Supporting information for

Copper-Catalyzed Domino Synthesis of Multisubstituted Benzo[b]thiophene Through Radical Cyclization Using Xanthate as Sulfur Surrogate

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Table of contents

1. General information 2
2. Experimental procedure 2
3. Optimization reaction condition **2a** 4
4. Plausible mechanism for thioketone formation 5
5. ^{1}H and ^{13}C Spectral data for all compounds 6
6. ^{1}H and ^{13}C spectra copy for all compounds 16
7. Experimental procedure for synthetic application 48
8. Crystal data for **2b**, **2i** and **3c** 55

1. General information

All reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra Synthesis Pvt. Ltd. and used for column chromatography using hexanes and ethyl acetate mixture as eluent. Unless otherwise noted, all of the starting materials are prepared by known methodologies without any modification. All the reactions were carried out in temperature controlled IKA oil bath magnetic stirrers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz (100 MHz and 125 MHz for ^{13}C) instrument. ^{1}H NMR spectra were reported relative to residual of DMSO-d^6 and $CDCl_3$ (δ 2.50 and 7.26 ppm). However, when the residual peak was overlapping with compound peak, the spectra were reported with residual TMS peak. ^{13}C NMR were reported relative to DMSO-d^6 and $CDCl_3$ (δ39.52 and 77.16 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and are corrected with benzoic acid as reference. Infrared spectra were recorded on a FTIR(ATR) 4000 Series spectrometer. The wave numbers of recorded IR signals are quoted in cm^{-1}. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

Solvents used for extraction and column chromatography were laboratory grade and used as received. Reaction solvents used were obtained from Fischer Scientific India Pvt. Ltd. various aldehydes were purchased from Alfa-aesar, Sigma-Aldrich Company, Avra synthesis, Spectrochem Pvt. Ltd. and TCI chemicals. $Cu(OAc)_2$ purchased from Alfa-aesar and potassium ethyl xanthogenate were obtained from Sigma-Aldrich and used directly as received.

2. Experimental procedure

2.1. General procedure for synthesis of 2-thioaroyl 3-hydroxy benzo[b]thiophene from 2-iodophenyl ketones 2

An oven dried reaction tube was loaded with 1-(2-iodophenyl)-propan-1-one (0.5 mmol), potassium ethyl xanthate (1.5 mmol), AcOH (1.0 mmol) and $Cu(OAc)_2$ (0.1 mmol) then DMSO (3 mL) was added. The reaction tube was closed with glass-stopper and stirred at 120 ºC in a pre-heated oil bath for recommended time. After the complete conversion of starting material to 2-thioaroyl 3-hydroxy benzo[b]thiophene, the reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with ethyl acetate and the combined organic extraction was dried over anhydrous Na_2SO_4. Solvent was removed under reduced

pressure and the residue was purified by silica gel column chromatography using hexanes/ethyl acetate mixture to afford the 2-thioaroyl 3-hydroxy benzo[b]thiophene **2**.

2.2. General procedure for synthesis of benzothiophene fused thioflavones from 1-(2-iodophenyl)-3-(2-methoxyphenyl)propan-1-one 3

An oven dried reaction tube was loaded with 1-(2-iodophenyl)-3-(2-methoxyphenyl)propan-1-one (0.5 mmol), potassium ethyl xanthate (1.5 mmol), AcOH (1.0 mmol) and $Cu(OAc)_2$ (0.1 mmol) then DMSO (3 mL) was added. The reaction tube was closed with glass-stopper and stirred at 120 ºC for recommended time in a pre-heated oil bath. After the complete conversion of 1-(2-iodophenyl)-3-(2-methoxyphenyl)propan-1-one to benzothiophene fused thioflavones, the reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with ethyl acetate and the combined organic extraction was dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexanes/ethyl acetate mixture to afford the benzothiophene fused thioflavones **3**.

2.3. General procedure for synthesis of 2-thioaroyl 3-hydroxy benzo[b]thiophene from 2-bromophenyl ketones 2

An oven dried reaction tube was loaded with 2-bromophenyl ketones (0.5 mmol), potassium ethyl xanthate (1.5 mmol), AcOH (1.0 mmol) and $Cu(OAc)_2$ (0.1 mmol), then DMSO (3 mL) was added. The reaction tube was closed with glass-stopper and stirred at 120 ºC in a pre-heated oil bath for recommended time. After the complete conversion of 2-bromophenyl ketones to 2-thioaroyl 3-hydroxy benzo[b]thiophene, the reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with ethyl acetate and the combined organic extraction was dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexanes/ethyl acetate mixture to afford the 2-thioaroyl 3-hydroxy benzo[b]thiophene.

2.4. General procedure for synthesis of 2-benzylbenzo[b]thiophen-3-yl acetate from 2-iodophenyl ketones 15

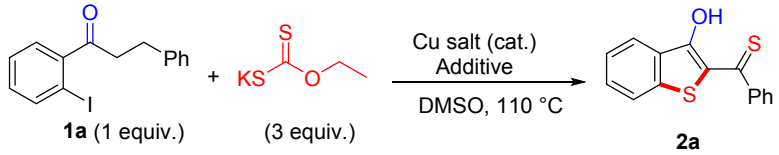
An oven dried reaction tube was loaded with 2-iodophenyl ketones (0.5 mmol), potassium ethyl xanthate (1.5 mmol), AcOH (1.0 mmol) and $Cu(OAc)_2$ (0.1 mmol), then DMSO (3 mL) was added. The reaction tube was closed with glass-stopper and stirred at 60 ºC in a pre-heated oil bath for recommended time. After the complete conversion of 2-iodophenyl ketones to 2-benzylbenzo[b]thiophen-3-yl acetate, the reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with

ethyl acetate and the combined organic extraction was dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexanes/ethyl acetate mixture to afford the 2-benzylbenzo[b]thiophen-3-yl.

2.5. General procedure for synthesis of gram scale synthesis of 2-thioaroyl 3-hydroxy benzo[b]thiophene 2a

Under open atmosphere, 2-iodophenyl ketones **1a** (1.68 g, 5 mmol), potassium ethyl xanthate (1.92 g, 15 mmol), $Cu(OAc)_2$ (183 mg, 1 mmol) and AcOH (656 mg, 2 equiv.) were successively added to an oven dried round bottom flask. Then, 15 mL of DMSO was added and closed with glass-stopper. The reaction tube was then immersed in a 120 ºC pre-heated oil bath. The reaction was allowed till the completion of starting material. Then, the reaction mixture was brought to room temperature; water was added and extracted with ethyl acetate (3×30 mL). Brine wash (1×25 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and silica gel column chromatography separation of crude product using hexanes and ethyl acetate mixture (15:5) afforded the corresponding 2-thioaroyl 3-hydroxy benzo[b]thiophene **2a** in 85% (1.16 g).

3.0. Optimization for the synthesis of 2-thioaroyl 3-hydroxy benzo[b]thiophene[a]



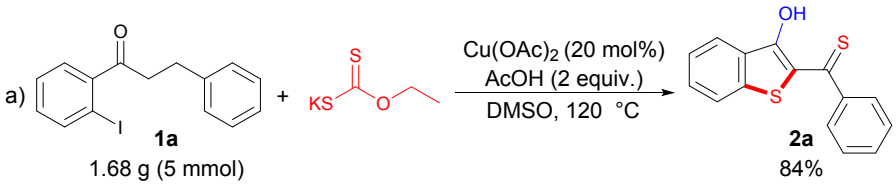
1a (1 equiv.) (3 equiv.) **2a**

Entry	Cu salt (mol%)	Additive (equiv.)	Time (h)	Yield (%)
1	$Cu(OAc)_2$ (10)	AcOH (2)	1	60
2	$Cu(OTf)_2$ (10)	AcOH (2)	1	40
3	CuI (10)	AcOH (2)	1	37
4	CuBr (10)	AcOH (2)	1	36
5	CuCl (10)	AcOH (2)	1	12
6	$Cu(OAc)_2$ (10)	NaOAc (2)	2	0
7	$Cu(OAc)_2$ (10)	CF_3SO_3H (2)	24	0
8	$Cu(OAc)_2$ (10)	CF_3CO_2H(2)	23	0
9	$Cu(OAc)_2$ (20)	AcOH (2)	1	69
10	**$Cu(OAc)_2$ (20)**	**AcOH (2)**	**1**	**85[b]**
11	$Cu(OAc)_2$ (20)	AcOH (2)	1	71[c]
12	$Cu(OAc)_2$ (20)	AcOH (1)	1	33
13	$Cu(OAc)_2$ (20)	AcOH (3)	1	28
14	$Cu(OAc)_2$ (20)	AcOH (2)	6	60[d]
15	-	AcOH (2)	1	7
16	$Cu(OAc)_2$ (20)	-	1	0

[a]Standard reaction conditions: **1a** (0.5 mmol), xanthate (3 equiv.), Cu catalyst, additive in 3 mL of solvent. [b]Reaction was carried out at 120 °C. [c]Reaction was carried out at 130 °C. [d]Reaction was carried with DMF as solvent.

A trial reaction was kept with 2-iodophenyl ketone **1a** in presence of potassium ethyl xanthate (3 equiv.), $Cu(OAc)_2$ (10 mol%) as catalyst and acetic acid (2 equiv.) as additive in DMSO as solvent at 110 °C. To our delight, the desired product **2a** was isolated with 60% yield within a short time span of

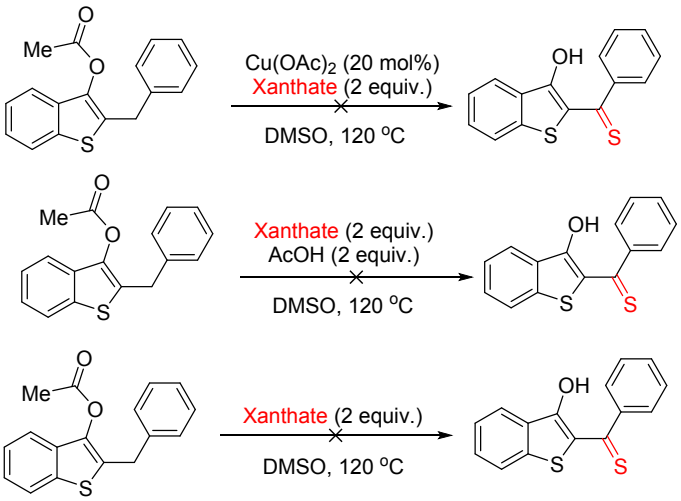
1 h (Table S1, Entry 1). Encouraged by this, a thorough optimization of the reaction conditions was carried out. Various Cu-salts were screened, however, other copper salts failed to provide better results (Entries 2-5). Other additives were used in place of AcOH, but, none of the other additives yielded the desired product (Entries 6-8), thus, suggesting that AcOH plays a crucial role in the product formation. Following this, the catalyst loading was varied. On increasing the catalyst loading to 20 mol%, an increase in the yield to 69% was observed (Entry 9). Next, the reaction temperature was increased to 120 °C and a drastic improvement in the yield of the product to 85% was observed (Entry 10). Further, increasing the temperature to 130 °C, lead to drop in the yield (Entry 11). Screening the equivalents of additive also did not improve the reaction yield (Entries 12-13). The reaction was also kept with DMF as solvent and the product was isolated in 60% yield with longer reaction time of 6 h (Entry 14). Two individual reactions, one without Cu-salt and other without AcOH were performed, only trace amount of product formation was observed in the case of without metal, this might be at higher temperature thioester formation can be observed through radical pathway. However, without AcOH the reaction was completely extinct (Entry 15 and 16).



In order to demonstrate the efficiency of this domino reaction in gram scale, the reaction was carried out with 5 mmol (1.68 g) of 2-iodophenyl ketone **1a** under standard optimized condition without changing any reaction parameters. The desired product **2a** was isolated in 84% yield.

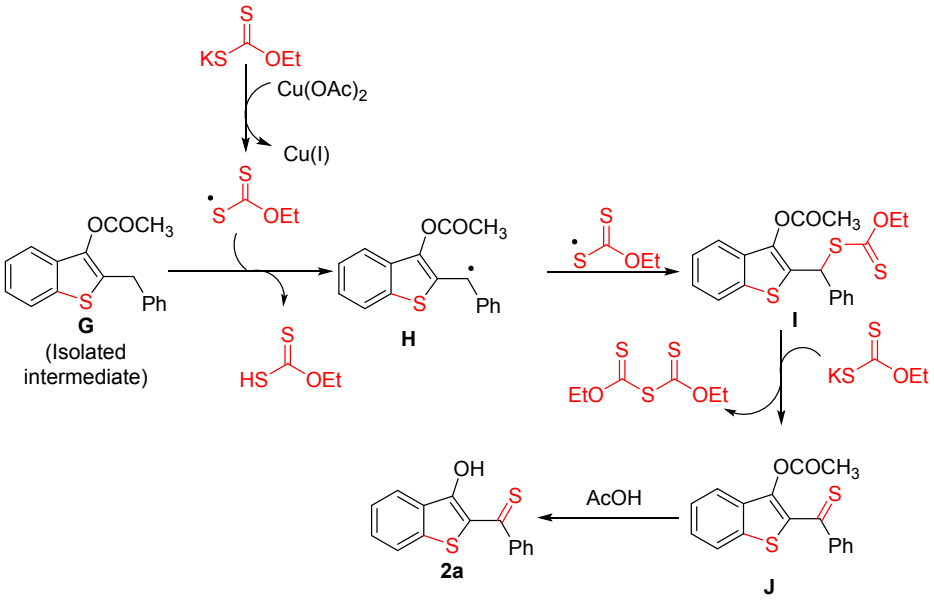
4.0 Plausible mechanism for the benzylic thioketone formation

To delineate the pathway for the formation of benzylic thioketone, the following control experiments were carried out. Initially, the intermediate **G** was subjected to the optimized reaction condition in the absence of acetic acid, however, no product formation was observed. The reaction also failed to proceed in the absence of copper acetate. One reaction was kept with intermediate G and only xanthate to check whether the reaction proceeds, however, the desired product formation was not observed. These experiments indicate that the formation of benzylic thioketone necessitates the presence of $Cu(OAc)_2$, xanthate as well as acetic acid.



Scheme 1. Control experiments

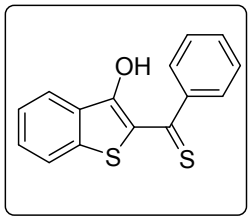
The intermediate **G** possess highly labile methylene group for oxidation since it is a benzylic carbon from either side. Initially, the thiyl radical is generated which abstracts proton from **G** to give xanthic acid and the radical intermediate **H**. The intermediate **H** further reacts with xanthate radical to give **I** which is followed by thioester cleavage to give thioketone containing intermediate **J**. Further, acid hydrolysis of intermediate **J** leads to the formation of the desired product **2a.**



Scheme 2. Plausible mechanism for formation of **2a** from **G**

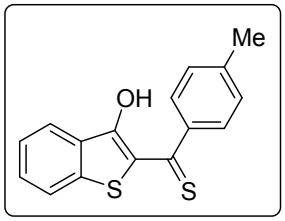
5.0. Experimental spectral data for 2:

(3-Hydroxybenzo[b]thiophen-2-yl)(phenyl)methanethione (2a): 115 mg; 85% yield; red solid; mp 98-100 °C; R_f 0.70 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.43 (m, 4H), 7.45-7.50 (m, 1H), 7.51-7.62 (m, 3H), 8.02 (d, J = 8.2 Hz, 1H), 14.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 122.9, 125.0,

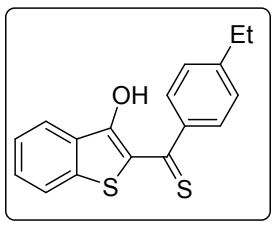


125.1, 127.1, 128.3, 130.7, 131.5, 131.7, 140.0, 147.7, 166.2, 215.3; FTIR (ATR) 3419, 2953, 2852, 1593, 1488, 1423, 758 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_{10}OS_2Na$ $[M+Na]^+$: 293.0070; found: 293.0064.

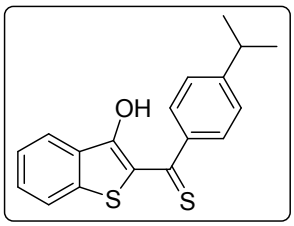
(3-Hydroxybenzo[b]thiophen-2-yl)(p-tolyl)methanethione (2b): 118 mg; 83% yield; red solid; mp 115-117 °C; R_f 0.65 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.50-7.65 (m, 4H), 8.10 (d, *J* = 8.4 Hz, 1H), 14.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 122.5, 122.8, 125.0, 125.1, 127.3, 128.9, 131.5, 131.6, 139.8, 141.4, 145.2, 166.0, 215.4; FTIR (ATR) 3499, 2959, 2922, 1594, 1490, 820, 765 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{13}OS_2$ $[M+H]^+$: 285.0407; found: 285.0403.



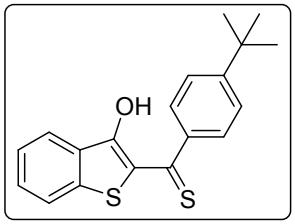
(4-Ethylphenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2c): 113 mg; 76% yield; red liquid; R_f 0.58 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, *J* = 7.6 Hz, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.60-7.66 (m, 3H), 8.10 (d, *J* = 8.4 Hz, 1H), 14.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3, 28.9, 122.5, 122.8, 124.9, 125.0, 127.4, 127.8, 131.5, 131.6, 139.9, 145.4, 147.6, 166.0, 215.4; FTIR (ATR) 3487, 2964, 2927, 1491, 1424, 770, 737 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{14}OS_2$ $[M+H]^+$: 299.0564; found: 299.0539.



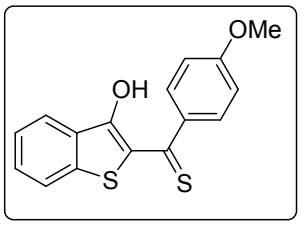
(3-Hydroxybenzo[b]thiophen-2-yl)(4-isopropylphenyl)methanethione (2d): 115 mg; 74% yield; red semi solid; R_f 0.65 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (d, *J* = 6.9 Hz, 6H), 2.93-3.03 (m, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.60-7.67 (m, 3H), 8.11 (d, *J* = 8.1 Hz, 1H), 14.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.8, 34.2, 122.5, 122.8, 124.9, 125.0, 126.4, 127.5, 131.5, 139.9, 145.5, 152.2, 166.0, 215.4; FTIR (ATR) 3510, 2960, 2921, 1594, 1491, 782, 735 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{18}H_{17}OS_2$ $[M+H]^+$: 313.0720; found: 313.0713.



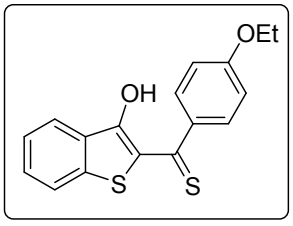
(4-(*tert*-Butyl)phenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2e): 112 mg; 69% yield; red solid; mp 112-114 °C; R_f 0.65 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (s, 9H), 7.29-7.34 (m, 1H), 7.35-7.40 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.50-7.60 (m, 3H), 8.01 (d, *J* = 8.8 Hz, 1H), 14.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.3, 35.0, 122.4, 122.7, 124.9, 125.0, 125.2, 127.2, 128.5, 131.5, 140.0, 145.1, 154.4, 166.0, 215.3; FTIR (ATR) 3476, 2961, 2926, 1637, 1489, 1425, 769, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{19}H_{19}OS_2$ $[M+H]^+$: 327.0877; found: 327.0819.



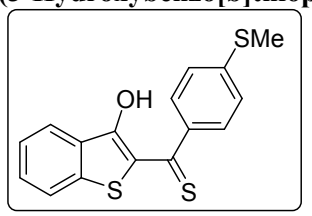
(3-Hydroxybenzo[b]thiophen-2-yl)(4-methoxyphenyl)methanethione (2f): 106 mg; 71% yield; red solid; mp 124-126 °C; R_f 0.58 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 3H), 6.87 (d, *J* = 8.2 Hz, 2H), 7.30-7.36 (m, 1H), 7.45-7.52 (m, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 1H), 14.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 113.5, 122.0, 122.7, 124.9, 129.6, 131.4, 131.7, 139.7, 140.8, 162.1, 165.8, 214.4; FTIR (ATR) 3441, 2956, 2925, 1599, 1490, 1422, 769, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{12}O_2S_2Na$ $[M+Na]^+$: 323.0176; found: 323.0166.



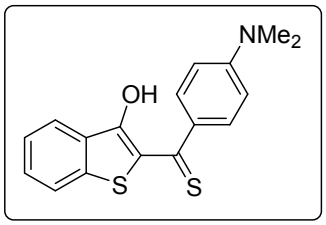
(4-Ethoxyphenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2g): 107 mg; 68% yield; red solid; mp 116-118 °C; R_f 0.41 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (t, *J* = 6.8 Hz, 3H), 4.11 (q, *J* = 6.8 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.60-7.70 (m, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 14.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.8, 63.9, 114.0, 122.0, 122.7, 125.0, 129.6, 131.4, 131.6, 139.6, 140.6, 161.6, 165.8, 214.4; FTIR (ATR) 3323, 2952, 2923, 1597, 1490, 759, 727 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{15}O_2S_2$ $[M+H]^+$: 315.0513; found: 315.0435.



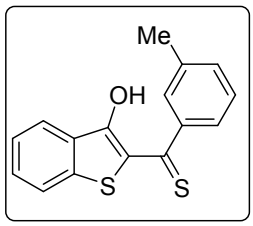
(3-Hydroxybenzo[b]thiophen-2-yl)(4-(methylthio)phenyl)methanethione (2h): 123 mg; 78% yield; red solid; mp 135-137 °C; R_f 0.61 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.54 (s, 3H), 7.25-7.30 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.62-7.70 (m, 3H), 8.10 (d, *J* = 8.4 Hz, 1H), 14.7 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2, 122.2, 122.8, 125.0, 125.1, 125.2, 127.9, 131.5, 131.6, 139.7, 143.2, 144.2, 166.1, 214.1; FTIR (ATR) 3492, 2978, 2912, 1487, 1417, 754, 730 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{13}OS_3$ $[M+H]^+$: 317.0128; found: 317.0094.



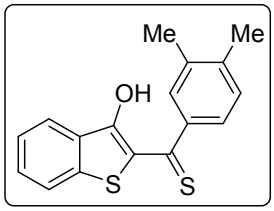
(4-(Dimethylamino)phenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2i): 59 mg; 38% yield; red solid; mp 128-130 °C; R_f 0.50 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 6H), 6.59 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 14.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.2, 110.7, 120.7, 122.5, 124.6, 124.7, 130.5, 130.7, 131.9, 136.2, 139.3, 152.8, 164.7, 213.0; FTIR (ATR) 3423, 2952, 2923, 1557, 1490, 752, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{16}NOS_2$ $[M+H]^+$: 314.0673; found: 314.0686.



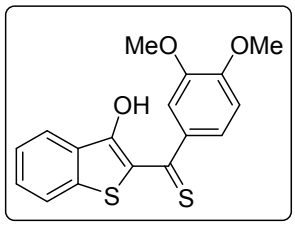
(3-Hydroxybenzo[b]thiophen-2-yl)(m-tolyl)methanethione (2j): 89 mg; 63% yield; red solid; mp 94-96 °C; R_f 0.61 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H), 7.21-7.29 (m, 2H), 7.31-7.42 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.53-7.59 (m, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 14.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 122.8, 122.9, 124.2, 125.0, 125.1, 127.8, 128.1, 131.5, 131.6, 131.7, 138.2, 140.0, 147.8, 166.1, 215.7; FTIR (ATR) 3445, 2954, 2922, 1486, 1424, 757, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{13}OS_2$ $[M+H]^+$: 285.0407; found: 285.0393.



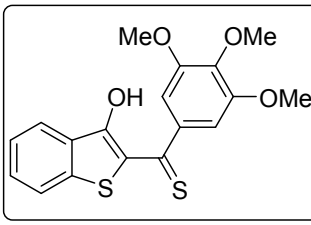
(3,4-Dimethylphenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2k): 113 mg; 76% yield; red solid; mp 121-123 °C; R_f 0.41 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 6H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.40-7.46 (m, 2H), 7.49 (s, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 14.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 122.5, 122.8, 124.7, 124.9, 125.0, 128.6, 129.4, 131.5, 131.6, 136.8, 139.9, 140.2, 145.7, 165.9, 215.6; FTIR (ATR) 3446, 2923, 2854, 1489, 1425, 766, 734 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{15}OS_2$ $[M+H]^+$: 299.0564; found: 299.0525.



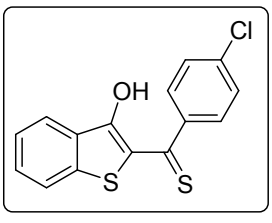
(3,4-Dimethoxyphenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2l): 120 mg; 73% yield; red solid; mp 141-143 °C; R_f 0.45 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.91-3.98 (m, 6H), 6.91 (d, J = 8.5 Hz, 1H), 7.33 (s, 1H), 7.37-7.46 (m, 2H), 7.52-7.61 (m, 1H), 7.65 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 14.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 56.2, 110.2, 111.3, 121.0, 122.0, 122.7, 125.0, 131.5, 131.7, 139.8, 140.8, 148.6, 151.7, 166.0, 214.1; FTIR (ATR) 3405, 2957, 2925, 1504, 1417, 1145, 749, 729 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{15}O_3S_2$ $[M+H]^+$: 331.0462; found: 331.0384.



(3-Hydroxybenzo[b]thiophen-2-yl)(3,4,5-trimethoxyphenyl)methanethione (2m): 104 mg; 58% yield; red solid; mp 138-140 °C; R_f 0.41 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.92-3.95 (m, 9H), 6.98 (s, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 14.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.3, 61.0, 105.2, 122.3, 122.8, 125.0, 125.1, 131.6, 131.7, 140.0, 140.4, 142.9, 152.8, 166.4, 214.1; FTIR (ATR) 3436, 2954, 2925, 1580, 1491, 1409, 1131, 833, 728 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{18}H_{17}O_4S_2$ $[M+H]^+$: 361.0568; found: 361.0525.

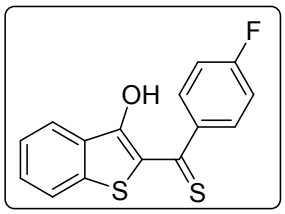


(4-Chlorophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2n): 102 mg; 67% yield; red viscous liquid; R_f 0.61 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400



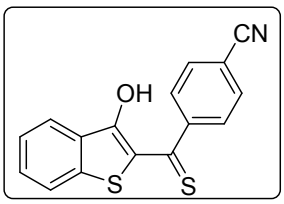
MHz) δ 7.40-7.47 (m, 3H), 7.56-7.67 (m, 4H), 8.11 (d, *J* = 8.4 Hz, 1H), 14.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.6, 122.8, 125.1, 125.2, 128.5, 128.6, 131.4, 132.0, 137.0, 139.8, 145.8, 166.5, 213.4; FTIR (ATR) 3442, 2964, 2930, 1495, 1412, 778, 730 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_{10}ClOS_2$ $[M+H]^+$: 304.9861; found : 304.9875.

(4-Fluorophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2o): 106 mg; 74% yield; red



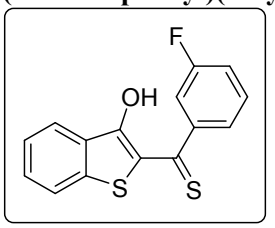
solid; mp 117-119 °C; R_f 0.55 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13 (t, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.63-7.75 (m, 3H), 8.12 (d, *J* = 8.0 Hz, 1H), 14.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 115.4 (d, *J* = 21.8 Hz), 122.5, 122.8, 125.1, 129.5 (d, *J* = 8.8 Hz), 131.5, 131.9, 139.8, 143.8 (d, *J* = 3.8 Hz), 164.3 (d, *J* = 250.6 Hz), 166.4, 213.6; FTIR (ATR) 3453, 2912, 2851, 1646, 1489, 1432, 835, 733 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_9FOS_2Na$ $[M+H]^+$: 310.9976; found : 310.9971.

4-(3-Hydroxybenzo[b]thiophene-2-carbonothioyl)benzonitrile (2p): 115 mg; 78% yield; red solid;



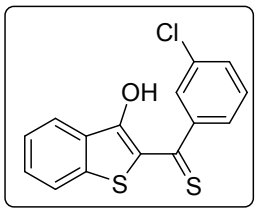
mp 172-174 °C; R_f 0.45 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (t, *J* = 8.4 Hz, 1H), 7.60-7.67 (m, 2H), 7.70-7.78 (m, 4H), 8.13 (d, *J* = 8.4 Hz, 1H), 14.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.0, 118.3, 122.8, 122.9, 125.3, 125.4, 127.6, 131.2, 132.2, 132.4, 140.0, 150.7, 167.0, 211.9; FTIR (ATR) 3432, 2956, 2851, 2232, 1594, 1493, 1433, 841, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{10}NOS_2$ $[M+H]^+$: 296.0203; found : 296.0209.

(3-Fluorophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2q): 111 mg; 77% yield; red



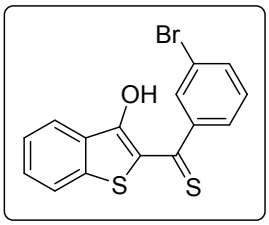
solid; mp 116-118 °C; R_f 0.48 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) 7.10-7.16 (m, 1H), 7.28-7.40 (m, 4H), 7.50-7.60 (m, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 14.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.5 (d, *J* = 23.3 Hz), 117.5 (d, *J* = 21.1 Hz), 122.7, 122.8, (d, *J* = 3.1 Hz), 122.9, 125.2, 129.9 (d, *J* = 8.2 Hz), 131.4, 132.0, 140.0, 149.1 (d, *J* = 7.1 Hz), 162.3 (d, *J* = 246.6 Hz), 166.7, 212.9; FTIR (ATR) 3441, 2967, 2922, 2853, 1478, 1438, 1235, 1075, 764, 729 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_{10}FOS_2$ $[M+H]^+$: 289.0157; found : 289.0162.

(3-Chlorophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2r): 123 mg; 81% yield; red

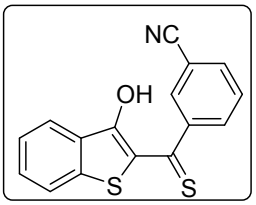


solid; mp 120-122 °C; R_f 0.63 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.40 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.48-7.54 (m, 1H), 7.55-7.63 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 14.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 122.9, 125.2, 125.3, 127.3, 129.6, 130.5, 131.4, 132.0, 134.4, 140.0, 148.8, 166.6, 212.8; FTIR (ATR) 3450, 1639, 1483, 1425, 1201, 1073, 776, 730 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_{10}ClOS_2$ $[M+H]^+$: 304.9861; found: 304.9872.

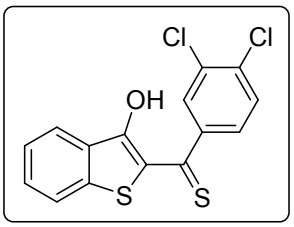
(3-Bromophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2s): 92 mg; 53% yield; red solid; mp 131-133 °C; R_f 0.52 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.36 (m, 1H), 7.40-7.47 (m, 1H), 7.55-7.68 (m, 4H), 7.80 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 14.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.4, 122.8, 122.9, 125.2, 125.7, 129.8, 130.1, 131.4, 132.1, 133.5, 140.0, 149.0, 166.7, 212.7; FTIR (ATR) 3388, 2965, 2930, 2851, 1487, 1425, 774, 729 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_{10}BrOS_2$ $[M+H]^+$: 348.9356; found : 348.9369.



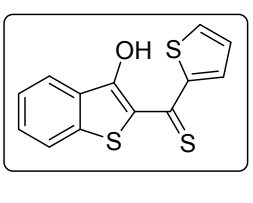
3-(3-Hydroxybenzo[b]thiophene-2-carbonothioyl)benzonitrile (2t): 112 mg; 76% yield; red solid; mp 152-154 °C; R_f 0.35 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (t, *J* = 7.6 Hz, 1H), 7.52-7.66 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 14.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.7, 118.1, 122.7, 123.0, 125.3, 125.4, 129.3, 130.5, 131.1, 131.2, 132.4, 133.6, 139.8, 147.9, 166.9, 211.2; FTIR (ATR) 3427, 3068, 3037, 2228, 1595, 1488, 1436, 750, 728 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{10}NOS_2$ $[M+H]^+$: 296.0203; found : 296.0216.



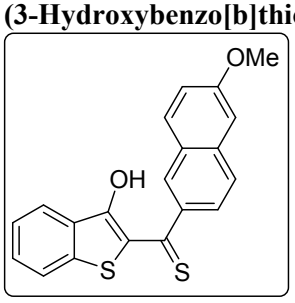
(3,4-Dichlorophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2u): 106 mg; 63% yield; red solid; mp 158-160 °C; R_f 0.45 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.47 (m, 1H), 7.49-7.56 (m, 2H), 7.60-7.66 (m, 1H), 7.67-7.70 (m, 1H), 7.77 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 14.64 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.6, 122.9, 125.2, 125.3, 126.4, 129.1, 130.3, 131.4, 132.3, 135.0, 139.9, 146.7, 166.9, 211.3; FTIR (ATR) 3423, 2918, 2851, 1639, 1461, 1423, 818, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_8Cl_2OS_2Na$ $[M+Na]^+$: 360.9291; found : 360.9302.



(3-Hydroxybenzo[b]thiophen-2-yl)(thiophen-2-yl)methanethione (2v): 113 mg; 82% yield; red solid; mp 124-126 °C; R_f 0.61 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13-7.21 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.63-7.79 (m, 2H), 7.90-7.95 (m, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 14.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 119.7, 122.6, 124.9, 125.1, 128.4, 129.6, 130.0, 131.7, 134.8, 139.5, 152.5, 166.7, 201.0; FTIR (ATR) 3445, 2954, 2921, 2851, 1487, 1402, 1223, 765, 728 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{13}H_8OS_3Na$ $[M+Na]^+$: 298.9635; found : 298.9642.

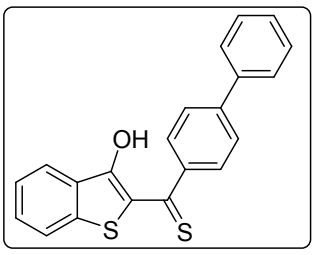


(3-Hydroxybenzo[b]thiophen-2-yl)(6-methoxynaphthalen-2-yl)methanethione (2w): 106 mg; 61% yield; red solid; mp 176-178 °C; R_f 0.50 (15% ethyl acetate in

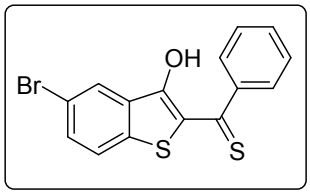


hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H), 7.10-7.18 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.70-7.80 (m, 3H), 8.03-8.13 (m, 2H), 14.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.5, 105.8, 120.0, 122.7, 122.8, 125.0, 125.1, 125.8, 126.9, 127.1, 127.7, 130.9, 131.6, 131.7, 136.0, 140.0, 143.1, 159.3, 166.0, 215.1; FTIR (ATR) 3440, 2921, 2967, 2923, 1475, 1423, 1222, 1095, 805, 726 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{20}H_{15}O_2S_2$ $[M+H]^+$: 351.0513; found : 351.0494.

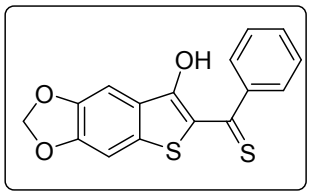
[1,1'-Biphenyl]-4-yl(3-hydroxybenzo[b]thiophen-2-yl)methanethione (2x): 98 mg; **5**7% yield; red solid; mp 140-142 °C; R_f 0.55 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.50 (m, 4H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.63-7.71 (m, 5H), 7.78 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 14.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.6, 122.8, 125.1, 127.0, 127.3, 127.9, 128.1, 129.0, 131.5, 131.7, 139.9, 140.1, 143.7, 146.5, 166.2, 214.7; FTIR (ATR) 3441, 2922, 2853, 1492, 1426, 758, 728 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{21}H_{15}OS_2$ $[M+H]^+$: 347.0564; found : 347.0511.



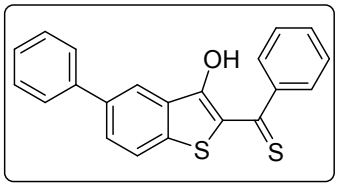
(5-Bromo-3-hydroxybenzo[b]thiophen-2-yl)(phenyl)methanethione (2y): 137 mg; 79% yield; red solid; mp 150-152 °C; R_f 0.41 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.61-7.67 (m, 2H), 8.25 (s, 1H),), 14.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.9, 123.4, 124.3, 127.1, 127.4, 128.4, 131.0, 133.1, 134.5, 138.1, 147.6, 164.3, 216.8; FTIR (ATR) 3423, 2953, 2921, 2852, 1484, 1445, 802, 730 cm^{-1}.



(7-Hydroxythieno[2',3':4,5]benzo[1,2-d][1,3]dioxol-6-yl)(phenyl)methanethione (2z): 111 mg; 71% yield; red solid; mp 112-114 °C; R_f 0.41 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.02 (s, 2H), 6.89 (s, 1H), 7.18 (s, 1H), 7.30-7.42 (m, 4H), 7.56 (d, *J* = 7.6 Hz, 2H), 14.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 101.6, 102.4, 122.8, 125.8, 127.1, 128.3, 130.5, 137.3, 147.5, 147.6, 152.9, 165.8, 212.2; FTIR (ATR) 3476, 2961, 2923, 2854, 1636, 1465, 1434, 1261, 803, 733 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{11}O_3S_2$ $[M+H]^+$: 315.0149; found : 315.0121.

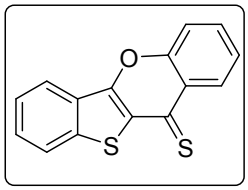


(3-Hydroxy-5-phenylbenzo[b]thiophen-2-yl)(phenyl)methanethione (2aa): 126 mg; 73% yield; reddish liquid; R_f 0.52 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.44 (m, 1H), 7.46-7.52 (m, 5H), 7.66-7.73 (m, 5H), 7.83 (d, *J* = 8.8 Hz, 1H), 8.31 (s, 1H), 14.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.9, 123.2, 127.2, 127.3, 127.4, 128.3,

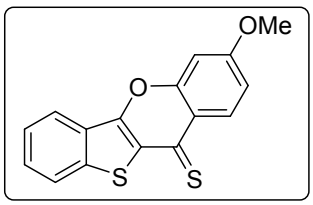


128.4, 129.1, 130.8, 131.3, 132.1, 138.5, 138.9, 140.0, 147.7, 166.2, 215.4; FTIR (ATR) 3473, 2963, 2928, 2850, 1638, 1467, 1434, 1261, 805, 731 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{21}H_{15}OS_2$ $[M+H]^+$: 347.0564; found : 347.0569.

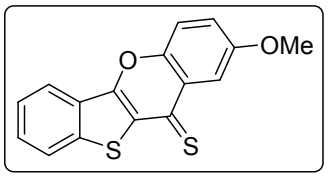
Experimental spectral data for 3:

11*H*-Benzo[4,5]thieno[3,2-b]chromen-11-one (3a): 123 mg; 92% yield; yellow solid; mp 111-113 

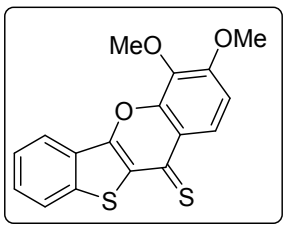
°C; R_f 0.65 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (t, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.6, 1H), 7.68 (d, *J* = 7.6, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7,48 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.6, 123.5, 123.8, 125.5, 126.0, 128.2, 128.3, 129.6, 129.9, 134.0, 135.1, 142.0, 145.3, 151.1, 195.0; FTIR (ATR) 2917, 2847, 1644, 1577, 1244, 761, 729 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_9OS_2$ $[M+H]^+$: 269.0094; found : 269.0086.

3-Methoxy-11H-benzo[4,5]thieno[3,2-b]chromen-11-one (3b): 116 mg; 78% yield; yellowish 

liquid; R_f 0.41 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.96 (s, 3H), 6.97-7.05 (m, 2H), 7.45 (t, *J* = 7.6, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.56-8.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 100.2, 115.7, 123.1, 123.2, 123.6, 125.4, 129.4, 129.6, 129.7, 134.3, 141.6, 145.0, 152.9, 164.8, 193.6; FTIR (ATR) 2921, 2851, 1636, 1269, 808, 733 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{11}O_2S_2$ $[M+H]^+$: 299.0200; found : 299.0201.

2-Methoxy-11H-benzo[4,5]thieno[3,2-b]chromen-11-one (3c): 105 mg; 71% yield; red solid; mp 

121-123 °C; R_f 0.31 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.97 (s, 3H), 7.35-7.45 (m, 1H), 7.50 (t, *J* = 7.6, 1H), 7.57-7.67 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 107.5, 119.9, 123.4, 123.8, 124.3, 125.5, 128.9, 129.7, 129.8, 134.9, 141.8, 145.4, 145.9, 157.7, 193.6; FTIR (ATR) 2928, 2852, 1635, 1616, 1248, 752, 725 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{10}O_2S_2Na$ $[M+Na]^+$: 321.0019; found : 321.0002.

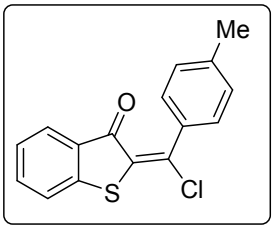
3,4-Dimethoxy-11H-benzo[4,5]thieno[3,2-b]chromene-11-thione (3d): 111 mg; 68% yield; yellow 

viscous liquid; R_f 0.41 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.05 (s, 3H), 4.11 (s, 3H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.7,

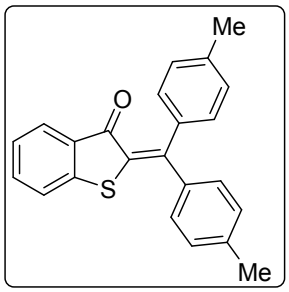
61.9, 110.9, 123.5, 123.7, 123.8, 124.0, 125.5, 129.7, 129.8, 134.2, 136.9, 141.9, 145.0, 146.1, 157.2, 194.3; FTIR (ATR) 2984, 2935, 1742, 1635, 1610, 1241, 808, 757 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{17}H_{12}O_3S_2$ $[M+H]^+$: 329.0306; found : 329.0307.

Experimental spectral data for application:

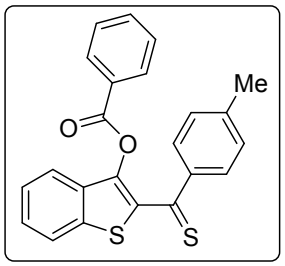
(Z)-2-(chloro(p-tolyl)methylene)benzo[b]thiophen-3(2H)-one (5): 131 mg; 92% yield; yellowish liquid; R_f 0.56 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 7.24 (d, *J* = 7.2 Hz, 3H), 7.24 (m, 3H), 7.50 (t, *J* = 7.5, 1H), 7.72 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 123.6, 125.6, 127.2, 128.9, 129.2, 132.3, 132.9, 133.1, 135.4, 141.4, 143.6, 144.1, 183.6; FTIR (ATR) 3060, 2986, 1734, 1635, 1266, 1245, 746, 704 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{16}H_{11}ClOSNH_4$ $[M+NH_4]^+$: 304.0562; found : 304.0541.



2-(Di-*p*-tolylmethylene)benzo[b]thiophen-3(2H)-one (6): 160 mg; 94% yield; red solid; mp 98-100 °C; R_f 0.56 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.3-2.4 (m, 6H), 7.18-7.25 (m, 7H), 7.30-7.38 (m, 3H), 7.48 (t, J = 7.4, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 14.67; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 123.3, 125.0, 127.0, 129.0, 129.2, 129.5, 129.7, 130.1, 132.9, 134.6, 136.8, 138.9, 139.5, 139.7, 145.8, 151.7, 186.8; FTIR (ATR) 2922, 2854, 1735, 1671, 1587, 1280, 818, 743 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{19}OS$ $[M+H]^+$: 343.1156; found : 343.1157.



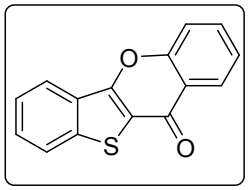
2-(4-Methylphenylcarbonothioyl)benzo[b]thiophen-3-yl benzoate (7): 143 mg; 74% yield; yellowish liquid; R_f 0.48 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.02 (s, 3H), 6.91 (d, J = 6.9 2H), 7.34 (t, J = 7.3, 3H), 7.45-7.54 (m, 4H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.73-7.77 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 122.9, 123.7, 125.4, 128.0, 128.1, 128.2, 128.5, 128.7, 130.1, 130.2, 133.8, 138.2, 139.7, 140.5, 142.0, 145.1, 163.5, 224.6; FTIR (ATR) 2923, 2854, 1747, 1688, 1282, 1240, 745, 708 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{17}O_2S_2$ $[M+H]^+$: 389.0669; found : 389.0668.



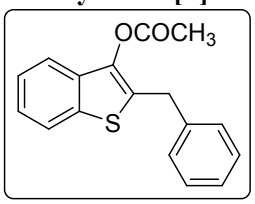
((3-Oxobenzo[b]thiophen-2(3H)-ylidene)(p-tolyl)methyl) benzothioate (8): 44 mg; 22% yield with 6:1 E/Z ratio; reddish liquid; R_f 0.41 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.40-7.55 (m, 6H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.70-7.74 (m, 1H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 122.8, 123.2, 123.5, 125.6, 127.3, 128.0, 128.4, 128.8, 129.0, 129.1,

129.2, 130.5, 133.0, 133.9, 134.3, 134.7, 135.5, 136.2, 139.3, 139.8, 141.5, 144.4, 184.2, 185.9; FTIR (ATR) 3058, 2983, 1731, 1691, 1291, 1266, 740, 706 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{17}O_2S_2$ $[M+H]^+$: 389.0669; found : 389.0672.

11*H*-benzo[4,5]thieno[3,2-b]chromen-11-one (9): 98 mg; 78% yield; yellow liquid; R_f 0.41 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.62 (m, 3H), 7.63-7.70 (m, 1H), 7.71-7.79 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.2, 122.6, 122.8, 123.9, 125.1, 125.2, 126.1, 128.9, 129.4, 129.5, 133.9, 140.1, 153.9, 156.2, 173.5; FTIR (ATR) 2938, 2857, 1698, 1496, 1249, 757, 705 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{15}H_8O_2SNa$ $[M+Na]^+$: 275.0142; found : 275.0125.



2-benzylbenzo[b]thiophen-3-yl acetate (15): 94 mg; 67% yield; yellow liquid; R_f 0.45 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H), 4.09 (s, 2H), 7.23-7.35 (m, 7H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6, 33.0, 120.1, 122.8, 124.5, 124.7, 126.9, 128.7, 128.8, 130.9, 133.0, 136.0, 137.4, 138.7, 168.7; HRMS (*m*/*z*) calculated for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0612; found : 305.0605.



6. ^1H and ^{13}C spectra for all compounds

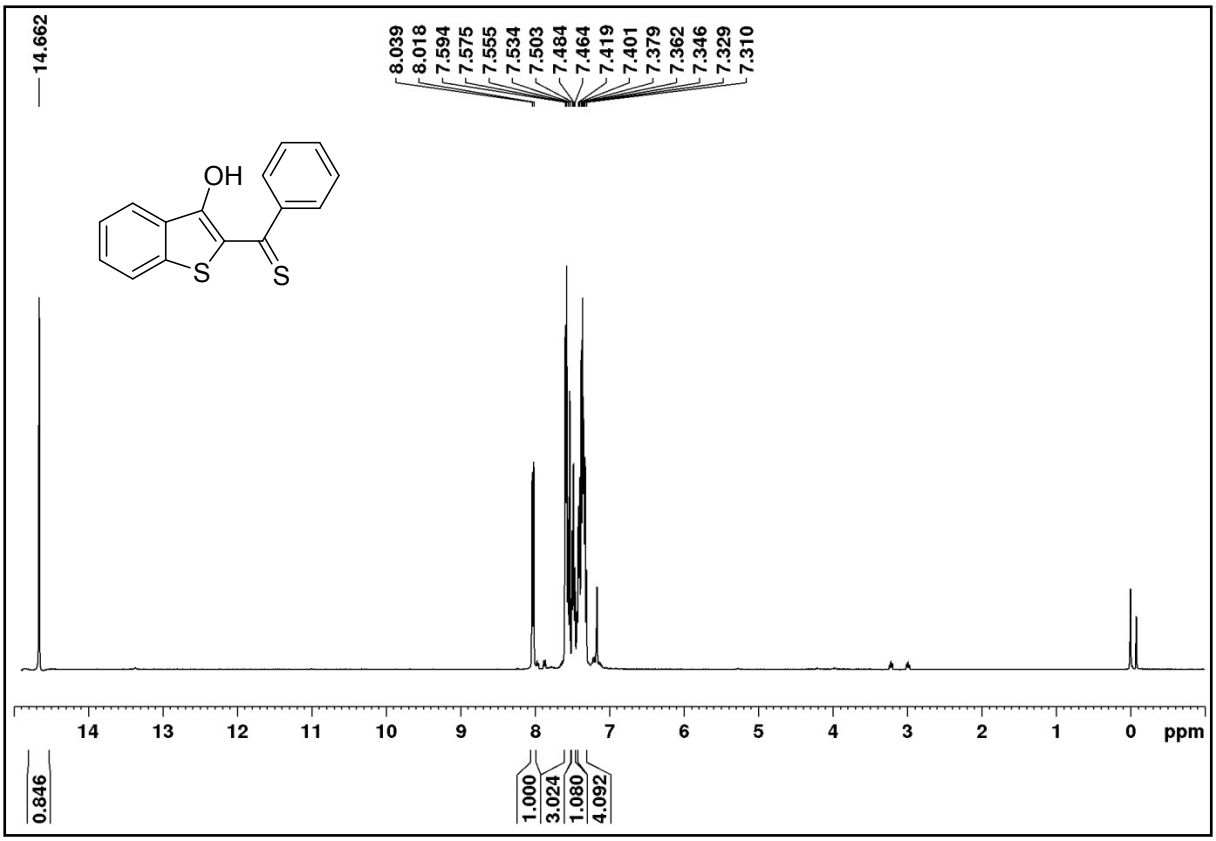


Figure 1: 400 MHz ^{1}H-NMR spectrum of **2a** in $CDCl_3$

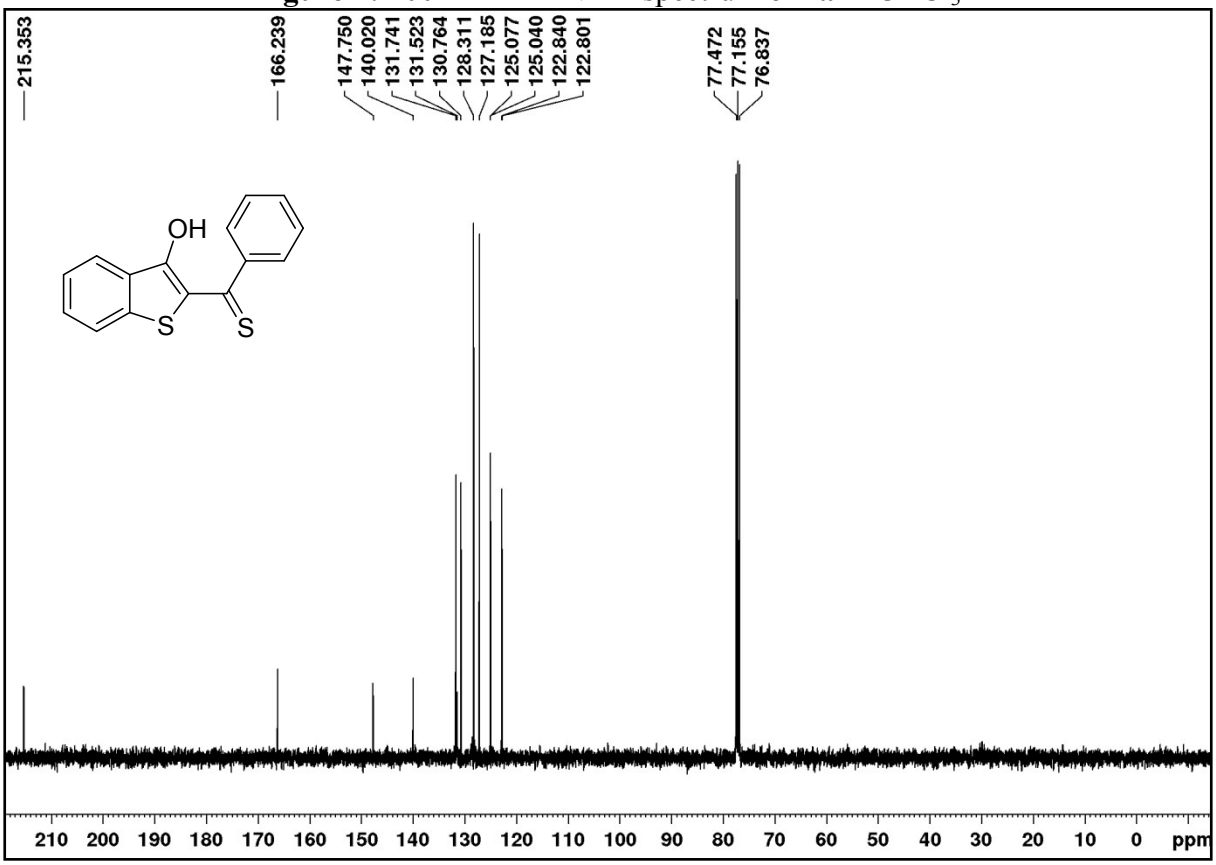


Figure 2: 100 MHz ^{13}C-NMR spectrum of **2a** in $CDCl_3$

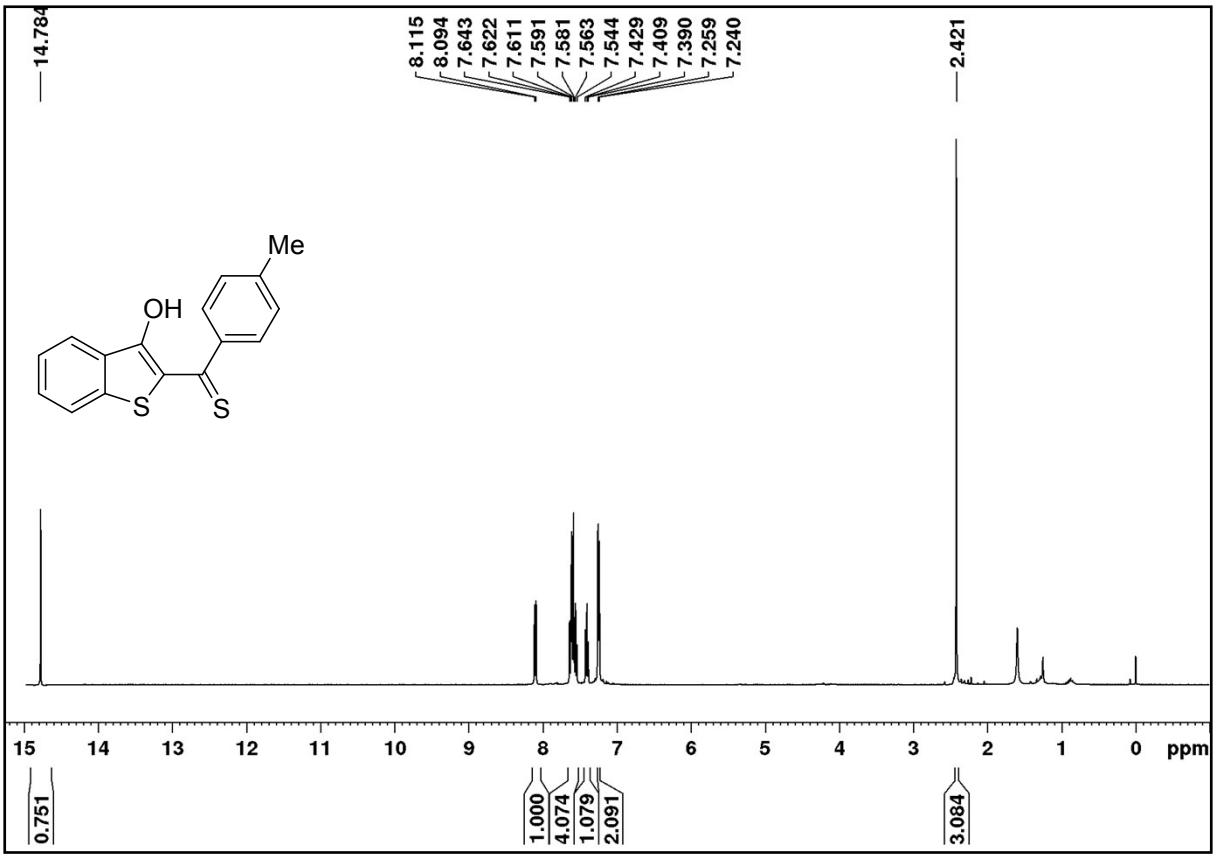


Figure 3: 400 MHz ^{1}H-NMR spectrum of **2b** in $CDCl_3$

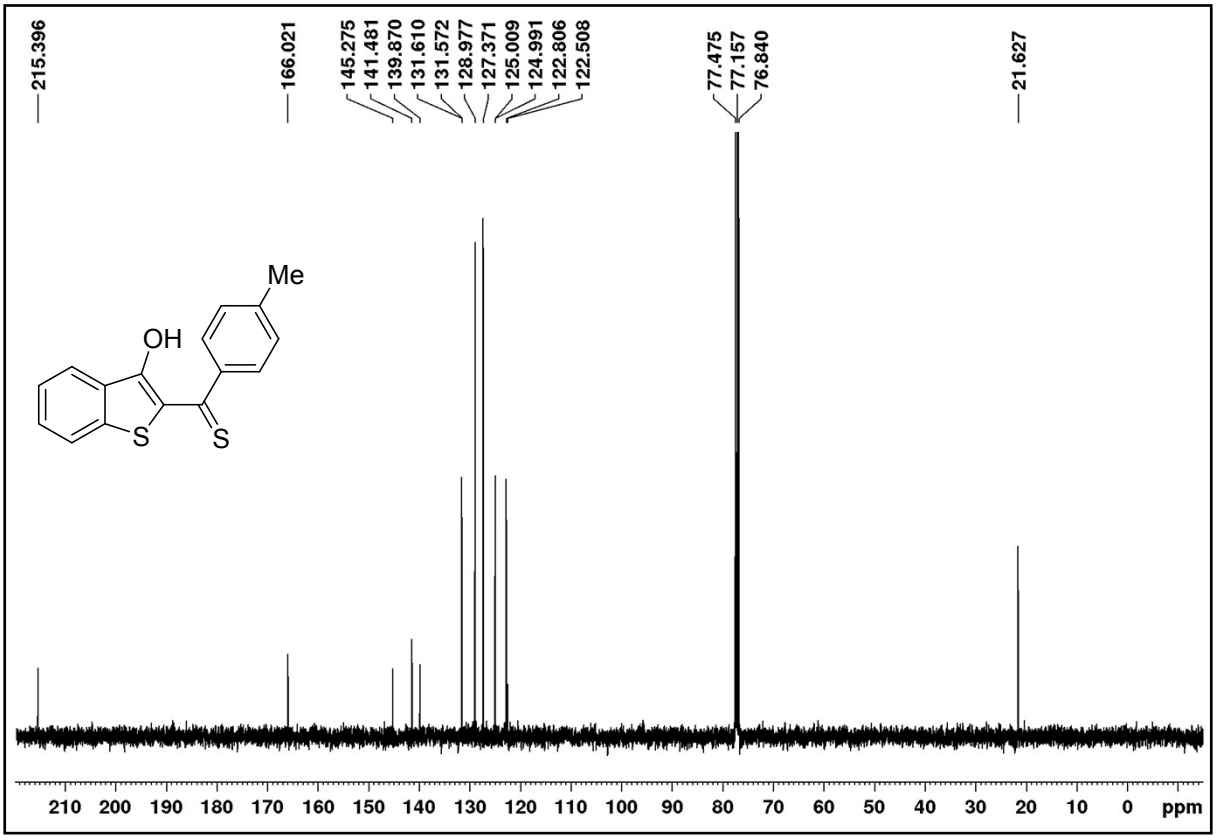


Figure 4: 100 MHz ^{13}C-NMR spectrum of **2b** in $CDCl_3$

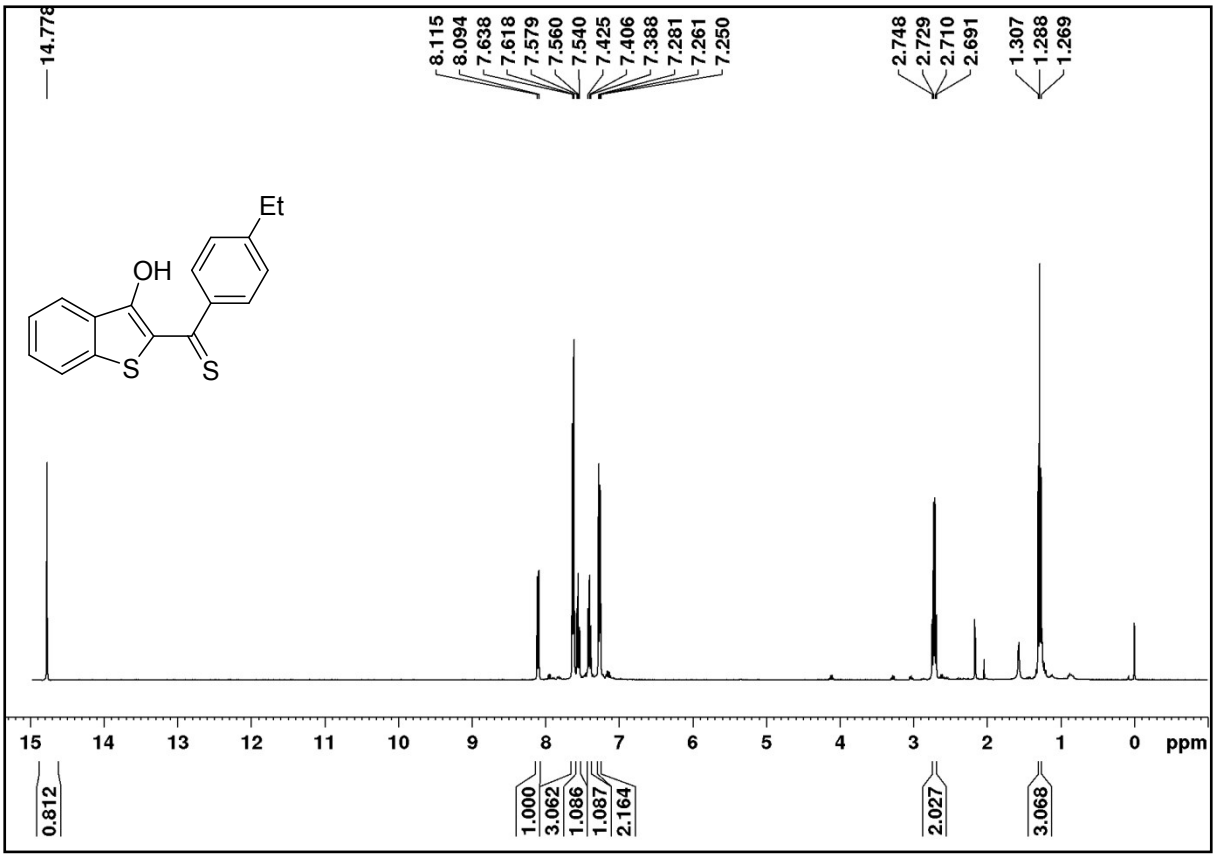


Figure 5: 400 MHz ^{1}H-NMR spectrum of **2c** in $CDCl_3$

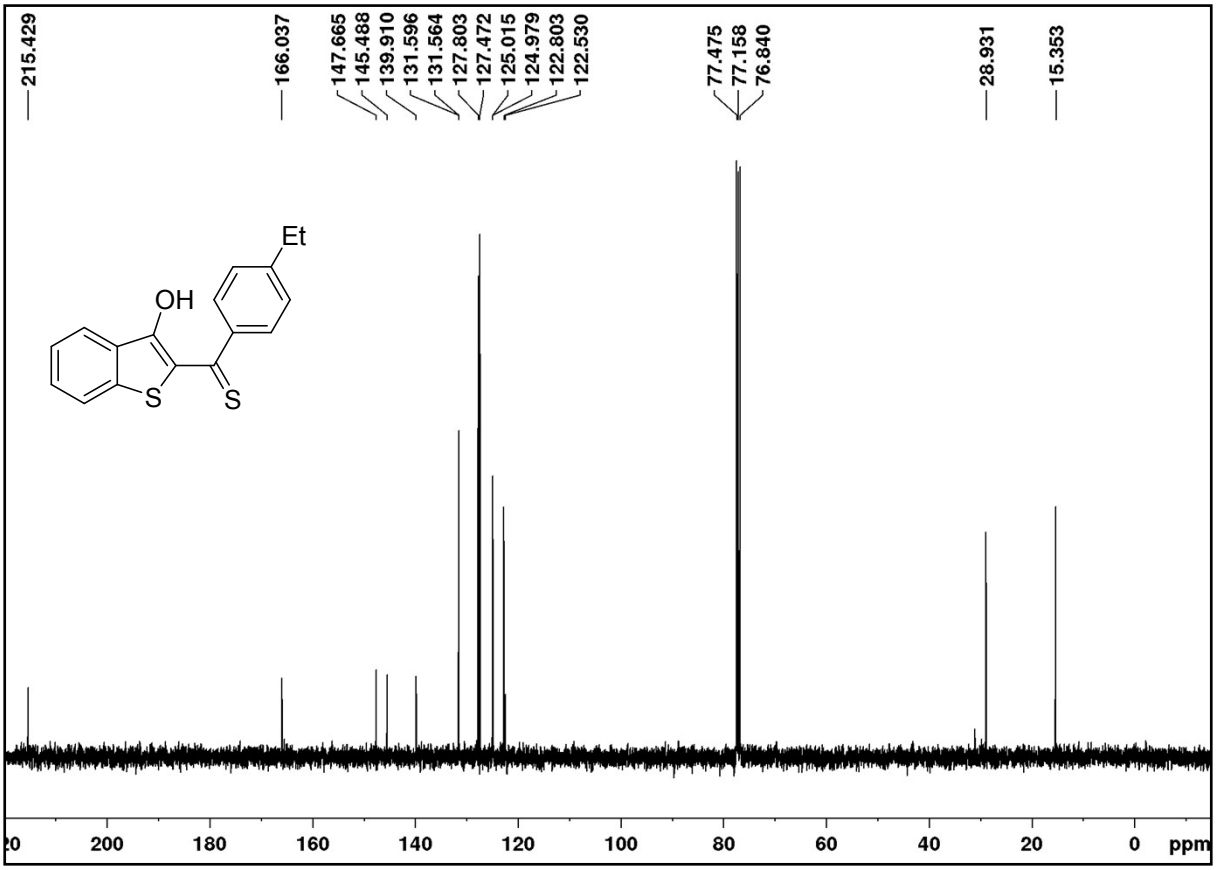


Figure 6: 100 MHz ^{13}C-NMR spectrum of **2c** in $CDCl_3$

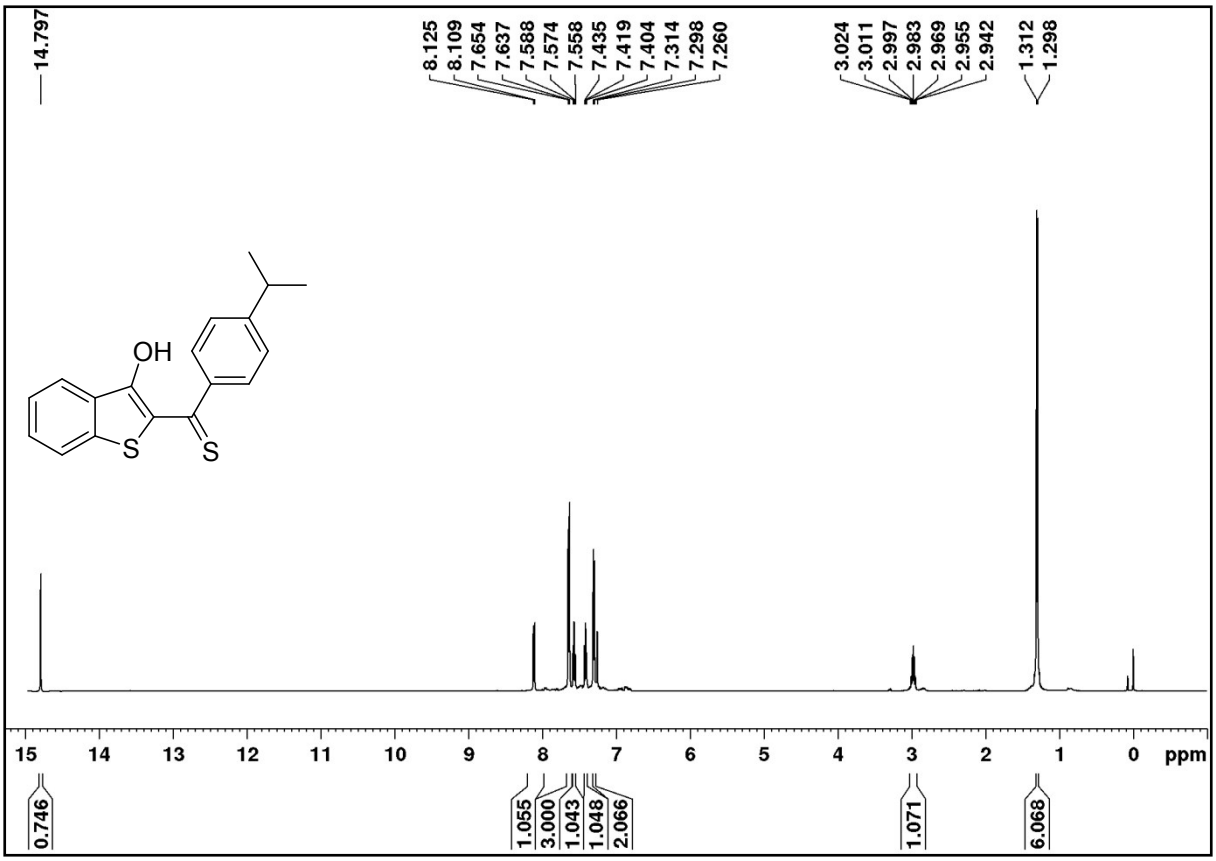


Figure 7: 400 MHz ^{1}H-NMR spectrum of **2d** in $CDCl_3$

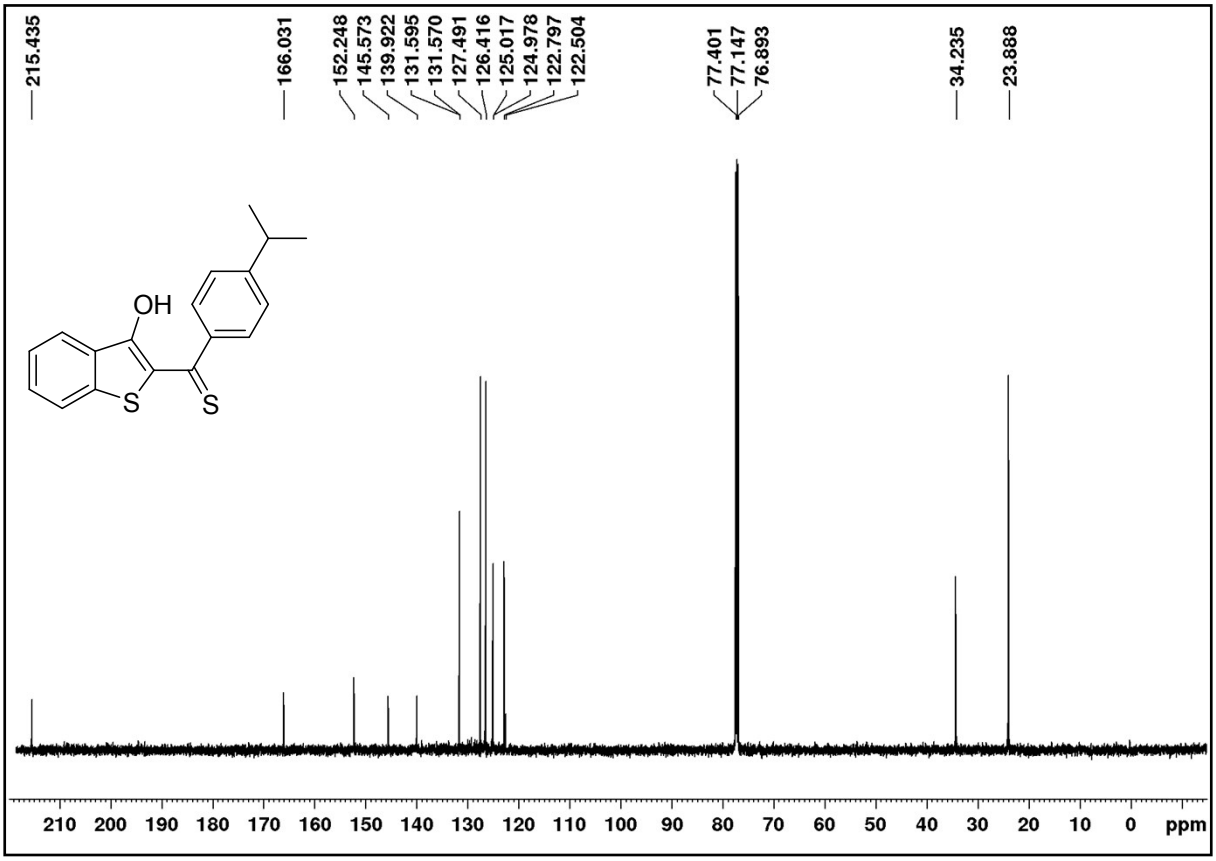


Figure 8: 100 MHz ^{13}C-NMR spectrum of **2d** in $CDCl_3$

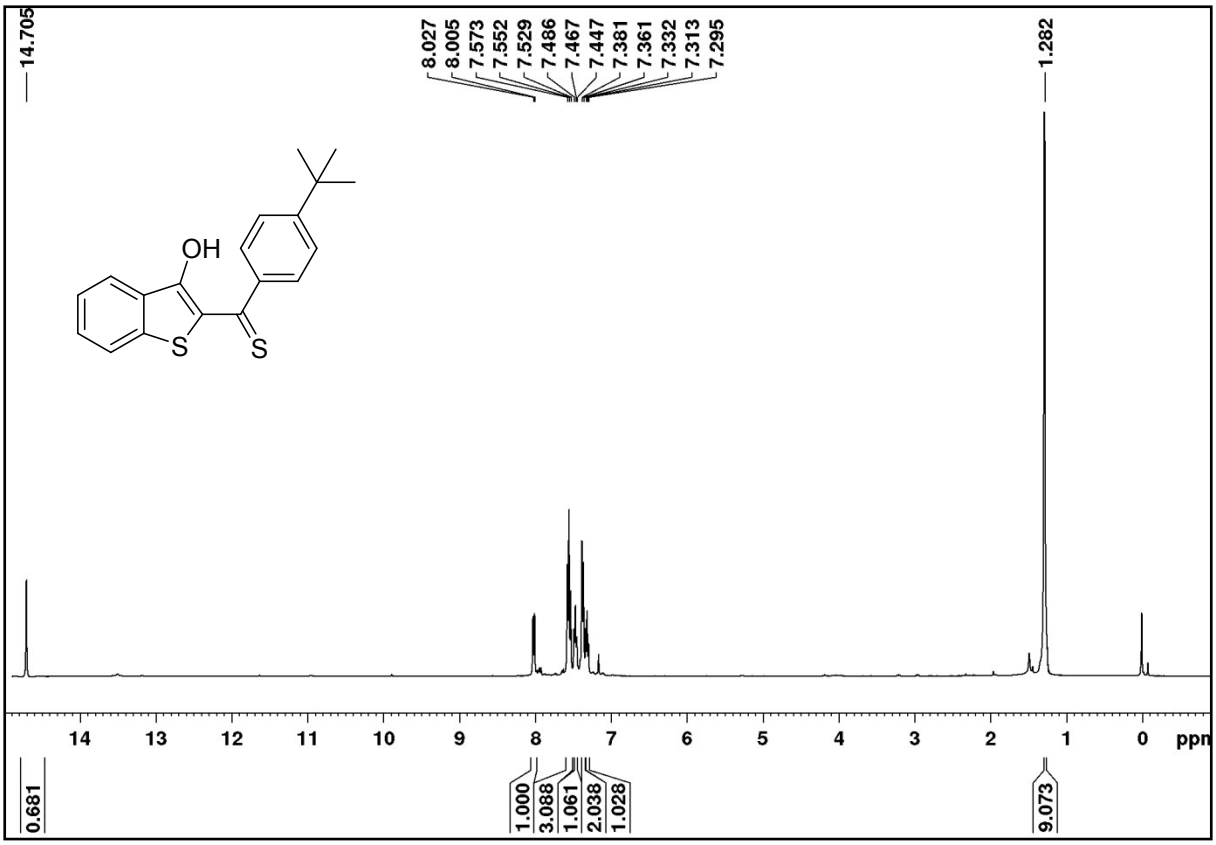


Figure 9: 400 MHz ^{1}H-NMR spectrum of **2e** in $CDCl_3$

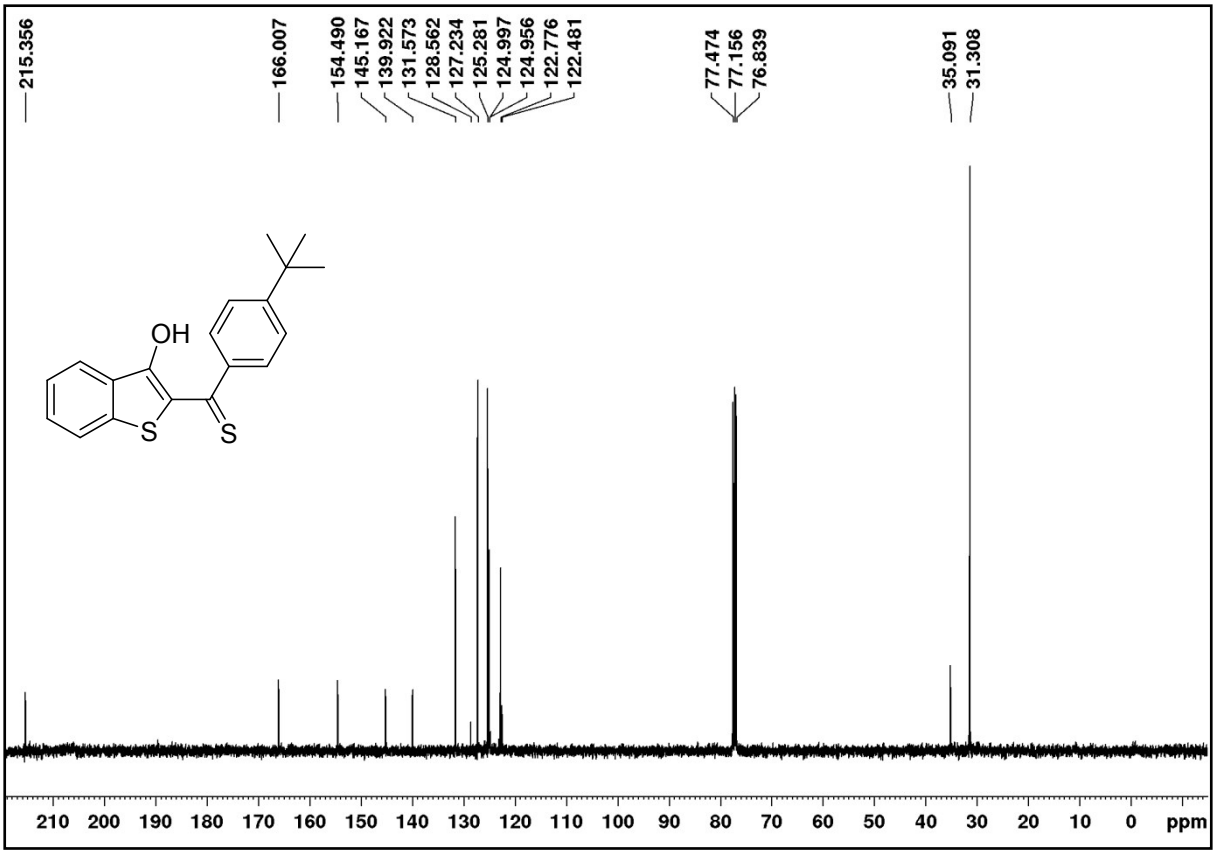


Figure 10: 100 MHz ^{13}C-NMR spectrum of **2e** in $CDCl_3$

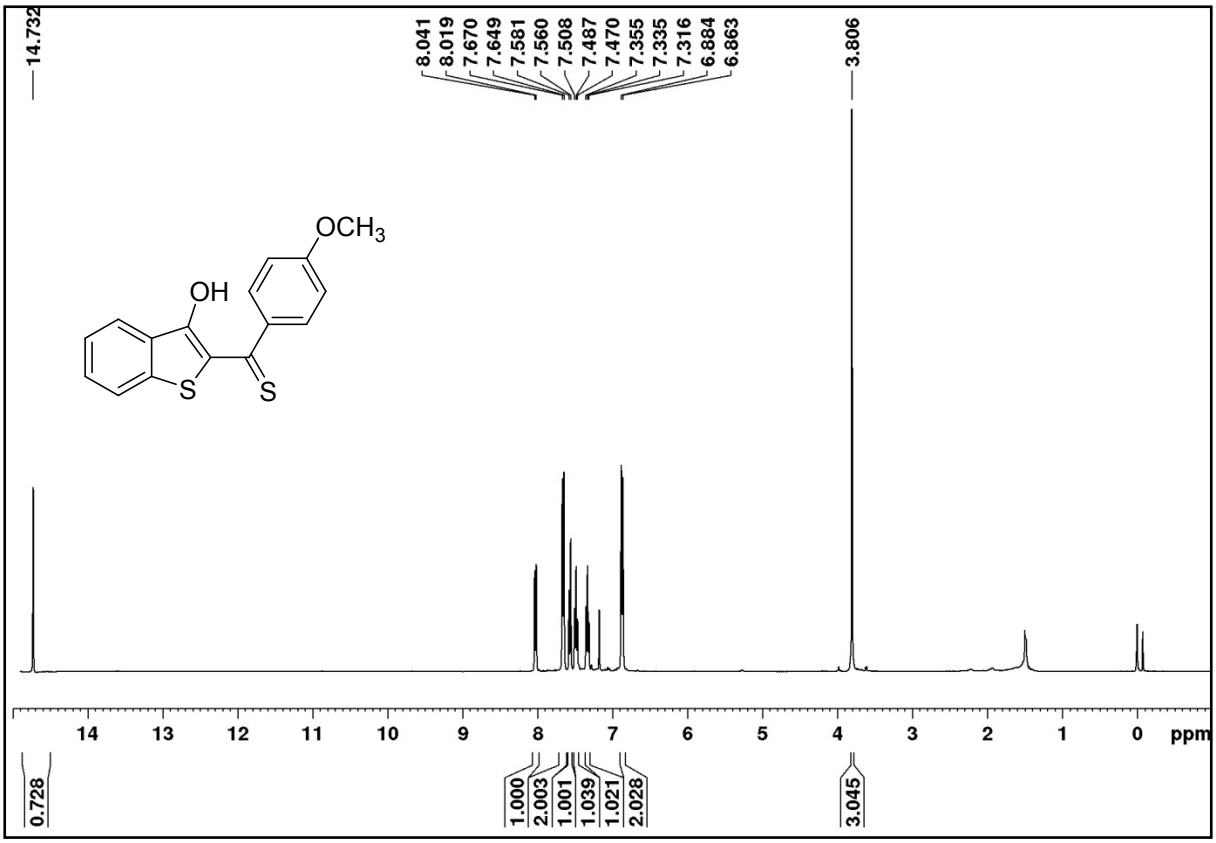


Figure 11: 400 MHz ^{1}H-NMR spectrum of **2f** in $CDCl_3$

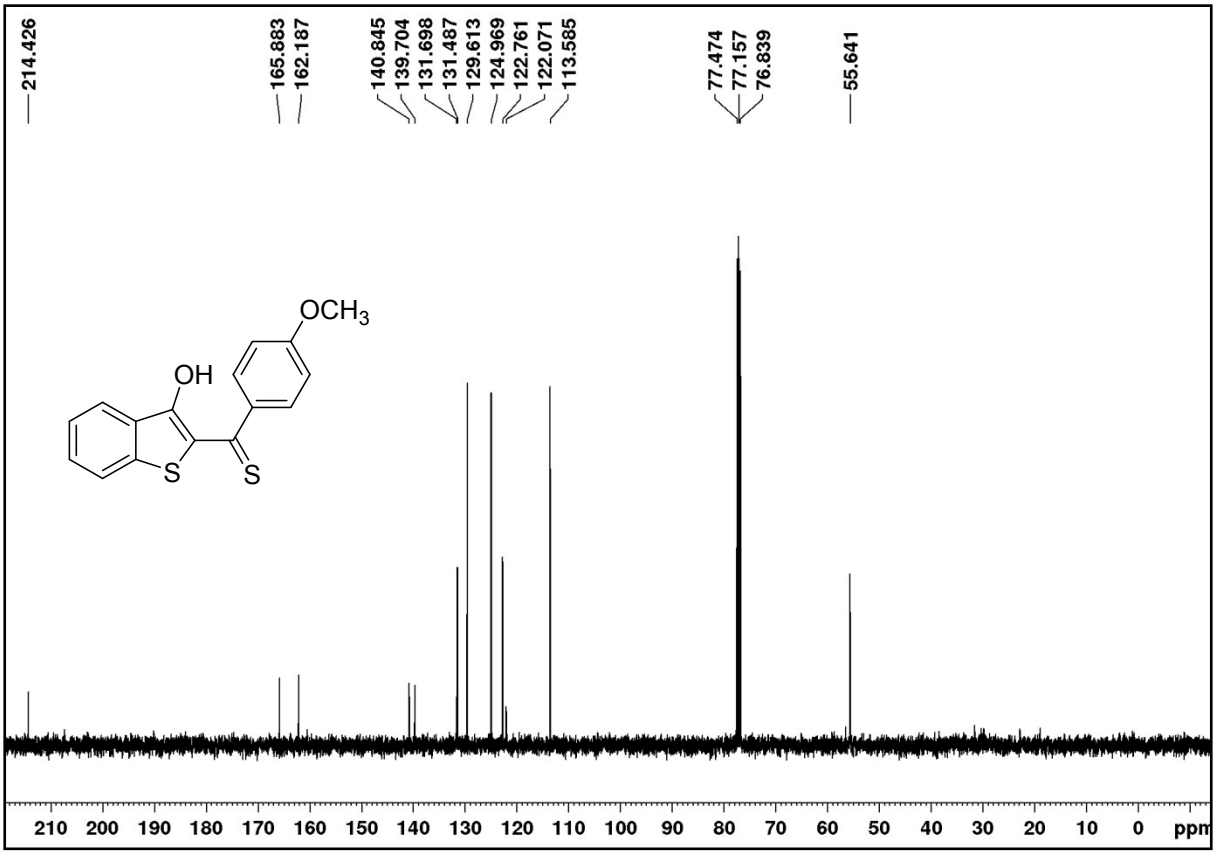


Figure 12: 100 MHz ^{13}C-NMR spectrum of **2f** in $CDCl_3$

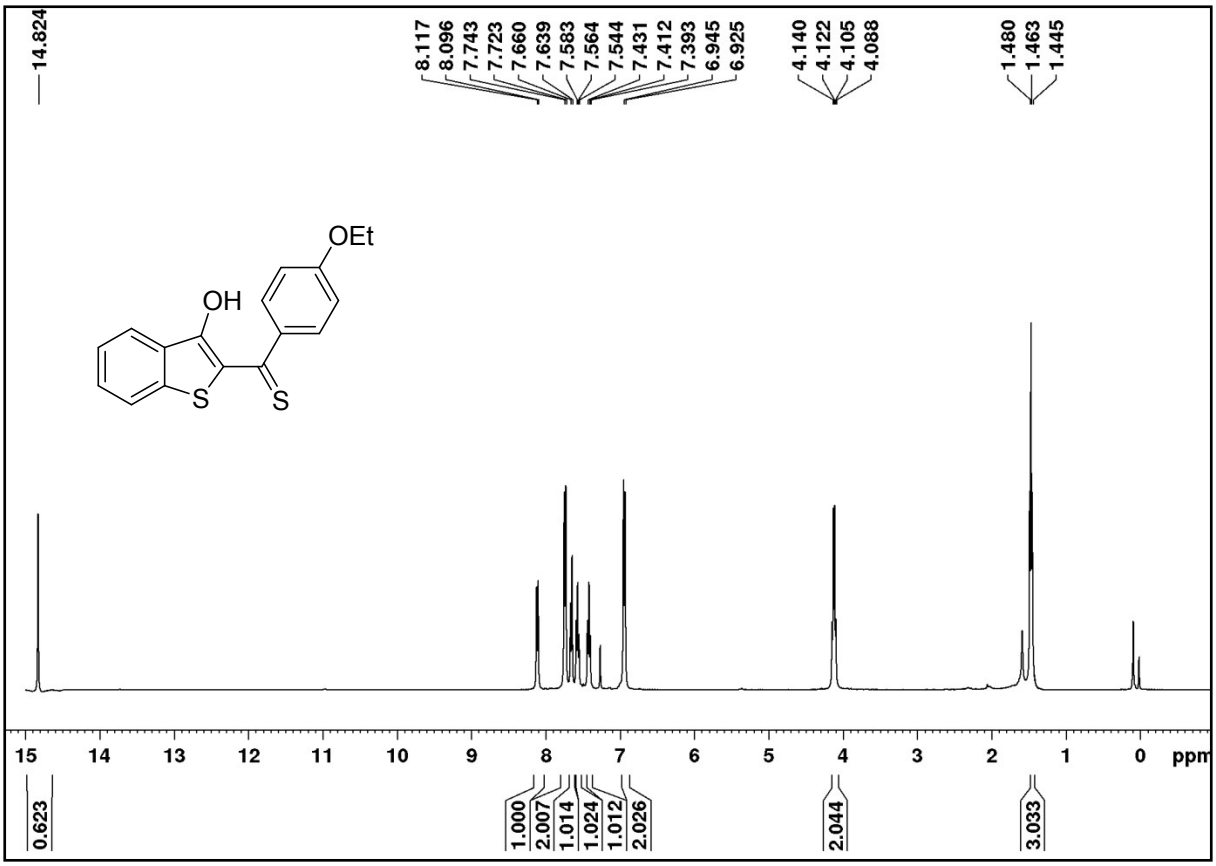


Figure 13: 400 MHz ^{1}H-NMR spectrum of **2g** in $CDCl_3$

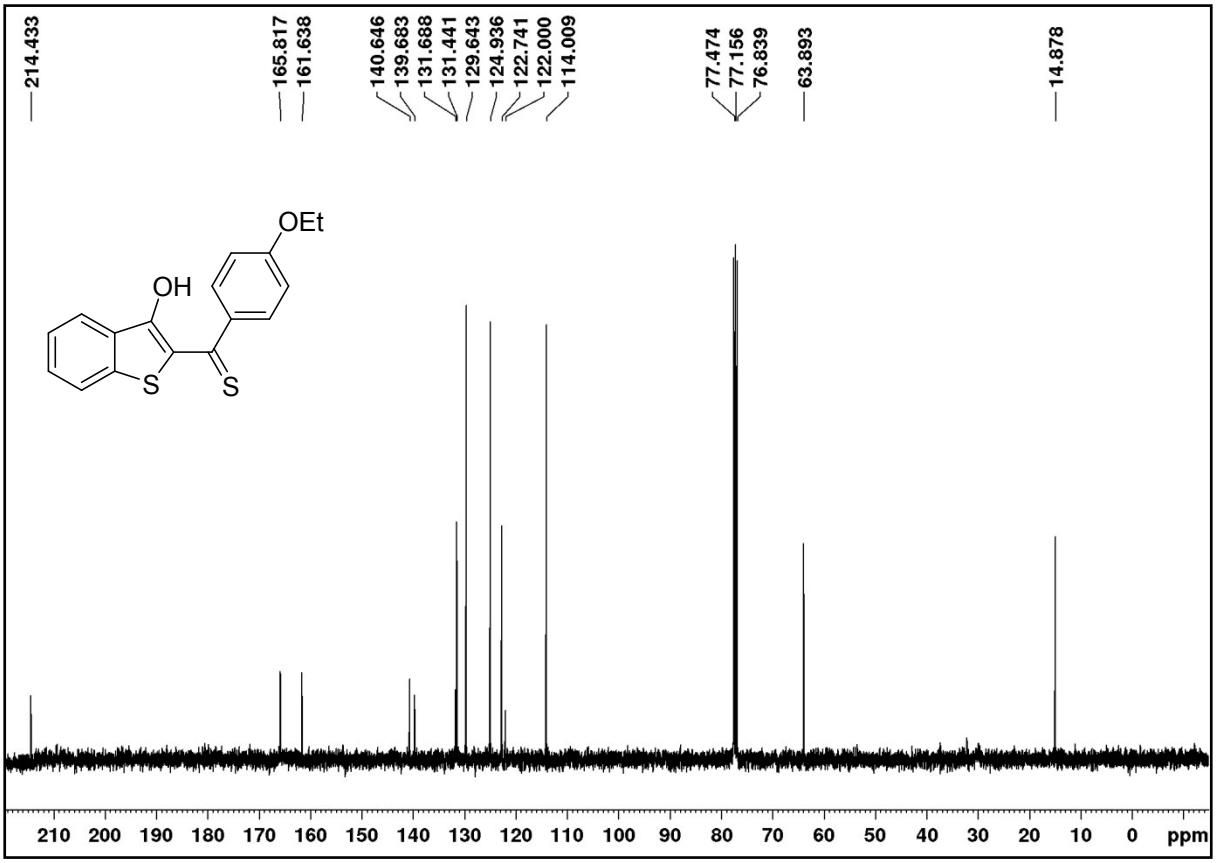


Figure 14: 100 MHz ^{13}C-NMR spectrum of **2g** in $CDCl_3$

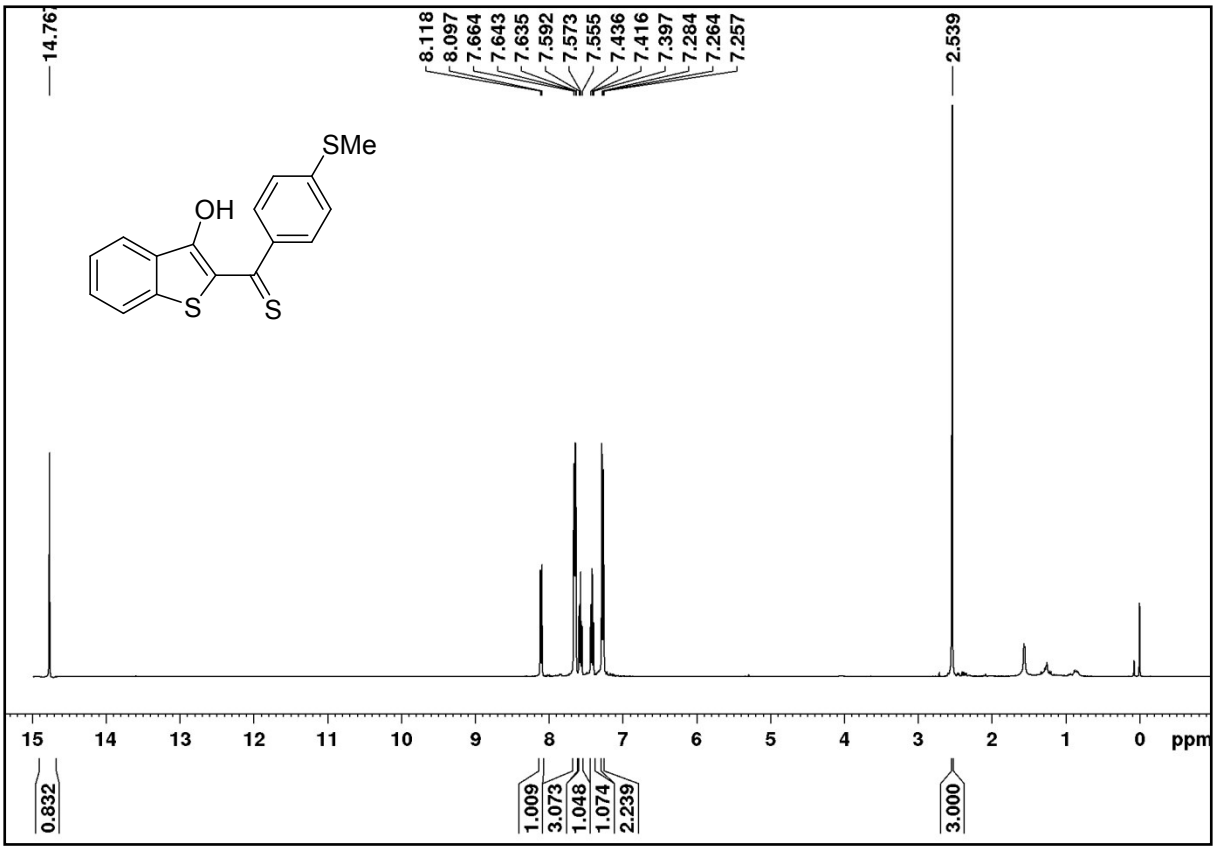


Figure 15: 400 MHz ^{1}H-NMR spectrum of **2h** in $CDCl_3$

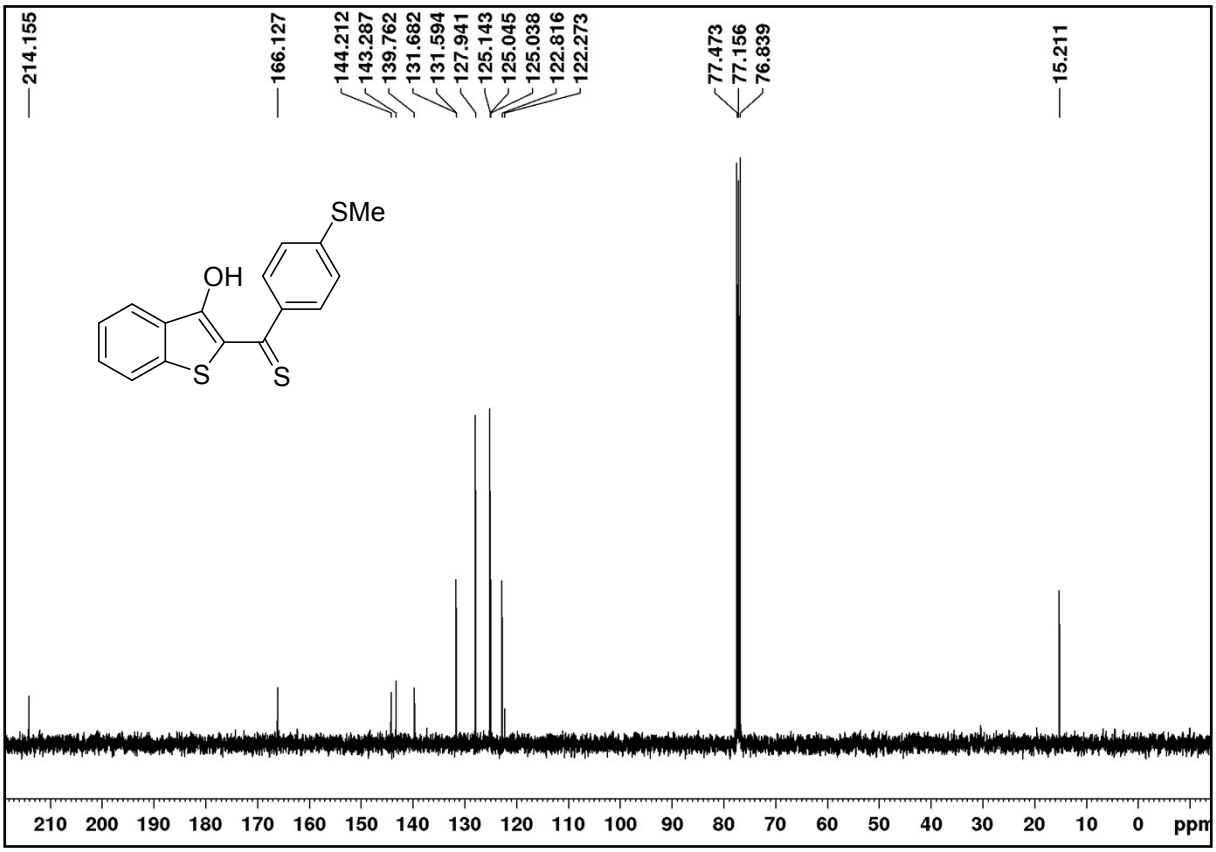


Figure 16: 100 MHz ^{13}C-NMR spectrum of **2h** in $CDCl_3$

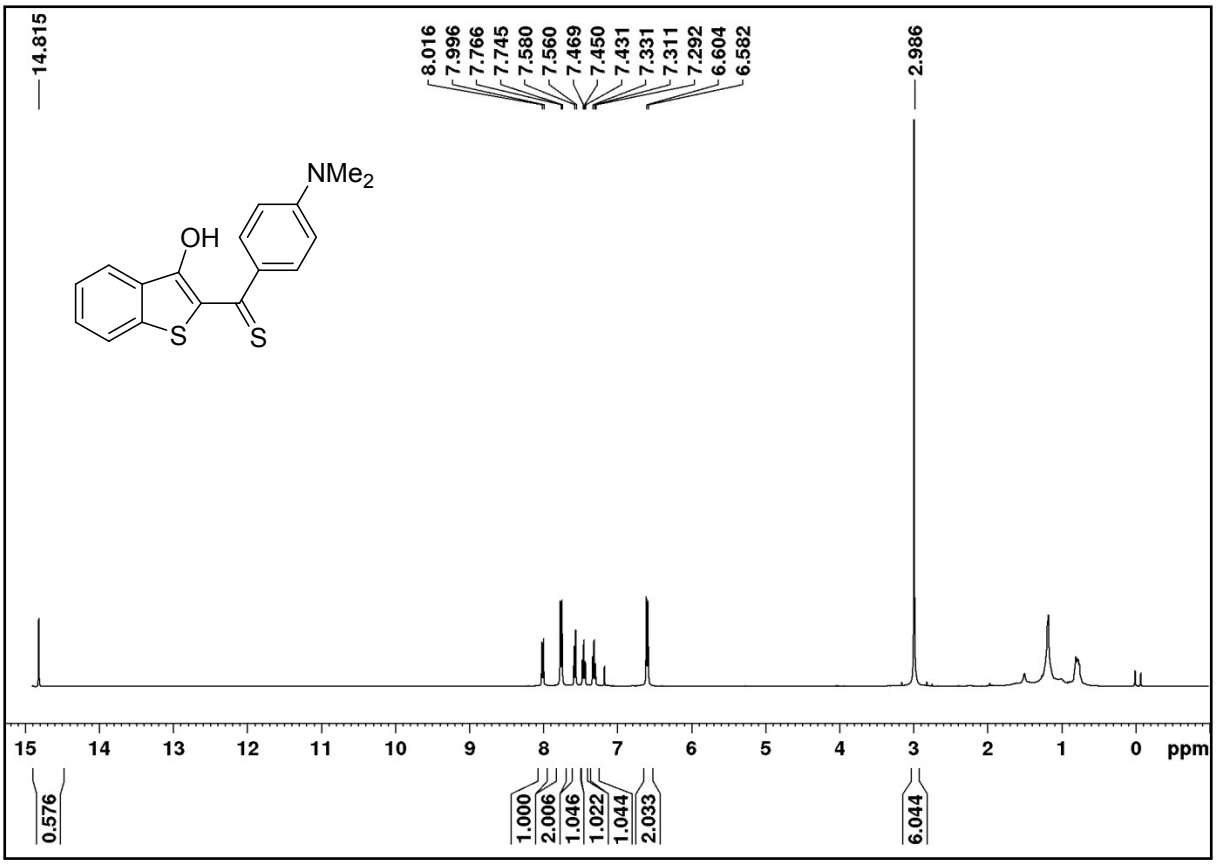


Figure 17: 400 MHz ^{1}H-NMR spectrum of **2i** in $CDCl_3$

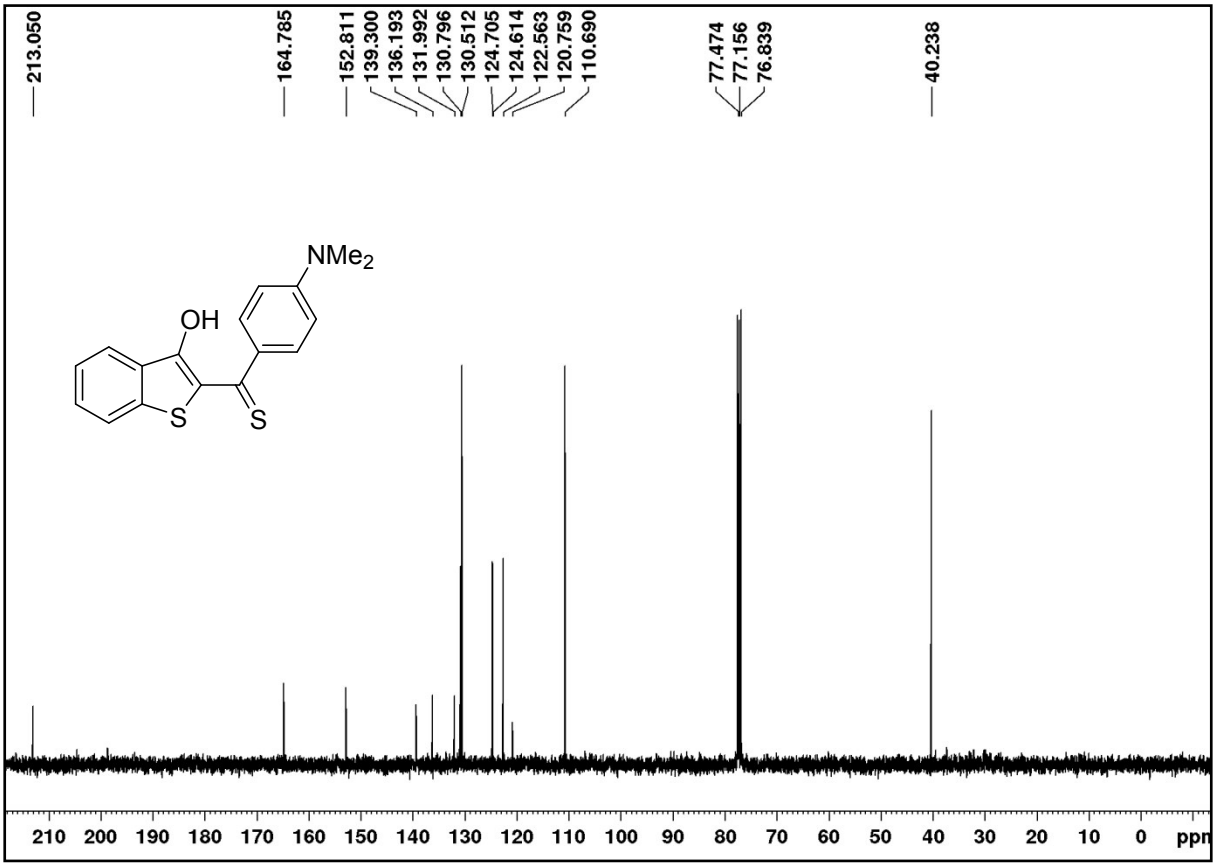


Figure 18: 100 MHz ^{13}C-NMR spectrum of **2i** in $CDCl_3$

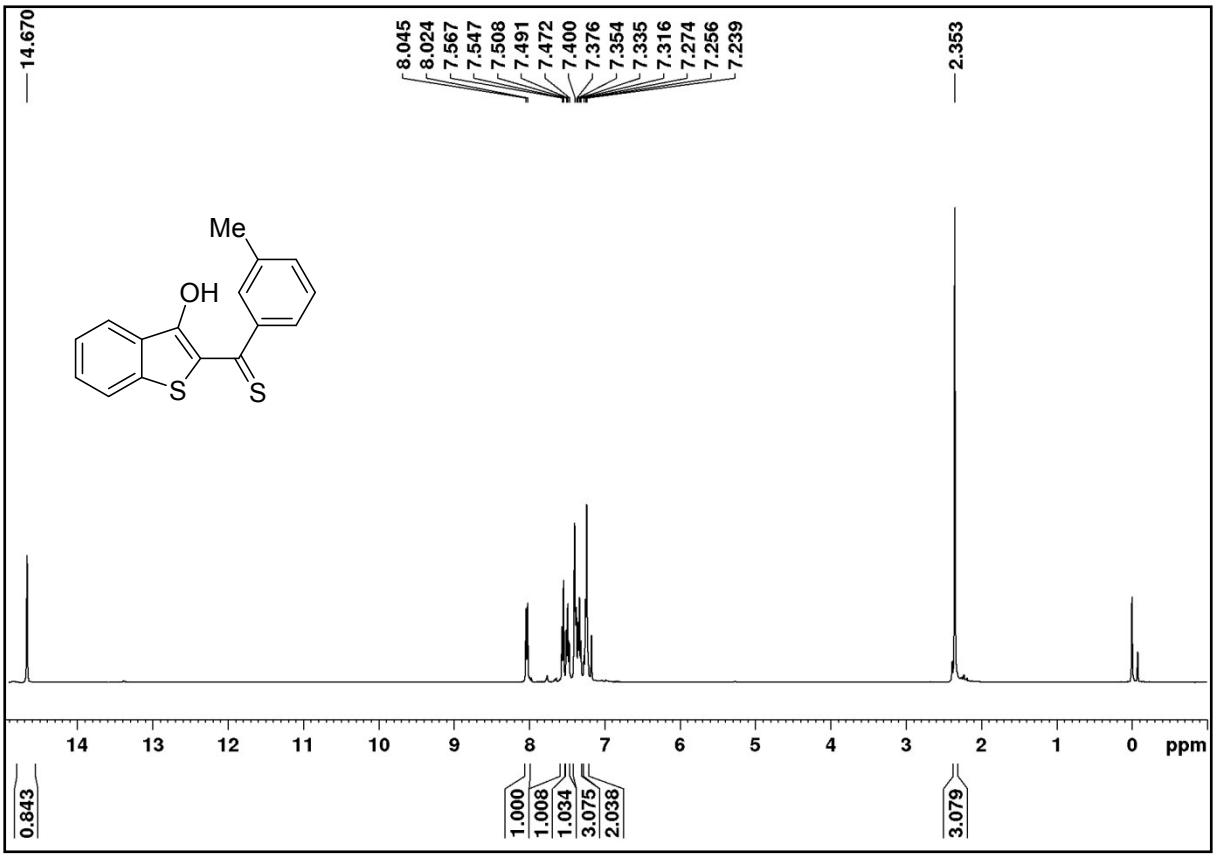


Figure 19: 400 MHz ^{1}H-NMR spectrum of **2j** in $CDCl_3$

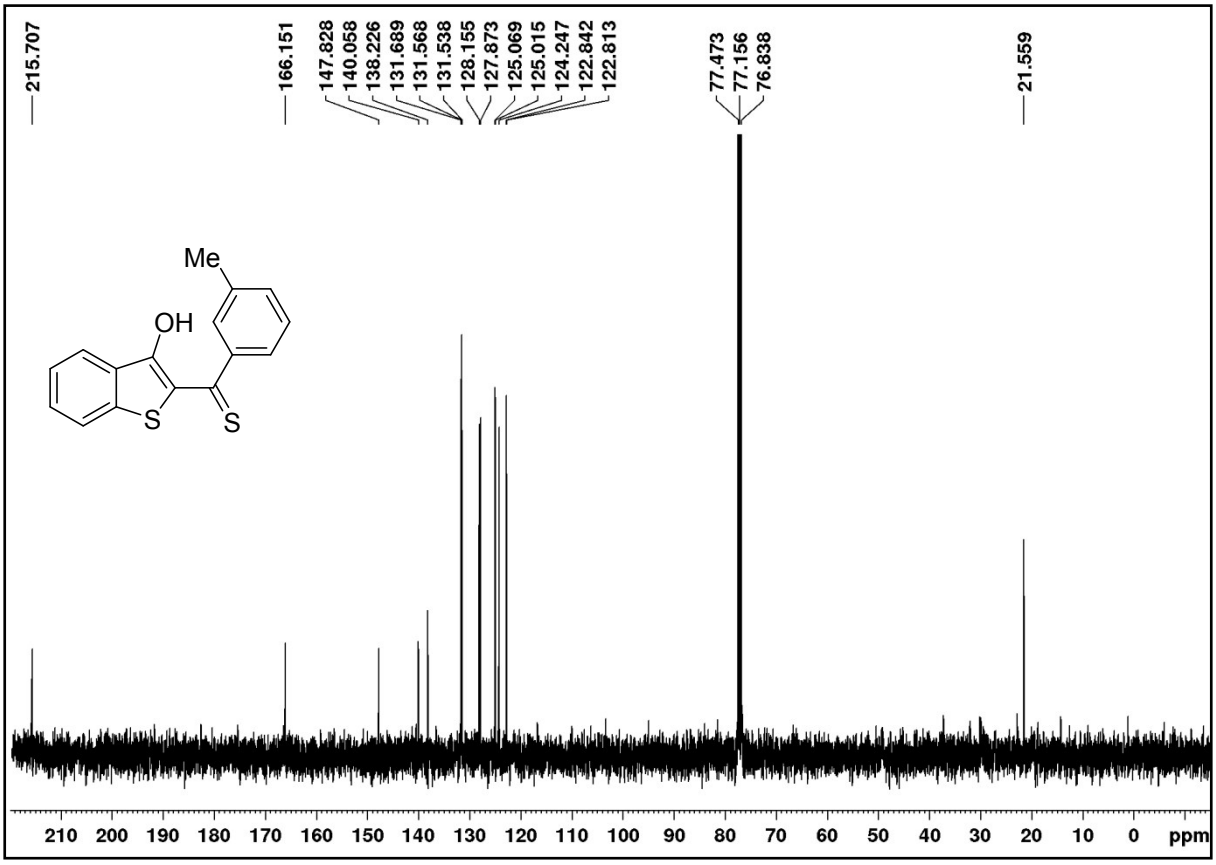


Figure 20: 100 MHz ^{13}C-NMR spectrum of **2j** in $CDCl_3$

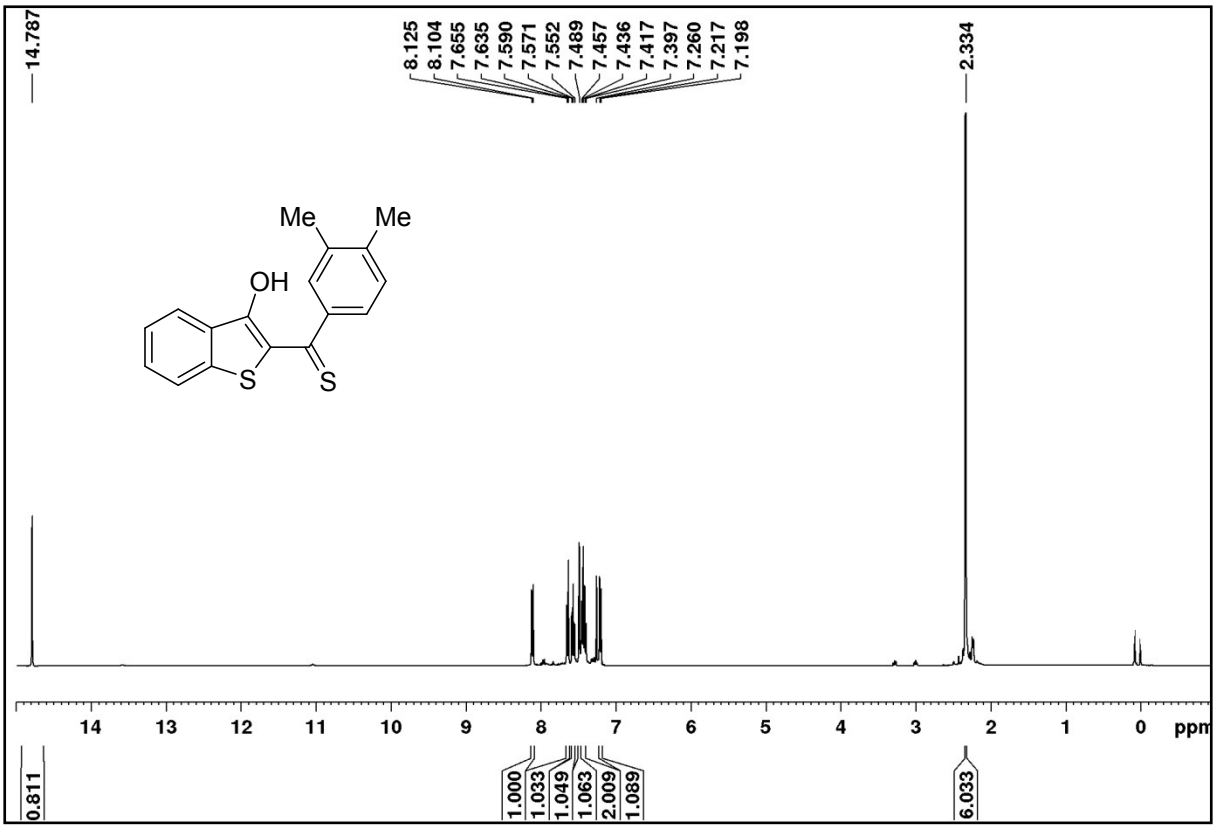


Figure 21: 400 MHz ^{1}H-NMR spectrum of **2k** in $CDCl_3$

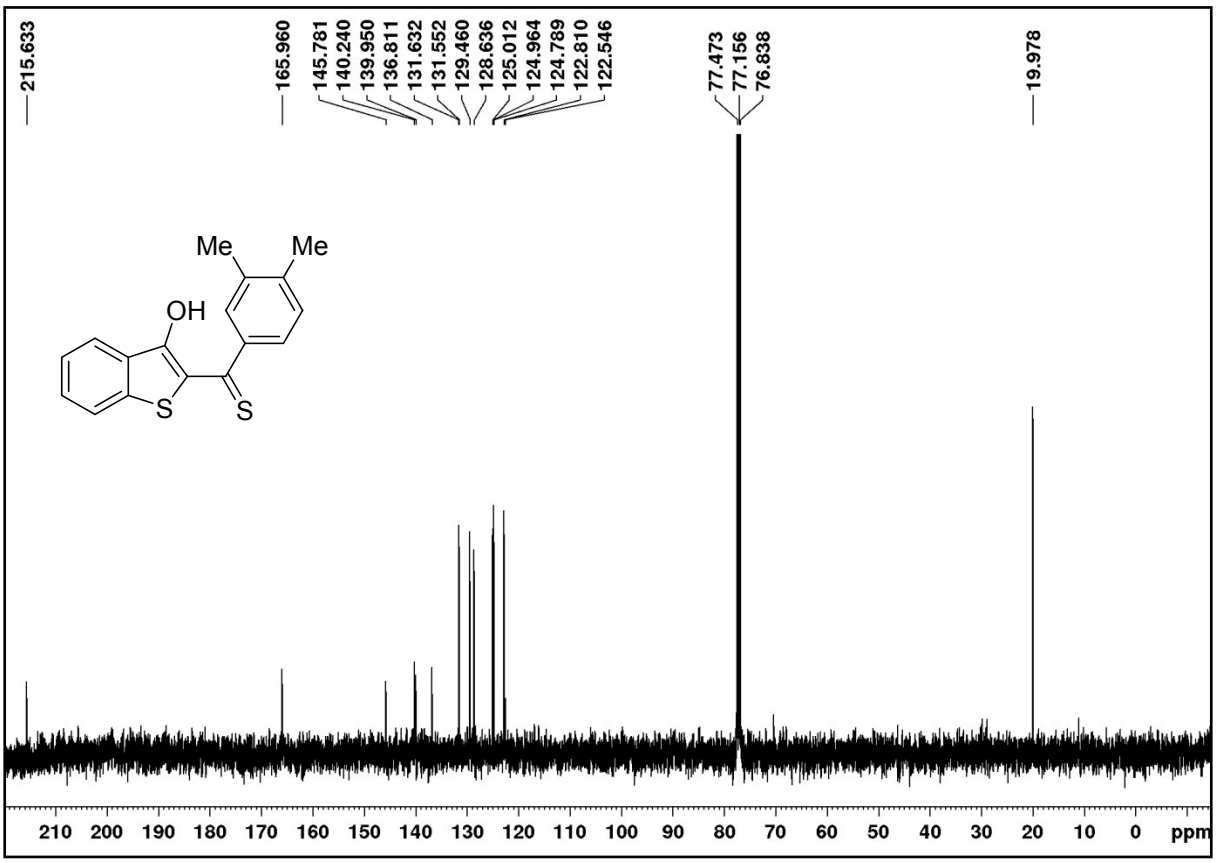


Figure 22: 100 MHz ^{13}C-NMR spectrum of **2k** in $CDCl_3$

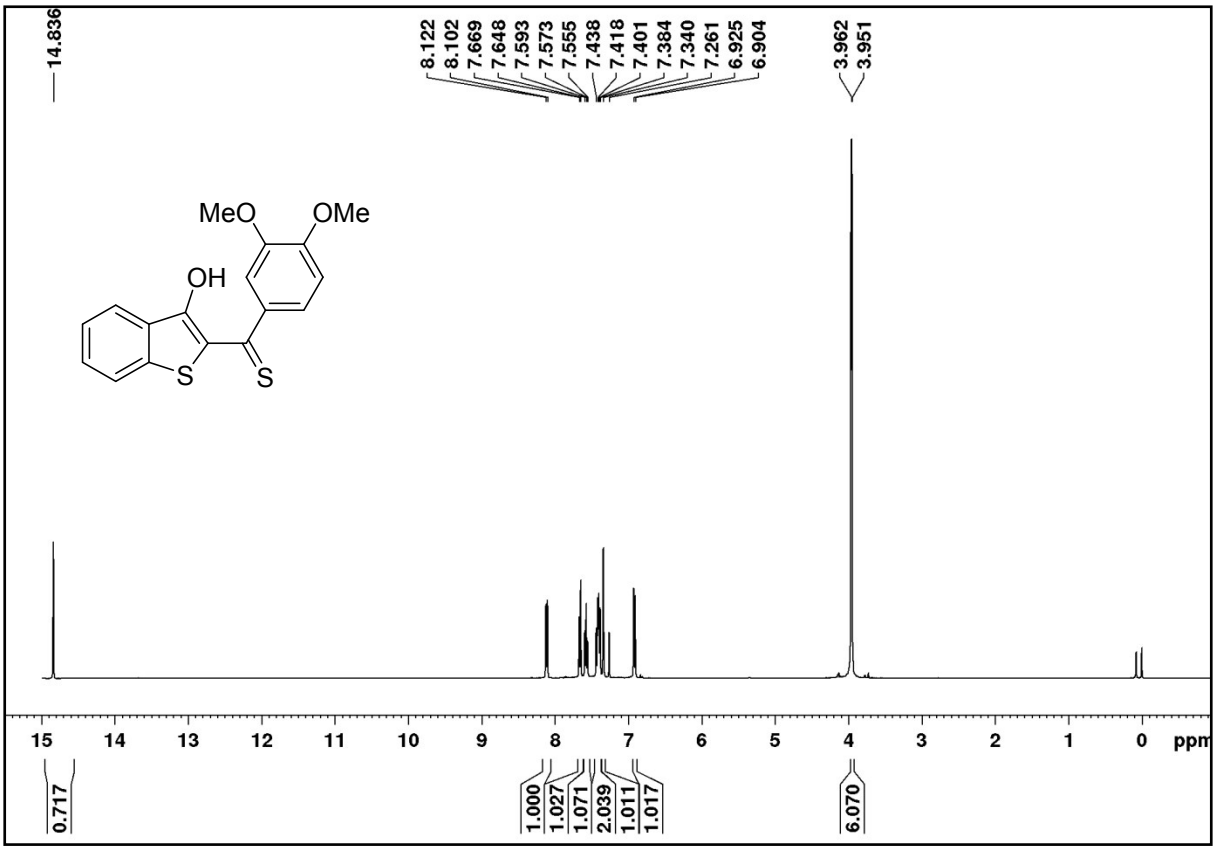


Figure 23: 400 MHz ^{1}H-NMR spectrum of **2l** in $CDCl_3$

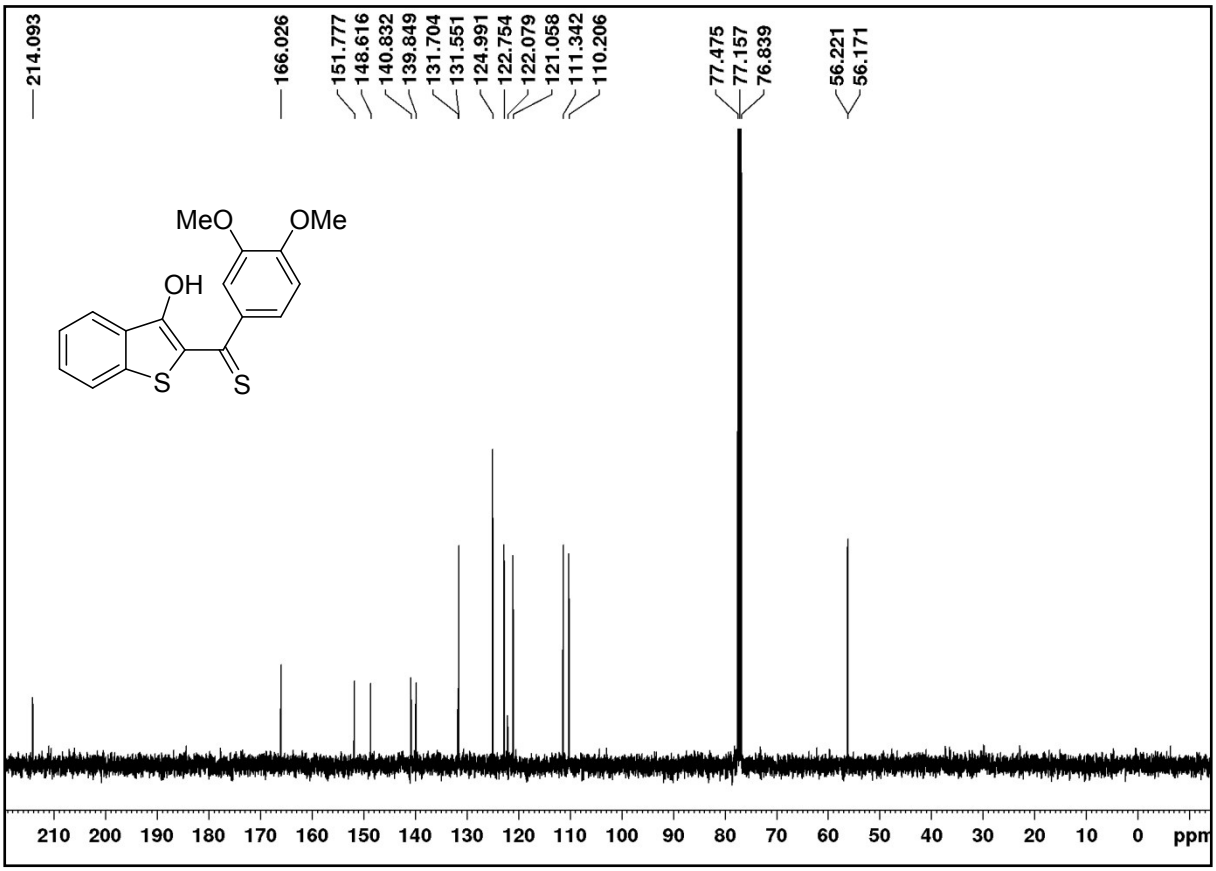


Figure 24: 100 MHz ^{13}C-NMR spectrum of **2l** in $CDCl_3$

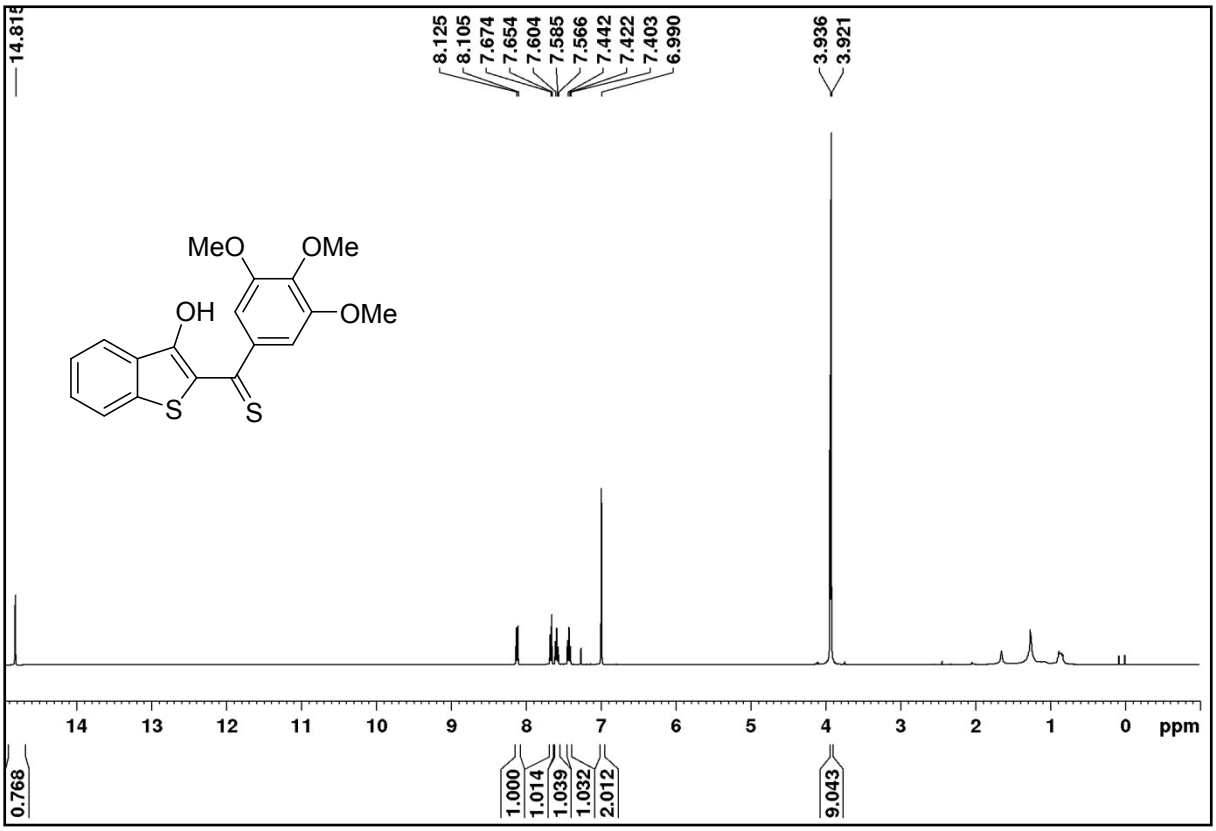


Figure 25: 400 MHz ^{1}H-NMR spectrum of **2m** in $CDCl_3$

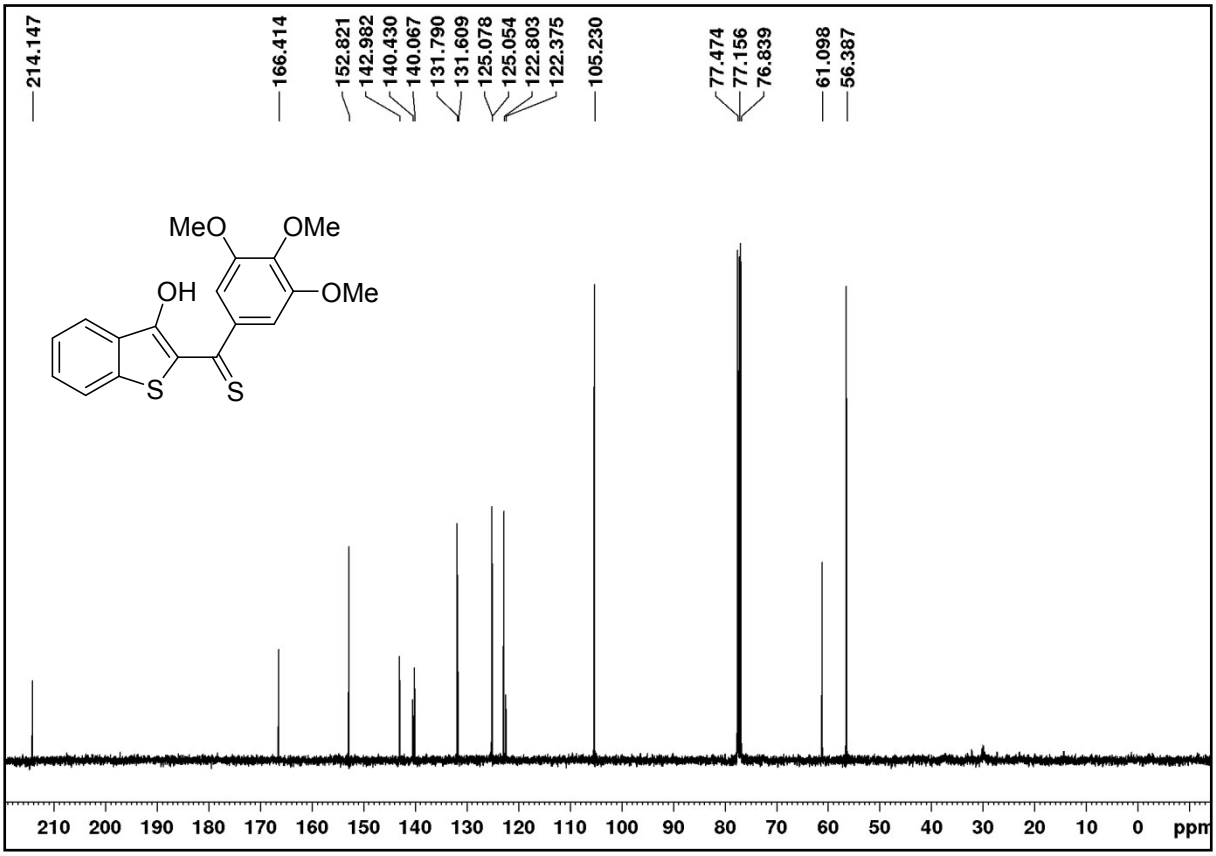


Figure 26: 100 MHz ^{13}C-NMR spectrum of **2m** in $CDCl_3$

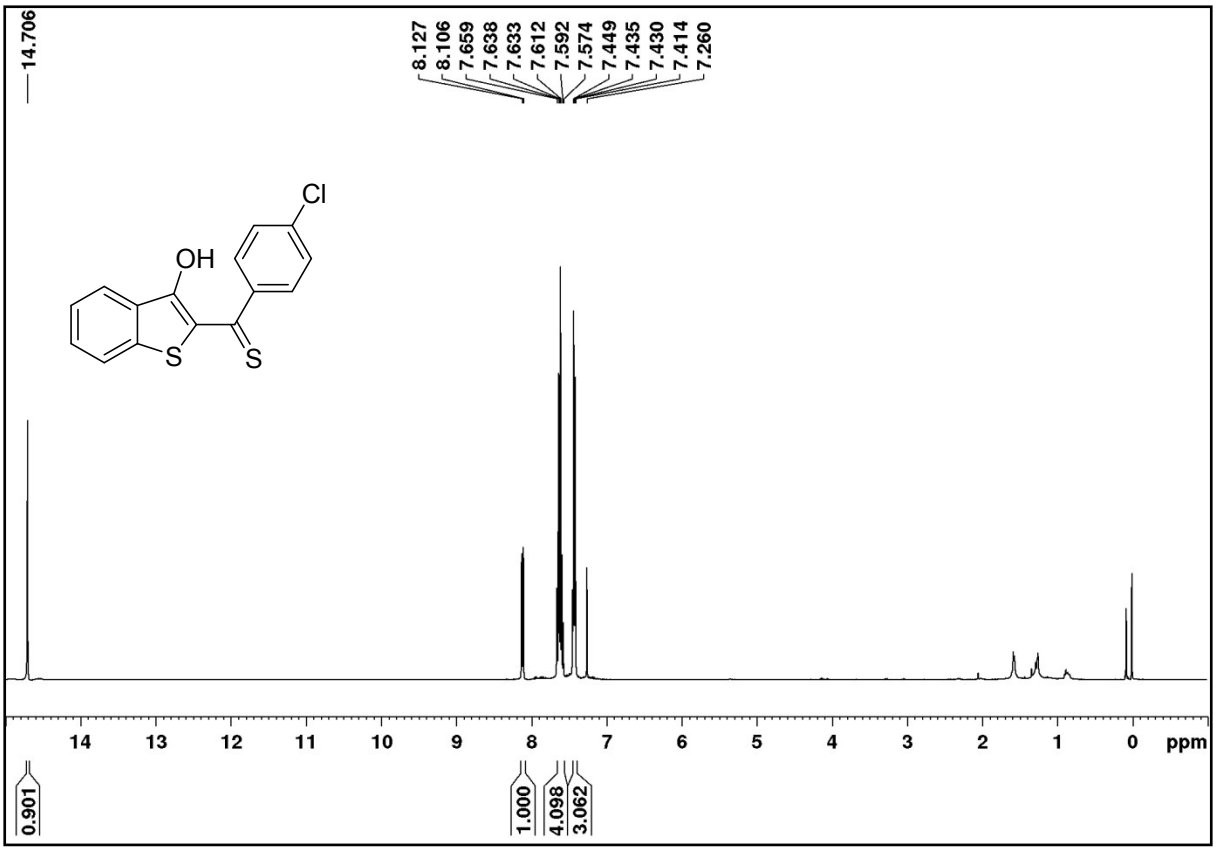


Figure 27: 400 MHz ^{1}H-NMR spectrum of **2n** in $CDCl_3$

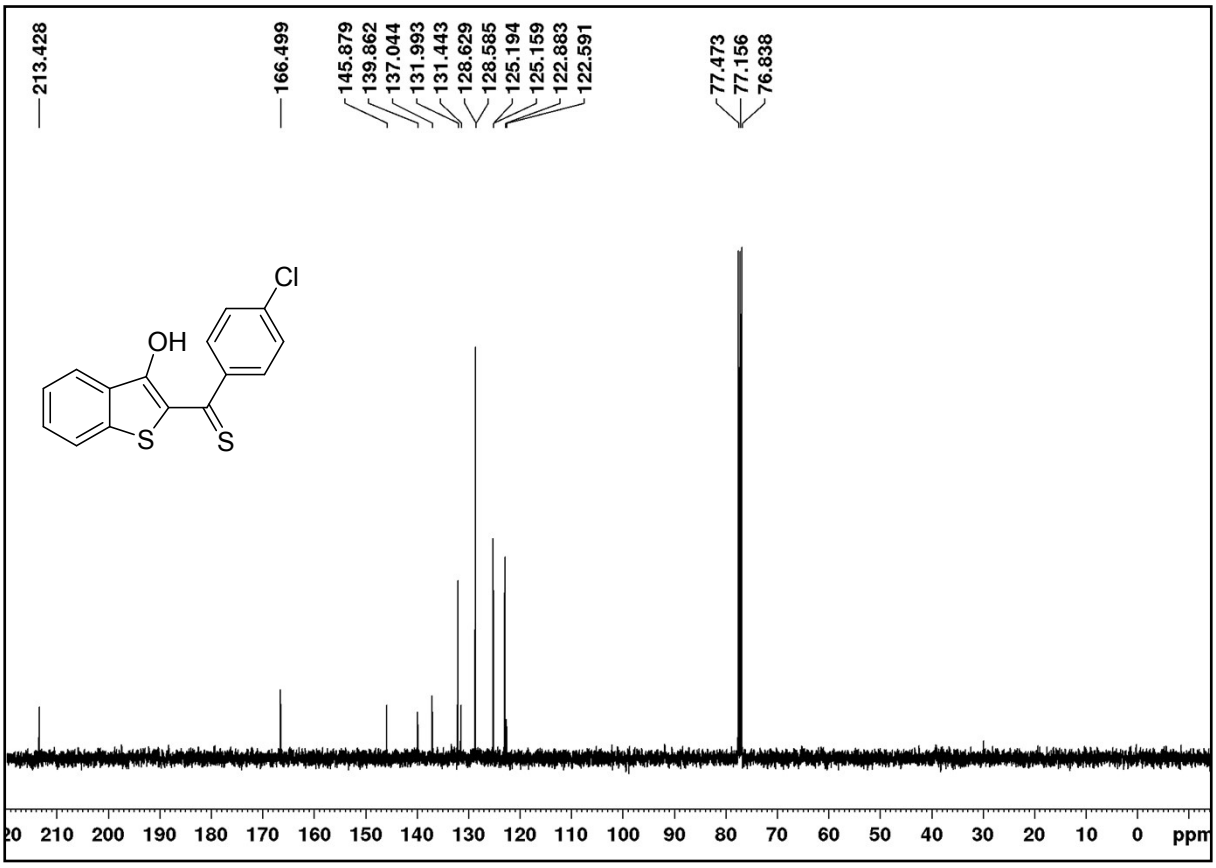


Figure 28: 100 MHz ^{13}C-NMR spectrum of **2n** in $CDCl_3$

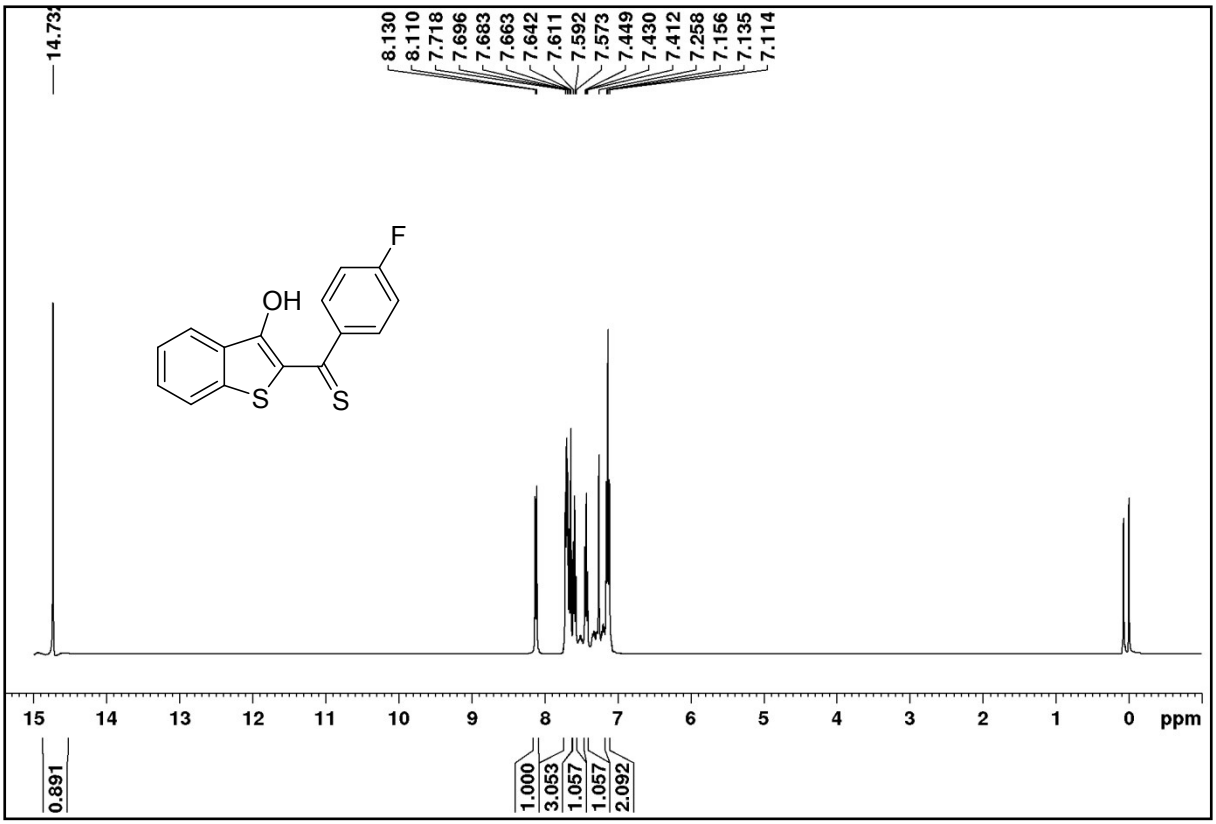


Figure 29: 400 MHz ^{1}H-NMR spectrum of **2o** in $CDCl_3$

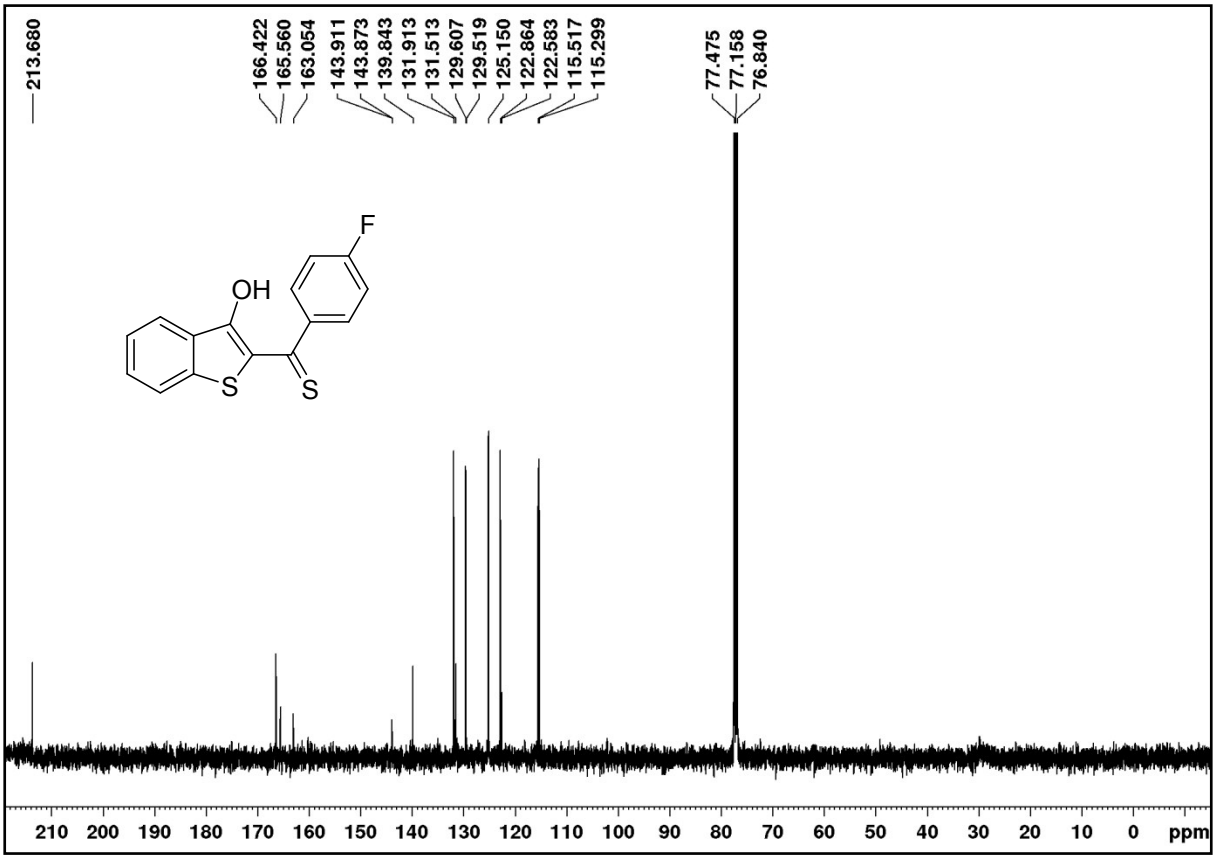


Figure 30: 100 MHz ^{13}C-NMR spectrum of **2o** in $CDCl_3$

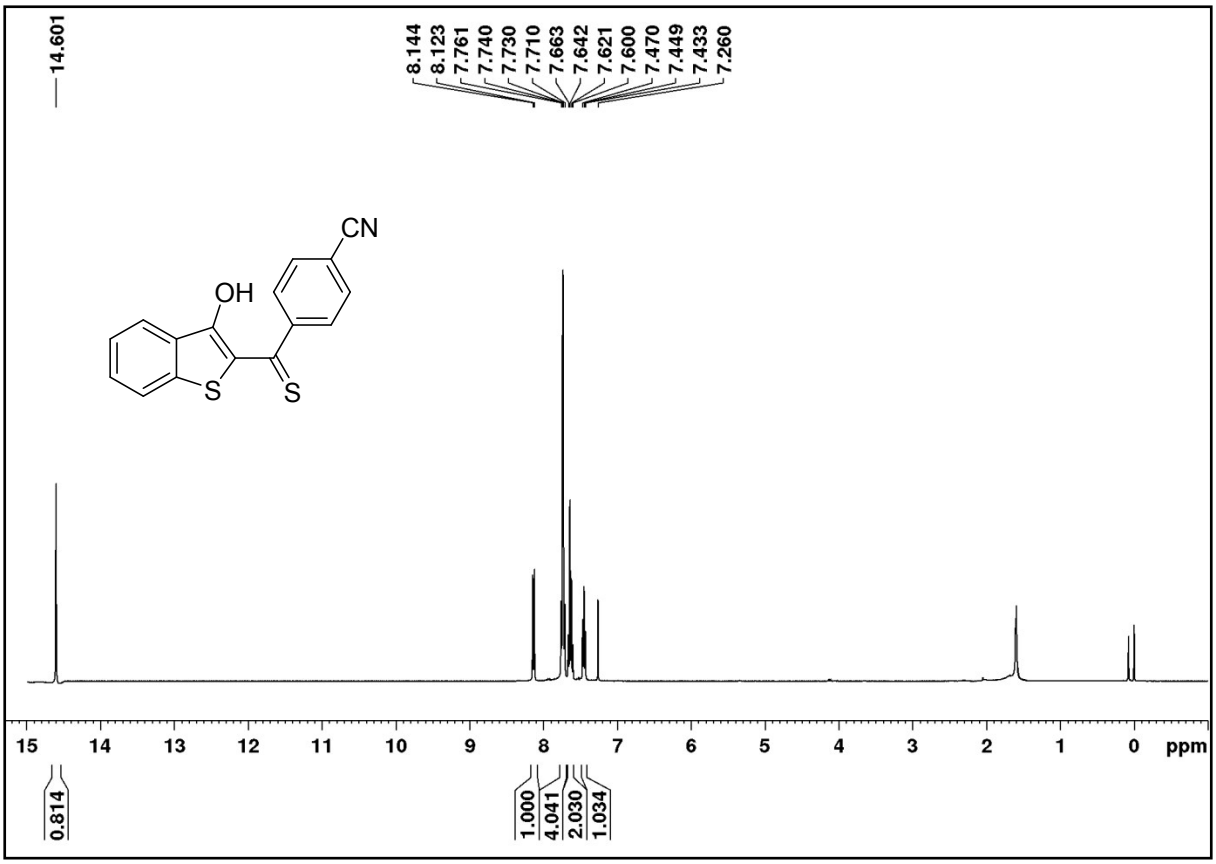


Figure 31: 400 MHz ^{1}H-NMR spectrum of **2p** in $CDCl_3$

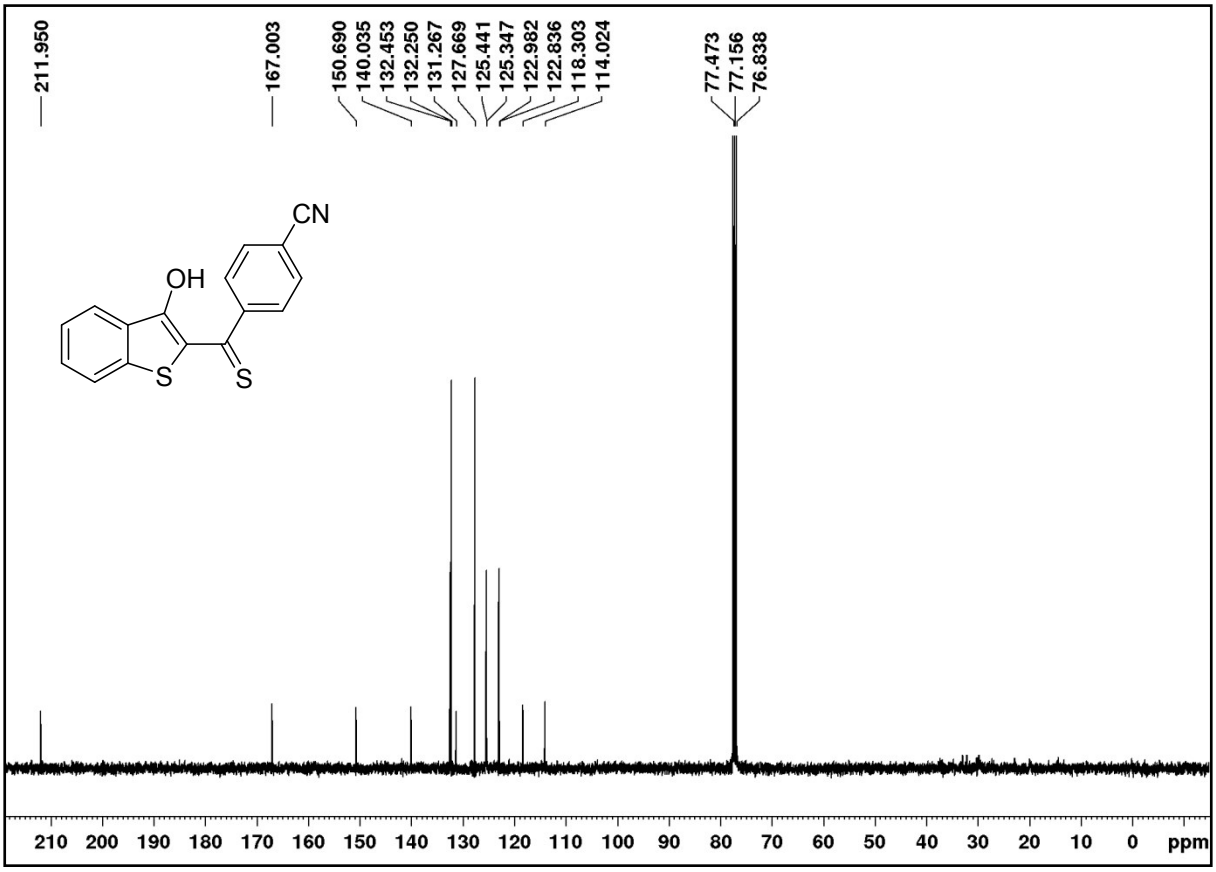


Figure 32: 100 MHz ^{13}C-NMR spectrum of **2p** in $CDCl_3$

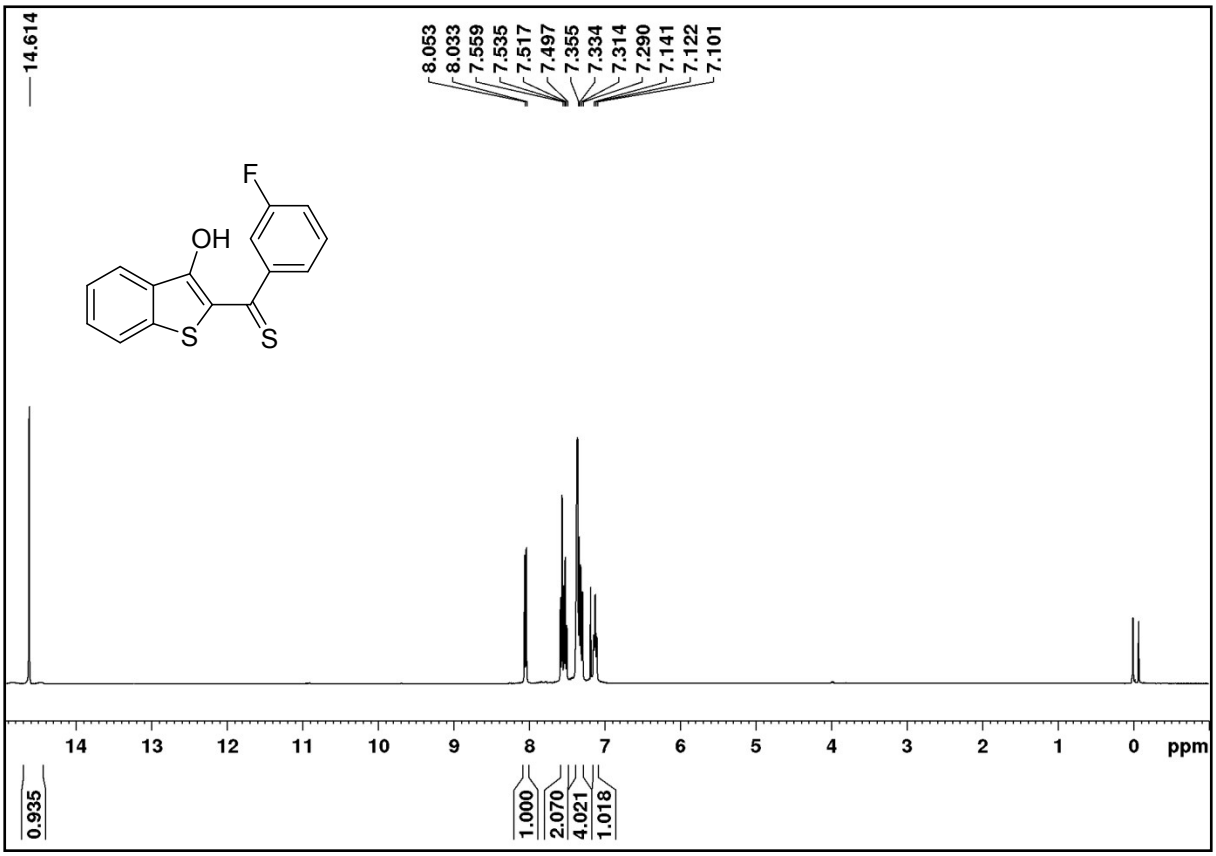


Figure 33: 400 MHz ^{1}H-NMR spectrum of **2q** in $CDCl_3$

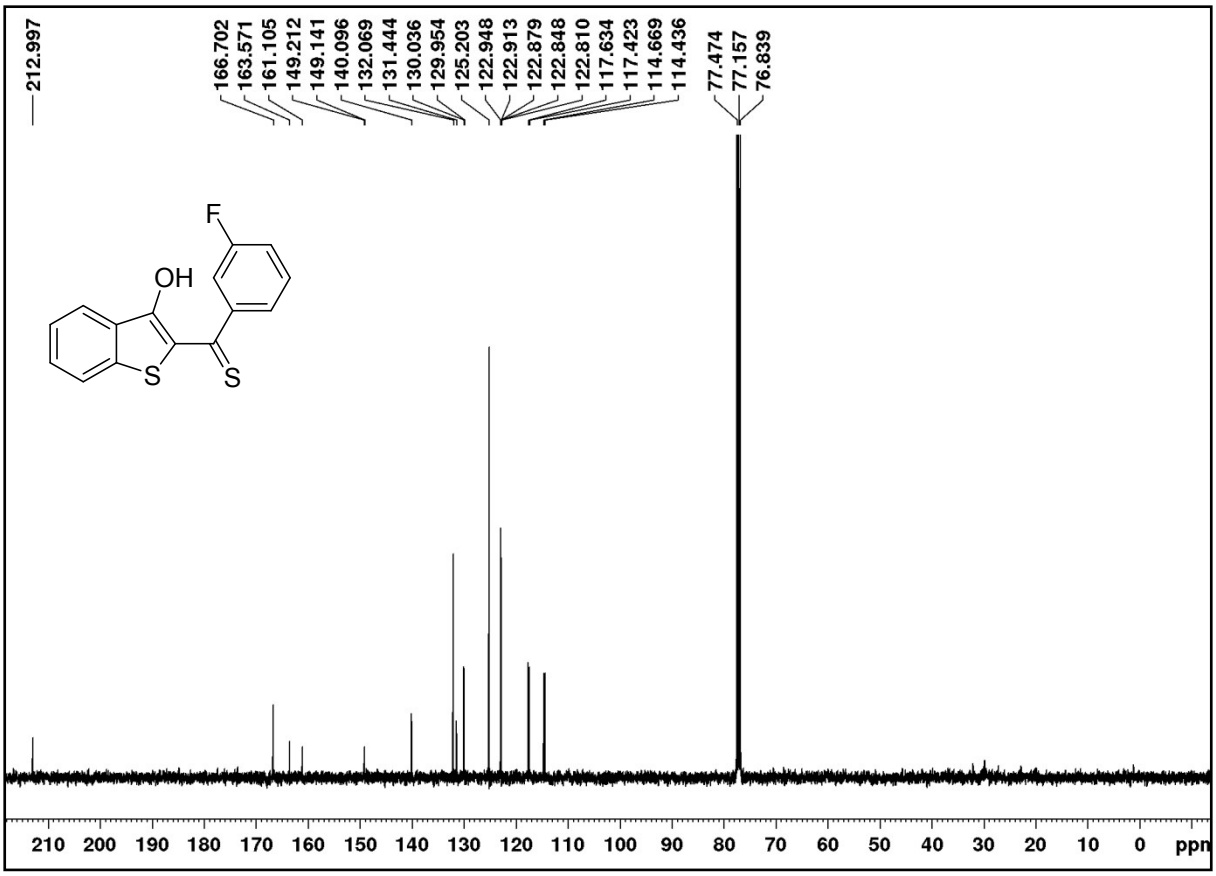


Figure 34: 100 MHz ^{13}C-NMR spectrum of **2q** in $CDCl_3$

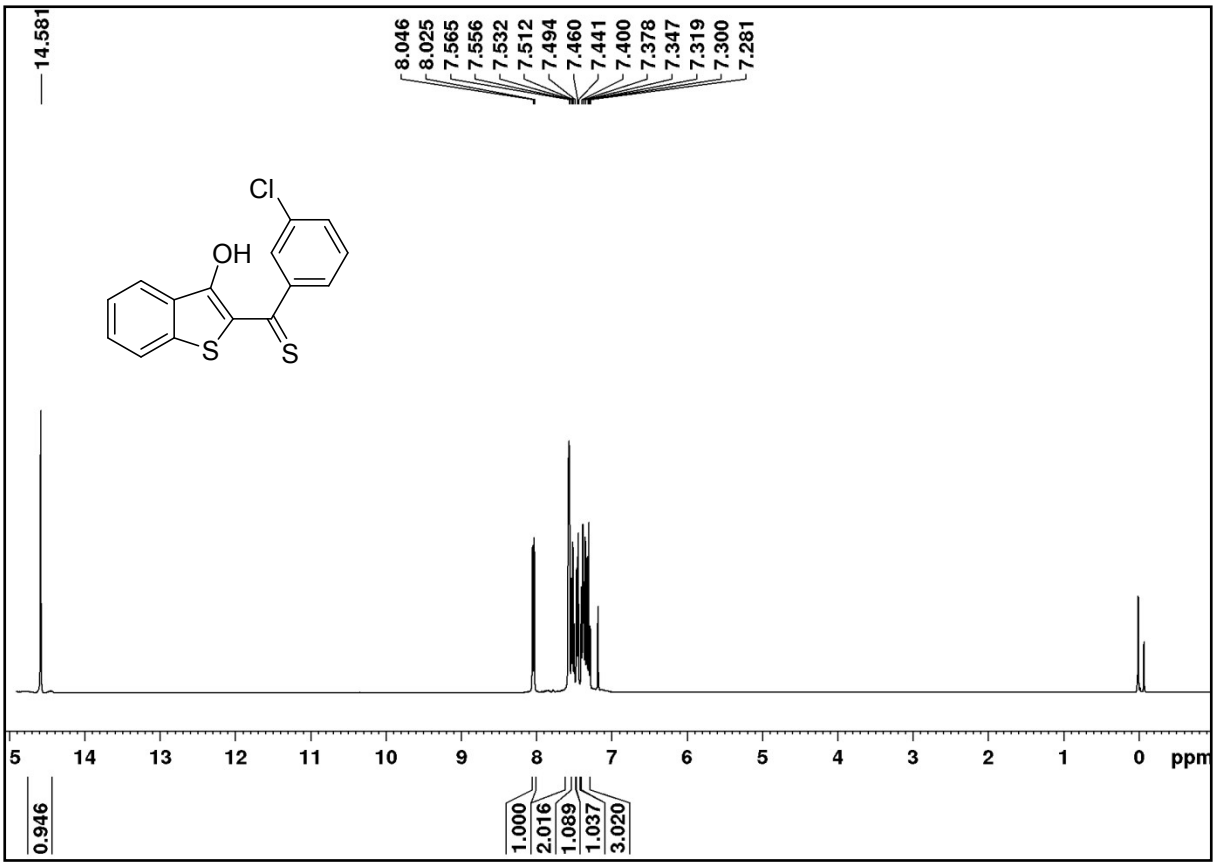


Figure 35: 400 MHz ^{1}H-NMR spectrum of **2r** in $CDCl_3$

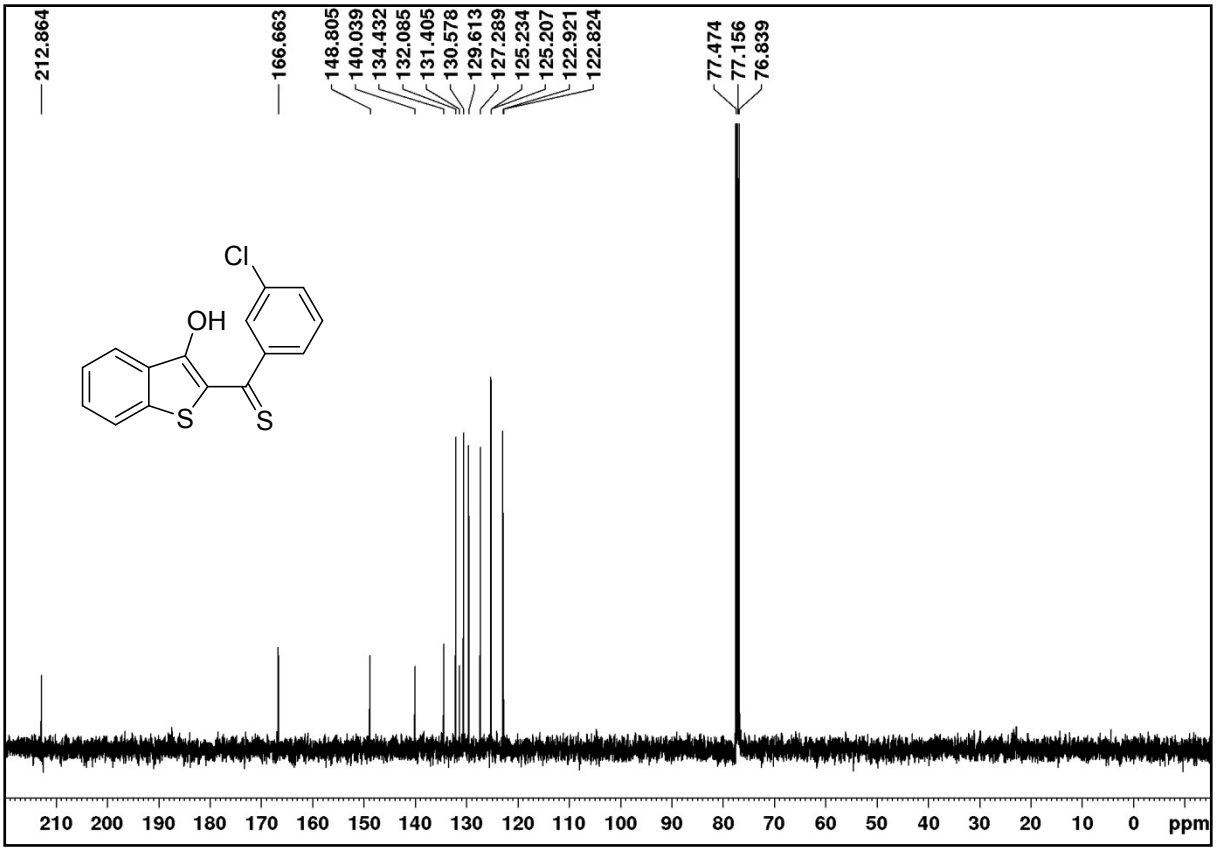


Figure 36: 400 MHz ^{1}H-NMR spectrum of **2r** in $CDCl_3$

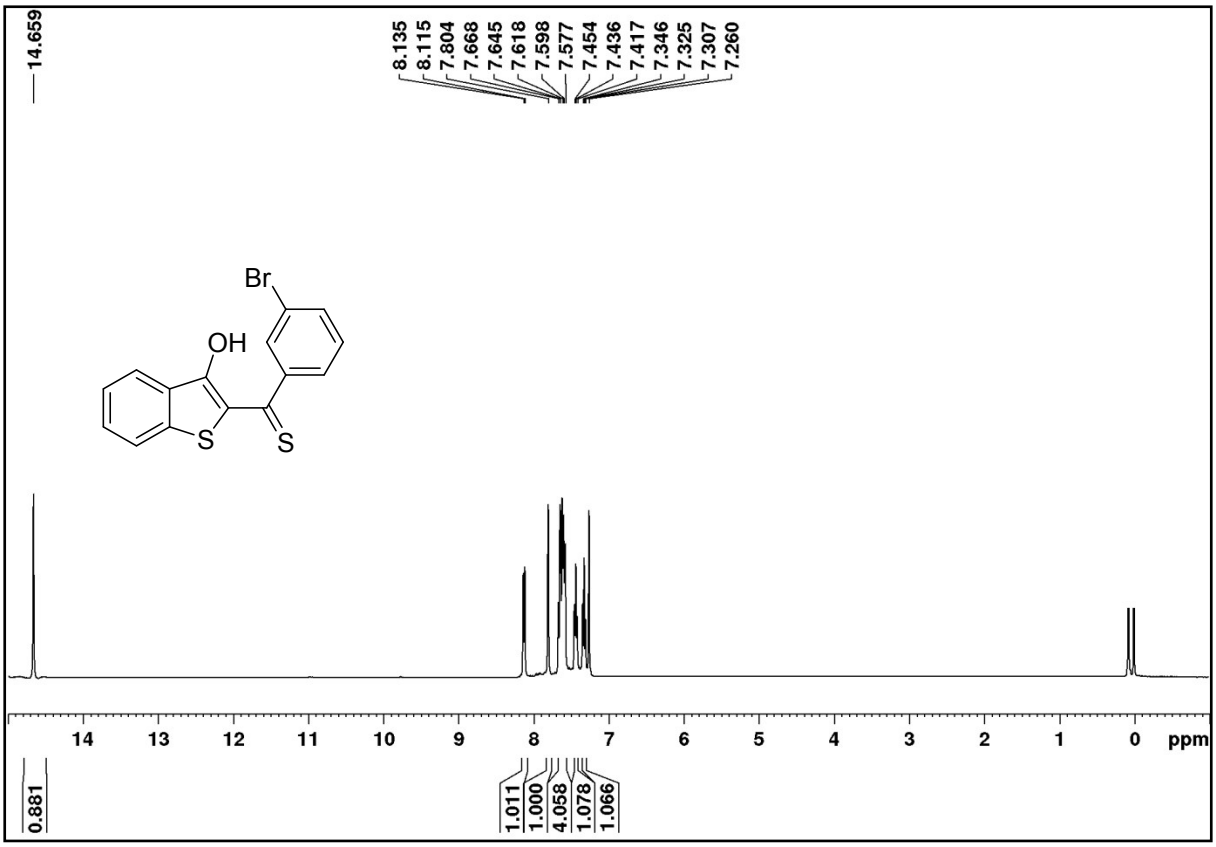


Figure 37: 400 MHz ^{1}H-NMR spectrum of **2s** in $CDCl_3$

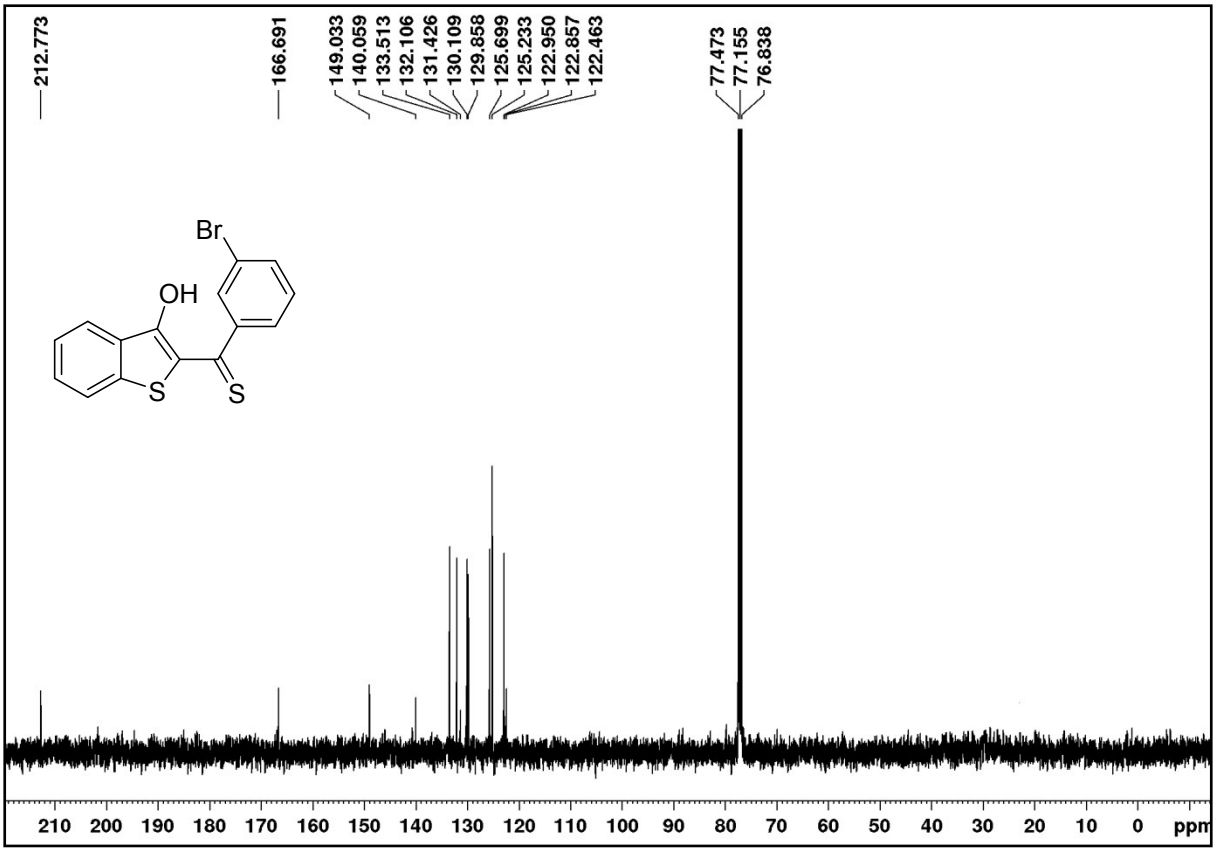


Figure 38: 400 MHz ^{1}H-NMR spectrum of **2s** in $CDCl_3$

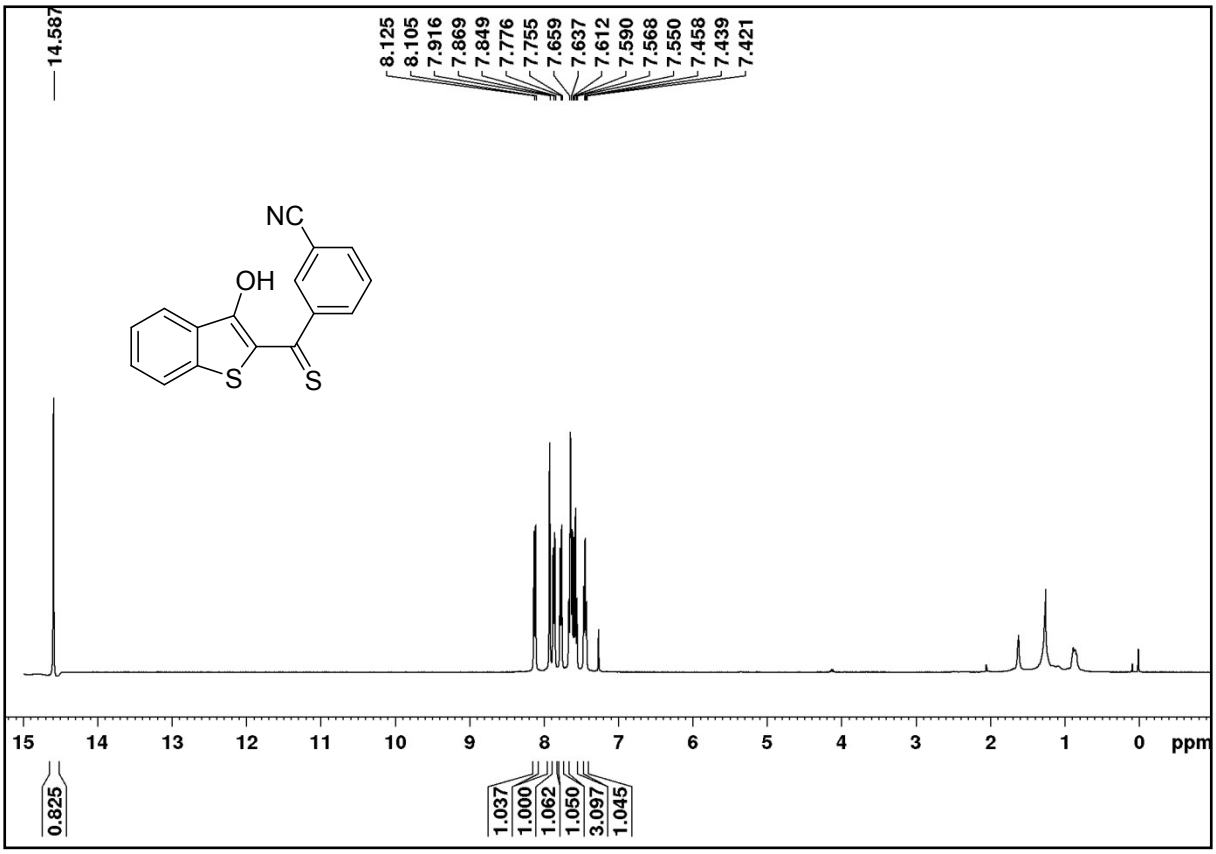


Figure 39: 400 MHz ^{1}H-NMR spectrum of **2t** in $CDCl_3$

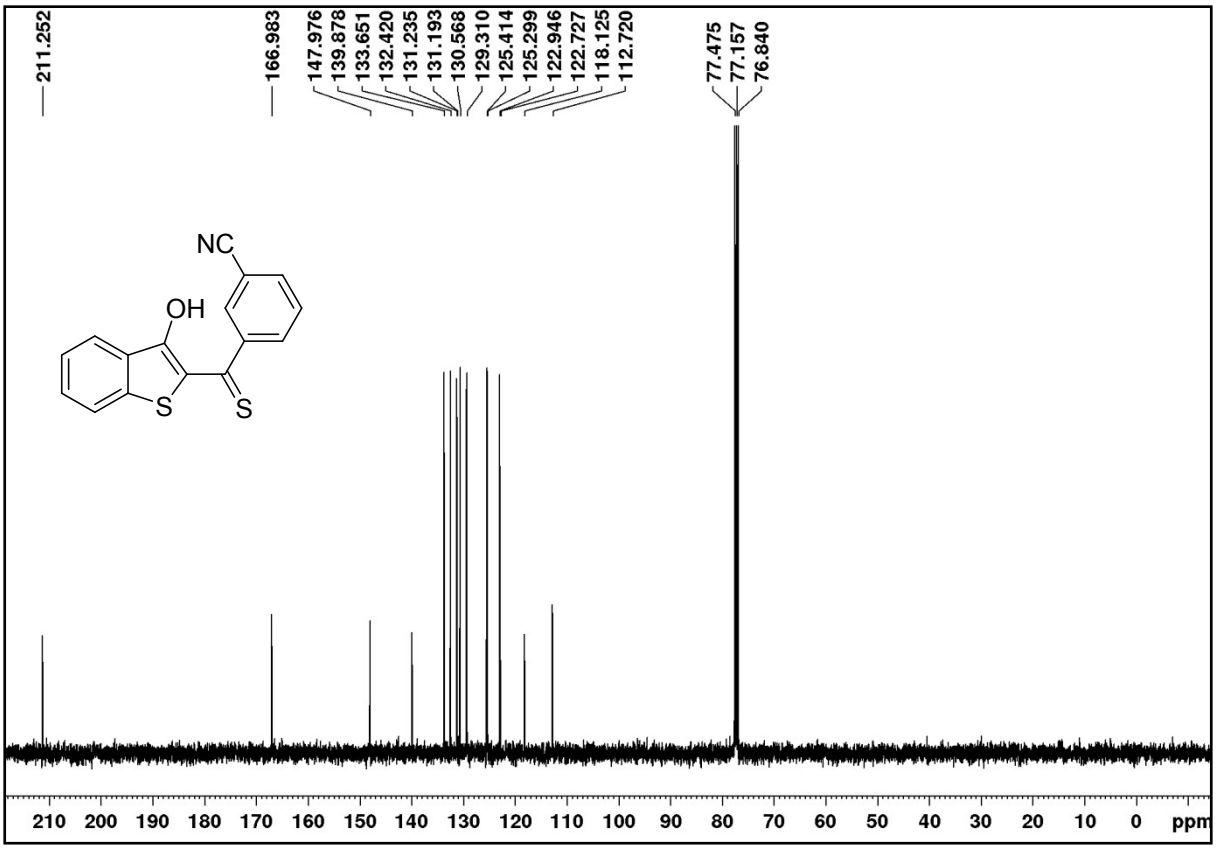


Figure 40: 100 MHz ^{13}C-NMR spectrum of **2t** in $CDCl_3$

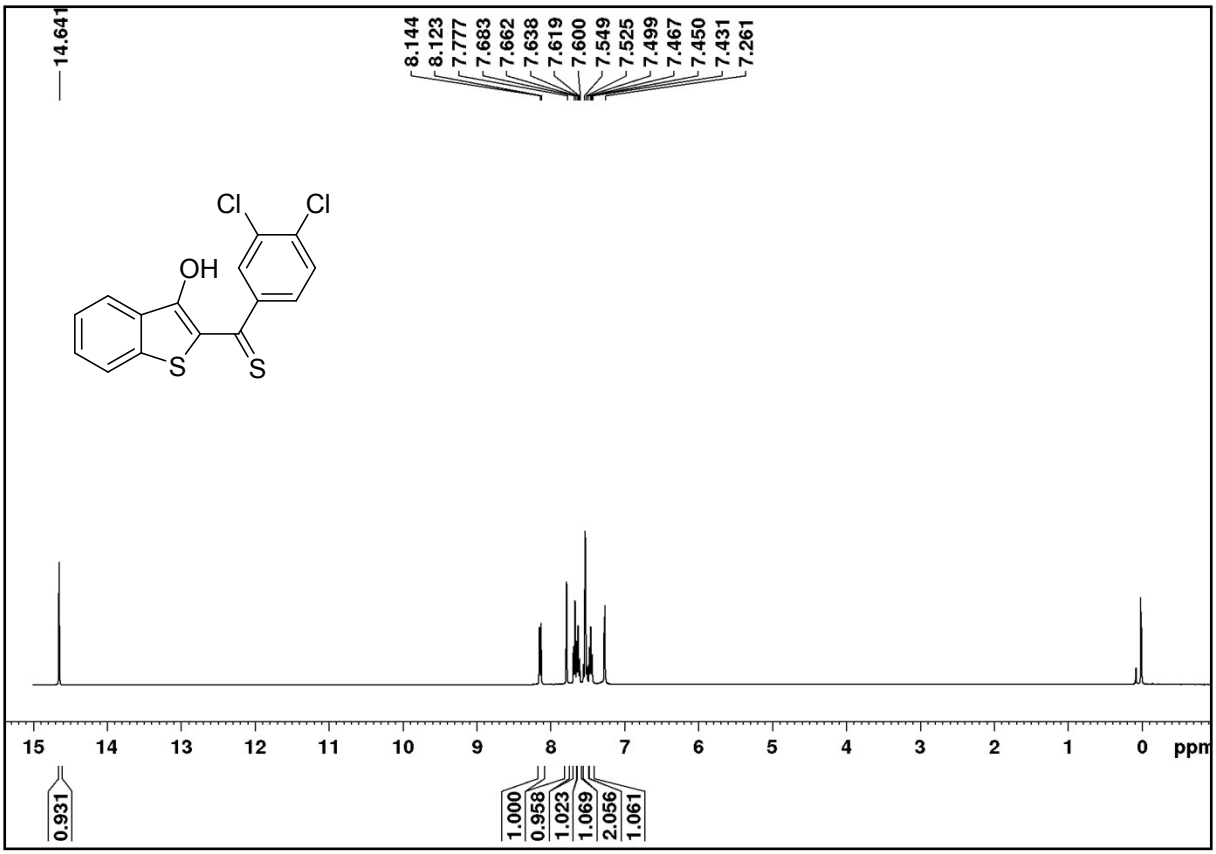


Figure 41: 400 MHz ^{1}H-NMR spectrum of **2u** in $CDCl_3$

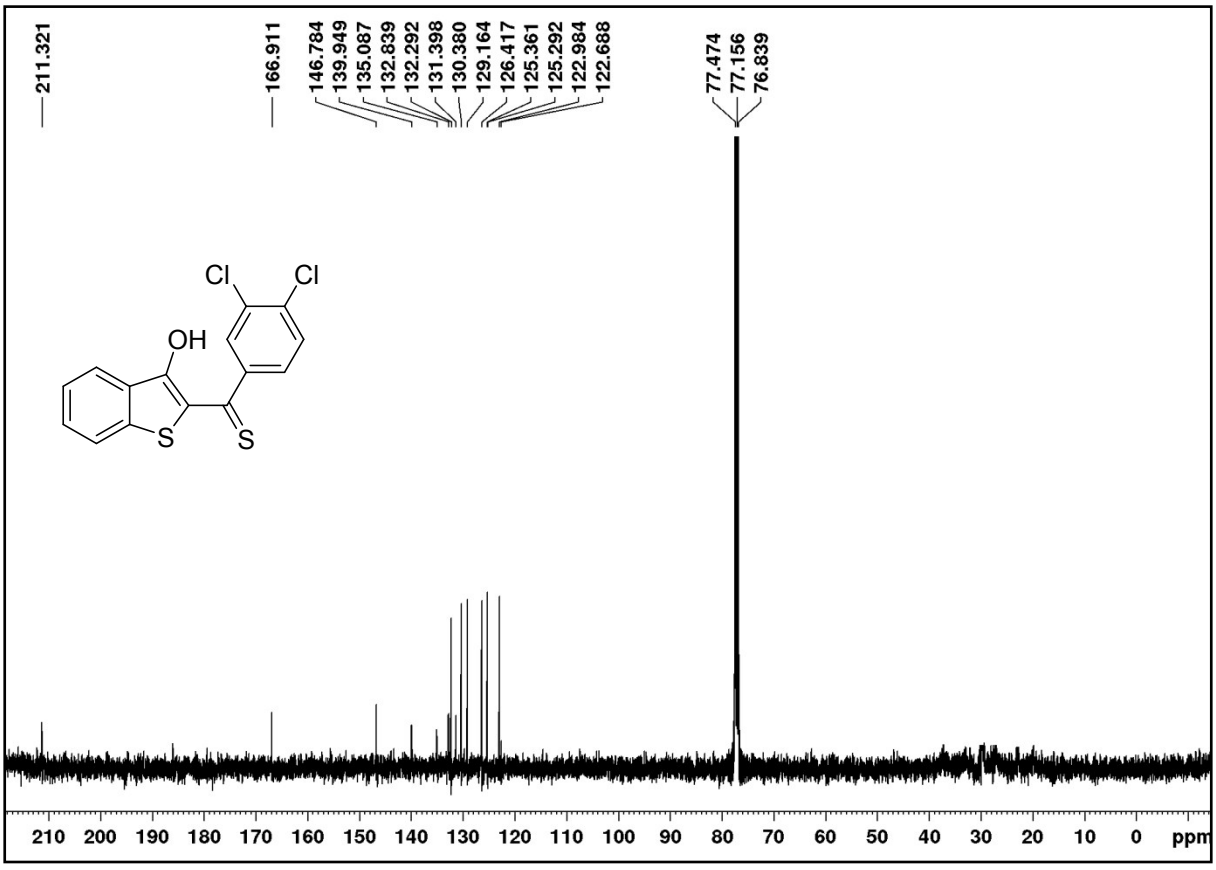


Figure 42: 400 MHz ^{1}H-NMR spectrum of **2u** in $CDCl_3$

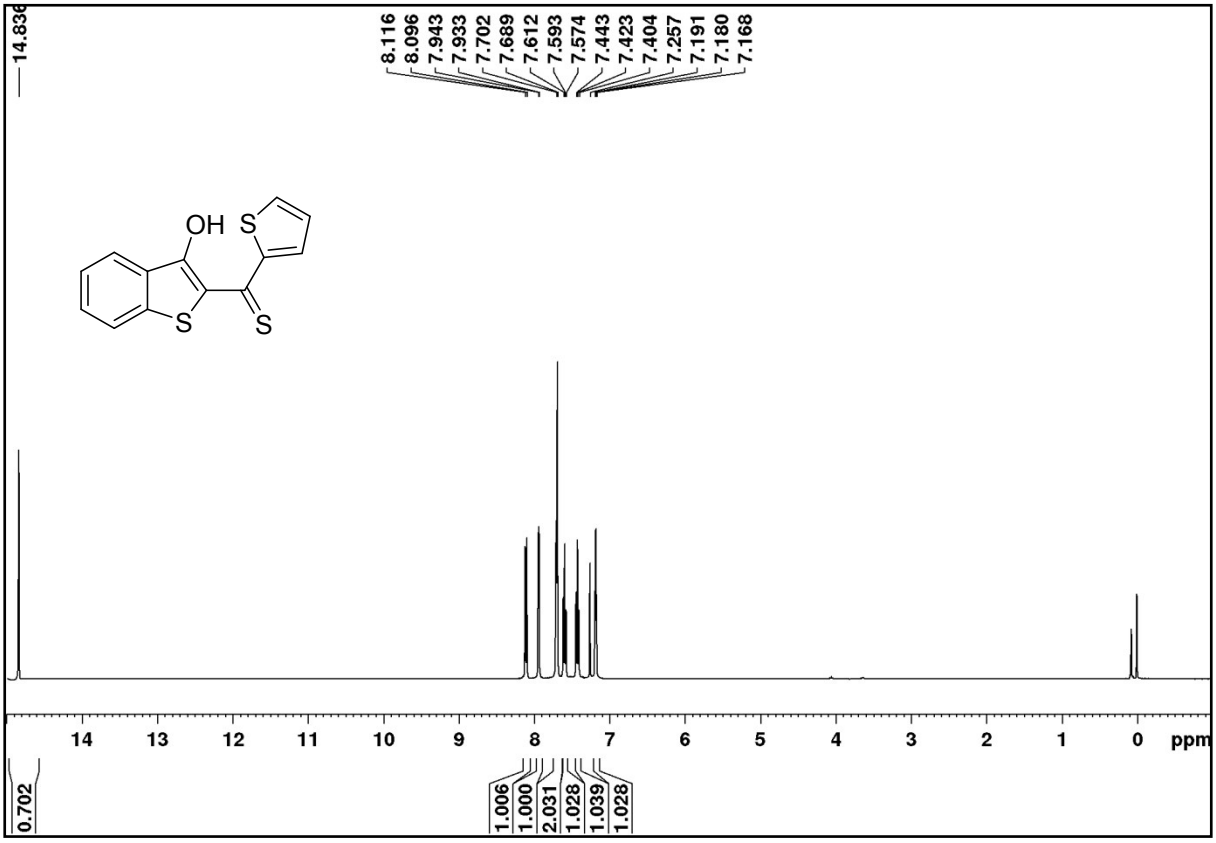


Figure 43: 400 MHz ^{1}H-NMR spectrum of **2v** in $CDCl_3$

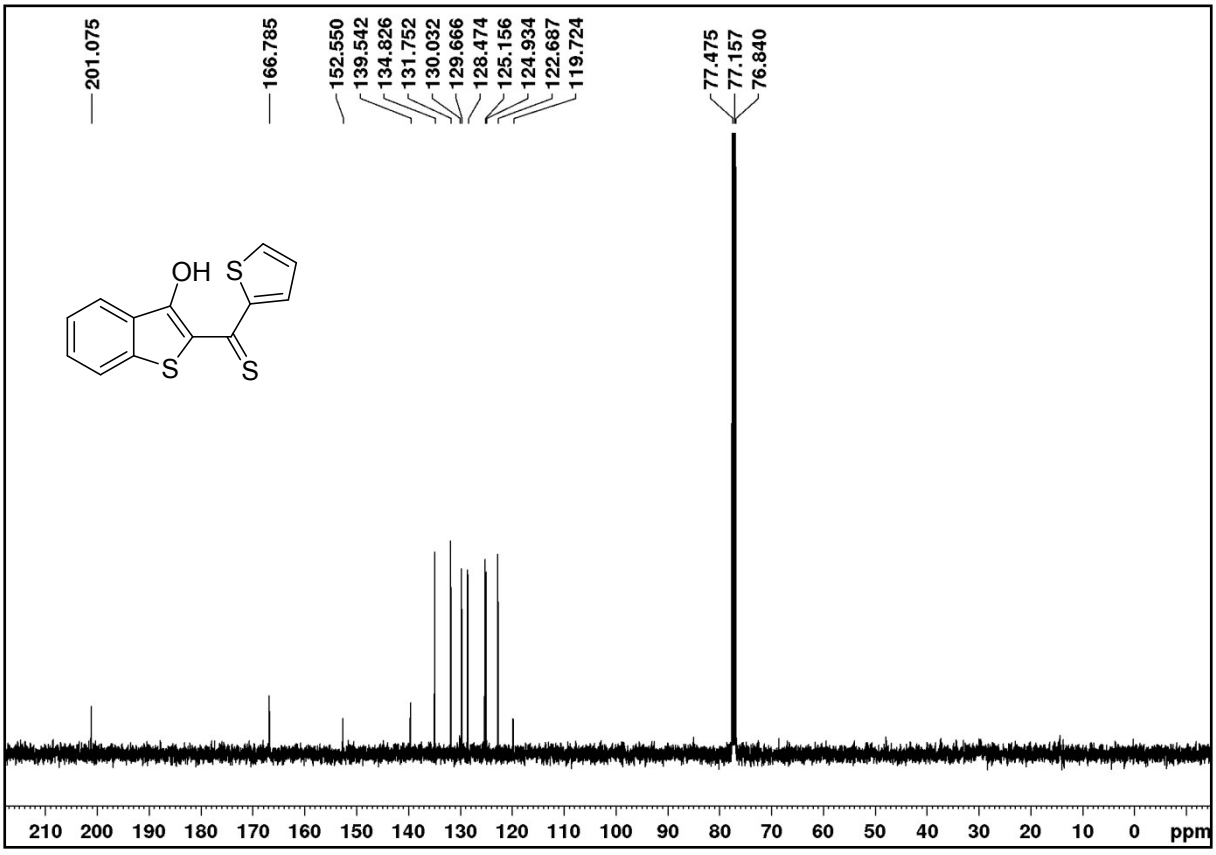


Figure 44: 100 MHz ^{13}C-NMR spectrum of **2v** in $CDCl_3$

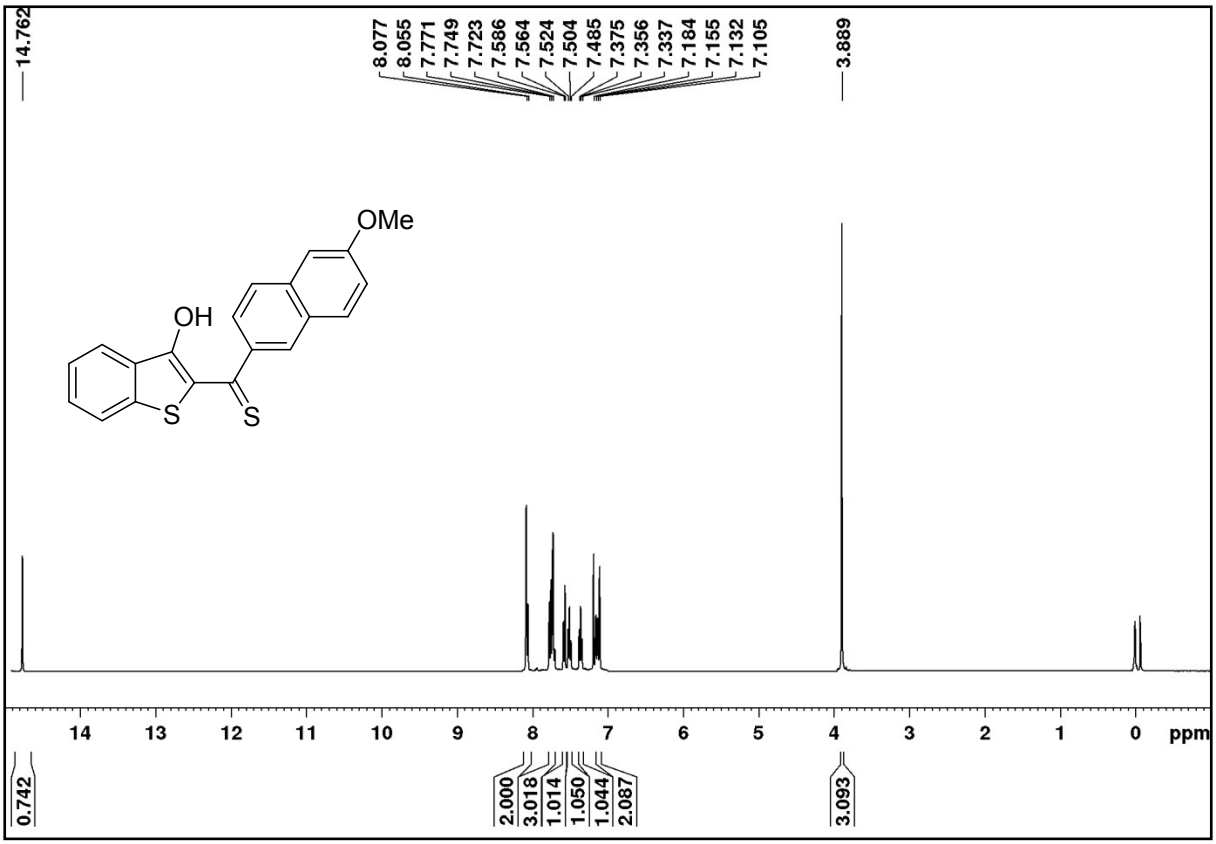


Figure 45: 400 MHz ^{1}H-NMR spectrum of **2w** in $CDCl_3$

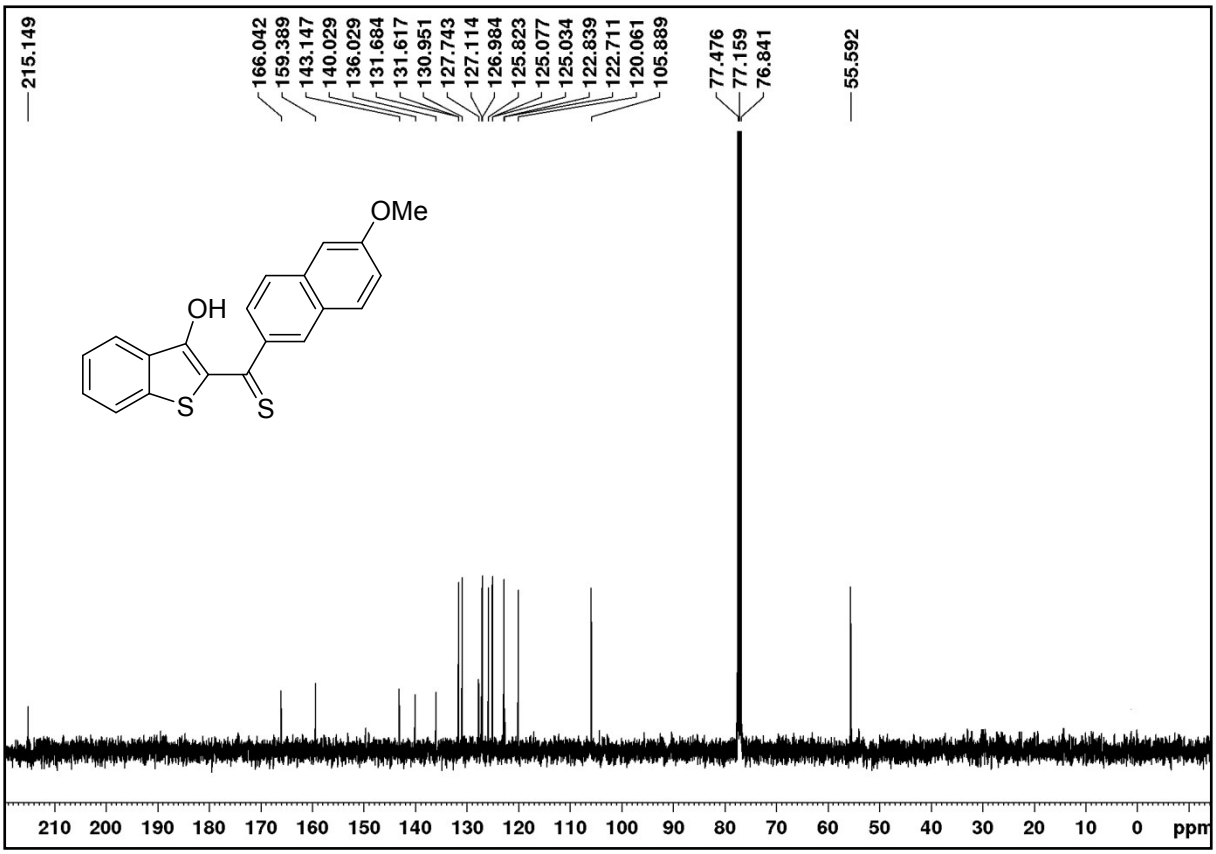


Figure 46: 100 MHz ^{13}C-NMR spectrum of **2w** in $CDCl_3$

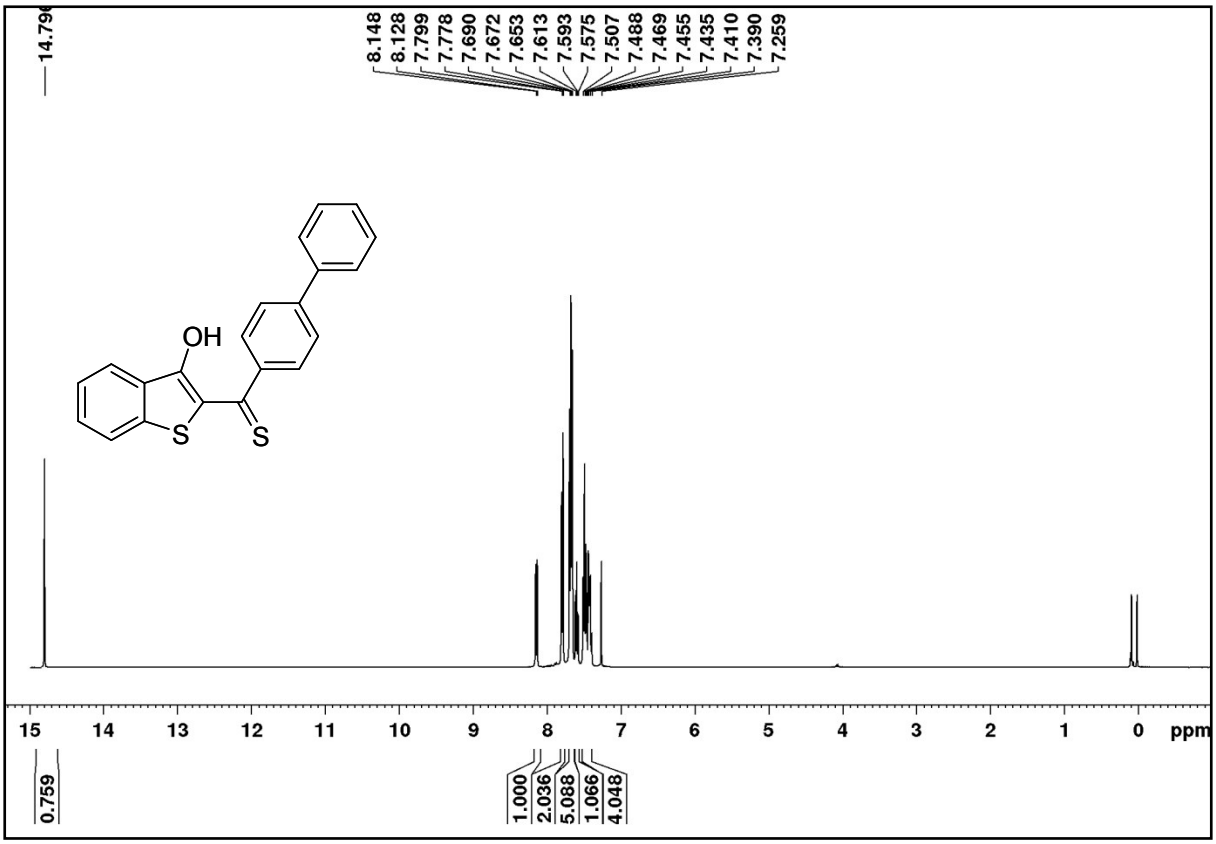


Figure 47: 400 MHz ^{1}H-NMR spectrum of **2x** in $CDCl_3$

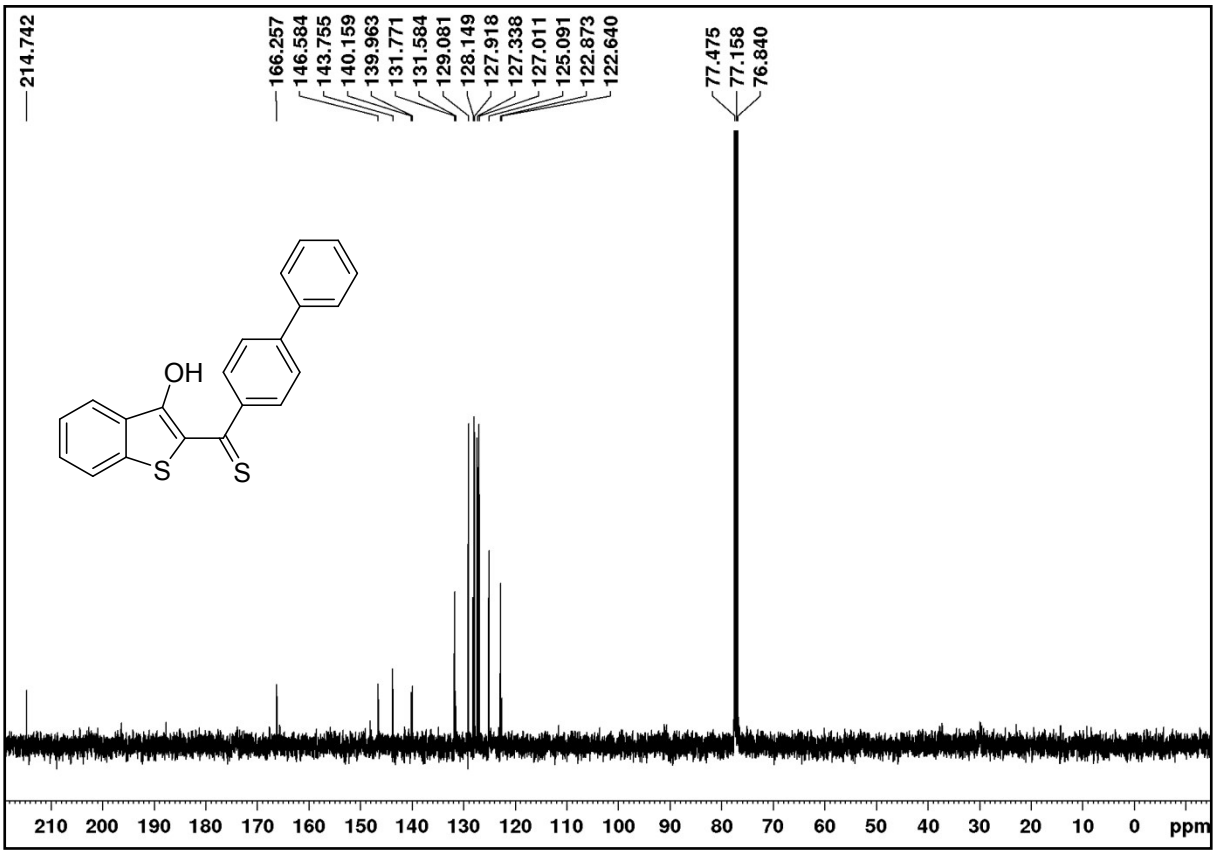


Figure 48: 100 MHz ^{13}C-NMR spectrum of **2x** in $CDCl_3$

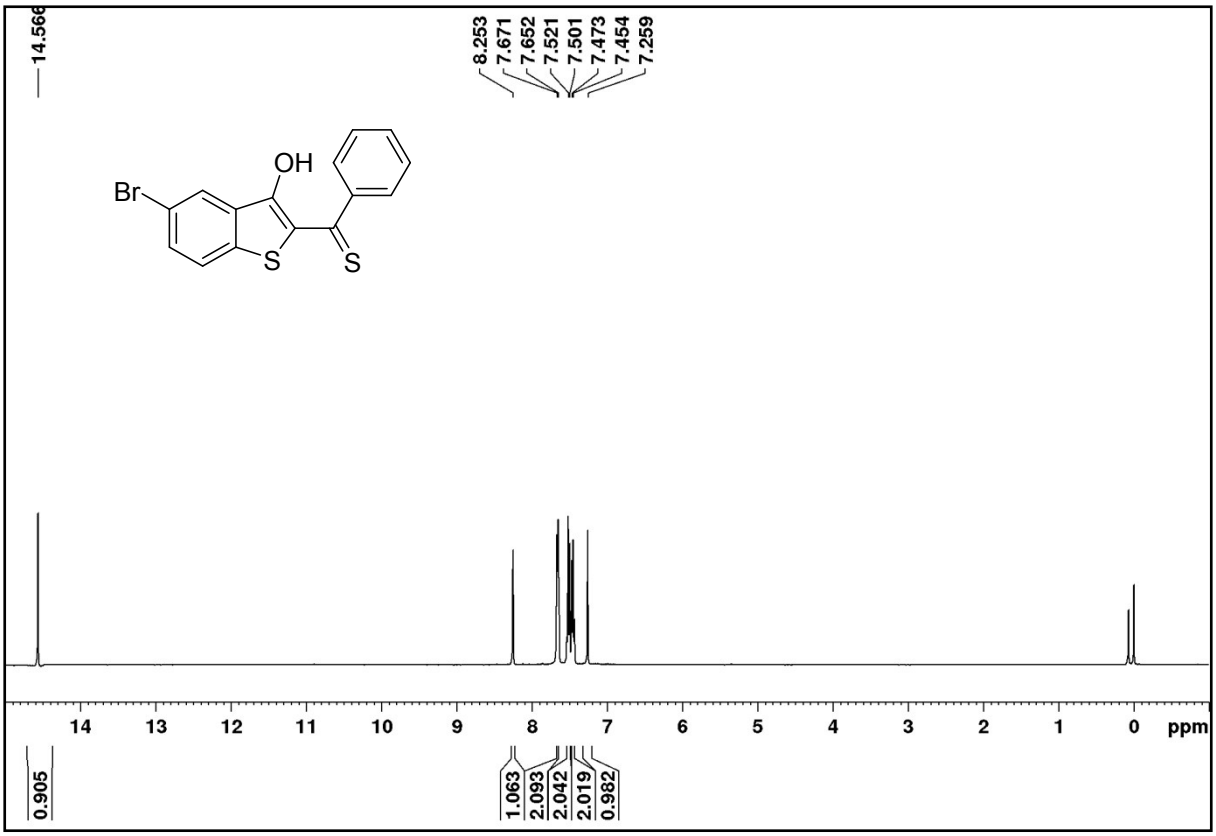


Figure 49: 400 MHz ^{1}H-NMR spectrum of **2y** in $CDCl_3$

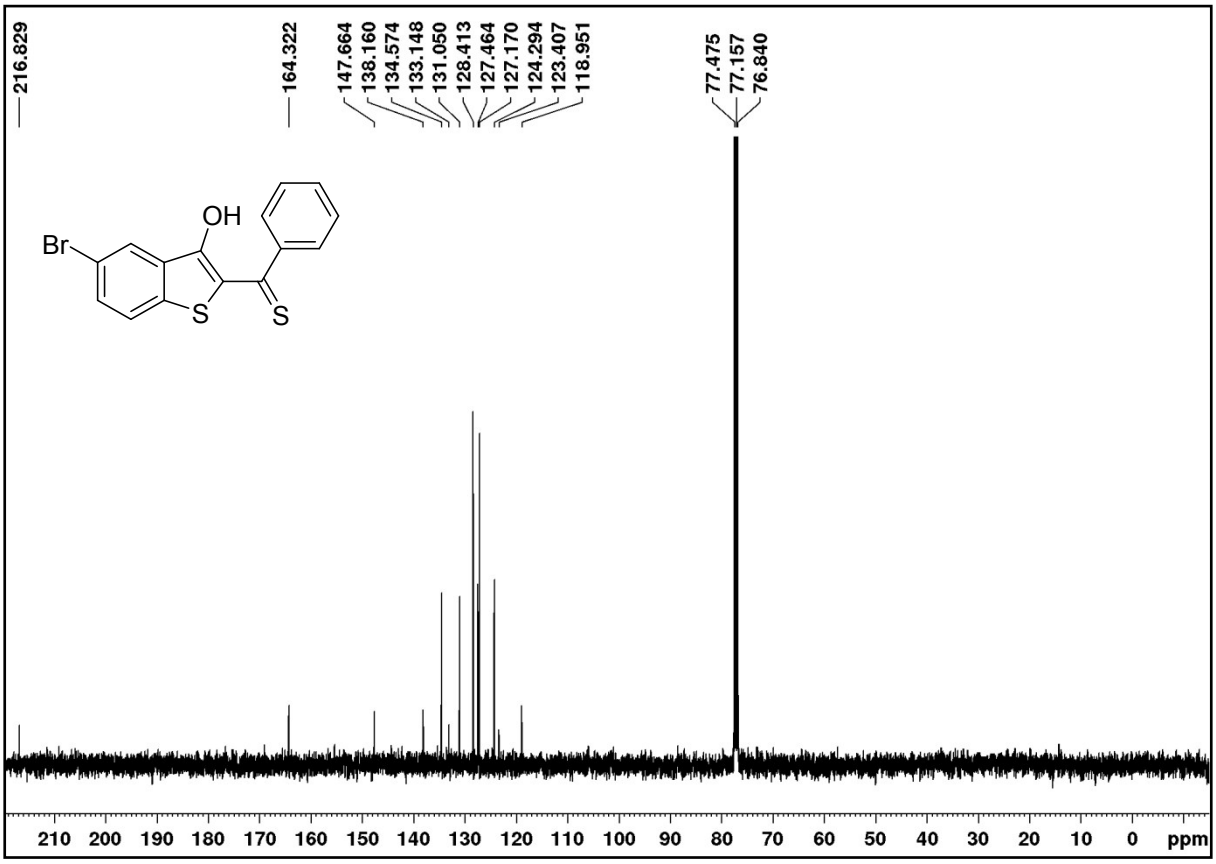


Figure 50: 100 MHz ^{13}C-NMR spectrum of **2y** in $CDCl_3$

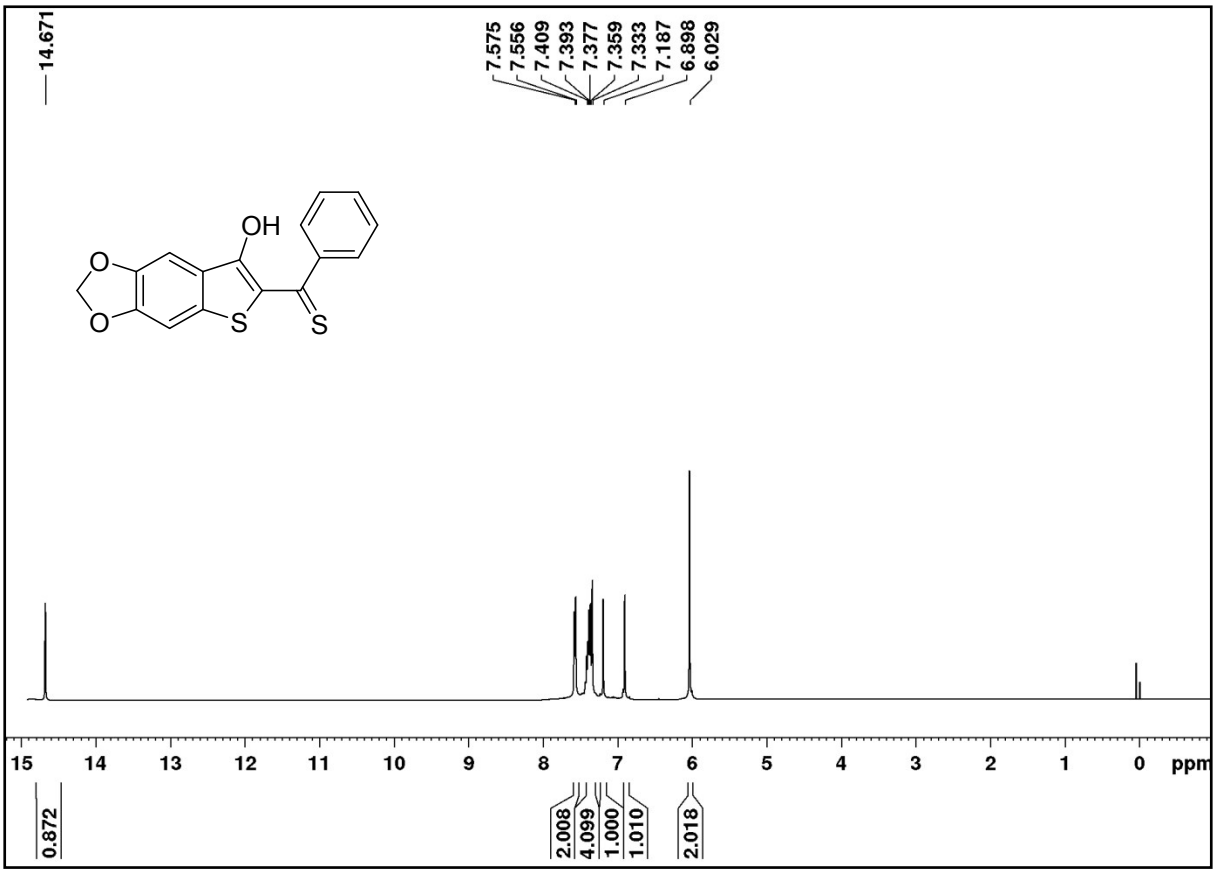


Figure 51: 400 MHz ^{1}H-NMR spectrum of **2z** in $CDCl_3$

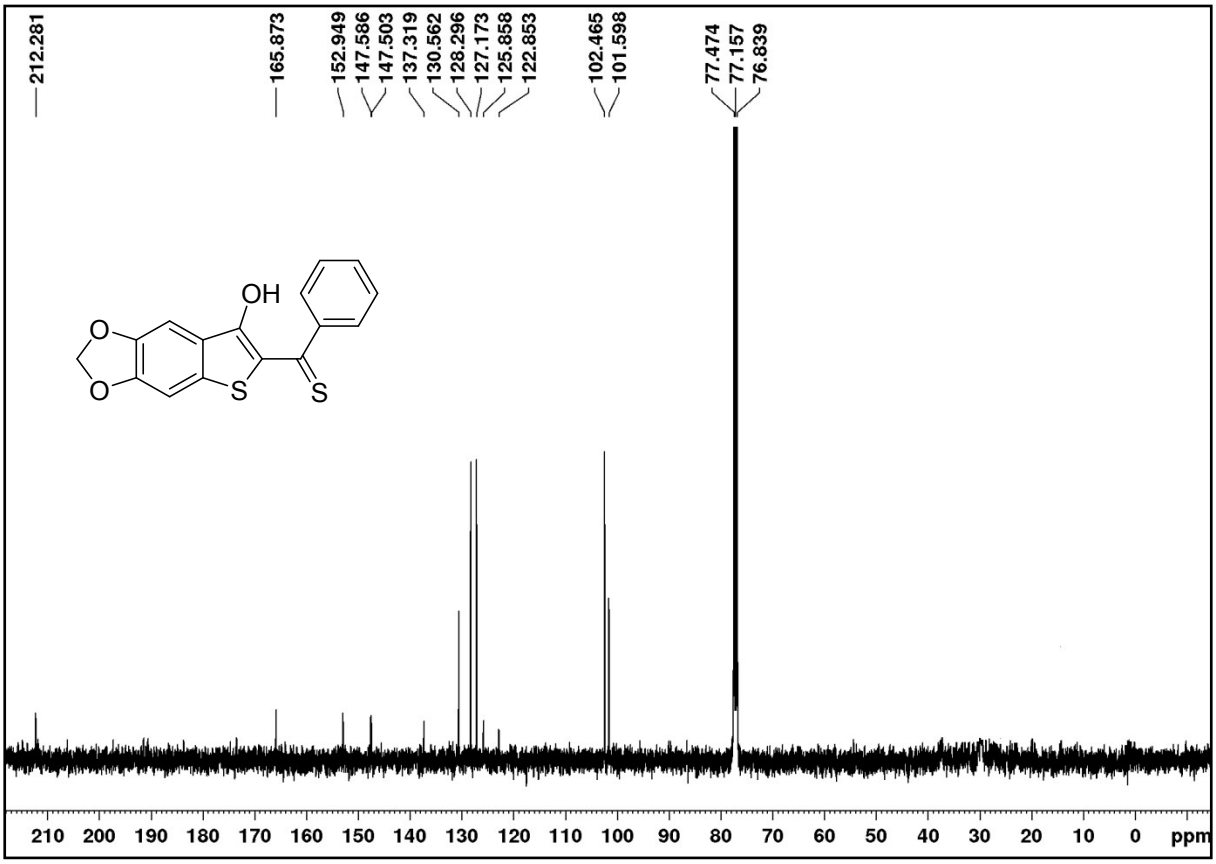


Figure 52: 100 MHz ^{13}C-NMR spectrum of **2z** in $CDCl_3$

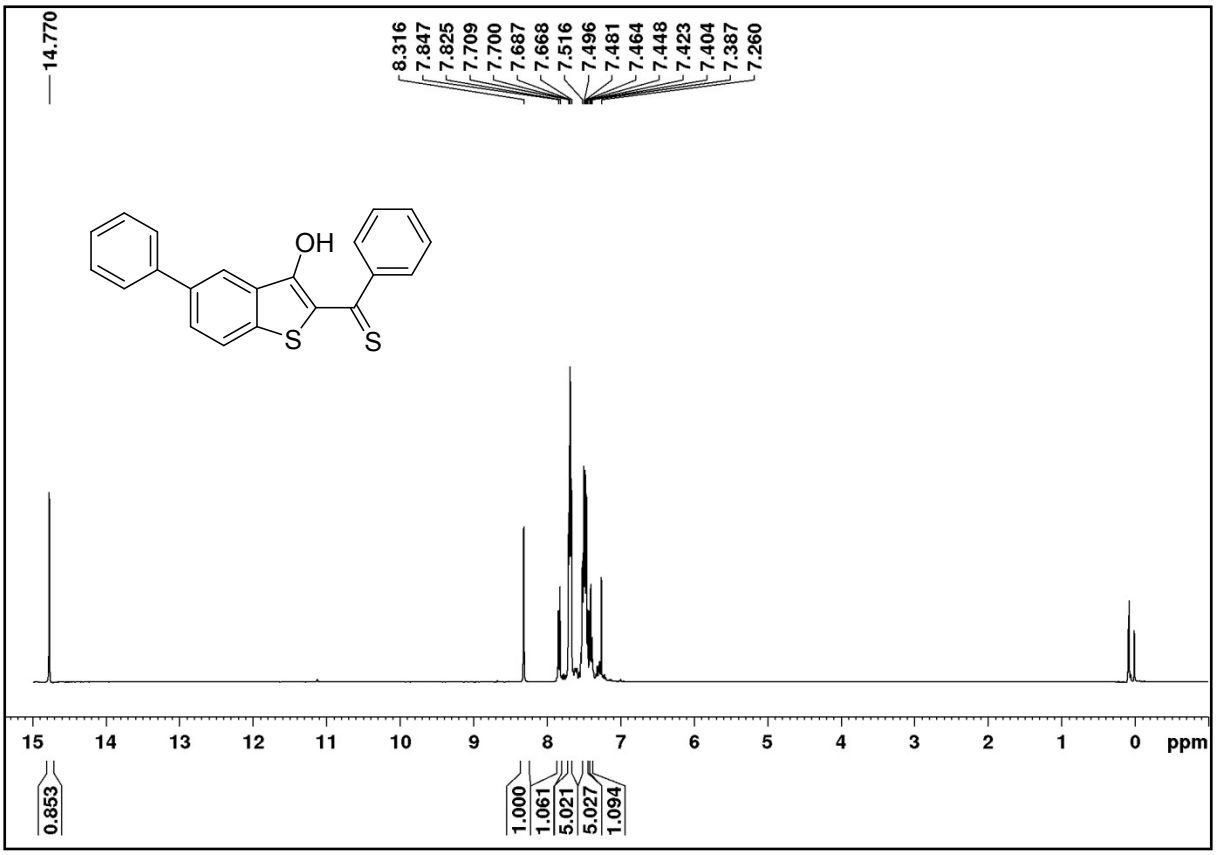


Figure 53: 400 MHz ^{1}H-NMR spectrum of **2aa** in $CDCl_3$

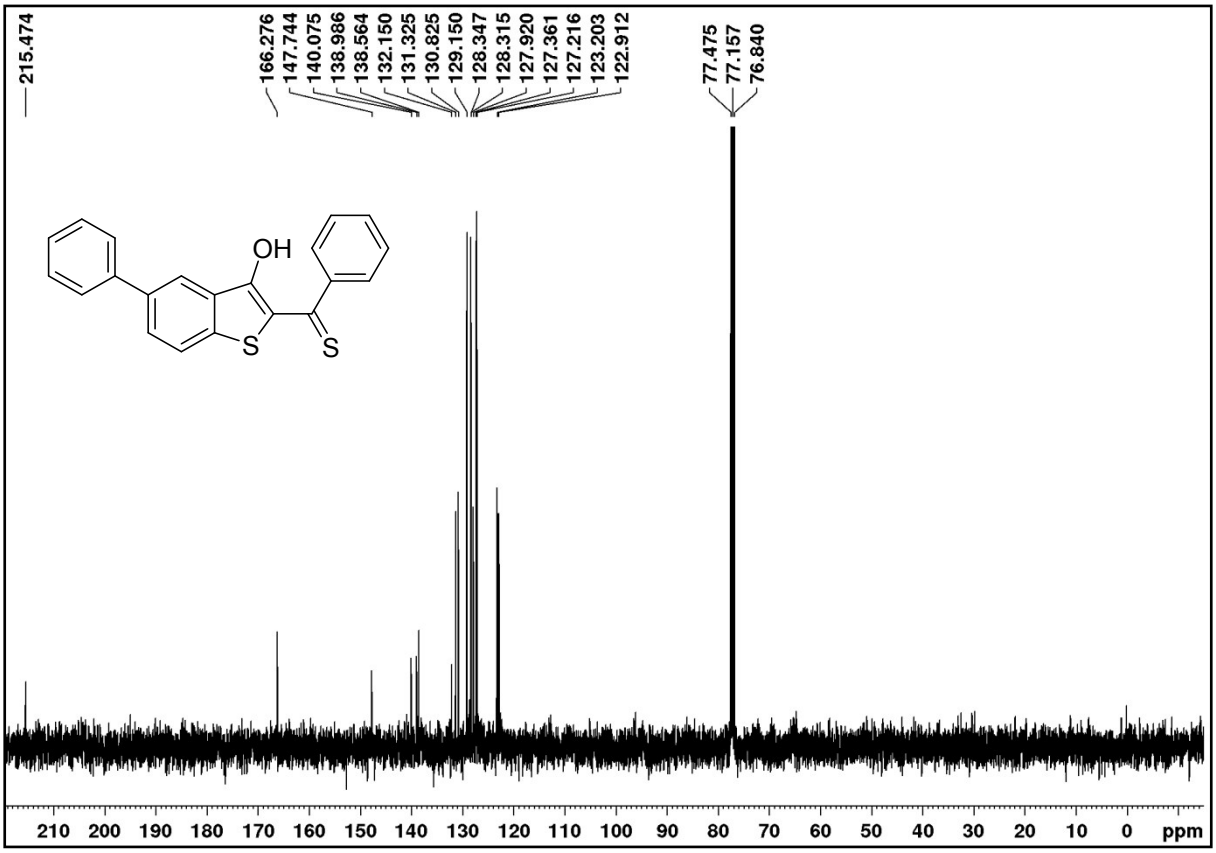


Figure 54: 100 MHz ^{13}C-NMR spectrum of **2aa** in $CDCl_3$

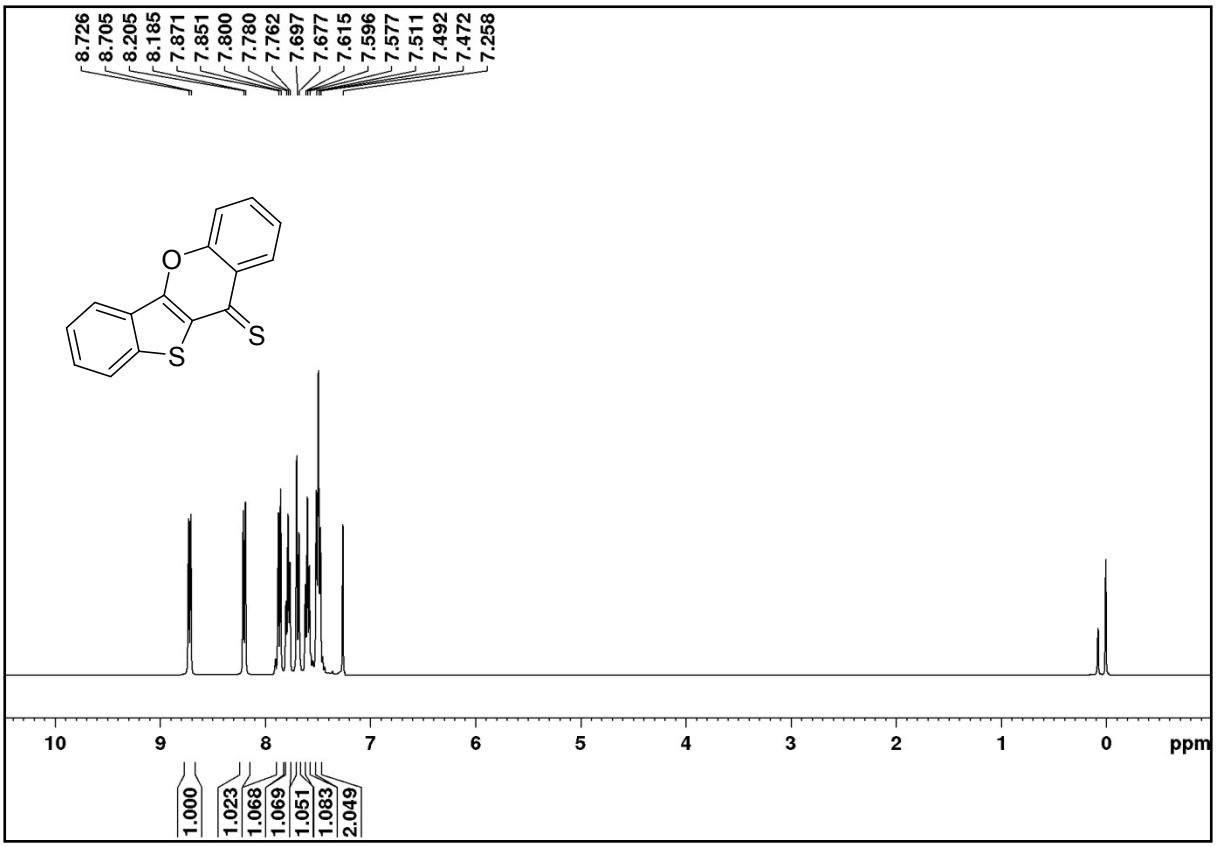


Figure 55: 400 MHz ^{1}H-NMR spectrum of **3a** in $CDCl_3$

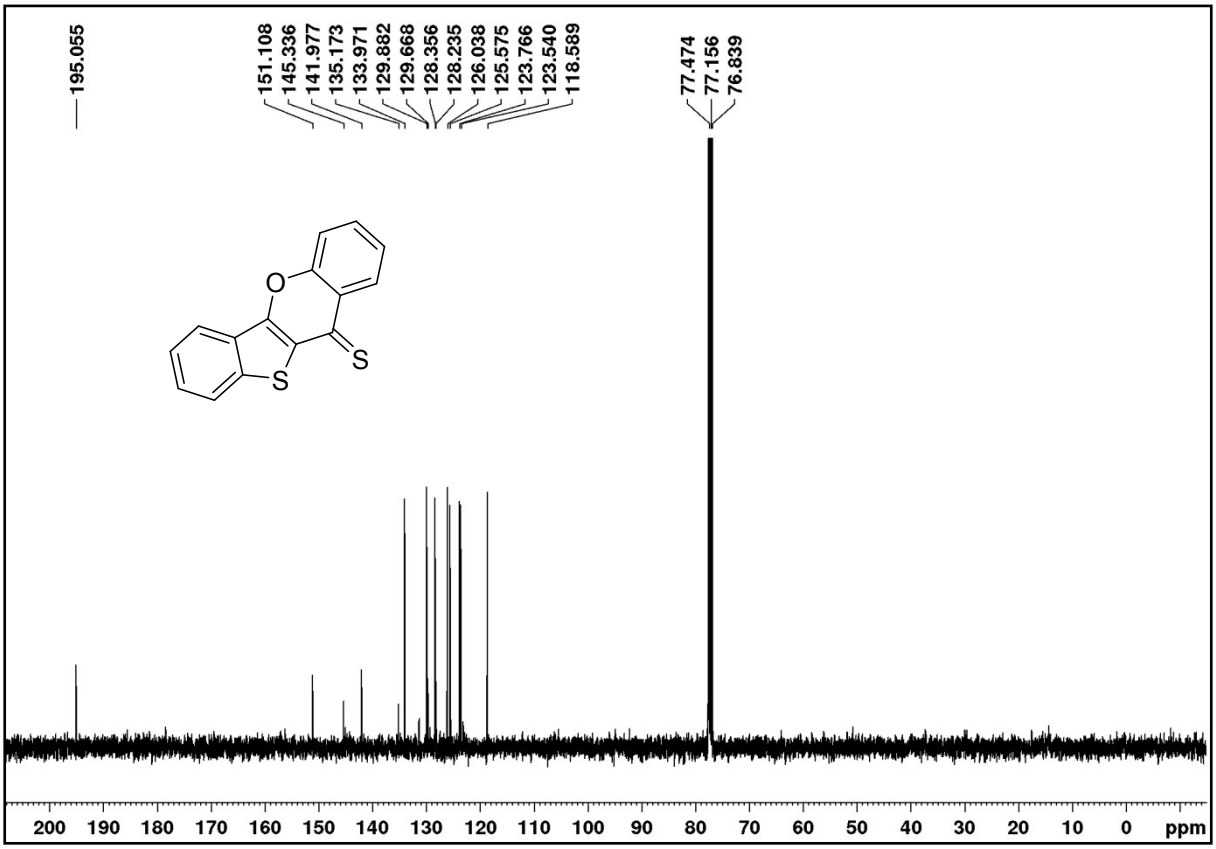


Figure 56: 100 MHz ^{13}C-NMR spectrum of **3a** in $CDCl_3$

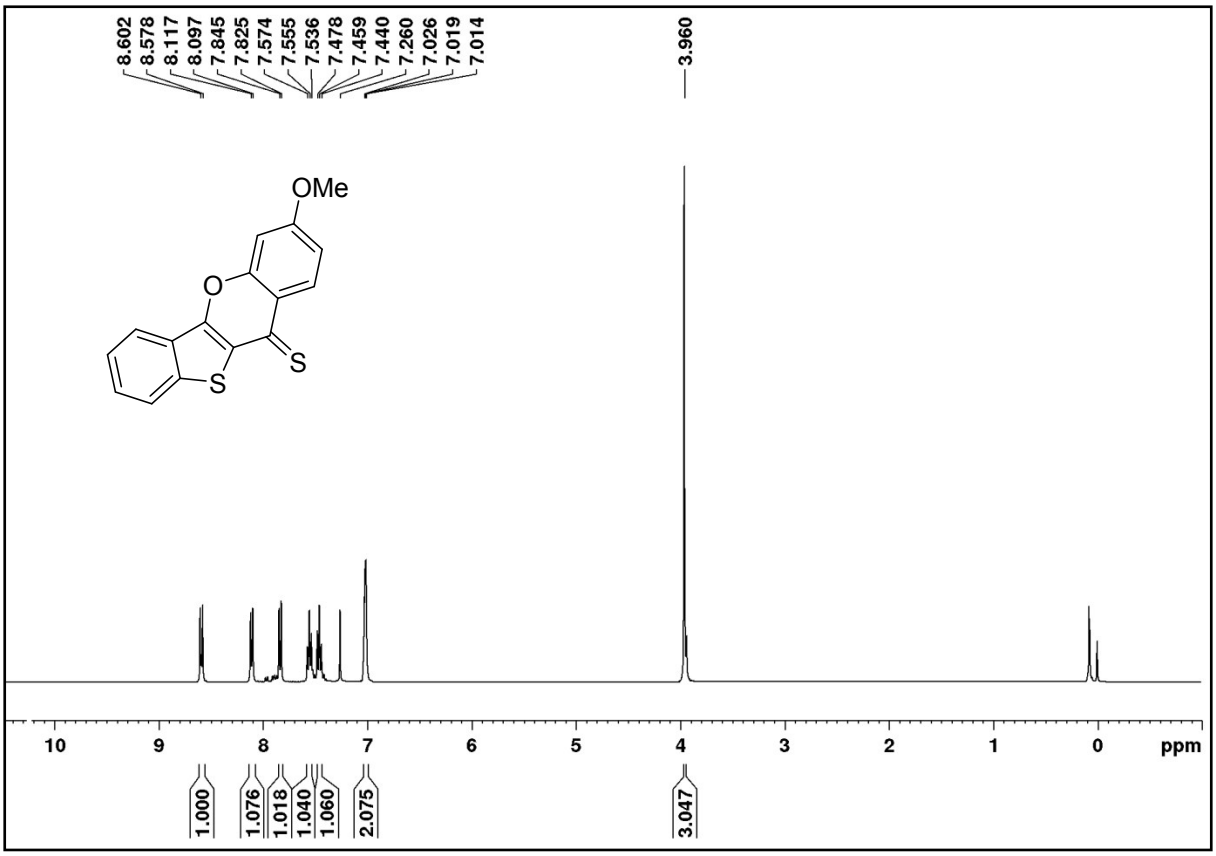


Figure 57: 400 MHz ^{1}H-NMR spectrum of **3b** in $CDCl_3$

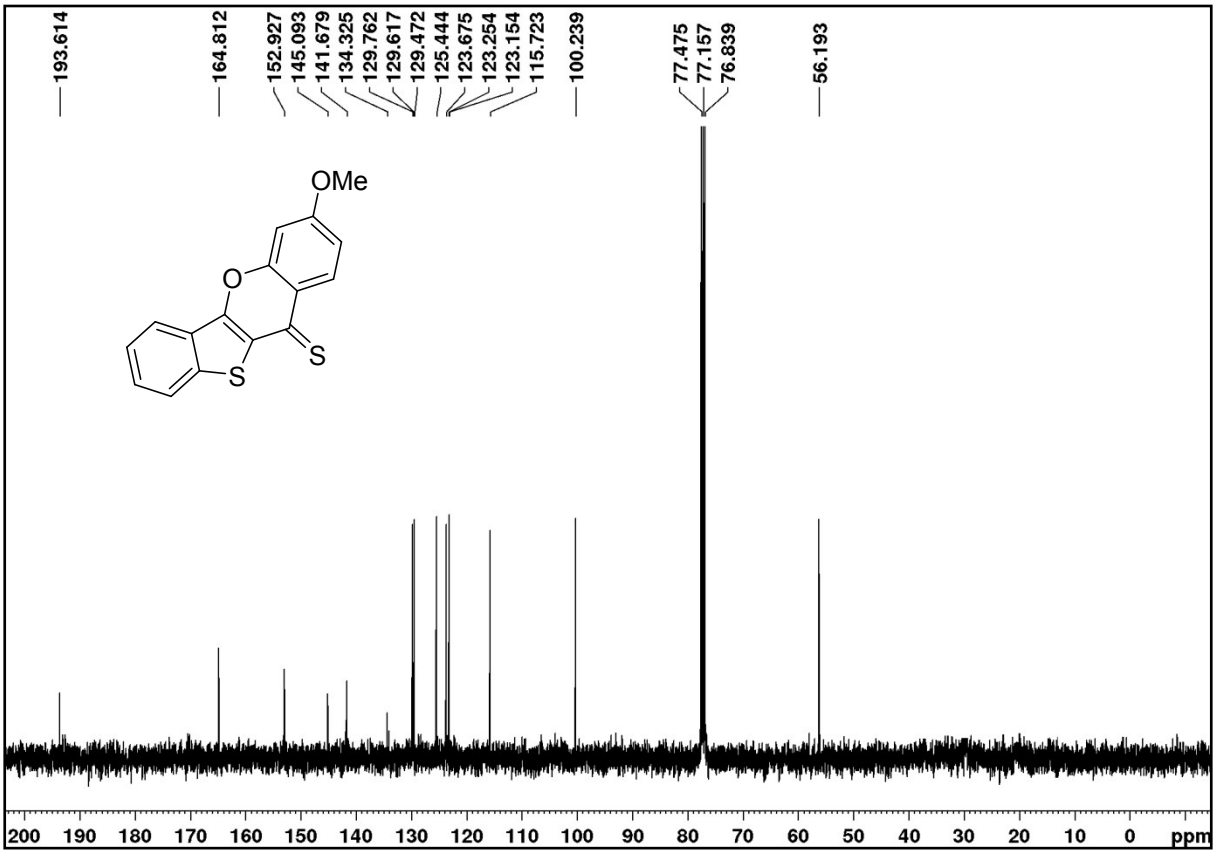


Figure 58: 100 MHz ^{13}C-NMR spectrum of **3b** in $CDCl_3$

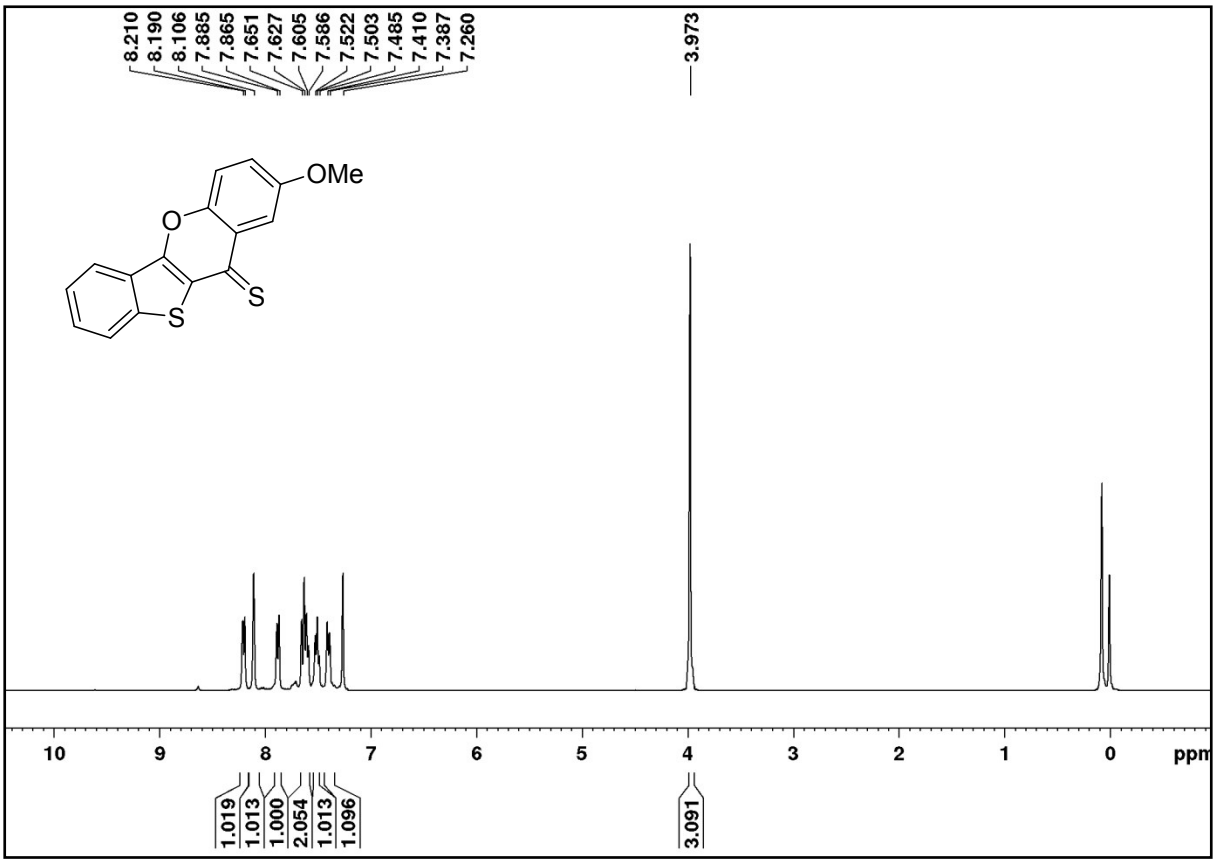


Figure 59: 400 MHz ^{1}H-NMR spectrum of **3c** in $CDCl_3$

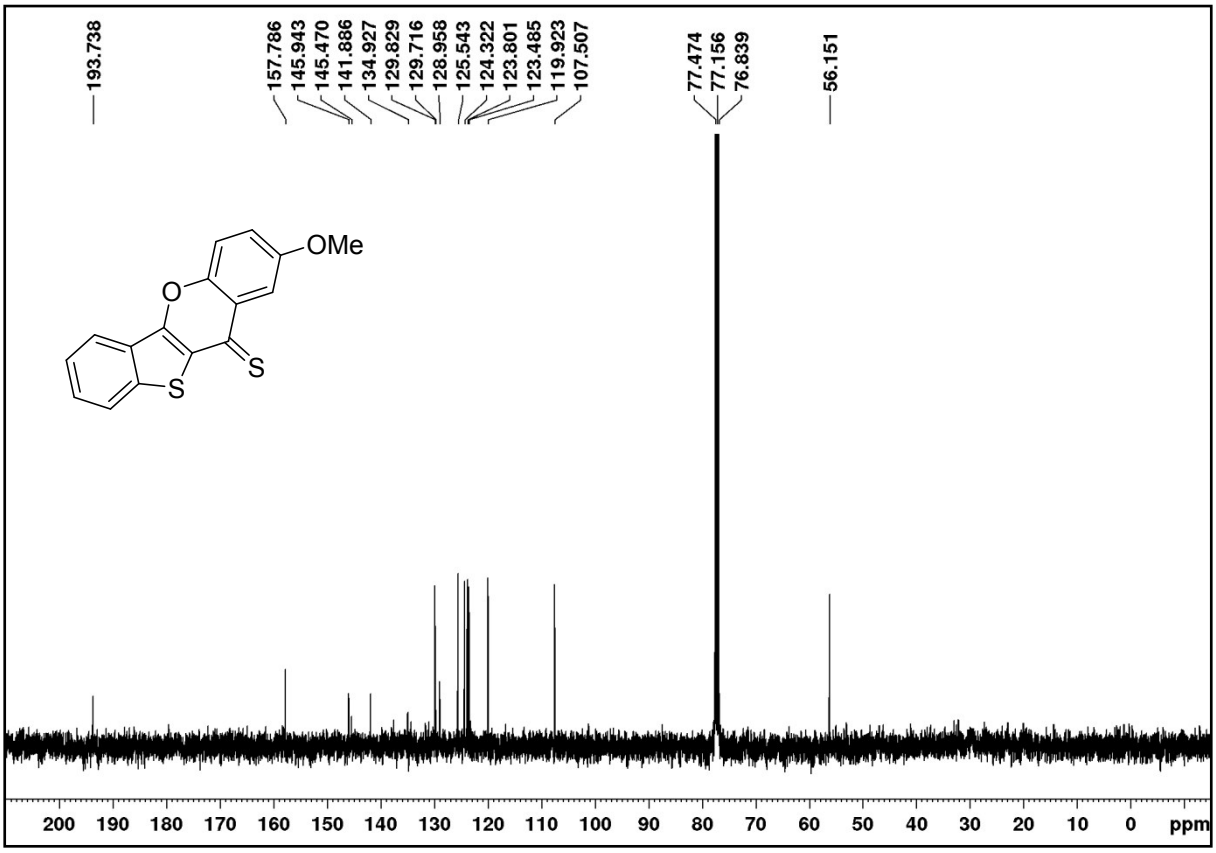


Figure 60: 100 MHz ^{13}C-NMR spectrum of **3c** in $CDCl_3$

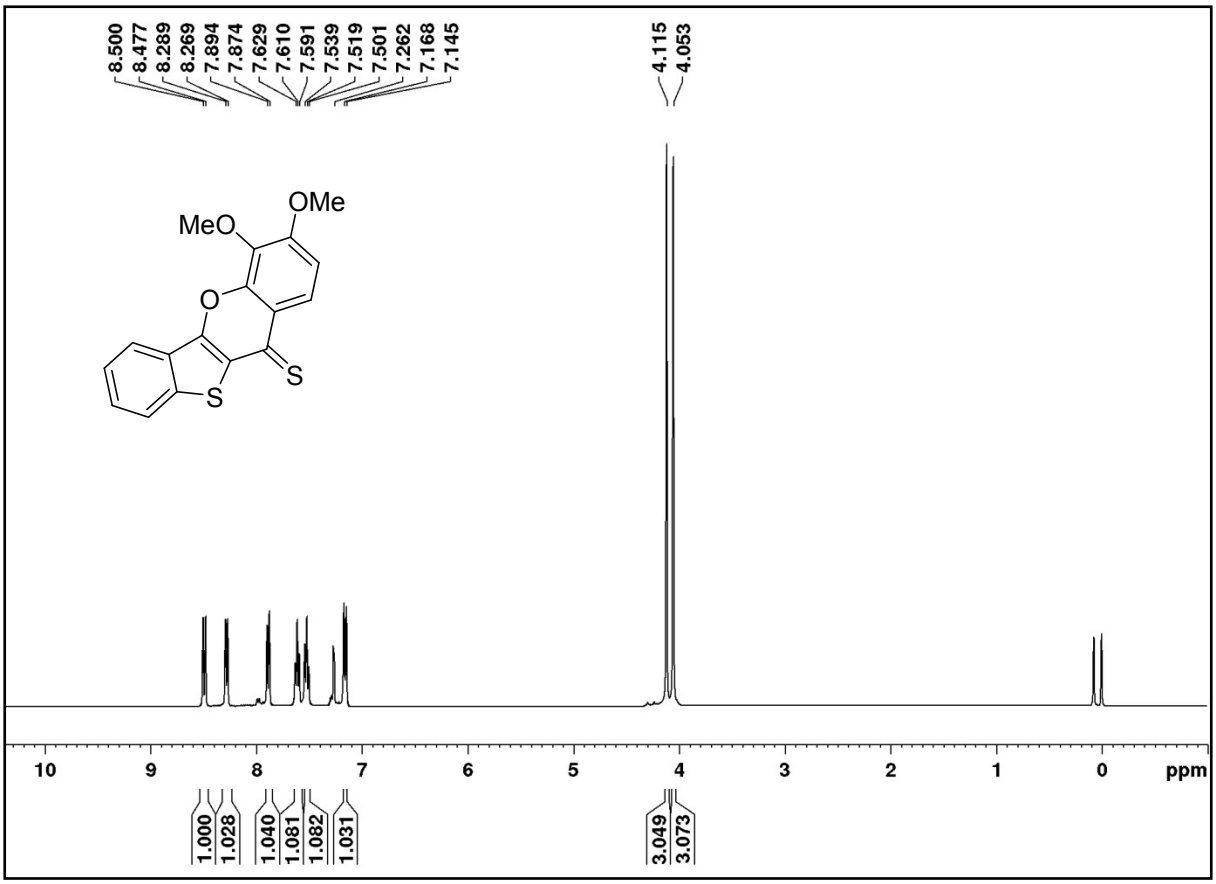


Figure 61: 400 MHz ^{1}H-NMR spectrum of **3d** in $CDCl_3$

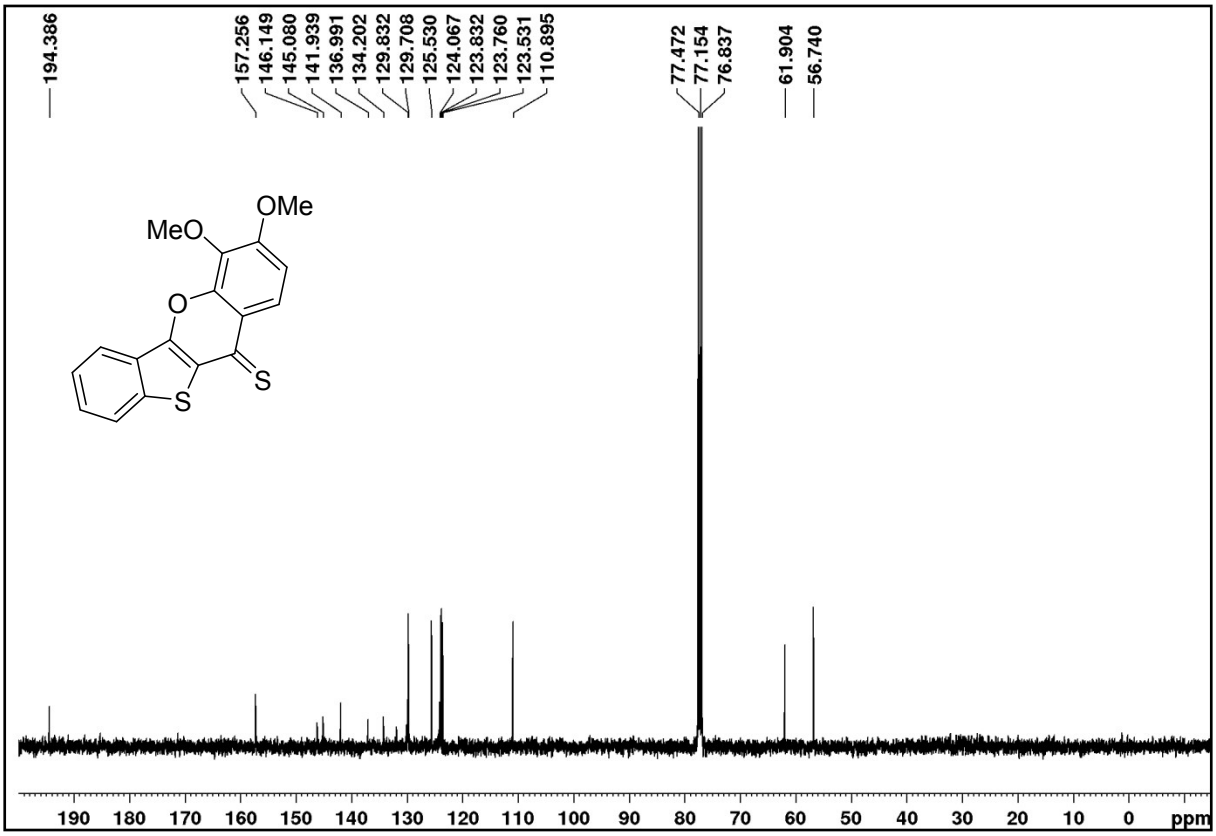


Figure 62: 100 MHz ^{13}C-NMR spectrum of **3d** in $CDCl_3$

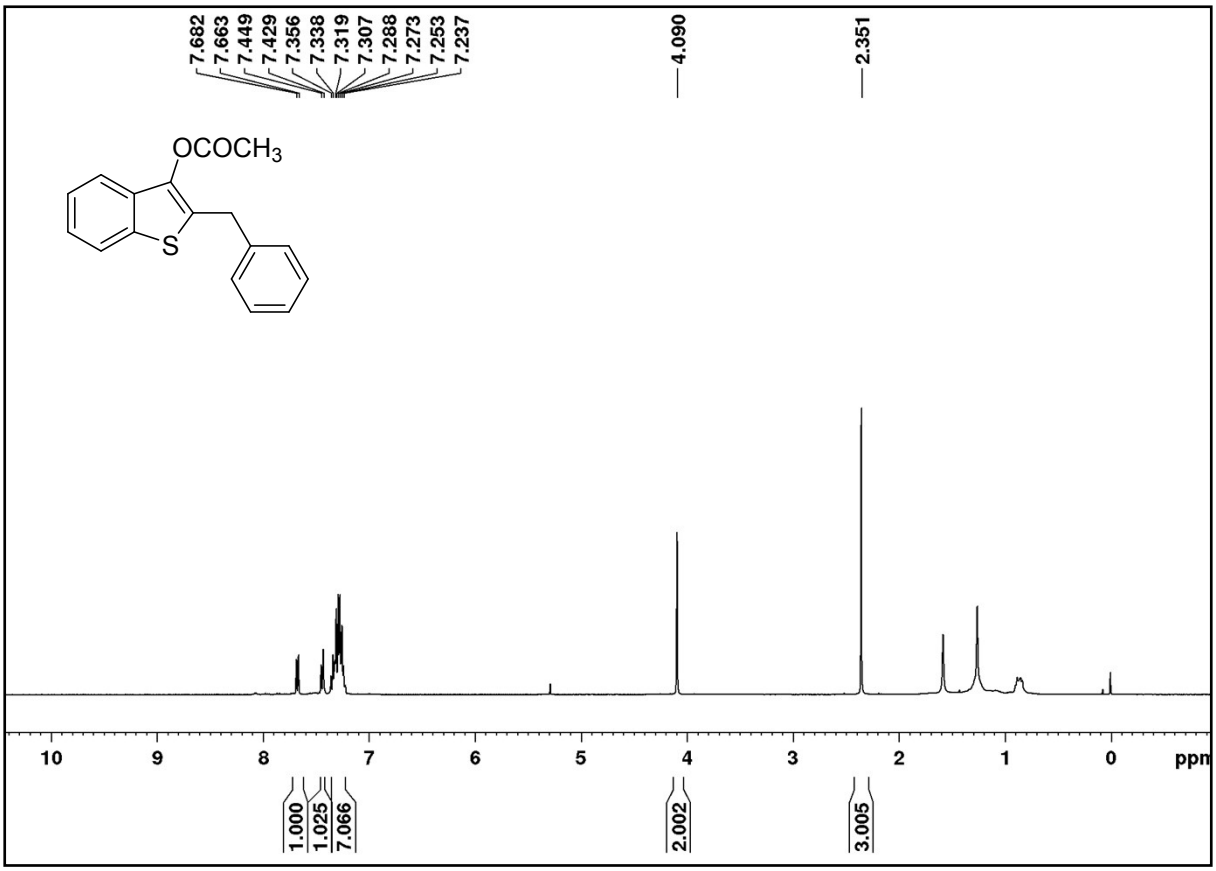


Figure 63: 400 MHz ^{1}H-NMR spectrum of **15** in $CDCl_3$

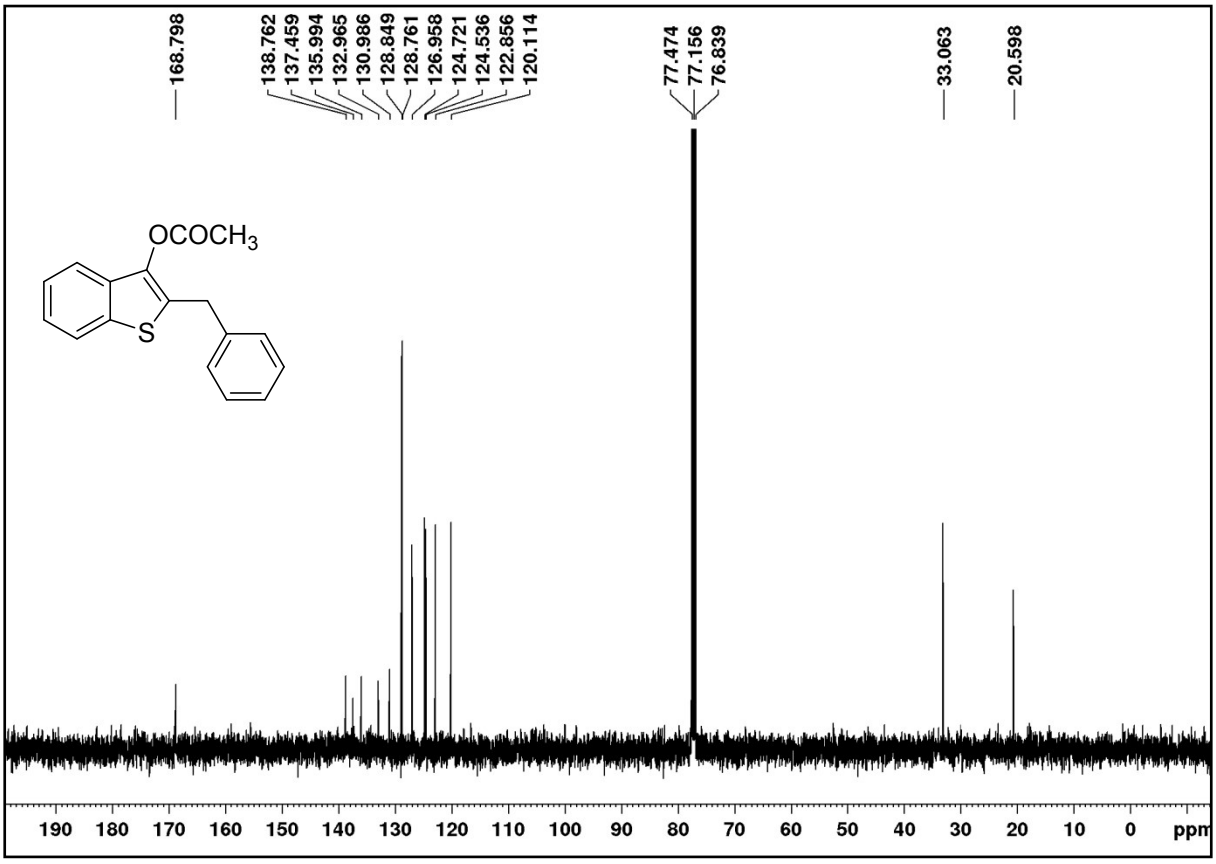
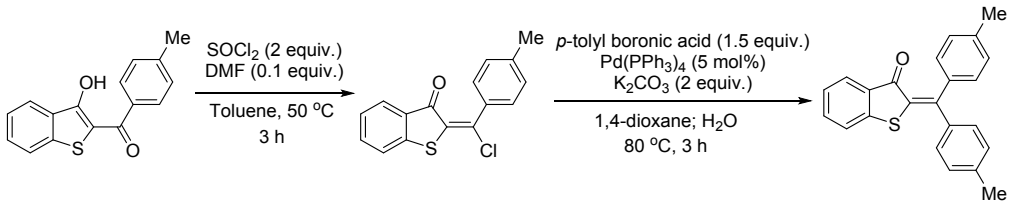


Figure 64: 100 MHz ^{13}C-NMR spectrum of **15** in $CDCl_3$

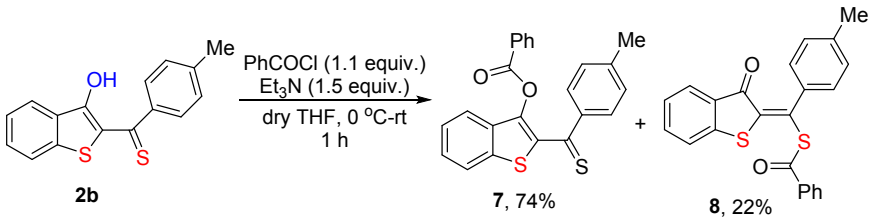
7.0. Synthesis of 4-fold photo switch 2-(di-p-tolylmethylene)benzo[b]thiophen-3(2H)-one



Preparation of vinyl chlorides (5): (3-hydroxybenzo[b]thiophen-2-yl)(p-tolyl)methanethione was dissolved in toluene to receive a 1 M solution thionyl chloride (2.0 equiv) and DMF (0.1 equiv) were added and the solution was stirred at 50 °C for 3 hours. Saturated sodium carbonate solution was added until the solution was neutralized and the product was extracted with dichloromethane (3 x 25 mL). The solvent was removed in vacuo and the product was purified by column chromatography over a short plug of silica or by crystallization.

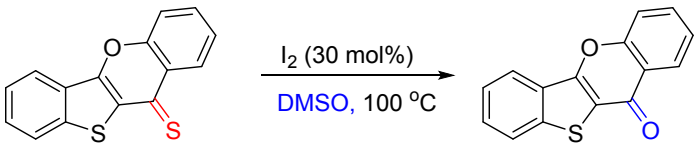
Typical Procedure for Suzuki-Miyaura Reactions (6): (Z)-2-(chloro(p-tolyl)methylene)benzo[b]thiophen-3(2H)-one was dissolved in dioxane to receive a 1 M solution. Corresponding boronic acids (1.5 equiv), potassium carbonate (2.0 equiv) and water (10 vol %) were added and the solution was degassed before $Pd(PPh_3)_4$ (5 mol %) was added. The reaction was heated to 80 °C under continuous stirring for 0.5 to 24 hours, subsequently 5 mL of a saturated aq. sodium carbonate solution was added and the product was extracted with dichloromethane (3 x 10 ml). The solvent was removed in vacuo and the product was purified by column chromatography and if possible by crystallization.

Synthesis of 2-(4-methylphenylcarbonothioyl)benzo[b]thiophen-3-yl benzoate from (3-hydroxybenzo[b]thiophen-2-yl)(p-tolyl)methanethione (7):



Typical Procedure for acylation reactions (7): (3-hydroxybenzo[b]thiophen-2-yl)(p-tolyl)methanethione was dissolved in dry THF and the reaction mixture was brought to 0°C then the corresponding acid chloride (1.1 equiv.) and Et_3N (1.5 equiv.) were added. The reaction was allowed to stir for 1 hour and the reaction was monitored by TLC. After the complete conversion of starting material, the reaction was quenched with addition of water and washed with EtOAc and the organic layer was collected. The solvent was removed in vacuo and the product was purified by column chromatography and if possible by crystallization.

General procedure for synthesis of 11*H*-benzo[4,5]thieno[3,2-b]chromen-11-one (9):



Under open atmosphere, 11*H*-benzo[4,5]thieno[3,2-b]chromene-11-thione **3a** (134 mg, 0.5 mmol) was dissolved in 3 mL of DMSO then 30 mol% of iodine was added and closed with glass-stopper. The reaction tube was then immersed in a 100 ºC pre-heated oil bath. The reaction was allowed until the completion of starting material. Then, the reaction mixture was brought to room temperature; water was added and extracted with ethyl acetate (3×7 mL). Brine wash (1×15 mL) and $Na_2S_2O_3.5H_2O$ was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and silica gel column separation of crude product using hexanes and ethyl acetate mixture (15:5) afforded the corresponding 11*H*-benzo[4,5]thieno[3,2-b]chromen-11-one **9**.

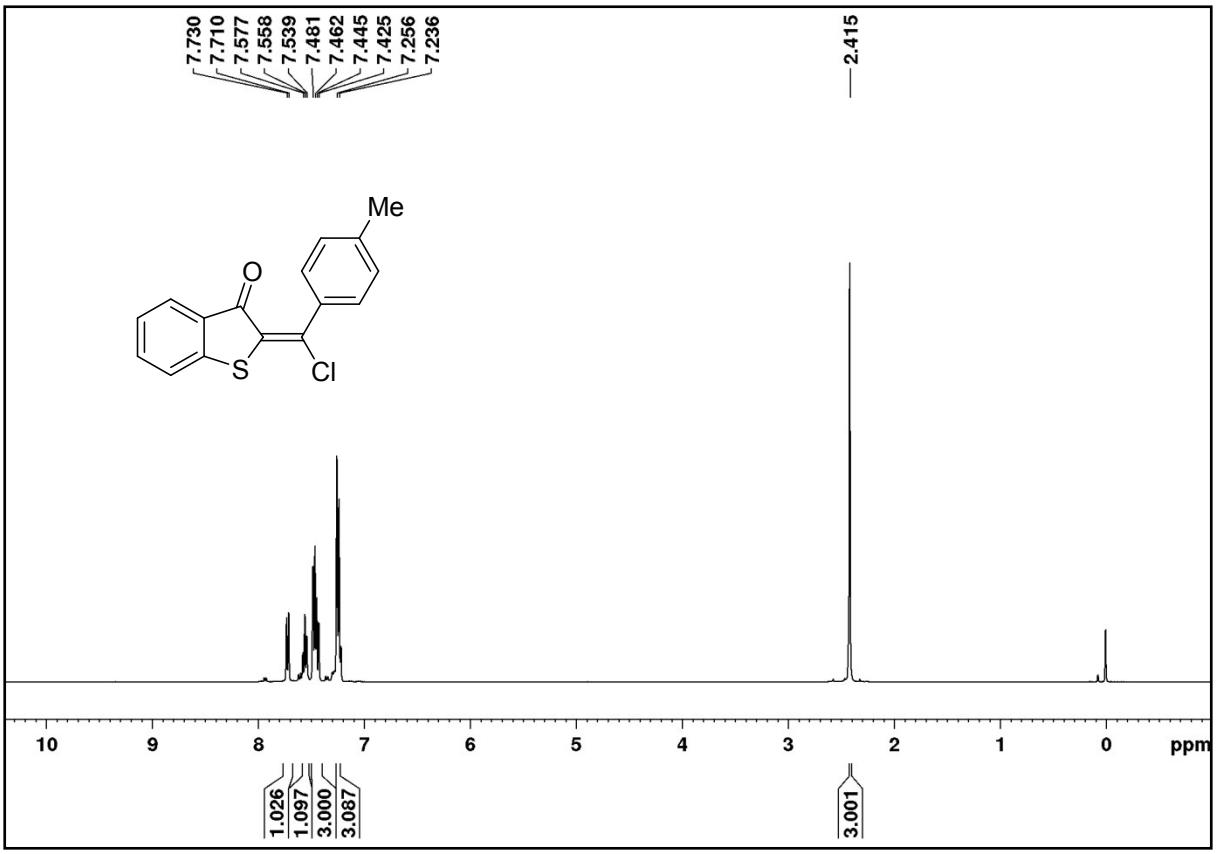


Figure 65: 400 MHz ^{1}H-NMR spectrum of **5** in $CDCl_3$

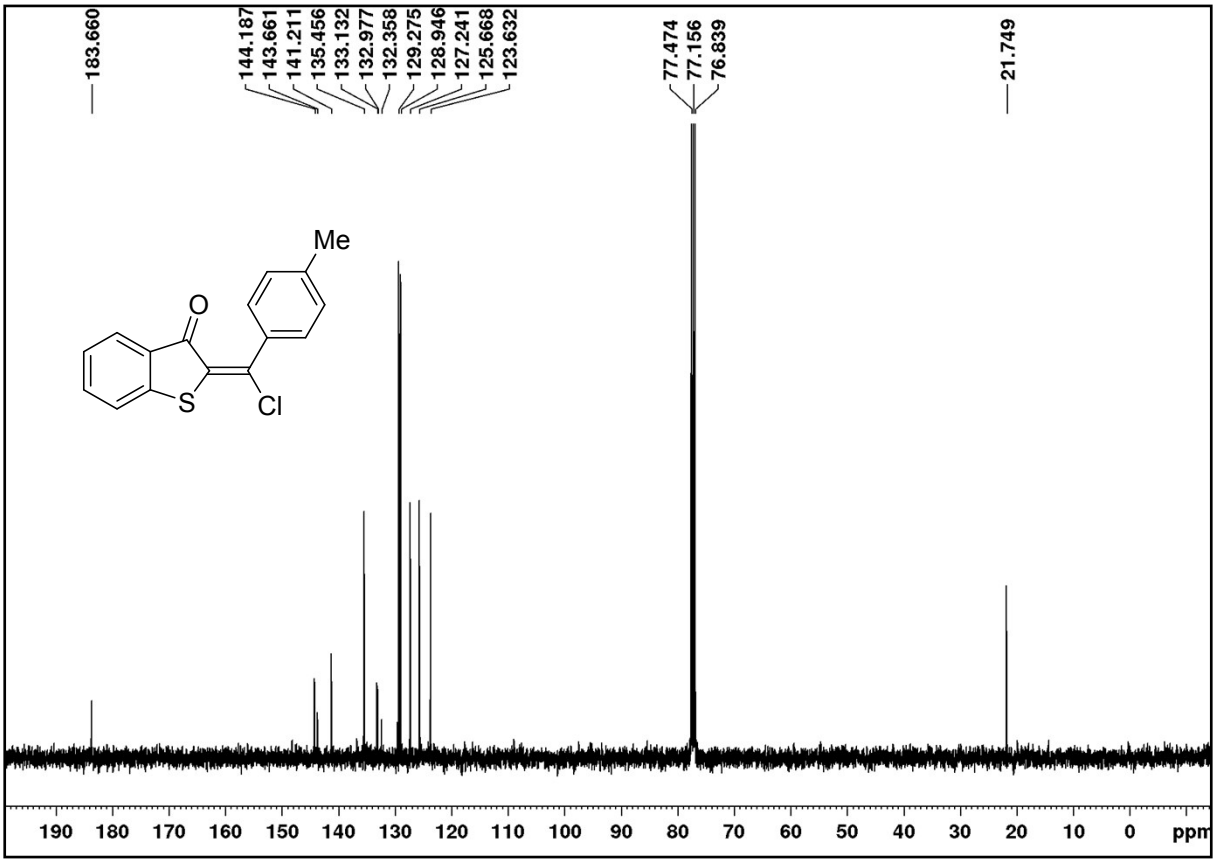


Figure 66: 100 MHz ^{13}C-NMR spectrum of **5** in $CDCl_3$

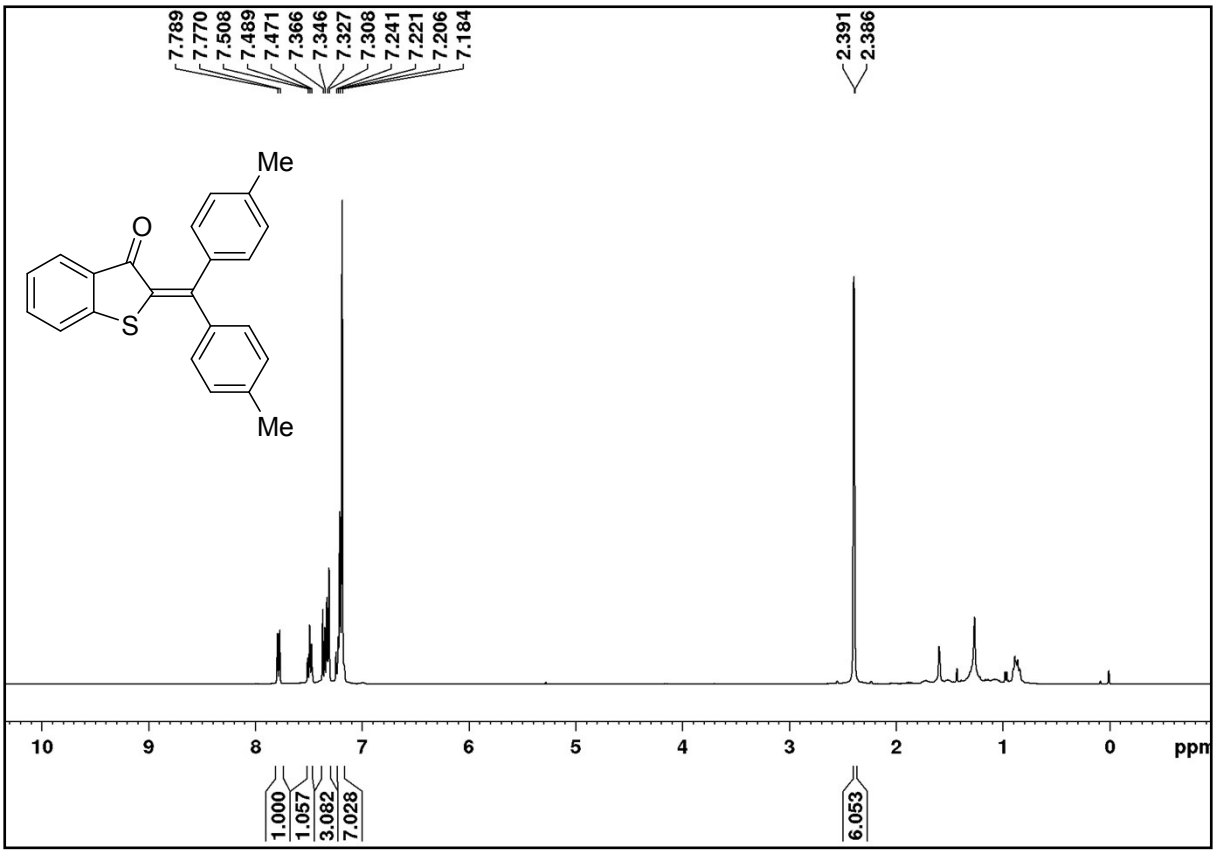


Figure 67: 400 MHz ^{1}H-NMR spectrum of **6** in $CDCl_3$

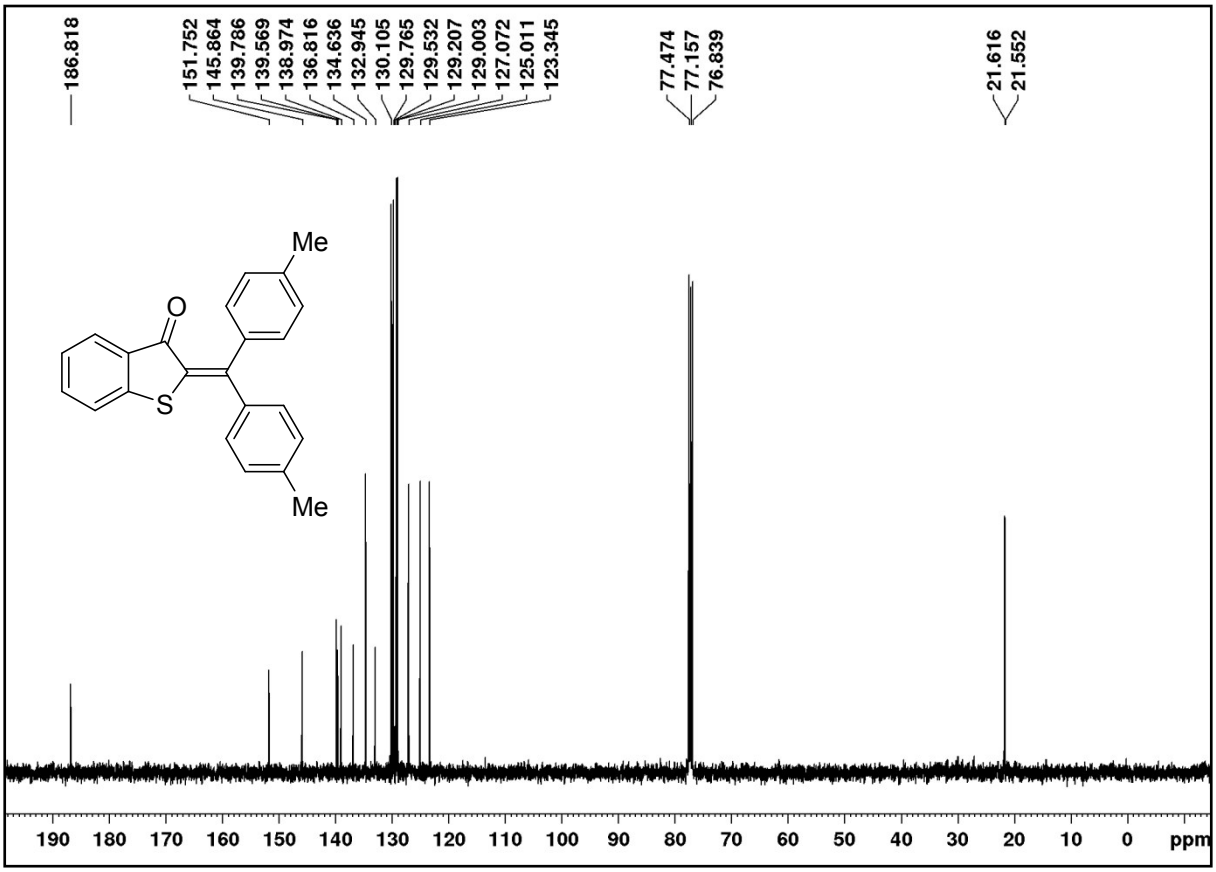


Figure 68: 100 MHz ^{13}C-NMR spectrum of 6 in $CDCl_3$

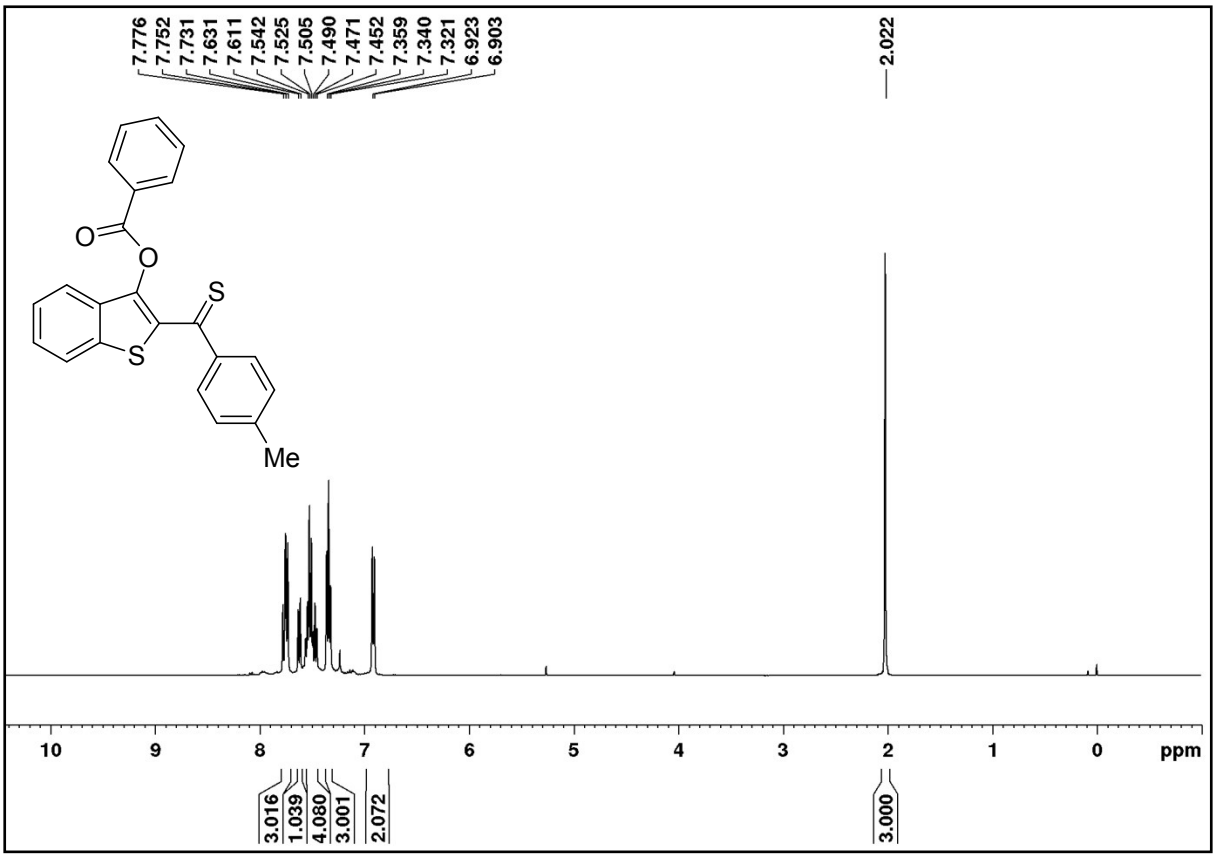


Figure 69: 400 MHz ^{1}H-NMR spectrum of **7** in $CDCl_3$

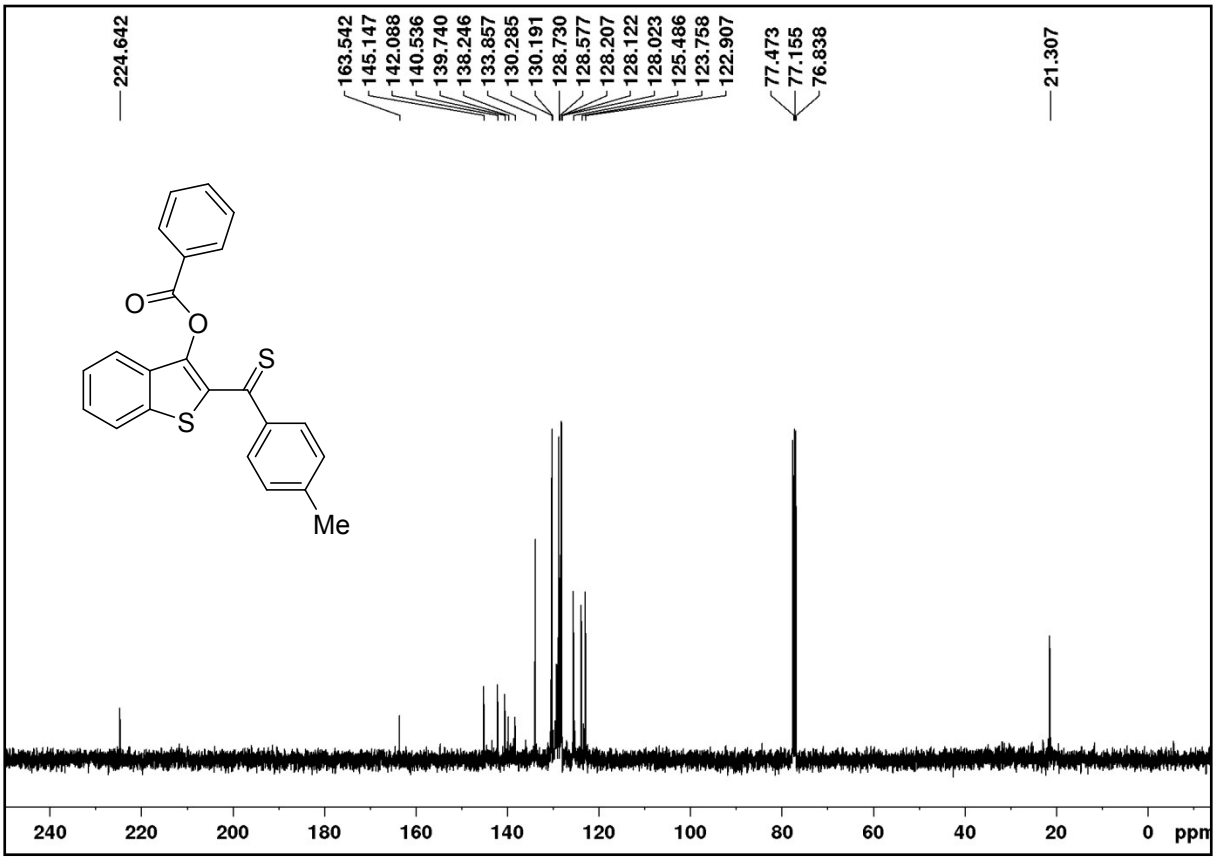


Figure 70: 100 MHz ^{13}C-NMR spectrum of **7** in $CDCl_3$

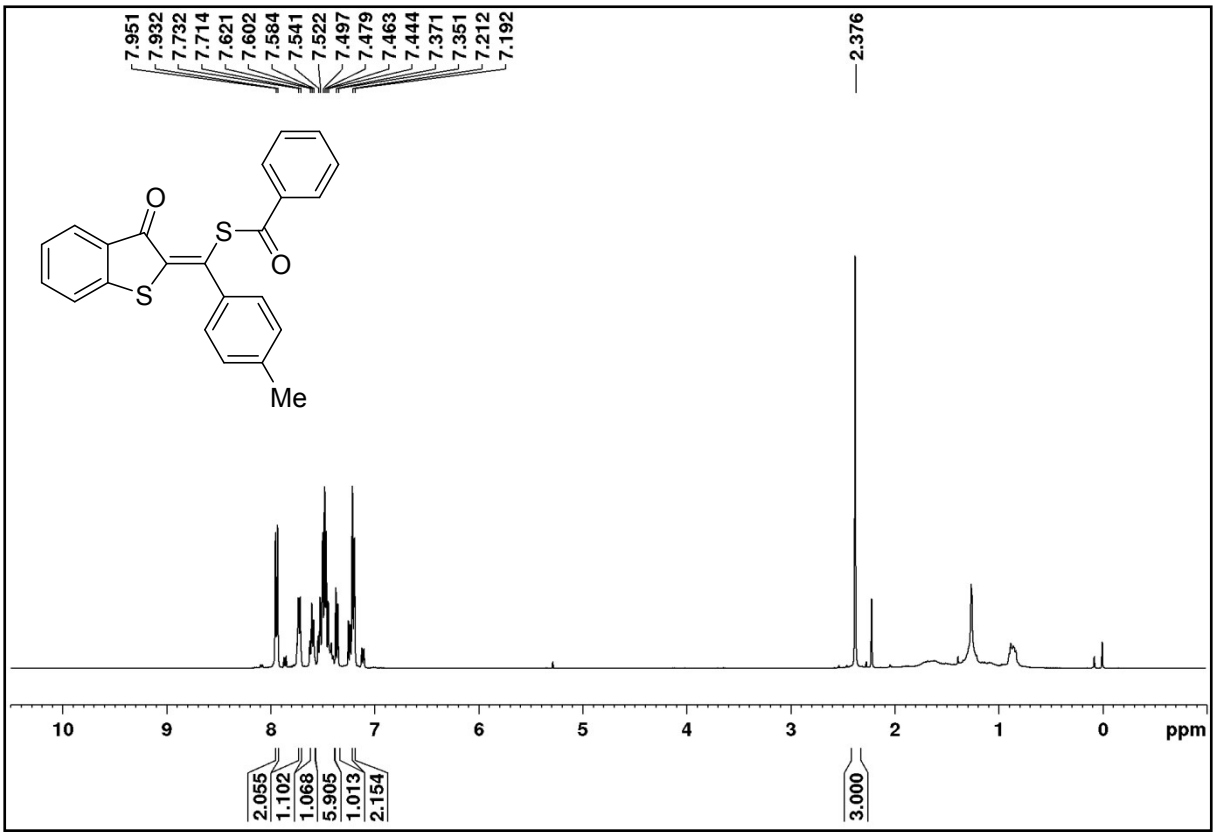


Figure 71: 400 MHz ^{1}H-NMR spectrum of **8** in $CDCl_3$

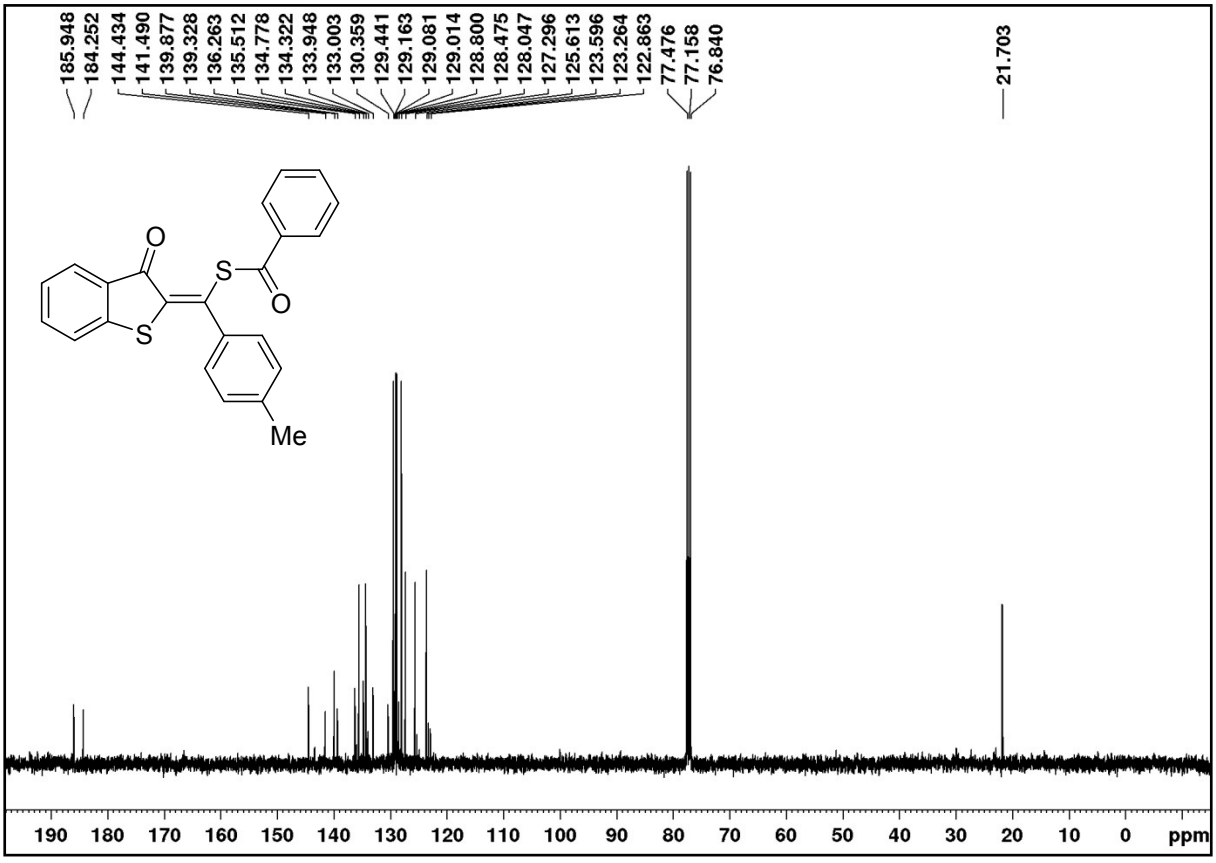


Figure 72: 100 MHz ^{13}C-NMR spectrum of **8** in $CDCl_3$

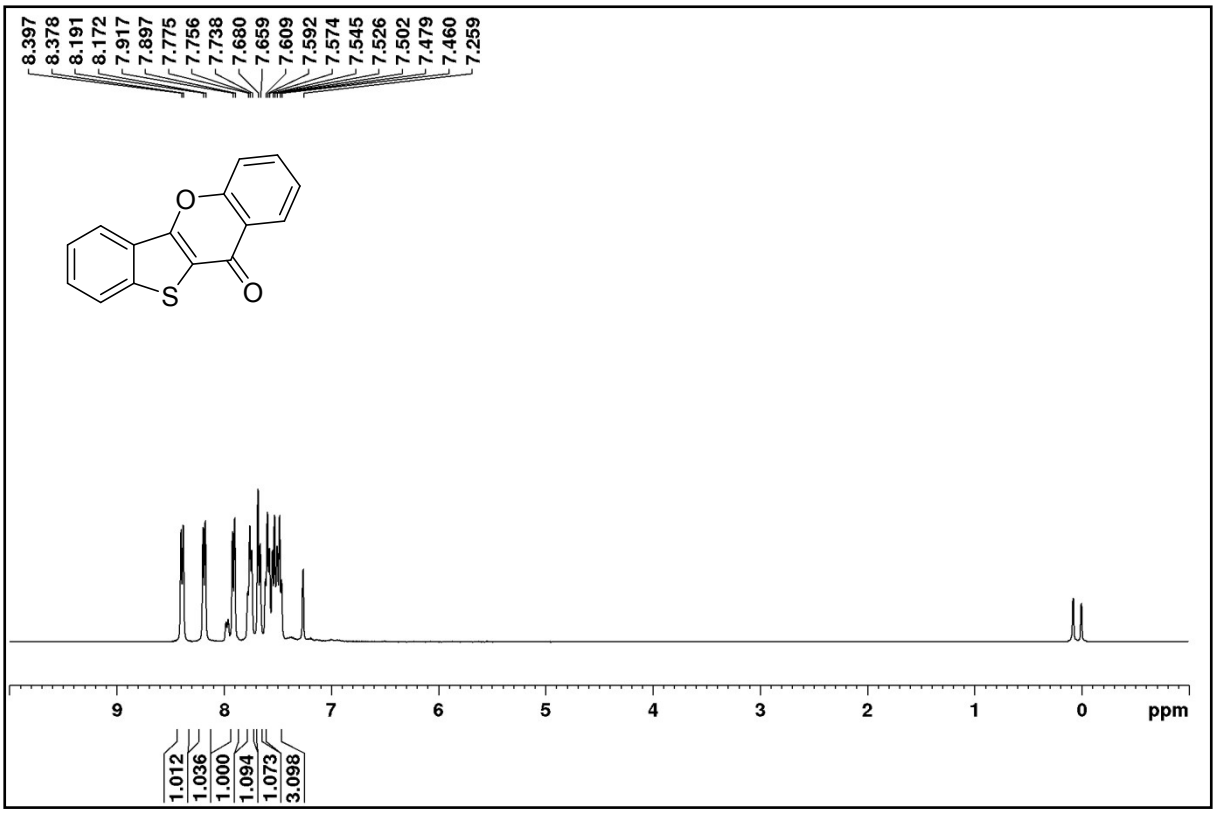


Figure 73: 400 MHz ^{1}H-NMR spectrum of **9** in $CDCl_3$

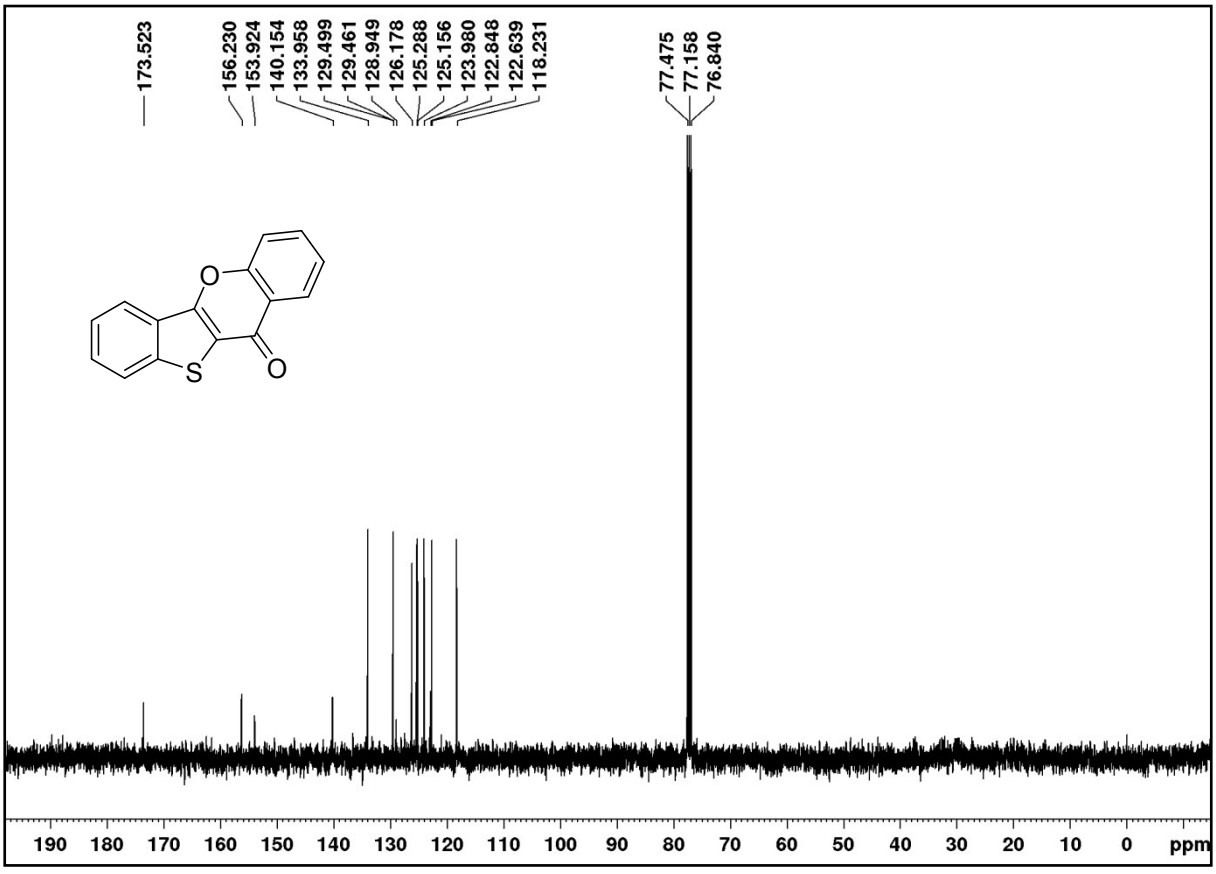


Figure 74: 100 MHz ^{13}C-NMR spectrum of **9** in $CDCl_3$

8.0. Single crystal XRD data for Compound

Single crystals of (3-hydroxybenzo[b]thiophen-2-yl)(p-tolyl)methanethione **2b** and (4-(dimethylamino)phenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanethione **2i and 3c** derivatives are suitable for X-ray analysis was obtained by slow evaporation of 0.01 M solution in 1:1 mixture of MeOH:DCM. Thermal ellipsoids are shown at the 50% probability level and hydrogens are omitted for clarity.

5.1 XRD Data for Compound 2b (CCDC No. 2031230)

Bond precision: C-C = 0.0031 A Wavelength=0.71073
Cell: a=13.9263(10) b=12.3383(9) c=7.8707(6)
alpha=90 beta=97.311(3) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1341.40(17)	1341.40(17)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C_{16} H_{12} O S_2	?
Sum formula	C_{16} H_{12} O S_2	C_{16} H_{12} O S_2
Mr	284.38	284.38
Dx,g cm^{-3}	1.408	1.408
Z	4	4
Mu (mm^{-1})	0.384	0.384
F000	592.0	592.0
F000'	593.19	
h,k,lmax	16,14,9	16,14,9
Nref	2368	2350
Tmin,Tmax	0.929,0.955	0.910,0.955
Tmin'	0.908	

Correction method= # Reported T Limits: Tmin= 0.910 Tmax= 0.955
AbsCorr = MULTI-SCAN
Data completeness= 0.992 Theta(max)= 24.994
R(reflections)= 0.0334(1855) wR2(reflections)= 0.0892(2350)
S = 1.009 Npar= 177

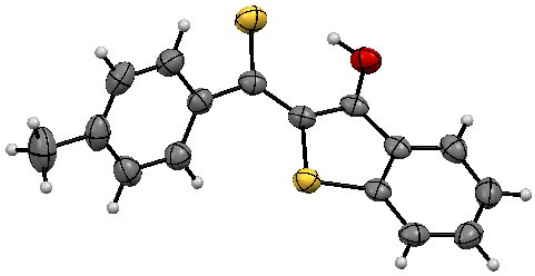


Figure S1. Single-crystal X-ray structure of compound **2b** (CCDC No. 2031230) Ellipsoids represent 50% probability level.

5.2 XRD Data for Compound 2i (CCDC No. 2031231)

Bond precision: C-C = 0.0029 A Wavelength=0.71073
Cell: a= 9.1370(3) b= 9.3396(4) c= 9.3410(3)
alpha= 105.2378(17) beta= 102.3386(17) gamma= 91.2454(18)
Temperature: 296 K

	Calculated	Reported
Volume	748.76(5)	748.76(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C_{17} H_{15} N O S_2	?
Sum formula	C_{17} H_{15} N O S_2	C_{17} H_{15} N O S_2
Mr	313.42	313.42
Dx,g cm^{-3}	1.390	1.390
Z	2	2
Mu (mm^{-1})	0.353	0.353
F000	328.0	328.0
F000'	328.60	
h,k,lmax	10,11,11	10,11,11
Nref	2631	2625
Tmin,Tmax	0.919,0.948	
Tmin'	0.916	

Correction method= # Reported T Limits: Tmin=0.919Tmax=0.948
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 24.994
R(reflections)= 0.0328(2248) wR2(reflections)= 0.0914(2625)
S = 1.036 Npar= 196

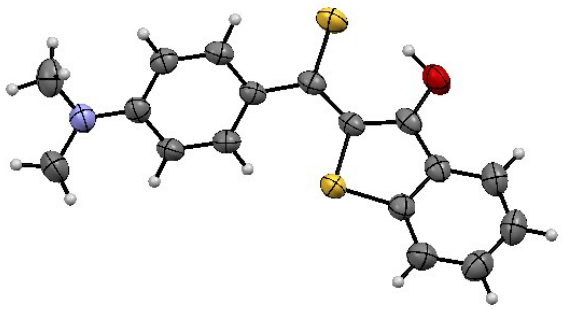


Figure S2. Single-crystal X-ray structure of compound **2i** (CCDC No. 2031231) Ellipsoids represent 50% probability level.

5.3 XRD Data for Compound 3c (CCDC No. 2043956)

Bond precision: C-C = 0.0028 A Wavelength= 11.0434(5)
Cell: a= 6.9373(3) b= 9.0024(4) c= 9.3410(3)
alpha= 88.3339(18) beta= 86.4577(18) gamma= 76.6509(16)
Temperature: 296 K

	Calculated	Reported
Volume	669.69(5)	669.69(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{16}H_{10}O_2S_2$	?
Sum formula	$C_{16}H_{10}O_2S_2$	$C_{16}H_{10}O_2S_2$
Mr	298.36	298.36
Dx,g cm^{-3}	1.480	1.480
Z	2	2
Mu (mm^{-1})	0.394	0.394
F000	308.0	308.0
F000'	308.62	
h,k,lmax	8,10,13	8,10,13
Nref	2354	8889
Tmin,Tmax	0.932,0.954	0.932,0.954
Tmin'	0.932	

Correction method= # Reported T Limits: Tmin= 0.932 Tmax=0.954
AbsCorr = MULTI-SCAN
Data completeness= 3.776 Theta(max)= 24.991
R(reflections)= 0.0365(7875) wR2(reflections)= 0.1279(8889)
S = 0.951 Npar= 183

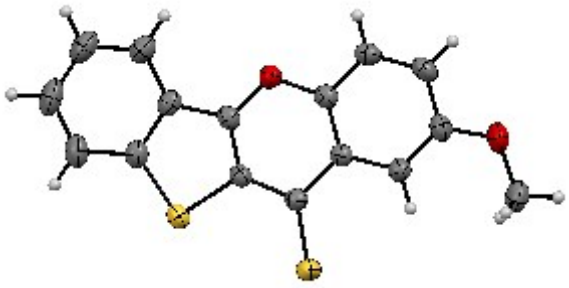


Figure S3. Single-crystal X-ray structure of compound **3c** (CCDC No. 2043956) Ellipsoids represent 50% probability level.