Supporting Information

Hypervalent Iodine-mediated One-pot Synthesis of C3,6-Dithioquinolin-2-ones

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MATERIALS AND METHODS

1. General information.

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

Solvents

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

Chromatography

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

Spectroscopy and Instruments

NMR spectra were recorded on Bruker-600 spectrometer operating at (600 MHz, 565 MHz and 151 MHz), for ^{1}H, ^{19}F and ^{13}C 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 ^{1}H 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.

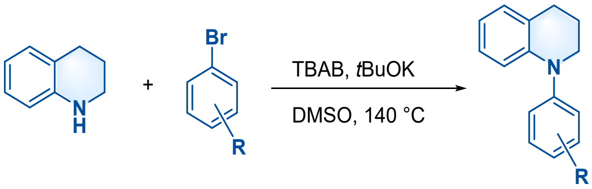
Instrument

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

EXPERIMENTAL DATA

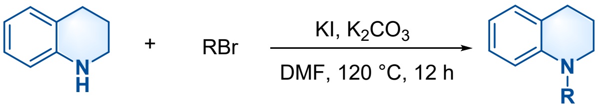
2. Substrates preparation.

2.1. Method A [1] (preparation of substrates 1a-1h)



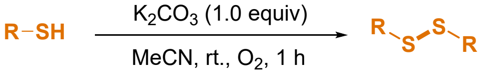
In a dry round-bottom flask, the corresponding substituted bromobenzene (2.0 mmol) and 1,2,3,4-tetrahydroquinoline (3.0 mmol) were added to 1,2,3,4-tetrahydroquinoline, followed by the addition of 3 mL of dimethyl sulfoxide (DMSO). Subsequently, tetrabutylammonium bromide (TBAB, 32.0 mg, 5 mol%) and potassium tert-butoxide (337.0 mg, 3.0 mmol) were added. The reaction mixture was heated at 140 °C and monitored frequently by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with water, and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate) to obtain the desired product.

2.2. Method B [2] (preparation of substrates 1i-1m)



Anhydrous potassium carbonate (691.1 mg, 5.0 mmol) and potassium iodide (1037.5 mg, 6.25 mmol) were added to a solution of 1,2,3,4-tetrahydroquinoline (333.0 mg, 2.5 mmol) and corresponding RBr (5.0 mmol) in DMF (50.0 mL). The mixture was stirred at 120 °C. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with EtOAc and H_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give desired product.

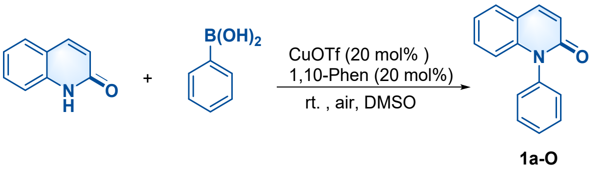
2.3. Method C [3] (preparation of substrates 2b-2m)



To a round bottle (50.0 mL) were added thiophenol (5.0 mmol), anhydrous potassium carbonate (0.69 g, 5.0 mmol), and MeCN (10.0 mL) sequentially, and the reaction was conducted at room temperature under oxygen atmosphere for 1 hour. And the desired disulfides were obtained quantitatively, after filter and concentration.

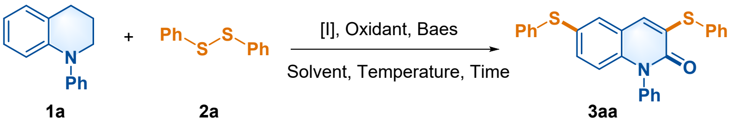
2.4. Method D [4] (preparation of substrates 1a-O)

Quinolin-2(1H)-one **1a'** (60.0 mg, 0.413 mmol), phenylboronic acid (75.0 mg, 0.619 mmol), CuOTf (42.0 mg, 0.082 mmol) and 1,10-Phen (16.0 mg, 0.082 mmol) were added sequentially into dimethyl sulfoxide (DMSO) (1.0 mL) to form a mixture, which was then stirred at room temperature under open air for 16 h. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (7:3) as the eluent to obtain compound **1a-O** as a pale yellow solid (62.0 mg, 68% yield).



3. Optimization of reaction conditions

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



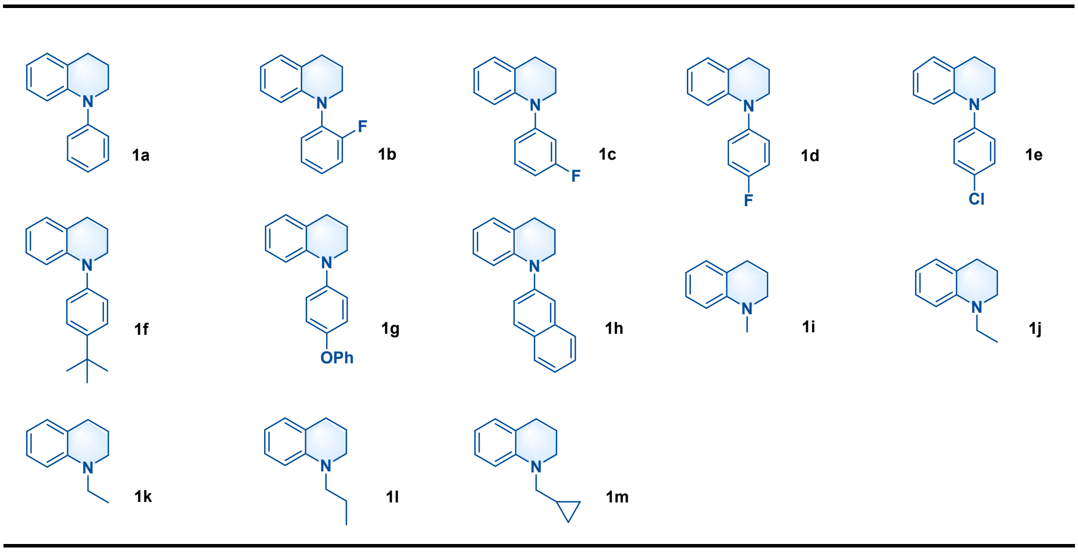
	[I]	Oxidant	Baes	Sovent	Temp.	Yield (%)[b]
1.	**I_2**	**IBX**	**Cs_2CO_3**	**DCE:H_2O**	**100 ℃**	**80**

2.	I_2	IBX	Cs_2CO_3	DCE:H_2O	100 °C	24 [c]
3.	-	IBX	Cs_2CO_3	DCE:H_2O	100 °C	0
4.	NaI	IBX	Cs_2CO_3	DCE:H_2O	100 °C	0
5.	KI	IBX	Cs_2CO_3	DCE:H_2O	100 °C	0
6.	NIS	IBX	Cs_2CO_3	DCE:H_2O	100 °C	0
7.	I_2	-	Cs_2CO_3	DCE:H_2O	100 °C	0
8.	I_2	$NaIO_4$	Cs_2CO_3	DCE:H_2O	100 °C	54
9.	I_2	DMP	Cs_2CO_3	DCE:H_2O	100 °C	12
10.	I_2	PIDA	Cs_2CO_3	DCE:H_2O	100 °C	0
11.	I_2	HTIB	Cs_2CO_3	DCE:H_2O	100 °C	0
12.	I_2	PIFA	Cs_2CO_3	DCE:H_2O	100 °C	0
13.	I_2	PhIO	Cs_2CO_3	DCE:H_2O	100 °C	0
14.	I_2	IBX	-	DCE:H_2O	100 °C	32
15.	I_2	IBX	Li_2CO_3	DCE:H_2O	100 °C	64
16.	I_2	IBX	$NaHCO_3$	DCE:H_2O	100 °C	61
17.	I_2	IBX	Na_2CO_3	DCE:H_2O	100 °C	69
18.	I_2	IBX	t - BuONa	DCE:H_2O	100 °C	66
19.	I_2	IBX	NaOH	DCE:H_2O	100 °C	51
20.	I_2	IBX	NaOEt	DCE:H_2O	100 °C	37
21.	I_2	IBX	K_2CO_3	DCE:H_2O	100 °C	73
22.	I_2	IBX	KOH	DCE:H_2O	100 °C	54
23.	I_2	IBX	Cs_2CO_3	toluene :H_2O	100 °C	0
24.	I_2	IBX	Cs_2CO_3	1,4-dioxane:H_2O	100 °C	0
25.	I_2	IBX	Cs_2CO_3	CH_3CN:H_2O	100 °C	0
26.	I_2	IBX	Cs_2CO_3	CH_2Cl_2:H_2O	100 °C	19
27.	I_2	IBX	Cs_2CO_3	$CHCl_3$:H_2O	100 °C	47
28.	I_2	IBX	Cs_2CO_3	DCE	100 °C	0
29.	I_2	IBX	Cs_2CO_3	H_2O	100 °C	0
30.	I_2	IBX	Cs_2CO_3	DCE:H_2O	80 °C	71
31.	I_2	IBX	Cs_2CO_3	DCE:H_2O	60 °C	57
32.	I_2	IBX	Cs_2CO_3	DCE:H_2O	40 °C	trace
33.	I_2	IBX	Cs_2CO_3	DCE:H_2O	100 °C	64 [d]

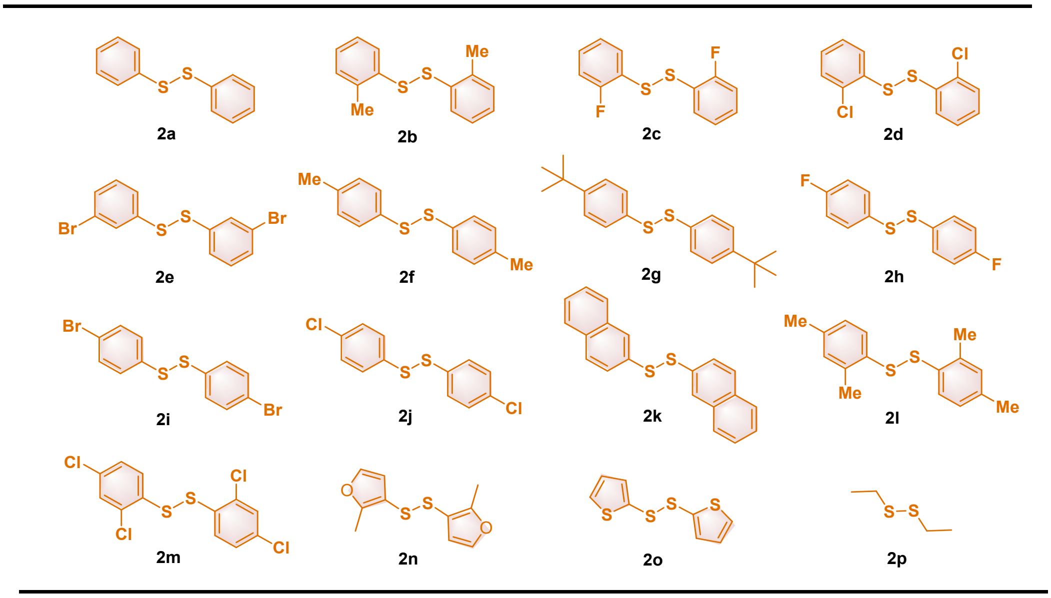
[a]Reaction conditions, unless specified otherwise: **1a** (0.2 mmol), **2a** (0.3 mmol), [I] (0.2 mmol), Oxidant (0.6 mmol) Baes (0.4 mmol) and solvent (DCE:H_2O = 4:1, 3.0 mL) were stirred at 100 °C under O_2 for 12 h. [b]Isolated yield. [c]I_2 (0.04 mmol), IBX = 2-iodoxybenzoic acid, NIS = N-Iodosuccinimide, DMP = Dess-Martin periodinane, PIDA = (diacetoxyiodo)benzene, HTIB = [hydroxy(tosyloxy)iodo]benzene, PIFA = Bis (trifluoroacetoxy) iodobenzene, PhIO = iodosyl benzene, DCE = 1,2-dichloroethane, [d]Ar instead of O_2.

4. Summary of substrates

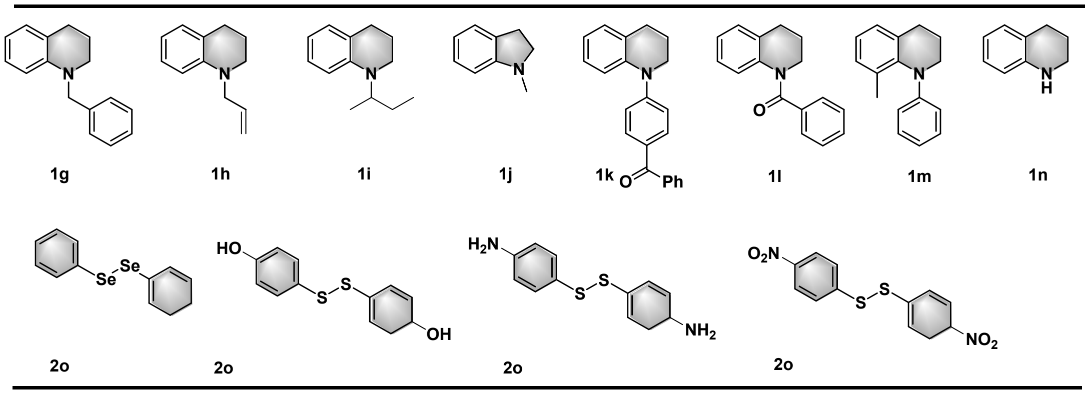
Scheme S1. Scope of N-substituted tetrahydroquinoline compounds.



Scheme S2. Scope of sulfide compounds.



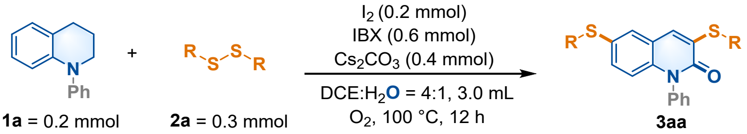
Scheme S3. Other unsuccessful substrates.



5. Typical procedure for the synthesis of 3aa.

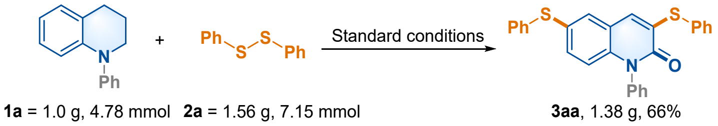
Diphenyl disulfide **2a** (65.0 mg, 0.3 mmol), Cs_2CO_3 (130.0 mg, 0.4 mmol), IBX (168 mg, 0.6 mmol), I_2 (51 mg, 0.2 mmol), DCE (2.4 ml), deionized water (0.6 ml) and N-phenyltetrahydroquinoline **1a** (42.0 mg, 0.2 mmol) were added sequentially to a reaction tube, and the mixture was stirred at 100 °C for 12 h under an O_2 atmosphere. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative thin-layer chromatography on silica gel using petroleum ether/ethyl acetate (6:1) as the eluent to give **3aa** as a pale yellow solid (69 mg, 80% yield).

Special Note: IBX is considered to have potential explosiveness under high temperatures or strong impacts. When handling IBX in the laboratory, we always wear appropriate personal protective equipment, including safety goggles, lab coats, and nitrile gloves. During the weighing of IBX, we use a balance in a stable environment and operate with extreme caution to avoid any accidental dropping or impact. When weighing, transferring, and using IBX, appropriate tools should be used and operations should be carried out carefully. During weighing, transfer in small amounts multiple times. When storing, it should be placed in a stable location that is not easily collided with. In addition, a sand bath is used to precisely control the temperature to avoid local overheating. Meanwhile, a pressure-resistant reaction tube is adopted, which can withstand the pressure generated during the reaction.

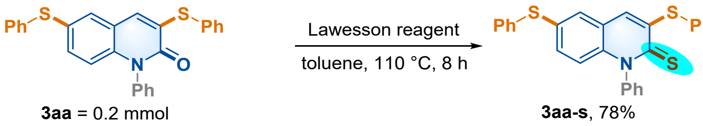


6. Synthetic application.

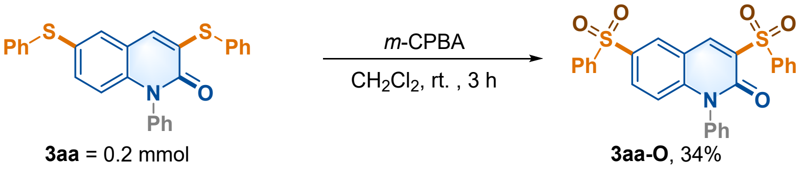
(1) Diphenyl disulfide **2a** (1.56 g, 7.15 mmol), Cs_2CO_3 3.09 g, 9.53 mmol), IBX (4.0 g, 14.2 mmol), I_2 (1.21 g, 4.76 mmol), DCE (50.0 ml), deionized water (12.0 ml) and N-phenyltetrahydroquinoline **1a** (1.0 g, 4.78 mmol) were added sequentially to a reaction tube, and the mixture was stirred at 100 °C for 12 h under an O_2 atmosphere. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative thin-layer chromatography on silica gel using petroleum ether/ethyl acetate (6:1) as the eluent to give **3aa** as a yellow solid (1.38 g, 66% yield).



(2) An oven-dried reaction tube was charged with compound **3aa** (87.0 mg, 0.2 mmol, 1 equiv.), the Lawesson reagent (41.0 mg, 0.1 mmol, 0.5 equiv.) and toluene (3.0 mL). After being stirred at 110 °C for 8 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel with ethyl acetate/petroleum ether (v/v = 1/10) as the eluent, affording the desired product **3aa-S** as a pale-yellow oil (71.0 mg, 78% yield).



(3) An oven-dried reaction tube was charged with compound **3aa** (87.0 mg, 0.2 mmol, 1.0 equiv.), m-chloroperoxybenzoic acid (*m*-CPBA, 345.0 mg, 2.0 mmol, 10 equiv.) and DCM (3.0 mL). After being stirred at room temperature for 3 hours, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel with ethyl acetate/petroleum ether (v/v = 2/3) as the eluent, affording the desired product **3aa-O** as a white solid (34mg, 34% yield).



7. Single crystal X-ray diffraction.

Light pink block-like single crystals of **3aj** 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. All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. Thermal ellipsoides are drawn at 50% probability level. And an ORTEP representation of the structure is shown below.

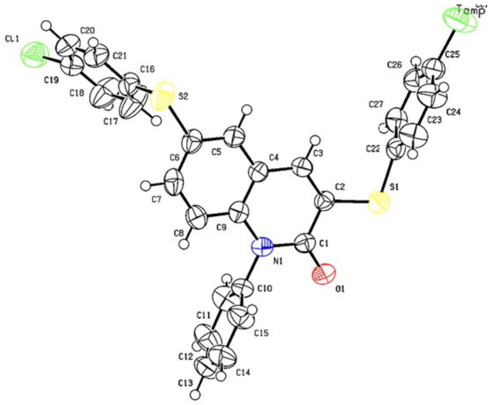


Figure S1. ORTEP drawing of **3aj** with the numbering scheme.

Table S2. Crystal data and structure refinement for **3aj**.

Identification code	2377686
Empirical formula	$C_{27}H_{17}Cl_2NOS_2$
Formula weight	506.43
Temperature	298
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 17.9420(13).
	b = 11.8982(8).
	c = 22.5176(15).
Volume	4807.0(6)
ρ_{calc} g/cm^3	1.400
μ/mm^{-1}	0.280
Z	0.465
F(000)	889.0
Crystal size	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2^{Θ} range for data collection	4.488 to 58.698
Index ranges	$-22 \le h \le 24$, $-16 \le k \le 14$, $-29 \le l \le 29$
Reflections collected	35595
Independent reflections	5893 [R_{int} = 0.0597, R_{sigma} = 0.0532]
Data / restraints / parameters	5893/0/298
Goodness-of-fit on F^2	1.074
Final R indices [I>=2^{σ} (I)]	R_1 = 0.0662, wR_2 = 0.1659
Final R indices (all data)	R_1 = 0.1126, wR_2 = 0.1989
Largest diff. peak and hole	0.31/-0.48

Table S3. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **3aj**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	x	y	z	U(eq)
S1	5439.9(5)	28.0(7)	2714.3(3)	56.5(3)
S2	5000.6(5)	2839.6(8)	5922.0(4)	67.1(3)
Cl1	3024.3(6)	7194.7(7)	5794.7(5)	78.7(3)
Cl2	8572.3(5)	2317.4(8)	2636.2(6)	93.3(4)
O1	3990.0(11)	-712.2(17)	2998.5(9)	59.1(6)
N1	3852.5(13)	-15.8(17)	3935.1(10)	41.8(5)
C2	4989.6(15)	351.8(19)	3385.3(11)	39.6(6)
C3	5248.2(15)	987(2)	3834.8(12)	42.1(6)
C1	4252.6(15)	-168.7(19)	3409.6(12)	42.2(6)
C9	4123.9(15)	616.8(19)	4417.6(11)	39.5(6)
C4	4819.2(15)	1142(2)	4361.8(11)	39.5(6)
C5	5071.8(15)	1822(2)	4830.9(12)	46.4(7)
C10	3114.0(15)	-499(2)	3948.6(12)	42.7(6)
C22	6301.1(16)	750(2)	2765.6(11)	45.5(7)
C8	3714.3(16)	734(2)	4939.8(13)	49.7(7)
C6	4658.0(17)	1967(2)	5340.3(12)	49.7(7)
C7	3982.4(17)	1398(3)	5399.0(12)	53.8(7)
C27	6385.4(17)	1800(2)	2504.2(13)	51.7(7)
C16	4453.0(17)	4075(2)	5838.8(12)	51.8(7)
C26	7082.8(18)	2297(2)	2471.7(14)	54.7(8)
C25	7683.9(17)	1743(2)	2702.3(14)	53.4(7)
C19	3597.7(17)	6008(2)	5804.7(14)	55.9(7)
C21	4481.6(18)	4856(3)	6290.5(14)	60.2(8)
C20	4059.8(19)	5826(3)	6274.9(14)	62.4(8)
C23	6918.1(18)	223(3)	3008.8(15)	61.7(8)
C24	7608.7(18)	720(2)	2979.0(15)	65.3(9)
C11	2532.2(17)	70(3)	3696.1(14)	61.0(8)
C15	3000.4(19)	-1531(2)	4207.0(15)	65.3(9)
C13	1723(2)	-1452(3)	3954.1(15)	76.7(11)
C12	1832.7(19)	-412(4)	3697.1(15)	77.1(11)
C14	2299(2)	-1997(3)	4212.4(17)	76.0(11)
C18	3575(2)	5268(3)	5345.7(17)	85.0(12)

C17	4006(2)	4310(3)	5359.2(16)	87.9(13

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3aj**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
S1	51.5(5)	76.0(5)	41.9(4)	-14.7(3)	1.0(3)	-9.1(4)
S2	65.2(6)	87.4(6)	48.9(5)	-21.1(4)	-20.2(4)	20.8(4)
Cl1	65.1(6)	64.6(5)	106.5(8)	-12.7(4)	-3.0(5)	2.3(4)
Cl2	54.8(6)	77.6(6)	147.6(11)	12.1(6)	-1.7(6)	-12.7(5)
O1	55.7(13)	66.4(13)	55.2(13)	-18.8(10)	-2.1(10)	-12.6(10)
N1	41.0(13)	40.7(11)	43.8(13)	0.5(9)	-4.0(10)	-4.0(9)
C2	40.2(15)	40.8(13)	37.7(14)	-2.3(10)	-3.4(11)	0.3(10)
C3	39.3(15)	44.3(13)	42.7(15)	1.7(11)	-1.7(12)	-5.3(11)
C1	43.5(16)	37.7(13)	45.4(16)	-0.8(11)	-2.8(13)	-1.1(11)
C9	40.9(15)	37.9(12)	39.6(14)	3.5(10)	-4.1(11)	8.3(11)
C4	42.2(15)	40.5(12)	35.9(14)	0.3(10)	-1.8(11)	1.2(11)
C5	40.7(16)	53.3(15)	45.1(16)	-5.3(12)	-6.1(12)	2.2(12)
C10	40.7(16)	40.4(13)	47.1(16)	4.3(11)	0.0(12)	-6.8(11)
C22	48.6(17)	54.0(15)	34.0(14)	-5.5(11)	2.6(12)	1.4(13)
C8	45.1(16)	54.2(15)	49.7(17)	6.7(13)	2.9(13)	5.8(12)
C6	48.5(18)	59.3(16)	41.2(16)	-9.2(12)	-7.9(13)	11.1(13)
C7	51.5(19)	71.4(19)	38.5(16)	-1.9(13)	2.1(13)	14.8(15)
C27	51.0(18)	54.8(16)	49.3(17)	1.9(13)	-2.3(14)	11.2(14)
C16	48.7(18)	67.7(17)	38.9(15)	-12.4(12)	-7.2(13)	3.5(14)
C26	61(2)	45.2(15)	58.2(18)	3.3(13)	1.7(16)	2.6(14)
C25	46.5(18)	47.9(16)	65.9(19)	-2.7(13)	0.6(14)	-1.6(13)
C19	47.3(18)	58.4(17)	62(2)	-8.5(14)	-1.3(15)	-6.1(14)
C21	59(2)	75(2)	45.9(18)	-11.7(14)	-15.2(15)	-3.9(16)
C20	69(2)	62.2(19)	57(2)	-17.6(14)	-4.9(17)	-9.5(16)
C23	62(2)	54.4(17)	68(2)	19.5(14)	-11.7(17)	0.1(15)
C24	50.0(19)	59.1(18)	87(2)	16.1(16)	-19.2(17)	4.4(15)
C11	56(2)	68.9(18)	58(2)	17.5(15)	-7.4(15)	-0.6(16)
C15	58(2)	51.6(17)	86(2)	14.7(15)	6.1(17)	-5.0(15)
C13	58(2)	112(3)	61(2)	-16(2)	15.7(18)	-38(2)
C12	44(2)	128(3)	59(2)	13(2)	-7.6(16)	-4(2)
C14	73(3)	63(2)	92(3)	5.7(19)	18(2)	-21.9(19)
C18	93(3)	85(2)	77(3)	-23.2(19)	-40(2)	24(2)
C17	115(3)	88(3)	61(2)	-34.3(18)	-40(2)	35(2)

Table S5. Bond lengths for **3aj**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.756(3)	C22	C23	1.385(4)
S1	C22	1.772(3)	C22	C27	1.390(4)
S2	C16	1.778(3)	C8	C7	1.387(4)
S2	C6	1.780(3)	C6	C7	1.395(4)
Cl1	C19	1.747(3)	C27	C26	1.386(4)
Cl2	C25	1.741(3)	C16	C17	1.374(4)
O1	C1	1.223(3)	C16	C21	1.379(4)
N1	C1	1.396(3)	C26	C25	1.366(4)
N1	C9	1.408(3)	C25	C24	1.374(4)
N1	C10	1.445(3)	C19	C18	1.358(4)
C2	C3	1.346(3)	C19	C20	1.362(4)
C2	C1	1.461(4)	C21	C20	1.381(4)
C3	C4	1.426(4)	C23	C24	1.375(4)
C9	C8	1.394(4)	C11	C12	1.380(4)
C9	C4	1.401(4)	C15	C14	1.376(5)
C4	C5	1.406(4)	C13	C14	1.352(5)
C5	C6	1.377(4)	C13	C12	1.381(5)
C10	C11	1.368(4)	C18	C17	1.377(5)
C10	C15	1.374(4)			

Table S6. Bond angles for **3aj**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C22	103.82(12)	C5	C6	C7	119.1(3)
C16	S2	C6	102.32(13)	C5	C6	S2	120.0(2)
C1	N1	C9	123.1(2)	C7	C6	S2	120.9(2)
C1	N1	C10	115.9(2)	C8	C7	C6	120.5(3)
C9	N1	C10	120.9(2)	C26	C27	C22	120.3(3)

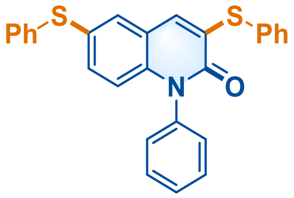
C3	C2	C1	121.5(2)	C17	C16	C21	117.6(3)
C3	C2	S1	127.7(2)	C17	C16	S2	125.0(2)
C1	C2	S1	110.82(17)	C21	C16	S2	117.3(2)
C2	C3	C4	120.8(2)	C25	C26	C27	119.1(3)
O1	C1	N1	120.8(2)	C26	C25	C24	121.5(3)
O1	C1	C2	123.0(2)	C26	C25	Cl2	120.1(2)
N1	C1	C2	116.2(2)	C24	C25	Cl2	118.4(2)
C8	C9	C4	120.0(2)	C18	C19	C20	120.4(3)
C8	C9	N1	121.5(2)	C18	C19	Cl1	119.8(3)
C4	C9	N1	118.5(2)	C20	C19	Cl1	119.8(2)
C9	C4	C5	118.5(2)	C16	C21	C20	121.6(3)
C9	C4	C3	119.8(2)	C19	C20	C21	119.1(3)
C5	C4	C3	121.7(2)	C24	C23	C22	120.4(3)
C6	C5	C4	121.6(3)	C25	C24	C23	119.5(3)
C11	C10	C15	120.4(3)	C10	C11	C12	119.2(3)
C11	C10	N1	119.6(2)	C10	C15	C14	120.0(3)
C15	C10	N1	120.1(3)	C14	C13	C12	120.1(3)
C23	C22	C27	119.2(3)	C11	C12	C13	120.2(3)
C23	C22	S1	120.2(2)	C13	C14	C15	120.1(3)
C27	C22	S1	120.2(2)	C19	C18	C17	120.2(3)
C7	C8	C9	120.2(3)	C16	C17	C18	120.9(3)

Table S7. Hydrogen atom coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **3aj**.

Atom	x	y	z	U(eq)
H3	5712.3	1329.83	3801.37	50
H5	5529.52	2183.39	4796.41	56
H8	3259.97	365.66	4980.58	60
H7	3709.64	1464.04	5748.46	65
H27	5971.99	2170.96	2350.46	62
H26	7140.85	2997.97	2295.17	66
H21	4792.62	4725.86	6613.64	72
H20	4090.85	6348.13	6581.18	75
H23	6864.92	-471.49	3193.46	74
H24	8021.69	367.03	3144.79	78
H11	2607.25	773.56	3525.97	73
H15	3397.74	-1913.91	4378.31	78
H13	1251.56	-1777.77	3949.62	92
H12	1434.06	-34.29	3524.01	92
H14	2220.68	-2689.34	4394.05	91
H18	3268.28	5409.16	5021.31	102
H17	3993.29	3815.48	5039.51	105

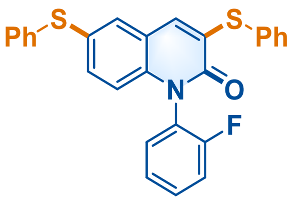
8. NMR data of the obtained compounds.

(1) 1-phenyl-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3aa)



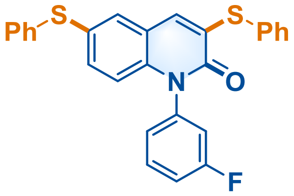
Petroleum ether and ethyl acetate (6:1) were used as eluents. yellow solid (69 mg, 80% yield); m.p.: 146-148 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.42 (d, *J* = 2.1 Hz, 1H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.31 (s, 1H), 7.27 (d, *J* = 2.8 Hz, 1H), 7.26 – 7.18 (m, 5H), 6.94 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 138.3, 137.3, 136.6, 136.4, 135.8, 132.7, 130.6, 130.3, 130.2, 130.1, 130.1, 129.9, 129.8, 129.3, 129.2, 128.7, 128.7, 126.8, 121.4, 117.0. HRMS (ESI-Orbitrap) m/z: [M+H]$^{+}$ Calcd. for $C_{27}H_{19}NOS_2$: 438.0980; found: 438.0985.

(2) 1-(2-fluorophenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ba)



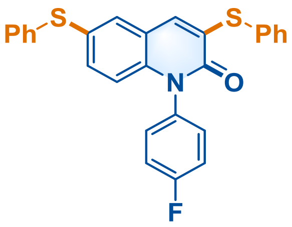
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (64 mg, 71% yield); m.p.: 139-141 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.57 (td, *J* = 8.1, 6.0 Hz, 1H), 7.50 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.18 (m, 7H), 7.12 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.06 (dt, *J* = 8.8, 2.2 Hz, 1H), 6.91 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.6 (d, *J* = 249.3 Hz), 159.2, 138.6 (d, *J* = 9.8 Hz), 137.8, 136.4, 136.3, 135.8, 132.7, 131.5 (d, *J* = 8.8 Hz), 130.6, 130.3, 130.2, 130.1, 130.0, 129.9, 129.3, 129.2, 126.9, 124.7 (d, *J* = 3.3 Hz), 121.3, 116.7 (d, *J* = 2.4 Hz), 116.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.95. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{18}FNOS_2$: 456.0886; found: 456.0892.

(3) 1-(3-fluorophenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ca)



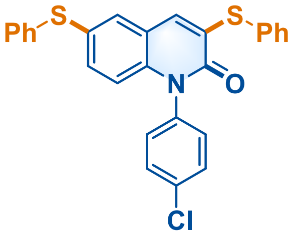
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (66 mg, 73% yield); m.p.: 138-139 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.57 (td, *J* = 8.1, 6.1 Hz, 1H), 7.50 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.18 (m, 7H), 7.12 (ddd, *J* = 7.8, 1.9, 0.9 Hz, 1H), 7.06 (dt, *J* = 8.8, 2.2 Hz, 1H), 6.91 (s, 1H), 6.60 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.6 (d, *J* = 249.3 Hz), 159.3, 138.6 (d, *J* = 9.5 Hz), 137.9, 136.4, 136.4, 135.8, 132.7, 131.5 (d, *J* = 8.9 Hz), 130.6, 130.3, 130.2, 130.1, 130.0, 129.9, 129.3, 129.2, 126.9, 124.7 (d, *J* = 3.3 Hz), 121.3, 116.7 (d), 116.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.00. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{18}FNOS_2$: 456.0886; found: 456.0891.

(4) 1-(4-fluorophenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3da)



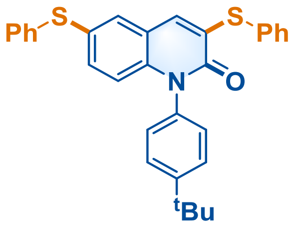
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (69 mg, 76% yield); m.p.: 139-141 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, J = 6.5, 3.0 Hz, 2H), 7.51 – 7.48 (m, 3H), 7.39 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 6.4 Hz, 4H), 7.26 – 7.17 (m, 6H), 6.91 (s, 1H), 6.60 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8 (d, J = 249.3 Hz), 159.5, 138.2, 136.5, 136.4, 135.8, 133.1 (d, J = 3.3 Hz), 132.7, 130.7, 130.6, 130.2, 130.2, 130.0, 129.8, 129.3, 129.1, 126.9, 121.4, 117.4 (d, J = 22.8 Hz), 116.8. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -111.72. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{18}FNOS_2$: 456.0886; found: 456.0890.

(5) 1-(4-chlorophenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ea)



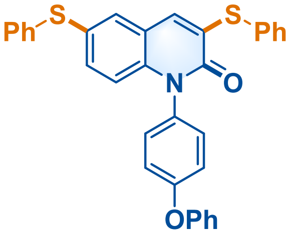
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (68 mg, 73% yield); m.p.: 160-162 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, J = 6.5, 3.0 Hz, 2H), 7.57 (d, 2H), 7.50 (t, 3H), 7.39 (d, J = 2.1 Hz, 1H), 7.26 – 7.18 (m, 8H), 6.91 (s, 1H), 6.60 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 137.9, 136.4, 136.3, 135.8, 135.7, 135.3, 132.6, 130.6, 130.3, 130.3, 130.2, 130.1, 130.0, 129.8, 129.3, 129.2, 126.9, 121.4, 116.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{18}ClNOS_2$ 470.0445; found: 470.0434.

(6) 1-(4-(tert-butyl)phenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3fa)



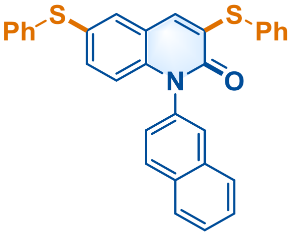
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (75 mg, 77% yield); m.p.: 167-168 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, 2H), 7.59 (d, 2H), 7.49 (dd, *J* = 4.9, 2.0 Hz, 3H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.24 (s, 1H), 7.23 – 7.16 (m, 7H), 6.91 (s, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 152.3, 138.5, 136.7, 136.4, 135.8, 134.5, 132.6, 130.6, 130.3, 130.1, 130.1, 129.9, 129.7, 129.3, 128.6, 128.1, 127.3, 126.8, 121.4, 117.2, 34.9, 31.5. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{31}H_{27}NOS_2$: 494.1606; found: 494.1611.

(7) 1-(4-phenoxyphenyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ga)



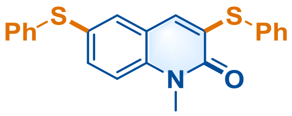
Petroleum ether and ethyl acetate (6:1) were used as eluents. Brown solid (69 mg, 66% yield); m.p.: 163-164 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, 2H), 7.50 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.39 (t, 3H), 7.26 – 7.17 (m, 11H), 7.13 (d, 2H), 6.91 (s, 1H), 6.69 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.6, 158.3, 156.3, 138.4, 136.6, 136.4, 135.8, 132.7, 131.7, 130.6, 130.2, 130.1, 130.1, 129.9, 129.8, 129.3, 128.8, 126.9, 124.3, 121.4, 119.9, 119.7, 117.0. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{33}H_{23}N_2O_2S_2$: 530.1242; found: 530.1248.

(8) 1-(naphthalen-2-yl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ha)



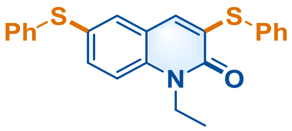
Petroleum ether and ethyl acetate (6:1) were used as eluents. yellow solid (60 mg, 62% yield); m.p.: 147-149 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, 2H), 7.60 – 7.55 (m, 2H), 7.51 (dd, 3H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.25 – 7.16 (m, 6H), 6.95 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.7, 138.4, 136.6, 136.5, 135.8, 134.6, 134.0, 133.4, 132.7, 130.7, 130.5, 130.2, 130.2, 129.9, 129.8, 129.3, 128.7, 128.3, 128.1, 127.9, 127.2, 126.9, 126.8, 126.1, 121.4, 117.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{21}NOS_2$: 488.1137; found: 488.1140.

(9) 1-methyl-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ia)



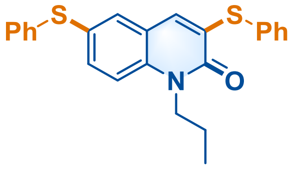
Petroleum ether and ethyl acetate (5:1) were used as eluents. Light yellow solid (43 mg, 58% yield); m.p.: 152-154 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.48 – 7.45 (m, 4H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 3H), 6.81 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 137.2, 136.8, 135.8, 135.6, 133.2, 131.2, 130.3, 130.1, 129.7, 129.6, 129.2, 128.3, 126.7, 121.6, 115.2, 30.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{17}NOS_2$: 376.0824; found: 376.0827.

(10) 1-ethyl-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ja)



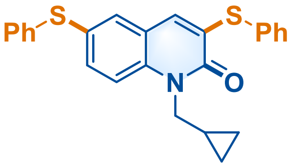
Petroleum ether and ethyl acetate (6:1) were used as eluents. Light yellow solid (34 mg, 44% yield); m.p.: 155-158 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (dd, 2H), 7.48 – 7.45 (m, 4H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.22 – 7.17 (m, 3H), 6.80 (s, 1H), 4.42 – 4.39 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.0, 136.8, 136.1, 135.9, 135.7, 133.2, 131.5, 130.3, 130.1, 129.7, 129.7, 129.6, 129.3, 128.0, 126.8, 122.0, 115.1, 38.3, 12.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{19}NOS_2$: 390.0980; found: 390.0984.

(11) 3,6-bis(phenylthio)-1-propylquinolin-2(1*H*)-one (3ka)



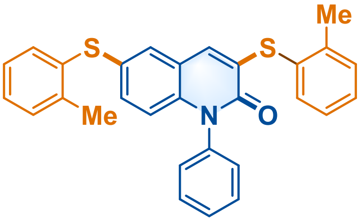
Petroleum ether and ethyl acetate (6:1) were used as eluents. Light yellow solid (46 mg, 57% yield); m.p.: 142-144 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.51 – 7.48 (m, 3H), 7.48 – 7.46 (m, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.20 (m, 6H), 6.83 (s, 1H), 4.33 – 4.29 (m, 2H), 1.86 – 1.81 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.2, 136.8, 136.4, 135.8, 135.6, 133.1, 131.4, 130.3, 130.1, 129.7, 129.6, 129.6, 129.3, 128.0, 126.8, 121.9, 115.3, 44.8, 20.9, 11.5. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{24}H_{21}NOS_2$: 404.1137; found: 404.1141.

(12) 1-(cyclopropylmethyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3la)



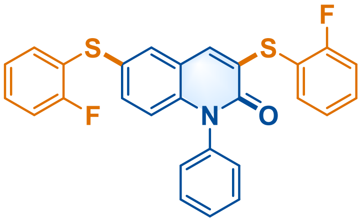
Petroleum ether and ethyl acetate (10:1) were used as eluents. Light yellow solid (30 mg, 37% yield); m.p.: 155-156 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.49 (q, *J* = 3.2, 2.6 Hz, 4H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.29 – 7.20 (m, 5H), 6.84 (s, 1H), 4.31 (d, *J* = 7.0 Hz, 2H), 1.31 – 1.28 (m, 1H), 0.66 – 0.61 (m, 2H), 0.58 – 0.55 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 136.8, 136.6, 135.9, 135.6, 133.1, 131.4, 130.3, 130.1, 129.7, 129.7, 129.6, 129.2, 128.0, 126.7, 121.9, 115.5, 47.0, 9.9, 4.3. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{25}H_{21}NOS_2$: 416.1137; found: 416.1141.

(13) 1-phenyl-3,6-bis(o-tolylthio)quinolin-2(1*H*)-one (3ab)



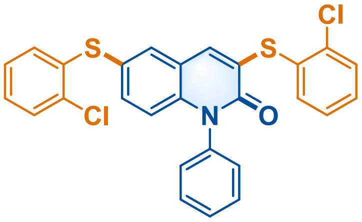
Petroleum ether and ethyl acetate (6:1) were used as eluents. Reddish-brown solid (73 mg, 79% yield); m.p.: 175-178 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 3.9 Hz, 2H), 7.35 – 7.31 (m, 4H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.17 – 7.06 (m, 4H), 6.71 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 2.51 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 143.3, 138.6, 137.7, 137.3, 137.0, 135.2, 134.7, 131.3, 131.3, 131.2, 130.6, 130.4, 130.2, 129.2, 129.2, 128.9, 128.9, 128.8, 128.7, 127.5, 127.4, 126.7, 121.4, 116.9, 20.6, 20.5. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{23}NOS_2$: 466.1293; found: 466.1299.

(14) 3,6-bis((2-fluorophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ac)



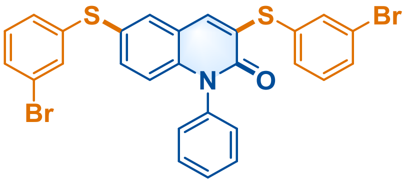
Petroleum ether and ethyl acetate (6:1) were used as eluents. yellow solid (72 mg, 76% yield); m.p.: 168-170 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (td, *J* = 7.5, 1.8 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.21 (td, *J* = 8.9, 2.0 Hz, 2H), 7.12 (td, *J* = 7.6, 1.8 Hz, 1H), 7.03 (dtd, *J* = 15.0, 7.9, 1.2 Hz, 2H), 6.91 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 250.3 Hz), 161.6, 159.4, 138.6, 137.7, 137.2, 133.9, 132.6, 132.5, 132.5, 130.6, 130.3, 130.2, 129.4, 129.2, 129.2, 128.8, 127.4 (d), 125.6 (d, *J* = 3.8 Hz), 124.8 (d, *J* = 3.7 Hz), 123.4 (d, *J* = 17.5 Hz), 121.3, 117.2, 116.9 (d, *J* = 22.3 Hz), 116.0 (d, *J* = 21.7 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -105.60, -109.31. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{17}F_2NOS_2$: 474.0792; found: 474.0797.

(15) 3,6-bis((2-chlorophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ad)



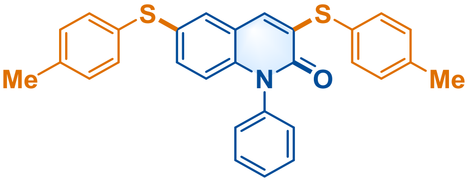
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (75 mg, 74% yield); m.p.: 166-168 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.61 (tt, *J* = 6.7, 1.7 Hz, 3H), 7.55 – 7.52 (m, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.35 – 7.32 (m, 3H), 7.29 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.88 (s, 1H), 6.84 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 1398, 139.2, 137.6, 137.1, 136.9, 134.2, 133.7, 132.6, 132.6, 131.4, 130.9, 130.6, 130.4, 129.8, 129.4, 129.4, 128.8, 128.2, 127.3, 127.2, 126.0, 121.5, 117.4. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{17}Cl_2NOS_2$: 506.0201; found: 506.0206.

(16) 3,6-bis((3-bromophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ae)



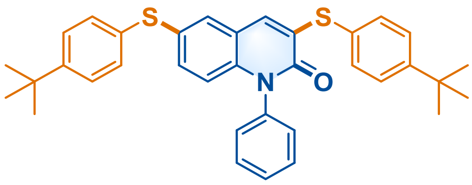
Petroleum ether and ethyl acetate (6:1) were used as eluents. yellow solid (91 mg, 77% yield); m.p.: 163-165 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (t, *J* = 1.8 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.57 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 5H), 7.12 – 7.07 (m, 2H), 7.04 (s, 1H), 6.65 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 139.5, 139.0, 137.7, 137.1, 135.3, 133.9, 133.7, 132.8, 132.7, 131.8, 131.6, 131.4, 131.3, 130.5, 130.4, 129.7, 129.4, 128.7, 127.7, 127.3, 123.6, 123.2, 121.3, 117.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{17}Br_2NOS_2$: 593.9191; found: 593.9196.

(17) 1-phenyl-3,6-bis(p-tolylthio)quinolin-2(1*H*)-one (3af)



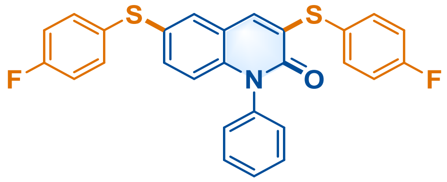
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (76 mg, 82% yield); m.p.: 181-183 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 7.6 Hz, 2H), 7.53 – 7.50 (m, 3H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.17 – 7.13 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 140.1, 137.9, 137.4, 137.3, 136.8, 135.8, 132.4, 131.7, 131.0, 130.9, 130.3, 130.1, 129.9, 129.8, 129.5, 129.2, 128.8, 126.4, 121.4, 116.9, 21.5, 21.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{23}NOS_2$: 466.1293; found: 4562.1299.

(18) 3,6-bis((4-(*tert*-butyl)phenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ag)



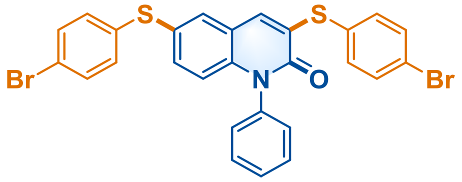
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (84 mg, 77% yield); m.p.: 170-173 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 15.9, 7.9 Hz, 4H), 7.54 – 7.51 (m, 3H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.18 (dd, *J* = 8.7, 3.3 Hz, 3H), 6.93 (s, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 1.39 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 153.1, 150.4, 137.9, 137.4, 136.6, 135.5, 132.5, 131.9, 130.3, 130.3, 129.8, 129.7, 129.4, 129.2, 128.8, 127.2, 126.4, 121.3, 116.9, 35.0, 34.6, 31.4, 31.3. HRMS (ESI-Orbitrap) m/z: [M+H]$^{+}$ Calcd. for $C_{35}H_{35}NOS_2$: 550.2232; found: 550.2238.

(19) 3,6-bis((4-fluorophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ah)



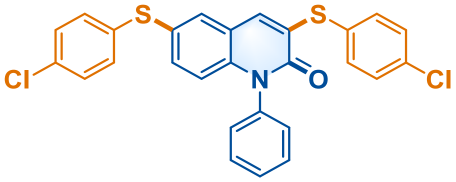
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (70 mg, 74% yield); m.p.: 172-174 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.20 (t, *J* = 8.6 Hz, 2H), 7.16 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.87 (s, 1H), 6.59 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 17.4 Hz), 161.5, 159.4, 138.1, 138.0, 137.9, 137.2, 136.5, 133.1, 133.0, 131.8, 131.0 (d, *J* = 3.5 Hz), 130.3, 130.0, 129.8, 129.5, 129.4, 128.7, 125.4 (d, *J* = 3.4 Hz), 121.3, 117.5 (d, *J* = 22.0 Hz), 117.1, 116.5 (d, *J* = 22.1 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.46, -114.19. HRMS (ESI-Orbitrap) m/z: [M+H]$^{+}$ Calcd. for $C_{27}H_{17}F_2NOS_2$: 474.0792; found: 474.0799.

(20) 3,6-bis((4-bromophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3ai)



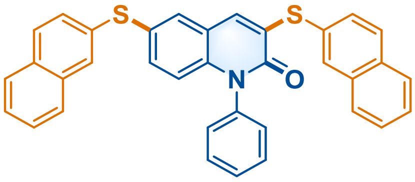
Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (86 mg, 73% yield); m.p.: 163-165 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 14.2, 8.1 Hz, 4H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.23 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.98 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 138.7, 137.1, 137.0, 136.1, 135.7, 133.3, 133.1, 132.3, 131.2, 131.1, 130.7, 130.4, 129.5, 129.4, 128.7, 128.0, 124.4, 121.3, 120.7, 117.2. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{27}H_{17}Br_2NOS_2$: 593.9191; found: 593.9197.

(21) 3,6-bis((4-chlorophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3aj)



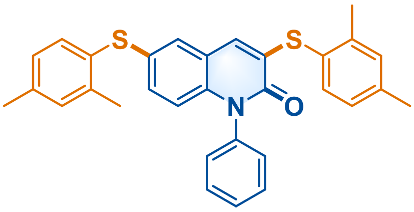
Petroleum ether and ethyl acetate (6:1) were used as eluents. Light pink solid (78 mg, 78% yield); m.p.: 164-165 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 – 7.52 (m, 5H), 7.48 – 7.45 (m, 2H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.15 – 7.12 (m, 2H), 6.97 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 138.5, 137.1, 136.8, 136.1, 135.7, 135.2, 132.9, 132.8, 131.0, 130.9, 130.5, 130.3, 130.3, 129.3, 128.8, 128.6, 128.2, 121.2, 117.1. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{27}H_{17}Cl_2NOS_2$: 506.0201; found: 506.0208.

(22) 3,6-bis(naphthalen-2-ylthio)-1-phenylquinolin-2(1*H*)-one (3ak)



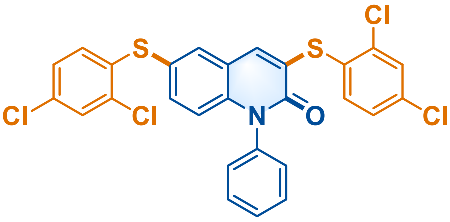
Petroleum ether and ethyl acetate (6:1) were used as eluents. yellow solid (76 mg, 71% yield); m.p.: 147-149 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.68 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.58 – 7.54 (m, 3H), 7.45 – 7.41 (m, 2H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.27 – 7.24 (m, 2H), 6.97 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 138.3, 137.3, 136.3, 135.7, 134.1, 133.7, 133.7, 133.5, 132.5, 132.1, 131.7, 130.4, 130.4, 130.3, 129.9, 129.3, 128.9, 128.8, 128.7, 128.0, 127.9, 127.8, 127.8, 127.4, 127.3, 127.3, 126.9, 126.7, 126.2, 121.4, 117.0. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{35}H_{23}NOS_2$: 538.1293; found: 538.1301.

(23) 3,6-bis((2,4-dimethylphenyl)thio)-1-phenylquinolin-2(1*H*)-one (3al)



Petroleum ether and ethyl acetate (6:1) were used as eluents. Brown solid (68 mg, 69% yield); m.p.: 156-158 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.31 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.25 (d, *J* = 2.3 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.98 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.92 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.67 (s, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 2.43 (d, *J* = 14.0 Hz, 6H), 2.30 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 143.2, 140.6, 139.6, 138.1, 137.4, 137.4, 137.1, 135.5, 132.8, 132.2, 131.6, 130.4, 130.2, 130.2, 130.1, 129.1, 128.8, 128.6, 128.4, 127.9, 127.6, 125.3, 121.5, 116.8, 21.4, 21.1, 20.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{27}NOS_2$: 494.1606; found: 494.1613.

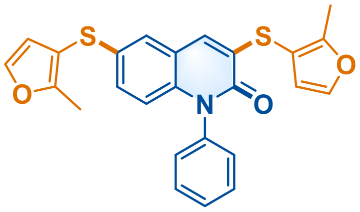
(24) 3,6-bis((2,4-dichlorophenyl)thio)-1-phenylquinolin-2(1*H*)-one (3am)



Petroleum ether and ethyl acetate (6:1) were used as eluents. White solid (83 mg, 73% yield); m.p.: 157-159 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.56 – 7.53 (m, 2H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.28 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.05 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.94 (s, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 140.4, 139.4, 138.1, 137.0, 136.9, 135.6, 134.3, 133.4, 133.2, 132.7, 132.5, 131.2, 130.8, 130.4, 130.3, 129.7, 129.5, 128.7, 128.6, 128.2, 127.7, 125.8, 121.5, 117.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for

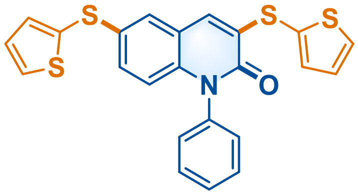
$C_{27}H_{15}Cl_4NOS_2$: 573.9421; found: 573.9429.

(25) 3,6-bis((2-methylfuran-3-yl)thio)-1-phenylquinolin-2(1*H*)-one (3an)



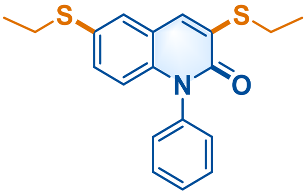
Petroleum ether and ethyl acetate (5:1) were used as eluents. Brown solid (50 mg, 57% yield); m.p.: 131-133 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.99 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.95 (s, 1H), 6.53 (d, *J* = 8.8 Hz, 1H), 6.45 (d, *J* = 1.9 Hz, 1H), 6.32 (d, *J* = 1.9 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 157.8, 156.7, 142.0, 141.4, 137.3, 136.8, 135.0, 132.0, 130.2, 129.2, 129.1, 128.7, 127.5, 124.6, 121.3, 116.7, 115.4, 115.3, 108.2, 105.5, 12.0, 11.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{19}NO_3S_2$: 446.0879; found: 446.0884.

(26) 1-phenyl-3,6-bis(thiophen-2-ylthio)quinolin-2(1*H*)-one (3ao)



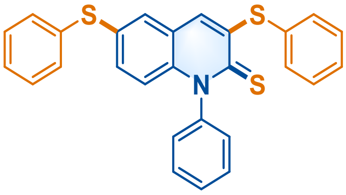
Petroleum ether and ethyl acetate (6:1) were used as eluents. Yellow solid (81mg, 91% yield); m.p.: 160-161 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.26 – 7.23 (m, 2H), 7.12 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.04 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.98 (s, 1H), 6.58 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.1, 137.8, 137.6, 137.1, 136.6, 135.5, 132.9, 132.1, 131.9, 131.2, 130.3, 130.1, 129.3, 129.1, 128.7, 128.0, 127.6, 126.6, 121.1, 116.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{15}NOS_4$: 450.0109; found: 450.0115.

(27) 3,6-bis(ethylthio)-1-phenylquinolin-2(1*H*)-one (3ap)



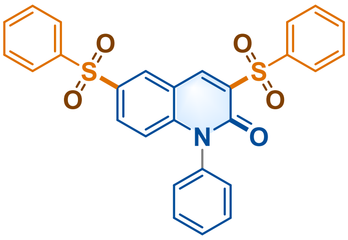
Petroleum ether and ethyl acetate (6:1) were used as eluents. Light yellow solid (32 mg, 48% yield); m.p.: 121-123 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.43 (s, 1H), 7.29 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.59 (d, *J* = 8.8 Hz, 1H), 3.01 (q, *J* = 7.4 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 2H), 1.46 (t, *J* = 7.4 Hz, 3H), 1.31 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.7, 137.4, 137.2, 134.0, 130.6, 130.2, 130.1, 129.7, 129.1, 128.7, 128.0, 121.2, 116.5, 28.8, 25.0, 14.6, 13.2. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{19}H_{19}NOS_2$: 342.0980; found: 342.0964.

(28) 1-phenyl-3,6-bis(phenylthio)quinoline-2(1*H*)-thione (3aa-s)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Light Yellow solid (70 mg, 78% yield); m.p.: 121-123 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 4H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.28 – 7.22 (m, 7H), 7.16 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.81 (s, 1H), 6.57 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 180.9, 146.4, 141.7, 138.9, 136.1, 135.2, 132.4, 131.9, 131.7, 131.0, 130.7, 130.3, 130.0, 129.4, 129.4, 129.1, 128.3, 127.5, 124.9, 123.9, 118.3. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ Calcd. for $C_{27}H_{19}NS_3$: 454.0752; found: 454.0757.

(29) 1-phenyl-3,6-bis(phenylsulfonyl)quinolin-2(1*H*)-one (3aa-O)

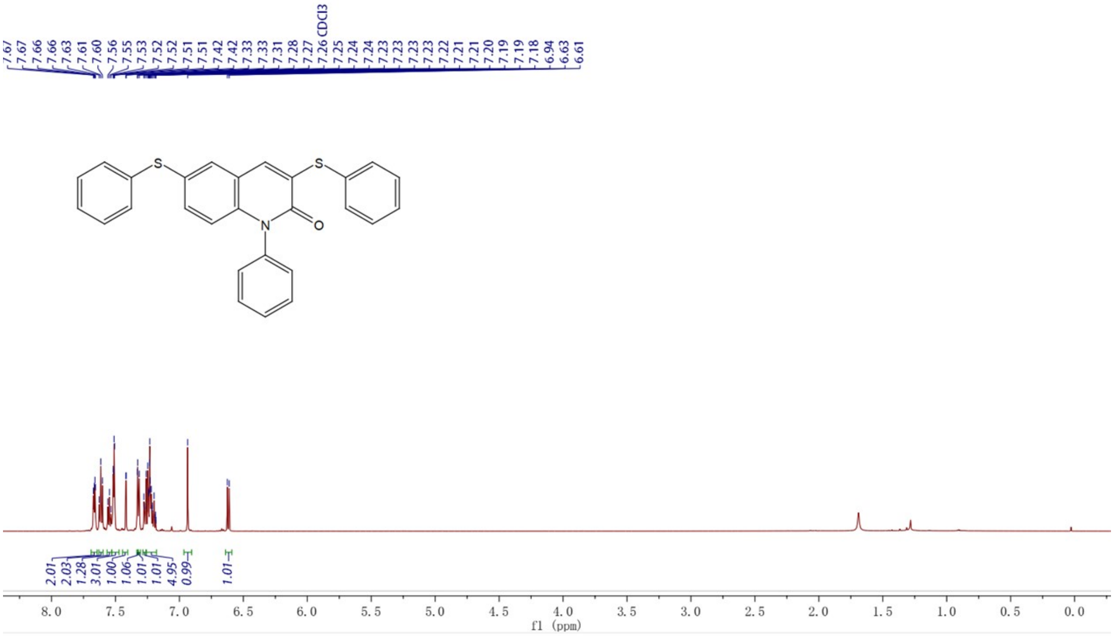


Petroleum ether and ethyl acetate (1:1) were used as eluents. White solid (34 mg, 34% yield); m.p.:

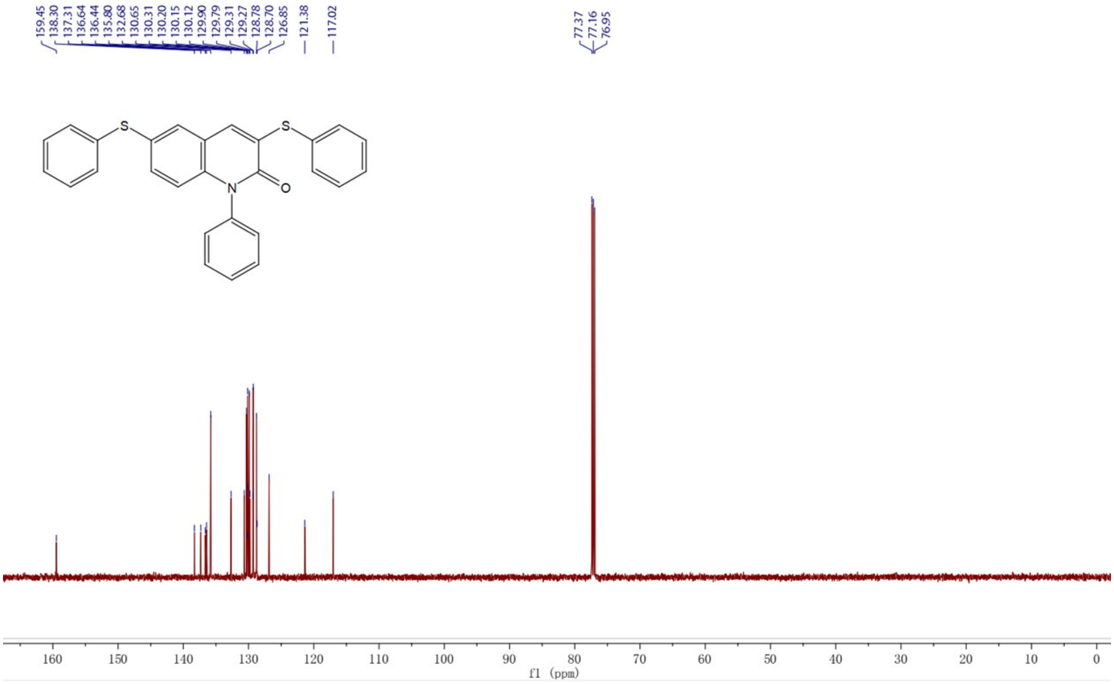
151-154 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.91 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.55 – 7.48 (m, 7H), 7.17 – 7.12 (m, 2H), 6.75 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6, 145.6, 143.5, 141.1, 138.7, 136.7, 135.7, 134.1, 134.0, 133.7, 131.4, 131.0, 130.7, 130.0, 129.6, 129.0, 128.4, 127.8, 117.9, 117.5. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{19}NO_5S_2$: 502.0777; found: 502.0783.

9. NMR spectra of the obtained compounds.

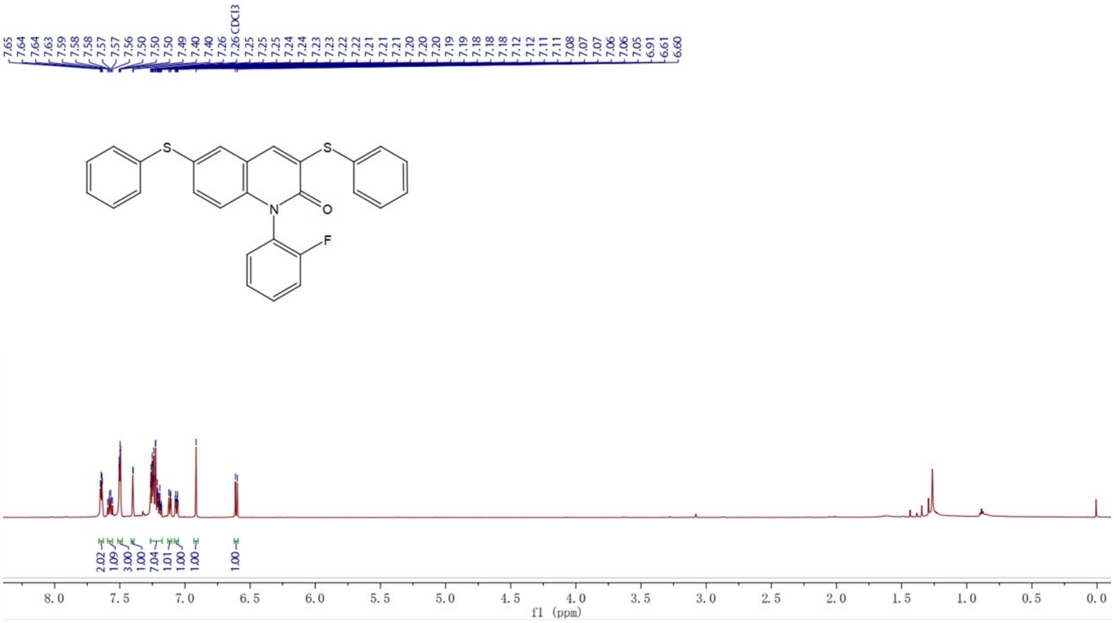
(1) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aa



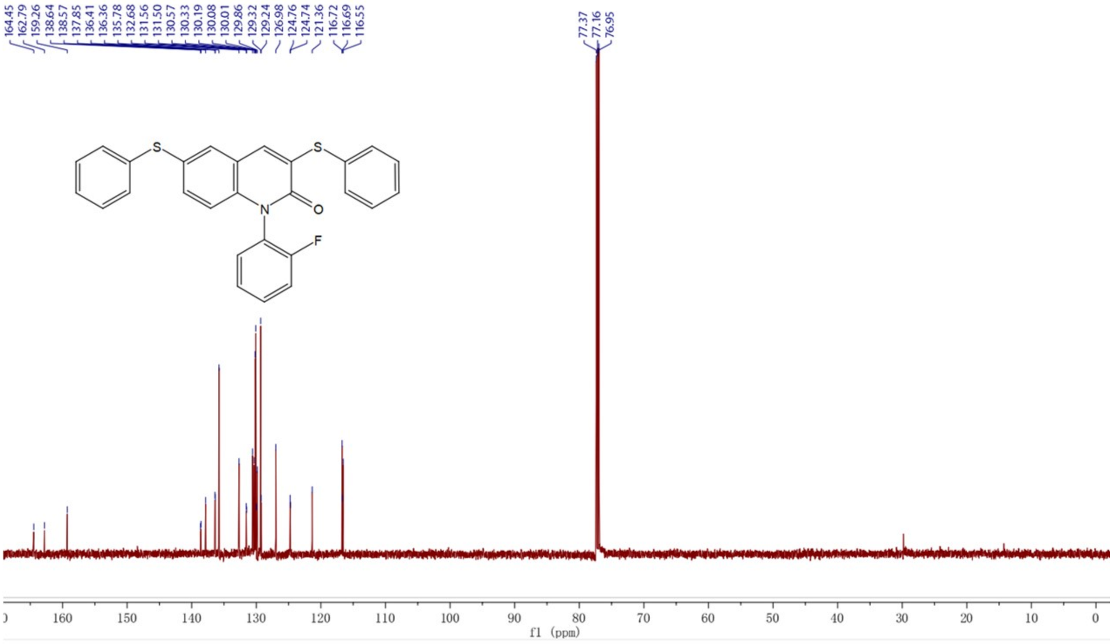
(2) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aa



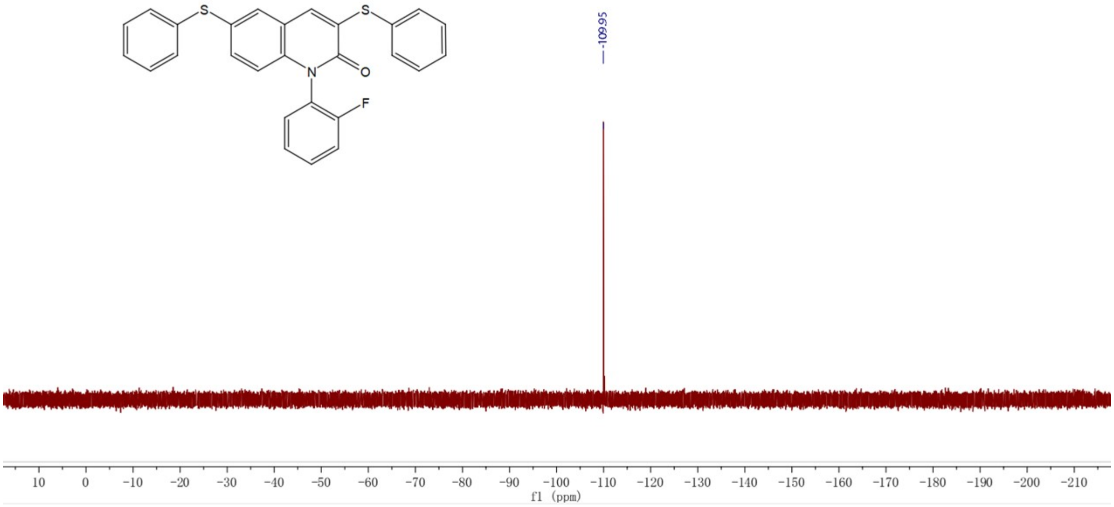
(3) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ba



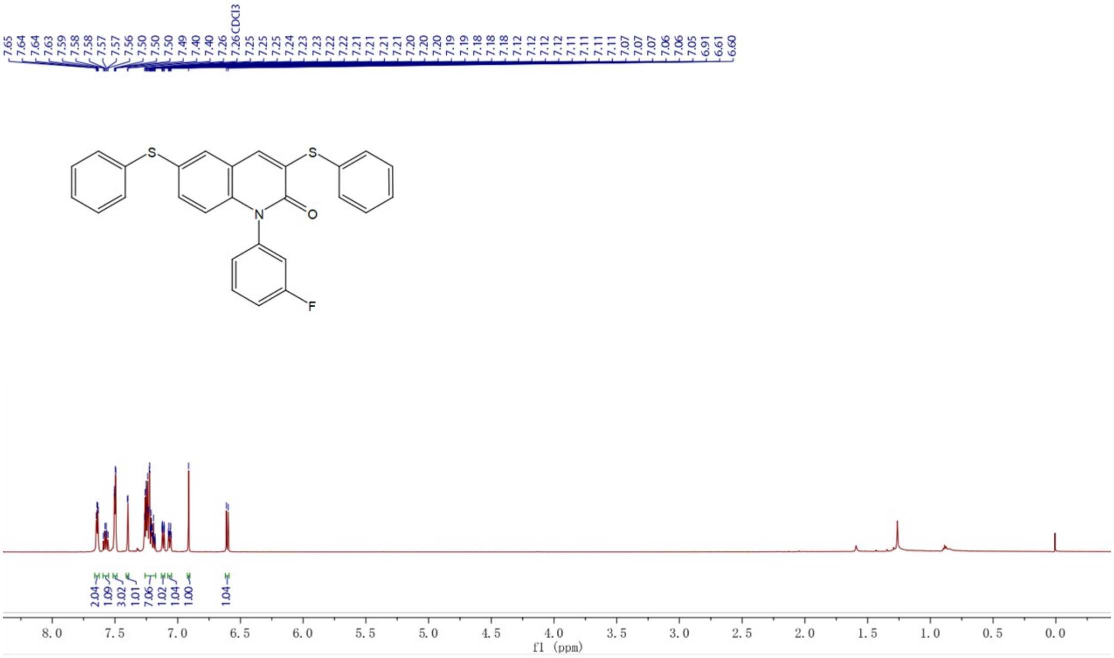
(4) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ba



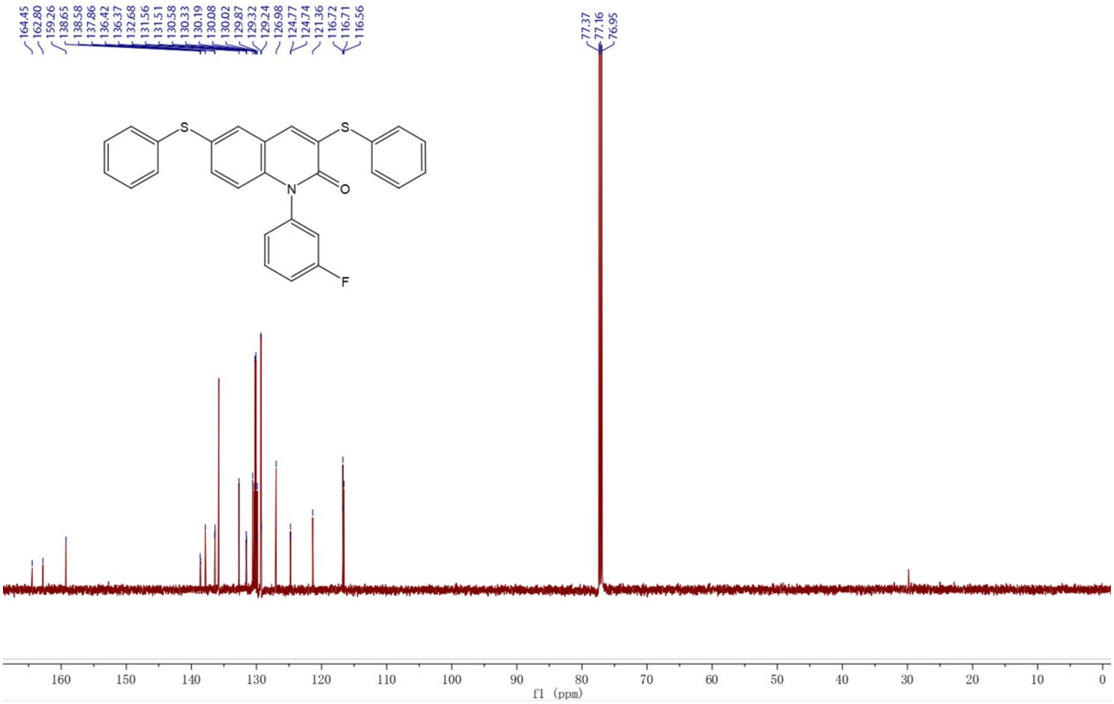
(5) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3ba



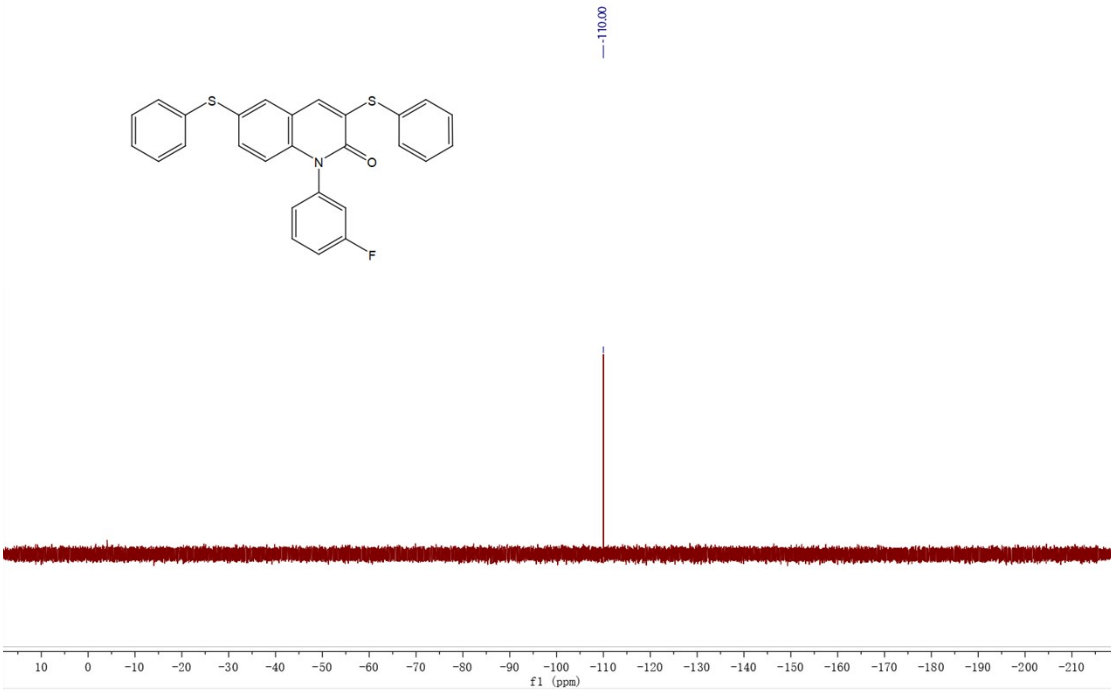
(6) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ca



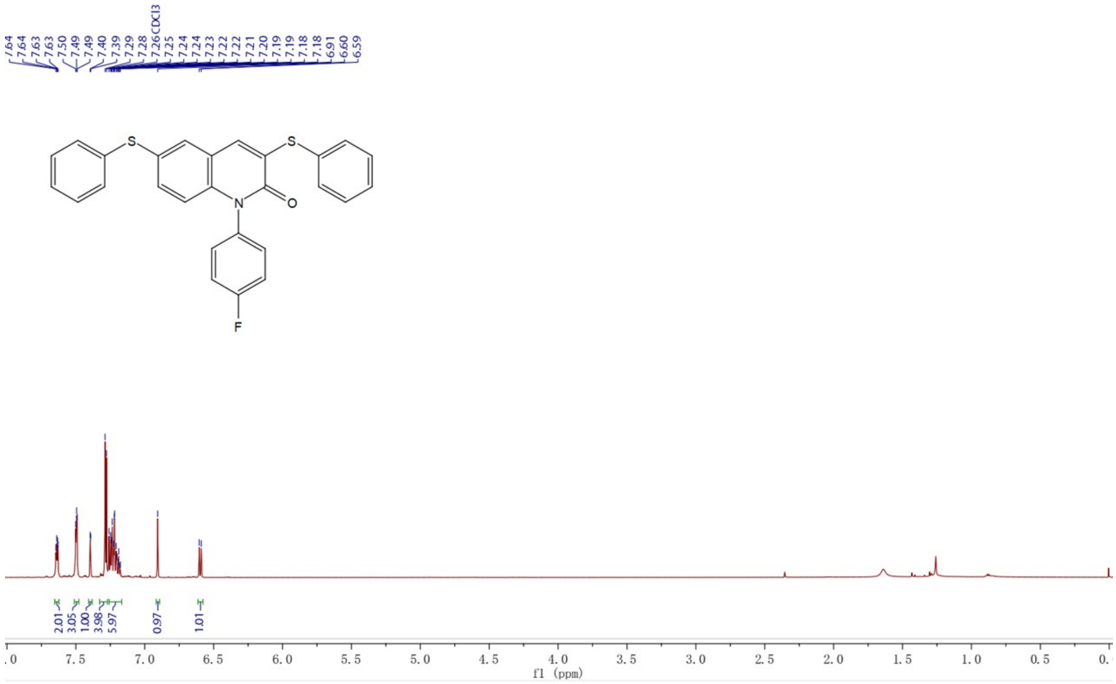
(7) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ca



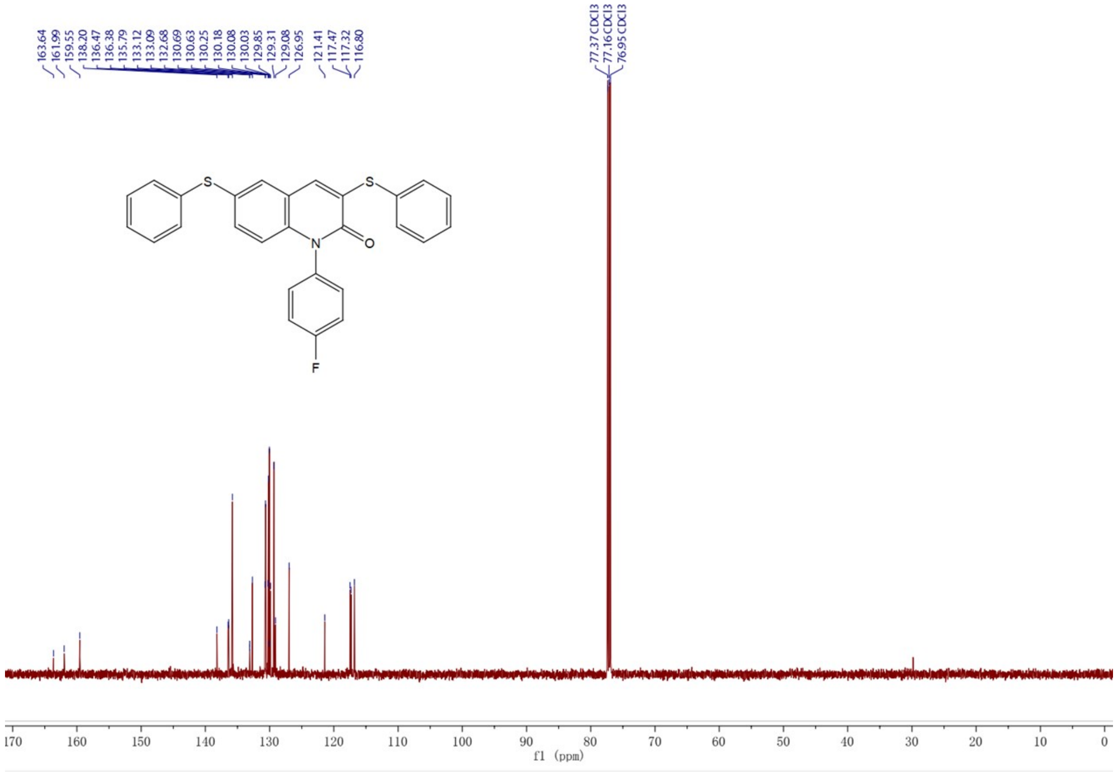
(8) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3ca



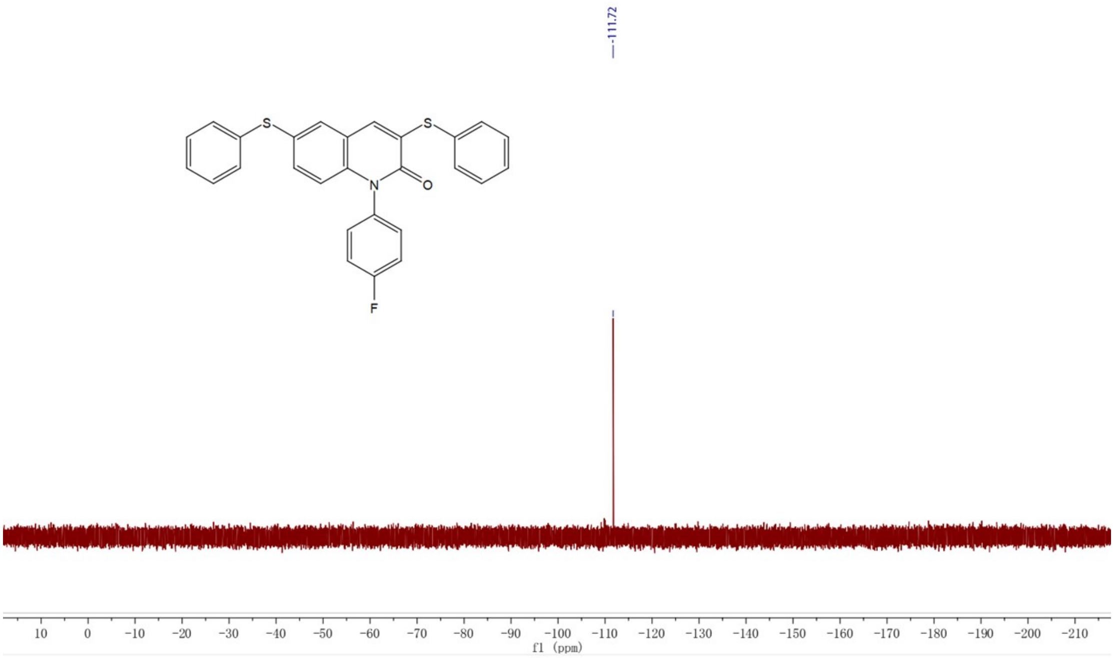
(9) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3da



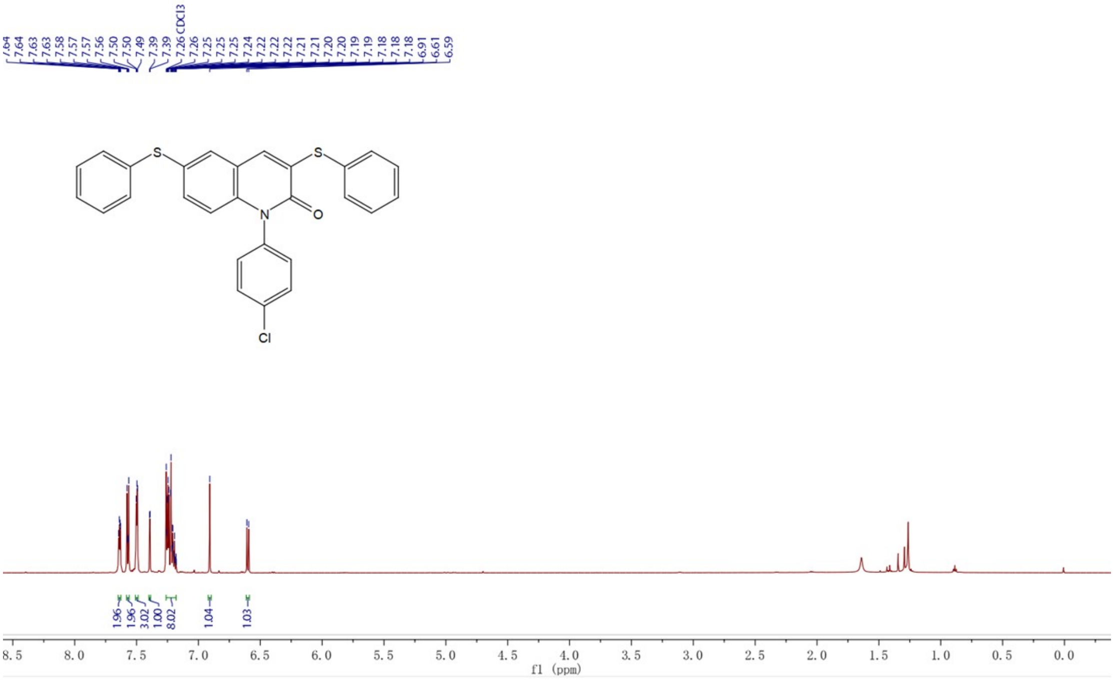
(10) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3da



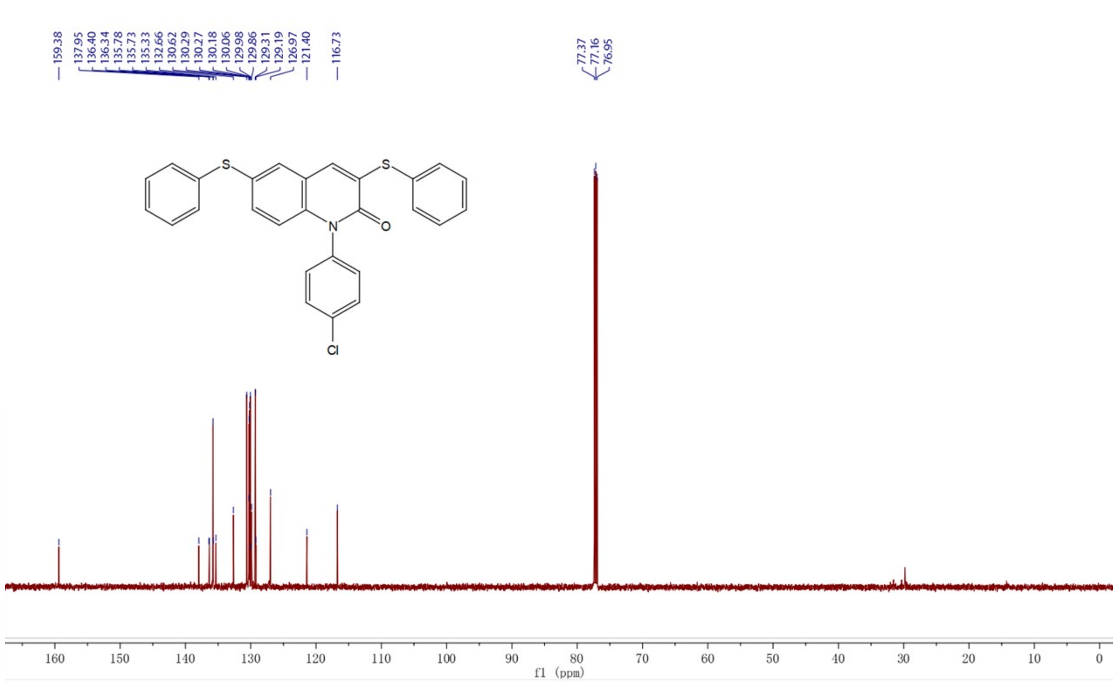
(11) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3da



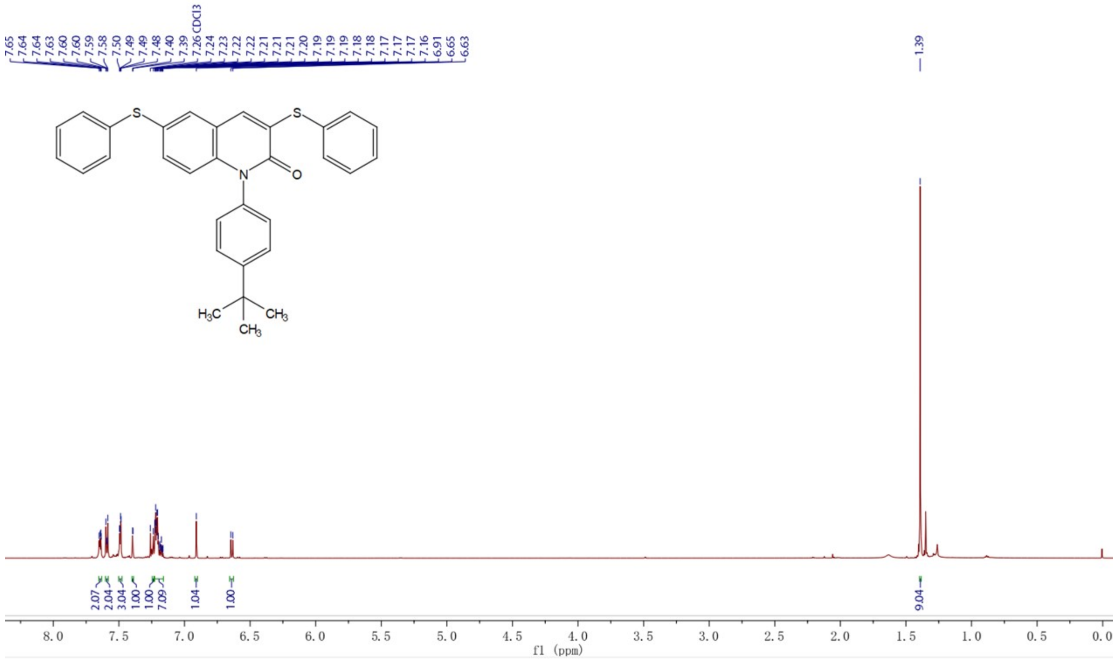
(12) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ea



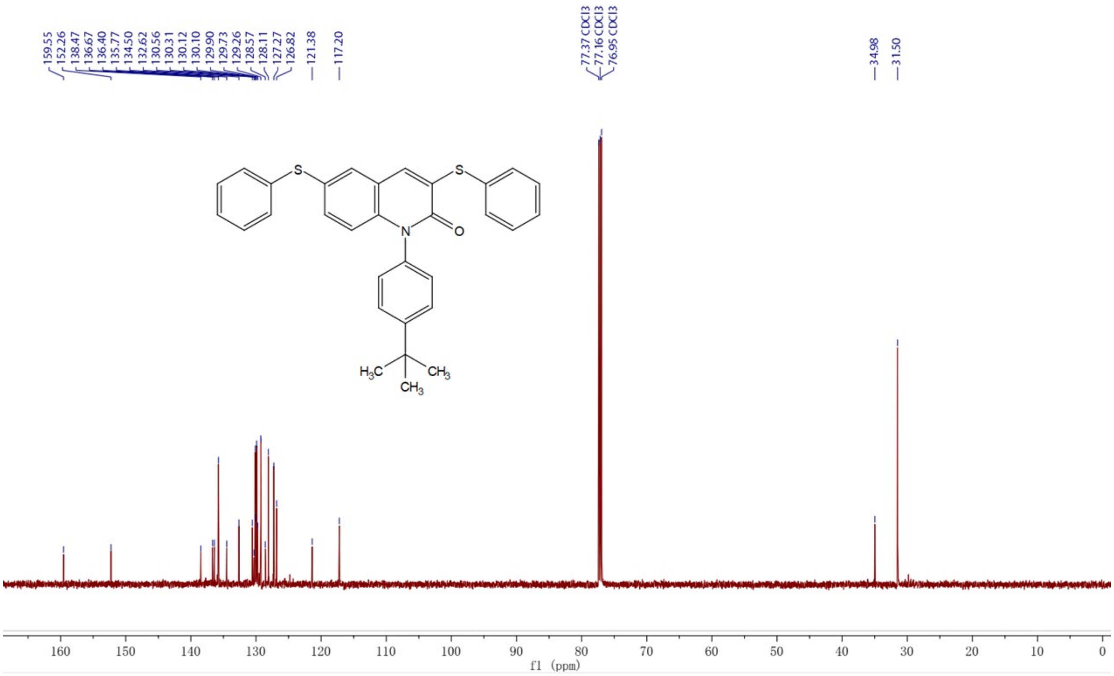
(12) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ea



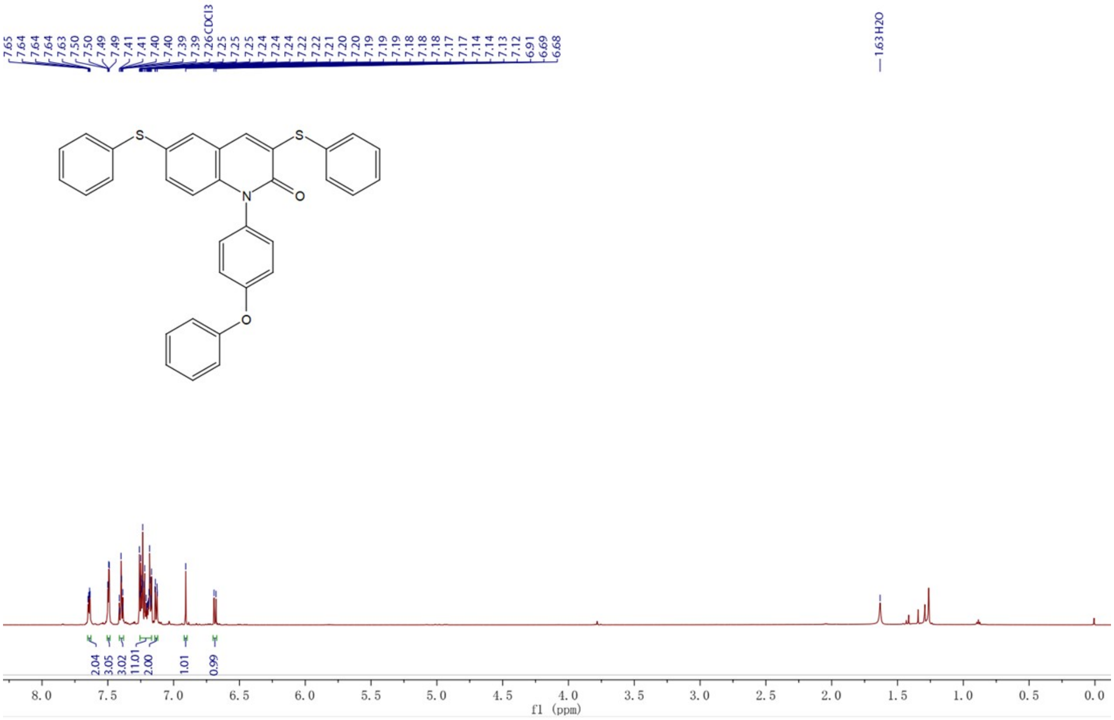
(13) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3fa



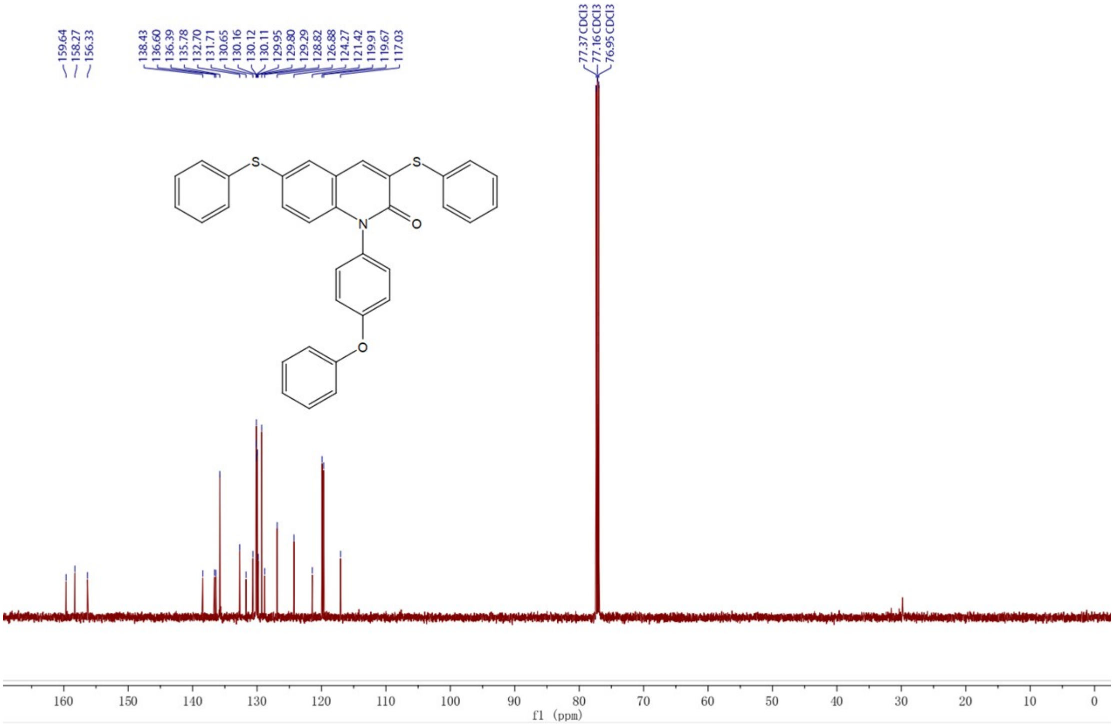
(14) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3fa



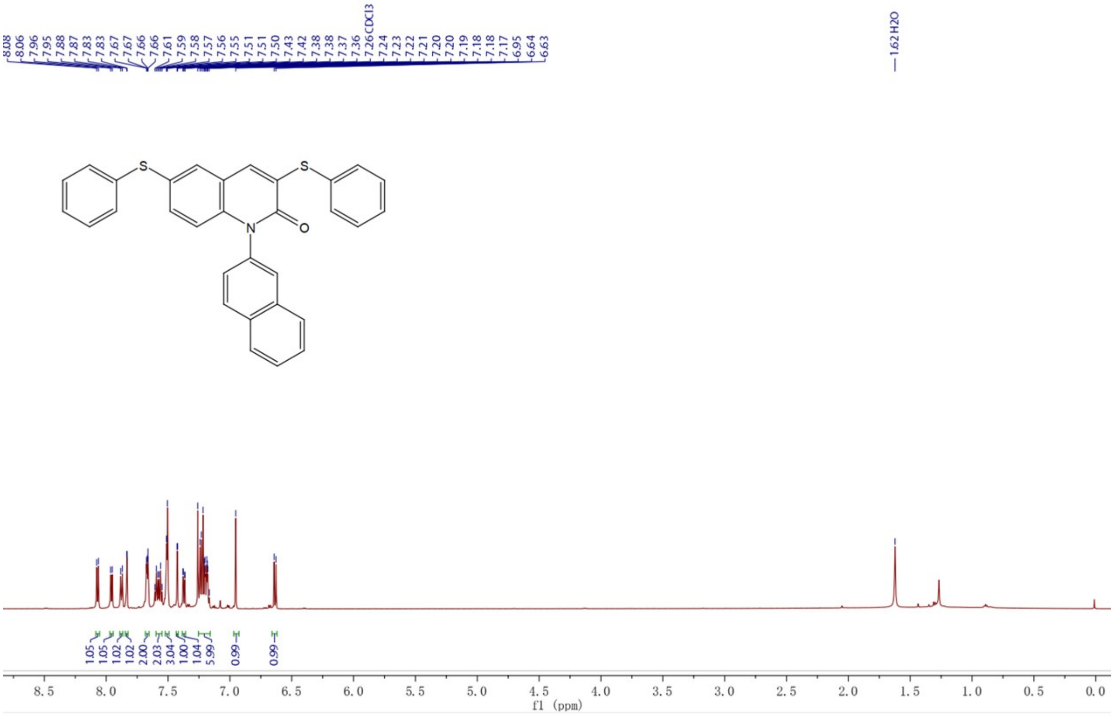
(15) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ga



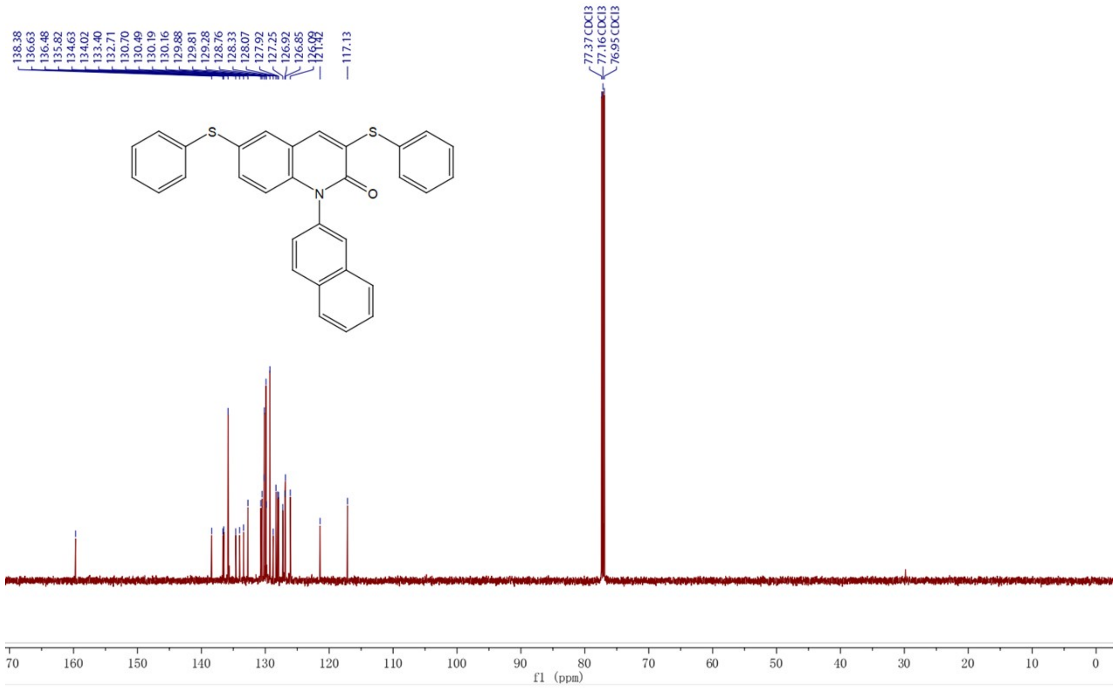
(16) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ga



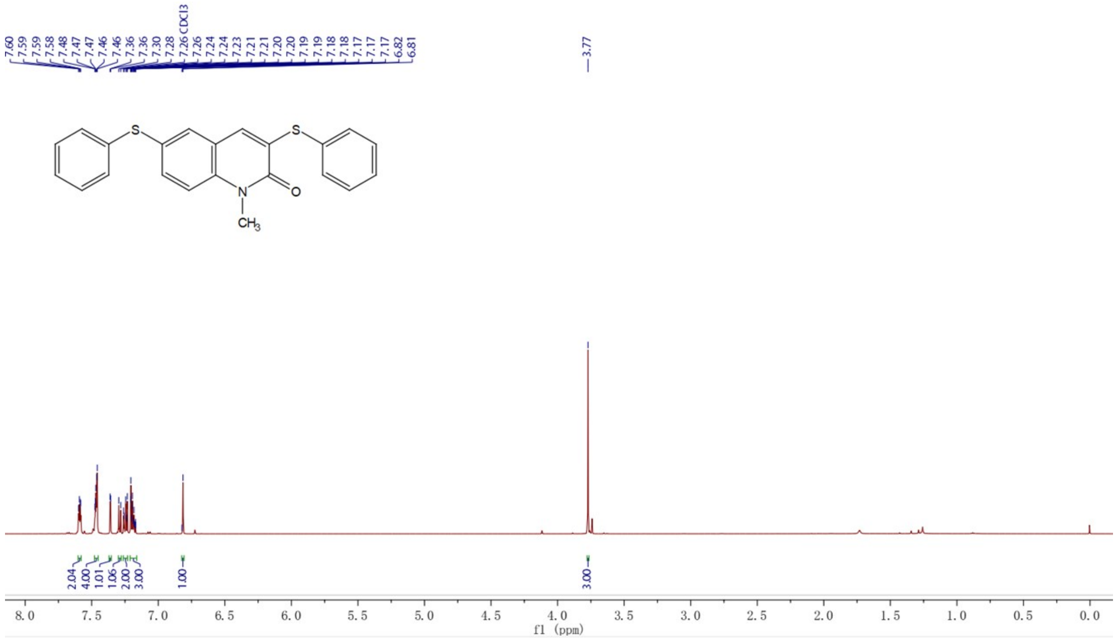
(17) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ha



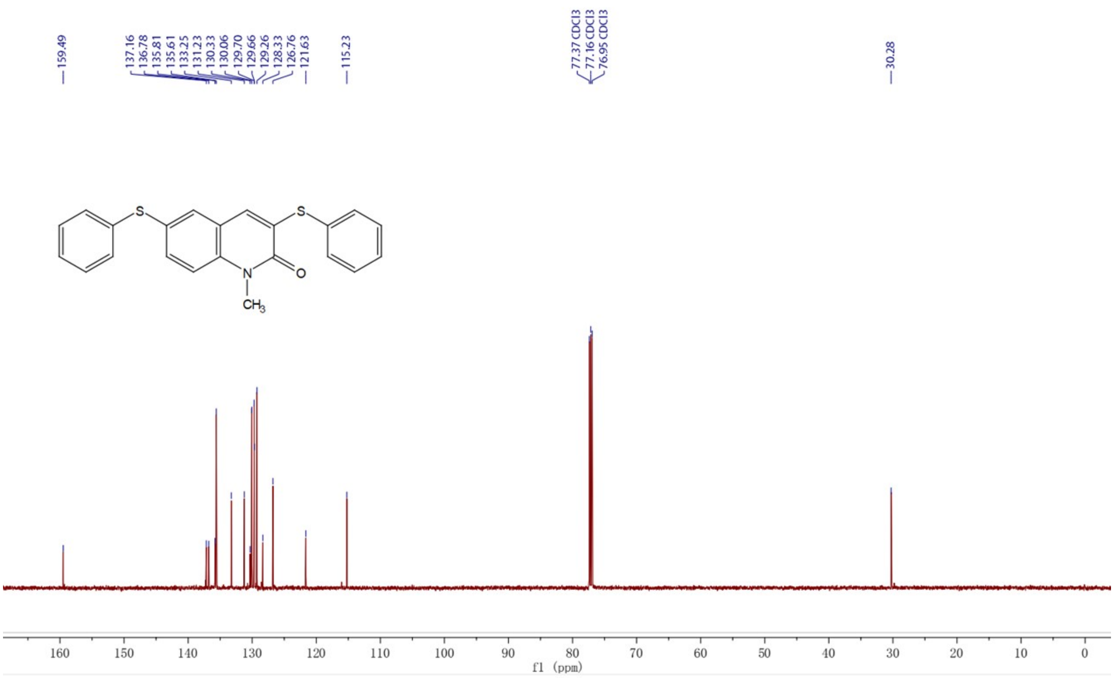
(18) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ha



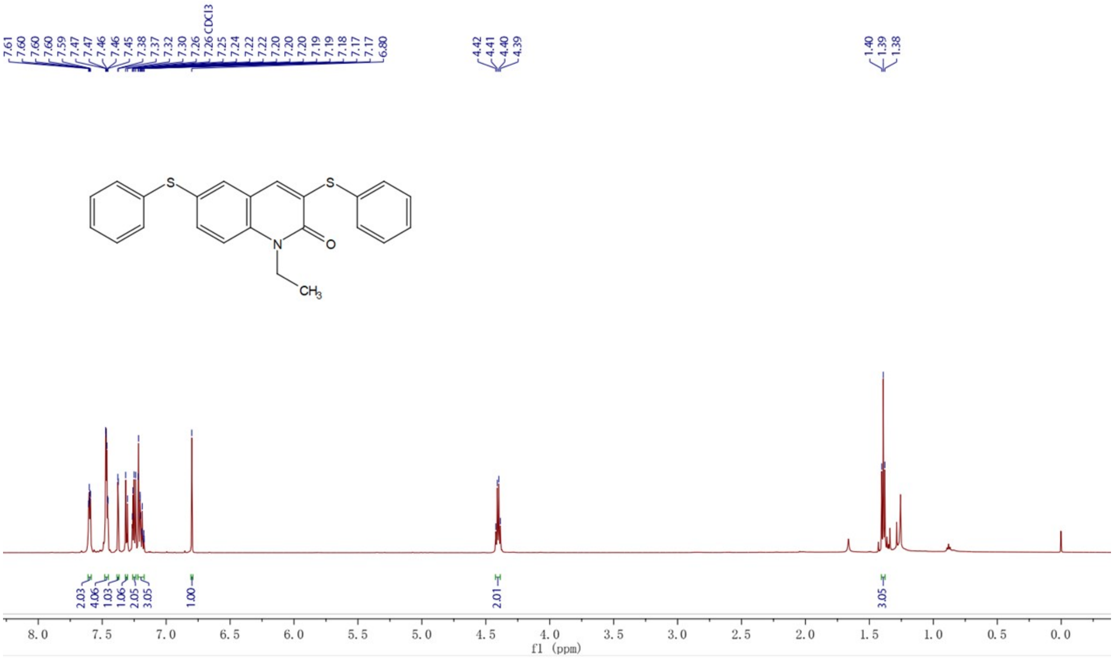
(19) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ia



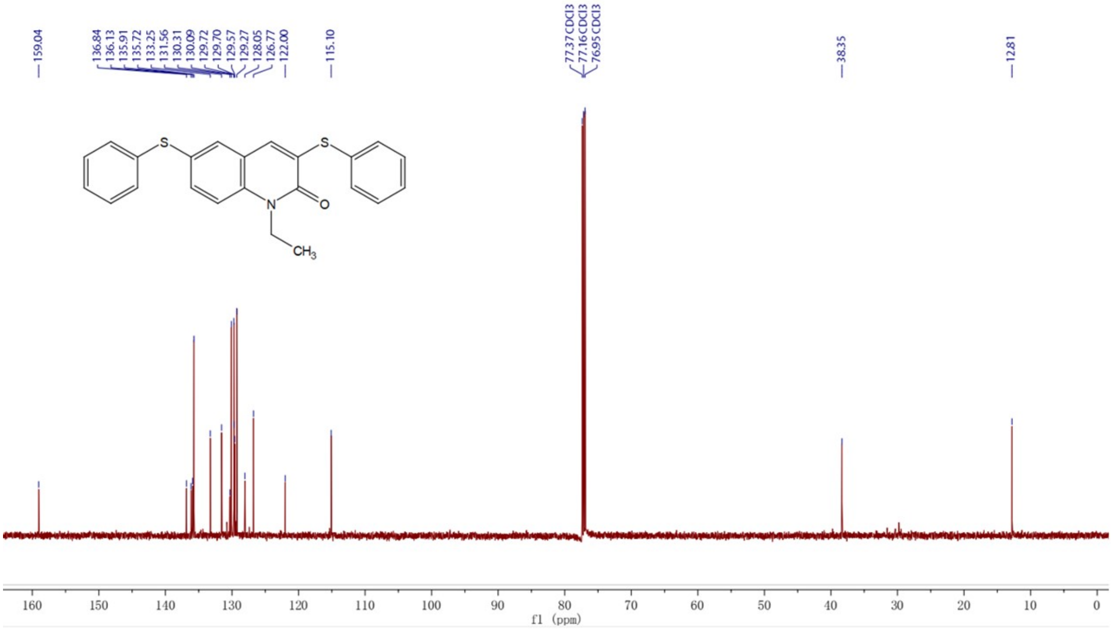
(20) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ia



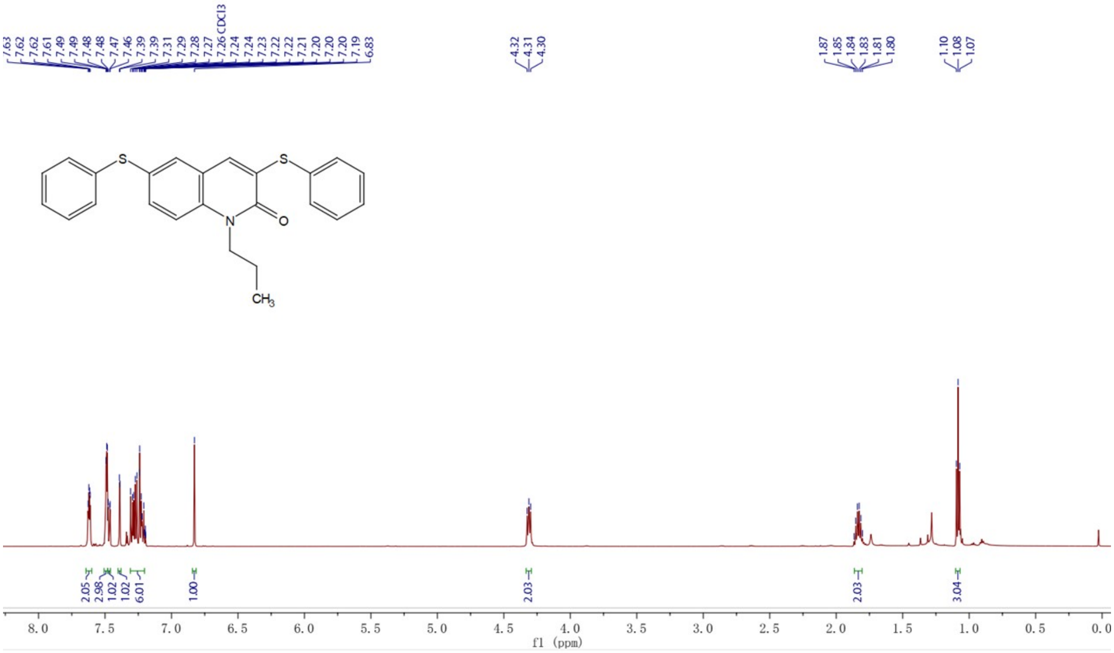
(21) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ja



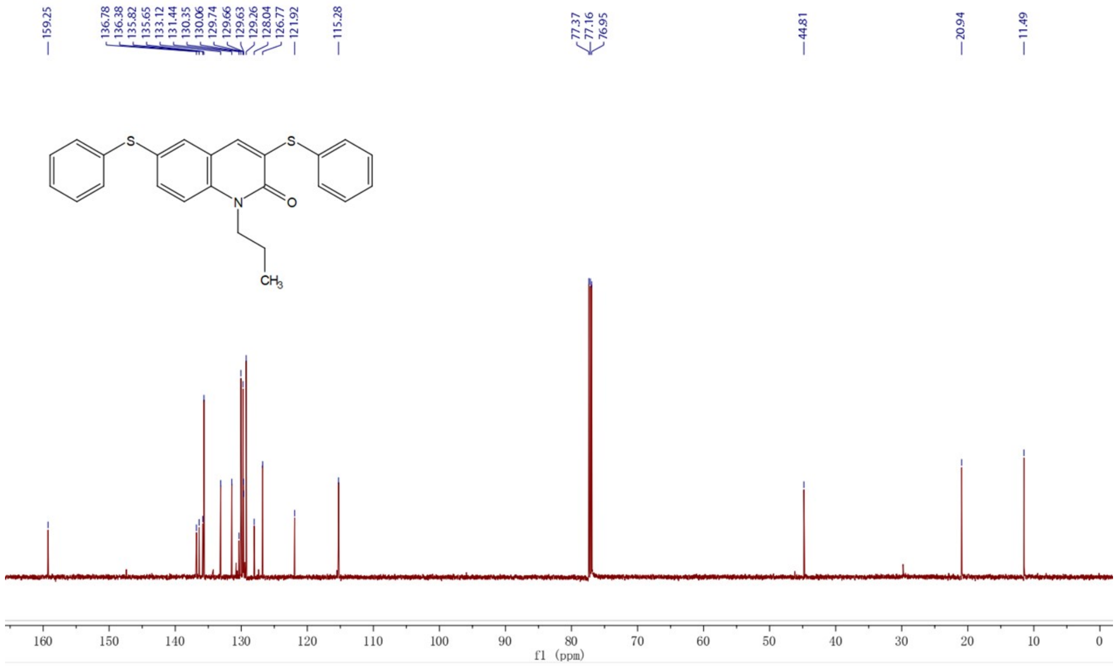
(22) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ja



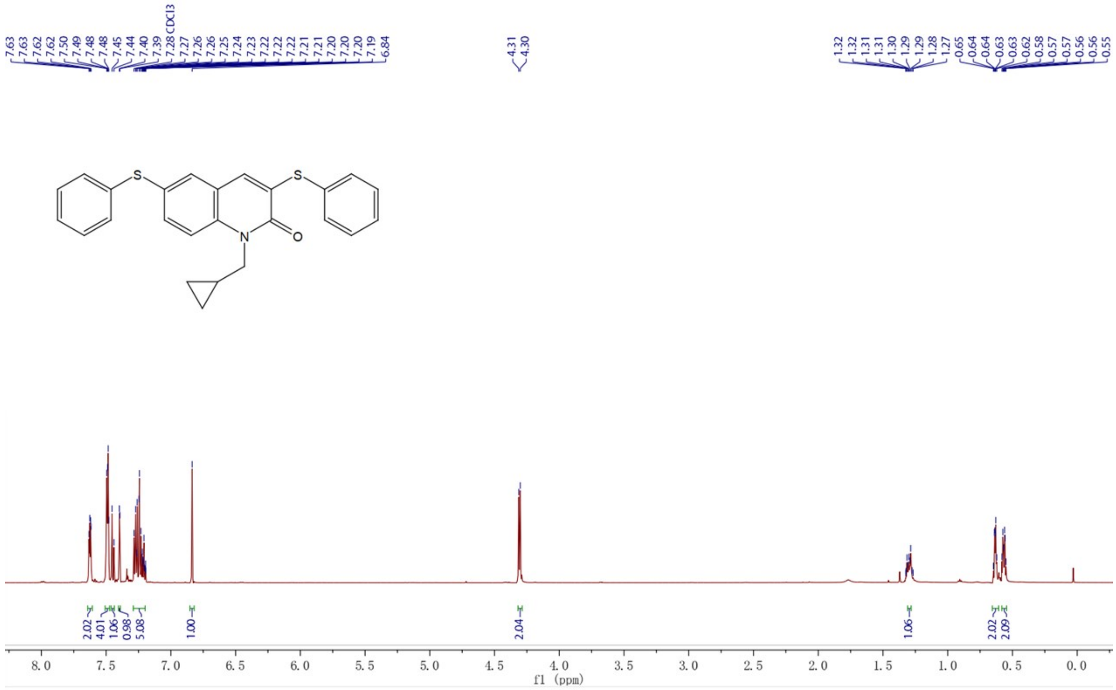
(24) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ka



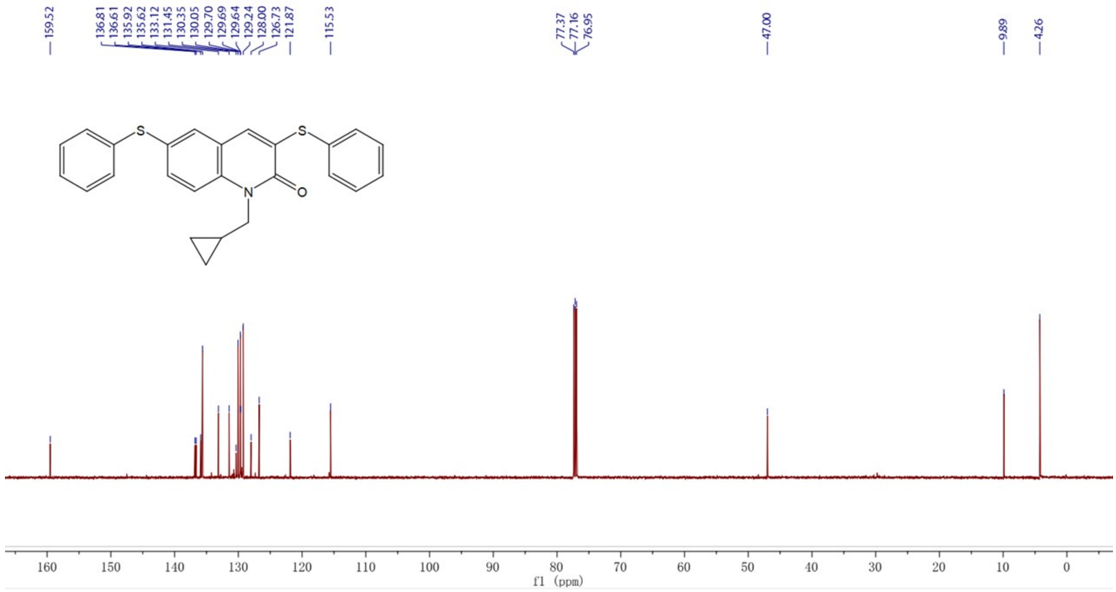
(25) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ka



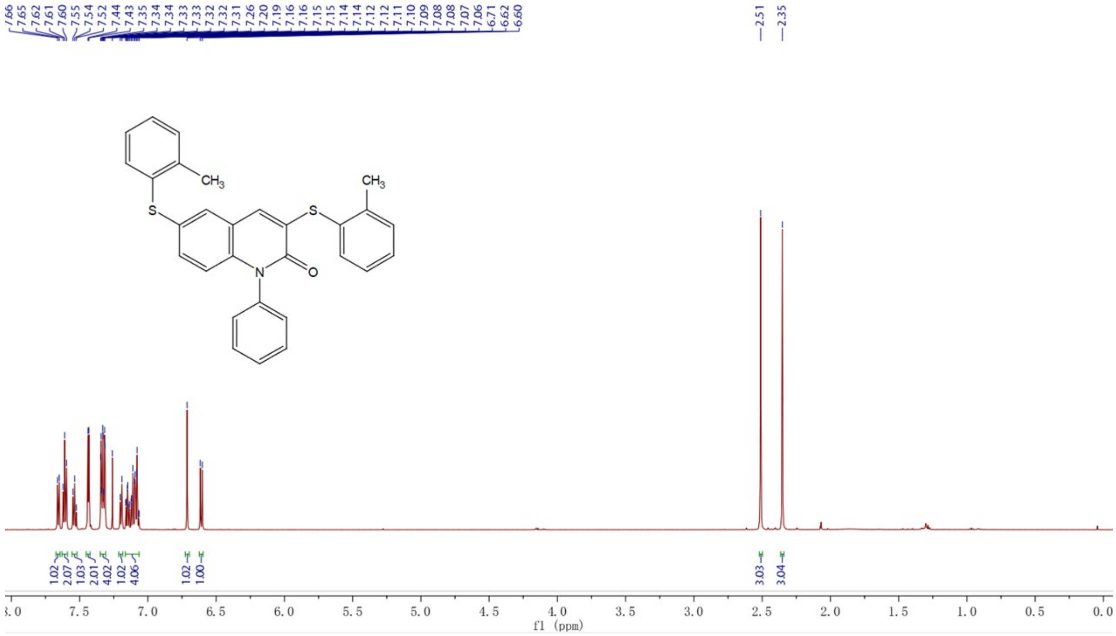
(26) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ia



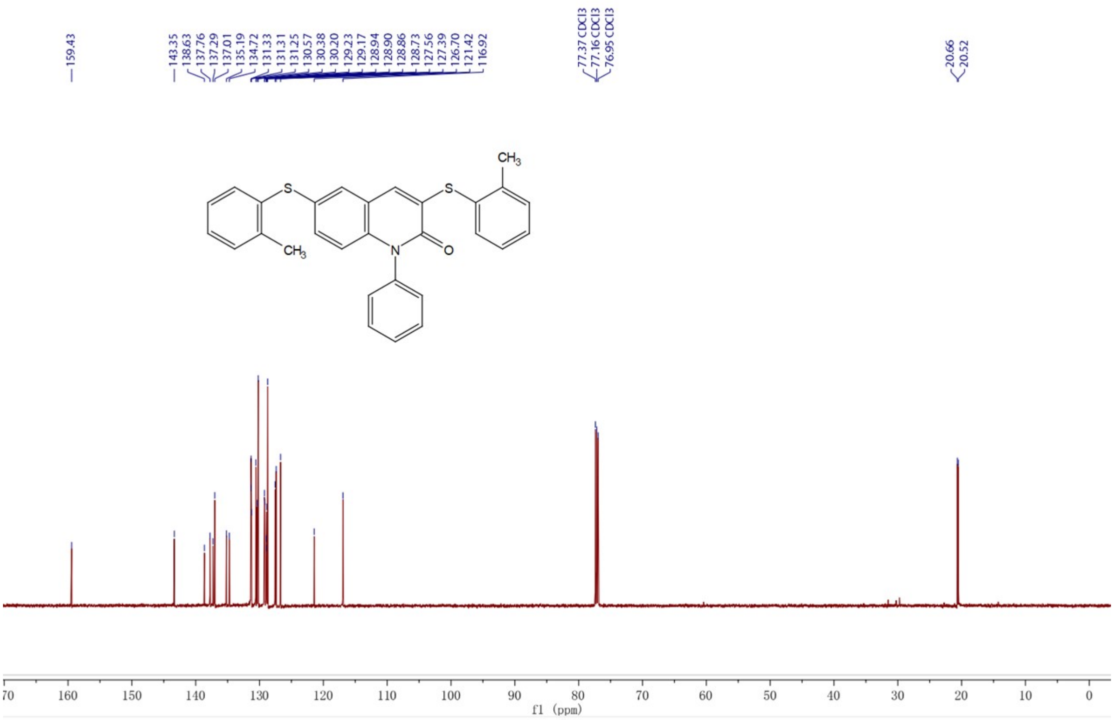
(27) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ia



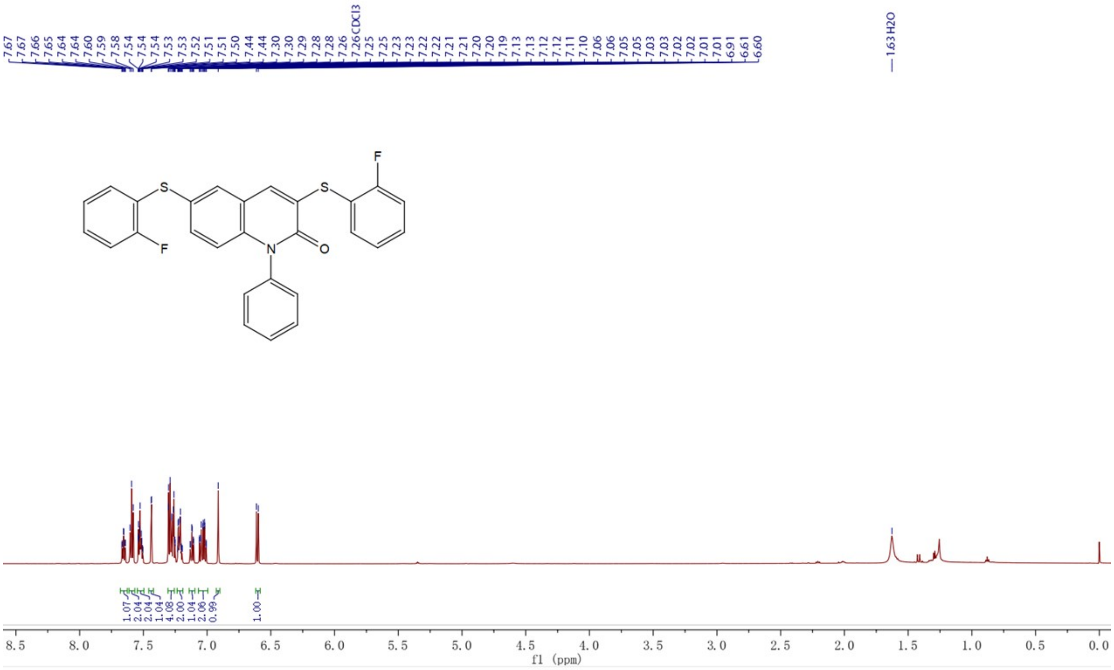
(28) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ab



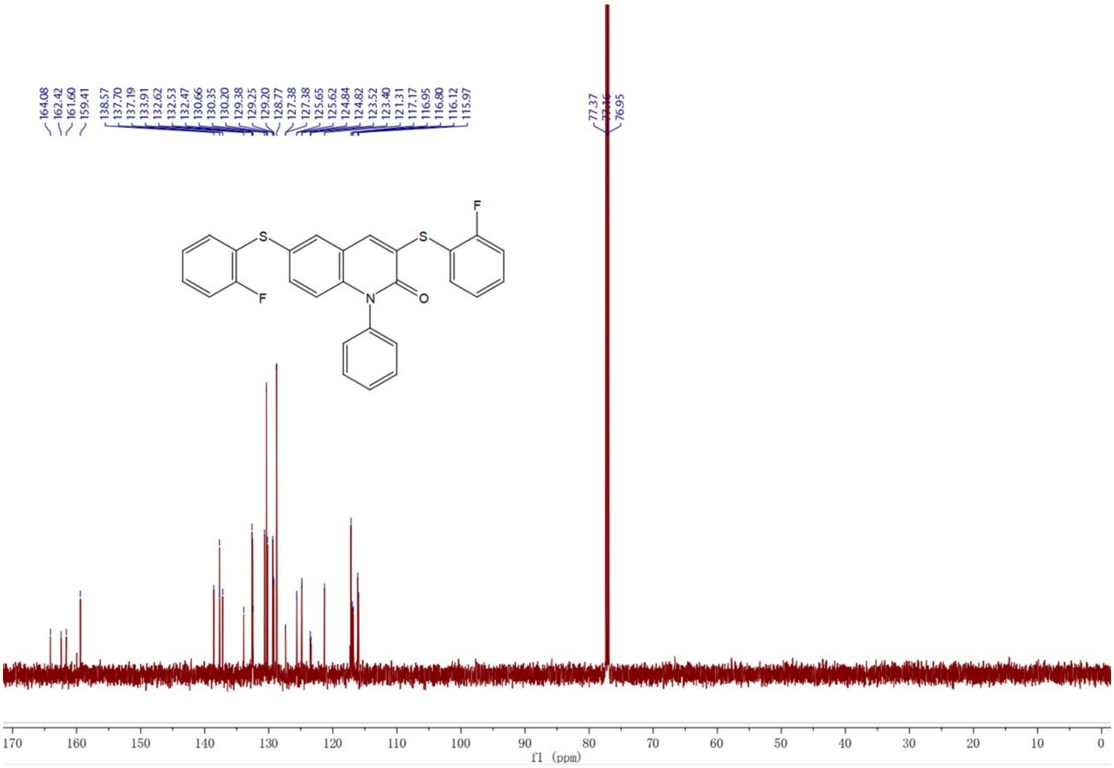
(29) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ab



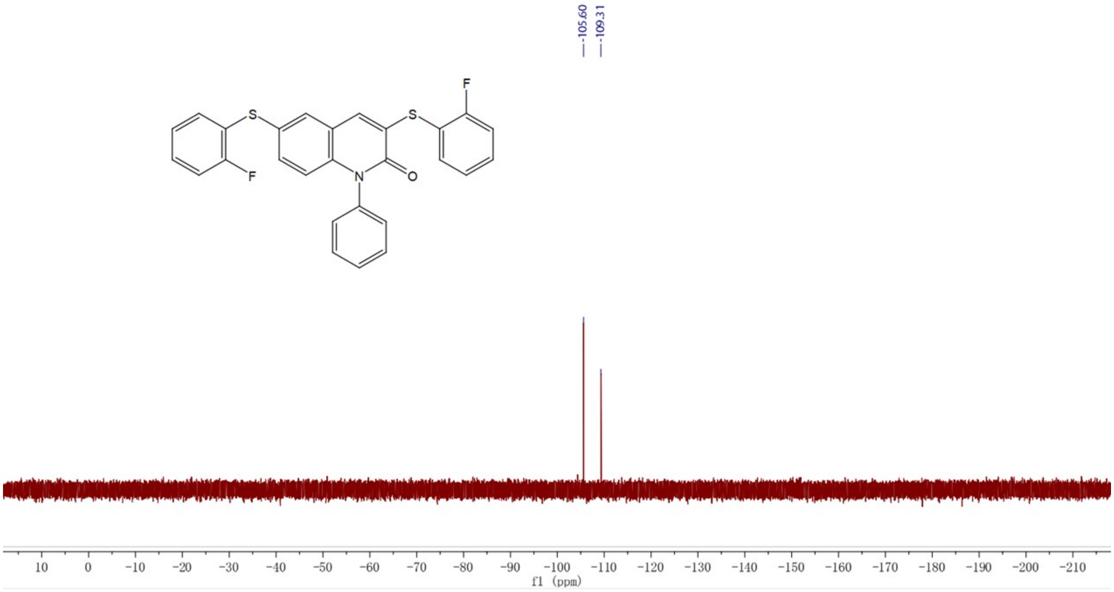
(30) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ac



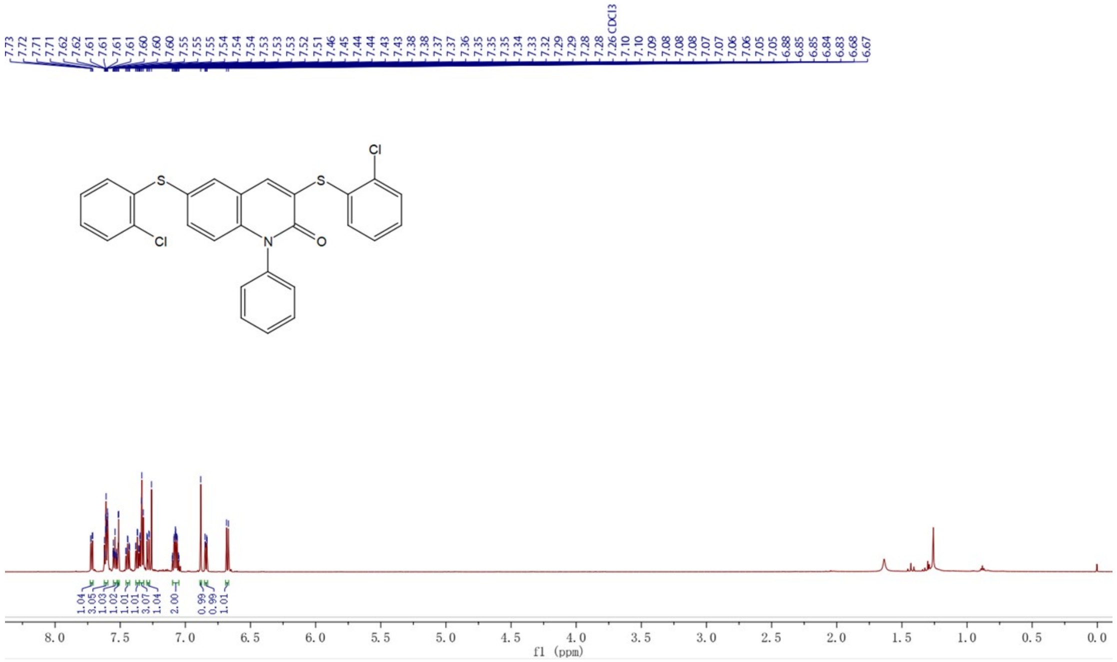
(31) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ac



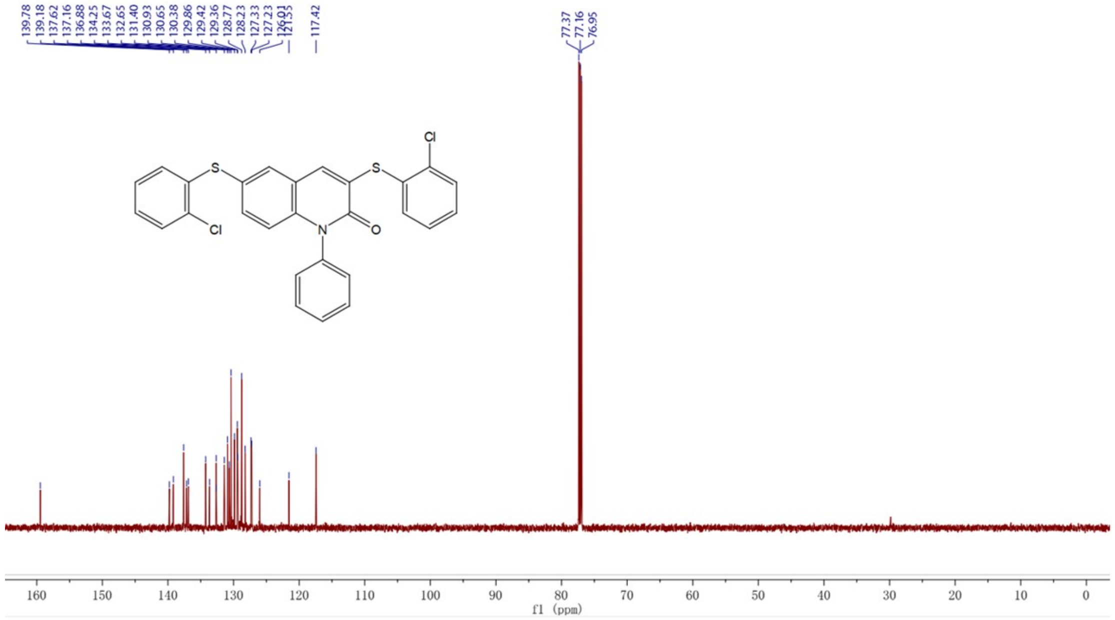
(32) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3ac



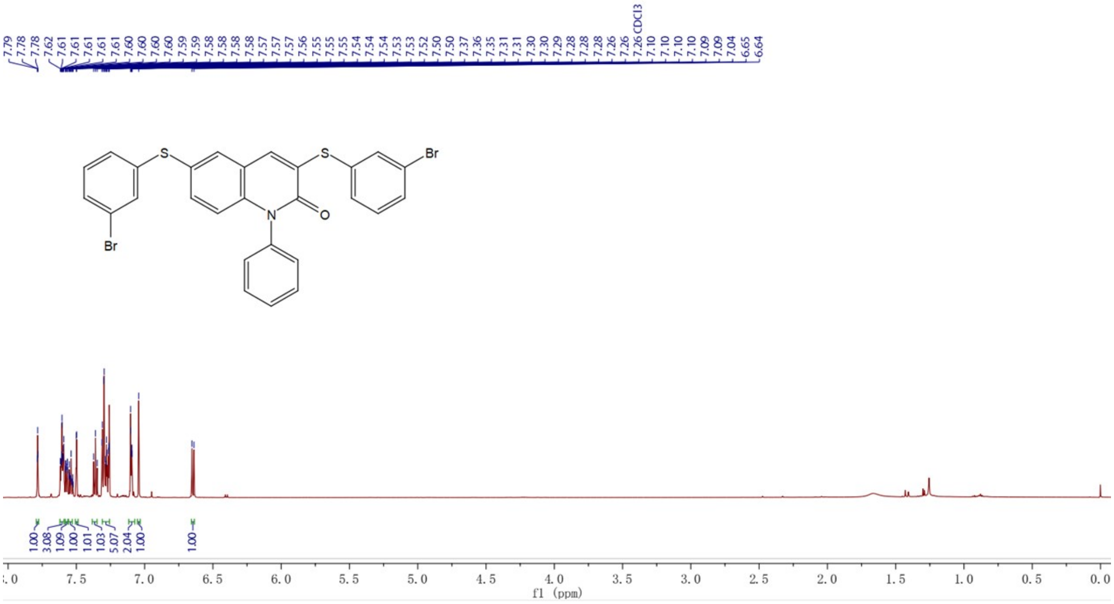
(35) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ad



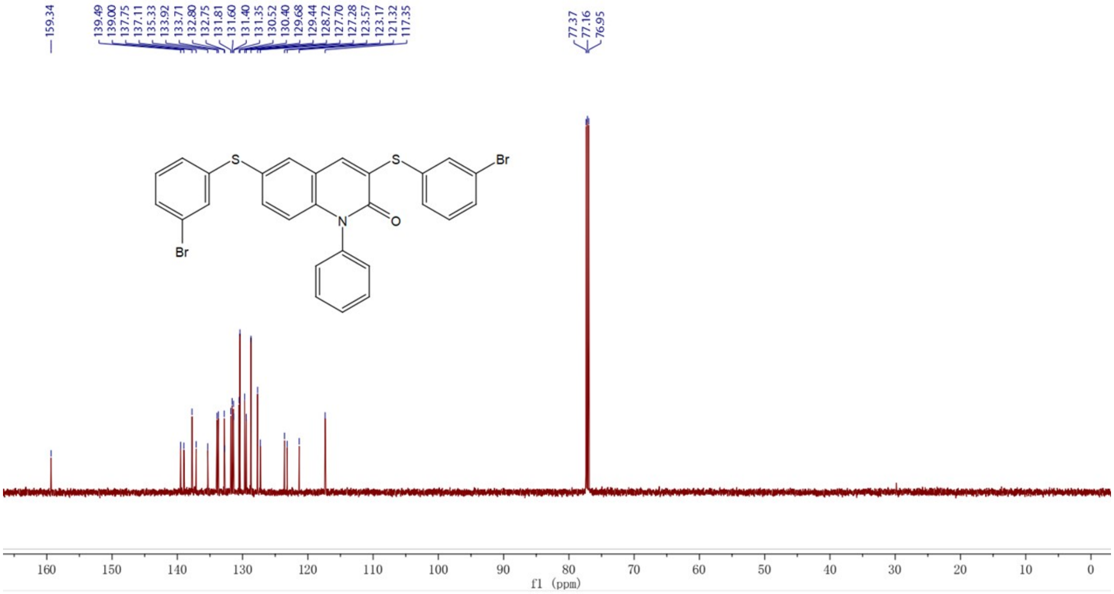
(36) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ad



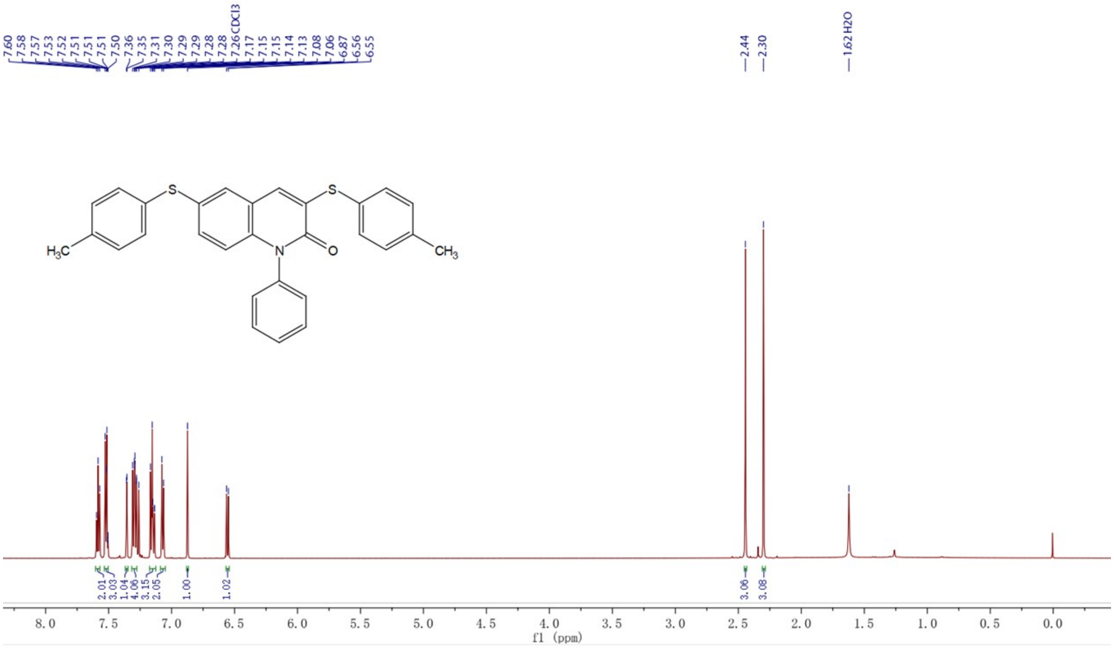
(37) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ae



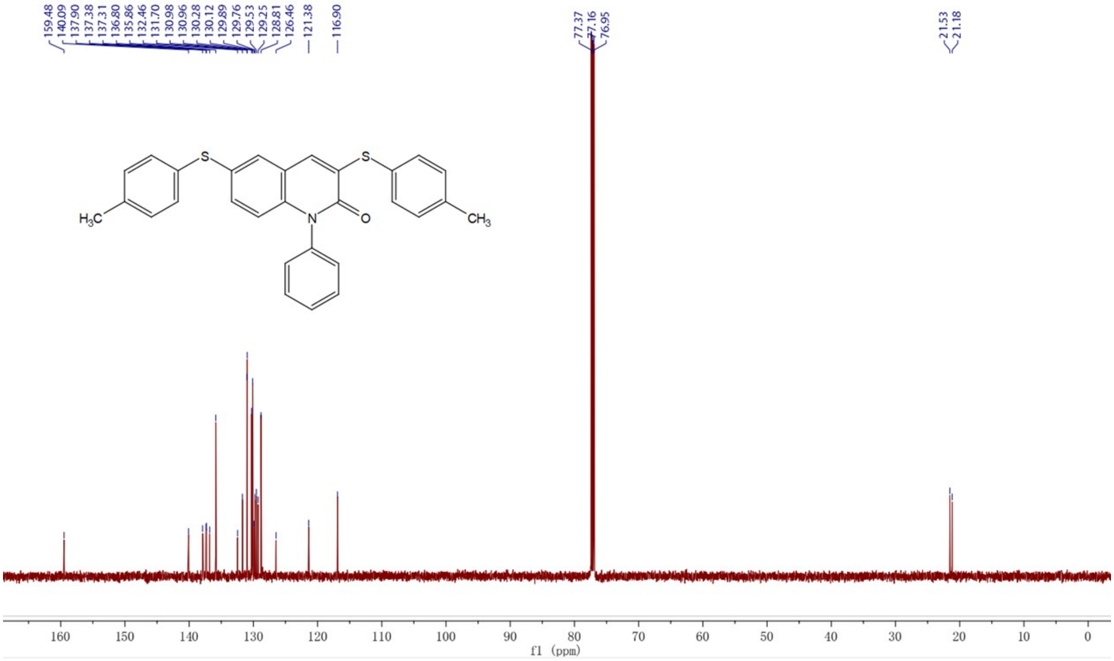
(38) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ae



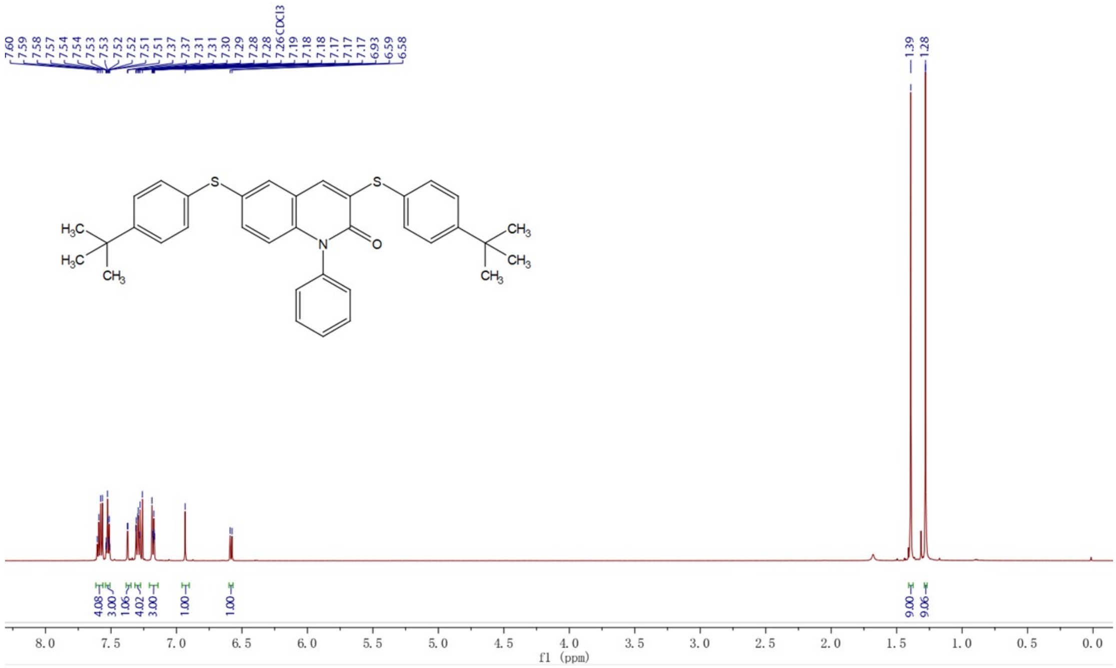
(39) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3af



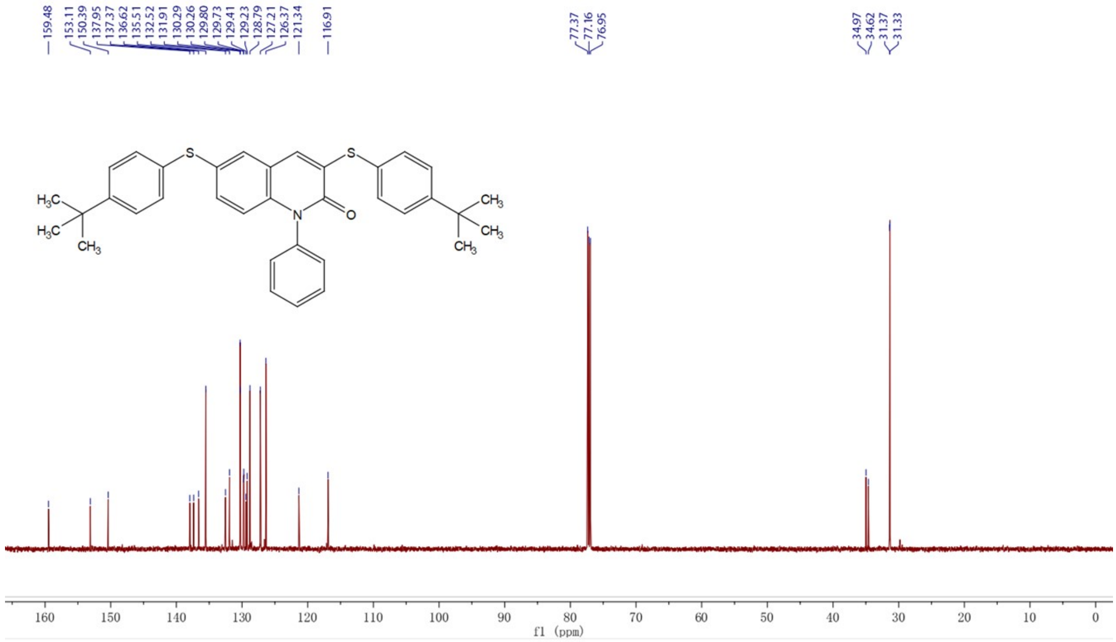
(40) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3af



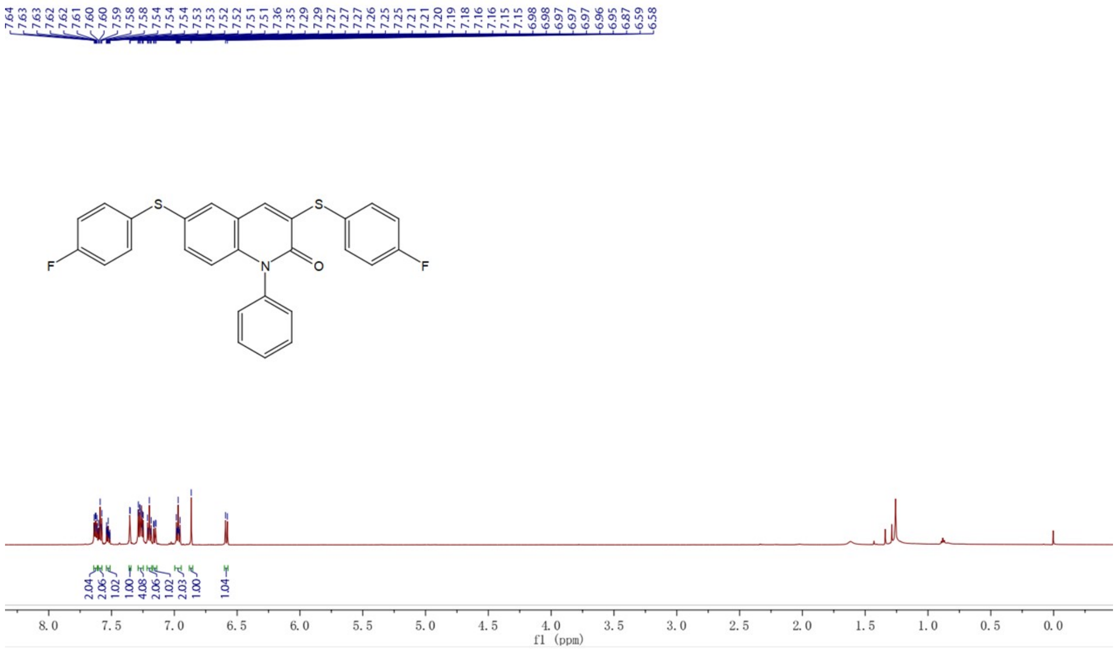
(41) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ag



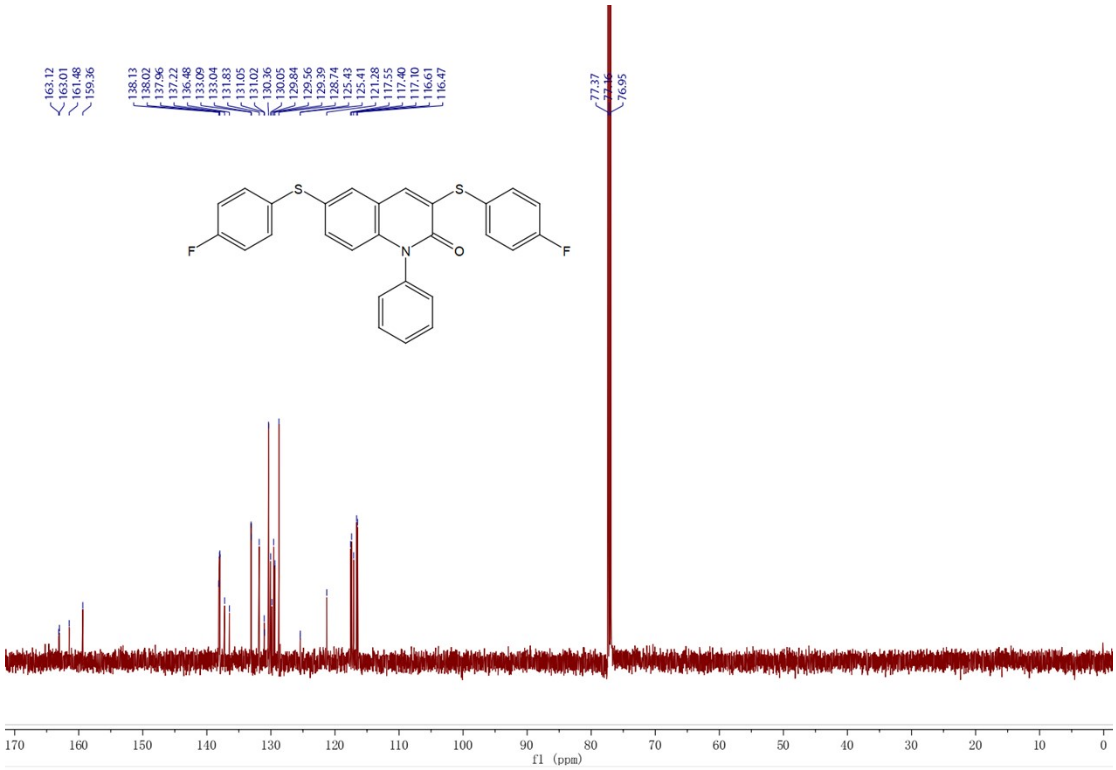
(42) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ag



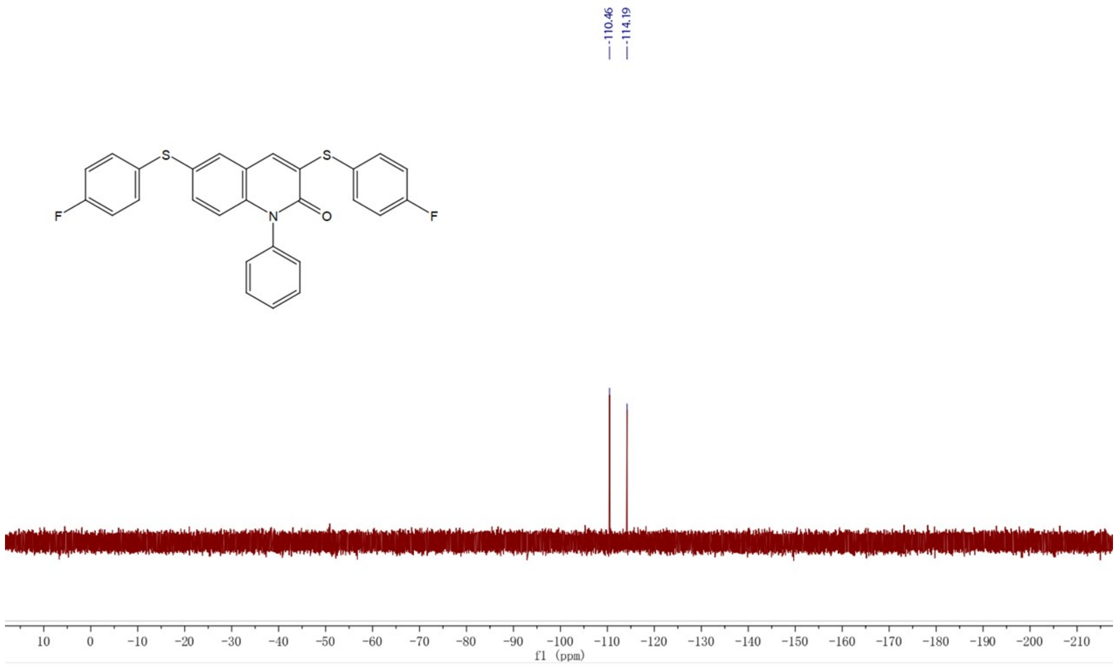
(43) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ah



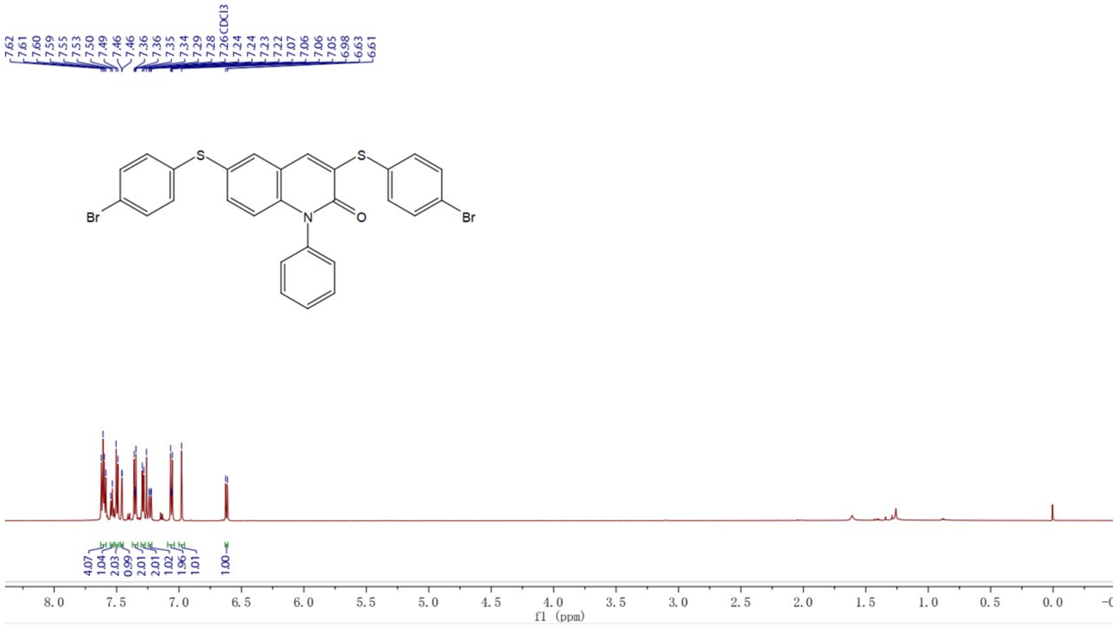
(44) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ah



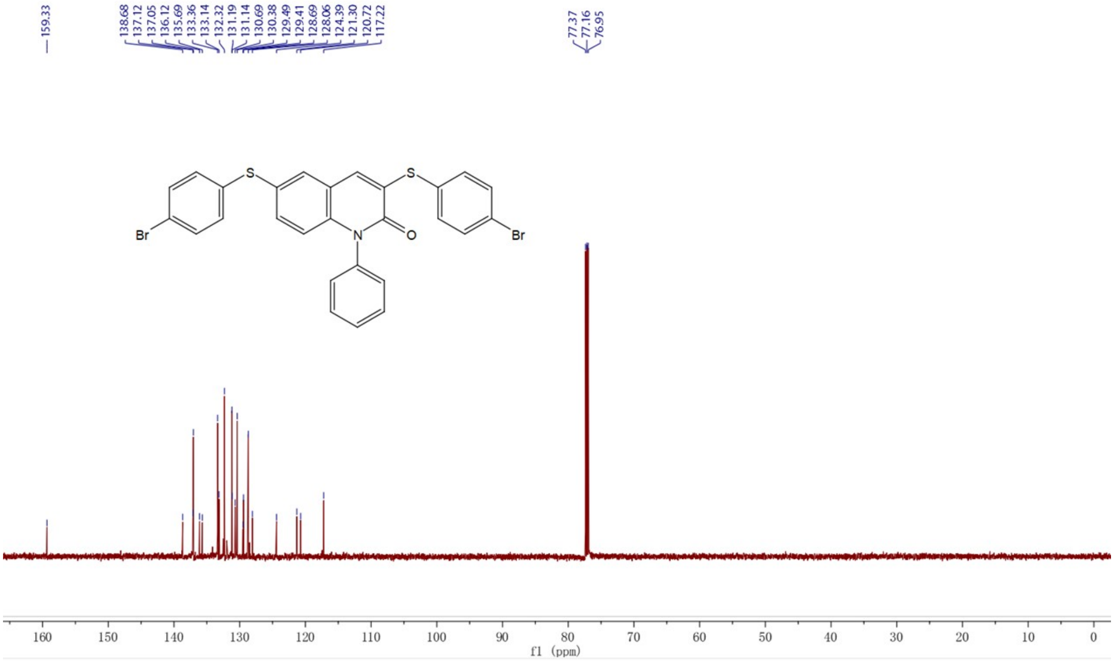
(46) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3ah



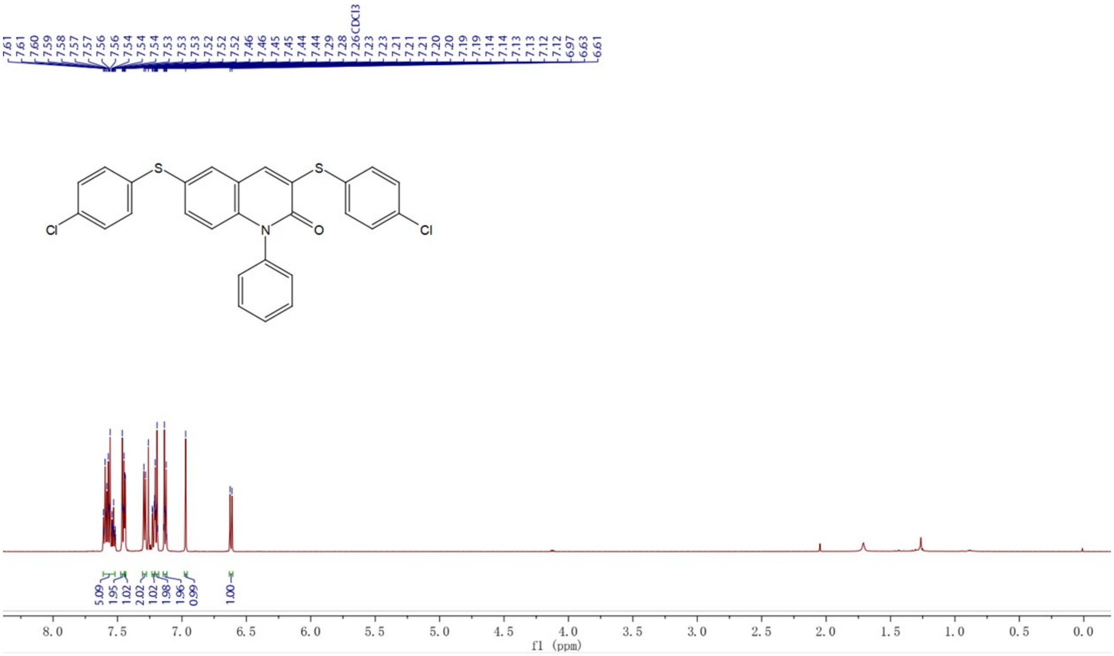
(47) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ai



(48) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ai

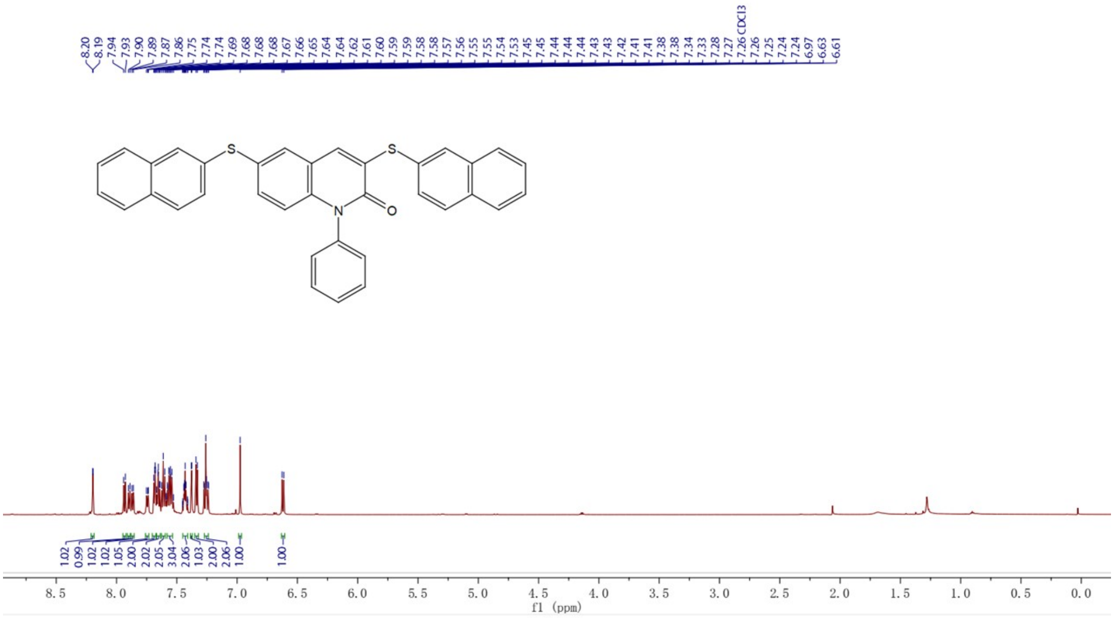


(50) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aj

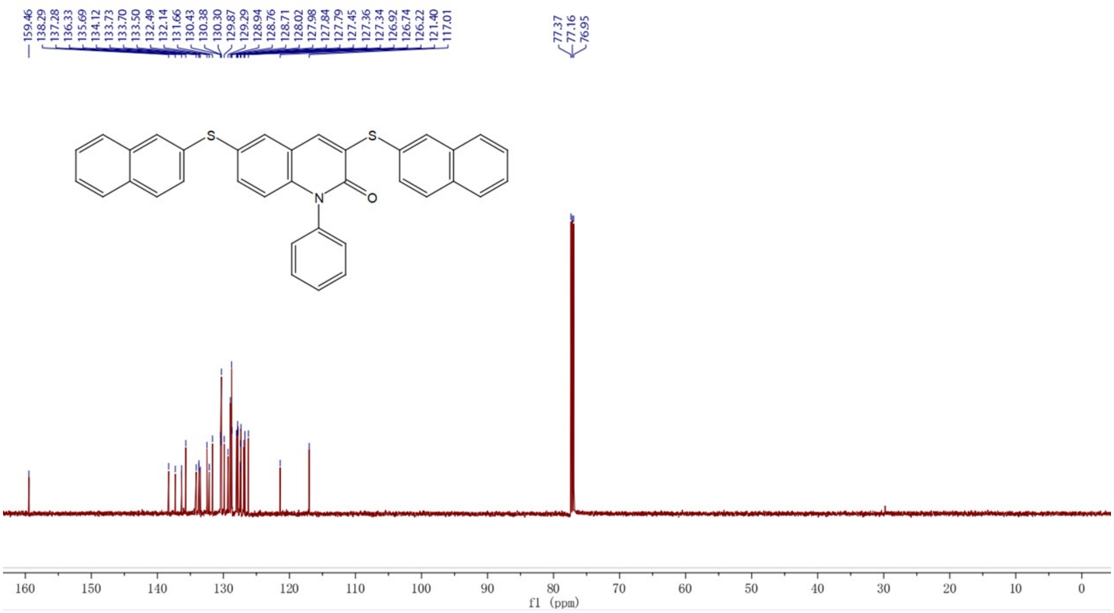


(51) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aj

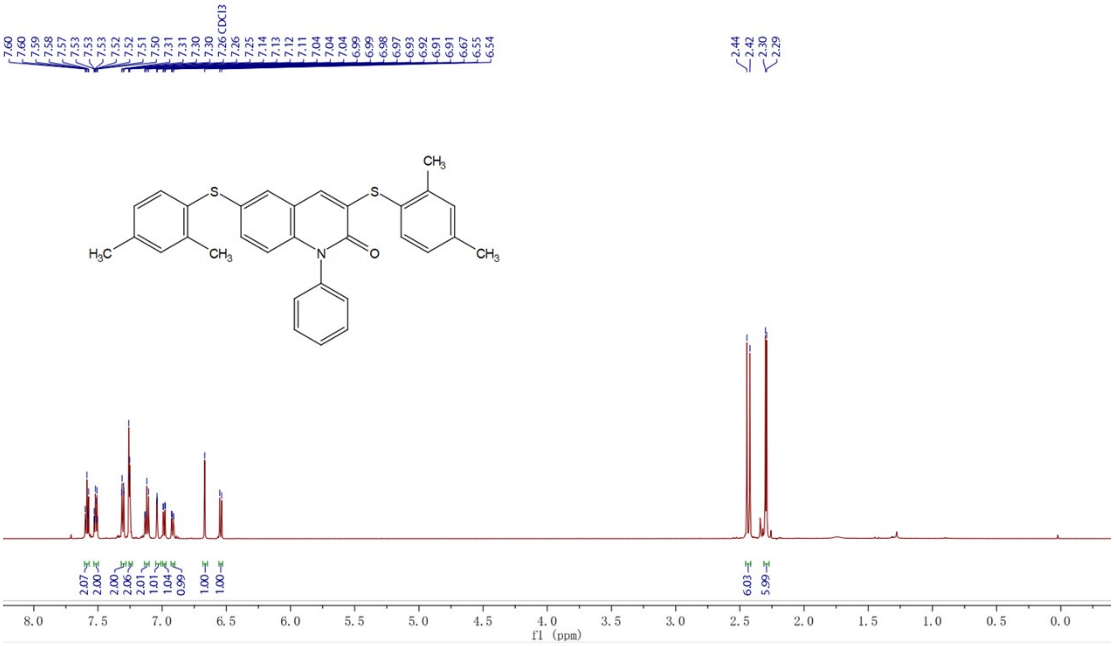
(52) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ak



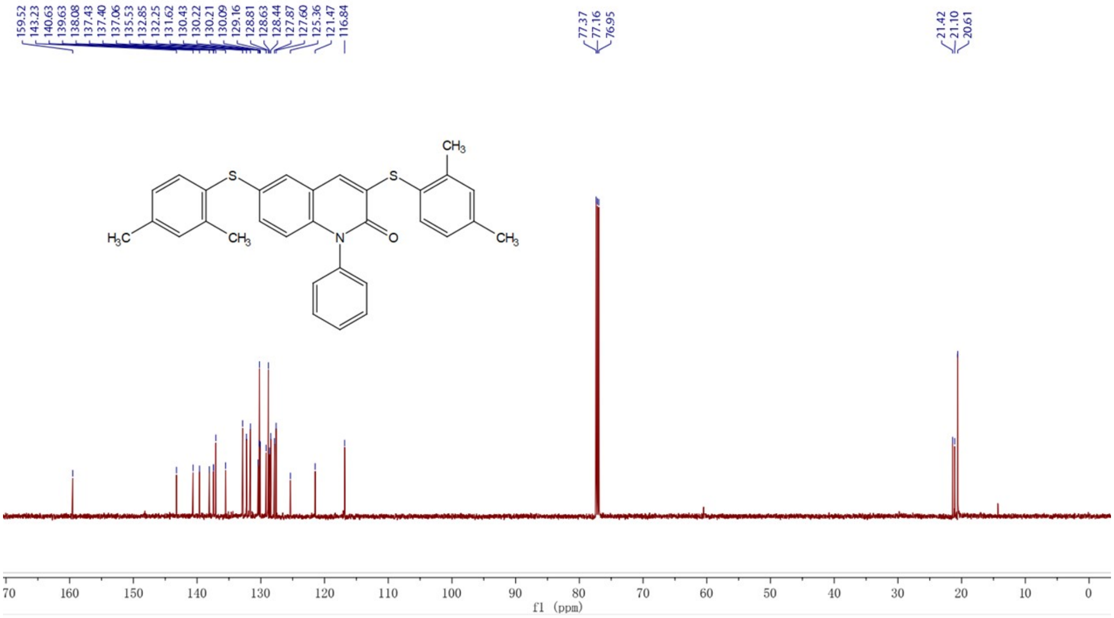
(53) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ak



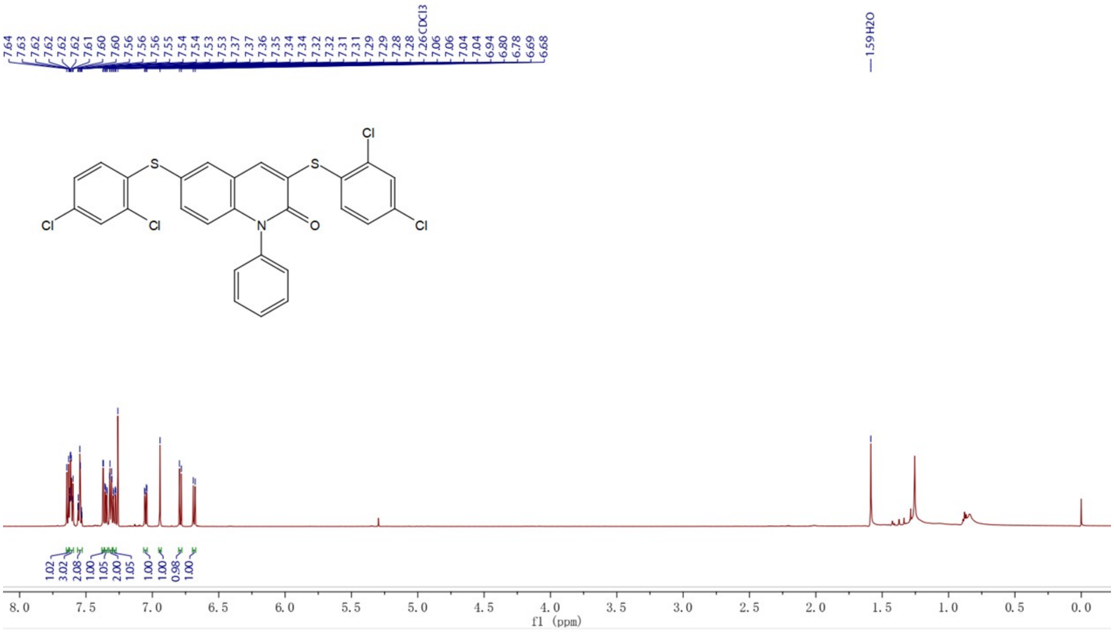
(54) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3al



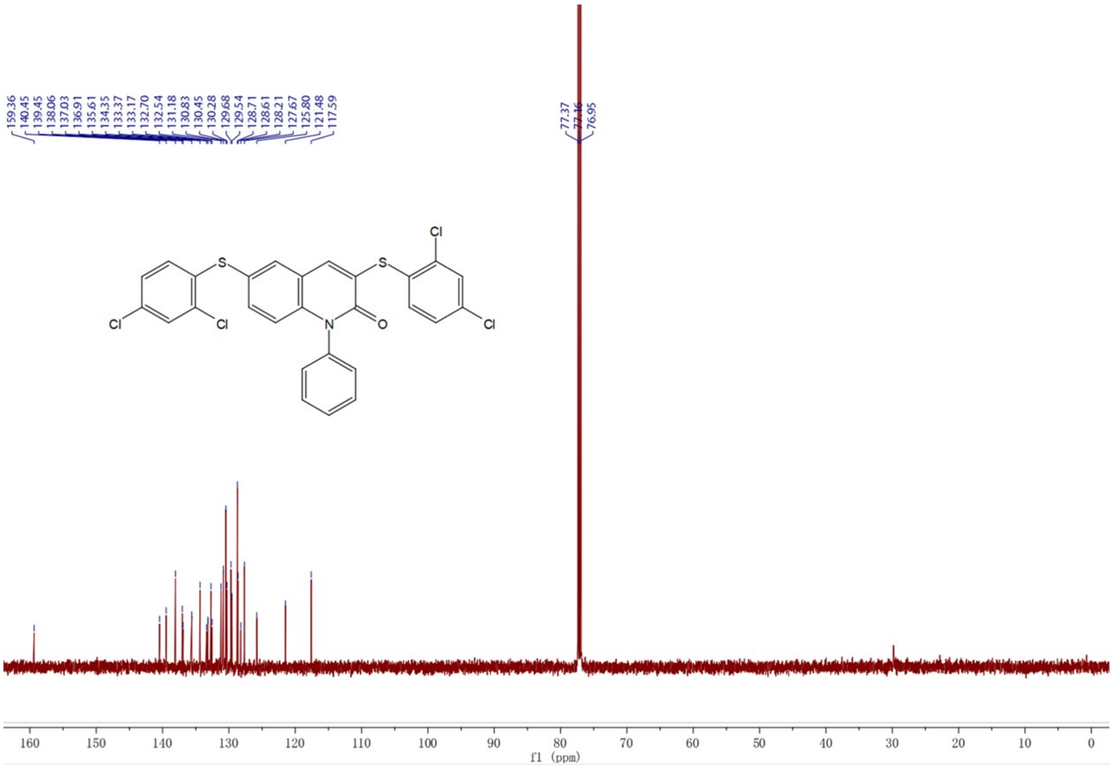
(55) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3al



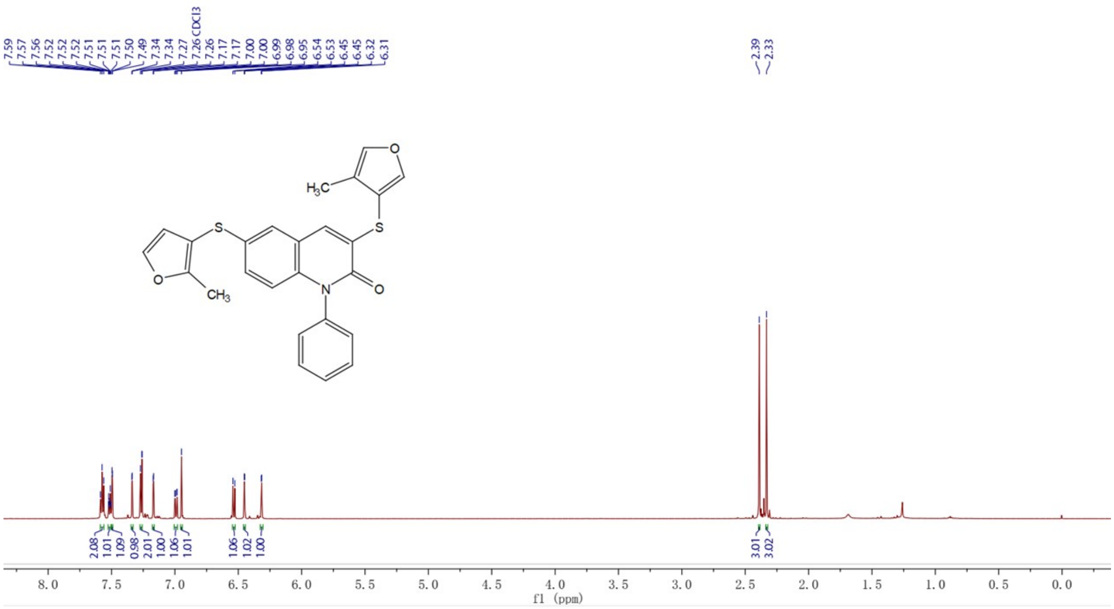
(56) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3am



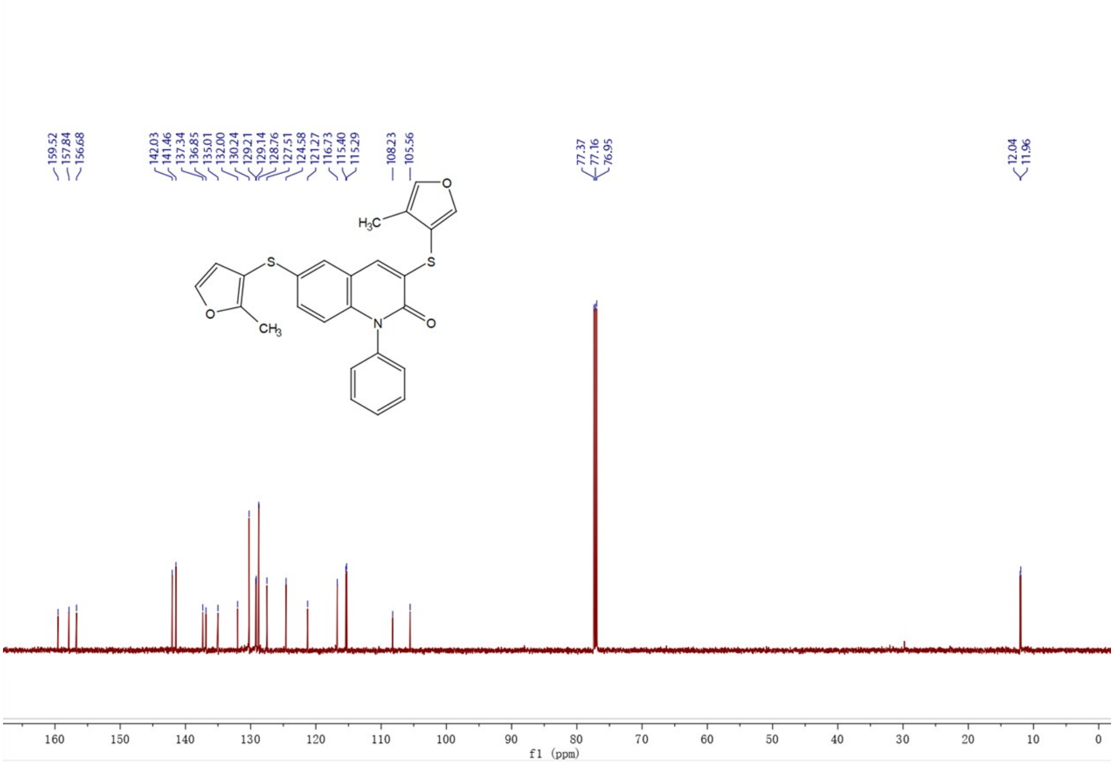
(57) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3am



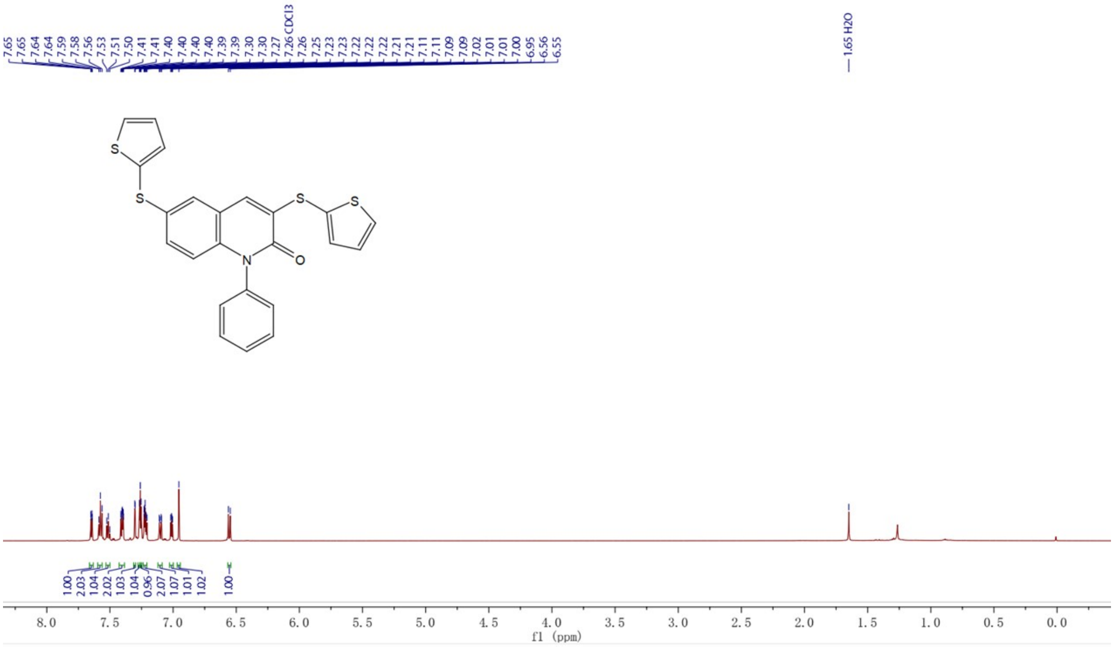
(58) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3an



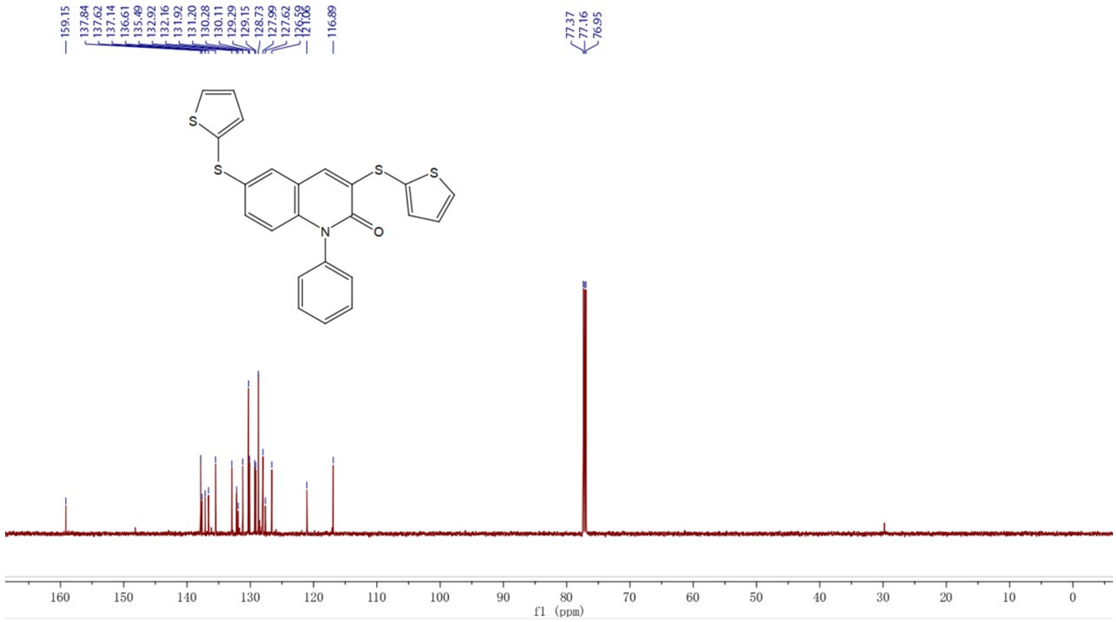
(59) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3an



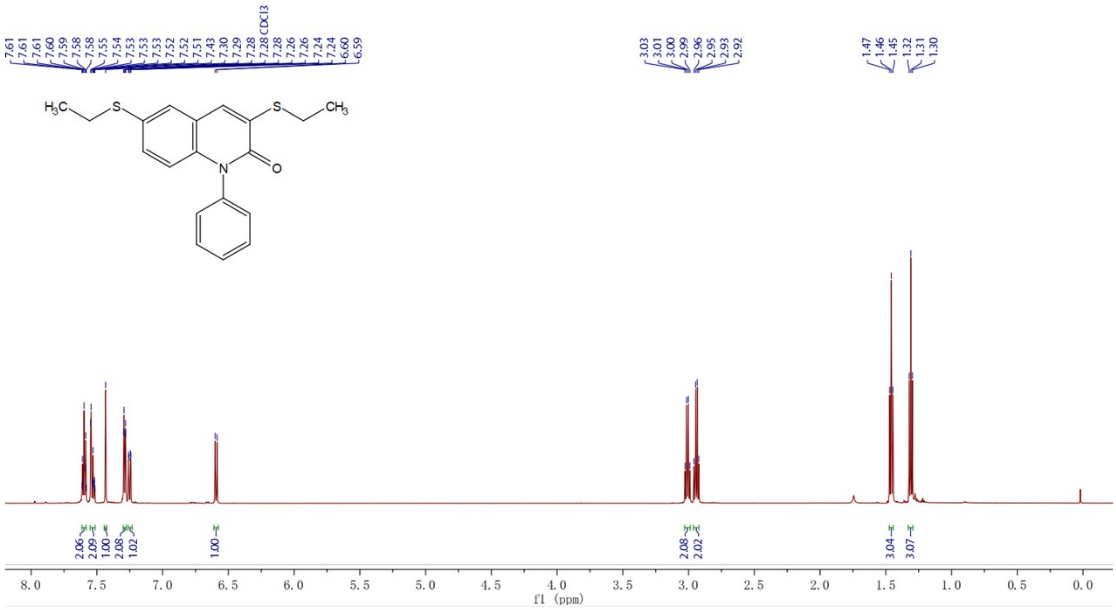
(60) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ao



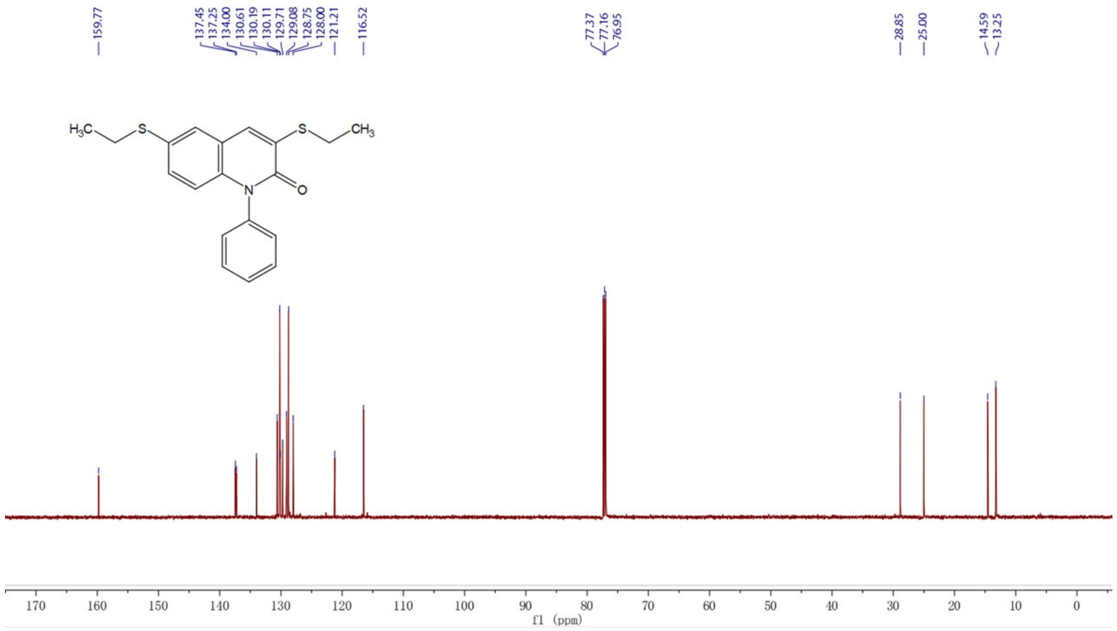
(61) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ao



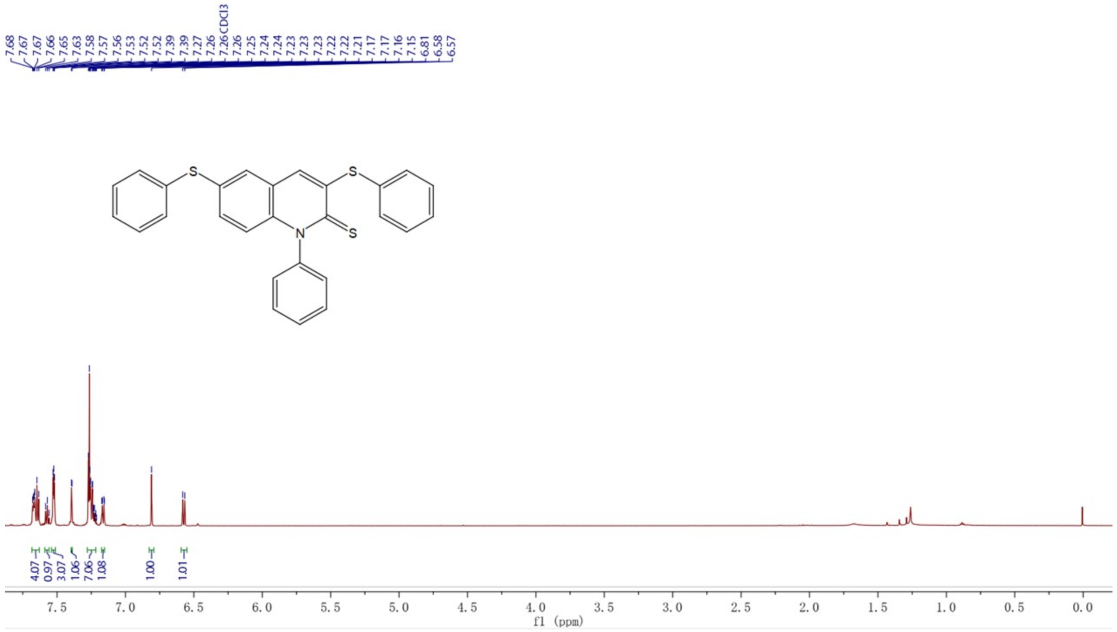
(62) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ap



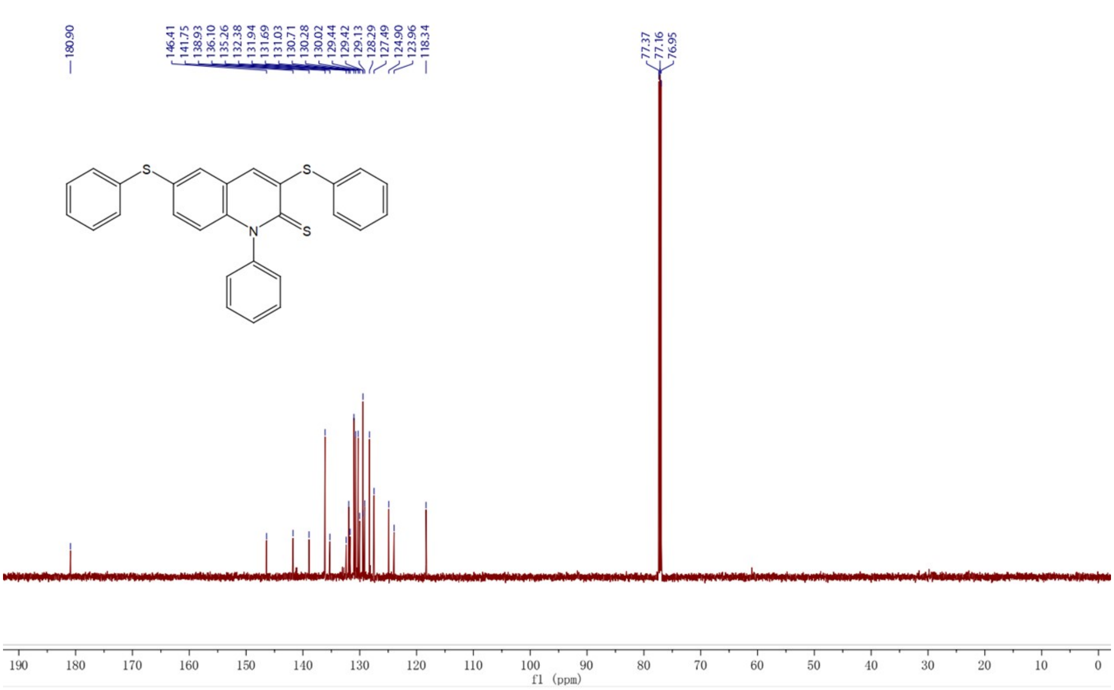
(63) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ap



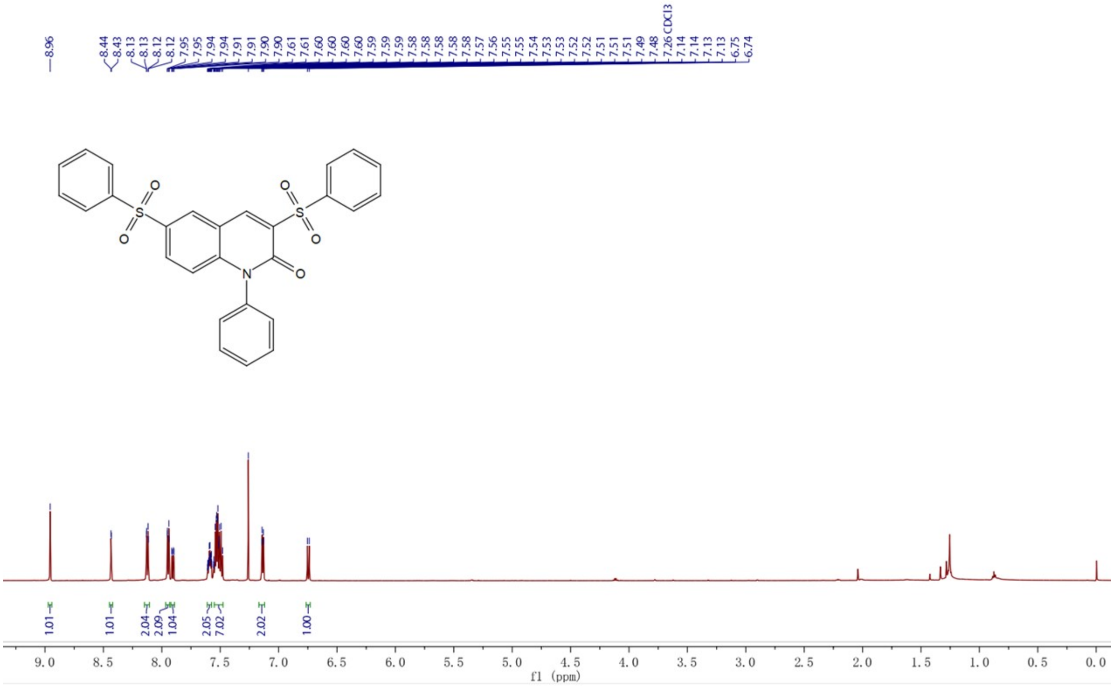
(64) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aa-S



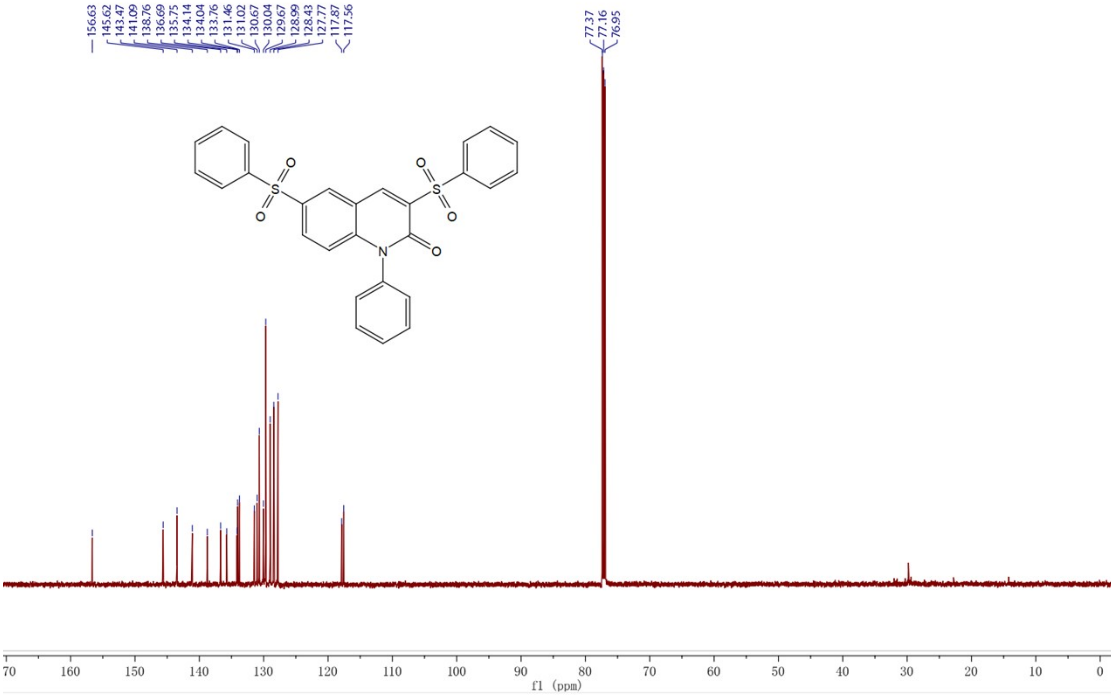
(65) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aa-S



(66) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of biphenyl 3aa-O

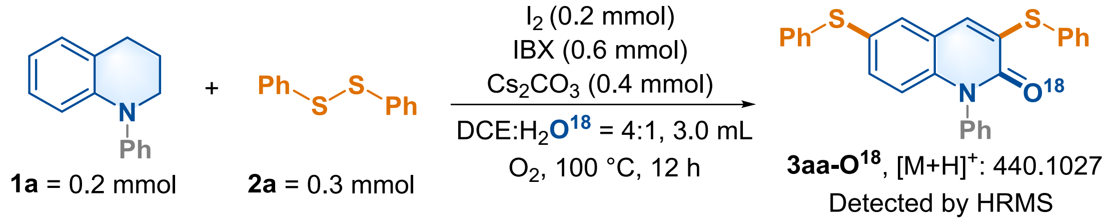


(67) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3aa-O



10. HRMS and LC-MS analyses

(1) HRMS analyses

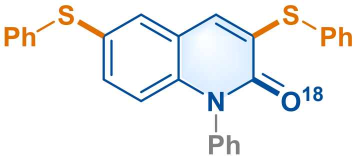


1a = 0.2 mmol

2a = 0.3 mmol

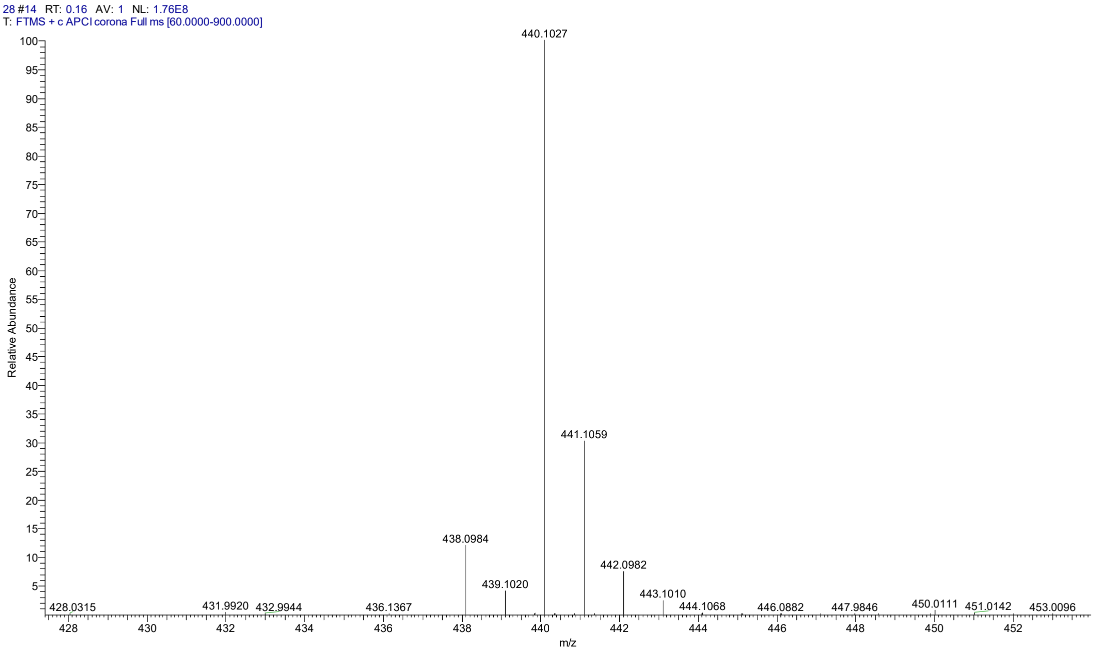
I_2 (0.2 mmol)
IBX (0.6 mmol)
Cs_2CO_3 (0.4 mmol)
DCE:H_2O^{18} = 4:1, 3.0 mL
O_2, 100 °C, 12 h

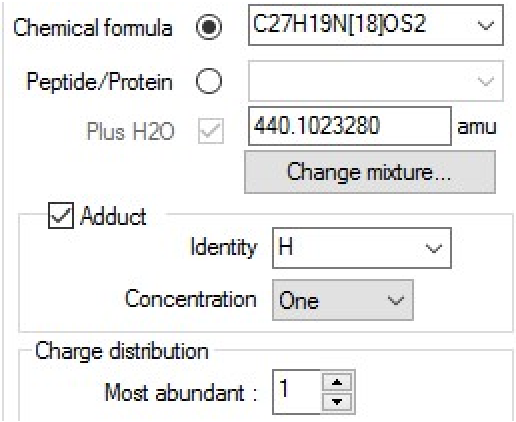
3aa-O^{18}, $[M+H]^+$: 440.1027
Detected by HRMS



3aa-O^{18}, $[M+H]^+$: 440.1027
Detected by HRMS
Chemical Formula: $C_{27}H_{19}NO^{18}S_2$

Figure S5. HRMS analysis experiment report of **3aa-O^{18}**.





Chemical formula ● C27H19N[18]OS2

Peptide/Protein ○

Plus H2O ☑ 440.1023280 amu

☑ Adduct

Identity H

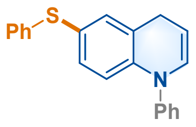
Concentration One

Charge distribution

Most abundant : 1

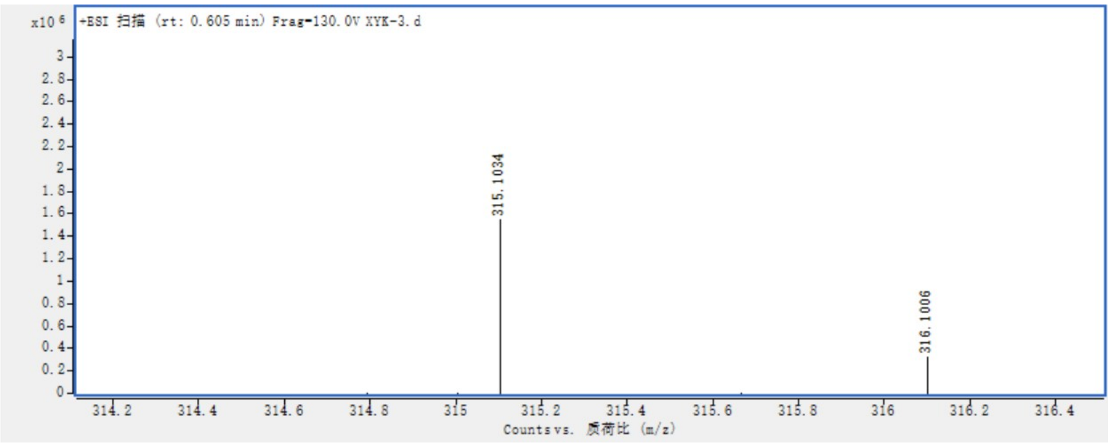
(2) LC-MS analyses

The model reaction was carried out under standard reaction conditions for 6 hours. Subsequently, the reaction mixture was analyzed by liquid chromatography-mass spectrometry (LC-MS), and 3aa-S1 could be observed.

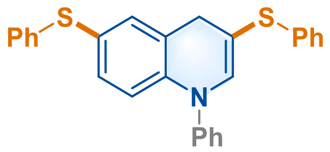


3aa-S2, $[M]^+$: 315.1034
Detected by LC-MS
Chemical Formula: $C_{21}H_{17}NS$

Figure S6. LC-MS analysis experiment report of the reaction mixture.



The model reaction was carried out under standard reaction conditions for 6 hours. Subsequently, the reaction mixture was analyzed by liquid chromatography-mass spectrometry (LC-MS), and 3aa-S2 could be observed.

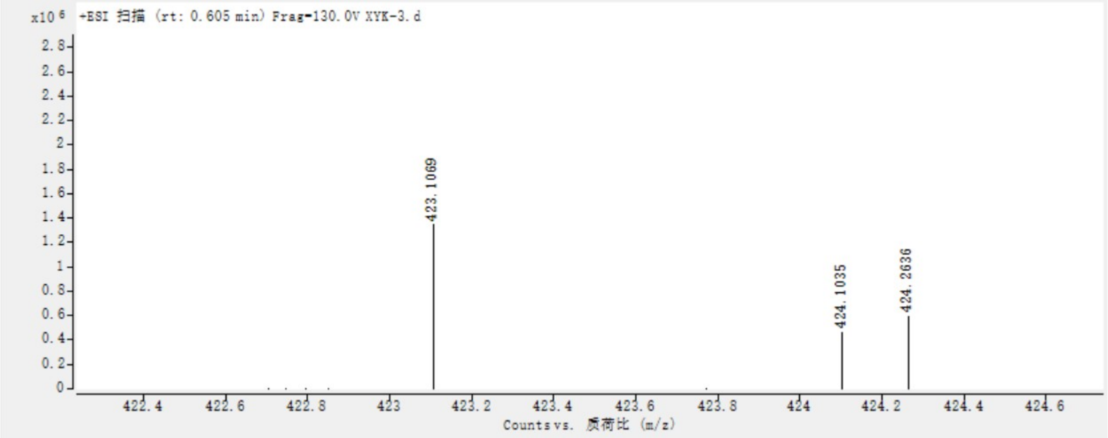


3aa-S2, $[M]^+$: 423.1069

Detected by LC-MS

Chemical Formula: $C_{27}H_{21}NS_2$

Figure S7. LC-MS analysis experiment report of the reaction mixture.



11. Reference

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