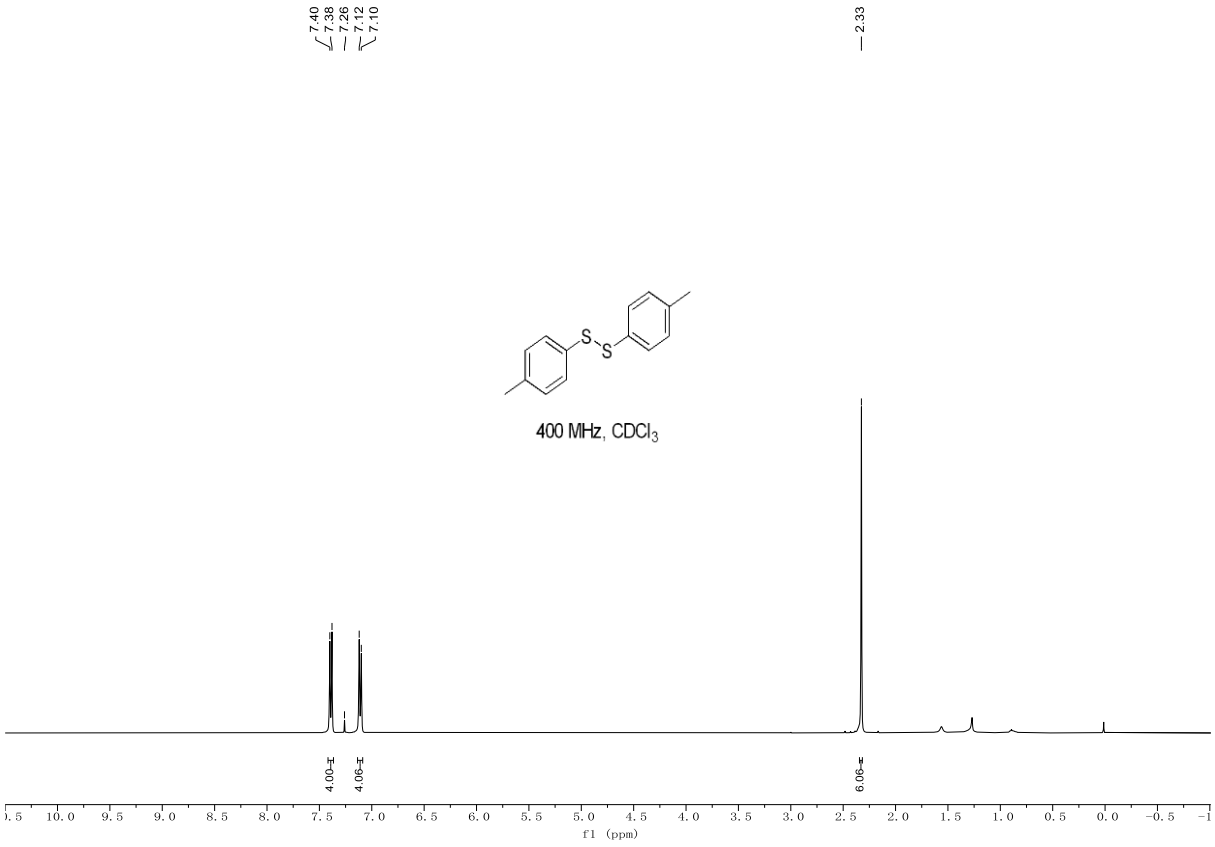
6-^{13}C NMR



100 MHz, $CDCl_3$



2A'-^{1}H NMR



2A'-^{13}C NMR