Electronic Supplementary Information

Directing-group-free Strategy for the Iodine-catalyzed Regioselective Dichalcogenation of Indoles, Understanding the Full Catalytic Cycles

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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 I2 stain. Column chromatography was performed on silica gel (200-300 mesh).

Spectroscopy and Instruments

NMR spectra were recorded on Bruker-400/500/600 spectrometer operating at (600 MHz, 565 MHz and 151 MHz), (500 MHz, 471 MHz and 126 MHz), (400 MHz, 376 MHz and 101 MHz), for 1H, 19F and 13C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ^{1}H-NMR: $CDCl_3$, 7.26, For ^{13}C-NMR: $CDCl_3$, 77.16, ^{19}F-NMR spectra were referenced using a unified chemical shift scale based on the 1H resonance of tetramethylsilane (1% v/v solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet, coupling constants in Hz, integration.

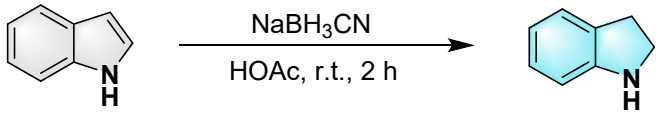
Instrument

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

EXPERIMENTAL DATA

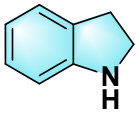
2. Substrates preparation.

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



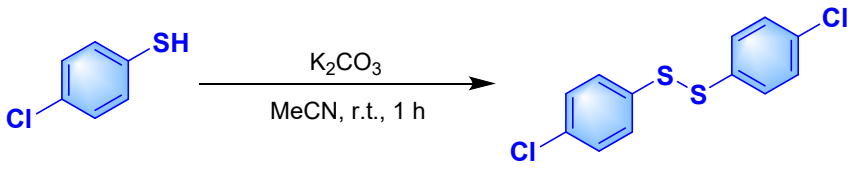
Procedure for indoline (1f): To a suspended solution of indole (1.33 g, 11.4 mmol) in HOAc (20.0 mL), $NaBH_3CN$ (1.89 g, 35.0 mmol) was added dropwise at 0 °C. The heterogeneous mixture was stirred for 2 h at room temperature. Quenched with saturated NH_4Cl (20.0 mL), and extracted with ether (4 × 75.0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

NMR Spectroscopy (1f):



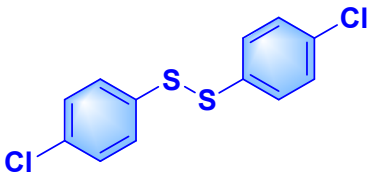
^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.60 (q, *J* = 8.4 Hz, 3H), 3.10 (t, *J* = 8.4 Hz, 2H), known compound.

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



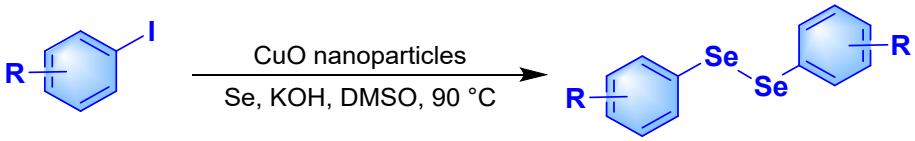
Procedure for 1,2-bis(4-chlorophenyl)disulfane (2f): To a round bottle (50 mL) were added 4-chlorobenzenethiol (5.0 mmol), anhydrous potassium carbonate (0.69 g, 5.0 mmol), and MeCN (10 mL) sequentially, and the reaction was conducted at room temperature under air atmosphere for 1 hour. And the desired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

NMR Spectroscopy (2f):



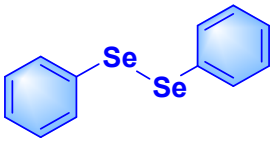
^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), known compound.

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



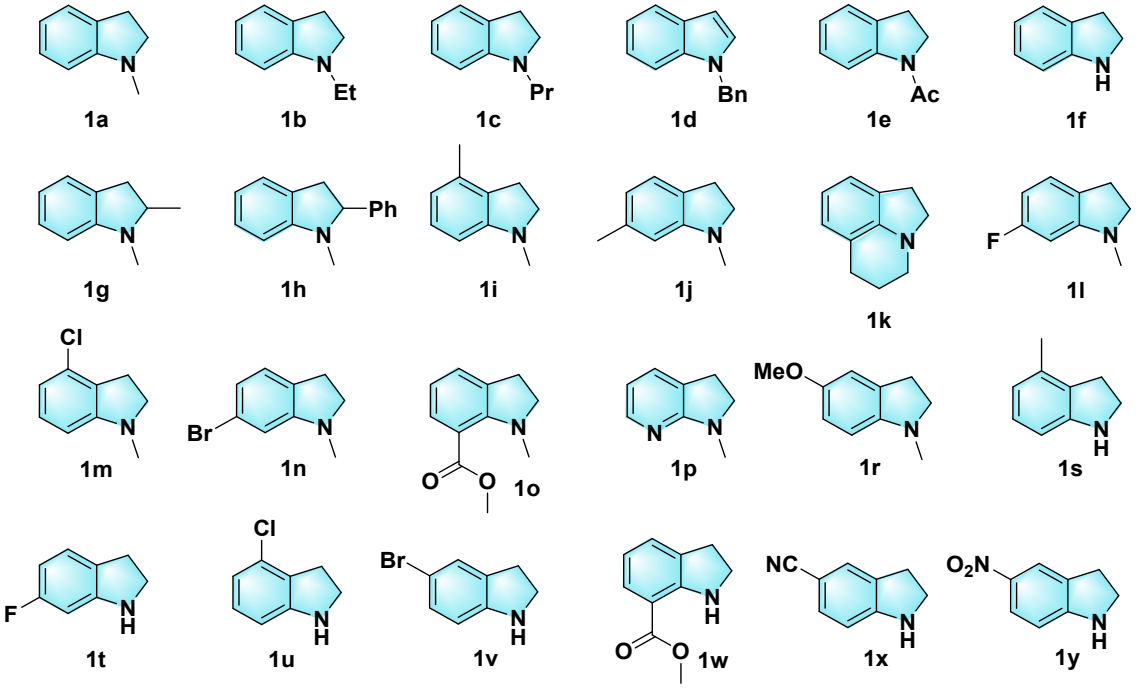
Procedure for 1,2-diphenyldiselane (2q): To a stirred solution of Se metal (2.0 mmol) and iodobenzene (1.0 mmol) in dry DMSO (2.0 mL) was added CuO nanoparticles (10.0 mol%) followed by KOH (2.0 equiv) under argon atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction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

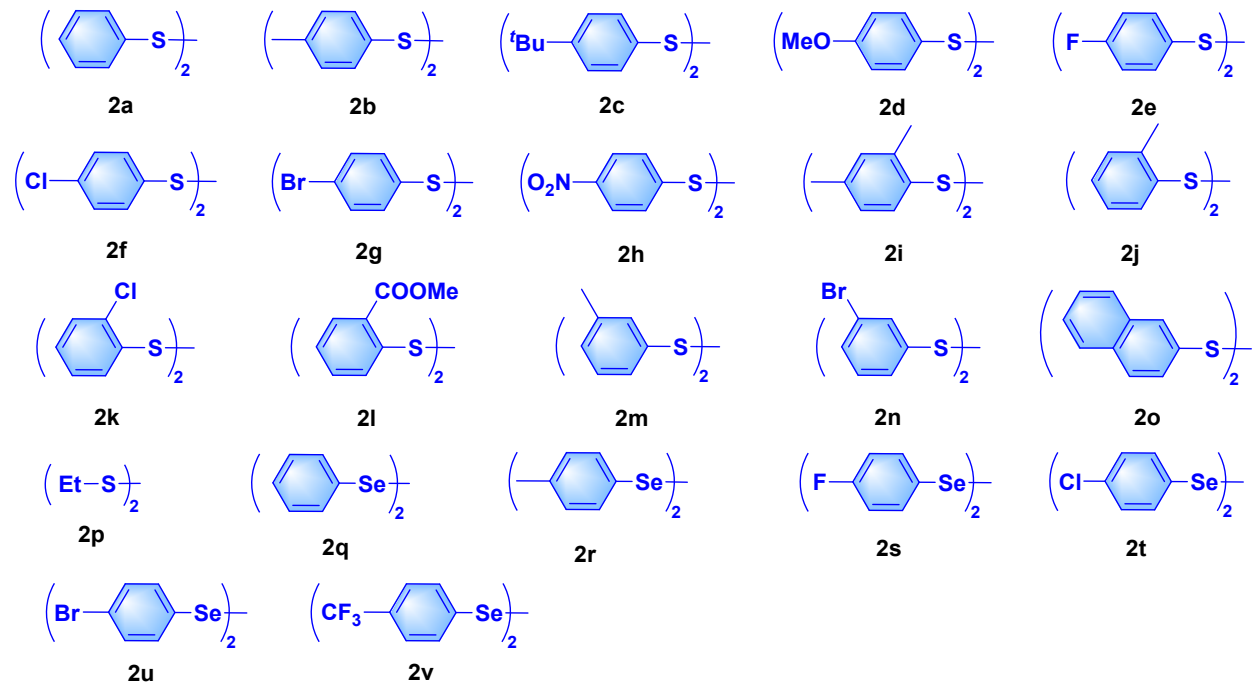


^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.81–7.52 (m, 4H), 7.36–7.24 (m, 6H), known compound.

Scheme S1. Scope of indolines.



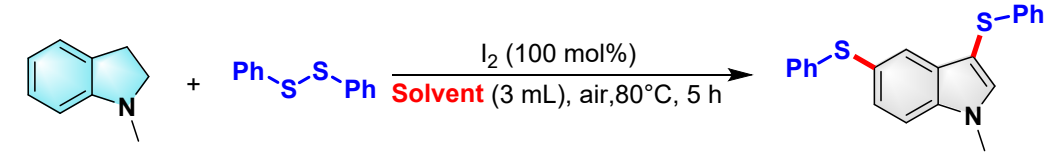
Scheme S2. Scope of dichalconides.



3. Optimization of reaction conditions.

3.1. Optimization of reaction conditions A.

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

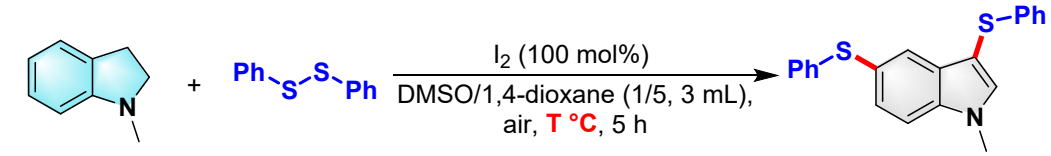


1a = 0.30 mmol **2a** = 0.25 mmol **3aa**

Entry	Solvent	Yield (%)[b]
1	1,4-dioxane	84
2	CH_3CN	18
3	Toluene	26
4	DCE	44
5	DMF	trace
6	DMSO	73
7	DMSO/1,4-dioxane (1/1)	71
8	DMSO/1,4-dioxane (1/2)	87
9	DMSO/1,4-dioxane (1/3)	79
10	DMSO/1,4-dioxane (1/4)	87
11	**DMSO/1,4-dioxane (1/5)**	**94**
12	DMSO/1,4-dioxane (2/1)	52

[a]Reaction conditions A, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.25 mmol) and I_2 (100 mol%), **solvent** (3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

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

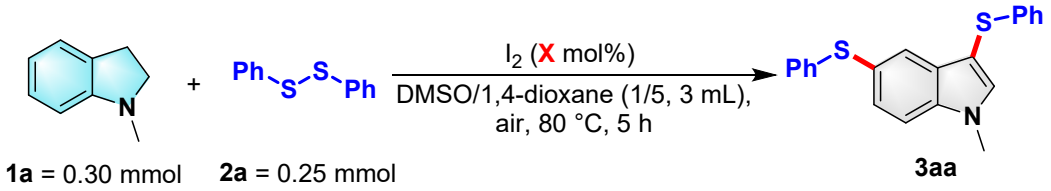


1a = 0.30 mmol **2a** = 0.25 mmol **3aa**

Entry	T [°C]	Yield (%)[b]
1	60	39
2	**80**	**94**
3	100	55

[a]Reaction conditions A, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.25 mmol) and I_2 (100 mol%), DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at **T °C** under air for 5 h. [b]Isolated yield.

Table S3. Screening the amount of I_2.[a]

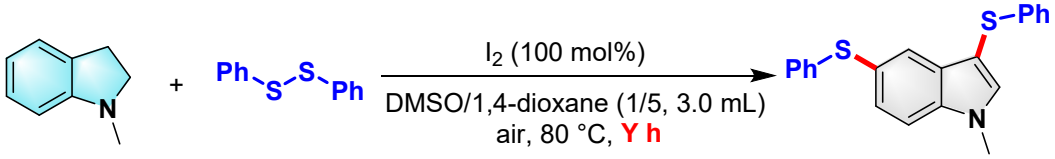


1a = 0.30 mmol **2a** = 0.25 mmol **3aa**

Entry	X (mol %)	Yield (%)[b]
1	50	47
2	80	75
3	**100**	**94**
4	120	88
5	150	86

[a]Reaction conditions A, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.25 mmol) and I_2 (X mol%), DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

Table S4. Screening the reaction time.[a]

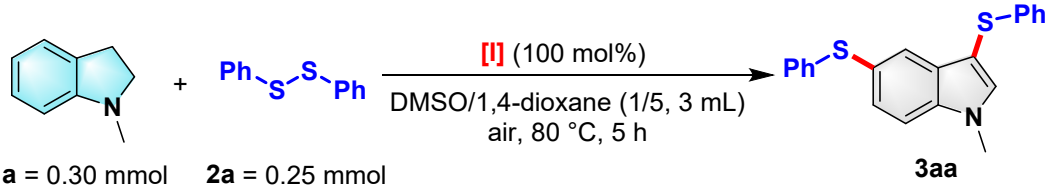


1a = 0.30 mmol **2a** = 0.25 mmol **3aa**

Entry	Y (h)	Yield (%)[b]
1	3	62
2	**5**	**94**
3	8	72
4	10	77

[a]Reaction conditions A, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.25 mmol) and I_2 (100 mol%), DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for Y h. [b]Isolated yield.

Table S5. Screening the iodized salt.[a]



1a = 0.30 mmol **2a** = 0.25 mmol **3aa**

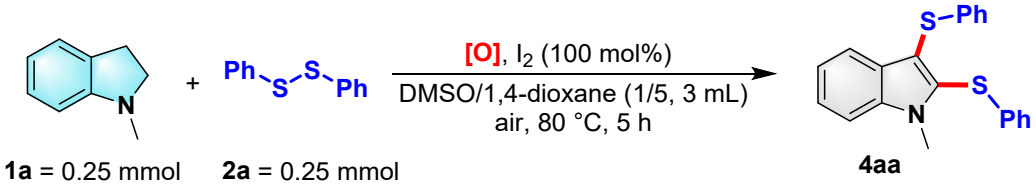
Entry	[I] (100 mol%)	Yield (%)[b]
1	NaI	31
2	KI	26
3	NH_4I	45

4	NIS	61

[a]Reaction conditions A, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.25 mmol) and **[I]** (100 mol%), DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

3.2. Optimization of reaction conditions B.

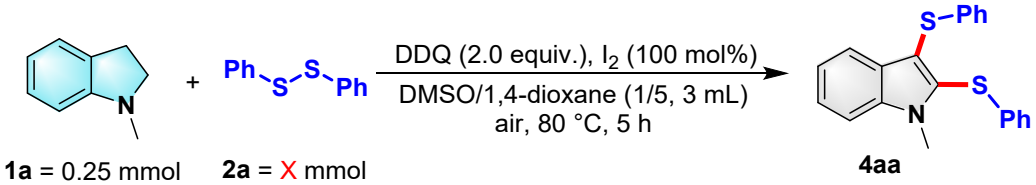
Table S6. Screening the oxidants[a]



Entry	Oxidant	Yield (%)[b]
1	$K_2S_2O_8$	12
2	TBHP	0
3	DTBP	0
4	**DDQ**	**36**

[a]Reaction conditions B, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.50 mmol), I_2 (100 mol%), **oxidant** (2.0 equiv.) and DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

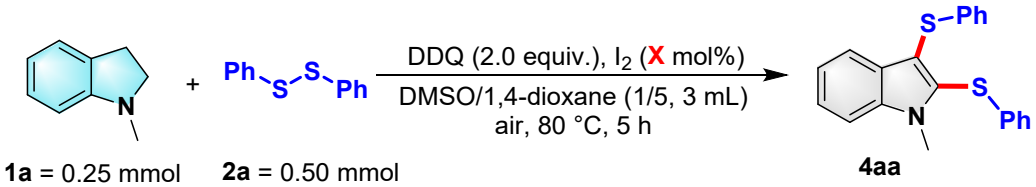
Table S7. Screening the amount of 2a.[a]



Entry	X (mmol)	Yield (%)[b]
1	0.30	43
2	0.40	57
3	**0.5**	**64**
4	0.6	55

[a]Reaction conditions B, unless specified otherwise: **1a** (0.30 mmol), **2a** (X mmol), I_2 (100 mol%), DDQ (2.0 equiv.) and DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

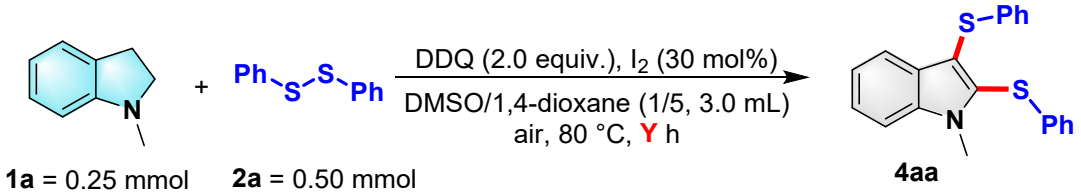
Table S8. Screening the amount of I_2.[a]



Entry	X (mmol)	Yield (%)[b]
1	80	60
2	50	59
3	**30**	**62**
4	20	54

[a]Reaction conditions B, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.50 mmol), I_2 (X mol%), DDQ (2.0 equiv.) and DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for 5 h. [b]Isolated yield.

Table S9. Screening the reaction time.[a]



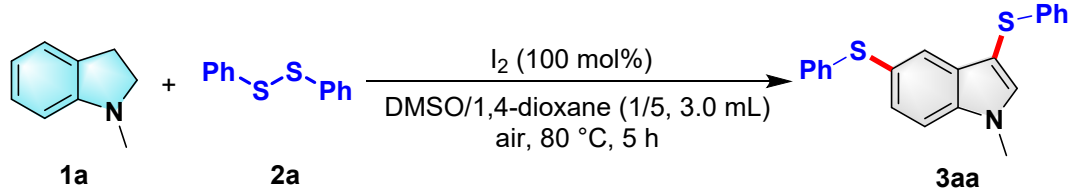
1a = 0.25 mmol **2a** = 0.50 mmol **4aa**

Entry	Y (h)	Yield (%)[b]
1	10	77
2	15	85
3	**20**	**91**
4	24	88

[a]Reaction conditions B, unless specified otherwise: **1a** (0.30 mmol), **2a** (0.50 mmol) I_2 (30 mol%), DDQ (2.0 equiv.) and DMSO/1,4-dioxane (1/5, 3.0 mL) were stirred at 80 °C under air for Y h. [b]Isolated yield.

4. Typical procedure for the synthesis of 3aa and 4aa

(1) Typical procedure for the synthesis of 3aa:

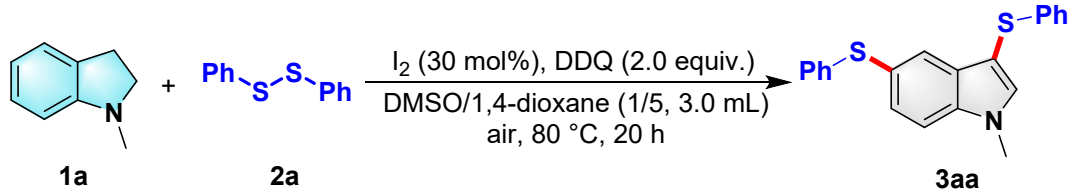


1a **2a** **3aa**

Under air atmosphere, 1-methylindoline **1a** (40.0 mg, 0.30 mmol), 1,2-diphenyldisulfane **2a** (54.5 mg, 0.25 mmol), I_2 (63.3 mg, 0.25 mmol), DMSO (0.5 mL) and 1,4-dioxane (2.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, and the resulting reaction mixture was heated at 80 °C for 5 h. After cooling to room temperature, the resulting mixture was washed with 10% Na_2CO_3 aqueous solution, and then extracted with ethyl acetate, the combined organic layers were dried with anhydrous Na_2SO_4, and then concentrated by removing the solvent under vacuum. The residue was purified by column chromatography on silica gel, and eluting with petroleum ether/ethyl acetate (5/1, v/v) to give

the product **3aa** as a white solid (81.5 mg, 94% yield).

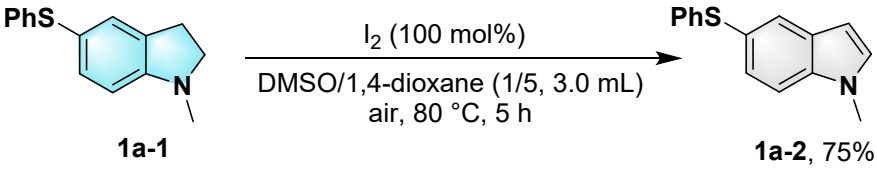
(2) Typical procedure for the synthesis of 4aa:



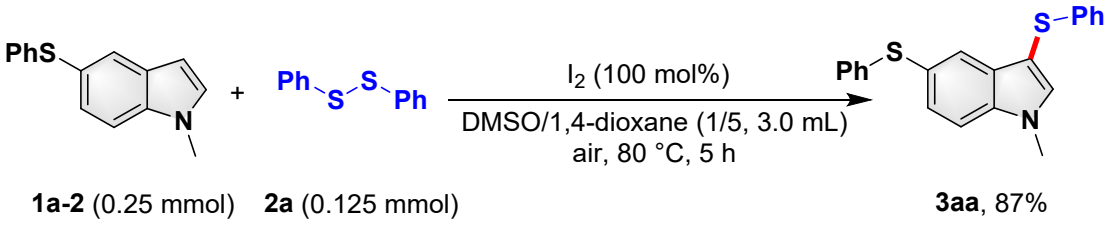
Under air atmosphere, 1-methylindoline **1a** (33.3 mg, 0.25 mmol), 1,2-diphenyldisulfane **2a** (109.0 mg, 0.50 mmol), I_2 (19.0 mg, 30 mol%), DDQ (113.5 mg, 0.50 mmol), DMSO (0.5 mL) and 1,4-dioxane (2.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, and the resulting reaction mixture was heated at 80 °C for 20 h. After cooling to room temperature, the resulting mixture was washed with 10% Na_2CO_3 aqueous solution, and then extracted with ethyl acetate, the combined organic layers were dried with anhydrous Na_2SO_4, and then concentrated by removing the solvent under vacuum. The residue was purified by column chromatography on silica gel, and eluting with petroleum ether/ethyl acetate (10/1, v/v) to give the product **4aa** as a white solid (79.4 mg, 91% yield).

5. Control experiments.

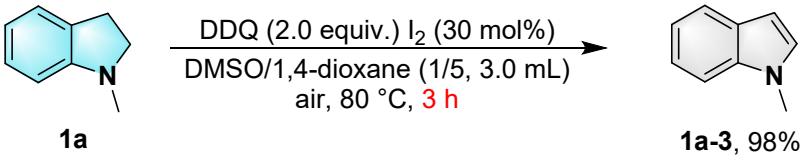
(1) 1-methyl-5-(phenylthio)indoline **1a-1** (60.3 mg, 0.25 mmol) and I_2 (100 mol%), 1,4-dioxane/DMSO (5/1, 3.0 mL) were stirred at 80 °C under air for 5 h. The reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **1a-2** (44.8 mg, 75% yield).



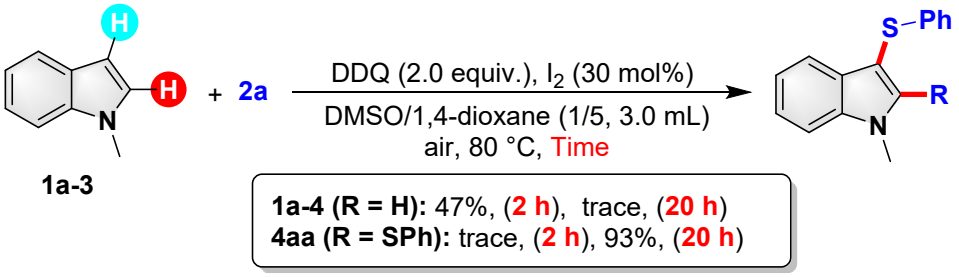
(2) Under the optimized reaction conditions A, the reaction of **1a-2** (59.7 mg, 0.25 mmol) and **2a** (27.3 mg, 0.125 mmol) were carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **3aa** as white solid (75.5 mg, 87% yield).



(3) 1-methylindoline **1a** (33.3 mg, 0.25 mmol) I_2 (30 mol%) and DDQ (113.5 mg, 0.50 mmol), 1,4-dioxane/DMSO (5/1, 3.0 mL) were stirred at 80 °C under air for 20 h. The reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **1a-3** (32.1 mg, 98% yield).

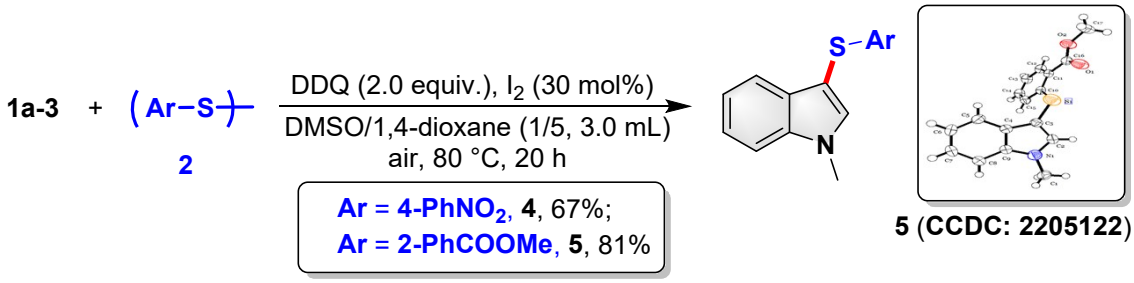


(4) Under the optimized reaction conditions B, the reaction of **1a-3** (33.3 mg, 0.25 mmol) and **2a** (109.0 mg, 0.50 mmol) were carried. Then, the crude reaction mixture was analyzed by TLC in 2 hours and20 hours respectively. The reaction mixture **(2 h)** was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **1a-4** as white solid (28.1 mg, 47% yield) and **4aa** (trace). The reaction mixture **(20 h)** was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **4aa** as white solid (80.7 mg, 93% yield) and **1a-4** (trace).



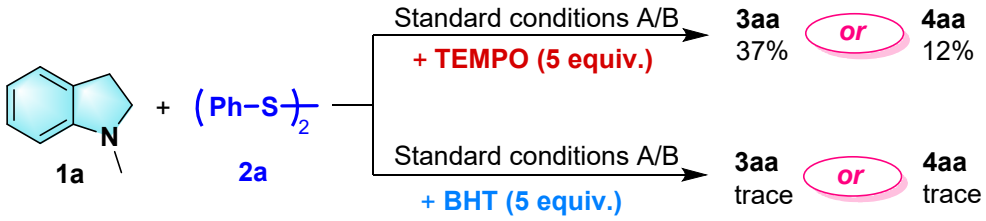
(5) Conditions 1: Under the optimized reaction conditions B, the reaction of **1a-3** (33.3 mg, 0.25 mmol) and 1,2-bis(4-nitrophenyl)disulfane (154.0 mg, 0.50 mmol) were carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **4** as white solid (47.6 mg, 67% yield).

Conditions 2: Under the optimized reaction conditions B, the reaction of **1a-3** (33.3 mg, 0.25 mmol) and dimethyl 2,2'-disulfanediyldibenzoate (167.0 mg, 0.50 mmol) were carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **5** as white solid (60.1 mg, 81% yield).

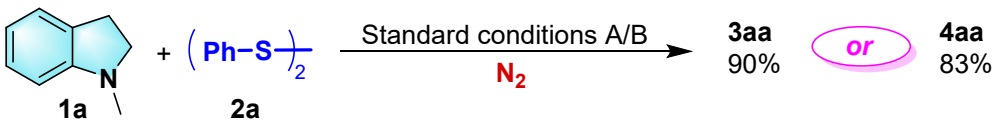


(6) Conditions 1: Under the standard condition A, two free radical trapping reagents, 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**) and hydroxytoluene (**BHT**) was introducing to this reaction A. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **3aa** as white solid (32.1 mg, 37% yield and trace products, respectively).

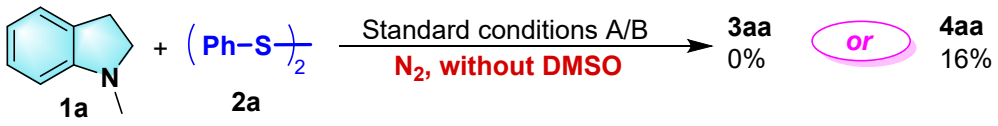
Conditions 2: Under the standard condition B, two free radical trapping reagents, 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**) and hydroxytoluene (**BHT**) was introducing to this reaction B. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/dichloromethane (10:1) to give product **4aa** as white solid (10.4 mg, 21% yield and trace products, respectively).



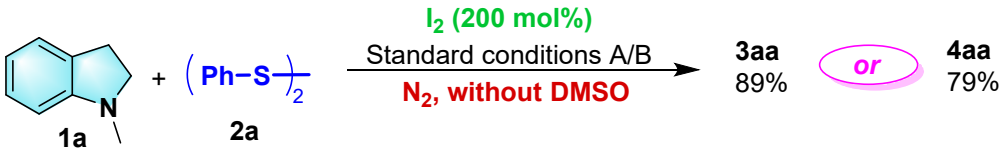
(7) Under the standard condition A/B, N_2 instead of air was used. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/dichloromethane (10:1) as the eluent to give **3aa** as a white solid (78.1 mg, 90% yield) or **4aa** as a white solid (72.0 mg, 83% yield).



(8) Under the standard condition A/B of both N_2 atmosphere and the absence of DMSO. Then, the crude reaction mixture was analyzed by TLC, and **3aa** not observed. Another 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/dichloromethane (10:1) as the eluent to give **4aa** as a white solid (13.9 mg, 16% yield).

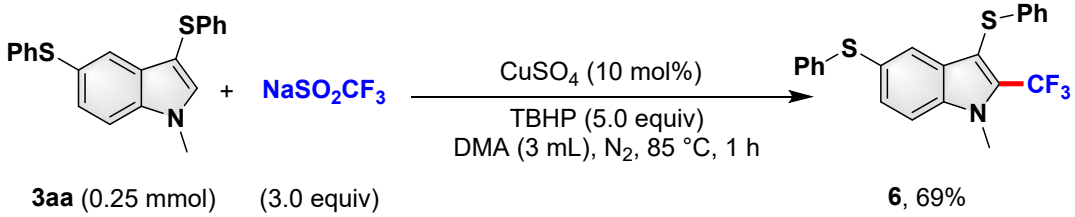


(9) Under the standard condition A/B of both N_2 atmosphere and the absence of DMSO, two equivalents of I_2 were employed in this scenario. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/dichloromethane (10:1) as the eluent to give **3aa** as a white solid (77.2 mg, 89% yield) or **4aa** as a white solid (68.5 mg, 79% yield).

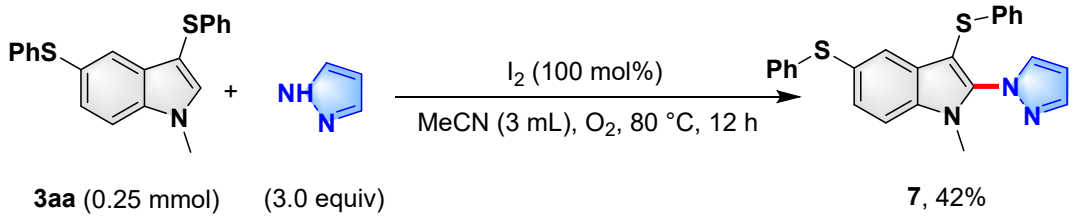


6. Synthetic utility.

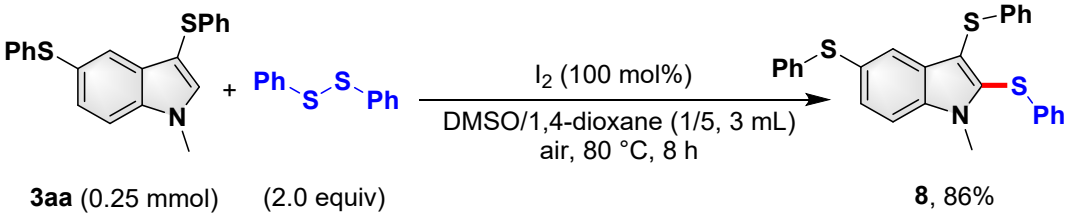
(1) To a solution of **3aa** (86.8 mg, 0.25 mmol) in DMA (3.0 mL) was added CF_3SO_2Na (3.0 equiv), $CuSO_4$ (10 mol%), TBHP (5.0 equiv) under N_2. After stirring at 85 °C for 1 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **6** as a white solid (71.6 mg, 69% yield).



(2) To a solution of **3aa** (86.8 mg, 0.25 mmol) in MeCN (3.0 mL) was added pyrazol (3.0 equiv), I_2 (1.0 equiv) under O_2. After stirring at 80 °C for 12 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **7** as a white solid (43.4 mg, 42% yield).

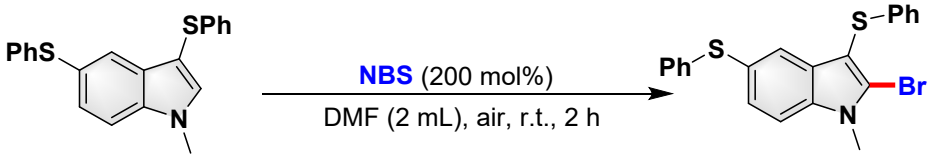


(3) To a solution of **3aa** (86.8 mg, 0.25 mmol) in DMSO/1,4-dioxane (1/5, 3.0 mL) was added 1,2-diphenyldisulfane (2.0 equiv), I_2 (1.0 equiv) under air. After stirring at 80 °C for 8 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **8** as a white solid (97.8 mg, 86% yield).



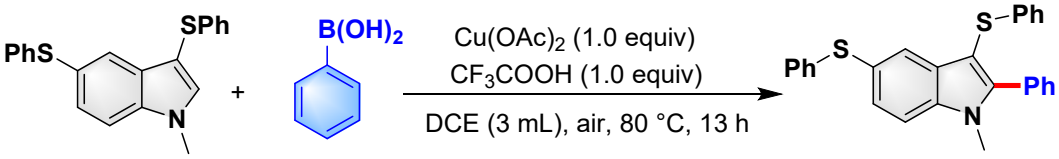
3aa (0.25 mmol) (2.0 equiv) **8**, 86%

(4) To a solution of **3aa** (86.8 mg, 0.25 mmol) in DMF (2.0 mL) was added *N*-Bromosuccinimide (2.0 equiv) under air. After stirring at room temperature for 2 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **9** as a white solid (81.6 mg, 77% yield).



3aa (0.25 mmol) **9**,77%

(5) To a solution of **3aa** (86.8 mg, 0.25 mmol) in DCE (3.0 mL) was added phenylboronic acid (2.0 equiv), $Cu(OAc)_2$ (1.0 equiv) and CF_3COOH (1.0 equiv) under air. After stirring at 80 °C for 13 h, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:10) as eluent to afford the pure product **10** as a white solid (45.5 mg, 43% yield).



3aa (0.25 mmol) (2.0 equiv) **10**,43%

7. Single crystal X-ray diffraction

(1) Single crystal X-ray diffraction of 3aa

White block-like single crystals of **3aa** 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.

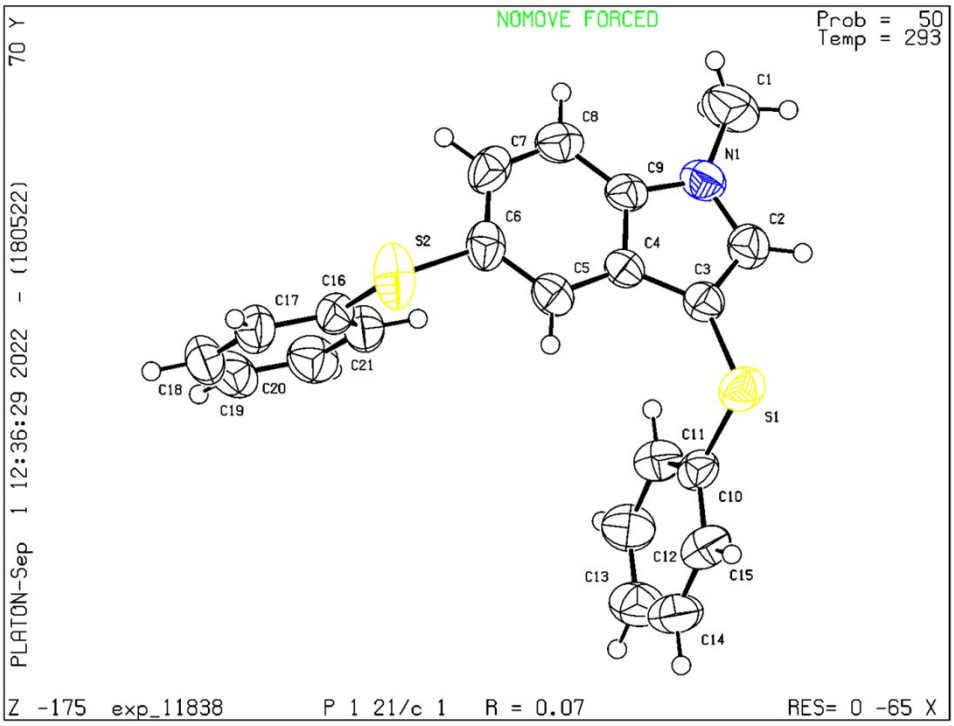


Figure S1. ORTEP drawing of **3aa** with the numbering scheme.

Table S10. Crystal data and structure refinement for **3aa**

Identification code	3aa	
Empirical formula	$C_{21}H_{17}NS_2$	
Formula weight	347.48	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.0377(12) Å	α = 90°.
	b = 20.8920(13) Å	β = 111.387(12)°.
	c = 8.4833(8) Å	γ = 90°.

Volume	1821.5(3) $Å^3$
Z	4
F(000)	728.0
Crystal size	0.20x 0.15 x 0.10 mm^3
2^{Θ} range for data collection	7.068 to 58.82
Index ranges	-13⩽h⩽14, -26⩽k⩽28, -11⩽l⩽10
Reflections collected	11884
Independent reflections	4287 [R(int) = 0.0344,R(sigma) = 0.0536]
Data / restraints / parameters	4287/0/219
Goodness-of-fit on F^2	1.058
Final R indices [I>=2^{σ}(I)]	R1 = 0.0653,wR2 = 0.1079
Final R indices (all data)	R1 = 0.1087,wR2 = 0.1244
Largest diff. peak and hole	0.21/-0.24 e.$Å^{-3}$

Table S11. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3aa**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7862.1(8)	6547.2(3)	7445.6(9)	60.2(2)
S2	9939.9(8)	3975.7(4)	6164.3(12)	76.3(3)
N1	7530(2)	5217.9(10)	10517(3)	55.6(6)
C9	8085(2)	4845.9(11)	9624(3)	45.6(6)
C4	8250(2)	5226.2(11)	8350(3)	42.3(6)
C3	7763(2)	5847.9(11)	8513(3)	47.3(6)
C16	8676(3)	3536.0(11)	4654(3)	49.4(6)
C5	8805(2)	4956.4(12)	7269(3)	48.4(6)
C10	6699(2)	6441.1(11)	5374(3)	48.3(6)
C2	7340(3)	5815.6(13)	9829(3)	55.4(7)
C11	5759(3)	5966.9(13)	4925(3)	57.6(7)
C15	6734(3)	6874.1(13)	4149(4)	62.1(8)
C6	9174(3)	4324.4(12)	7478(3)	54.9(7)
C17	9036(3)	3124.5(12)	3627(4)	61.8(8)
C8	8467(3)	4209.3(12)	9853(3)	56.1(7)
C21	7377(3)	3588.4(12)	4431(3)	57.2(7)
C7	9010(3)	3956.6(12)	8778(4)	61.0(8)
C18	8115(4)	2773.9(14)	2393(4)	72.8(10)
C20	6455(3)	3227.2(14)	3189(4)	67.5(8)
C12	4868(3)	5934.6(15)	3290(4)	67.9(8)
C14	5831(3)	6834.1(15)	2519(4)	71.7(9)

C19	6827(4)	2820.0(14)	2181(4)	74.0(9)
C1	7217(4)	5006.9(16)	11964(4)	82.3(10)
C13	4895(3)	6367.5(17)	2088(4)	75.2(9)

Table S12. Anisotropic Displacement Parameters ($Å^2×10^3$) for **3aa**. 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	65.8(5)	47.0(4)	62.3(4)	3.3(3)	16.6(4)	-5.2(3)
S2	53.9(5)	80.0(6)	97.5(6)	-39.2(5)	30.6(5)	-8.2(4)
N1	60.3(15)	64.6(14)	45.0(12)	3.8(10)	22.8(12)	1.9(12)
C9	41.6(15)	49.6(14)	36.6(13)	-0.4(11)	3.6(12)	-4.9(11)
C4	36.6(14)	47.8(14)	36.8(12)	-3.4(10)	6.6(12)	-3.6(11)
C3	46.4(16)	49.2(14)	43.7(14)	-0.4(11)	13.5(13)	-0.3(12)
C16	61.6(18)	39.1(13)	51.2(15)	0.2(11)	24.8(15)	0.5(12)
C5	44.4(15)	53.9(15)	43.4(13)	-6.9(11)	12.0(13)	-9.7(12)
C10	45.1(16)	47.4(14)	55.2(15)	7.6(12)	21.5(14)	11.0(12)
C2	54.7(18)	58.3(16)	53.2(16)	-2.8(13)	19.4(15)	7.2(13)
C11	54.0(19)	61.7(17)	58.0(17)	12.7(13)	21.4(16)	3.6(14)
C15	60(2)	55.5(16)	74(2)	17.2(14)	27.8(18)	8.3(14)
C6	46.6(17)	51.2(16)	59.5(17)	-16.5(13)	10.7(15)	-4.2(12)
C17	78(2)	51.7(16)	68.0(19)	-2.1(14)	40.5(19)	5.4(15)
C8	57.2(19)	53.3(16)	48.4(15)	4.0(12)	8.2(15)	-10.8(14)
C21	65(2)	52.2(16)	57.0(17)	-7.0(13)	24.7(16)	0.2(14)
C7	56.3(19)	41.6(14)	66.2(18)	-6.0(13)	-0.3(16)	0.0(13)
C18	117(3)	53.9(17)	58.5(18)	-10.8(14)	45(2)	-4.8(19)
C20	67(2)	70.2(19)	60.0(18)	-1.9(15)	17.1(17)	-10.9(16)
C12	56(2)	79(2)	62.5(19)	4.6(16)	13.9(17)	-2.2(16)
C14	74(2)	80(2)	63(2)	27.4(16)	26(2)	21.4(18)
C19	103(3)	64.7(19)	49.9(17)	-8.7(14)	23(2)	-22.8(19)
C1	99(3)	97(2)	62.4(19)	9.0(17)	44(2)	-7(2)
C13	65(2)	96(2)	56.8(18)	11.2(18)	12.2(17)	13.4(19)

Table S13. Bond Lengths for **3aa**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	**C3**	1.743(2)	**C5**	**C6**	1.374(3)
S1	**C10**	1.772(3)	**C10**	**C11**	1.384(4)
S2	**C16**	1.768(3)	**C10**	**C15**	1.389(3)
S2	**C6**	1.782(3)	**C11**	**C12**	1.379(4)
N1	**C9**	1.375(3)	**C15**	**C14**	1.381(4)

N1	**C2**	1.362(3)	**C6**	**C7**	1.408(4)
N1	**C1**	1.459(3)	**C17**	**C18**	1.375(4)
C9	**C4**	1.406(3)	**C8**	**C7**	1.367(4)
C9	**C8**	1.387(3)	**C21**	**C20**	1.390(4)
C4	**C3**	1.431(3)	**C18**	**C19**	1.369(4)
C4	**C5**	1.395(3)	**C20**	**C19**	1.371(4)
C3	**C2**	1.360(3)	**C12**	**C13**	1.371(4)
C16	**C17**	1.382(3)	**C14**	**C13**	1.369(4)
C16	**C21**	1.381(4)			

Table S14. Bond Angles for **3aa**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	**S1**	**C10**	104.50(12)	**C11**	**C10**	**C15**	118.9(3)
C16	**S2**	**C6**	103.68(12)	**C15**	**C10**	**S1**	116.9(2)
C9	**N1**	**C1**	125.6(2)	**C3**	**C2**	**N1**	110.6(2)
C2	**N1**	**C9**	108.2(2)	**C12**	**C11**	**C10**	120.0(2)
C2	**N1**	**C1**	126.2(2)	**C14**	**C15**	**C10**	120.2(3)
N1	**C9**	**C4**	108.2(2)	**C5**	**C6**	**S2**	119.8(2)
N1	**C9**	**C8**	129.7(2)	**C5**	**C6**	**C7**	120.6(2)
C8	**C9**	**C4**	122.1(2)	**C7**	**C6**	**S2**	119.5(2)
C9	**C4**	**C3**	106.3(2)	**C18**	**C17**	**C16**	120.6(3)
C5	**C4**	**C9**	119.2(2)	**C7**	**C8**	**C9**	117.5(2)
C5	**C4**	**C3**	134.5(2)	**C16**	**C21**	**C20**	119.8(3)
C4	**C3**	**S1**	127.86(18)	**C8**	**C7**	**C6**	121.6(2)
C2	**C3**	**S1**	125.0(2)	**C19**	**C18**	**C17**	120.4(3)
C2	**C3**	**C4**	106.7(2)	**C19**	**C20**	**C21**	120.5(3)
C17	**C16**	**S2**	116.6(2)	**C13**	**C12**	**C11**	121.0(3)
C21	**C16**	**S2**	124.3(2)	**C13**	**C14**	**C15**	120.6(3)
C21	**C16**	**C17**	119.1(3)	**C18**	**C19**	**C20**	119.6(3)
C6	**C5**	**C4**	118.9(2)	**C14**	**C13**	**C12**	119.3(3)
C11	**C10**	**S1**	124.15(19)				

Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3aa**.

Atom	*x*	*y*	*z*	U(eq)
H5	8924.61	5200.32	6419.97	58
H2	6971.89	6154.76	10207.49	67
H11	5727.44	5670.29	5727.01	69
H15	7367.64	7191.9	4427.11	74

H17	9909.69	3084.21	3771.82	74
H8	8357.88	3963.71	10705.98	67
H21	7118.47	3864.58	5109.57	69
H7	9277.74	3531.37	8907.52	73
H18	8367.34	2503.83	1696.68	87
H20	5580.65	3262.04	3041.25	81
H12	4239.54	5614.33	2996.8	82
H14	5857.75	7126.82	1706.92	86
H19	6208.21	2576.41	1358.42	89
H1A	6491.6	4717.6	11585.32	124
H1B	6996.66	5371.33	12494.75	124
H1C	7956.1	4792.99	12762.33	124
H13	4284.23	6344.55	991.85	90

(2) Single crystal X-ray diffraction of 4ka

White block-like single crystals of **4ka** 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 296(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.

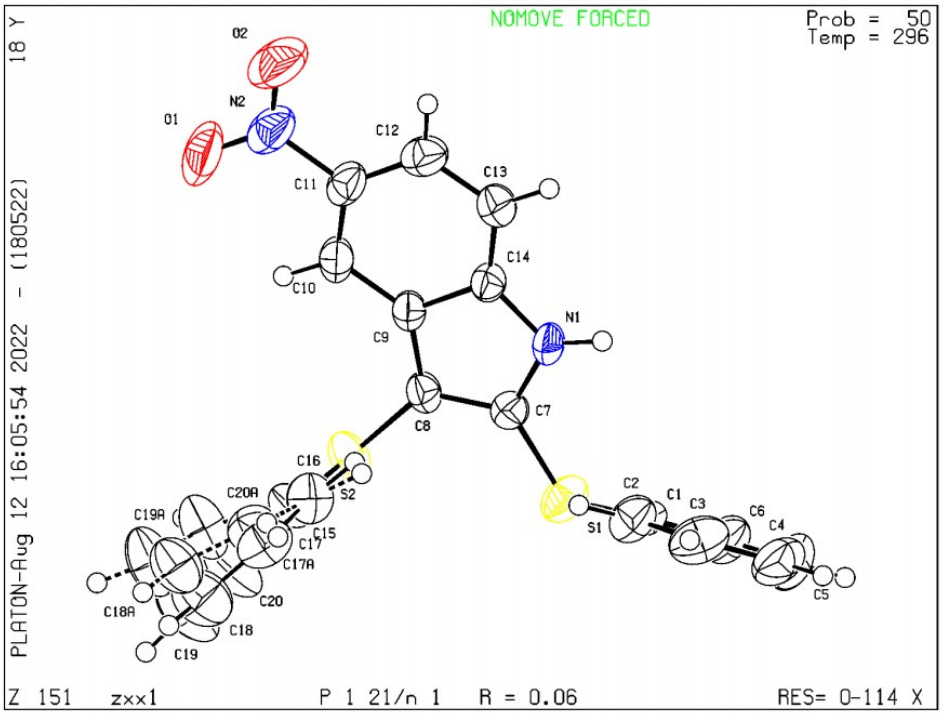


Figure S2. ORTEP drawing of **4ka** with the numbering scheme.

Table S16. Crystal data and structure refinement for **4ka**

Identification code	4ka	
Empirical formula	$C_{20}H_{14}N_2O_2S_2$	
Formula weight	378.45	
Temperature	296(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/n1$	
Unit cell dimensions	a = 13.2398(11) Å	α = 90°.
	b = 10.6639(9) Å	β = 103.117(9) °.
	c = 13.3695(12) Å	γ = 90°.
Volume	1838.4(3) $Å^3$	
Z	4	
F(000)	784	
Crystal size	0.18x 0.14 x 0.13mm^3	
2^{Θ} range for data collection	1.954 to 29.282	
Index ranges	-14<=h<=18, -14<=k<=13, -18<=l<=10	
Reflections collected	8828	
Independent reflections	4214 [R(int) = 0.0355]	
Data / restraints / parameters	4214 / 146 / 272	
Goodness-of-fit on F^2	1.044	
Final R indices [I>=2σ (I)]	R1 = 0.0614, wR2 = 0.1158	

Final R indices (all data)	R1 = 0.1026, wR2 = 0.1381
Largest diff. peak and hole	0.248 and -0.271 e.Å^{-3}

Table S17. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4ka**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S(1)	4661(1)	3807(1)	2243(1)	54(1)
S(2)	6885(1)	3679(1)	4156(1)	49(1)
O(1)	7850(2)	7431(3)	7166(2)	85(1)
O(2)	6885(2)	9067(3)	7113(2)	89(1)
N(1)	4535(2)	5998(2)	3305(2)	42(1)
N(2)	7081(2)	8051(3)	6768(2)	62(1)
C(1)	4005(2)	4692(3)	1169(2)	41(1)
C(2)	4396(2)	5780(3)	849(2)	55(1)
C(3)	3867(3)	6370(3)	-37(2)	67(1)
C(4)	2959(3)	5869(4)	-606(2)	73(1)
C(5)	2578(3)	4776(4)	-292(2)	73(1)
C(6)	3088(2)	4195(3)	594(2)	57(1)
C(7)	5086(2)	4941(2)	3188(2)	38(1)
C(8)	5965(2)	4885(2)	3963(2)	39(1)
C(9)	5961(2)	5969(2)	4588(2)	36(1)
C(10)	6635(2)	6428(3)	5469(2)	45(1)
C(11)	6379(2)	7550(3)	5854(2)	47(1)
C(12)	5495(2)	8240(3)	5413(2)	50(1)
C(13)	4823(2)	7805(3)	4546(2)	47(1)
C(14)	5058(2)	6664(3)	4145(2)	37(1)
C(15)	7938(2)	4351(3)	3726(2)	48(1)
C(16)	7924(2)	5494(3)	3260(2)	56(1)
C(17)	8755(7)	5914(11)	2877(7)	59(2)
C(17A)	8842(11)	6010(20)	3097(13)	58(3)
C(18)	9584(8)	5171(9)	2939(7)	82(2)
C(18A)	9771(13)	5423(14)	3380(13)	70(3)
C(19)	9573(6)	3977(8)	3311(9)	91(3)
C(19A)	9826(9)	4376(14)	3975(16)	83(4)
C(20)	8746(6)	3533(7)	3676(8)	75(2)

C(20A)	8943(8)	3878(14)	4215(14)	69(3)

Table S18. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4ka**. 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}
S(1)	70(1)	41(1)	45(1)	-4(1)	0(1)	-1(1)
S(2)	41(1)	41(1)	67(1)	12(1)	13(1)	8(1)
O(1)	57(1)	114(2)	69(2)	-12(2)	-17(1)	-22(2)
O(2)	94(2)	101(2)	72(2)	-42(2)	16(1)	-33(2)
N(1)	35(1)	49(1)	36(1)	-2(1)	-6(1)	8(1)
N(2)	57(2)	84(2)	47(2)	-16(2)	12(1)	-31(2)
C(1)	45(2)	44(2)	33(1)	-9(1)	8(1)	-1(1)
C(2)	59(2)	58(2)	47(2)	-4(2)	9(1)	-13(2)
C(3)	98(3)	56(2)	50(2)	4(2)	23(2)	-6(2)
C(4)	94(3)	75(3)	41(2)	-3(2)	-1(2)	19(2)
C(5)	69(2)	82(3)	56(2)	-7(2)	-10(2)	-8(2)
C(6)	60(2)	59(2)	50(2)	-7(2)	7(2)	-14(2)
C(7)	39(1)	40(2)	35(1)	-1(1)	7(1)	1(1)
C(8)	32(1)	42(2)	41(1)	4(1)	5(1)	6(1)
C(9)	30(1)	41(2)	35(1)	2(1)	3(1)	1(1)
C(10)	32(1)	60(2)	41(2)	4(1)	1(1)	-1(1)
C(11)	40(2)	60(2)	38(2)	-5(1)	6(1)	-17(1)
C(12)	56(2)	48(2)	48(2)	-10(2)	15(1)	-6(1)
C(13)	42(2)	49(2)	49(2)	-1(1)	5(1)	8(1)
C(14)	34(1)	42(2)	32(1)	2(1)	4(1)	2(1)
C(15)	45(2)	44(2)	60(2)	6(1)	19(1)	7(1)
C(16)	57(2)	51(2)	58(2)	8(2)	11(1)	-1(1)
C(17)	79(4)	54(4)	48(4)	2(3)	19(3)	-18(3)
C(17A)	63(6)	61(6)	51(6)	-1(5)	16(5)	-7(5)
C(18)	77(5)	91(5)	90(5)	13(4)	43(4)	-6(4)
C(18A)	57(5)	76(7)	85(8)	10(6)	29(6)	-3(5)
C(19)	74(4)	96(5)	118(6)	26(4)	57(4)	27(4)
C(19A)	52(5)	84(7)	116(8)	35(6)	24(6)	5(5)
C(20)	67(4)	64(4)	106(5)	25(4)	45(4)	24(3)
C(20A)	50(5)	62(6)	99(7)	34(6)	23(5)	6(4)

Table S19. Bond Lengths for **4ka**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	**C(1)**	1.772(3)	**C(11)**	**C(12)**	1.395(4)
S(1)	**C(7)**	1.747(3)	**C(12)**	**H(12)**	0.9300
S(2)	**C(8)**	1.749(3)	**C(12)**	**C(13)**	1.373(3)
S(2)	**C(15)**	1.775(3)	**C(13)**	**H(13)**	0.9300
O(1)	**N(2)**	1.230(3)	**C(13)**	**C(14)**	1.393(4)
O(2)	**N(2)**	1.227(3)	**C(15))**	**C(16)**	1.368(4)
N(1)	**H(1)**	0.8600	**C(15))**	**C(20)**	1.393(6)
N(1)	**C(7)**	1.371(3)	**C(15)**	**C(20A)**	1.434(10)
N(1)	**C(14)**	1.375(3)	**C(16)**	**H(16)**	0.9300
N(2)	**C(11)**	1.459(3)	**C(16)**	**H(16A)**	0.9300
C(1)	**C(2)**	1.378(4)	**C(16))**	**C(17)**	1.389(8)
C(1)	**C(6)**	1.386(4)	**C(16)**	**C(17A)**	1.395(14)
C(2)	**H(2)**	0.9300	**C(17)**	**H(17)**	0.9300
C(2)	**C(3)**	1.383(4)	**C(17)**	**C(18)**	1.341(8)
C(3)	**H(3)**	0.9300	**C(17A)**	**H(17A)**	0.9300
C(3)	**C(4)**	1.377(5)	**C(17A))**	**C(18A)**	1.355(13)
C(4)	**H(4)**	0.9300	**C(18))**	**H(18)**	0.9300
C(4)	**C(5)**	1.373(5)	**C(18)**	**C(19)**	1.369(8)
C(5)	**H(5)**	0.9300	**C(18A)**	**H(18A)**	0.9300
C(5)	**C(6)**	1.372(4)	**C(18A)**	**C(19A)**	1.363(13)
C(6)	**H(6)**	0.9300	**C(19**	**H(19)**	0.9300
C(7)	**C(8)**	1.373(3)	**C(19)**	**C(20)**	1.379(7)
C(8)	**C(9)**	1.427(3)	**C(19A))**	**H(19A)**	0.9300
C(9)	**C(10)**	1.395(3)	**C(19A)**	**C(20A)**	1.388(12)
C(9)	**C(14)**	1.417(3)	**C(20)**	**H(20)**	0.9300
C(10)	**H(10)**	0.9300	**C(20A)**	**H(20A)**	0.9300
C(10)	**C(11)**	1.374(4)			

Table S20. Bond Angles for **4ka**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(7)	**S(1)**	**C(1)**	103.63(12)	**C(13)**	**C(12)**	**H(12)**	120.0
C(8)	**S(2)**	**C(15)**	103.15(13)	**C(12)**	**C(13)**	**H(13)**	121.3
C(7)	**N(1)**	**H(1)**	125.2	**C(12)**	**C(13)**	**C(14)**	117.5(2)

C(7)	**N(1)**	**C(14)**	109.6(2)	**C(14)**	**C(13)**	**H(13)**	121.3
C(14)	**N(1)**	**H(1)**	125.2	**N(1)**	**C(14)**	**C(9)**	107.0(2)
O(1)	**N(2)**	**C(11)**	118.2(3)	**N(1)**	**C(14)**	**C(13)**	130.5(2)
O(2)	**N(2)**	**O(1)**	122.5(3)	**C(13)**	**C(14)**	**C(9)**	122.5(2)
O(2)	**N(2)**	**C(11)**	119.3(3)	**C(16)**	**C(15)**	**S(2)**	125.2(2)
C(2)	**C(1)**	**S(1)**	123.4(2)	**C(16**	**C(15)**	**C(20)**	117.9(4)
C(2)	**C(1)**	**C(6)**	119.6(3)	**C(16)**	**C(15)**	**C(20A)**	115.9(5)
C(6)	**C(1)**	**S(1)**	116.9(2)	**C(20)**	**C(15)**	**S(2)**	115.5(4)
C(1)	**C(2)**	**H(2)**	120.1	**C(20A)**	**C(15)**	**S(2)**	115.2(5)
C(1)	**C(2)**	**C(3)**	119.7(3)	**C(15**	**C(16**	**H(16)**	119.1
C(3)	**C(2)**	**H(2)**	120.1	**C(15)**	**C(16)**	**H(16A)**	120.0
C(2)	**C(3)**	**(3)**	119.8	**C(15)**	**C(16)**	**C(17)**	121.7(6)
C(4)	**C(3)**	**C(2)**	120.4(3)	**C(15)**	**C(16)**	**C(17A)**	120.0(10)
C(4)	**C(3)**	**H(3)**	119.8	**C(17)**	**C(16)**	**H(16)**	119.1
C(3)	**C(4)**	**H(4)**	120.1	**C(17A)**	**C(16)**	**H(16A)**	120.0
C(5)	**C(4)**	**C(3)**	119.7(3)	**C(16)**	**C(17)**	**H(17)**	120.3
C(5)	**C(4)**	**H(4)**	120.1	**C(18)**	**C(17)**	**C(16)**	119.5(9)
C(4)	**C(5)**	**H(5)**	119.8	**C(18)**	**C(17)**	**H(17)**	120.3
C(6)	**C(5)**	**C(4)**	120.3(3)	**C(16))**	**C(17A)**	**H(17A)**	118.6
C(6)	**C(5)**	**H(5)**	119.8	**C(18A)**	**C(17A)**	**C(16)**	122.9(18)
C(1)	**C(6)**	**H(6)**	119.9	**C(18A)**	**C(17A)**	**H(17A)**	118.6
C(5)	**C(6)**	**C(1)**	120.2(3)	**C(17)**	**C(18)**	**H(18)**	120.1
C(5)	**C(6)**	**H(6)**	119.9	**C(17)**	**C(18)**	**C(19)**	119.8(9)
N(1)	**C(7)**	**S(1)**	124.00(18)	**C(19)**	**C(18)**	**H(18)**	120.1
N(1)	**C(7)**	**C(8)**	109.4(2)	**C(17A)**	**C(18A)**	**H(18A)**	121.1
C(8)	**C(7)**	**S(1)**	126.5(2)	**C(17A)**	**C(18A)**	**C(19A)**	117.8(16)
C(7)	**C(8)**	**S(2)**	125.9(2)	**C(19A)**	**C(18A)**	**H(18A)**	121.1
C(7)	**C(8)**	**C(9)**	106.9(2)	**C(18)**	**C(19)**	**H(19)**	119.2
C(9)	**C(8)**	**S(2)**	127.15(18)	**C(18)**	**C(19)**	**C(20)**	121.5(7)
C(10)	**C(9)**	**C(8)**	133.8(2)	**C(20)**	**C(19)**	**H(19)**	119.2
C(10)	**C(9)**	**C(14)**	119.1(2)	**C(18A)**	**C(19A)**	**H(19A)**	119.6
C(14)	**C(9)**	**C(8)**	107.1(2)	**C(18A)**	**C(19A**	**C(20A)**	120.8(12)
C(9)	**C(10)**	**H(10)**	121.4	**C(20A)**	**C(19A)**	**H(19A)**	119.6
C(11)	**C(10)**	**C(9)**	117.2(2)	**C(15)**	**C(20)**	**H(20)**	120.6
C(11)	**C(10)**	**H(10)**	121.4	**C(19)**	**C(20))**	**C(15)**	118.8(6)

C(10)	**C(11)**	**N(2)**	118.0(3)	**C(19)**	**C(20)**	**H(20)**	120.6
C(10)	**C(11)**	**C(12)**	123.8(2)	**C(15)**	**C(20A)**	**H(20A)**	119.9
C(12)	**C(11)**	**N(2)**	118.3(3)	**C(19A)**	**C(20A)**	**C(15)**	120.2(10)
C(11)	**C(12)**	**H(12)**	120.0	**C(19A)**	**C(20A)**	**H(20A)**	119.9
C(13)	**C(12)**	**C(11)**	119.9(3)				

Table S21. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4ka**.

Atom	***x***	***y***	***z***	**U(eq)**
H(1)	3951	6212	2913	51
H(2)	5014	6116	1227	66
H(3)	4126	7110	-250	80
H(4)	2604	6270	-1201	87
H(5)	1971	4428	-682	87
H(6)	2817	3465	811	69
H(10)	7232	5994	5782	54
H(12)	5360	8994	5708	60
H(13)	4233	8255	4237	57
H(16)	7343	6004	3197	67
H(16A)	7303	5928	3051	67
H(17)	8737	6705	2580	71
H(17A)	8815	6788	2779	69
H(18)	10164	5466	2730	98
H(18A)	10352	5726	3176	84
H(19)	10135	3452	3319	109
H(19A)	10464	3991	4223	100
H(20)	8728	2703	3886	90
H(20A)	9002	3235	4695	83

(3) Single crystal X-ray diffraction of 5.

White block-like single crystals of **5** 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.

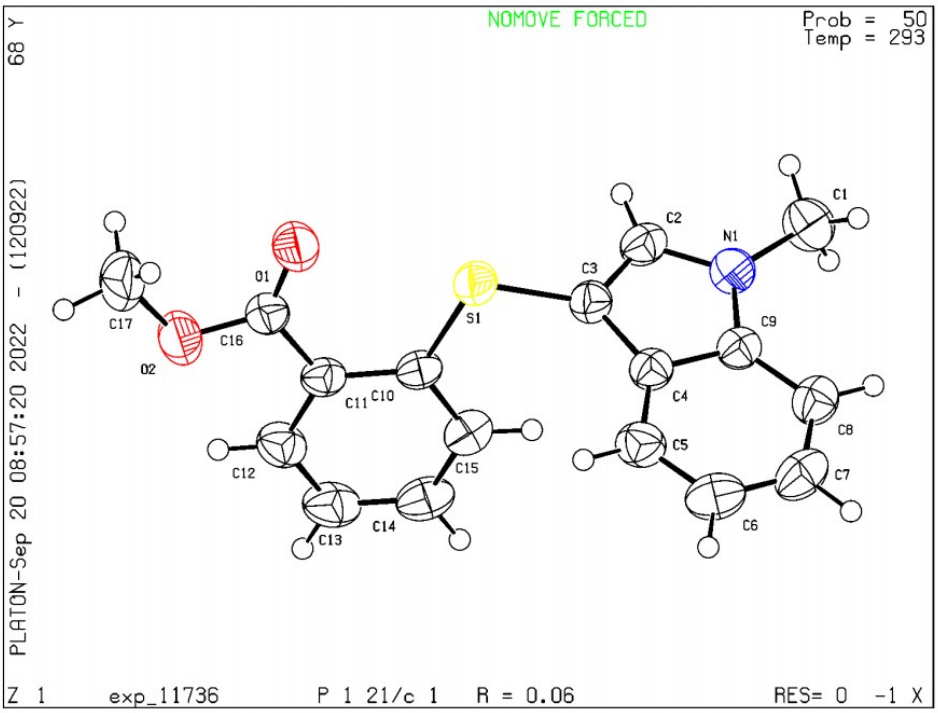


Figure S3. ORTEP drawing of **5** with the numbering scheme.

Table S22. Crystal data and structure refinement for **5**

Identification code	5	
Empirical formula	$C_{17}H_{15}NO_2S$	
Formula weight	297.36	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9527(7)) Å	α = 90°.
	b = 13.3537(10) Å	β = 98.396(7) °.
	c = 13.9904(10) Å	γ = 90°.
Volume	1469.8(2) $Å^3$	
Z	4	
F(000)	624.0	
Crystal size	0.15x 0.12 x 0.10mm^3	
2^{Θ} range for data collection	4.238 to 58.778	
Index ranges	-7≤h≤10, -18≤k≤16, -18≤l≤19	
Reflections collected	7087	

Independent reflections	3370 [Rint = 0.0377, Rsigma = 0.0655]
Data / restraints / parameters	3370/0/193
Goodness-of-fit on F^2	1.038
Final R indices [I>=2σ (I)]	R1 = 0.0582, wR2 = 0.1122
Final R indices (all data)	R1 = 0.0955, wR2 = 0.1301
Largest diff. peak and hole	0.23/-0.22 e.Å^{-3}

Table S23. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	3009.4(8)	4525.3(5)	6995.1(4)	48.3(2)
O2	1671(2)	3957.1(14)	9885.9(11)	64.3(5)
O1	2771(3)	4945.8(15)	8871.7(12)	69.6(6)
N1	2780(2)	4627.6(15)	4183.1(13)	44.8(5)
C11	1216(3)	3509.4(17)	8252.3(15)	39.6(5)
C9	3795(3)	3791.4(18)	4336.4(15)	39.9(5)
C10	1615(3)	3580.0(17)	7309.0(15)	38.7(5)
C4	4022(3)	3573.5(18)	5330.6(15)	40.0(6)
C16	1971(3)	4213.4(19)	9009.8(16)	44.8(6)
C3	3066(3)	4308.5(18)	5769.4(15)	42.1(6)
C15	879(3)	2886.0(19)	6629.3(17)	48.8(6)
C8	4540(3)	3217.4(19)	3682.1(17)	49.4(6)
C2	2354(3)	4925.7(18)	5044.8(16)	45.2(6)
C12	93(3)	2771.5(19)	8468.5(19)	50.9(6)
C5	5025(3)	2757.4(19)	5666.1(18)	52.2(7)
C13	-643(3)	2109(2)	7778(2)	59.1(7)
C14	-228(3)	2165.9(19)	6861.7(19)	54.9(7)
C7	5508(3)	2415(2)	4046(2)	58.7(7)
C1	2293(3)	5120(2)	3256.5(17)	59.4(7)
C6	5751(3)	2187(2)	5025(2)	62.0(7)
C17	2436(4)	4590(2)	10666.1(18)	78.8(10)

Table S24. Anisotropic Displacement Parameters (Å^2×10^3) for **5**. 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	57.3(4)	43.5(4)	45.9(4)	-7.0(3)	13.8(3)	-11.1(3)
O2	84.9(13)	65.2(13)	44.9(9)	-0.5(10)	16.7(9)	-21.3(11)
O1	107.5(16)	54.8(12)	48.8(10)	-7.7(10)	19.2(10)	-31.7(12)

N1	43.6(11)	46.1(12)	43.8(11)	0.6(10)	3.2(9)	2.1(10)
C11	36.9(12)	33.8(13)	48.5(13)	-0.3(11)	7.8(10)	3.8(11)
C9	34.6(12)	39.8(14)	45.2(12)	-3.6(11)	5.2(10)	-4.5(11)
C10	34.9(12)	33.4(12)	47.2(12)	-2.6(11)	3.9(10)	4.0(10)
C4	37.9(13)	39.0(13)	42.8(12)	-3.1(11)	5.4(10)	-4.3(11)
C16	50.5(15)	38.4(14)	47.5(14)	1.9(12)	13.6(11)	4.5(12)
C3	44.5(13)	40.5(14)	42.1(12)	-2.7(11)	9.4(10)	-3.7(12)
C15	47.4(14)	45.6(15)	53.1(14)	-8.0(12)	6.5(11)	0.6(12)
C8	45.5(14)	53.3(17)	49.7(13)	-7.4(13)	7.8(11)	-5.0(13)
C2	42.8(14)	40.3(14)	53.6(14)	-6.0(12)	11.0(11)	2.4(12)
C12	46.1(15)	46.4(15)	62.4(15)	5.5(13)	15.3(12)	-1.6(13)
C5	56.7(16)	45.8(15)	52.2(14)	3.4(13)	1.5(12)	4.3(13)
C13	48.8(16)	45.2(16)	85(2)	-0.3(15)	16.7(14)	-11.5(14)
C14	46.1(15)	42.6(15)	73.8(18)	-13.5(14)	1.1(13)	-6.8(13)
C7	48.2(15)	59.0(18)	71.0(18)	-19.0(16)	15.1(13)	3.3(14)
C1	60.8(17)	62.7(19)	51.5(14)	8.1(14)	-3.1(12)	7.7(15)
C6	56.2(17)	48.8(17)	79.5(19)	-3.1(16)	4.3(14)	12.1(14)
C17	114(3)	81(2)	43.1(14)	-9.3(16)	17.3(15)	-25(2)

Table S25. Bond Lengths for **5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	**C10**	1.777(2)	**C9**	**C8**	1.391(3)
S1	**C3**	1.746(2)	**C10**	**C15**	1.394(3)
O2	**C16**	1.327(3)	**C4**	**C3**	1.433(3)
O2	**C17**	1.443(3)	**C4**	**C5**	1.391(3)
O1	**C16**	1.197(3)	**C3**	**C2**	1.364(3)
N1	**C9**	1.376(3)	**C15**	**C14**	1.375(3)
N1	**C2**	1.359(3)	**C8**	**C7**	1.374(3)
N1	**C1**	1.455(3)	**C12**	**C13**	1.375(3)
C11	**C10**	1.405(3)	**C5**	**C6**	1.367(3)
C11	**C16**	1.477(3)	**C13**	**C14**	1.372(3)
C11	**C12**	1.393(3)	**C7**	**C6**	1.388(4)
C9	**C4**	1.407(3)			

Table S26. Bond Angles for **5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	**S1**	**C10**	103.39(11)	**C5**	**C4**	**C3**	134.9(2)
C16	**O2**	**C17**	115.8(2)	**O2**	**C16**	**C11**	112.9(2)
C9	**N1**	**C1**	125.4(2)	**O1**	**C16**	**O2**	122.1(2)
C2	**N1**	**C9**	108.43(19)	**O1**	**C16**	**C11**	125.0(2)

C2	**N1**	**C1**	126.1(2)	**C4**	**C3**	**S1**	128.73(18)
C10	**C11**	**C16**	120.5(2)	**C2**	**C3**	**S1**	124.20(18)
C12	**C11**	**C10**	119.4(2)	**C2**	**C3**	**C4**	106.51(19)
C12	**C11**	**C16**	120.1(2)	**C14**	**C15**	**C10**	121.5(2)
N1	**C9**	**C4**	108.04(19)	**C7**	**C8**	**C9**	117.1(2)
N1	**C9**	**C8**	129.9(2)	**N1**	**C2**	**C3**	110.6(2)
C8	**C9**	**C4**	122.1(2)	**C13**	**C12**	**C11**	121.5(2)
C11	**C10**	**S1**	120.95(17)	**C6**	**C5**	**C4**	119.4(2)
C15	**C10**	**S1**	121.23(17)	**C14**	**C13**	**C12**	119.0(2)
C15	**C10**	**C11**	117.8(2)	**C13**	**C14**	**C15**	120.6(2)
C9	**C4**	**C3**	106.4(2)	**C8**	**C7**	**C6**	121.7(2)
C5	**C4**	**C9**	118.7(2)	**C5**	**C6**	**C7**	121.0(3)

Table S27. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5**.

Atom	*x*	*y*	*z*	U(eq)
H15	1144.16	2910.77	6003.82	59
H8	4389.02	3370.55	3026.64	59
H2	1670.31	5474.51	5128.89	54
H12	-166.27	2725.42	9094.05	61
H5	5199.19	2600.73	6320.8	63
H13	-1409.69	1630.19	7930.6	71
H14	-700.54	1712.87	6393.24	66
H7	6014.66	2012.65	3625.63	70
H1A	3273.95	5191.78	2935.37	89
H1B	1832.3	5769.14	3358.53	89
H1C	1452.04	4723.8	2864.03	89
H6	6417.74	1639.76	5247.74	74
H17A	1878.24	5229.25	10622.87	118
H17B	3619.83	4679.59	10621.91	118
H17C	2318.67	4281.71	11272.85	118

8. Computational Details.

All density functional theory (DFT) calculations with tightSCF and defgrid3 were carried out using ORCA 5.0.3 packges[4-5]. Geometry optimization of all intermediates and transition states were carried out at the (U)M06-2X[6] level of theory using a basis set of def2-TZVP[7] and the conductor-like polarizable continuum model (CPCM) solvent model[8] accounting for the effect of mixed solvents (V_{DMSO}: $V_{1,4\text{-dioxane}}$ = 1 : 5) . Frequency analyses at 353.15 K were also performed at the same level of theory as geometry optimization to confirm whether optimized stationary points were either local minimum (no imaginary frequency) or transition state (only one imaginary frequency), as well as to evaluate zero-point vibrational

energies (ZPE) and thermal corrections. Shermo 2.3.4 was used to refine the thermodynamic data[9]. And the intrinsic reaction coordinates (IRC) were done to verified the transition state with the reactant and product. The 3D diagrams of molecules were generated using CYLview2.0[10] andVMD 1.9.3[11]. The Frontier Molecular Orbitals were generated using Multiwfn 3.7[12].

(1) The Hypothesized reaction mechanisms of indoline C5–H functionalization.

(a) Mechanism of Electrophilic Aromatic Substitution.

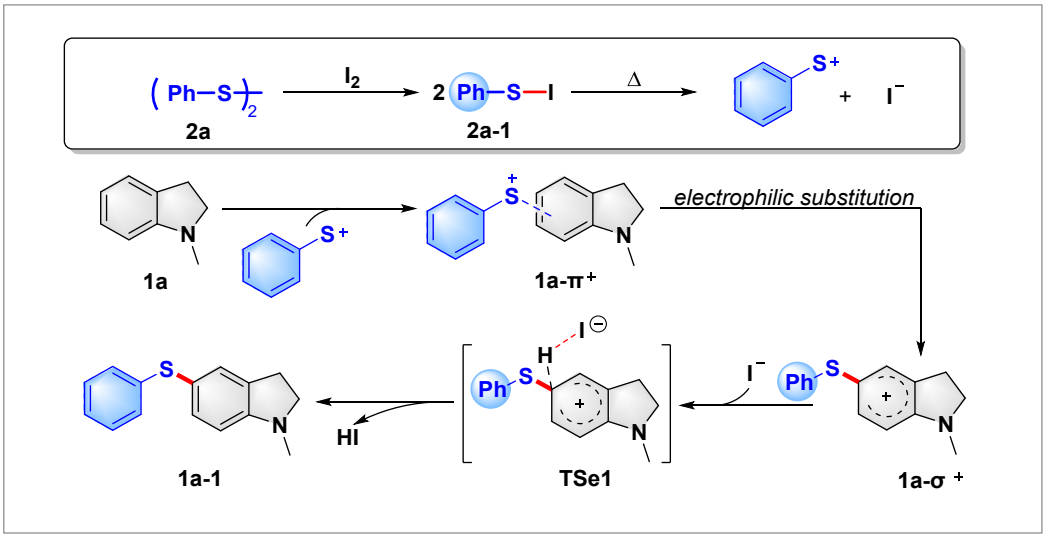
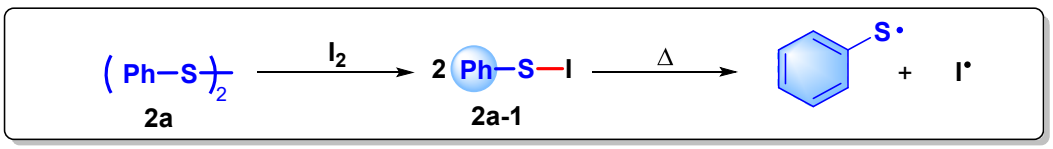


Table S28. The thermodynamic data and the image frequency of transition states in electrophilic aromatic substitution.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
1a	-404.3027160	-404.1206424	-404.1093001	-404.1081817	-404.1611783	
PhSI	-927.4612116	-927.368249	-927.3583559	-927.3572375	-927.4103003	
PhS^+	-629.5445557	-629.453119	-629.4452929	-629.4441745	-629.4901595	
I^-	-297.8119955	-297.8119955	-297.8103179	-297.8091996	-297.8324251	
1a-π^+	-1033.945477	-1033.666688	-1033.647168	-1033.646049	-1033.716184	
1a-σ^+	-1033.947344	-1033.670006	-1033.649237	-1033.648118	-1033.722211	
TSe1	-1033.900574	-1033.628414	-1033.607918	-1033.6068	-1033.68028	876.64i
1a-1	-1033.534133	-1033.269508	-1033.249468	-1033.248349	-1033.320712	

(b) Mechanism of Radical Addition .



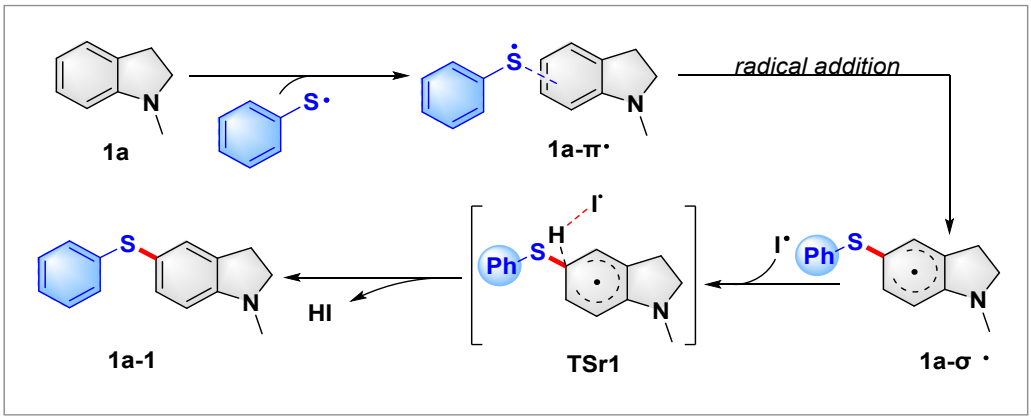


Table S29. The thermodynamic data and the image frequency of transition states in radical addition.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
I_2	-595.2566864	-595.2561743	-595.252695	-595.2515766	-595.2874058	
PhS·	-629.7866477	-629.6952811	-629.6877678	-629.6866494	-629.7319149	
I·	-297.6129165	-297.6129165	-297.611239	-297.6101206	-297.6341213	
1a-π·	-1034.098198	-1033.824164	-1033.802698	-1033.80158	-1033.878058	
1a-σ·	-1033.879139	-1033.825969	-1033.804513	-1033.803395	-1033.878058	
TSr1	-1331.751323	-1331.481603	-1331.458239	-1331.457121	-1331.53817	1029.70i
1a-1	-1033.534133	-1033.269508	-1033.249468	-1033.248349	-1033.320712	
HI	-298.226218	-298.226218	-298.226218	-298.226218	-298.226218	

(c) Mechanism of Nucleophilic Substitution.

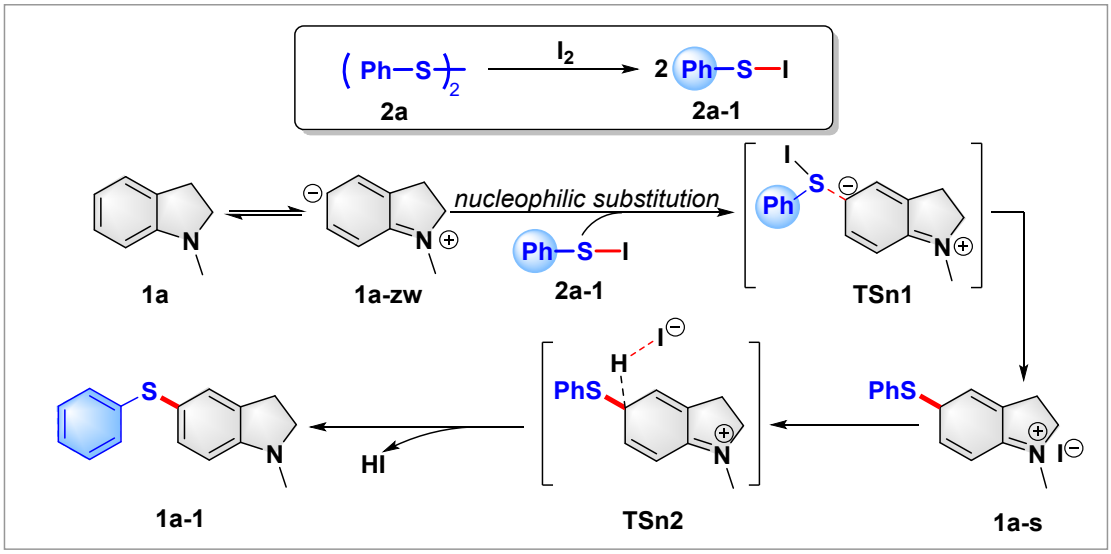


Table S30. The thermodynamic data and the image frequency of transition states in nucleophilic dubstitution.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
1a-zw	-404.2990042	-404.117869	-404.1068372	-404.1057189	-404.1584638	
TSn1	-1331.75194	-1331.476097	-1331.452693	-1331.451574	-1331.533367	267.22i
1a-s	-1331.77739	-1331.499808	-1331.476109	-1331.47499	-1331.557556	
TSn2	-1331.751198	-1331.481586	-1331.45818	-1331.457062	-1331.538299	1030.75i
1a-1	-1033.534133	-1033.269508	-1033.249468	-1033.248349	-1033.320712	

(2) The Hypothesized reaction mechanisms of indoline oxidative dehydrogenation.

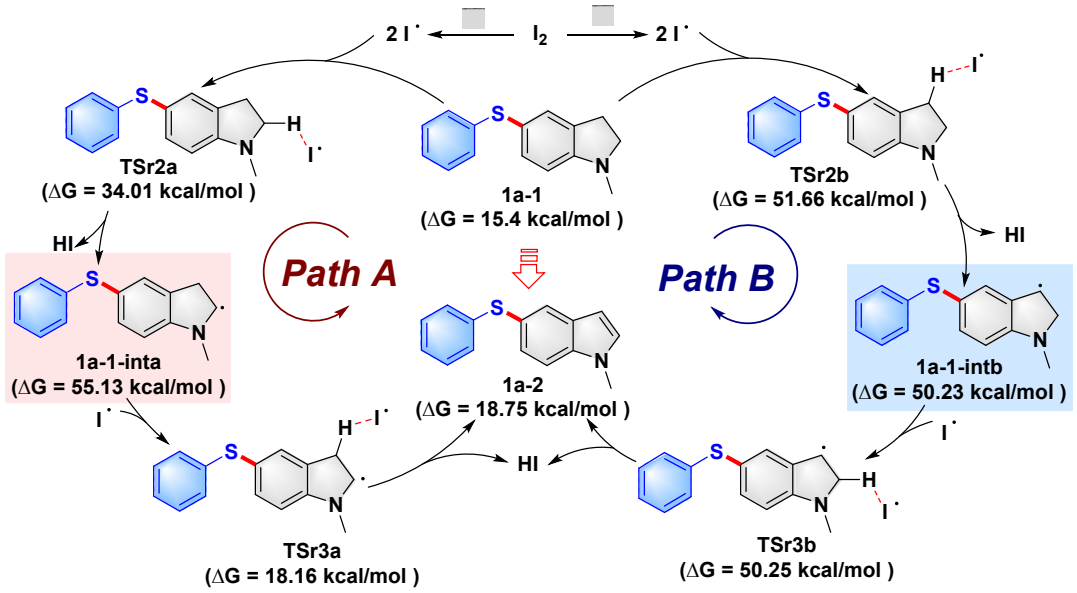


Table S31. The thermodynamic data and the image frequency of transition states in oxidative dehydrogenation.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
TSr2a	-1628.778441	-1628.518167	-1628.492866	-1628.491747	-1628.578475	987.69i
1a-1-inta	-1032.882403	-1032.632047	-1032.611686	-1032.610568	-1032.684477	
TSr3a	-1330.568237	-1330.321578	-1330.29927	-1330.298151	-1330.377505	945.63i
TSr2b	-1331.114624	-1330.860167	-1330.838178	-1330.83706	-1330.916216	638.86i
1a-1-intb	-1032.88995	-1032.63981	-1032.619452	-1032.618333	-1032.692277	
TSr3b	-1032.890007	-1032.639853	-1032.619536	-1032.618417	-1032.692244	855.38i
1a-2	-1032.341024	-1032.099595	-1032.080136	-1032.079017	-1032.15035	

(3) The Hypothesized reaction mechanisms of indole C3–H functionalization.

(a) Mechanism of Electrophilic Aromatic Substitution.

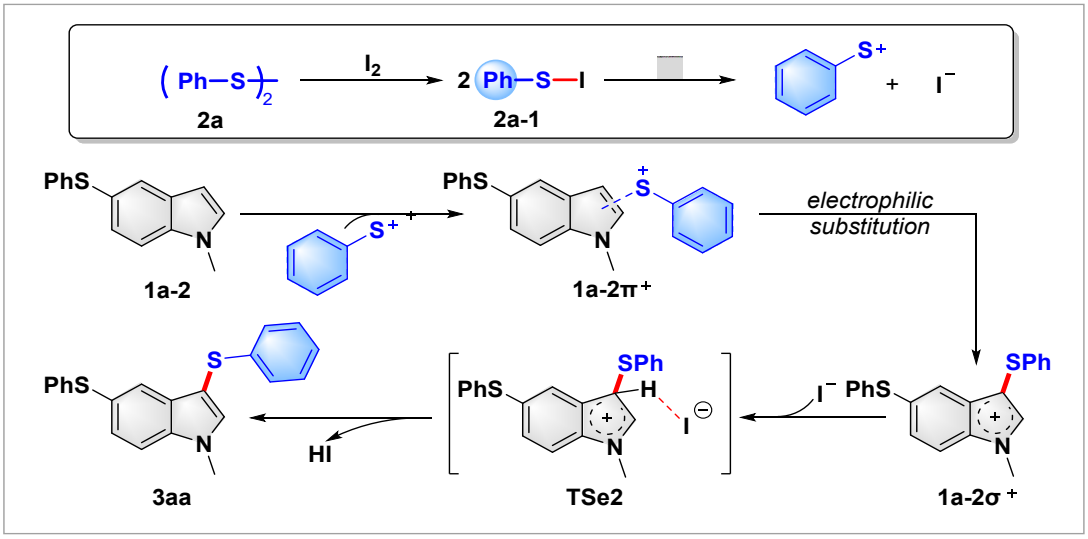


Table S32. The thermodynamic data and the image frequency of transition states in electrophilic aromatic substitution.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
1a-2	-1032.341024	-1032.099595	-1032.080136	-1032.079017	-1032.15035	
1a-2π$^+$	-1661.967838	-1661.631475	-1661.603261	-1661.602142	-1661.690832	
1a-2σ$^+$	-1661.983593	-1661.647006	-1661.618703	-1661.617584	-1661.707477	
TSe2	-1959.797572	-1959.468208	-1959.437174	-1959.436056	-1959.53278	918.03i
3aa	-1661.573882	-1661.249836	-1661.221655	-1661.220536	-1661.310018	

(b) Mechanism of Radical Addition.

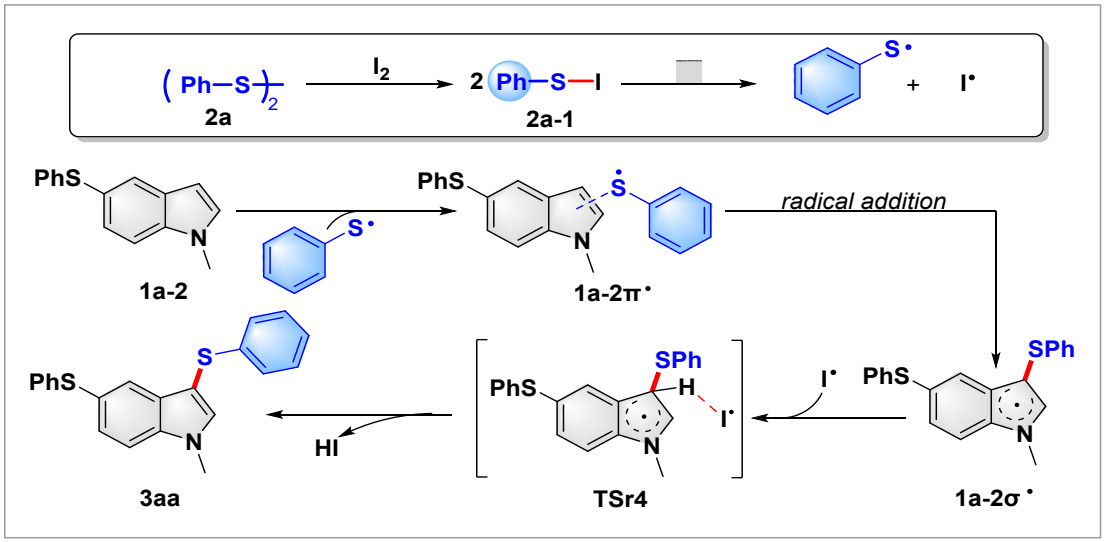


Table S33. The thermodynamic data and the image frequency of transition states in radical addition.

Structure	Eele(a.u.)	E0(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	Image frequency (cm^{-1})
1a-2	-1032.341024	-1032.099595	-1032.080136	-1032.079017	-1032.15035	
1a-2π·	-1662.139654	-1661.805993	-1661.776629	-1661.775511	-1661.868418	
1a-2σ·	-1662.136829	-1661.803365	-1661.773863	-1661.772745	-1661.865632	
TSr4	-1959.795408	-1959.465795	-1959.434895	-1959.433777	-1959.529513	1004.19i
3aa	-1661.573882	-1661.249836	-1661.221655	-1661.220536	-1661.310018	

Note: at the M06-2X/def2-TZVP level of theory with CPCM(mixed solvent).

(4) The free energy and Boltzmann distribution (P%) of the intermediate sigma complexes at 4, 5, 6 and 7 positions of 1a.

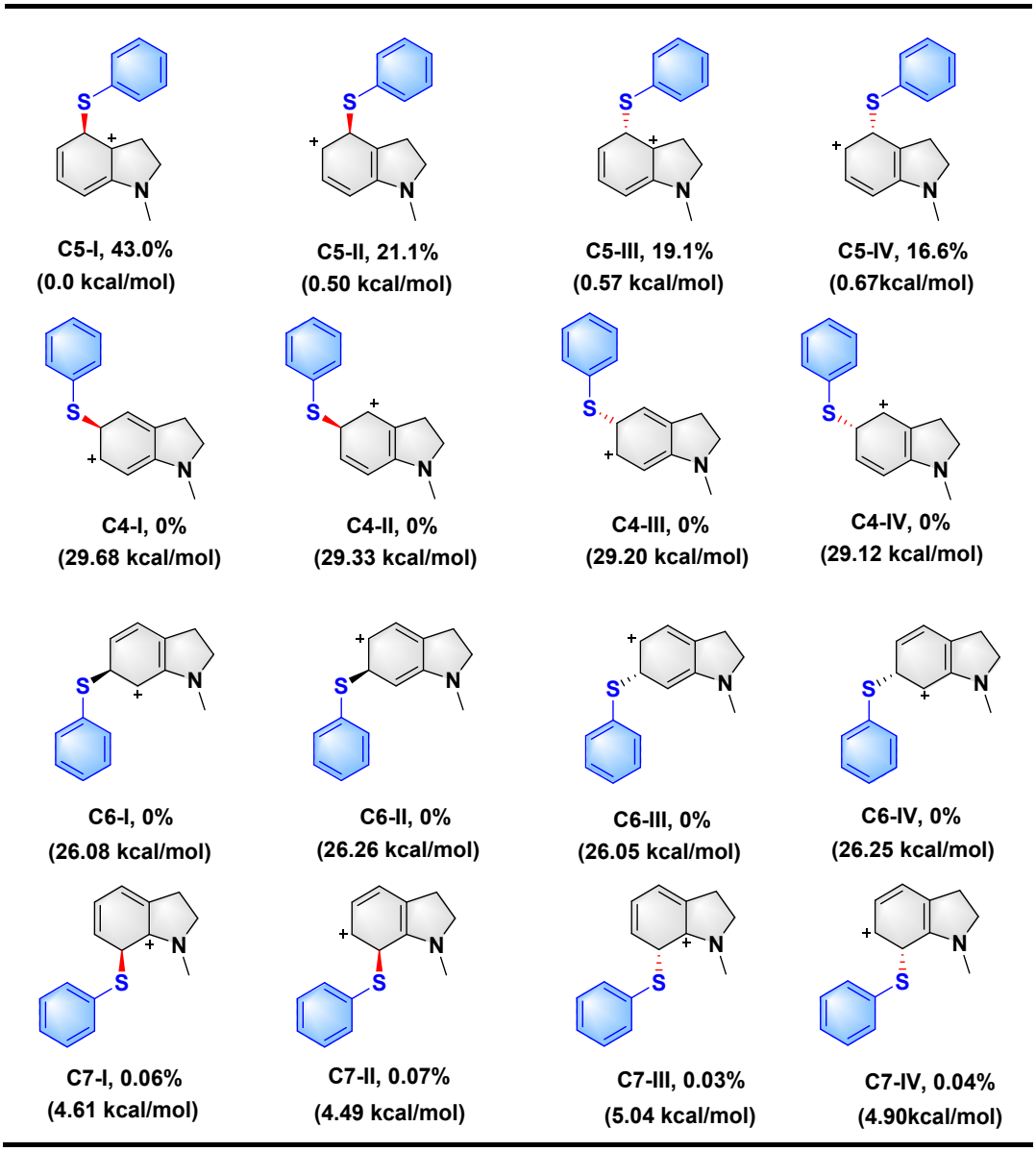


Table S34. The thermodynamic data and Boltzmann distribution (P%) of the intermediate sigma complexes at 4, 5, 6 and 7 positions of **1a**.

Structures	Eele(a.u.)	ZPE(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	dG(kcal/mol)	P%
C4-I	-1033.896488	-1033.621184	-1033.600316	-1033.599197	-1033.673124	29.68	0.00
C4-II	-1033.896523	-1033.621346	-1033.600422	-1033.599304	-1033.673418	29.33	0.00
C4-III	-1033.896999	-1033.621759	-1033.600855	-1033.599737	-1033.673758	29.20	0.00
C4-IV	-1033.896487	-1033.621428	-1033.600458	-1033.59934	-1033.673567	29.12	0.00
C5-I	-1033.947344	-1033.670006	-1033.649237	-1033.648118	-1033.722211	0.00	43.01
C5-II	-1033.946908	-1033.669436	-1033.64875	-1033.647632	-1033.721594	0.50	21.10
C5-III	-1033.946915	-1033.66943	-1033.648748	-1033.64763	-1033.721541	0.57	19.06
C5-IV	-1033.946905	-1033.669382	-1033.648714	-1033.647595	-1033.72146	0.67	16.63
C6-I	-1033.901327	-1033.626339	-1033.605482	-1033.604364	-1033.678409	26.08	0.00
C6-II	-1033.90132	-1033.626278	-1033.605455	-1033.604337	-1033.678263	26.26	0.00
C6-III	-1033.901331	-1033.626357	-1033.605489	-1033.604371	-1033.678439	26.05	0.00
C6-IV	-1033.90132	-1033.626282	-1033.60546	-1033.604341	-1033.678274	26.25	0.00
C7-I	-1033.940486	-1033.663194	-1033.642526	-1033.641408	-1033.715104	4.61	0.06
C7-II	-	-	-	-	-	4.49	0.07

	1033.9404 58 -	1033.6632 09 -	1033.6425 2 -	1033.64 1402 -	1033.715 186 -		
C7-III	1033.9444 07 -	1033.6662 95 -	1033.6462 41 -	1033.64 5123 -	1033.716 722 -	5.04	0.03
C7-IV	1033.9444 34	1033.6663 78	1033.6462 94	1033.64 5176	1033.716 849	4.90	0.04

Note: at the M06-2X/def2-TZVP level of theory with CPCM (mixed solvent).

(5) The free energy and Boltzmann distribution (P%) of the intermediate sigma complexes at 2 and 3 positions of 1a-2.

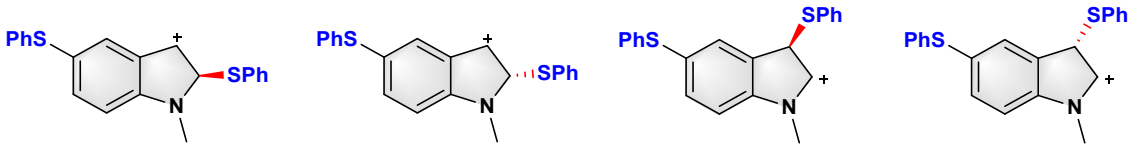


Table S35. The thermodynamic data and Boltzmann distribution (P%) of the intermediate sigma complexes at 2,3 positions of **1a-2**.

Structures	Eele(a.u.)	ZPE(a.u.)	U(a.u.)	H(a.u.)	G(a.u.)	dG(kcal/mol)	P%
C2-I	- 1661.9605 89	- 1661.6247 91	- 1661.5 96193	- 1661.59 5075	- 1661.68 5783	13.61	0.00
C2-II	- 1661.9606 08	- 1661.6249 44	- 1661.5 96261	- 1661.59 5143	- 1661.68 6006	13.47	0.00
C3-I	- 1661.9835 93	- 1661.6470 06	- 1661.6 18703	- 1661.61 7584	- 1661.70 7477	0.00	52.14
C2-II	- 1661.9836 46	- 1661.6469 89	- 1661.6 18729	- 1661.61 761	- 1661.70 7381	0.06	47.86

Note: at the M06-2X/def2-TZVP level of theory with CPCM (mixed solvent).

(6) All Opted Species Cartesian Coordinates.

Table S36. The Cartesian Coordinates of **1a**.

N	-7.818971	0.340639	-0.288220
C	-7.649563	0.807001	1.094137
C	-8.556976	-0.123710	1.909148
C	-10.867734	-1.031053	1.034157
C	-11.640141	-1.276061	-0.106385
C	-11.141222	-0.959676	-1.362340
C	-9.872605	-0.398537	-1.519939
C	-9.111237	-0.172845	-0.380565
C	-9.614308	-0.476707	0.892302
C	-7.344011	1.228704	-1.326099
H	-6.601613	0.766772	1.388021
H	-7.997959	1.846735	1.178317
H	-8.011869	-1.021966	2.212458
H	-8.951866	0.352732	2.804514
H	-11.256151	-1.264947	2.018645
H	-12.629392	-1.703522	-0.008772
H	-11.748858	-1.141478	-2.240277
H	-9.500853	-0.148706	-2.505132
H	-6.310440	1.501458	-1.115796
H	-7.373439	0.728568	-2.293349
H	-7.945790	2.146500	-1.384526

Table S37. The Cartesian Coordinates of **PhSI**.

C	-9.410431	0.706111	-0.557058
C	-9.505162	-1.387776	0.620943
C	-10.892737	-1.372056	0.527559
C	-11.539052	-0.318112	-0.107004
C	-10.800648	0.725024	-0.648546
S	-8.466179	1.993687	-1.318374
I	-8.136145	3.503841	0.517452
H	-7.680131	-0.353088	0.144197
H	-9.002228	-2.209359	1.114305
H	-11.470924	-2.184029	0.949668
H	-12.618799	-0.306232	-0.180266
H	-11.294199	1.553117	-1.140996

Table S38. The Cartesian Coordinates of **PhS**$^{+}$.

C	-9.216134	1.048077	-0.277317
C	-8.666260	-0.255859	0.070213
C	-9.510048	-1.297623	0.345046
C	-10.907200	-1.085602	0.287387
C	-11.482994	0.162509	-0.045074
C	-10.662465	1.221456	-0.325621
S	-8.222366	2.301235	-0.611048

H	-7.580502	-0.363384	0.101925
H	-9.122434	-2.281292	0.608672
H	-11.571652	-1.924036	0.511136
H	-12.567162	0.268566	-0.075256
H	-11.052883	2.205854	-0.590263

Table S39. The Cartesian Coordinates of **1a-π**$^{+}$.

N	-1.014333	0.807621	-1.214104
C	-0.184098	1.095982	0.033455
C	-0.483570	-0.034429	1.017881
C	-1.244608	-2.461952	0.390311
C	-1.767855	-3.262524	-0.616501
C	-2.049774	-2.739621	-1.878579
C	-1.815697	-1.400628	-2.158741
C	-1.286900	-0.634994	-1.137317
C	-1.001772	-1.121794	0.121377
C	-0.275600	1.203143	-2.453607
S	-2.569127	1.767468	-1.280006
C	-3.270913	1.373912	0.280113
C	-3.970261	0.178112	0.453951
C	-4.507011	-0.120027	1.696956
C	-4.367975	0.781023	2.747409
C	-3.696824	1.985046	2.564174
C	-3.140691	2.284317	1.330077
H	-3.603146	2.687062	3.381991
H	-4.794500	0.546758	3.714455
H	-5.042101	-1.049058	1.842414
H	-4.083343	-0.507743	-0.376640
H	-2.607493	3.213537	1.173779
H	-1.960764	-4.309147	-0.420430
H	-2.457307	-3.380195	-2.648982
H	-2.048875	-0.981539	-3.128833
H	-1.030276	-2.871865	1.368929
H	0.853709	1.057439	-0.292308
H	-0.421190	2.097133	0.381262
H	-1.233649	0.247557	1.758495
H	0.421102	-0.330366	1.546520
H	-0.009452	2.253531	-2.362153
H	0.612674	0.579683	-2.519184
H	-0.918481	1.046556	-3.316063

Table S40. The Cartesian Coordinates of **1a-σ**$^{+}$.

C	-0.097076	0.778548	-0.359310
C	0.194987	-0.656043	-0.600281

C	1.420851	-1.192162	-0.527108
C	2.516318	-0.311041	-0.227964
C	2.313393	1.114358	-0.030692
C	1.090290	1.635231	-0.095704
N	3.770831	-0.614325	-0.098596
C	4.625274	0.550840	0.199232
C	3.658395	1.744863	0.222526
C	4.388750	-1.921829	-0.215893
S	-1.204682	0.910044	1.122394
C	-2.711990	0.249689	0.455031
C	-3.423149	0.954963	-0.514338
C	-4.613567	0.440928	-1.006484
C	-5.107504	-0.764714	-0.519201
C	-4.404878	-1.460484	0.455526
C	-3.201990	-0.959746	0.939154
H	-0.678034	1.190616	-1.189573
H	-0.657102	-1.287747	-0.825206
H	1.584168	-2.247644	-0.687993
H	0.917424	2.694883	0.052465
H	5.385659	0.622060	-0.578037
H	5.118610	0.372927	1.154659
H	3.679101	2.257812	1.182030
H	3.902605	2.467844	-0.553878
H	3.634782	-2.689752	-0.348414
H	5.067663	-1.912846	-1.068596
H	4.958368	-2.115590	0.692536
H	-3.045827	1.904054	-0.876011
H	-5.162505	0.988238	-1.761903
H	-6.041347	-1.158984	-0.898736
H	-4.786481	-2.398863	0.836710
H	-2.642203	-1.504187	1.689024

Table S41. The Cartesian Coordinates of **TSe1**.

C	-9.343493	0.093323	0.888532
C	-8.734694	0.067060	-0.409730
C	-7.495569	-0.577408	-0.637268
C	-6.879792	-1.196369	0.432773
C	-7.504545	-1.210413	1.728333
C	-8.691614	-0.608606	1.957406
N	-5.718856	-1.864807	0.479644
C	-5.571955	-2.610100	1.733362
C	-6.602677	-1.958011	2.669936
C	-4.934410	-2.193947	-0.687154
S	-10.776788	1.015295	1.323295

C	-11.152451	1.879416	-0.180025
C	-10.561443	3.113503	-0.437256
C	-10.878607	3.790226	-1.606618
C	-11.782593	3.239018	-2.507702
C	-12.374517	2.010430	-2.242950
C	-12.062445	1.325854	-1.075700
H	-9.628695	-0.801832	-0.094939
H	-9.201676	0.634490	-1.205054
H	-7.087202	-0.593477	-1.636520
H	-9.154507	-0.619977	2.936516
H	-4.550769	-2.524549	2.101089
H	-5.792777	-3.667582	1.560986
H	-7.142824	-2.680768	3.277289
H	-6.123397	-1.243457	3.342043
H	-3.936681	-2.487793	-0.367189
H	-4.849780	-1.321873	-1.334652
H	-5.385289	-3.016307	-1.251252
H	-9.861317	3.535606	0.272375
H	-10.422474	4.749978	-1.811340
H	-12.029257	3.771428	-3.417276
H	-13.081004	1.583432	-2.942649
H	-12.518900	0.368419	-0.858200

Table S42. The Cartesian Coordinates of **1a-1**.

C	-9.763485	-1.113520	-0.822855
C	-10.178627	-0.169531	-1.764896
C	-9.437402	0.991457	-2.009417
C	-8.265816	1.196468	-1.273560
C	-7.832121	0.236047	-0.331658
C	-8.569537	-0.907866	-0.102107
S	-10.716006	-2.589035	-0.560804
N	-7.387947	2.256521	-1.319006
C	-6.131827	1.847137	-0.686107
C	-6.556323	0.745640	0.299178
C	-7.337891	3.152465	-2.446538
C	-11.716185	-2.177074	0.857228
C	-12.443262	-3.223961	1.441732
C	-13.256183	-2.977673	2.545953
C	-13.348895	-1.691332	3.081893
C	-12.624712	-0.652320	2.497917
C	-11.811049	-0.886696	1.388205
H	-11.098888	-0.348698	-2.324400
H	-9.773490	1.709352	-2.757913
H	-8.237010	-1.652851	0.624289

H	-5.439585	1.442562	-1.450620
H	-5.641625	2.701440	-0.199831
H	-6.772149	1.174324	1.291448
H	-5.788988	-0.028516	0.427017
H	-6.703956	4.013668	-2.196125
H	-6.927582	2.665743	-3.352195
H	-8.343827	3.528772	-2.676412
H	-12.363961	-4.233722	1.031993
H	-13.815240	-3.800522	2.995430
H	-13.981820	-1.499989	3.949641
H	-12.692367	0.357730	2.906543
H	-11.252043	-0.065922	0.935979

Table S43. The Cartesian Coordinates of **I•**.

I	0.668790	1.656051	0.000000

Table S44. The Cartesian Coordinates of **PhS•**.

S	-0.862794	2.349388	-0.624735
C	-1.904084	1.037091	-0.275029
C	-1.377309	-0.228019	0.063235
C	-2.220842	-1.284814	0.343205
C	-3.602462	-1.105548	0.293048
C	-4.141692	0.136636	-0.038279
C	-3.305616	1.198989	-0.319930
H	-0.302832	-0.352806	0.098577
H	-1.809228	-2.251734	0.601336
H	-4.260827	-1.936352	0.512577
H	-5.215137	0.268622	-0.075171
H	-3.710678	2.168647	-0.578834

Table S45. The Cartesian Coordinates of **1a-*π*•**.

C	-3.363684	-0.998653	-2.213155
C	-3.362982	-2.092579	-1.356372
C	-2.401214	-2.230766	-0.354035
C	-1.442031	-1.235276	-0.228120
C	-1.424272	-0.137251	-1.102596
C	-2.382373	-0.011217	-2.085078
N	-0.412266	-1.137218	0.701020
C	0.575943	-0.201728	0.148874
C	-0.258156	0.741805	-0.729484
C	0.106186	-2.341406	1.310786

S	-5.653688	-0.492285	0.304366
H	-4.119588	-0.915224	-2.983110
C	-4.517944	0.764939	0.575027
C	-4.566708	1.949606	-0.185986
C	-3.676256	2.977649	0.058556
C	-2.716280	2.843591	1.060141
C	-2.640405	1.671681	1.808791
C	-3.527627	0.638741	1.568218
H	-4.119793	-2.859321	-1.468764
H	-2.411601	-3.091428	0.301992
H	-2.369475	0.838602	-2.757906
H	1.112778	0.306127	0.949171
H	1.302819	-0.752855	-0.464813
H	0.296864	1.115310	-1.588441
H	-0.605690	1.600516	-0.148929
H	0.867053	-2.070860	2.042041
H	-0.690081	-2.873895	1.829740
H	0.555299	-3.014855	0.567621
H	-5.317586	2.042054	-0.960347
H	-3.726518	3.887160	-0.526098
H	-2.021456	3.651669	1.252125
H	-1.883975	1.566365	2.576013
H	-3.475794	-0.277997	2.141754

Table S46. The Cartesian Coordinates of **1a-σ˙**.

N	-1.014333	0.807621	-1.214104
C	-0.184098	1.095982	0.033455
C	-0.483570	-0.034429	1.017881
C	-1.244608	-2.461952	0.390311
C	-1.767855	-3.262524	-0.616501
C	-2.049774	-2.739621	-1.878579
C	-1.815697	-1.400628	-2.158741
C	-1.286900	-0.634994	-1.137317
C	-1.001772	-1.121794	0.121377
C	-0.275600	1.203143	-2.453607
S	-2.569127	1.767468	-1.280006
C	-3.270913	1.373912	0.280113
C	-3.970261	0.178112	0.453951
C	-4.507011	-0.120027	1.696956
C	-4.367975	0.781023	2.747409
C	-3.696824	1.985046	2.564174
C	-3.140691	2.284317	1.330077
H	-3.603146	2.687062	3.381991

H	-4.794500	0.546758	3.714455
H	-5.042101	-1.049058	1.842414
H	-4.083343	-0.507743	-0.376640
H	-2.607493	3.213537	1.173779
H	-1.960764	-4.309147	-0.420430
H	-2.457307	-3.380195	-2.648982
H	-2.048875	-0.981539	-3.128833
H	-1.030276	-2.871865	1.368929
H	0.853709	1.057439	-0.292308
H	-0.421190	2.097133	0.381262
H	-1.233649	0.247557	1.758495
H	0.421102	-0.330366	1.546520
H	-0.009452	2.253531	-2.362153
H	0.612674	0.579683	-2.519184
H	-0.918481	1.046556	-3.316063

Table S47. The Cartesian Coordinates of **TSr1**.

C	-8.631010	0.681494	0.699452
C	-7.863254	0.597057	-0.479391
C	-6.898869	-0.384903	-0.636988
C	-6.609954	-1.214005	0.446956
C	-7.268755	-1.041850	1.682630
C	-8.242466	-0.097020	1.827899
N	-5.682139	-2.224189	0.531148
C	-5.992031	-3.027734	1.719801
C	-6.684281	-2.031178	2.660635
C	-5.223466	-2.913420	-0.653369
S	-9.617221	2.117955	1.057447
C	-10.710466	2.353160	-0.314368
C	-11.486869	3.513984	-0.246098
C	-12.398551	3.807529	-1.246575
C	-12.547933	2.953175	-2.334222
C	-11.772871	1.805318	-2.405097
C	-10.854893	1.499971	-1.405246
H	-9.962190	-0.410127	0.327788
H	-8.063473	1.282251	-1.292860
H	-6.365525	-0.477555	-1.573740
H	-8.772930	0.025225	2.764992
H	-5.083704	-3.460946	2.135460
H	-6.676065	-3.841918	1.445021
H	-7.427957	-2.503030	3.299208
H	-5.948984	-1.535036	3.299120
H	-4.418625	-3.593402	-0.378006
H	-4.834067	-2.199347	-1.377465

H	-6.029930	-3.491616	-1.122559
H	-11.374069	4.185847	0.597039
H	-12.993324	4.709423	-1.175741
H	-13.257714	3.183712	-3.117776
H	-11.874799	1.132150	-3.247115
H	-10.264614	0.599225	-1.487879

Table S48. The Cartesian Coordinates of **HI**.

I	-2.019822	0.940600	0.000000
H	-3.636578	0.940600	0.000000

Table S49. The Cartesian Coordinates of **TSr2b**

N	6.144942	4.828152	-4.151069
C	4.978235	3.875472	-4.292643
C	5.590811	2.516505	-4.587870
C	8.045923	1.809188	-4.998615
C	9.361678	2.275504	-4.935780
C	9.675212	3.591577	-4.554056
C	8.661644	4.500565	-4.229737
C	7.333796	4.060077	-4.293192
C	7.020014	2.703331	-4.665909
C	6.061970	5.776570	-3.016790
C	12.813952	1.261826	-6.829650
C	13.547174	1.680196	-7.943845
C	12.988411	2.580933	-8.858229
C	11.690514	3.062842	-8.661601
C	10.943976	2.646057	-7.553641
C	11.515831	1.750991	-6.649326
S	10.650342	1.118646	-5.248686
H	10.718408	3.911855	-4.508816
H	8.900949	5.521037	-3.944598
H	7.816661	0.783786	-5.290320
H	5.055352	1.798556	-5.196268
H	5.422443	1.715284	-3.330969
H	13.256005	0.565489	-6.116721
H	14.557850	1.304968	-8.098230
H	13.564714	2.905382	-9.722514
H	11.255345	3.762585	-9.373553
H	9.930222	3.019824	-7.411419
H	5.136355	6.370289	-3.107940
H	6.072544	5.291534	-2.026240
H	6.909455	6.482209	-3.064869
H	4.315005	3.870824	-3.404837
H	4.369271	4.232257	-5.155632

I	4.983637	0.969812	-1.779832

Table S50. The Cartesian Coordinates of **TSr2a**.

N	5.898932	4.946883	-4.251580
C	5.285089	3.881079	-4.879032
C	6.309417	3.301287	-5.827563
C	8.882525	3.432236	-5.407851
C	9.854861	4.119269	-4.670990
C	9.500737	5.175026	-3.767511
C	8.208536	5.547797	-3.577829
C	7.231041	4.839536	-4.313551
C	7.574463	3.797560	-5.227176
C	5.189309	5.813664	-3.327998
C	12.004288	1.209384	-5.496812
C	12.203289	0.199817	-6.429747
C	12.089613	0.472913	-7.786141
C	11.778329	1.757377	-8.218970
C	11.590240	2.776071	-7.296738
C	11.698575	2.492077	-5.937914
S	11.542474	3.789779	-4.742741
H	10.291222	5.673359	-3.220333
H	7.942701	6.334486	-2.885533
H	9.140579	2.621562	-6.076113
H	6.160372	3.763356	-6.812956
H	6.273357	2.219458	-5.952522
H	12.083726	1.004730	-4.436956
H	12.437759	-0.801268	-6.092658
H	12.238893	-0.317894	-8.509778
H	11.687946	1.968809	-9.276333
H	11.360160	3.782403	-7.623858
H	5.200785	5.330028	-2.345844
H	5.688797	6.776675	-3.274408
H	4.166751	5.929007	-3.673955
H	5.321354	3.033511	-3.937504
H	4.243691	4.021263	-5.146985
I	7.920635	-0.134415	-6.786270
I	6.287352	1.900479	-2.572951

Table S51. The Cartesian Coordinates of **1a-1-intb**.

N	5.9818	5.2548	-4.7913
C	5.2548	4.0032	-5.1514
C	6.3036	3.0531	-5.5911
C	9.0099	3.1110	-5.0730
C	9.9782	3.7610	-4.3651

C	9.6271	5.0384	-3.5459
C	8.3650	5.5528	-3.5858
C	7.3276	4.8297	-4.4475
C	7.5900	3.6821	-5.0355
C	5.2713	6.0043	-3.7452
C	12.9729	1.1555	-5.9761
C	13.2197	0.5326	-7.1541
C	12.4986	0.9930	-8.4345
C	11.6171	2.0211	-8.3833
C	11.3366	2.7290	-7.0447
C	11.9712	2.3238	-5.9179
S	11.6471	3.1420	-4.3707
H	10.3798	5.5167	-2.9545
H	8.1113	6.4382	-3.0413
H	9.2337	2.2241	-5.6282
H	6.2883	2.9329	-6.6542
H	6.1723	1.5785	-4.9141
H	13.4740	0.8356	-5.0864
H	13.9157	-0.2792	-7.1945
H	12.6934	0.5012	-9.3646
H	11.1160	2.3410	-9.2730
H	10.6407	3.5407	-7.0043
H	4.2953	6.2680	-4.0957
H	5.1834	5.3970	-2.8686
H	5.8180	6.8934	-3.5097
H	4.4171	3.3899	-3.8964
H	4.5522	4.2305	-5.9258
I	5.6842	-0.5096	-3.7105
I	3.3399	2.1710	-2.0502

Table S52. The Cartesian Coordinates of **1a-1-inta**.

N	5.71657899	4.74702225	4.79089778
C	5.17091949	3.38338888	5.05006161
C	6.33758881	2.53082268	5.33322738
C	8.98730303	2.97241236	4.73690315
C	9.83521914	3.80972325	4.06688462
C	9.29893109	5.11690295	3.40773373
C	7.99001627	5.46401382	3.55183446
C	7.08828011	4.52926128	4.36299164
C	7.51346384	3.36458910	4.81152821
C	4.88037366	5.49460936	3.84009528
C	13.18352176	1.42164665	5.23598529
C	13.56763387	0.70857063	6.32132981
C	12.87281665	0.93324941	7.67816177

C	11.87360654	1.84028109	7.78473170
C	11.43655951	2.65064809	6.55062111
C	12.05376317	2.45762321	5.35997406
S	11.56068594	3.40179914	3.93683556
H	9.96127243	5.74709686	2.84400858
H	7.60740475	6.36520515	3.11940157
H	9.33921835	2.06617607	5.18676674
H	6.40125375	2.27530767	6.37008330
H	6.25777703	0.98170533	4.31085530
H	13.66530291	1.26555842	4.29233658
H	14.35368831	-0.01060934	6.23588517
H	13.17889794	0.37278346	8.53675945
H	11.38890007	1.99313741	8.72600174
H	10.64637124	3.36585163	6.63299560
H	3.89395731	5.59980739	4.23975530
H	4.83617173	4.96253285	2.91105017
H	5.30452414	6.46567931	3.67526582
H	4.29059522	2.65490122	3.59694950
H	4.47811678	3.44854775	5.86402869
I	6.00037929	-0.61202354	3.13027295
I	3.32832253	1.86616887	2.03108471

Table S53. The Cartesian Coordinates of **TSr3b**.

N	-8.086960	1.180902	2.894484
C	-6.736531	0.839008	2.744538
C	-6.667157	-0.264286	1.868278
C	-8.475267	-1.319529	0.358402
C	-9.806956	-1.232942	0.063456
C	-10.648690	-0.287155	0.727253
C	-10.173303	0.571750	1.674904
C	-8.803986	0.474110	2.004646
C	-7.949671	-0.459923	1.353086
C	-8.551177	2.340886	3.629787
S	-10.516887	-2.357390	-1.104260
C	-11.210644	-1.261718	-2.315206
C	-12.289881	-1.733444	-3.060441
C	-12.836746	-0.944952	-4.063265
C	-12.325413	0.322063	-4.316986
C	-11.253905	0.791827	-3.567323
C	-10.688348	0.003279	-2.574315
H	-11.696911	-0.255911	0.456042
H	-10.821812	1.288539	2.159831
H	-7.832252	-2.021571	-0.156496
H	-6.039673	1.092620	3.532553

H	-6.401125	1.701927	1.773948
H	-5.757796	-0.771917	1.586427
H	-9.545942	2.144136	4.023493
H	-8.578127	3.214317	2.974841
H	-7.868491	2.525480	4.455541
H	-12.701460	-2.713521	-2.851648
H	-13.673172	-1.320206	-4.639159
H	-12.759527	0.939349	-5.092575
H	-10.846278	1.776335	-3.759123
H	-9.842906	0.372309	-2.007320
I	-6.429635	3.203251	0.453550

Table S54. The Cartesian Coordinates of **TSr3a**.

N	5.765698	4.835941	5.141567
C	4.933244	3.853869	5.510342
C	5.547755	2.609653	5.356913
C	7.887052	2.085387	4.316156
C	9.031201	2.707866	3.844917
C	9.125177	4.110475	3.773728
C	8.081905	4.918209	4.180407
C	6.937152	4.281054	4.651047
C	6.817997	2.883381	4.720656
C	5.525021	6.263065	5.267314
C	12.685460	1.107142	4.650912
C	13.522113	0.998220	5.750940
C	13.104650	1.445911	6.999848
C	11.839892	2.000847	7.136351
C	10.990477	2.110015	6.041058
C	11.412975	1.663054	4.792783
S	10.410764	1.721331	3.328324
H	10.038157	4.555581	3.400477
H	8.156968	5.996876	4.137944
H	7.835363	1.005956	4.380730
H	6.094955	2.680470	6.775505
H	5.039613	1.659503	5.409773
H	13.017820	0.762295	3.678725
H	14.506774	0.564690	5.629053
H	13.760586	1.363325	7.856510
H	11.501011	2.352544	8.102934
H	10.005132	2.539486	6.168805
H	5.594467	6.733700	4.287644
H	6.264731	6.702517	5.935491
H	4.529334	6.411484	5.675422
H	3.966310	4.087203	5.930497

I	7.008297	2.777553	8.374779

Table S55. The Cartesian Coordinates of **1a-2**.

C	-9.151870	-0.066232	-1.337394
C	-7.937960	-0.225148	-0.635342
C	-7.718956	-1.322833	0.169108
C	-8.737248	-2.276506	0.250528
C	-9.958116	-2.142613	-0.452963
C	-10.158756	-1.010692	-1.252119
S	-9.375180	1.353354	-2.373530
N	-8.782991	-3.446144	0.954992
C	-9.991907	-4.051460	0.718620
C	-10.744286	-3.295077	-0.133830
C	-7.725671	-3.947272	1.807537
C	-9.715502	2.653083	-1.215905
C	-9.718779	3.954478	-1.721078
C	-10.002430	5.024529	-0.886282
C	-10.278110	4.812308	0.460297
C	-10.271300	3.517264	0.960543
C	-9.995150	2.436860	0.130397
H	-7.173548	0.535218	-0.732297
H	-6.788845	-1.441500	0.710338
H	-11.085509	-0.869912	-1.794571
H	-10.217499	-4.994652	1.191567
H	-11.733548	-3.530369	-0.489544
H	-7.534932	-3.252870	2.626447
H	-8.034687	-4.905594	2.216844
H	-6.808063	-4.082580	1.234300
H	-9.495773	4.125818	-2.767693
H	-10.001769	6.029078	-1.290309
H	-10.494078	5.648687	1.112017
H	-10.485384	3.338599	2.006911
H	-9.999454	1.432176	0.532412

Table S56. The Cartesian Coordinates of **1a-2π^+**.

C	-5.831109	0.403568	-0.888843
C	-5.393026	0.566314	0.526307
C	-5.244001	-0.661348	1.329059
C	-5.172290	-1.829173	0.676170
C	-5.398796	-1.949137	-0.747373
C	-5.800172	-0.805602	-1.497288
N	-4.849396	-3.099589	1.150511
C	-4.852584	-3.933705	0.118681
C	-5.194776	-3.273161	-1.077385

C	-4.514200	-3.407914	2.531076
S	-6.184289	1.808962	-1.865479
C	-6.651685	3.037065	-0.670101
C	-5.794940	4.101572	-0.410438
C	-6.176789	5.083016	0.496199
C	-7.401936	4.994504	1.144216
C	-8.256390	3.929500	0.880021
C	-7.888927	2.953473	-0.034977
H	-5.950009	1.336232	1.060500
H	-5.091728	-0.562752	2.396819
H	-6.067298	-0.914436	-2.541098
H	-4.611570	-4.977352	0.263989
H	-5.277259	-3.738825	-2.044863
H	-5.359609	-3.168724	3.173874
H	-4.287747	-4.467901	2.599840
H	-3.645241	-2.823641	2.831563
H	-4.837131	4.156791	-0.911364
H	-5.512484	5.913215	0.697853
H	-7.694352	5.757917	1.853604
H	-9.214122	3.862874	1.379572
H	-8.553367	2.127269	-0.255767
C	-2.750913	0.066730	-0.337758
C	-2.146129	-0.990423	0.343771
C	-1.459258	-1.966597	-0.362726
C	-1.369881	-1.886910	-1.748662
C	-1.958917	-0.827270	-2.428050
C	-2.650931	0.150364	-1.725829
S	-3.651195	1.297902	0.555371
H	-2.220623	-1.043321	1.423304
H	-0.991661	-2.786126	0.167691
H	-0.833453	-2.649122	-2.299285
H	-1.881839	-0.761273	-3.505483
H	-3.118377	0.976934	-2.247221

Table S57. The Cartesian Coordinates of **1a-2σ**$^{+}$.

C	-8.679641	0.086889	-0.497405
C	-9.247143	-1.184374	-0.326500
C	-8.461450	-2.310452	-0.138902
C	-7.095376	-2.111859	-0.130732
C	-6.511536	-0.865955	-0.302073
C	-7.292840	0.256094	-0.484688
N	-6.055851	-3.071067	0.041761
C	-4.900541	-2.507834	-0.027138

C	-5.024942	-1.038645	-0.216705
C	-6.320916	-4.482631	0.297234
S	-9.820425	1.413178	-0.732243
C	-8.765023	2.838249	-0.763039
C	-8.406787	3.458570	0.431019
C	-7.588383	4.579592	0.405003
C	-7.134952	5.082797	-0.808957
C	-7.500415	4.466760	-1.999545
C	-8.316279	3.342665	-1.979963
S	-4.394328	-0.233232	1.312023
C	-2.649780	-0.508821	1.117870
C	-2.013054	-1.475078	1.891411
C	-0.641573	-1.659742	1.769019
C	0.087262	-0.887759	0.873720
C	-0.551357	0.076317	0.101197
C	-1.918740	0.273148	0.225752
H	-10.325000	-1.288192	-0.337284
H	-8.906730	-3.287207	-0.005162
H	-6.840927	1.230836	-0.612253
H	-3.983011	-3.070102	0.088475
H	-4.463303	-0.668289	-1.074608
H	-6.888011	-4.882590	-0.541097
H	-5.373750	-5.002462	0.402271
H	-6.907104	-4.560351	1.211221
H	-8.766805	3.061411	1.371761
H	-7.308679	5.061706	1.332754
H	-6.498995	5.958514	-0.826657
H	-7.151379	4.859963	-2.945566
H	-8.604063	2.854859	-2.902579
H	-2.589636	-2.075068	2.584188
H	-0.145121	-2.408421	2.372570
H	1.155435	-1.034527	0.778813
H	0.017150	0.681808	-0.592613
H	-2.421402	1.031402	-0.362252

Table S58. The Cartesian Coordinates of **TSe2**.

C	-10.628868	1.878305	0.224813
C	-11.067448	2.454310	-0.982436
C	-10.229092	2.563412	-2.076431
C	-8.942827	2.057185	-1.936853
C	-8.488543	1.501442	-0.736352
C	-9.327518	1.420977	0.366204
N	-7.911371	1.967264	-2.871702
C	-6.861903	1.369155	-2.318398

C	-7.099110	1.132846	-0.947533
C	-7.996289	2.481656	-4.229084
S	-6.161226	0.081173	0.101734
S	-11.806187	1.796057	1.548569
H	-6.510592	2.428523	-0.527802
C	-7.116477	-1.415657	0.119903
C	-6.858688	-2.297022	1.170123
C	-7.532811	-3.507022	1.241040
C	-8.478820	-3.840934	0.278592
C	-8.740520	-2.956604	-0.759368
C	-8.059843	-1.747573	-0.847525
C	-11.223394	0.399730	2.477315
C	-11.093724	-0.851439	1.874208
C	-10.652358	-1.933146	2.619267
C	-10.359329	-1.779175	3.972006
C	-10.504745	-0.538073	4.573945
C	-10.928031	0.556652	3.826247
H	-12.089746	2.802708	-1.058388
H	-10.574727	3.002531	-3.003020
H	-8.973180	0.990128	1.294582
H	-5.954170	1.199224	-2.879328
H	-7.071136	2.246743	-4.747123
H	-8.836223	2.012646	-4.739207
H	-8.141870	3.560550	-4.200877
H	-6.133451	-2.032418	1.930669
H	-7.325488	-4.184782	2.059504
H	-9.012457	-4.780373	0.341573
H	-9.476391	-3.205787	-1.513503
H	-8.265578	-1.074172	-1.669949
H	-11.327924	-0.970056	0.822945
H	-10.541625	-2.899638	2.144518
H	-10.018672	-2.627496	4.551780
H	-10.276871	-0.411590	5.624530
H	-11.020512	1.531980	4.286735
I	-5.895230	4.035575	0.165310

Table S59. The Cartesian Coordinates of **3aa**.

C	-7.690496	-0.252270	-1.133020
C	-6.666571	-0.947981	-0.461813
C	-6.922434	-2.124839	0.217609
C	-8.239145	-2.580311	0.237275
C	-9.276503	-1.887067	-0.423110
C	-8.993240	-0.720637	-1.130251
N	-8.787283	-3.679714	0.851159

C	-10.132038	-3.686915	0.617456
C	-10.483583	-2.615962	-0.162728
C	-8.045796	-4.654591	1.625006
S	-12.078825	-2.222119	-0.741601
S	-7.250780	1.209061	-2.038678
C	-12.438542	-0.703829	0.110241
C	-11.747814	-0.279764	1.241897
C	-12.100806	0.913604	1.859678
C	-13.142524	1.686607	1.363091
C	-13.832925	1.258265	0.235093
C	-13.481828	0.072247	-0.394082
C	-8.447455	2.403535	-1.501859
C	-8.788834	3.410889	-2.402080
C	-9.675612	4.410755	-2.023991
C	-10.239628	4.404364	-0.754827
C	-9.900601	3.395648	0.140187
C	-9.002735	2.401952	-0.223550
H	-5.661962	-0.545537	-0.477031
H	-6.130066	-2.655695	0.729529
H	-9.780239	-0.186541	-1.651023
H	-10.754181	-4.467919	1.027166
H	-7.557806	-4.171655	2.471861
H	-8.739435	-5.406158	1.992456
H	-7.290500	-5.135411	1.003053
H	-10.937880	-0.877120	1.640337
H	-11.553946	1.238050	2.736470
H	-13.411043	2.616713	1.846944
H	-14.644600	1.852856	-0.164830
H	-14.013485	-0.250807	-1.281447
H	-8.366771	3.405986	-3.399730
H	-9.934967	5.187993	-2.731664
H	-10.939693	5.177111	-0.464996
H	-10.333193	3.381967	1.132649
H	-8.739038	1.625239	0.483254

Table S60. The Cartesian Coordinates of **C4-I**.

C	-1.402398	-0.646017	-0.808487
C	-1.289262	-2.003508	-0.711912
C	-0.031386	-2.615542	-0.588133
C	1.140473	-1.848549	-0.580653
C	1.053732	-0.470280	-0.666656
C	-0.221864	0.211689	-0.742252
N	2.448470	-2.260649	-0.523430

C	3.269988	-1.091754	-0.173363
C	2.425877	0.103703	-0.646199
C	2.804753	-3.541611	0.050145
S	-0.389934	0.924620	1.026035
C	-1.855329	1.899499	0.862571
C	-1.809472	3.111987	0.175831
C	-2.946338	3.902278	0.107779
C	-4.117474	3.492261	0.736548
C	-4.157814	2.287838	1.428318
C	-3.029052	1.482292	1.486387
H	-2.370207	-0.167608	-0.881487
H	-2.174688	-2.623655	-0.709411
H	0.022761	-3.693295	-0.490184
H	-0.229752	1.087837	-1.390809
H	4.241419	-1.148093	-0.659210
H	3.416956	-1.055284	0.912603
H	2.508047	0.986969	-0.011308
H	2.690048	0.407043	-1.666154
H	2.257572	-4.340715	-0.447521
H	3.868480	-3.709392	-0.107803
H	2.595075	-3.575934	1.125900
H	-0.888044	3.429902	-0.296584
H	-2.915971	4.842425	-0.427155
H	-5.001176	4.115367	0.687642
H	-5.069162	1.971270	1.918325
H	-3.051928	0.535304	2.010724

Table S61. The Cartesian Coordinates of **C4-II**.

C	-1.500986	-0.803763	0.409797
C	-1.324681	-2.103569	0.030030
C	-0.043830	-2.678596	-0.000516
C	1.082909	-1.938052	0.378577
C	0.933964	-0.614819	0.755322
C	-0.358368	0.039252	0.752080
N	2.393766	-2.334863	0.468199
C	3.223491	-1.122776	0.545734
C	2.267042	-0.059820	1.112283
C	2.891130	-3.454823	-0.303187
S	-0.238622	1.141806	-0.807772
C	-1.744808	2.058621	-0.684669
C	-2.780599	1.802513	-1.580354
C	-3.933233	2.574030	-1.531160
C	-4.055535	3.581723	-0.582192
C	-3.022453	3.830275	0.315484

C	-1.861158	3.075086	0.262373
H	-2.482866	-0.349119	0.415441
H	-2.173422	-2.701175	-0.271879
H	0.065020	-3.705313	-0.329444
H	-0.513398	0.744513	1.568705
H	3.561725	-0.841541	-0.458613
H	4.093222	-1.294632	1.175784
H	2.334659	0.004452	2.204678
H	2.430406	0.943196	0.715781
H	2.291363	-4.341936	-0.105454
H	2.878590	-3.243027	-1.379007
H	3.914526	-3.661676	0.004100
H	-2.679340	1.005758	-2.306447
H	-4.737344	2.383100	-2.229656
H	-4.958580	4.177128	-0.542091
H	-3.118170	4.618000	1.051152
H	-1.044521	3.270248	0.946723

Table S62. The Cartesian Coordinates of **C4-III**.

C	-0.895487	1.365581	-0.009063
C	-1.886378	1.435981	0.927919
C	-2.621535	0.295438	1.289216
C	-2.345645	-0.946336	0.704442
C	-1.384597	-1.034561	-0.288655
C	-0.553977	0.096555	-0.645551
N	-2.920556	-2.168720	0.948841
C	-2.596919	-3.047360	-0.184889
C	-1.304950	-2.442725	-0.760293
C	-4.243535	-2.267169	1.530155
S	1.069496	-0.343073	0.277991
C	2.133434	0.970195	-0.235054
C	2.683409	0.955976	-1.516102
C	3.568380	1.955594	-1.890736
C	3.912291	2.954908	-0.986694
C	3.368325	2.962365	0.292588
C	2.470874	1.974182	0.670632
H	-0.315862	2.238329	-0.278995
H	-2.114084	2.378055	1.406922
H	-3.405311	0.386147	2.031737
H	-0.268639	0.148063	-1.695417
H	-2.478353	-4.075630	0.149046
H	-3.402424	-3.004619	-0.927310
H	-1.212412	-2.535317	-1.841223
H	-0.412468	-2.901819	-0.312490

H	-4.276195	-1.737544	2.481138
H	-5.010510	-1.857660	0.862003
H	-4.462471	-3.316580	1.718052
H	2.419297	0.165193	-2.207452
H	3.995690	1.950276	-2.884847
H	4.607948	3.730389	-1.280548
H	3.638170	3.740102	0.994876
H	2.030691	1.975887	1.659863

Table S63. The Cartesian Coordinates of **C4-IV**.

C	-0.463538	1.058249	1.115533
C	-1.713120	1.284931	1.617988
C	-2.666765	0.255711	1.672626
C	-2.351878	-1.035753	1.231916
C	-1.094954	-1.290917	0.711068
C	-0.095993	-0.250205	0.581690
N	-3.120841	-2.172548	1.251741
C	-2.489056	-3.154779	0.357380
C	-1.012533	-2.725490	0.326204
C	-4.567020	-2.097877	1.266735
S	-0.157938	0.095248	-1.301813
C	1.147062	1.272916	-1.481549
C	0.835557	2.600318	-1.768385
C	1.859194	3.510424	-1.990814
C	3.184413	3.099636	-1.909476
C	3.492321	1.775562	-1.615123
C	2.475330	0.856055	-1.408357
H	0.266778	1.853897	1.050769
H	-1.989157	2.271783	1.962393
H	-3.657173	0.475499	2.053068
H	0.928380	-0.573085	0.766825
H	-2.632649	-4.164310	0.735835
H	-2.933428	-3.083437	-0.642455
H	-0.524222	-2.879856	-0.637028
H	-0.421217	-3.254967	1.082423
H	-4.903297	-1.491616	2.106443
H	-4.959772	-1.673946	0.334866
H	-4.965376	-3.102869	1.393106
H	-0.200492	2.911243	-1.815779
H	1.621134	4.540552	-2.221200
H	3.981156	3.813050	-2.076381
H	4.524836	1.457146	-1.555627
H	2.705159	-0.180567	-1.194320

Table S64. The Cartesian Coordinates of **C5-I**.

C	-4.055867	-0.356420	-0.477154
C	-4.166459	-1.831670	-0.616383
C	-3.120743	-2.664160	-0.550354
C	-1.816470	-2.088567	-0.348181
C	-1.629145	-0.654524	-0.236320
C	-2.675758	0.166044	-0.307905
N	-0.682892	-2.709448	-0.239610
C	0.457811	-1.800466	-0.015896
C	-0.157141	-0.392199	-0.043817
C	-0.438205	-4.138712	-0.293512
S	-5.093682	0.115575	0.985021
C	-5.201332	1.869387	0.728980
C	-4.576677	2.729763	1.627179
C	-4.693186	4.104783	1.461171
C	-5.417040	4.618457	0.393587
C	-6.035404	3.757223	-0.506983
C	-5.938014	2.384270	-0.336148
H	-4.546372	0.115537	-1.334560
H	-5.163919	-2.227357	-0.768332
H	-3.246946	-3.732166	-0.650245
H	-2.557405	1.240876	-0.225528
H	1.189668	-1.972938	-0.804256
H	0.909506	-2.057501	0.942330
H	0.031230	0.145249	0.883420
H	0.244569	0.198320	-0.865437
H	-1.350384	-4.673629	-0.533645
H	0.314433	-4.329978	-1.057709
H	-0.057104	-4.465628	0.673958
H	-4.002684	2.322223	2.449648
H	-4.210789	4.772044	2.163696
H	-5.502470	5.689474	0.262581
H	-6.605166	4.155451	-1.336621
H	-6.436163	1.710690	-1.023077

Table S65. The Cartesian Coordinates of **C5-II**.

C	-2.457643	-0.396415	0.197553
C	-2.572258	-1.877161	0.149393
C	-1.522437	-2.705160	0.204488
C	-0.212522	-2.120771	0.332911
C	-0.028884	-0.685017	0.429863
C	-1.080475	0.130615	0.376531
N	0.929401	-2.733814	0.380146
C	2.075989	-1.815567	0.521613

C	1.447557	-0.413672	0.567331
C	1.182955	-4.160790	0.308116
S	-3.176639	0.240193	-1.388659
C	-3.378894	1.953610	-0.968467
C	-4.337683	2.344191	-0.035327
C	-4.504087	3.688959	0.260527
C	-3.731071	4.647079	-0.387076
C	-2.784332	4.258005	-1.325203
C	-2.600047	2.910654	-1.612357
H	-3.123022	-0.017646	0.979857
H	-3.574051	-2.279612	0.054582
H	-1.650367	-3.776930	0.164385
H	-0.964474	1.206956	0.440481
H	2.737911	-1.967742	-0.330658
H	2.612401	-2.082495	1.431860
H	1.668636	0.090006	1.506626
H	1.809817	0.212059	-0.246104
H	0.254855	-4.708734	0.189031
H	1.839001	-4.352881	-0.540632
H	1.684129	-4.471561	1.224584
H	-4.952950	1.596926	0.451415
H	-5.246786	3.990033	0.988035
H	-3.869525	5.696401	-0.160608
H	-2.181280	5.000875	-1.831088
H	-1.854625	2.599508	-2.333147

Table S66. The Cartesian Coordinates of **C5-III**.

C	-3.895432	-0.381358	-0.391400
C	-4.001944	-1.861541	-0.467362
C	-2.948278	-2.685127	-0.419159
C	-1.639563	-2.095466	-0.304343
C	-1.458276	-0.657332	-0.246916
C	-2.512954	0.154224	-0.300195
N	-0.496349	-2.705038	-0.243097
C	0.649041	-1.781239	-0.131309
C	0.018457	-0.379639	-0.126029
C	-0.241277	-4.133239	-0.273487
S	-4.879881	0.145007	1.088662
C	-5.011147	1.885725	0.762432
C	-4.359121	2.787932	1.597759
C	-4.492417	4.153700	1.377286
C	-5.260668	4.616348	0.317321
C	-5.906693	3.713290	-0.520565
C	-5.792369	2.349614	-0.294513

H	-4.422195	0.052898	-1.247366
H	-5.002392	-2.268142	-0.558556
H	-3.071252	-3.756750	-0.474392
H	-2.398896	1.231970	-0.259892
H	1.187440	-2.019206	0.785847
H	1.309985	-1.958741	-0.979373
H	0.376141	0.221206	-0.960052
H	0.242670	0.153155	0.796243
H	-1.167247	-4.684555	-0.393346
H	0.428396	-4.346224	-1.106362
H	0.245131	-4.420567	0.658546
H	-3.751004	2.419739	2.414256
H	-3.988558	4.853650	2.031226
H	-5.359037	5.680170	0.143675
H	-6.511008	4.071809	-1.343874
H	-6.311403	1.643726	-0.931764

Table S67. The Cartesian Coordinates of **C5-IV**.

C	-2.424862	-0.384261	0.271763
C	-2.541863	-1.865407	0.299713
C	-1.490425	-2.692300	0.339272
C	-0.175909	-2.105809	0.372884
C	0.013020	-0.667532	0.385542
C	-1.039907	0.147341	0.348403
N	0.966646	-2.719057	0.397527
C	2.119245	-1.798483	0.434784
C	1.494801	-0.394051	0.432359
C	1.215531	-4.148696	0.391468
S	-3.233749	0.179882	-1.298942
C	-3.405375	1.912133	-0.948221
C	-4.316940	2.351962	0.009963
C	-4.459753	3.709894	0.253433
C	-3.710143	4.631415	-0.470418
C	-2.810623	4.192974	-1.432778
C	-2.650186	2.832661	-1.668891
H	-3.045495	0.032485	1.071402
H	-3.547358	-2.269059	0.276233
H	-1.620142	-3.764485	0.356320
H	-0.920864	1.225251	0.352723
H	2.698366	-2.016878	1.331739
H	2.740843	-1.998746	-0.437659
H	1.815483	0.182053	-0.433572
H	1.763600	0.162605	1.328211
H	0.282783	-4.699381	0.341655

H	1.834945	-4.387794	-0.472717
H	1.755119	-4.411600	1.301187
H	-4.913492	1.631991	0.557293
H	-5.165742	4.049385	1.000311
H	-3.830116	5.690894	-0.284254
H	-2.226014	4.907432	-1.997763
H	-1.941421	2.483279	-2.408870

Table S68. The Cartesian Coordinates of **C6-I**.

C	-2.640748	2.421228	-0.293383
C	-2.563973	0.963473	-0.385863
C	-1.245191	0.359455	-0.566213
C	-0.140652	1.160361	-0.608191
C	-0.282264	2.565081	-0.436590
C	-1.522094	3.197770	-0.297380
N	1.182712	0.841993	-0.761477
C	2.001911	1.961713	-0.285536
C	1.072291	3.170941	-0.454841
C	1.637097	-0.511753	-0.533074
S	-3.282728	0.388718	1.268338
C	-3.366159	-1.354153	0.964876
C	-4.398516	-1.879994	0.190047
C	-4.479879	-3.250562	-0.005539
C	-3.542204	-4.094573	0.580129
C	-2.517774	-3.569525	1.357778
C	-2.422972	-2.197075	1.547634
H	-3.625188	2.861181	-0.186027
H	-3.298312	0.592043	-1.110048
H	-1.180216	-0.719448	-0.628792
H	-1.577598	4.272504	-0.188512
H	2.265347	1.820358	0.768736
H	2.916228	2.041476	-0.869353
H	1.199127	3.634234	-1.442038
H	1.197971	3.954556	0.290630
H	1.094553	-1.199802	-1.180774
H	2.695955	-0.572892	-0.776014
H	1.489887	-0.813740	0.511186
H	-5.131950	-1.216236	-0.251257
H	-5.280012	-3.660550	-0.607899
H	-3.612089	-5.164340	0.430598
H	-1.789342	-4.226478	1.814916
H	-1.623018	-1.776264	2.143934

Table S69. The Cartesian Coordinates of **C6-II**.

C	-4.095940	2.449931	0.522626
C	-4.032898	0.990701	0.605068
C	-2.712259	0.364436	0.602245
C	-1.599250	1.145528	0.486887
C	-1.738477	2.552237	0.331389
C	-2.974257	3.206725	0.367481
N	-0.273584	0.802564	0.451983
C	0.487261	1.904698	-0.146761
C	-0.384041	3.131893	0.152309
C	0.115444	-0.560571	0.165392
S	-4.973345	0.438120	-0.942734
C	-4.975983	-1.313011	-0.678759
C	-4.127213	-2.117975	-1.434924
C	-4.161394	-3.496628	-1.271215
C	-5.029552	-4.065702	-0.347926
C	-5.871679	-3.259407	0.410642
C	-5.852529	-1.882714	0.242744
H	-5.078139	2.907043	0.549881
H	-4.668435	0.627979	1.420993
H	-2.657879	-0.715398	0.657432
H	-3.025410	4.282224	0.264216
H	1.479424	1.968296	0.294448
H	0.588055	1.754997	-1.227684
H	-0.351295	3.914627	-0.603792
H	-0.106427	3.589499	1.110968
H	-0.342511	-1.236414	0.887056
H	-0.187400	-0.860063	-0.845622
H	1.196748	-0.643836	0.253417
H	-3.446397	-1.663089	-2.143492
H	-3.506851	-4.123793	-1.862295
H	-5.051652	-5.140180	-0.218824
H	-6.550050	-3.703961	1.127169
H	-6.514385	-1.248656	0.819882

Table S70. The Cartesian Coordinates of **C6-III**.

C	-2.669654	2.432172	-0.220299
C	-2.594450	0.977902	-0.358695
C	-1.275478	0.377931	-0.552647
C	-0.169739	1.178335	-0.565947
C	-0.310502	2.577289	-0.350234
C	-1.550066	3.206998	-0.196272
N	1.153122	0.864644	-0.726336
C	1.974048	1.967908	-0.217489
C	1.044442	3.182434	-0.344813

C	1.608242	-0.496688	-0.554469
S	-3.324206	0.351408	1.270298
C	-3.393515	-1.382569	0.916418
C	-4.406281	-1.892093	0.105861
C	-4.475524	-3.257136	-0.129210
C	-3.546191	-4.112471	0.453492
C	-2.541853	-3.603804	1.267198
C	-2.458151	-2.236487	1.495679
H	-3.653871	2.869784	-0.102085
H	-3.324127	0.633270	-1.100986
H	-1.212039	-0.698699	-0.647797
H	-1.604573	4.277995	-0.054880
H	2.886600	2.065784	-0.801399
H	2.241005	1.793419	0.830874
H	1.168961	3.938177	0.429165
H	1.172213	3.682415	-1.313782
H	1.064838	-1.157714	-1.229189
H	2.666764	-0.547356	-0.801279
H	1.462966	-0.842480	0.476365
H	-5.134262	-1.220488	-0.332680
H	-5.260390	-3.654423	-0.759551
H	-3.607039	-5.178037	0.273203
H	-1.819693	-4.269270	1.721984
H	-1.672892	-1.828349	2.119601

Table S71. The Cartesian Coordinates of **C6-IV**.

C	-4.094946	2.446546	0.521685
C	-4.029634	0.987290	0.601808
C	-2.707917	0.363209	0.598293
C	-1.596181	1.146271	0.485930
C	-1.737350	2.553063	0.333126
C	-2.974318	3.205332	0.368691
N	-0.269650	0.805315	0.452087
C	0.489334	1.909862	-0.144925
C	-0.383675	3.135169	0.156689
C	0.120537	-0.556457	0.159959
S	-4.971071	0.435131	-0.944891
C	-4.977314	-1.315744	-0.679031
C	-4.125606	-2.122964	-1.429267
C	-4.162952	-3.501330	-1.263670
C	-5.037084	-4.067699	-0.344460
C	-5.882237	-3.259100	0.408354
C	-5.860014	-1.882753	0.238423
H	-5.077608	2.902357	0.549895

H	-4.663457	0.622644	1.418349
H	-2.651769	-0.716703	0.650505
H	-3.027540	4.280858	0.266747
H	1.481614	1.973941	0.295895
H	0.589638	1.762412	-1.226211
H	-0.351983	3.919409	-0.597941
H	-0.107020	3.591409	1.116220
H	-0.336116	-1.235500	0.879424
H	-0.182837	-0.852338	-0.851968
H	1.201990	-0.638902	0.246867
H	-3.439969	-1.669976	-2.134387
H	-3.506254	-4.130542	-1.850167
H	-5.061400	-5.141973	-0.214081
H	-6.565188	-3.701665	1.121745
H	-6.524121	-1.246373	0.810406

Table S72. The Cartesian Coordinates of **C7-I**.

C	-2.711485	1.376503	1.862112
C	-1.523603	1.179139	1.282676
C	-1.214920	-0.047404	0.491922
C	-2.280236	-1.076420	0.589687
C	-3.563697	-0.797093	1.171583
C	-3.766185	0.377688	1.791051
N	-2.213188	-2.293734	0.155495
C	-3.465210	-3.046641	0.379280
C	-4.432710	-2.012756	0.980862
C	-1.078474	-2.960778	-0.455865
C	0.331851	1.405076	-1.294213
C	0.225011	2.782445	-1.460928
C	1.374701	3.562315	-1.489051
C	2.621483	2.970081	-1.338236
C	2.724940	1.593377	-1.167243
C	1.582676	0.807121	-1.153688
S	-1.134322	0.406481	-1.312826
H	-2.912544	2.295417	2.395660
H	-0.742239	1.927001	1.325803
H	-0.240684	-0.466895	0.750546
H	-4.718972	0.591407	2.260590
H	-3.239787	-3.873252	1.053254
H	-3.795664	-3.451519	-0.576103
H	-5.252078	-1.799185	0.295360
H	-4.858277	-2.357488	1.920908
H	-0.881366	-3.876078	0.102078
H	-1.332085	-3.213732	-1.485270

H	-0.206567	-2.314503	-0.440897
H	-0.751855	3.236945	-1.565612
H	1.292719	4.633151	-1.622547
H	3.515237	3.580358	-1.355130
H	3.696744	1.130633	-1.054129
H	1.656688	-0.267660	-1.037228

Table S73. The Cartesian Coordinates of **C7-II**.

C	-2.859275	1.571002	1.170334
C	-1.782961	1.473383	0.384388
C	-1.332537	0.175168	-0.195759
C	-2.306834	-0.921652	0.028927
C	-3.412983	-0.787728	0.936306
C	-3.683727	0.412446	1.475559
N	-2.273399	-2.100881	-0.503297
C	-3.377029	-2.966078	-0.036482
C	-4.093754	-2.127663	1.035503
C	-1.334519	-2.611478	-1.485290
C	1.322026	0.906384	0.158972
C	1.832360	0.900412	-1.137555
C	2.717687	1.893052	-1.531471
C	3.104148	2.879556	-0.630416
C	2.601226	2.878100	0.664298
C	1.704122	1.894593	1.061487
S	0.215527	-0.377264	0.682921
H	-3.134762	2.523133	1.602775
H	-1.161516	2.332753	0.168197
H	-1.076483	0.267446	-1.253064
H	-4.532692	0.535934	2.137277
H	-2.948997	-3.892161	0.344040
H	-4.004660	-3.196139	-0.897813
H	-5.162612	-2.056133	0.846359
H	-3.951399	-2.558427	2.026202
H	-1.904062	-3.014227	-2.322531
H	-0.673879	-1.819810	-1.824786
H	-0.749331	-3.410165	-1.029661
H	1.537439	0.120202	-1.829108
H	3.113070	1.891225	-2.538929
H	3.800251	3.648945	-0.938792
H	2.901472	3.644889	1.366517
H	1.298584	1.891283	2.065191

Table S74. The Cartesian Coordinates of **C7-III**..

C	-4.415592	2.132917	-0.215484

C	-4.392160	0.841988	-0.560599
C	-3.117961	0.061287	-0.582605
C	-1.927259	0.932572	-0.569956
C	-1.995395	2.281461	-0.058576
C	-3.193805	2.865971	0.086316
N	-0.721729	0.635915	-0.937701
C	0.233408	1.737543	-0.685974
C	-0.584971	2.783959	0.086252
C	-0.247091	-0.554521	-1.621410
C	-1.574745	-1.638148	1.093131
C	-1.469522	-2.894763	0.499197
C	-0.251348	-3.558351	0.505383
C	0.857618	-2.973583	1.108473
C	0.749934	-1.726391	1.713101
C	-0.465919	-1.055737	1.705905
S	-3.122428	-0.779417	1.096037
H	-5.357077	2.662164	-0.157745
H	-5.300268	0.289406	-0.761804
H	-3.101263	-0.712136	-1.346625
H	-3.267517	3.900285	0.399228
H	0.585906	2.094950	-1.654203
H	1.078517	1.336701	-0.127704
H	-0.295449	2.798186	1.137705
H	-0.455961	3.785351	-0.317511
H	-1.077289	-1.207030	-1.870139
H	0.264671	-0.236286	-2.529516
H	0.456544	-1.080921	-0.975076
H	-2.338414	-3.341953	0.032428
H	-0.167246	-4.532684	0.041936
H	1.806704	-3.494121	1.111188
H	1.611492	-1.274379	2.187191
H	-0.560487	-0.080432	2.168961

Table S75. The Cartesian Coordinates of **C7-IV**.

C	-5.860868	-1.803564	-0.185501
C	-5.656939	-0.976296	0.844217
C	-4.297746	-0.439136	1.157813
C	-3.358275	-0.601156	0.032306
C	-3.572054	-1.611963	-0.976919
C	-4.785695	-2.169981	-1.096729
N	-2.256352	0.043733	-0.182994
C	-1.521435	-0.469826	-1.359602
C	-2.309749	-1.717104	-1.788283
C	-1.738024	1.213675	0.504312

C	-2.040450	-1.032939	2.780853
C	-0.961391	-1.638207	2.138056
C	0.328079	-1.181808	2.377021
C	0.538080	-0.124262	3.254621
C	-0.537919	0.472300	3.903836
C	-1.827765	0.017738	3.671738
S	-3.679811	-1.625604	2.475606
H	-6.844244	-2.218113	-0.361880
H	-6.448223	-0.721992	1.536706
H	-4.319391	0.558939	1.587818
H	-4.990671	-2.876973	-1.891252
H	-0.495450	-0.677486	-1.058438
H	-1.517422	0.317761	-2.113997
H	-2.501593	-1.734361	-2.858452
H	-1.765952	-2.624458	-1.522479
H	-2.451235	1.570706	1.239683
H	-0.798540	0.953306	0.993925
H	-1.553881	1.985422	-0.242837
H	-1.137942	-2.458459	1.451963
H	1.166228	-1.649802	1.877202
H	1.543181	0.233633	3.437243
H	-0.371640	1.290536	4.592337
H	-2.672212	0.476043	4.171411

Table S76. The Cartesian Coordinates of **C2-I**.

C	-2.215234	0.349482	2.163795
C	-1.591646	-0.897052	1.760476
C	-2.120775	-1.734305	0.835198
C	-3.357465	-1.346985	0.255835
C	-4.016926	-0.123217	0.666912
C	-3.397165	0.736757	1.629339
N	-4.073218	-1.963531	-0.661609
C	-5.270132	-1.200846	-0.941404
C	-5.175950	-0.041264	-0.030863
C	-3.799175	-3.258156	-1.264443
S	-1.481335	1.294995	3.457243
C	0.224856	1.298352	2.971990
C	1.190174	1.168859	3.966332
C	2.536495	1.221765	3.629528
C	2.920962	1.381250	2.304307
C	1.953304	1.503636	1.313686
C	0.605831	1.475865	1.643603
S	-5.178115	-0.607636	-2.691472
C	-6.804536	0.084990	-2.837745

C	-7.903236	-0.752565	-3.019948
C	-9.167664	-0.202089	-3.168237
C	-9.332756	1.178614	-3.150289
C	-8.234622	2.011662	-2.978103
C	-6.967229	1.467445	-2.816501
H	-0.656123	-1.166193	2.236446
H	-1.632192	-2.658990	0.563748
H	-3.876895	1.664427	1.912386
H	-6.169803	-1.809118	-0.823431
H	-5.921176	0.740219	0.005323
H	-2.725717	-3.382353	-1.381443
H	-4.201797	-4.052236	-0.636133
H	-4.275279	-3.288425	-2.241999
H	0.888416	1.021496	4.995772
H	3.284712	1.123656	4.405440
H	3.970818	1.410483	2.043443
H	2.246461	1.633185	0.279756
H	-0.145838	1.594850	0.872639
H	-7.763337	-1.826289	-3.047483
H	-10.022608	-0.850838	-3.307423
H	-10.319885	1.605186	-3.273649
H	-8.362326	3.086219	-2.966233
H	-6.106172	2.108294	-2.674589

Table S77. The Cartesian Coordinates of **C2-II**.

C	-1.325455	1.267340	0.012049
C	-0.785310	-0.063499	-0.193066
C	-1.518388	-1.106370	-0.654324
C	-2.881974	-0.847538	-0.952881
C	-3.436861	0.481342	-0.785083
C	-2.621796	1.538704	-0.268279
N	-3.805830	-1.672294	-1.400472
C	-5.055542	-0.962675	-1.567015
C	-4.734472	0.424126	-1.171770
C	-3.633922	-3.066088	-1.776910
S	-0.243684	2.568830	0.502785
C	0.656793	1.813264	1.830821
C	0.037806	0.974357	2.755067
C	0.778323	0.438861	3.799553
C	2.124308	0.756040	3.940949
C	2.733149	1.605900	3.026168
C	2.006557	2.127115	1.963789
S	-6.278075	-1.669658	-0.372175
C	-7.725939	-0.790101	-0.898302

C	-8.220843	0.245289	-0.110264
C	-9.381512	0.904774	-0.493594
C	-10.036138	0.538196	-1.662594
C	-9.537270	-0.494306	-2.449648
C	-8.386142	-1.166686	-2.066258
H	0.263525	-0.218580	0.030581
H	-1.080331	-2.082762	-0.802930
H	-3.046074	2.522579	-0.117478
H	-5.448575	-1.073738	-2.580165
H	-5.466020	1.219316	-1.172241
H	-2.880704	-3.522277	-1.140079
H	-4.583576	-3.578335	-1.637683
H	-3.331544	-3.133060	-2.821675
H	-1.016970	0.745404	2.662930
H	0.296790	-0.218938	4.511720
H	2.695684	0.342328	4.761575
H	3.781350	1.855546	3.128733
H	2.485119	2.771858	1.237234
H	-7.698652	0.528915	0.794700
H	-9.770436	1.706736	0.120189
H	-10.938745	1.055763	-1.960932
H	-10.050023	-0.783008	-3.357884
H	-8.000302	-1.982667	-2.665041

Table S78. The Cartesian Coordinates of **C3-I**.

C	-8.679641	0.086889	-0.497405
C	-9.247143	-1.184374	-0.326500
C	-8.461450	-2.310452	-0.138902
C	-7.095376	-2.111859	-0.130732
C	-6.511536	-0.865955	-0.302073
C	-7.292840	0.256094	-0.484688
N	-6.055851	-3.071067	0.041761
C	-4.900541	-2.507834	-0.027138
C	-5.024942	-1.038645	-0.216705
C	-6.320916	-4.482631	0.297234
S	-9.820425	1.413178	-0.732243
C	-8.765023	2.838249	-0.763039
C	-8.406787	3.458570	0.431019
C	-7.588383	4.579592	0.405003
C	-7.134952	5.082797	-0.808957
C	-7.500415	4.466760	-1.999545
C	-8.316279	3.342665	-1.979963
S	-4.394328	-0.233232	1.312023
C	-2.649780	-0.508821	1.117870

C	-2.013054	-1.475078	1.891411
C	-0.641573	-1.659742	1.769019
C	0.087262	-0.887759	0.873720
C	-0.551357	0.076317	0.101197
C	-1.918740	0.273148	0.225752
H	-10.325000	-1.288192	-0.337284
H	-8.906730	-3.287207	-0.005162
H	-6.840927	1.230836	-0.612253
H	-3.983011	-3.070102	0.088475
H	-4.463303	-0.668289	-1.074608
H	-6.888011	-4.882590	-0.541097
H	-5.373750	-5.002462	0.402271
H	-6.907104	-4.560351	1.211221
H	-8.766805	3.061411	1.371761
H	-7.308679	5.061706	1.332754
H	-6.498995	5.958514	-0.826657
H	-7.151379	4.859963	-2.945566
H	-8.604063	2.854859	-2.902579
H	-2.589636	-2.075068	2.584188
H	-0.145121	-2.408421	2.372570
H	1.155435	-1.034527	0.778813
H	0.017150	0.681808	-0.592613
H	-2.421402	1.031402	-0.362252

Table S79. The Cartesian Coordinates of **C3-II**..

C	-8.631206	0.047310	-0.458023
C	-9.123940	-1.250515	-0.659408
C	-8.311091	-2.364506	-0.523000
C	-6.996164	-2.126262	-0.176732
C	-6.486616	-0.852952	0.026730
C	-7.293537	0.256741	-0.113595
N	-5.944786	-3.064687	0.030269
C	-4.851157	-2.463143	0.344889
C	-5.029278	-0.986948	0.351472
C	-6.129566	-4.501896	-0.135295
S	-9.796137	1.354363	-0.679771
C	-8.855894	2.795454	-0.250552
C	-8.805609	3.216970	1.075412
C	-8.077932	4.351102	1.409486
C	-7.407537	5.063891	0.422221
C	-7.464879	4.645116	-0.901426
C	-8.189870	3.510382	-1.241788
S	-4.031405	-0.302913	-1.033510
C	-2.391854	-0.515413	-0.383940

C	-1.543033	-1.453305	-0.964432
C	-0.242544	-1.587655	-0.494447
C	0.202080	-0.798075	0.557868
C	-0.649725	0.135496	1.138929
C	-1.944091	0.286314	0.664220
H	-10.164688	-1.385660	-0.926439
H	-8.698144	-3.362392	-0.680092
H	-6.896454	1.251794	0.036653
H	-3.933899	-3.006472	0.531473
H	-4.714922	-0.522202	1.286128
H	-6.437094	-4.692830	-1.161879
H	-5.190914	-5.000816	0.083767
H	-6.908653	-4.827389	0.551326
H	-9.332563	2.656508	1.837272
H	-8.038037	4.679041	2.440162
H	-6.843100	5.949486	0.684587
H	-6.946412	5.201580	-1.671432
H	-8.238753	3.176098	-2.270371
H	-1.900706	-2.070971	-1.778510
H	0.419605	-2.312923	-0.949225
H	1.214307	-0.907233	0.925353
H	-0.302010	0.754894	1.955492
H	-2.606295	1.024519	1.100258

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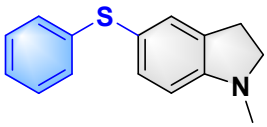
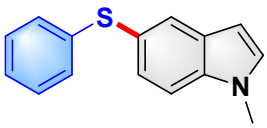
10. Analytic data of the obtained compounds.

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



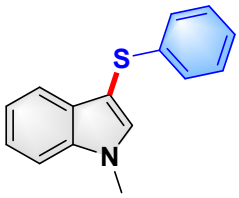
Yellow liquid, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 1H), 7.25–7.22 (m, 3H), 7.17–7.15 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.41 (t, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 8.3 Hz, 2H), 2.83 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 153.96, 140.48, 135.02, 131.70, 131.00, 128.75, 126.95, 124.99, 118.66, 107.21, 55.83, 35.58, 28.35. **HRMS (ESI):** Calcd. for $C_{15}H_{15}NS$ $[M+H]^+$: 242.0925, found: 242.0919.

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



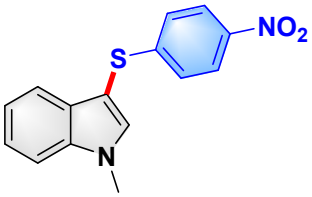
Known compound, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.24–7.21 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*)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

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



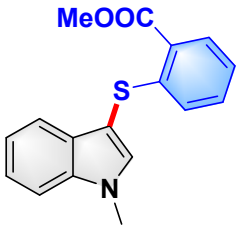
Known compound, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 (s, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.21 (ddt, *J* = 13.2, 7.2, 3.4 Hz, 3H), 7.18–7.15 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 3.87 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ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

(4) 1-methyl-3-((4-nitrophenyl)thio)-1*H*-indole (4)



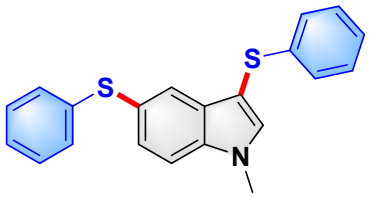
Known compound, (47.6 mg, 67% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 150.21, 144.93, 137.74, 135.41, 129.23, 125.04, 123.83, 123.10, 121.07, 119.32, 110.13, 97.93, 33.32.

(5) methyl 2-((1-methyl-1*H*-indol-3-yl)thio)benzoate (5)



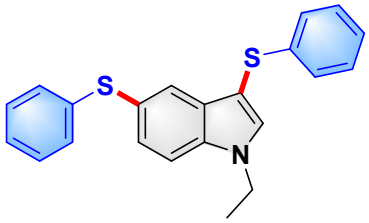
Known compound, (60.1 mg, 81% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36–7.32 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.16–7.13 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 4.03 (s, 3H), 3.87 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 167.07, 144.80, 137.83, 135.56, 132.25, 131.17, 129.83, 126.36, 125.90, 123.61, 122.70, 120.62, 119.80, 109.87, 100.63, 52.11, 33.18.

(6) 1-methyl-3,5-bis(phenylthio)-1*H*-indole (3aa)



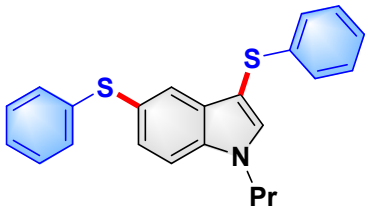
White solid, (81.5 mg, 94% yield), m.p.: 124-125 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.3 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.23–7.20 (m, 2H), 7.20–7.16 (m, 4H), 7.15–7.12 (m, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 3H). **^{13}C-NMR** (125 MHz, Chloroform-*d*) δ 139.15, 139.12, 137.38, 135.89, 130.73, 128.85, 128.76, 128.56, 128.04, 126.00, 125.89, 125.57, 124.97, 124.57, 110.96, 101.24, 33.33. **HRMS (ESI):** Calcd. for $C_{21}H_{17}NS_2$ [M+H]$^+$: 348.0875, found: 348.0869.

(7) 1-ethyl-3,5-bis(phenylthio)-1*H*-indole (3ba)



White solid, (55.1 mg, 61% yield), m.p.: 115-116 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.47 (s, 1H), 7.43 (s, 2H), 7.24–7.19 (m, 6H), 7.16–7.09 (m, 4H), 4.24 (q, *J* = 7.3 Hz, 2H), 1.56 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (125 MHz, Chloroform-*d*) δ 139.24, 139.15, 136.52, 134.20, 130.89, 128.87, 128.78, 128.44, 128.07, 126.01, 125.95, 125.58, 124.95, 124.48, 111.04, 101.22, 41.60, 15.45. **HRMS (ESI):** Calcd. for $C_{22}H_{19}NS_2$ [M+H]$^+$: 362.1032, found: 362.1027.

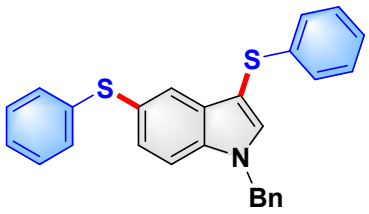
(8) 3,5-bis(phenylthio)-1-propyl-1*H*-indole (3ca)



White solid, (69.4 mg, 74% yield), m.p.: 89-90 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.45 (s, 1H), 7.42 (d, *J* = 1.1 Hz, 2H), 7.25–7.19 (m, 6H), 7.16–7.13 (m, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 4.15 (t, *J* = 7.1 Hz, 2H), 1.96 (h, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.28, 139.12, 136.77, 135.07, 130.84, 128.87, 128.78, 128.40, 128.09, 125.95, 125.90, 125.59, 124.93,

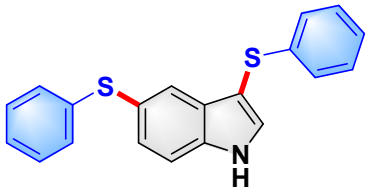
124.44, 111.17, 101.03, 48.60, 23.47, 11.56. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NS_2$ $[M+H]^+$: 376.1188, found: 376.1184.

(9) 1-benzyl-3,5-bis(phenylthio)-1*H*-indole (3da)



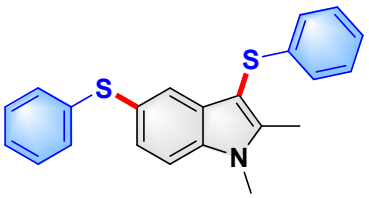
Yellow liquid, (69.8 mg, 66% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.96–7.81 (m, 1H), 7.46 (s, 1H), 7.42–7.35 (m, 5H), 7.25–7.21 (m, 8H), 7.18–7.16 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 5.37 (s, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.02, 138.80, 136.98, 136.29, 135.22, 130.98, 129.08, 128.90, 128.81, 128.50, 128.45, 128.20, 127.14, 126.12, 125.75, 125.69, 125.19, 125.05, 111.41, 102.17, 50.70. **HRMS (ESI):** Calcd. for $C_{27}H_{21}NS_2$ $[M+H]^+$: 424.1188, found: 424.1182.

(10) 3,5-bis(phenylthio)-1*H*-indole (3fa)



White solid, (35.0 mg, 42% yield), m.p.: 108-109 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.89 (s, 1H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.41–7.39 (m, 2H), 7.26–7.20 (m, 6H), 7.18–7.15 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.86, 138.74, 136.32, 131.55, 130.10, 128.95, 128.85, 128.34, 126.23, 125.78, 125.55, 125.19, 125.15, 112.84, 103.43. **HRMS (ESI):** Calcd. for $C_{20}H_{15}NS_2$ $[M+H]^+$: 334.0719, found: 334.0713.

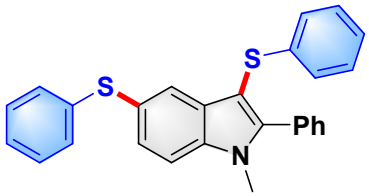
(11) 1,2-dimethyl-3,5-bis(phenylthio)-1*H*-indole (3ga)



White solid, (68.6 mg, 76% yield), m.p.: 120-122 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.23–7.17 (m, 6H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.10–7.06

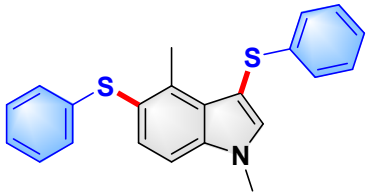
(m, 3H), 3.78 (s, 3H), 2.56 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 143.92, 139.52, 139.29, 137.03, 130.74, 128.78, 128.72, 127.94, 127.81, 125.65, 125.37, 125.31, 124.69, 124.12, 110.20, 98.77, 30.53, 10.97. **HRMS (ESI):** Calcd. for $C_{22}H_{19}NS_2$ $[M+H]^+$: 362.1032, found: 362.1026.

(12) 1-methyl-2-phenyl-3,5-bis(phenylthio)-1*H*-indole (3ha)



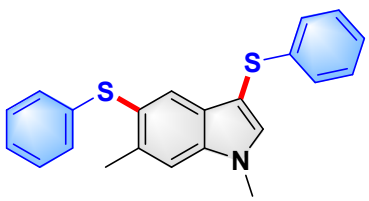
White solid, (84.6 mg, 80% yield), m.p.: 126-127 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 1.4 Hz, 1H), 7.55–7.50 (m, 6H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.28 (dd, *J* = 5.2, 3.5 Hz, 4H), 7.24–7.18 (m, 3H), 7.16–7.11 (m, 3H), 3.79 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 146.88, 139.58, 139.31, 137.58, 130.82, 130.66, 130.23, 129.09, 128.93, 128.86, 128.81, 128.46, 128.12, 125.98, 125.90, 125.63, 125.00, 124.81, 111.20, 100.33, 31.96. **HRMS (ESI):** Calcd. for $C_{27}H_{21}NS_2$ $[M+H]^+$: 424.1188, found: 424.1182.

(13) 1,4-dimethyl-3,5-bis(phenylthio)-1*H*-indole (3ia)



White solid, (60.5 mg, 67% yield), m.p.: 150-152 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.22–7.18 (m, 4H), 7.10–7.06 (m, 4H), 7.03 (dt, *J* = 8.3, 1.6 Hz, 2H), 3.84 (s, 3H), 2.83 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 141.31, 139.31, 138.33, 137.17, 137.15, 130.77, 128.79, 128.43, 126.76, 125.29, 124.89, 124.68, 123.34, 108.40, 101.19, 33.20, 15.60. **HRMS (ESI):** Calcd. for $C_{22}H_{19}NS_2$ $[M+H]^+$: 362.1032, found: 362.1027.

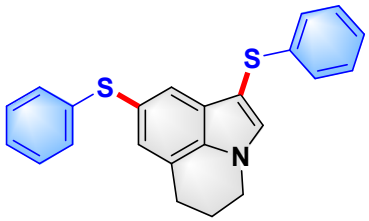
(14) 1,6-dimethyl-3,5-bis(phenylthio)-1*H*-indole (3ja)



White solid, (49.6 mg, 55% yield), m.p.: 129-131 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 5.7 Hz, 1H), 7.36 (s, 1H), 7.32 (s, 1H), 7.23–7.15 (m, 6H), 7.13–7.05 (m, 4H), 3.84 (s, 3H), 2.56 (s, 3H). **^{13}C-**

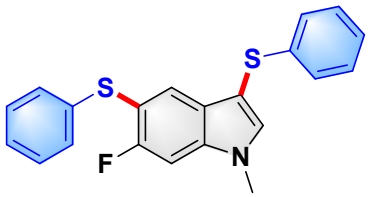
NMR (151 MHz, Chloroform-*d*) δ 139.31, 138.95, 138.42, 136.33, 135.25, 128.94, 128.83, 128.74, 127.97, 126.88, 126.05, 125.05, 124.93, 123.73, 111.60, 101.10, 33.21, 21.52. **HRMS (ESI):** Calcd. for $C_{22}H_{19}NS_2$ $[M+H]^+$: 362.1032, found: 362.1028.

(15) 1,8-bis(phenylthio)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (3ka)



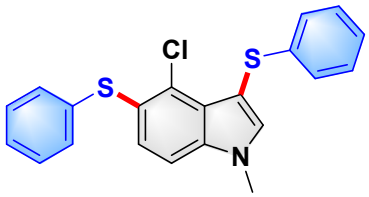
White solid, (72.7 mg, 78% yield), m.p.: 110-111 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.37 (s, 1H), 7.26–7.23 (m, 4H), 7.22 (d, *J* = 6.5 Hz, 5H), 7.17–7.10 (m, 2H), 4.19 (t, 2H), 3.01 (t, *J* = 6.1 Hz, 2H), 2.29 (p, *J* = 6.0 Hz, 2H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.64, 139.51, 134.98, 133.10, 128.85, 128.77, 128.38, 127.93, 126.11, 125.60, 125.46, 124.96, 124.56, 123.74, 123.61, 101.10, 44.44, 24.43, 22.72. **HRMS (ESI):** Calcd. for $C_{23}H_{19}NS_2$ $[M+H]^+$: 374.1032, found: 374.1028.

(16) 6-fluoro-1-methyl-3,5-bis(phenylthio)-1*H*-indole (3la)



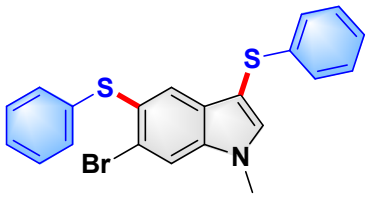
Brown solid, (67.5 mg, 74% yield), m.p.: 126-128 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.0 Hz, 1H), 7.35 (s, 1H), 7.24–7.17 (m, 7H), 7.14 (dd, *J* = 10.4, 7.5 Hz, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 160.40, 158.80, 138.76 (d, *J* = 3.0 Hz), 138.15 (d, *J* = 10.6 Hz), 137.40, 128.91, 128.81, 127.94, 127.70, 126.69, 126.21 (d, *J* = 1.5 Hz), 125.87, 125.17, 113.23 (d, *J* = 19.6 Hz), 101.93, 97.41 (d, *J* = 28.7 Hz), 33.39. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -113.22. **HRMS (ESI):** Calcd. for $C_{21}H_{16}FNS_2$ $[M+H]^+$: 366.0781, found: 366.0777.

(17) 4-chloro-1-methyl-3,5-bis(phenylthio)-1*H*-indole (3ma)



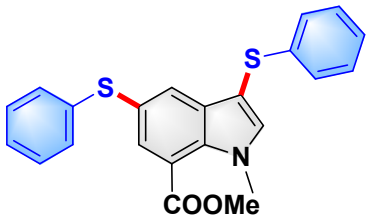
White solid, (65.7 mg, 69% yield), m.p.: 166-168 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.35 (s, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.28–7.24 (m, 4H), 7.21 (dd, *J* = 14.1, 7.9 Hz, 4H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 140.86, 138.46, 137.66, 136.62, 129.83, 129.61, 129.07, 128.68, 128.47, 126.82, 126.41, 126.06, 125.52, 124.85, 109.14, 101.83, 33.38. **HRMS (ESI):** Calcd. for $C_{21}H_{16}ClNS_2$ $[M+H]^+$: 382.0485, found: 382.0482.

(18) 6-bromo-1-methyl-3,5-bis(phenylthio)-1*H*-indole (3na)



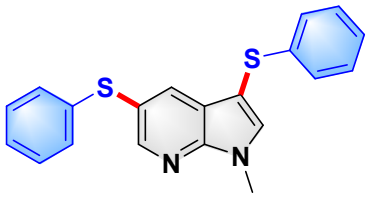
White solid, (68.9 mg, 65% yield), m.p.: 143-145 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.73 (s, 1H), 7.33 (s, 1H), 7.23 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.19–7.16 (m, 5H), 7.12–7.08 (m, 3H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.54, 138.06, 136.95, 136.13, 129.92, 129.03, 128.93, 128.77, 126.61, 126.36, 126.21, 126.14, 125.21, 122.18, 114.88, 102.01, 33.37. **HRMS (ESI):** Calcd. for $C_{21}H_{16}BrNS_2$ $[M+H]^+$: 425.9980, found: 425.9977.

(19) methyl 1-methyl-3,5-bis(phenylthio)-1*H*-indole-7-carboxylate (3oa)



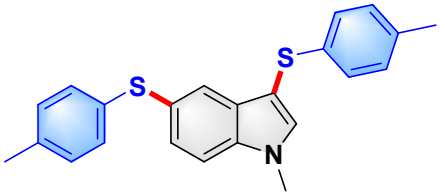
White solid, (24.3 mg, 24% yield), m.p.: 106-107 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.1 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.76–7.71 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.42 (d, *J* = 11.4 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.29 (t, *J* = 6.8 Hz, 1H), 6.99 (s, 1H), 3.69 (s, 3H), 2.13 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 184.92, 183.57, 143.25, 142.92, 135.45, 135.25, 134.79, 133.60, 133.45, 132.69, 132.24, 131.37, 126.82, 125.94, 125.16, 123.75, 121.80, 120.54, 118.23, 110.20, 103.76, 30.03, 8.86. **HRMS (ESI):** Calcd. for $C_{23}H_{19}NO_2S_2$ $[M+H]^+$: 406.0930, found: 406.0925

(20) 1-methyl-3,5-bis(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (3pa)



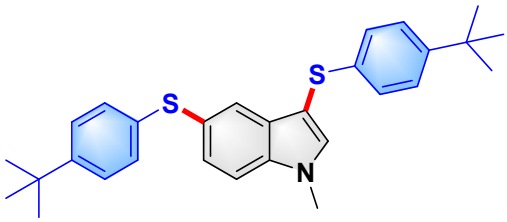
White solid, (53.1 mg, 61% yield), m.p.: 132-134 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.09 (s, 1H), 7.52 (s, 1H), 7.24–7.19 (m, 4H), 7.18–7.14 (m, 3H), 7.14–7.10 (m, 3H), 3.97 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 148.83, 148.00, 138.45, 138.09, 136.14, 133.85, 129.04, 128.88, 128.24, 126.26, 126.06, 125.34, 122.71, 122.36, 100.43, 31.68. **HRMS (ESI):** Calcd. for $C_{20}H_{16}N_2S_2$ $[M+H]^+$: 349.0828, found: 349.0824.

(21) 1-methyl-3,5-bis(*p*-tolylthio)-1*H*-indole (3ab)



White solid, (76.9 mg, 82% yield), m.p.: 123-125 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 4.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.06 (td, *J* = 5.0, 2.3 Hz, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 137.14, 135.76, 135.56, 135.46, 135.05, 134.83, 130.65, 129.69, 129.54, 129.05, 127.82, 126.52, 125.65, 125.02, 110.79, 101.85, 33.27, 21.02, 20.93. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NS_2$ $[M+H]^+$: 376.1188, found: 376.1183.

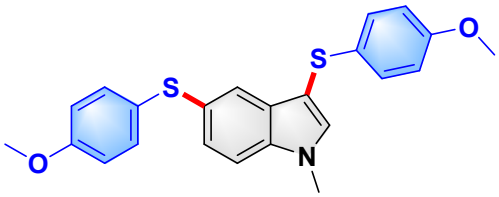
(22) 3,5-bis((4-(*tert*-butyl)phenyl)thio)-1-methyl-1*H*-indole (3ac)



Yellow liquid, (78.0 mg, 68% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 9.9 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H), 1.32 (s, 9H), 1.30 (s, 9H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 148.90, 148.15, 137.22, 135.69, 135.66, 135.30, 130.86, 128.31, 128.23, 126.10, 125.91, 125.79, 125.52,

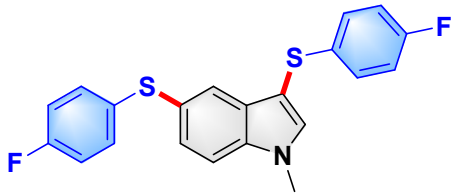
125.18, 110.74, 101.85, 34.41, 34.33, 33.24, 31.34, 31.32. **HRMS (ESI):** Calcd. for $C_{29}H_{33}NS_2$ $[M+H]^+$: 460.2127, found: 460.2123.

(23) 3,5-bis((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (3ad)



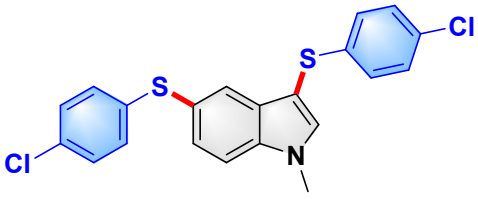
White liquid, (78.3 mg, 77% yield), **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 1.1 Hz, 1H), 7.32–7.28 (m, 5H), 7.17 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.77 (s, 6H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 158.85, 158.00, 136.81, 135.04, 132.44, 130.47, 129.44, 129.07, 128.21, 127.47, 126.43, 123.24, 114.73, 114.55, 110.63, 102.97, 55.36, 33.15. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NO_2S_2$ $[M+H]^+$: 408.1086, found: 408.1079.

(24) 3,5-bis((4-fluorophenyl)thio)-1-methyl-1*H*-indole (3ae)



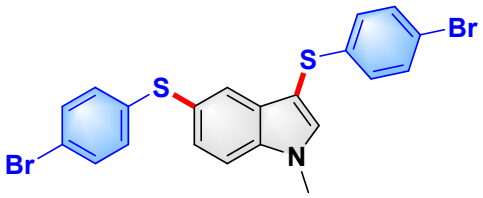
White solid, (66.1 mg, 69% yield), m.p.: 87-89 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.36 (d, *J* = 4.4 Hz, 2H), 7.36 (s, 1H), 7.22–7.19 (m, 2H), 7.12–7.09 (m, 2H), 6.96–6.92 (m, 2H), 6.91–6.88 (m, 2H), 3.85 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 162.13 (d, *J* = 83.1 Hz), 160.50 (d, *J* = 81.5 Hz), 137.20, 135.60, 133.86 (d, *J* = 3.0 Hz), 133.33 (d, *J* = 3.0 Hz), 131.16 (d, *J* = 7.6 Hz), 130.43, 128.25 (d, *J* = 7.6 Hz), 127.61, 125.94, 124.56, 115.97 (d, *J* = 21.1 Hz), 115.77 (d, *J* = 22.7 Hz), 110.92, 101.91, 33.27. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -116.23, -117.77. **HRMS (ESI):** Calcd. for $C_{21}H_{15}F_2NS_2$ $[M+H]^+$: 384.0687, found: 384.0684.

(25) 3,5-bis((4-chlorophenyl)thio)-1-methyl-1*H*-indole (3af)



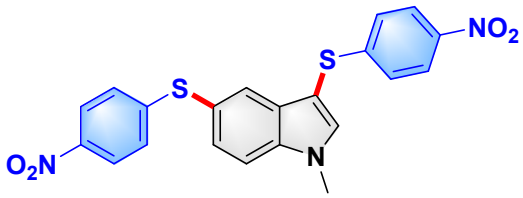
White solid, (77.8 mg, 75% yield), m.p.: 126-128 °C, **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.40 (s, 3H), 7.18 (d, *J* = 6.6 Hz, 2H), 7.15 (d, *J* = 6.7 Hz, 2H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.03 (d, *J* = 6.7 Hz, 2H), 3.88 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 137.63, 137.60, 137.46, 136.02, 131.54, 130.79, 130.45, 129.40, 128.97, 128.83, 128.44, 127.27, 125.57, 124.50, 111.19, 100.85, 33.42. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Cl_2NS_2$ $[M+H]^+$: 416.0096, found: 416.0090.

(26) 3,5-bis((4-bromophenyl)thio)-1-methyl-1*H*-indole (3ag)



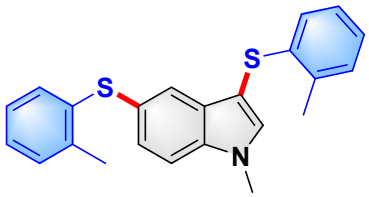
White solid, (67.8 mg, 54% yield), m.p.: 150-152 °C, **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 1.7 Hz, 1H), 7.40 (d, *J* = 2.6 Hz, 3H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.96 (d, *J* = 6.8 Hz, 2H), 3.88 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 138.37, 138.36, 137.49, 136.07, 131.86, 131.71, 130.44, 129.54, 128.54, 127.55, 125.68, 124.26, 119.35, 118.57, 111.23, 100.69, 33.44. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Br_2NS_2$ $[M+H]^+$: 503.9085, found: 503.9080.

(27) 1-methyl-3,5-bis((4-nitrophenyl)thio)-1*H*-indole (3ah)



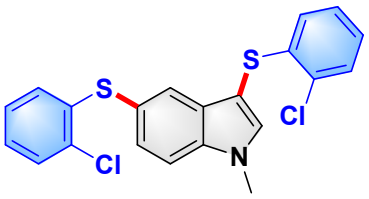
Yellow solid, (74.3 mg, 68% yield), m.p.: 96-97 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 2.4 Hz, 2H), 8.00 (d, *J* = 2.4 Hz, 2H), 7.80 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 150.10, 149.30, 145.09, 145.00, 138.20, 136.94, 130.52, 129.83, 127.00, 125.70, 125.05, 123.95, 123.92, 121.51, 112.02, 98.87, 33.66. **HRMS (ESI):** Calcd. for $C_{21}H_{13}N_3O_4S_2$ $[M+H]^+$: 438.0577, found: 438.0573.

(28) 1-methyl-3,5-bis(*o*-tolylthio)-1*H*-indole (3ai)



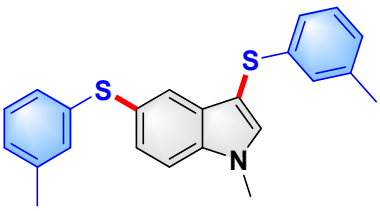
White solid, (70.3 mg, 75% yield), m.p.: 160-162 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.38–7.35 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (q, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.19, 137.76, 137.33, 136.61, 135.90, 134.48, 130.91, 130.10, 129.91, 128.63, 128.05, 126.40, 126.27, 125.78, 125.36, 124.62, 124.50, 110.97, 100.61, 33.34, 20.30, 19.94. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NS_2$ $[M+H]^+$: 376.1188, found: 376.1183.

(29) 3,5-bis((2-chlorophenyl)thio)-1-methyl-1*H*-indole (3aj)



White solid, (73.7 mg, 71% yield), m.p.: 164-167 °C, **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.94–7.74 (m, 1H), 7.50–7.41 (m, 3H), 7.36–7.29 (m, 2H), 7.05–6.93 (m, 4H), 6.67 (ddd, *J* = 7.2, 3.4, 1.8 Hz, 2H), 3.92 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 139.11, 138.21, 137.97, 136.62, 130.83, 130.16, 129.74, 129.38, 127.55, 127.38, 126.96, 126.91, 126.26, 125.92, 125.63, 122.32, 111.48, 99.68, 33.52. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Cl_2NS_2$ $[M+H]^+$: 416.0096, found: 416.0091.

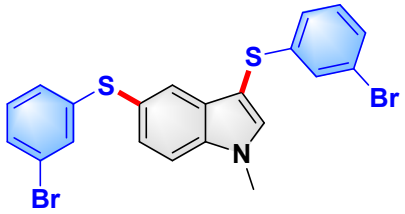
(30) 1-methyl-3,5-bis(*m*-tolylthio)-1*H*-indole (3ak)



White solid, (62.8 mg, 67% yield), m.p.: 116-118 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 1.4 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.12–7.09 (m, 2H), 7.05 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.00, 138.87, 138.66, 138.53, 137.39, 135.87, 130.85, 128.83, 128.76, 128.67, 128.50, 126.71, 126.60, 126.00,

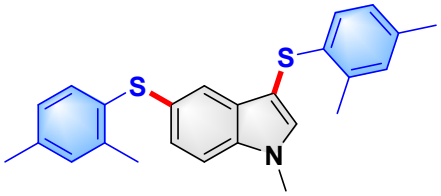
125.80, 125.33, 124.77, 123.25, 110.95, 101.43, 33.28, 21.43, 21.38. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NS_2$ $[M+H]^+$: 376.1188, found: 376.1185.

(31) 3,5-bis((3-bromophenyl)thio)-1-methyl-1*H*-indole (3al)



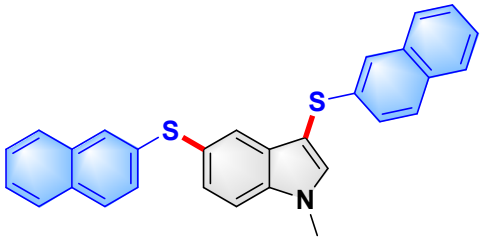
White solid, (75.3 mg, 60% yield), m.p.: 120-121 °C, **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 9.5 Hz, 3H), 7.24 (dd, *J* = 11.5, 5.7 Hz, 4H), 7.10–7.01 (m, 4H), 3.91 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 142.00, 141.71, 137.70, 136.35, 130.58, 130.15, 130.12, 130.11, 129.86, 129.11, 128.40, 128.19, 128.02, 126.36, 125.94, 124.34, 123.38, 122.99, 111.43, 100.20, 33.51. **HRMS (ESI)**: Calcd. for $C_{21}H_{15}Br_2NS_2$ $[M+H]^+$: 503.9085, found: 503.9081.

(32) 3,5-bis((2,4-dimethylphenyl)thio)-1-methyl-1*H*-indole (3am)



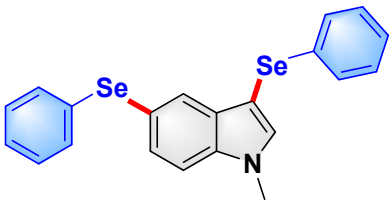
White solid, (81.6 mg, 81% yield), m.p.: 137-139 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.33 (d, *J* = 6.3 Hz, 1H), 7.31 (s, 1H), 7.28 (d, *J* = 4.8 Hz, 1H), 7.04–6.97 (m, 3H), 6.88 (t, *J* = 6.8 Hz, 1H), 6.77 (t, *J* = 6.6 Hz, 1H), 6.74–6.71 (m, 1H), 3.84 (s, 3H), 2.46 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.77, 136.96, 136.28, 135.40, 134.84, 134.50, 134.44, 133.26, 131.15, 130.85, 130.78, 130.51, 127.22, 127.03, 126.77, 126.34, 125.88, 123.84, 110.70, 101.36, 33.22, 20.92, 20.76, 20.33, 19.92. **HRMS (ESI):** Calcd. for $C_{25}H_{25}NS_2$ $[M+H]^+$: 404.1501, found: 404.1497.

(33) 1-methyl-3,5-bis(naphthalen-2-ylthio)-1*H*-indole (3an)



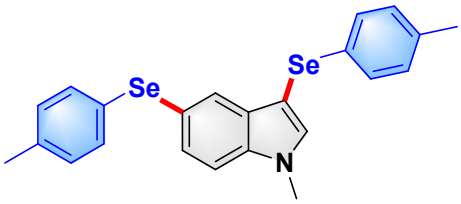
White solid, (80.5 mg, 72% yield), m.p.: 142-143 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.74 (ddd, *J* = 14.0, 6.3, 3.3 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.62–7.58 (m, 4H), 7.53 (s, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.43–7.39 (m, 6H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.28 (s, 1H), 3.85 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 136.63, 136.29, 135.92, 133.82, 133.77, 131.70, 131.47, 130.78, 128.41, 128.34, 128.33, 127.73, 127.68, 127.15, 126.96, 126.72, 126.41, 126.39, 125.55, 125.49, 125.17, 124.97, 124.91, 123.81, 111.04, 101.33, 33.32. **HRMS (ESI):** Calcd. for $C_{29}H_{21}NS_2$ $[M+H]^+$: 448.1188, found: 448.1184.

(34) 1-methyl-3,5-bis(phenylselanyl)-1*H*-indole (3ao)



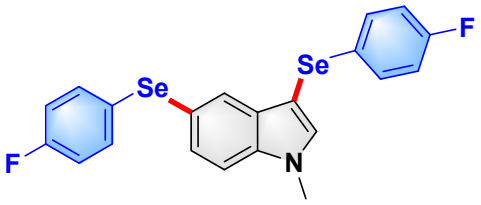
Brown solid, (89.5 mg, 81% yield), m.p.: 107-109 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.53 (d, *J* = 6.9 Hz, 1H), 7.36–7.33 (m, 4H), 7.29–7.27 (m, 2H), 7.21–7.13 (m, 6H), 3.85 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.28, 136.25, 133.79, 133.75, 131.83, 130.75, 129.54, 129.06, 128.99, 128.95, 127.81, 126.24, 125.79, 120.27, 110.77, 96.46, 33.18. **HRMS (ESI):** Calcd. for $C_{21}H_{17}NSe_2$ $[M+H]^+$: 443.9764, found: 443.9759.

(35) 1-methyl-3,5-bis(*p*-tolylselanyl)-1*H*-indole (3ap)



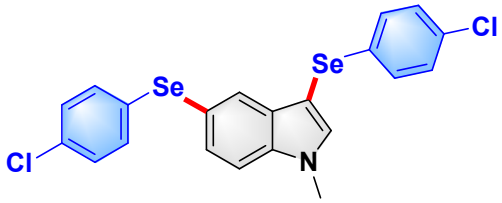
White solid, (81.2 mg, 69% yield), m.p.: 112-113 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.32 (s, 1H), 7.32–7.29 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 3.82 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.11, 136.31, 135.94, 135.65, 131.78, 131.53, 129.91, 129.85, 129.81, 129.63, 129.45, 128.95, 127.15, 120.98, 110.63, 96.91, 33.12, 21.07, 20.99. **HRMS (ESI):** Calcd. for $C_{23}H_{21}NSe_2$ $[M+H]^+$: 472.0077, found: 472.0072.

(36) 3,5-bis((4-fluorophenyl)selanyl)-1-methyl-1*H*-indole (3aq)



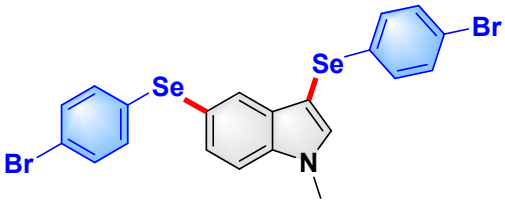
White solid, (75.4 mg, 63% yield), m.p.: 106-109 °C, **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.34 (q, *J* = 8.7, 7.7 Hz, 4H), 7.25 (dd, *J* = 8.1, 5.6 Hz, 2H), 6.90 (dt, *J* = 19.4, 8.6 Hz, 4H), 3.85 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.05 (d, *J* = 39.4 Hz), 160.61 (d, *J* = 37.4 Hz), 137.16, 136.10, 133.47 (d, *J* = 7.1 Hz), 131.54, 131.05 (d, *J* = 8.1 Hz), 128.87, 127.80 (d, *J* = 17.2 Hz), 126.85, 121.10, 116.35, 116.17 (d, *J* = 6.1 Hz), 115.99, 110.88, 96.76, 33.23. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -115.65, -116.79. **HRMS (ESI):** Calcd. for $C_{21}H_{15}F_2NSe_2$ $[M+H]^+$: 479.9576, found: 479.9570.

(37) 3,5-bis((4-chlorophenyl)selanyl)-1-methyl-1*H*-indole (3ar)



White solid, (100.7 mg, 79% yield), m.p.: 116-118 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.37 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.17–7.14 (m, 4H), 7.12 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.35, 136.31, 132.44, 132.14, 131.89, 131.87, 131.85, 131.58, 130.24, 129.42, 129.16, 129.05, 127.50, 120.28, 110.95, 96.22, 33.24. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Cl_2NSe_2$ $[M+H]^+$: 511.8985, found: 511.8975.

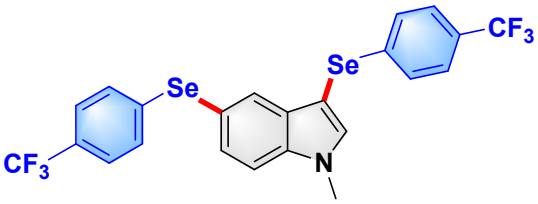
(38) 3,5-bis((4-bromophenyl)selanyl)-1-methyl-1*H*-indole (3as)



White solid, (61.4 mg, 41% yield), m.p.: 126-127 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.50 (d, *J* = 6.3 Hz, 1H), 7.37–7.34 (m, 2H), 7.32–7.29 (m, 2H), 7.27–7.25 (m, 2H), 7.16 (dq, *J* = 5.9, 1.9 Hz, 2H), 7.09 (dq, *J* = 6.5, 2.1 Hz, 2H), 3.86 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.39, 136.39,

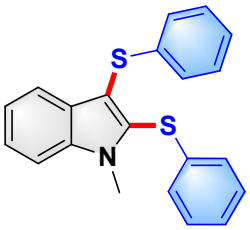
132.73, 132.33, 132.09, 131.97, 131.58, 130.52, 129.53, 127.61, 120.38, 120.10, 119.74, 111.03, 96.08, 33.27. **HRMS (ESI):** Calcd. for $C_{21}H_{15}Br_2NSe_2$ $[M+H]^+$: 599.7962, found: 599.7958.

(39) 1-methyl-3,5-bis((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole (3at)



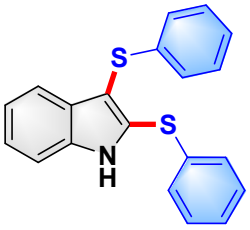
Yellow solid, (92.6 mg, 64% yield), m.p.: 129-131 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 4.2 Hz, 2H), 7.39 (dd, *J* = 8.1, 5.2 Hz, 4H), 7.31 (dd, *J* = 14.8, 8.2 Hz, 4H), 3.92 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 139.68, 139.40, 137.70, 136.86, 131.72, 130.33, 129.53, 128.49, 128.27, 128.23, 128.03 (d, *J* = 4.5 Hz), 127.83, 125.65 (d, *J* = 3.0 Hz), 125.09 (d, *J* = 3.0 Hz), 123.29 (d, *J* = 3.0 Hz), 118.91, 111.30, 95.30, 33.31. **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -62.51, -62.56. **HRMS (ESI):** Calcd. for $C_{23}H_{15}F_6NSe_2$ $[M+H]^+$: 579.9512, found: 579.9506.

(40) 1-methyl-2,3-bis(phenylthio)-1*H*-indole (4aa)



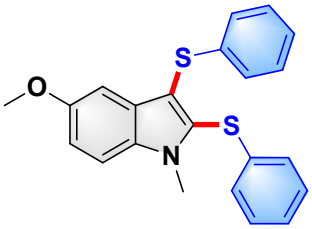
Known compound, (79.4 mg, 91% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.25 (ddd, *J* = 14.7, 6.6, 1.2 Hz, 3H), 7.20 (d, *J* = 4.3 Hz, 5H), 7.15–7.09 (m, 3H), 3.86 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.62, 138.59, 135.92, 134.38, 129.29, 129.28, 128.77, 127.49, 126.68, 126.30, 125.10, 124.10, 121.19, 120.46, 111.15, 110.32, 31.20. Calcd. for $C_{21}H_{17}NS_2$.

(41) 2,3-bis(phenylthio)-1*H*-indole (4ba)



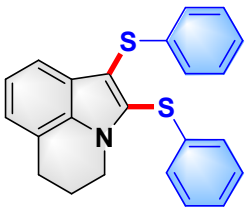
Known compound, (78.7 mg, 85% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.33–7.25 (m, 6H), 7.20 (td, *J* = 7.4, 6.6, 3.5 Hz, 5H), 7.14–7.09 (m, 1H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.12, 136.95, 134.45, 133.63, 130.02, 129.70, 129.47, 128.82, 127.31, 126.65, 125.18, 123.96, 121.31, 119.98, 111.28. Calcd. for $C_{20}H_{15}NS_2$.

(42) 5-methoxy-1-methyl-2,3-bis(phenylthio)-1*H*-indole (4ca)



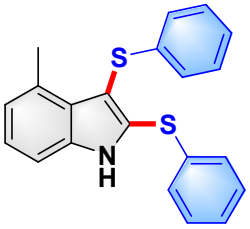
White solid, (82.0 mg, 87% yield), m.p.: 149-151 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.9 Hz, 1H), 7.22–7.17 (m, 3H), 7.16–7.11 (m, 5H), 7.08 (d, *J* = 7.4 Hz, 3H), 7.04 (d, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 155.31, 138.64, 136.01, 134.28, 133.69, 129.92, 129.19, 128.69, 127.34, 126.39, 126.16, 124.94, 114.99, 111.21, 110.05, 100.99, 55.84, 31.28. **HRMS (ESI):** Calcd. for $C_{22}H_{19}NOS_2$ $[M+H]^+$: 378.0981, found: 378.0975.

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



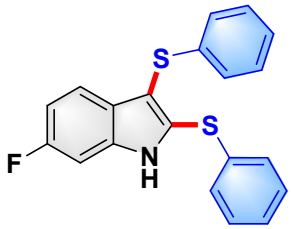
White solid, (77.4 mg, 83% yield), m.p.: 120-121 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.24–7.18 (m, 6H), 7.17–7.07 (m, 6H), 4.14–4.10 (m, 2H), 3.04 (t, *J* = 6.1 Hz, 2H), 2.24 (p, *J* = 6.0 Hz, 2H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.82, 135.99, 135.91, 132.37, 129.20, 128.69, 127.59, 127.54, 126.69, 126.21, 124.99, 122.42, 121.18, 120.74, 117.66, 109.97, 43.11, 24.81, 22.75. **HRMS (ESI):** Calcd. for $C_{23}H_{19}NS_2$ $[M+H]^+$: 374.1032, found: 374.1027.

(44) 4-methyl-2,3-bis(phenylthio)-1*H*-indole (4ea)



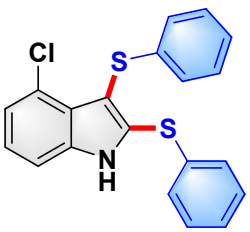
White solid, (70.36 mg, 81% yield), m.p.: 113-115 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.35–7.25 (m, 5H), 7.23–7.16 (m, 4H), 7.14–7.07 (m, 3H), 6.96 (d, *J* = 5.1 Hz, 1H), 2.73 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 140.41, 137.27, 134.95, 134.35, 132.05, 129.95, 129.46, 128.87, 128.07, 127.35, 125.54, 124.74, 123.75, 123.00, 109.09, 107.96, 18.77. **HRMS (ESI):** Calcd. for $C_{21}H_{17}NS_2$ $[M+H]^+$: 348.0875, found: 348.0871.

(45) 6-fluoro-2,3-bis(phenylthio)-1*H*-indole (4fa)



Known compound, (68.5 mg, 78% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.52 (d, *J* = 5.3 Hz, 1H), 7.32–7.23 (m, 5H), 7.22–7.09 (m, 5H), 7.03 (d, *J* = 9.2 Hz, 1H), 6.98–6.92 (m, 1H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 160.89 (d, *J* = 241.9 Hz), 137.74, 136.81 (d, *J* = 12.6 Hz), 134.32, 133.66 (d, *J* = 3.8 Hz), 129.64, 129.47, 128.85, 127.36, 126.73, 126.40, 125.34, 121.01 (d, *J* = 10.1 Hz), 110.19 (d, *J* = 25.2 Hz), 109.82, 97.77 (d, *J* = 27.7 Hz). **^{19}F-NMR** (471 MHz, Chloroform-*d*) δ -117.83. Calcd. for $C_{20}H_{14}FNS_2$.

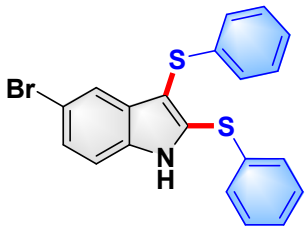
(46) 4-chloro-2,3-bis(phenylthio)-1*H*-indole (4ga)



White solid, (76.1 mg, 83% yield), m.p.: 141-144 °C, ^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.36 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.34–7.29 (m, 3H), 7.24–7.17 (m, 5H), 7.16–7.13 (m, 2H), 7.11 (t, *J* = 7.1 Hz, 1H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 139.91, 138.14, 137.59, 133.01, 130.93, 129.69, 128.79,

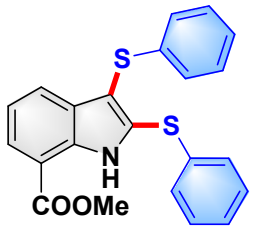
128.01, 126.43, 126.25, 126.23, 124.99, 123.95, 122.72, 110.02, 106.67. **HRMS (ESI):** Calcd. for $C_{20}H_{14}ClNS_2$ $[M+H]^+$: 368.0329, found: 368.0324.

(47) 5-bromo-2,3-bis(phenylthio)-1*H*-indole (4ha)



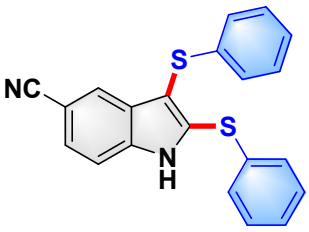
Known compound, (63.7 mg, 62% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.76 (s, 1H), 7.33 (dtd, *J* = 12.7, 7.0, 2.0 Hz, 6H), 7.22–7.18 (m, 3H), 7.13 (dd, *J* = 8.1, 1.9 Hz, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 137.61, 136.04, 135.38, 133.25, 131.89, 130.56, 129.61, 128.89, 127.85, 126.68, 126.58, 125.37, 122.22, 114.79, 112.53, 107.71. Calcd. for $C_{20}H_{14}BrNS_2$.

(48) methyl 2,3-bis(phenylthio)-1*H*-indole-7-carboxylate (4ia)



White solid, (41.0 mg, 42% yield), m.p.: 157-159 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.94 (d, *J* = 6.7 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.32–7.27 (m, 3H), 7.17 (s, 3H), 7.15–7.08 (m, 3H), 3.97 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 167.31, 137.86, 136.73, 135.72, 133.55, 131.07, 130.33, 129.50, 128.81, 127.66, 126.62, 125.78, 125.26, 120.57, 112.84, 108.62, 52.09. **HRMS (ESI):** Calcd. for $C_{22}H_{17}NO_2S_2$ $[M+H]^+$: 392.0773, found: 392.0767.

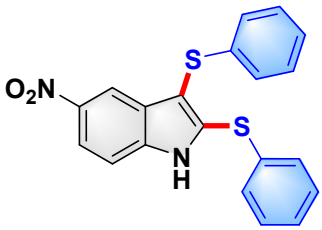
(49) 2,3-bis(phenylthio)-1*H*-indole-5-carbonitrile (4ja)



Known compound, (36.7 mg, 41% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 7.91 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.41–7.37 (m, 3H), 7.36–7.31 (m, 3H), 7.24–7.20 (m, 2H), 7.16–7.13 (m, 3H). **^{13}C-**

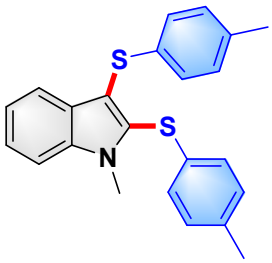
NMR (126 MHz, Chloroform-*d*) δ 138.47, 138.19, 136.95, 132.24, 131.37, 130.03, 129.79, 129.02, 128.39, 126.95, 126.35, 125.78, 124.90, 120.04, 112.04, 108.45, 104.42. Calcd. for $C_{21}H_{14}N_2S_2$.

(50) 5-nitro-2,3-bis(phenylthio)-1*H*-indole (4ka)



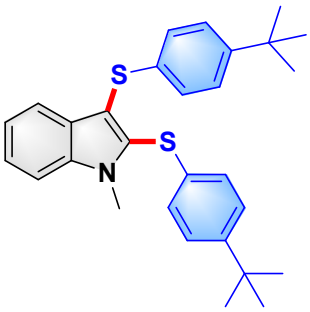
Known compound, (44.4 mg, 47% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 2.2 Hz, 2H), 8.14 (d, *J* = 6.7 Hz, 1H), 7.44–7.41 (m, 2H), 7.39–7.35 (m, 4H), 7.24–7.21 (m, 2H), 7.18–7.13 (m, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 142.96, 139.55, 139.35, 136.85, 131.82, 131.65, 129.93, 129.89, 129.03, 128.61, 127.08, 125.85, 118.99, 116.41, 111.12, 109.70. Calcd. for $C_{20}H_{14}N_2O_2S_2$.

(51) 1-methyl-2,3-bis(*p*-tolylthio)-1*H*-indole (4ab)



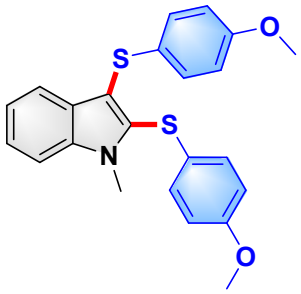
Known compound, (81.6 mg, 87% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.78–7.74 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.41–7.37 (m, 1H), 7.27–7.23 (m, 1H), 7.12 (s, 2H), 7.08–7.05 (m, 4H), 7.02 (s, 2H), 3.85 (s, 3H), 2.35–2.31 (m, 6H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.49, 136.29, 135.02, 134.88, 134.82, 132.28, 130.02, 129.52, 129.28, 127.98, 127.12, 123.90, 121.01, 120.42, 111.43, 110.19, 31.15, 21.03, 20.99. Calcd. for $C_{23}H_{21}NS_2$.

(52) 2,3-bis((4-(*tert*-butyl)phenyl)thio)-1-methyl-1*H*-indole (4ac)



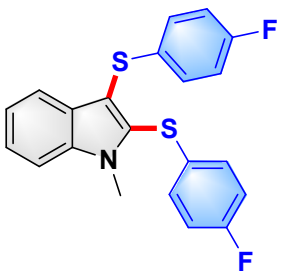
White solid, (83.8 mg, 73% yield), m.p.: 96-99 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.26–7.20 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H), 1.30 (d, *J* = 1.8 Hz, 18H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 149.51, 148.15, 138.44, 135.18, 134.87, 132.34, 129.38, 127.68, 126.78, 126.25, 125.75, 123.86, 120.96, 120.47, 111.41, 110.13, 34.46, 34.35, 31.36, 31.28, 31.17. **HRMS (ESI):** Calcd. for $C_{29}H_{33}NS_2$ $[M+H]^+$: 460.2127, found: 460.2121.

(53) 2,3-bis((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4ad)



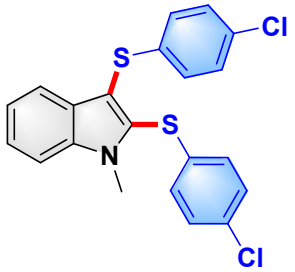
Known compound, (89.5 mg, 88% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.77–7.69 (m, 1H), 7.39–7.32 (m, 2H), 7.24–7.16 (m, 3H), 7.13 (ddd, *J* = 8.6, 3.9, 2.0 Hz, 2H), 6.78–6.72 (m, 4H), 3.83 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 158.75, 157.98, 138.26, 135.39, 130.51, 129.53, 129.19, 129.13, 126.10, 123.77, 120.92, 120.28, 114.88, 114.45, 111.97, 110.09, 55.35, 55.32, 31.09. Calcd. for $C_{23}H_{21}NO_2S_2$.

(54) 2,3-bis((4-fluorophenyl)thio)-1-methyl-1*H*-indole (4ae)



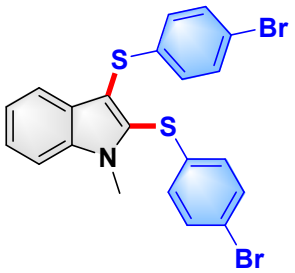
Brown solid, (78.5 mg, 87% yield), m.p.: 109-111 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.16–7.13 (m, 2H), 7.10 (ddt, *J* = 8.2, 5.2, 2.6 Hz, 2H), 6.91 (dddd, *J* = 22.0, 8.8, 6.1, 2.1 Hz, 4H), 3.86 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 162.41 (d, *J* = 71.8 Hz), 160.45 (d, *J* = 70.6 Hz), 138.43, 134.57, 133.41 (d, *J* = 3.8 Hz), 130.66 (d, *J* = 2.5 Hz), 129.92 (d, *J* = 7.6 Hz), 129.08, 128.93 (d, *J* = 7.6 Hz), 124.24, 121.32, 120.25, 116.40 (d, *J* = 22.7 Hz), 115.80 (d, *J* = 22.7 Hz), 111.53, 110.35, 31.16. **^{19}F-NMR** (471 MHz, Chloroform-*d*) δ -115.20, -117.37. **HRMS (ESI):** Calcd. for $C_{21}H_{15}F_2NS_2$ $[M+H]^+$: 384.0687, found: 384.0681.

(55) 2,3-bis((4-chlorophenyl)thio)-1-methyl-1*H*-indole (4af)



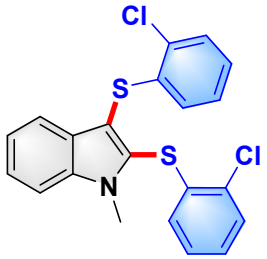
Known compound, (87.1 mg, 84% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.56, 137.05, 134.27, 133.94, 132.45, 131.03, 129.41, 129.06, 128.85, 128.79, 127.95, 124.43, 121.50, 120.29, 110.93, 110.48, 31.23. Calcd. for $C_{21}H_{15}Cl_2NS_2$.

(56) 2,3-bis((4-bromophenyl)thio)-1-methyl-1*H*-indole (4ag)



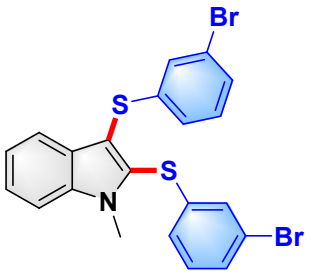
Known compound, (96.8 mg, 77% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.42–7.38 (m, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.27–7.23 (m, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.53, 137.66, 134.91, 133.74, 132.28, 131.70, 128.99, 128.92, 128.18, 128.15, 124.40, 121.47, 120.26, 118.80, 110.78, 110.42, 31.20. Calcd. for $C_{21}H_{15}Br_2NS_2$.

(57) 2,3-bis((2-chlorophenyl)thio)-1-methyl-1*H*-indole (4ah)



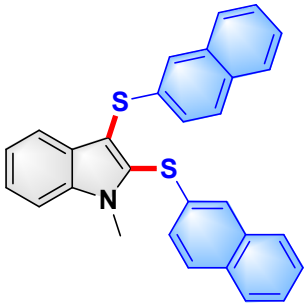
Known compound, (68.5 mg, 66% yield), **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.33 (ddd, *J* = 13.7, 7.9, 1.3 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.08–7.05 (m, 1H), 7.00 (tdd, *J* = 7.8, 4.7, 1.5 Hz, 2H), 6.95–6.91 (m, 1H), 6.65 (d, *J* = 6.4 Hz, 1H), 6.59 (d, *J* = 6.4 Hz, 1H), 3.86 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.89, 137.59, 135.15, 133.49, 131.34, 130.56, 129.79, 129.38, 129.16, 127.74, 127.43, 126.99, 126.84, 126.65, 125.63, 124.44, 121.48, 120.39, 110.50, 110.11, 31.21. Calcd. for $C_{21}H_{15}Cl_2NS_2$.

(58) 2,3-bis((3-bromophenyl)thio)-1-methyl-1*H*-indole (4ai)



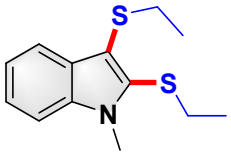
Known compound, (74.2 mg, 59% yield), **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.30–7.26 (m, 2H), 7.25–7.16 (m, 3H), 7.07 (t, *J* = 7.9 Hz, 1H), 7.04–6.99 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 3.87 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 140.88, 138.59, 137.93, 133.56, 130.57, 130.08, 129.85, 129.53, 129.10, 128.92, 128.24, 125.85, 125.04, 124.50, 123.28, 122.89, 121.58, 120.28, 110.55, 110.52, 31.31. Calcd. for $C_{21}H_{15}Br_2NS_2$.

(59) 1-methyl-2,3-bis(naphthalen-2-ylthio)-1*H*-indole (4aj)



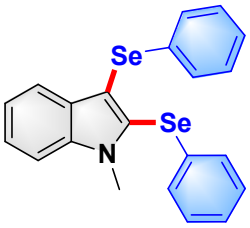
White solid, (84.9 mg, 76% yield), m.p.: 115-116 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.74–7.70 (m, 2H), 7.66–7.61 (m, 2H), 7.58–7.53 (m, 4H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.44–7.40 (m, 3H), 7.40–7.35 (m, 2H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.62, 136.06, 134.51, 133.74, 133.12, 131.84, 131.47, 129.41, 128.95, 128.28, 127.72, 127.67, 127.12, 126.97, 126.68, 126.30, 126.07, 125.90, 125.59, 125.47, 125.16, 124.58, 124.13, 121.26, 120.48, 110.35, 31.27. **HRMS (ESI):** Calcd. for $C_{29}H_{21}NS_2$ $[M+H]^+$: 448.1188, found: 448.1180.

(60) 2,3-bis(ethylthio)-1-methyl-1*H*-indole (4ak)



White solid, (49.6 mg, 79% yield), m.p.: 87-90 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 6.8 Hz, 1H), 3.93 (s, 3H), 2.89 (q, *J* = 7.4 Hz, 2H), 2.83 (q, *J* = 7.4 Hz, 2H), 1.25 (q, *J* = 7.4 Hz, 6H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 137.86, 136.15, 129.91, 123.15, 120.39, 119.76, 112.24, 109.89, 31.28, 30.90, 30.69, 15.19, 14.89. **HRMS (ESI):** Calcd. for $C_{13}H_{17}NS_2$ $[M+H]^+$: 252.0875, found: 252.0873.

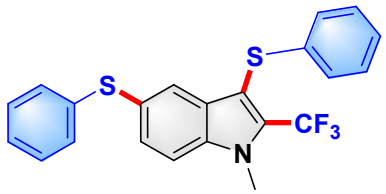
(61) 1-methyl-2,3-bis(phenylselanyl)-1*H*-indole (4al)



White solid, (82.0 mg, 83% yield), m.p.: 121-123 °C, **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.30 (dd, *J* = 4.8, 3.0 Hz, 2H), 7.25–7.21 (m,

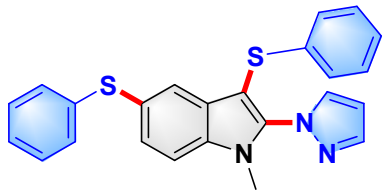
3H), 7.18 (dt, *J* = 5.4, 2.4 Hz, 3H), 7.14 (dt, *J* = 4.6, 3.2 Hz, 3H), 3.90 (s, 3H). **^{13}C-NMR** (126 MHz, Chloroform-*d*) δ 138.94, 133.79, 133.68, 131.62, 130.52, 130.15, 129.45, 129.42, 128.96, 126.80, 125.80, 123.64, 121.35, 120.97, 110.23, 109.04, 32.83. **HRMS (ESI):** Calcd. for $C_{21}H_{17}NSe_2$ $[M+H]^+$: 443.9764, found: 443.9758.

(62) 1-methyl-3,5-bis(phenylthio)-2-(trifluoromethyl)-1*H*-indole (6)



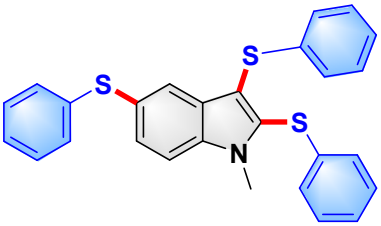
White solid, (71.6 mg, 69% yield), m.p.: 73-75 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.26–7.16 (m, 7H), 7.16–7.11 (m, 3H), 3.96 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 137.97, 137.54, 137.41, 130.72, 130.04 (d, *J* = 36.2 Hz), 129.46, 129.00, 128.92, 128.87, 127.03, 126.95, 126.47, 126.11, 125.63, 122.12, 111.35, 106.47, 32.00 (d, *J* = 3.0 Hz, 1H). **^{19}F-NMR** (565 MHz, Chloroform-*d*) δ -56.51. **HRMS (ESI):** Calcd. for $C_{22}H_{16}F_3NS_2$ $[M+H]^+$: 416.0749, found: 416.0742.

(63) 1-methyl-3,5-bis(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (7)



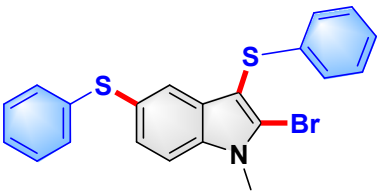
White solid, (43.4 mg, 42% yield), m.p.: 106-108 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.89 (s, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.26–7.23 (m, 2H), 7.22 (s, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 3H), 6.49 (t, *J* = 2.1 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 142.52, 139.72, 138.71, 138.02, 135.07, 133.47, 129.48, 129.02, 129.01, 128.95, 128.37, 126.27, 126.00, 125.87, 125.81, 125.39, 111.30, 107.05, 95.91, 30.98. **HRMS (ESI):** Calcd. for $C_{24}H_{19}N_3S_2$ $[M+H]^+$: 414.1093, found: 414.1089.

(64) 1-methyl-2,3,5-tris(phenylthio)-1*H*-indole (8)



White solid, (97.8 mg, 86% yield), m.p.: 129-131 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.46–7.44 (m, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.25–7.21 (m, 6H), 7.16 (ddt, *J* = 13.3, 6.5, 3.4 Hz, 6H), 7.12–7.08 (m, 3H), 3.82 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.52, 138.15, 138.06, 135.53, 135.48, 129.99, 129.46, 129.30, 128.92, 128.74, 128.63, 127.72, 127.01, 126.45, 125.87, 125.86, 125.77, 125.32, 111.59, 111.28, 31.31. **HRMS (ESI):** Calcd. for $C_{27}H_{21}NS_3$ $[M+H]^+$: 456.0909, found: 456.0903.

(65) 2-bromo-1-methyl-3,5-bis(phenylthio)-1*H*-indole (9)

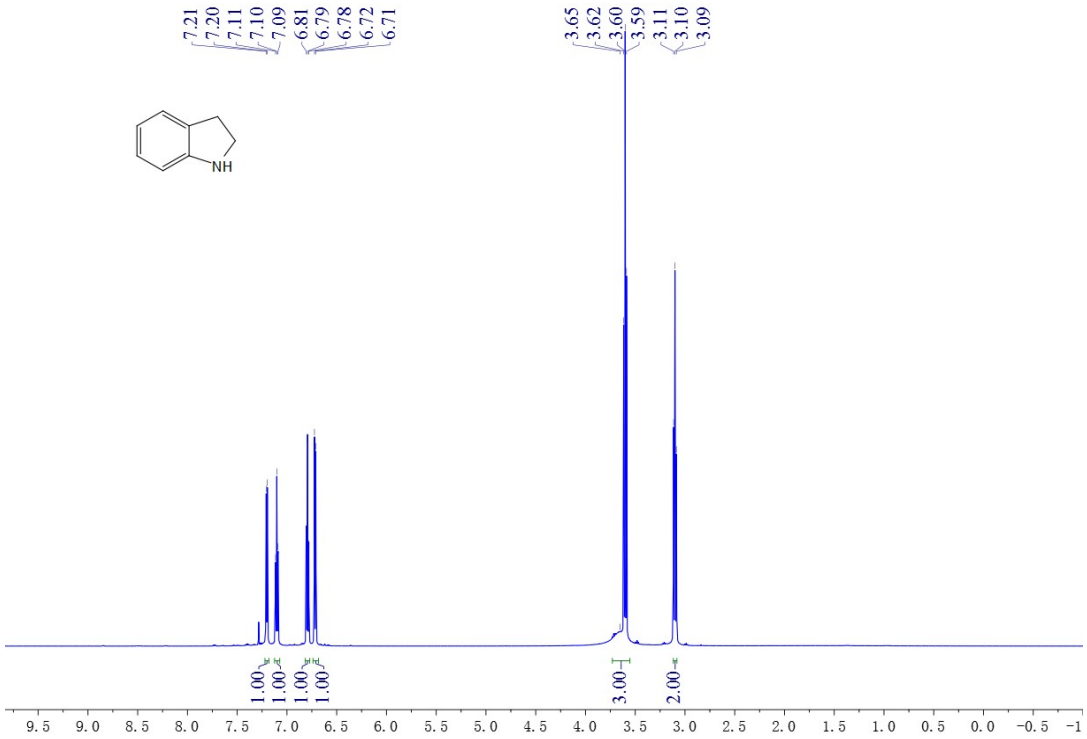


White solid, (81.6 mg, 77% yield), m.p.: 118-119 °C, **^{1}H-NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.19–7.15 (m, 3H), 7.14–7.07 (m, 5H), 3.80 (s, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*) δ 138.08, 137.11, 136.10, 135.29, 130.90, 129.33, 128.83, 127.71, 127.01, 126.67, 126.51, 125.30, 122.74, 114.73, 111.75, 110.60, 31.37. **HRMS (ESI):** Calcd. for $C_{21}H_{16}BrNS_2$ $[M+H]^+$: 425.9980.1080, found: 425.9975.

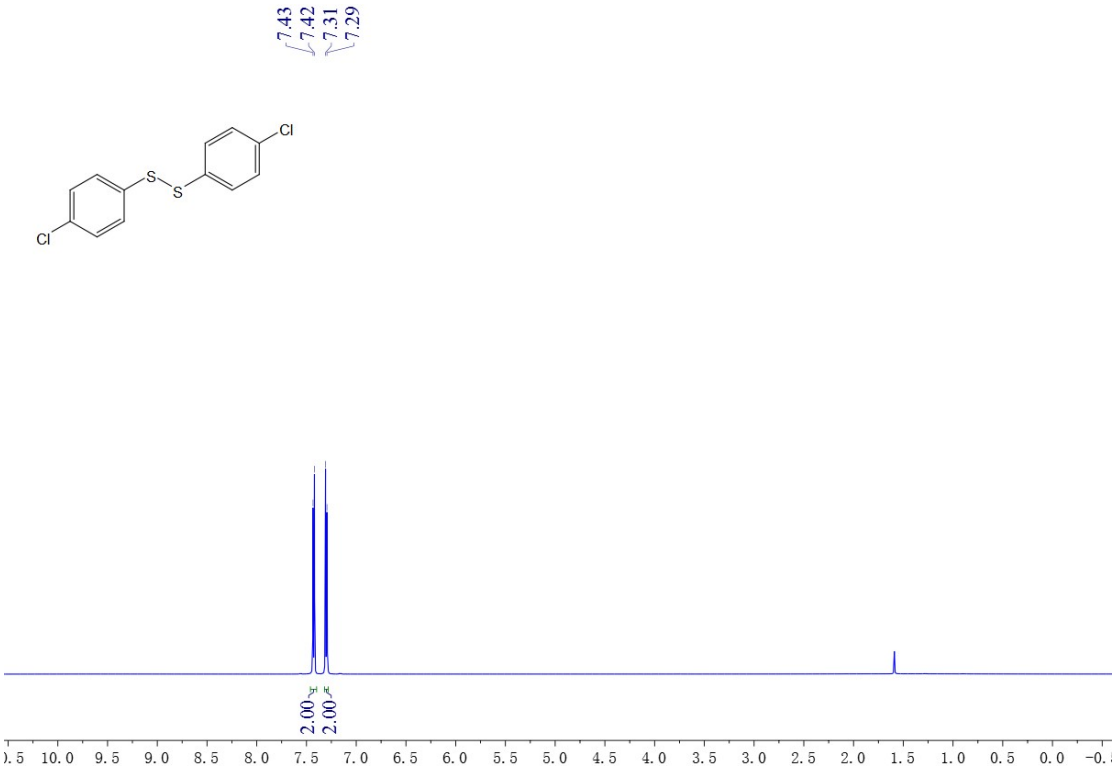
SPECTROSCOPIC DATA

11. NMR spectra of the obtained compounds.

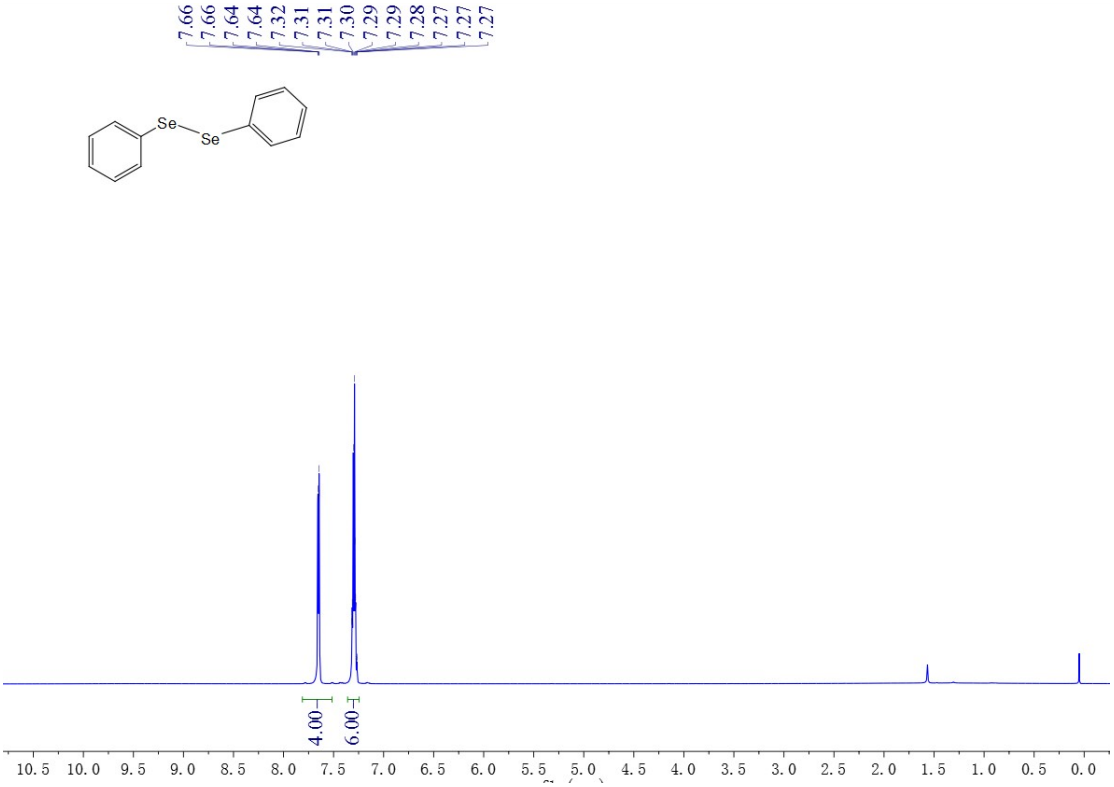
(1) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1f



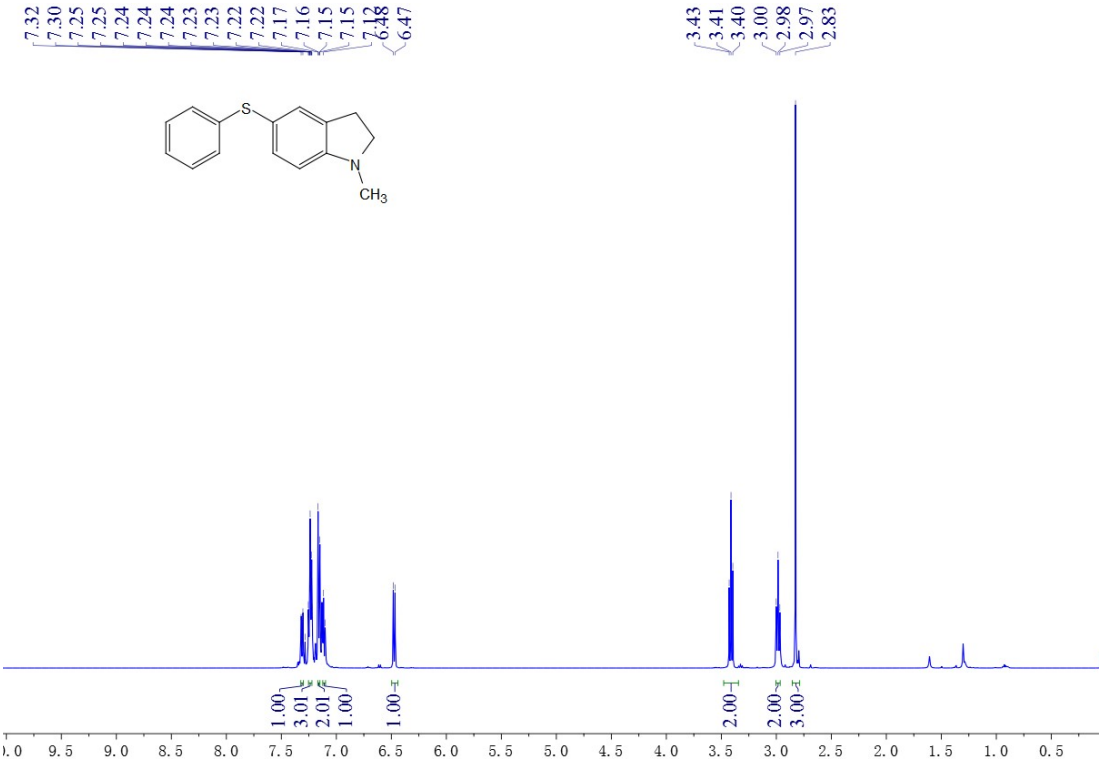
(2) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 2f



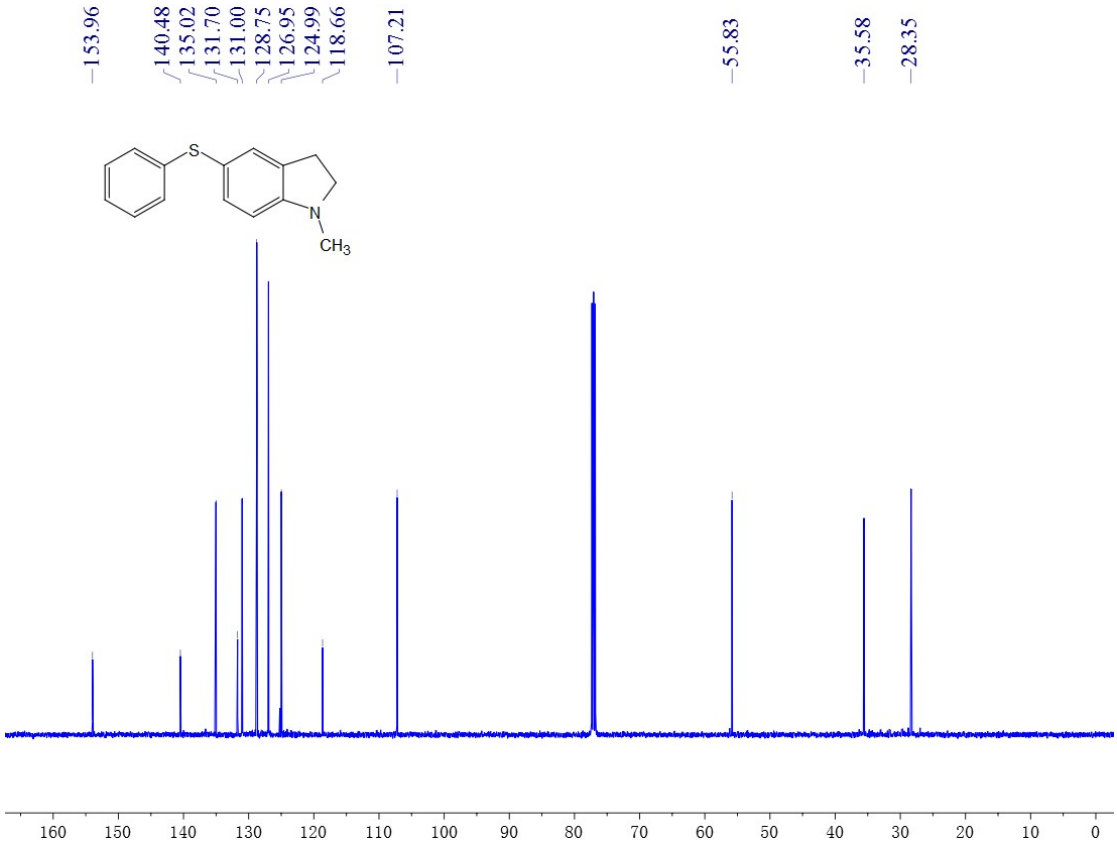
(3) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 2q



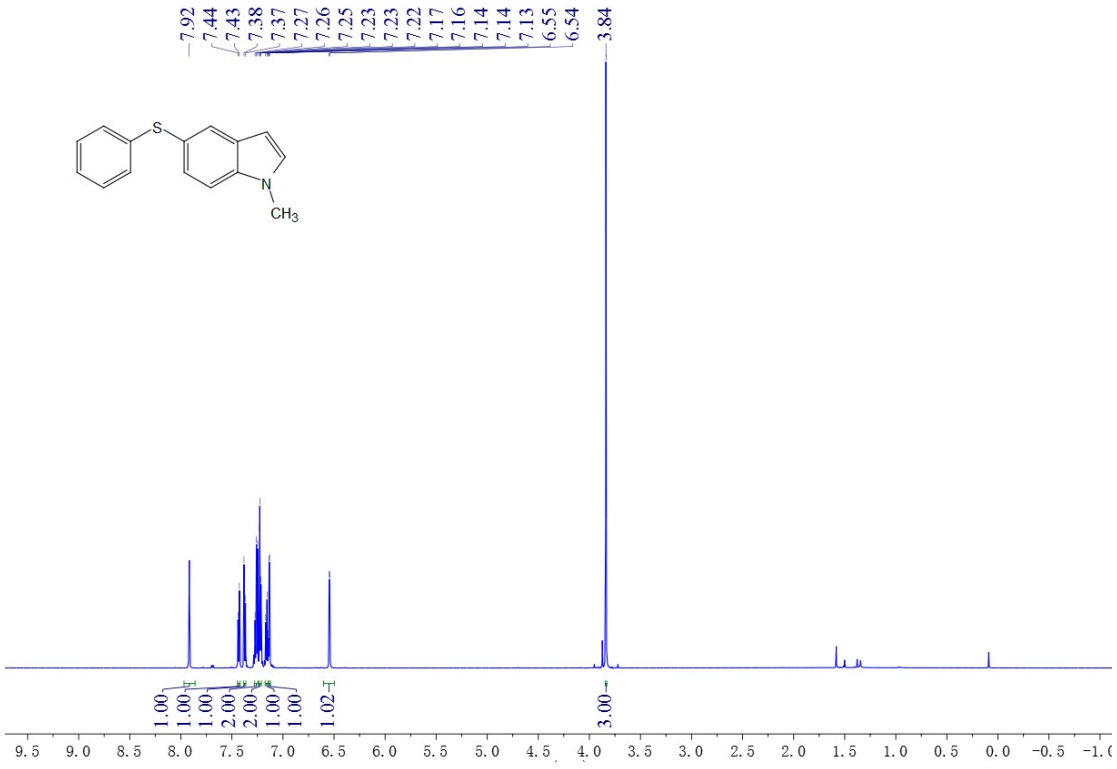
(4) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 1a-1



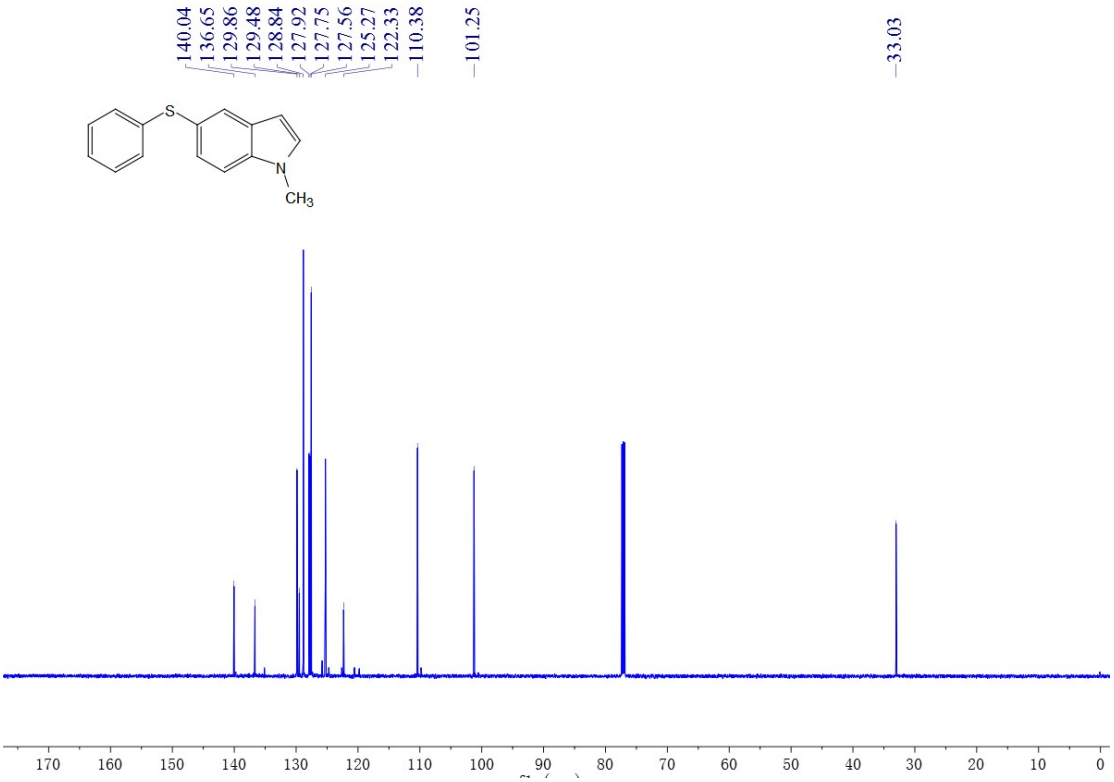
(5) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 1a-1



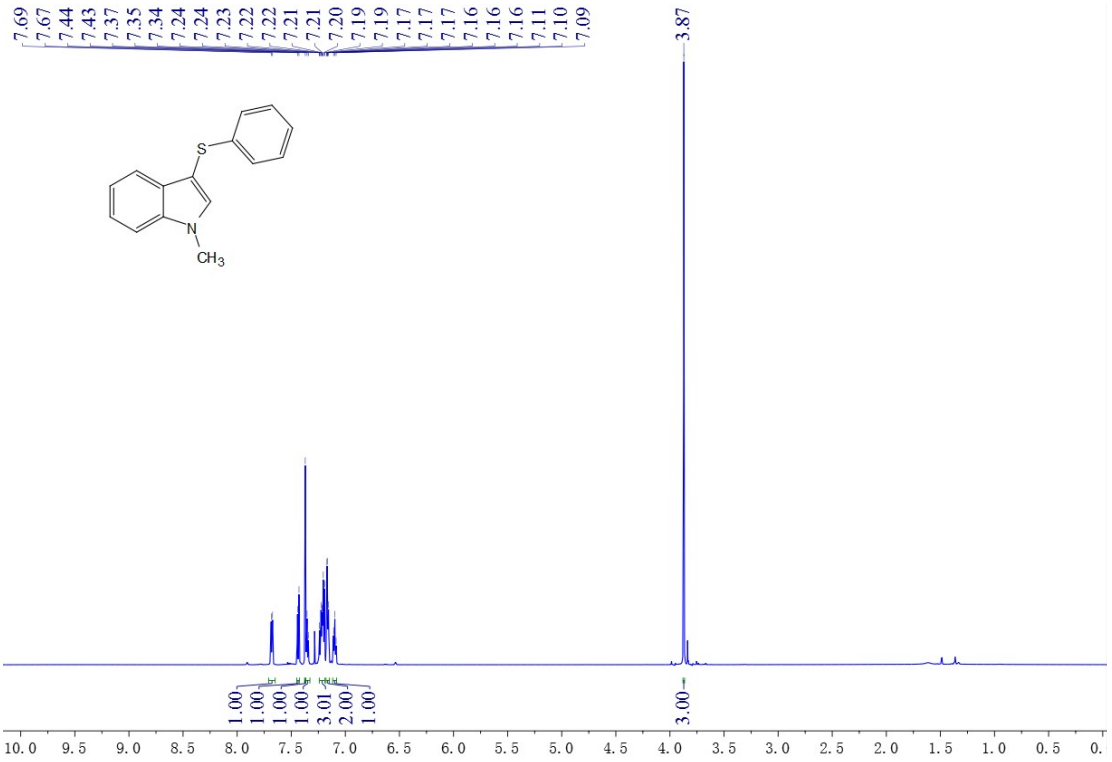
(6) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-2



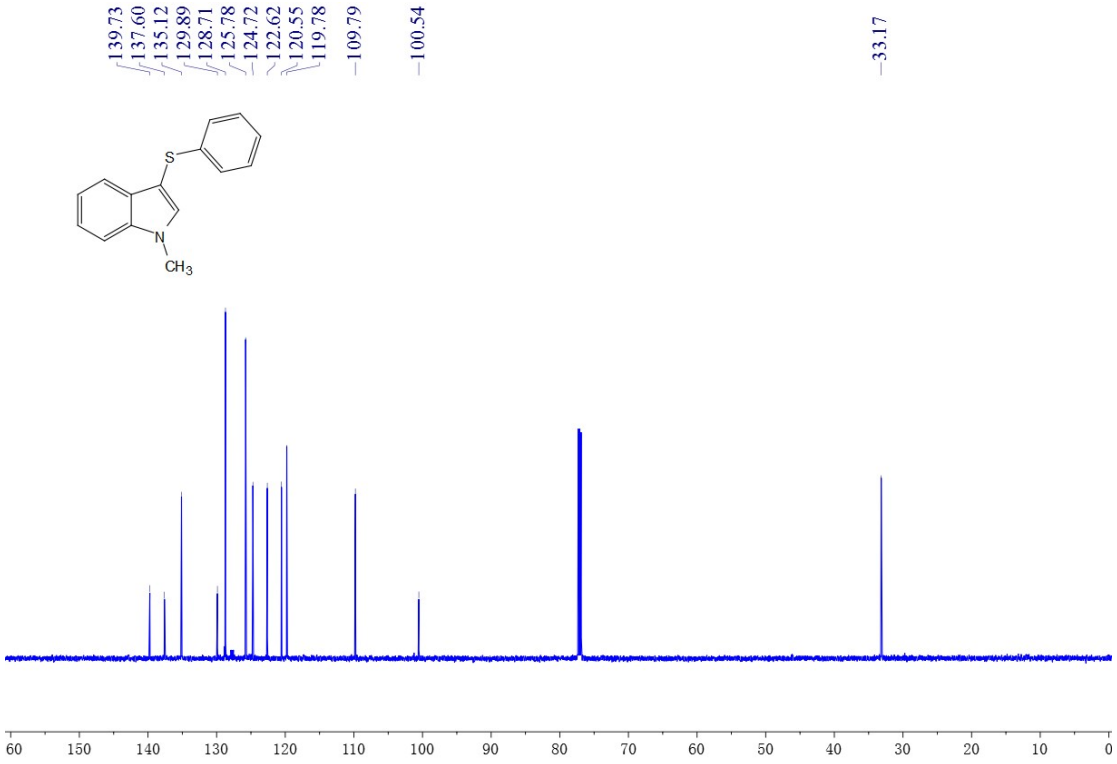
(7) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-2



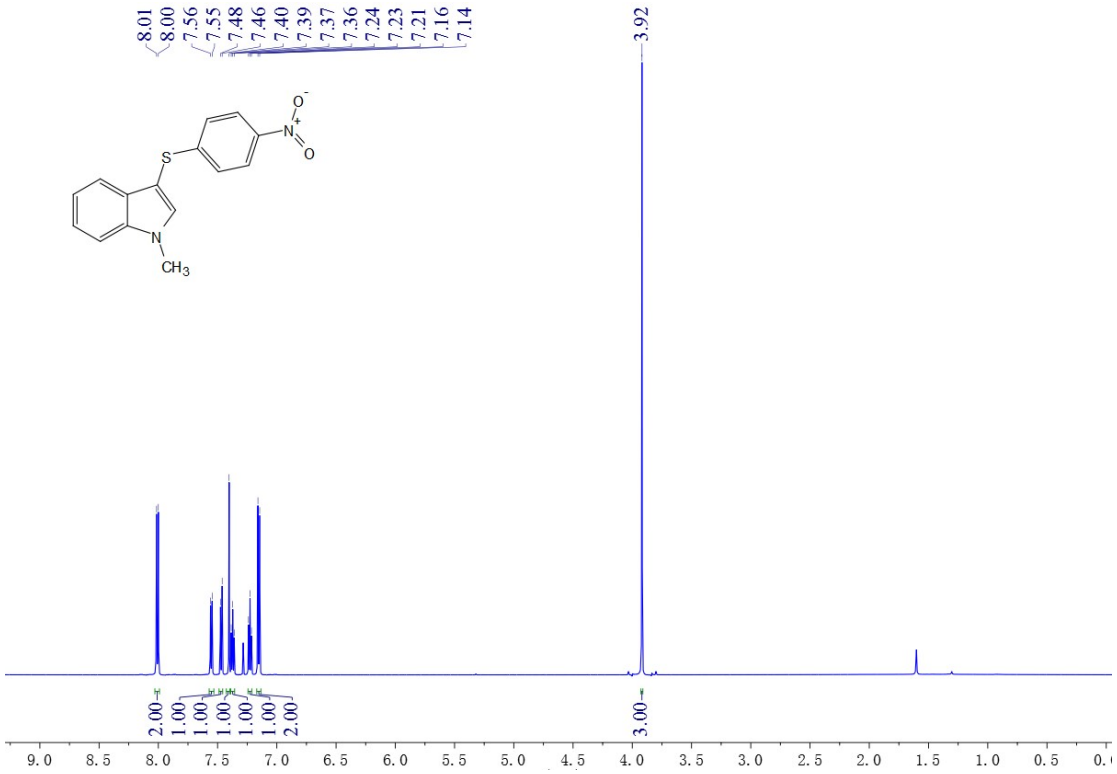
(8) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 1a-4



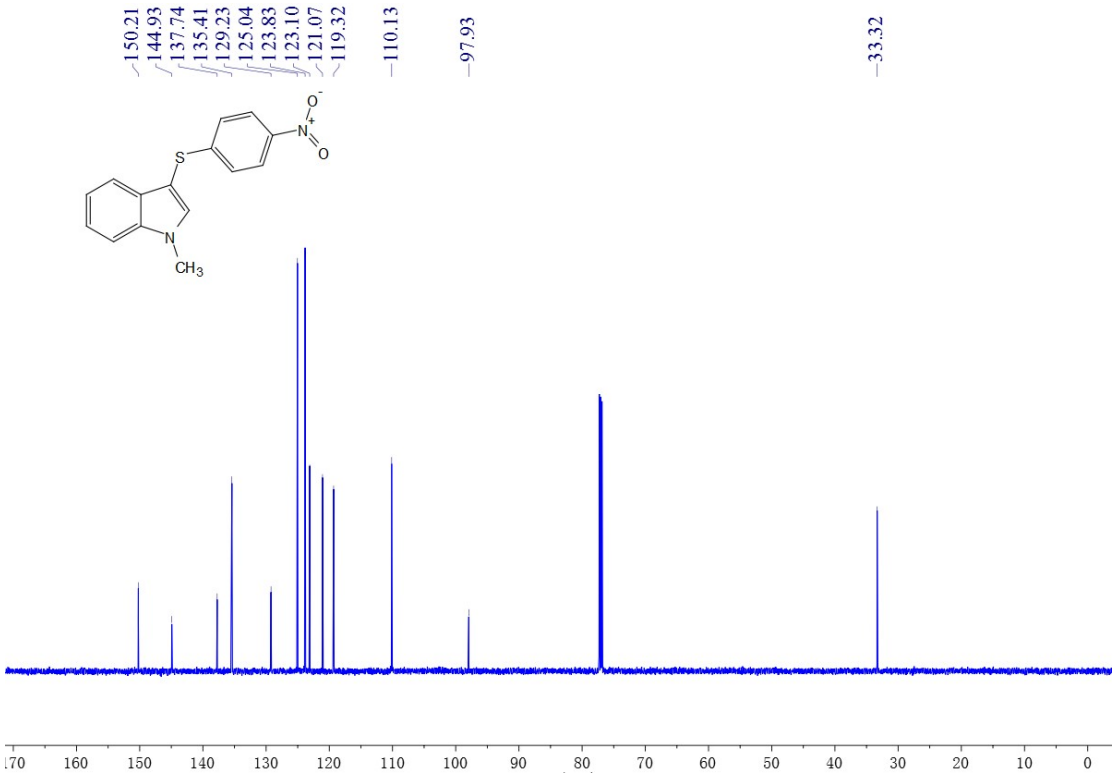
(9) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 1a-4



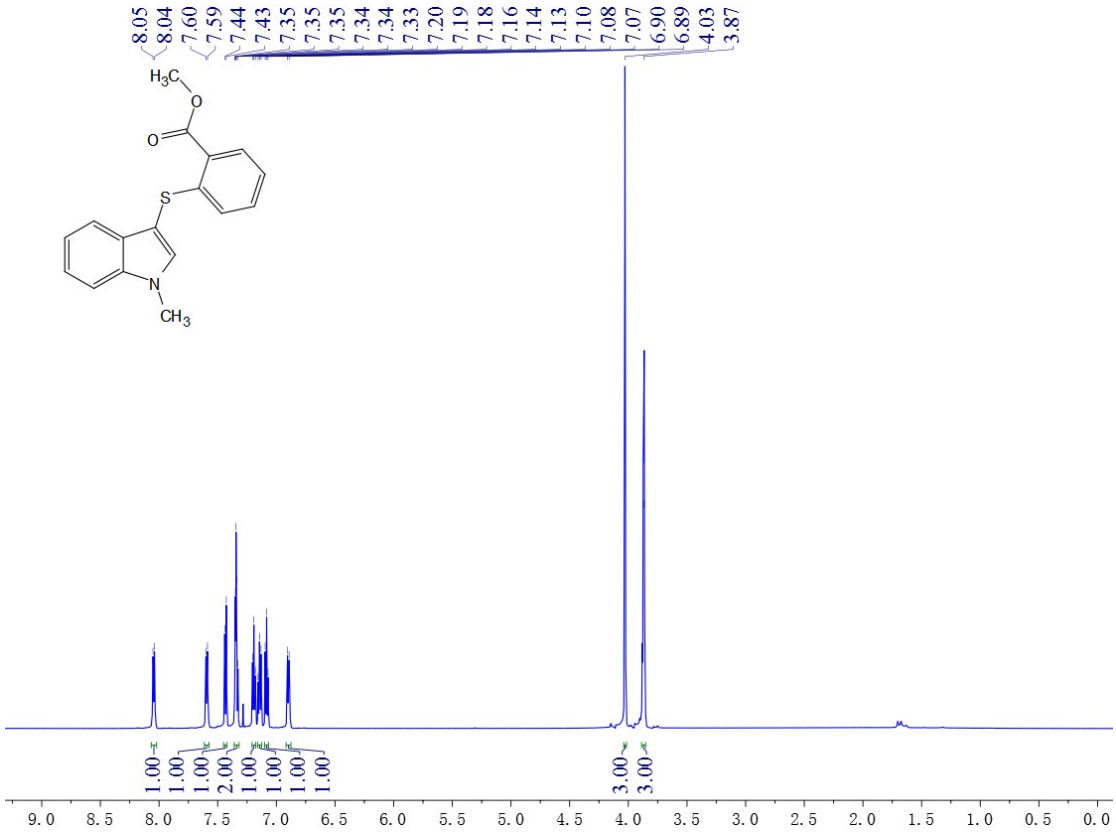
(10) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 4



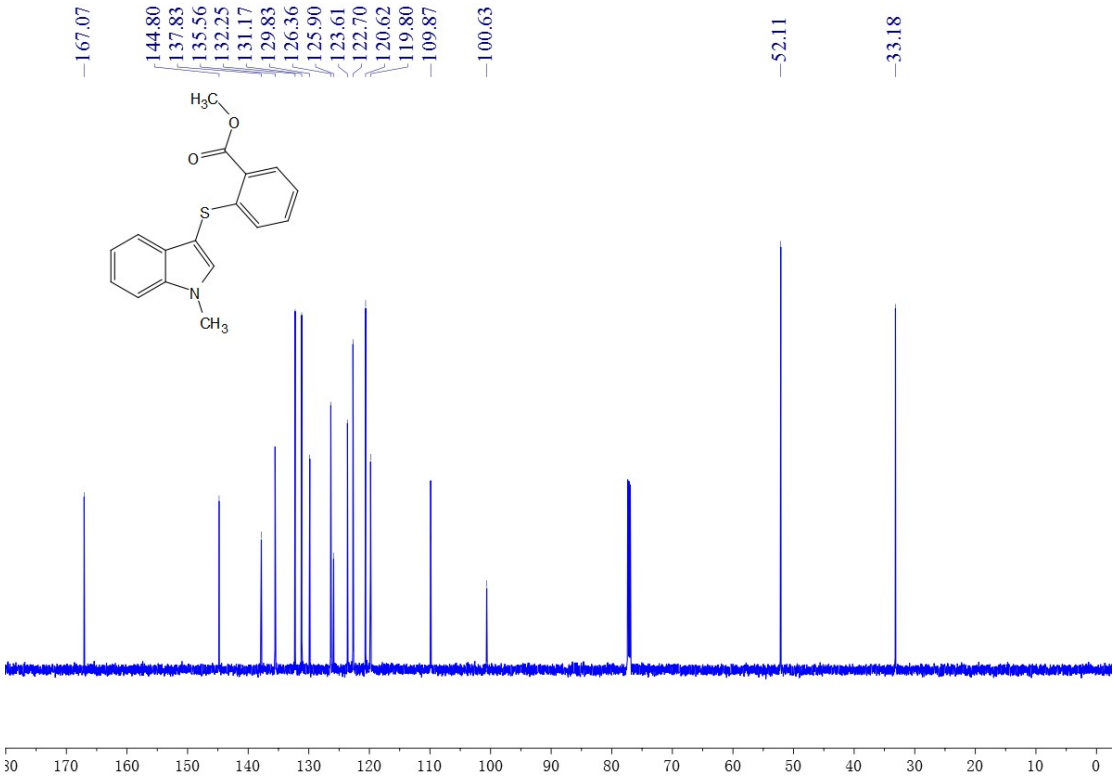
(11) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 4



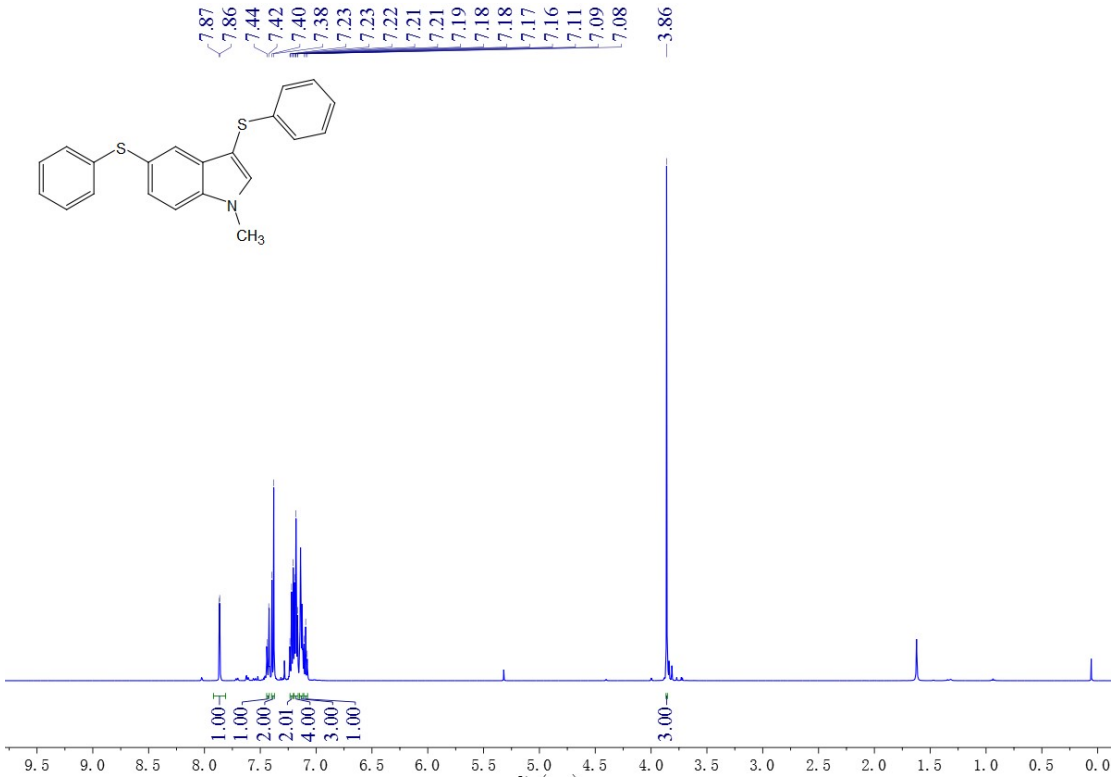
(12) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 5



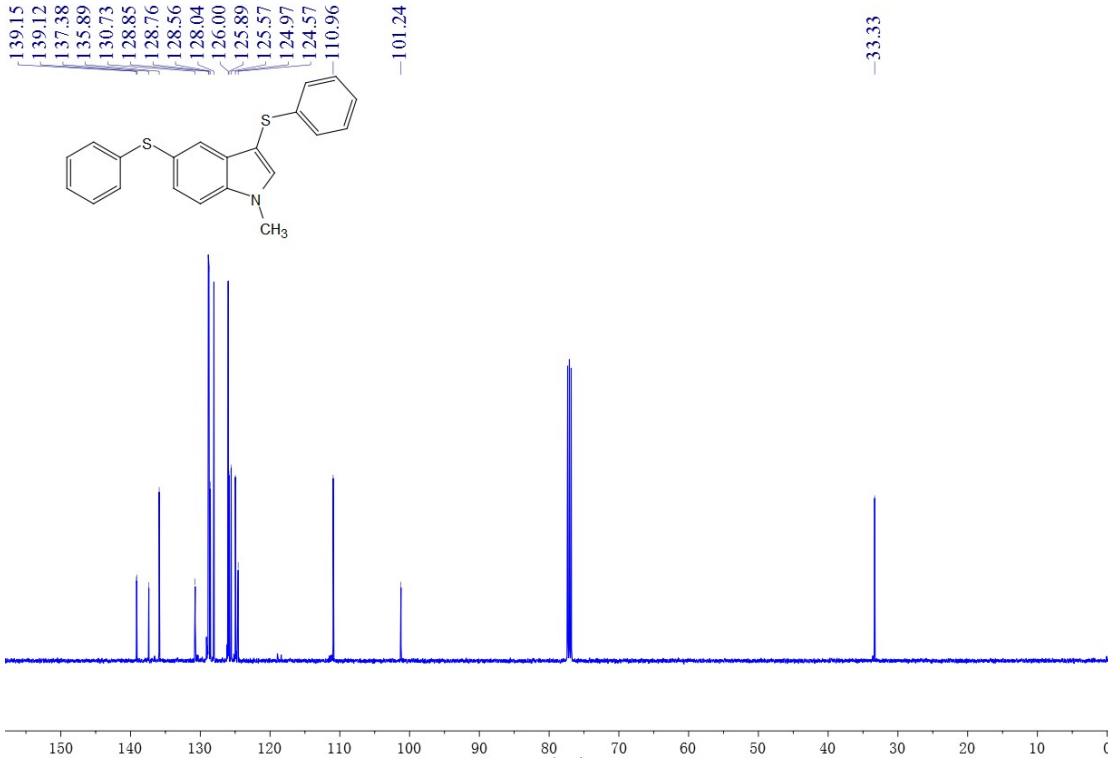
(13) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 5



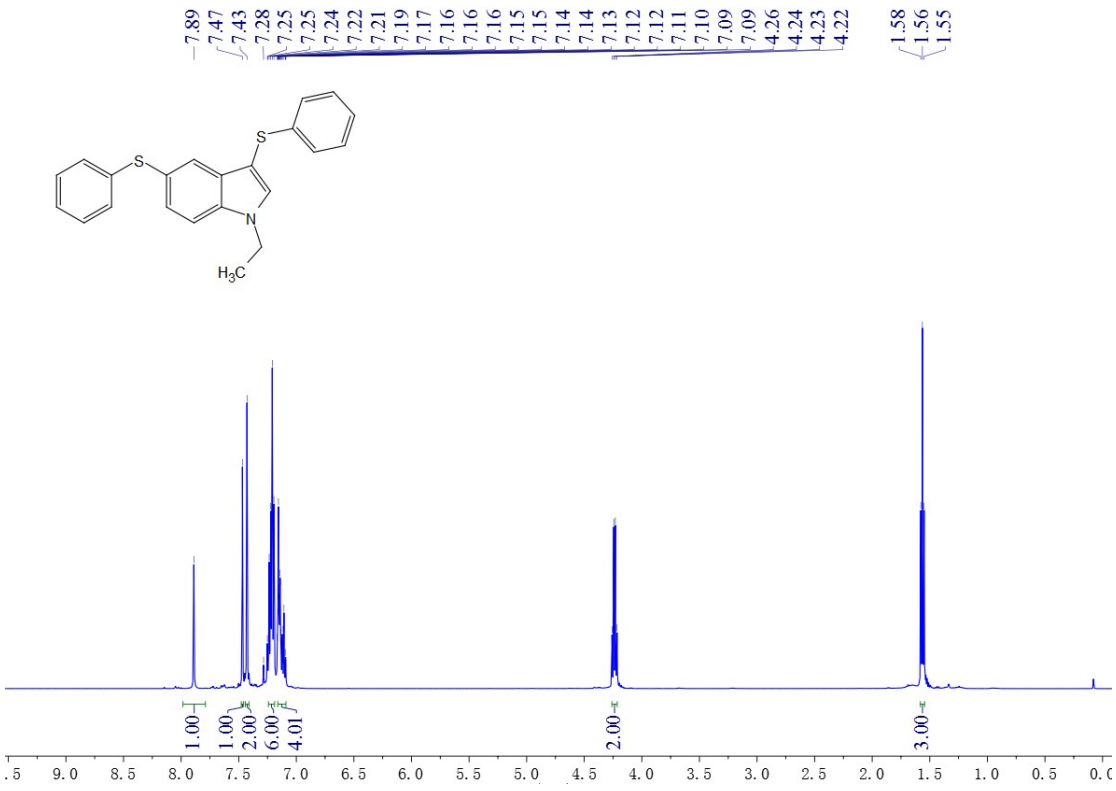
(14) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3aa



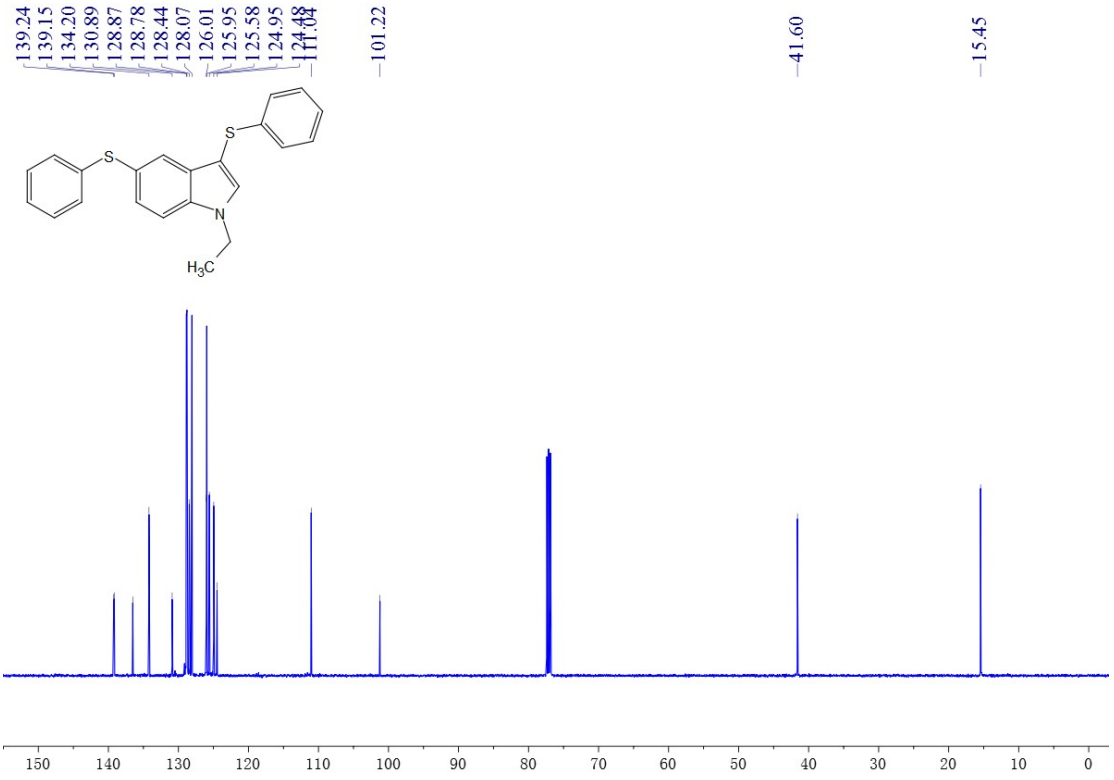
(15) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3aa



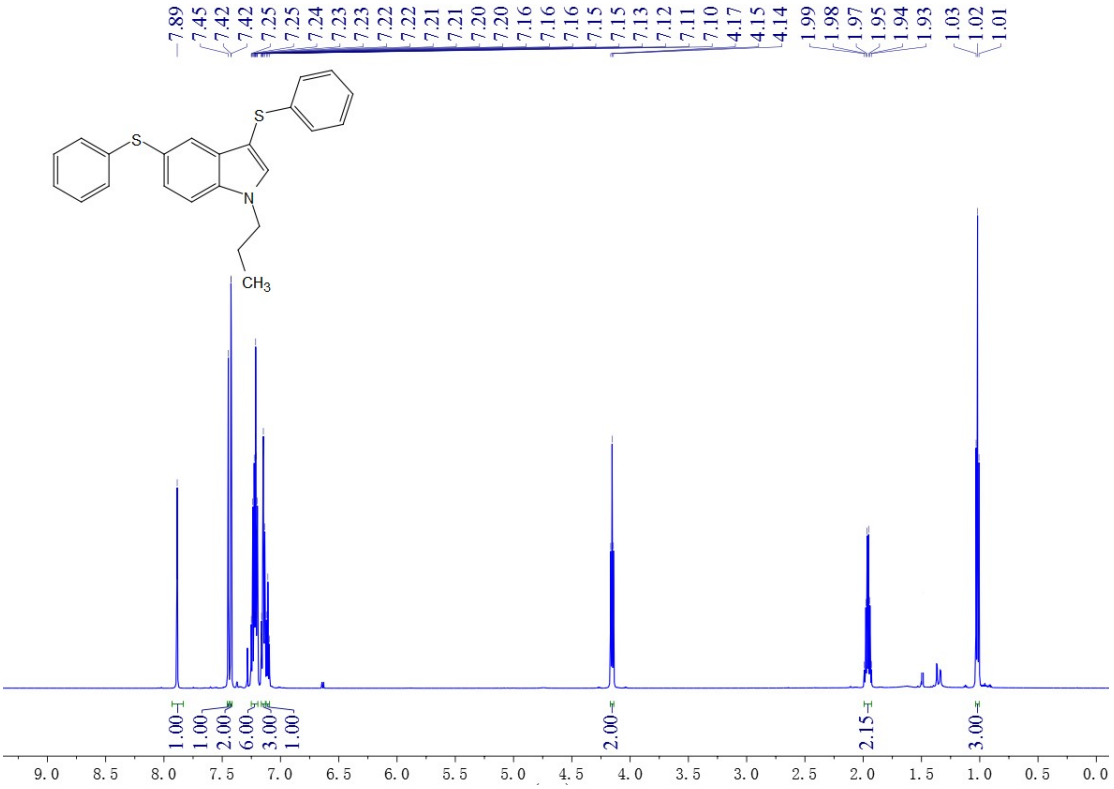
(16) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ba



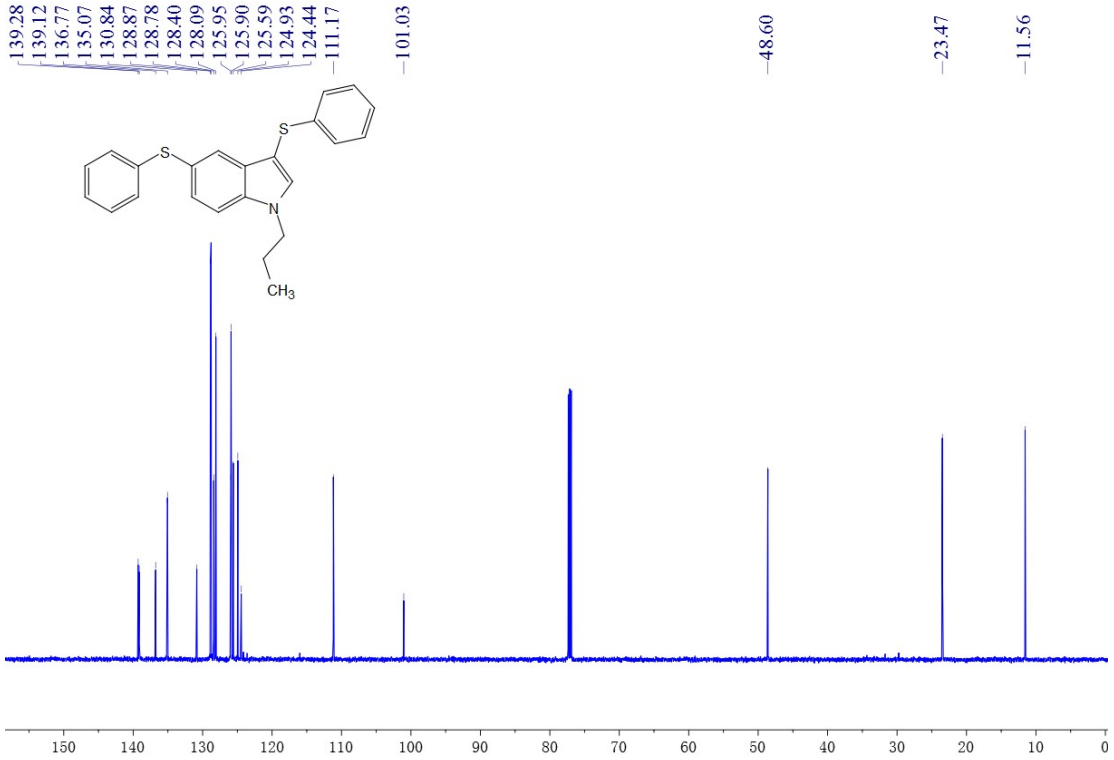
(17) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3ba



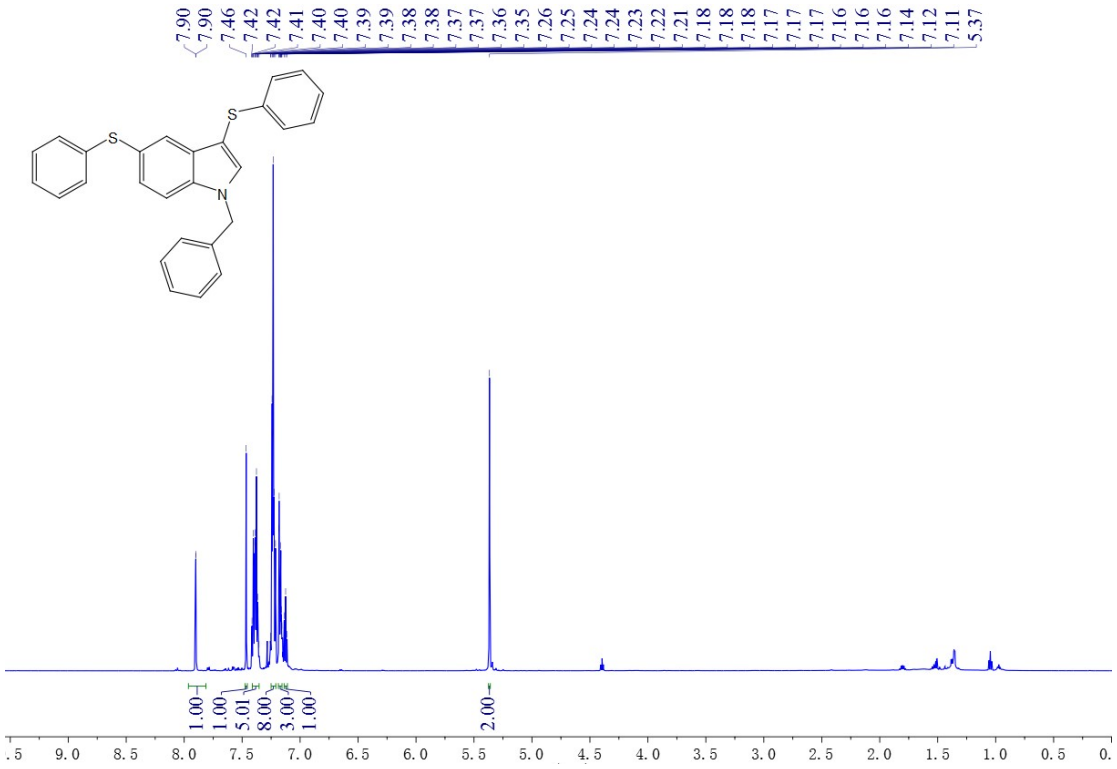
(18) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ca



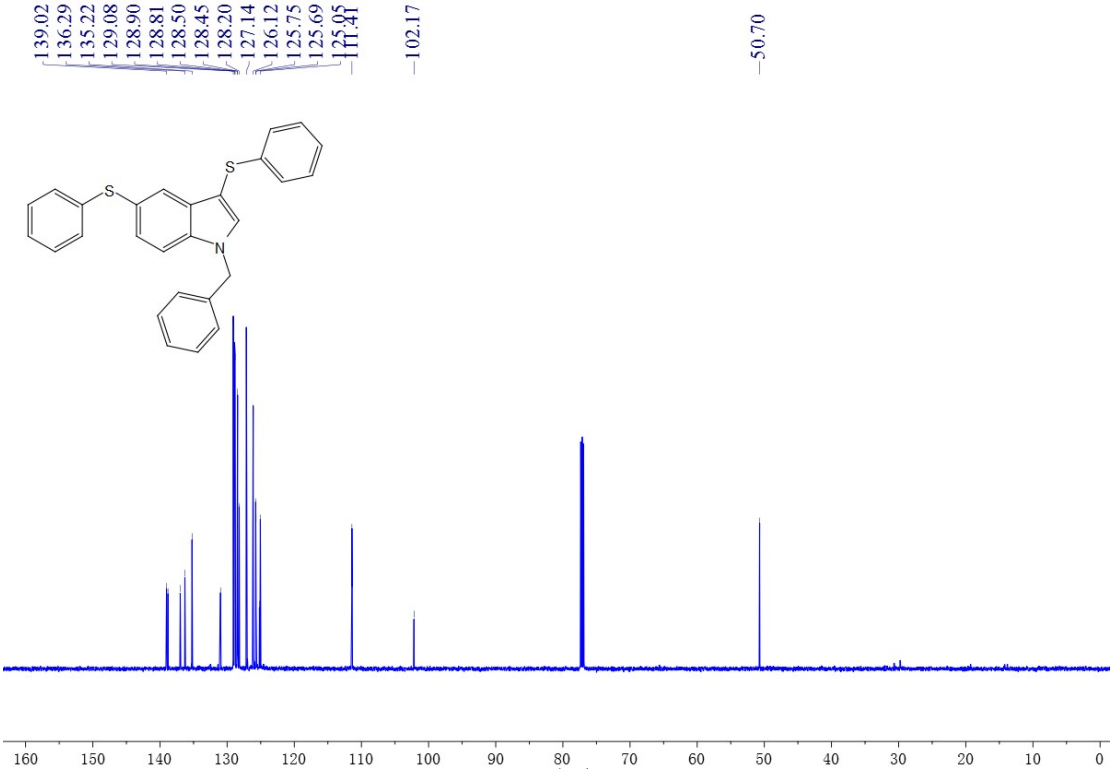
(19) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ca



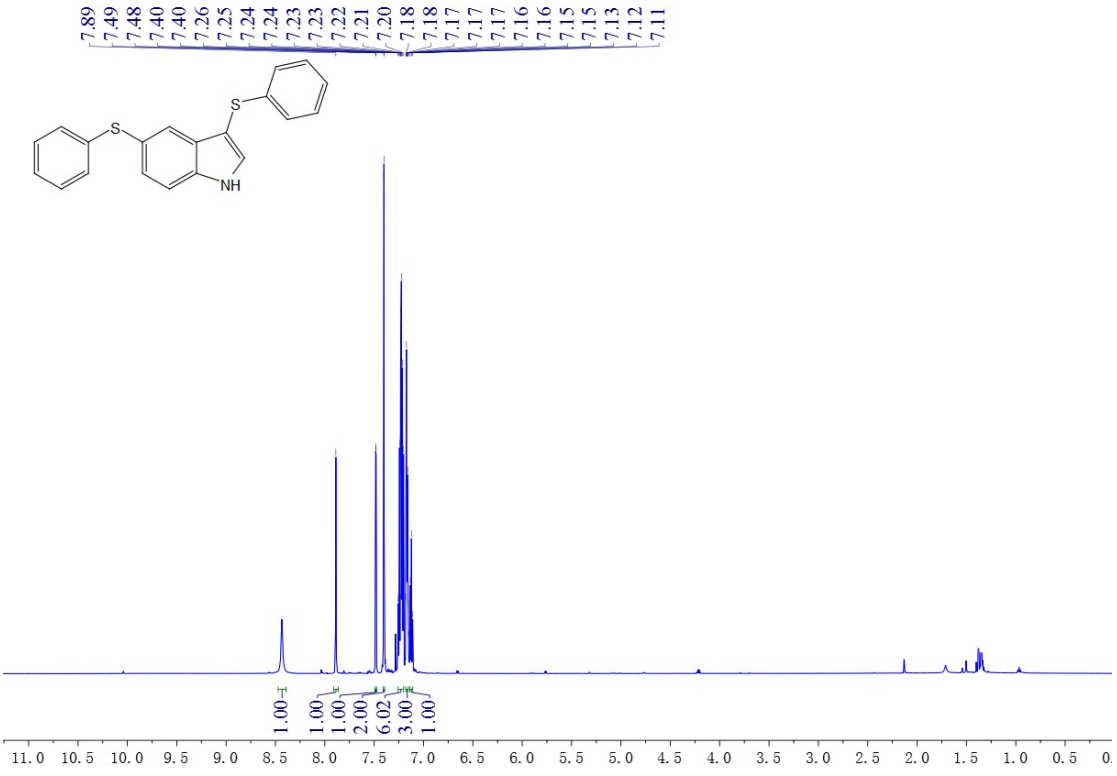
(20) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3da



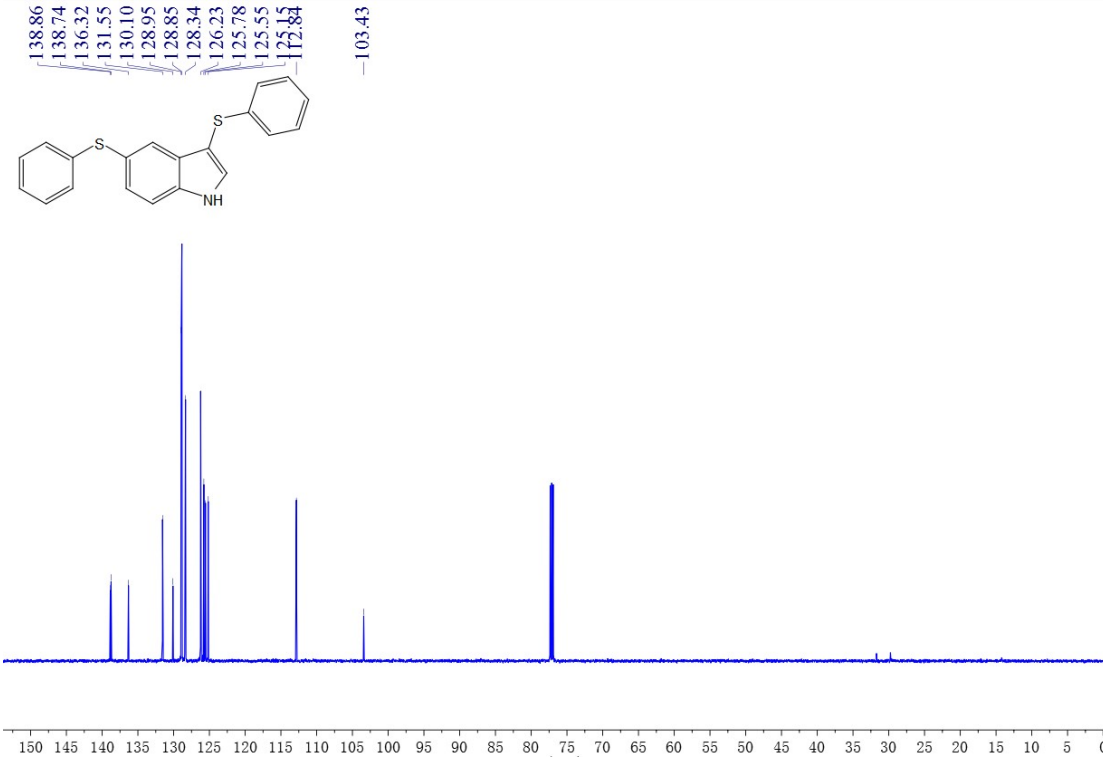
(21) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3da



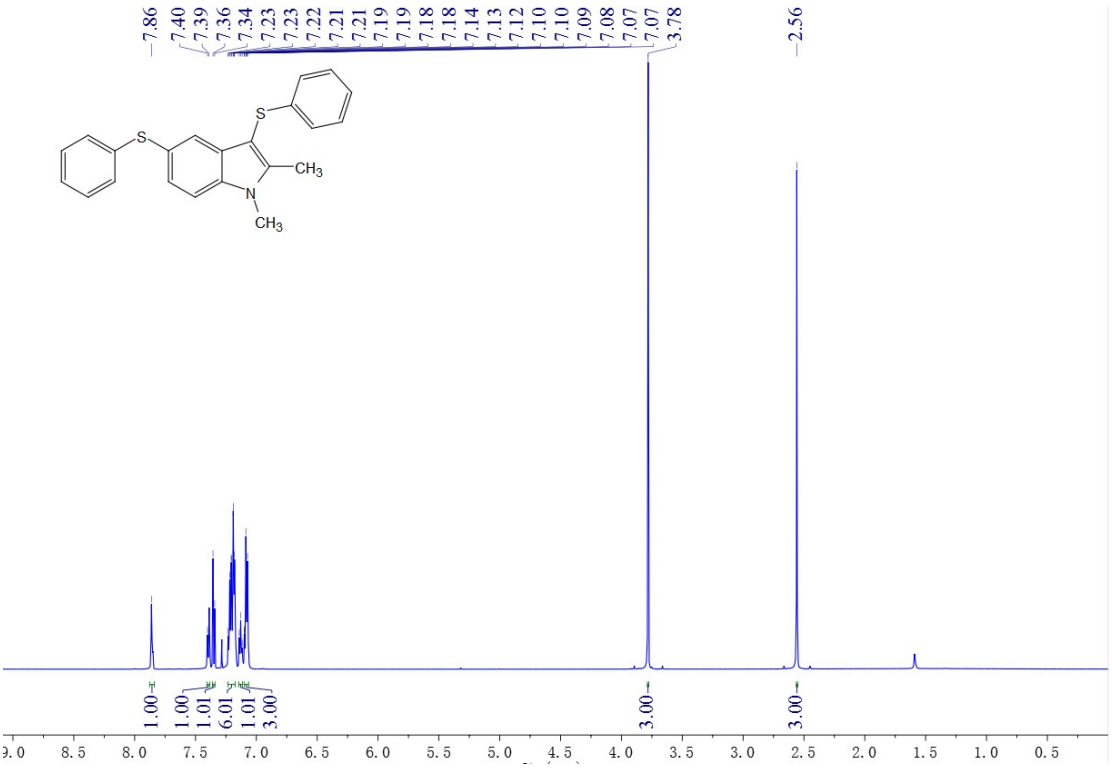
(22) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3fa



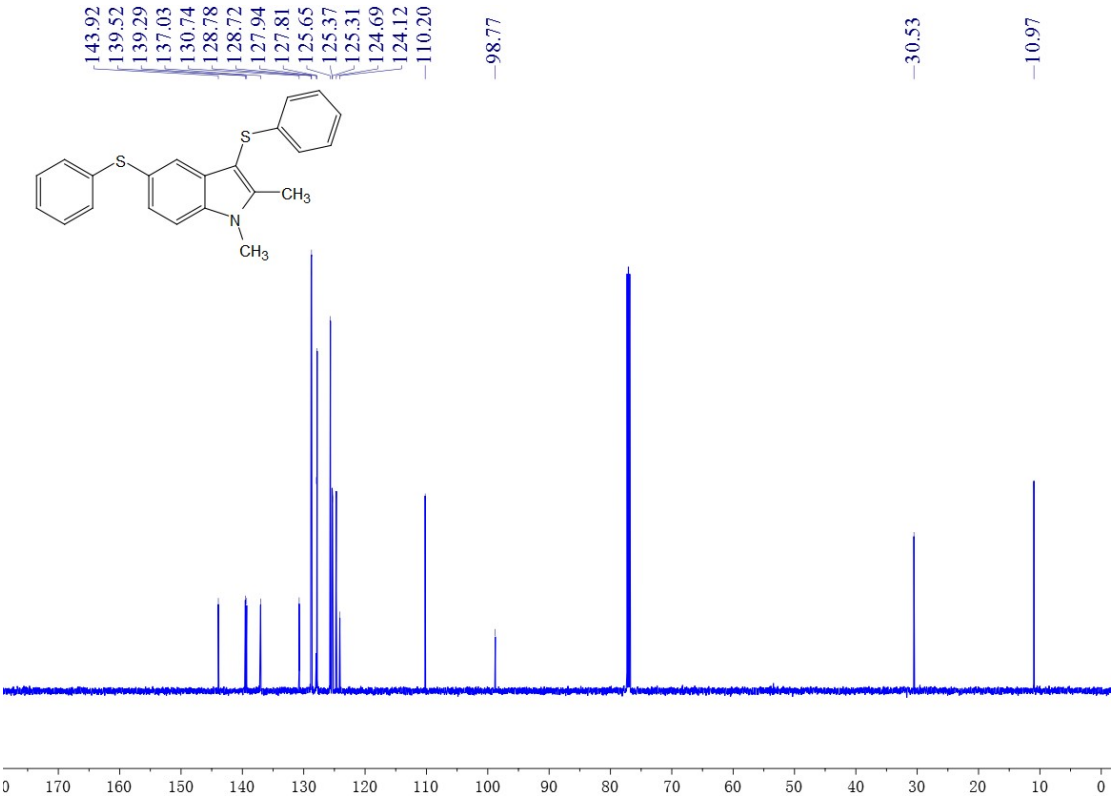
(23) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3fa



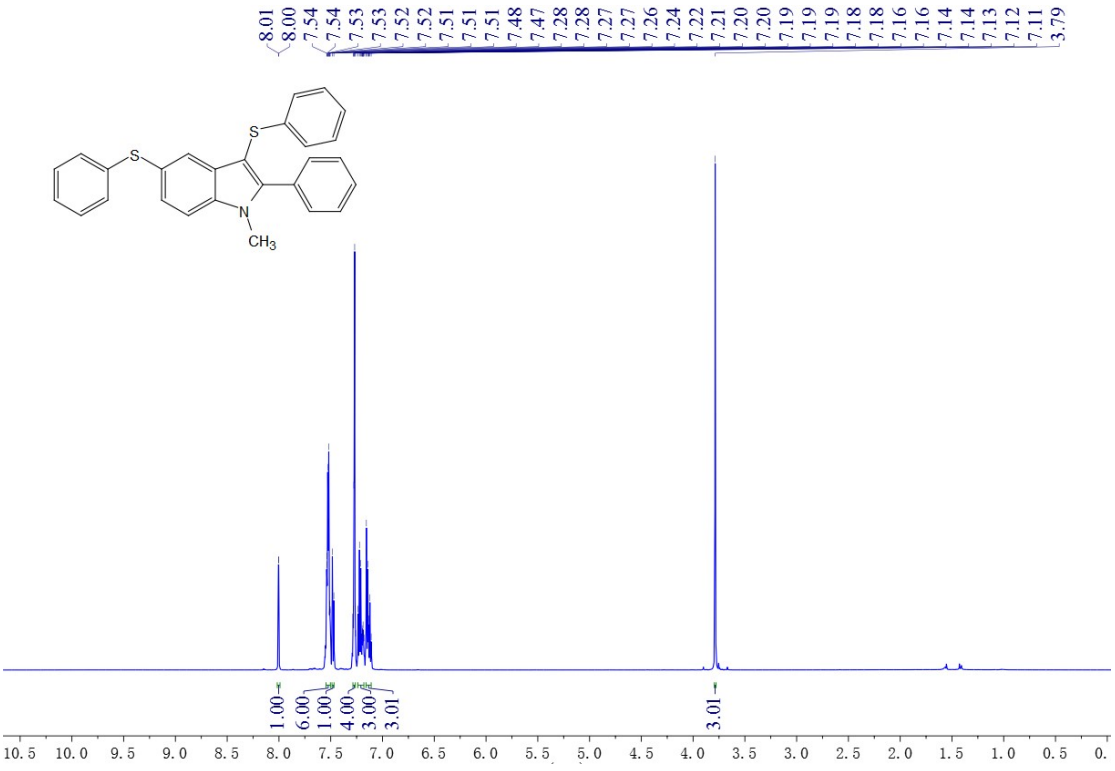
(24) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ga



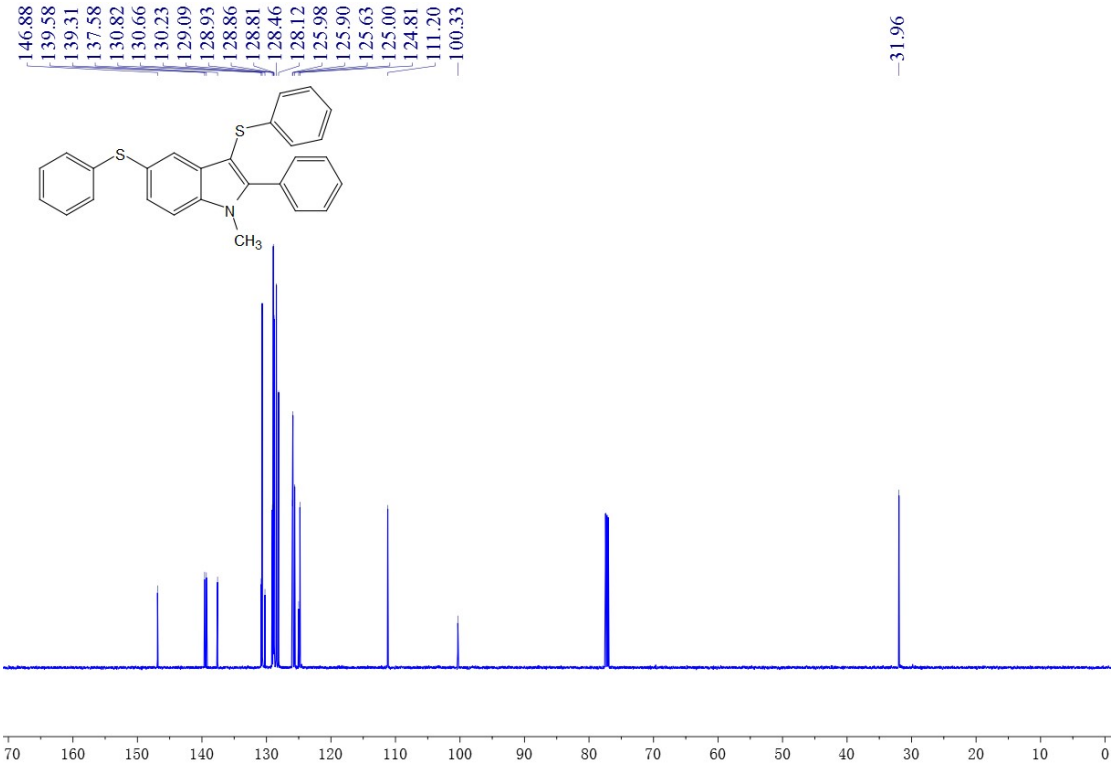
(25) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ga



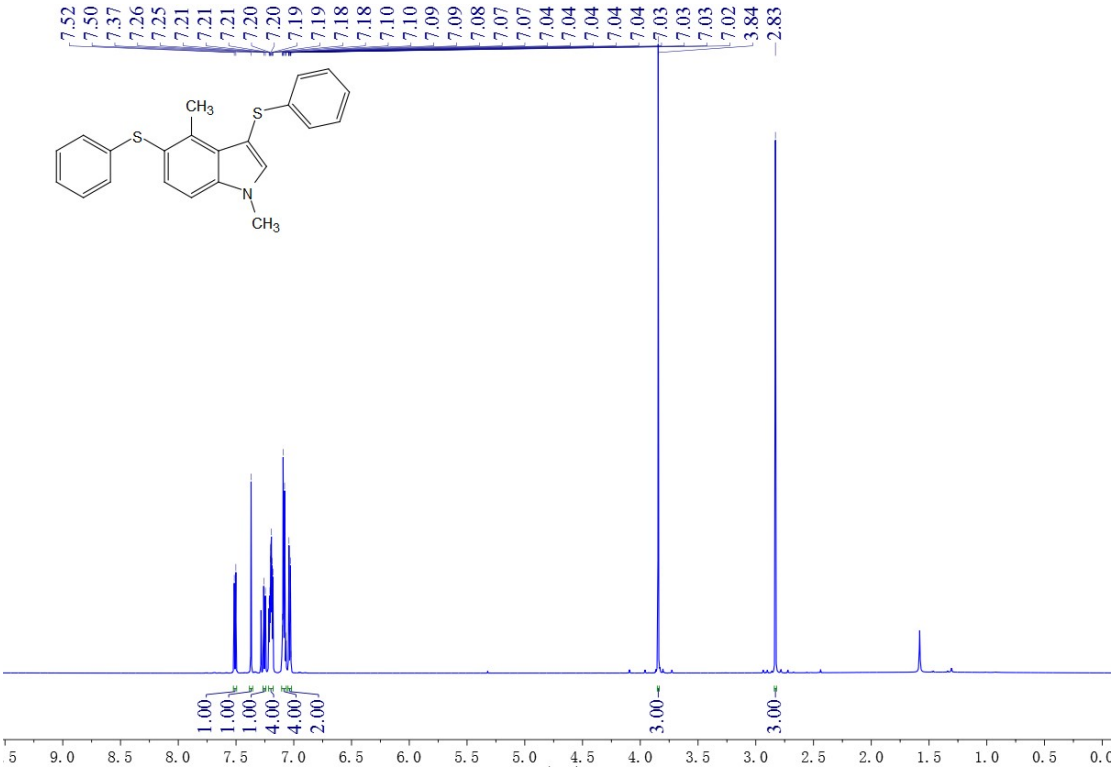
(26) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ha



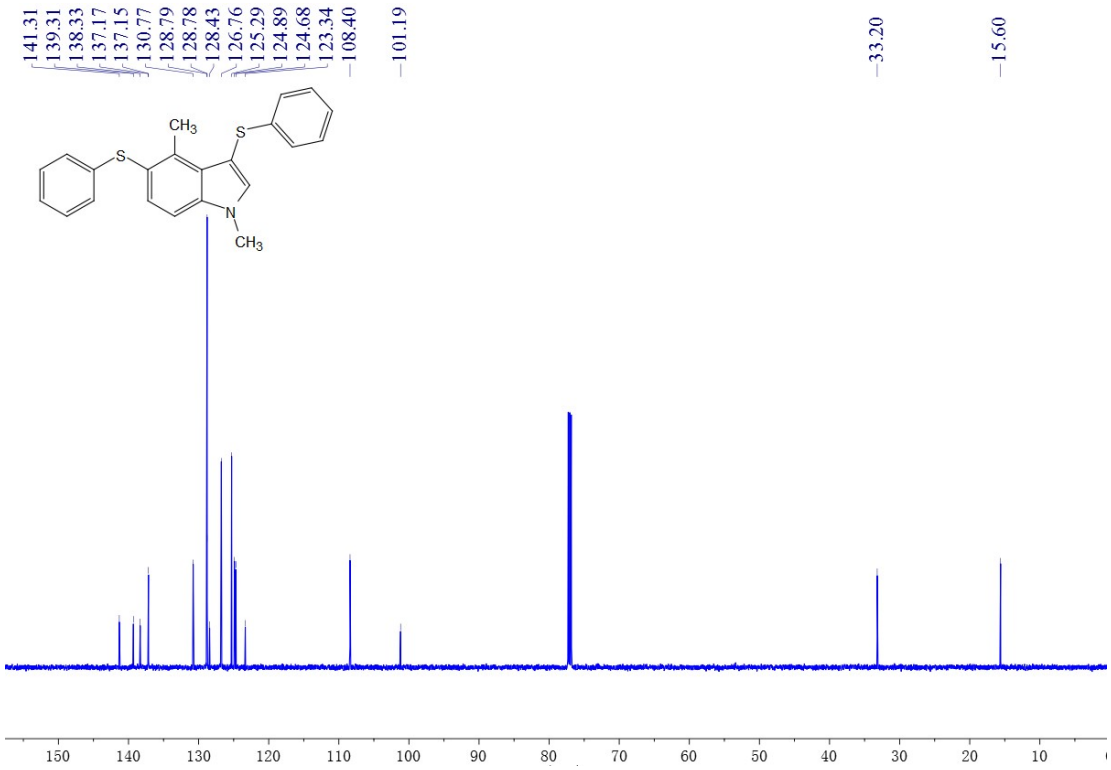
(27) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ha



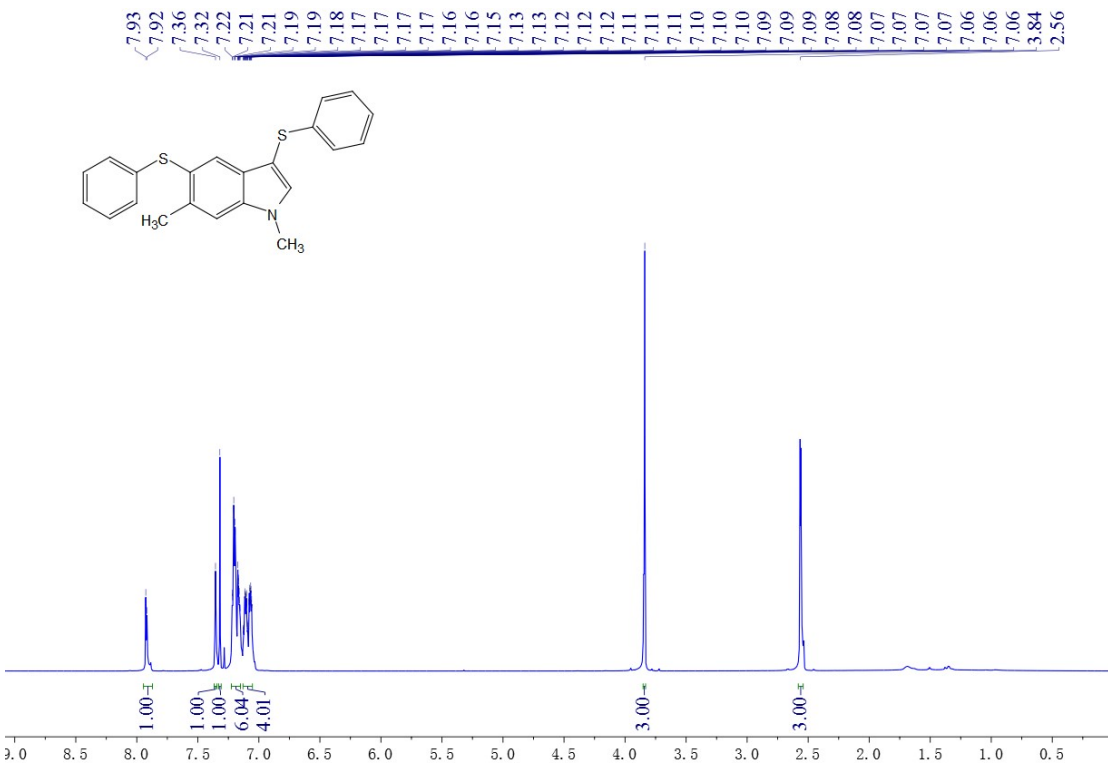
(28) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ia



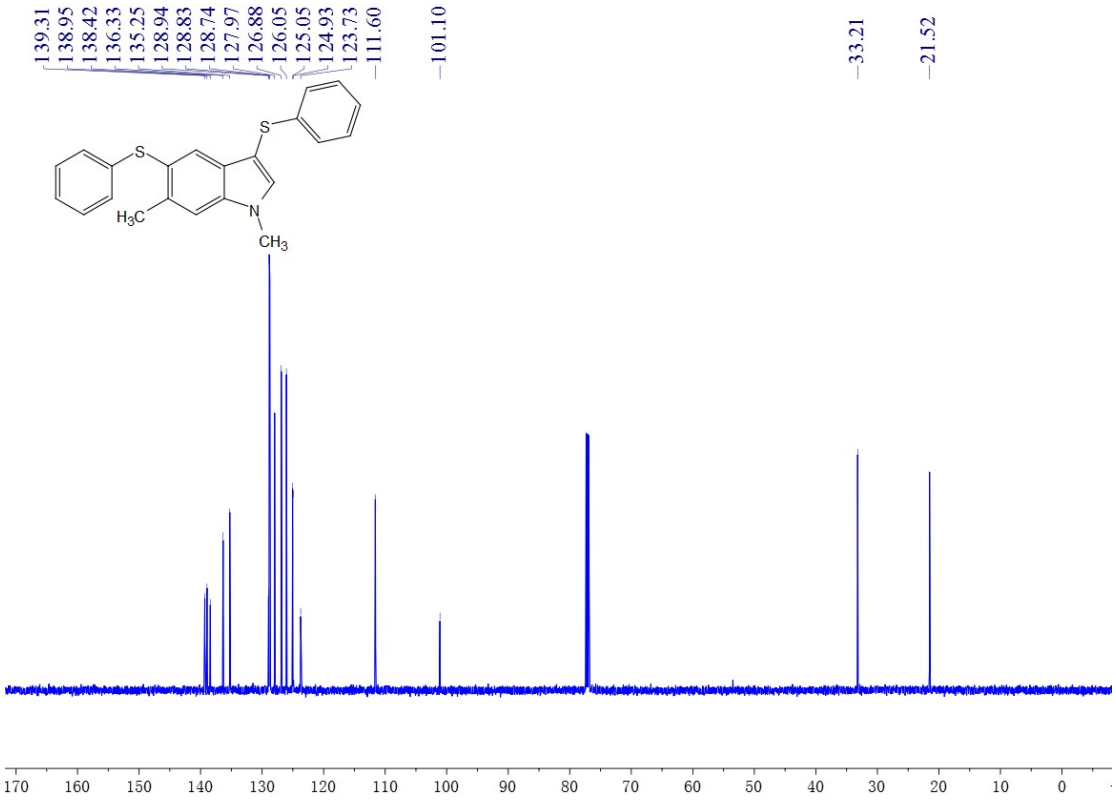
(29) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ia



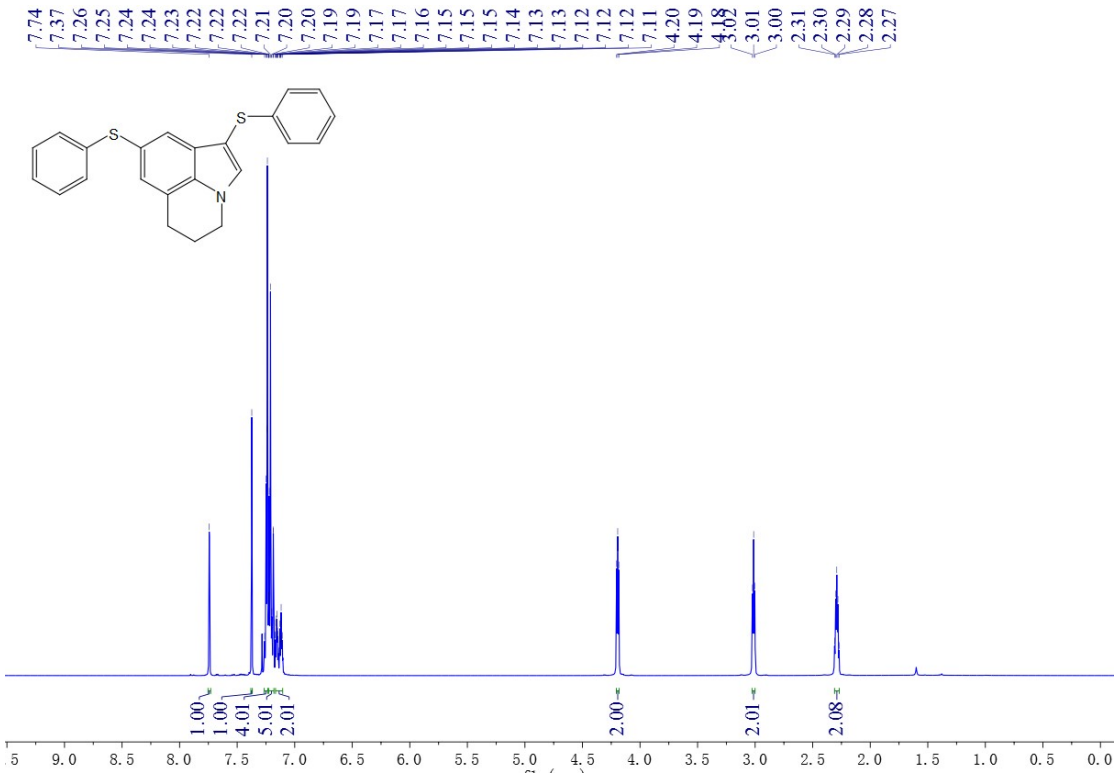
(30) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ja



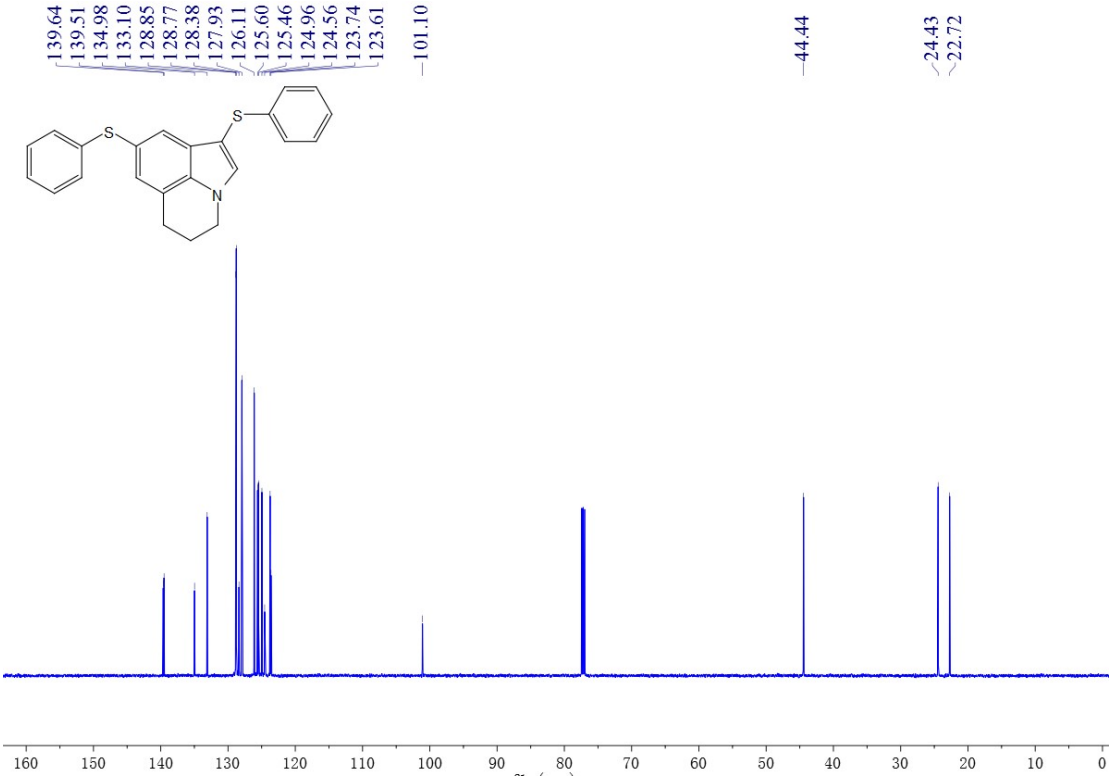
(31) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ja



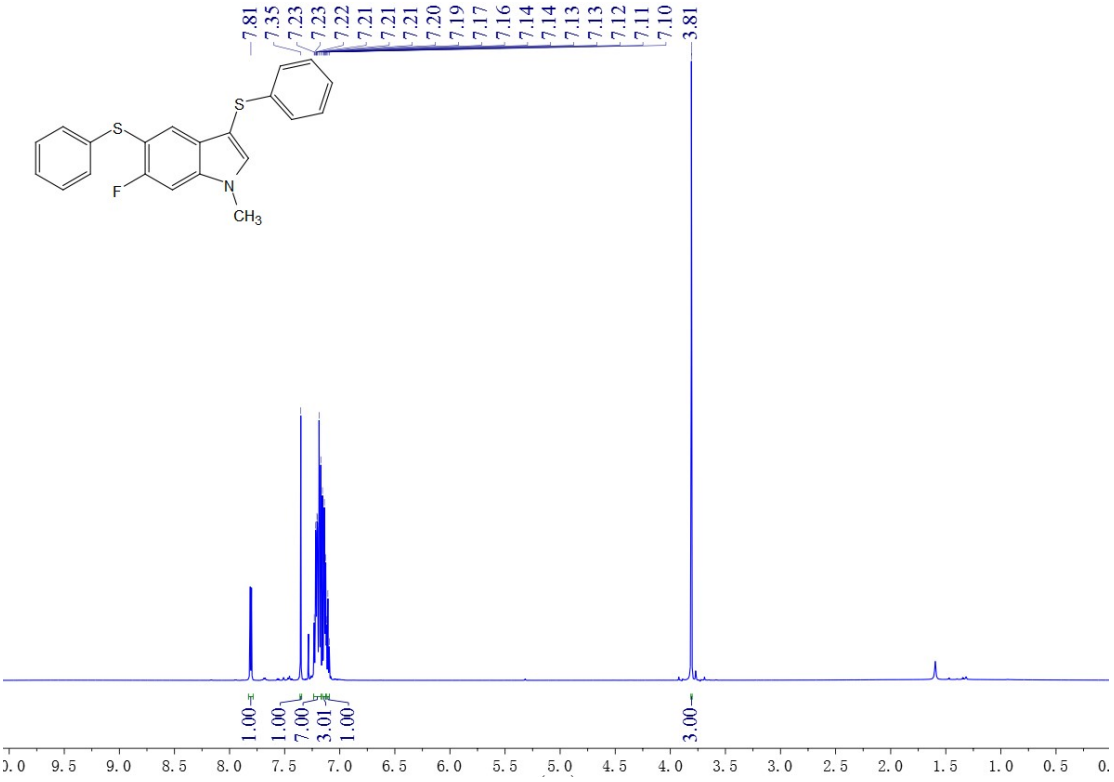
(32) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ka



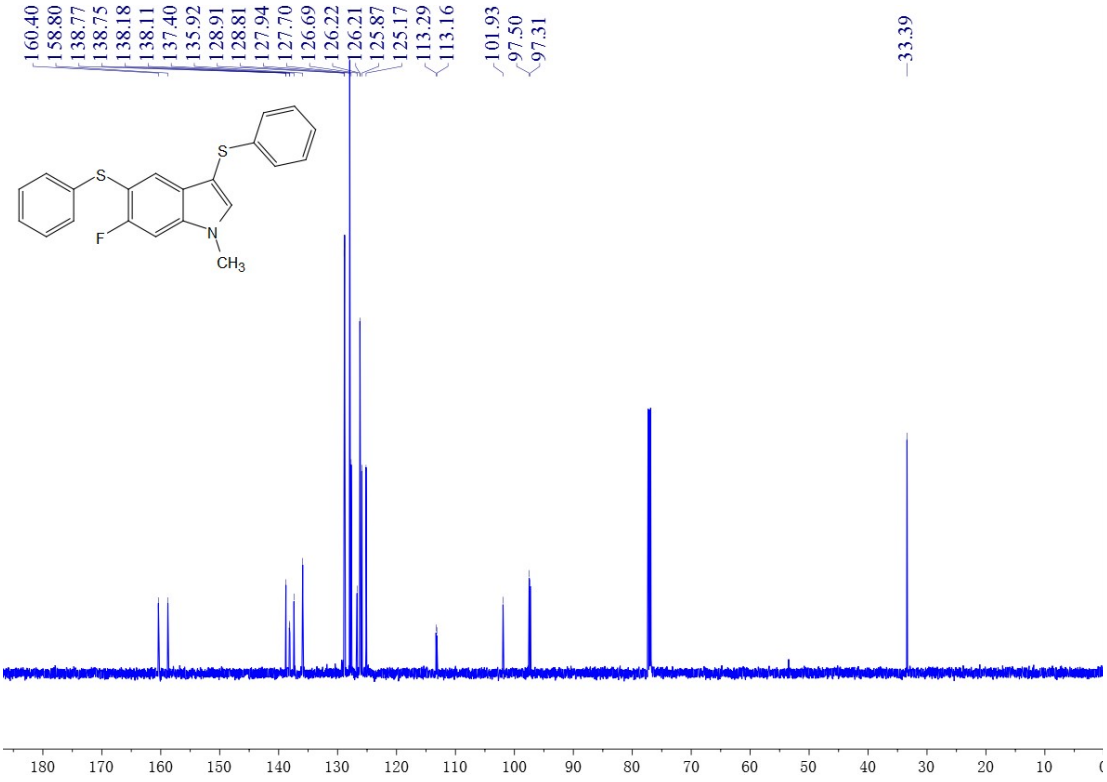
(33) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ka



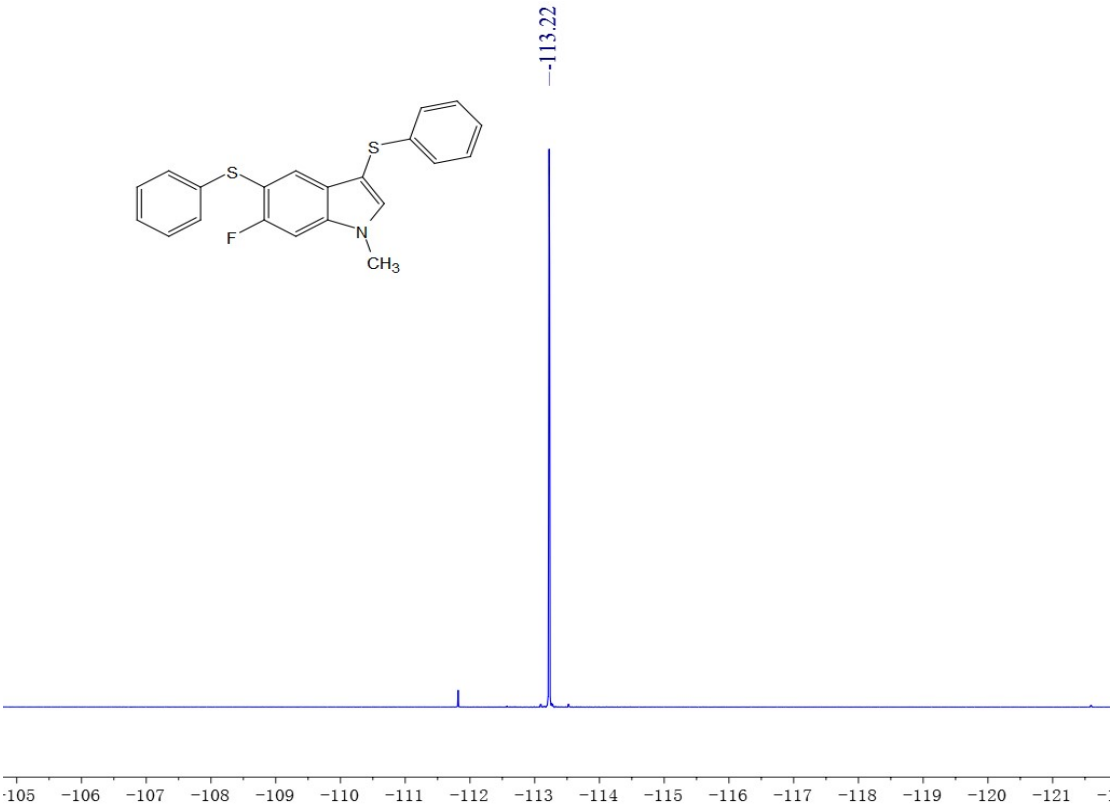
(34) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3la



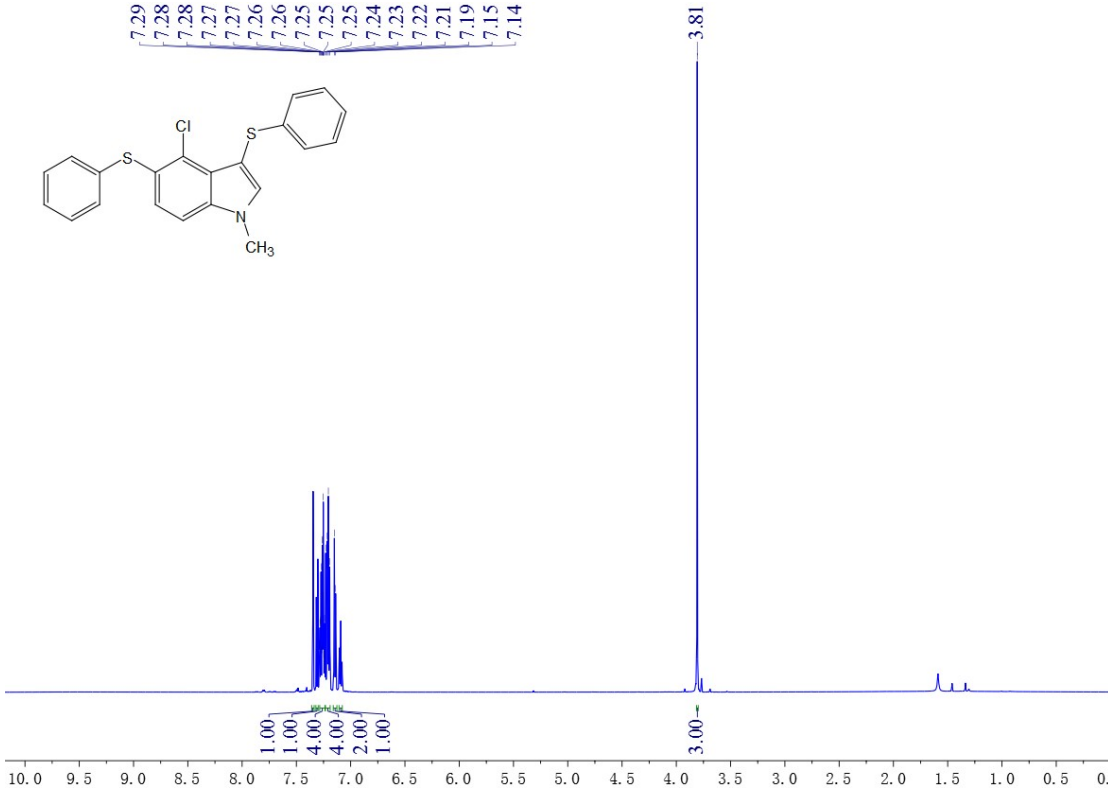
(35) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3la



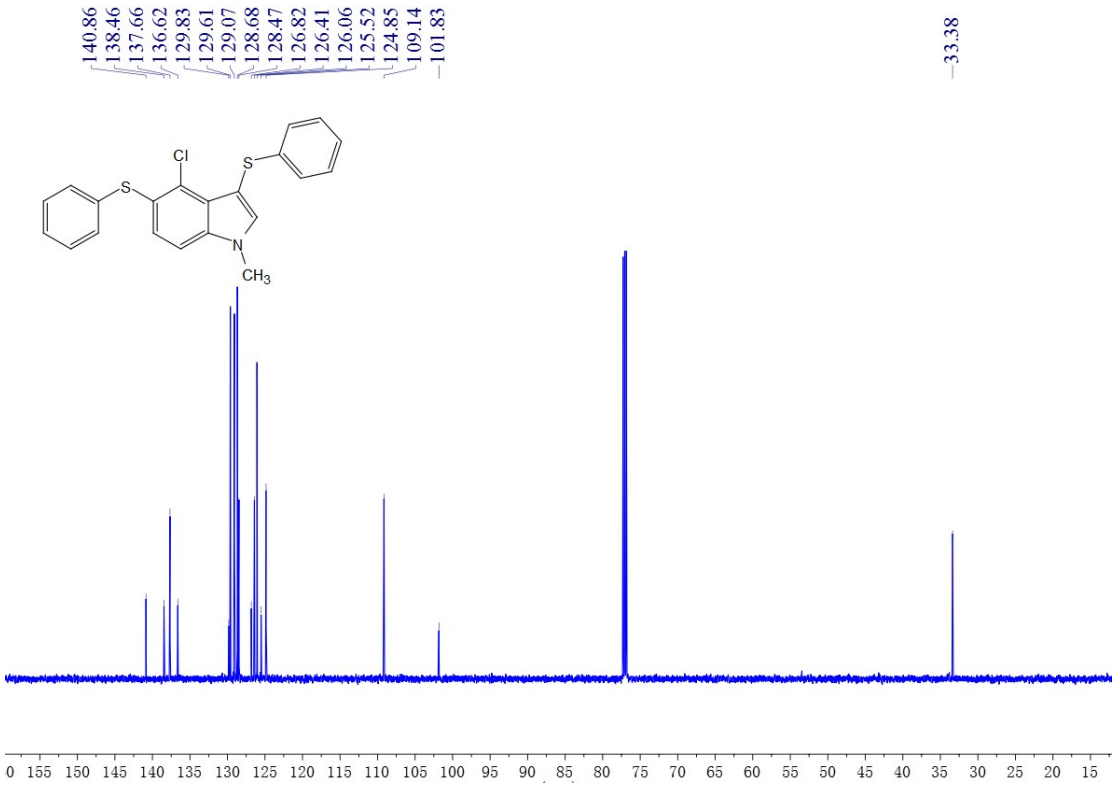
(36) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 3la



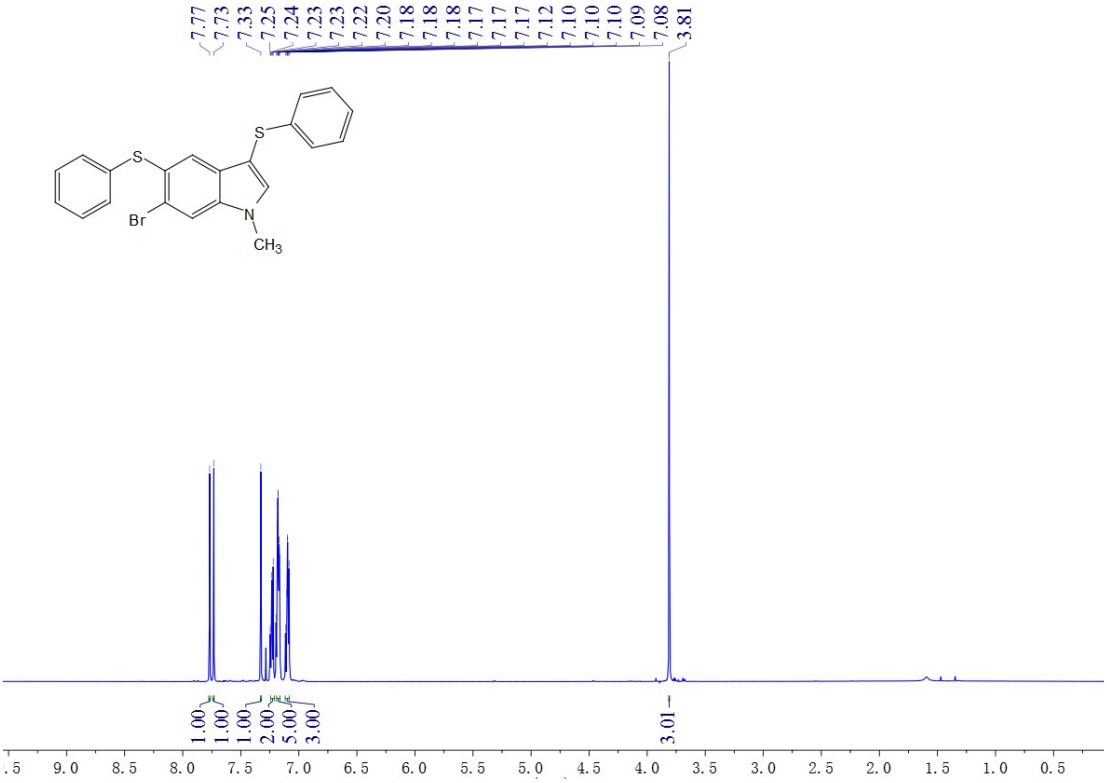
(37) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ma



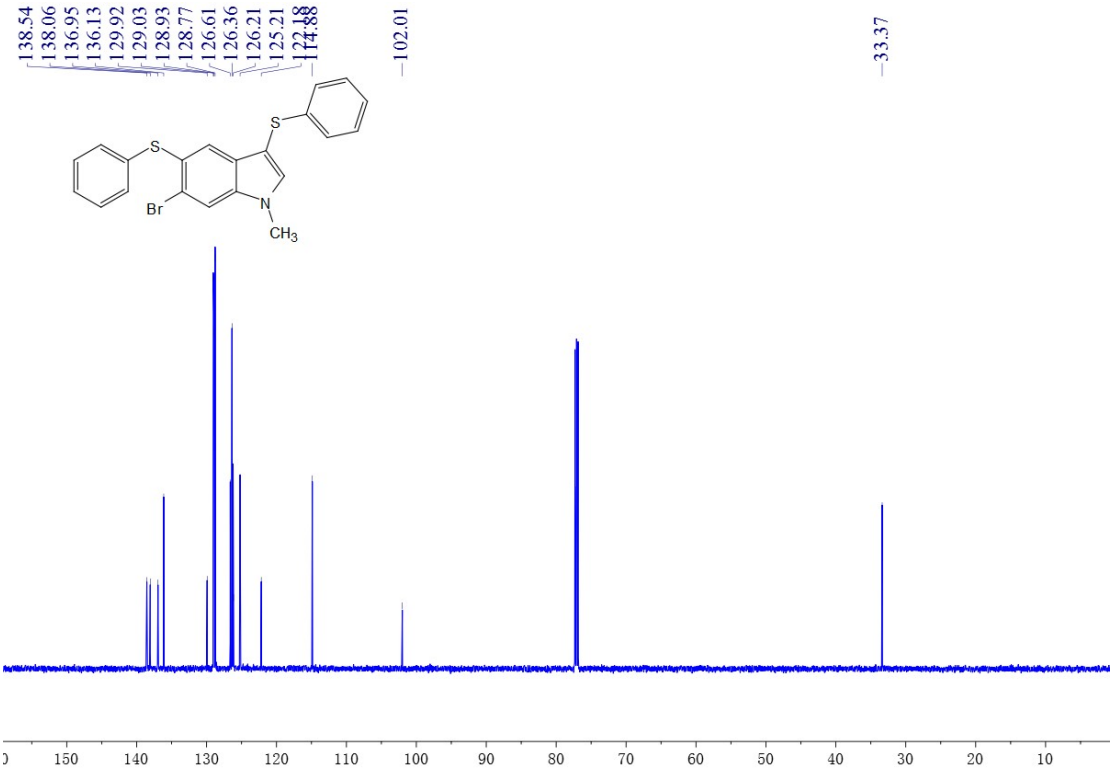
(38) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ma



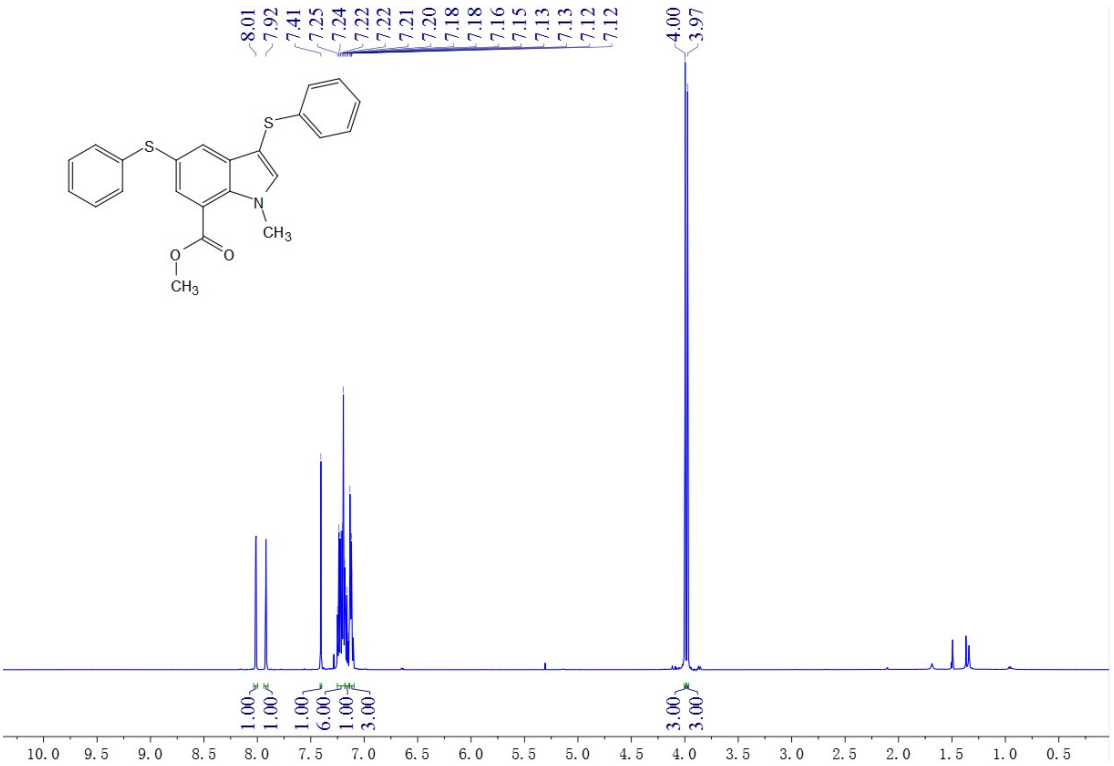
(39) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3na



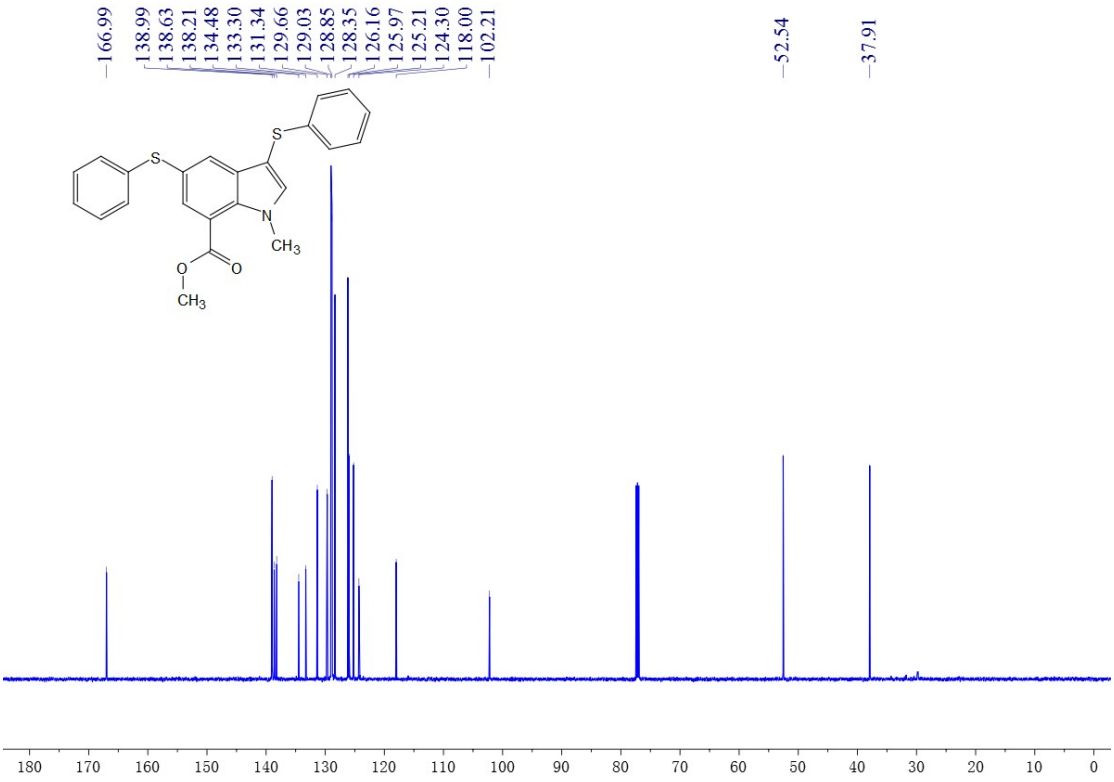
(40) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3na



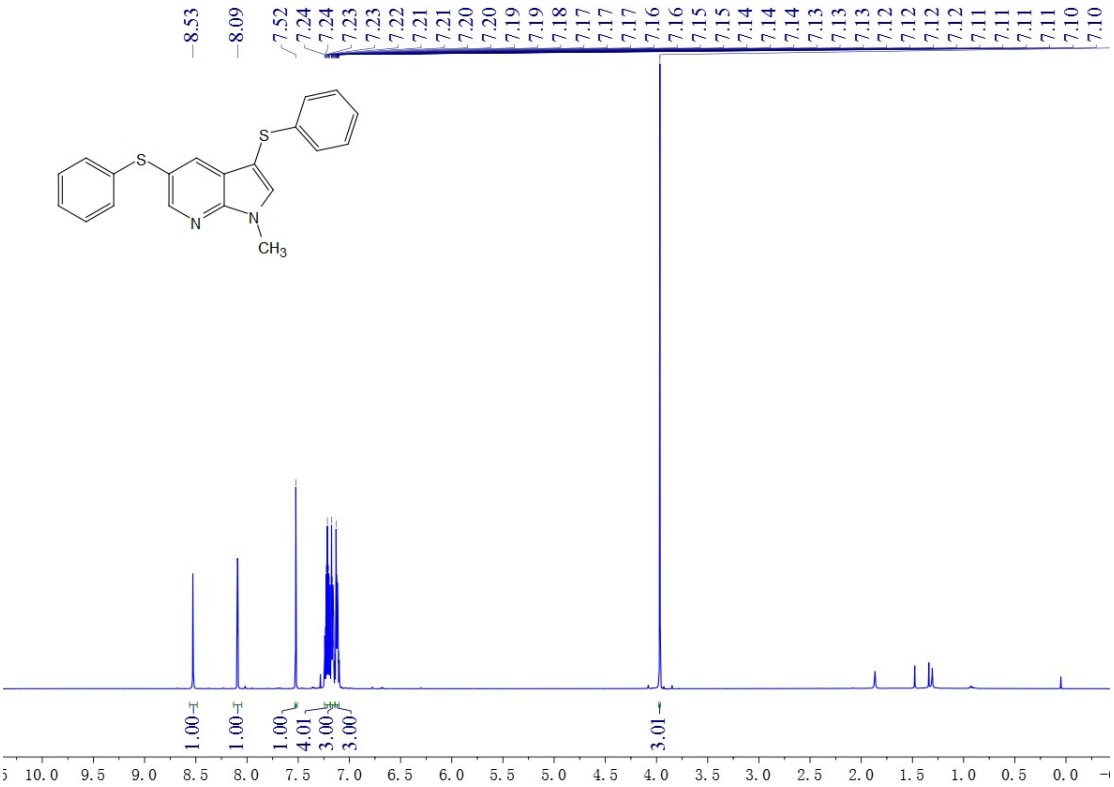
(41) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3oa



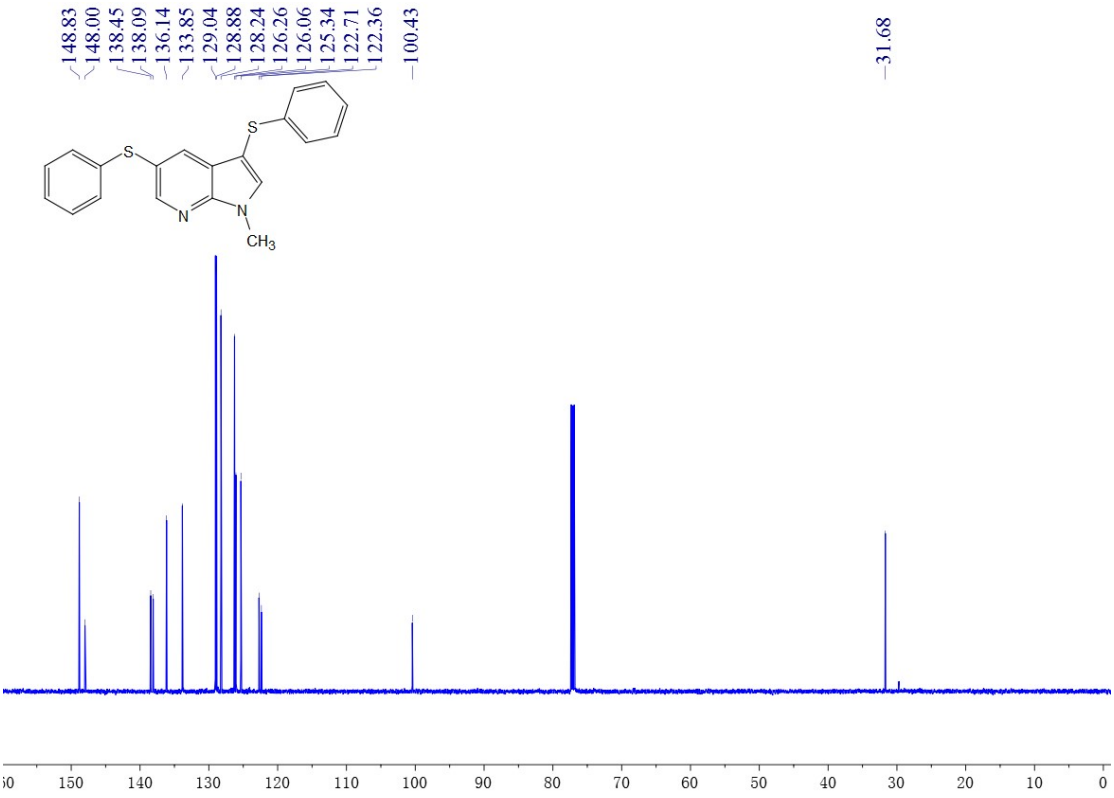
(42) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3oa



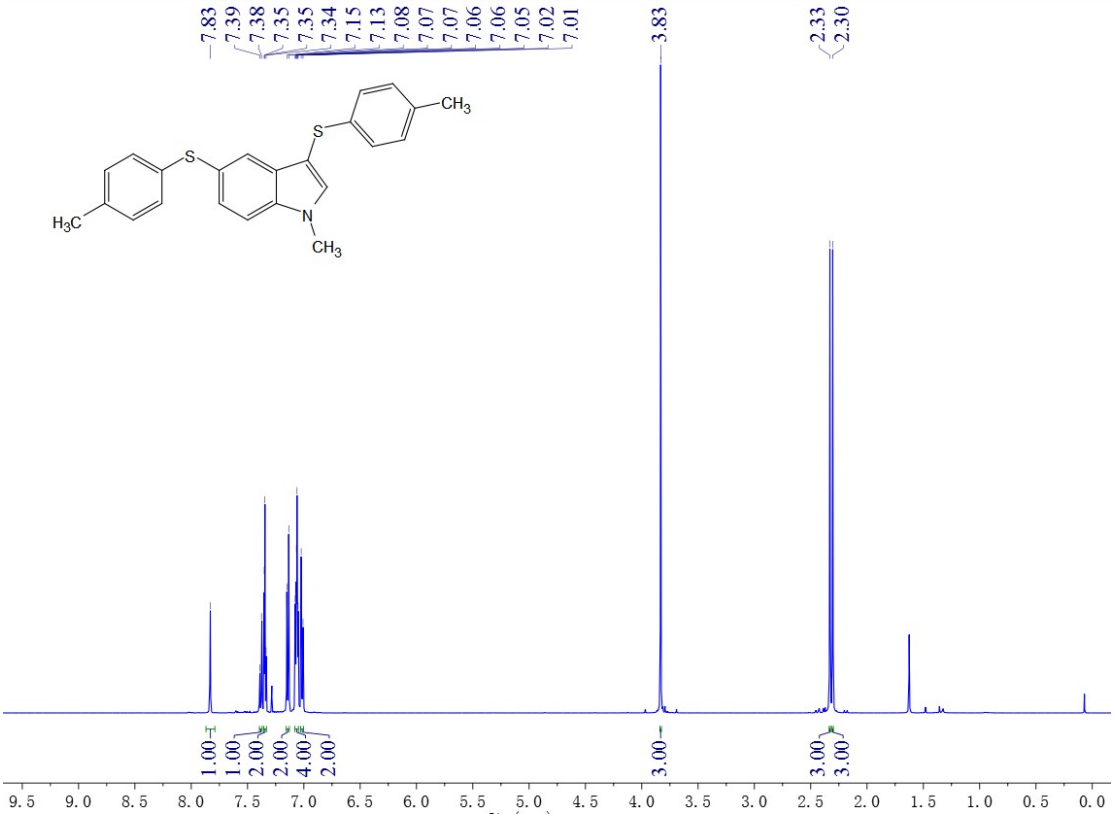
(43) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3pa



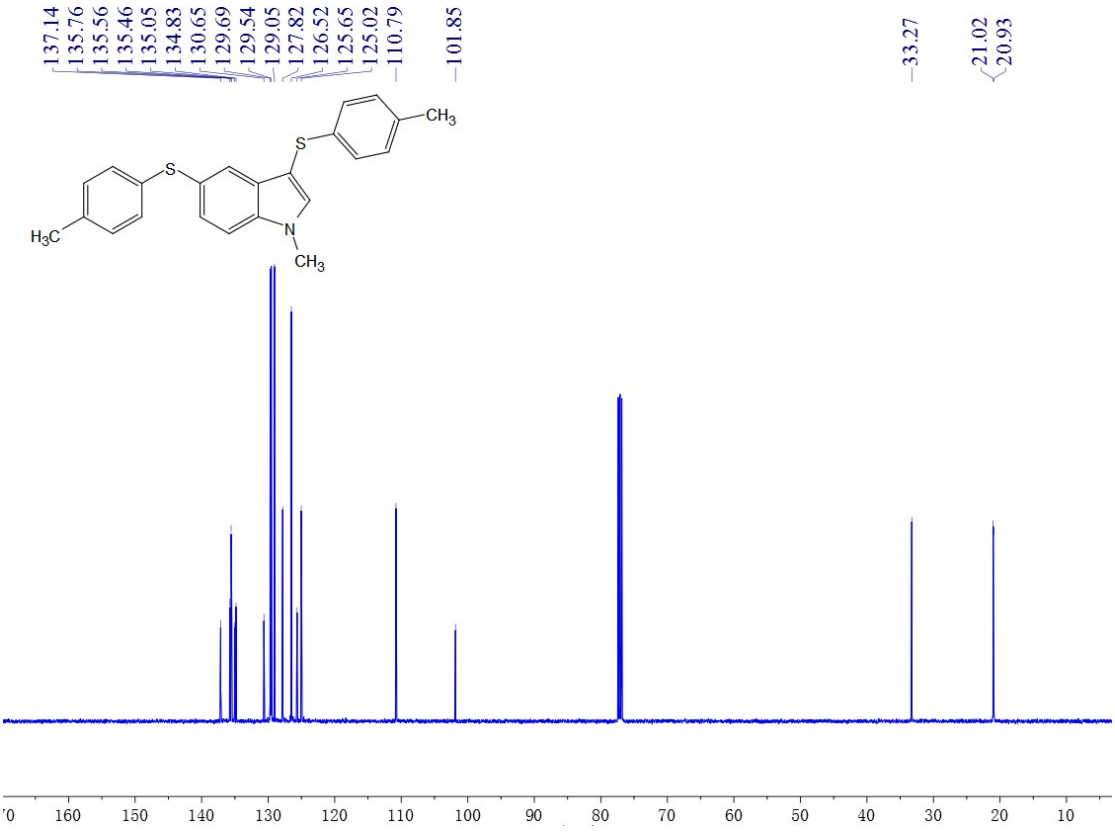
(44) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3pa



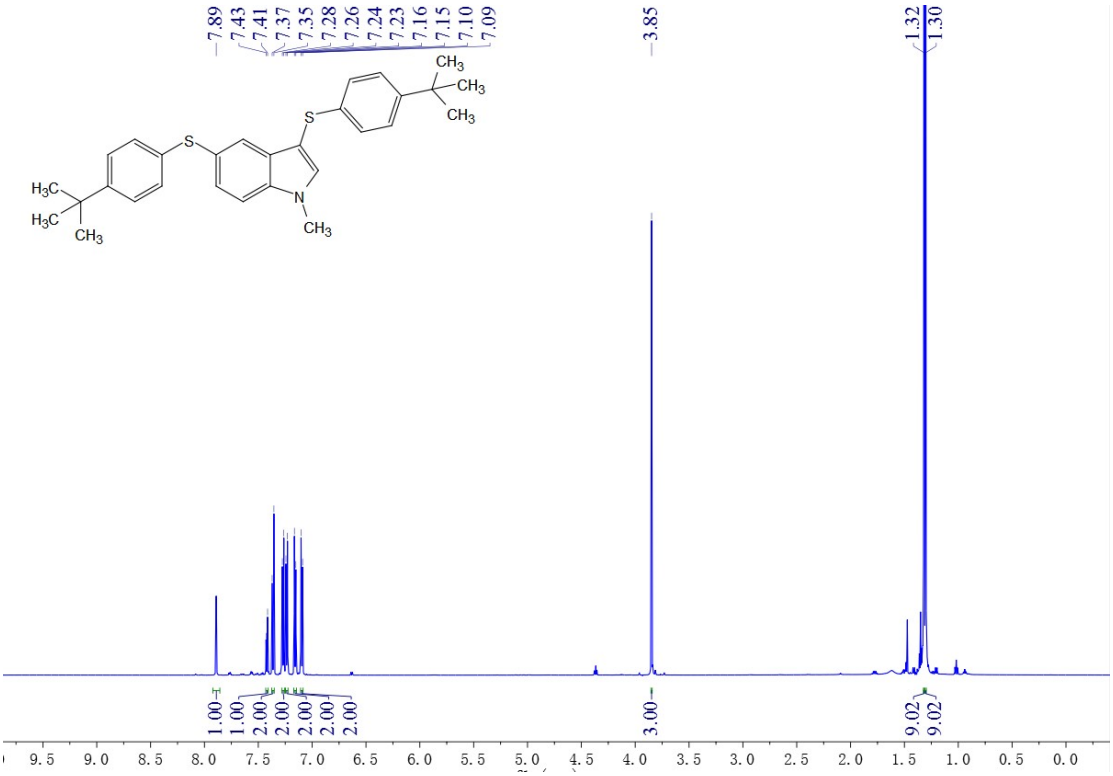
(45) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ab



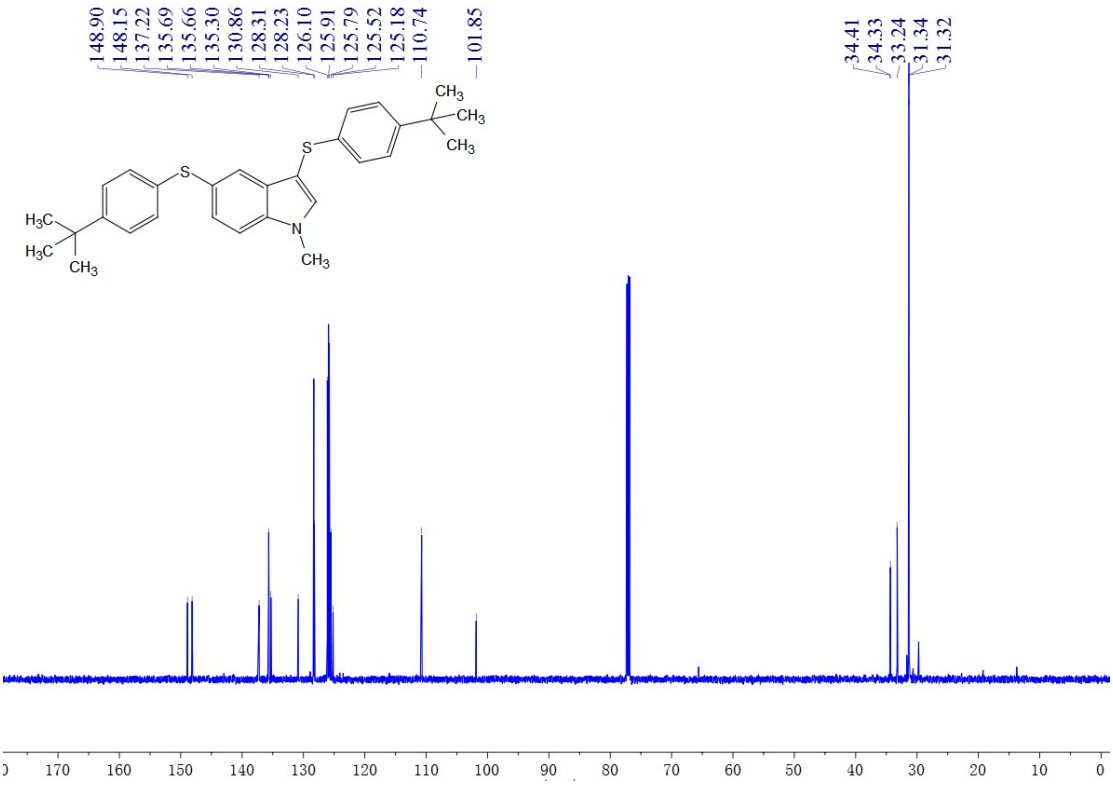
(46) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3ab



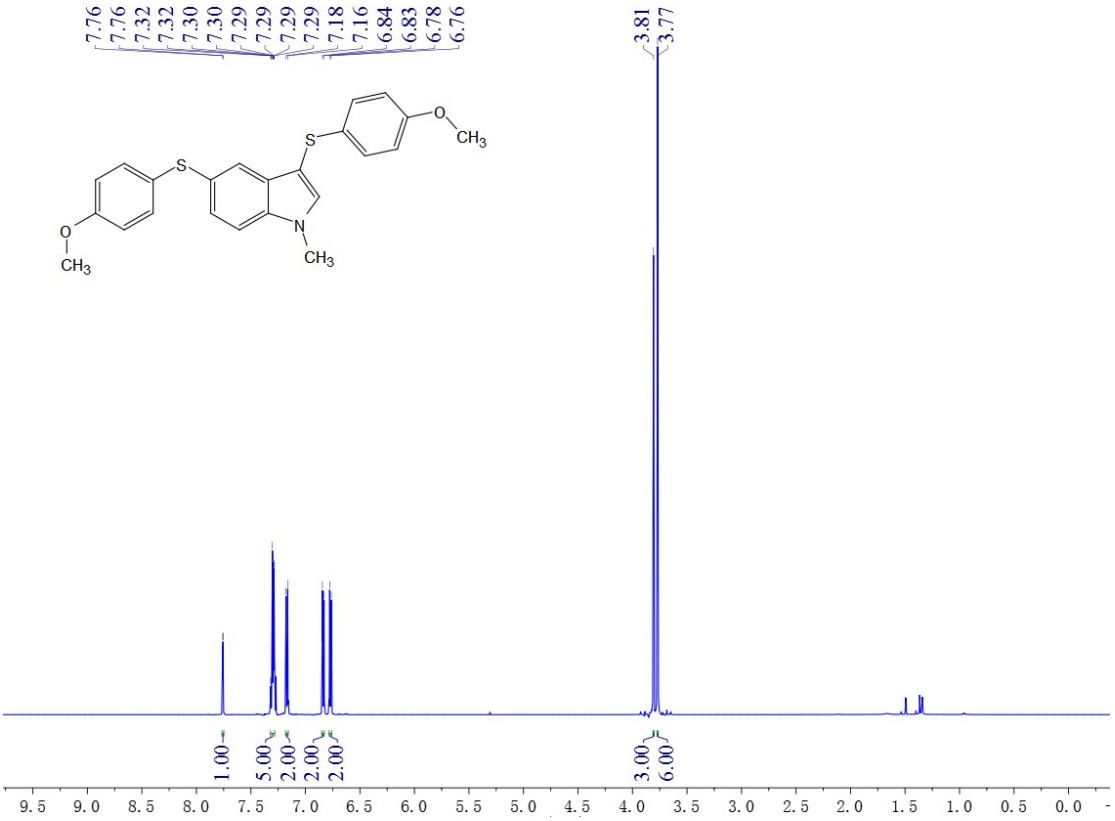
(47) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ac



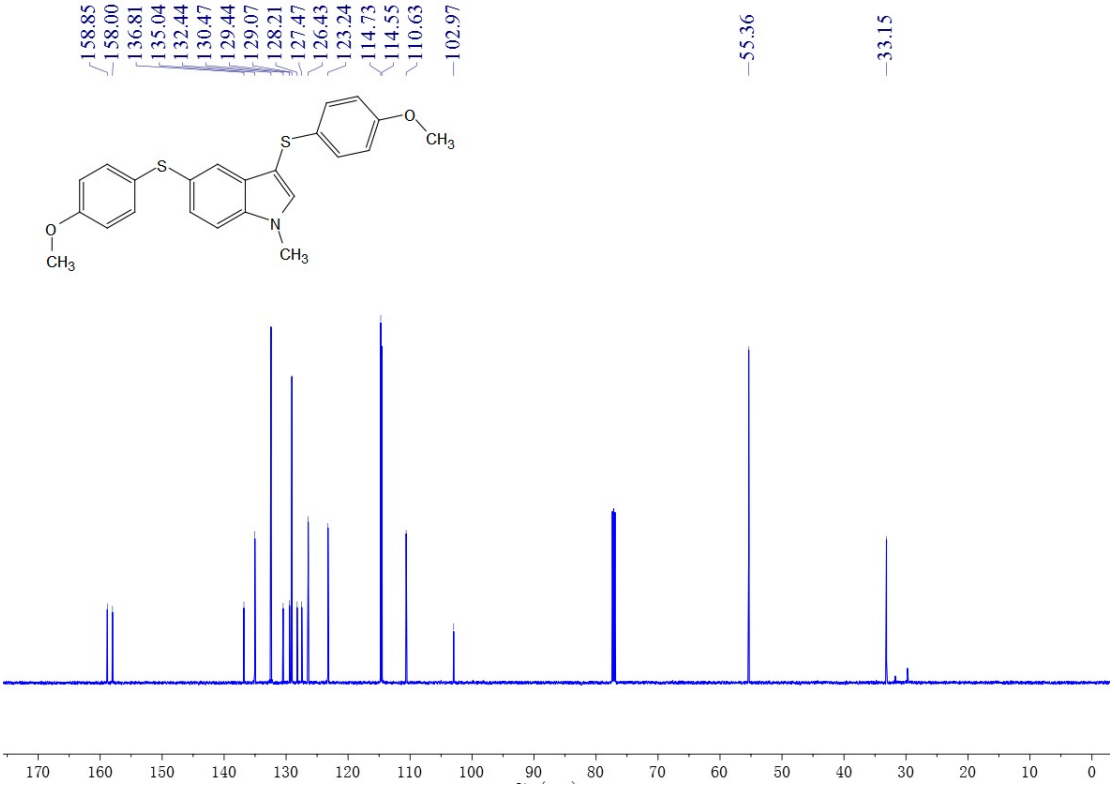
(48) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ac



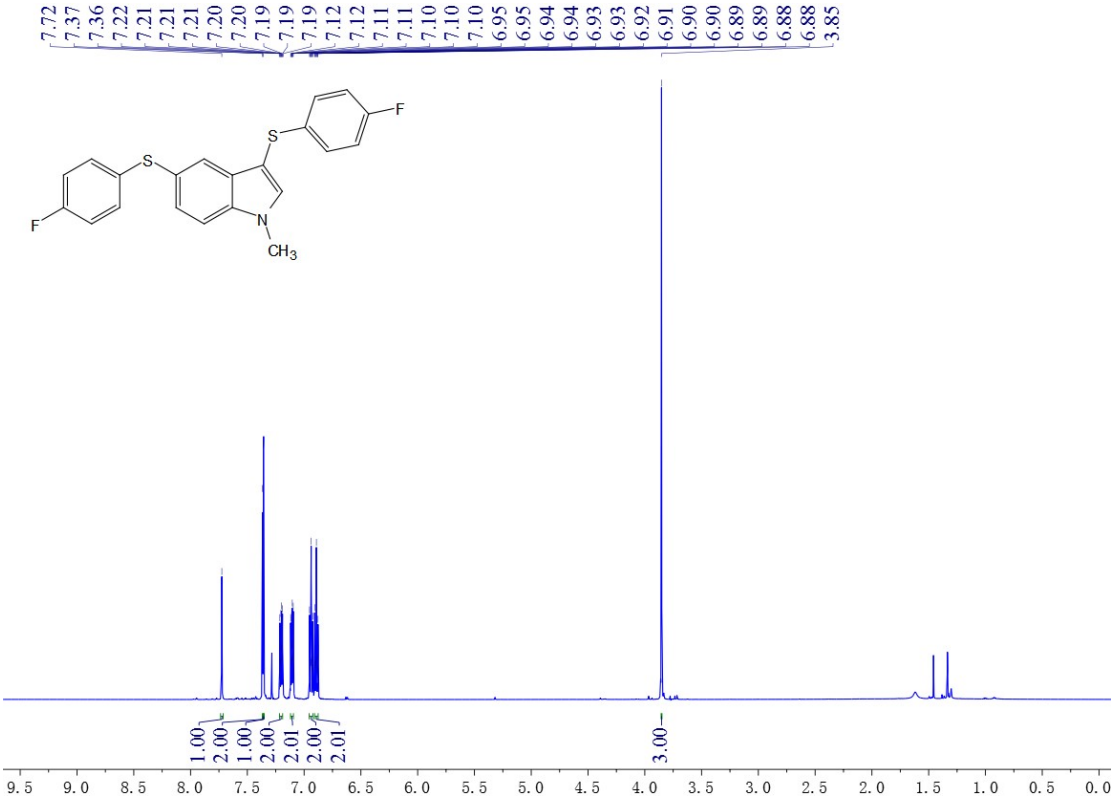
(49) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ad



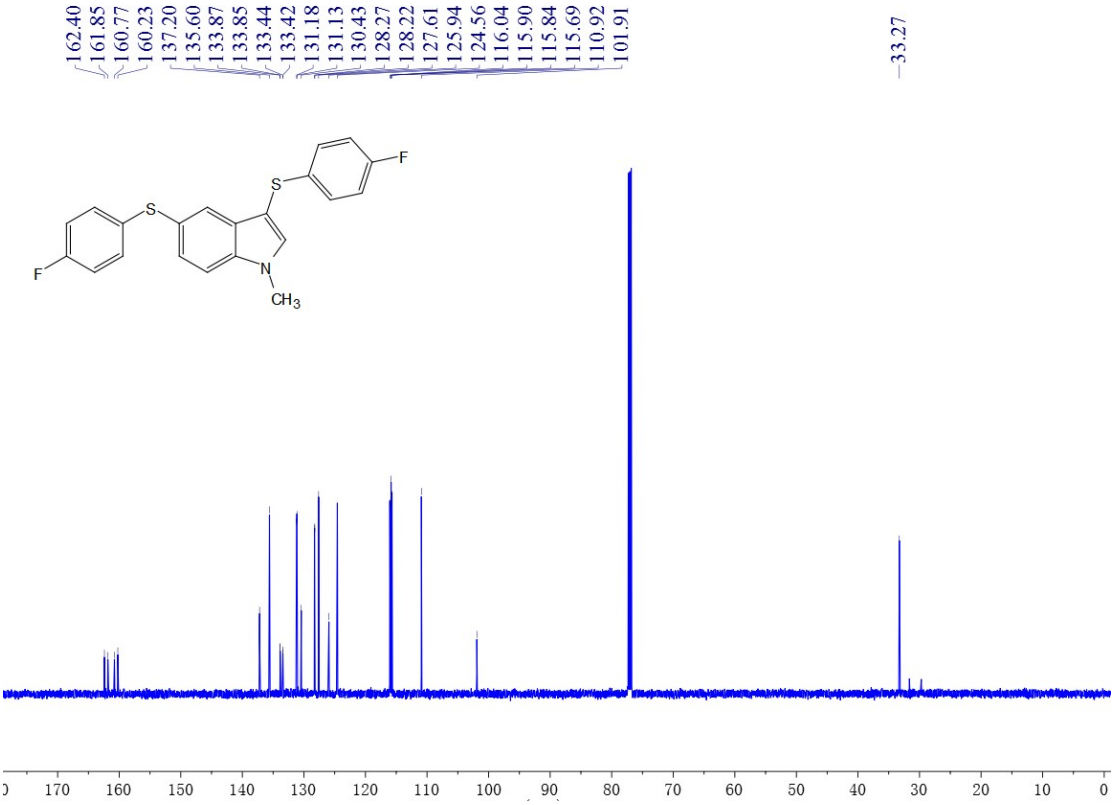
(50) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ad



(51) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ae

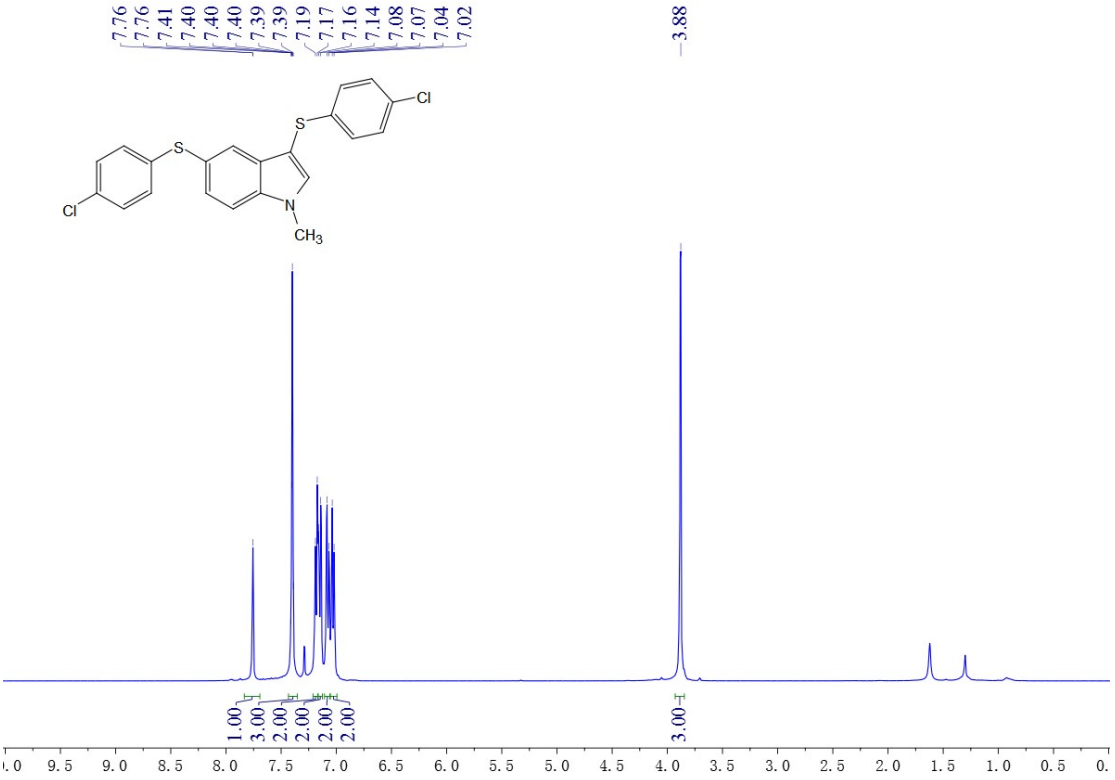


(52) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ae

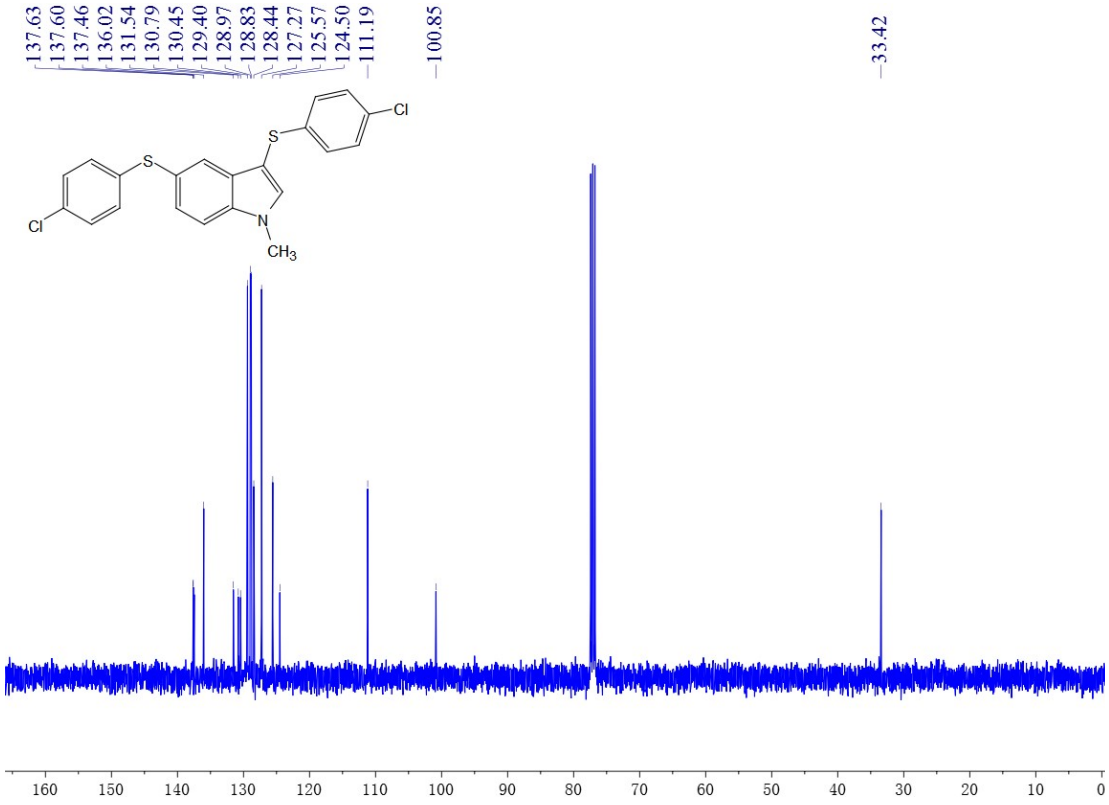


(53) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 3ae

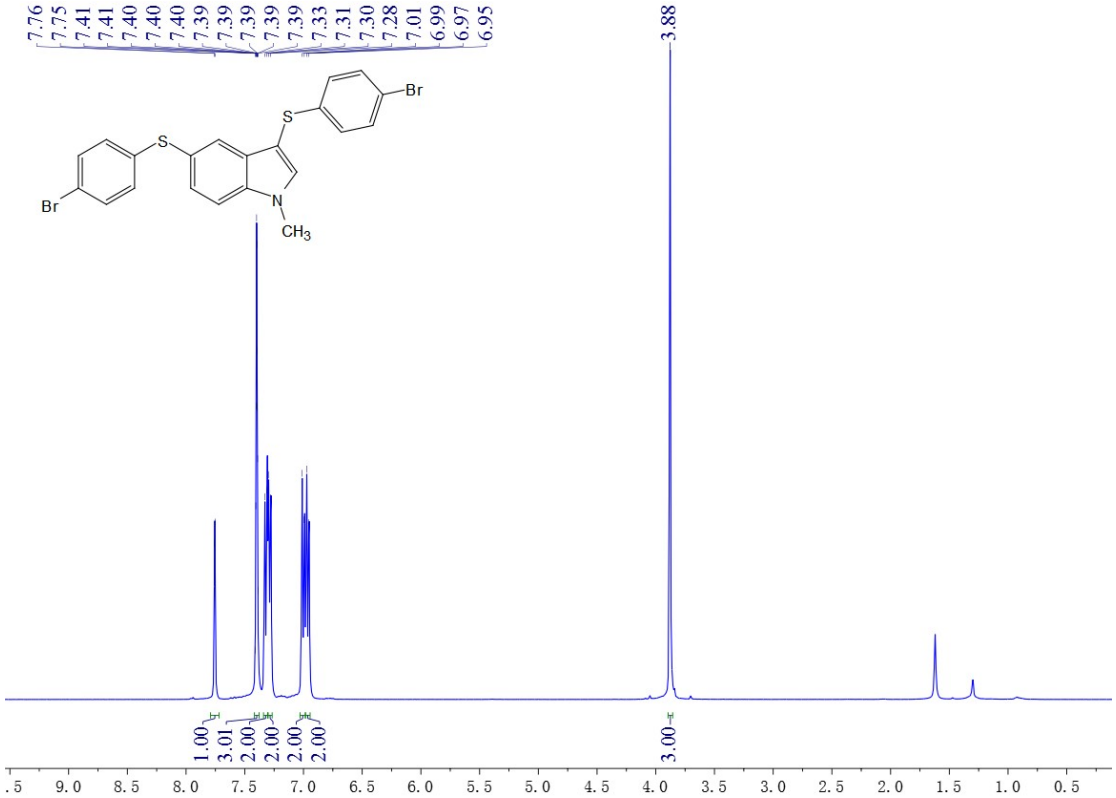
(54) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3af



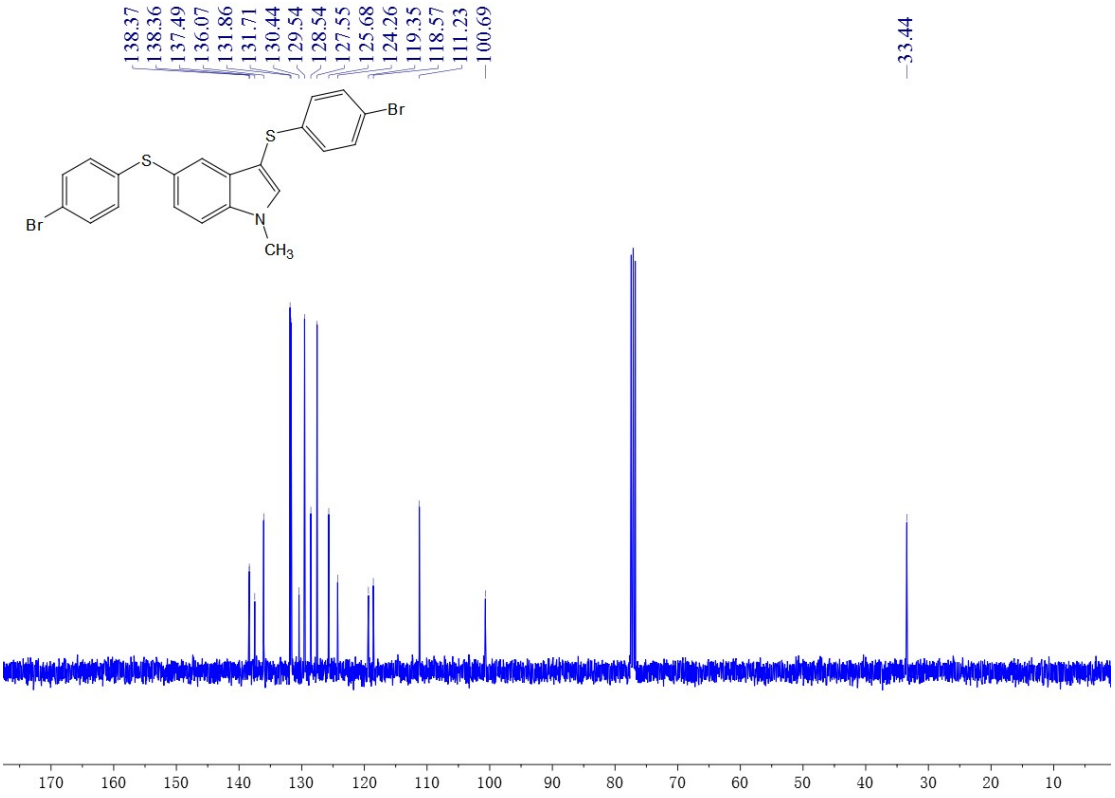
(55) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3af



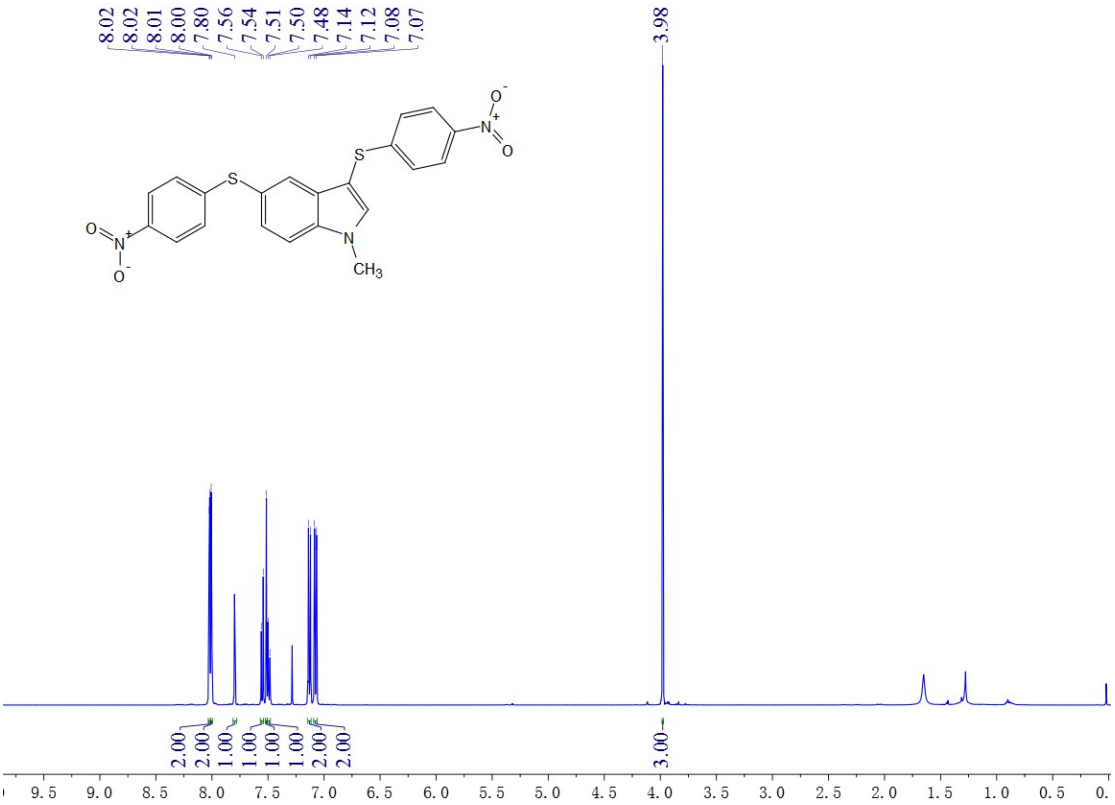
(56) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ag



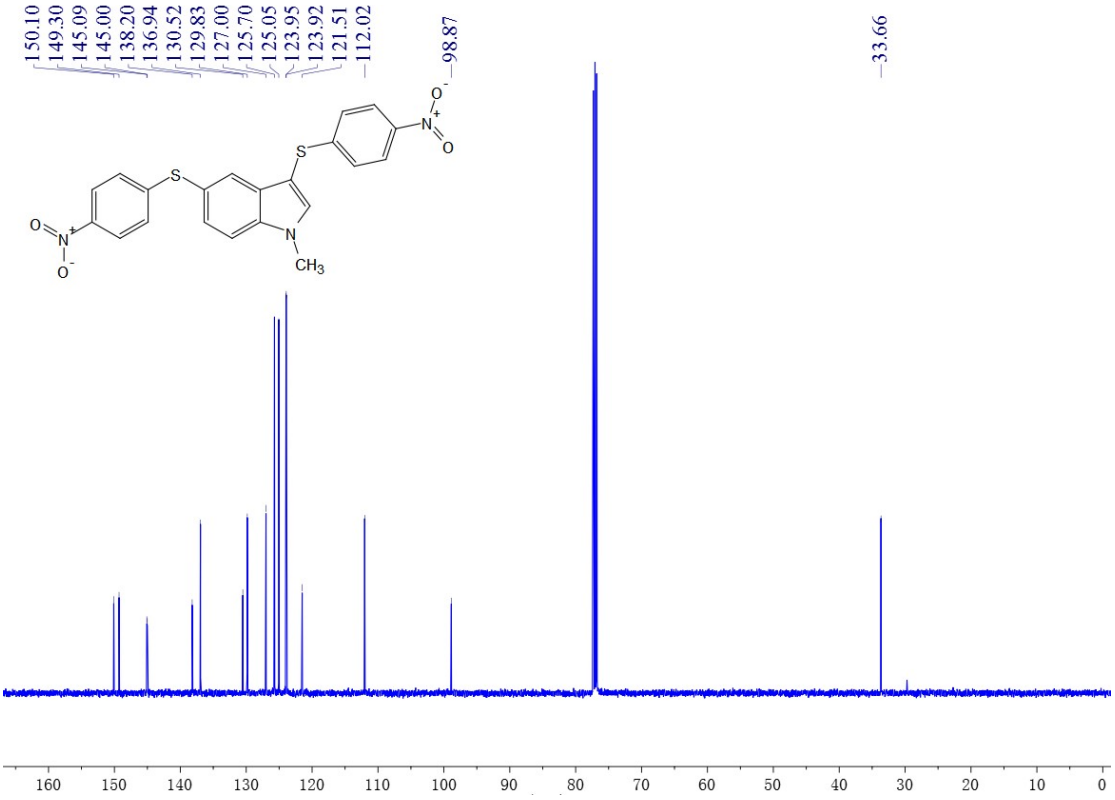
(57) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ag



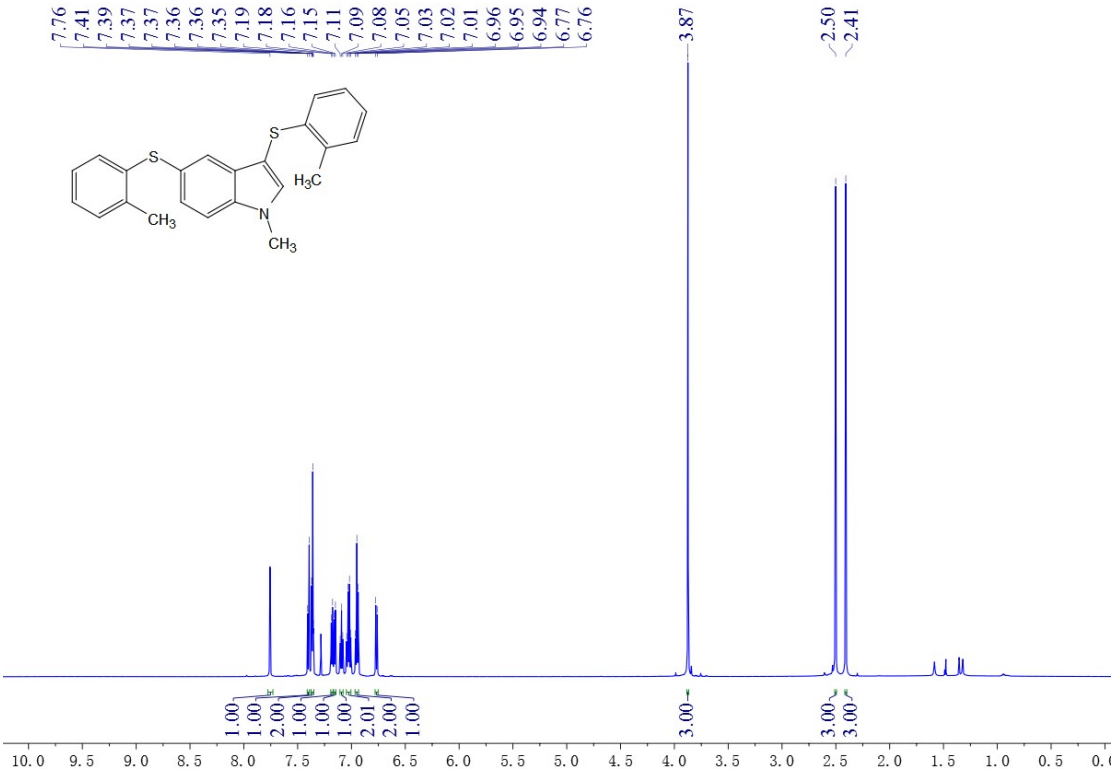
(58) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ah



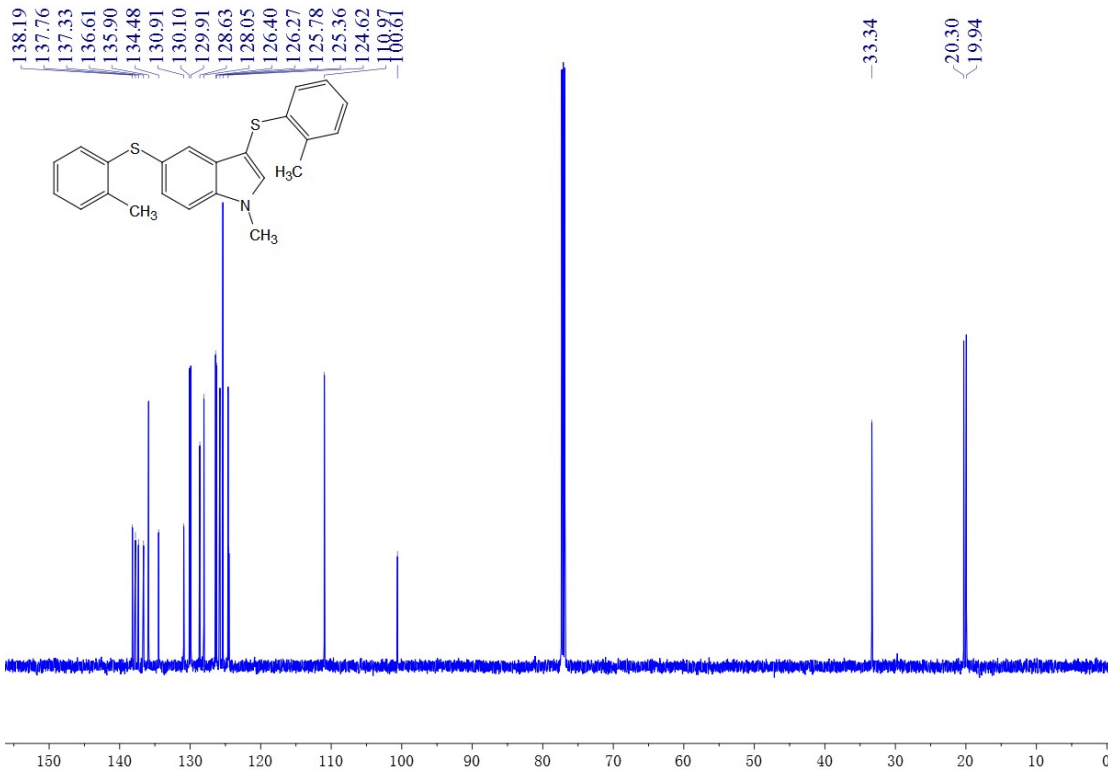
(59) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3ah



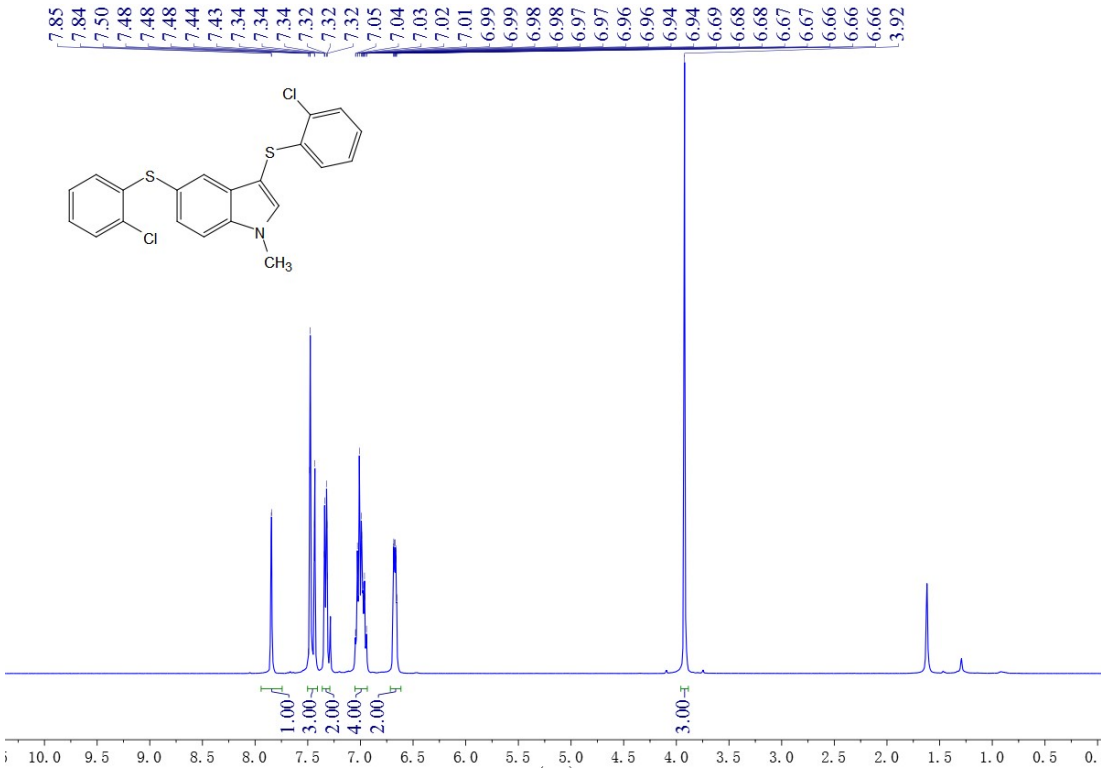
(60) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ai



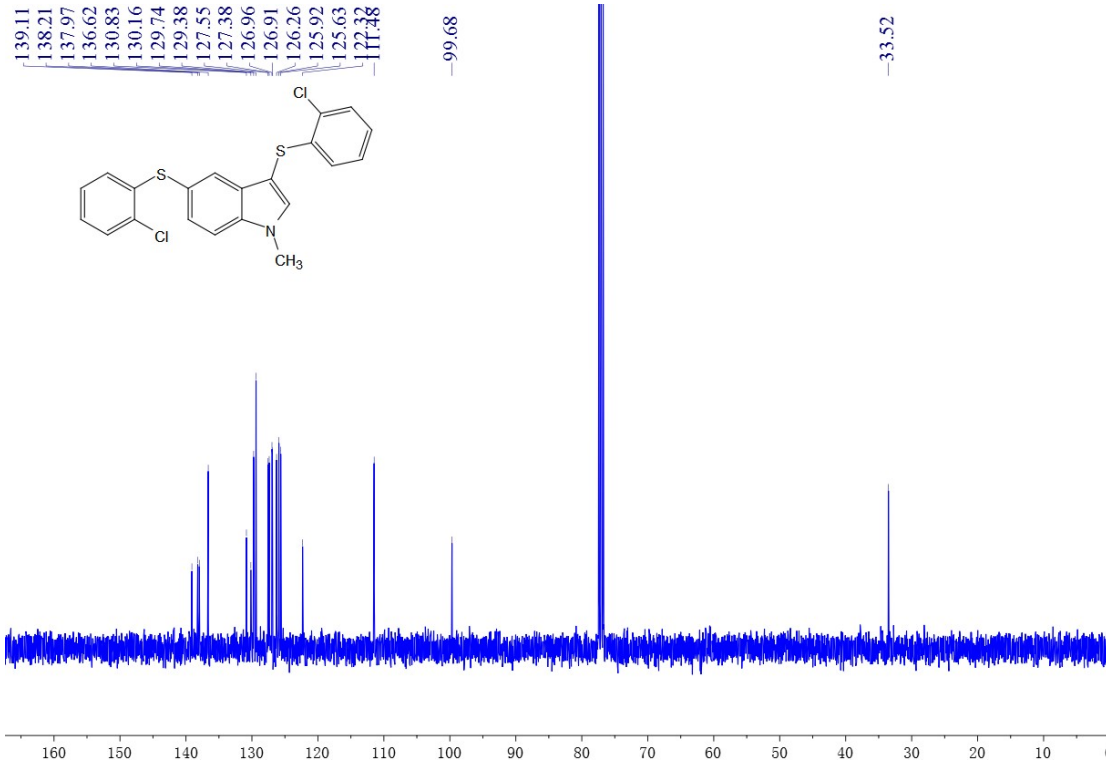
(61) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ai



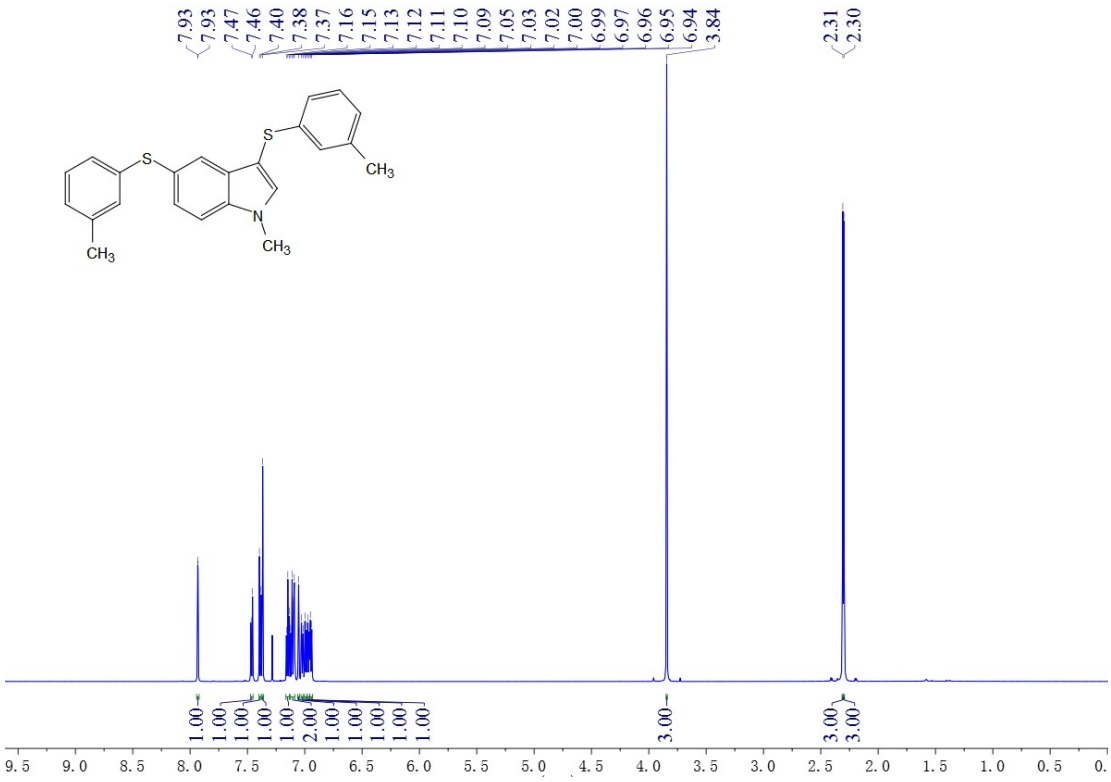
(62) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3aj



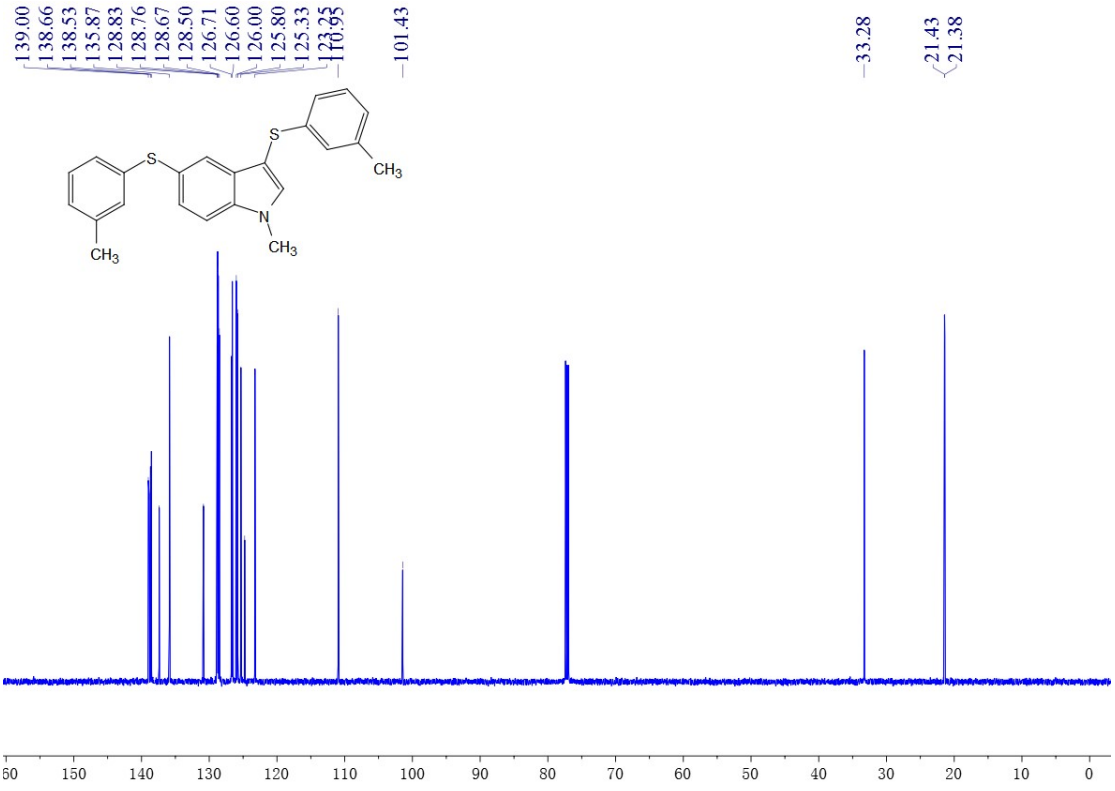
(63) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3aj



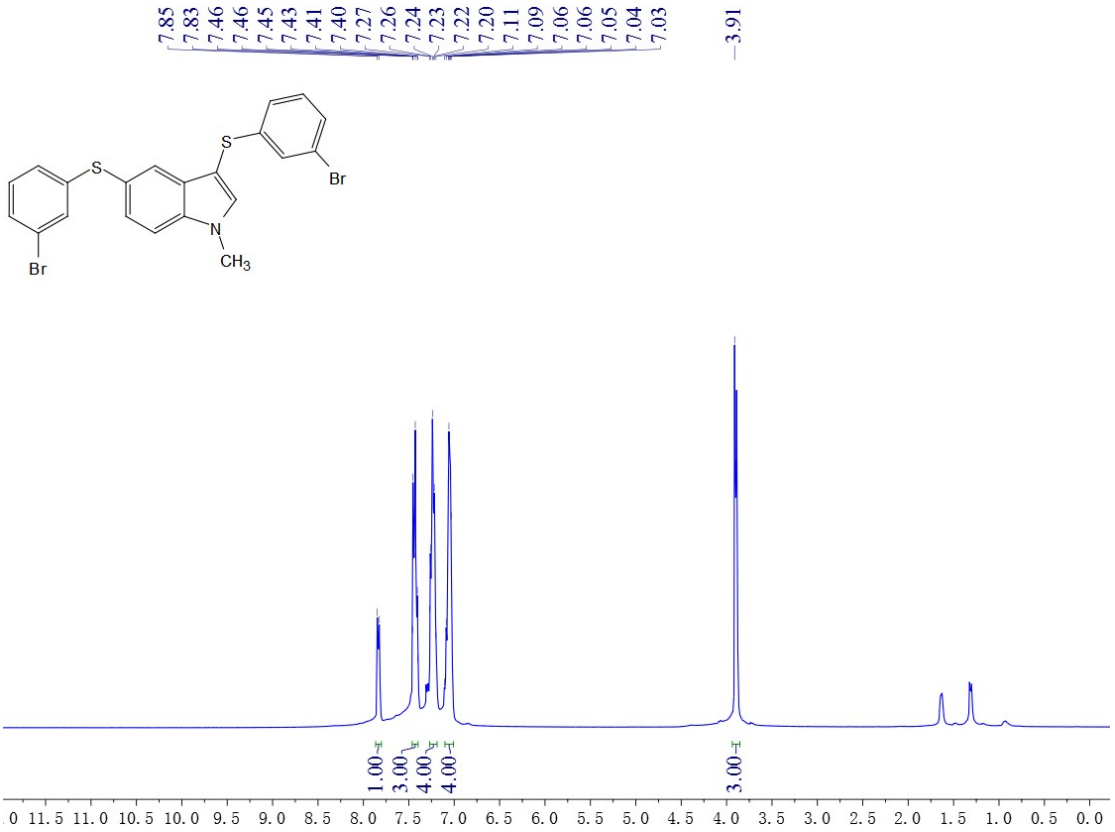
(64) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ak



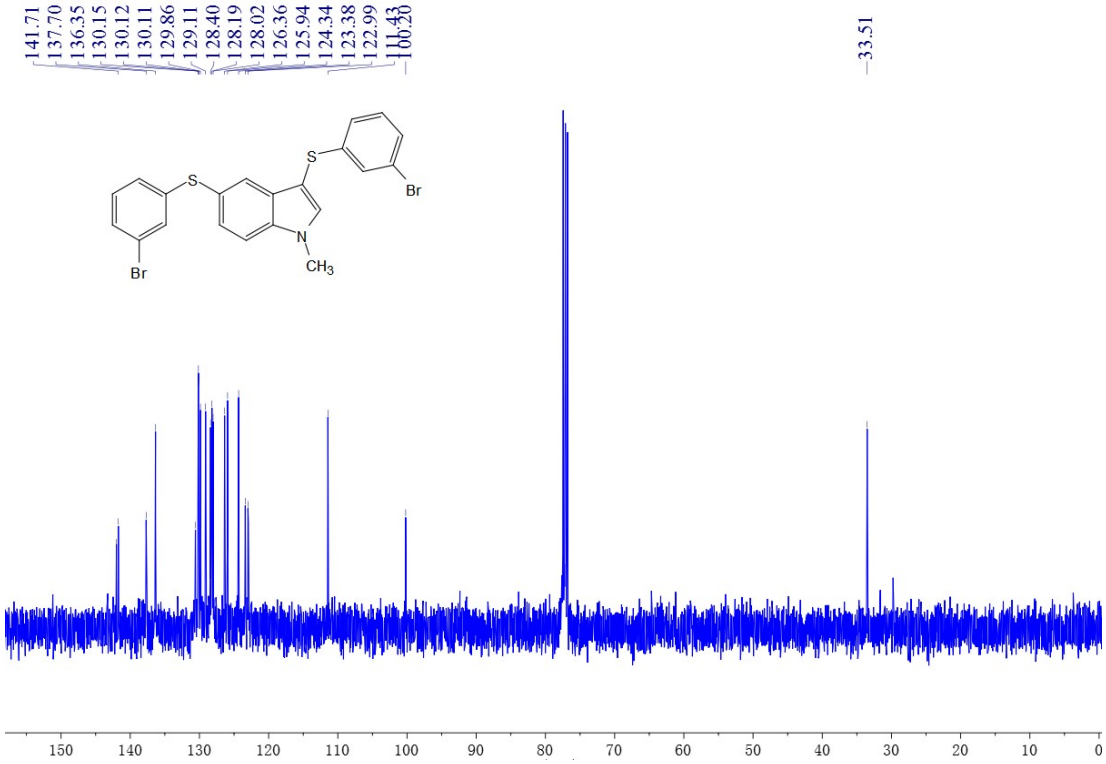
(65) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ak



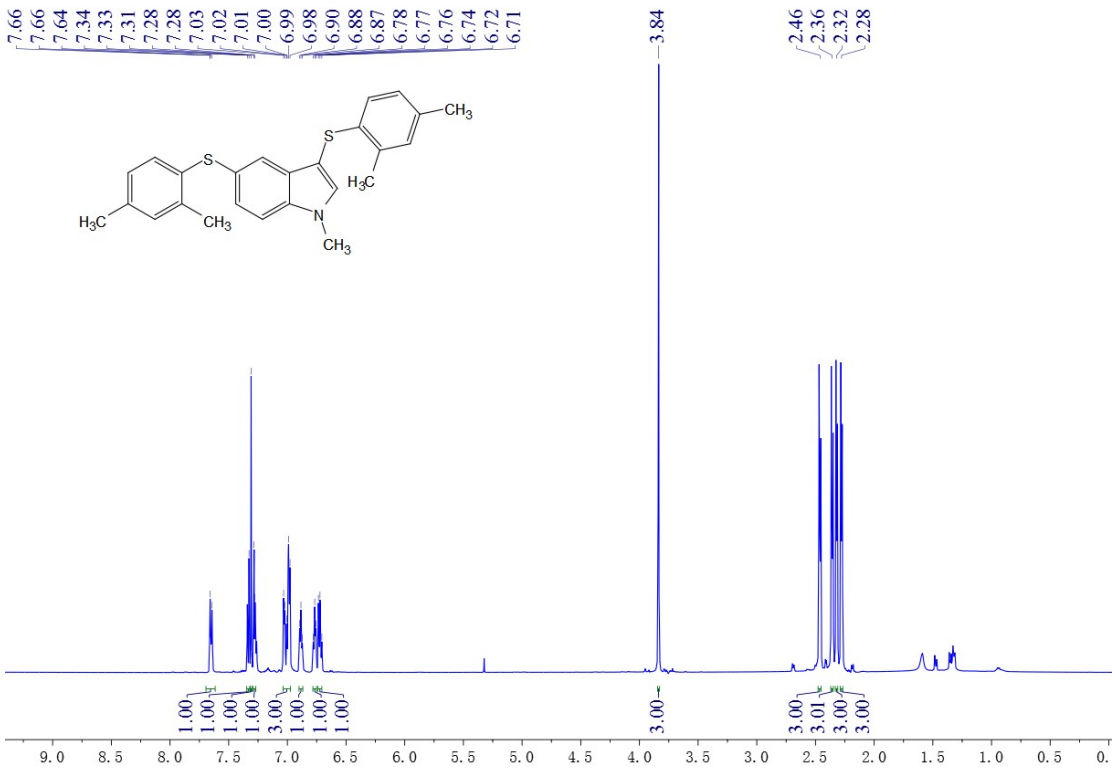
(66) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3al



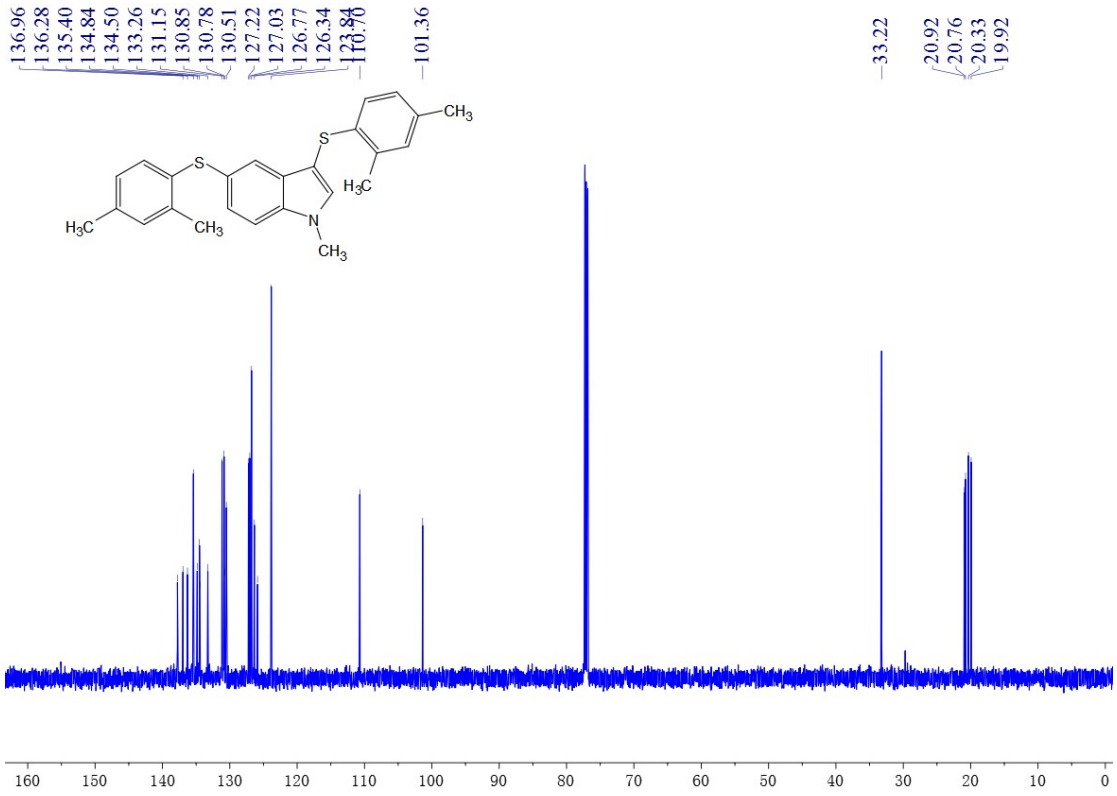
(67) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3al



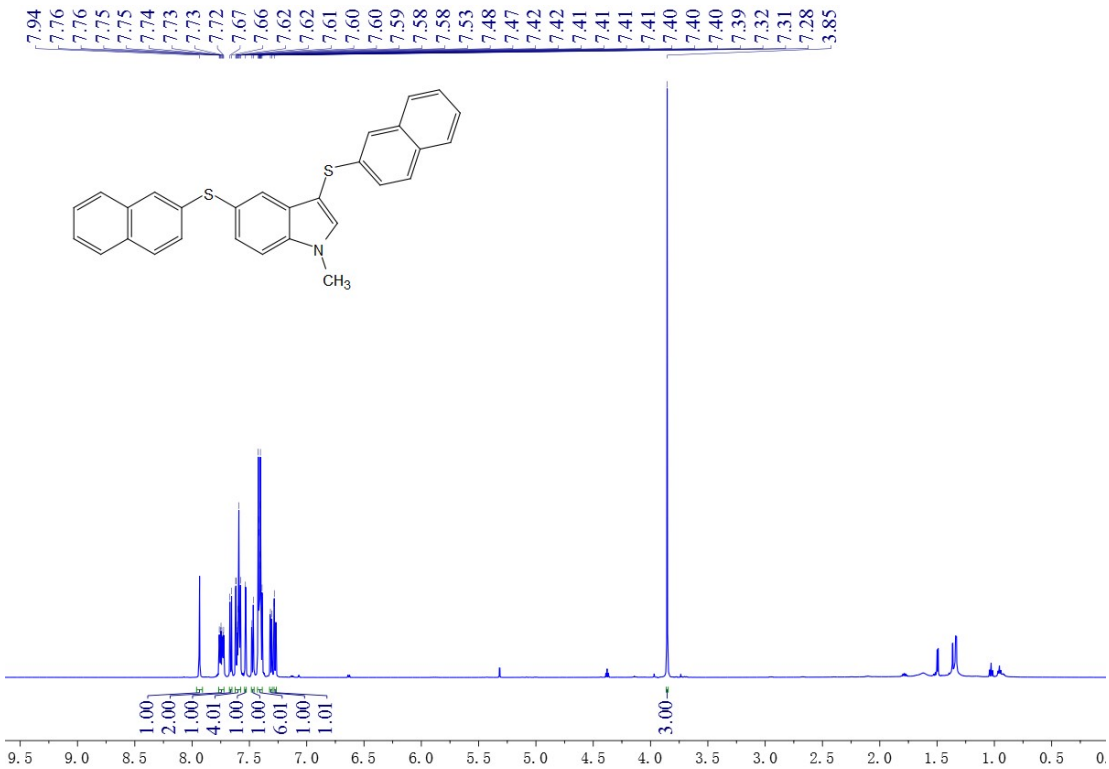
(68) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3am



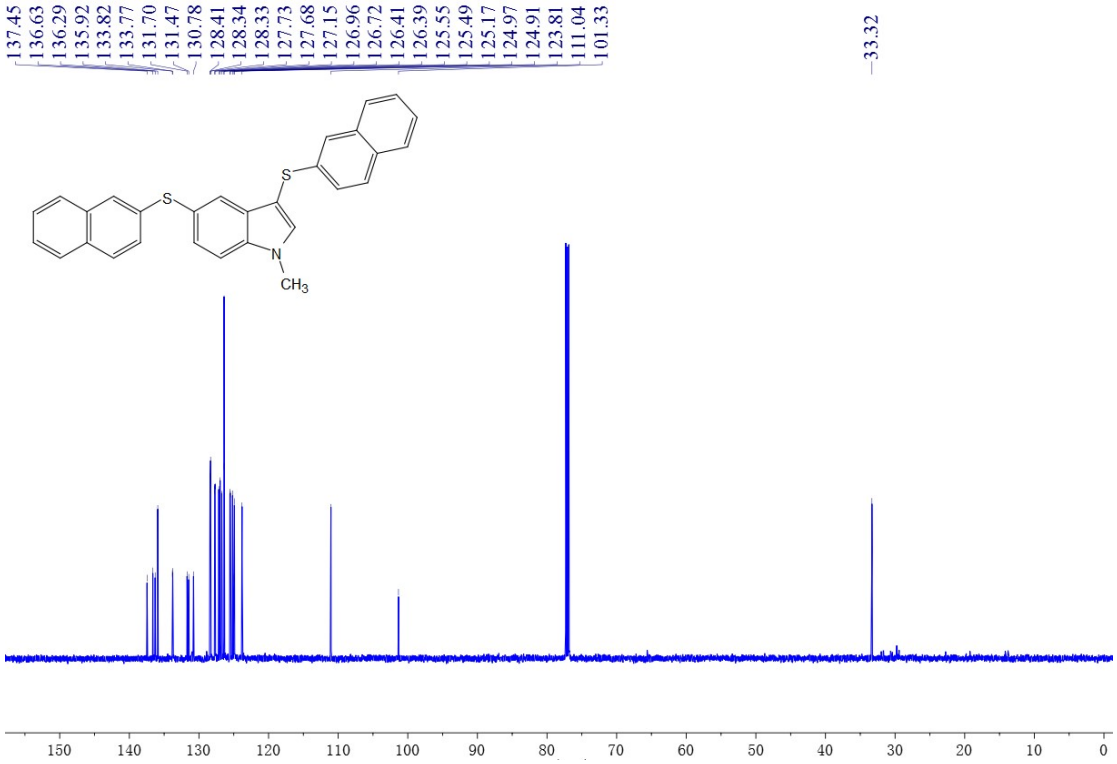
(69) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3am



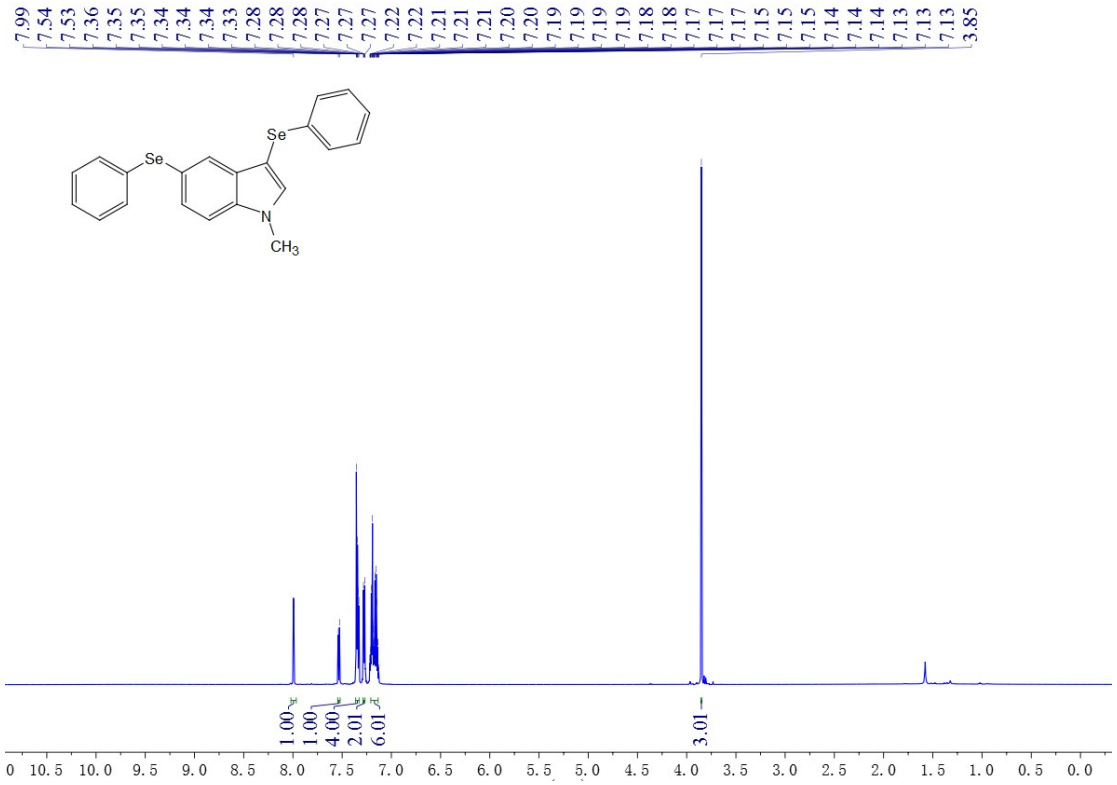
(70) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3an



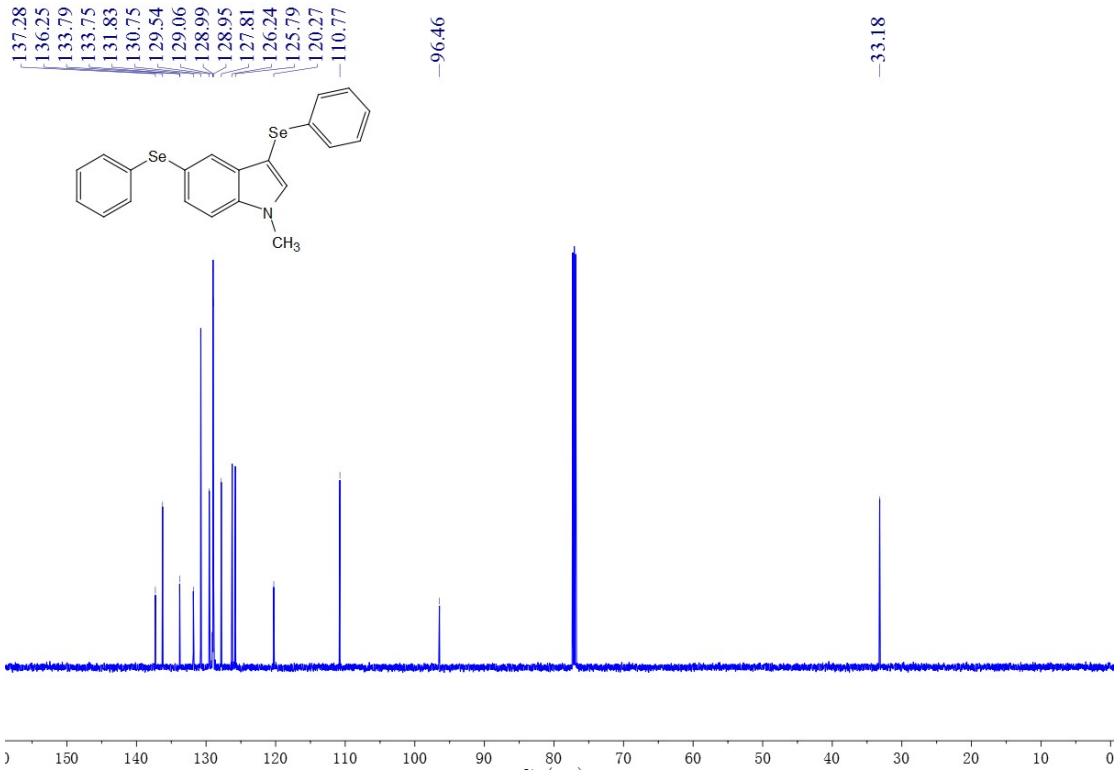
(71) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3an



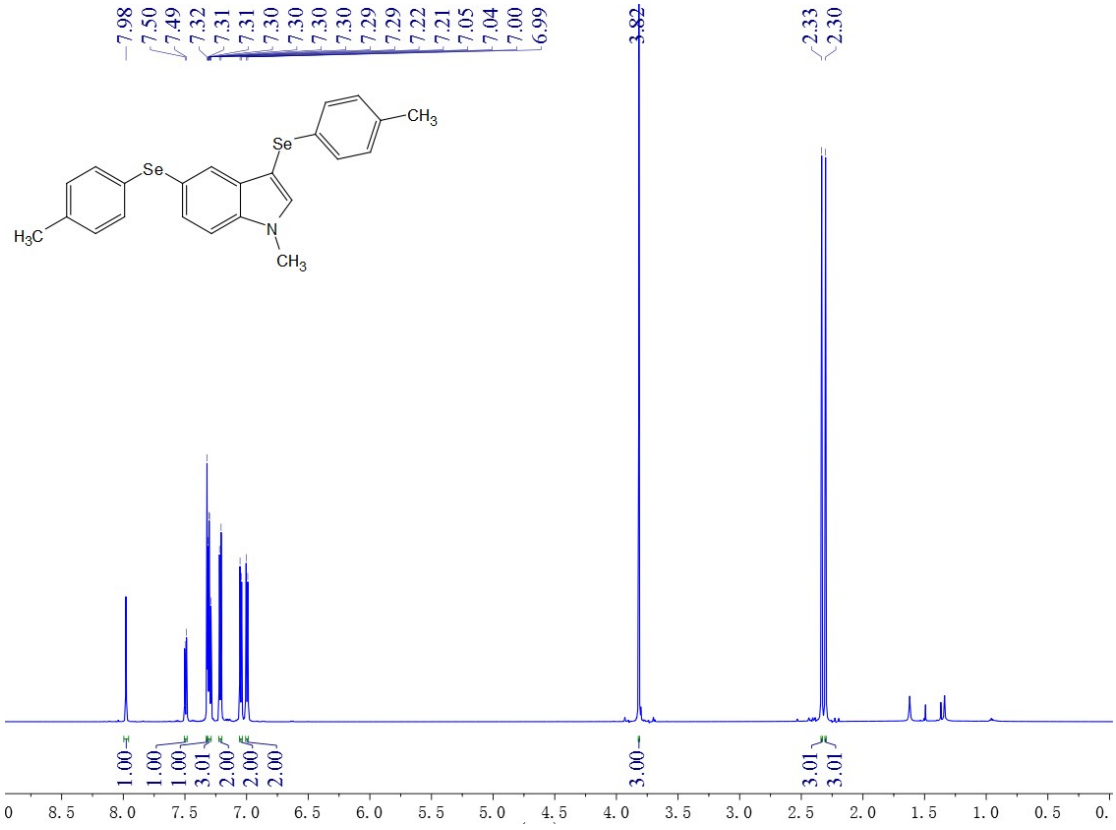
(72) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ao



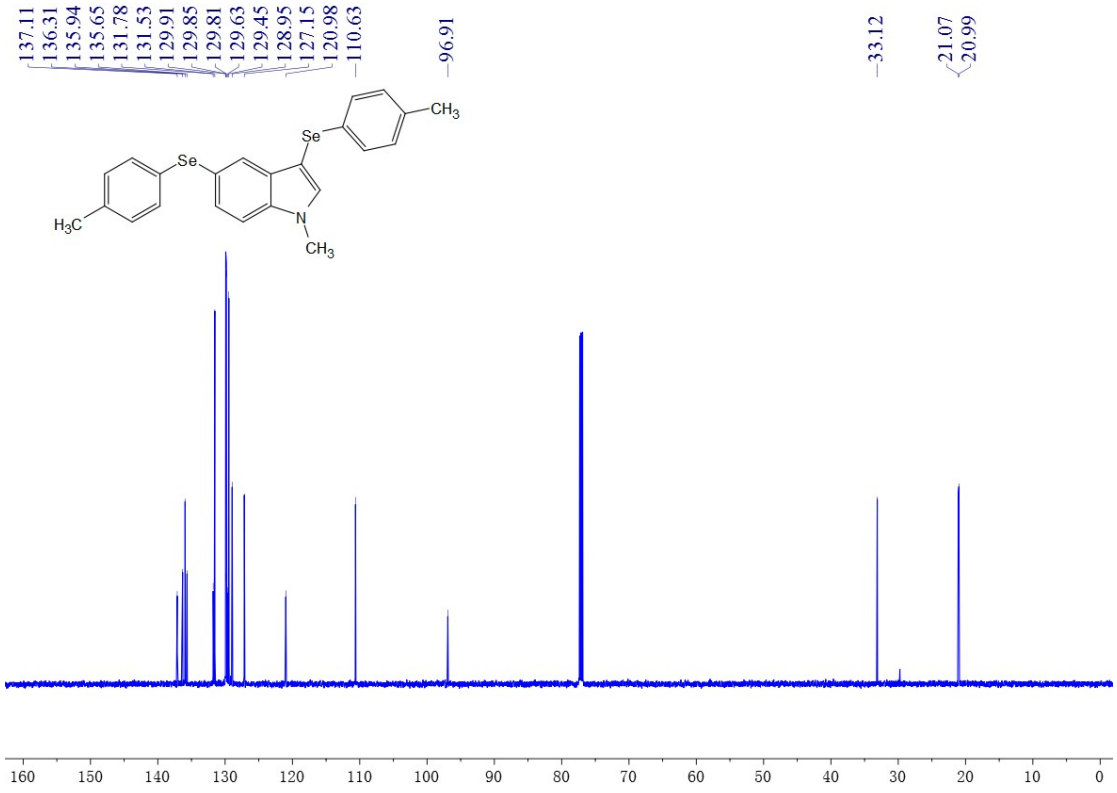
(73) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ao



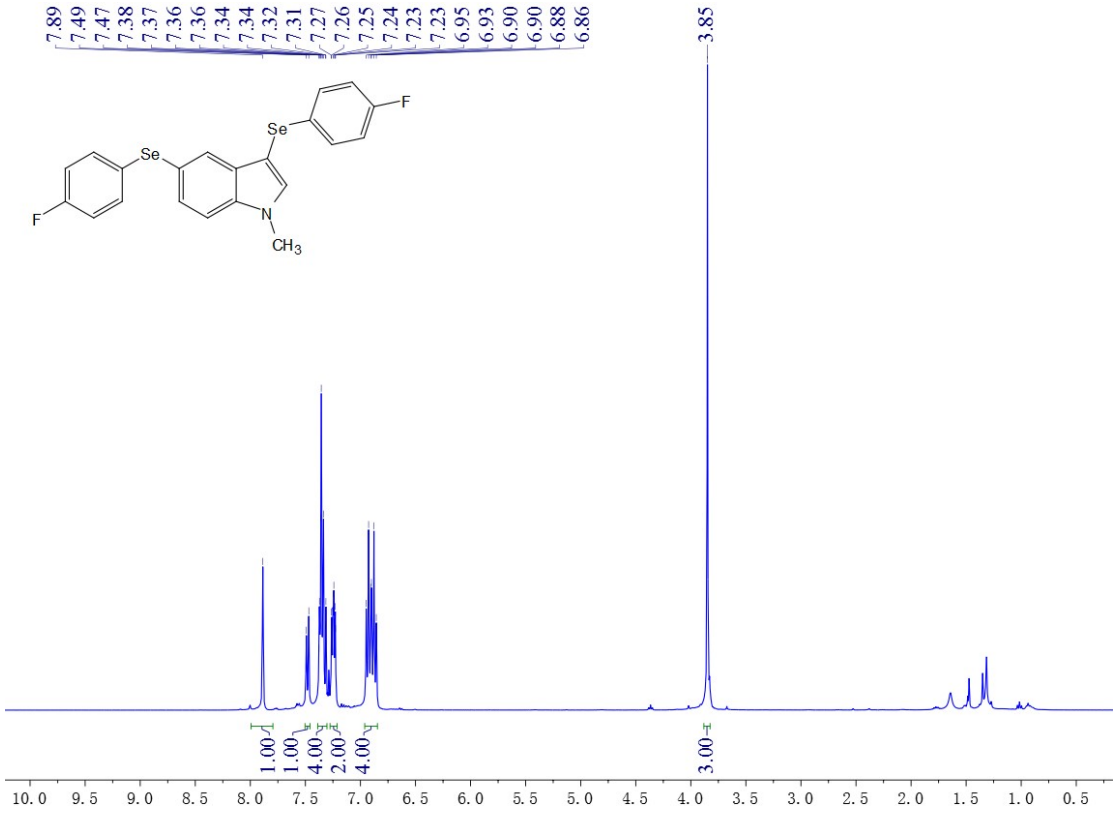
(74) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ap



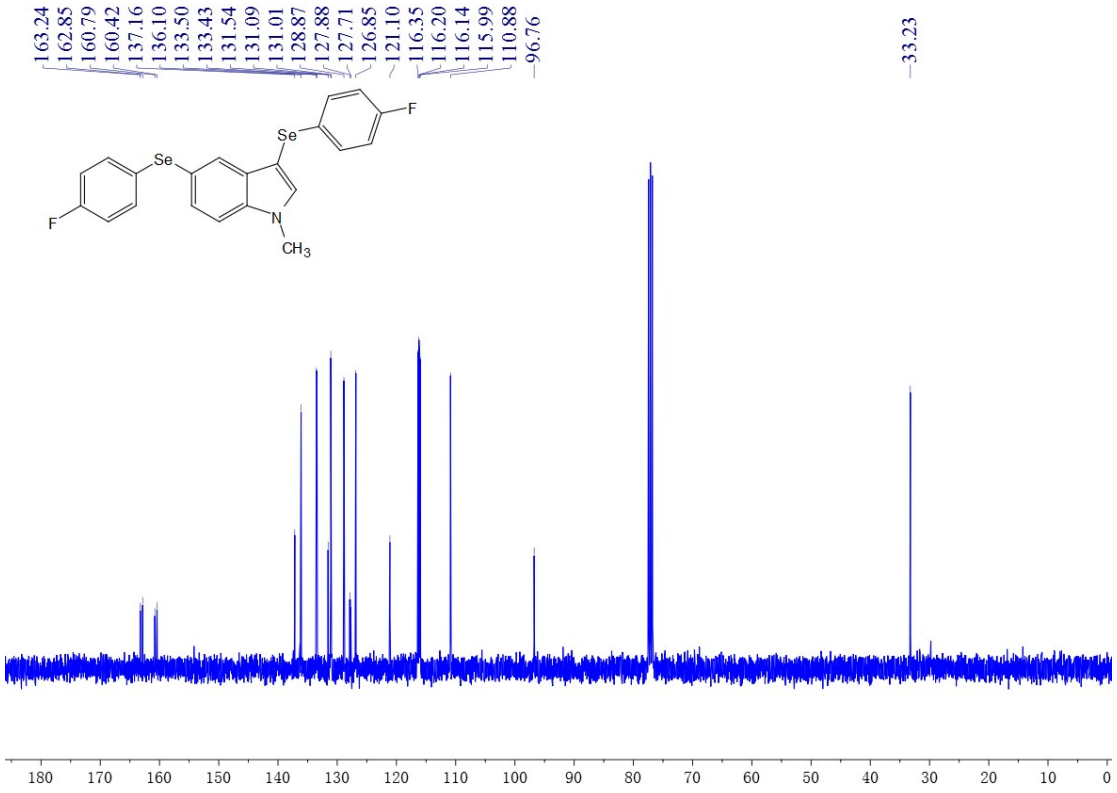
(75) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ap



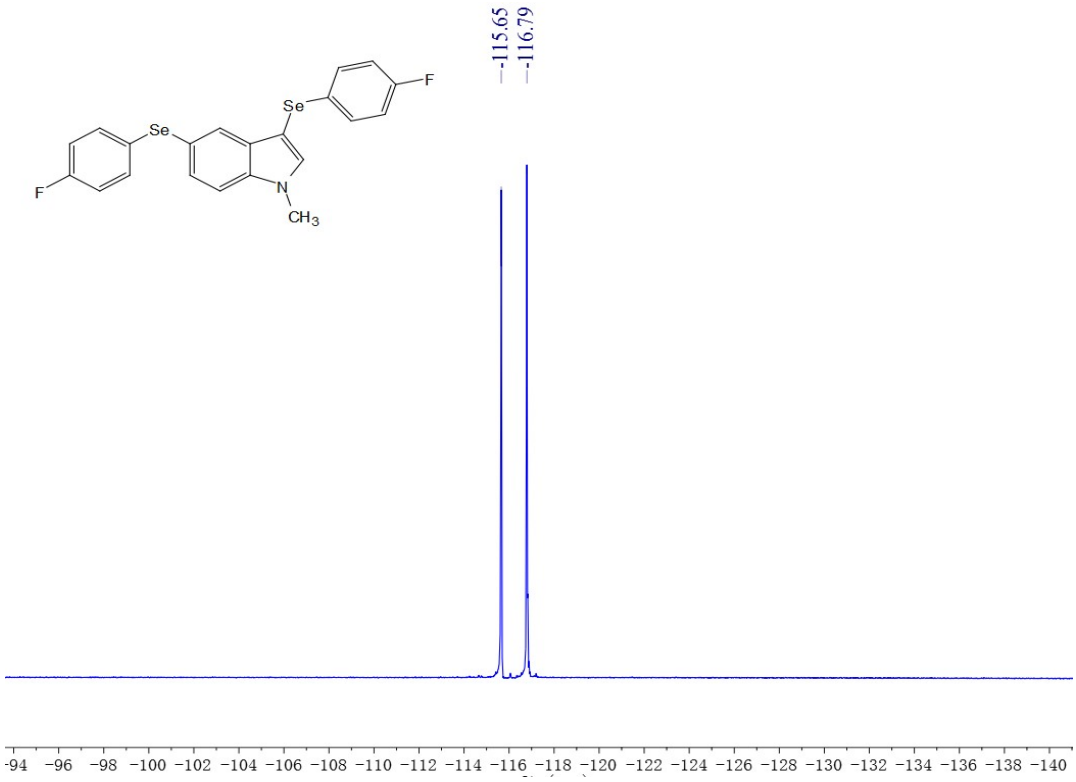
(76) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3aq



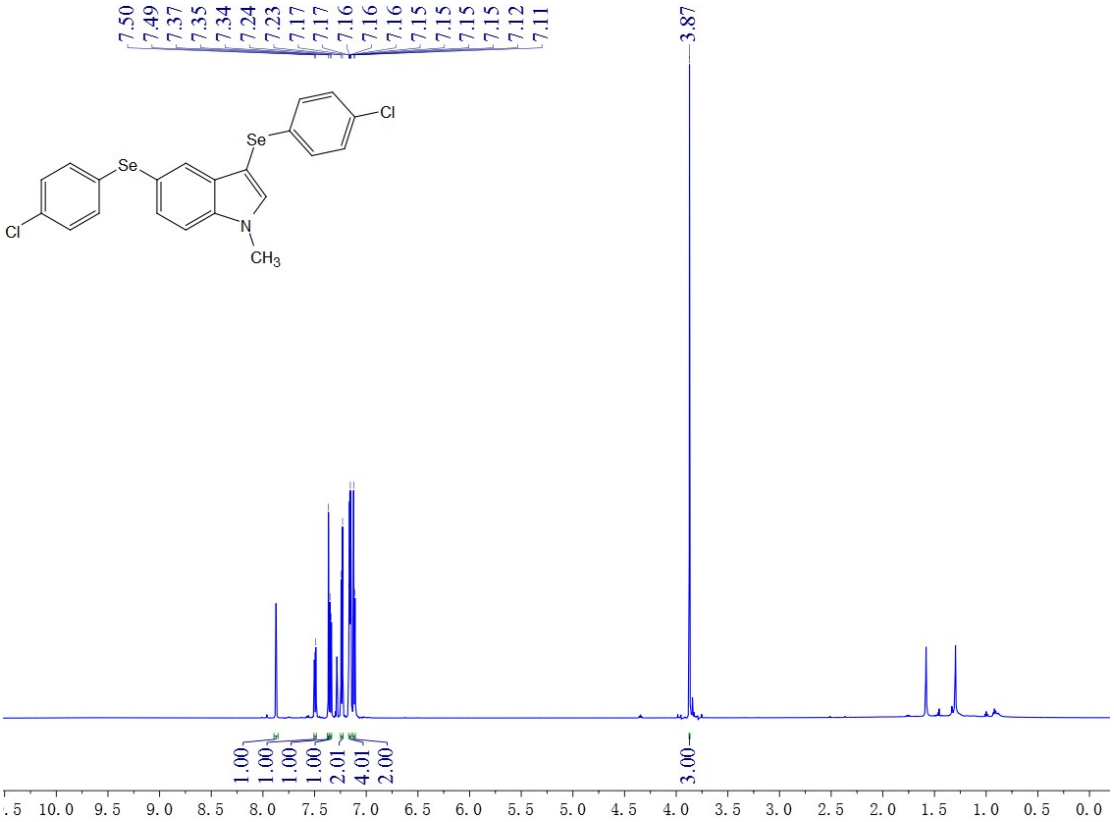
(77) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3aq



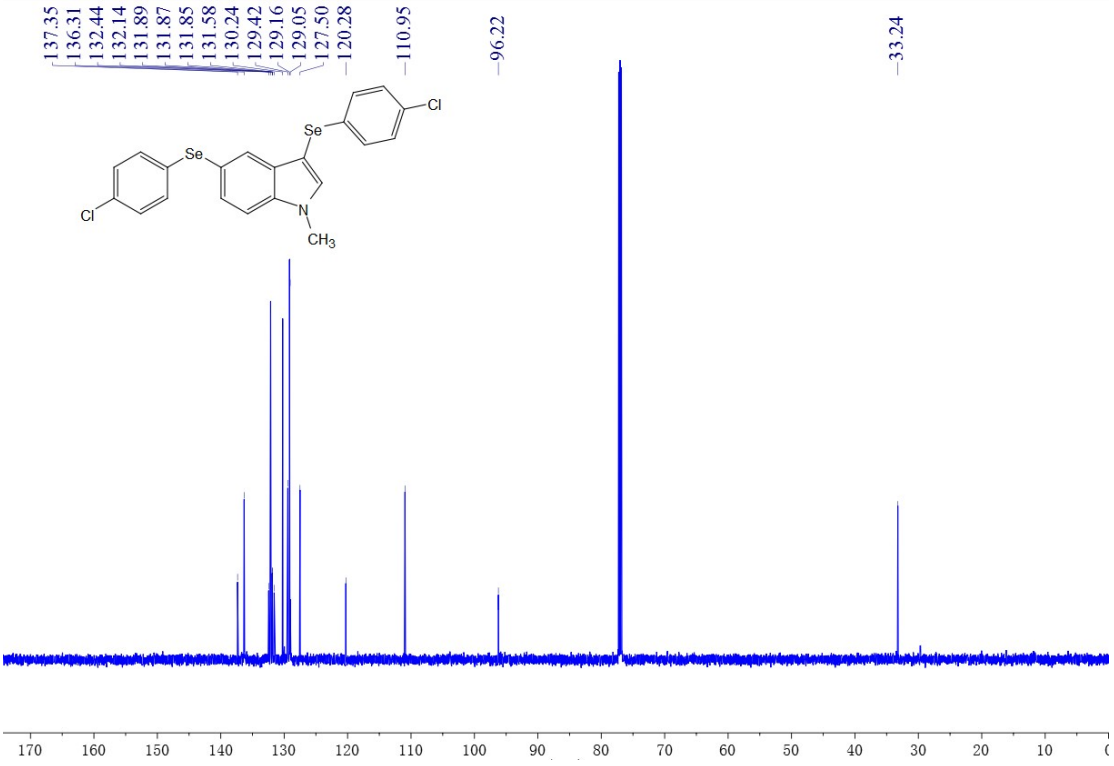
(78) ^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 3aq



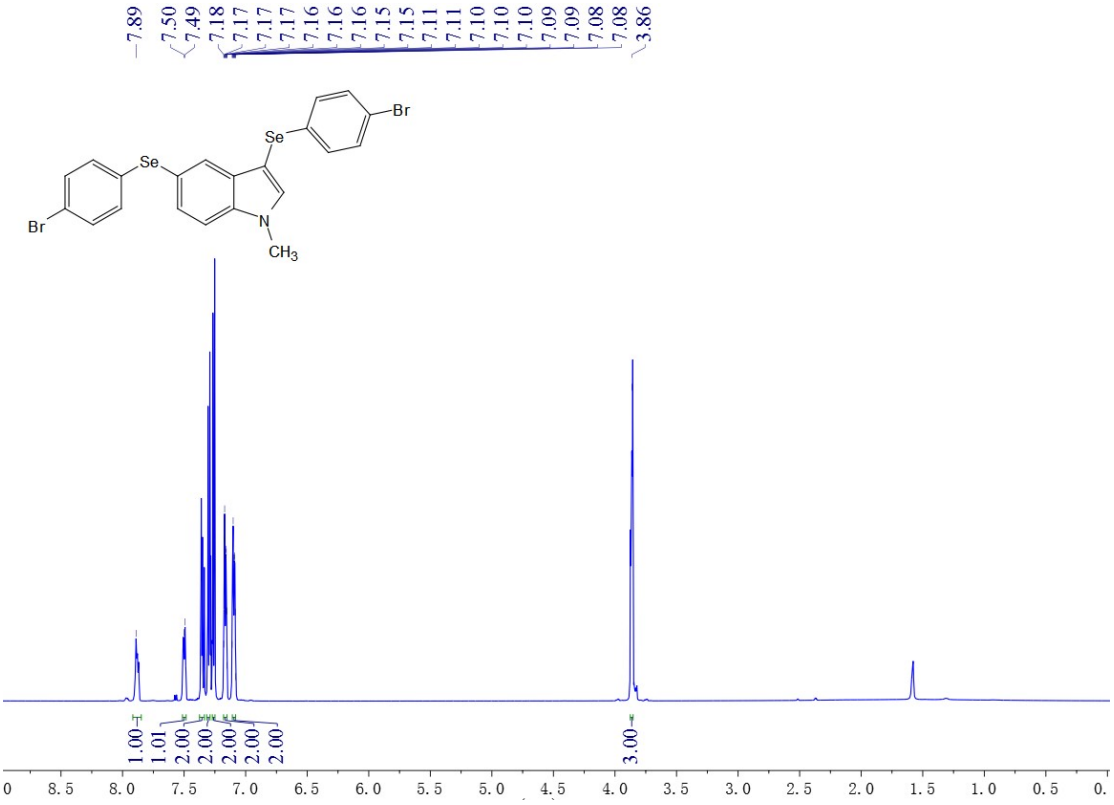
(79) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3ar



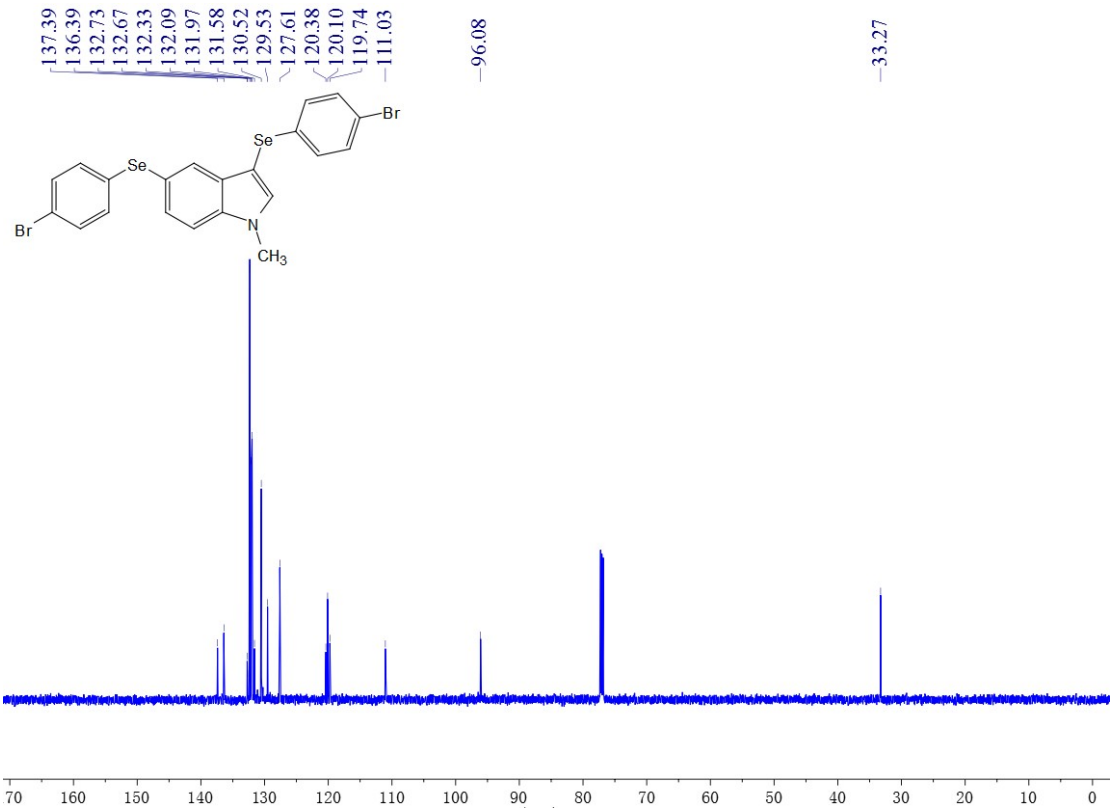
(80) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3ar



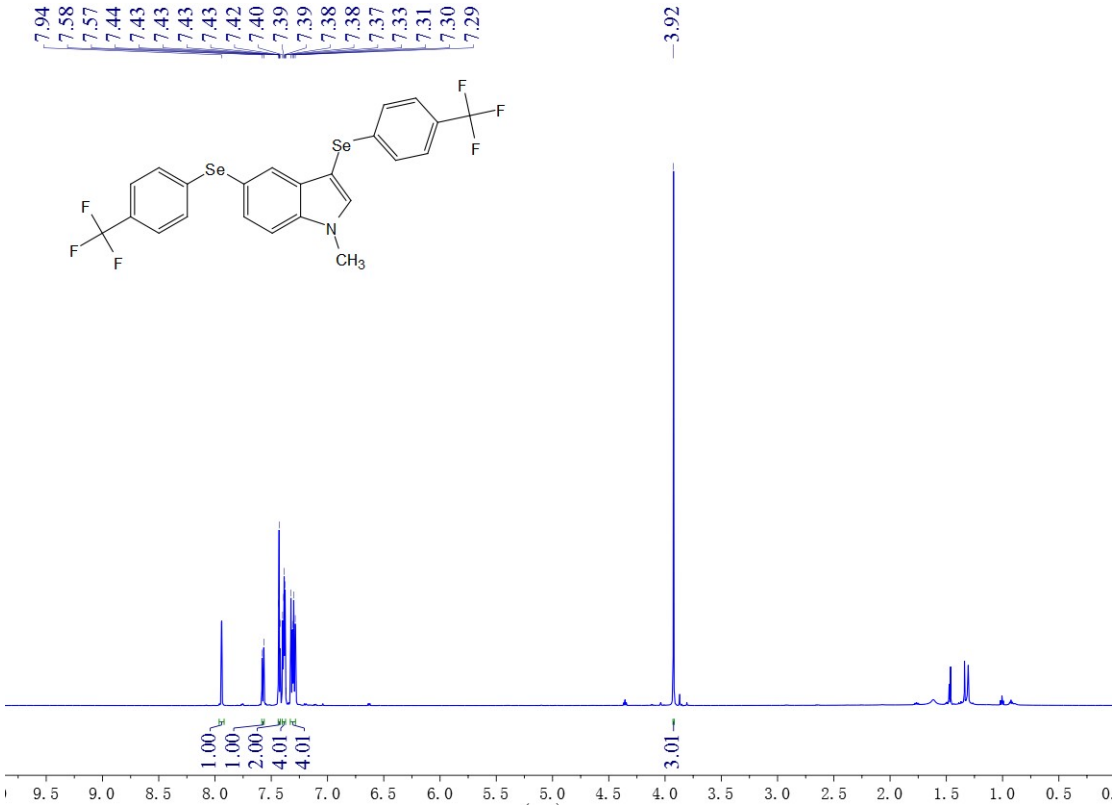
(81) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3as



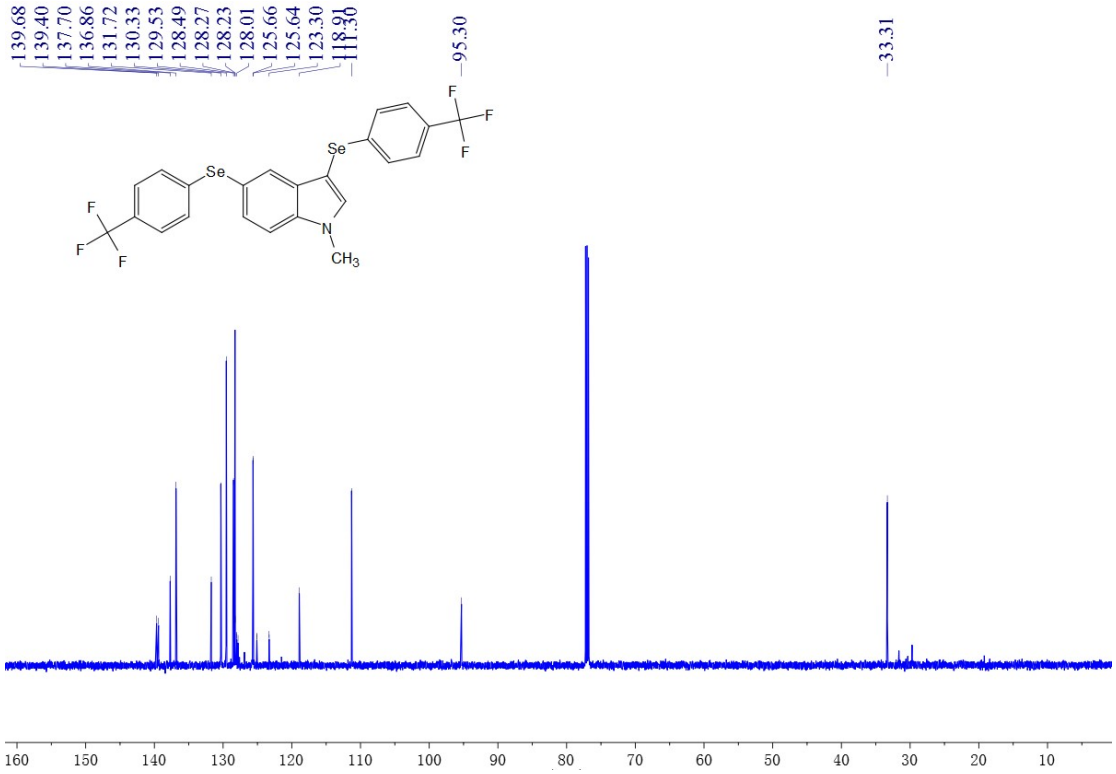
(82) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3as



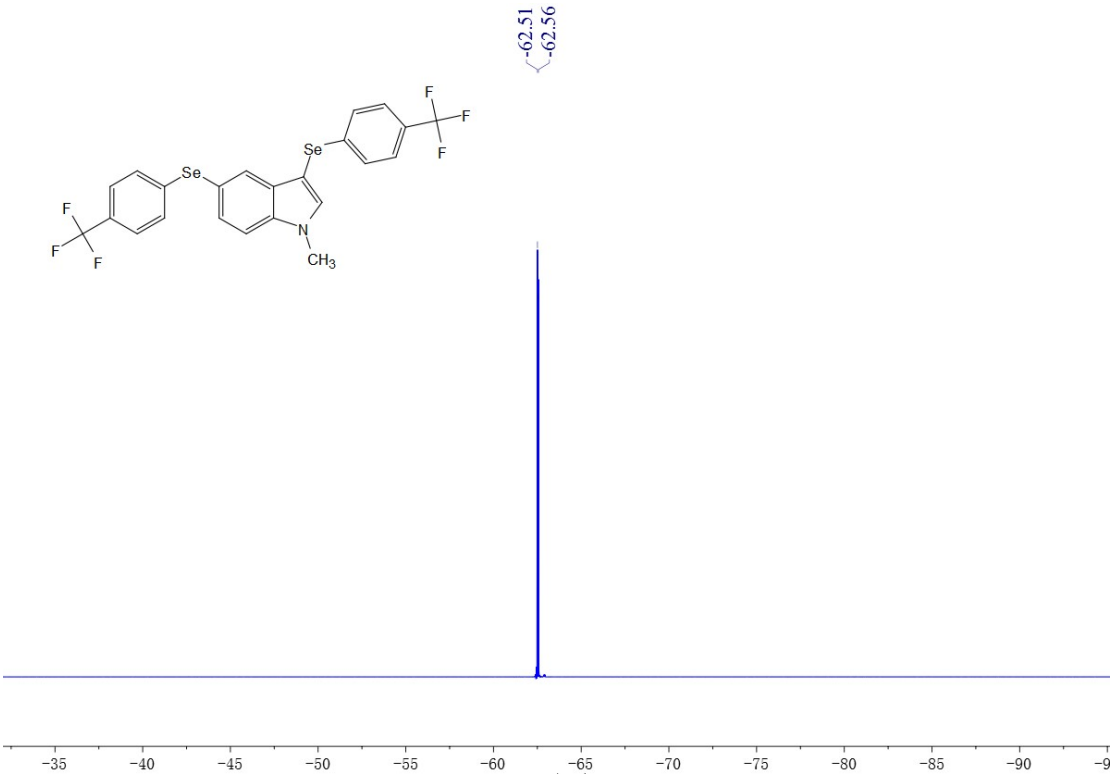
(83) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 3at



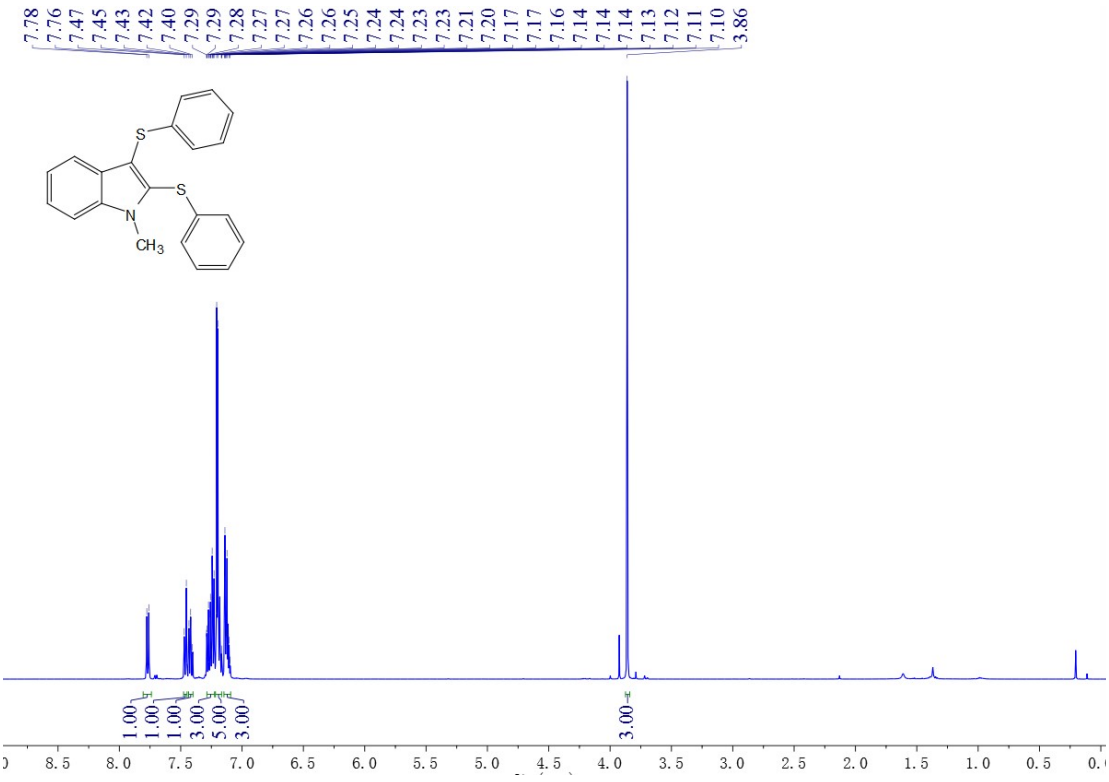
(84) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 3at



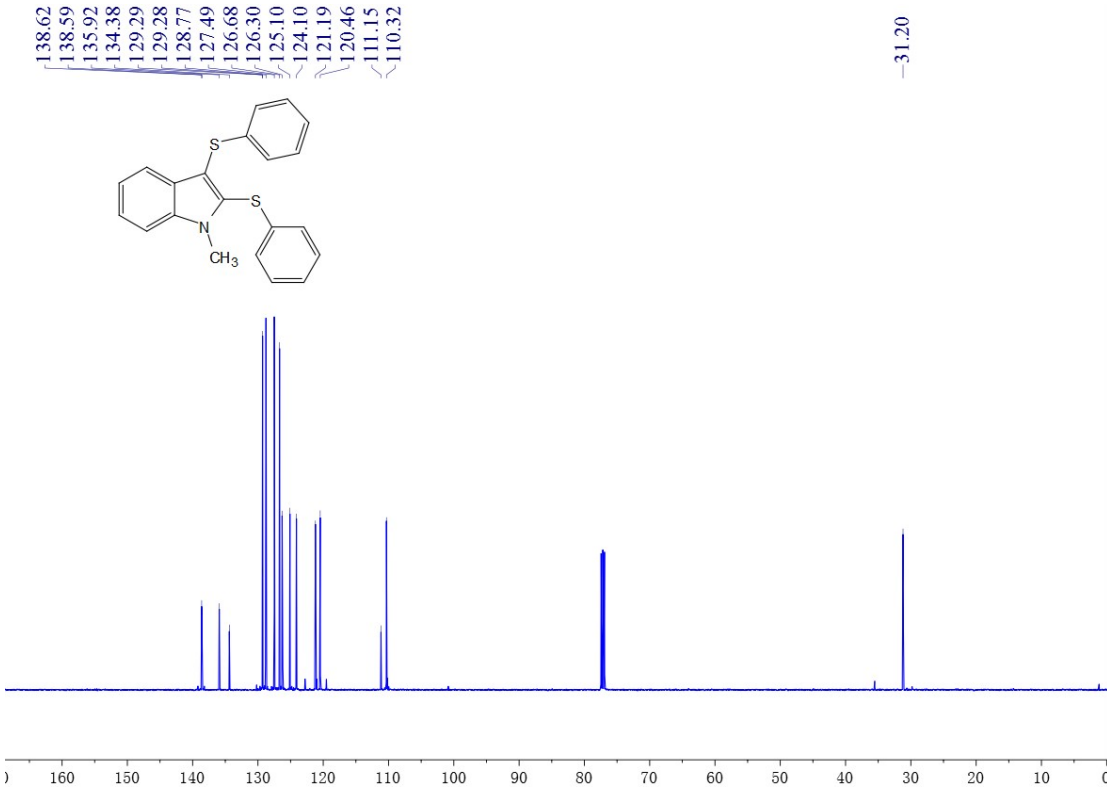
(85) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 3at



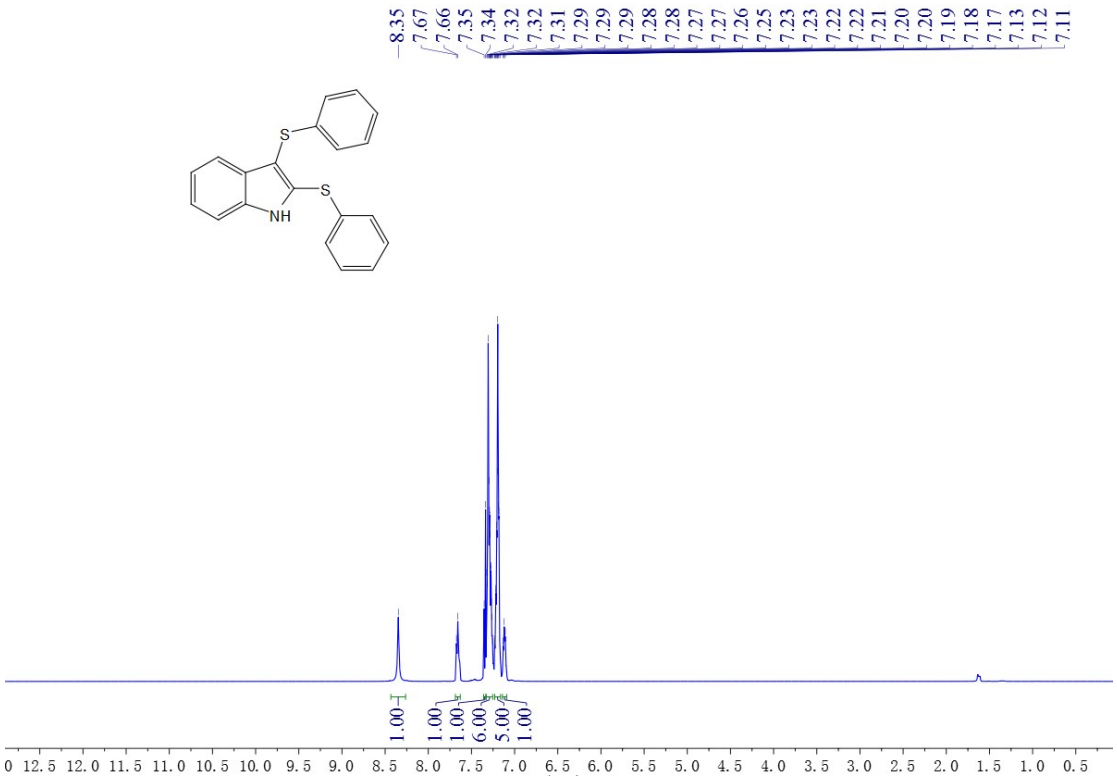
(86) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aa



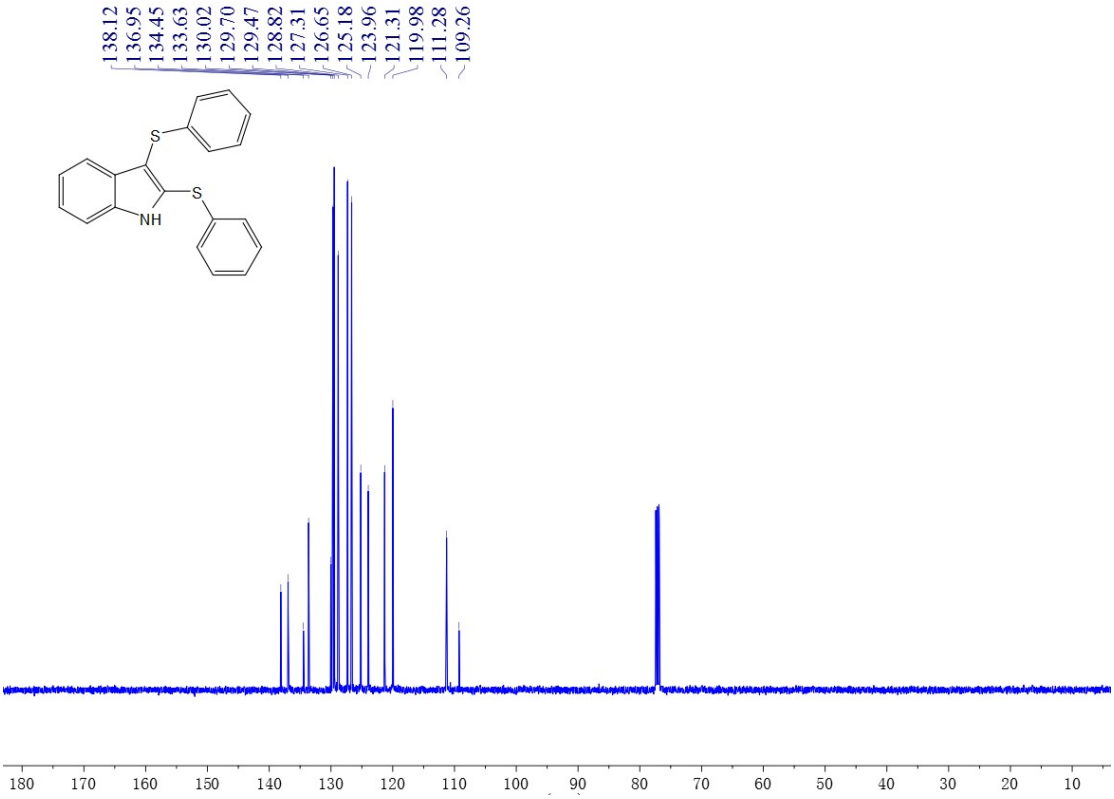
(87) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4aa



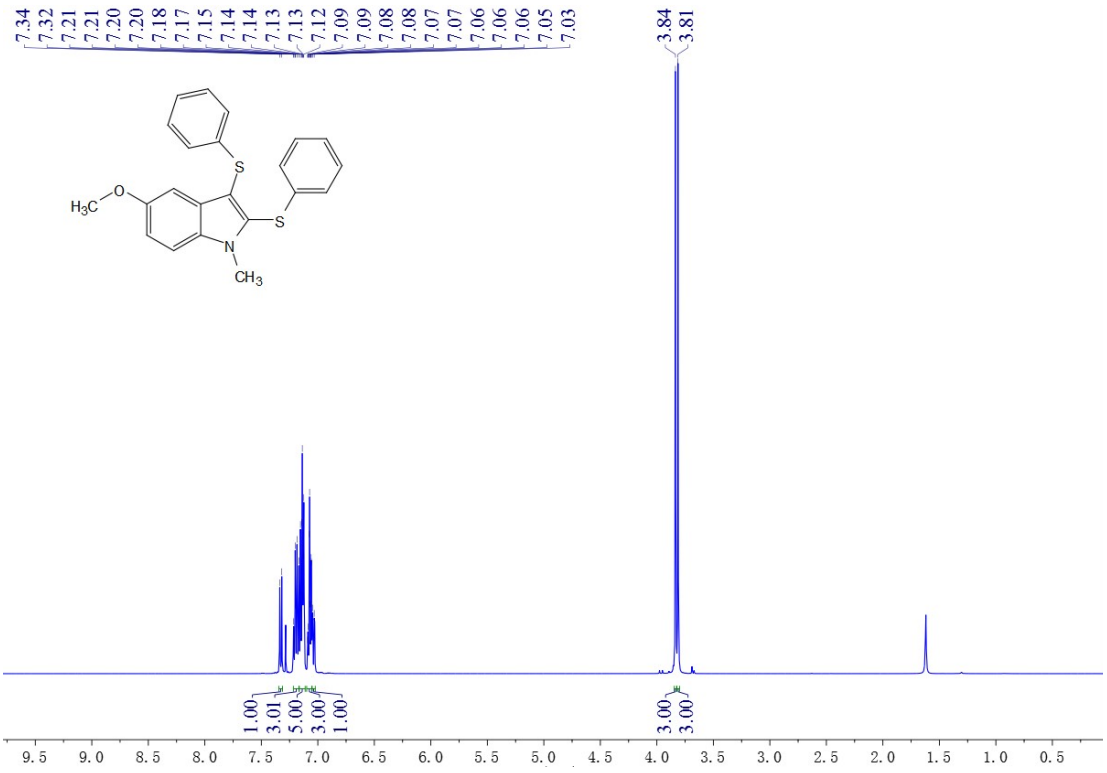
(88) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ba



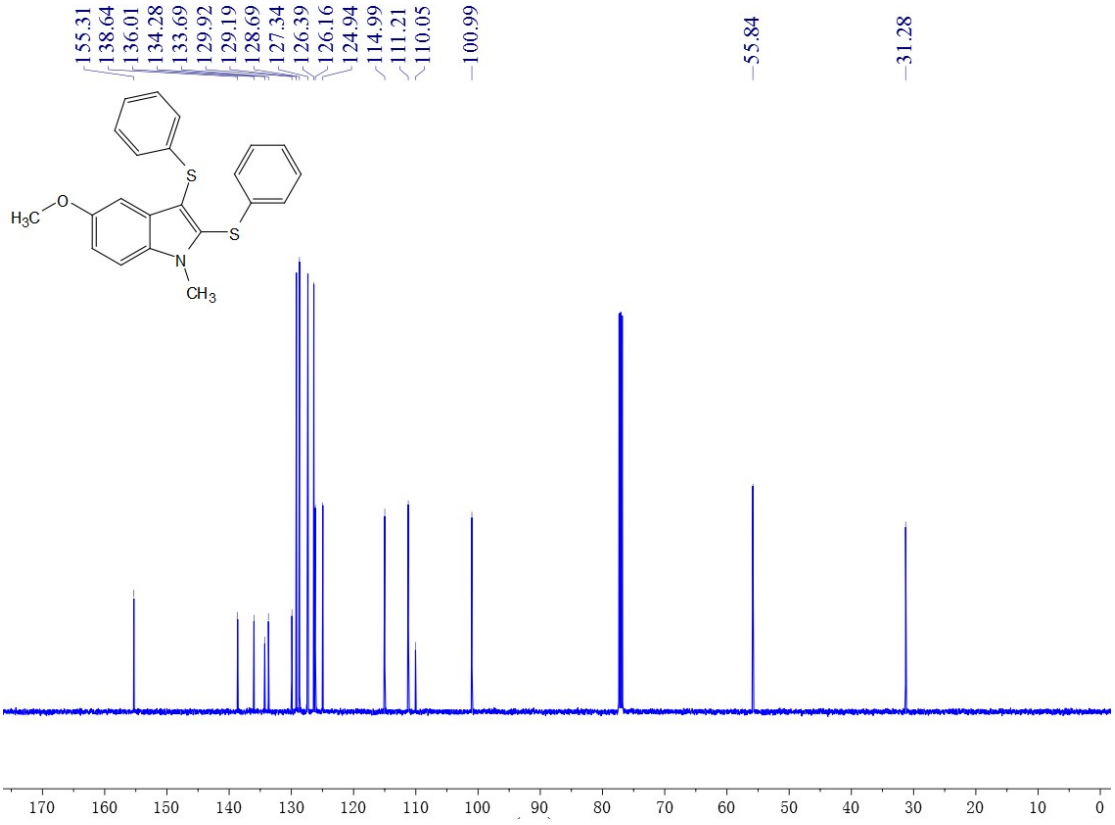
(89) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ba



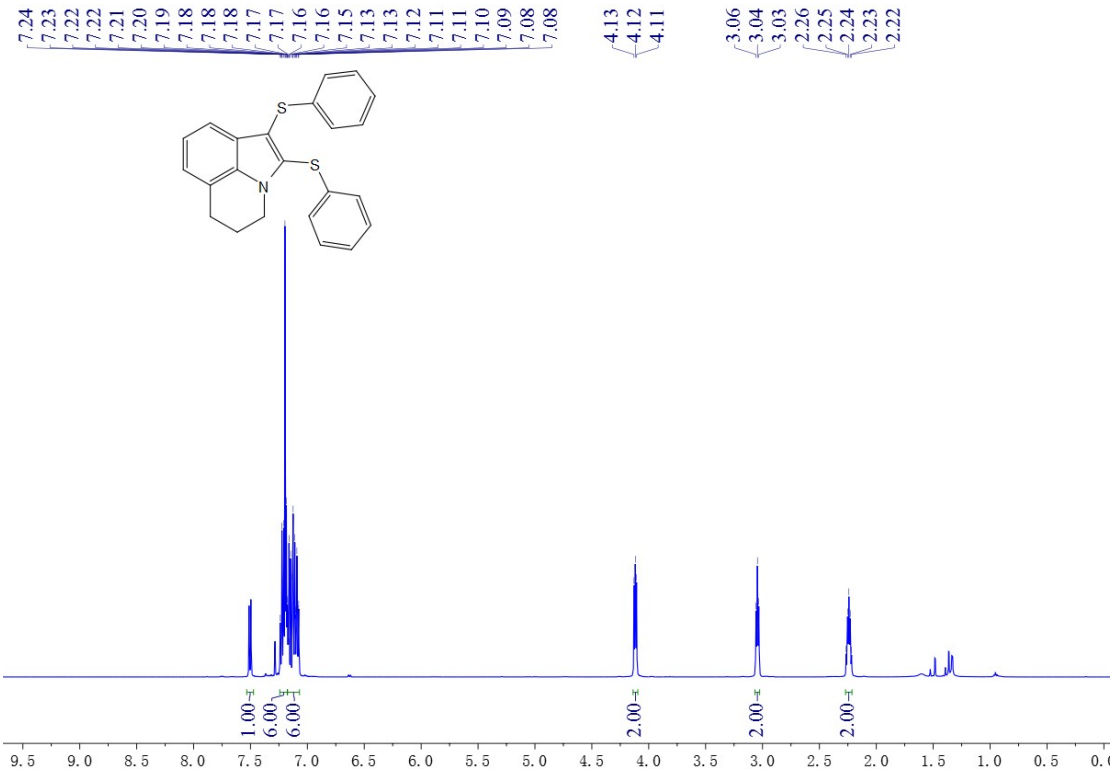
(90) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ca



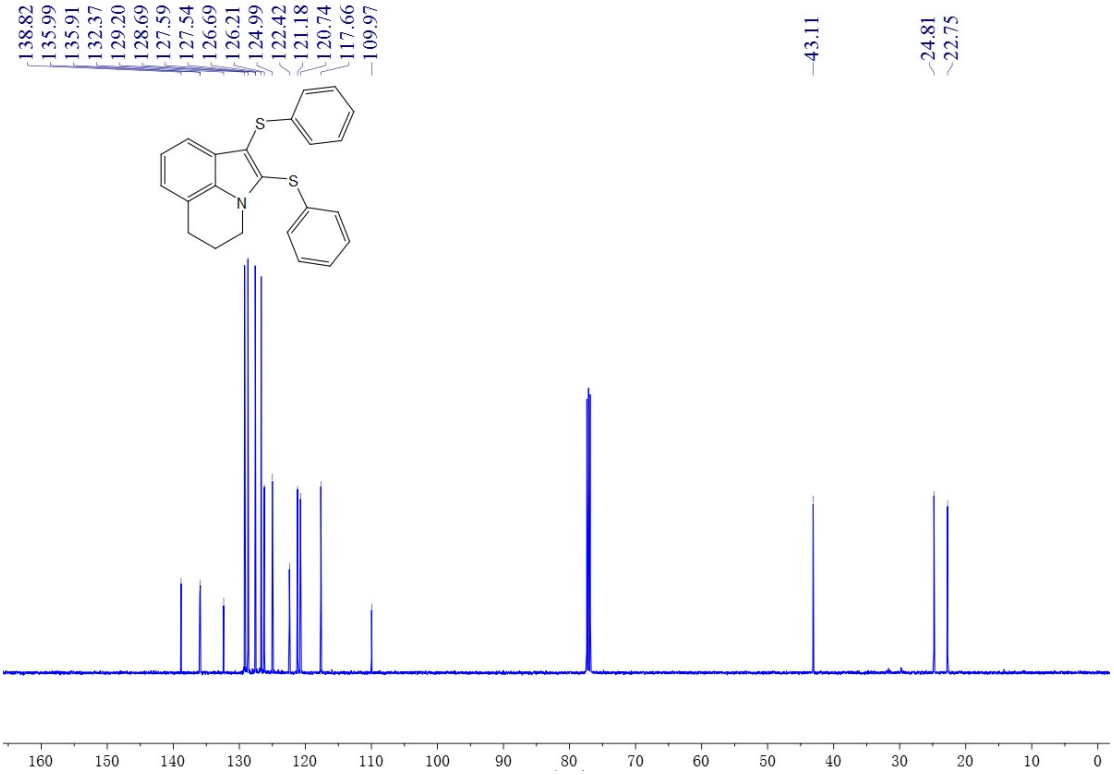
(91) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ca



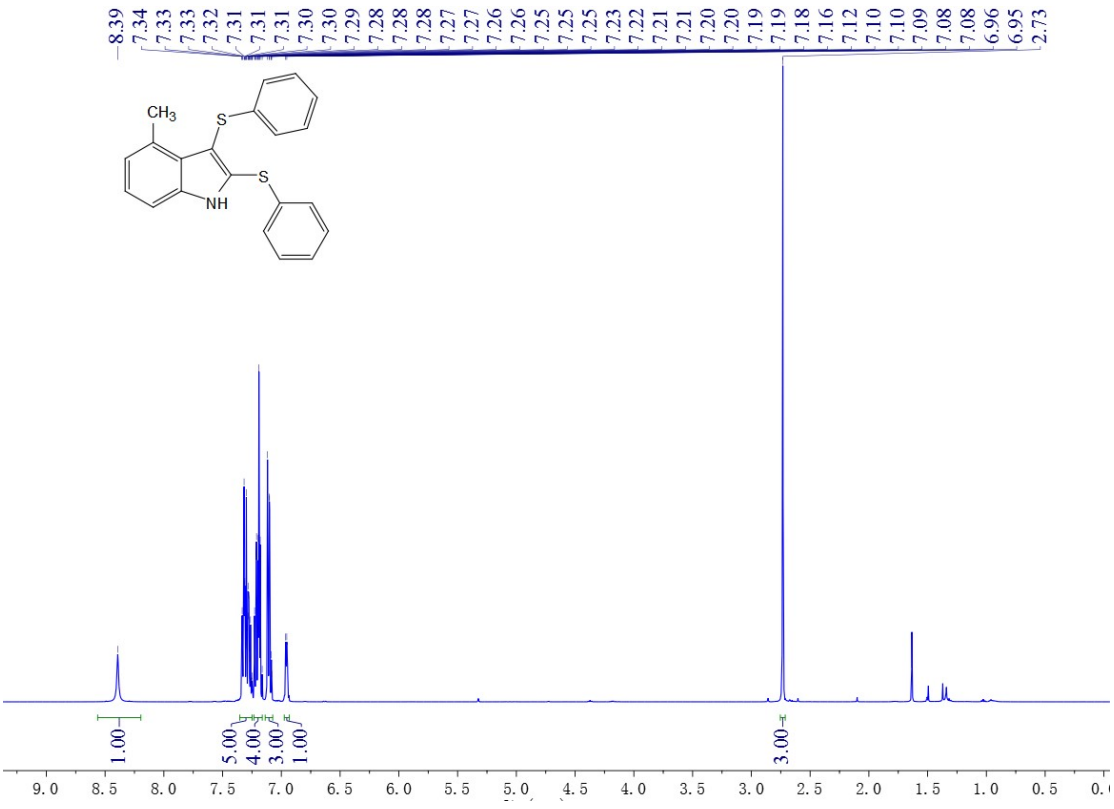
(92) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4da



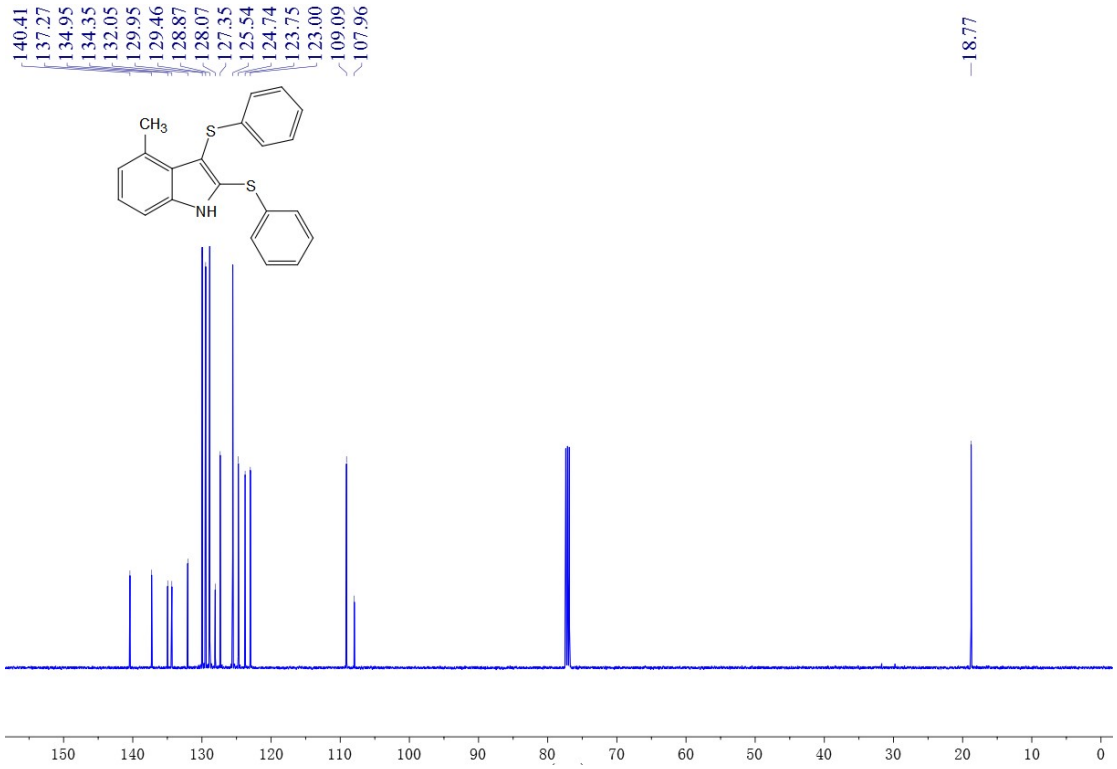
(93) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4da



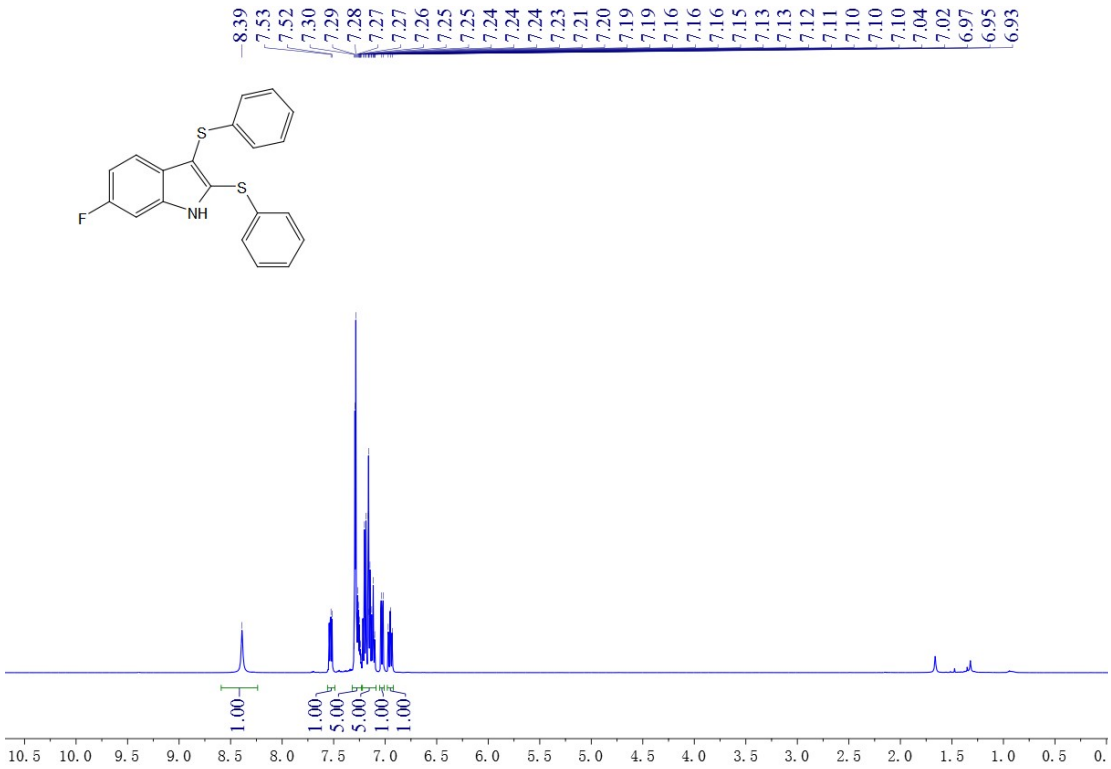
(94) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ea



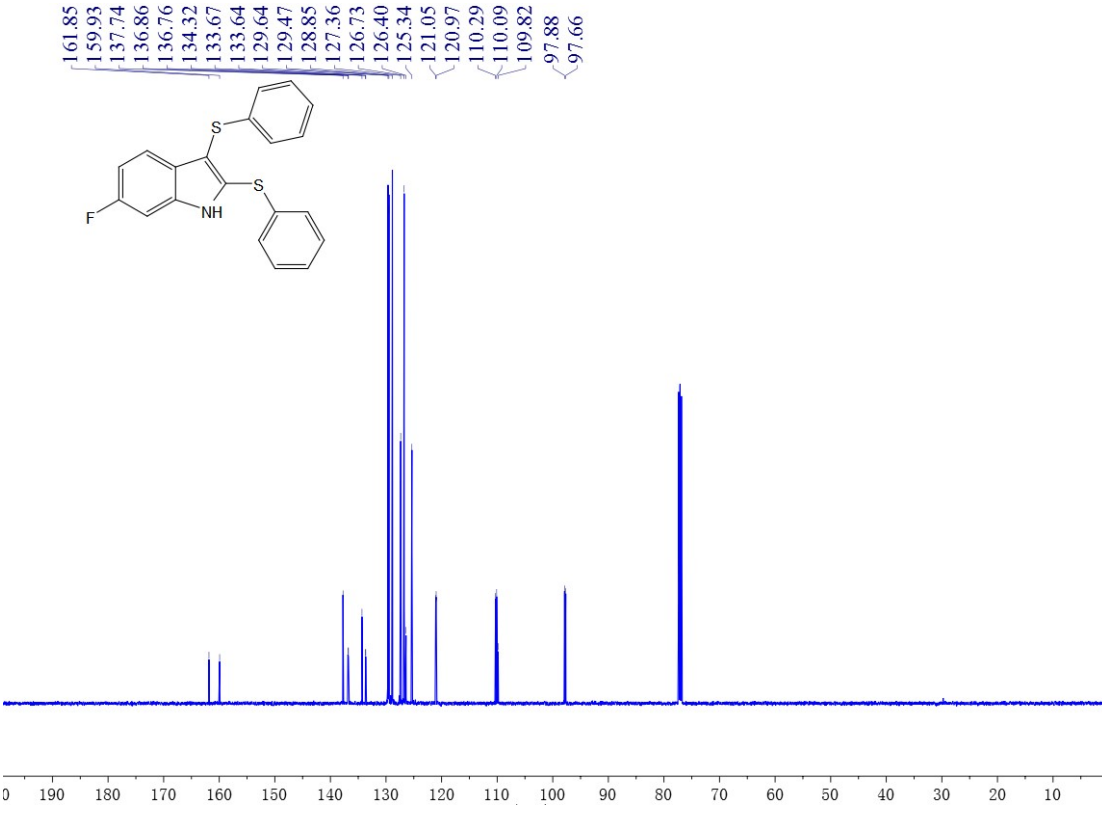
(95) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ea



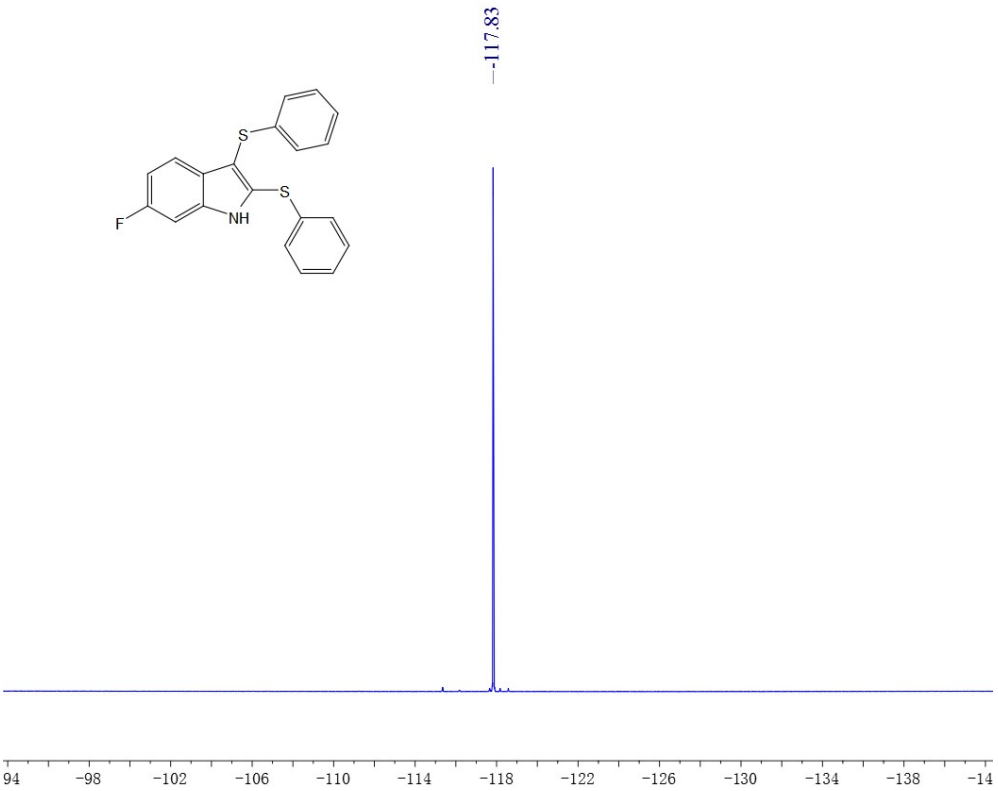
(96) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4fa



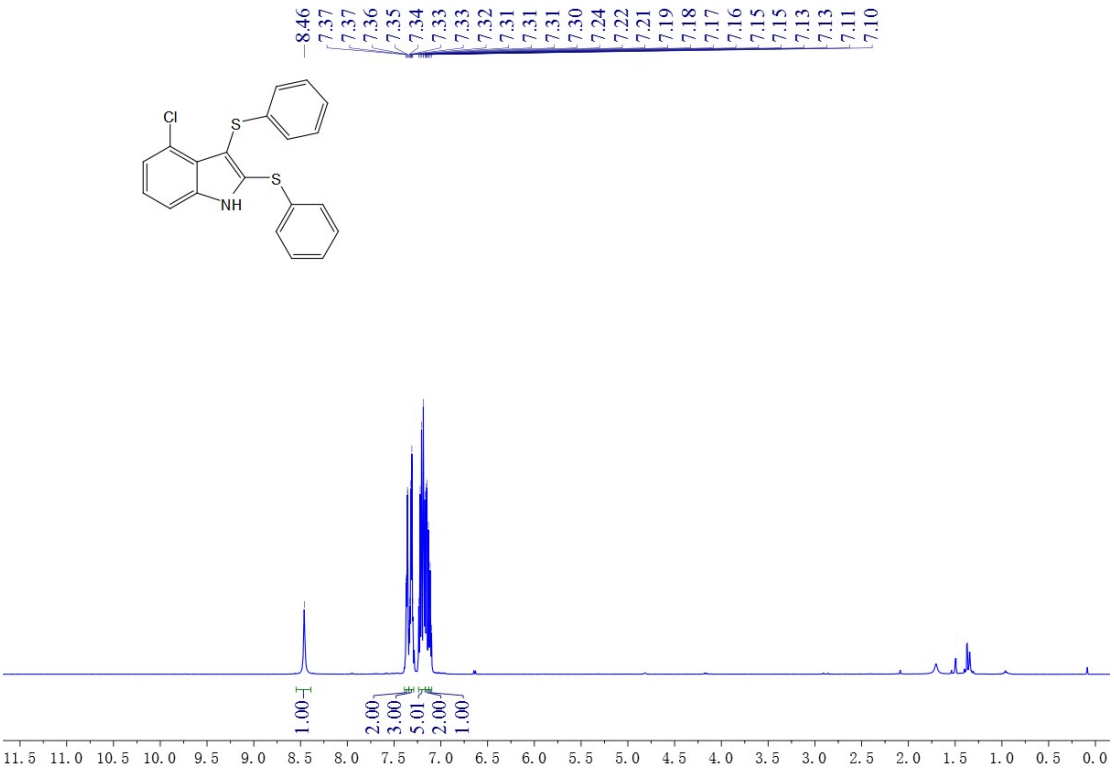
(97) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4fa



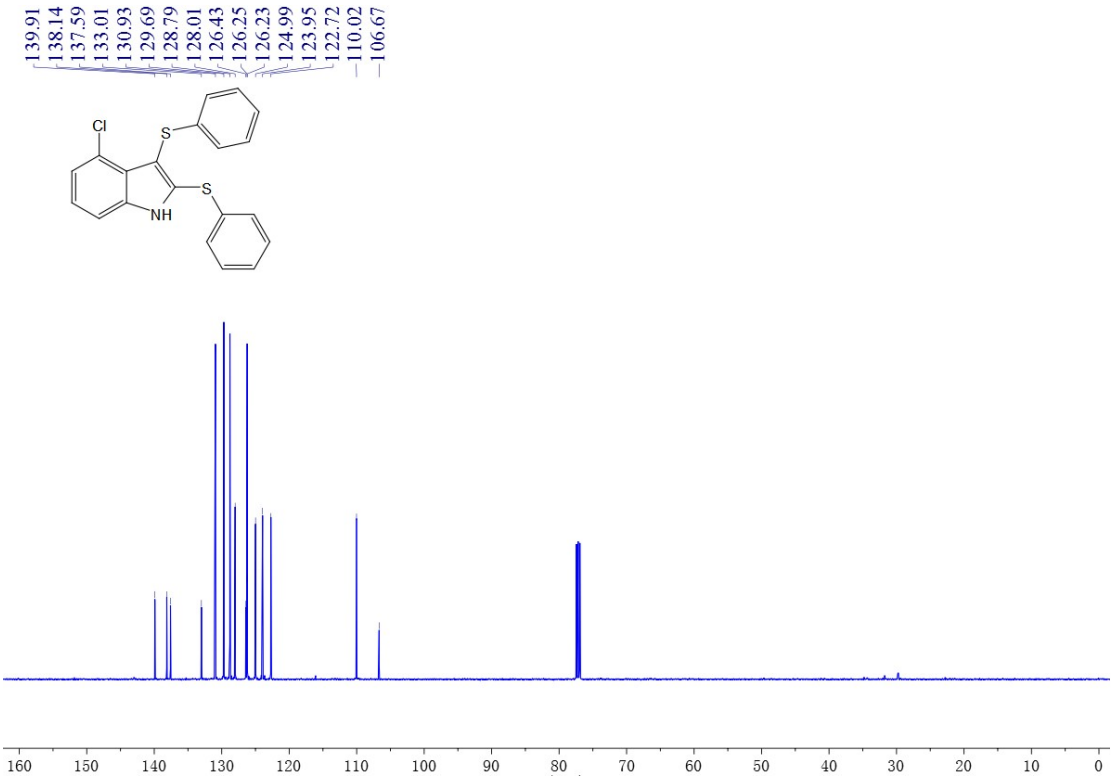
(98) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 4fa



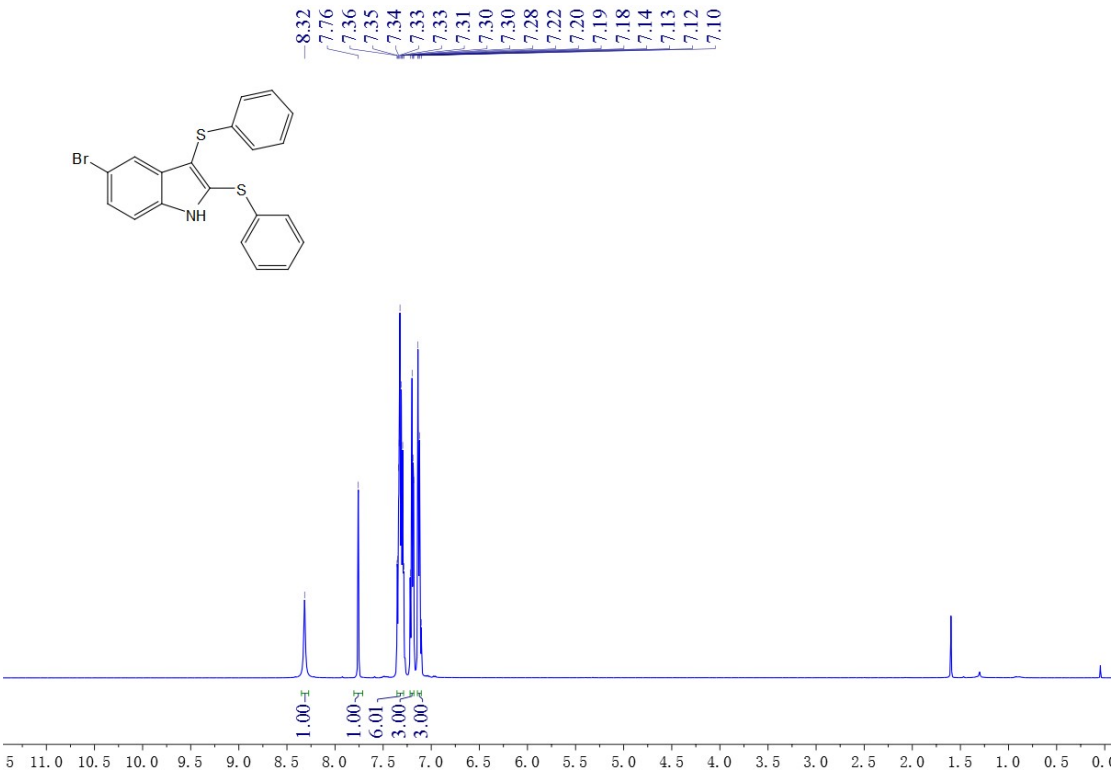
(99) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ga



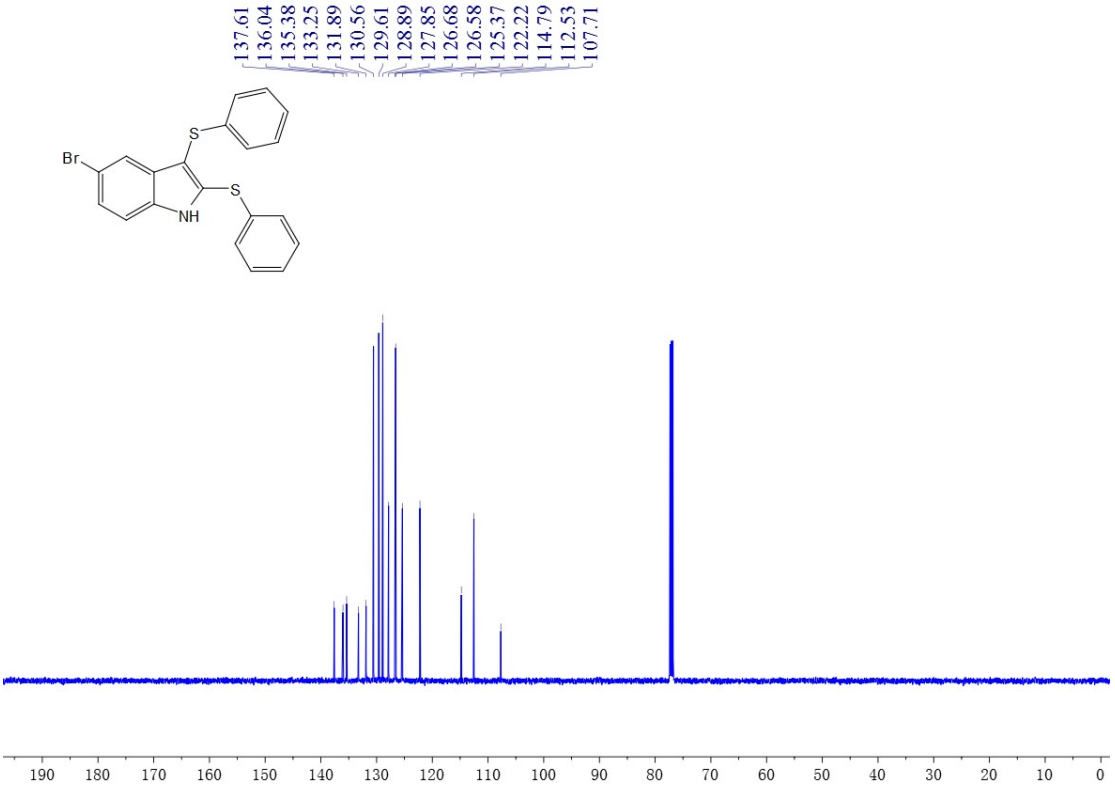
(100) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ga



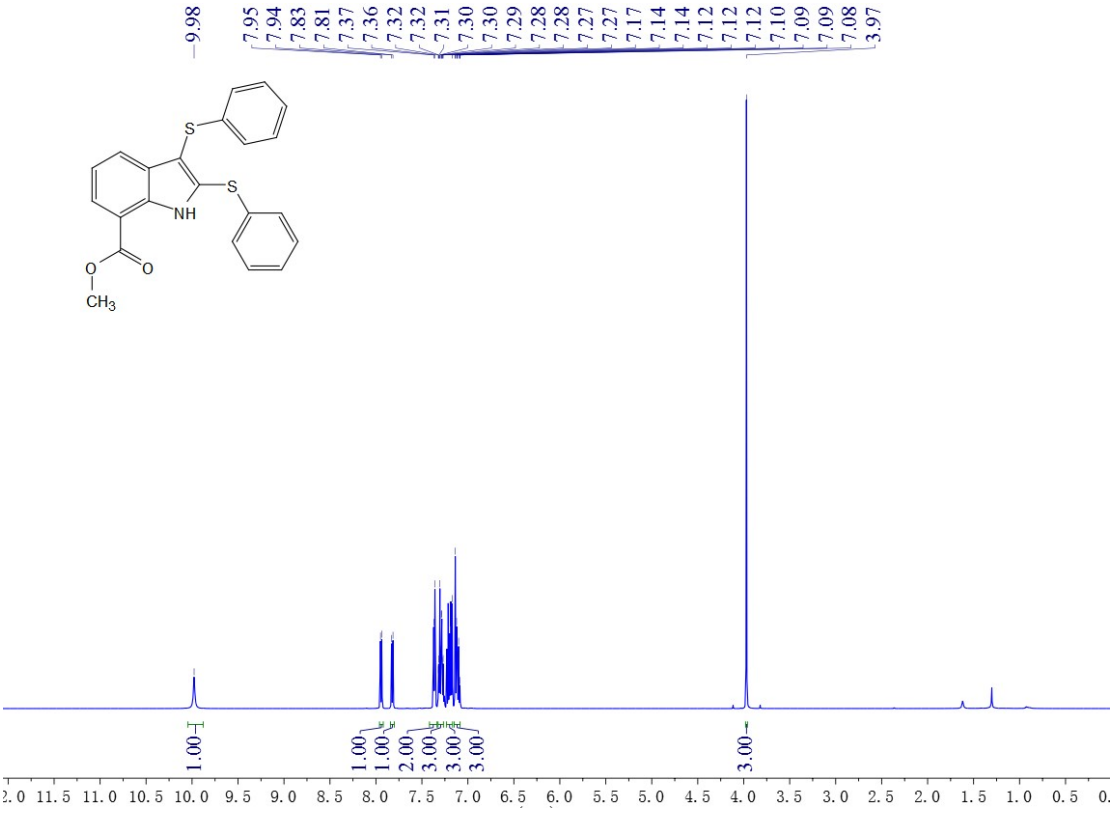
(101) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ha



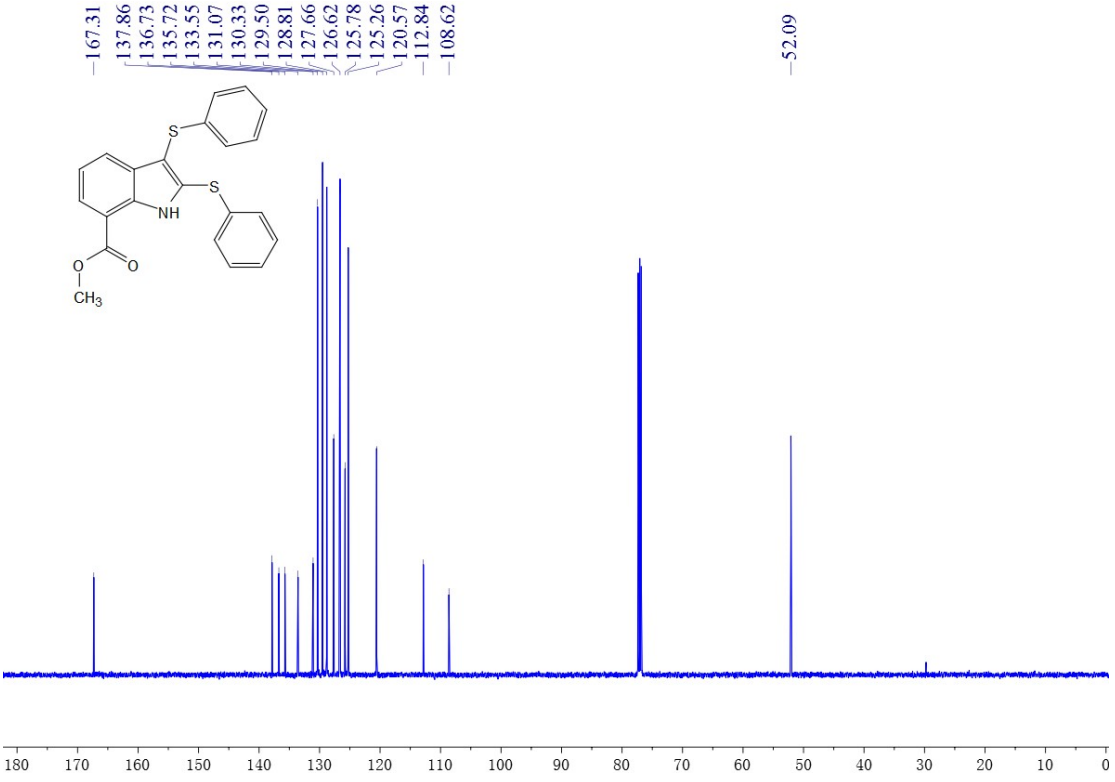
(102) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ha



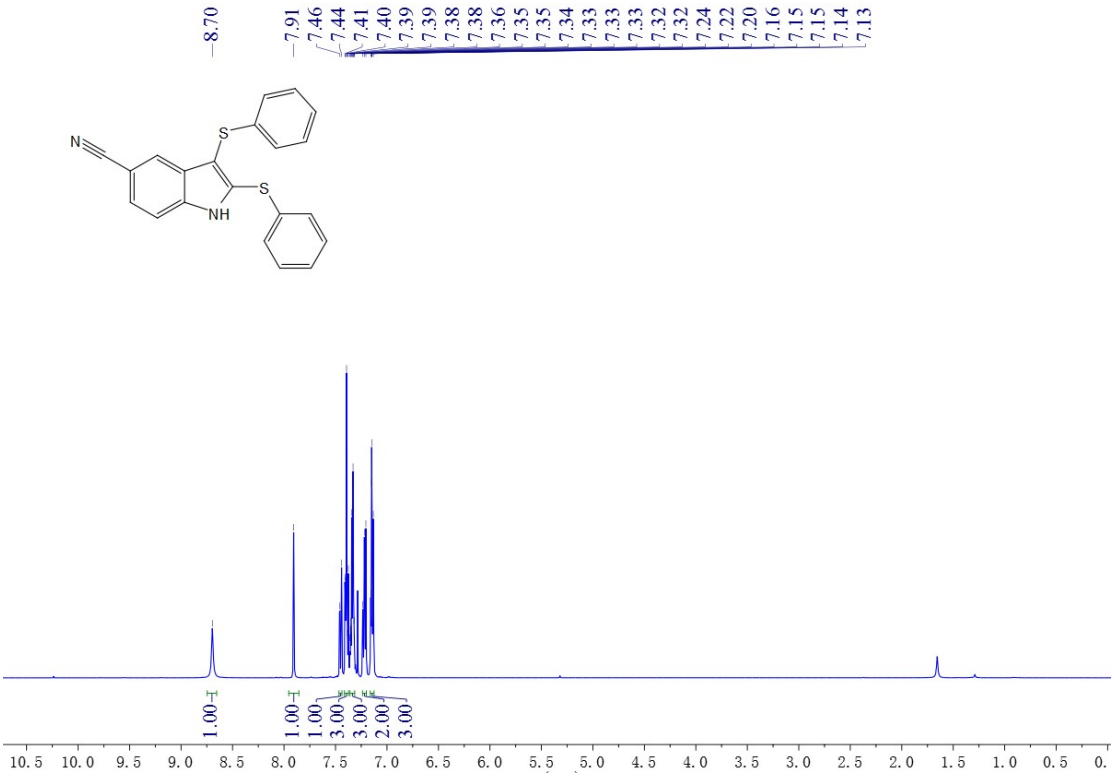
(103) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ia



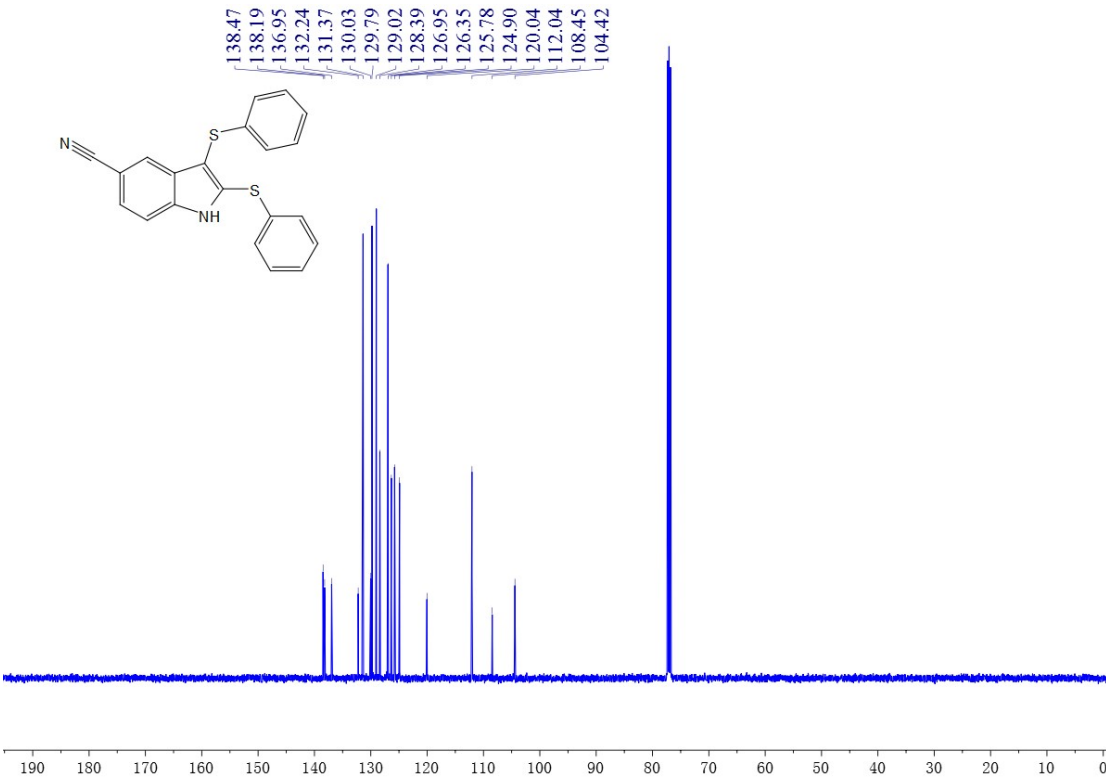
(104) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ia



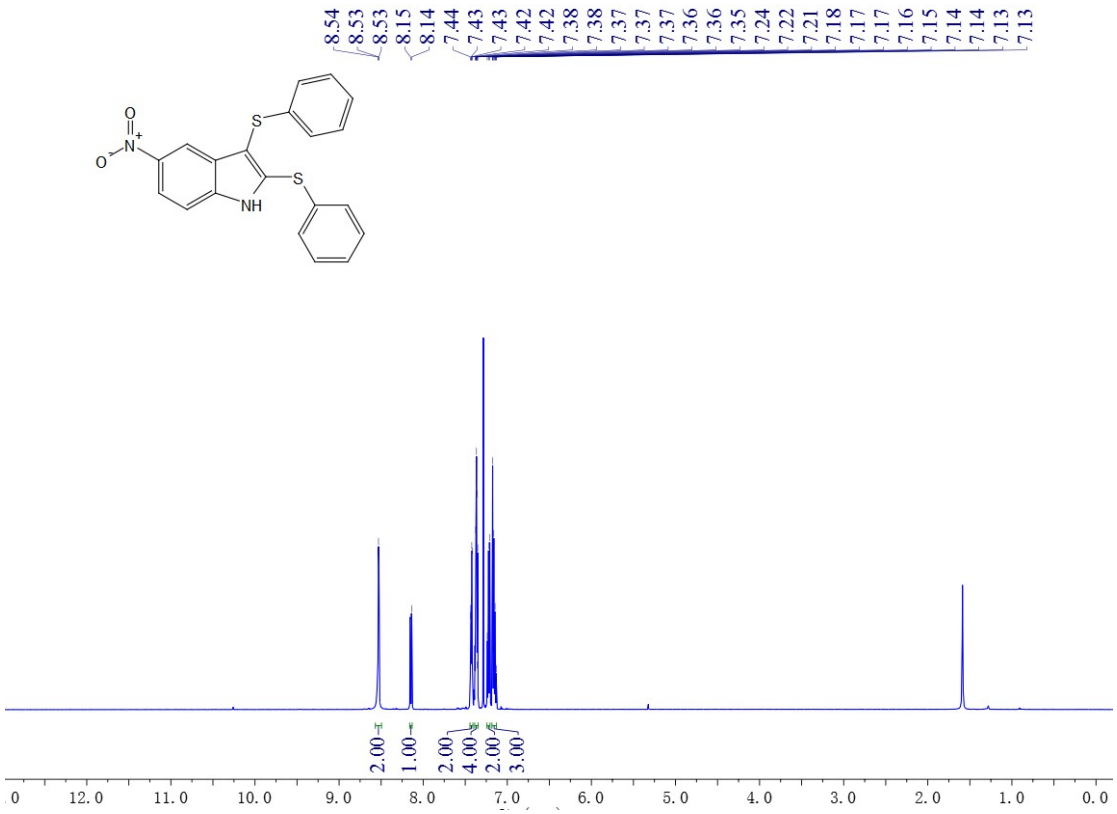
(105) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ja



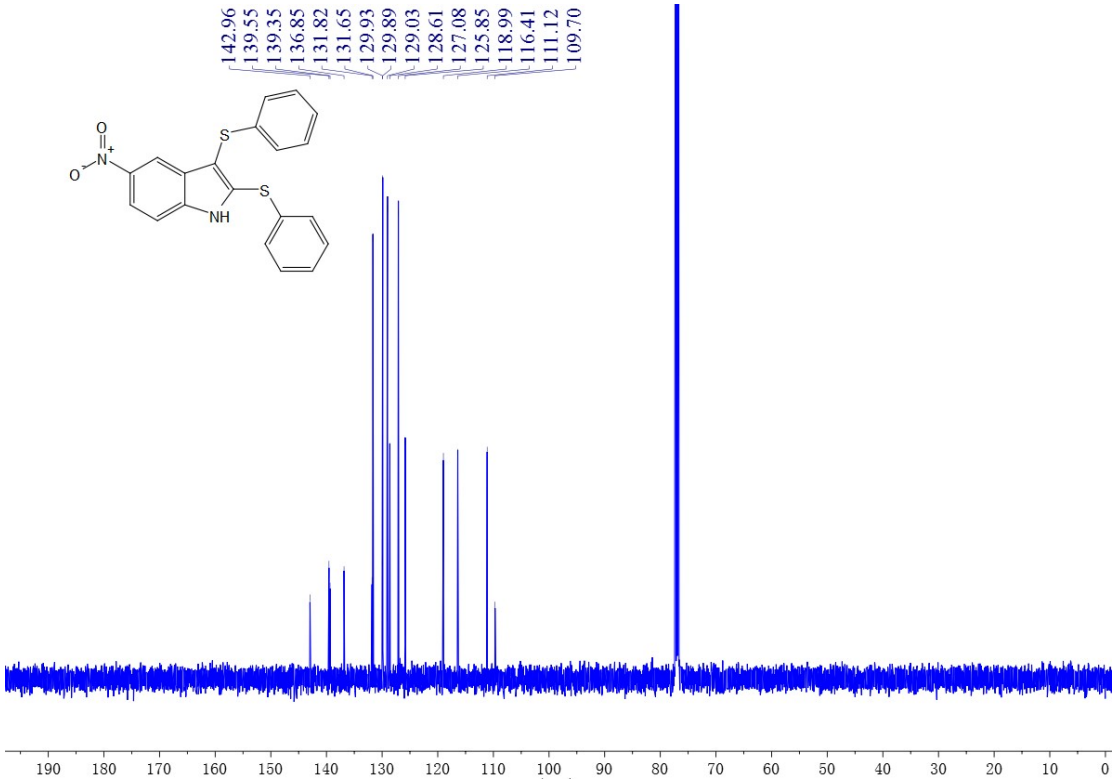
(106) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ja



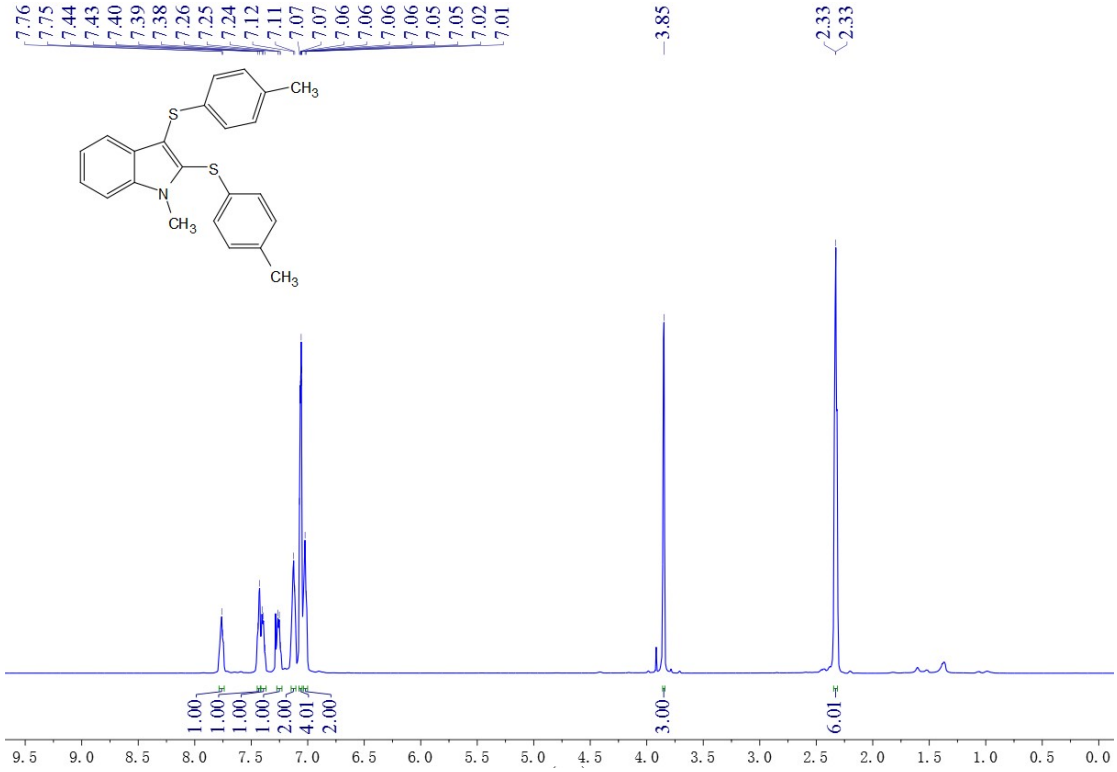
(107) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ka



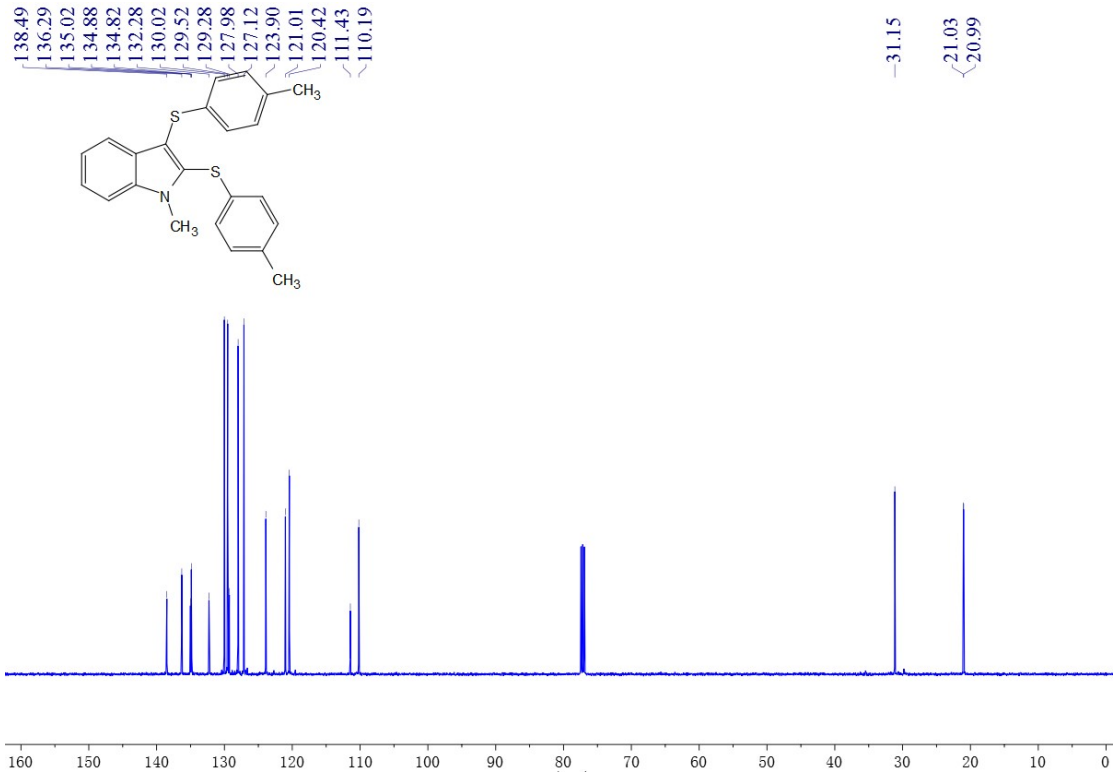
(108) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ka



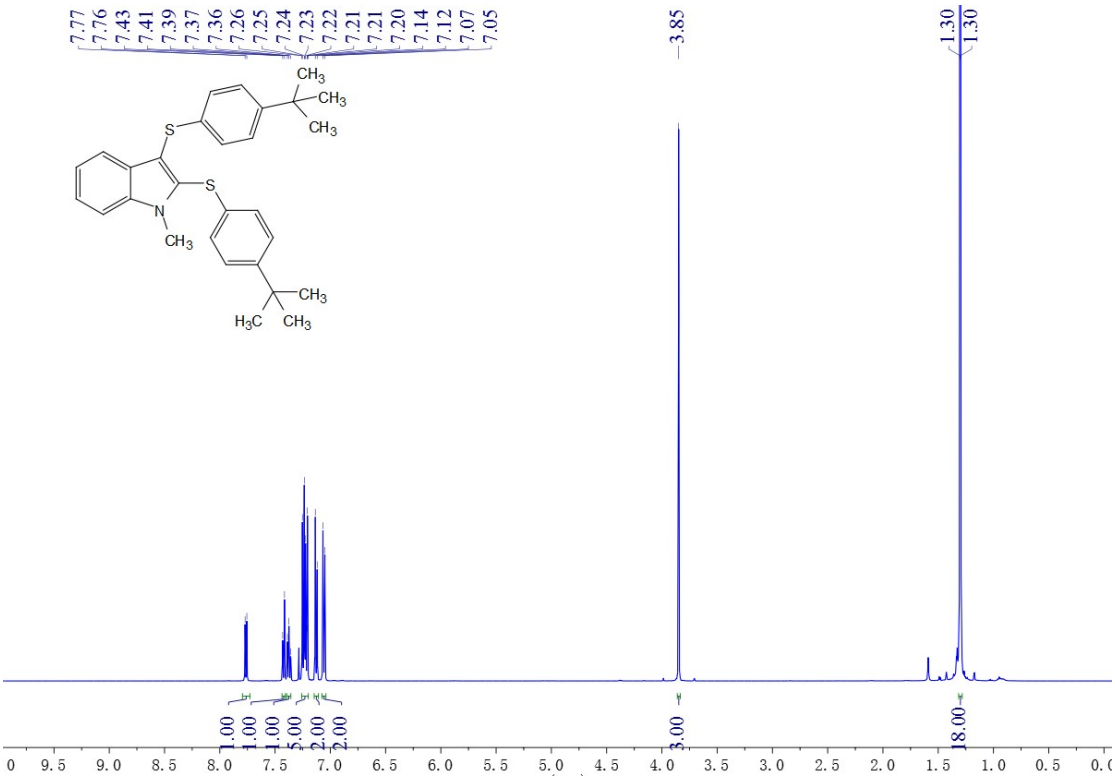
(109) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ab



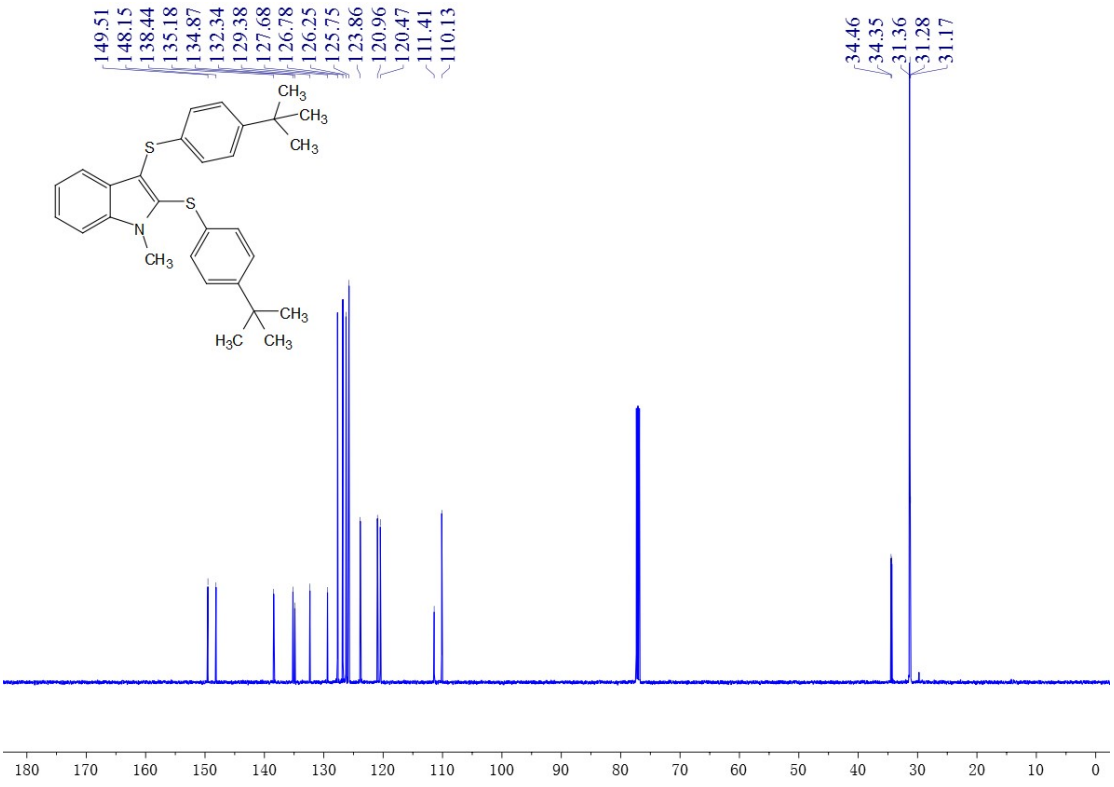
(110) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ab



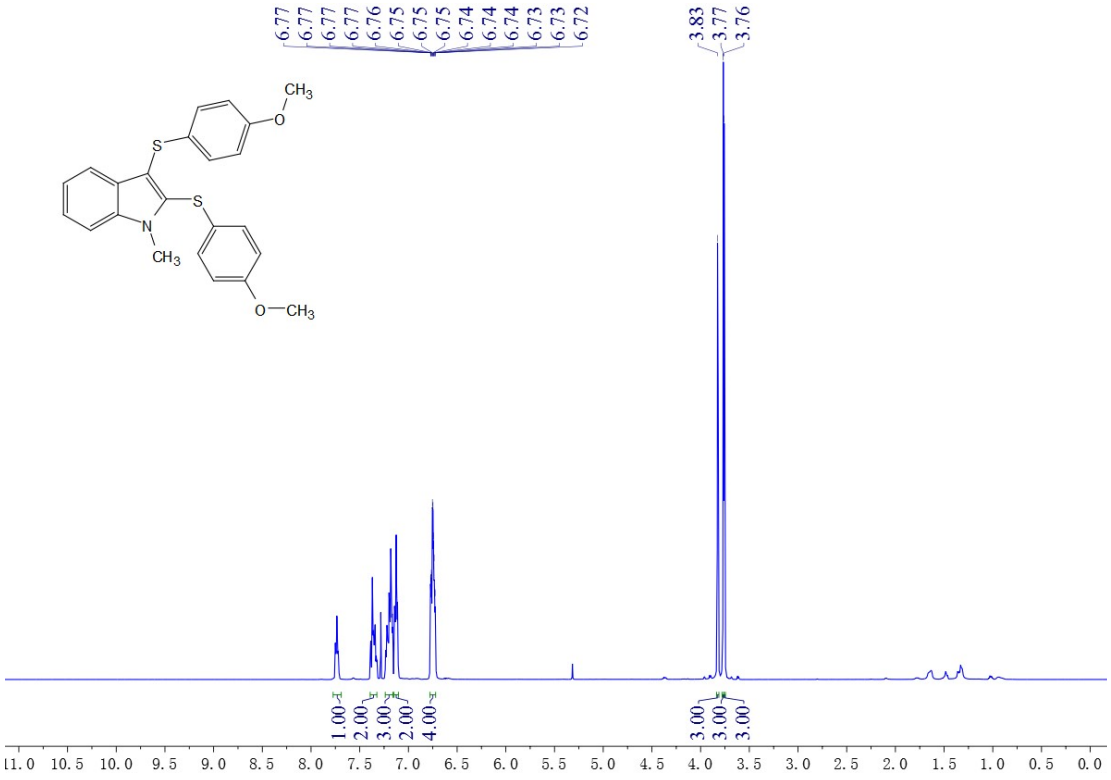
(111) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ac



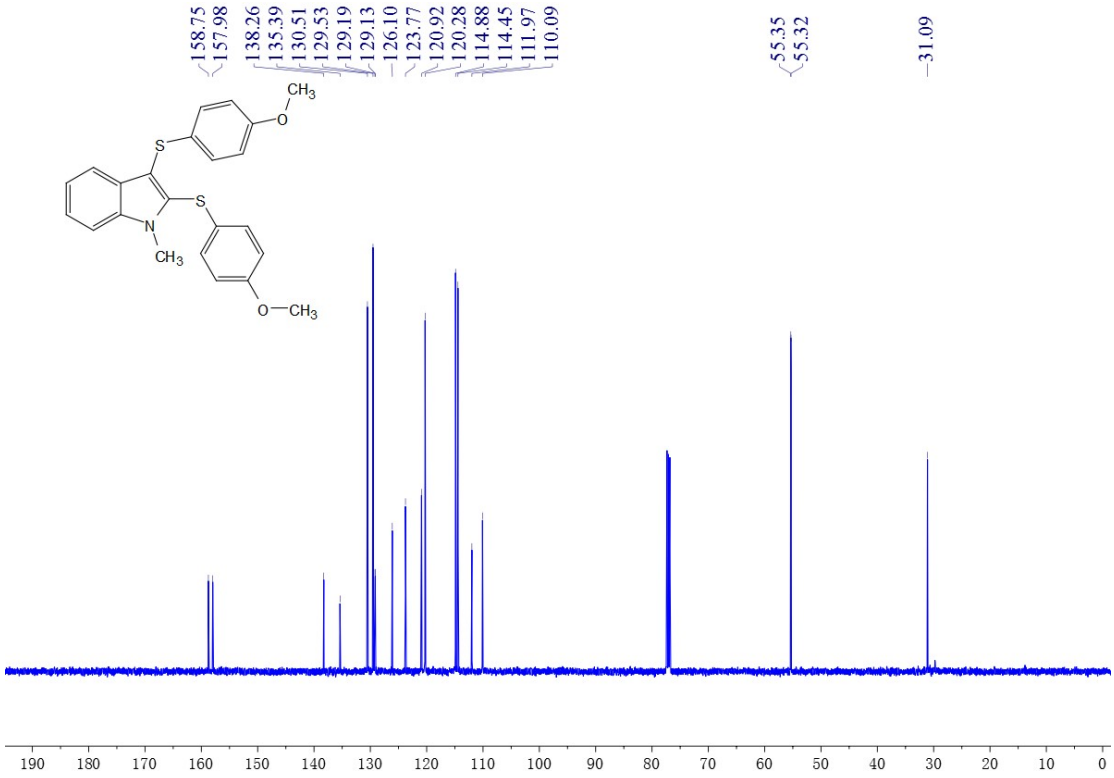
(112) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ac



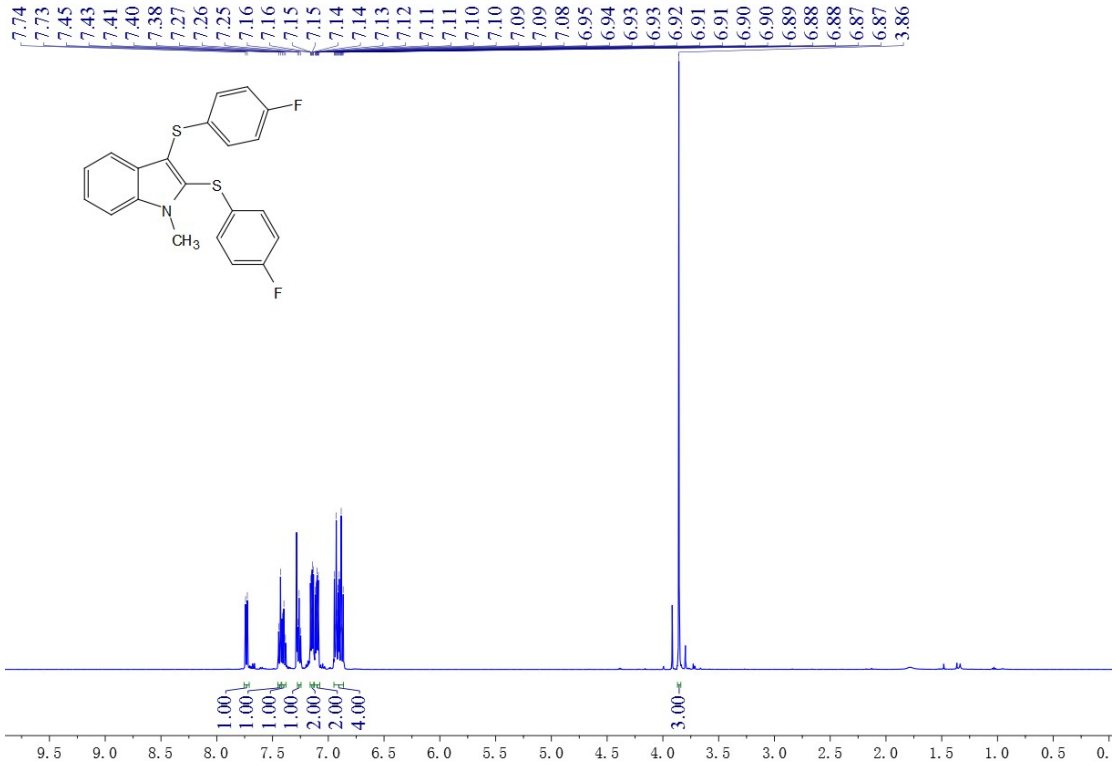
(113) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ad



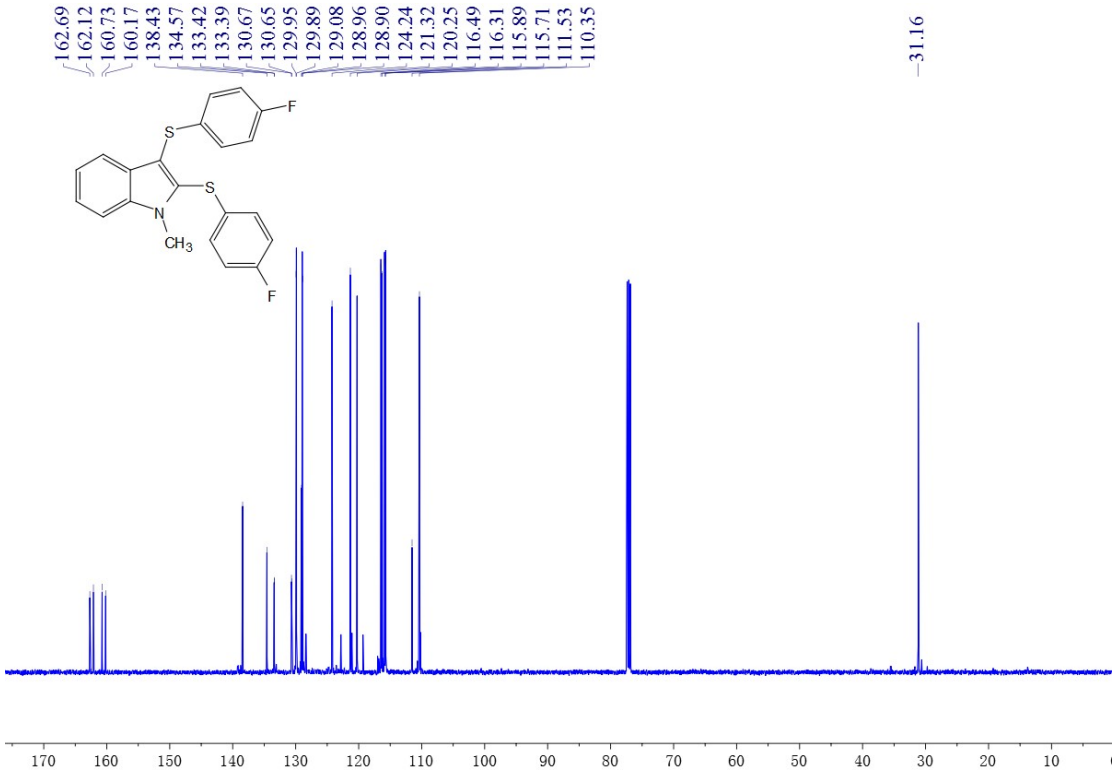
(114) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ad



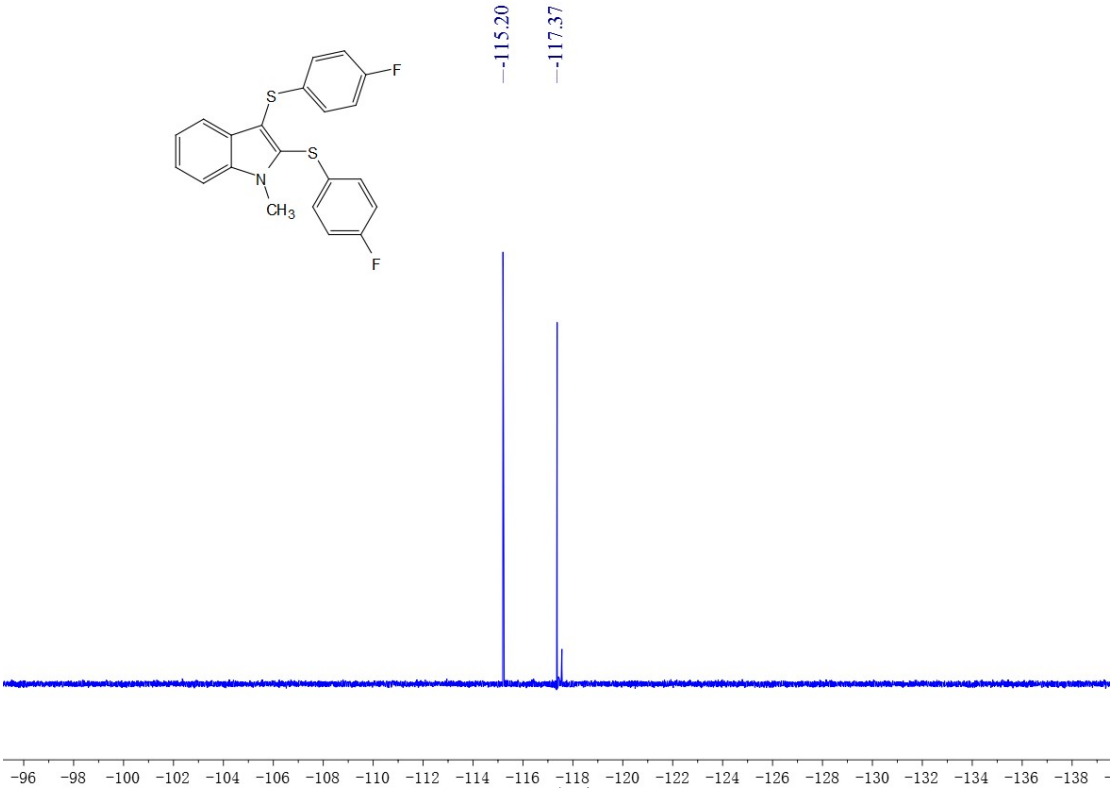
(115) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ae



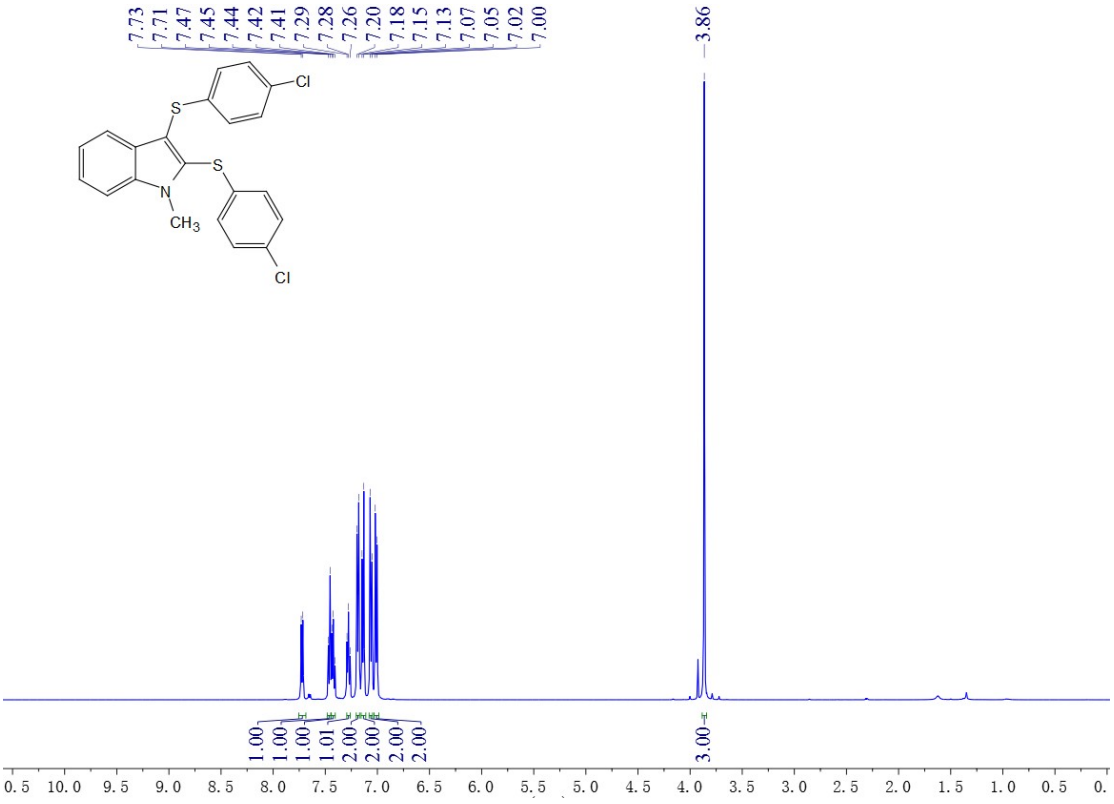
(116) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ae



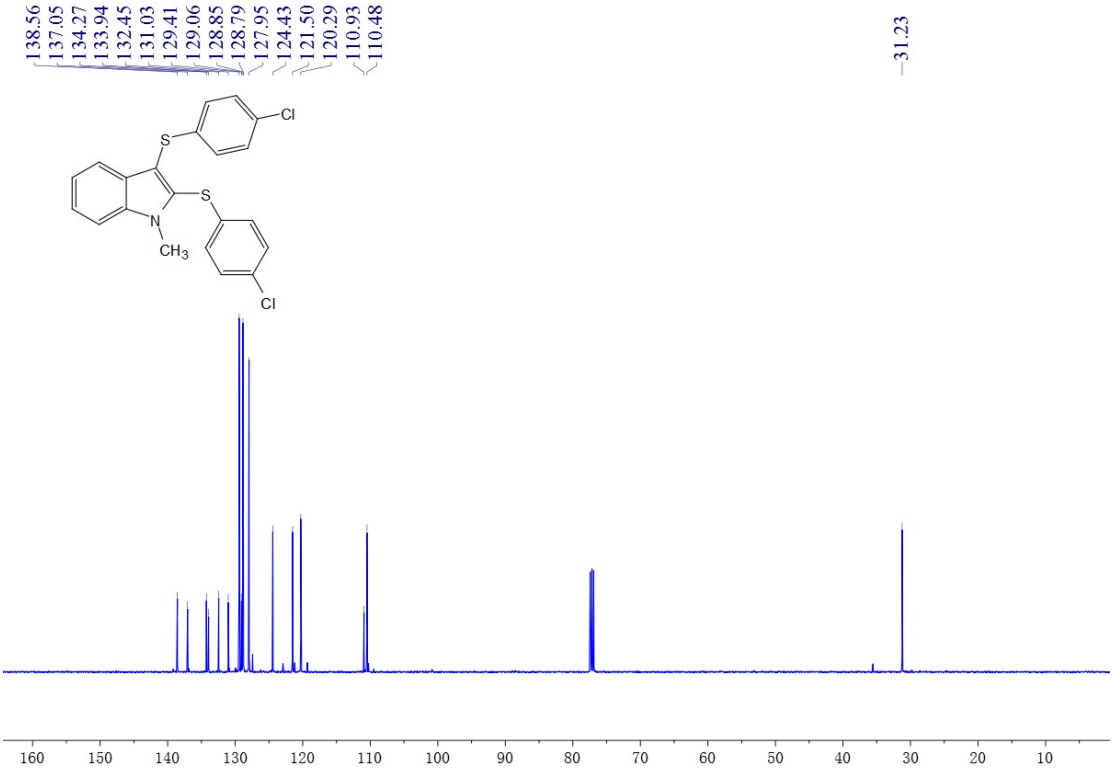
(117) ^{19}F-NMR (126 MHz, $CDCl_3$) spectrum of 4ae



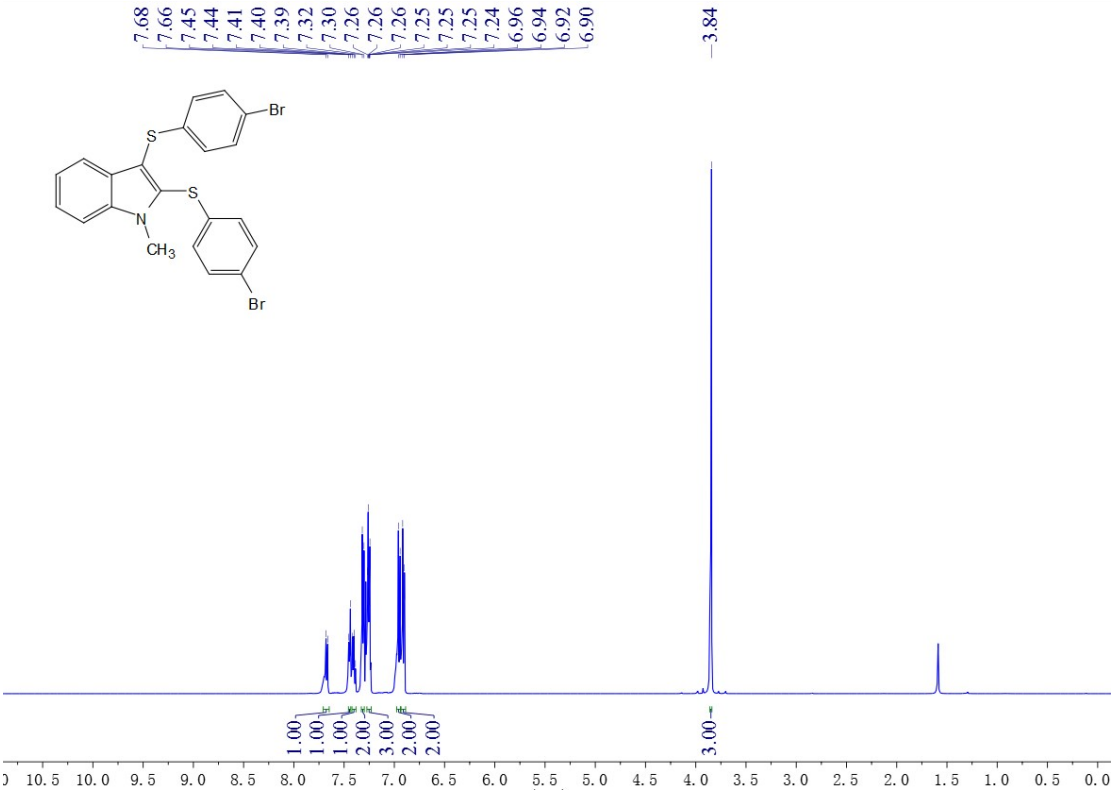
(118) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4af



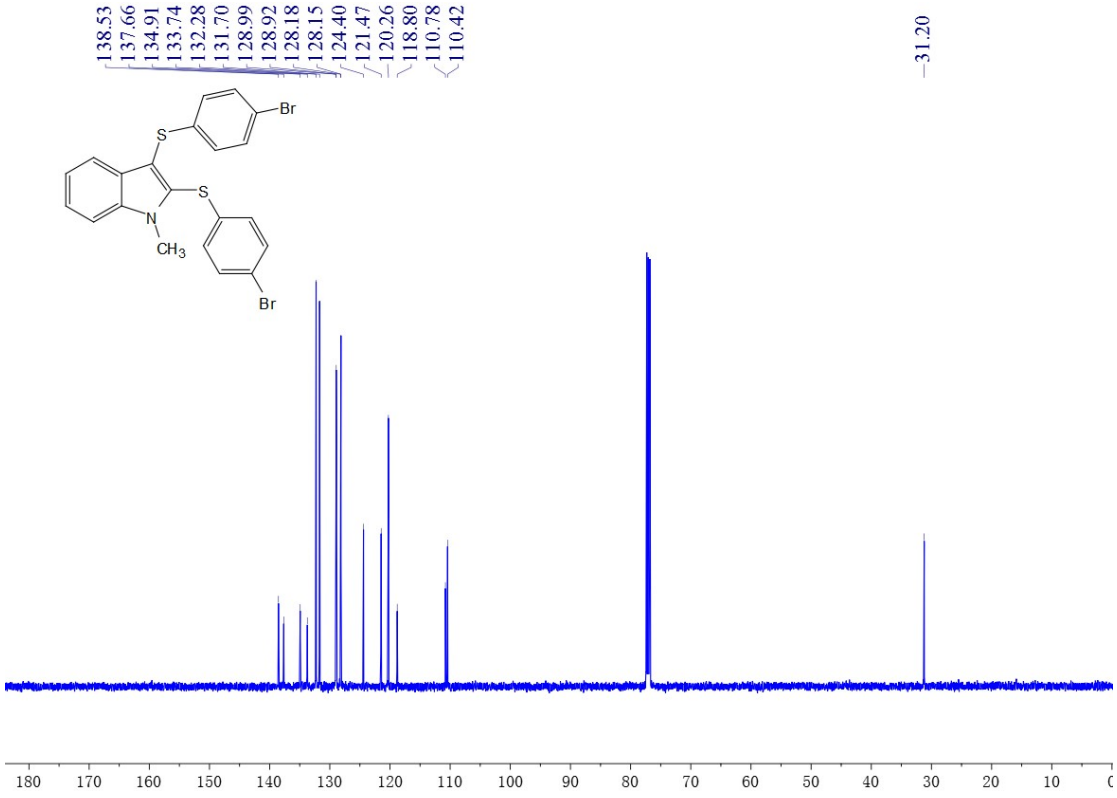
(119) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4af



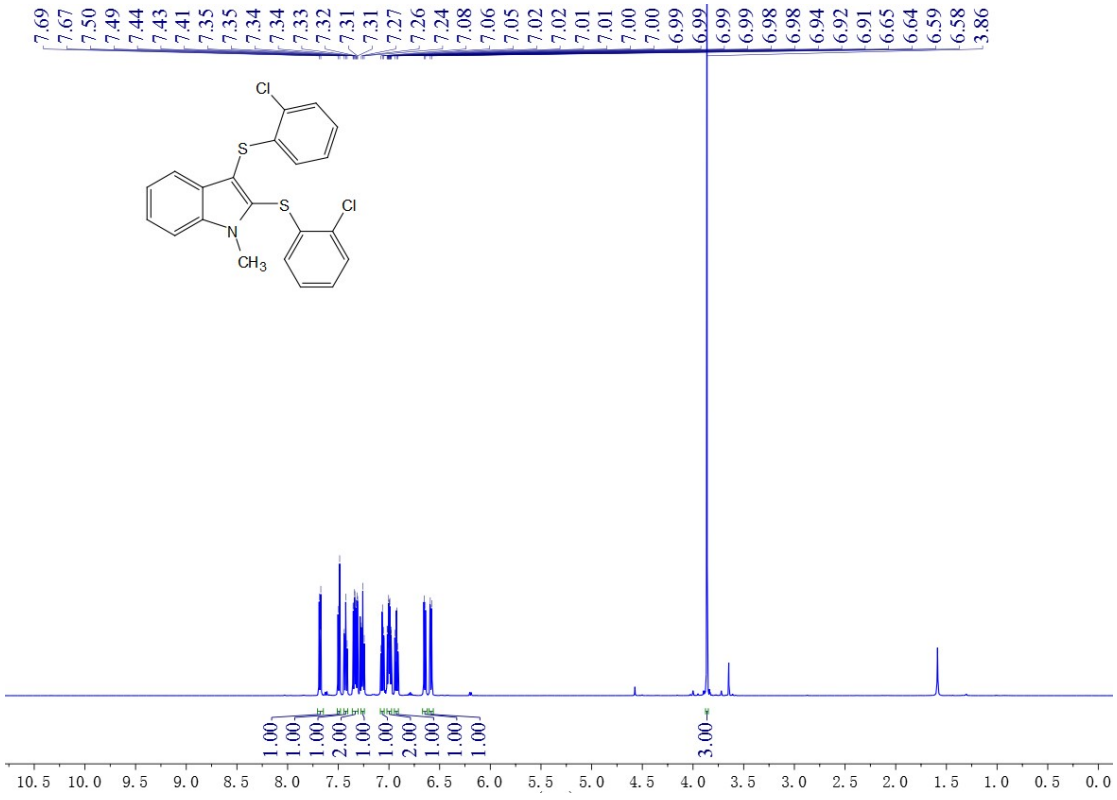
(120) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ag



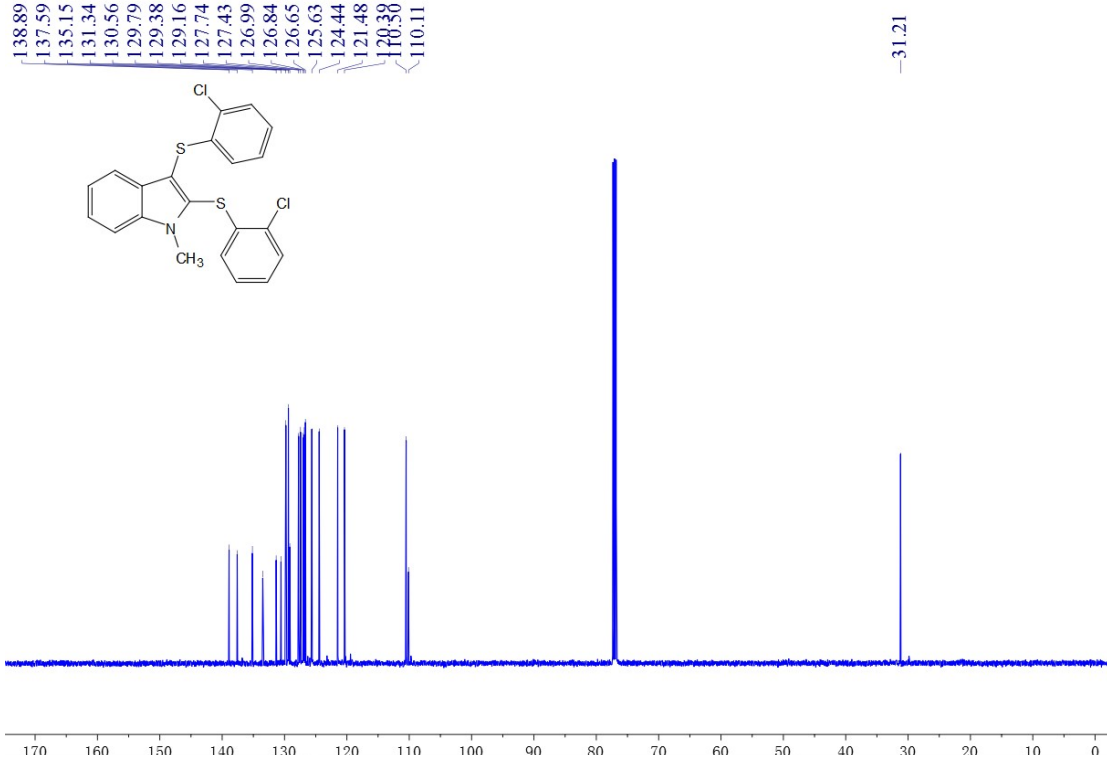
(121) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ag



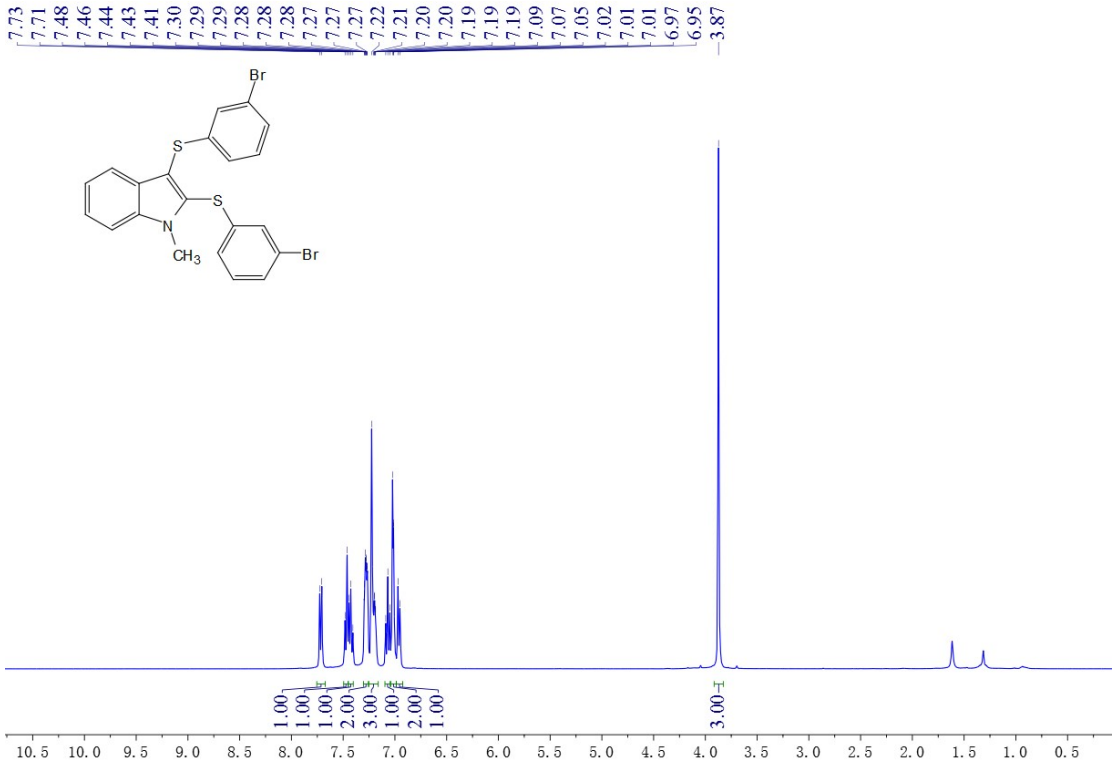
(122) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ah



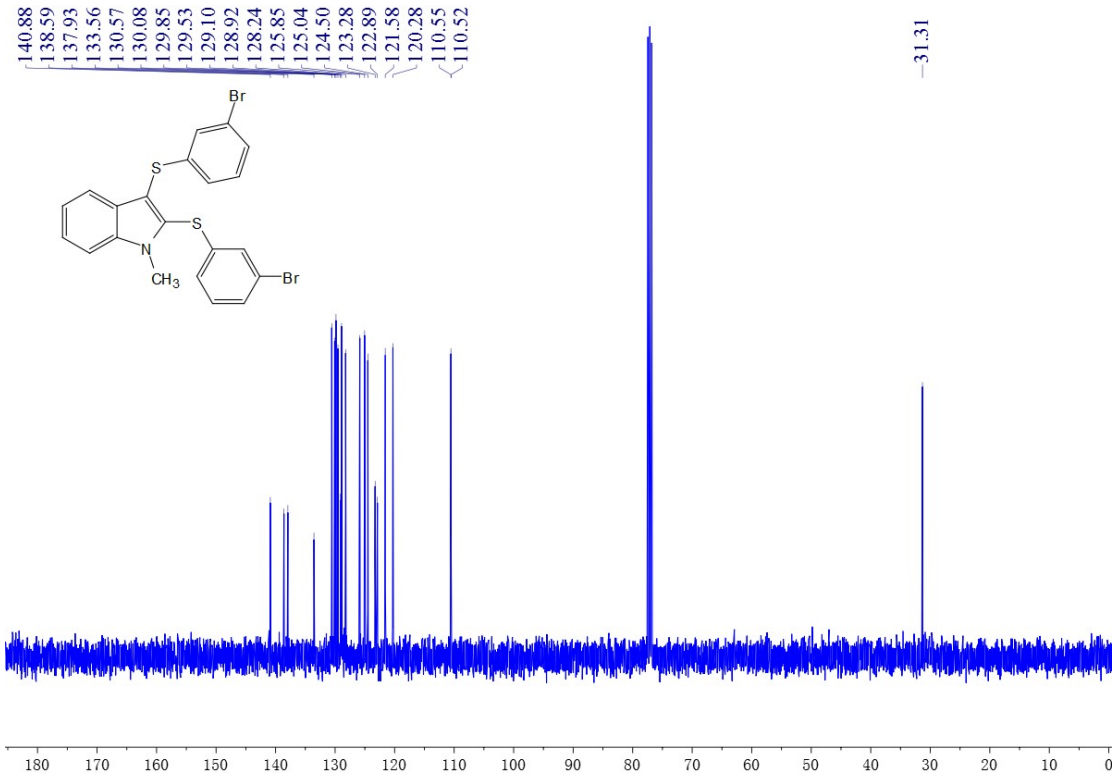
(123) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ah



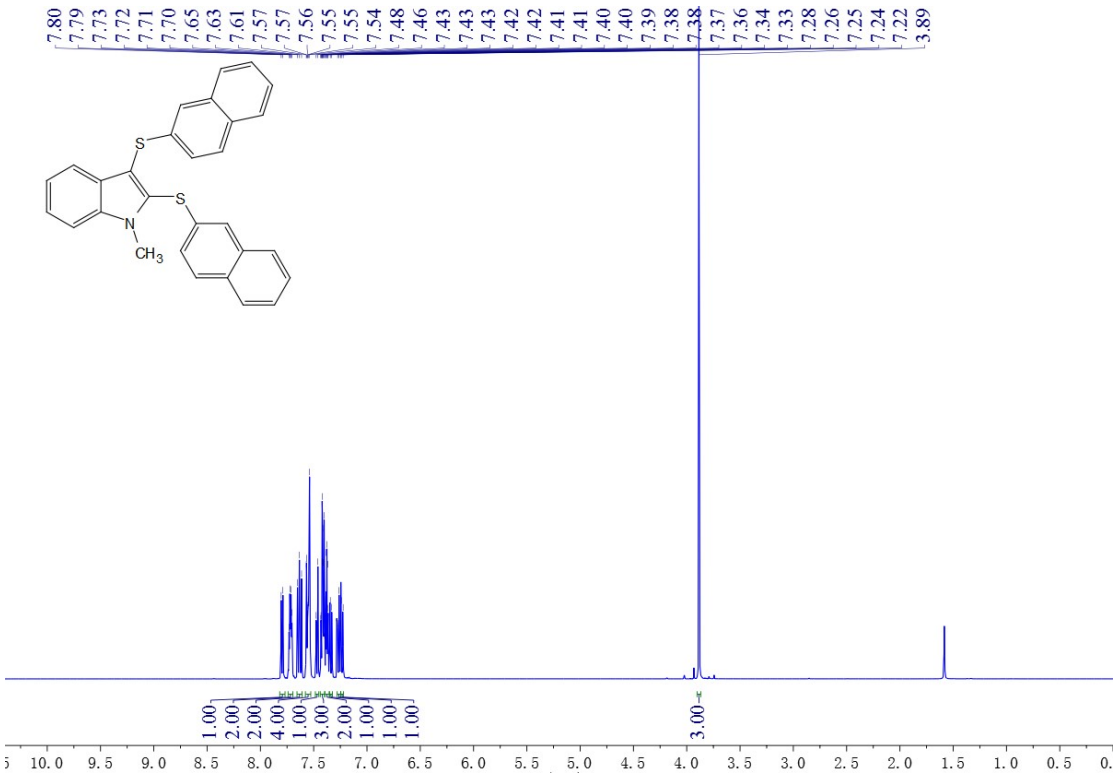
(124) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 4ai



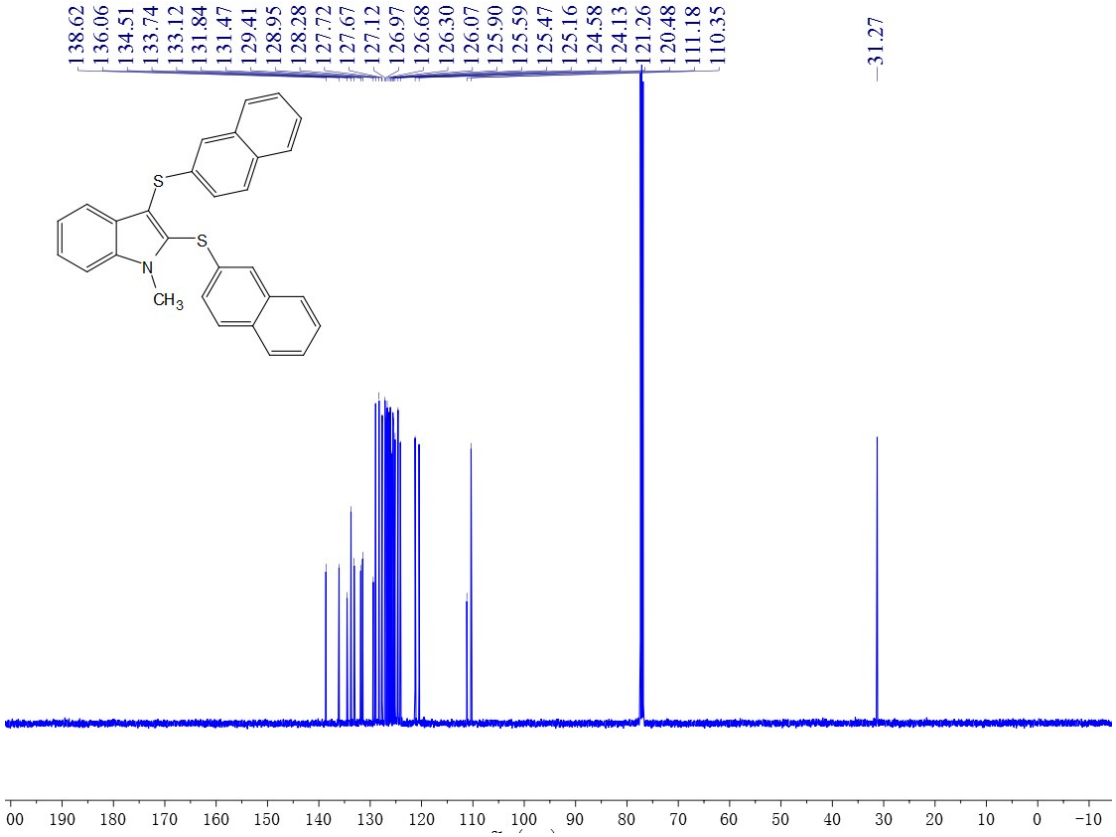
(125) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 4ai



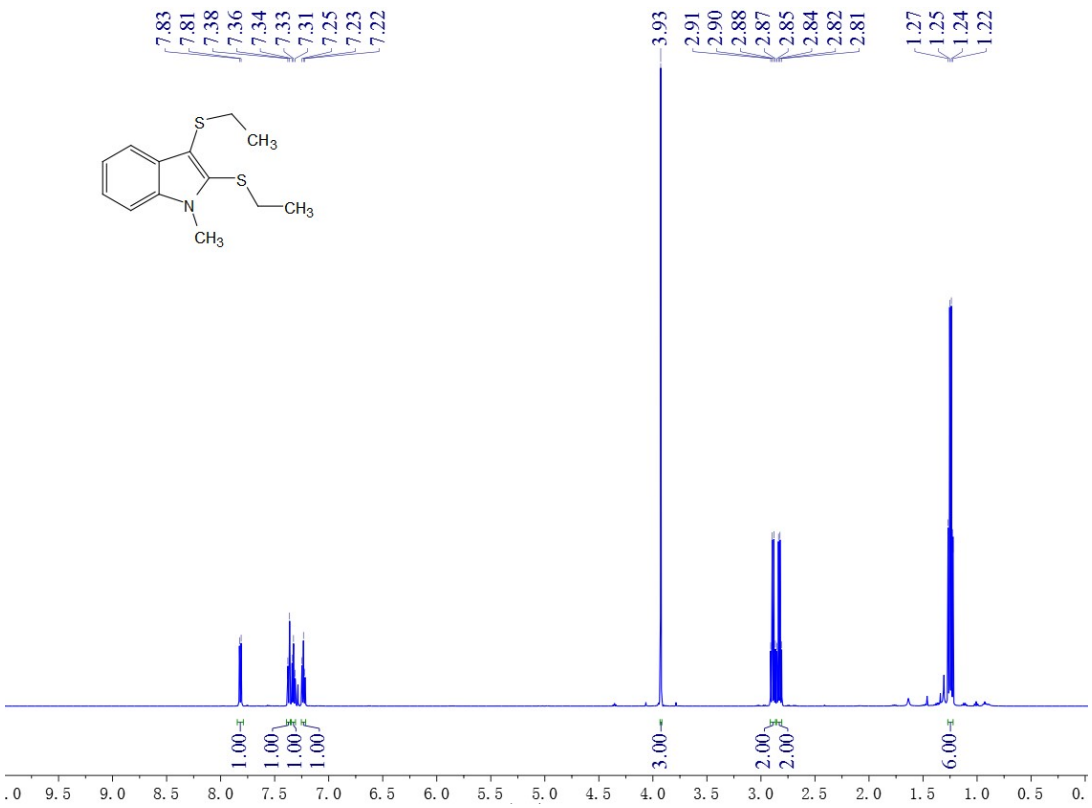
(126) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aj



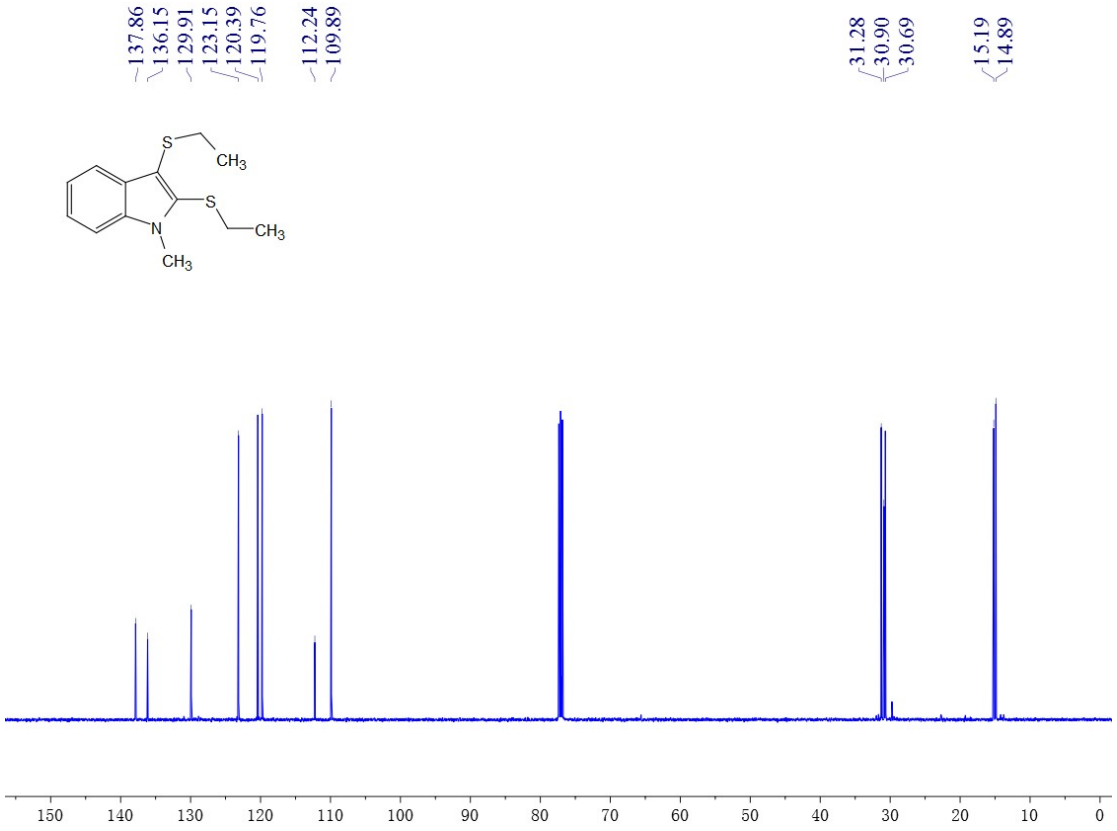
(127) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4aj



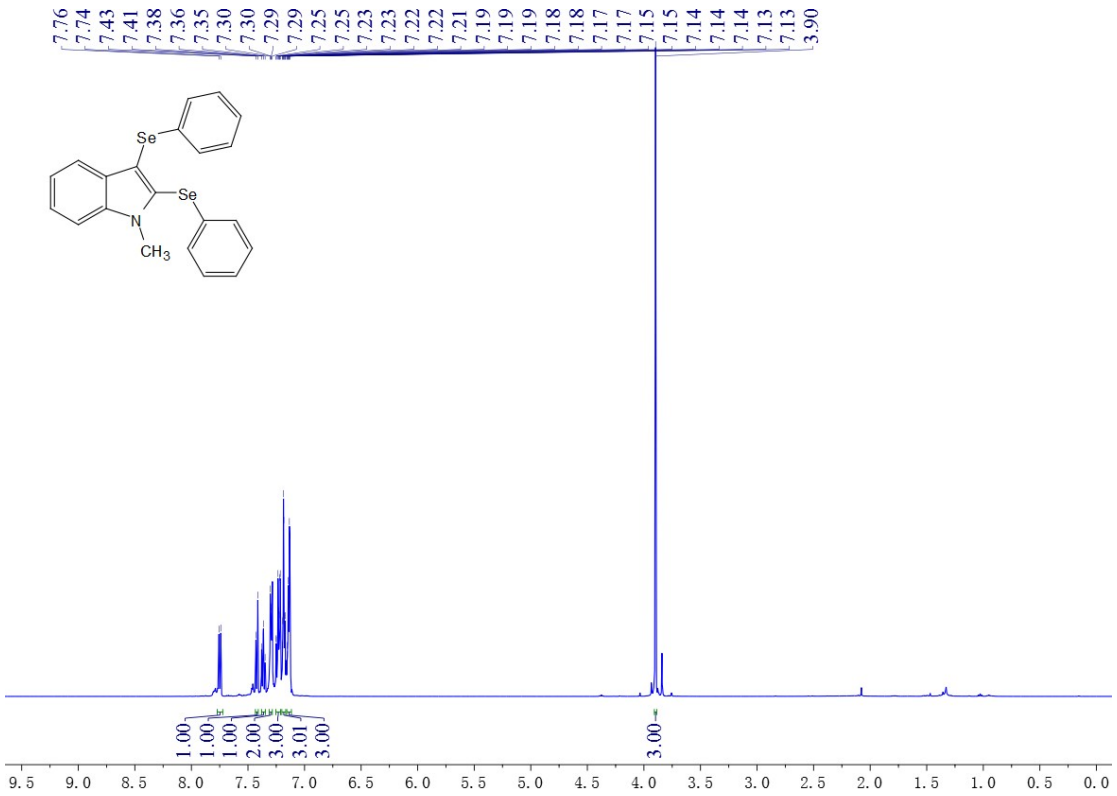
(128) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ak



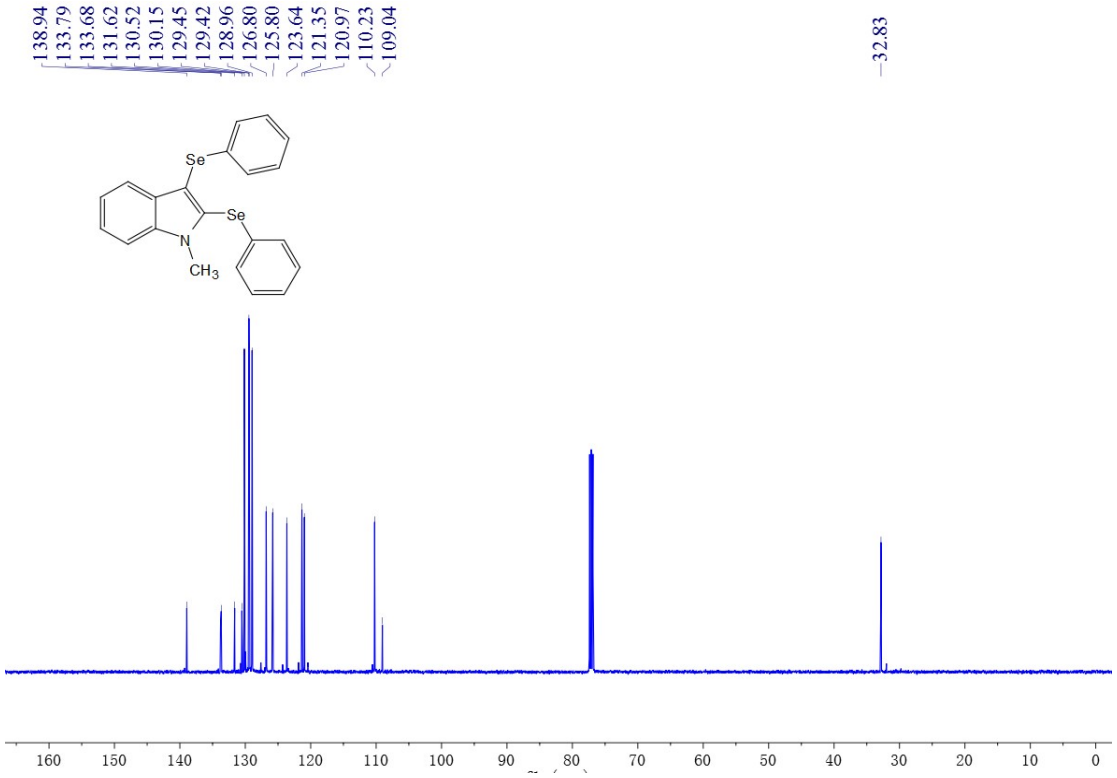
(129) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4ak



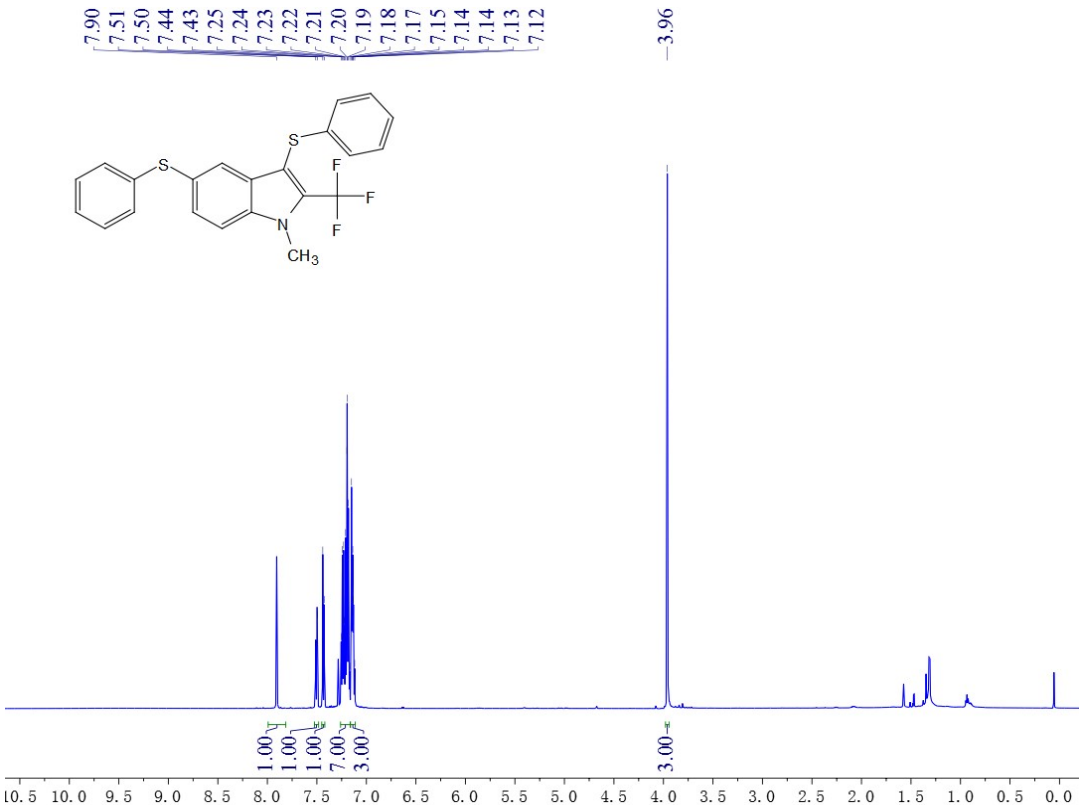
(130) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4al



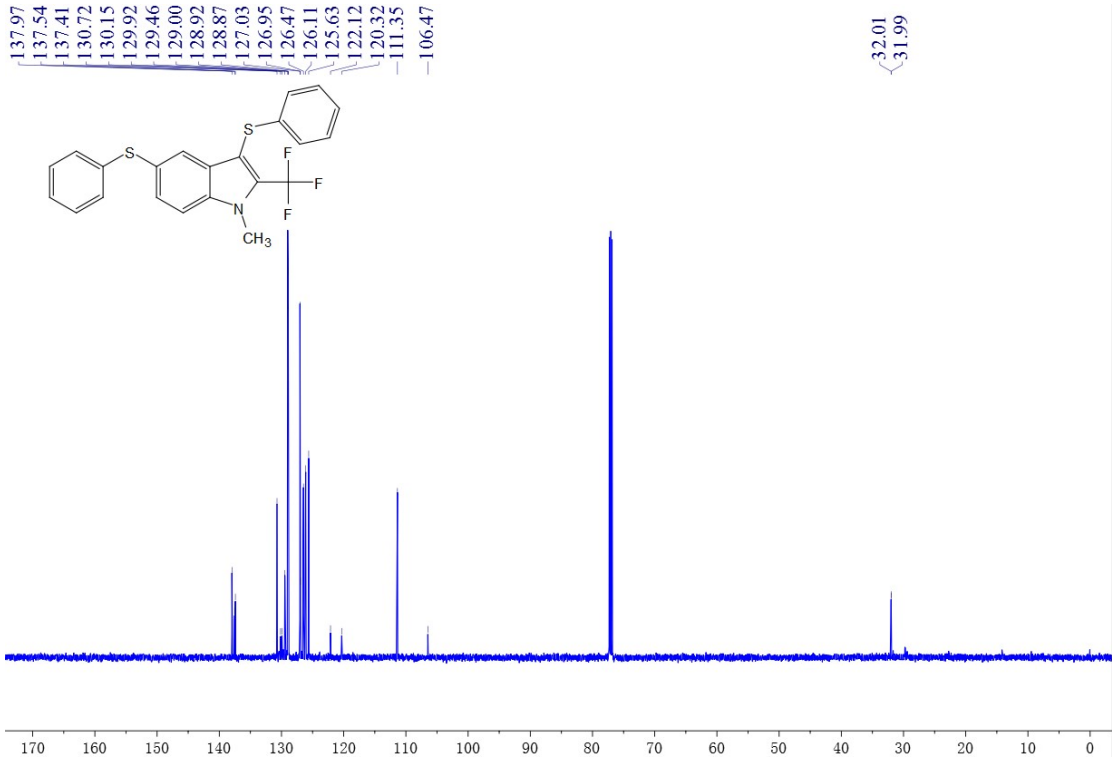
(131) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4al



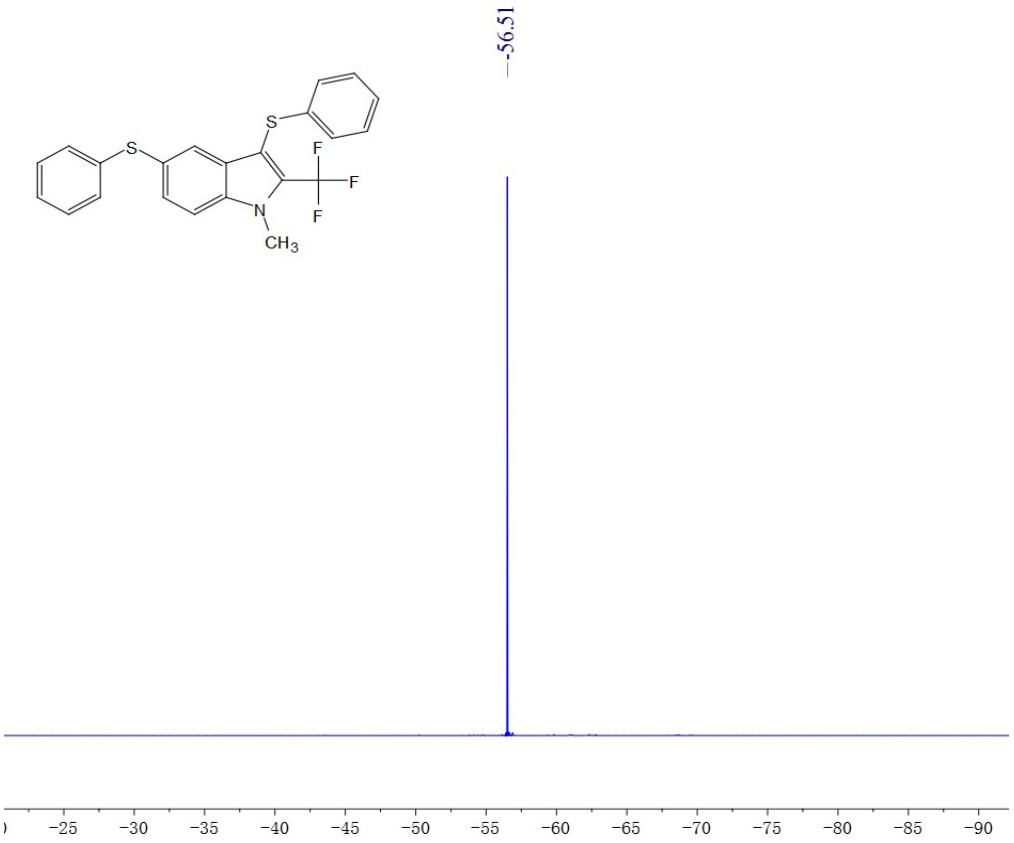
(132) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 6



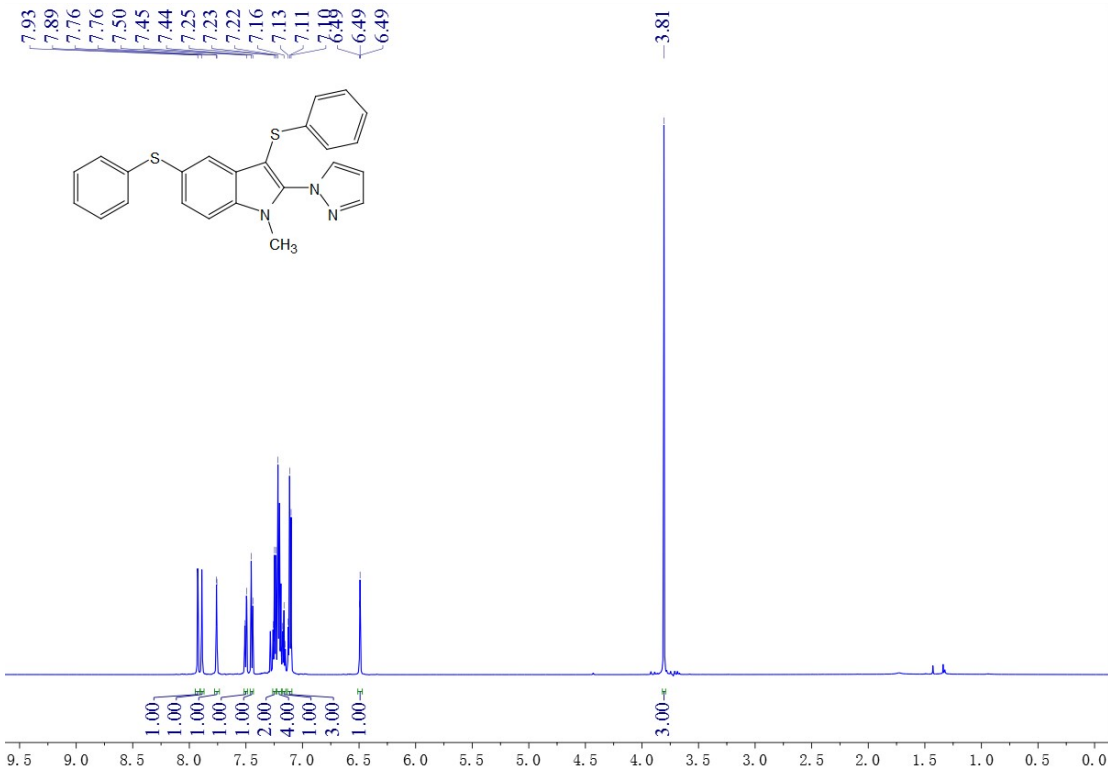
(133) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 6



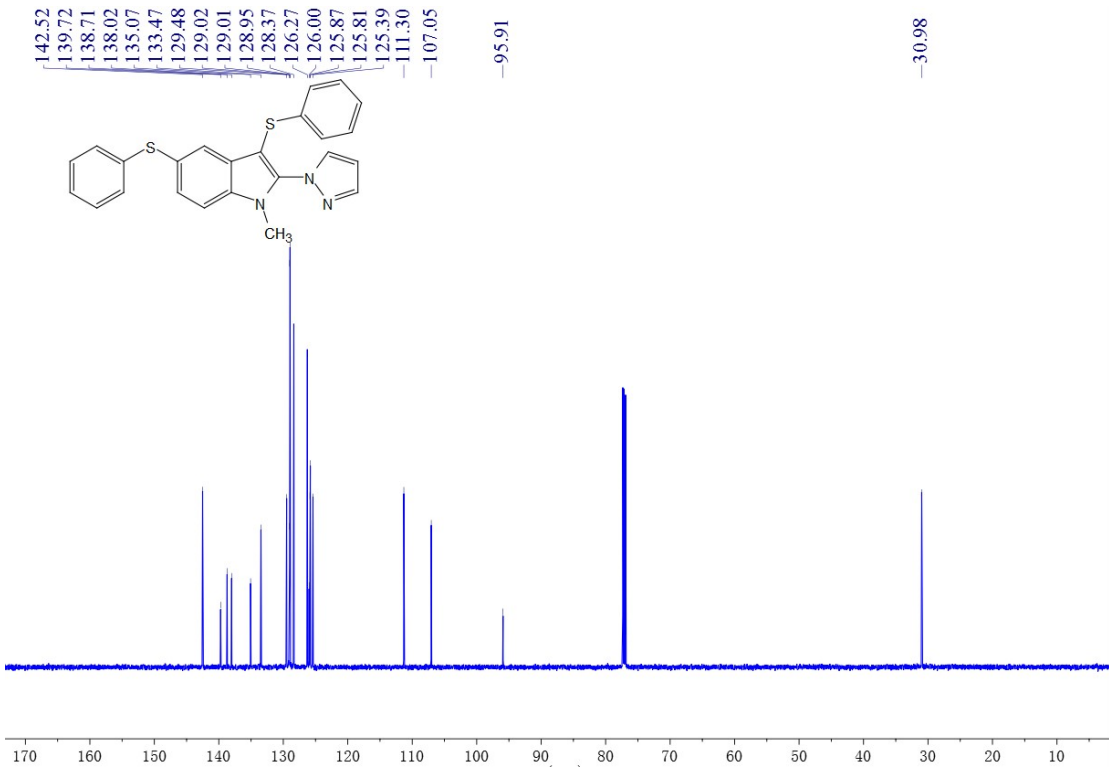
(134) ^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of 6



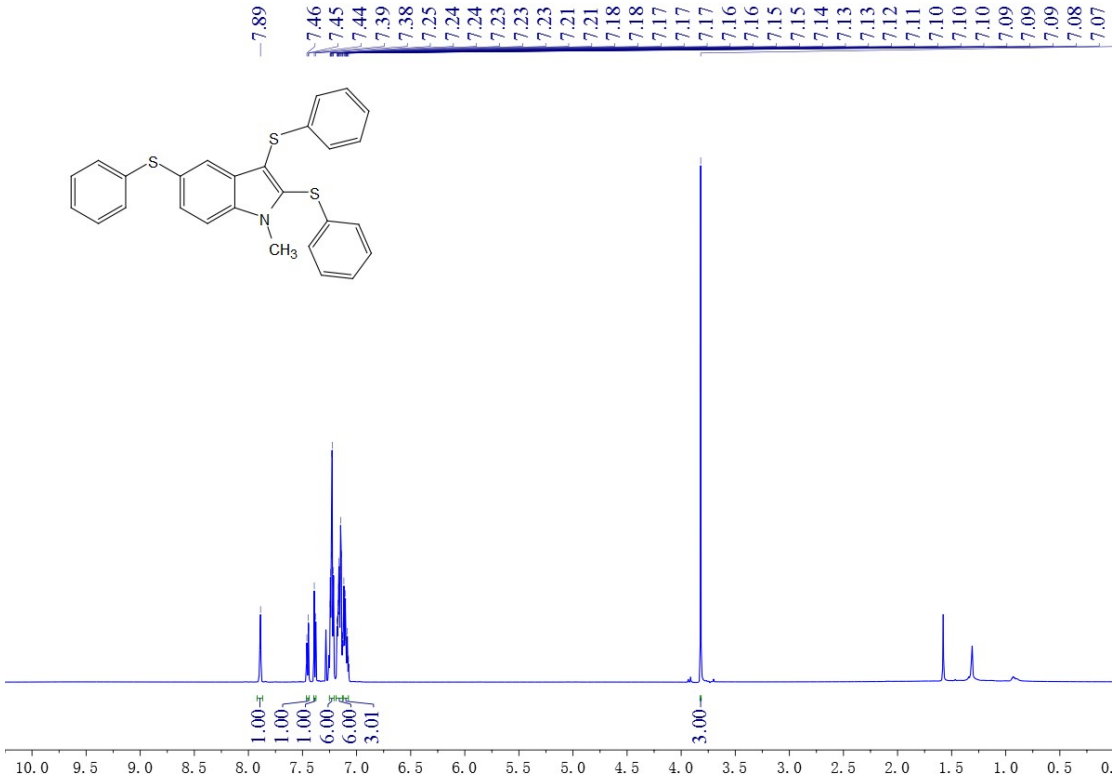
(135) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 7



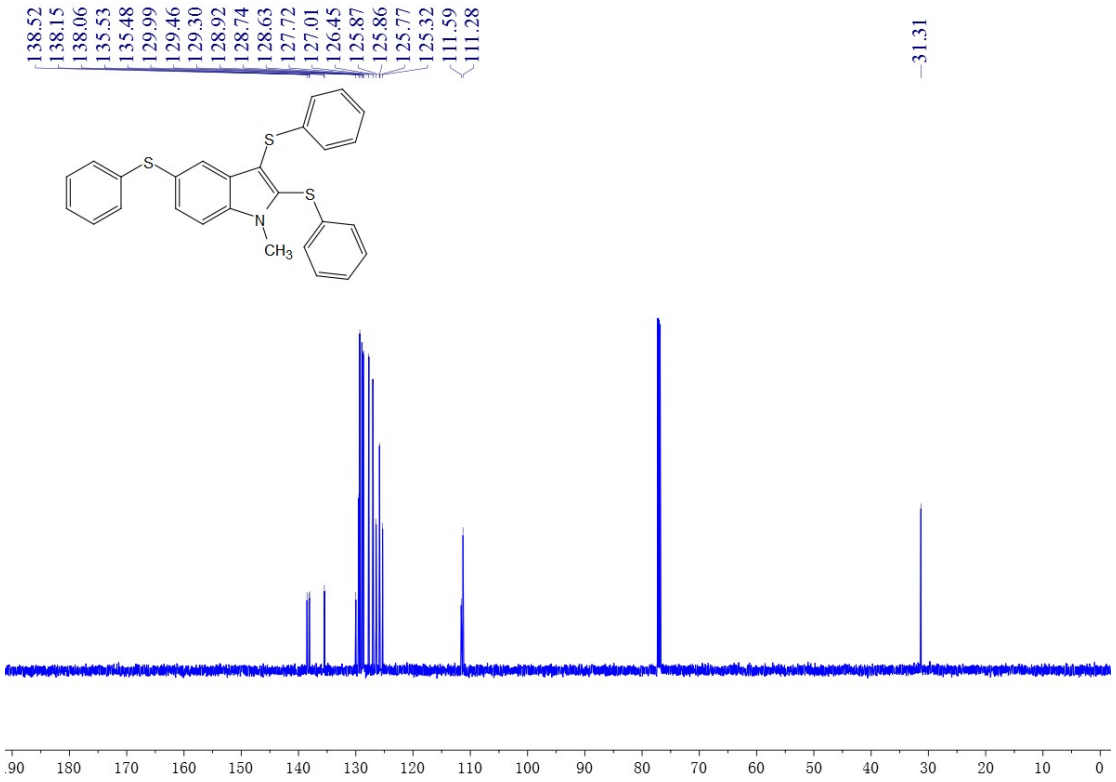
(136) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 7



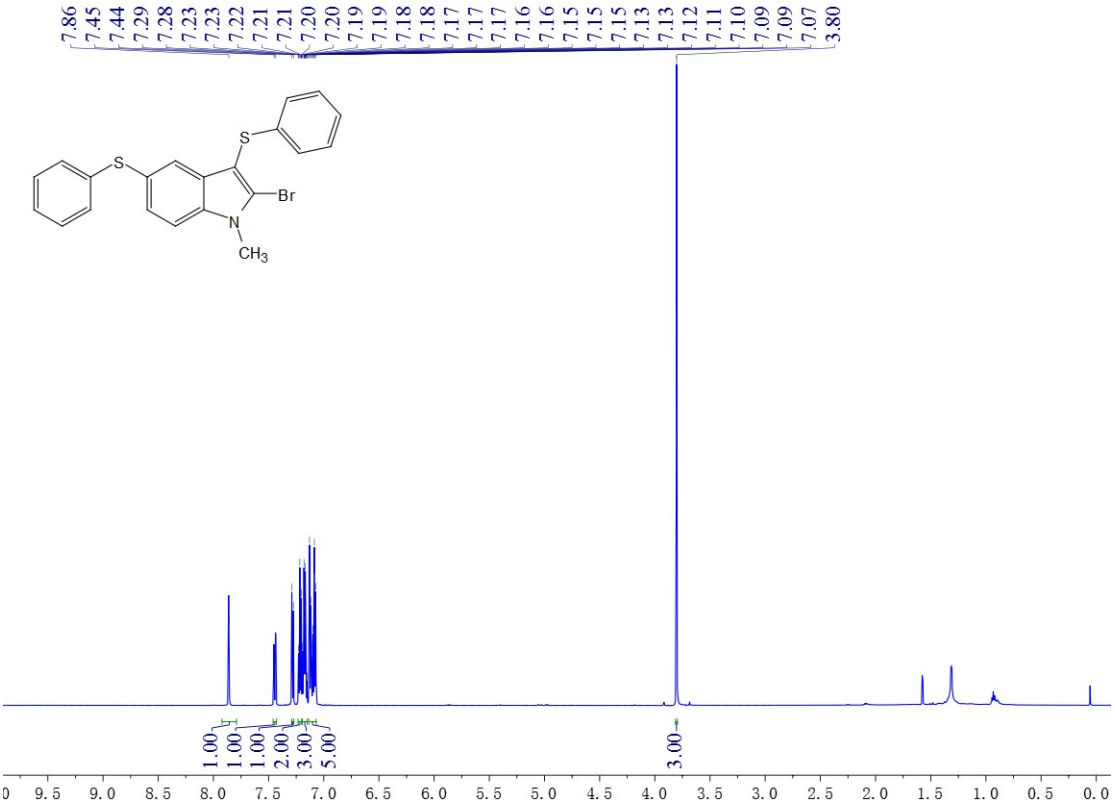
(137) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 8



(138) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 8



(139) ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of 9



(140) ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of 9