Electronic Supplementary Information

Iodine-Dependent Oxidative Regioselective Aminochalcogenation of Indolines

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MATERIALS AND METHODS

1. General information.

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 50–60 °C at an appropriate pressure. Purified compounds were further dried under vacuum (10^{-6}–10^{-3} bar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

Solvents

All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification and used as received.

Chromatography

Thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254) was performed using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light and I_2 stain. Column chromatography was performed on silica gel (200-300 mesh).

Spectroscopy and Instruments

NMR spectra were recorded on Bruker-400/500/600 spectrometer operating at (600 MHz, 565 MHz and 151 MHz) for 1H, 19F and 13C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ^{1}H-NMR: $CDCl_3$, 7.26; For ^{13}C-NMR: $CDCl_3$, 77.16; ^{19}F-NMR spectra were referenced using a unified chemical shift scale based on the 1H resonance of tetramethylsilane (1% v/v solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration.

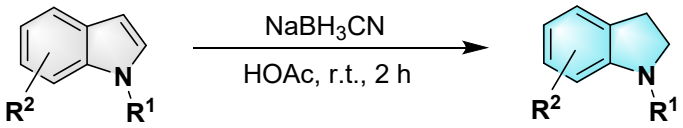
Instrument

All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

EXPERIMENTAL DATA

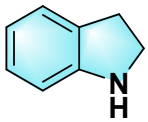
2. Substrates preparation.

(1) General Procedure for the preparation of indoline derivatives (1a-1n)[1]:



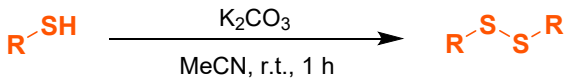
Procedure for indoline (1f): To a suspended solution of indole (1.33 g, 11.4 mmol) in HOAc (20.0 mL), $NaBH_3CN$ (1.89 g, 35.0 mmol) was added dropwise at 0 °C. The heterogeneous mixture was stirred for 2 h at room temperature. Quenched with saturated NH_4Cl (20.0 mL), and extracted with ether (4 × 75.0 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel (petroleum ether) afforded **1f** as a yellow oil. Similarly, the other indoline derivatives were prepared from the corresponding indoles.

NMR Spectroscopy (1f):



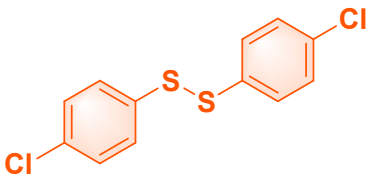
^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.60 (q, *J* = 8.4 Hz, 3H), 3.10 (t, *J* = 8.4 Hz, 2H), known compound.

(2) General Procedure for the preparation of disulfide derivatives (3a-3q)[2]:



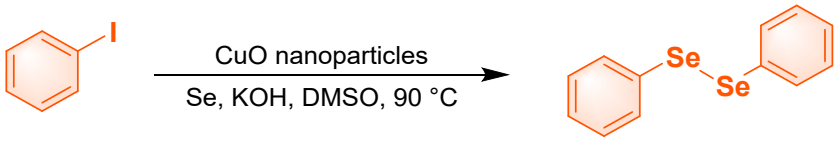
Procedure for 1,2-bis(4-chlorophenyl)disulfane (3e): To a round bottle (50 mL) were added 4-chlorobenzenethiol (5.0 mmol), anhydrous potassium carbonate (0.69 g, 5.0 mmol), and MeCN (10 mL) sequentially, and the reaction was conducted at room temperature under air atmosphere for 1 hour. And the desired disulfides were obtained quantitatively, after filter and concentration. Other disulfide derivatives were prepared in a similar approach.

NMR Spectroscopy (3e):



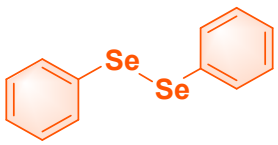
[1]H-NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), known compound.

(3) General Procedure for the preparation of 1,2-diphenyldiselane (3r)[3]:



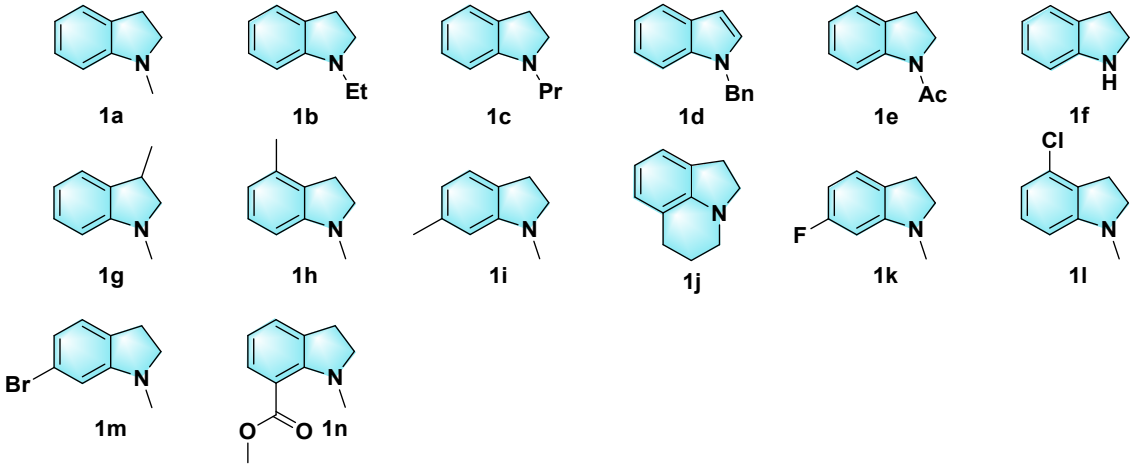
Procedure for 1,2-diphenyldiselane (3r): To a stirred solution of Se metal (2.0 mmol) and iodobenzene (1.0 mmol) in dry DMSO (2.0 mL) was added CuO nanoparticles (10.0 mol%) followed by KOH (2.0 equiv) under argon atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and it was then quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on a silica gel column chromatography (Pet Ether) to give the pure diselenides.

NMR Spectroscopy (3r):

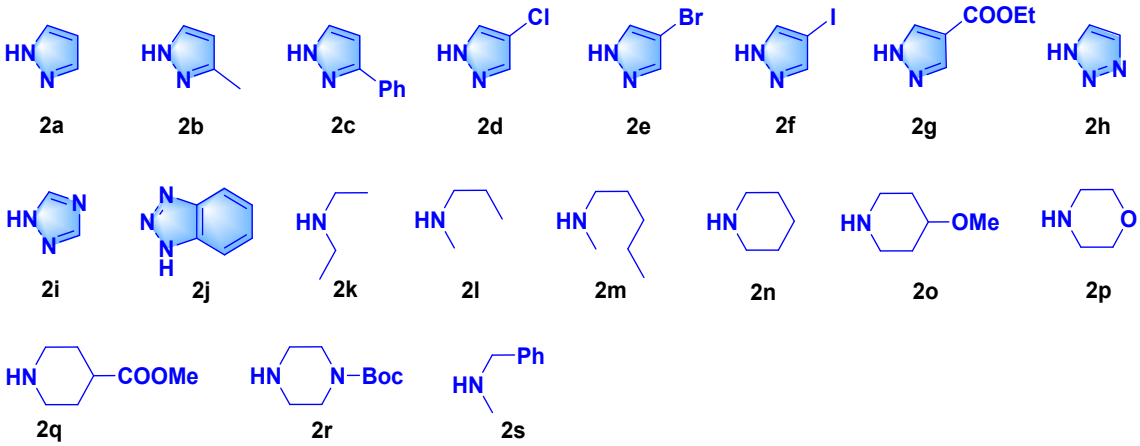


[1]H-NMR (600 MHz, Chloroform-*d*) δ 7.81–7.52 (m, 4H), 7.36–7.24 (m, 6H), known compound.

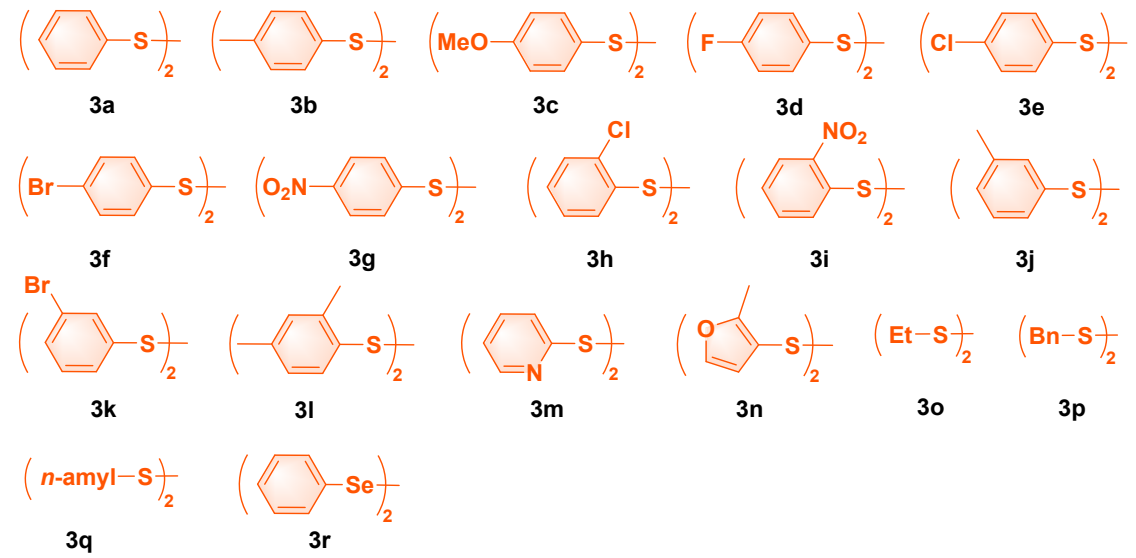
Scheme S1. Scope of indolines.



Scheme S2. Scope of amines and *N*-containing heterocycles.

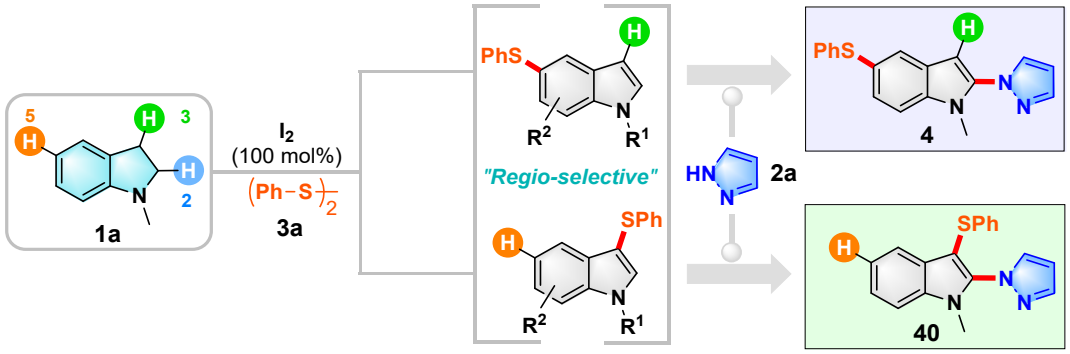


Scheme S3. Scope of disulfides.



3. Optimization of reaction conditions.

Table S1. Optimization of the reaction conditions.[a]

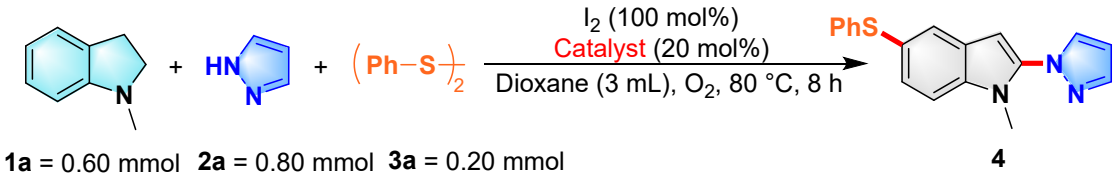


Entry	Catalyst	Solvent	4(%) [b]	40 (%) [b]
1	CuCl	1,4-dioxane	43	-
2	CuBr	1,4-dioxane	50	-
3	CuI	1,4-dioxane	62	-
4	$CuBr_2$	1,4-dioxane	59	-
5	CuI	1,4-dioxane	trace	48 [c]
6	CuI	*Other sol.*	-	< 48 [c]
7	CuI	*Other sol.*	< 62	-
8	CuI	DCE	74	-
9	CuI	DCE	(55, 61) [d]	-
10	CuI	DCE	(64, 70) [e]	-
11	CuI	DCE	(79, **93**, 67) [f]	-
12	CuI	1,4-dioxane	-	71 [c, g]

[a]Reaction conditions, unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), I_2 (100 mol%), catalyst (20 mol%) and solvent (3.0 mL) were stirred at 80 °C under O_2 for 8 h. [b]Isolated yield. [c]DDQ (2.0 equiv.) were added. [d]At 60 °C and 100 °C. [e]80 mol% and 120 mol% of I_2, respectively. [f]10 h, 12 h and 14 h of reaction time, respectively. [g]**1a** (0.20 mmol) and I_2 (30 mol%) were used.

Details:

Table S2. Screening the catalyst of reaction.[a]

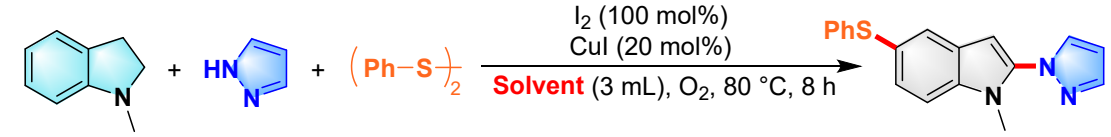


Entry	Catalyst	Yield (%)[b]
1	CuCl	43
2	CuBr	50
3	**CuI**	**62**
4	$CuCl_2$	26
5	$CuBr_2$	59

6	$Cu(OTf)_2$	17
7	$Cu(OAc)_2$	23
8	-	trace

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), **catalyst** (20 mol%), I_2 (100 mol%) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 8 h. [b]Isolated yield.

Table S3. Screening the solvent of reaction.[a]

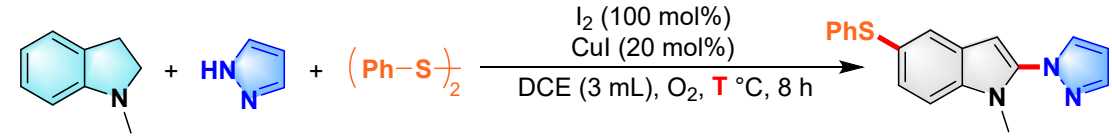


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	Solvent	Yield (%)[b]
1	CH_3CN	trace
2	**DCE**	**74**
3	DMF	trace
4	DMSO	22
5	Toluene	68

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%) and **solvent** (3.0 mL) were stirred at 80 °C under O_2 for 8 h. [b]Isolated yield.

Table S4. Screening the temperature of reaction.[a]

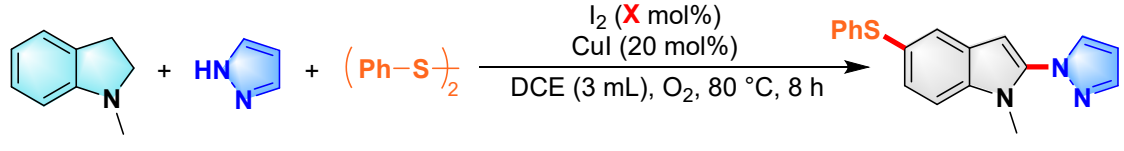


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	T [°C]	Yield (%)[b]
1	60	55
2	100	61

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%) and 1,4-dioxane (3.0 mL) were stirred at **T** °C under O_2 for 8 h. [b]Isolated yield.

Table S5. Screening the amount of I_2.[a]

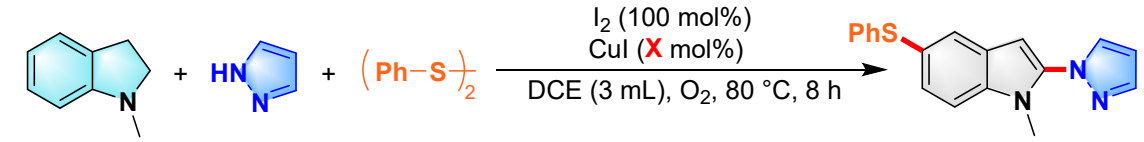


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	X (mol %)	Yield (%)[b]
1	80	64
2	120	70

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (**X** mol%) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 8 h. [b]Isolated yield.

Table S6. Screening the amount of CuI.[a]

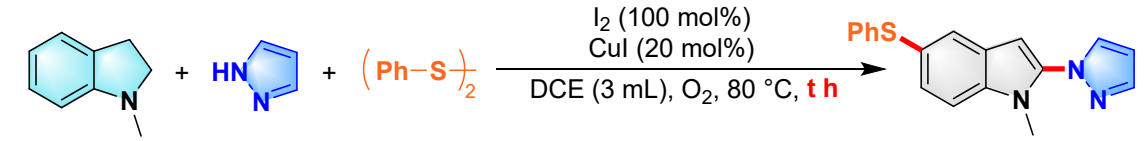


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	X (mol %)	Yield (%)[b]
1	10	32
2	30	72

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (**X** mol%), I_2 (100 mol%) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 8 h. [b]Isolated yield.

Table S7. Screening the reaction time.[a]

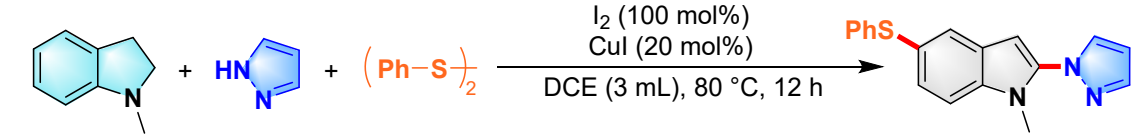


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	t (h)	Yield (%)[b]
1	10	79
2	**12**	**93**
3	14	67

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for **t h**. [b]Isolated yield.

Table S8. Screening Air and N_2 atmosphere.[a]



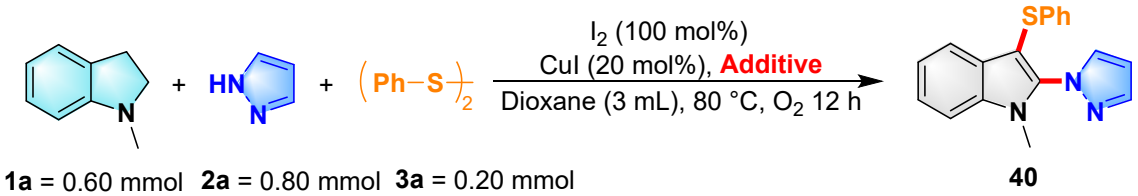
1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	atmosphere	Yield (%)[b]
1	Air	47

2	N_2	14

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under **Air** or **N_2** for 12 h. [b]Isolated yield.

Table S9. Screening the additives of reaction.[a]

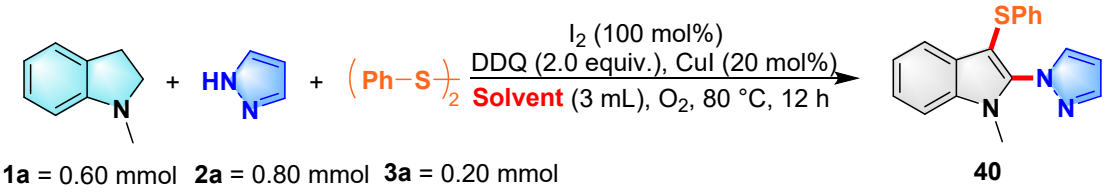


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **40**

Entry	Additives	Yield (%)[b]
1	DMSO (1 mL)	trace
2	$K_2S_2O_8$ (2.0 equiv.)	trace
3	TBHP (2.0 equiv.)	trace
4	**DDQ** (2.0 equiv.)	**48**

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%), 1,4-dioxane (3.0 mL) and **additives** were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

Table S10. Screening the solvent of reaction.[a]

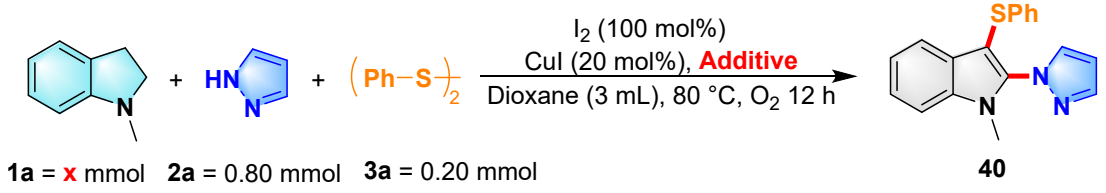


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **40**

Entry	Solvent	Yield (%)[b]
1	CH_3CN	trace
2	DCE	24
3	DMF	trace
4	DMSO	trace
5	Toluene	31

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%), DDQ (2.0 equiv.) and **solvent** (3.0 mL) were stirred at 80 °C under O_2 for12 h. [b]Isolated yield.

Table S11. Screening the amount of 1a.[a]



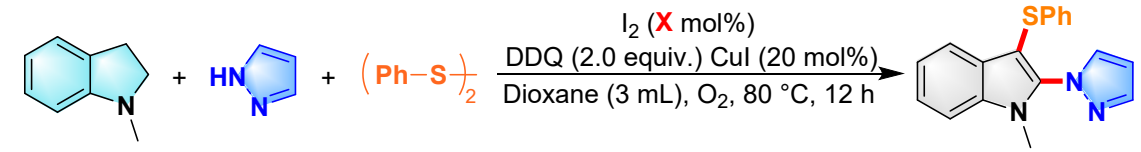
1a = **x** mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **40**

Entry	x (mmol)	Yield (%)[b]

1	0.50	53
2	0.40	56
3	0.30	60
4	**0.20**	**64**

[a]Reaction conditions unless specified otherwise: **1a** (x mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (100 mol%) DDQ (2.0 equiv.) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

Table S12. Screening the amount of I_2.[a]



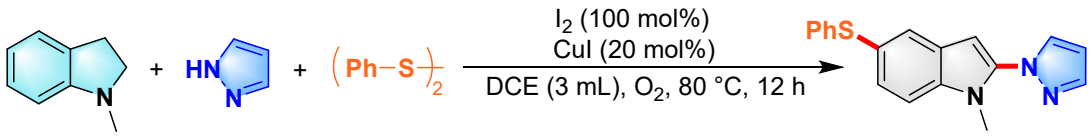
1a = 0.20 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **40**

Entry	X (mol %)	Yield (%)[b]
1	80	59
2	50	68
3	**30**	**71**
4	10	59

[a]Reaction conditions unless specified otherwise: **1a** (0.20 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%), I_2 (X mol%) DDQ (2.0 equiv.) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

4. Typical procedure for the synthesis of 4 and 40

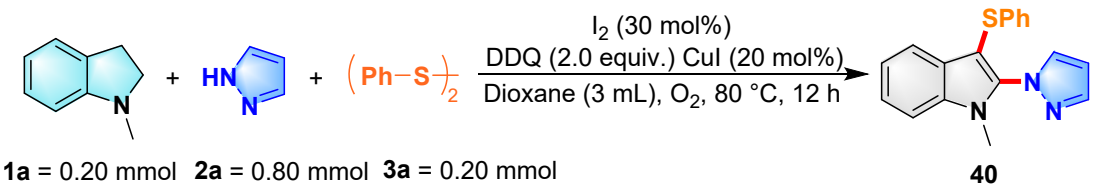
(1) Typical procedure for the synthesis of 4:



1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

The mixture of 1-methylindoline **1a** (79.8 mg, 0.60 mmol), **2a** (54.5 mg, 0.80 mmol), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%, 7.6 mg), I_2 (100 mol%, 50.6 mg) and DCE (3.0 mL) were stirred at 80 °C under O_2 for 12 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/acetic ether (10:1) as the eluent to give **4** as a white solid (113.5 mg, 93% yield).

(2) Typical procedure for the synthesis of 40:



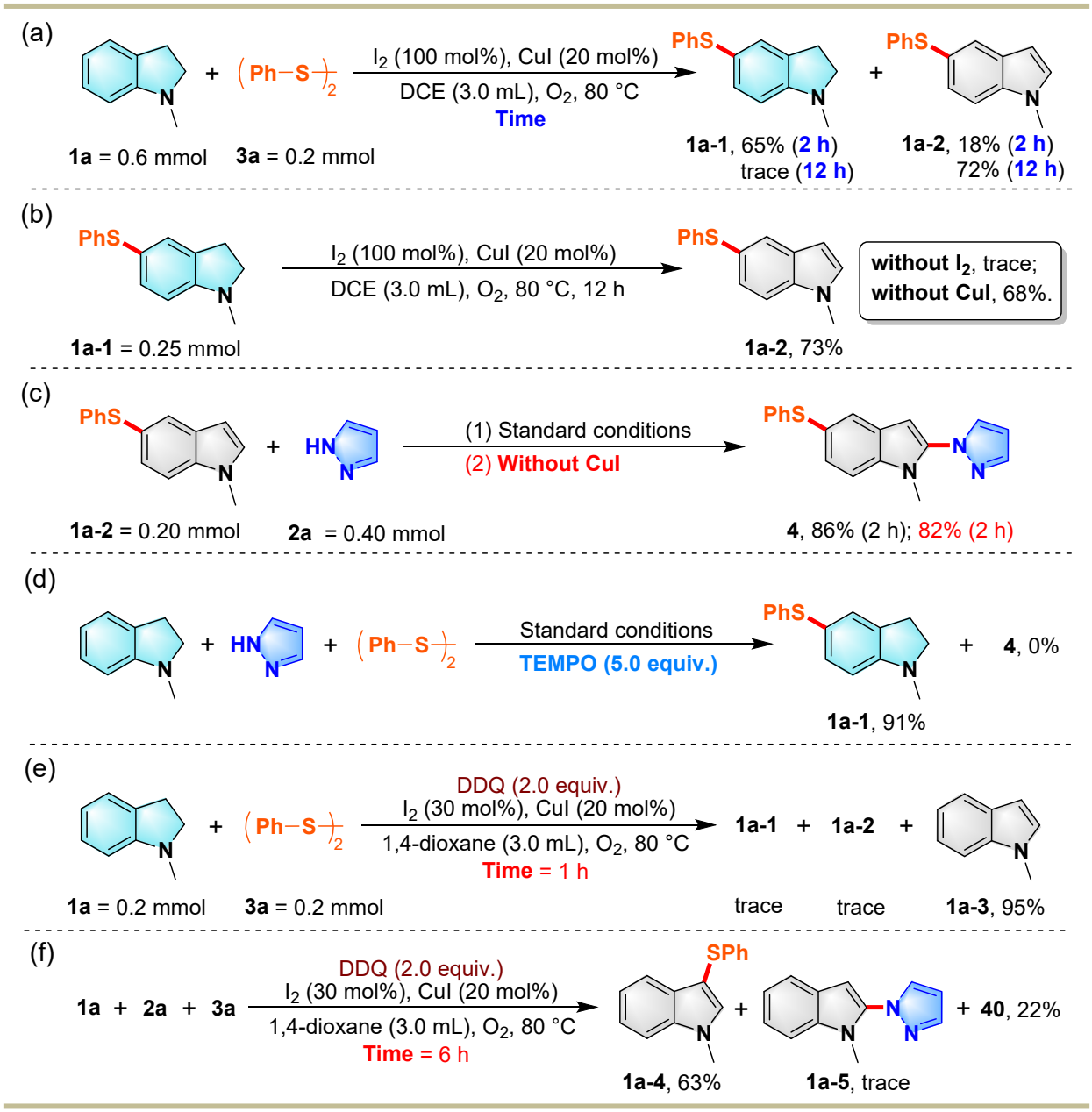
1a = 0.20 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol

40

The mixture of 1-methylindoline **1a** (26.6 mg, 0.20 mmol), **2a** (54.5 mg, 0.80 mmol), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%,7.6 mg), I_2 (30 mol%, 15.2 mg) DDQ (2.0 equiv., 90.8 mg) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 12 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/acetic ether (10:1) as the eluent to give **40** as a white solid (43.3 mg, 71% yield).

5. Control experiments.

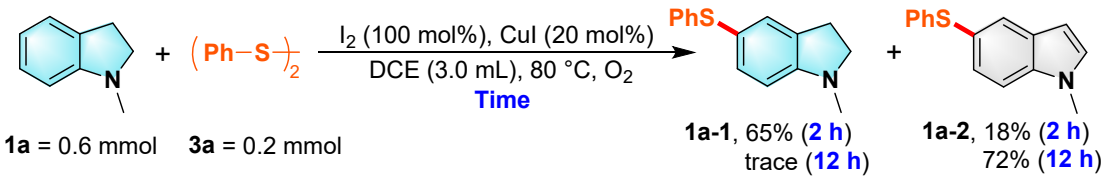
Scheme S4. Control experiments.



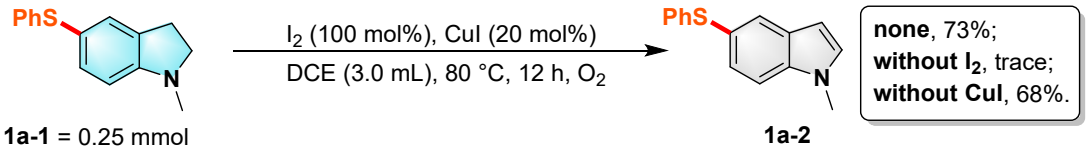
Details:

(1) Under the optimized reaction conditions, the reaction of **1a** (79.8 mg, 0.60 mmol) and **3a** (43.6 mg, 0.20 mmol) were carried. Then, the crude reaction mixture was analyzed by TLC in 2 and 12 hours respectively. The reaction mixture **(2 h)** was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10:1) to give product **1a-1** as yellow liquid (62.7 mg, 65% yield) and **1a-2** as white solid (17.2 mg, 18% yield). The reaction mixture **(12 h)** was purified by preparative TLC on

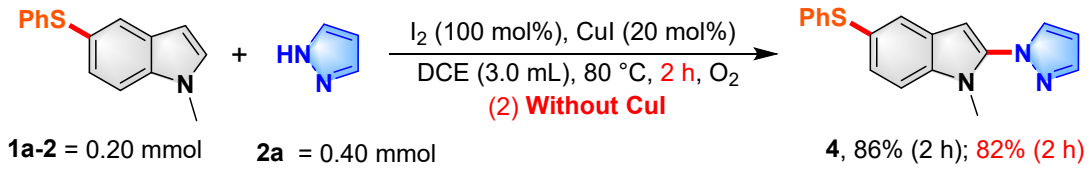
silica eluting with petroleum ether/acetic ether (10:1) to give product **1a-2** as white solid (68.8 mg, 72% yield) and **1a-1** (trace).



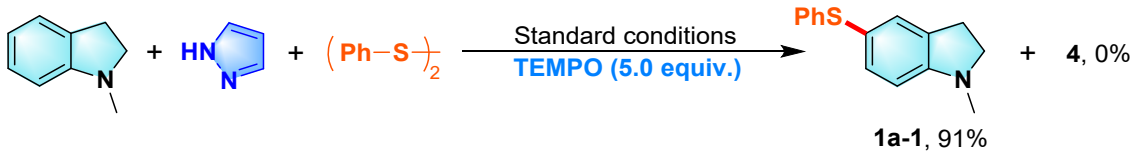
(2) Under the optimized reaction conditions, 1-methyl-5-(phenylthio)indoline **1a-1** (60.3 mg, 0.25 mmol) underwent the reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10:1), resulting in a yield of (73%, 43.6 mg) for product **1a-2**. It is worth noting that in the absence of iodine (I_2), only trace amounts of product **1a-2** were obtained, while in the absence of CuI, the yield of product **1a-2** was (68%, 40.6 mg).



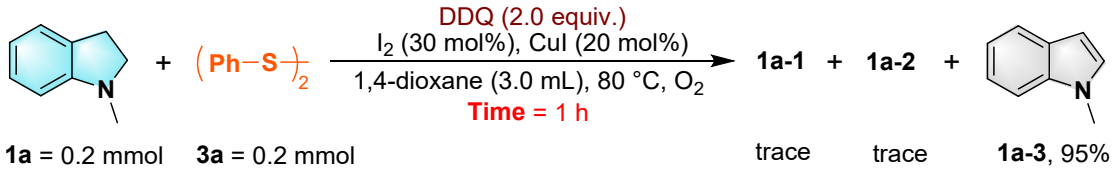
(3) Under the optimized reaction conditions, 1-methyl-5-(phenylthio)-1*H*-indole **1a-2** (47.8 mg, 0.20 mmol) and pyrazol **2a** (27.2 mg, 0.4 mmol) were reacted for 2 hours, then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10:1), resulting in a yield of 86% for product **4** (52.5 mg). It is worth noting that in the absence of CuI, the yield of product **4** can also reach 82% (50.0 mg). .



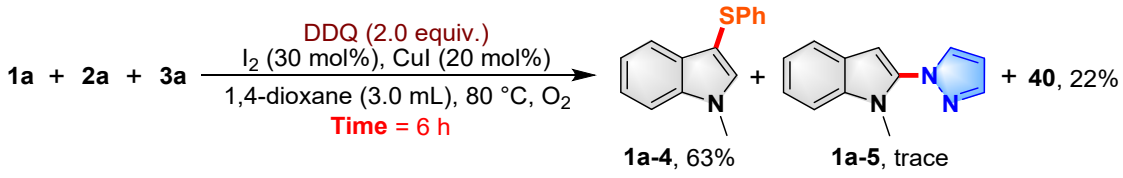
(4) Under the standard conditions, the radical trapping reagents, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10:1) to give product **1a-1** as yellow liquid (87.7 mg, 91% yield). However, product **4** was not obtained.



(5) The mixture of 1-methylindoline **1a** (26.6 mg, 0.20 mmol), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%,7.6 mg), I_2 (30 mol%, 15.2 mg) DDQ (2.0 equiv., 90.8 mg) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 1 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/acetic ether (10:1) as the eluent to give trace amount of **1a-1** and **1a-2**, as well as 95% yield of **1a-3** as yellow liquid (24.9 mg).

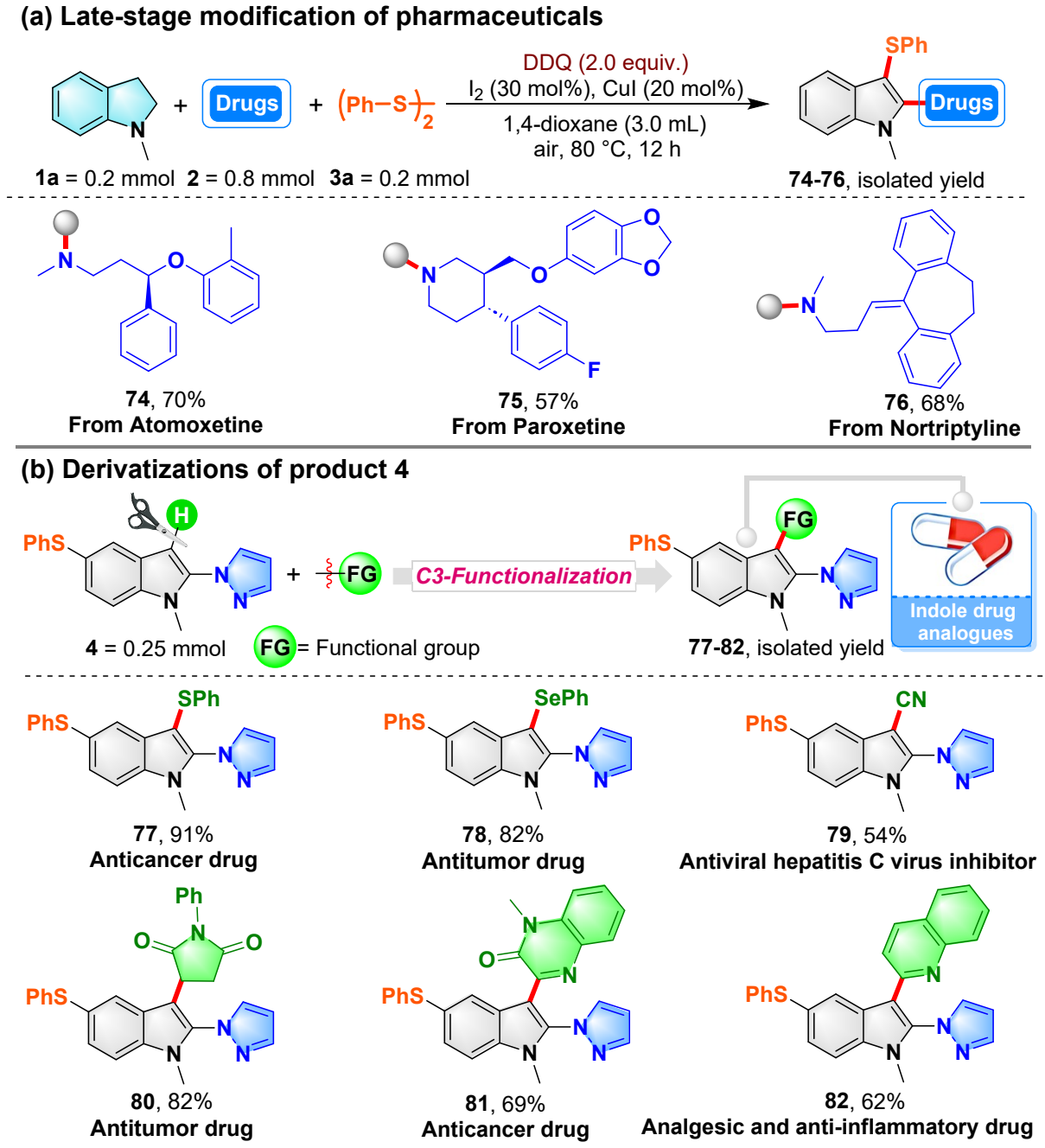


(6) The mixture of 1-methylindoline **1a** (26.6 mg, 0.20 mmol), **2a** (54.5 mg, 0.80 mmol), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%,7.6 mg), I_2 (30 mol%, 15.2 mg) DDQ (2.0 equiv., 90.8 mg) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 6 h. The resultant mixture was concentrated by evaporating the solvent under vacuum, and the remaining residue was further purified using preparative TLC on silica gel. Petroleum ether/acetic ether (10:1) was used as the eluent for this purification step. As a result, product **1a-4** was obtained with a yield of 63% (30.1 mg), and a trace amount of **1a-5** was also observed. Additionally, product **40** was obtained with a yield of 22% (13.4 mg).



6. Synthetic utility.

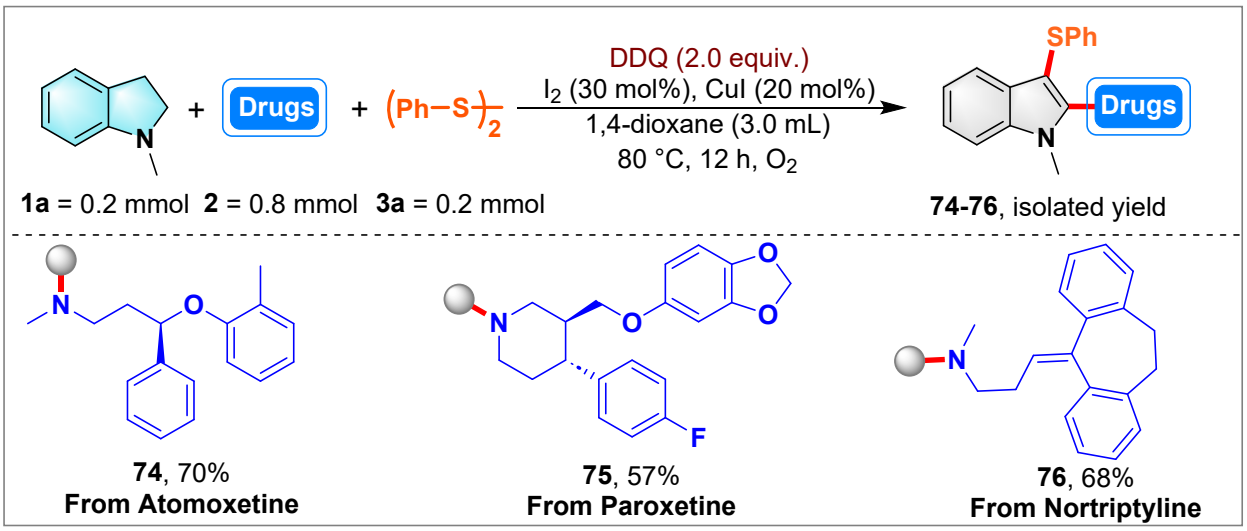
Scheme S5. Synthetic applications and derivatizations.



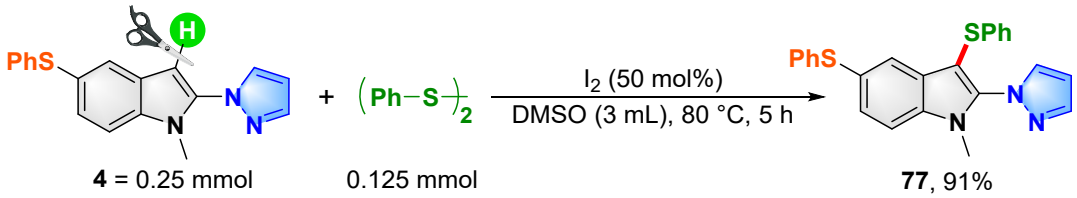
Details:

(1) The mixture of 1-methylindoline **1a** (26.6 mg, 0.20 mmol), drugs (0.80 mmol, including atomoxetine, paroxetine and nortriptyline), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%,7.6 mg), I_2 (30 mol%, 15.2 mg) DDQ (2.0 equiv., 90.8 mg) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2

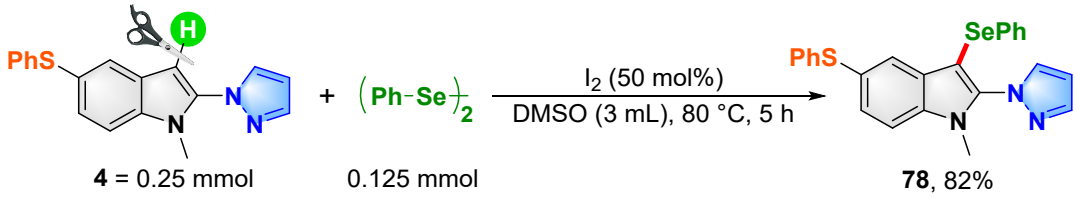
for 12 h. The mixture obtained after solvent evaporation under vacuum was subjected to purification by thin-layer chromatography on silica gel using a eluent consisting of petroleum ether/ethyl acetate (10:1). As a result, three products, namely **74** (68.9 mg, 70%), **75** (64.5 mg, 57%), and **76** (68.0 mg, 68%), were successfully separated and isolated, respectively.



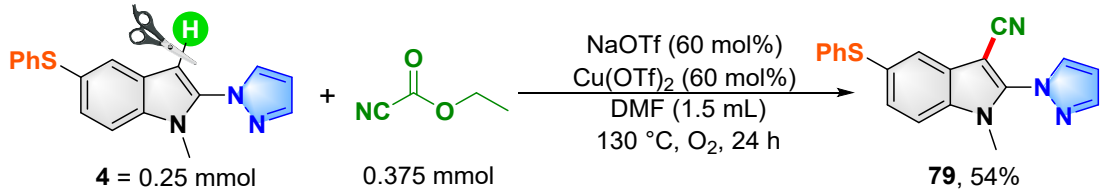
(2) To a solution of **4** (76.3 mg, 0.25 mmol) in DMSO (3.0 mL) was added 1,2-diphenyldisulfane (27.3 mg, 0.125 mmol), I_2 (50 mol%, 31.6 mg). After stirring at 80 °C for 5 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **77** as a white solid (94.0 mg, 91% yield).



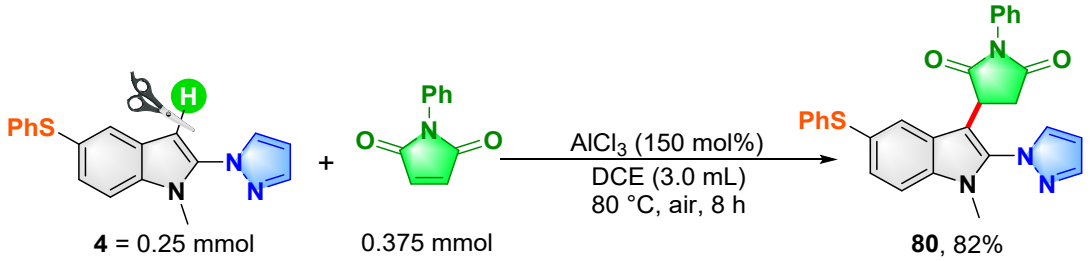
(3) To a solution of **4** (76.3 mg, 0.25 mmol) in DMSO (3.0 mL) was added 1,2-diphenyldiselane (39.1 mg, 0.125 mmol), I_2 (50 mol%, 31.6 mg). After stirring at 80 °C for 5 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **78** as a white solid (94.5 mg, 82% yield).



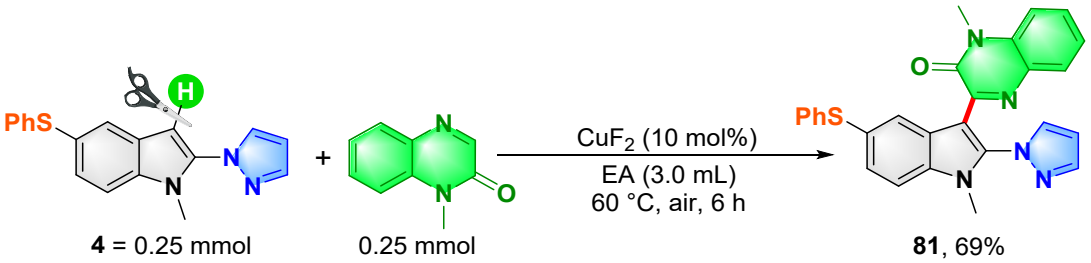
(4) To a solution of **4** (76.3 mg, 0.25 mmol) in DMF (1.5 mL) was added ethyl carbonocyanidate (37.1 mg, 0.375 mmol), NaOTf (60 mol%, 25.8 mg) and $Cu(OTf)_2$ (60 mol%, 54.3 mg). After stirring at 130 °C for 24 h under O_2, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **79** as a white solid (44.6 mg, 54% yield).



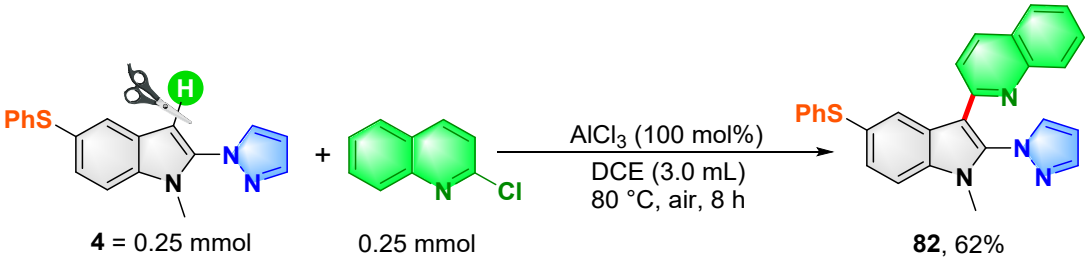
(5) To a solution of **4** (76.3 mg, 0.25 mmol) in DCE (3.0 mL) was added 1-phenyl-1*H*-pyrrole-2,5-dione (64.9 mg, 0.375 mmol) and $AlCl_3$ (150 mol%, 50.0 mg). After stirring at 80 °C for 8 h under air the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **80** as a yellow solid (98.0 mg, 82% yield).



(6) To a solution of **4** (76.3 mg, 0.25 mmol) in EA (3.0 mL) was added 1-methylquinoxalin-2(1*H*)-one 40.0 mg, 0.25 mmol) and CuF_2 (10 mol%, 2.5 mg). After stirring at 60 °C for 6 h under air the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate/petroleum (1:5) as eluent to afford the pure product **81** as a yellow solid (79.9 mg, 82% yield).



(7) To a solution of **4** (76.3 mg, 0.25 mmol) in DCE (3.0 mL) was added 2-chloroquinoline (40.8 mg, 0.25 mmol) and $AlCl_3$ (100 mol%, 33.3 mg). After stirring at 80 °C for 8 h under air the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **82** as a white solid (67.0 mg, 62% yield).



7. Single crystal X-ray diffraction

(1) Single crystal X-ray diffraction of 10

White block-like single crystals of **10** were grown by layering a dichlormethane solution with *n*-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 293(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 25.242°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below.

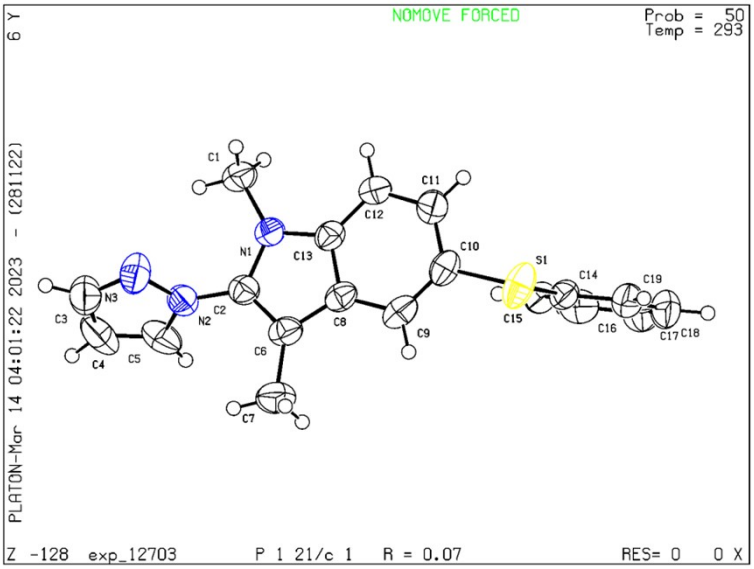


Figure S1. ORTEP drawing of **10** with the numbering scheme.

Table S13. Crystal data and structure refinement for **10**

Identification code	10	
Empirical formula	$C_{19}H_{17}N_3S$	
Formula weight	319.41	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.7135(7) Å	α = 90°.
	b = 22.940(2) Å	β = 100.290(11)°.
	c = 9.6284(11) Å	γ = 90°.
Volume	1821.5(3) $Å^3$	
Z	4	
F(000)	672.0	
Crystal size	0.20x 0.14 x 0.10 mm^3	
2^{Θ} range for data collection	7.106 to 58.88	
Index ranges	-10≤h≤7, -31≤k≤30, -11≤l≤13	
Reflections collected	8754	
Independent reflections	3848 [Rint = 0.0410, Rsigma = 0.0634]	
Data / restraints / parameters	3848/0/210	
Goodness-of-fit on F^2	1.041	
Final R indices [I>=2^{σ}(I)]	R1 = 0.0707, wR2 = 0.1590	
Final R indices (all data)	R1 = 0.1152, wR2 = 0.1860	
Largest diff. peak and hole	0.47/-0.37 e.$Å^{-3}$	

Table S14. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters

(Å^2×10^3) for **10**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2025.1(10)	1598.5(4)	5914.8(8)	67.0(3)
N1	6682(3)	3143.0(10)	3387(2)	45.6(6)
N2	6600(3)	4191.6(10)	3140(3)	49.5(6)
N3	8244(3)	4385.3(12)	3733(3)	67.7(7)
C2	5925(3)	3675.0(12)	3607(3)	44.7(6)
C14	516(3)	1322.7(12)	4458(3)	44.9(6)
C8	4388(3)	2991.6(13)	4477(3)	45.5(7)
C15	373(3)	1520.5(13)	3089(3)	48.8(7)
C13	5737(3)	2718.1(12)	3916(3)	44.7(6)
C6	4513(3)	3606.7(13)	4269(3)	49.4(7)
C9	3231(3)	2640.1(14)	5093(3)	52.2(7)
C12	5959(4)	2114.8(13)	3934(3)	55.6(8)
C19	-614(4)	886.2(13)	4763(4)	57.8(8)
C10	3435(3)	2051.4(14)	5115(3)	51.1(7)
C11	4806(4)	1787.2(14)	4535(3)	58.0(8)
C1	8190(4)	3045.4(14)	2687(4)	59.7(8)
C5	5794(5)	4566.4(14)	2160(4)	66.9(9)
C16	-885(4)	1285.9(14)	2035(3)	61.3(8)
C18	-1863(4)	658.3(15)	3705(4)	69.7(9)
C3	8400(5)	4885.8(16)	3095(4)	73.3(10)
C17	-2021(4)	858.8(16)	2345(4)	71.0(10)
C4	6917(6)	5015.2(14)	2109(4)	78.6(11)
C7	3359(4)	4068.3(16)	4690(4)	77.4(11)

Table S14. Anisotropic Displacement Parameters (Å^2×10^3) for **10**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	54.7(5)	99.1(7)	45.1(5)	13.1(4)	2.9(3)	-26.6(5)
N1	39.4(11)	45.8(13)	52.8(14)	4.7(11)	11.6(10)	2.9(10)
N2	49.0(13)	43.3(13)	54.9(14)	-1.8(11)	6.2(11)	0.4(11)
N3	58.7(16)	67.7(18)	75.8(18)	4.9(15)	9.6(14)	-18.2(14)
C2	40.5(13)	45.7(16)	45.5(15)	-1.5(13)	1.3(12)	2.0(12)
C14	35.7(13)	49.0(15)	50.1(16)	2.4(13)	7.5(11)	-0.9(12)
C8	33.7(12)	57.9(18)	42.7(15)	-5.4(13)	1.1(11)	-1.0(12)
C15	44.3(14)	54.0(17)	48.1(16)	3.4(13)	8.5(13)	0.3(13)
C13	35.2(13)	50.9(16)	47.0(15)	2.1(13)	4.5(12)	0.0(12)
C6	39.8(14)	57.3(18)	50.0(16)	-12.1(14)	5.1(12)	2.8(13)
C9	38.0(14)	76(2)	43.2(15)	-7.7(15)	9.6(12)	-3.4(14)

C12	44.4(15)	51.7(18)	74(2)	3.4(15)	20.1(14)	6.7(14)
C19	53.1(17)	55.3(18)	67(2)	7.2(15)	16.2(15)	-3.3(15)
C10	39.7(14)	66(2)	46.0(16)	-0.2(14)	3.1(12)	-10.9(14)
C11	49.3(16)	53.6(18)	71(2)	5.5(15)	9.4(15)	-3.5(15)
C1	52.4(17)	59.2(18)	73(2)	5.8(16)	27.7(16)	7.9(15)
C5	80(2)	47.1(18)	69(2)	3.8(16)	-1.0(18)	18.3(17)
C16	60.5(18)	69(2)	52.2(18)	-6.6(16)	4.1(15)	7.2(17)
C18	61(2)	59(2)	92(3)	-13.6(19)	18.8(19)	-19.2(17)
C3	79(2)	59(2)	90(3)	-9(2)	36(2)	-15.7(19)
C17	56.6(19)	75(2)	77(2)	-23(2)	0.6(17)	-6.4(18)
C4	121(3)	37.2(17)	83(3)	4.5(17)	33(2)	8(2)
C7	62(2)	70(2)	104(3)	-22(2)	26(2)	7.8(18)

Table S16. Bond Lengths for **10**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	**C14**	1.772(3)	**C8**	**C6**	1.431(4)
S1	**C10**	1.776(3)	**C8**	**C9**	1.410(4)
N1	**C2**	1.386(3)	**C15**	**C16**	1.382(4)
N1	**C13**	1.369(3)	**C13**	**C12**	1.394(4)
N1	**C1**	1.461(3)	**C6**	**C7**	1.486(4)
N2	**N3**	1.368(3)	**C9**	**C10**	1.359(4)
N2	**C2**	1.401(3)	**C12**	**C11**	1.368(4)
N2	**C5**	1.344(4)	**C19**	**C18**	1.374(4)
N3	**C3**	1.318(4)	**C10**	**C11**	1.418(4)
C2	**C6**	1.365(4)	**C5**	**C4**	1.352(5)
C14	**C15**	1.380(4)	**C16**	**C17**	1.382(4)
C14	**C19**	1.393(4)	**C18**	**C17**	1.372(5)
C8	**C13**	1.403(4)	**C3**	**C4**	1.382(5)

Table S17. Bond Angles for **10**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	**S1**	**C10**	103.42(13)	**N1**	**C13**	**C12**	129.7(2)
C2	**N1**	**C1**	126.7(2)	**C12**	**C13**	**C8**	122.4(3)
C13	**N1**	**C2**	107.6(2)	**C2**	**C6**	**C8**	104.9(2)
C13	**N1**	**C1**	125.7(2)	**C2**	**C6**	**C7**	127.8(3)
N3	**N2**	**C2**	120.7(2)	**C8**	**C6**	**C7**	127.3(3)
C5	**N2**	**N3**	111.3(3)	**C10**	**C9**	**C8**	119.6(3)
C5	**N2**	**C2**	127.9(3)	**C11**	**C12**	**C13**	117.6(3)
C3	**N3**	**N2**	104.1(3)	**C18**	**C19**	**C14**	120.0(3)
N1	**C2**	**N2**	120.3(2)	**C9**	**C10**	**S1**	120.7(2)

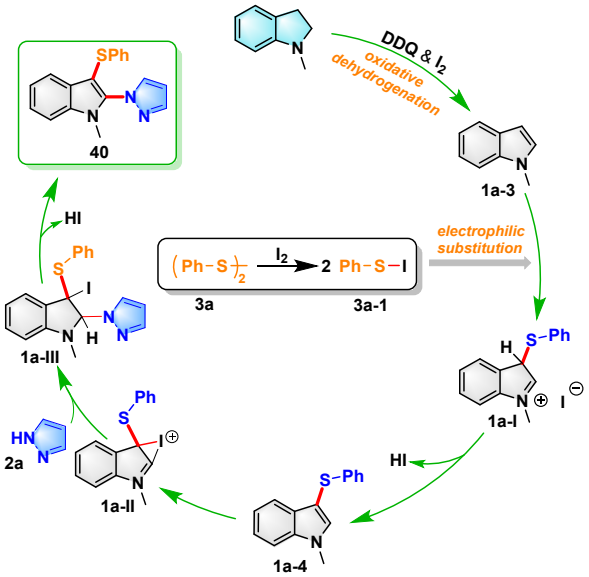
C6	**C2**	**N1**	111.3(2)	**C9**	**C10**	**C11**	120.7(3)
C6	**C2**	**N2**	128.4(3)	**C11**	**C10**	**S1**	118.6(2)
C15	**C14**	**S1**	124.6(2)	**C12**	**C11**	**C10**	121.2(3)
C15	**C14**	**C19**	119.4(3)	**N2**	**C5**	**C4**	107.1(3)
C19	**C14**	**S1**	115.9(2)	**C15**	**C16**	**C17**	120.4(3)
C13	**C8**	**C6**	108.3(2)	**C17**	**C18**	**C19**	120.7(3)
C13	**C8**	**C9**	118.4(3)	**N3**	**C3**	**C4**	111.9(3)
C9	**C8**	**C6**	133.4(3)	**C18**	**C17**	**C16**	119.5(3)
C14	**C15**	**C16**	120.0(3)	**C5**	**C4**	**C3**	105.6(3)
N1	**C13**	**C8**	107.8(2)				

Table S18. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **10.**

Atom	*x*	*y*	*z*	U(eq)
H15	1123.35	1811.53	2875.84	59
H9	2333.37	2810.05	5482.77	63
H12	6857.25	1941.25	3552.46	67
H19	-523.11	749.09	5681.76	69
H11	4925.52	1383.77	4563.11	70
H1A	8524.51	3406.87	2307.62	89
H1B	7874.65	2768.84	1935.92	89
H1C	9159.95	2896.26	3357.75	89
H5	4674.06	4524.98	1620.01	80
H16	-967.34	1416.13	1110.72	74
H18	-2608.44	364.95	3912.88	84
H3	9391.02	5123.58	3285.97	88
H17	-2885.92	708.63	1638.52	85
H4	6730.45	5342.44	1531.41	94
H7A	3784.03	4443.96	4466.49	116
H7B	3368.46	4044.28	5686.41	116
H7C	2177.32	4014.98	4187.58	116

8. Plausible reaction pathways

Scheme S6. C2,3-aminochalcogenation pathways.



Based on the control experiments results and related studies, the following reaction pathways are proposed. Initially, 1-methylindoline **1a** is converted to 1-methyl-1*H*-indole **1a-3** through rapid oxidative dehydrogenation in the presence of DDQ and I_2. The regio-selectively electrophilic addition of the 1-methyl-1*H*-indole **1a-3** at C3 position by **3a-1** (generating *via* the reaction of **3a** and I_2) generated of the intermediate **1a-I**, followed by reductive elimination of HI affords the product **1a-4**, which then reacts with I_2, leading to the formation of the corresponding iodonium **1a-II**. Nucleophilic attack of pyrazol **2a** at the C2 position of **1-II** yields the formation of **1a-III**. Finally, reductive elimination of intermediate **1-III** produces the target product **40** while liberating HI.

9. Reference.

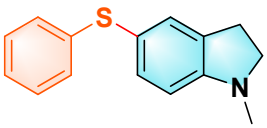
1. H. Y. Li, J. Y. Jie, S. X. Wu, X. B. Yang and H. Xu, Rh(III)-Catalyzed direct C-7 amination of indolines with anthranils. *Org. Chem. Front.*, 2017, **4**, 250–254.

2. W. S. Ouyang, X. Q. Cai, X. J. Chen, J. Wang, J. H. Rao, Y. Gao, Y. P. Huo, Q. Chen and X. W. Li, Sequential C–H activation enabled expedient delivery of polyfunctional arenes. *Chem. Commun.*, 2021, **57**, 8075–8078.

3. D. Singh, A. M. Deobald and L. R. S. Camargo, Tabarelli, G.; Rodrigues, O. E. D.; Braga, A. L. An Efficient One-Pot Synthesis of Symmetrical Diselenides or Ditellurides from Halides with CuO Nanopowder/Se^0 or Te^0/Base. *Org. Lett.*, 2010, **12**, 3288–3291.

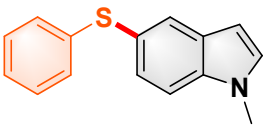
10. Analytic data of the obtained compounds.

(1) 1-methyl-5-(phenylthio)indoline (1a-1)



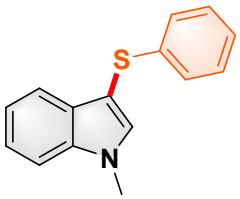
Yellow liquid, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 1H), 7.25–7.22 (m, 3H), 7.17–7.15 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.41 (t, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 8.3 Hz, 2H), 2.83 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.96, 140.48, 135.02, 131.70, 131.00, 128.75, 126.95, 124.99, 118.66, 107.21, 55.83, 35.58, 28.35. **HRMS (ESI):** Calcd. for $C_{15}H_{15}NS$ $[M+H]^+$: 242.0925; found: 242.0919.

(2) 1-methyl-5-(phenylthio)-1*H*-indole (1a-2)



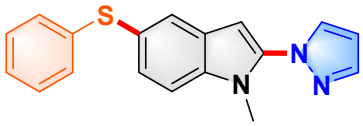
Known compound, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.24–7.21 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 140.04, 136.65, 129.86, 129.48, 128.84, 127.92, 127.75, 127.56, 125.27, 122.33, 110.38, 101.25, 33.03.

(3) 1-methyl-3-(phenylthio)-1*H*-indole (1a-4)



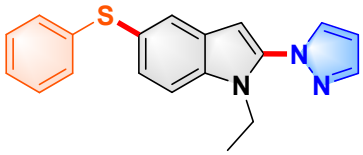
Known compound, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 (s, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.21 (ddt, *J* = 13.2, 7.2, 3.4 Hz, 3H), 7.18–7.15 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 3.87 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.73, 137.60, 135.12, 129.89, 128.71, 125.78, 124.72, 122.62, 120.55, 119.78, 109.79, 100.54, 33.17.

(4) 1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4)



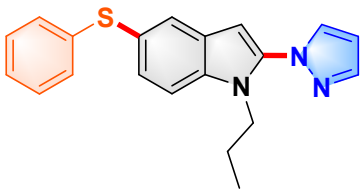
White solid, (113.5 mg, 93% yield), m.p.: 137-138 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.23–7.19 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 6.52 (t, *J* = 2.1 Hz, 1H), 3.74 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.10, 139.46, 136.53, 135.59, 132.33, 128.88, 128.69, 127.89, 127.34, 126.98, 125.50, 124.00, 110.83, 107.09, 95.82, 30.28. Calcd. for $C_{18}H_{15}N_3S$ $[M+H]^+$: 306.1059; found: 306.1048.

(5) 1-ethyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (5)



Yellow liquid, (97.0 mg, 76% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.7 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.29–7.25 (m, 4H), 7.18 (d, *J* = 6.8 Hz, 1H), 6.54 (s, 1H), 6.53 (t, *J* = 2.1 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.07, 139.50, 135.99, 134.56, 132.41, 128.94, 128.63, 127.96, 127.48, 127.21, 125.55, 123.88, 110.99, 107.06, 96.14, 38.75, 15.31. Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1208.

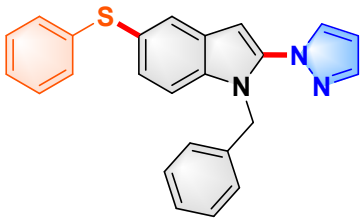
(6) 5-(phenylthio)-1-propyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (6)



Yellow liquid, (70.0 mg, 51% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.0 Hz, 1H), 7.85 (d, *J* = 1.3 Hz, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.28–7.22 (m, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.53 (s, 1H), 6.51 (t, *J* = 2.1 Hz,

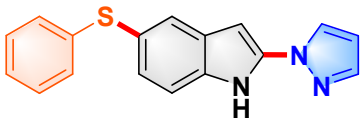
1H), 4.16 (t, *J* = 12 Hz, 2H), 1.76–1.73 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.97, 139.43, 136.23, 134.95, 132.49, 128.90, 128.54, 127.95, 127.38, 127.06, 125.52, 123.82, 111.17, 106.99, 96.21, 45.36, 23.15, 11.37. **HRMS (ESI):** Calcd. for $C_{20}H_{19}N_3S$ $[M+H]^+$: 334.1372; found: 334.1367.

(7) 1-benzyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (7)



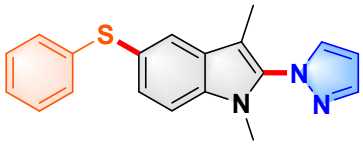
White solid, (102.1 mg, 67% yield), m.p.: 123-124 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.7 Hz, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.28–7.25 (m, 7H), 7.19–7.16 (m, 1H), 7.04 (d, *J* = 6.1 Hz, 2H), 6.61 (s, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 5.44 (s, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.16, 139.11, 137.05, 136.40, 135.25, 132.50, 128.95, 128.72, 128.71, 128.27, 127.58, 127.26, 127.13, 126.67, 125.70, 124.54, 111.58, 107.17, 96.72, 47.22. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S$ $[M+H]^+$: 382.1372; found: 382.1364.

(8) 5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (9)



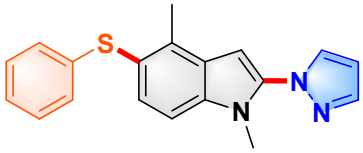
White solid, (78 mg, 67% yield), m.p.: 144-145 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 8.02 (d, *J* = 2.4 Hz, 1H), 7.85–7.77 (m, 2H), 7.34–7.30 (m, 2H), 7.27–7.22 (m, 4H), 7.15 (t, *J* = 7.1 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 6.43 (s, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.12, 139.48, 136.27, 133.53, 128.89, 128.13, 127.95, 127.92, 126.59, 125.49, 124.10, 112.17, 108.36, 87.17. **HRMS (ESI):** Calcd. for $C_{17}H_{13}N_3S$ $[M+H]^+$: 292.0903; found: 292.0898.

(9) 1,3-dimethyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (10)



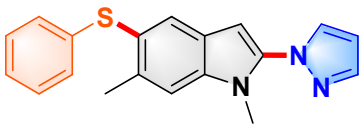
White solid, (114.8 mg, 90% yield), m.p.: 138-139 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.26–7.23 (m, 2H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.56 (t, *J* = 2.1 Hz, 1H), 3.55 (s, 3H), 2.22 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.95, 139.87, 134.77, 132.93, 129.41, 128.85, 127.50, 127.43, 126.47, 125.30, 122.69, 110.63, 106.81, 105.86, 29.59, 8.02. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1209.

(10) 1,4-dimethyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (11)



White solid, (91.9 mg, 72% yield), m.p.: 127-128 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.12–7.09 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.62 (s, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 3.74 (s, 3H), 2.66 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.06, 139.55, 135.92, 135.77, 135.73, 132.36, 130.96, 128.84, 127.19, 126.48, 124.83, 121.64, 108.47, 107.04, 95.45, 30.24, 16.97. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1205.

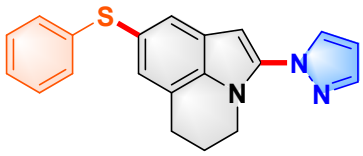
(11) 1,6-dimethyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (12)



White solid, (105.9 mg, 83% yield), m.p.: 142-143 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.33 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.50 (s, 1H), 3.71 (s, 3H), 2.54 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.98, 139.18, 136.60,

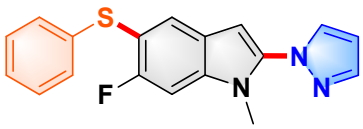
136.33, 135.91, 132.41, 129.28, 128.87, 126.70, 125.15, 124.98, 123.20, 111.41, 106.97, 95.74, 30.15, 21.60. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1207.

(12) 8-(phenylthio)-2-(1*H*-pyrazol-1-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (13)



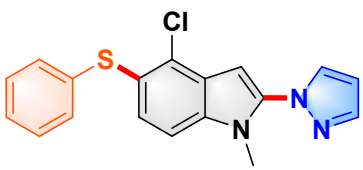
White solid, (115.2 mg, 87% yield), m.p.: 115-116 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.71 (s, 1H), 7.27–7.22 (m, 4H), 7.18 (s, 1H), 7.15 (t, *J* = 6.3 Hz, 1H), 6.51 (s, 1H), 6.45 (s, 1H), 4.30 (t, *J* = 5.1 Hz, 2H), 3.01 (t, *J* = 6.1 Hz, 2H), 2.27 (p, *J* = 5.8 Hz, 2H).**^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.82, 139.96, 135.65, 132.84, 131.35, 128.84, 127.69, 125.54, 125.31, 124.91, 123.59, 123.40, 107.13, 93.26, 43.22, 24.67, 22.68. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3S$ $[M+H]^+$: 332.1216; found: 332.1209.

(13) 1,6-dimethyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (14)



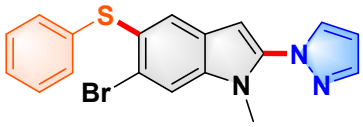
White solid, (82.7 mg, 64% yield), m.p.: 103-104 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 8.3, 5.7 Hz, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.51 (s, 1H), 3.68 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 159.45 (d, *J* = 241.6 Hz), 142.17, 137.62, 136.65 (d, *J* = 4.5 Hz), 136.46 (d, *J* = 10.6 Hz), 132.38, 129.02, 128.97, 127.82, 125.85, 123.04, 112.74 (d, *J* = 21.1 Hz), 107.16, 97.29 (d, *J* = 28.7 Hz), 95.97, 30.44. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -112.80. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3S$ $[M+H]^+$: 324.0965; found: 324.0957.

(14) 4-chloro-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (15)



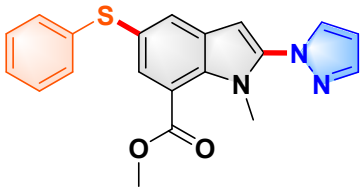
White solid, (97.6 mg, 72% yield), m.p.: 151-152 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.29–7.26 (m, 3H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.67 (s, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.32, 137.24, 136.79, 136.06, 132.31, 130.13, 129.43, 129.04, 128.55, 126.28, 126.03, 123.05, 109.24, 107.34, 95.03, 30.68. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0660.

(15) 6-bromo-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (16)



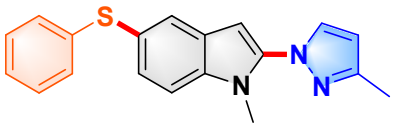
White solid, (65.9 mg, 43% yield), m.p.: 156-157 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.79 (s, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.73 (s, 1H), 7.32–7.29 (m, 2H), 7.24–7.20 (m, 3H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.45 (s, 1H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.25, 137.25, 136.92, 136.35, 132.29, 129.12, 128.85, 127.84, 126.30, 126.21, 125.68, 121.86, 114.71, 107.29, 95.65, 30.50. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 384.0165; found: 384.0158.

(16) methyl 1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole-7-carboxylate (17)



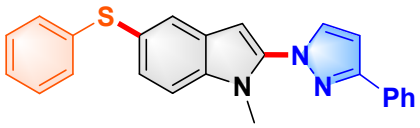
White solid, (62.4 mg, 43% yield), m.p.: 120-121 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 1.8 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 2.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.62 (s, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 3.98 (s, 3H), 3.63 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 167.05, 142.36, 138.41, 133.21, 132.58, 131.33, 130.97, 129.38, 129.04, 128.35, 127.77, 125.94, 123.93, 117.69, 107.37, 97.25, 52.45, 33.87. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3O_2S$ $[M+H]^+$: 364.1114; found: 364.1109.

(17) 1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-5-(phenylthio)-1*H*-indole (18)



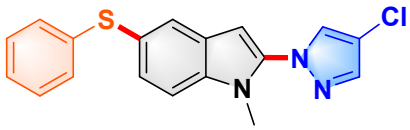
White solid, (94.4 mg, 74% yield), m.p.: 94-95 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.5 Hz, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.27–7.23 (m, 2H), 7.21 (d, *J* = 6.5 Hz, 2H), 7.17–7.13 (m, 1H), 6.49 (s, 1H), 6.30 (d, *J* = 2.1 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.52, 139.56, 136.78, 135.58, 133.03, 128.88, 128.56, 127.83, 127.31, 127.08, 125.46, 123.77, 110.78, 107.07, 95.64, 30.25, 13.78. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1204.

(18) 1-methyl-2-(3-phenyl-1*H*-pyrazol-1-yl)-5-(phenylthio)-1*H*-indole (19)



White solid, (73.2 mg, 48% yield), m.p.: 107-108 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 1.4 Hz, 1H), 7.95 (s, 1H), 7.88 (d, *J* = 1.1 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.50–7.46 (m, 3H), 7.42–7.39 (m, 2H), 7.28–7.25 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.58 (s, 1H), 3.83 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.95, 139.52, 136.59, 135.69, 133.59, 132.66, 128.89, 128.79, 128.73, 128.44, 127.85, 127.37, 127.05, 125.94, 125.49, 123.95, 110.85, 104.52, 95.67, 30.48. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S$ $[M+H]^+$: 382.1372; found: 382.1361.

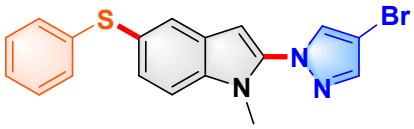
(19) 2-(4-chloro-1*H*-pyrazol-1-yl)-1-methyl-5-(phenylthio)-1*H*-indole (20)



White solid, (97.6 mg, 72% yield), m.p.: 144-145 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.79 (s, 1H), 7.77 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.28–7.25 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 3.73 (s, 3H). **^{13}C-**

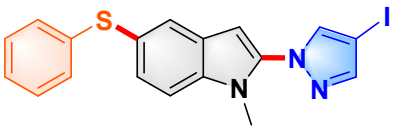
NMR (151 MHz, Chloroform-*d*) δ 140.67, 139.25, 135.64, 135.56, 130.01, 128.94, 128.07, 127.35, 126.75, 125.64, 124.46, 112.09, 110.94, 96.24, 30.29. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0677.

(20) 2-(4-bromo-1*H*-pyrazol-1-yl)-1-methyl-5-(phenylthio)-1*H*-indole (21)



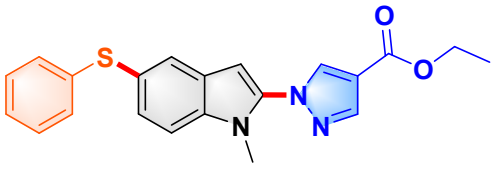
White solid, (87.3 mg, 57% yield), m.p.: 157-158 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.82 (s, 1H), 7.80 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 3.73 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.71, 139.26, 135.56, 135.54, 132.20, 128.96, 128.95, 128.08, 127.36, 126.76, 125.65, 124.47, 110.95, 96.30, 95.34, 30.30. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$:384.0165; found: 384.0154.

(21) 2-(4-iodo-1*H*-pyrazol-1-yl)-1-methyl-5-(phenylthio)-1*H*-indole (22)



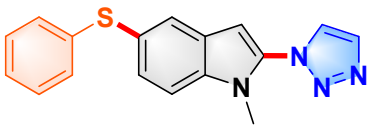
White solid, (106.6 mg, 62% yield), m.p.: 166-167 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 3.1 Hz, 2H), 7.82 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.23–7.21 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 3.72 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 147.06, 139.25, 136.48, 135.56, 135.37, 128.94, 128.08, 127.35, 126.77, 125.64, 124.43, 110.93, 96.32, 58.63, 30.31. **HRMS (ESI):** Calcd. for $C_{18}H_{14}IN_3S$ $[M-H]^+$: 429.9880; found: 429.9871.

(22) ethyl 1-(1-methyl-5-(phenylthio)-1*H*-indol-2-yl)-1*H*-pyrazole-4-carboxylate (23)



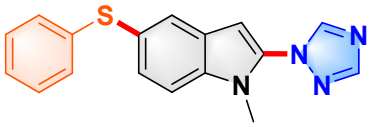
White solid, (122.1 mg, 81% yield), m.p.: 219-220 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 8.24 (s, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.27–7.23 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.57 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.51, 143.02, 139.17, 135.65, 135.48, 135.31, 129.04, 128.93, 128.12, 127.36, 126.70, 125.66, 124.62, 116.68, 110.97, 96.53, 60.67, 30.38, 14.45. **HRMS (ESI):** Calcd. for $C_{21}H_{19}N_3O_2S$ $[M+H]^+$: 378.1271; found: 378.1260.

(23) 1-methyl-5-(phenylthio)-2-(1*H*-1,2,3-triazol-1-yl)-1*H*-indole (24)



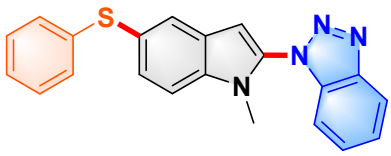
Yellow solid, (96.7 mg, 79% yield), m.p.: 81-82 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 1.1 Hz, 1H), 7.91 (d, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.27–7.24 (m, 2H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.64 (s, 1H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.92, 135.75, 133.72, 132.33, 129.30, 128.98, 128.27, 127.35, 126.61, 126.56, 125.79, 125.04, 111.16, 97.36, 30.39. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1588; found: 307.1579.

(24) 1-methyl-5-(phenylthio)-2-(1*H*-1,2,4-triazol-1-yl)-1*H*-indole (25)



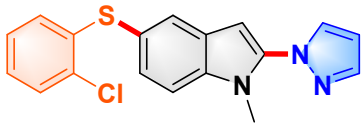
Yellow solid, (62.4 mg, 51% yield), m.p.: 98-99 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.24 (s, 1H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.26–7.23 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 2H), 7.16 (d, J = 7.2 Hz, 1H), 6.61 (s, 1H), 3.70 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.36, 145.60, 138.96, 135.80, 132.04, 129.27, 128.96, 128.24, 127.35, 126.54, 125.76, 124.95, 111.03, 97.50, 30.18. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1588; found: 307.1570.

(25) 1-(1-methyl-5-(phenylthio)-1*H*-indol-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (26)



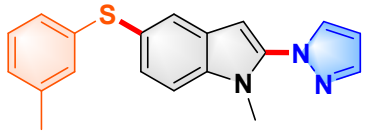
White solid, (98.3 mg, 69% yield), m.p.: 116-117 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 1.0 Hz, 1H), 7.64–7.60 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.29–7.25 (m, 4H), 7.18 (t, *J* = 6.8 Hz, 1H), 6.78 (s, 1H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 145.48, 138.99, 135.83, 134.57, 131.11, 129.22, 129.09, 128.97, 128.31, 127.41, 126.98, 125.78, 124.95, 124.92, 120.34, 111.13, 110.25, 98.09, 30.30. **HRMS (ESI):** Calcd. for $C_{21}H_{16}N_4S$ $[M+H]^+$: 357.1168; found: 357.1159.

(26) 5-((2-chlorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (27)



White solid, (94.9 mg, 70% yield), m.p.: 147-148 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.3 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 1H), 7.06–7.01 (m, 2H), 6.73–6.69 (m, 1H), 6.56 (s, 1H), 6.53 (t, *J* = 2.1 Hz, 1H), 3.77 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.18, 139.57, 136.73, 136.03, 132.34, 130.69, 129.64, 129.36, 128.89, 127.44, 127.25, 127.02, 125.80, 121.43, 111.23, 107.18, 95.92, 30.36. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0661.

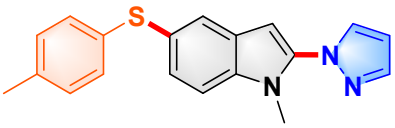
(27) 1-methyl-2-(1*H*-pyrazol-1-yl)-5-(*m*-tolylthio)-1*H*-indole (28)



White solid, (100.8 mg, 79% yield), m.p.: 133-134 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (t, *J* = 1.8 Hz, 2H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.12 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.55 (s, 1H), 6.55–6.53 (m, 1H), 3.76 (s, 3H), 2.33 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.12, 139.15, 138.74, 136.56, 135.60, 132.37, 128.84, 128.68, 128.63, 127.20, 127.02,

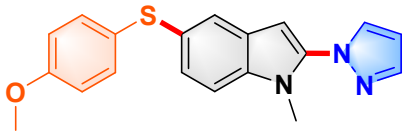
126.57, 125.22, 124.26, 110.88, 107.15, 95.83, 30.33, 21.46. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1207.

(28) 1-methyl-2-(1*H*-pyrazol-1-yl)-5-(*p*-tolylthio)-1*H*-indole (29)



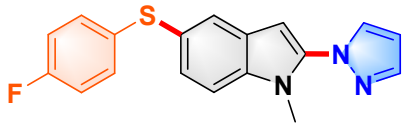
White solid, (94.4 mg, 74% yield), m.p.: 150-151 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 4.7 Hz, 1H), 7.82 (d, *J* = 6.7 Hz, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.45–7.41 (m, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 9.1 Hz, 2H), 7.10 (t, *J* = 6.9 Hz, 2H), 6.52 (dd, *J* = 4.3, 2.4 Hz, 2H), 3.73 (s, 3H), 2.34 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.07, 136.48, 135.78, 135.38, 135.29, 132.34, 129.75, 128.97, 128.00, 126.92, 126.37, 125.27, 110.73, 107.08, 95.74, 30.27, 21.03. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1205.

(29) 5-((4-methoxyphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (30)



Yellow liquid (119.3 mg, 89% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.75 (s, 1H), 7.72 (s, 1H), 7.37–7.31 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.51 (t, *J* = 4.5 Hz, 1H), 6.48 (s, 1H), 3.81 (s, 3H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.78, 142.04, 136.41, 135.06, 132.33, 132.27, 128.44, 127.11, 126.69, 124.67, 114.74, 110.59, 107.04, 95.62, 55.39, 30.22. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3OS$ $[M+H]^+$: 336.1165; found: 336.1157.

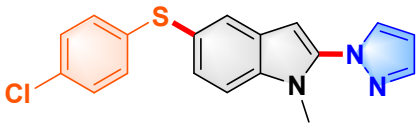
(30) 5-((4-fluorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (31)



White solid, (86.6 mg, 67% yield), m.p.: 174-175 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 1.2 Hz, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.41 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.23 (ddt, *J* = 8.2, 5.0, 2.5 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 6.52 (d, *J* =

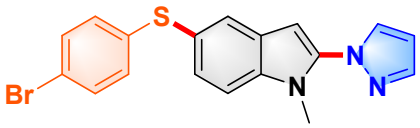
3.4 Hz, 2H), 3.73 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.46 (d, *J* = 246.1 Hz), 142.11, 136.60, 135.47, 134.01 (d, *J* = 3.0 Hz), 132.32, 130.64 (d, *J* =7.6 Hz), 127.94, 126.96, 126.49, 124.96, 116.00 (d, *J* = 21.1 Hz), 110.86, 107.11, 95.74, 30.28. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -116.61. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3S$ $[M+H]^+$: 324.0965; found: 324.0957.

(31) 5-((4-chlorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (32)



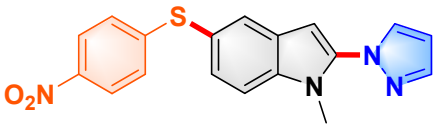
White solid, (127.5 mg, 94% yield), m.p.: 196-197 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.84 (s, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.53 (s, 1H), 6.53–6.52 (m, 1H), 3.74 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.14, 138.21, 136.66, 135.69, 132.32, 131.29, 129.00, 128.94, 128.62, 127.47, 127.03, 123.48, 110.99, 107.13, 95.82, 30.31. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0661.

(32) 5-((4-bromophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (33)



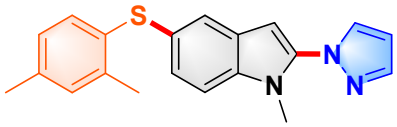
White solid, (95.0 mg, 62% yield), m.p.: 217-218 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.7 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 6.8 Hz, 2H), 6.54 (s, 1H), 6.52 (t, *J* = 2.1 Hz, 1H), 3.75 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.15, 139.00, 136.68, 135.72, 132.32, 131.83, 129.18, 128.70, 127.60, 127.05, 123.23, 119.06, 111.02, 107.14, 95.83, 30.32. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 384.0165; found: 384.0156.

(33) 1-methyl-5-((4-nitrophenyl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (34)



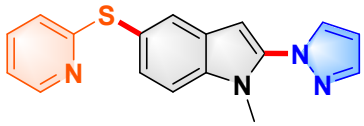
Yellow solid, (68.6 mg, 49% yield), m.p.: 244-245 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 9.0 Hz, 2H), 7.91 (s, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.49–7.45 (m, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.58 (s, 1H), 6.54 (t, *J* = 2.1 Hz, 1H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.83, 144.89, 142.28, 137.03, 136.27, 132.32, 129.41, 129.01, 127.36, 125.51, 123.91, 120.04, 111.52, 107.28, 95.96, 30.44. **HRMS (ESI):** Calcd. for $C_{18}H_{14}N_4O_2S$ $[M+H]^+$: 351.0910; found: 351.0897.

(34) 5-((2,4-dimethylphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (35)



White solid, (99.9 mg, 75% yield), m.p.: 123-124 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.68 (s, 1H), 7.36–7.32 (m, 2H), 7.07 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 6.48 (s, 1H), 3.72 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.03, 137.68, 136.36, 136.32, 135.13, 133.51, 132.31, 131.20, 130.37, 127.27, 127.04, 126.96, 125.52, 125.12, 110.67, 107.02, 95.64, 30.22, 20.94, 20.40. **HRMS (ESI):** Calcd. for $C_{20}H_{19}N_3S$ $[M+H]^+$: 334.1372; found: 334.1361.

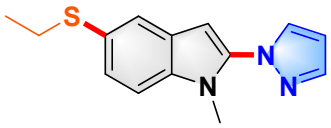
(35) 1-methyl-2-(1*H*-pyrazol-1-yl)-5-(pyridin-2-ylthio)-1*H*-indole (36)



Orange solid, (99.1 mg, 81% yield), m.p.: 202-203 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 4.8 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.52 (d, *J* = 6.9 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.40–7.37 (m, 1H), 6.95 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.55 (s, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 3.74 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 163.60, 149.31, 142.16, 136.70, 136.61, 136.09, 132.37,

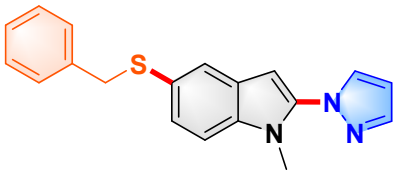
129.89, 129.09, 127.19, 120.97, 120.38, 119.29, 111.16, 107.18, 96.00, 30.34. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1012; found: 307.1003.

(36) 5-(ethylthio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (37)



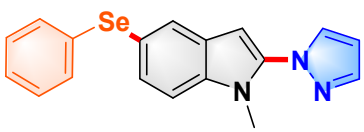
Yellow liquid, (68.9 mg, 67% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 2.2 Hz, 1H), 7.74 (d, *J* = 1.4 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 6.49 (s, 1H), 3.70 (s, 3H), 2.94 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.99, 136.29, 134.93, 132.32, 126.89, 126.68, 126.40, 124.65, 110.19, 106.98, 95.48, 30.24, 30.17, 14.75. **HRMS (ESI):** Calcd. for $C_{14}H_{15}N_3S$ $[M+H]^+$: 259.1059; found: 259.1050.

(37) 5-(benzylthio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (38)



Yellow solid, (76.6 mg, 60% yield), m.p.: 105-106 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.2 Hz, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.1 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.30–7.27 (m, 3H), 7.26–7.24 (m, 3H), 6.51 (t, *J* = 2.1 Hz, 1H), 6.47 (s, 1H), 4.12 (s, 2H), 3.70 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.01, 138.41, 136.26, 135.17, 132.34, 128.96, 128.39, 127.51, 126.96, 126.64, 126.10, 125.60, 110.18, 107.02, 95.67, 41.69, 30.19. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1204.

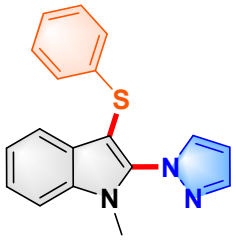
(38) 1-methyl-5-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (39)



White solid, (127.1 mg, 91% yield), m.p.: 155-156 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.57 (d, *J* = 6.8 Hz,

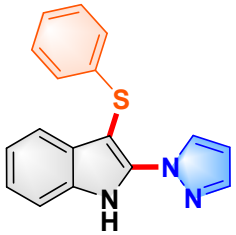
1H), 7.39 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.25–7.22 (m, 2H), 7.22–7.20 (m, 1H), 6.53 (q, *J* = 2.1, 1.6 Hz, 2H), 3.74 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.10, 135.51, 133.98, 132.37, 130.64, 129.75, 129.16, 129.14, 128.45, 127.25, 126.26, 119.86, 110.90, 107.11, 95.70, 30.25. **HRMS (ESI):** Calcd. for $C_{18}H_{15}N_3Se$ $[M+H]^+$: 354.0504; found: 354.0496.

(39) 1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (40)



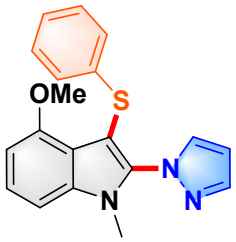
White solid (43.3 mg, 71% yield), m.p.: 112-114 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.8 Hz, 1H), 7.76–7.73 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.23–7.20 (m, 2H), 7.16–7.13 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.50–6.48 (m, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.35, 139.05, 138.55, 135.35, 133.51, 128.95, 128.15, 126.04, 125.15, 123.84, 121.60, 120.21, 110.12, 106.87, 95.56, 30.72. **HRMS (ESI):** Calcd. for $C_{18}H_{15}N_3S$ $[M+H]^+$: 306.1059; found: 306.1052.

(40) 3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (41)



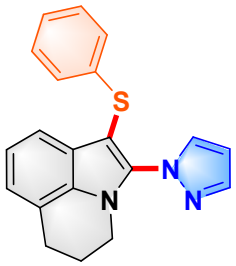
Yellow solid (32.0 mg, 55% yield), m.p.: 126-127 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 10.65 (s, 1H), 8.79 (d, *J* = 2.6 Hz, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 3H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.55–6.49 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.10, 137.98, 137.79, 132.88, 130.37, 130.05, 129.13, 125.57, 125.25, 123.25, 121.52, 119.41, 111.34, 108.35, 86.73. **HRMS (ESI):** Calcd. for $C_{17}H_{13}N_3S$ $[M+H]^+$: 292.0903; found: 292.0892.

(41) 4-methoxy-1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (42)



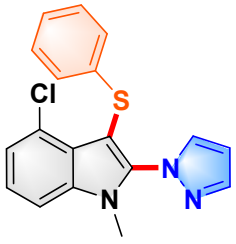
White solid (56.3 mg, 84% yield), m.p.: 94-95 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 13.6, 7.3 Hz, 3H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.47–6.44 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 155.62, 142.23, 139.17, 138.65, 133.39, 130.24, 128.94, 128.91, 125.82, 125.05, 114.31, 111.12, 106.79, 101.27, 94.86, 55.83, 30.81. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3OS$ $[M+H]^+$: 336.1165; found: 336.1157.

(42) 1-(phenylthio)-2-(1*H*-pyrazol-1-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (43)



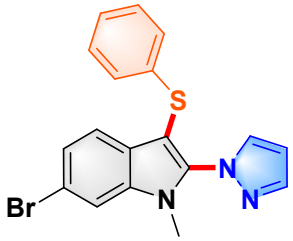
White solid (54.3 mg, 82% yield), m.p.: 128-129 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.1 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.24 (dt, *J* = 22.2, 7.6 Hz, 5H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.49 (t, *J* = 5.3 Hz, 1H), 4.38–4.31 (m, 2H), 3.14–3.08 (m, 2H), 2.36–2.31 (m, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.08, 138.97, 137.80, 132.99, 132.32, 129.03, 126.80, 125.93, 125.12, 122.65, 121.66, 120.72, 117.41, 106.88, 93.16, 43.58, 24.74, 22.78. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3S$ $[M+H]^+$: 332.1216; found: 332.1208.

(43) 4-chloro-1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (44)



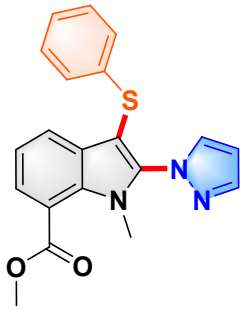
White solid (51.5 mg, 76% yield), m.p.: 156-157 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30–7.27 (m, 1H), 7.24–7.20 (m, 3H), 7.13–7.09 (m, 3H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.75 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.54, 140.56, 140.16, 136.63, 133.78, 128.89, 127.41, 125.91, 125.01, 124.24, 124.02, 123.04, 108.93, 106.93, 95.89, 30.97. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0659.

(44) 6-bromo-1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (45)



White solid (48.3 mg, 63% yield), m.p.: 161-162 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 1.6 Hz, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.23–7.20 (m, 2H), 7.19 (s, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.47–6.46 (m, 1H), 3.77 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.52, 139.50, 138.04, 134.45, 133.41, 132.29, 130.56, 129.06, 128.81, 125.96, 125.35, 112.09, 107.06, 94.70, 85.32, 30.94. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 384.0165; found: 384.0155.

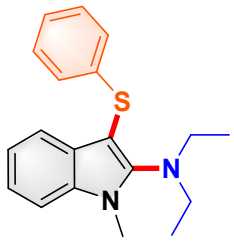
(45) methyl 1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole-7-carboxylate (46)



White solid (34.1 mg, 47% yield), m.p.: 194-195 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89–7.86 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.11–7.07 (m, 3H), 6.50–6.48 (m, 1H), 4.02 (s, 3H), 3.70 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 167.65, 142.62, 140.95, 137.85, 133.59, 133.03, 129.99,

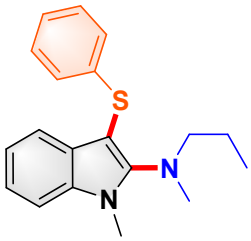
128.96, 127.02, 126.22, 125.34, 124.50, 120.69, 117.24, 107.10, 97.42, 52.42, 34.48. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3O_2S$ $[M+H]^+$: 364.1114; found: 364.1107.

(46) *N*,*N*-diethyl-1-methyl-3-(phenylthio)-1*H*-indol-2-amine (47)



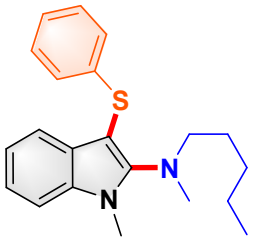
Yellow liquid (25.4 mg, 41% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.54 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.19–7.15 (m, 3H), 7.11–7.08 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 3.31 (q, *J* = 7.2 Hz, 4H), 1.01 (t, *J* = 7.2 Hz, 6H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.41, 139.79, 134.72, 129.52, 128.58, 125.24, 124.23, 121.73, 120.40, 118.55, 109.59, 92.88, 48.40, 28.92, 13.75. **HRMS (ESI):** Calcd. for $C_{19}H_{22}N_2S$ $[M+H]^+$: 311.1576; found: 311.1568.

(47) *N*,1-dimethyl-3-(phenylthio)-*N*-propyl-1*H*-indol-2-amine (48)



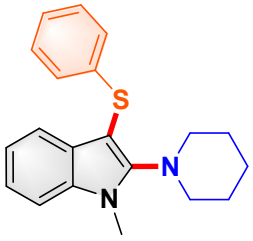
Yellow liquid (30.4 mg, 49% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28–7.24 (m, 1H), 7.18 (dddt, *J* = 11.5, 7.1, 5.6, 3.1 Hz, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 3.24–3.20 (m, 2H), 2.94 (s, 3H), 1.56–1.51 (m, 2H), 0.89–0.86 (m, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.51, 140.31, 134.66, 129.74, 128.62, 125.21, 124.25, 121.65, 120.45, 118.37, 109.34, 90.80, 57.87, 41.62, 29.09, 21.35, 11.46. **HRMS (ESI):** Calcd. for $C_{19}H_{22}N_2S$ $[M+H]^+$: 311.1576; found: 311.1568.

(48) *N*,1-dimethyl-*N*-pentyl-3-(phenylthio)-1*H*-indol-2-amine (49)



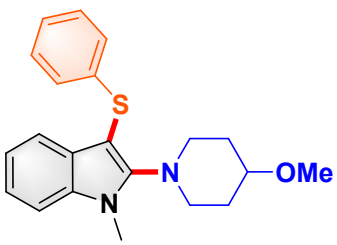
Yellow liquid (35.8 mg, 53% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.21–7.16 (m, 3H), 7.13 (s, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 3.28–3.24 (m, 2H), 2.95 (s, 3H), 1.54–1.49 (m, 2H), 1.30–1.23 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.50, 140.35, 134.70, 129.81, 128.63, 125.24, 124.27, 121.66, 120.47, 118.39, 109.37, 90.82, 56.05, 41.76, 29.23, 29.11, 27.92, 22.54, 14.13. **HRMS (ESI):** Calcd. for $C_{21}H_{26}N_2S$ $[M+H]^+$: 339.1189; found: 339.1882.

(49) 1-methyl-3-(phenylthio)-2-(piperidin-1-yl)-1*H*-indole (50)



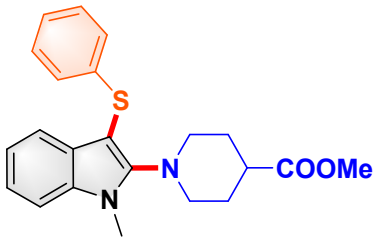
Yellow liquid (37.4 mg, 58% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.32–3.29 (m, 4H), 1.71 (q, *J* = 5.6 Hz, 4H), 1.63 (q, *J* = 5.9 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.71, 140.85, 134.85, 129.78, 128.65, 125.08, 124.19, 121.58, 120.41, 118.35, 109.22, 89.30, 52.60, 29.03, 26.74, 24.18. **HRMS (ESI):** Calcd. for $C_{20}H_{22}N_2S$ $[M+H]^+$: 323.1576; found: 323.1570.

(50) 2-(4-methoxypiperidin-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (51)



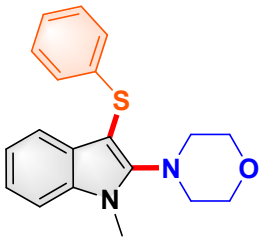
Yellow liquid (49.3 mg, 70% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.29–7.27 (m, 1H), 7.23–7.19 (m, 2H), 7.19–7.15 (m, 1H), 7.14–7.11 (m, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 3.40–3.34 (m, 5H), 2.10–2.05 (m, 2H), 1.74–1.67 (m, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.85, 140.61, 134.84, 129.66, 128.71, 125.09, 124.31, 121.82, 120.54, 118.44, 109.35, 89.89, 55.69, 32.02, 29.03. **HRMS (ESI):** Calcd. for $C_{21}H_{24}N_2OS$ $[M+H]^+$: 353.1682; found: 353.1674.

(51) methyl 1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperidine-4-carboxylate (52)



Yellow liquid (20.5 mg, 27% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09–7.05 (m, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.40 (t, *J* = 11.2 Hz, 2H), 3.26 (d, *J* = 12.3 Hz, 2H), 2.50–24.5 (m,1H), 2.02–1.98 (m, 2H), 1.90–1.84 (m, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 175.55, 151.71, 140.52, 134.75, 129.56, 128.68, 125.09, 124.32, 121.86, 120.53, 118.47, 109.35, 90.23, 51.78, 51.09, 40.86, 29.10, 28.95. **HRMS (ESI):** Calcd. for $C_{22}H_{24}N_2O_2S$ $[M+H]^+$: 381.1631; found: 381.1622.

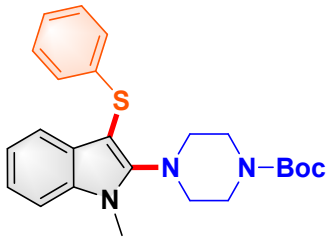
(52) 4-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)morpholine (53)



Yellow solid (35.0 mg, 54% yield), m.p.: 121-122 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.22–7.17 (m, 3H), 7.12–7.07 (m, 3H), 3.86–3.84 (m, 4H), 3.75 (s, 3H), 3.36 (s, 4H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.67, 140.41, 134.77, 129.61, 128.74, 125.14, 124.43, 122.10, 120.71,

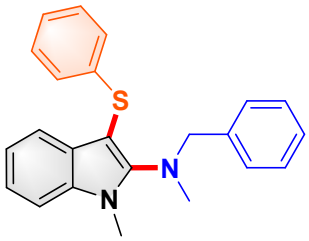
118.65, 109.46, 90.80, 67.59, 51.52, 29.07. **HRMS (ESI):** Calcd. for $C_{19}H_{20}N_2OS$ $[M+H]^+$: 325.1369; found: 325.1361.

(53) *tert*-butyl 4-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperazine-1-carboxylate (54)



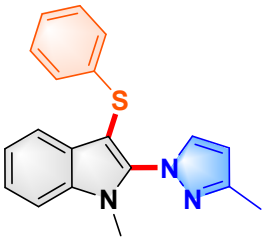
Brown solid (58.4 mg, 69% yield), m.p.: 196-197 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.21–7.15 (m, 3H), 7.07 (dd, *J* = 8.3, 7.0 Hz, 3H), 3.73 (s, 3H), 3.57 (s, 4H), 3.30 (s, 4H), 1.52 (s, 9H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 154.81, 150.86, 140.28, 134.79, 129.50, 128.77, 125.08, 124.46, 122.13, 120.71, 118.64, 109.49, 90.75, 79.97, 29.08, 28.49, 28.48. **HRMS (ESI):** Calcd. for $C_{24}H_{29}N_3O_2S$ $[M+H]^+$: 424.2053; found: 424.2043.

(54) *N*-benzyl-*N*,1-dimethyl-3-(phenylthio)-1*H*-indol-2-amine (55)



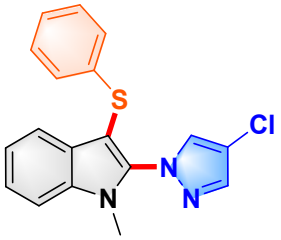
Yellow solid (44.4 mg, 62% yield), m.p.: 92-93 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.48–7.39 (m, 5H), 7.39–7.34 (m, 2H), 7.31–7.25 (m, 3H), 7.24–7.22 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.56 (s, 2H), 3.82 (s, 3H), 2.96 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.45, 140.28, 138.67, 134.77, 129.71, 128.82, 128.66, 128.51, 127.38, 125.38, 125.37, 124.49, 122.00, 120.67, 118.66, 109.56, 91.35, 60.26, 41.47, 29.33. **HRMS (ESI):** Calcd. for $C_{23}H_{22}N_2S$ $[M+H]^+$: 359.1576; found: 359.1569.

(55) 1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-3-(phenylthio)-1*H*-indole (56)



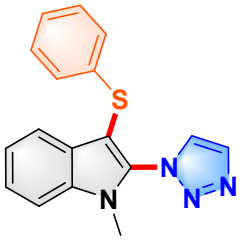
Green liquid (49.1 mg, 77% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.21–7.17 (m, 2H), 7.12–7.07 (m, 3H), 6.25 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.76, 139.30, 138.74, 135.33, 134.20, 128.88, 128.15, 125.90, 124.98, 123.64, 121.45, 120.09, 110.00, 106.88, 94.99, 30.73, 13.78. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1208.

(56) 2-(4-chloro-1*H*-pyrazol-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (57)



Yellow solid (50.9 mg, 75% yield), m.p.: 107-109 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.72 (d, *J* = 6.7 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.13–7.10 (m, 3H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 140.95, 138.04, 138.02, 135.30, 131.06, 129.01, 127.90, 126.19, 125.35, 124.16, 121.77, 120.36, 111.76, 110.17, 96.34, 30.69. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0669; found: 340.0663.

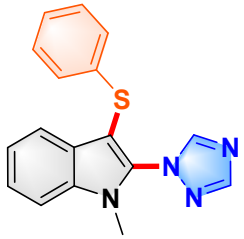
(57) 1-methyl-3-(phenylthio)-2-(1*H*-1,2,3-triazol-1-yl)-1*H*-indole (58)



White solid (36.1 mg, 59% yield), m.p.: 117-118 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.1 Hz, 1H), 7.86 (d, *J* = 1.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz,

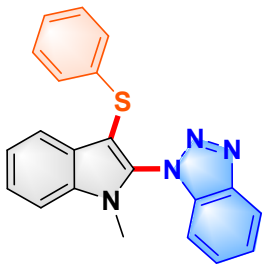
1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (dd, *J* = 17.0, 7.6 Hz, 3H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.58, 135.56, 134.90, 133.31, 129.08, 127.96, 127.41, 126.23, 125.55, 124.61, 122.04, 120.49, 110.38, 97.36, 30.89. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1588; found: 307.1579.

(58) 1-methyl-3-(phenylthio)-2-(1*H*-1,2,4-triazol-1-yl)-1*H*-indole (59)



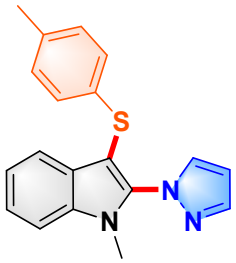
White solid (49.0 mg, 80% yield), m.p.: 124-125 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.24 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.32–7.29 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (q, *J* = 7.6 Hz, 3H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.29, 146.57, 137.85, 135.54, 134.93, 129.10, 127.93, 126.20, 125.56, 124.54, 122.00, 120.52, 110.25, 97.50, 30.74. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1588; found: 307.1579.

(59) 1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (60)



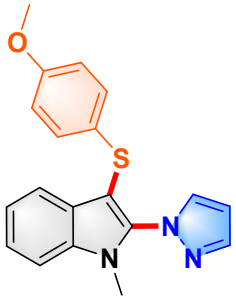
Pink solid (45.6 mg, 64% yield), m.p.: 147-148 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.51–7.45 (m, 3H), 7.35–7.32 (m, 2H), 7.16–7.12 (m, 2H), 7.11–7.06 (m, 3H), 3.64 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 145.27, 137.05, 136.00, 134.89, 133.40, 128.95, 128.84, 127.97, 126.93, 125.56, 124.74, 124.63, 121.88, 120.65, 120.28, 110.46, 110.43, 30.36. **HRMS (ESI):** Calcd. for $C_{21}H_{16}N_4S$ $[M+H]^+$: 357.1168; found: 357.1159.

(60) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(*p*-tolylthio)-1*H*-indole (61)



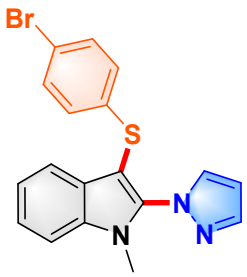
White solid (51.7 mg, 81% yield), m.p.: 111-112 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.5 Hz, 1H), 7.76–7.72 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.04–7.01 (m, 4H), 6.50–6.47 (m, 1H), 3.79 (s, 3H), 2.29 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.29, 138.89, 135.30, 134.99, 134.86, 133.55, 129.71, 128.18, 126.39, 123.75, 121.50, 120.23, 110.04, 106.79, 96.20, 30.67, 20.91.**HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1210.

(61) 3-((4-methoxyphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (62)



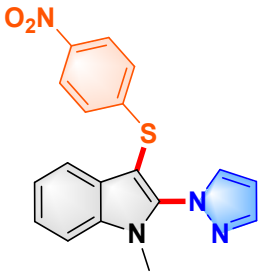
White solid (52.9 mg, 79% yield), m.p.: 85-86 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.79–7.74 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.51 (t, *J* = 2.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.03, 142.28, 138.59, 135.21, 133.66, 128.90, 128.80, 128.10, 123.74, 121.46, 120.19, 114.66, 110.04, 106.80, 97.61, 55.33, 30.58. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3OS$ $[M+H]^+$: 336.1165; found: 336.1154.

(62) 3-((4-bromophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (63)



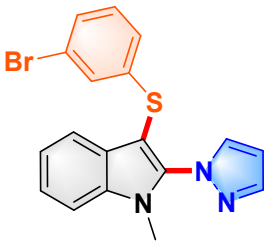
White solid (31.4 mg, 41% yield), m.p.: 85-86 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 8.6, 2.1 Hz, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.49 (t, *J* = 2.1 Hz, 1H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.44, 139.08, 137.79, 135.32, 133.41, 131.88, 127.81, 127.60, 123.99, 121.75, 120.01, 118.75, 110.20, 106.98, 95.07, 30.71. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 384.0165; found: 384.0156.

(63) 1-methyl-3-((4-nitrophenyl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (64)



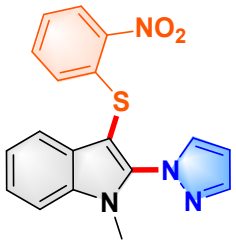
Yellow solid (53.2 mg, 76% yield), m.p.: 165-166 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 2H), 6.50–6.48 (m, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 148.59, 145.22, 142.63, 139.37, 135.41, 133.19, 127.40, 125.26, 124.32, 124.07, 122.10, 119.73, 110.45, 107.23, 93.12, 30.78. **HRMS (ESI):** Calcd. for $C_{18}H_{14}N_4O_2S$ $[M+H]^+$: 351.0910; found: 351.0901.

(64) 3-((3-bromophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (65)



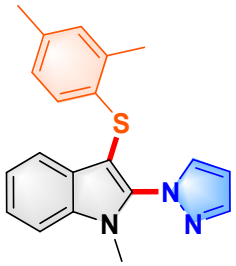
White solid (45.2 mg, 59% yield), m.p.: 95-96 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.43–7.40 (m, 1H), 7.29 (s, 1H), 7.26 (t, *J* = 1.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.50–6.48 (m, 1H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.44, 141.06, 139.17, 135.33, 133.36, 130.24, 128.39, 128.22, 127.86, 124.45, 123.98, 122.97, 121.79, 119.99, 110.22, 107.00, 94.52, 30.75. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 384.0165; found: 384.0154.

(65) 1-methyl-3-((2-nitrophenyl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (66)



Yellow solid (51.1 mg, 73% yield), m.p.: 165-166 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 6.9 Hz, 1H), 7.83 (d, *J* = 1.4 Hz, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.48–6.45 (m, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 144.97, 142.54, 139.73, 139.07, 135.56, 133.73, 133.34, 127.72, 127.51, 126.03, 124.88, 124.23, 121.99, 119.92, 110.38, 107.26, 94.36, 30.82. **HRMS (ESI):** Calcd. for $C_{18}H_{14}N_4O_2S$ $[M+H]^+$: 351.0910; found: 351.0917.

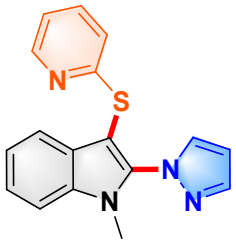
(66) 3-((2,4-dimethylphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (67)



White solid (46.6 mg, 70% yield), m.p.: 117-118 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* =

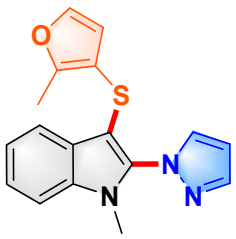
8.0 Hz, 1H), 6.46 (t, *J* = 1.9 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.24, 138.97, 135.40, 134.78, 134.60, 133.97, 133.47, 131.00, 128.27, 127.27, 125.83, 123.72, 121.45, 120.27, 110.03, 106.76, 95.52, 30.71, 20.76, 19.88. **HRMS (ESI):** Calcd. for $C_{20}H_{19}N_3S$ $[M+H]^+$: 334.1372; found: 334.1368.

(67) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(pyridin-2-ylthio)-1*H*-indole (68)



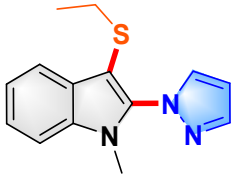
Yellow solid (37.3 mg, 61% yield), m.p.: 139-140 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 4.9 Hz, 1H), 7.84 (d, *J* = 1.7 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.49–7.46 (m, 1H), 7.42–7.37 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 6.97 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.44, 149.42, 142.40, 139.29, 136.87, 135.42, 133.55, 127.84, 123.92, 121.70, 120.05, 120.02, 119.66, 110.19, 106.97, 94.00, 30.77. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1012; found: 307.1003.

(68) 1-methyl-3-((2-methylfuran-3-yl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (69)



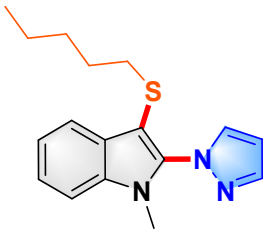
Yellow solid (53.8 mg, 87% yield), m.p.: 78-79 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.89–7.86 (m, 2H), 7.38 (dd, *J* = 5.6, 1.1 Hz, 2H), 7.30 (t, *J* = 6.7 Hz, 1H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.58 (t, *J* = 2.1 Hz, 1H), 6.08 (s, 1H), 3.67 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.74, 142.14, 140.30, 137.64, 134.81, 133.94, 127.94, 123.60, 121.23, 120.00, 114.32, 112.00, 109.95, 106.75, 99.71, 30.28, 11.72. **HRMS (ESI):** Calcd. for $C_{17}H_{15}N_3OS$ $[M+H]^+$: 310.1009; found: 310.1006.

(69) 3-(ethylthio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (70)



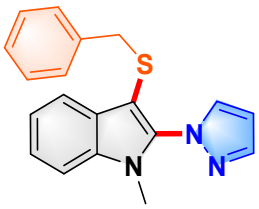
Yellow liquid (27.8 mg, 54% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (t, *J* = 2.6 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.56 (t, *J* = 2.1 Hz, 1H), 3.69 (s, 3H), 2.58 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.04, 138.28, 134.99, 133.81, 128.53, 123.51, 121.01, 120.13, 109.90, 106.57, 99.27, 30.33, 30.27, 15.12. **HRMS (ESI):** Calcd. for $C_{14}H_{15}N_3S$ $[M+H]^+$: 258.1059; found: 258.1052.

(70) 1-methyl-3-(pentylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (71)



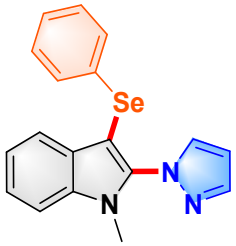
Yellow liquid (34.1 mg, 57% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (dt, *J* = 3.2, 1.8 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.42–7.38 (m, 2H), 7.32–7.29 (m, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 3.69 (s, 3H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.41–1.37 (m, 2H), 1.22 (d, *J* = 3.8 Hz, 4H), 0.85 (t, *J* = 5.8 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.03, 138.22, 135.01, 133.83, 128.45, 123.49, 121.00, 120.10, 109.92, 106.56, 99.57, 36.49, 30.55, 30.29, 29.34, 22.23, 14.02. **HRMS (ESI):** Calcd. for $C_{17}H_{21}N_3S$ $[M+H]^+$: 300.1529; found: 300.1525.

(71) 3-(benzylthio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (72)



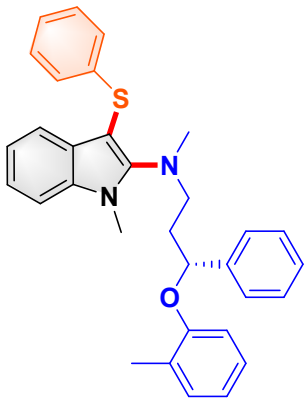
White solid (42.7 mg, 67% yield), m.p.: 106-107 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.43–7.39 (m, 2H), 7.30 (ddd, *J* = 8.0, 6.0, 2.1 Hz, 1H), 7.25–7.20 (m, 3H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.05–7.01 (m, 2H), 6.43 (t, *J* = 2.2 Hz, 1H), 3.84 (s, 2H), 3.64 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.04, 138.58, 138.51, 135.04, 133.55, 128.93, 128.36, 128.16, 126.97, 123.56, 121.13, 120.03, 110.01, 106.42, 98.85, 40.67, 30.28. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1209.

(72) 1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (73)



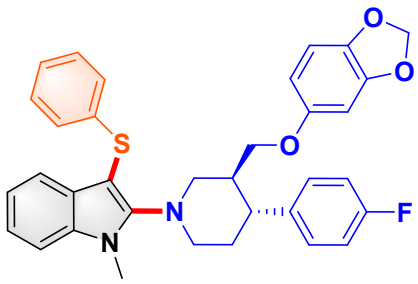
White solid (134.1 mg, 95%), m.p.: 97-98 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 6.52–6.49 (m, 1H), 3.78 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.30, 139.21, 135.74, 133.67, 133.41, 129.25, 128.98, 126.01, 123.86, 121.57, 121.20, 110.10, 106.75, 92.49, 30.64. **HRMS (ESI):** Calcd. for $C_{18}H_{15}N_3Se$ $[M+H]^+$: 354.0504; found: 354.0494.

(73) (*R*)-*N*,1-dimethyl-*N*-(3-phenyl-3-(*o*-tolyloxy)propyl)-3-(phenylthio)-1*H*-indol-2-amine (74)



Yellow liquid (68.9 mg, 70% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.29 (m, 4H), 7.27 (td, *J* = 6.8, 1.6 Hz, 3H), 7.22 – 7.18 (m, 3H), 7.13 (dd, *J* = 14.8, 7.2 Hz, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.96 (td, *J* = 7.8, 1.8 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.17 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.65 (s, 3H), 3.55 (tdd, *J* = 12.8, 8.4, 5.8 Hz, 2H), 2.97 (s, 3H), 2.31 (s, 3H), 2.26 – 2.20 (m, 1H), 2.09 – 2.04 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 156.05, 151.73, 142.03, 140.22, 134.74, 130.67, 129.76, 128.79, 128.68, 127.55, 127.02, 126.60, 125.78, 125.31, 124.44, 121.90, 120.62, 120.30, 118.53, 112.73, 109.50, 91.28, 77.52, 52.35, 42.21, 37.56, 29.07, 16.64. **HRMS (ESI):** Calcd. for $C_{32}H_{32}N_2OS$ $[M+H]^+$: 493.2308; found: 493.2297.

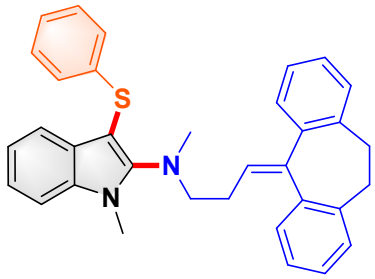
(74) 2-((3*S*,4*R*)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (75)



Yellow liquid (64.5 mg, 57% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.28–7.22 (m, 5H), 7.20–7.18 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 2.5 Hz, 1H), 6.15 (d, *J* = 6.1 Hz, 1H), 5.94 (s, 2H), 3.82 (s, 3H), 3.73 (ddd, *J* = 12.3, 4.0, 1.7 Hz, 1H), 3.65 (ddd, *J* = 12.4, 8.3, 2.9 Hz, 2H), 3.54–3.49 (m, 2H), 3.41 (d, *J* = 12.1 Hz, 1H), 2.68–2.63 (m, 1H), 2.45 (dtt, *J* = 11.2, 7.8, 3.7 Hz, 1H), 2.06–1.99 (m, 1H), 1.95 (dd, *J* = 13.1, 3.6 Hz, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.70 (d, *J* = 244.6 Hz), 154.31, 151.84, 148.23, 141.75, 140.75, 139.63 (d, *J* = 3.0 Hz), 134.92, 129.86, 128.90 (d, *J* = 7.6 Hz), 128.83, 125.26, 124.48, 121.92, 120.69, 118.52, 115.70, 115.56, 109.44, 107.91, 105.78, 101.18, 98.20, 89.88, 69.44, 55.70, 52.15, 44.22, 42.88, 35.38, 29.36. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -116.00. **HRMS (ESI):** Calcd. for $C_{34}H_{31}FN_2O_3S$ $[M+H]^+$: 567.2112; found: 567.2101.

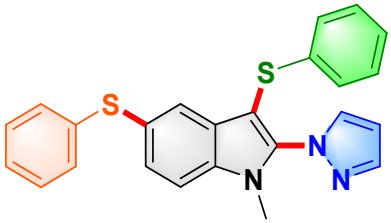
(75) *N*-(3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*,1-dimethyl-3-

(phenylthio)-1*H*-indol-2-amine (76)



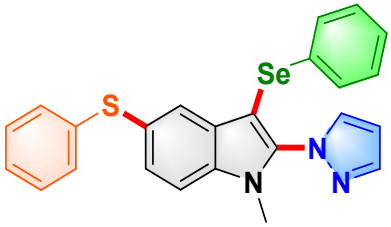
Yellow liquid (68.0 mg, 68% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.24 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.18 – 7.14 (m, 3H), 7.12 – 7.09 (m, 3H), 7.09 – 7.03 (m, 3H), 5.85 (t, *J* = 7.4 Hz, 1H), 3.66 (s, 3H), 3.44 – 3.28 (m, 4H), 3.04 – 2.94 (m, 1H), 2.89 (s, 3H), 2.83 – 2.70 (m, 1H), 2.36 (q, *J* = 8.2, 7.3 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.04, 144.02, 141.33, 140.31, 140.00, 139.33, 137.14, 134.75, 130.09, 129.79, 129.04, 128.75, 128.61, 128.24, 128.13, 127.53, 127.17, 126.12, 125.84, 125.31, 124.41, 121.86, 120.61, 118.51, 109.47, 91.10, 55.82, 41.72, 33.85, 32.14, 29.18, 28.57. **HRMS (ESI):** Calcd. for $C_{34}H_{32}N_2S$ $[M+H]^+$: 501.2359; found: 501.2348.

(76) 1-methyl-3,5-bis(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (77)



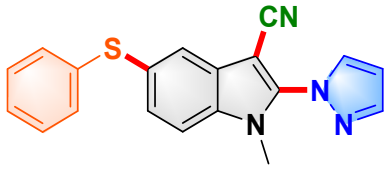
White solid, (94.0 mg, 91% yield), m.p.: 106-108 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.89 (s, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.26–7.23 (m, 2H), 7.22 (s, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 3H), 6.49 (t, *J* = 2.1 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.52, 139.72, 138.71, 138.02, 135.07, 133.47, 129.48, 129.02, 129.01, 128.95, 128.37, 126.27, 126.00, 125.87, 125.81, 125.39, 111.30, 107.05, 95.91, 30.98. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S_2$ $[M+H]^+$: 414.1093; found: 414.1089.

(77) 1-methyl-3-(phenylselanyl)-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (78)



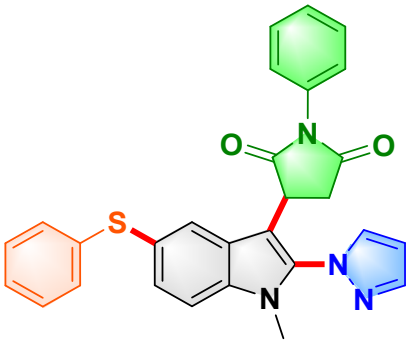
White solid, (94.5 mg, 82% yield), m.p.: 129-130 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 1.2 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.26–7.21 (m, 6H), 7.19–7.15 (m, 4H), 6.51–6.49 (m, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 13C NMR (151 MHz, Chloroform-d) δ 142.43, 139.80, 138.87, 135.47, 133.60, 132.85, 129.83, 129.53, 129.27, 129.25, 128.95, 128.27, 126.99, 126.21, 125.75, 125.72, 111.26, 106.88, 92.78, 30.83. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3SSe$ $[M+H]^+$: 462.0597; found: 462.0561.

(78) 1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole-3-carbonitrile (79)



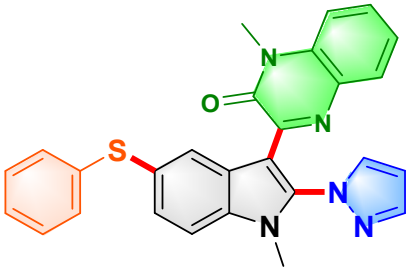
White solid, (44.6 mg, 54% yield), m.p.: 143-144 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.6 Hz, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.31–7.29 (m, 4H), 7.25–7.21 (m, 1H), 6.63–6.62 (m, 1H), 3.88 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 143.44, 141.26, 137.19, 134.05, 132.46, 129.71, 129.33, 129.30, 129.20, 126.68, 126.49, 123.97, 114.18, 111.68, 108.70, 79.22, 31.74. **HRMS (ESI):** Calcd. for $C_{19}H_{14}N_4S$ $[M+H]^+$: 331.1012; found: 331.1007.

(79) 1-methyl-3,5-bis(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (80)



Yellow solid, (98.0 mg, 82% yield), m.p.: 155-156 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, J = 1.9 Hz, 1H), 7.87 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 8.3 Hz, 2H), 7.26 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.24–7.22 (m, 2H), 7.20–7.16 (m, 3H), 6.57 (t, *J* = 2.0 Hz, 1H), 4.29 (dd, *J* = 10.0, 5.7 Hz, 1H), 3.56 (s, 3H), 3.25 (dd, *J* = 18.6, 10.0 Hz, 1H), 3.08 (dd, *J* = 18.6, 5.7 Hz, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 176.65, 174.92, 142.66, 138.63, 134.55, 134.05, 133.65, 131.97, 129.26, 129.20, 129.06, 128.69, 128.45, 126.50, 125.97, 125.39, 125.30, 124.29, 111.46, 107.78, 105.79, 36.86, 36.25, 29.73. **HRMS (ESI):** Calcd. for $C_{28}H_{22}N_4O_2S$ $[M+H]^+$: 479.1536; found: 479.1531.

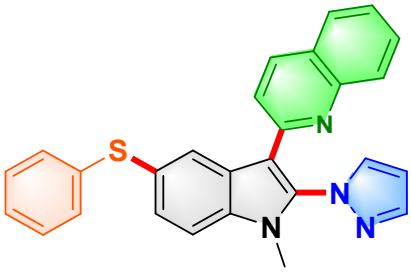
(80) 1-methyl-3-(1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (81)



Yellow solid, (79.9 mg, 69% yield), m.p.: 245-246 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 1.7 Hz, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.25–7.21 (m, 4H), 7.13 (t, *J* = 6.5 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.75 (s, 3H), 3.61 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.96, 151.04, 142.09, 139.21, 136.49, 134.96, 133.55, 133.23, 133.06, 130.09, 129.96, 129.40, 128.89, 128.08, 127.85, 126.66, 125.52, 125.44, 123.53, 113.50, 111.06, 106.99, 106.50, 30.44, 29.45.

HRMS (ESI): Calcd. for $C_{27}H_{21}N_5OS$ $[M+H]^+$: 464.1540; found: 464.1542.

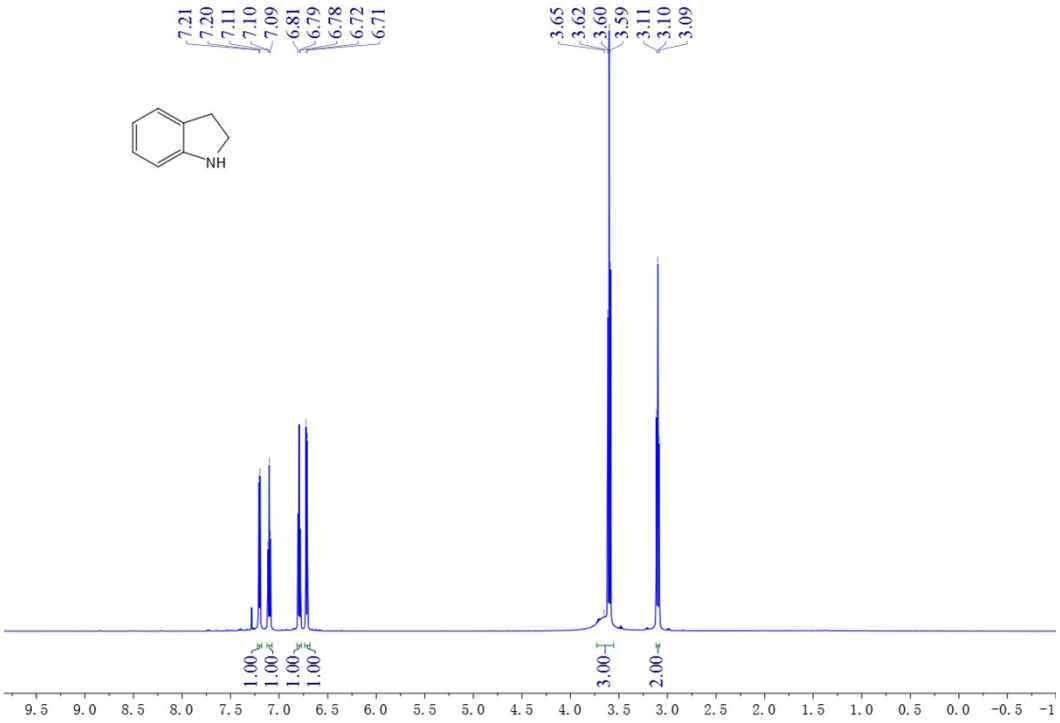
(81) 2-(1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)quinoline (82)



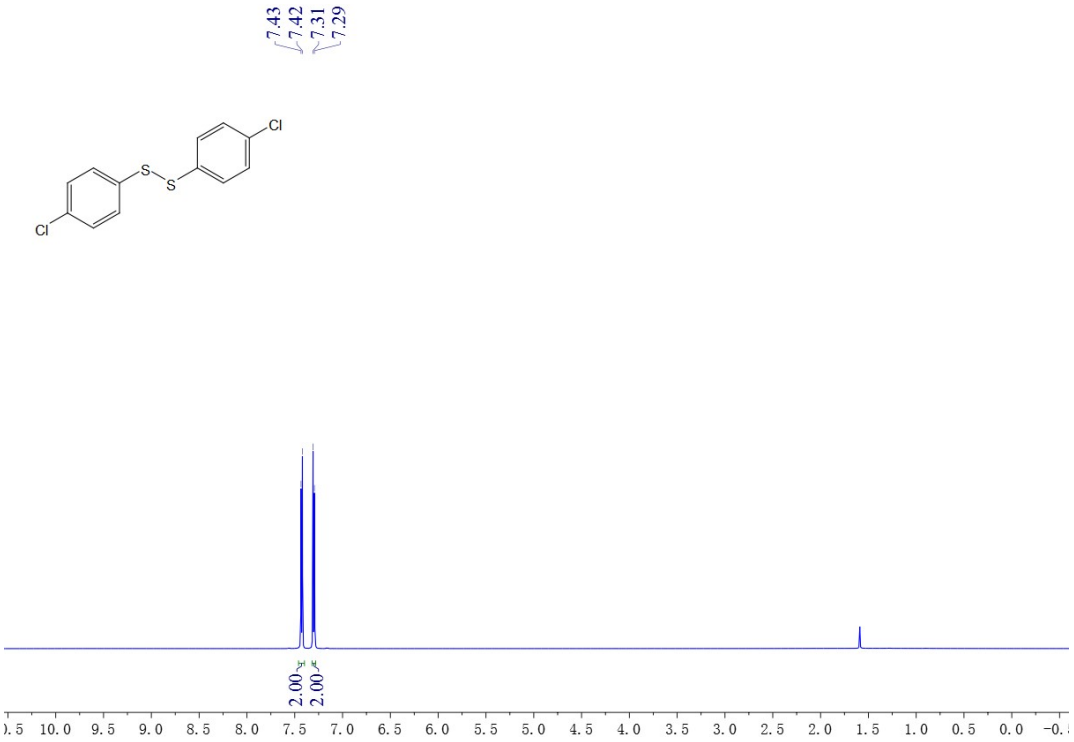
White solid, (67.0 mg, 62% yield), m.p.: 171-172 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.12–8.09 (m, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.72–7.69 (m, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.31–7.26 (m, 4H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 3.65 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 148.27, 142.73, 138.93, 136.16, 134.94, 134.17, 134.00, 129.53, 129.45, 129.40, 128.94, 128.56, 128.32, 127.32, 126.41, 126.01, 125.98, 125.95, 125.71, 120.34, 111.42, 110.83, 107.74, 29.72. **HRMS (ESI):** Calcd. for $C_{27}H_{20}N_4S$ $[M+H]^+$: 433.1481; found: 433.1477.

11. NMR spectra of the obtained compounds.

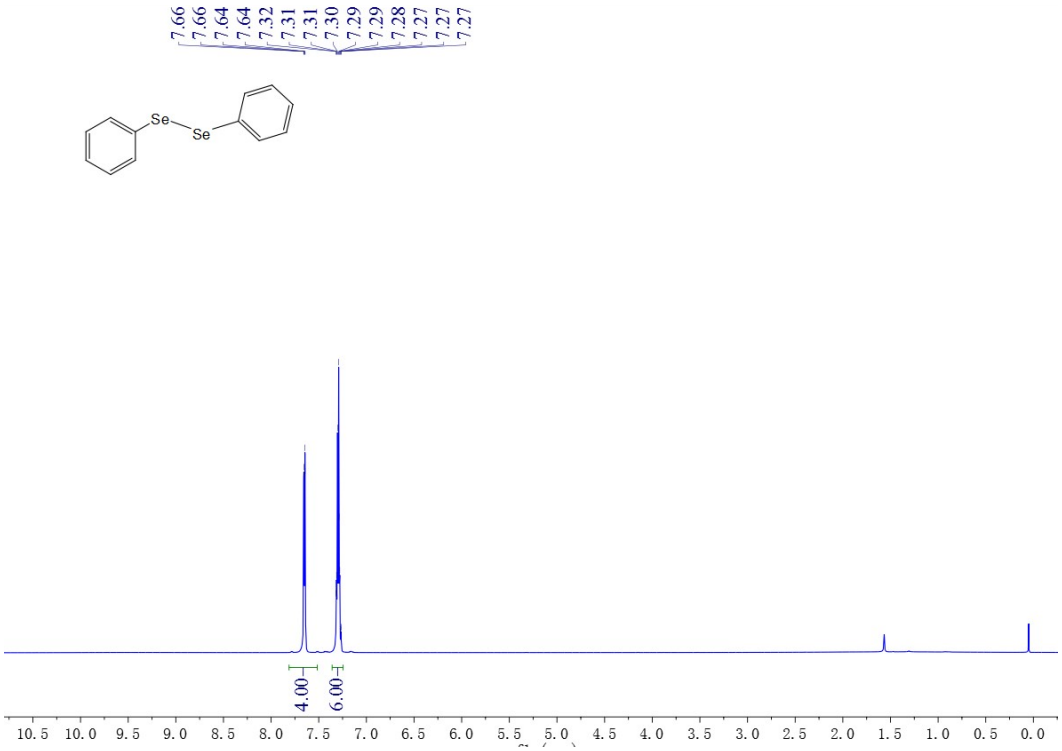
(1) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1f



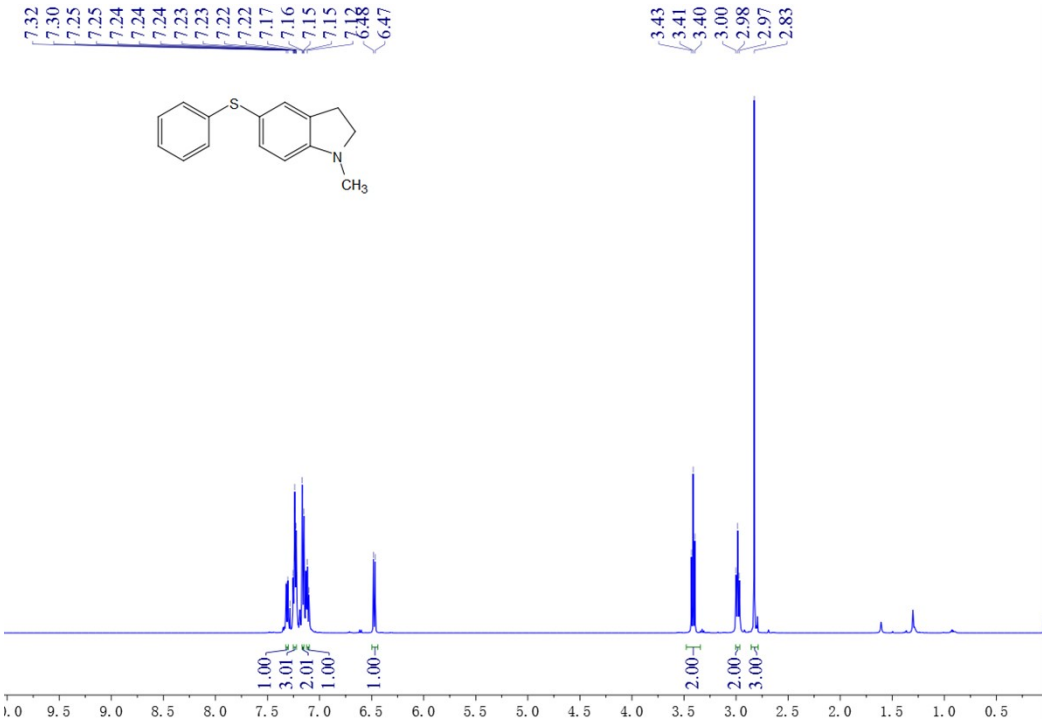
(2) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 2e



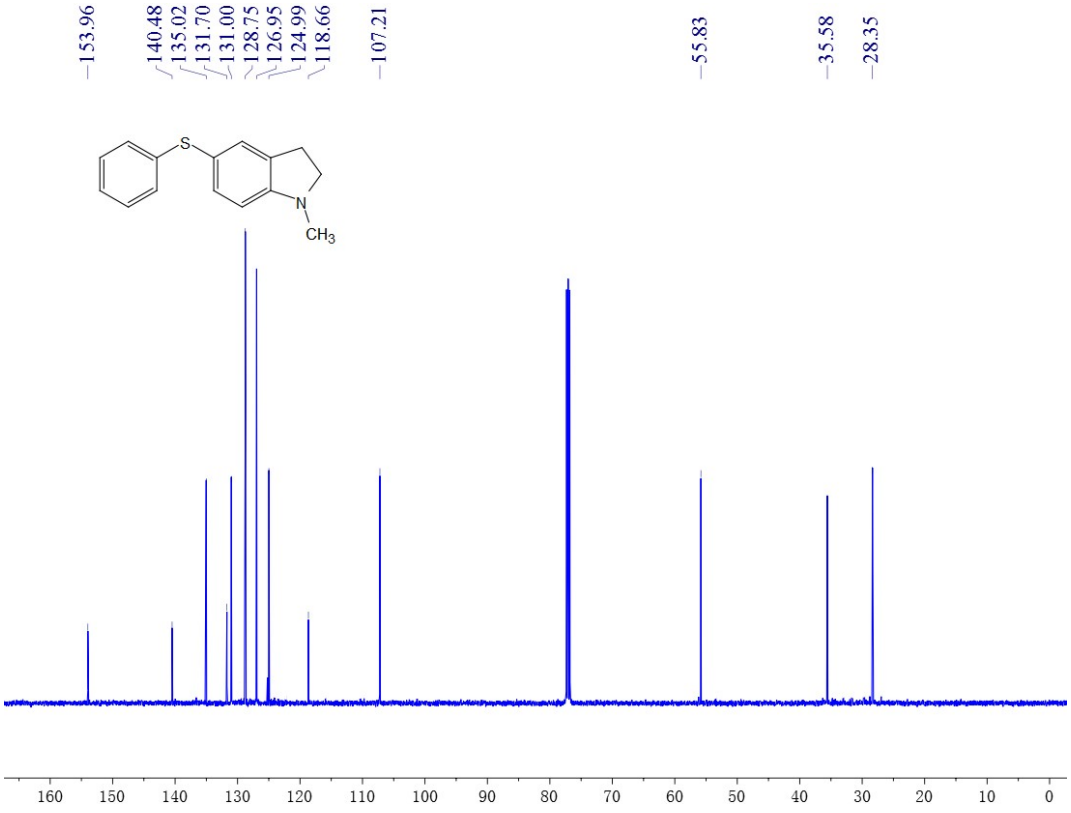
(3) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 2r



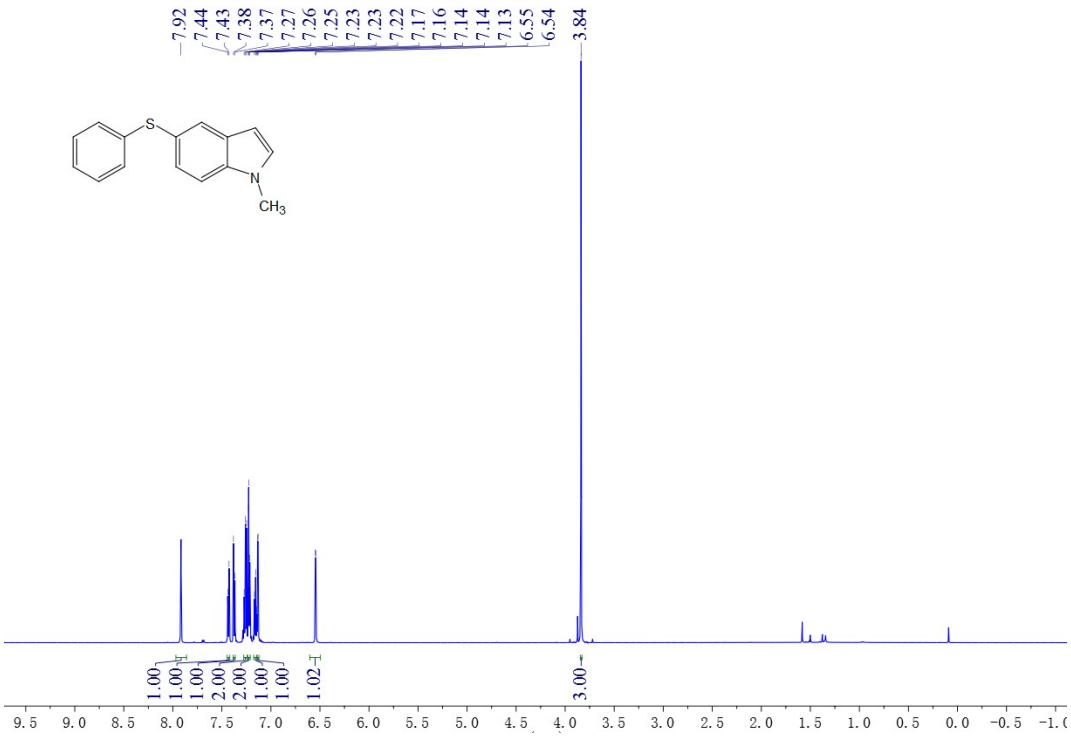
(4) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-1



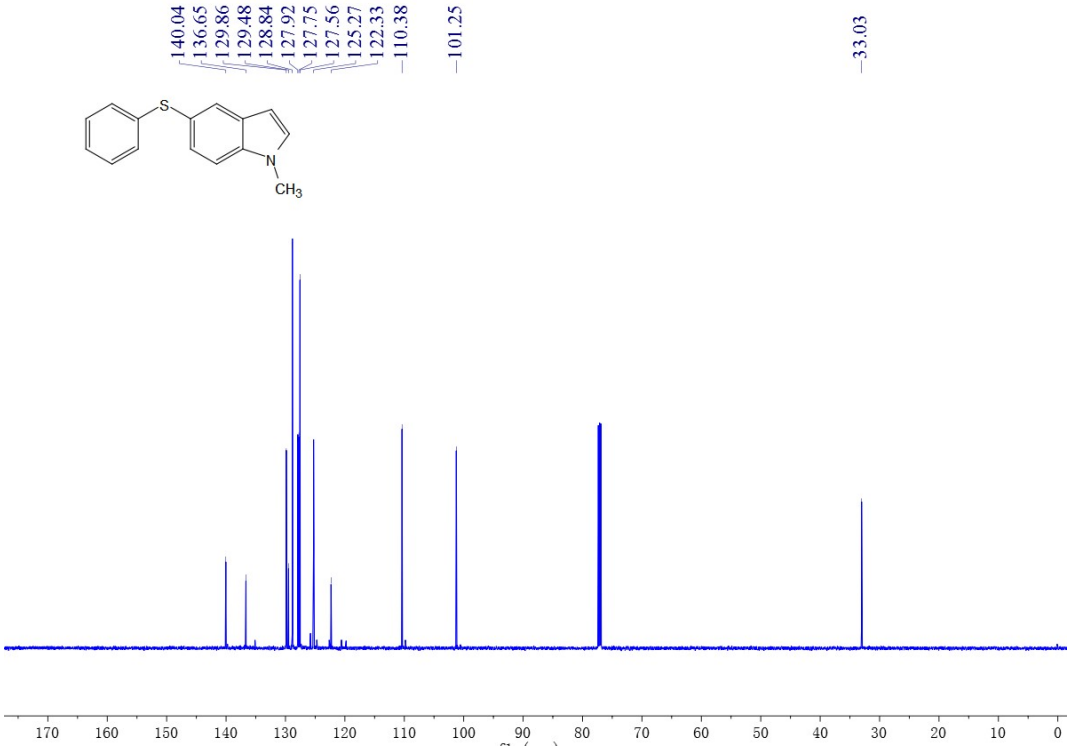
(5) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-1



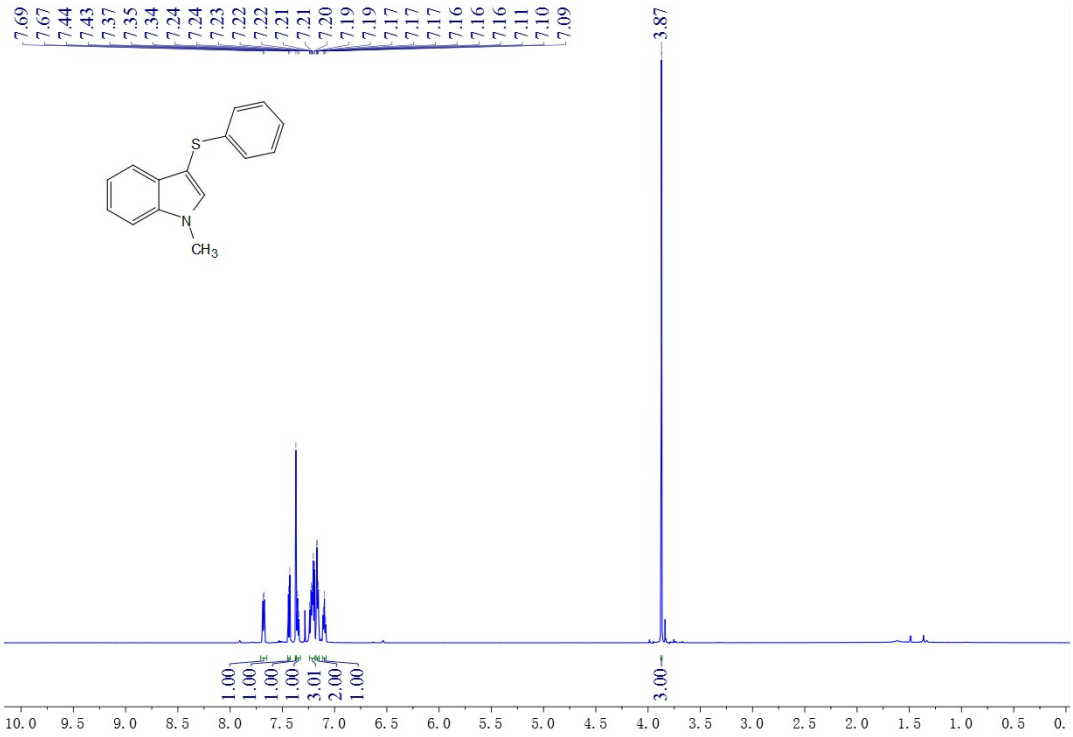
(6) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-2



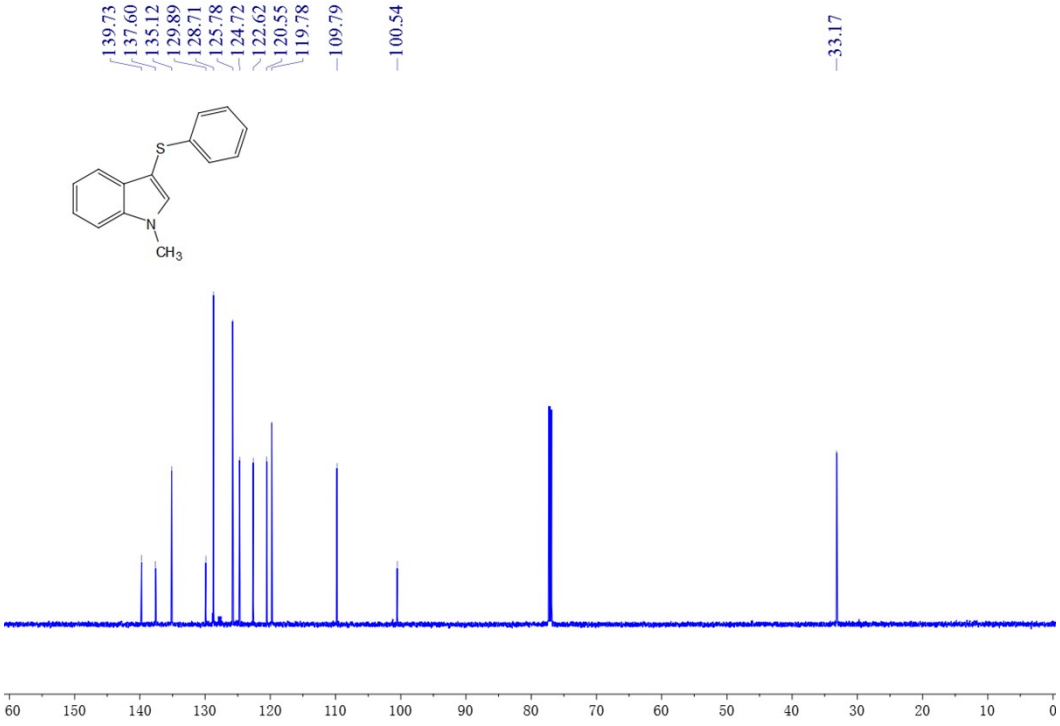
(7) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-2



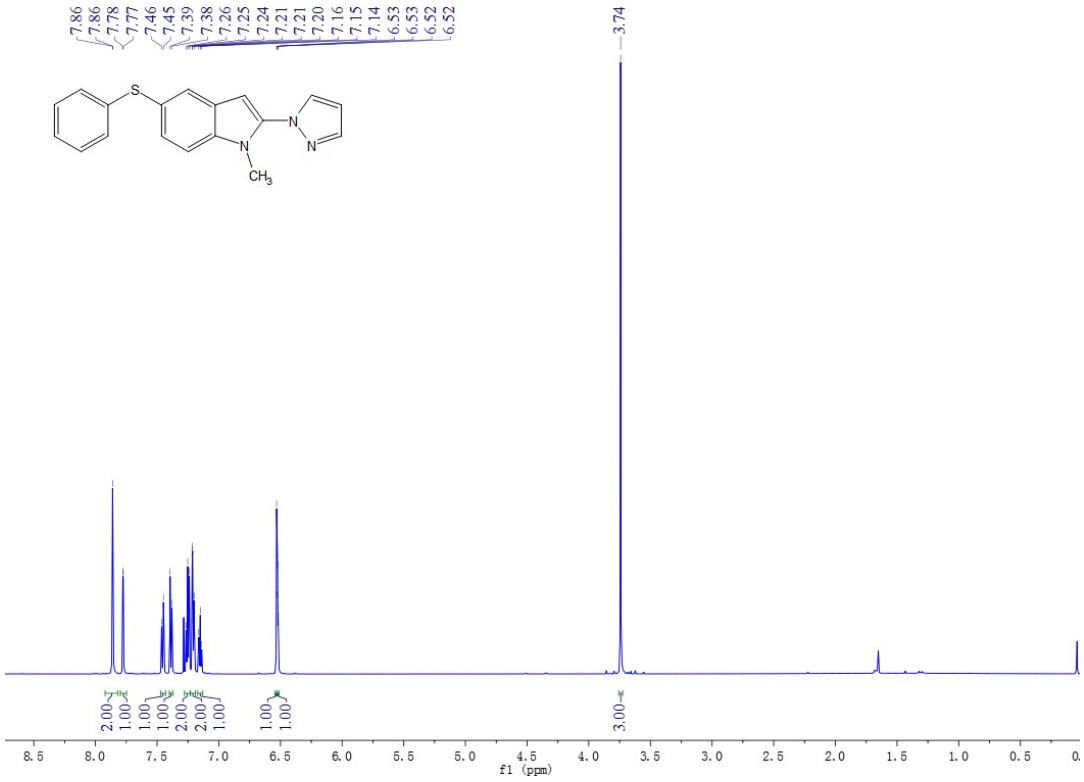
(8) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-4



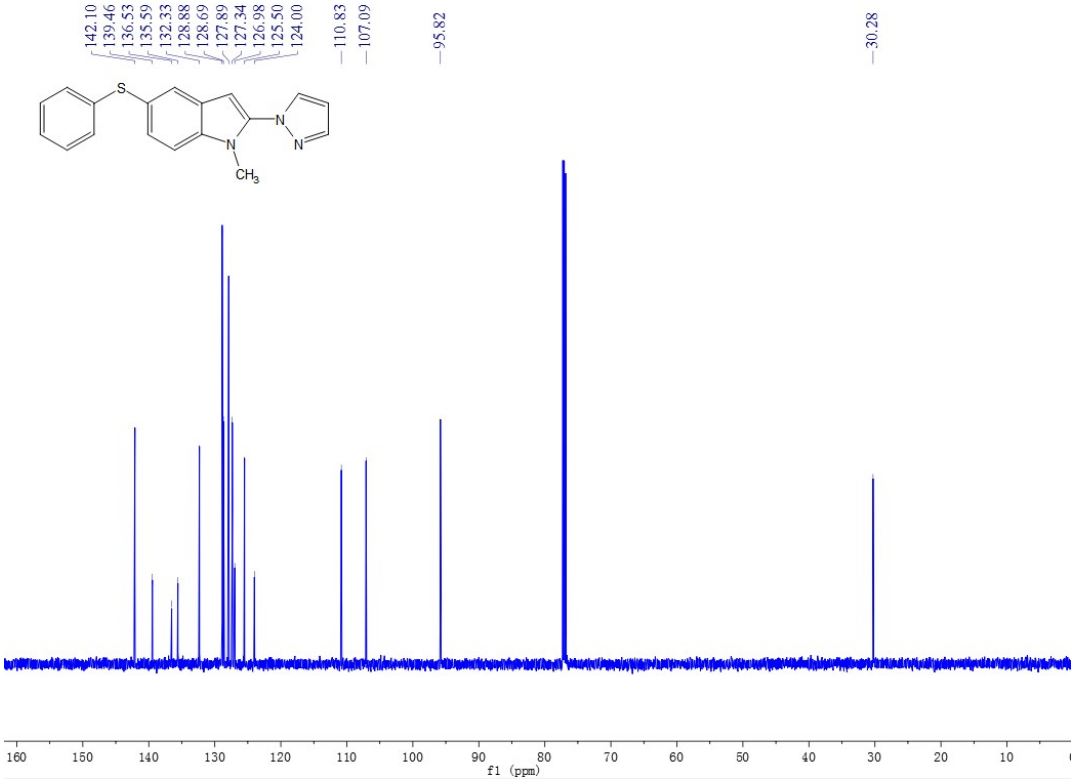
(9) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-4



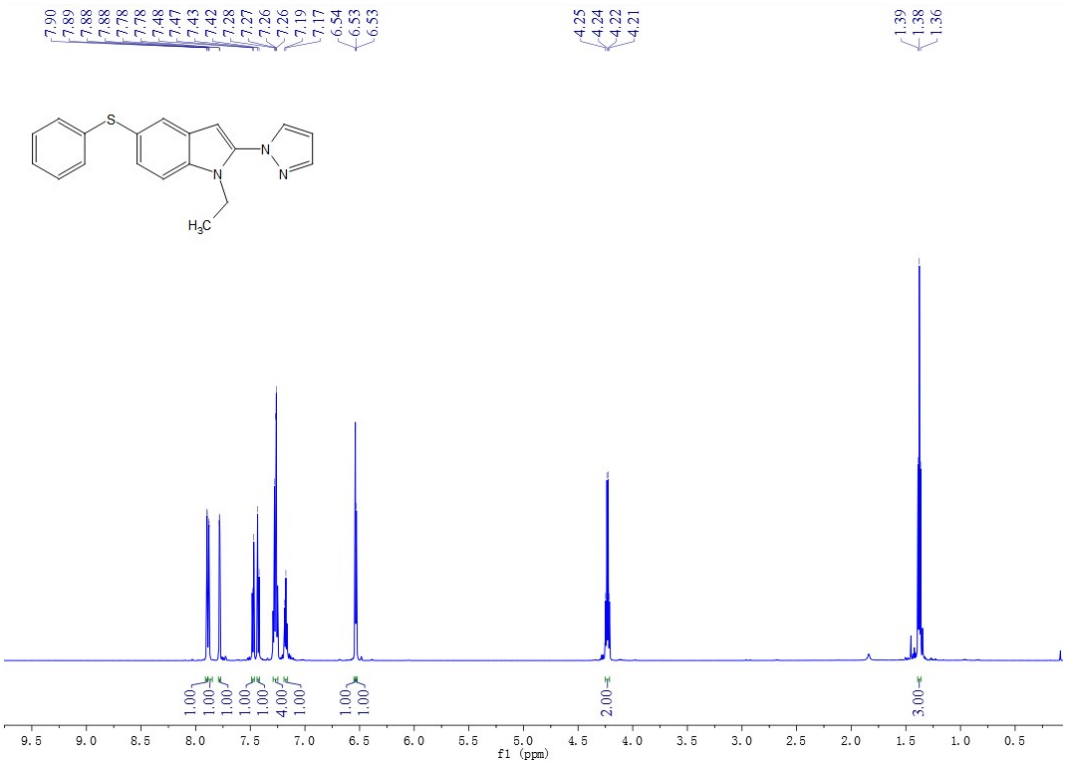
(10) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 4



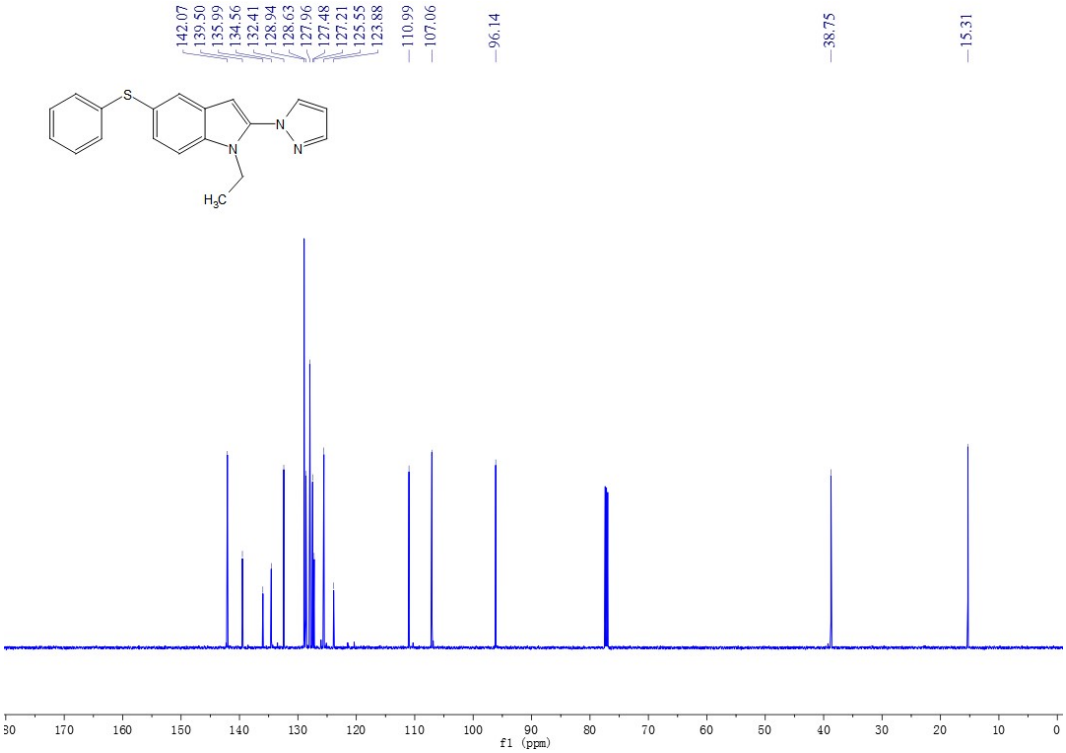
(11) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 4



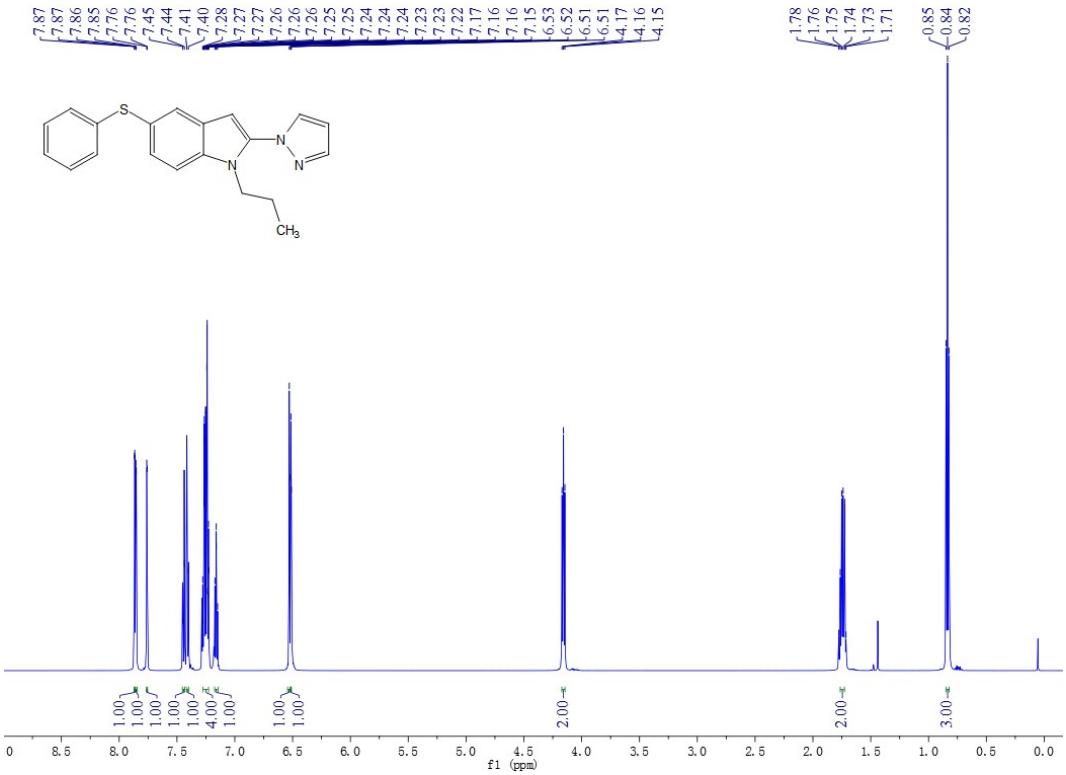
(12) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 5



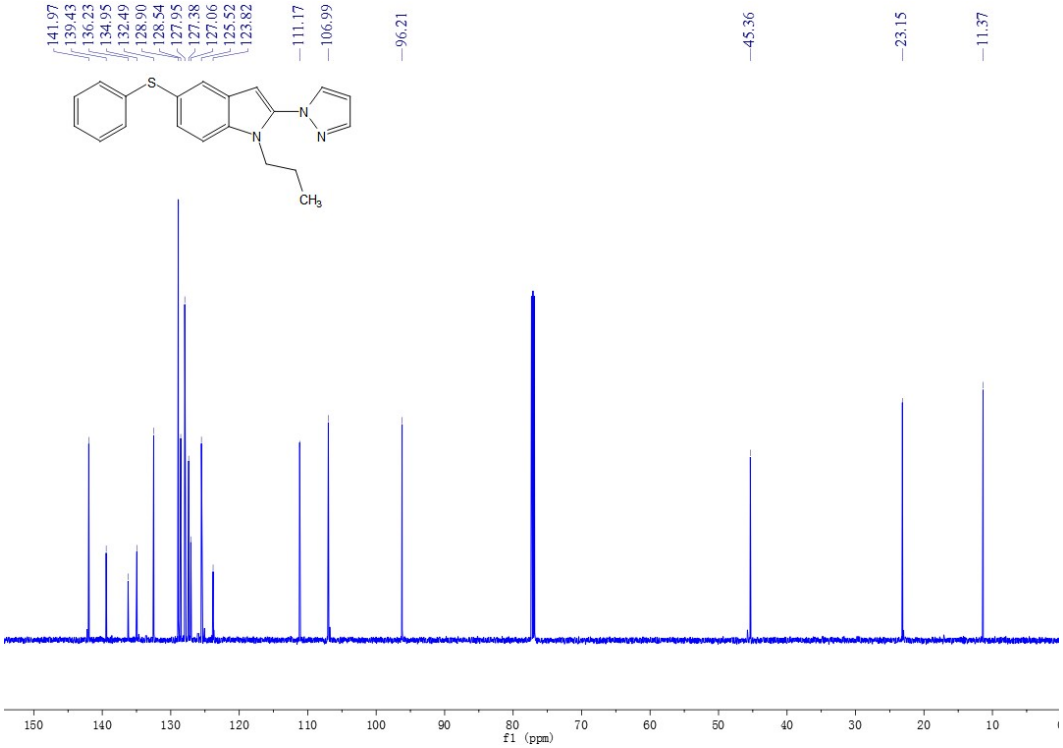
(13) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 5



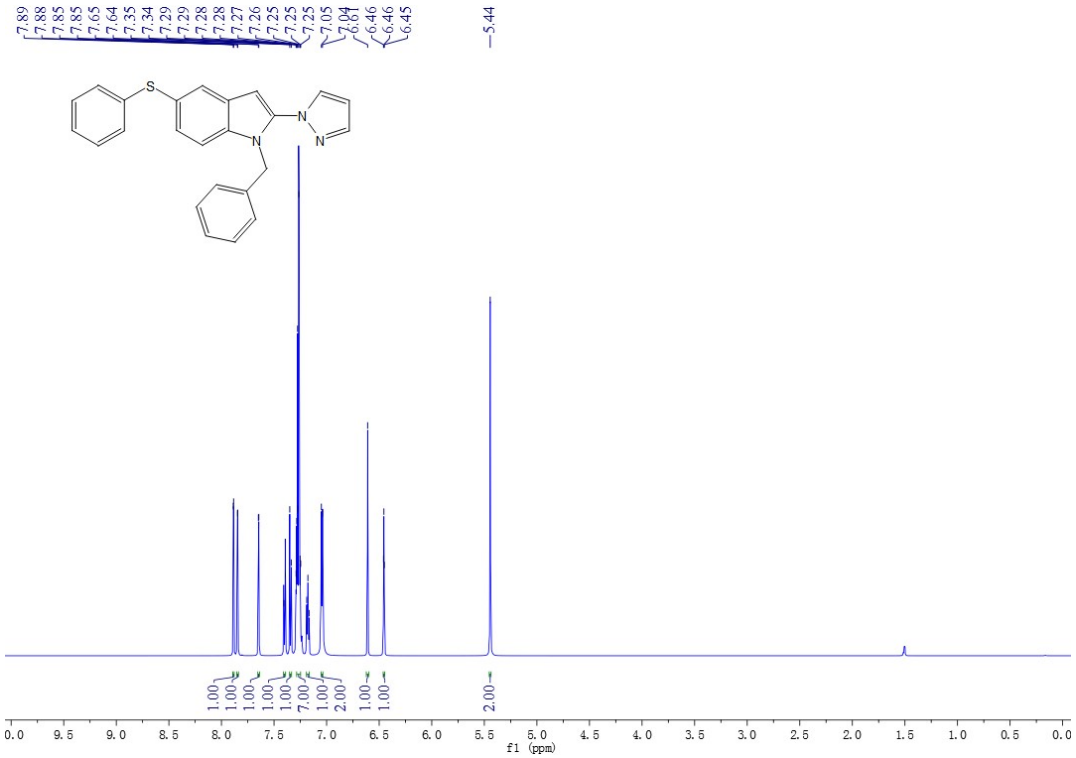
(14) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 6



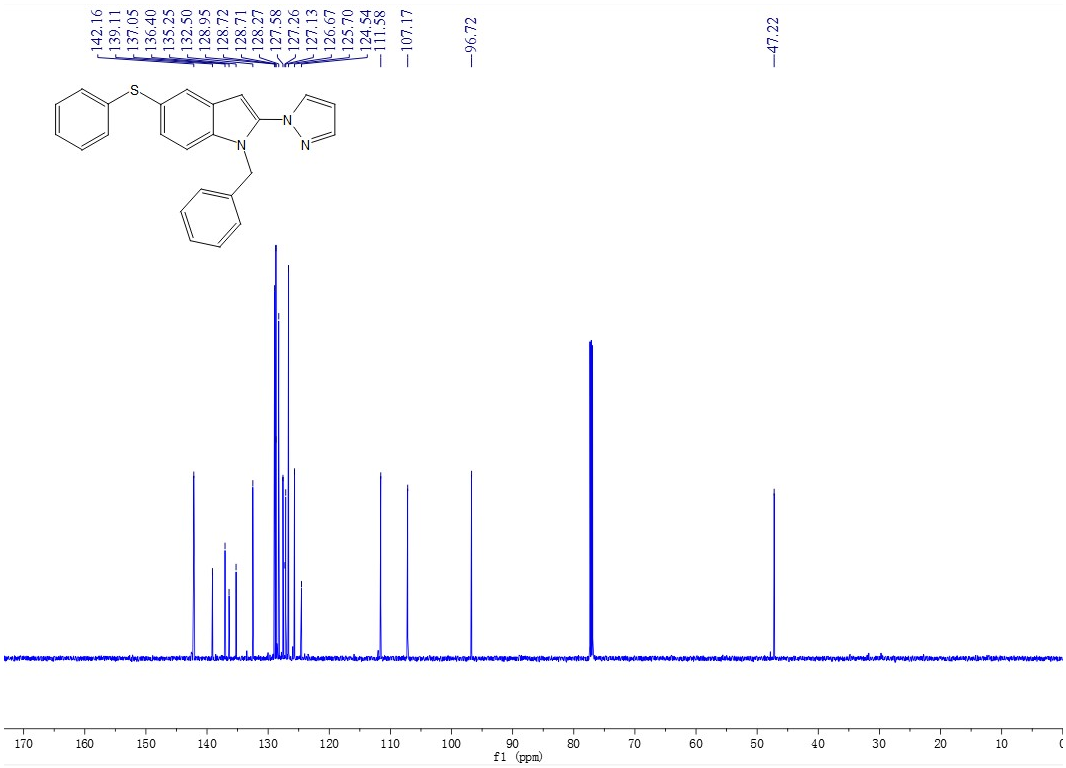
(15) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 6



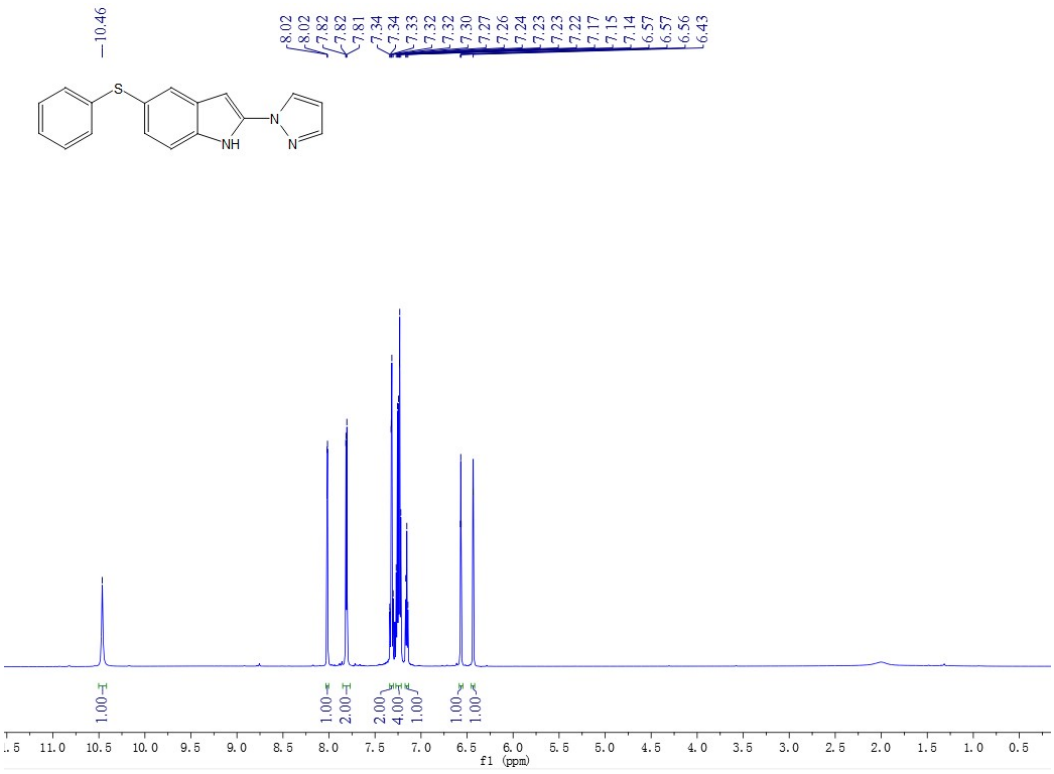
(16) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 7



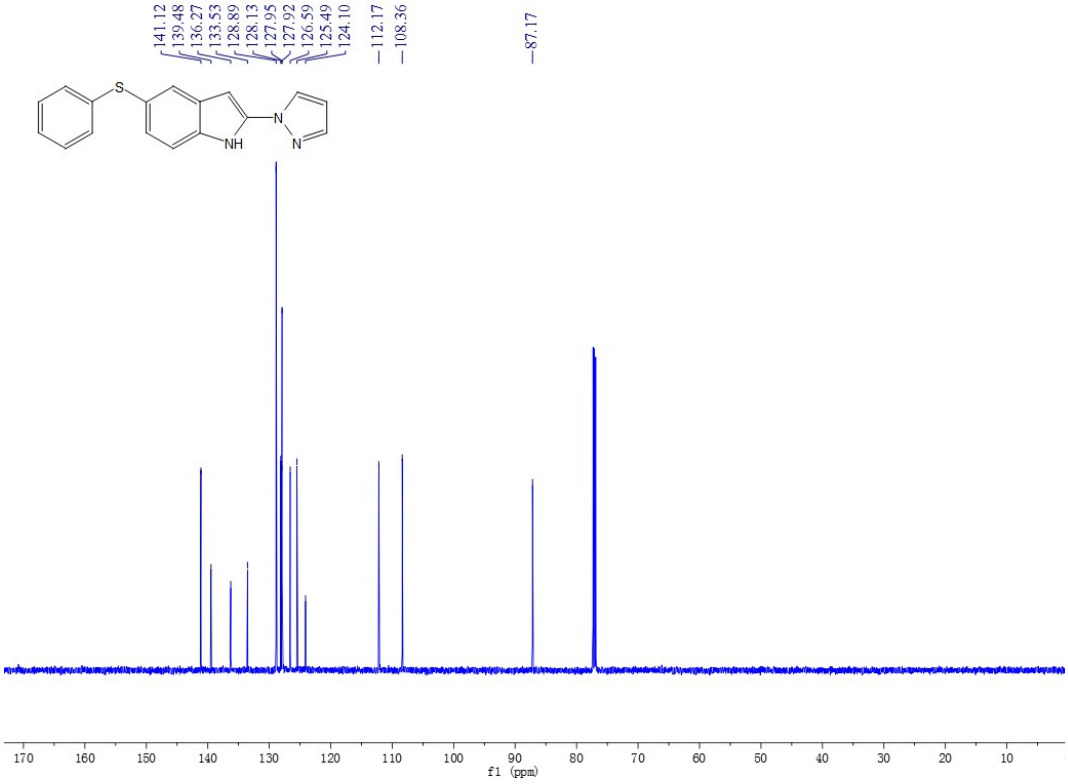
(17) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 7



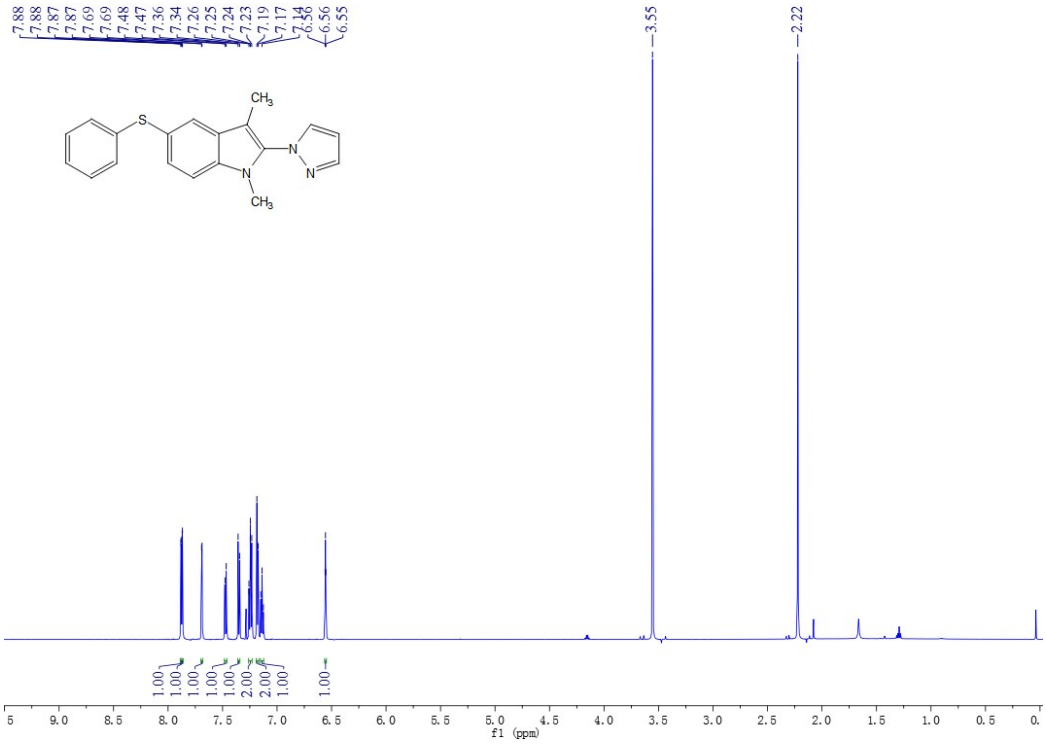
(18) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 9



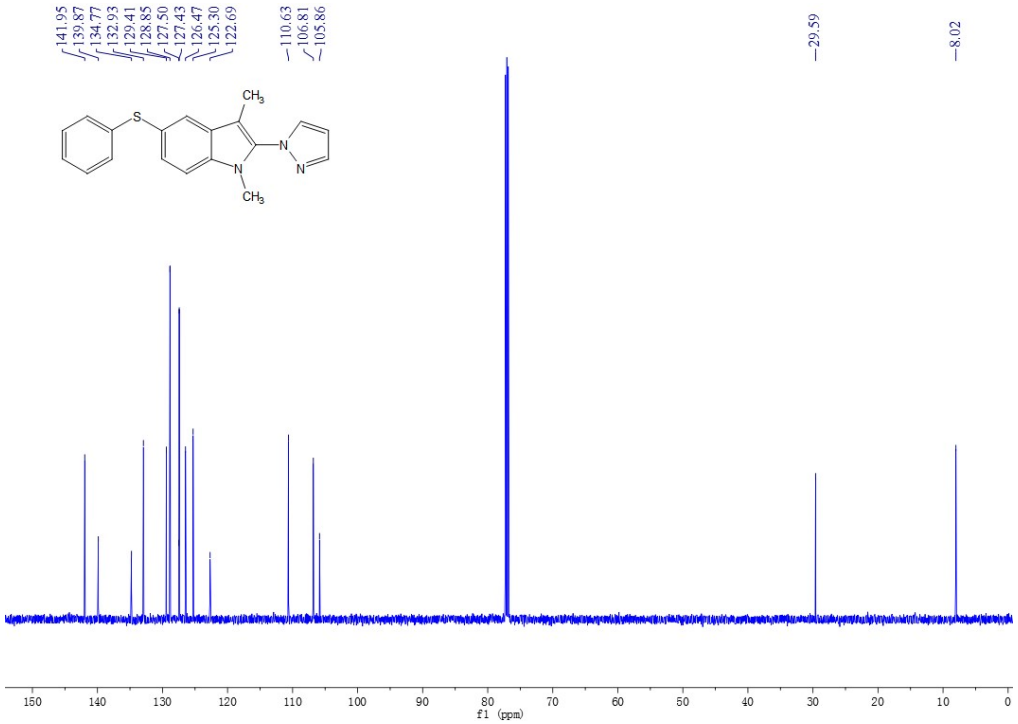
(19) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 9



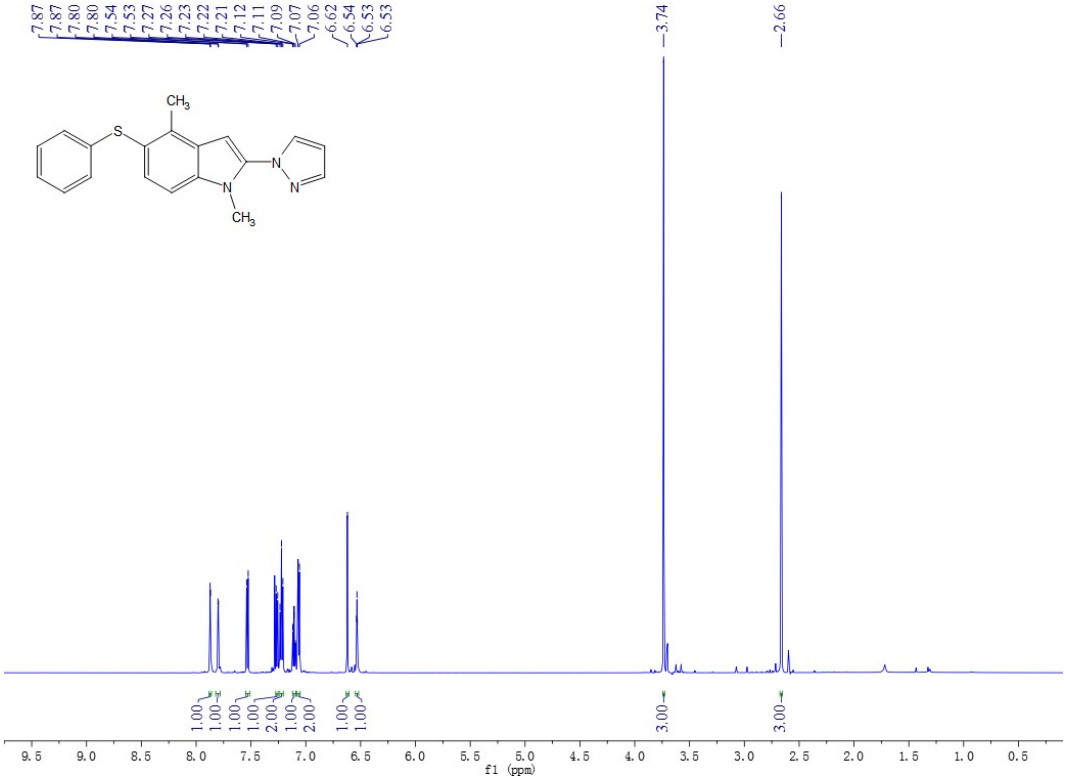
(20) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 10



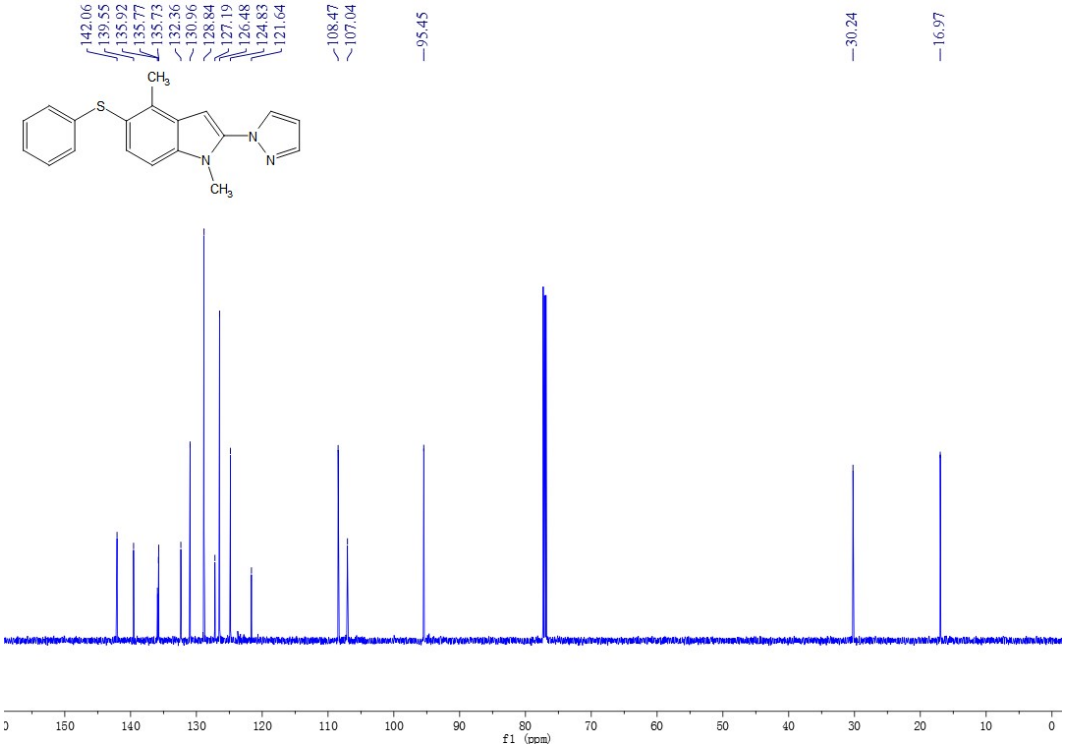
(21) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 10



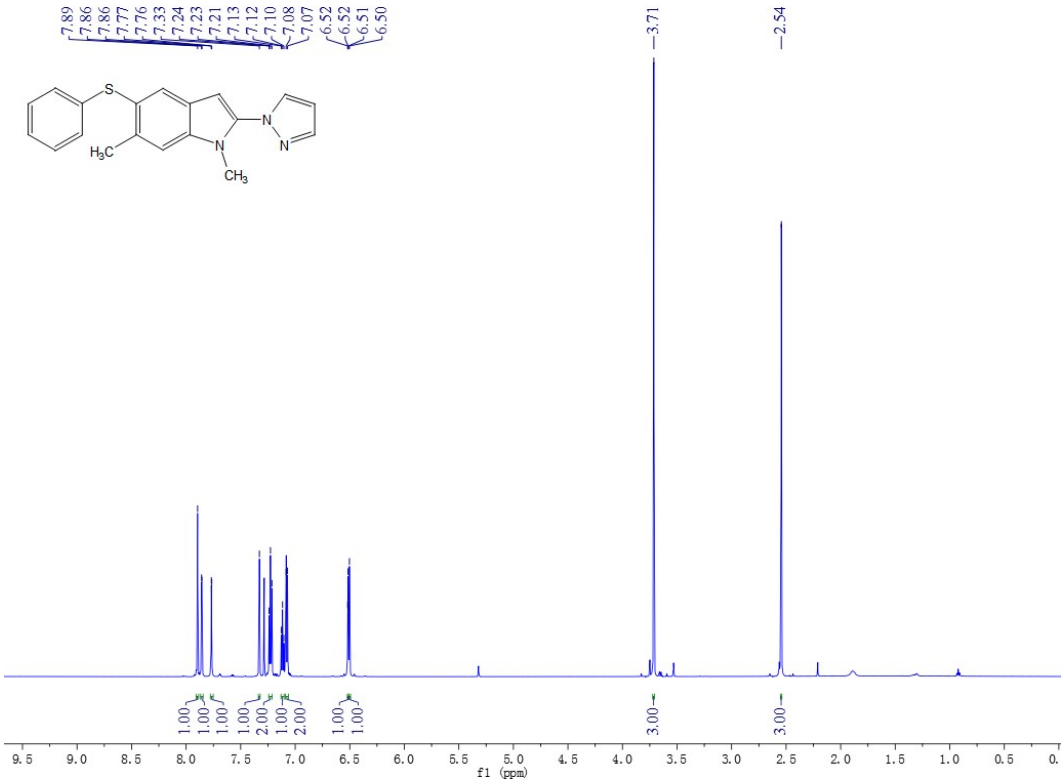
(22) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 11



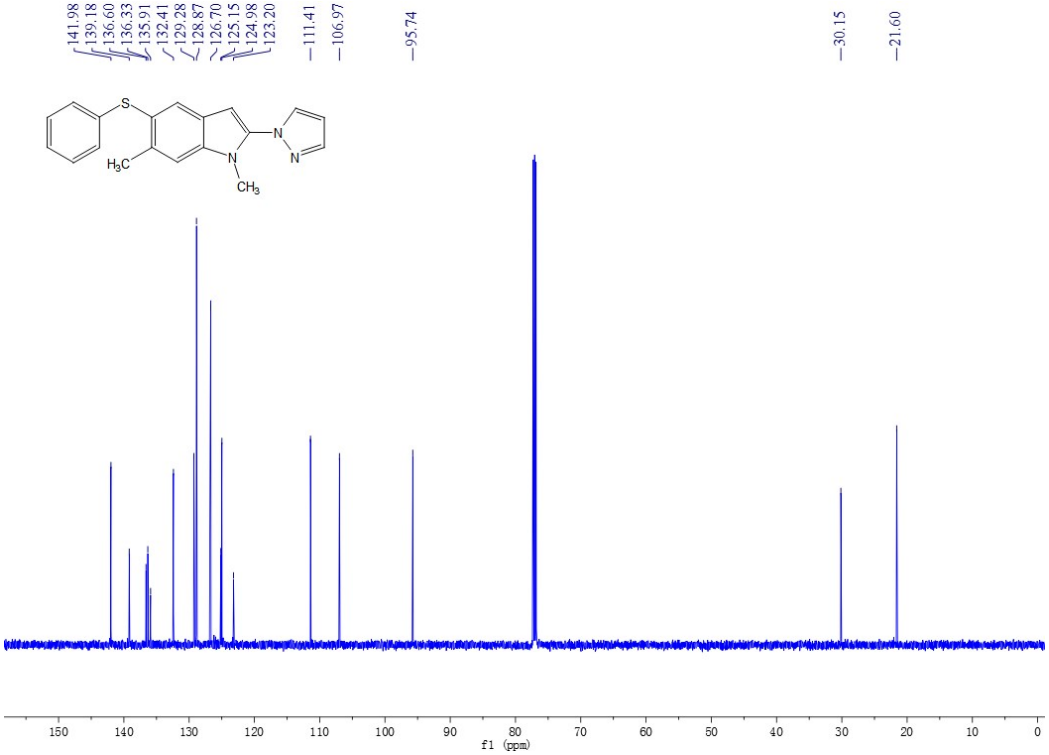
(23) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 11



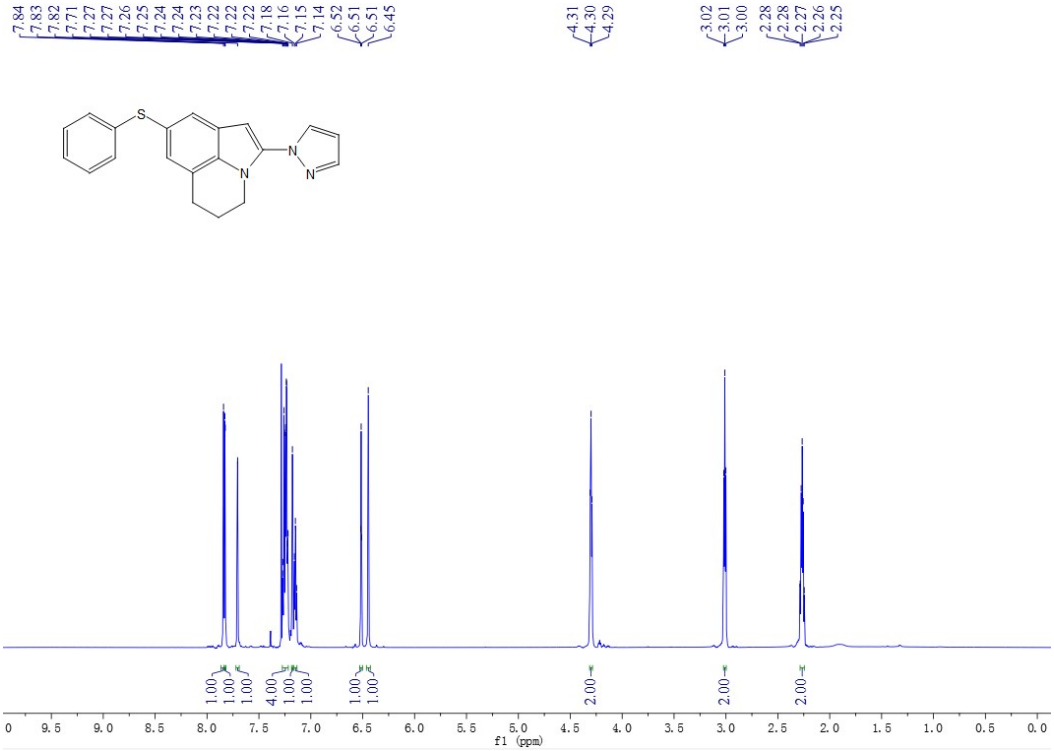
(24) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 12



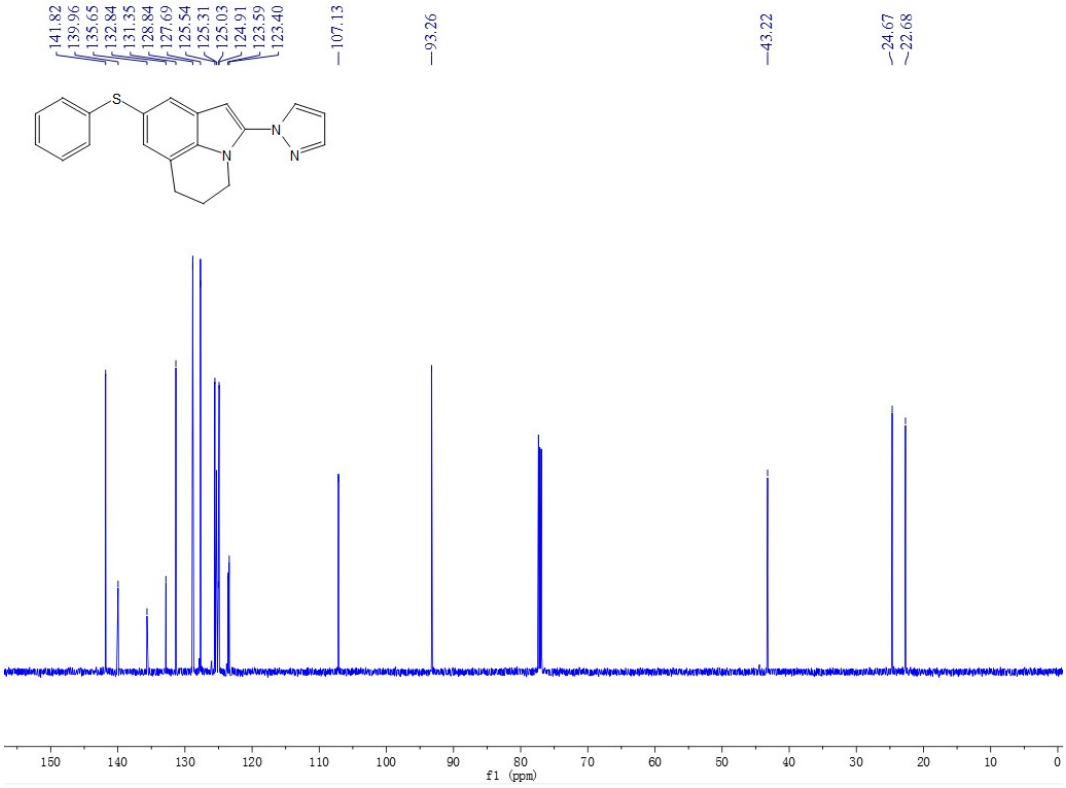
(25) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 12



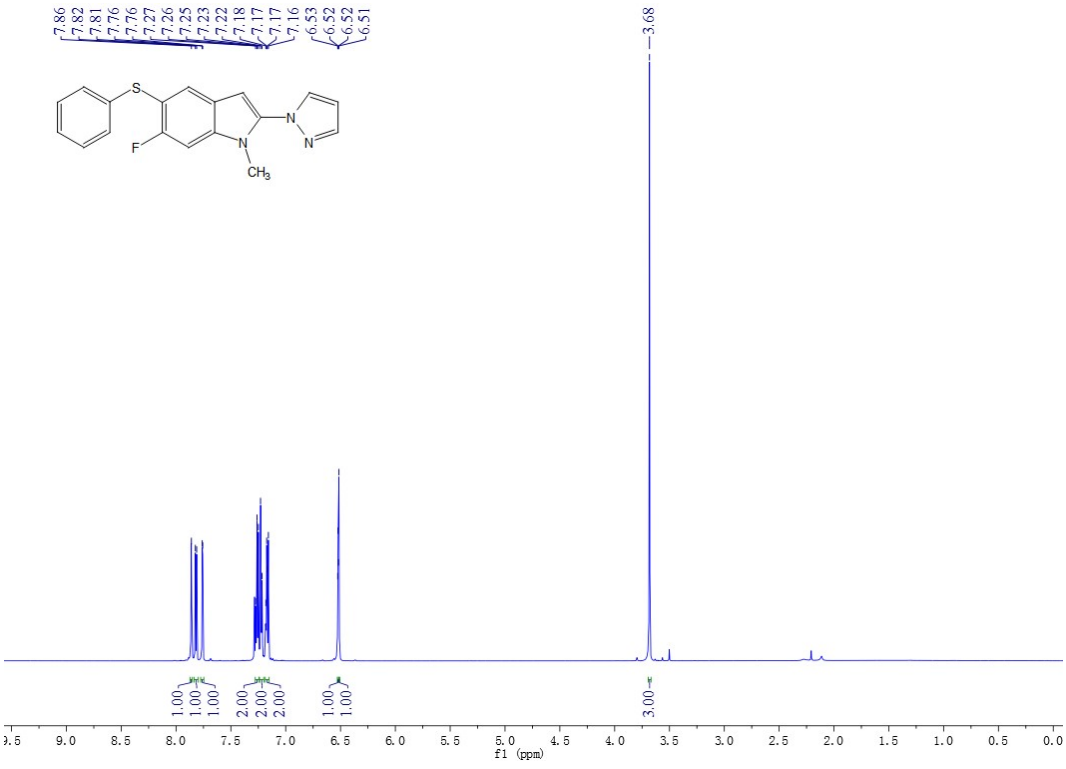
(26) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 13



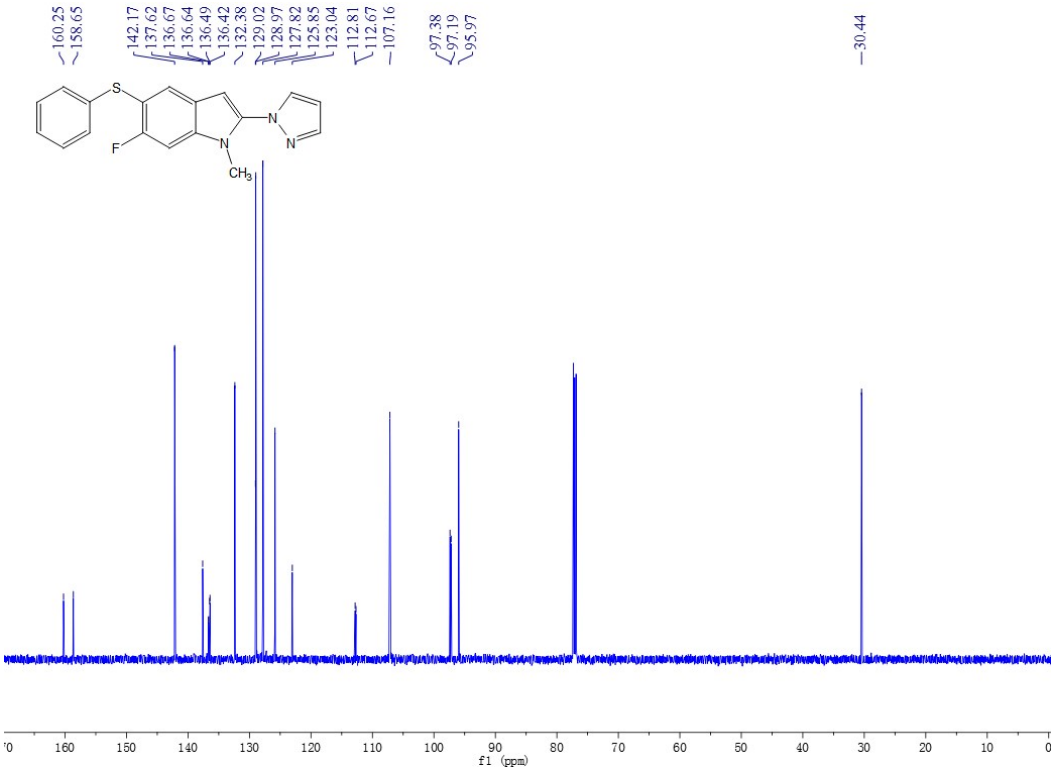
(27) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 13



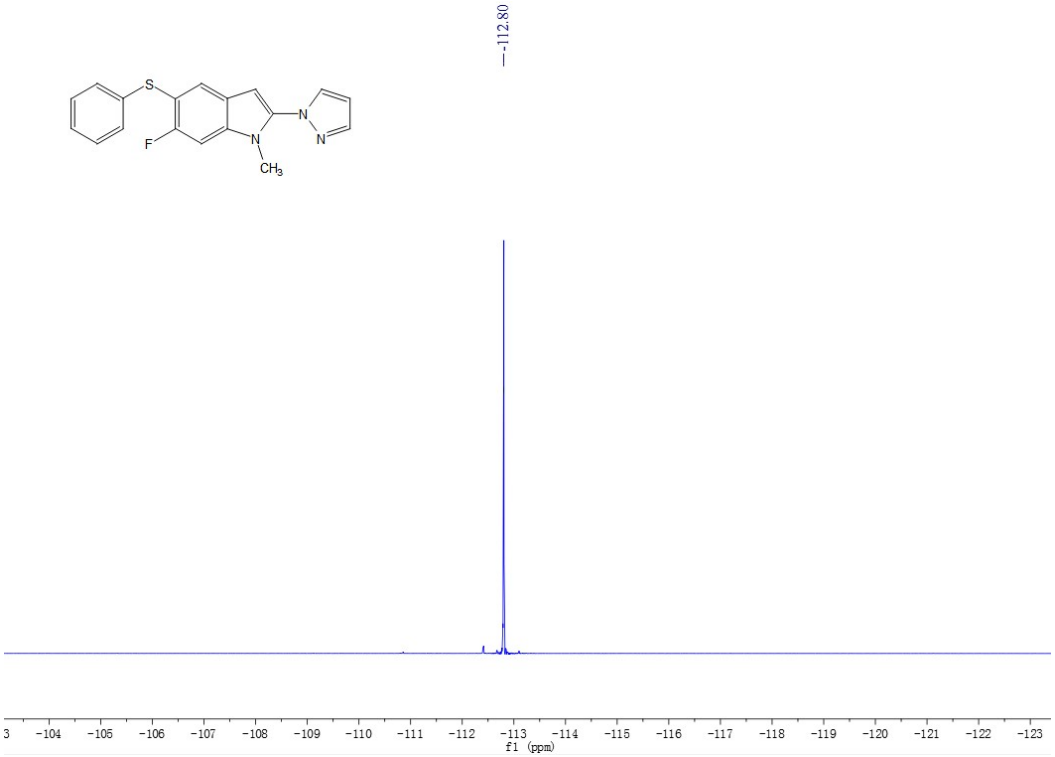
(28) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 14



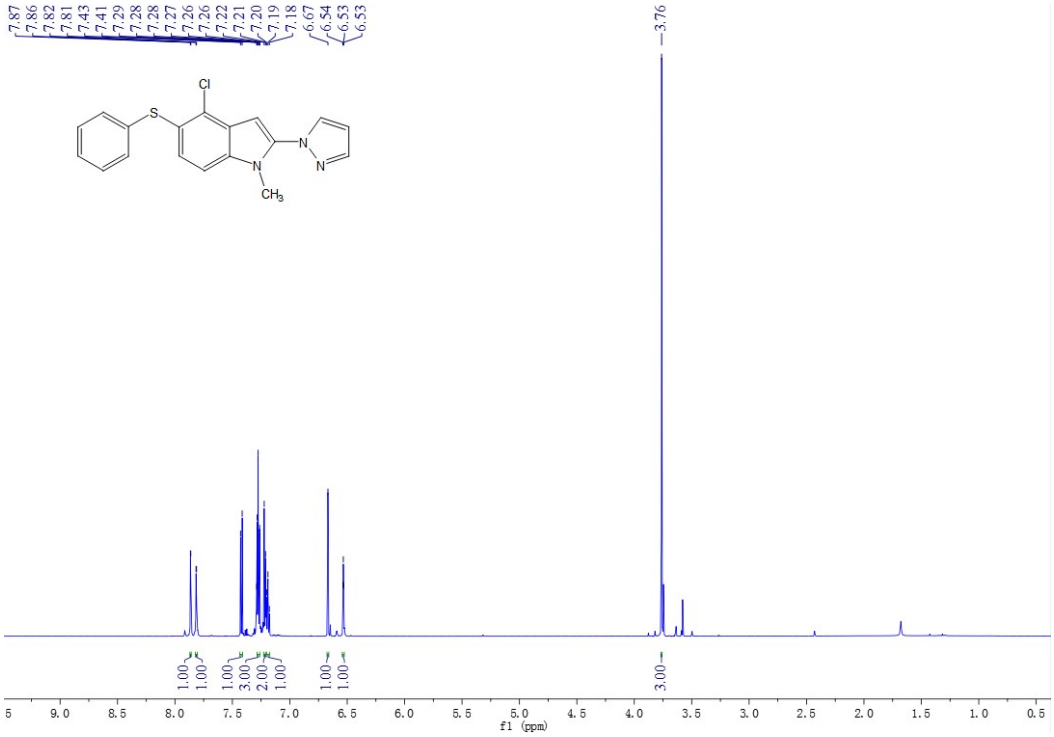
(29) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 14



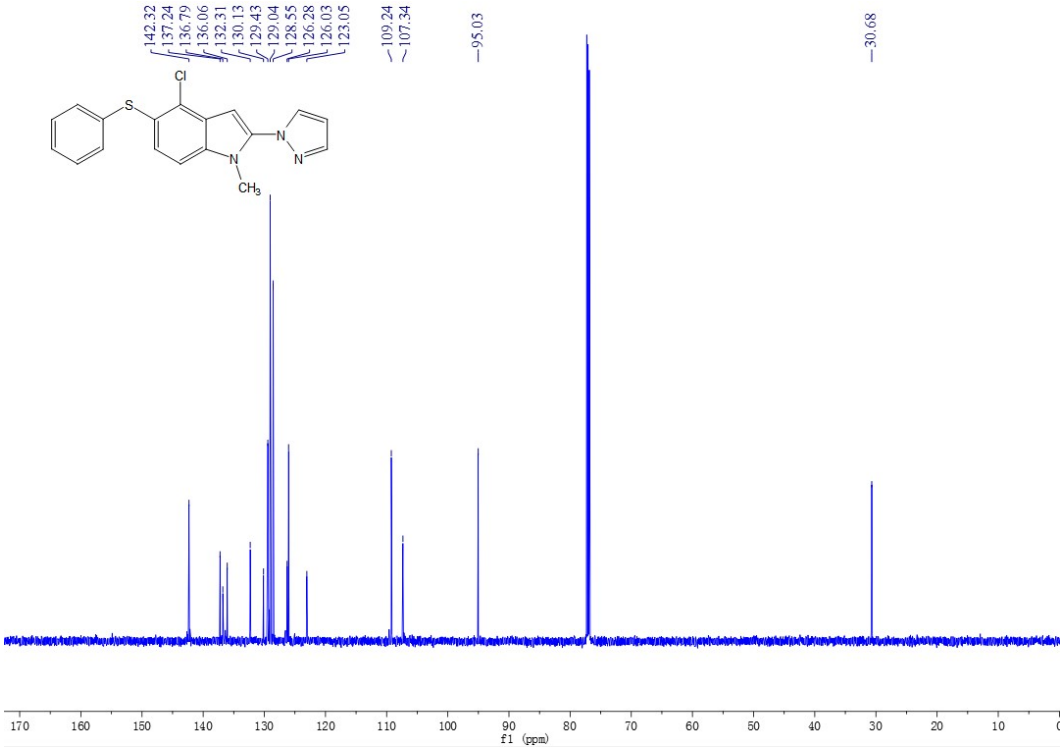
(30) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 14



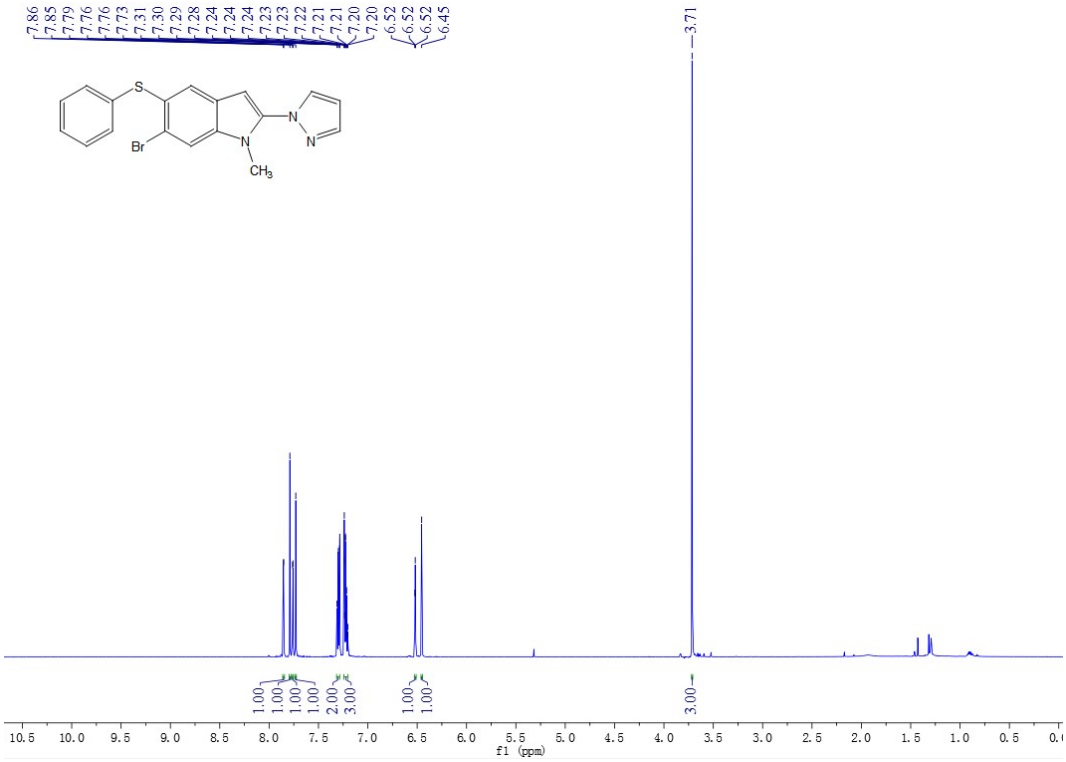
(31) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 15



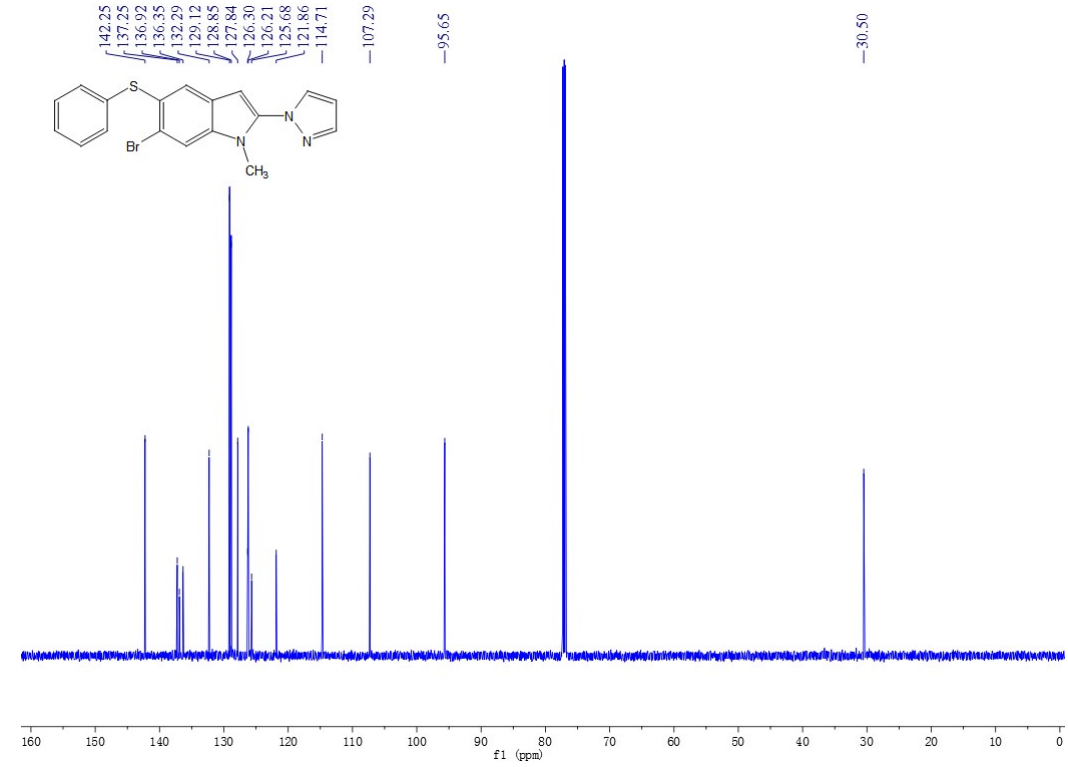
(32) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 15



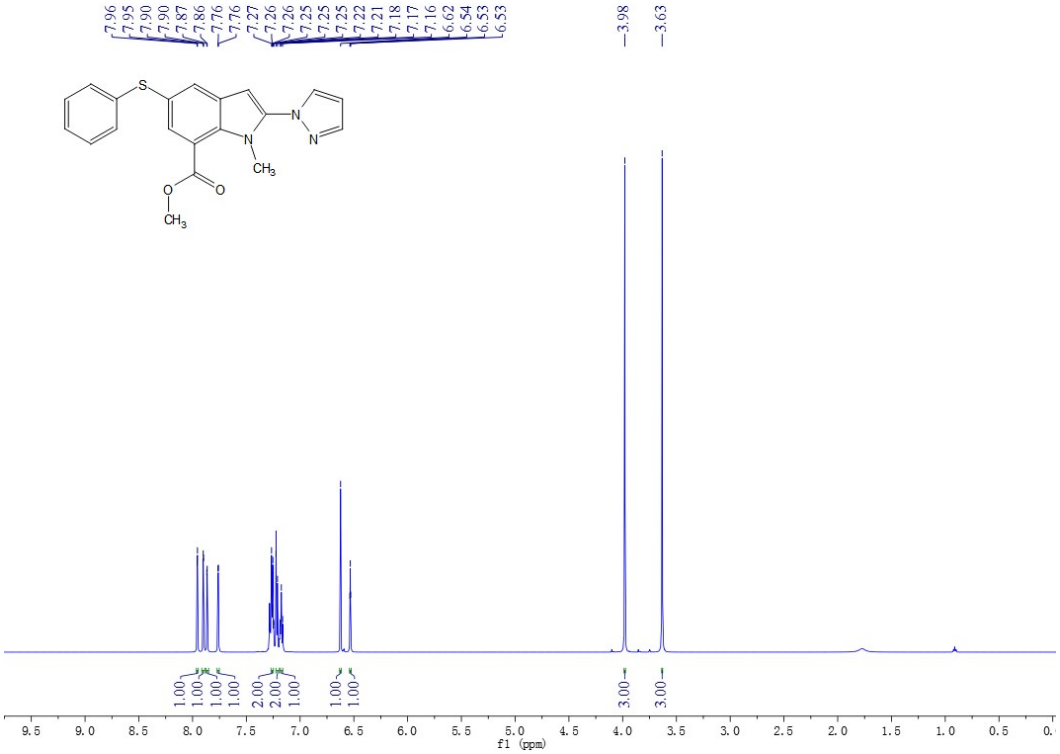
(33) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 16



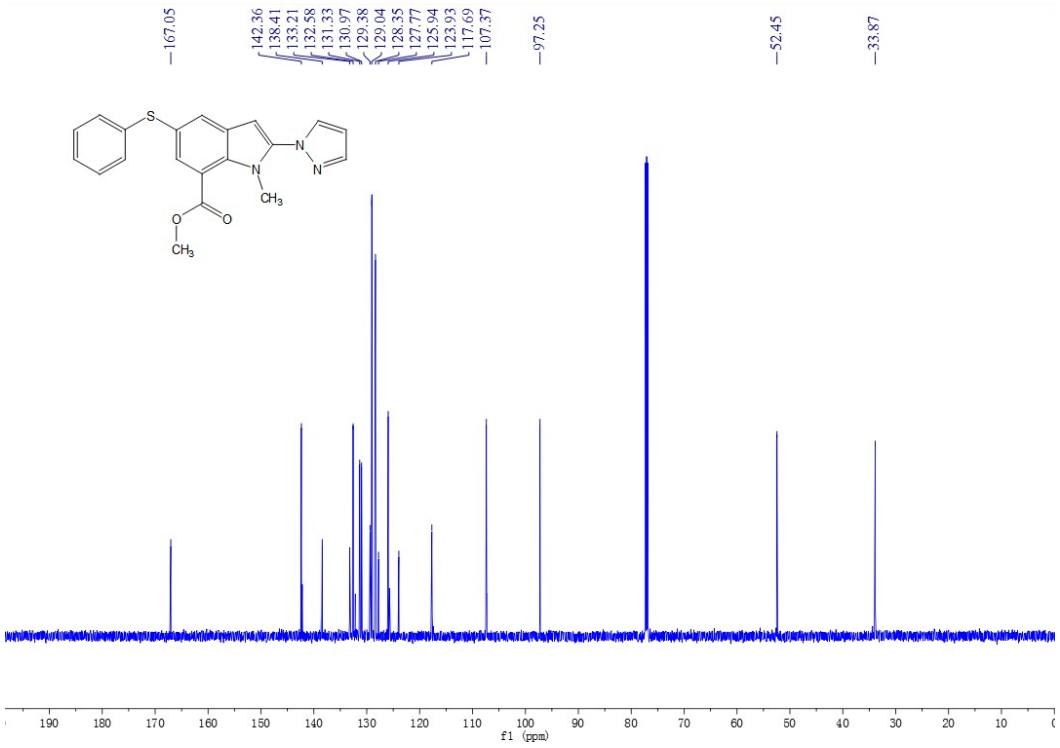
(34) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 16



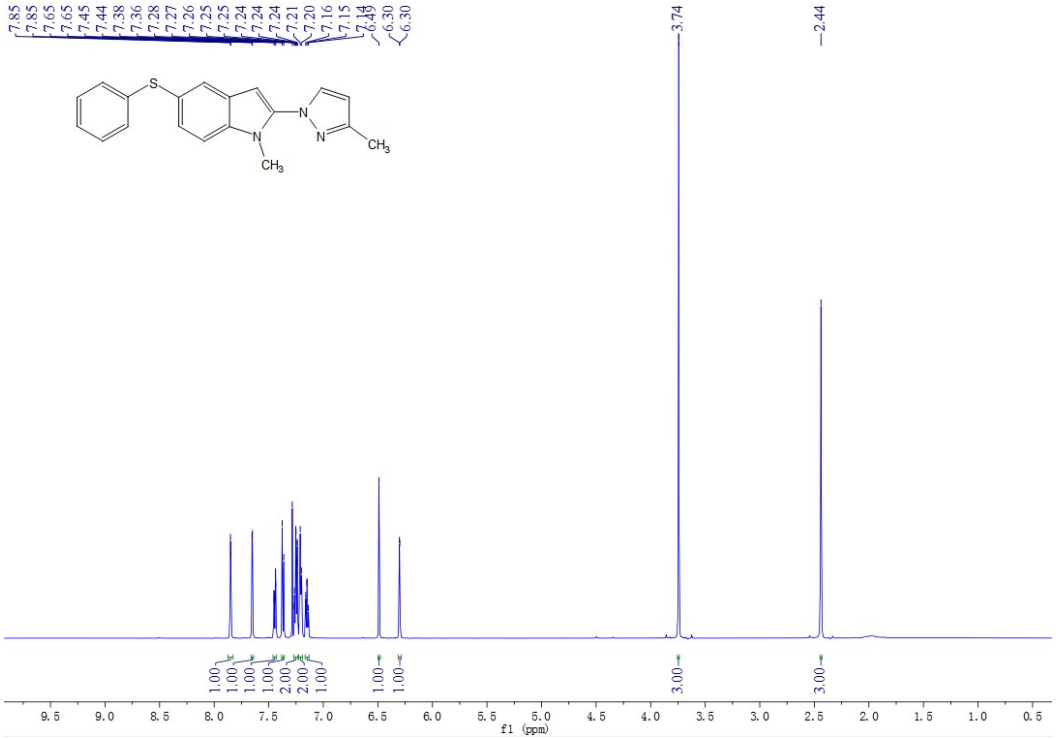
(35) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 17



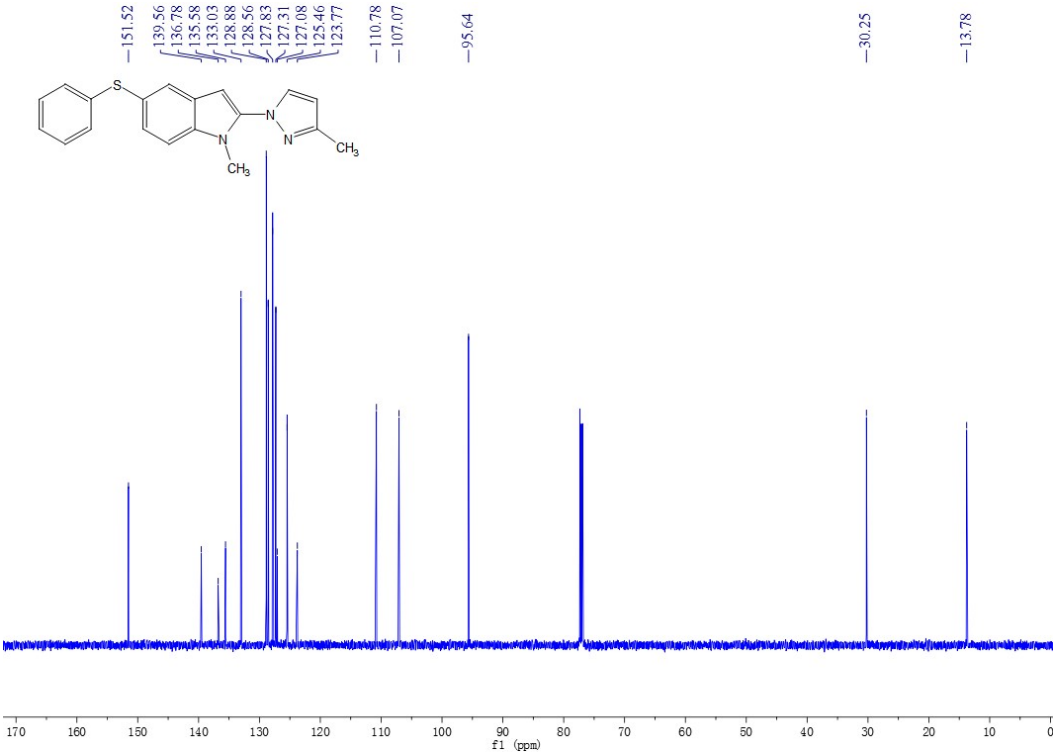
(36) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 17



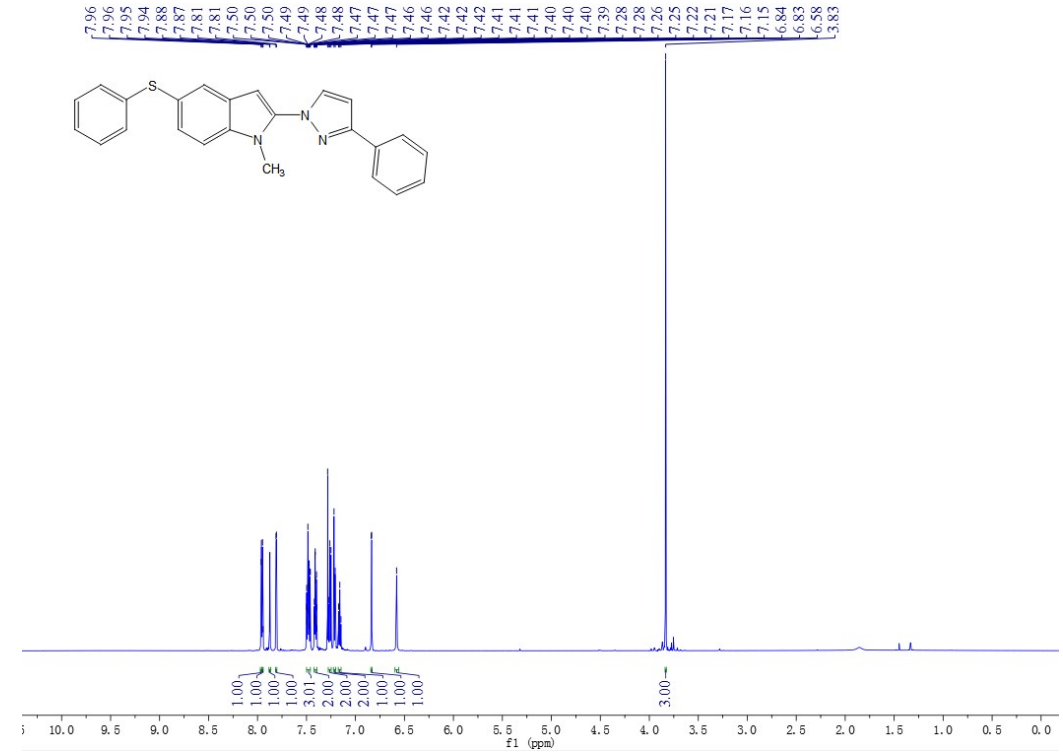
(37) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 18



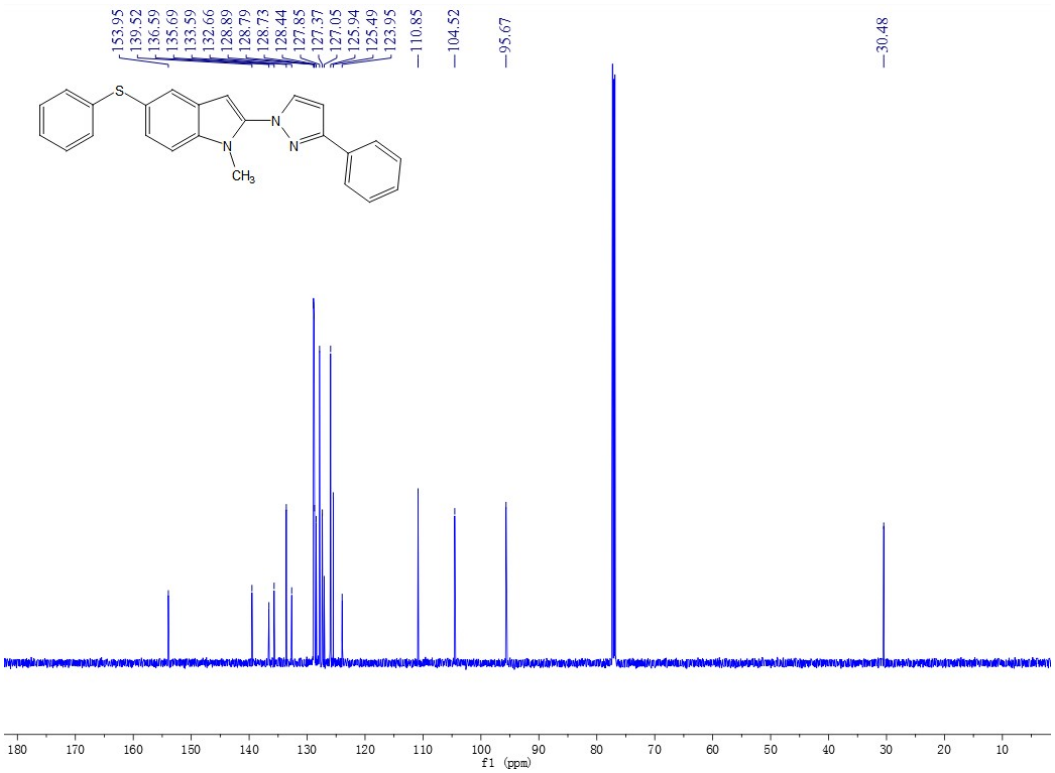
(38) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 18



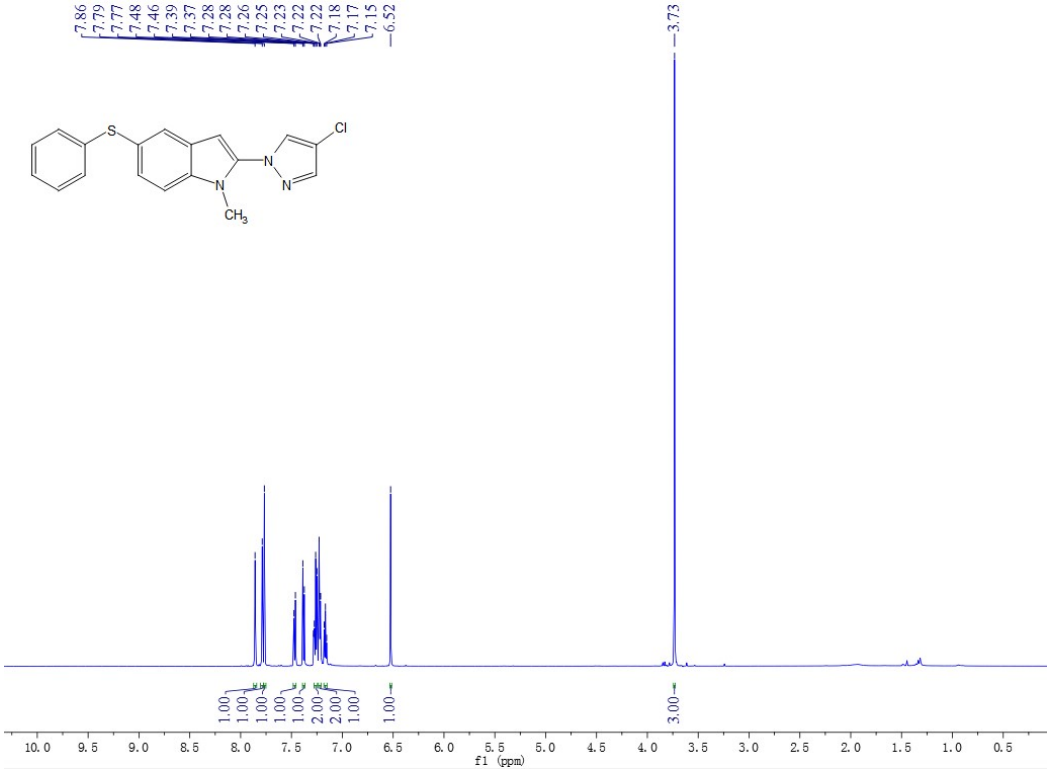
(39) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 19



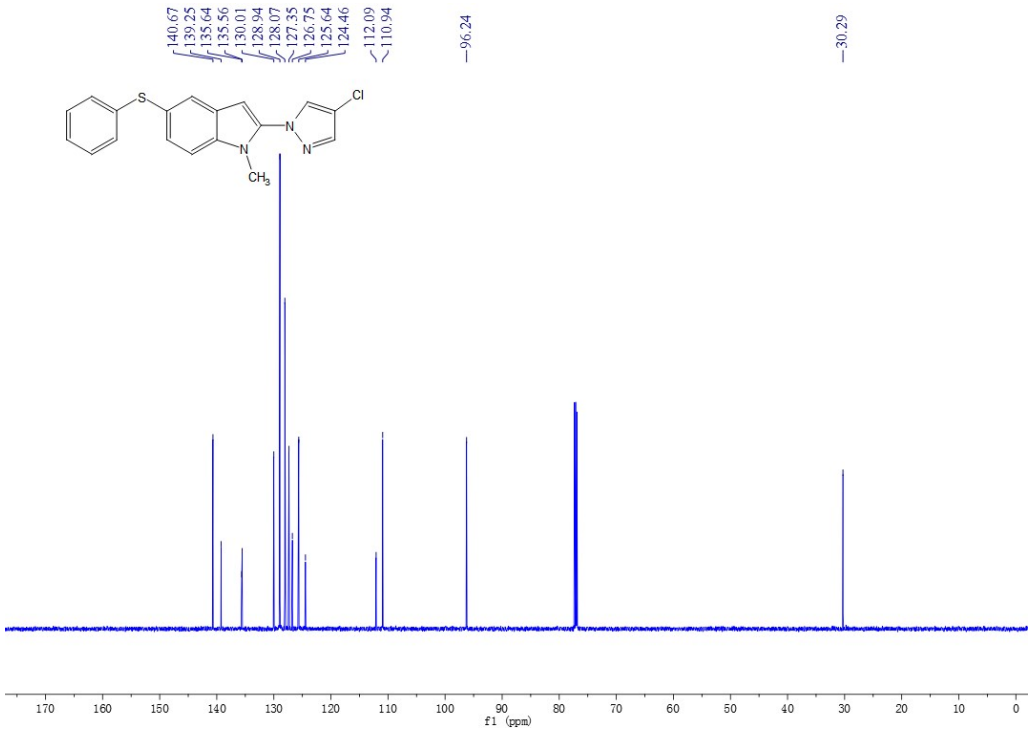
(40) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 19



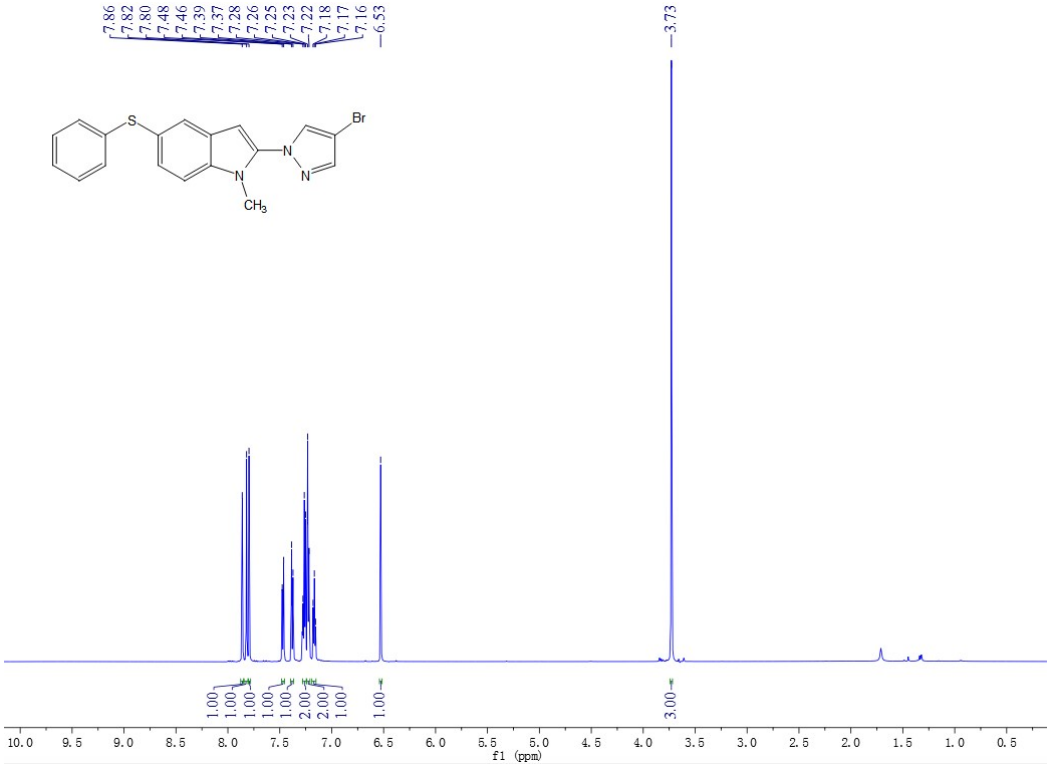
(41) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 20



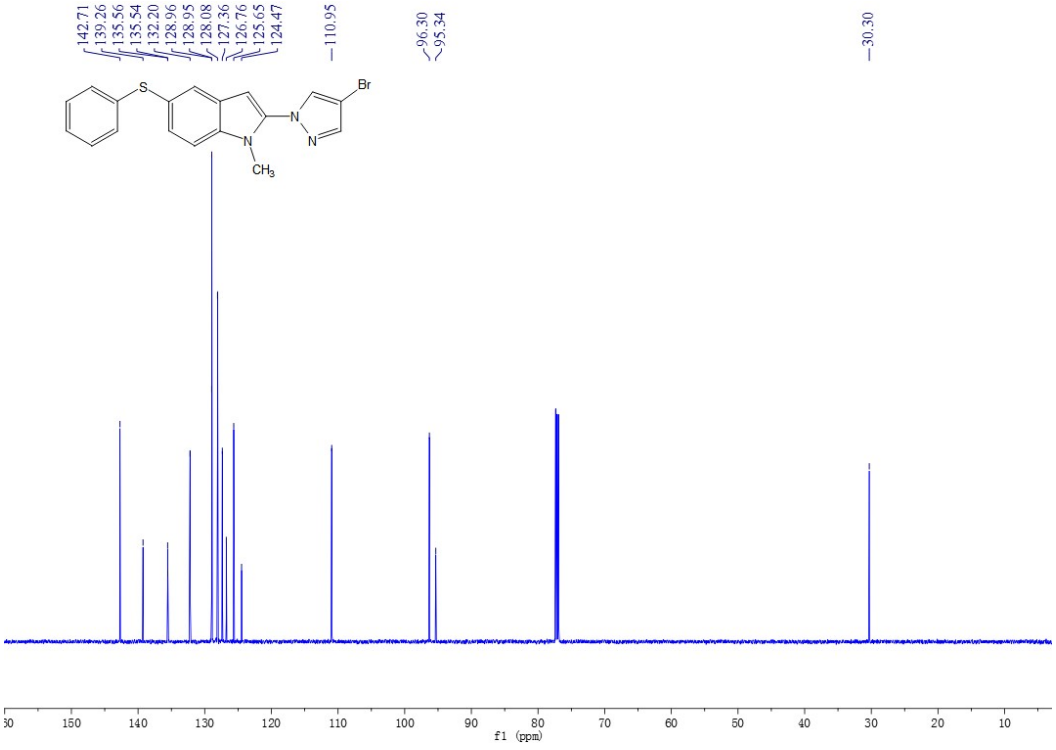
(42) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 20



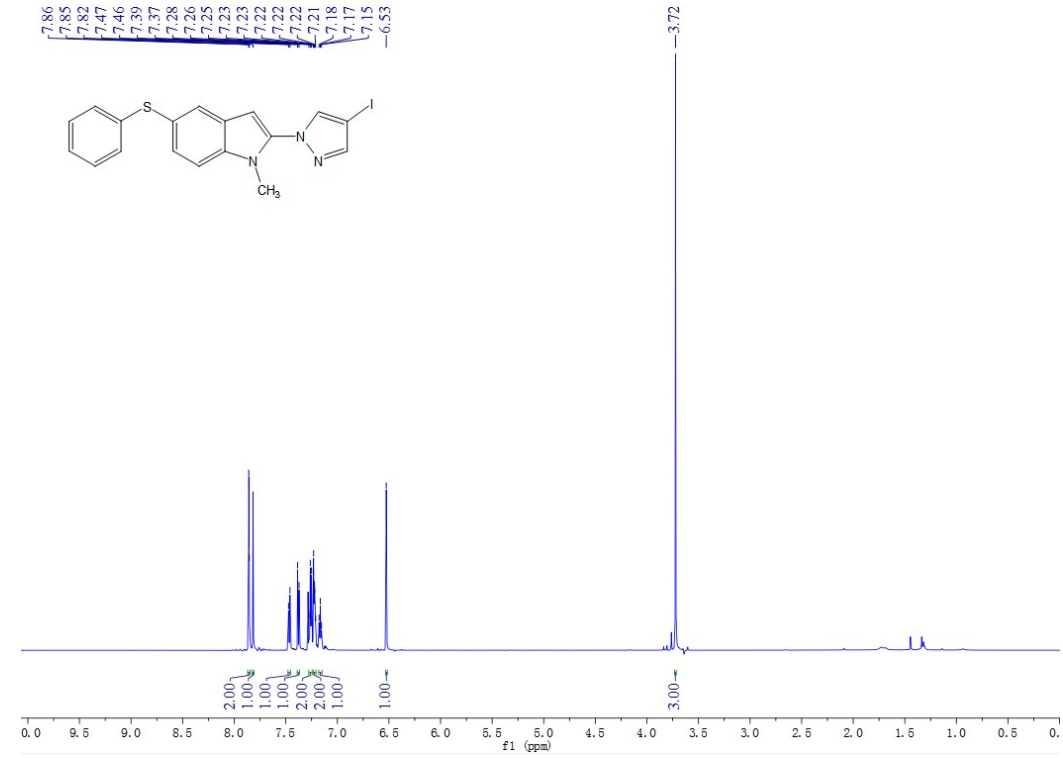
(43) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 21



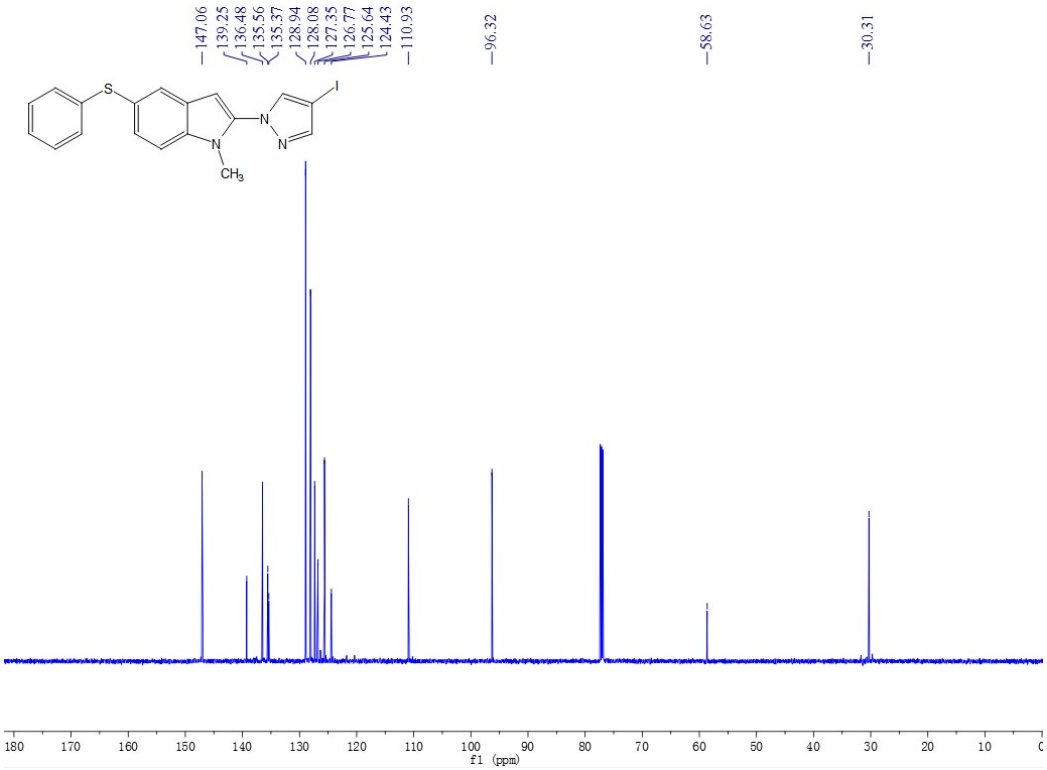
(44) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 21



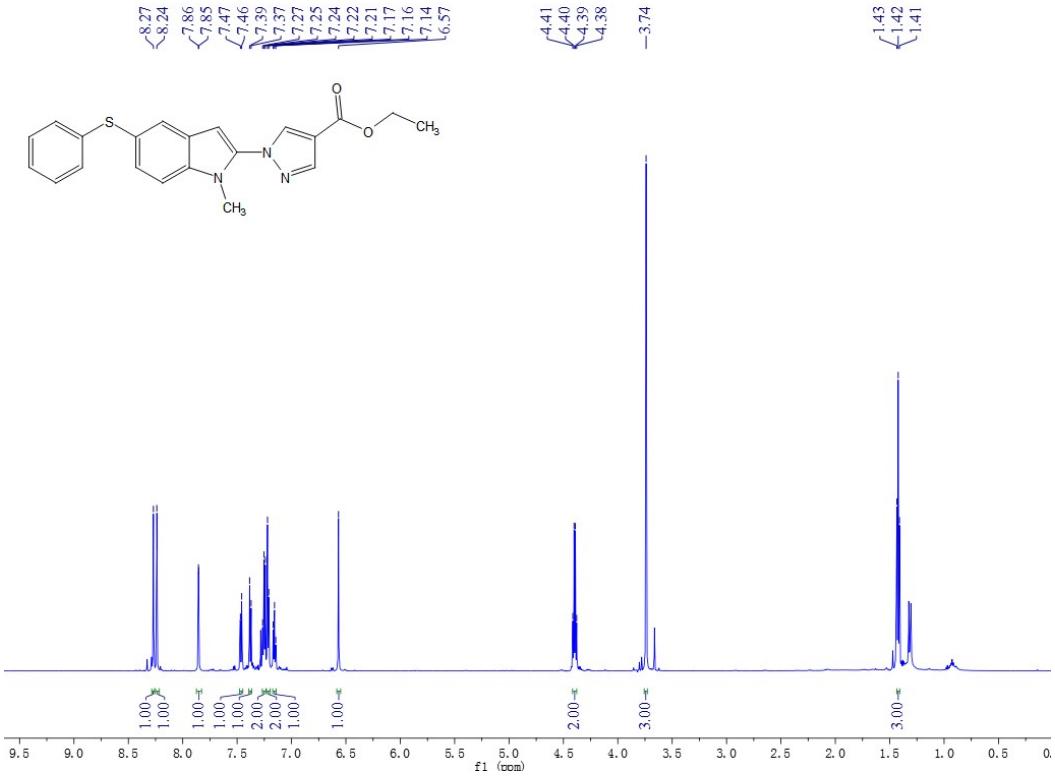
(45) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 22



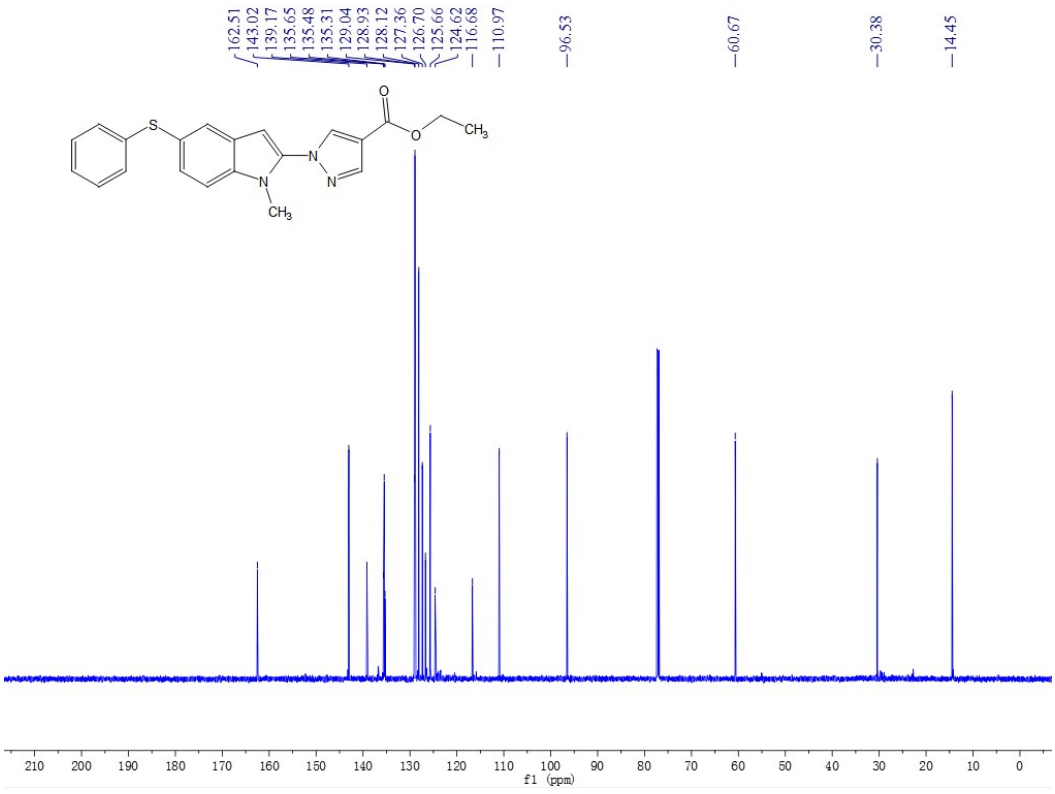
(46) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 22



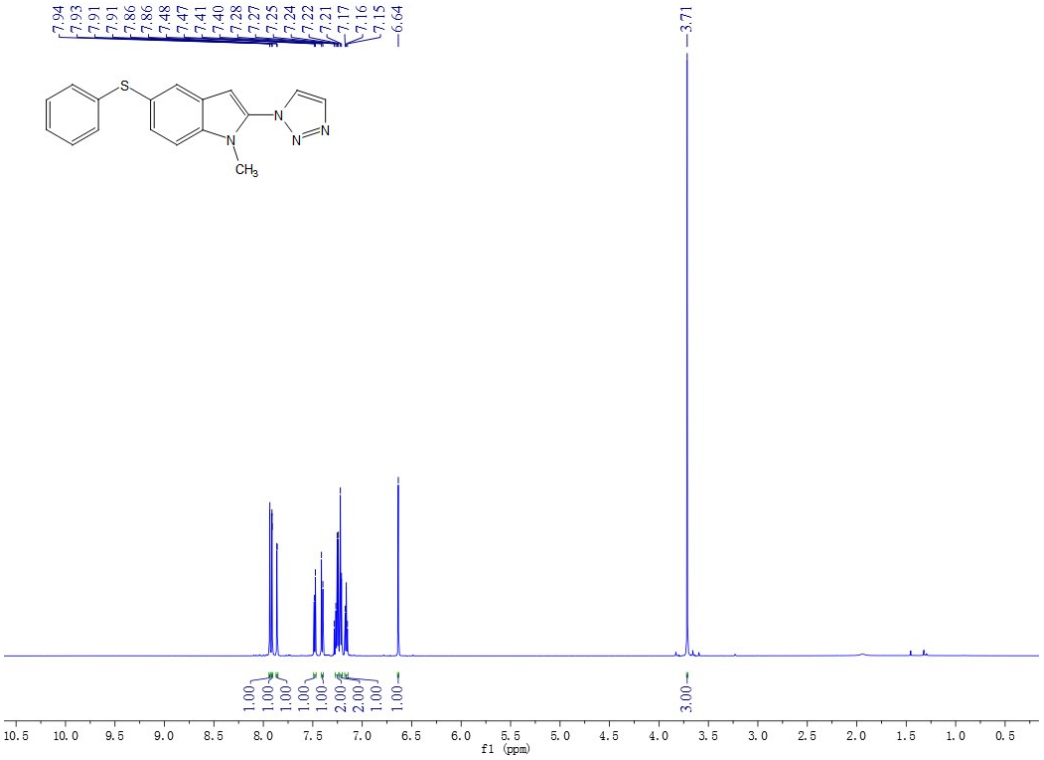
(47) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 23



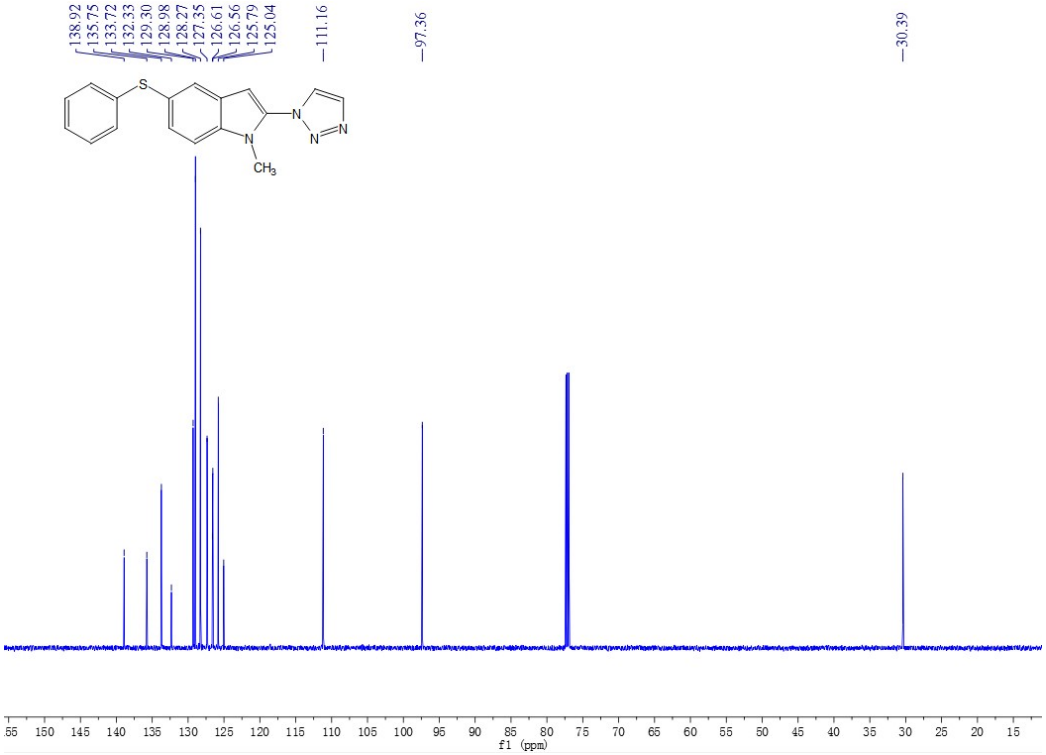
(48) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 23



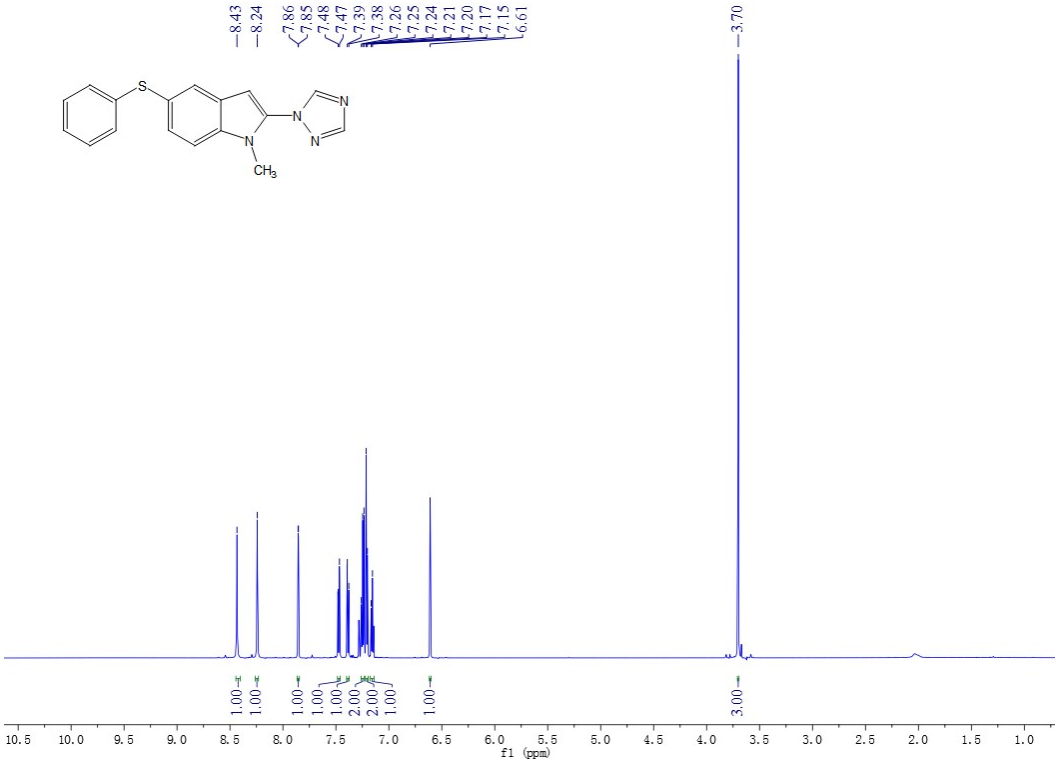
(49) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 24



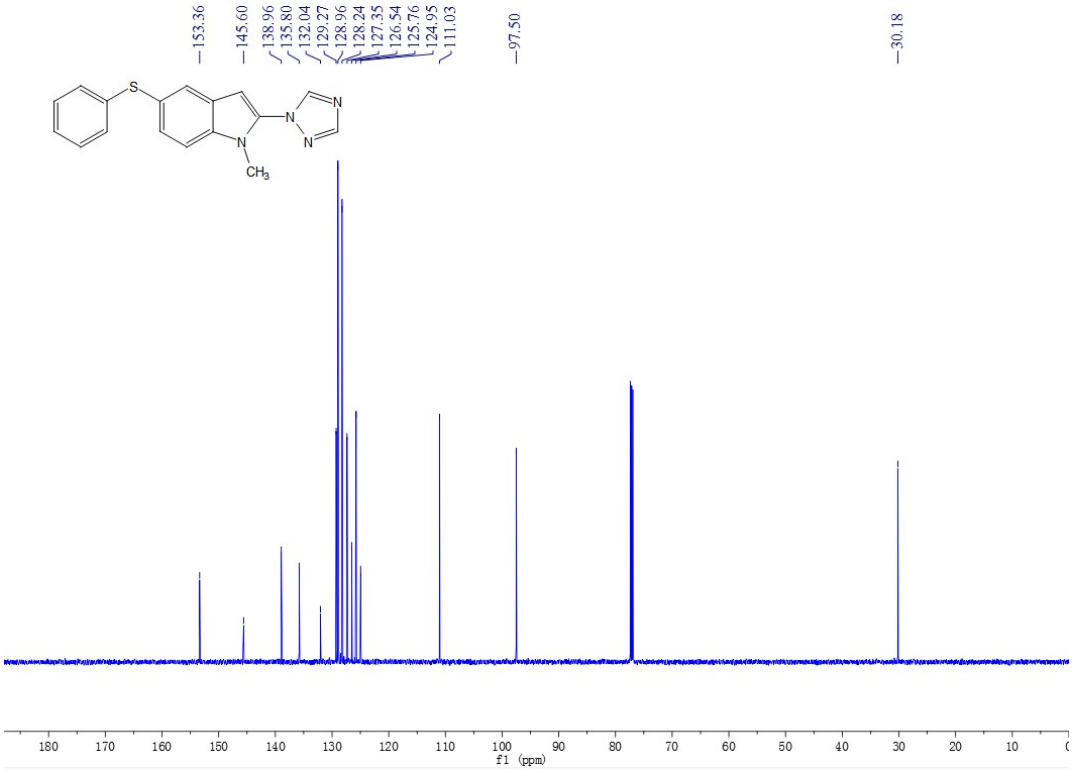
(50) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 24



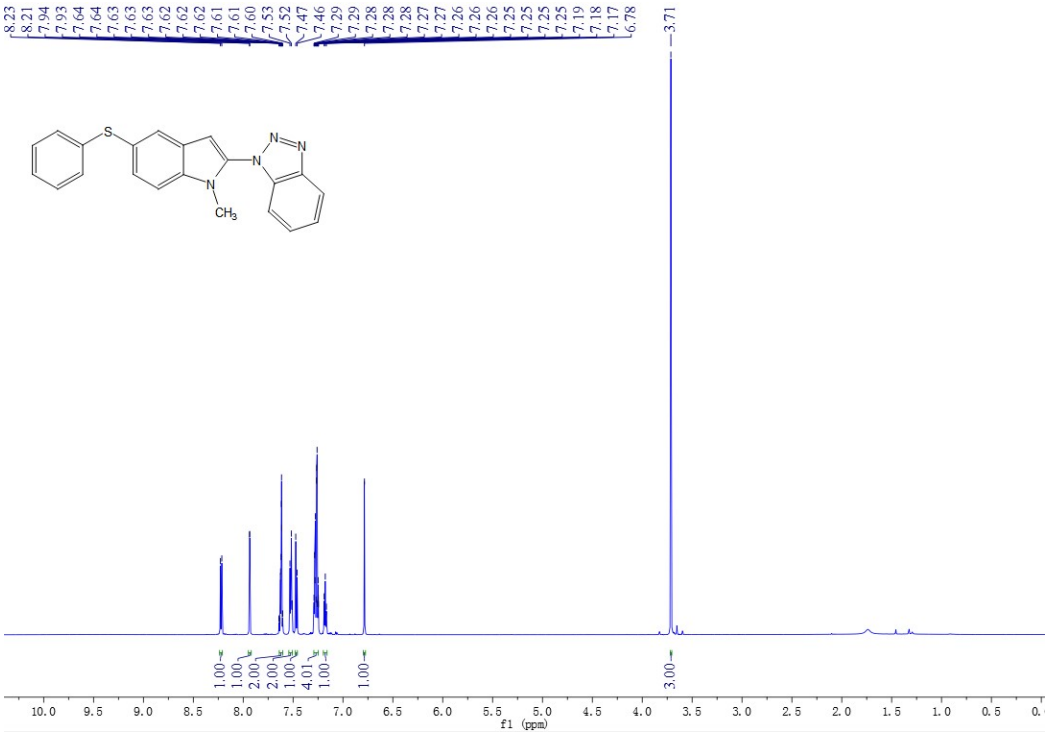
(51) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 25



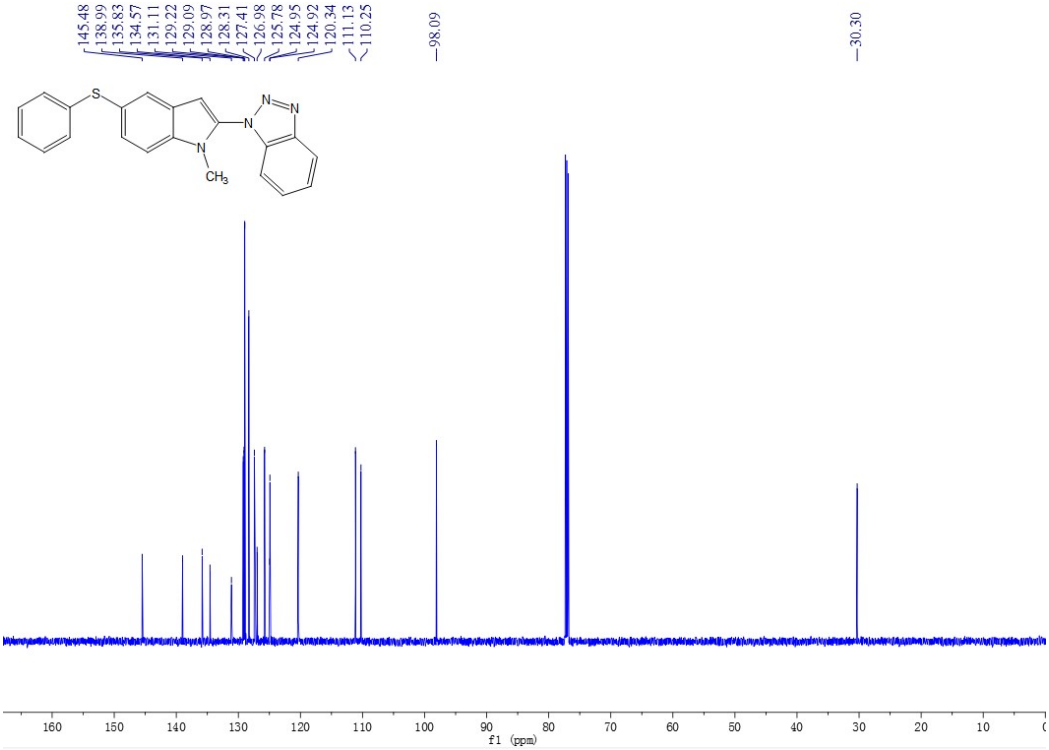
(52) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 25



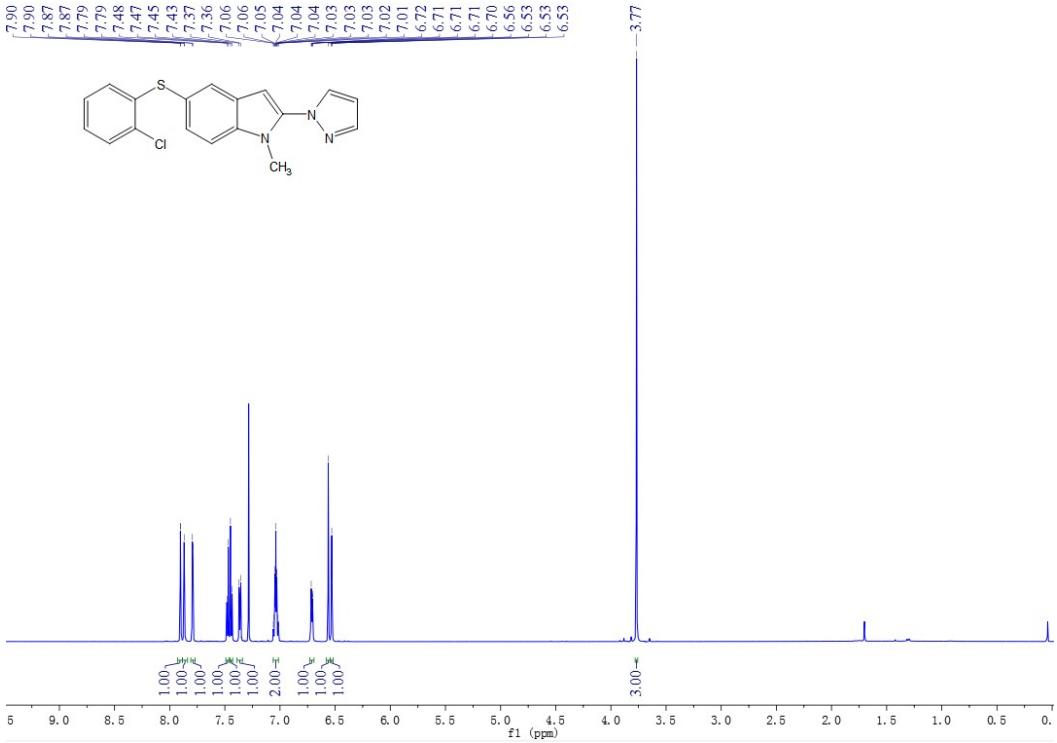
(53) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 26



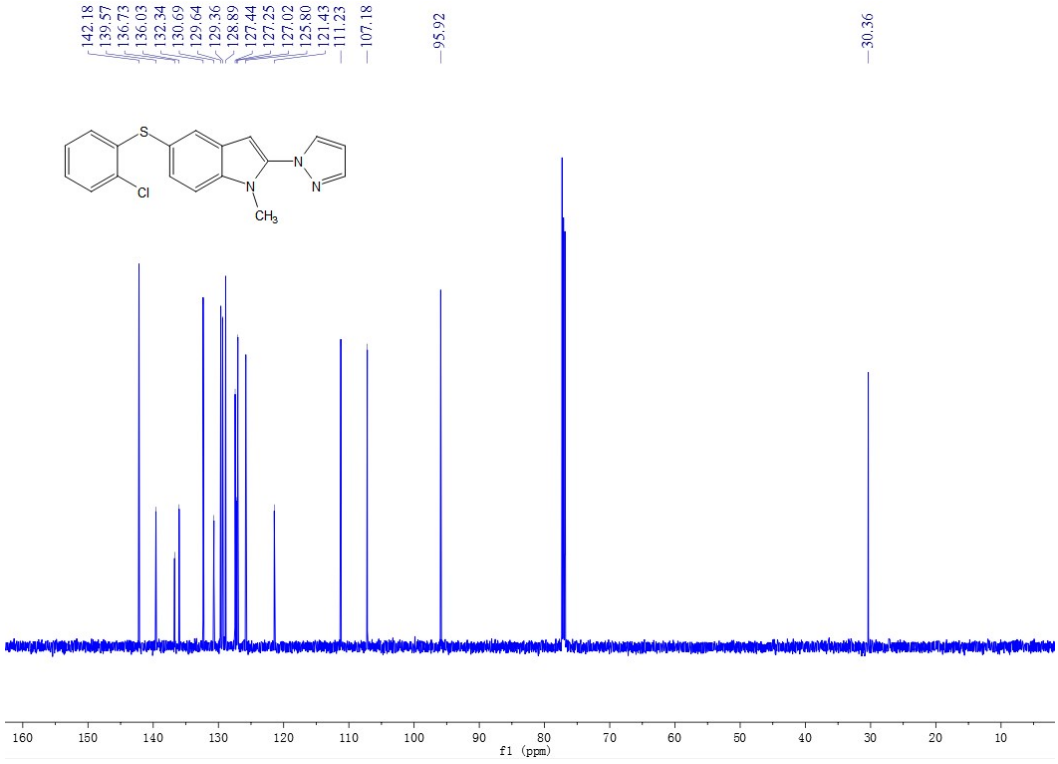
(54) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 26



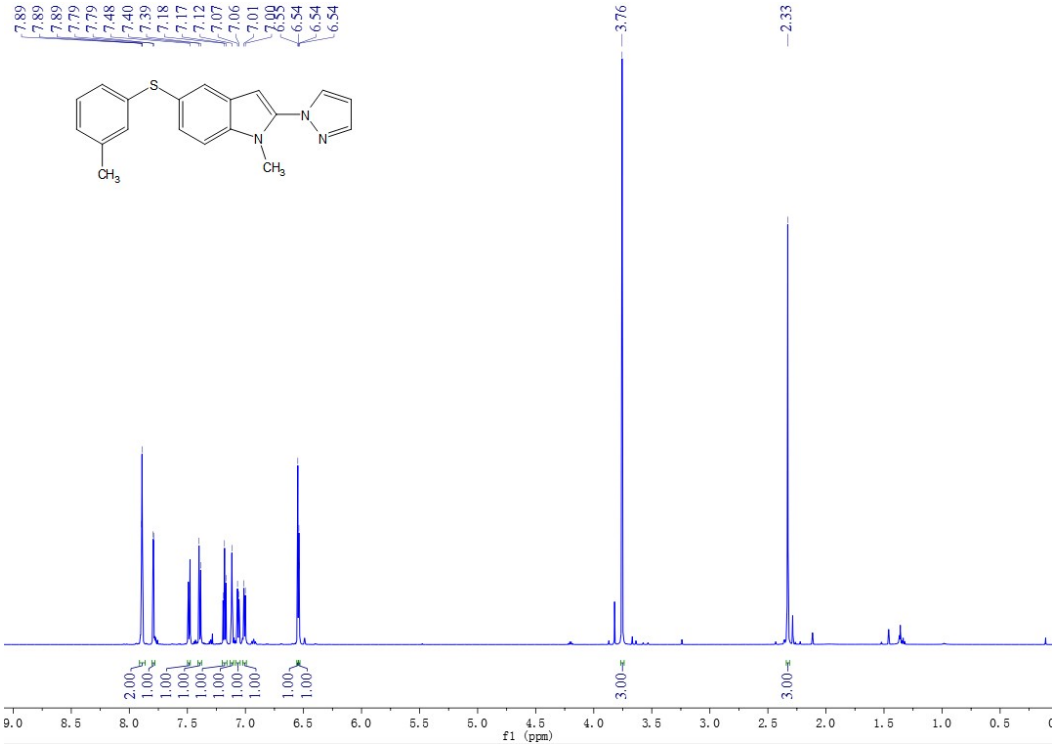
(55) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 27



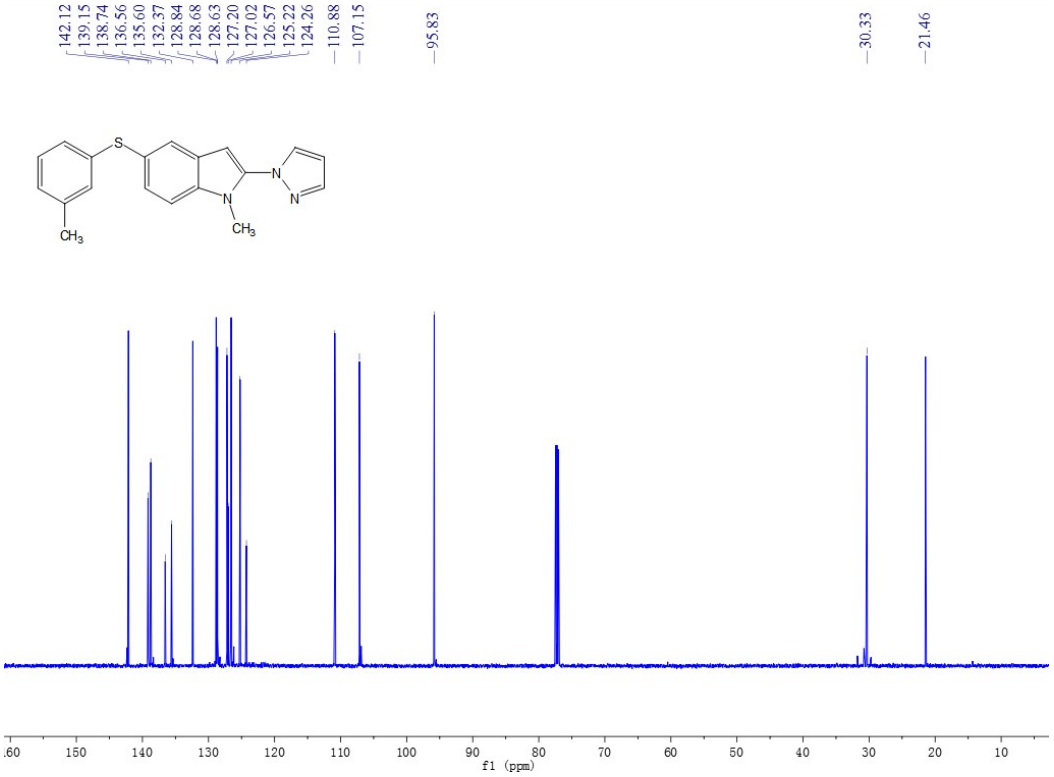
(56) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 27



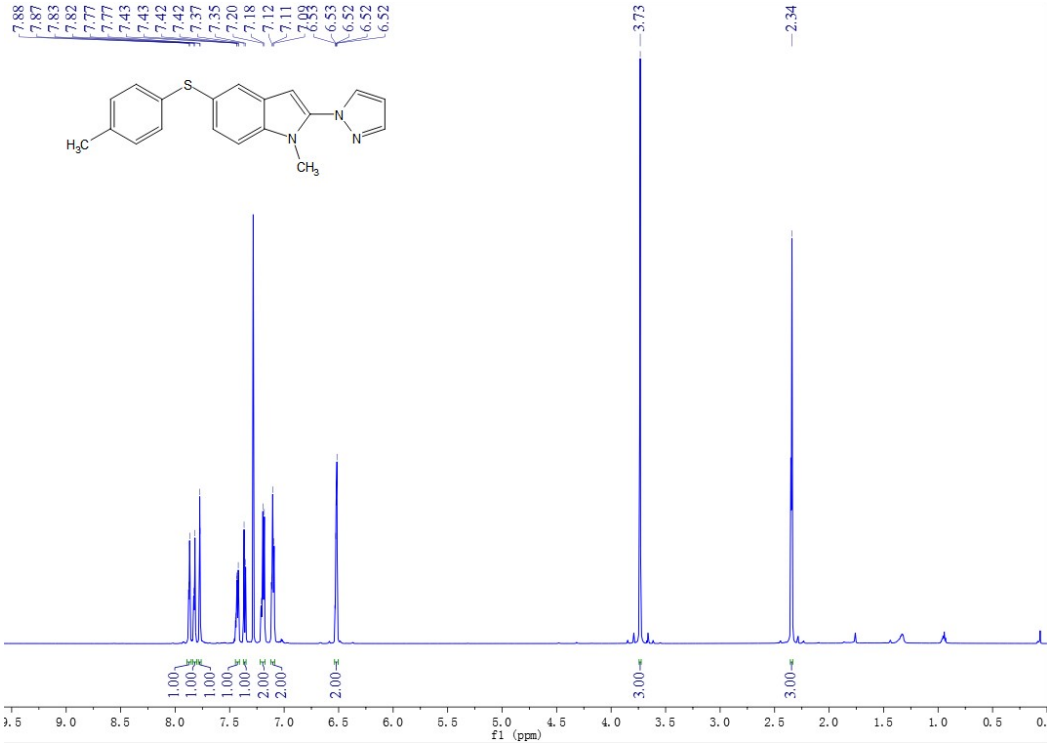
(57) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 28



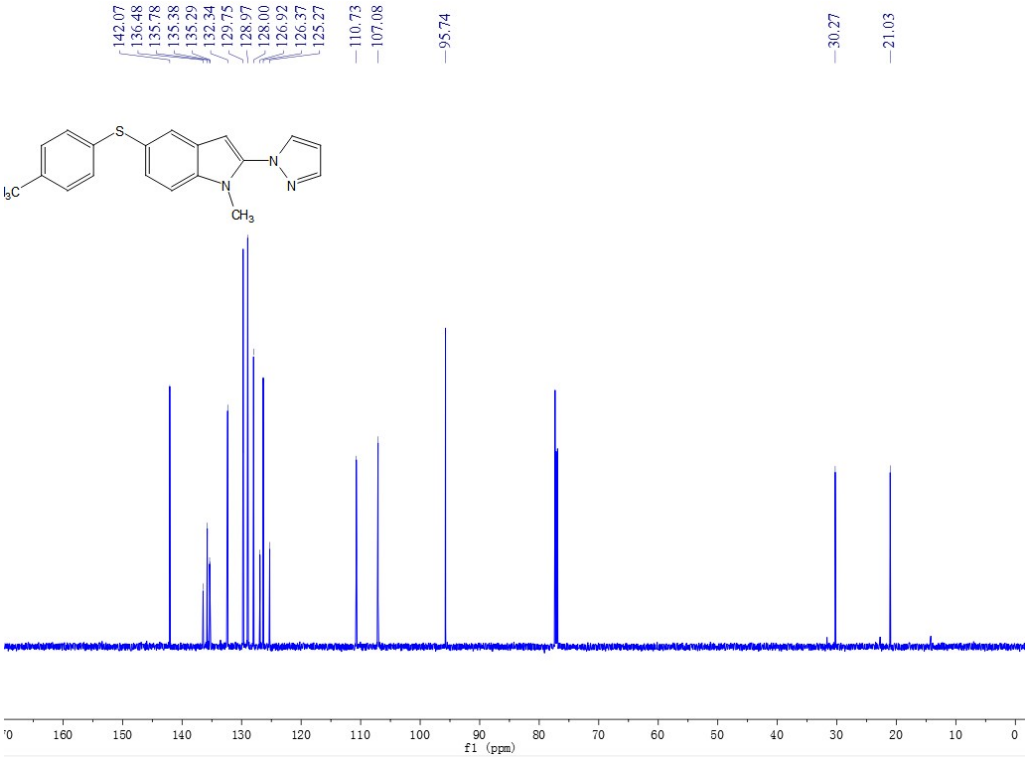
(58) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 28



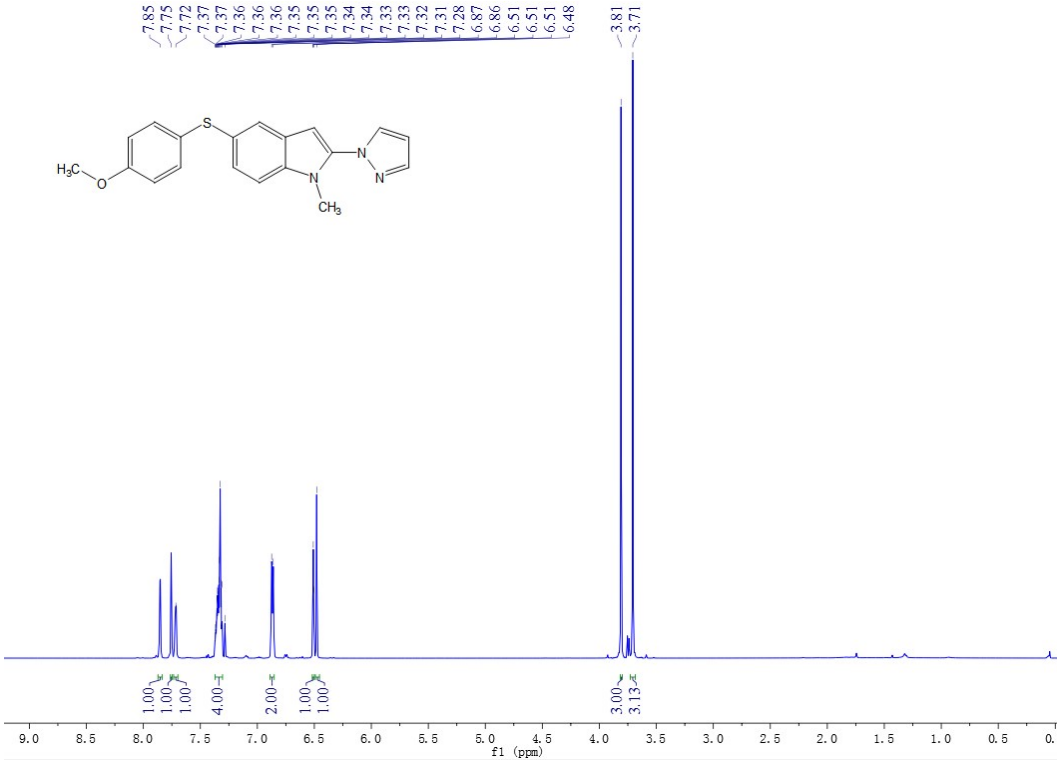
(59) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 29



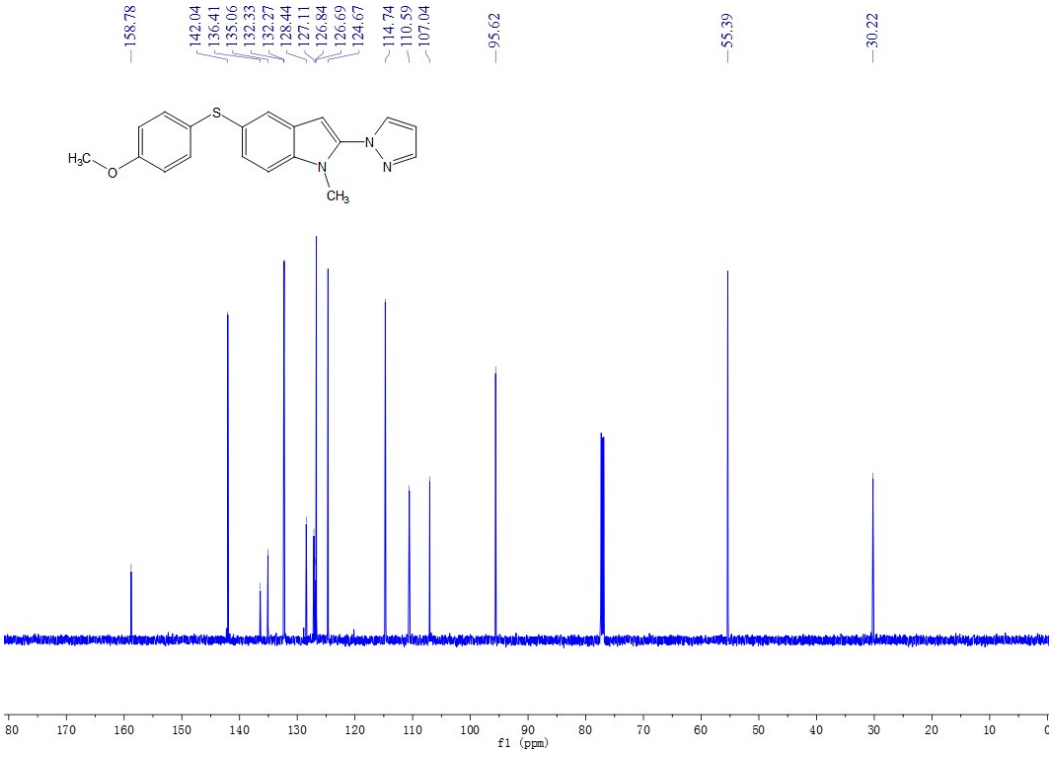
(60) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 29



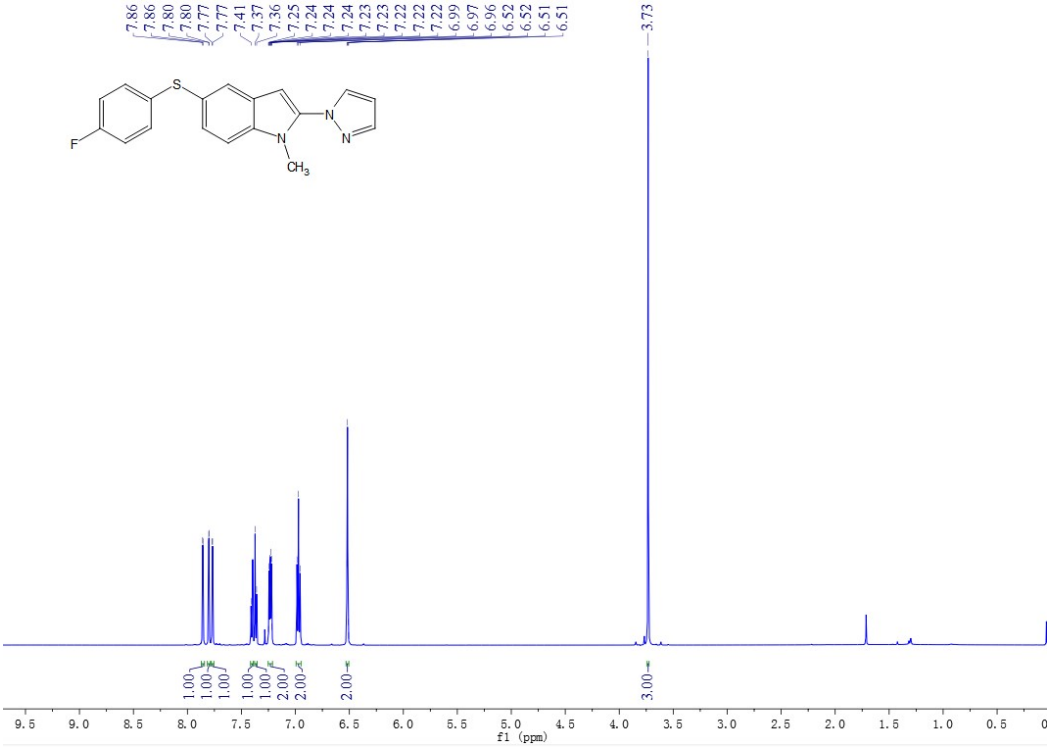
(61) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 30



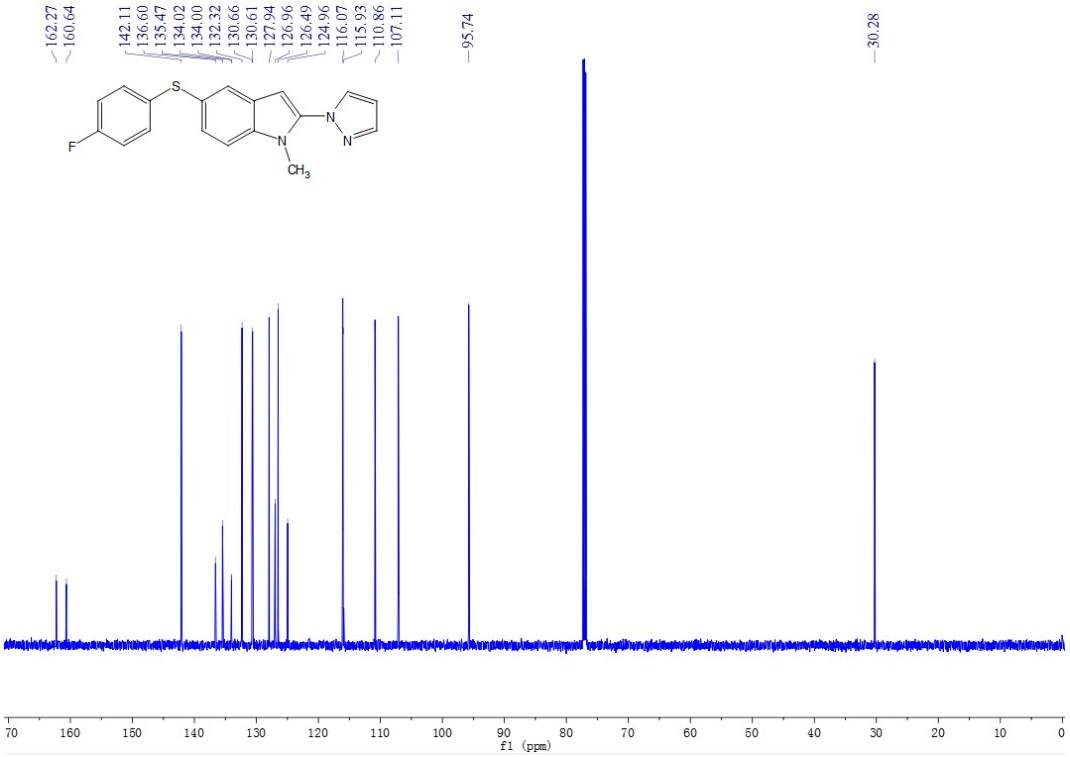
(62) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 30



(63) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 31

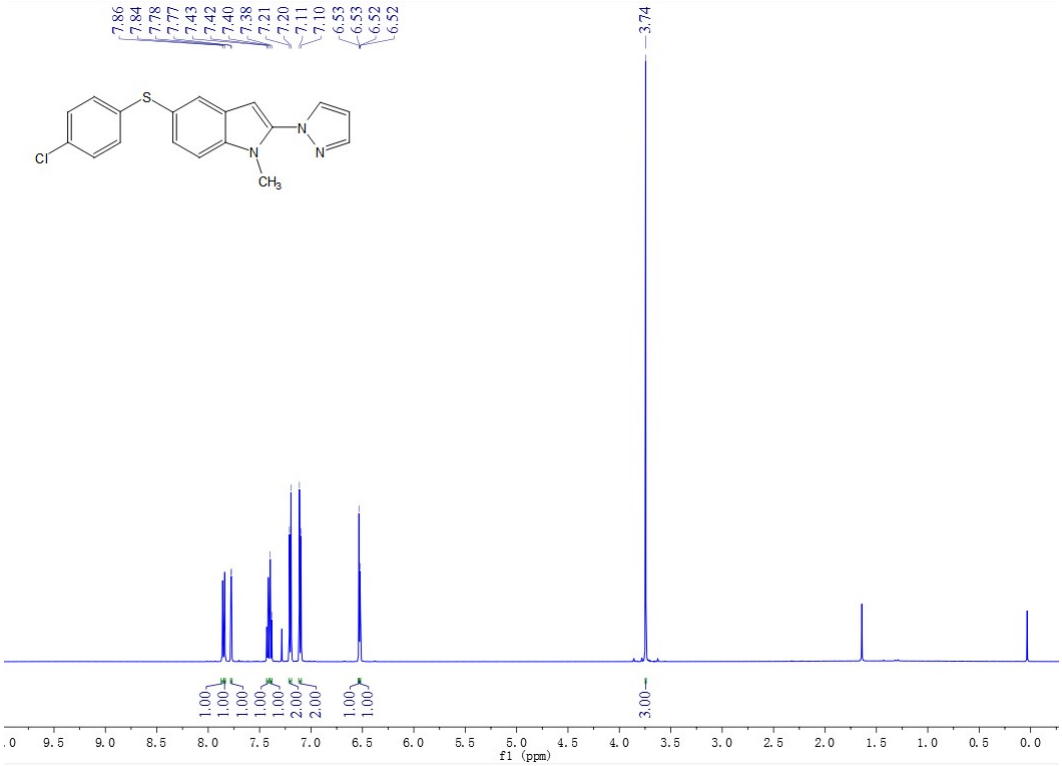


(64) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 31

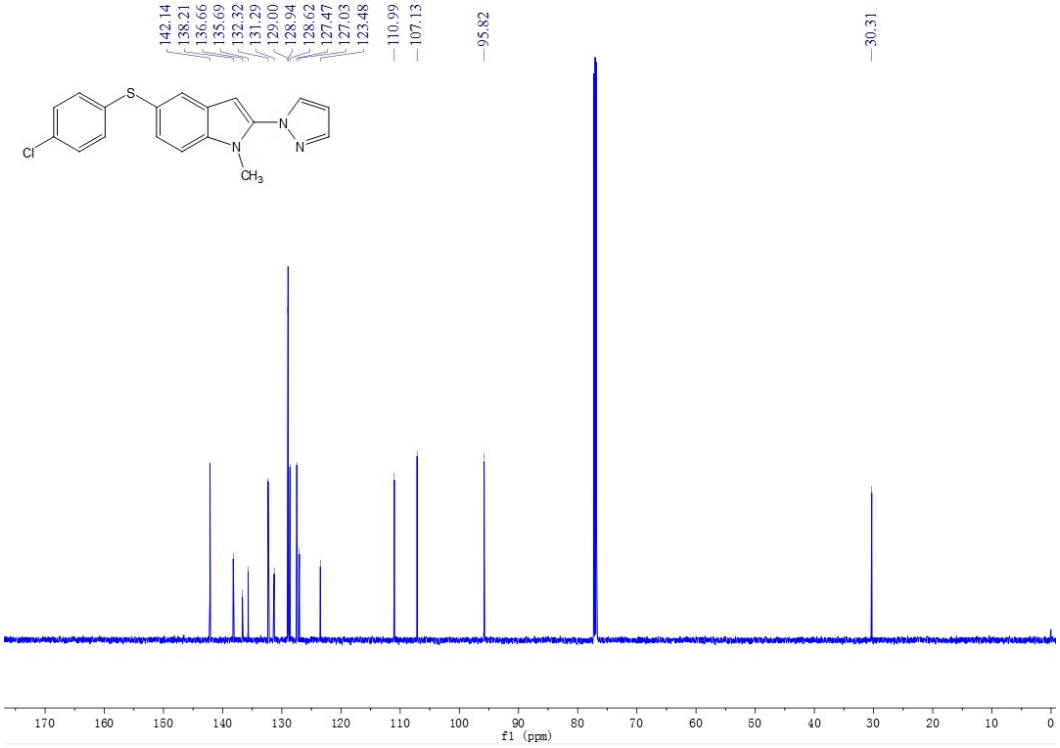


(65) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 31

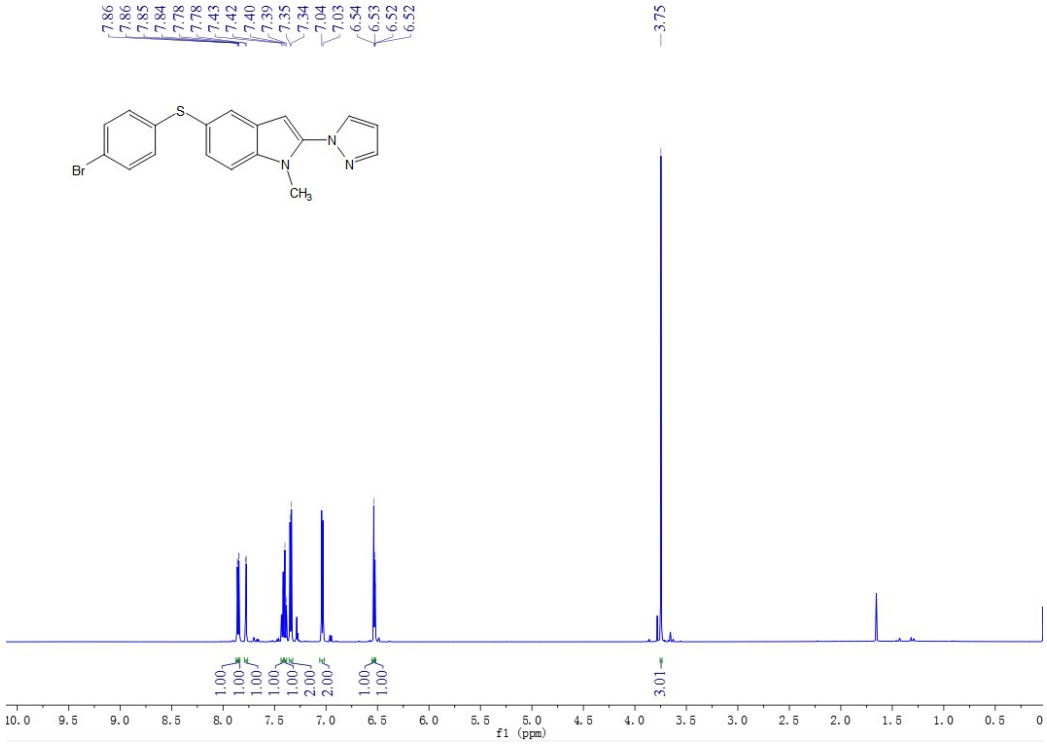
(66) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 32



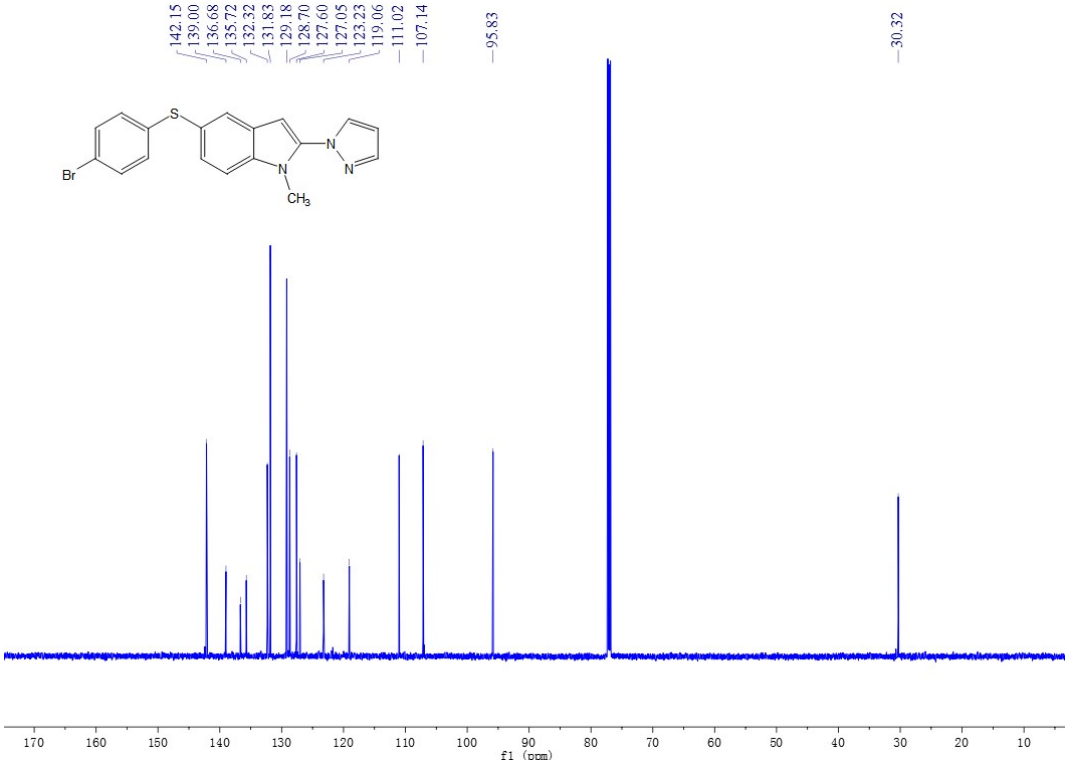
(67) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 32



(68) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 33

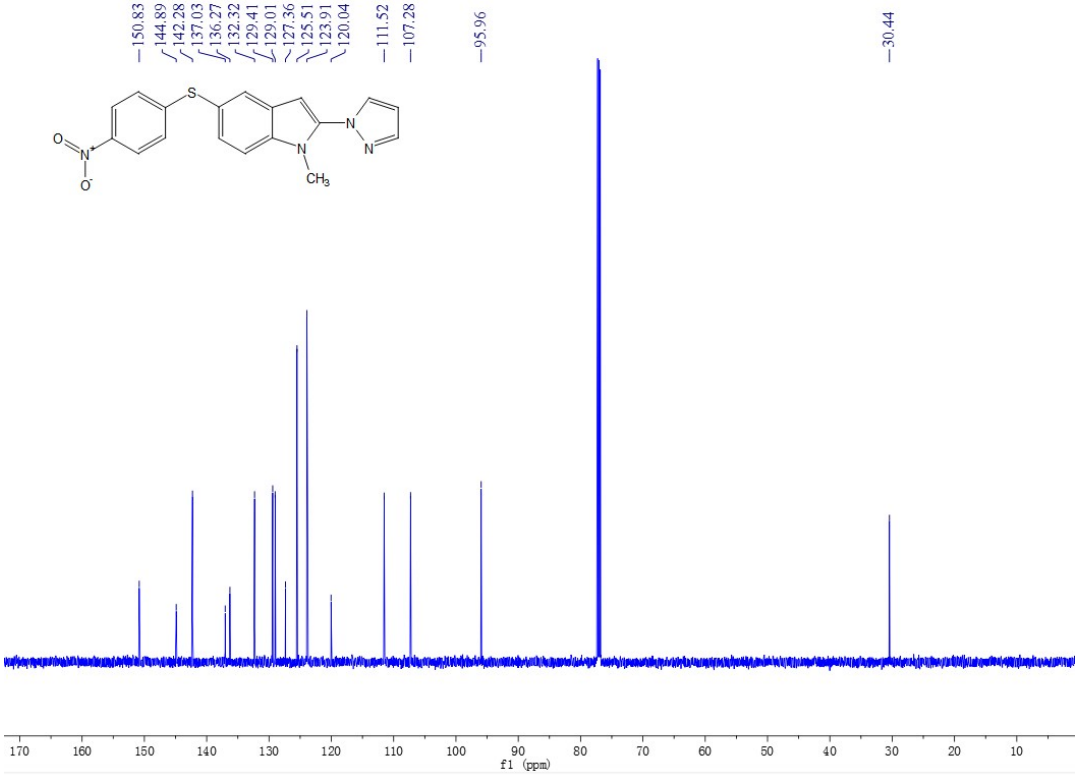


(69) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 33

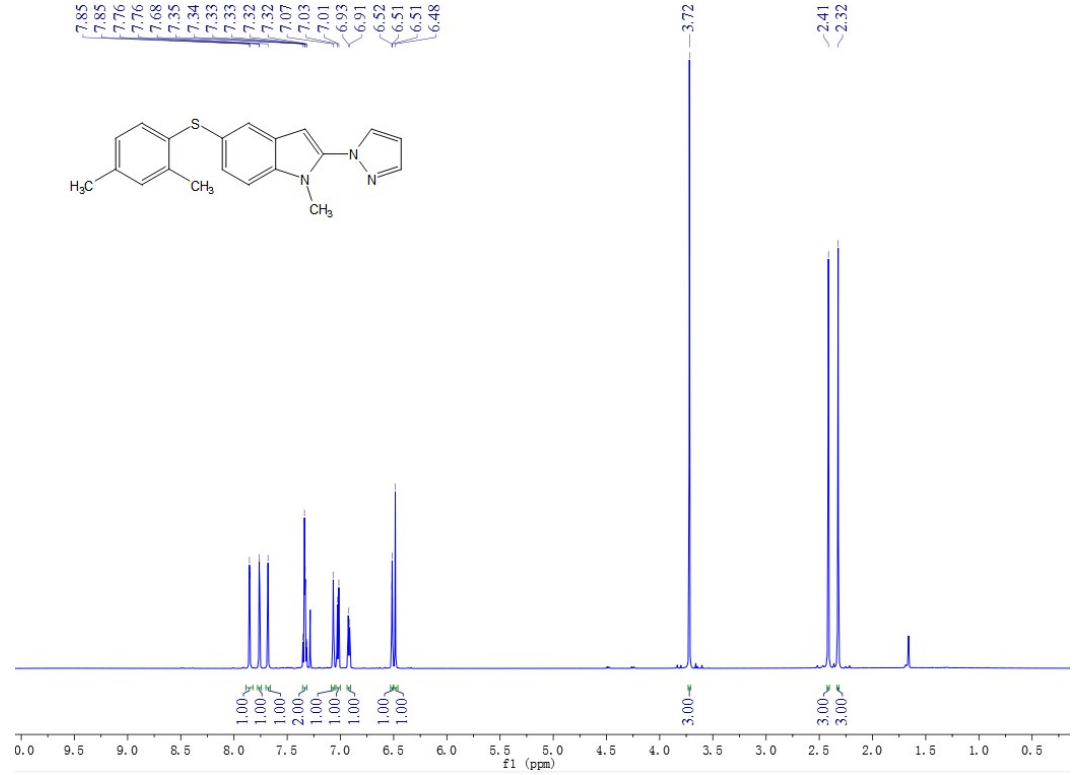


(70) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 34

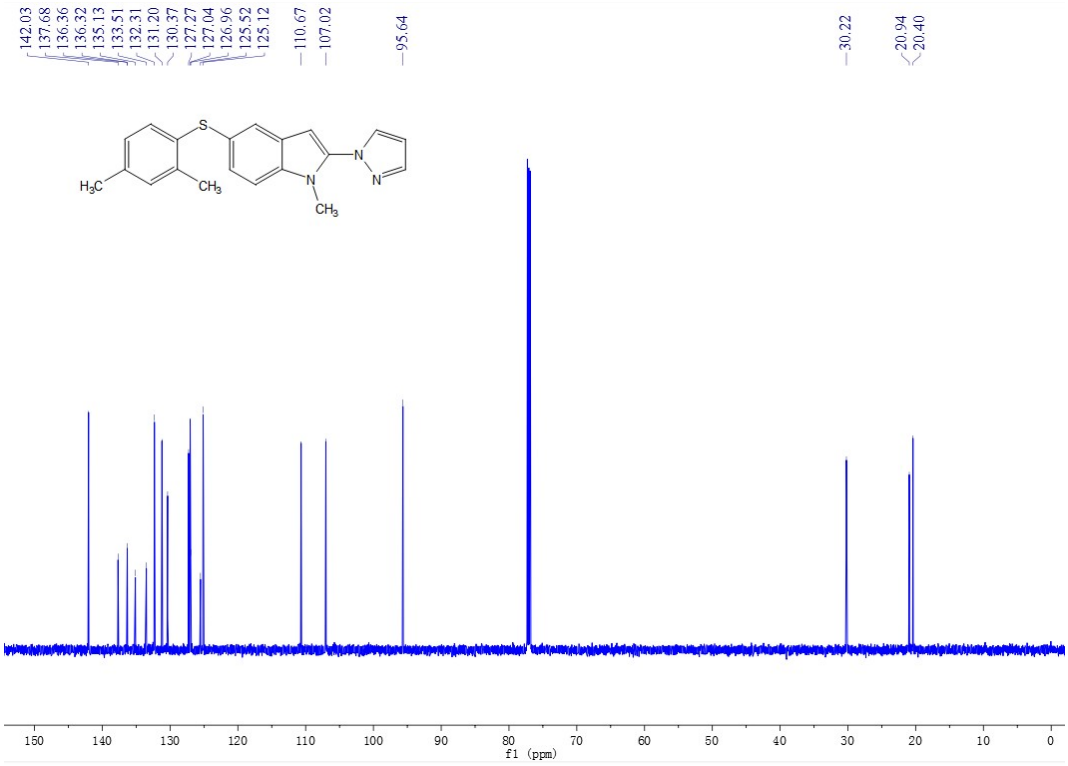
(71) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 34



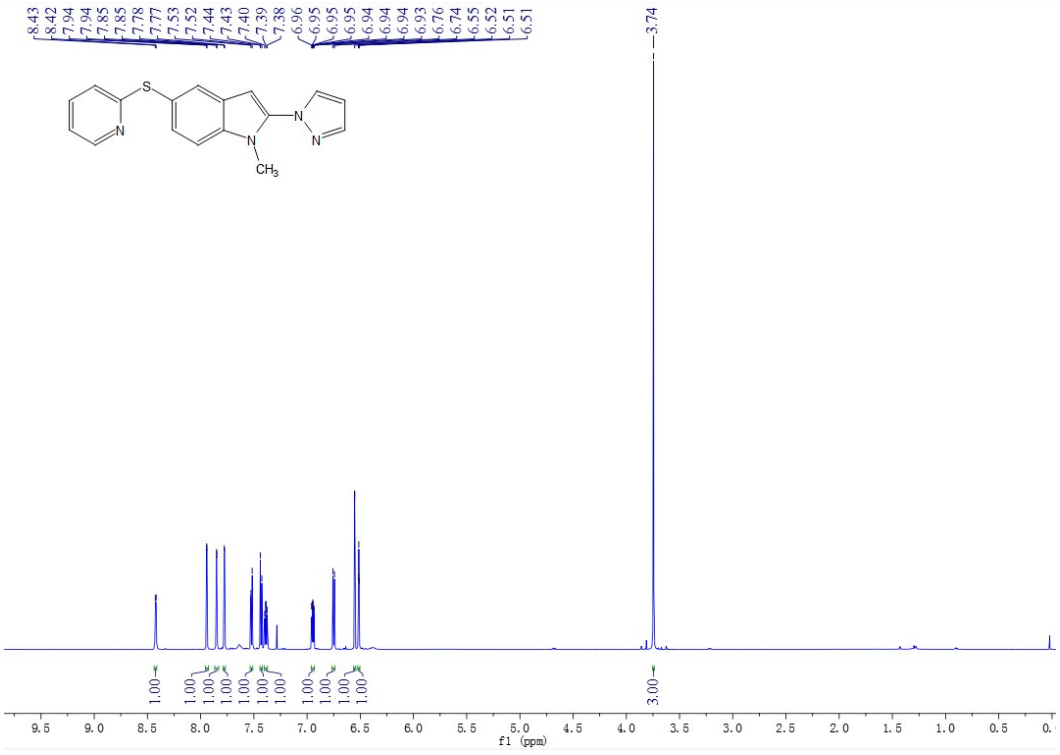
(72) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 35



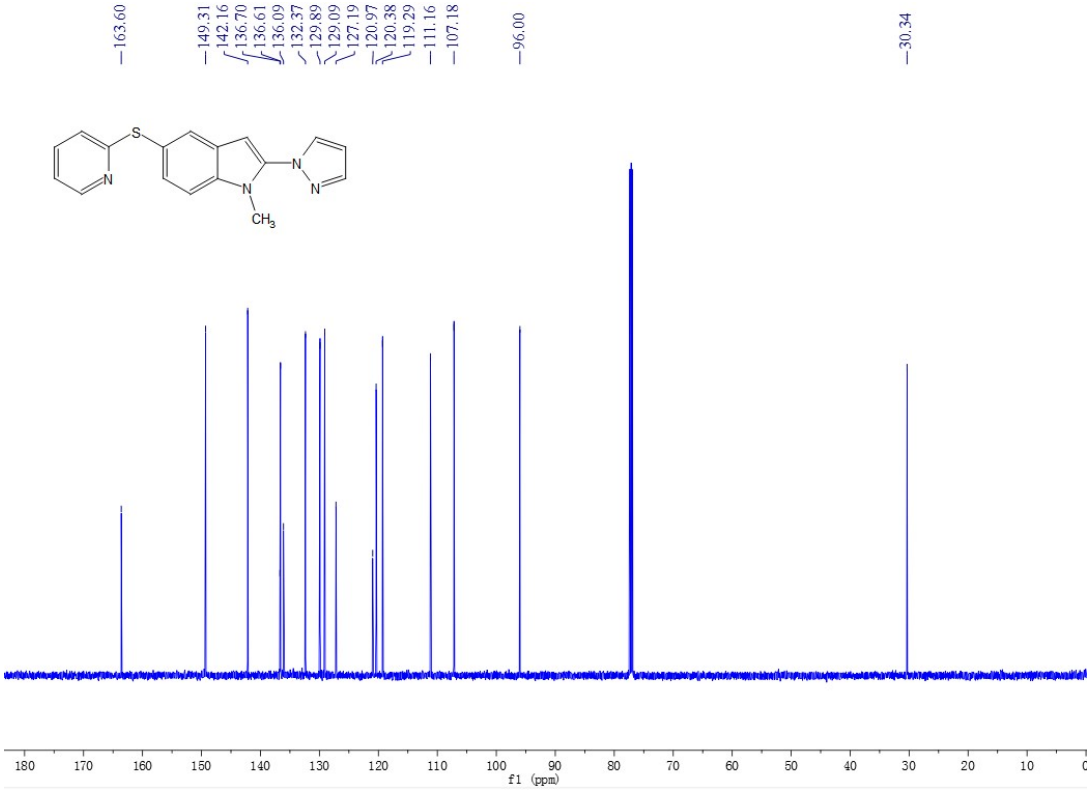
(73) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 35



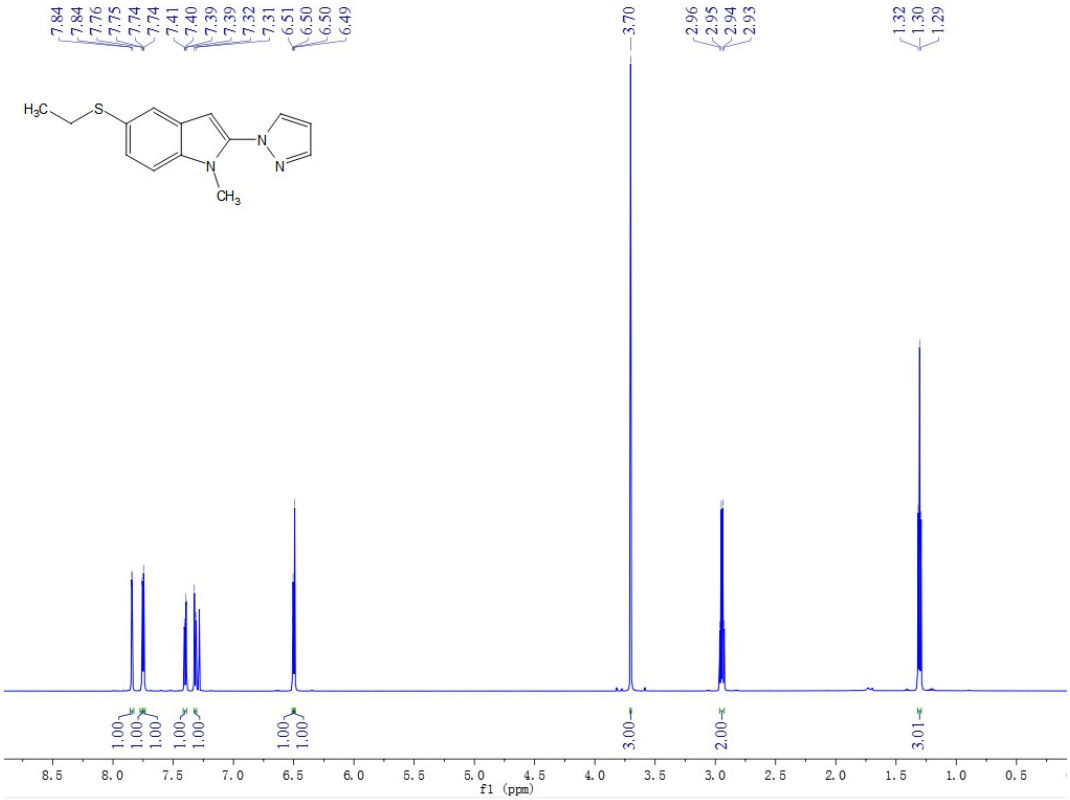
(74) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 36



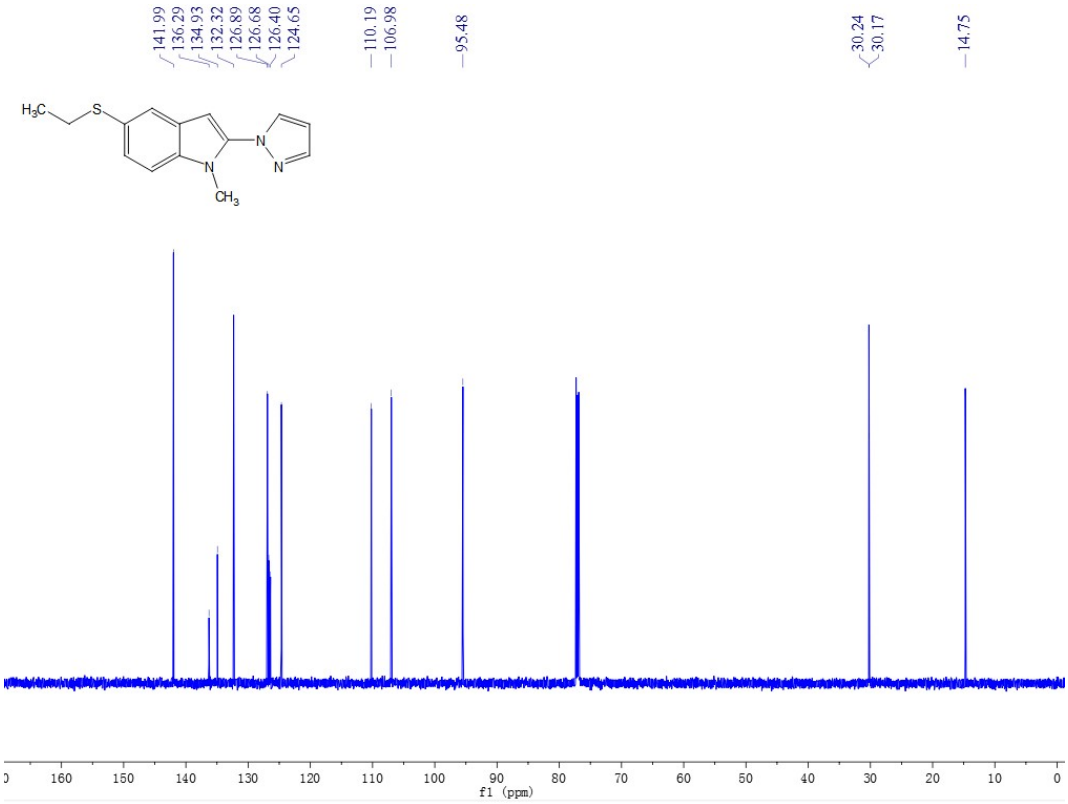
(75) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 36



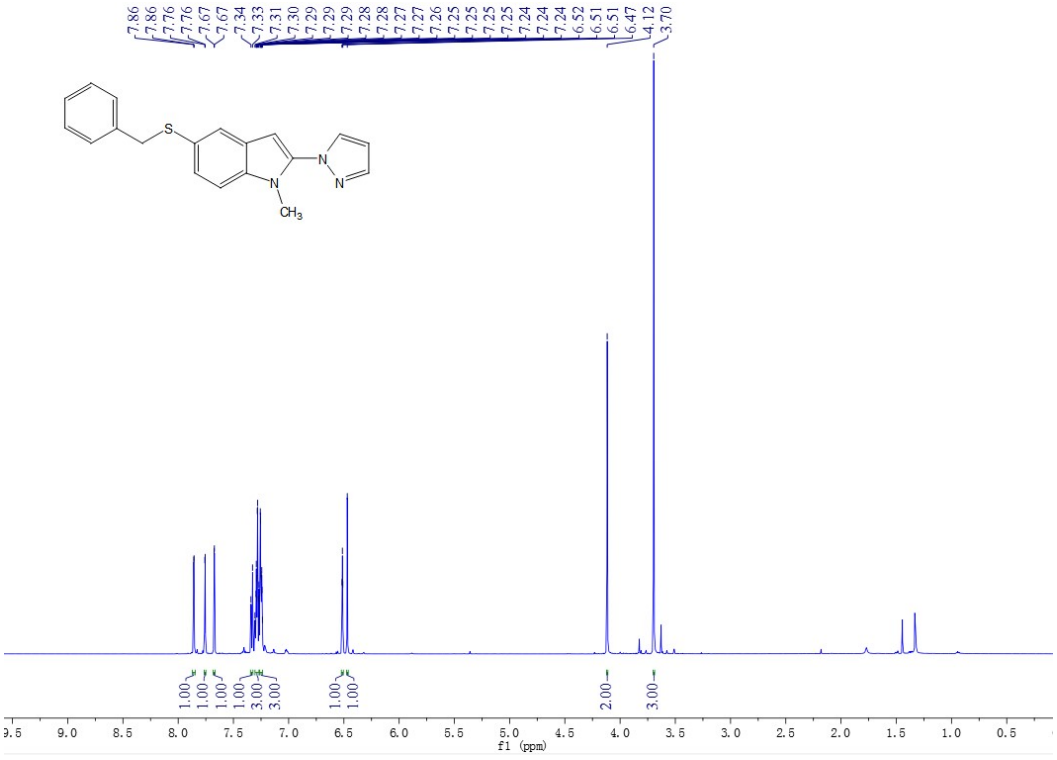
(76) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 37



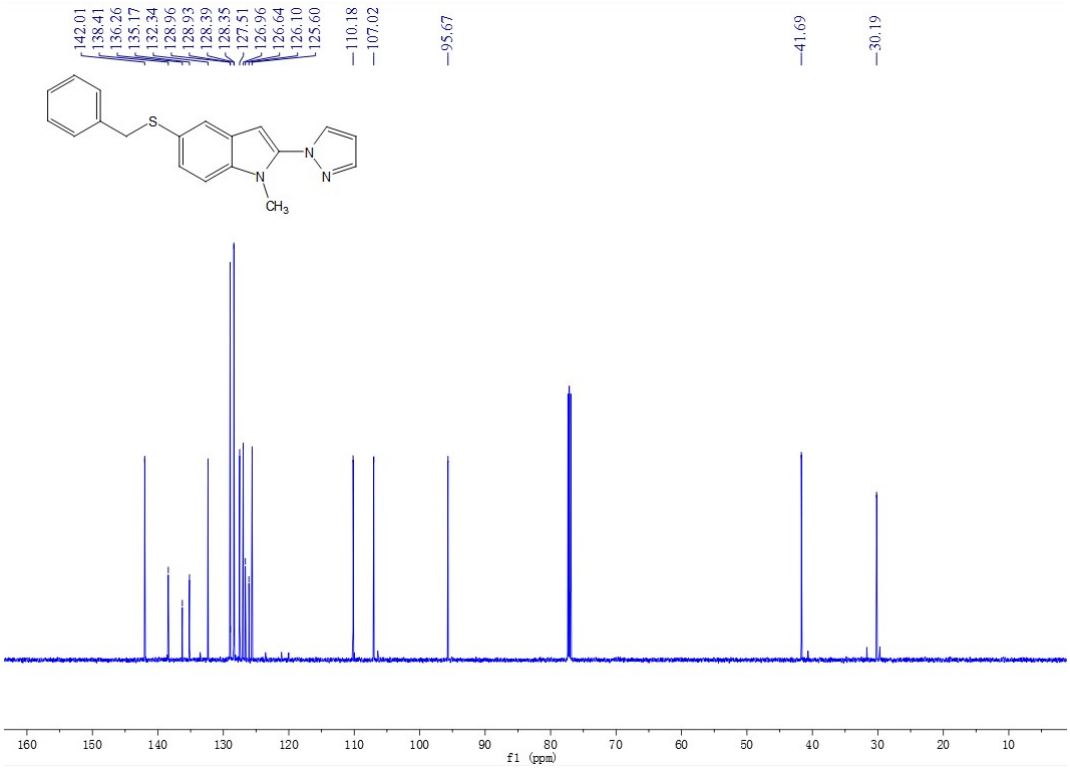
(77) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 37



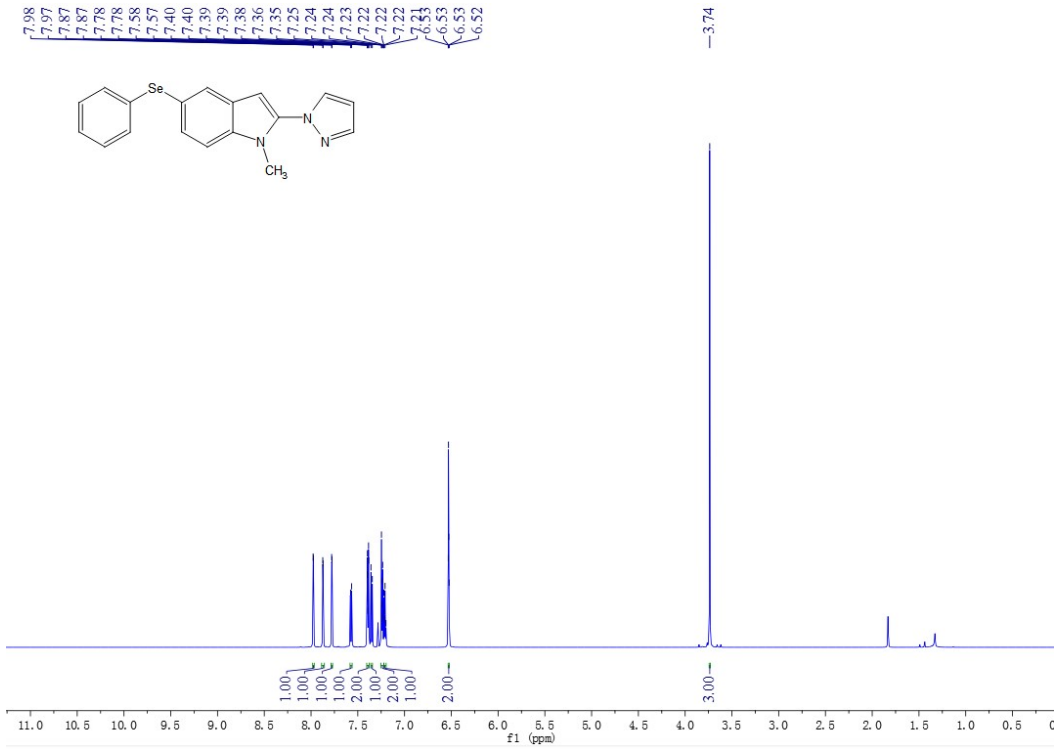
(78) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 38



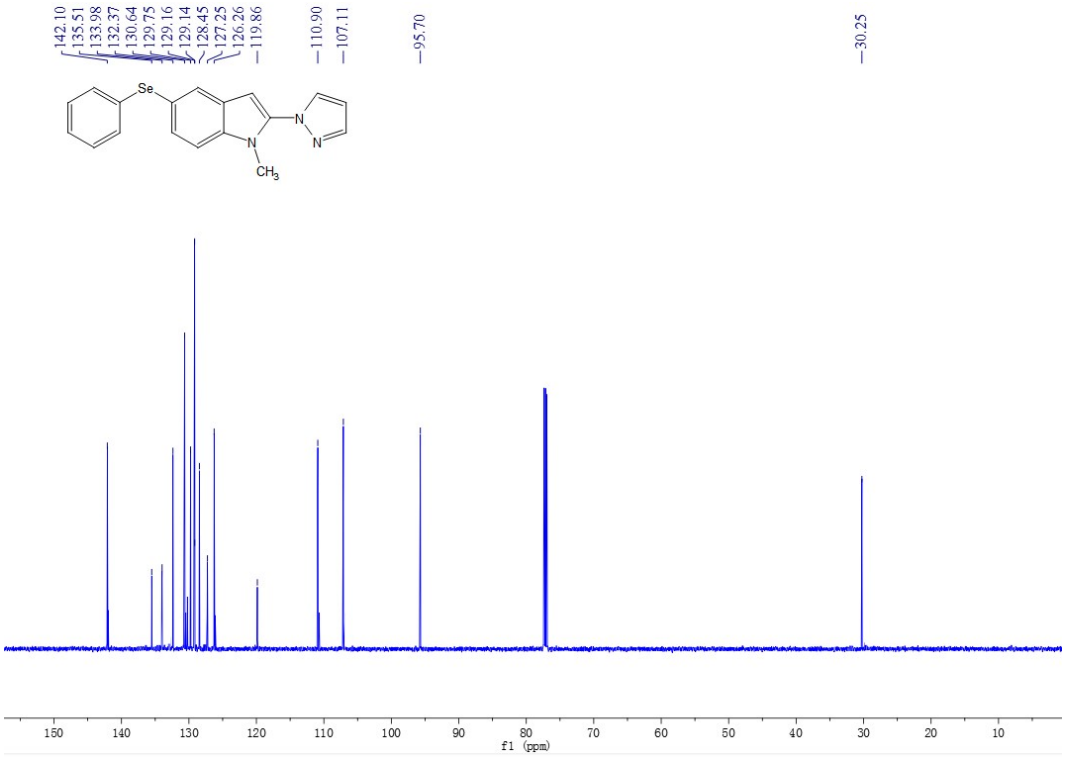
(79) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 38



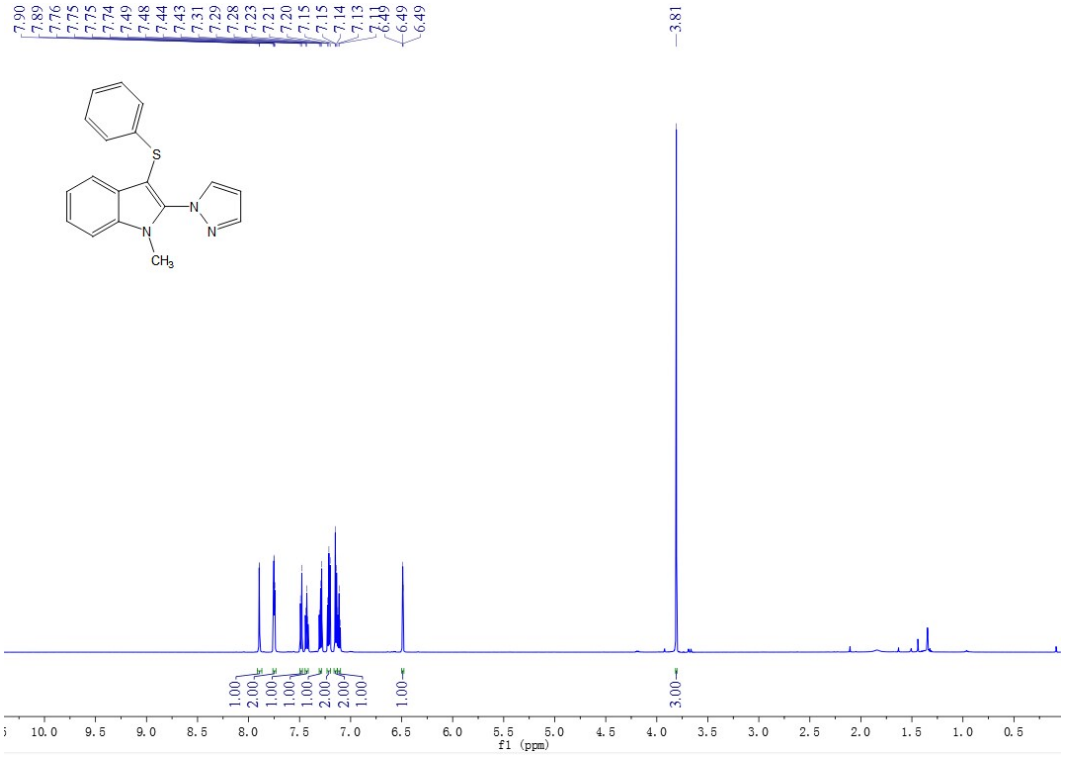
(80) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 39



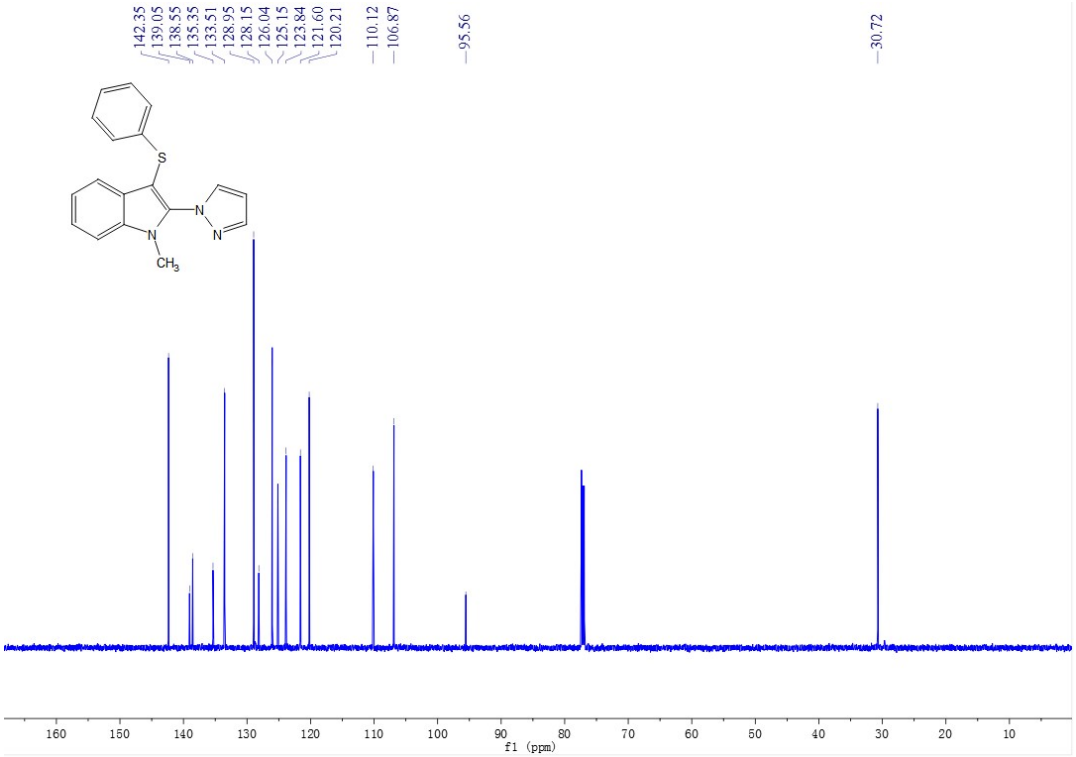
(81) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 39



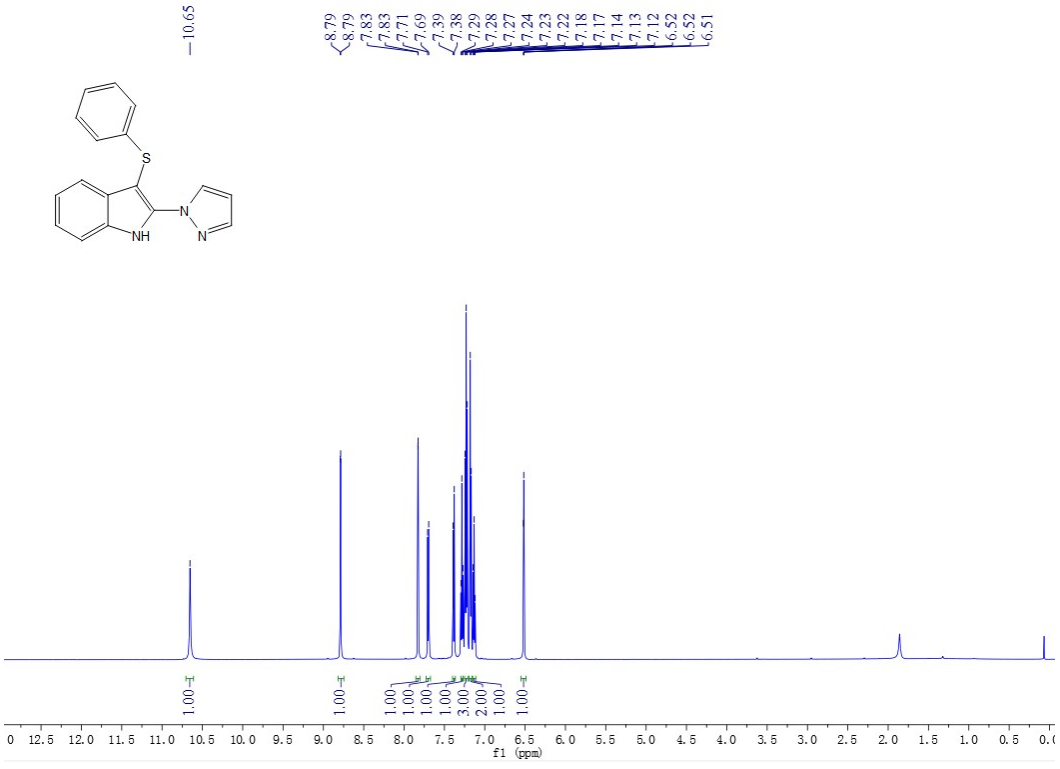
(82) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 40



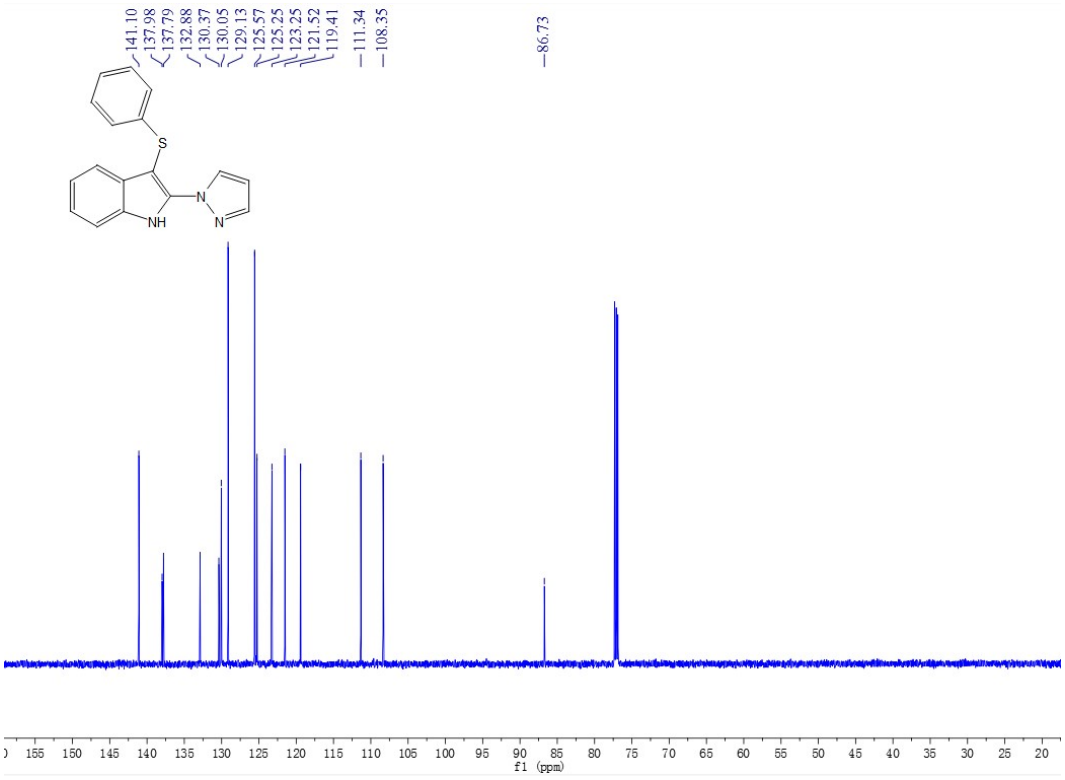
(83) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 40



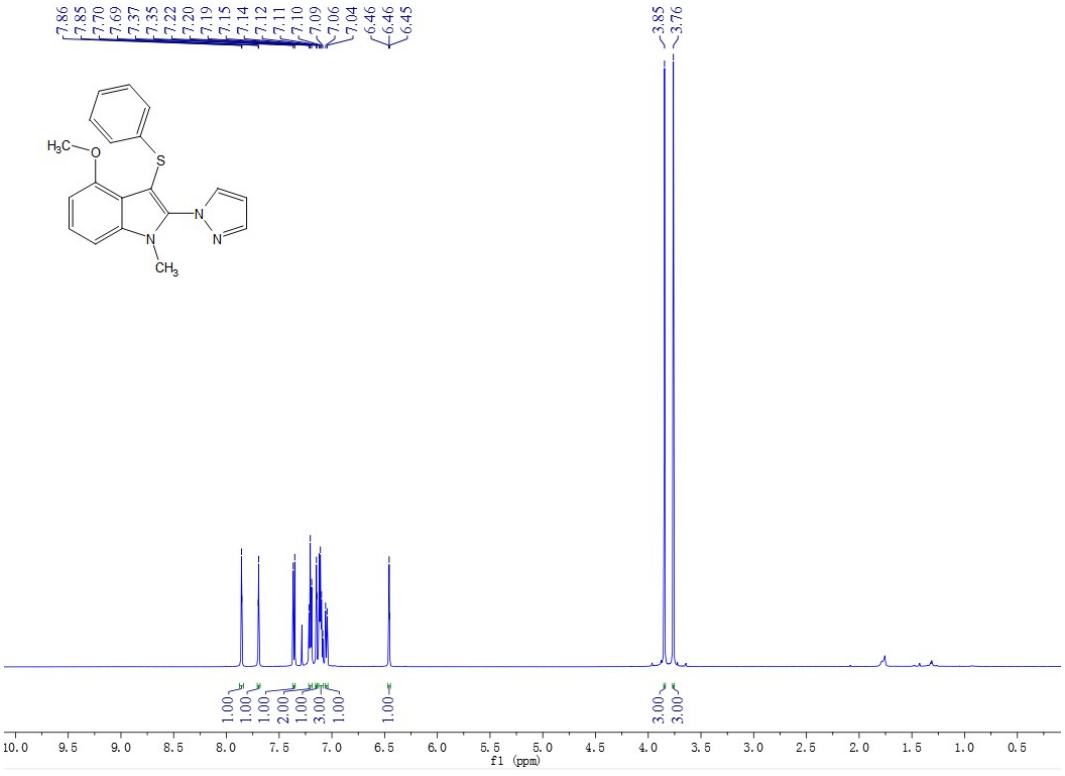
(84) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 41



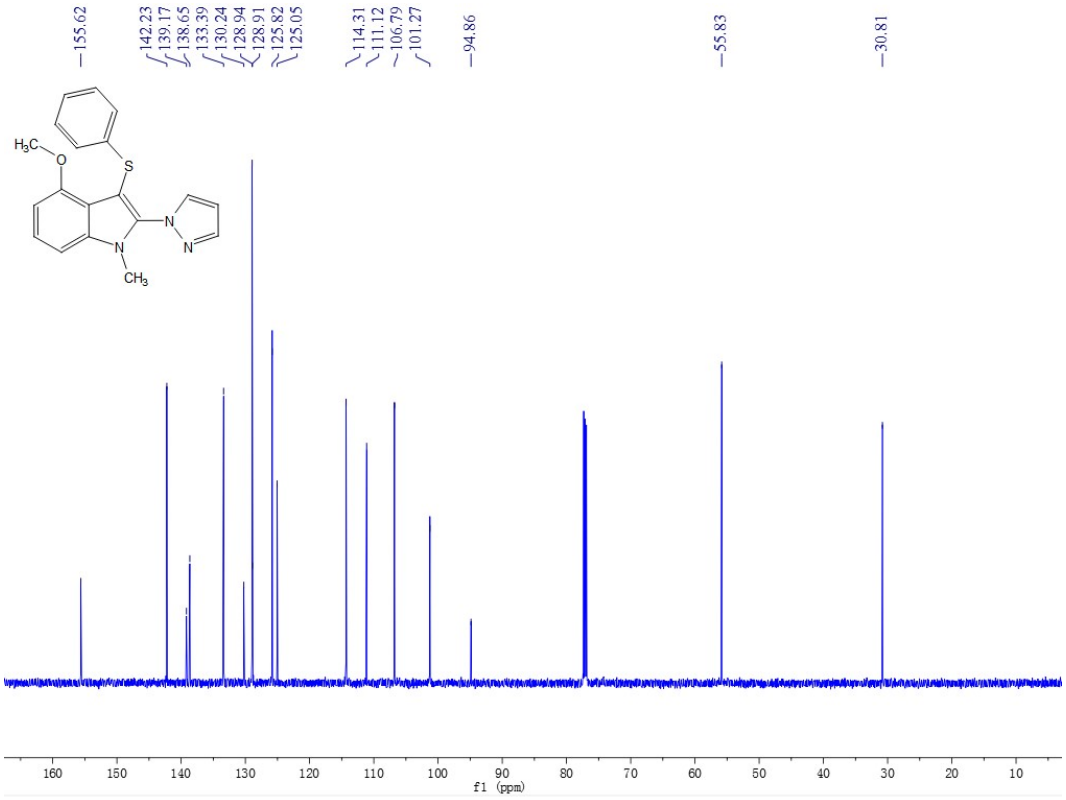
(85) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 41



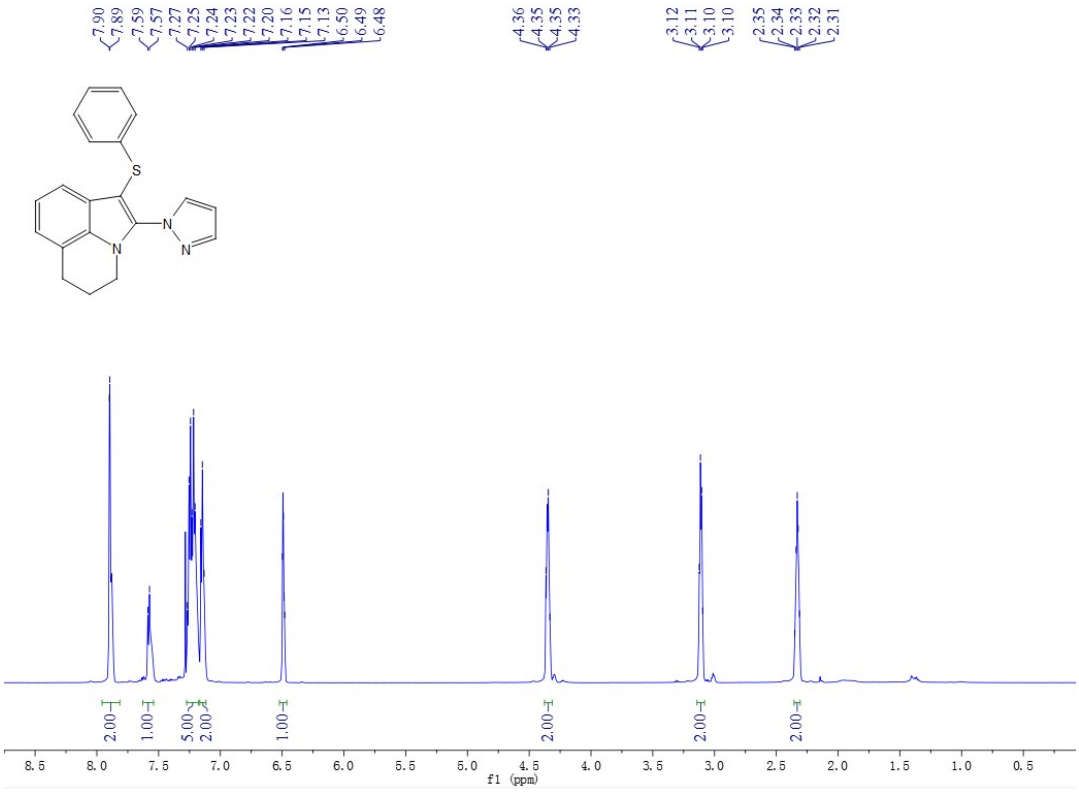
(86) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 42



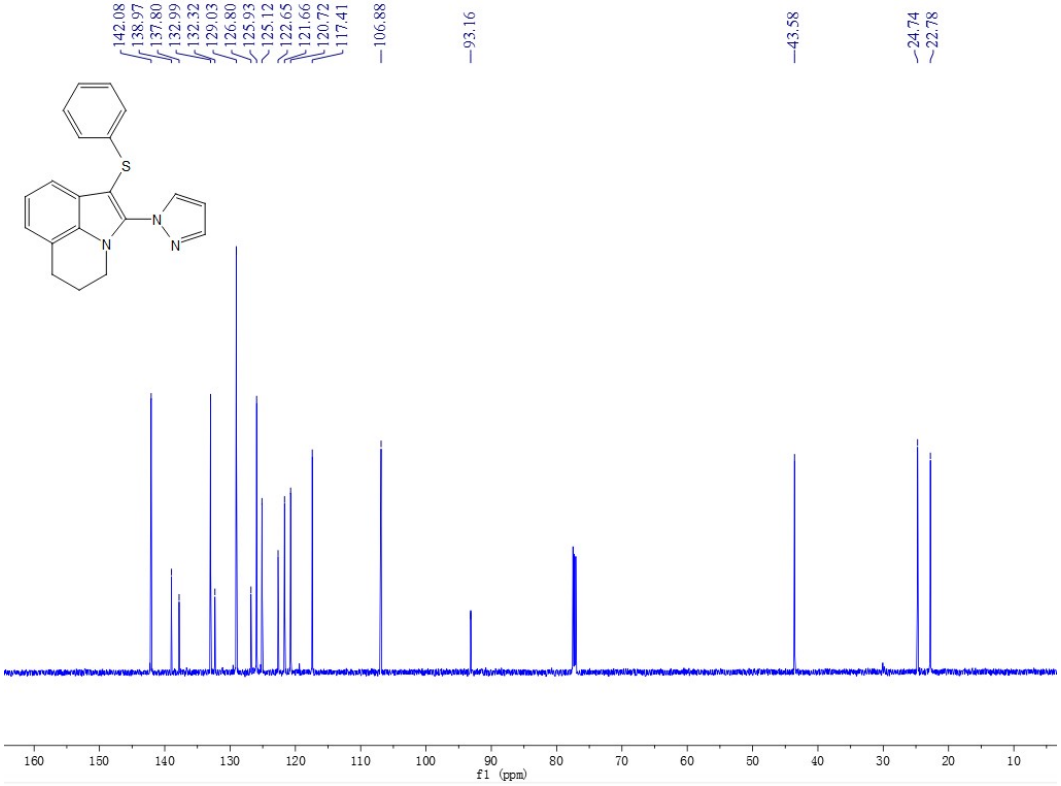
(87) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 42



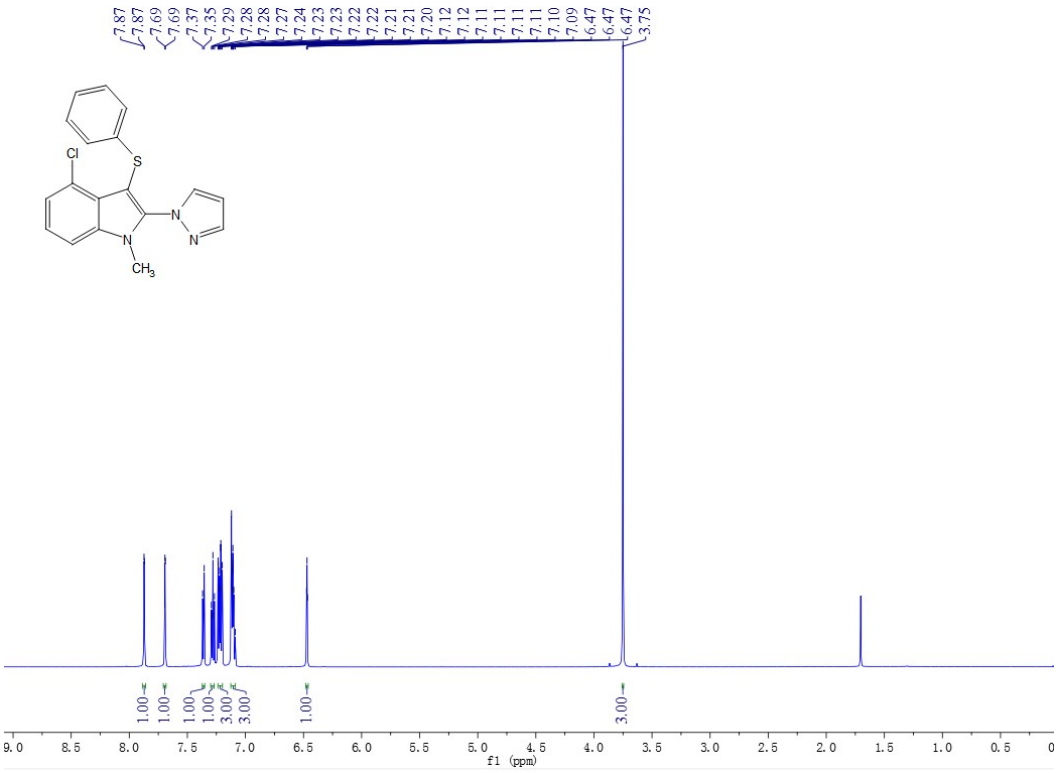
(88) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 43



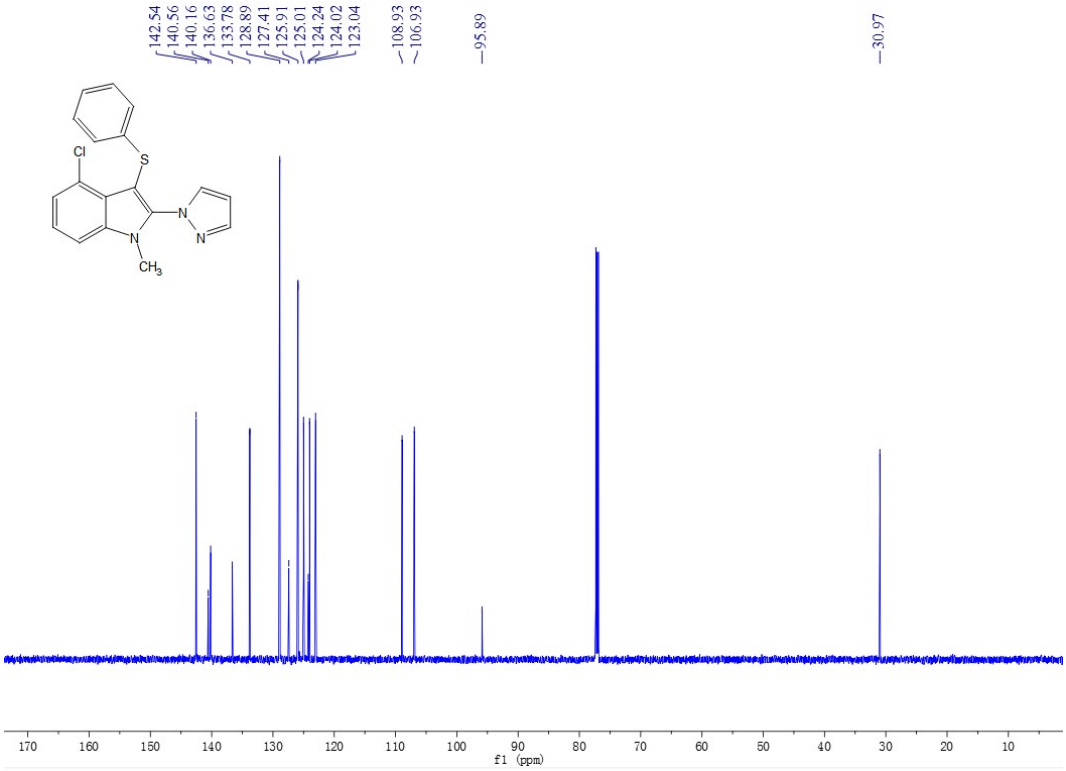
(89) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 43



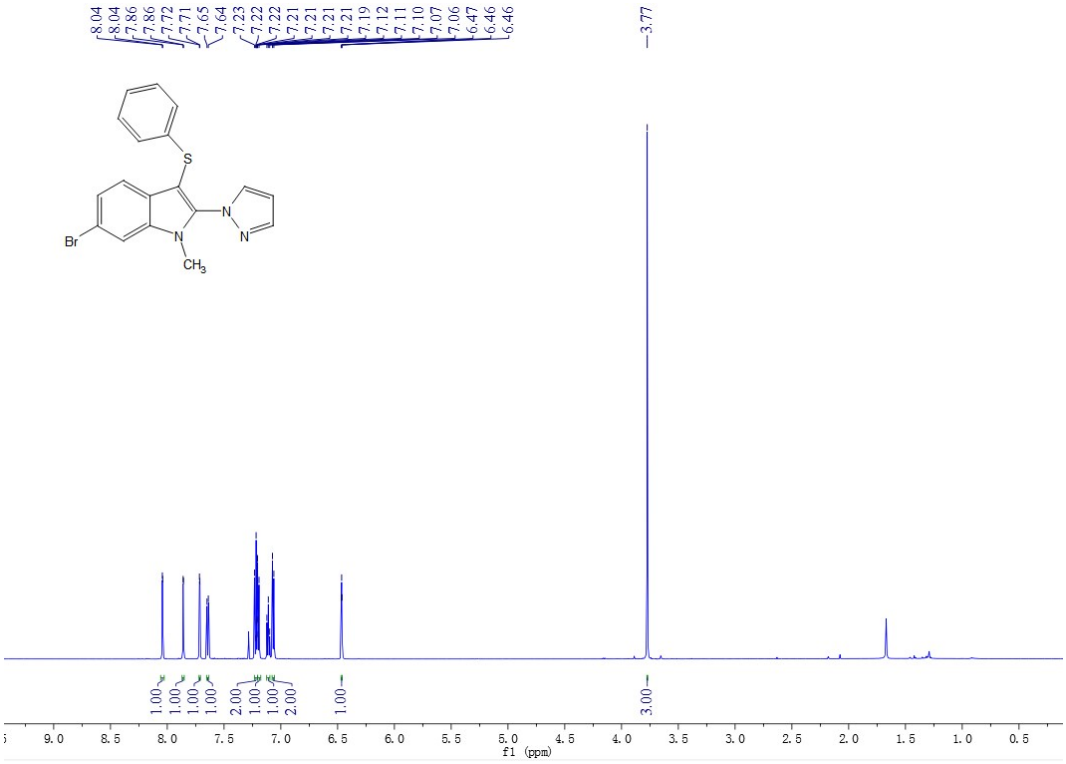
(90) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 44



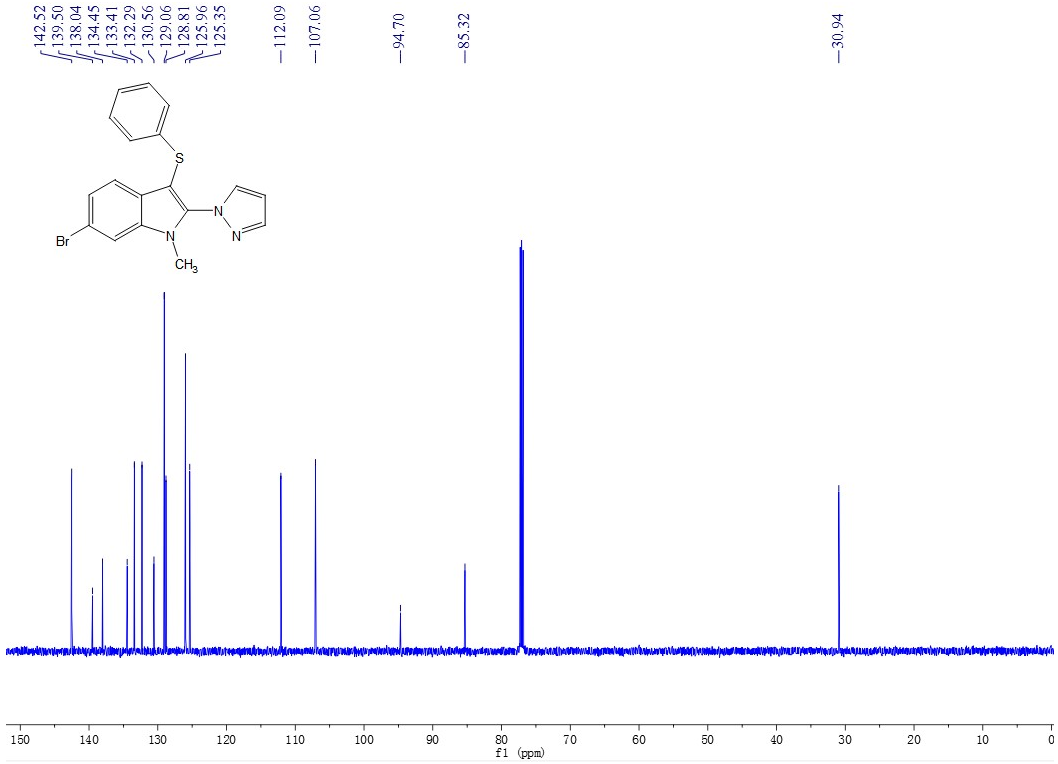
(91) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 44



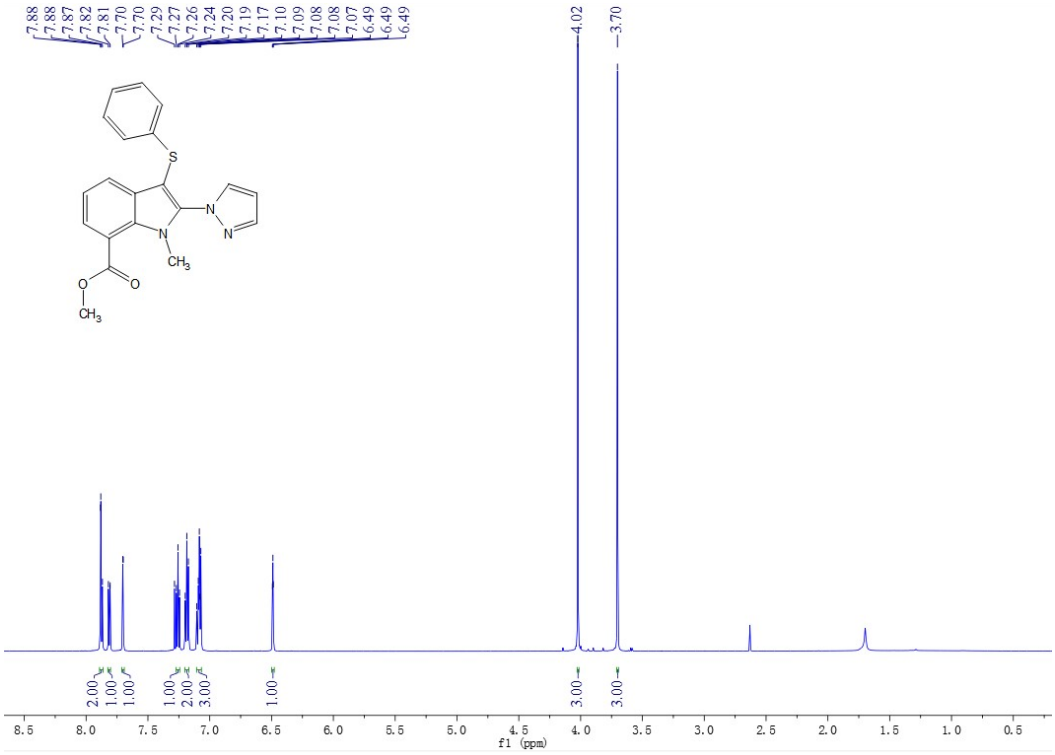
(92) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 45



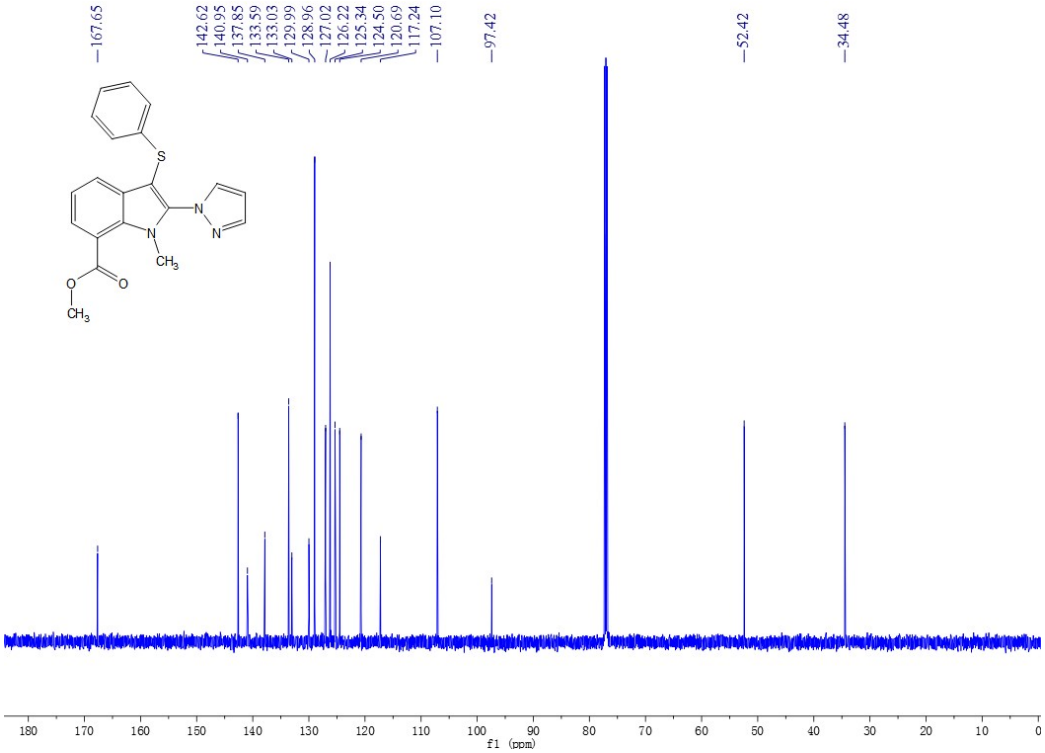
(93) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 45



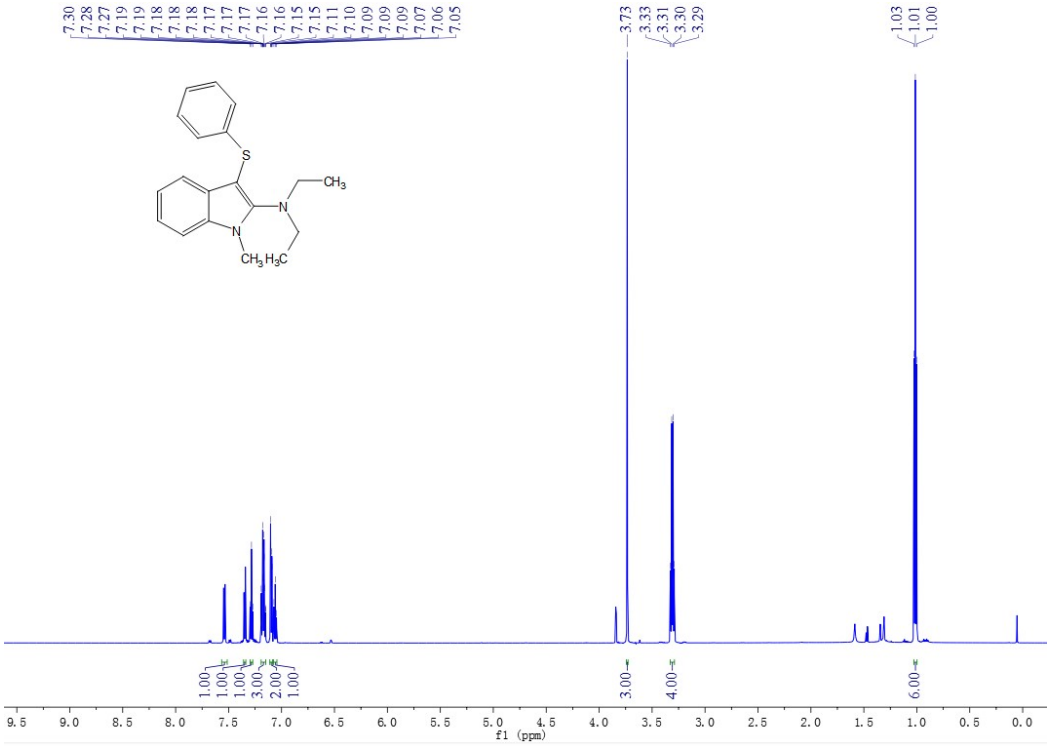
(94) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 46



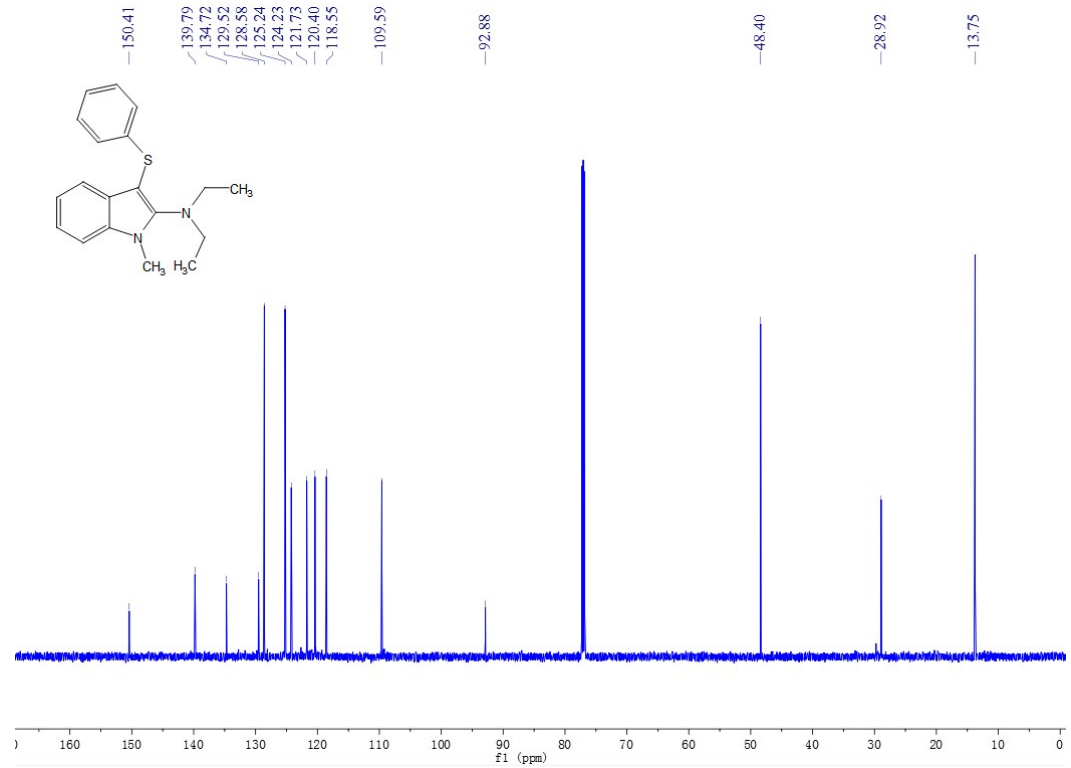
(95) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 46



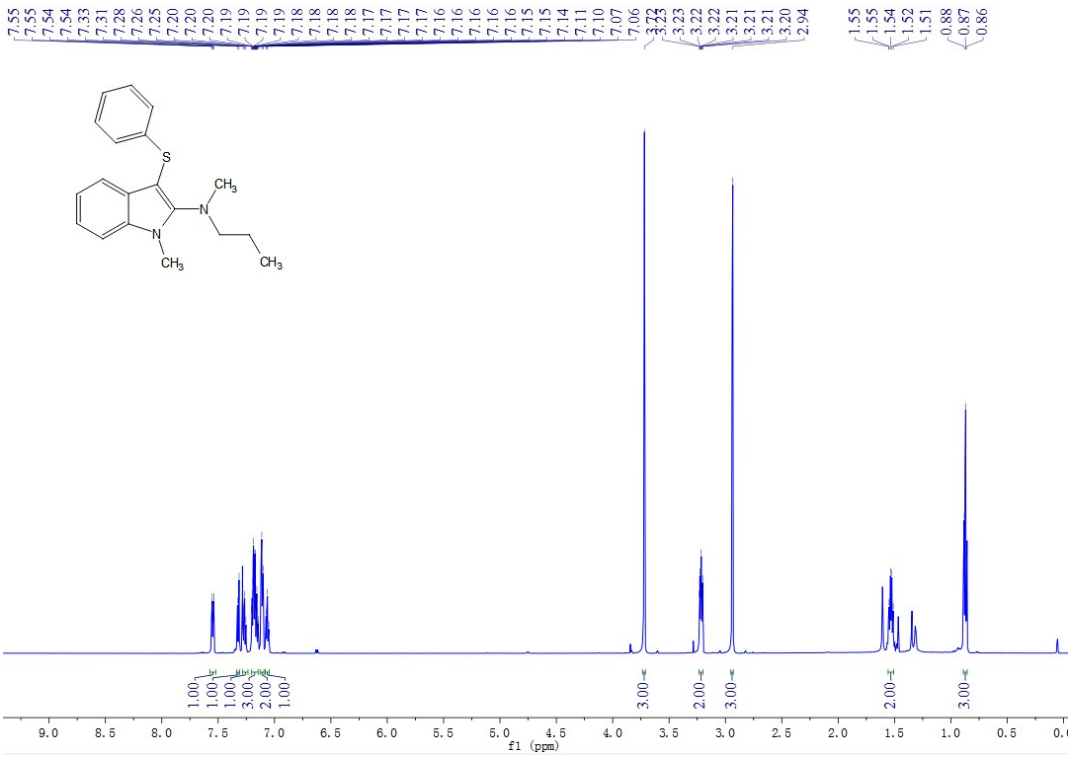
(96) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 47



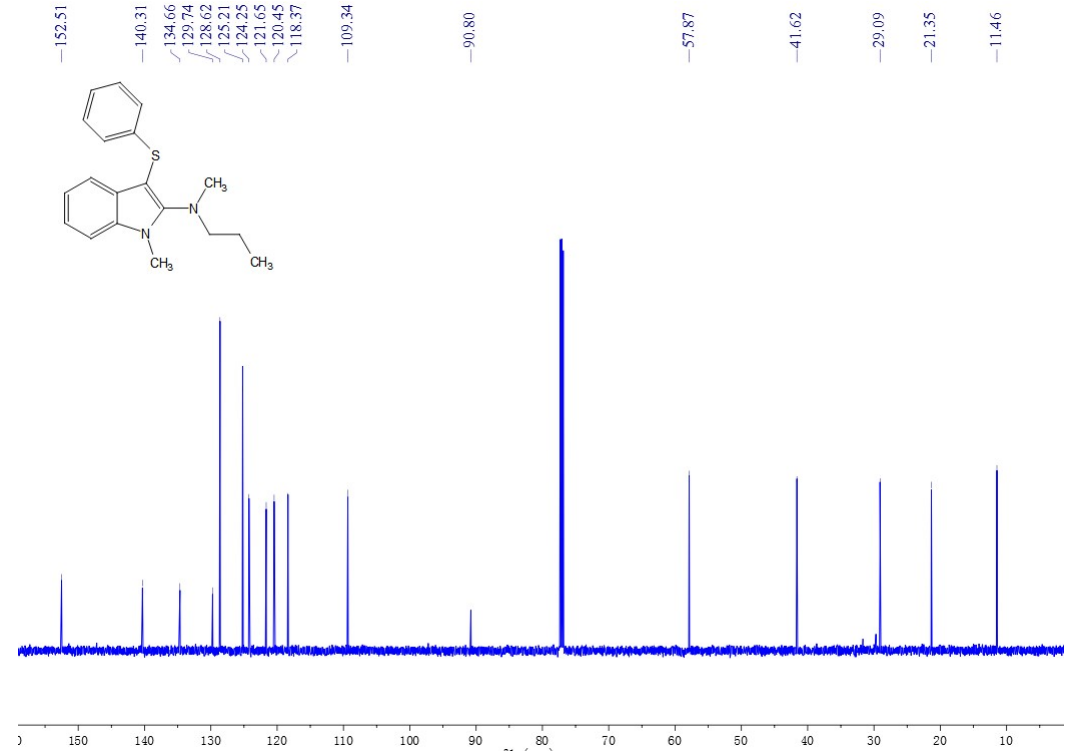
(97) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 47



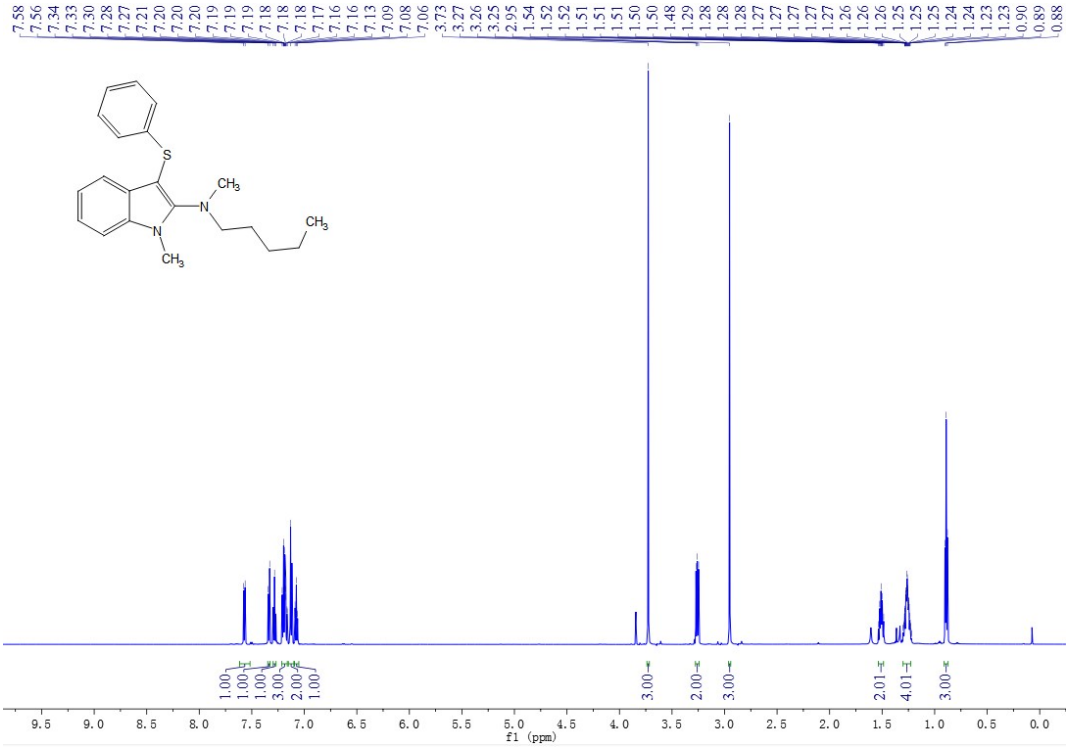
(98) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 48



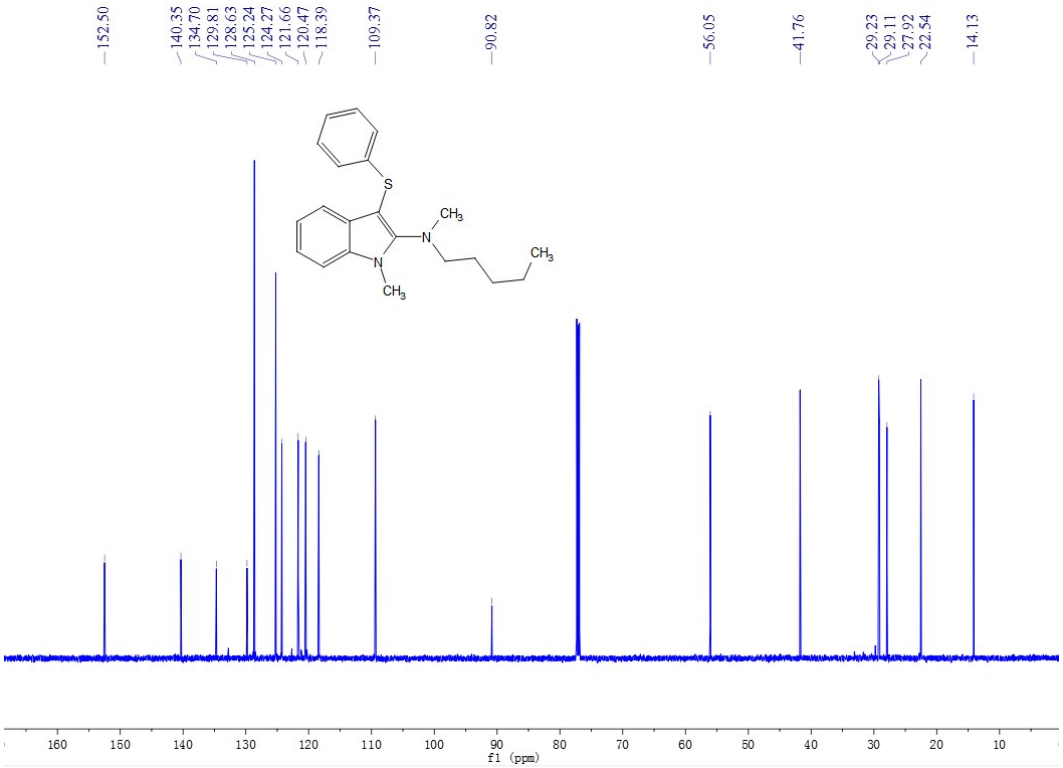
(99) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 48



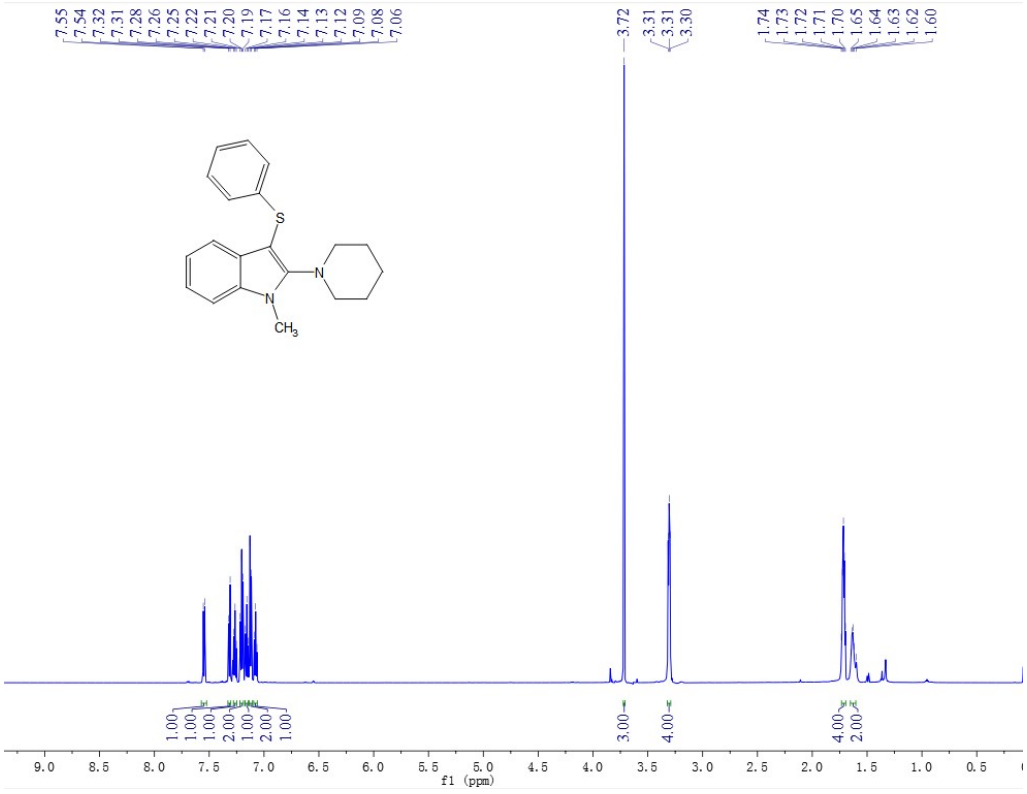
(100) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 49



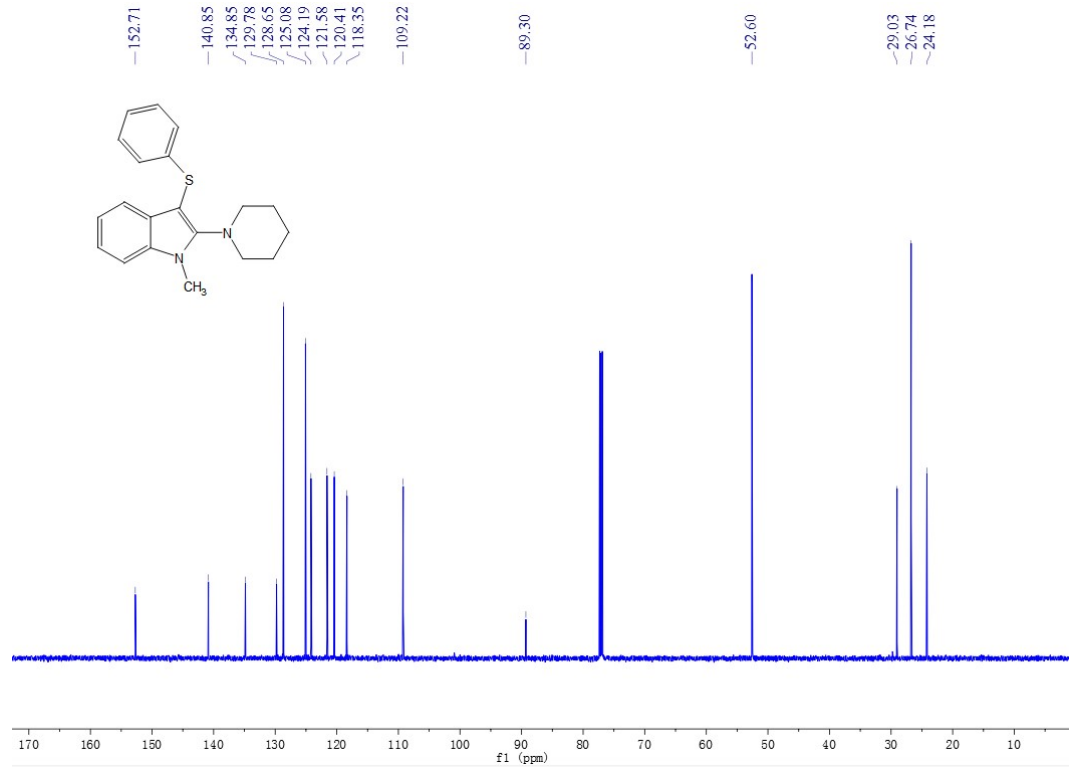
(101) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 49



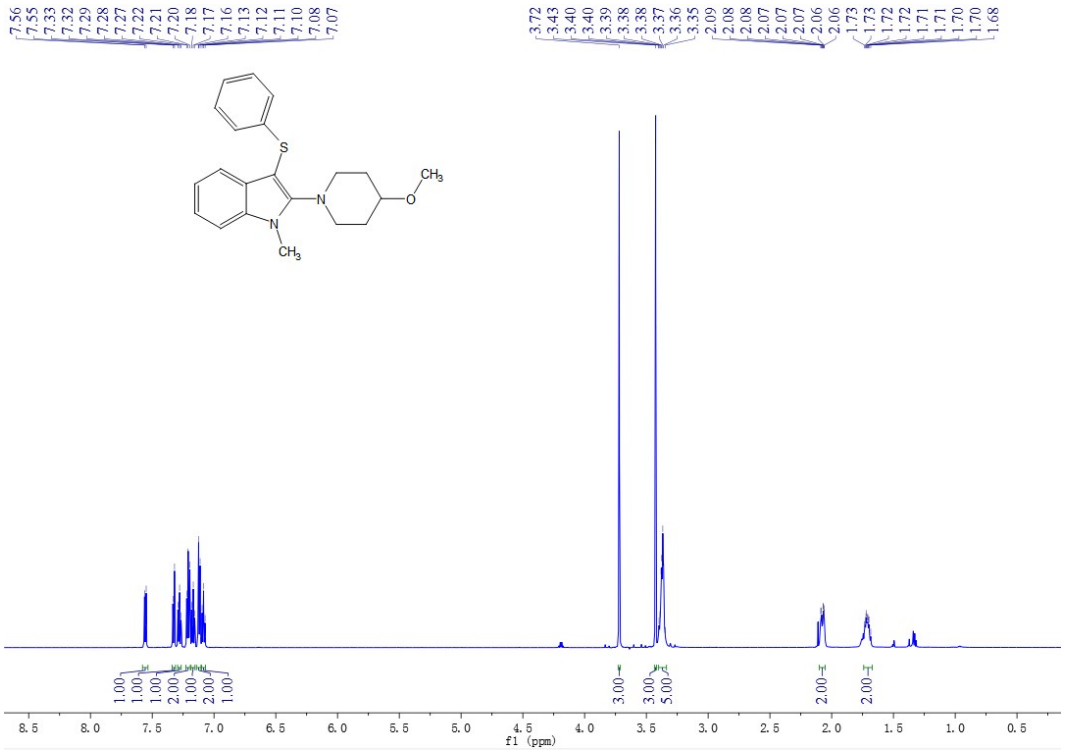
(102) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 50



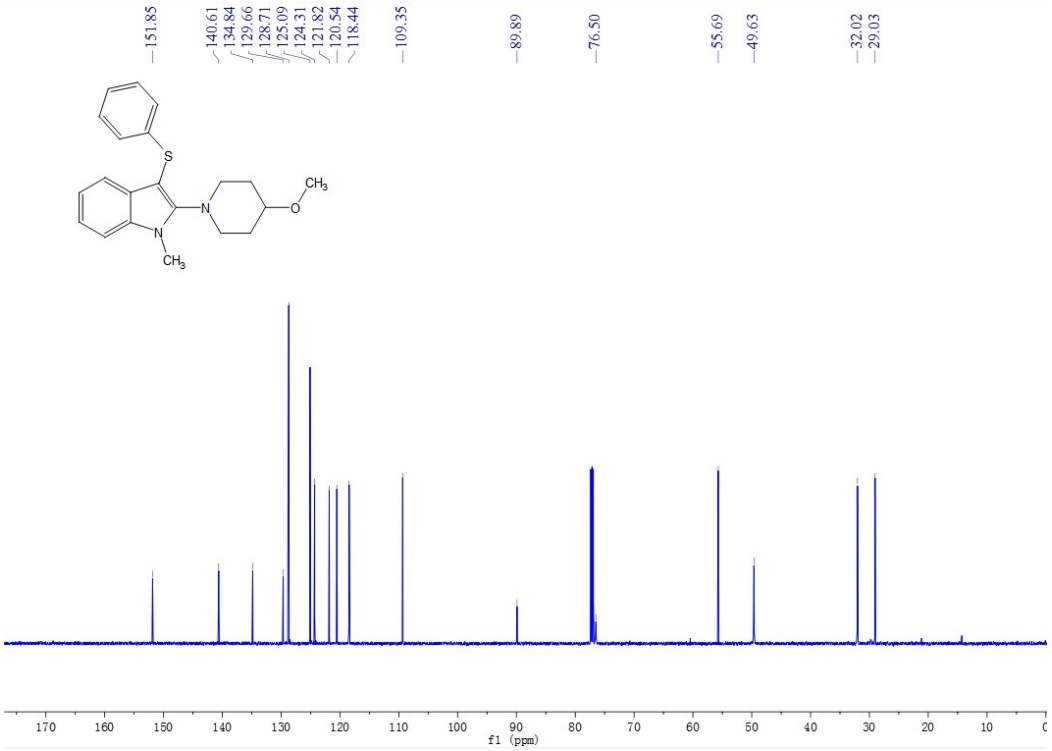
(103) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 50



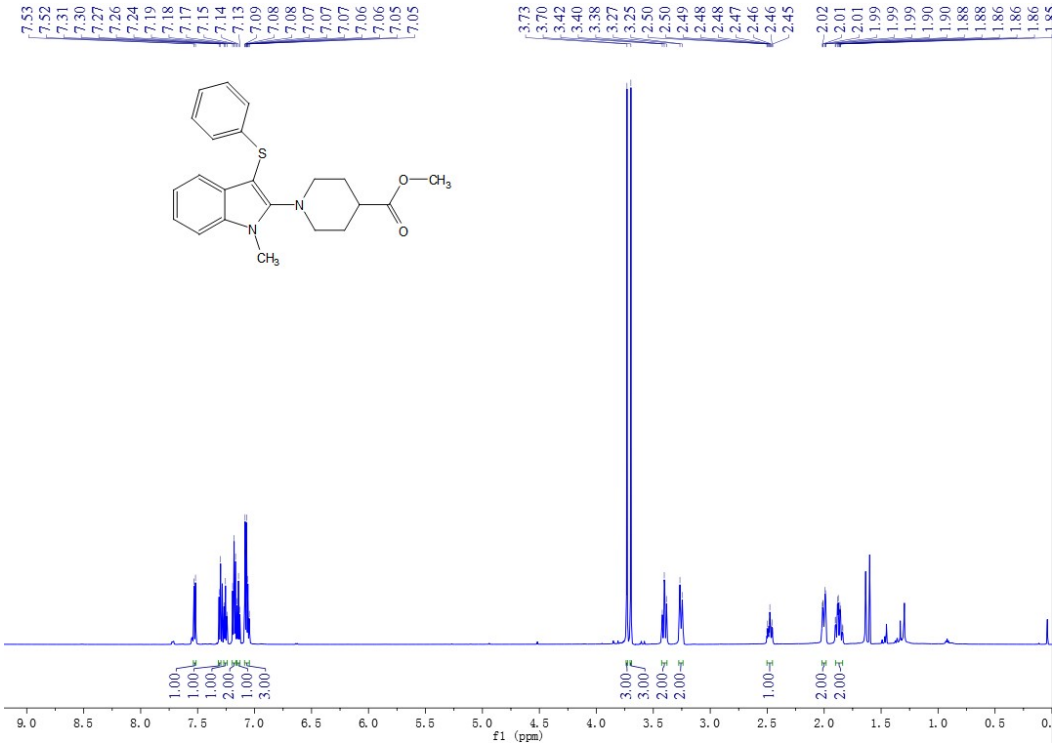
(104) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 51



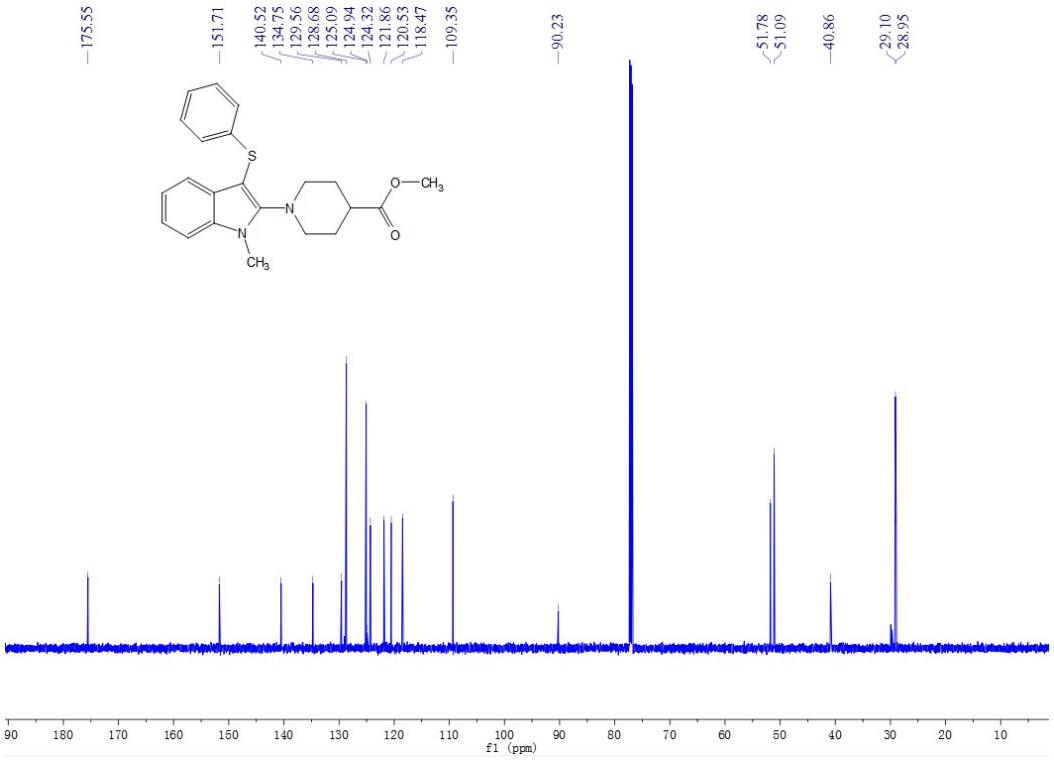
(105) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 51



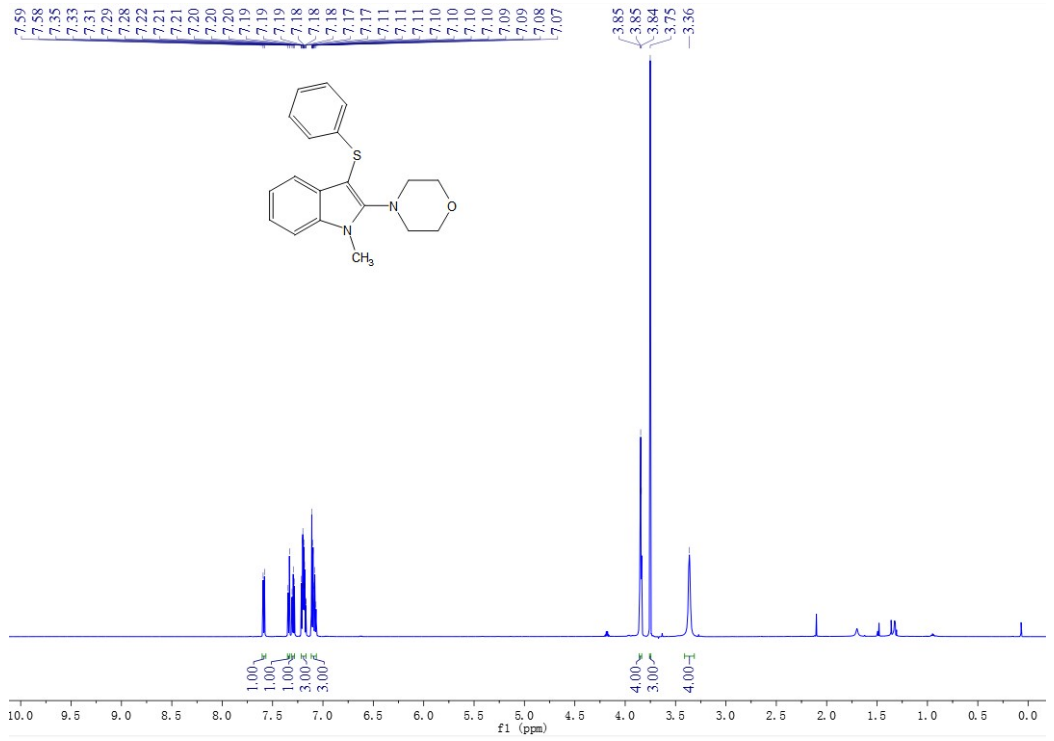
(106) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 52



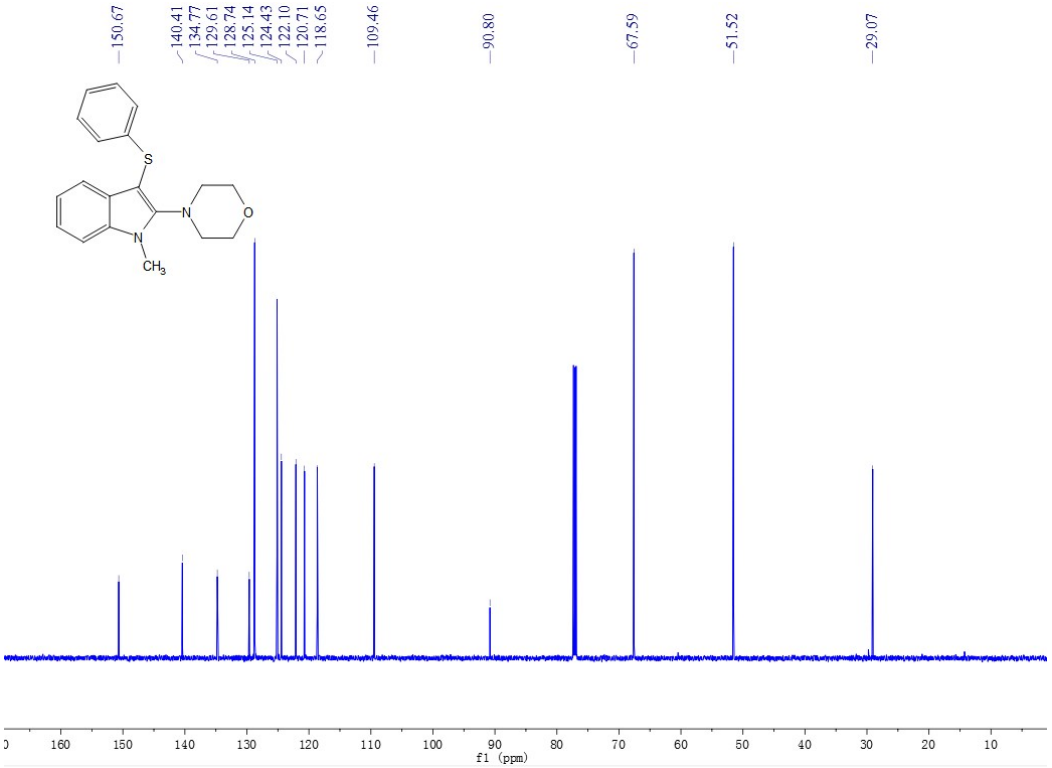
(107) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 52



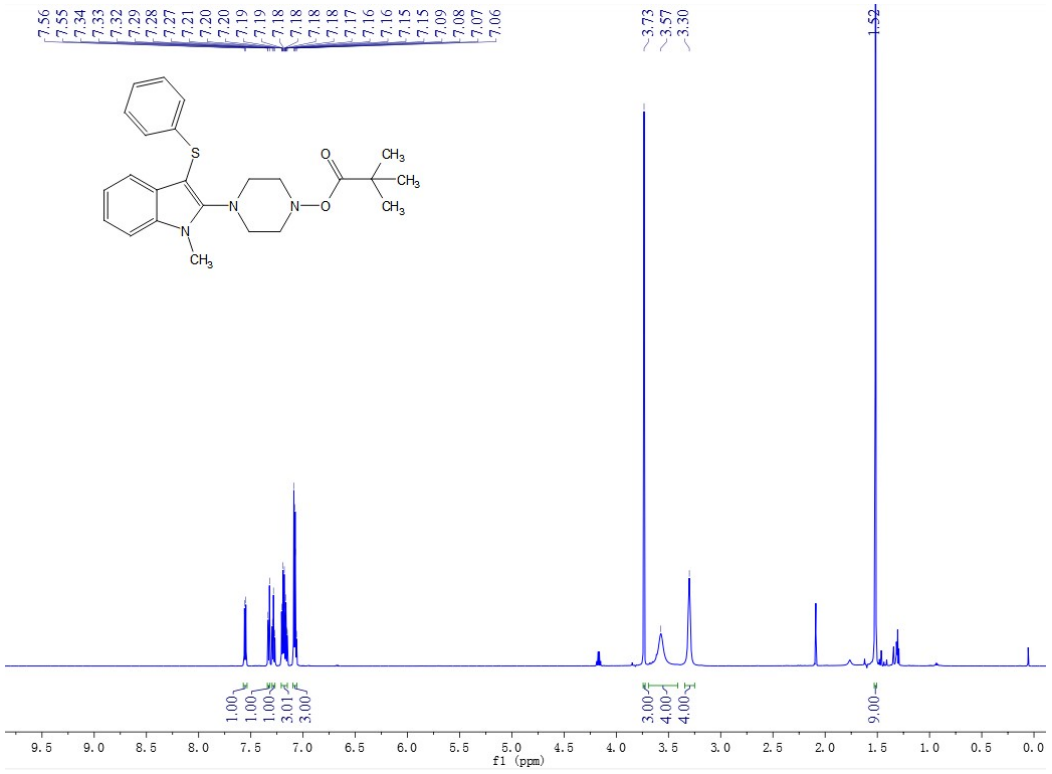
(108) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 53



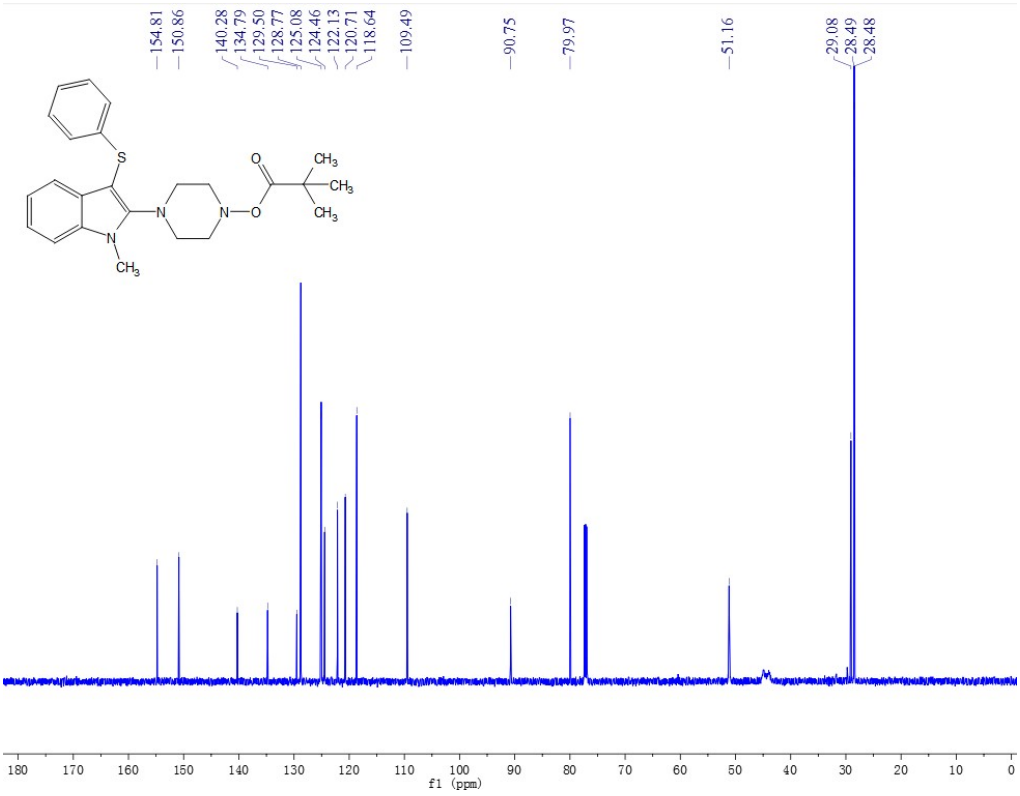
(109) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 53



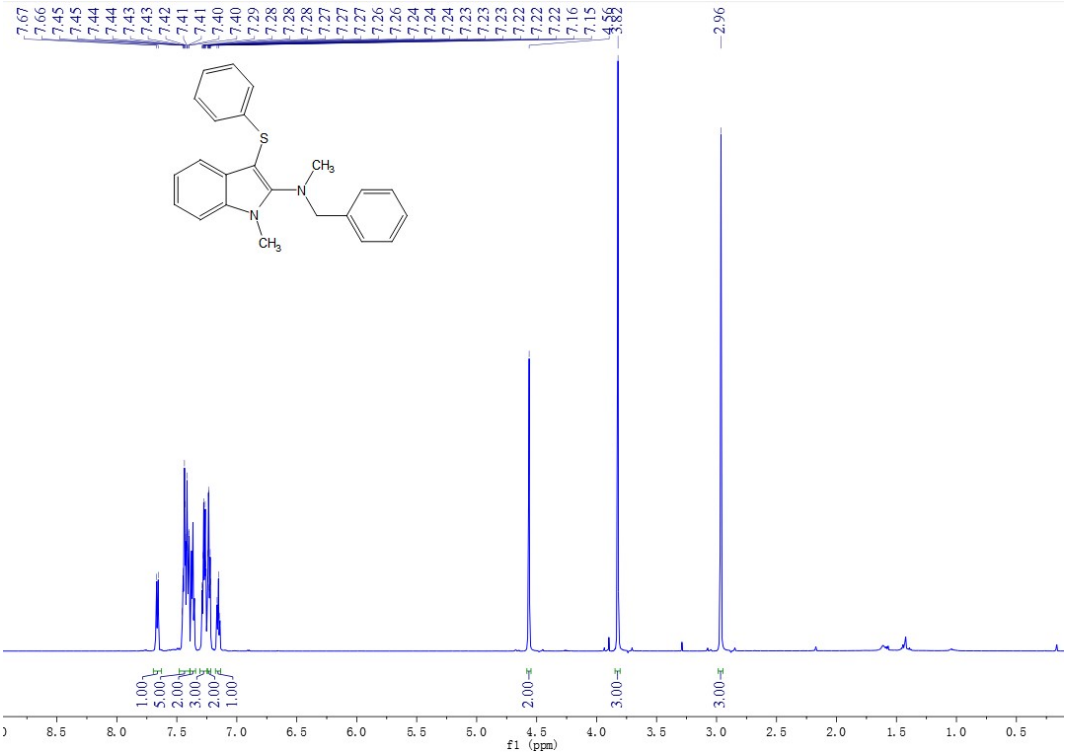
(110) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 54



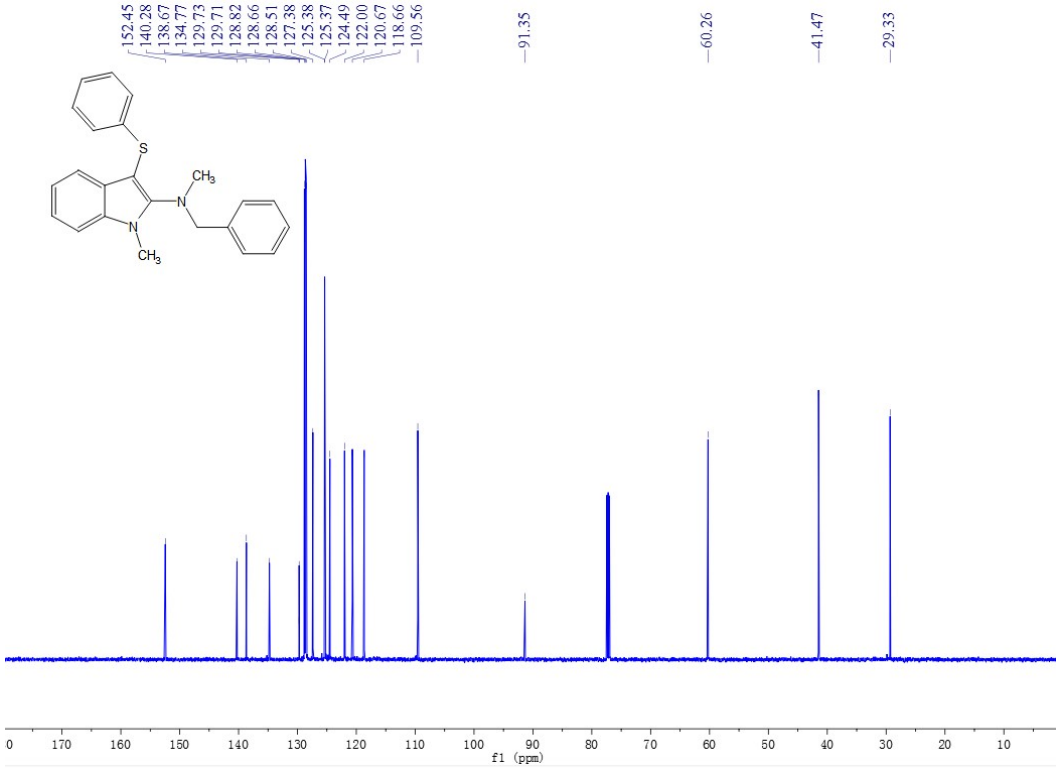
(111) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 54



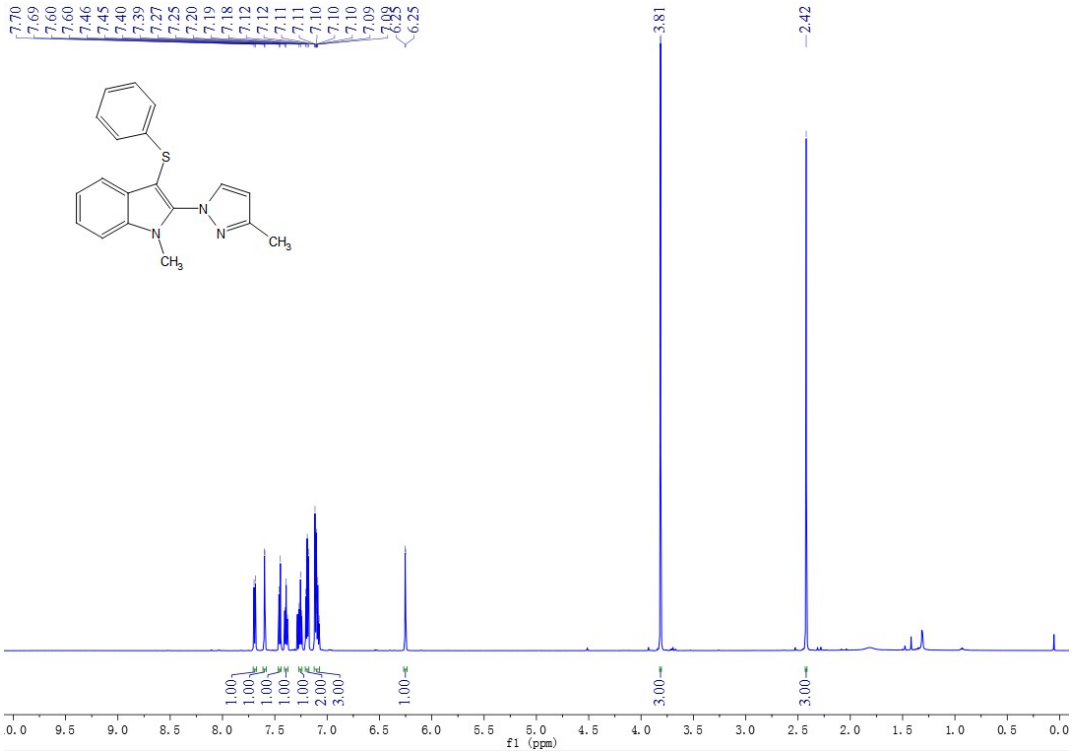
(112) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 55



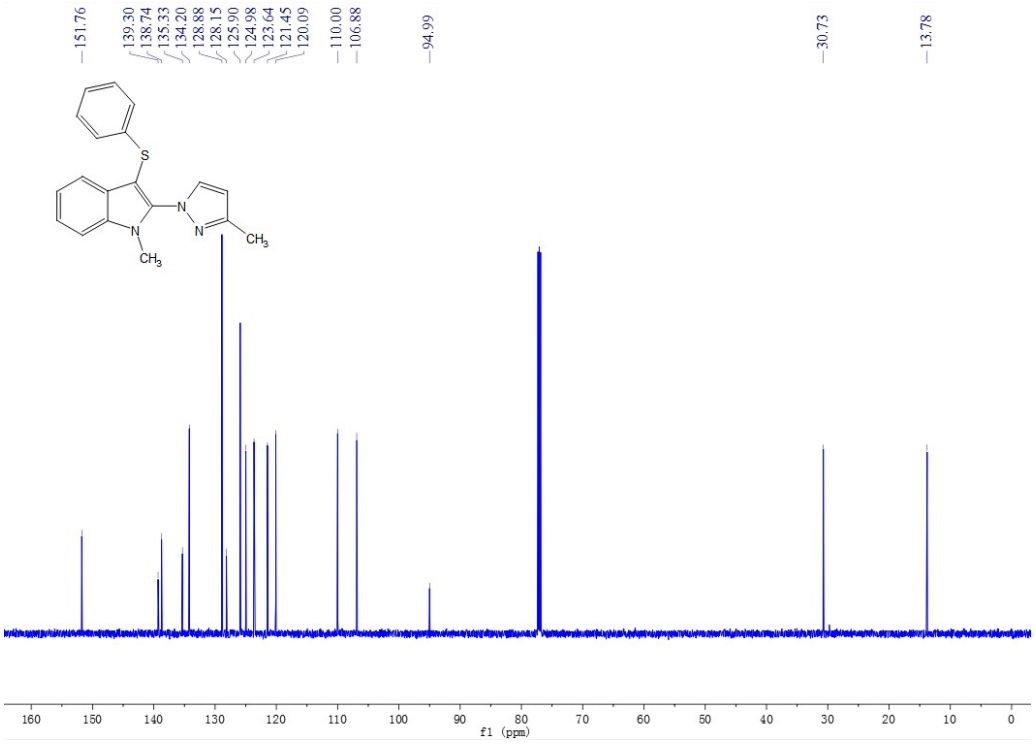
(113) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 55



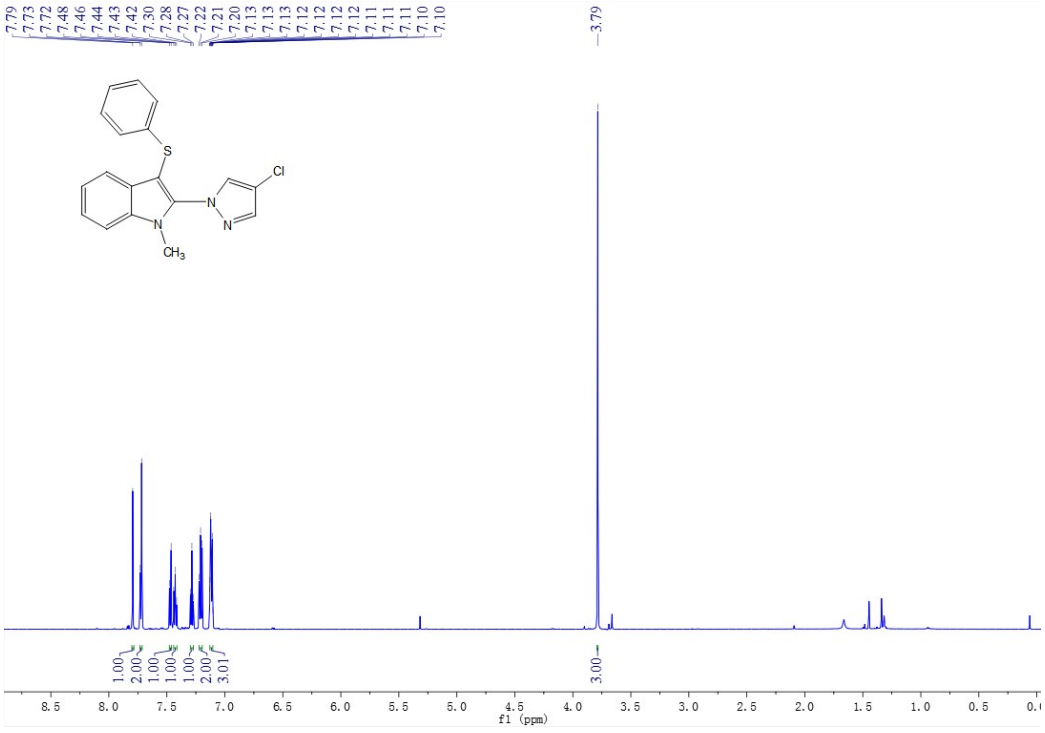
(114) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 56



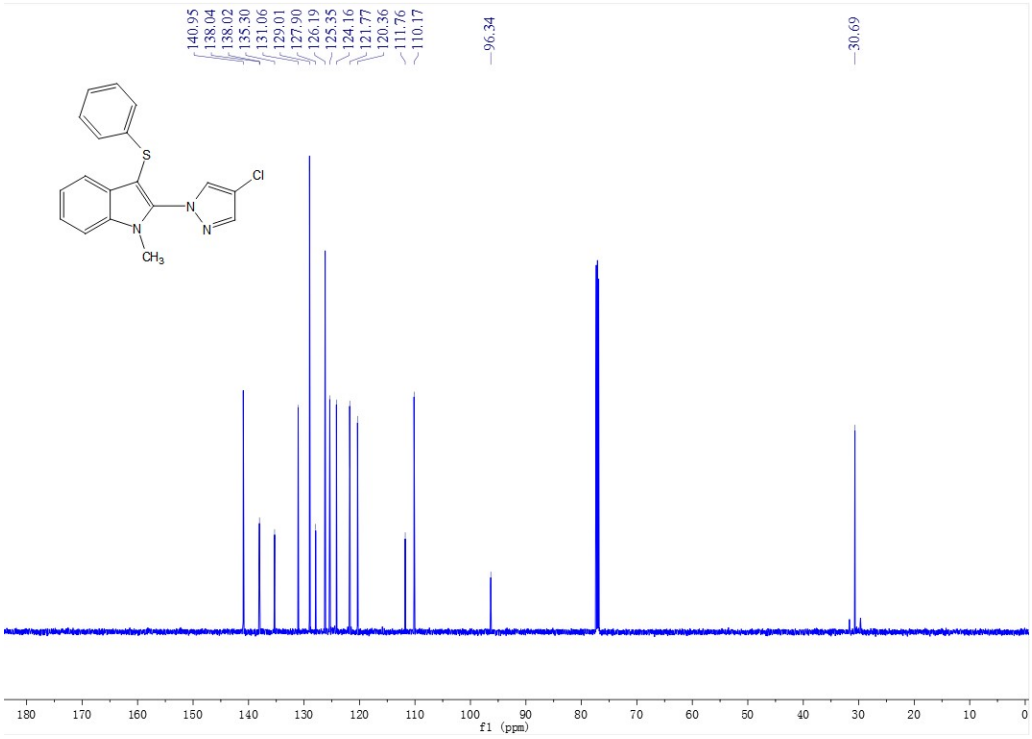
(115) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 56



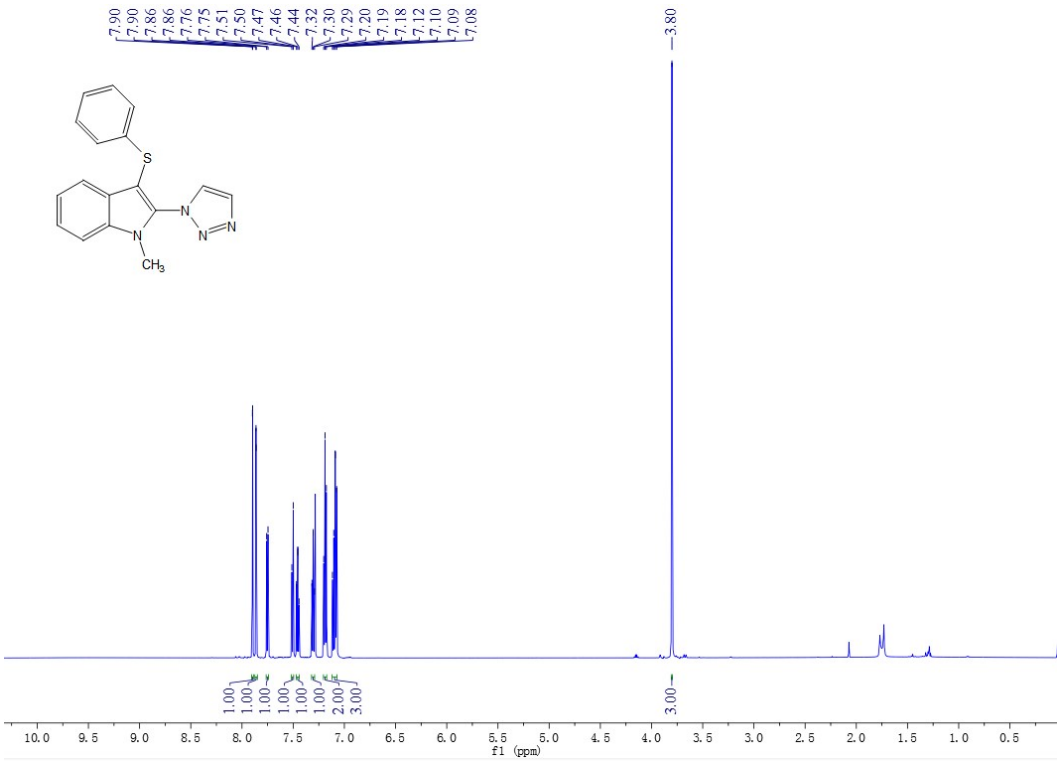
(116) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 57



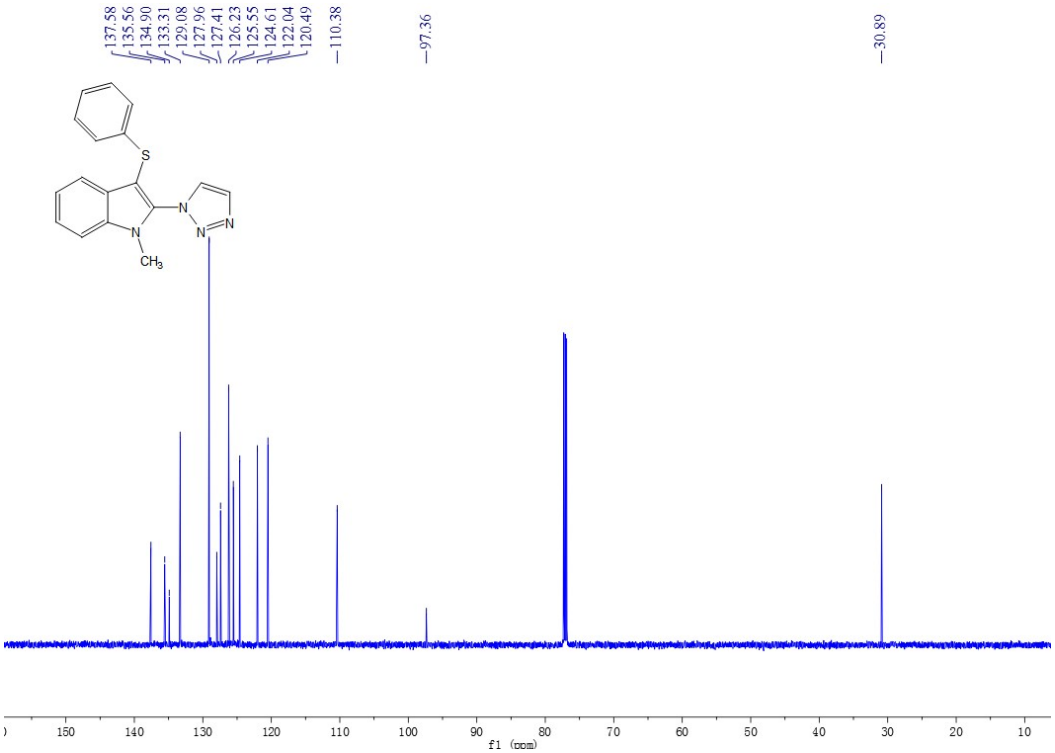
(117) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 57



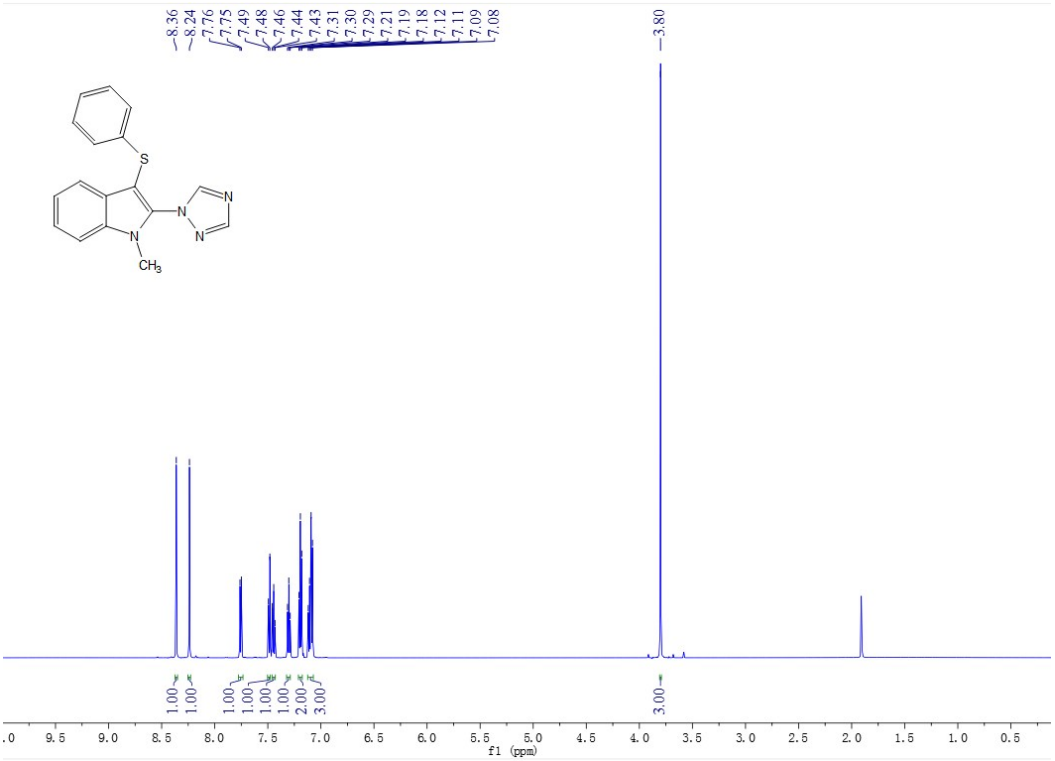
(118) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 58



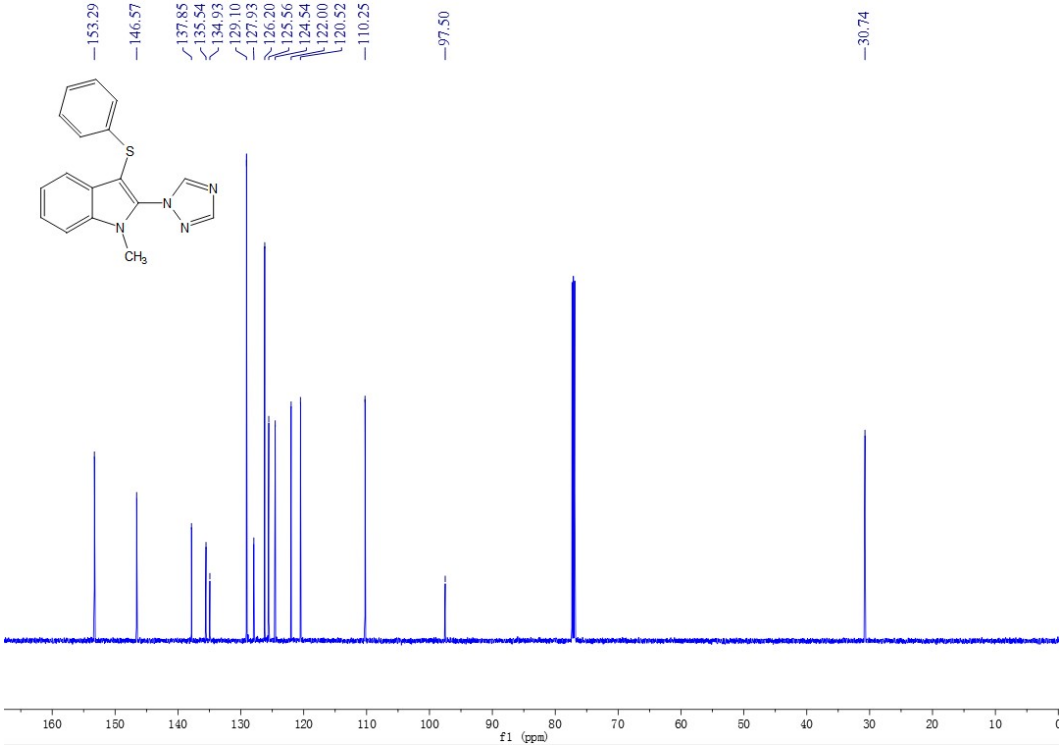
(119) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 58



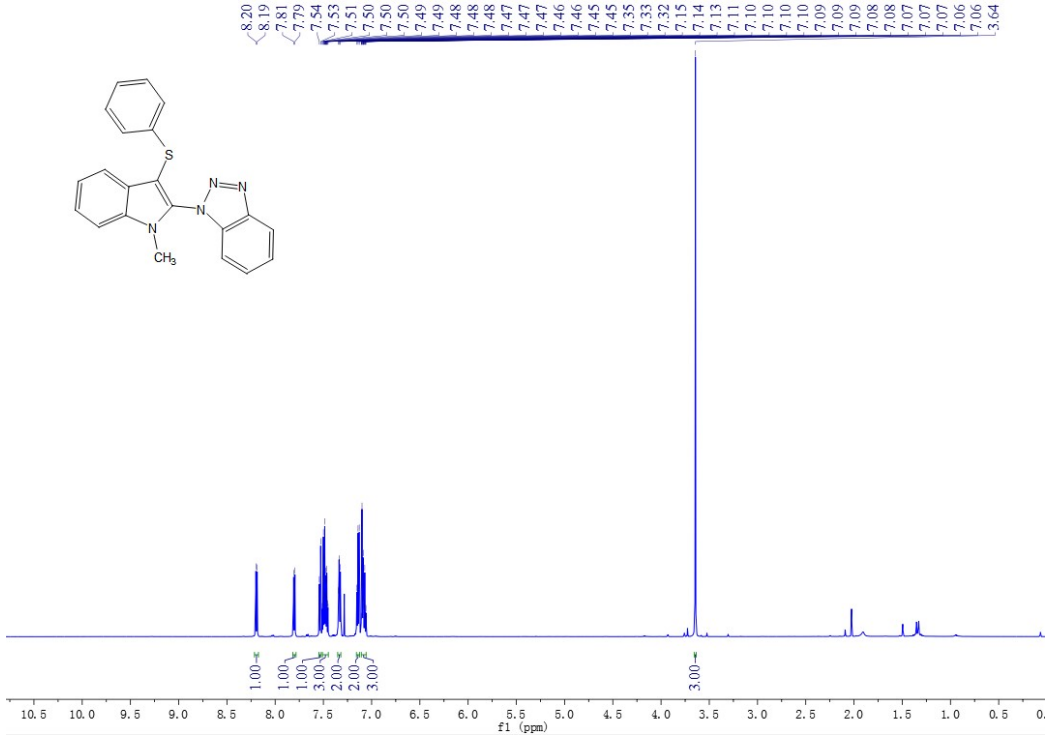
(120) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 59



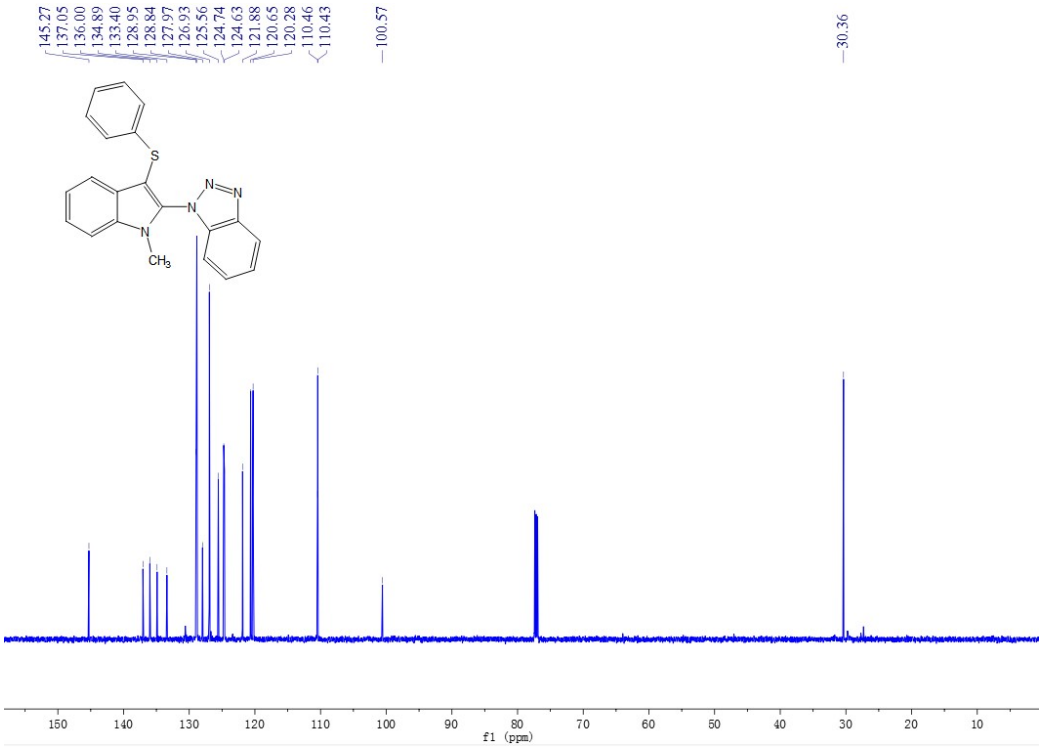
(121) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 59



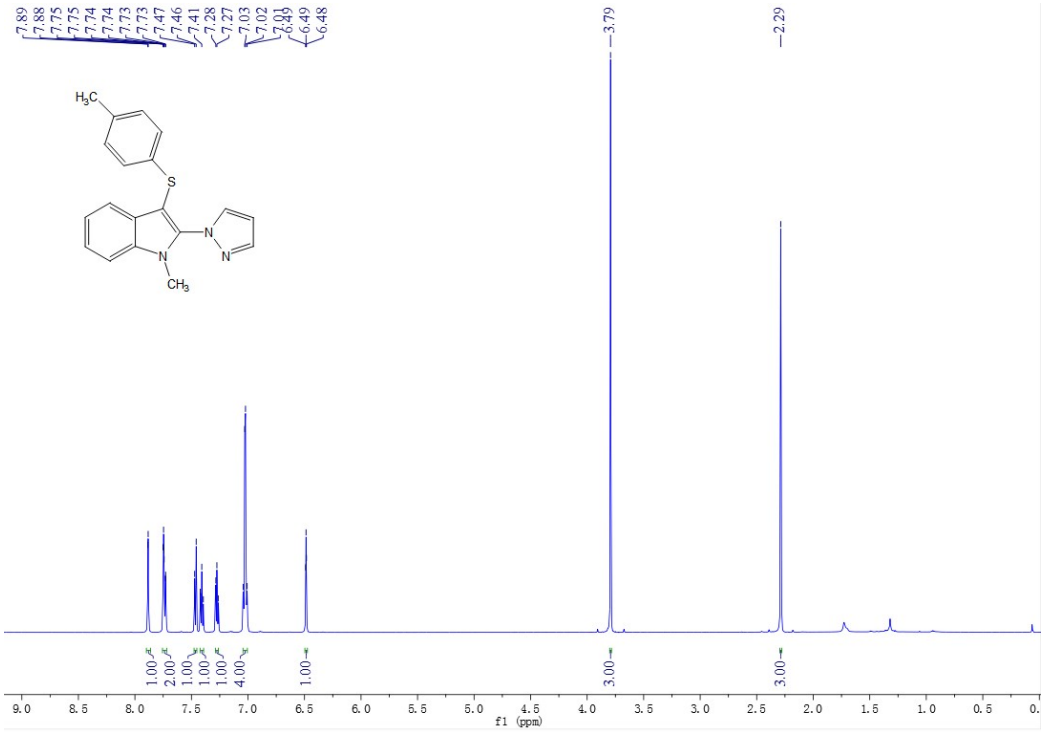
(122) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 60



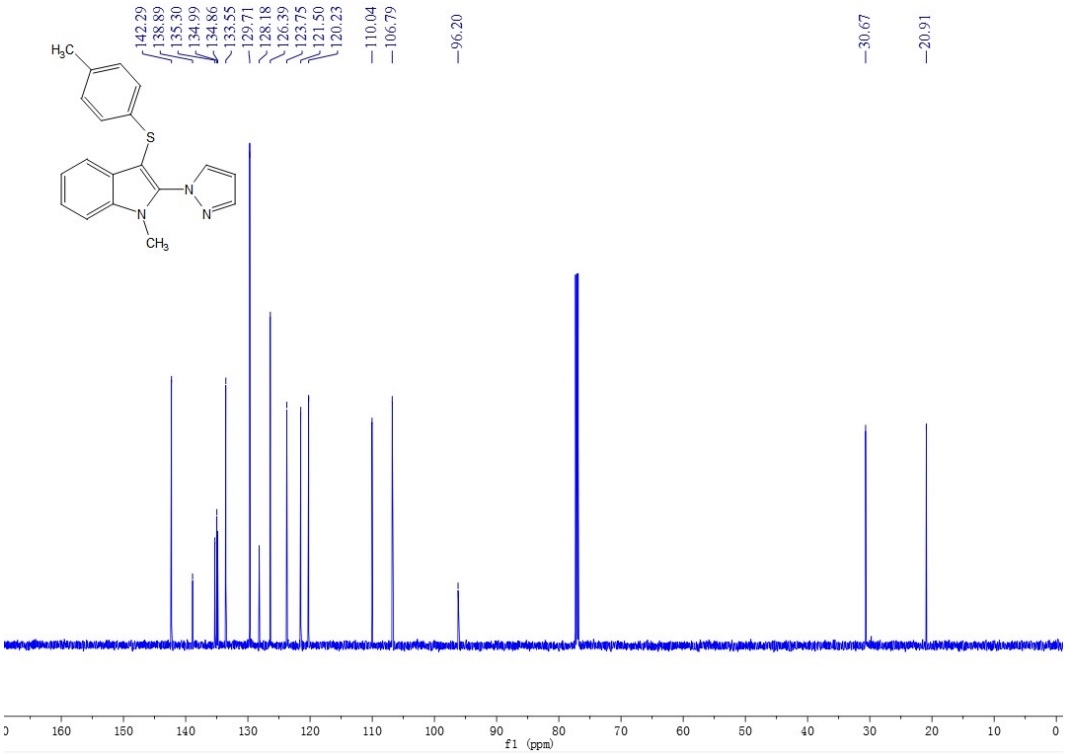
(123) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 60



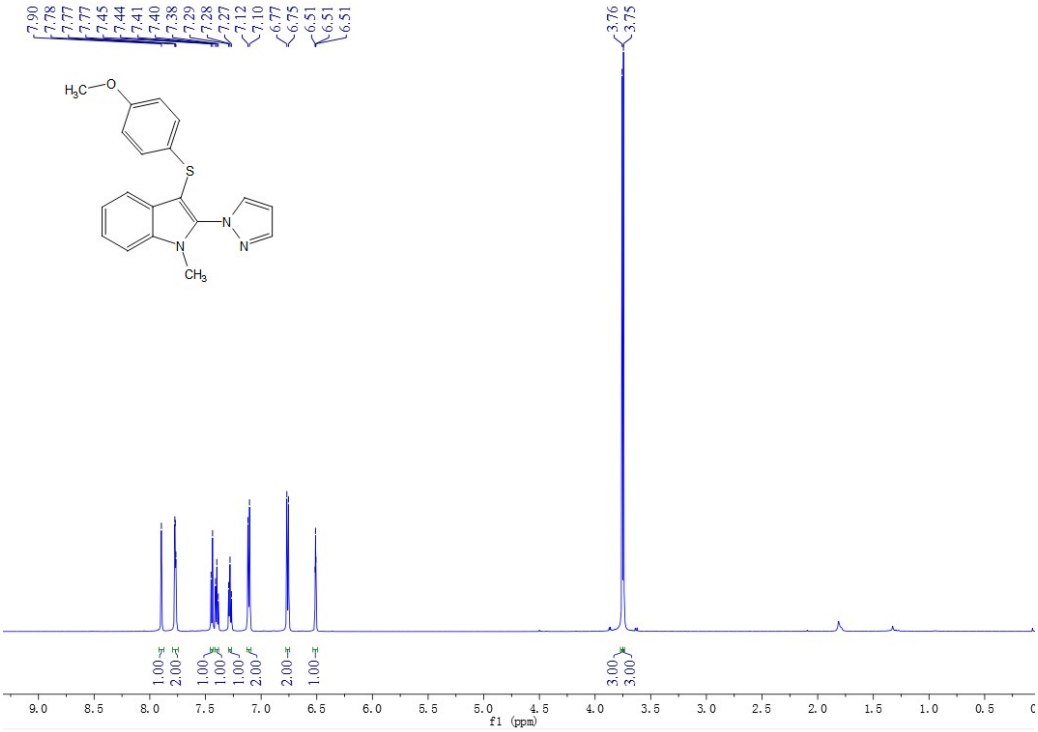
(124) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 61



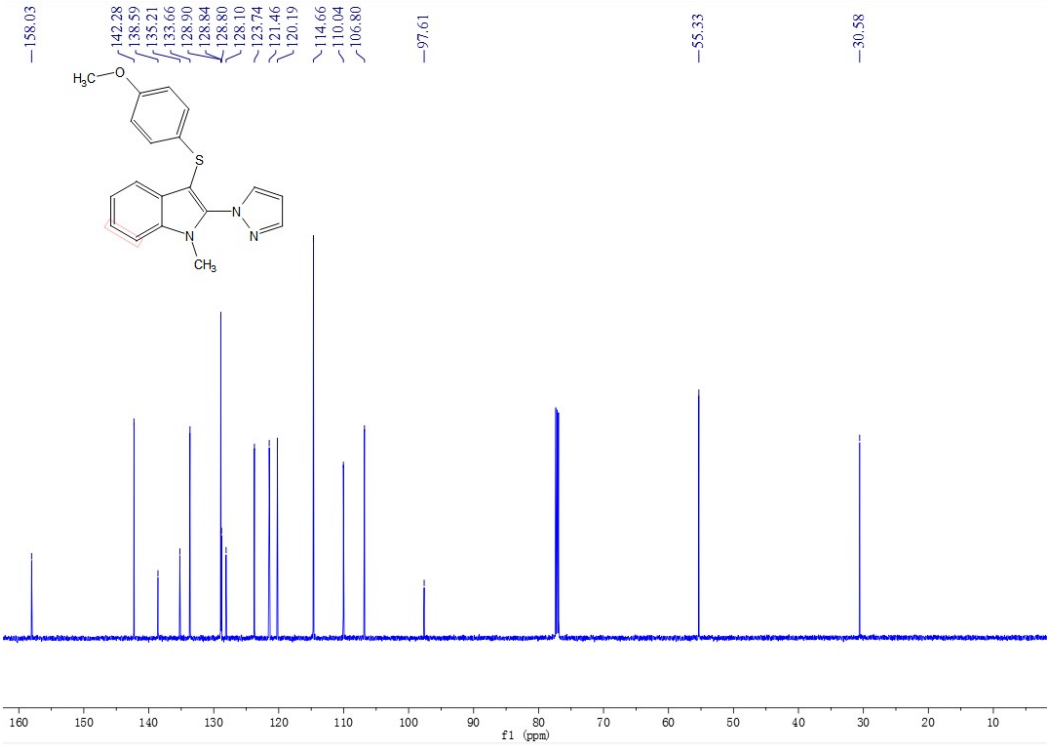
(125) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 61



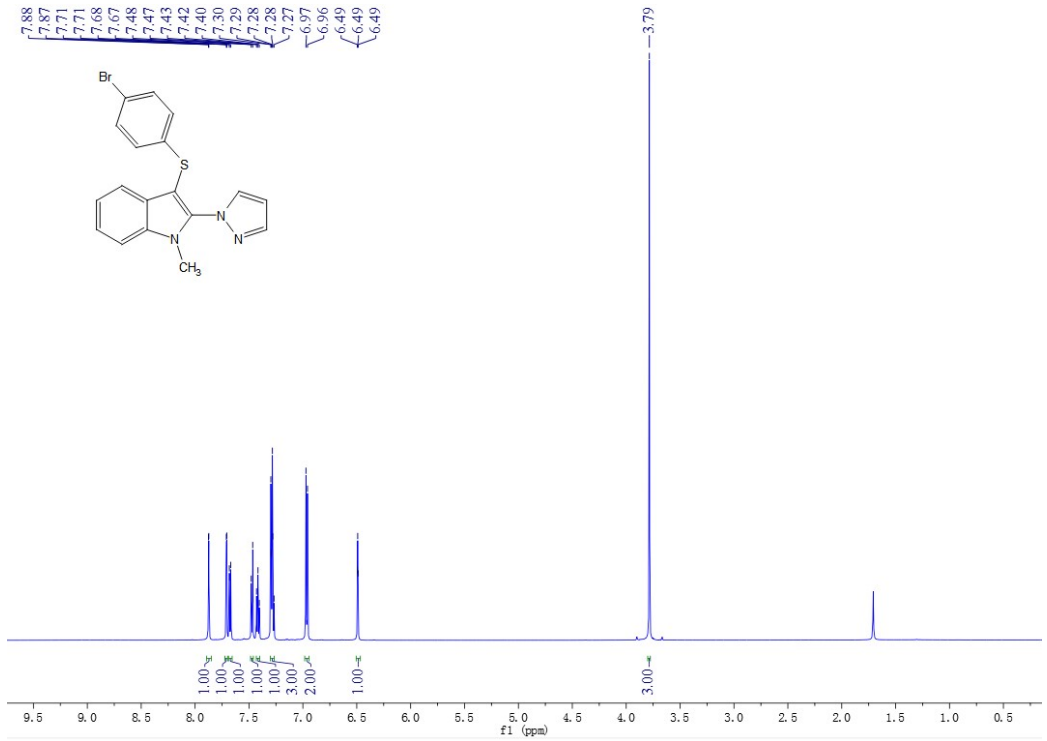
(126) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 62



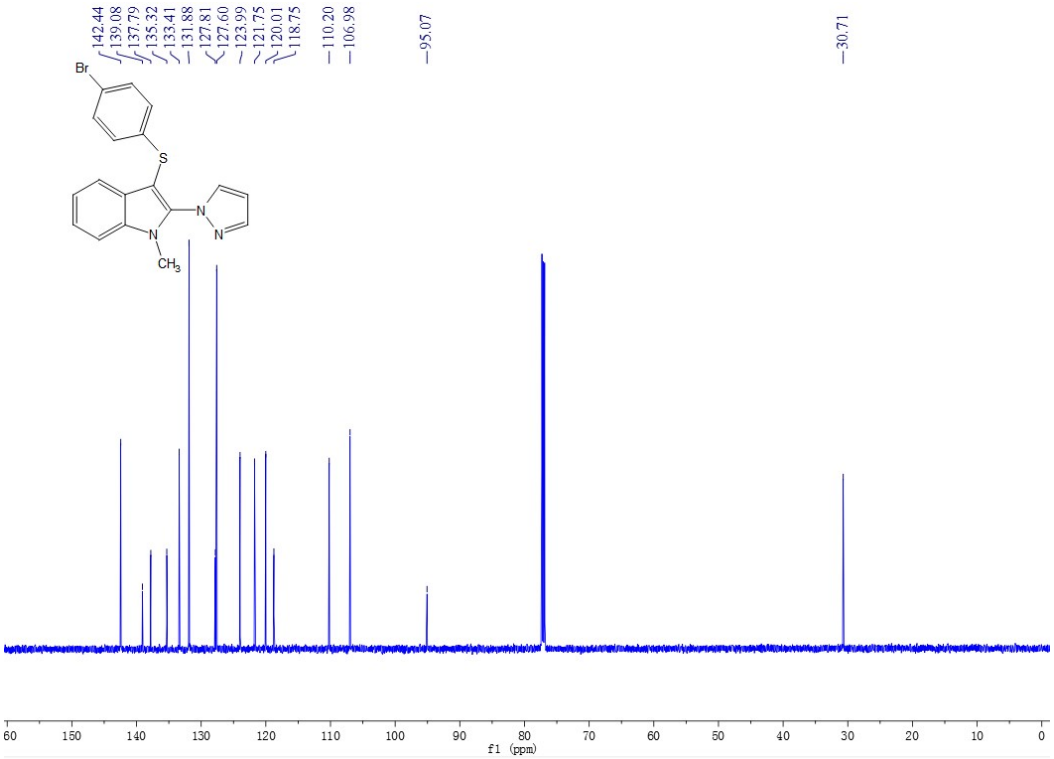
(127) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 62



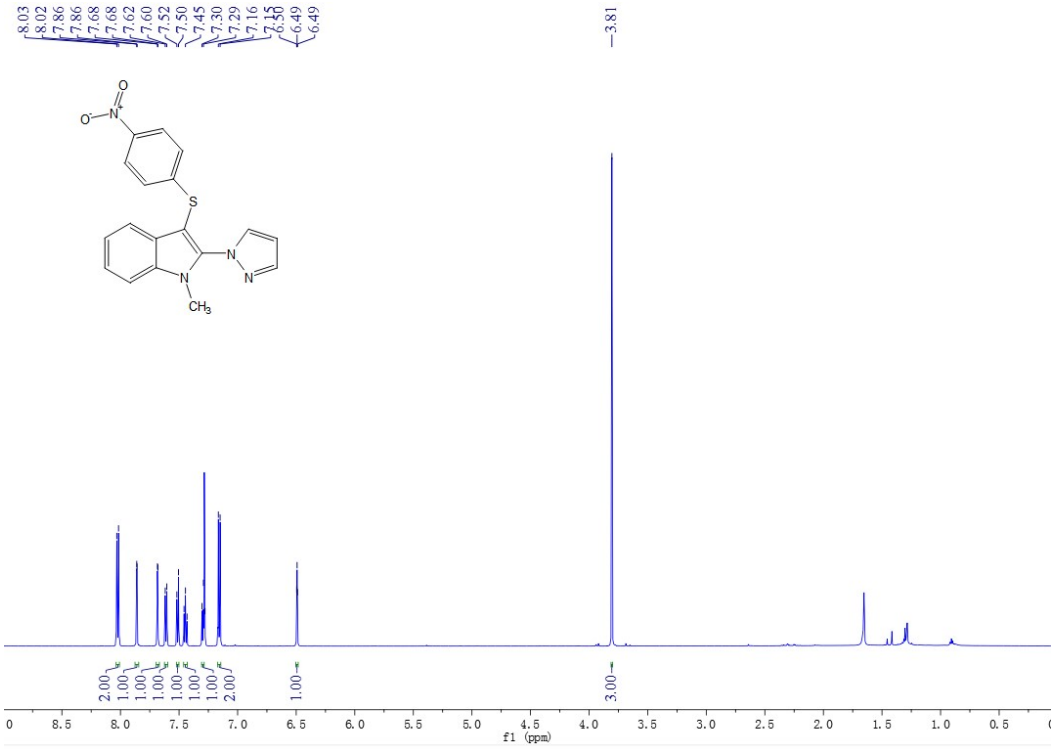
(128) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 63



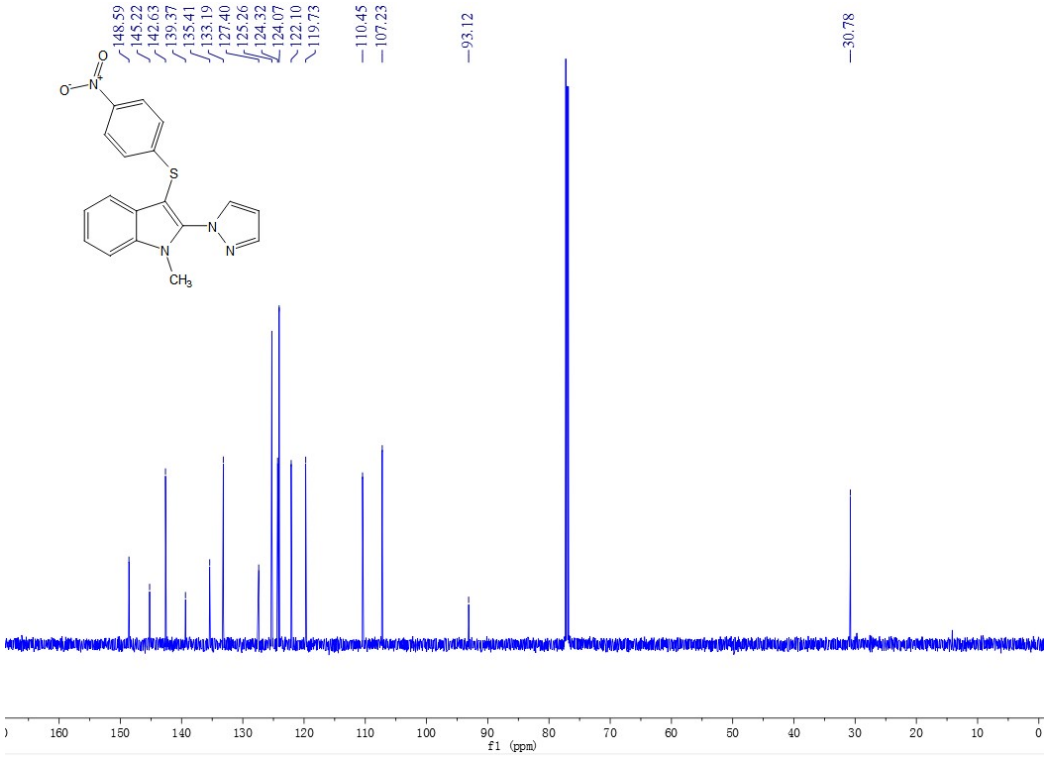
(129) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 63



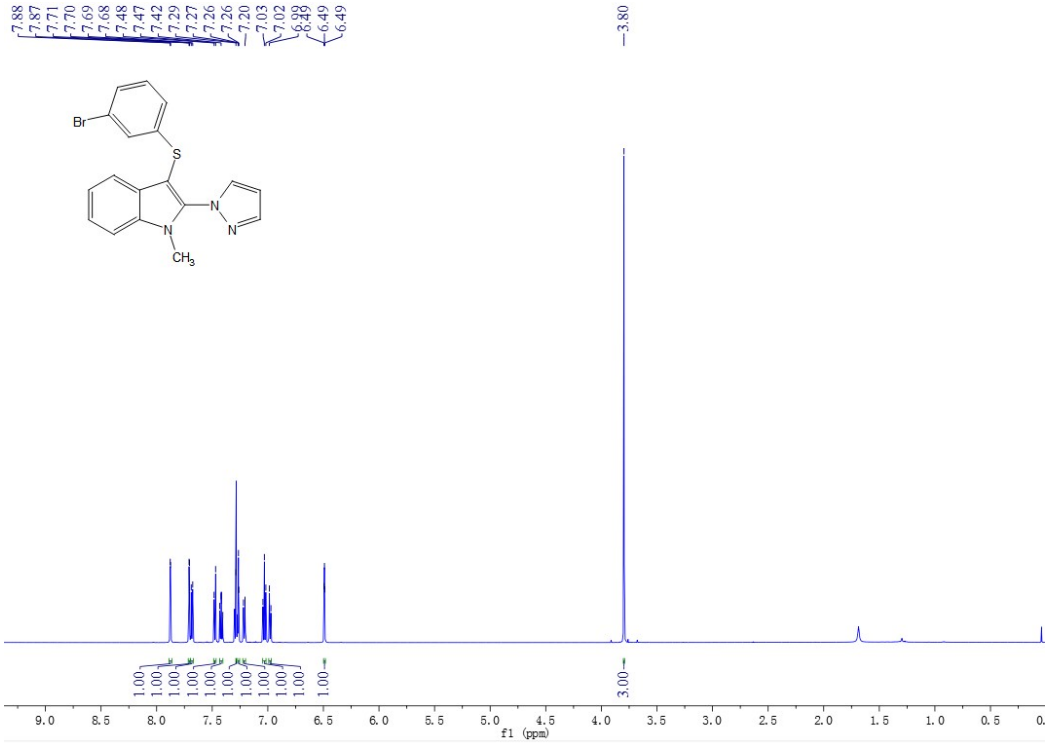
(130) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 64



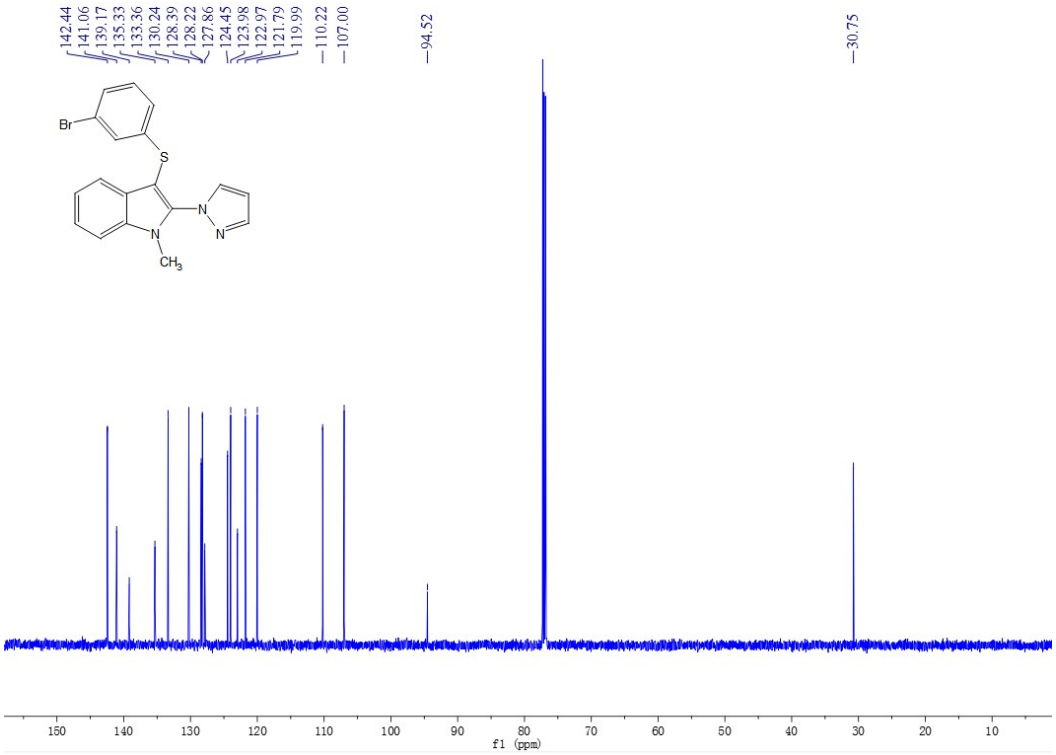
(131) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 64



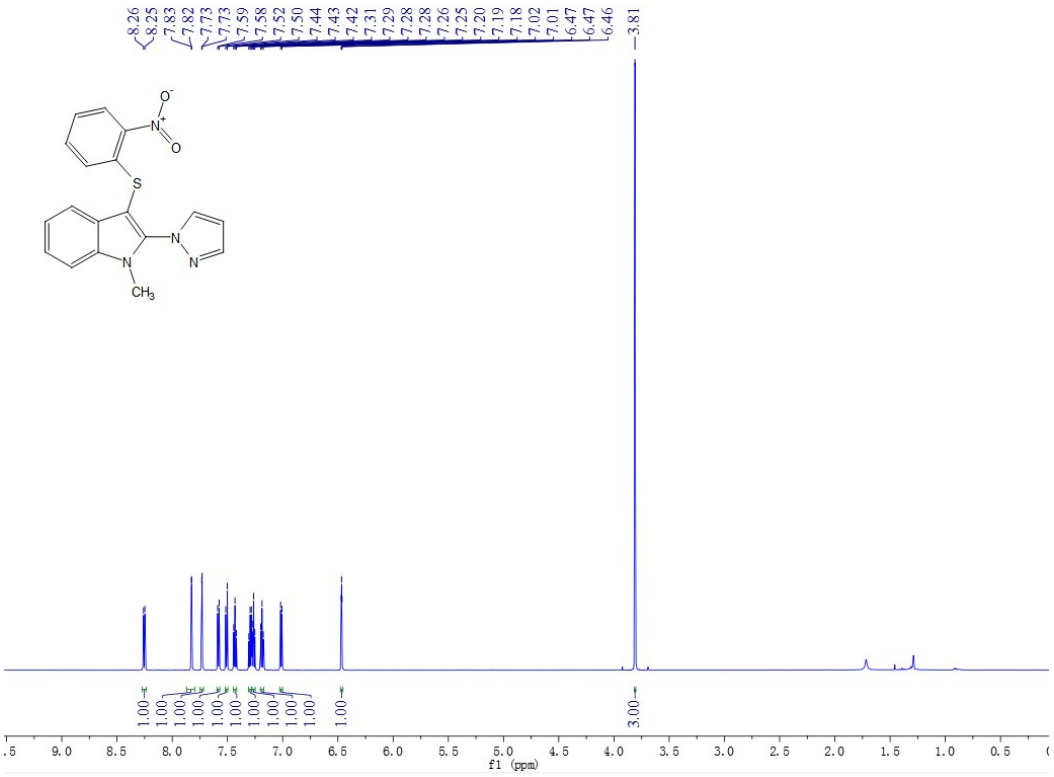
(132) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 65



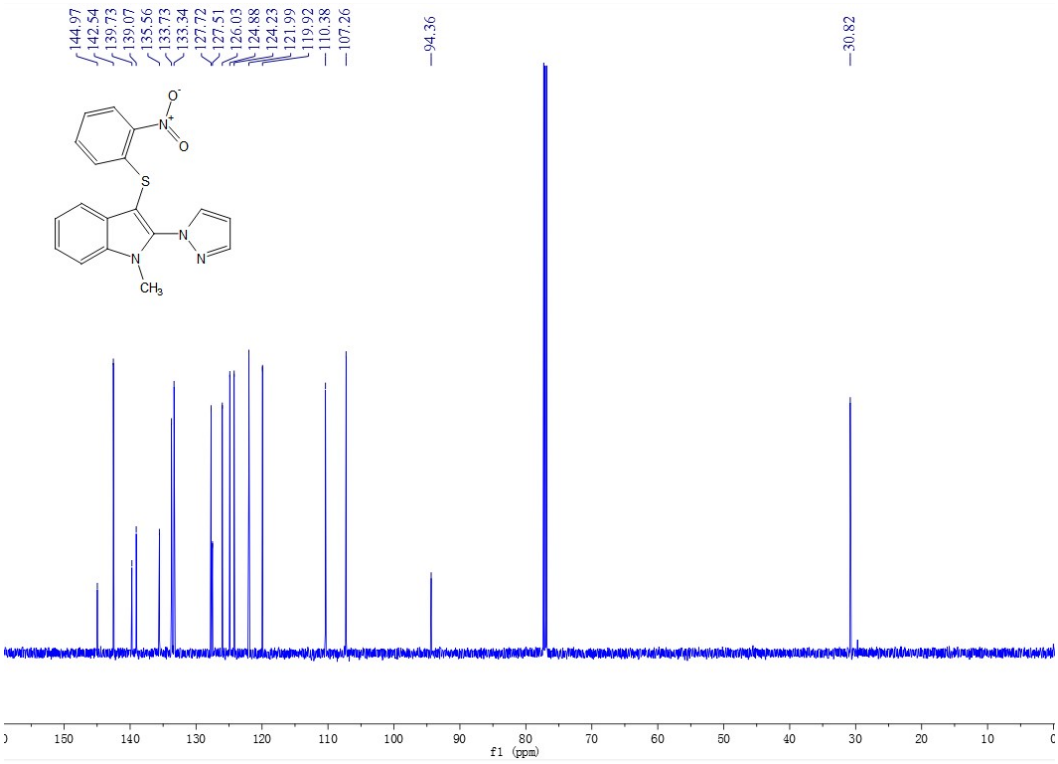
(133) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 65



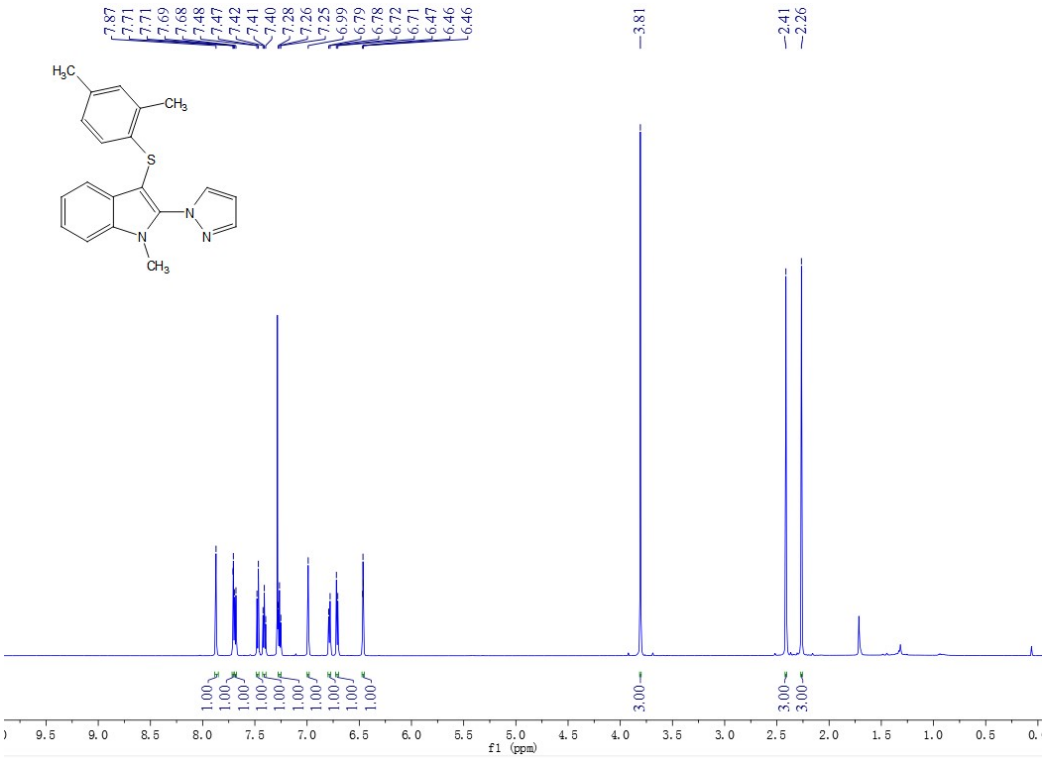
(134) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 66



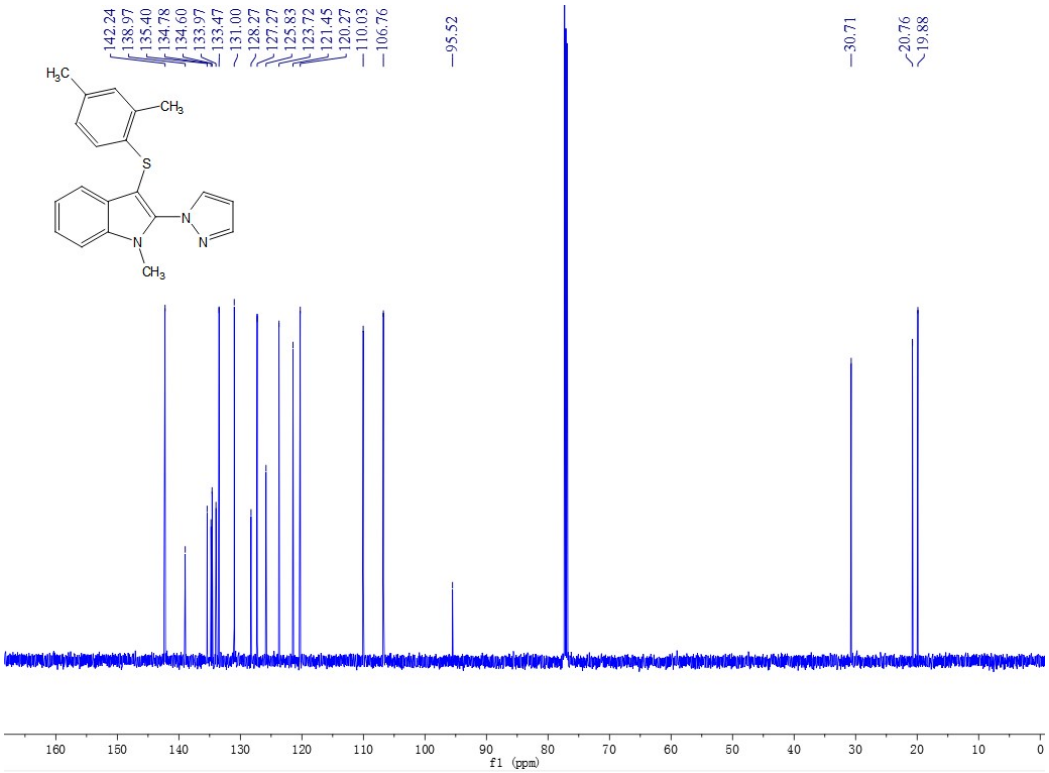
(135) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 66



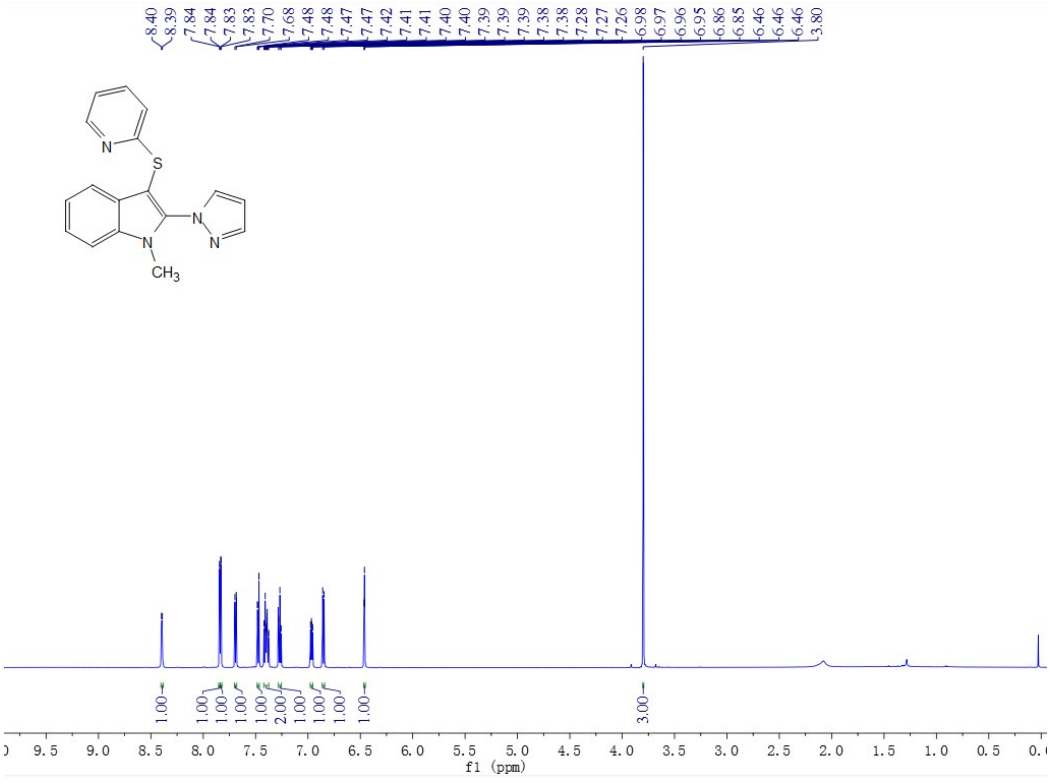
(136) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 67



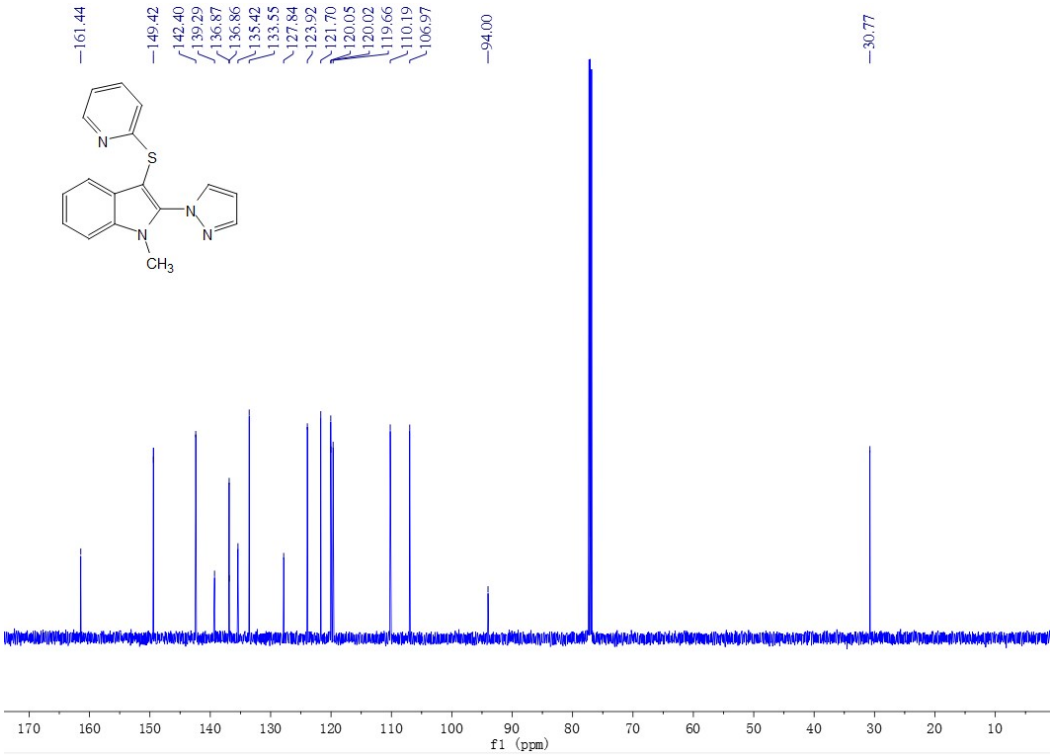
(137) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 67



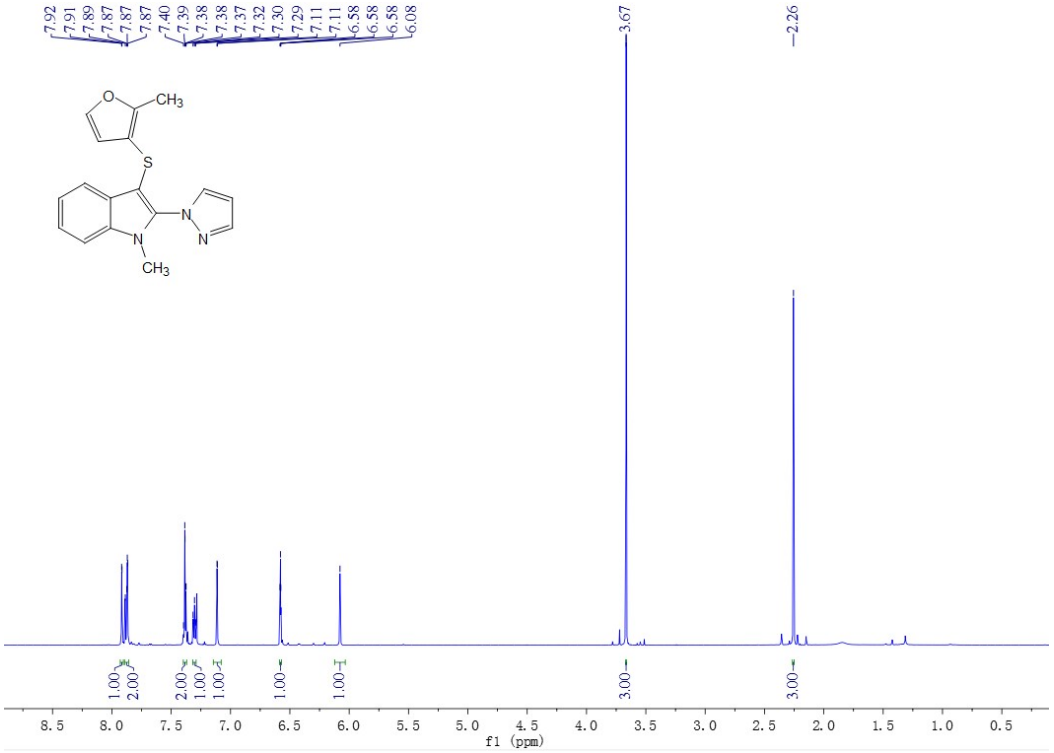
(138) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 68



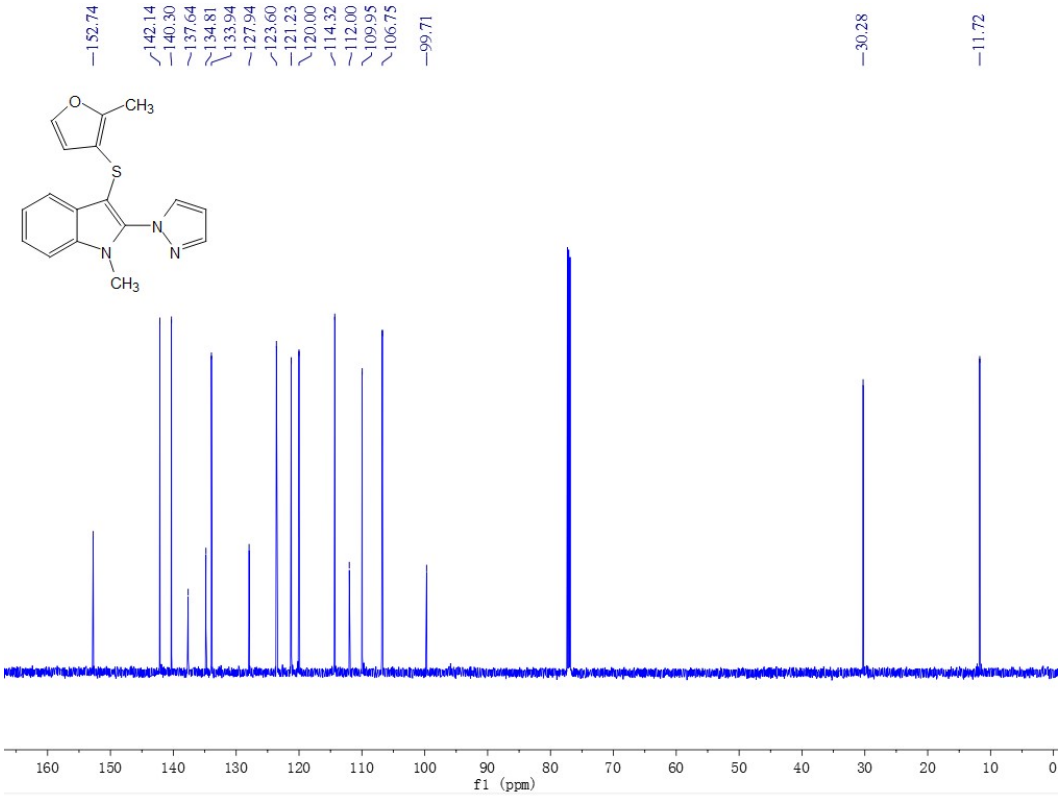
(139) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 68



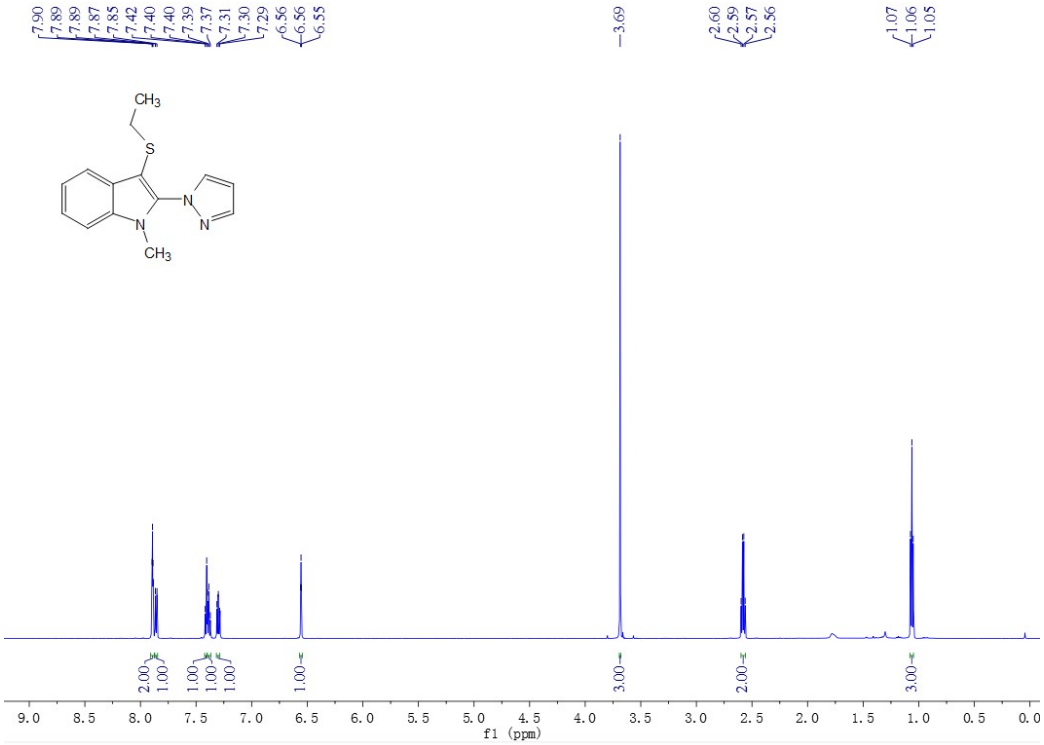
(140) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 69



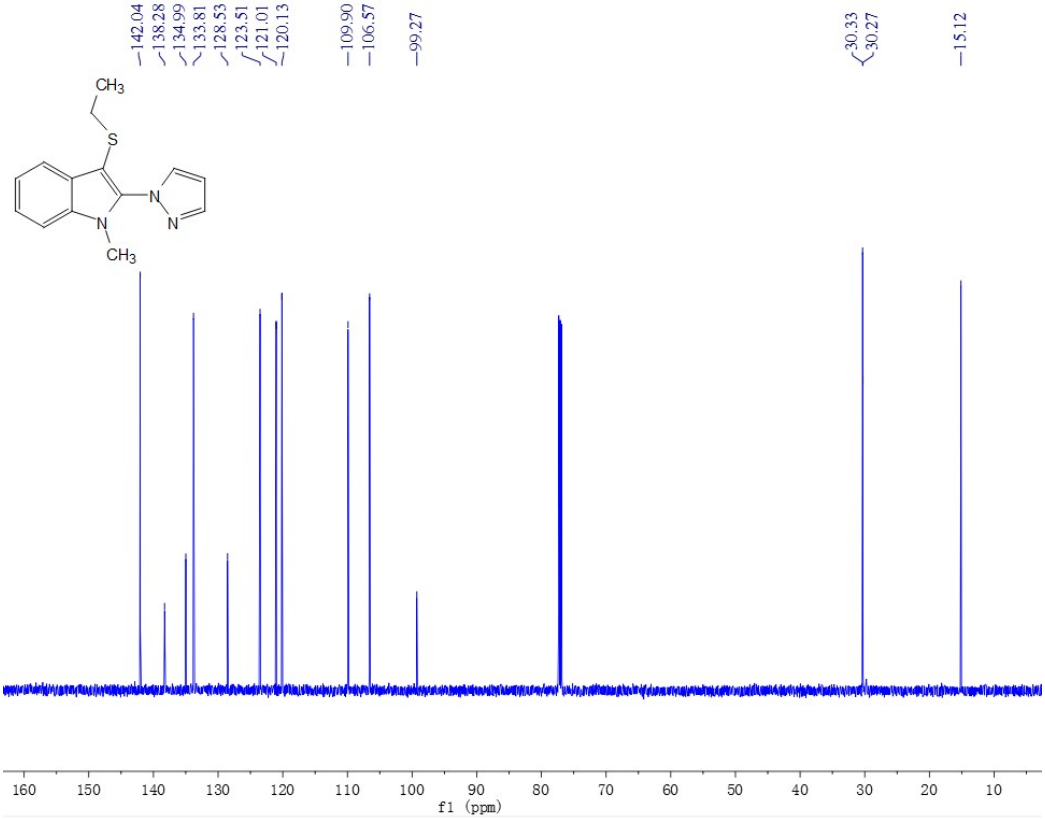
(141) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 69



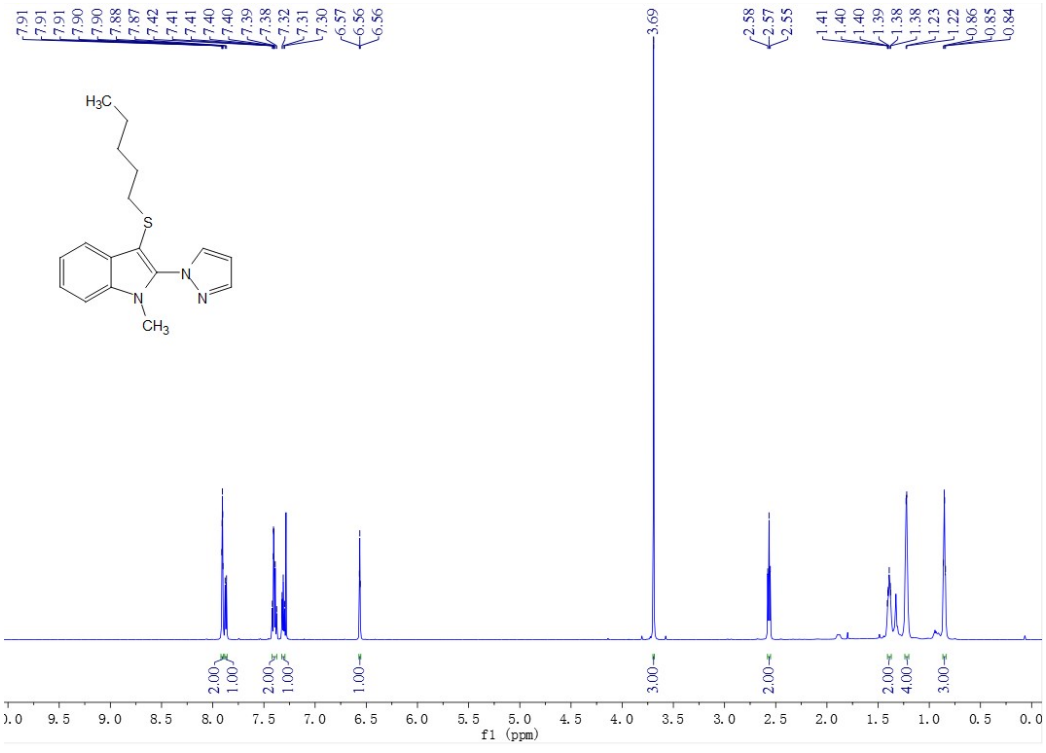
(142) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 70



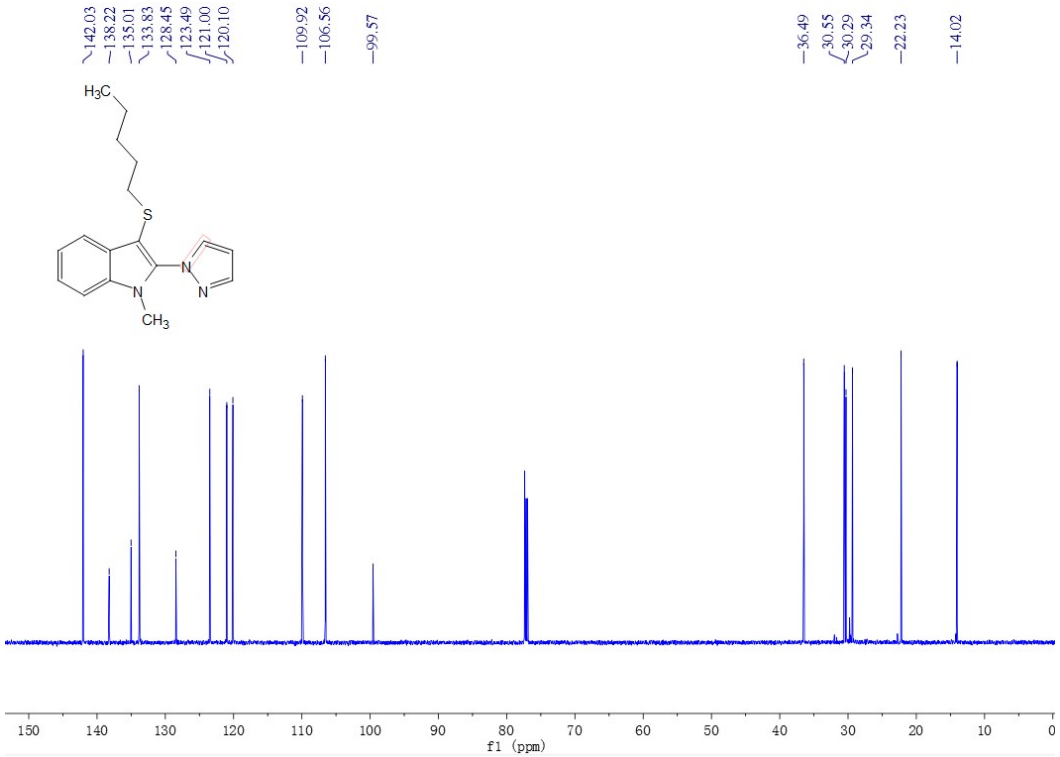
(143) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 70



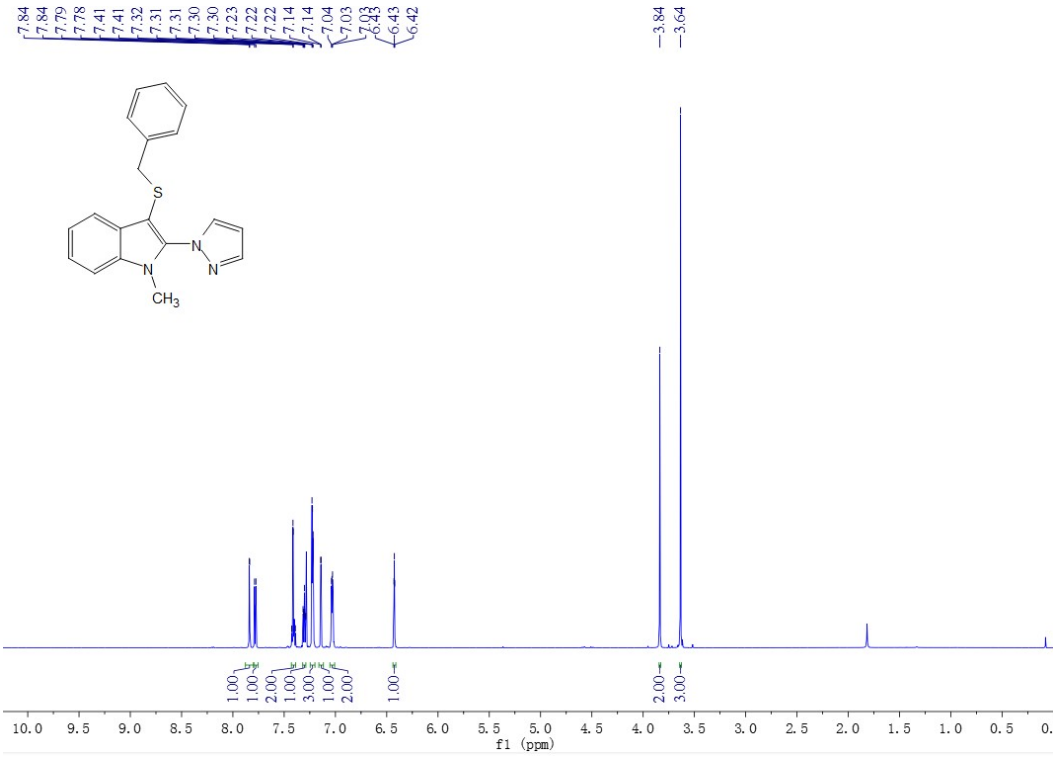
(144) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 71



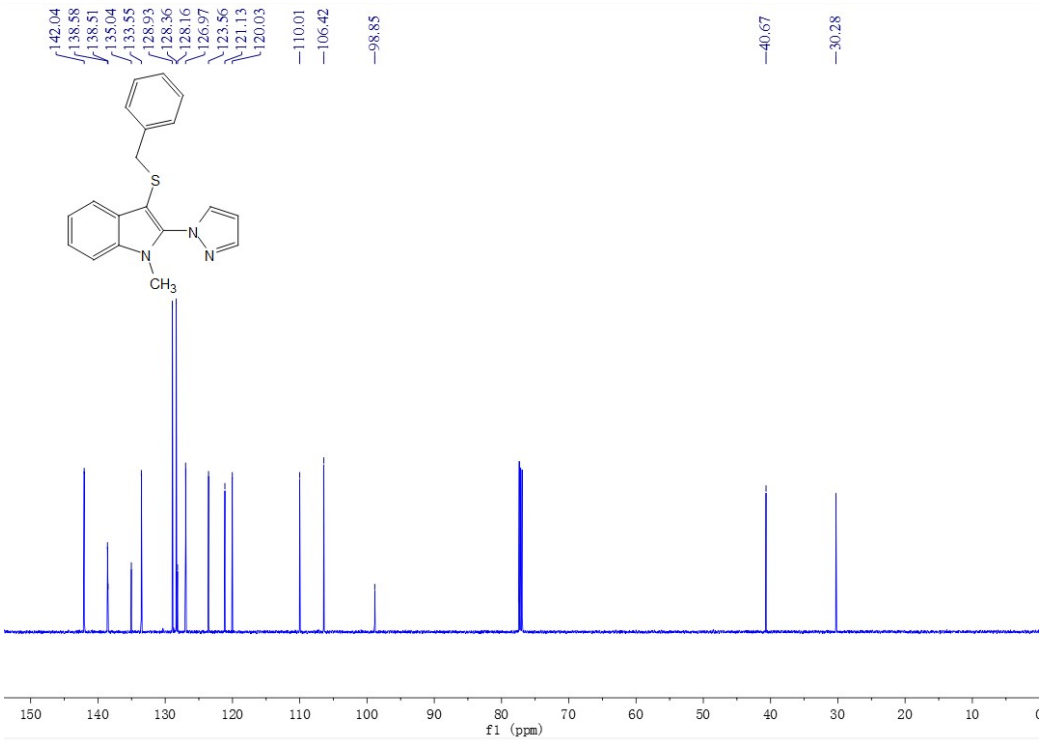
(145) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 71



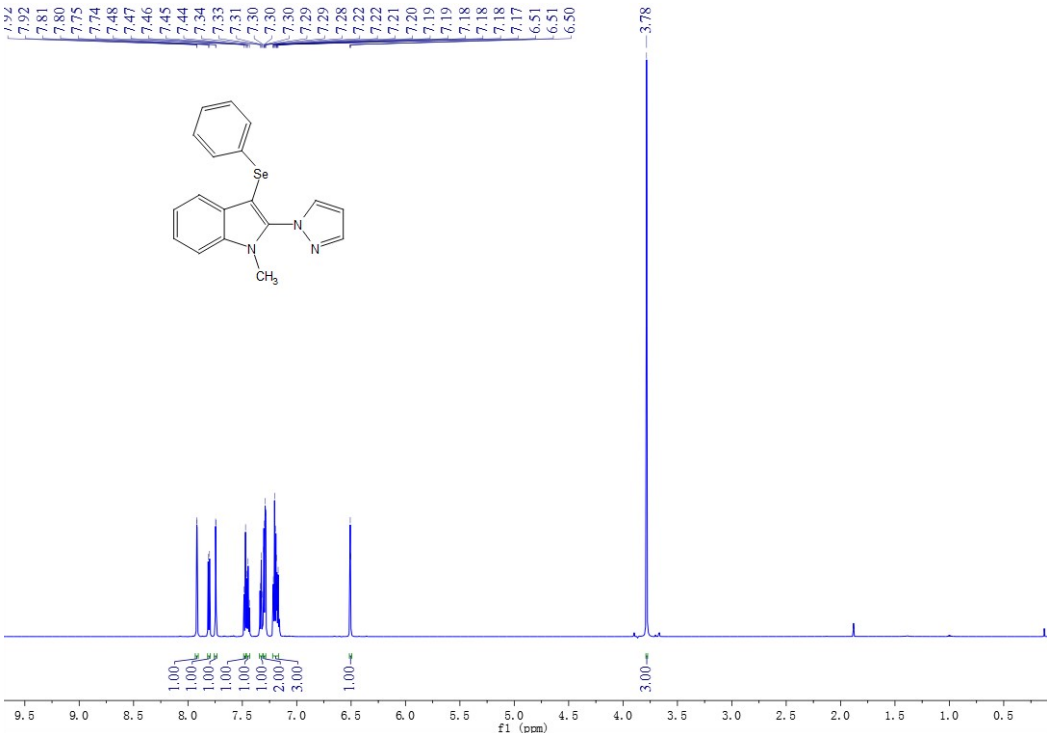
(146) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 72



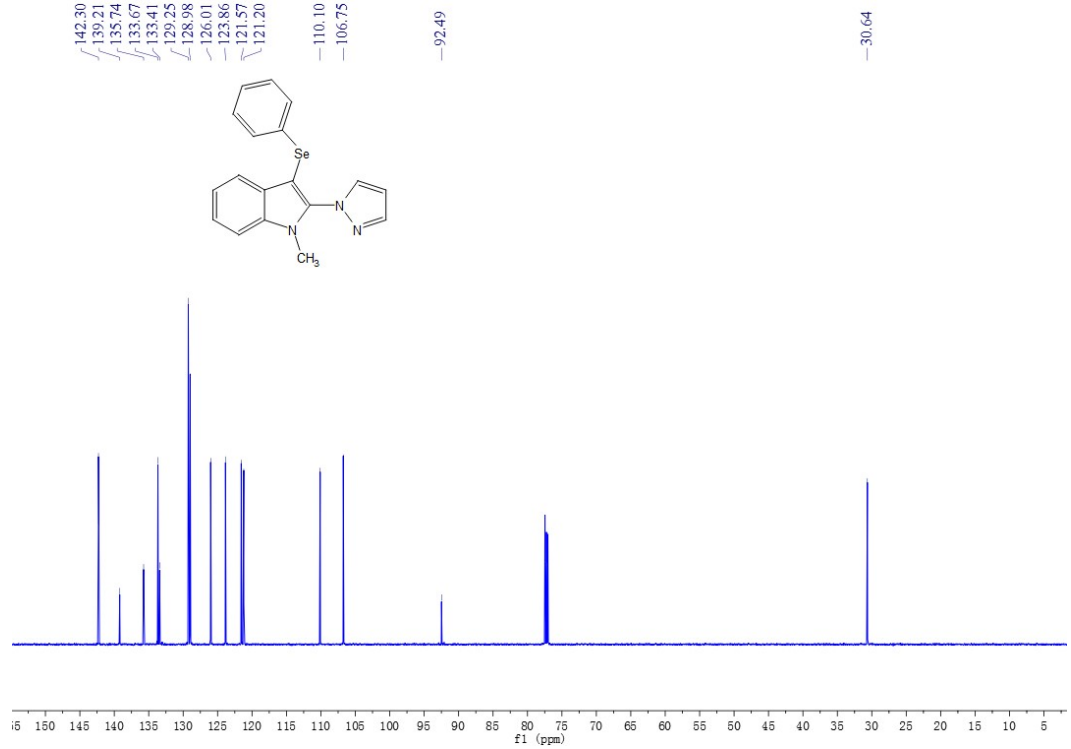
(147) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 72



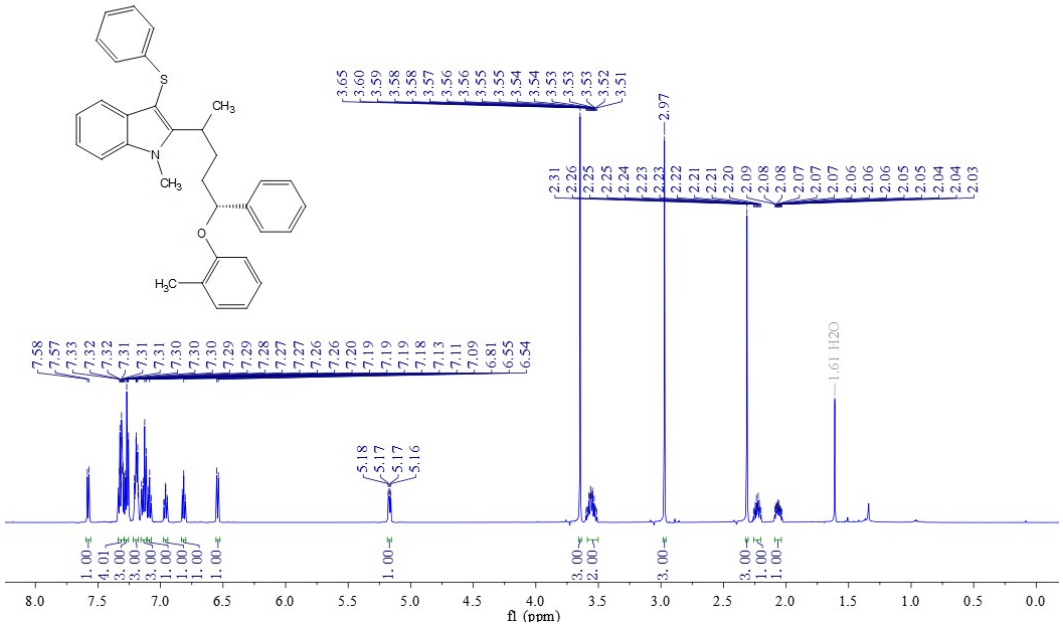
(148) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 73



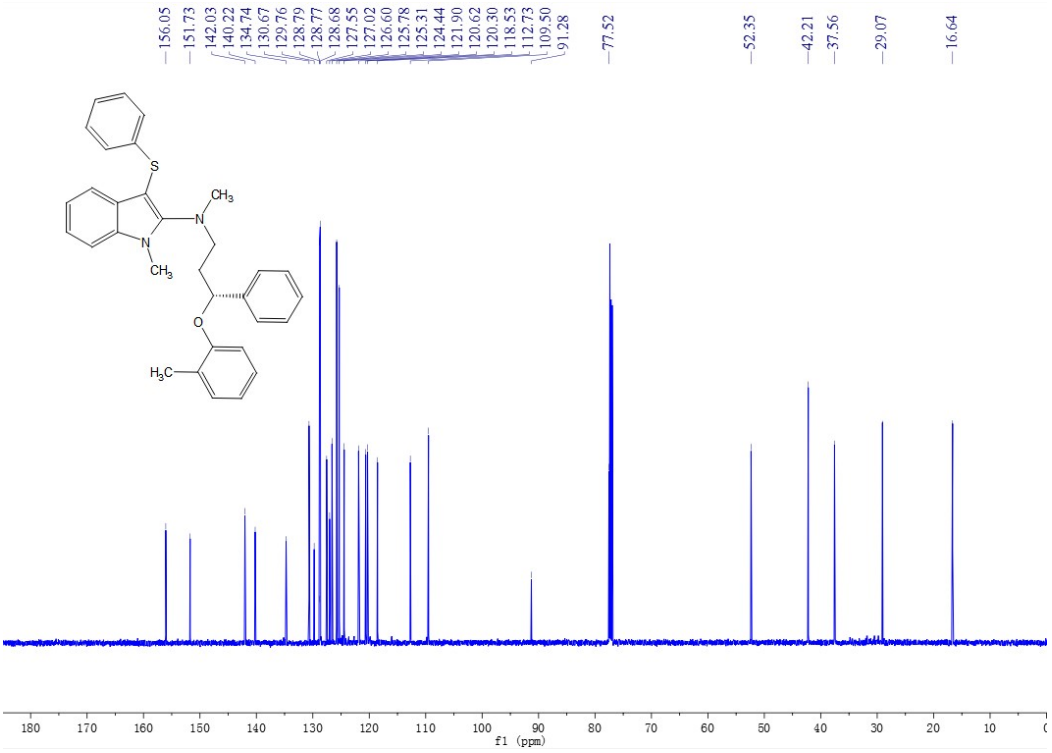
(149) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 73



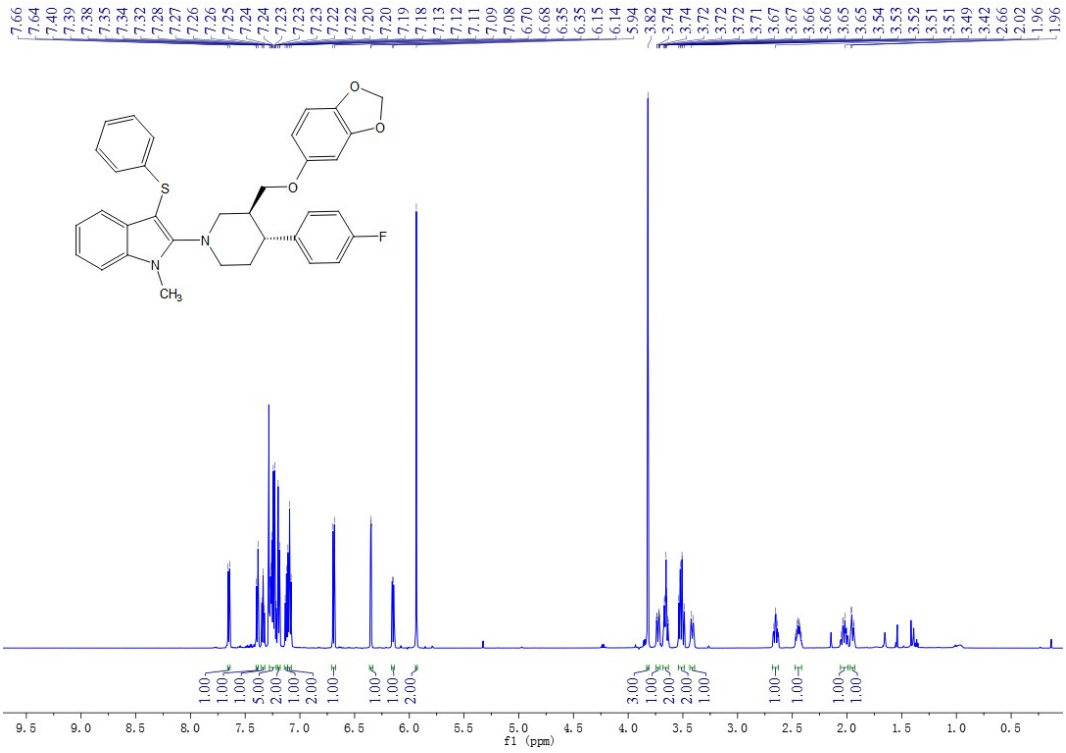
(150) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 74



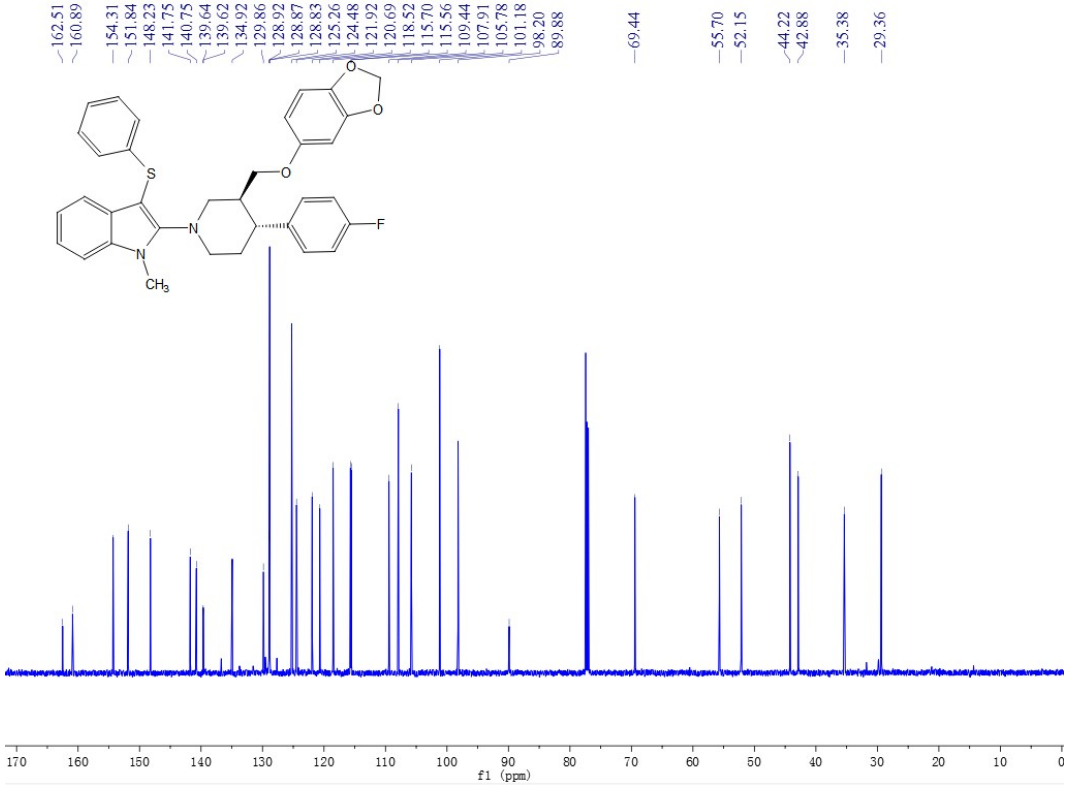
(151) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 74



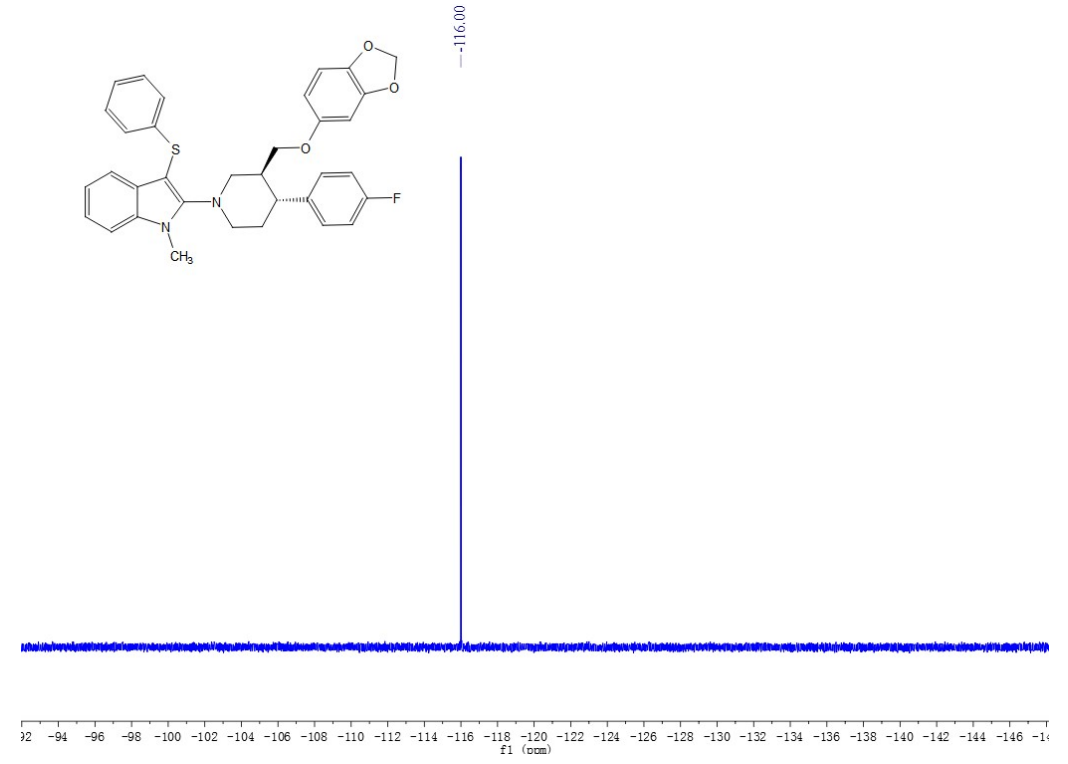
(152) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 75



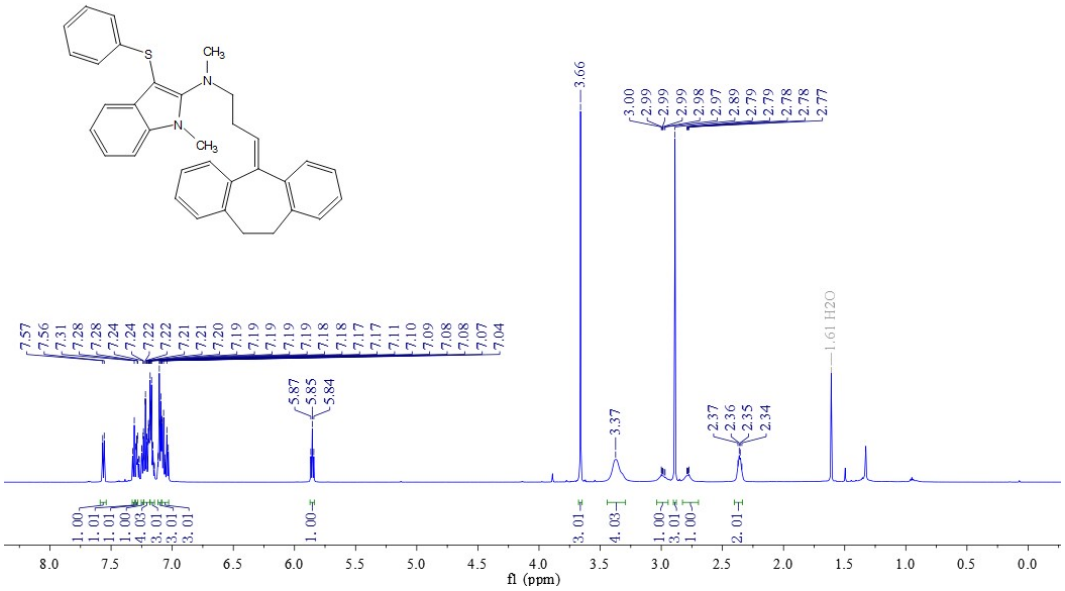
(153) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 75



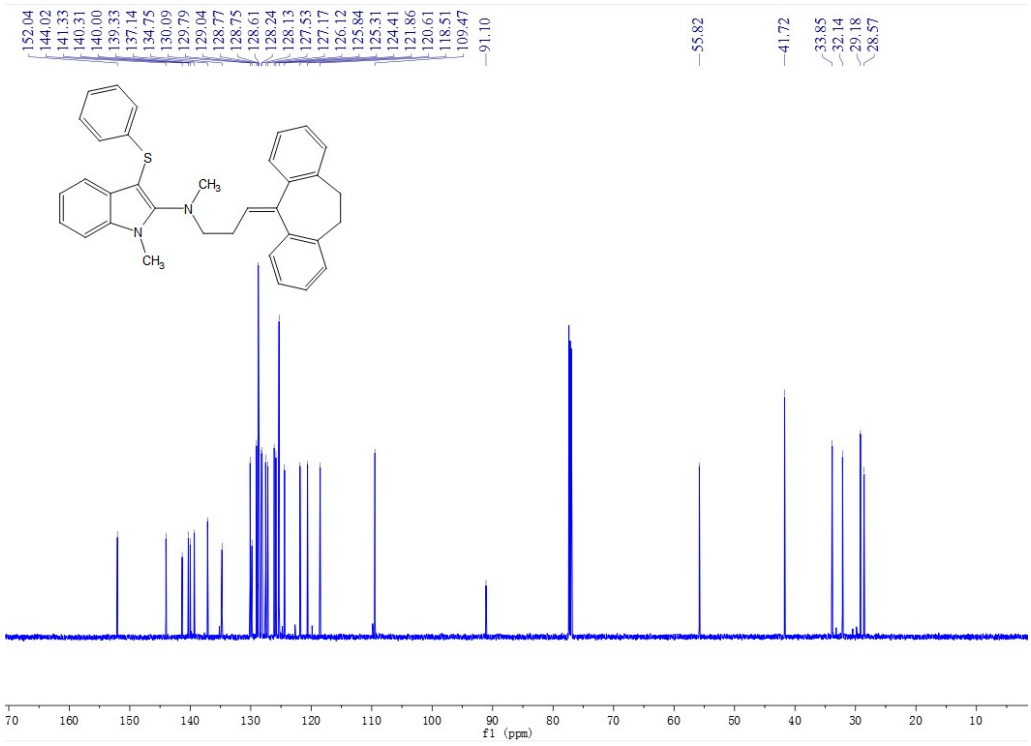
(154) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 75



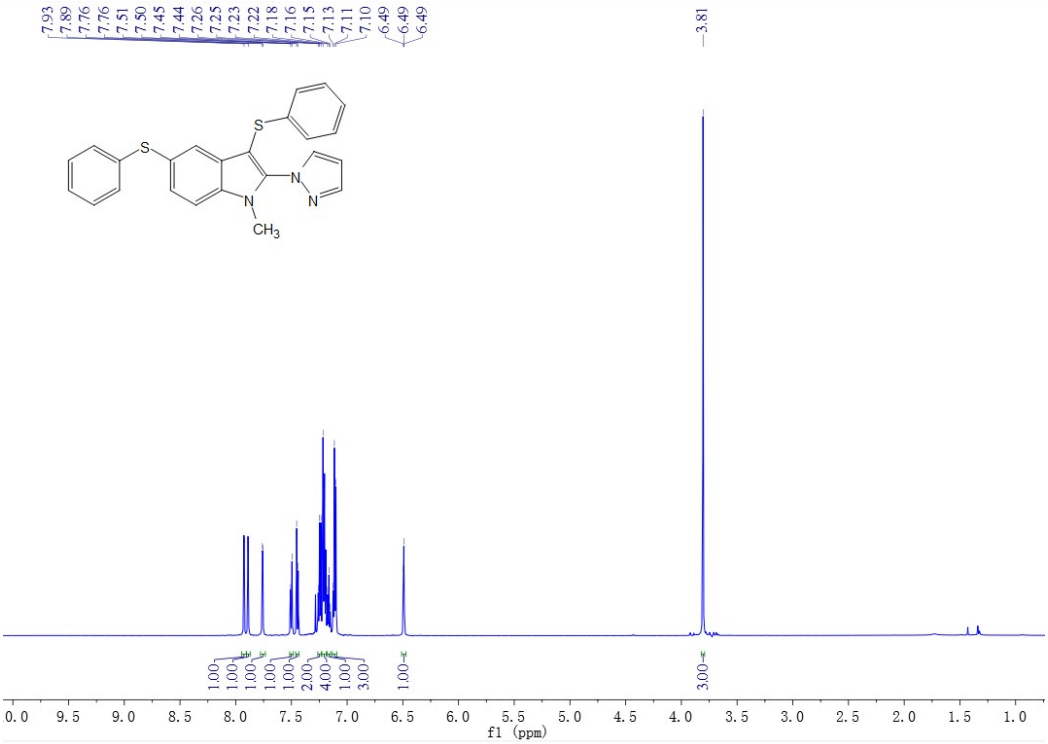
(155) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 76



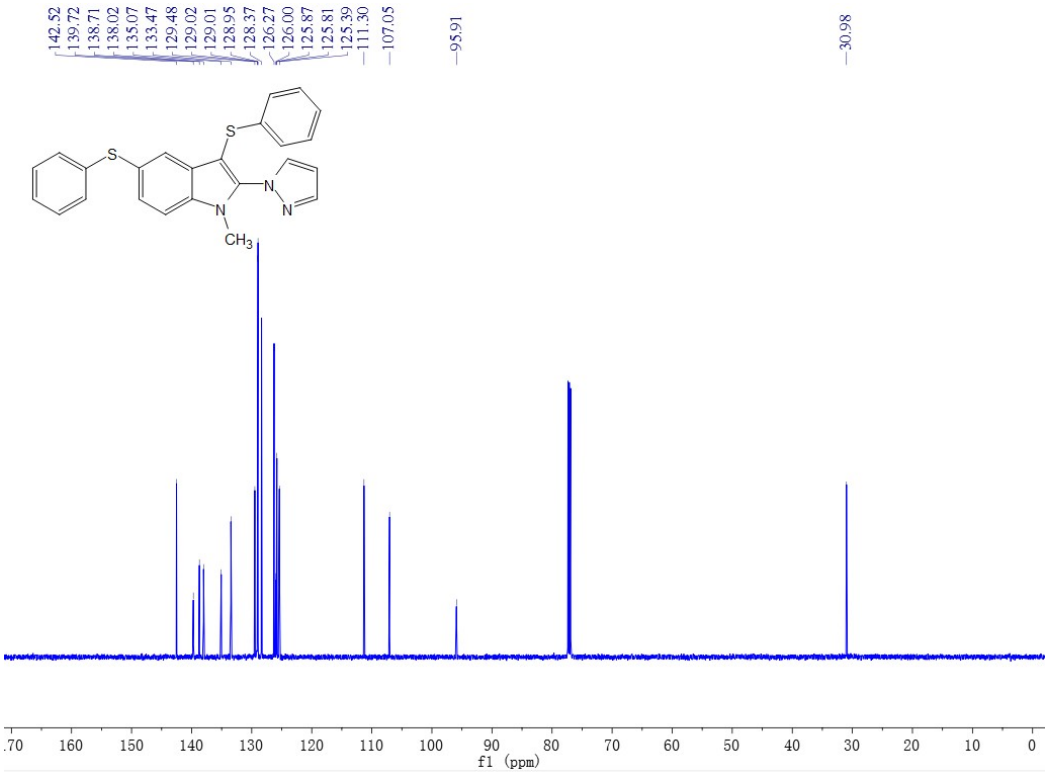
(156) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 76



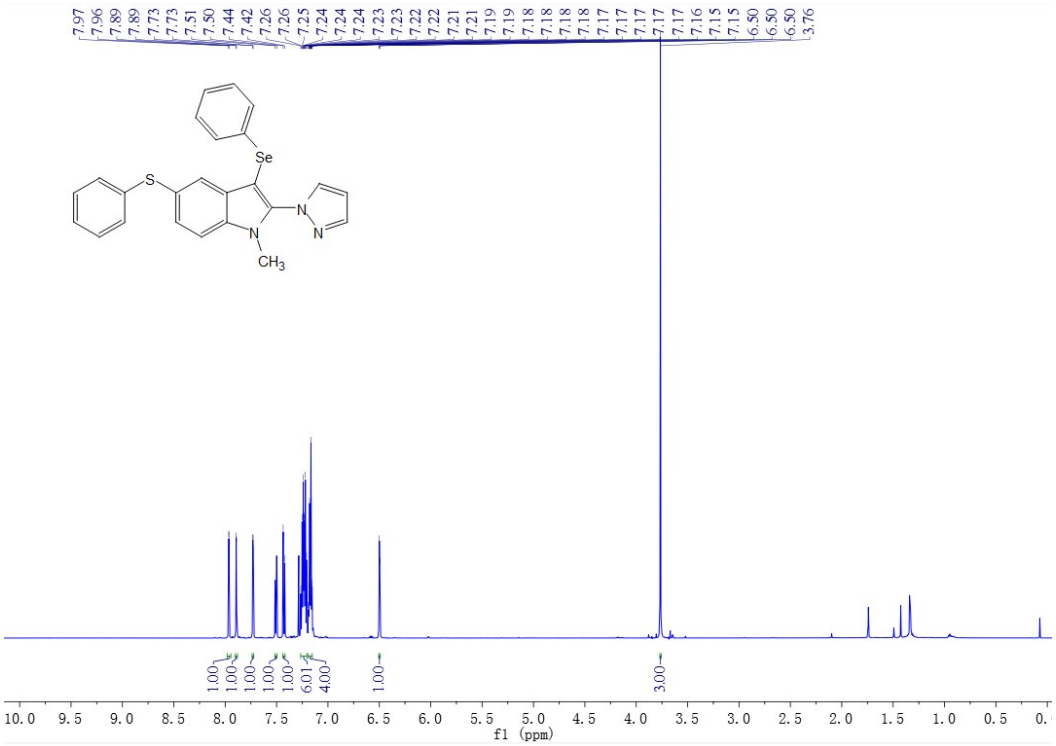
(157) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 77



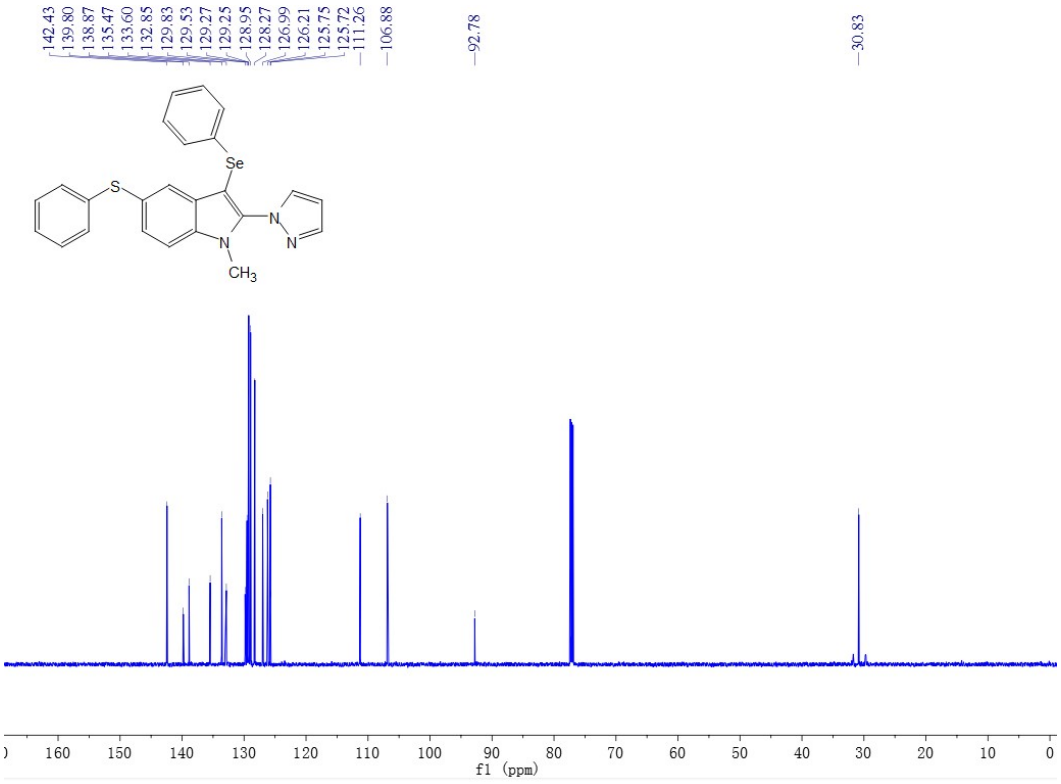
(158) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 77



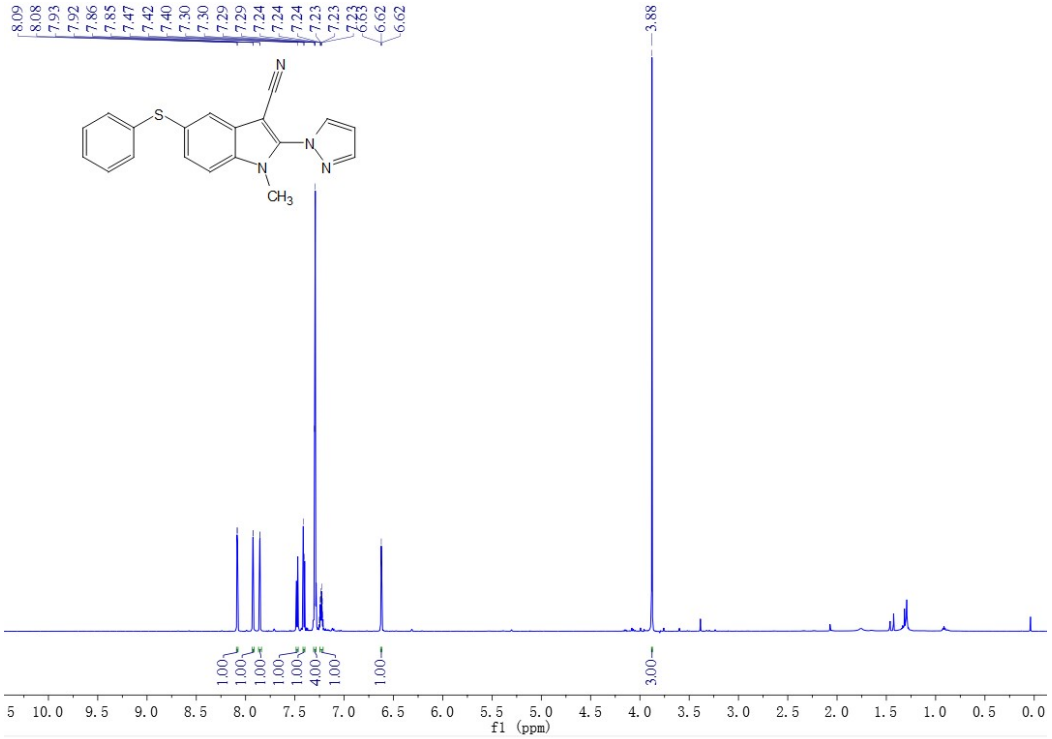
(159) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 78



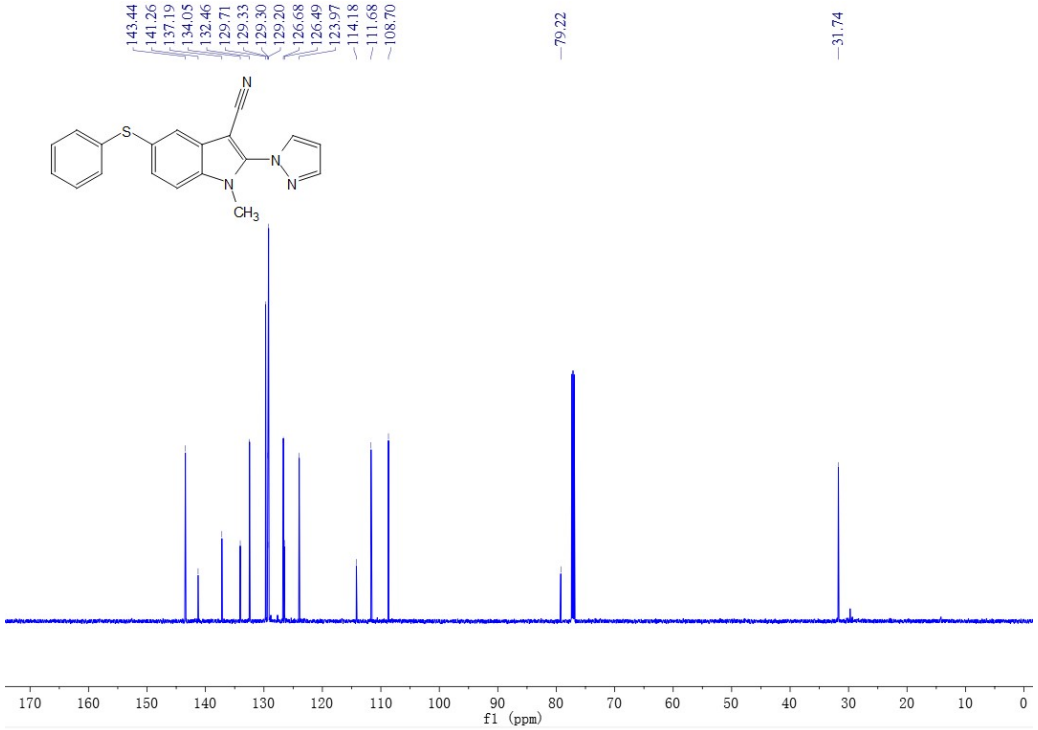
(160) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 78



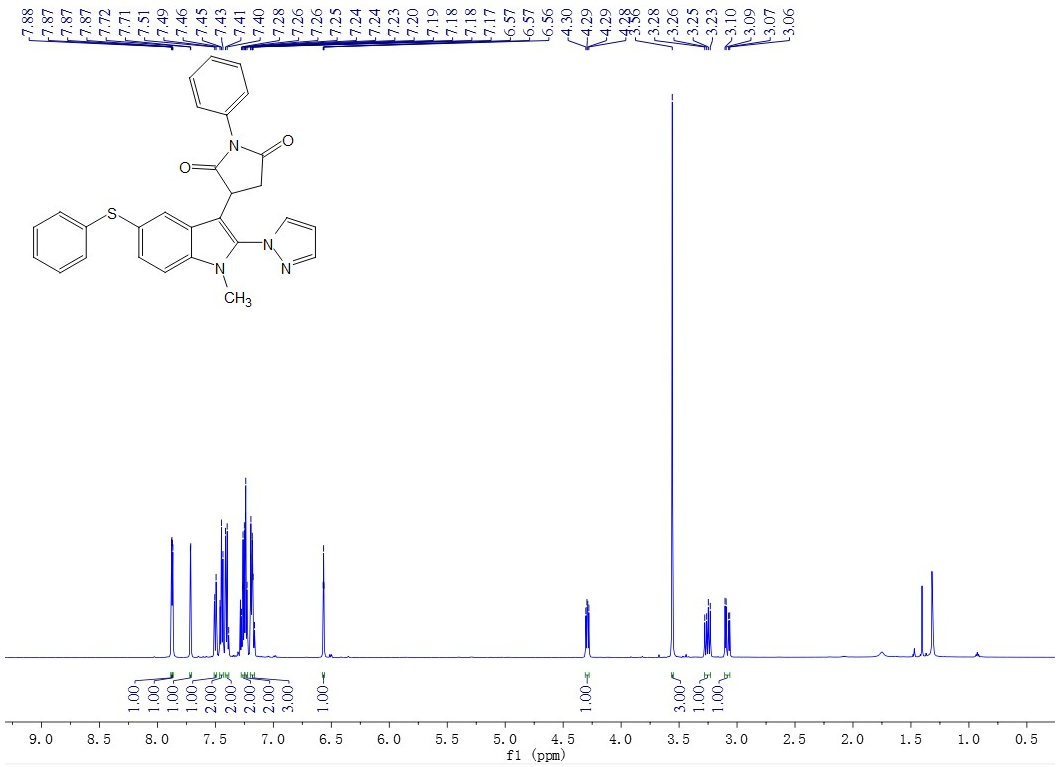
(161) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 79



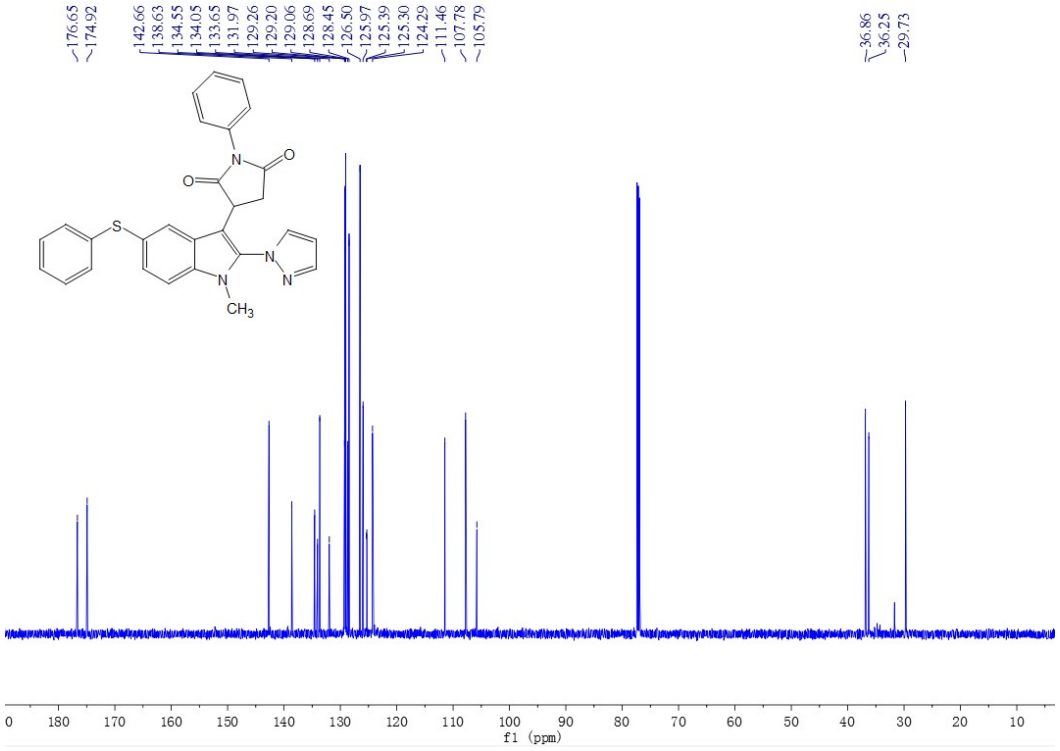
(162) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 79



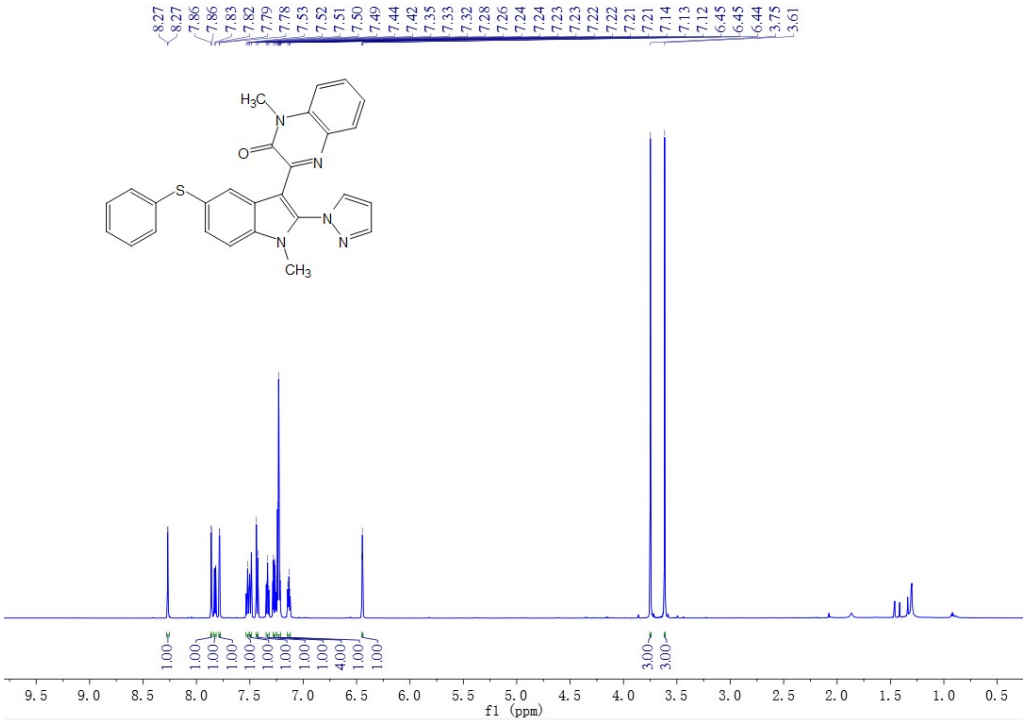
(163) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 80



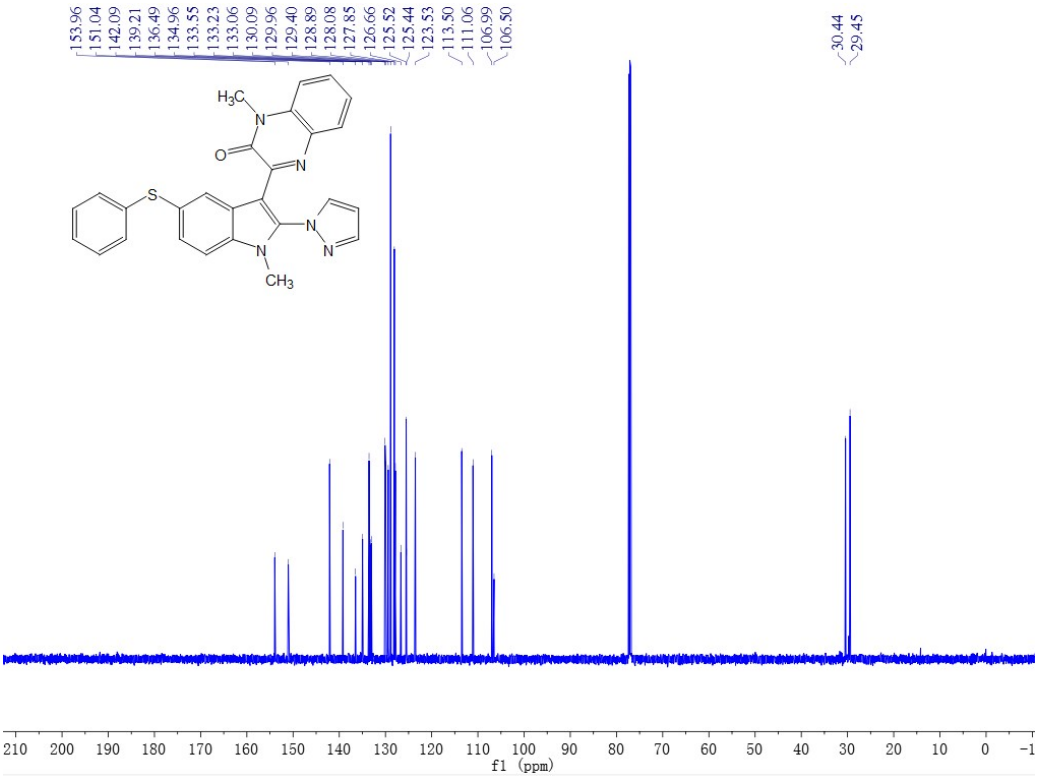
(164) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 80



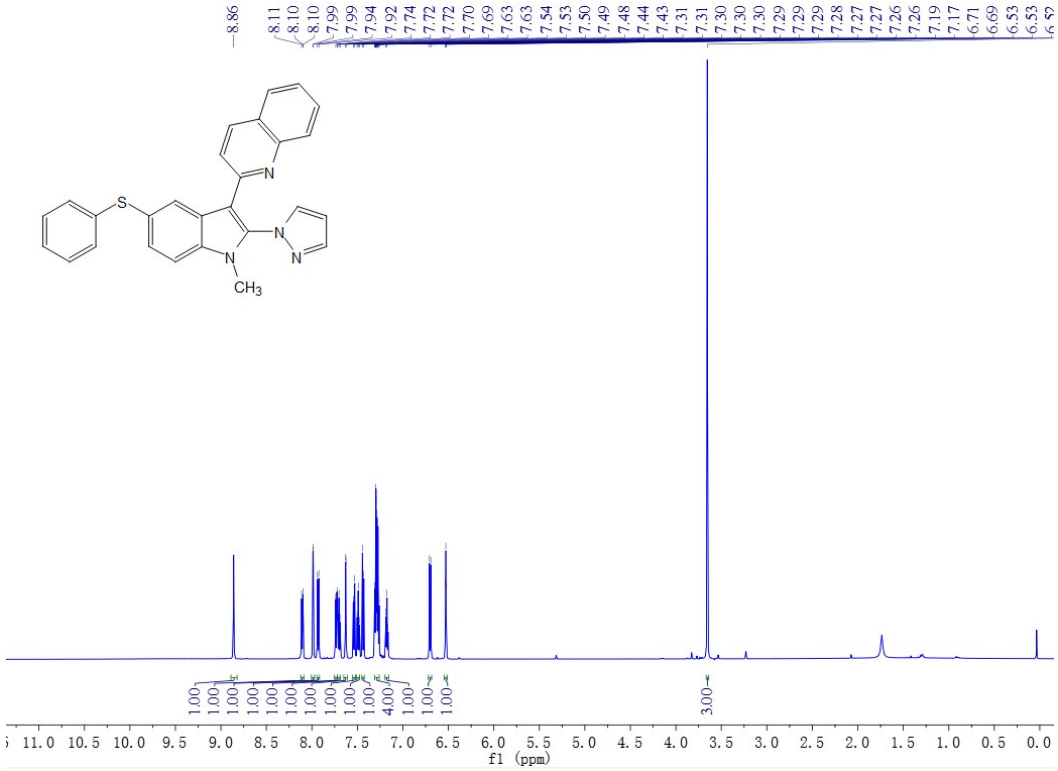
(165) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 81



(166) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 81



(167) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 82



(168) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 82