Supporting Information

Anchoring-Migration Strategy Enables Metal-Free C2-Selective Cross-Coupling of Benzothiophenes

Hong-Tao Deng[1], Wen-Ning Zhu[1], Chen Zhao[1], Xiao-Fei Liu[1], Ji-Rong Huang[1,*]

[1]*School of Pharmacy, Tongji Medical College, Huazhong University of Science and Technology; Wuhan, 430030, China.*

[*]*Corresponding author. Email: huangjr@hust.edu.cn.*

Contents

1. General Information

1.1 Methods and materials

All reactions were carried out in anhydrous solvents under ambient atmosphere unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on GF254 silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., China). Column chromatography was performed on silica gel (200−300 mesh) using appropriate eluents; preparative TLC (Yantai Jiangyou Silica Gel Development Co., Ltd., China) was used when required. TLC visualization was achieved with UV light (254 and 365 nm), an iodine chamber, and $KMnO_4$ stain. Unless otherwise stated, starting materials were obtained from commercial suppliers and used without further purification.

1.2 Instrumentation

^{1}H NMR and ^{13}C NMR spectra were measured on AscendTM 400 MHz Bruker unit (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR), AscendTM 600 MHz Bruker unit (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 564 MHz for ^{19}F NMR) or AVANCE NEO 600 MHz Bruker unit (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR). Chemical shifts were reported in parts per million (ppm) referenced to the appropriate solvent peaks (δ 7.26 ppm for $CDCl_3$, δ 2.50 ppm for DMSO-d_6; δ 77.16 ppm for $CDCl_3$, δ 39.97 ppm for DMSO-d_6 in fully decoupled ^{13}C spectra). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, m = multiplet, br = broad), integration, and coupling constants in Hertz (Hz). NMR yields were determined using 1,3,5-trimethoxybenzene or 3,4,5-trichloropyridine as internal standard. HRMS data were obtained using either APCI (Atmospheric Pressure Chemical Ionisation) or ESI (Electrospray Ionisation) on Bruker microTOF II (Bruker, Karlsruhe, Germany) and SolariX 7.0T (BrukerDaltonics, USA), respectively. M.p. (melting points) were obtained using an X-5 microscopic apparatus (Gongyi Yuhua Instrument Co., Ltd, China). Photoderivatization was operated at RLH-18CU Multi-Position Parallel Photochemical Reaction System (Roger tech., Ltd, China.)

2. The Preparation of Substrates

2.1 Preparation of benzothiophene substrates

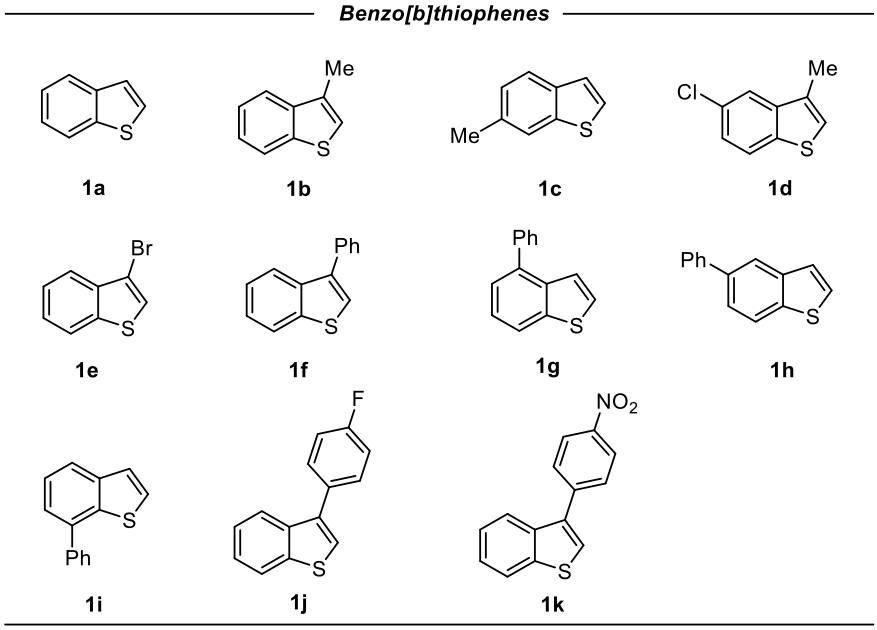


Figure 1S. Structures of benzothiophene substrates

As shown in **Figure 1S**, benzothiophene substrates were obtained from commercial purchase (**1a**, **1b**, **1d**, **1e**) or prepared by following the literature procedures[1-3] (**1c**, **1f-1k**).

2.2 Synthesis of benzothiophene sulfoxides

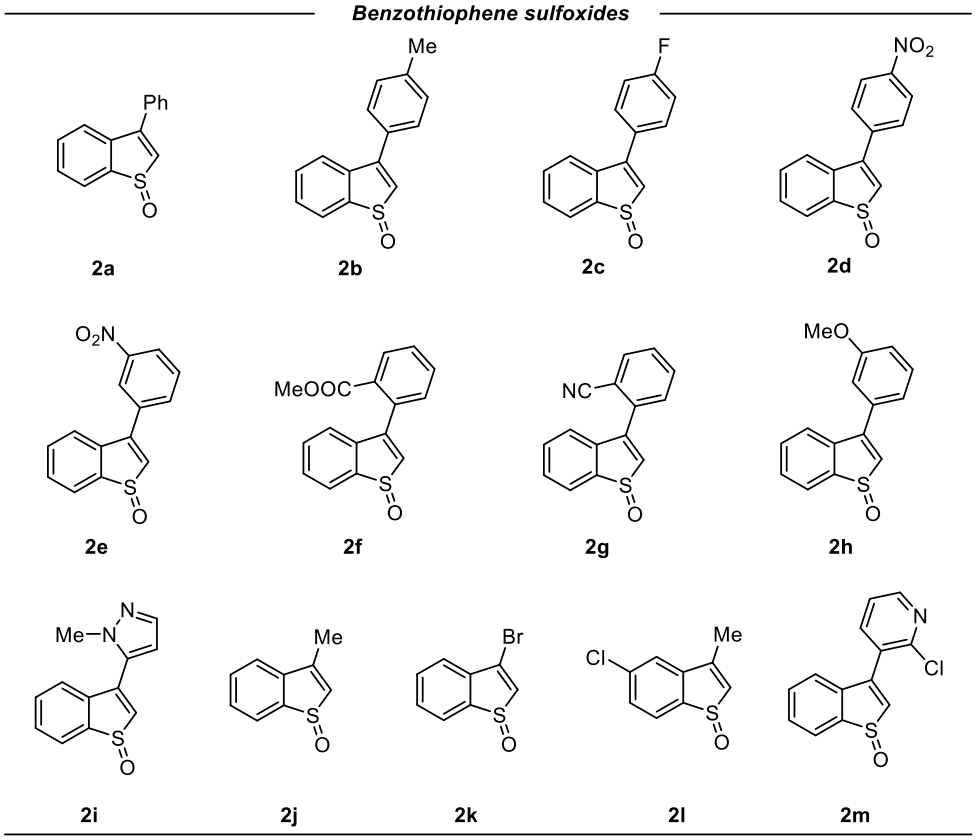
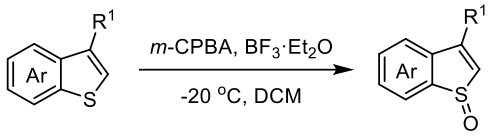


Figure 2S. Structures of benzothiophene sulfoxides

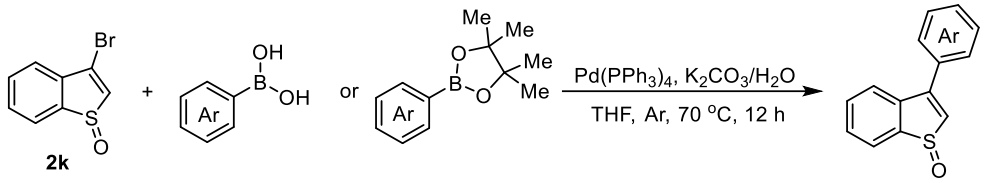
Method A: Synthesis of **2a**, **2c**, **2d** and **2j**–**2l**



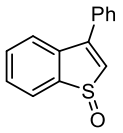
Benzothiophene (1.0 equiv.) and $BF_3{\cdot}Et_2O$ (8.0 equiv.) were dissolved in CH_2Cl_2 (0.1 M) and cooled to −20 °C under argon. A solution of 3-chloroperoxybenzoic acid (*m*-CPBA, 1.5 equiv.) in a minimal volume of CH_2Cl_2 was then added dropwise in three portions over 1.5 hours. Upon completion, a small amount of saturated K_2CO_3 solution was added at −20 °C, followed by additional solid K_2CO_3. The reaction mixture was filtered through a plug of anhydrous Na_2SO_4 and K_2CO_3, and the plug was washed with CH_2Cl_2 to afford a solution of the benzothiophene sulfoxide. The crude product was purified by recrystallization from CH_2Cl_2/petroleum ether (PE) or by column chromatography (CH_2Cl_2 as eluent).

Note: Benzothiophene sulfoxides unsubstituted at C2 and C3 (**1a**, **1f**–**1i**) were stable in solution but tended to decompose when concentrated to high concentrations; therefore, these intermediates were used as freshly prepared *in-situ* solutions.

Method B: Synthesis of **2b**, **2e-2i**, **2m**

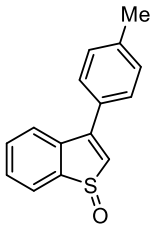


To a THF (0.1 M) solution of **2k** (1.0 equiv.) and arylboron reagent (1.2 equiv.) was added an aqueous K_2CO_3 solution (1.0 M, 6.25 equiv.) and $Pd(PPh_3)_4$ (5 mol%). The reaction mixture was stirred at 70 °C under an argon atmosphere for 12 hours. After cooling to room temperature, the mixture was diluted with water and extracted with ethyl acetate (EtOAc). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (PE/EtOAc as eluent) to afford the desired product.



3-phenylbenzo[*b*]thiophene 1-oxide (2a)

The compound was prepared according to a known procedure and has been previously characterized[4].



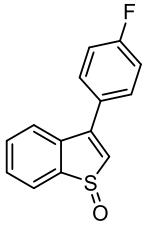
3-(*p*-tolyl)benzo[*b*]thiophene 1-oxide (2b)

Following **Method B**, the compound **2b** was prepared from 2.0 mmol of **2k** and 2.4 mmol of *p*-tolylboronic acid, and was isolated as a yellow solid (430.8 mg, 83% yield). M.p. = 42.8–43.5 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 1H), 7.60 – 7.50 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.68, 146.74, 140.31, 137.53, 132.12, 131.84, 129.87 (2C), 129.78, 129.08, 128.11 (2C), 126.76, 124.60, 21.55.

HRMS (ESI) calcd. for $C_{15}H_{13}OS^+$ ($M+H^+$) 241.0682, found 241.0686.



3-(4-fluorophenyl)benzo[*b*]thiophene 1-oxide (2c)

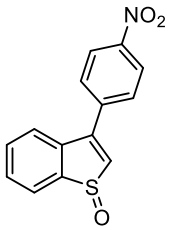
Following **Method A**, the compound **2c** was prepared from 2.0 mmol of **1j** and isolated as a yellow solid (302.9 mg, 62% yield). M.p. = 134.2 – 134.6 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 1H), 7.57 – 7.50 (m, 5H), 7.24 – 7.18 (m, 2H), 6.98 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.77 (d, *J* = 251.5 Hz), 147.58, 146.65, 137.23, 132.89, 131.97, 130.11 (d, *J* = 8.1 Hz, 2C), 129.28, 128.70 (d, *J* = 3.3 Hz), 126.88, 124.36,116.39 (d, *J* = 22.2 Hz, 2C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ 110.16 – 110.26 (m).

HRMS (ESI) calcd. for $C_{14}H_9FNaOS^+$ ($M+Na^+$) 267.0250, found 267.0251.



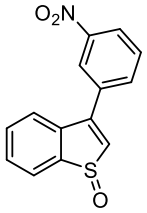
3-(4-nitrophenyl)benzo[*b*]thiophene 1-oxide (2d)

Following **Method A**, the compound **2d** was prepared from 20.0 mmol of **1k** and isolated as a yellow solid (4.39 g, 81% yield). M.p. = 134.2 – 134.6 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.8 Hz, 2H), 8.06 – 8.02 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.50 – 7.46 (m, 1H), 7.14 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.79, 146.56, 146.37, 139.01, 136.50, 135.18, 132.28, 129.75, 129.27 (2C), 127.21, 124.52 (2C), 124.14.

HRMS (ESI) calcd. for $C_{14}H_9NaO_3S^+$ ($M+Na^+$) 294.0195, found 294.0198.



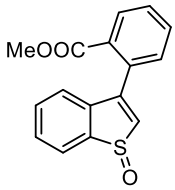
3-(3-nitrophenyl)benzo[*b*]thiophene 1-oxide (2e)

Following **Method B**, the compound **2e** was prepared from 1.0 mmol of **2k** and 1.2 mmol of (3-nitrophenyl)boronic acid and was isolated as a white solid (257.1 mg, 95% yield). M.p. = 181.8 – 183.4 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (t, *J* = 2.0 Hz, 1H), 8.37 (ddd, *J* = 7.6, 2.4, 1.2 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.89 (ddd, *J* = 7.6, 1.6, 1.2 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.51 – 7.47 (m, 1H), 7.15 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.76, 146.53, 146.06, 136.44, 134.96, 134.30, 134.08, 132.27, 130.49, 129.69, 127.17, 124.74, 124.02, 123.12.

HRMS (ESI) calcd. for $C_{14}H_{10}NO_3S^+$ ($M+H^+$) 272.0376, found 272.0374.



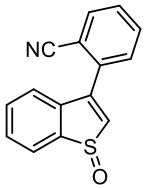
methyl 2-(1-oxidobenzo[*b*]thiophen-3-yl)benzoate (2f)

Following **Method B**, the compound **2f** was prepared from 2.0 mmol of **2k** and 2.4 mmol of (2-(methoxycarbonyl)phenyl)boronic acid, and was isolated as a light-yellow solid (237.8 mg, 42% yield). M.p. = 69.7 – 71.3 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.66 (td, *J* = 7.8, 1.2 Hz, 1H), 7.58 (td, *J* = 7.8, 1.2 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 3.60 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.66, 149.17, 145.46, 138.75, 135.65, 132.97, 132.48, 131.85, 130.96, 130.49, 130.44, 129.64, 128.78, 126.30, 123.53, 52.26.

HRMS (ESI) calcd. for $C_{16}H_{13}O_3S^+$ ($M+H^+$) 285.0580, found 285.0585.



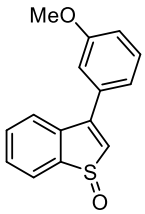
2-(1-oxidobenzo[*b*]thiophen-3-yl)benzonitrile (2g)

Following **Method B**, the compound **2g** was prepared from 1.0 mmol of **2k** and 1.2 mmol of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile, and was isolated as a light-yellow solid (214.2 mg, 85% yield). M.p. = 180.2 – 182.6 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.60 – 7.56 (m, 3H), 7.31 – 7.29 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.08, 144.23, 136.85, 136.70, 135.83, 134.12, 133.28, 132.12, 130.08, 129.86, 129.60, 126.95, 124.29, 117.12, 112.00.

HRMS (ESI) calcd. for $C_{15}H_9NNaOS^+$ ($M+Na^+$) 274.0297, found 274.0302.



3-(3-methoxyphenyl)benzo[*b*]thiophene 1-oxide (2h)

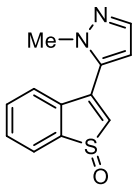
Following **Method B**, the compound **2h** was prepared from 2.0 mmol of **2k** and 2.4 mmol of (3-methoxyphenyl)boronic acid, and was isolated as a white solid (388.6 mg, 76% yield). M.p. = 74.5 – 76.8 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 1H), 7.60 – 7.50 (m, 3H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.07 – 7.03 (m, 2H), 7.00 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.09, 148.58, 146.61, 137.37, 133.92, 132.75, 131.93, 130.30, 129.20, 126.78, 124.62, 120.48, 115.49, 113.80, 55.56.

HRMS (ESI) calcd. for $C_{15}H_{13}O_2S^+$ ($M+H^+$) 257.0631, found 257.0629.

NMR spectra are in agreement with the reported data[5].



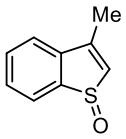
3-(1-methyl-1H-pyrazol-5-yl)benzo[*b*]thiophene 1-oxide (2i)

Following **Method B**, compound **2i** was prepared from 1.0 mmol of **2k** and 1.2 mmol of 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole, and was isolated as a light-yellow solid (200.8 mg, 87% yield). M.p. = 129.3 – 132.9 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 8.00 (m, 1H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.51 – 7.49 (m, 1H), 7.08 (s, 1H), 6.54 (d, *J* = 1.8 Hz, 1H), 3.95 (s, 3H).

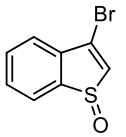
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.75, 139.28, 137.19, 136.85, 135.23, 133.87, 132.32, 129.73, 126.84, 124.51, 108.28, 38.07.

HRMS (ESI) calcd. for $C_{12}H_{10}N_2NaOS^+$ ($M+Na^+$) 253.0406, found 253.0405.



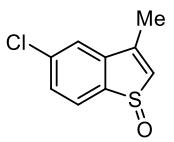
3-methylbenzo[*b*]thiophene 1-oxide (2j)

The compound was prepared according to a known procedure and has been previously characterized[4].



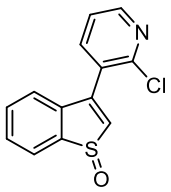
3-bromobenzo[*b*]thiophene 1-oxide (2k)

The compound was prepared according to a known procedure and has been previously characterized[4].



5-chloro-3-methylbenzo[*b*]thiophene 1-oxide (2l)

The compound was prepared according to a known procedure and has been previously characterized[4].



3-(2-chloropyridin-3-yl)benzo[*b*]thiophene 1-oxide (2m)

Following **Method B**, the compound **2m** was prepared from 2.0 mmol of **2k** and 2.4 mmol of (2-chloropyridin-3-yl)boronic acid, and was isolated as a yellow solid (436.0 mg, 83% yield). M.p. = 145.5 – 147.8 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.54 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.01 – 7.99 (m, 1H), 7.76 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.41 (dd, *J* = 7.2, 4.8 Hz, 1H), 7.18 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.12 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.66, 149.73, 145.77, 143.98, 139.49, 136.78, 136.50, 132.06, 129.44, 128.44, 126.67, 124.45, 122.75.

HRMS (ESI) calcd. for $C_{13}H_8ClNNaOS^+$ ($M+Na^+$) 283.9907, found 283.9914.

2.3 Synthesis of 4-hydroxycoumarin derivatives

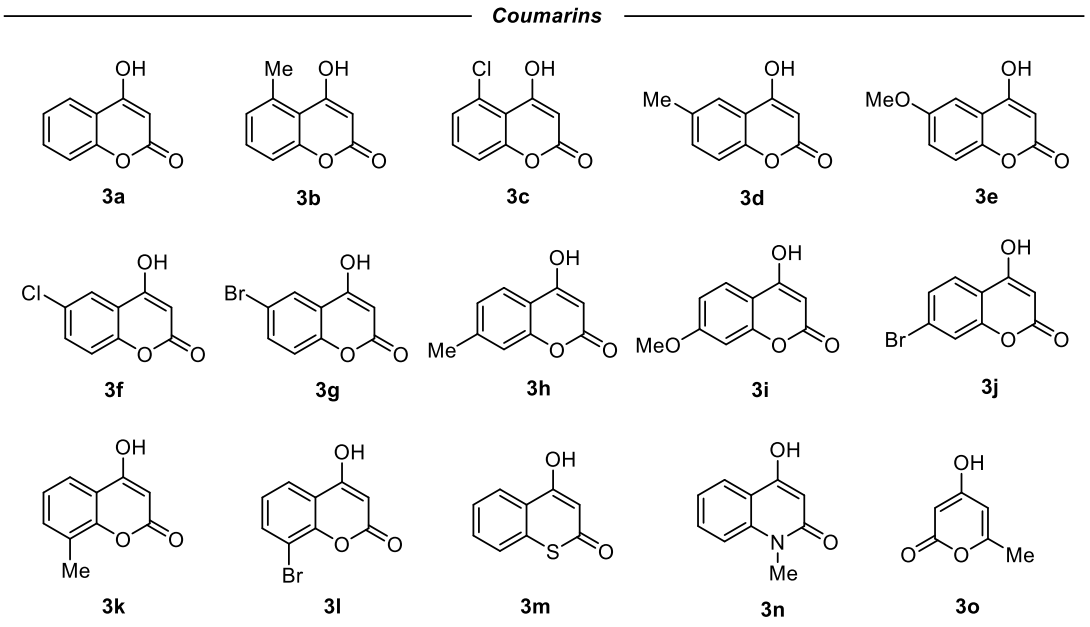
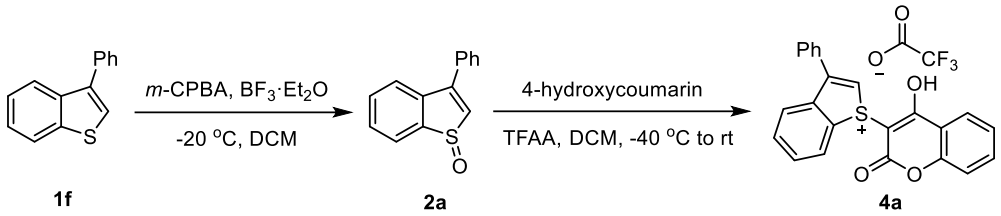


Figure 3S. Structures of 4-hydroxycoumarin derivatives

As shown in **Figure 3S**, 4-hydroxycoumarin derivatives were obtained from commercial purchase (**3a**, **3d**, **3f**, **3h**, **3i**, **3m-3o**) or prepared by following the literature procedures[6, 7] (**3b**, **3c**, **3e**, **3g**, **3j-3l**).

2.4 Synthesis of benzothiophene sulfonium salts



1-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3-phenyl-1*H*-benzo[*b*]thiophen-1-ium trifluoroacetate (4a)

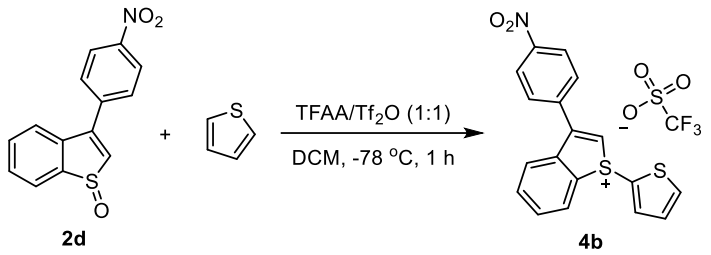
Following **Method A**, compound **2a** was prepared *in situ* from **1f** (4.0 mmol, 1.0 equiv.). The resulting solution of **2a** was adjusted to a concentration of 0.1 M and cooled to −40 °C. Trifluoroacetic anhydride (TFAA, 6.0 mmol, 1.5 equiv.) was added, followed by 4-hydroxycoumarin (4.0 mmol, 1.0 equiv.). The mixture was then allowed to warm to room temperature and stirred for 30 min. When TLC indicated complete consumption of **2a**, the solvent was removed under reduced pressure and the crude material was recrystallized from CH_2Cl_2/PE to afford **4a** as a white solid (429.8 mg, 62% yield). M.p. = 188.7 – 189.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.70 – 7.67 (m, 3H), 7.65 – 7.58 (m, 4H), 7.54 (s, 1H), 7.29 – 7.25 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.48, 161.47, 154.38, 152.29, 140.43, 134.90, 133.53, 132.23, 131.67, 130.33, 129.74, 129.30 (2C), 128.50 (2C), 125.83, 125.80, 125.16, 123.73, 121.52, 117.19, 117.09.

^{19}F NMR (565 MHz, DMSO-d_6) δ -73.39.

HRMS (ESI) calcd. for $C_{23}H_{15}O_3S^+$ (M^+) 371.0736, found 371.0735.



3-(4-nitrophenyl)-1-(thiophen-2-yl)-1*H*-benzo[*b*]thiophen-1-ium trifluoromethanesulfonate (4b)

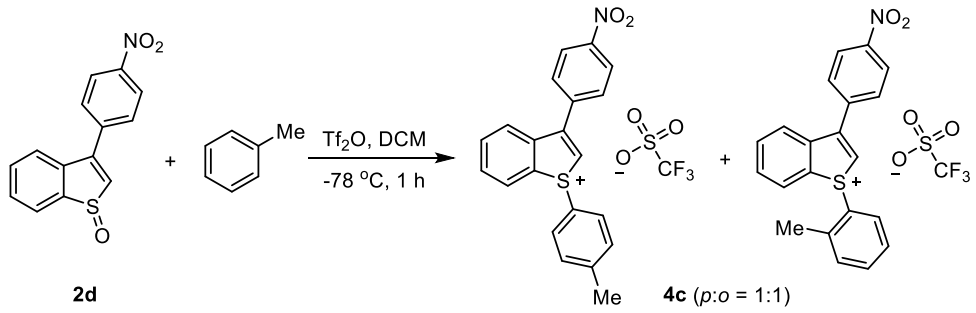
A suspension of 3-(4-nitrophenyl)benzothiophene 1-oxide (**2d**, 0.2 mmol, 1.0 equiv.) and thiophene (0.4 mmol, 2.0 equiv.) in CH_2Cl_2 (2.0 mL) was stirred in a sealed tube at -78 °C. A mixture of TFAA (0.3 mmol, 1.5 equiv.) and trifluoromethanesulfonic anhydride (Tf_2O, 0.3 mmol, 1.5 equiv.) was then added to the reaction. Upon complete consumption of **2d** (after stirring at −78 °C for 1 hour), the solvent was removed under reduced pressure and the residue was purified by preparative TLC (CH_2Cl_2/MeOH, 10:1) to give product **4b** as a brown oil (63.5 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.81 (m, 6H), 7.80 – 7.74 (m, 1H), 7.39 – 7.27 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.84, 149.49, 143.62, 138.72, 137.79, 136.54, 136.48, 134.30, 132.07, 130.32, 129.91 (2C), 128.52, 126.75, 124.86 (2C), 124.25, 124.23, 120.68 (q, *J* = 317.1 Hz), 116.43.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -78.32.

HRMS (ESI) calcd. for $C_{18}H_{12}NO_2S_2^+$ (M^+) 338.0304, found 338.0296.



Mixture of *ortho*- and *para*-tolyl benzothiophenium salts (4c)

A suspension of 3-(4-nitrophenyl)benzothiophene 1-oxide (**2d**, 0.5 mmol, 1.0 equiv.) and toluene (1.0 mmol, 2.0 equiv.) in CH_2Cl_2 (5.0 mL) was stirred in a sealed tube at -78 °C. Tf_2O (0.75 mmol, 1.5 equiv.) was then added to the reaction mixture. Upon complete consumption of **2d** (after stirring at −78 °C for 1 hour), the solvent was removed under reduced pressure and the residue was purified by preparative TLC (CH_2Cl_2/MeOH, 50:1) to give product **4c** as a light-yellow oil (164.8 mg, 67% yield, *o:p* = 1:1).

The NMR data for the isomeric mixture:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 – 8.42 (m, 4H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.04 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.92 (d, *J* = 3.0 Hz, 2H), 7.90 – 7.85 (m, 4H), 7.76 – 7.73 (m, 2H), 7.60 – 7.56 (m, 3H), 7.51 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.27 (m, 1H), 6.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.94 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.59, 152.15, 149.30, 147.05, 143.77, 139.38, 139.36, 136.60, 136.58, 135.37, 135.19, 133.83, 133.81, 133.72, 132.46 (2C), 131.74, 131.64, 130.86 (2C), 129.88 (2C), 129.82 (2C), 129.27, 128.17, 127.69, 127.68, 126.77, 126.47, 124.71 (4C), 123.16, 122.52, 121.63, 121.54, 119.50, 118.30, 21.75, 20.29.

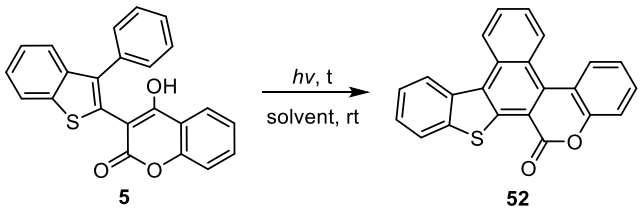
^{19}F NMR (565 MHz, Chloroform-*d*) δ -77.73.

HRMS (ESI) calcd. for $C_{21}H_{16}NO_2S^+$ (M^+) 346.0896, found 346.0903.

3. Optimization of the Reaction Conditions and Substrate Limitations

Optimization of the Reaction Conditions

Table 1S. Optimization of photocatalytic 6π electrocyclization for the conversion of **5** to polycyclic benzothiophene **52**



Entry	Solvent	Light Sources	t (h)	Conv. (%)	Yield (%)[a]
1	toluene	Sunlight	9	29	14
2	CH_3CN	Sunlight	9	100	13
3	DCM	Sunlight	9	77	34
4	THF	Sunlight	9	100	29
5	EA	Sunlight	9	80	24
6	DMF	Sunlight	6	100	12
7	DMSO	Sunlight	9	90	14
8	NMP	Sunlight	9	100	17
9	DMF	365 nm LEDs	3	100	52
10[b]	DMF	365 nm LEDs	3	100	90 (87)[c]
11[b]	DMF	380 nm LEDs	3	100	88
12[b]	DMF	390 nm LEDs	6	100	81
13[b]	DMF	405 nm LEDs	6	100	83
14[b]	DMF	415 nm LEDs	6	100	77
15[b]	DMF	425 nm LEDs	6	100	81
16[b]	DMF	435 nm LEDs	6	100	84
17[b]	DMF	455 nm LEDs	12	100	71
18[b]	DMF	White light	12	15	9

[a]Reaction conditions: Compound **5** (0.05 mmol, 1.0 equiv.) was dissolved in 0.5 mL solvent and irradiated at room temperature. The maximum daily sunlight exposure was

9 hours and the LEDs had a power rating of 15 W. Conversion and yield were determined by ^{1}H NMR analysis using 3,4,5-trichloropyridine as the internal standard. [b]The solution was degassed with argon for 3 minutes before irradiation. [c]Isolated yield.

Substrate Limitations

Although our anchoring–migration strategy enables C2 coupling of benzothiophene derivatives with a wide range of (hetero)arenes, broader substrate screening revealed that certain substrates either fail to undergo the initial anchoring step or do not efficiently undergo the subsequent migration (see Fig. 4S).

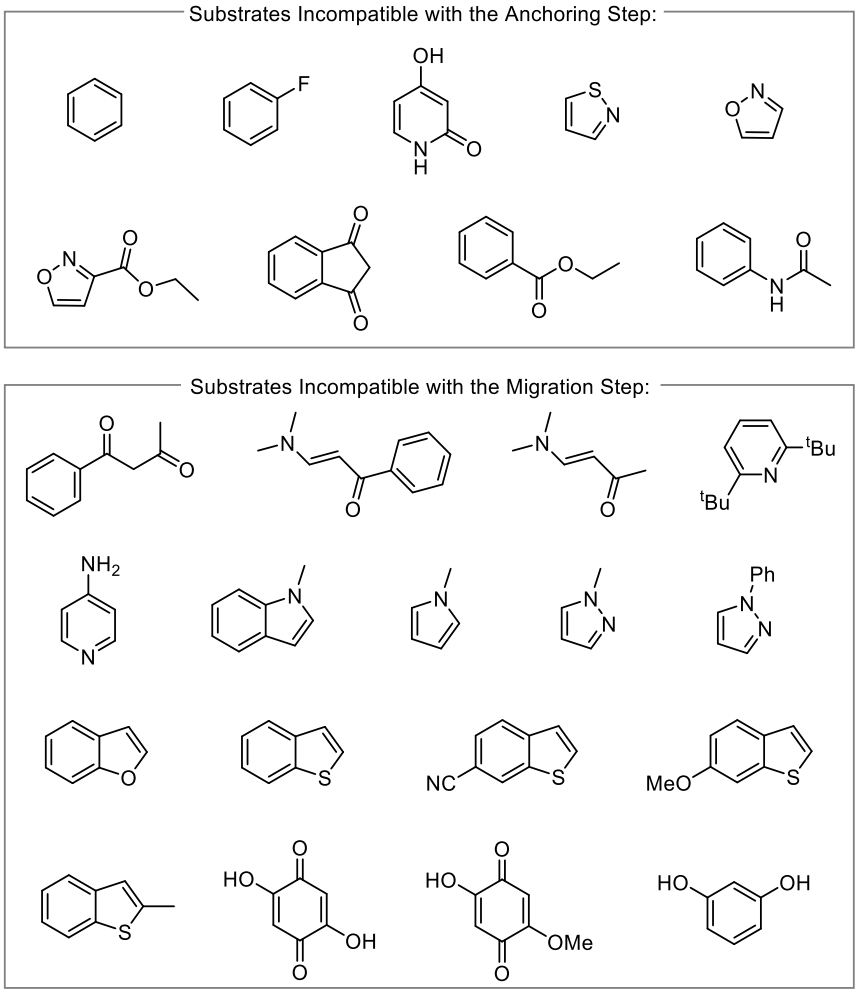
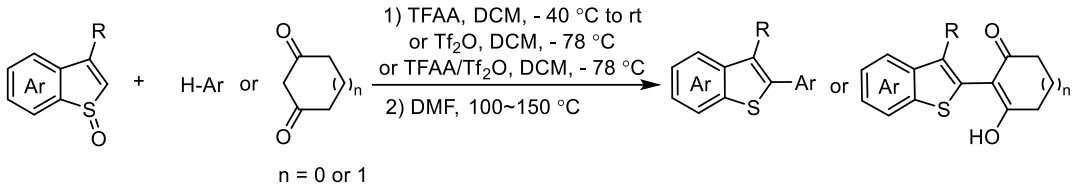


Figure 4S. Coupling partners that fail the anchoring–migration sequence

4. General Procedure



General Procedure A: A suspension of benzothiophene sulfoxide derivative (0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL) was stirred in a sealed tube at −40 °C. TFAA (0.30 mmol, 3.0 equiv.) and (hetero)arenes or 1,3-diketones (0.11 mmol, 1.1 equiv.) were added. The mixture was then allowed to warm to room temperature and stirred for 30 min. Upon complete consumption of the sulfoxide (monitored by TLC), the solvent was removed under reduced pressure. The residue was dissolved in DMF (1.0 mL) and heated to 130 °C for 3–6 hours, with progress monitored by TLC until the reaction was complete. After cooling to room temperature, the reaction was diluted with brine (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by preparative TLC (PE/EtOAc) to afford the desired products.

Adjustment based on the optimal conditions:

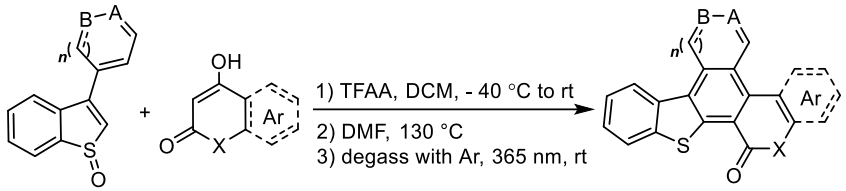
For the synthesis of compounds **42**, **49**, **50**: The *in-situ* formed benzothiophene sulfonium salts were dissolved in DMF (1.0 mL) and heated to 100 °C for 3 hours.

For the synthesis of compounds **43**, **45**, **46**: (Hetero)arenes (2.0 equiv.), TFAA (1.5 equiv.), Tf_2O (1.5 equiv.), DMF (1.25 M); −78 °C, 1 hour for anchoring; 130 °C, 24 hours for migration.

Note: To facilitate the purification of the final product **43**, the benzothiophenium salt **4b** generated from 0.2 mmol of benzothiophene sulfoxide **2d** was isolated prior to the migration step.

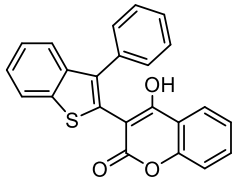
For the synthesis of compound **44**: Toluene (2.0 equiv.), Tf_2O (1.5 equiv.), DMF (1.25 M); −78 °C, 1 hour for anchoring; 130 °C, 12 hours for migration.

For the synthesis of compound **47** and **48**: Mesitylene (2.0 equiv.), Tf_2O (1.5 equiv.), DMF (1.25 M); −78 °C, 1 hour for anchoring; 150 °C, 12 hours for migration.



General Procedure B: A suspension of C3-(hetero)aryl-substituted benzothiophene sulfoxides (0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL) was stirred in a sealed tube at −40 °C. TFAA (0.30 mmol, 3.0 equiv.) and 4-hydroxycoumarin derivative (0.11 mmol, 1.1 equiv.) were added. The mixture was then allowed to warm to room temperature and stirred for 30 min. Upon complete consumption of the sulfoxide (monitored by TLC), the solvent was removed under reduced pressure. The residue was dissolved in DMF (1.0 mL) and heated to 130 °C for 3–6 hours, with progress monitored by TLC until the reaction was complete. After cooling to room temperature, the reaction mixture was degassed by bubbling argon for 3 min and irradiated with 365 nm LEDs for 3 hours at room temperature. The precipitated solid in the reaction solution was collected by filtration and washed with EtOAc to give a portion of the pure product. The filtrate was then diluted with brine (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The remaining crude material was purified by preparative TLC (PE/EtOAc) to afford the additional portion of the desired product.

5. Characterization Data of Products



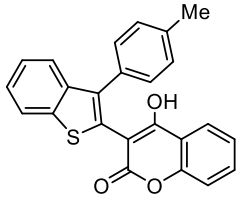
4-hydroxy-3-(3-phenylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (5)

Following **General Procedure A**, the compound **5** was prepared from 0.1 mmol of **2a** and 0.11 mmol of **3a**, and was isolated as a yellow solid (27.4 mg, 74% yield). Alternatively, the product could also be obtained in 68% yield via in-situ oxidation of 3-phenylbenzothiophene **1a** followed by **General Procedure A**. M.p. = 188.7 – 189.5 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.06 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.47 – 7.30 (m, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 164.11, 161.72, 153.17, 140.45, 139.69, 138.24, 135.13, 133.48, 129.34 (2C), 128.93 (2C), 128.03, 125.27, 124.91, 124.61, 124.40, 123.25, 123.07, 116.83, 116.17, 98.27.

HRMS (ESI) calcd. for $C_{23}H_{14}NaO_3S^+$ ($M+Na^+$) 393.0556, found 393.0573.



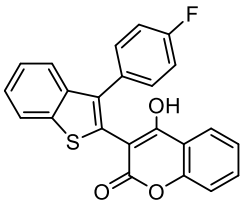
4-hydroxy-3-(3-(*p*-tolyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (6)

Following **General Procedure A**, the compound **6** was prepared from 0.1 mmol of **2b** and 0.11 mmol of **3a**, and was isolated as a yellow solid (26.0 mg, 68% yield). M.p. = 122.4 – 123.8 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (dt, J = 7.8, 1.2 Hz, 1H), 7.86 (dd, J = 7.8, 1.8 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.60 – 7.59 (m, 1H), 7.46 – 7.43 (m, 1H), 7.43 – 7.40 (m, 1H), 7.38 (dd, J = 8.4, 0.6 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.26 (d, J = 7.8, 2H), 7.20 (d, J = 7.8, 2H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 163.76, 161.66, 153.16, 140.47, 139.81, 138.36, 137.28, 133.53, 132.14, 129.57 (2C), 129.20 (2C), 125.25, 124.86, 124.67, 124.39, 123.34, 123.06, 116.85, 116.10, 98.52, 21.27.

HRMS (ESI) calcd. for $C_{24}H_{16}NaO_3S^+$ ($M+Na^+$) 407.0712, found 407.0719.



3-(3-(4-fluorophenyl)benzo[*b*]thiophen-2-yl)-4-hydroxy-2*H*-chromen-2-one (7)

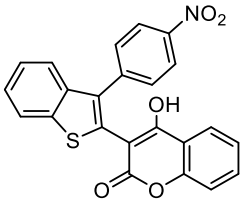
Following **General Procedure A**, the compound **7** was prepared from 0.1 mmol of **2c** and 0.11 mmol of **3a**, and was isolated as a yellow oil (33.3 mg, 86% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 – 8.06 (m, 1H), 7.86 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.60 – 7.58 (m, 1H), 7.49 – 7.33 (m, 6H), 7.28 – 7.23 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.93, 162.01 (d, J = 245.4 Hz), 161.63, 153.18, 140.40, 139.63, 137.30, 133.54, 131.40(d, J = 4.0Hz), 131.36 (d, J = 8.1Hz, 2C), 129.94, 125.35, 124.97, 124.64, 124.39, 123.15, 123.08, 116.83, 116.13, 115.93 (d, J = 21.2Hz, 2C), 98.17.

^{19}F NMR (376 MHz, Chloroform-*d*) δ 106.49 – 117.32 (m).

HRMS (ESI) calcd. for $C_{23}H_{13}FNaO_3S^+$ ($M+Na^+$) 411.0462, found 411.0473.



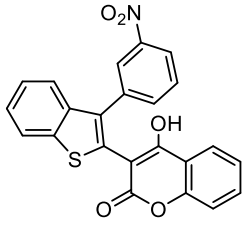
4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (8)

Following **General Procedure A**, the compound **8** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3a**, and was isolated as a yellow solid (37.0 mg, 89% yield). M.p. = 204.4 – 206.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, J = 8.8 Hz, 2H), 8.05 (dd, J = 7.2, 2.0 Hz, 1H), 7.81 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 – 7.57 (m, 4H), 7.47 – 7.40 (m, 2H), 7.31 – 7.25 (m, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.85, 153.50, 146.86, 142.93, 140.31, 138.93, 134.93, 132.93, 130.64 (2C), 125.18, 125.03, 124.73, 124.14 (2C), 124.06, 123.04, 122.56, 118.02, 116.66, 115.96, 96.03.

HRMS (ESI) calcd. for $C_{23}H_{13}NaO_5S^+$ ($M+Na^+$) 438.0407, found 438.0414.



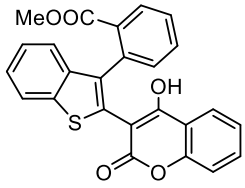
4-hydroxy-3-(3-(3-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (9)

Following **General Procedure A**, the compound **9** was prepared from 0.1 mmol of **2e** and 0.11 mmol of **3a**, and was isolated as a yellow solid (34.1 mg, 82% yield). M.p. > 300 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 – 8.16 (m, 2H), 8.10 (dd, J = 7.2, 1.6 Hz, 1H), 7.84 (dd, J = 8.0, 2.0 Hz, 1H), 7.79 (dt, J = 7.6, 1.6 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.51 – 7.43 (m, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 164.65, 161.69, 153.28, 148.30, 140.43, 139.06, 136.80, 136.05, 135.74, 133.56, 131.93, 130.67, 125.57, 125.26, 124.59, 124.48, 124.03, 123.21, 122.95, 122.81, 116.84, 116.39, 97.40.

HRMS (ESI) calcd. for $C_{23}H_{13}NaO_5S^+$ ($M+Na^+$) 438.0407, found 438.0417.



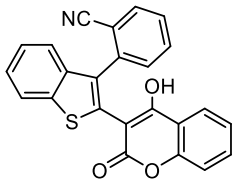
methyl 2-(2-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)benzo[*b*]thiophen-3-yl)benzoate (10)

Following **General Procedure A**, the compound **10** was prepared from 0.2 mmol of **2f** and 0.22 mmol of **3a**, and was isolated as a yellow solid (32.6 mg, 47% yield). M.p. = 205.3 – 206.7 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.21 – 7.16 (m, 2H), 3.75 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.86, 163.03, 162.66, 153.49, 140.94, 139.20, 137.72, 135.48, 133.42, 132.87, 132.05, 130.74, 129.60, 128.88, 128.69, 125.36, 124.61, 124.31, 124.01, 122.75, 121.85, 116.73, 115.56, 98.46, 53.45.

HRMS (ESI) calcd. for $C_{25}H_{16}NaO_5S^+$ ($M+Na^+$) 451.0611, found 451.0617.



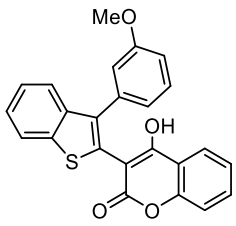
2-(2-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)benzo[*b*]thiophen-3-yl)benzonitrile (11)

Following **General Procedure A**, the compound **11** was prepared from 0.1 mmol of **2g** and 0.11 mmol of **3a**, and was isolated as a yellow solid (36.1 mg, 91% yield). M.p. = 168.7 – 169.9 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 2H), 7.63 (t, *J* = 6.6 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.47 – 7.44 (m, 1H), 7.42 – 7.40 (m, 1H), 7.37 – 7.29 (m, 3H), 7.20 – 7.15 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.45, 161.78, 153.35, 140.48, 139.09, 139.05, 134.85, 133.19, 132.91, 132.59, 132.01, 131.61, 128.17, 125.03, 124.49, 124.32, 123.77, 123.02, 122.31, 118.38, 116.52, 116.19, 112.67, 97.96.

HRMS (ESI) calcd. for $C_{24}H_{13}NNaO_3S^+$ ($M+Na^+$) 418.0508, found 418.0507.



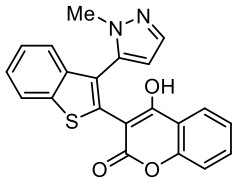
4-hydroxy-3-(3-(3-methoxyphenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (12)

Following **General Procedure A**, the compound **12** was prepared from 0.2 mmol of **2h** and 0.22 mmol of **3a**, and was isolated as a yellow solid (51.4 mg, 56% yield). M.p. = 102.8 – 104.7 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.59 – 7.56 (m, 1H), 7.44 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27– 7.25 (m, 1H), 7.04 – 7.01 (m, 2H), 6.89 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.86, 161.50, 160.01, 153.48, 141.10, 139.27, 139.18, 135.26, 133.22, 130.18, 126.59, 125.71, 124.87, 124.26, 124.09, 123.93, 122.66, 121.56, 116.87, 114.48, 114.45, 114.43, 99.52, 55.41.

HRMS (ESI) calcd. for $C_{24}H_{16}NaO_4S^+$ ($M+Na^+$) 423.0662, found 423.0687.



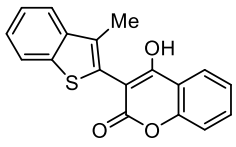
4-hydroxy-3-(3-(1-methyl-1*H*-pyrazol-5-yl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (13)

Following **General Procedure A**, the compound **13** was prepared from 0.1 mmol of **2i** and 0.11 mmol of **3a**, and was isolated as a yellow solid (25.4 mg, 68% yield). M.p. = 275.4 – 278.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 – 8.06 (m, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.48 – 7.41 (m, 3H), 7.39 – 7.31 (m, 3H), 6.21 (d, *J* = 2.0 Hz, 1H), 3.58 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 165.05, 161.06, 152.86, 139.55, 138.82, 138.08, 136.09, 132.74, 126.25, 124.76, 124.72, 124.21, 123.82, 122.63, 122.31, 116.88, 116.28, 106.85, 96.27, 79.20, 36.85.

HRMS (ESI) calcd. for $C_{21}H_{14}N_2NaO_3S^+$ ($M+Na^+$) 397.0617, found 397.0623.



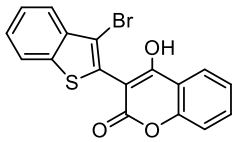
4-hydroxy-3-(3-methylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (14)

Following **General Procedure A**, the compound **14** was prepared from 0.1 mmol of **2j** and 0.11 mmol of **3a**, and was isolated as a yellow solid (12.4 mg, 40% yield). M.p. = 181.0 – 183.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (dd, J = 8.0, 1.6 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.81 – 7.79 (m, 1H), 7.72 – 7.68 (m, 1H), 7.45 – 7.38 (m, 4H), 2.21 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 174.92, 159.93, 154.11, 148.36, 141.93, 134.32, 133.98, 131.92, 129.78, 125.58, 125.05, 124.63, 124.09, 121.49, 117.84, 117.10, 72.25, 14.69.

HRMS (ESI) calcd. for $C_{18}H_{12}NaO_3S^+$ ($M+Na^+$) 331.0399, found 331.0393.



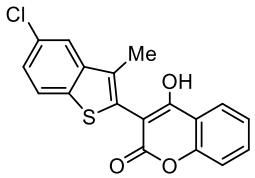
3-(3-bromobenzo[*b*]thiophen-2-yl)-4-hydroxy-2*H*-chromen-2-one (15)

Following **General Procedure A**, the compound **15** was prepared from 0.2 mmol of **2k** and 0.22 mmol of **3a**, and was isolated as a light-red solid (24.8 mg, 20% yield). M.p. = 234.8 – 235.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 8.4 Hz, 1H), 8.12 – 8.09 (m, 2H), 7.72 – 7.68 (m, 1H), 7.63 – 7.57 (m, 2H), 7.55 – 7.48 (m 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.76, 157.07, 152.71, 152.51, 141.87, 132.16, 126.44, 126.15, 125.77, 125.62, 123.86, 121.64, 120.05, 119.62, 117.81, 113.07, 107.99.

HRMS (ESI) calcd. for $C_{17}H_9BrNaO_3S^+$ ($M+Na^+$) 394.9348, found 394.9354.



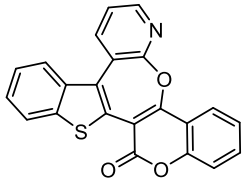
3-(5-chloro-3-methylbenzo[*b*]thiophen-2-yl)-4-hydroxy-2*H*-chromen-2-one (16)

Following **General Procedure A**, the compound **16** was prepared from 0.2 mmol of **2l** and 0.22 mmol of **3a**, and was isolated as a yellow solid (44.6 mg, 65% yield). M.p. > 300 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.98 (d, J = 8.4 Hz, 2H), 7.86 (s, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.43 – 7.38 (m, 3H), 2.20 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.19, 161.54, 153.35, 141.79, 138.72, 133.38, 132.30, 131.10, 129.52, 124.80, 124.57, 124.51, 124.36, 122.04, 116.85, 116.82, 97.72, 12.88.

HRMS (ESI) calcd. for $C_{18}H_{11}ClNaO_3S^+$ ($M+Na^+$) 365.0010, found 365.0011.



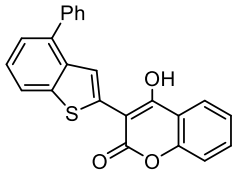
1*H*-benzo[4',5']thieno[3',2':4,5]chromeno[3',4':6,7]oxepino[2,3-*b*]pyridin-1-one (18)

Following **General Procedure A**, the compound **18** was prepared from 0.1 mmol of **2m** and 0.11 mmol of **3a**, and was isolated as a yellow solid (30.1 mg, 81% yield). M.p. = 166.3 – 167.6 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.43 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.99 – 7.97 (m, 2H), 7.66 – 7.64 (m, 1H), 7.50 – 7.46 (m, 3H), 7.43 – 7.40 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.69, 161.18, 160.47, 153.03, 148.59, 141.46, 139.25, 136.44, 133.29, 133.26, 130.80, 125.83, 125.79, 125.29, 125.10, 123.03, 123.01, 122.89, 122.33, 117.23, 116.54, 111.49.

HRMS (ESI) calcd. for $C_{22}H_{11}NNaO_3S^+$ ($M+Na^+$) 392.0352, found 392.0359.



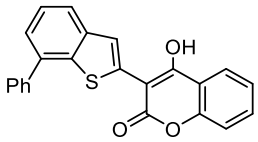
4-hydroxy-3-(4-phenylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (19).

A solution of 4-phenylbenzo[*b*]thiophene 1-oxide was prepared *in situ* from **1g** (0.1 mmol) according to **Method A** and used directly. Subsequently, compound **19** was prepared according to **General Procedure A** and isolated as a yellow solid (24.7 mg, 67% yield). M.p. = 226.2 – 227.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (s, 1H), 7.99 (dd, J = 8.0, 1.6 Hz, 1H), 7.82 (d, J = 6.8 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.55 – 7.47 (m, 3H), 7.45 – 7.41 (m, 1H), 7.26 – 7.20 (m, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 169.94, 162.43, 152.99, 141.89, 140.77, 139.47, 137.87, 135.22, 131.42, 129.20 (2C), 129.03 (2C), 127.45, 125.34, 124.20, 123.08, 122.42, 121.32, 120.88, 117.14, 116.16, 96.26.

HRMS (ESI) calcd. for $C_{23}H_{14}NNaO_3S^+$ ($M+Na^+$) 393.0556, found 393.0556.



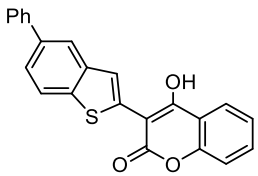
4-hydroxy-3-(7-phenylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (20)

A solution of 7-phenylbenzo[*b*]thiophene 1-oxide was prepared *in situ* from **1i** (0.1 mmol) according to **Method A** and used directly. Following **General Procedure A**, compound **20** was obtained by concentrating the reaction mixture and washing the resulting solid with a small amount of CH_2Cl_2 to afford the pure product as a light-yellow solid (31.3 mg, 85% yield). M.p. = 215.6 – 217.8 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 1H), 8.12 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 (dd, J = 8.0, 1.2 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.68 – 7.63 (m, 1H), 7.58 – 7.54 (m, 2H), 7.48 – 7.39 (m, 4H), 7.37 – 7.34 (m, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 163.27, 161.45, 152.28, 140.67, 140.40, 138.10, 135.73, 135.70, 133.08, 129.37 (2C), 128.42 (2C), 125.32, 124.80, 124.46, 124.45, 124.19, 122.98, 117.03, 116.77, 100.06.

HRMS (ESI) calcd. for $C_{23}H_{14}NNaO_3S^+$ ($M+Na^+$) 393.0556, found 393.0556.



4-hydroxy-3-(5-phenylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (21)

A solution of 5-phenylbenzo[*b*]thiophene 1-oxide was prepared *in situ* from **1h** (0.2 mmol) according to **Method A** and used directly. Following **General Procedure A**,

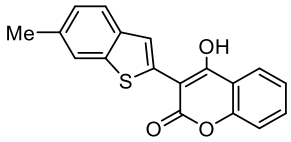
compound **21** was obtained by concentrating the reaction mixture and washing the resulting solid with CH_2Cl_2 to afford the pure product as a yellow solid (21.1 mg, 29% yield). M.p. = 234.9 – 236.1 °C.

Note: A relatively large amount of CH_2Cl_2 was required to completely remove impurities from the product, resulting in partial loss of material and a slightly reduced isolated yield.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (s, 1H), 8.15 (dd, J = 7.8, 1.2 Hz, 1H), 8.12 (d, J = 1.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.68 – 7.65 (m, 1H), 7.60 (dd, J = 8.4, 1.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.43 – 7.36 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 163.86, 161.63, 152.36, 141.05, 140.29, 138.85, 136.74, 136.65, 132.96, 129.41 (2C), 127.59, 127.33 (2C), 124.61, 124.35, 124.09, 123.23, 122.47, 121.38, 117.44, 116.75, 99.90.

HRMS (ESI) calcd. for $C_{23}H_{14}NNaO_3S^+$ ($M+Na^+$) 393.0556, found 393.0556.



4-hydroxy-3-(6-methylbenzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (22)

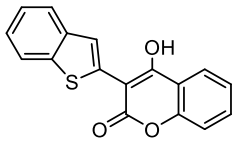
A solution of 6-methylbenzo[*b*]thiophene 1-oxide was prepared *in situ* from **1c** (0.2 mmol) according to **Method A** and used directly. Following **General Procedure A**, compound **22** was obtained by concentrating the reaction mixture and washing the resulting solid with CH_2Cl_2 to afford the pure product as a yellow solid (16.1 mg, 26% yield). M.p. > 300 °C.

Note: A relatively large amount of CH_2Cl_2 was required to completely remove impurities from the product, resulting in partial loss of material and a slightly reduced isolated yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (s, 1H), 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 7.61 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.28 – 7.24 (m, 2H), 7.07 (dd, J = 8.0, 1.6 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 162.27, 152.86, 139.18, 138.41, 137.79, 131.69, 131.53, 125.46, 125.18, 123.22, 122.00, 121.37, 120.75, 119.13, 116.20, 96.88, 21.66.

HRMS (ESI) calcd. for $C_{18}H_{12}NaO_3S^+$ ($M+Na^+$) 331.0399, found 331.0401.

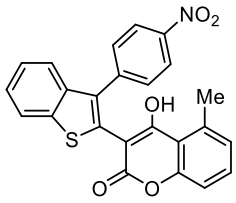


3-(benzo[*b*]thiophen-2-yl)-4-hydroxy-2*H*-chromen-2-one (23)

A solution of benzo[*b*]thiophene 1-oxide was prepared *in situ* from **1a** (0.2 mmol) according to **Method A** and used directly. Following **General Procedure A**, compound **23** was obtained by concentrating the reaction mixture and washing the resulting solid with a small amount of CH_2Cl_2 to afford the pure product as a yellow solid (32.1 mg, 55% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.22 (d, J = 0.6 Hz, 1H), 8.14 (dd, J = 7.8, 1.2 Hz, 1H), 7.94 – 7.92 (m, 1H), 7.86 – 7.84 (m, 1H), 7.68 – 7.65 (m, 1H), 7.43 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H).

NMR spectra are in agreement with the reported data[8].



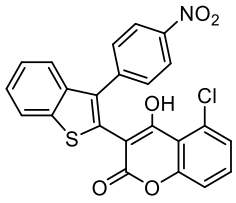
4-hydroxy-5-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (24)

Following **General Procedure A**, the compound **24** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3b**, and was isolated as a light-yellow solid (31.8 mg, 74% yield). M.p. = 154.7 – 157.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, J = 8.8 Hz, 2H), 8.10 – 8.08 (m, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.63 – 7.61 (m, 1H), 7.51 – 7.42 (m, 3H), 7.18 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 167.44, 161.08, 154.64, 147.13, 142.31, 140.60, 139.15, 138.29, 136.45, 132.61, 131.96, 130.72 (2C), 128.06, 125.55, 125.20, 124.23 (2C), 123.19, 122.91, 115.23, 115.03, 97.42, 23.55.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_5S^+$ ($M+Na^+$) 452.0563, found 452.0562.



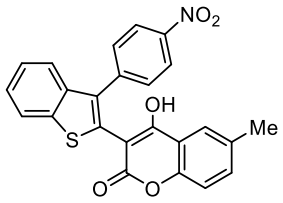
5-chloro-4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (25)

Following **General Procedure A**, the compound **25** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3c**, and was isolated as a light-yellow solid (28.3 mg, 63% yield). M.p. = 176.8 – 178.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 6.8 Hz, 1H), 7.66 – 7.61 (m, 3H), 7.55 (t, J = 8.0 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.36 (d, J = 7.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.40, 155.16, 147.09, 142.34, 140.57, 139.04, 136.22, 132.97, 131.10, 130.69 (2C), 130.17, 128.01, 125.51, 125.18, 124.61, 124.25 (2C), 123.17, 122.86, 116.65, 114.61, 98.08.

HRMS (ESI) calcd. for $C_{23}H_{12}ClNNaO_5S^+$ ($M+Na^+$) 472.0017, found 472.0019.



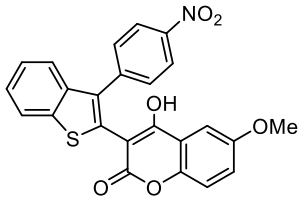
4-hydroxy-6-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (26)

Following **General Procedure A**, the compound **26** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3d**, and was isolated as a light-yellow solid (26.0 mg, 61% yield). M.p. > 300 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.10 – 8.08 (m, 1H), 7.65 – 7.62 (m, 4H), 7.50 – 7.42 (m, 3H), 7.25 (d, J = 8.4 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.69, 161.72, 151.45, 147.07, 142.35, 140.44, 138.92, 135.89, 134.35, 133.85, 132.50, 130.67 (2C), 125.52, 125.23, 124.24 (2C), 124.10, 123.17, 122.84, 116.63, 116.16, 97.37, 20.79.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_5S^+$ ($M+Na^+$) 452.0563, found 452.0554.



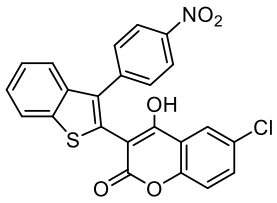
4-hydroxy-6-methoxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (27)

Following **General Procedure A**, the compound **27** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3e**, and was isolated as a light-yellow solid (34.9 mg, 78% yield). M.p. = 155.6 – 158.4 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.09 – 8.07 (m, 1H), 7.66 – 7.62 (m, 3H), 7.49 – 7.42 (m, 2H), 7.31 – 7.29 (m, 2H), 7.22 (dd, J = 8.8, 3.2 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.96, 161.75, 155.83, 147.72, 147.02, 142.49, 140.39, 138.91, 135.61, 133.05, 130.66 (2C), 125.45, 125.19, 124.23 (2C), 123.14, 122.77, 121.23, 118.12, 117.23, 106.29, 97.34, 56.14.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_6S^+$ ($M+Na^+$) 468.0512, found 468.0512.



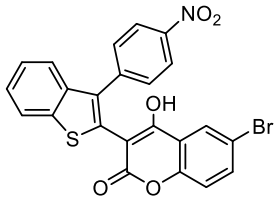
6-chloro-4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (28)

Following **General Procedure A**, the compound **28** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3f**, and was isolated as a light-yellow solid (33.1 mg, 74% yield). M.p. = 238.5 – 240.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, J = 8.8 Hz, 2H), 8.07 – 8.02 (m, 1H), 7.78 (d, J = 2.4 Hz, 1H), 7.66 – 7.60 (m, 4H), 7.46 – 7.39 (m, 2H), 7.34 (d, J = 8.8 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 165.67, 161.53, 152.09, 146.87, 142.81, 140.30, 138.83, 134.99, 134.21, 132.49, 130.62 (2C), 128.17, 125.22, 125.05, 124.16 (2C), 123.91, 123.02, 122.56, 119.67, 118.82, 96.60.

HRMS (ESI) calcd. for $C_{23}H_{12}ClNNaO_5S^+$ ($M+Na^+$) 472.0017, found 472.0015.



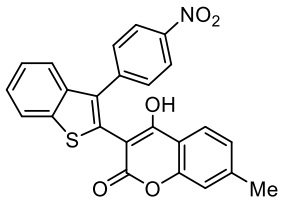
6-bromo-4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (29)

Following **General Procedure A**, the compound **29** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3g**, and was isolated as an orange-yellow solid (39.0 mg, 79% yield). M.p. = 237.7 – 249.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, J = 8.8 Hz, 2H), 7.97 – 7.93 (m, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.37 – 7.33 (m, 2H), 7.11 (d, J = 8.8 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 170.30, 162.16, 153.02, 146.34, 144.30, 139.95, 138.89, 133.73, 132.51, 130.52, 127.47, 124.53, 124.31, 124.01, 123.87, 122.66, 121.82, 118.77, 114.84, 92.45.

HRMS (ESI) calcd. for $C_{23}H_{12}BrNNaO_5S^+$ ($M+Na^+$) 515.9512, found 515.9515.



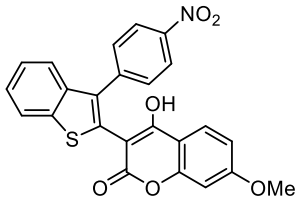
4-hydroxy-7-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (30)

Following **General Procedure A**, the compound **30** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3h**, and was isolated as a light-yellow solid (32.9 mg, 77% yield). M.p. = 186.6 – 188.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.08 (dd, J = 7.2, 2.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.65 – 7.62 (m, 3H), 7.50 – 7.42 (m, 2H), 7.18 (s, 1H), 7.13 (dd, J = 8.0, 1.6 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.95, 161.75, 153.40, 147.04, 144.41, 142.41, 140.42, 138.91, 135.81, 132.66, 130.66 (2C), 125.61, 125.49, 125.21, 124.28, 124.22 (2C), 123.16, 122.82, 116.81, 114.05, 96.59, 21.59.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_5S^+$ ($M+Na^+$) 452.0563, found 452.0576.



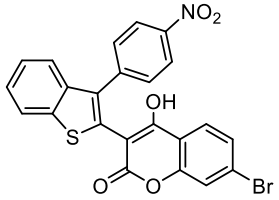
4-hydroxy-7-methoxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (31)

Following **General Procedure A**, the compound **31** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3i**, and was isolated as a light-yellow solid (21.3 mg, 48% yield). M.p. = 224.4 – 226.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.08 (dd, J = 6.8, 1.2 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.64 – 7.61 (m, 3H), 7.49 – 7.42 (m, 2H), 6.94 (d, J = 2.4 Hz, 1H), 6.90 (dd, J = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 165.10, 163.69, 161.88, 155.20, 147.03, 142.47, 140.40, 138.91, 135.75, 132.83, 130.67 (2C), 125.75, 125.47, 125.20, 124.22 (2C), 123.15, 122.80, 112.57, 109.61, 100.91, 94.94, 56.45.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_6S^+$ ($M+Na^+$) 468.0512, found 468.0515.



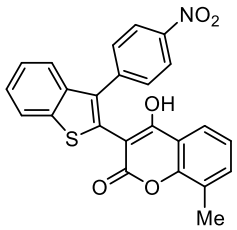
7-bromo-4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (32)

Following **General Procedure A**, the compound **32** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3j**, and was isolated as a light-yellow solid (43.3 mg, 88% yield). M.p. = 209.9 – 212.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.8 Hz, 2H), 8.03 (dd, J = 6.4, 2.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.58 (d, J = 1.6 Hz, 1H), 7.46 – 7.39 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 165.68, 161.43, 153.71, 146.92, 142.58, 140.32, 138.79, 135.39, 133.30, 130.62 (2C), 127.38, 126.32, 125.90, 125.40, 125.16, 124.15 (2C), 123.06, 122.70, 119.55, 116.85, 96.75.

HRMS (ESI) calcd. for $C_{23}H_{12}BrNNaO_5S^+$ ($M+Na^+$) 515.9512, found 515.9521.



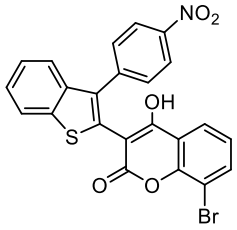
4-hydroxy-8-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (33)

Following **General Procedure A**, the compound **33** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3k**, and was isolated as a yellow solid (36.0 mg, 84% yield). M.p. = 157.7 – 161.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.10 – 8.08 (m, 1H), 7.70 – 7.62 (m, 4H), 7.51 – 7.43 (m, 3H), 7.21 (t, J = 7.6 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.85, 161.53, 151.59, 147.09, 142.31, 140.44, 138.96, 136.03, 134.52, 132.24, 130.69 (2C), 125.71, 125.57, 125.25, 124.27 (2C), 124.04, 123.19, 122.89, 122.15, 116.11, 97.33, 15.60.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_5S^+$ ($M+Na^+$) 452.0563, found 452.0569.



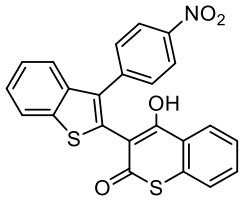
8-bromo-4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-chromen-2-one (34)

Following **General Procedure A**, the compound **34** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3l**, and was isolated as a yellow solid (26.3 mg, 53% yield). M.p. = 164.8 – 166.4 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, J = 8.8 Hz, 2H), 8.05 (dd, J = 6.8, 2.0 Hz, 1H), 7.86 (dd, J = 8.0, 1.6 Hz, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 – 7.61 (m, 3H), 7.47 – 7.39 (m, 2H), 7.19 (t, J = 8.0 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 166.70, 161.08, 150.11, 146.87, 142.86, 140.30, 138.87, 135.87, 134.95, 134.38, 130.64 (2C), 125.21, 125.05, 125.00, 124.50, 124.17 (2C), 123.03, 122.56, 120.06, 109.42, 95.84.

HRMS (ESI) calcd. for $C_{23}H_{12}BrNNaO_5S^+$ ($M+Na^+$) 515.9512, found 515.9515.



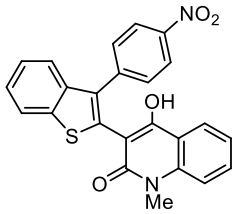
4-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-thiochromen-2-one (35)

Following **General Procedure A**, the compound **35** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3m**, and was isolated as a light-yellow solid (35.5 mg, 82% yield). M.p. = 216.5 – 218.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 7.2 Hz, 1H), 7.63 – 7.57 (m, 5H), 7.50 – 7.42 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 181.08, 166.27, 147.11, 142.27, 140.68, 139.23, 136.13, 135.90, 131.85, 130.59 (2C), 127.70, 127.05, 125.99, 125.42, 125.15, 124.68, 124.19 (2C), 123.18, 122.87, 109.07.

HRMS (ESI) calcd. for $C_{23}H_{13}NNaO_4S_2^+$ ($M+Na^+$) 454.0178, found 454.0180.



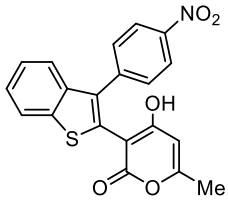
4-hydroxy-1-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)quinolin-2(1*H*)-one (36)

Following **General Procedure A**, the compound **36** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3n**, and was isolated as a brown solid (21.2 mg, 50% yield). M.p. = 158.3 – 161.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, J = 8.8 Hz, 2H), 8.09 (dd, J = 6.8, 1.6 Hz, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 – 7.62 (m, 4H), 7.51 – 7.42 (m, 3H), 7.24 (t, J = 7.6 Hz, 1H), 3.58 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 162.03, 159.68, 146.98, 142.54, 140.55, 140.02, 139.19, 135.57, 133.79, 132.44, 130.70 (2C), 125.33, 125.09, 124.31, 124.13 (2C), 123.12, 122.80, 122.09, 115.84, 115.19, 103.67, 29.80.

HRMS (ESI) calcd. for $C_{24}H_{16}N_2NaO_4S^+$ ($M+Na^+$) 451.0723, found 451.0711.



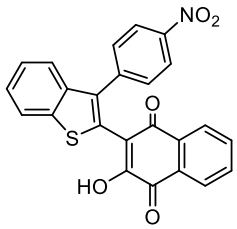
4-hydroxy-6-methyl-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2*H*-pyran-2-one (37)

Following **General Procedure A**, the compound **37** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3o**, and was isolated as a yellow solid (31.2 mg, 82% yield). M.p. = 138.0 – 140.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 8.8 Hz, 2H), 8.04 – 8.02 (m, 1H), 7.62 – 7.59 (m, 3H), 7.46 – 7.38 (m, 2H), 6.03 (d, J = 1.2 Hz, 1H), 2.18 (d, J = 0.8 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 168.81, 163.99, 163.13, 146.96, 142.84, 139.97, 138.45, 134.60, 133.04, 130.56 (2C), 125.37, 125.18, 124.21 (2C), 123.03, 122.55, 100.35, 94.55, 19.96.

HRMS (ESI) calcd. for $C_{20}H_{13}NNaO_5S^+$ ($M+Na^+$) 402.0407, found 402.0415.



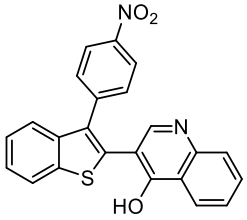
2-hydroxy-3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)naphthalene-1,4-dione (40)

Following **General Procedure A**, the compound **40** was prepared from 0.1 mmol of **2d** and 0.11 mmol of 2-hydroxynaphthalene-1,4-dione, and was isolated as a marron solid (29.2 mg, 68% yield). M.p. = 196.4 – 198.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, J = 8.8 Hz, 2H), 8.04 – 8.00 (m, 1H), 7.91 (dd, J = 7.6, 1.6 Hz, 1H), 7.88 (dd, J = 7.6, 1.6 Hz, 1H), 7.75 (td, J = 7.6, 1.6 Hz, 1H), 7.69 (dd, J = 7.6, 1.2 Hz, 1H), 7.66 – 7.62 (m, 3H), 7.43 – 7.38 (m, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 183.17, 180.47, 146.54, 143.62, 140.25, 138.54, 136.35, 134.73, 134.16, 133.46, 132.46, 131.27, 130.54 (2C), 130.12, 126.25, 126.02, 124.87, 124.82, 124.03 (2C), 122.83, 122.20, 113.24.

HRMS (ESI) calcd. for $C_{24}H_{13}NNaO_5S^+$ (M+Na$^+$) 450.0407, found 450.0397.



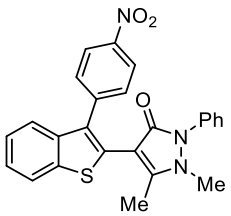
3-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)quinolin-4-ol (41)

Following **General Procedure A**, the compound **41** was prepared from 0.1 mmol of **2d** and 0.11 mmol of quinolin-4-ol, and was isolated as a yellow solid (9.7 mg, 24% yield). M.p. > 300 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.04 (br, 1H), 8.30 (d, J = 8.8 Hz, 2H), 8.16 (dd, J = 8.0, 1.6 Hz, 1H), 8.07 – 8.05 (m, 1H), 7.76 (s, 1H), 7.70 – 7.66 (m, 3H), 7.58 – 7.55 (m, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.45 – 7.37 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ174.51, 146.44, 142.80, 140.61, 140.59, 139.18, 138.91, 138.04, 136.22, 132.15, 131.33, 131.15, 125.49, 125.24, 124.69, 124.10, 124.05, 122.39, 121.79, 118.54, 112.71.

HRMS (ESI) calcd. for $C_{23}H_{15}N_2NaO_3S^+$ (M+H$^+$) 399.0798, found 399.0801.



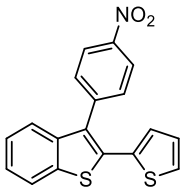
1,5-dimethyl-4-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (42)

Following **General Procedure A**, the compound **42** was prepared from 0.1 mmol of **2d** and 0.11 mmol of 1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one, and was isolated as a yellow solid (10.5 mg, 23% yield). M.p. = 132.5 – 133.5 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.89 (m, 1H), 7.70 – 7.66 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.31 (m, 5H), 3.10 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 164.22, 153.35, 146.94, 143.07, 140.58, 138.59, 134.86, 134.13, 131.44, 130.81, 129.50, 127.39, 125.05, 124.80, 124.77, 124.06, 122.63, 122.44, 103.46, 35.66, 12.05.

HRMS (ESI) calcd. for $C_{25}H_{19}N_3NaO_3S^+$ ($M+Na^+$) 464.1039, found 464.1046.



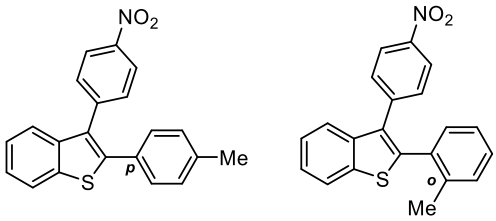
3-(4-nitrophenyl)-2-(thiophen-2-yl)benzo[*b*]thiophene (43)

Following **General Procedure A**, the compound **43** was prepared from 0.2 mmol of **2d** and 0.4 mmol of thiophene, and was isolated as a yellow oil (20.9 mg, 31% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.8 Hz, 2H), 7.86 – 7.84 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.08 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.76, 142.51, 140.31, 138.53, 135.26, 134.43, 131.84 (2C), 130.97, 127.89, 127.55, 127.32, 125.41, 125.21, 124.25 (2C), 122.75, 122.26.

HRMS (ESI) calcd. for $C_{18}H_{11}NNaO_2S_2^+$ ($M+Na^+$) 360.0123, found 360.0131.



Mixture of C2-(*o*-/*p*-tolyl)benzothiophenes (44)

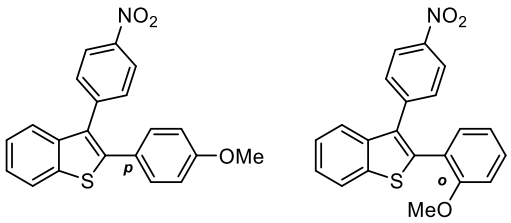
Following **General Procedure A**, the mixture of **44** was prepared form 0.1 mmol of **2d** and 0.2 mmol of toluene, and was isolated as a yellow oil (18.0 mg, 52% yield, *o:p* = 1:1).

The NMR data for the isomeric mixture:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.93 – 7.89 (m, 2H), 7.72 – 7.70 (m, 1H), 7.56 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.42 (m, 5H), 7.41 – 7.36 (m, 3H), 7.34 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.20 – 7.15 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.09, 146.82, 143.00, 142.43, 142.11, 141.67, 139.93, 139.85, 139.12, 138.73, 138.64, 137.32, 135.87, 132.74, 132.40, 132.37, 132.35, 132.27, 131.59, 131.53 (2C), 130.73 (2C), 130.58, 130.56, 130.50, 129.72 (2C), 129.59 (2C), 129.55, 129.15, 125.91, 125.09, 125.05, 125.00, 124.08 (2C), 123.82 (2C), 122.66, 122.64, 122.54, 122.47, 121.69, 21.37, 20.28.

HRMS (ESI) calcd. for $C_{21}H_{15}NNaO_2S^+$ ($M+Na^+$) 368.0716, found 368.0731.



Mixture of 2-(*o*-/*p*-anisyl)benzothiophenes (45)

Following **General Procedure A**, the mixture of **45** was prepared from 0.1 mmol of **2d** and 0.2 mmol of anisole, and was isolated as a yellow oil (18.2 mg, 50% yield, *o:p* = 1:2).

The NMR data for the ***para*-isomer**:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.4 Hz, 2H), 7.90 – 7.88 (m, 1H), 7.56 –7.55 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H).

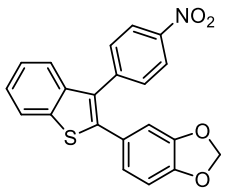
^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.86, 147.05, 143.05, 141.87, 139.95, 138.96, 132.56, 131.53 (2C), 131.08 (2C), 130.09, 125.03, 124.90, 124.09 (2C), 122.53, 122.42, 120.81, 114.32 (2C), 55.43.

The NMR data for the ***ortho*-isomer**:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.88 (m, 1H), 7.68 – 7.66 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.31 (m, 1H), 7.28 (dd, *J* = 7.2 Hz, 1.8 Hz, 1H), 6.94 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 6.84 – 6.81 (m, 1H), 3.50 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.74, 146.72, 143.52, 137.06, 139.90, 138.95, 138.22, 132.63, 130.53 (2C), 125.78, 124.87, 124.83, 123.63 (2C), 122.46, 122.27, 111.40, 55.15.

HRMS (ESI) of both isomers calcd. for $C_{21}H_{15}NNaO_2S^+$ ($M+Na^+$) 384.0665, found 384.0659.



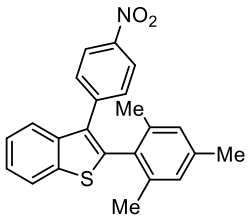
5-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)benzo[*d*][1,3]dioxole (46)

Following **General Procedure A**, the compound **46** was prepared from 0.1 mmol of **2d** and 0.2 mmol of benzo[*d*][1,3]dioxole, and was isolated as a yellow oil (7.7 mg, 21% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.91 – 7.86 (m, 1H), 7.56 – 7.50 (m, 3H), 7.42 – 7.35 (m, 2H), 6.79 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 5.97 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.05, 147.99, 147.12, 142.82, 141.68, 139.83, 138.93, 131.48 (2C), 130.48, 127.24, 125.11, 125.07, 124.14 (2C), 124.04, 122.64, 122.43, 110.08, 108.77, 101.56.

HRMS (ESI) calcd. for $C_{21}H_{13}NNaO_4S^+$ ($M+Na^+$) 398.0457, found 398.0489.



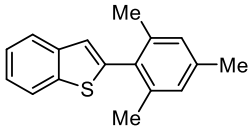
2-mesityl-3-(4-nitrophenyl)benzo[*b*]thiophene (47)

Following **General Procedure A**, the compound **47** was prepared from 0.1 mmol of **2d** and 0.2 mmol of mesitylene, and was isolated as a yellow oil (25.6 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.95 – 7.90 (m, 1H), 7.76 – 7.71 (m, 1H), 7.45 – 7.40 (m, 4H), 6.87 (s, 2H), 2.29 (s, 3H), 2.07 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.79, 142.39, 141.16, 140.37, 138.85, 138.84, 137.81, 132.26, 130.02 (2C), 129.03, 128.55 (2C), 124.86 (2C), 123.79 (2C), 122.69, 122.67, 21.26, 20.67 (2C).

HRMS (ESI) calcd. for $C_{23}H_{19}NNaO_2S^+$ ($M+Na^+$) 396.1029, found 396.1032.

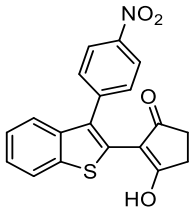


2-mesitylbenzo[*b*]thiophene (48)

A solution of benzo[*b*]thiophene 1-oxide was prepared *in situ* from **1a** (0.1 mmol) according to **Method A** and used directly. Subsequently, compound **48** was prepared according to **General Procedure A** and isolated as a yellow oil (24.1 mg, 48% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 1H), 7.84 – 7.81 (m, 1H), 7.43 – 7.34 (m, 2H), 7.07 (t, *J* = 1.2 Hz, 1H), 7.00 (s, 2H), 2.38 (s, 3H), 2.22 (d, *J* = 1.6 Hz, 6H).

NMR spectra are in agreement with the reported data[9].



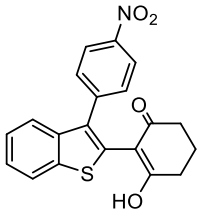
3-hydroxy-2-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)cyclopent-2-en-1-one (49)

Following **General Procedure A**, the compound **49** was prepared from 0.1 mmol of **2d** and 0.11 mmol of cyclopentane-1,3-dione, and was isolated as a brown oil (17.9 mg, 51% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.97 – 7.42 (m, 1H), 7.60 – 7.58 (m, 3H), 7.36 – 7.33 (m, 2H), 2.32 (s, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 195.41, 146.20, 144.50, 139.41, 138.52, 134.40, 130.62 (2C), 130.50, 124.82, 124.38, 123.85 (2C), 122.78, 121.69, 108.69, 70.25, 31.75, 31.66.

HRMS (ESI) calcd. for $C_{19}H_{13}NNaO_4S^+$ ($M+Na^+$) 374.0457, found 374.0447.



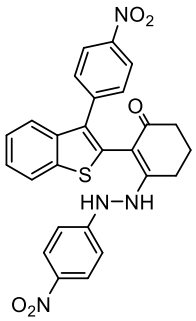
3-hydroxy-2-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)cyclohex-2-en-1-one (50)

Following **General Procedure A**, the compound **50** was prepared from 0.1 mmol of **2d** and 0.11 mmol of cyclohexane-1,3-dione, and was isolated as a yellow solid (18.5 mg, 51% yield). M.p. = 148.6 – 150.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 8.8 Hz, 2H), 8.01 – 7.97 (m, 1H), 7.62 – 7.60 (m, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.42 – 7.36 (m, 2H), 2.38 – 2.32 (m, 4H), 1.85 (p, J = 6.4 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 197.66, 146.72, 143.02, 140.06, 138.51, 135.43, 133.45, 130.48 (2C), 124.93, 124.85, 124.05 (2C), 122.87, 122.29, 108.87, 36.56, 26.75, 20.56.

HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_4S^+$ ($M+Na^+$) 388.0614, found 388.0616.



2-(3-(4-nitrophenyl)benzo[*b*]thiophen-2-yl)-3-(2-(4-nitrophenyl)hydrazineyl)cyclohex-2-en-1-one (51)

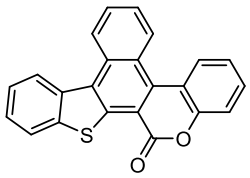
A suspension of **50** (0.1 mmol, 1.0 equiv.) and (4-nitrophenyl)hydrazine (0.1 mmol, 1.0 equiv.) in EtOH (1.0 mL) was stirred in a sealed tube at room temperature. Acetic acid was then added, and the mixture was stirred overnight. Upon completion, the reaction

was quenched with saturated aqueous K_2CO_3, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by preparative TLC to afford the title compound **51** as a yellow solid (13.5 mg, 27% yield). The product was found to be unstable at room temperature. M.p. = 246.8 – 248.4 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.03 (s, 1H), 8.62 (s, 1H), 8.39 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.67 – 7.65 (m, 3H), 7.43 – 7.39 (m, 2H), 6.22 (br, 2H), 2.37 – 2.25 (m, 4H), 1.90 – 1.86 (m, 1H), 1.81 – 1.74 (m, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 194.70, 166.26, 154.88, 153.81, 147.05, 145.44, 138.89, 136.14, 130.80, 126.15, 124.83, 124.14, 123.63, 123.19, 123.02, 122.54, 117.67, 116.04, 110.61, 105.11, 100.99, 32.01, 29.89, 22.56.

HRMS (ESI) calcd. for $C_{26}H_{20}N_4NaO_5S^+$ (M+Na^+) 523.1047, found 523.1044.

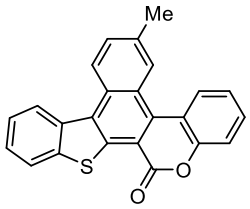


1*H*-benzo[4',5']thieno[2',3':3,4]naphtho[2,1-*c*]chromen-1-one (52)

Following **General Procedure B**, the compound **52** was prepared from 0.1 mmol of **2a** and 0.11 mmol of **3a**, and was isolated as a yellow solid (22.3 mg, 63% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.15 (dd, J = 8.4, 3.0 Hz, 1H), 8.95 (dd, J = 8.4, 2.4 Hz, 1H), 8.83 – 8.82 (m, 1H), 8.48 (dd, J = 8.4, 2.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.94 – 7.91 (m, 1H), 7.74 – 7.71 (m, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.46 – 7.43 (m, 1H).

NMR spectra are in agreement with the reported data[10].



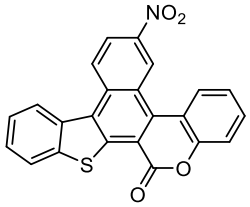
8-methyl-1*H*-benzo[4',5']thieno[2',3':3,4]naphtho[2,1-*c*]chromen-1-one (53)

Following **General Procedure B**, the compound **53** was prepared from 0.1 mmol of **2b** and 0.11 mmol of **3a**, and was isolated as a yellow solid (24.4 mg, 67% yield). M.p. = 223.5 – 225.6 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 8.8 Hz, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 8.67 (s, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.71 – 7.69 (m, 1H), 7.63 – 7.53 (m, 4H), 7.45 – 7.40 (m, 1H), 2.63 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.15, 151.54, 142.89, 135.84, 135.77, 134.67, 134.26, 132.18, 131.83, 131.06, 130.24, 128.67, 128.05, 127.10, 126.02, 124.99, 124.64, 124.40, 124.23, 123.29, 118.67, 117.96, 115.29, 22.02.

HRMS (ESI) calcd. for $C_{24}H_{14}NaO_2S^+$ ($M+Na^+$) 389.0607, found 389.0597.



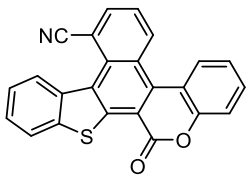
8-nitro-1*H*-benzo[4',5']thieno[2',3':3,4]naphtho[2,1-*c*]chromen-1-one (54)

Following **General Procedure B**, the compound **54** was prepared from 0.1 mmol of **2d** and 0.11 mmol of **3a**, and was isolated as a yellow solid (19.3 mg, 49% yield). Compound **54** exhibits poor solubility in both organic and aqueous media. M.p. > 300 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 9.33 (d, *J* = 8.4 Hz, 1H), 8.84 (d, *J* = 7.8 Hz, 1H), 8.72 (d, *J* = 7.8 Hz, 1H), 8.45 (d, *J* = 7.2 Hz, 1H), 8.17 (d, *J* = 6.6 Hz, 1H), 7.73 – 7.59 (m, 5H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.48, 151.86, 144.99, 143.10, 140.52, 136.24, 135.69, 134.12, 131.56, 130.94, 128.43, 127.06, 126.10, 125.98, 125.92, 125.52, 124.51, 123.81, 123.72, 118.47, 117.77, 116.98.

HRMS (ESI) calcd. for $C_{23}H_{11}NNaO_4S^+$ ($M+Na^+$) 420.0301, found 420.0268.



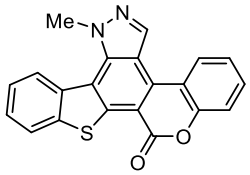
1-oxo-1*H*-benzo[4',5']thieno[2',3':3,4]naphtho[2,1-*c*]chromene-10-carbonitrile (55)

Following **General Procedure B**, the compound **55** was prepared from 0.1 mmol of **2g** and 0.11 mmol of **3a**, and was isolated as a yellow solid (25.7 mg, 68% yield). Compound **55** exhibits poor solubility in both organic and aqueous media. M.p. > 300 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 – 9.22 (m, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.35 – 8.32 (m, 2H), 8.12 – 8.10 (m, 1H), 7.88 – 7.84 (m, 1H), 7.69 – 7.60 (m, 4H), 7.51 – 7.47 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.27, 151.81, 142.50, 139.83, 138.78, 134.45, 133.78, 133.30, 131.77, 131.09, 129.88, 128.52, 127.97, 127.57, 127.18, 125.94, 124.94, 123.61, 122.72, 119.06, 118.41, 117.79, 116.56, 109.10.

HRMS (ESI) calcd. for $C_{24}H_{11}NNaO_2S^+$ ($M+Na^+$) 400.0403, found 400.0445.



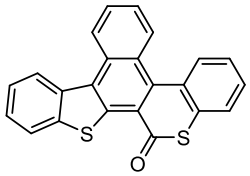
9-methylbenzo[4,5]thieno[2,3-*g*]chromeno[4,3-*e*]indazol-1(9H)-one (56)

Following **General Procedure B**, the compound **56** was prepared from 0.1 mmol of **2i** and 0.11 mmol of **3a**, and was isolated as a white solid (20.7 mg, 58% yield). Compound **56** exhibits poor solubility in both organic and aqueous media. M.p. > 300 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.95 (s, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.61 – 7.52 (m, 4H), 4.69 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.92, 151.83, 142.50, 140.86, 140.79, 140.64, 138.05, 136.23, 132.43, 131.24, 126.36, 126.25, 125.14, 124.73, 124.50, 123.37, 120.45, 118.52, 118.15, 111.17, 42.74.

HRMS (ESI) calcd. for $C_{21}H_{12}N_2NaO_2S^+$ ($M+Na^+$) 379.0512, found 379.0537.



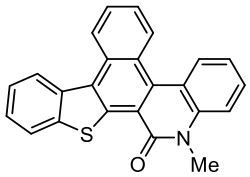
1*H*-benzo[4',5']thieno[2',3':3,4]naphtho[2,1-*c*]thiochromen-1-one (57)

Following **General Procedure B**, the compound **57** was prepared from 0.1 mmol of **2a** and 0.11 mmol of **3m**, and was isolated as a yellow solid (26.7 mg, 73% yield). M.p. = 145.5 – 148.7 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 8.4 Hz, 1H), 8.84 (d, *J* = 8.0 Hz, 1H), 8.75 – 8.73 (m, 1H), 8.26 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.67 – 7.61 (m, 3H), 7.59 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 185.86, 143.71, 138.50, 134.29, 134.05, 133.49, 133.37, 132.29, 131.09, 130.49, 130.28, 129.05, 128.51, 126.89, 126.73, 126.04, 126.00, 125.31, 125.04, 124.63, 123.98, 123.27, 123.04.

HRMS (ESI) calcd. for $C_{23}H_{12}NaOS_2^+$ ($M+Na^+$) 391.0222, found 391.0178.



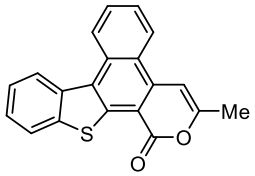
2-methylbenzo[*k*]benzo[4,5]thieno[2,3-*i*]phenanthridin-1(2*H*)-one (58)

Following **General Procedure B**, the compound **58** was prepared from 0.1 mmol of **2a** and 0.11 mmol of **3n**, and was isolated as a light-yellow solid (15.3 mg, 42% yield). M.p. = 248.7 – 251.2 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.85 (d, *J* = 8.0 Hz, 1H), 8.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.15 – 8.13 (m, 1H), 7.89 – 7.85 (m, 1H), 7.70 – 7.54 (m, 5H), 7.42 – 7.38 (m, 1H), 3.96 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.51, 143.49, 138.28, 136.57, 134.68, 133.12, 133.03, 130.28, 129.89, 129.62, 129.60, 129.27, 127.53, 125.58, 125.33, 124.79, 124.47, 124.31, 123.30, 122.30, 119.66, 119.30, 114.90, 30.64.

HRMS (ESI) calcd. for $C_{24}H_{15}NNaOS^+$ ($M+Na^+$) 388.0767, found 388.0771.



3-methyl-1*H*-benzo[*f*]benzo[4,5]thieno[3,2-*h*]isochromen-1-one (59)

Following **General Procedure B**, the compound **59** was prepared from 0.1 mmol of **2a** and 0.11 mmol of **3o**, and was isolated as a light-yellow solid (19.7 mg, 62% yield). M.p. = 201.4 – 204.3 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 9.0 Hz, 1H), 8.83 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.92 – 7.89 (m, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 2.50 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.50, 156.62, 141.87, 140.51, 137.11, 136.65, 135.16, 133.22, 130.41, 129.34, 125.93, 125.67, 125.48, 125.40, 124.91, 124.22, 124.18, 123.23, 99.94, 20.37.

HRMS (ESI) calcd. for $C_{20}H_{12}NaO_2S^+$ ($M+Na^+$) 339.0450, found 339.0483.

6. Mechanistic Studies

Radical trapping reaction:

The effect of the radical scavengers TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) and 1,1-diphenylethylene on the reaction outcome was examined. Substrate **4a** was subjected to the standard conditions in the presence of 2.0 equiv. of each scavenger.

4a **5**

A suspension of **4a** (0.1 mmol, 1.0 equiv.) and TEMPO (0.2 mmol, 2.0 equiv.) or 1,1-diphenylethylene (0.2 mmol, 2.0 equiv.) in DMF (1.0 mL) was placed in a sealed tube and stirred at 130 °C for 3 hours. After cooling to room temperature, the reaction mixture was diluted with brine (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered. After concentration, the crude reaction mixture was analyzed by ^{1}H NMR and HRMS (ESI).

Results of the trapping experiments:

When the reaction was run in the presence of TEMPO (2.0 equiv.) or 1,1-diphenylethylene (2.0 equiv.), product formation was not inhibited, and the desired product was isolated in 86% and 83% yield, respectively (Table S1). Importantly, neither ^{1}H NMR of the crude reaction mixture nor HRMS revealed any adducts originating from the radical scavengers, suggesting that scavenger-derived compounds are not formed under these conditions.

Table 2S. Results of radical-trapping experiments

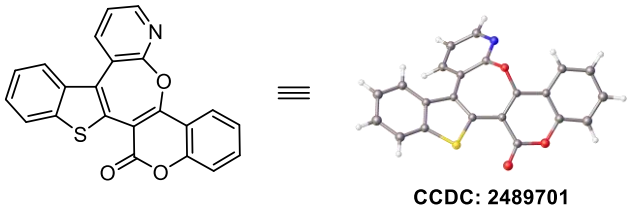
Entry	Additive (2.0 equiv.)	Yield of **5** (%)[a]
1	TEMPO	95 (86)[b]
2	1,1-diphenylethylene	91 (83)[b]

[a]Yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield.

7. Crystallographic Data

Crystals of **18** suitable for X-ray analysis were obtained by vapor diffusion of PE into acetone, while crystals of **51** were grown from DCM/EtOAc. The crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC 2489701 and 2489711).

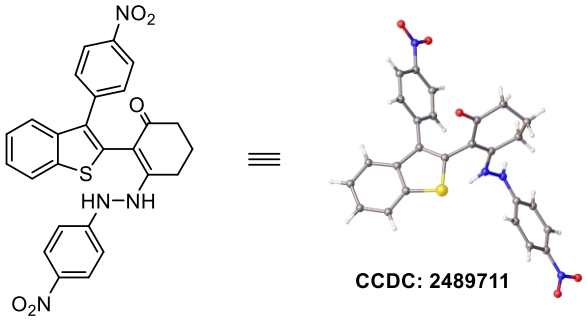
Table 3S. Crystallographic data and structure refinement for **18**.



Identification code	20241226_201-2
Empirical formula	$C_{22}H_{21}NO_3S$
Formula weight	379.483
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5234(1)
b/Å	9.8694(1)
c/Å	17.1274(1)
α/°	90
β/°	96.145(1)
γ/°	90
Volume/Å^3	1600.56(3)
Z	7
ρ_{calc}g/cm^3	2.756
μ/mm^{-1}	3.521
F(000)	1406.7
Crystal size/mm^3	0.2 × 0.17 × 0.07

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.34 to 147.94
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 11, -21 ≤ l ≤ 20
Reflections collected	16960
Independent reflections	3218 [R_{int} = 0.0427, R_{sigma} = 0.0292]
Data/restraints/parameters	3218/0/245
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0795
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0807
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.29

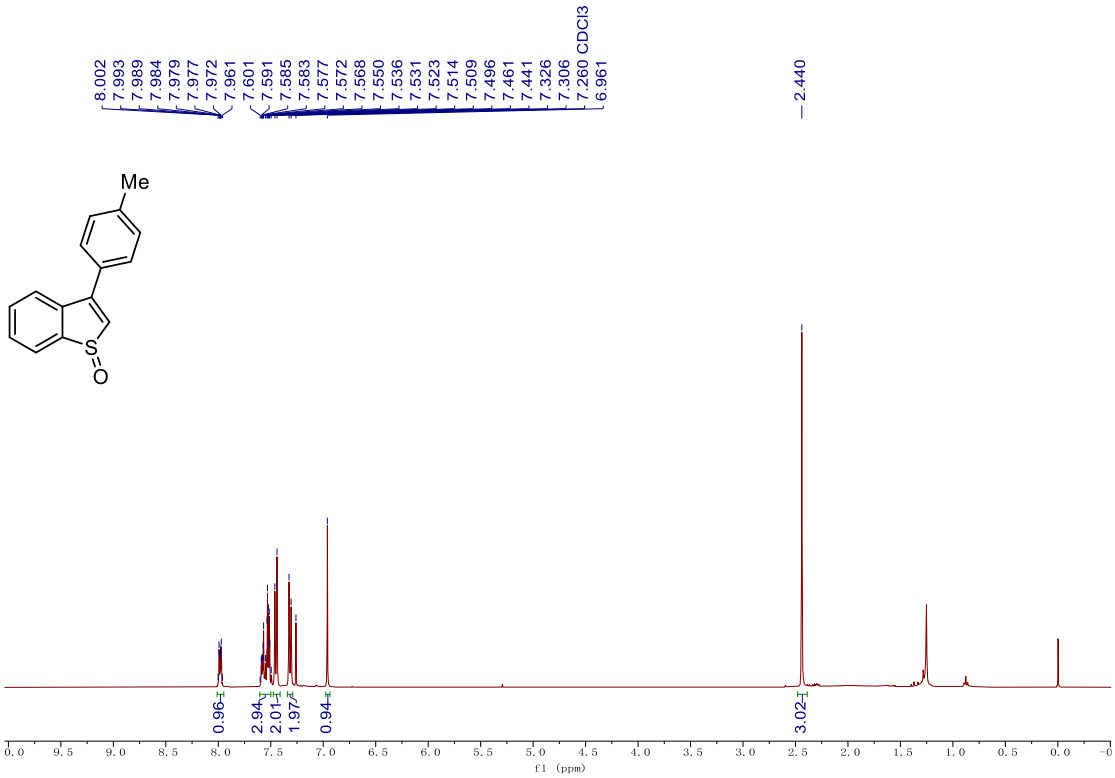
Table 4S. Crystallographic data and structure refinement for **51**.



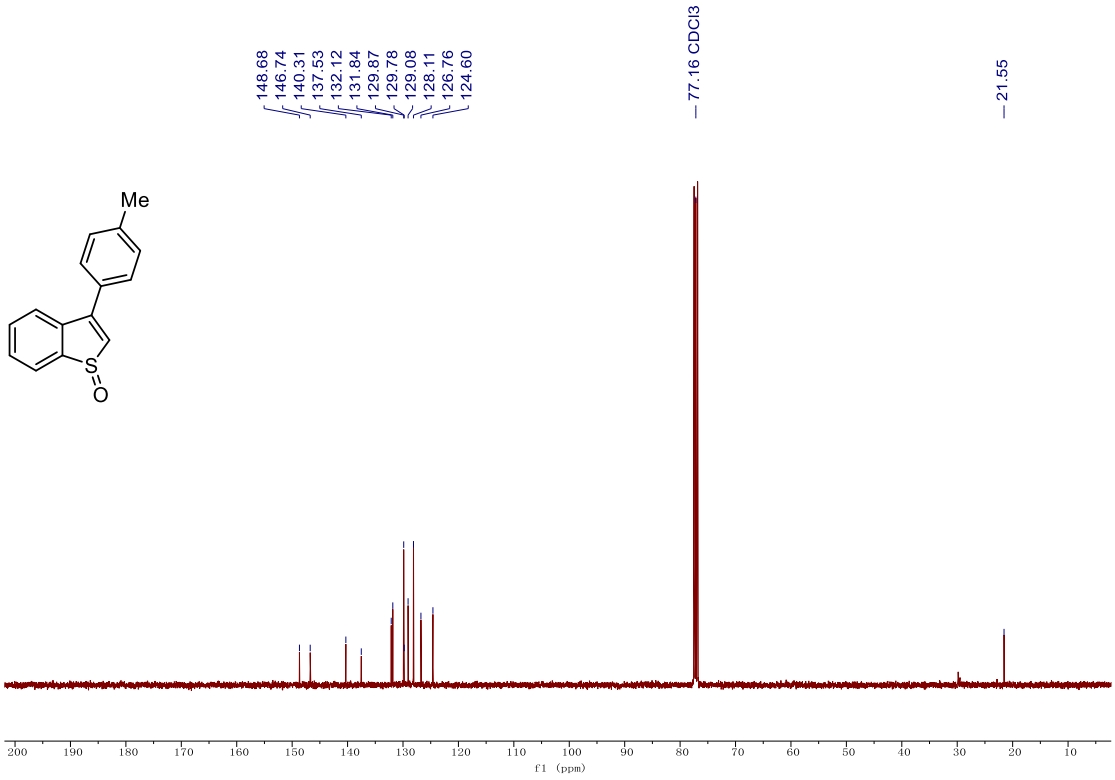
Identification code	20250703_DHT-385-1
Empirical formula	$C_{26}H_{20}N_4O_5S·(1/3\ C_4H_8O_2)$
Formula weight	529.90
Temperature/K	99.98(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.04690(10)
b/Å	11.59320(10)
c/Å	22.39950(10)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	2868.68(4)
Z	4
ρ_{calc}g/cm^3	1.227
μ/mm^{-1}	1.374
F(000)	1104.0
Crystal size/mm^3	0.5 × 0.3 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.894 to 148.678
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	51808
Independent reflections	5774 [R_{int} = 0.0501, R_{sigma} = 0.0227]
Data/restraints/parameters	5774/0/326
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0588, wR_2 = 0.1769
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1777
Largest diff. peak/hole / e Å^{-3}	0.97/-0.43
Flack parameter	0.030(7)

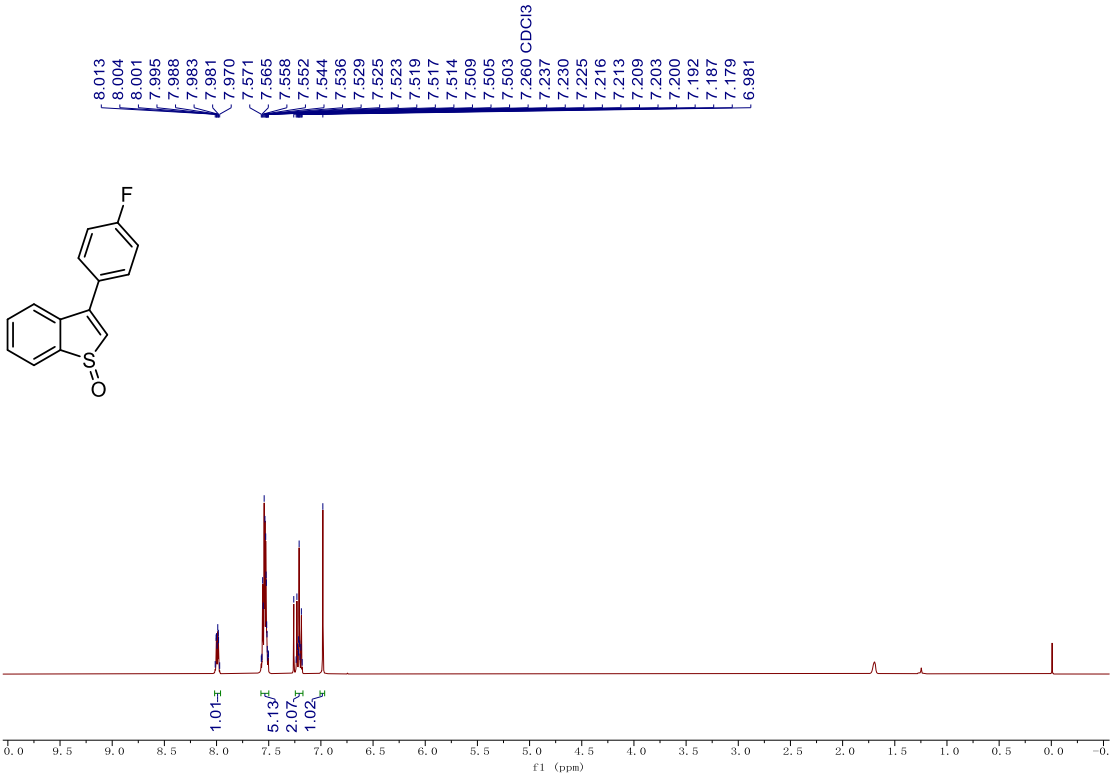
8. NMR Spectra



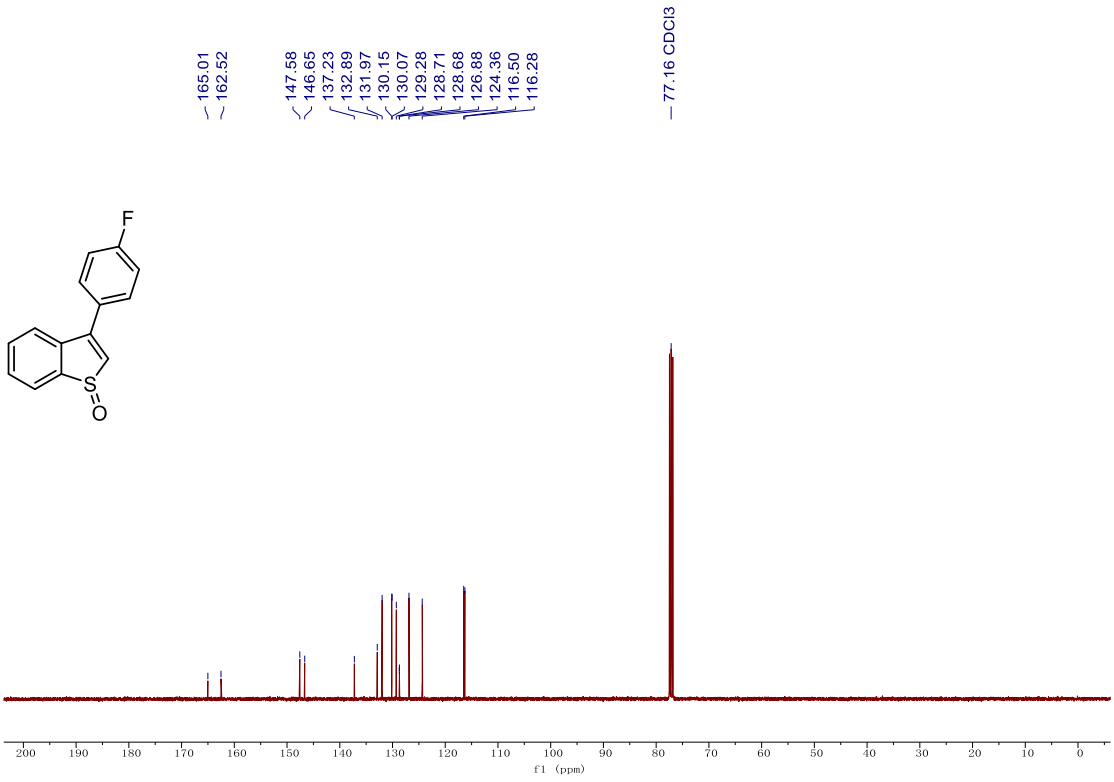
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2b**



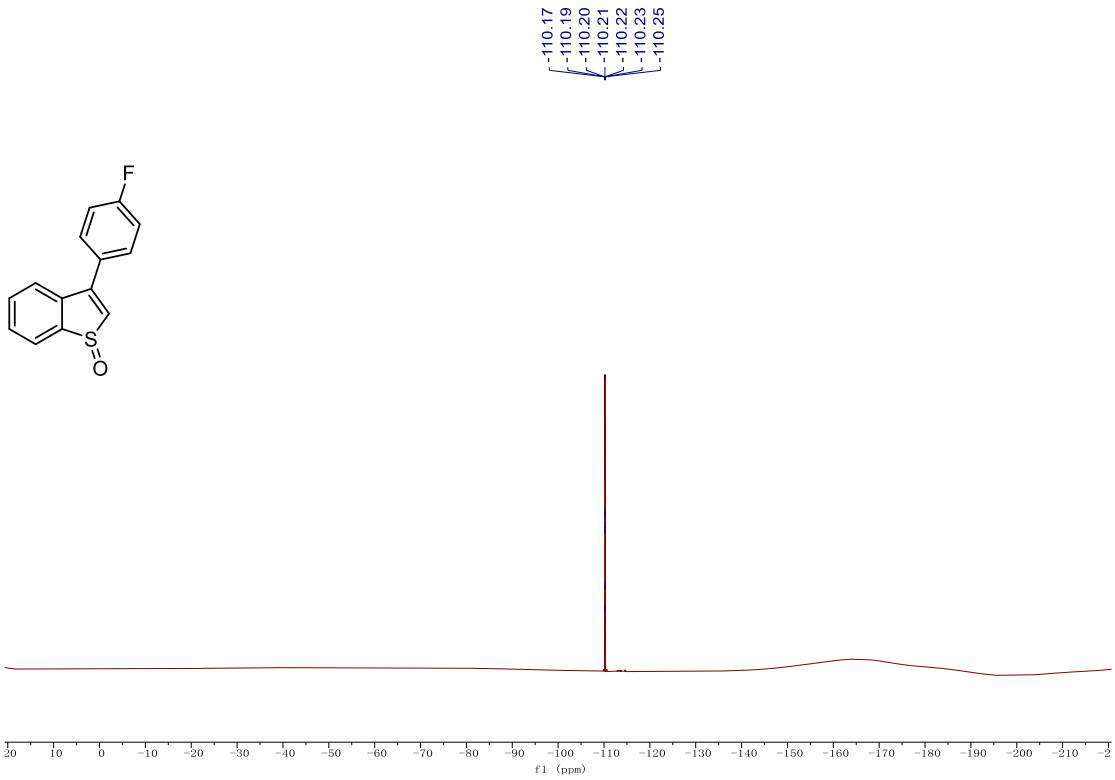
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2b**



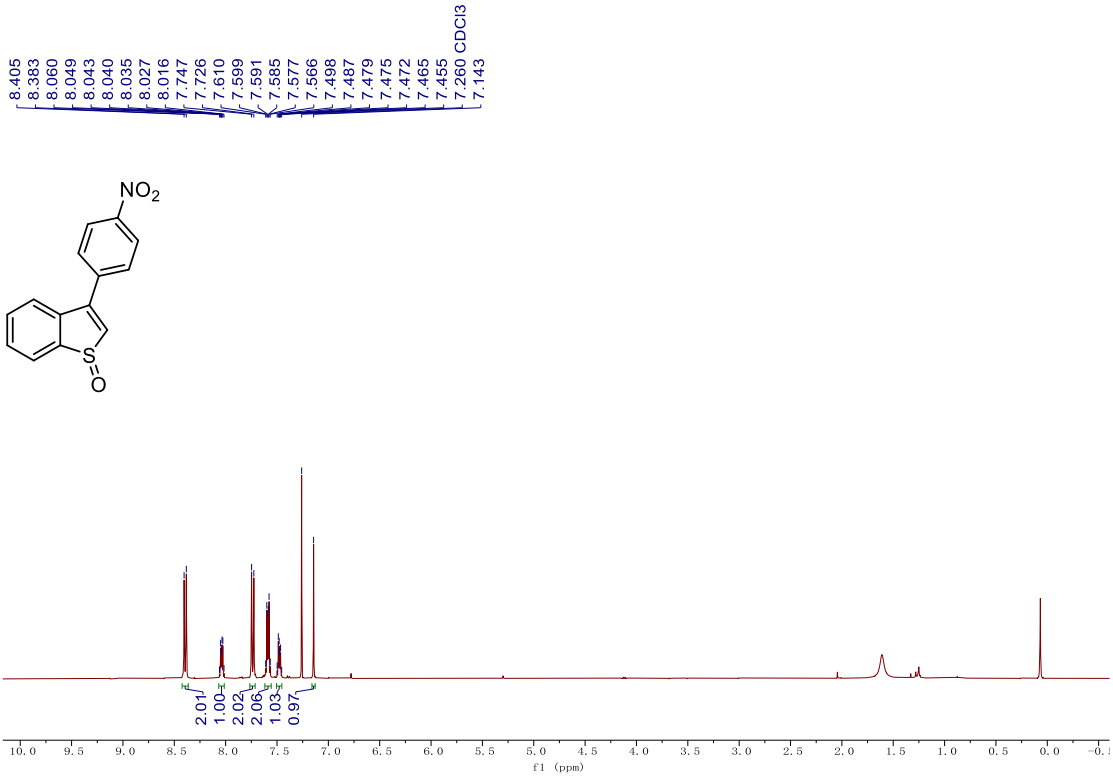
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2c**



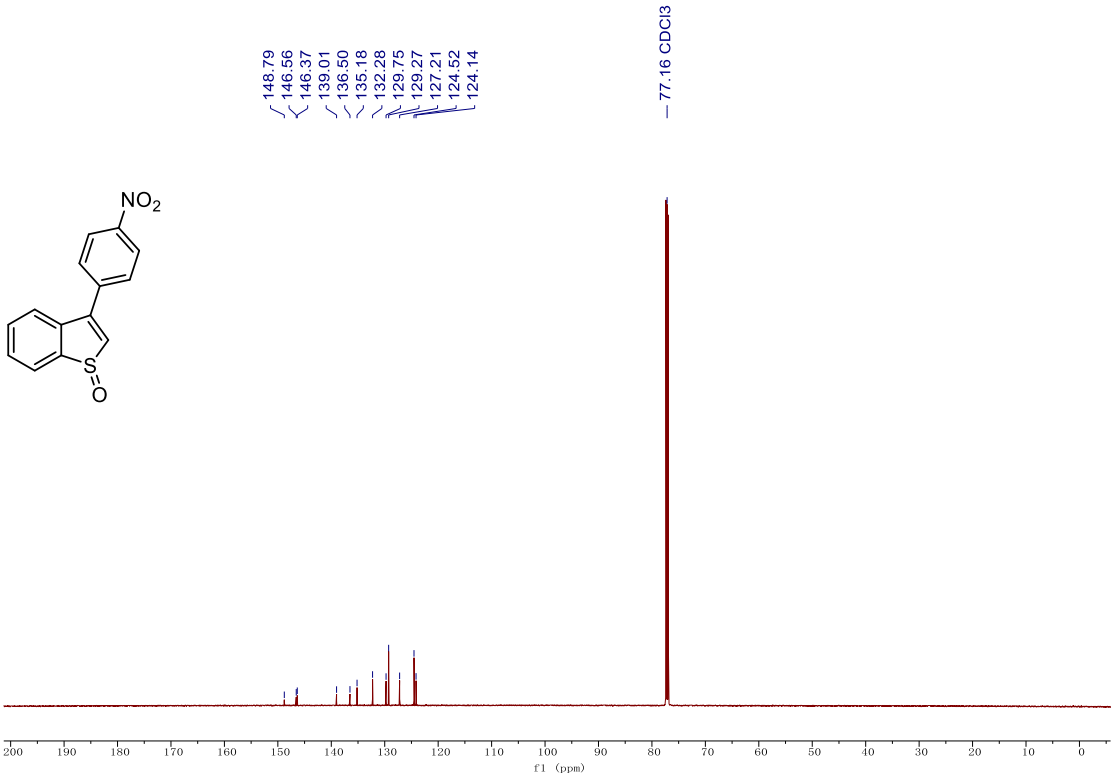
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2c**



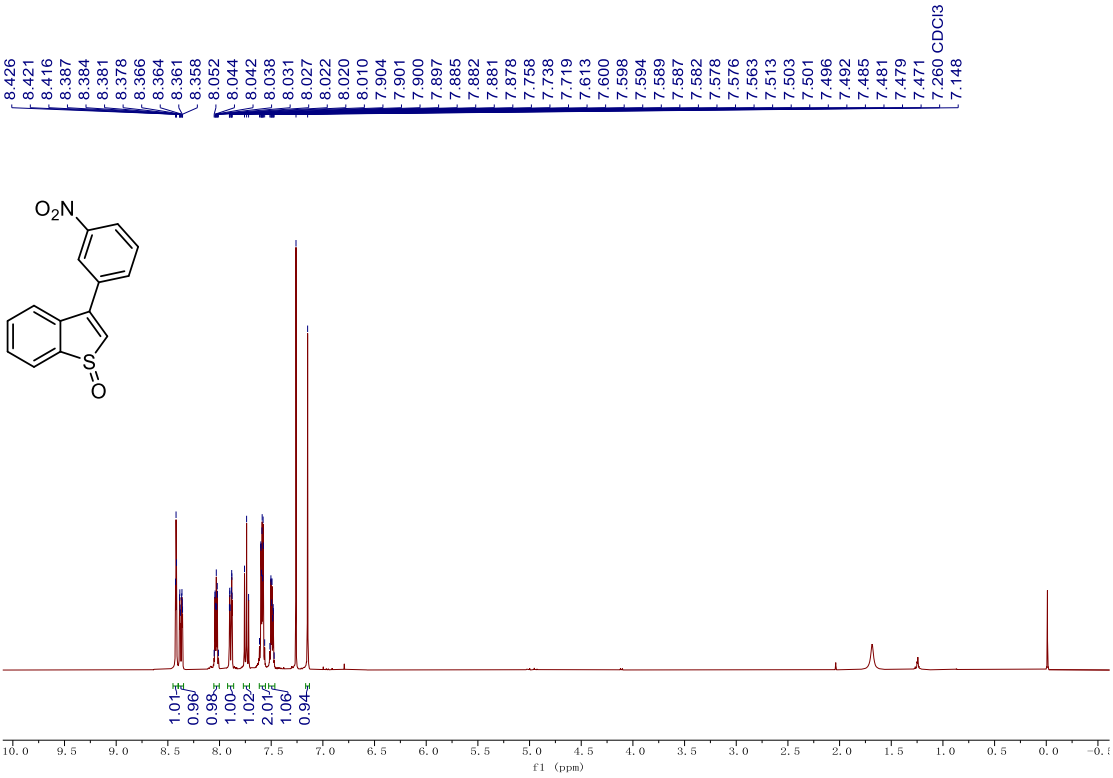
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2c**



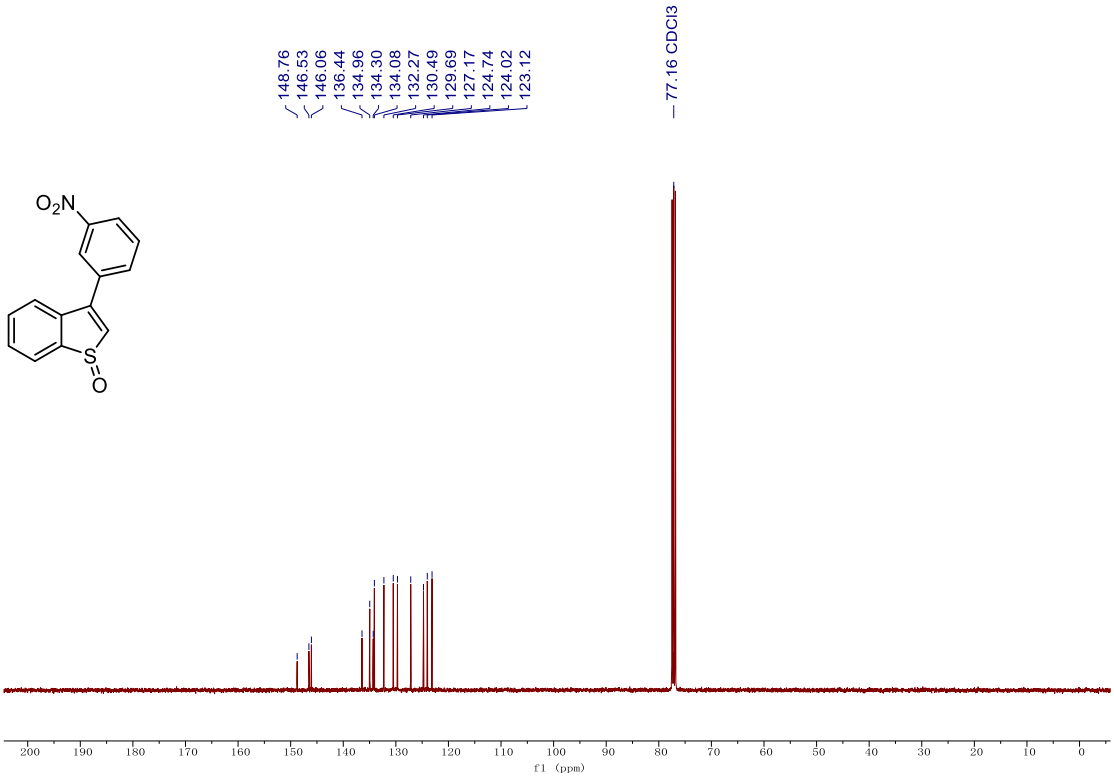
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2d**



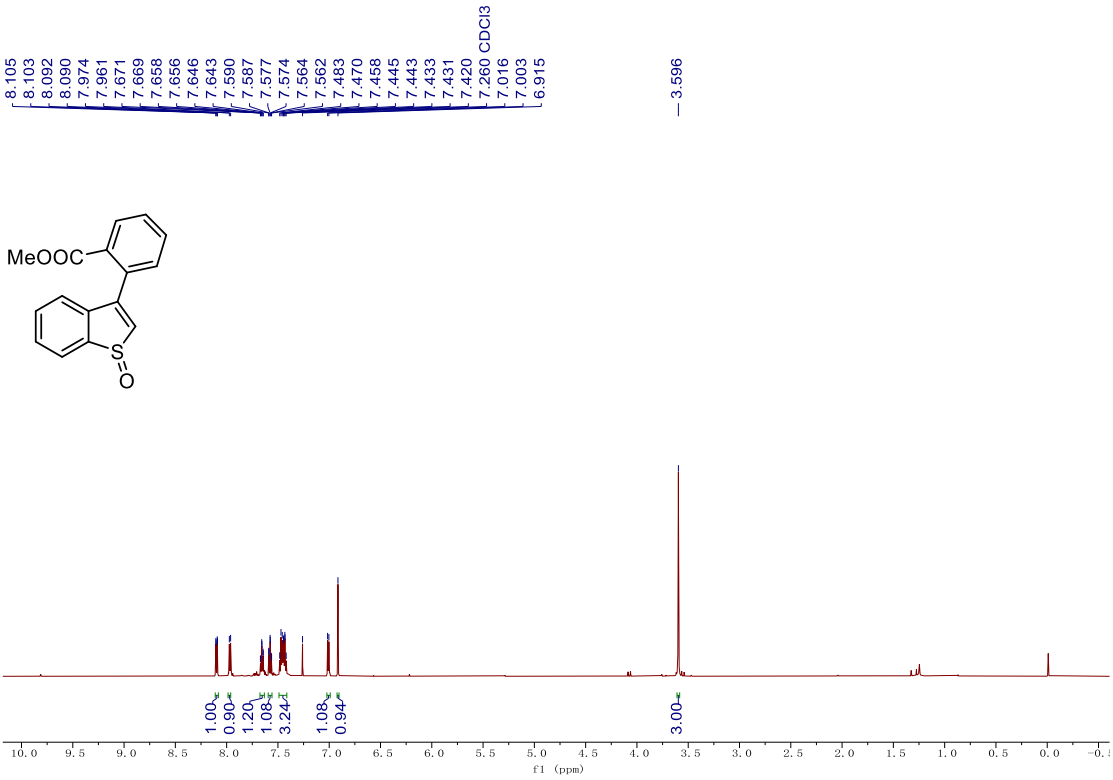
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **2d**



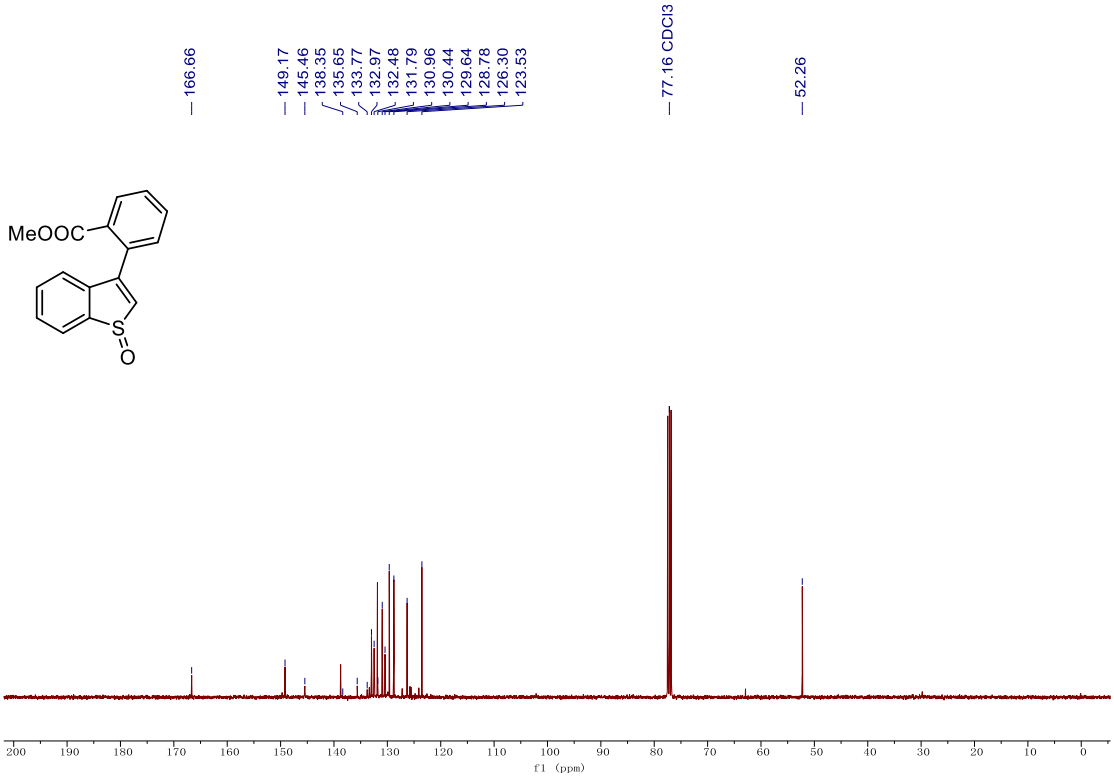
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2e**



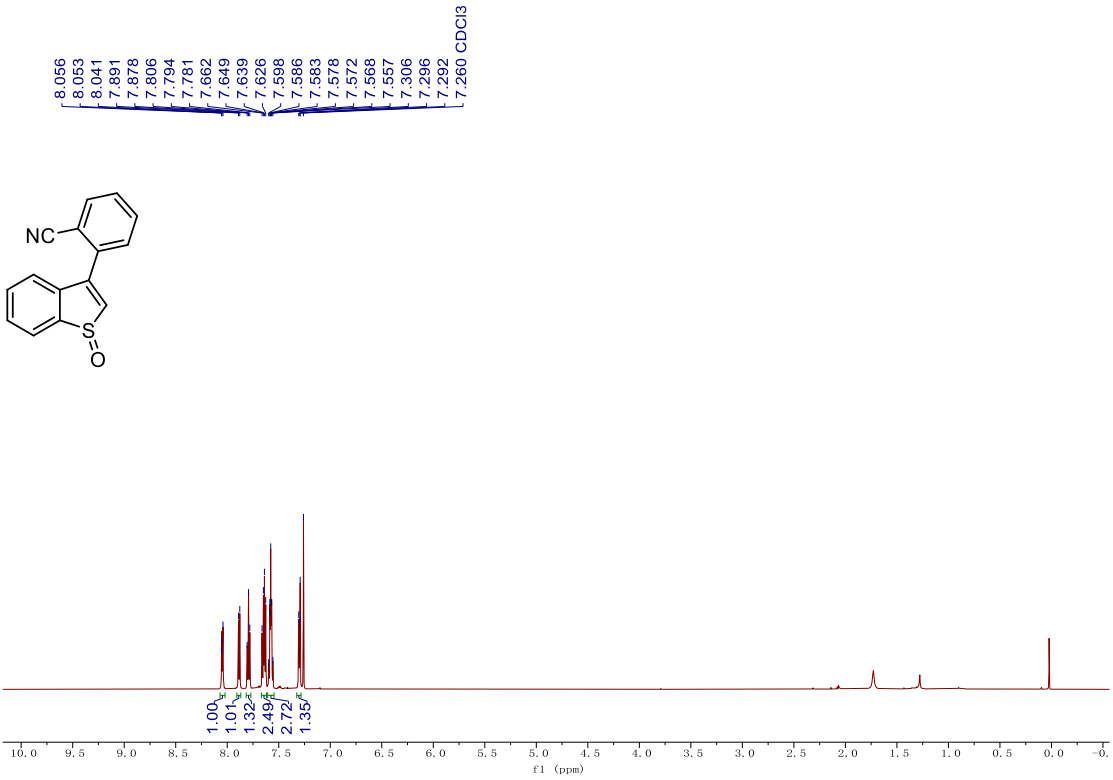
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2e**



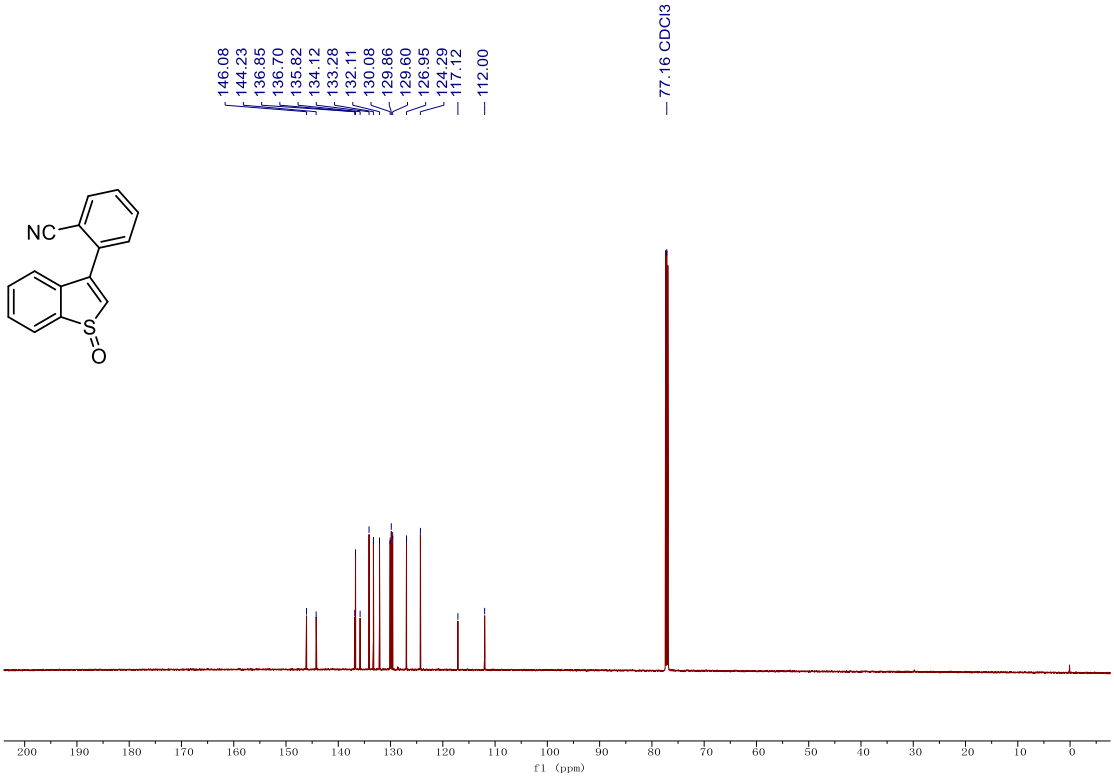
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **2f**



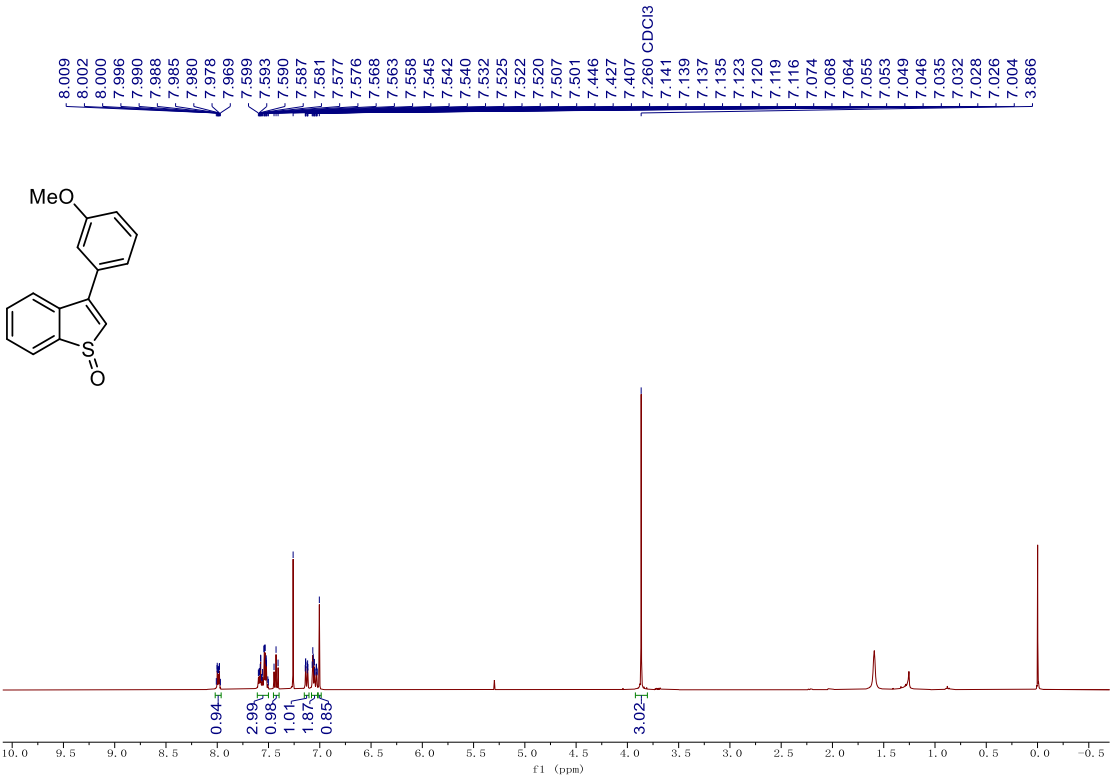
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2f**



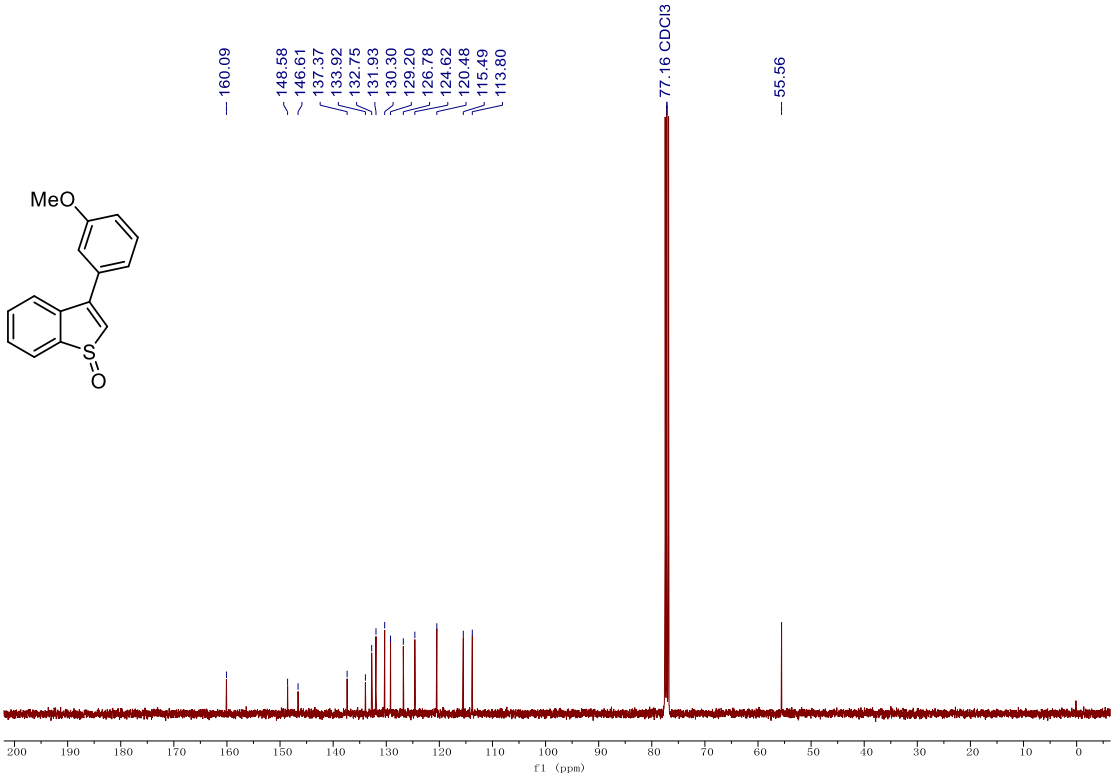
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **2g**



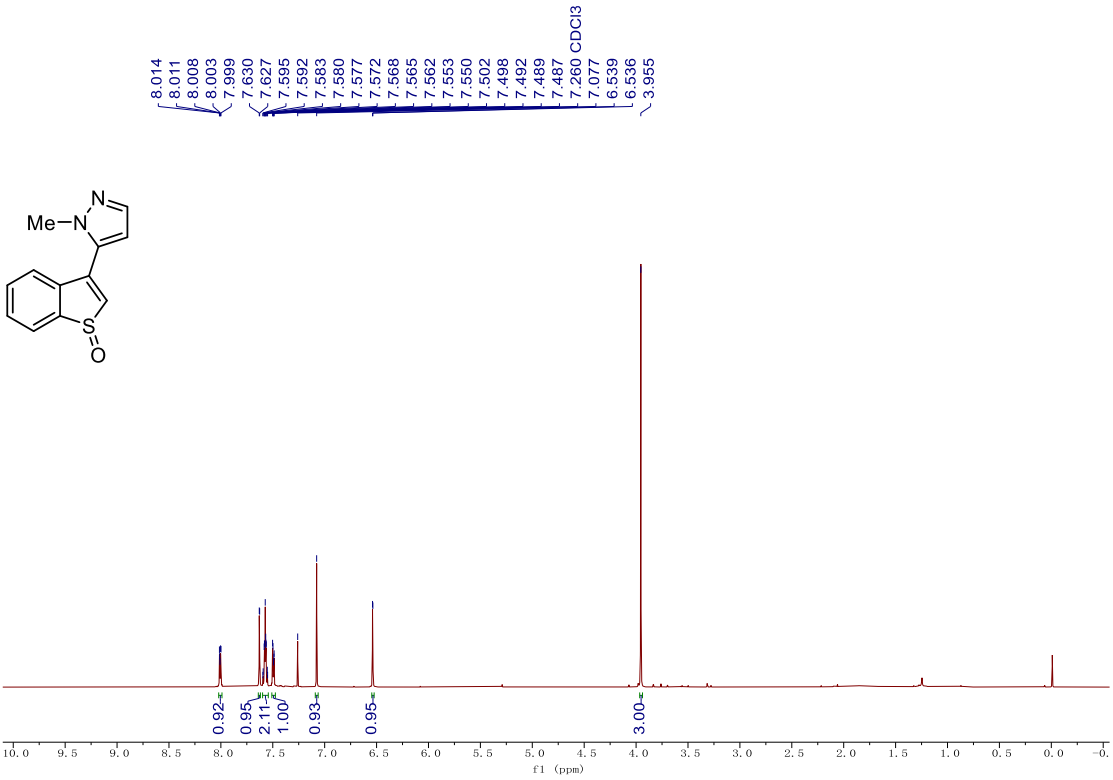
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **2g**



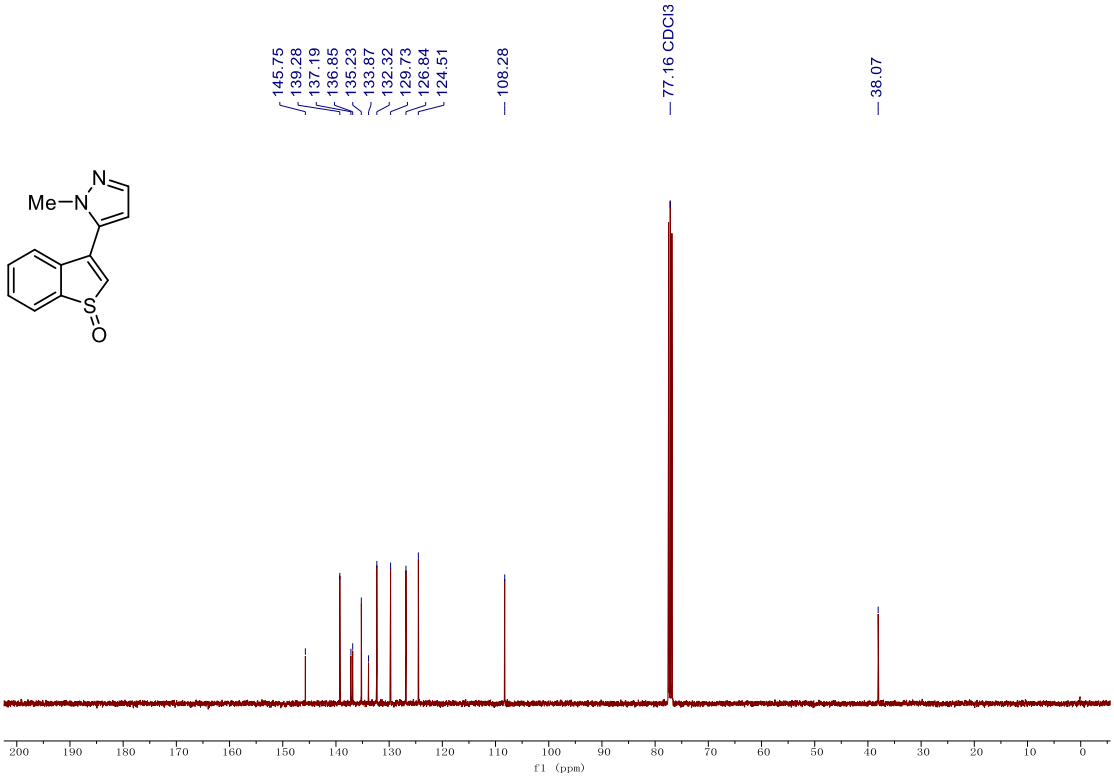
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2h**



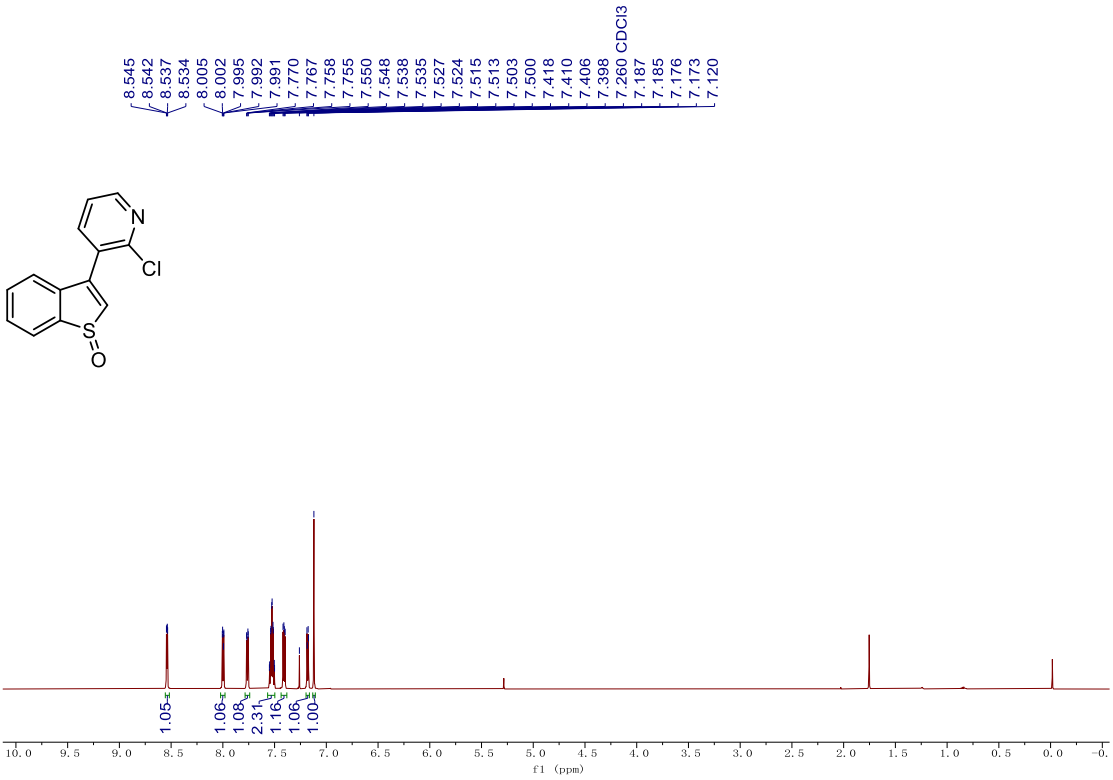
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2h**



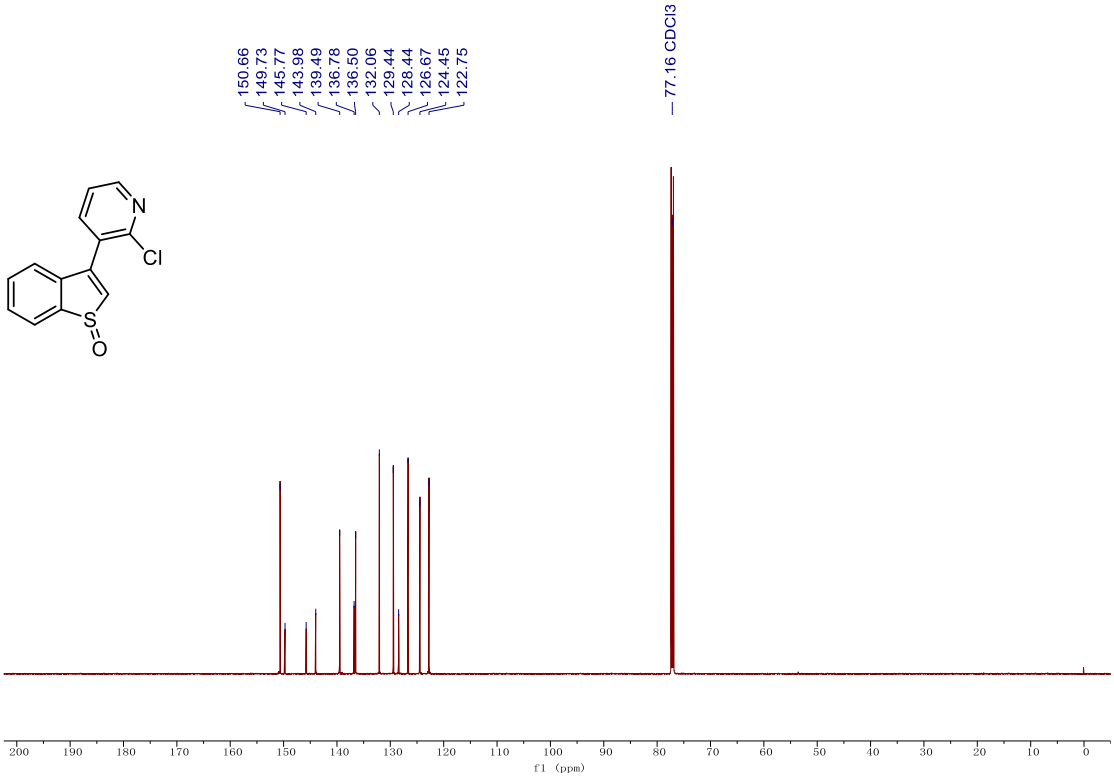
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **2i**



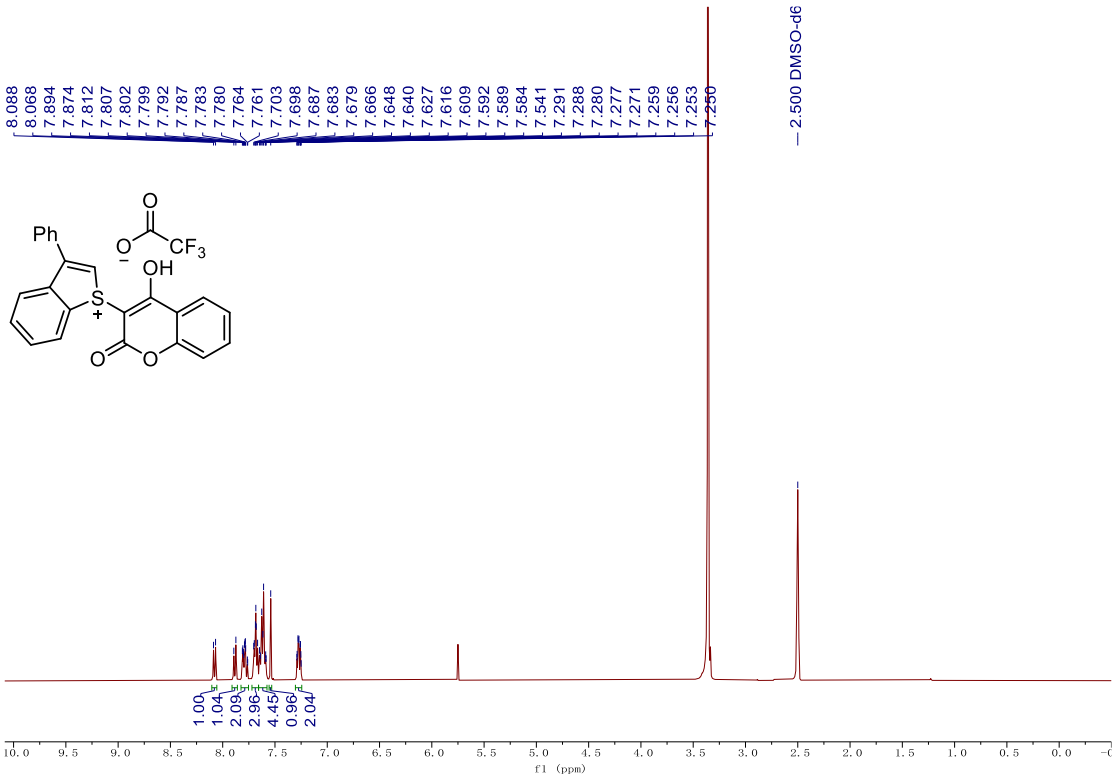
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2i**



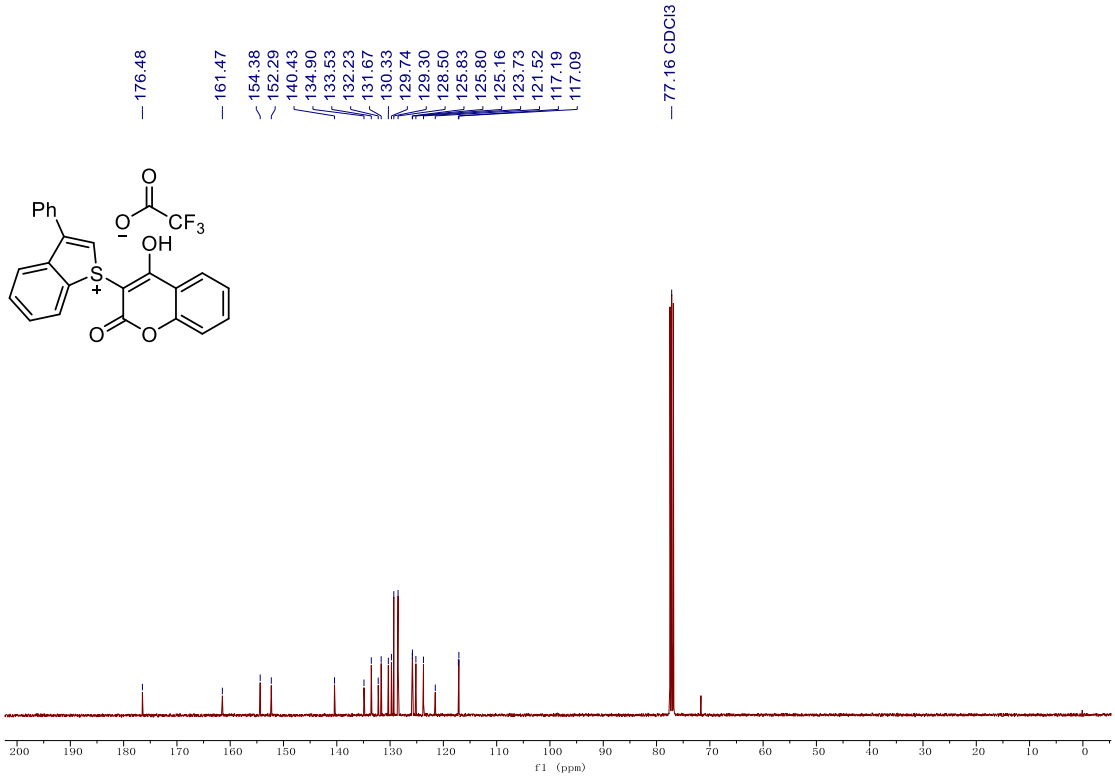
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **2m**



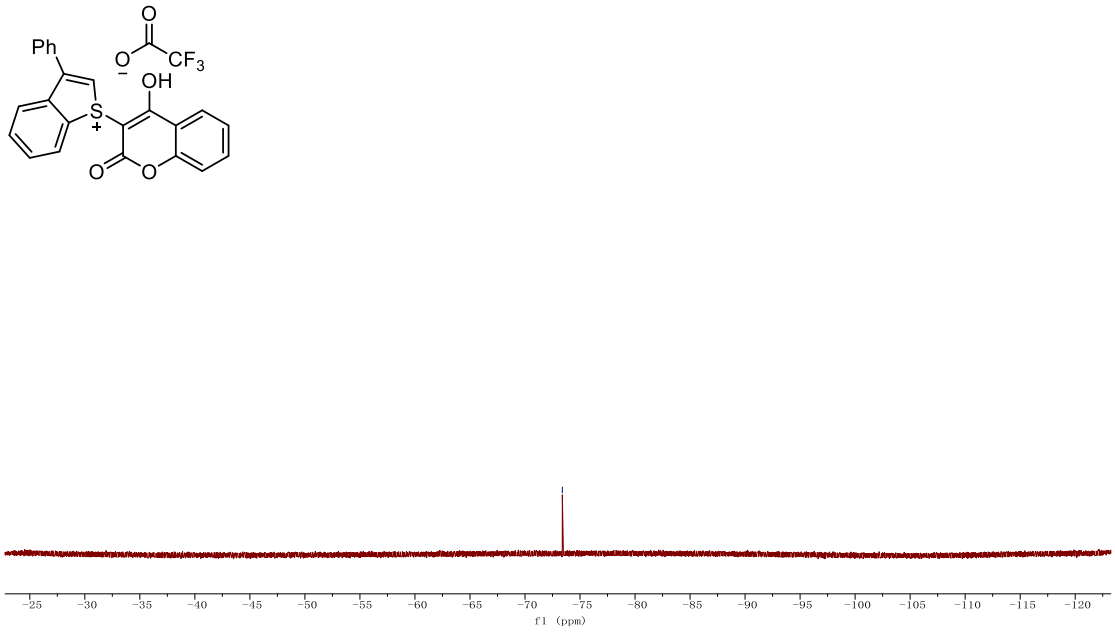
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **2m**



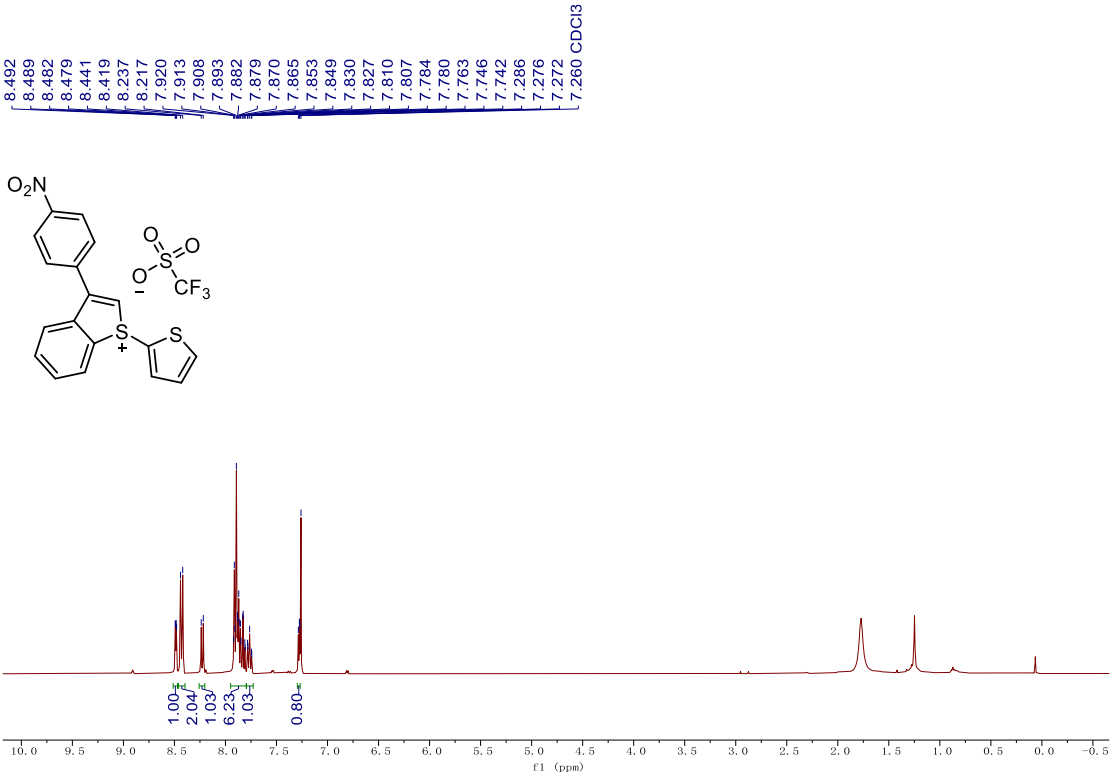
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4a**



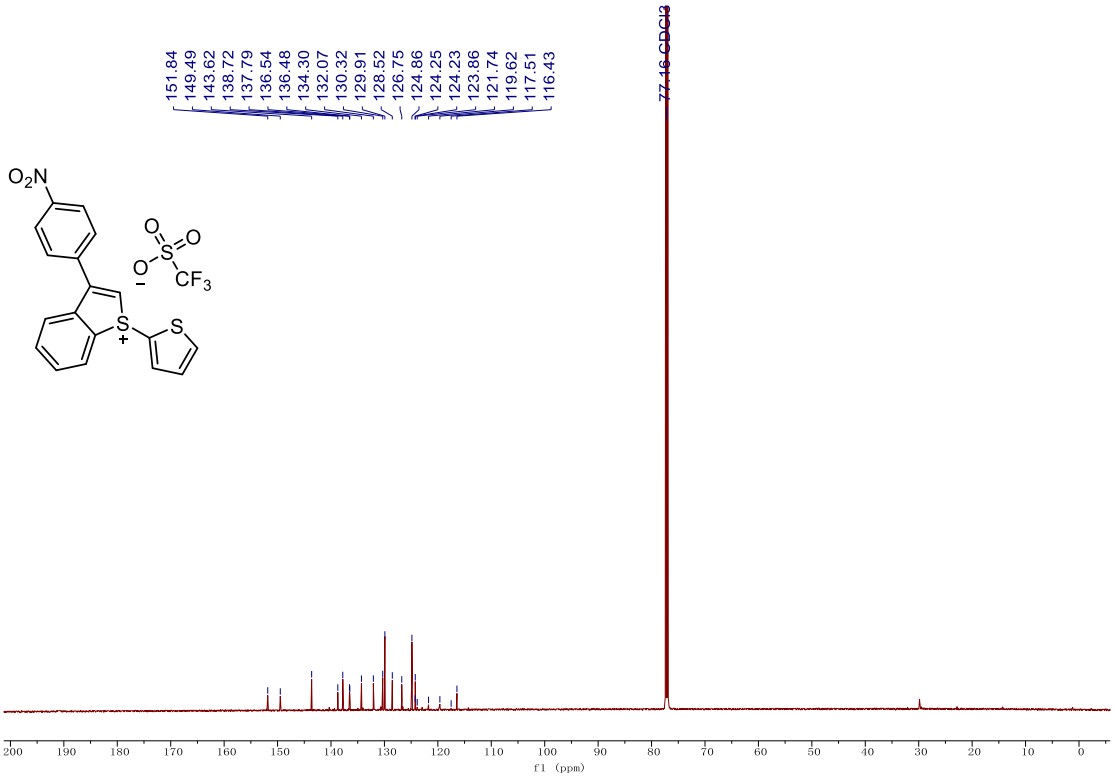
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4a**



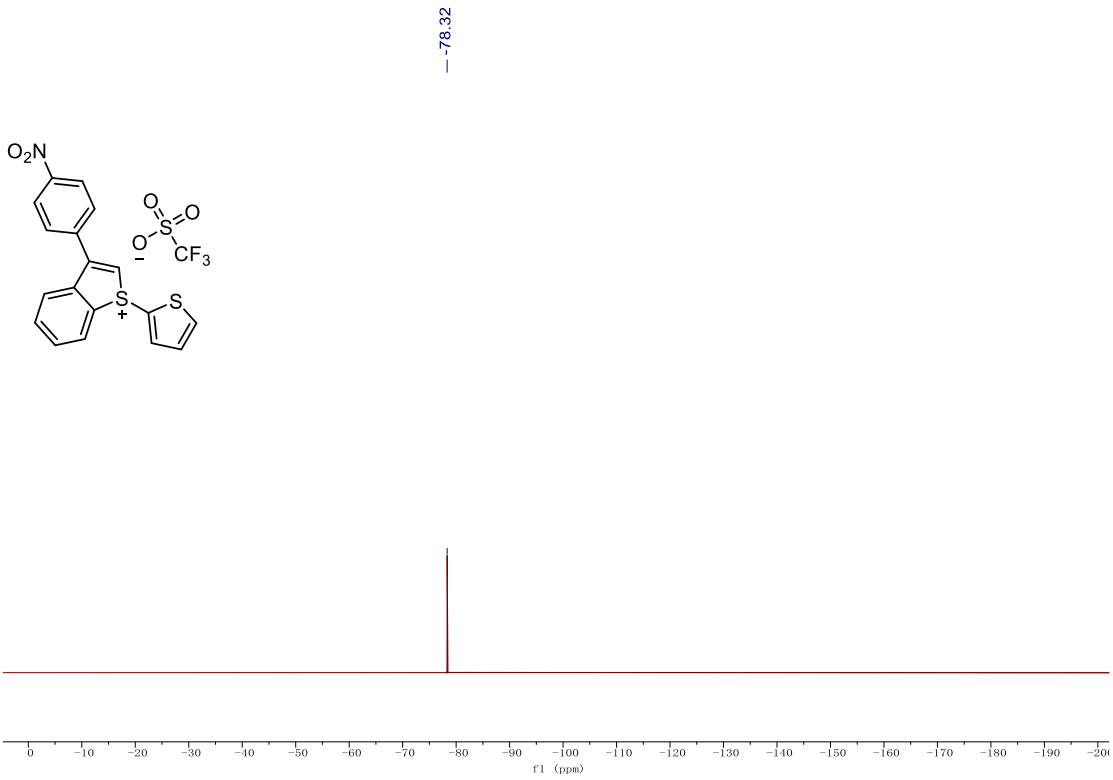
^{19}F NMR (565 MHz, DMSO-d_6) Spectrum of **4a**



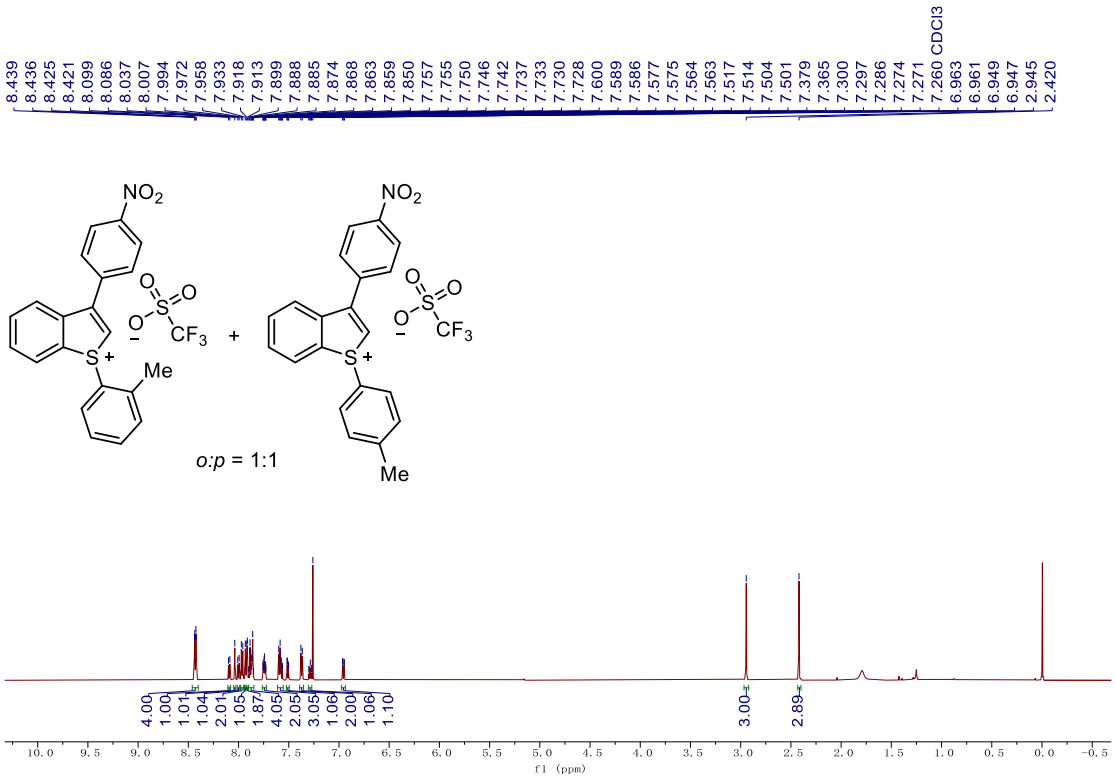
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4b**



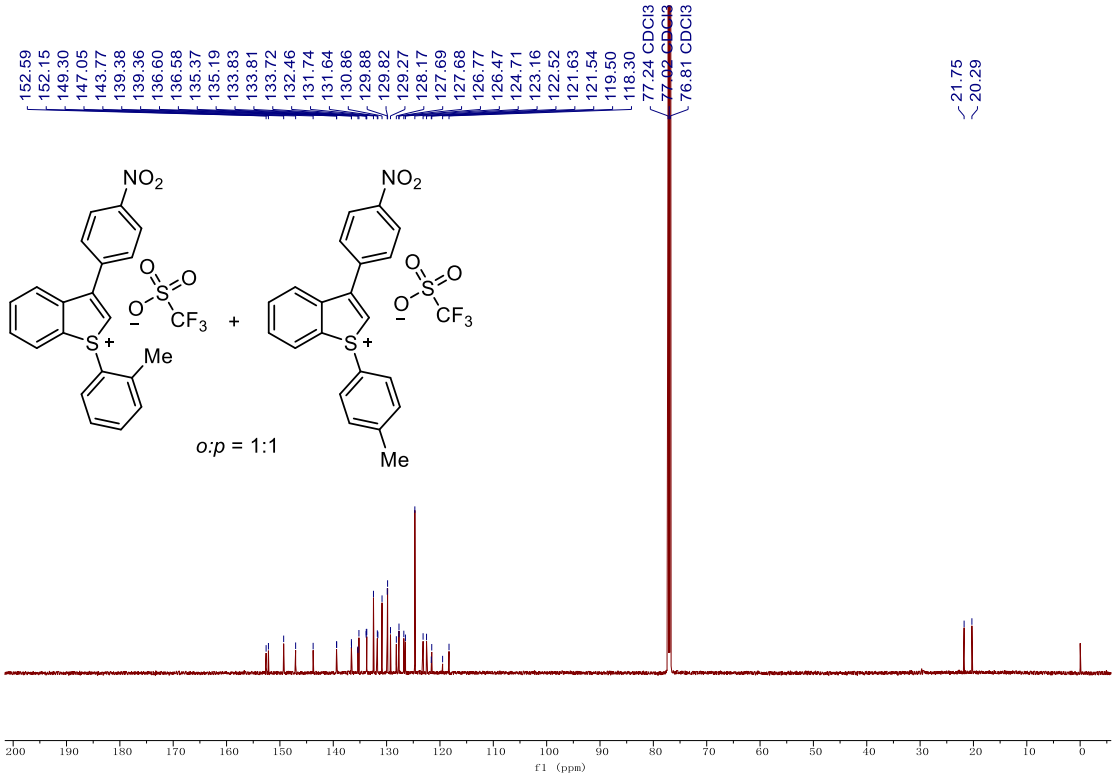
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **4b**



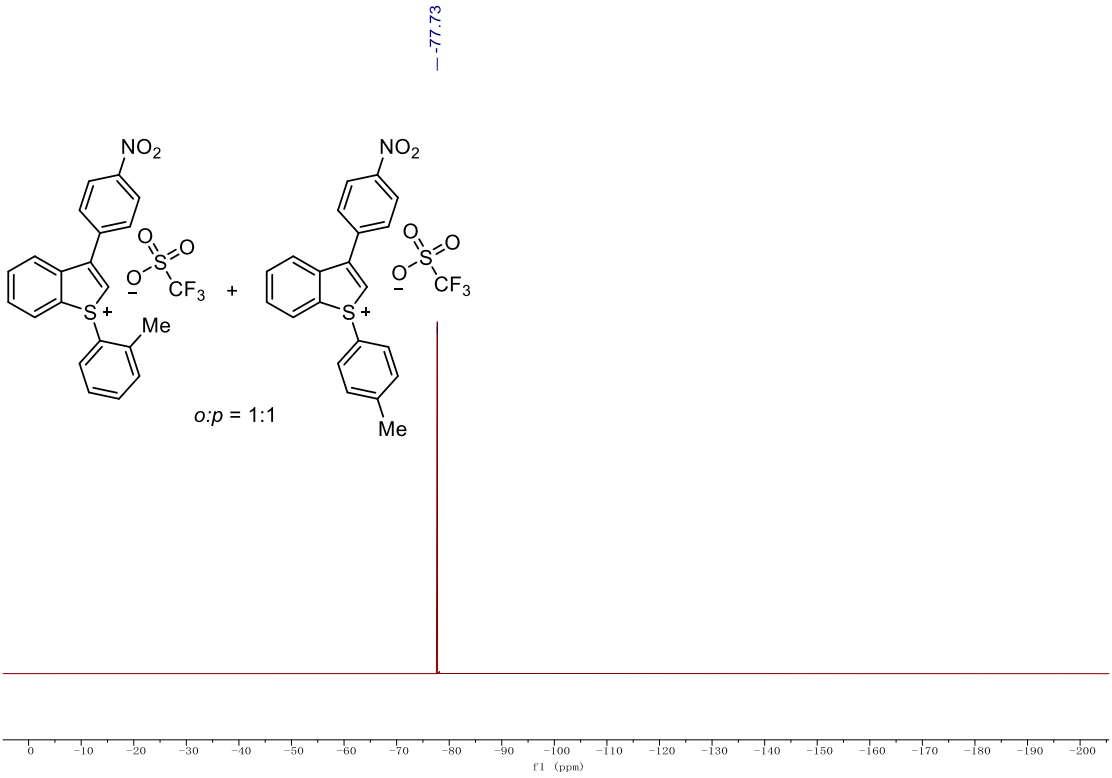
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **4b**



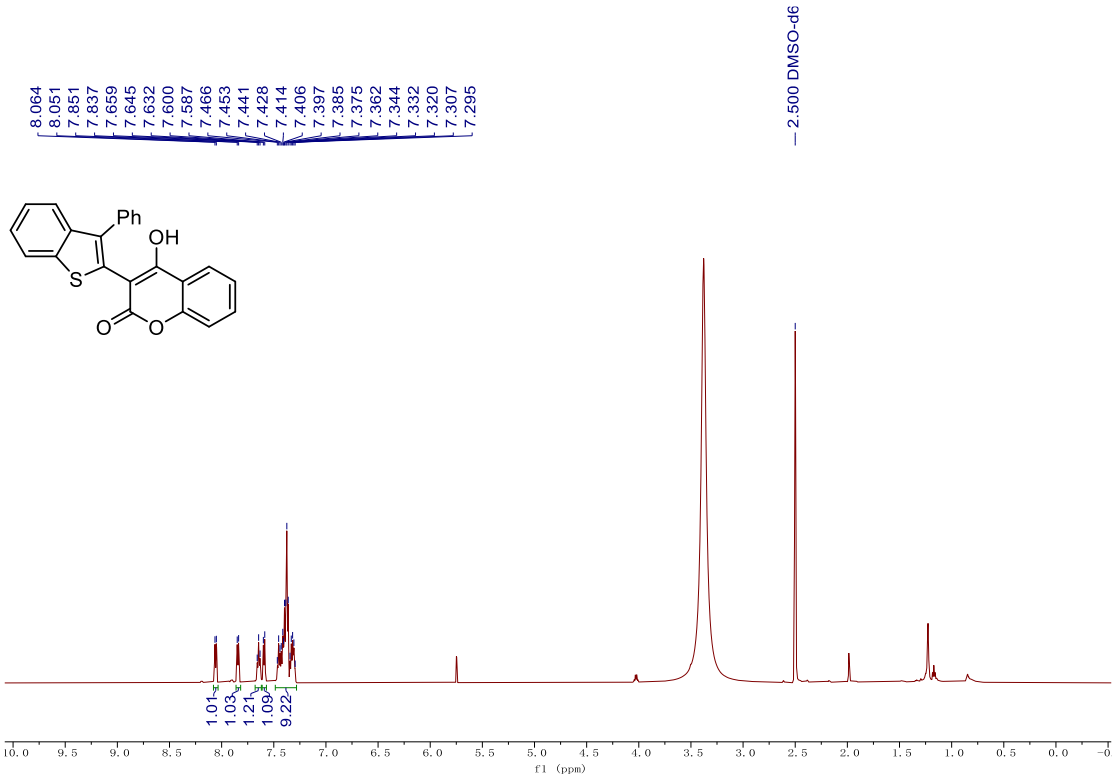
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **4c**



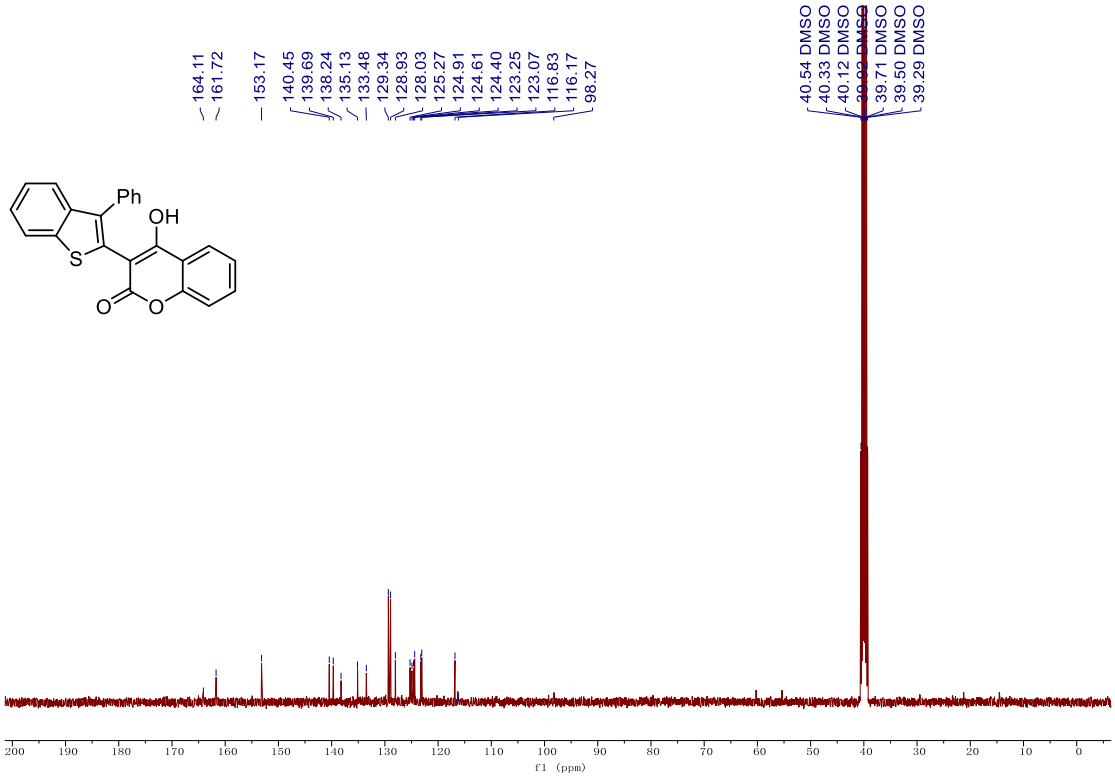
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **4c**



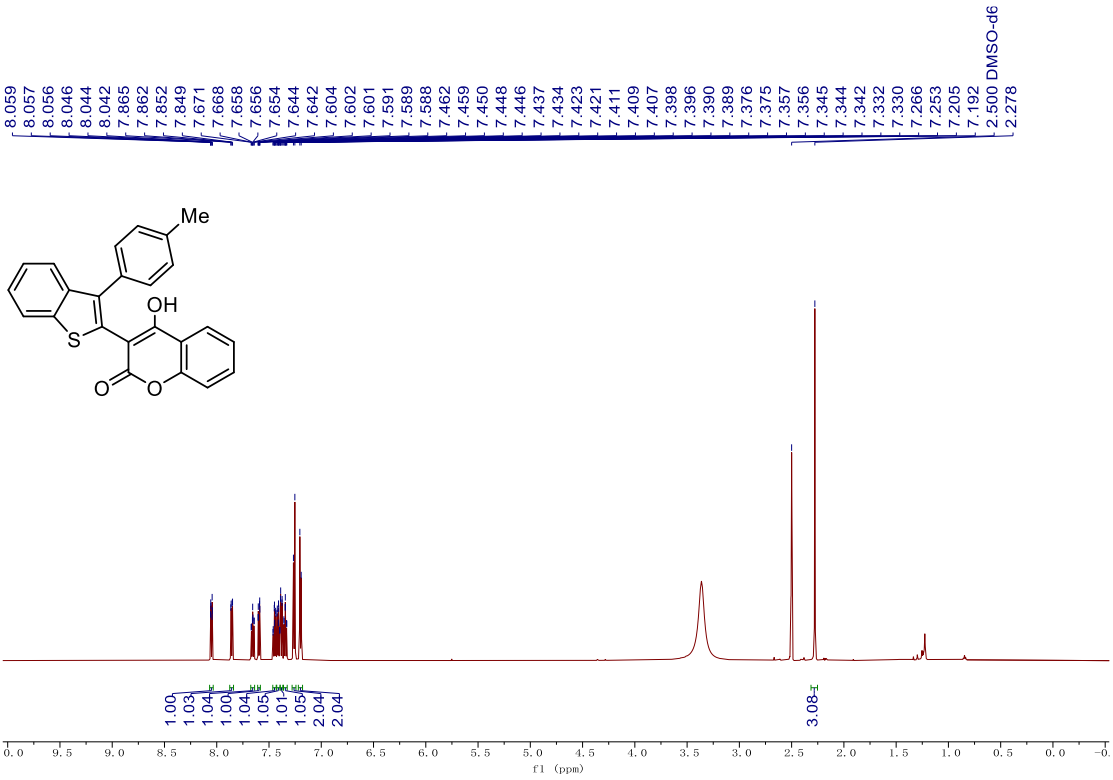
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **4c**



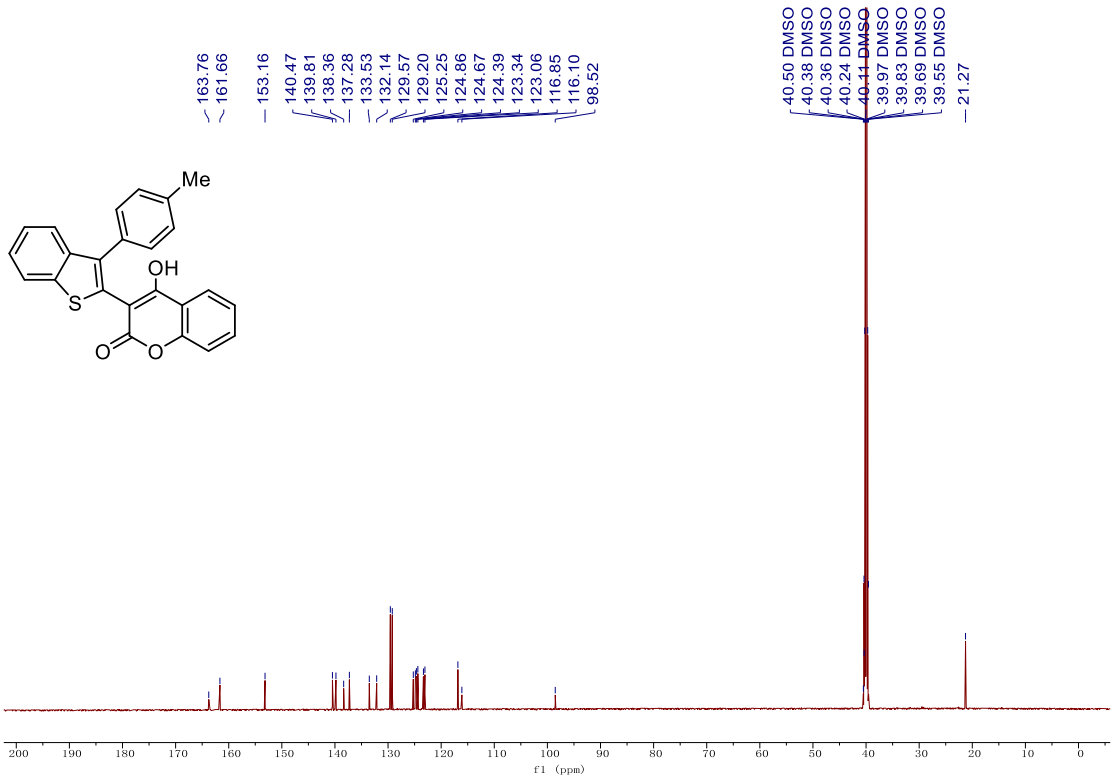
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **5**



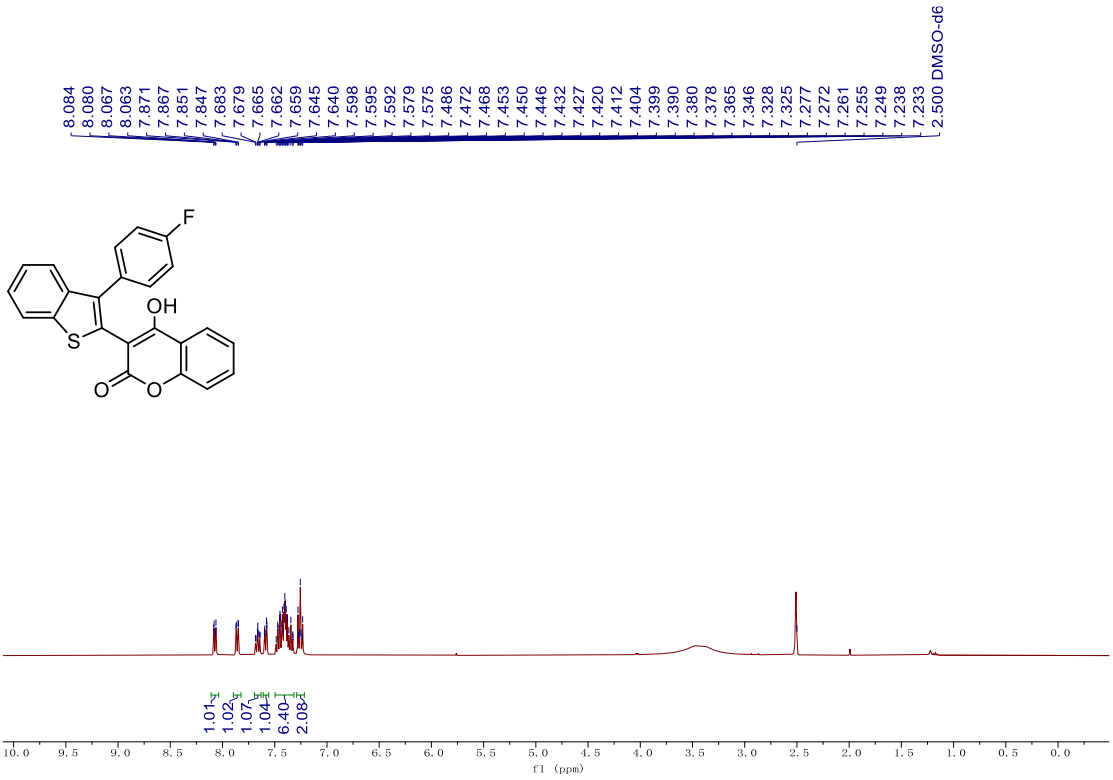
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of **5**



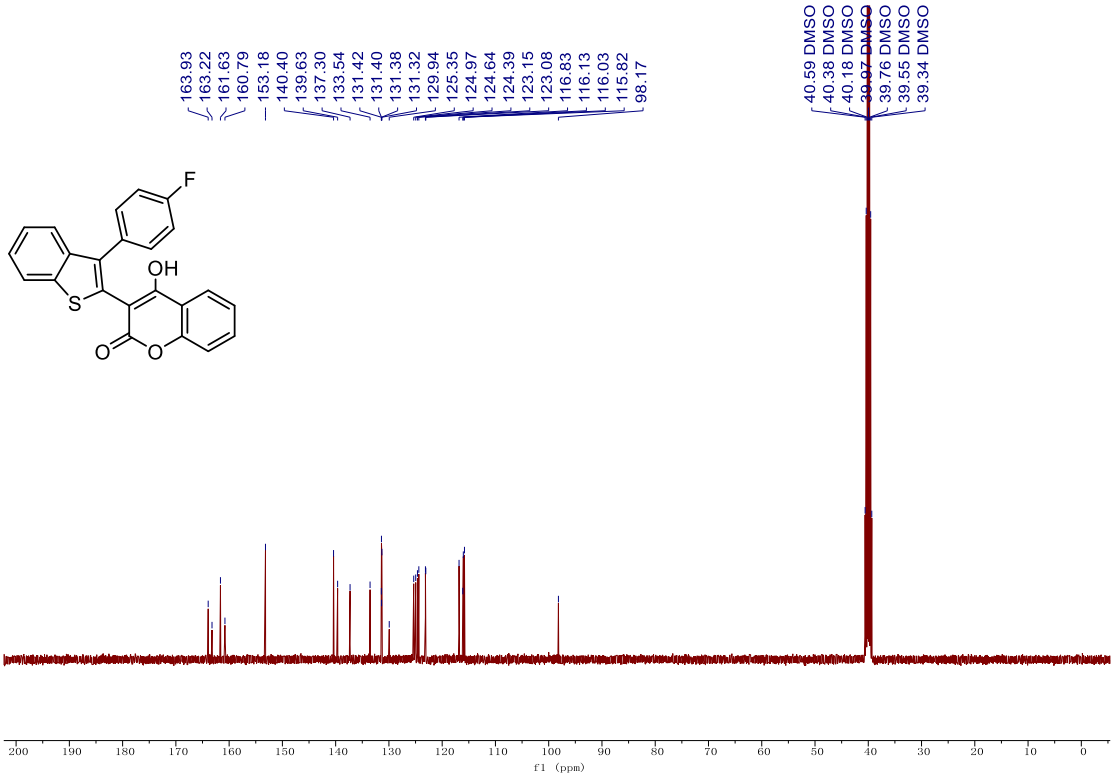
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **6**



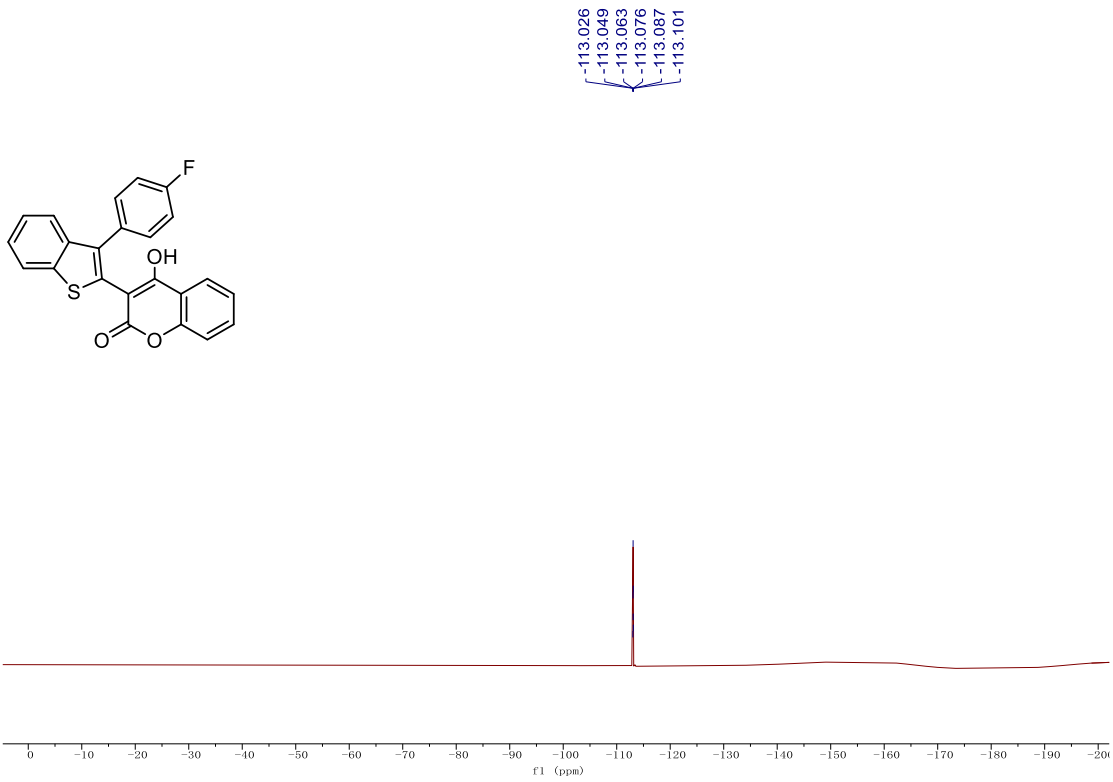
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **6**



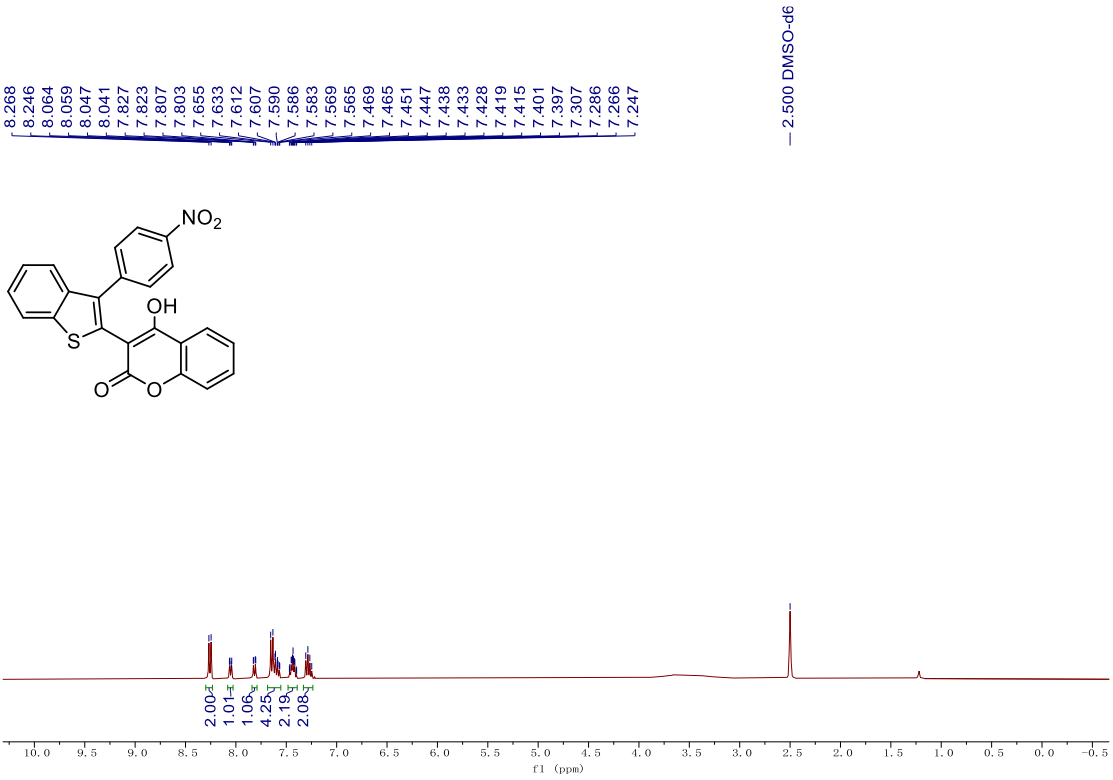
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **7**



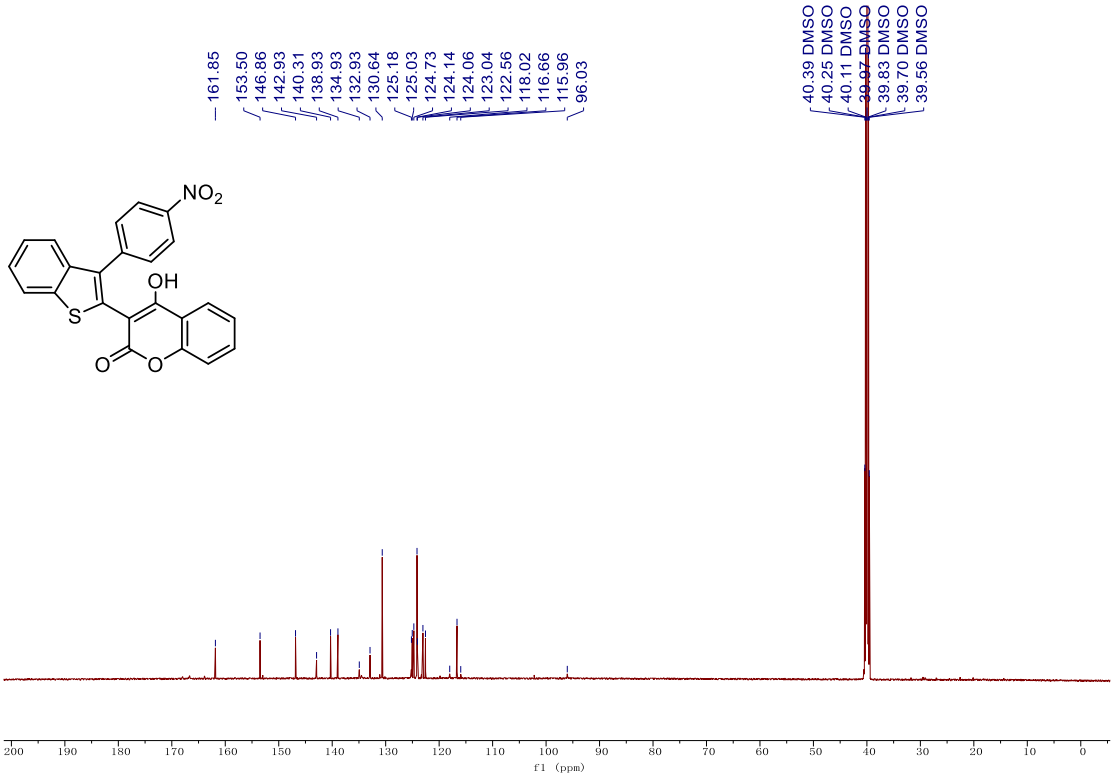
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of **7**



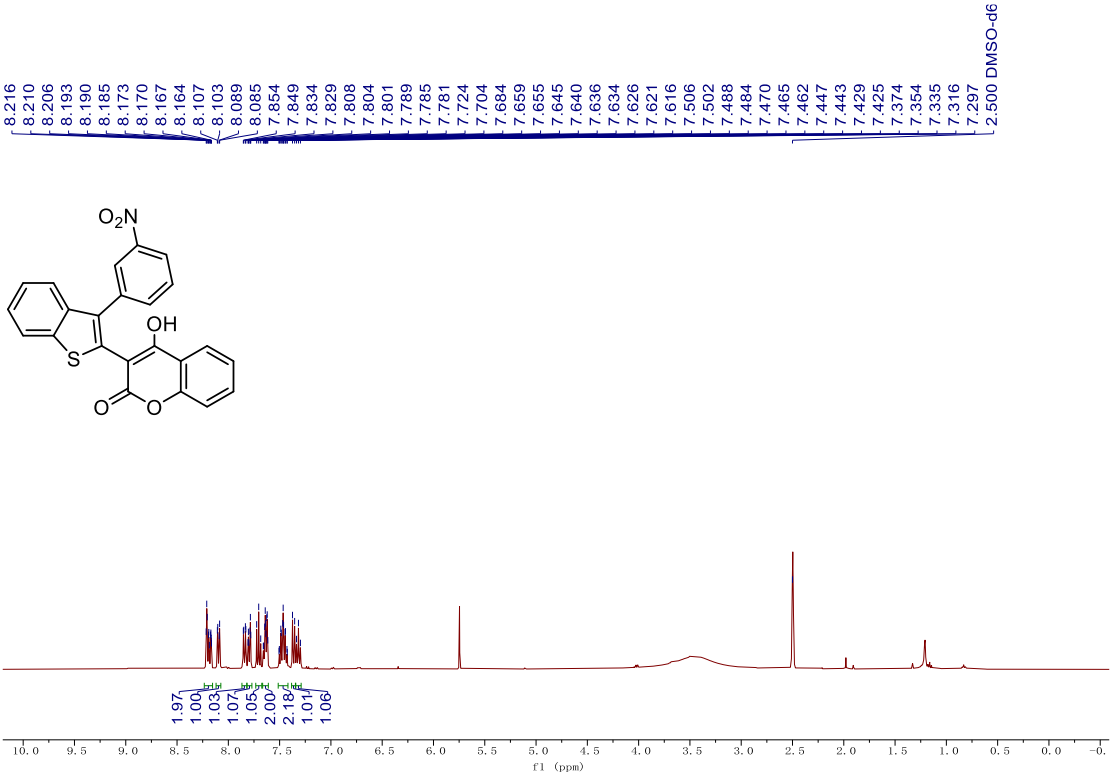
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **7**



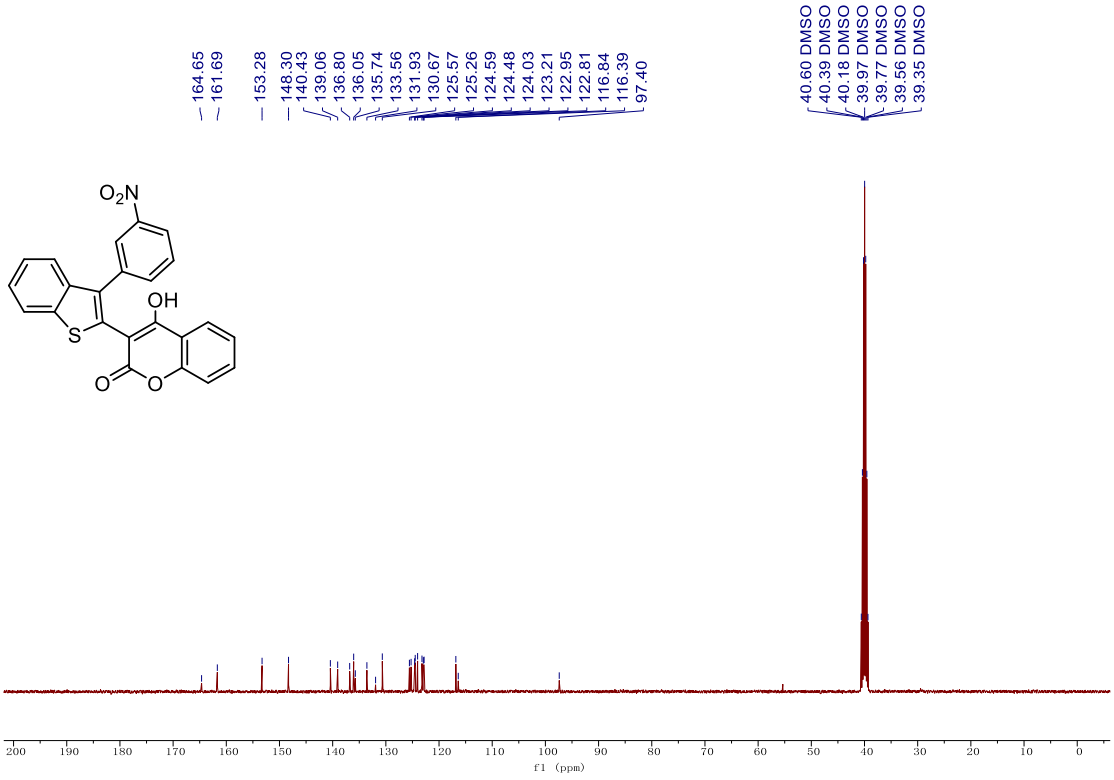
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **8**



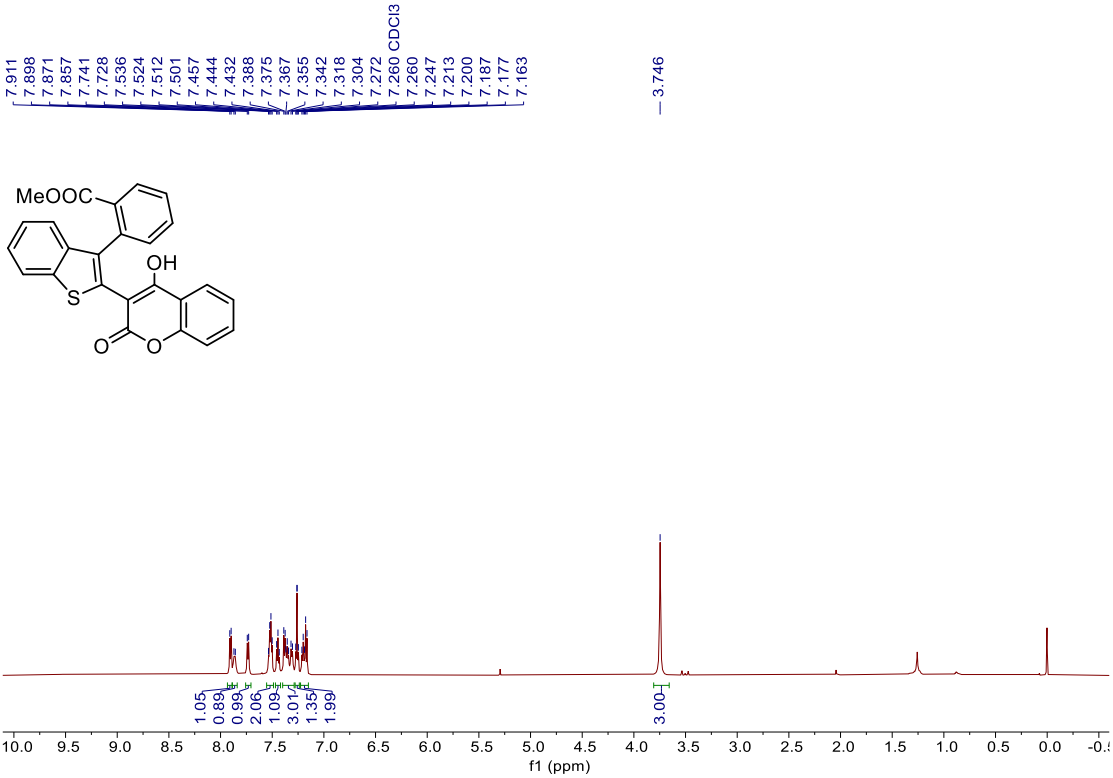
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **8**



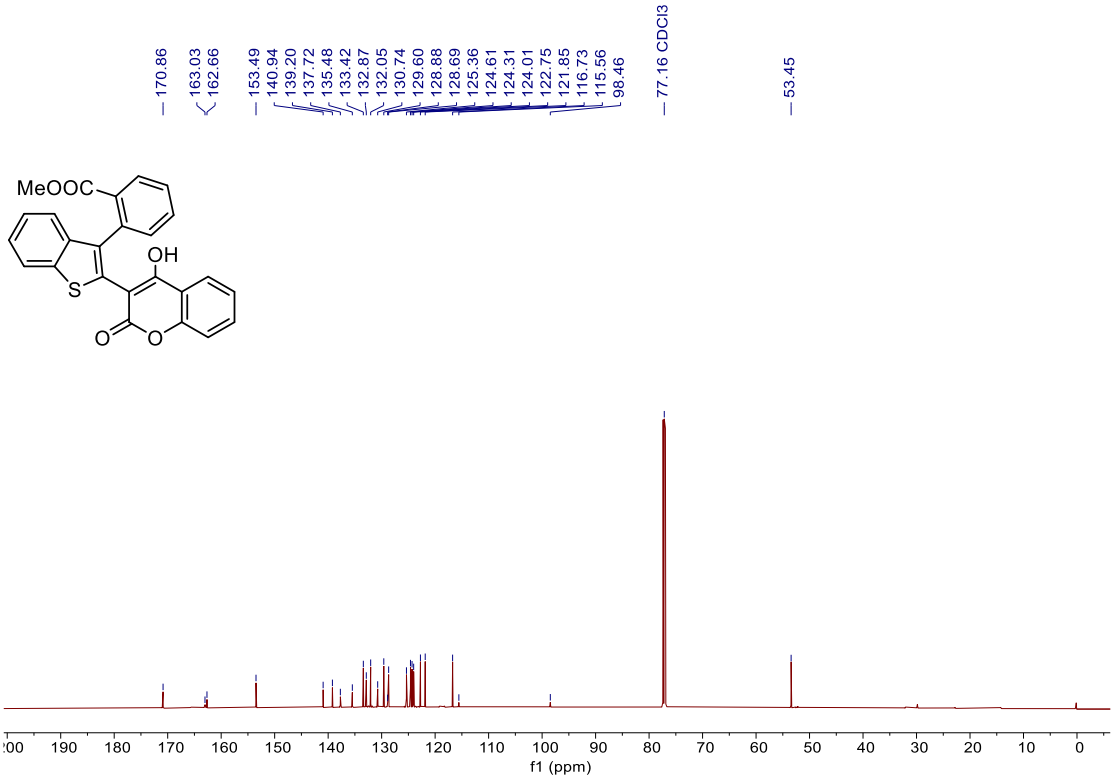
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **9**



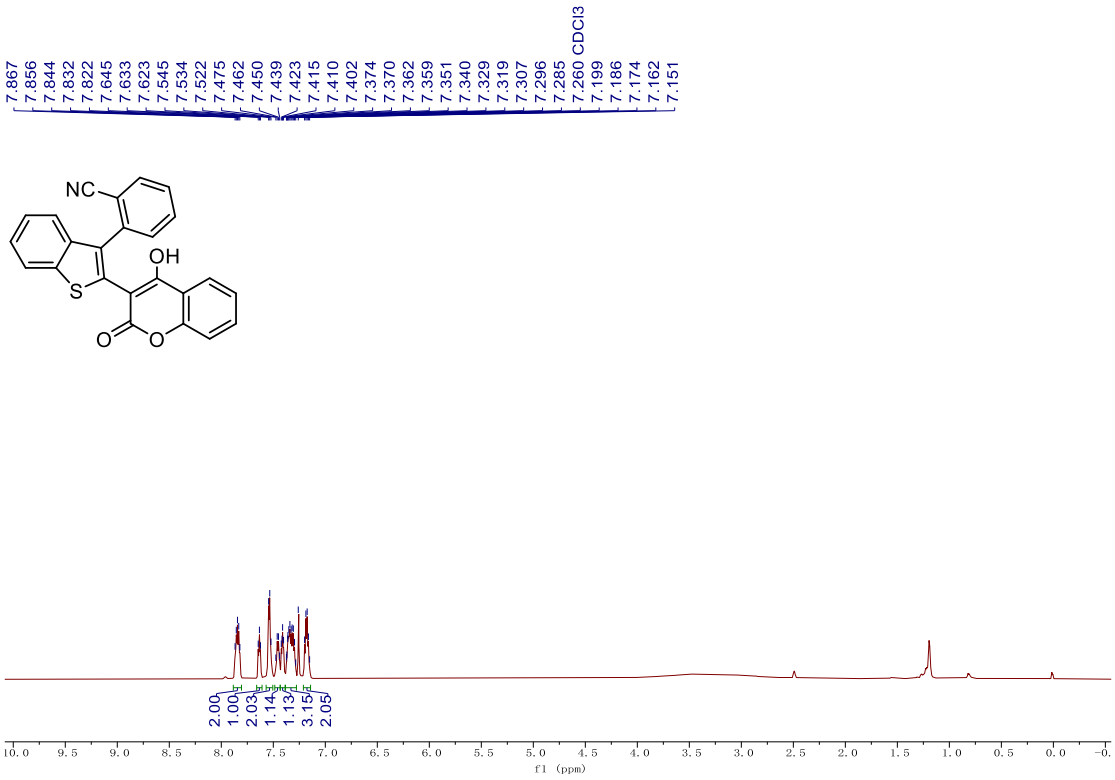
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of **9**



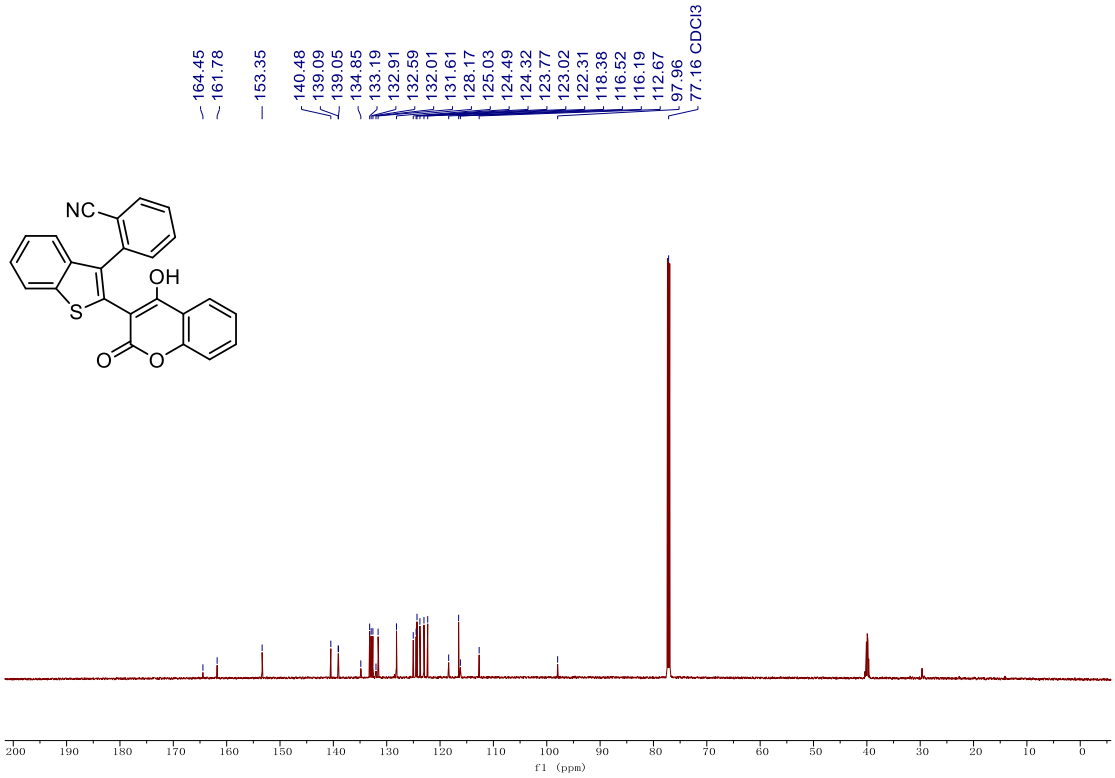
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **10**



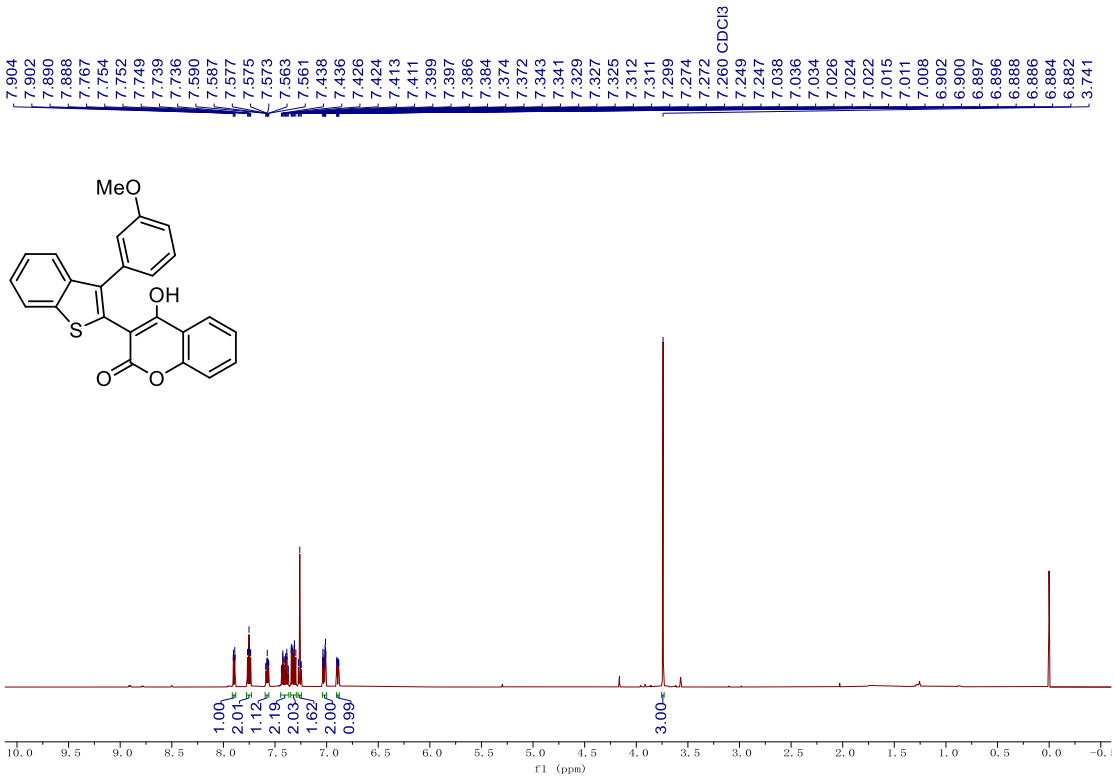
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **10**



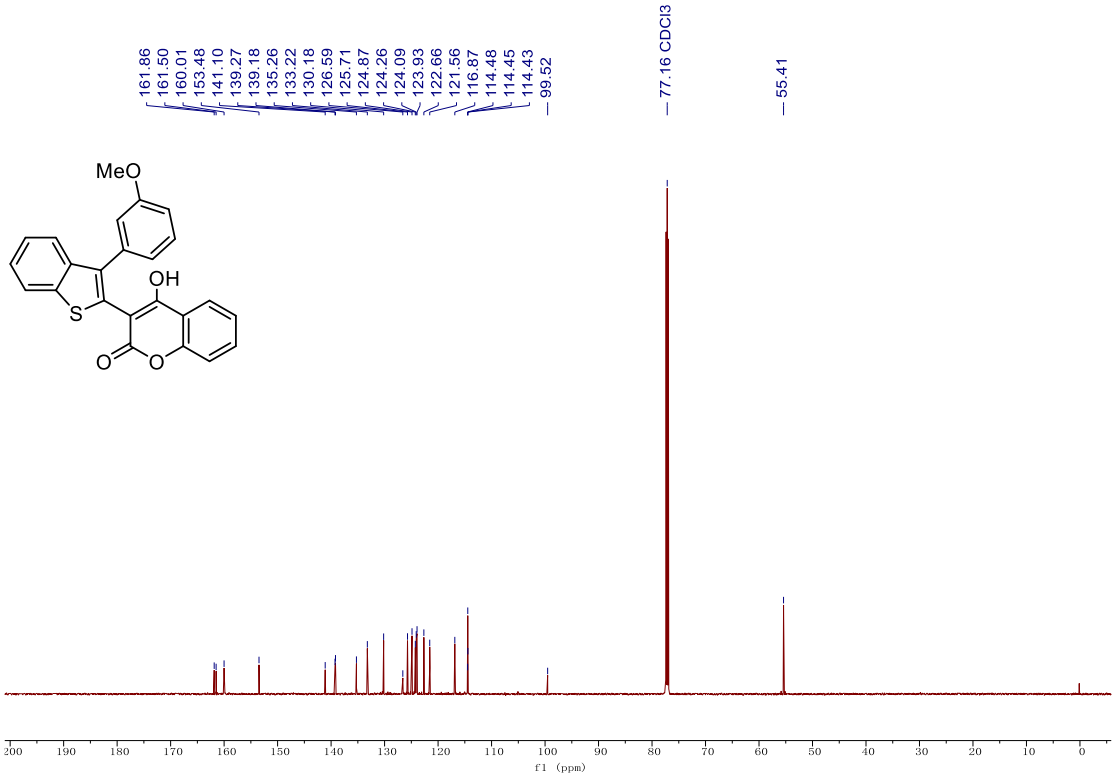
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **11**



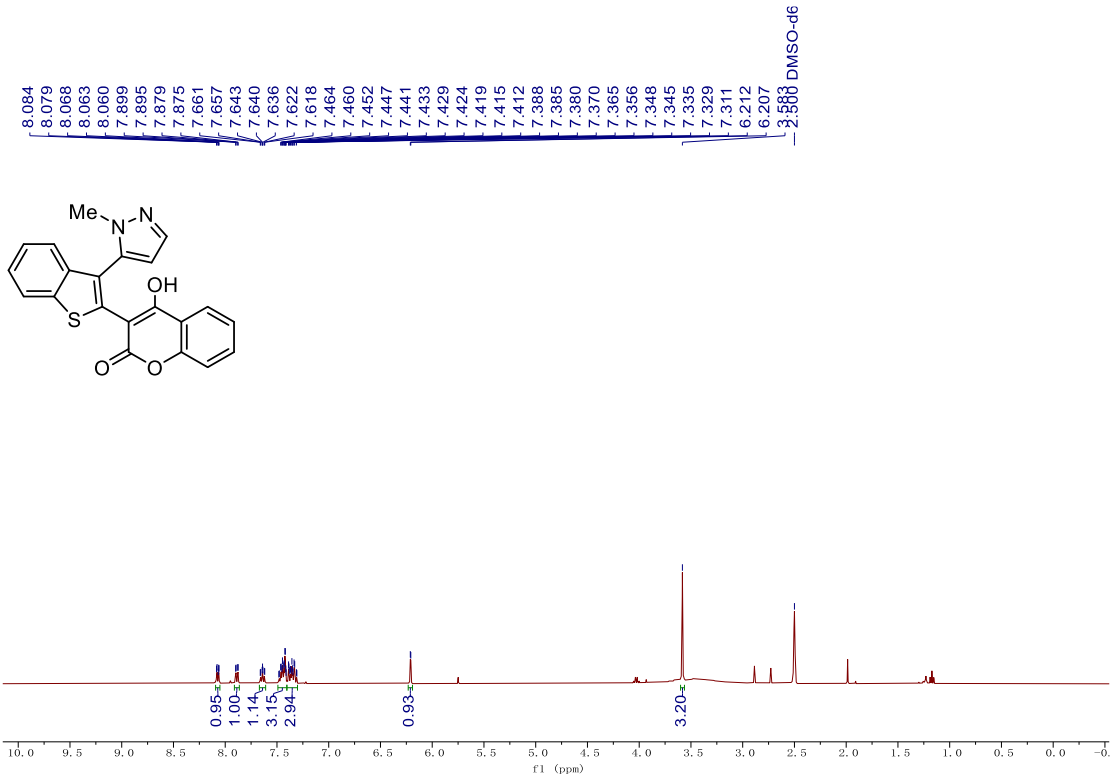
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **11**



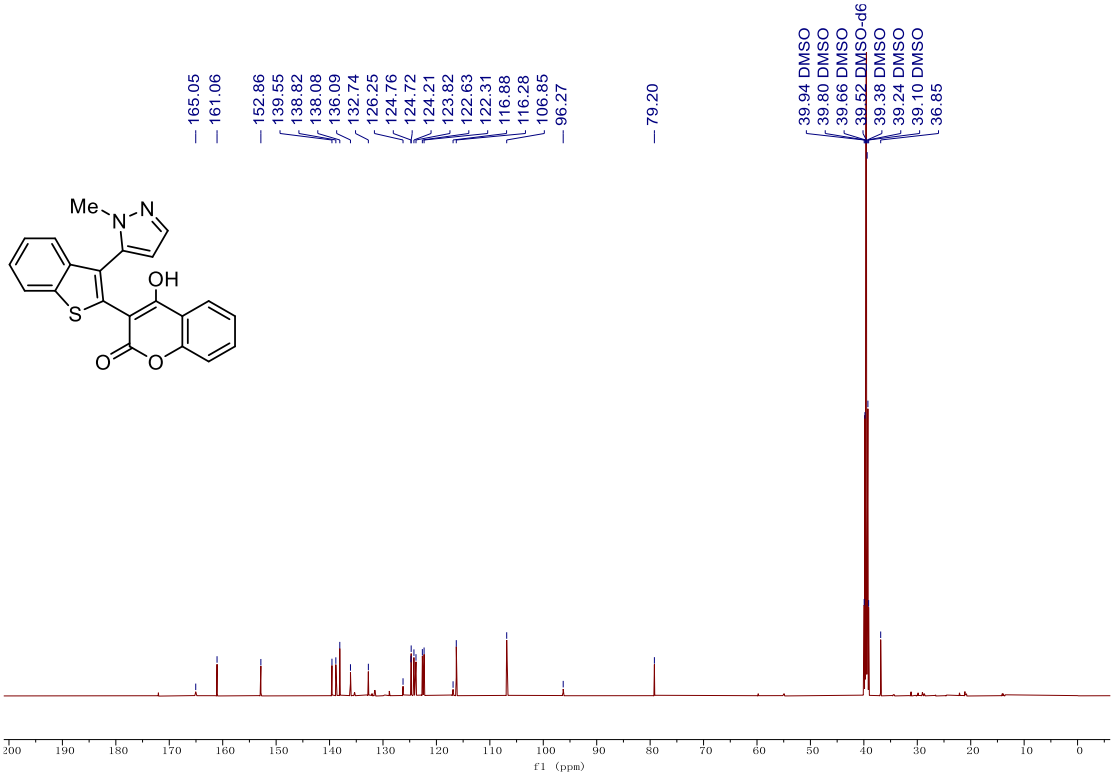
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **12**



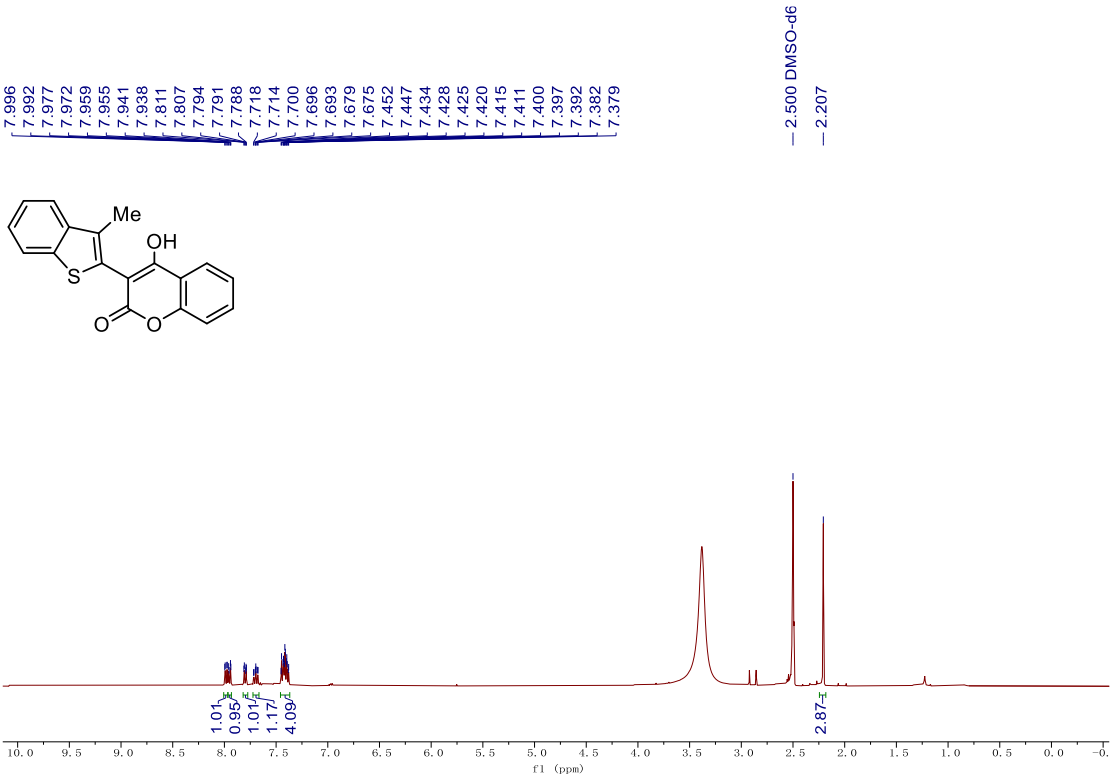
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **12**



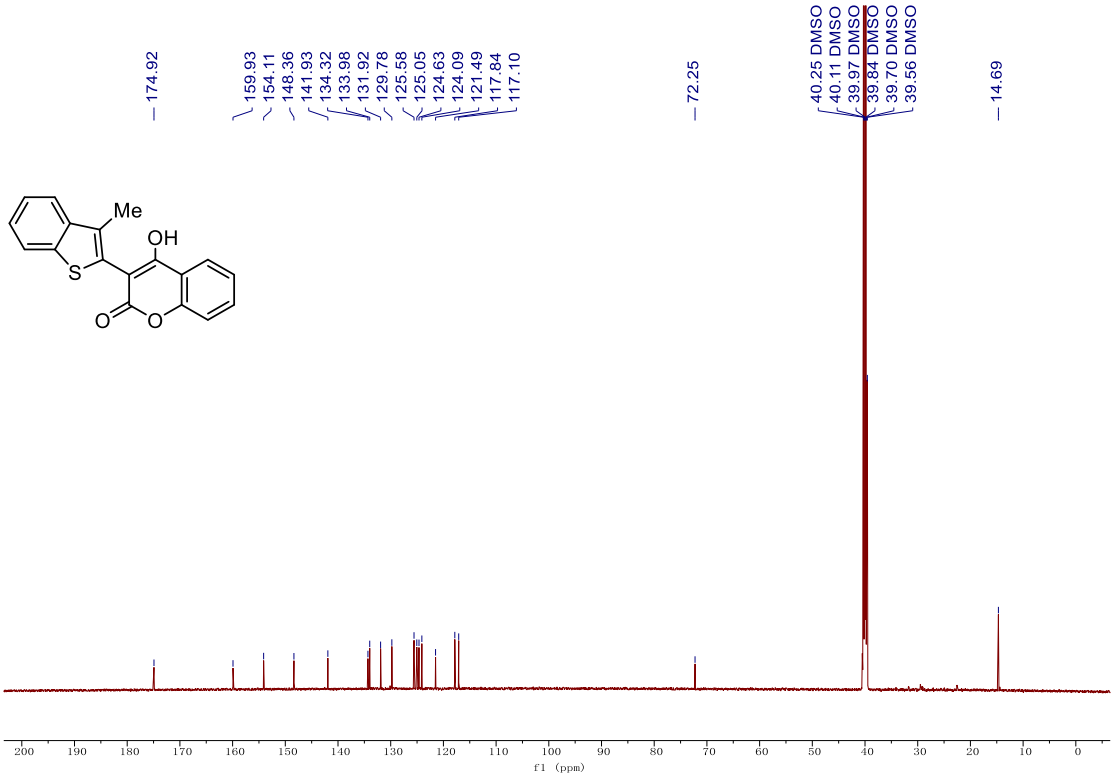
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **13**



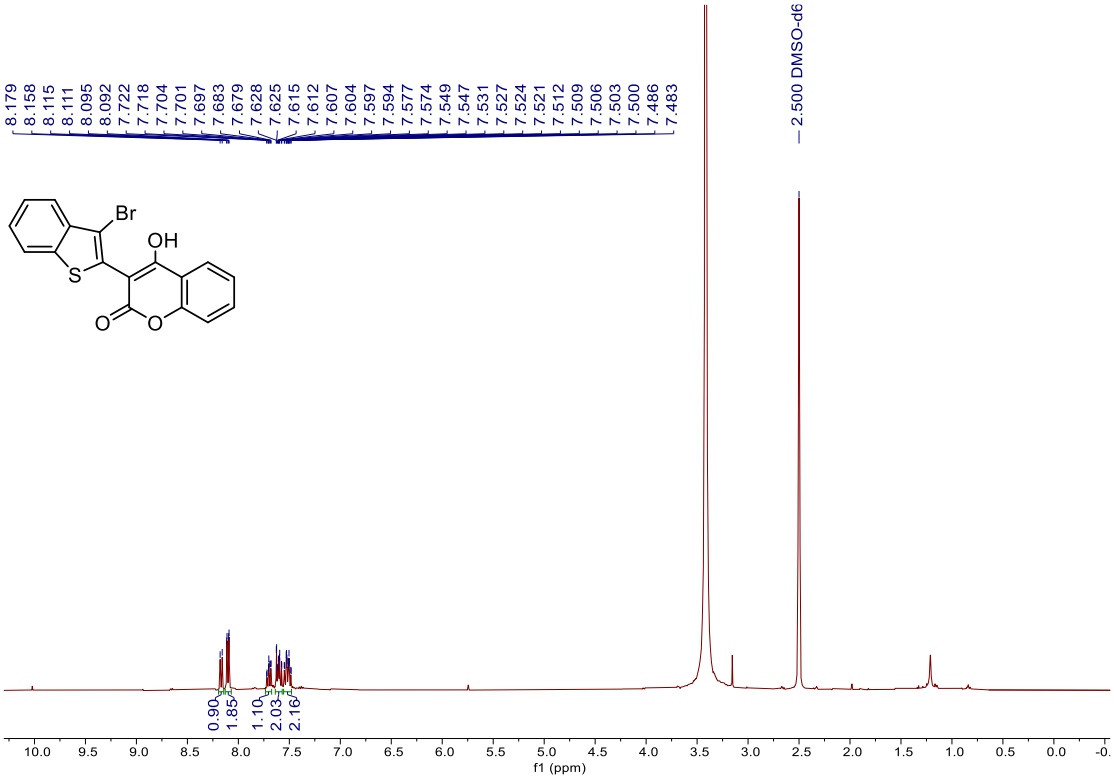
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **13**



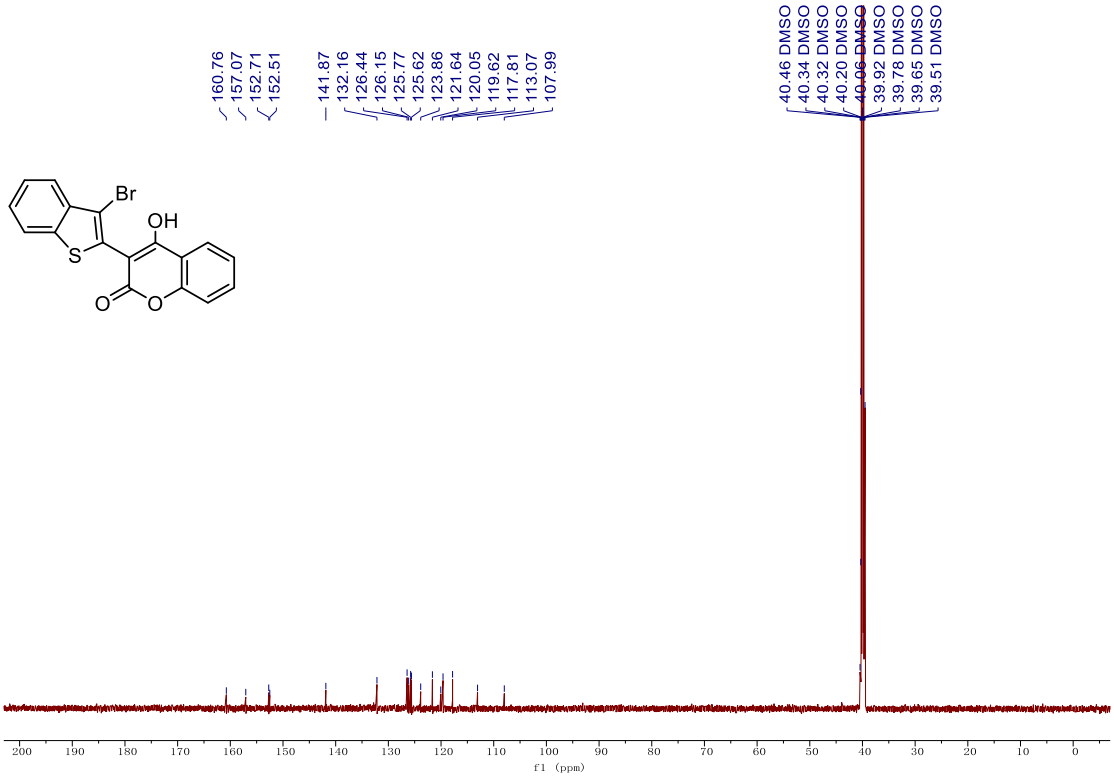
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **14**



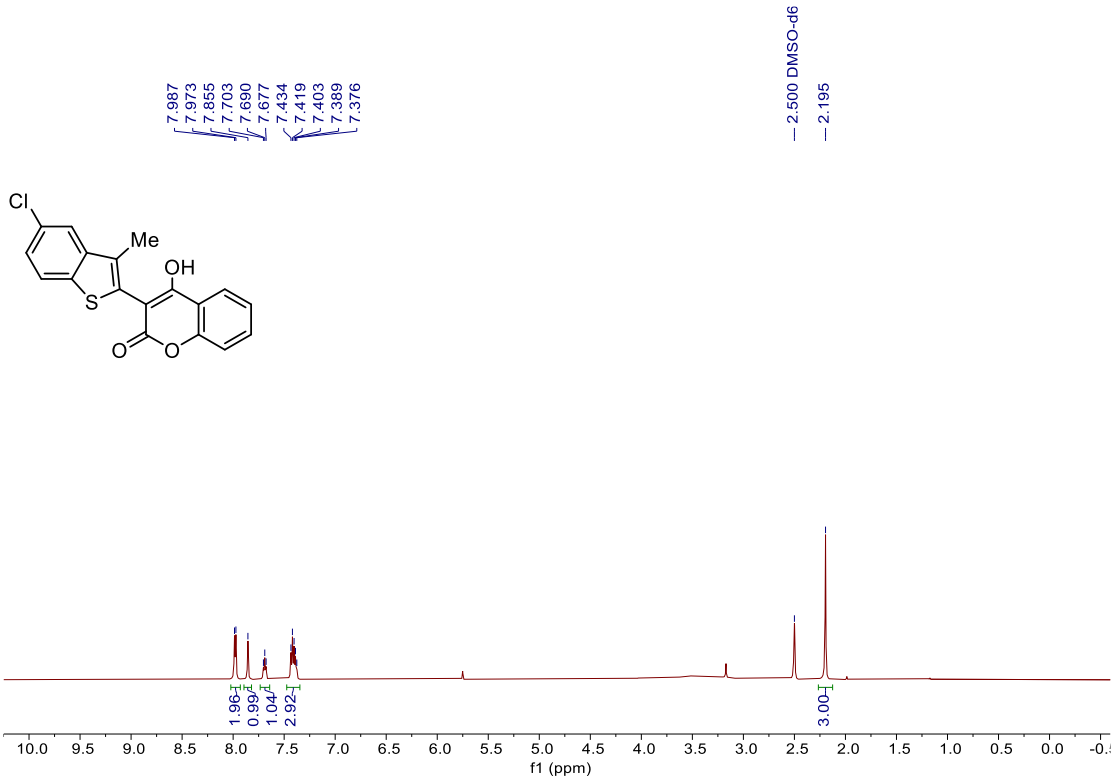
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **14**



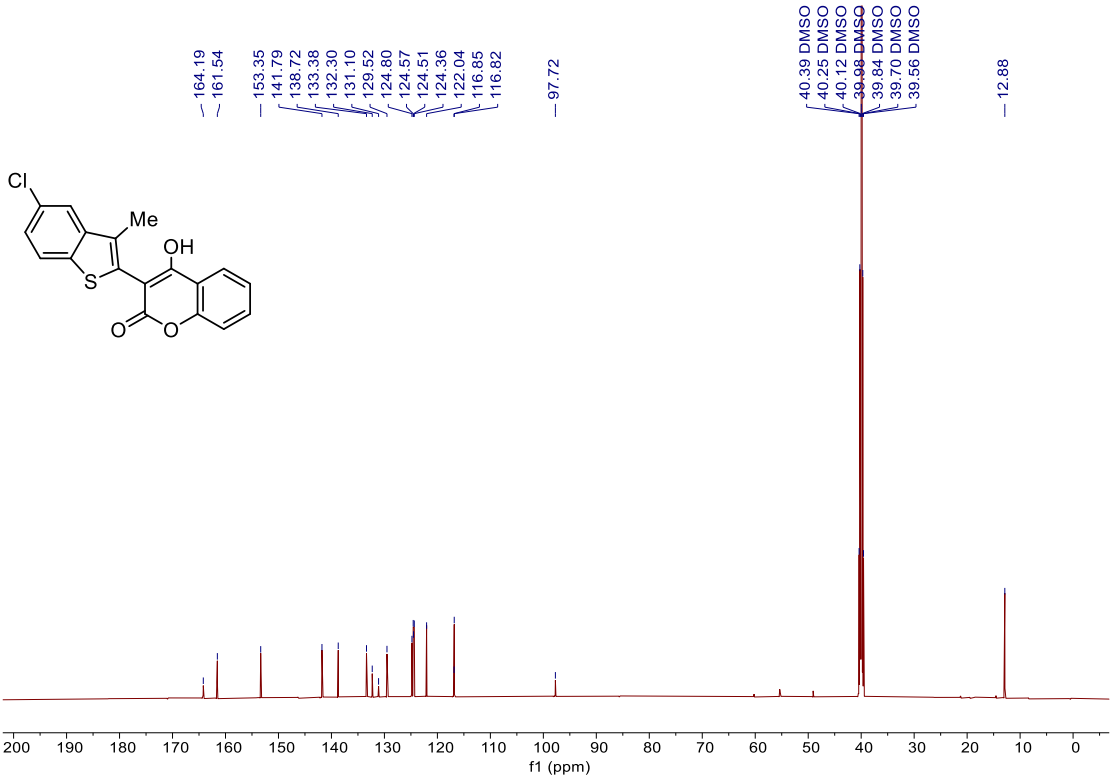
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **15**



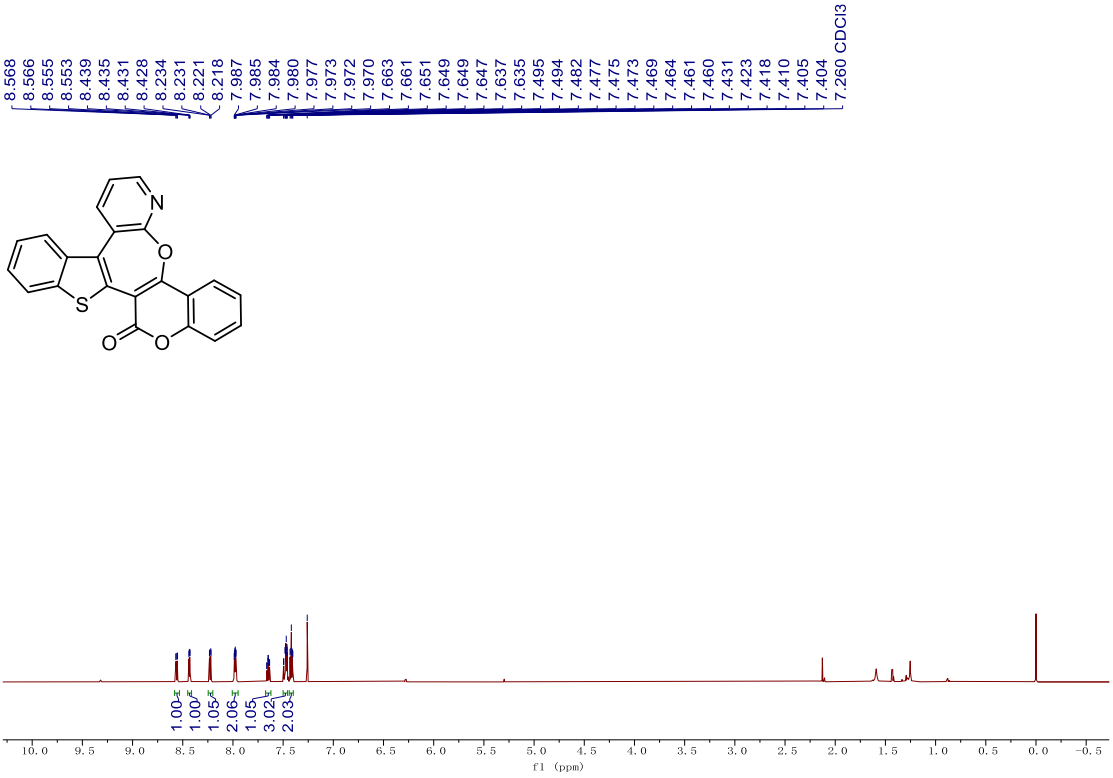
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **15**



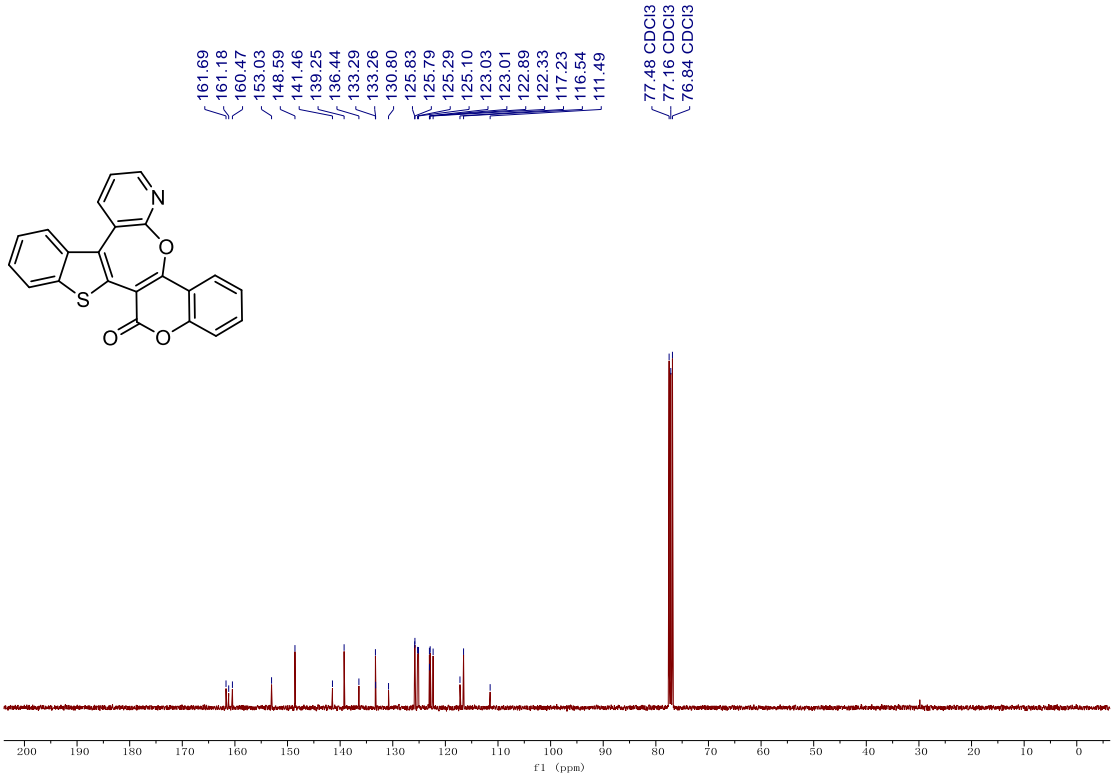
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **16**



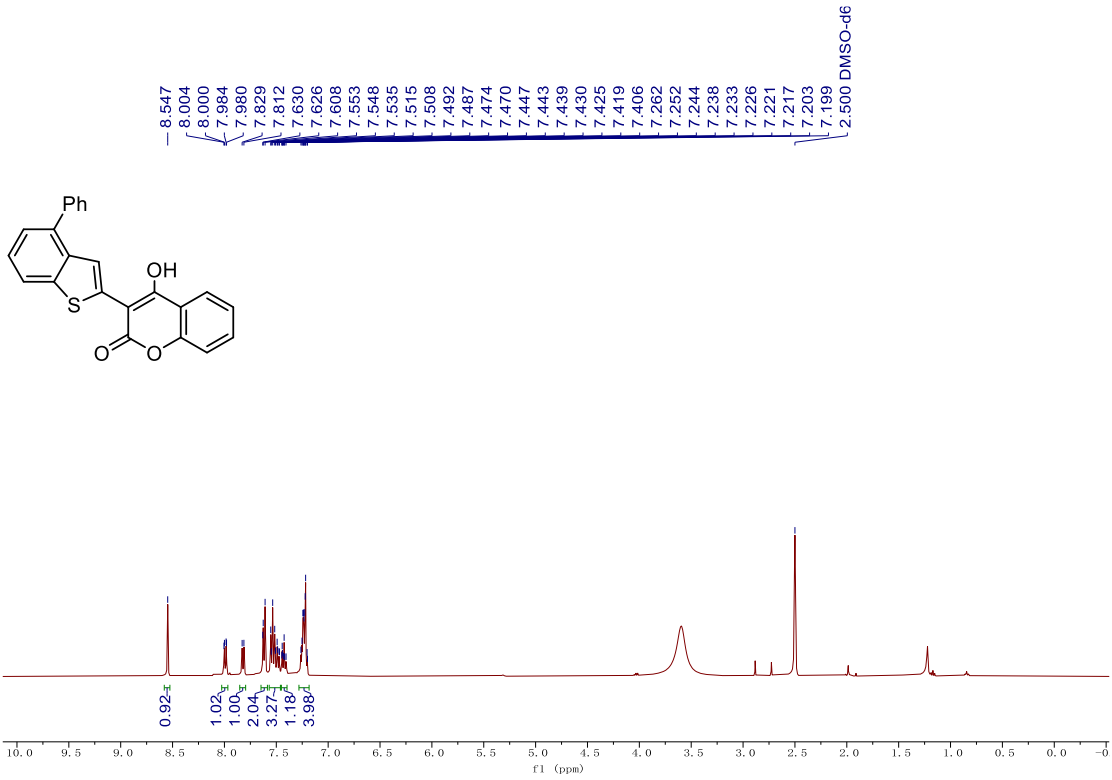
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **16**



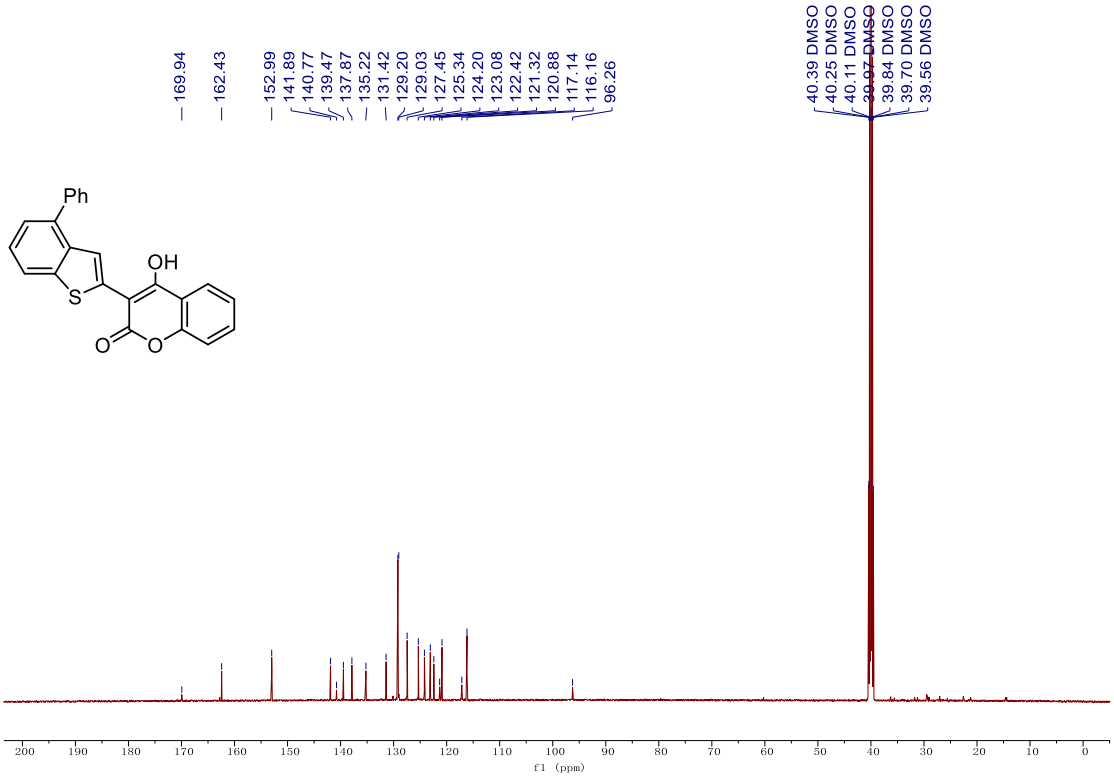
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **18**



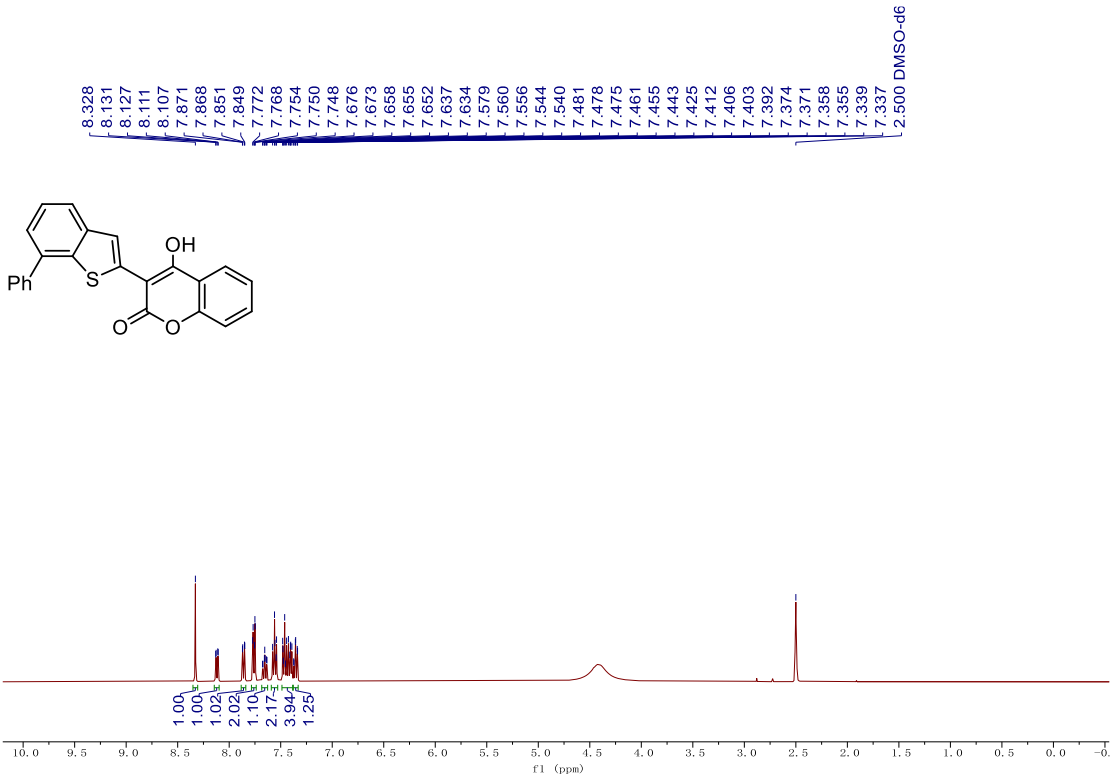
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **18**



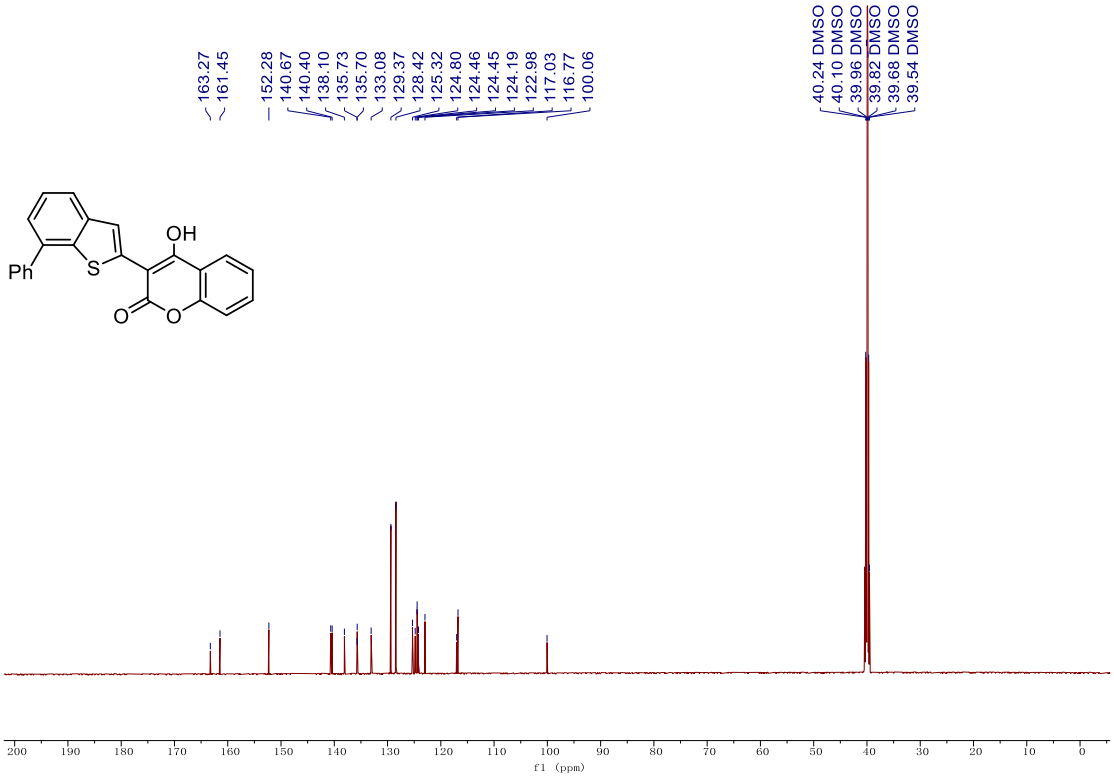
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **19**



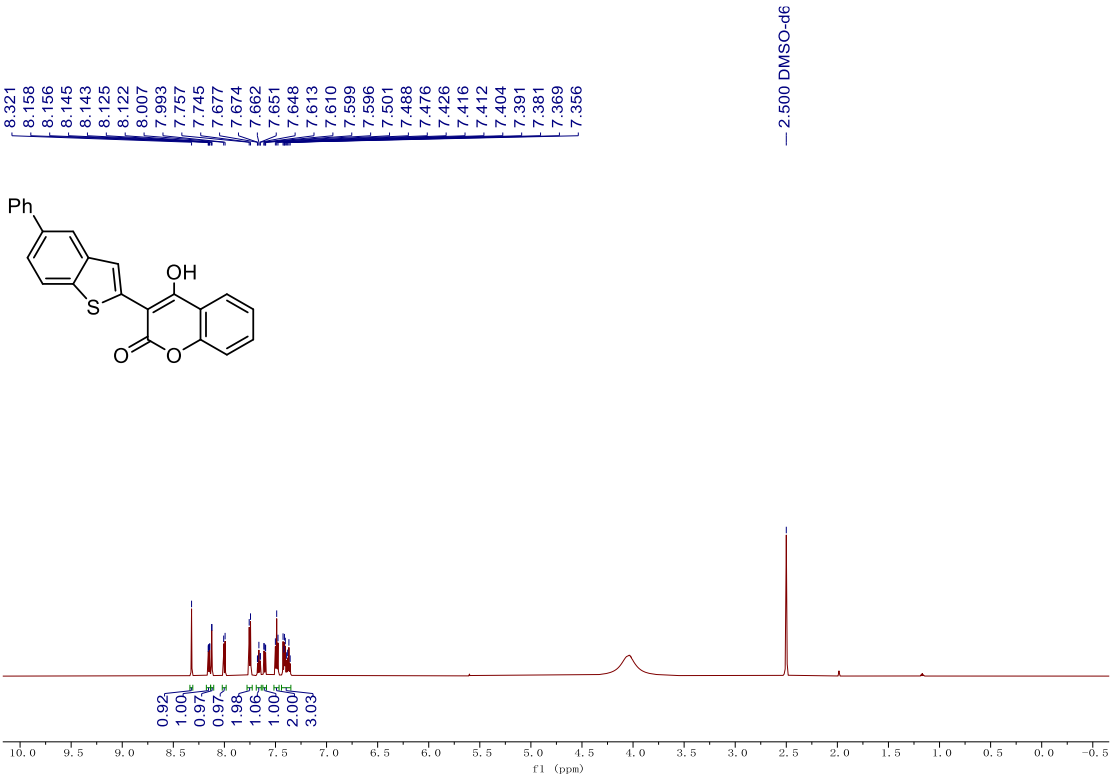
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **19**



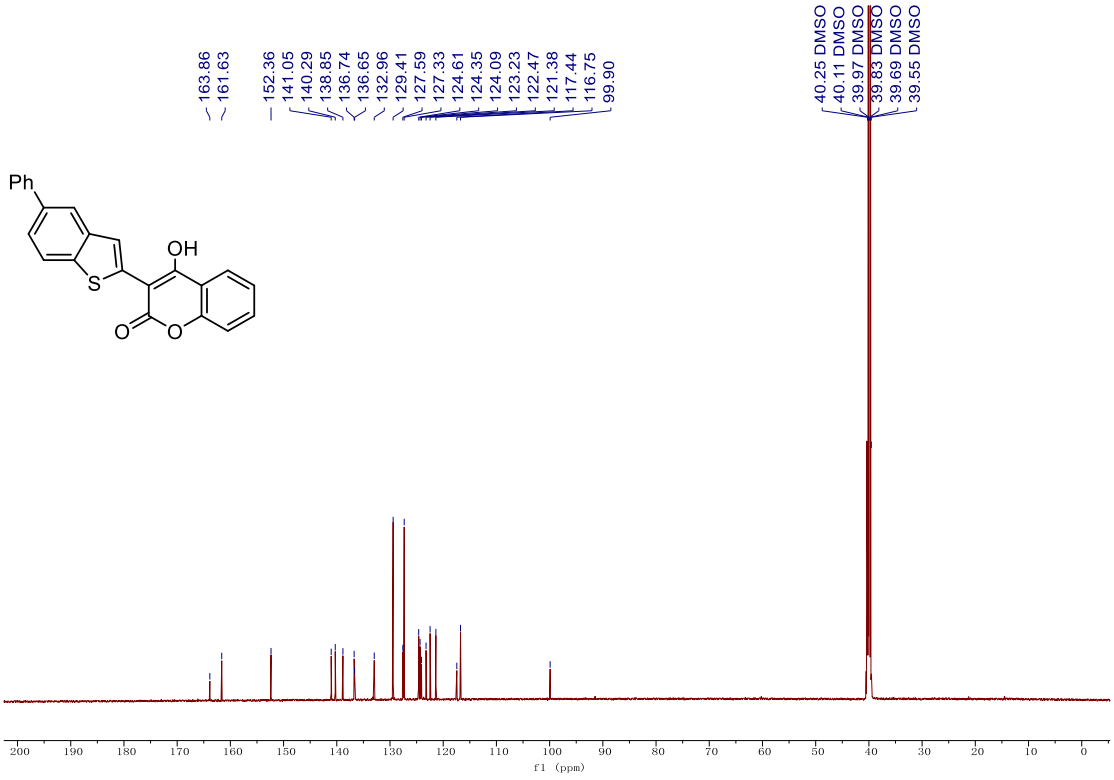
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **20**



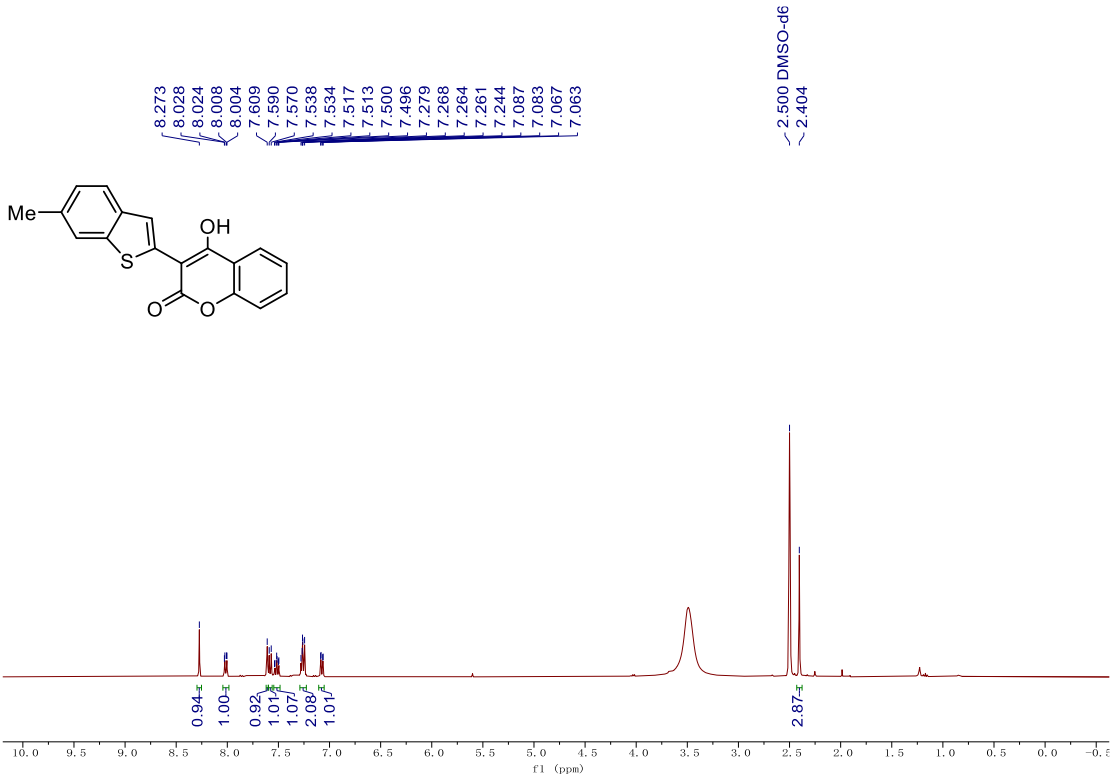
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **20**



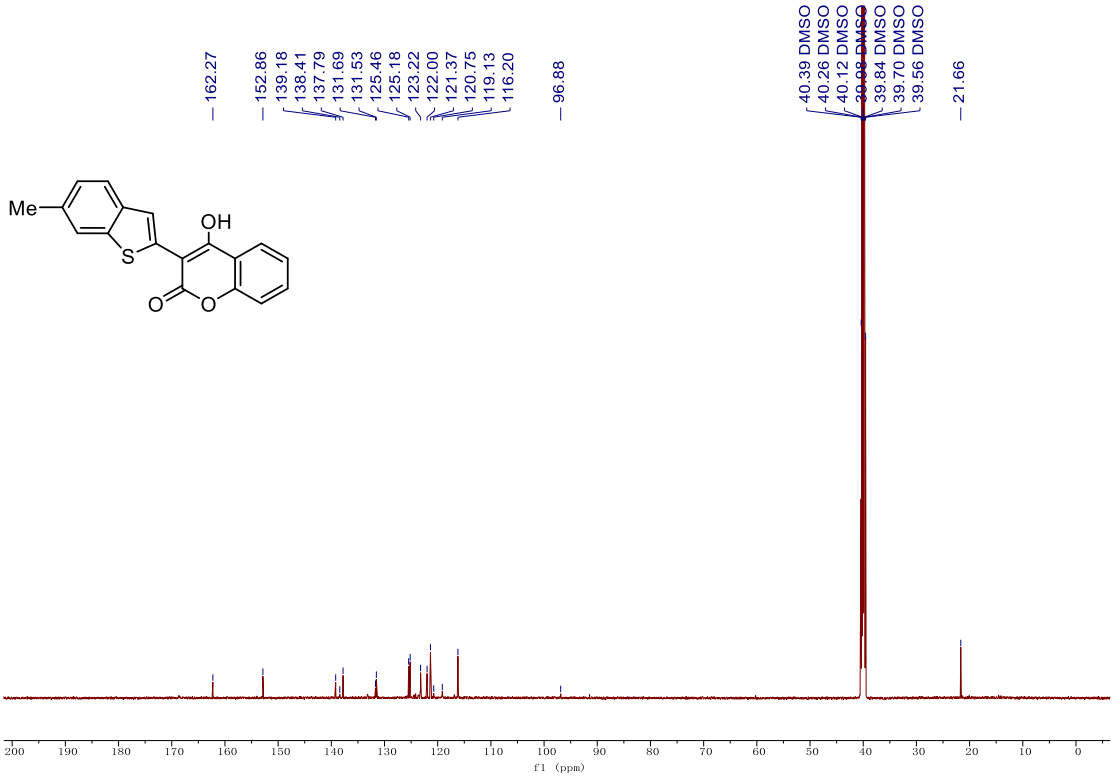
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **21**



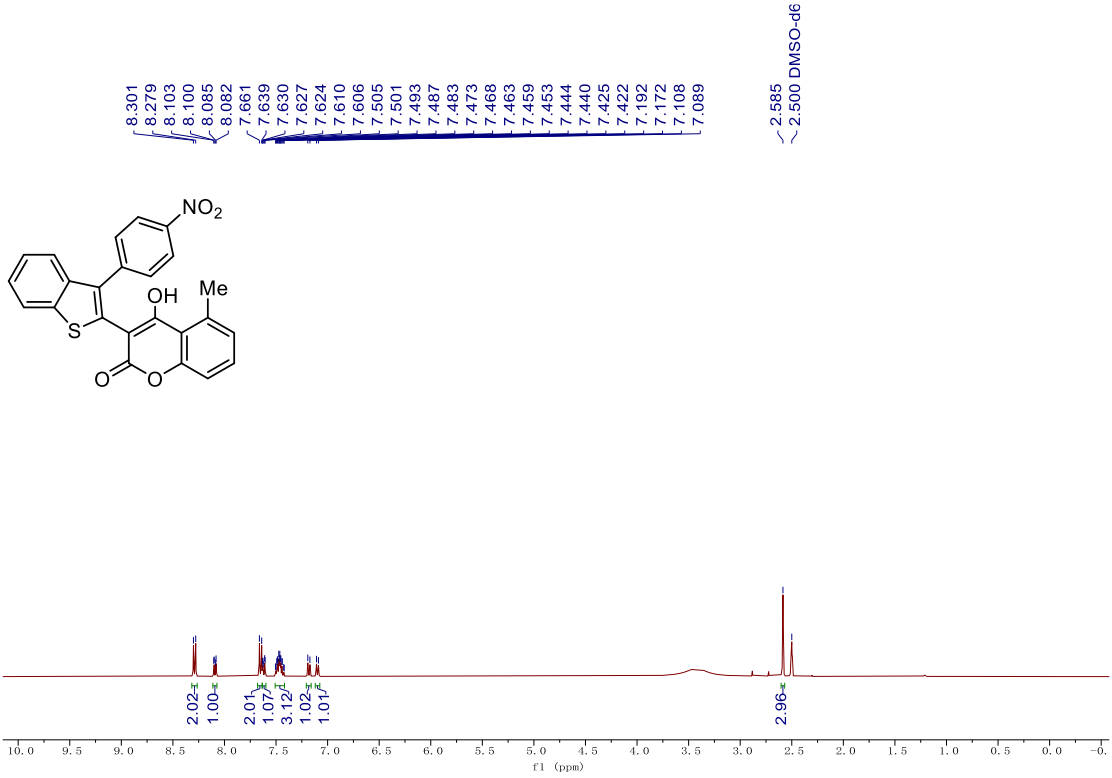
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **21**



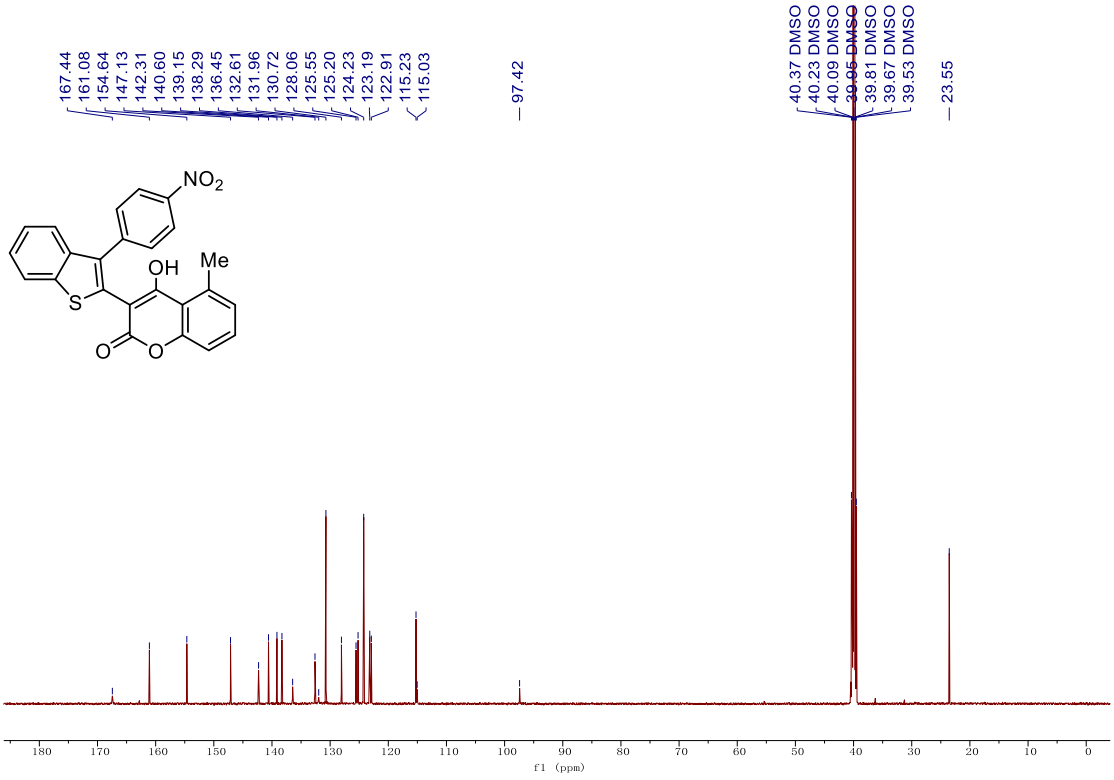
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **22**



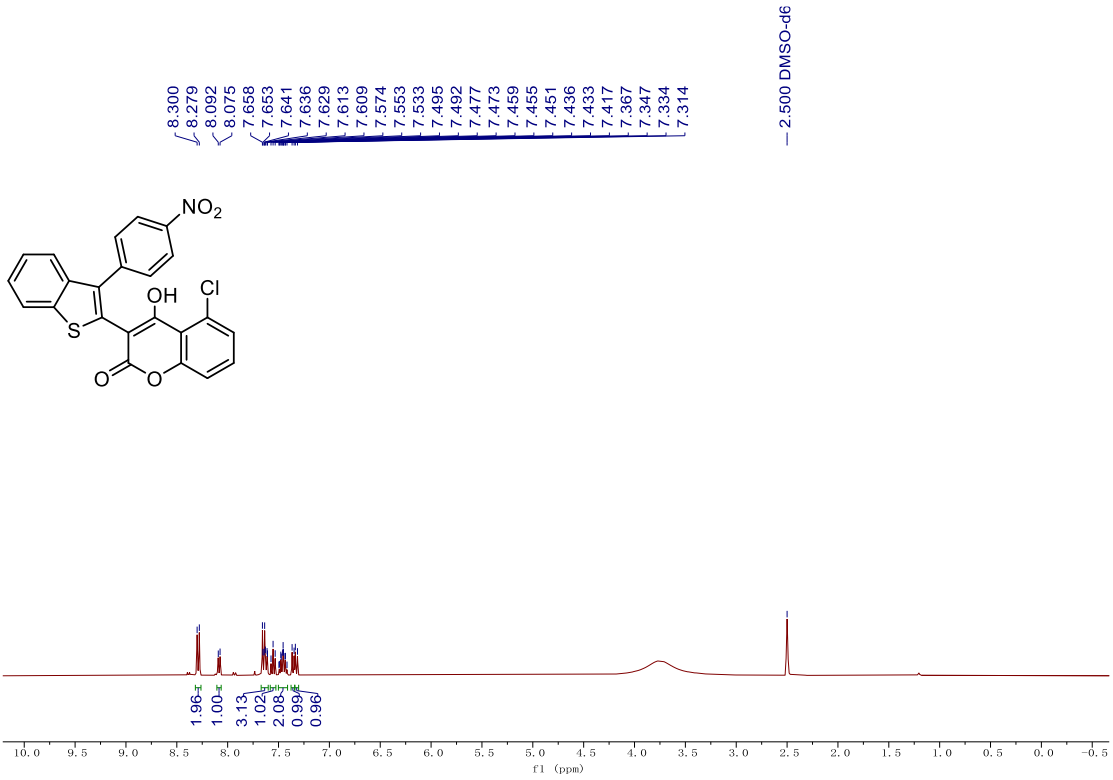
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **22**



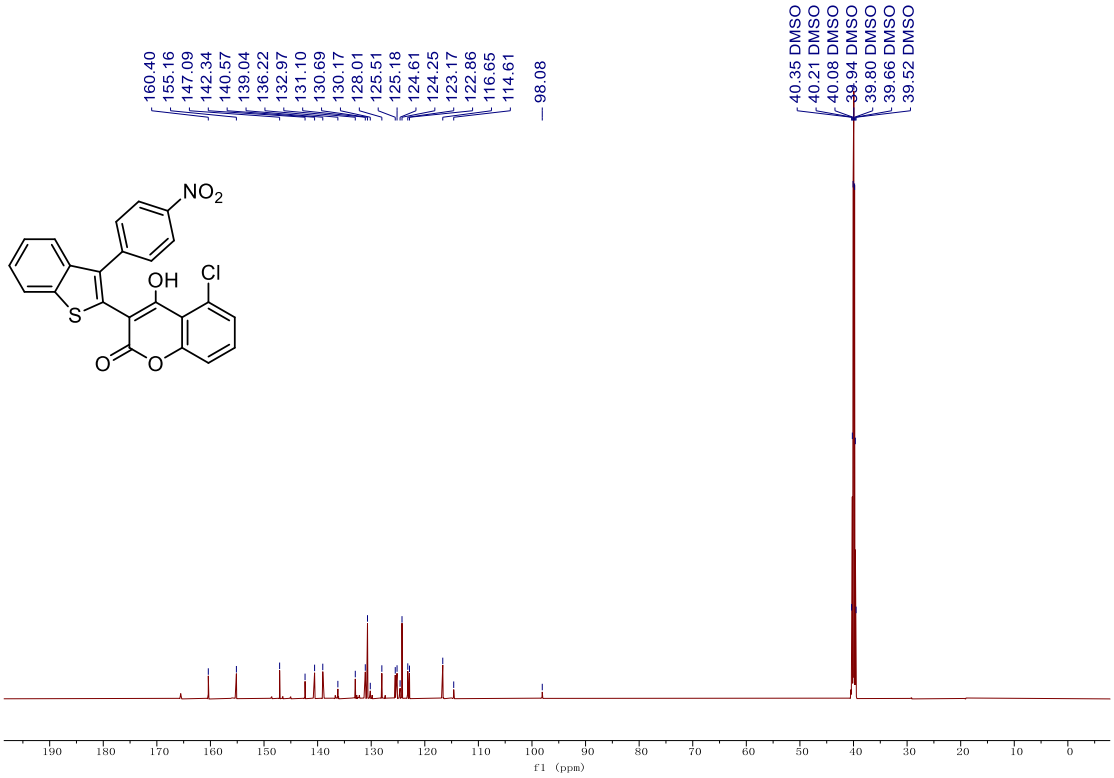
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **24**



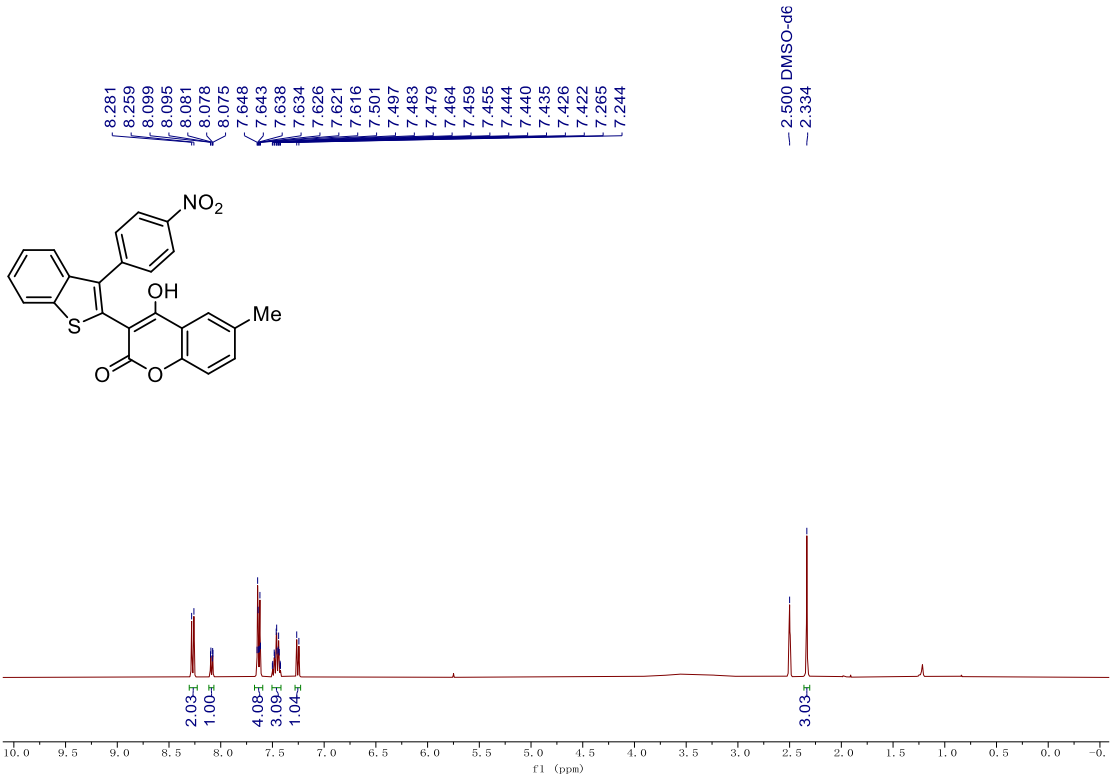
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **24**



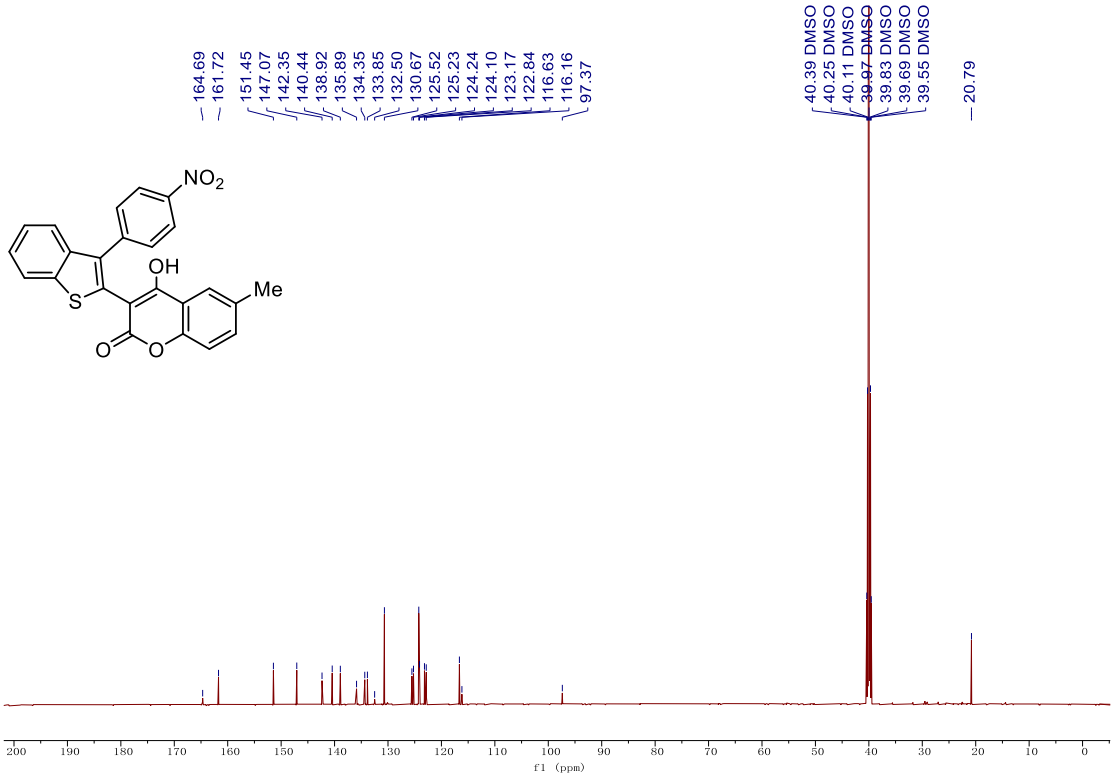
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **25**



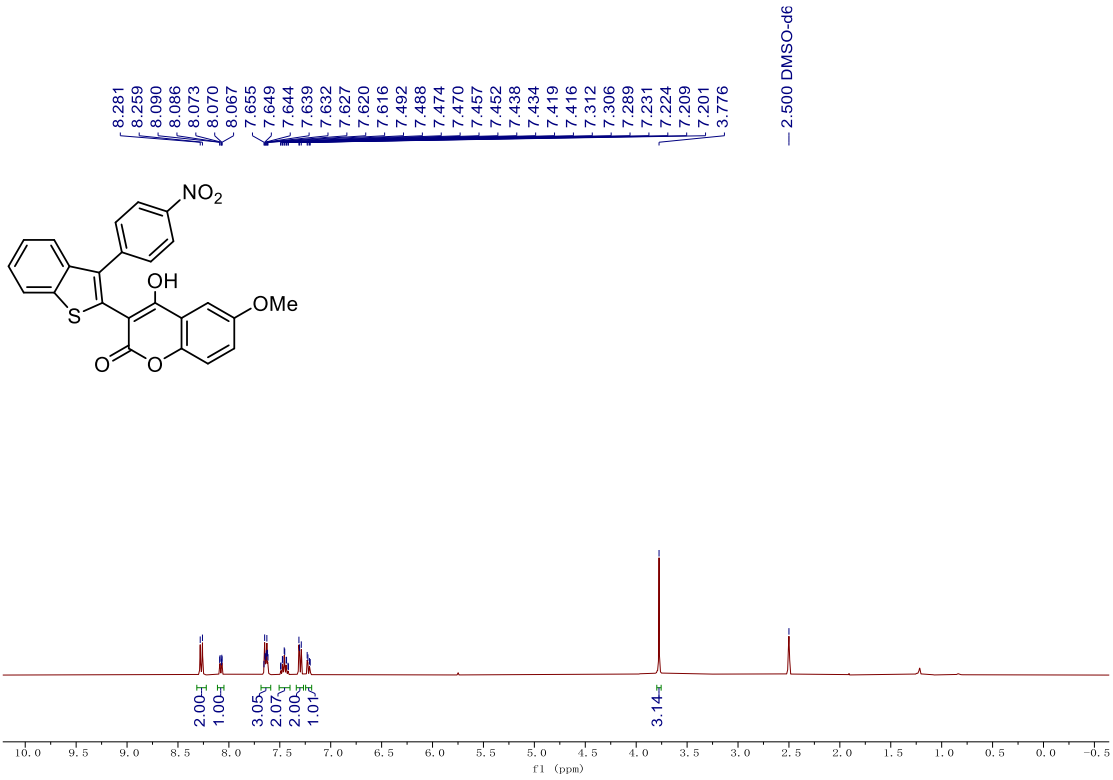
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **25**



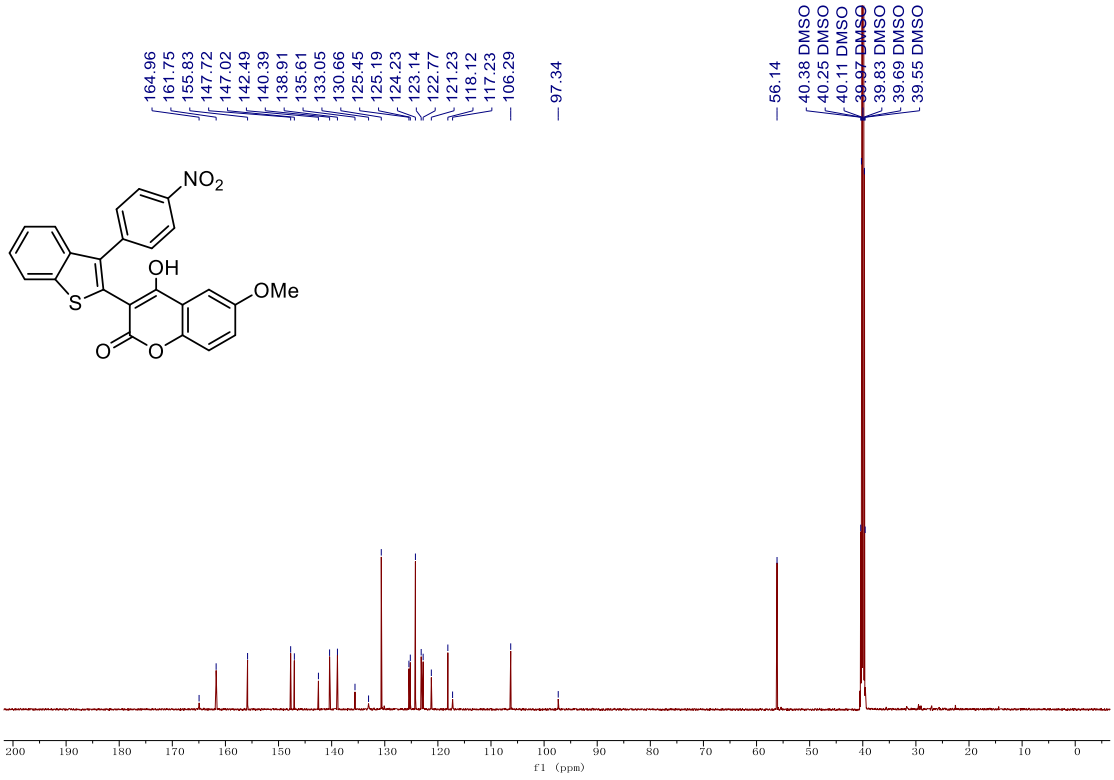
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **26**



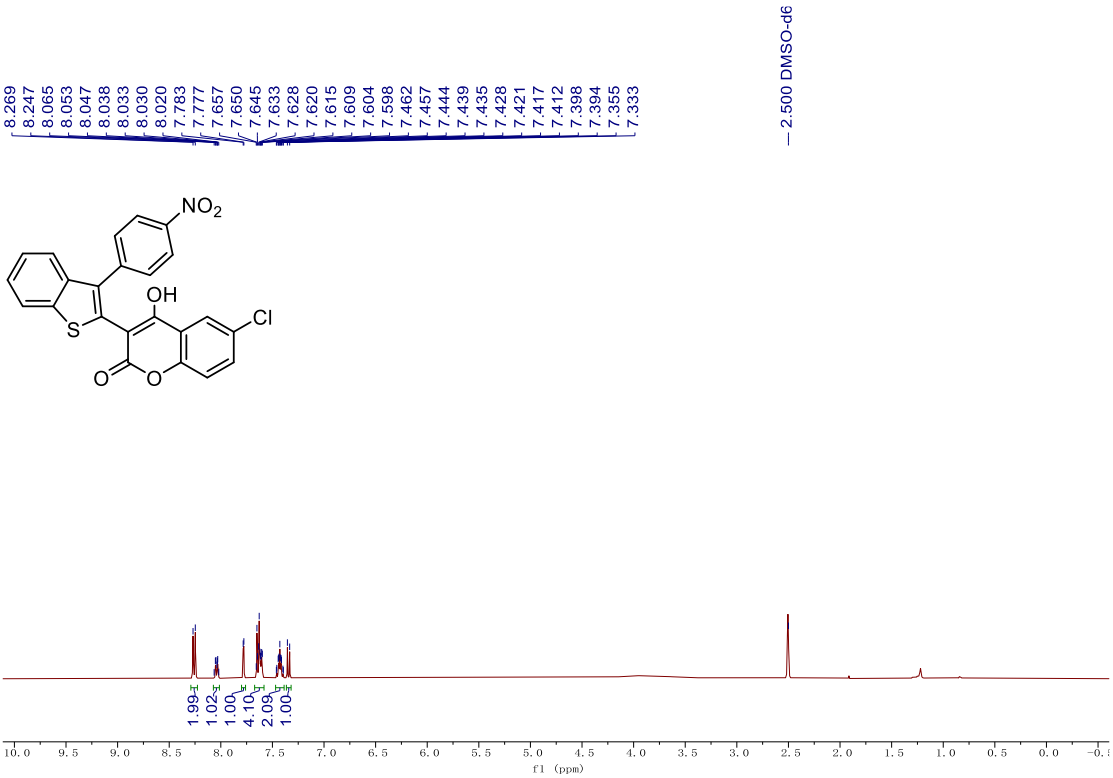
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **26**



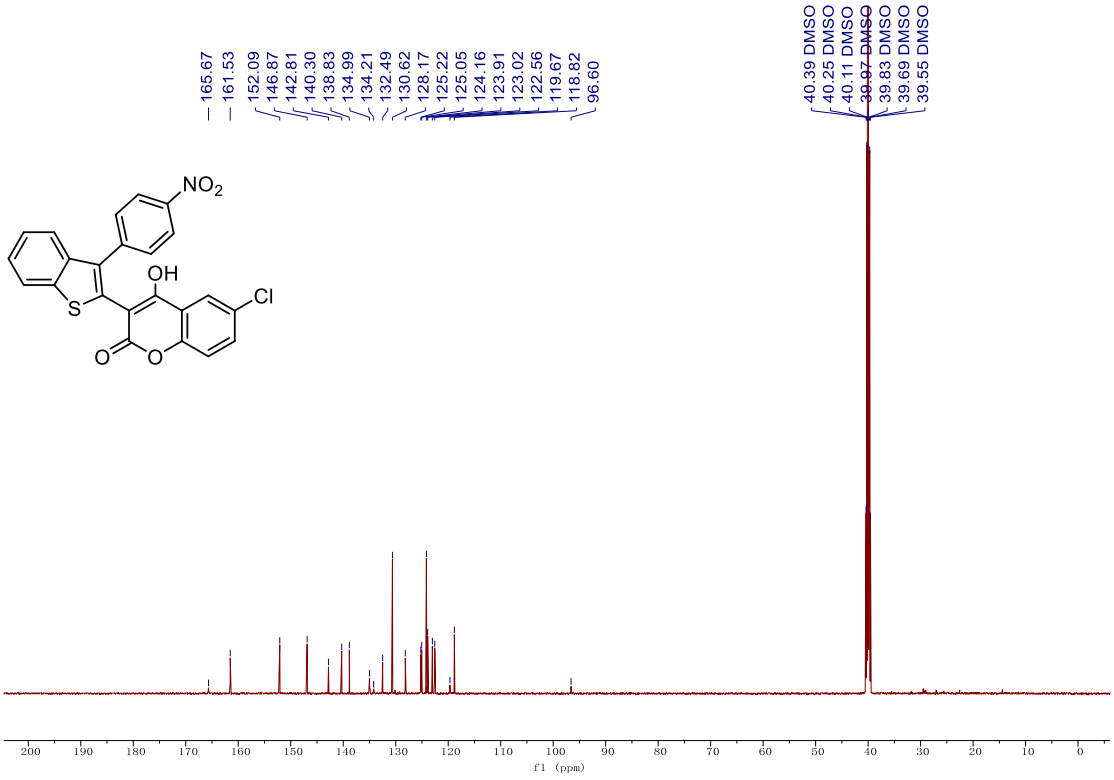
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **27**



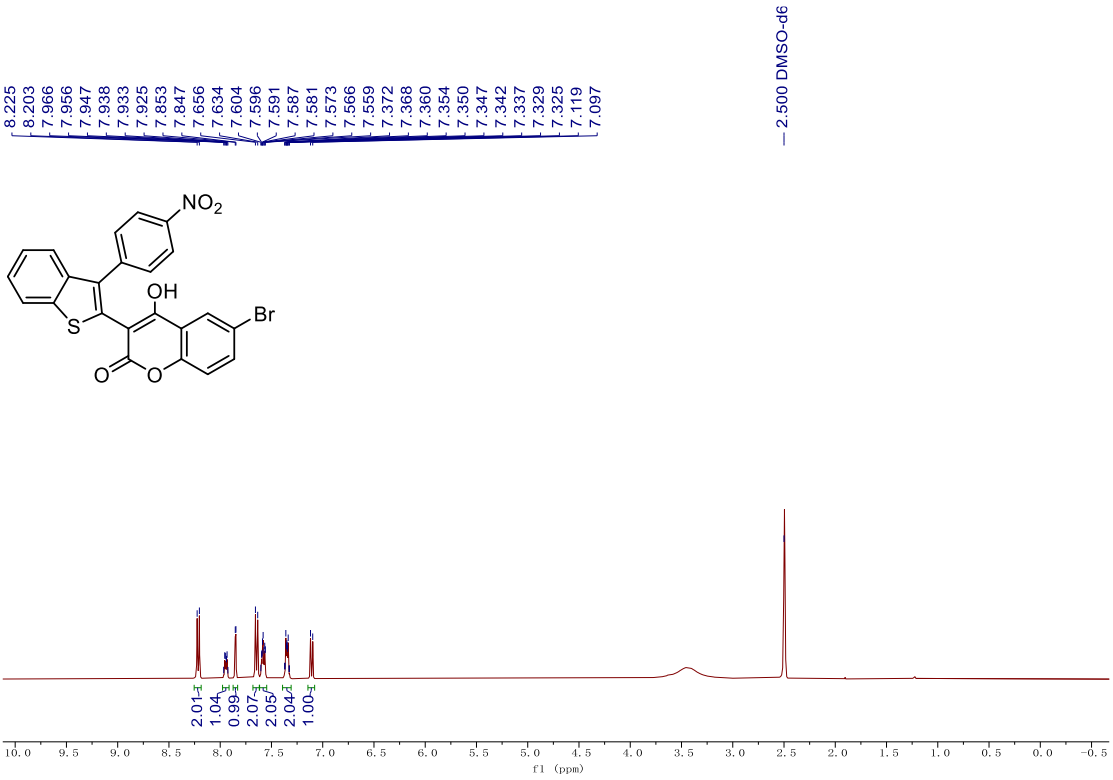
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **27**



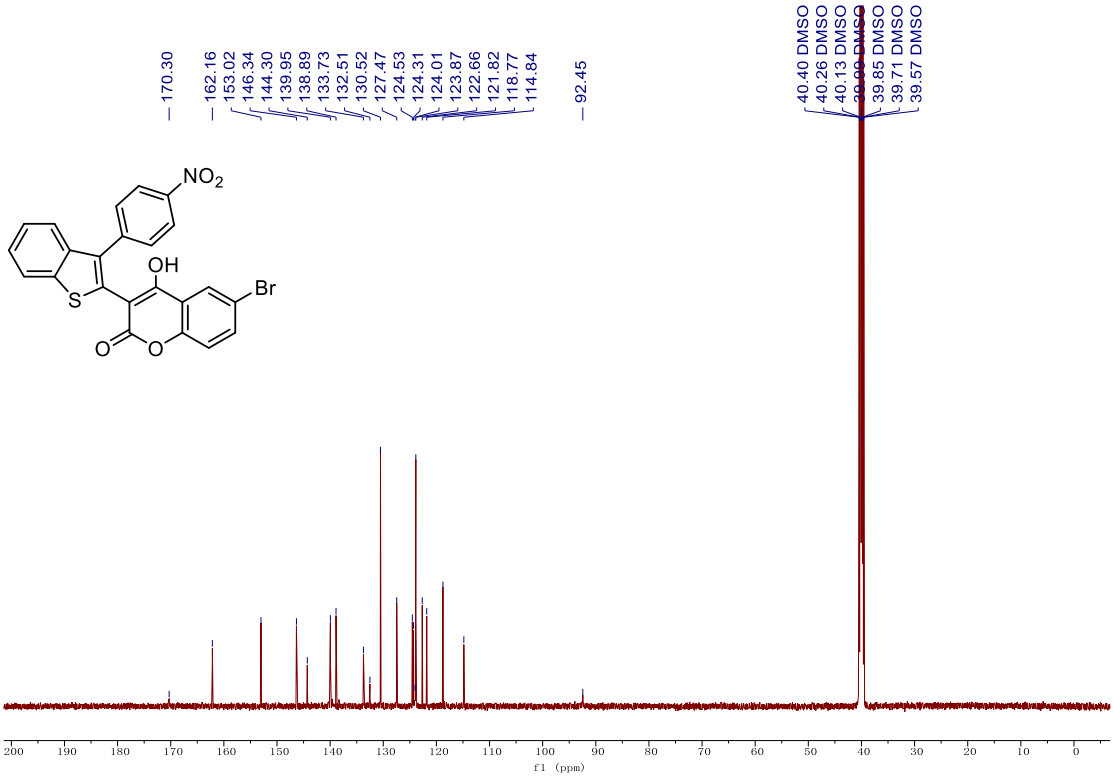
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **28**



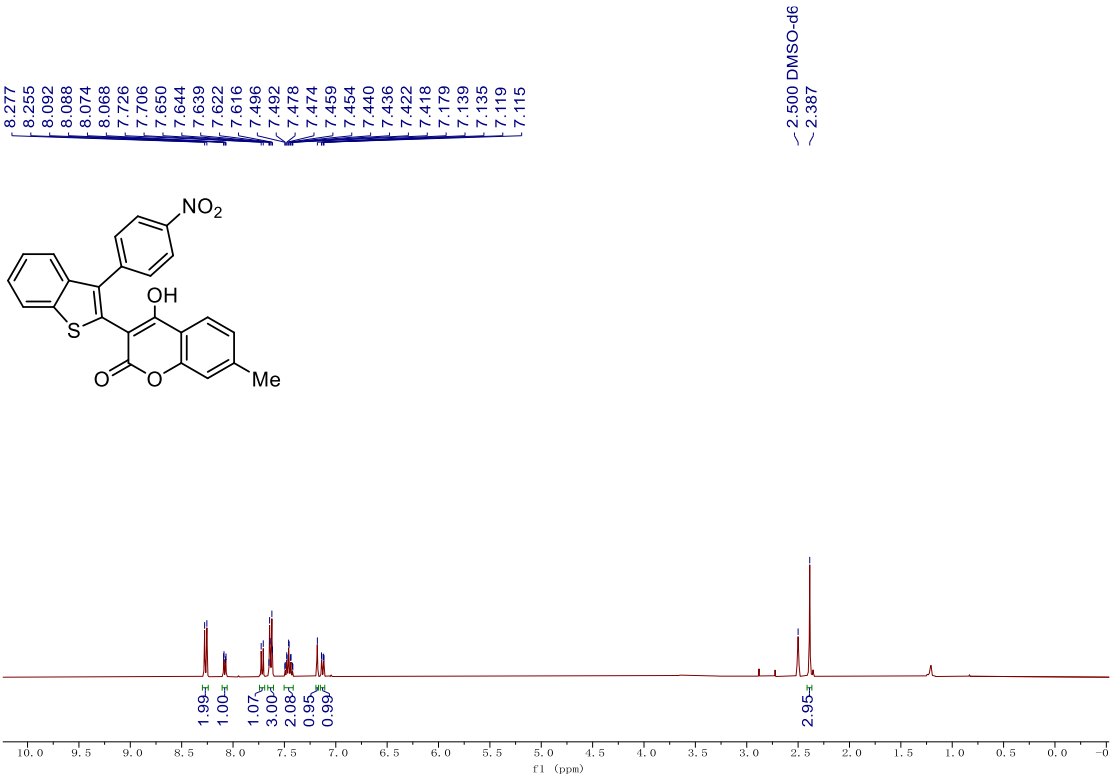
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **28**



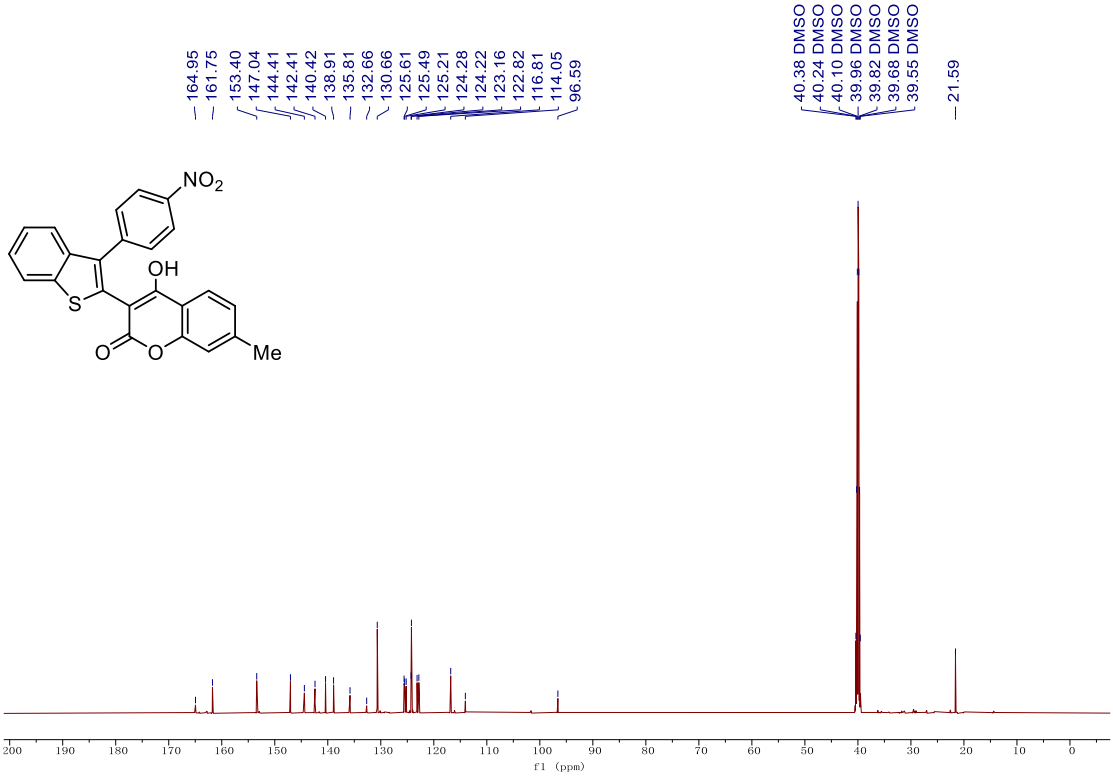
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **29**



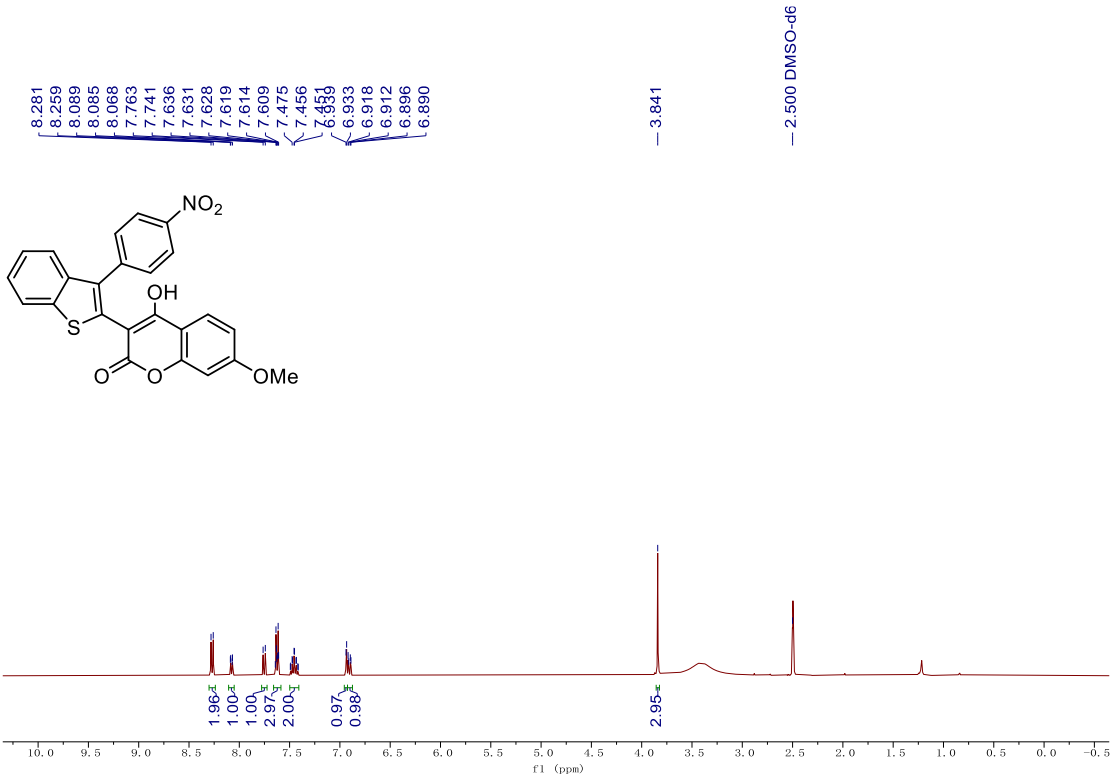
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **29**



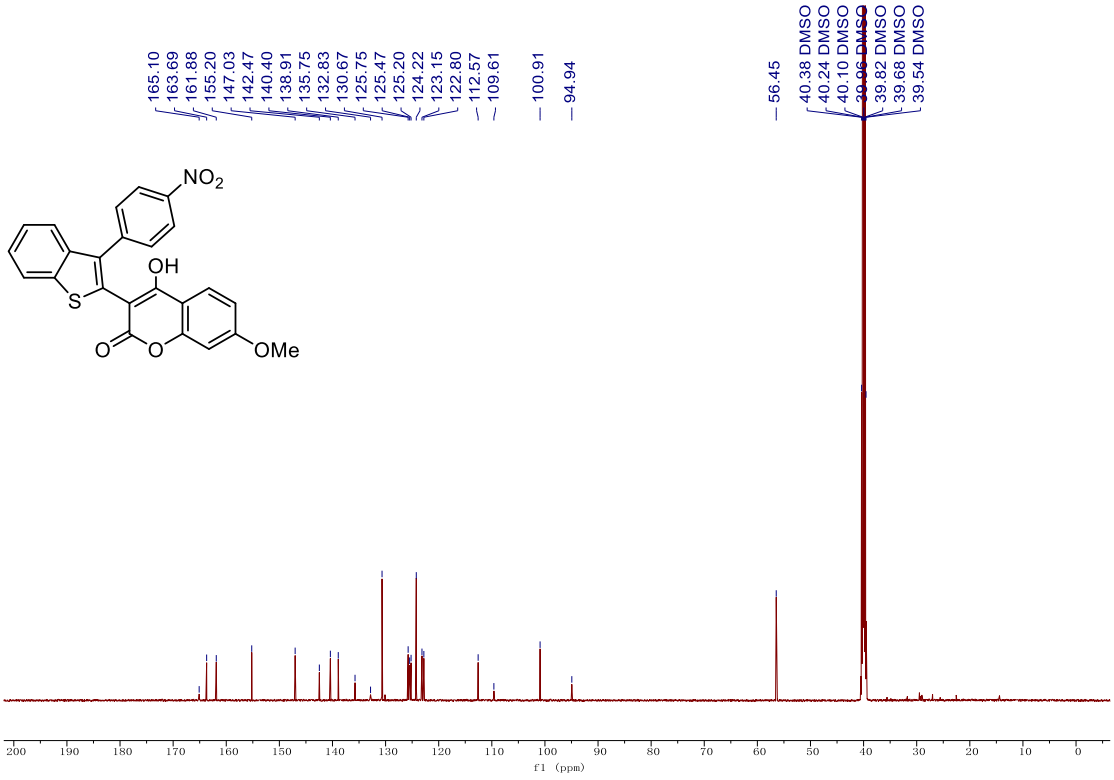
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **30**



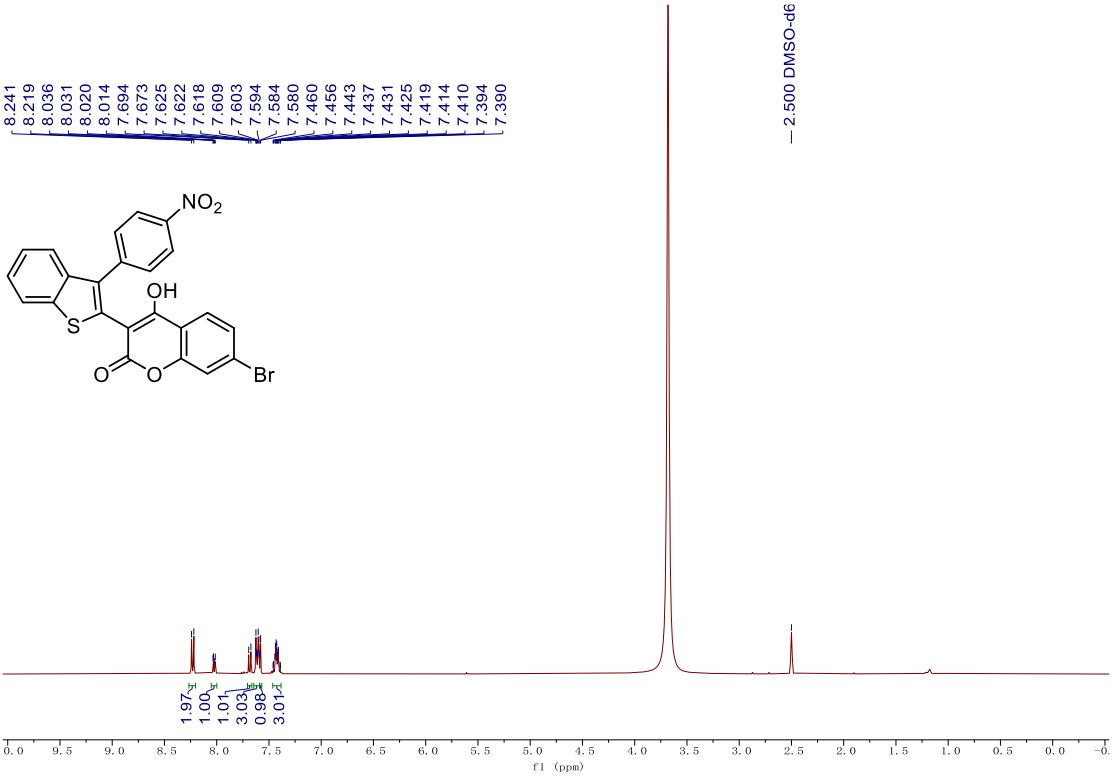
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **30**



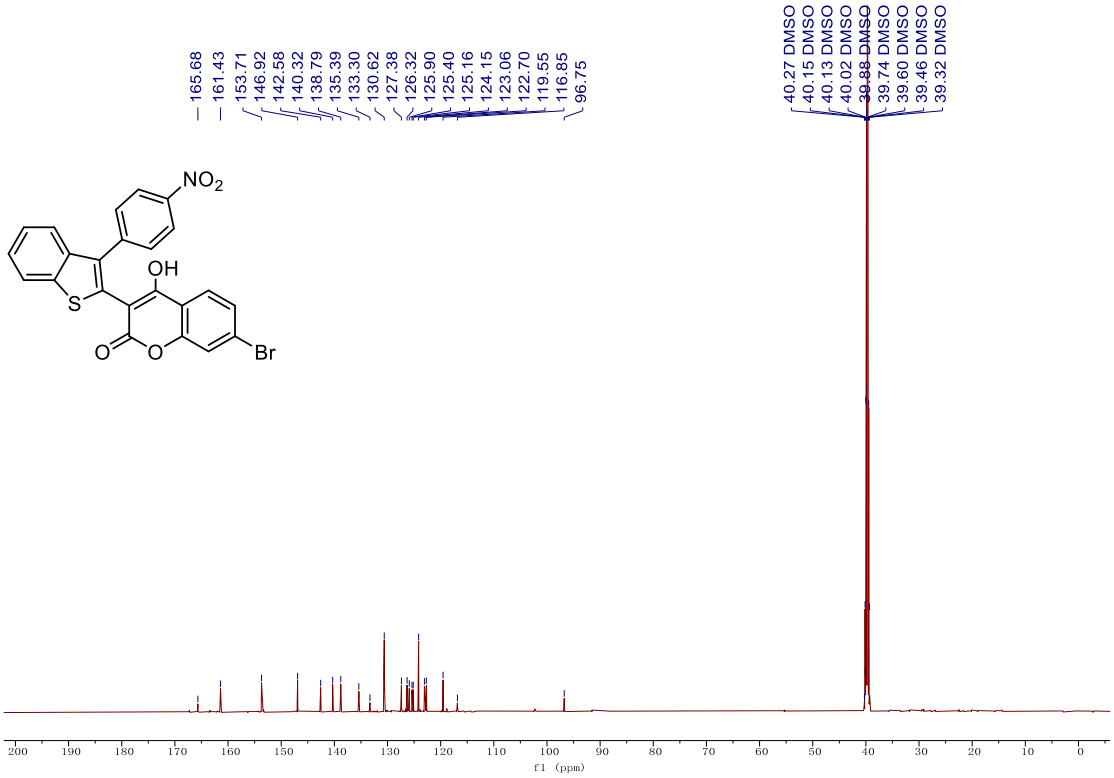
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **31**



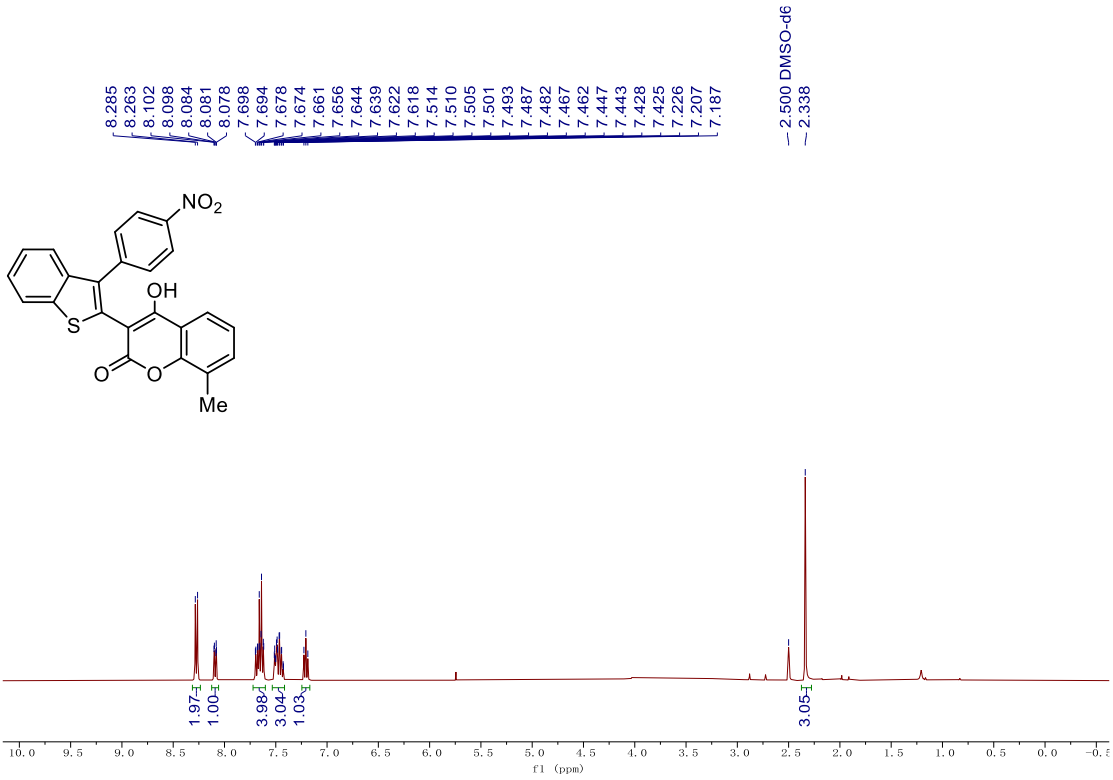
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **31**



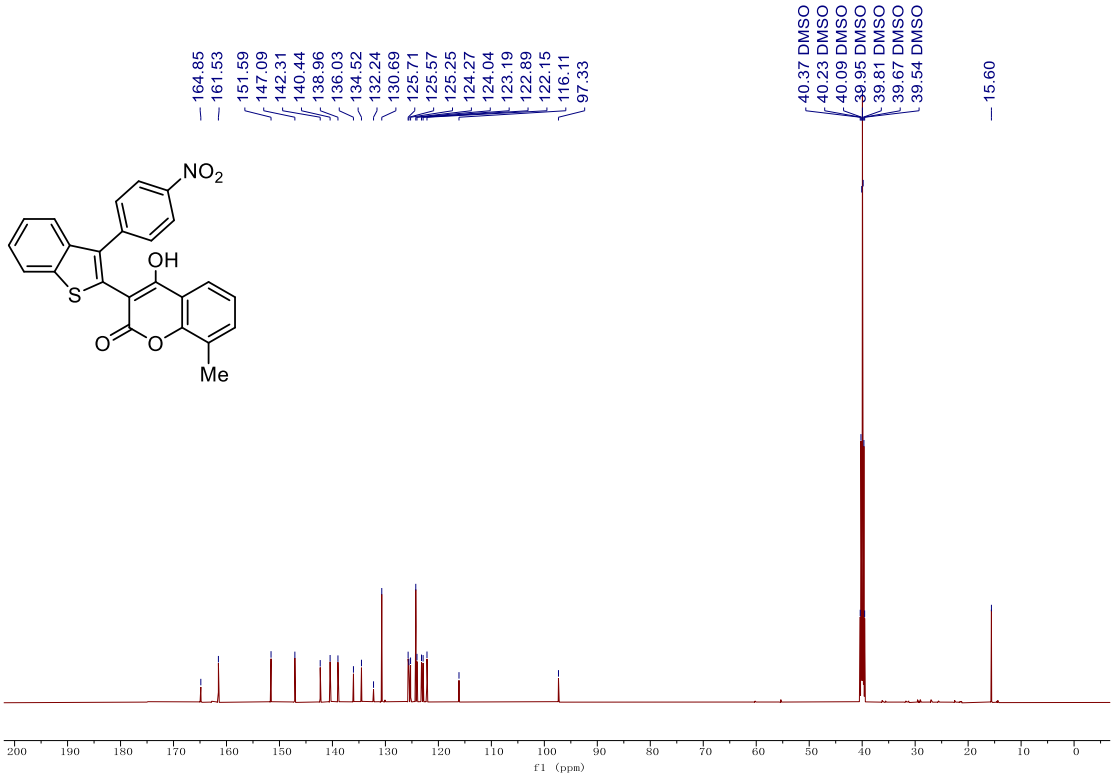
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **32**



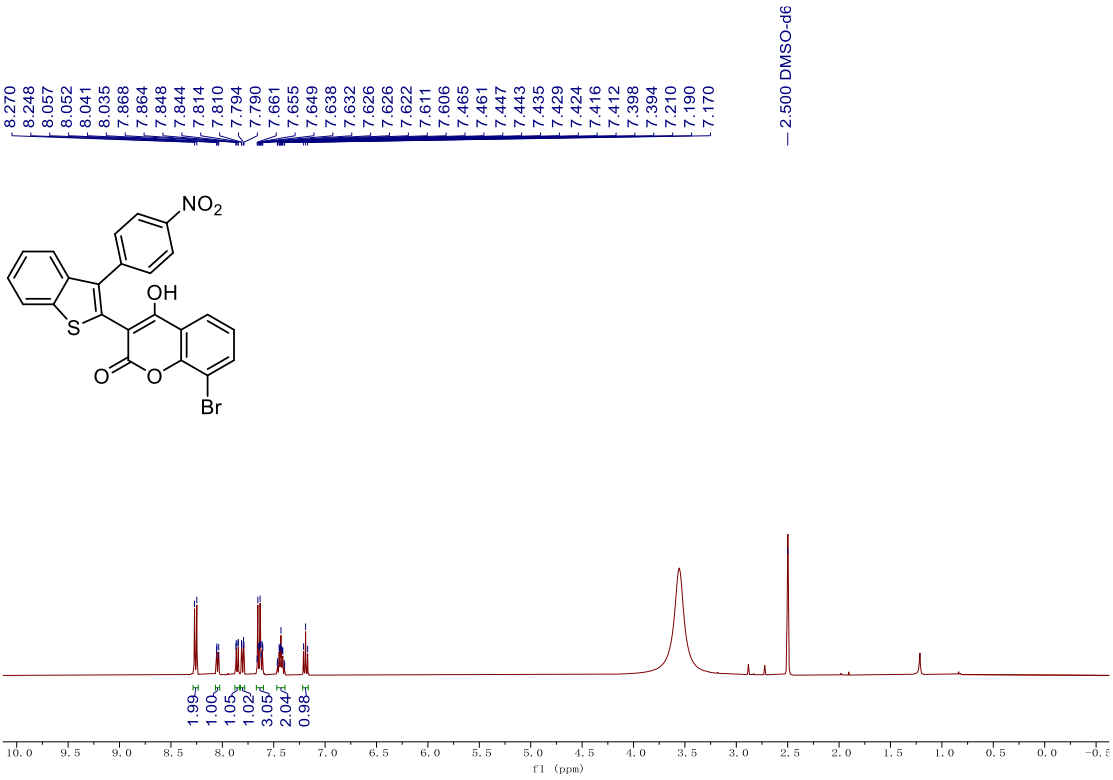
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **32**



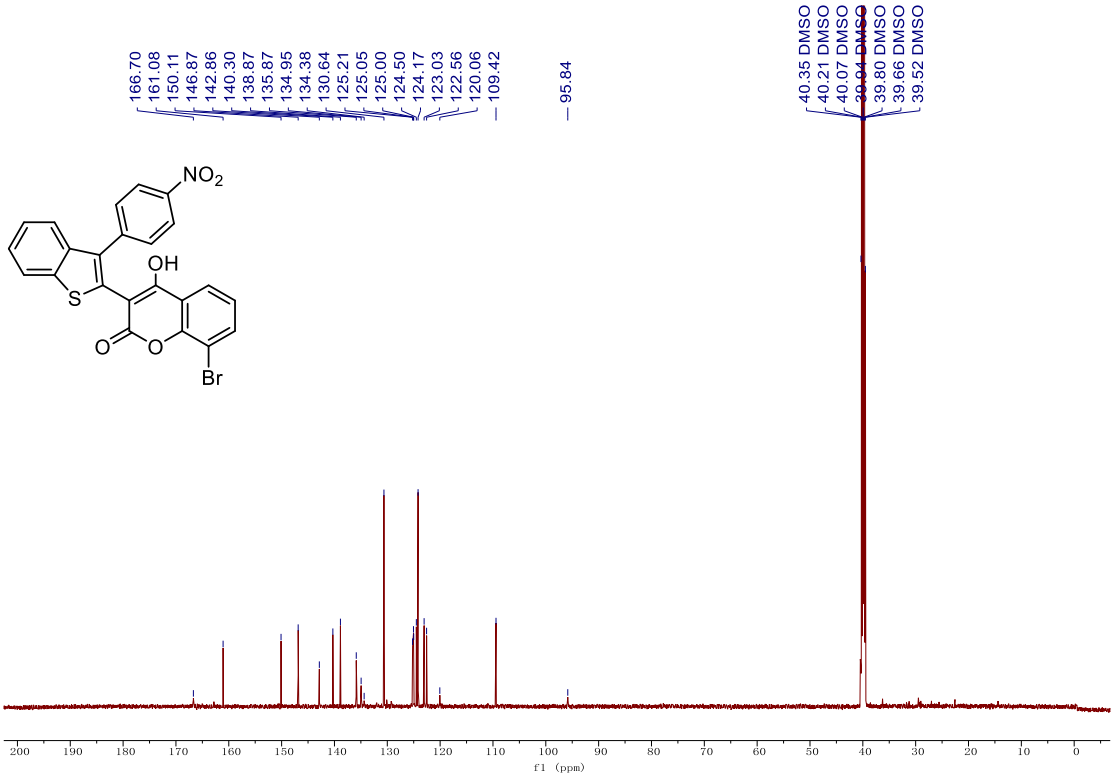
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **33**



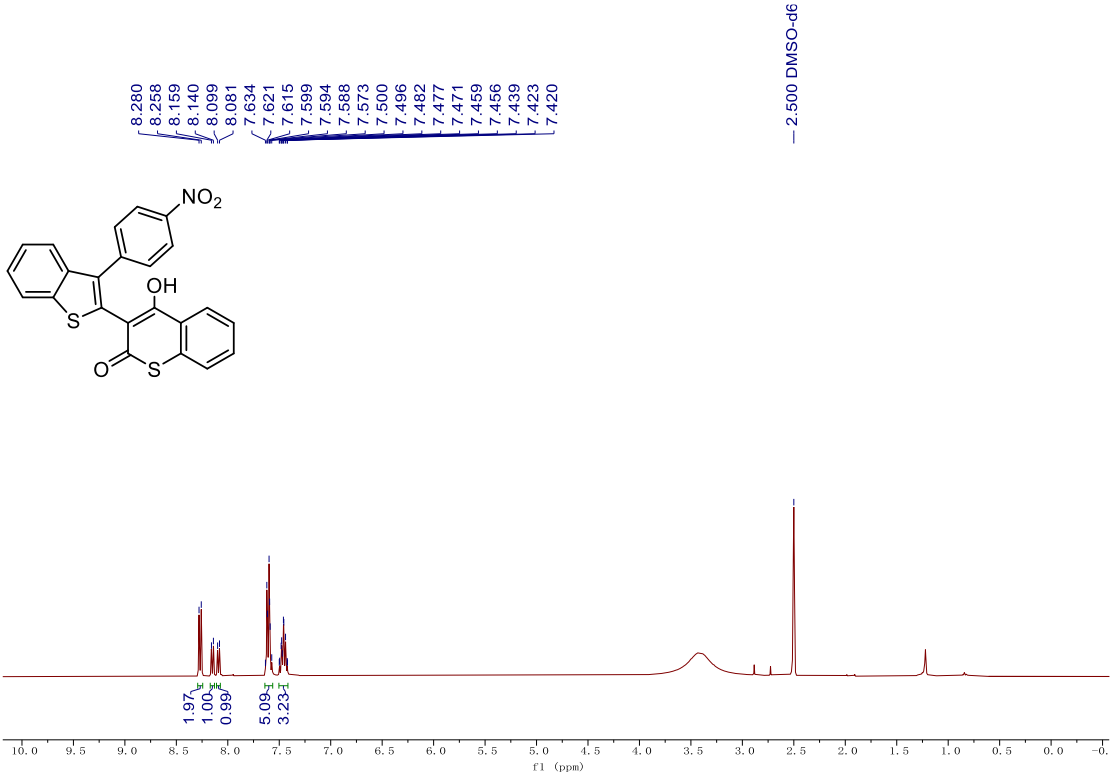
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **33**



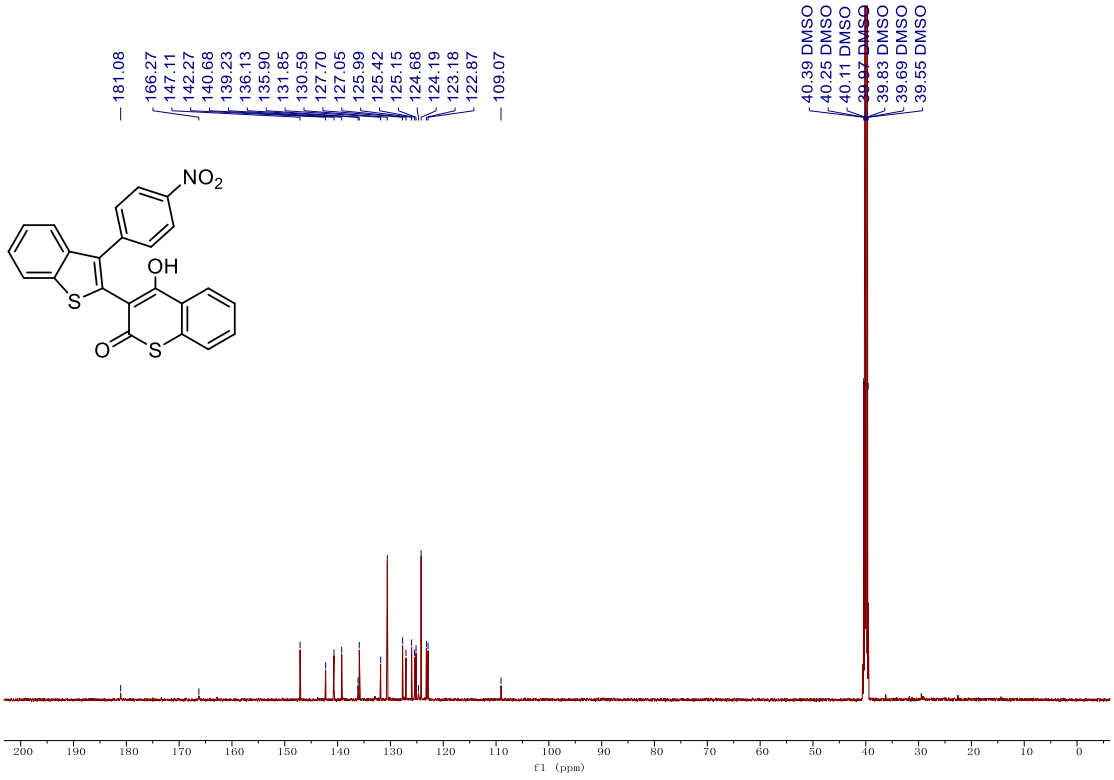
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **34**



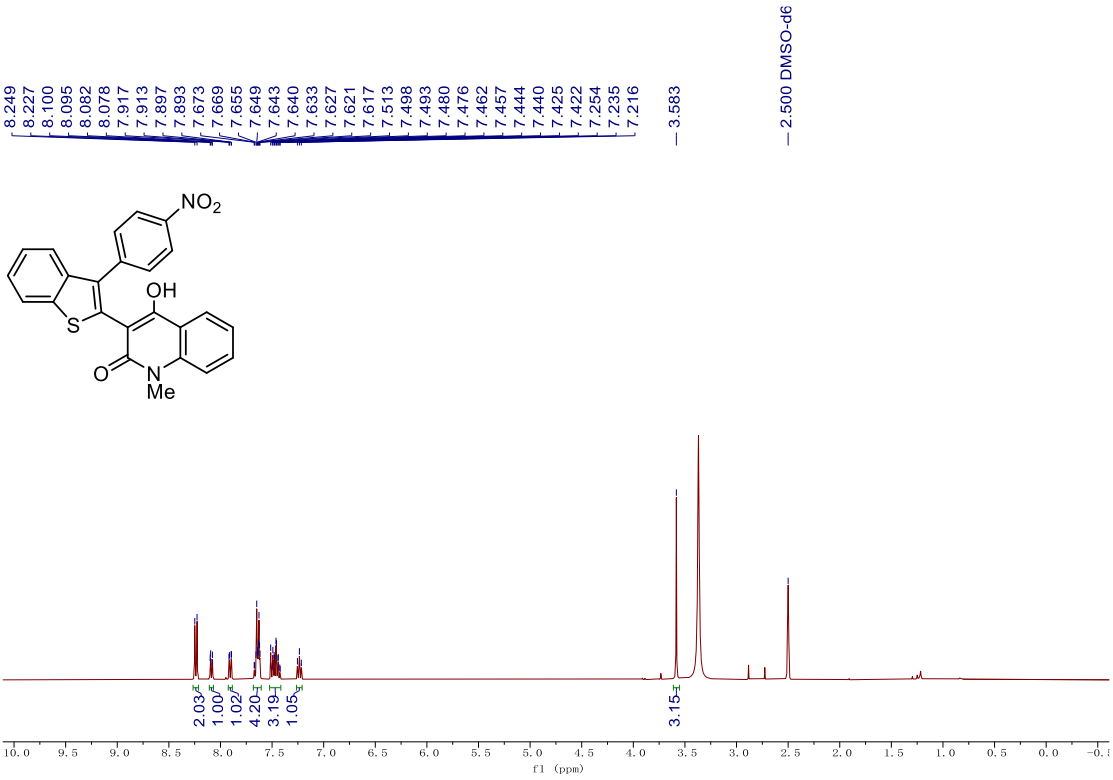
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **34**



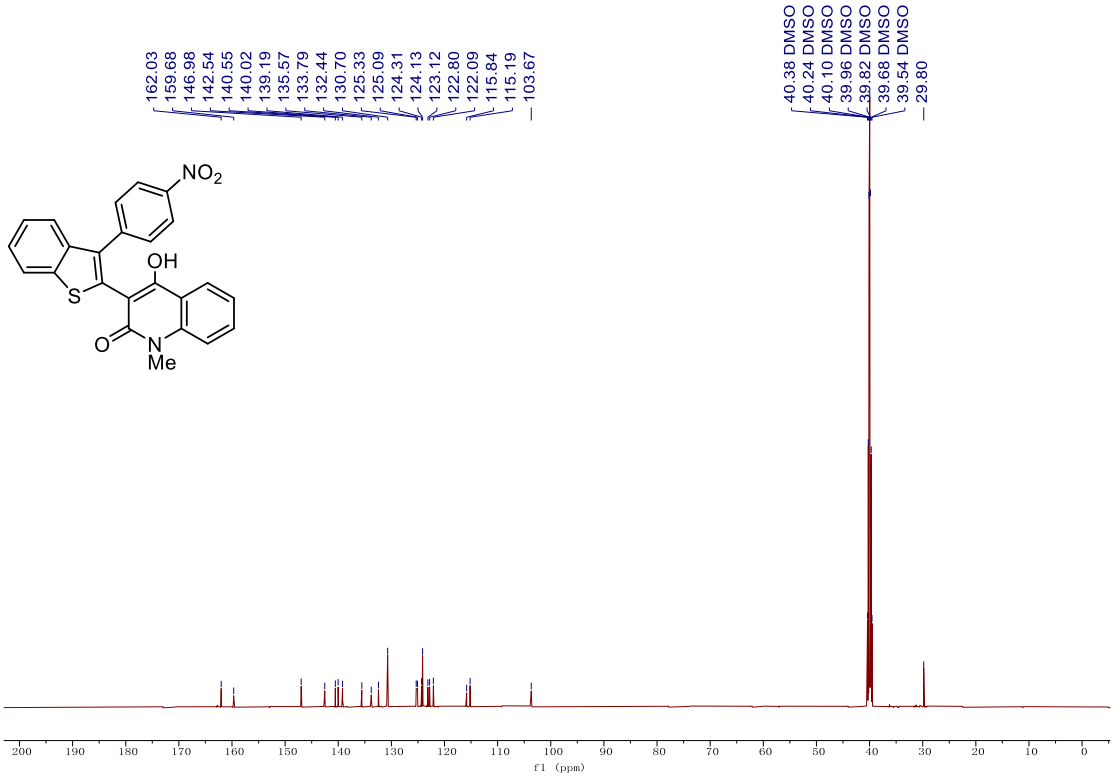
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **35**



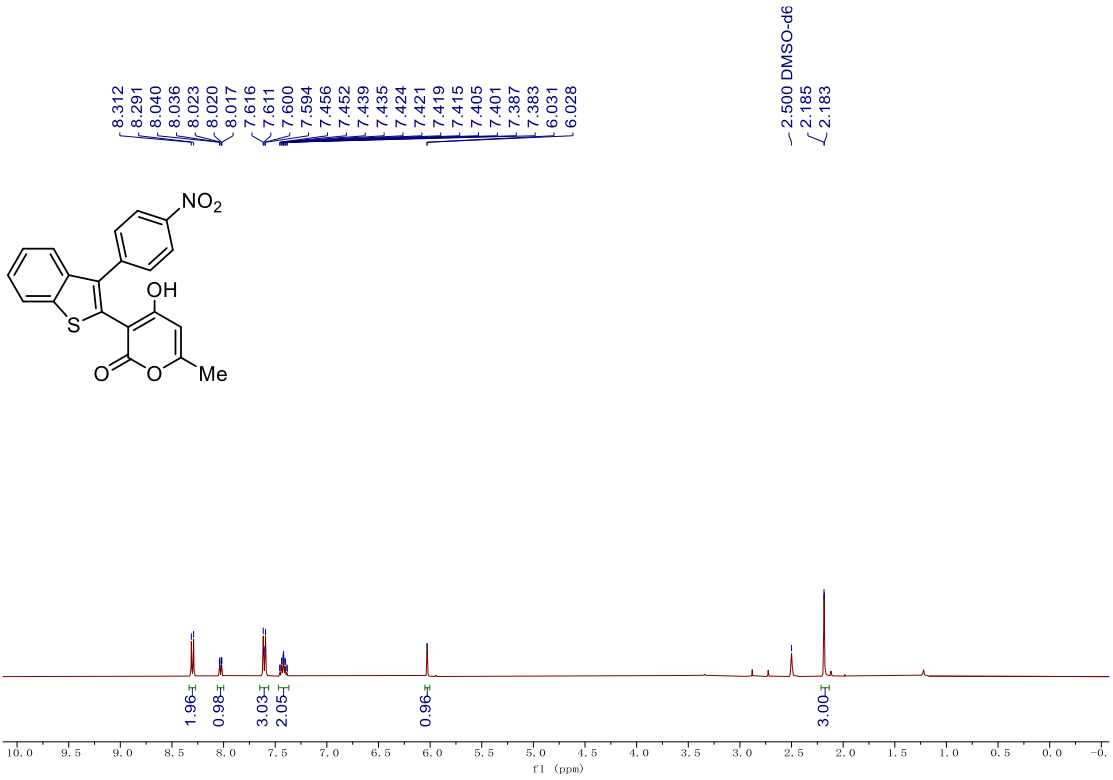
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **35**



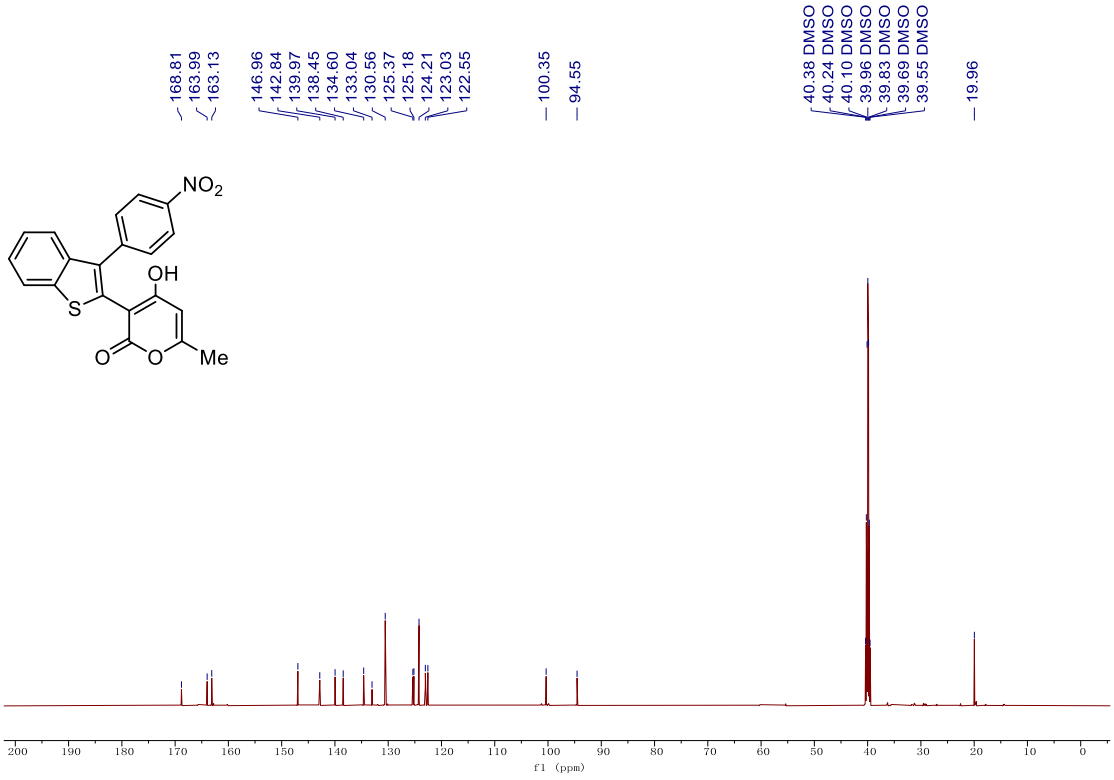
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **36**



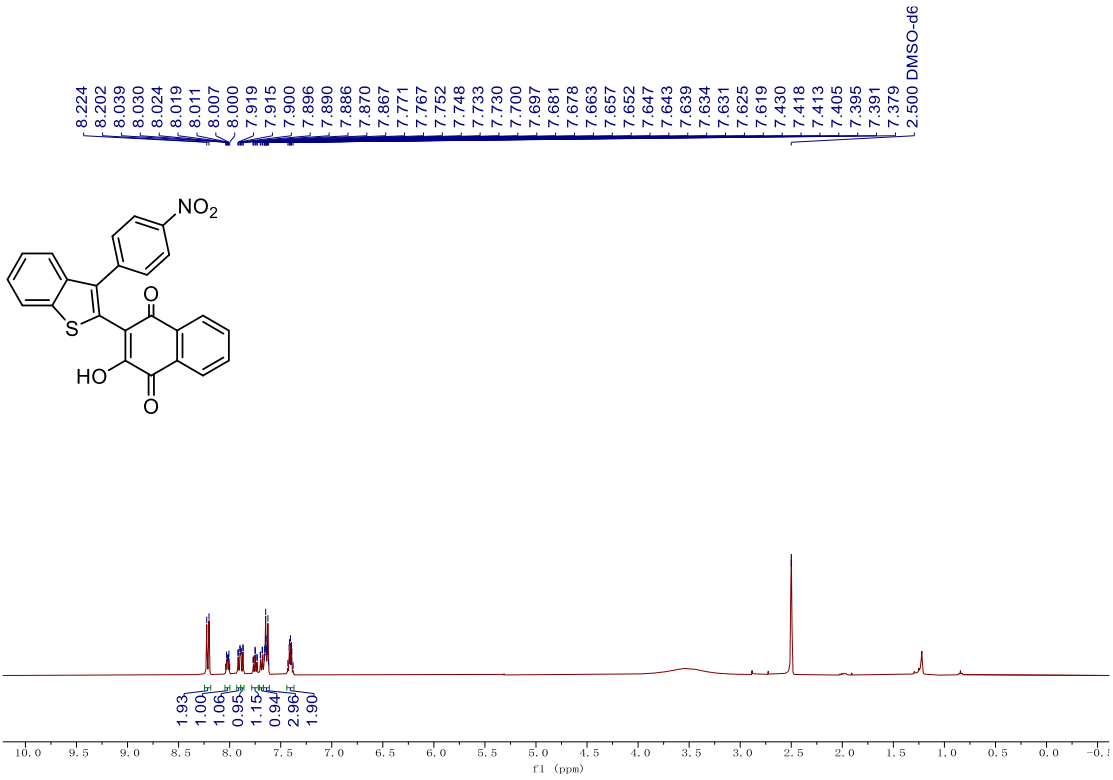
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **36**



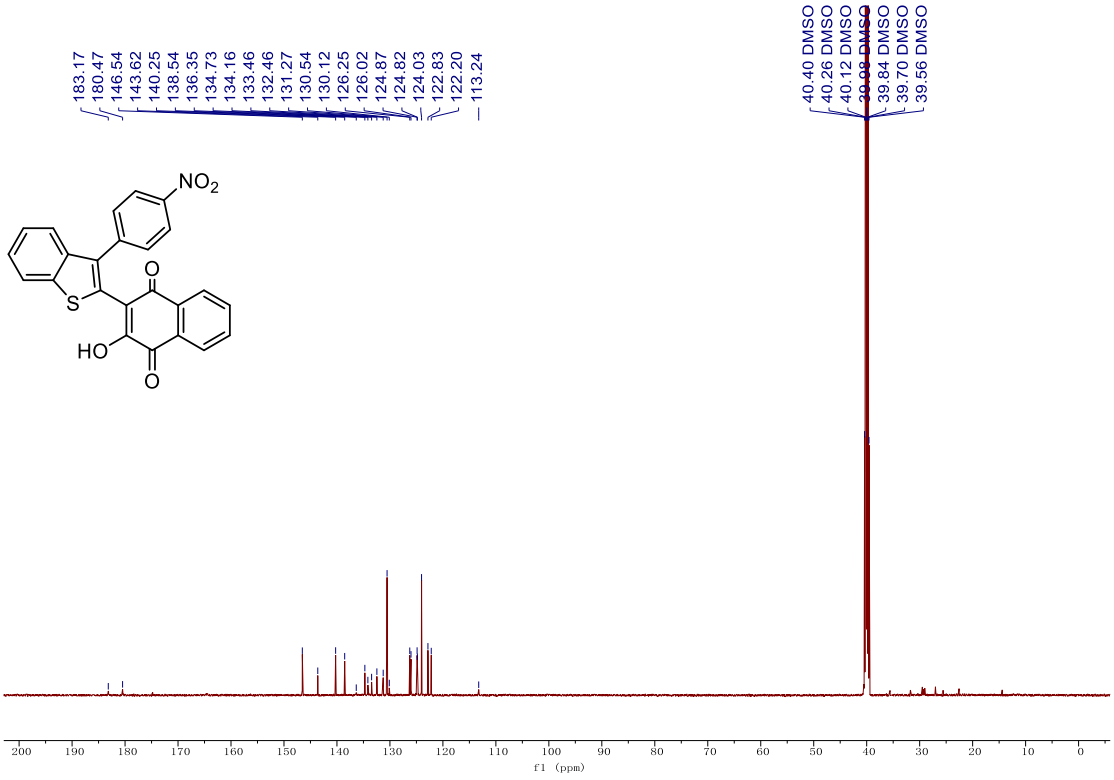
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **37**



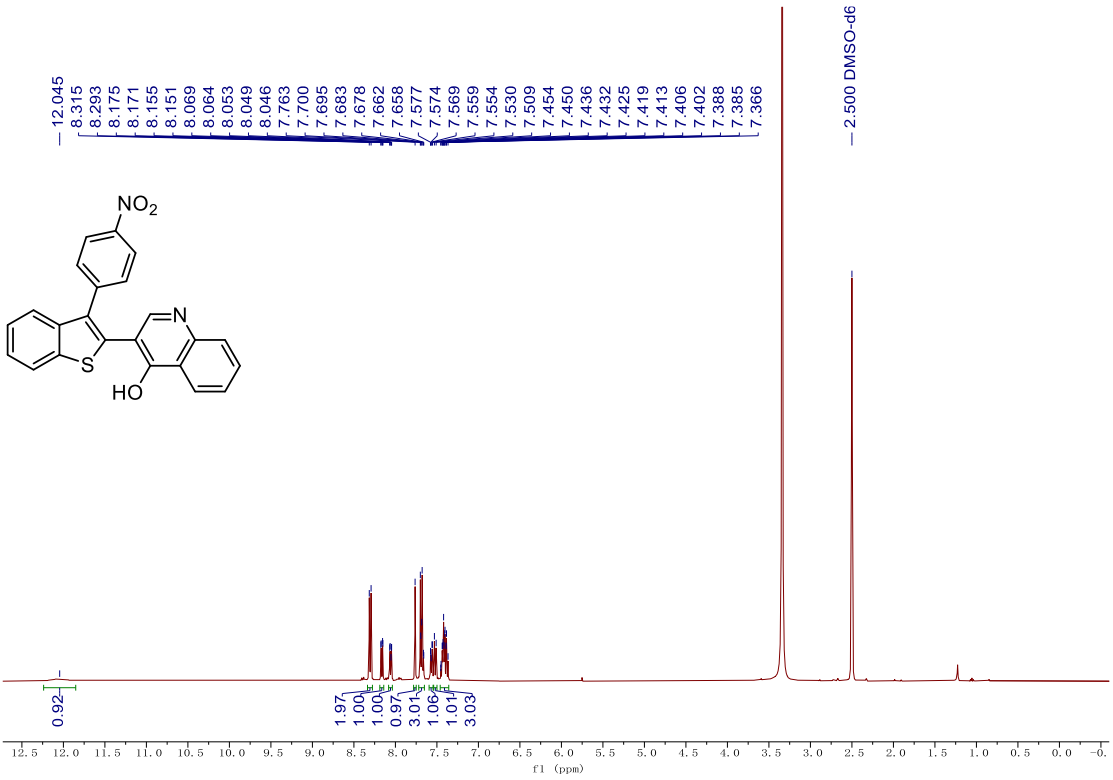
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **37**



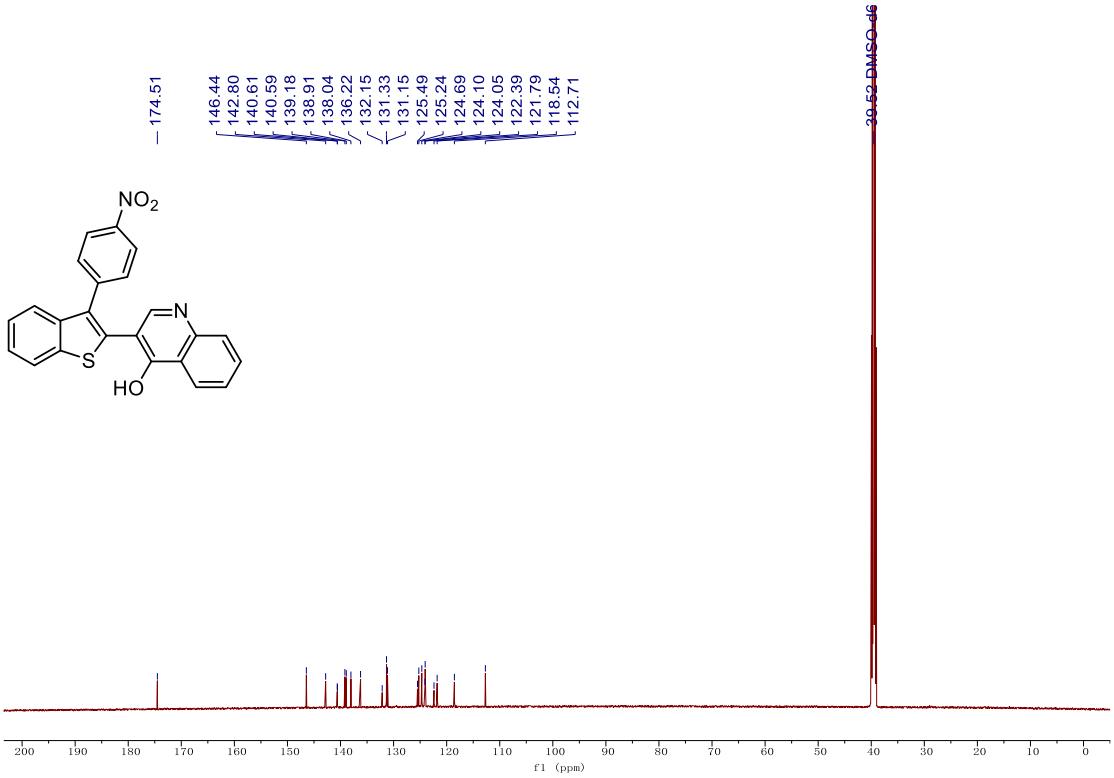
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **40**



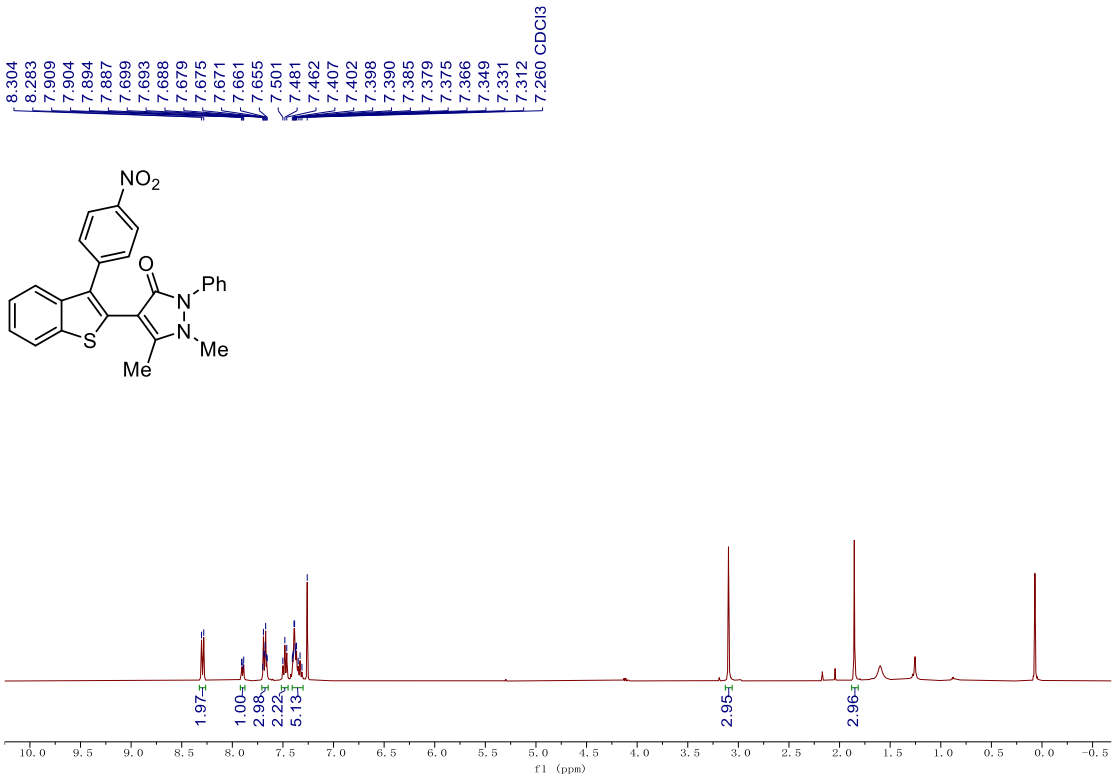
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **40**



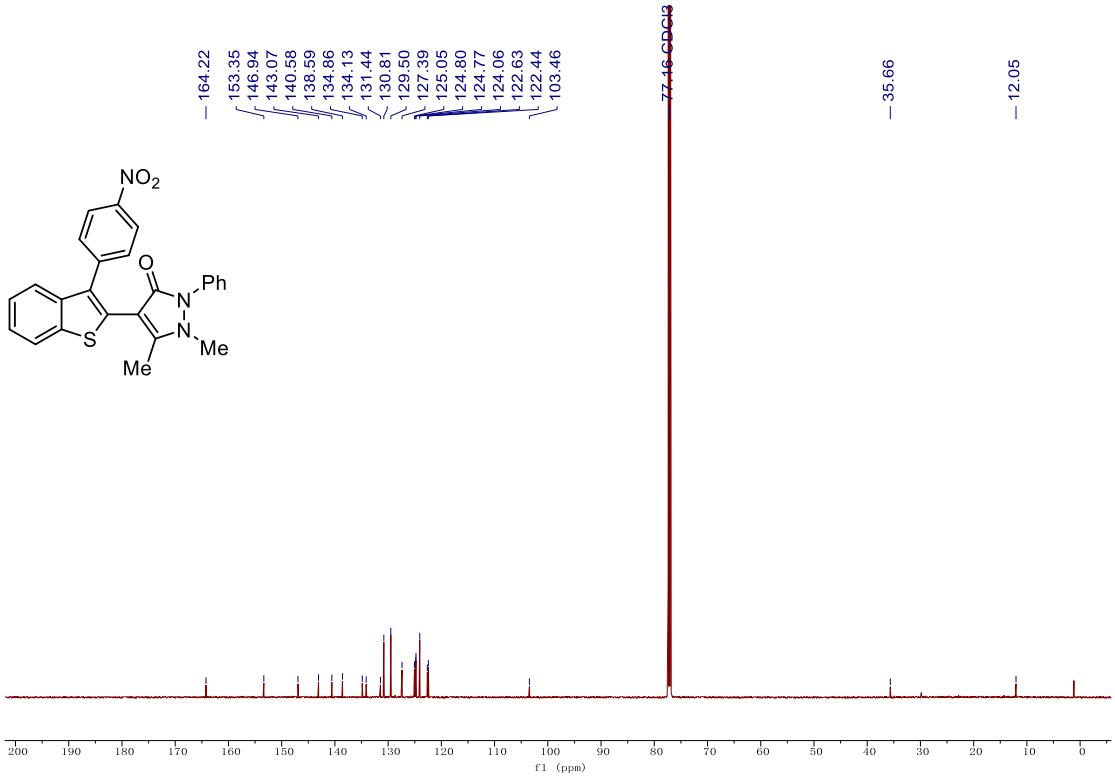
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **41**



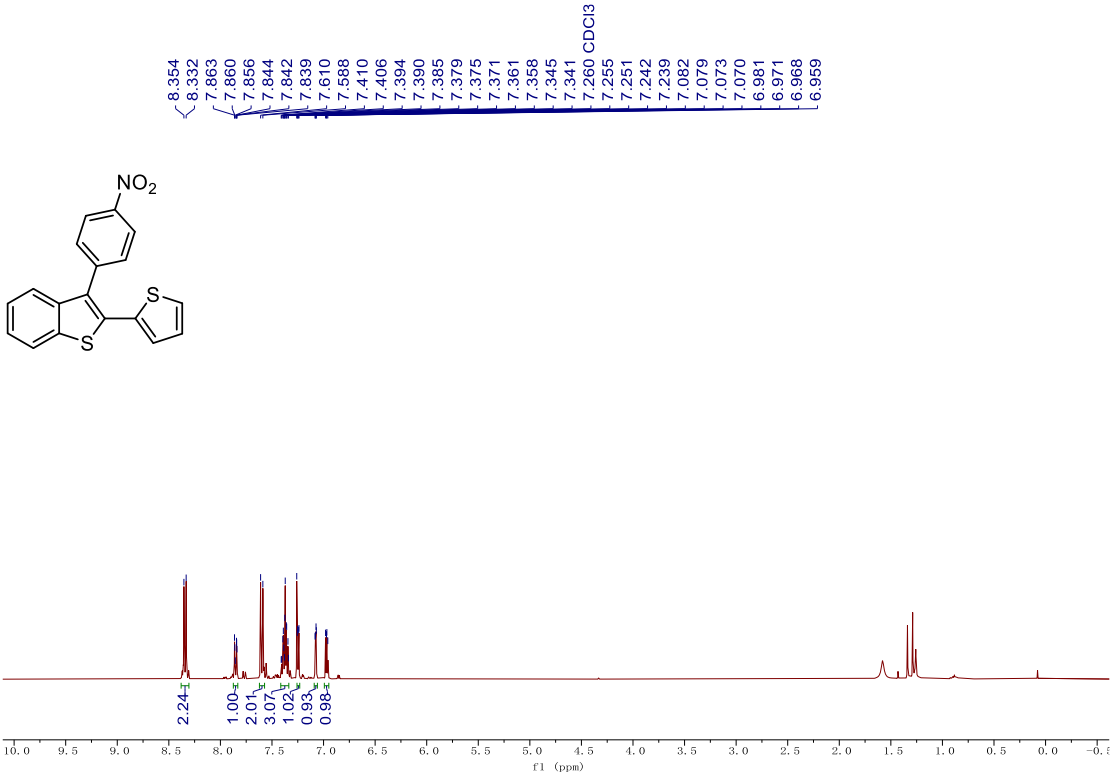
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **41**



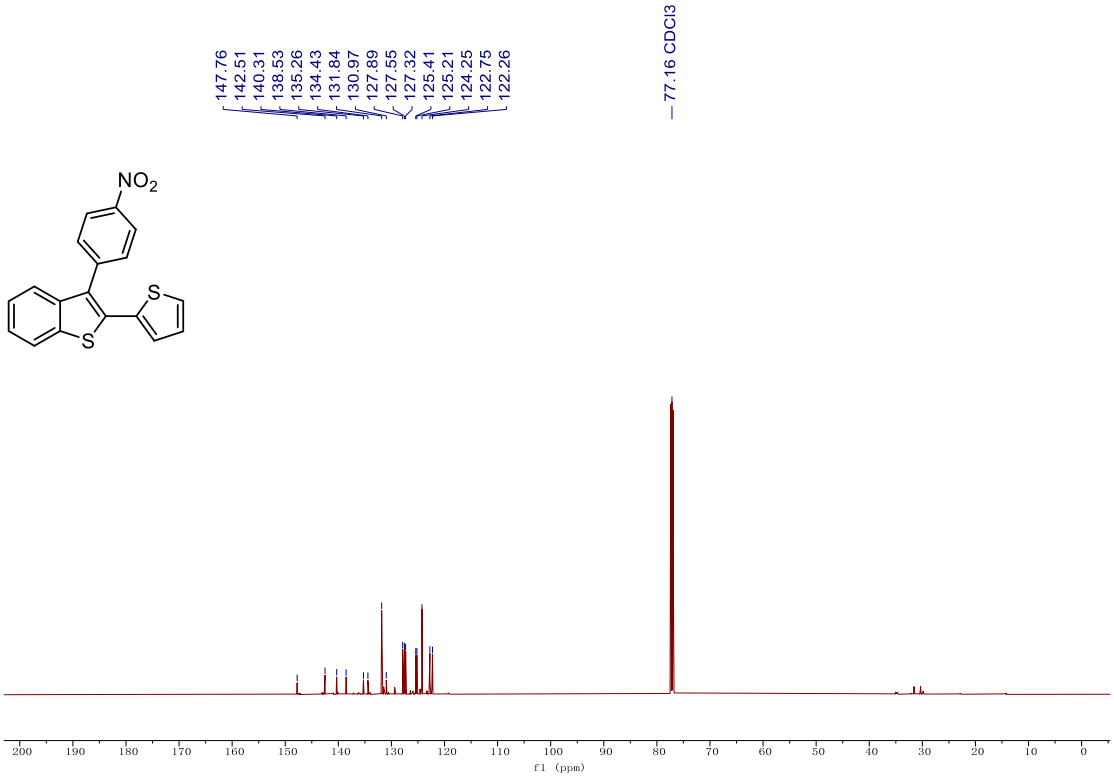
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **42**



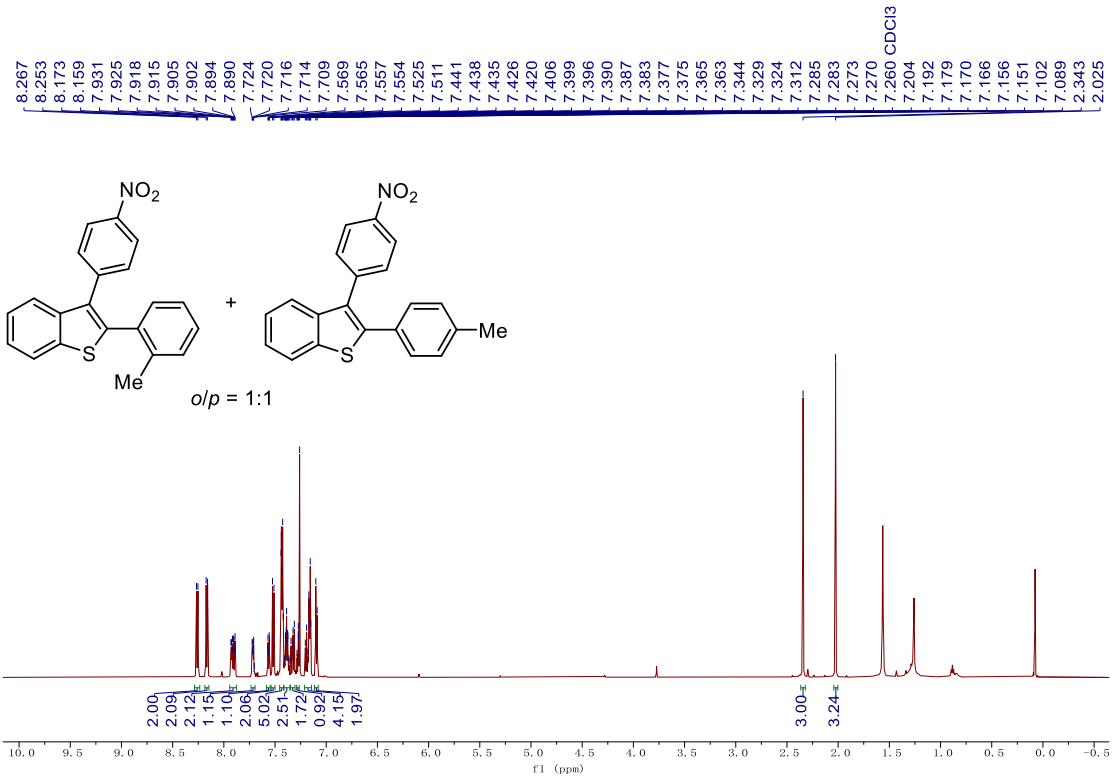
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **42**



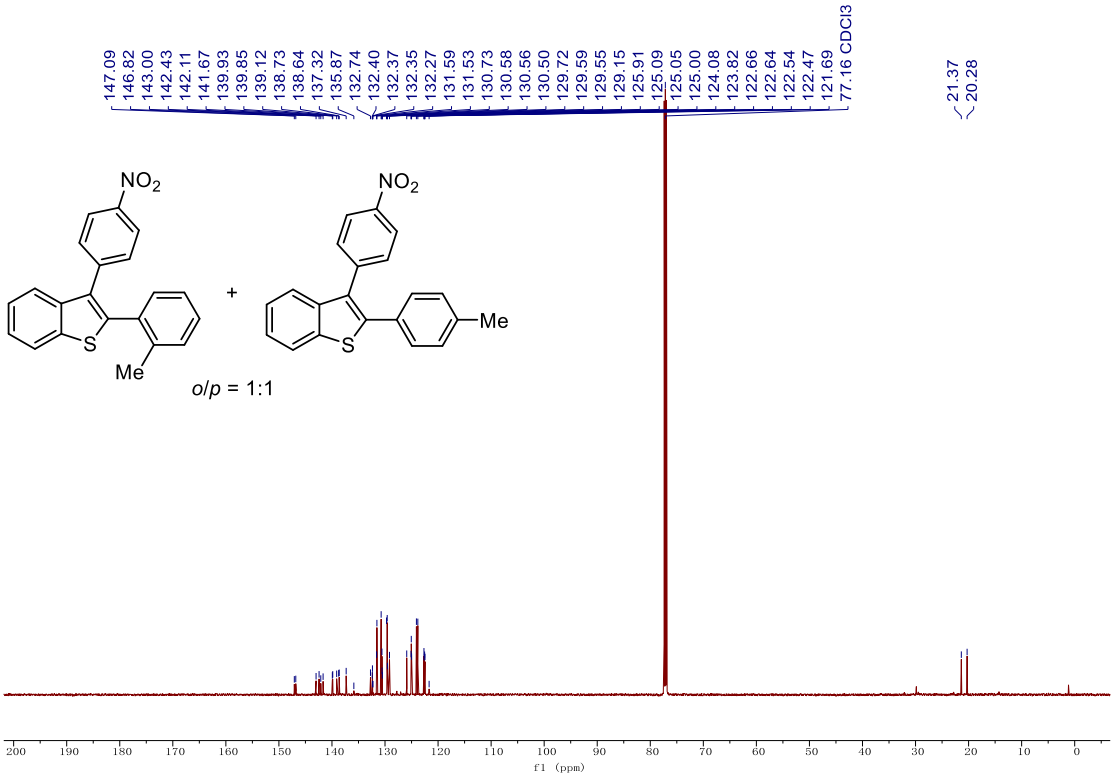
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **43**



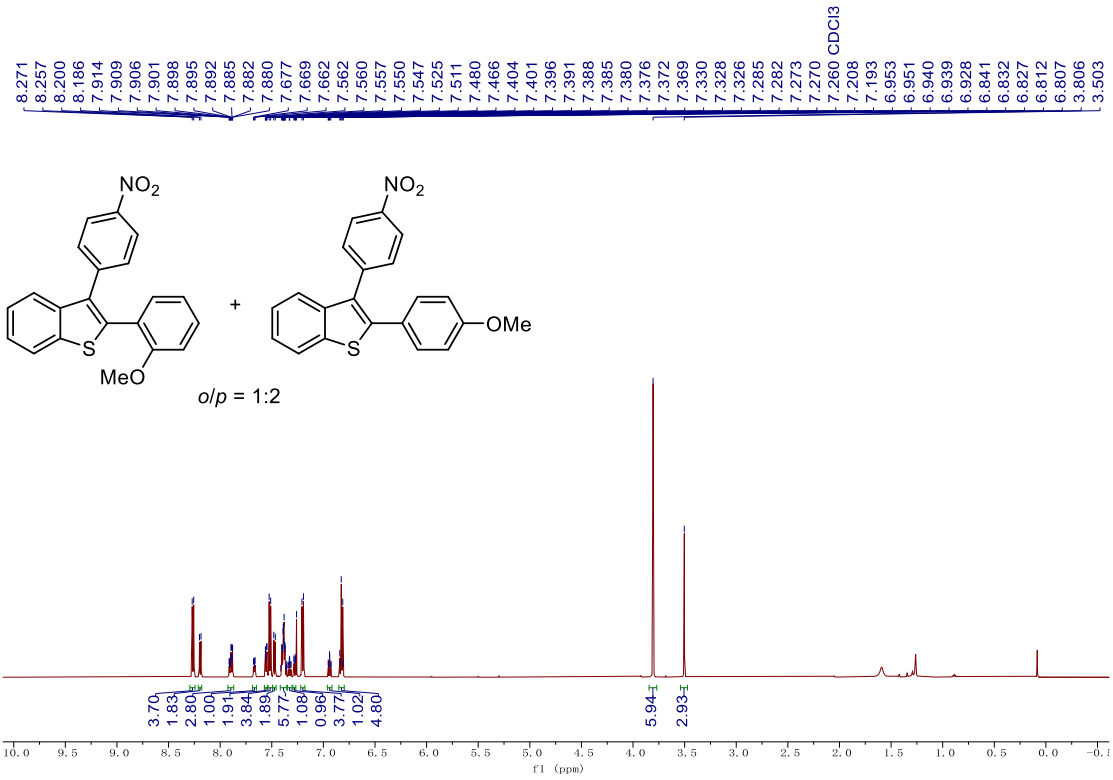
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **43**



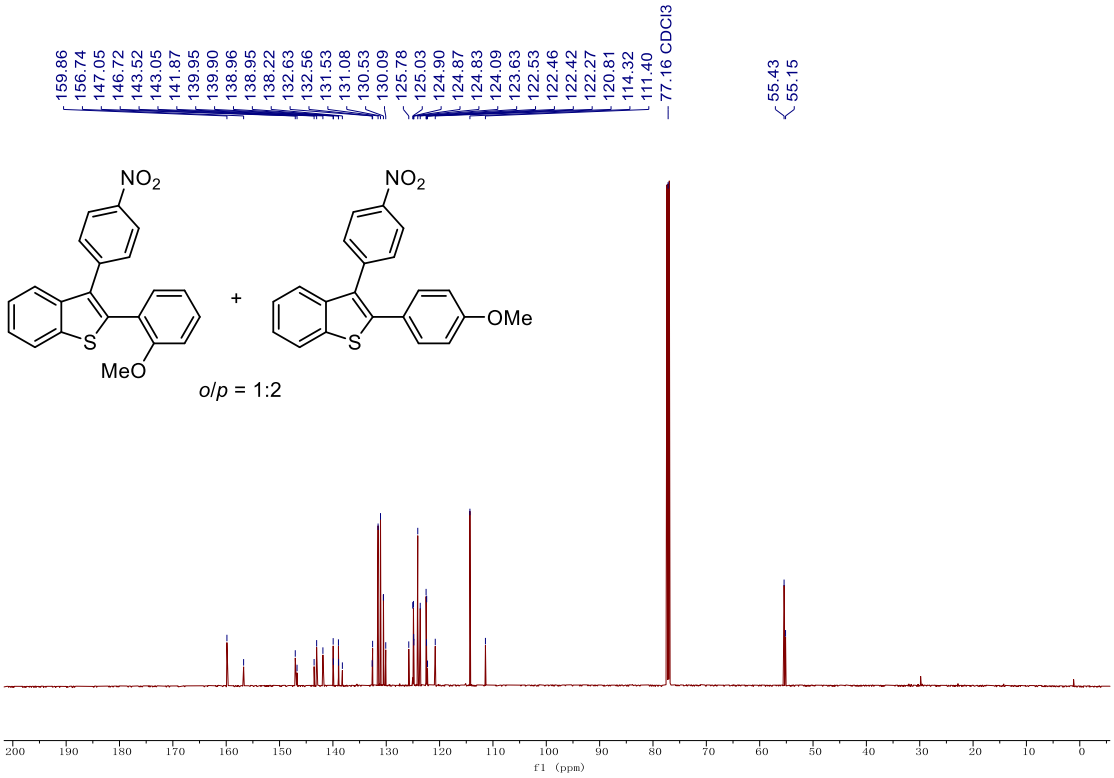
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **44**



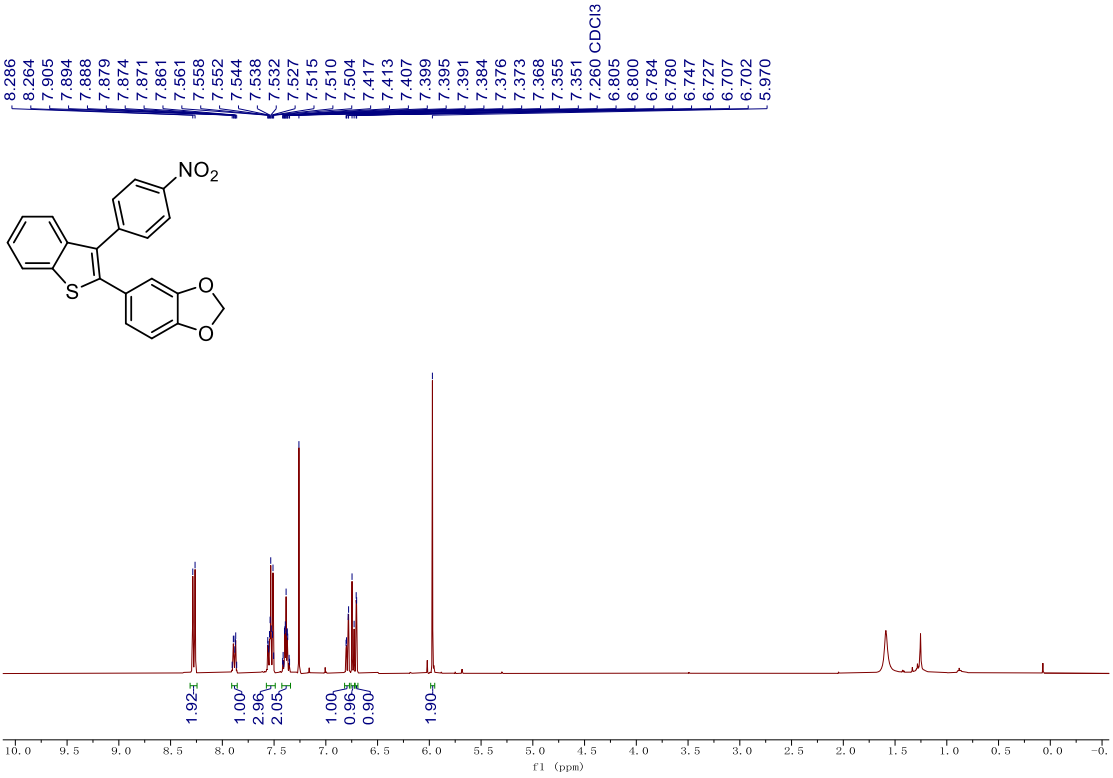
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **44**



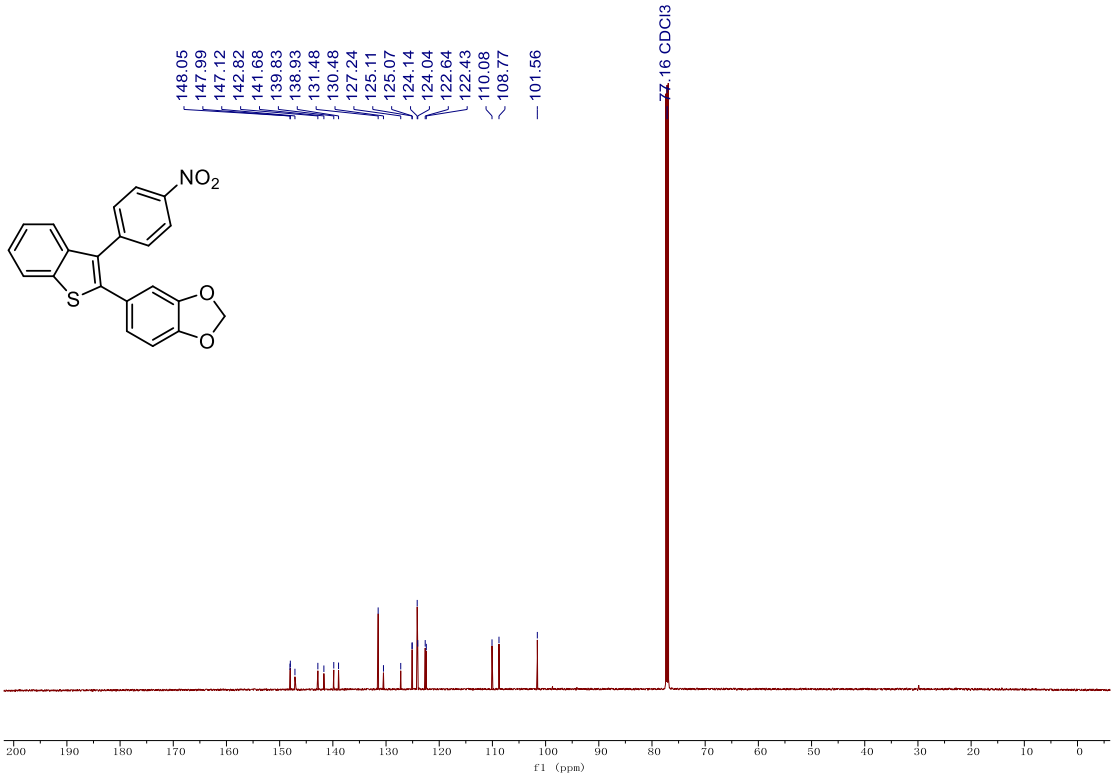
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **45**



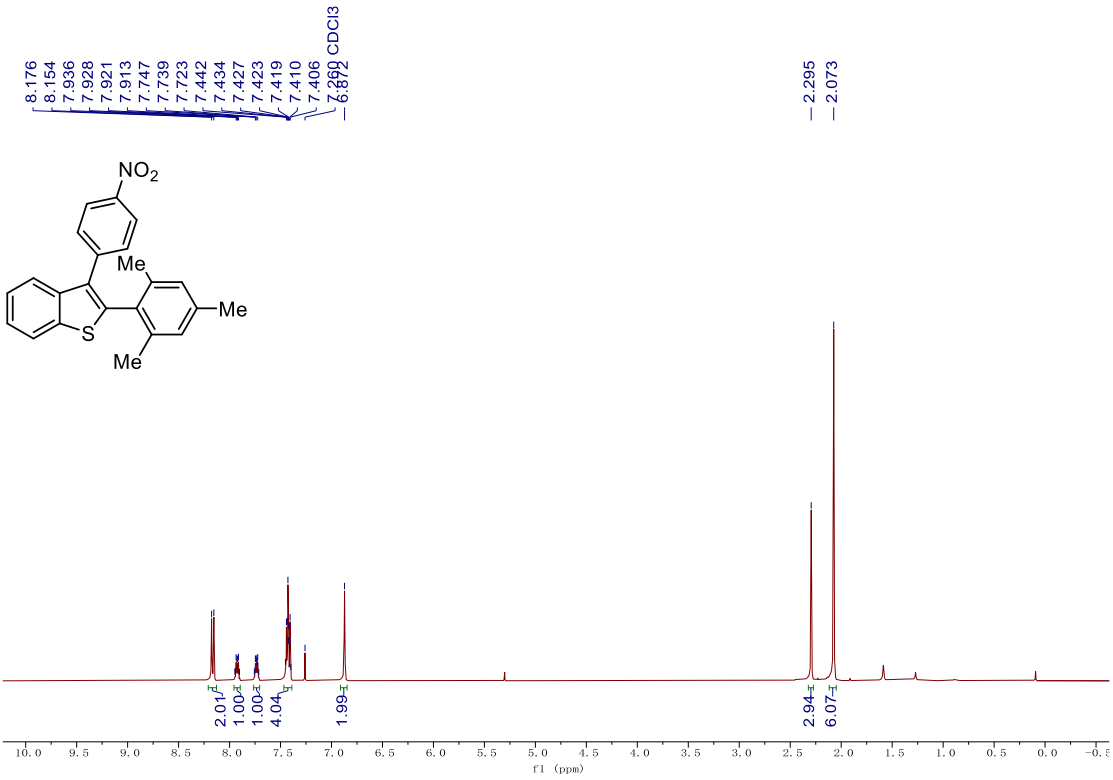
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **45**



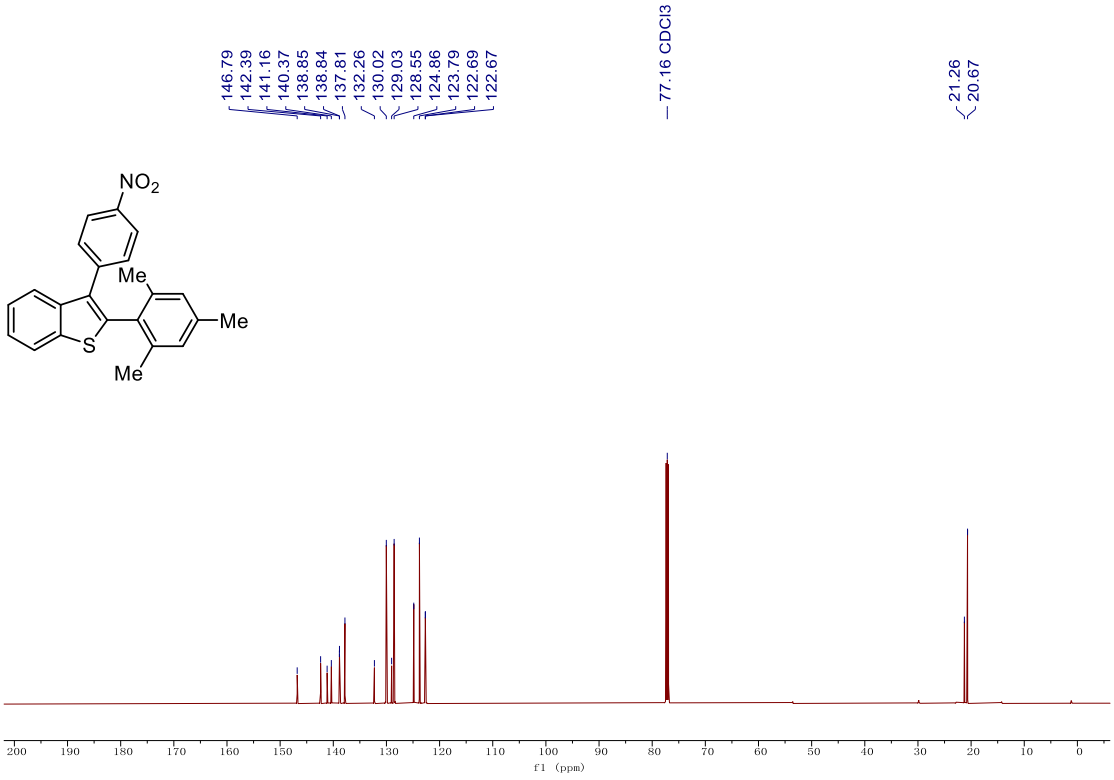
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **46**



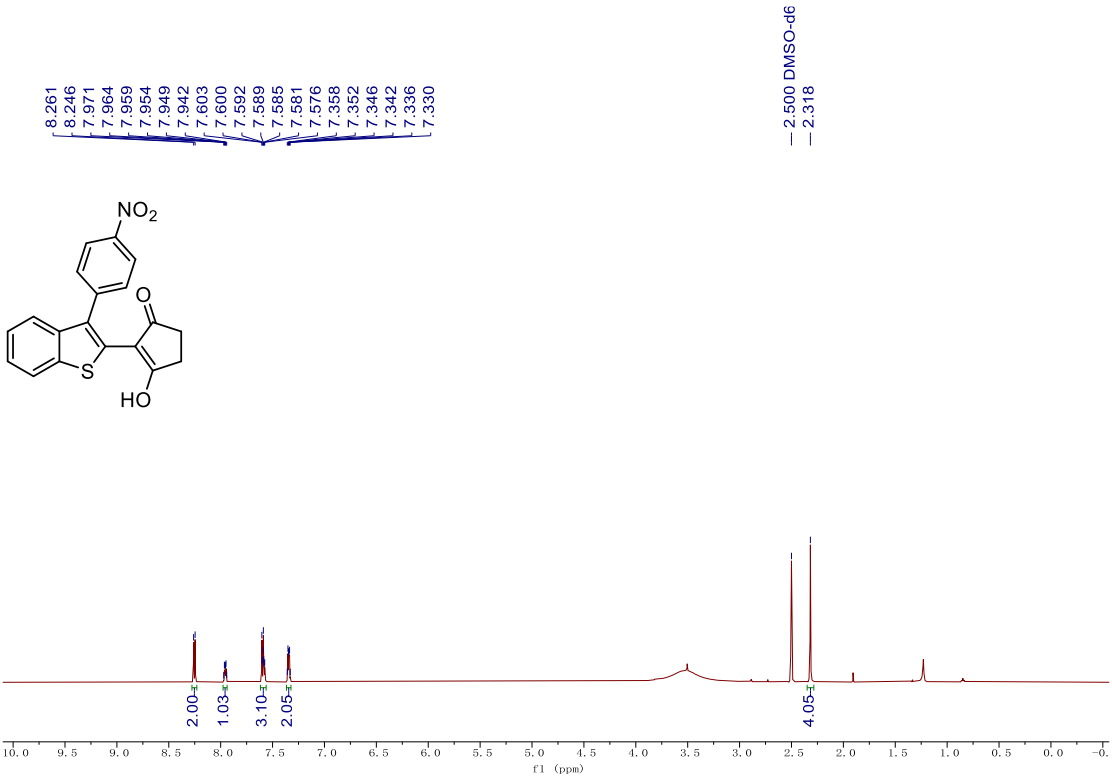
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **46**



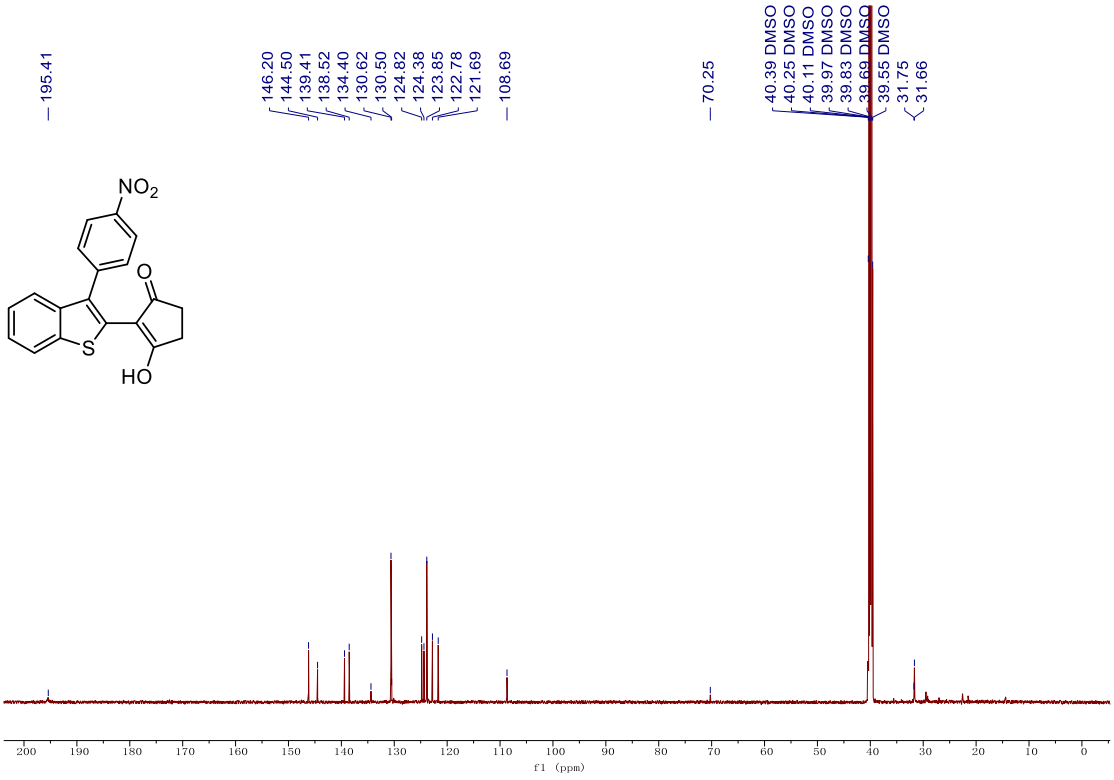
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **47**



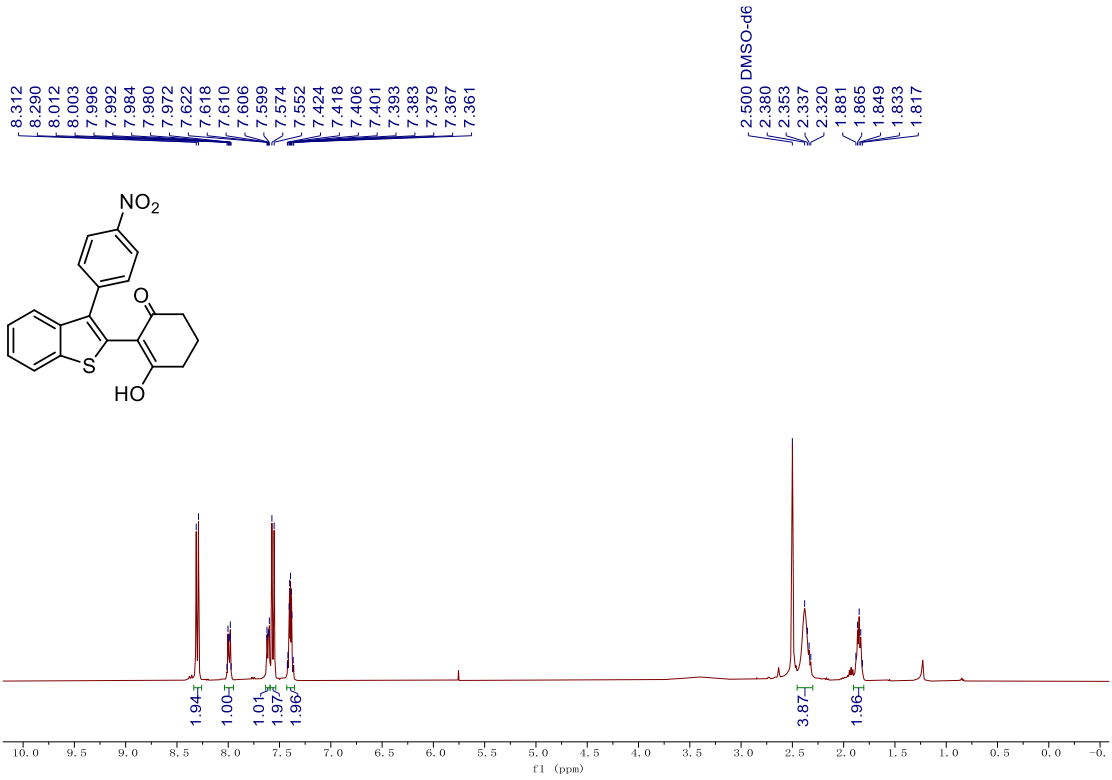
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **47**



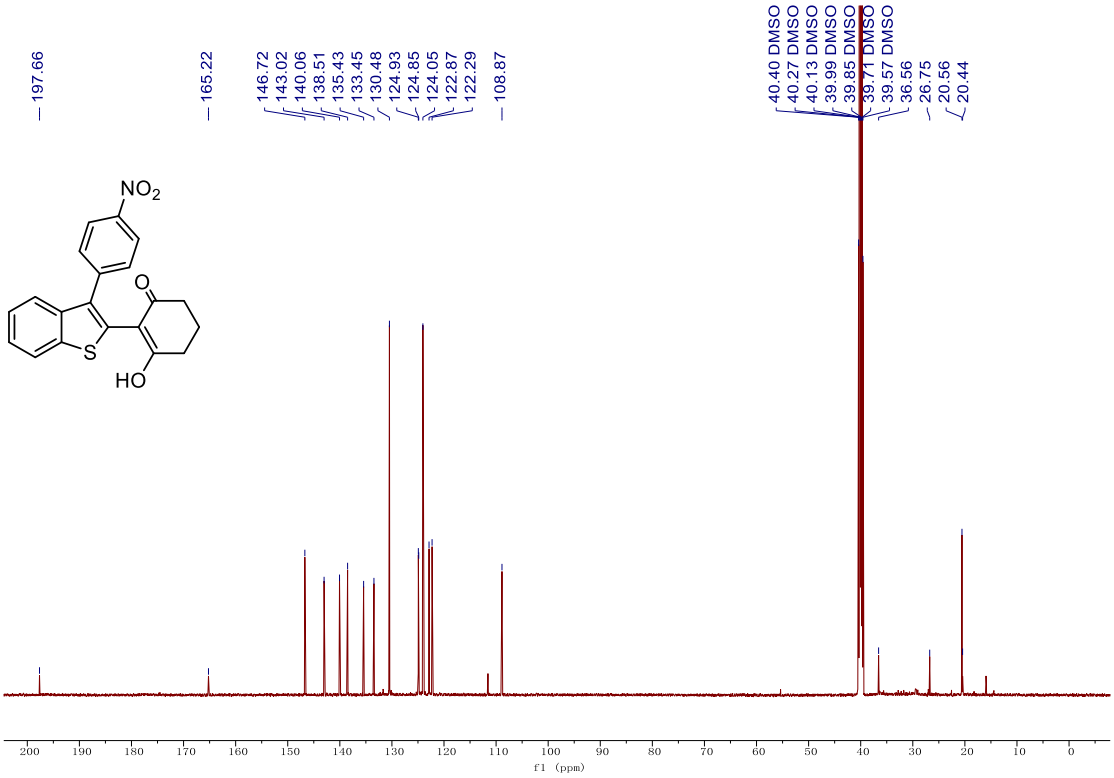
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **49**



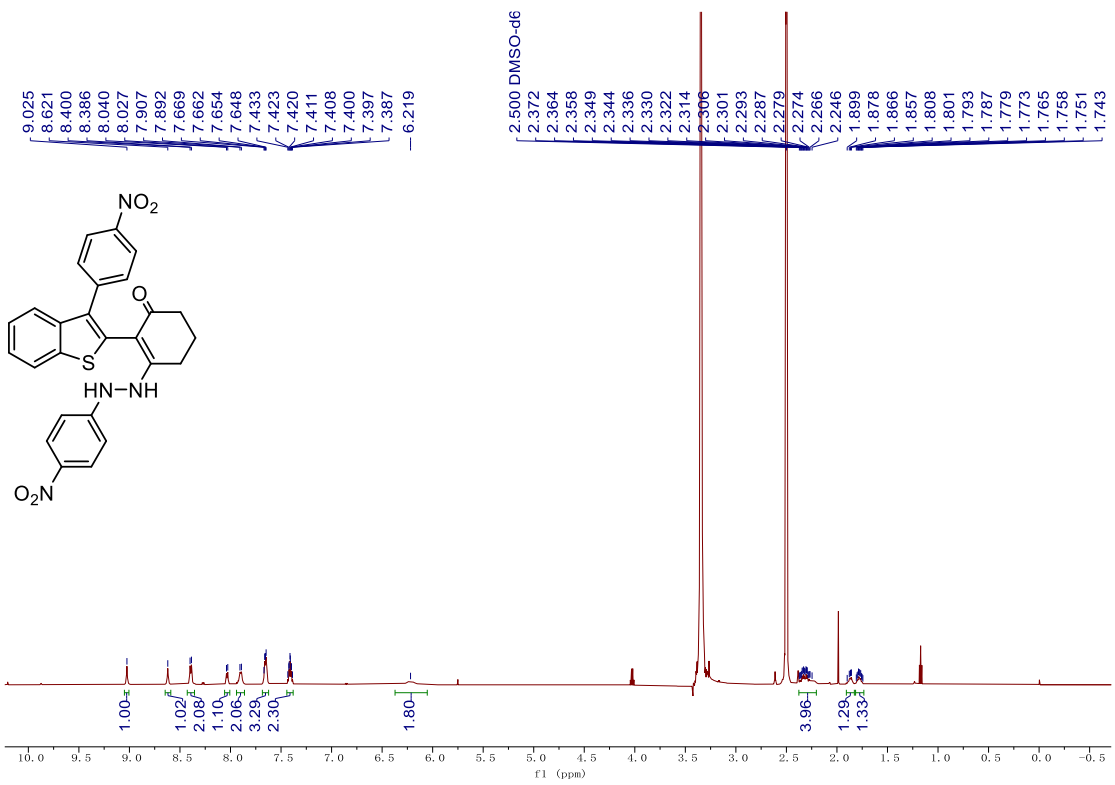
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **49**



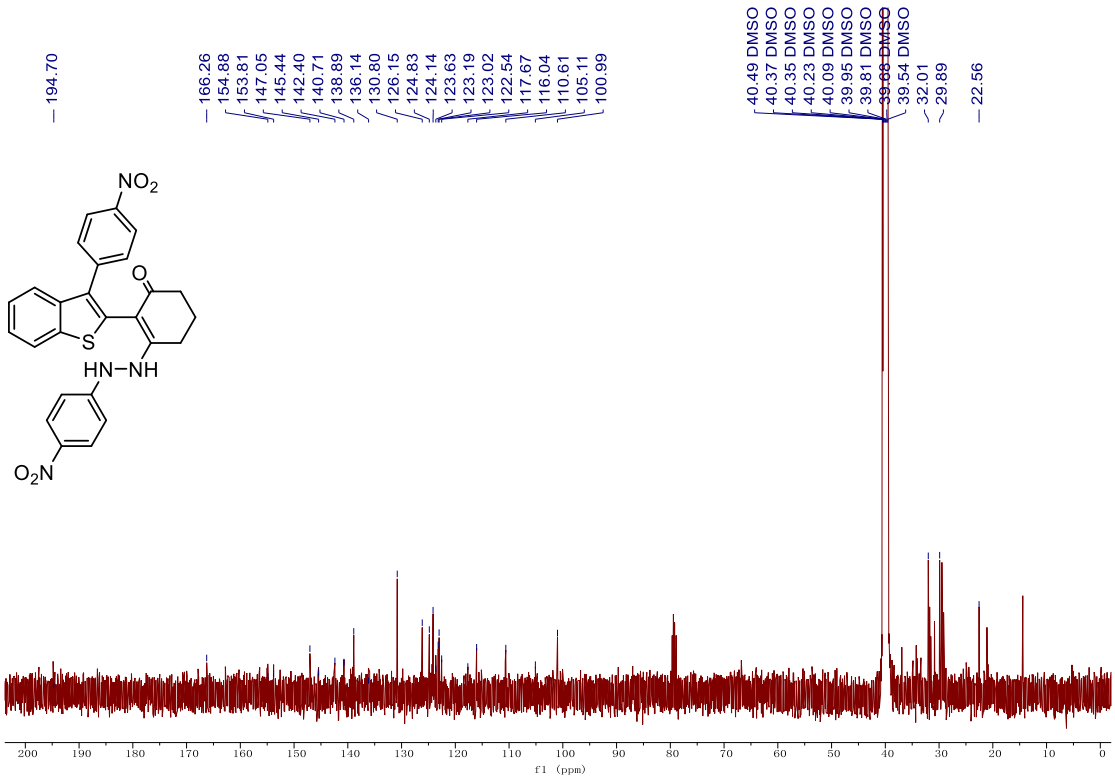
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **50**



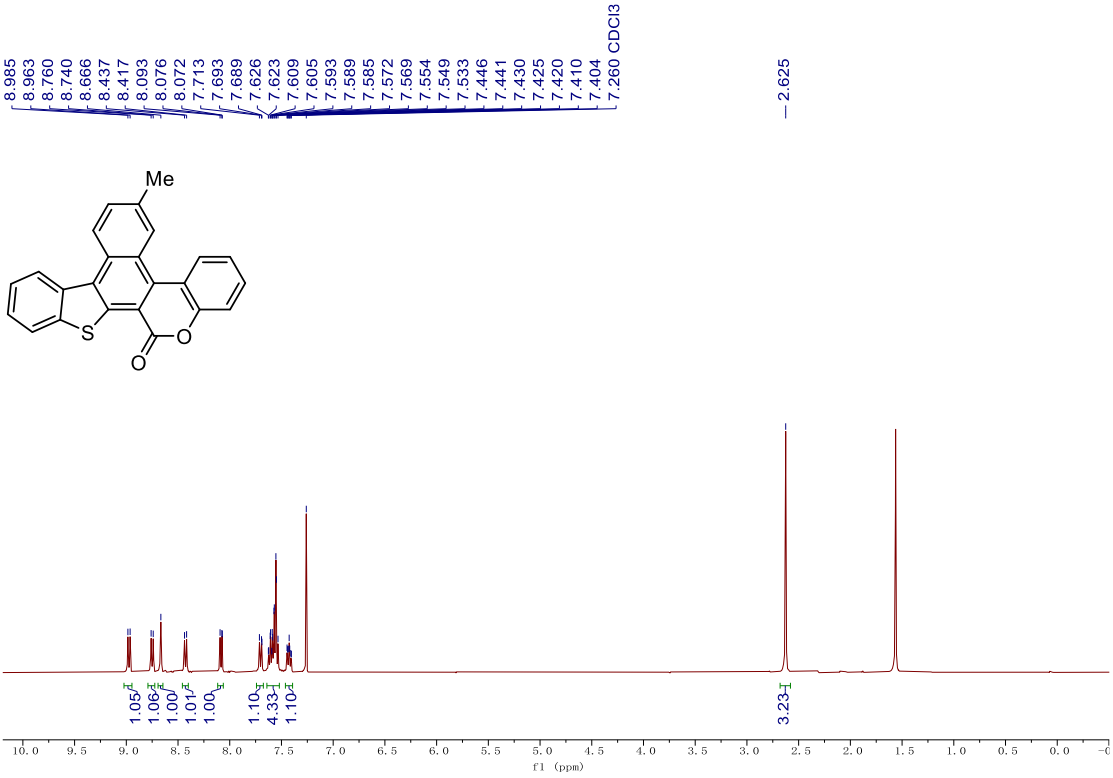
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **50**



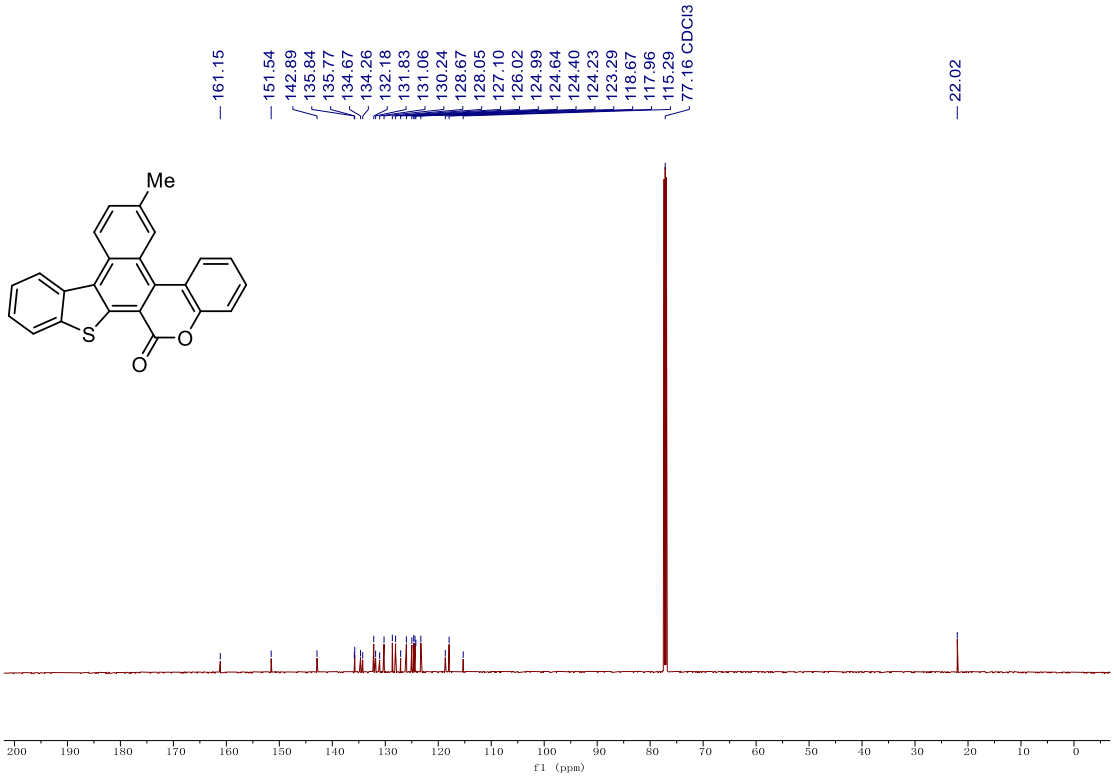
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **51**



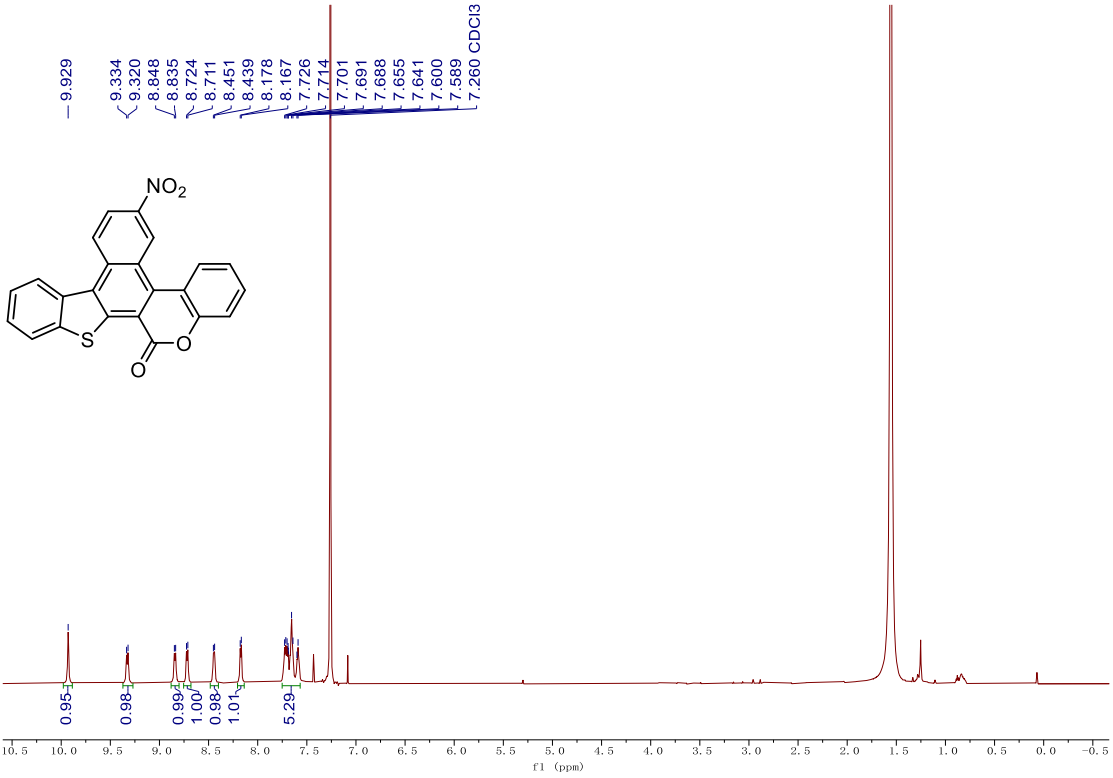
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **51**



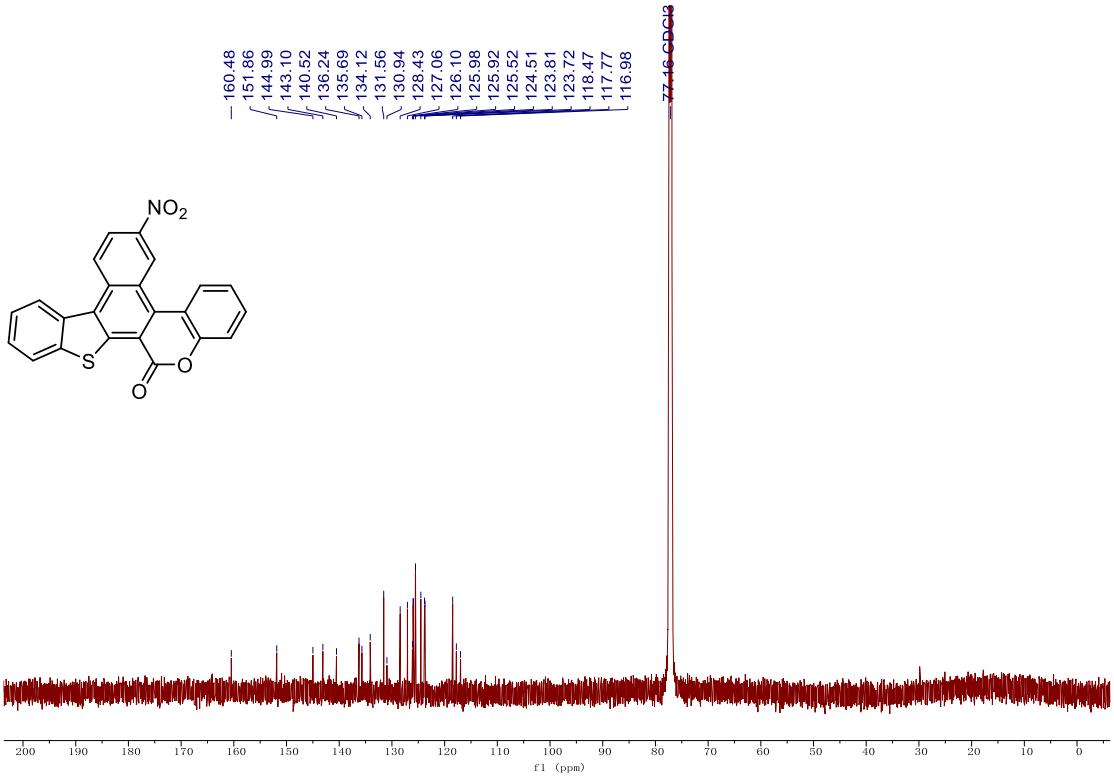
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **53**



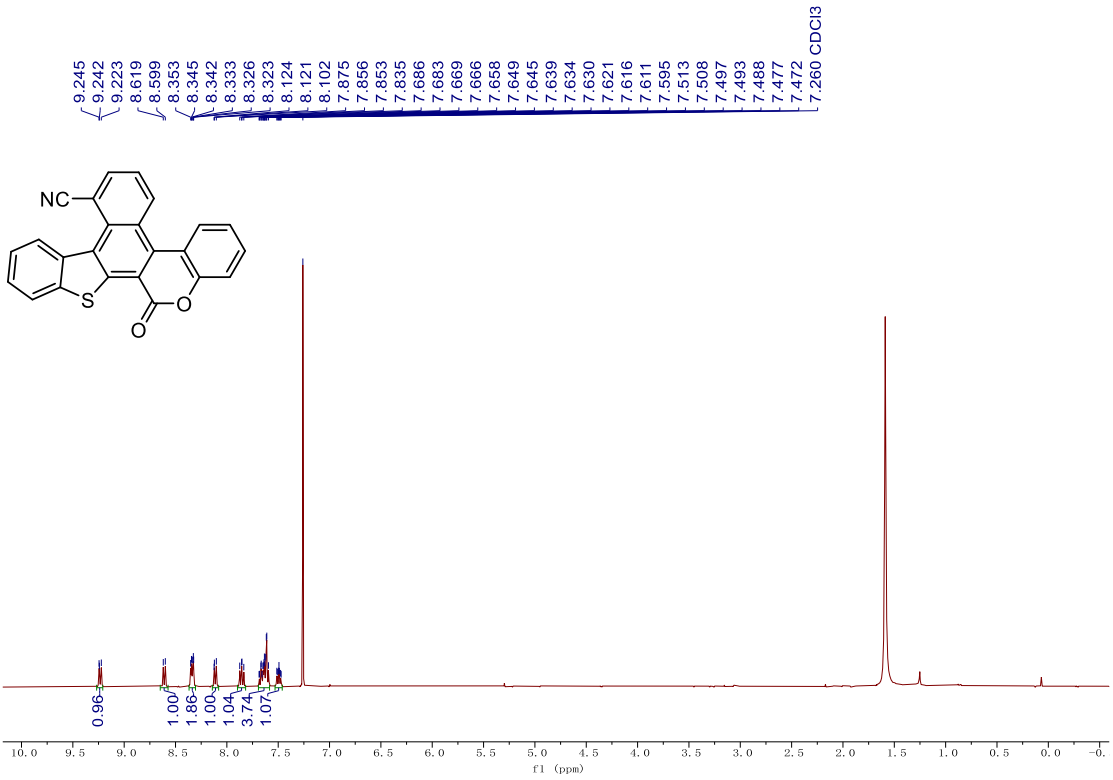
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **53**



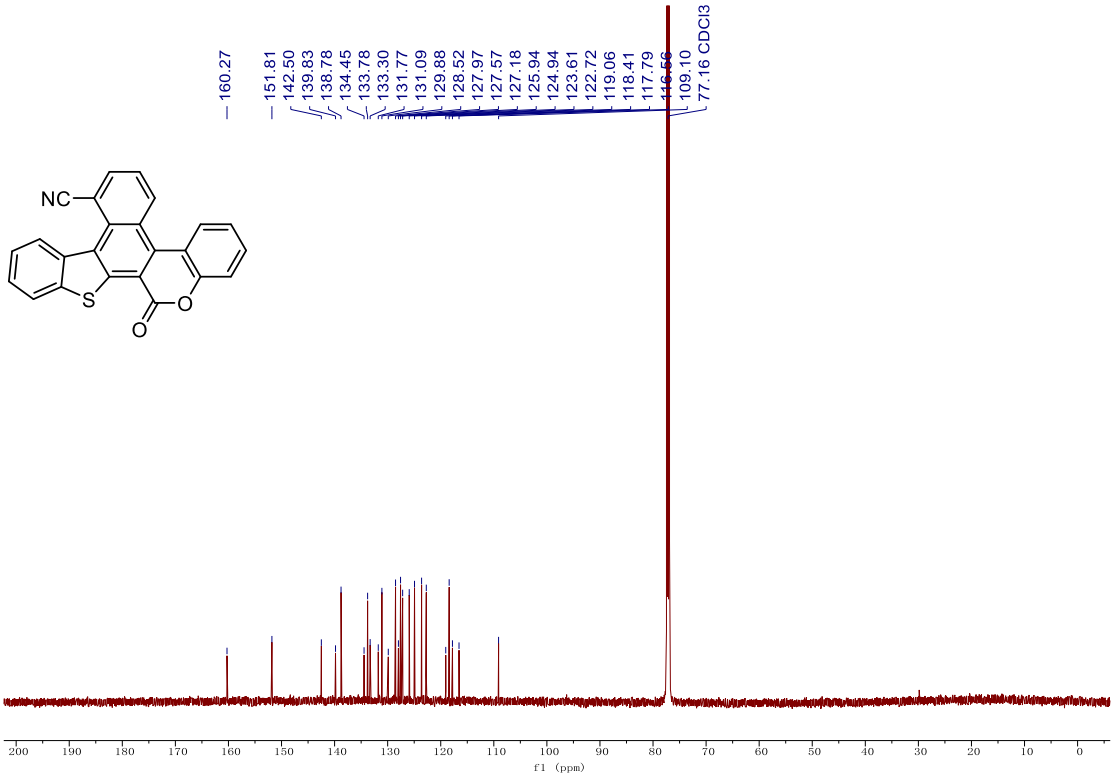
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **54**



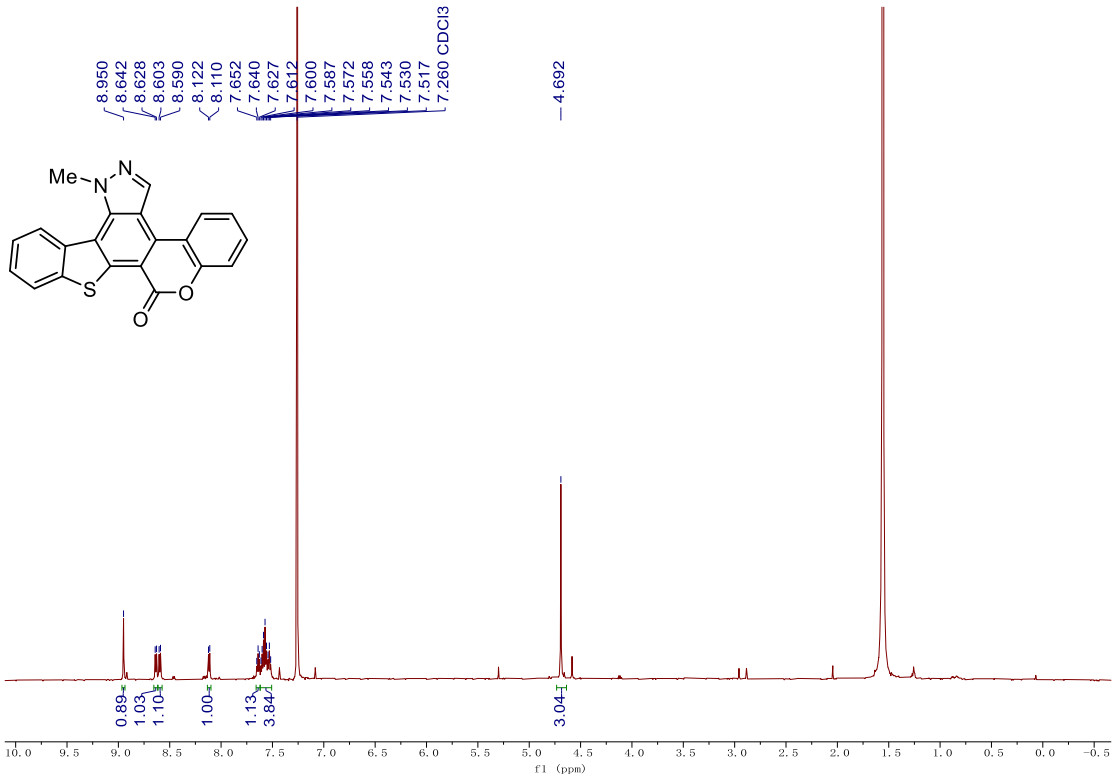
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **54**



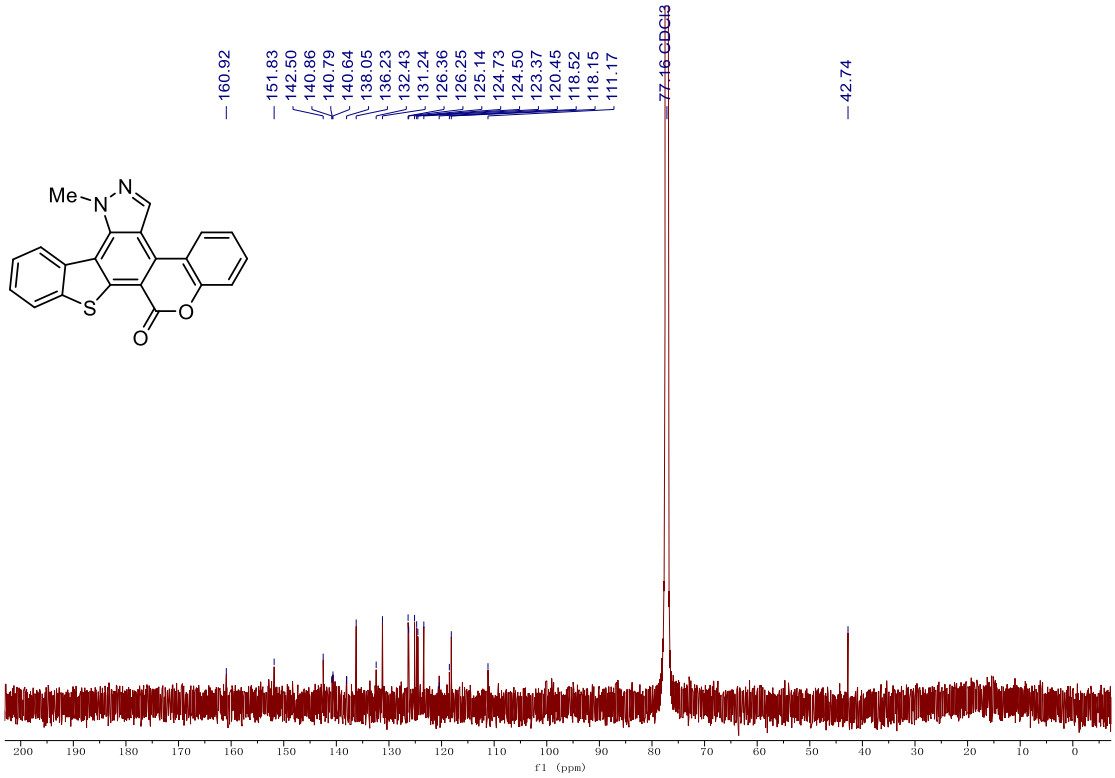
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **55**



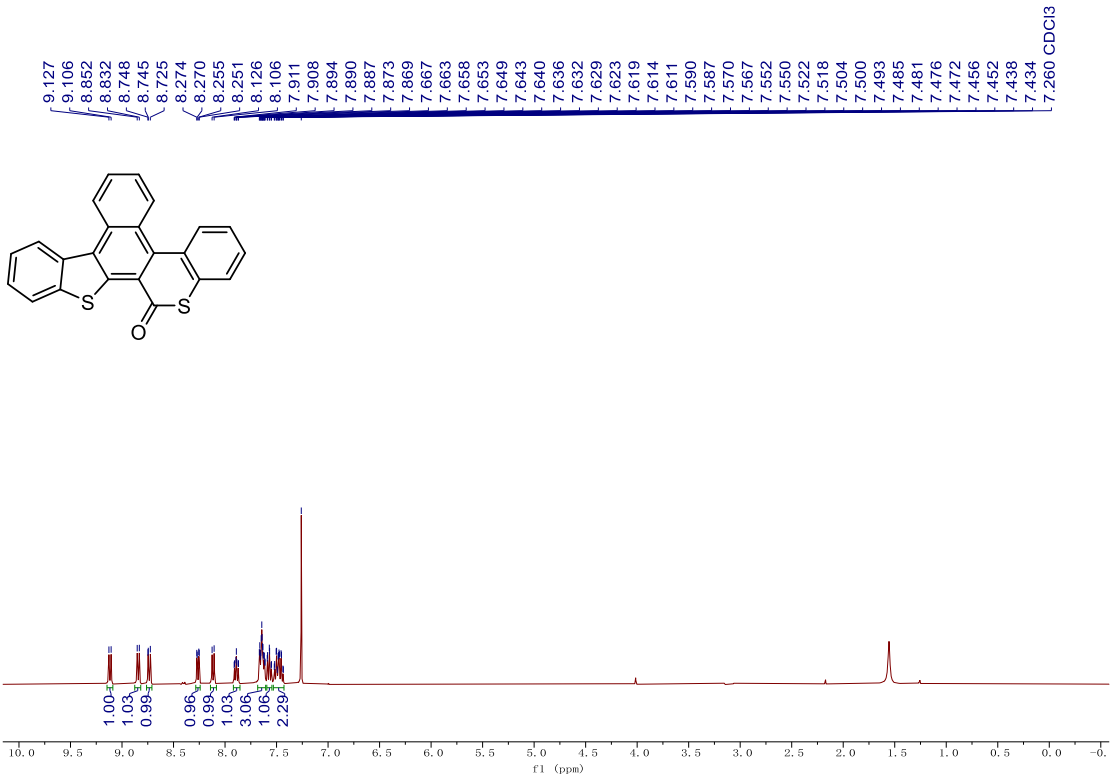
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **55**



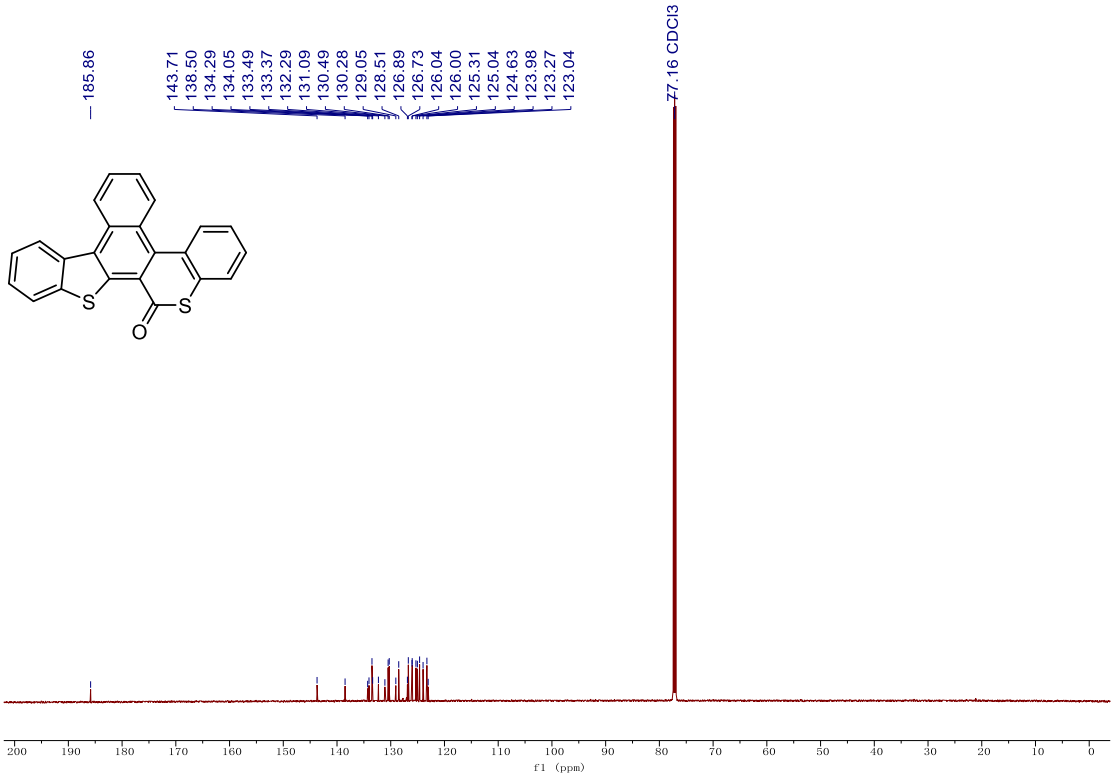
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **56**



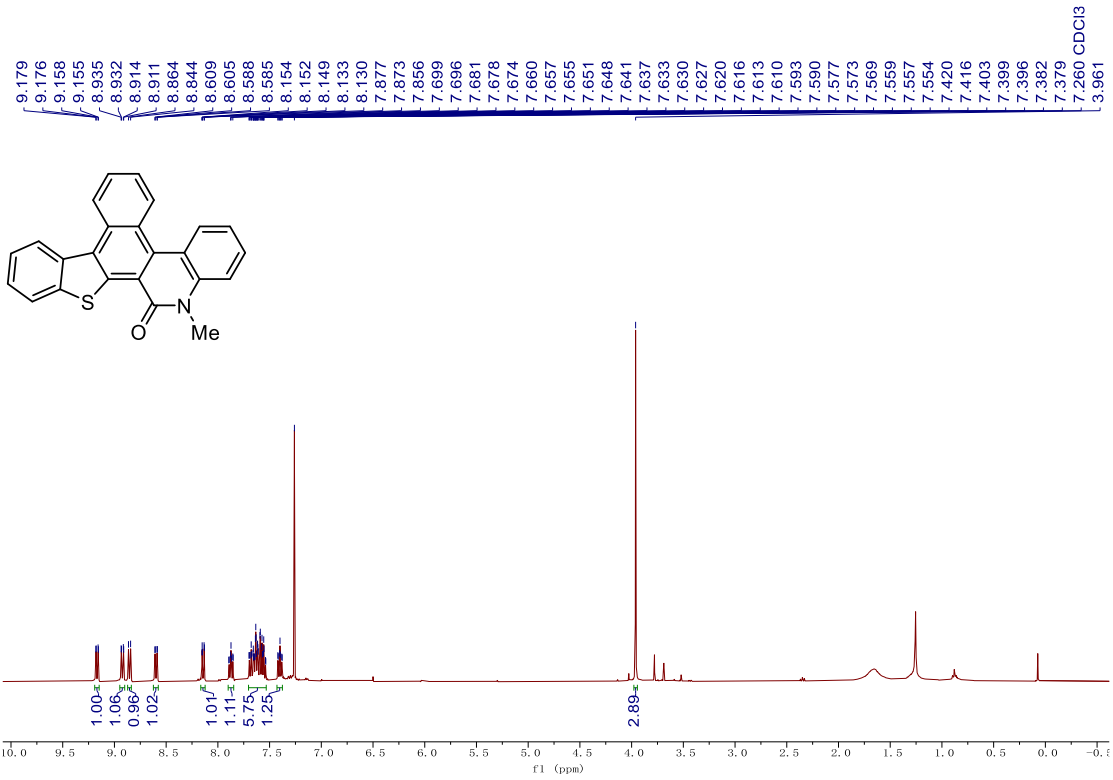
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **56**



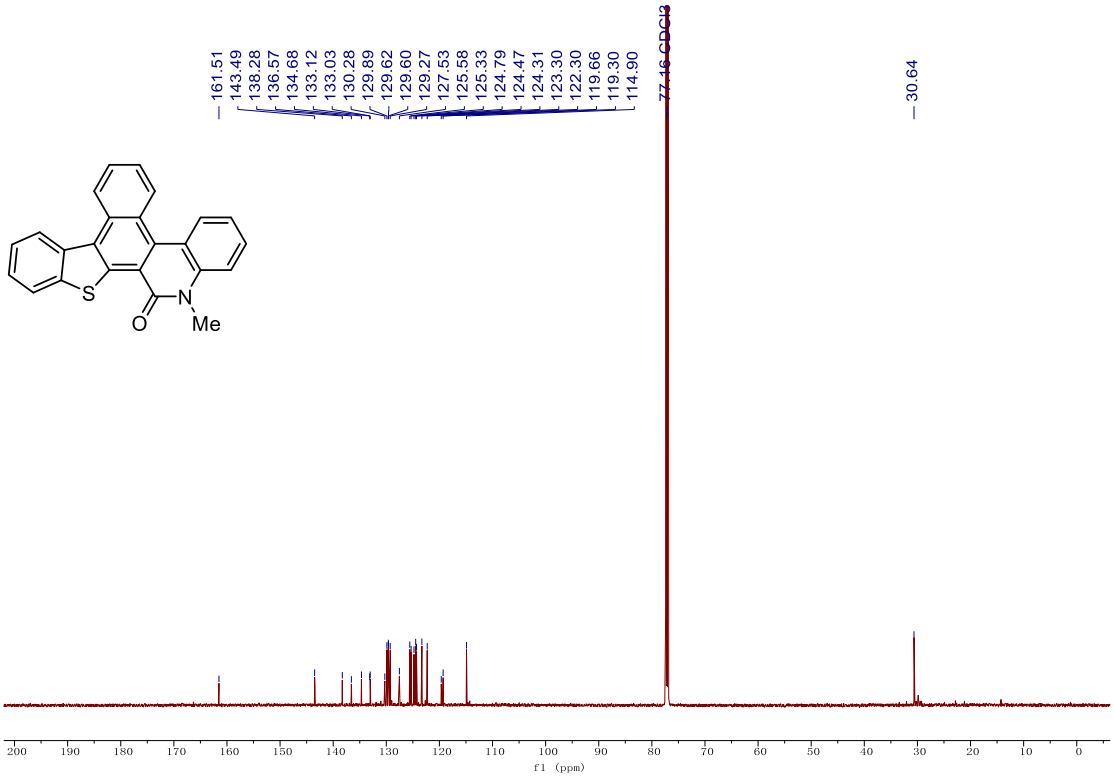
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **57**



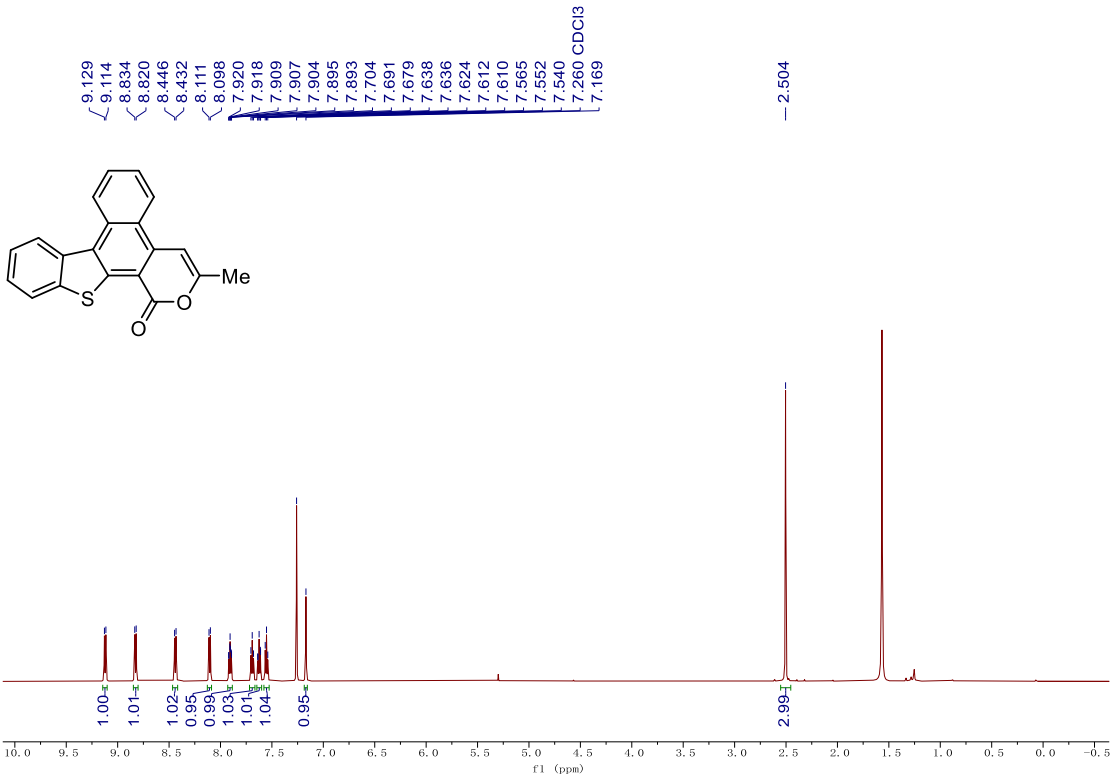
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **57**



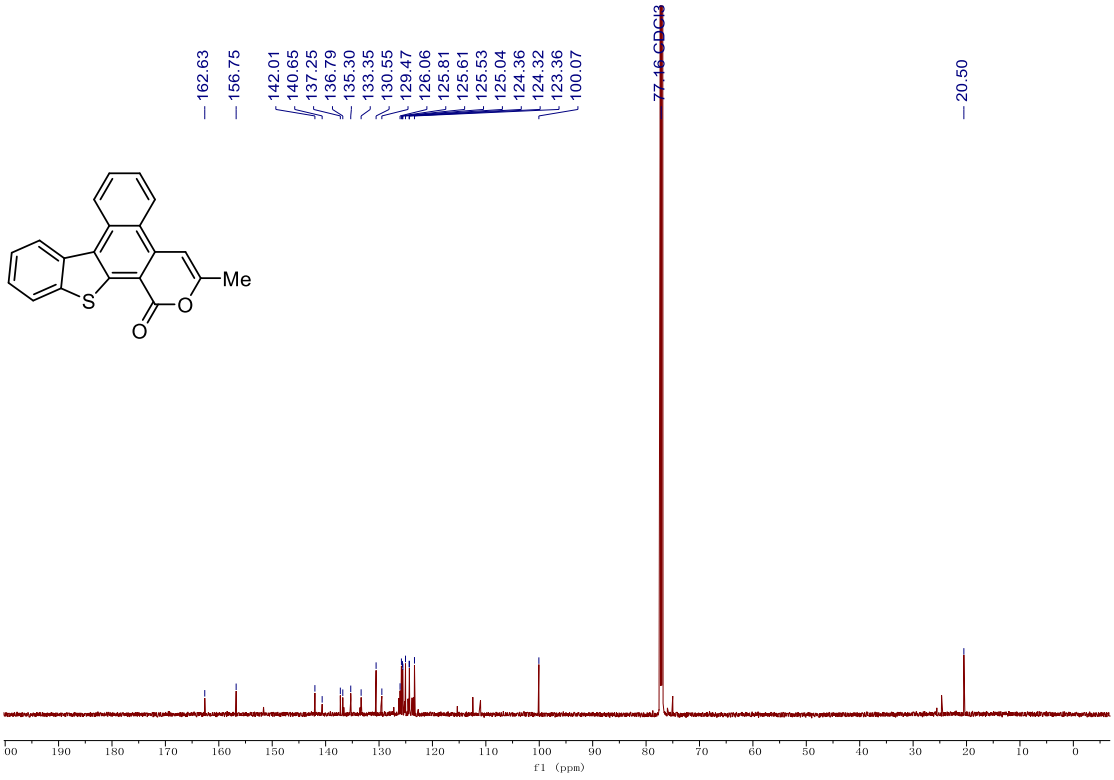
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **58**



^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **58**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **59**



^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **59**

9. References

[1] X.-Y. Shen, M. Li, T.-P. Zhou, J.-R. Huang. Benzo[*b*]naphtho[1,2-*d*]thiophene sulfoxides: biomimetic synthesis, photophysical properties, and applications. *Angew. Chem. Int. Ed.* 2022, **61**, e202203908.

[2] P. Tosatti, A. Pfaltz. Iridium-catalyzed asymmetric hydrogenation of benzo[*b*]thiophene 1,1-dioxides. *Angew. Chem. Int. Ed.* 2017, **56**, 4579–4582.

[3] M.-Z. Guo, M.-J. Mou, Z. Chen, S.-F. Ni, M. Li, L.-R. Wen, L.B. Zhang. Electrochemical reduction of benzo[*b*]thiophene 1,1-dioxides with HFIP as hydrogen donor. *Chin. J. Chem.* 2024, **42**, 585–591.

[4] Z. He, H. J. Shrives, J. A. Fernández-Salas, A. Abengózar, J. Neufeld, K. Yang, A. P. Pulis, D. J. Procter. Synthesis of C2-substituted benzothiophenes via an interrupted Pummerer/[3,3]-sigmatropic/1,2-migration cascade of benzothiophene S-oxides. *Angew. Chem. Int. Ed.* 2018, **57**, 5759–5764.

[5] Z. He, T. Biremond, G. J. P. Perry, D. J. Procter. Para-coupling of phenols with C2/C3-substituted benzothiophene S-oxides. *Tetrahedron* 2020, **76**, 131315–131320.

[6] J. Padwal, W. Lewis, C. J. Moddy. Synthesis of the reported structure of crassiflorone, a naturally occurring quinone isolated from the African ebony Diospyros crassiflora, and regioisomeric pentacyclic furocoumarin naphthoquinones *Org. Biomol. Chem.* 2011, **9**, 3484–3493.

[7] Y.-X. Chen, S. Wu, X. Shen, D.-F. Xu, Q. Wang, S.-H. Ji, H. Zhu, G. Wu, C. Sheng, Y.-R. Cai. Two-phase electrosynthesis of dihydroxycoumestans: discovery of a new scaffold for topoisomerase I poison. *Chem. Eur. J.* 2024, **30**, e202401400.

[8] Q. Zhu, J. Wu, R. Fathi, Z. Yang. Phenyliodonium zwitterion as an efficient electrophile in the palladium-catalyzed Suzuki-type reaction: a novel method for the synthesis of 3-aryl-4-hydroxycoumarins. *Org. Lett.* 2022, **4**, 3333–3336.

[9] C. Mi, B.-B. Zhang, G. Zhang, A. Peng, Z.X. Wang, Q. Shi, H. Huang. An efficient C−Si/C−H cross-coupling reaction enabled by a radical pathway. *Chem. Eur. J.* 2024, **30**, e202303857.

[10] M. Zhang, H.-Y. An, B.-G. Zhao, J.-H. Xu. Aromatic annulation strategy for naphthalenes fused at 1,2- and 3,4-positions with two heterocycles. *Org. Biomol. Chem.* 2006, **4**, 33–35.