Supporting information for

Cu-Catalyzed One-pot Synthesis of Thiochromeno-quinolinone and Thiochromeno-thioflavone via Oxidative Double Hetero Michael Addi-tion using in-situ Generated Nucleophiles

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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 thiochromeno-quinolinone from 2-iodobenzaldehyde

An oven dried reaction tube was loaded with 2-iodobenzaldehyde (0.5 mmol), 2-nitro chalcone (0.5 mmol), potassium ethyl xanthate (1.5 mmol), NaOAc (1.0 mmol) and $Cu(OAc)_2$ (0.05 mmol) then DMSO (2 mL) was added. The reaction tube was closed with glass-stopper and stirred at 100 ºC in a pre-heated oil bath for recommended time. After complete formation of (2-aminophenyl)(2-phenyl-2H-thiochromen-3-yl)methanone, 2 equivalents of KOH was added to the reaction mixture with in the same pot and further heated at 100 ^{o}C. After the complete conversion of 2-amino thiochromene to thiochromeno-quinolinone, 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 thiochromeno-quinolinone.

2.2. General procedure for synthesis of thiochromeno-thioflavone from 2-iodobenzaldehyde

An oven dried reaction tube was loaded with 2-iodobenzaldehyde (0.5 mmol), 2-bromo chalcone (0.5 mmol), potassium ethyl xanthate (1.5 mmol), NaOAc (1.0 mmol) and $Cu(OAc)_2$ (0.05 mmol) then DMSO (2 mL) was added. The reaction tube was closed with glass-stopper and stirred at 100 ºC for recommended time in a pre-heated oil bath. After complete formation of 2-bromophenyl)(2-phenyl-2H-thiochromen-3-yl)methanone, the reaction temperature was increased to 130 ^oC without changing any other parameters. After the complete conversion of 2-amino thiochromene to thiochromeno-thioflavone, 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 thiochromeno-quinolinone.

2.3. General procedure for synthesis of thiochromeno-quinolinone from 2-bromobenzaldehyde

An oven dried reaction tube was loaded with 2-bromobenzaldehyde (0.5 mmol), 2-nitro chalcone (0.5 mmol), potassium ethyl xanthate (1.5 mmol), NaOAc (1.0 mmol) and $Cu(OAc)_2$ (0.05 mmol), then DMSO (2 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 complete formation of (2-aminophenyl)(2-phenyl-2H-thiochromen-3-yl)methanone, 2 equivalents of KOH was added to the reaction mixture with in the same pot and further heated at 120 ^oC. After the complete conversion of 2-amino thiochromene to thiochromeno-quinolinone, 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 thiochromeno-quinolinone.

2.4. General procedure for synthesis of thiochromeno-thioflavone from 2-bromobenzaldehyde

An oven dried reaction tube was loaded with 2-bromobenzaldehyde (0.5 mmol), 2-bromo chalcone (0.5 mmol), potassium ethyl xanthate (1.5 mmol), NaOAc (1.0 mmol) and $Cu(OAc)_2$ (0.05 mmol) then DMSO (2 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 complete formation of 2-bromophenyl)(2-phenyl-2H-thiochromen-3-yl)methanone, the reaction temperature was increased to 130 ^oC without changing any other parameters. The reaction was allowed until the completion of starting material. After that 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 thiochromeno-thioflavone **7**.

General procedure for synthesis of gram scale synthesis of thiochromeno-quinolinone 4a:

Under open atmosphere, 2-iodobenzaldehyde **1a** (928 mg, 4 mmol), 2-nitrochalcone **2a** (1.01 g, 4 mmol), potassium ethyl xanthate (1.92 g, 12 mmol), $Cu(OAc)_2$ (72 mg, 0.4 mmol) and NaOAc (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 100 ºC pre-heated oil bath. After complete formation of *o*-amino thiochromene **3a**, 2 equivalents of KOH was added to the reaction mixture and further heated at 100 ^oC. The reaction was allowed till the completion of intermediate **3a**. 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 thiochromeno-quinolinone **4a** in 85% (1.16 g).

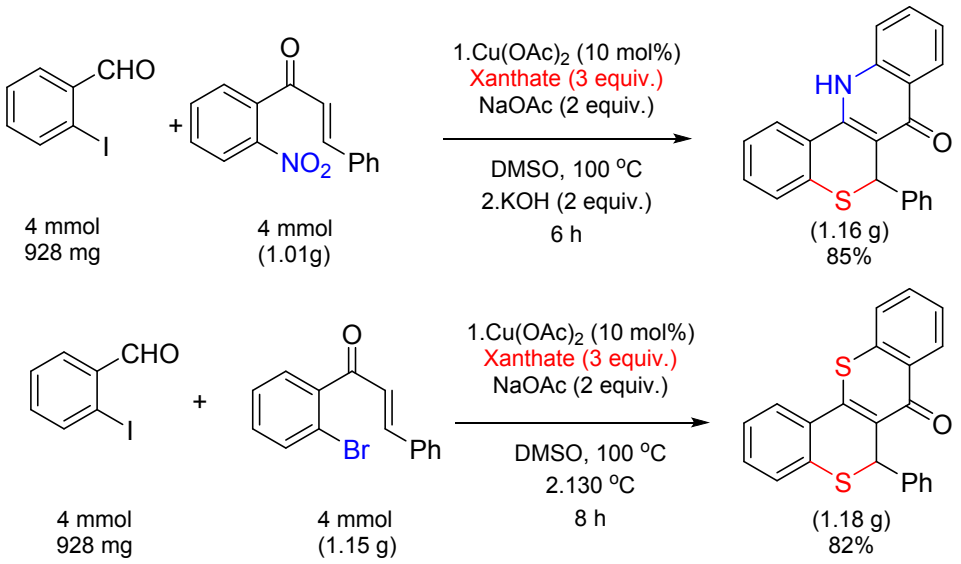
General procedure for synthesis gram scale synthesis of thiochromeno-thioflavone 7a:

Under an open atmosphere, 2-iodobenzaldehyde **1a** (928 mg, 4 mmol), 2-bromochalcone **2a** (1.01 g, 4 mmol), potassium ethyl xanthate (1.92 g, 12 mmol), $Cu(OAc)_2$ (72 mg, 0.4 mmol) and NaOAc (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 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 (3×30 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 thiochromeno-quinolinone **4a** in 82% (1.16 g).

3. Gram Synthesis of thiochromeno-quinolone and thiochromeno-thioflavone:

In order to showcase the efficacy of the one-pot synthesis of thiochromeno-quinolone and thiochromeno-thioflavone on gram scale, the reaction was performed in 4 mmol (928 mg) scale under standard optimized condition without altering any reaction parameters. The reaction proceeded smoothly and provided the corresponding thiochromeno-quinolone **4a** and thiochromeno-thioflavone **7a** in 85% (1.16 g) and 82% (1.18 g) yield respectively (Scheme S1).

Scheme S1: Gram scale synthesis of 4a and 7a

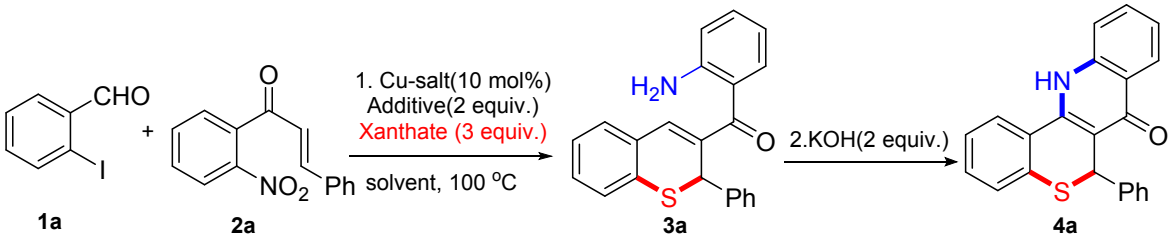


4.0. Optimization for the reaction condition of 4a:

Our initial efforts commenced with 2-iodobenzaldehyde **1a** and 2-nitrochalcone **2a** as the model substrate, using xanthate as the sulfur surrogate and $Cu(OAc)_2$ as the catalyst. The starting material 2-nitrochalcone was easily synthetic accessible by simple aldol condensation reaction, enabling structurally diverse substrate availability. The reaction was allowed to stir at 100 °C for 24 h in DMF. The desired product thiochromeno-quinolone **4a** was detected in 21% along with isolable intermediate **3a** (Table S1, entry 1). To our delight, the yield was increased to 58% when 2 equiv. of KOH was added to the reaction mixture after the formation of isolable intermediate **3a** in the same pot (entry 2). Catalytic amount of copper salt was essential for the C-S bond formation followed by double hetero Michael addition reaction. Therefore, we have started to screen the different metal salts such as CuI, CuCl, $CuBr_2$ and $CuCl_2$ (entries 3-6). Among them, $Cu(OAc)_2$ was proved to be the better catalyst for this tetracyclic thiochromeno-quinolone formation. Keeping the $Cu(OAc)_2$ as constant then we started to screen different additives. The use of inorganic bases such as KOH, Cs_2CO_3 and K_2CO_3 (entries 7-9) were ineffective. However, while screening the NaOAc as additive (entry 10), the desired product **4a** was obtained in 78% yield after 3 h. A change of organic bases such as DIPEA, Et_3N and pyridine (entry 11-13) did not provide impressive yield. However, exchanging the DMF by DMSO, the reaction successfully yielded 86%of the desired product **4a** within 3 h (entry 14). Replacement of DMSO with other solvents did not give impressive yield (entry 15-17). Whereas increasing or reducing the reaction temperature leads to the drop in the yield (entry 18). However without copper catalyst the reaction did not proceed for the product formation (entry 19). Similarly, without NaOAc in the presence of catalytic amount of $Cu(OAc)_2$ also the yield was significantly reduced (entry 20). At the optimized reaction conditions, **1a** (1 equiv.) reacted with **2a** (1 equiv.) along with 3 equiv. of

xanthate in the presence of 10 mol% $Cu(OAc)_2$ and NaOAc (2 equiv.) in DMSO at 100 °C yielded 86 % of the tetracyclic thiochromeno-quinolone **4a**.

Table S1: Optimization of reaction condition for 4a



Entry	Cu salt	Additive	Solvent	Time (h)	Yield (%)
1	$Cu(OAc)_2$	AgOAc	DMF	24	21[a]
2	$Cu(OAc)_2$	AgOAc	DMF	5	58
3	CuI	AgOAc	DMF	5	47
4	CuCl	AgOAc	DMF	5	38
5	$CuBr_2$	AgOAc	DMF	7	45
6	$CuCl_2$	AgOAc	DMF	8	32
7	$Cu(OAc)_2$	KOH	DMF	24	26[b]
8	$Cu(OAc)_2$	K_2CO_3	DMF	24	nd[b]
9	$Cu(OAc)_2$	Cs_2CO_3	DMF	24	nd[b]
10	$Cu(OAc)_2$	NaOAc	DMF	3	78
11	$Cu(OAc)_2$	DIPEA	DMF	22	22[c]
12	$Cu(OAc)_2$	Et_3N	DMF	18	26
13	$Cu(OAc)_2$	Pyridine	DMF	24	12
14	$Cu(OAc)_2$	NaOAc	DMSO	3	86
15	$Cu(OAc)_2$	NaOAc	PhMe	3	nd[b]
16	$Cu(OAc)_2$	NaOAc	1,4-dioxane	3	nd[b]
17	$Cu(OAc)_2$	NaOAc	CH_3CN	3	nd[b]
18	$Cu(OAc)_2$	NaOAc	DMSO	3	76[d]
19	-	NaOAc	DMSO	3	trace
20	$Cu(OAc)_2$	-	DMSO	3	37

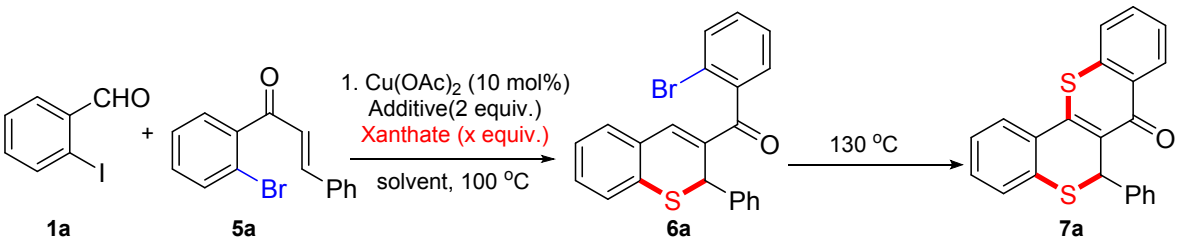
Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), xanthate (3 equiv), $Cu(OAc)_2$ (10 mol%), additive (2 equiv) and solvent at 100 °C then KOH (2 equiv.). [a]Without KOH as base. [b]Starting materials remained. [c]The reaction yielded an inseparable complex mixture but product was isolable. [d] Reaction was carried at 90 °C

4.1. Optimization for the reaction condition of 7a:

Furthermore, we anticipated to extend this methodology for the synthesis of thiochromeno-thioflavone via intermolecular followed by intramolecular double sulfa-Michael addition using in-situ generated thiolate anions. To achieve our hypothesis, the initial reaction was performed with 2-iodobenzaldehyde **1a** (1 equiv.) and 2′-bromochalcone **5a** (1 equiv.) with 3 equiv. of xanthate as sulfur surrogate in the presence of 10 mol% $Cu(OAc)_2$ and NaOAc (2 equiv.) in DMSO at 100 °C. The reaction was even allowed for a longer reaction time of 24 h. However, the desired product formation was not observed. Instead, the 2′-bromo substituted thiochromene **6a** was isolated in 92% yield (Table S2, entry 1). Since the second step of the

one-pot reaction contains the C-S bond formation using less reactive bromo substituent, we felt increasing the reaction temperature will leads to the expected product formation. Therefore, the next reaction was carried out in one-pot manner. The first step was carried out at 100 °C. After the formation of intermediate **6a**, the temperature of the reaction mixture was increased to 130 °C (entry 2). To our delight, the thiochromene fused thioflavone **7a** was isolated in 82% yield after 7 h. Having this initial result, we started screening other parameters such as ratio of the xanthate, solvent and reaction temperature (entries 3-9). Nevertheless, the initial result stands out to be the best reaction condition. Also, the reaction was performed in domino manner at 130 °C, however the yield was drastically reduced (entry 10). This proves that the one-pot path way favours the tetracyclic ring formation over the domino reaction.

Table S2: Optimization of reaction condition for 7a



1a **5a** **6a** **7a**

Entry	Additives	Xanthate	Solvent	Yield (%)
1	NaOAc	3.0	DMSO	0[c]
2	NaOAc	3.0	DMSO	82
3	-	3.0	DMSO	18
4	NaOAc	2	DMSO	62
5	NaOAc	2.5	DMSO	69
6	NaOAc	3.5	DMSO	78
7	NaOAc	3.0	DMF	35
8	NaOAc	3.0	H_2O	0
9	NaOAc	3.0	DMSO	82[d]
10	NaOAc	3.0	DMSO	21[e]

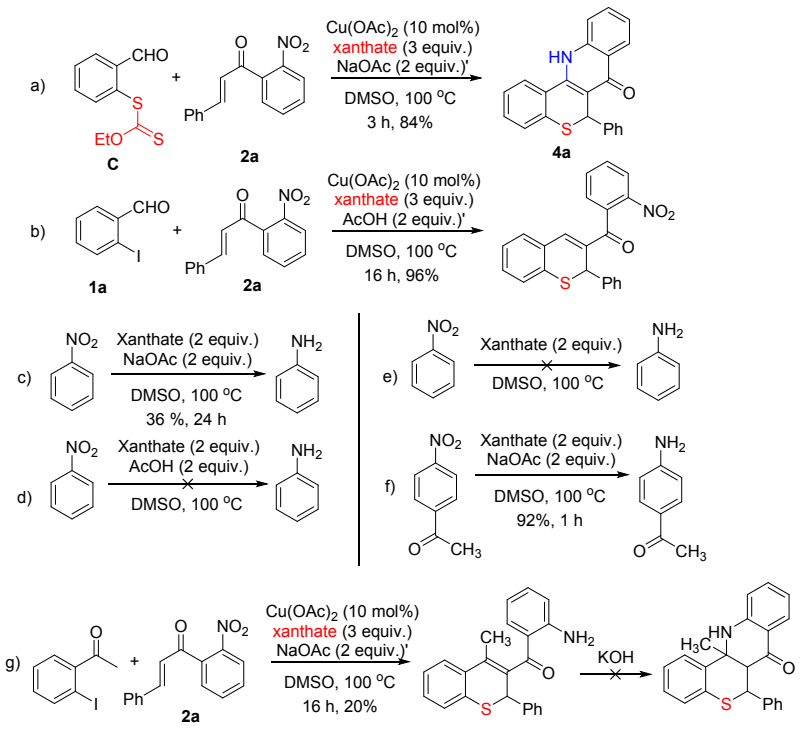
[a]**1a** (0.5 mmol), **5a** (0.5 mmol), xanthate (x equiv.), $Cu(OAc)_2$ (10 mol%), additive (2 equiv.) and solvent (2 mL) at 100 °C then reaction temperature was increased to 130 °C.[b]isolated yield. [c]The complte reaction allowed at 100 °C. [d]After the formation of intermediate **6a**, temperature was increased to 140 °C. [e]Reaction was carried out domino in 130 °C.

5.Control experiments

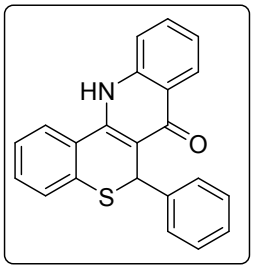
Apart from the main control experiments, we have carried few more reactions to get the insight into the reaction mechanism. The initial reaction was kept with expected intermediate **C** under the optimized reaction condition, and the reaction proceeded effortlessly to the

product formation (Scheme S2a). The reduction of the aromatic nitro compound to corresponding amine was achieved by the combination of xanthate and additive was confirmed by primary control experiments. However, to understand the role of additive, few more reactions were carried out. The acetic acid may be generated by abstraction of proton by counter anion OAc ion, which can act as a proton source for the reduction of nitro group via proton coupled electron transfer (PCET) mechanism. Therefore, the subsequent reaction was carried out with AcOH as additive under the optimized reaction condition. However, the product formation was completely extinct, and only the corresponding *o*-nitro substituted thiochromene was observed in 96% (Scheme S2b). The next reaction was carried out with simple nitro aniline in the presence of 2 equiv. of xanthates and NaOAc (2 equiv.) in DMSO at 100 ^{o}C. The yield was reduced drastically regardless the longer reaction time (Scheme S2c). No product formation was observed, when we replaced NaOAc using AcOH or without additive (Scheme S2d-S2e). However, when we used electron withdrawing group substituted nitrobenzene, the reaction was completed in a shorter reaction time with high chemoselectivity (Scheme S2f). Also, we have carried out the reaction by replacing 2-iodobenzaldehyde by 2-iodoacetophenone under the optimized reaction condition (Scheme S2g). The desired tetracyclic moiety was not observed, only the corresponding thiochromene intermediate was isolated in 20% yield.

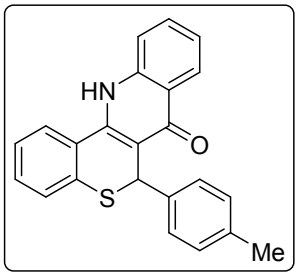
Scheme S2: Control experiments



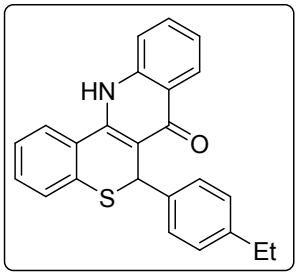
6.0. Experimental spectral data for 4:



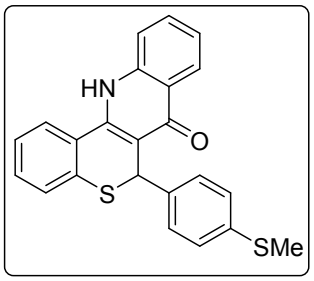
6-Phenyl-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4a): 147 mg; 86% yield; yellow solid; mp 196-198 ^{o}C; R_f 0.70 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 5.84 (s, 1H), 7.03-7.20 (m, 5H), 7.35-7.50 (m, 4H), 7.69-7.78 (m, 1H), 7.87-8.00 (m, 1H), 8.08-8.23 (m, 2H), 11.70 (s, 1H); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 37.7, 115.5, 118.9, 123.4, 123.8, 125.1, 126.2, 126.4, 126.9, 127.0, 128.1, 128.2, 129.1, 131.0, 132.2, 133.9, 139.9, 141.7, 142.7, 173.9; FTIR (ATR) 2923, 2852, 1661, 1632, 1262, 1034, 998, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{15}NOSNa$ $[M+Na]^{+}$: 364.0772; found: 364.0781.



6-(*p*-Tolyl)-6,12-Dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4b): 151 mg; 85% yield; yellow solid; mp 201-203 ^{o}C; R_f 0.74 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 2.16 (s, 3H), 5.80 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.30-7.40 (m, 1H), 7.41-7.46 (m, 3H), 7.72-7.78 (m, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.13-8.19 (m, 2H), 11.70(s, 1H) ; ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 20.5, 37.4, 115.6, 118.9, 123.3, 123.8, 125.1, 126.1, 126.3, 126.9, 128.1, 128.6, 129.1, 130.9, 132.1, 134.0, 136.1, 138.6, 139.9, 142.6, 173.8; FTIR (ATR) 2923, 2854, 1658, 1631, 1265, 1022, 998, 755 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{18}NOS$ $[M+H]^{+}$: 356.1109; found: 356.1102.

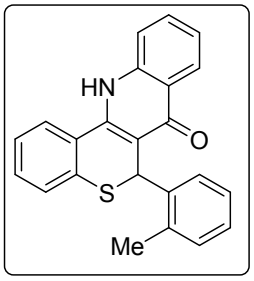


6-(4-Ethylphenyl)-6,12-Dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4c): 153 mg; 83% yield; yellow solid; mp 205-205 ^{o}C; R_f 0.58 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 1.04 (t, *J* = 7.2 Hz, 3H), 2.43 (q, *J* = 7.6 Hz, 2H), 5.80(s, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.41-7.43 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.10 - 8.70 (m, 2H), 11.70 (s, 1H); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 15.5, 27.6, 37.4, 115.6, 118.9, 123.3, 123.8, 125.1, 126.1, 126.3, 127.0, 127.5, 128.1, 129.2, 131.0, 132.1, 134.0, 139.0, 139.9, 142.4, 142.6, 173.9; FTIR (ATR) 2923, 1619, 1511, 1353, 1022, 1002 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{24}H_{20}NOS$ $[M+H]^{+}$: 370.1265; found: 370.1258.

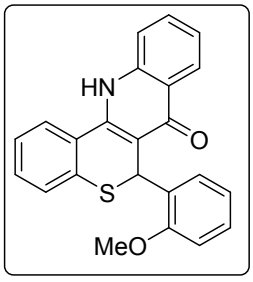


6-(4-(Methylthio)Phenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4d): 140 mg; 72% yield; yellow solid; mp 198-201 ^{o}C; R_f 0.5 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 500 MHz) δ δ 2.35 (s, 3H), 5.81 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 8.0 Hz , 1H), 7.42-7.46 (m, 3H), 7.74 (dt, *J* = 1.0,7.0 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 8.14 - 8.19 (m, 2H), 11.73(s,

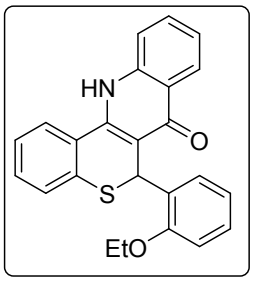
1H) ; ^{13}C NMR (DMSO-d^6, 125 MHz) δ 14.6, 37.3, 115.5, 118.9, 123.4, 123.8, 125.1, 125.6, 126.2, 126.4, 127.6, 128.1, 129.2, 131.2, 132.2, 133.9, 136.7, 138.3, 139.9, 142.7, 173.9; FTIR (ATR) 2985, 2938, 1727, 1253, 1033, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{17}NOS_2Na$ $[M+Na]^+$: 410.0649; found: 410.0645.



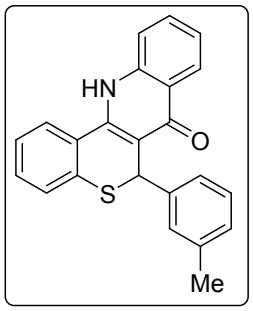
6-(*o*-Tolyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4e): 143 mg; 81% yield; yellow solid; mp 208-211 °C; R_f 0.58 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.12 (s, 3H), 5.78 (s, 1H), 6.85-6.92 (m, 2H), 6.95-7.00 (m, 1H), 7.00-7.05 (m, 1H), 7.35-7.45 (m, 4H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.10-8.20 (m, 2H), 11.71(s, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 21.0, 37.6, 115.4, 118.9, 123.3, 123.8, 124.0, 125.1, 126.1, 126.3, 127.6, 127.8, 127.9, 128.2, 129.1, 131.0, 132.1, 134.0, 137.1, 139.9, 141.7, 142.7, 173.9; FTIR (ATR) 3054, 1623, 1554, 1492, 1025, 998 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{18}NOS$ $[M+H]^+$: 356.1109; found: 356.1107.



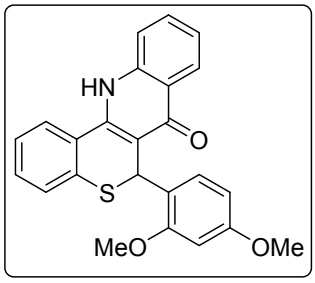
6-(2-Methoxyphenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4f): 145 mg; 78% yield; yellow solid; mp 221-223 °C; R_f 0.41 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 3.93 (s, 3H), 6.01 (s, 1H), 6.50-6.55 (m, 2H), 6.95-7.05 (m, 1H), 7.08-7.15 (m, 1H), 7.30-7.45 (m, 4H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, , 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 11.71(s, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 31.6, 55.6, 111.0, 114.0, 118.9, 119.5, 123.2, 123.7, 125.0, 126.0, 126.4, 126.5, 128.0, 128.3, 128.7, 129.2, 130.8, 132.0, 134.3, 140.0, 143.5, 155.9, 173.7; FTIR (ATR) 2923, 2854, 1627, 1496, 1249, 1025, 998, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{18}NO_2S$ $[M+Na]^+$: 372.1058; found: 372.1050.



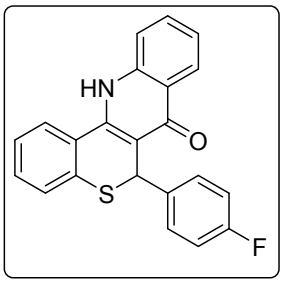
6-(2-Ethoxyphenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4g): 141 mg; 73% yield; yellow solid; mp 218-220 °C; R_f 0.45 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 500 MHz) δ 1.49 (t, *J* = 6.8 Hz, 3H), 4.15-4.25 (m, 2H), 6.02 (s, 1H), 6.50-6.55 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 7.30-7.45 (m, 5H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 11.75 (s, 1H); ^{13}C NMR (DMSO-d^6, 125 MHz) δ 14.9, 31.8, 63.6, 111.9, 114.0, 118.9, 119.4, 123.3 123.8, 125.0, 125.9, 126.4, 126.5, 128.0, 128.3, 128.9, 129.2, 130.9, 132.1, 134.5, 140.0, 143.6, 155.3, 173.9; FTIR (ATR) 2923, 2857, 1623, 1508, 1241, 1025, 998, 748 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{24}H_{20}NO_2S$ $[M+H]^+$: 386.1214; found: 386.1208.



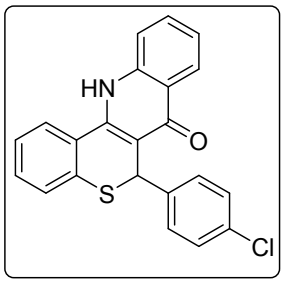
6-(*m*-Tolyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4h): 140 mg; 79% yield; yellow solid; mp 204-206 ^{o}C; R_f 0.58 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 2.56 (s, 3H), 5.87 (s, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.32-7.40 (m, 3H), 7.45 (t, *J* = 7.2 Hz, , 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.22(d, *J* = 7.6 Hz, 1H), 11.8 (s, 1H); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 19.4, 34.7, 115.2, 118.9, 123.4, 123.7, 125.0, 125.6, 125.9, 126.3, 126.5, 127.1, 128.4, 129.4, 130.7, 131.1, 132.2, 133.4, 135.2, 139.0, 139.9, 143.4, 178.8; FTIR (ATR) 3058, 1708, 1623, 1488, 1025, 1002, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{18}NOS$ $[M+H]^{+}$: 356.1109; found: 356.1100.



6-(2,4-Dimethoxyphenyl)-6,12-Dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4i): 136 mg; 68% yield; yellow solid; mp 177-179 ^{o}C; R_f 0.32 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 3.62 (s, 3H), 3.91 (s, 3H), 5.93 (s, 1H), 6.08 (d, *J* = 8.4, 1H), 6.40 (d, *J* = 8.4, 1H), 6.55 (d, *J* = 1.2, 1H), 7.30-7.47 (m, 4H), 7.72 (t, *J* = 7.6, 1H), 7.93 (d, *J* = 8.4, 1H), 8.08 (d, *J* = 8.0, 1H), 8.19 (d, *J* = 7.6, 1H), 11.73 (s, 1H); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 31.7, 55.2, 55.8, 98.8, 103.5, 114.4, 119.0, 121.1, 123.3, 123.8, 125.1, 126.0, 126.5, 127.3, 128.2, 129.4, 130.1, 132.2, 134.6, 140.0, 143.5, 157.0, 159.9, 173.8; FTIR (ATR) 2923, 2850, 1735, 1619, 1265, 1025, 995, 755 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{24}H_{20}NO_3S$ $[M+H]^{+}$: 402.1163; found: 402.1159.

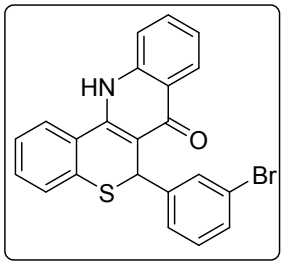


6-(4-Fluorophenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4j): 146 mg; 81% yield; yellow solid; mp 196-198 ^{o}C; R_f 0.54 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 500 MHz) δ 5.86 (s, 1H), 6.94 (t, *J* = 8.5 Hz, 2H), 7.16-7.21 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.40-7.45 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 8.13-8.19 (m, 2H), 11.74 (s, 1H); ^{13}C NMR (DMSO-d^{6}, 125 MHz) δ 37.0, 114.8 (d, *J* = 21.2 Hz), 115.5, 118.9, 123.4, 123.8, 125.1, 126.2, 126.4, 128.0, 128.9 (d, *J* = 8.1 Hz), 129.2, 131.0, 132.2, 133.8, 137.9 (d, *J* = 2.8 Hz), 139.9, 142.7, 161.1 (d, *J* = 247.6 Hz), 173.9; FTIR (ATR) 2923, 2857, 1731, 1623, 1238, 1022, 998, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{15}FNOS$ $[M+H]^{+}$: 360.0858; found: 360.0853.

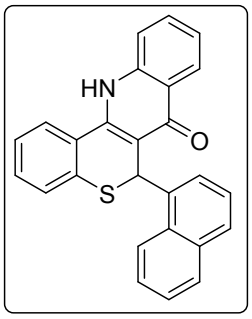


6-(4-Chlorophenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4k): 159 mg; 84% yield; yellow solid; mp 212-214 ^{o}C; R_f 0.58 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^{6}, 500 MHz) δ 5.85 (s, 1H), 7.15-7.20 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.41-7.46 (m, 3H), 7.70-7.75 (m, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 8.12-8.17 (m, 2H), 11.74(s, 1H); ^{13}C

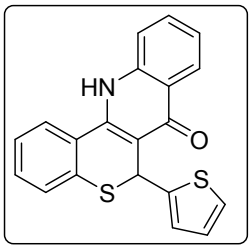
NMR (DMSO-d^6, 125 MHz) δ 37.0, 115.2, 118.9, 123.4, 123.8, 125.0, 126.3, 126.4, 127.7, 128.0, 128.8, 129.1, 131.1, 131.5, 132.2, 133.6, 139.9, 140.7, 142.7, 173.9; FTIR (ATR) 2923, 1627, 1496, 1403, 1361, 1091, 1018, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{15}ClNOS$ $[M+H]^+$: 376.0562; found: 376.0557.



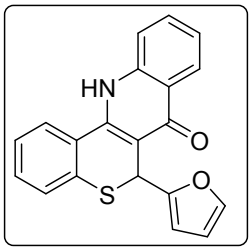
6-(3-Bromophenyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4l): 161 mg; 76% yield; yellow solid; mp 188-190 °C; R_f 0.61 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 5.87 (s, 1H), 7.05-7.13 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.38-7.48 (m, 5H), 7.70-7.77 (m, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.10-8.20 (m, 2H), 11.74(s, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 37.1, 115.0, 119.0, 121.3, 123.4, 123.8, 125.0, 125.8, 126.3, 126.4, 127.9, 129.1, 129.7, 129.8, 130.2, 131.1, 132.2, 133.5, 139.9, 142.7, 144.6, 173.8; FTIR (ATR) 2981, 2923, 1731, 1253, 1022, 740 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{15}BrNOS$ $[M+H]^+$: 420.0057; found: 420.0048.



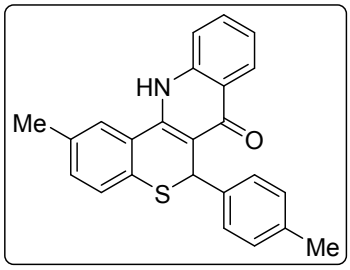
6-(Naphthalen-1-yl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4m): 162 mg; 83% yield; yellow solid; mp 225-227 °C; R_f 0.65 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 500 MHz) δ 6.60 (s, 1H), 6.80 (d, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.30-7.38 (m, 2H), 7.41-7.46 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.66-7.71 (m, 2H), 7.72-7.76 (m, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.52 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 34.3, 114.8, 118.9, 123.4, 123.8, 123.9, 124.2, 124.8, 125.0, 125.8, 126.2, 126.3, 126.6, 127.8, 128.0, 128.8, 129.4, 129.9, 130.9, 132.2, 133.8, 134.2, 135.8, 140.0, 143.7, 173.9; FTIR (ATR) 3054, 2923, 1619, 1585, 1511, 1238, 1022, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{26}H_{18}NOS$ $[M+H]^+$: 392.1109; found: 392.1101.



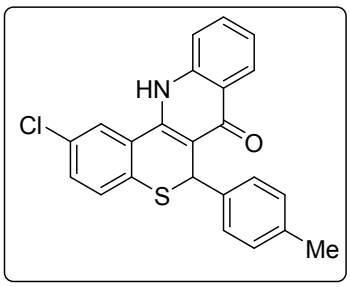
6-(Thiophen-2-yl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4n): 149 mg; 85% yield; yellow solid; mp 168-170 °C; R_f 0.51 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 6.07 (s, 1H), 6.72 (s, 2H), 7.16 (d, *J* = 4.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.44-7.48 (m, 2H), 7.50-7.53 (m, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.12-8.18 (m, 2H), 11.72 (s, 1H) ; ^{13}C NMR (DMSO-d^6, 100 MHz) δ 34.0, 116.7, 119.0, 123.5, 123.9, 124.8, 125.2, 125.3, 126.4, 126.5, 127.7, 129.4, 131.2, 132.3, 133.9, 139.9, 142.1, 145.9, 173.5; FTIR (ATR) 2923, 2854, 1731, 1619, 1261, 1025, 998, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{20}H_{14}NOS_2$ $[M+H]^+$: 348.0516; found: 348.0510.



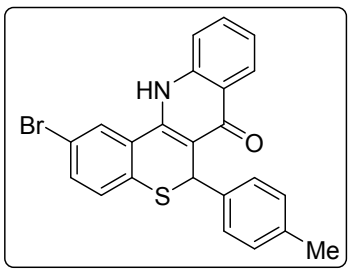
6-(Furan-2-yl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4o): 129 mg; 78% yield; yellow solid; mp 178-180 °C; R_f 0.58 (50% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.71 (d, *J* = 3.0, 1H), 5.83 (s, 1H), 6.12 (s, 1H), 7.36 (t, *J* = 7.5, 1H), 7.42-7.48 (m, 4H), 7.70-7.75 (m, 1H), 7.91 (d, *J* = 8.4, 1H), 8.12-8.18 (m, 2H), 11.71 (s, 1H); ^{13}C NMR (DMSO-d^6, 125 MHz) δ 32.3, 107.6, 110.4, 113.7, 119.0, 123.4, 123.9, 125.1, 126.2, 126.5, 127.9, 129.2, 131.0, 132.2, 133.7, 139.9, 142.6, 142.7, 152.9, 173.5; FTIR (ATR) 2923, 2854, 1735, 1631, 1245, 1025, 995, 755 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{20}H_{14}NO_2S$ $[M+H]^+$: 332.0745; found: 332.0737.



2-Methyl-6-(p-tolyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4p): 150 mg; 81% yield; yellow solid; mp 187-189 °C; R_f 0.72 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.14 (s, 3H), 2.41 (s, 3H), 5.76 (s, 1H), 6.91 (d, *J* =7.6 Hz, 2H), 7.02 (d, *J* =7.6 Hz, 2H), 7.20-7.27 (m, 1H), 7.30-7.40 (m, 2H), 7.70-7.76 (m, 1H), 7.92 (d, *J* =8.0 Hz, 1H), 7.97 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 11.64 (s, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 20.4, 20.8, 37.4, 115.7, 118.8, 123.2, 123.8, 125.0, 126.6, 126.9, 128.5, 128.9, 130.5, 131.7, 132.0, 135.4, 135.9, 138.6, 139.8, 142.6, 173.8; FTIR (ATR) 2923, 2853, 1733, 1610, 1261, 1034, 750 cm^{-1}; HRMS (m/z) calculated for $C_{24}H_{20}NOS$ [M+H]+ : 370.1265; found: 370.1259.



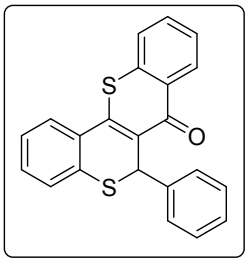
2-Chloro-6-(p-tolyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4q): 134 mg; 69% yield; yellow solid; mp 188-190 °C; R_f 0.60 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 500 MHz) δ 2.16 (s, 3H), 5.85 (s, 1H), 6.95 (d, *J* =8.0 Hz, 2H), 7.04 (d, *J* =8.0 Hz, 2H), 7.36-7.41 (m, 1H), 7.44-7.50 (m, 2H), 7.73-7.78 (m, 1H), 7.92 (d, *J* =8.0 Hz, 1H), 8.15 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 8.26 (s, 1H), 11.74 (s, 1H); ^{13}C NMR (DMSO-d^6, 125 MHz) δ 20.5, 37.5, 115.8, 118.9, 123.4, 123.8, 125.1, 126.0, 126.9, 128.6, 129.7, 130.4, 130.5, 130.7, 132.2, 133.0, 136.2, 138.2, 139.9, 141.6, 173.8; FTIR (ATR) 2923, 2854, 1735, 1619, 1265, 1037, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{17}ClNOS$ $[M+H]^+$: 390.0719; found: 390.0710.



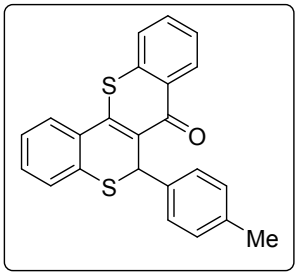
2-Bromo-6-(p-tolyl)-6,12-dihydro-7H-thiochromeno[4,3-b]quinolin-7-one (4r): 160 mg; 73% yield; yellow solid; mp 198-200 °C; R_f 0.65 (50% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.15 (s, 3H), 5.82 (s, 1H), 6.93 (d, *J* =8.0 Hz, 2H), 7.02 (d, *J* =8.0 Hz, 2H), 7.35-7.40 (m, 2H), 7.57 (d, *J* = 8.0, 1H), 7.71-7.76 (m, 1H), 7.89 (d, *J* =8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 11.71 (s, 1H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 20.4, 37.4, 115.8, 118.6, 118.9, 123.4, 123.8, 125.0, 126.9, 128.6,

128.7, 130.0, 130.9, 132.2, 133.3, 133.5, 136.2, 138.2, 139.9, 141.5, 173.8; FTIR (ATR) 2927, 2852, 1731, 1617, 1265, 1033, 752 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{16}BrNOSNa$ $[M+Na]^+$: 456.0033; found: 456.0030.

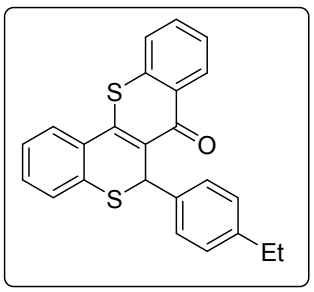
6.1. Experimental spectral data for 7



6-Phenyl-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7a): 148 mg; 82% yield; brownish yellow solid; mp 168-170 ^oC; R_f 0.5 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.09 (s, 1H), 7.08-7.14 (m, 3H), 7.18-7.23 (m, 2H), 7.23-7.28 (m, 1H), 7.31 (td, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.53 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.64 (td, *J* = 7.0 Hz, 1.2 Hz, 1H), 7.67 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.88 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.0, 126.37, 126.42, 126.7, 127.3, 127.4, 127.8, 128.4, 129.26, 129.33, 129.6, 130.2, 131.3, 131.4, 131.8, 133.8, 136.4, 140.5, 145.1, 178.2; FTIR (KBr) 3064, 1676, 1617, 1434, 732 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{14}ONaS_2$ $[M+Na]^+$: 381.0384; found: 381.0371.

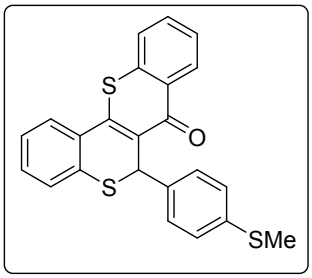


6-(*p*-Tolyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7b): 157 mg; 81% yield; brownish yellow solid; mp 184-186 ^oC; R_f 0.41 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.18 (s, 3H), 6.05 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.24 (td, *J* = 6.8 Hz, 1.6 Hz, 1H), 7.29 (td, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.50 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.61 (td, *J* = 7.0 Hz, 1.6 Hz, 1H), 7.64 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.86 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 8.53 (dd, *J* = 8.2 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 38.8, 126.3, 126.4, 126.6, 127.1, 127.7, 129.1, 129.3, 129.4, 129.6, 130.2, 131.2, 131.4, 131.8, 133.8, 136.3, 137.1, 137.6, 144.9, 178.2; FTIR (KBr) 3058, 2913, 1610, 1510, 1436, 757 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{17}OS_2$ $[M+H]^+$: 373.0720; found: 373.0719.

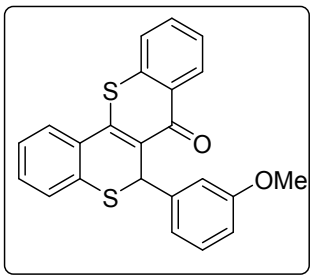


6-(*p*-Tolyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7c): 153 mg; 79% yield; yellow semi liquid; R_f 0.80 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.10 (t, *J* = 7.6 Hz, 3H), 2.48 (q, *J* = 7.6 Hz, 2H), 6.05 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.20-7.31 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.55-7.65 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3, 28.4, 38.7 ,126.2, 126.3, 126.6, 127.1, 127.6, 127.9, 129.3, 129.4, 129.5, 130.1, 131.1, 131.3, 131.7, 133.8, 136.3, 137.8, 143.4, 144.8, 178.2; FTIR (KBr) 3058,

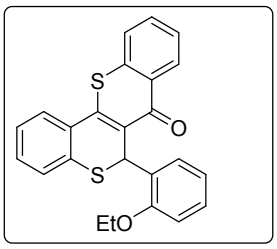
2962, 2923, 1708, 1585, 1527, 1338, 740 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{24}H_{19}OS_2$ $[M+H]^+$: 387.0877; found: 387.0862.



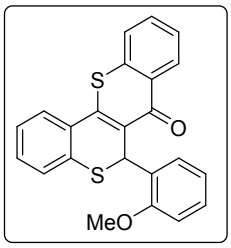
6-[4-(Methylthio)phenyl]-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7d): 153 mg; 76% yield; brownish yellow solid; mp 177-179 ^oC; R_f 0.3 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 6.06 (s, 1H), 7.08-7.16 (m, 4H), 7.20 (dd, *J* = 7.2 Hz, 1.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.53 (td, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.63 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 8.55 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 39.0, 126.4, 127.2, 127.3, 127.4, 127.7, 128.4, 129.2, 129.3, 129.6, 130.2, 130.3, 131.3, 131.8, 132.3, 136.3, 136.4, 140.6, 145.2, 178.3; FTIR (KBr) 2919, 2855, 1651, 1612, 1589, 1499, 739 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{16}ONaS_3$ $[M+Na]^+$: 427.0255; found: 427.0236.



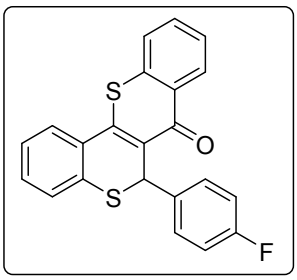
6-(3-Methoxyphenyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7e): 132 mg; 68% yield; brownish yellow viscous liquid; Rf 0.30 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.61 (s, 3H), 6.06 (s, 1H), 6.63 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.75-6.82 (m, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.20-7.25 (m, 1H), 7.28 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.39 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.49 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.55 -7.65(m, 2H), 7.84 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 8.52 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.9, 55.1, 112.8, 113.1, 119.7, 126.4, 126.6, 127.7, 129.1, 129.2, 129.3, 129.5, 130.1, 131.2, 131.3, 131.8, 133.7, 136.3, 142.0, 145.1, 159.5, 178.1; FTIR (KBr) 3012, 2844, 1654, 1617, 1581, 755 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{17}O_2S_2$ $[M+H]^+$: 389.0669; found: 389.0664.



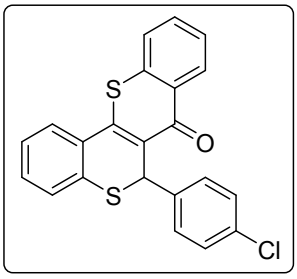
6-(2-Ethoxyphenyl)-6H,7H-Thiochromeno[4,3-b]thiochromen-7-one (7f): 123 mg; 61% yield; yellow viscous liquid; R_f 0.45 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.56 (t, *J* = 7.2 Hz, 3H), 4.19 (q, *J* = 6.8 Hz ,2H), 6.43 (s, 1H), 6.51 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.20-7.28 (m, 3H), 7.50 (t, J = 7.2 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 8.48 (d, J = 8.0 Hz,1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.1, 33.2, 64.1, 112.0, 119.7, 126.0, 126.3, 126.6, 127.0, 127.6, 128.0, 128.1, 128.6, 129.4, 129.5, 130.1, 131.3, 131.7, 134.6, 136.3, 145.9, 155.7, 178.1; FTIR (KBr) 3058, 2977, 2931, 1708, 1589, 1442, 1342, 1241, 740 cm^{-1}; HRMS (m/z) calculated for $C_{24}H_{19}O_2S_2$ $[M+H]^+$: 403.0826; found: 403.0816.



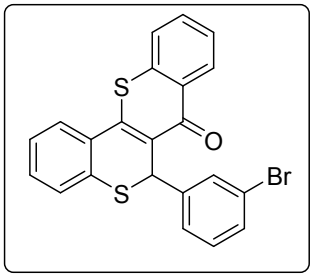
6-(2-Methoxyphenyl)-6H,7H-Thiochromeno[4,3-b]thiochromen-7-one (7g): 144 mg; 74% yield; yellow viscous liquid; R_f 0.46 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98 (s, 3H), 6.41 (s, 1H), 6.50-6.57 (m, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 8.0 Hz 1H), 7.21-7.30 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.88-8.00 (m, 1H), 8.48 (d, J = 8.0 Hz, 1H); ^{13}C NMR (CDCl3, 100 MHz) δ 33.0, 55.8, 111.0, 119.8, 126.1, 126.3, 126.6, 127.1, 127.6, 127.8, 128.1, 128.7, 129.4, 129.6, 130.0, 131.1, 131.2, 131.7, 134.3, 136.2, 145.9, 156.3, 178.0; FTIR (ATR) 3058, 2923, 1712, 1592, 1438, 1346, 1249, 744 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{17}O_2S_2$ $[M+H]^+$: 389.0669; found: 389.0673.



6-(4-Fluorophenyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7h): 147 mg; 78% yield; brownish yellow solid; mp 208-210 °C; R_f 0.70 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.97 (s, 1H), 6.69-6.75 (m, 2H), 7.06-7.12 (m, 2H), 7.17-7.27 (m, 2H) 7.32-7.36 (m, 1H), 7.43-7.49 (m, 1H), 7.53-7.61 (m, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.3, 115.2 (d, *J* = 21.4 Hz), 126.4 (d, *J* = 8.1 Hz), 126.7, 127.8, 128.8, 128.9, 129.0, 129.2, 129.3, 129.5, 130.1, 131.2, 131.3, 132.0, 133.4, 136.2, 145.1, 160.9, 178.1; FTIR (ATR) 3062, 2923, 1708, 1612, 1504, 1346, 748 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{14}FOS_2$ $[M+H]^+$: 377.0470; found: 377.0459.

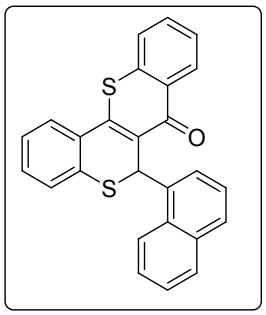


6-(4-Chlorophenyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7i): 158 mg; 80% yield; brownish yellow solid; mp 208-210 °C; R_f 0.45 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.29 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.35 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.56 (td, *J* = 8.2 Hz, 1.6 Hz, 1H), 7.66 (td, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.4, 126.5, 126.6, 126.7, 127.9, 128.5, 128.7, 129.1, 129.4, 129.6, 130.1, 131.3, 131.4, 132.0, 133.3, 133.4, 136.3, 139.0, 145.3, 178.2; FTIR (KBr) 3058, 1679, 1610, 1534, 1436, 822, 744 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{13}ONaS_2Cl$ $[M+Na]^+$: 414.9994; found: 414.9996.

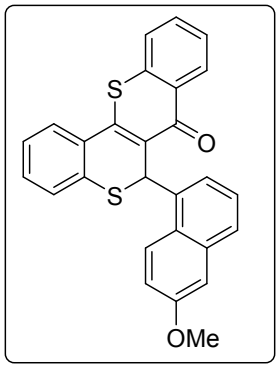


6-(3-Bromophenyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7j): 145 mg; 66% yield; brownish yellow viscous liquid; R_f 0.46 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.95 (s, 1H), 6.87 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.10-7.20 (m, 2H), 7.20-7.35 (m, 3H), 7.44 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.50-7.60 (m, 2H), 7.76 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 8.45 (dd, *J* = 8.0 Hz, 1.2

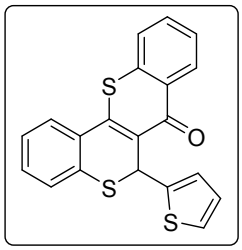
Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.5, 122.4, 125.9, 126.4, 126.6, 126.7, 127.8, 128.6, 129.3, 129.5, 129.8, 130.0, 130.4, 130.6, 131.2, 131.4, 132.0, 133.2, 136.3, 142.7, 145.5, 178.0; FTIR (ATR) 3058, 2923, 1712, 1589, 1434, 1346, 748 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{22}H_{14}BrOS_2$ $[M+H]^+$: 436.9669; found: 436.9658.



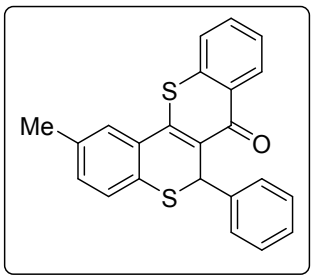
6-(Naphthalen-1-yl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7k): 151 mg; 73% yield; brownish yellow viscous liquid; R_f 0.46 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.80-6.91 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.18-7.31 (m, 3H), 7.48-7.55 (m, 2H), 7.60-7.70 (m, 3H), 7.70-7.75 (m, 1H), 7.81 (d, *J* = 8.0, 1H), 7.98-8.02 (m, 1H), 8.40-8.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.4, 123.7, 124.6, 124.8, 125.8, 126.4, 126.5, 126.8, 127.8, 128.5, 129.2, 129.5, 129.8, 130.1, 130.3, 131.2, 131.8, 133.8, 134.2, 134.6, 136.3, 146.1, 178.1; FTIR (ATR) 3058, 2927, 1708, 1650, 1616, 1434, 1276, 759 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{26}H_{17}OS_2$ $[M+H]^+$:409.0720; found: 409.0712.



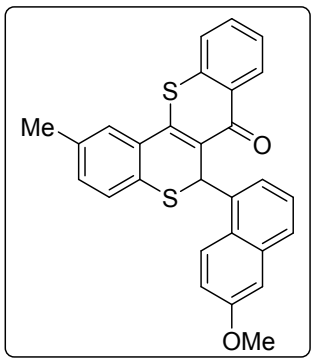
6-(6-Methoxynaphthalen-1-yl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7l): 135 mg; 61% yield; yellow viscous liquid; R_f 0.53 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (s, 3H), 6.21 (s, 1H), 6.96-7.00 (m, 2H), 7.23-7.29 (m, 2H), 7.37-7.48 (m, 4H), 7.50-7.56 (m, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 8.55(d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.2, 55.3, 105.5, 118.7, 125.7, 126.4, 126.5, 126.6, 127.2, 127.7, 128.4, 129.1, 129.4, 129.5, 129.6, 130.2, 131.2, 131.4, 131.8, 133.7, 133.9, 135.2, 136.4, 136.4, 145.2, 157.7, 178.2; FTIR (ATR) 3058, 2923, 1712, 1604, 1342, 1265, 758 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{27}H_{19}O_2S_2$ $[M+H]^+$:439.0826; found: 439.0842.



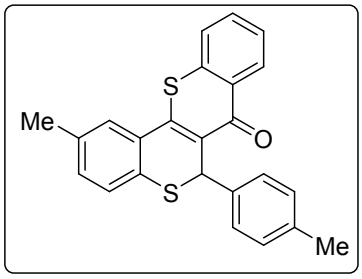
6-(Thiophen-2-yl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7m): 136 mg; 74% yield; brownish yellow viscous liquid; R_f 0.29 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.34 (d, *J* = 0.4 Hz, 1H), 6.70 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H), 6.79 (dt, *J* = 3.6 Hz, 0.8 Hz, 1H), 6.95 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 7.30 (td, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.37 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.48 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.50-7.54 (m, 1H), 7.59-7.63 (m, 2H), 7.86 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 8.56 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.2, 122.9, 124.6, 125.8, 126.3, 126.4, 126.6, 126.8, 127.8, 129.56, 129.60, 130.2, 131.1, 131.4, 131.8, 133.5, 136.3, 144.3, 144.7, 177.7; FTIR (KBr) 3052, 1610, 1590, 1438, 754 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{20}H_{12}ONaS_3$ $[M+Na]^+$: 386.9948; found: 386.9954.



3-Methyl-6-phenyl-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7n): 149 mg; 80% yield; brownish viscous liquid; R_f 0.46 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.1 (s, 3H), 6.03 (s, 1H), 7.89 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.0 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.33 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.42 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.54 (td, *J* = 7.61 Hz, 1.6 Hz, 1H), 7.64 (td, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.89 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 8.55 (dd, J = 8.0 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.9, 38.7, 126.4, 126.6, 126.7, 127.7, 127.8, 129.2, 129.4, 129.6, 130.2, 131.3, 131.4, 131.9, 133.7, 136.4, 137.4, 137.6, 145.1, 178.7; FTIR (KBr) 3055, 2926, 1623, 1541, 1426, 754 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{23}H_{16}ONaS_2$ $[M+Na]^+$: 395.0535; found: 395.0543.

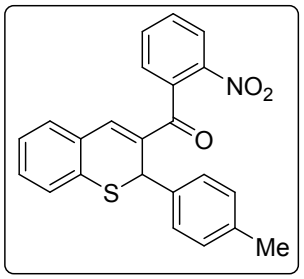


6-(6-Methoxynaphthalen-1-yl)-2-methyl-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7o): 116 mg; 51% yield; yellow viscous liquid; R_f 0.55 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.82 (s, 3H), 6.19 (s, 1H), 6.95-7.03 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.25-7.30 (m, 1H), 7.36-7.40 (m, 1H), 7.40-7.44 (m, 1H), 7.45-7.50 (m, 1H), 7.51-7.56 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.67-7.72 (m, 2H), 8.56 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 39.2, 55.3, 105.6, 118.6, 125.7, 126.4, 126.5, 127.1, 127.2, 127.7, 128.4, 129.2, 129.5, 129.6, 130.1, 130.2, 131.3, 131.8, 132.3, 133.8, 135.3, 136.2, 136.4, 145.3, 157.7, 178.3; FTIR (ATR) 3058, 2954, 1604, 1342, 1265, 740 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{28}H_{21}O_2S_2$ $[M+H]^+$: 453.0982; found: 453.0981.

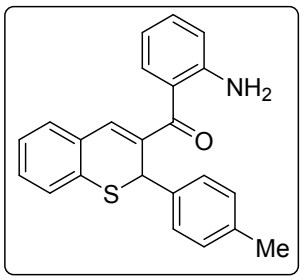


2-Methyl-6-(p-tolyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one (7p): 153 mg; 79% yield; brown solid; mp 195-198; R_f 0.80 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 3H), 2.37 (s, 3H), 6.03 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.07-7.14 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.48-7.52 (m, 1H), 7.55-7.61 (m, 1H), 7.62 -7.66 (m, 1H), 7.67 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 21.3, 38.8, 126.3, 127.1, 127.2, 127.6, 129.0, 129.1, 129.4, 129.5, 130.2, 130.3, 131.3, 131.7, 132.2, 136.1, 136.3, 137.0, 137.6, 144.9, 178.2; FTIR (ATR) 3054, 2919, 1708, 1604, 1531, 740 cm^{-1}; HRMS (*m*/*z*) calculated for $C_{24}H_{19}OS_2$ $[M+H]^+$: 387.0877; found: 387.0873.

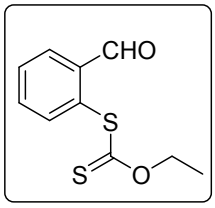
6.2.Experimental spectral data for reaction intermediates:



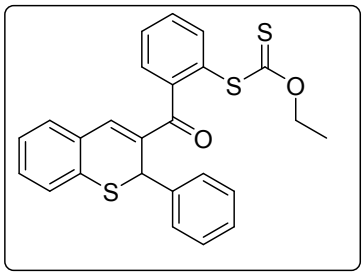
(2-Nitrophenyl)(2-(p-tolyl)-2H-thiochromen-3-yl)methanone (9): yellow solid; R_f 0.60 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 5.46 (s, 1H), 7.00-7.10 (m, 4H), 7.13-7.25 (m, 5H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 39.2, 124.8, 125.7, 126.6, 127.8, 129.1, 129.4, 130.1, 130.5, 131.1, 131.6, 133.3, 133.5, 134.0, 135.7, 137.6, 138.5, 140.9, 146.6, 192.4; FTIR (ATR) 2923, 2854, 1735, 1654, 1527, 1241, 752 cm^{-1}.



(2-Aminophenyl)(2-(p-tolyl)-2H-thiochromen-3-yl)methanone (6): yellow solid; R_f 0.80 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 5.32 (s, 1H), 5.57 (bs, 2H), 6.60-6.72 (m, 2H), 6.95-7.05 (m, 2H), 7.10-7.29 (m, 8H), 7.60 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 41.1, 115.9, 117.1, 118.9, 125.7, 126.6, 127.6, 129.5, 130.4, 130.5, 130.6, 132.0, 133.0, 133.9, 134.4, 137.0, 137.4, 138.9, 150.0, 197.4; FTIR (ATR) 3019, 2923, 1731, 1616, 1230, 752 cm^{-1}.



***O*-Ethyl S-(2-formylphenyl) carbonodithioate (C):** colorless liquid; R_f 0.80 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, *J* = 7.2 Hz, 3H), 4.66 (q, *J* = 6.8 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 10.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 71.8, 127.2, 128.7, 133.3, 134.0, 134.3, 139.8, 191.7, 209.9; FTIR (ATR) 2923, 2854, 1689, 1265, 1033, 755 cm^{-1}.



***O*-Ethyl S-(2-(2-phenyl-2H-thiochromene-3-carbonyl)phenyl) carbonodithioate (9):** yellow liquid; R_f 0.70 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21-1.30 (m, 3H), 4.35-4.60 (m, 2H), 5.49 (s, 1H), 7.05-7.10 (m, 1H), 7.15-7.30 (m, 9H), 7.36-7.43 (m, 1H), 7.50-7.57 (m, 2H), 7.60-7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6, 39.0, 70.6, 125.7, 126.8, 127.6, 127.7, 128.2, 128.6, 130.2, 130.3, 130.4, 131.4, 133.3, 133.5, 138.1, 141.6, 142.6, 144.3, 195.0, 212.6; FTIR (ATR) 2923, 2857, 1735, 1646, 1226, 1033, 752 cm^{-1}.

7. ^{1}H and ^{13}C spectra for all compounds

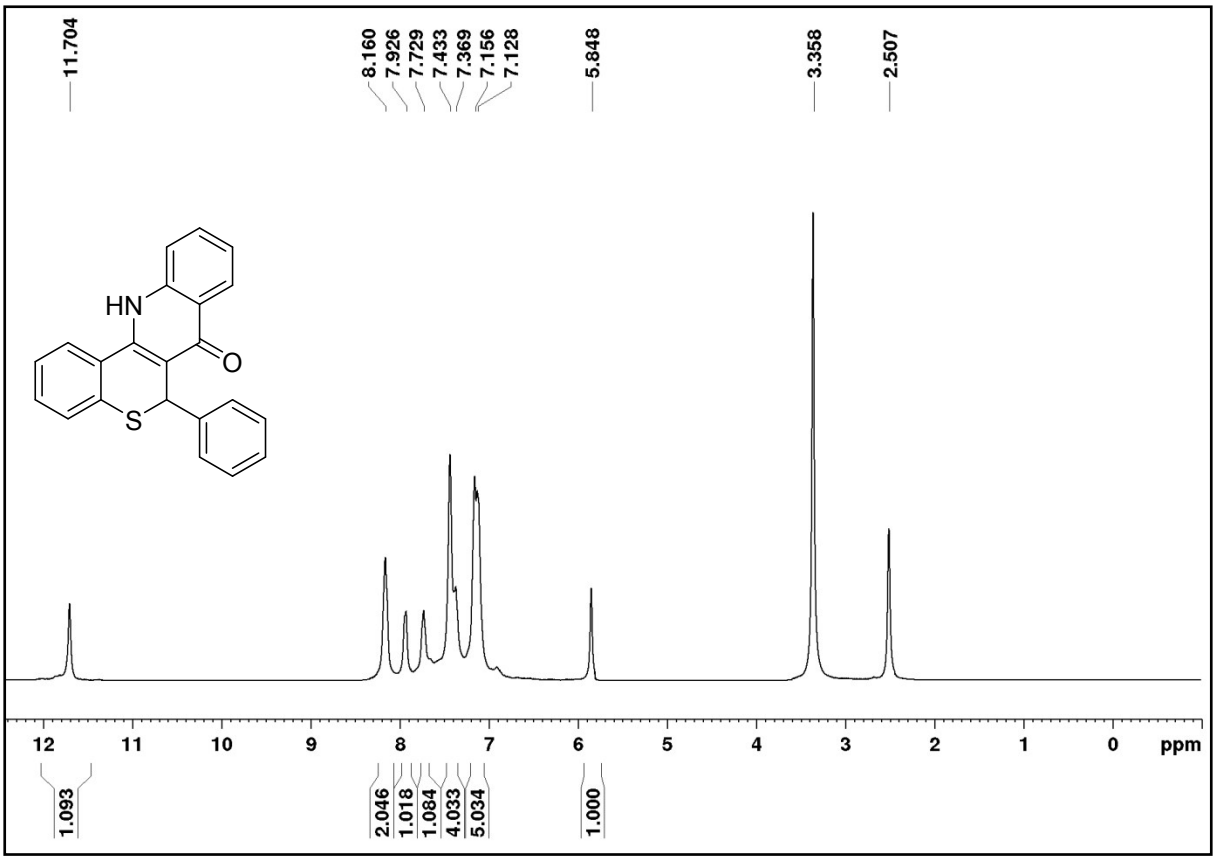


Figure 1: 400 MHz ^{1}H-NMR spectrum of **4a** in DMSO-d6

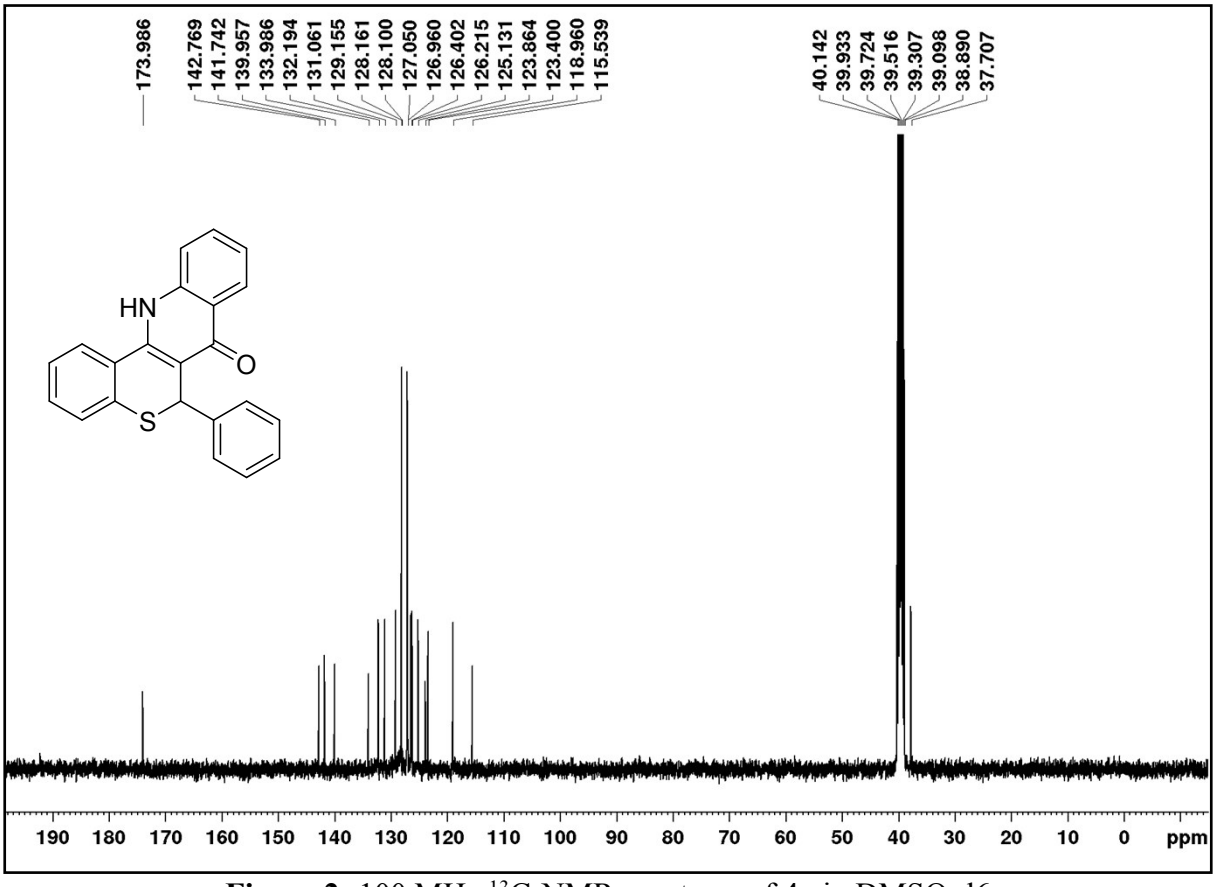


Figure 2: 100 MHz ^{13}C-NMR spectrum of **4a** in DMSO-d6

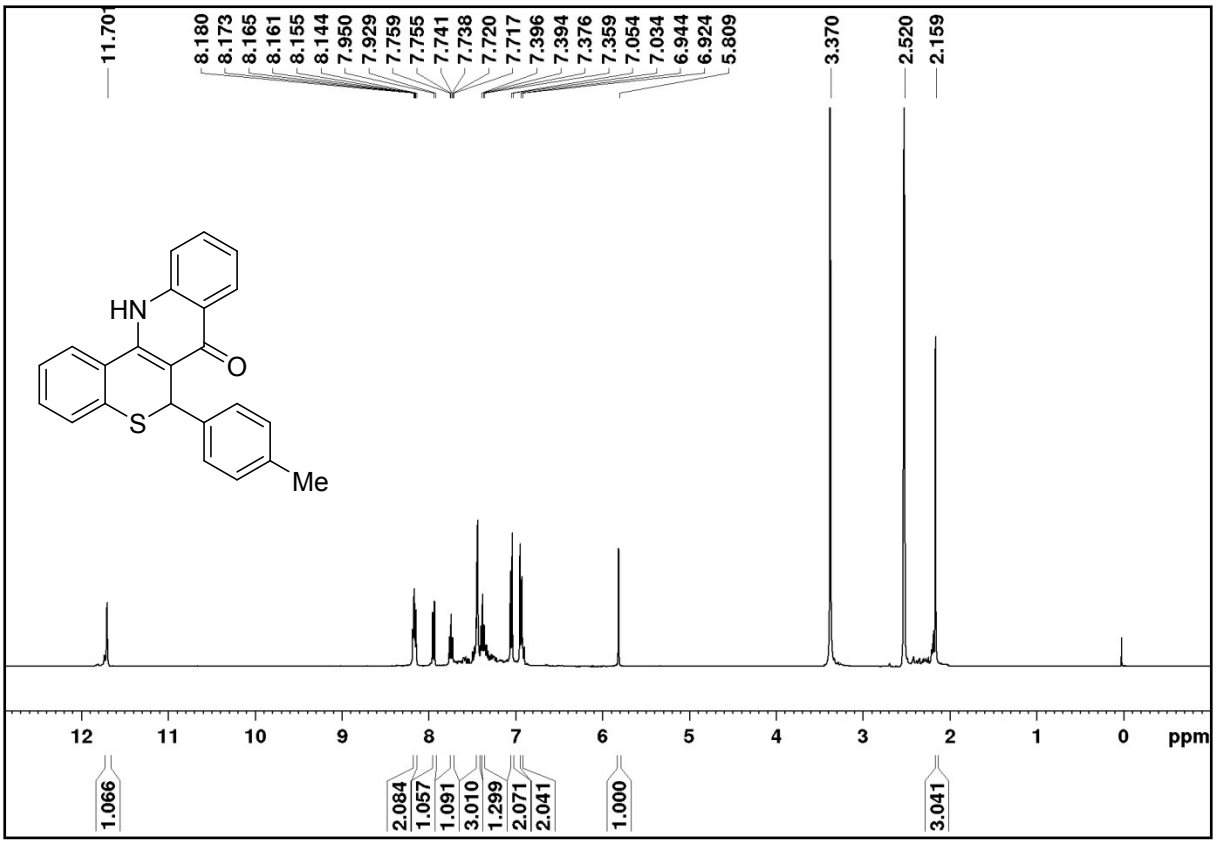


Figure 3: 400 MHz ^{1}H-NMR spectrum of **4b** in DMSO-d6

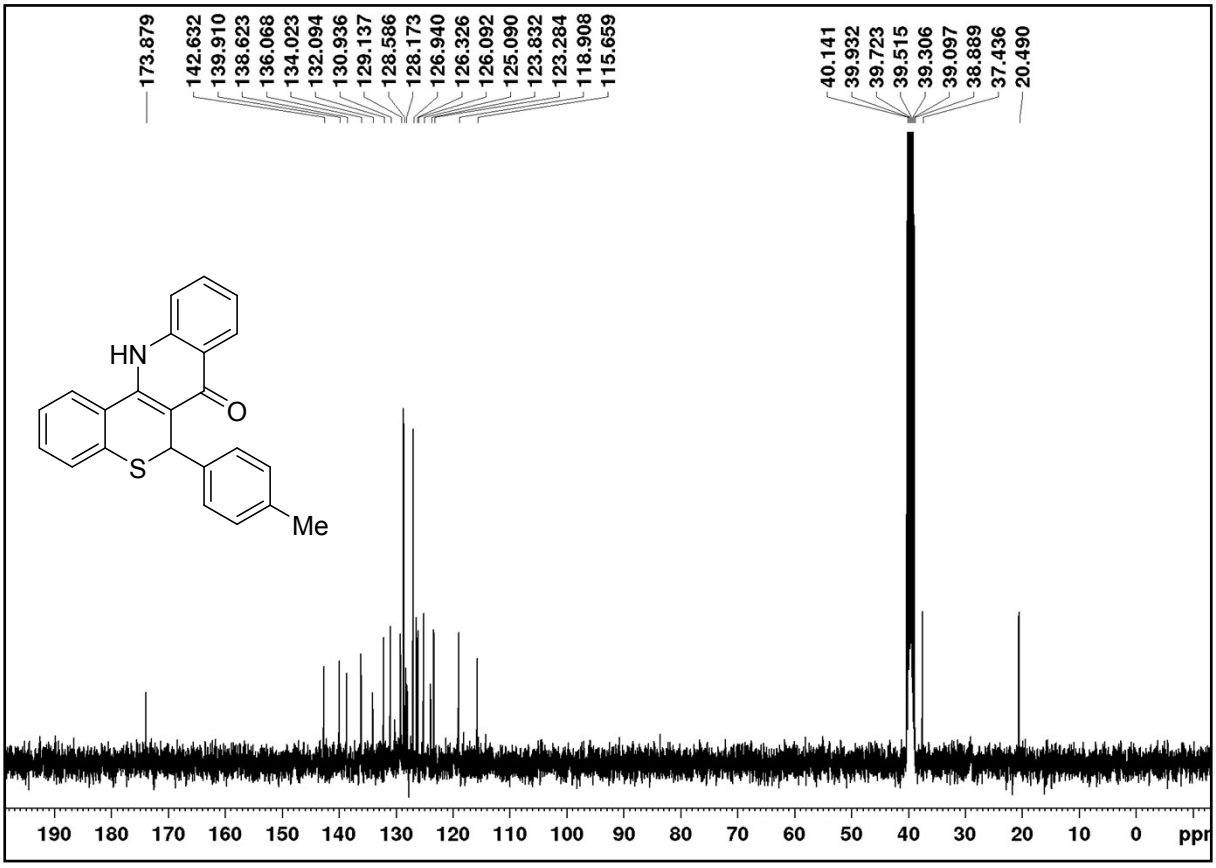


Figure 4: 100 MHz ^{13}C-NMR spectrum of **4b** in DMSO-d6

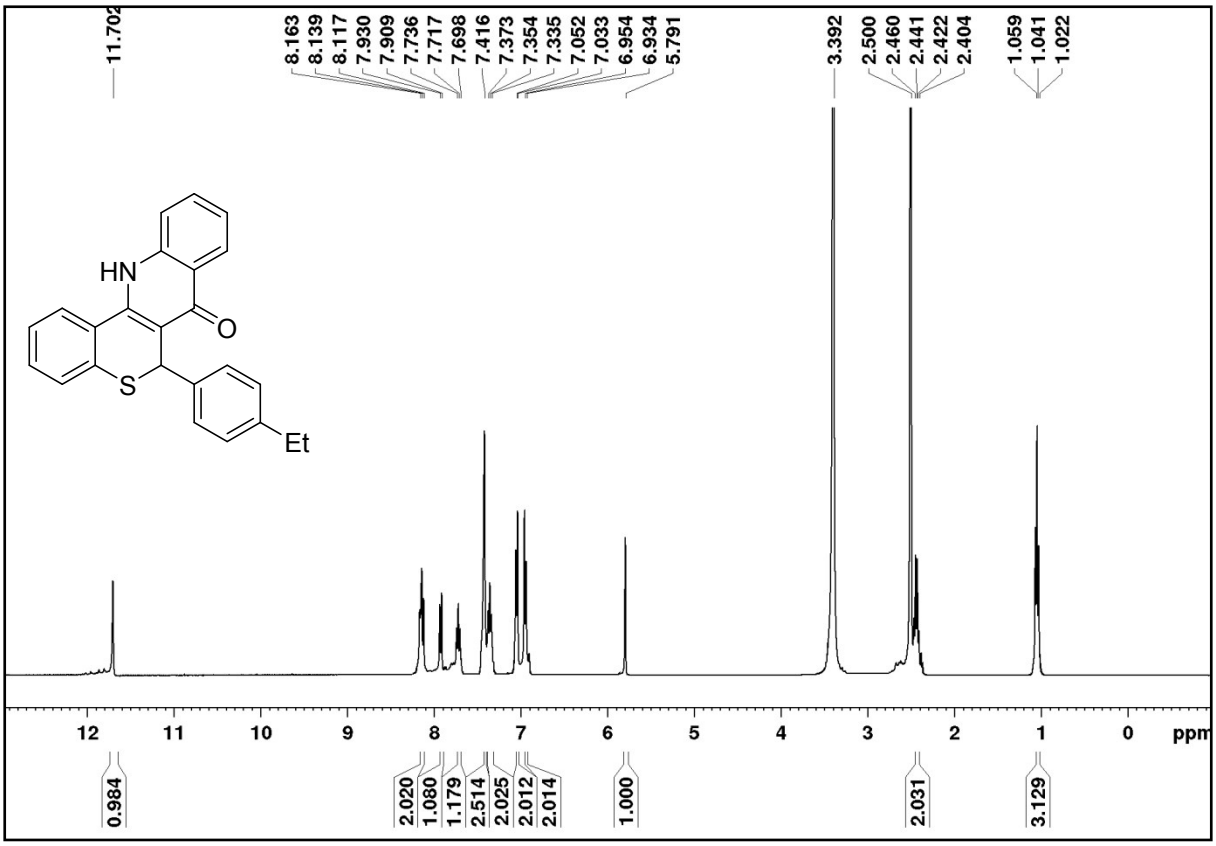


Figure 5: 400 MHz ^{1}H-NMR spectrum of **4c** in DMSO-d6

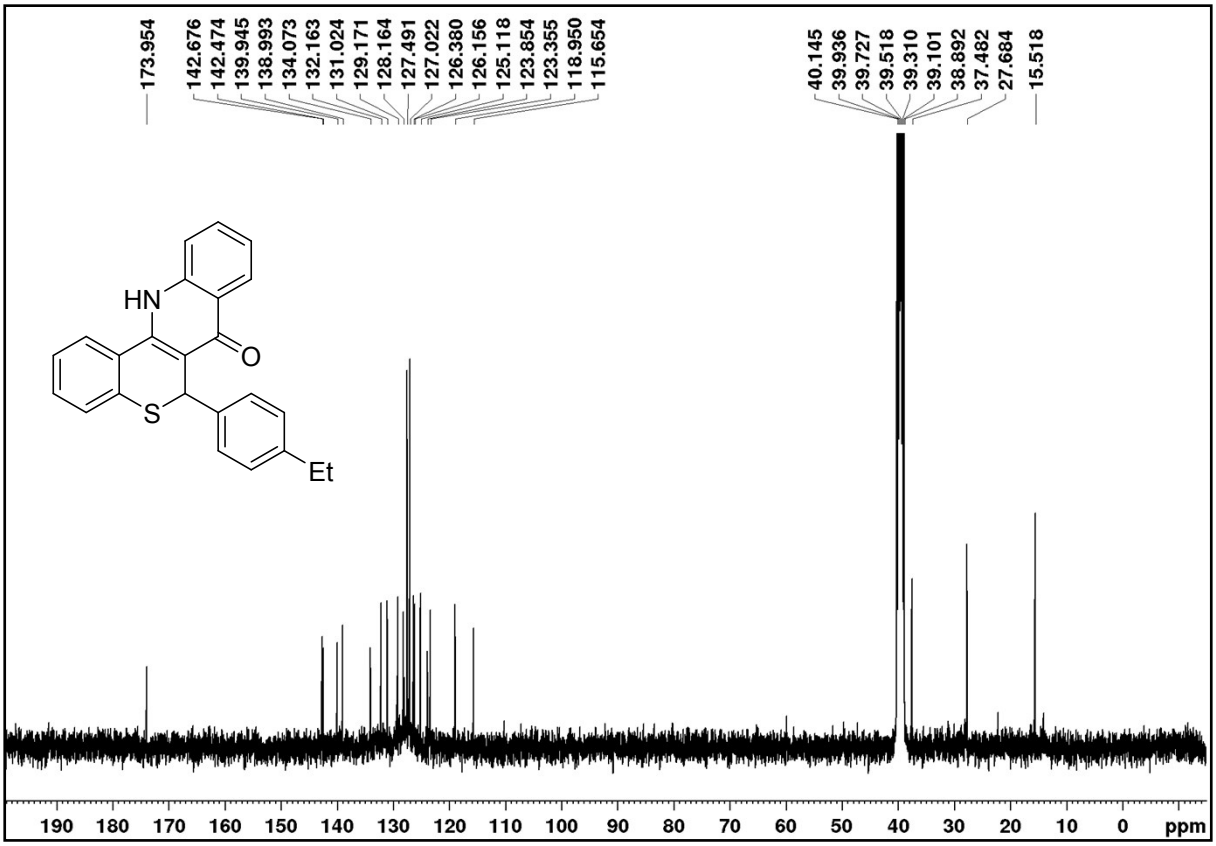


Figure 6: 100 MHz ^{13}C-NMR spectrum of **4c** in DMSO-d6

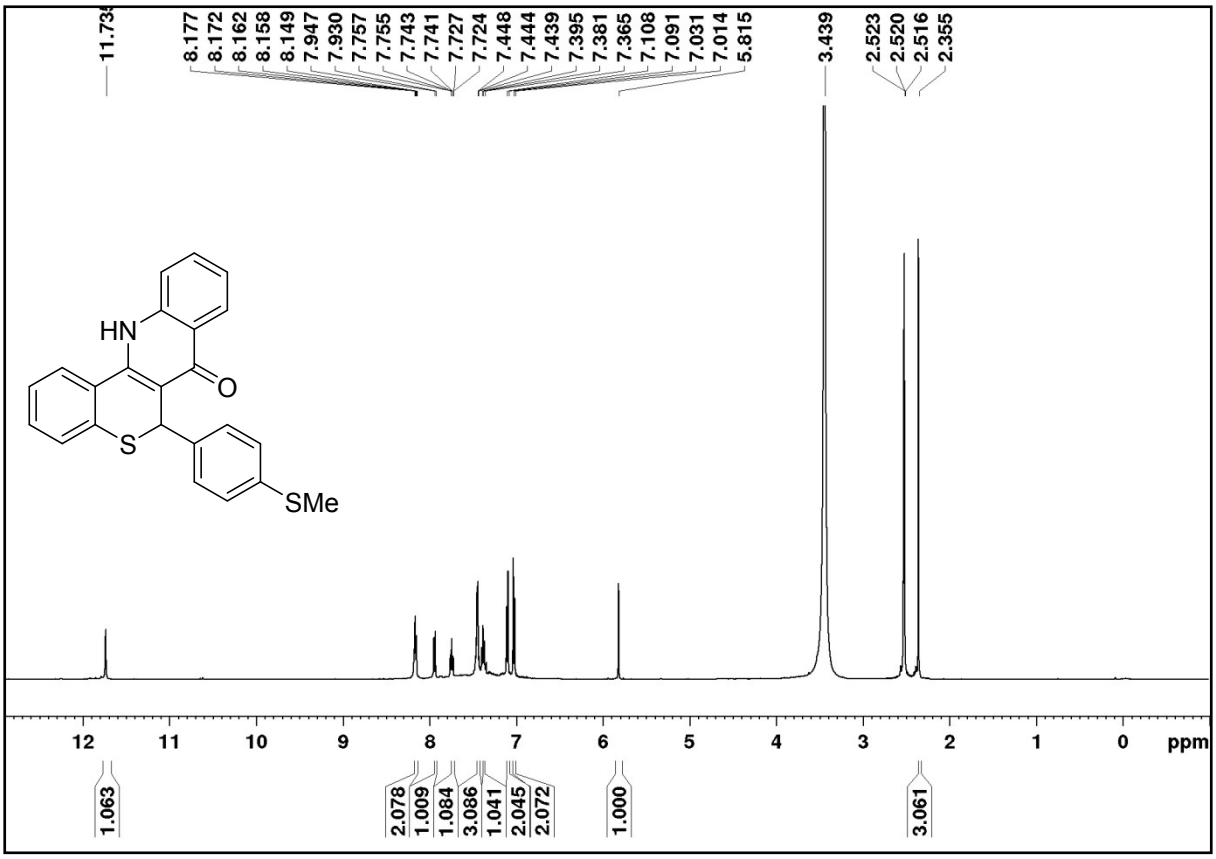


Figure 7: 500 MHz ^{1}H-NMR spectrum of **4d** in DMSO-d6

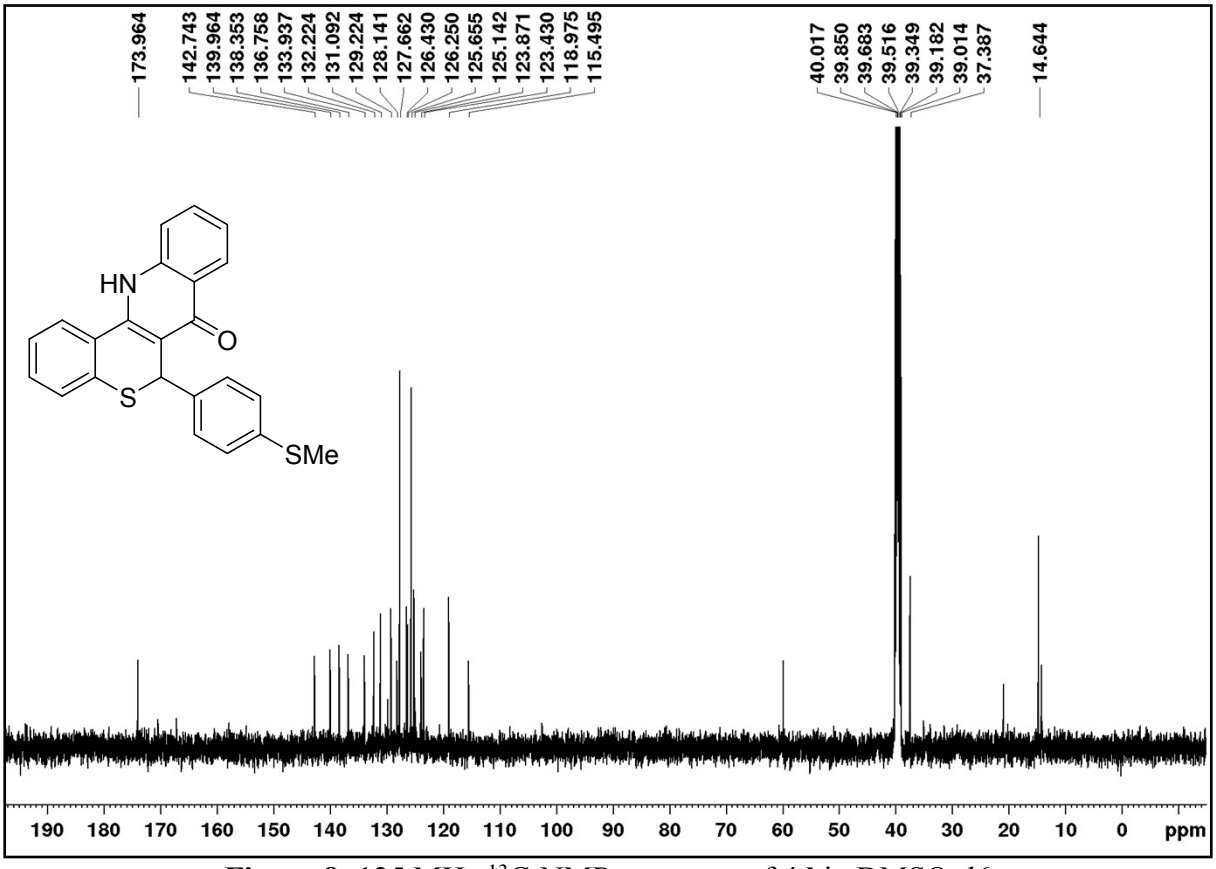


Figure 8: 125 MHz ^{13}C-NMR spectrum of **4d** in DMSO-d6

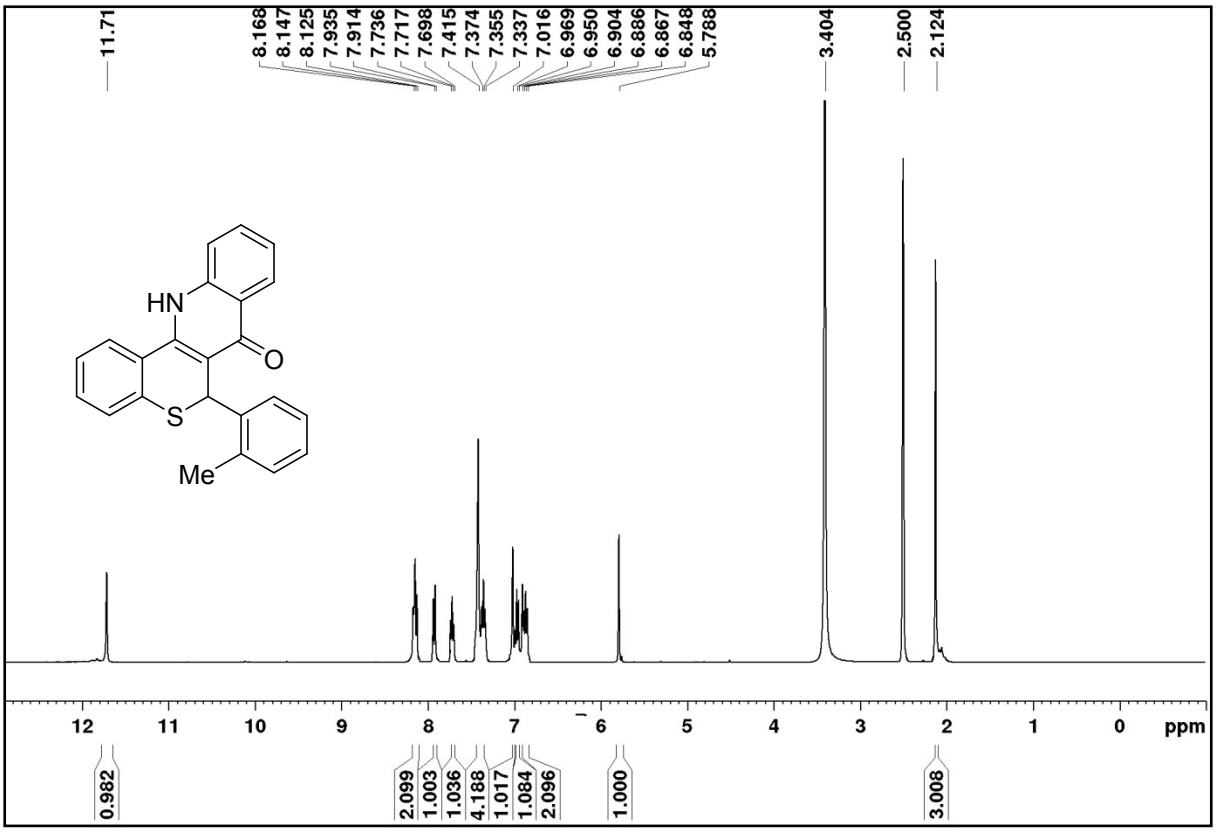


Figure 9: 400 MHz ^{1}H-NMR spectrum of **4e** in DMSO-d6

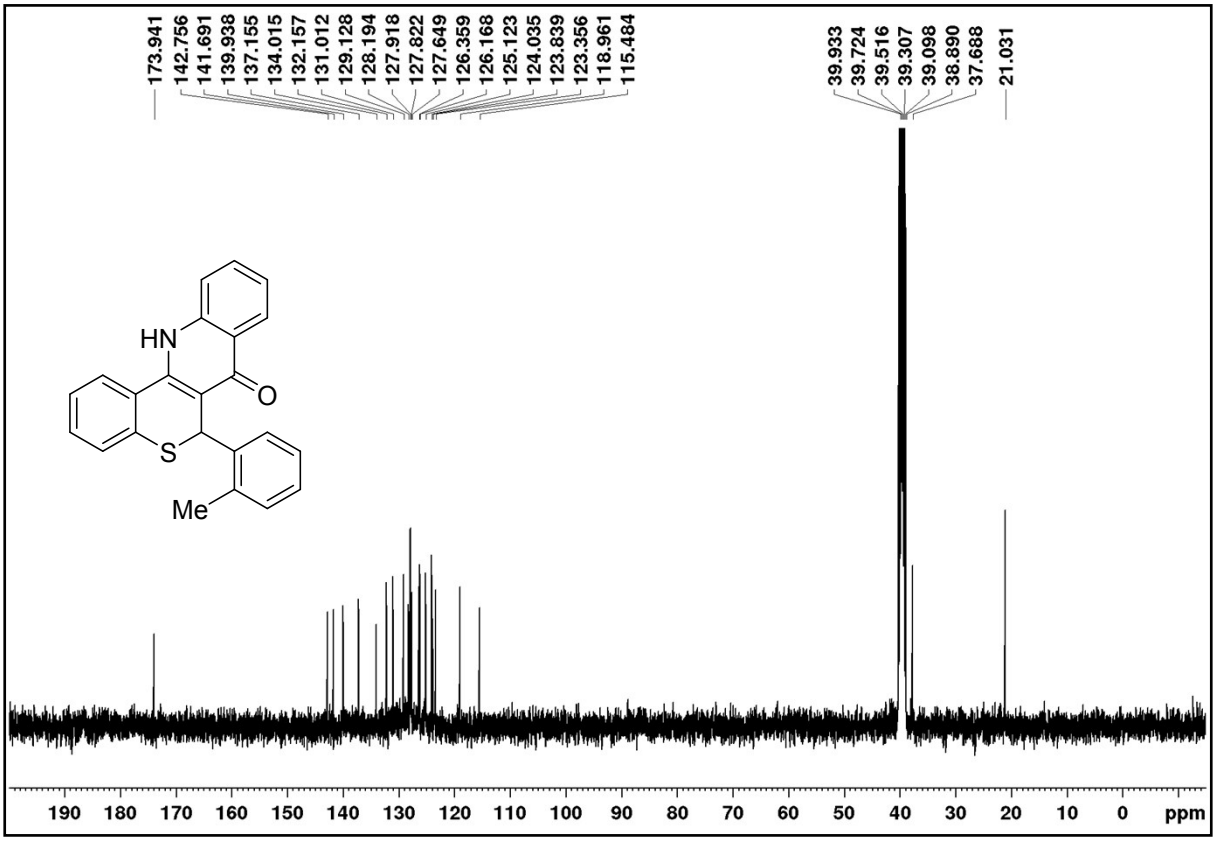


Figure 10: 100 MHz ^{13}C-NMR spectrum of **4e** in DMSO-d6

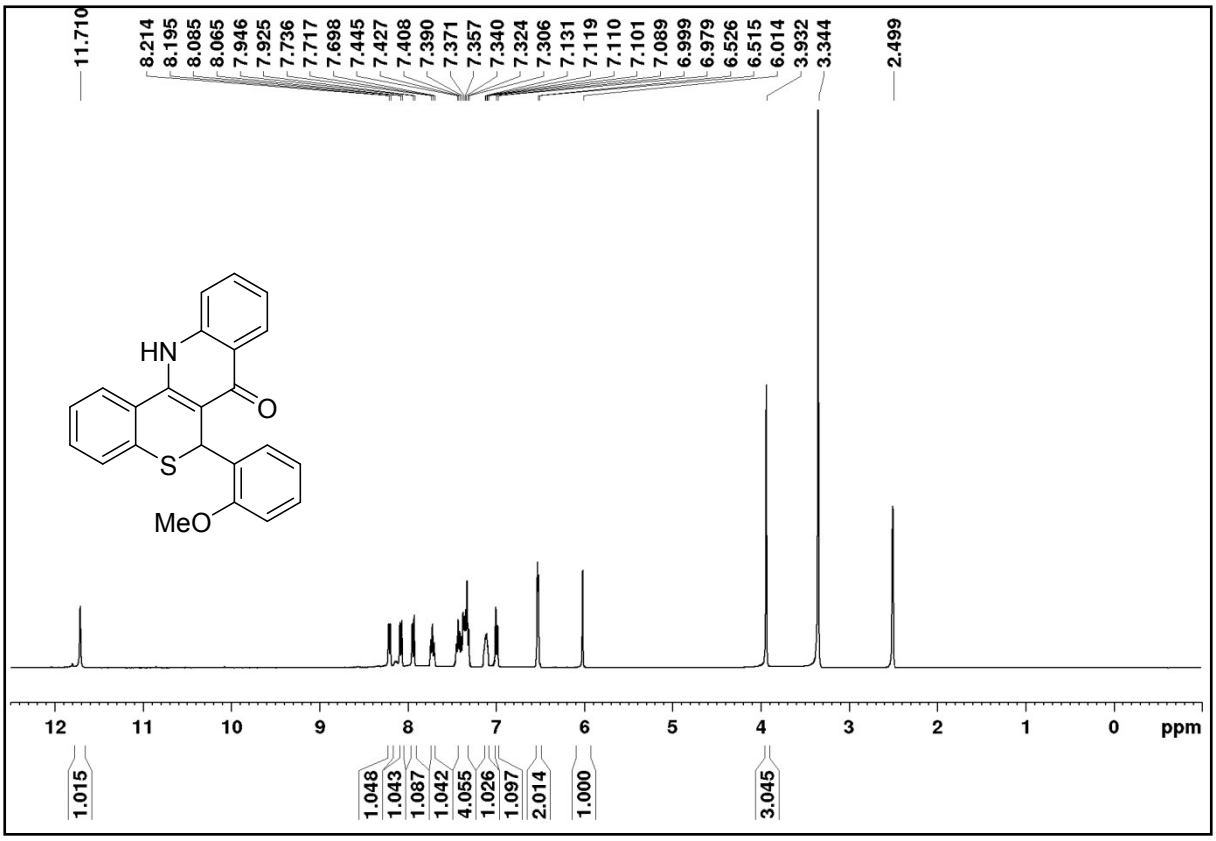


Figure 11: 400 MHz ^{1}H-NMR spectrum of **4f** in DMSO-d6

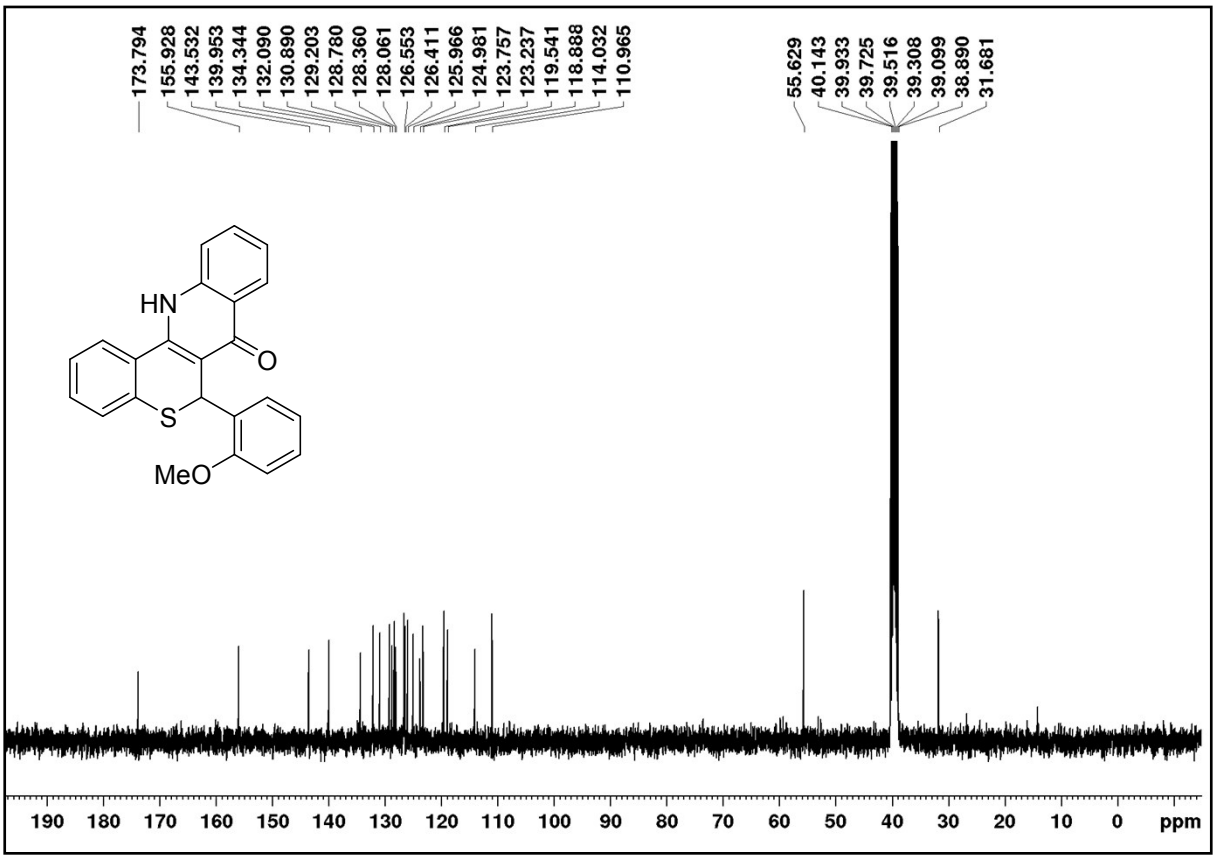


Figure 12: 100 MHz ^{13}C-NMR spectrum of **4f** in DMSO-d6

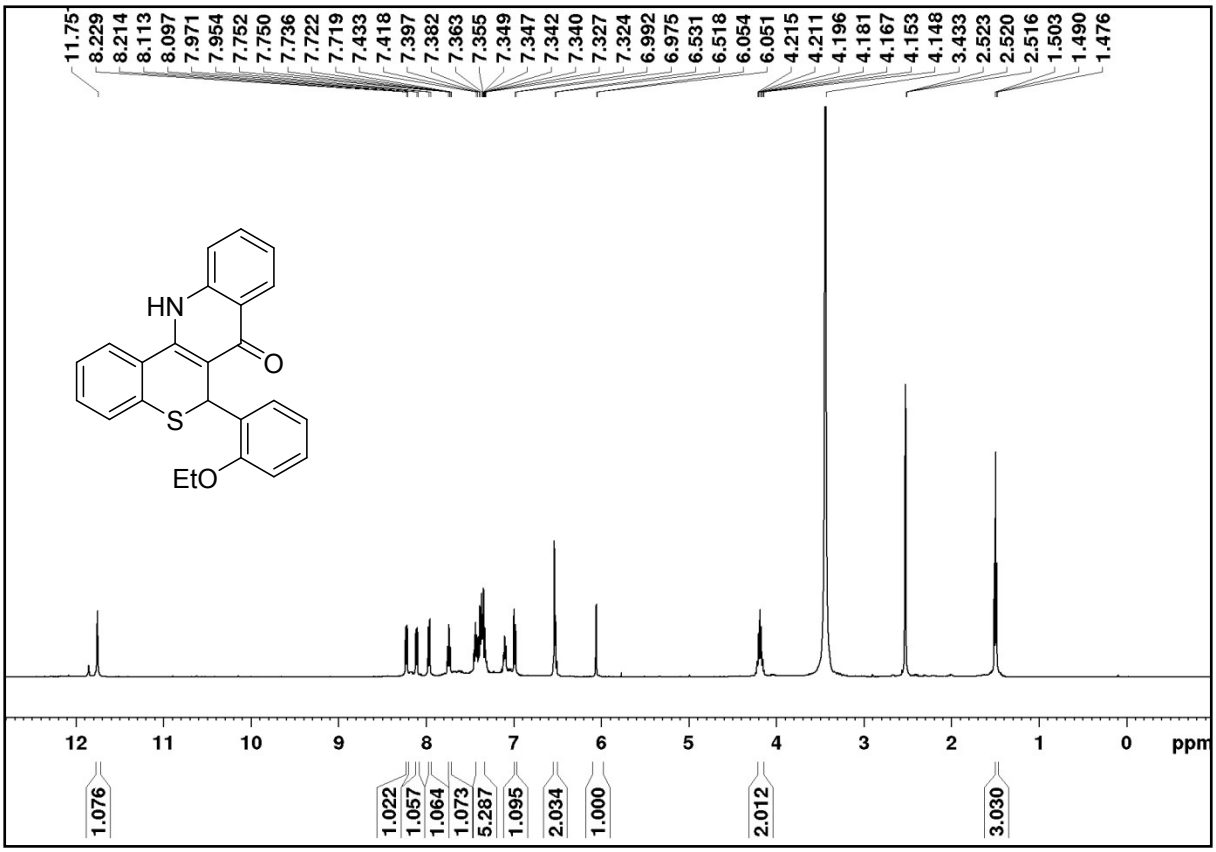


Figure 13: 500 MHz ^{1}H-NMR spectrum of **4g** in DMSO-d6

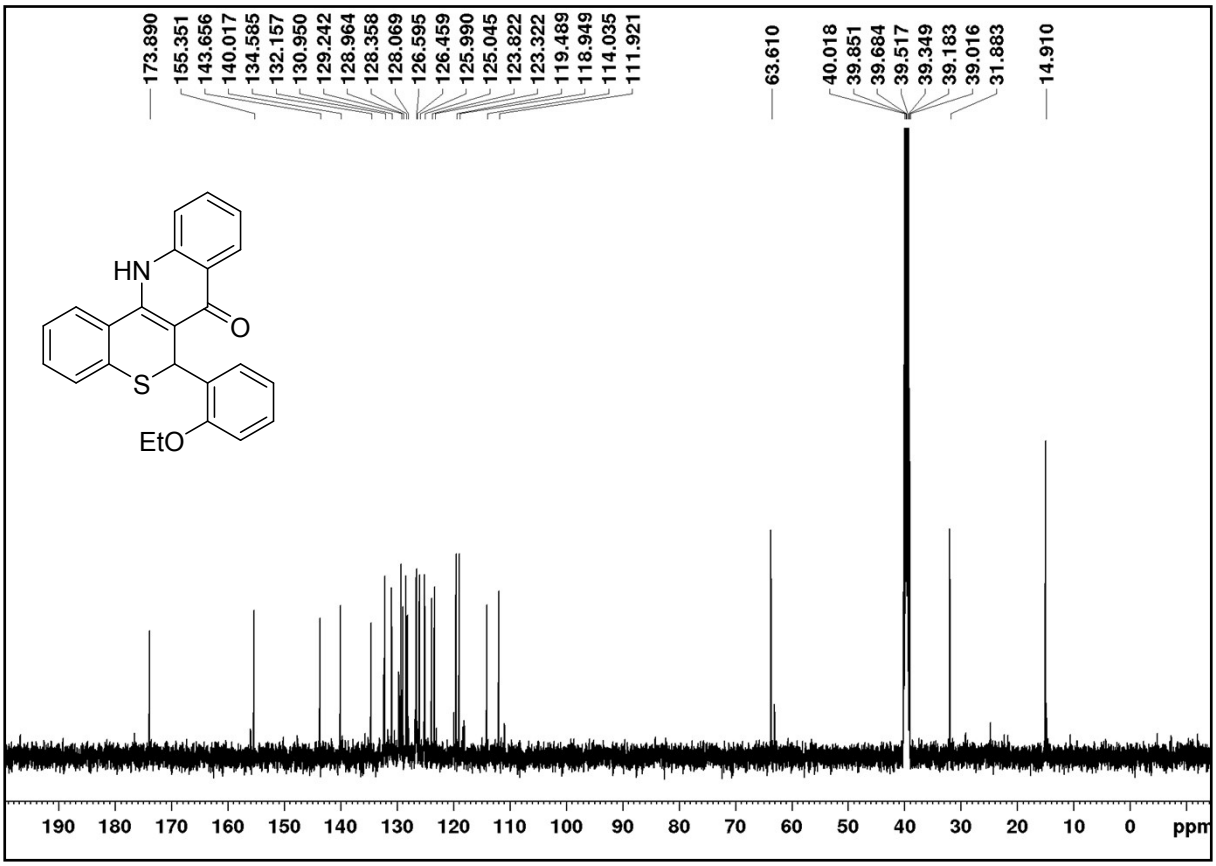


Figure 14: 125 MHz ^{13}C-NMR spectrum of **4g** in DMSO-d6

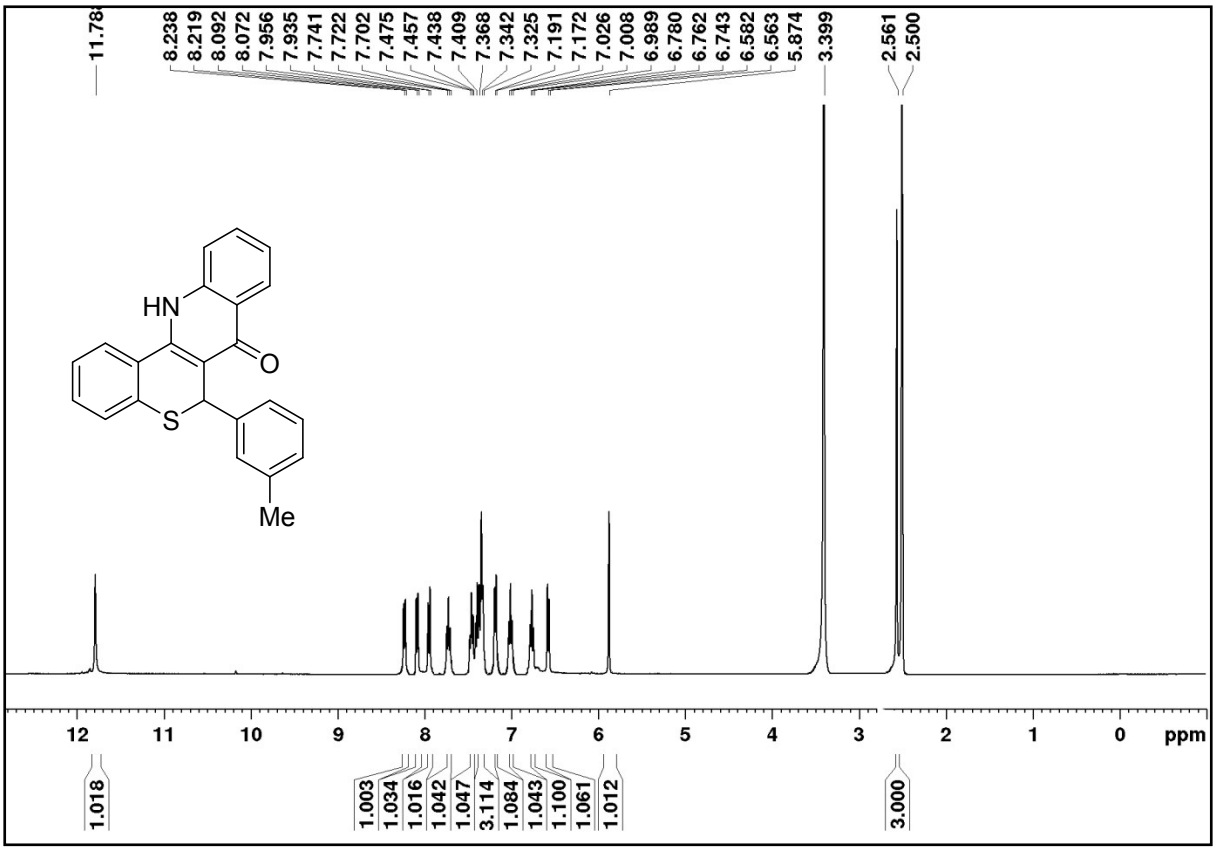


Figure 15: 400 MHz ^{1}H-NMR spectrum of **4h** in DMSO-d6

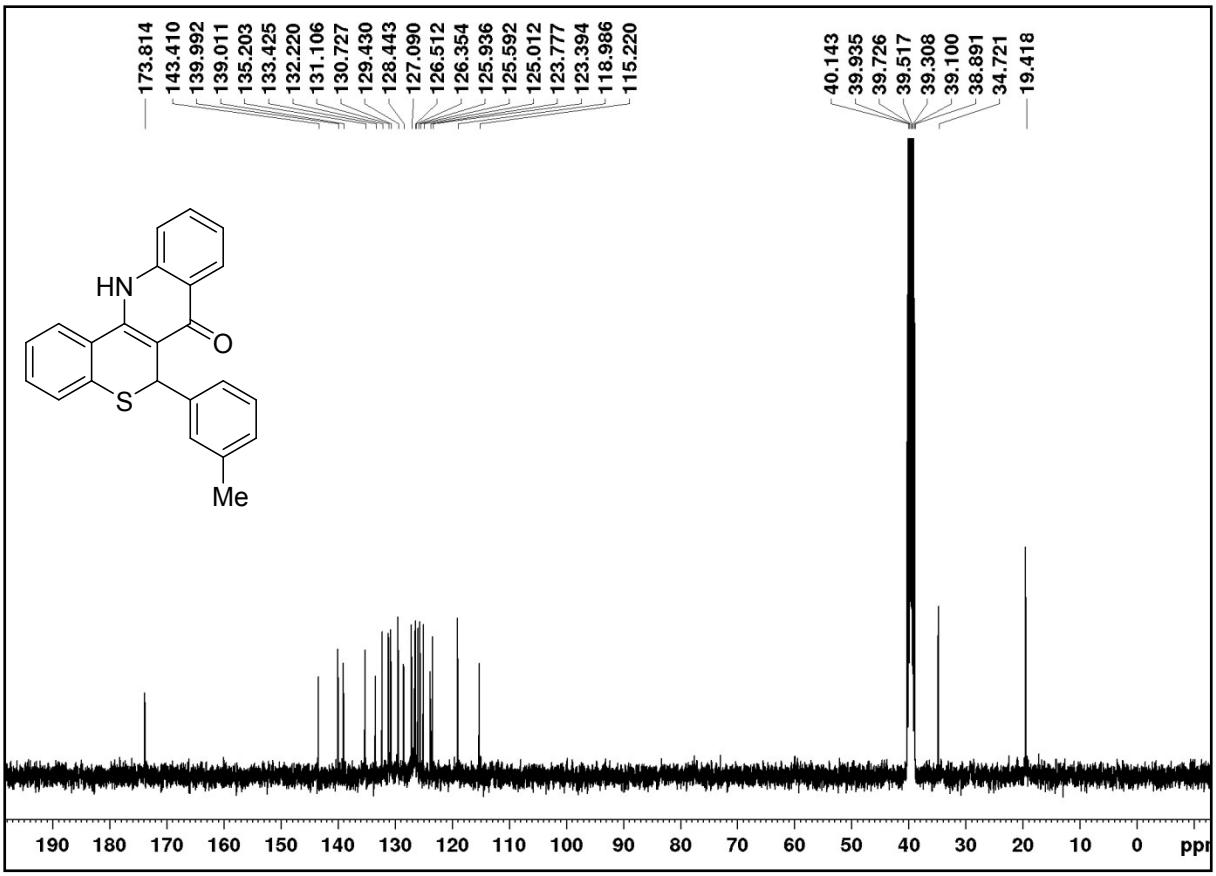


Figure 16: 100 MHz ^{13}C-NMR spectrum of **4h** in DMSO-d6

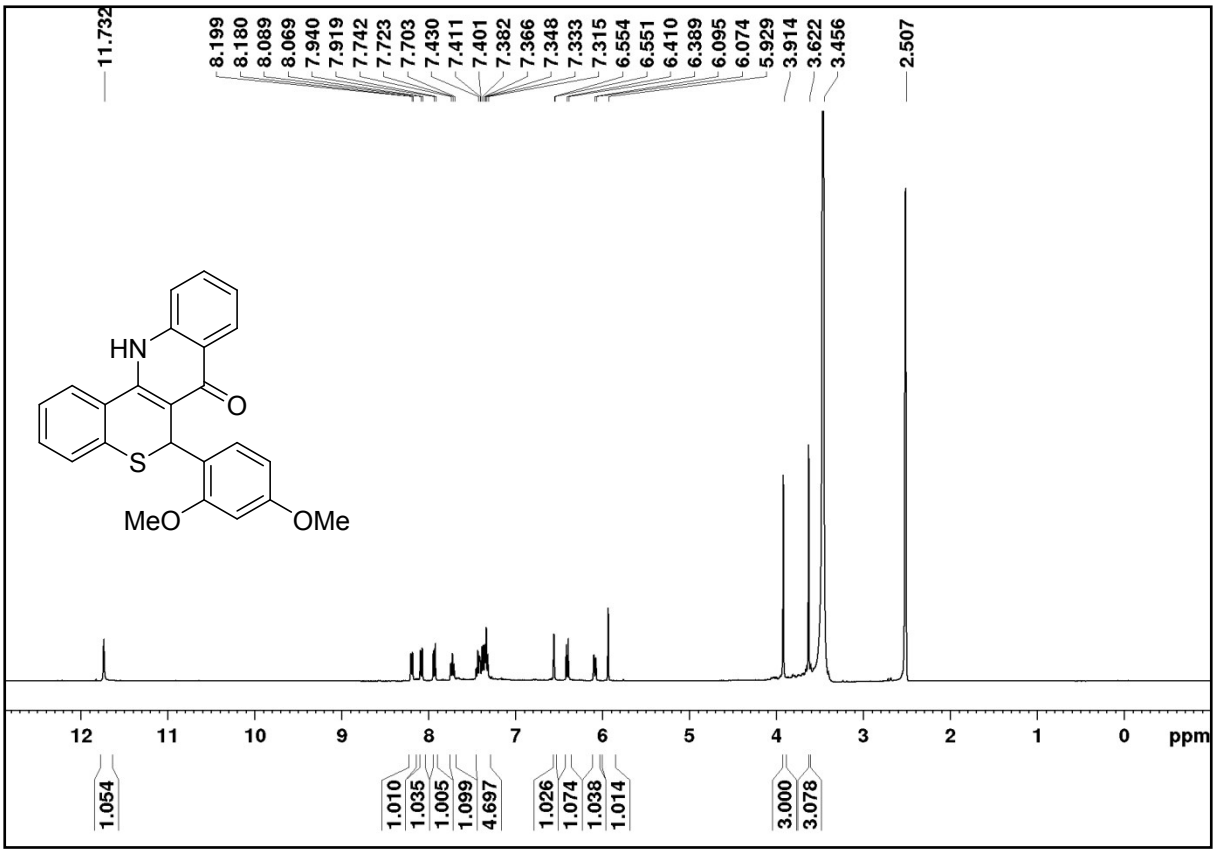


Figure 17: 400 MHz ^{1}H-NMR spectrum of **4i** in DMSO-d6

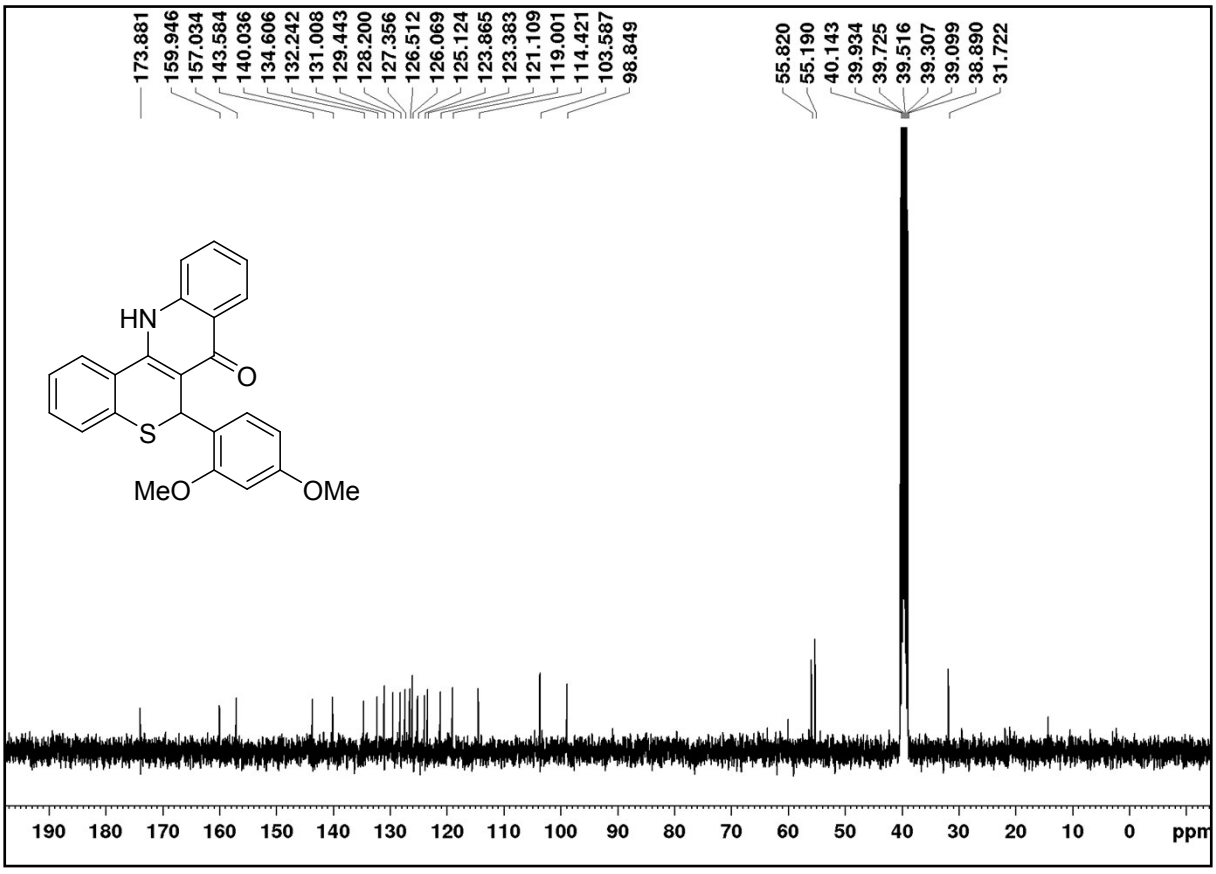


Figure 18: 100 MHz ^{13}C-NMR spectrum of **4i** in DMSO-d6

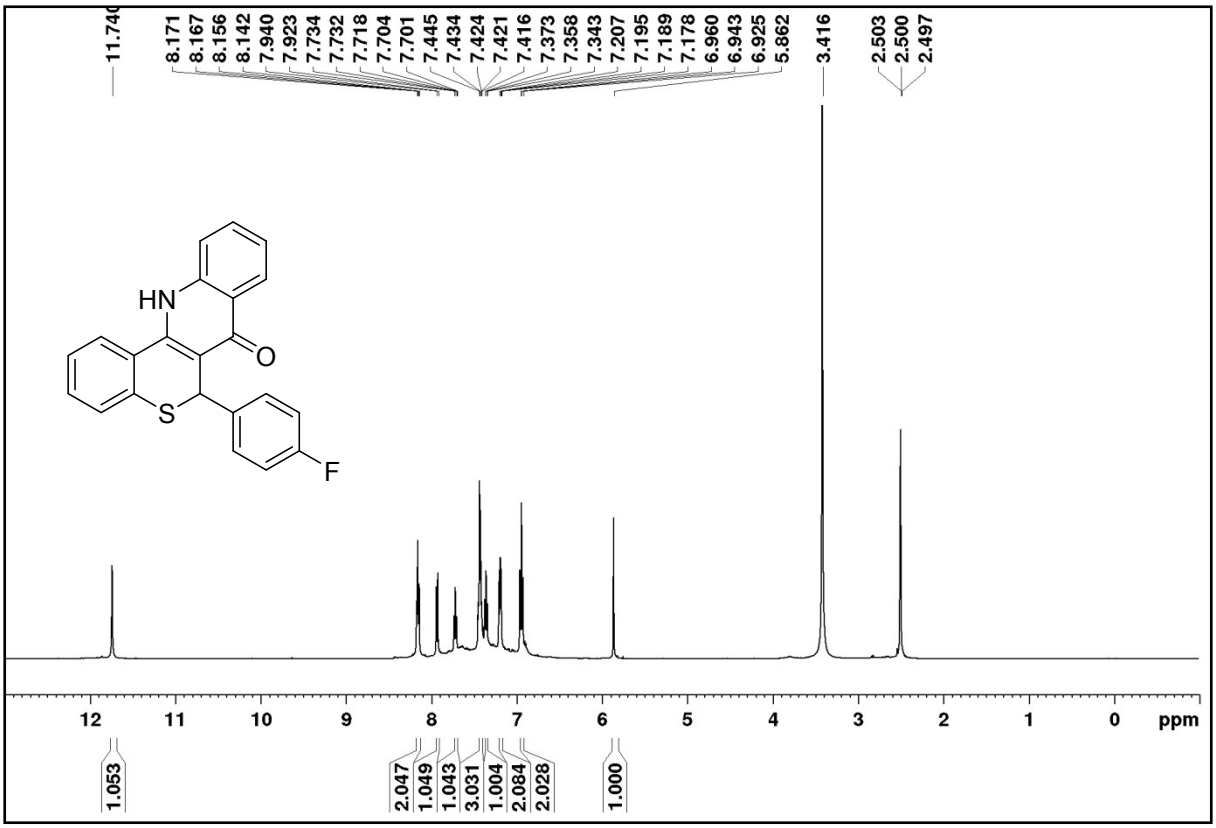


Figure 19: 500 MHz ^{1}H-NMR spectrum of **4j** in DMSO-d6

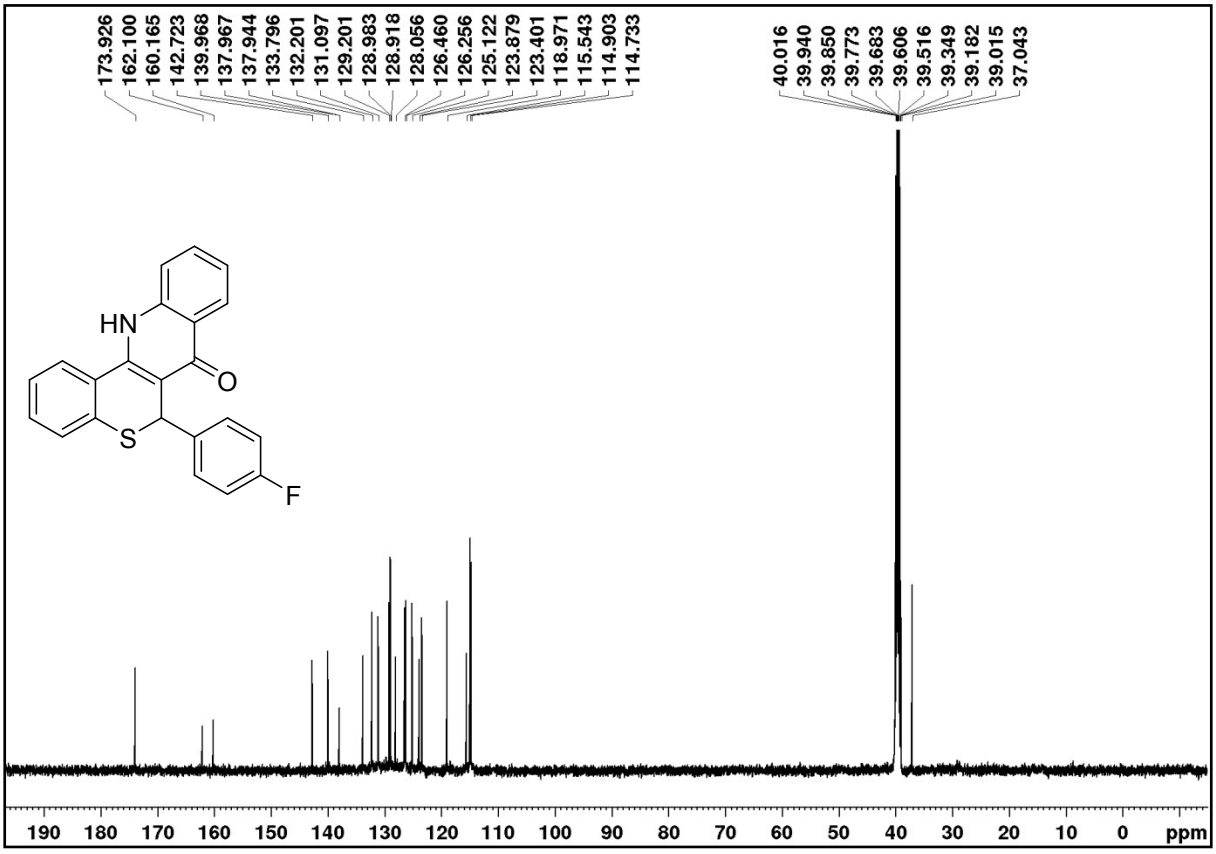


Figure 20: 125 MHz ^{13}C-NMR spectrum of **4j** in DMSO-d6

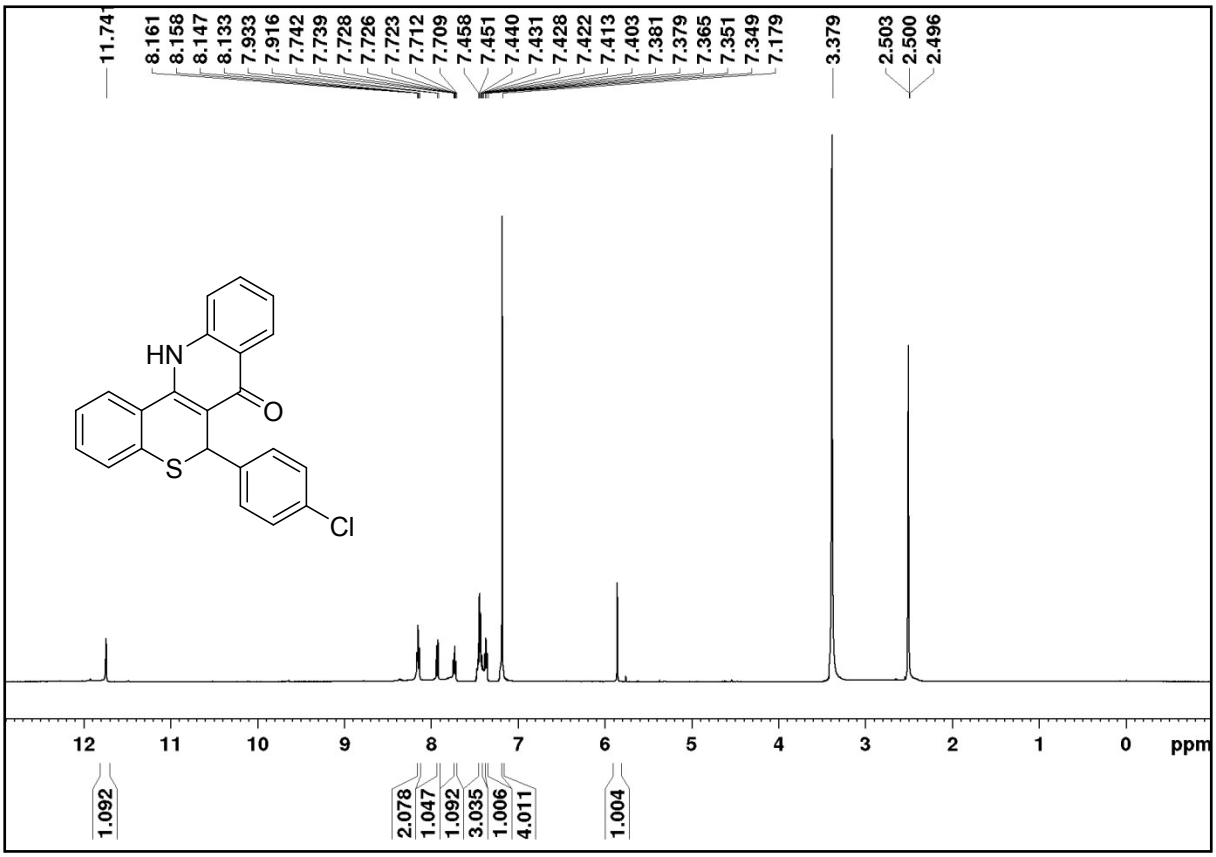


Figure 21: 500 MHz ^{1}H-NMR spectrum of **4k** in DMSO-d6

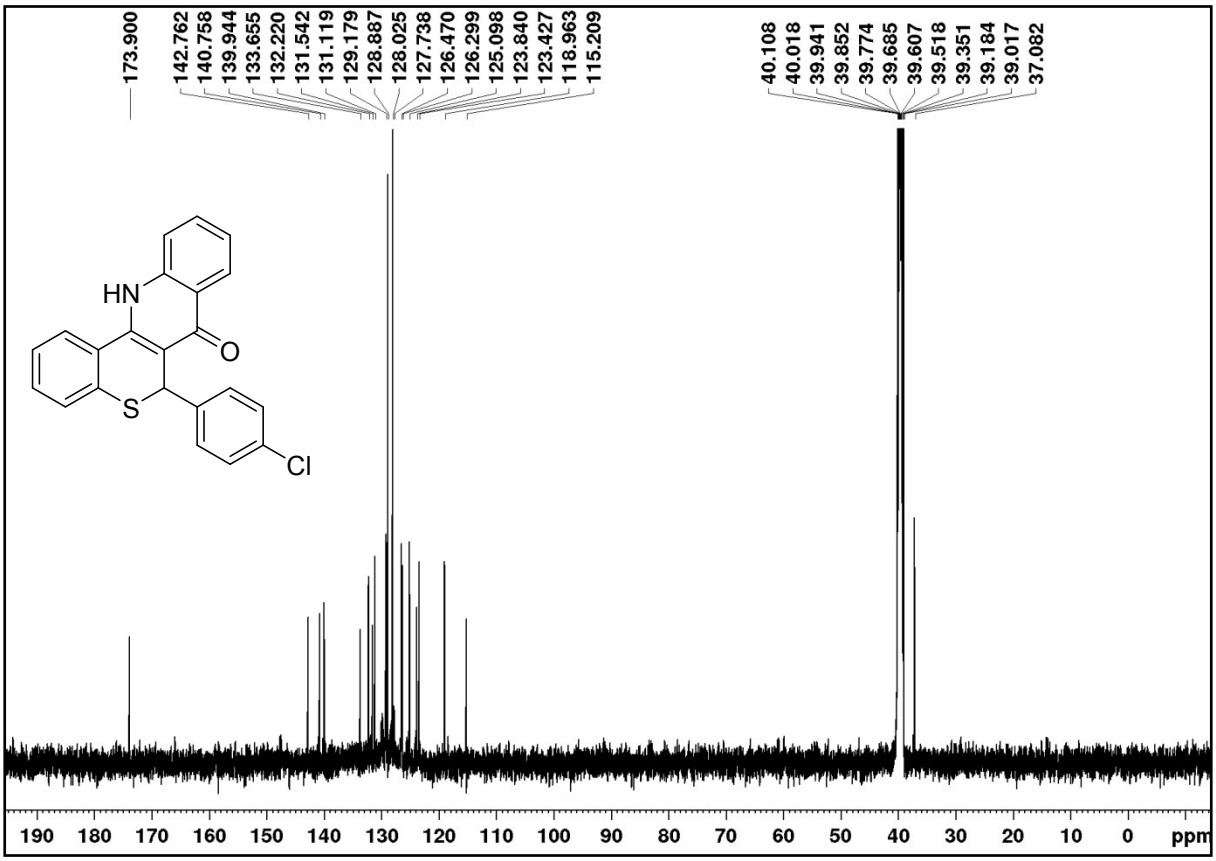


Figure 22: 125 MHz ^{13}C-NMR spectrum of **4k** in DMSO-d6

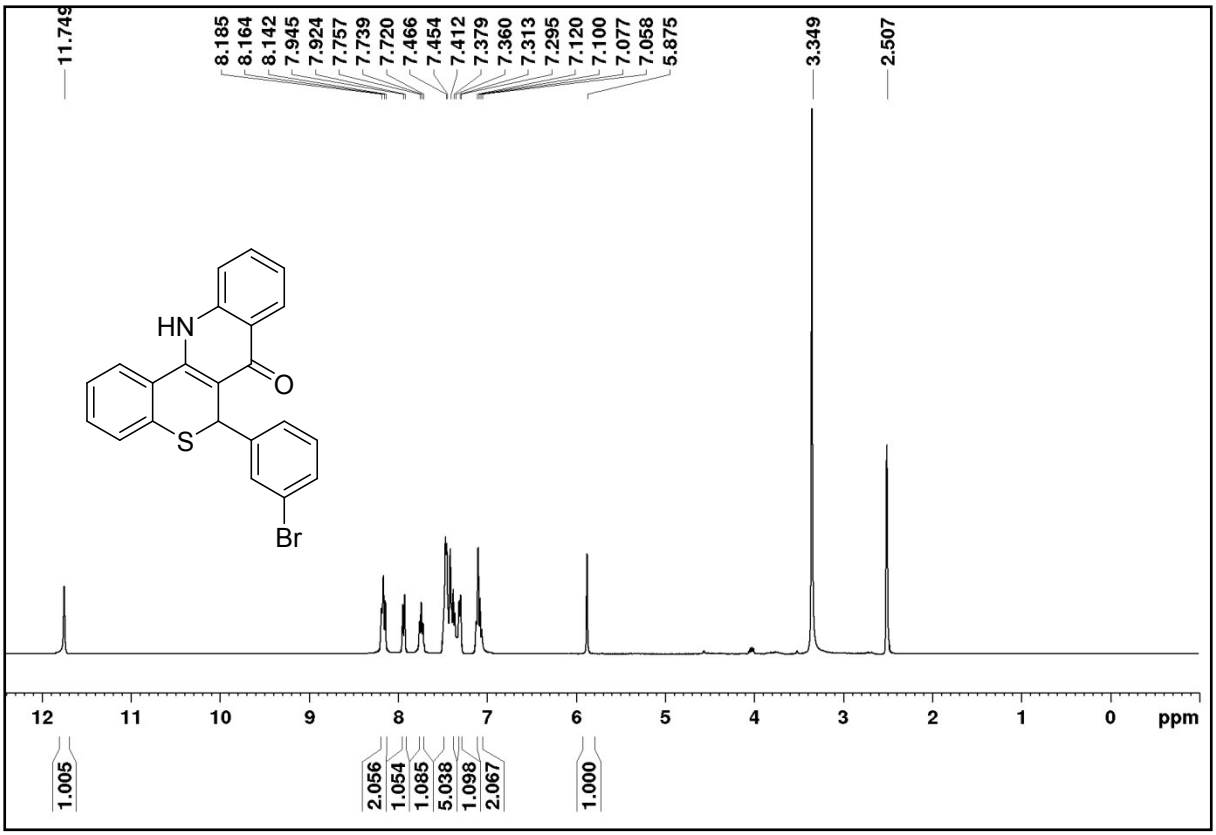


Figure 23: 400 MHz ^{1}H-NMR spectrum of **4l** in DMSO-d6

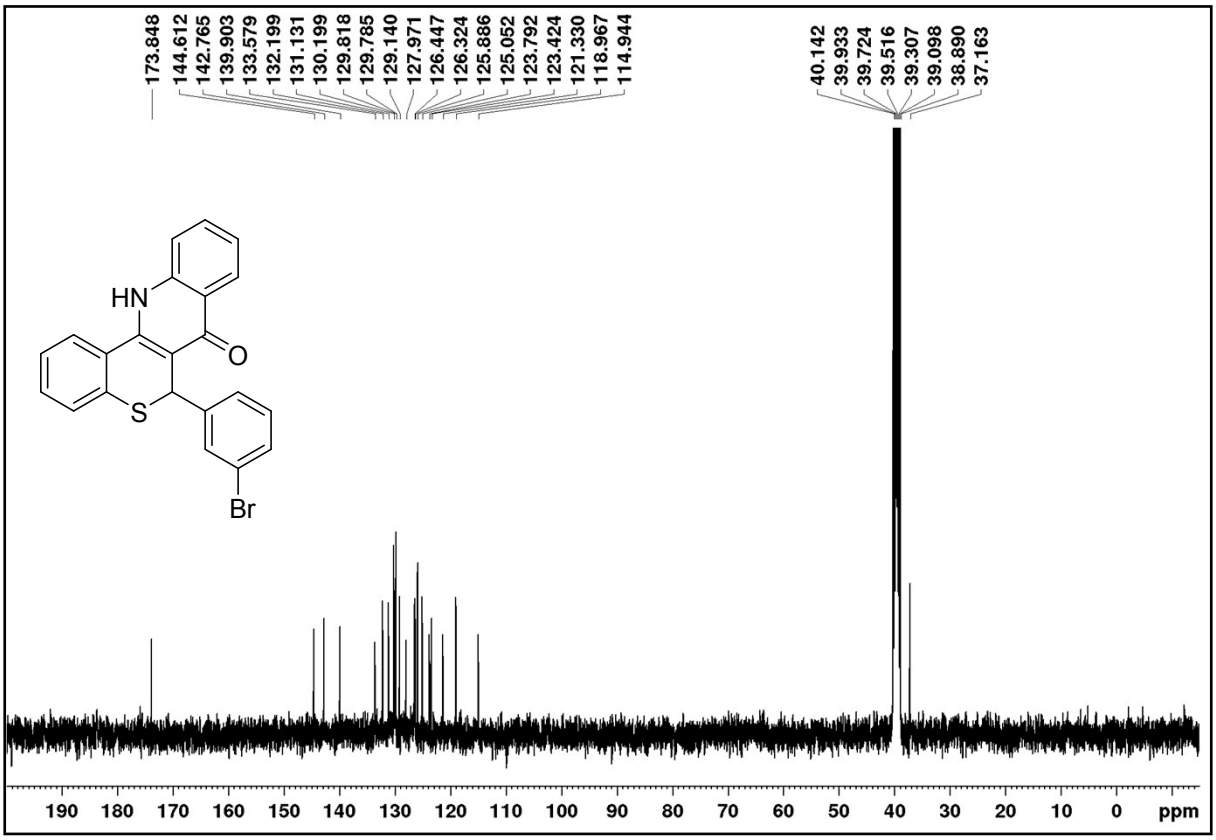


Figure 24: 100 MHz ^{13}C-NMR spectrum of **4l** in DMSO-d6

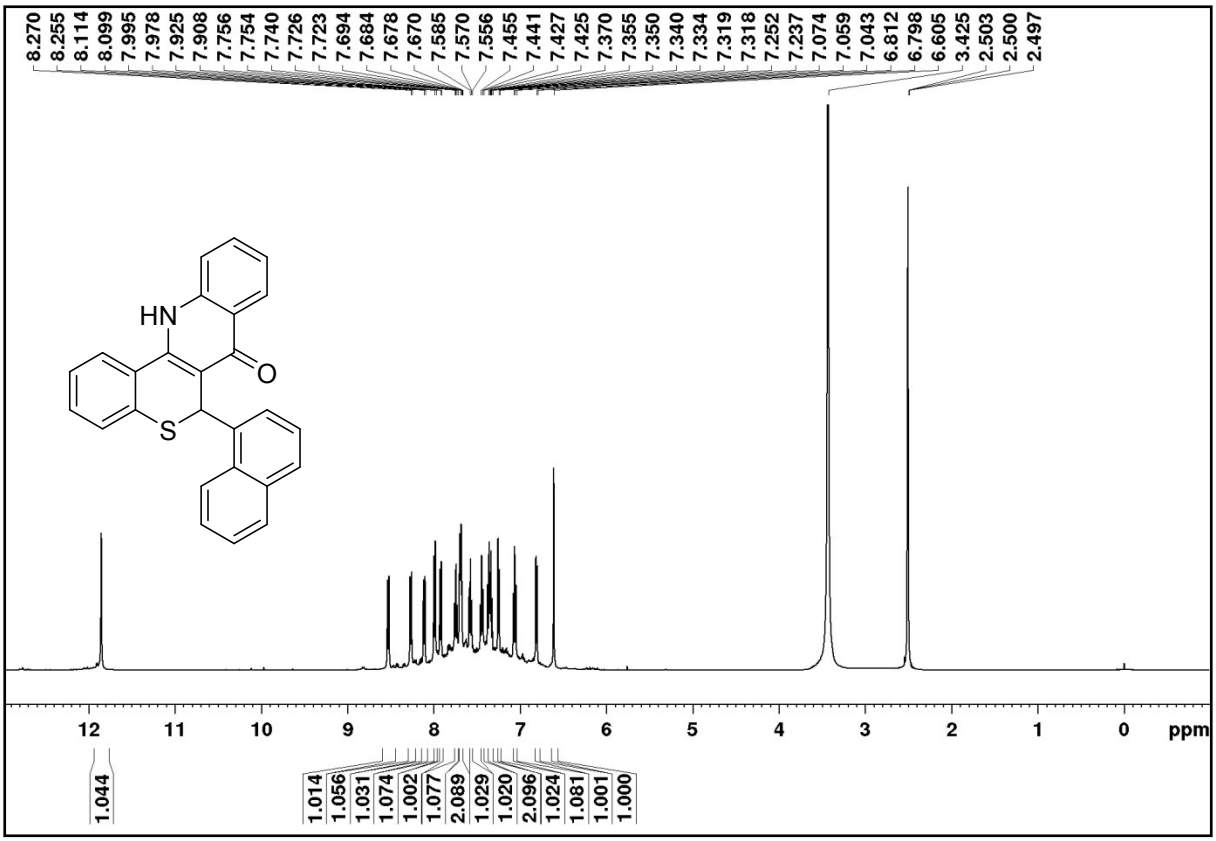


Figure 25: 500 MHz ^{1}H-NMR spectrum of **4m** in DMSO-d6

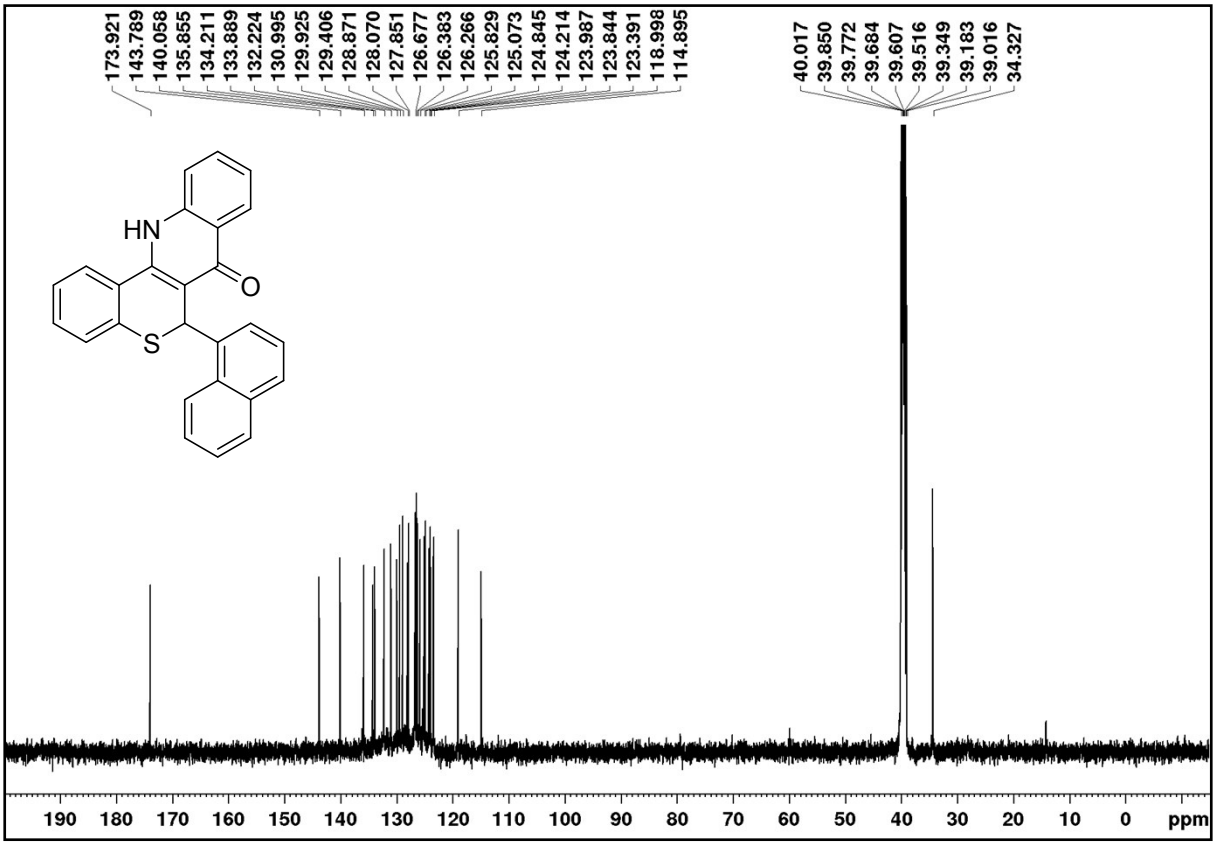


Figure 26: 125 MHz ^{13}C-NMR spectrum of **4m** in DMSO-d6

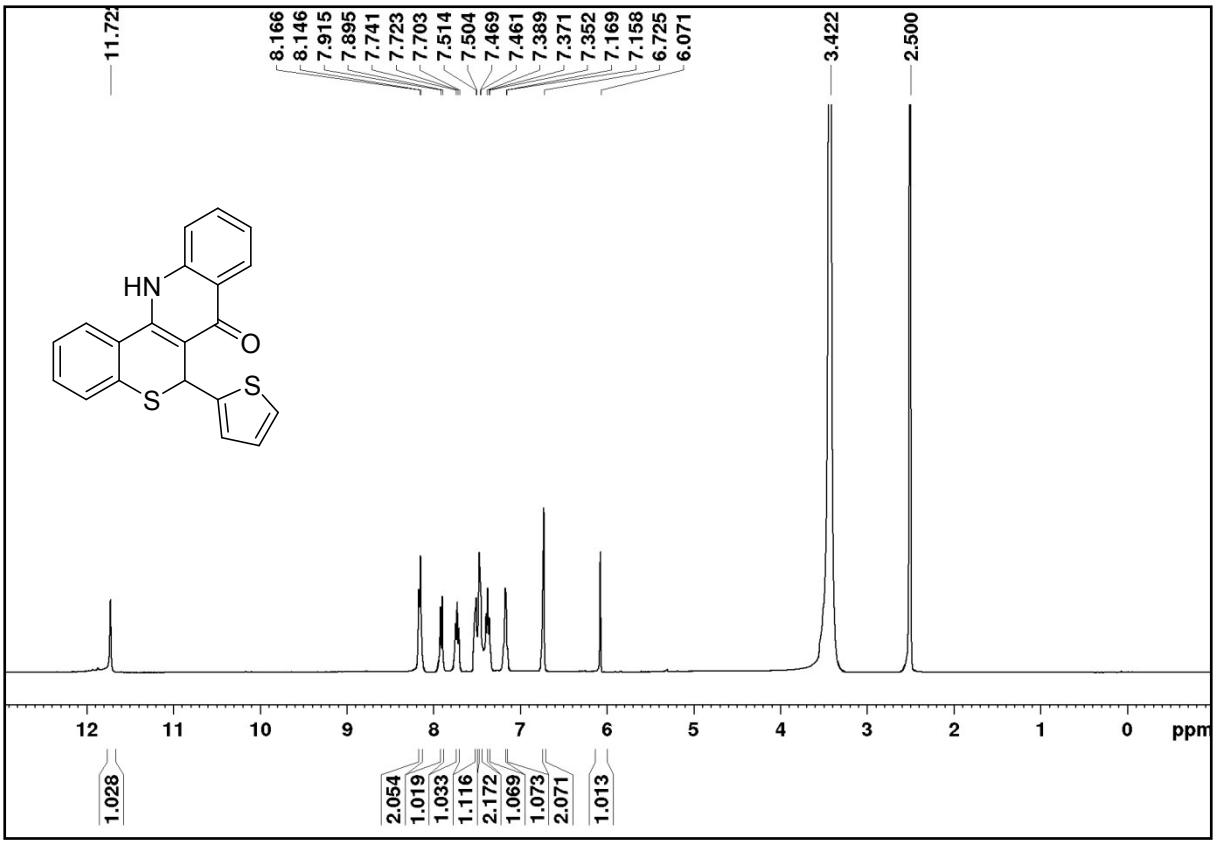


Figure 27: 400 MHz ^{1}H-NMR spectrum of **4n** in DMSO-d6

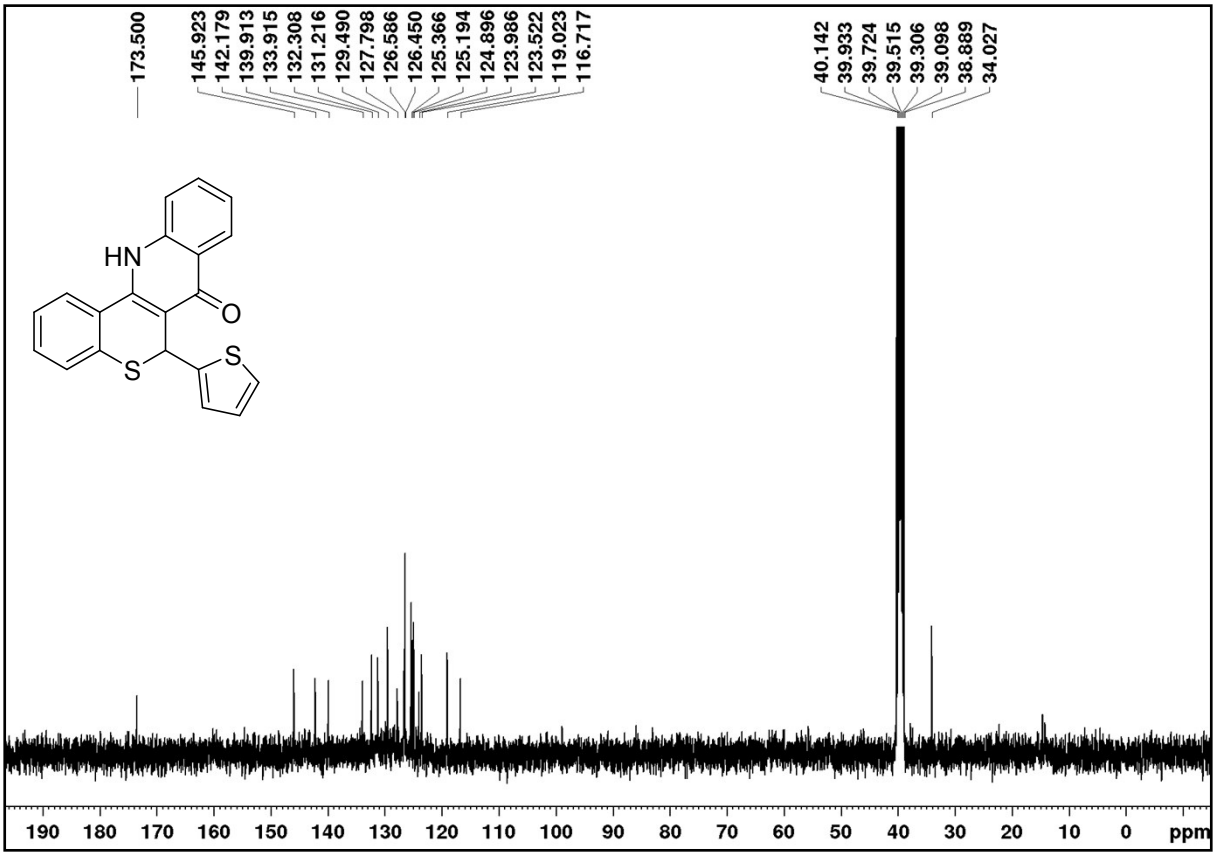


Figure 28: 100 MHz ^{13}C-NMR spectrum of **4n** in DMSO-d6

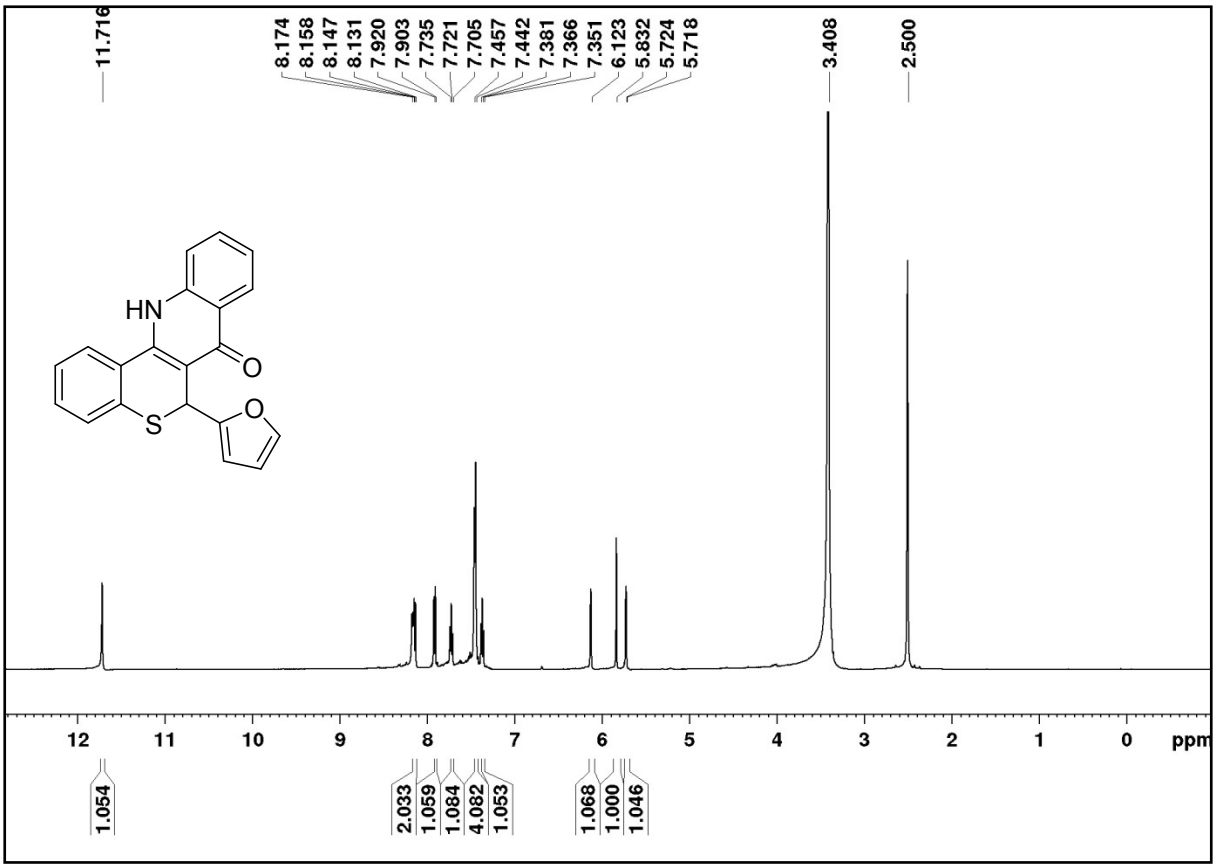


Figure 29: 500 MHz ^{1}H-NMR spectrum of **4o** in DMSO-d6

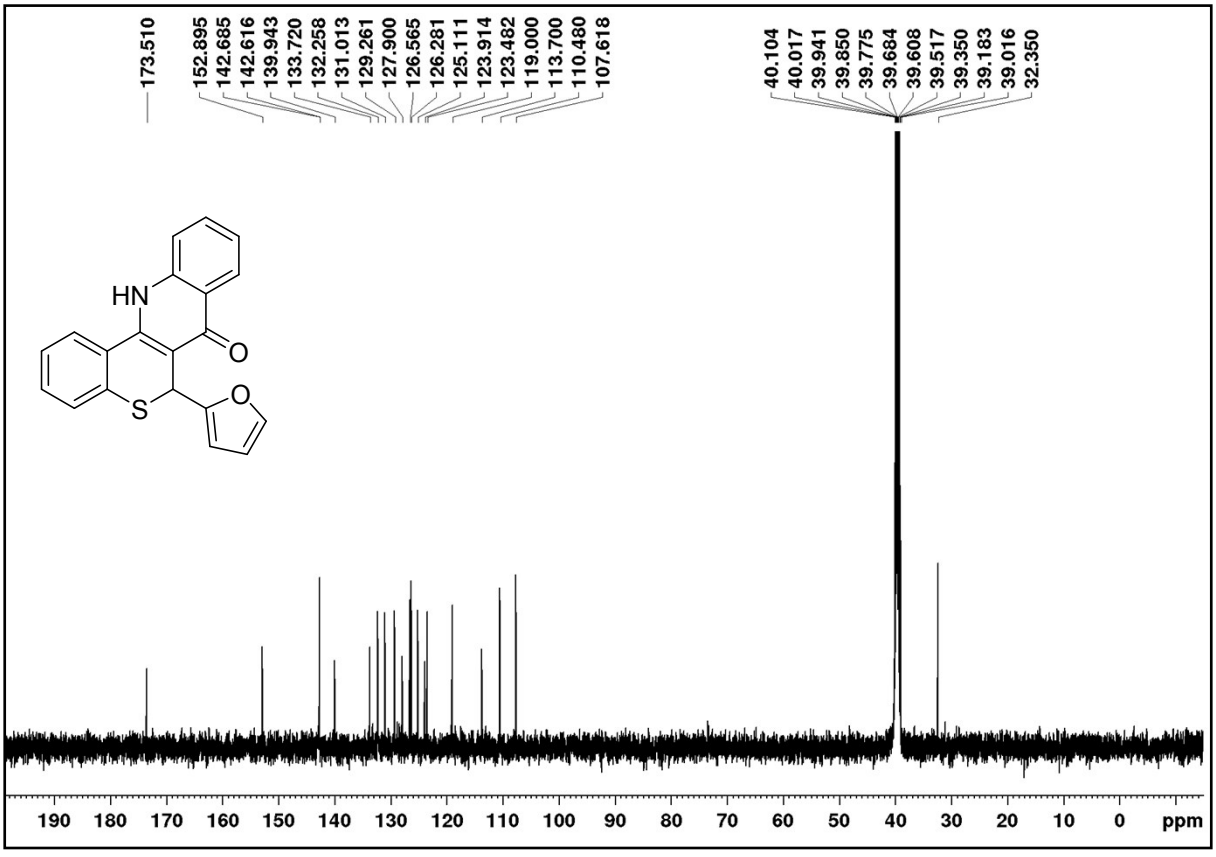


Figure 30: 125 MHz ^{13}C-NMR spectrum of **4o** in DMSO-d6

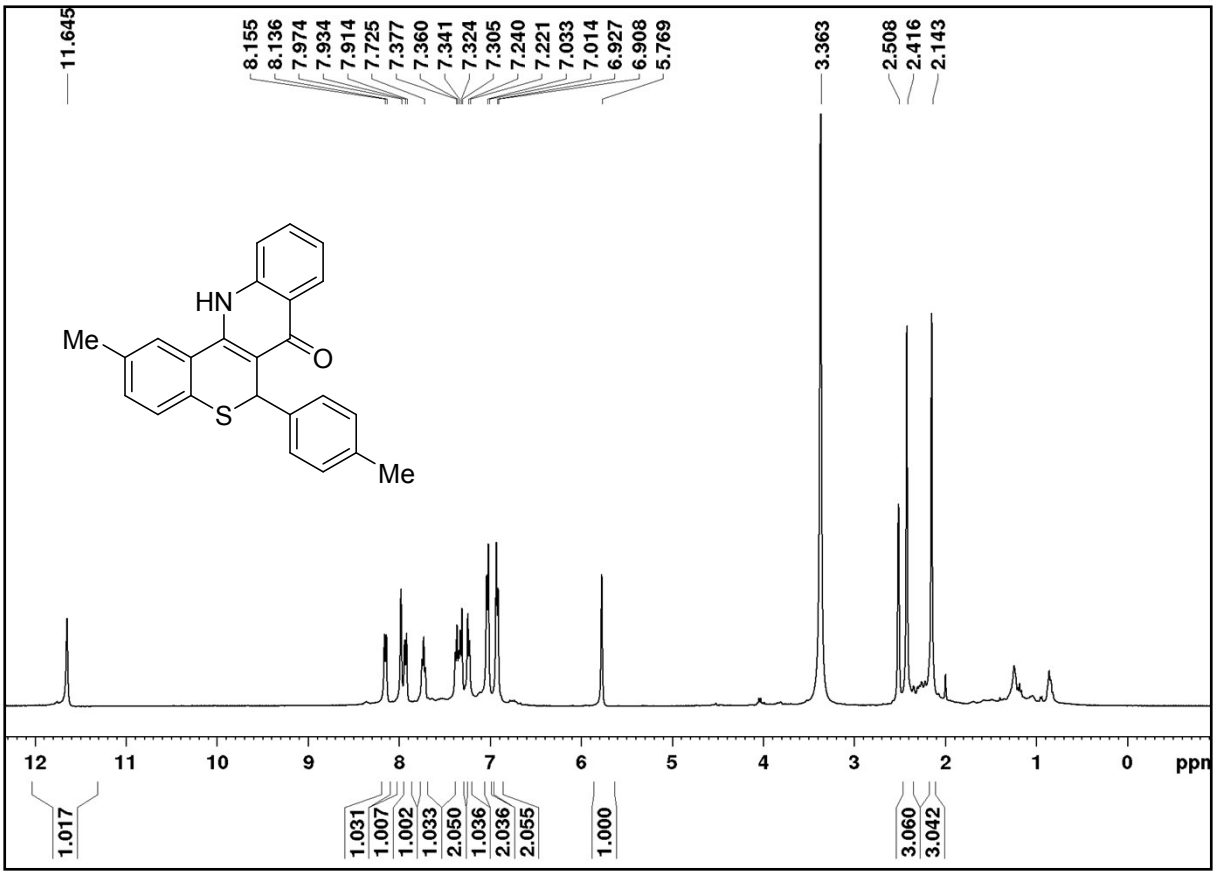


Figure 31: 400 MHz ^{1}H-NMR spectrum of **4p** in DMSO-d6

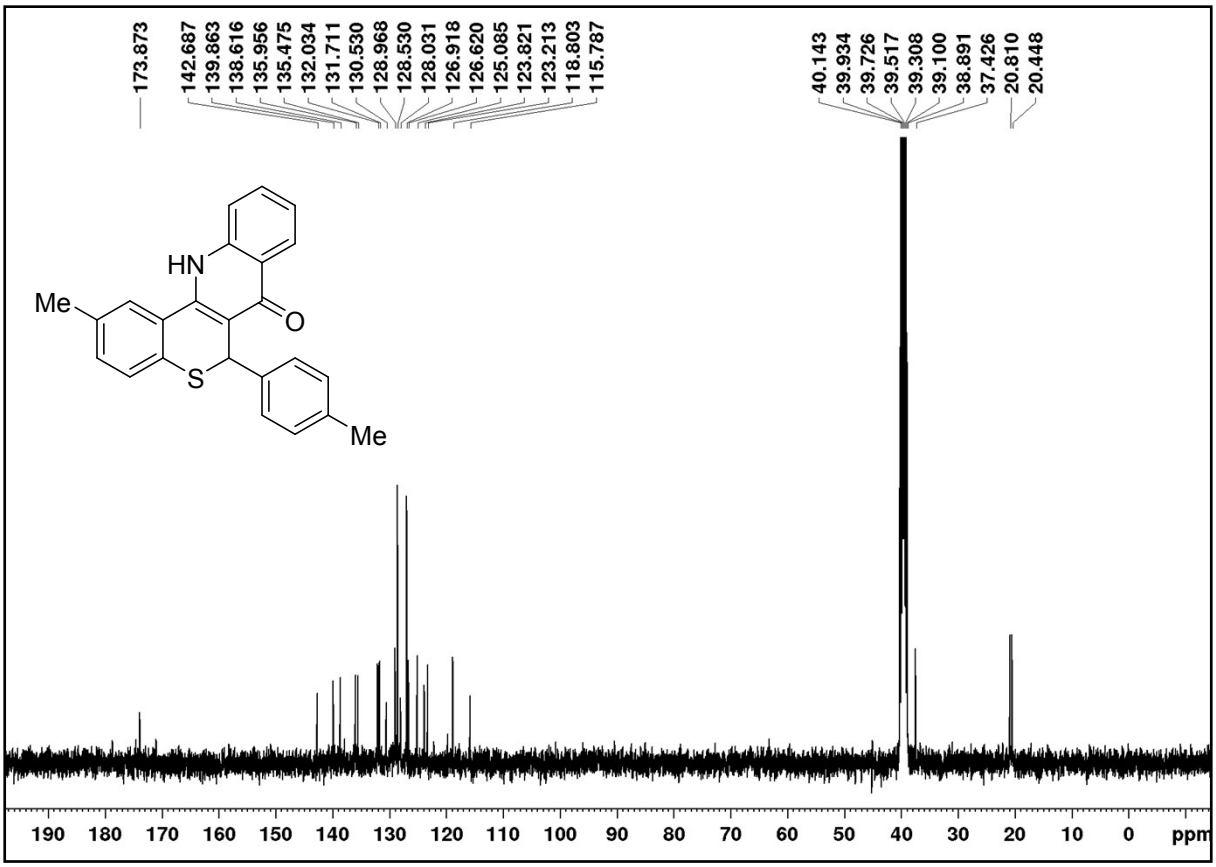


Figure 32: 100 MHz ^{13}C-NMR spectrum of **4p** in DMSO-d6

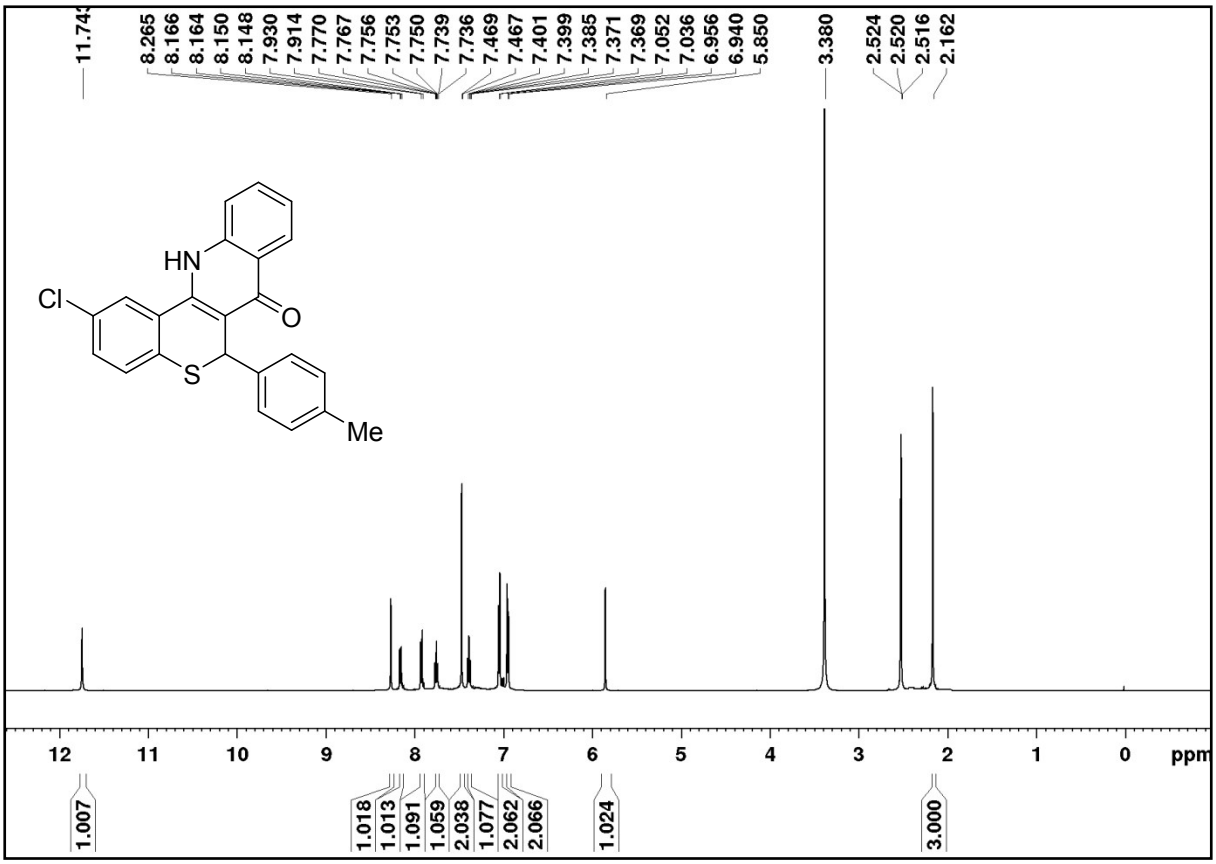


Figure 33: 500 MHz ^{1}H-NMR spectrum of **4q** in DMSO-d6

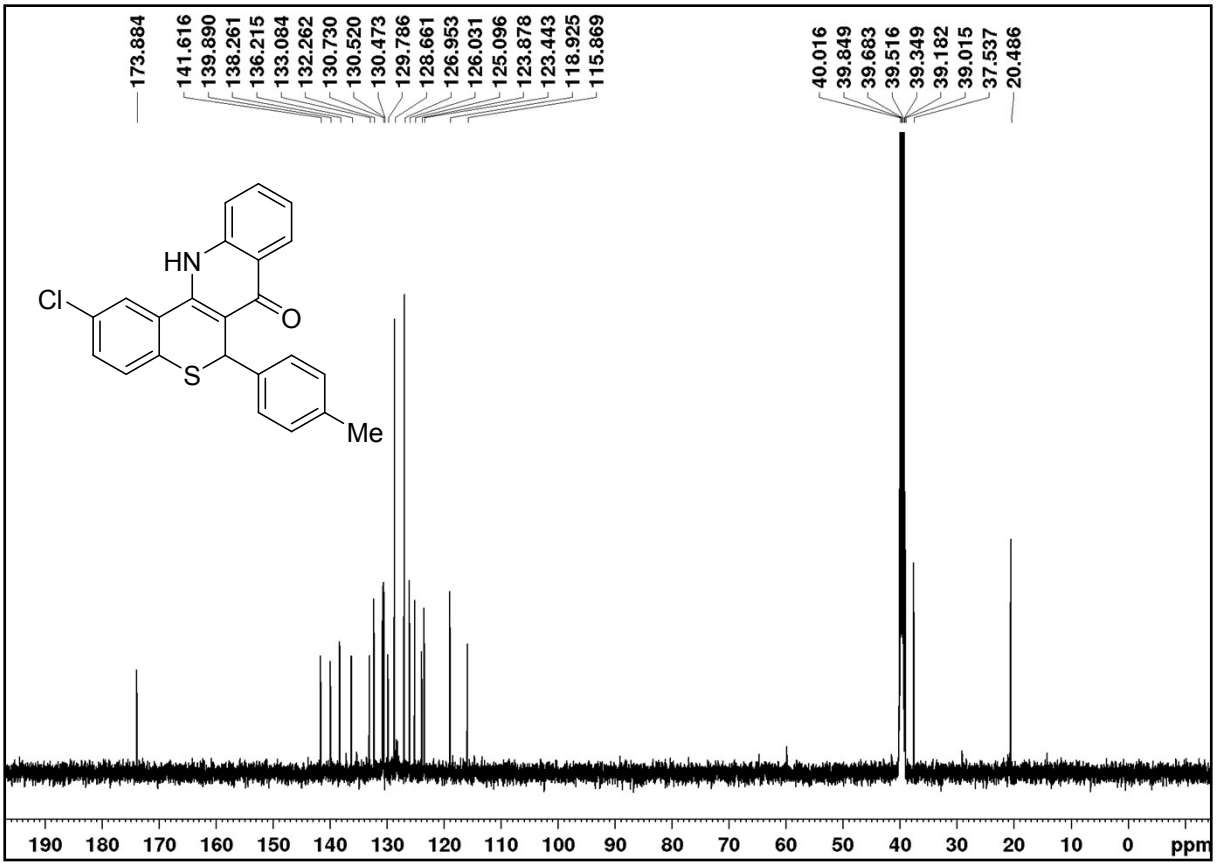


Figure 34: 125 MHz ^{13}C-NMR spectrum of **4q** in DMSO-d6

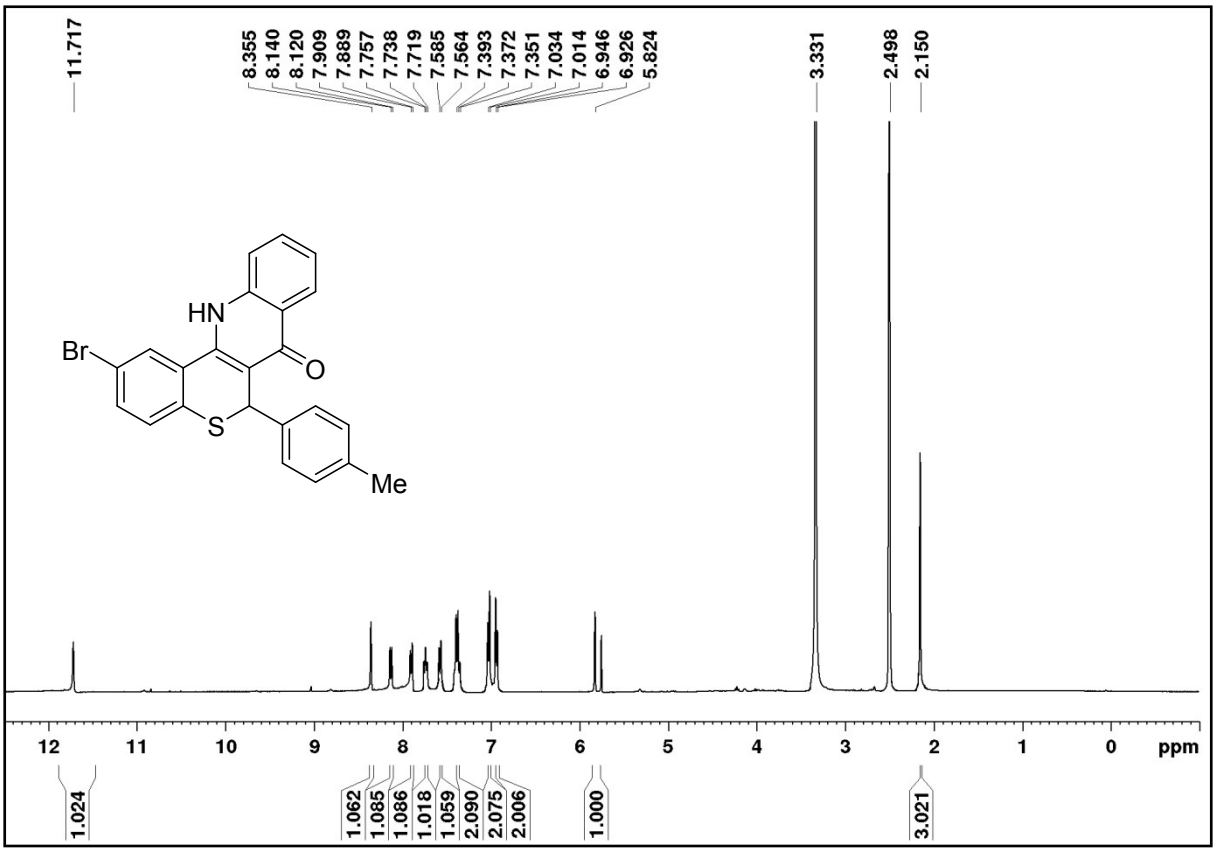


Figure 35: 400 MHz ^{1}H-NMR spectrum of **4r** in DMSO-d6

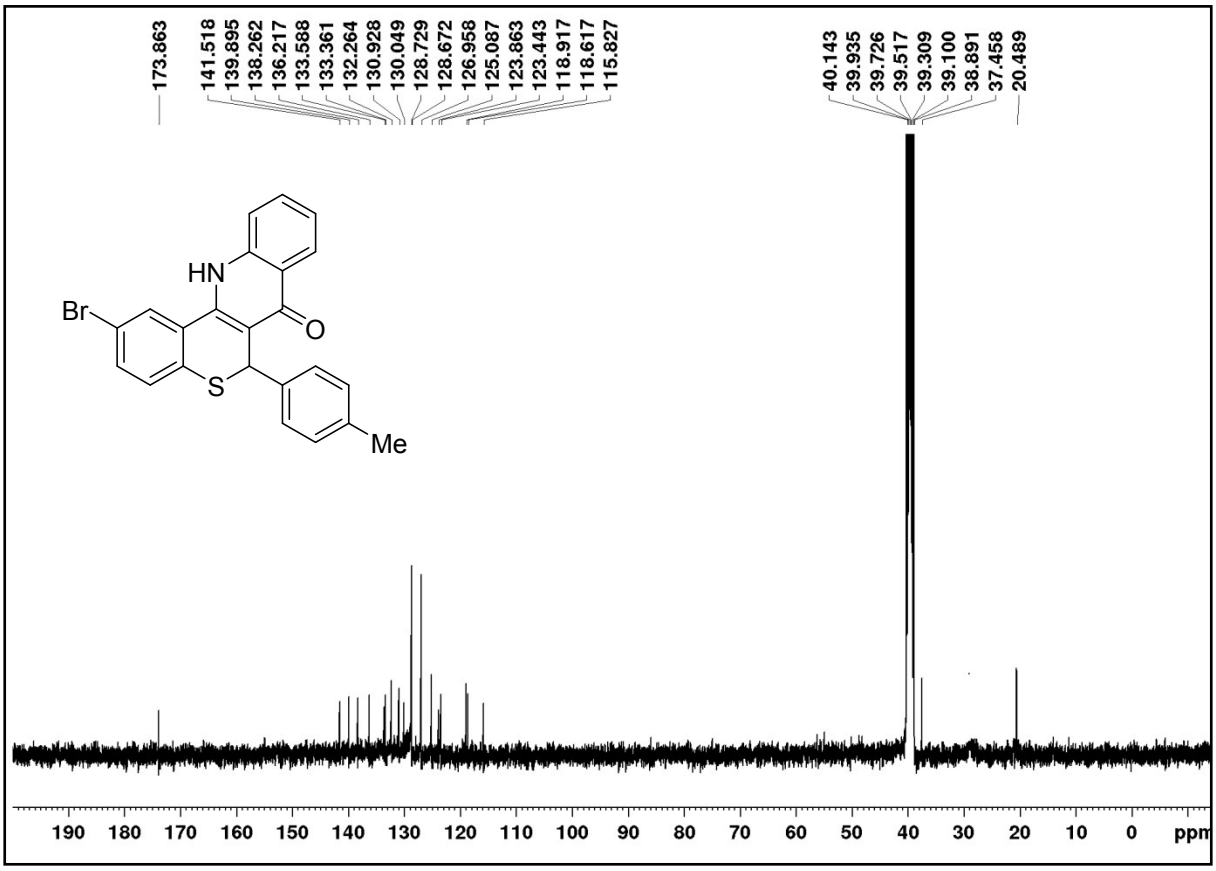


Figure 36: 100 MHz ^{13}C-NMR spectrum of **4r** in DMSO-d6

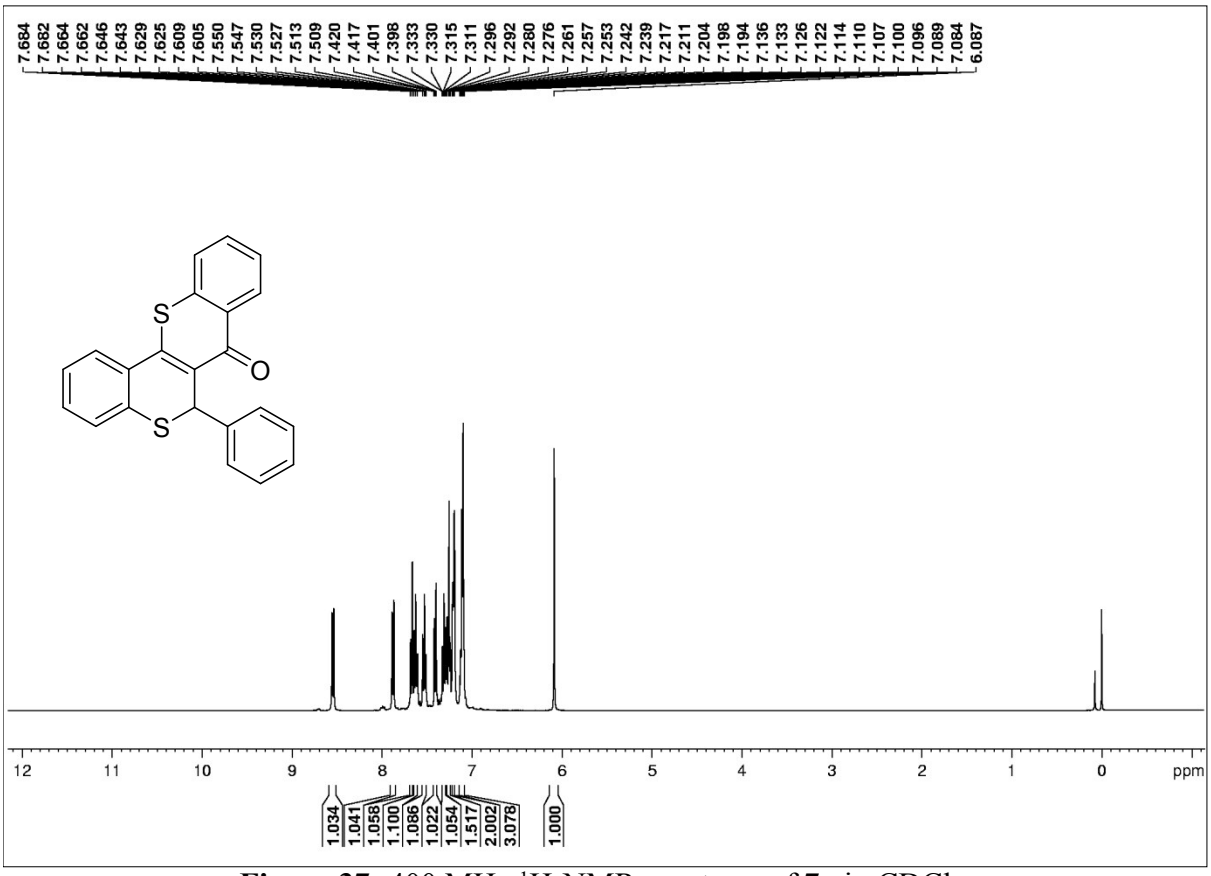


Figure 37: 400 MHz ^{1}H-NMR spectrum of **7a** in $CDCl_3$

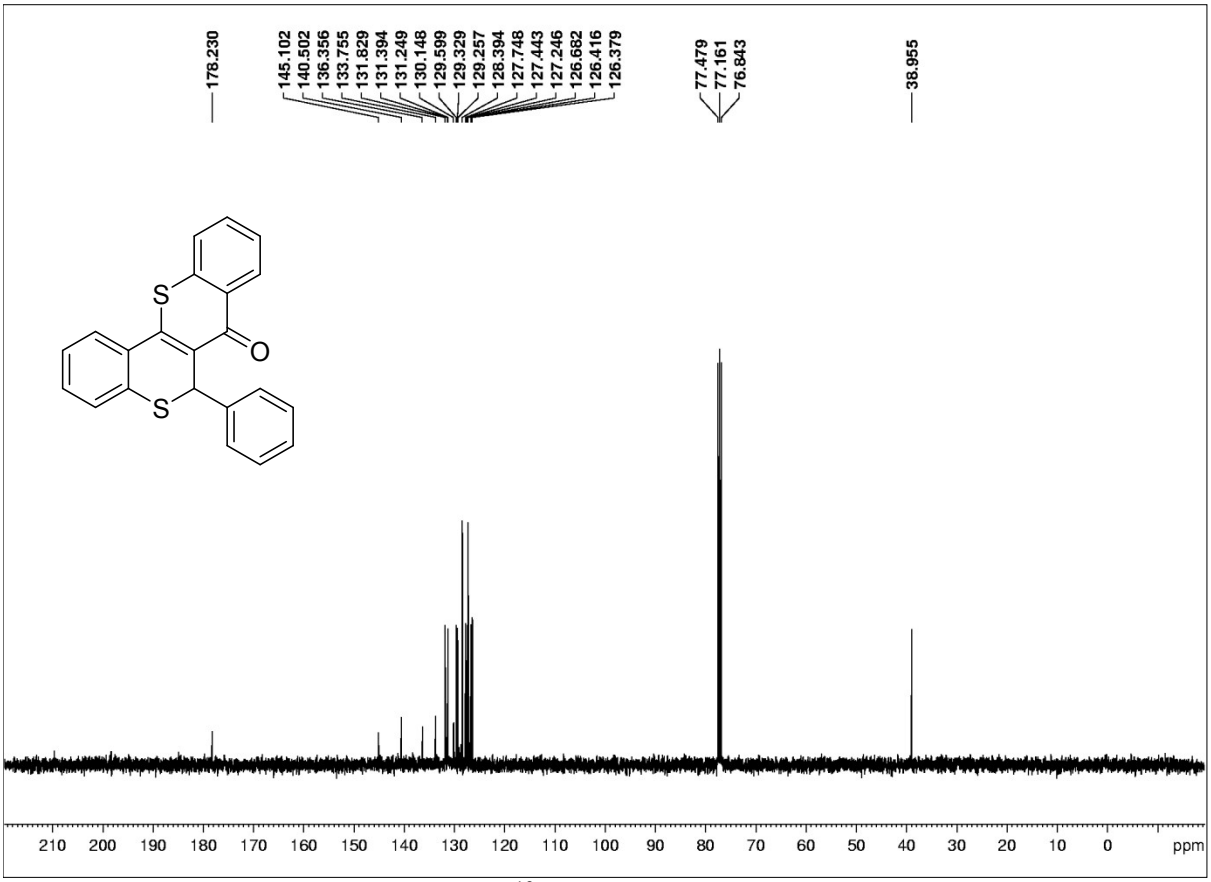


Figure 38: 100 MHz ^{13}C-NMR spectrum of **7a** in $CDCl_3$

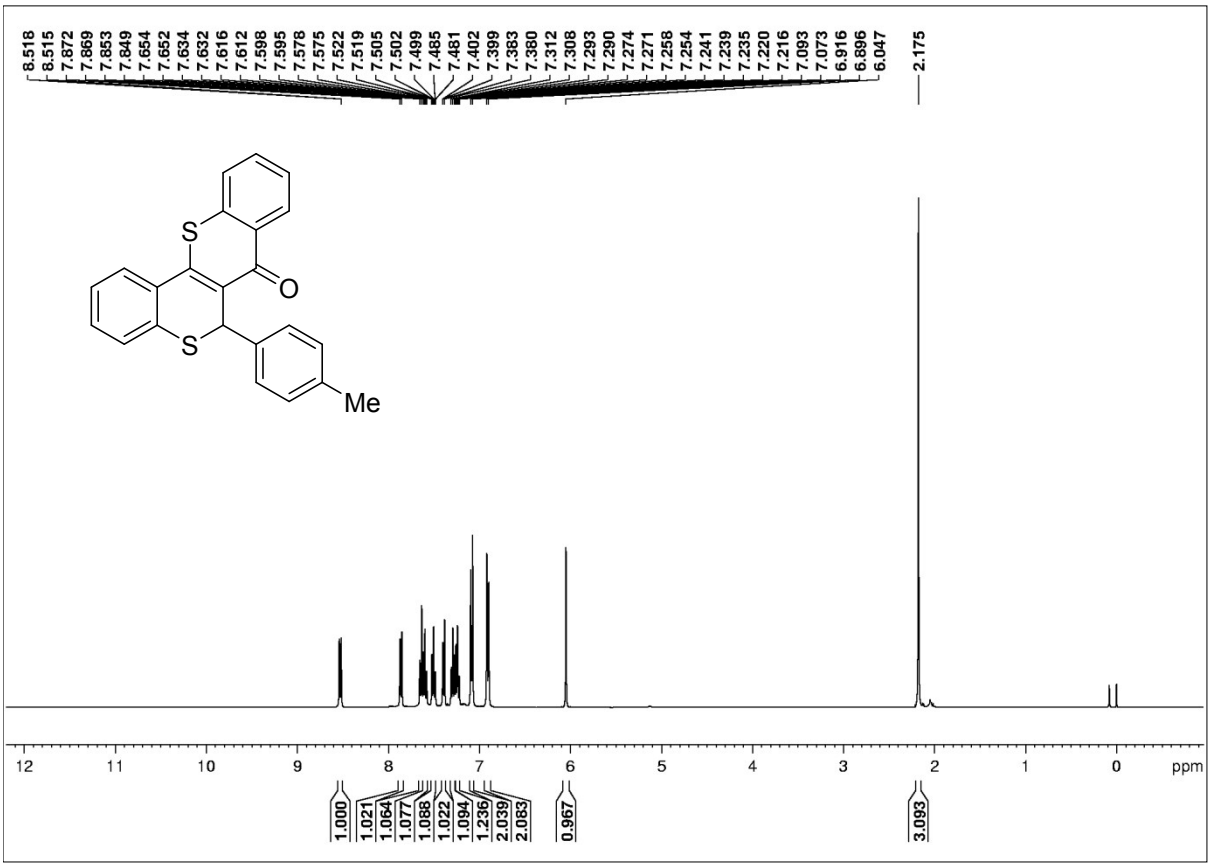


Figure 39: 400 MHz ^{1}H-NMR spectrum of **7b** in $CDCl_3$

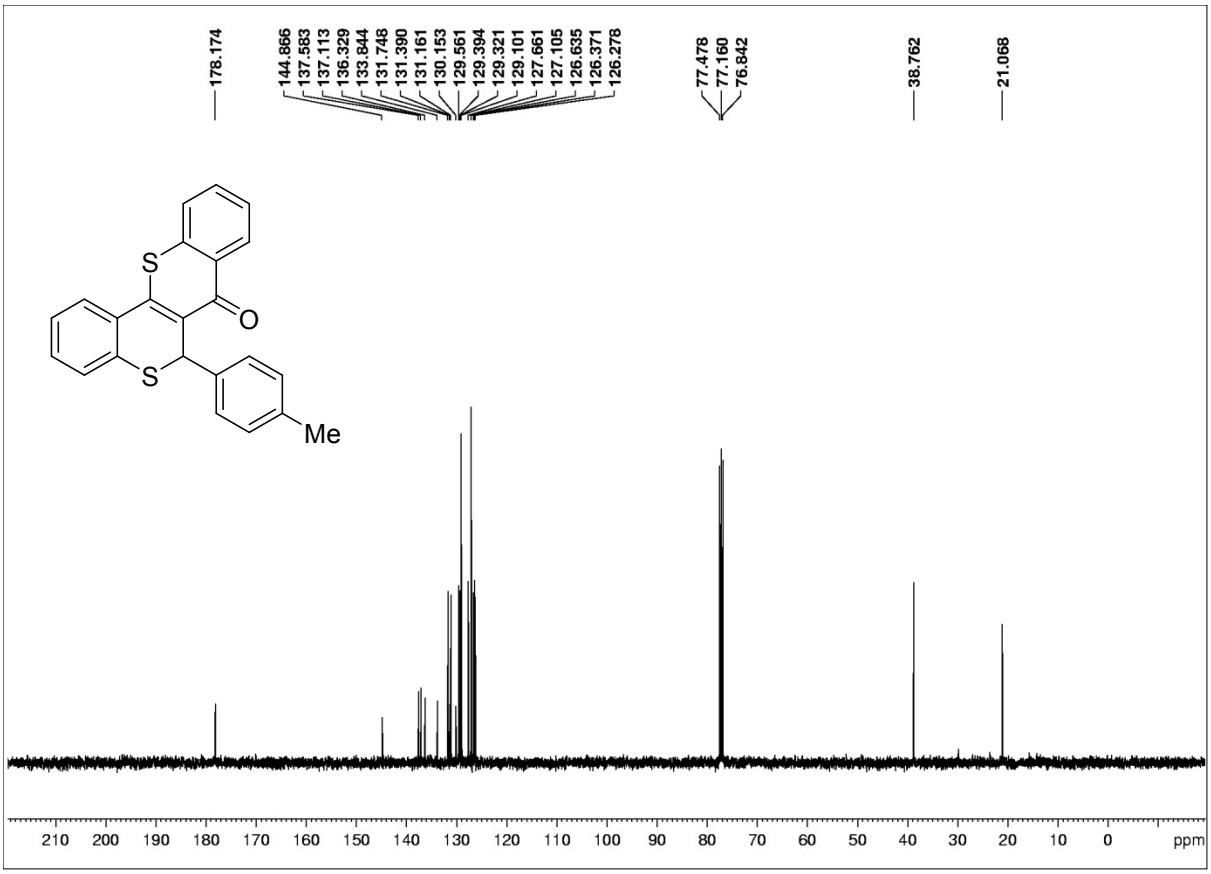


Figure 40: 100 MHz ^{13}C-NMR spectrum of **7b** in $CDCl_3$

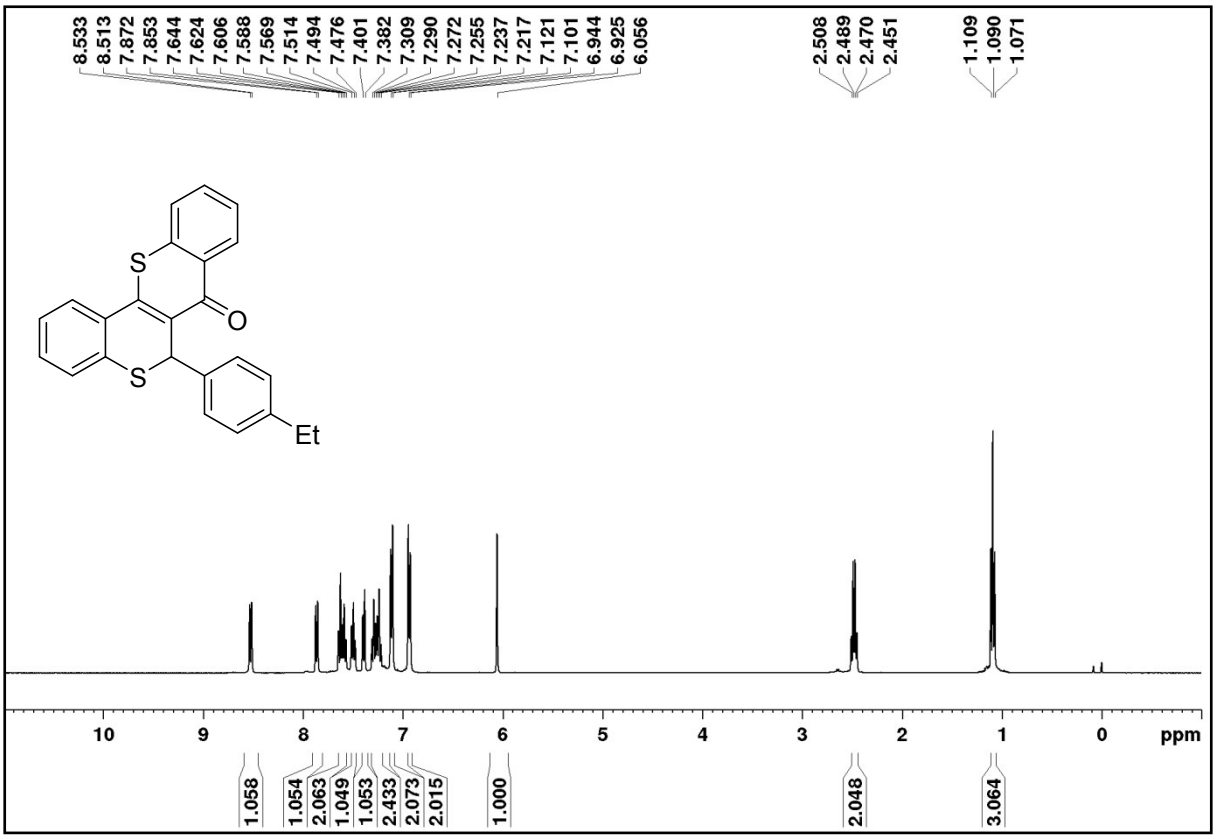


Figure 41: 400 MHz ^{1}H-NMR spectrum of **7c** in $CDCl_3$

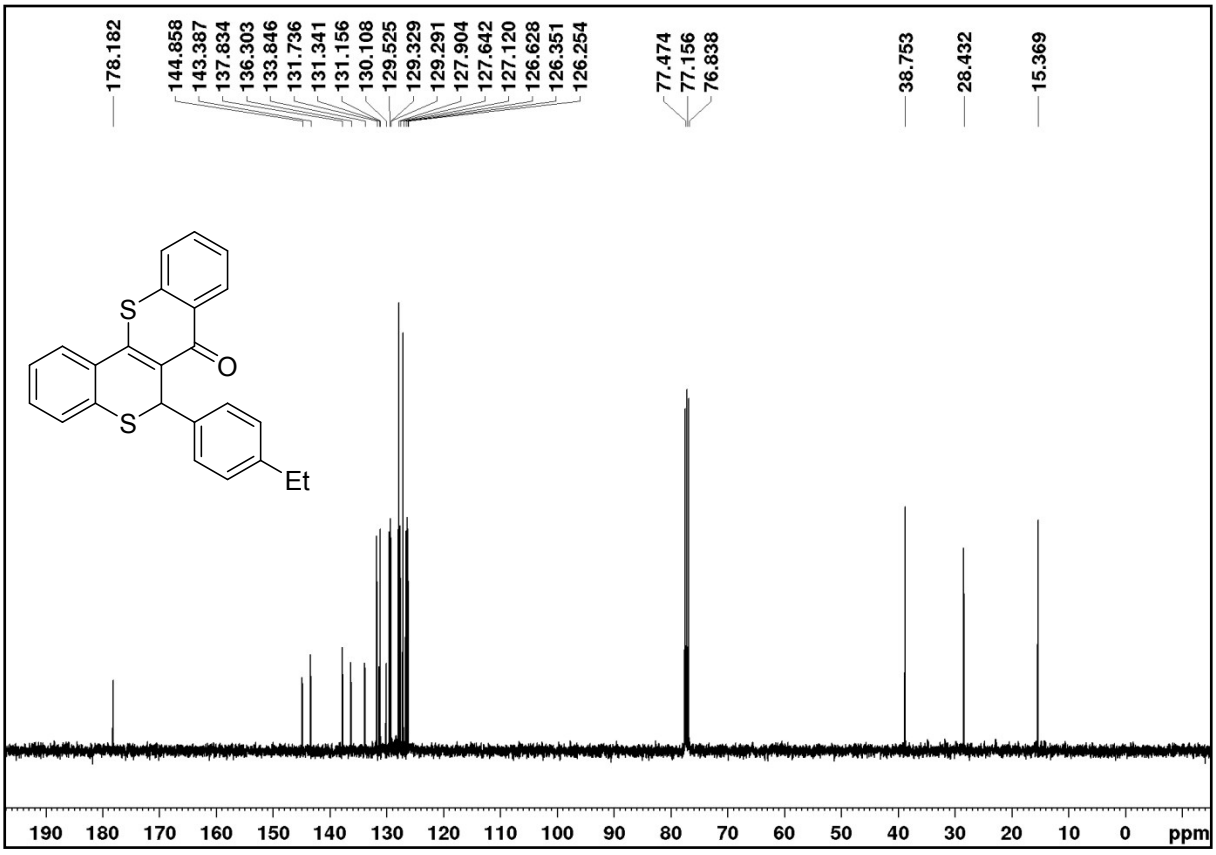


Figure 42: 100 MHz ^{13}C-NMR spectrum of **7c** in $CDCl_3$

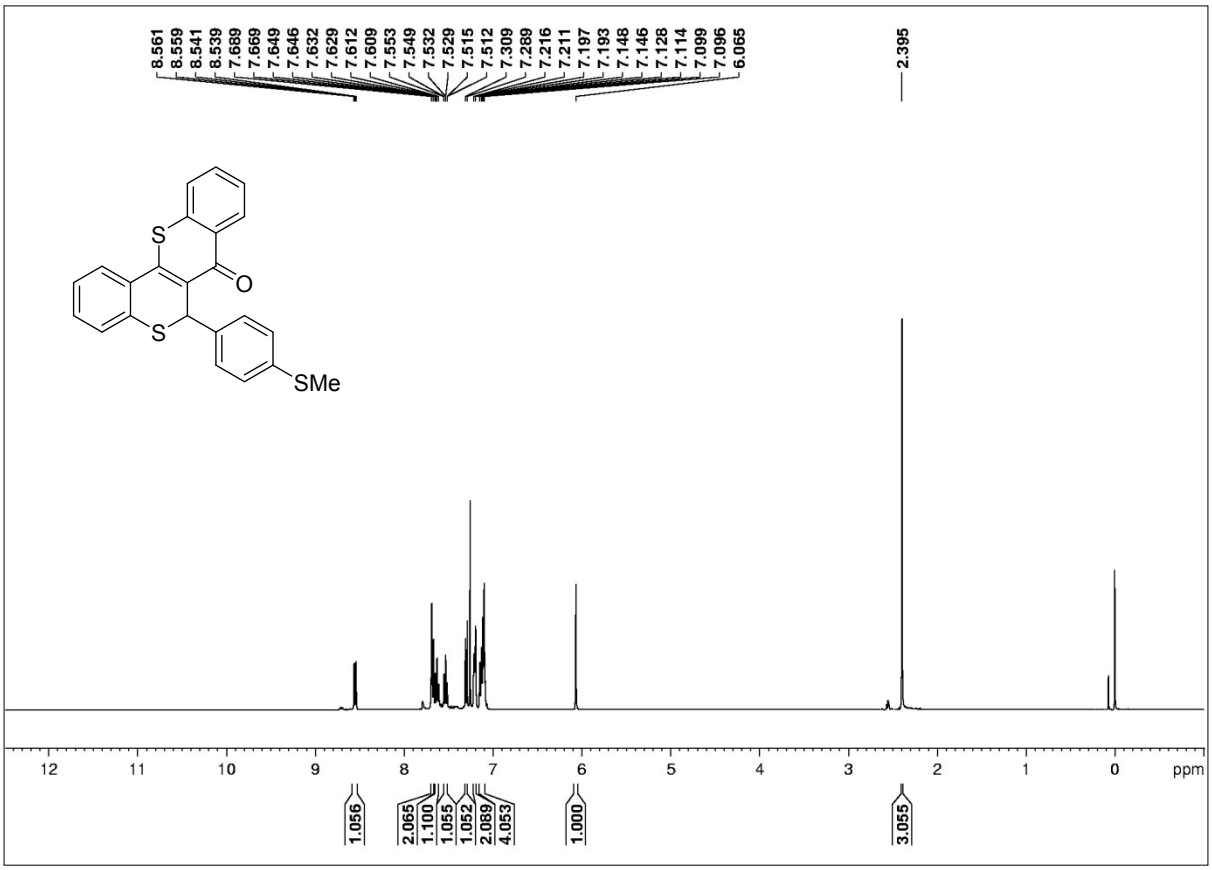


Figure 43: 400 MHz ^{1}H-NMR spectrum of **7d** in $CDCl_3$

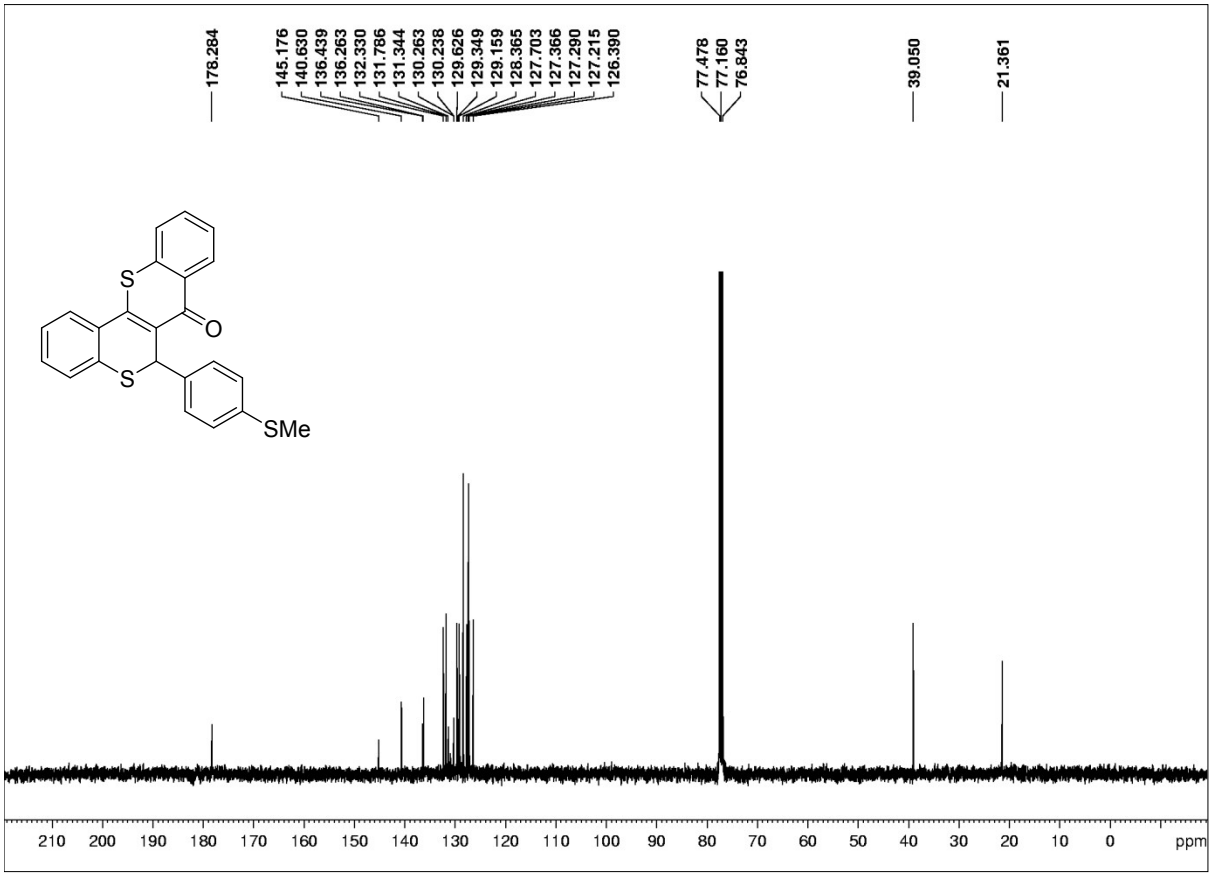


Figure 44: 400 MHz ^{1}H-NMR spectrum of **7d** in $CDCl_3$

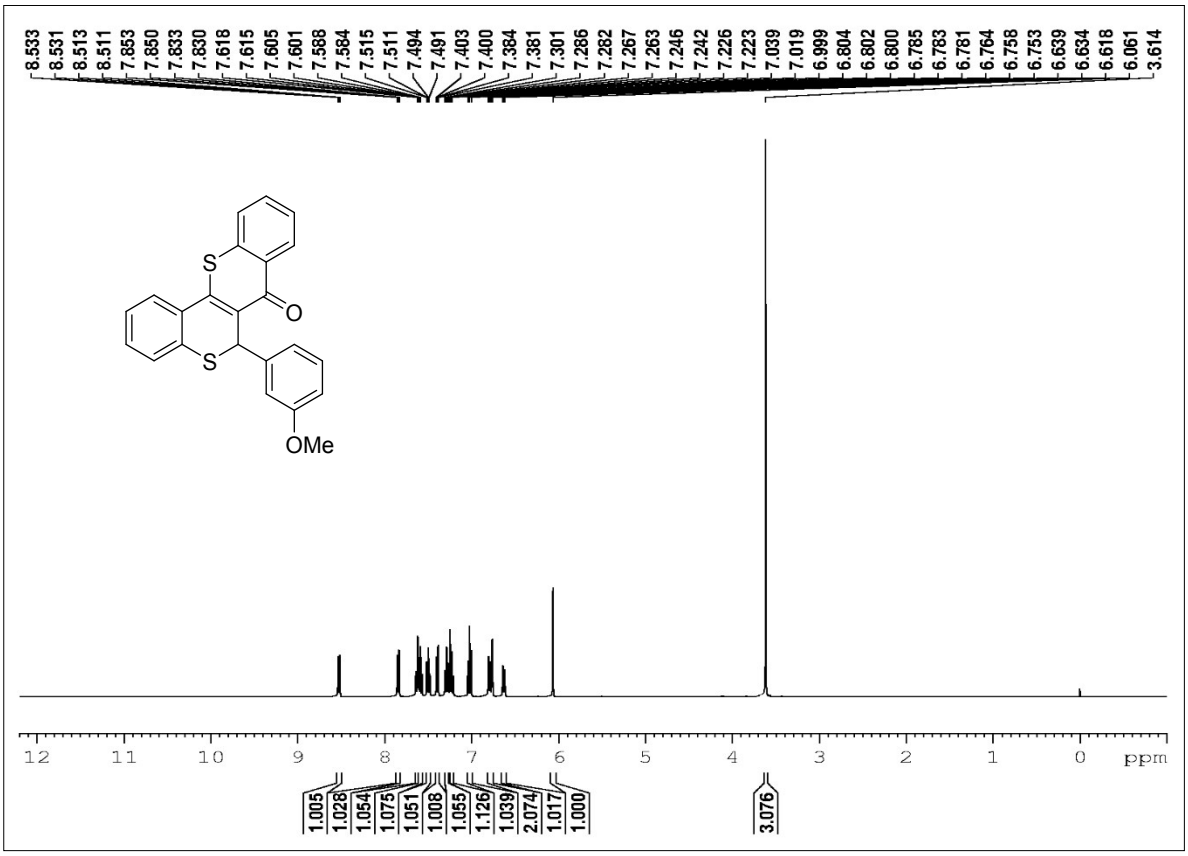


Figure 45: 400 MHz ^{1}H-NMR spectrum of **7e** in $CDCl_3$

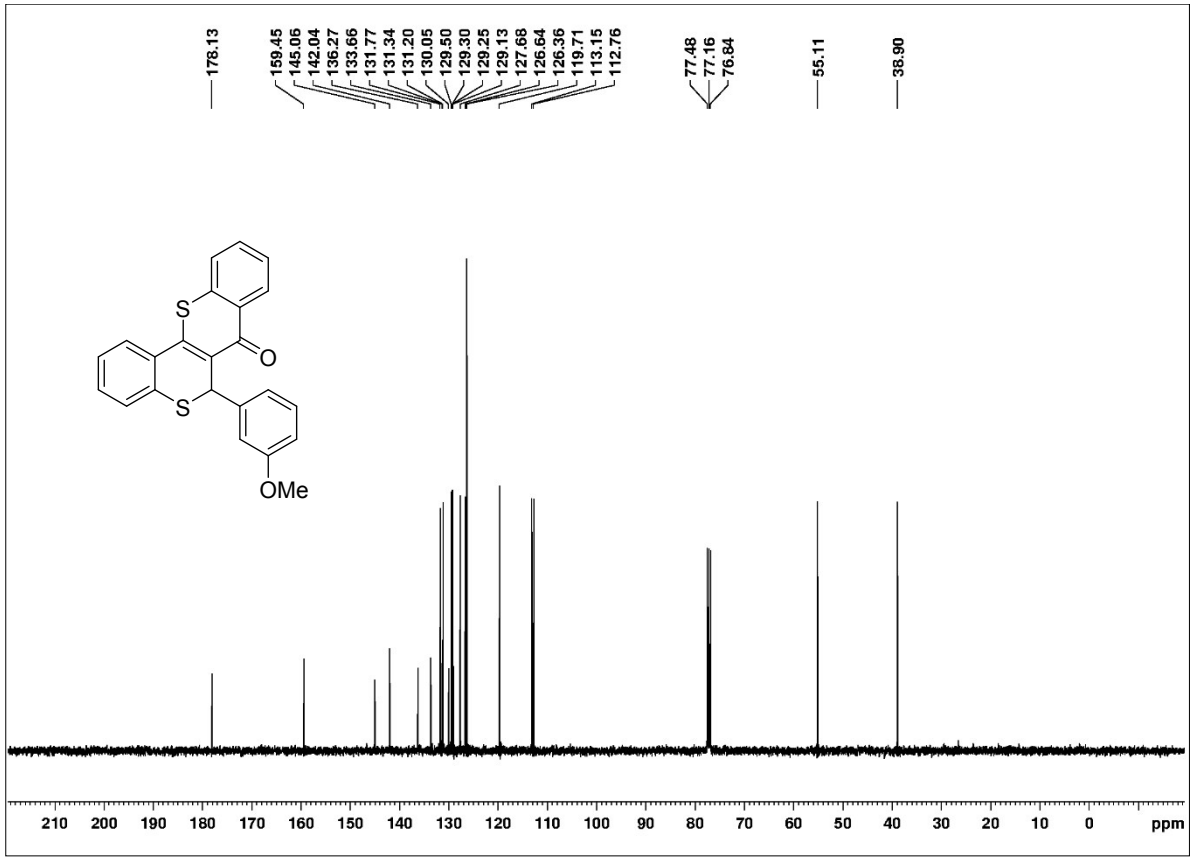


Figure 46: 100 MHz ^{13}C-NMR spectrum of **7e** in $CDCl_3$

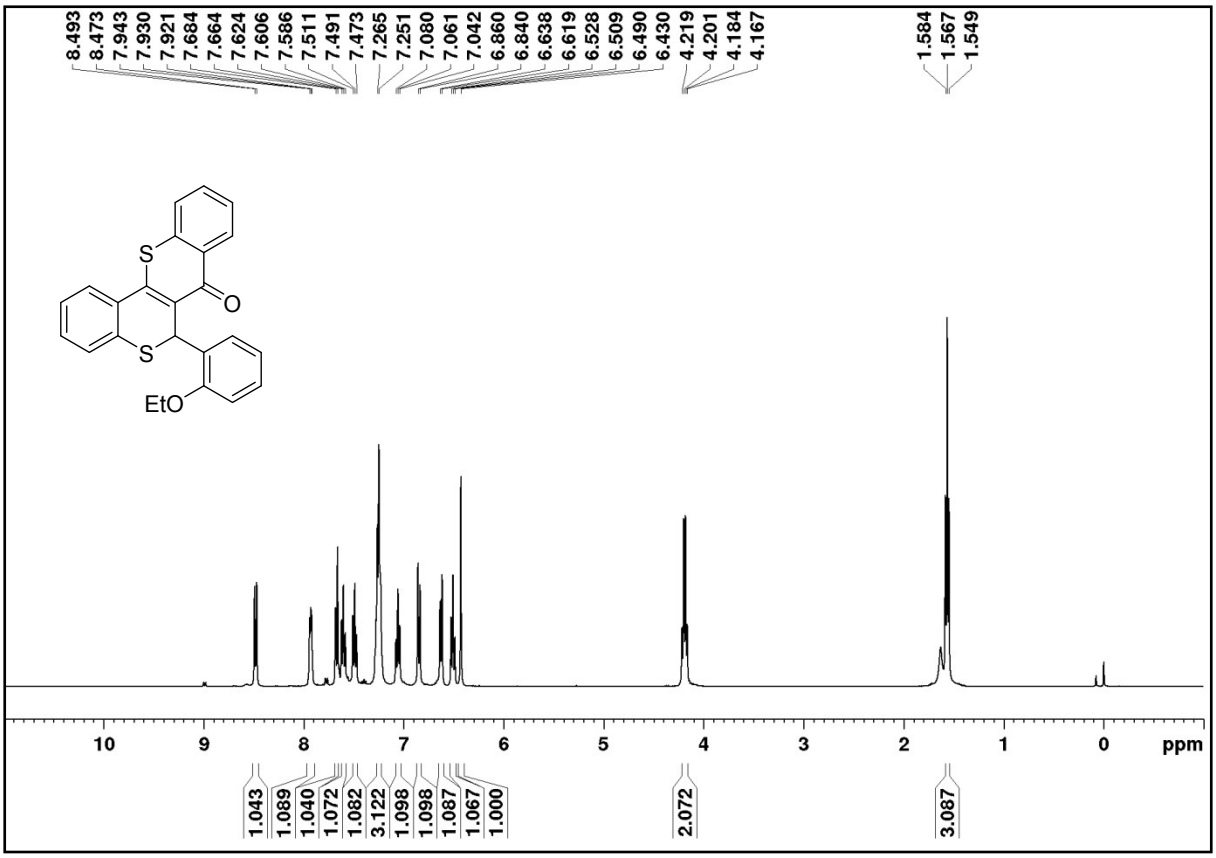


Figure 47: 400 MHz ^{1}H-NMR spectrum of **7f** in $CDCl_3$

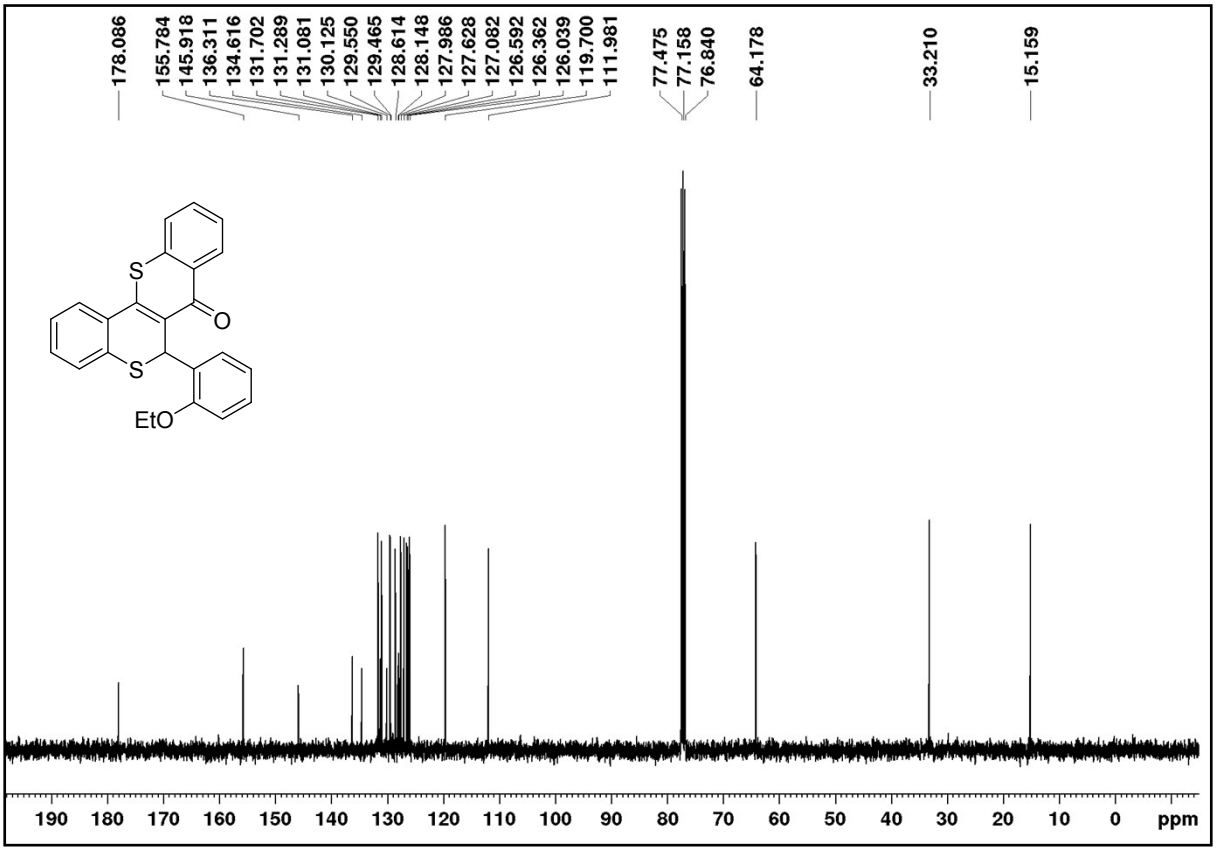


Figure 48: 100 MHz ^{13}C-NMR spectrum of **7f** in $CDCl_3$

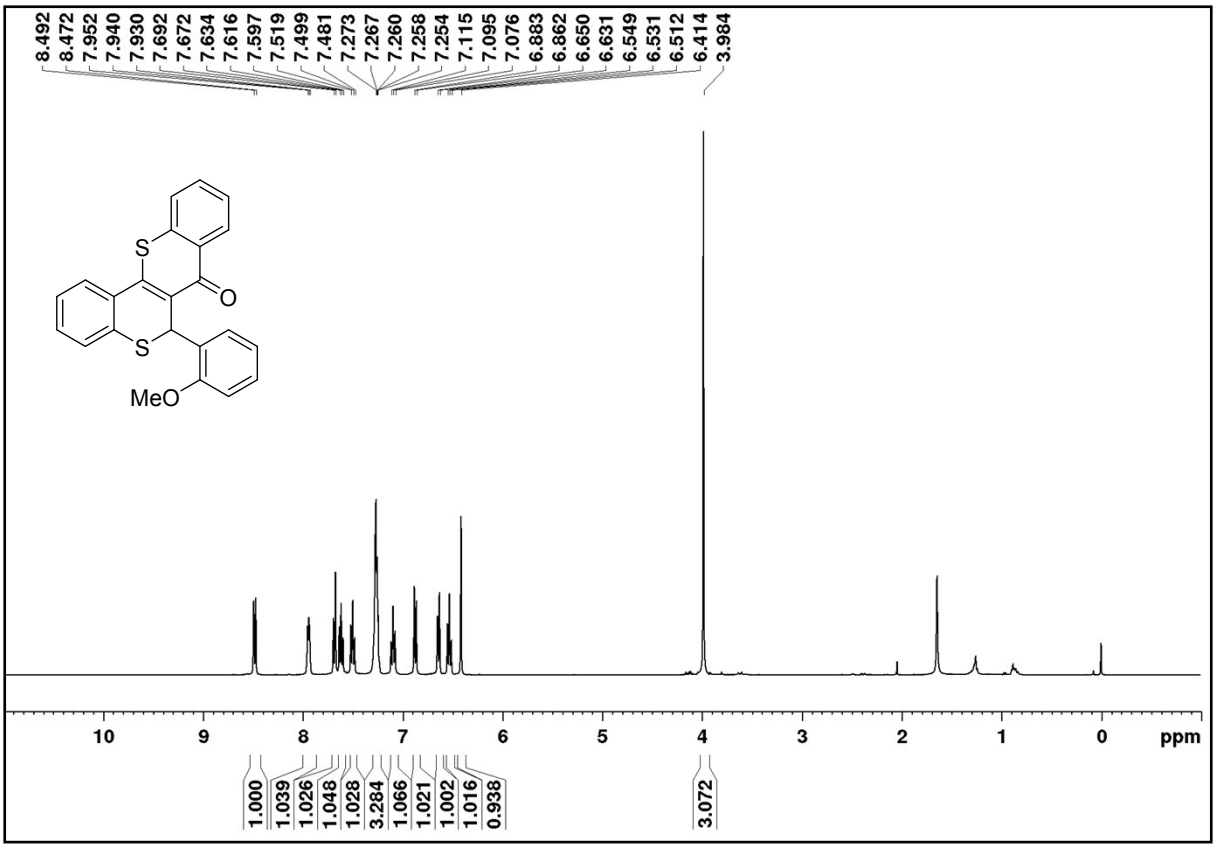


Figure 49: 400 MHz ^{1}H-NMR spectrum of **7g** in $CDCl_3$

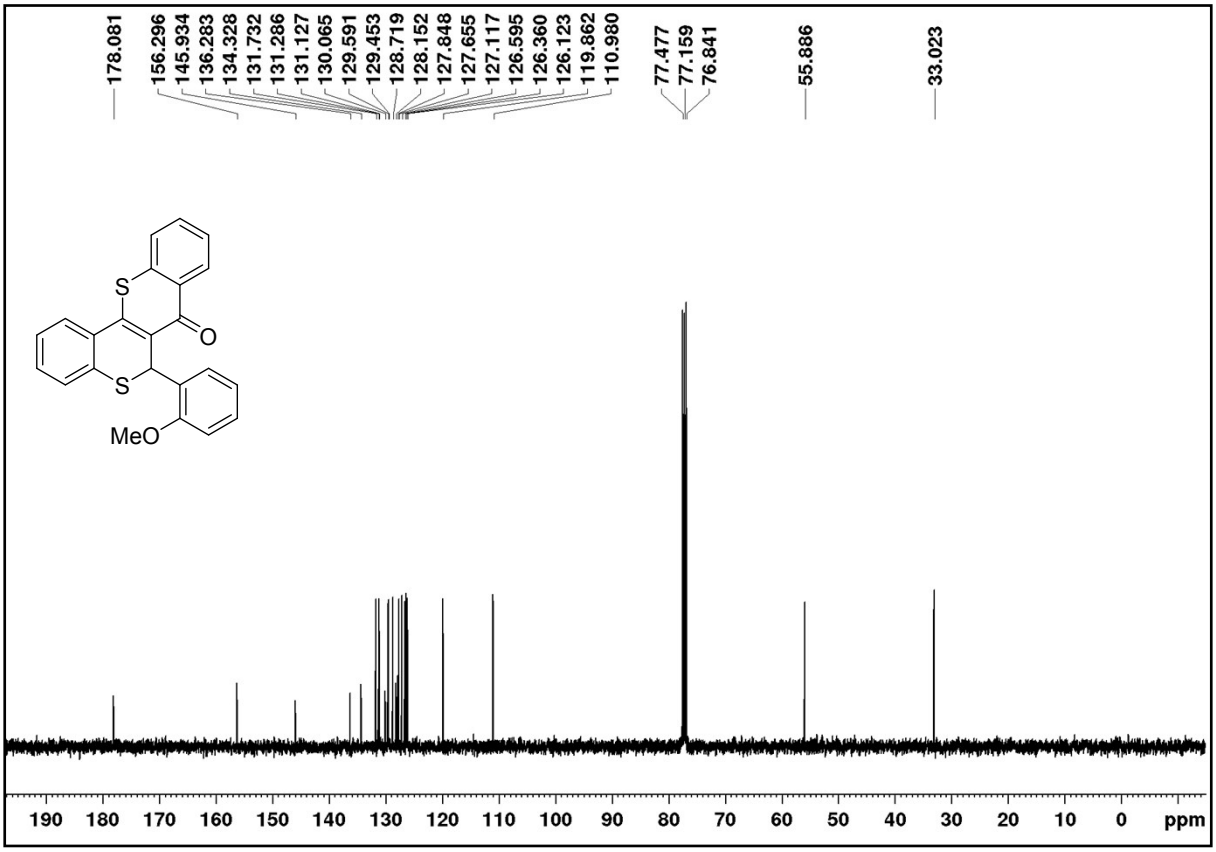


Figure 50: 100 MHz ^{13}C-NMR spectrum of **7g** in $CDCl_3$

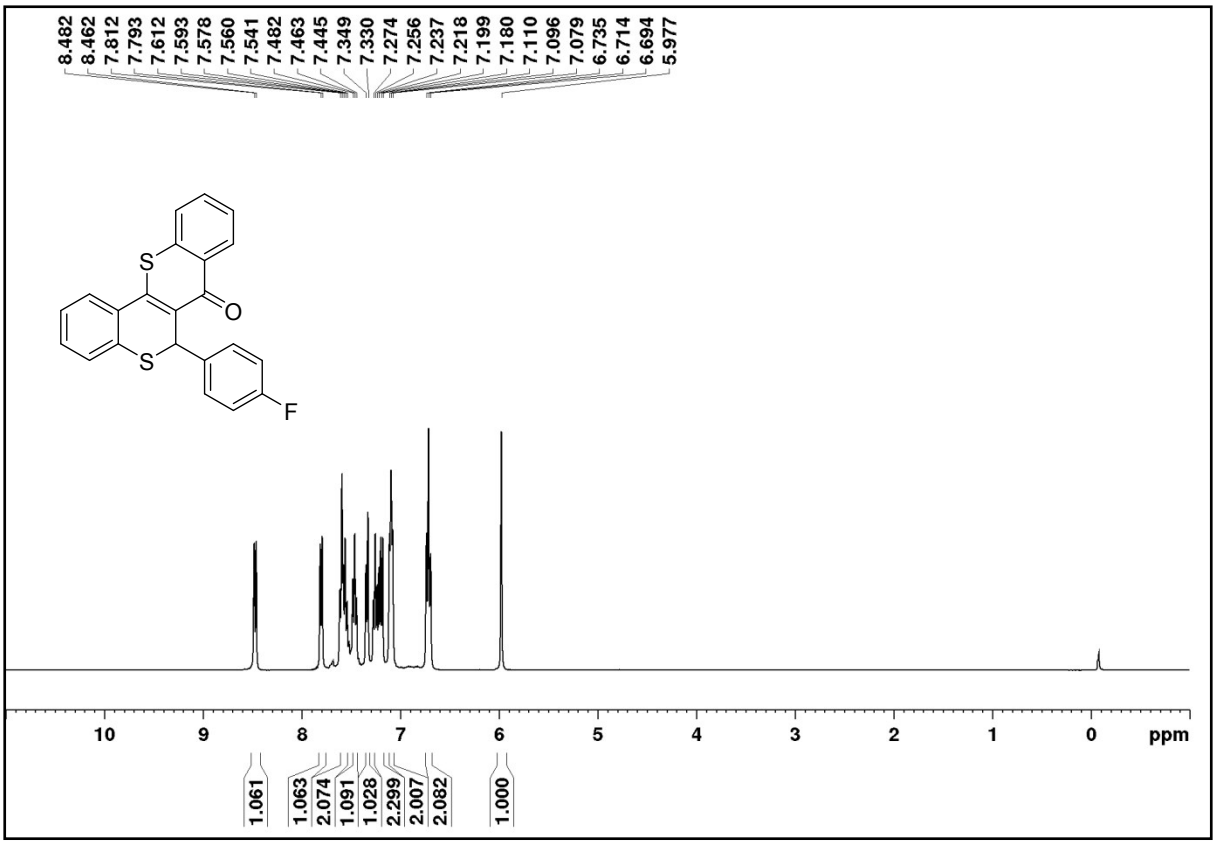


Figure 51: 400 MHz ^{1}H-NMR spectrum of **7h** in $CDCl_3$

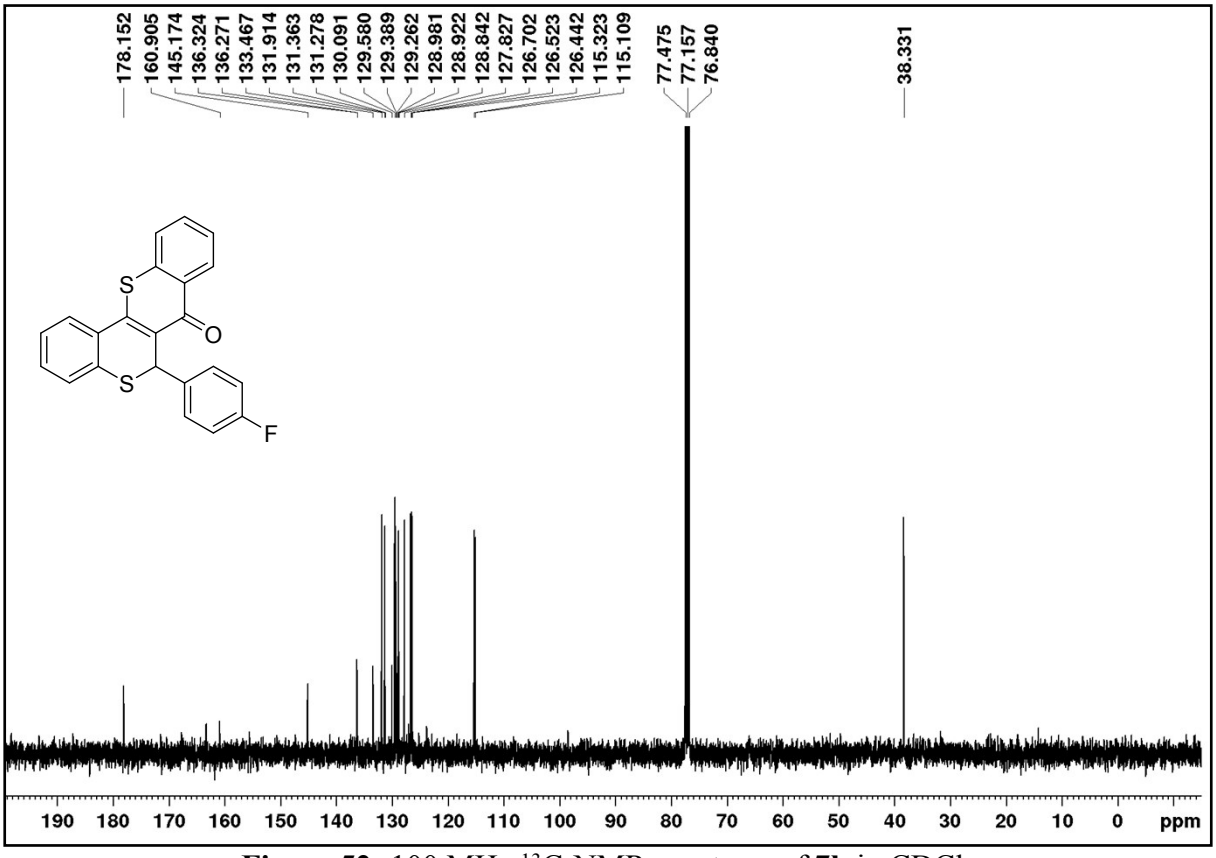


Figure 52: 100 MHz ^{13}C-NMR spectrum of **7h** in $CDCl_3$

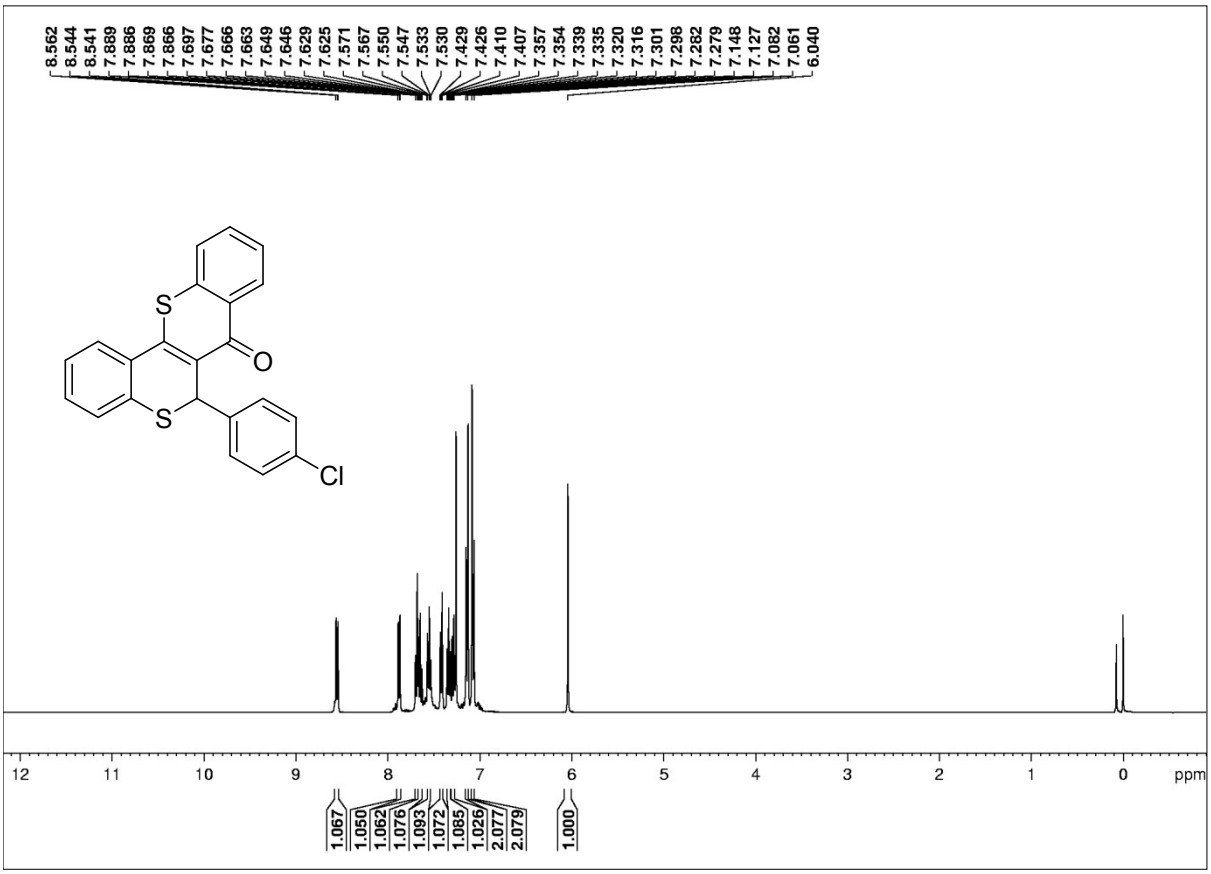


Figure 53: 400 MHz ^{1}H-NMR spectrum of **7i** in $CDCl_3$

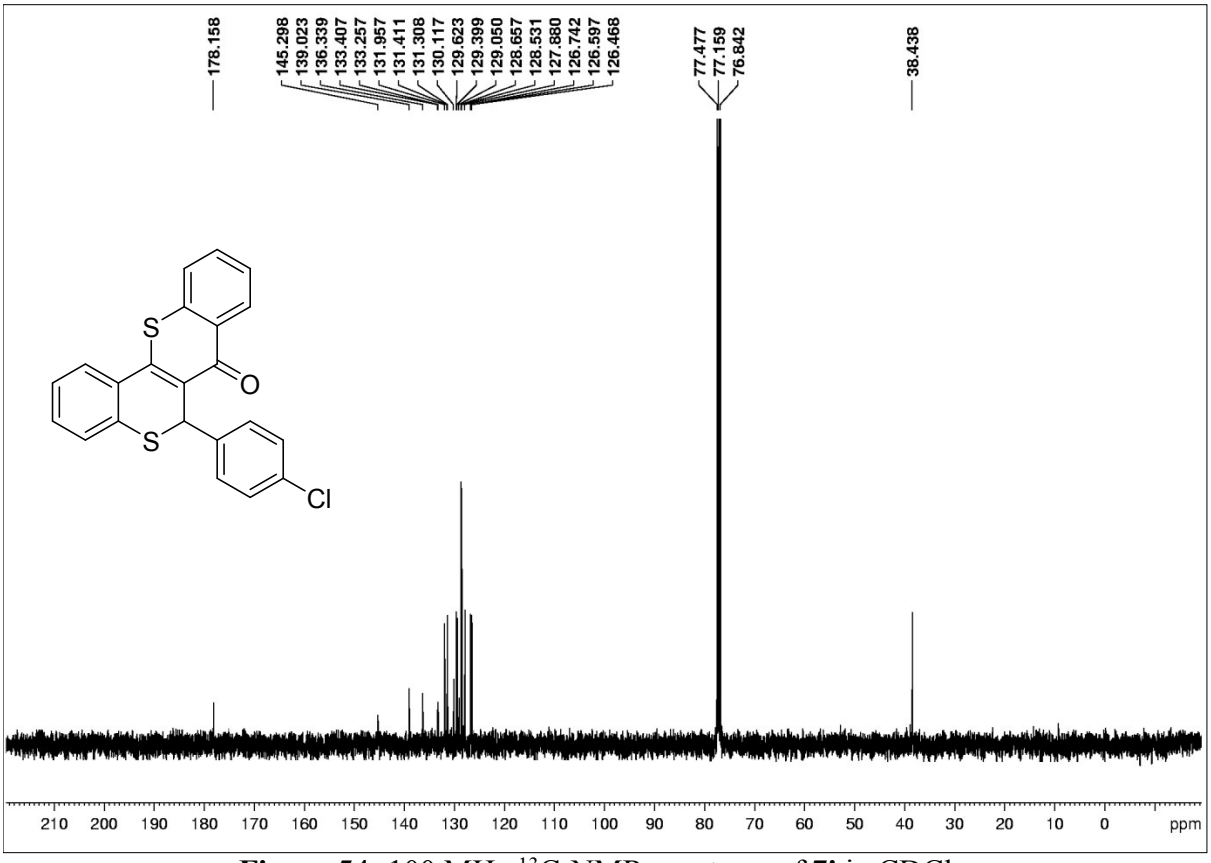


Figure 54: 100 MHz ^{13}C-NMR spectrum of **7i** in $CDCl_3$

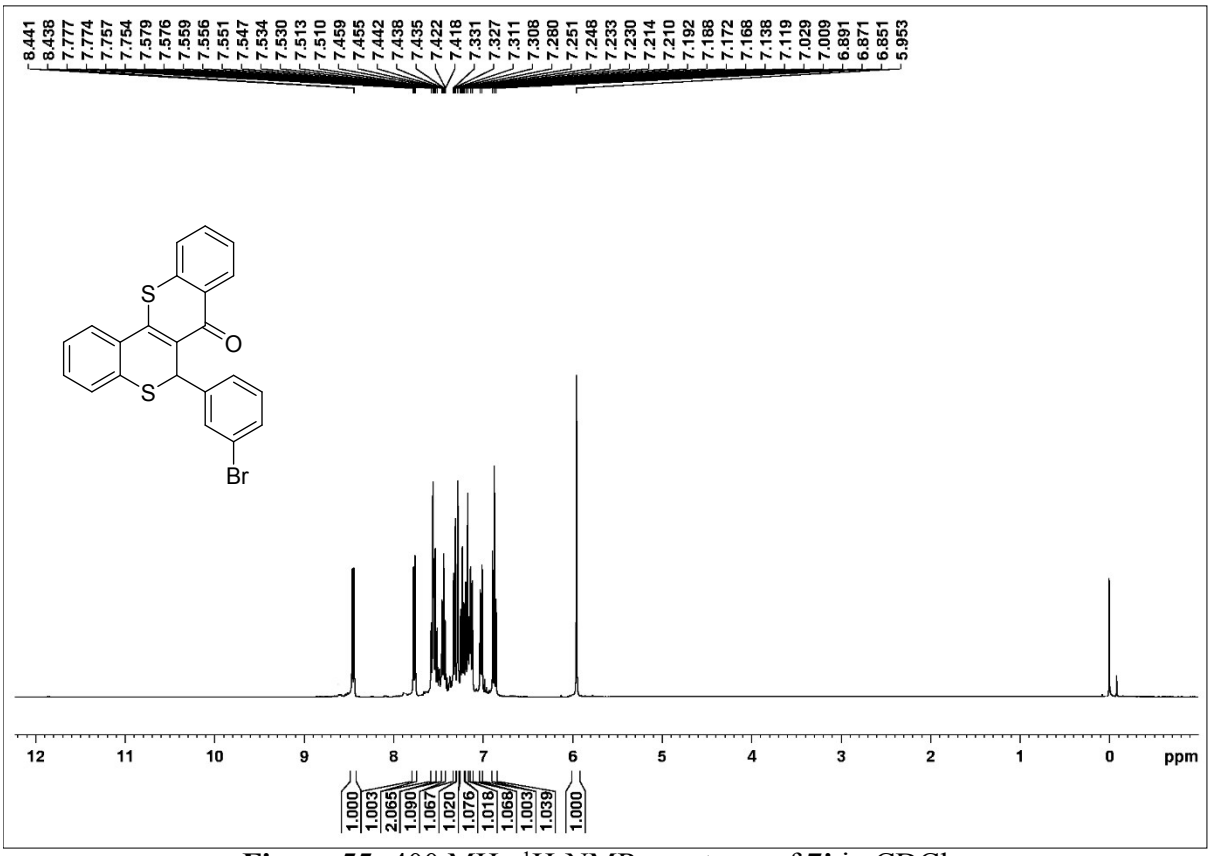


Figure 55: 400 MHz ^{1}H-NMR spectrum of **7j** in $CDCl_3$

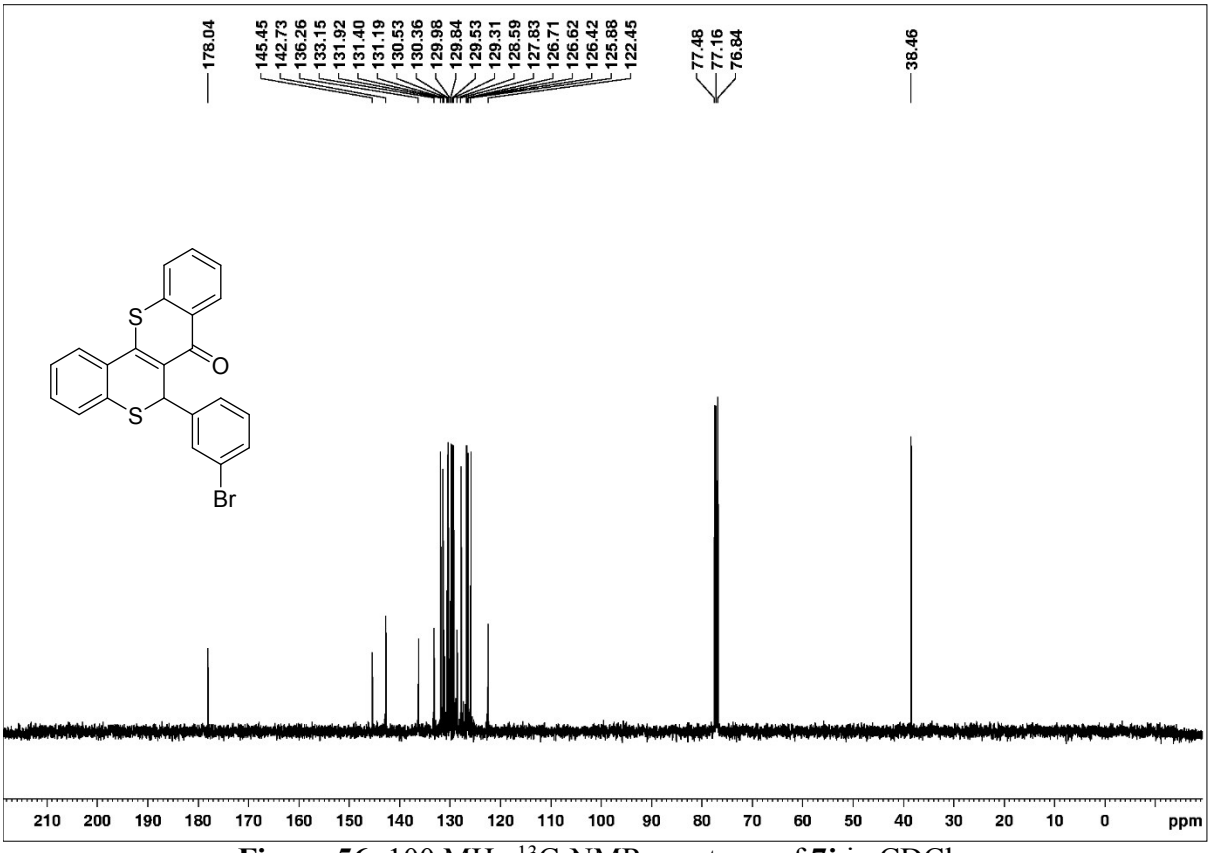


Figure 56: 100 MHz ^{13}C-NMR spectrum of **7j** in $CDCl_3$

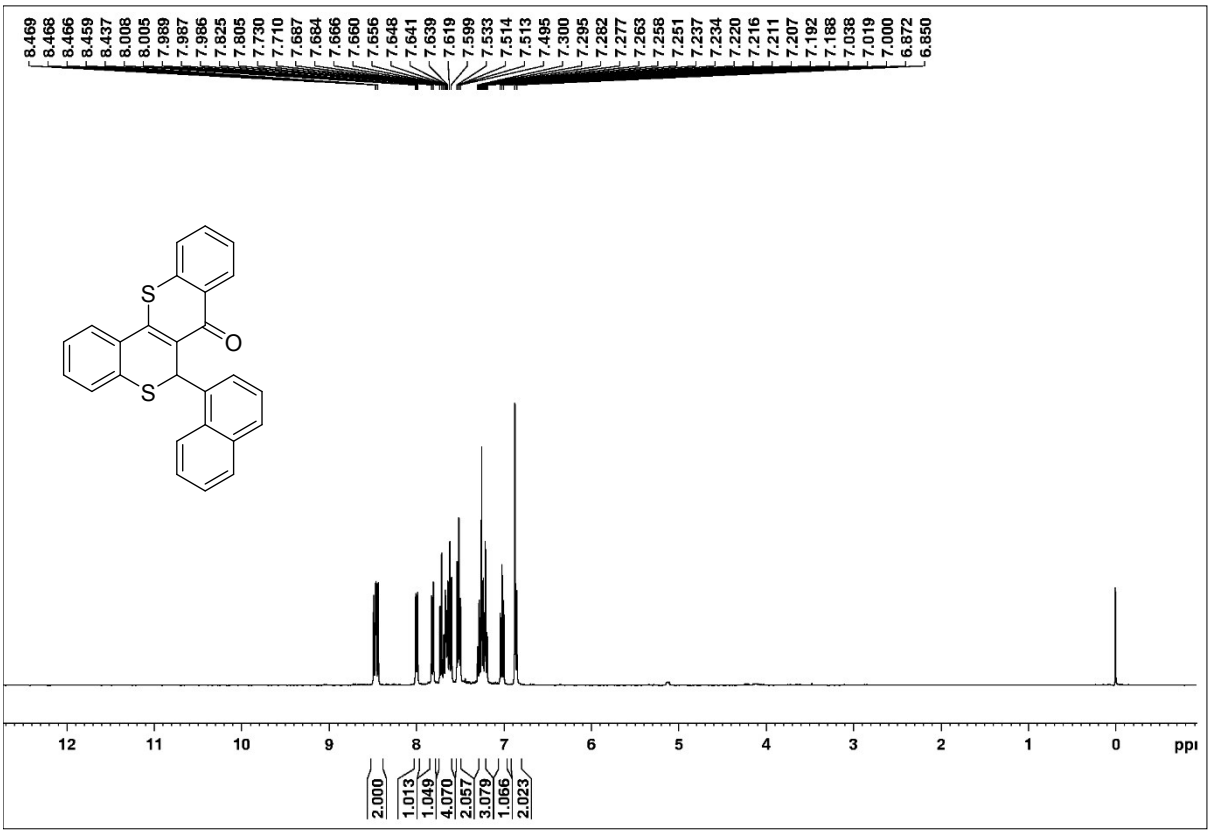


Figure 57: 400 MHz ^{1}H-NMR spectrum of **7k** in $CDCl_3$

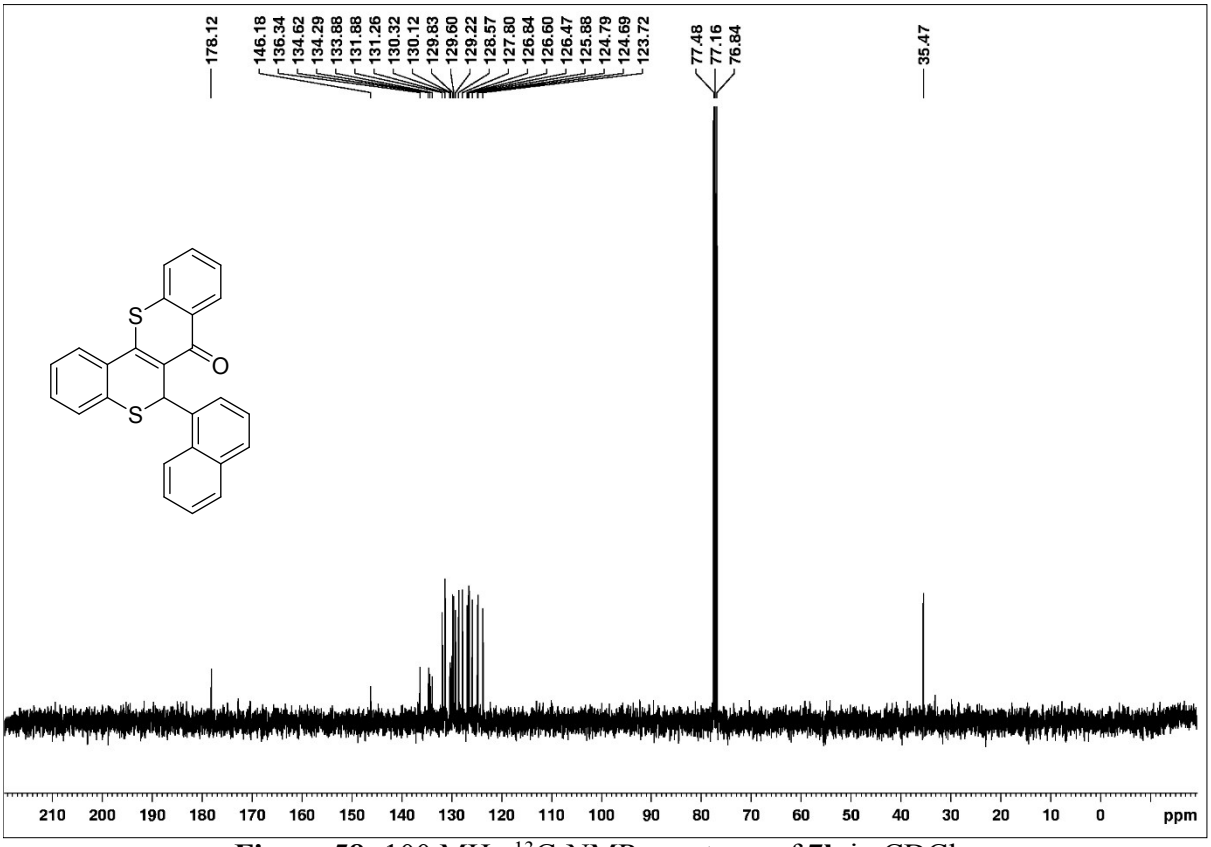


Figure 58: 100 MHz ^{13}C-NMR spectrum of **7k** in $CDCl_3$

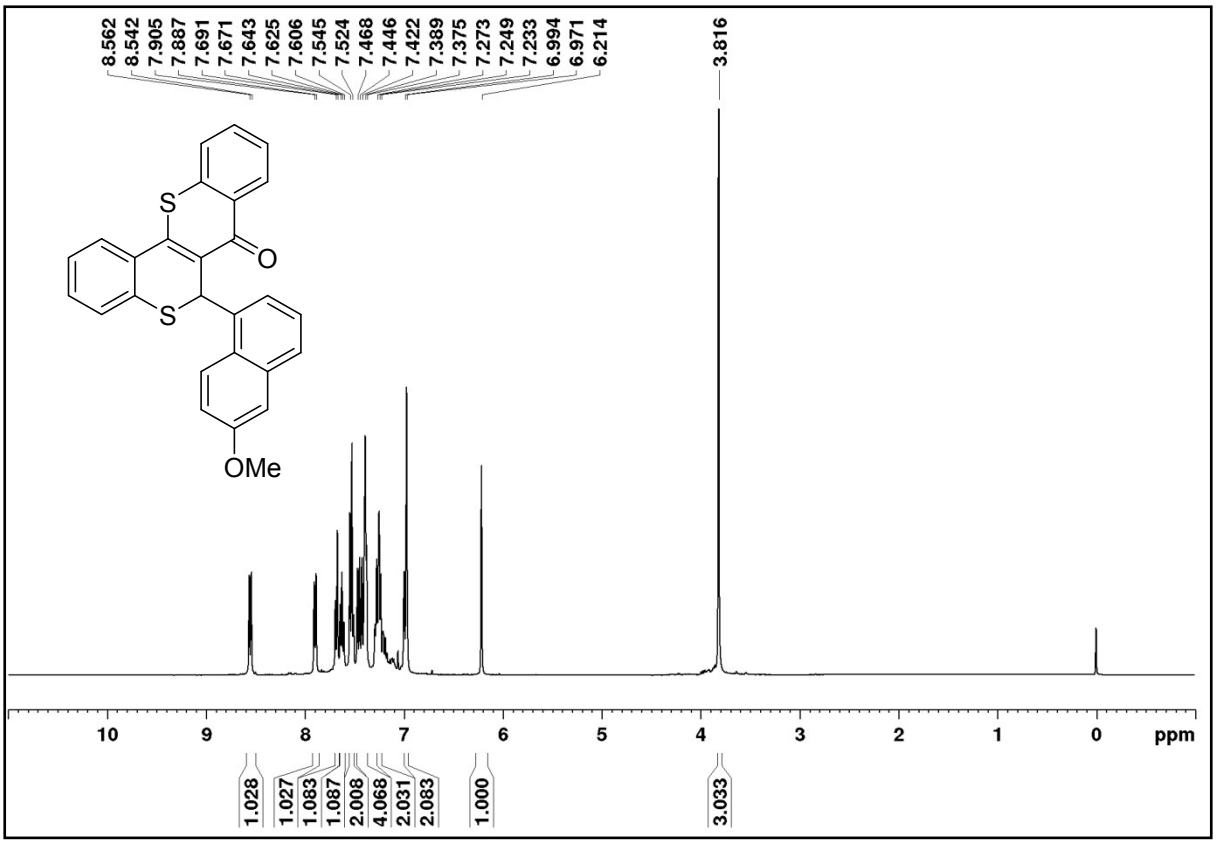


Figure 59: 400 MHz ^{1}H-NMR spectrum of **7l** in $CDCl_3$

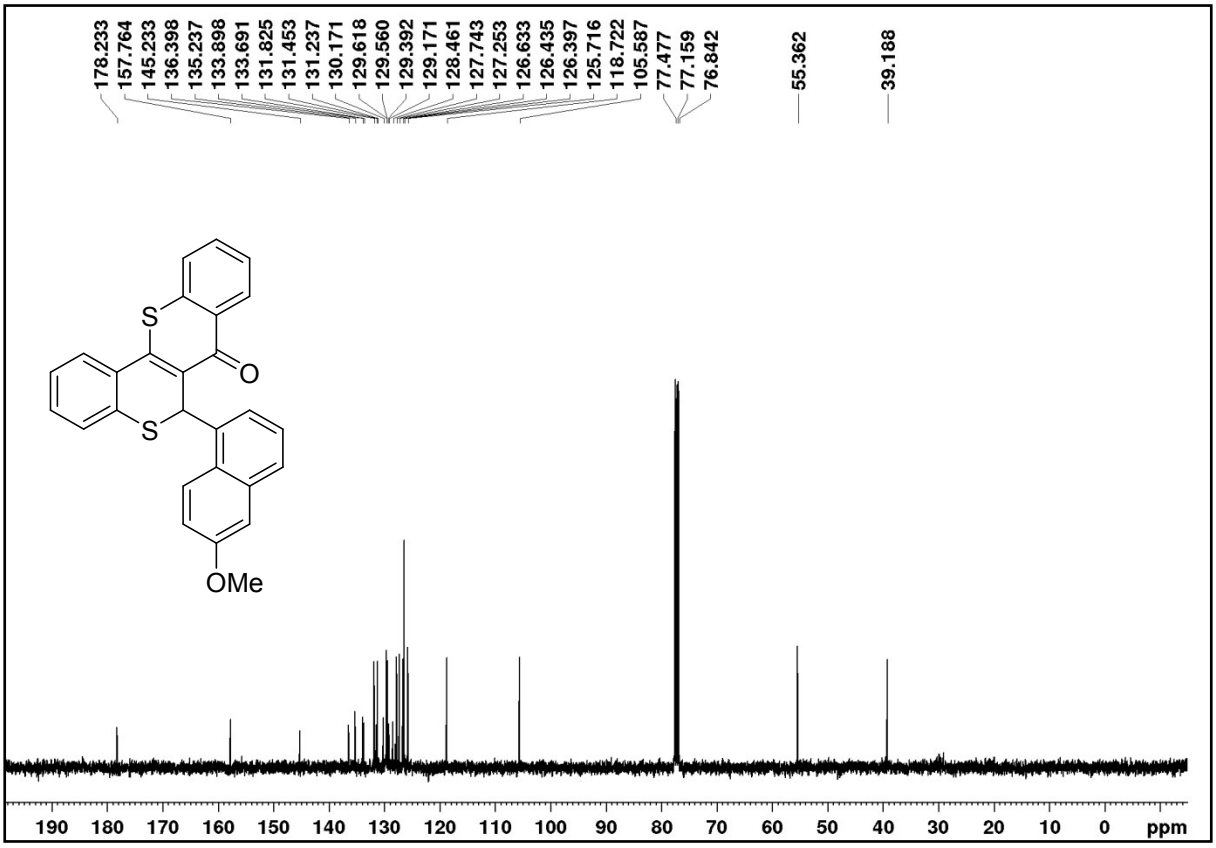


Figure 60: 100 MHz ^{13}C-NMR spectrum of **7l** in $CDCl_3$

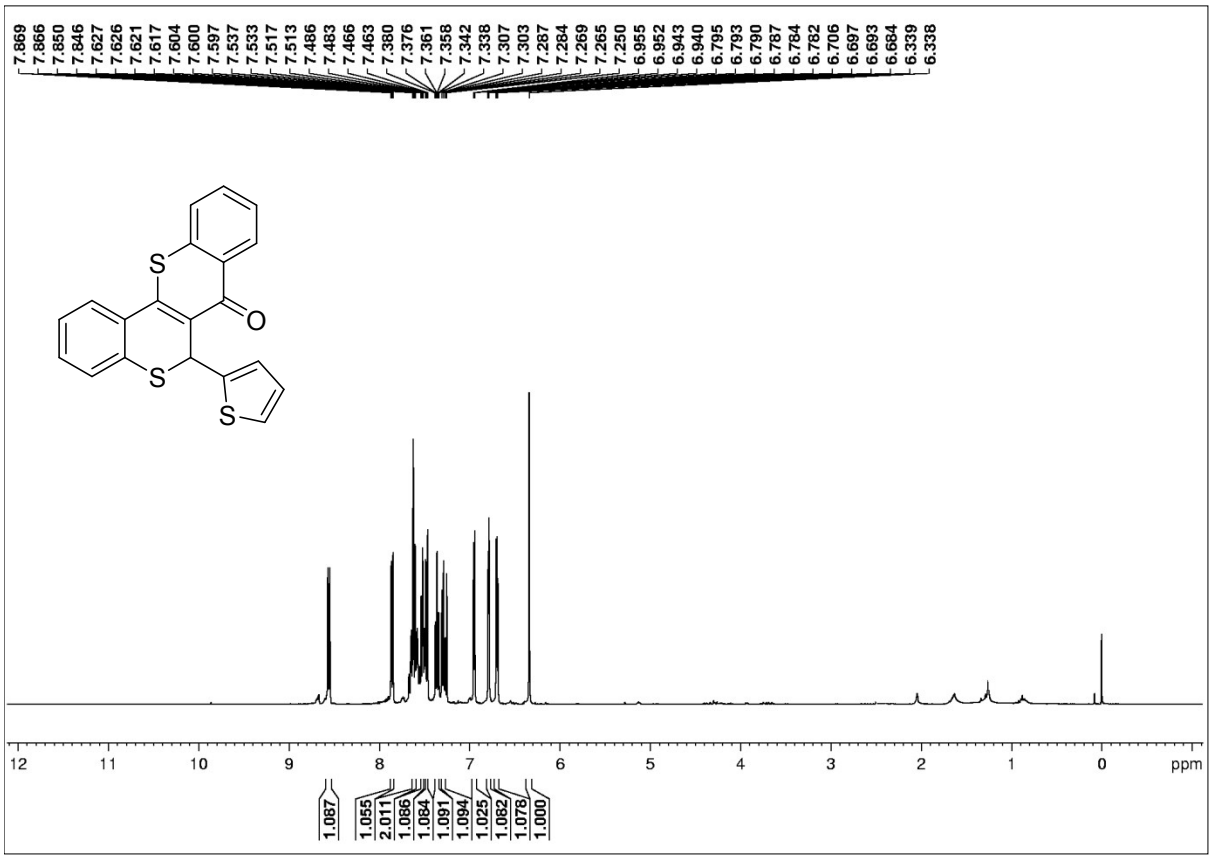


Figure 61: 400 MHz ^{1}H-NMR spectrum of **7m** in $CDCl_3$

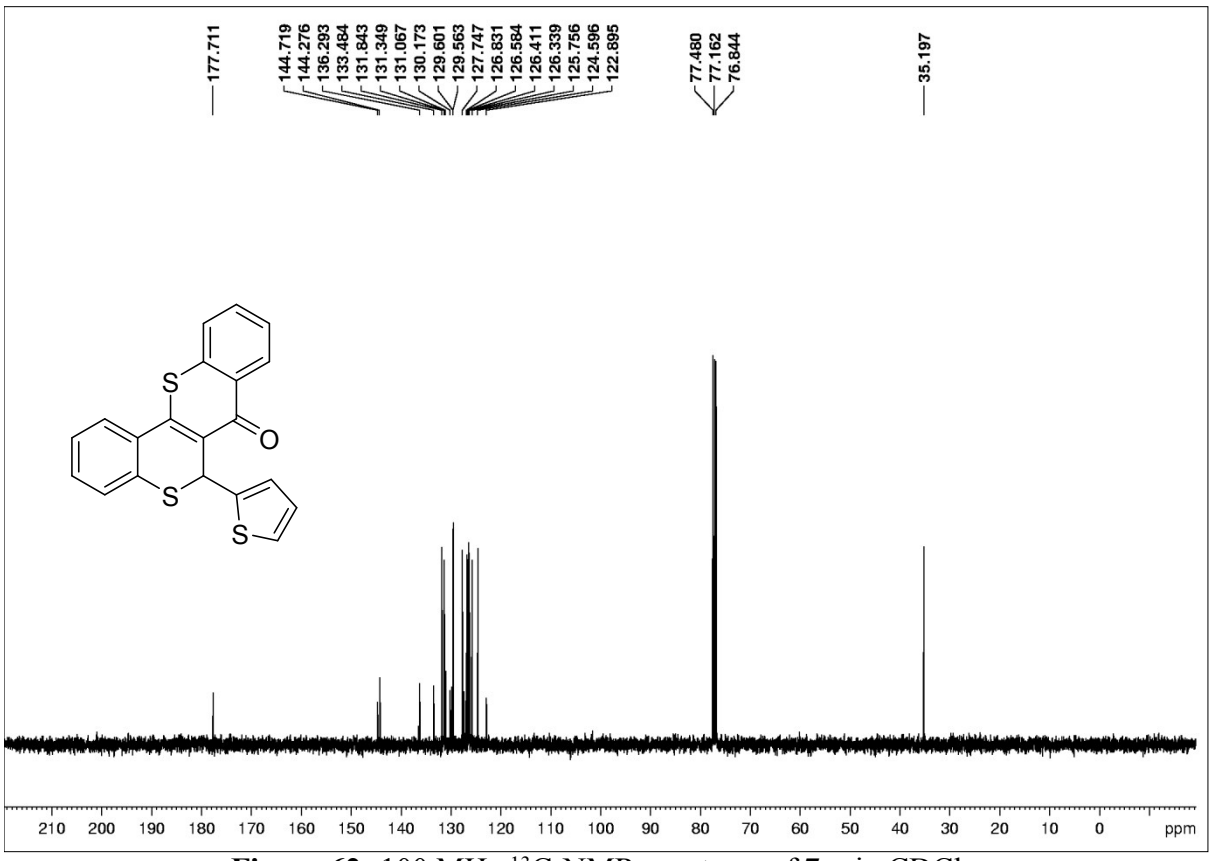


Figure 62: 100 MHz ^{13}C-NMR spectrum of **7m** in $CDCl_3$

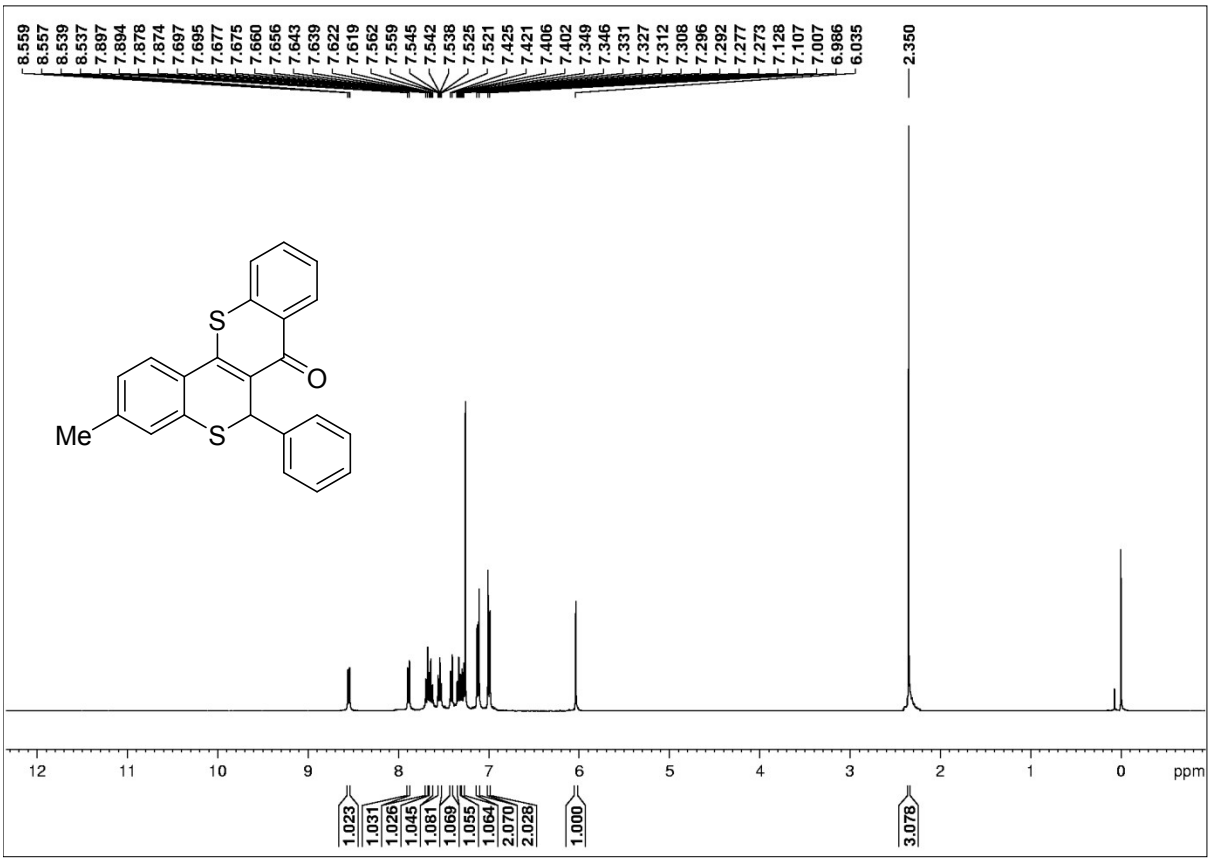


Figure 63: 400 MHz ^{1}H-NMR spectrum of **7n** in $CDCl_3$

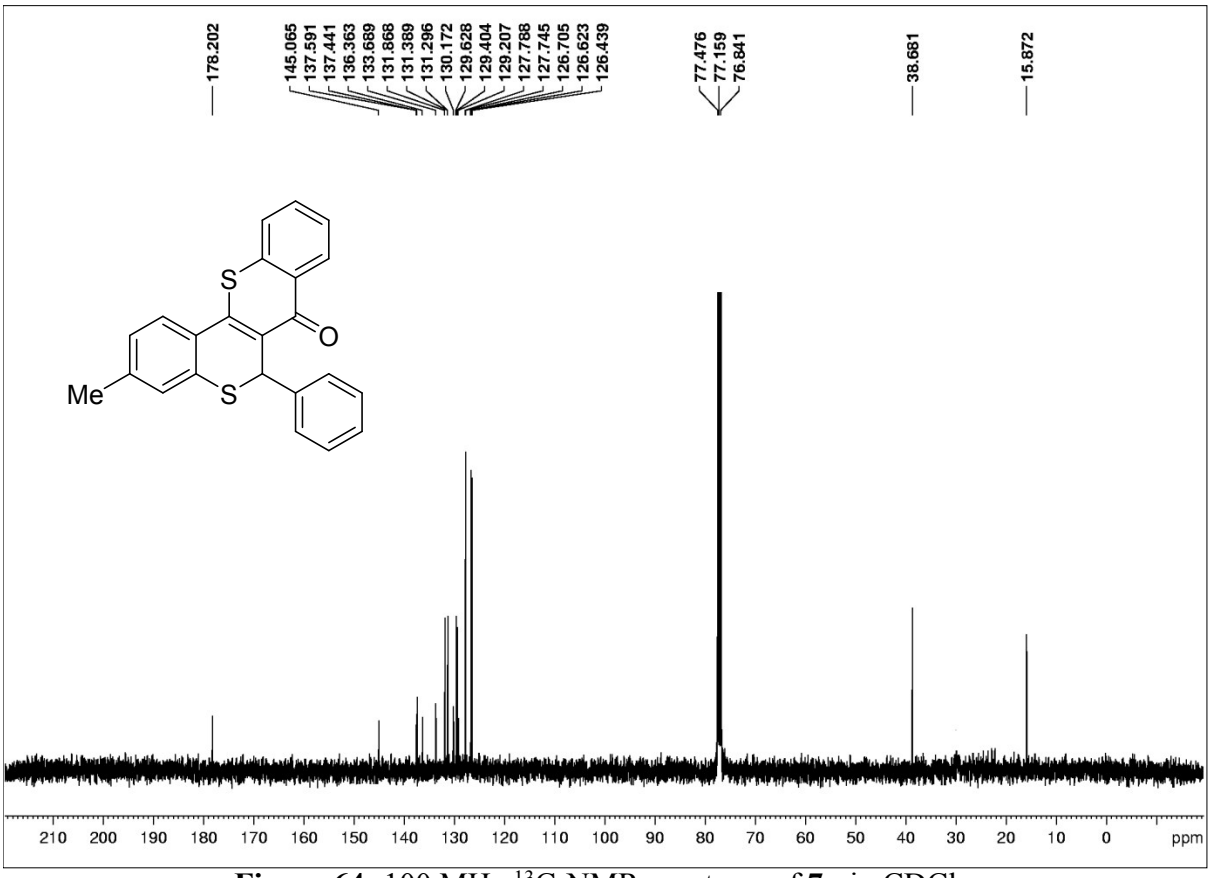


Figure 64: 100 MHz ^{13}C-NMR spectrum of **7n** in $CDCl_3$

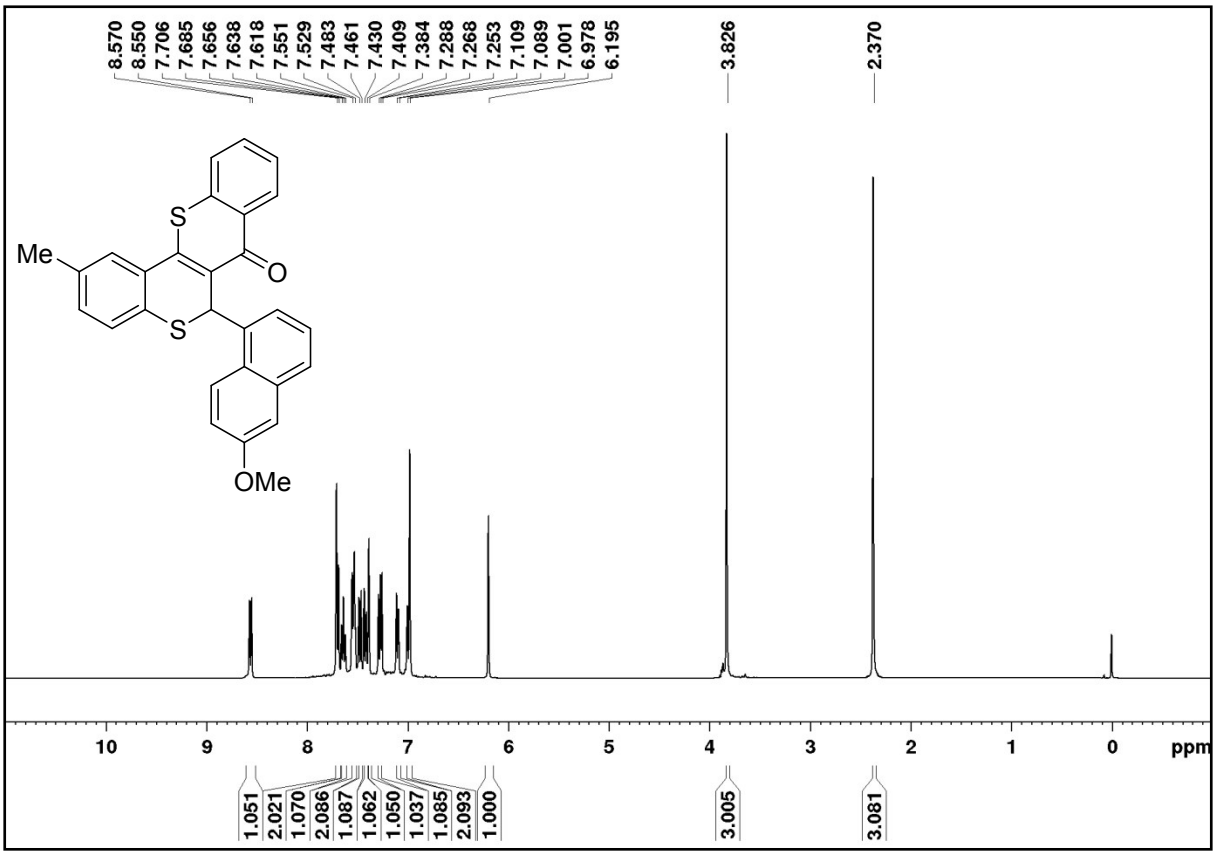


Figure 65: 400 MHz ^{1}H-NMR spectrum of **7o** in $CDCl_3$

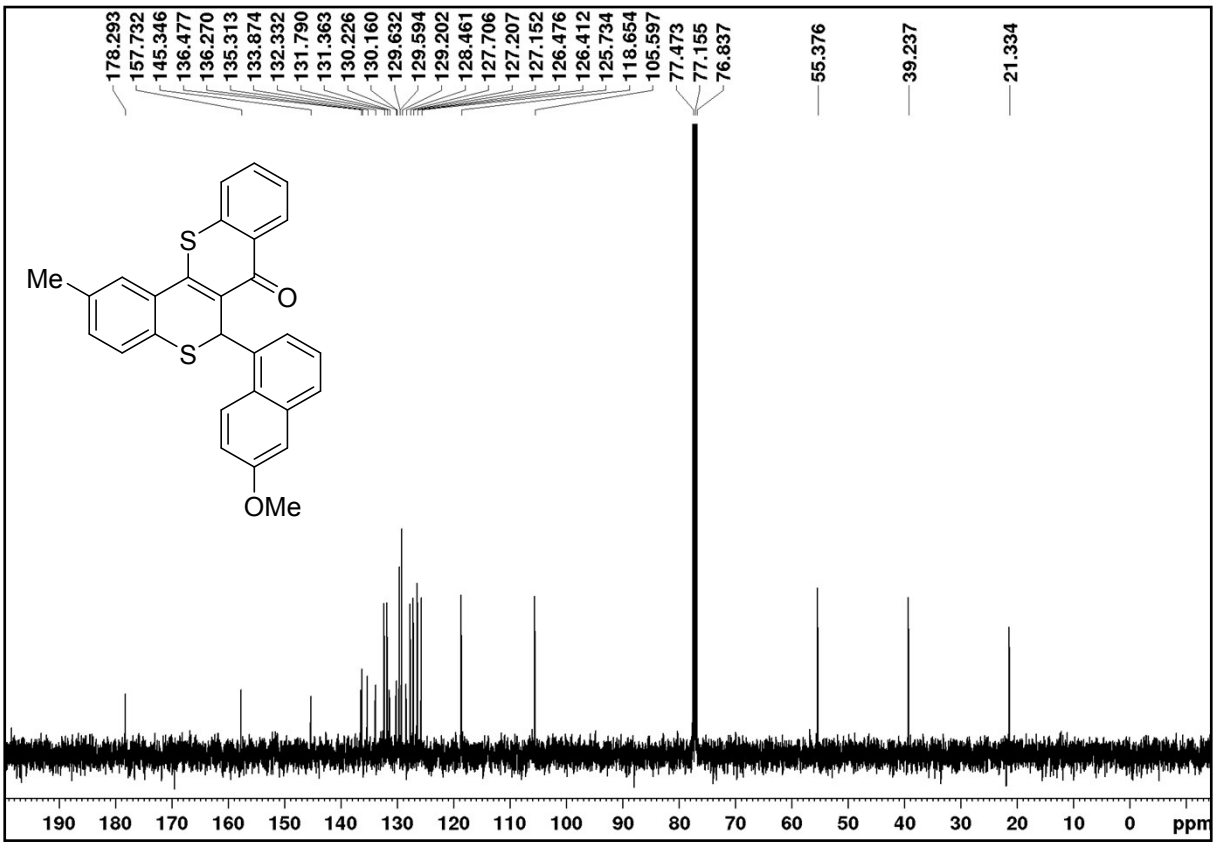


Figure 66: 100 MHz ^{13}C-NMR spectrum of **7o** in $CDCl_3$

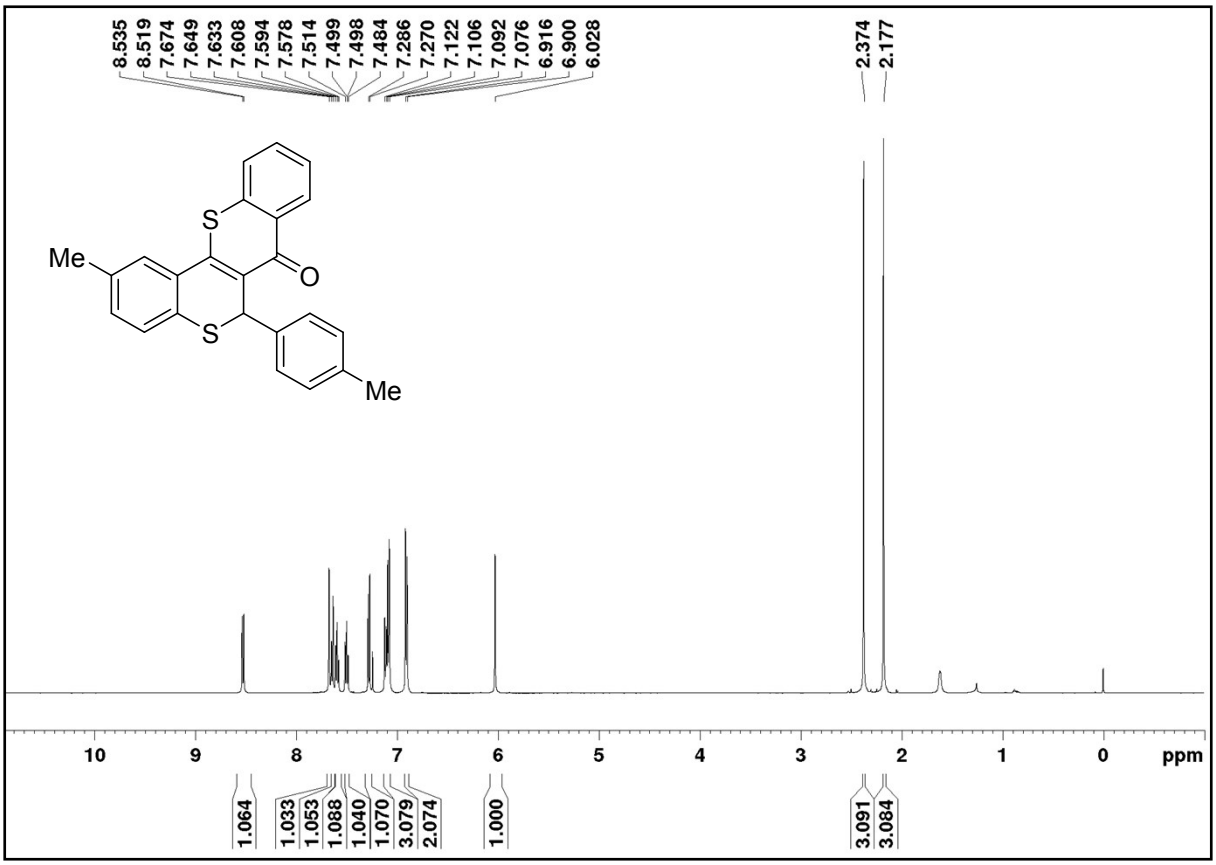


Figure 67: 500 MHz ^{1}H-NMR spectrum of **7p** in $CDCl_3$

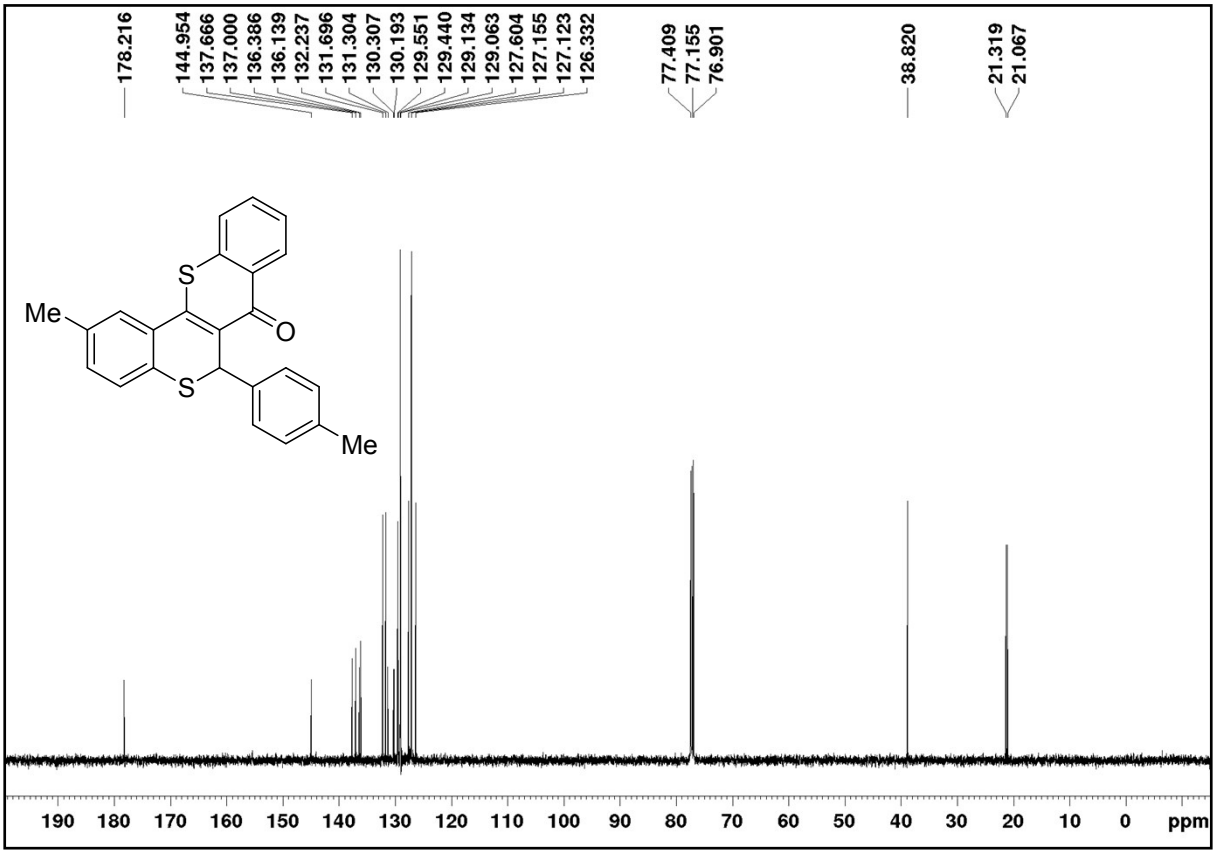


Figure 68: 125 MHz ^{13}C-NMR spectrum of **7p** in $CDCl_3$

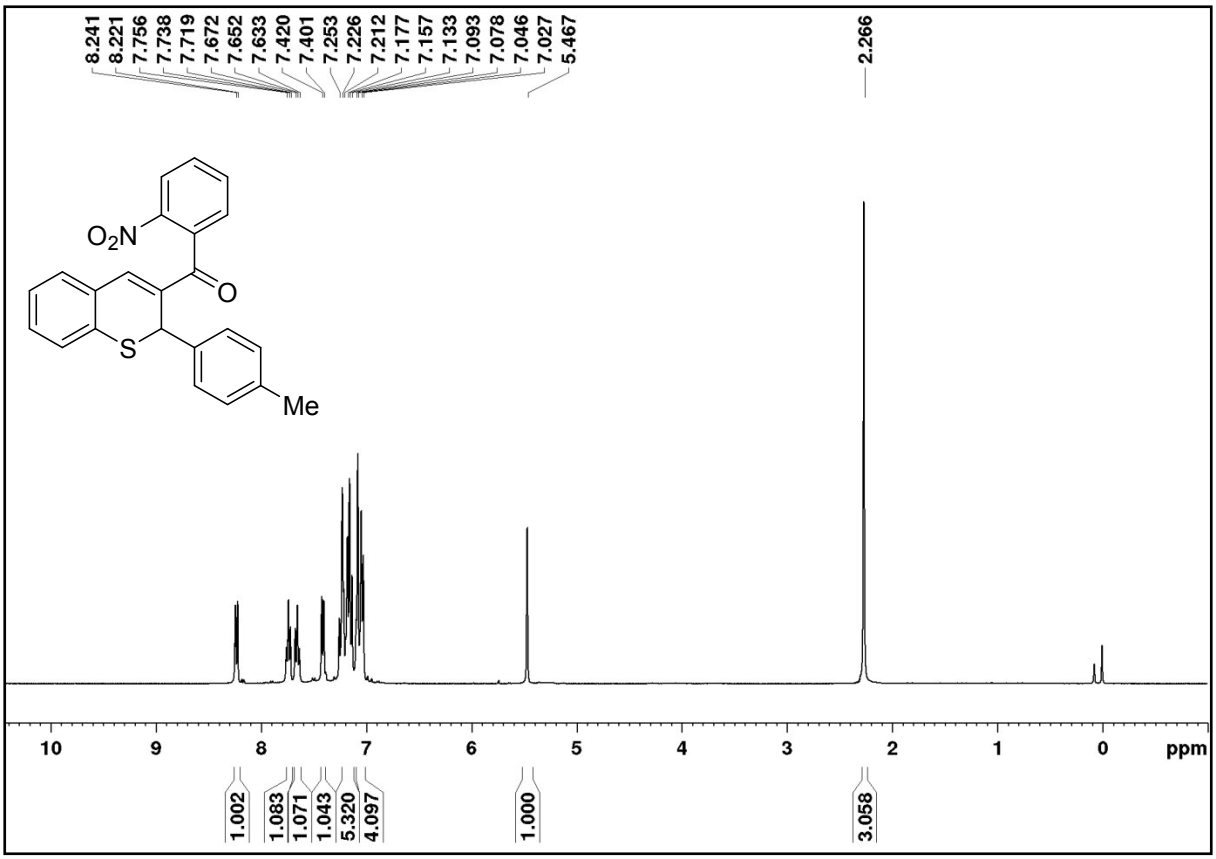


Figure 69: 400 MHz ^{1}H-NMR spectrum of **9** in $CDCl_3$

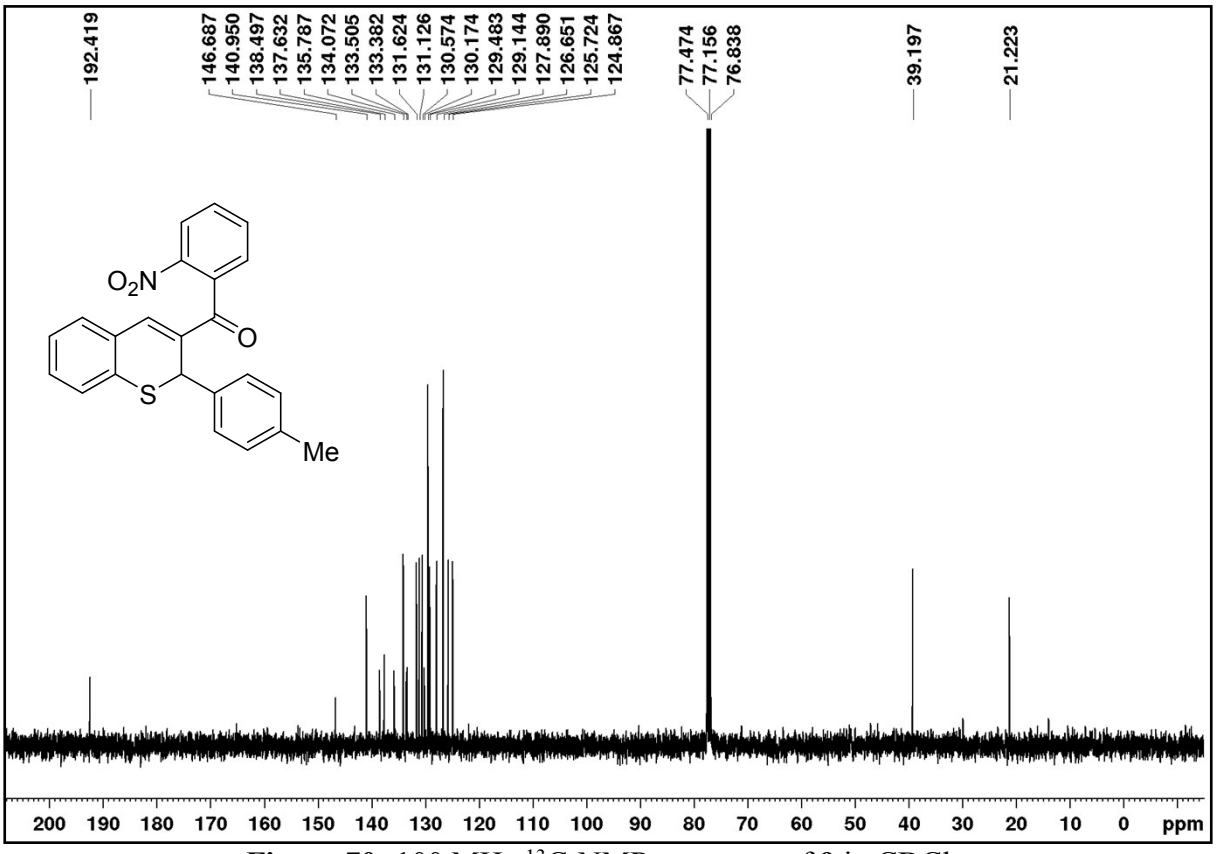


Figure 70: 100 MHz ^{13}C-NMR spectrum of **9** in $CDCl_3$

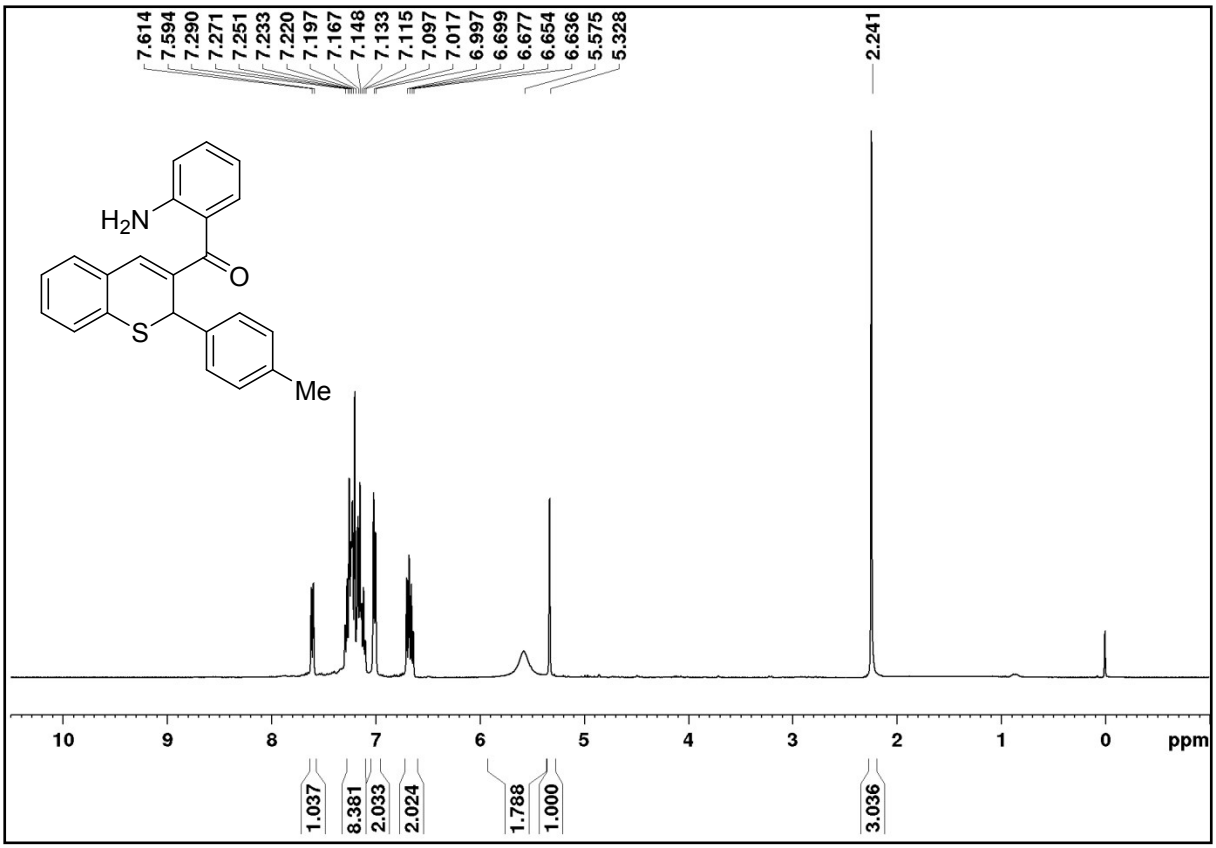


Figure 71: 400 MHz ^{1}H-NMR spectrum of **3** in $CDCl_3$

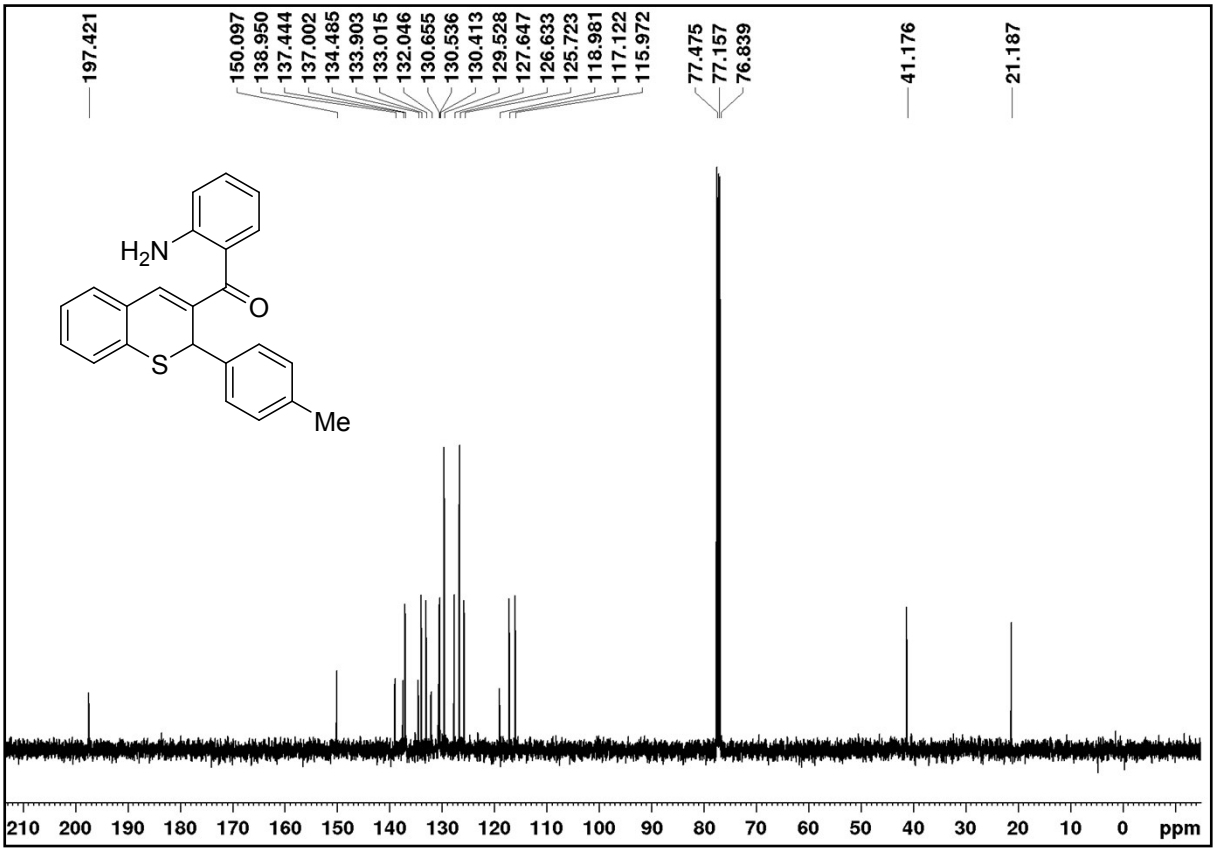


Figure 72: 100 MHz ^{13}C-NMR spectrum of **3** in $CDCl_3$

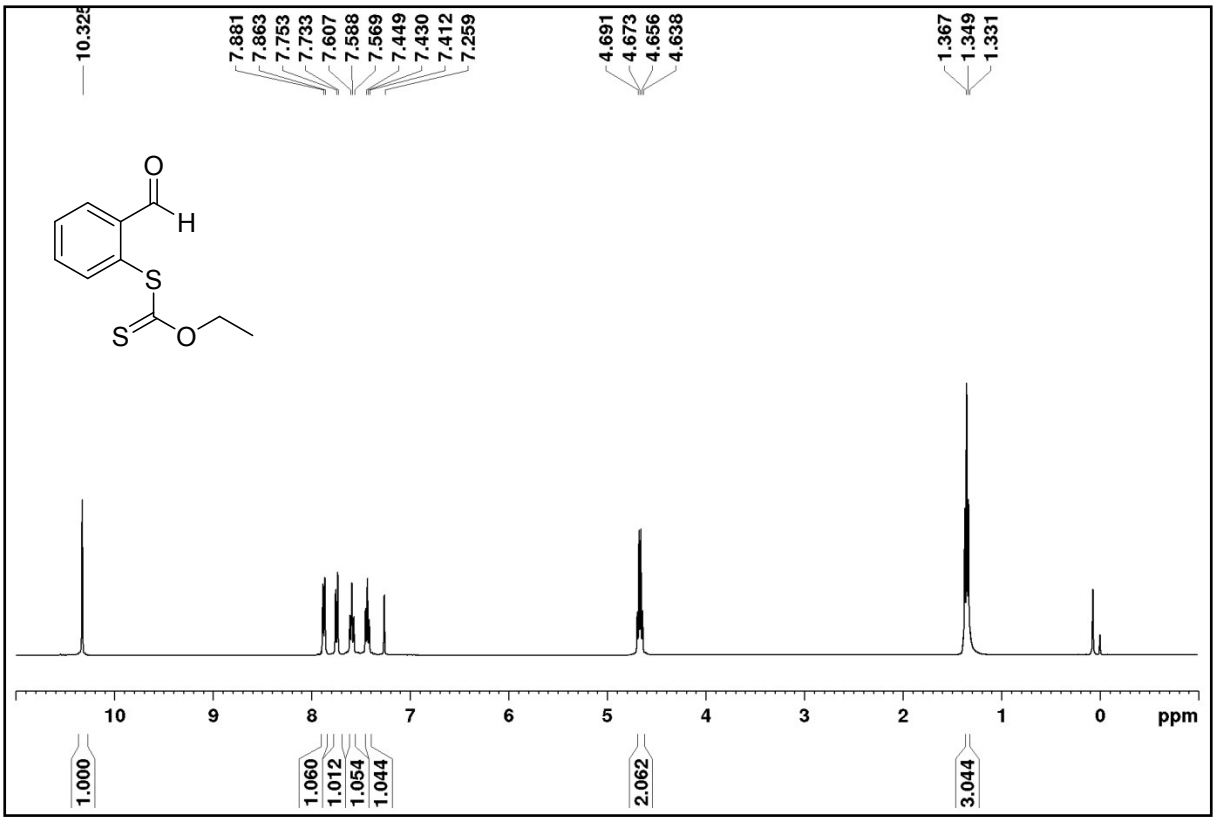


Figure 73: 400 MHz ^{1}H-NMR spectrum of **C** in $CDCl_3$

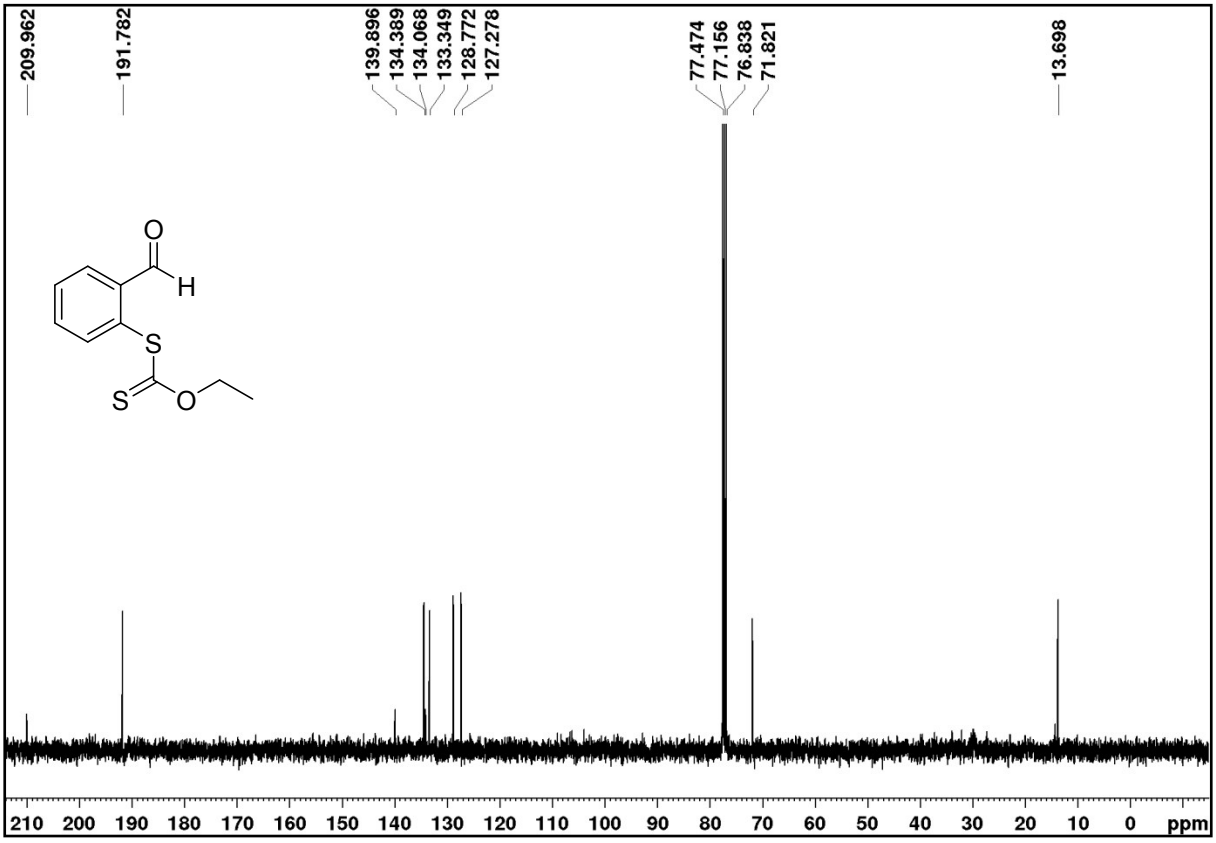


Figure 74: 100 MHz ^{13}C-NMR spectrum of **C** in $CDCl_3$

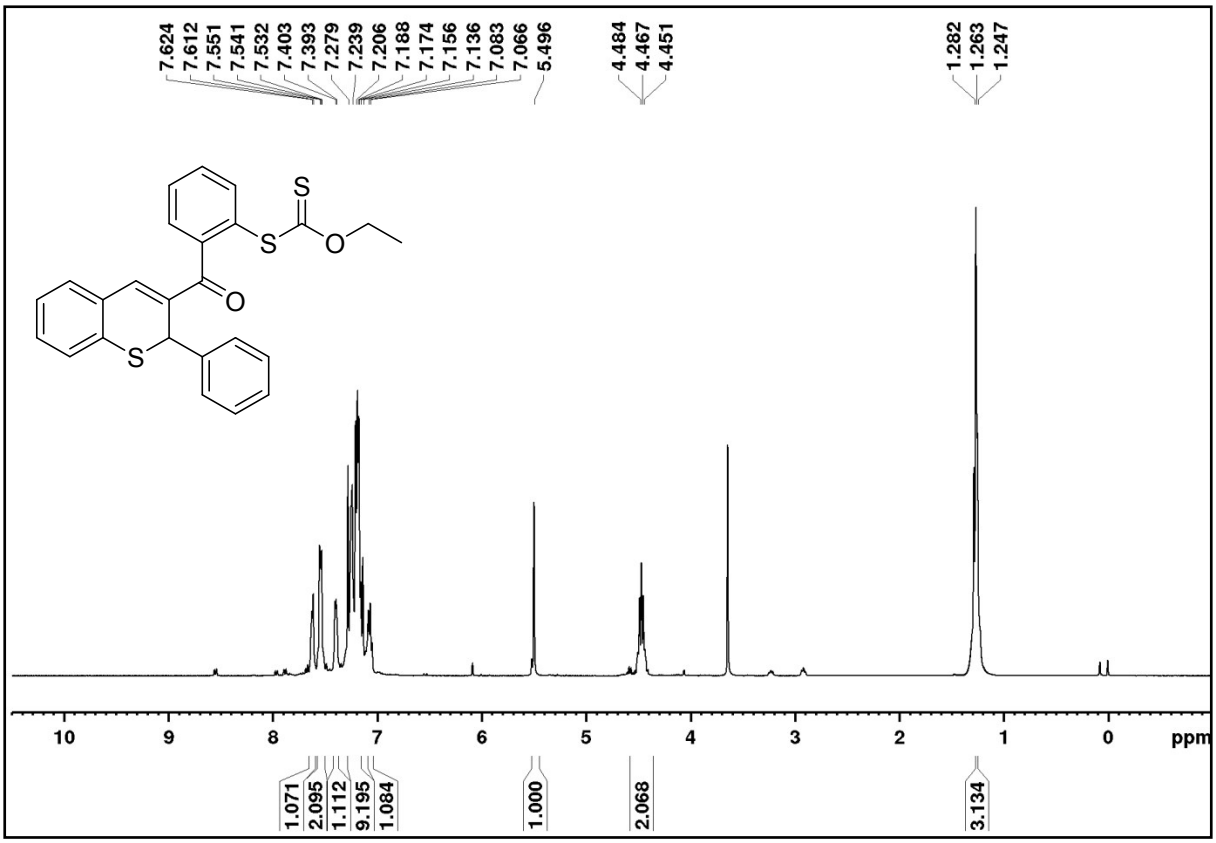


Figure 75: 400 MHz ^{1}H-NMR spectrum of **6'** in $CDCl_3$

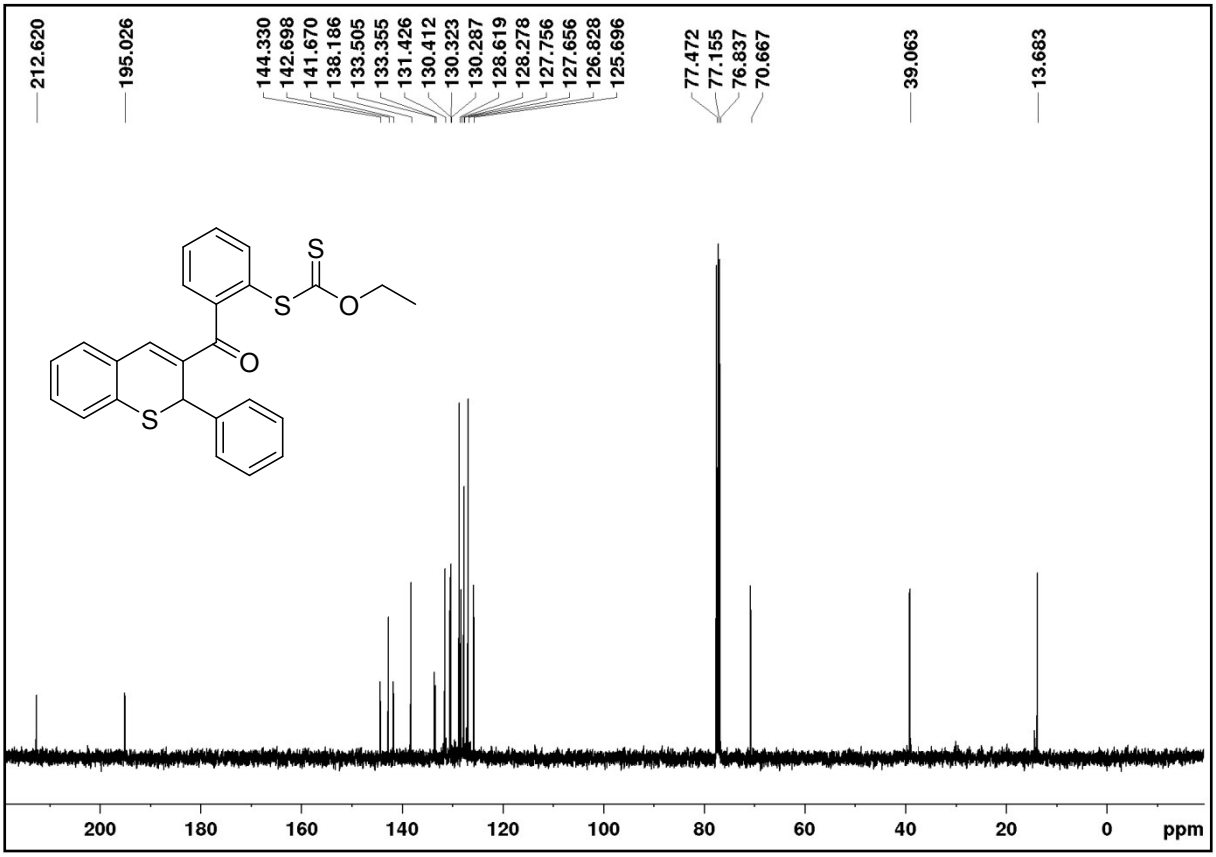


Figure 76: 100 MHz ^{13}C-NMR spectrum of **6'** in $CDCl_3$

4. Single crystal XRD data for Compound

Single crystals of 6-(p-tolyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one **7b** and 6-(4-fluorophenyl)-6H,7H-thiochromeno[4,3-b]thiochromen-7-one **7h** 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.

4. XRD Data for Compound 7b (CCDC No. 1991010)

Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=11.1152(3) b=12.7185(4) c=12.9078(5)
alpha=90 beta=103.7030(14) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1772.82(10)	1772.82(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C_{23} H_{16} O S_2	C_{23} H_{16} O S_2
Sum formula	C_{23} H_{16} O S_2	C_{23} H_{16} O S_2
Mr	372.48	372.48
Dx,g cm^{-3}	1.396	1.396
Z	4	4
Mu (mm^{-1})	0.309	0.309
F000	776.0	776.0
F000'	777.26	
h,k,lmax	13,15,15	13,15,15
Nref	3123	3124
Tmin,Tmax	0.926,0.970	
Tmin'	0.926	

Correction method= # Reported T Limits: Tmin=0.926Tmax=0.970
AbsCorr = MULTI-SCAN
Data completeness= 1.000 Theta(max)= 24.999
R(reflections)= 0.0341(2490) wR2(reflections)= 0.0843(3124)
S = 0.988 Npar= 236

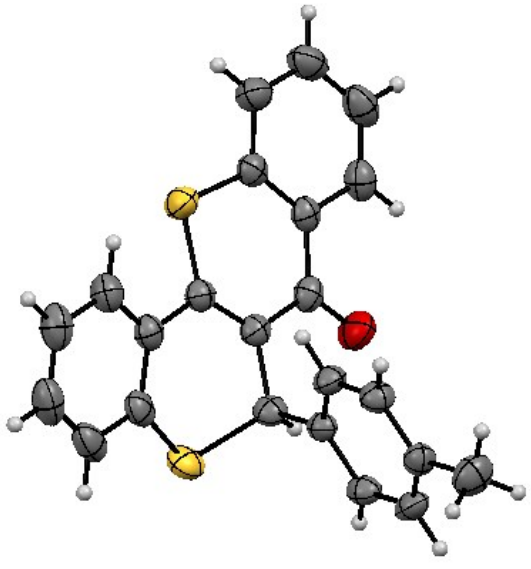


Figure S1. Single-crystal X-ray structure of compound **7b** (CCDC No. 1991010) Ellipsoids represent 50% probability level.

4. XRD Data for Compound 7h (CCDC No. 1991009**)**

Bond precision: C-C = 0.0044 A Wavelength=0.71073
Cell: a=11.3658(11) b=12.2954(9) c=12.4661(14)
alpha=90 beta=102.113(5) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1703.3(3)	1703.3(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C_{22} H_{13} F O S_2	C_{22} H_{13} F O S_2
Sum formula	C_{22} H_{13} F O S_2	C_{22} H_{13} F O S_2
Mr	376.44	376.44
Dx,g cm^{-3}	1.468	1.468
Z	4	4
Mu (mm^{-1})	0.331	0.331
F000	776.0	776.0
F000'	777.32	
h,k,lmax	13,14,14	13,14,14
Nref	2999	3000
Tmin,Tmax	0.957,0.974	0.952,0.974
Tmin'	0.952	

Correction method= # Reported T Limits: Tmin=0.952 Tmax=0.974
AbsCorr = MULTI-SCAN
Data completeness= 1.000 Theta(max)= 24.999
R(reflections)= 0.0425(1766) wR2(reflections)= 0.0995(3000)
S = 0.999 Npar= 235

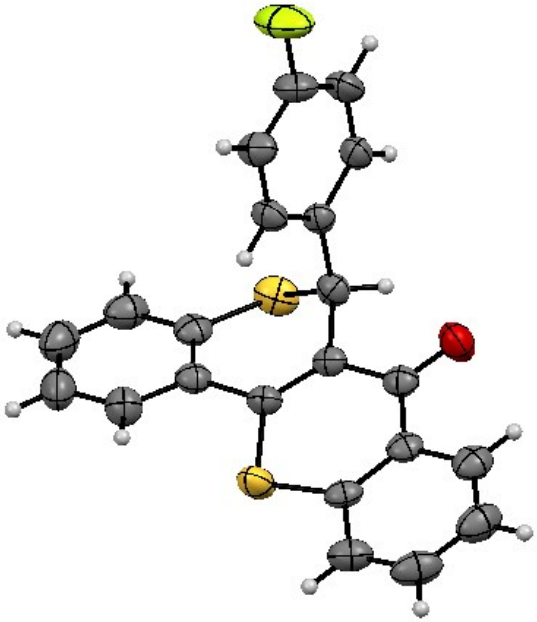


Figure S2. Single-crystal X-ray structure of compound **7h** (CCDC No. 1991009) Ellipsoids represent 50% probability level.