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Electronic Supporting Information

Solvent-Controlled Switchable Multicomponent Tandem Oxidative Triple Functionalization 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.

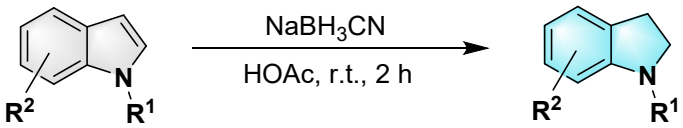
Instrument

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

EXPERIMENTAL DATA

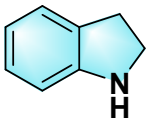
2. Substrates preparation.

(1) General procedure for the preparation of indoline derivatives (1a-1m)[1]:



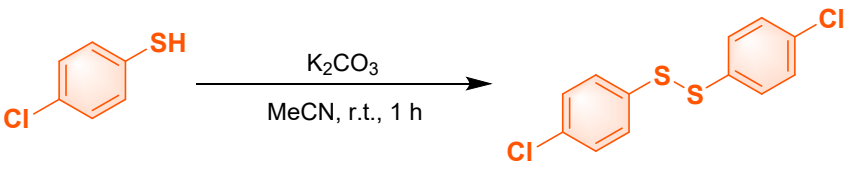
Procedure for indoline (1f): To a suspended solution of indole (1.33 g, 11.4 mmol) in HOAc (20.0 mL), $NaBH_3CN$ (1.89 g, 35.0 mmol) was added dropwise at 0 °C. The heterogeneous mixture was stirred for 2 h at room temperature. Quenched with saturated NH_4Cl (20.0 mL), and extracted with ether (4 × 75.0 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):



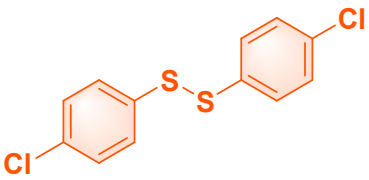
^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.60 (q, *J* = 8.4 Hz, 3H), 3.10 (t, *J* = 8.4 Hz, 2H), known compound.

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



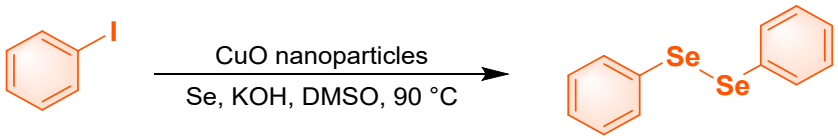
Procedure for 1,2-bis(4-chlorophenyl)disulfane (3e): To a round bottle (50 mL) were added 4-chlorobenzenethiol (5.0 mmol), anhydrous potassium carbonate (0.69 g, 5.0 mmol), and MeCN (10 mL) sequentially, and the reaction was conducted at room temperature under air atmosphere for 1 hour. And the desired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

NMR Spectroscopy (3e):



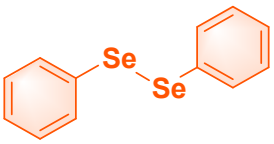
^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), known compound.

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



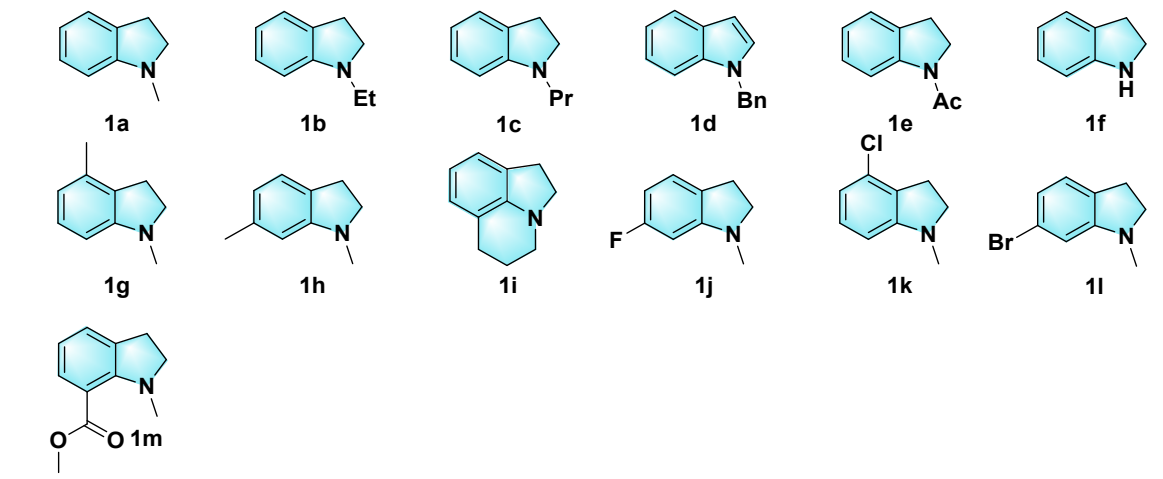
Procedure for 1,2-diphenyldiselane (3p): To a stirred solution of Se metal (2.0 mmol) and iodobenzene (1.0 mmol) in dry DMSO (2.0 mL) was added CuO nanoparticles (10.0 mol%) followed by KOH (2.0 equiv) under argon atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction 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 (petroleum ether) to give the pure diselenides.

NMR Spectroscopy (3p):

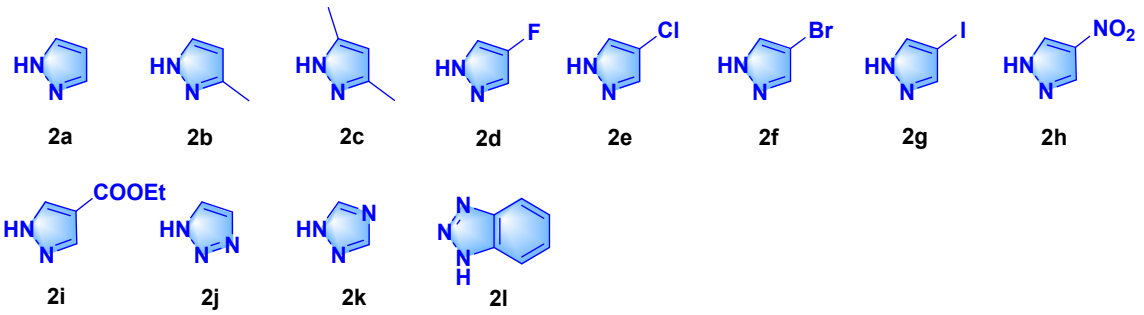


^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.81–7.52 (m, 4H), 7.36–7.24 (m, 6H), known compound.

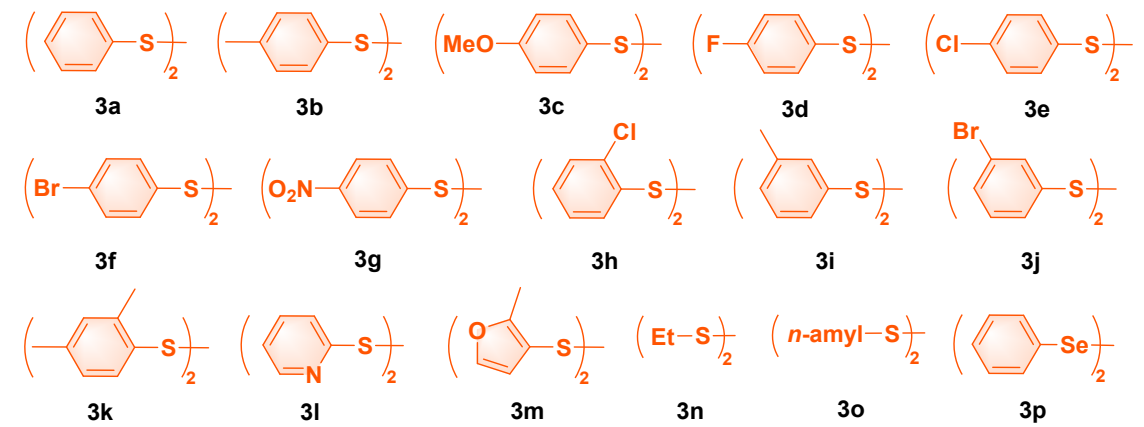
Scheme S1. Scope of indolines.



Scheme S2. Scope of azoles.

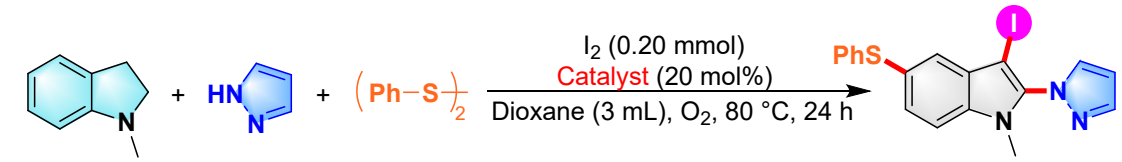


Scheme S3. Scope of disulfides.



3. Optimization of reaction conditions.

Table S1. Screening the catalyst of reaction.[a]

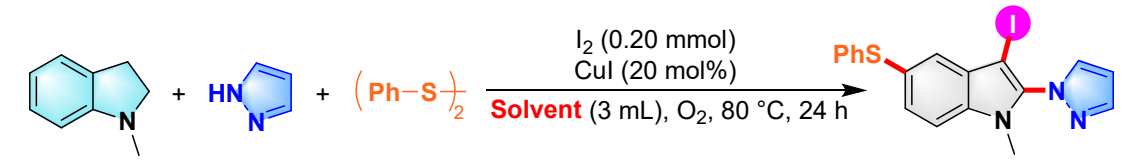


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	Catalyst	Yield (%)[b]
1	**CuI**	**47**
2	CuCl	trace
3	CuBr	30
4	$CuCl_2$	trace
5	$CuBr_2$	42
6	$Cu(OAc)_2$	trace
7	$Cu(OTf)_2$	19
8	$CuSO_4$	trace

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), **catalyst** (20 mol%, loading amount based on **3a**), I_2 (0.20 mmol) and 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 24 h. [b]Isolated yield.

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

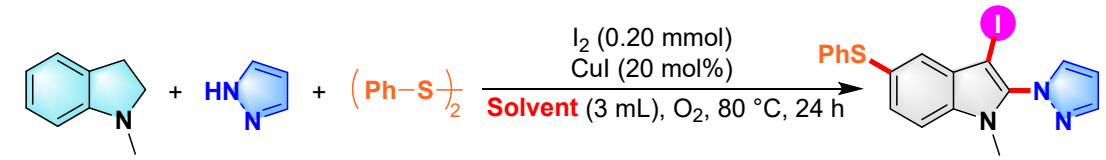


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	Solvent	Yield (%)[b]
1	CH_3CN	trace
2	DCE	26
3	DMF	trace
4	DMSO	16
5	**Toluene**	**45**

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%, loading amount based on **3a**), I_2 (0.20 mmol) and **solvent** (3.0 mL) were stirred at 80 °C under O_2 for 24 h. [b]Isolated yield.

Table S3. Screening the ratio of solvent mixture.[a]

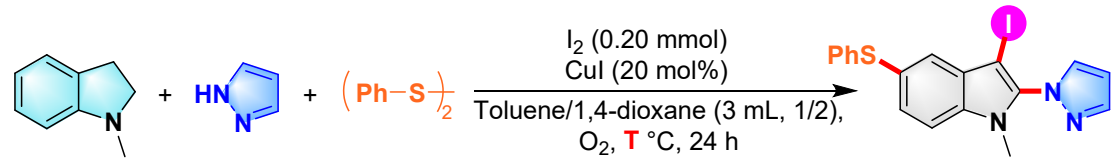


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	Solvent	Yield (%)[b]
1	Toluene/1,4-dioxane (1/1)	69
2	**Toluene/1,4-dioxane (1/2)**	**73**
3	Toluene/1,4-dioxane(2/1)	69

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%, loading amount based on **3a**), I_2 (0.20 mmol) and **solvent** (3.0 mL) were stirred at 80 °C under O_2 for 24 h. [b]Isolated yield.

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

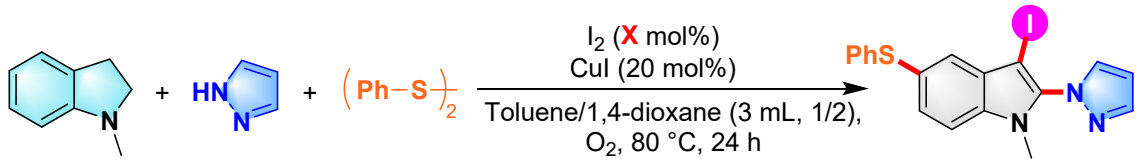


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	T [°C]	Yield (%)[b]
1	60	31
2	100	60

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%, loading amount based on **3a**), I_2 (0.20 mmol) and toluene/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at **T** °C under O_2 for 24 h. [b]Isolated yield.

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

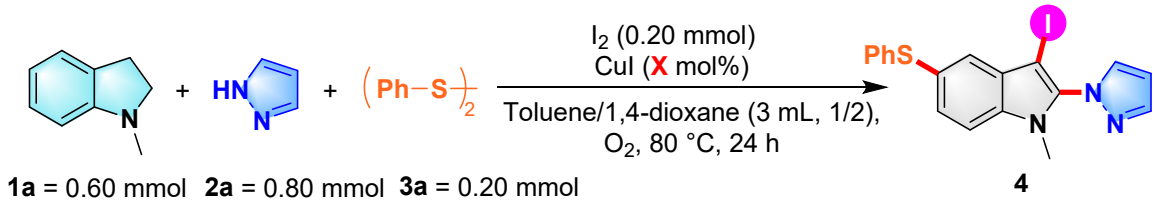


1a = 0.60 mmol **2a** = 0.80 mmol **3a** = 0.20 mmol **4**

Entry	X (mol %)	Yield (%)[b]
1	50	26
2	150	67

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%, loading amount based on **3a**), I_2 (**X** mol%, loading amount based on **3a**) and toluene/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at 80 °C under O_2 for 24 h. [b]Isolated yield.

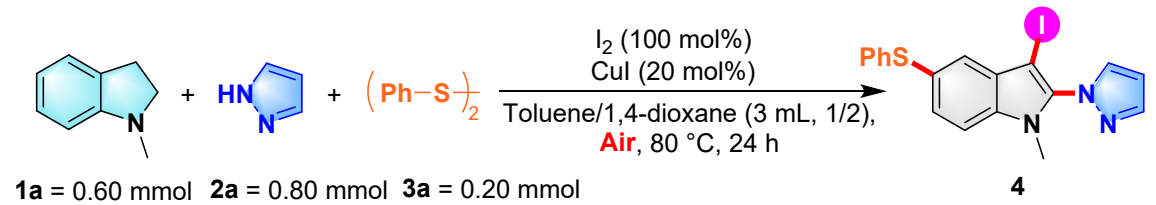
Table S6. Screening the amount of CuI.[a]



Entry	X (mol %)	Yield (%)[b]
1	80	44
2	120	70

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (X mol%, loading amount based on **3a**), I_2 (0.20 mmol) and toluene/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at 80 °C under O_2 for 24 h. [b]Isolated yield.

Table S7. Screening Air atmosphere.[a]

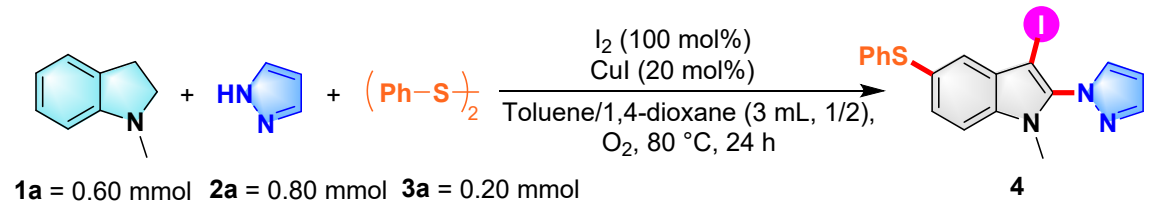


Entry	atmosphere	Yield (%)[b]
1	Air	47

[a]Reaction conditions unless specified otherwise: **1a** (0.60 mmol), **2a** (0.80 mmol), **3a** (0.20 mmol), CuI (20 mol%, loading amount based on **3a**), I_2 (0.20 mmol) and toluene/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at 80 °C under **Air** for 24 h. [b]Isolated yield.

4. Typical procedure for the synthesis of 4 and 43

(1) Typical procedure for the synthesis of 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 (50.6 mg, 0.2 mmol) and toluene/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at 80 °C under O_2 for 24 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 (125.6 mg, 73% yield).

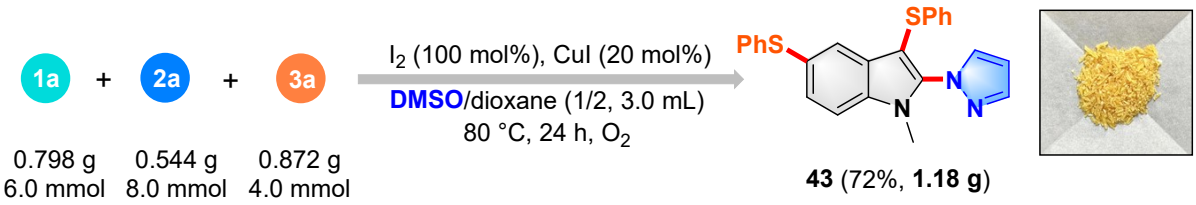
(2) Typical procedure for the gram-scale synthesis of 4:

To a suspended solution of 1-methylindoline **1a** (0.798 g, 6.0 mmol), **2a** (0.544 g, 8.0 mmol), **3a** (0.436 g, 2.0 mmol), CuI (20 mol%, 76 mg), I_2 (0.50 g, 2.0 mmol) and toluene/1,4-dioxane (30 mL, v/v = 1/2) were placed in a 50 mL round-bottom flask. The heterogeneous mixture was stirred for 24 h at 80 °C under O_2. Quenched with saturated NH_4Cl (40.0 mL), and extracted with ethyl acetate (4 × 75.0 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude reaction mixture was purified by column chromatography on silica gel afforded **4** (61%, 1.05 g) as white solid.

(3) Typical procedure for the synthesis of 43:

The mixture of 1-methylindoline **1a** (79.8 mg, 0.60 mmol), **2a** (54.5 mg, 0.80 mmol), **3a** (87.2 mg, 0.40 mmol), CuI (20 mol%,15.2 mg), I_2 (101.2 mg, 0.40 mmol) and DMSO/1,4-dioxane (3.0 mL, v/v = 1/2) were stirred at 80 °C under O_2 for 24 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 **43** as yellow solid (125.6 mg, 76% yield).

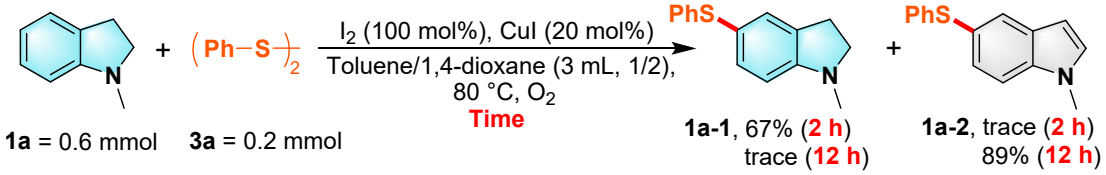
(4) Typical procedure for the gram-scale synthesis of 43:



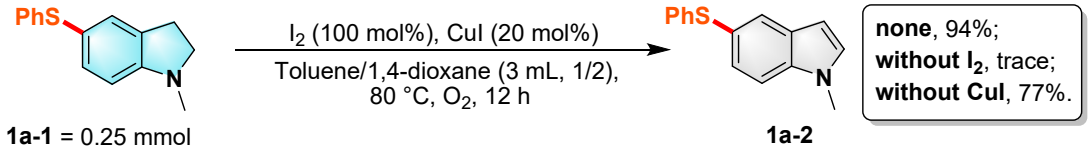
To a suspended solution of 1-methylindoline **1a** (0.798 g, 6.0 mmol), **2a** (0.544 g, 8.0 mmol), **3a** (0.872 g, 4.0 mmol), CuI (20 mol%, 152 mg), I_2 (1.01 g, 4.0 mmol) and DMSO/1,4-dioxane (30 mL, v/v = 1/2) were placed in a 50 mL round-bottom flask. The heterogeneous mixture was stirred for 24 h at 80 °C under O_2. Quenched with saturated NH_4Cl (40.0 mL), and extracted with ethyl acetate (4 × 75.0 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude reaction mixture was purified by column chromatography on silica gel afforded **43** (72%, 1.18 g) as yellow solid.

5. Control experiments.

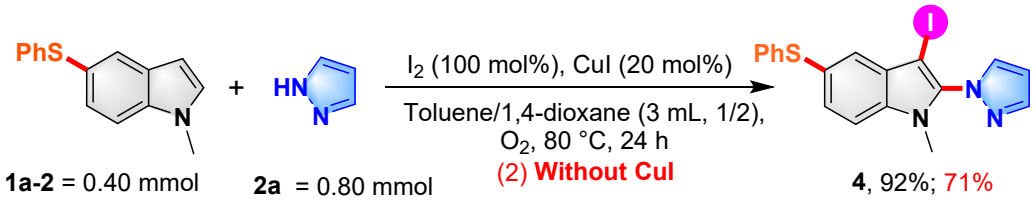
(1) Under the optimized reaction conditions, the reaction of **1a** (79.8 mg, 0.60 mmol) and **3a** (43.6 mg, 0.20 mmol) were carried. Then, the crude reaction mixture was analyzed by TLC in 2 and 12 hours respectively. The reaction mixture **(2 h)** was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10/1) to give product **1a-1** as yellow liquid (64.6 mg, 67% yield) and **1a-2** (trace). 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 (85.1 mg, 89% yield) and **1a-1** (trace).



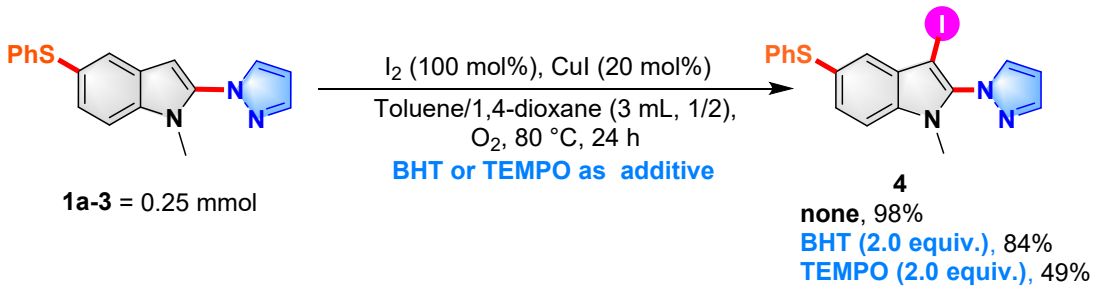
(2) Under the optimized reaction conditions, 1-methyl-5-(phenylthio)indoline **1a-1** (60.3 mg, 0.25 mmol) underwent the reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10/1), resulting in a yield of (94%, 56.2 mg) for product **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 77% (46.0 mg).



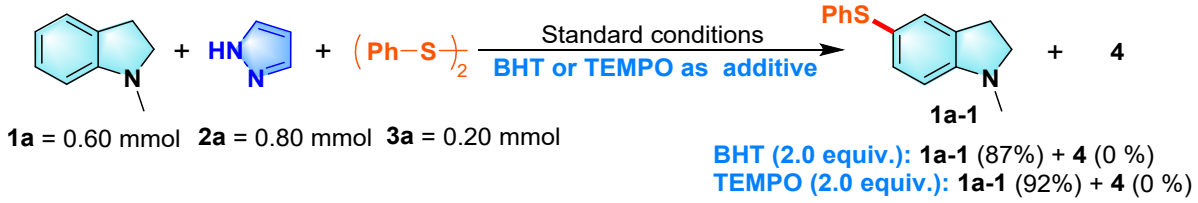
(3) Under the optimized reaction conditions, 1-methyl-5-(phenylthio)-1*H*-indole **1a-2** (95.6 mg, 0.40 mmol) and pyrazol **2a** (54.4 mg, 0.8 mmol) were reacted for 24 hours, then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10/1), resulting in a yield of 92% for product **4** (158.2 mg). It is worth noting that in the absence of CuI, the yield of product **4** can also reach 71% (122.1 mg).



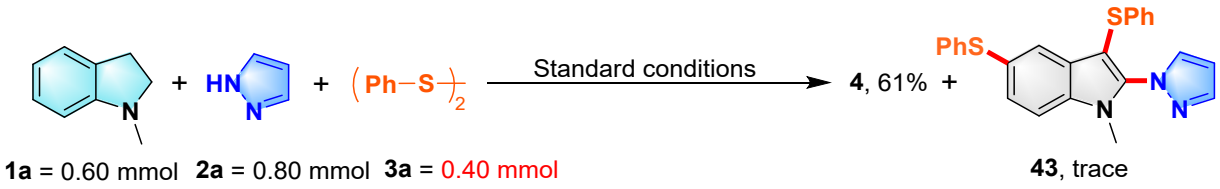
(4) Under the optimized reaction conditions, 1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole **1a-3** (76.3 mg, 0.25 mmol) were reacted for 24 hours, then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10/1), resulting in a yield of 98% for product **4** (105.4 mg). It is worth noting that Butylated hydroxytoluene (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were introducing to this reaction, the products **4** were obtained in yields of 84% (90.3 mg) and 49% (52.7 mg) respectively.



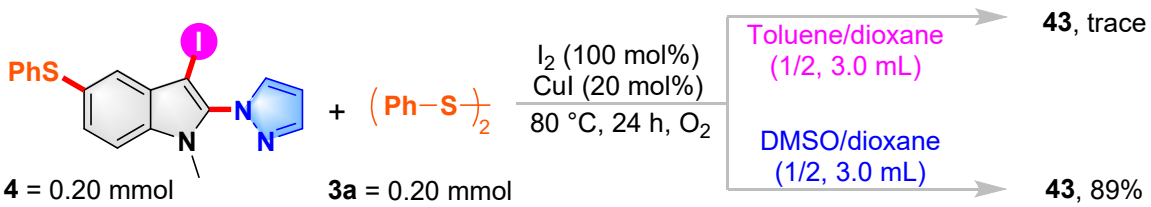
(5) Under the standard conditions, the radical trapping reagents, Butylated hydroxytoluene (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/acetic ether (10:1) to give product **1a-1** in yields of 87% (83.9 mg) and 92% (88.7 mg), respectively. However, product **4** was not obtained.



(6) The mixture of 1-methylindoline **1a** (79.8 mg, 0.60 mmol), **2a** (54.5 mg, 0.80 mmol), **3a** (87.2 mg, 0.40 mmol), CuI (20 mol%,15.2 mg), I_2 (101.2 mg, 0.40 mmol) and toluene/1,4-dioxane (3.0 mL, 1/2) were stirred at 80 °C under O_2 for 24 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 **4** was obtained with a yield of 61% (104.9 mg), and a trace amount of **43** was also observed.



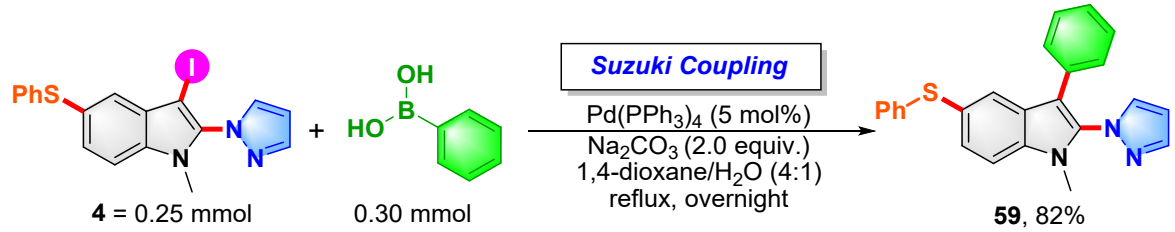
(7) The mixture of **4** (86.0 mg, 0.20 mmol), **3a** (43.6 mg, 0.20 mmol), CuI (20 mol%, 7.6 mg), I_2 (50.6 mg, 0.20 mmol) and toluene/1,4-dioxane (3.0 mL, 1/2) were individually stirred at 80°C in the solution of toluene/1,4-dioxane (3.0 mL, 1/2) and DMSO/1,4-dioxane (3.0 mL, 1/2) under O_2 for 24 hours. 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 **43** (73.5 mg) was obtained in 89% yield when the reaction was carried out in DMSO/1,4-dioxane solution, while only trace amounts of **43** were obtained when the reaction was carried out in the toluene/1,4-dioxane solution.



6. Synthetic utility.

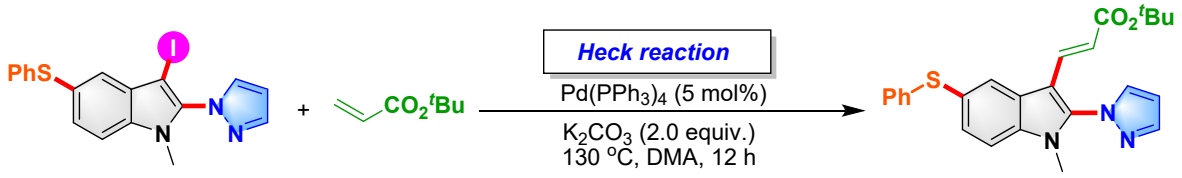
(1) To a mixture of **4** (107.5 mg, 0.25 mmol), sodium carbonate (53.0 mg, 0.50 mmol), phenylboronic acid (36.6 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (14.4 mg, 0.013 mmol) in 1, 4-dioxane/H_2O (4/1) 3 mL was

taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 100 °C for 12 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4, concentrated *via* rotavapor and subJected for column chromatography to afford product **59** (78.1 mg, 82%) as white solid.



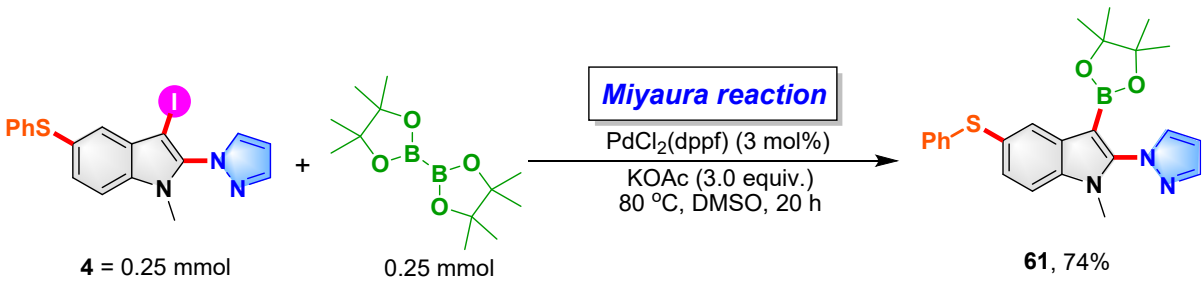
4 = 0.25 mmol 0.30 mmol **59**, 82%

(2) To a mixture of **4** (107.5 mg, 0.25 mmol), potassium carbonate (69.1 mg, 0.50 mmol), *tert*-butylacrylate (64.0 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.013) in DMA (3.0 mL) was taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 130 °C for 12 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4, concentrated *via* rotavapor and subJected for column chromatography to afford product **60** (97.0 mg, 90%) as white solid.



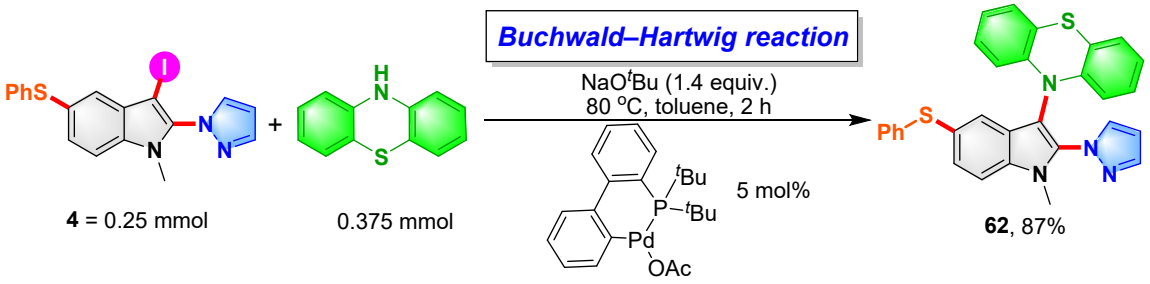
4 = 0.25 mmol 0.50 mmol **60**, 90%

(3) To a mixture of **4** (107.5 mg, 0.25 mmol), potassium acetate (73.5 mg, 0.75 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (63.5 mg, 0.25 mmol) and $PdCl_2$(dppf) (5.5 mg, 3 mol%) in DMSO (3.0 mL) was taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 80 °C for 20 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4, concentrated *via* rotavapor and subJected for column chromatography to afford product **61** (79.7 mg, 74%) as yellow solid.



4 = 0.25 mmol 0.25 mmol **61**, 74%

(4) To a mixture of **4** (107.5 mg, 0.25 mmol), sodium *tert*-butoxide (33.6 mg, 0.35 mmol), 10*H*-phenothiazine (74.6 mg, 0.375 mmol) and Palladium catalyst (5.8 mg, 5 mol%) in toluene (3.0 mL) was taken under argon atmosphere in a sealed tube vial. The reaction mixture was stirred at 80 °C for 2 h in oil bath. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4, concentrated *via* rotavapor and subJected for column chromatography to afford product **62** (109.2 mg, 87%) as white solid.



7. Single crystal X-ray diffraction

(1) Single crystal X-ray diffraction of 23

White block-like single crystals of **23** 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.

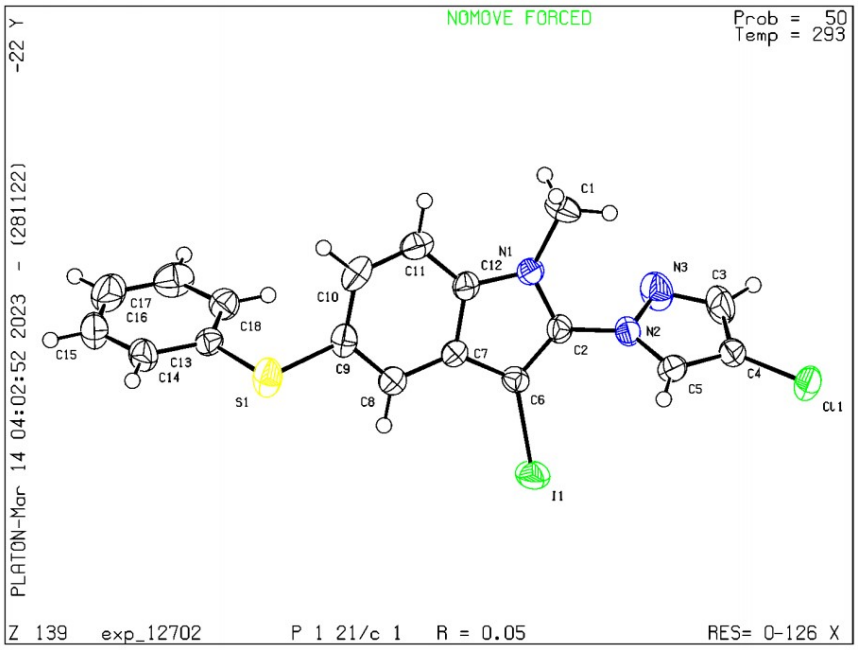


Figure S1. ORTEP drawing of **23** with the numbering scheme.

Table S8. Crystal data and structure refinement for **23**

Identification code	23	
Empirical formula	$C_{18}H_{13}ClIN_3S$	
Formula weight	465.72	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9812(9) Å	α = 90°.
	b = 19.5103(15) Å	β = 109.106(13)
	c = 12.0639(13) Å	γ = 90°.
Volume	1775.1(3) $Å^3$	
Z	4	
F(000)	912.0	
Crystal size	0.20x 0.12 x 0.11 mm^3	
2^{Θ} range for data collection	6.838 to 58.86	
Index ranges	$-10 \le h \le 5$, $-20 \le k \le 26$, $-16 \le l \le 16$	
Reflections collected	10221	
Independent reflections	4139 [Rint = 0.0315, Rsigma = 0.0453]	
Data / restraints / parameters	4139/0/218	
Goodness-of-fit on F^2	1.106	
Final R indices [I>=2^{σ} (I)]	R1 = 0.0490, wR2 = 0.0916	
Final R indices (all data)	R1 = 0.0661, wR2 = 0.0989	
Largest diff. peak and hole	1.04/-0.94 e.$Å^{-3}$	

Table S9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **23**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	5945.0(4)	2754.4(2)	4250.2(3)	48.84(12)
Cl1	-1339.3(16)	1643.4(6)	3166.2(11)	55.9(3)
S1	8976.5(17)	5579.7(6)	6178.4(9)	49.7(3)
N1	3417(4)	3698.4(17)	6446(3)	32.5(7)
N2	2412(4)	2659.4(17)	5349(3)	34.0(8)
C6	5012(5)	3345(2)	5328(3)	29.7(8)
C7	5711(5)	3984.3(19)	5844(3)	27.8(8)
C2	3636(5)	3196(2)	5707(3)	31.3(8)
C12	4679(5)	4186(2)	6534(3)	31.3(8)
N3	2103(6)	2219(2)	6127(3)	54.7(11)
C8	7073(5)	4407(2)	5769(3)	32.0(8)
C5	1343(5)	2542(2)	4243(3)	35.7(9)
C13	10652(5)	5613(2)	7558(3)	32.8(9)
C9	7360(5)	5015(2)	6375(3)	35.8(9)
C18	10783(6)	5182(2)	8485(4)	39.6(10)
C4	309(5)	2002(2)	4306(4)	37.4(9)
C14	11945(6)	6107(2)	7681(4)	43.5(10)
C11	4975(6)	4805(2)	7142(3)	40.1(10)
C10	6295(6)	5213(2)	7040(3)	41.7(10)
C1	2000(6)	3748(3)	6944(4)	48.6(12)
C17	12186(7)	5251(3)	9518(4)	54.4(13)
C3	814(7)	1826(3)	5472(4)	54.8(13)
C15	13312(7)	6167(3)	8703(5)	57.3(13)
C16	13451(7)	5746(3)	9633(5)	63.4(15)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **23**. 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}
I1	57.7(2)	40.07(18)	62.1(2)	-9.38(14)	37.86(17)	-2.86(14)
Cl1	45.6(7)	58.3(7)	64.3(7)	-30.1(6)	18.6(6)	-17.0(6)
S1	59.4(8)	44.4(6)	38.0(5)	10.0(5)	5.9(5)	-19.1(6)
N1	26.2(17)	38.4(18)	32.2(16)	-5.4(15)	8.5(14)	0.6(14)
N2	31.0(18)	36.1(19)	34.7(17)	-0.5(14)	10.5(15)	-6.8(14)
C6	25.2(19)	33(2)	30.7(18)	1.4(16)	9.3(16)	3.3(16)
C7	28(2)	28.3(19)	23.6(17)	2.1(15)	4.3(15)	2.9(16)
C2	27(2)	35(2)	29.7(18)	-0.9(16)	5.5(16)	-2.9(16)
C12	25(2)	37(2)	27.6(18)	-0.1(16)	2.6(16)	2.0(16)

N3	59(3)	57(3)	46(2)	13(2)	15(2)	-16(2)
C8	30(2)	35(2)	27.7(18)	3.5(17)	5.9(16)	2.1(17)
C5	37(2)	38(2)	32.3(19)	-4.9(17)	12.0(18)	-0.1(18)
C13	35(2)	26.3(19)	37(2)	-4.1(17)	12.6(18)	1.8(17)
C9	38(2)	32(2)	31.6(19)	6.4(17)	3.2(18)	-5.7(18)
C18	42(2)	33(2)	44(2)	-0.5(18)	15(2)	-0.1(19)
C4	34(2)	36(2)	47(2)	-10.3(19)	18.9(19)	-5.6(18)
C14	46(3)	34(2)	56(3)	-4(2)	23(2)	-8(2)
C11	40(2)	46(3)	34(2)	-5.4(18)	10.8(19)	7(2)
C10	48(3)	31(2)	36(2)	-5.5(18)	1(2)	2(2)
C1	41(3)	61(3)	55(3)	-4(2)	30(2)	4(2)
C17	57(3)	63(3)	39(2)	6(2)	10(2)	13(3)
C3	56(3)	49(3)	62(3)	4(2)	24(3)	-22(2)
C15	44(3)	57(3)	72(3)	-21(3)	22(3)	-17(2)
C16	46(3)	79(4)	56(3)	-18(3)	6(3)	-3(3)

Table S11. Bond Lengths for **23**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	**C6**	2.051(4)	**C12**	**C11**	1.391(5)
Cl1	**C4**	1.711(4)	**N3**	**C3**	1.318(6)
S1	**C13**	1.762(4)	**C8**	**C9**	1.372(5)
S1	**C9**	1.771(4)	**C5**	**C4**	1.355(6)
N1	**C2**	1.374(5)	**C13**	**C18**	1.376(5)
N1	**C12**	1.365(5)	**C13**	**C14**	1.383(6)
N1	**C1**	1.446(5)	**C9**	**C10**	1.401(6)
N2	**C2**	1.400(5)	**C18**	**C17**	1.383(6)
N2	**N3**	1.353(5)	**C4**	**C3**	1.374(6)
N2	**C5**	1.347(5)	**C14**	**C15**	1.358(7)
C6	**C7**	1.423(5)	**C11**	**C10**	1.358(6)
C6	**C2**	1.352(5)	**C17**	**C16**	1.371(7)
C7	**C12**	1.406(5)	**C15**	**C16**	1.365(7)
C7	**C8**	1.391(5)			

Table S12. Bond Angles for **23**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	**S1**	**C9**	104.91(18)	**C9**	**C8**	**C7**	118.4(4)
C2	**N1**	**C1**	126.9(4)	**N2**	**C5**	**C4**	106.1(4)
C12	**N1**	**C2**	107.5(3)	**C18**	**C13**	**S1**	125.3(3)
C12	**N1**	**C1**	125.3(3)	**C18**	**C13**	**C14**	118.9(4)
N3	**N2**	**C2**	121.9(3)	**C14**	**C13**	**S1**	115.8(3)

C5	**N2**	**C2**	125.8(3)	**C8**	**C9**	**S1**	117.9(3)
C5	**N2**	**N3**	112.2(3)	**C8**	**C9**	**C10**	121.1(4)
C7	**C6**	**I1**	126.7(3)	**C10**	**C9**	**S1**	120.7(3)
C2	**C6**	**I1**	126.6(3)	**C13**	**C18**	**C17**	119.7(4)
C2	**C6**	**C7**	106.7(3)	**C5**	**C4**	**Cl1**	126.5(3)
C12	**C7**	**C6**	106.4(3)	**C5**	**C4**	**C3**	105.7(4)
C8	**C7**	**C6**	134.0(4)	**C3**	**C4**	**Cl1**	127.7(3)
C8	**C7**	**C12**	119.6(3)	**C15**	**C14**	**C13**	120.5(4)
N1	**C2**	**N2**	120.6(3)	**C10**	**C11**	**C12**	117.6(4)
C6	**C2**	**N1**	110.8(3)	**C11**	**C10**	**C9**	121.6(4)
C6	**C2**	**N2**	128.2(3)	**C16**	**C17**	**C18**	120.9(5)
N1	**C12**	**C7**	108.6(3)	**N3**	**C3**	**C4**	112.2(4)
N1	**C12**	**C11**	129.7(4)	**C14**	**C15**	**C16**	121.3(5)
C11	**C12**	**C7**	121.6(4)	**C15**	**C16**	**C17**	118.7(5)
C3	**N3**	**N2**	103.7(4)				

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **23**.

Atom	*x*	*y*	*z*	U(eq)
H8	7772.3	4281.3	5318.73	38
H5	1318.61	2782.65	3572.92	43
H18	9931.8	4844.32	8417.05	47
H14	11877.98	6398.69	7058.52	52
H11	4291.79	4934.24	7600.58	48
H10	6498.5	5633.67	7422.26	50
H1A	1389.82	4175.86	6717.44	73
H1B	2487.42	3724.92	7783.36	73
H1C	1184.01	3376.33	6660.32	73
H17	12273	4958.67	10142.44	65
H3	305.49	1470.56	5765	66
H15	14168.58	6502.18	8771.58	69
H16	14387.27	5794.25	10331.8	76

8. Reference.

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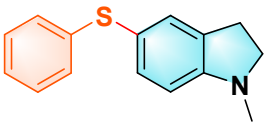
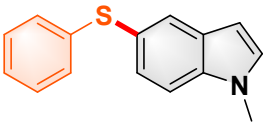
9. Analytic data of the obtained compounds.

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



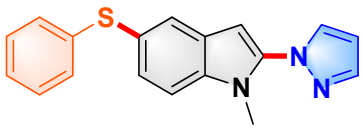
Yellow liquid, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 1H), 7.25–7.22 (m, 3H), 7.17–7.15 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.41 (t, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 8.3 Hz, 2H), 2.83 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.96, 140.48, 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.

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



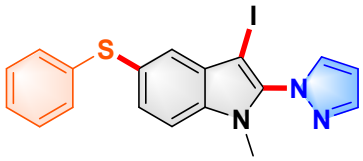
Known compound, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.24–7.21 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) 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.

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



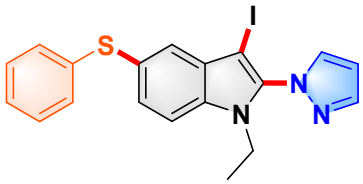
White solid, (113.5 mg, 93% yield), m.p.: 137-138 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.23–7.19 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 6.52 (t, *J* = 2.1 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.

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



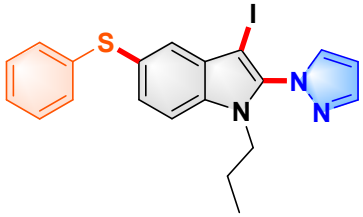
White solid, (125.6 mg, 73% yield), m.p.: 156-157 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.74 (d, *J* = 1.3 Hz, 1H), 7.49 (d, *J* = 6.8 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.29–7.25 (m, 2H), 7.22 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.60– 6.57(m, 1H), 3.66 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.52, 138.89, 137.08, 135.61, 133.32, 130.01, 129.44, 128.97, 128.17, 127.99, 125.77, 125.45, 111.34, 107.20, 54.18, 30.70. Calcd. for $C_{18}H_{14}IN_3S$ [M-H]$^-$: 429.9880; found: 429.9885.

1-ethyl-3-iodo-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (5)



White solid, (151.3 mg, 85% yield), m.p.: 133-134 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.76 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.30–7.23 (m, 4H), 7.18 (t, *J* = 7.1 Hz, 1H), 6.59 (t, *J* = 2.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.45, 138.91, 136.56, 134.56, 133.32, 129.94, 129.58, 128.99, 128.20, 128.13, 125.78, 125.31, 111.42, 107.18, 54.74, 39.45, 15.46. Calcd. for $C_{19}H_{16}IN_3S$ [M-H]$^-$: 444.0037; found: 444.0029.

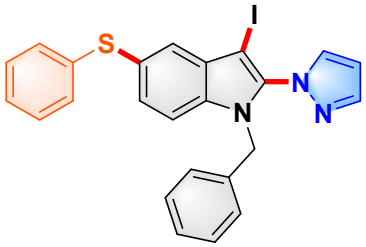
3-iodo-5-(phenylthio)-1-propyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (6)



White solid, (145.0 mg, 79% yield), m.p.: 141-142 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 6.9 Hz,

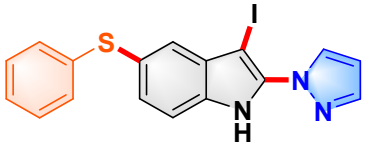
1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.25–7.23 (m, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 4.06–4.03 (m, 2H), 1.72–1.69 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.39, 138.87, 136.82, 135.00, 133.43, 129.86, 129.46, 128.98, 128.22, 128.03, 125.78, 125.27, 111.64, 107.14, 54.85, 46.09, 23.26, 11.38. **HRMS (ESI):** Calcd. for $C_{20}H_{18}IN_3S$ $[M-H]^-$: 458.0193; found: 458.0197.

1-benzyl-3-iodo-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (7)



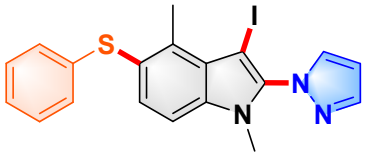
White solid, (178.5 mg, 88% yield), m.p.: 149-150 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.28–7.24 (m, 7H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.00–6.98 (m, 2H), 6.49 (t, *J* = 2.2 Hz, 1H), 5.31 (s, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.55, 138.52, 136.93, 136.42, 135.20, 133.45, 129.99, 129.61, 128.99, 128.77, 128.51, 127.80, 127.76, 126.70, 125.92, 111.95, 107.24, 55.57, 47.82. **HRMS (ESI):** Calcd. for $C_{24}H_{18}IN_3S$ $[M-H]^-$: 506.0193; found: 506.0195.

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



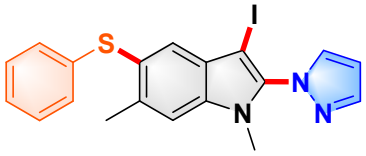
White solid, (103.2 mg, 62% yield), m.p.: 166-167 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 10.76 (s, 1H), 8.74 (d, *J* = 2.6 Hz, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.36 (d, *J* = 6.7 Hz, 1H), 7.29–7.25 (m, 3H), 7.24–7.22 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.62–6.59 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.43, 138.98, 135.93, 133.41, 131.45, 129.72, 129.58, 128.96, 128.13, 127.32, 125.72, 125.35, 112.54, 107.88, 44.06. **HRMS (ESI):** Calcd. for $C_{17}H_{12}IN_3S$ $[M+Na]^+$: 439.9689; found: 439.968.

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



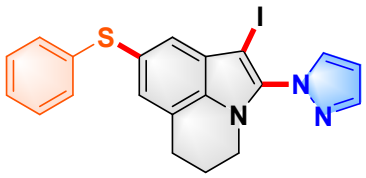
White solid, (131.7 mg, 74% yield), m.p.: 156-157 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.26–7.21 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.60–6.58 (m, 1H), 3.57 (s, 3H), 3.06 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.48, 139.12, 137.25, 136.78, 135.93, 133.57, 131.88, 128.91, 126.72, 125.40, 125.04, 123.85, 108.95, 107.18, 53.17, 30.45, 16.80. **HRMS (ESI):** Calcd. for $C_{19}H_{16}IN_3S$ $[M-H]^-$: 444.0037; found: 444.0035.

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



White solid, (140.6 mg, 79% yield), m.p.: 127-128 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.77 (s, 1H), 7.30 (s, 1H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.64 (s, 3H), 2.55 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.45, 138.74, 138.03, 136.52, 133.36, 130.13, 128.96, 127.70, 126.72, 125.17, 124.39, 111.83, 107.13, 53.90, 30.61, 21.59. **HRMS (ESI):** Calcd. for $C_{19}H_{16}IN_3S$ $[M-H]^-$: 444.0037; found: 444.0030.

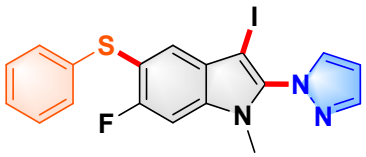
1-iodo-8-(phenylthio)-2-(1*H*-pyrazol-1-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (12)



White solid, (160.9 mg, 88% yield), m.p.: 177-178 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.89 (s, 1H), 7.58 (s, 1H), 7.28–7.25 (m, 2H), 7.24 (s, 1H), 7.23–7.20 (m, 2H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 4.15–4.12 (m, 2H), 2.99 (t, *J* = 6.1 Hz, 2H), 2.22 (p, J = 6.0 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.25, 139.45, 135.63, 132.87,

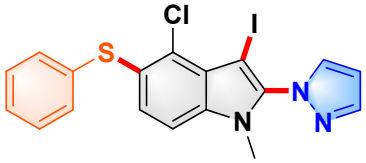
132.84, 128.94, 127.91, 127.82, 126.80, 125.57, 125.50, 124.88, 123.78, 107.07, 51.49, 43.09, 24.39, 22.49. **HRMS (ESI):** Calcd. for $C_{20}H_{16}IN_3S$ $[M-H]^-$: 456.0037; found: 456.0028.

6-fluoro-3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (13)



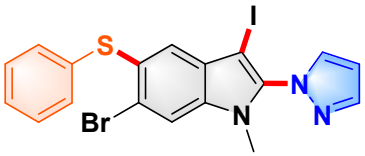
White solid, (120.1 mg, 67% yield), m.p.: 192-193 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.24–7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.62 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 160.33 (d, *J* = 243.1 Hz), 142.63, 137.39(d, *J* = 3.0 Hz), 137.13, 136.16 (d, *J* = 10.6 Hz), 133.27, 130.06, 129.03, 127.95, 126.05, 125.58, 114.21 (d, *J* = 21.1 Hz), 107.29, 97.62 (d, *J* = 30.2 Hz), 54.12, 30.90. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -110.79. **HRMS (ESI):** Calcd. for $C_{18}H_{13}FIN_3S$ $[M+Na]^+$: 471.9751; found: 471.9750.

4-chloro-3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (14)



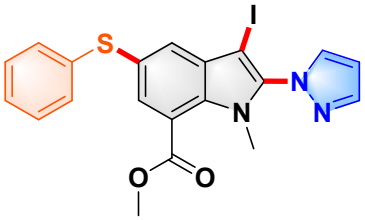
White solid, (131.8 mg, 71% yield), m.p.: 185-186 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.32–7.28 (m, 2H), 7.27–7.25 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.59 (t, *J* = 2.2 Hz, 1H), 3.57 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.65, 138.28, 136.36, 135.99, 133.65, 129.96, 129.57, 129.40, 129.19, 126.55, 126.01, 123.62, 109.63, 107.31, 52.08, 30.81. **HRMS (ESI):** Calcd. for $C_{18}H_{13}ClIN_3S$ $[M+Na]^+$: 487.9456; found: 487.9453.

6-bromo-3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1H-indole (15)



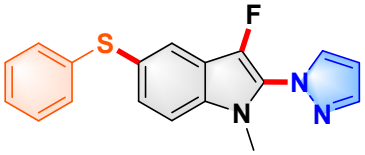
White solid, (119.9 mg, 59% yield), m.p.: 218-219 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.71 (s, 1H), 7.66 (s, 1H), 7.33–7.30 (m, 2H), 7.23 (dtd, *J* = 7.3, 2.8, 0.9 Hz, 3H), 6.59–6.57 (m, 1H), 3.63 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.67, 137.53, 136.80, 136.12, 133.26, 129.19, 128.86, 128.83, 128.79, 126.90, 126.38, 123.62, 115.13, 107.36, 53.92, 30.90. **HRMS (ESI):** Calcd. for $C_{18}H_{13}BrIN_3S$ $[M+Na]^+$: 531.8950; found: 531.8946.

methyl 3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole-7-carboxylate (16)



White solid, (125.2 mg, 64% yield), m.p.: 204-205 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 1.8 Hz, 1H), 7.92 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.29–7.27 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.60 (t, *J* = 2.2 Hz, 1H), 3.97 (s, 3H), 3.60 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 166.49, 142.76, 139.14, 137.89, 133.38, 133.28, 132.67, 131.80, 131.45, 129.13, 128.55, 126.18, 125.20, 118.29, 107.50, 56.15, 52.59, 34.36. **HRMS (ESI):** Calcd. for $C_{20}H_{16}IN_3O_2S$ $[M-H]^-$: 487.9935; found: 487.9929.

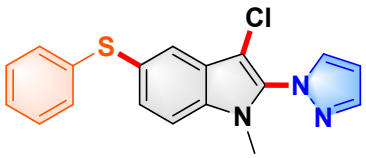
3-fluoro-1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (17)



White solid, (87.9 mg, 68% yield), m.p.: 124-125 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.71 (s, 1H), 7.64–7.60 (m, 1H), 7.22–7.18 (m, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.12–7.08 (m, 3H), 7.01 (t, *J* = 9.1 Hz, 1H), 6.49–6.46 (m, 1H), 3.74 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.67, 160.07, 142.43, 139.23, 138.13, 135.36 (d, *J* = 12.1

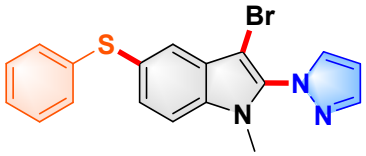
Hz), 133.41, 128.98, 126.09, 125.29, 124.33, 121.39 (d, J = 9.1 Hz), 110.91 (d, J = 24.2 Hz), 96.73 (d, J = 27.2 Hz, 1H), 96.08, 30.87. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -180.04. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3S$ $[M+H]^+$: 324.0965; found: 324.0963.

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



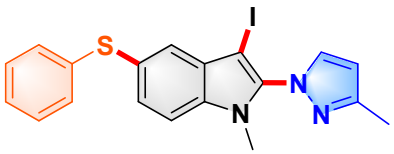
White solid, (62.4 mg, 46% yield), m.p.: 153-154 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, J = 1.8 Hz, 1H), 7.73 (d, J = 2.5 Hz, 1H), 7.69 (d, J = 1.7 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 6.8 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.1 Hz, 2H), 6.47 (t, J = 2.2 Hz, 1H), 3.78 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.52, 140.03, 138.02, 133.68, 133.42, 129.33, 129.05, 127.51, 126.04, 125.37, 124.27, 119.57, 111.33, 107.06, 95.25, 31.00. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0670; found: 340.0661.

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



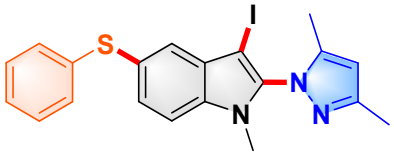
White solid, (68.9 mg, 45% yield), m.p.: 170-171 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, J = 1.4 Hz, 1H), 7.84 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 2.6 Hz, 1H), 7.47 (d, J = 6.8 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.22–7.19 (m, 2H), 7.12 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 7.2 Hz, 2H), 6.48–6.46 (m, 1H), 3.78 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.53, 139.86, 138.00, 133.97, 133.41, 129.90, 129.05, 126.83, 126.00, 125.36, 122.64, 115.04, 111.69, 107.06, 95.10, 30.99. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3S$ $[M+H]^+$: 484.0165; found: 484.0158.

3-iodo-1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-5-(phenylthio)-1*H*-indole (20)



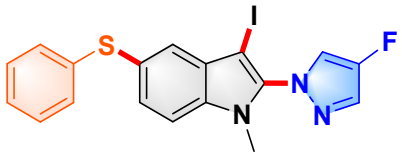
White solid, (142.4 mg, 80% yield), m.p.: 147-148 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.73 (s, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.28–7.25 (m, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 3.68 (s, 3H), 2.45 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.88, 139.00, 137.36, 135.63, 134.03, 129.89, 129.48, 128.98, 128.09, 127.97, 125.73, 125.18, 111.31, 107.23, 53.94, 30.75, 13.86. **HRMS (ESI):** Calcd. for $C_{19}H_{16}IN_3S$ $[M-H]^-$: 444.0037; found: 444.0032.

2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-iodo-1-methyl-5-(phenylthio)-1*H*-indole (21)



White solid, (97.3 mg, 53% yield), m.p.: 122-123 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.26 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.25–7.22 (m, 2H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.12 (s, 1H), 3.54 (s, 3H), 2.38 (s, 3H), 2.22 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.33, 143.25, 138.93, 136.18, 135.59, 129.94, 129.43, 129.02, 128.23, 128.21, 127.85, 125.81, 125.20, 111.41, 106.53, 57.32, 30.34, 13.94, 11.60. **HRMS (ESI):** Calcd. for $C_{20}H_{18}IN_3S$ $[M-H]^-$: 458.0193; found: 458.0189.

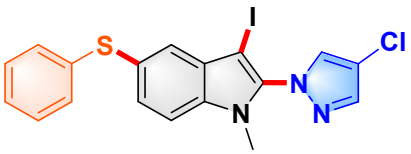
2-(4-fluoro-1*H*-pyrazol-1-yl)-3-iodo-1-methyl-5-(phenylthio)-1*H*-indole (22)



White solid, (120.1 mg, 67% yield), m.p.: 163-164 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 3.9 Hz, 1H), 7.74–7.72 (m, 2H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.23 (s, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 3.67 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.07 (d, *J* = 250.7 Hz), 138.72, 136.67, 135.51, 130.64 (d, *J* = 13.6 Hz), 130.19, 129.26, 129.00, 128.29, 127.96, 125.86, 125.81, 119.00 (d, *J* = 27.2 Hz), 111.40,

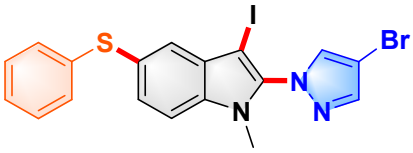
54.49, 30.66. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -175.01. **HRMS (ESI):** Calcd. for $C_{18}H_{13}FIN_3S$ $[M+Na]^+$: 471.9751 found: 471.9752.

2-(4-chloro-1*H*-pyrazol-1-yl)-3-iodo-1-methyl-5-(phenylthio)-1*H*-indole (23)



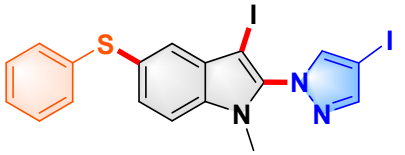
White solid, (126.2 mg, 68% yield), m.p.: 186-187 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 2H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.29–7.26 (m, 2H), 7.24–7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.18, 138.66, 136.24, 135.53, 130.89, 130.22, 129.27, 129.01, 128.35, 127.94, 125.90, 112.15, 111.43, 54.63, 30.73. **HRMS (ESI):** Calcd. for $C_{18}H_{13}ClIN_3S$ $[M+Na]^+$: 487.9456; found: 487.9451.

2-(4-bromo-1*H*-pyrazol-1-yl)-3-iodo-1-methyl-5-(phenylthio)-1*H*-indole (24)



White solid, (83.3 mg, 41% yield), m.p.: 191-192 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.73 (s, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.29–7.26 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.20–7.17 (m, 1H), 3.66 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 143.20, 138.66, 136.16, 135.54, 133.05, 130.23, 129.28, 129.01, 128.35, 127.95, 125.90, 111.42, 95.41, 54.69, 30.74. **HRMS (ESI):** Calcd. for $C_{18}H_{13}BrIN_3S$ $[M+Na]^+$: 531.8950; found: 531.8944.

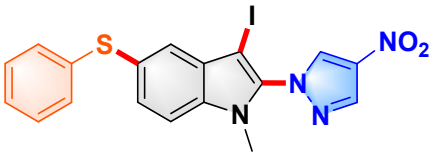
3-iodo-2-(4-iodo-1*H*-pyrazol-1-yl)-1-methyl-5-(phenylthio)-1*H*-indole (25)



White solid, (129.0 mg, 58% yield), m.p.: 180-181 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.88 (s, 1H), 7.72 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.28–

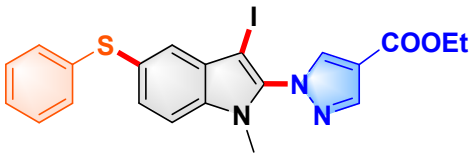
7.25 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 3.65 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 147.50, 138.67, 137.32, 136.00, 135.54, 130.21, 129.30, 129.01, 128.35, 127.94, 125.89, 125.87, 111.41, 58.75, 54.70, 30.76. **HRMS (ESI):** Calcd. for $C_{18}H_{13}I_2N_3S$ [M-H]$^-$: 555.8847; found: 555.8844.

3-iodo-1-methyl-2-(4-nitro-1*H*-pyrazol-1-yl)-5-(phenylthio)-1*H*-indole (26)



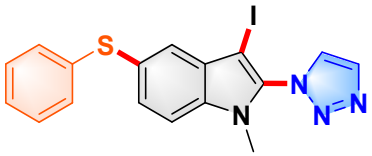
Yellow solid, (129.2 mg, 68% yield), m.p.: 231-232 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.43 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.29–7.27 (m, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.21–7.18 (m, 1H), 3.73 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.20, 137.90, 136.96, 135.63, 134.83, 132.49, 130.65, 129.06, 128.68, 127.86, 126.86, 126.13, 111.55, 55.46, 31.00. **HRMS (ESI):** Calcd. for $C_{18}H_{13}IN_4O_2S$ [M-H]$^-$: 474.9731; found: 474.9728.

ethyl 1-(3-iodo-1-methyl-5-(phenylthio)-1*H*-indol-2-yl)-1*H*-pyrazole-4-carboxylate (27)



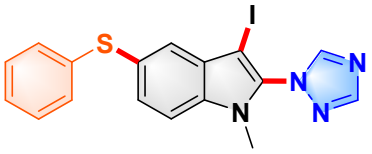
White solid, (171.0 mg, 85% yield), m.p.: 195-196 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.28 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.28–7.25 (m, 2H), 7.23–7.21 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 4.41 (t, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.39, 143.37, 138.58, 136.67, 136.00, 135.59, 130.29, 129.25, 129.01, 128.39, 127.96, 126.05, 125.92, 116.87, 111.45, 60.76, 54.84, 30.82, 14.44. **HRMS (ESI):** Calcd. for $C_{21}H_{18}IN_3O_2S$ [M-H]$^-$: 502.0092; found: 502.0088.

3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-1,2,3-triazol-1-yl)-1*H*-indole (28)



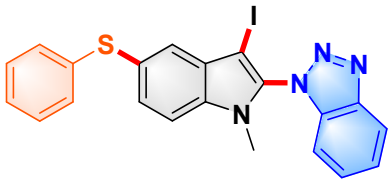
White solid, (133.1 mg, 77% yield), m.p.: 131-132 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (t, *J* = 1.8 Hz, 2H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.12 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 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 $C_{17}H_{13}IN_4S$ $[M-H]^-$: 430.9833; found: 430.8928.

3-iodo-1-methyl-5-(phenylthio)-2-(1*H*-1,2,4-triazol-1-yl)-1*H*-indole (29)



White solid, (125.9 mg, 73% yield), m.p.: 149-150 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.29 (s, 1H), 7.72 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.28–7.25 (m, 2H), 7.24–7.21 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 3.69 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.56, 138.41, 135.80, 133.20, 130.46, 129.22, 129.03, 128.51, 127.93, 126.40, 126.01, 111.48, 55.66, 30.82. **HRMS (ESI):** Calcd. for $C_{17}H_{13}IN_4S$ $[M-H]^-$: 430.9833; found: 430.9830.

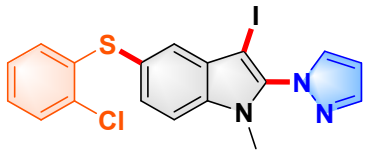
1-(3-iodo-1-methyl-5-(phenylthio)-1*H*-indol-2-yl)-1H-benzo[*d*][1,2,3]triazole (30)



White solid, (169.7 mg, 88% yield), m.p.: 124-125 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.65–7.62 (m, 1H), 7.56–7.53 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.31–7.29 (m, 1H), 7.28 (d, *J* = 2.9 Hz, 3H), 7.20 (t, *J* = 6.8 Hz, 1H), 3.60 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 145.42, 138.43, 136.02, 134.08,

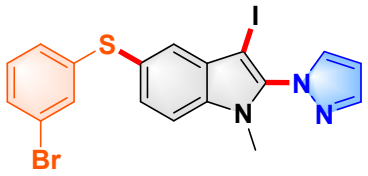
132.48, 130.46, 129.62, 129.18, 129.06, 128.60, 127.80, 126.40, 126.05, 124.94, 120.61, 111.62, 110.72, 56.93, 30.70. **HRMS (ESI):** Calcd. for $C_{21}H_{15}IN_4S$ $[M-H]^-$: 480.9989; found: 480.9980.

5-((2-chlorophenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (31)



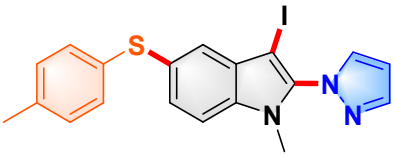
White solid, (142.9 mg, 77% yield), m.p.: 161-162 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 2.5 Hz, 1H), 7.78 (d, *J* = 1.2 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.38–7.36 (m, 1H), 7.05 (ddd, *J* = 7.1, 5.9, 1.9 Hz, 2H), 6.70 (d, *J* = 7.4 Hz, 1H), 6.59 (t, *J* = 2.2 Hz, 1H), 3.69 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.59, 139.07, 137.30, 136.09, 133.32, 130.99, 130.92, 129.75, 129.64, 129.44, 127.64, 127.09, 126.04, 122.84, 111.71, 107.27, 54.30, 30.77. **HRMS (ESI):** Calcd. for $C_{18}H_{13}ClIN_3S$ $[M+Na]^+$: 487.9456; found: 487.9453.

5-((3-bromophenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (32)



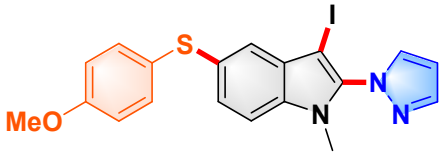
White solid, (103.6 mg, 51% yield), m.p.: 154-155 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 9.5 Hz, 1H), 7.27 (ddt, *J* = 11.0, 4.0, 2.5 Hz, 2H), 7.10–7.07 (m, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 3.68 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.57, 141.88, 137.28, 135.91, 133.34, 133.31, 130.39, 130.22, 130.18, 129.89, 129.57, 128.76, 128.52, 126.00, 125.98, 123.84, 123.03, 123.00, 111.64, 107.25, 54.31, 30.75. **HRMS (ESI):** Calcd. for $C_{18}H_{13}BrIN_3S$ $[M+Na]^+$: 531.8950; found: 531.8949.

3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-5-(p-tolylthio)-1*H*-indole (33)



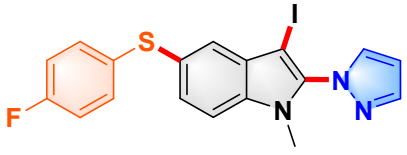
White solid, (131.7 mg, 74% yield), m.p.: 126-127 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.2 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.59–6.58 (m, 1H), 3.65 (s, 3H), 2.34 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.50, 137.01, 136.06, 135.38, 134.74, 133.34, 129.83, 129.35, 129.33, 129.21, 127.02, 126.68, 111.25, 107.20, 54.13, 30.70, 21.08. **HRMS (ESI):** Calcd. for $C_{19}H_{16}IN_3S$ $[M-H]^-$: 444.0037; found: 444.0030.

3-iodo-5-((4-methoxyphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (34)



Yellow liquid, (167.8 mg, 91% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.61 (d, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.57 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 3H), 3.61 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.97, 142.46, 136.95, 135.04, 133.36, 132.59, 129.26, 128.55, 127.99, 127.83, 125.24, 114.84, 111.17, 107.19, 55.44, 54.02, 30.69. **HRMS (ESI):** Calcd. for $C_{19}H_{16}IN_3OS$ $[M-H]^-$: 459.9986; found: 459.9982.

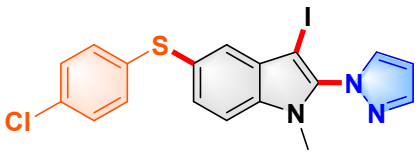
5-((4-fluorophenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (35)



White solid, (116.5 mg, 65% yield), m.p.: 143-144 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.25 (dd, *J* = 8.9, 5.1 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.59–6.57 (m, 1H), 3.65 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.60 (d, *J* = 246.1 Hz), 142.54, 137.16, 135.47, 133.46 (d, *J* = 3.0 Hz), 133.34, 131.04 (d, *J* = 7.6 Hz), 129.42, 129.21, 127.07, 126.42, 116.13

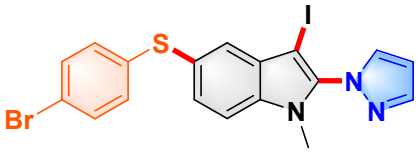
(d, J = 21.1 Hz), 111.43, 107.25, 54.14, 30.74. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -115.95. **HRMS (ESI):** Calcd. for $C_{18}H_{13}FIN_3S$ $[M+Na]^+$: 471.9751 found: 471.9747.

5-((4-chlorophenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (36)



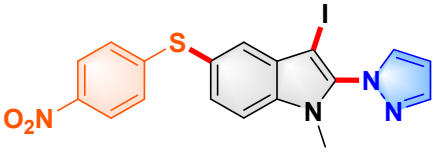
White solid, (155.9 mg, 84% yield), m.p.: 160-161 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, J = 1.9 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.45 (d, J = 6.8 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.59–6.58 (m, 1H), 3.67 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.56, 137.67, 137.23, 135.73, 133.31, 131.58, 129.95, 129.51, 129.29, 129.04, 128.16, 124.91, 111.52, 107.25, 54.19, 30.74. **HRMS (ESI):** Calcd. for $C_{18}H_{13}ClIN_3S$ $[M+Na]^+$: 487.9456; found: 487.9451.

5-((4-bromophenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (37)



White solid, (142.2 mg, 70% yield), m.p.: 178-179 °C;**^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, J = 1.9 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.35 (dd, J = 8.6, 2.8 Hz, 3H), 7.05 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 2.0 Hz, 1H), 3.67 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.57, 138.47, 137.25, 135.77, 133.31, 131.93, 130.05, 129.52, 129.43, 128.32, 124.63, 119.37, 111.55, 107.26, 54.22, 30.76. **HRMS (ESI):** Calcd. for $C_{18}H_{13}BrIN_3S$ $[M+Na]^+$: 531.8950; found: 531.8946.

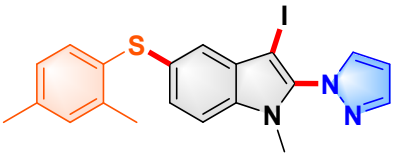
3-iodo-1-methyl-5-((4-nitrophenyl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (38)



Yellow solid, (131.1 mg, 69% yield), m.p.: 246-247 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.04 (d, J = 9.1 Hz, 2H), 7.92 (d, J = 1.9 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H), 7.78 (d, J = 1.2 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 9.0 Hz, 2H), 6.60–6.59 (m,

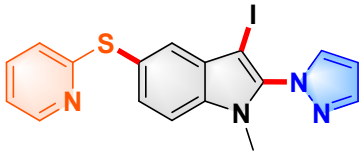
1H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.27, 145.00, 142.69, 137.63, 136.39, 133.29, 130.84, 129.87, 125.68, 123.97, 121.37, 112.06, 107.38, 54.34, 30.85. **HRMS (ESI):** Calcd. for $C_{18}H_{13}IN_4O_2S$ $[M-H]^-$: 474.9731; found: 474.9721.

5-((2,4-dimethylphenyl)thio)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (39)



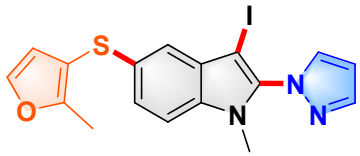
White solid, (141.4 mg, 77% yield), m.p.: 157-158 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.58 (t, *J* = 2.1 Hz, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.47, 137.81, 136.92, 136.57, 135.14, 133.32, 133.04, 131.28, 130.53, 129.42, 128.36, 127.35, 126.91, 125.90, 111.19, 107.15, 54.01, 30.66, 20.99, 20.45. **HRMS (ESI):** Calcd. for $C_{20}H_{18}IN_3S$ $[M-H]^-$: 458.0193; found: 458.0189.

3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-5-(pyridin-2-ylthio)-1*H*-indole (40)



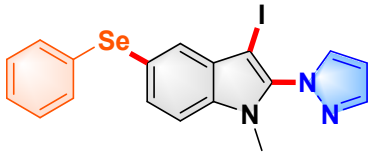
Orange solid (75.9 mg, 44% yield), m.p.: 201-202 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.82 (d, *J* = 1.3 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 6.96 (dd, *J* = 6.5, 4.9 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.59–6.56 (m, 1H), 3.67 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 163.00, 149.41, 142.57, 137.28, 136.68, 136.16, 133.33, 131.34, 129.88, 129.67, 122.26, 120.54, 119.49, 111.64, 107.28, 54.39, 30.78. **HRMS (ESI):** Calcd. for $C_{17}H_{13}IN_4S$ $[M+H]^+$: 432.9978; found: 432.9975.

3-iodo-1-methyl-5-((2-methylfuran-3-yl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (41)



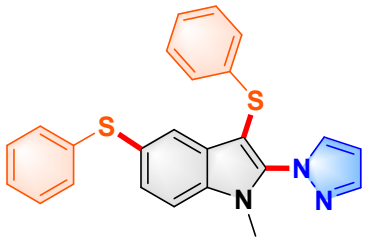
Yellow liquid (123.3 mg, 71% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.40 (s, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 2H), 6.56 (t, *J* = 2.2 Hz, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 3.61 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 155.65, 142.40, 141.08, 136.81, 134.44, 133.31, 129.67, 129.19, 124.80, 121.45, 115.19, 110.85, 110.05, 107.10, 53.70, 30.60, 11.99. **HRMS (ESI):** Calcd. for $C_{17}H_{14}IN_3OS$ $[M+H]^+$: 435.9975; found: 435.9971.

3-iodo-1-methyl-5-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (42)



White solid (126.2 mg, 66% yield), m.p.: 153-154 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.7 Hz, 1H), 7.84 (dd, *J* = 4.8, 1.9 Hz, 2H), 7.59 (d, *J* = 6.9 Hz, 1H), 7.38 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.25 (t, *J* = 7.1 Hz, 2H), 7.23–7.19 (m, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.66 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.50, 136.92, 135.54, 133.50, 133.32, 131.14, 130.81, 129.60, 129.20, 129.14, 126.45, 121.06, 111.32, 107.18, 54.01, 30.66. **HRMS (ESI):** Calcd. for $C_{18}H_{14}IN_3Se$ $[M-H]^-$: 477.9384; found: 477.9377.

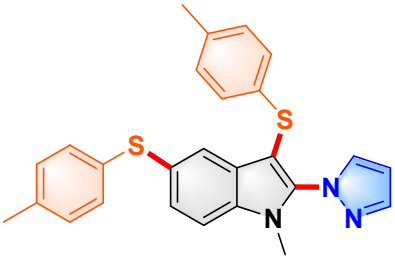
1-methyl-3,5-bis(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (43)



Yellow solid (125.6 mg, 76% 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,

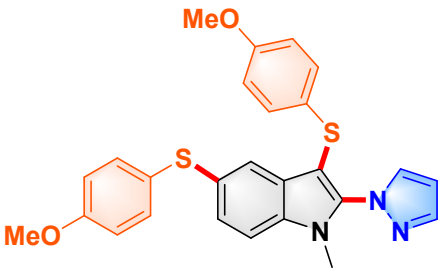
138.02, 135.07, 133.47, 129.48, 129.02, 129.01, 128.95, 128.37, 126.27, 126.00, 125.87, 125.81, 125.39, 111.30, 107.05, 95.91, 30.98. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S_2$ $[M+H]^+$: 414.1093; found: 414.1089.

1-methyl-2-(1*H*-pyrazol-1-yl)-3,5-bis(p-tolylthio)-1*H*-indole (44)



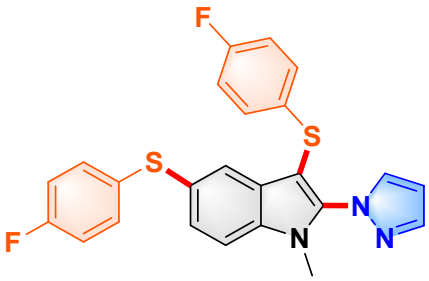
White solid (107.6 mg, 61% yield), m.p.: 156-157 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.86 (s, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 4H), 6.49 (t, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.41, 139.42, 136.03, 135.24, 134.78, 134.56, 134.34, 133.51, 129.75, 129.74, 129.39, 128.94, 128.67, 127.11, 126.71, 124.94, 111.08, 106.93, 96.53, 30.87, 21.03, 20.93. **HRMS (ESI):** Calcd. for $C_{26}H_{23}N_3S_2$ $[M+H]^+$:442.1406; found: 442.1403.

3,5-bis((4-methoxyphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (45)



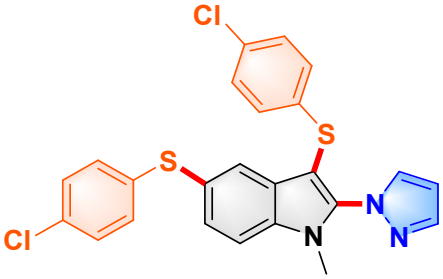
White solid (153.3 mg, 81% yield), m.p.: 92-93 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.79 (s, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.37–7.33 (m, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.52–6.49 (m, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.99, 158.21, 142.37, 138.98, 134.35, 133.62, 132.83, 129.43, 128.93, 128.76, 128.21, 127.62, 127.22, 123.08, 114.78, 114.66, 110.95, 106.92, 97.90, 55.38, 55.33, 30.73. **HRMS (ESI):** Calcd. for $C_{26}H_{23}N_3O_2S_2$ $[M+H]^+$: 474.1304; found: 474.1301.

3,5-bis((4-fluorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (46)



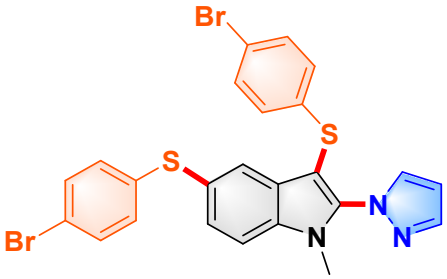
White solid (114.9 mg, 64% yield), m.p.: 177-178 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.6 Hz, 1H), 7.78 (s, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 2H), 7.23 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.05 (dd, *J* = 8.8, 5.1 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.51 (t, *J* = 2.1 Hz, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.29 (d, *J* = 68.0 Hz), 160.66 (d, *J* = 68.0 Hz), 142.55, 139.47, 134.78, 133.43, 132.98 (d, *J* = 3.0 Hz), 132.61 (d, *J* = 3.0 Hz), 131.50 (d, *J* = 7.6 Hz), 128.75 (d, *J* = 7.6 Hz), 128.68, 128.48, 127.30, 124.50, 116.13 (d, *J* = 10.6 Hz), 115.98 (d, *J* = 9.1 Hz), 111.27, 107.09, 96.82, 30.84. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -115.81, -116.87. **HRMS (ESI):** Calcd. for $C_{24}H_{17}F_2N_3S_2$ $[M+H]^+$: 450.0905; found: 450.0900.

3,5-bis((4-chlorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (47)



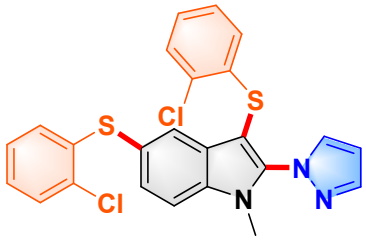
White solid (136.6 mg, 71% yield), m.p.: 165-166 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.6 Hz, 1H), 7.81 (s, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.47–7.43 (m, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.50 (t, *J* = 2.1 Hz, 1H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.64, 139.80, 137.16, 136.37, 135.09, 133.36, 131.81, 131.33, 129.72, 129.34, 129.07, 129.05, 128.73, 127.63, 125.92, 125.52, 111.49, 107.19, 95.72, 30.97. **HRMS (ESI):** Calcd. for $C_{24}H_{17}Cl_2N_3S_2$ $[M+H]^+$: 482.0314; found: 482.0317.

3,5-bis((4-bromophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (48)



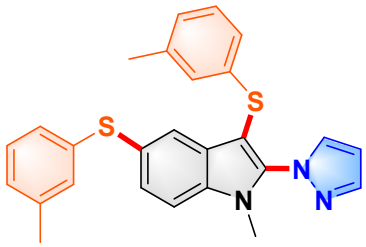
White solid (131.8 mg, 58% yield), m.p.: 182-183 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.81 (s, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 2.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.51–6.49 (m, 1H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.65, 137.93, 137.10, 135.13, 133.34, 131.97, 131.94, 129.86, 129.44, 128.72, 127.85, 125.68, 125.65, 119.61, 119.13, 111.51, 107.20, 95.52, 30.99. **HRMS (ESI):** Calcd. for $C_{24}H_{17}Br_2N_3S_2$ $[M+H]^+$: 569.9303; found: 569.9294.

3,5-bis((2-chlorophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (49)



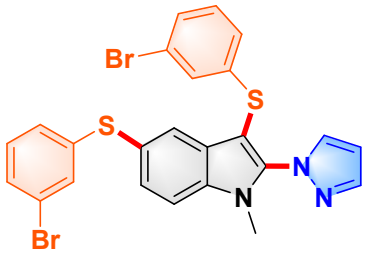
White solid (130.8 mg, 68% yield), m.p.: 158-159 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 1.3 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.06–7.02 (m, 2H), 7.02–6.98 (m, 2H), 6.72–6.71 (m, 1H), 6.71–6.68 (m, 1H), 6.50–6.48 (m, 1H), 3.85 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.67, 140.34, 138.73, 136.97, 135.71, 133.32, 131.18, 130.67, 130.56, 129.61, 129.45, 129.00, 127.85, 127.43, 127.17, 127.02, 126.24, 126.13, 126.02, 123.68, 111.73, 107.31, 94.16, 31.16. **HRMS (ESI):** Calcd. for $C_{24}H_{17}Cl_2N_3S_2$ $[M+H]^+$: 482.0314; found: 482.0311.

1-methyl-2-(1*H*-pyrazol-1-yl)-3,5-bis(*m*-tolylthio)-1*H*-indole (50)



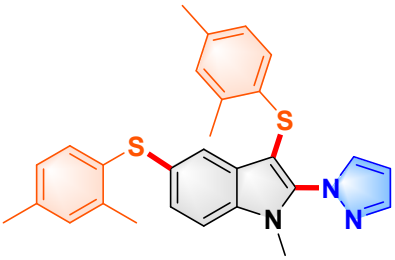
White solid (125.2 mg, 72% yield), m.p.: 155-156 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.7 Hz, 1H), 7.89 (s, 1H), 7.79–7.76 (m, 1H), 7.50 (d, *J* = 9.9 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.14 (t, *J* = 8.9 Hz, 1H), 7.11–7.06 (m, 2H), 7.03–6.96 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.88 (s, 1H), 6.49 (s, 1H), 3.82 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.47, 139.66, 138.78, 138.73, 138.44, 137.82, 135.04, 133.49, 129.44, 129.09, 129.02, 128.87, 128.80, 126.83, 126.74, 126.33, 125.85, 125.51, 123.27, 111.24, 107.00, 95.91, 30.99, 21.42, 21.38. **HRMS (ESI):** Calcd. for $C_{26}H_{23}N_3S_2$ $[M+H]^+$: 442.1406; found: 442.1405.

3,5-bis((3-bromophenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (51)



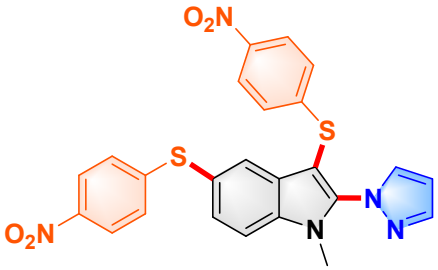
White solid (152.2 mg, 67% yield), m.p.: 197-198 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.1 Hz, 2H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 10.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.28–7.27 (m, 1H), 7.26–7.23 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.10–7.07 (m, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.51–6.49 (m, 1H), 3.82 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.71, 141.62, 140.43, 140.05, 135.38, 133.36, 130.39, 130.23, 130.13, 130.05, 128.88, 128.62, 128.53, 128.52, 126.40, 126.22, 124.61, 123.12, 123.01, 111.78, 107.30, 94.90, 31.14. **HRMS (ESI):** Calcd. for $C_{24}H_{17}Br_2N_3S_2$ $[M+H]^+$: 569.9303; found: 569.9328.

3,5-bis((2,4-dimethylphenyl)thio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (52)



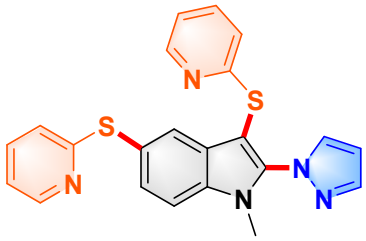
White solid (150.1 mg, 80% yield), m.p.: 133-134 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.71 (d, *J* = 6.2 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34–7.30 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.96 (s, 1H), 6.91 (d, *J* = 6.6 Hz, 1H), 6.78 (d, *J* = 7.1 Hz, 1H), 6.68 (t, *J* = 8.1 Hz, 1H), 6.46 (t, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 2.34 (d, *J* = 5.7 Hz, 6H), 2.33 (s, 3H), 2.27 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.34, 139.37, 138.14, 136.64, 135.11, 134.86, 134.60, 133.44, 133.41, 132.68, 131.25, 131.02, 130.97, 129.01, 127.51, 127.30, 127.29, 127.26, 126.28, 123.63, 111.04, 106.87, 95.84, 30.88, 20.97, 20.79, 20.37, 19.88. **HRMS (ESI):** Calcd. for $C_{28}H_{27}N_3S_2$ $[M+H]^+$: 470.1719; found: 470.1714.

1-methyl-3,5-bis((4-nitrophenyl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (53)



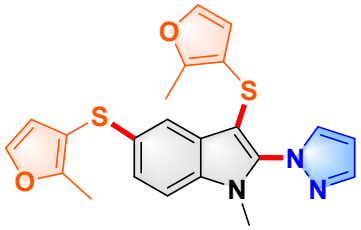
Yellow solid (102.6 mg, 51% yield), m.p.: 244-245 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.04 (s, 2H), 8.03 (s, 2H), 7.88 (dd, *J* = 3.2, 1.6 Hz, 2H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.51 (t, *J* = 2.2 Hz, 1H), 3.88 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 149.72, 147.67, 145.44, 145.12, 143.00, 140.68, 135.91, 133.11, 130.91, 128.79, 127.20, 125.85, 125.32, 124.19, 123.98, 122.73, 112.35, 107.62, 93.58, 31.26. **HRMS (ESI):** Calcd. for $C_{24}H_{17}N_5O_4S_2$ $[M+H]^+$: 504.0795; found: 504.0791.

1-methyl-2-(1*H*-pyrazol-1-yl)-3,5-bis(pyridin-2-ylthio)-1*H*-indole (54)



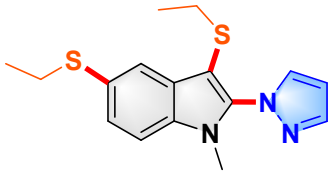
Yellow solid (84.7 mg, 51% yield), m.p.: 207-208 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 4.9 Hz, 1H), 8.35 (d, *J* = 4.2 Hz, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.84 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.39 (dt, *J* = 13.4, 7.8 Hz, 2H), 6.97–6.93 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.79, 160.59, 149.61, 149.31, 142.63, 140.24, 136.82, 136.64, 135.75, 133.54, 130.95, 129.06, 127.70, 122.79, 120.64, 120.25, 119.92, 119.50, 111.69, 107.16, 94.41, 31.10. **HRMS (ESI):** Calcd. for $C_{22}H_{17}N_5S_2$ $[M+H]^+$: 416.0998; found: 416.0995.

1-methyl-3,5-bis((2-methylfuran-3-yl)thio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (55)



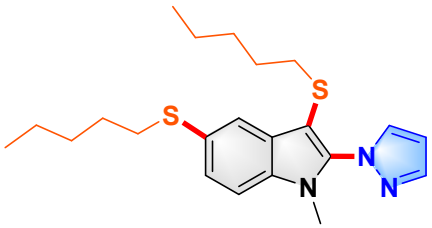
Yellow solid (117.9 mg, 70% yield), m.p.: 86-87 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.4 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 1.9 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 1.9 Hz, 1H), 6.57–6.56 (m, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 5.98 (d, *J* = 1.9 Hz, 1H), 3.62 (s, 3H), 2.41 (s, 3H), 2.18 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 155.99, 153.14, 142.21, 141.07, 140.29, 137.93, 133.88, 133.37, 129.71, 128.55, 123.83, 118.84, 115.34, 114.34, 111.50, 110.57, 109.77, 106.81, 99.40, 30.40, 11.90, 11.58. **HRMS (ESI):** Calcd. for $C_{22}H_{19}N_3O_2S_2$ $[M+H]^+$: 422.0991; found: 422.0986.

3,5-bis(ethylthio)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (56)



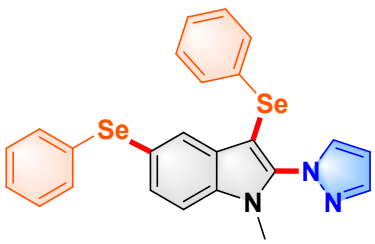
Yellow solid (74.8 mg, 59% yield), m.p.: 89-90 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91–7.88 (m, 1H), 7.88 (d, *J* = 2.5 Hz, 2H), 7.42 (d, *J* = 10.1 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.54 (t, *J* = 2.0 Hz, 1H), 3.66 (s, 3H), 2.98 (q, *J* = 7.3 Hz, 2H), 2.55 (q, *J* = 7.3 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.12, 138.75, 134.04, 133.74, 129.19, 127.53, 127.35, 123.06, 110.44, 106.66, 98.94, 30.44, 30.36, 29.96, 15.08, 14.66. **HRMS (ESI):** Calcd. for $C_{16}H_{19}N_3S_2$ $[M+H]^+$: 318.1093; found: 318.1085.

1-methyl-3,5-bis(pentylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (57)



Yellow liquid (72.2 mg, 45% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90–7.85 (m, 3H), 7.42 (d, *J* = 6.7 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.54 (t, *J* = 2.1 Hz, 1H), 3.66 (s, 3H), 2.99–2.95 (m, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.47–1.42 (m, 2H), 1.38–1.32 (m, 4H), 1.19 (h, *J* = 3.7 Hz, 4H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.84–0.81 (m, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.10, 138.64, 133.97, 133.75, 129.08, 127.95, 127.18, 122.78, 110.41, 106.62, 99.24, 36.49, 35.95, 30.98, 30.51, 30.43, 29.30, 29.08, 22.31, 22.19, 14.02, 13.97. **HRMS (ESI):** Calcd. for $C_{22}H_{31}N_3S_2$ $[M+H]^+$: 402.2032; found: 402.2027.

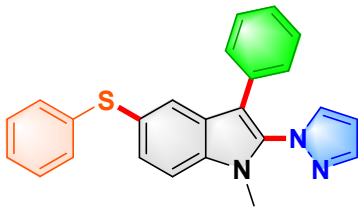
1-methyl-3,5-bis(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (58)



White solid (166.6 mg, 82% yield), m.p.: 129-130 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.51 (d, *J* = 6.8 Hz,

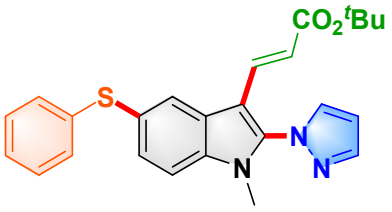
1H), 7.43 (d, J = 8.5 Hz, 1H), 7.27–7.24 (m, 3H), 7.24–7.21 (m, 3H), 7.17 (t, J = 7.0 Hz, 4H), 6.50 (t, J = 2.2 Hz, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.44, 139.81, 138.87, 135.47, 133.61, 132.86, 129.83, 129.53, 129.28, 129.26, 128.96, 128.28, 126.99, 126.23, 125.77, 125.73, 111.28, 106.89, 92.79, 30.84. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3Se_2$ $[M+H]^+$: 510.0101; found: 510.0098.

1-methyl-3-phenyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (59)



White solid (78.1 mg, 82% yield), m.p.: 127-128 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.95 (d, J = 4.2 Hz, 1H), 7.91–7.89 (m, 1H), 7.75 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 8.3 Hz, 3H), 7.54 (d, J = 8.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37–7.34 (m, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.17–7.14 (m, 2H), 7.11 (t, J = 6.8 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 3.83 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.38, 141.79, 139.56, 135.14, 134.87, 133.49, 129.00, 128.76, 128.71, 127.45, 126.79, 126.00, 125.19, 123.59, 118.47, 110.47, 106.92, 95.82, 30.90. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S$ $[M+H]^+$: 382.1372; found: 382.1375.

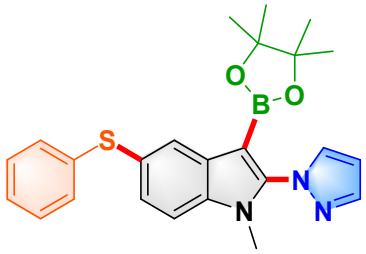
***tert*-butyl (*E*)-3-(1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)acrylate (60)**



White solid (97.0 mg, 90% yield), m.p.: 153-154 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, J = 1.5 Hz, 1H), 7.85–7.84 (m, 1H), 7.75–7.71 (m, 2H), 7.58 (d, J = 10.1 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.19 (t, J = 7.8 Hz, 2H), 7.10 (t, J = 7.5 Hz, 3H), 6.48–6.45 (m, 1H), 6.40 (d, J = 15.9 Hz, 1H), 3.78 (s, 3H), 1.56 (s, 9H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 166.64, 144.44, 142.49, 139.86, 138.07, 136.27, 133.44, 129.04, 128.48, 128.43, 126.07, 125.36,

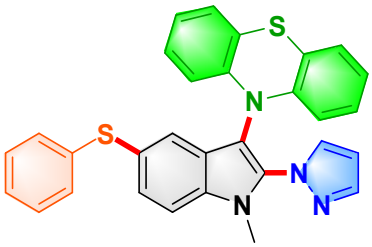
123.47, 120.75, 118.42, 110.65, 107.03, 96.38, 80.25, 30.97, 28.28. **HRMS (ESI):** Calcd. for $C_{25}H_{25}N_3O_2S$ $[M+H]^+$: 432.1740; found: 432.1731.

1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (61)



Yellow solid (79.7 mg, 74% yield), m.p.: 111-112 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.88–7.84 (m, 2H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 6.9 Hz, 3H), 6.46–6.43 (m, 1H), 3.80 (s, 3H), 1.39 (s, 12H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.32, 139.37, 138.95, 137.32, 133.45, 130.00, 128.93, 127.95, 127.66, 125.72, 124.95, 109.43, 106.85, 95.87, 83.70, 30.81, 24.93. **HRMS (ESI):** Calcd. for $C_{24}H_{26}BN_3O_2S$ $[M+H]^+$: 431.1948; found: 431.1956.

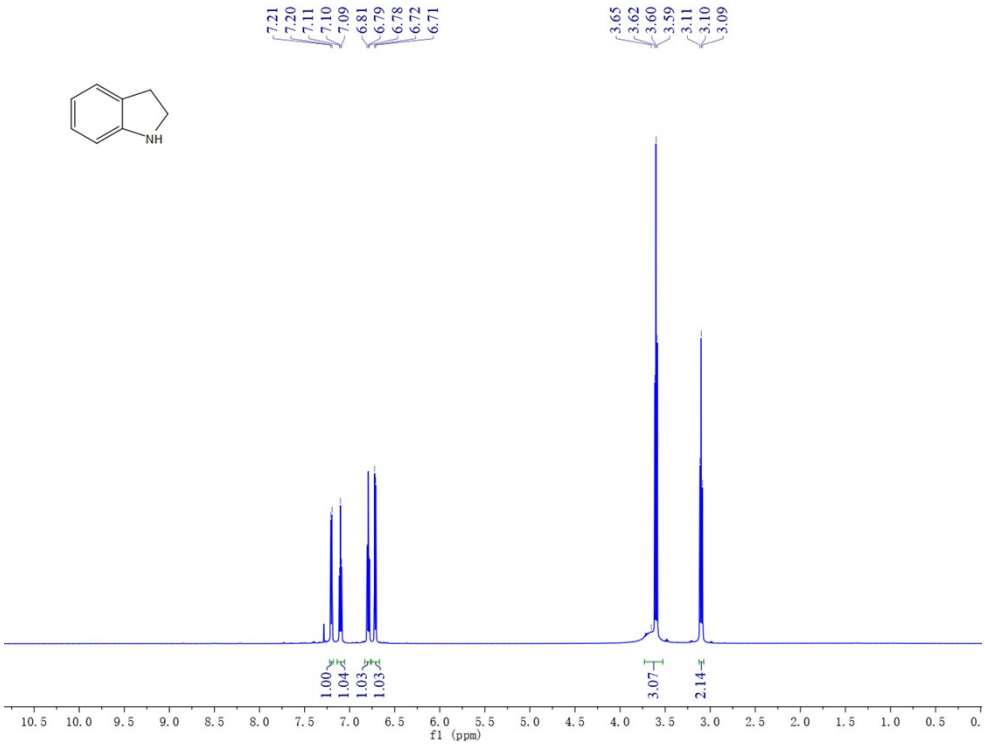
10-(1-methyl-5-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)-10*H*-phenothiazine (62)



White solid (109.2 mg, 87% yield), m.p.: 177-178 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 4H), 7.15 (t, *J* = 6.4 Hz, 1H), 7.05 (d, *J* = 5.7 Hz, 2H), 6.86 (p, *J* = 7.1 Hz, 4H), 6.49 (d, *J* = 7.6 Hz, 2H), 6.42 (t, *J* = 2.2 Hz, 1H), 3.95 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 144.11, 142.35, 133.59, 133.16, 132.41, 129.01, 128.94, 128.38, 127.28, 126.88, 125.87, 125.04, 124.94, 122.97, 121.04, 115.86, 111.61, 107.93, 107.54, 31.17. **HRMS (ESI):** Calcd. for $C_{30}H_{22}N_4S_2$ $[M+H]^+$: 503.1359; found: 503.1355.

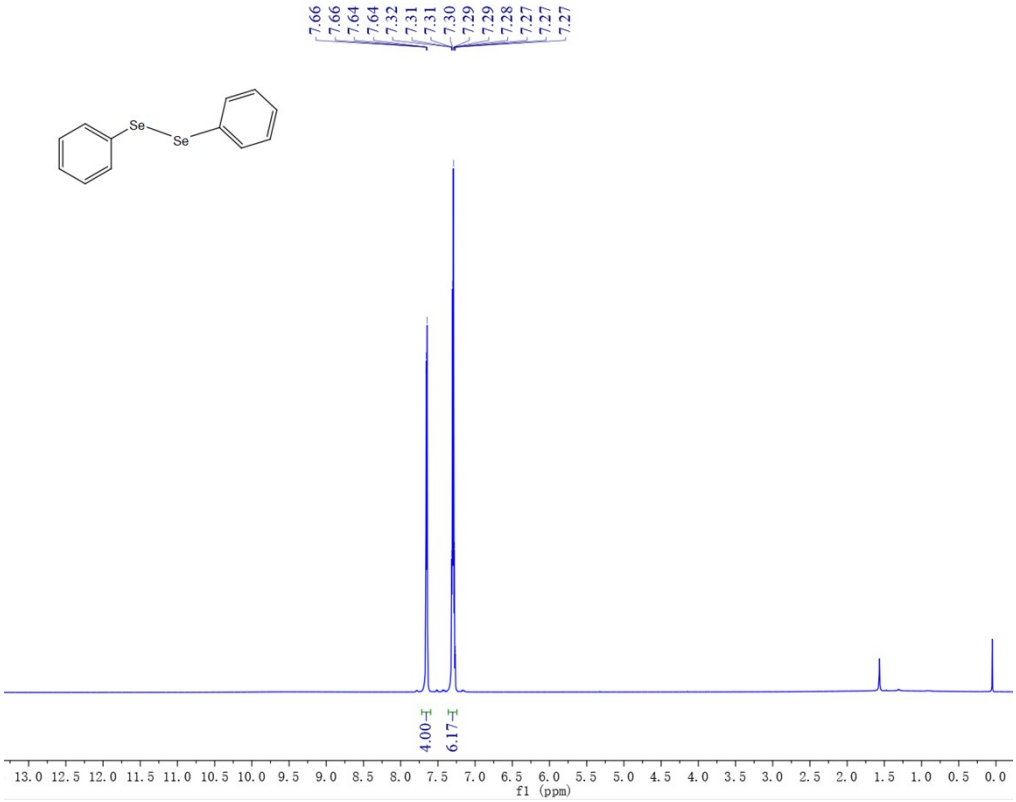
10. NMR spectra of the obtained compounds.

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

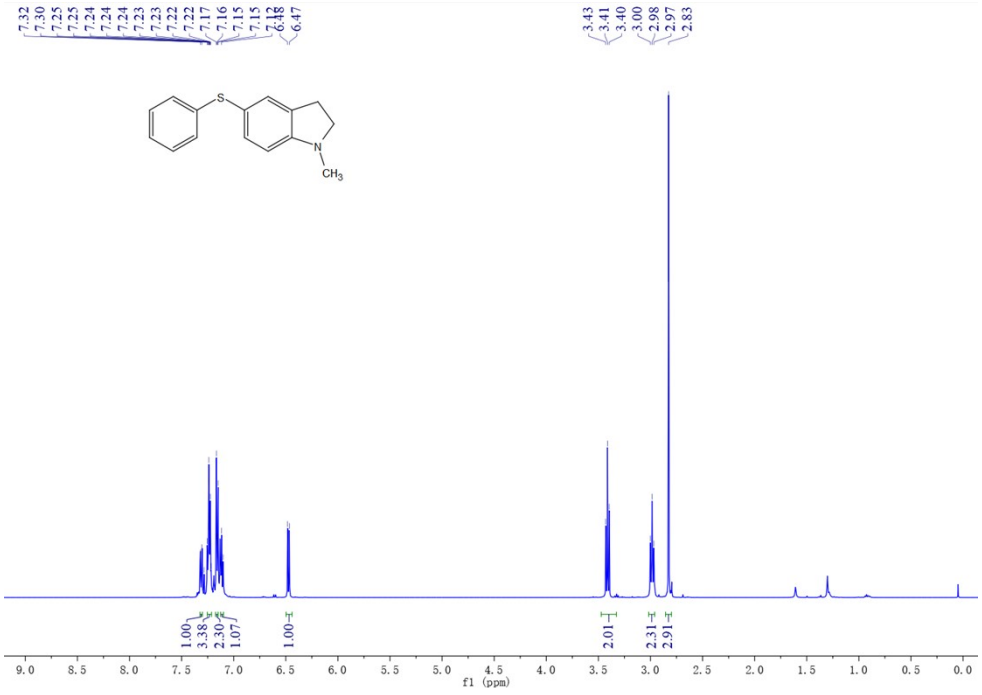


(2) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3e

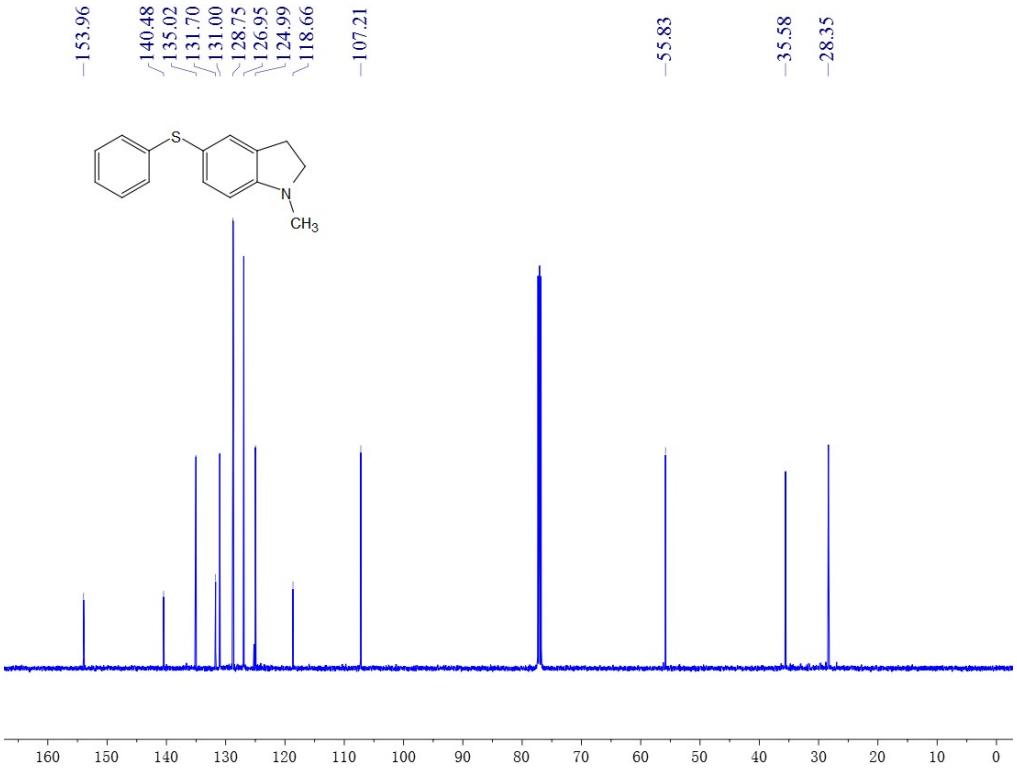
(3) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3p



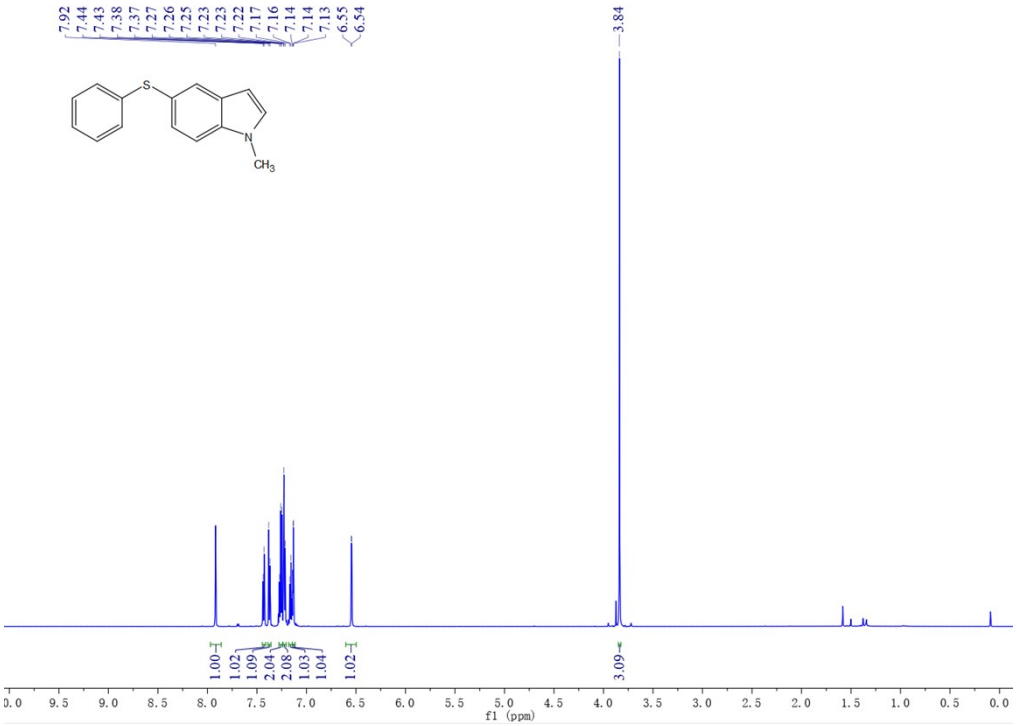
(4) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-1



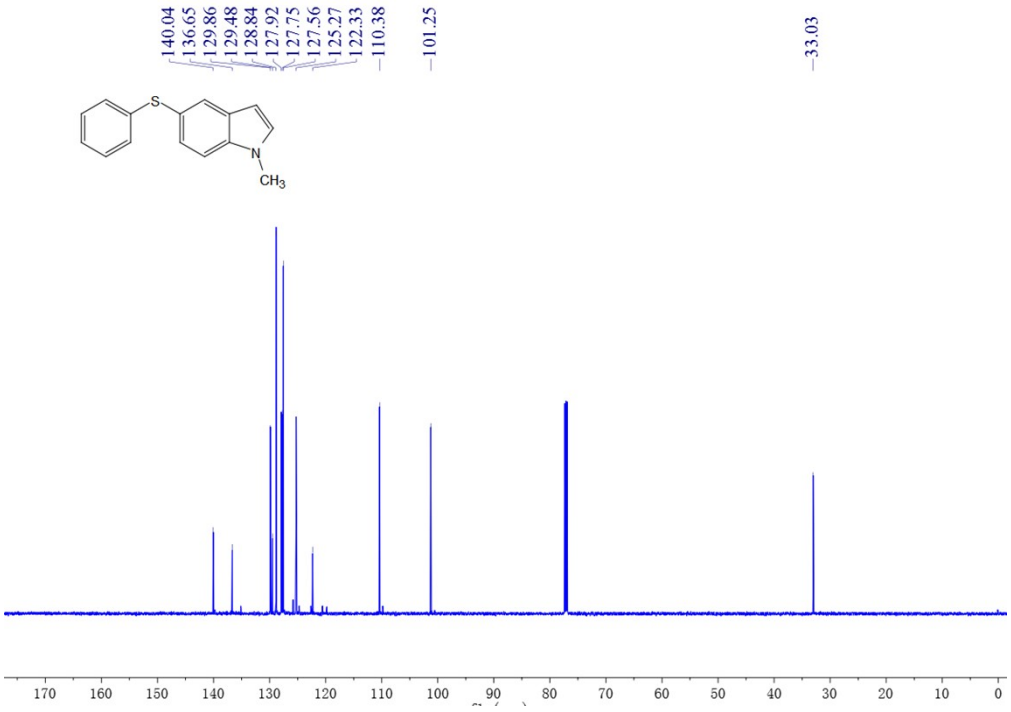
(5) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-1



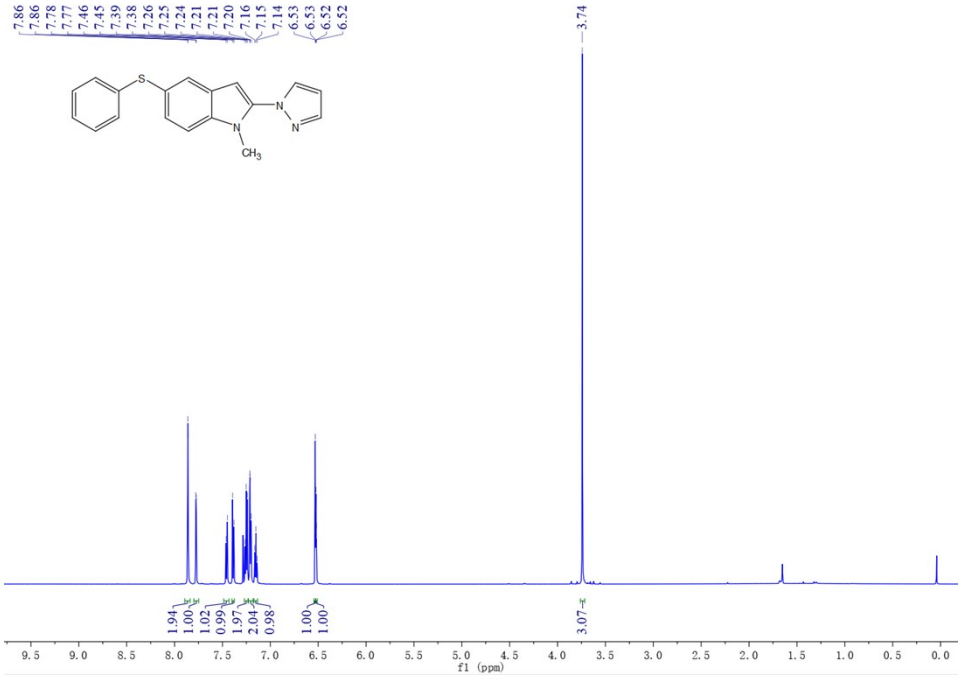
(6) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-2



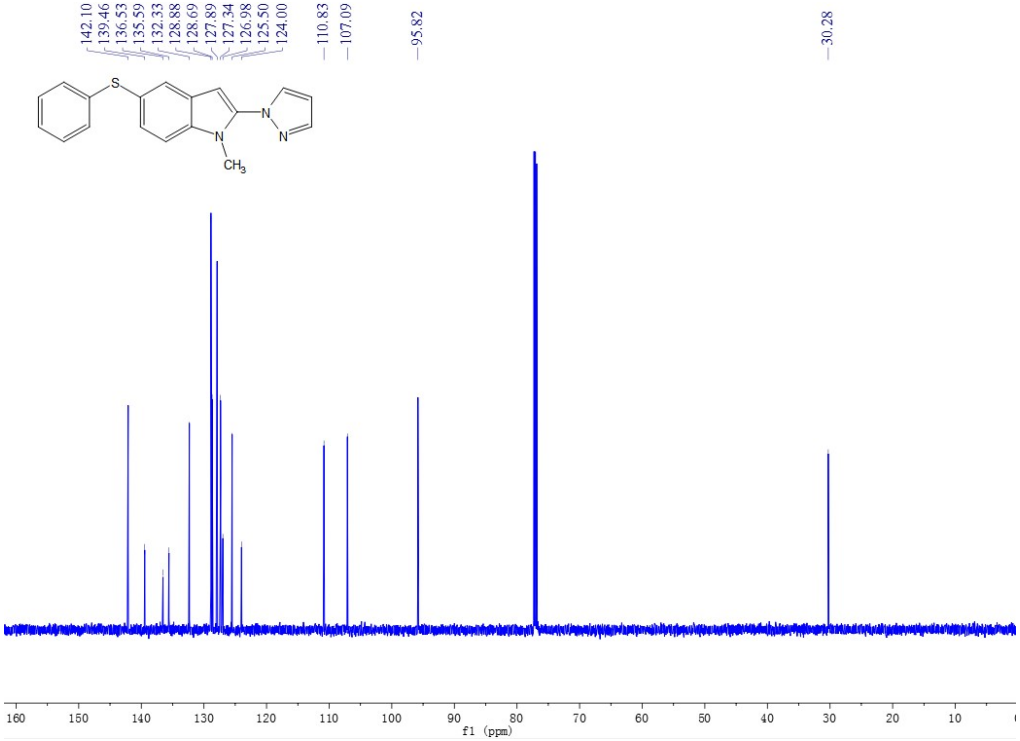
(7) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-2



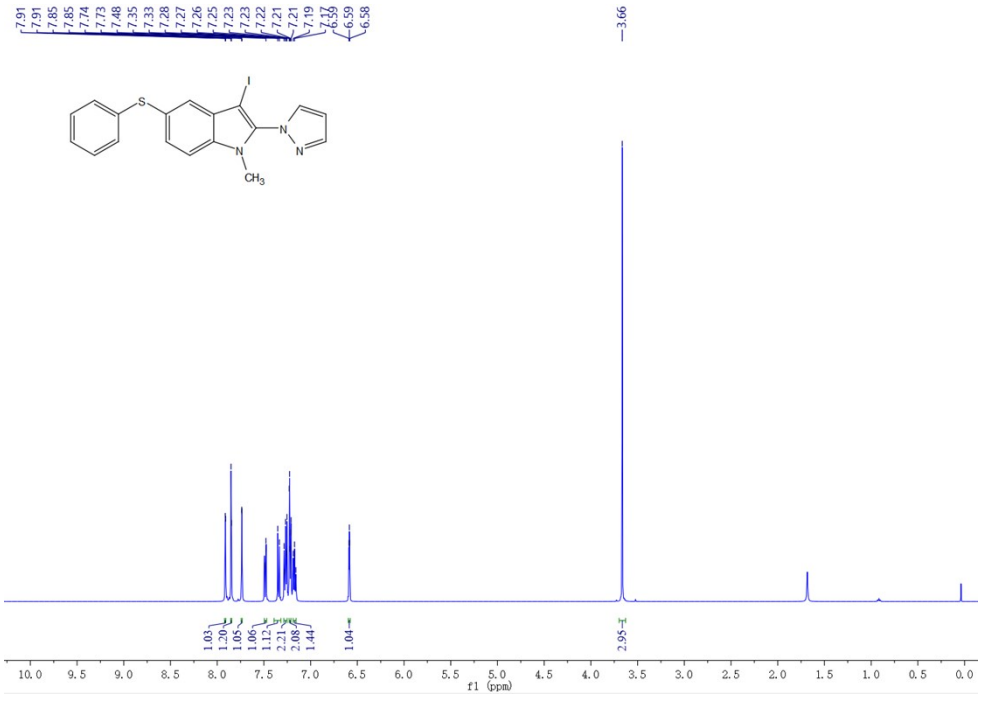
(8) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-3



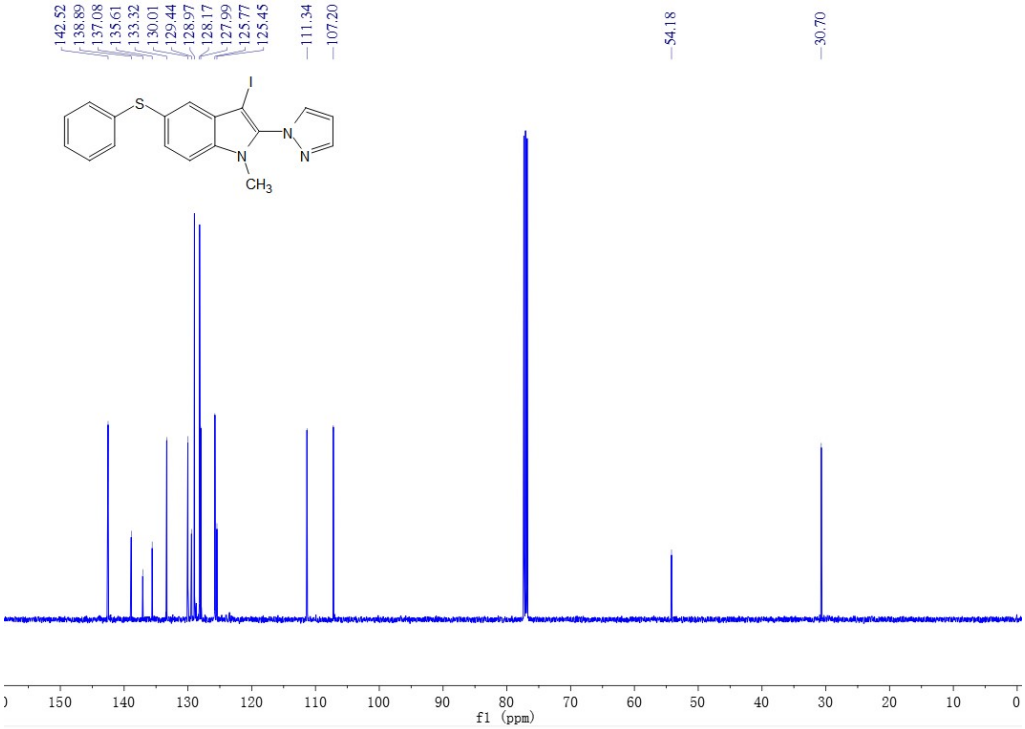
(9) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-3



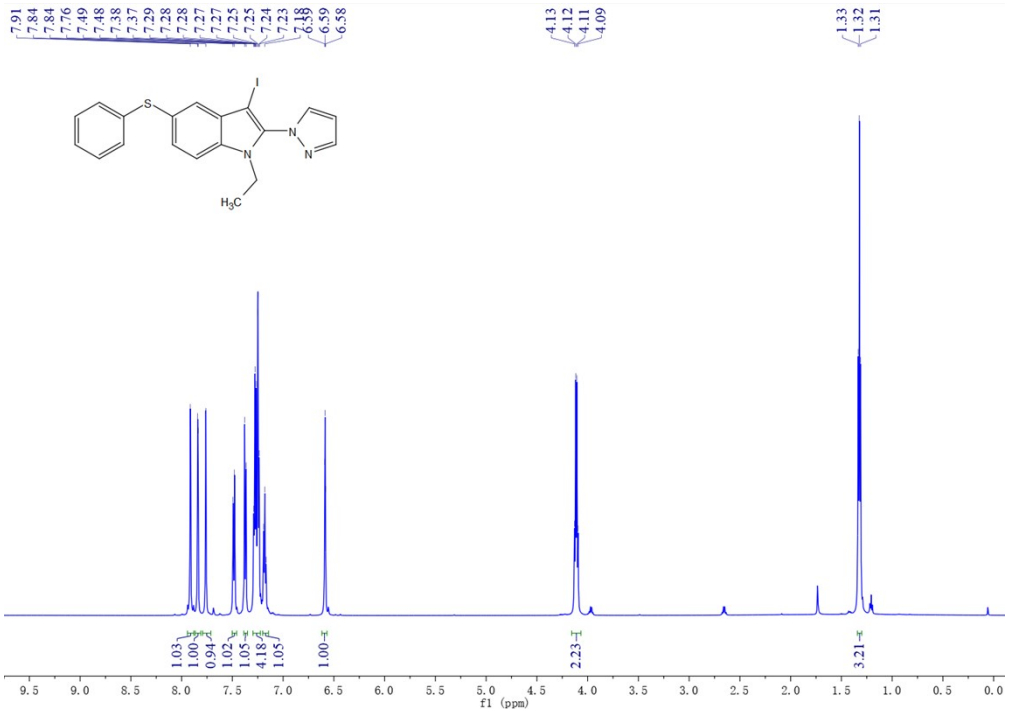
(10) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 4



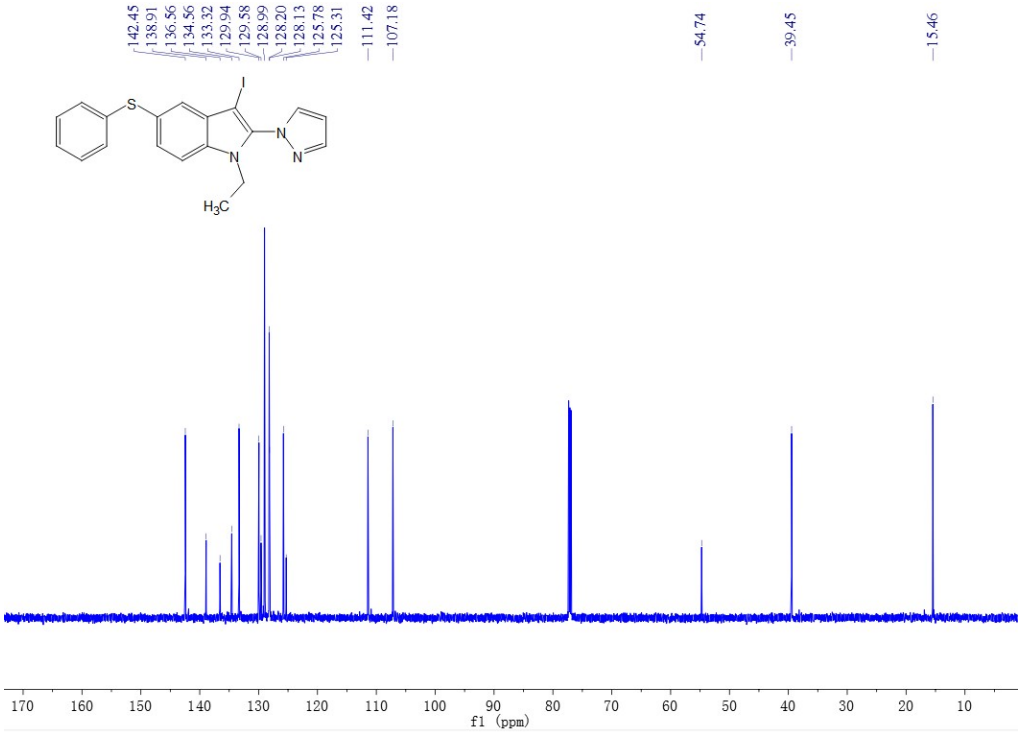
(11) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 4



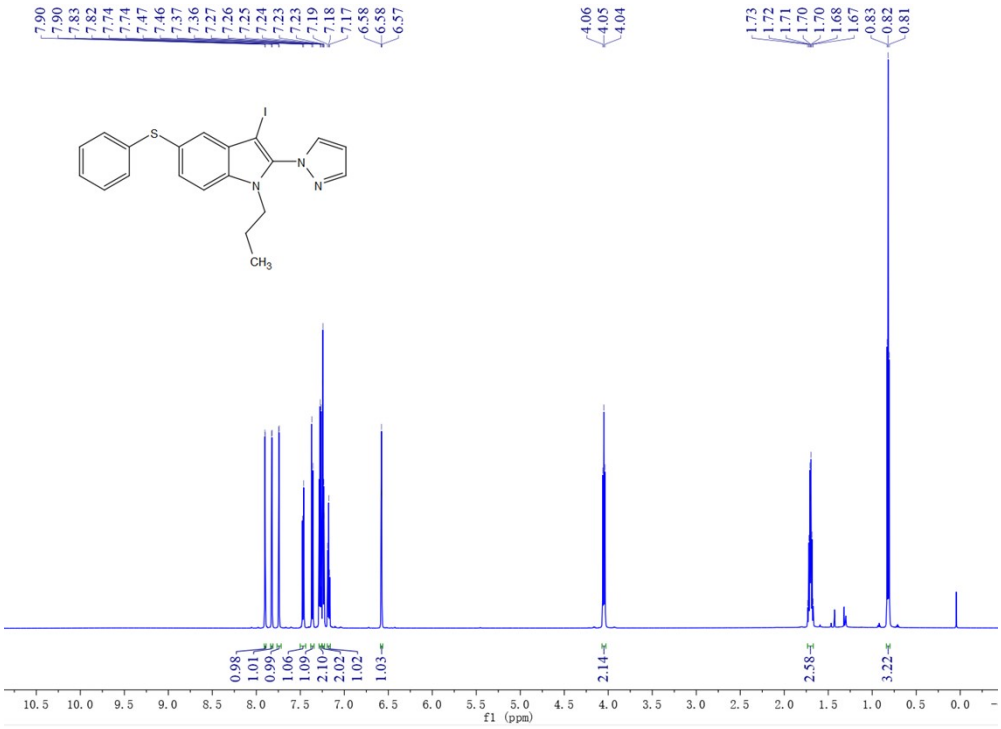
(12) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 5



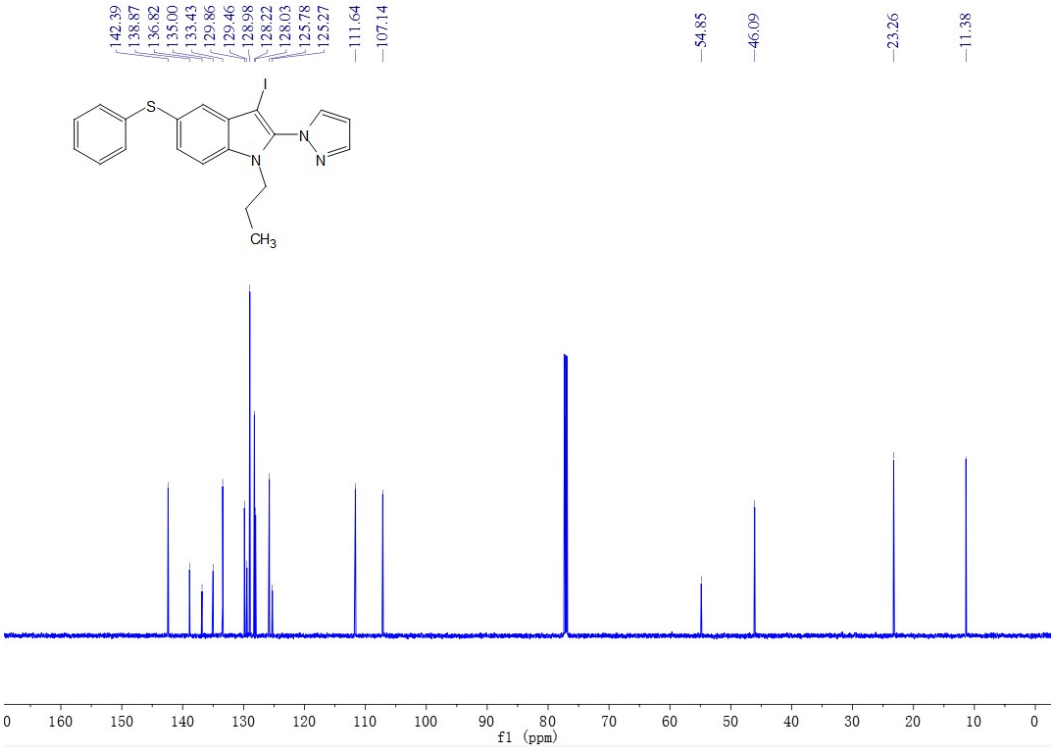
(13) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 5



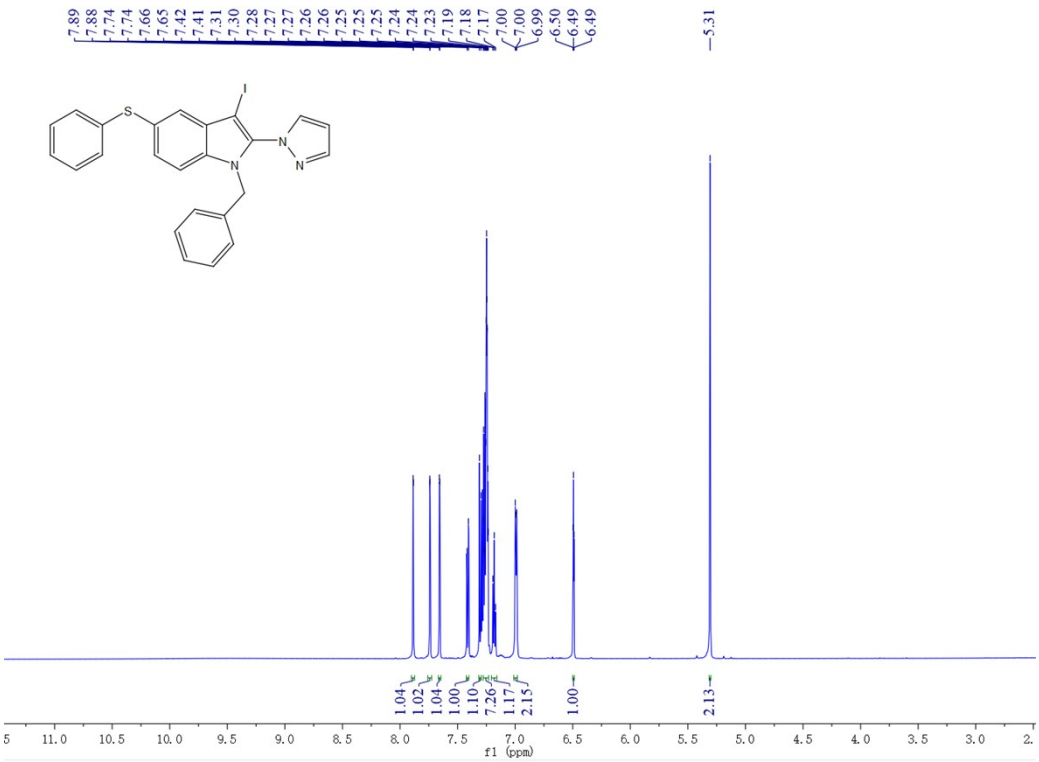
(14) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 6



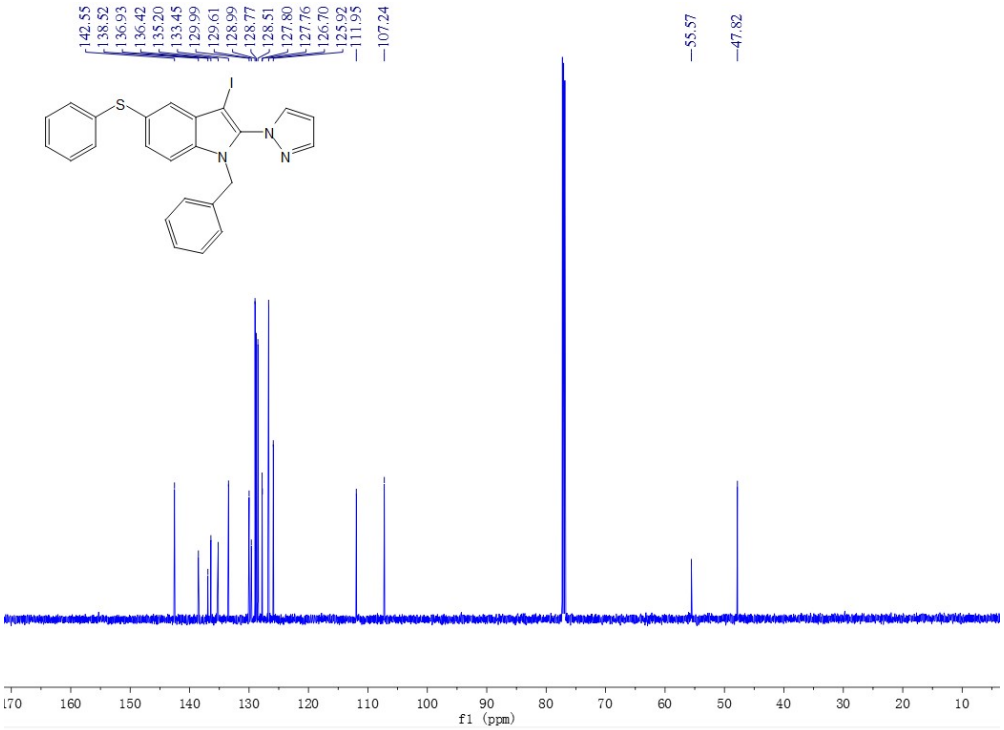
(15) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 6



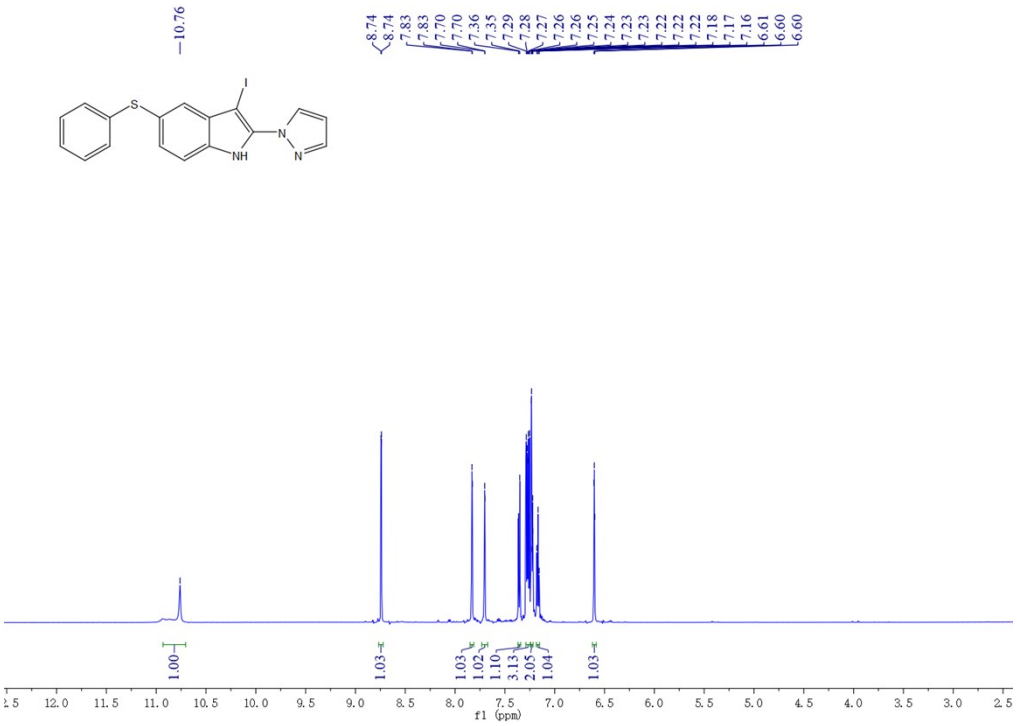
(16) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 7



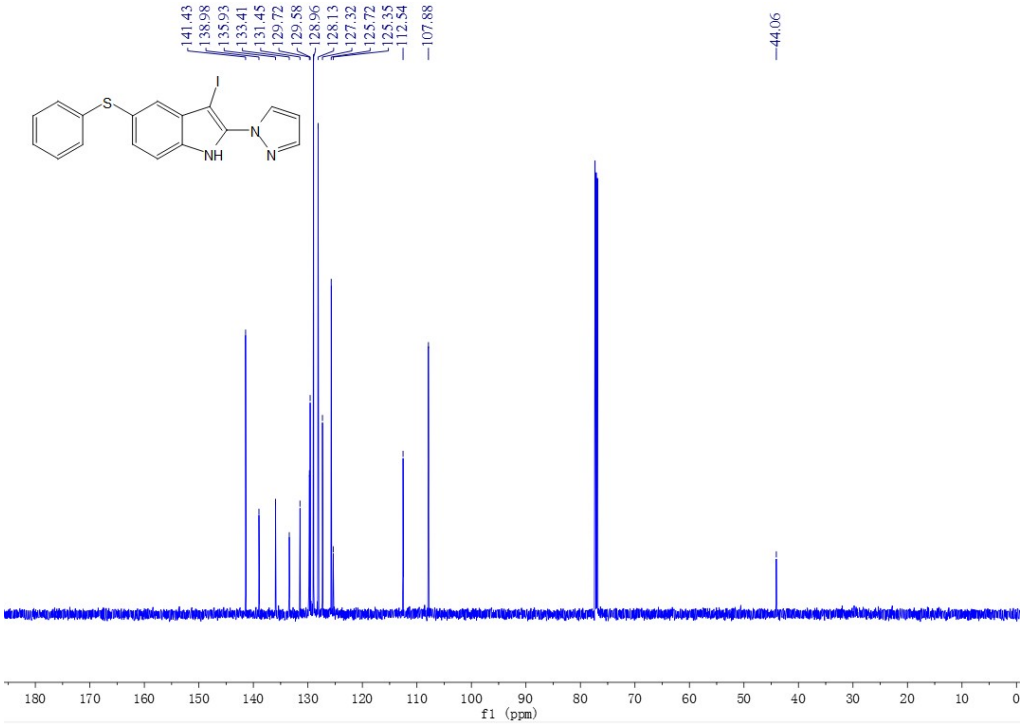
(17) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 7



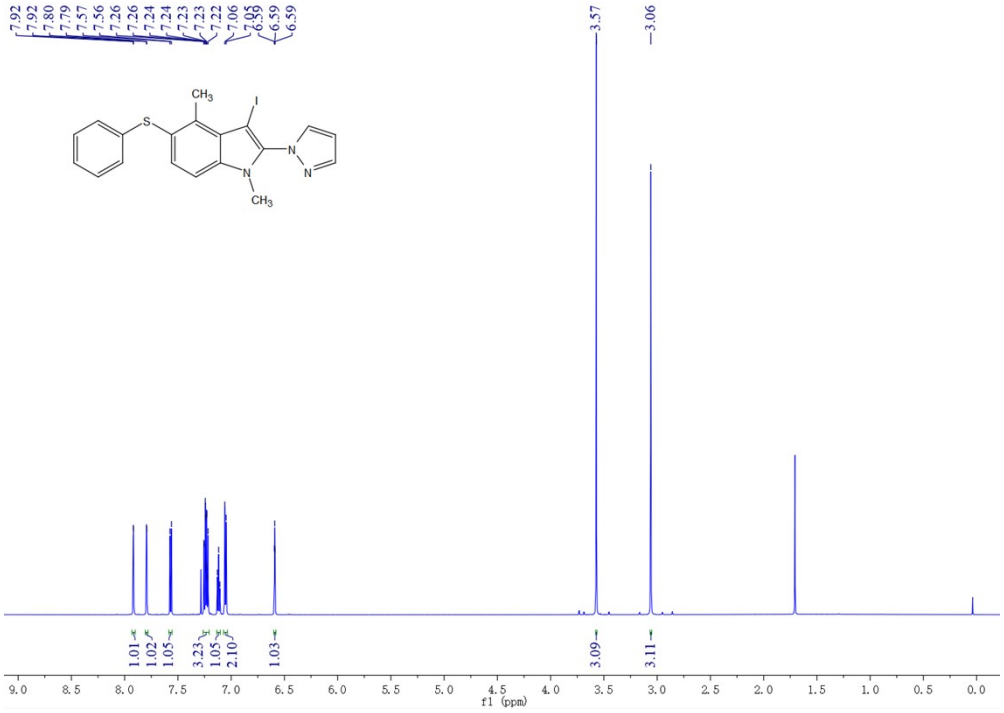
(18) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 8



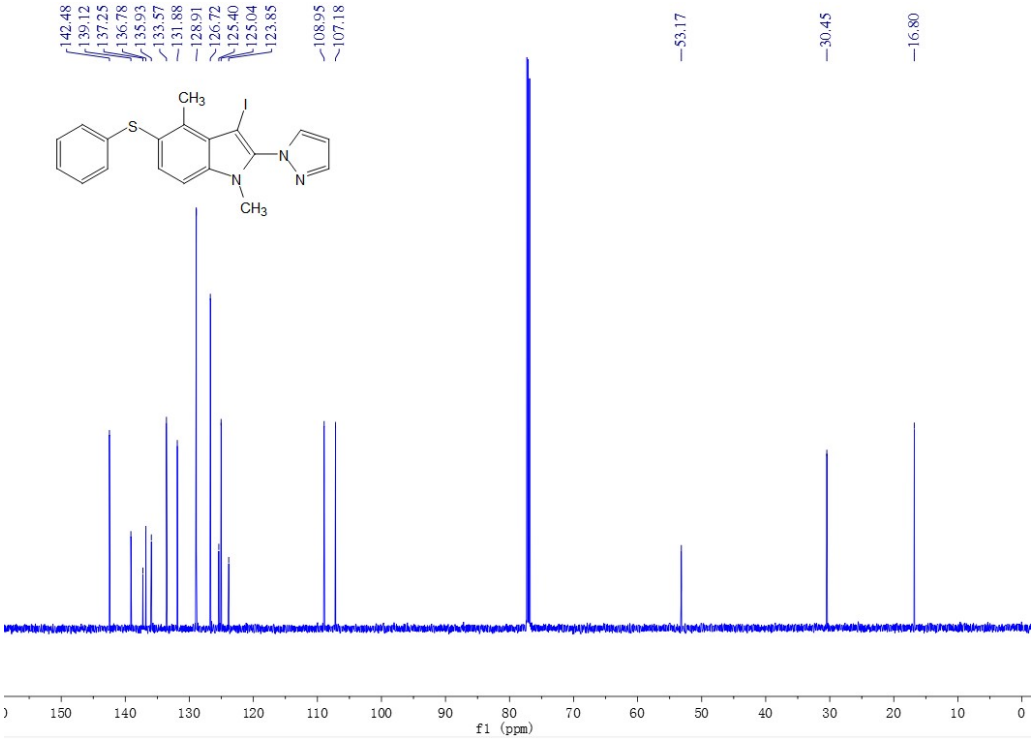
(19) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 8



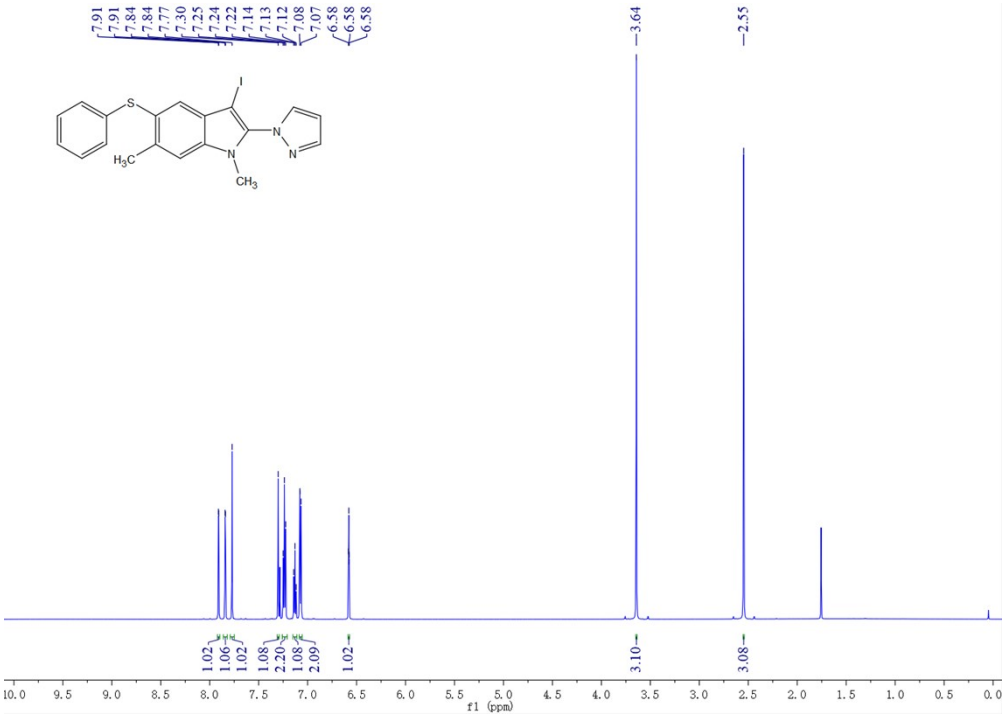
(20) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 10



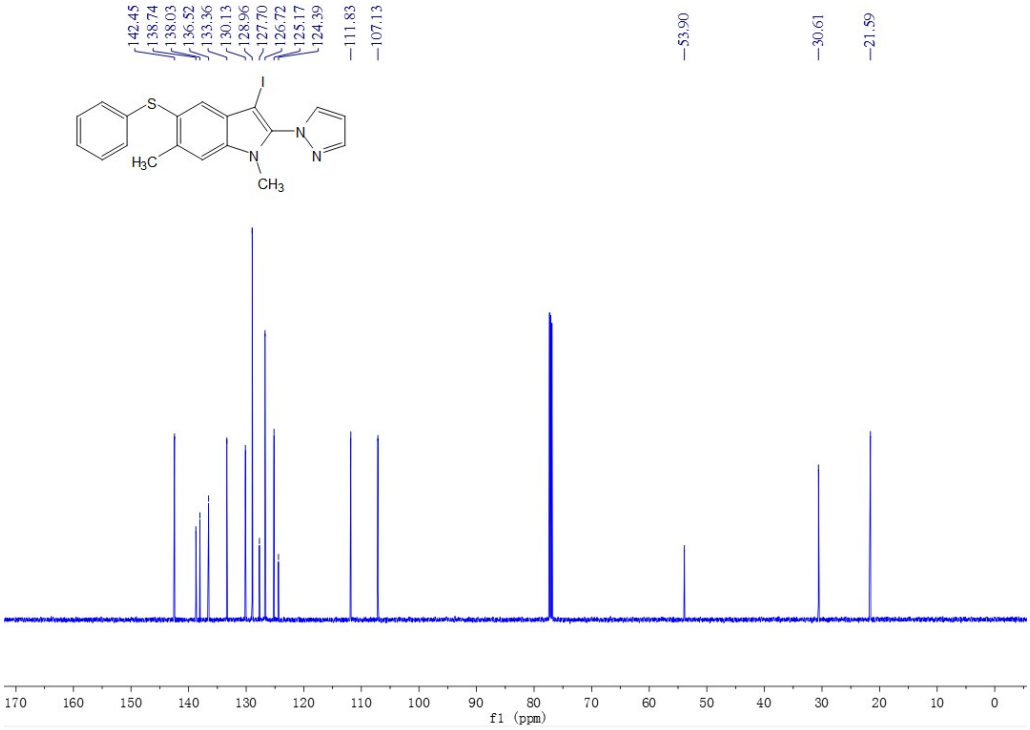
(21) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 10



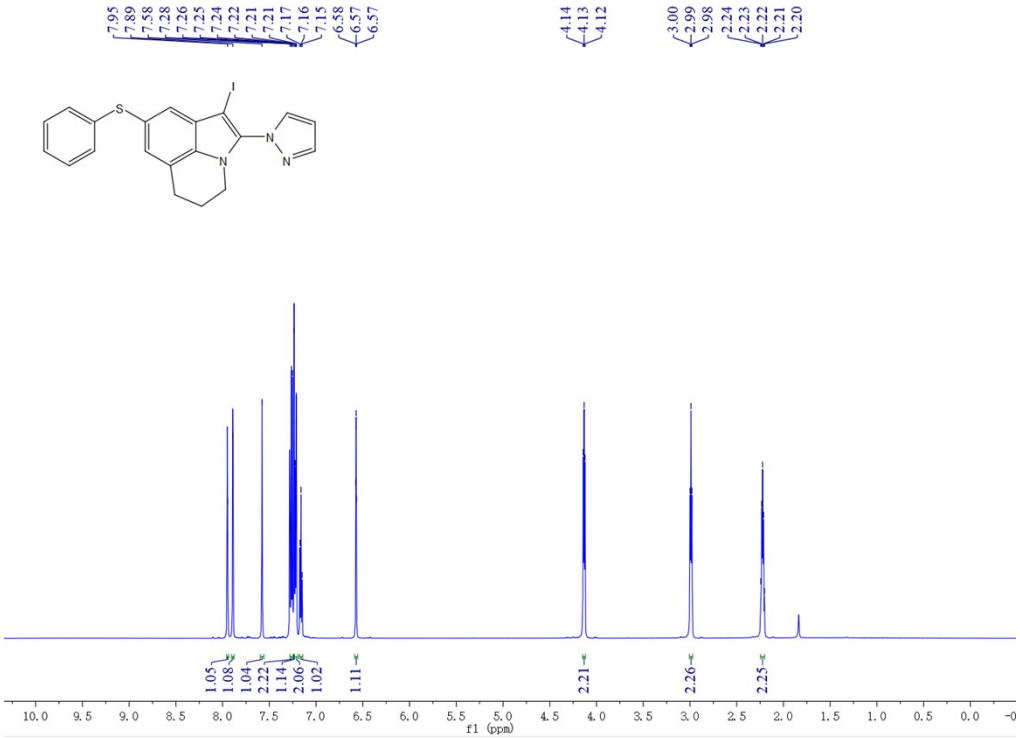
(22) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 11



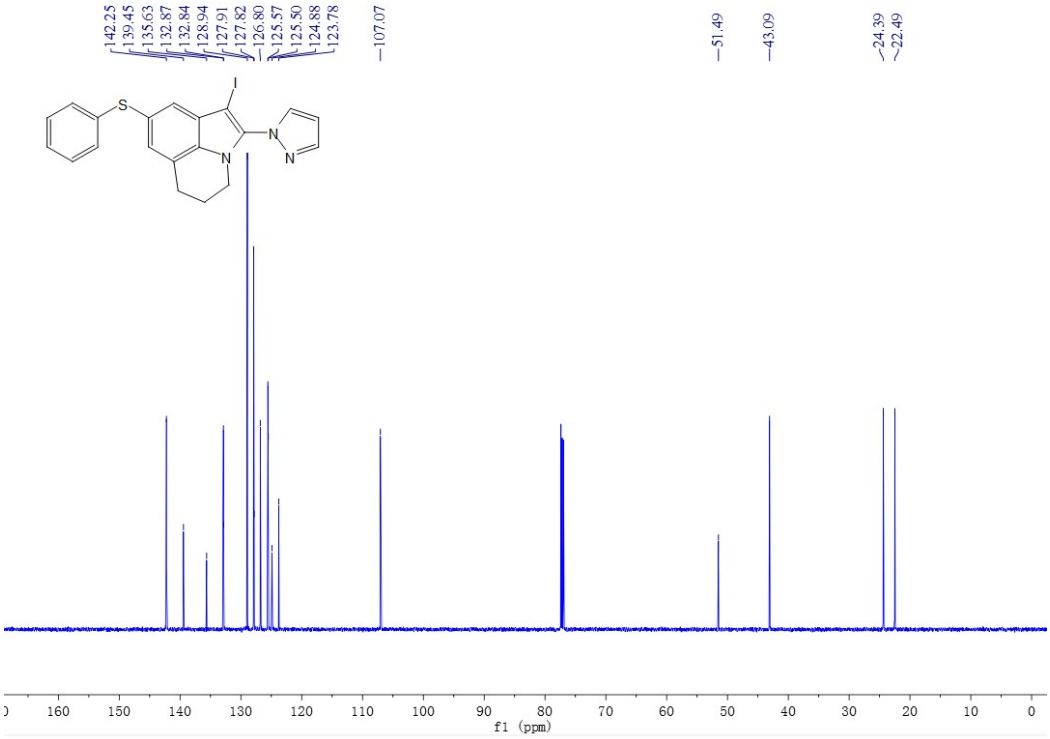
(23) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 11



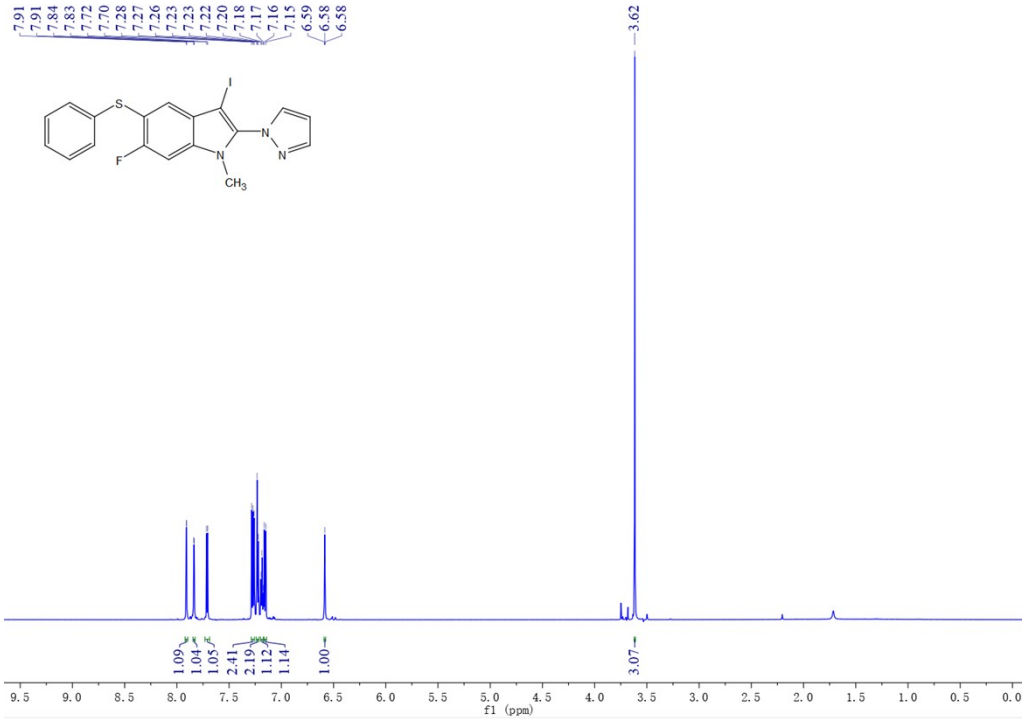
(24) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 12



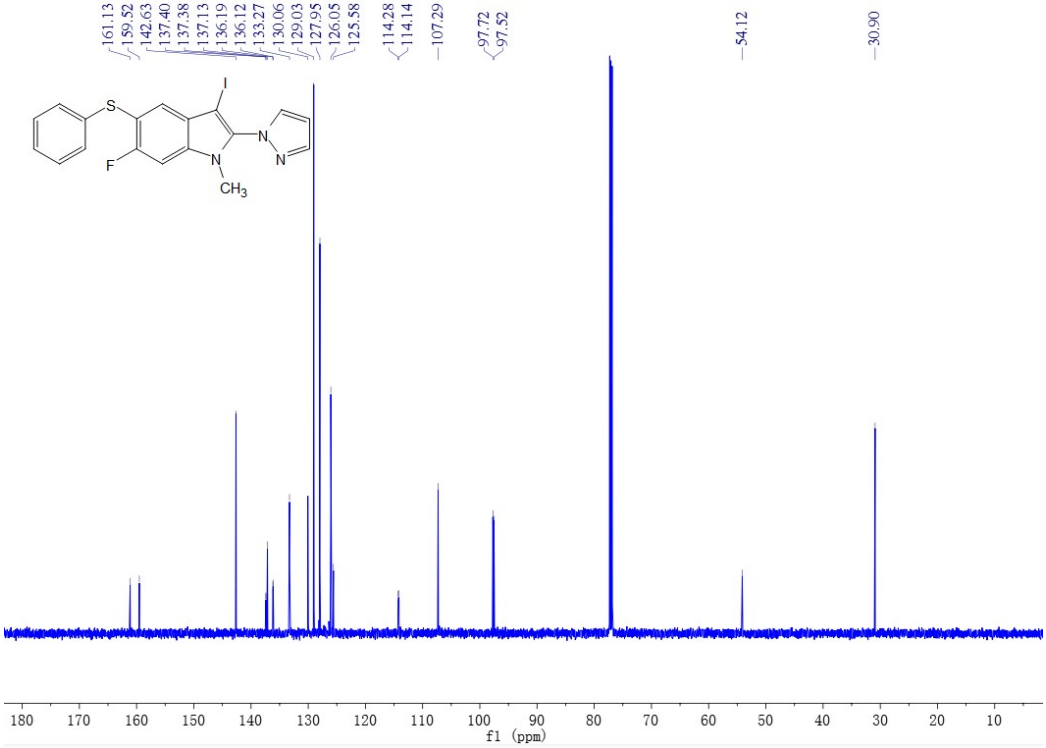
(25) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 12



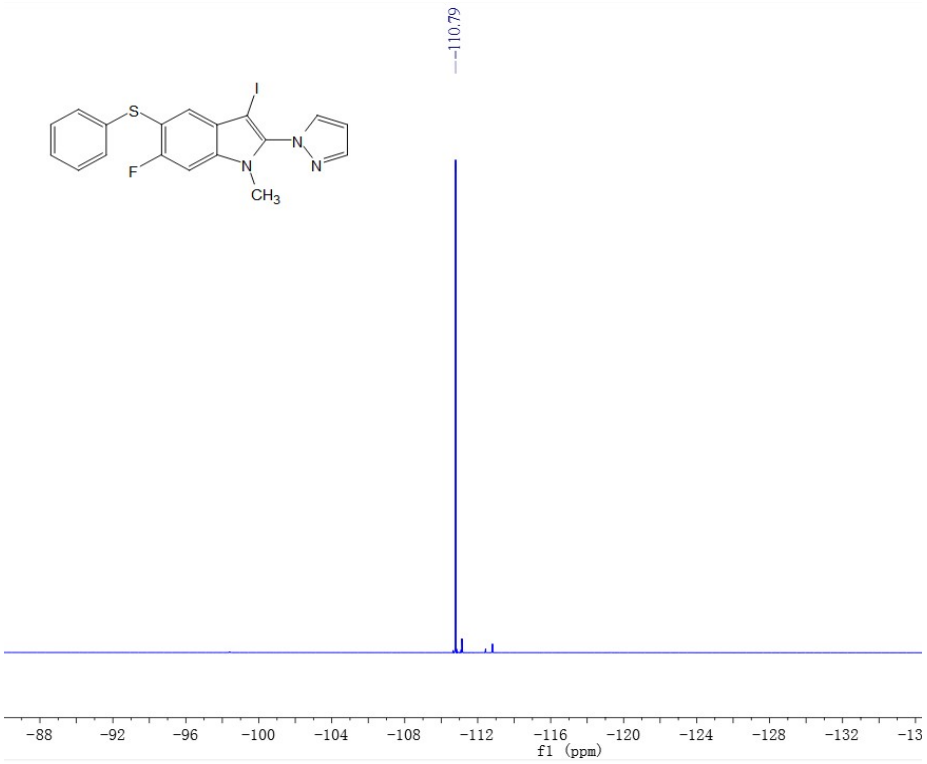
(26) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 13



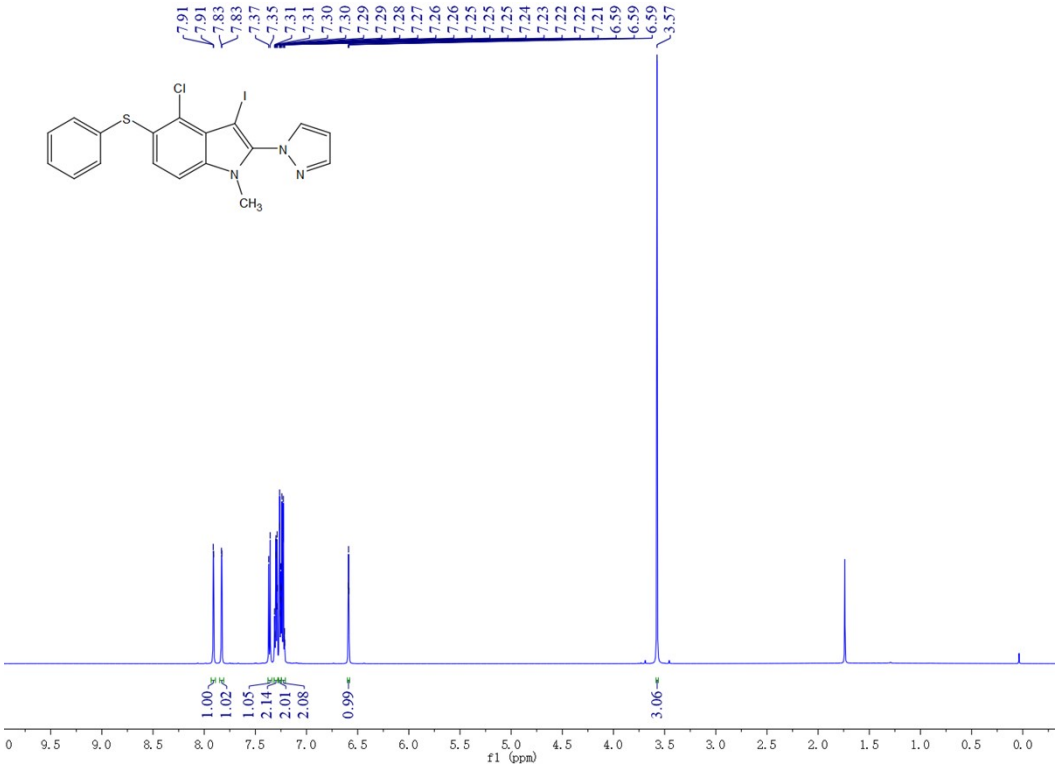
(27) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 13



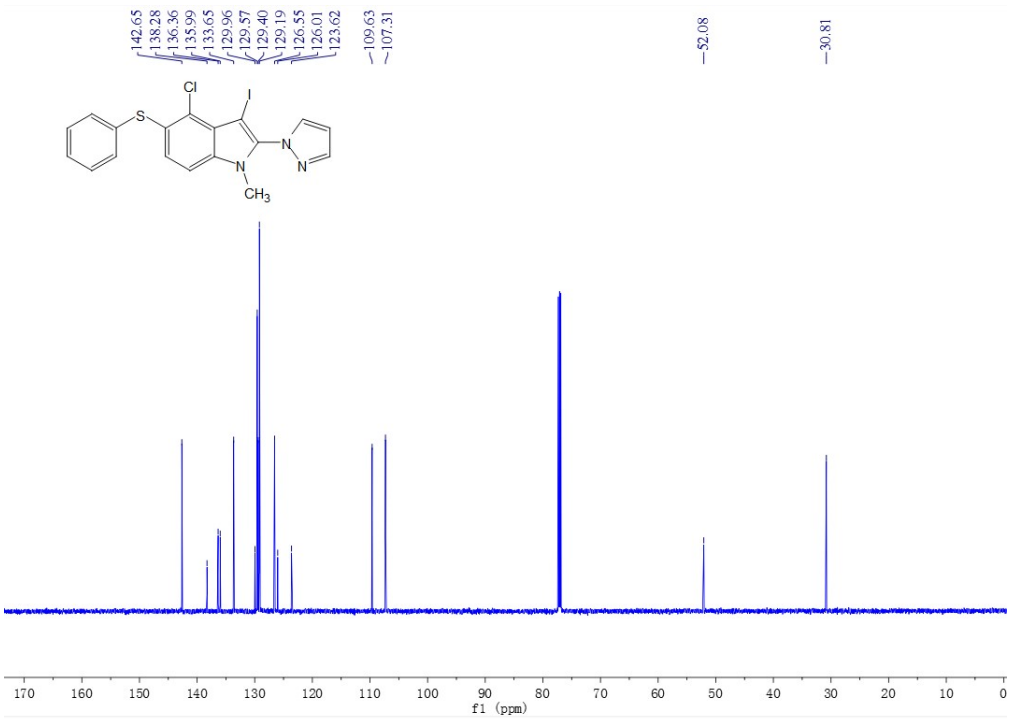
(28) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 13



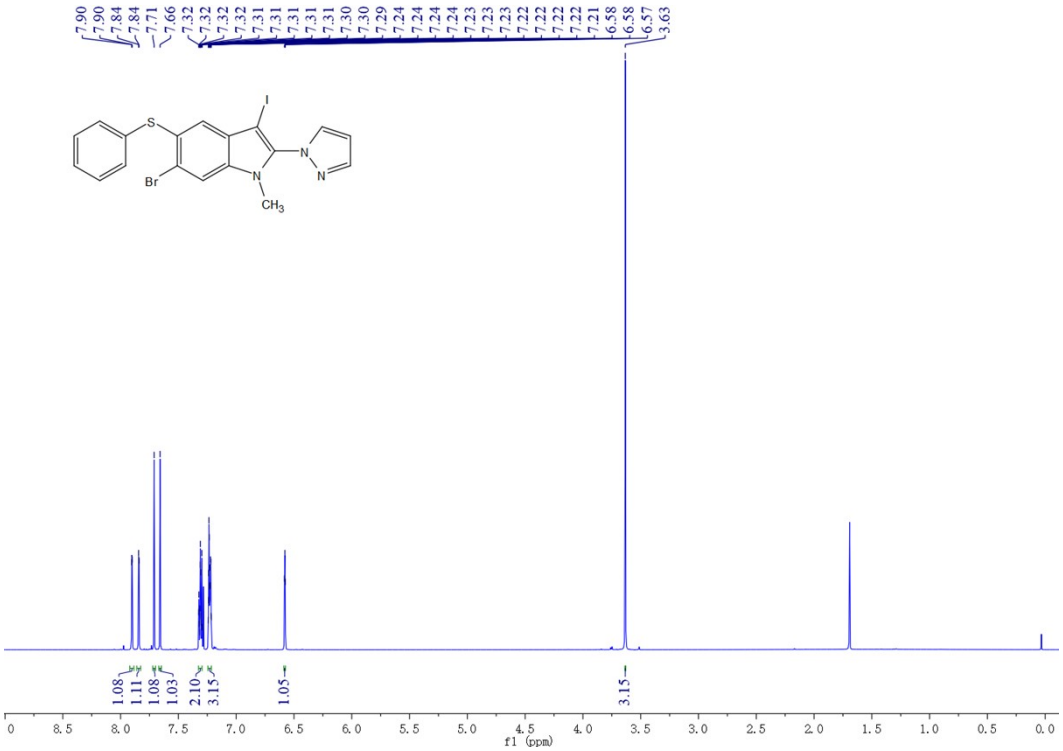
(29) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 14



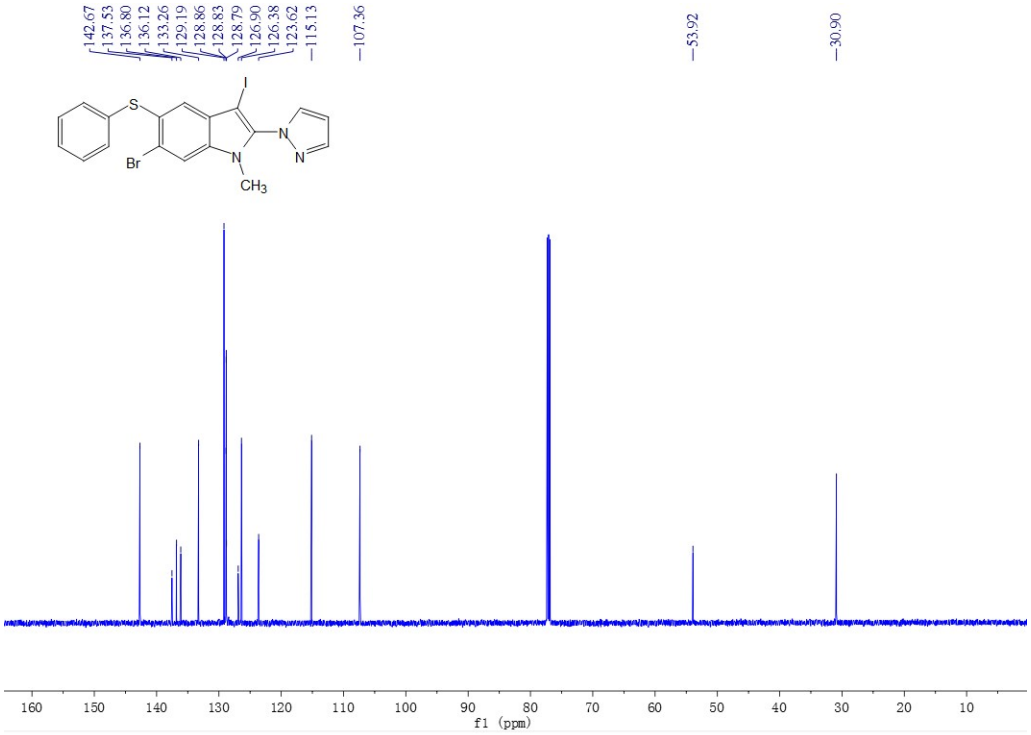
(30) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 14



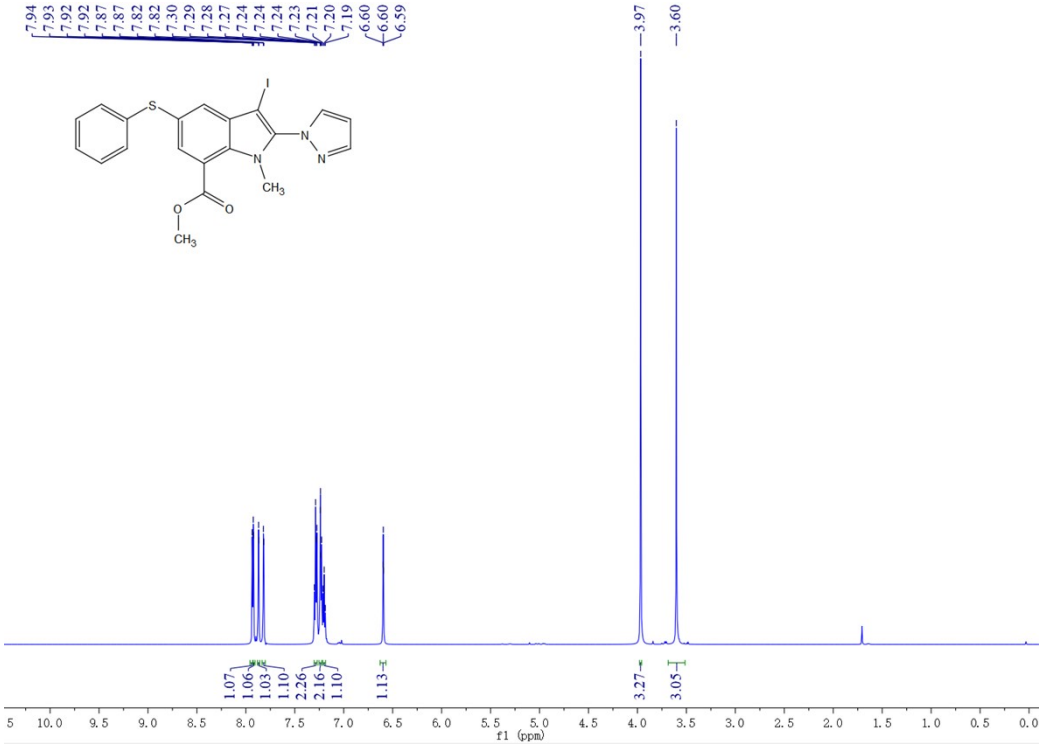
(31) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 15



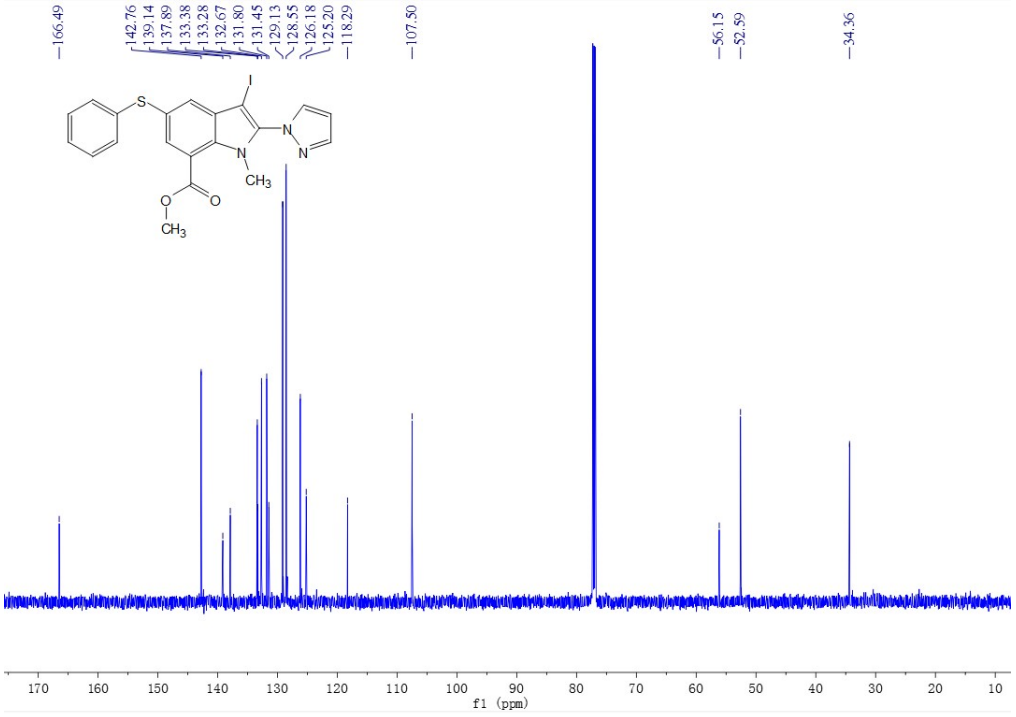
(32) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 15



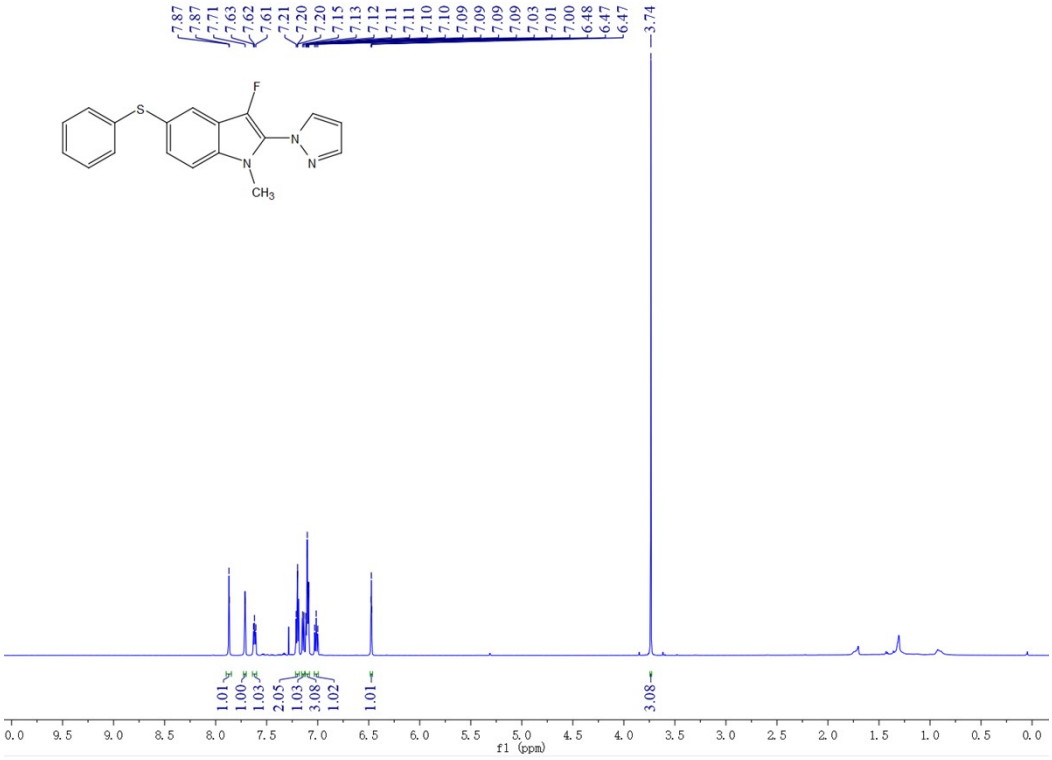
(33) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 16



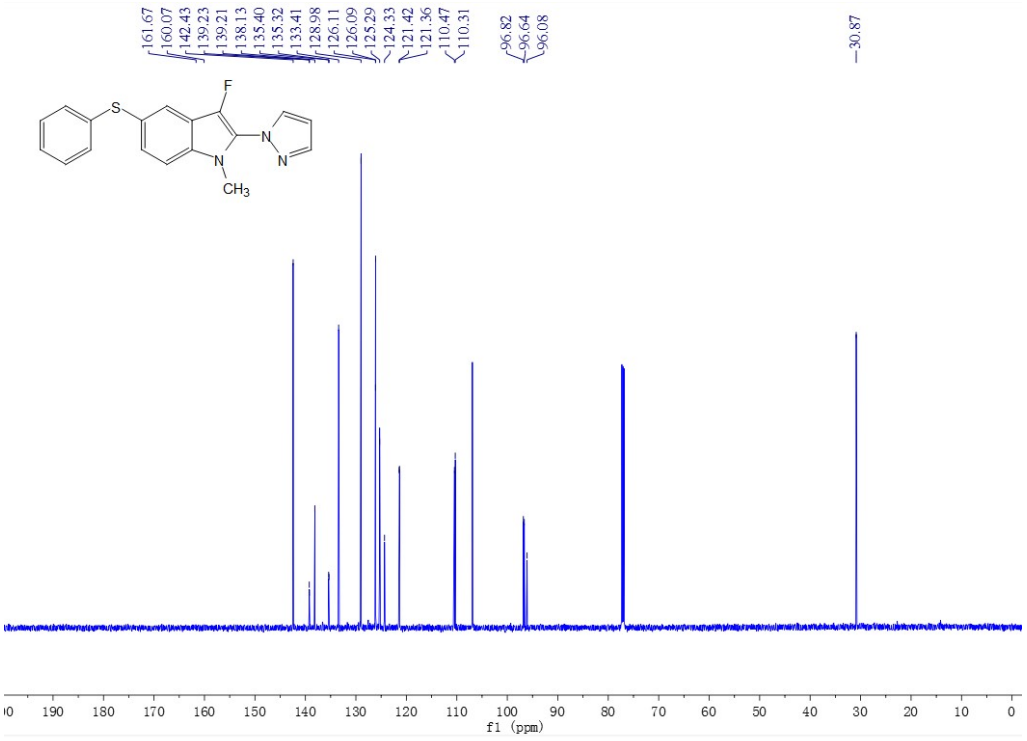
(34) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 16



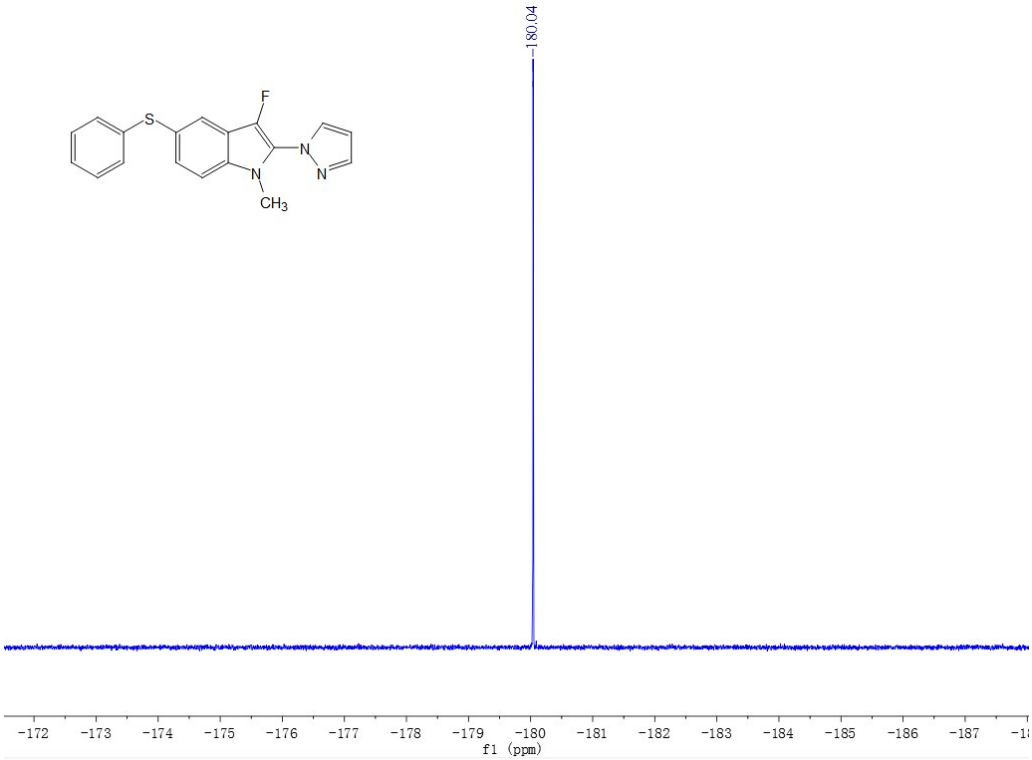
(35) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 17



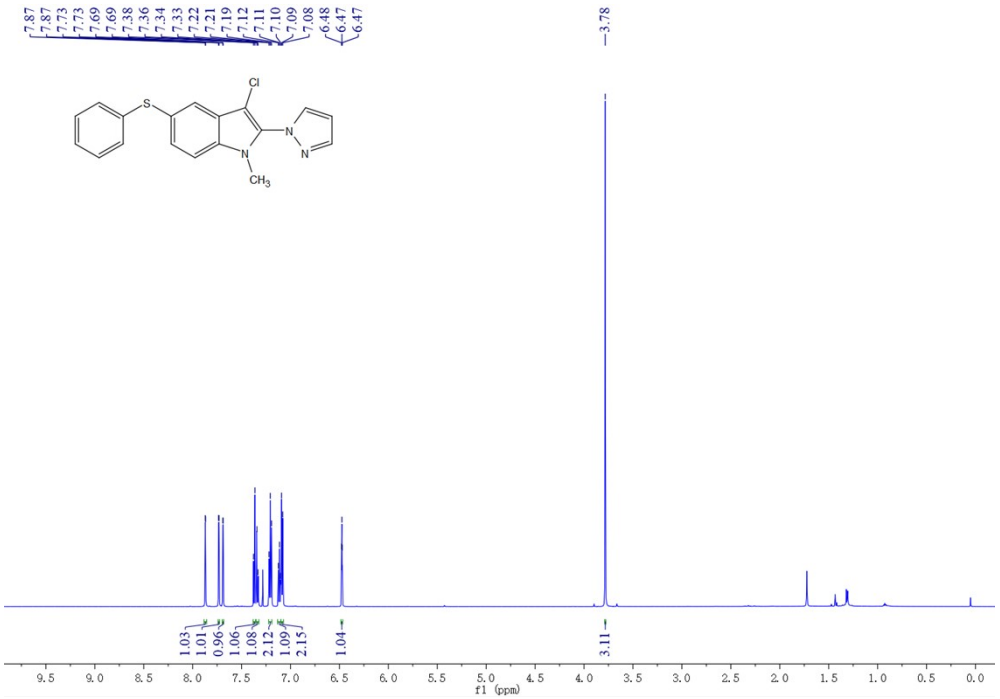
(36) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 17



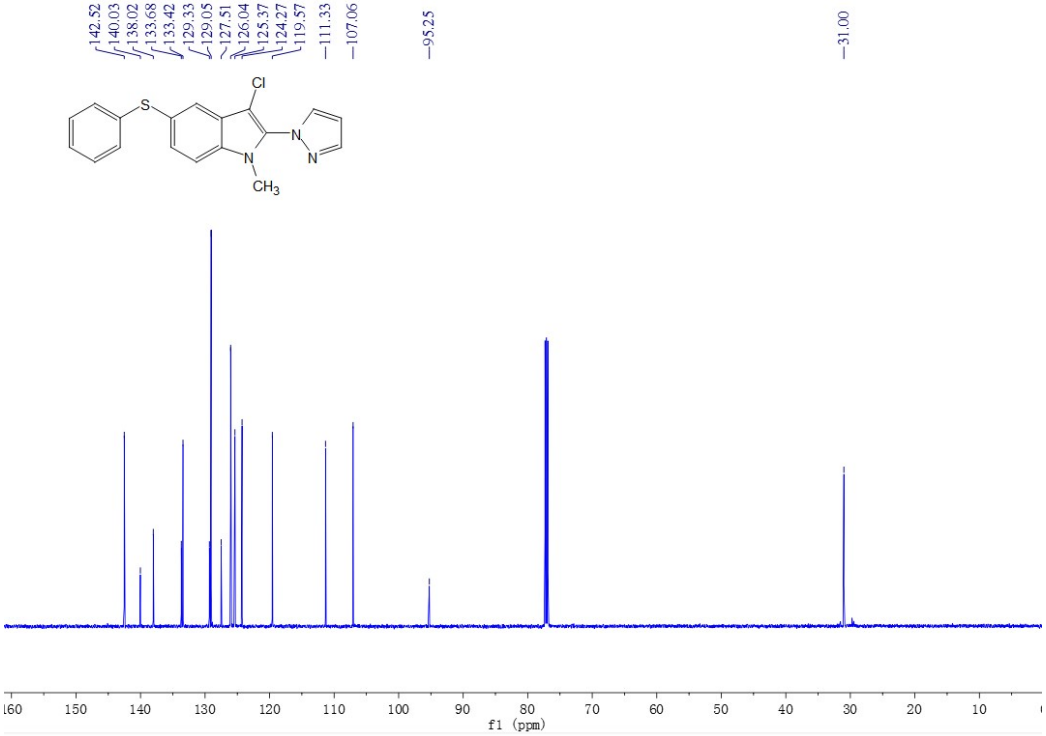
(37) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 17



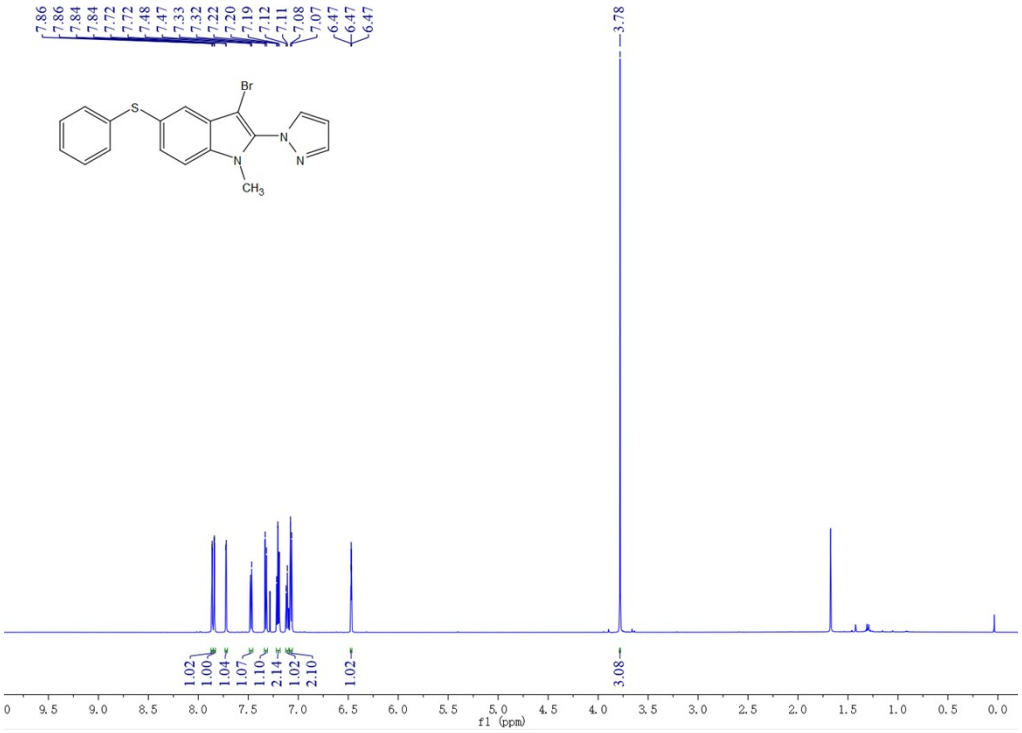
(38) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 18



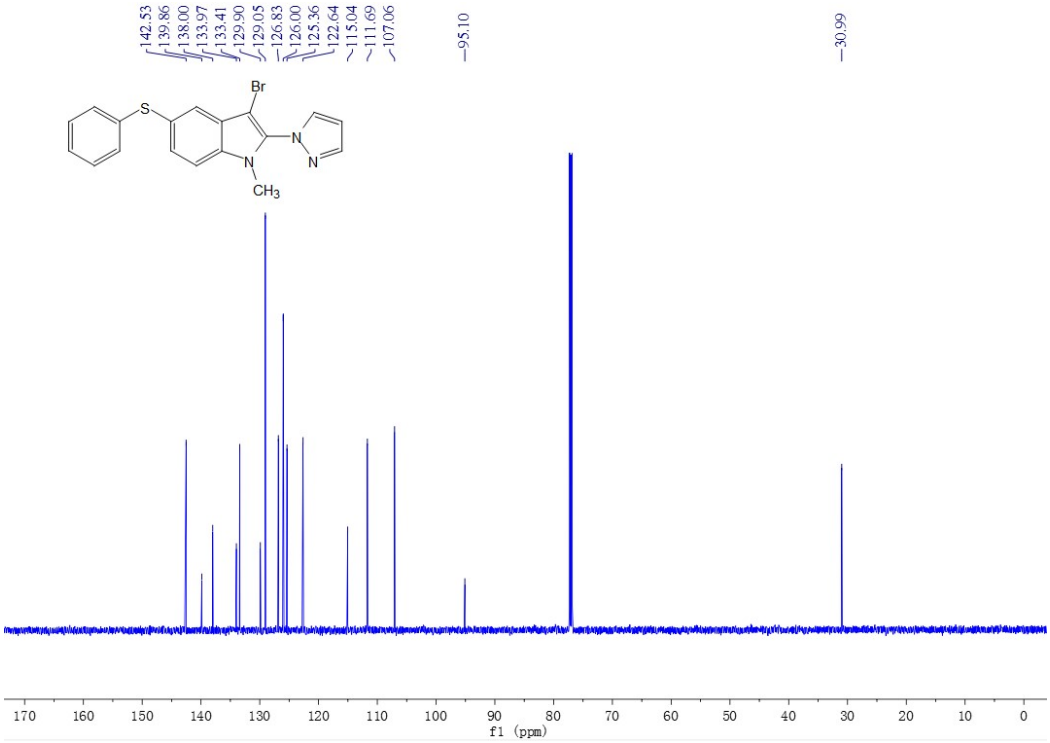
(39) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 18



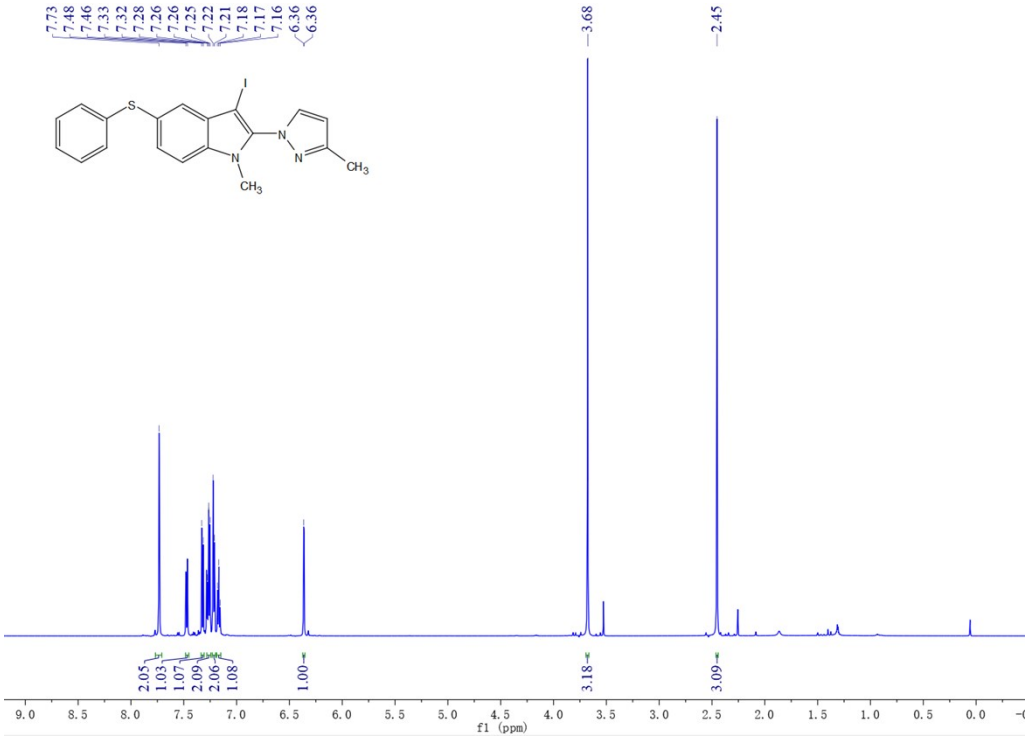
(40) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 19



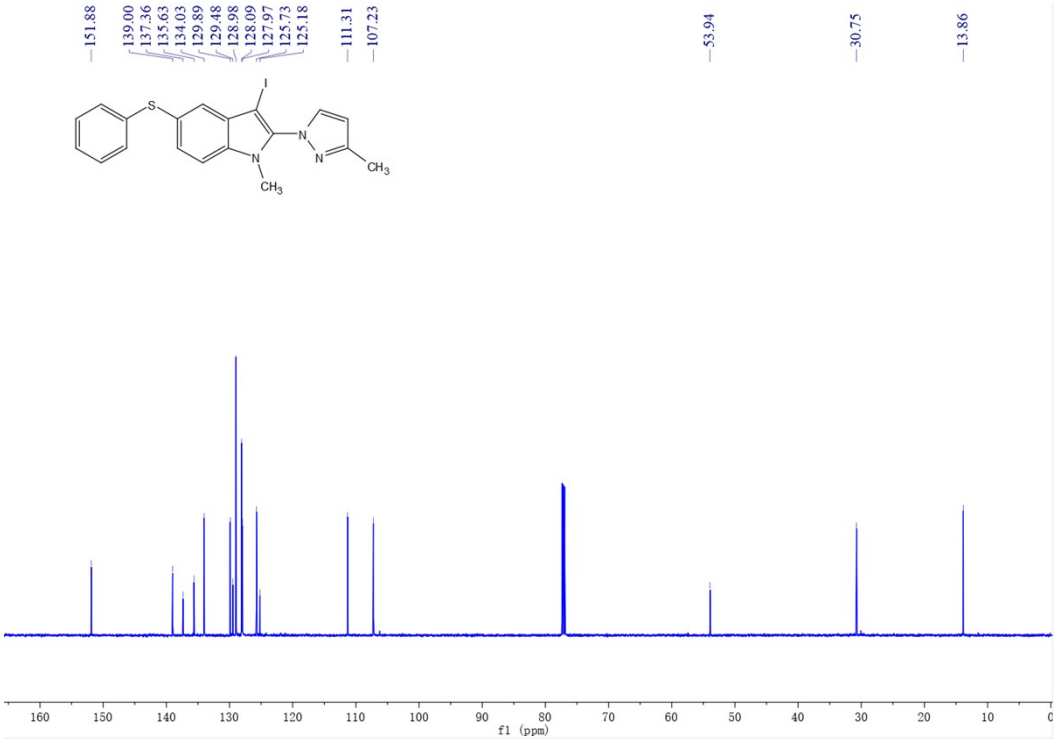
(41) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 19



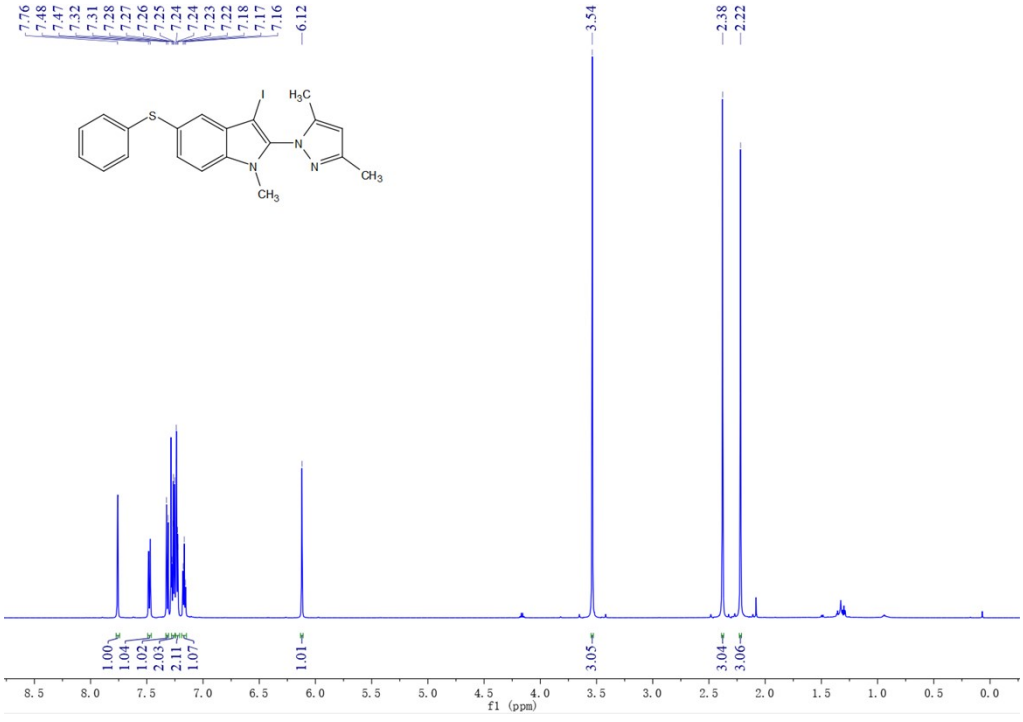
(42) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 20



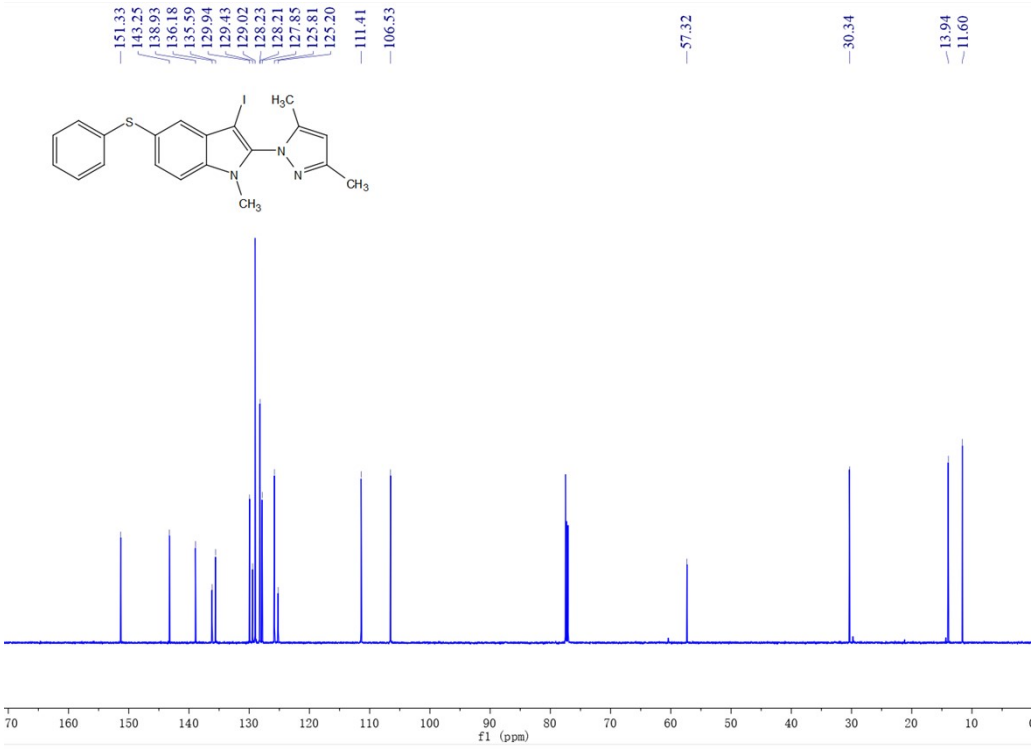
(43) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 20



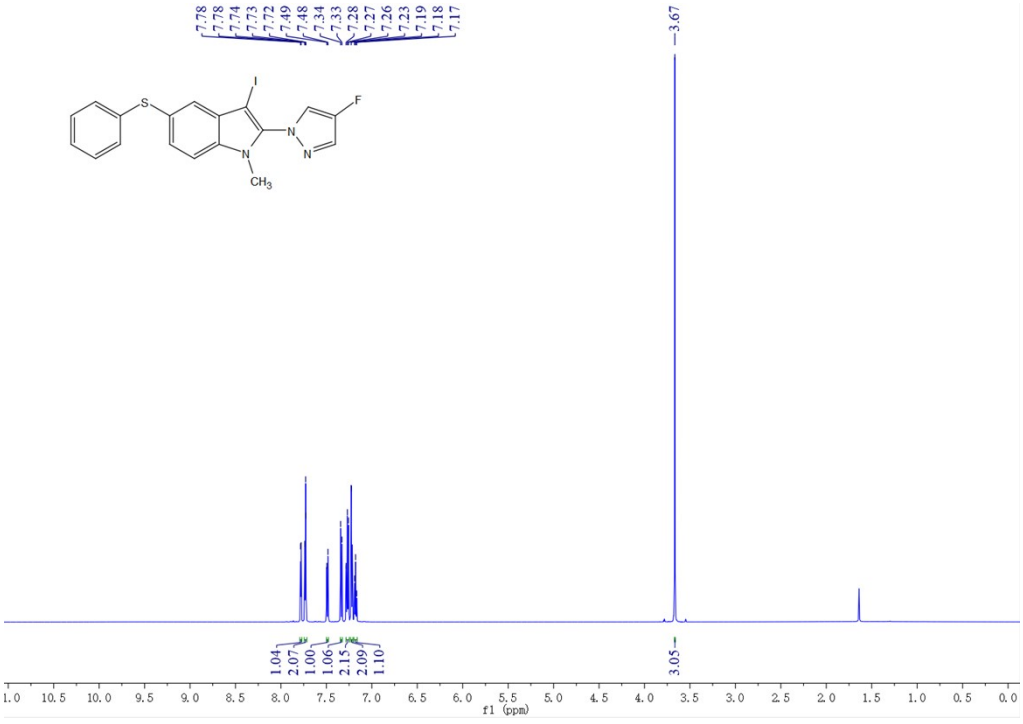
(44) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 21



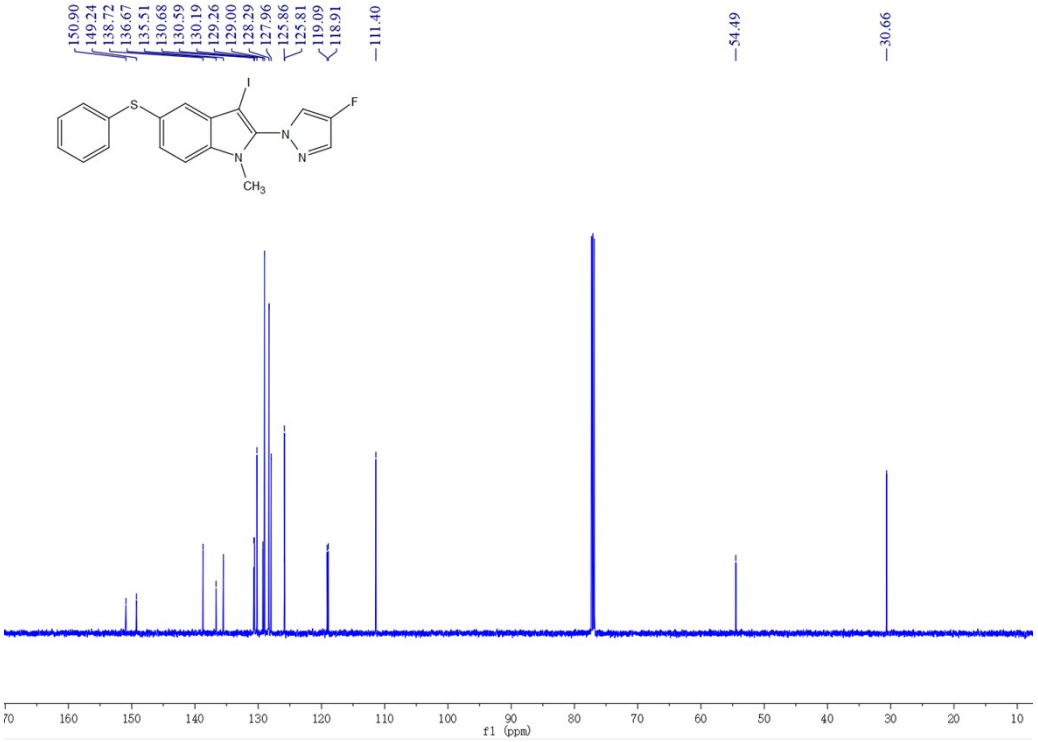
(45) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 21



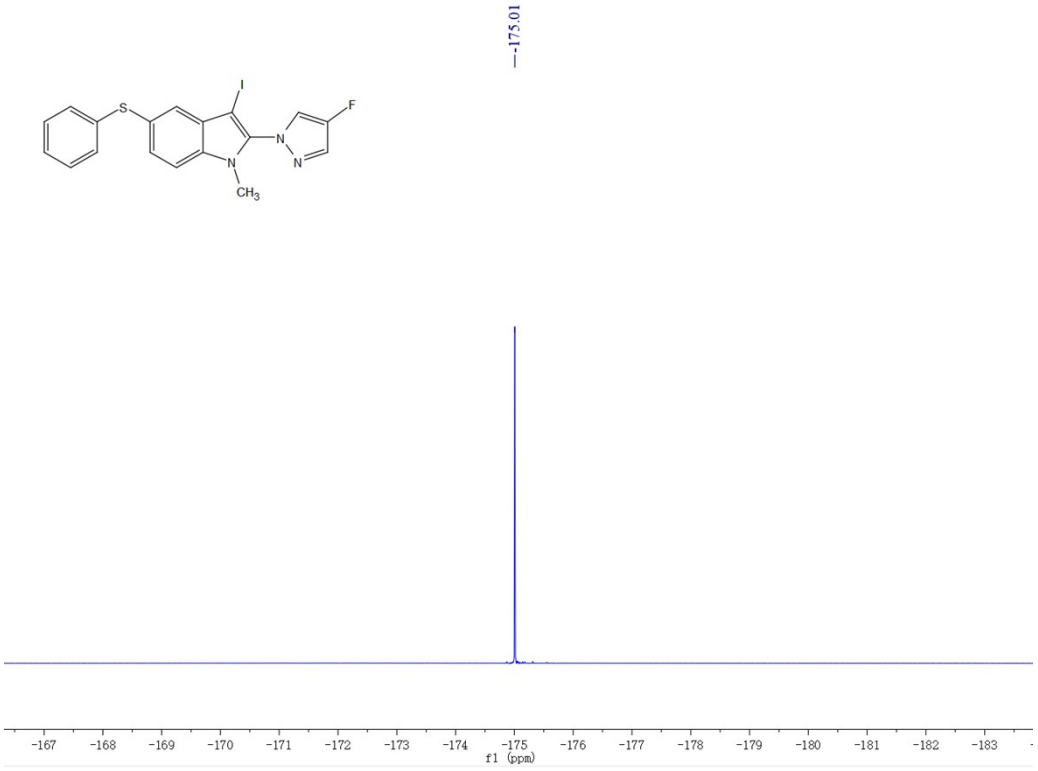
(46) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 22



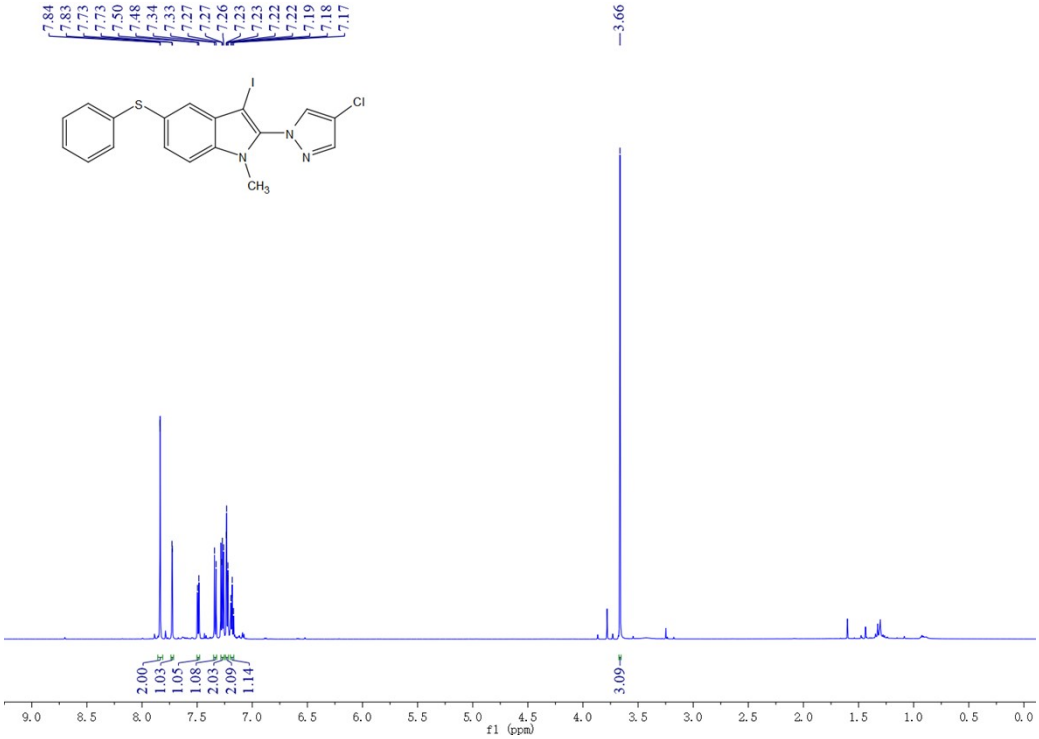
(47) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 22



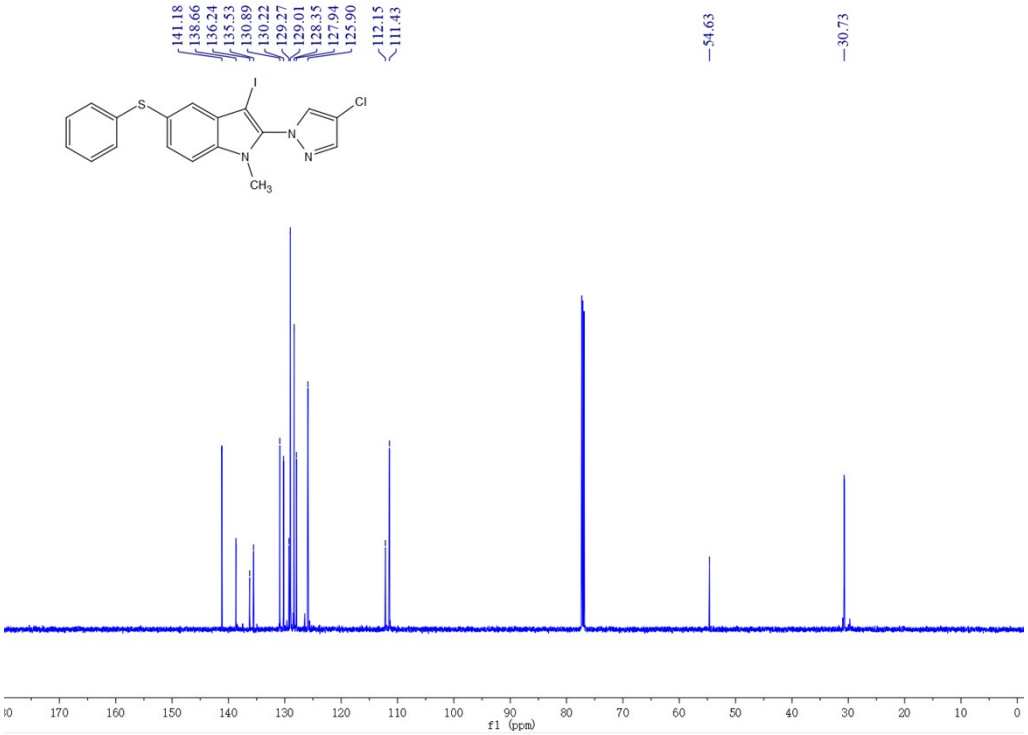
(48) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 22



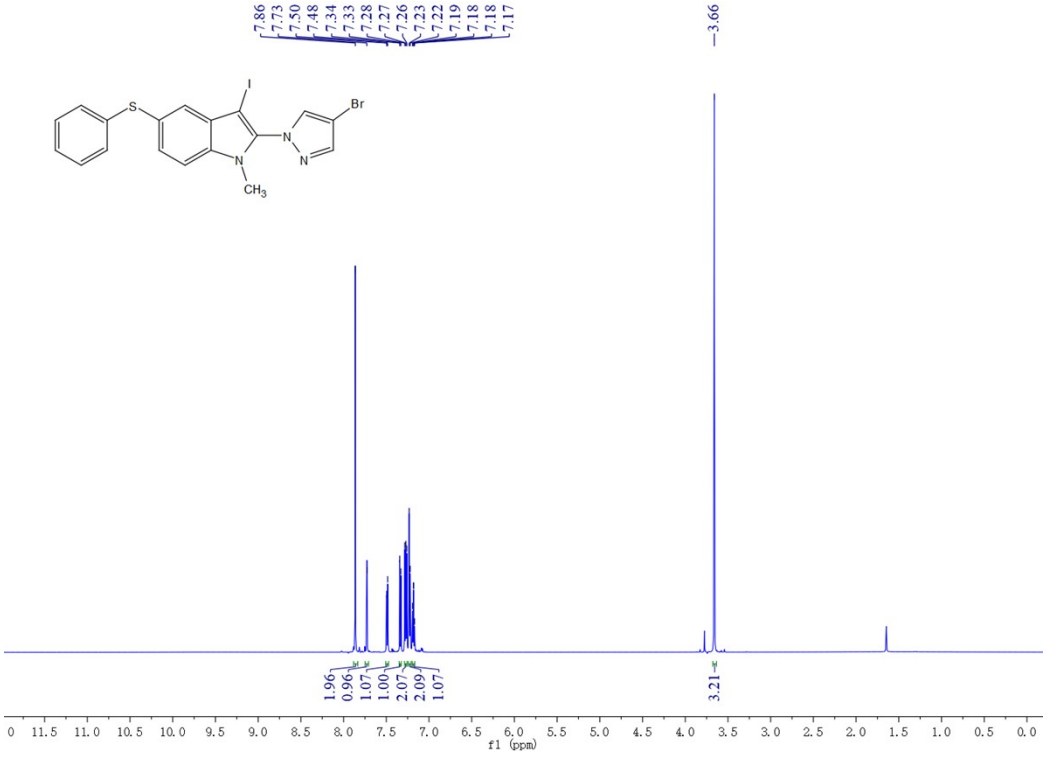
(49) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 23



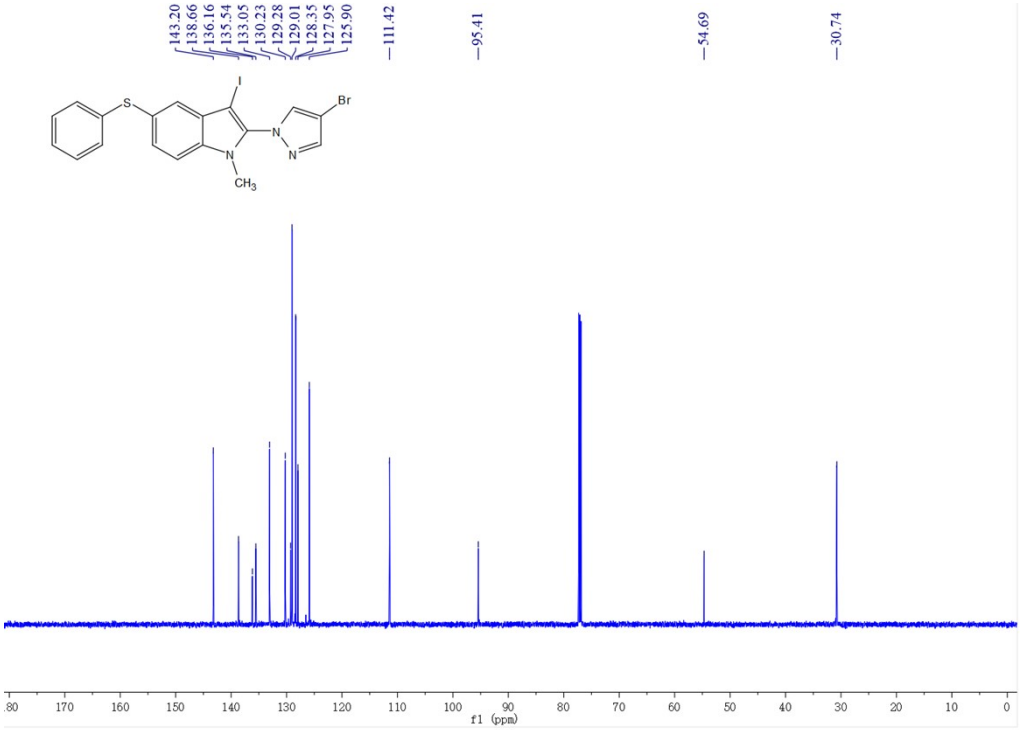
(50) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 23



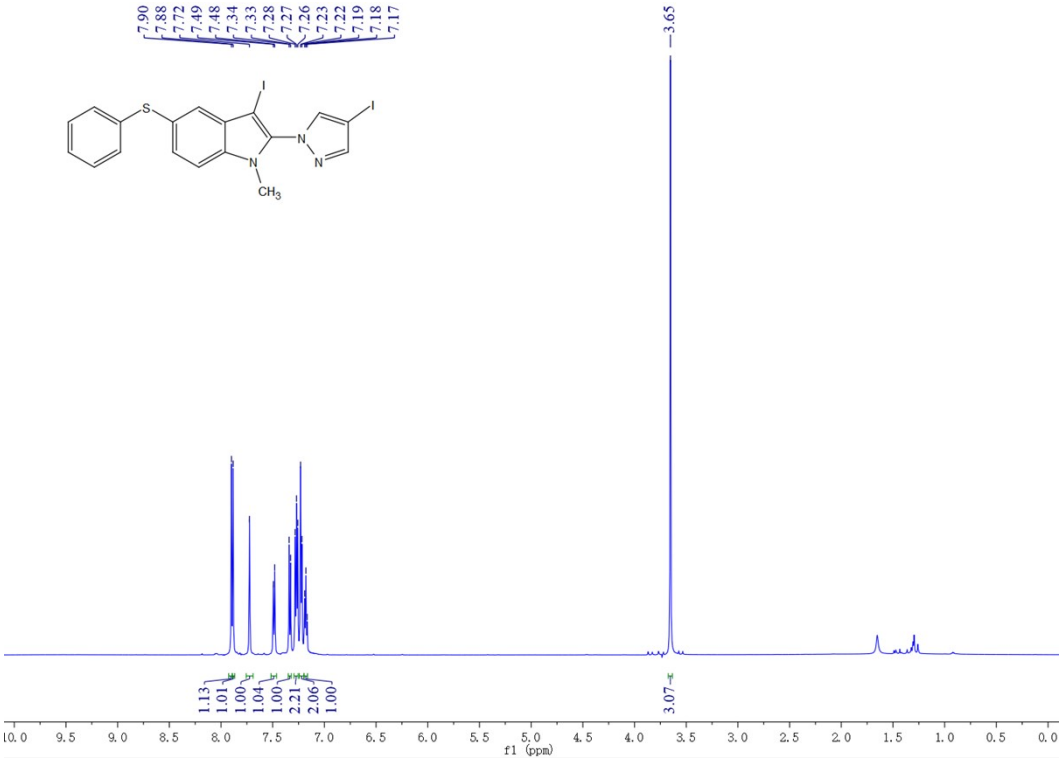
(51) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 24



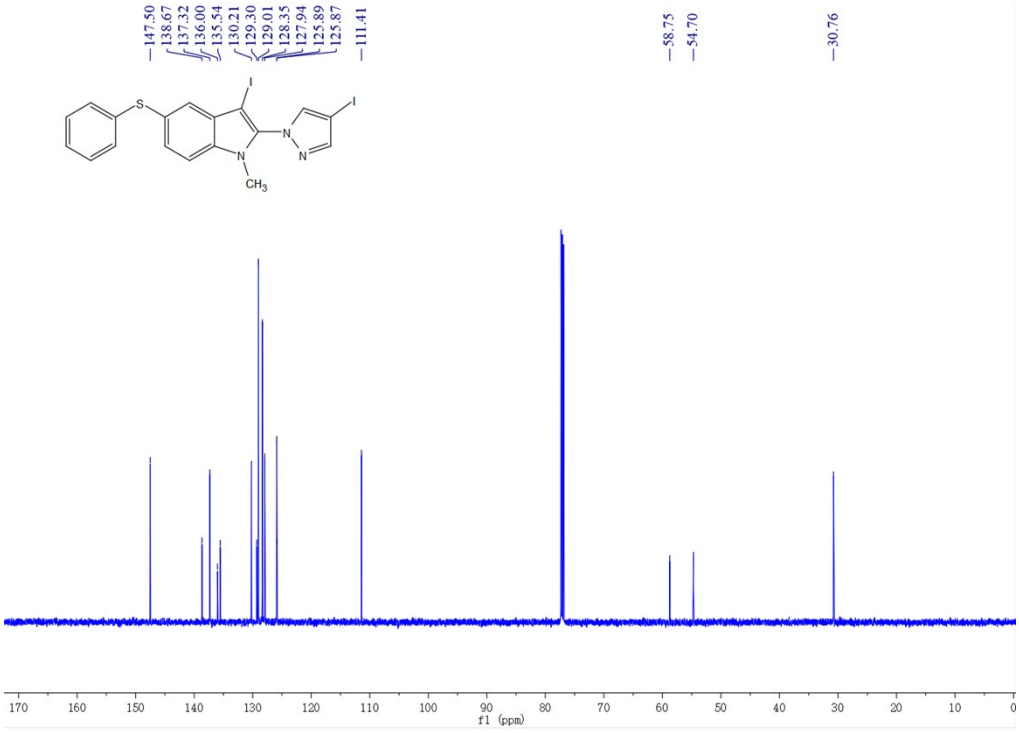
(52) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 24



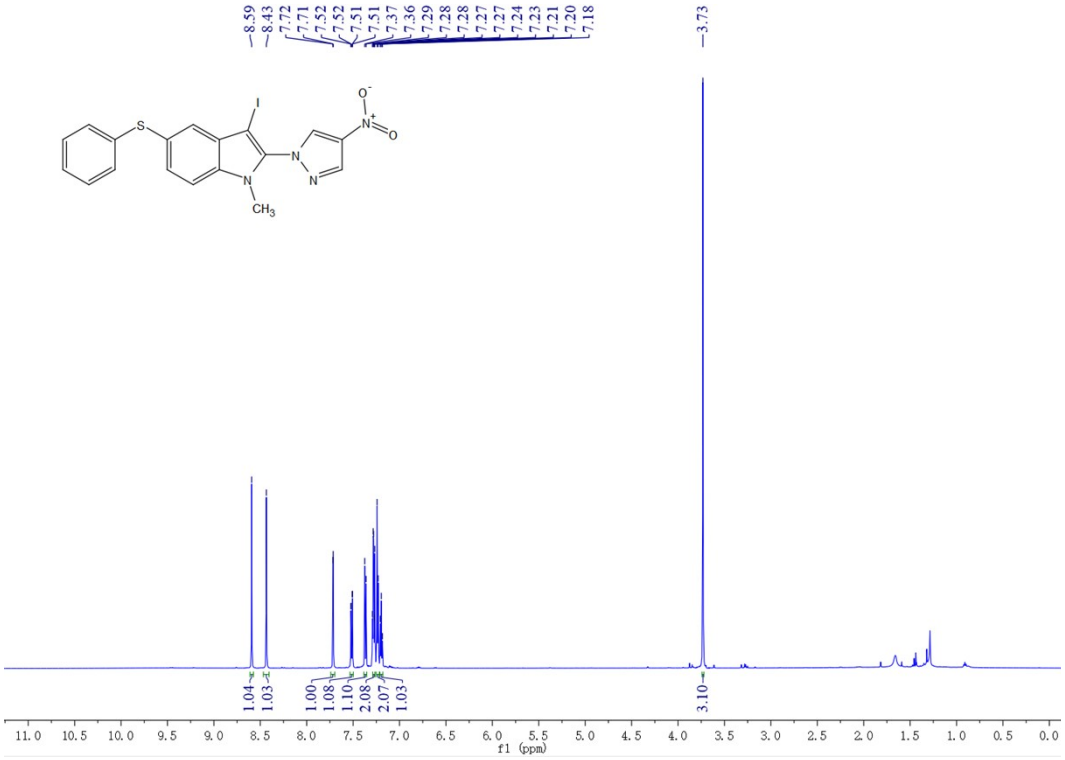
(53) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 25



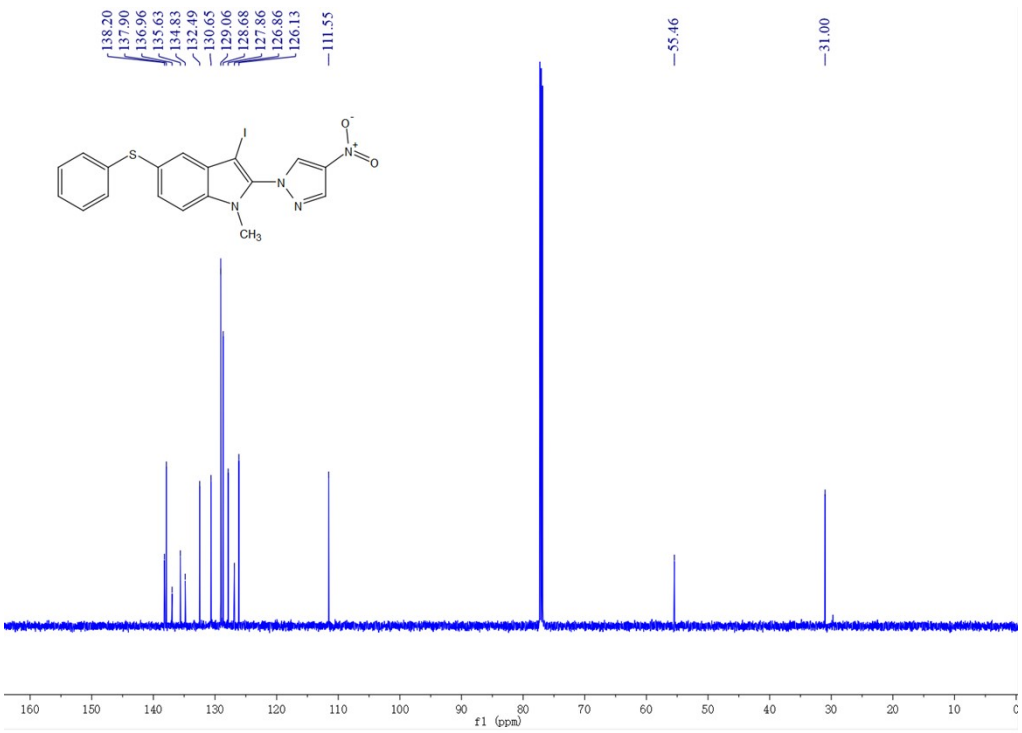
(54) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 25



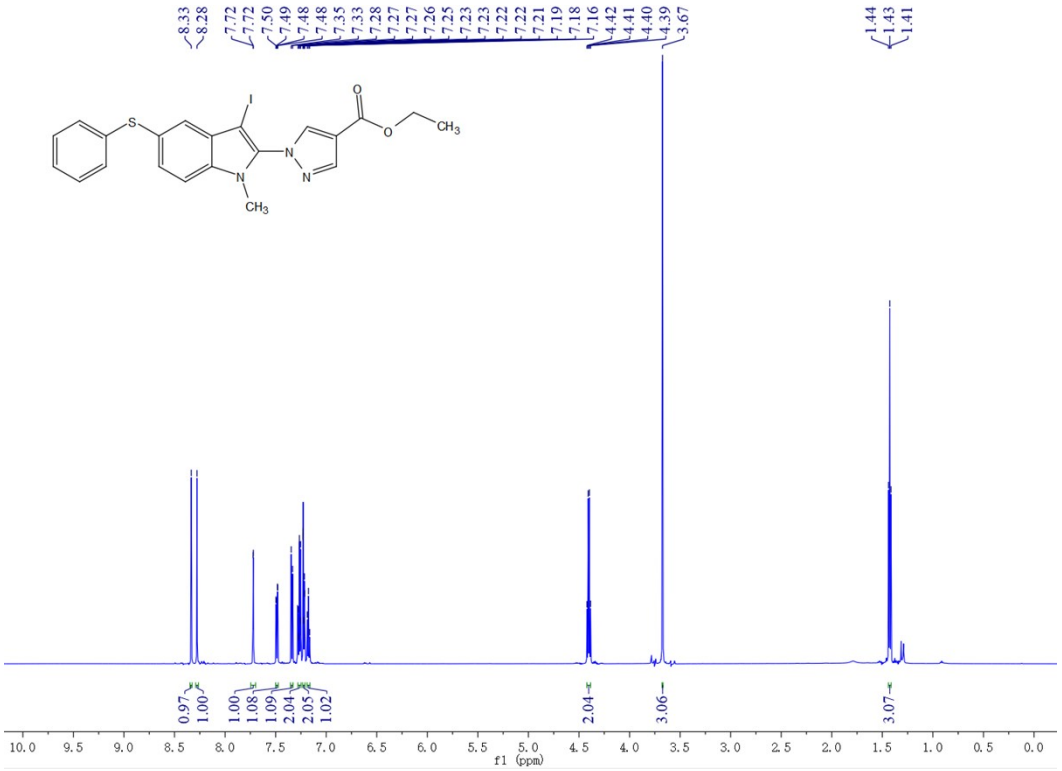
(55) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 26



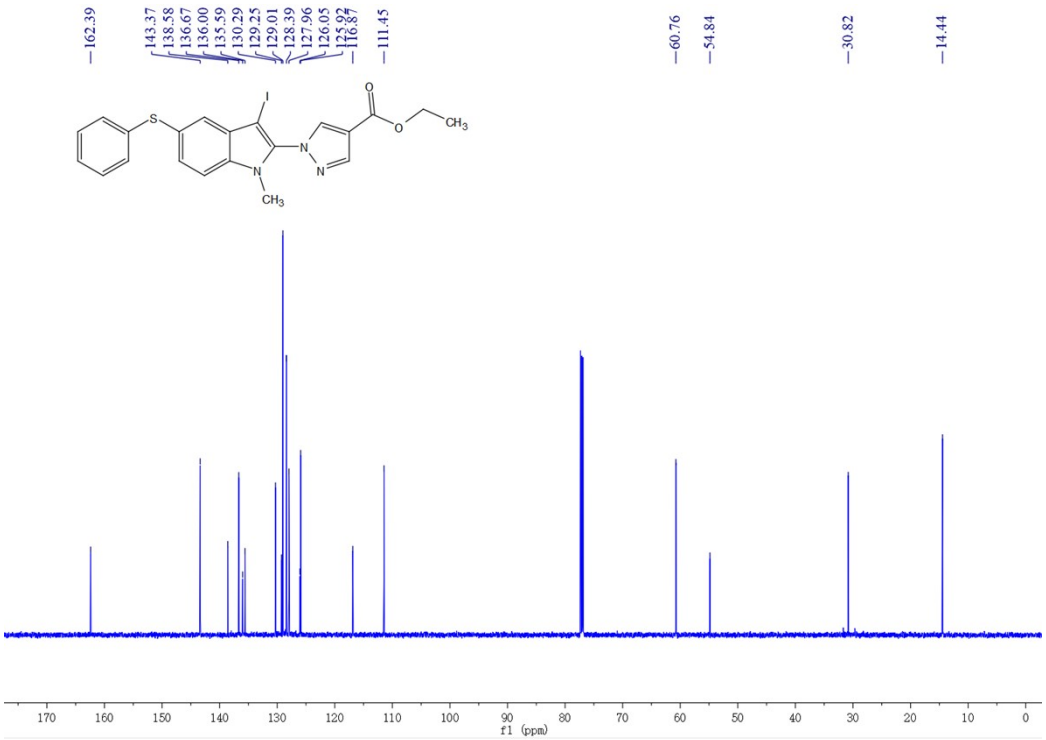
(56) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 26



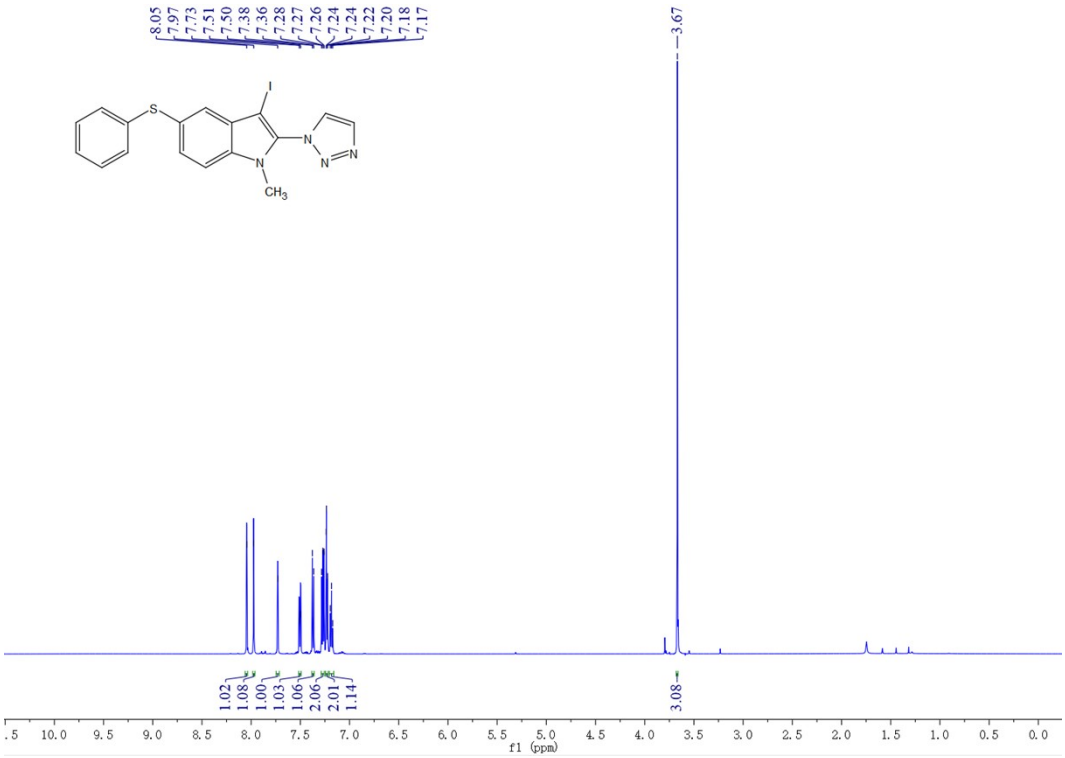
(57) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 27



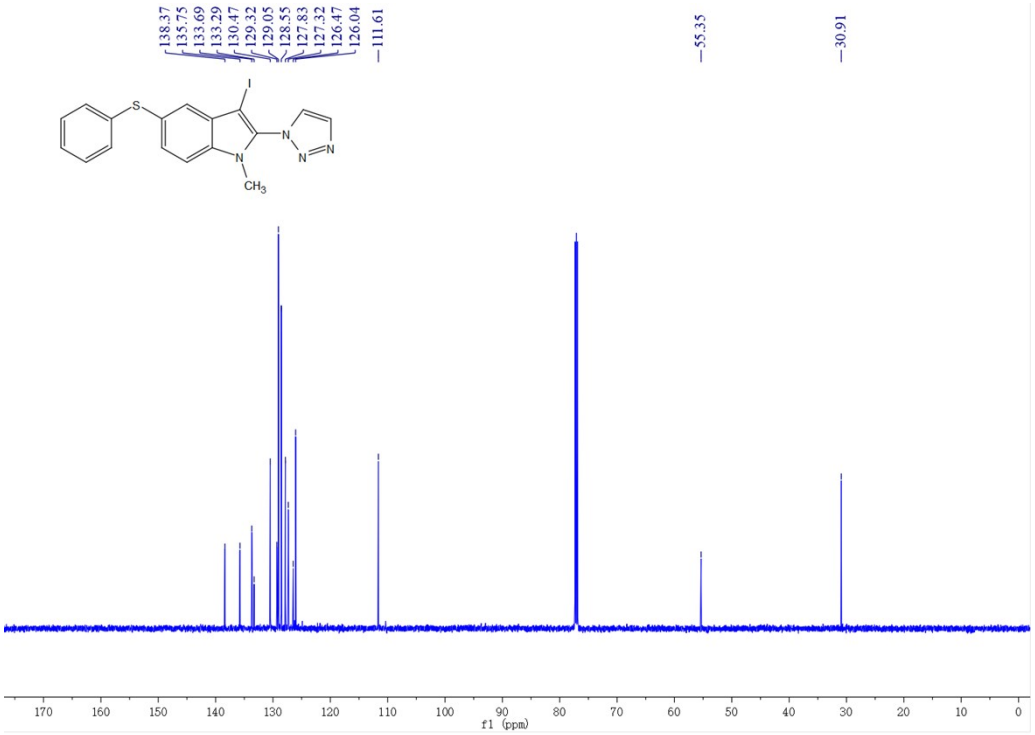
(58) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 27



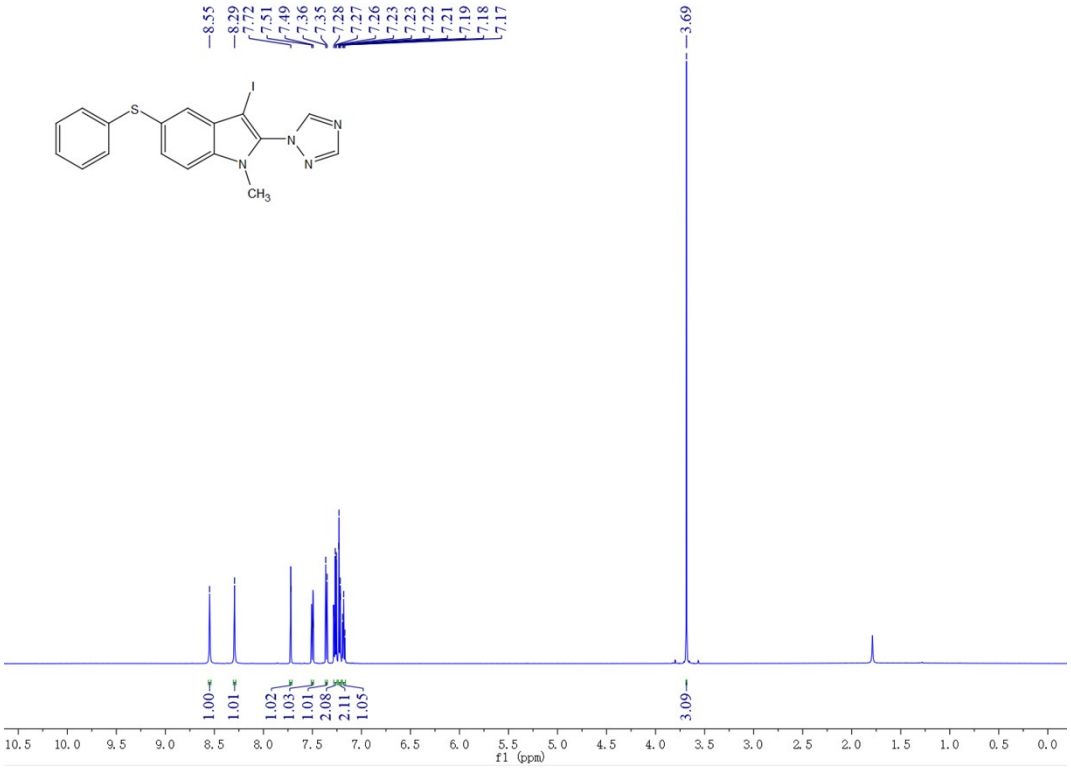
(59) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 28



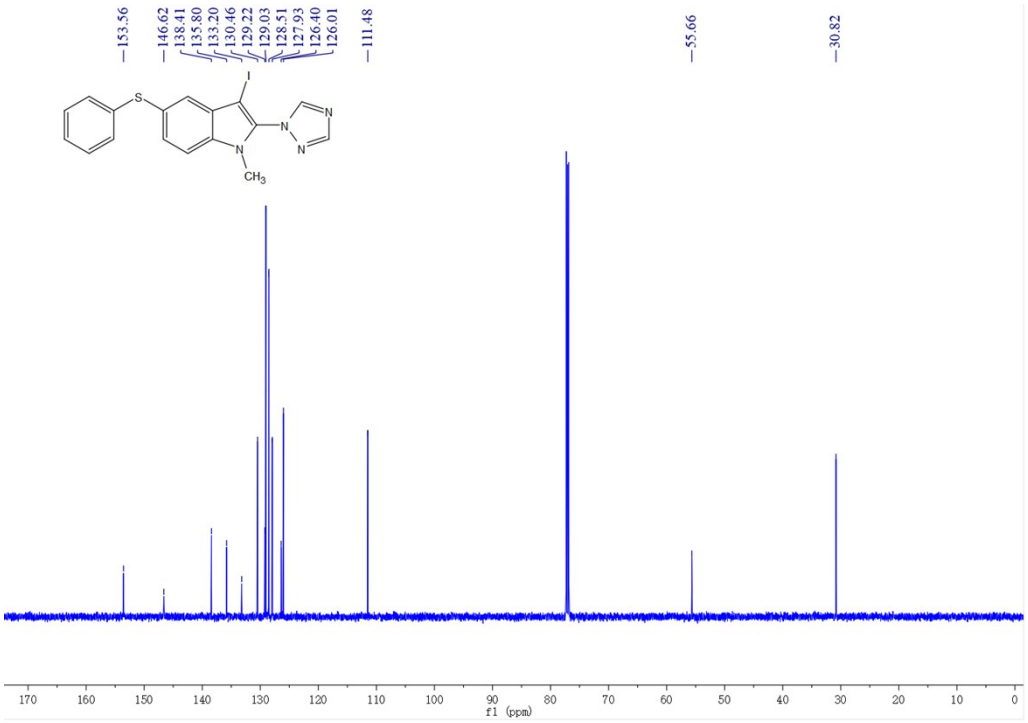
(60) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 28



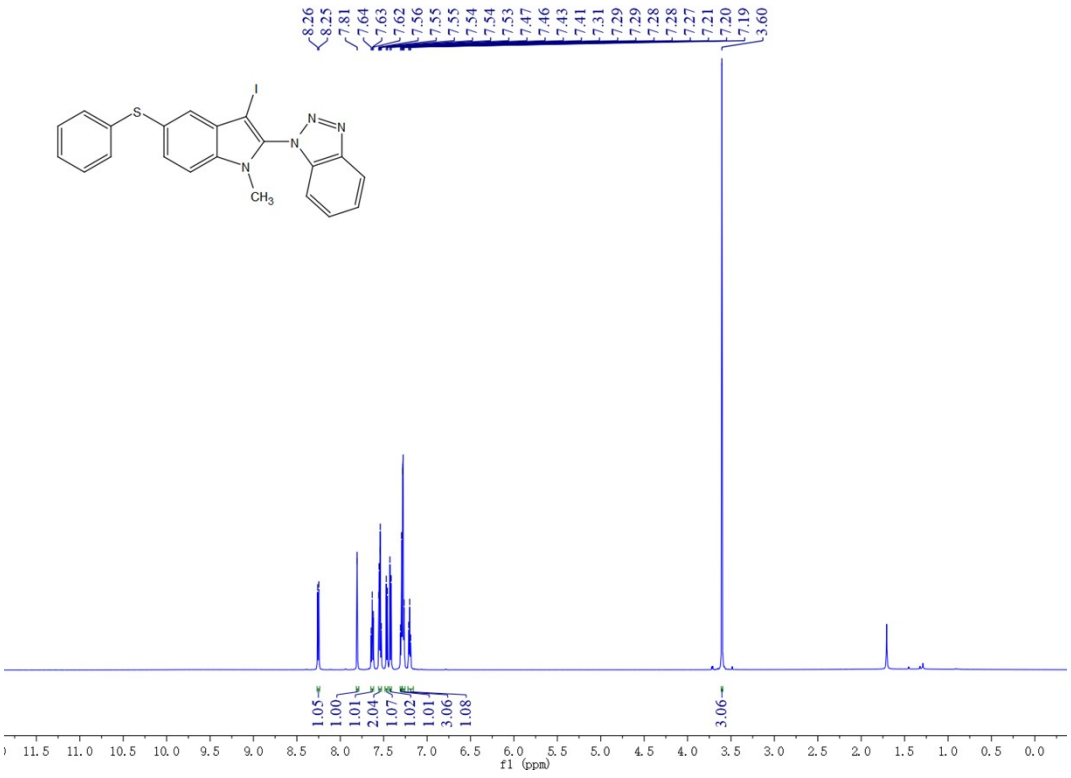
(61) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 29



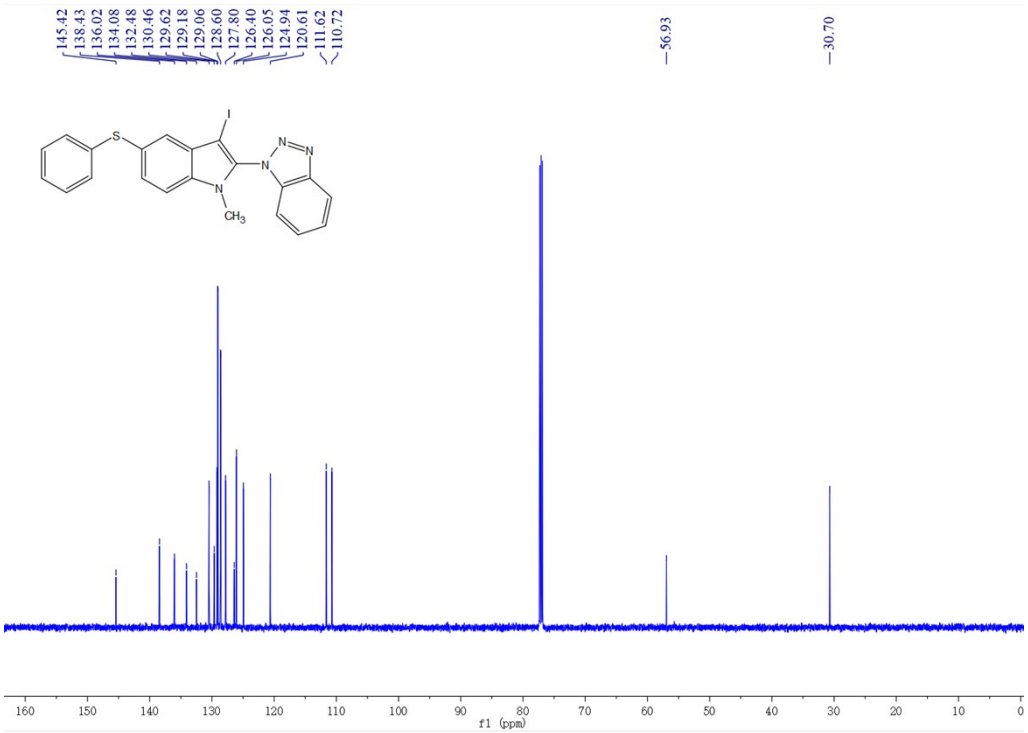
(62) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 29



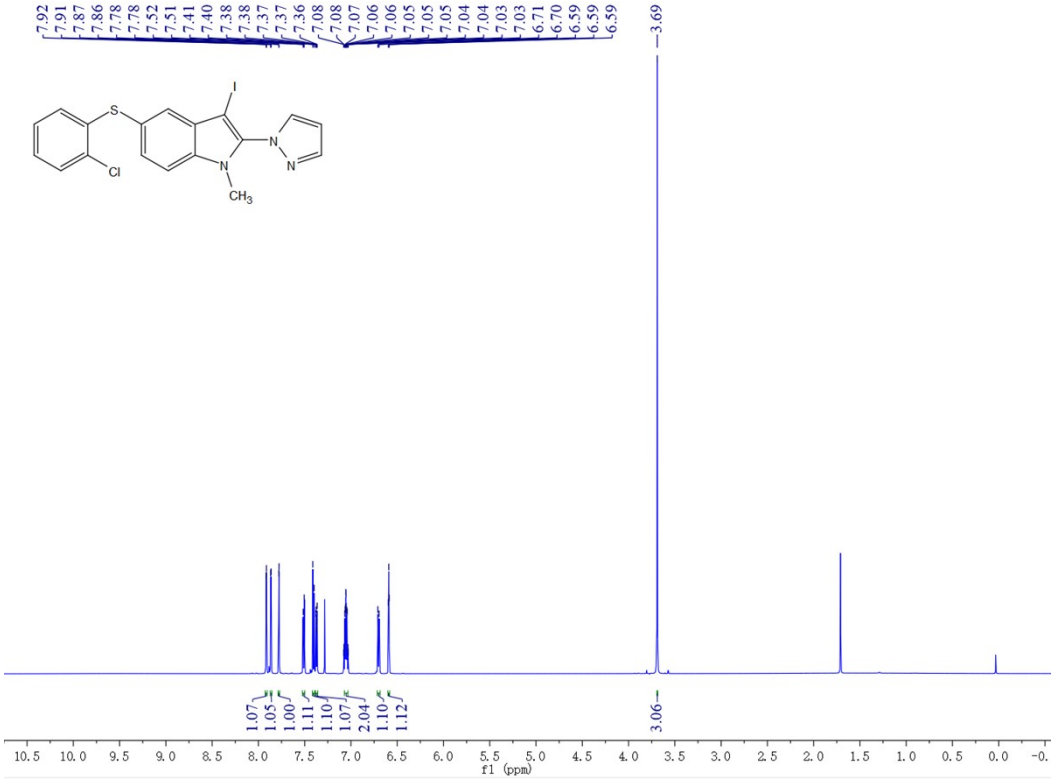
(63) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 30



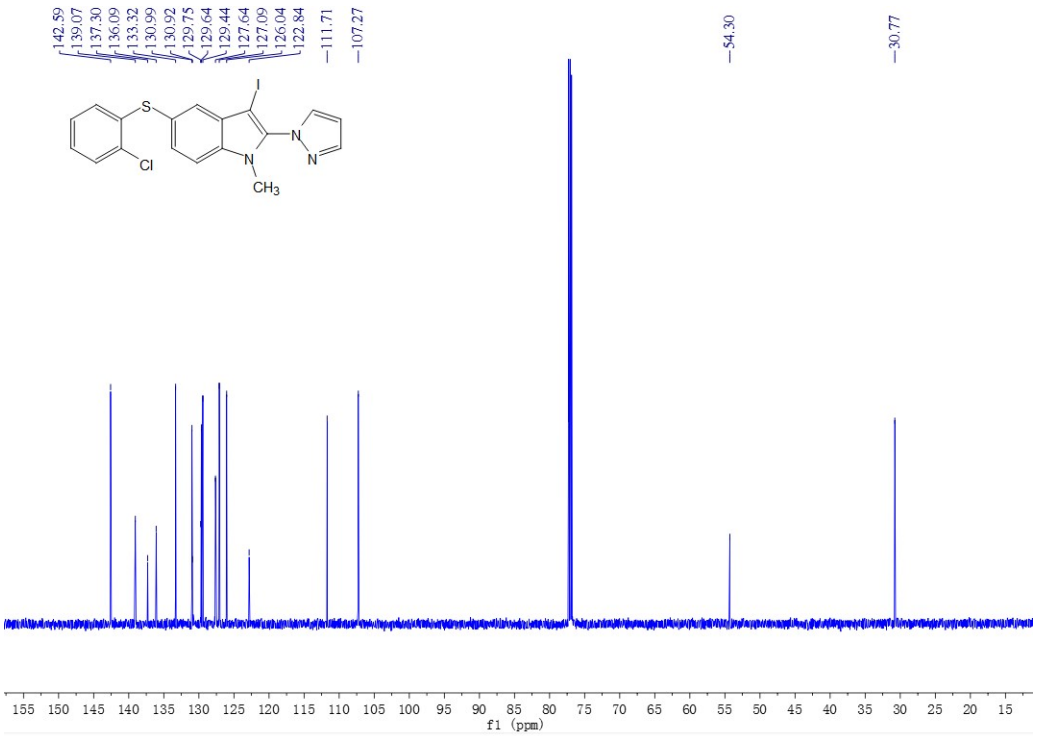
(64) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 30



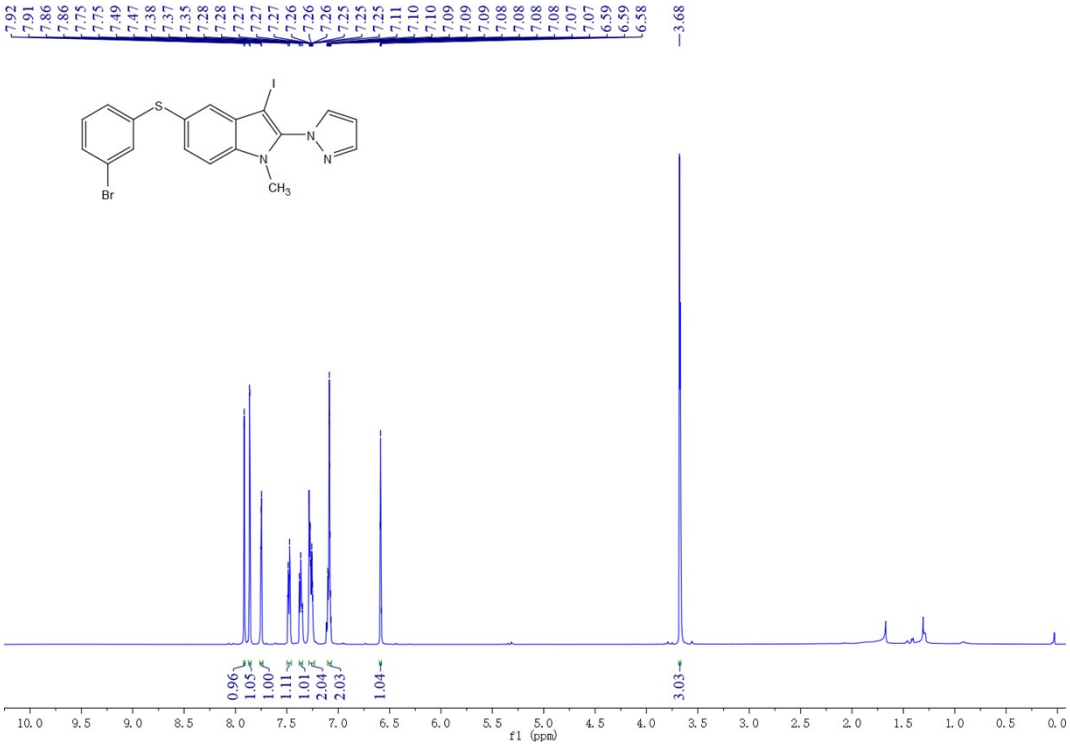
(65) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 31



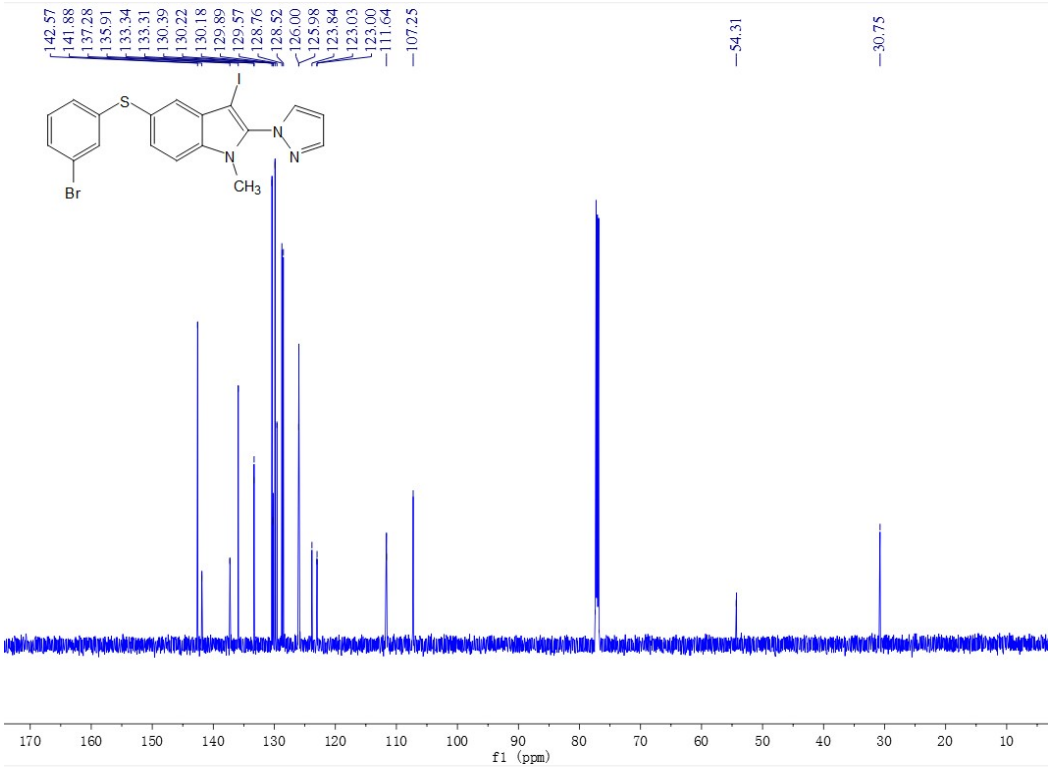
(66) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 31



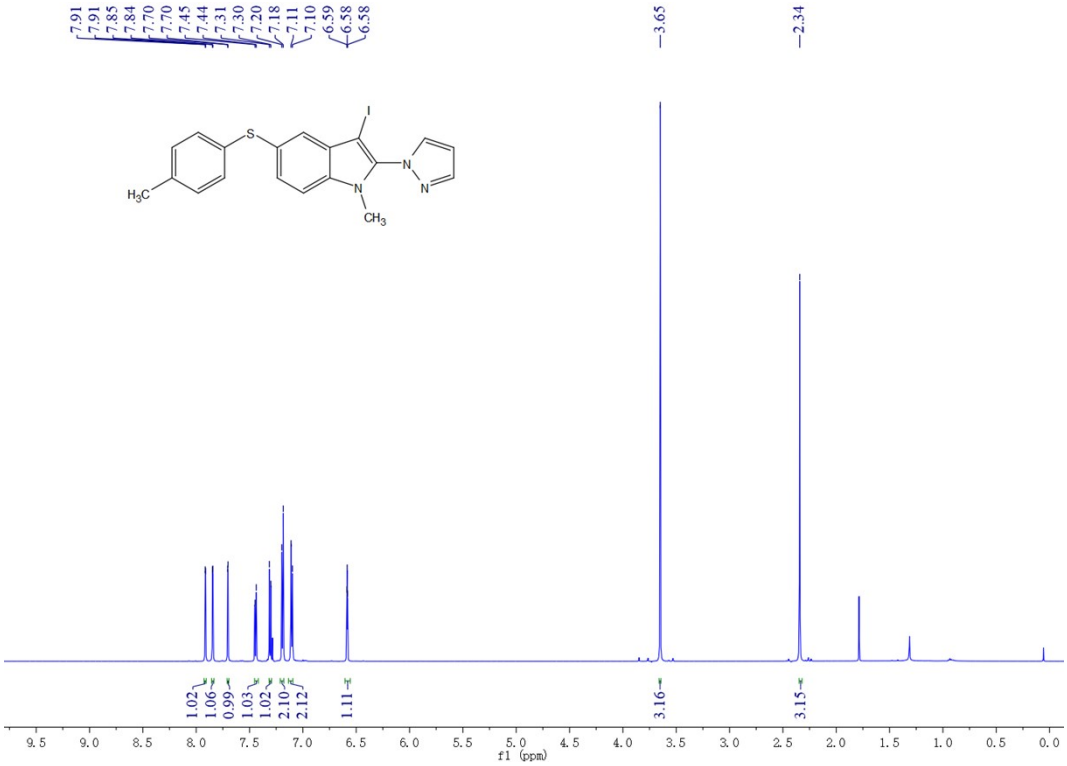
(67) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 32



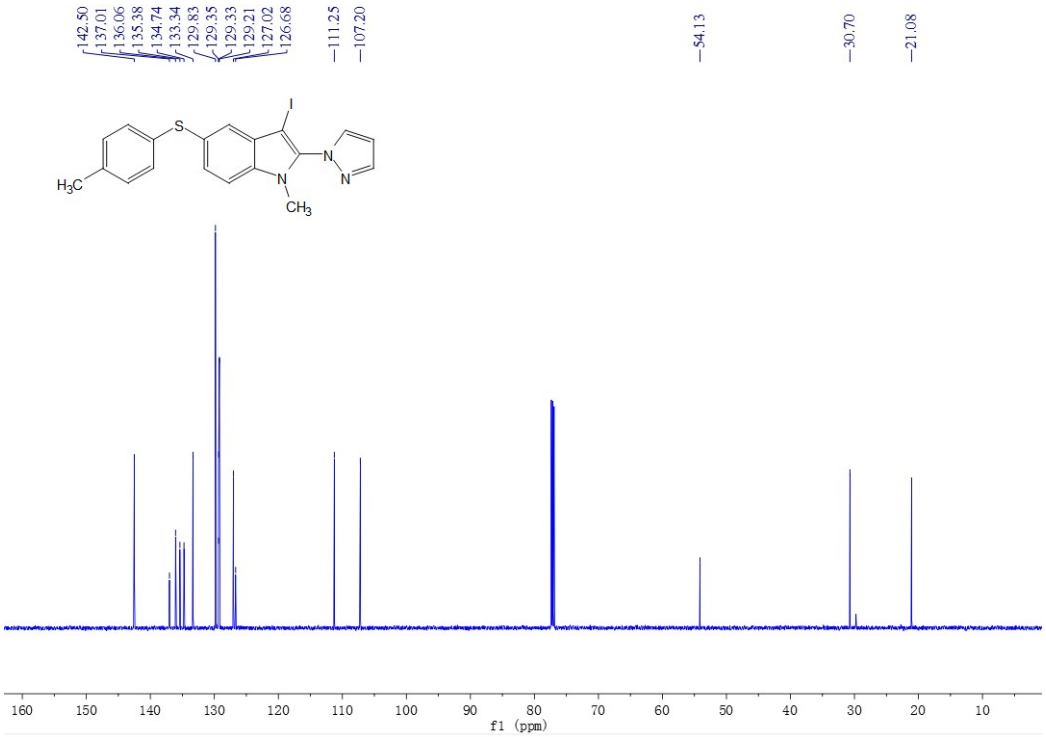
(68) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 32



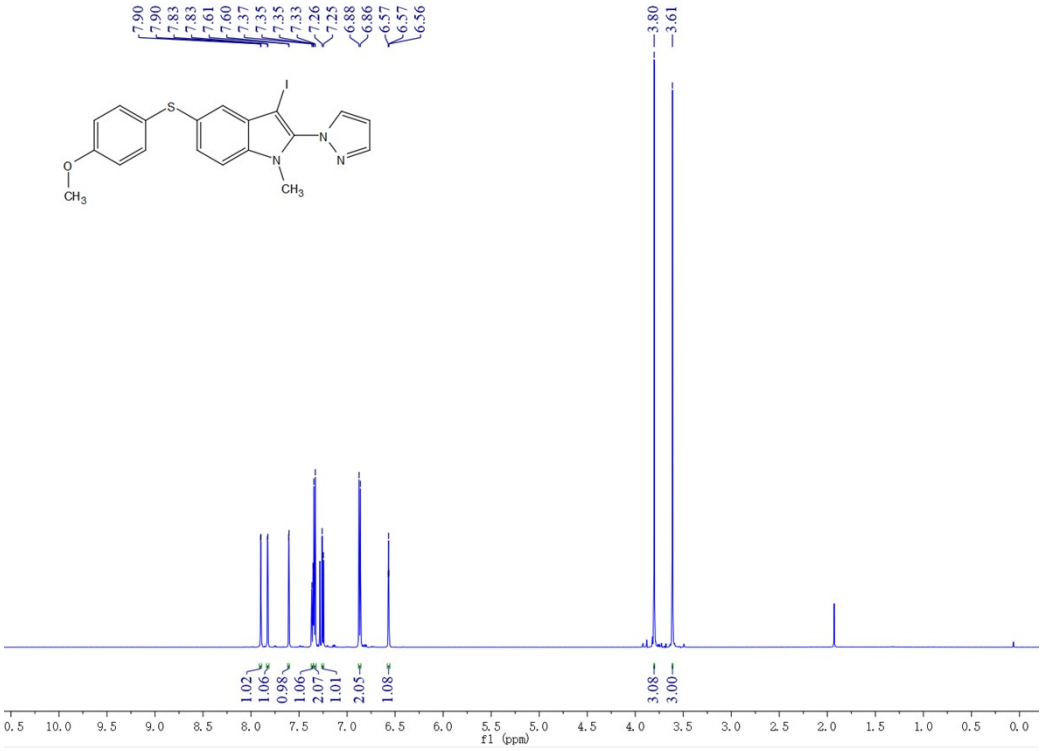
(69) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 33



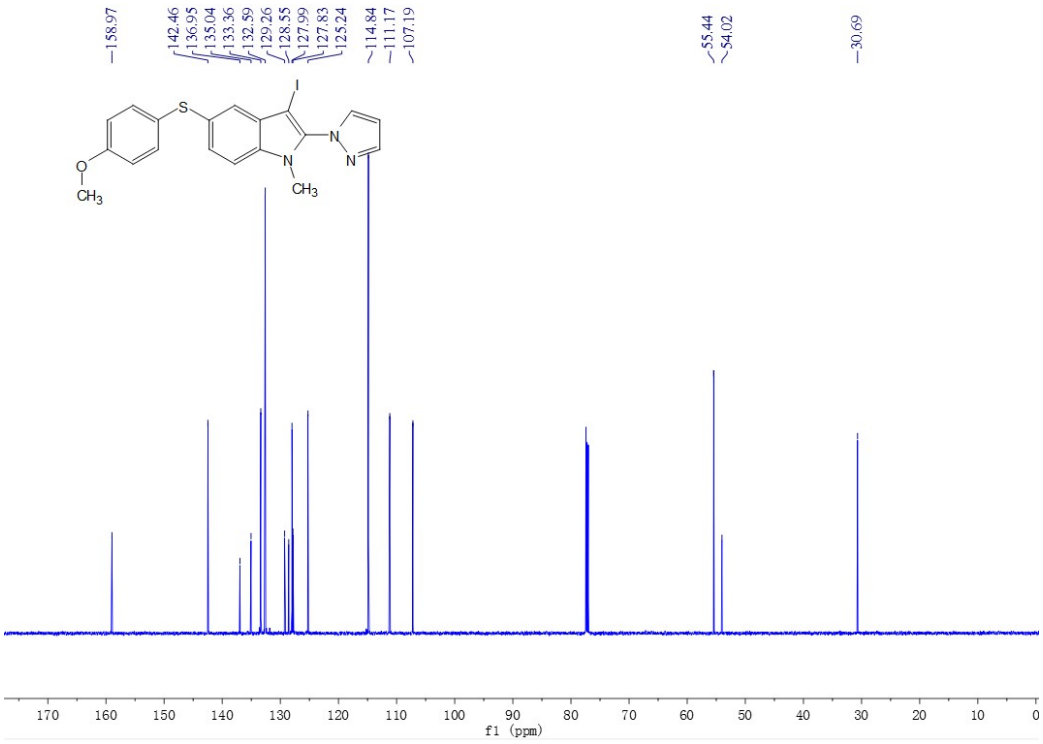
(70) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 33



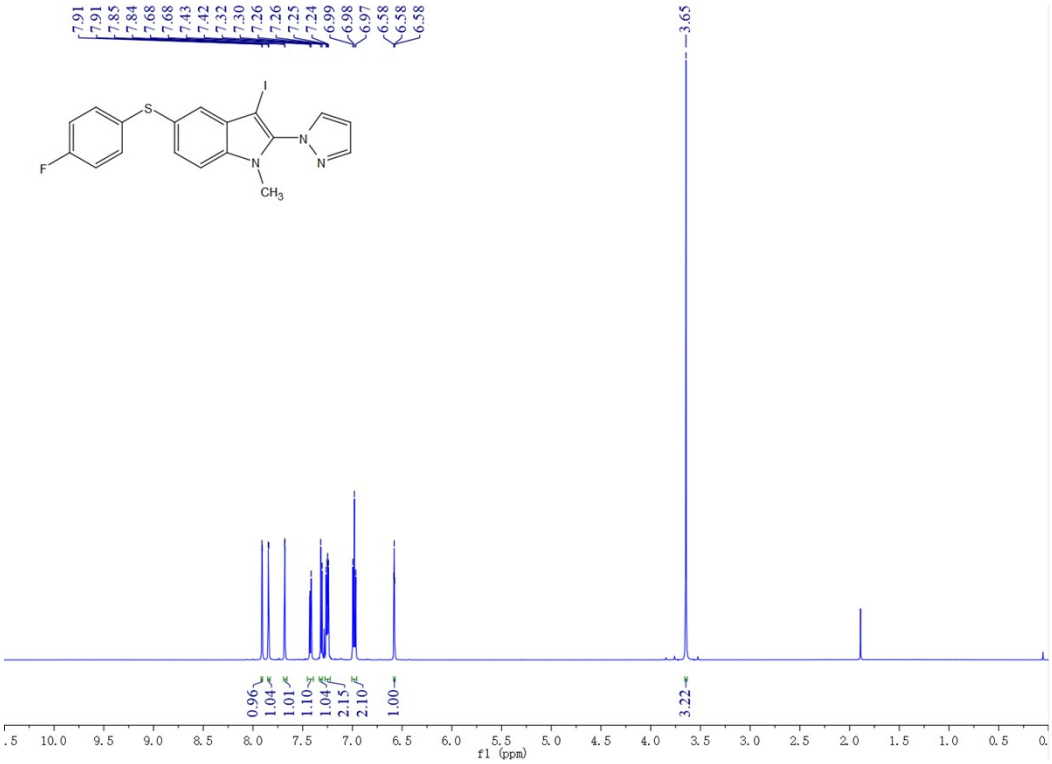
(71) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 34



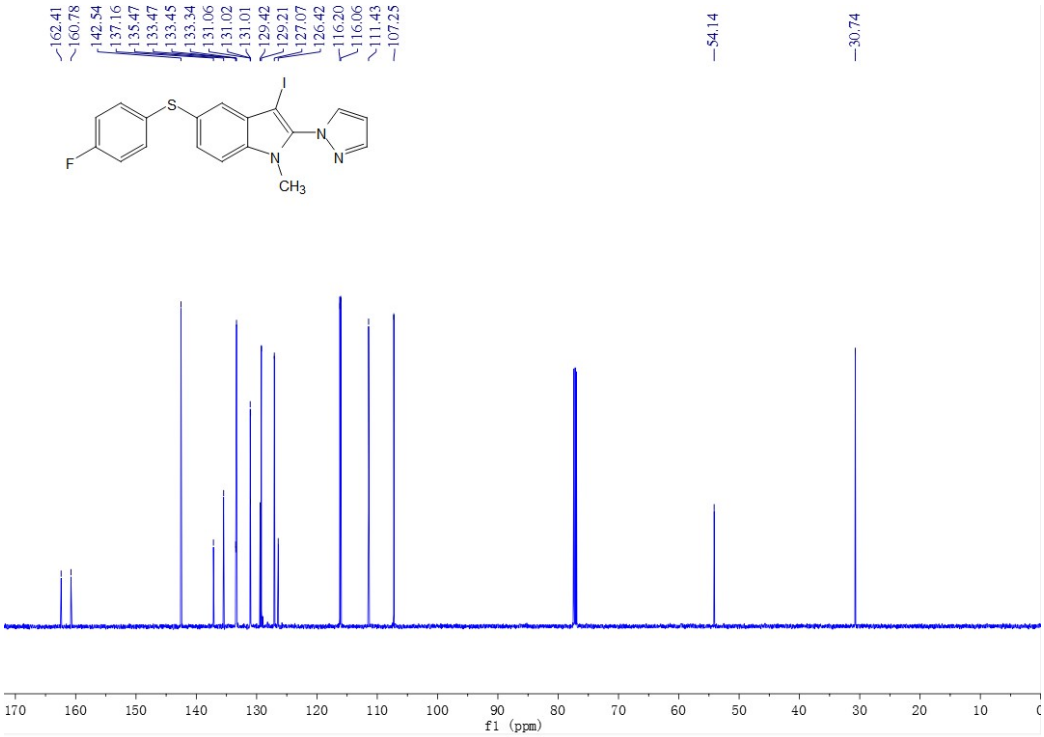
(72) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 34



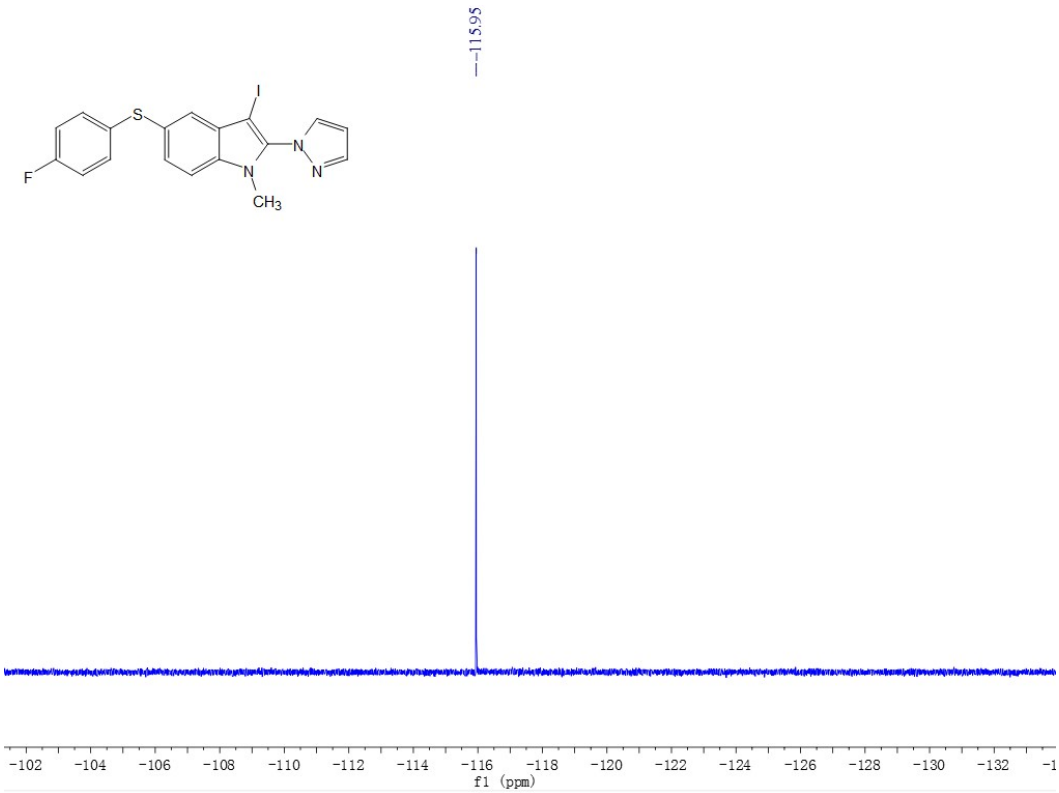
(73) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 35



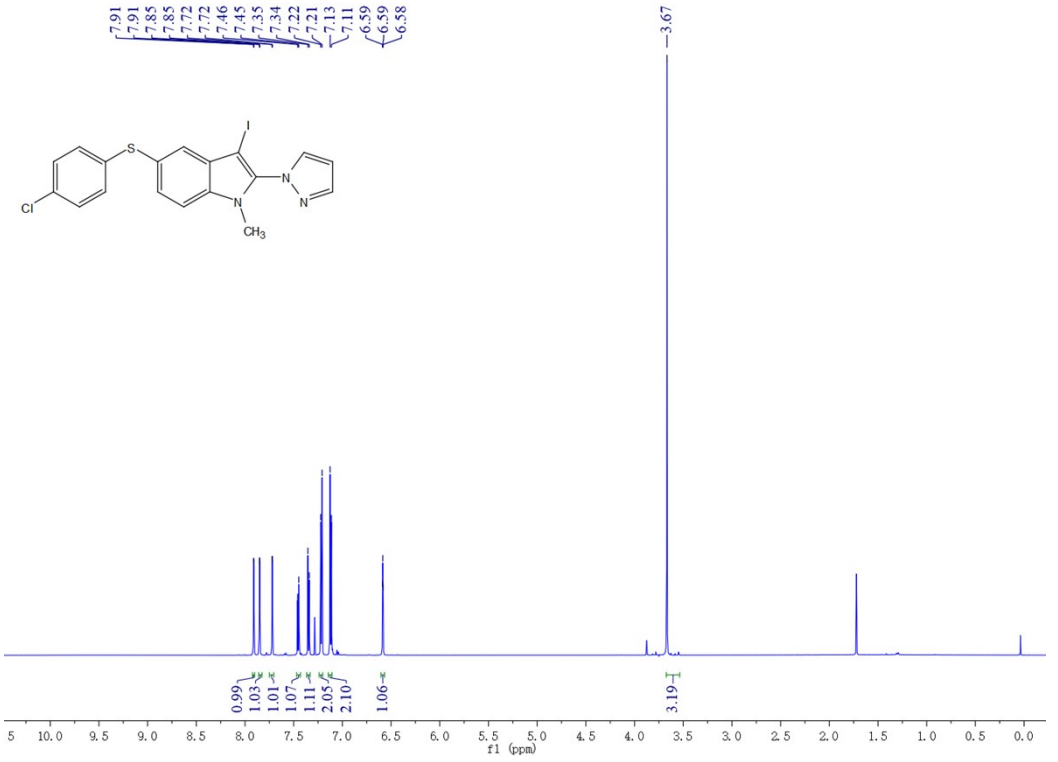
(74) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 35



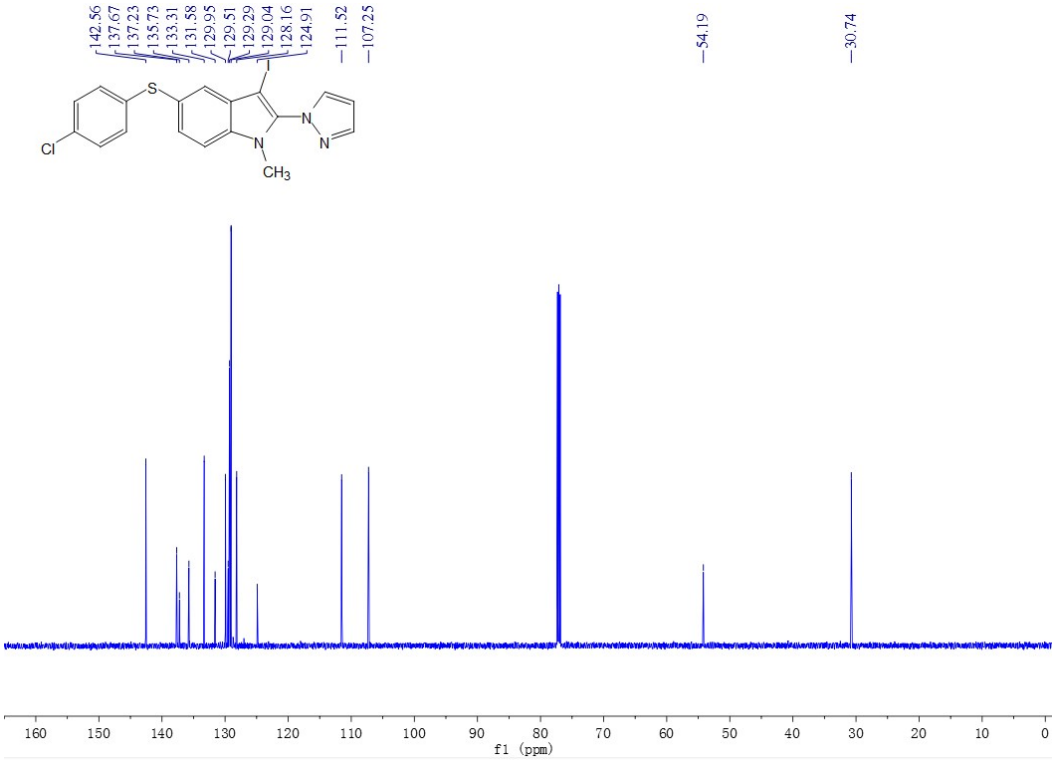
(75) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 35



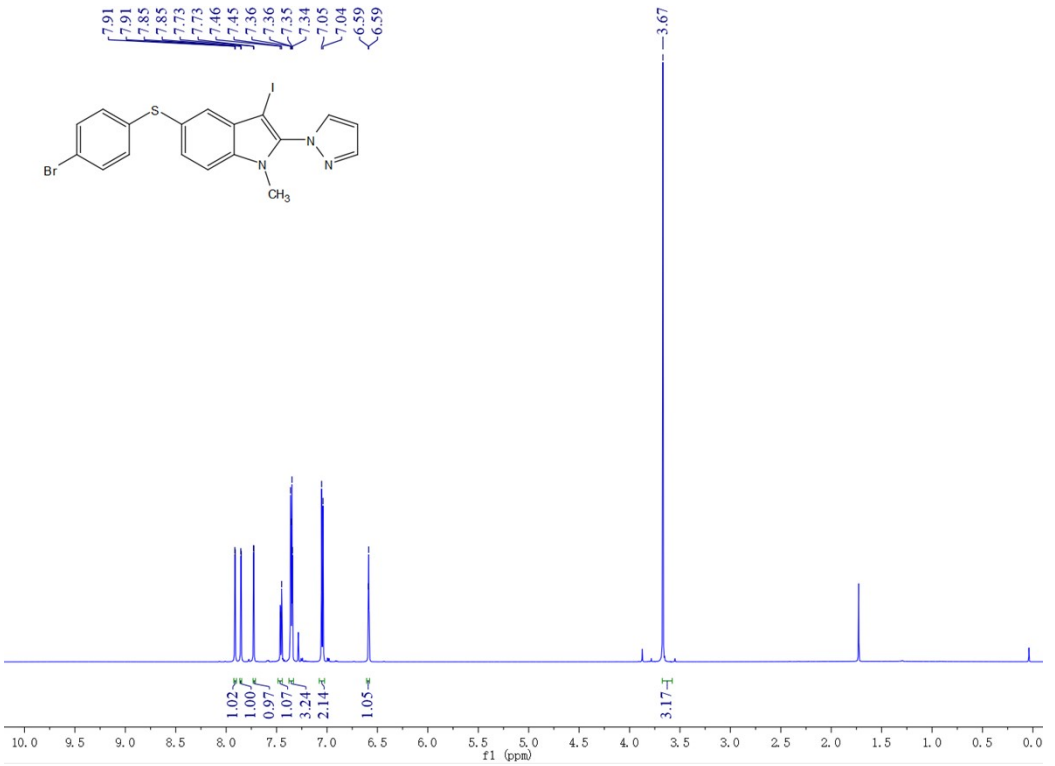
(76) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 36



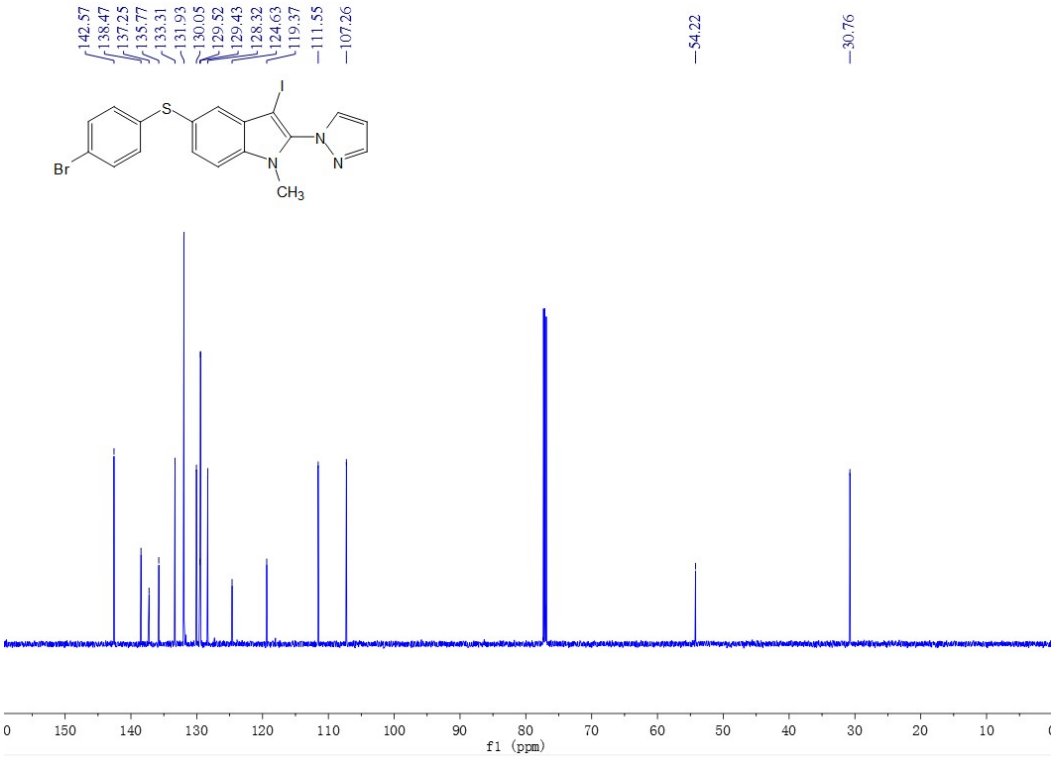
(77) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 36



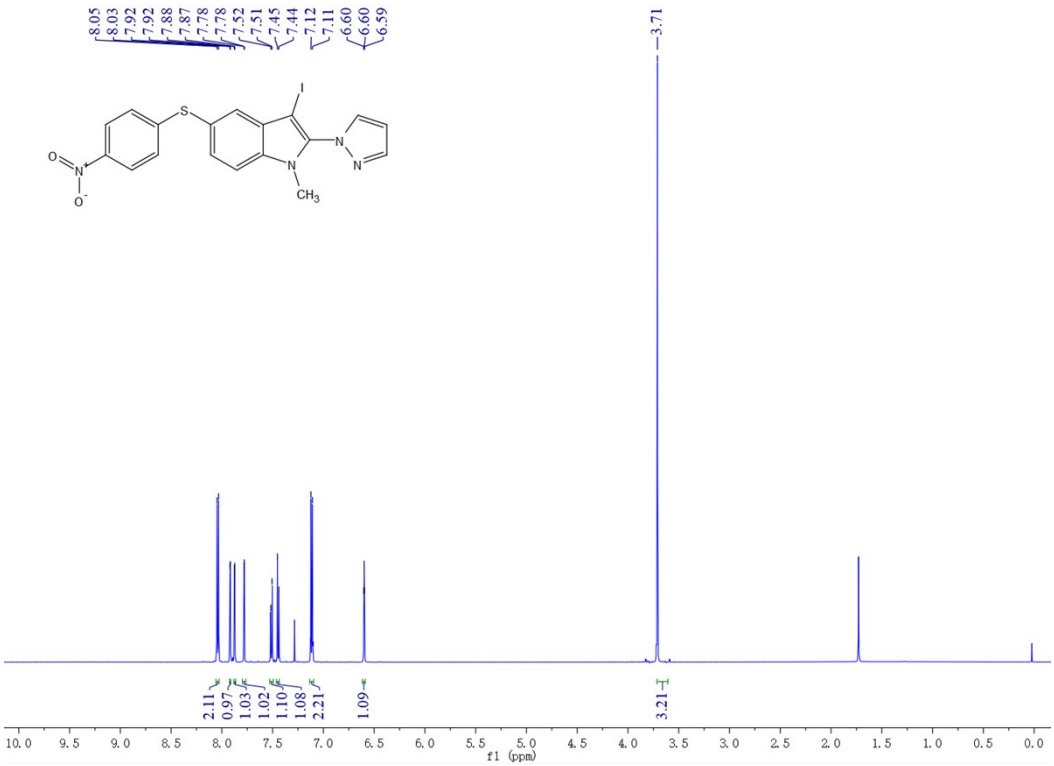
(78) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 37



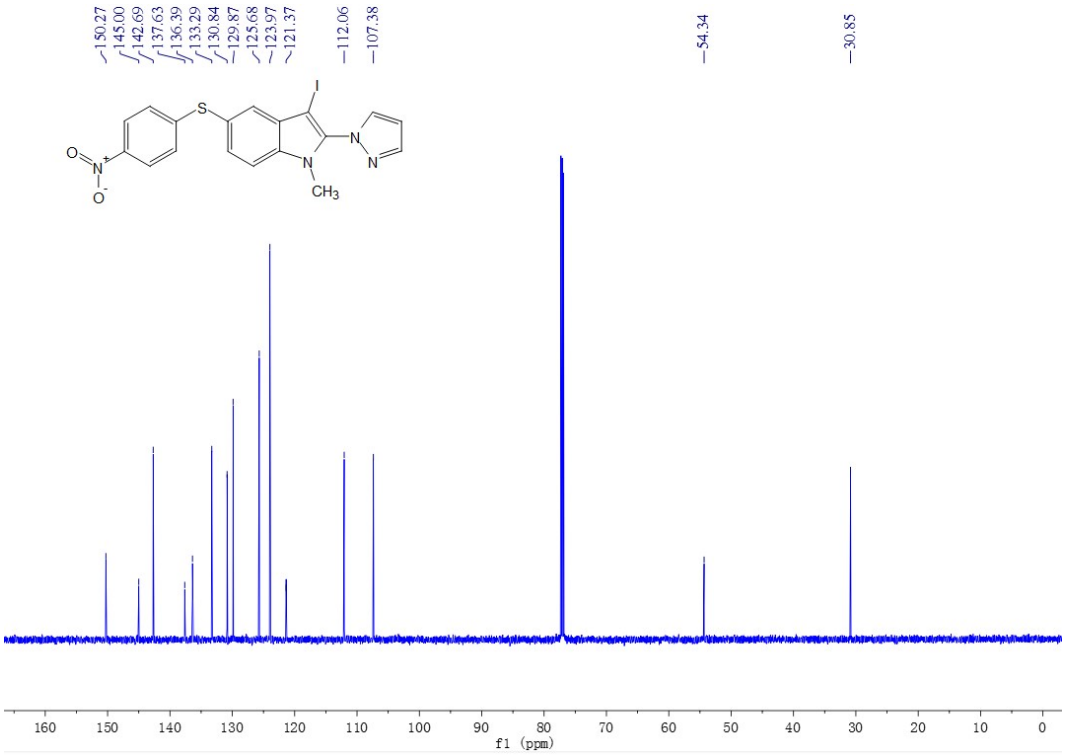
(79) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 37



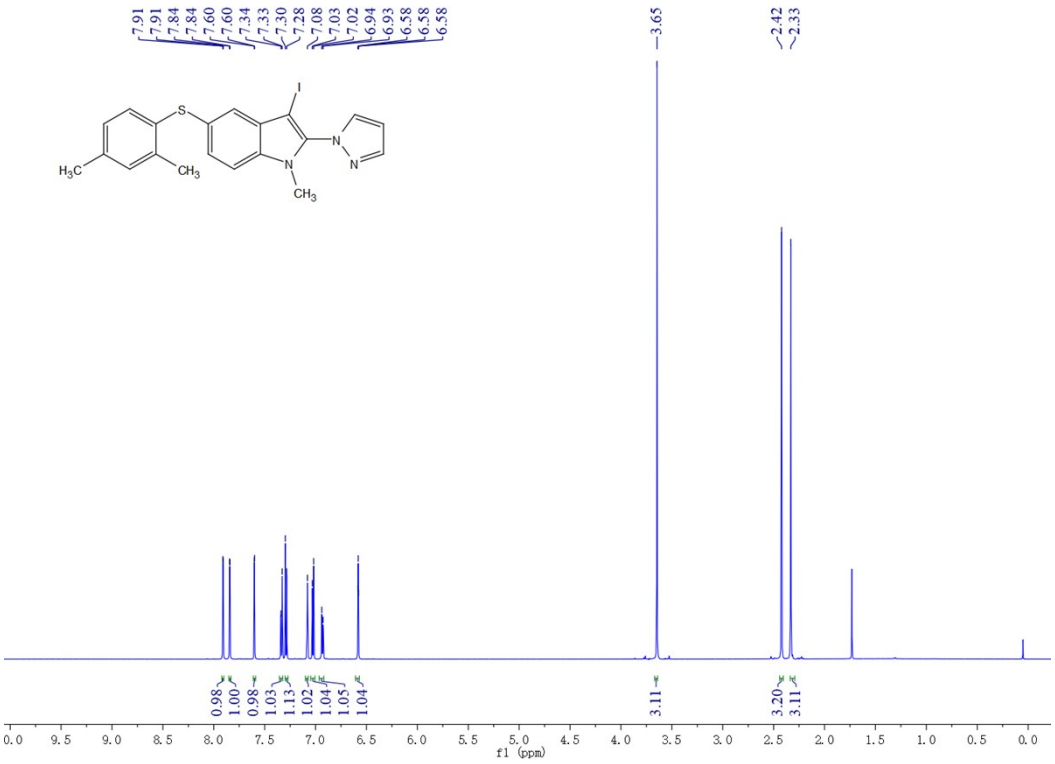
(80) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 38



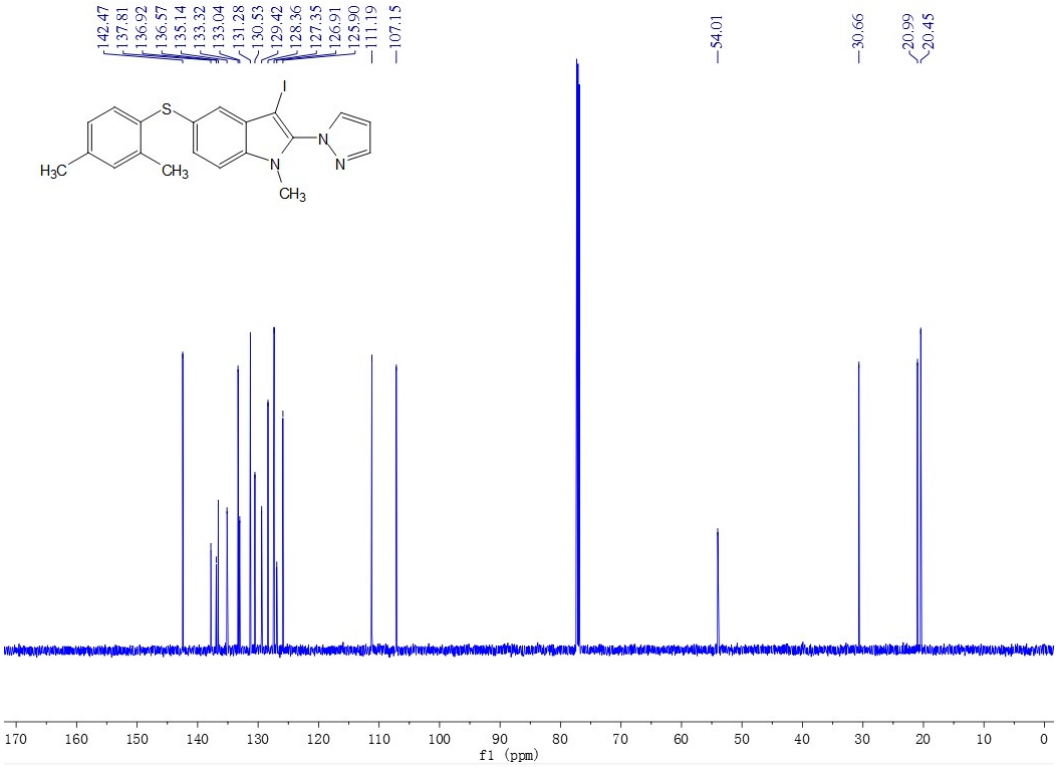
(81) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 38



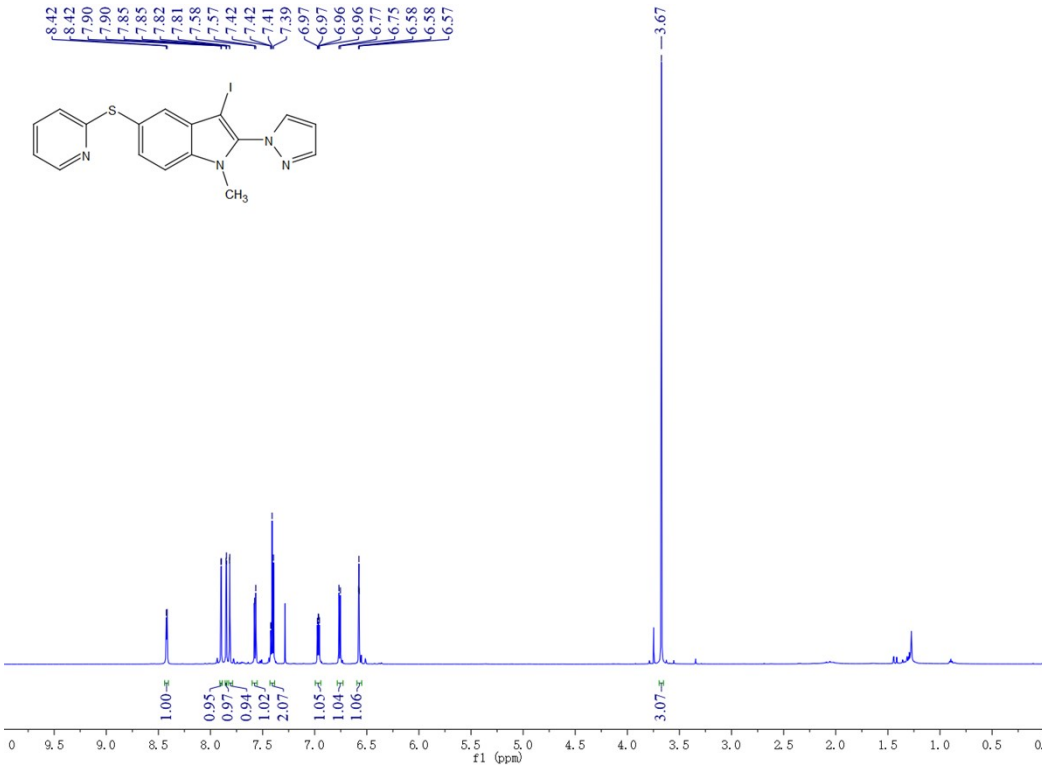
(82) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 39



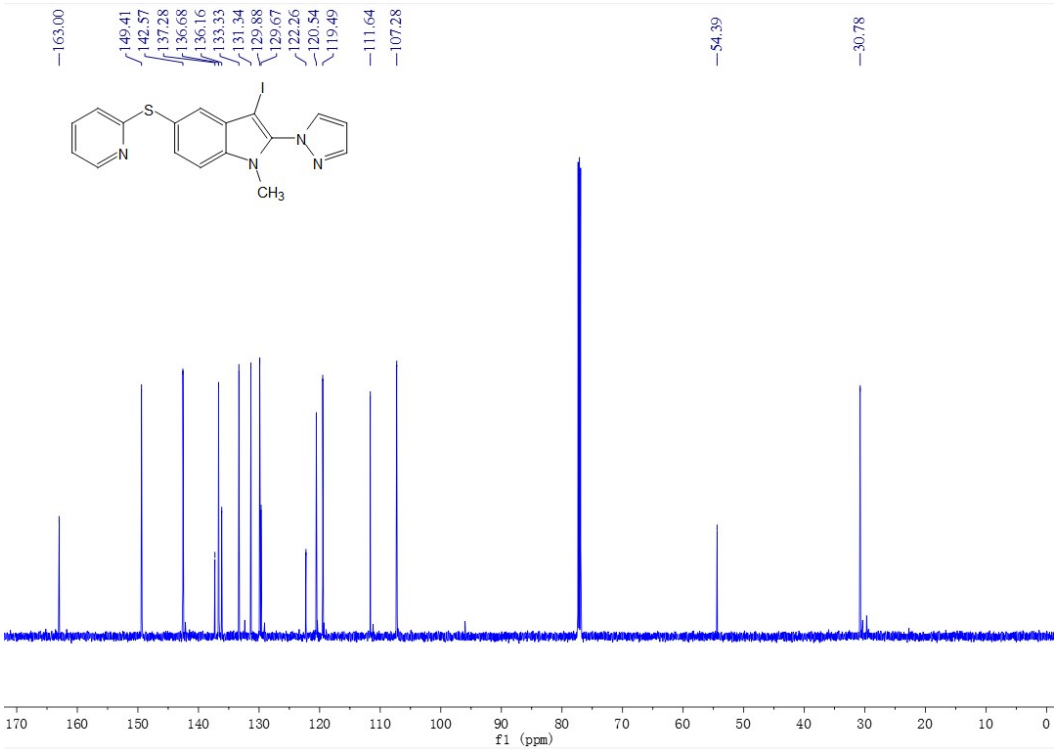
(83) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 39



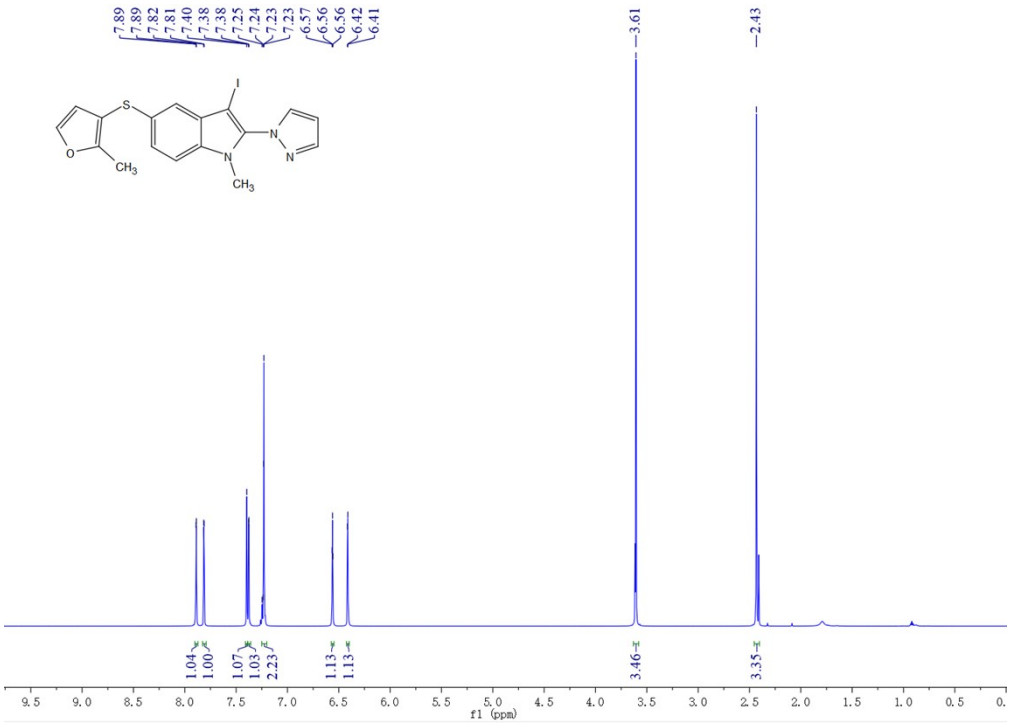
(84) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 40



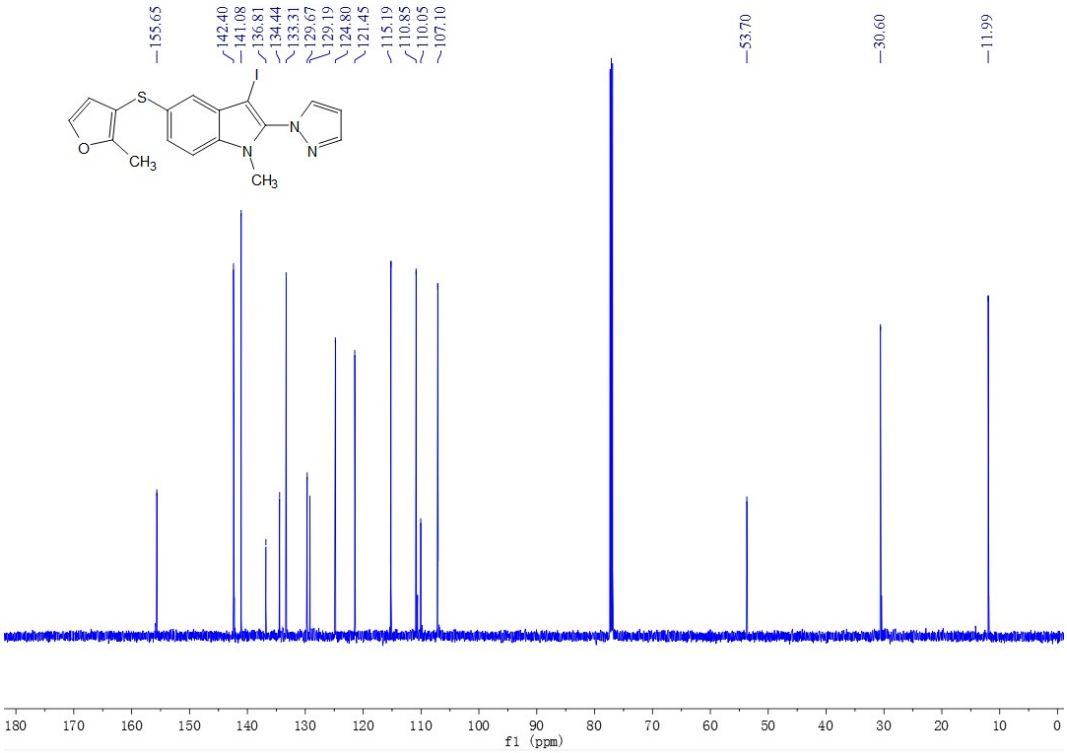
(85) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 40



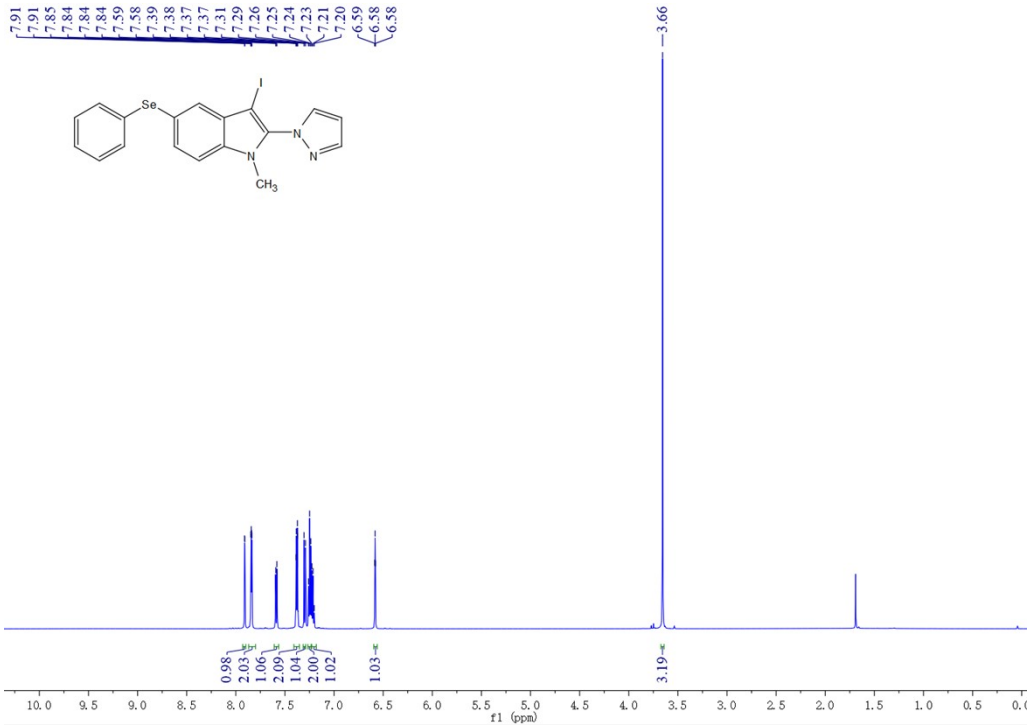
(86) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 41



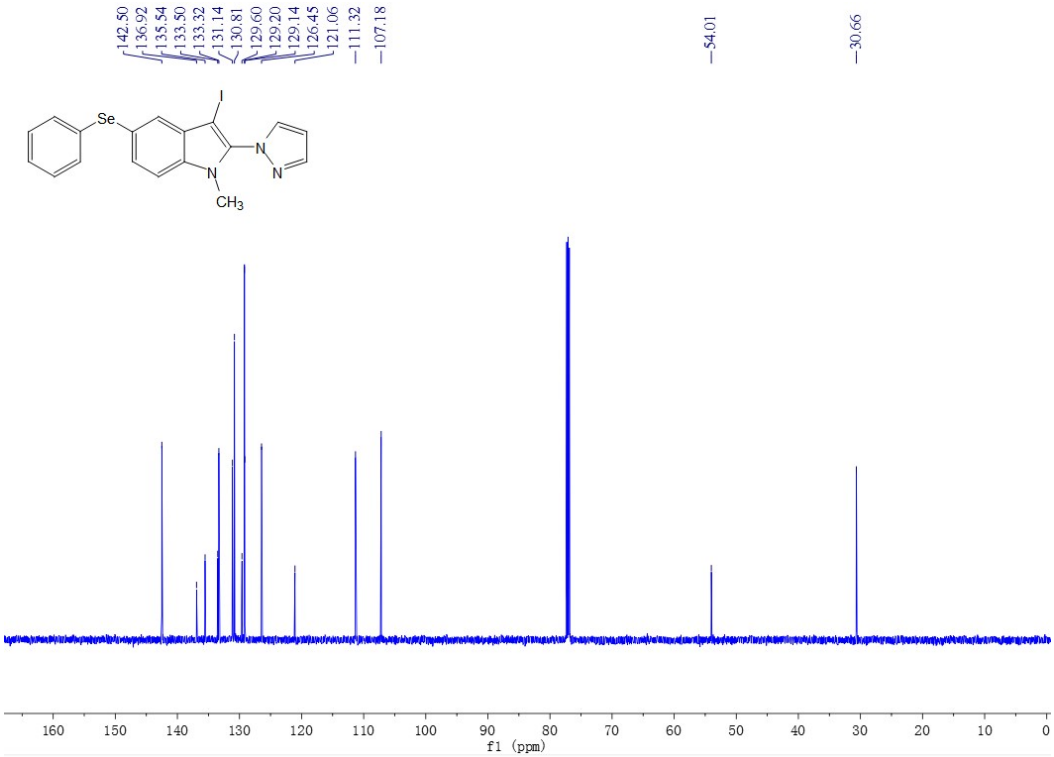
(87) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 41



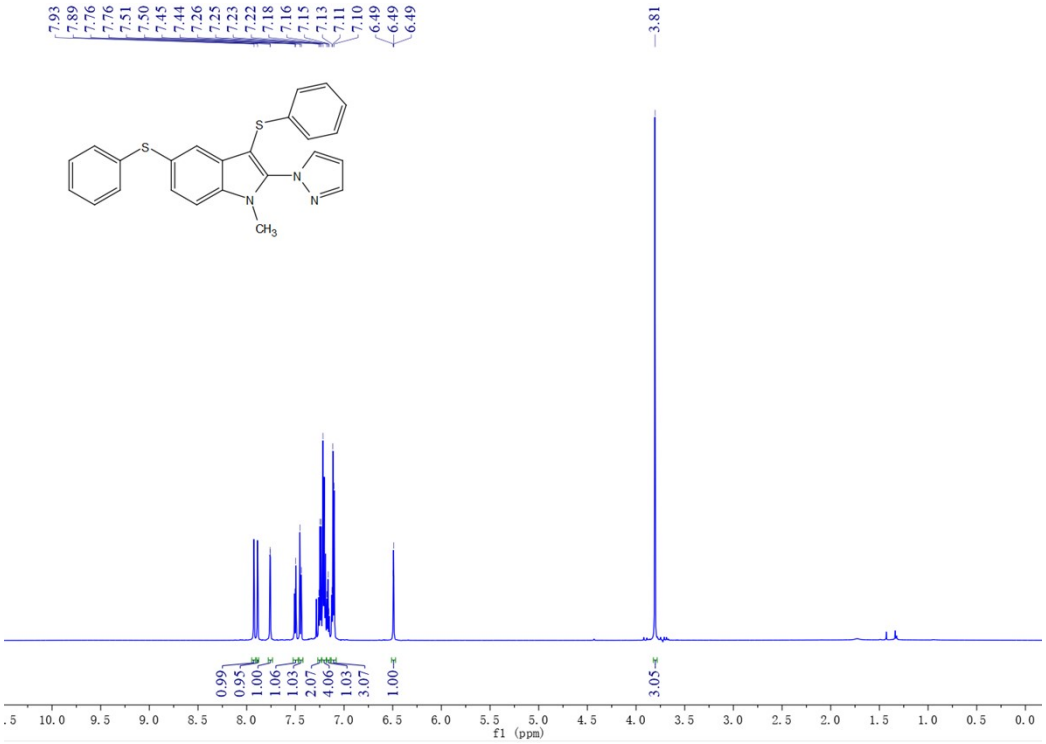
(88) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 42



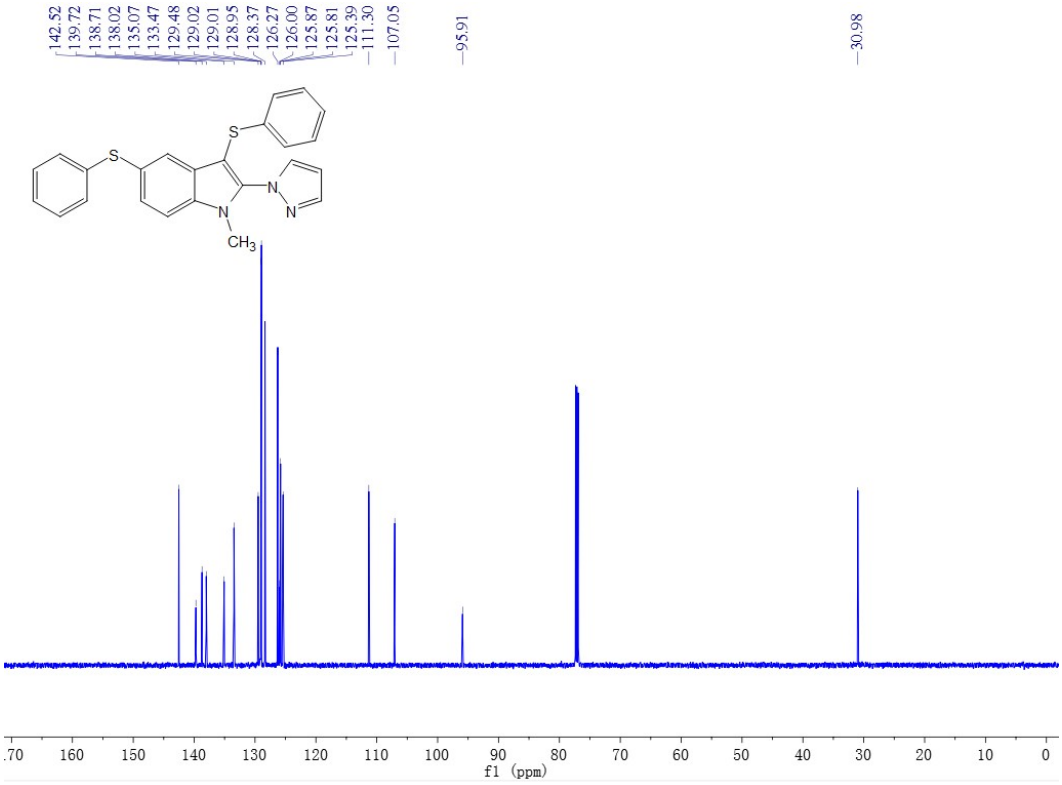
(89) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 42



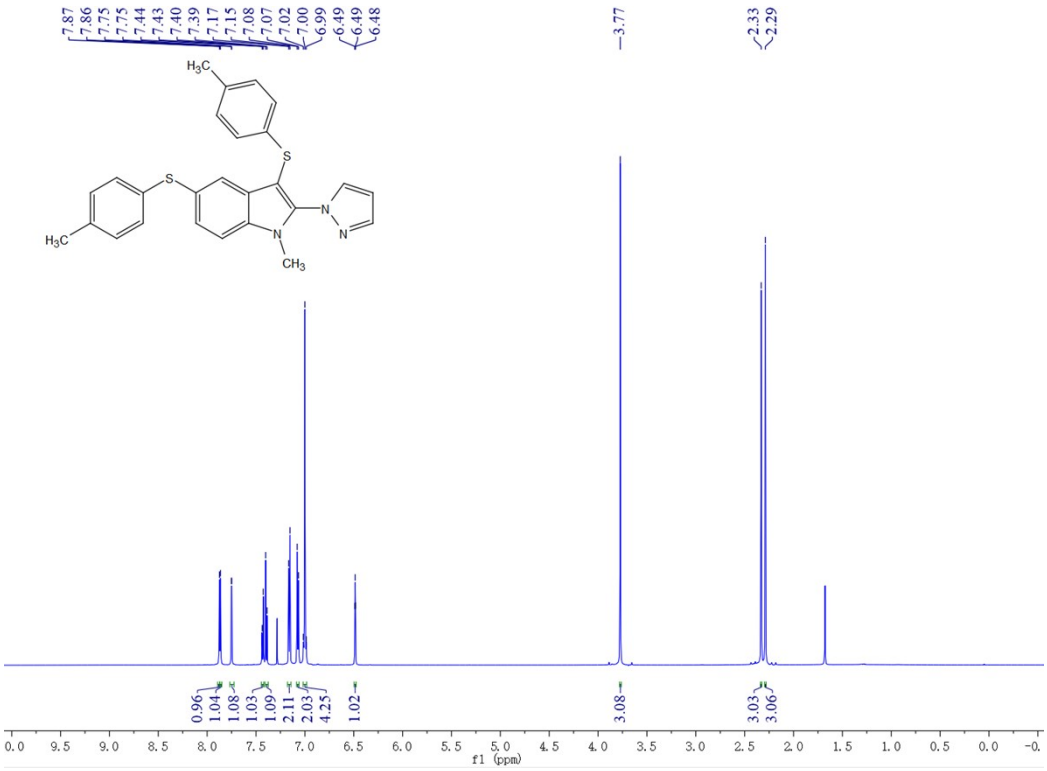
(90) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 43



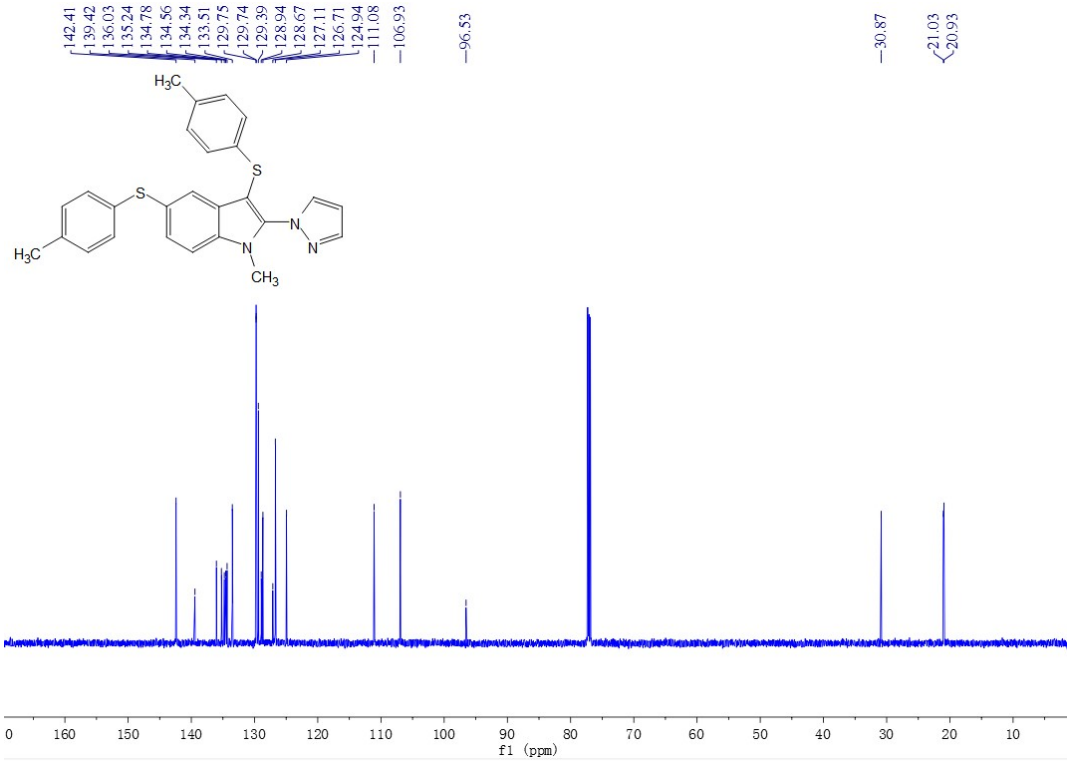
(91) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 43



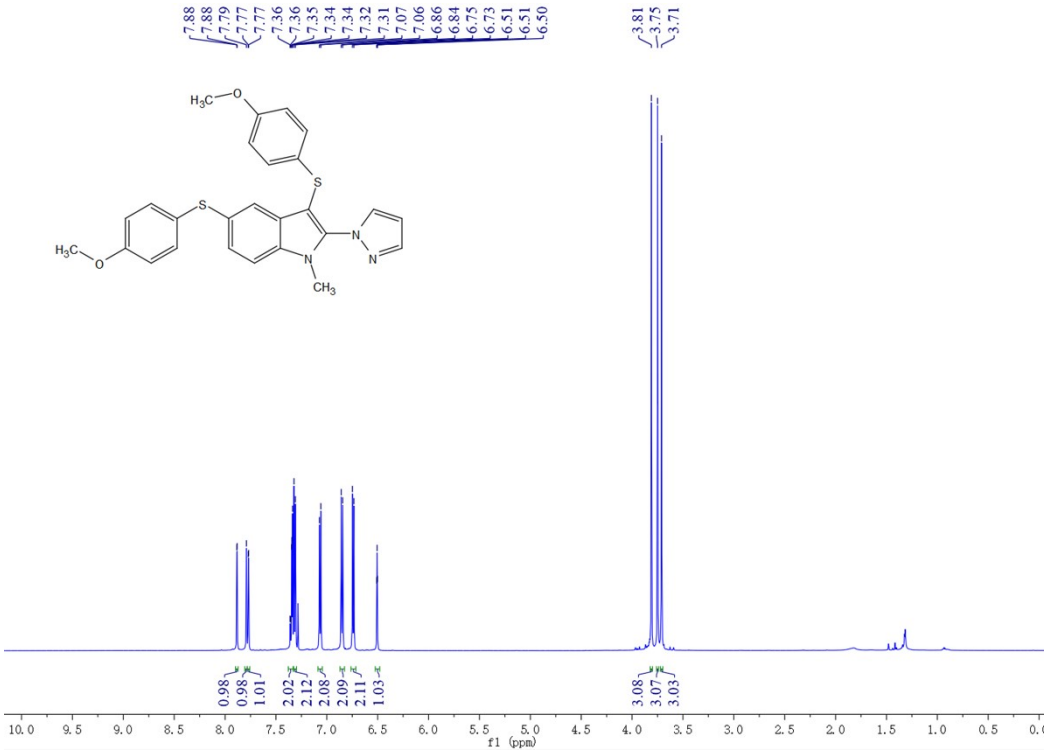
(92) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 44



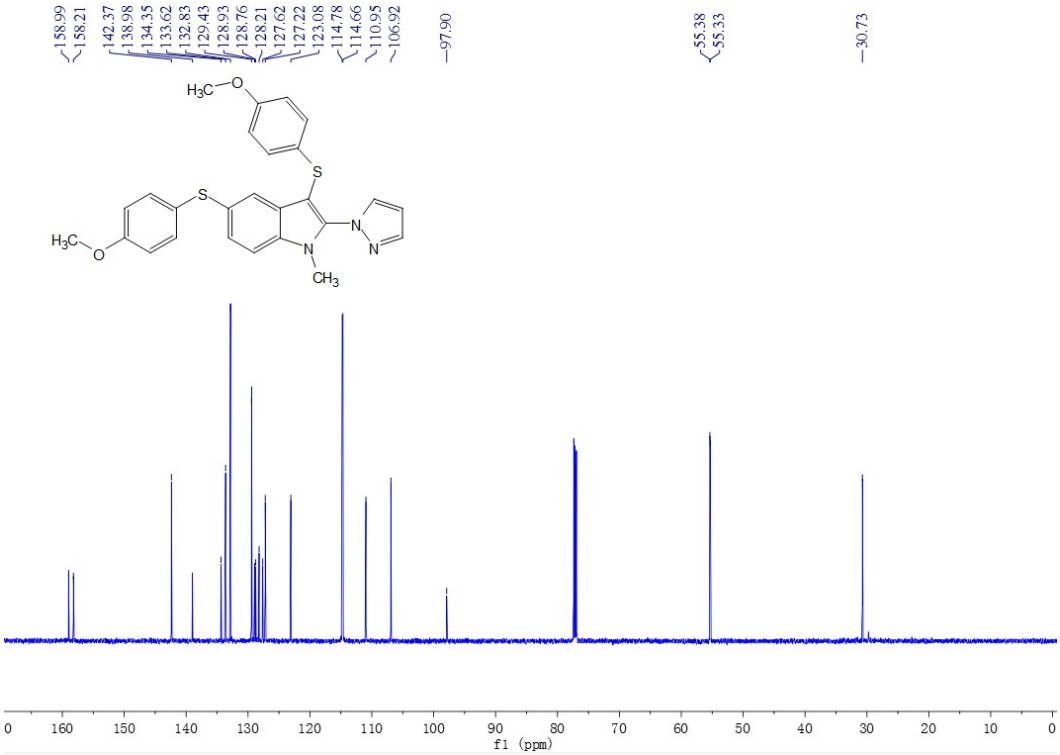
(93) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 44



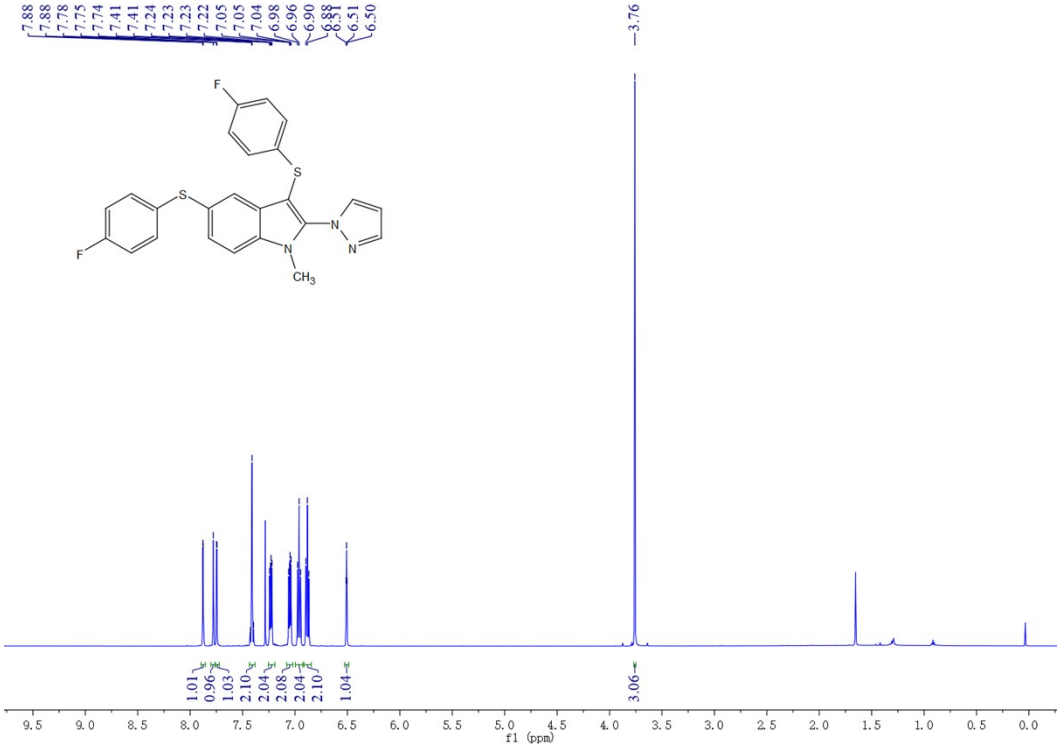
(94) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 45



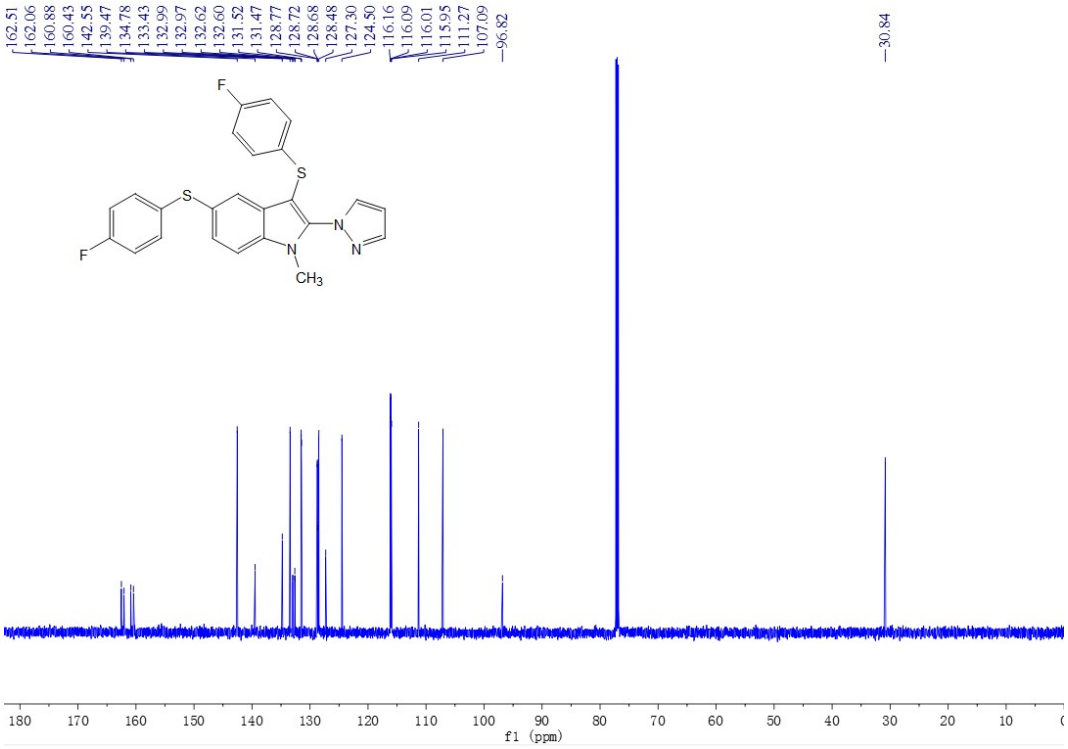
(95) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 45



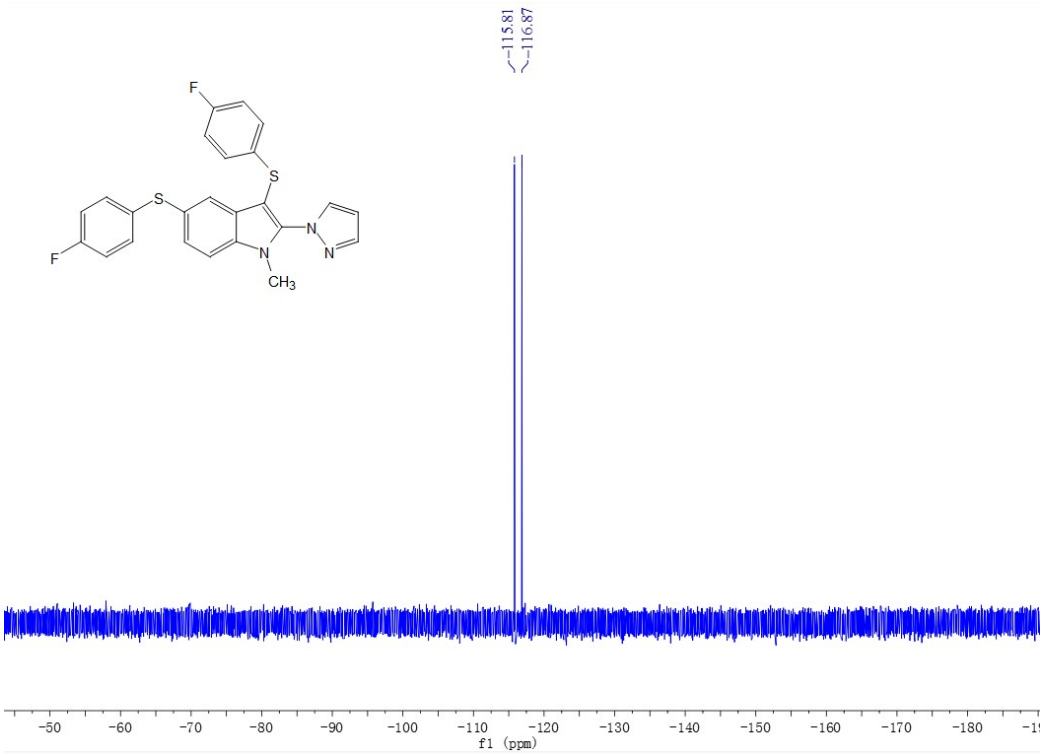
(96) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 46



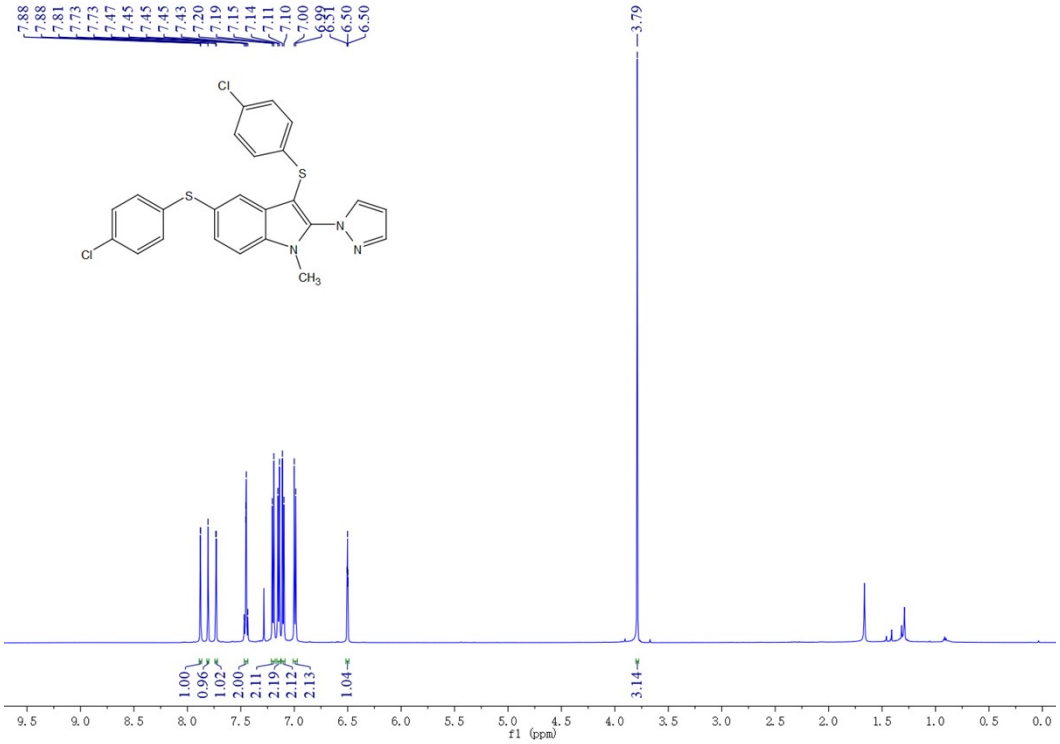
(97) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 46



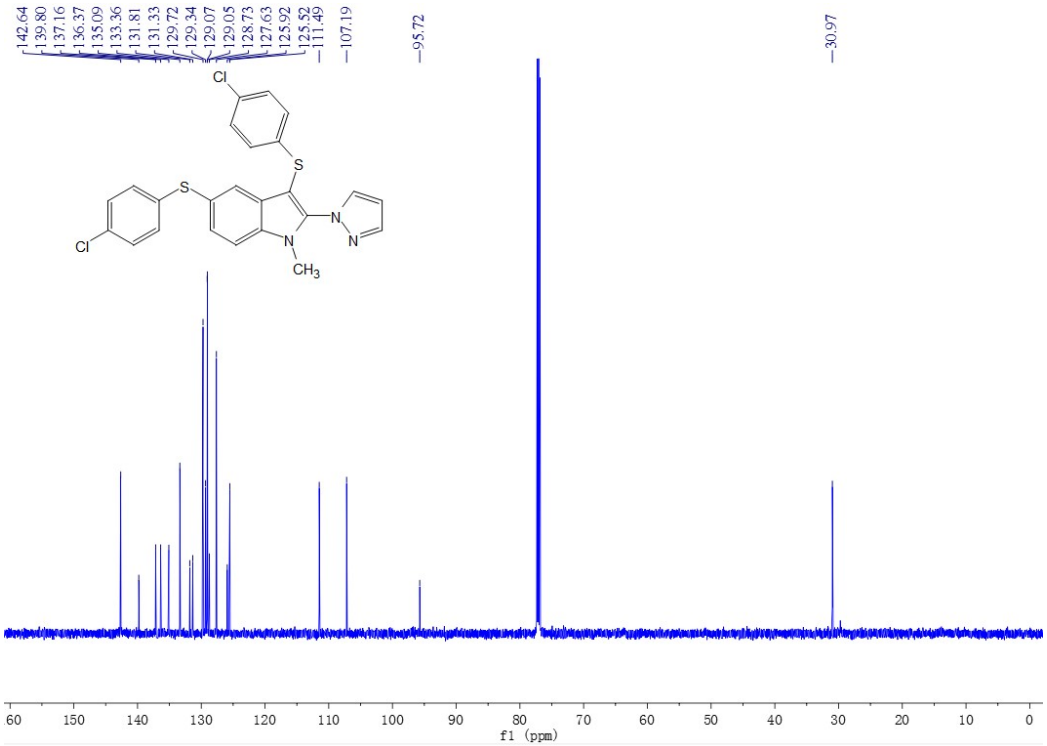
(98) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 46



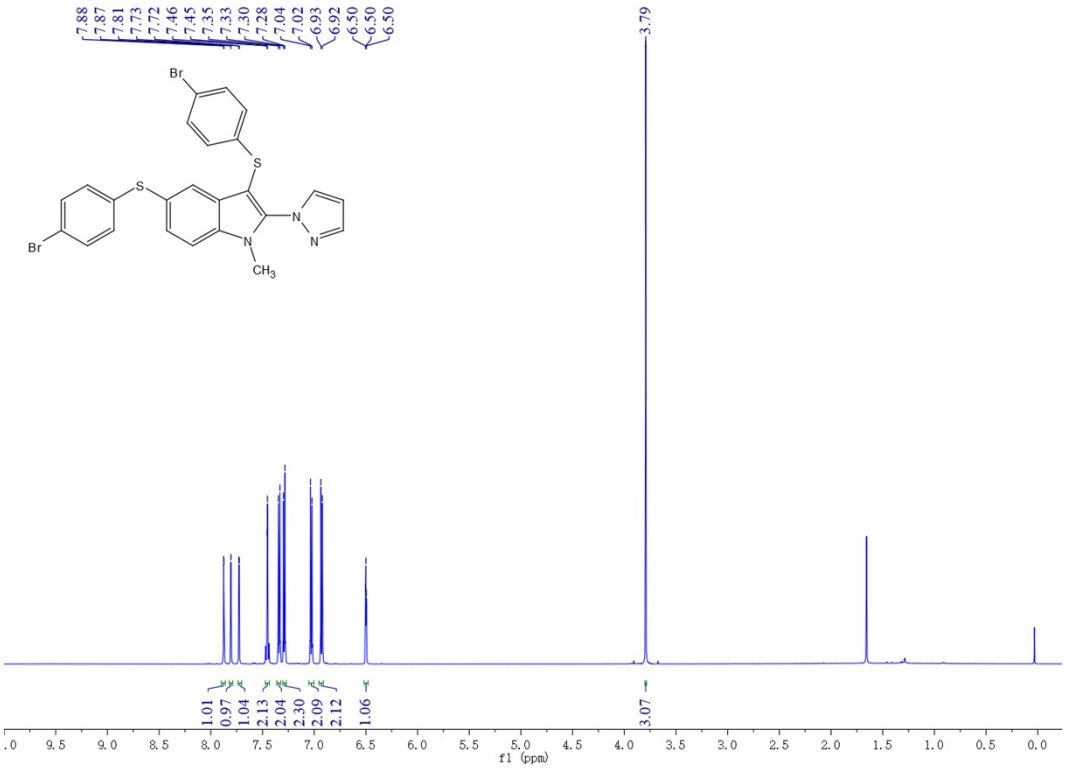
(99) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 47



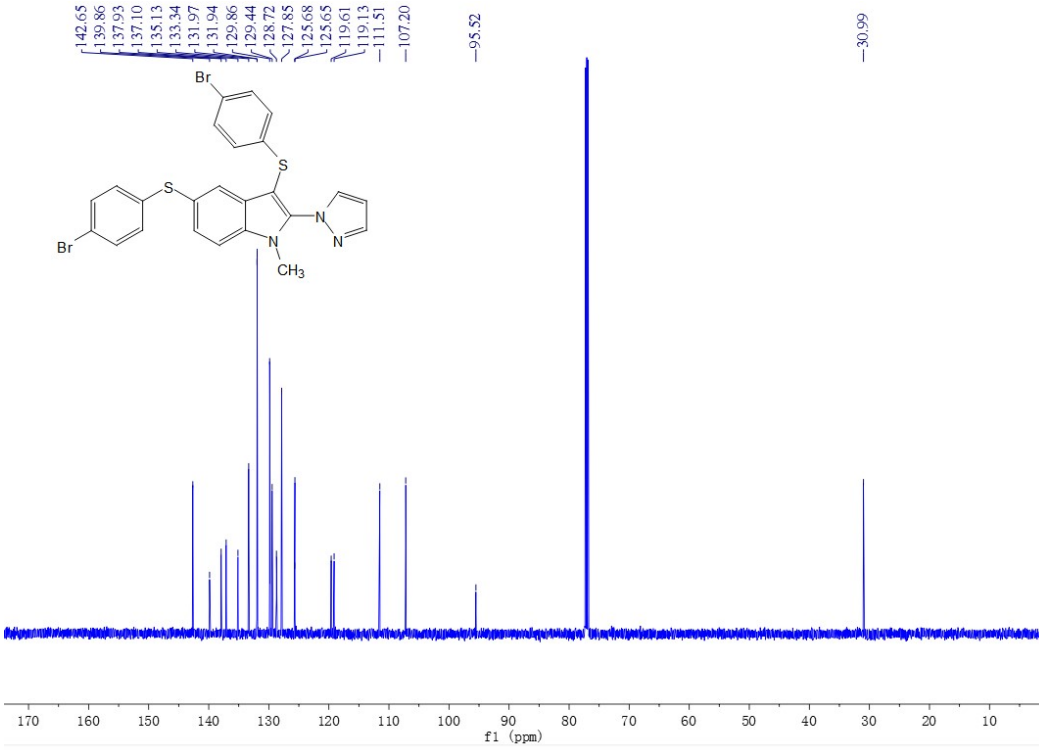
(100) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 47



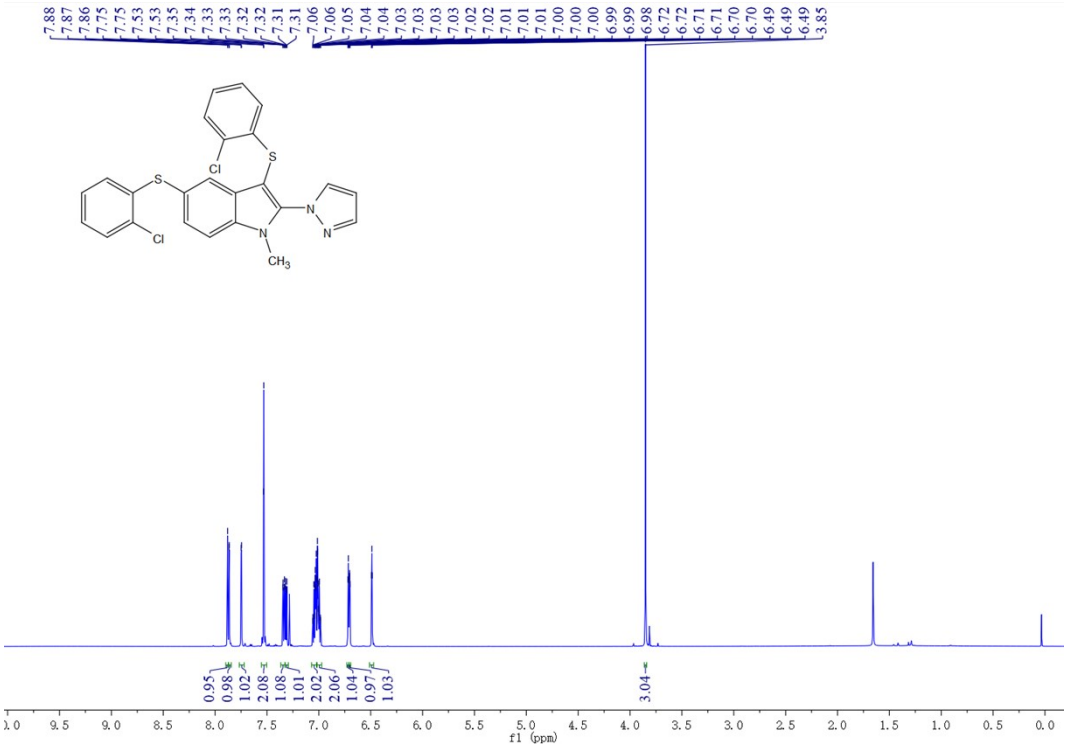
(101) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 48



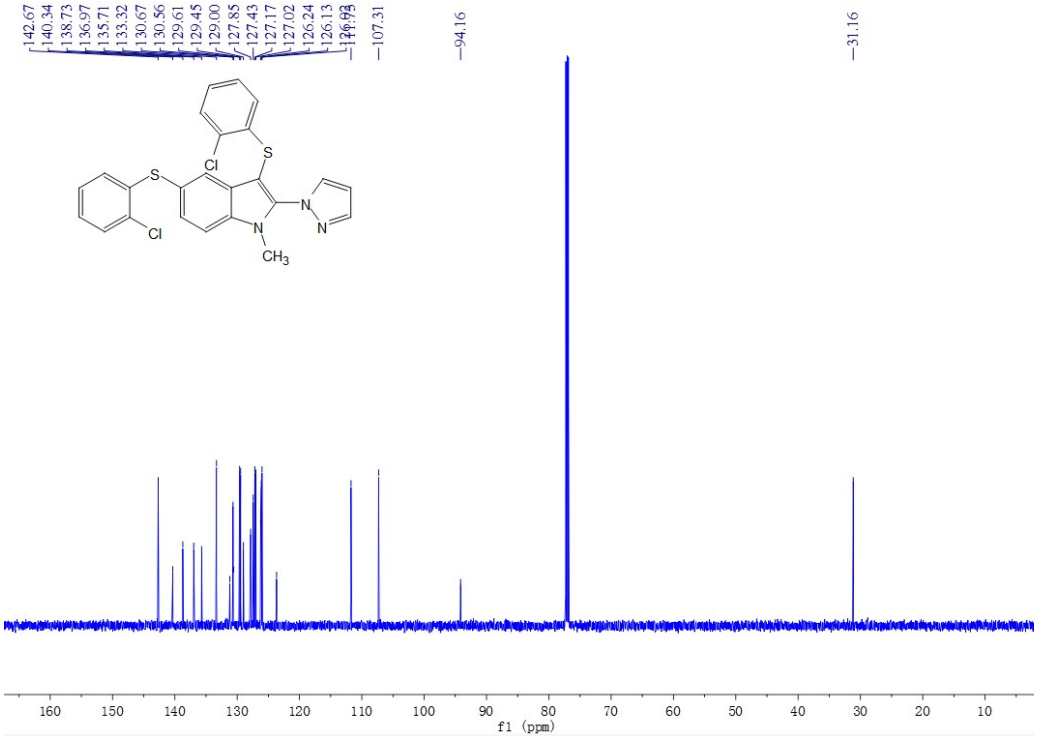
(102) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 48



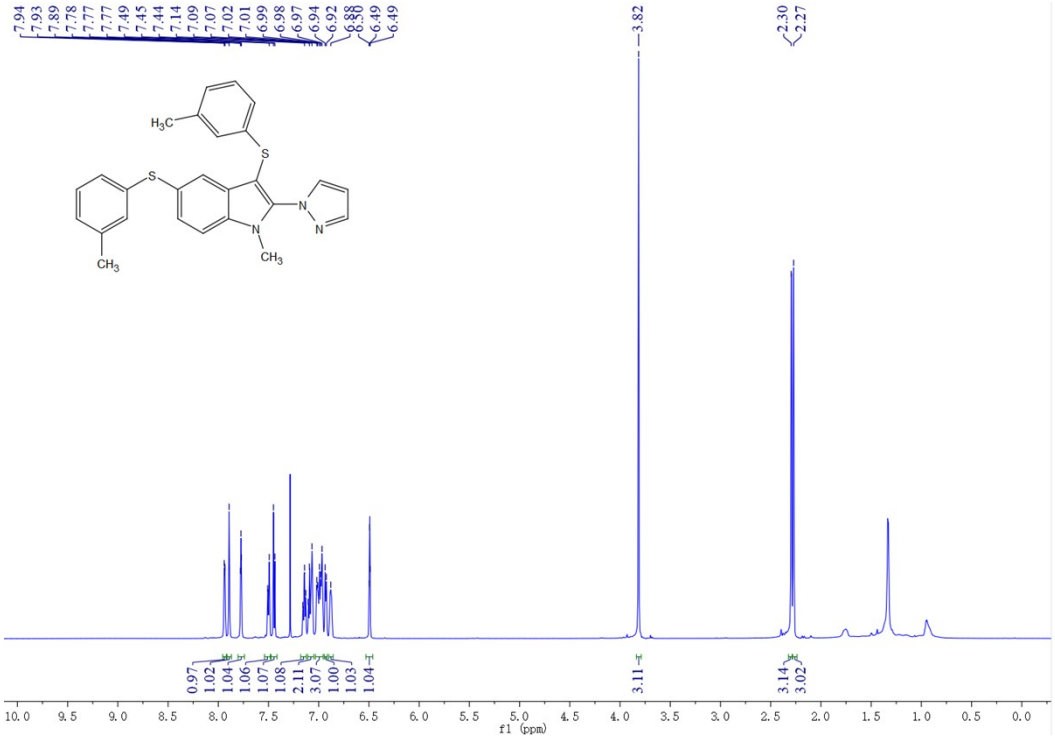
(103) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 49



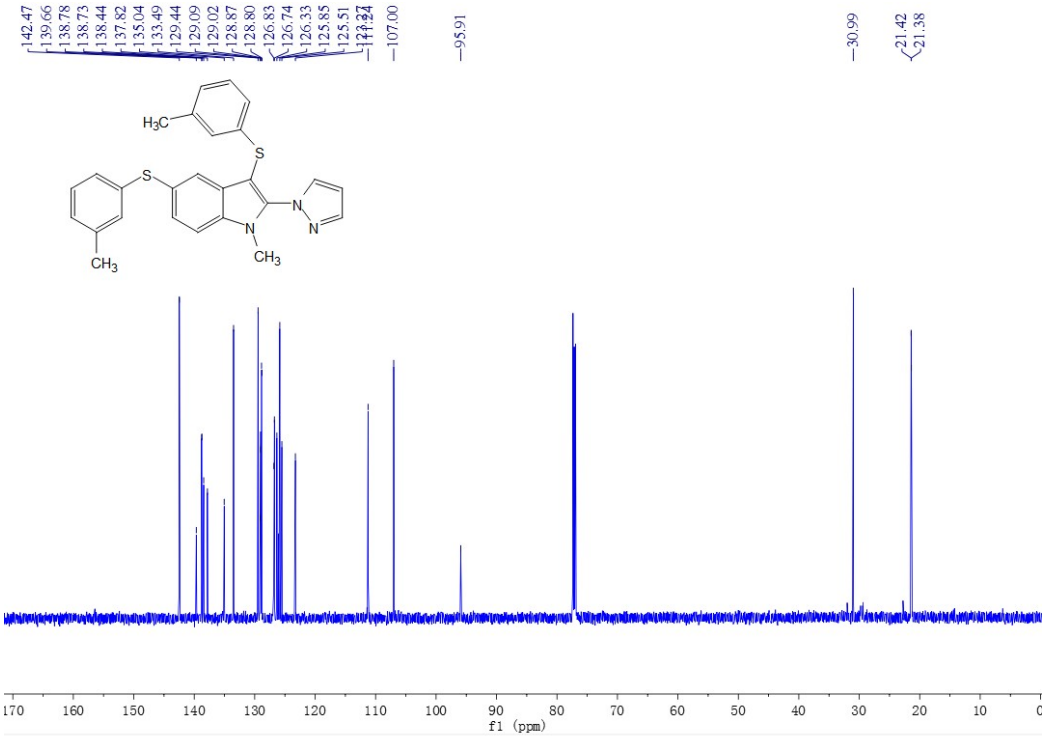
(104) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 49



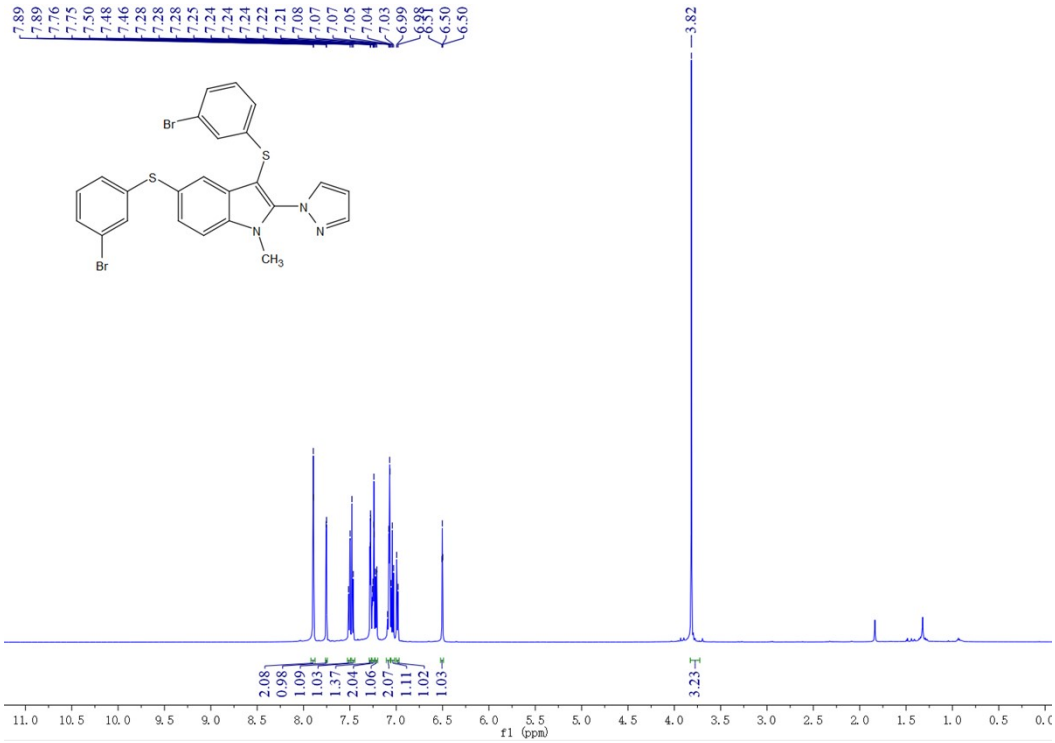
(105) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 50



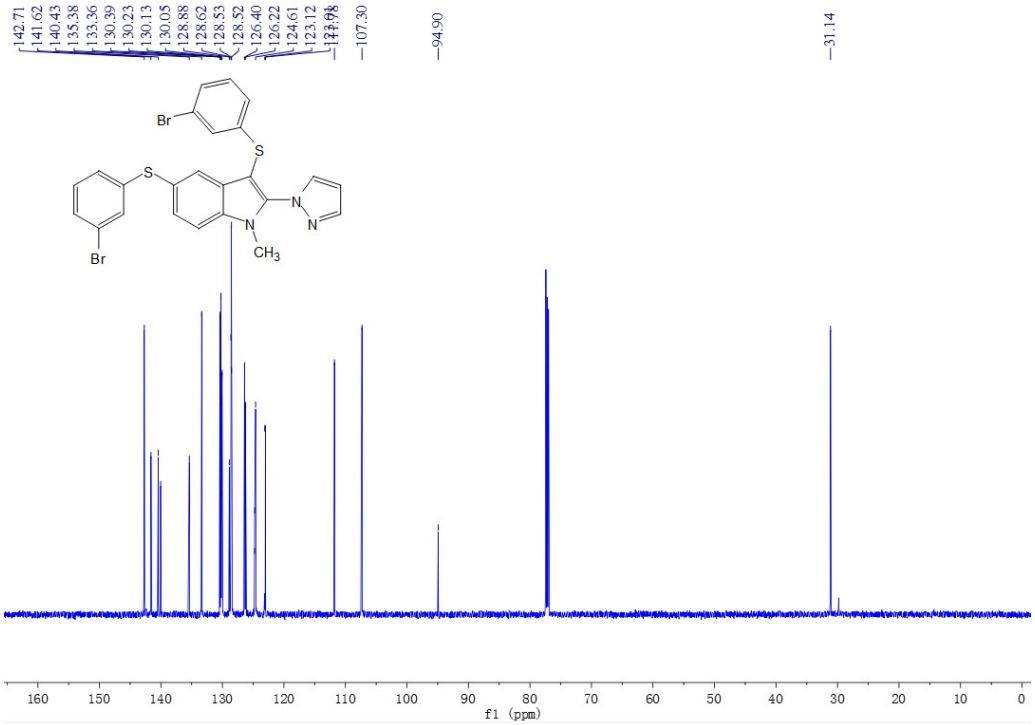
(106) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 50



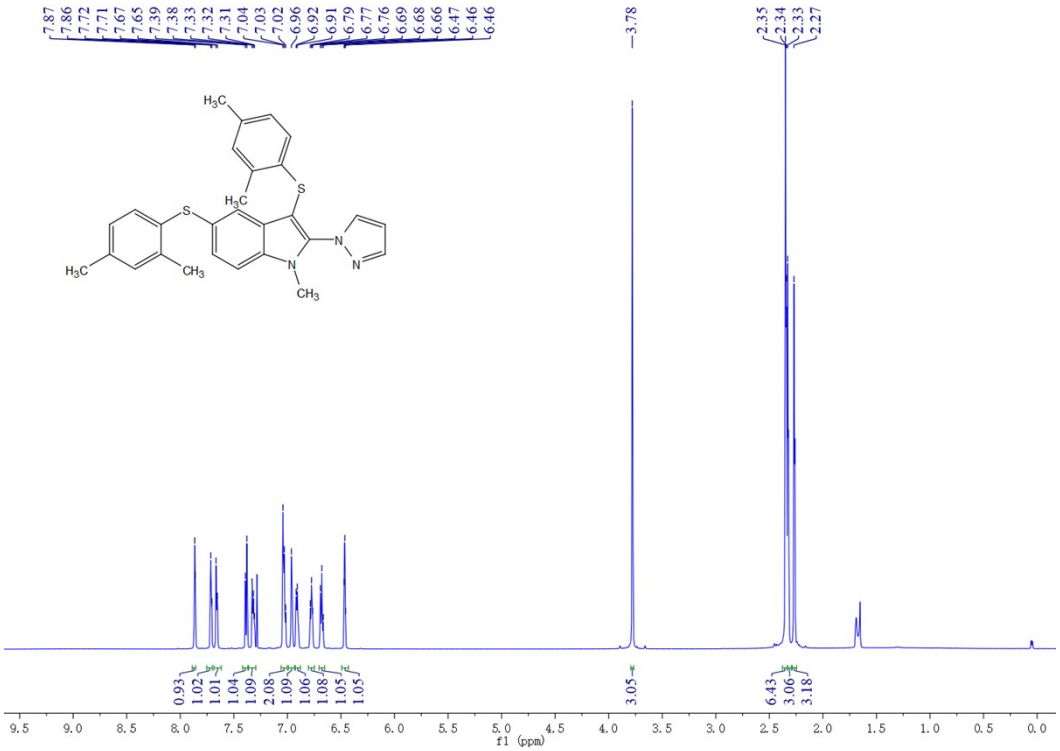
(107) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 51



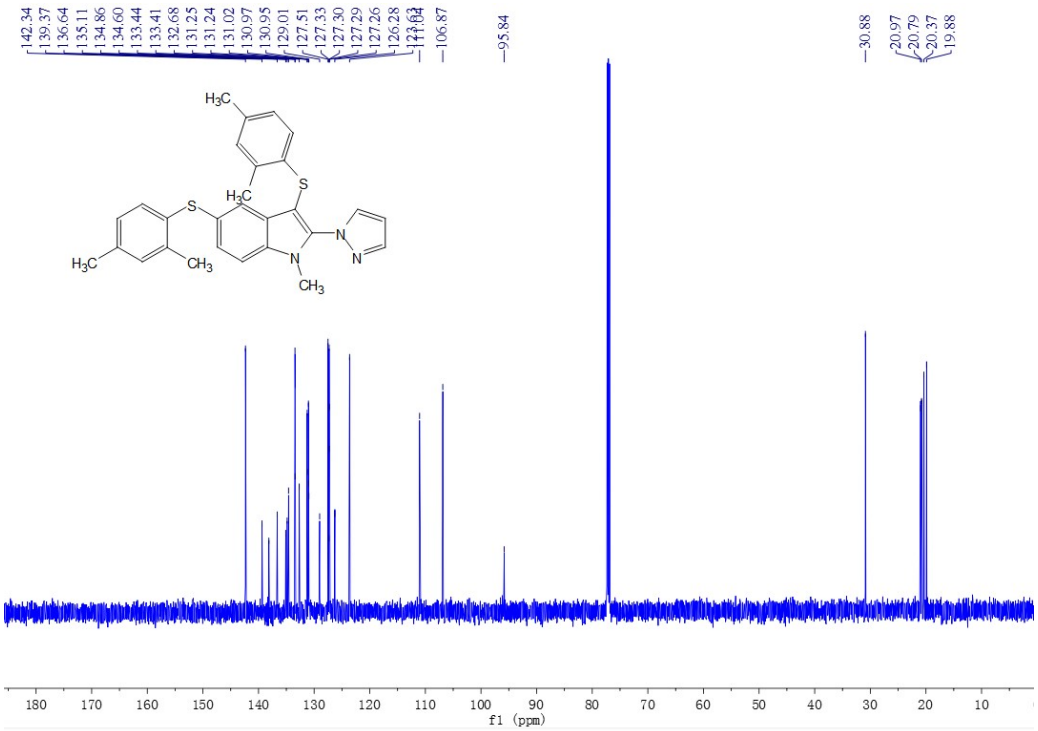
(108) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 51



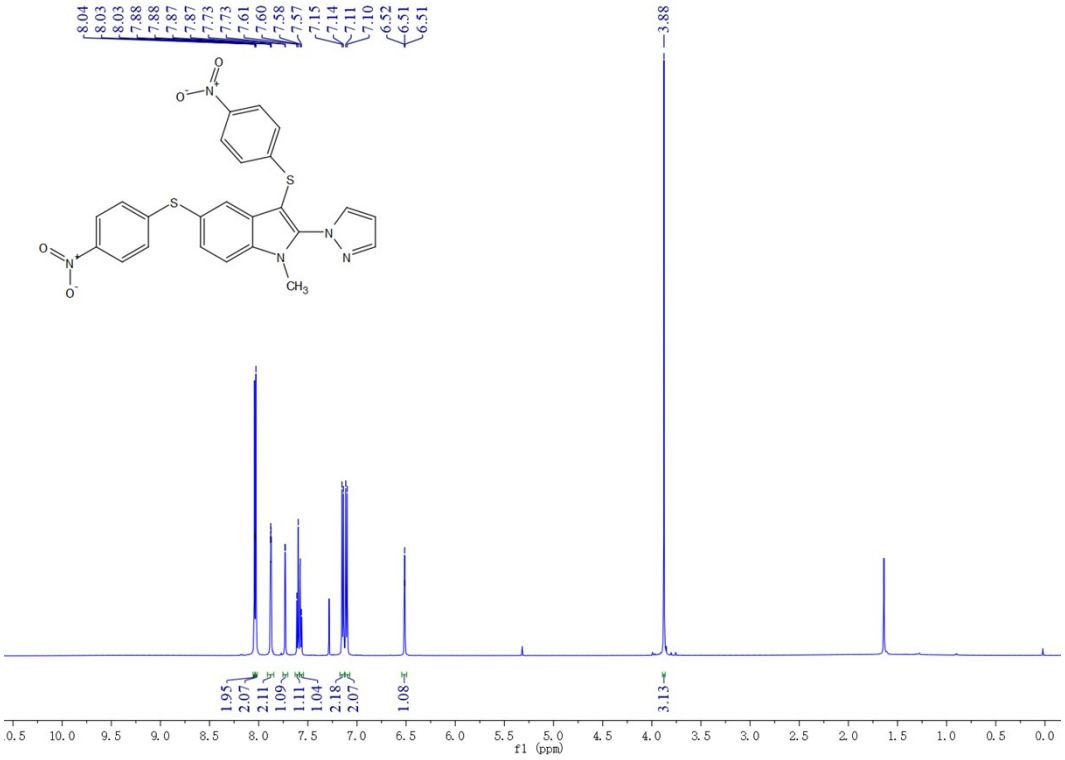
(109) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 52



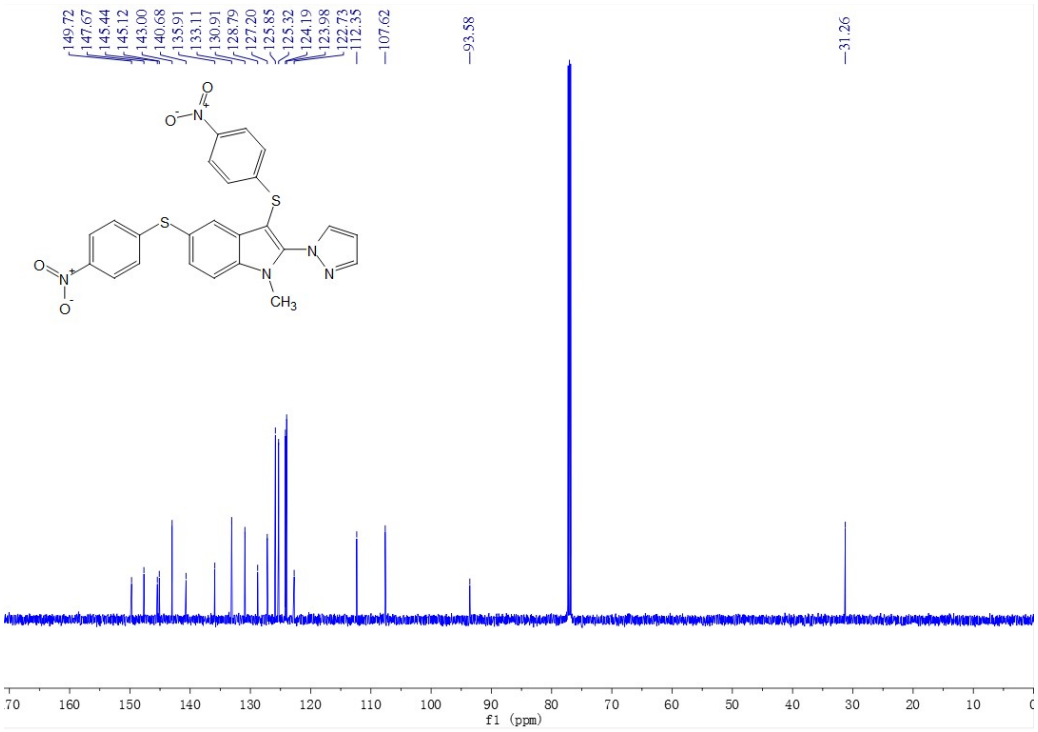
(110) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 52



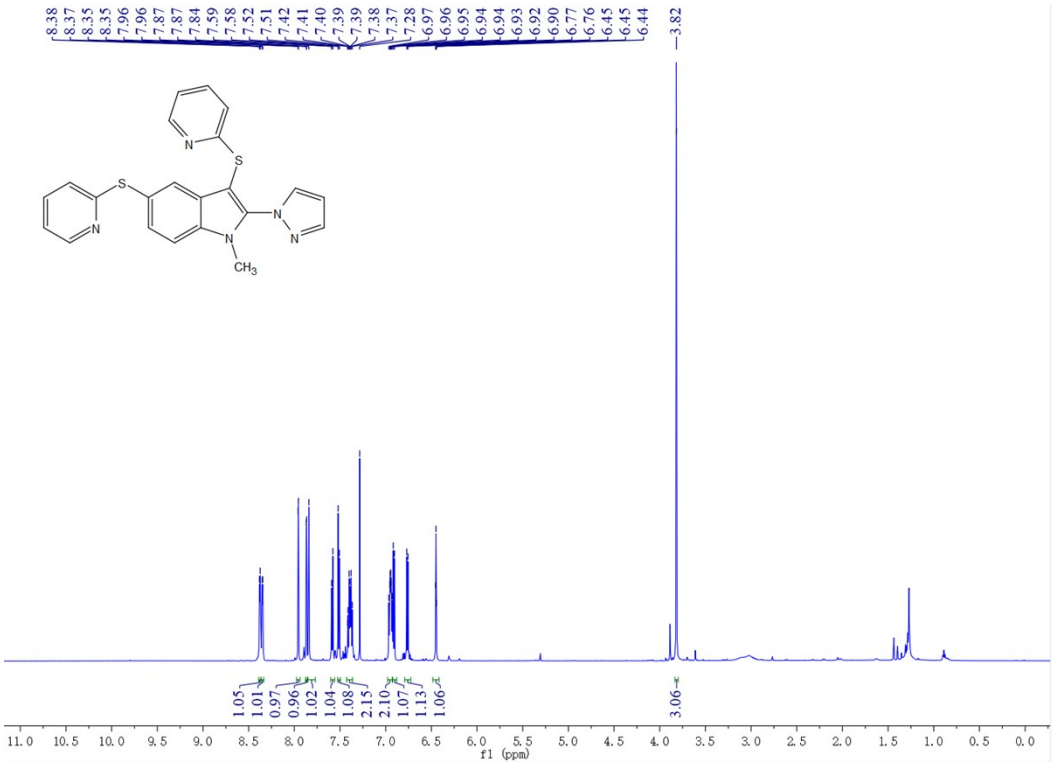
(111) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 53



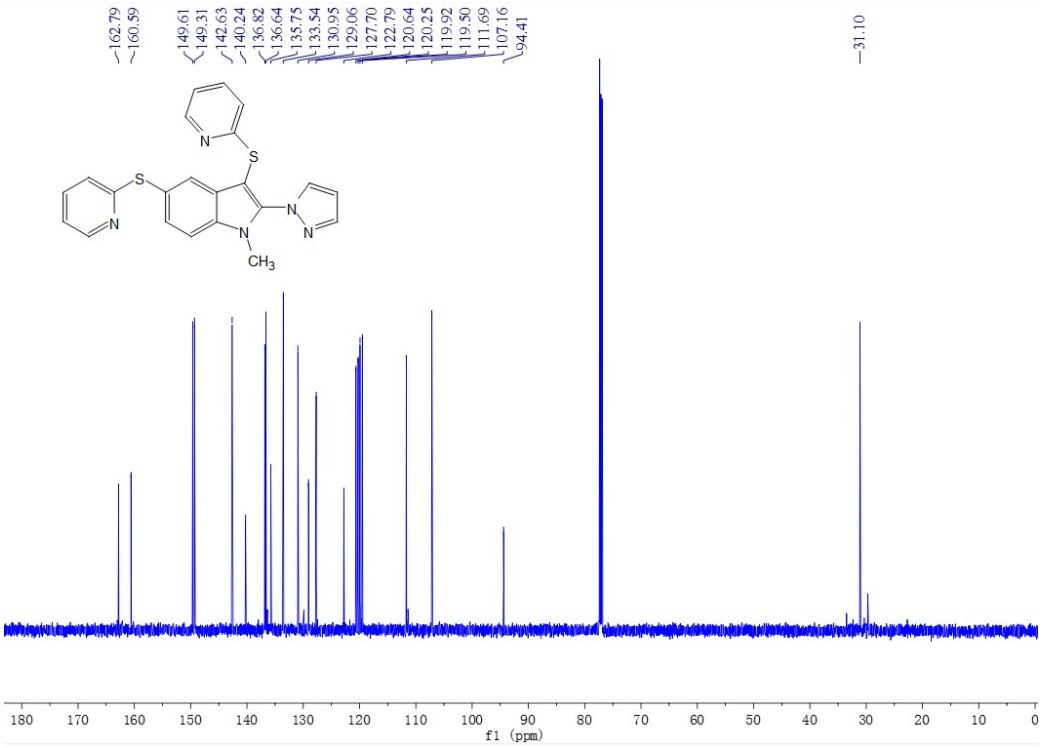
(112) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 53



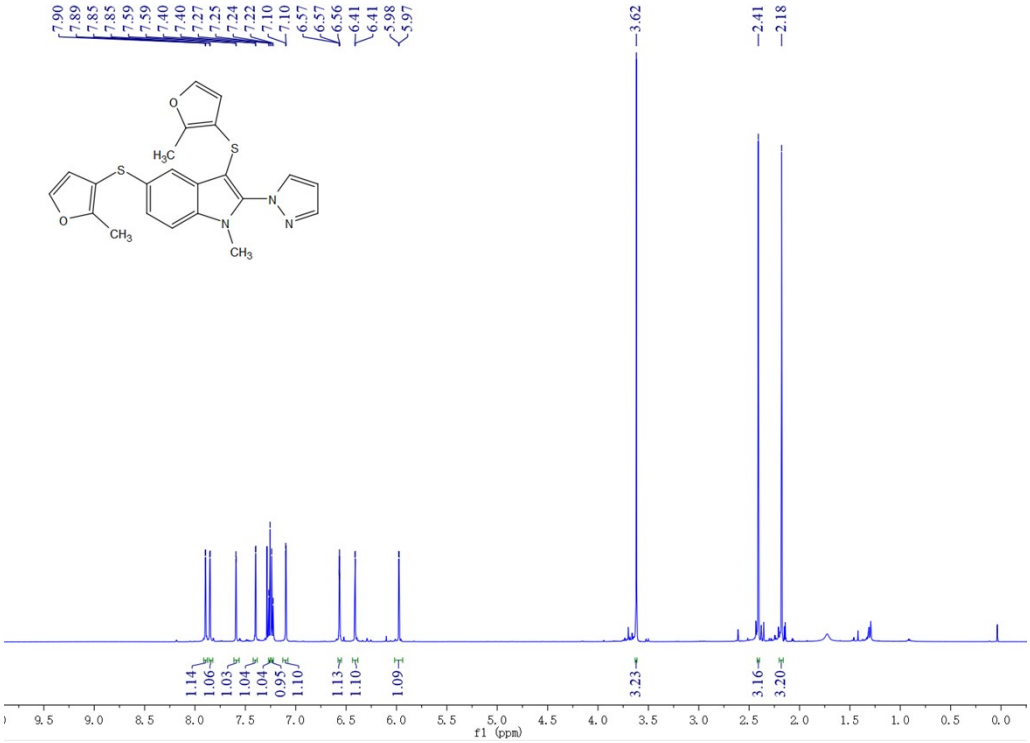
(113) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 54



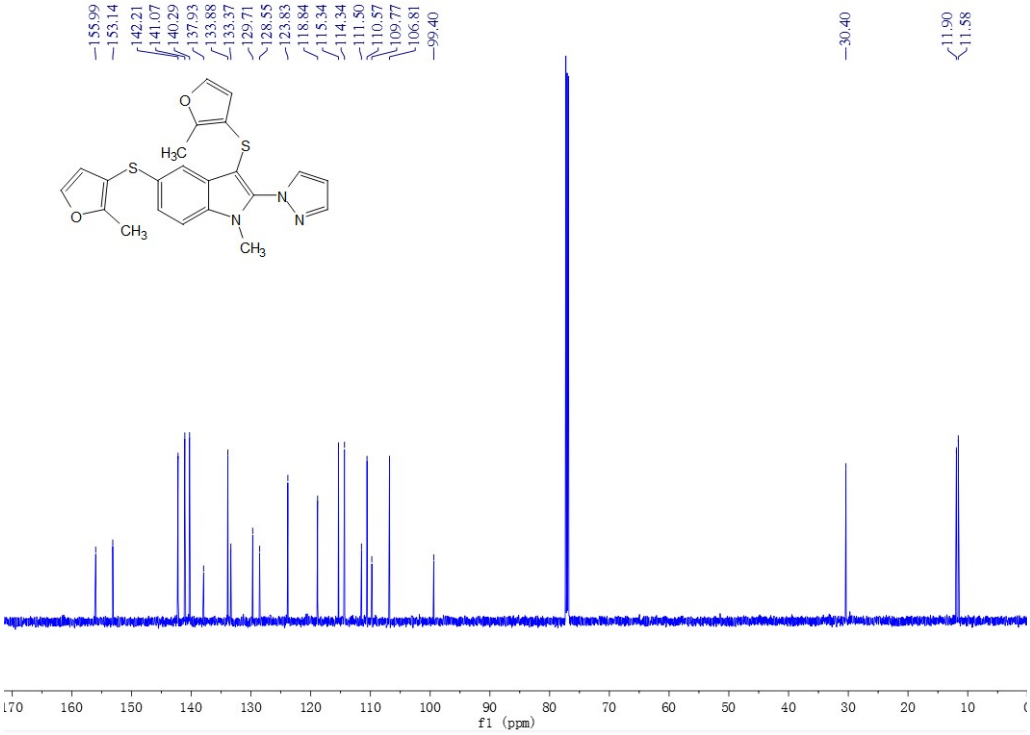
(114) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 54



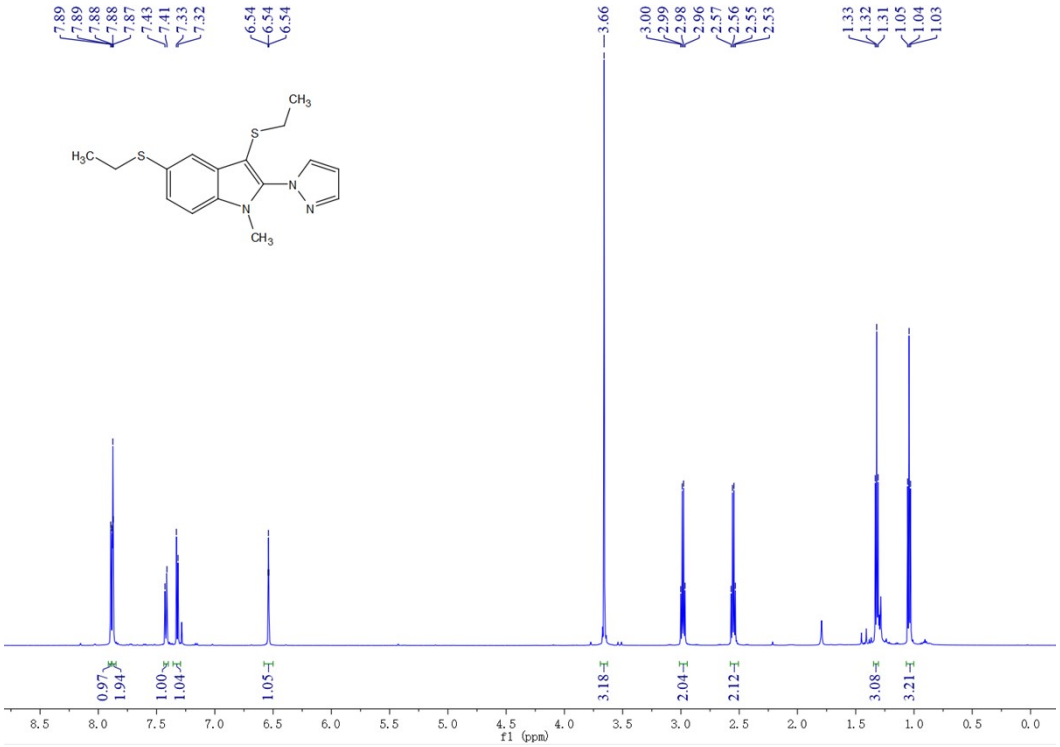
(115) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 55



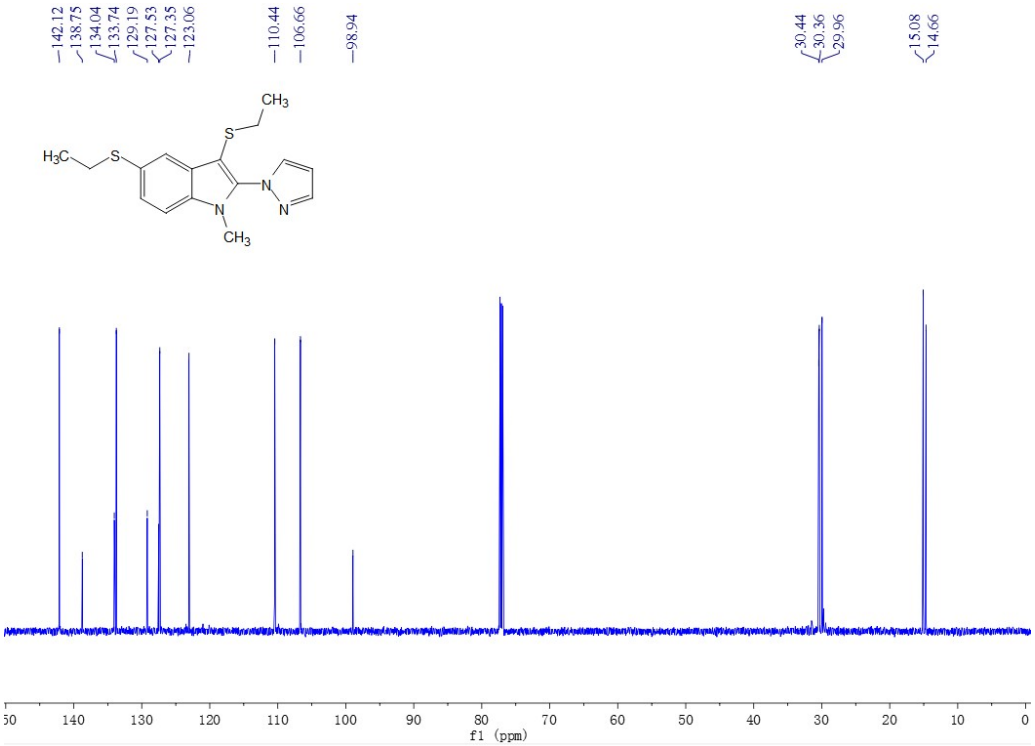
(116) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 55



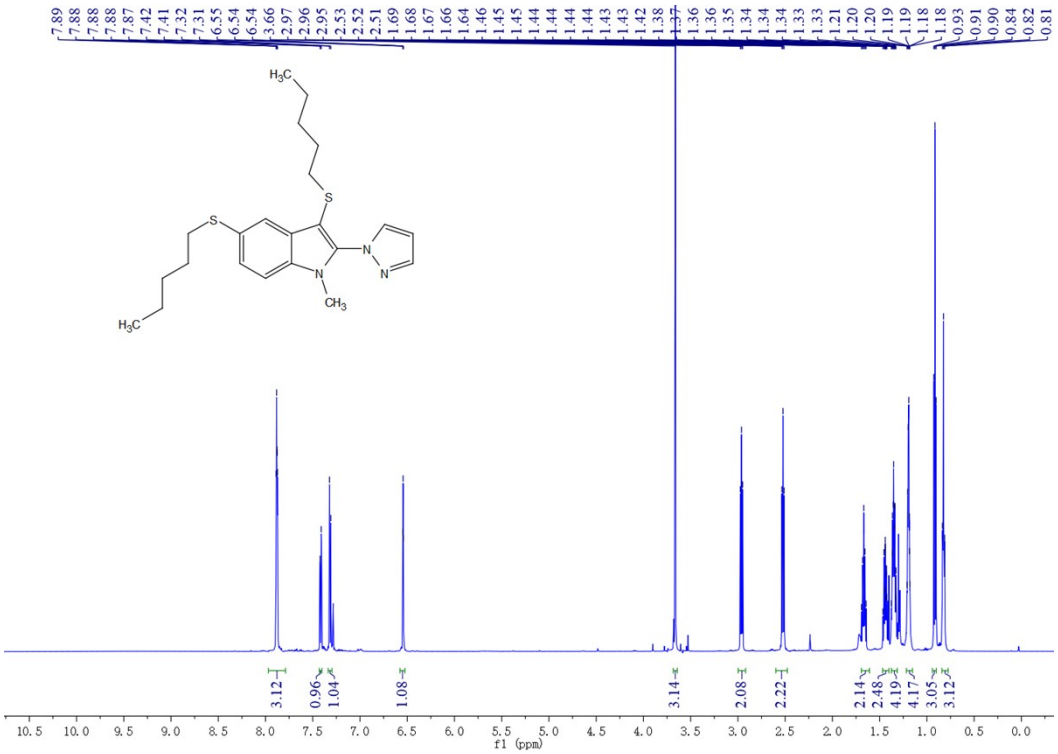
(117) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 56



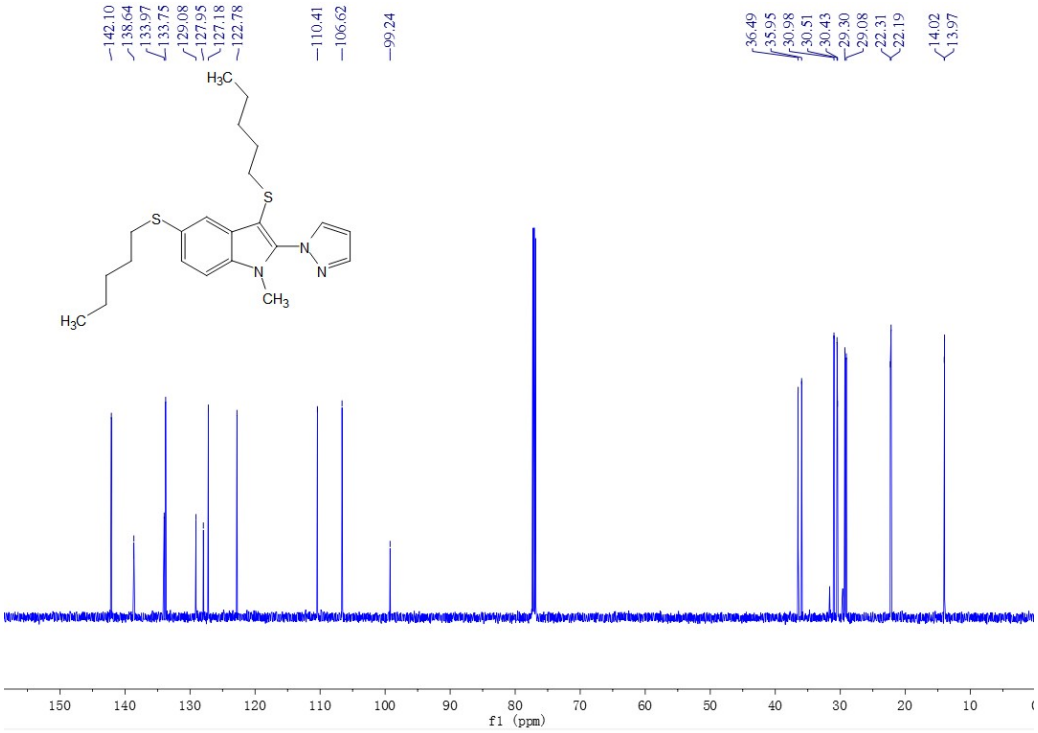
(118) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 56



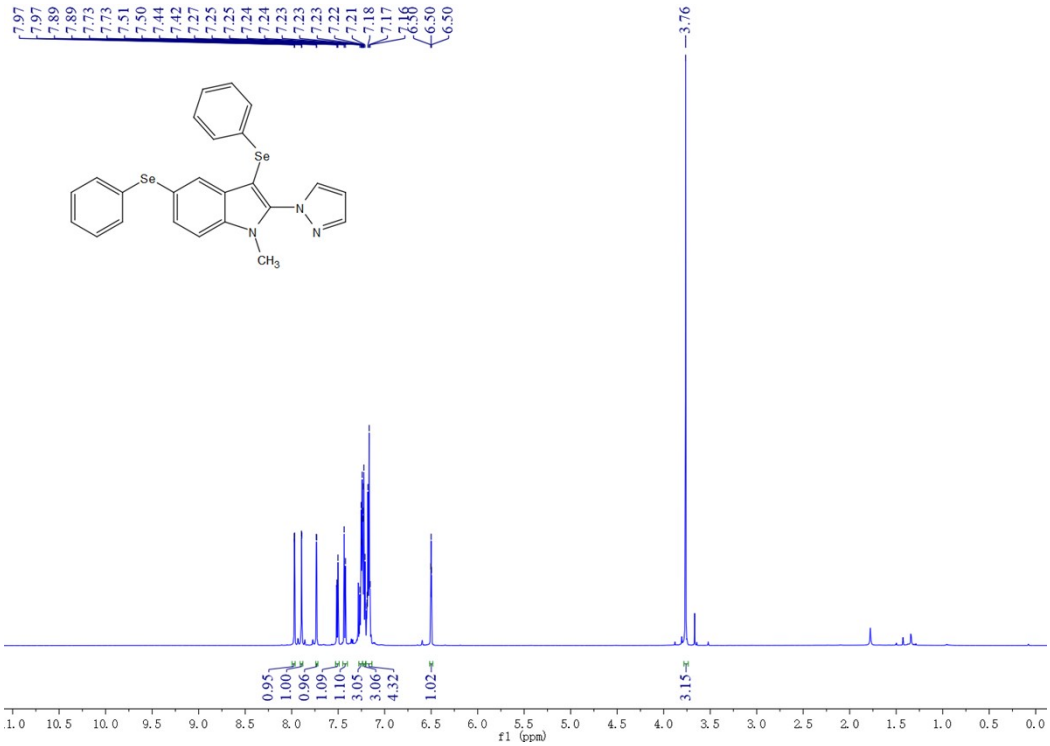
(119) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 57



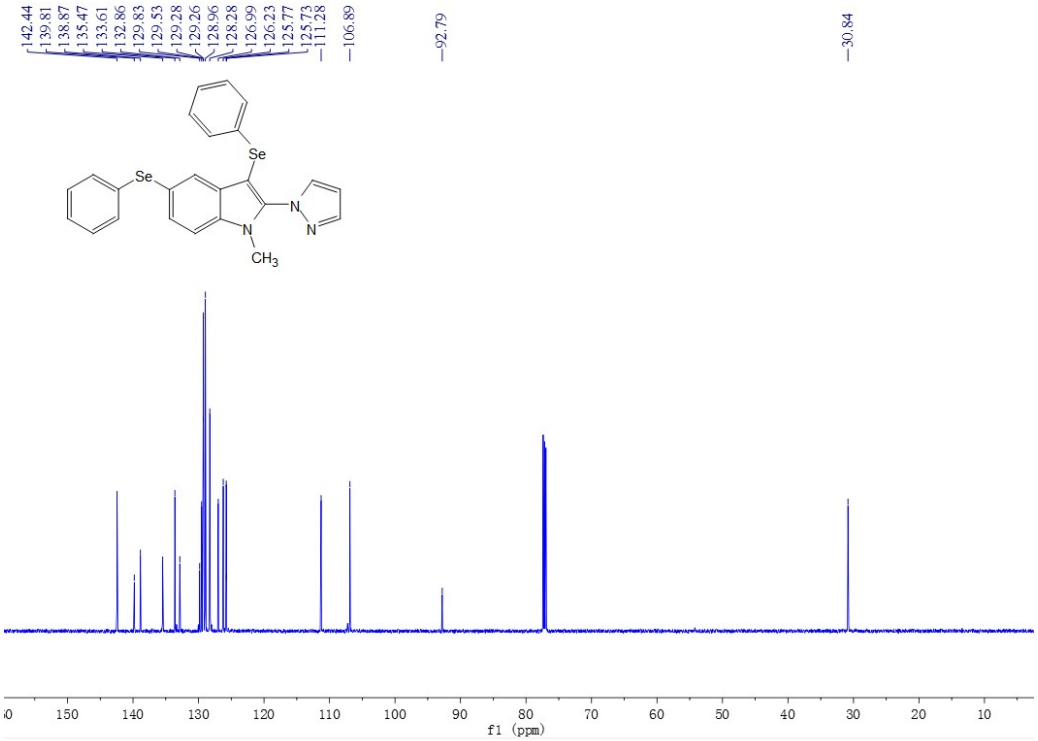
(120) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 57



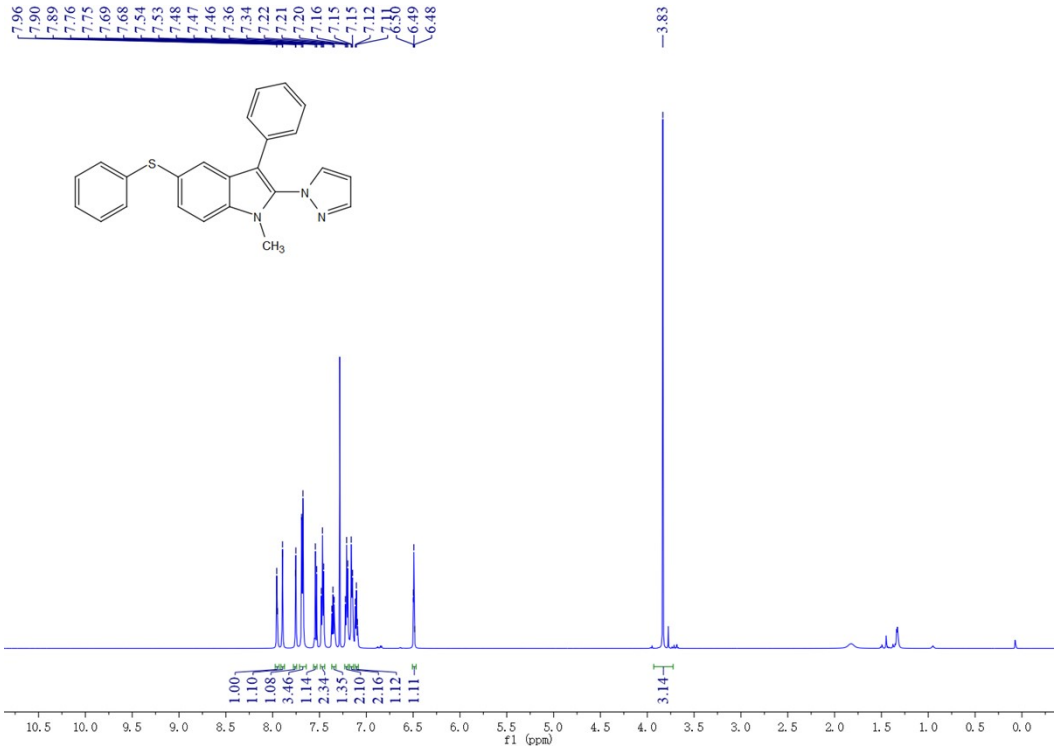
(121) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 58



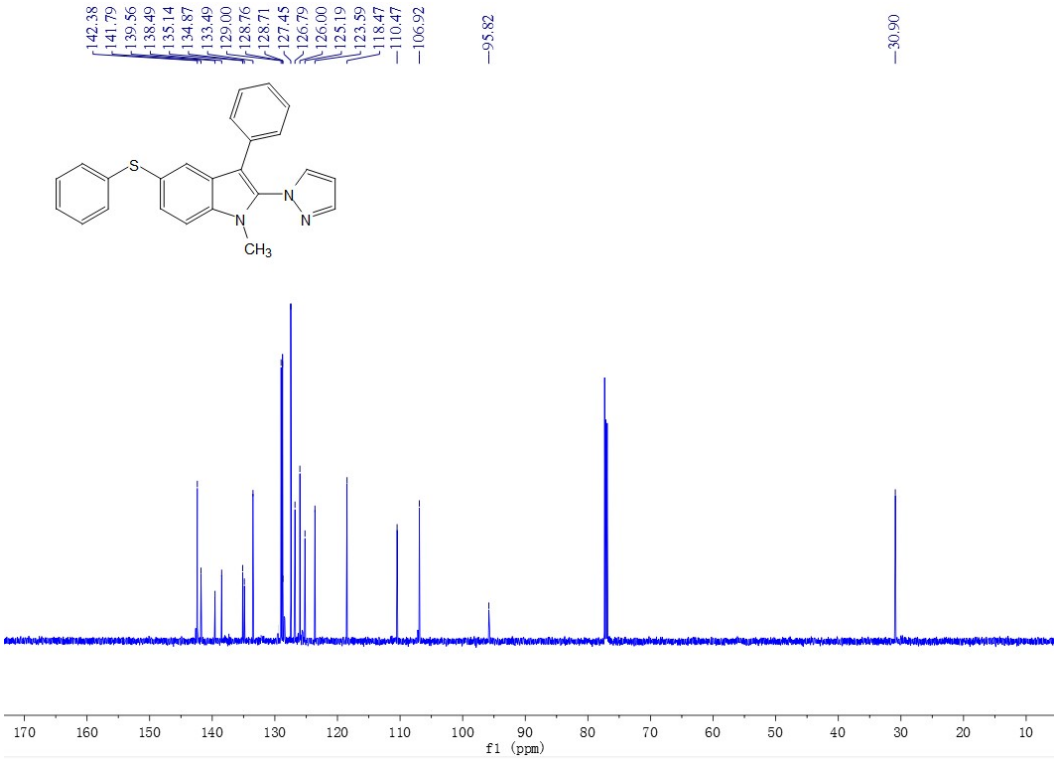
(122) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 58



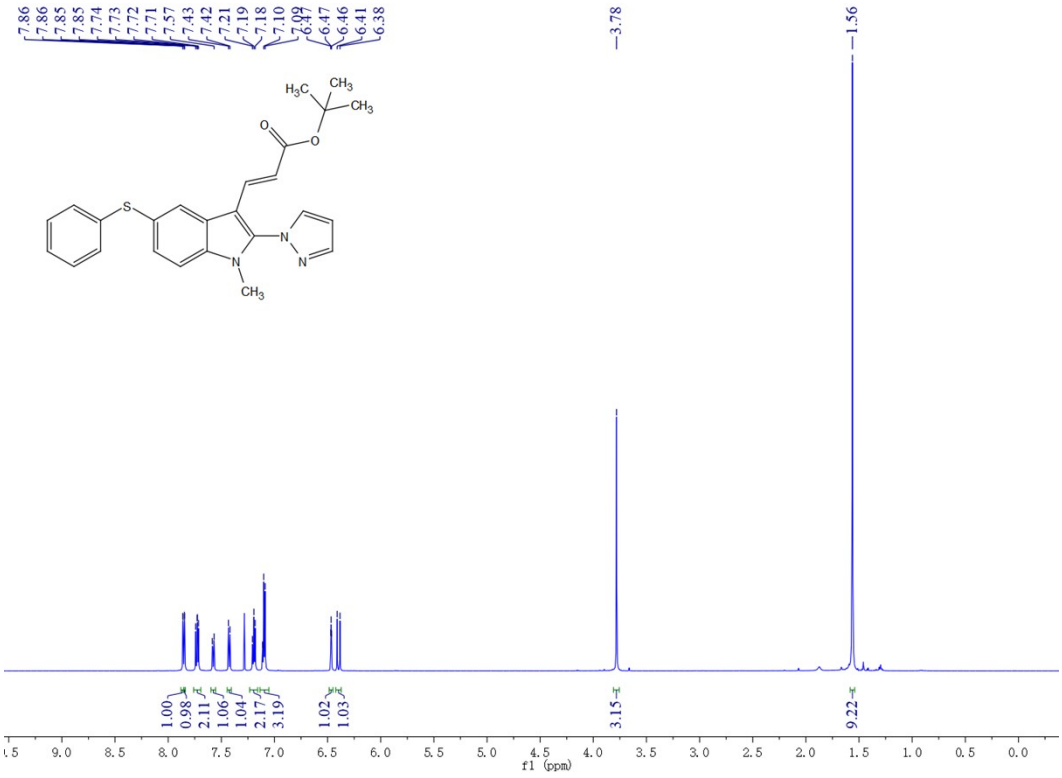
(123) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 59



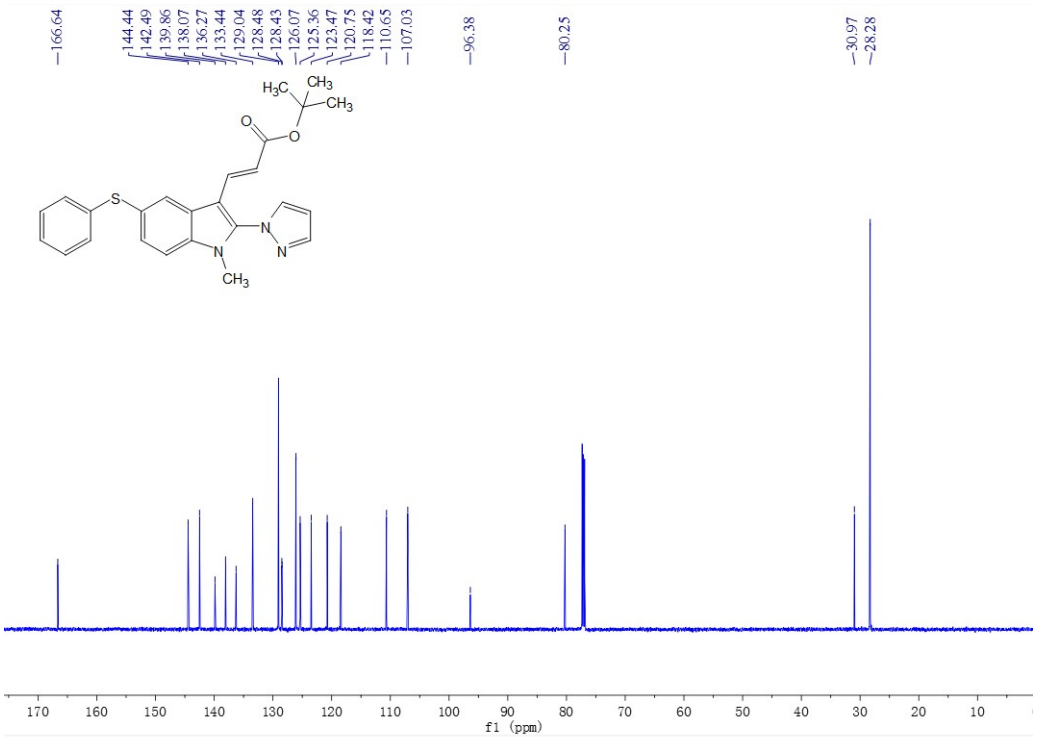
(124) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 59



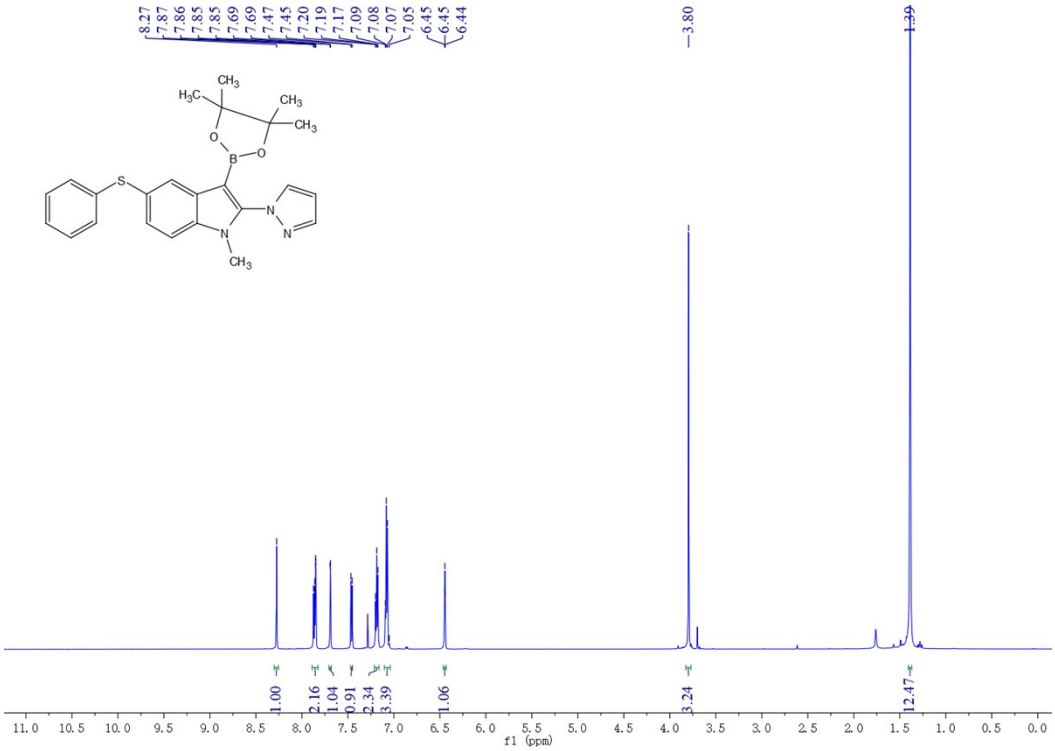
(125) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 60



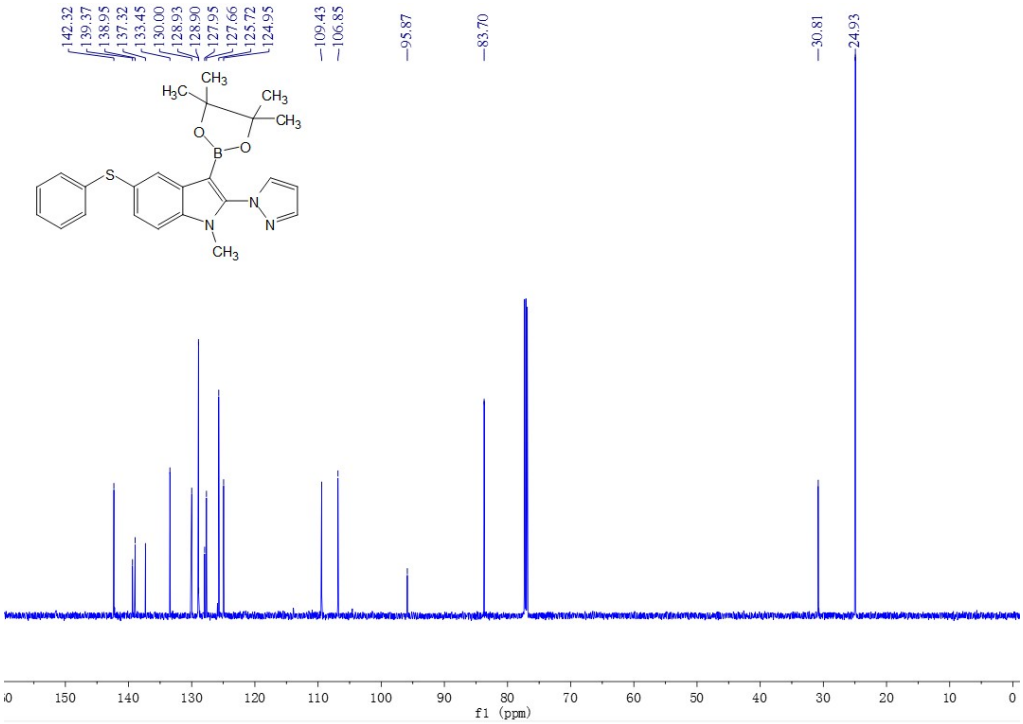
(126) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 60



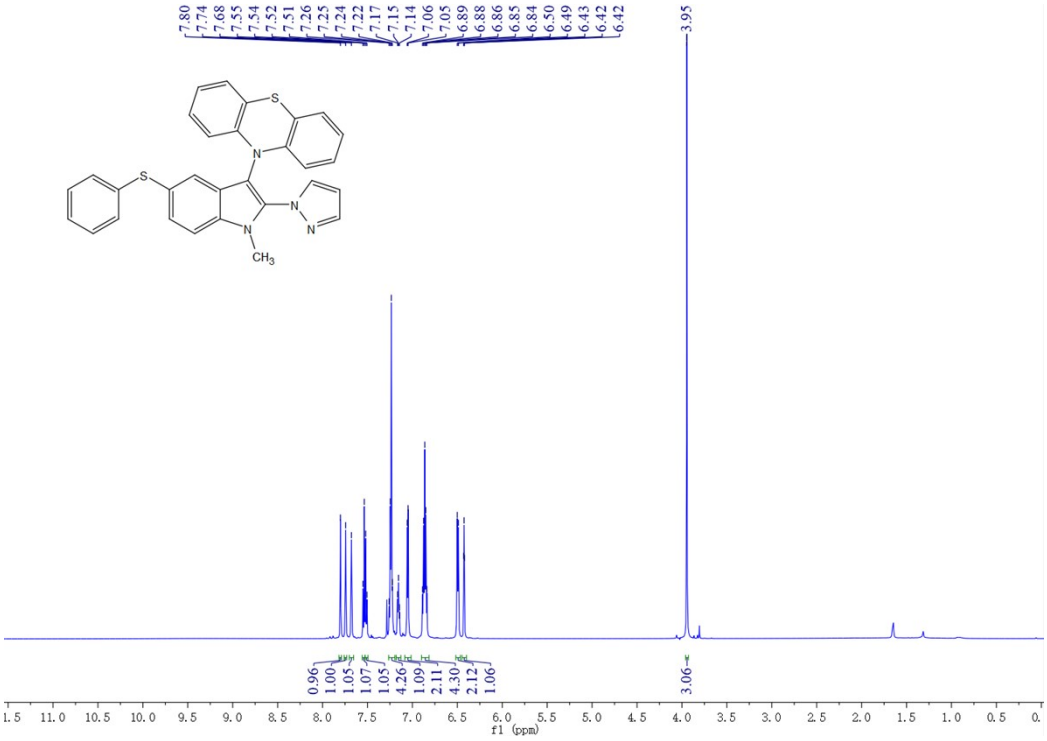
(127) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 61



(128) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 61



(129) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 62



(130) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 62