Electronic Supplementary Information

Organo-catalyzed C2,3−H Aminochalcogenation of Indoles with Secondary (Aliphatic) Amines

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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-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.

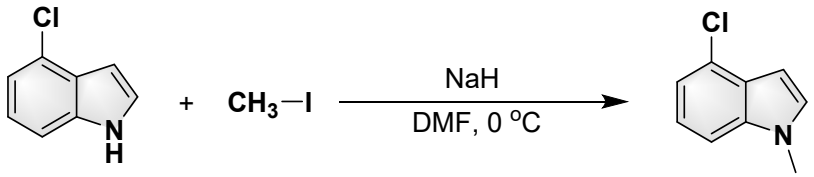
Instrument

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

EXPERIMENTAL DATA

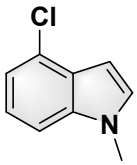
2. Substrates preparation.

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



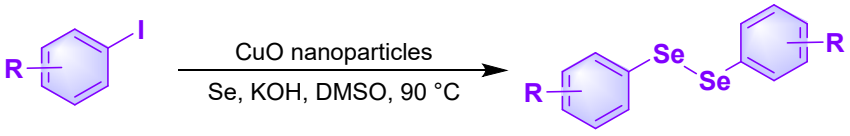
Procedure for 4-chloro-1-methyl-1*H*-indole (1k): To a suspended solution of NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) in DMF (5.0 mL), 4-chloro-1*H*-indole (1.51 g, 10.0 mmol) in DMF (5.0 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 15 min and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (0.83 mL, 13.0 mmol), and allowed to warm to room temperature. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (20.0 mL), and extracted with ether (3 × 20.0 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 **1k** as a yellow oil. Similarly, the other *N*-substituted indole derivatives were prepared from their corresponding indoles and halides.

NMR Spectroscopy (1k):



^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.26–7.22 (m, 1H), 7.22–7.17 (m, 2H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.65 (d, *J* = 3.2 Hz, 1H), 3.77 (s, 3H), known compound.

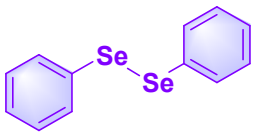
(2) General Procedure for the preparation of diselenoether derivatives (2a-2n)[2]:



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

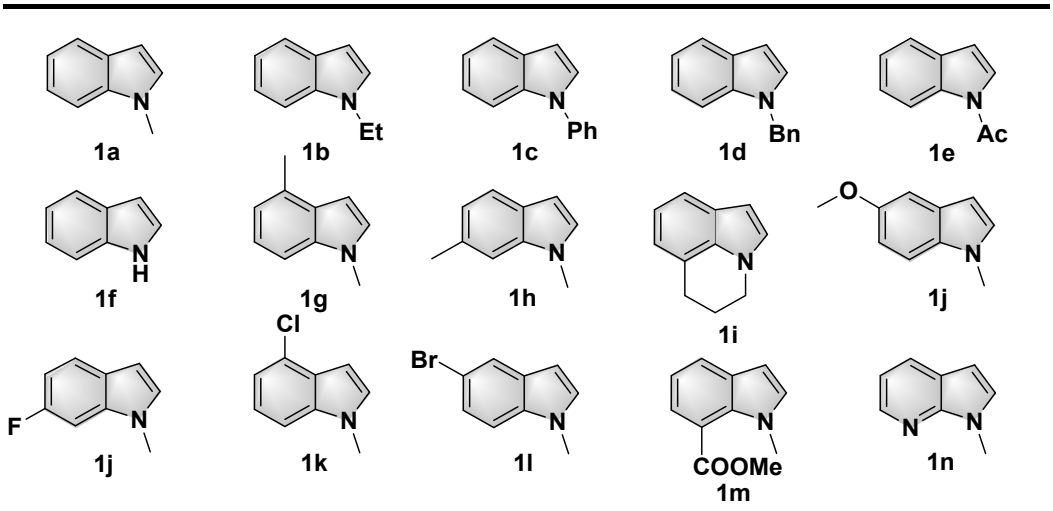
was complete, the reaction mixture was allowed to cool to room temperature and it was then quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on a silica gel column chromatography (Pet Ether) to give the pure diselenides.

NMR Spectroscopy (2a):

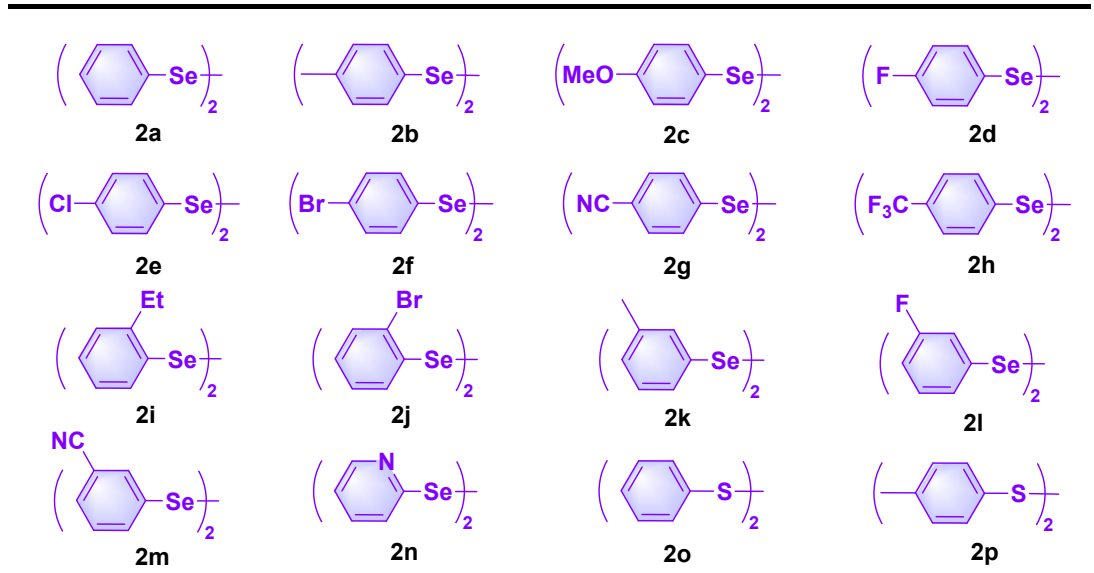


^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.81–7.52 (m, 4H), 7.36–7.24 (m, 6H), known compound.

Scheme S1. Scope of indoles.

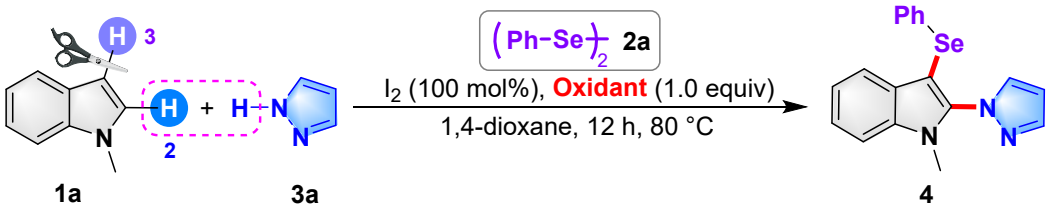


Scheme S2. Scope of diselenides and disulfides.



3. Optimization of reaction conditions.

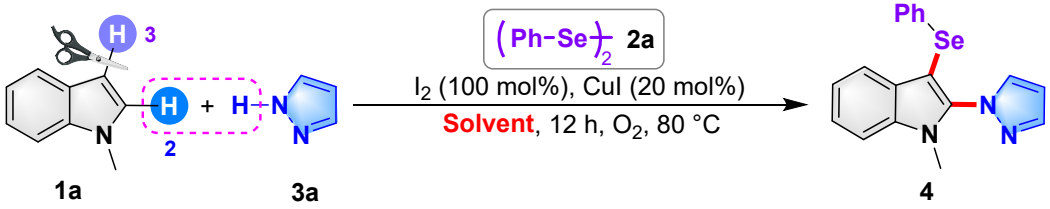
Table S1. Screening the oxidant of reaction.[a]



Entry	[I]	Oxidant	Solvent	Yield (%)[b]
1	I_2	O_2	1,4-dioxane	45
2	I_2	DDQ	1,4-dioxane	21
3	I_2	$K_2S_2O_8$	1,4-dioxane	12
4	I_2	DTBP	1,4-dioxane	72
5	I_2	TBHP	1,4-dioxane	92
6	**I_2**	**CuI + O_2**	**1,4-dioxane**	**95**
7	I_2	CuCl + O_2	1,4-dioxane	89
8	I_2	CuBr + O_2	1,4-dioxane	92
10	I_2	$CuCl_2$ + O_2	1,4-dioxane	83
11	I_2	$CuBr_2$ + O_2	1,4-dioxane	94
12	I_2	$Cu(OTf)_2$ + O_2	1,4-dioxane	70

[a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), **oxidant** (1.0 eq.) or **copper salts** (20 mol%), I_2 (100 mol%), 1,4-dioxane (3.0 mL) were stirred at 80 °C for 12 h. [b]Isolated yield.

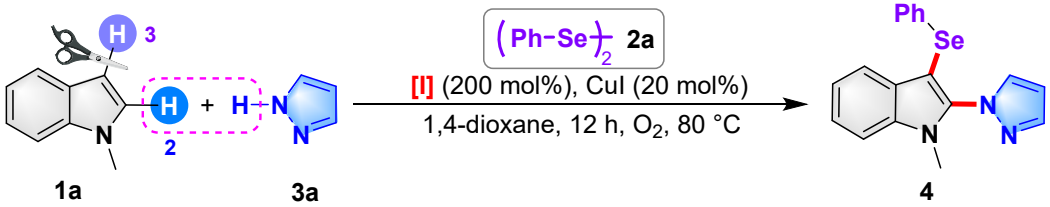
Table S2. Screening the solvent of reaction.[a]



Entry	[I]	Oxidant	Solvent	Yield (%)[b]
1	I_2	CuI + O_2	MeCN	89
2	I_2	CuI + O_2	DCE	82
3	I_2	CuI + O_2	DMF	trace
4	I_2	CuI + O_2	DMSO	60
5	I_2	CuI + O_2	Toluene	77

[a]Reaction conditions, unless specified otherwise: [a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), CuI (20 mol%), I_2 (100 mol%), **solvent** (3.0 mL) were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

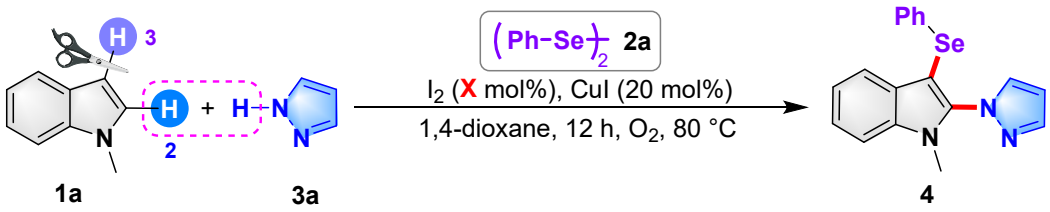
Table S3. Screening the iodized salts of reaction.[a]



Entry	[I]	Oxidant	Solvent	Yield (%)[b]
1	NH_4I	CuI + O_2	1,4-dioxane	trace
2	NaI	CuI + O_2	1,4-dioxane	trace
3	KI	CuI + O_2	1,4-dioxane	trace
4	NIS	CuI + O_2	1,4-dioxane	89

[a]Reaction conditions, unless specified otherwise: [a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), CuI (20 mol%), **iodized salts** (200 mol%), 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

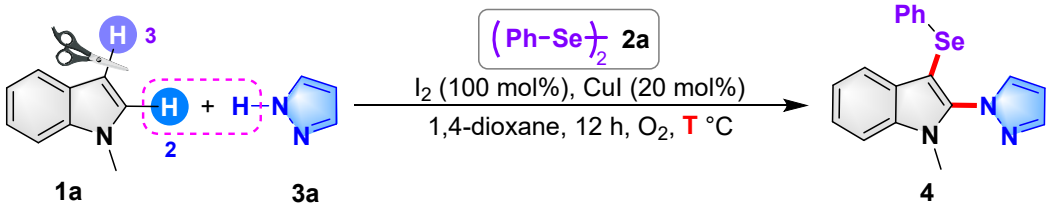
Table S4. Screening the amount of I_2 of reaction.[a]



Entry	[I]	X (mol %)	Oxidant	Solvent	Yield (%)[b]
1	I_2	20	CuI + O_2	1,4-dioxane	trace
2	I_2	50	CuI + O_2	1,4-dioxane	55
3	I_2	80	CuI + O_2	1,4-dioxane	78
4	I_2	150	CuI + O_2	1,4-dioxane	84

[a]Reaction conditions, unless specified otherwise: [a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), CuI (20 mol%), I_2 (**X** mol%), 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for 12 h. [b]Isolated yield.

Table S5. Screening the reaction temperature of reaction.[a]

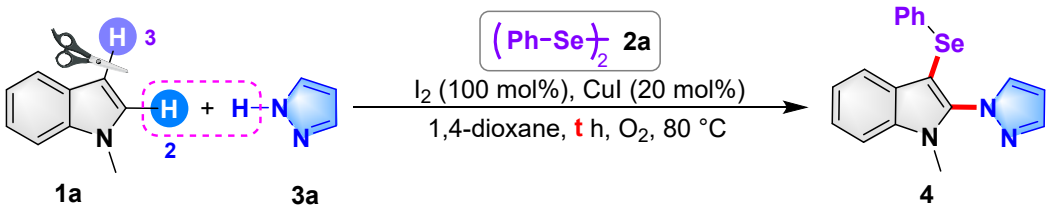


Entry	[I]	T (°C)	Oxidant	Solvent	Yield (%)[b]
1	I_2	60	CuI + O_2	1,4-dioxane	36

2	I_2	100	CuI + O_2	1,4-dioxane	92

[a]Reaction conditions, unless specified otherwise: [a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), CuI (20 mol%), I_2 (100 mol%), 1,4-dioxane (3.0 mL) were stirred at T °C under O_2 for 12 h. [b]Isolated yield.

Table S6. Screening the reaction time of reaction.[a]

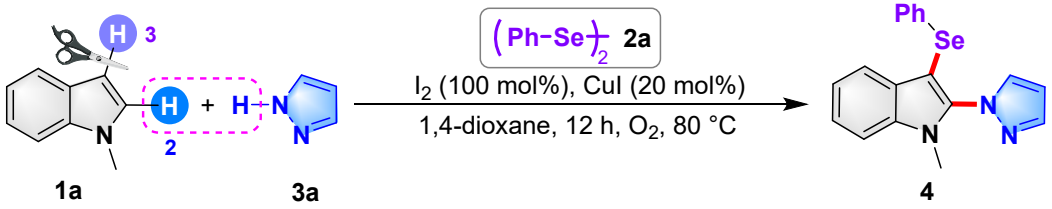


Entry	[I]	t (h)	Oxidant	Solvent	Yield (%)[b]
1	I_2	8	CuI + O_2	1,4-dioxane	65
2	I_2	10	CuI + O_2	1,4-dioxane	83
3	I_2	14	CuI + O_2	1,4-dioxane	90

[a]Reaction conditions, unless specified otherwise: [a]Reaction conditions, unless specified otherwise: **1a** (0.40 mmol), **2a** (0.20 mmol) and **3a** (0.80 mmol), CuI (20 mol%), I_2 (100 mol%), 1,4-dioxane (3.0 mL) were stirred at 80 °C under O_2 for t h. [b]Isolated yield.

4. Typical procedure for the synthesis of 4

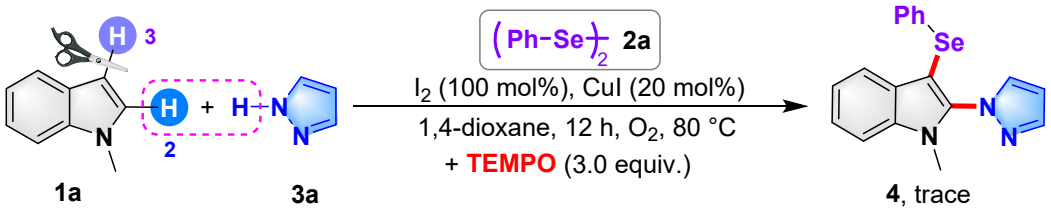
(1) Typical procedure for the synthesis of 4:



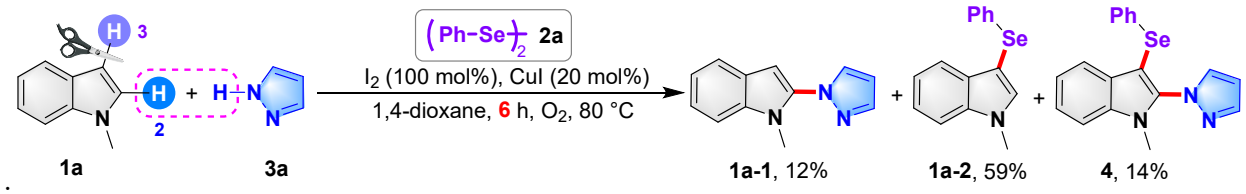
The mixture of **1a** (52.4 mg, 0.40 mmol), **2a** (62.6 mg, 0.20 mmol) and **3a** (54.5 mg, 0.80 mmol), CuI (20 mol%), I_2 (100 mol%), 1,4-dioxane (3 mL) were stirred at 80 °C under O_2 for 12 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (10:1) as the eluent to give **4** as a white solid (134.2 mg, 95% yield).

5. Control experiments.

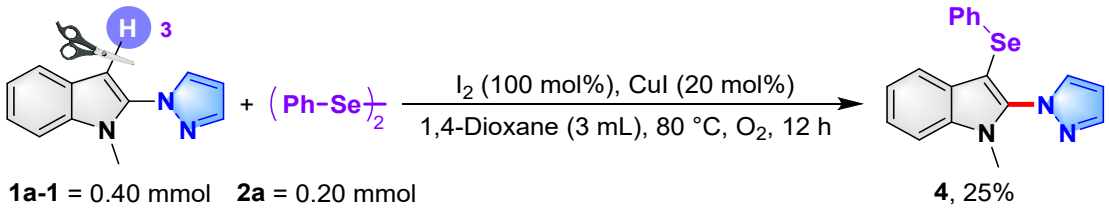
(1) Under the standard condition, the free radical trapping reagent 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**, 3.0 equivalents) was introducing to this reaction. Then, the crude reaction mixture was analyzed by TLC, and only yields trace amounts of product **4**.



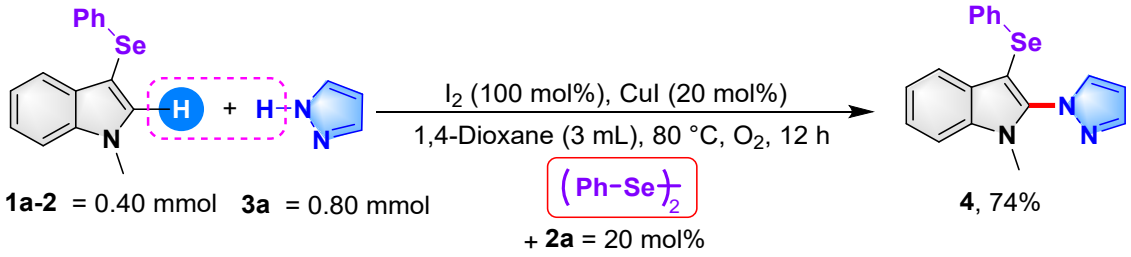
(2) The mixture of **1a** (52.4 mg, 0.40 mmol), **2a** (62.6 mg, 0.20 mmol) and **3a** (54.5 mg, 0.80 mmol), CuI (20 mol%), I_2 (100 mol%), 1,4-dioxane (3 mL) were stirred at 80 °C under O_2 for 6 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (10:1) as the eluent to give **1a-1** (9.5 mg, 12% yield), **1a-2** (67.7 mg, 59% yield) and **4** (19.8 mg, 14% yield), respectively.



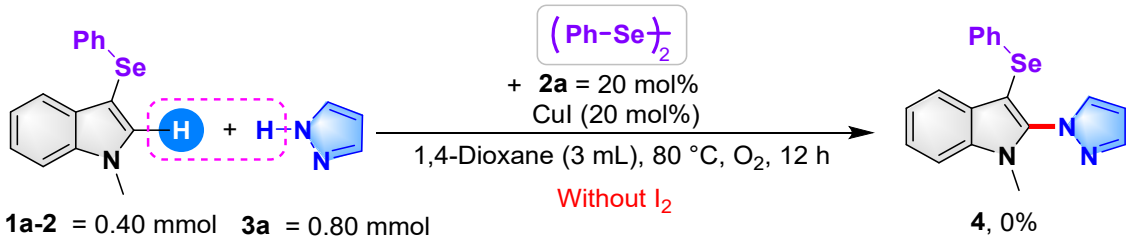
(3) Under the standard condition, the reaction of **1a-1** (78.8 mg, 0.40 mmol) and 1,2-diphenyldiselane **2a** (62.6 mg, 0.20 mmol) were carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (10:1) to give product **4** as white solid (35.3 mg, 25% yield).



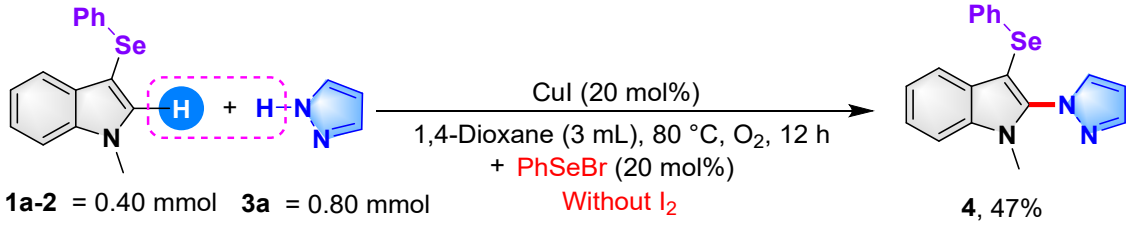
(4) Under the standard condition, the reaction of **1a-2** (114.8 mg, 0.40 mmol) and pyrazo **3a** (54.4 mg, 0.80 mmol) were carried and **2a** (26.2 mg, 20 mol%) was introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (10:1) to give product **4** as white solid (104.5 mg, 74% yield).



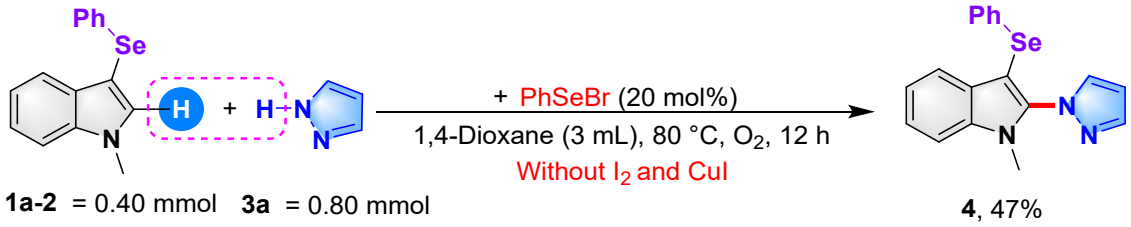
(5) Under the standard condition of the absence of I_2., the reaction of **1a-2** (114.8 mg, 0.40 mmol) and pyrazo **3a** (54.4 mg, 0.80 mmol) were carried and **2a** (26.2 mg, 20 mol%) was introducing to this reaction. Then, the crude reaction mixture was analyzed by TLC, the unobserved product **4**.



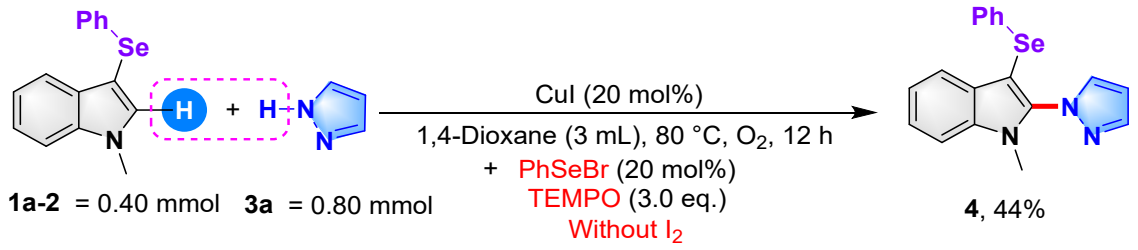
(6) Under the standard condition of the absence of I_2., the reaction of **1a-2** (114.8 mg, 0.40 mmol) and pyrazo **3a** (54.4 mg, 0.80 mmol) were carried and **PhSeBr** (18.8 mg, 20 mol%) was introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (10:1) to give product **4** as white solid (66.4 mg, 47% yield).



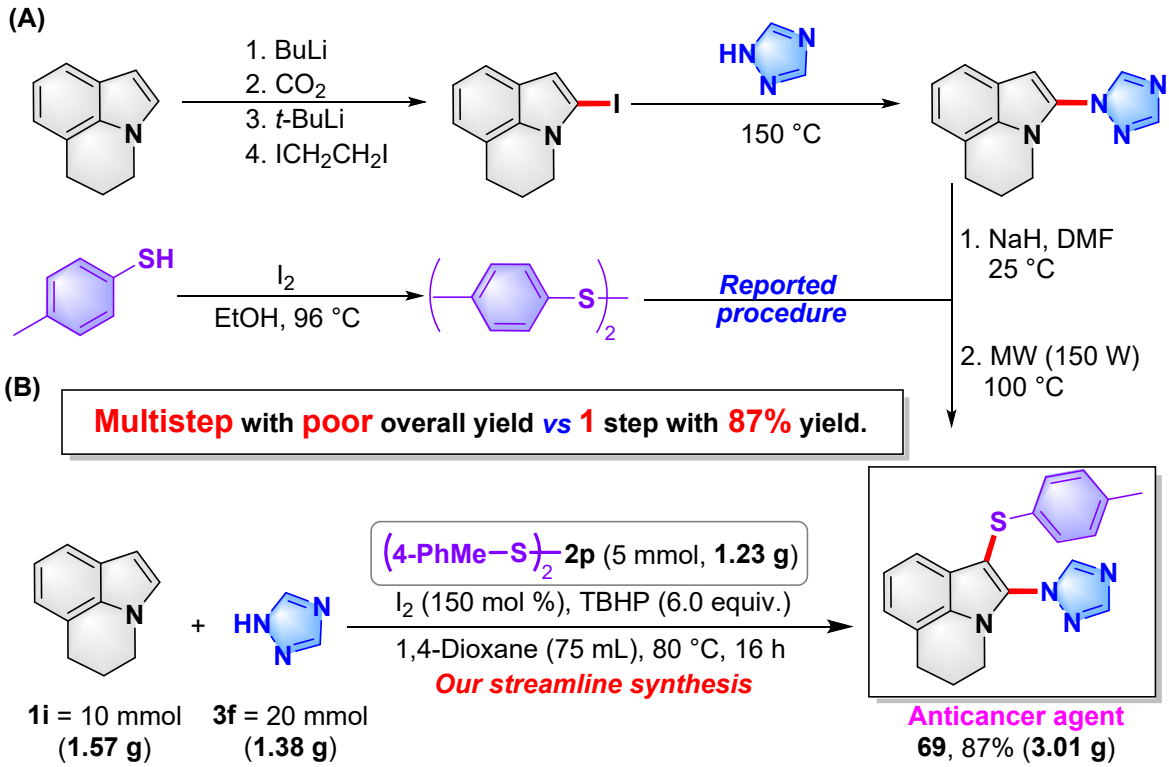
(7) Under the standard condition of the absence of I_2 and CuI, the reaction of **1a-2** (114.8 mg, 0.40 mmol) and pyrazo **3a** (54.4 mg, 0.80 mmol) were carried and **PhSeBr** (18.8 mg, 20 mol%) was introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (10:1) to give product **4** as white solid (19.8 mg, 14% yield).



(8) Under the standard condition of the absence of I_2., the reaction of **1a-2** (114.8 mg, 0.40 mmol) and pyrazo **3a** (54.4 mg, 0.80 mmol) were carried, **PhSeBr** (18.8 mg, 20 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**, 3.0 equivalents) were introducing to this reaction. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (10:1) to give product **4** as white solid (62.1 mg, 44% yield).



6. Synthetic utility.



(1) The mixture of **1i** (1.57 g, 10.0 mmol), **2p** (1.23 g, 5.0 mmol) and **3f** (1.38 g, 20.0 mmol), TBHP (6.0 equiv.), I_2 (150 mol%), 1,4-dioxane (75 mL) were stirred at 80 °C under air for 16 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by using petroleum ether/ethyl acetate (10:1) as the eluent to give **69** as a brown solid (3.01 g, 87% yield).

7. Single crystal X-ray diffraction

(1) Single crystal X-ray diffraction of 50.

White block-like single crystals of **50** 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.

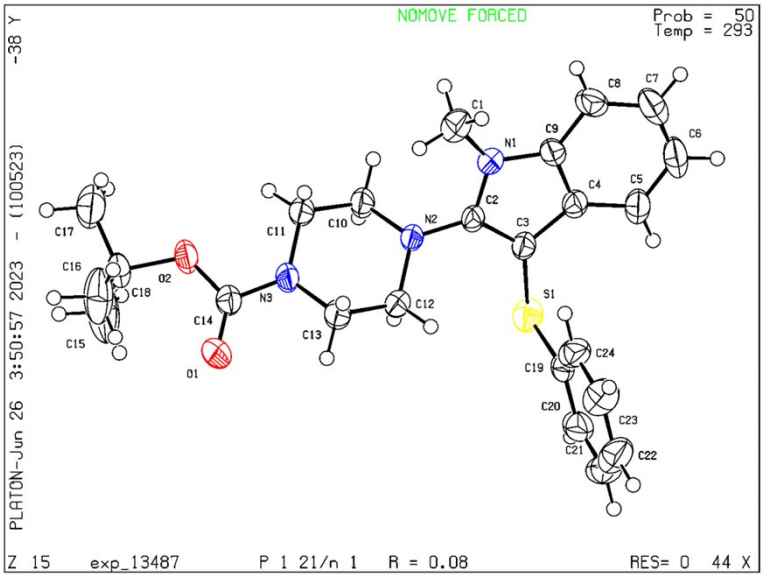


Figure S1. ORTEP drawing of **50** with the numbering scheme.

Table S7. Crystal data and structure refinement for **50**

Identification code	**50**	
Empirical formula	$C_{24}H_{29}N_3O_2S$	
Formula weight	423.56	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.7303(9) Å	α = 90°.
	b = 18.2774(19) Å	β = 100.470(10)°.
	c = 14.2998(14) Å	γ = 90°.
Volume	2243.8(4) Å^3	

Z	4
F(000)	904.0
Crystal size	0.20x 0.15 x 0.10 mm^3
2^{Θ} range for data collection	6.768 to 58.48
Index ranges	-10⩽h⩽11, -24⩽k⩽24, -19⩽l⩽17
Reflections collected	10860
Independent reflections	5155 [R(int) = 0.0465, R(sigma) = 0.0877]
Data / restraints / parameters	5155/0/275
Goodness-of-fit on F^2	1.055
Final R indices [I>=2^{σ}(I)]	R1 = 0.0768, wR2 = 0.1385
Final R indices (all data)	R1 = 0.1409, wR2 = 0.1671
Largest diff. peak and hole	0.26/-0.26 e.$Å^{-3}$

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **50**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	10564.4(9)	2915.9(5)	6163.4(5)	48.1(3)
O2	2091(2)	3880.3(11)	4136.8(13)	48.1(5)
N1	8185(3)	3874.7(12)	7930.3(15)	38.3(6)
N2	6867(3)	3447.9(12)	6428.7(16)	36.4(6)
O1	2626(3)	2699.0(13)	3850.7(17)	72.1(8)
N3	4187(3)	3348.4(13)	4993.6(17)	44.5(6)
C2	8253(3)	3529.4(14)	7075.6(18)	32.3(6)
C9	9657(3)	3874.8(14)	8482.2(18)	36.0(7)
C3	9775(3)	3319.3(15)	7074.3(19)	35.0(7)
C4	10670(3)	3533.8(15)	7970.4(19)	36.2(7)
C19	10768(3)	1985.2(17)	6510(2)	39.7(7)
C14	2924(3)	3258.8(17)	4296(2)	41.3(7)
C5	12242(4)	3455.3(17)	8385(2)	48.4(8)
C18	663(3)	3922.1(17)	3404(2)	44.8(8)
C11	4403(4)	3977.5(16)	5637(2)	48.9(8)
C12	6718(3)	2856.2(16)	5737(2)	47.3(8)
C8	10166(4)	4142.0(16)	9401(2)	49.1(8)
C24	10211(4)	1698.1(17)	7278(2)	48.8(8)
C10	6116(3)	4113.7(16)	5984(2)	45.5(8)
C20	11522(4)	1525(2)	5970(2)	56.4(9)
C7	11721(4)	4054.4(18)	9789(2)	57.7(9)
C6	12741(4)	3719.7(19)	9289(2)	58.7(9)

C13	5028(4)	2696.3(16)	5381(2)	54.3(9)
C1	6778(4)	4012.0(18)	8303(2)	54.6(9)
C21	11696(4)	796(2)	6186(3)	74.3(12)
C22	11140(4)	509(2)	6941(3)	72.0(11)
C23	10402(4)	957.6(19)	7489(3)	63.4(10)
C16	-479(4)	3344(2)	3520(3)	86.9(14)
C17	24(5)	4666(2)	3594(4)	107.8(17)
C15	1108(5)	3913(3)	2442(2)	116(2)

Table S9. Anisotropic Displacement Parameters ($Å^2×10^3$) for **50**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	43.7(5)	58.7(6)	43.1(4)	4.7(4)	11.0(4)	6.0(4)
O2	39.4(12)	42.9(13)	52.6(12)	1.6(10)	-16.3(10)	-1.5(10)
N1	35.8(14)	34.8(14)	42.5(13)	-3.6(11)	1.8(11)	6.4(11)
N2	32.1(13)	27.6(13)	44.1(13)	-2.1(11)	-7.1(11)	3.9(10)
O1	60.7(16)	56.2(16)	84.5(17)	-30.4(14)	-26.7(13)	7.6(13)
N3	35.6(14)	34.6(14)	54.9(15)	-5.3(12)	-14.2(12)	2.2(11)
C2	32.1(16)	24.9(15)	36.8(14)	4.1(12)	-2.0(12)	2.4(12)
C9	42.1(18)	24.4(15)	37.2(15)	2.9(13)	-4.3(13)	-3.9(13)
C3	31.8(16)	31.9(16)	38.7(15)	2.4(13)	-0.5(13)	3.6(13)
C4	37.1(17)	27.7(15)	40.8(15)	4.5(13)	-0.7(13)	0.9(13)
C19	21.5(14)	51.1(19)	43.9(15)	-10.7(15)	-0.8(12)	1.2(14)
C14	32.6(17)	42.0(19)	46.0(17)	-1.3(15)	-1.5(14)	0.7(14)
C5	36.4(17)	46(2)	57.0(19)	6.4(16)	-6.2(15)	0.9(15)
C18	33.8(17)	52(2)	42.6(16)	5.8(15)	-8.9(13)	-2.0(15)
C11	42.7(19)	34.2(18)	61.3(19)	-6.7(15)	-13.2(15)	5.7(14)
C12	40.9(18)	36.7(18)	58.0(18)	-9.1(15)	-8.0(15)	9.8(15)
C8	63(2)	34.1(18)	46.1(17)	-4.7(15)	-0.3(16)	-3.7(16)
C24	37.9(18)	44(2)	65(2)	-8.9(16)	12.6(16)	0.9(15)
C10	40.2(18)	30.0(16)	57.9(18)	-0.7(14)	-13.8(15)	2.4(14)
C20	35.9(19)	73(3)	58(2)	-25.2(19)	4.0(16)	1.3(18)
C7	69(3)	49(2)	43.9(18)	5.0(16)	-17.9(18)	-13.4(19)
C6	44(2)	56(2)	65(2)	12.4(19)	-21.5(18)	-8.3(17)
C13	47(2)	32.7(18)	72(2)	-8.9(16)	-17.6(17)	3.6(15)
C1	45(2)	60(2)	58.4(19)	-1.9(17)	8.9(16)	12.0(17)
C21	43(2)	64(3)	112(3)	-44(3)	3(2)	2(2)
C22	42(2)	39(2)	129(3)	-12(2)	0(2)	-1.0(17)
C23	48(2)	46(2)	96(3)	2(2)	14(2)	-6.9(18)

C16	39(2)	97(3)	114(3)	42(3)	-14(2)	-18(2)
C17	75(3)	71(3)	150(4)	-18(3)	-53(3)	19(2)
C15	67(3)	226(6)	52(2)	29(3)	-1(2)	19(3)

Table S10. Bond Lengths for **50**.

Atom	Atom	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C3	1.744(3)	**C3**	**C4**	1.429(4)
S1	C19	1.772(3)	**C4**	**C5**	1.399(4)
O2	C14	1.346(3)	**C19**	**C24**	1.384(4)
O2	C18	1.477(3)	**C19**	**C20**	1.387(4)
N1	C2	1.386(3)	**C5**	**C6**	1.375(4)
N1	C9	1.380(3)	**C18**	**C16**	1.482(4)
N1	C1	1.447(3)	**C18**	**C17**	1.513(5)
N2	C2	1.391(3)	**C18**	**C15**	1.497(4)
N2	C12	1.455(3)	**C11**	**C10**	1.508(4)
N2	C10	1.471(3)	**C12**	**C13**	1.499(4)
O1	C14	1.208(3)	**C8**	**C7**	1.379(4)
N3	C14	1.356(3)	**C24**	**C23**	1.390(4)
N3	C11	1.463(3)	**C20**	**C21**	1.369(5)
N3	C13	1.456(4)	**C7**	**C6**	1.382(5)
C2	C3	1.384(4)	**C21**	**C22**	1.366(5)
C9	C4	1.394(4)	**C22**	**C23**	1.373(5)
C9	C8	1.396(4)			

Table S11. Bond Angles for **50**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3	**S1**	**C19**	103.31(13)	**C24**	**C19**	**C20**	118.9(3)
C14	**O2**	**C18**	121.6(2)	**C20**	**C19**	**S1**	117.4(2)
C2	**N1**	**C1**	125.3(2)	**O2**	**C14**	**N3**	111.4(3)
C9	**N1**	**C2**	108.7(2)	**O1**	**C14**	**O2**	124.6(3)
C9	**N1**	**C1**	123.6(2)	**O1**	**C14**	**N3**	123.9(3)
C2	**N2**	**C12**	119.4(2)	**C6**	**C5**	**C4**	118.7(3)
C2	**N2**	**C10**	117.7(2)	**O2**	**C18**	**C16**	112.4(3)
C12	**N2**	**C10**	110.1(2)	**O2**	**C18**	**C17**	102.2(2)
C14	**N3**	**C11**	123.5(2)	**O2**	**C18**	**C15**	109.0(3)
C14	**N3**	**C13**	117.9(2)	**C16**	**C18**	**C17**	110.1(3)
C13	**N3**	**C11**	113.9(2)	**C16**	**C18**	**C15**	112.8(3)
N1	**C2**	**N2**	117.7(2)	**C15**	**C18**	**C17**	109.9(4)
C3	**C2**	**N1**	108.8(2)	**N3**	**C11**	**C10**	110.1(2)
C3	**C2**	**N2**	133.5(2)	**N2**	**C12**	**C13**	109.7(2)

N1	**C9**	**C4**	108.3(2)	**C7**	**C8**	**C9**	117.4(3)
N1	**C9**	**C8**	130.0(3)	**C19**	**C24**	**C23**	119.7(3)
C4	**C9**	**C8**	121.8(3)	**N2**	**C10**	**C11**	110.1(2)
C2	**C3**	**S1**	128.9(2)	**C21**	**C20**	**C19**	120.6(3)
C2	**C3**	**C4**	106.9(2)	**C8**	**C7**	**C6**	121.5(3)
C4	**C3**	**S1**	124.0(2)	**C5**	**C6**	**C7**	121.2(3)
C9	**C4**	**C3**	107.3(2)	**N3**	**C13**	**C12**	111.5(2)
C9	**C4**	**C5**	119.4(3)	**C22**	**C21**	**C20**	120.8(4)
C5	**C4**	**C3**	133.3(3)	**C21**	**C22**	**C23**	119.5(4)
C24	**C19**	**S1**	123.7(2)	**C22**	**C23**	**C24**	120.6(3)

Table S12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **50**.

Atom	***x***	***y***	***z***	**U(eq)**
H5	12935	3229	8055	58
H11A	3896	3885	6175	59
H11B	3930	4408	5306	59
H12A	7233	2422	6030	57
H12B	7214	2995	5209	57
H8	9484	4370	9738	59
H24	9710	1999	7653	59
H10A	6603	4257	5454	55
H10B	6249	4510	6443	55
H20	11912	1712	5456	68
H7	12092	4224	10401	69
H6	13784	3672	9569	70
H13A	4934	2323	4892	65
H13B	4565	2508	5900	65
H1A	6648	4530	8373	82
H1B	6853	3779	8911	82
H1C	5899	3819	7871	82
H21	12198	493	5815	89
H22	11260	13	7082	86
H23	10028	764	8005	76
H16A	-81	2876	3373	130
H16B	-1445	3438	3097	130
H16C	-649	3342	4164	130
H17A	-263	4668	4211	162
H17B	-876	4771	3119	162
H17C	805	5032	3572	162
H15A	1925	4262	2426	174

H15B	219	4040	1969	174
H15C	1464	3433	2313	174

9. Reference.

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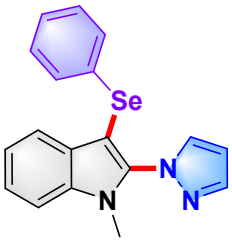
2. D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues, A. L. Braga, An Efficient One-Pot Synthesis of Symmetrical Diselenides or Ditellurides from Halides with CuO Nanopowder/Se0 or Te0/Base, *Org. Lett.,* 2010*,* **12***,* 3288–3291.

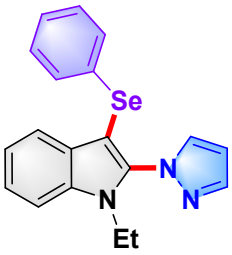
10. Analytic data of the obtained compounds.

(1) 1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4)



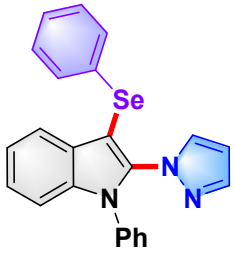
White solid (134.1 mg, 95%), m.p.: 97-98 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 6.52–6.49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

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



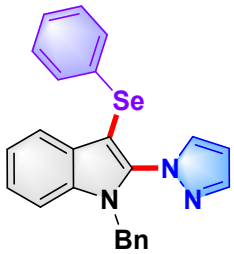
Yellow liquid (130.7 mg, 89%), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.44–7.40 (m, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 6.9 Hz, 2H), 7.20– .14 (m, 3H), 6.49 (t, *J* = 2.2 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.19, 138.60, 134.64, 133.63, 133.38, 129.19, 129.13, 128.95, 125.93, 123.74, 121.38, 121.33, 110.18, 106.66, 92.83, 39.18, 15.32. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ [M+H]$^+$: 368.0660; found: 368.0652.

(3) 1-phenyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (6)



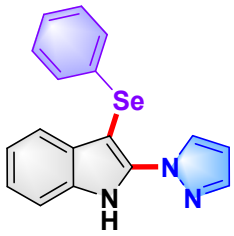
Yellow liquid (74.7 mg, 45%), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.44–7.37 (m, 5H), 7.36–7.33 (m, 3H), 7.22 (dt, *J* = 13.2, 6.9 Hz, 3H), 6.36 (t, *J* = 2.2 Hz, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.75, 138.67, 136.28, 136.16, 133.42, 132.64, 129.74, 129.44, 129.26, 128.87, 128.16, 126.84, 126.27, 124.50, 122.20, 121.38, 111.23, 106.82, 96.22. **HRMS (ESI):** Calcd. for $C_{23}H_{17}N_3Se$ [M+H]$^+$: 416.0660; found: 416.0651.

(4) 1-benzyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (7)



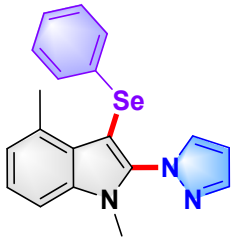
Red solid (99.5 mg, 58%), m.p.: 149-150 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.31–7.26 (m, 6H), 7.21–7.16 (m, 3H), 7.06 (d, *J* = 5.9 Hz, 2H), 6.42 (t, *J* = 2.2 Hz, 1H), 5.47 (s, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.32, 139.01, 136.92, 135.42, 133.77, 129.25, 129.14, 129.02, 128.74, 127.64, 126.75, 126.03, 124.09, 121.69, 121.33, 110.85, 106.80, 93.71, 47.64. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3Se$ [M+H]$^+$:430.0808; found: 430.0817.

(5) 3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (9)



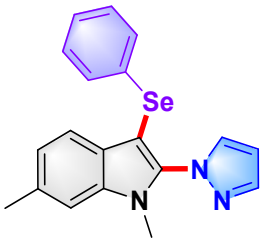
Red liquid (105.8 mg, 78%), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 10.96 (s, 1H), 8.83 (d, *J* = 2.6 Hz, 1H), 7.86 (d, *J* = 1.7 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32–7.28 (m, 3H), 7.27–7.24 (m, 1H), 7.23–7.18 (m, 3H), 6.54–6.52 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.18, 138.01, 133.44, 132.96, 131.17, 130.36, 129.45, 128.31, 126.05, 123.26, 121.47, 120.41, 111.32, 108.05, 83.12. **HRMS (ESI):** Calcd. for $C_{17}H_{13}N_3Se$ $[M+H]^+$:440.0347; found: 440.0340.

(6) 1,4-dimethyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (10)



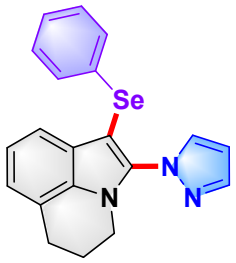
Brown solid (142.4 mg, 97% yield); m.p.: 150-151 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.34–7.29 (m, 2H), 7.23 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.21–7.18 (m, 2H), 7.16–7.13 (m, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.48–6.46 (m, 1H), 3.70 (s, 3H), 2.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.17, 139.80, 135.96, 135.69, 133.83, 132.89, 129.28, 128.11, 126.23, 125.62, 123.53, 123.30, 107.98, 106.54, 91.99, 30.52, 19.20. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ $[M+H]^+$: 368.0652; found: 368.0660.

(7) 1,6-dimethyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (11)



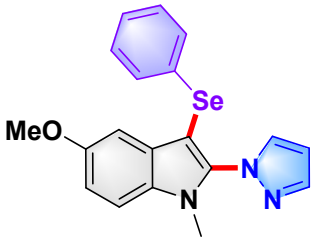
Brown solid (107.2 mg, 73% yield), m.p.: 136-137 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.27–7.25 (m, 3H), 7.20–7.16 (m, 2H), 7.16–7.13 (m, 2H), 6.49–6.47 (m, 1H), 3.73 (s, 3H), 2.59 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.18, 138.62, 136.04, 133.86, 133.66, 133.52, 129.20, 128.88, 126.76, 125.90, 123.31, 120.83, 110.00, 106.62, 92.34, 30.48, 22.11. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ $[M+H]^+$: 368.0652; found: 368.0660.

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



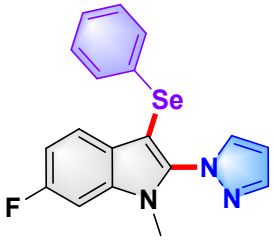
Yellow liquid (91.0 mg, 60% yield); **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.28–7.25 (m, 2H), 7.20–7.14 (m, 4H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.46 (t, *J* = 2.2 Hz, 1H), 4.27–4.25 (m, 2H), 3.08 (t, *J* = 6.1 Hz, 2H), 2.30 (p, *J* = 6.0 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.98, 137.74, 133.67, 133.14, 132.65, 129.19, 128.78, 127.50, 125.85, 122.46, 121.45, 120.56, 118.22, 106.58, 90.05, 43.27, 24.70, 22.72. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3Se$ $[M+H]^+$: 380.0660; found: 380.0650.

(9) 5-methoxy-1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (13)



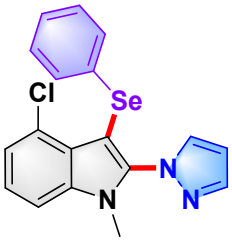
Yellow solid (104.2 mg, 68% yield), m.p.: 106-107 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.3 Hz, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.25–7.22 (m, 2H), 7.20–7.16 (m, 3H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 6.4 Hz, 1H), 6.48–6.45 (m, 1H), 3.86 (s, 3H), 3.72 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 155.54, 142.14, 139.27, 133.52, 133.45, 130.63, 129.62, 129.18, 128.74, 125.87, 114.29, 111.03, 106.61, 102.24, 91.92, 55.85, 30.67. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3OSe$ $[M+H]^+$: 384.0610; found: 384.0602.

(10) 6-fluoro-1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (14)



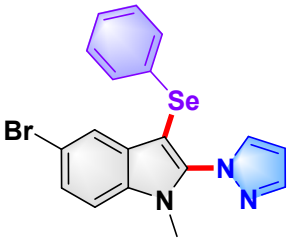
Yellow solid (130.6 mg, 88% yield), m.p.: 111-112 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.65 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.22 (d, *J* = 6.5 Hz, 2H), 7.19–7.11 (m, 4H), 7.04–7.00 (m, 1H), 6.48 (t, *J* = 2.2 Hz, 1H), 3.69 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 160.88 (d, *J* = 120.8 Hz), 142.34, 139.35 (d, *J* = 3.0 Hz), 135.63 (d, *J* = 12.1 Hz), 133.56, 132.96, 129.23, 129.03, 126.11, 125.19, 122.34 (d, *J* = 10.6 Hz), 110.31 (d, *J* = 24.2 Hz), 106.76, 96.59 (d, *J* = 25.7 Hz), 92.84, 30.74. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -116.96. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3Se$ $[M+H]^+$: 372.0410; found: 372.0400.

(11) 4-chloro-1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (15)



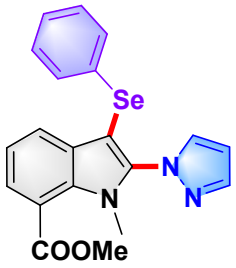
Yellow solid (137.8 mg, 89% yield), m.p.: 163-164 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.24 (td, *J* = 7.7, 1.3 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.70 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.39, 140.57, 136.86, 135.04, 133.93, 129.09, 128.95, 127.88, 125.85, 124.45, 123.83, 122.95, 108.92, 106.73, 92.12, 30.82. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3Se$ $[M+H]^+$: 388.0114; found: 388.0104.

(12) 5-bromo-1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (16)



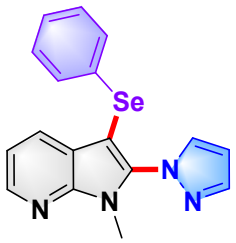
Brown solid (151.4 mg, 88% yield), m.p.: 109-110 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 1.3 Hz, 1H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.21–7.14 (m, 5H), 6.48 (d, *J* = 1.8 Hz, 1H), 3.73 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.44, 139.97, 134.34, 133.55, 132.88, 130.71, 129.30, 128.95, 126.78, 126.18, 123.60, 114.90, 111.65, 106.89, 91.90, 30.85. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3Se$ $[M+H]^+$: 431.9609; found: 431.9597.

(13) methyl 1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole-7-carboxylate (17)



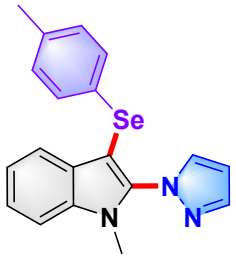
White solid (103.6 mg, 63% yield), m.p.: 131-132 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.81 (d, *J* = 6.9 Hz, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.22–7.18 (m, 2H), 7.18–7.12 (m, 3H), 6.49 (t, *J* = 2.1 Hz, 1H), 4.02 (s, 3H), 3.67 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 167.66, 142.49, 141.05, 133.68, 133.35, 132.71, 130.78, 129.21, 129.11, 127.01, 126.13, 125.57, 120.58, 117.11, 106.95, 94.30, 52.39, 34.32. **HRMS (ESI):** Calcd. for $C_{20}H_{17}N_3O_2Se$ $[M+H]^+$: 412.0559; found: 412.0550.

(14) 1-methyl-3-(phenylselanyl)-2-(1*H*-pyrazol-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (18)



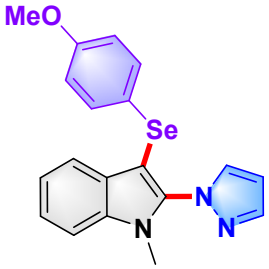
Red solid (106.2 mg, 75% yield), m.p.: 118-119 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 4.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (s, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.20 (td, *J* = 4.6, 2.4 Hz, 3H), 7.16–7.14 (m, 3H), 6.49 (t, *J* = 2.2 Hz, 1H), 3.89 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 146.67, 144.89, 142.49, 139.60, 133.39, 132.72, 129.28, 129.22, 129.09, 126.24, 122.18, 117.78, 106.95, 90.51, 29.35. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4Se$ $[M+H]^+$: 355.0456; found: 355.0448.

(15) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(*p*-tolylselanyl)-1*H*-indole (19)



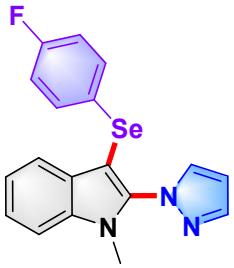
Red solid (85.1 mg, 58% yield), m.p.: 149-150 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.50 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 3H), 2.29 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.21, 138.99, 135.85, 135.67, 133.70, 130.00, 129.41, 129.35, 128.98, 123.74, 121.44, 121.20, 109.99, 106.65, 92.97, 30.55, 21.01. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ $[M+H]^+$: 368.0660; found: 368.0652.

(16) 3-((4-methoxyphenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (20)



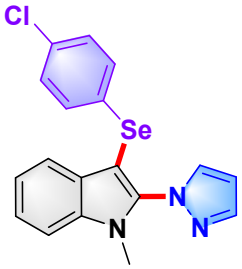
Brown solid (64.3 mg, 42% yield), m.p.: 124-125 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 6.9 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.60, 142.17, 138.67, 135.56, 133.75, 131.74, 128.87, 123.68, 122.91, 121.36, 121.14, 114.90, 109.95, 106.62, 94.05, 55.26, 30.44. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3OSe$ $[M+H]^+$: 384.0610; found: 384.0602.

(17) 3-((4-fluorophenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (21)



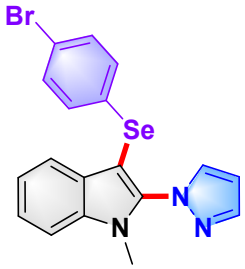
Yellow liquid (106.8 mg, 72% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.22 (dd, *J* = 8.8, 5.3 Hz, 2H), 6.87 (t, *J* = 8.8 Hz, 2H), 6.51 (t, *J* = 2.2 Hz, 1H), 3.73 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.74 (d, *J* = 244.6 Hz), 142.27, 138.93, 135.60, 133.61, 131.33 (d, *J* = 7.6 Hz), 128.68, 127.37 (d, *J* = 4.5 Hz), 123.86, 121.54, 120.98, 116.24 (d, *J* = 21.1 Hz), 110.06, 106.74, 93.24, 30.49. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -116.46. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3Se$ $[M+H]^+$: 372.0410; found: 372.0401.

(18) 3-((4-chlorophenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (22)



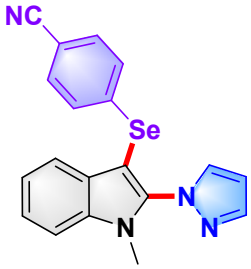
Red solid (126.9 mg, 82% yield), m.p.: 159-160 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.3 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.51–6.48 (m, 1H), 3.75 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.33, 139.12, 135.65, 133.55, 132.00, 131.48, 130.31, 129.23, 128.64, 123.93, 121.64, 120.95, 110.11, 106.80, 92.35, 30.56. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3Se$ $[M+H]^+$: 388.0114; found: 388.0104.

(19) 3-((4-bromophenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (23)



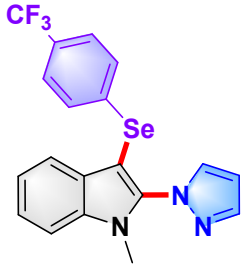
Red solid (132.7 mg, 77% yield), m.p.: 167-168 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31–7.28 (m, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.50 (t, *J* = 2.2 Hz, 1H), 3.75 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.35, 139.17, 135.67, 133.56, 132.29, 132.14, 130.56, 128.64, 123.96, 121.67, 120.96, 119.92, 110.14, 106.83, 92.19, 30.59. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3Se$ $[M+H]^+$: 431.9609; found: 431.9599.

(20) 4-((1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)selanyl)benzonitrile (24)



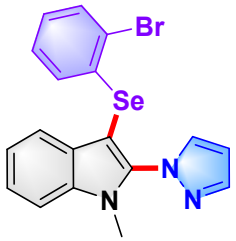
Gray solid (77.1 mg, 51% yield), m.p.: 140-141 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.49–7.47 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.30–7.27 (m, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.49 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.49, 141.43, 139.50, 135.74, 133.37, 132.35, 128.47, 128.35, 124.21, 121.93, 120.72, 118.91, 110.32, 109.09, 107.00, 90.75, 30.66. **HRMS (ESI):** Calcd. for $C_{19}H_{14}N_4Se$ $[M+H]^+$: 379.0456; found: 379.0446.

(21) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole (25)



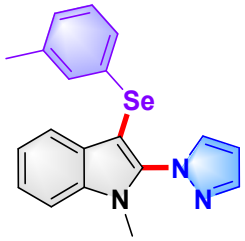
Red solid (94.3 mg, 56% yield), m.p.: 106-107 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.70–7.68 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.32–7.29 (m, 3H), 6.50 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.42, 139.43, 138.90, 135.75, 133.45, 128.58, 128.38, 125.87 (d, *J* = 4.5 Hz), 125.83, 125.80, 124.09, 121.80, 120.88, 110.22, 106.90, 91.31, 30.62. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -62.40. **HRMS (ESI):** Calcd. for $C_{19}H_{14}F_3N_3Se$ $[M+H]^+$: 422.0378; found: 422.0369.

(22) 3-((2-bromophenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (26)



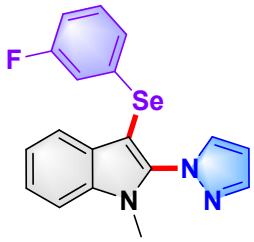
Red solid (146.2 mg, 85% yield), m.p.: 142-144 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89–7.84 (m, 1H), 7.72–7.68 (m, 2H), 7.51–7.46 (m, 2H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.02–6.97 (m, 2H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.49–6.46 (m, 1H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.42, 139.77, 136.29, 135.95, 133.50, 132.68, 128.75, 128.72, 128.05, 126.88, 124.07, 121.92, 121.80, 121.11, 110.25, 106.99, 91.85, 30.82. **HRMS (ESI):** Calcd. for $C_{18}H_{14}BrN_3Se$ $[M+H]^+$: 431.9609; found: 431.9597.

(23) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(*m*-tolylselanyl)-1*H*-indole (27)



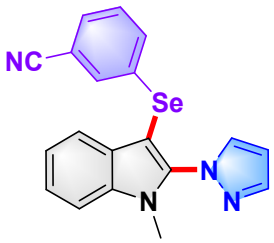
Yellow liquid (55.8 mg, 38% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.42–7.39 (m, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.10 (s, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.96–6.94 (m, 1H), 6.48 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.20, 139.07, 138.90, 135.67, 133.64, 133.06, 129.54, 129.00, 126.88, 126.00, 123.72, 121.43, 121.20, 109.97, 106.63, 92.44, 30.59, 21.35. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ $[M+H]^+$: 368.0660; found: 368.0652.

(24) 3-((3-fluorophenyl)selanyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (28)



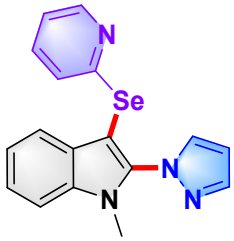
Yellow liquid (120.2 mg, 81% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.13 (td, *J* = 8.0, 5.8 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.85–6.80 (m, 1H), 6.50–6.48 (m, 1H), 3.77 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 163.09 (d, *J* = 249.2 Hz), 142.34, 139.28, 135.70, 135.54 (d, *J* = 6.0 Hz), 133.50, 130.32 (d, *J* = 9.1 Hz), 128.72, 124.30 (d, *J* = 3.0 Hz), 123.96, 121.69, 120.95, 115.65 (d, *J* = 22.7 Hz), 112.92 (d, *J* = 21.1 Hz), 110.15, 106.81, 91.82, 30.61. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -111.97. **HRMS (ESI):** Calcd. for $C_{18}H_{14}FN_3Se$ $[M+H]^+$: 372.0410; found: 372.0400.

(25) 3-((1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)selanyl)benzonitrile (29)



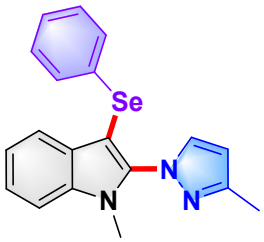
Yellow liquid (84.7 mg, 56% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.3 Hz, 1H), 7.71–7.63 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.46–7.41 (m, 3H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.54–6.47 (m, 1H), 3.76 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.44, 139.39, 135.70, 135.32, 133.39, 133.07, 131.71, 129.55, 129.51, 128.37, 124.18, 121.90, 120.67, 118.39, 113.22, 110.36, 106.99, 91.26, 30.63. **HRMS (ESI):** Calcd. for $C_{19}H_{14}N_4Se$ $[M+H]^+$: 379.0456; found: 379.0447.

(26) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(pyridin-2-ylselanyl)-1*H*-indole (30)



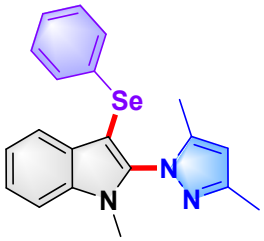
Yellow solid (46.7 mg, 33% yield), m.p.: 125-126 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 5.9 Hz, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32–7.29 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.97 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.46 (t, *J* = 2.2 Hz, 1H), 3.77 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.84, 149.79, 142.33, 139.38, 136.74, 135.81, 133.67, 128.64, 123.90, 122.95, 121.61, 121.06, 120.21, 110.11, 106.81, 91.72, 30.65. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4Se$ $[M+H]^+$: 355.0456; found: 355.0448.

(27) 1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-3-(phenylselanyl)-1*H*-indole (31)



Yellow liquid (130.7 mg, 89% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.24–7.21 (m, 2H), 7.18–7.12 (m, 3H), 6.25 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.64, 139.39, 135.69, 134.32, 133.53, 129.13, 128.95, 128.80, 125.81, 123.62, 121.37, 121.05, 109.93, 106.68, 92.02, 30.60, 13.80. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3Se$ $[M+H]^+$: 368.0660; found: 368.0652.

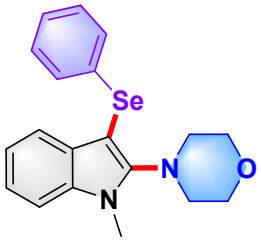
(28) 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-methyl-3-(phenylselanyl)-1*H*-indole (32)



Yellow liquid (73.2 mg, 48% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.70–7.65 (m, 1H), 7.40 (ddd, *J* = 13.9, 8.6, 7.4 Hz, 2H), 7.28–7.22 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 3H), 6.04 (s, 1H), 3.56 (s, 3H), 2.33 (s,

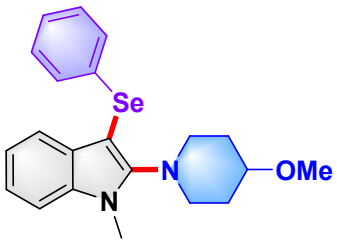
3H), 2.05 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.78, 143.45, 137.47, 135.75, 132.56, 129.44, 128.93, 128.68, 125.84, 123.72, 121.20, 109.96, 106.04, 95.63, 29.85, 13.77, 11.35. **HRMS (ESI):** Calcd. for $C_{20}H_{19}N_3Se$ $[M+H]^+$: 382.0817; found: 382.0808.

(29) 4-(1-methyl-3-(phenylselanyl)-1*H*-indol-2-yl)morpholine (33)



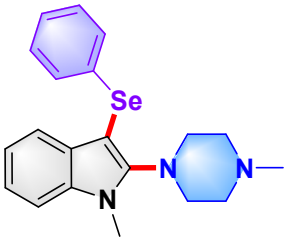
Red liquid (92.3 mg, 62% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 6.9 Hz, 1H), 7.23–7.19 (m, 2H), 7.16 (dddd, *J* = 10.3, 7.6, 6.5, 1.3 Hz, 3H), 7.11 (t, *J* = 7.1 Hz, 1H), 3.84 (t, *J* = 4.6 Hz, 4H), 3.75 (s, 3H), 3.34 (s, 4H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.40, 135.11, 134.94, 130.36, 128.99, 127.98, 125.28, 122.06, 120.60, 119.55, 109.38, 87.09, 67.63, 51.77, 28.94. **HRMS (ESI):** Calcd. for $C_{19}H_{20}N_2OSe$ $[M+H]^+$: 373.0814; found: 373.0804.

(30) 2-(4-methoxypiperidin-1-yl)-1-methyl-3-(phenylselanyl)-1*H*-indole (34)



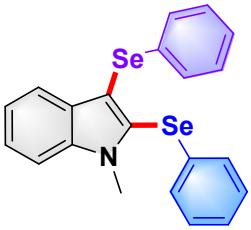
Red liquid (88.0 mg, 55% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.19 – 7.15 (m, 2H), 7.14 – 7.09 (m, 3H), 7.09 – 7.06 (m, 1H), 3.68 (s, 3H), 3.37 (s, 3H), 3.35 – 3.26 (m, 4H), 2.05 – 2.00 (m, 2H), 1.71 – 1.61 (m, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.60, 135.25, 134.98, 130.40, 128.95, 127.88, 125.15, 121.76, 120.42, 119.32, 109.26, 86.27, 55.66, 28.89. **HRMS (ESI):** Calcd. for $C_{21}H_{24}N_2OSe$ $[M+H]^+$: 401.1127; found: 401.1118.

(31) 1-methyl-2-(4-methylpiperazin-1-yl)-3-(phenylselanyl)-1*H*-indole (35)



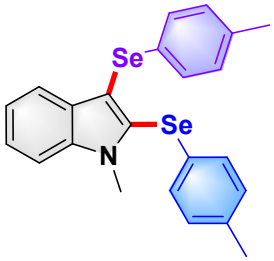
Red liquid (72.4 mg, 47% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.10 – 7.03 (m, 2H), 7.03 – 6.97 (m, 3H), 6.97 – 6.93 (m, 1H), 3.58 (s, 3H), 3.23 (s, 4H), 2.42 (s, 4H), 2.23 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.90, 135.31, 135.00, 130.50, 128.92, 127.94, 125.15, 121.85, 120.48, 119.43, 109.28, 86.79, 55.77, 51.25, 46.30, 28.98. **HRMS (ESI):** Calcd. for $C_{20}H_{23}N_3Se$ $[M+H]^+$: 386.1130; found: 386.1120.

(32) 1-methyl-2,3-bis(phenylselanyl)-1*H*-indole (36)



Colorless solid (151.7 mg, 86% yield), m.p.: 108-109 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.32–7.30 (m, 2H), 7.27–7.22 (m, 3H), 7.21–7.17 (m, 3H), 7.17–7.13 (m, 3H), 3.90 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.94, 133.79, 133.68, 131.62, 130.52, 130.15, 129.45, 129.42, 128.96, 126.80, 125.80, 123.64, 121.35, 120.97, 110.23, 109.04, 32.83. **HRMS (ESI):** Calcd. for $C_{21}H_{17}NSe_2$ $[M+H]^+$: 443.9764; found: 443.9754.

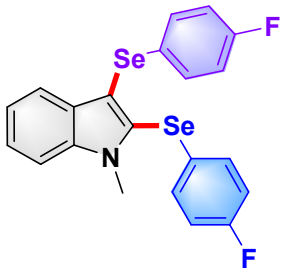
(33) 1-methyl-2,3-bis(*p*-tolylselanyl)-1*H*-indole (37)



Colorless solid (154.5 mg, 82% yield), m.p.: 114-115 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.28–7.24 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR**

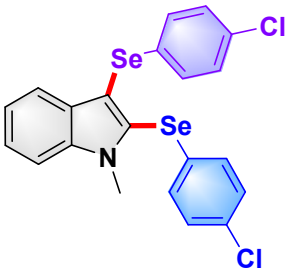
(151 MHz, Chloroform-*d*) δ 138.91, 136.83, 135.64, 134.11, 130.63, 130.57, 130.25, 129.90, 129.87, 129.80, 127.84, 123.51, 121.35, 120.87, 110.19, 109.20, 32.82, 21.11, 21.08. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NSe_2$ $[M+H]^+$: 472.0076; found: 472.0067.

(34) 2,3-bis((4-fluorophenyl)selanyl)-1-methyl-1*H*-indole (38)



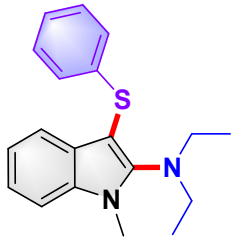
Yellow liquid (97.5 mg, 51% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.79 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.43 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.32 – 7.22 (m, 5H), 6.94 – 6.85 (m, 4H), 3.92 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.74 (d, *J* = 65.9 Hz), 161.10 (d, *J* = 64.1 Hz), 138.81, 133.88, 132.50 (d, *J* = 7.8 Hz), 131.68 (d, *J* = 7.4 Hz), 130.34, 127.93 (d, *J* = 3.1 Hz), 125.83 (d, *J* = 3.3 Hz), 123.83, 121.16 (d, *J* = 3.7 Hz), 116.60 (d, *J* = 21.9 Hz), 116.13, 115.99, 110.34, 109.36, 32.79. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -114.72, -116.63. **HRMS (ESI):** Calcd. for $C_{21}H_{15}F_2NSe_2$ $[M+H]^+$: 479.9576; found: 479.9564.

(35) 2,3-bis((4-chlorophenyl)selanyl)-1-methyl-1*H*-indole (39)



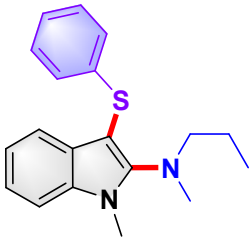
White solid (122.4 mg, 60% yield), m.p.: 129-130 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.44–7.41 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.16–7.11 (m, 4H), 7.11–7.06 (m, 4H), 3.90 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.90, 133.12, 131.95, 131.79, 131.41, 130.73, 130.31, 129.65, 129.56, 129.04, 129.03, 123.98, 121.27, 121.18, 110.40, 108.99, 32.87. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Cl_2NSe_2$ $[M+H]^+$: 511.8985; found: 511.8968.

(36) *N*,*N*-diethyl-1-methyl-3-(phenylthio)-1*H*-indol-2-amine (40)



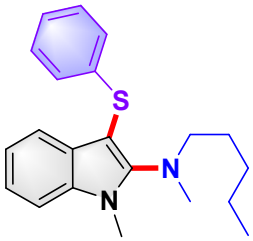
Yellow liquid (76.9 mg, 62% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.54 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.19–7.15 (m, 3H), 7.11–7.08 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 3.31 (q, *J* = 7.2 Hz, 4H), 1.01 (t, *J* = 7.2 Hz, 6H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.41, 139.79, 134.72, 129.52, 128.58, 125.24, 124.23, 121.73, 120.40, 118.55, 109.59, 92.88, 48.40, 28.92, 13.75. **HRMS (ESI):** Calcd. for $C_{19}H_{22}N_2S$ $[M+H]^+$: 311.1576; found: 311.1568.

(37) *N*,1-dimethyl-3-(phenylthio)-*N*-propyl-1*H*-indol-2-amine (41)



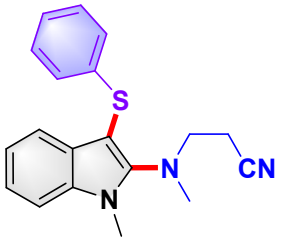
Yellow liquid (85.6 mg, 69% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28–7.24 (m, 1H), 7.18 (dddt, *J* = 11.5, 7.1, 5.6, 3.1 Hz, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 3.24–3.20 (m, 2H), 2.94 (s, 3H), 1.56–1.51 (m, 2H), 0.89–0.86 (m, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.51, 140.31, 134.66, 129.74, 128.62, 125.21, 124.25, 121.65, 120.45, 118.37, 109.34, 90.80, 57.87, 41.62, 29.09, 21.35, 11.46. **HRMS (ESI):** Calcd. for $C_{19}H_{22}N_2S$ $[M+H]^+$: 311.1576; found: 311.1568.

(38) *N*,1-dimethyl-*N*-pentyl-3-(phenylthio)-1*H*-indol-2-amine (42)



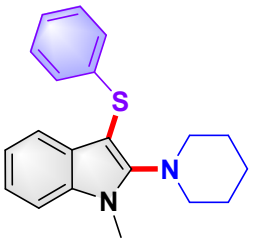
Yellow liquid (82.5 mg, 61% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.21–7.16 (m, 3H), 7.13 (s, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 3.28–3.24 (m, 2H), 2.95 (s, 3H), 1.54–1.49 (m, 2H), 1.30–1.23 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.50, 140.35, 134.70, 129.81, 128.63, 125.24, 124.27, 121.66, 120.47, 118.39, 109.37, 90.82, 56.05, 41.76, 29.23, 29.11, 27.92, 22.54, 14.13. **HRMS (ESI):** Calcd. for $C_{21}H_{26}N_2S$ $[M+H]^+$: 339.1189; found: 339.1882.

(39) 3-(methyl(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)amino)propanenitrile (43)



Brown liquid (46.2 mg, 36% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.22–7.18 (m, 3H), 7.12–7.05 (m, 3H), 3.81 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.92 (s, 3H), 2.46 (t, *J* = 6.4 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 149.58, 139.47, 134.75, 129.32, 128.91, 125.28, 124.79, 122.50, 120.90, 118.71, 118.71, 109.88, 92.40, 51.07, 42.42, 29.15, 17.46. **HRMS (ESI):** Calcd. for $C_{19}H_{19}N_3S$ $[M+H]^+$: 322.1372; found: 322.1364.

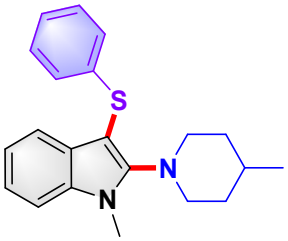
(40) 1-methyl-3-(phenylthio)-2-(piperidin-1-yl)-1*H*-indole (44)



Yellow liquid (110.8 mg, 86% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.32–3.29 (m, 4H), 1.71 (q, *J* = 5.6 Hz, 4H), 1.63 (q,

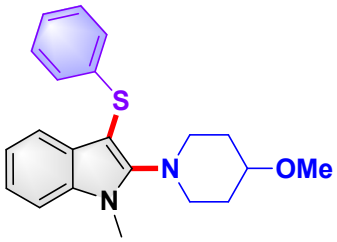
J = 5.9 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.71, 140.85, 134.85, 129.78, 128.65, 125.08, 124.19, 121.58, 120.41, 118.35, 109.22, 89.30, 52.60, 29.03, 26.74, 24.18. **HRMS (ESI):** Calcd. for $C_{20}H_{22}N_2S$ $[M+H]^+$: 323.1576; found: 323.1570.

(41) 1-methyl-2-(4-methylpiperidin-1-yl)-3-(phenylthio)-1*H*-indole (45)



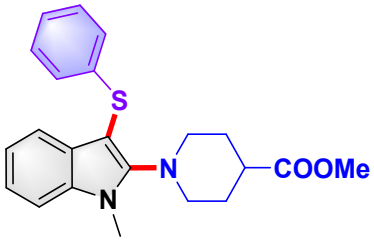
Yellow solid (125.0 mg, 93% yield), m.p.: 135-136 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 7.24–7.20 (m, 2H), 7.18 (t, J = 7.0 Hz, 1H), 7.15 (d, J = 1.1 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 3.72 (s, 3H), 3.43 (t, J = 11.1 Hz, 2H), 3.25 (d, J = 12.1 Hz, 2H), 1.76 (d, J = 12.5 Hz, 2H), 1.61–1.57 (m, 1H), 1.43–1.38 (m, 2H), 1.06 (d, J = 6.6 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.55, 140.89, 134.89, 129.84, 128.68, 125.13, 124.23, 121.61, 120.44, 118.35, 109.25, 89.42, 51.94, 35.15, 30.64, 29.07, 22.23. **HRMS (ESI):** Calcd. for $C_{21}H_{24}N_2S$ $[M+H]^+$: 337.1733; found: 337.1725.

(42) 2-(4-methoxypiperidin-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (46)



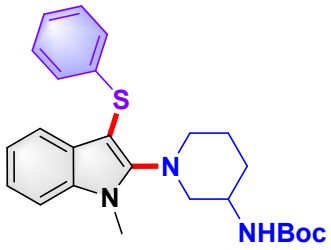
Yellow liquid (126.7 mg, 90% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.29–7.27 (m, 1H), 7.23–7.19 (m, 2H), 7.19–7.15 (m, 1H), 7.14–7.11 (m, 2H), 7.08 (t, J = 7.3 Hz, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 3.40–3.34 (m, 5H), 2.10–2.05 (m, 2H), 1.74–1.67 (m, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.85, 140.61, 134.84, 129.66, 128.71, 125.09, 124.31, 121.82, 120.54, 118.44, 109.35, 89.89, 55.69, 32.02, 29.03. **HRMS (ESI):** Calcd. for $C_{21}H_{24}N_2OS$ $[M+H]^+$: 353.1682; found: 353.1674.

(43) methyl 1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperidine-4-carboxylate (47)



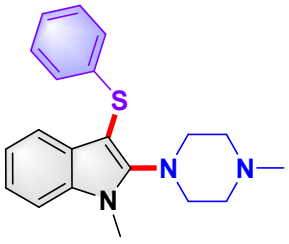
Yellow liquid (66.9 mg, 44% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09–7.05 (m, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.40 (t, *J* = 11.2 Hz, 2H), 3.26 (d, *J* = 12.3 Hz, 2H), 2.50–24.5 (m,1H), 2.02–1.98 (m, 2H), 1.90–1.84 (m, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 175.55, 151.71, 140.52, 134.75, 129.56, 128.68, 125.09, 124.32, 121.86, 120.53, 118.47, 109.35, 90.23, 51.78, 51.09, 40.86, 29.10, 28.95. **HRMS (ESI):** Calcd. for $C_{22}H_{24}N_2O_2S$ $[M+H]^+$: 381.1631; found: 381.1622.

(44) *tert*-butyl (1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperidin-3-yl)carbamate (48)



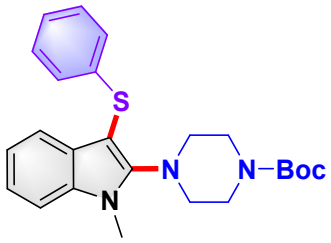
Purple solid (157.3 mg, 90% yield), m.p.: 138-139 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.20–7.17 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09–7.05 (m, 3H), 4.79 (s, 1H), 3.82 (s, 1H), 3.73 (s, 3H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.25 (dtd, *J* = 28.5, 12.6, 10.8, 5.0 Hz, 2H), 3.08 (dd, *J* = 11.6, 7.7 Hz, 1H), 2.00–1.64 (m, 4H), 1.48 (s, 9H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 155.20, 151.23, 140.36, 134.72, 129.43, 128.71, 125.08, 124.35, 121.95, 120.55, 118.52, 109.39, 90.52, 79.41, 56.93, 51.86, 29.08, 28.44. **HRMS (ESI):** Calcd. for $C_{25}H_{31}N_3O_2S$ $[M+H]^+$: 438.2209; found: 438.2203.

(45) 1-methyl-2-(4-methylpiperazin-1-yl)-3-(phenylthio)-1*H*-indole (49)



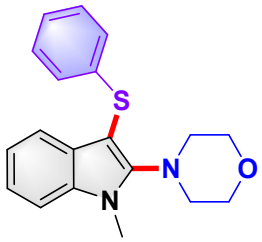
Yellow solid (83.6 mg, 62% yield), m.p.: 140-141 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.28–7.25 (m, 1H), 7.17 (q, *J* = 7.5 Hz, 3H), 7.09–7.03 (m, 3H), 3.71 (s, 3H), 3.39 (s, 4H), 2.57 (s, 4H), 2.38 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.23, 140.66, 134.81, 129.76, 128.65, 125.06, 124.25, 121.86, 120.57, 118.50, 109.32, 90.37, 55.76, 51.07, 46.36, 29.10. **HRMS (ESI):** Calcd. for $C_{20}H_{23}N_3S$ $[M+H]^+$: 338.1685; found: 338.1678.

(46) *tert*-butyl 4-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperazine-1-carboxylate (50)



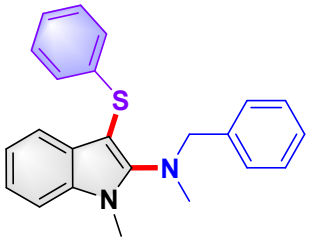
Brown solid (138.7 mg, 82% yield), m.p.: 196-197 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.21–7.15 (m, 3H), 7.07 (dd, *J* = 8.3, 7.0 Hz, 3H), 3.73 (s, 3H), 3.57 (s, 4H), 3.30 (s, 4H), 1.52 (s, 9H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 154.81, 150.86, 140.28, 134.79, 129.50, 128.77, 125.08, 124.46, 122.13, 120.71, 118.64, 109.49, 90.75, 79.97, 29.08, 28.49, 28.48. **HRMS (ESI):** Calcd. for $C_{24}H_{29}N_3O_2S$ $[M+H]^+$: 424.2053; found: 424.2043.

(47) 4-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)morpholine (51)



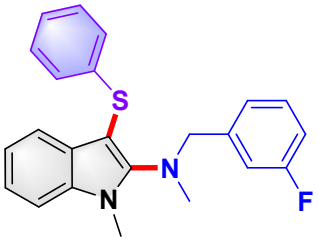
Yellow solid (101.1 mg, 78% yield), m.p.: 121-122 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.22–7.17 (m, 3H), 7.12–7.07 (m, 3H), 3.86–3.84 (m, 4H), 3.75 (s, 3H), 3.36 (s, 4H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.67, 140.41, 134.77, 129.61, 128.74, 125.14, 124.43, 122.10, 120.71, 118.65, 109.46, 90.80, 67.59, 51.52, 29.07. **HRMS (ESI):** Calcd. for $C_{19}H_{20}N_2OS$ $[M+H]^+$: 325.1369; found: 325.1361.

(48) *N*-benzyl-*N*,1-dimethyl-3-(phenylthio)-1*H*-indol-2-amine (52)



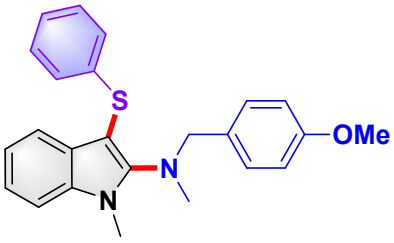
Yellow solid (111.7 mg, 78% yield), m.p.: 92-93 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.48–7.39 (m, 5H), 7.39–7.34 (m, 2H), 7.31–7.25 (m, 3H), 7.24–7.22 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.56 (s, 2H), 3.82 (s, 3H), 2.96 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.45, 140.28, 138.67, 134.77, 129.71, 128.82, 128.66, 128.51, 127.38, 125.38, 125.37, 124.49, 122.00, 120.67, 118.66, 109.56, 91.35, 60.26, 41.47, 29.33. **HRMS (ESI):** Calcd. for $C_{23}H_{22}N_2S$ $[M+H]^+$: 359.1576; found: 359.1569.

(49) *N*-(3-fluorobenzyl)-*N*,1-dimethyl-3-(phenylthio)-1*H*-indol-2-amine (53)



Brown solid (63.2 mg, 42% yield), m.p.: 95-97 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.31–7.27 (m, 2H), 7.22–7.16 (m, 3H), 7.13–7.07 (m, 5H), 7.00–6.95 (m, 1H), 4.49 (s, 2H), 3.78 (s, 3H), 2.87 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 163.02 (d, *J* = 246.1 Hz), 151.94, 141.42 (d, *J* = 6.0 Hz), 140.00, 134.65, 129.86 (d, *J* = 9.1 Hz), 129.54, 128.76, 125.28, 124.48, 124.06, 122.06, 120.66, 118.66, 115.18 (d, *J* = 21.1 Hz), 114.17 (d, *J* = 21.1 Hz), 109.51, 91.54, 59.57, 41.68, 29.24. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -113.30. **HRMS (ESI):** Calcd. for $C_{23}H_{21}FN_2S$ $[M+H]^+$: 377.1482; found: 377.1472.

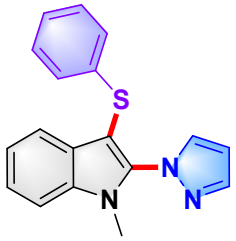
(50) *N*-(4-methoxybenzyl)-*N*,1-dimethyl-3-(phenylthio)-1*H*-indol-2-amine (54)



Colourless solid (97.8 mg, 63% yield), m.p.: 142-143 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.67–7.49 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.25–7.18 (m, 3H),

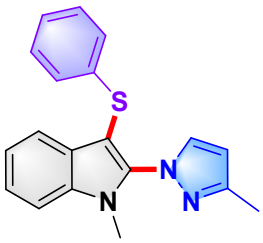
7.16 (s, 2H), 7.10 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 4.43 (s, 2H), 3.85 (s, 3H), 3.76 (s, 3H), 2.89 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.89, 152.36, 140.23, 134.71, 130.63, 129.85, 129.65, 128.72, 125.30, 124.38, 121.87, 120.56, 118.56, 113.78, 109.48, 91.28, 59.56, 55.30, 41.28, 29.25. **HRMS (ESI):** Calcd. for $C_{24}H_{24}N_2OS$ $[M+H]^+$: 389.1682; found: 389.1673.

(51) 1-methyl-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (55)



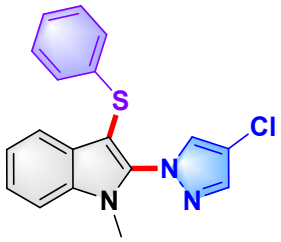
Yellow solid (108.6 mg, 89% yield), m.p.: 112-114 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, J = 1.8 Hz, 1H), 7.76–7.73 (m, 2H), 7.48 (d, J = 8.3 Hz, 1H), 7.43 (t, J = 7.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.23–7.20 (m, 2H), 7.16–7.13 (m, 2H), 7.11 (t, J = 7.3 Hz, 1H), 6.50–6.48 (m, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.35, 139.05, 138.55, 135.35, 133.51, 128.95, 128.15, 126.04, 125.15, 123.84, 121.60, 120.21, 110.12, 106.87, 95.56, 30.72. **HRMS (ESI):** Calcd. for $C_{18}H_{15}N_3S$ $[M+H]^+$: 306.1059; found: 306.1052.

(52) 1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-3-(phenylthio)-1*H*-indole (56)



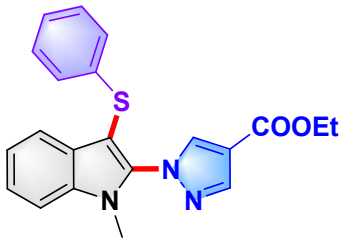
Green liquid (94.4 mg, 74% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.69 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.21–7.17 (m, 2H), 7.12–7.07 (m, 3H), 6.25 (d, J = 2.4 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 151.76, 139.30, 138.74, 135.33, 134.20, 128.88, 128.15, 125.90, 124.98, 123.64, 121.45, 120.09, 110.00, 106.88, 94.99, 30.73, 13.78. **HRMS (ESI):** Calcd. for $C_{19}H_{17}N_3S$ $[M+H]^+$: 320.1216; found: 320.1208.

(53) 2-(4-chloro-1*H*-pyrazol-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (57)



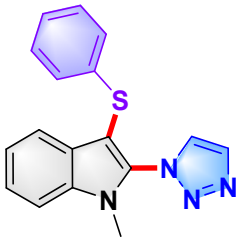
Yellow solid (93.6 mg, 69% yield), m.p.: 107-109 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.72 (d, *J* = 6.7 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.13–7.10 (m, 3H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 140.95, 138.04, 138.02, 135.30, 131.06, 129.01, 127.90, 126.19, 125.35, 124.16, 121.77, 120.36, 111.76, 110.17, 96.34, 30.69. **HRMS (ESI):** Calcd. for $C_{18}H_{14}ClN_3S$ $[M+H]^+$: 340.0669; found: 340.0663.

(54) ethyl 1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)-1*H*-pyrazole-4-carboxylate (58)



Red solid (128.2 mg, 85% yield), m.p.: 123-124 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.21 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.30–7.27 (m, 1H), 7.21–7.18 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.49, 143.21, 137.81, 137.68, 136.90, 135.33, 129.00, 127.87, 126.47, 125.49, 124.30, 121.83, 120.45, 116.44, 110.20, 97.05, 60.59, 30.74, 14.39. **HRMS (ESI):** Calcd. for $C_{21}H_{19}N_3O_2S$ $[M+H]^+$: 378.1271; found: 378.1262.

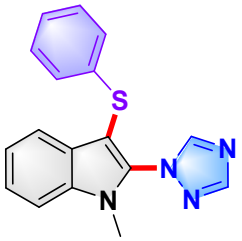
(55) 1-methyl-3-(phenylthio)-2-(1*H*-1,2,3-triazol-1-yl)-1*H*-indole (59)



White solid (94.3 mg, 77% yield), m.p.: 117-118 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.1 Hz, 1H), 7.86 (d, *J* = 1.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H),

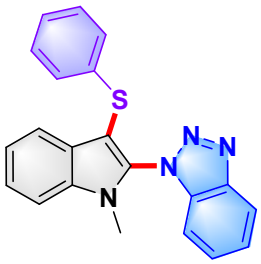
7.46 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (dd, *J* = 17.0, 7.6 Hz, 3H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.58, 135.56, 134.90, 133.31, 129.08, 127.96, 127.41, 126.23, 125.55, 124.61, 122.04, 120.49, 110.38, 97.36, 30.89. **HRMS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

(56) 1-methyl-3-(phenylthio)-2-(1*H*-1,2,4-triazol-1-yl)-1*H*-indole (60)



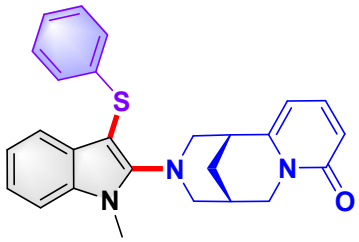
White solid (104.0 mg, 85% yield), m.p.: 124-125 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.24 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.32–7.29 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (q, *J* = 7.6 Hz, 3H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.29, 146.57, 137.85, 135.54, 134.93, 129.10, 127.93, 126.20, 125.56, 124.54, 122.00, 120.52, 110.25, 97.50, 30.74. **HRMS (ESI):** Calcd. for $C_{17}H_{14}N_4S$ $[M+H]^+$: 307.1588; found: 307.1579.

(57) 1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (61)



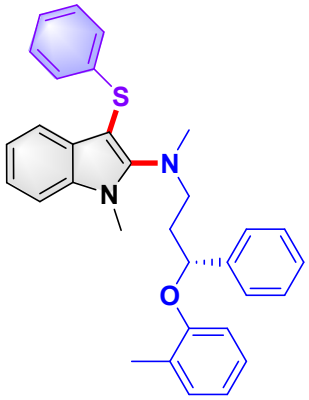
Pink solid (102.5 mg, 72% yield), m.p.: 147-148 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.51–7.45 (m, 3H), 7.35–7.32 (m, 2H), 7.16–7.12 (m, 2H), 7.11–7.06 (m, 3H), 3.64 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 145.27, 137.05, 136.00, 134.89, 133.40, 128.95, 128.84, 127.97, 126.93, 125.56, 124.74, 124.63, 121.88, 120.65, 120.28, 110.46, 110.43, 30.36. **HRMS (ESI):** Calcd. for $C_{21}H_{16}N_4S$ $[M+H]^+$: 357.1168; found: 357.1159.

(58) (1*R*,5*S*)-3-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)-1,2,3,4,5,6-hexahydro-8*H*-1,5-methanopyrido[1,2-*a*][1,5]diazocin-8-one (62)



Yellow liquid (102.5 mg, 72% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 9.1, 6.8 Hz, 1H), 7.24–7.17 (m, 4H), 7.12–7.09 (m, 1H), 7.06 (dd, *J* = 18.1, 7.2 Hz, 3H), 6.55 (d, *J* = 9.1 Hz, 1H), 6.07 (d, *J* = 6.9 Hz, 1H), 4.30 (d, *J* = 15.6 Hz, 1H), 3.95 (dd, *J* = 15.6, 6.5 Hz, 1H), 3.90 (d, *J* = 11.7 Hz, 1H), 3.74 (d, *J* = 11.2 Hz, 1H), 3.19 (d, *J* = 11.7 Hz, 1H), 3.15 (s, 3H), 3.10–3.04 (m, 2H), 2.49 (ddd, *J* = 7.1, 4.9, 2.7 Hz, 1H), 2.01 (q, *J* = 3.4 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 163.51, 151.01, 150.00, 139.93, 138.91, 134.52, 128.99, 128.81, 125.06, 124.52, 122.41, 120.68, 118.58, 116.94, 109.69, 105.14, 92.50, 59.39, 58.20, 50.00, 35.46, 28.04, 27.97, 25.40. **HRMS (ESI):** Calcd. for $C_{26}H_{25}N_3OS$ $[M+H]^+$: 428.1791; found: 428.1781.

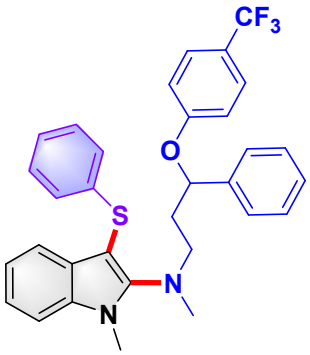
(59) (*R*)-*N*,1-dimethyl-*N*-(3-phenyl-3-(*o*-tolyloxy)propyl)-3-(phenylthio)-1*H*-indol-2-amine (63)



Yellow liquid (167.3 mg, 85% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.29 (m, 4H), 7.27 (td, *J* = 6.8, 1.6 Hz, 3H), 7.22 – 7.18 (m, 3H), 7.13 (dd, *J* = 14.8, 7.2 Hz, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.96 (td, *J* = 7.8, 1.8 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.17 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.65 (s, 3H), 3.55 (tdd, *J* = 12.8, 8.4, 5.8 Hz, 2H), 2.97 (s, 3H), 2.31 (s, 3H), 2.26 – 2.20 (m, 1H), 2.09 – 2.04 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 156.05, 151.73, 142.03, 140.22, 134.74, 130.67, 129.76, 128.79, 128.68, 127.55,

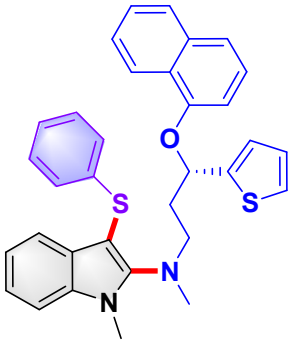
127.02, 126.60, 125.78, 125.31, 124.44, 121.90, 120.62, 120.30, 118.53, 112.73, 109.50, 91.28, 77.52, 52.35, 42.21, 37.56, 29.07, 16.64. **HRMS (ESI):** Calcd. for $C_{32}H_{32}N_2OS$ [M+H]$^+$: 493.2308; found: 493.2297.

(60) *N*,1-dimethyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)-3-(phenylthio)-1*H*-indol-2-amine (64)



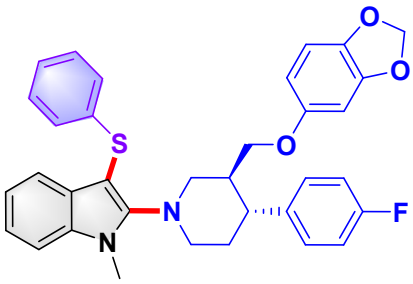
Yellow liquid (152.9 mg, 70% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.28–7.23 (m, 3H), 7.22–7.19 (m, 2H), 7.18–7.13 (m, 3H), 7.09 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 5.09 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.63 (s, 3H), 3.49 (t, *J* = 7.2 Hz, 2H), 2.94 (s, 3H), 2.15 (ddd, *J* = 14.1, 7.0, 2.1 Hz, 1H), 2.04–2.00 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 160.43, 151.39, 140.87, 140.02, 134.62, 129.63, 128.78, 128.71, 127.84, 126.67 (d, *J* = 4.5 Hz), 125.68, 125.22, 124.40, 121.90, 120.61, 118.44, 115.60, 109.38, 78.13, 51.94, 42.26, 37.40, 29.07. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -61.55. **HRMS (ESI):** Calcd. for $C_{32}H_{29}F_3N_2OS$ [M+H]$^+$: 547.2025; found: 547.2015.

(61) (*S*)-*N*,1-dimethyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)-3-(phenylthio)-1*H*-indol-2-amine (65)



Yellow liquid (149.5 mg, 70% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.54 – 7.48 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 3.9 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.17 (ddd, *J* = 15.4, 7.7, 3.1 Hz, 3H), 7.13 – 7.09 (m, 2H), 7.07 – 7.04 (m, 1H), 6.95 (d, *J* = 2.8 Hz, 1H), 6.93 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.63 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.65 (s, 3H), 3.60 (t, *J* = 7.4 Hz, 2H), 2.97 (s, 3H), 2.52 – 2.46 (m, 1H), 2.26 – 2.21 (m, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.36, 151.45, 145.03, 140.14, 134.72, 134.64, 129.77, 128.80, 127.56, 126.65, 126.39, 126.15, 125.71, 125.32, 124.79, 124.67, 124.47, 122.17, 121.95, 120.71, 120.67, 118.53, 109.52, 106.95, 91.41, 74.32, 52.05, 42.36, 37.61, 29.11. **HRMS (ESI):** Calcd. for $C_{33}H_{30}N_2OS_2$ $[M+H]^+$: 533.1727; found: 533.1729.

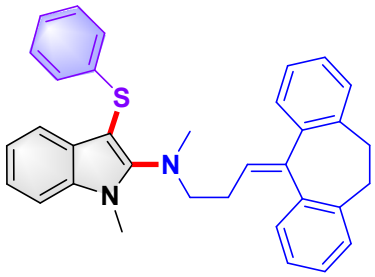
(62) 2-((3*S*,4*R*)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)-1-methyl-3-(phenylthio)-1*H*-indole (66)



Yellow liquid (187.9 mg, 83% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.28–7.22 (m, 5H), 7.20–7.18 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 2.5 Hz, 1H), 6.15 (d, *J* = 6.1 Hz, 1H), 5.94 (s, 2H), 3.82 (s, 3H), 3.73 (ddd, *J* = 12.3, 4.0, 1.7 Hz, 1H), 3.65 (ddd, *J* = 12.4, 8.3, 2.9 Hz, 2H), 3.54–3.49 (m, 2H), 3.41 (d, *J* = 12.1 Hz, 1H), 2.68–2.63 (m, 1H), 2.45 (dtt, *J* = 11.2, 7.8, 3.7 Hz, 1H), 2.06–1.99 (m, 1H), 1.95 (dd, *J* = 13.1, 3.6 Hz, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 161.70 (d, *J* = 244.6 Hz), 154.31, 151.84, 148.23, 141.75, 140.75, 139.63 (d, *J* = 3.0 Hz), 134.92, 129.86, 128.90 (d, *J* = 7.6 Hz), 128.83, 125.26, 124.48, 121.92, 120.69, 118.52, 115.70, 115.56, 109.44, 107.91, 105.78, 101.18, 98.20, 89.88, 69.44, 55.70, 52.15, 44.22, 42.88, 35.38, 29.36. **^{19}F-NMR** (565 MHz, Chloroform-d) δ -116.00. **HRMS (ESI):** Calcd. for $C_{34}H_{31}FN_2O_3S$ $[M+H]^+$: 567.2112; found: 567.2101.

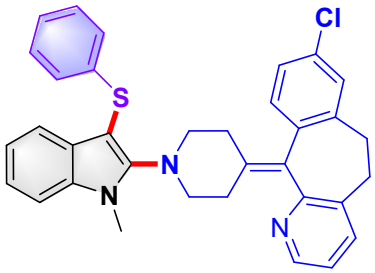
(63) *N*-(3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*,1-dimethyl-3-

(phenylthio)-1*H*-indol-2-amine (67)



Yellow liquid (158.0 mg, 79% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.24 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.18 – 7.14 (m, 3H), 7.12 – 7.09 (m, 3H), 7.09 – 7.03 (m, 3H), 5.85 (t, *J* = 7.4 Hz, 1H), 3.66 (s, 3H), 3.44 – 3.28 (m, 4H), 3.04 – 2.94 (m, 1H), 2.89 (s, 3H), 2.83 – 2.70 (m, 1H), 2.36 (q, *J* = 8.2, 7.3 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 152.04, 144.02, 141.33, 140.31, 140.00, 139.33, 137.14, 134.75, 130.09, 129.79, 129.04, 128.75, 128.61, 128.24, 128.13, 127.53, 127.17, 126.12, 125.84, 125.31, 124.41, 121.86, 120.61, 118.51, 109.47, 91.10, 55.82, 41.72, 33.85, 32.14, 29.18, 28.57. **HRMS (ESI):** Calcd. for $C_{34}H_{32}N_2S$ $[M+H]^+$: 501.2359; found: 501.2348.

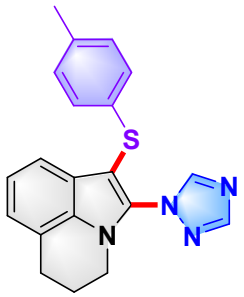
(64) 8-chloro-11-(1-(1-methyl-3-(phenylthio)-1*H*-indol-2-yl)piperidin-4-ylidene)-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (68)



Brown liquid (188.2 mg, 86% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 3.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.15–7.08 (m, 5H), 7.03 (dd, *J* = 19.1, 7.2 Hz, 3H), 3.72 (s, 3H), 3.46–3.37 (m, 2H), 3.29 (dt, *J* = 6.3, 3.5 Hz, 4H), 2.87–2.79 (m, 2H), 2.68–2.49 (m, 4H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 157.26, 151.47, 146.52, 140.51, 139.66, 137.85, 137.79, 137.64, 134.84, 133.77, 133.60, 132.87, 130.69, 129.04, 128.67, 126.11, 125.05, 124.29, 122.28, 121.80, 120.52,

118.41, 109.30, 89.74, 52.68, 52.60, 32.00, 31.82, 31.77, 31.51, 29.18. **HRMS (ESI):** Calcd. for $C_{34}H_{30}ClN_3S$ $[M+H]^+$: 546.1778; found: 546.1776.

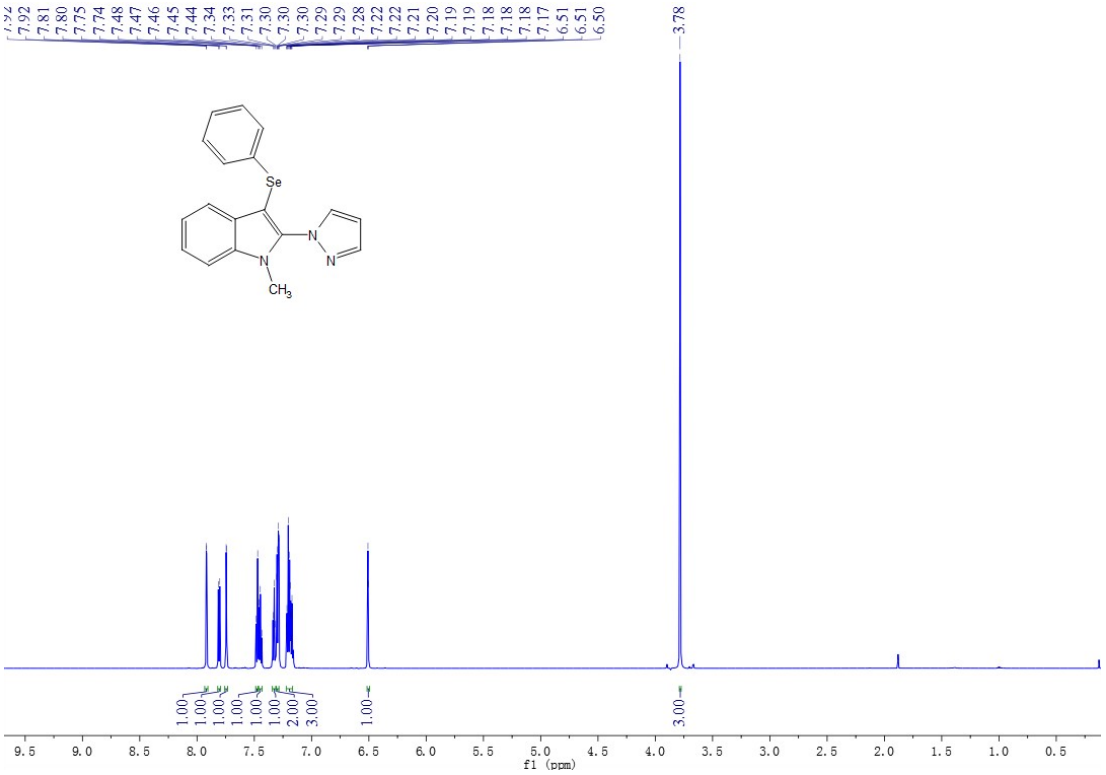
(65) 1-methyl-3-(*p*-tolylthio)-2-(1*H*-1,2,4-triazol-1-yl)-1*H*-indole (69)



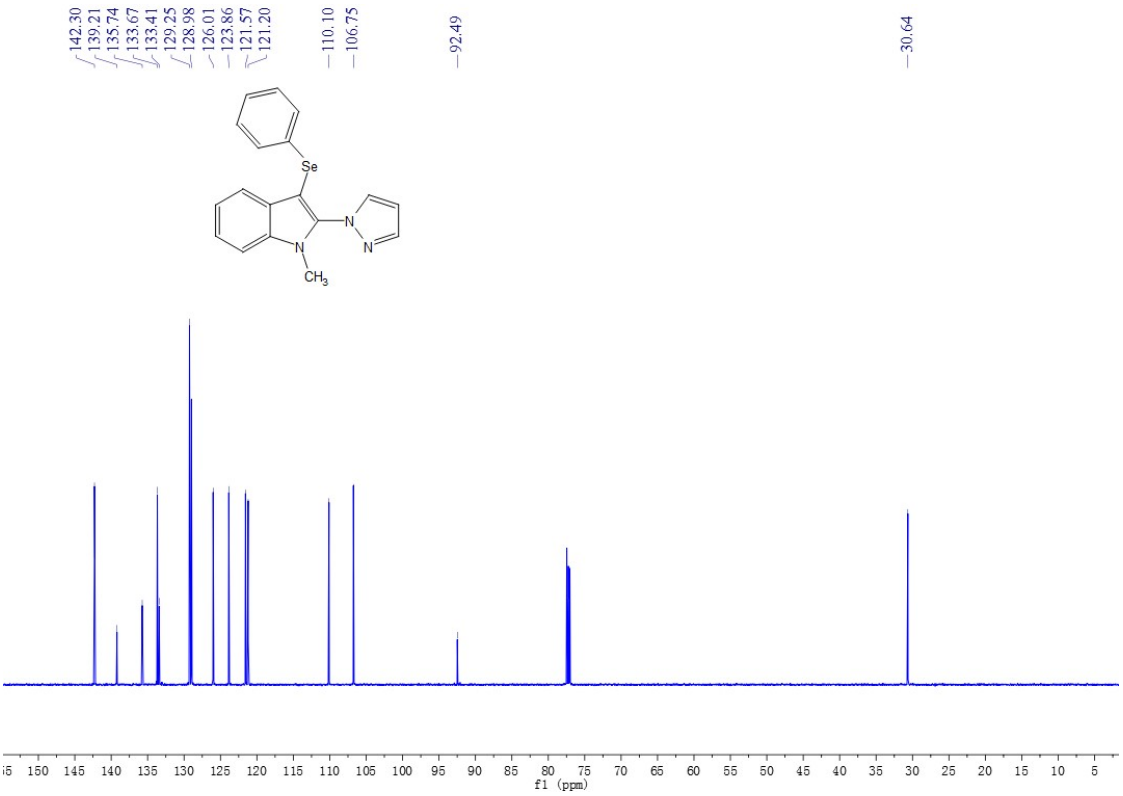
Brown solid (3.01 g, 87% yield), m.p.: 100-102 °C; **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.21 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.02–6.99 (m, 5H), 4.22–4.19 (m, 2H), 2.97 (t, *J* = 6.2 Hz, 2H), 2.32–2.30 (m, 2H), 2.28 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 153.03, 146.06, 135.68, 135.40, 133.32, 132.84, 132.45, 131.47, 129.95, 126.60, 122.65, 121.94, 121.23, 96.63, 43.26, 29.87, 22.66, 20.93. **HRMS (ESI):** Calcd. for $C_{20}H_{18}N_4S$ $[M+H]^+$: 347.1332; found: 347.1325.

11. NMR spectra of the obtained compounds.

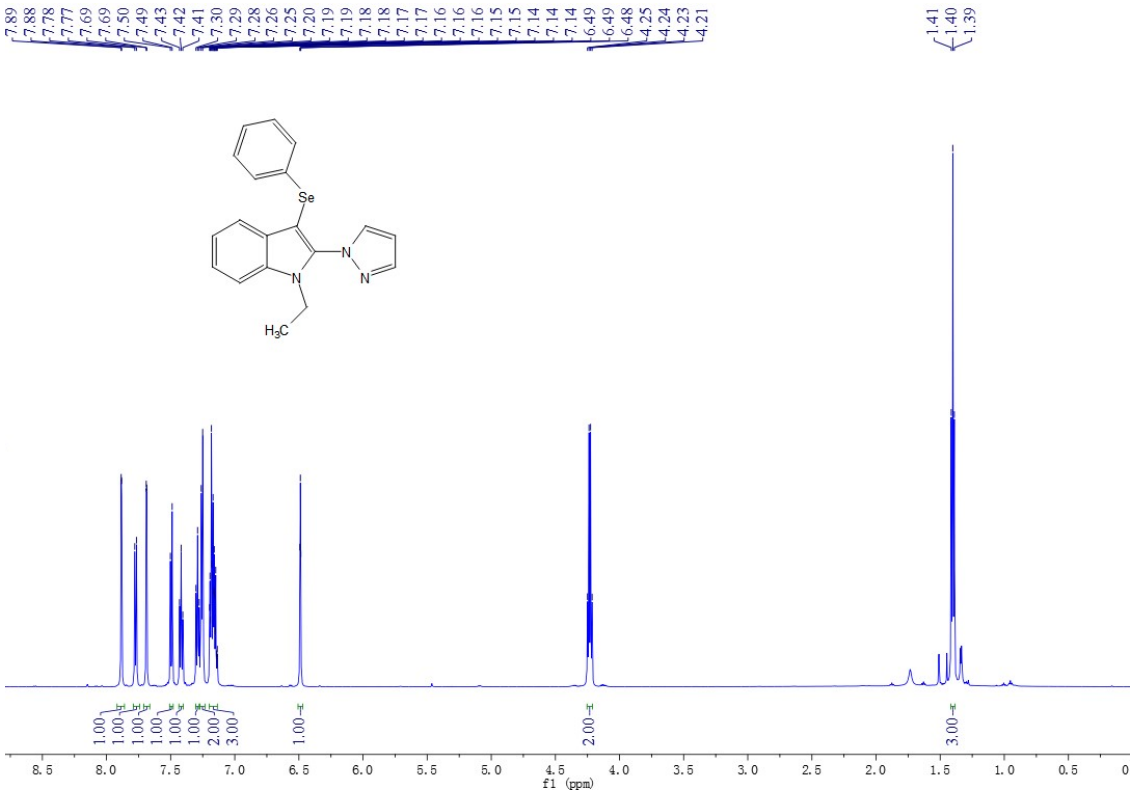
(1) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 4



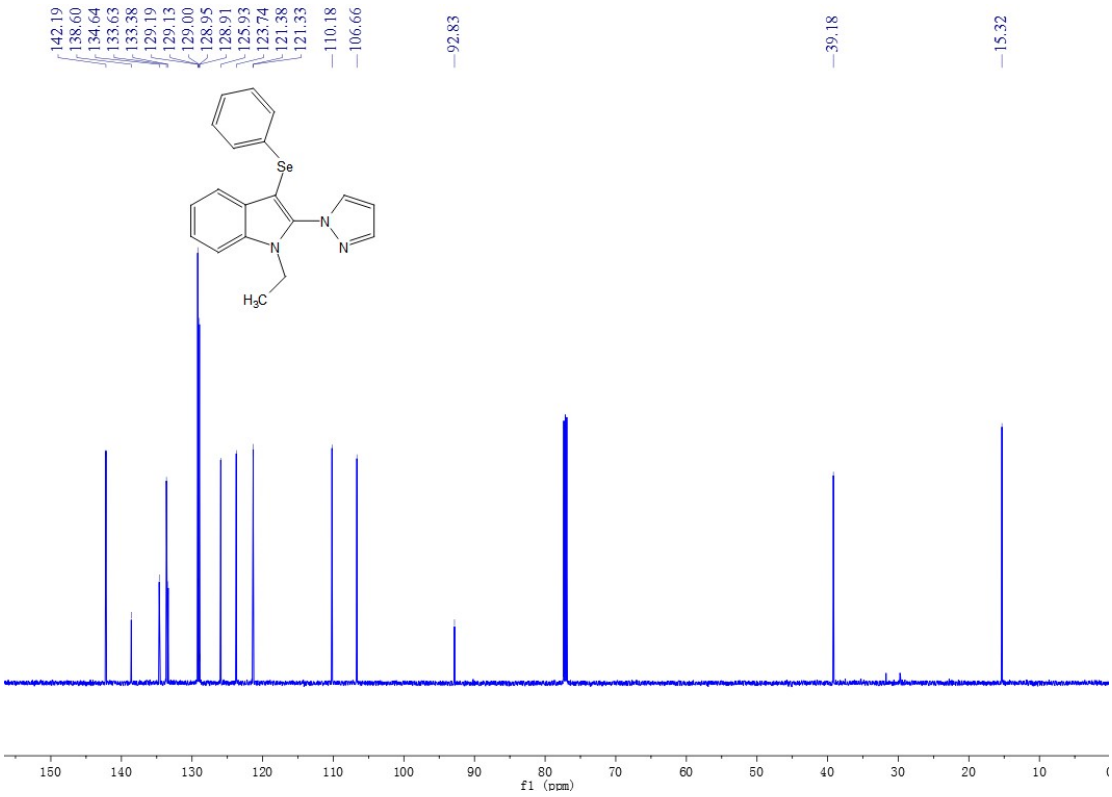
(2) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 4



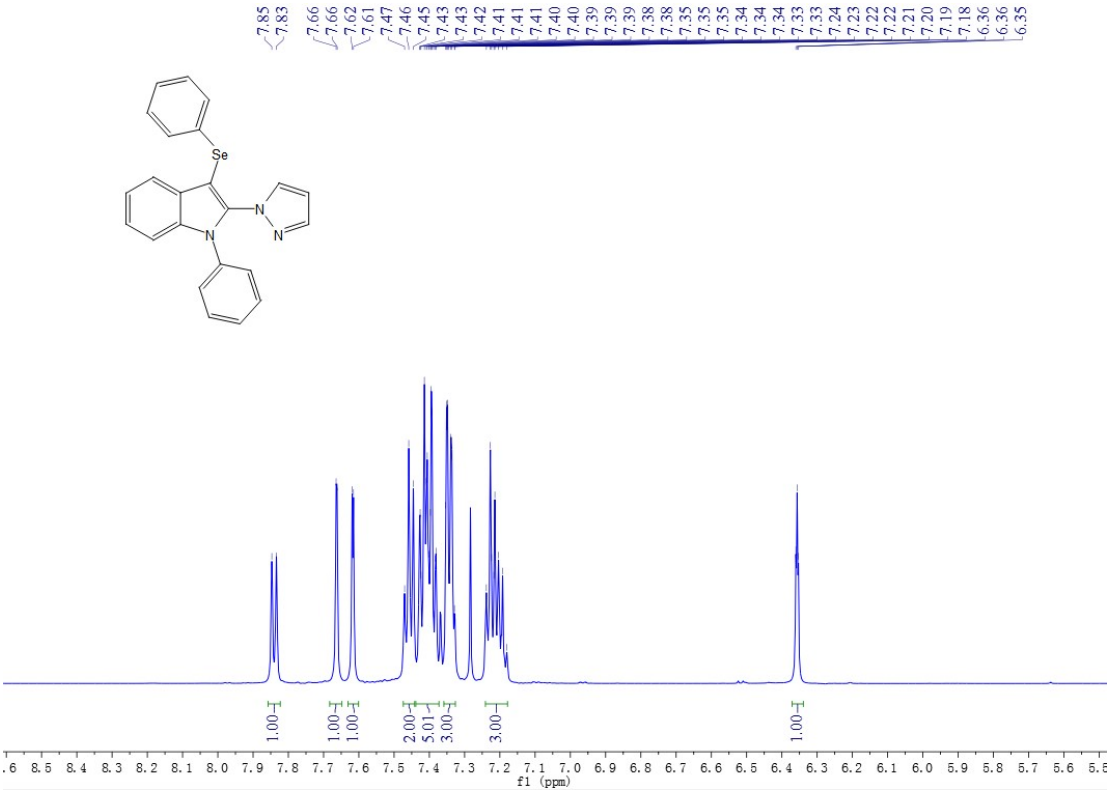
(3) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 5



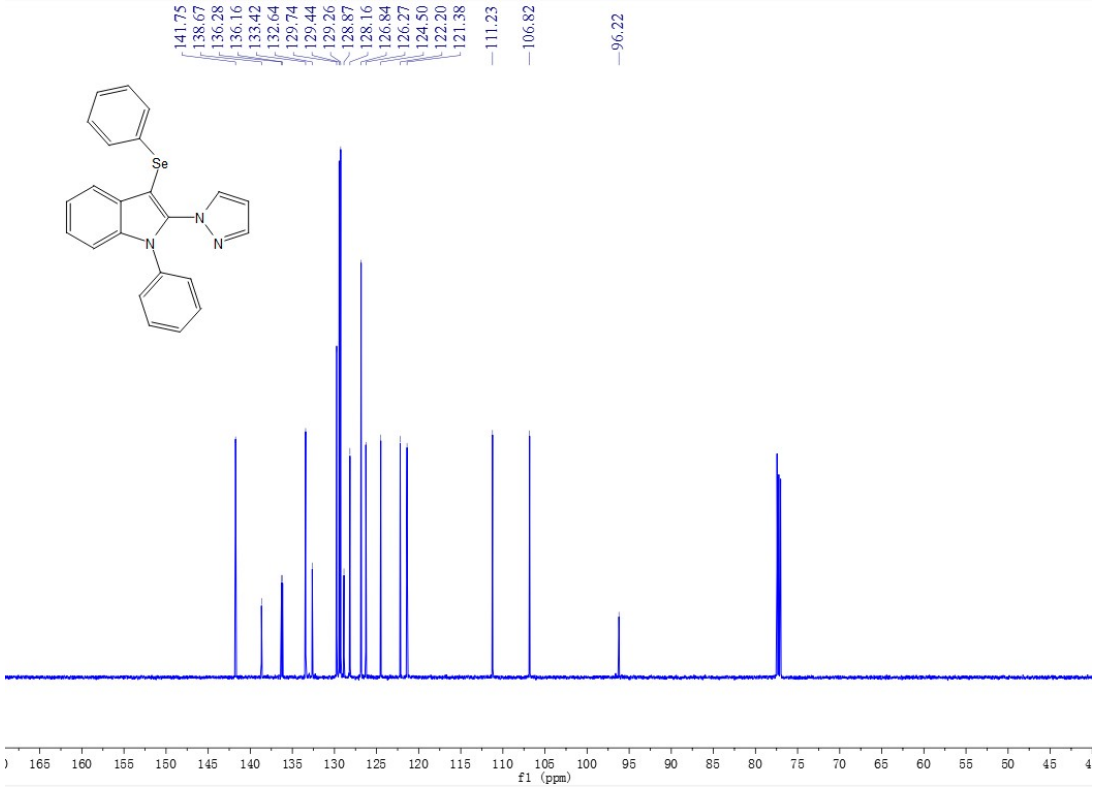
(4) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 5



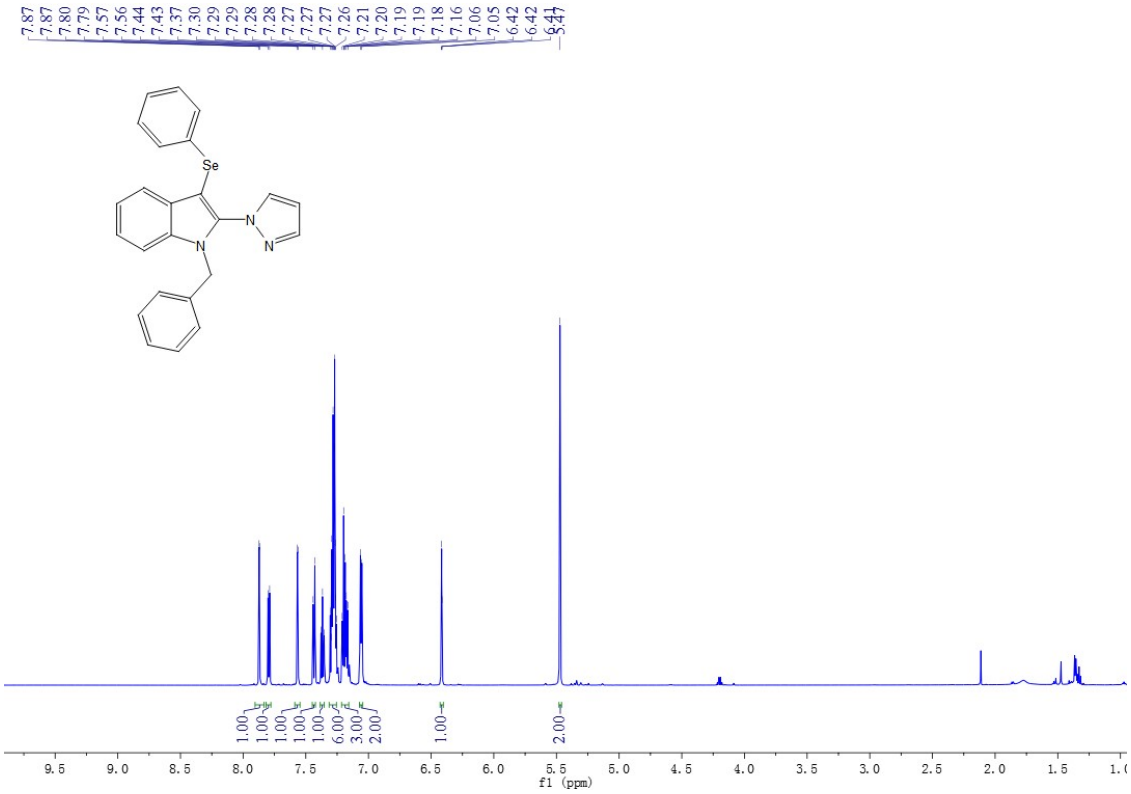
(5) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 6



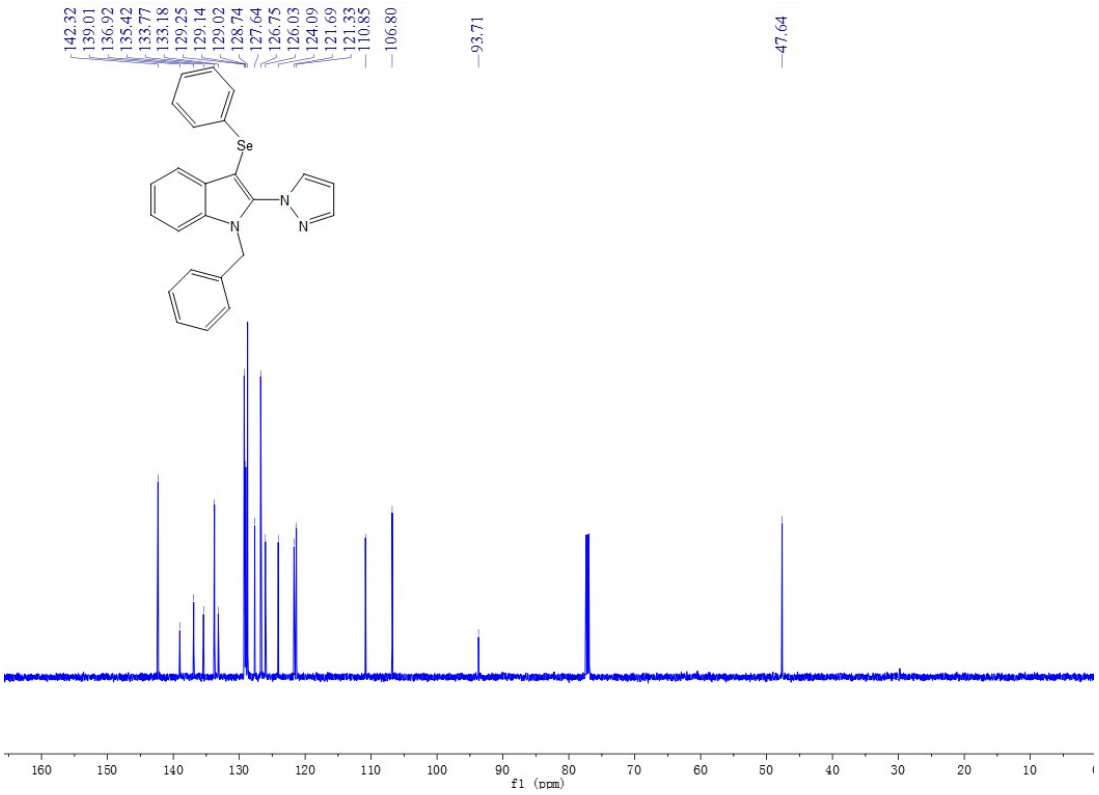
(6) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 6



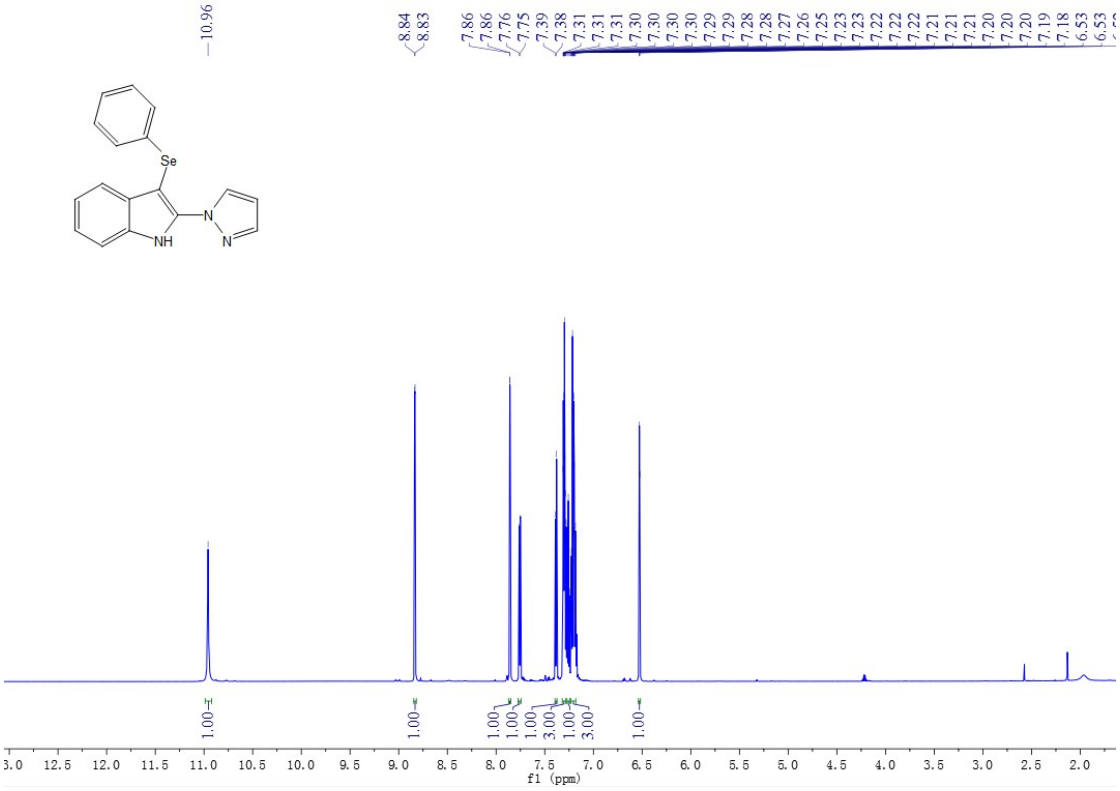
(7) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 7



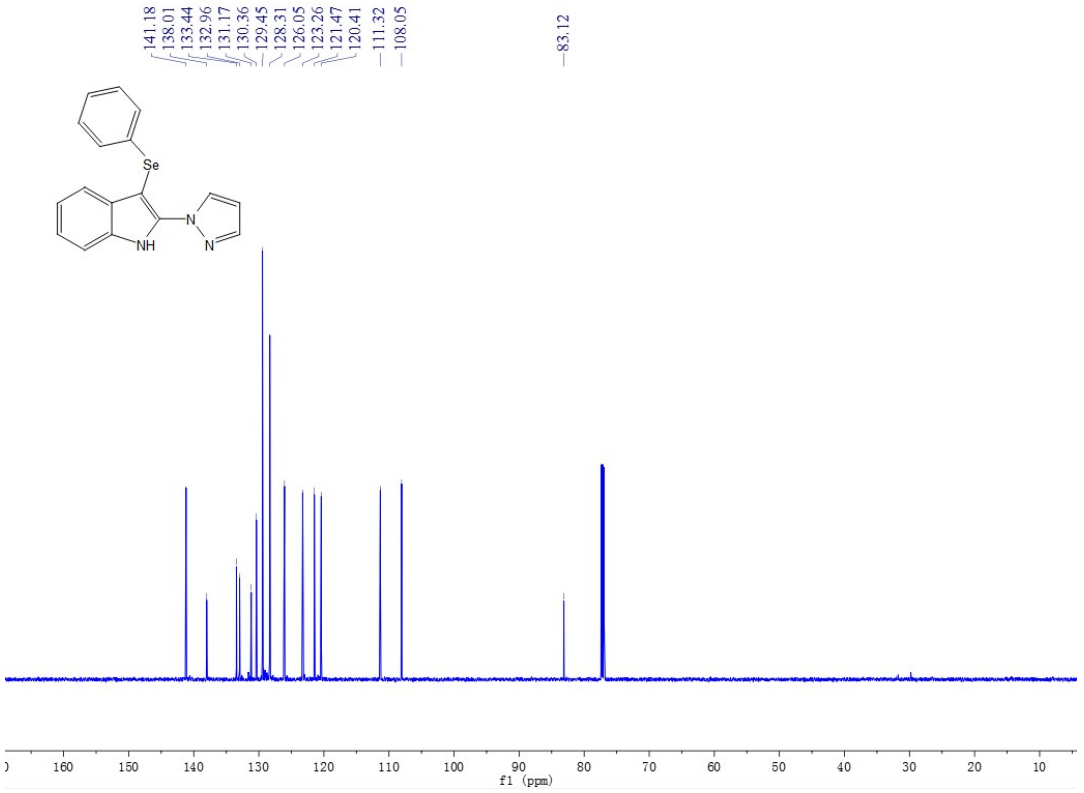
(8) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 7



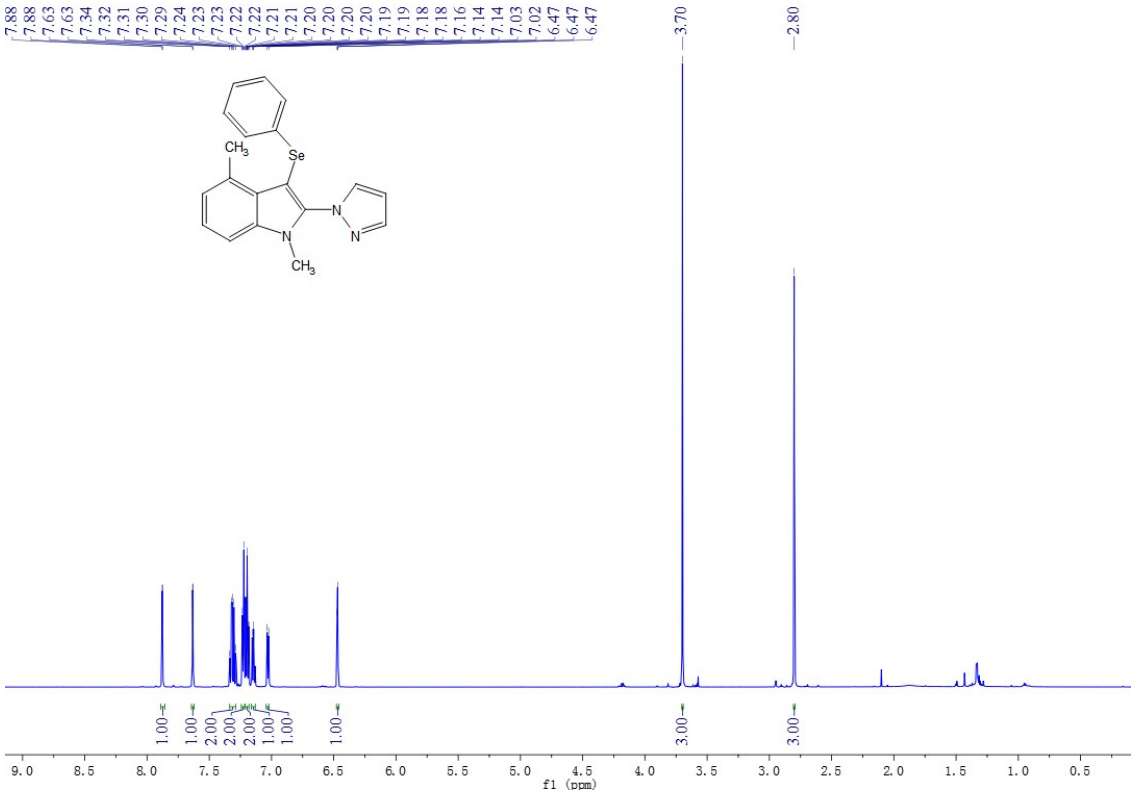
(9) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 9



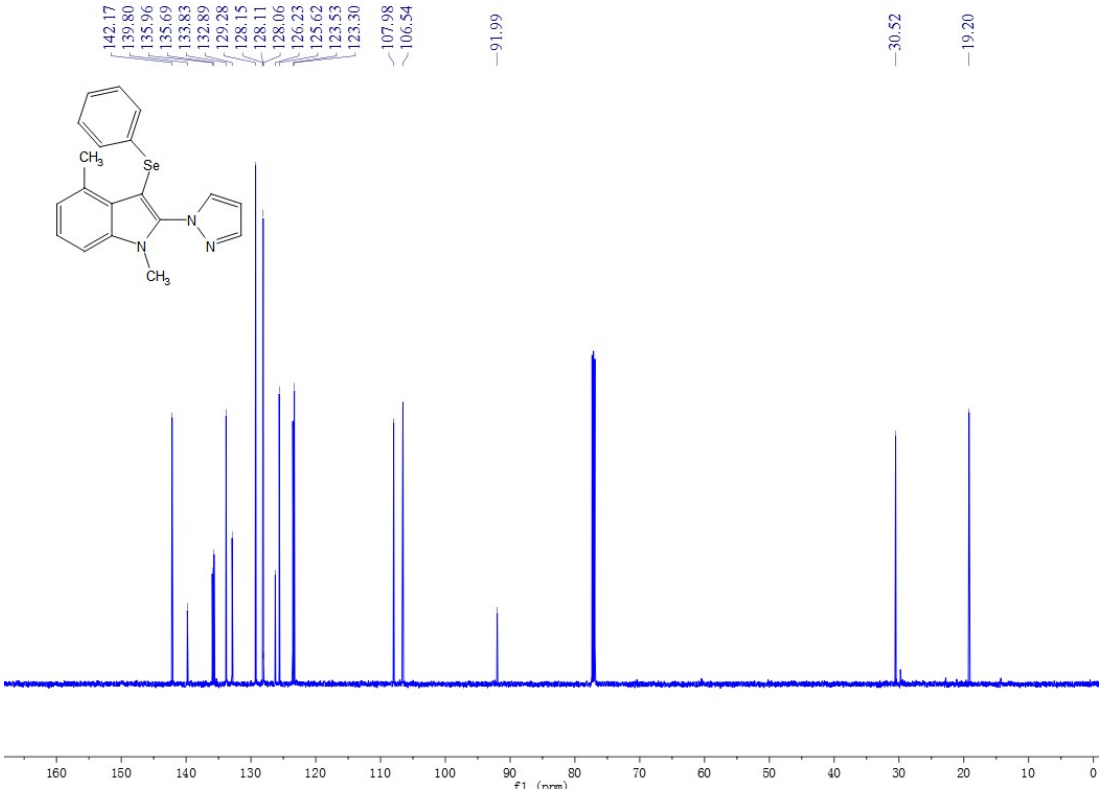
(10) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 9



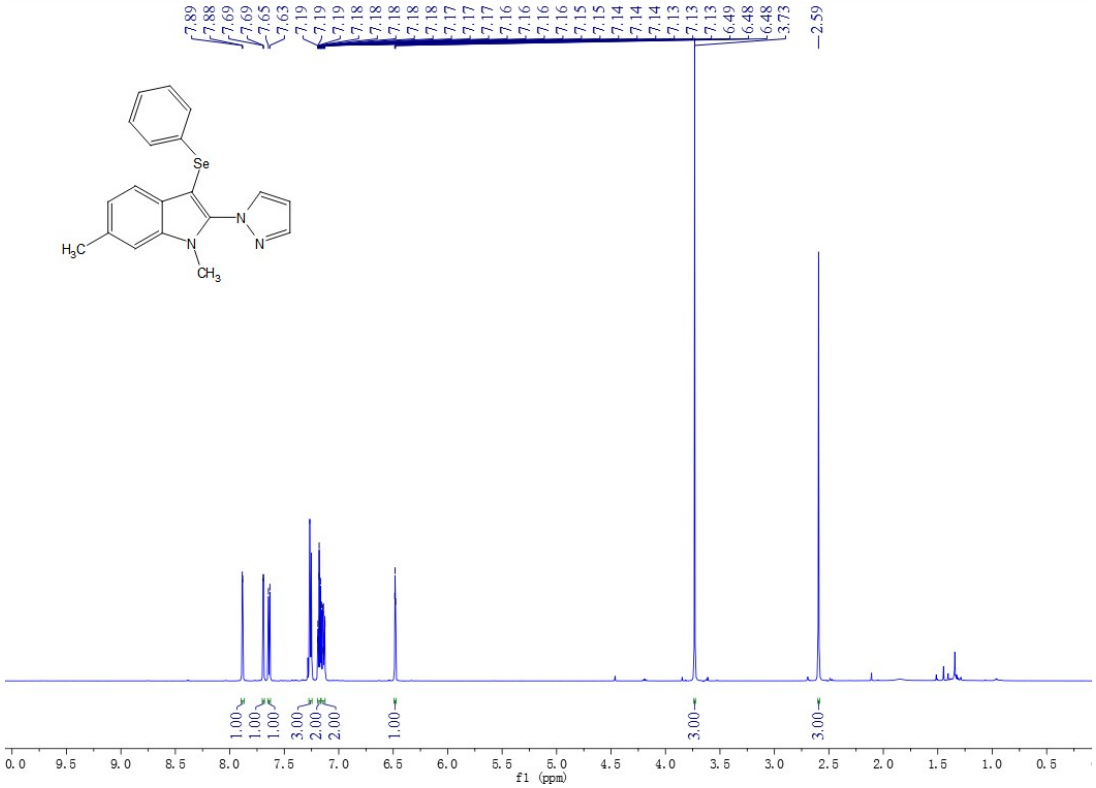
(11) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 10



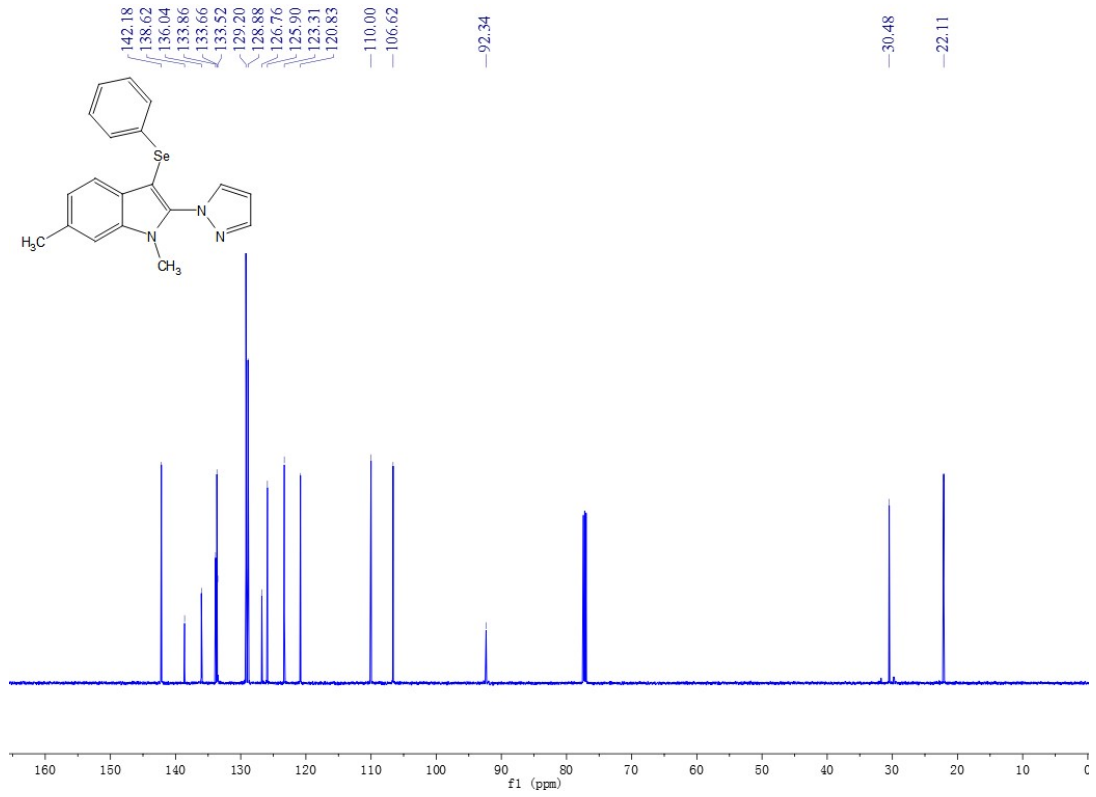
(12) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 10



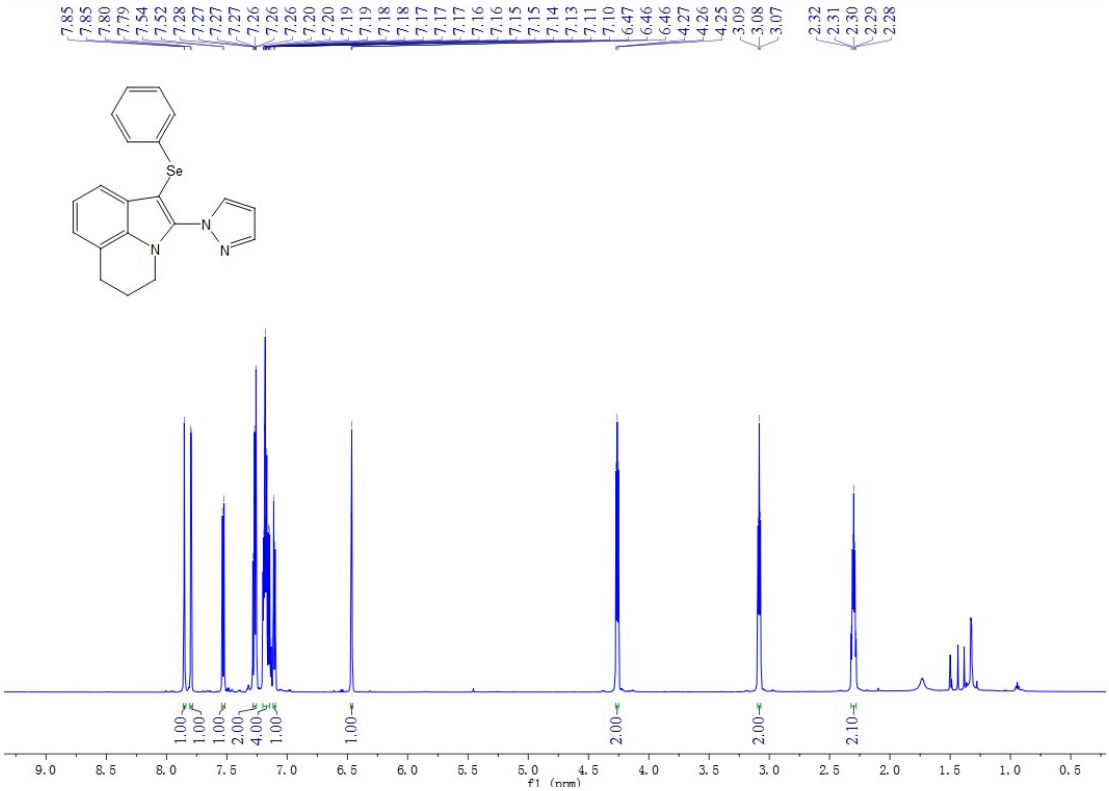
(13) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 11



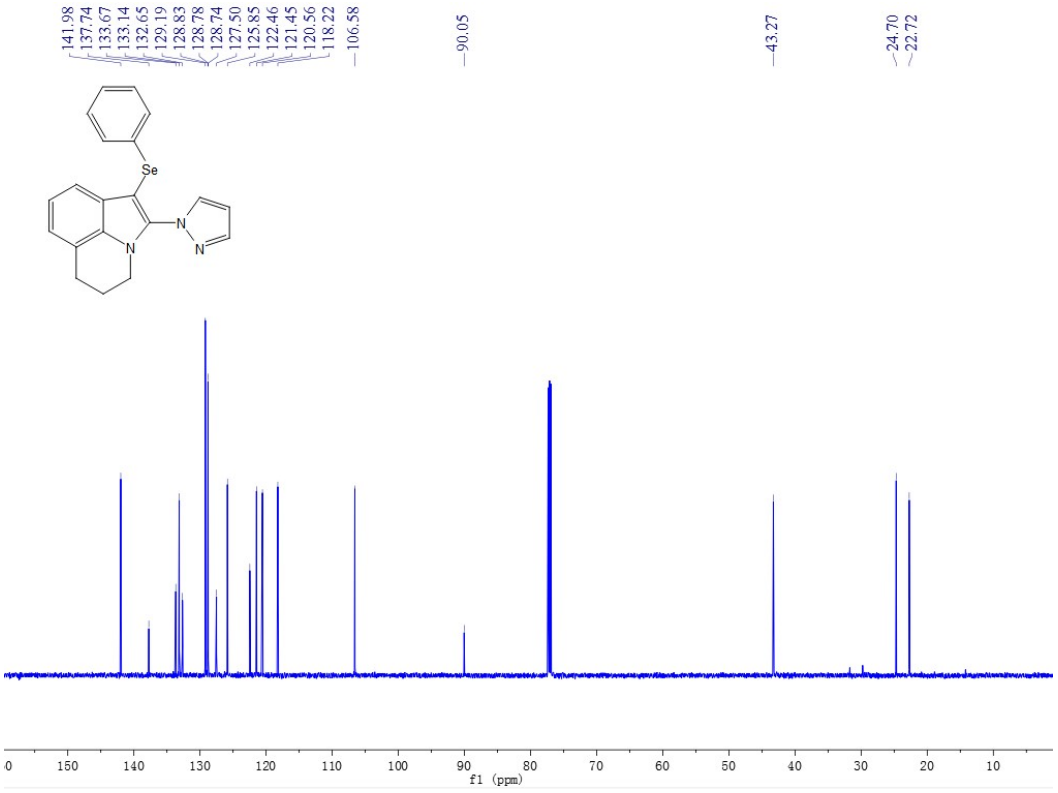
(14) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 11



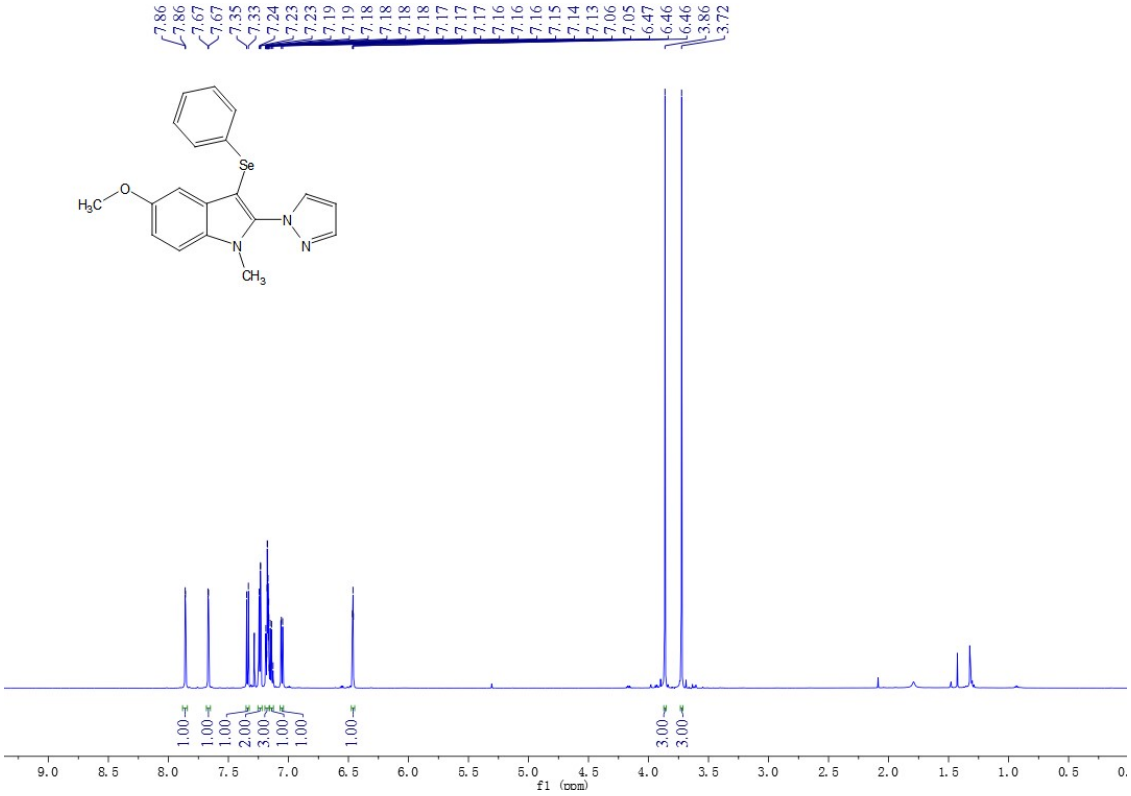
(15) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 12



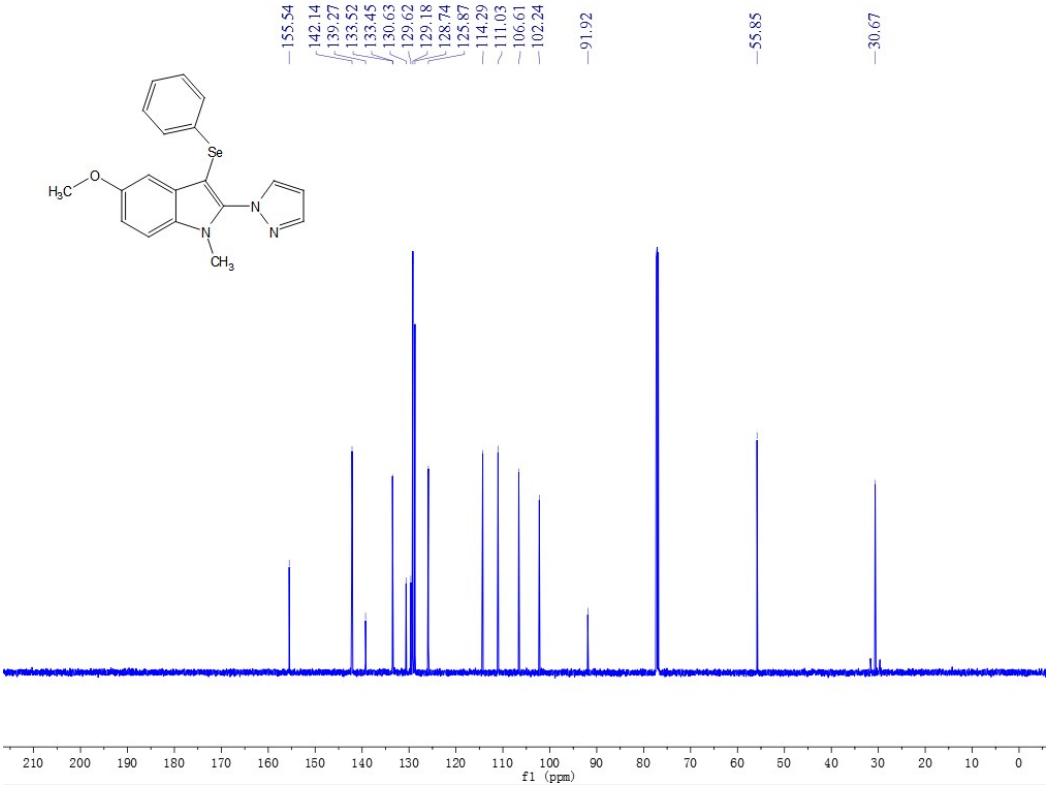
(16) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum o12



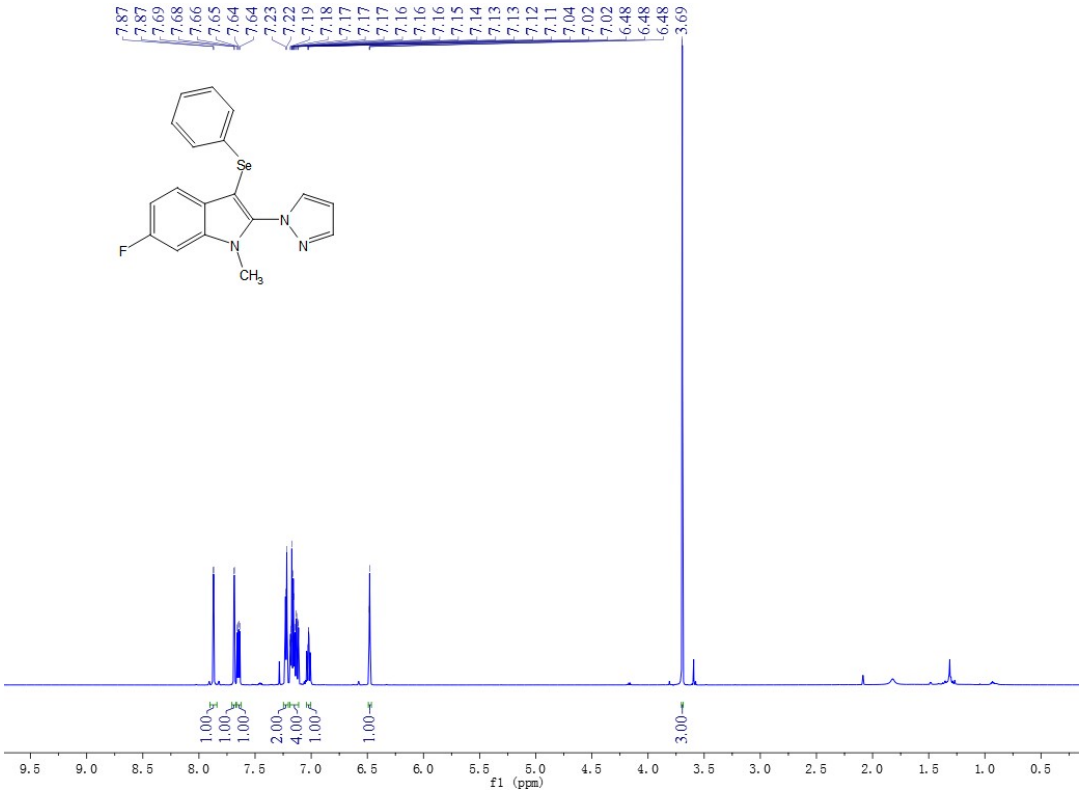
(17) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 13



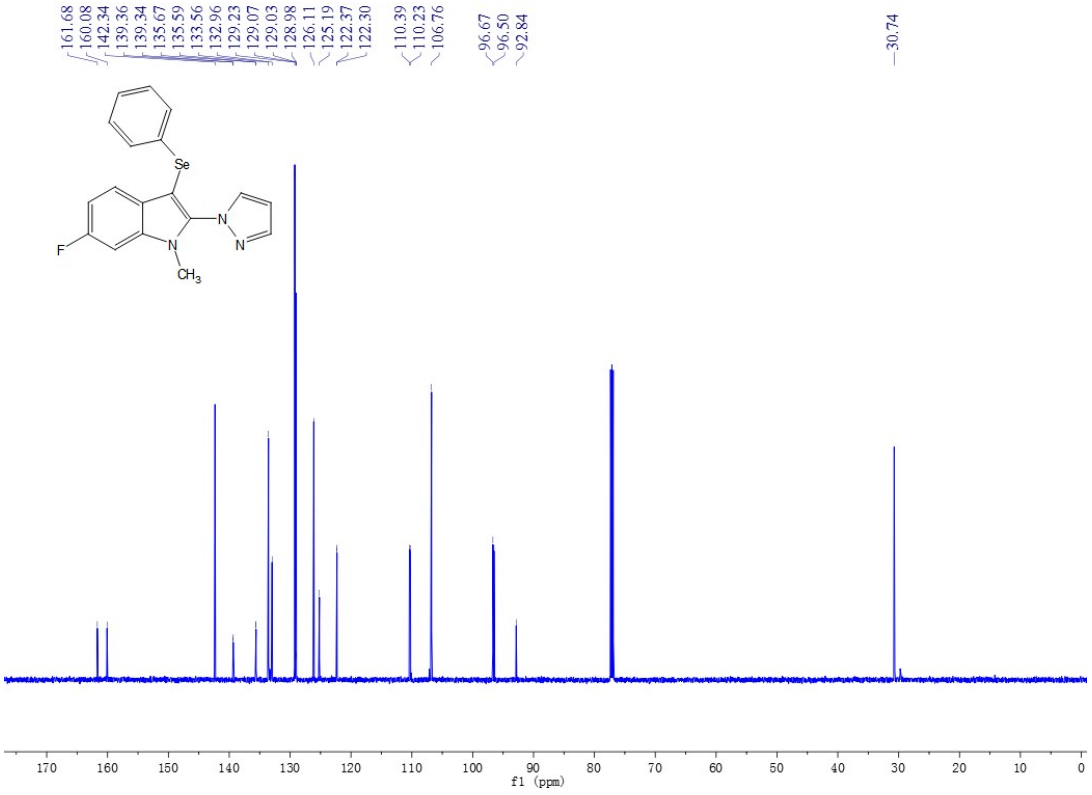
(18) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 13



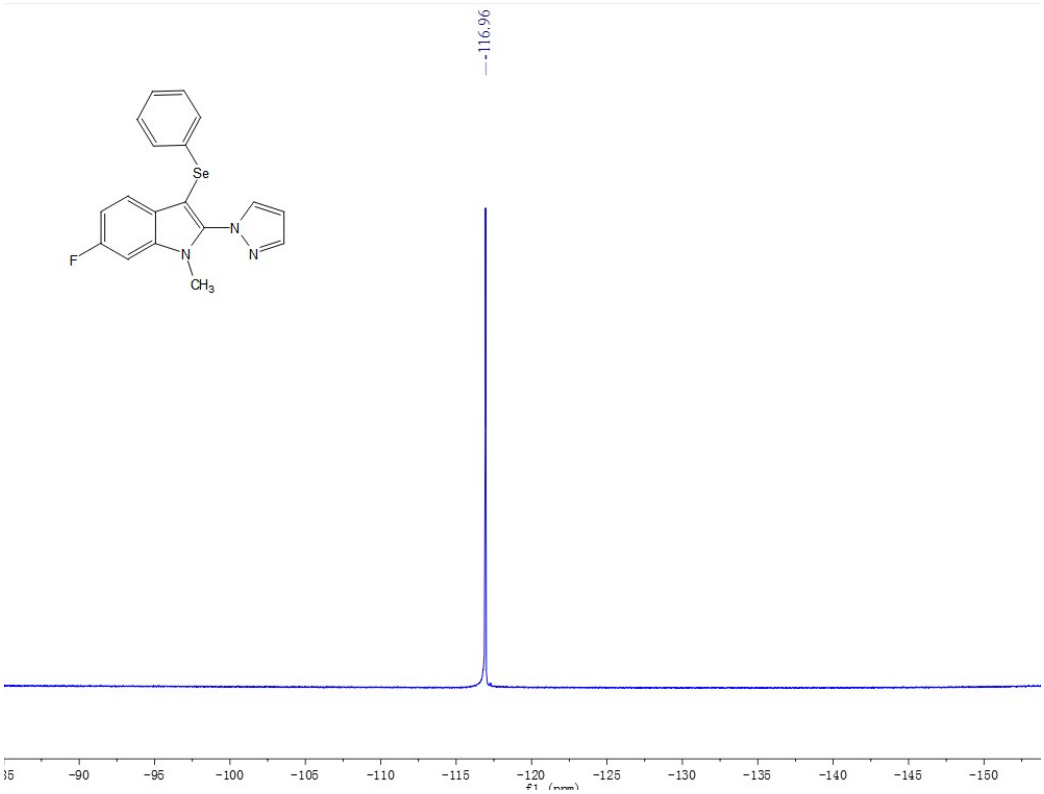
(19) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 14



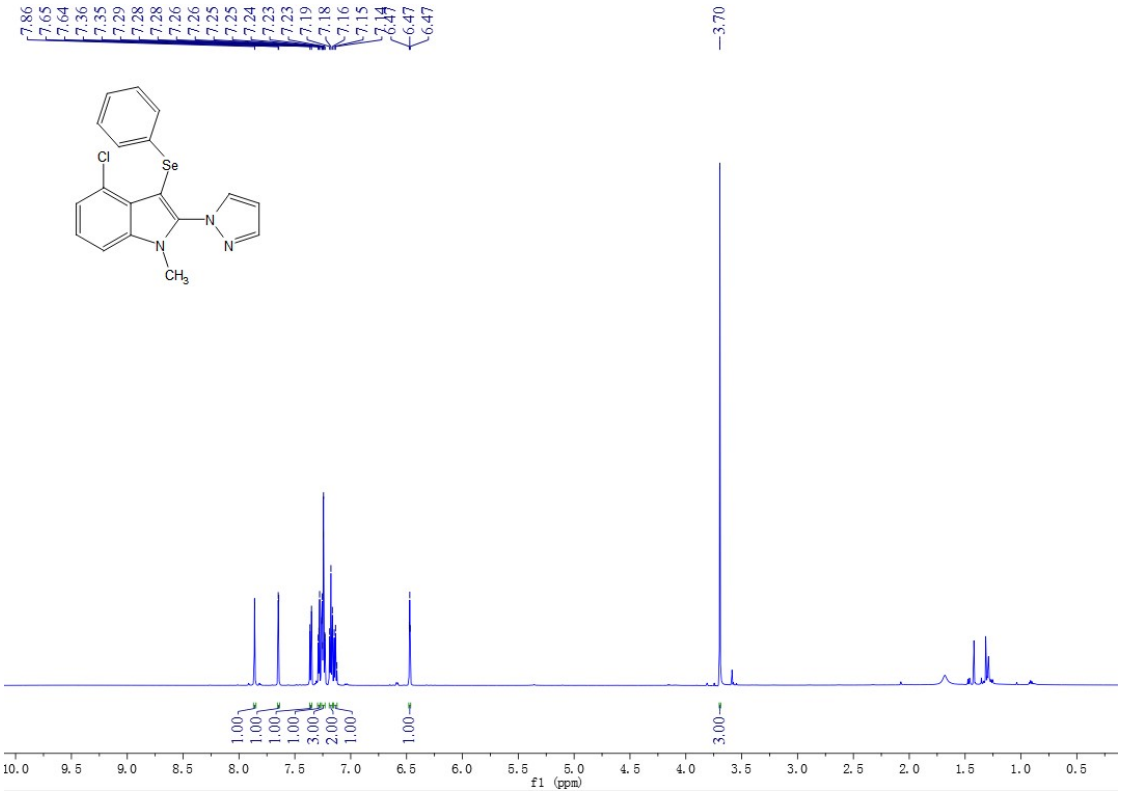
(20) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 14



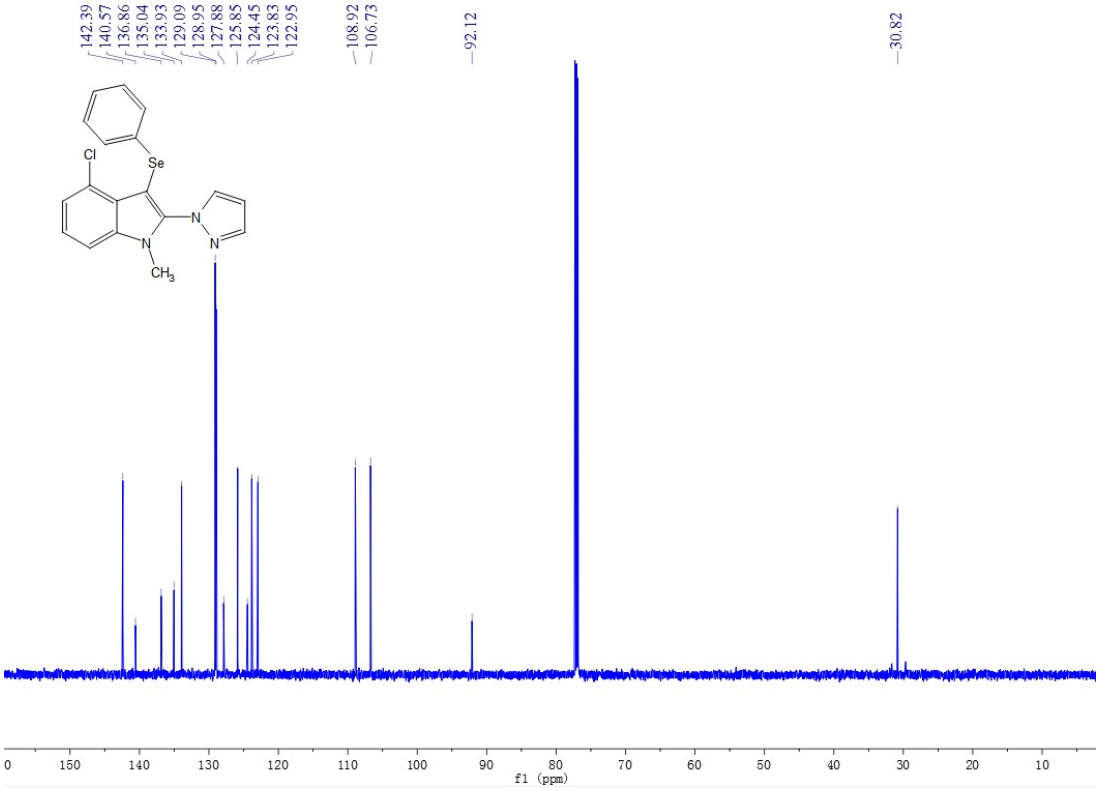
(21) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 14



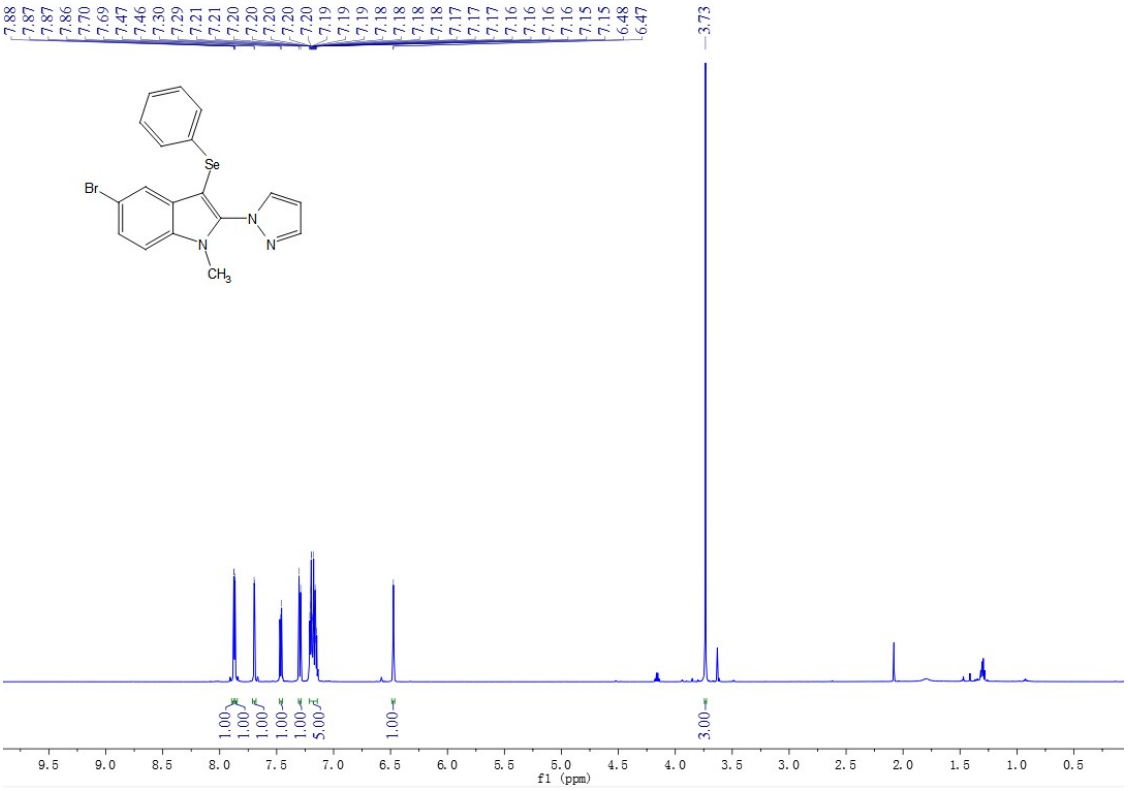
(22) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 15



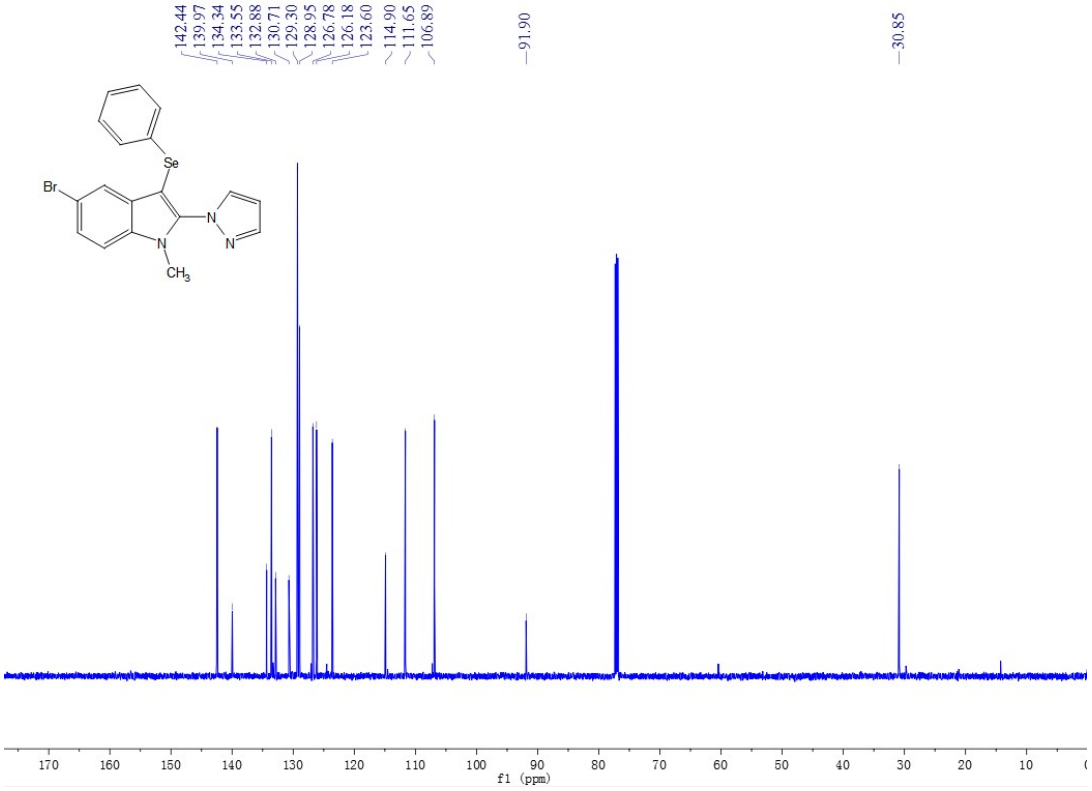
(23) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 15



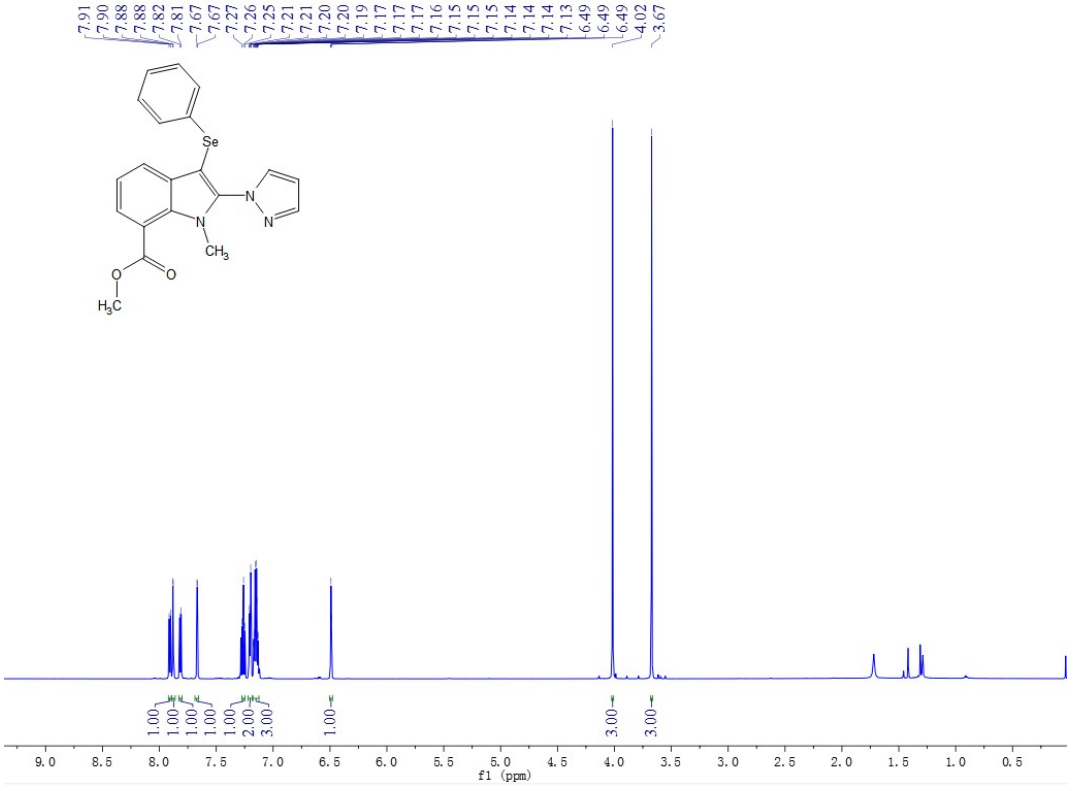
(24) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 16



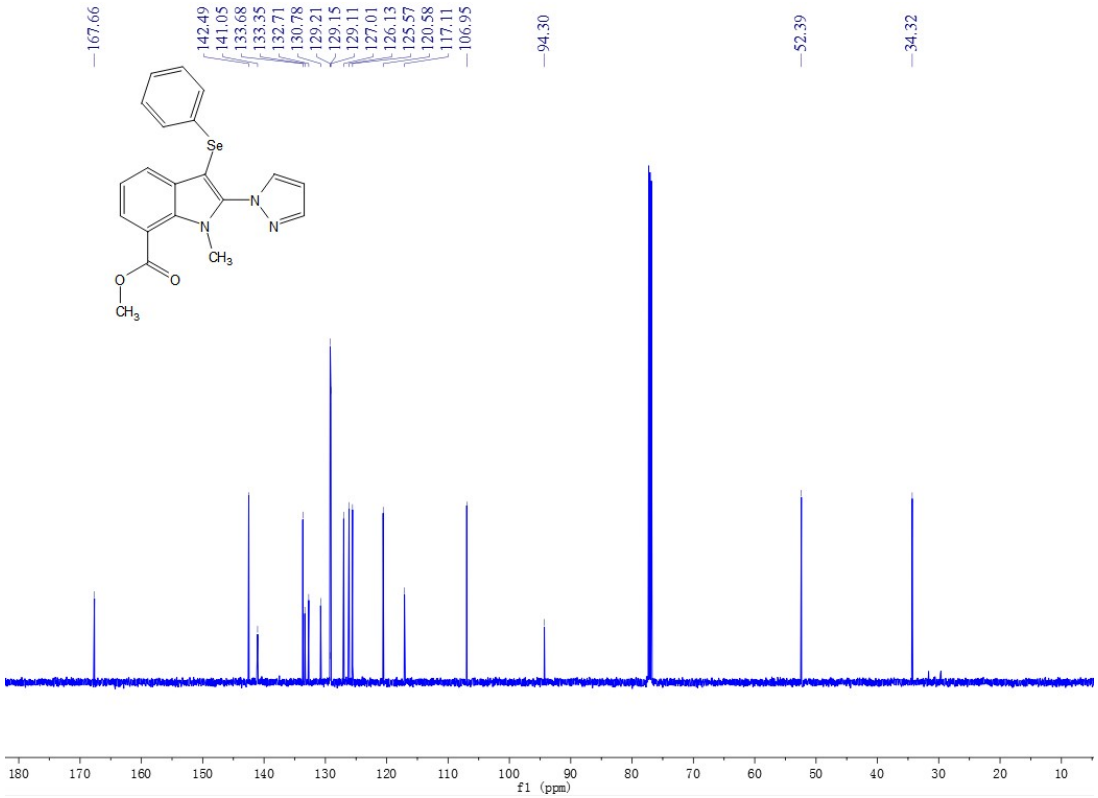
(25) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 16



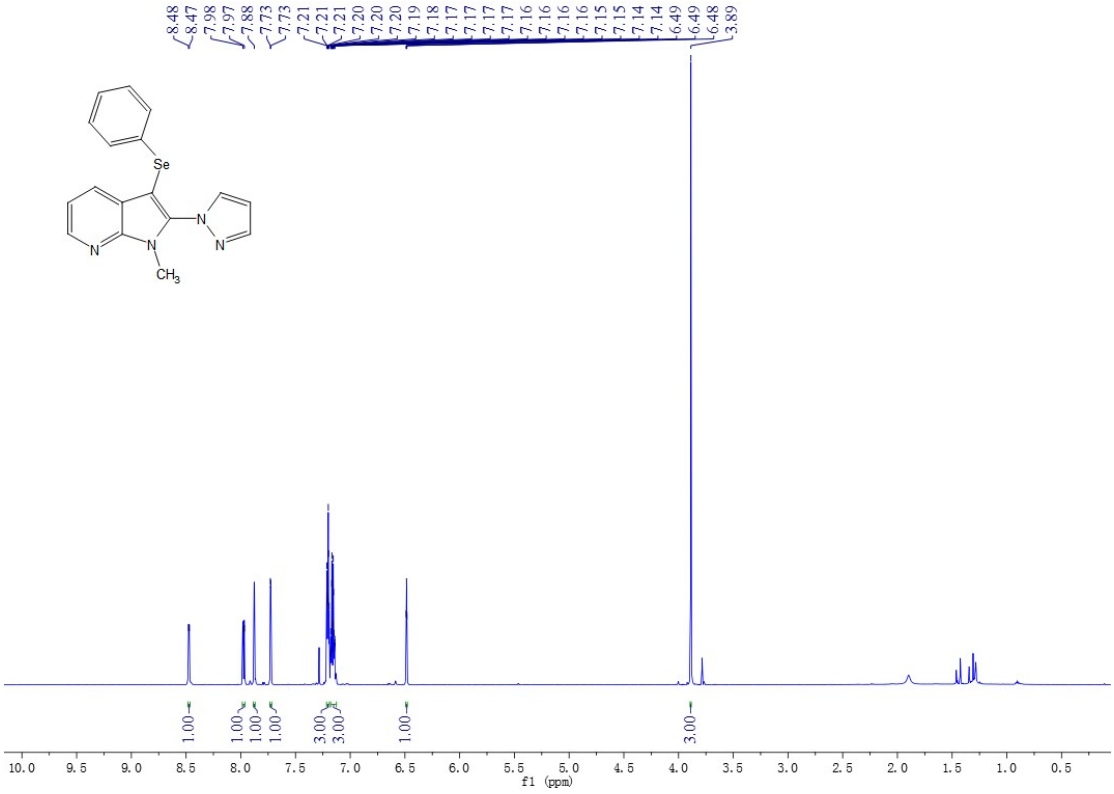
(26) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 17



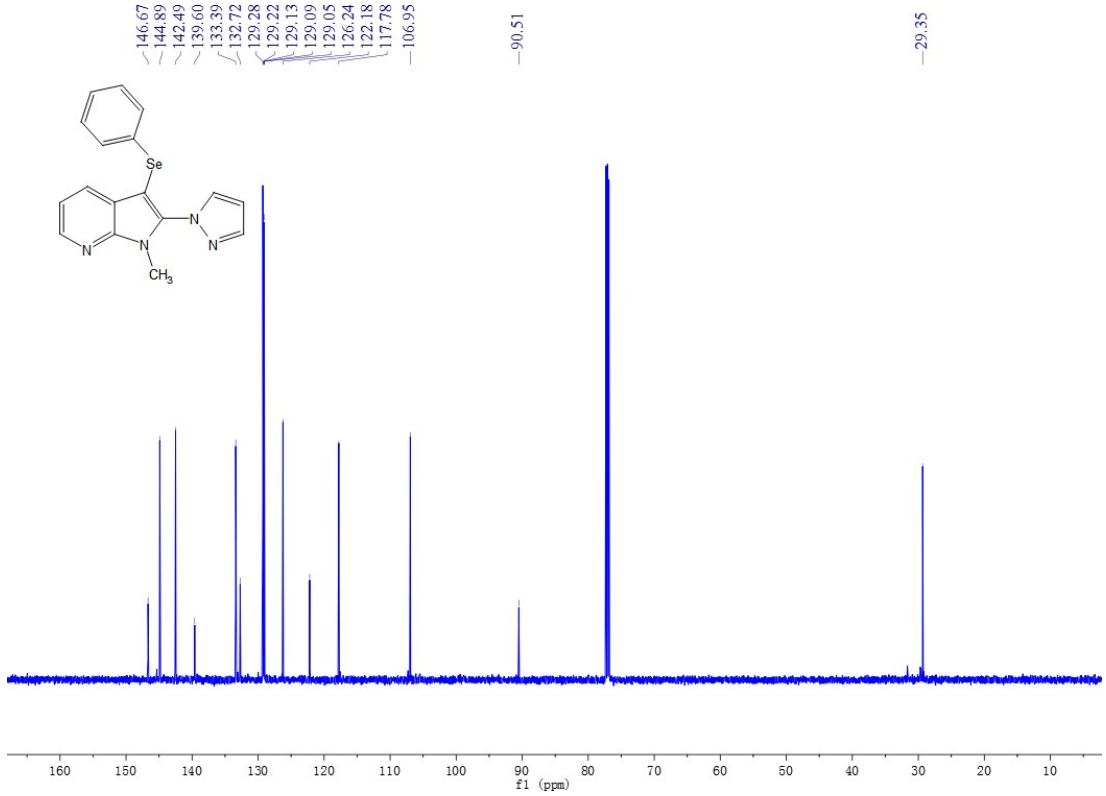
(27) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 17



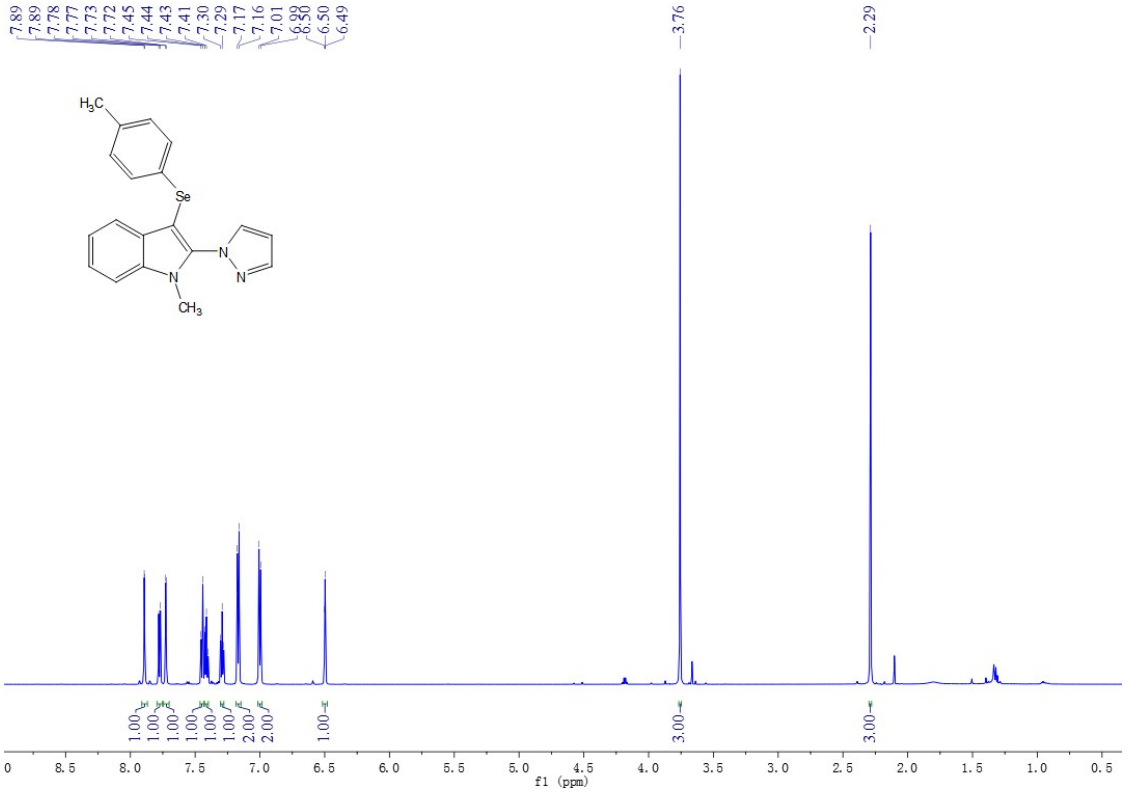
(28) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 18



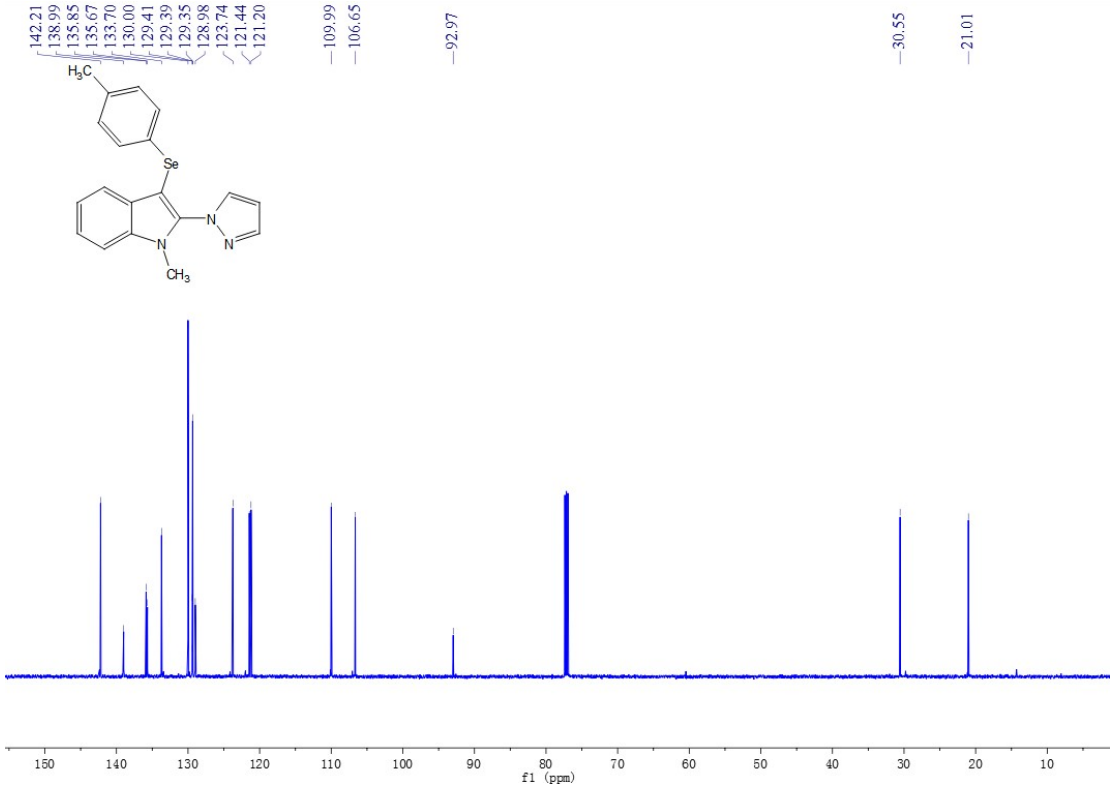
(29) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 18



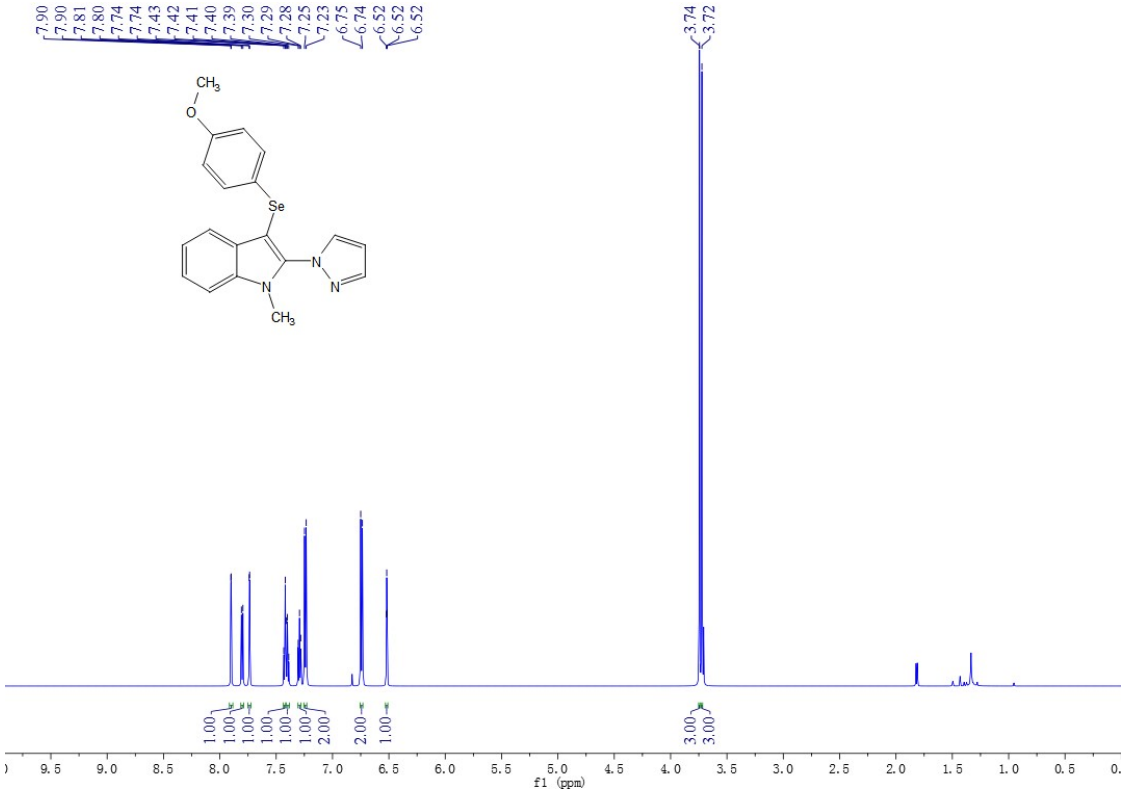
(30) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 19



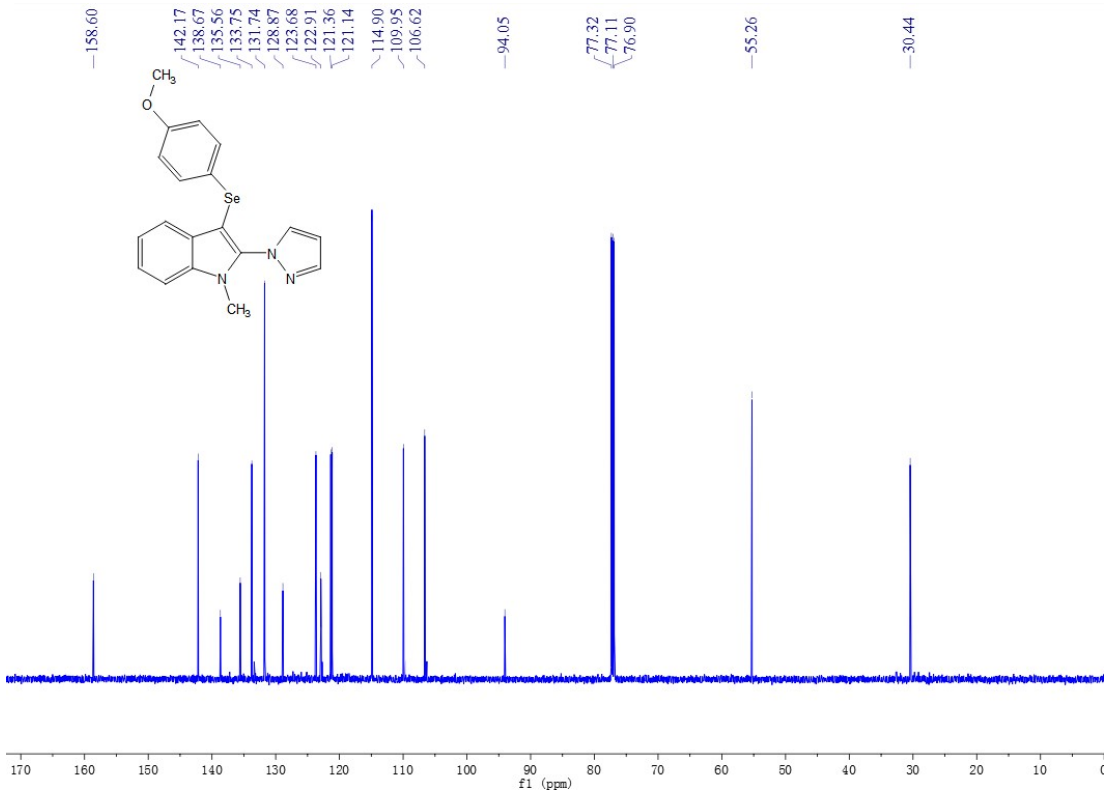
(31) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 19



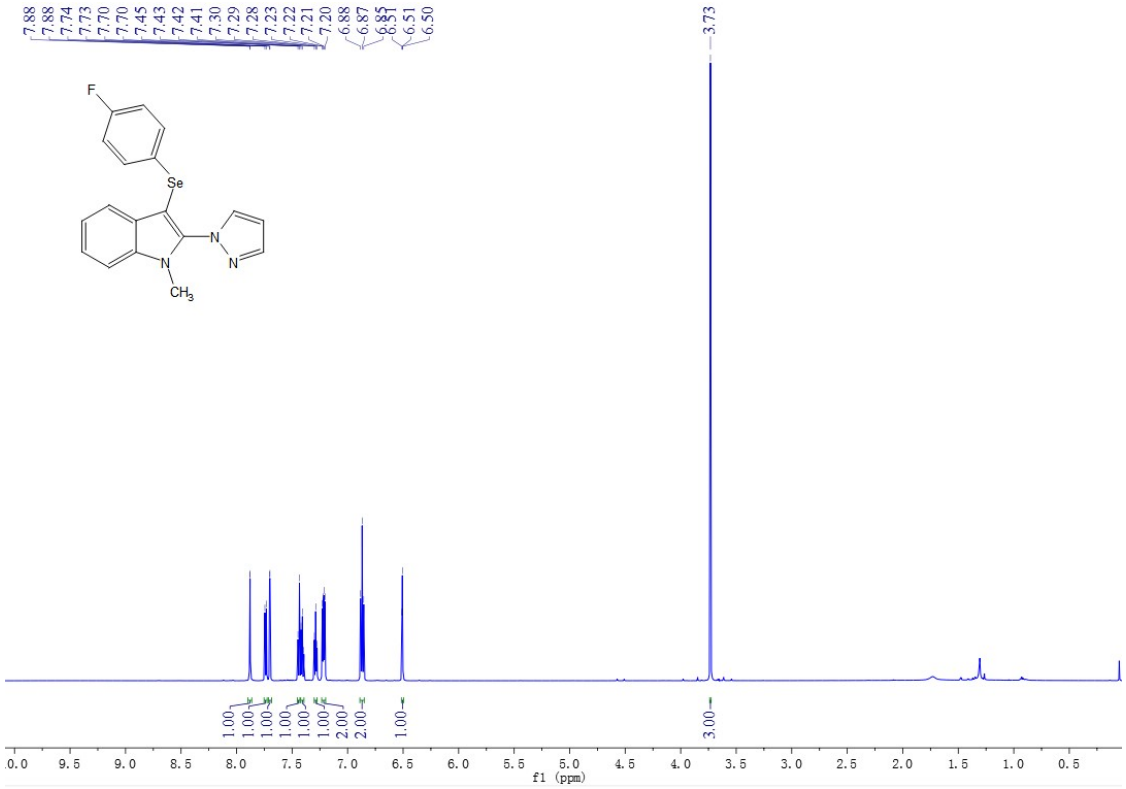
(32) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 20



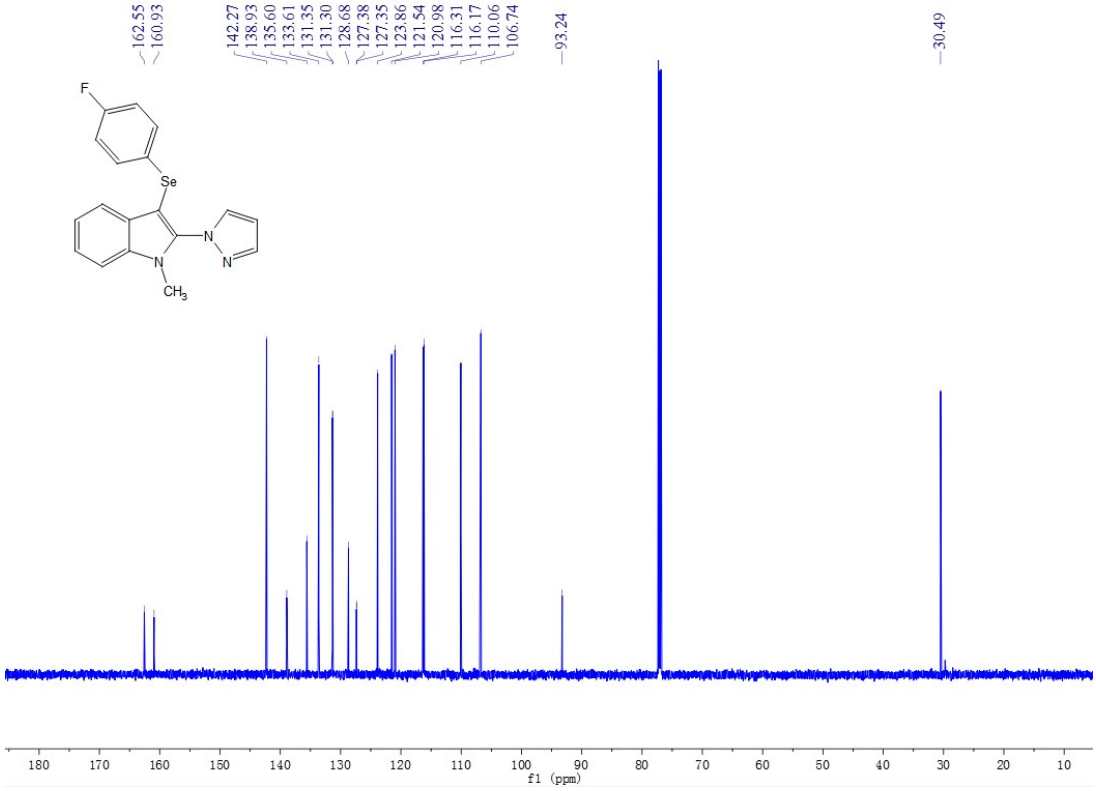
(33) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 20



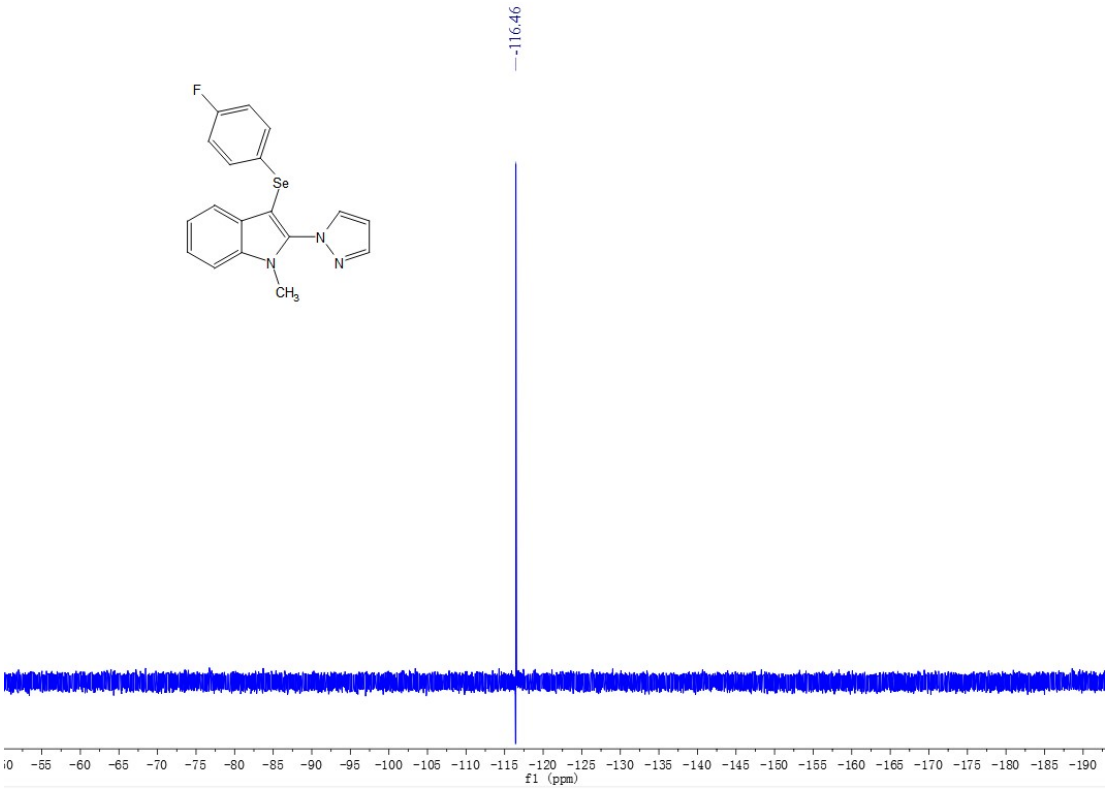
(34) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 21



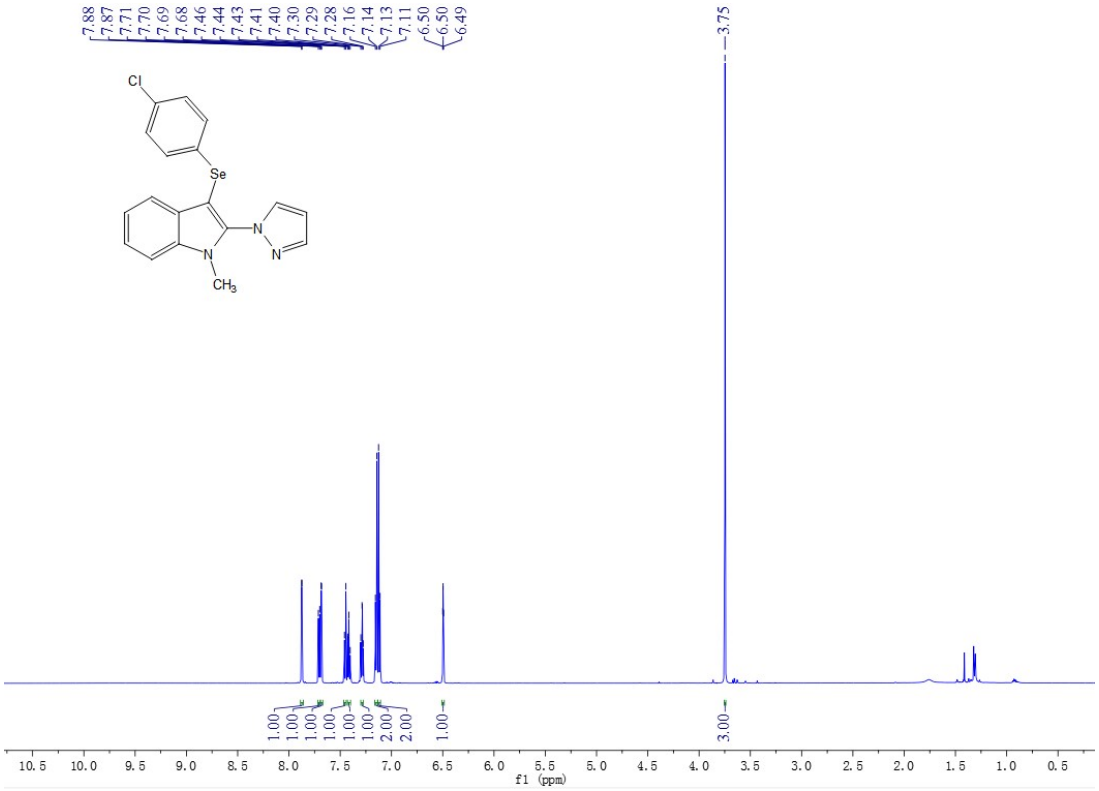
(35) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 21



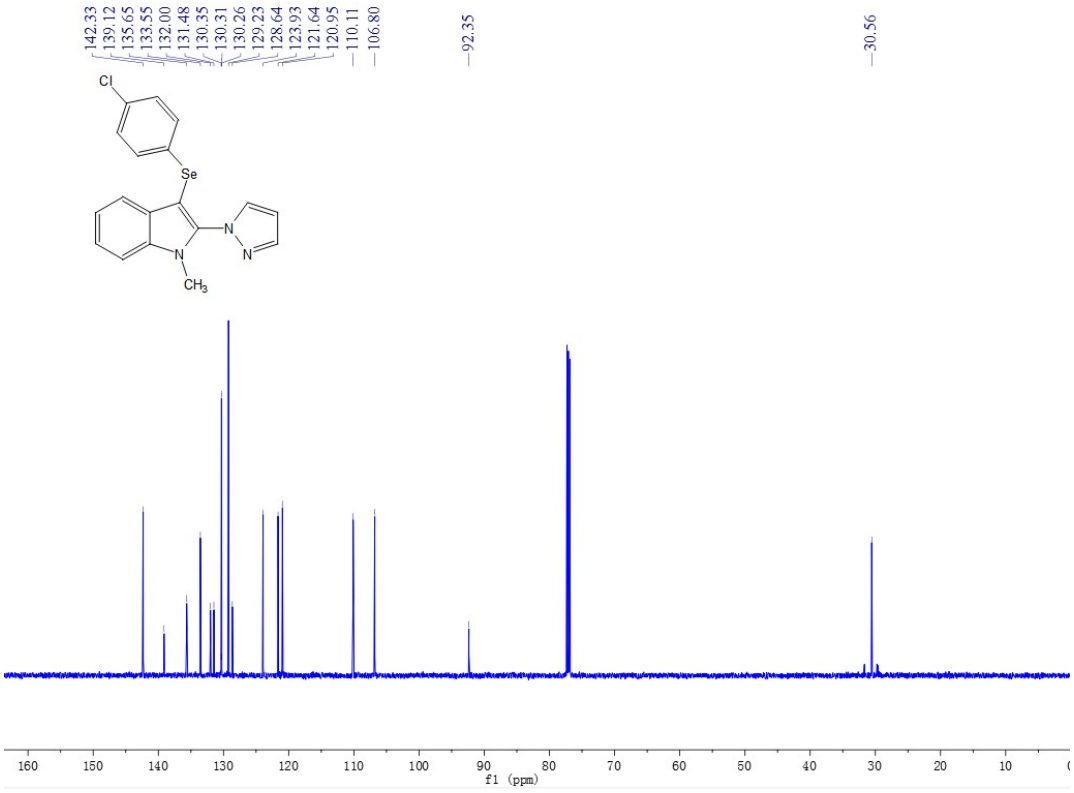
(36) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 21



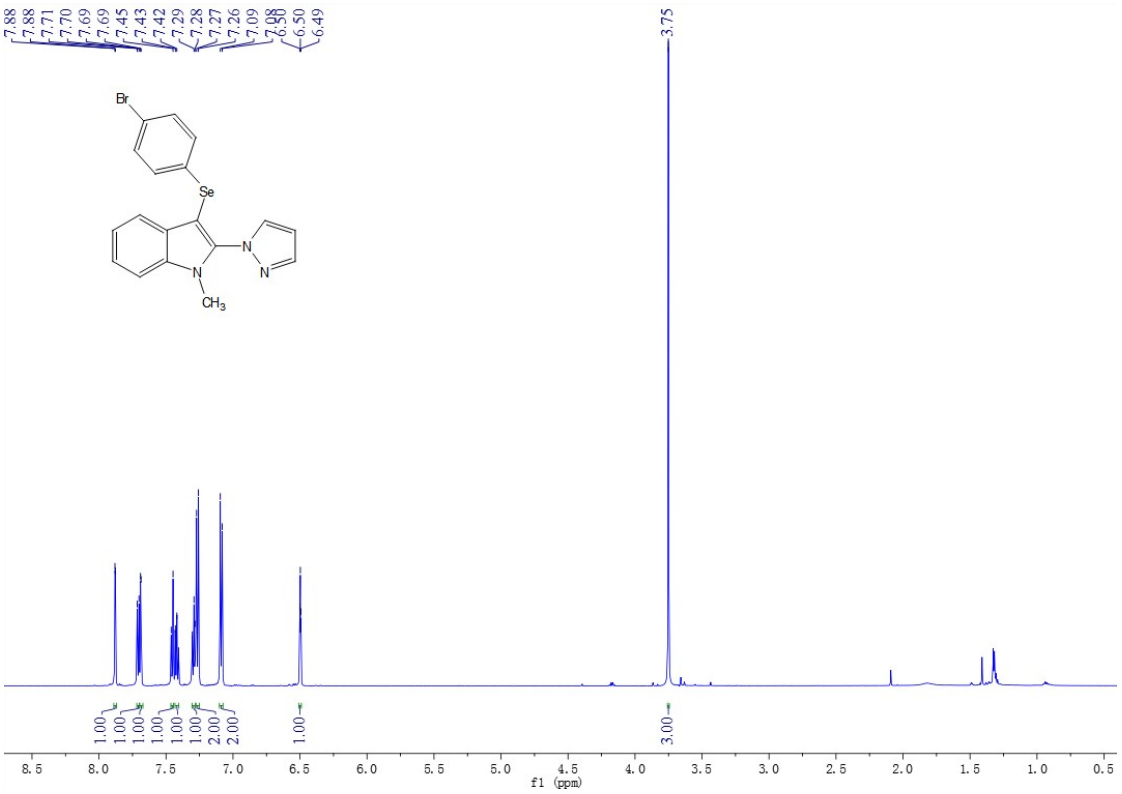
(37) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 22



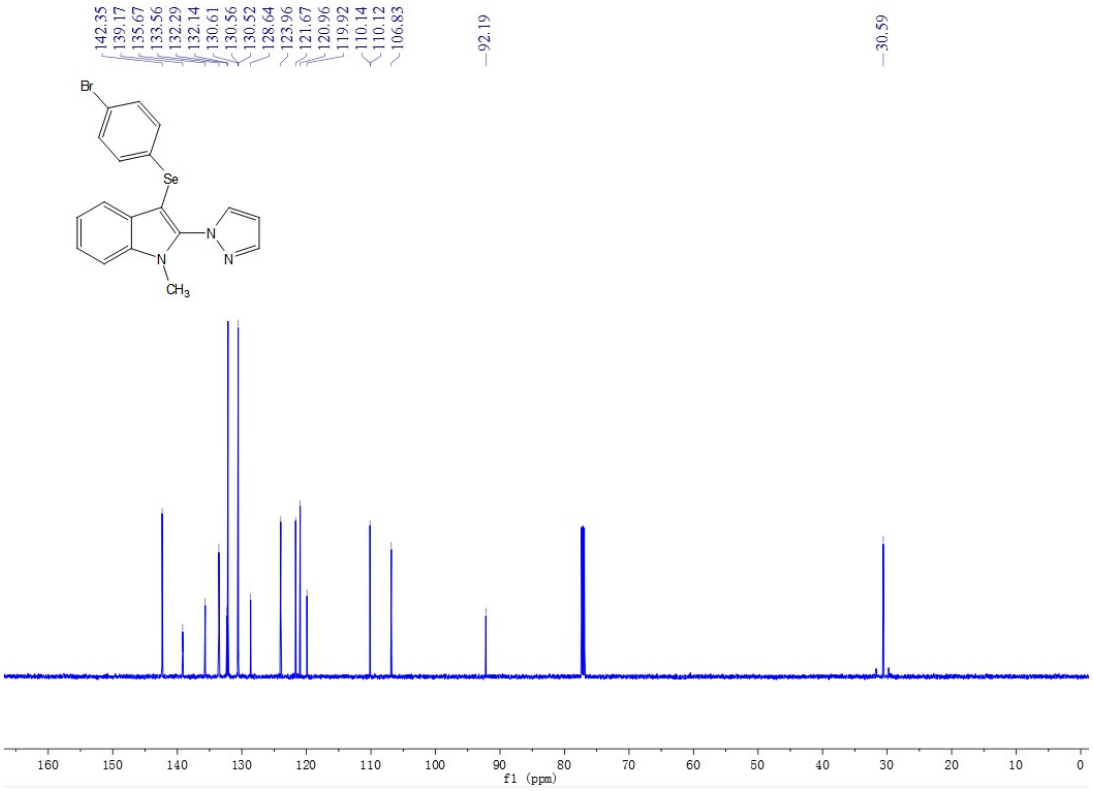
(38) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 22



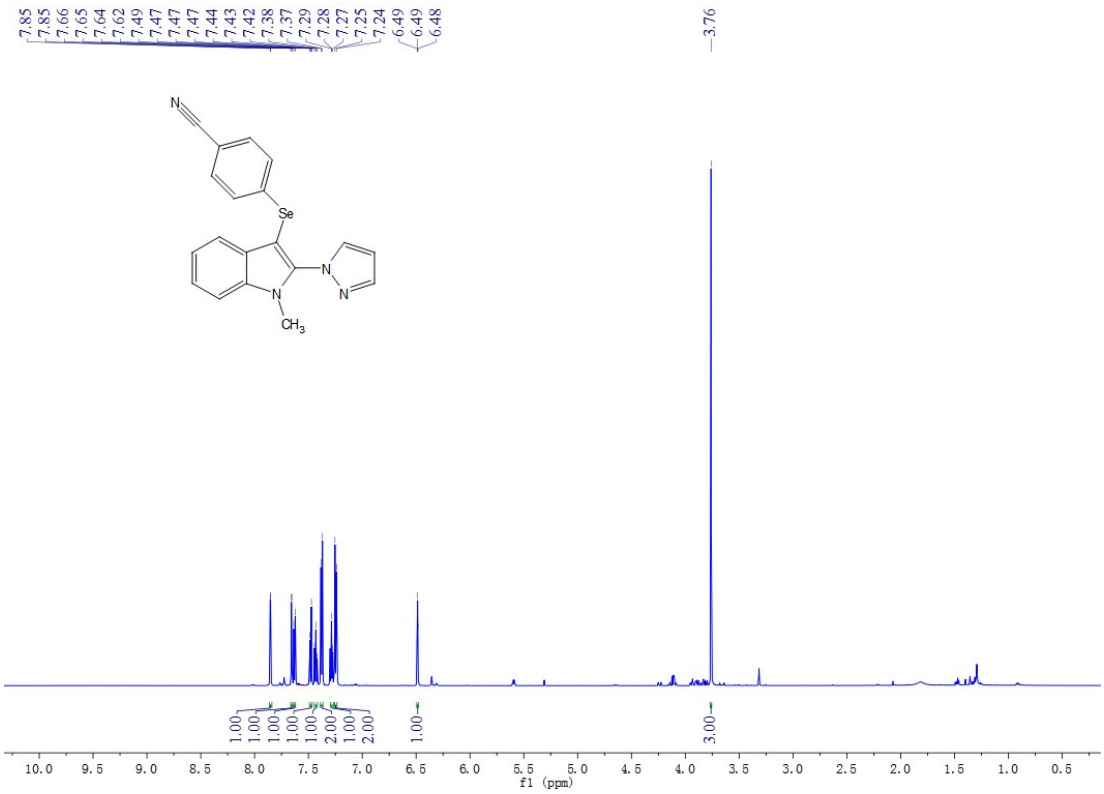
(39) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 23



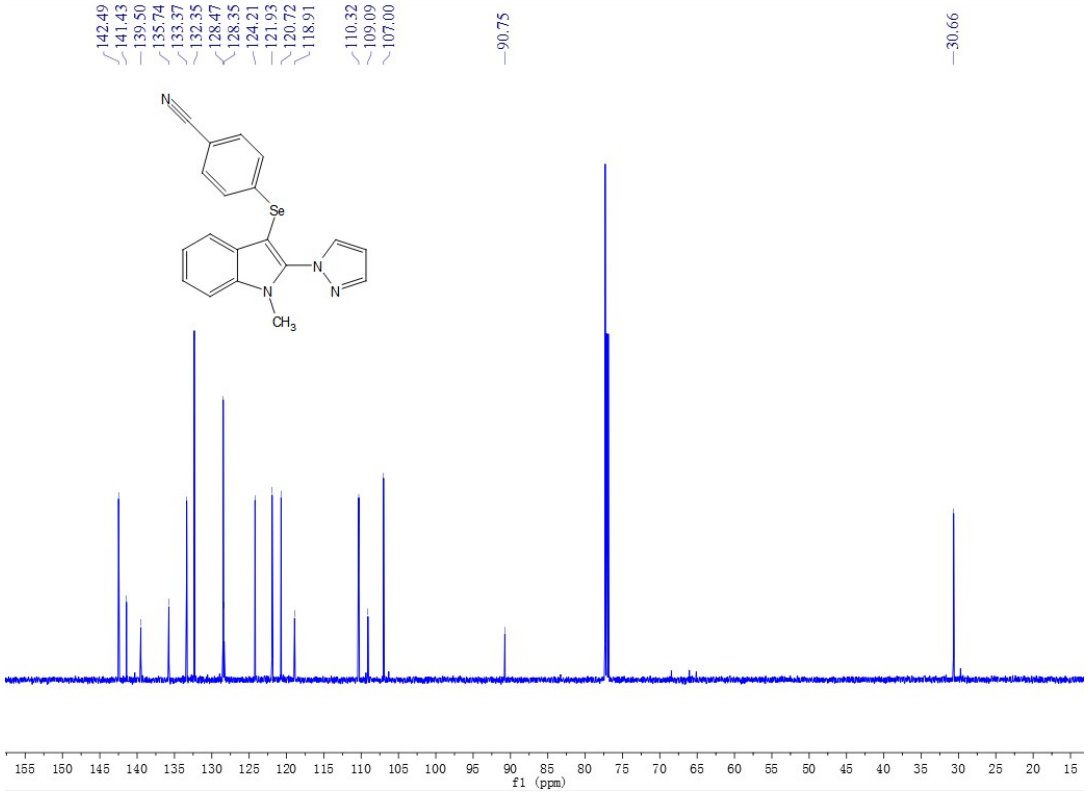
(40) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 23



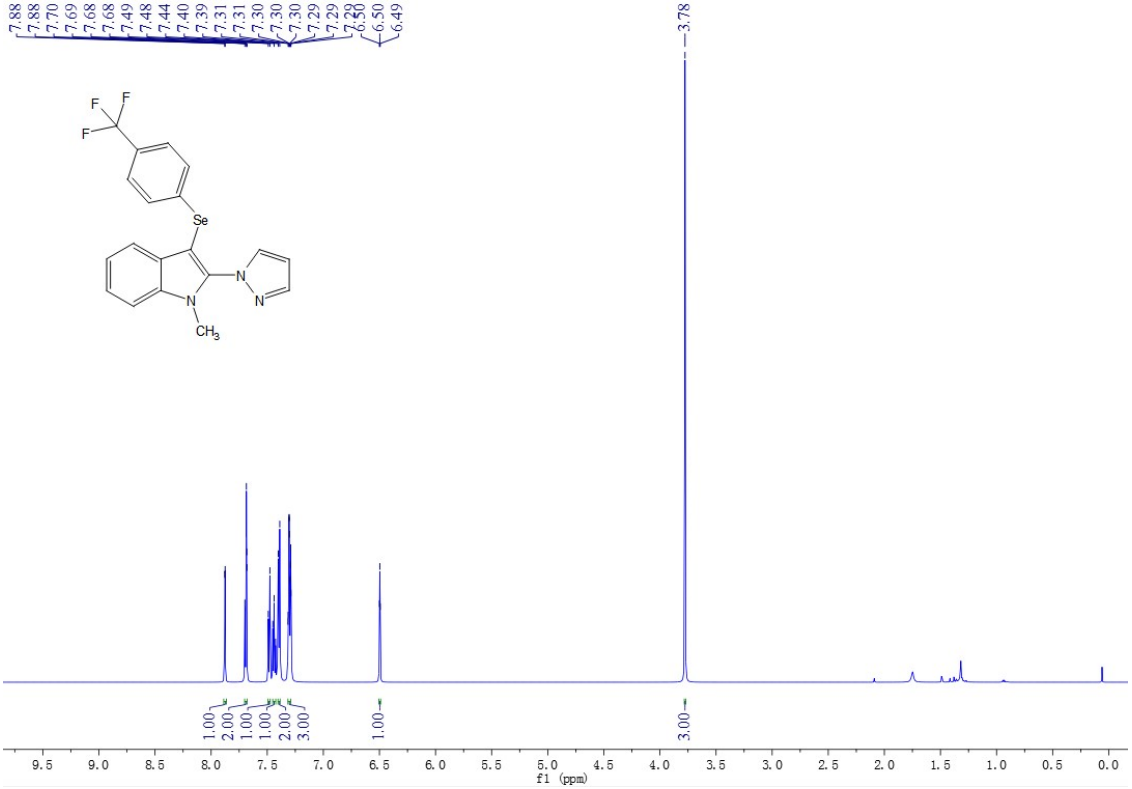
(41) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 24



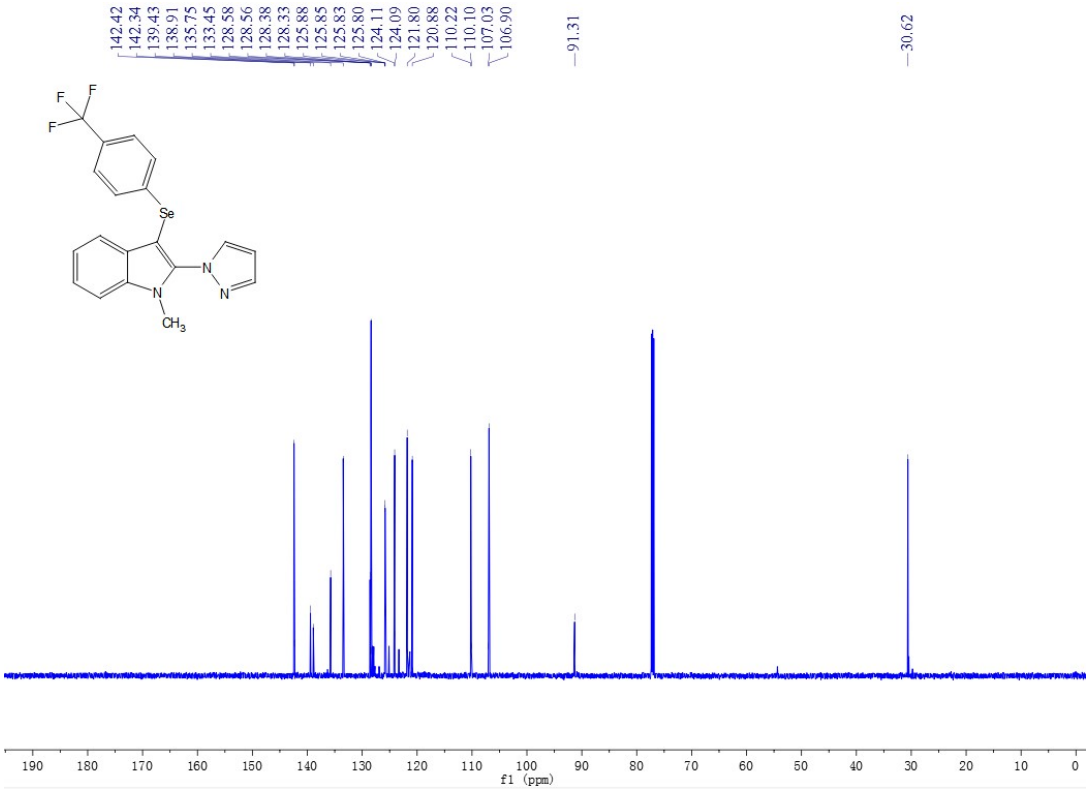
(42) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 24



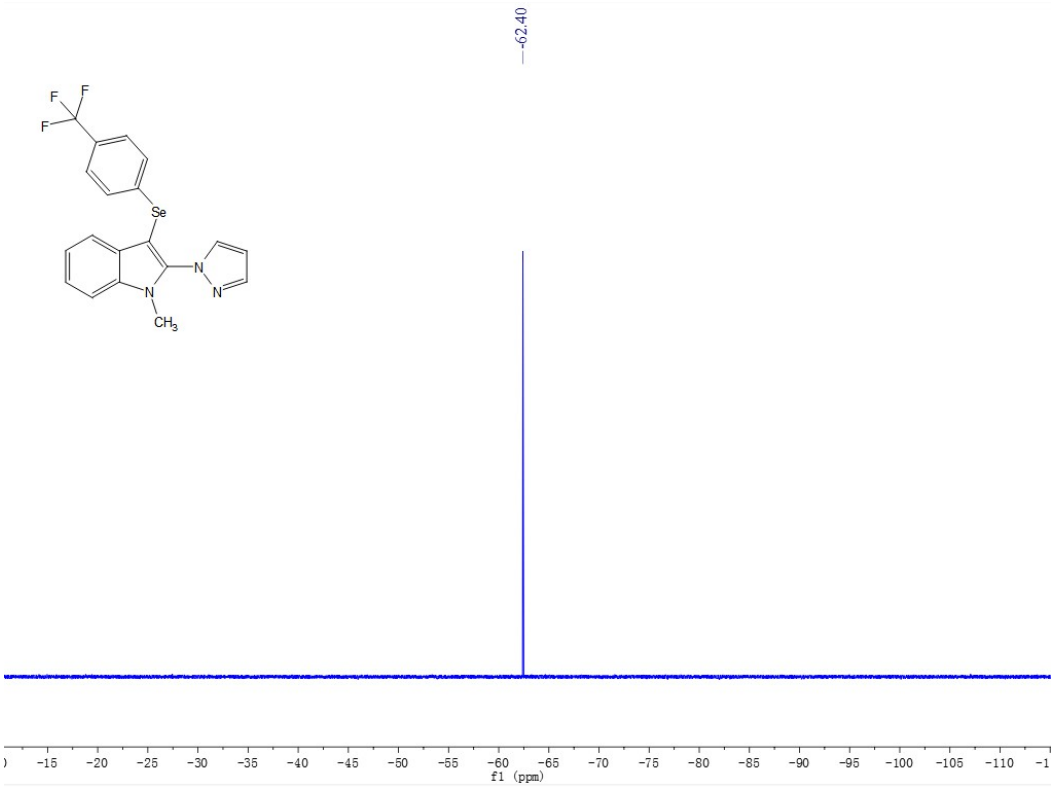
(43) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 25



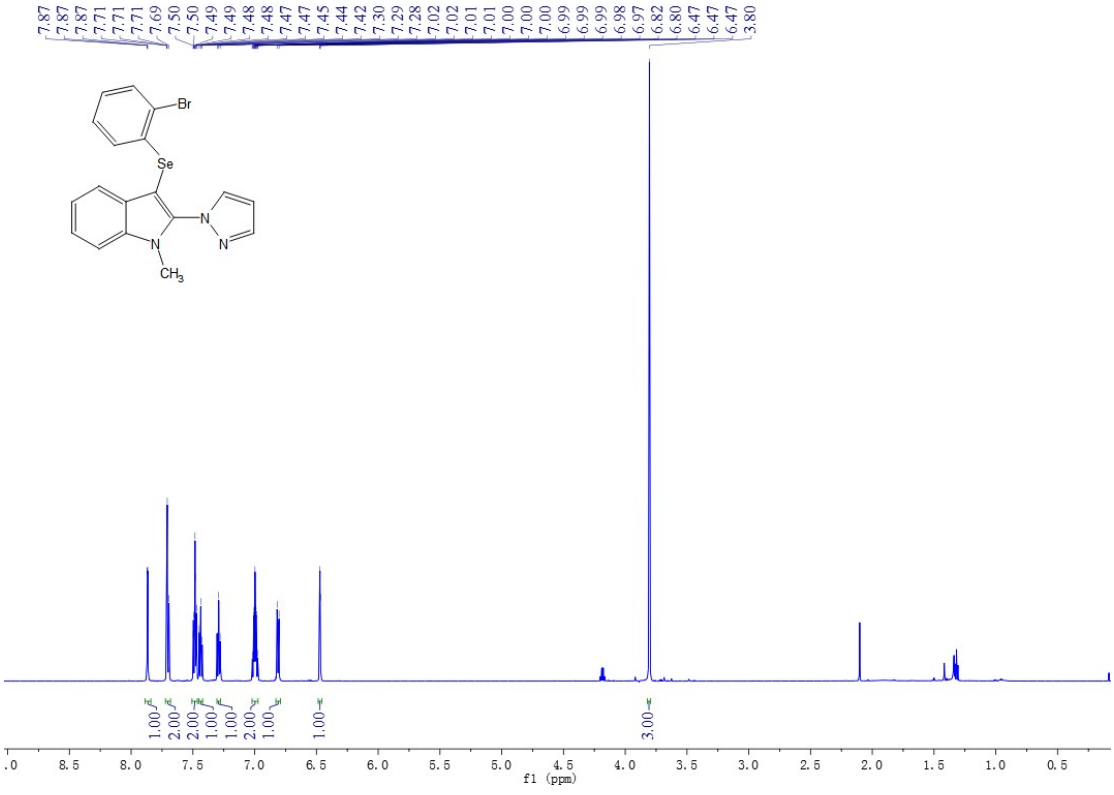
(44) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 25



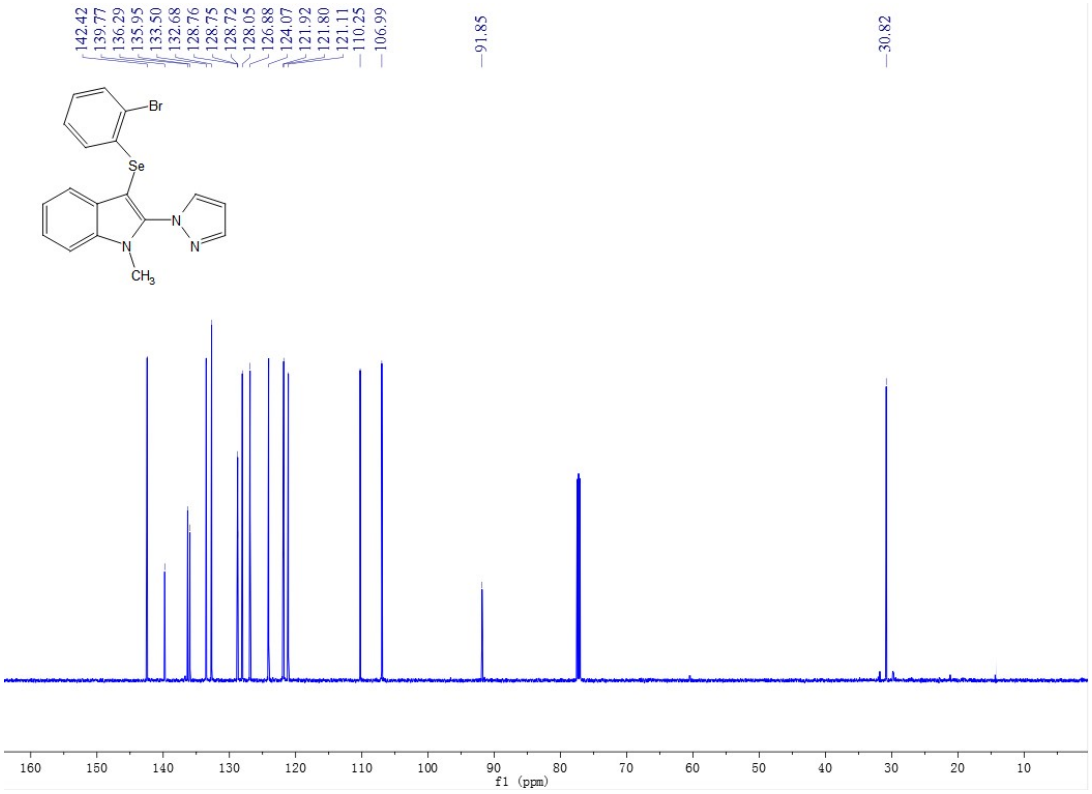
(45) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 25



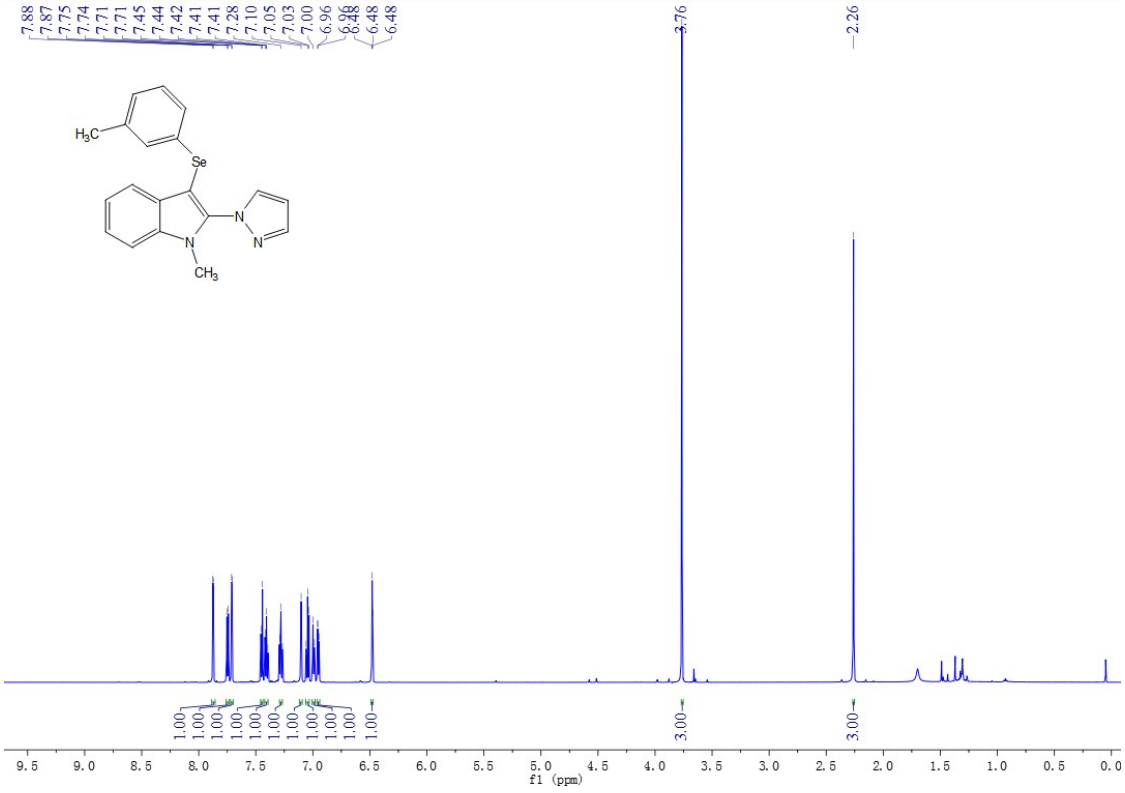
(46) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 26



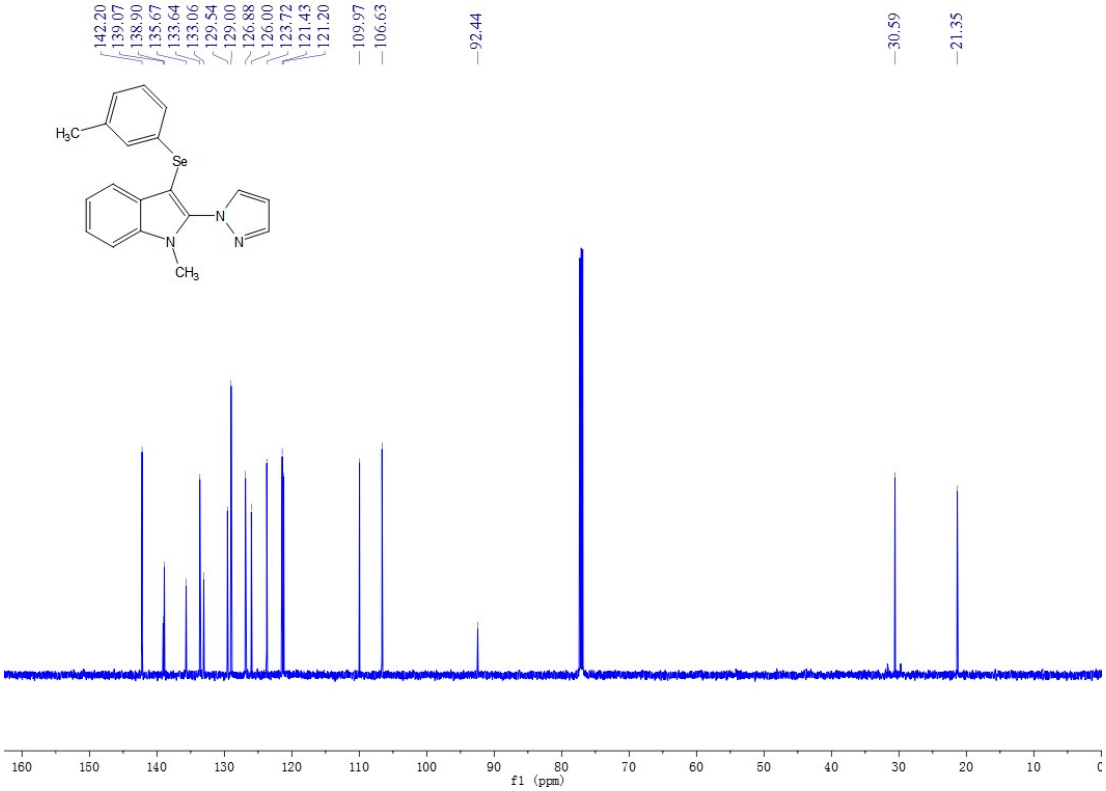
(47) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 26



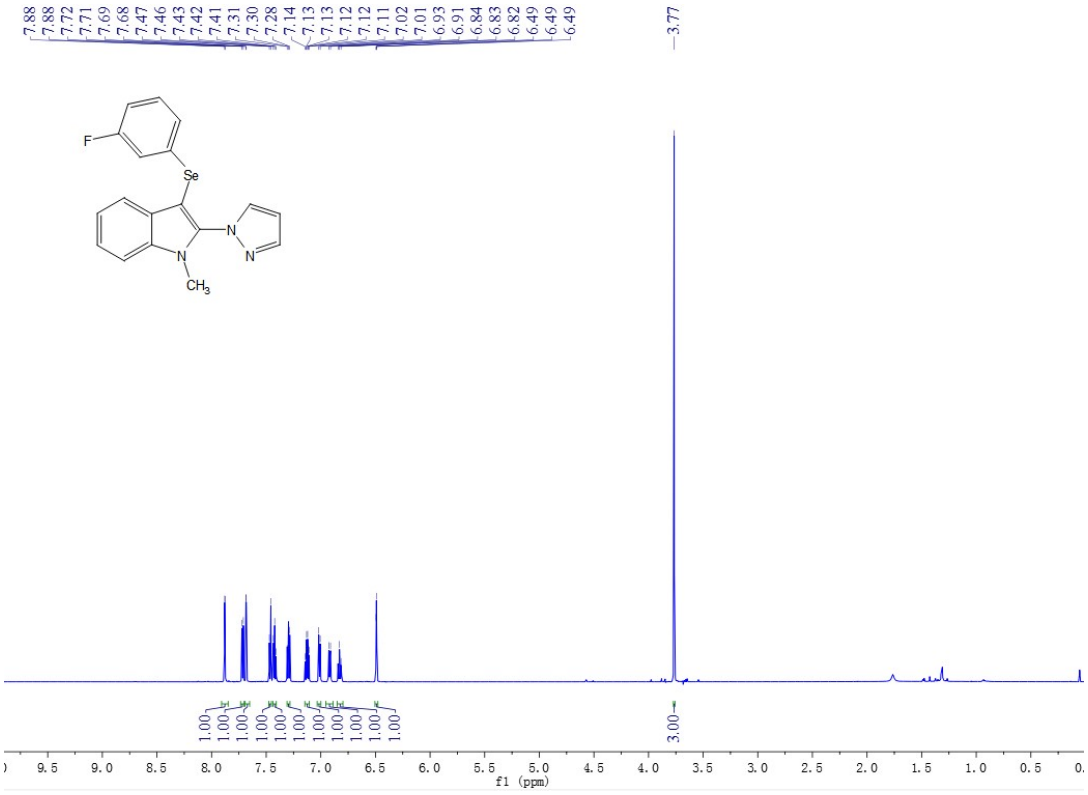
(48) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 27



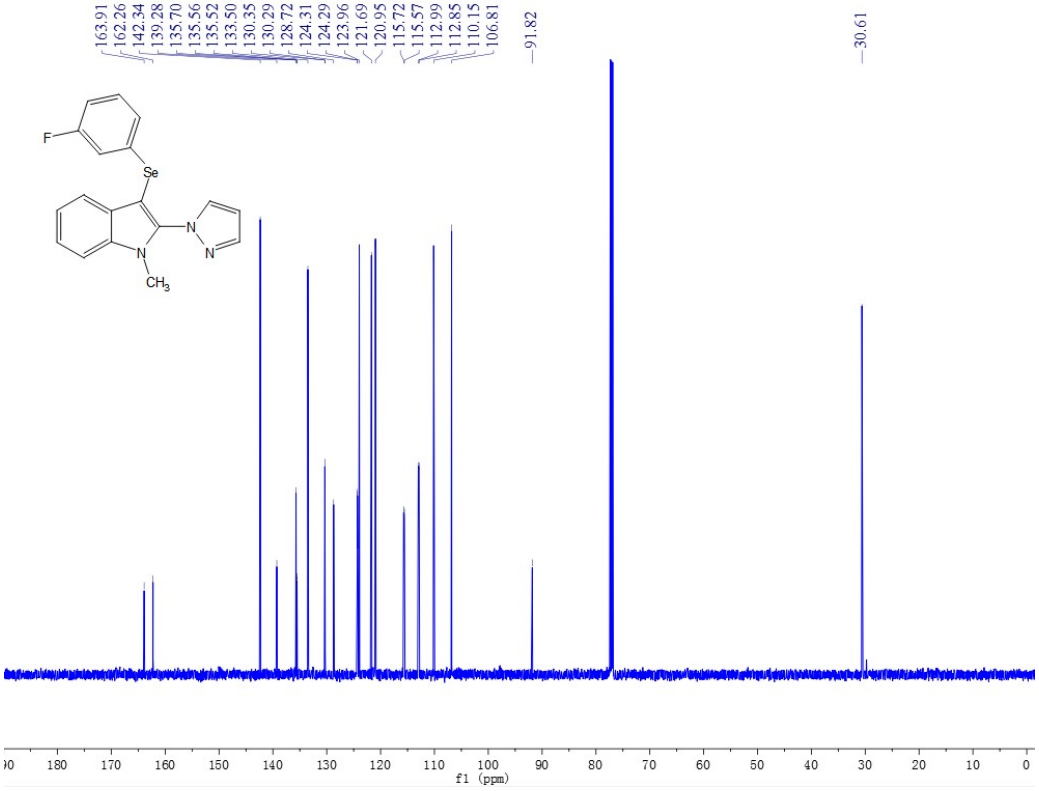
(49) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 27



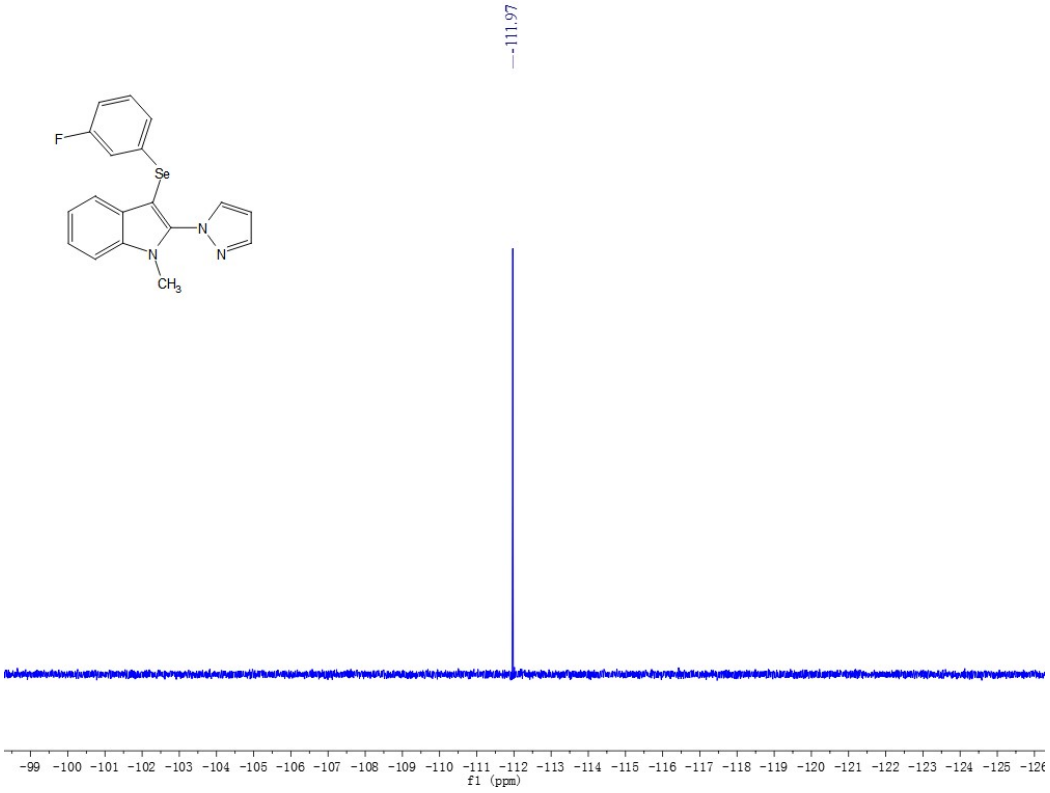
(50) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 28



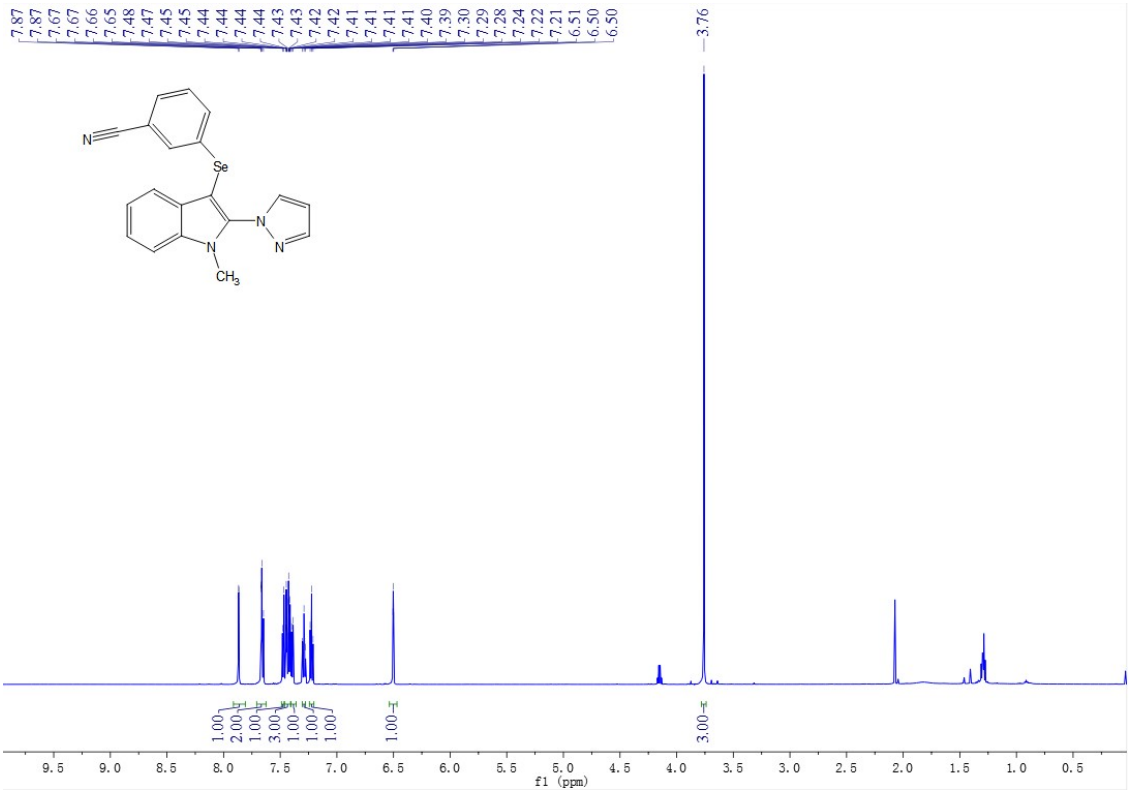
(51) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 28



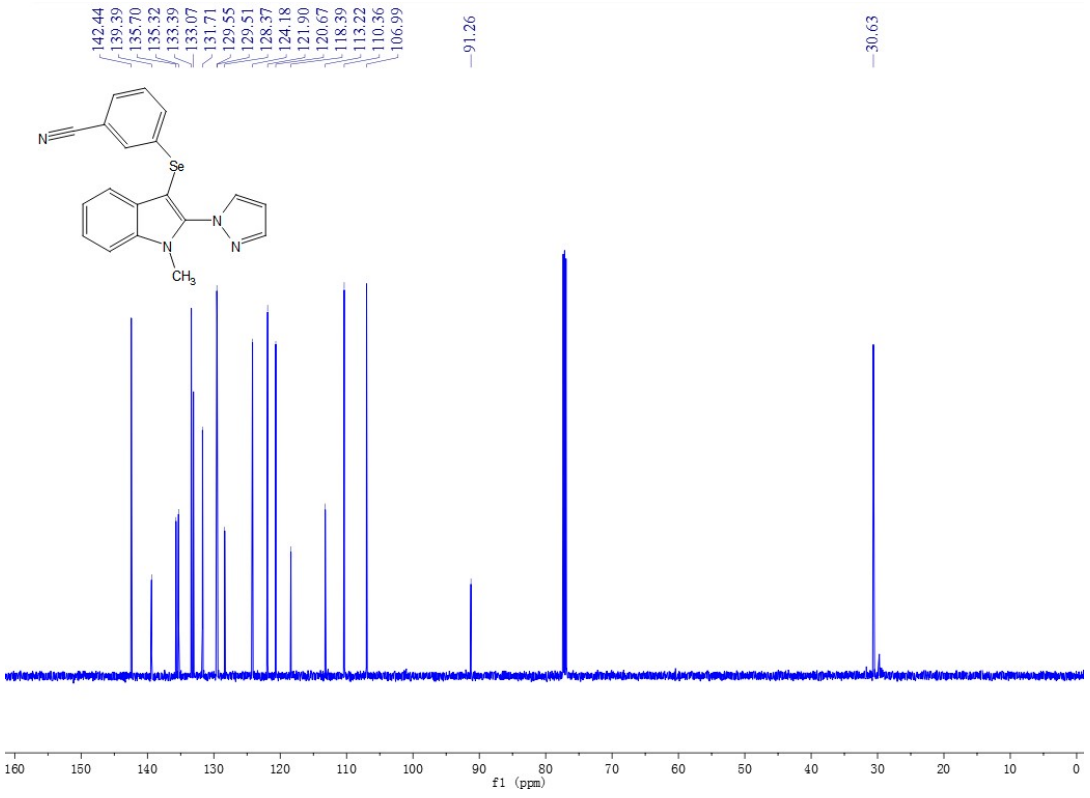
(52) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 28



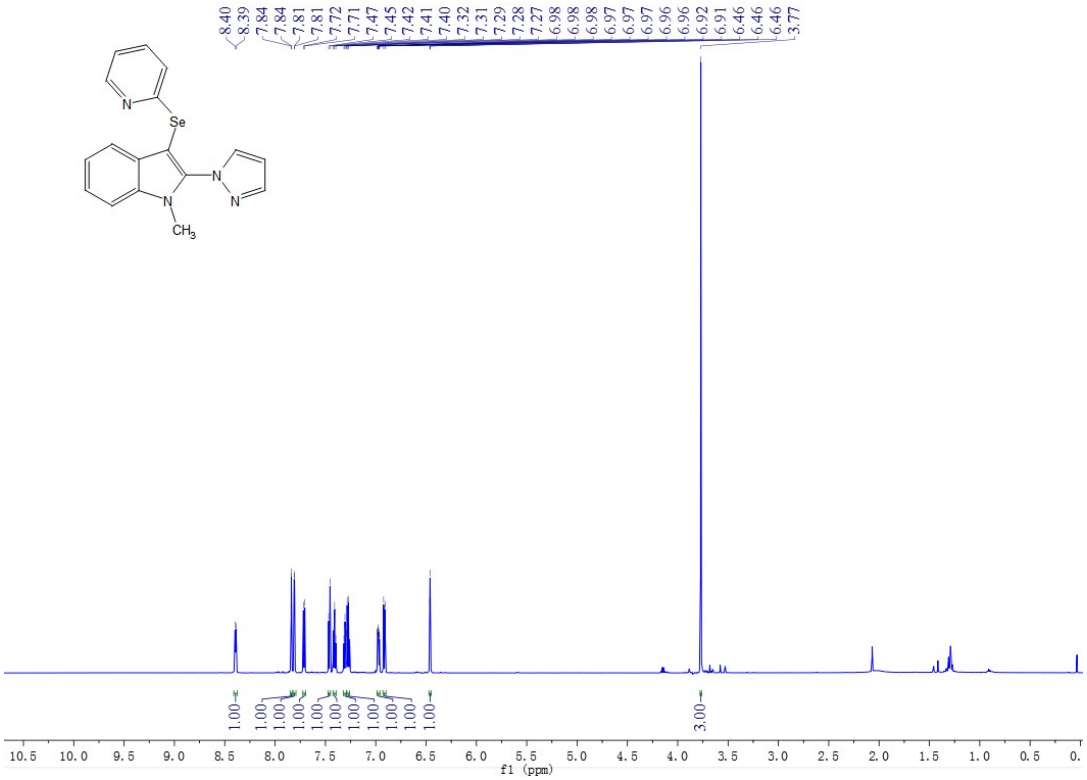
(53) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 29



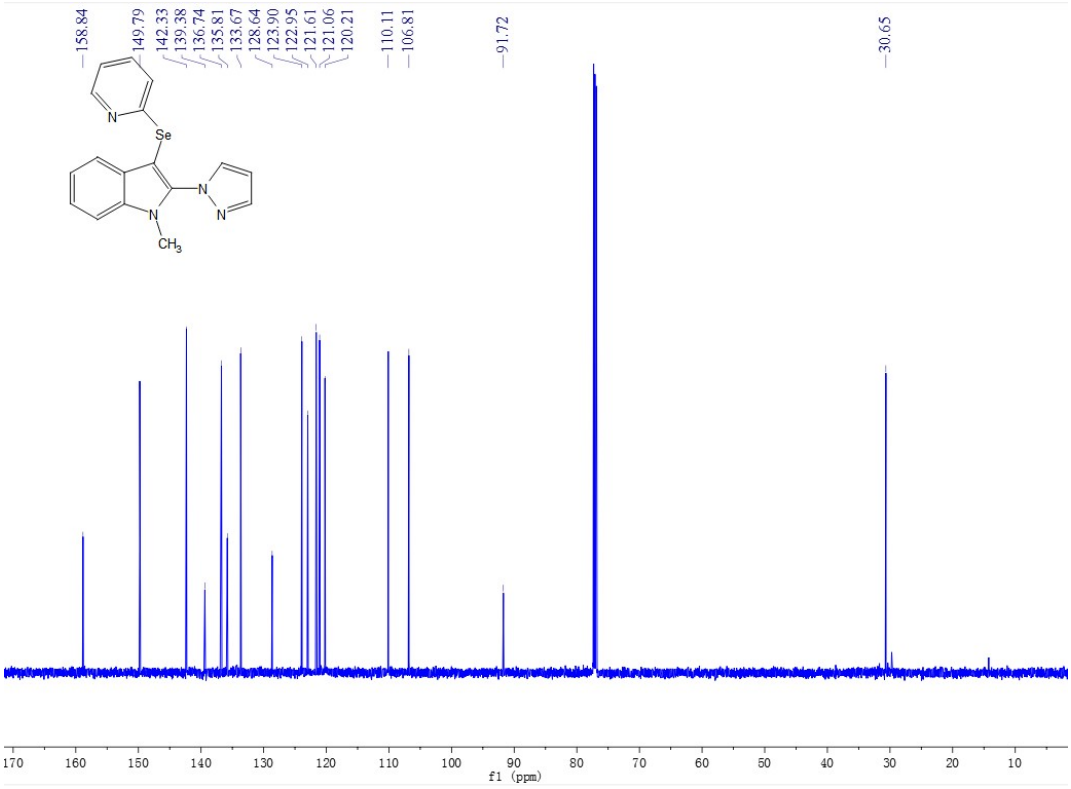
(54) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 29



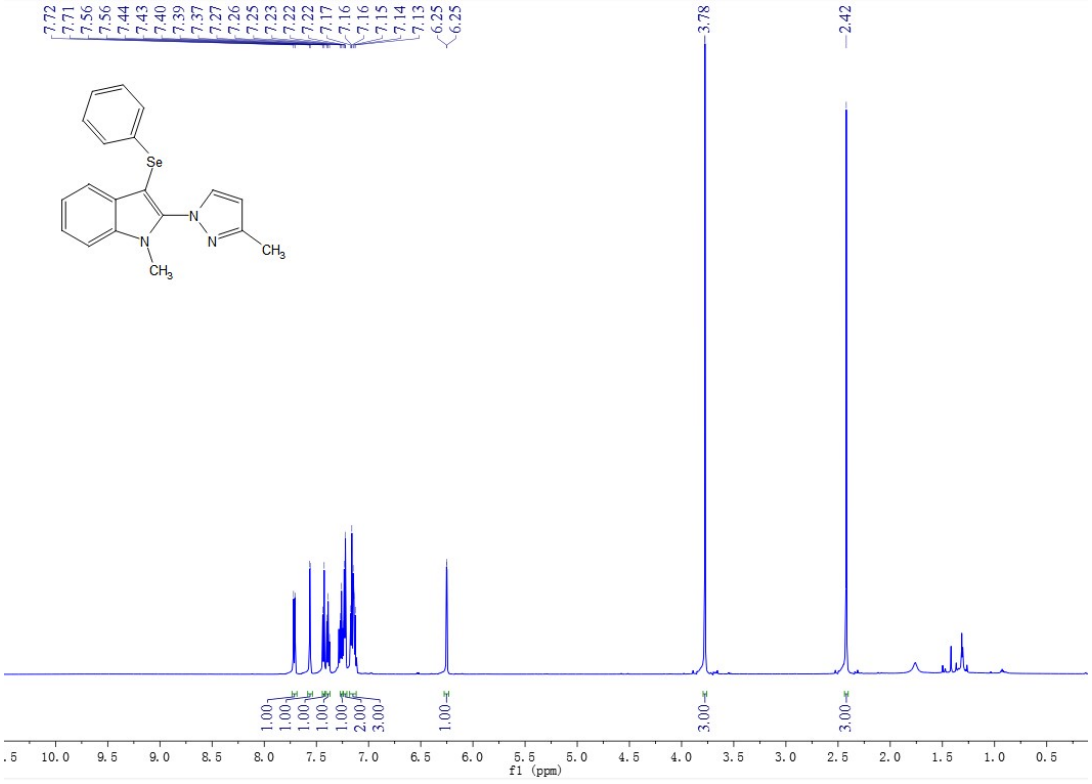
(55) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 30



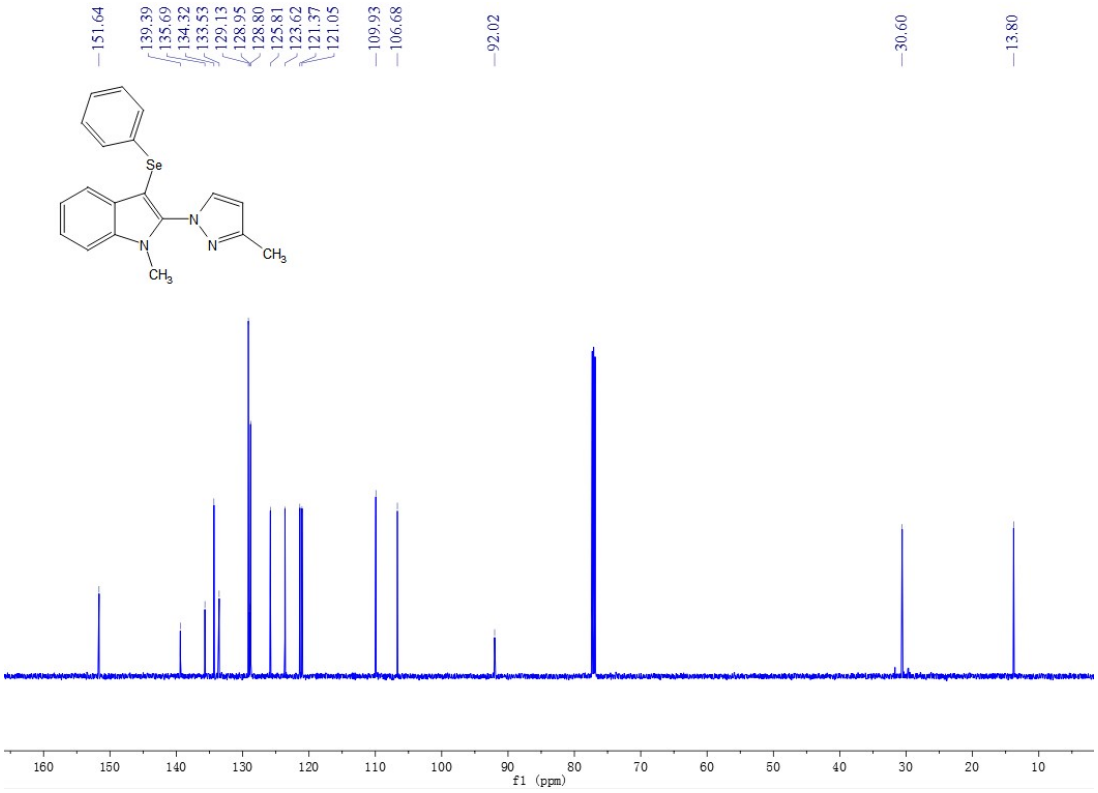
(56) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 30



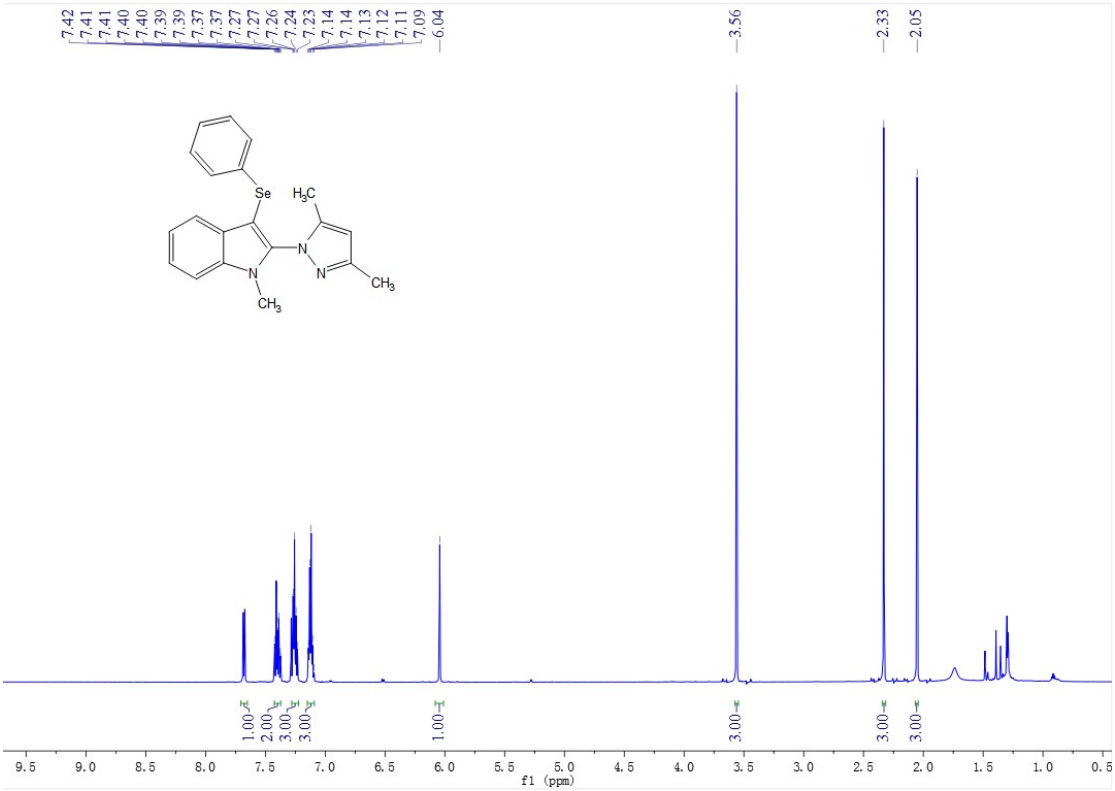
(57) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 31



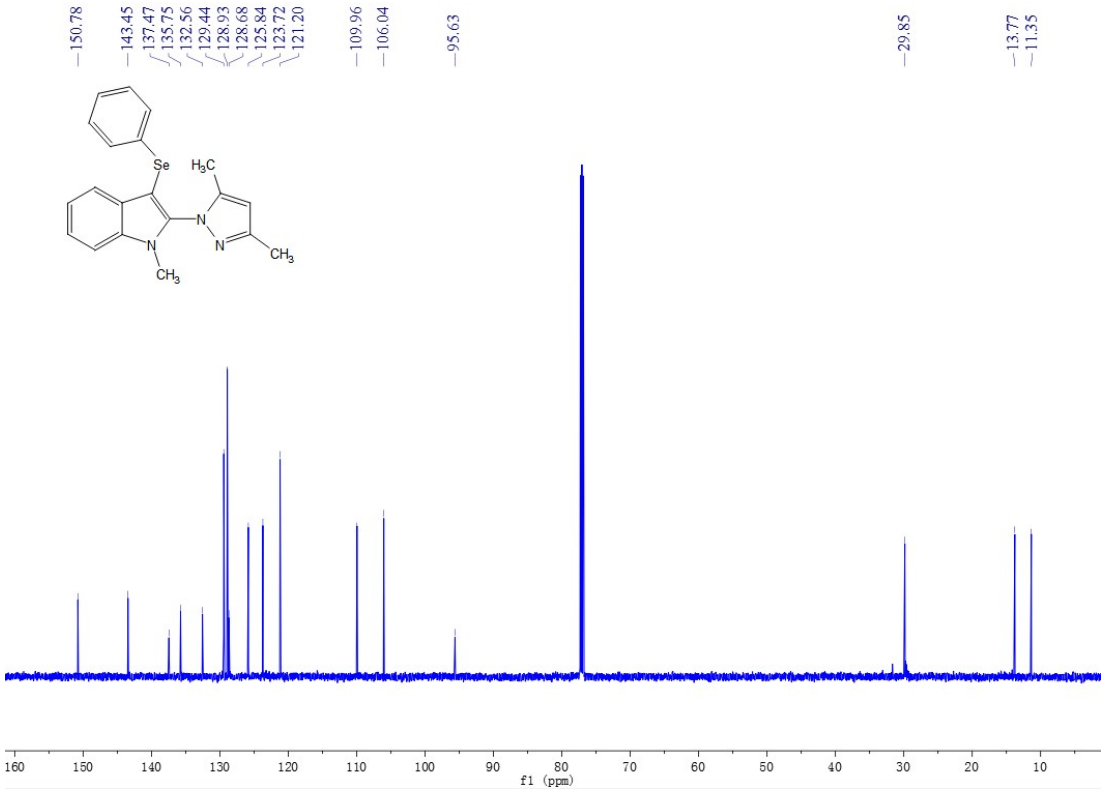
(58) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 31



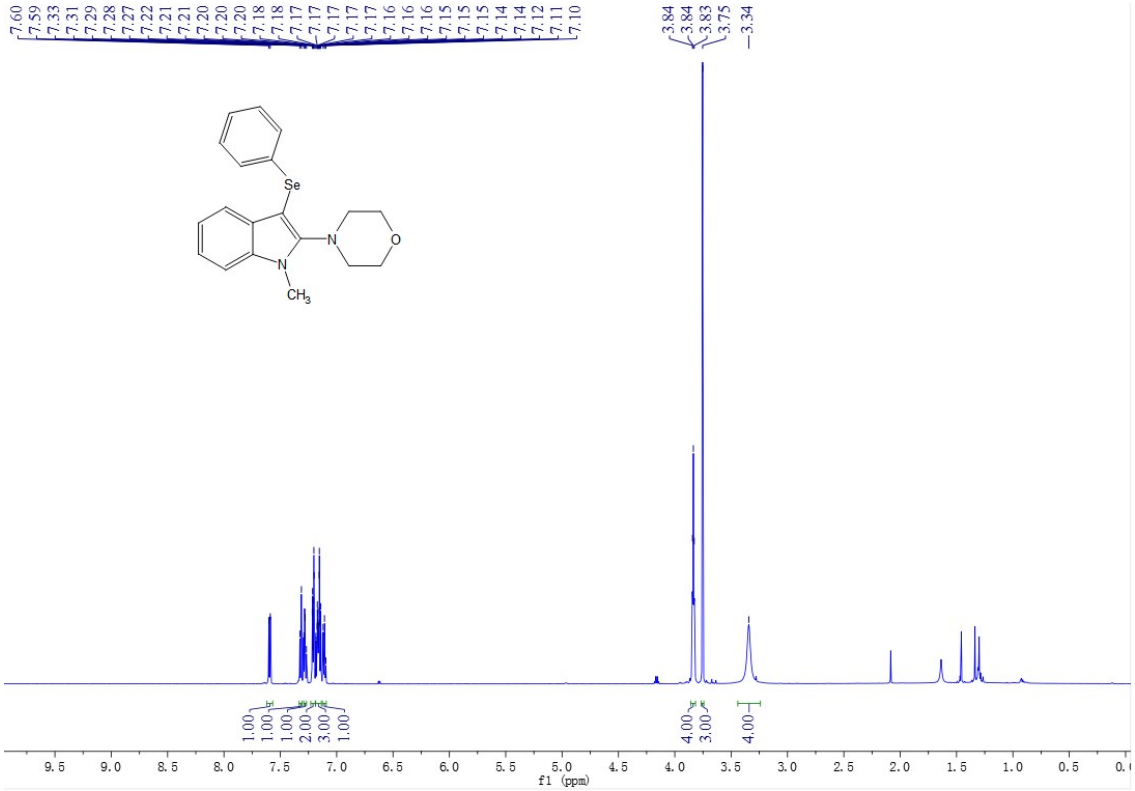
(59) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 32



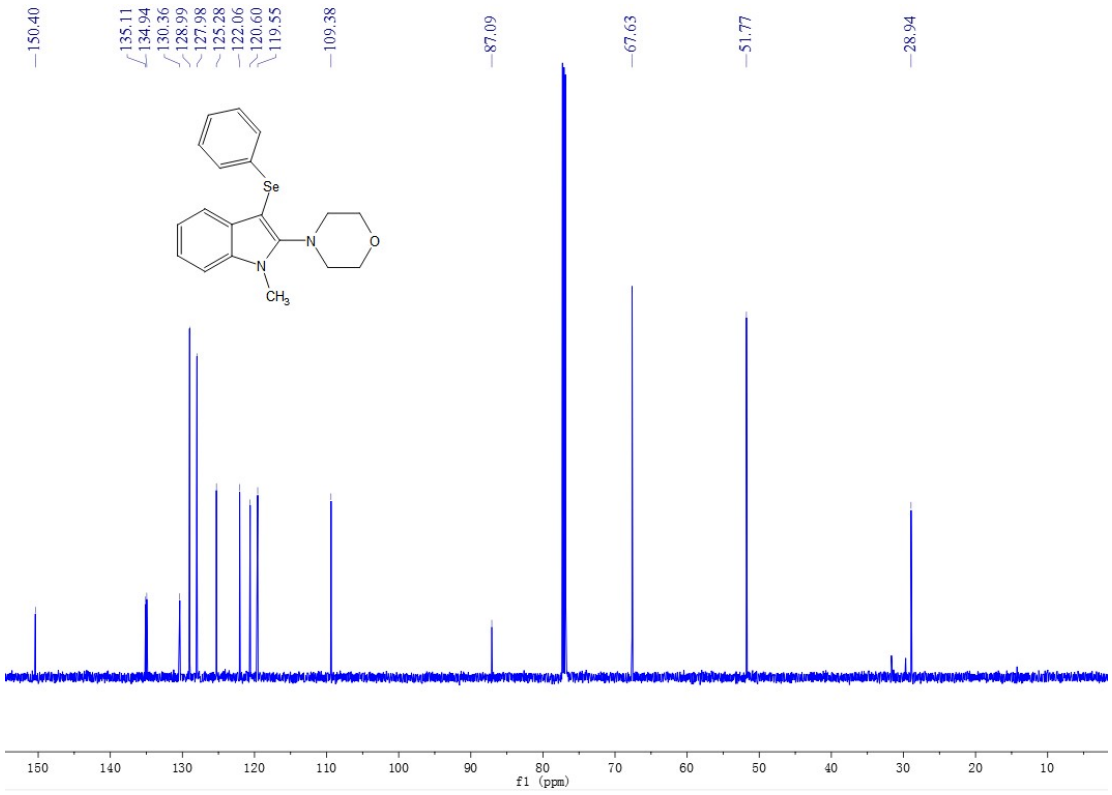
(60) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 32



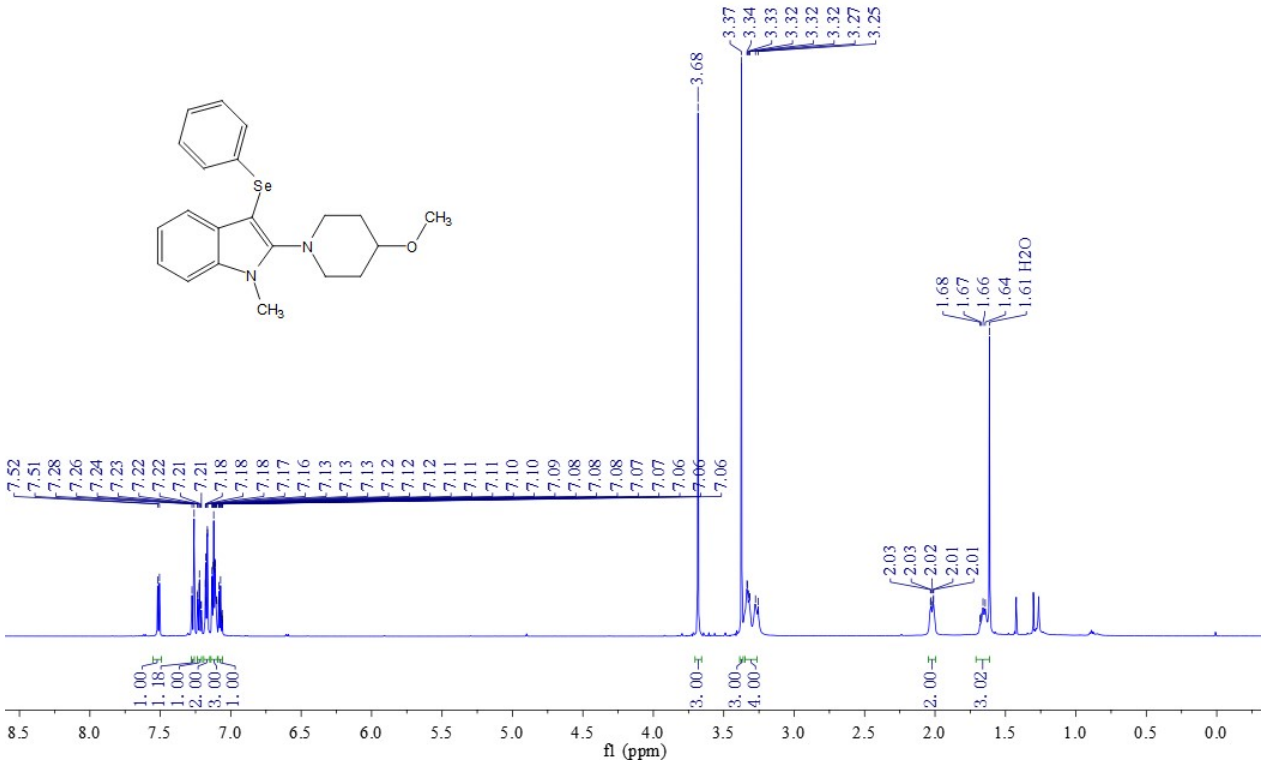
(61) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 33



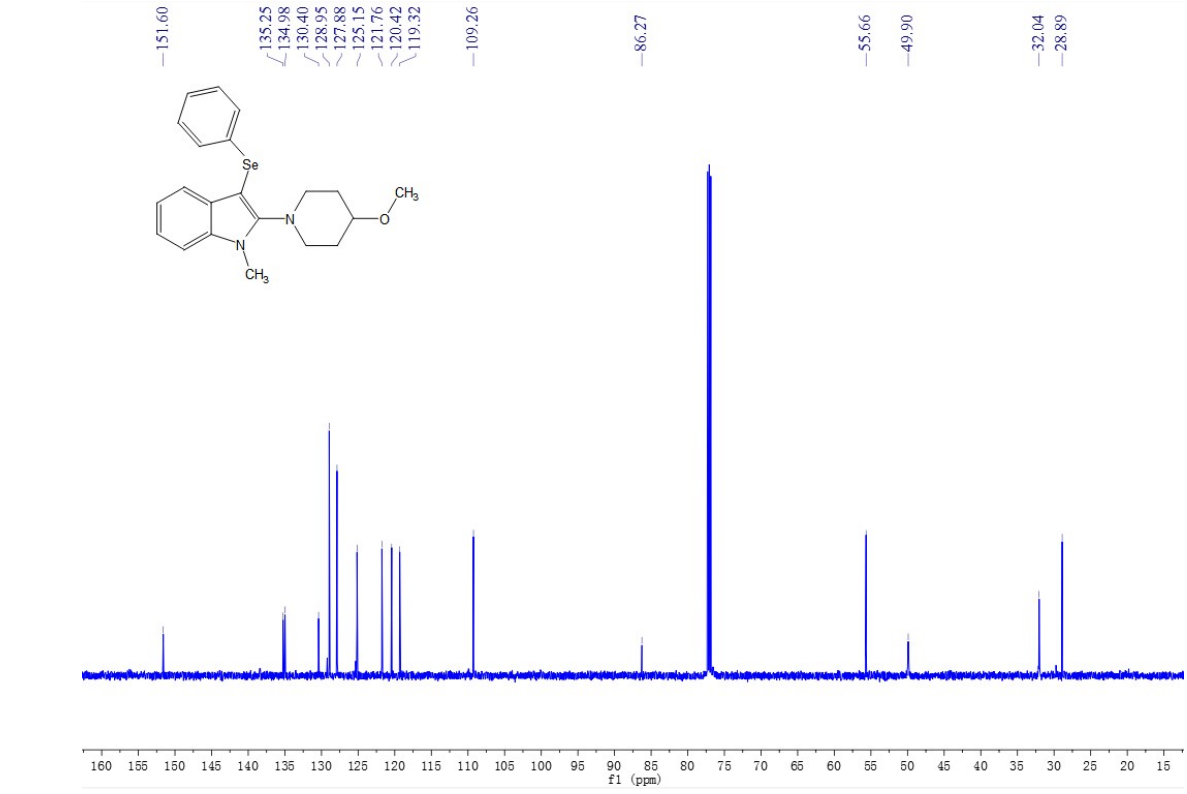
(62) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 33



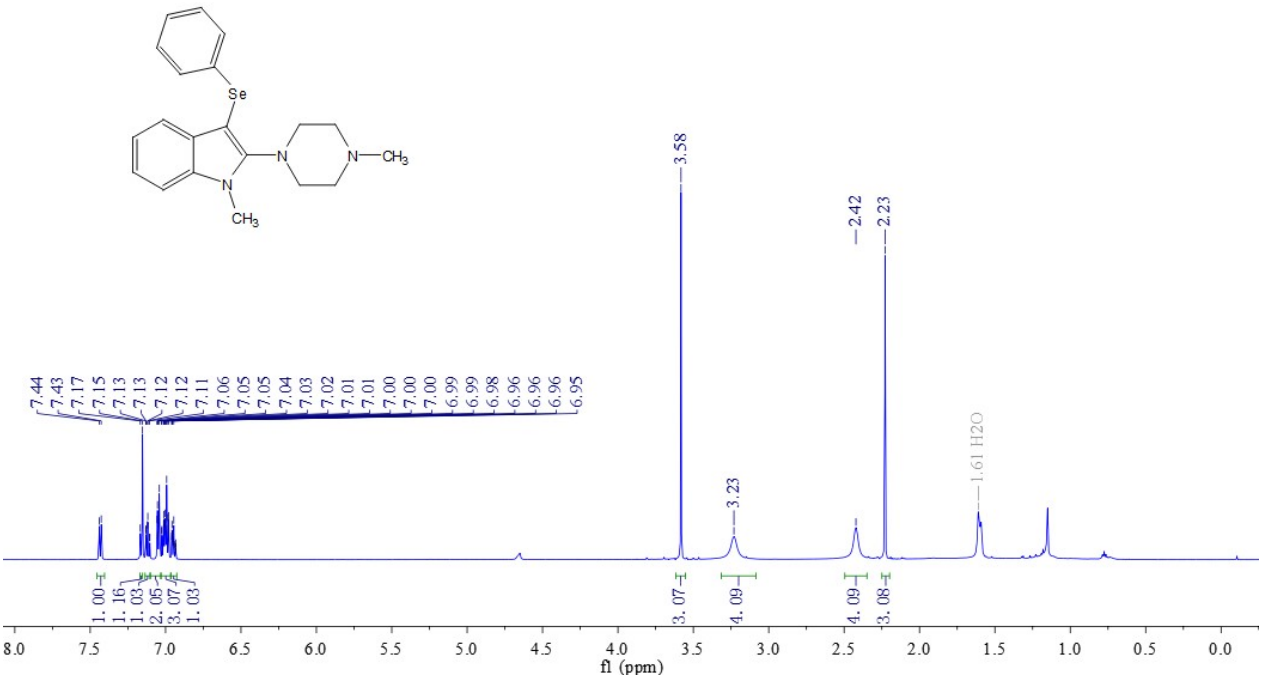
(63) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 34



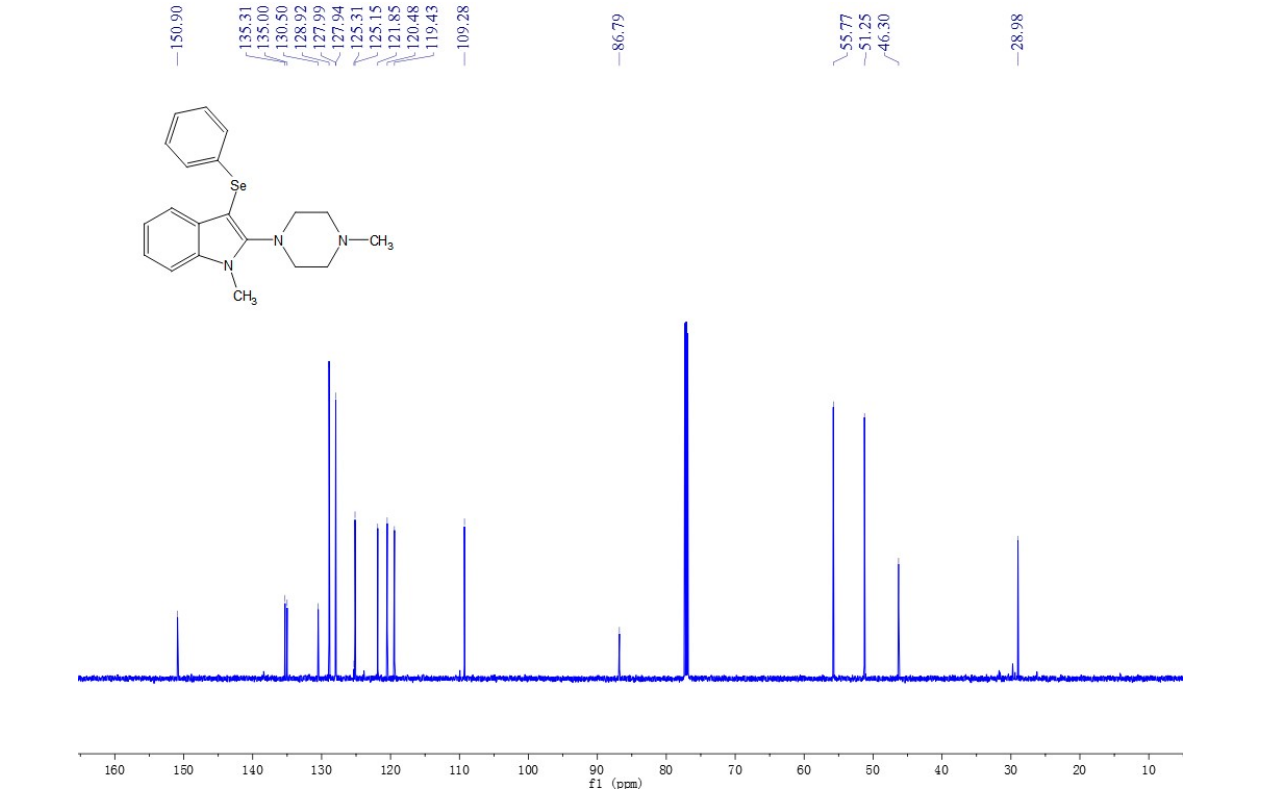
(64) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 34



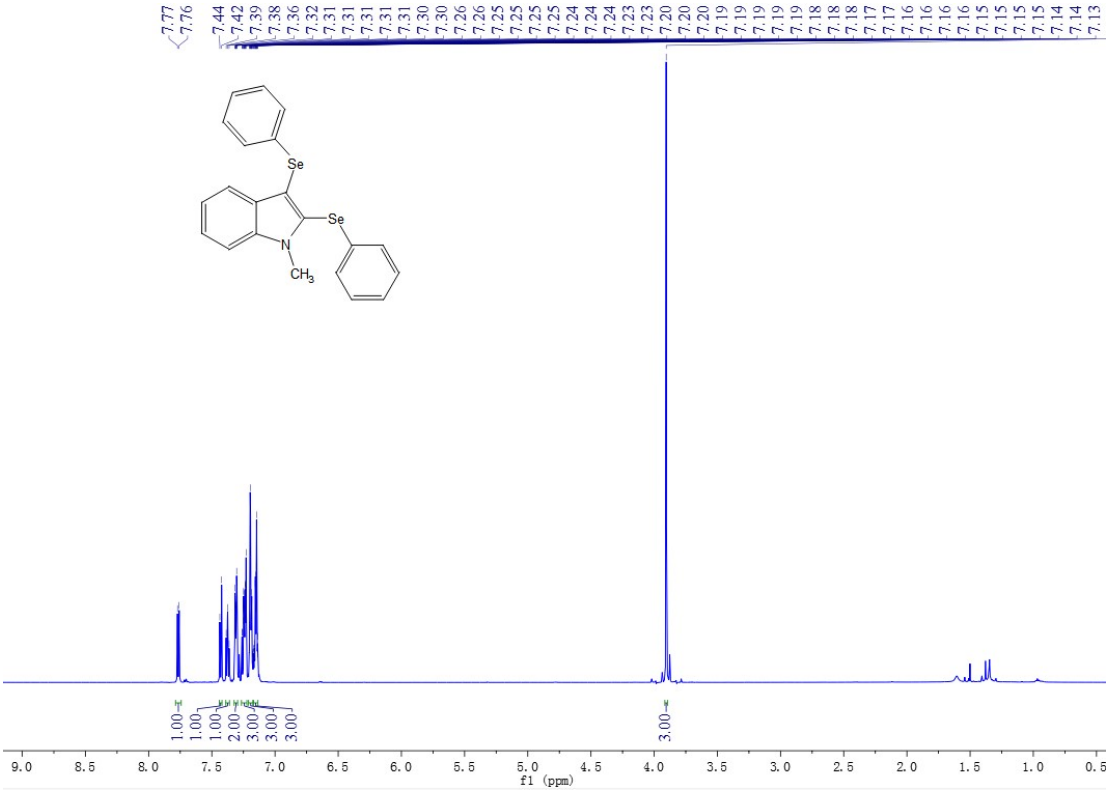
(65) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 35



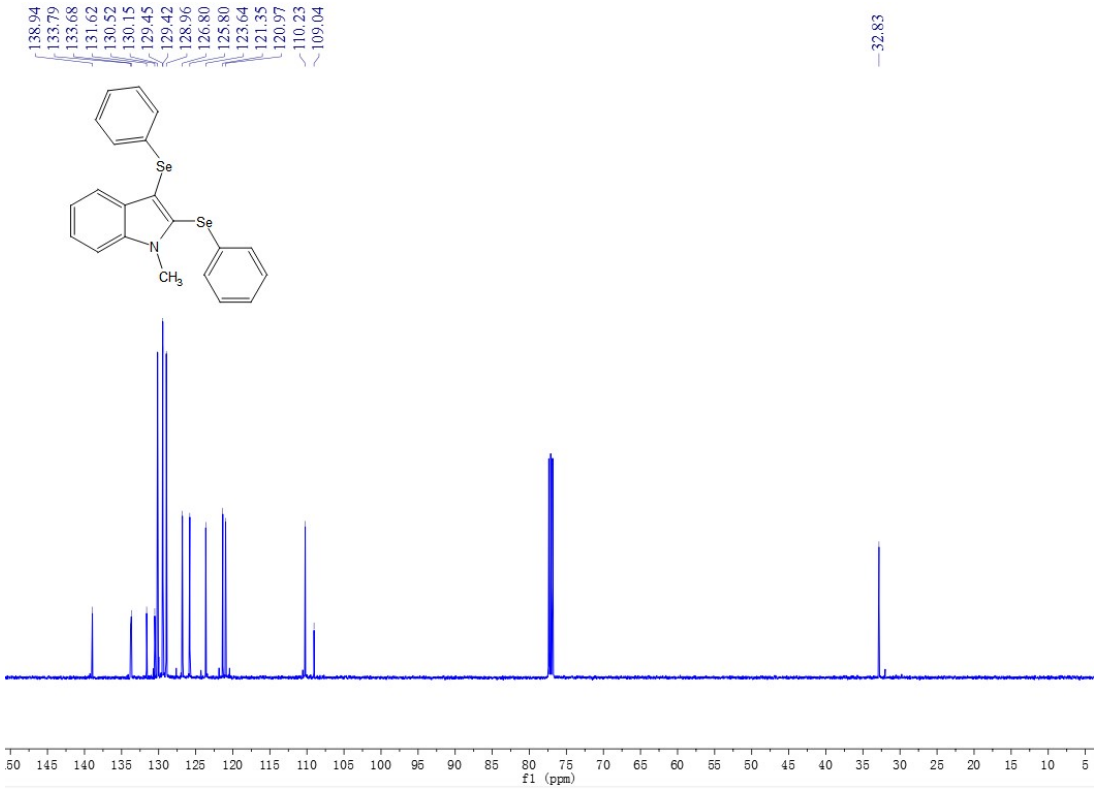
(66) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 35



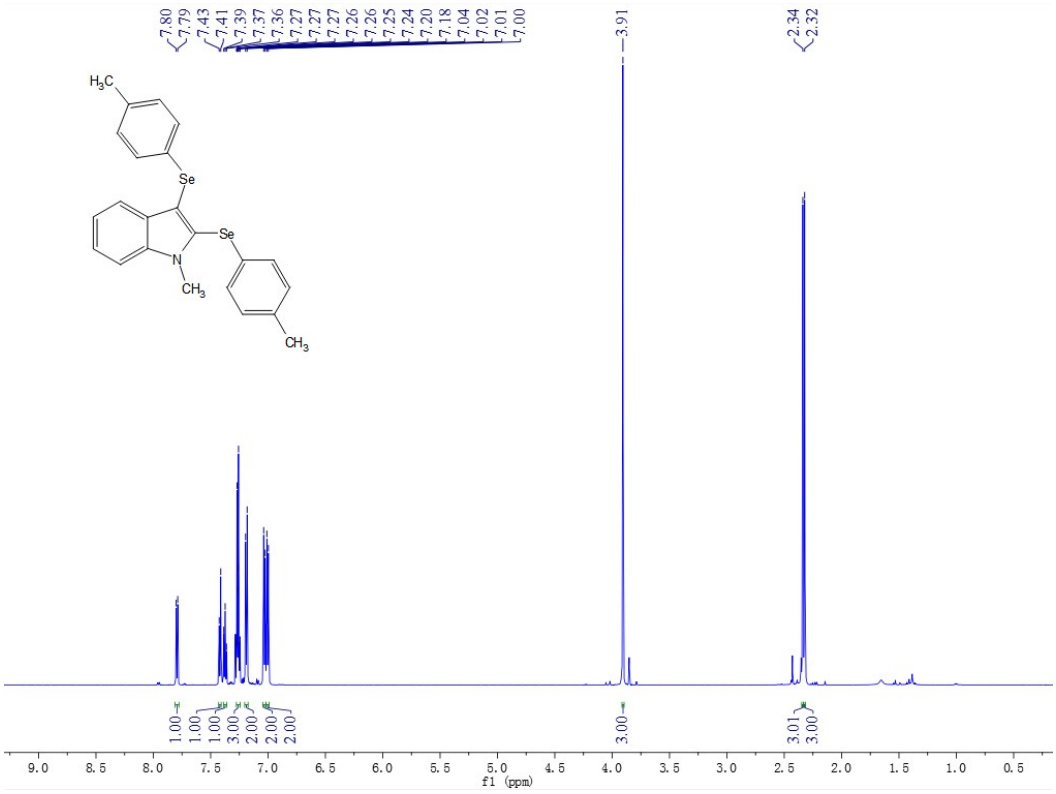
(67) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 36



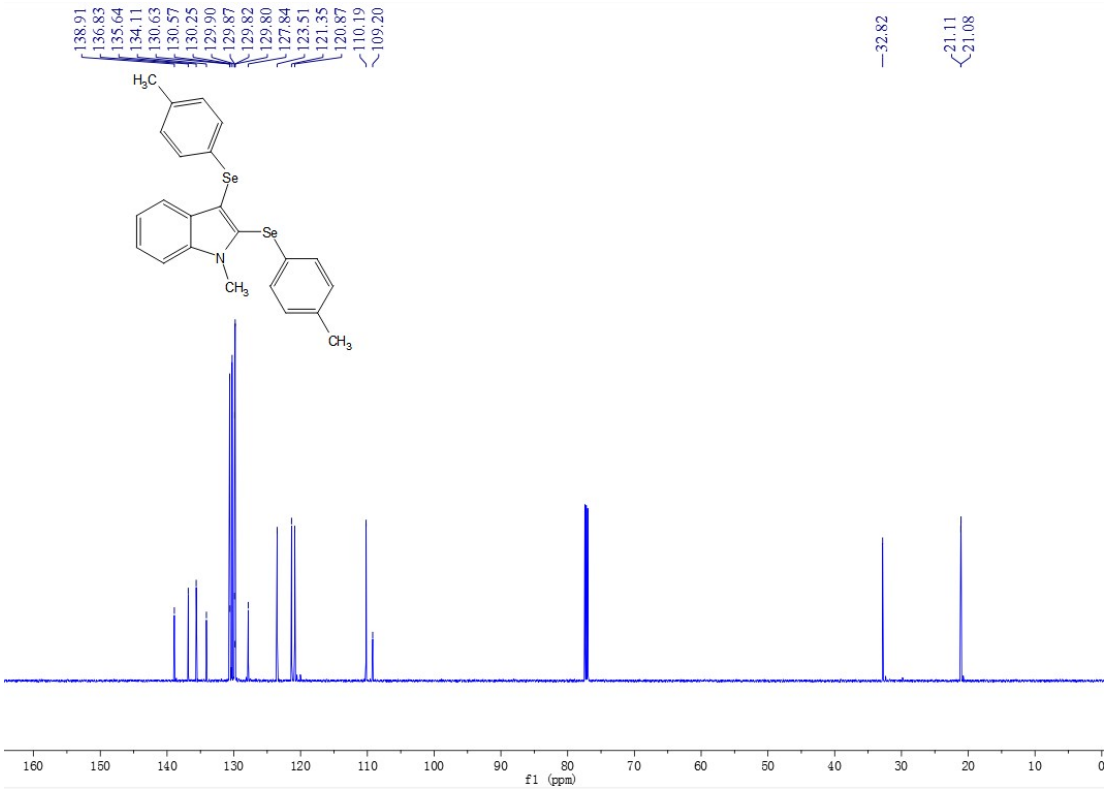
(68) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 36



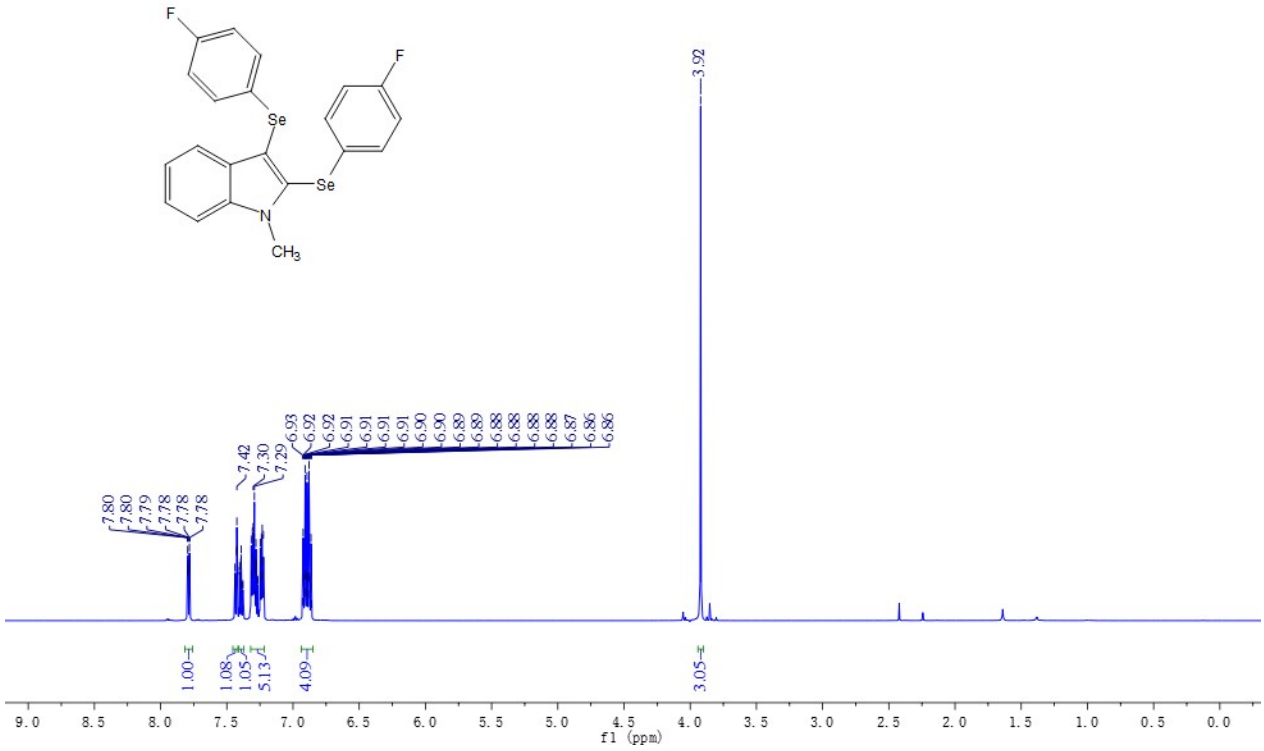
(69) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 37



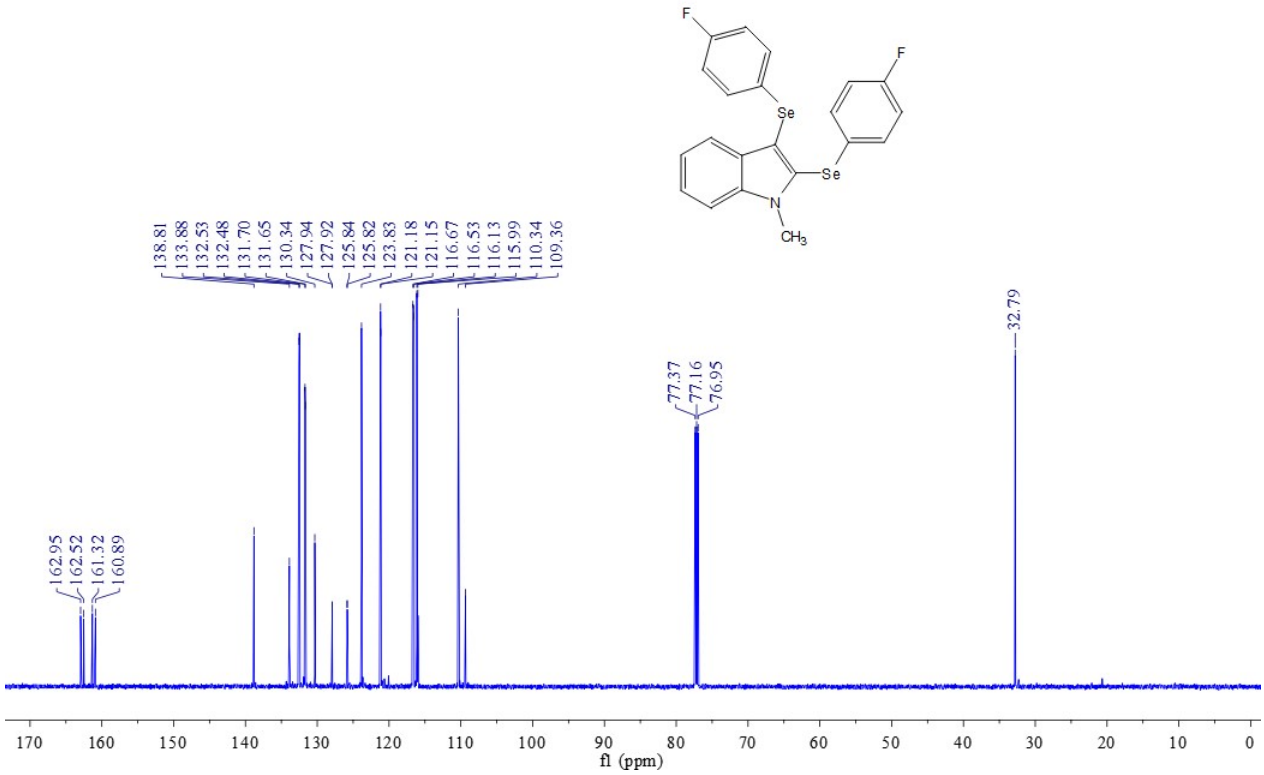
(70) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 37



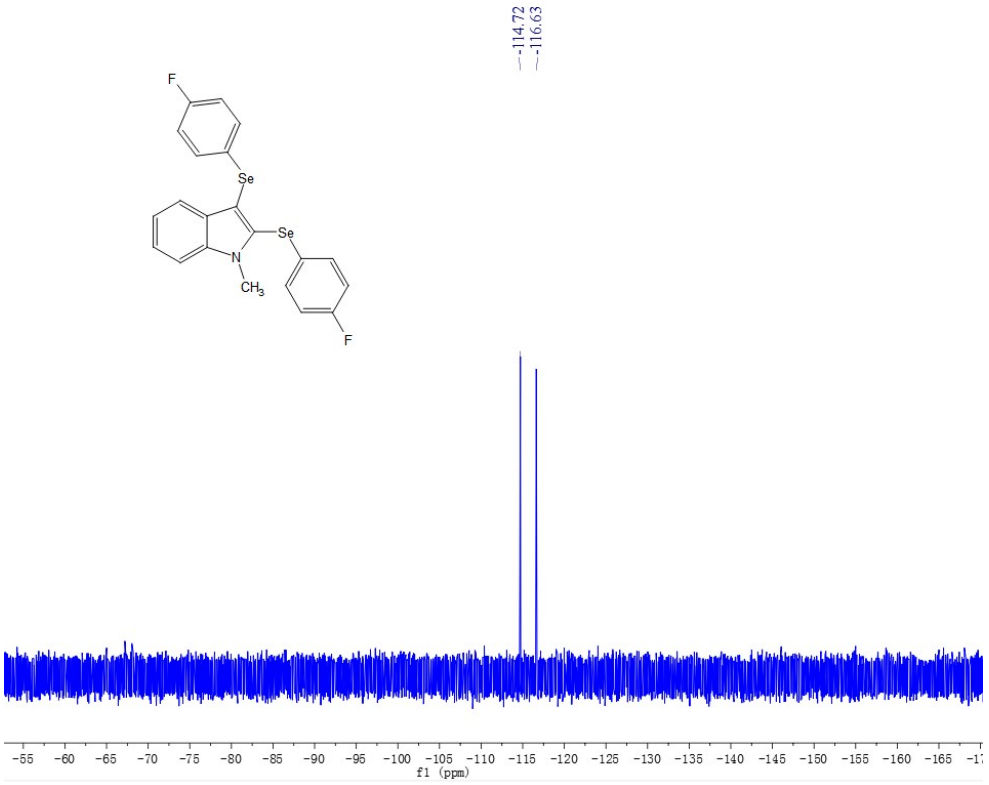
(71) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 38



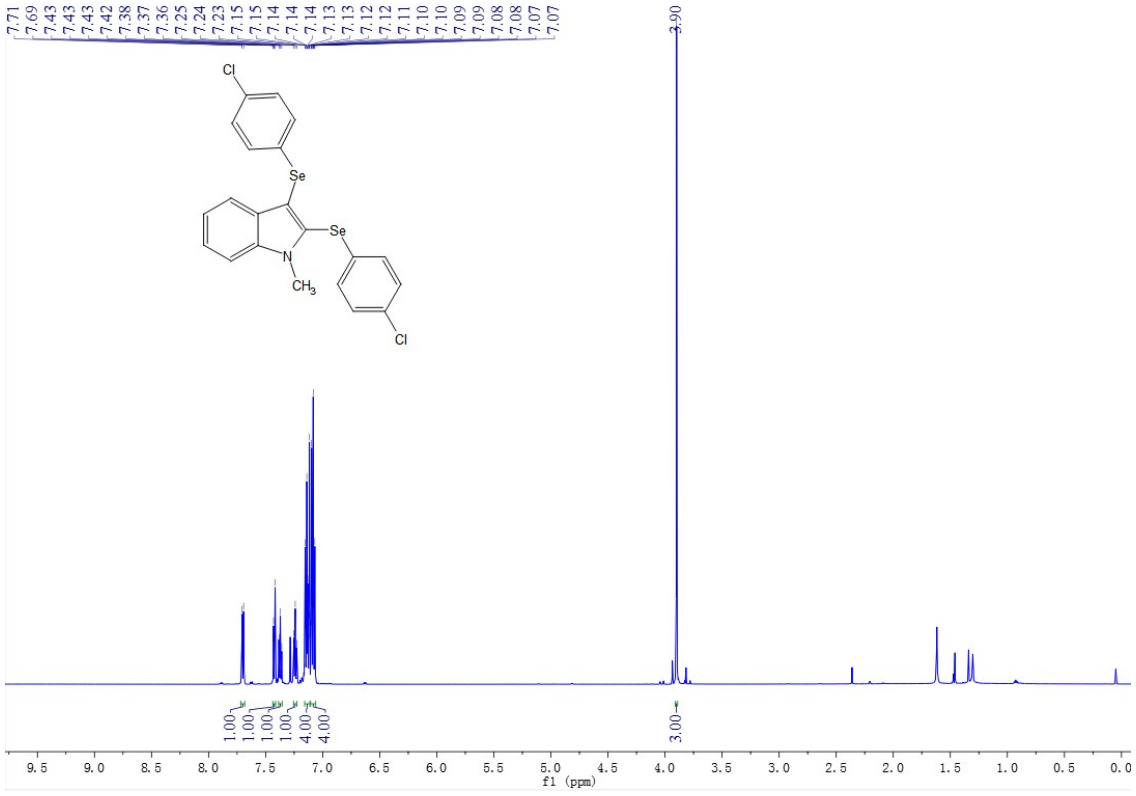
(72) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 38



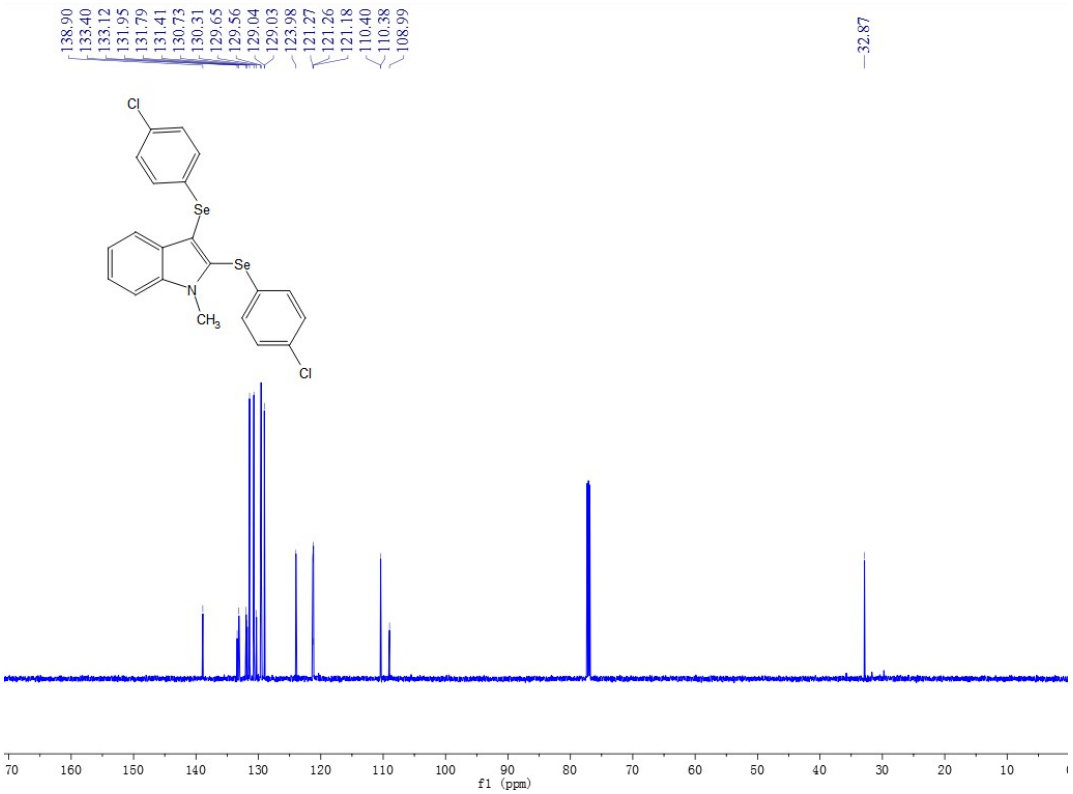
(73) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 38



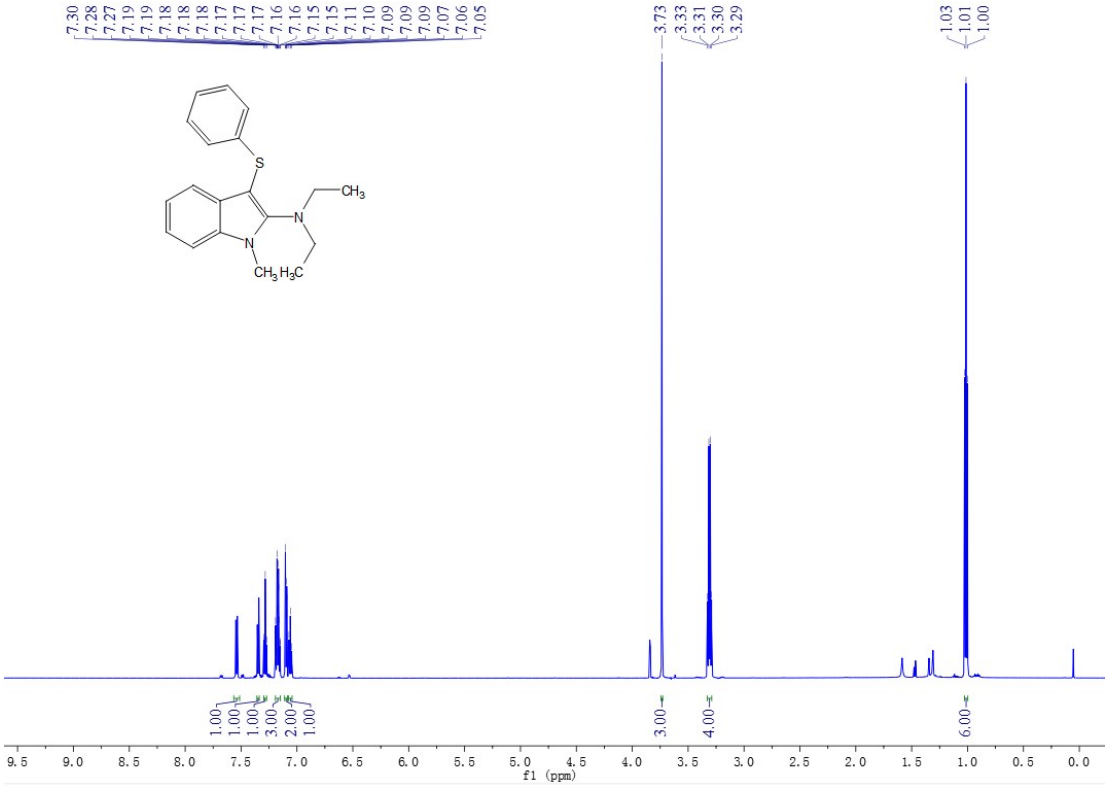
(74) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 39



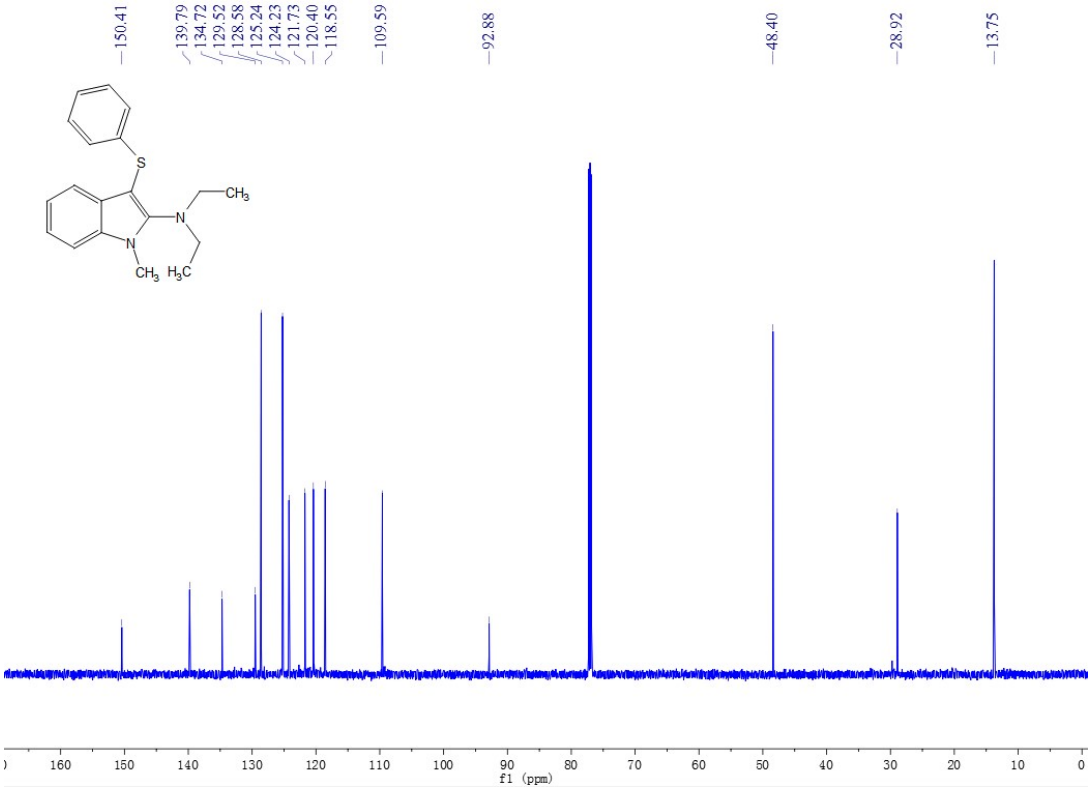
(75) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 39



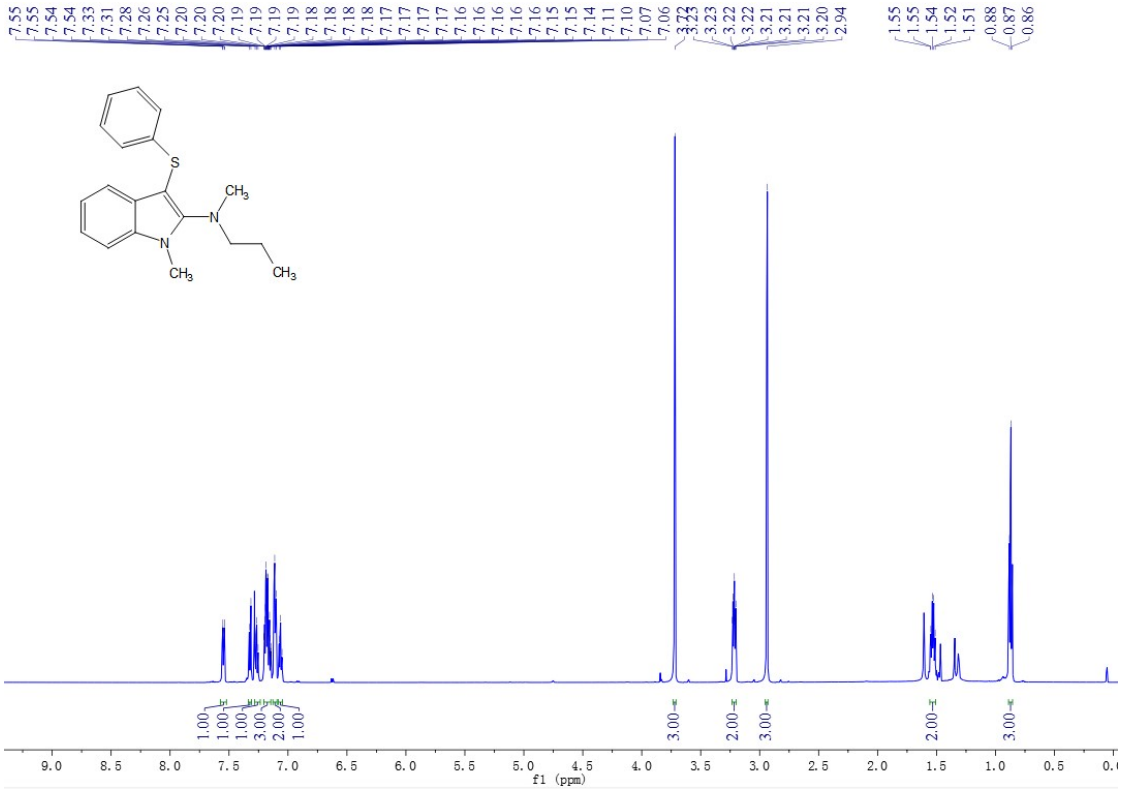
(76) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 40



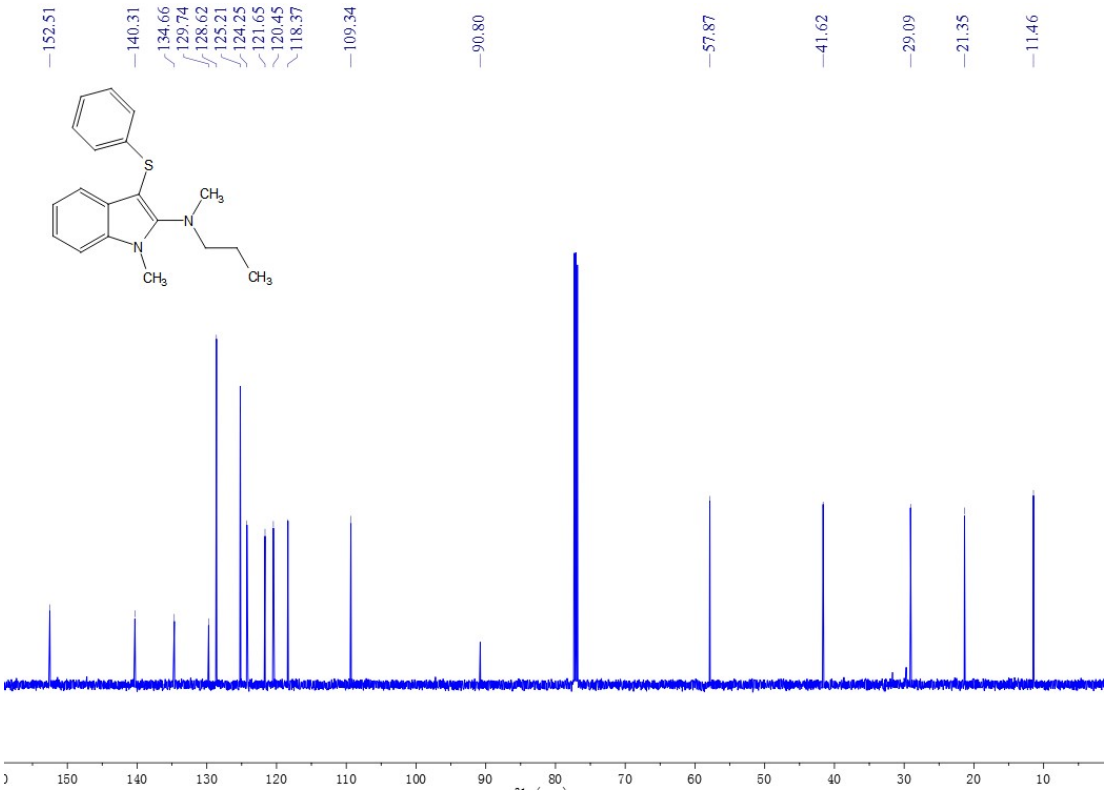
(77) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 40



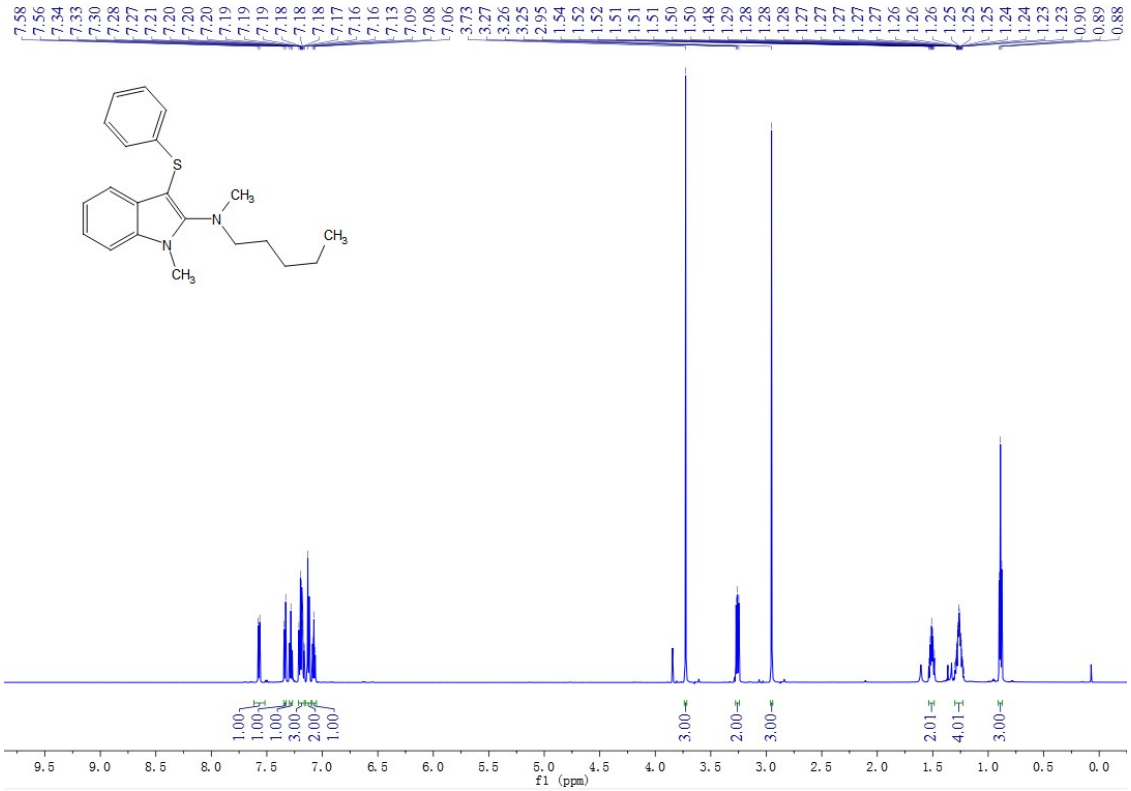
(78) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 41



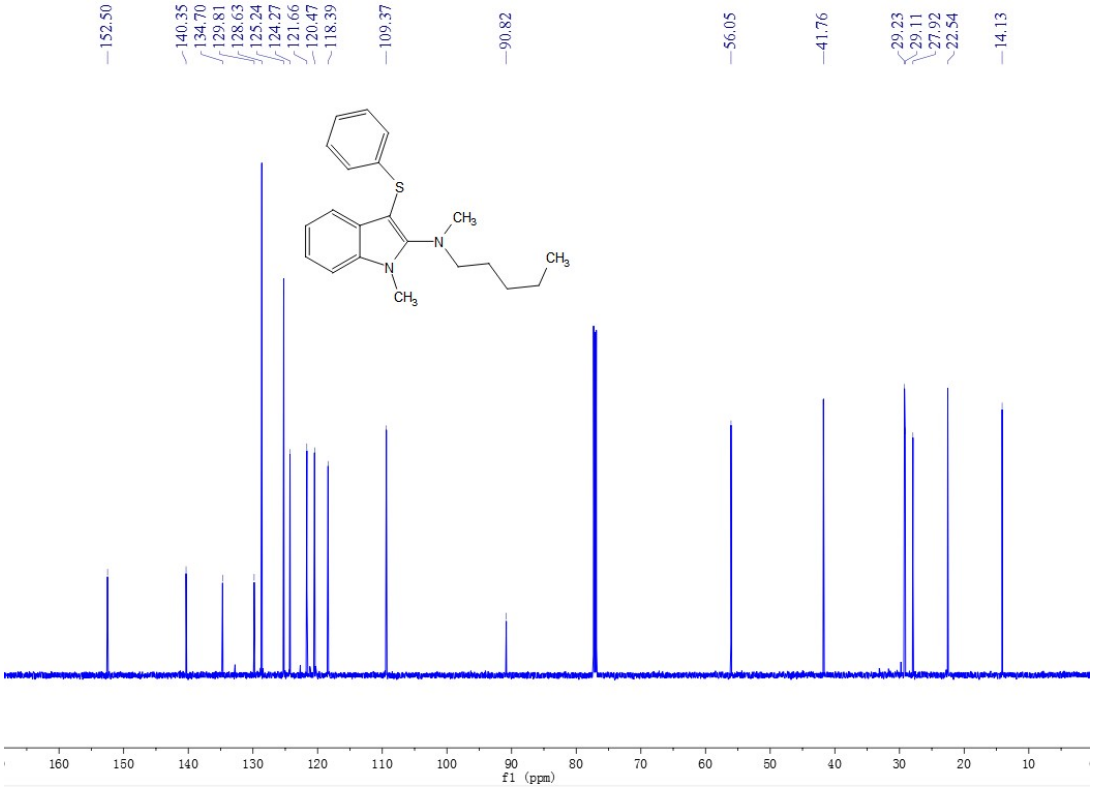
(79) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 41



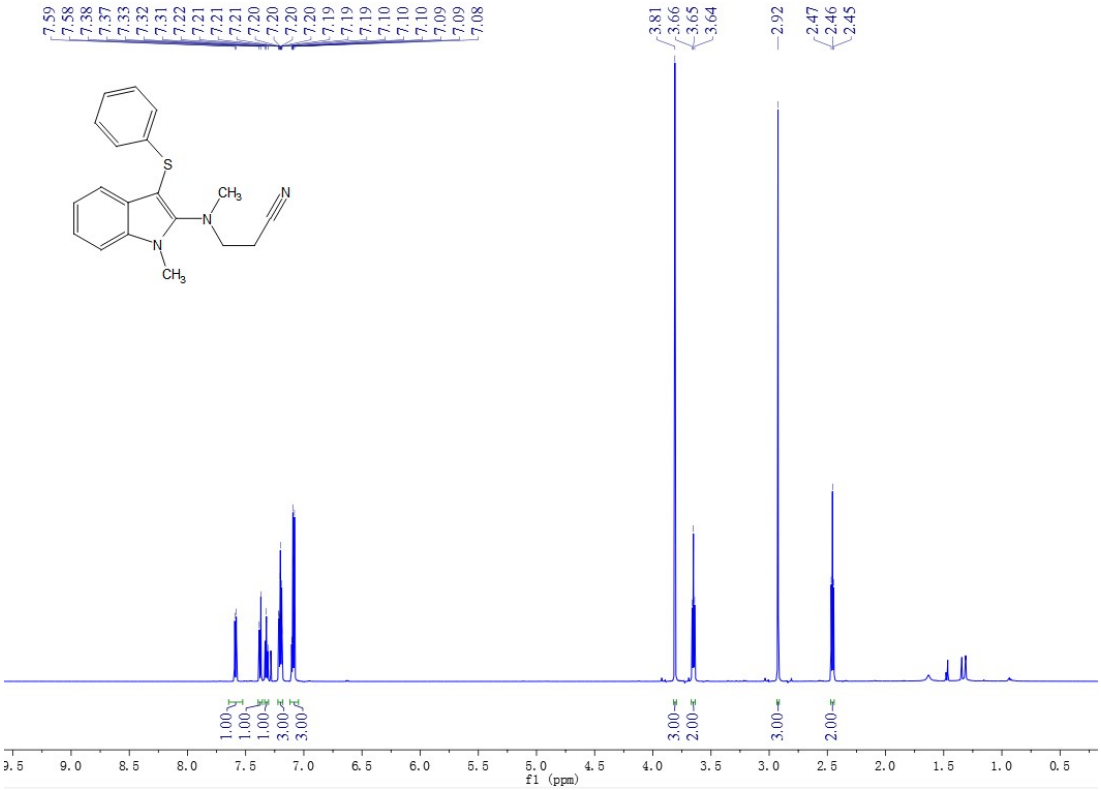
(80) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 42



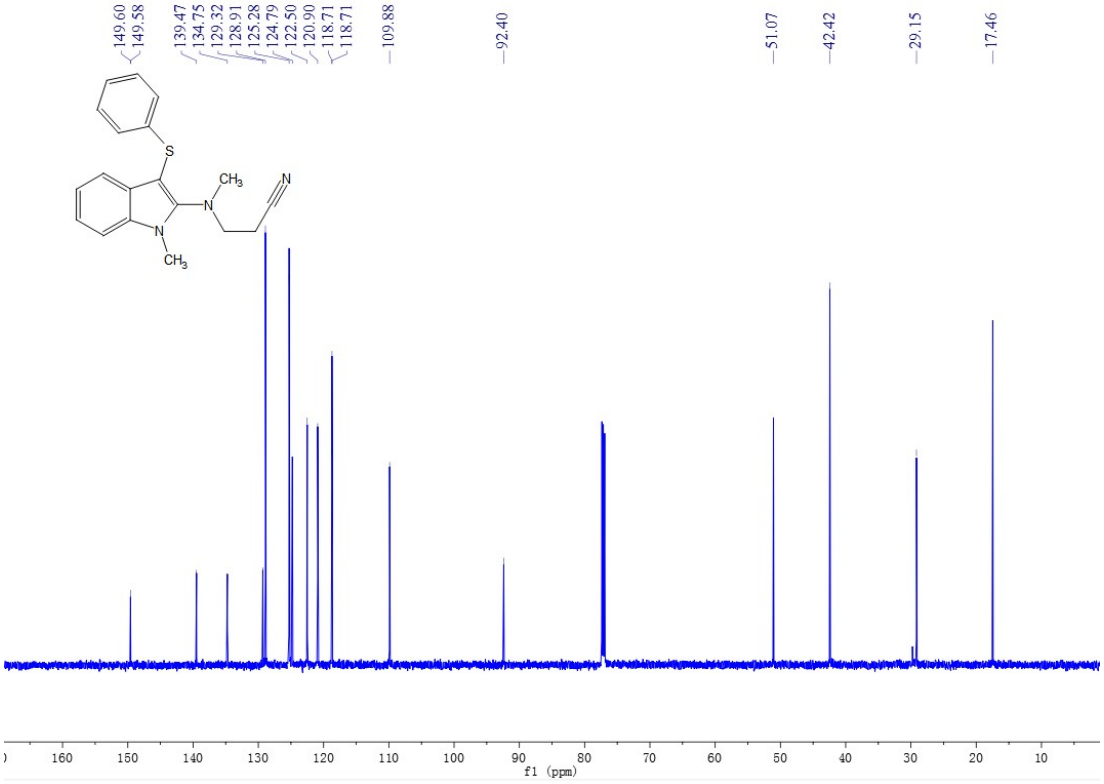
(81) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 42



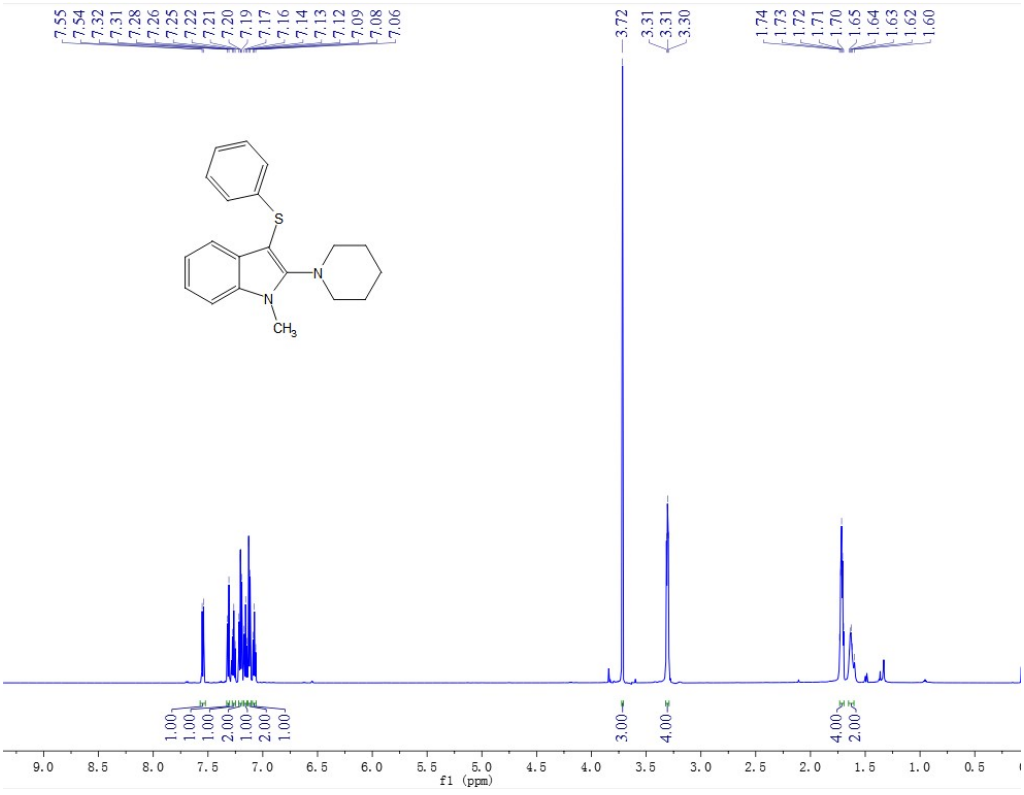
(82) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 43



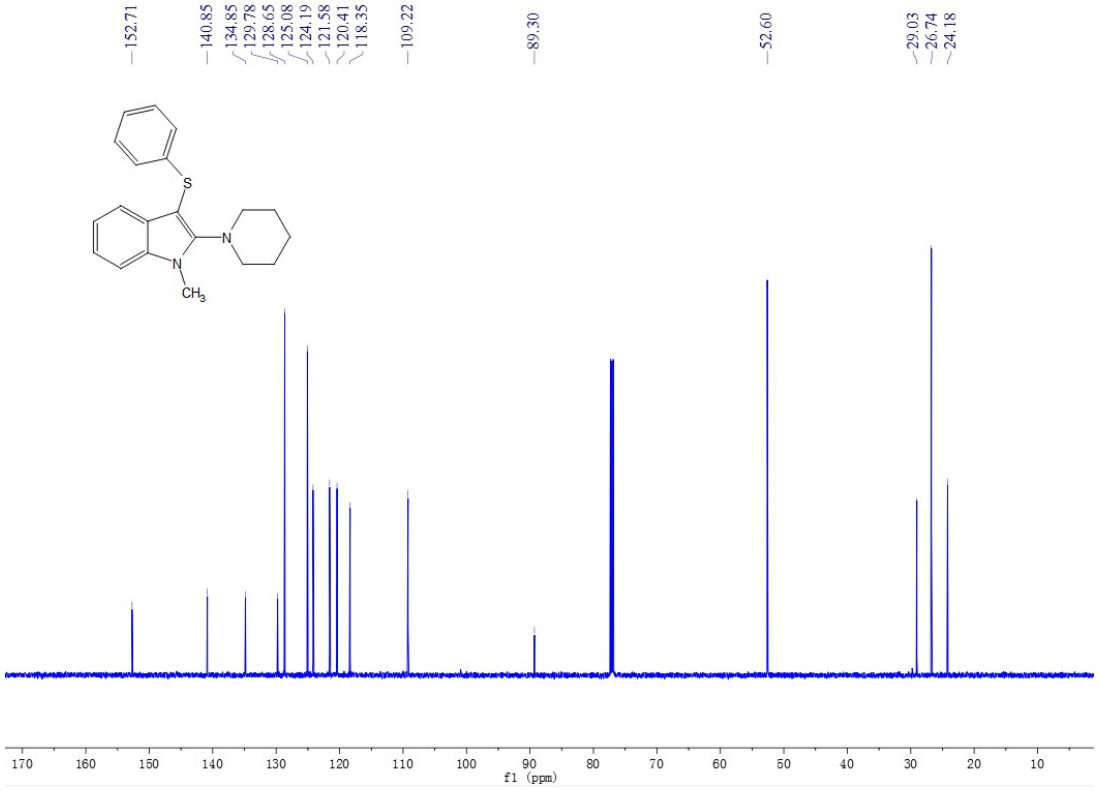
(83) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 43



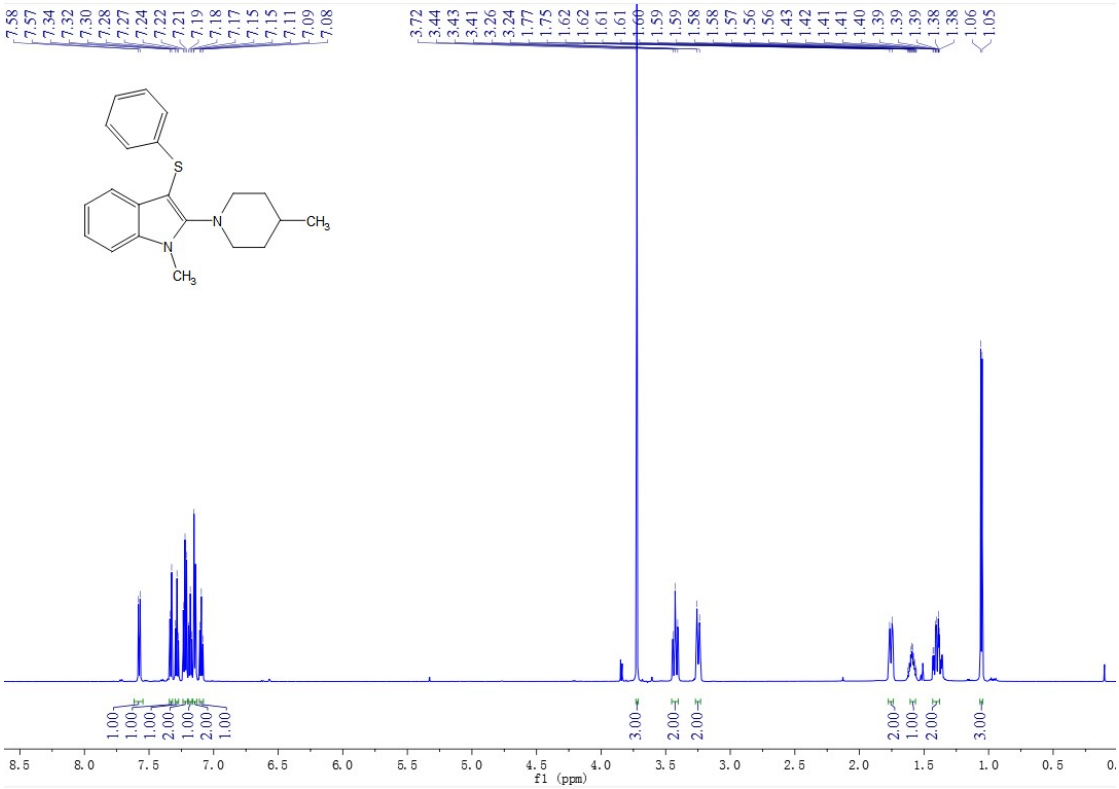
(84) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 44



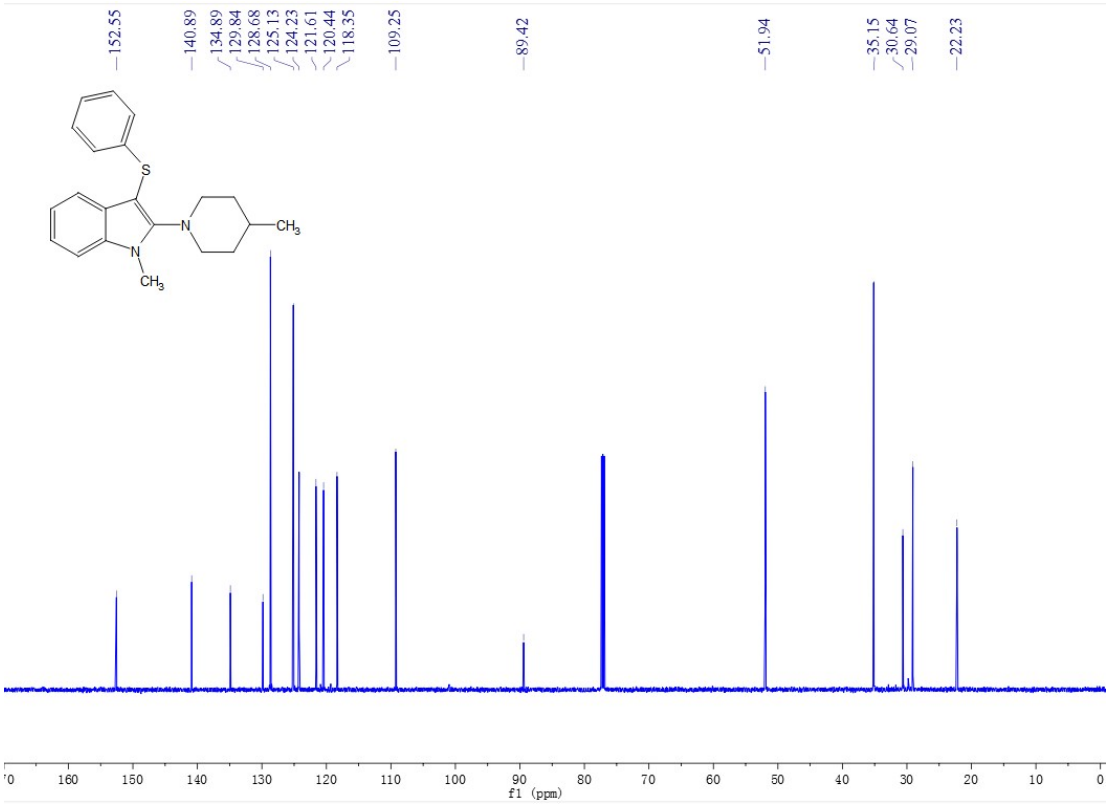
(85) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 44



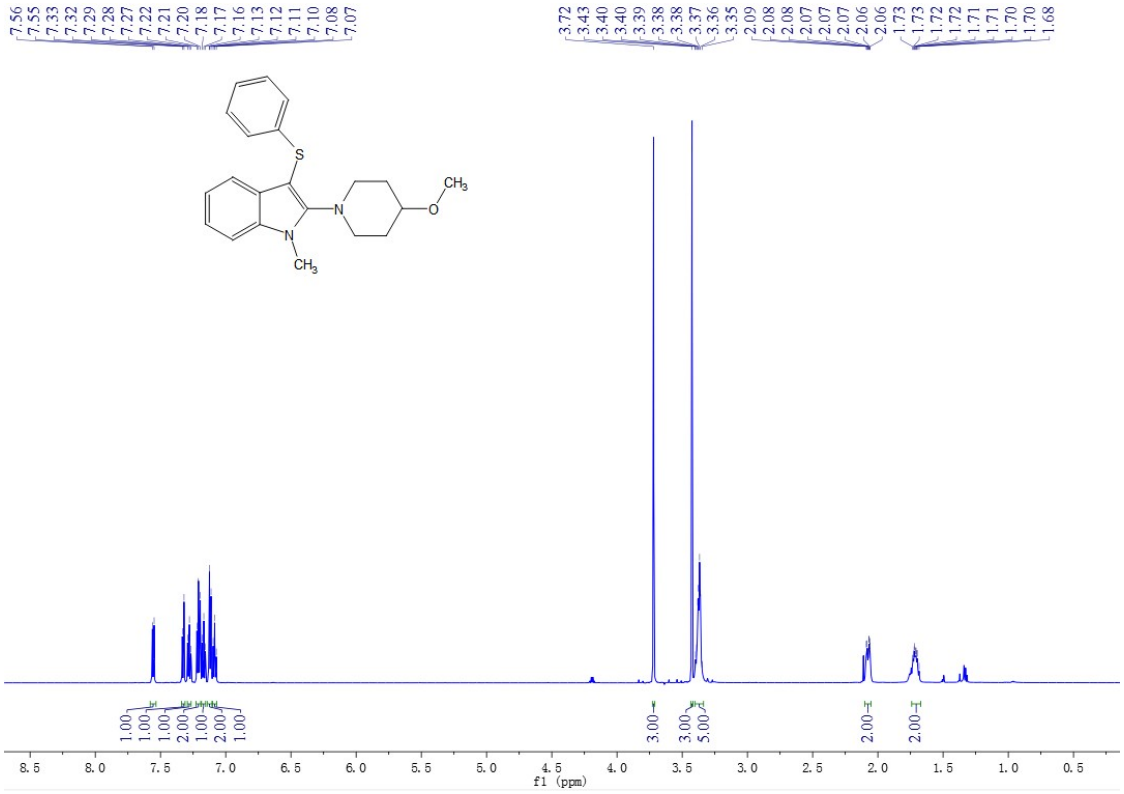
(86) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 45



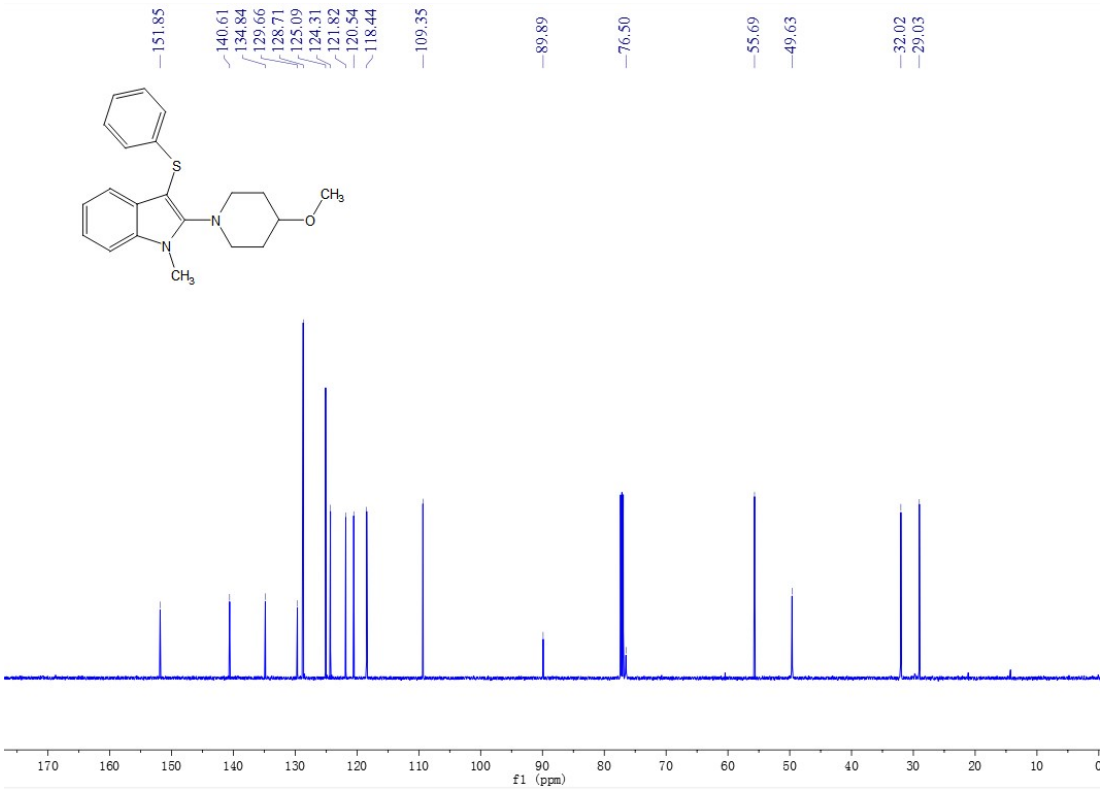
(87) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 45



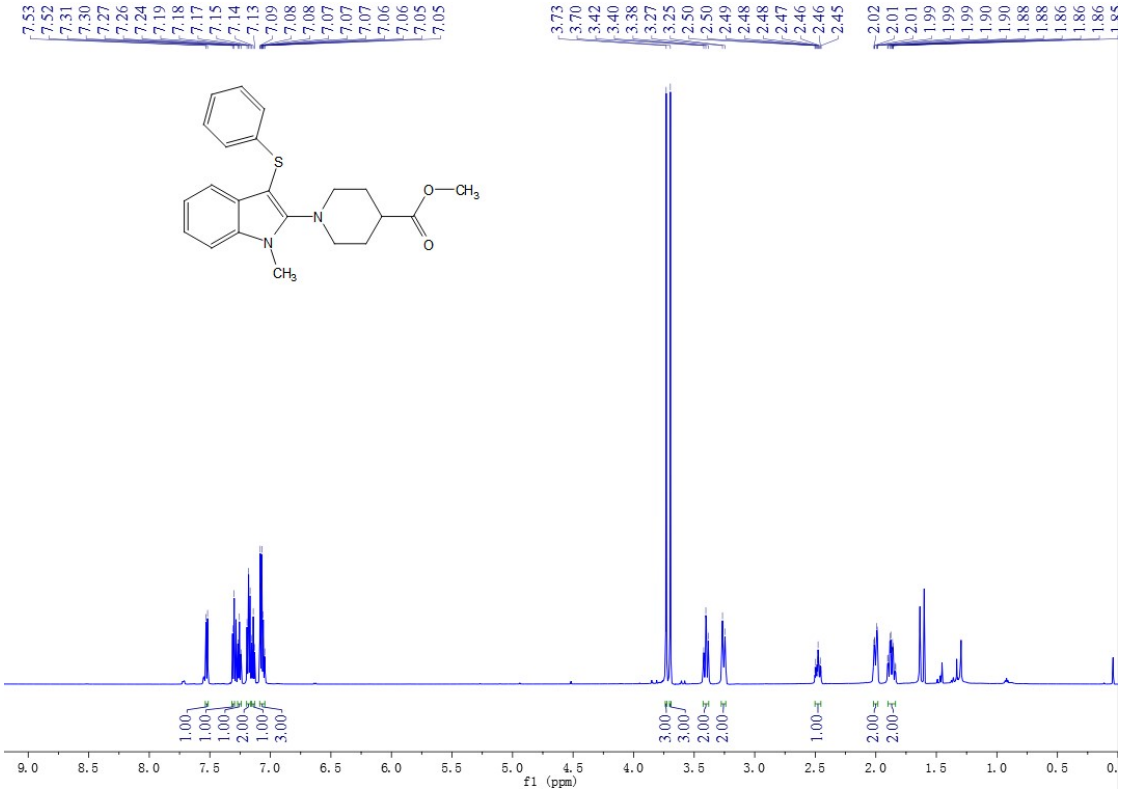
(88) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 46



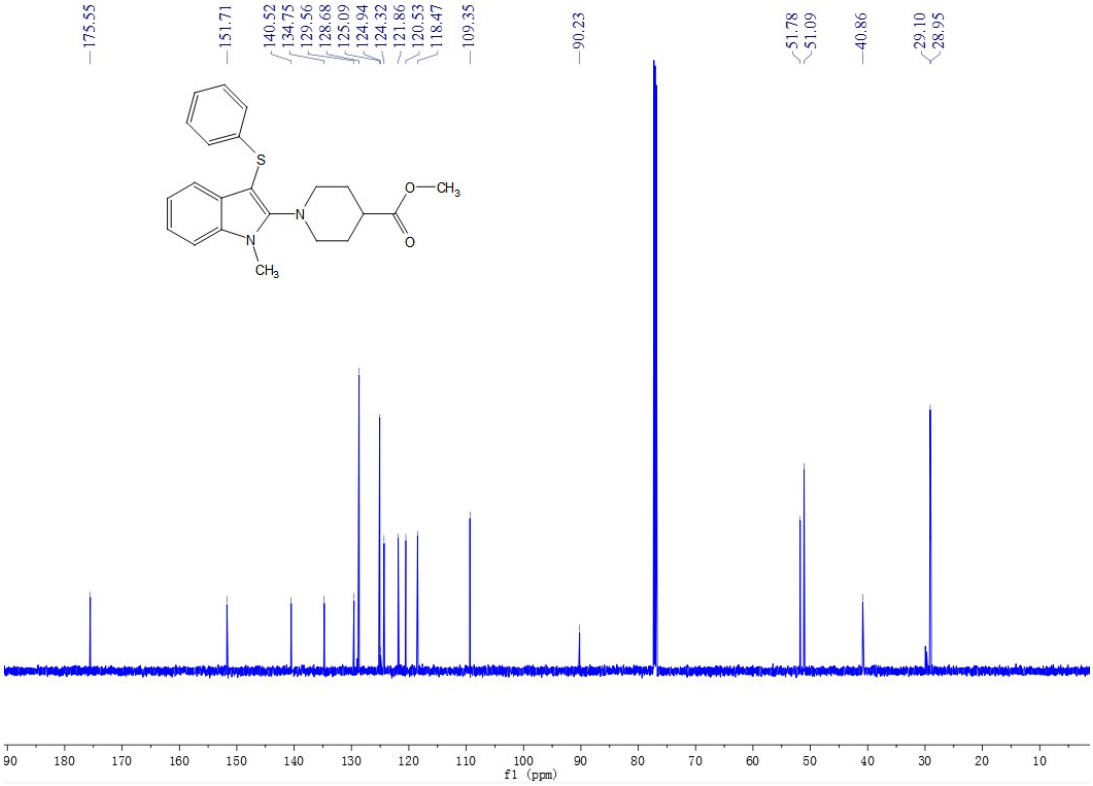
(89) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 46



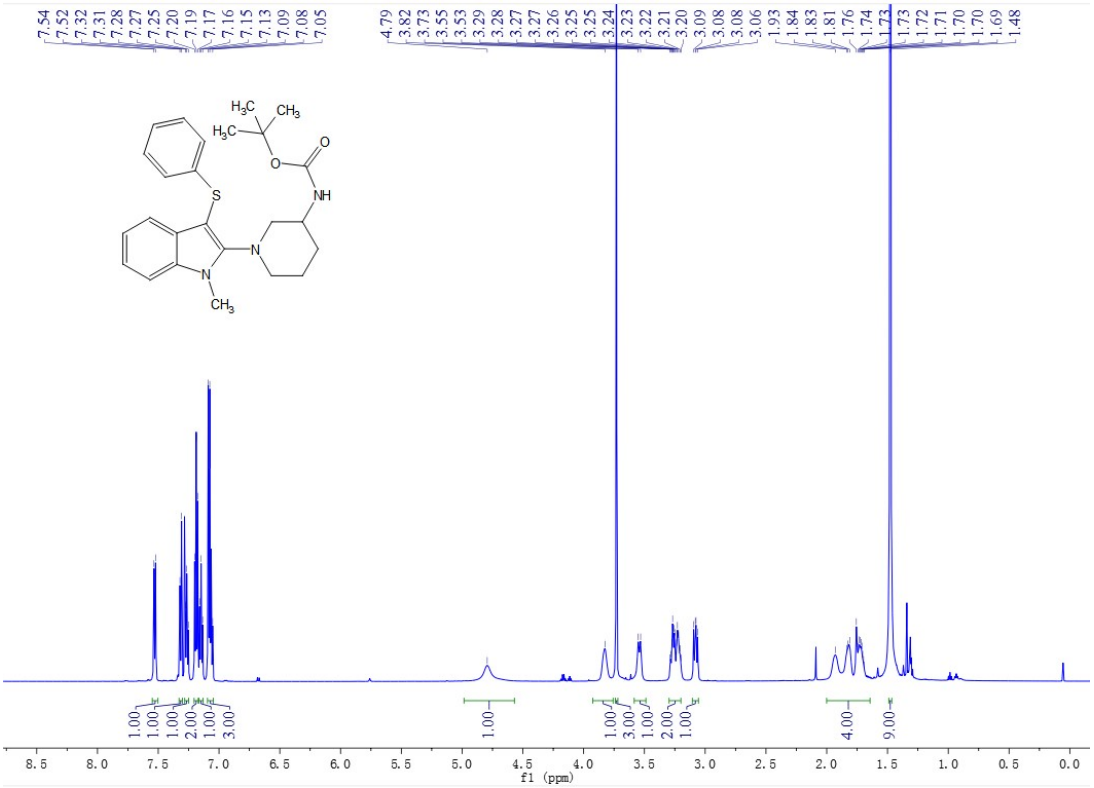
(90) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 47



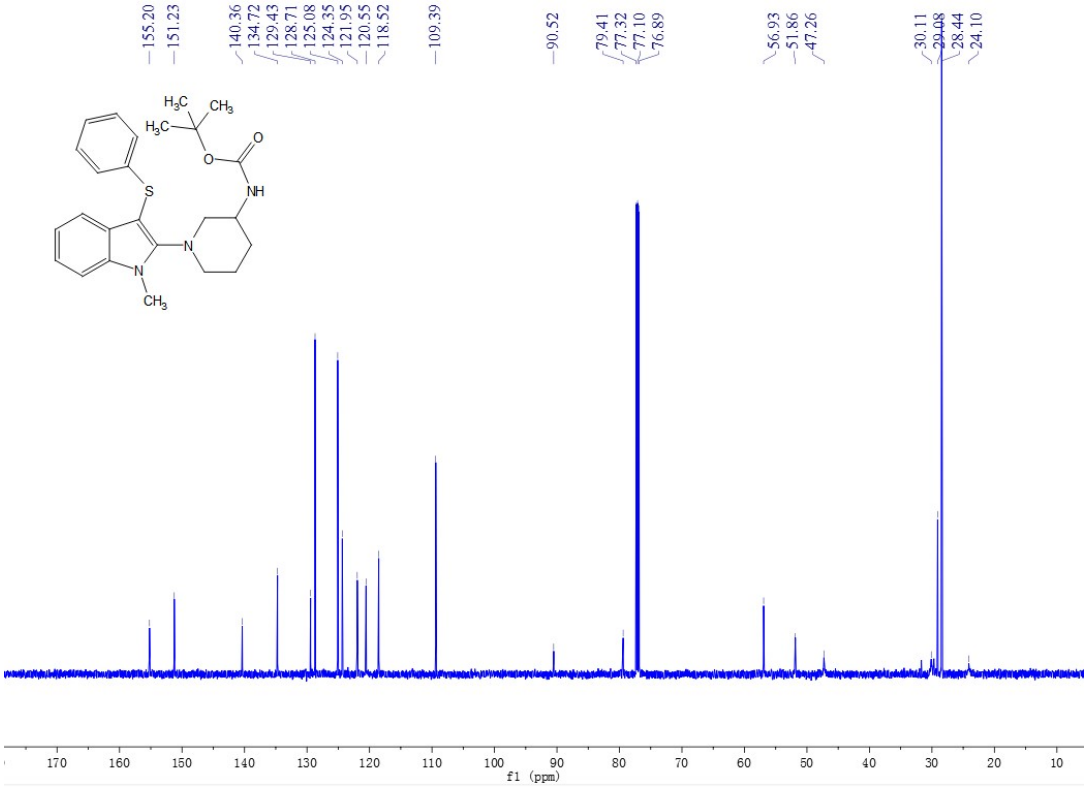
(91) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 47



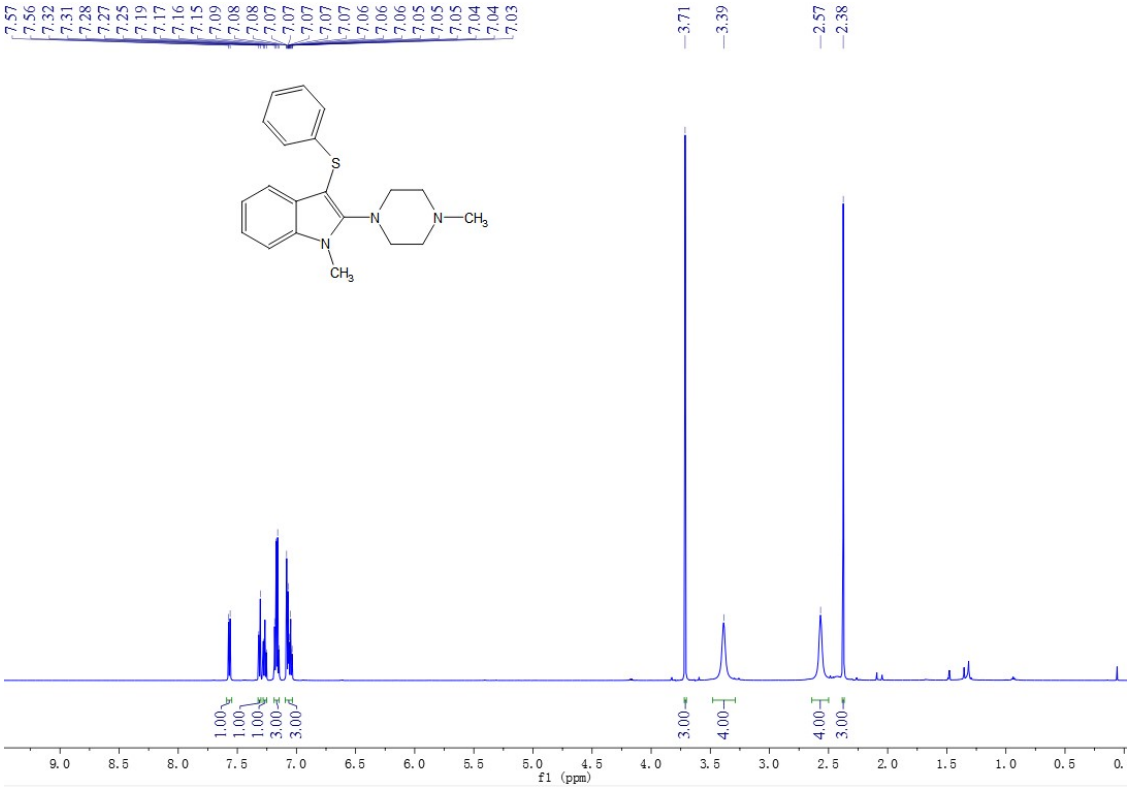
(92) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 48



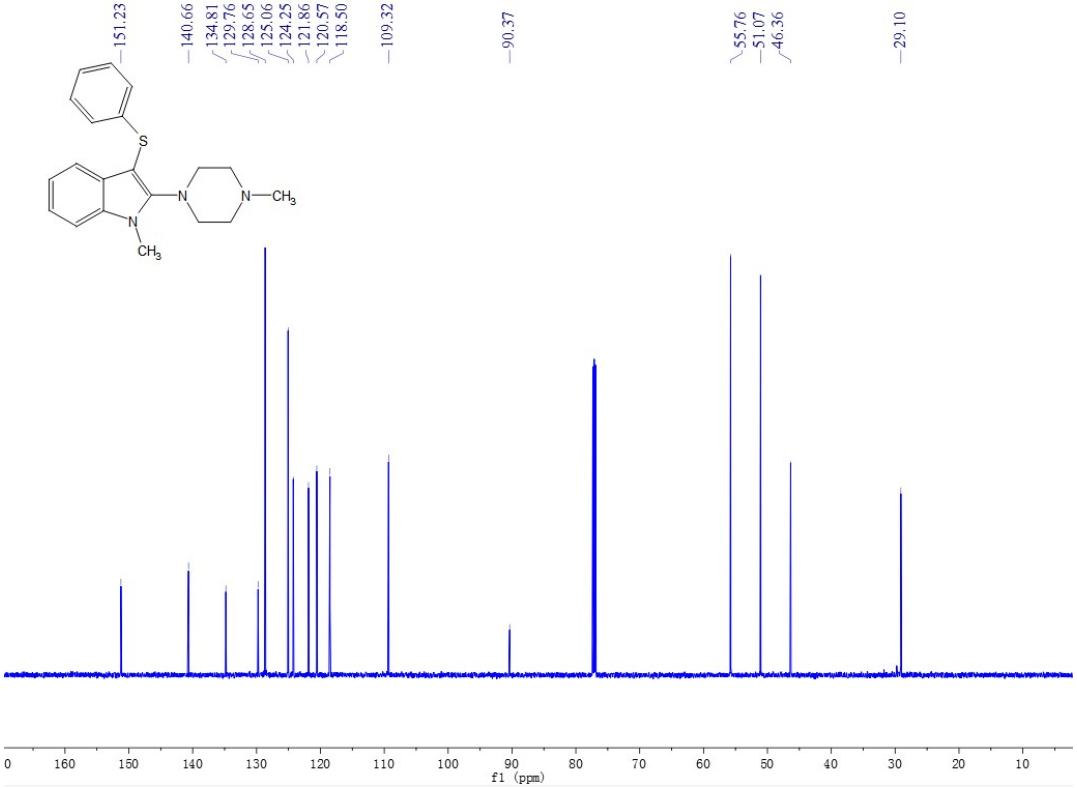
(93) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 48



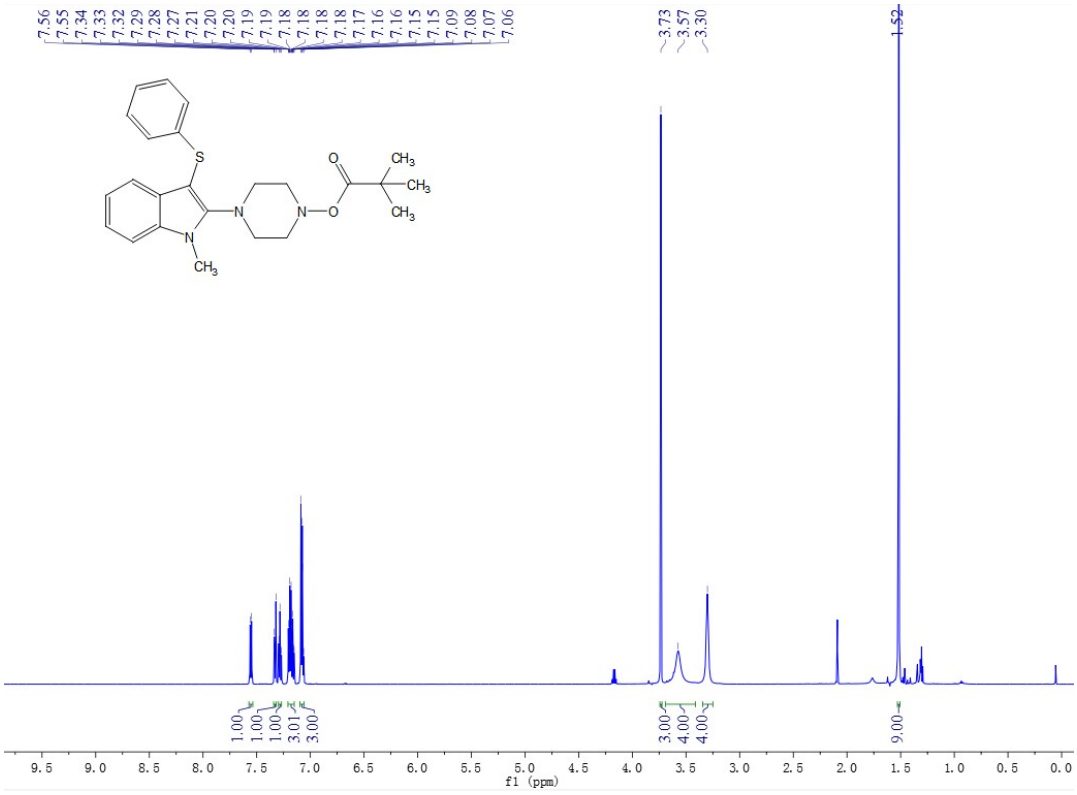
(94) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 49



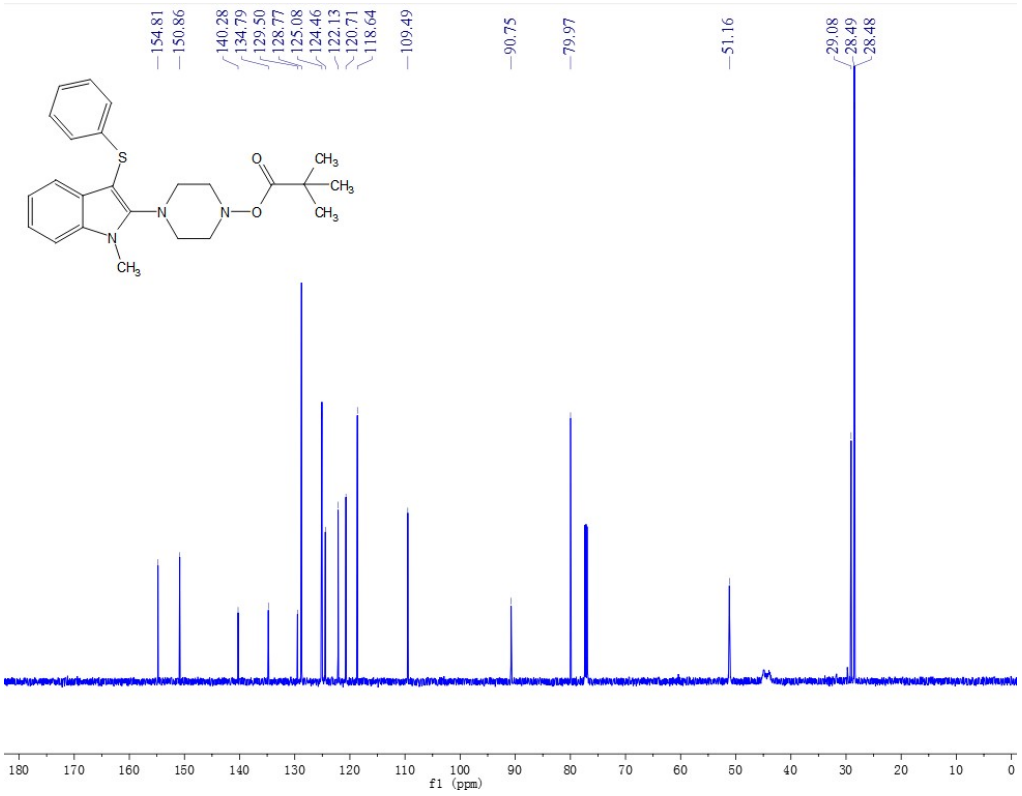
(95) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 49



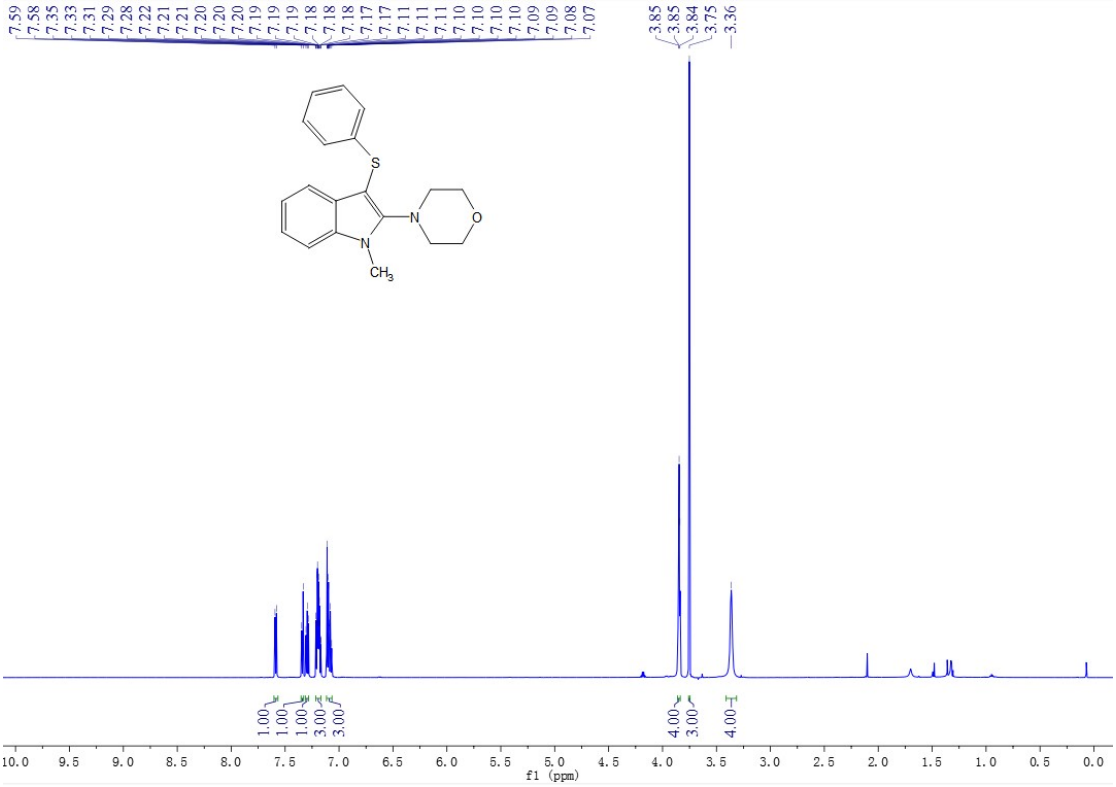
(96) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 50



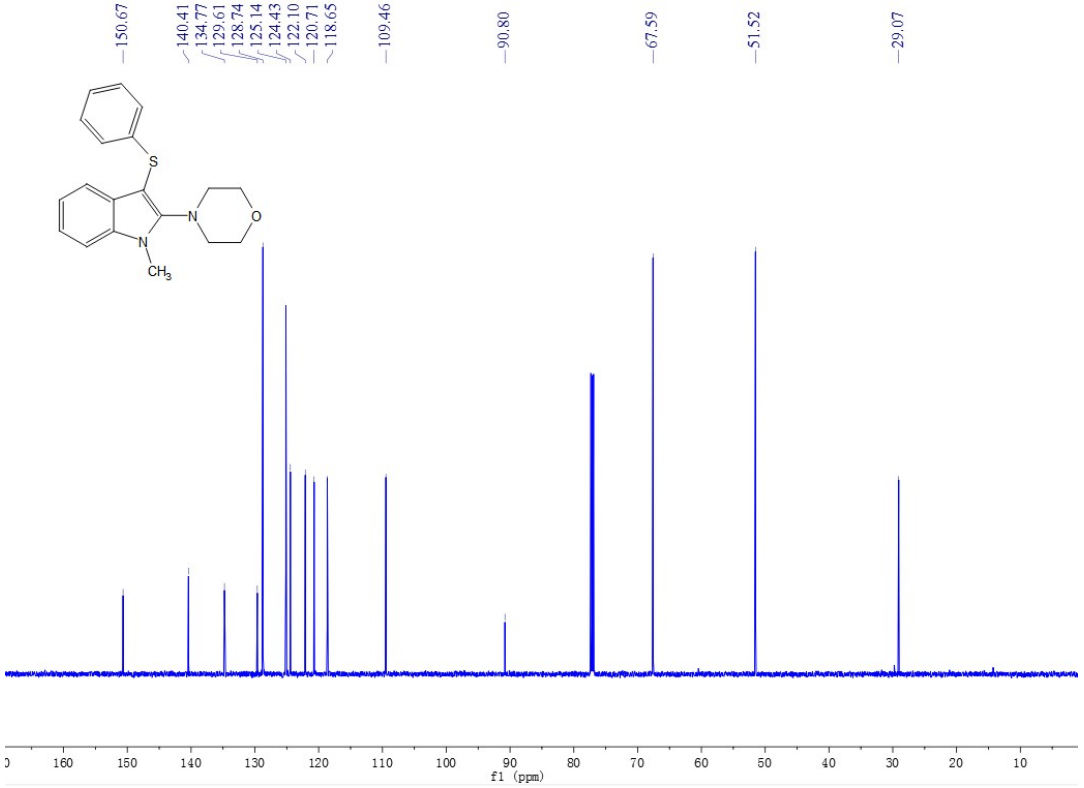
(97) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 50



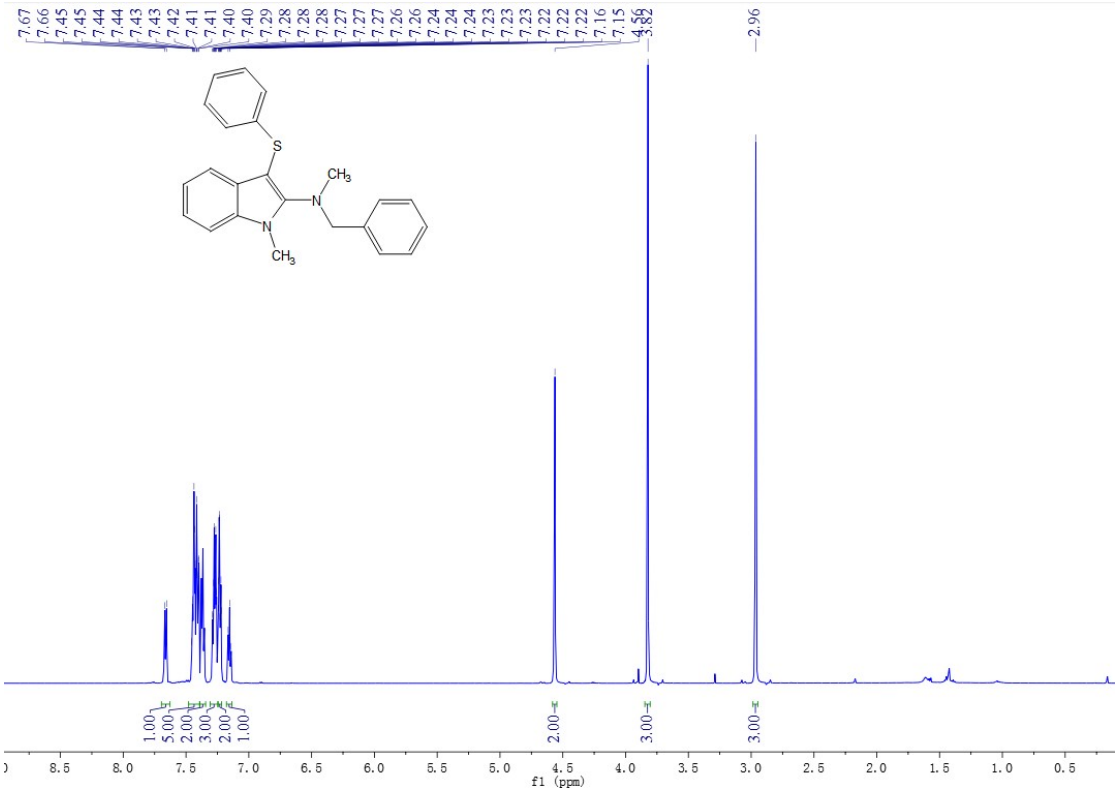
(98) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 51



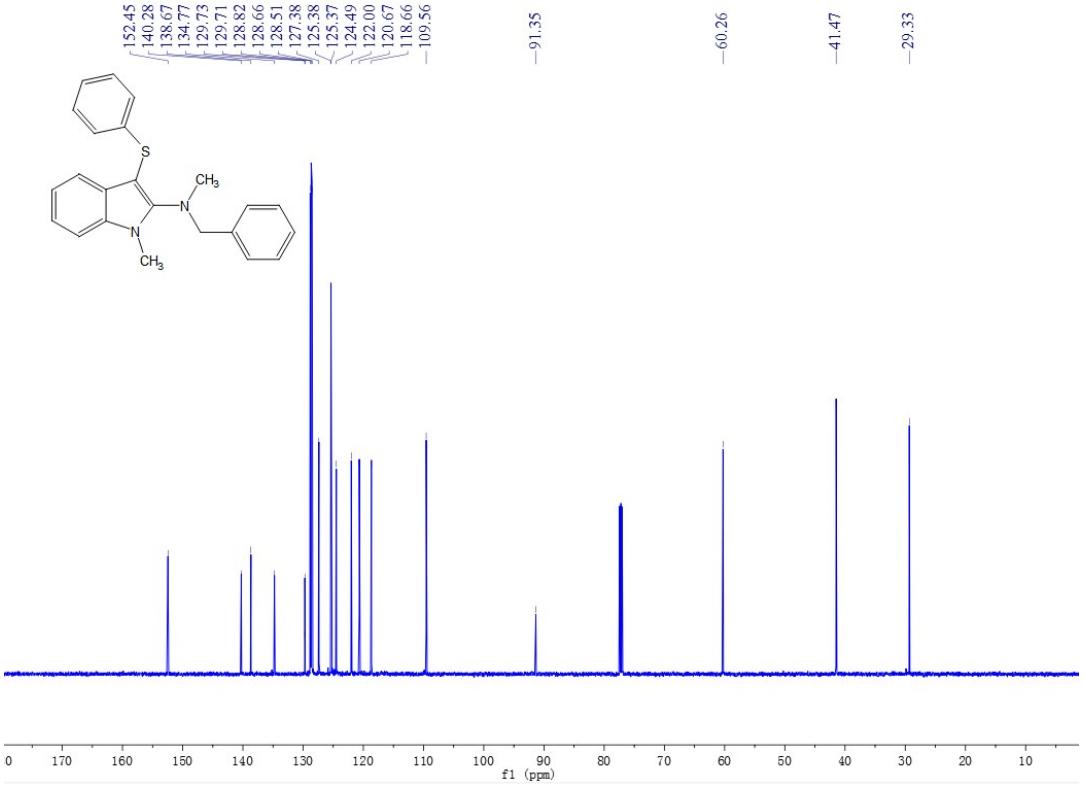
(99) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 51



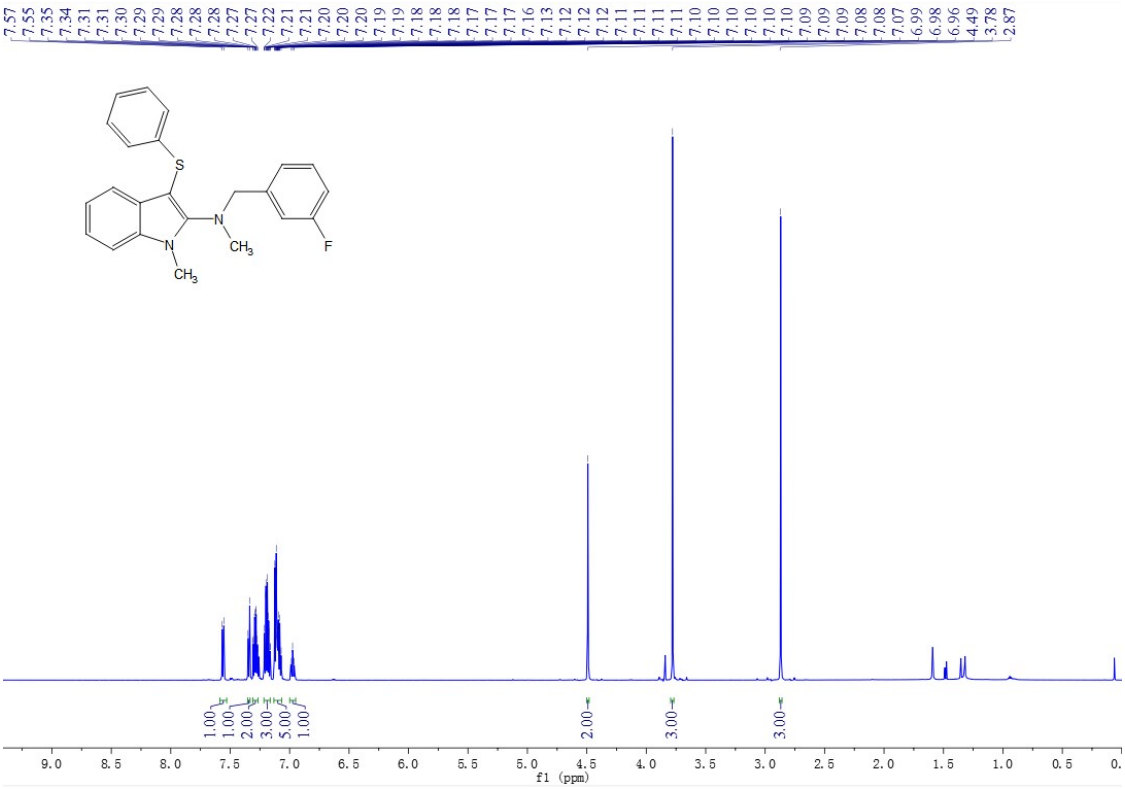
(100) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 52



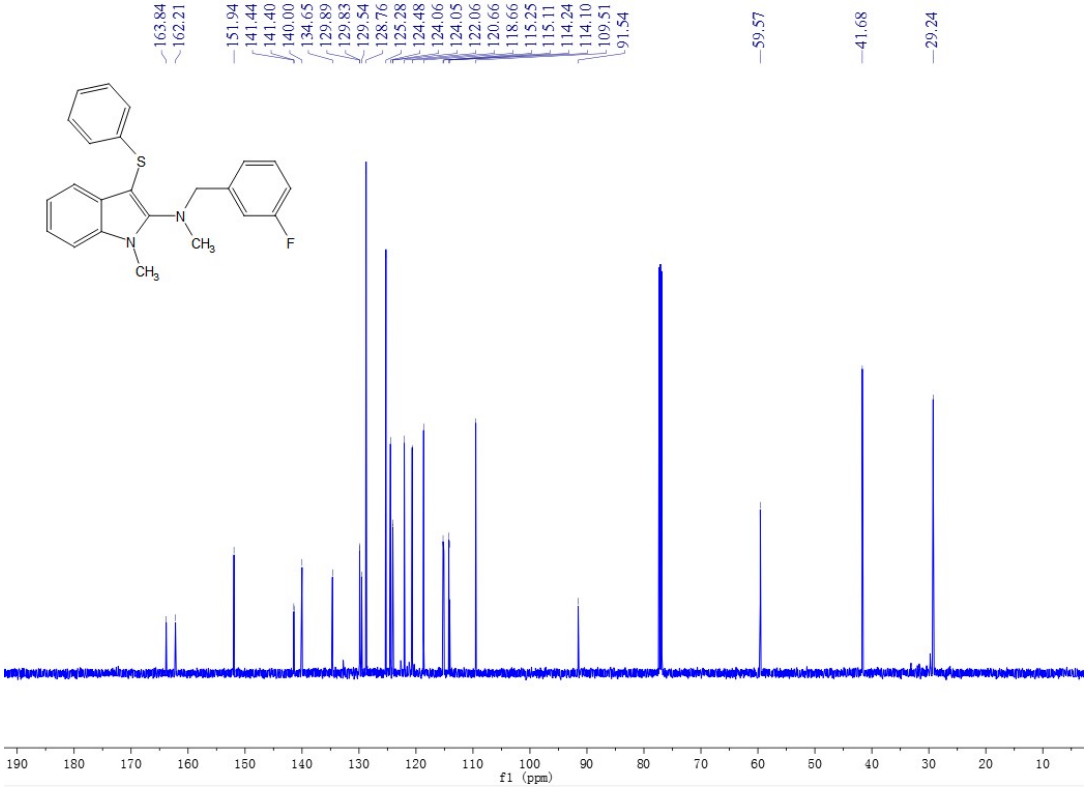
(101) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 52



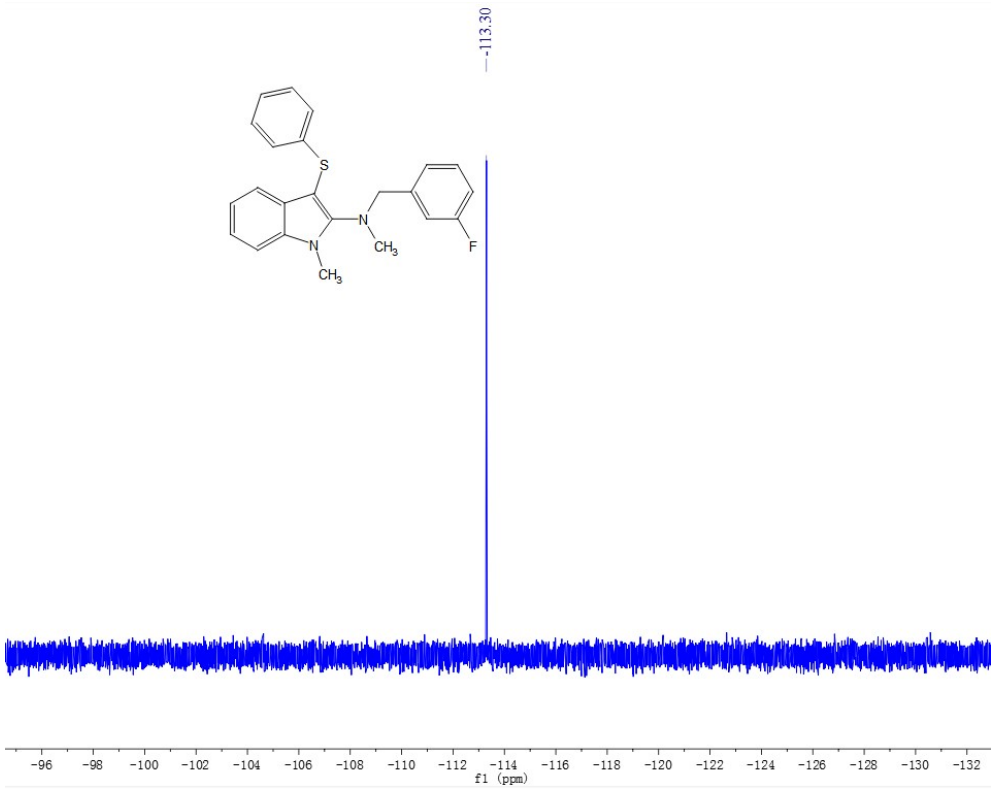
(102) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 53



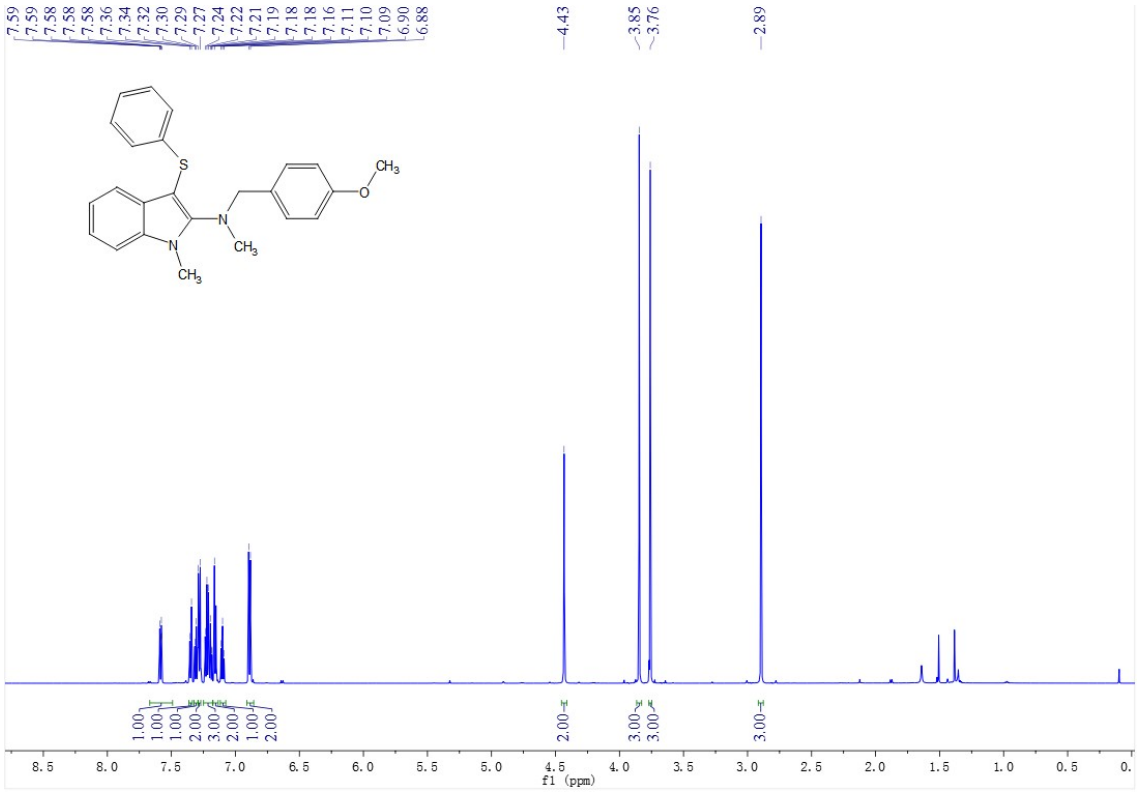
(103) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 53



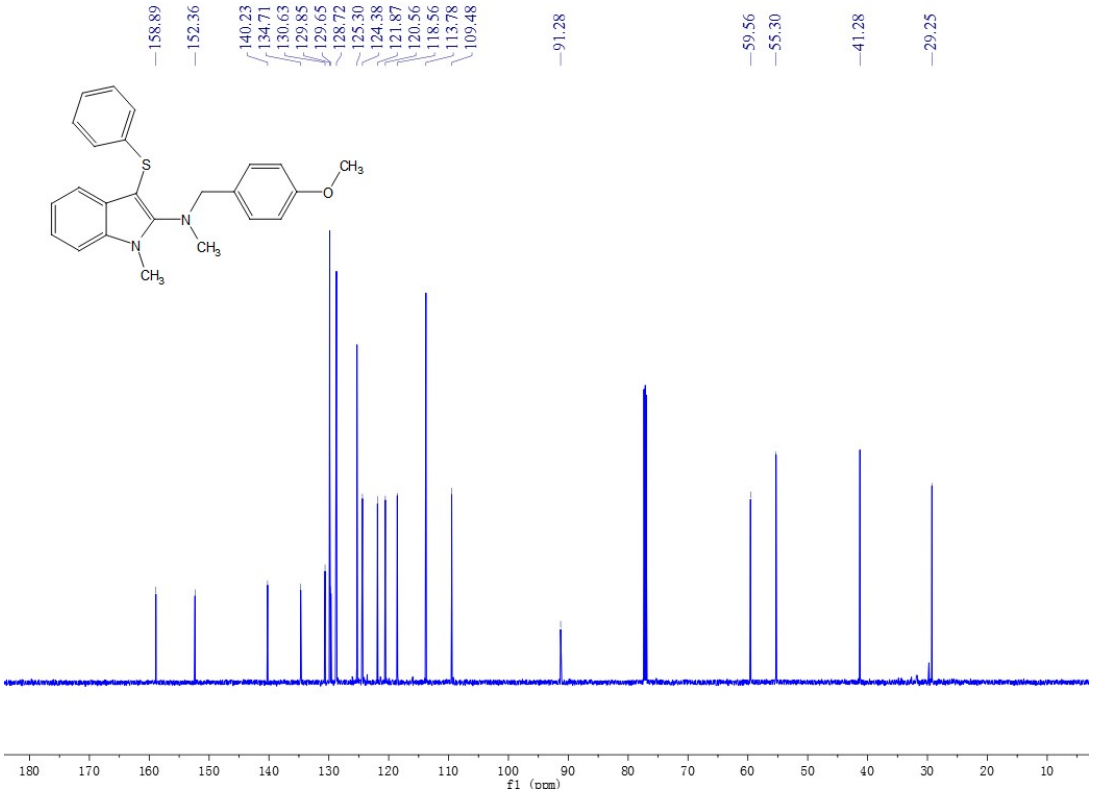
(104) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 53



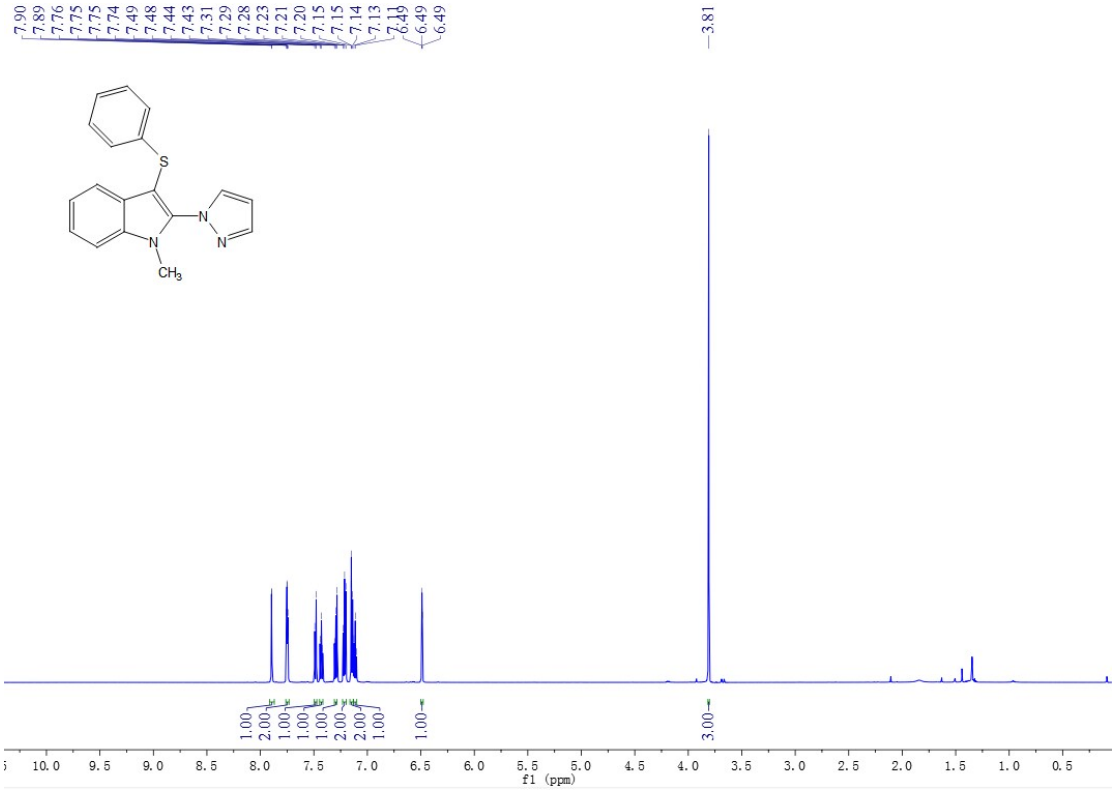
(105) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 54



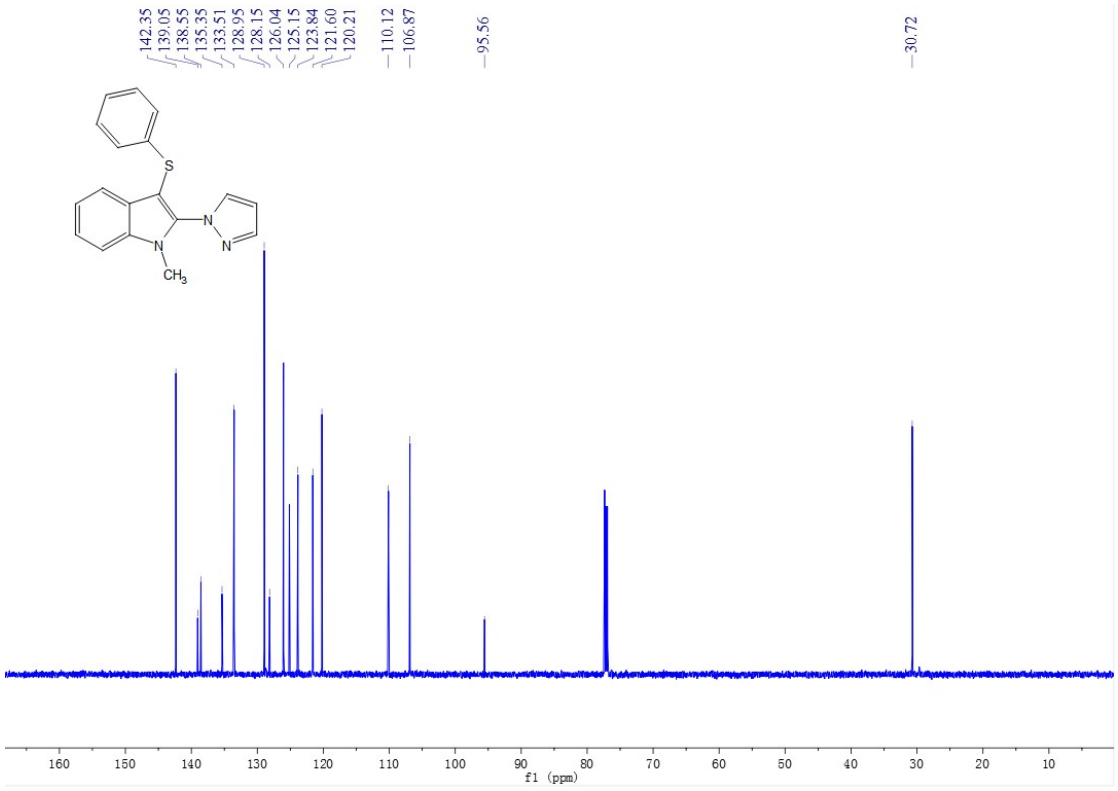
(106) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 54



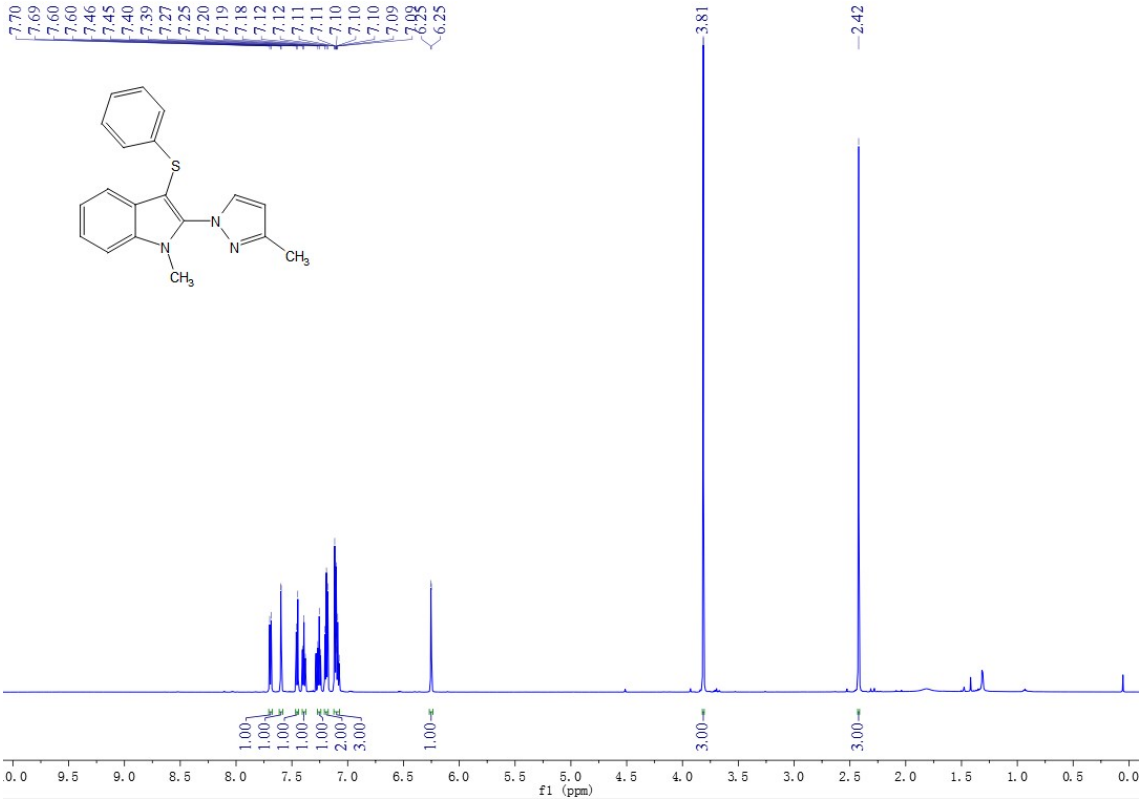
(107) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 55



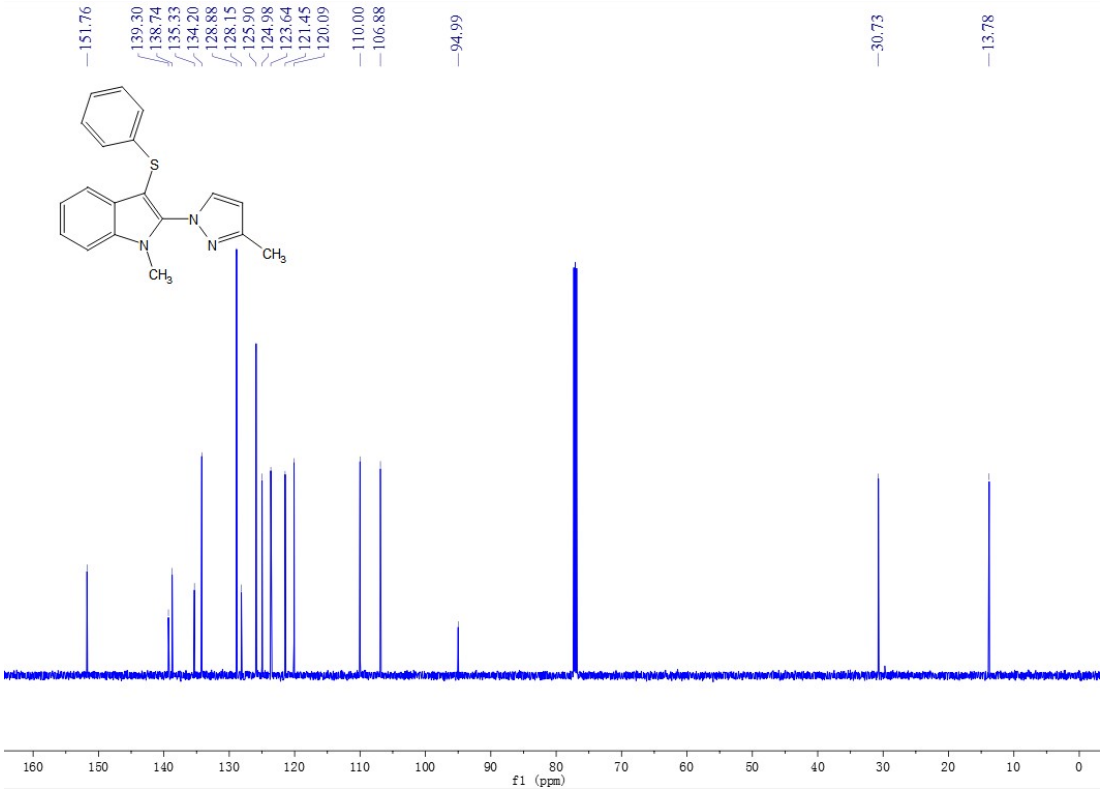
(108) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 55



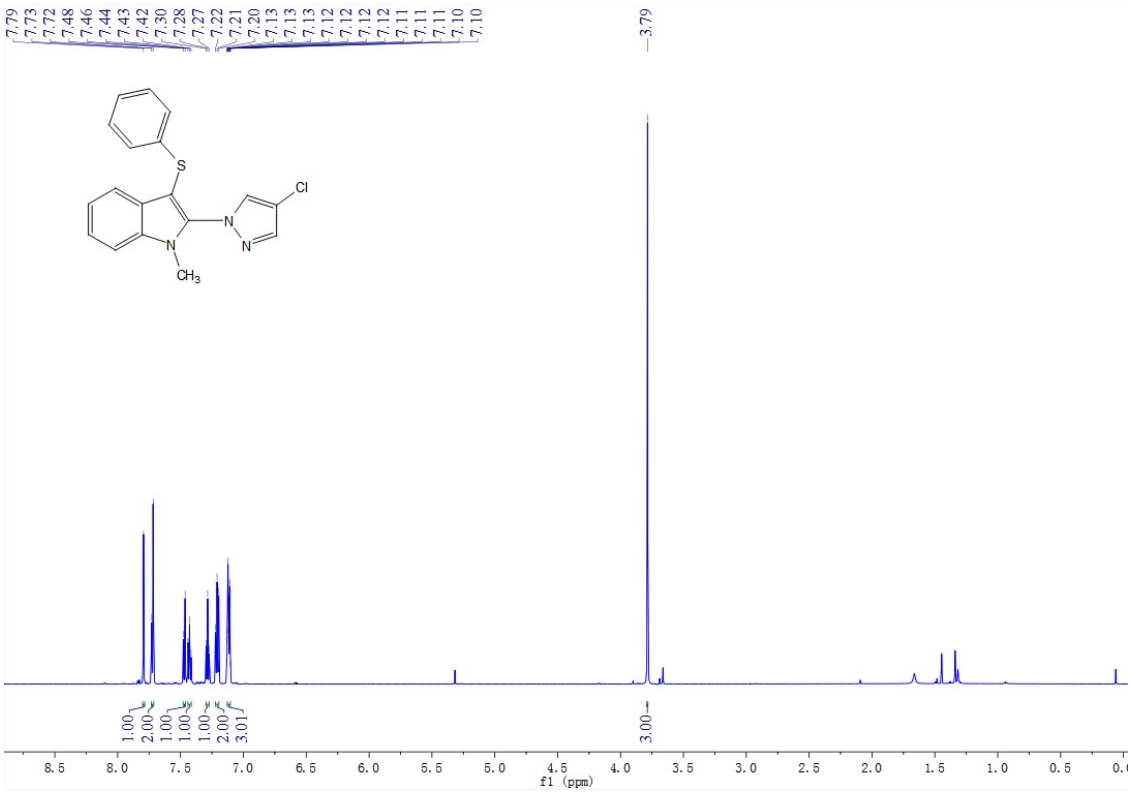
(109) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 56



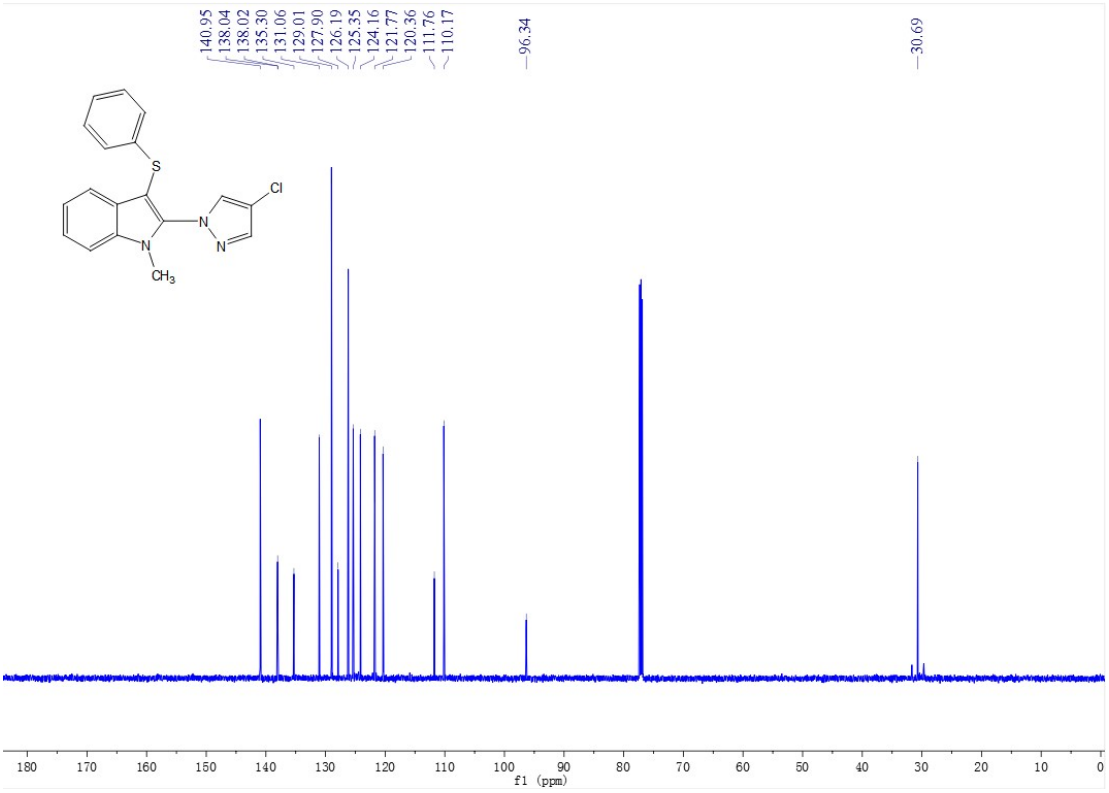
(110) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 56



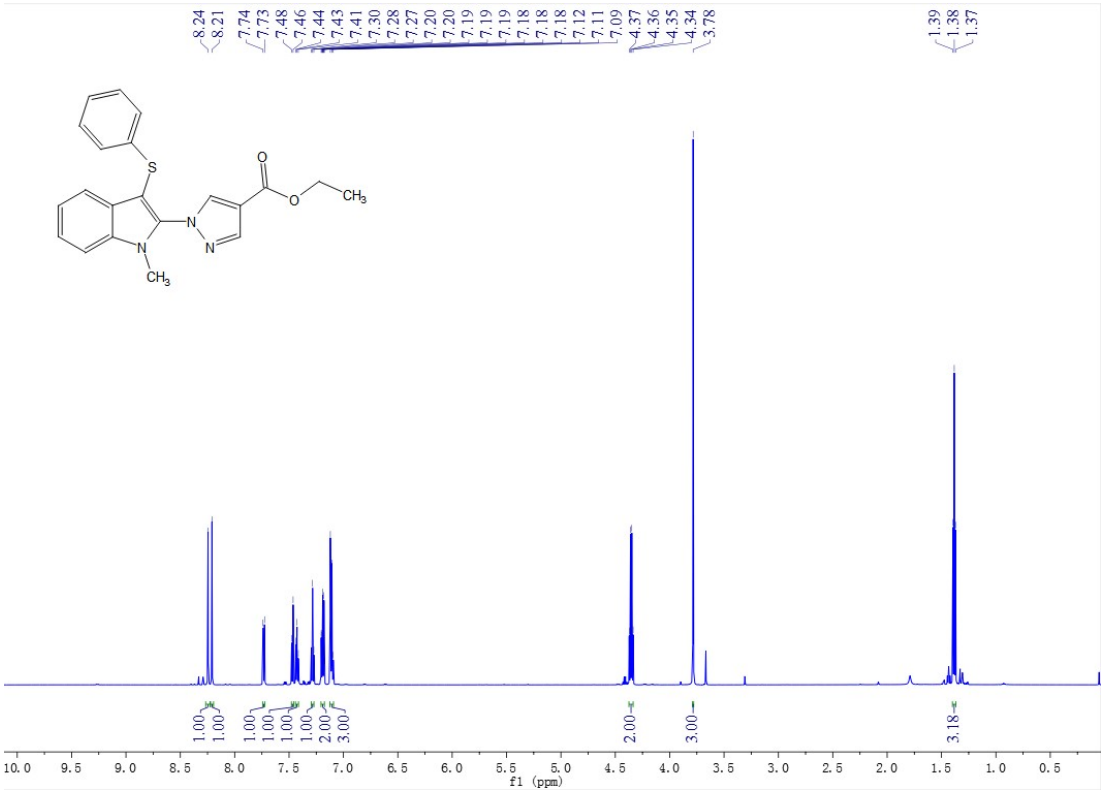
(111) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 57



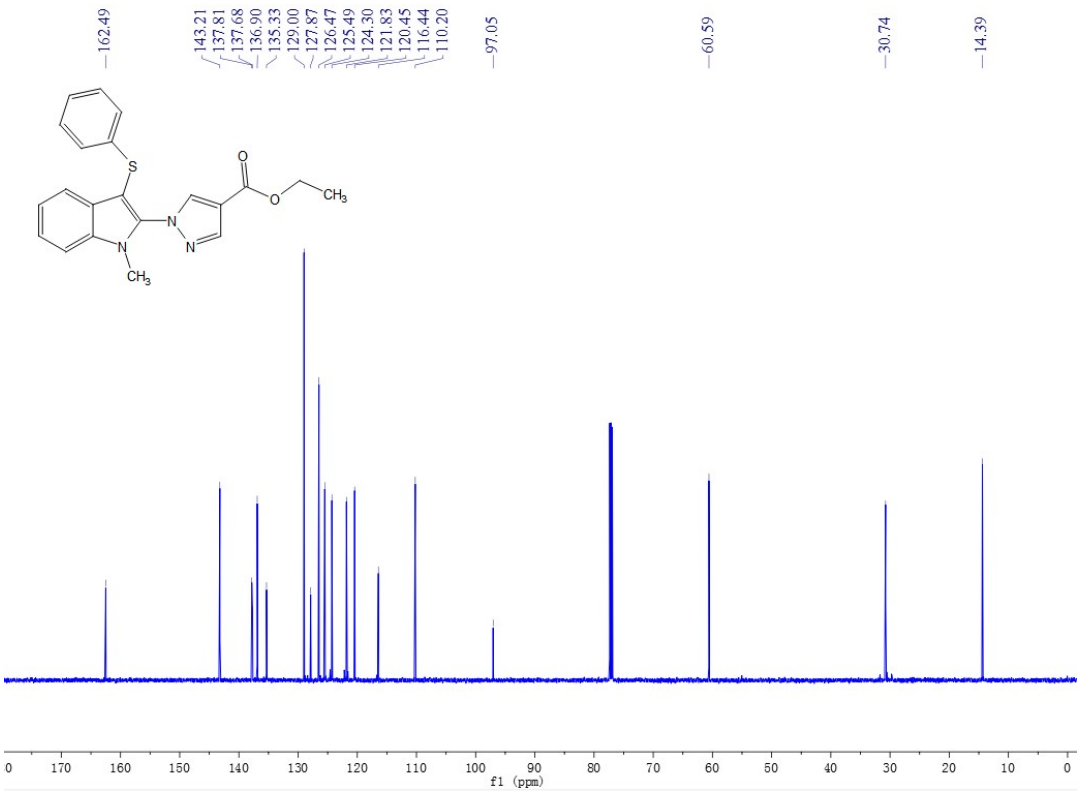
(112) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 57



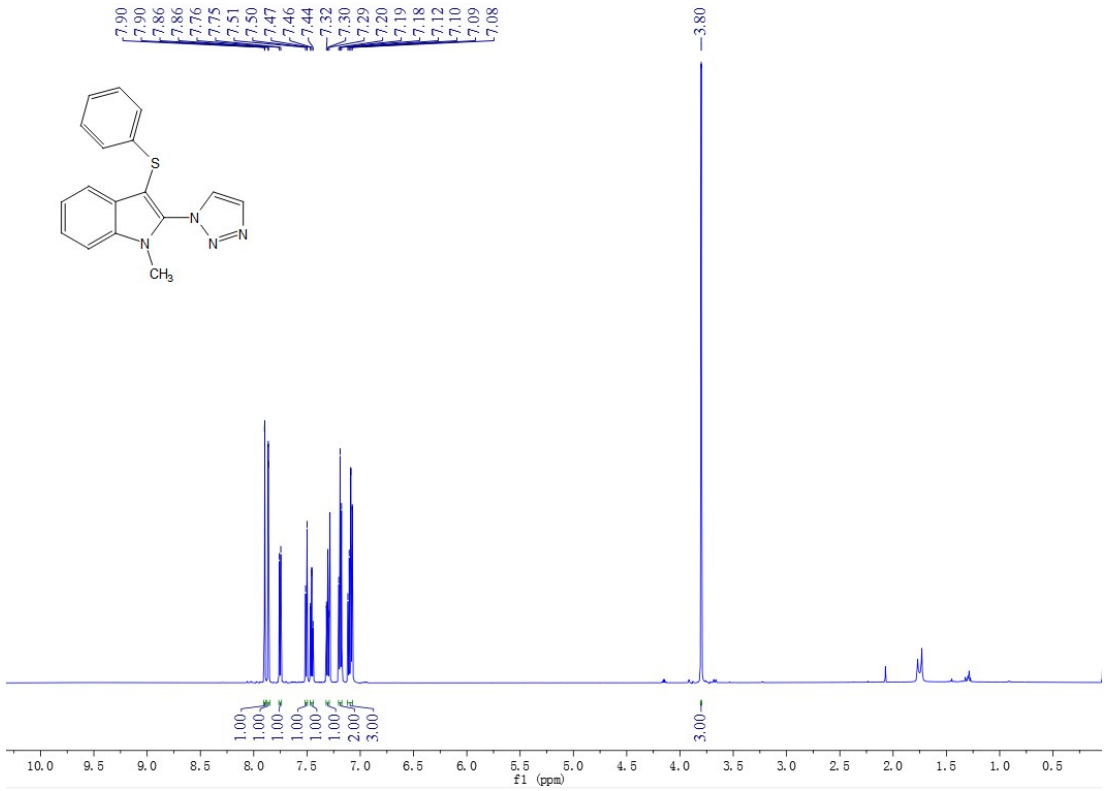
(113) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 58



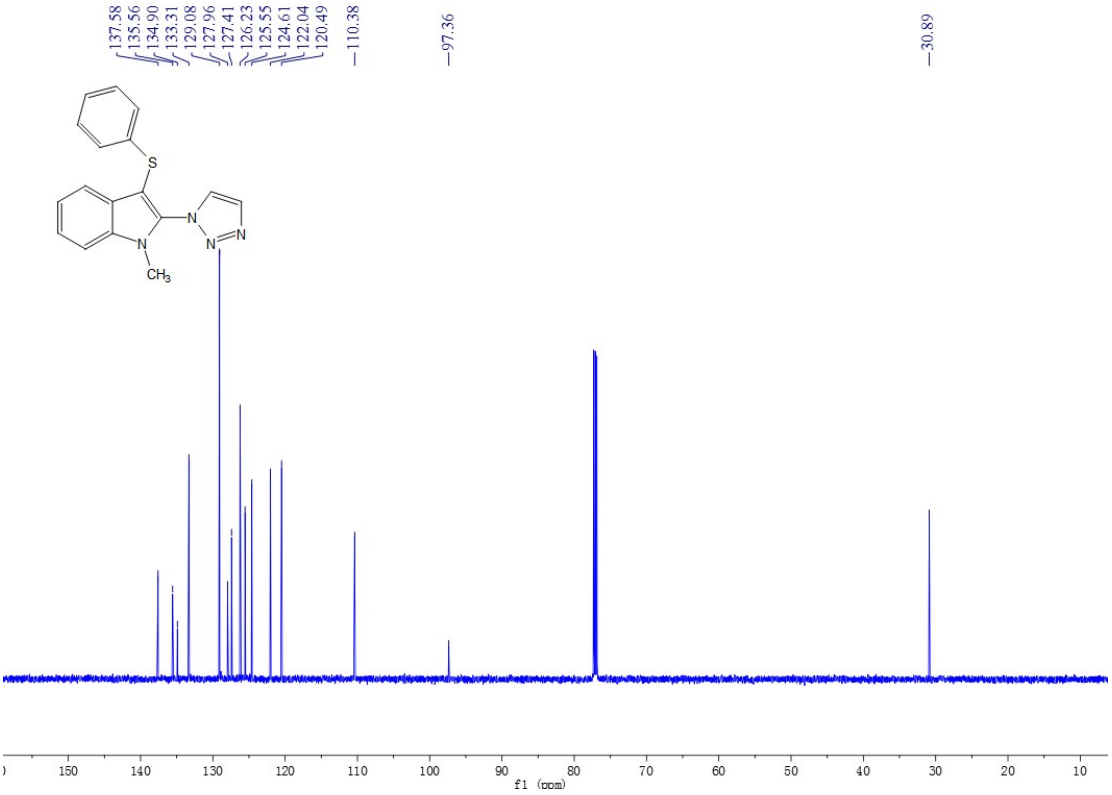
(114) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 58



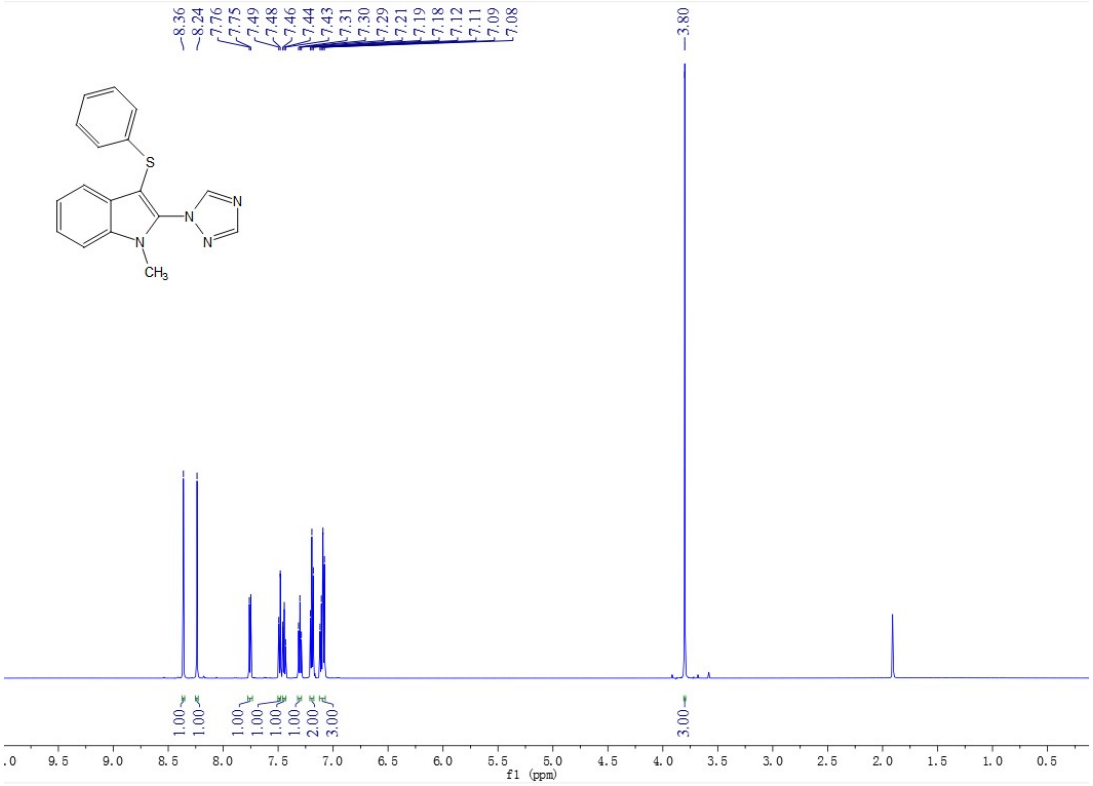
(115) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 59



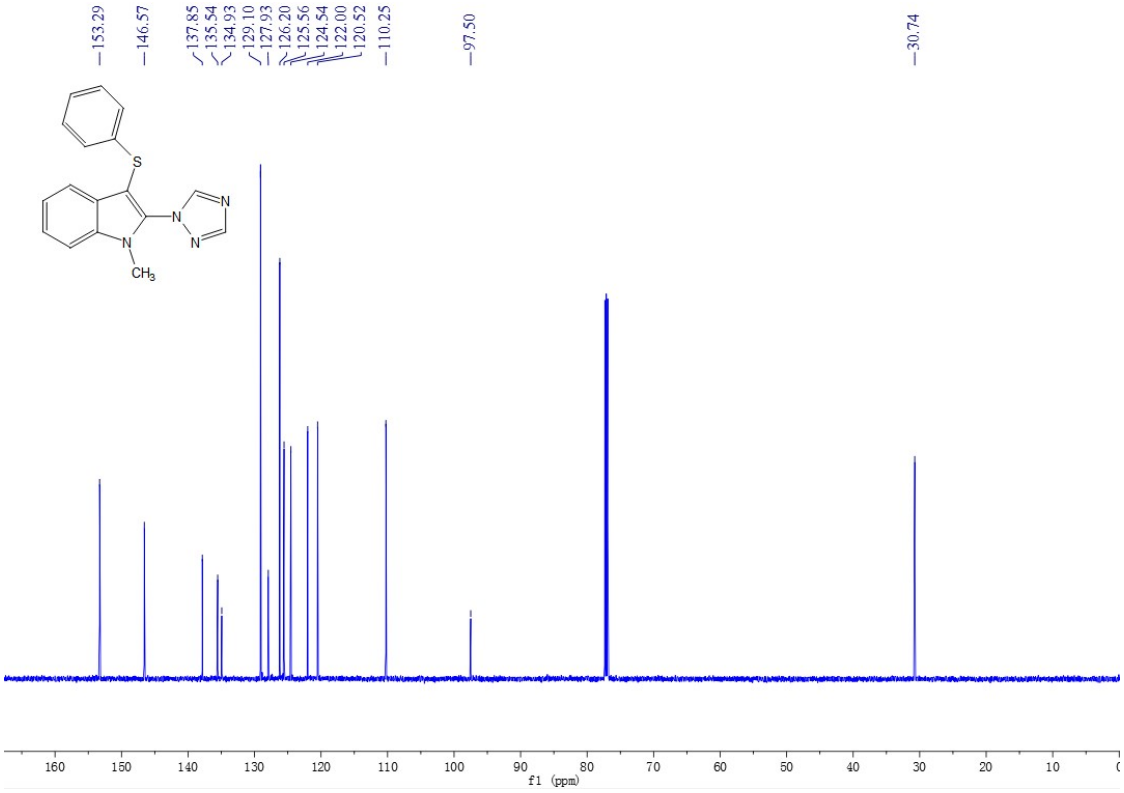
(116) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 59



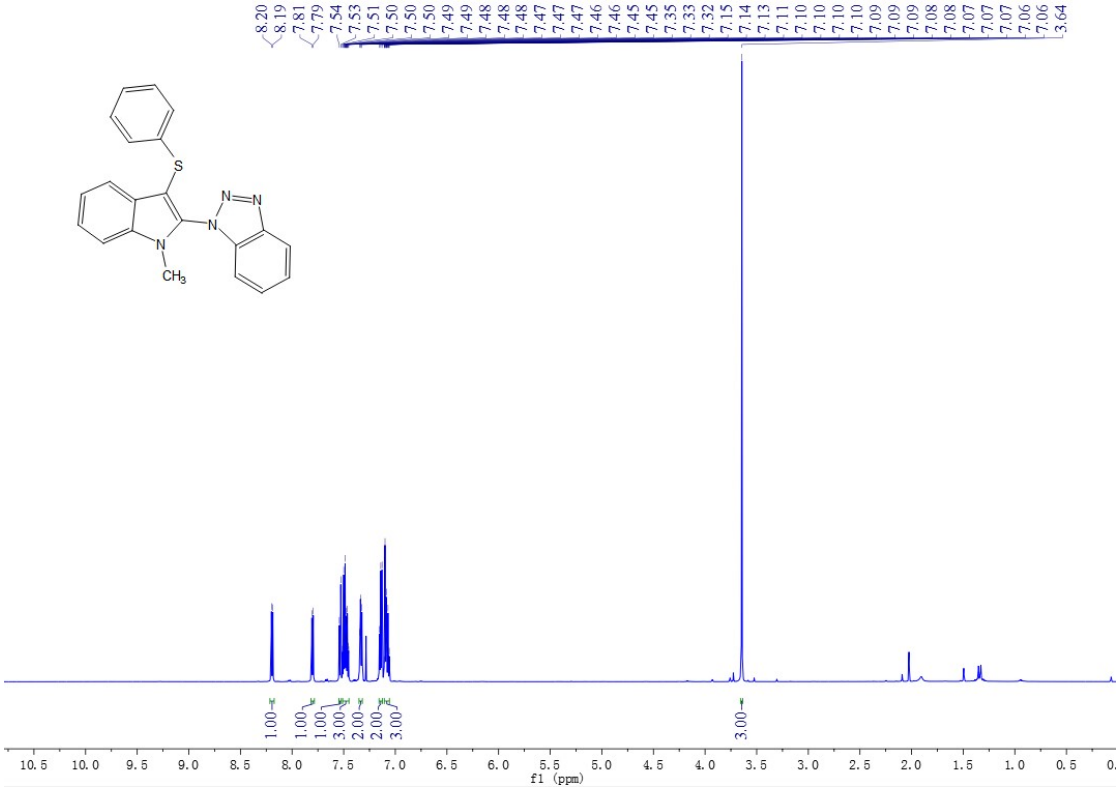
(117) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 60



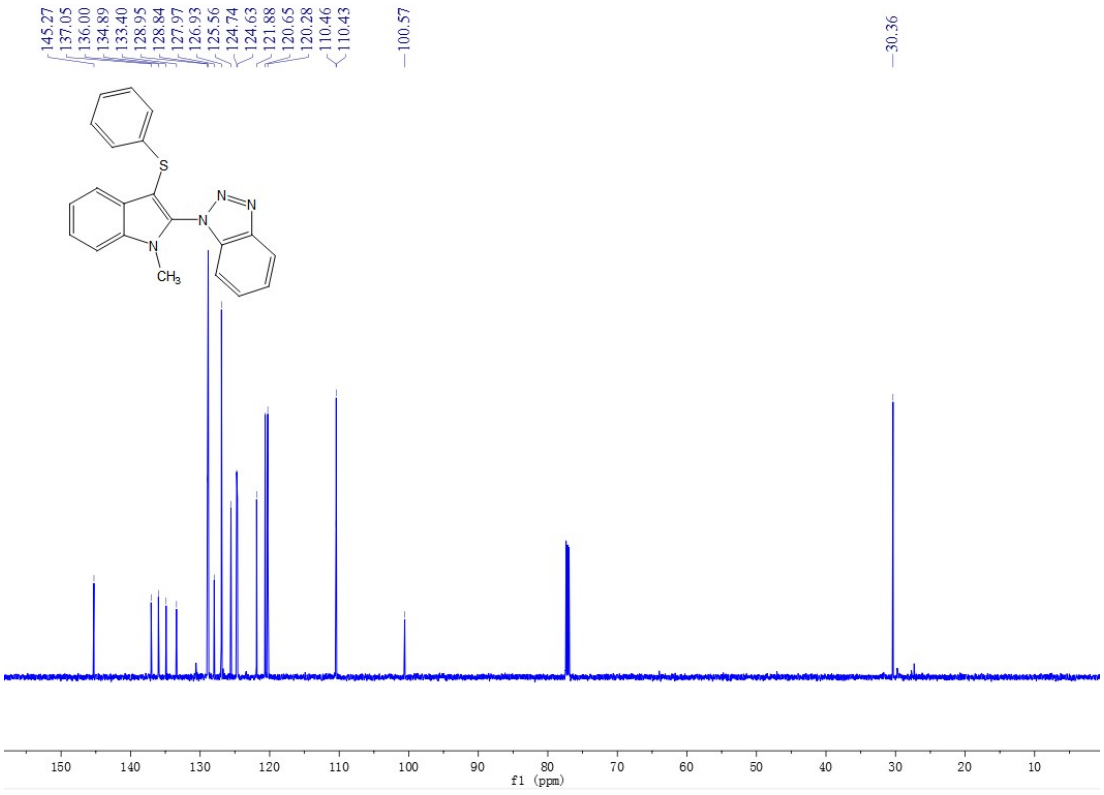
(118) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum 60



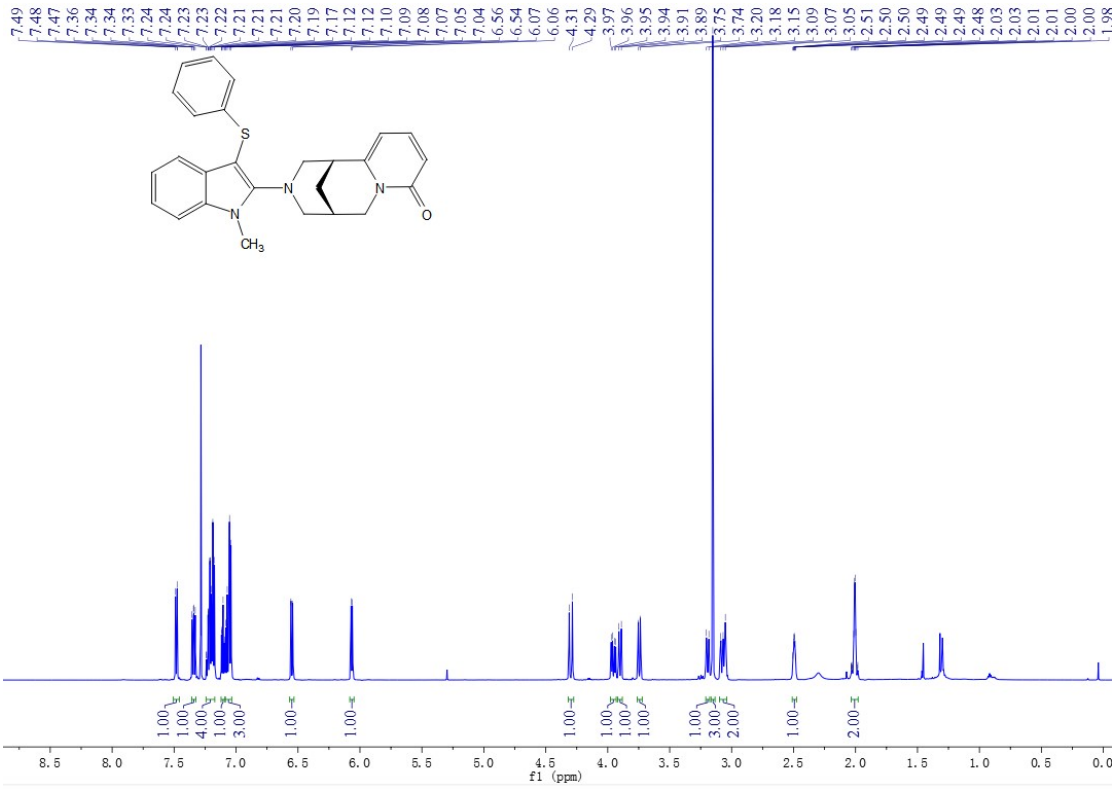
(119) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 61



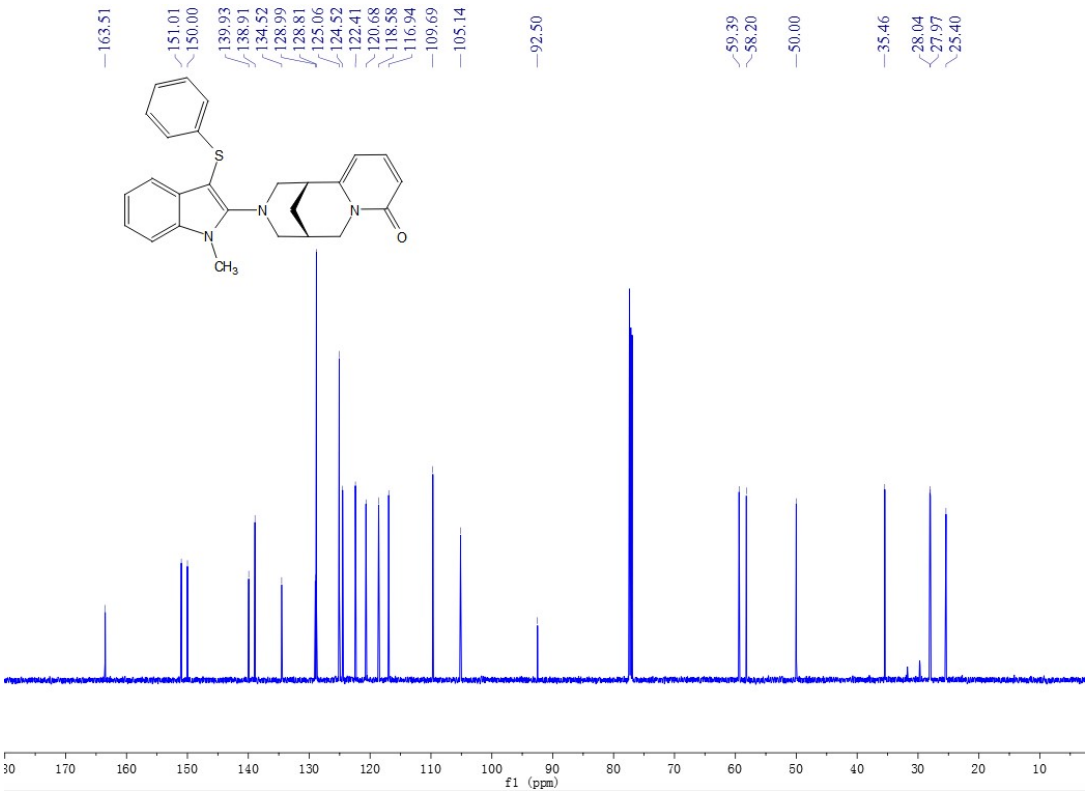
(120) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 61



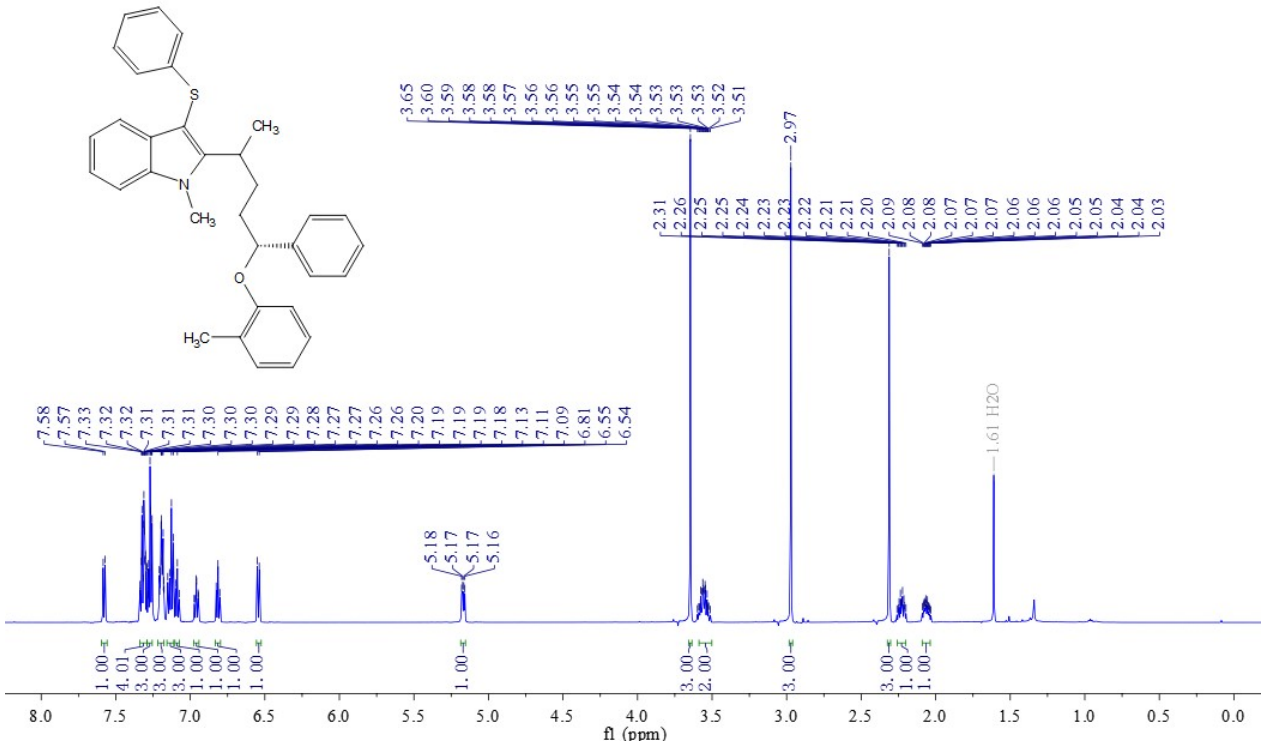
(121) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 62



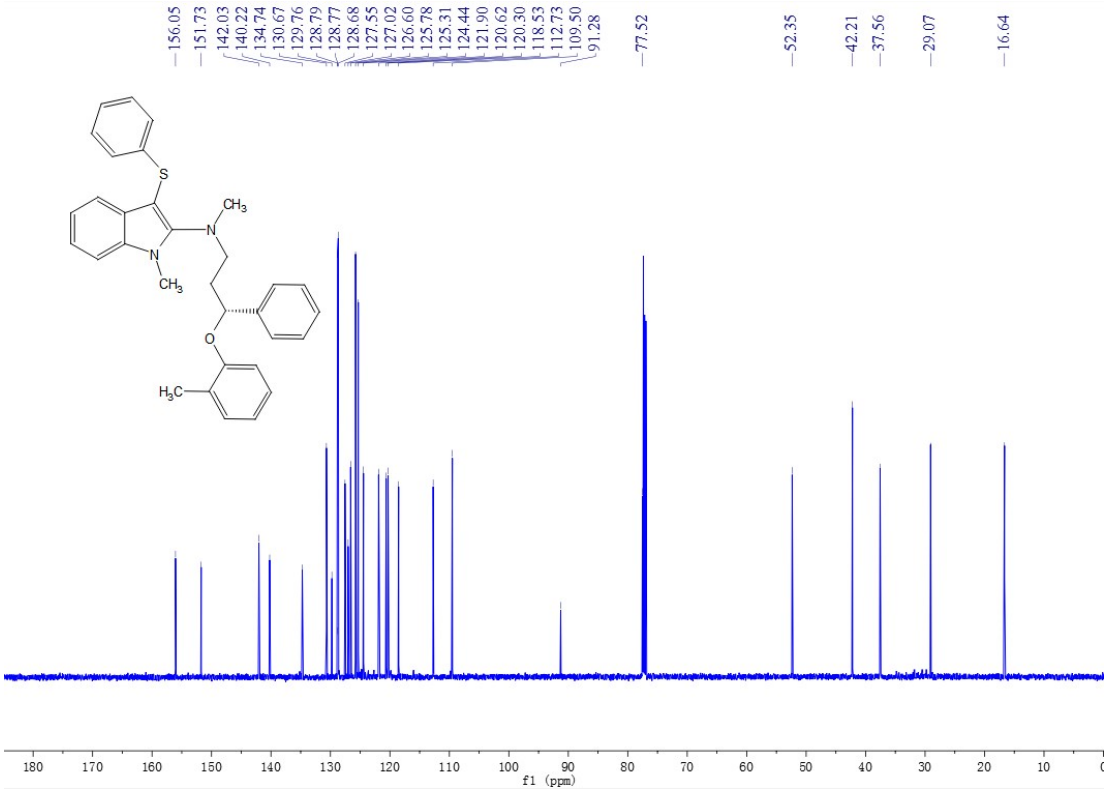
(122) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 62



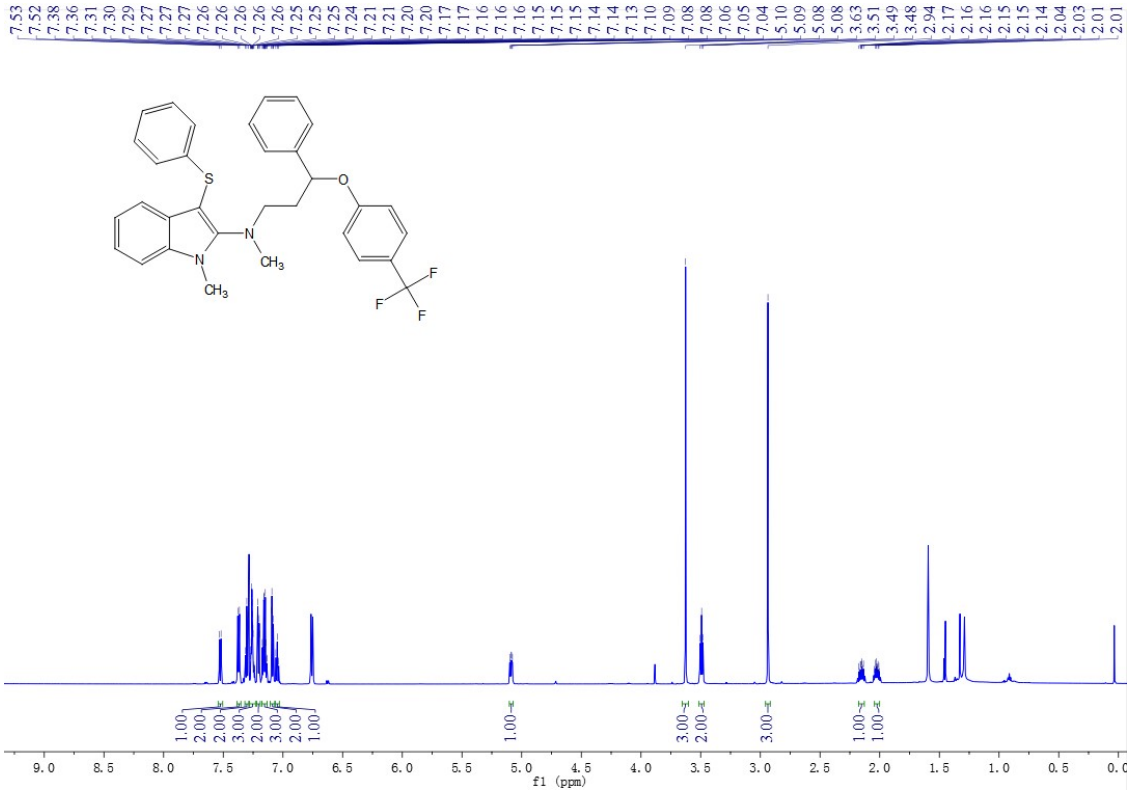
(123) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 63



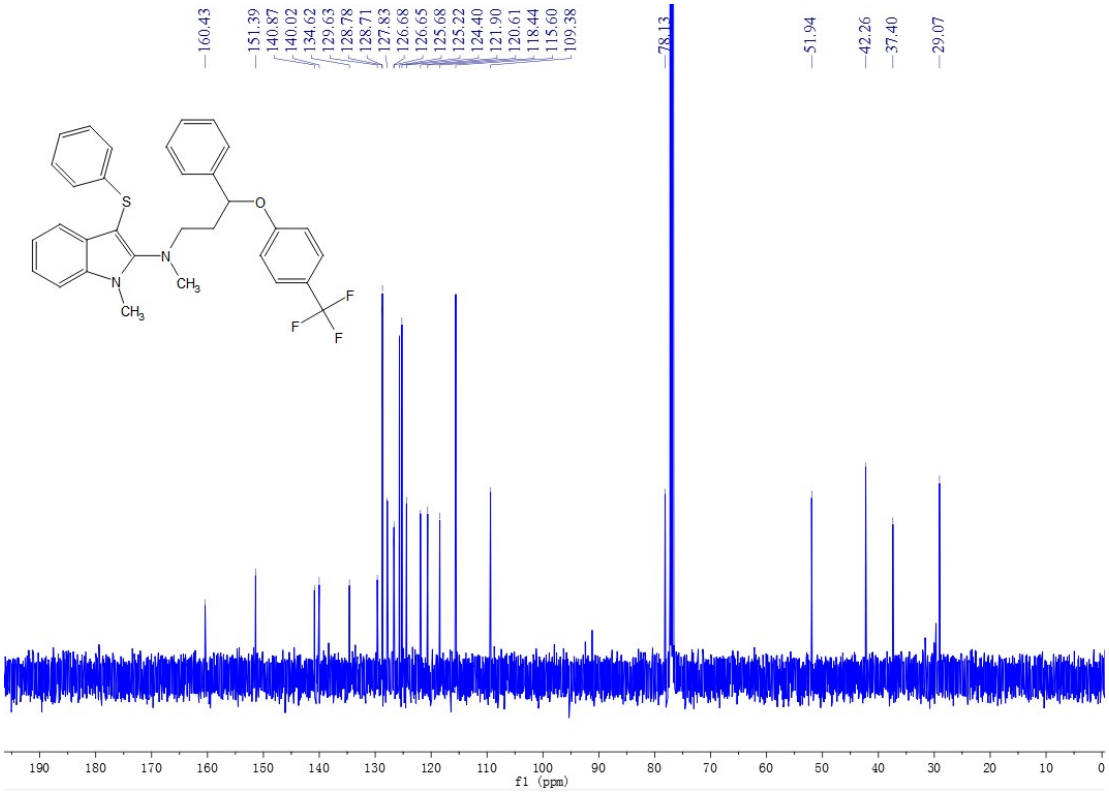
(124) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 63



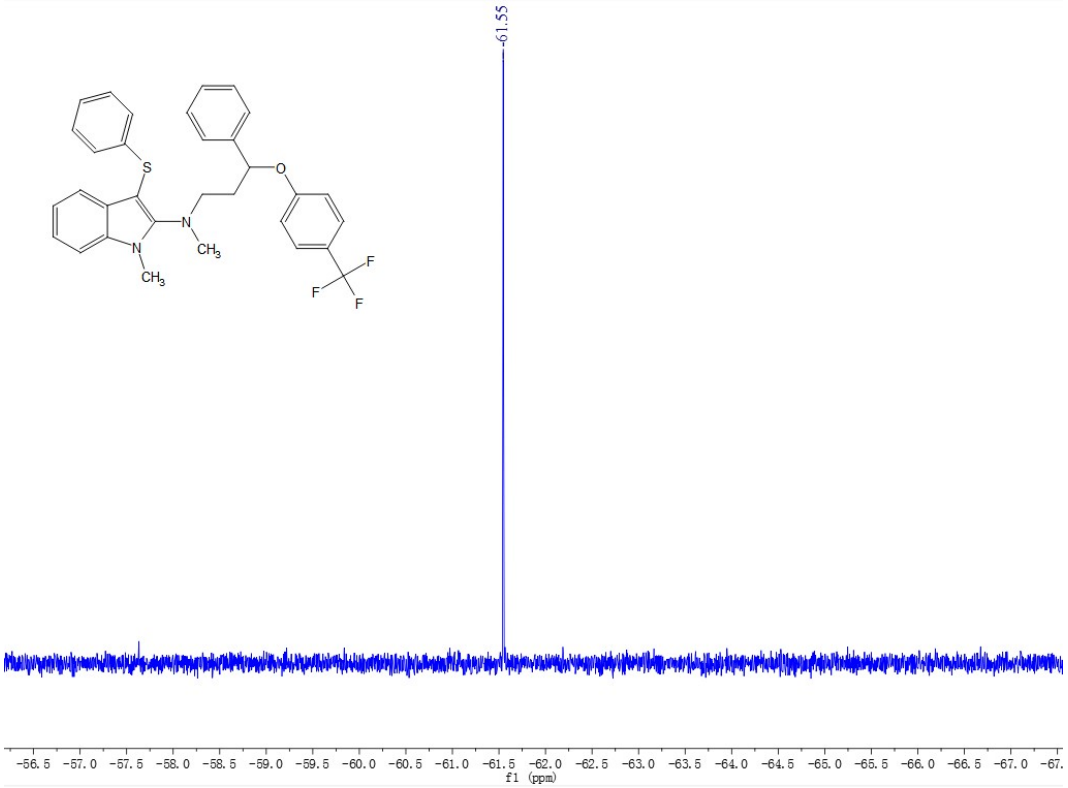
(125) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 64



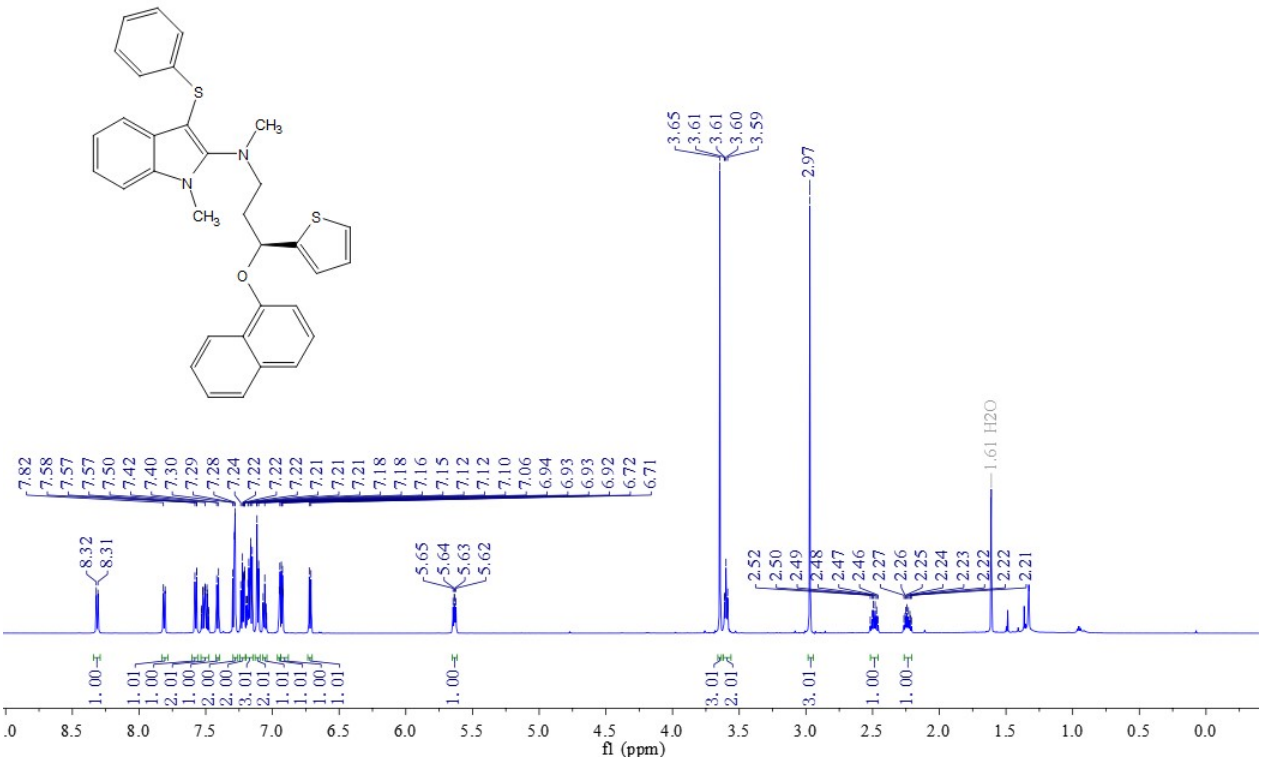
(126) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 64



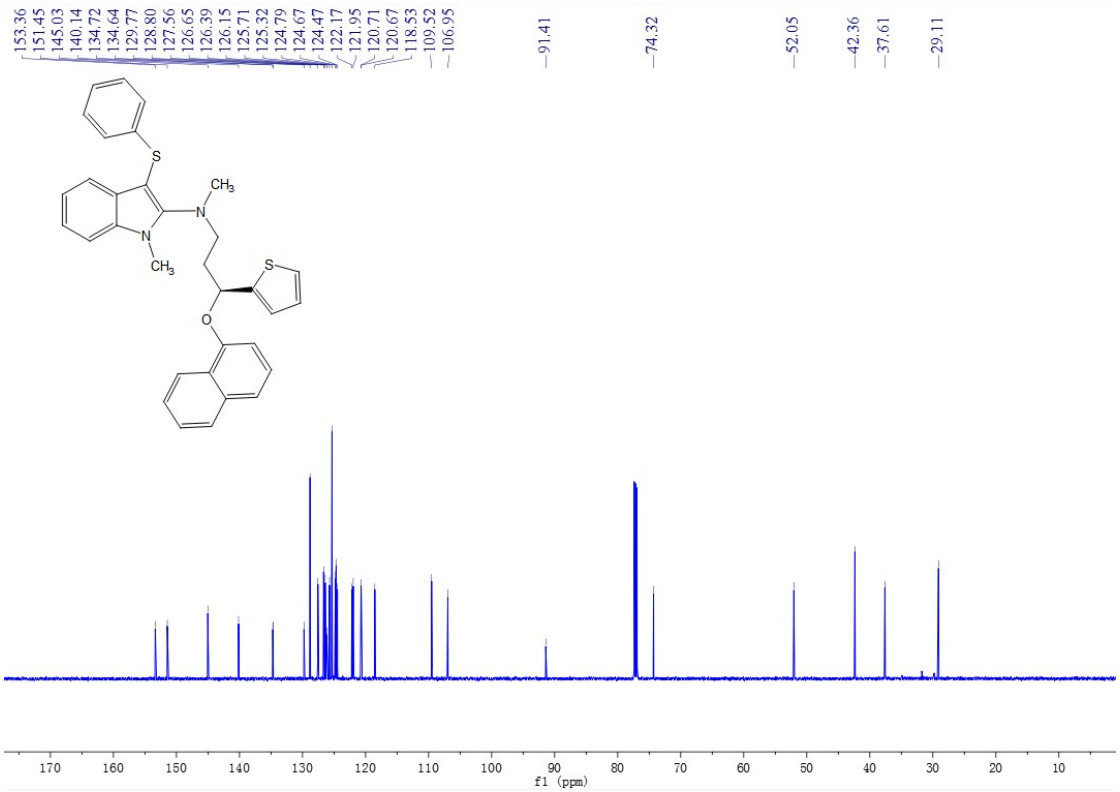
(127) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 64



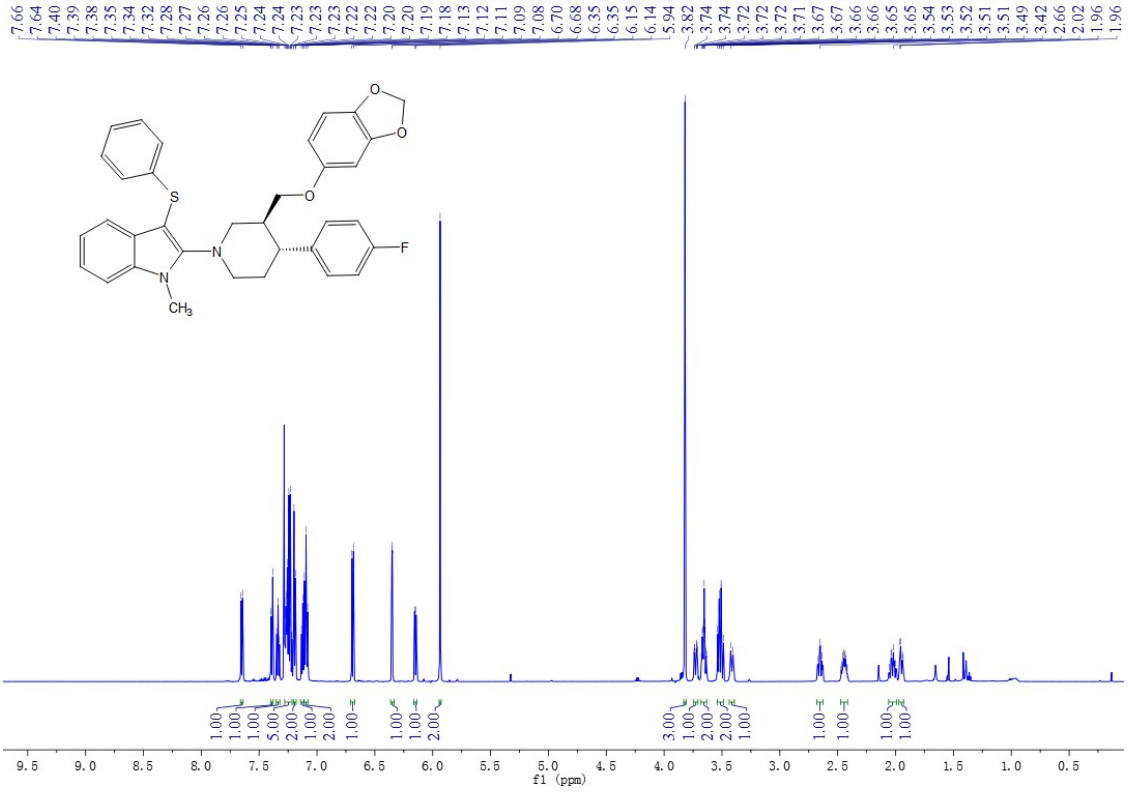
(128) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 65



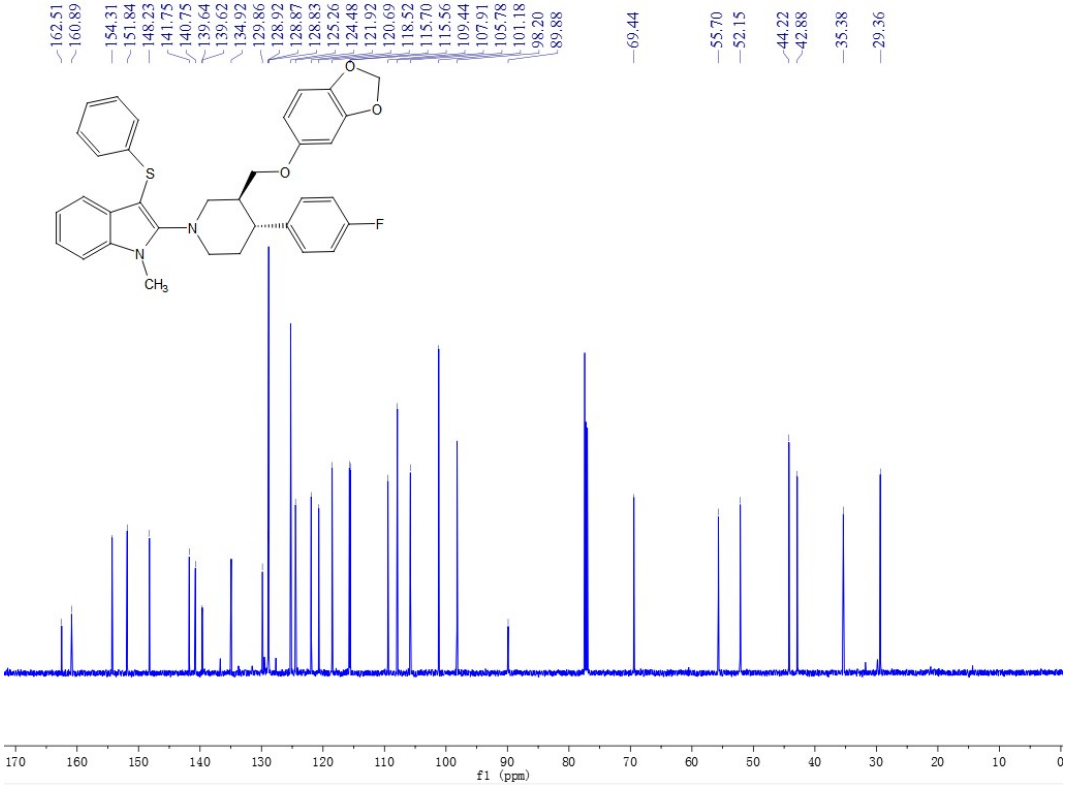
(129) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 65



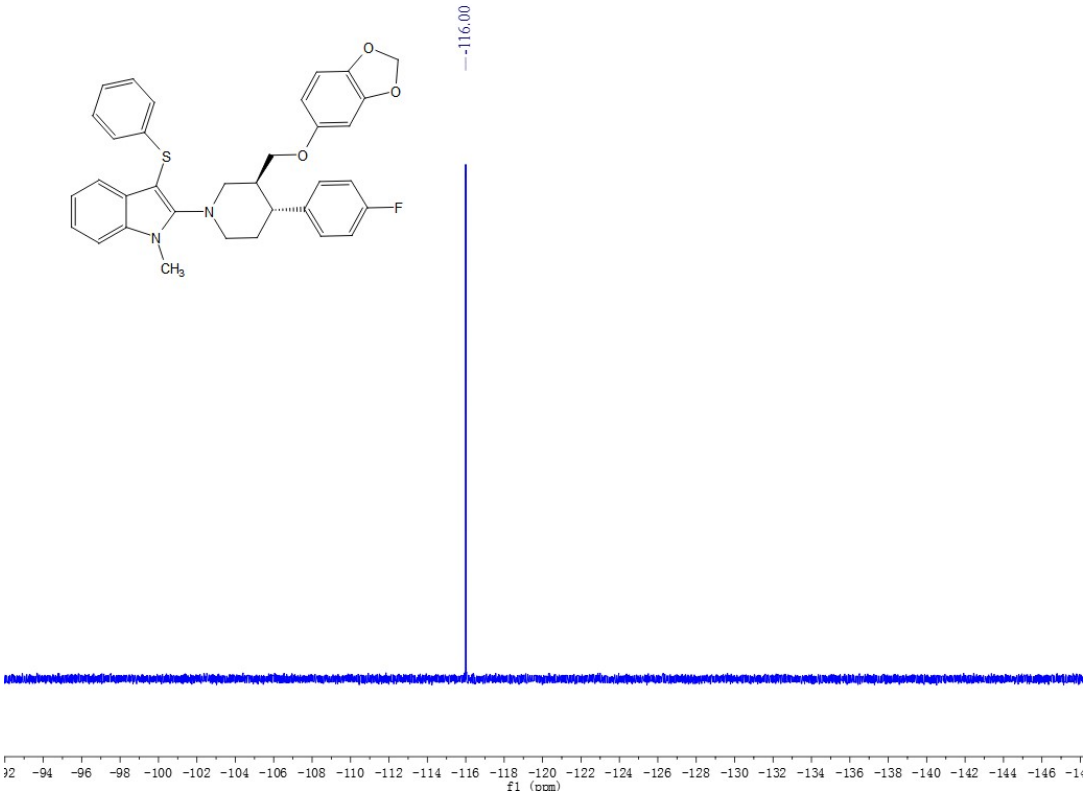
(130) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 66



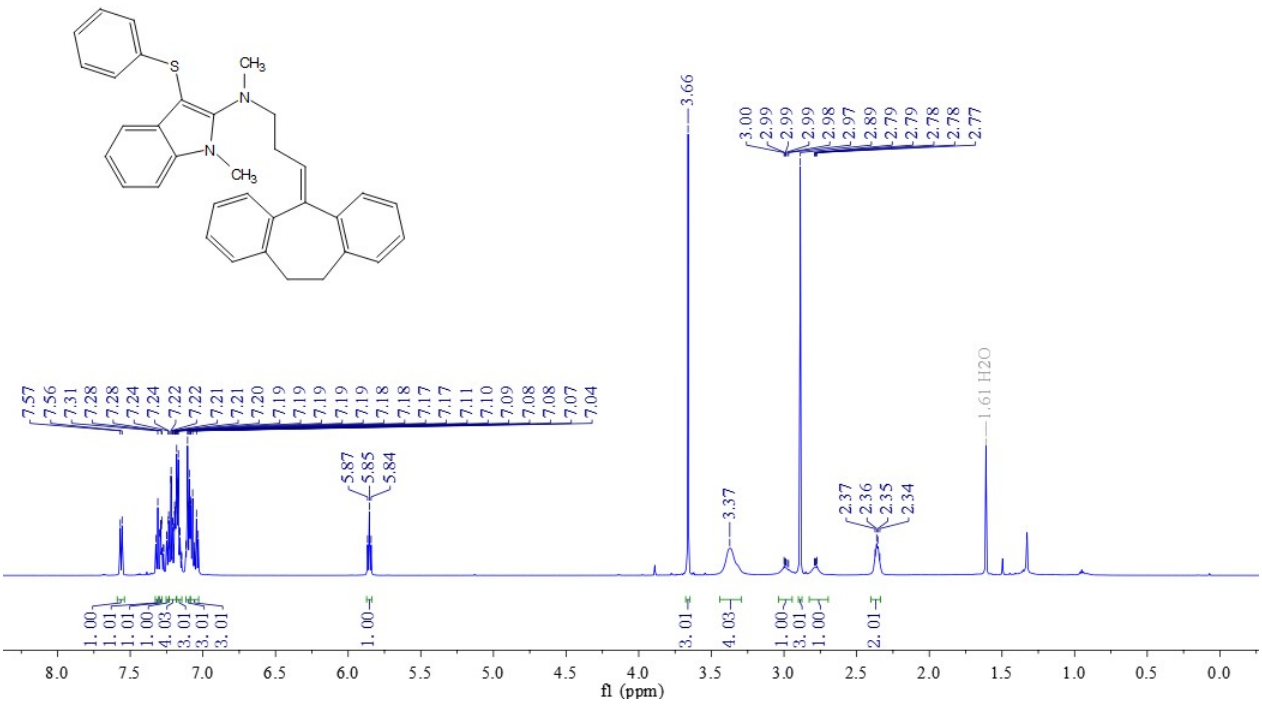
(131) **^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 66**



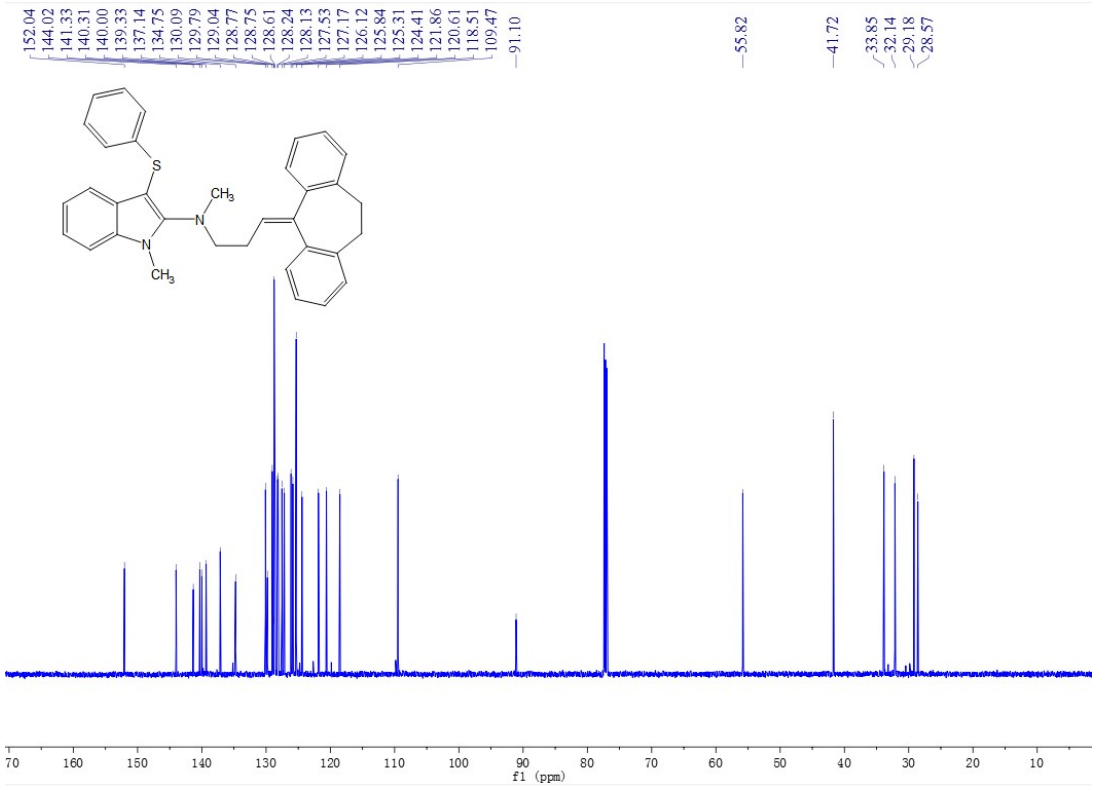
(132) **^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 66**



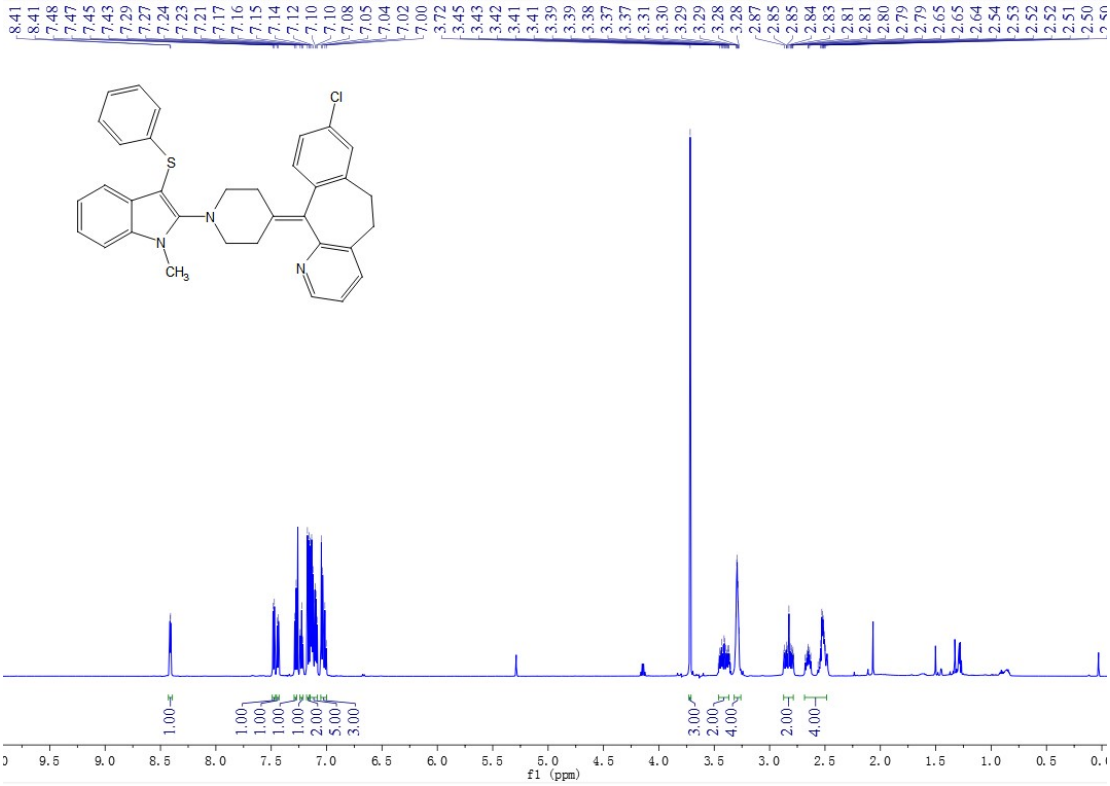
(133) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 67



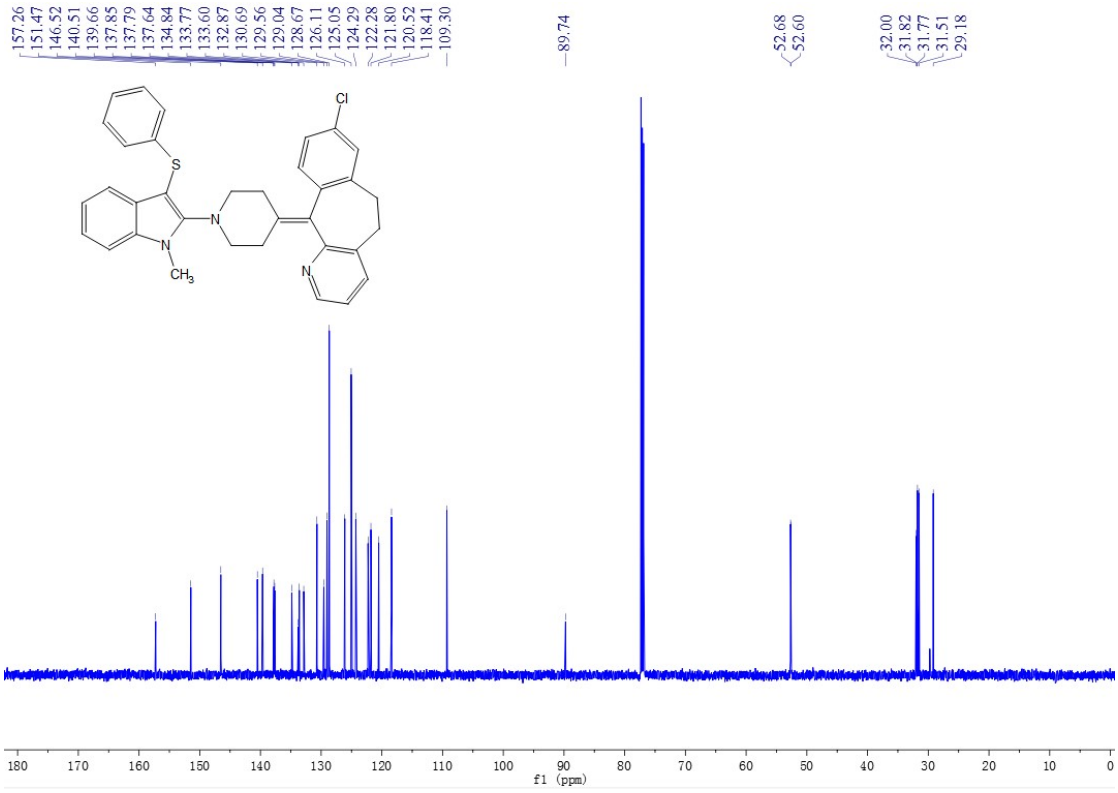
(134) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 67



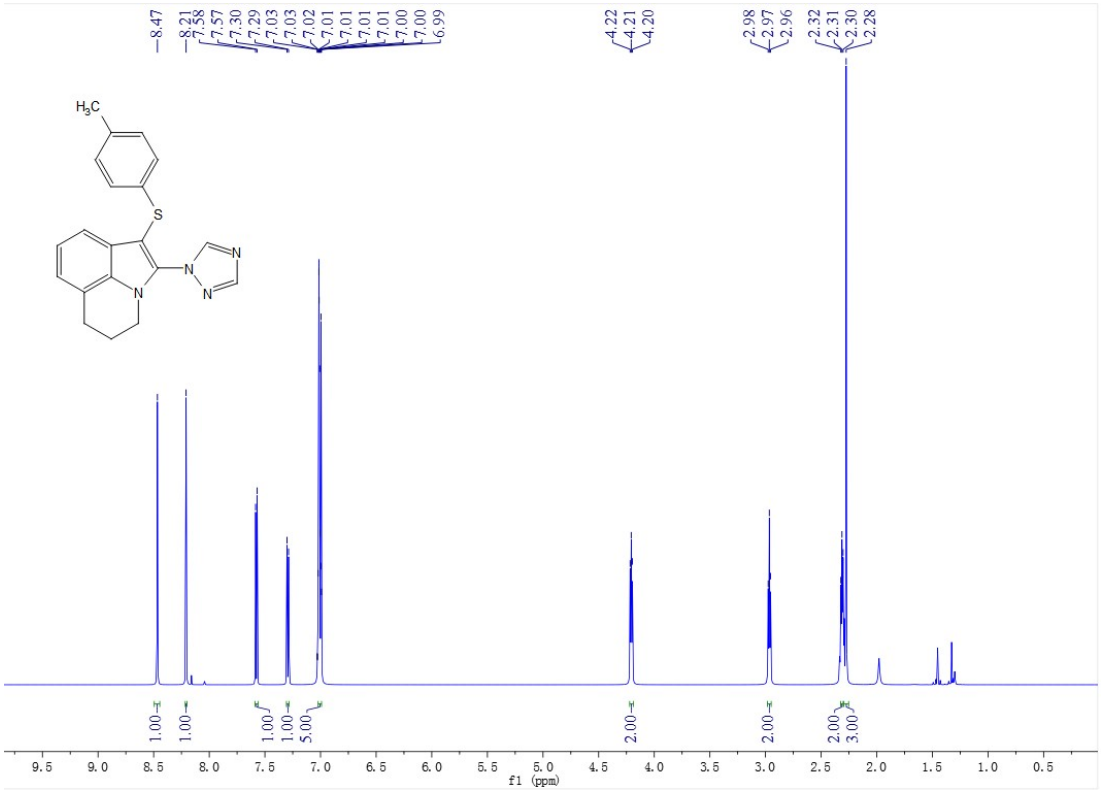
(135) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 68



(136) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 68



(137) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 69



(138) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 69