Supporting information

Annulation of Quinone methides with 2-Benzylidene Dithiolanes: Synthesis of Spirochroman Dithiolanes

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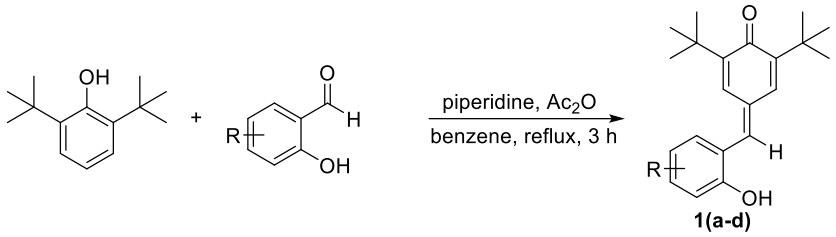
Contents:

1. General Information:

All the syntheses of Grignard reagents were carried out under nitrogen environment. Solvents were used as supplied and not dried, until required for specific condition. Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was executed on pre-coated, aluminium-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254, 365 nm) and stained with aqueous potassium permanganate solution and standard *p*-anisaldehyde solution. Infrared spectra of the compounds were recorded by using a Perkin Elmer 283 Spectrometer or by using attenuated total reflection spectrophotometer in reciprocal centimeter (cm^{-1}). HRMS spectra were recorded on Agilent 6530 Accurate-Mass Q-TOF LC/MS spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian Mercury 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C), and an Agilent 500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C).The center of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.00 ppm (^{13}C in $CDCl_3$).Data is reported as follows: chemical shift multiplicity [s= singlet, d= doublet, t= triplet, q= quartet, p= pentet, m= multiplet and bs = broad singlet], coupling constant (in Hz), integration and assignment). Melting points was recorded. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Fluorochem and TCI Europe unless otherwise specified.

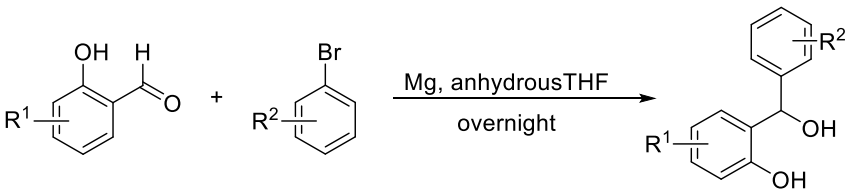
2. General procedures:

2.1 General procedure for the synthesis of *p*-Quinone methides[1] (1a-1d)



A solution of 2,6-di-*tert*-butyl phenol (1 equiv) and the corresponding salicylaldehyde (1.3 equiv.) was placed in a Dean-Stark apparatus. Once the mixture was dissolved in benzene (2 mL/mmol), the resulting solution was heated to reflux. Piperidine (4 equiv.) was added dropwise within 30 minutes. The reaction mixture was continued to reflux for 3 hours. After cooling just below the boiling point of the reaction mixture, acetic anhydride (2 equiv.) was added dropwise. The reaction was monitored by TLC analysis until the intermediate was fully consumed (about 5~10 minutes). Subsequently, the solution was poured on ice-water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, washed with brine and dried over anhydrous Na_2SO_4. After the solvent of the filtrate was removed under reduced pressure, the crude products were purified by flash column chromatography to afford **1(a-d)**. The characterization data of the products matched with the literature reports.

2.2 General procedure for the synthesis of *o*-Quinone methides[2] (4a-4l)



A 100 mL two-necked flask was equipped with a condenser and a rubber septum. Magnesium (4 equiv.) and anhydrous THF (1.5 mL/mmol) were introduced under argon atmosphere. The reaction was initiated with small amount of iodine and 0.5 mL of 1,2-dibromoethane was added (ethylene gas evolved right after the addition). After the disappearance of brown colour, aryl/alkyl bromide (2 equiv) solution (1.0 mmol of aryl/alkyl bromide was dissolved in 3 mL THF) was added drop-wise to the solution in an hour and the mixture was refluxed for another one hour. The resulting solution was used for next step directly. To a solution of derivatives of salicylaldehyde (1 equiv.) in dry THF (2 mL/ 1 mmol) was added aryl magnesium bromide solution at 0 °C. The solution was warmed to ambient temperature and stirred overnight. The reaction mixture was cooled to 0 °C and then saturated aq. NH_4Cl was added. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude products were further purified by using flash column chromatography in ethyl acetate/hexane solvent combination to afford product **4(a-l)**. The characterization data of the products matched with the literature reports.

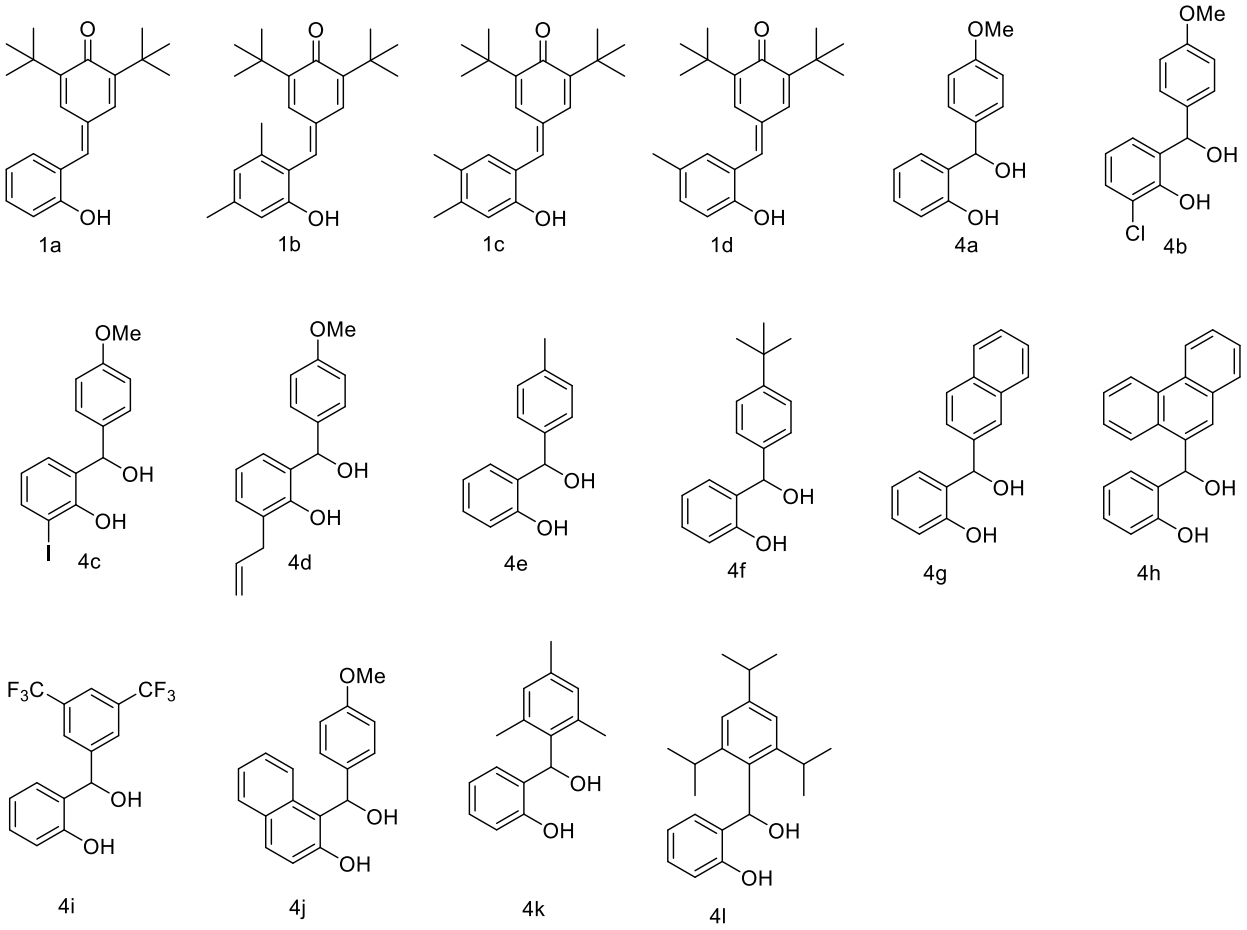
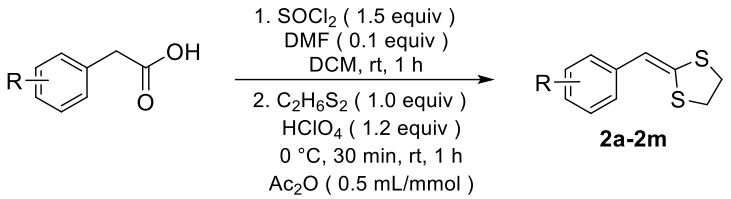


Figure-1: Synthesized Quinone Methides

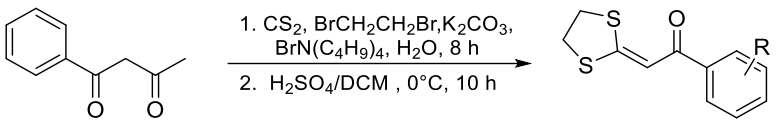
2.3a General procedure for the synthesis of Phenyl dithiolanes[3] (2a-2m)



To a solution of derivatives of phenylacetic acid (1 equiv.) in dichloromethane (1.0 mL/mmol) was added thionyl chloride (1.5 equiv.) and dimethylformamide (0.05 equiv.) and the mixture was stirred at room temperature for 1 hour. The solvent was removed in vacuo to give derivatives of phenylacetyl chloride (7.81 g, 100%) as oil, which was used without further purification. Analytical data matches the literature precedent.

Ethane-1,2-dithiol (1 equiv.) was added drop-wise to 2-phenylacetyl chloride (1 equiv.) at 0 ℃ and stirred for 30 min. Then, $HClO_4$ (70%, 1.2 equiv.) was carefully added drop-wise and stirred for another 5 min. The mixture was allowed to warm to room temperature and stirred for 30 min. Then cooled to 0 ℃ and freshly distilled Ac_2O (15 mL) was carefully added drop-wise. The dithiolanylium salt was precipitated with anhydrous Et_2O and filtrated under argon. The red solid was washed with Et_2O and dissolved in anhydrous CH_3CN. Afterwards, Et_3N was added until the red color disappeared and the solvents were removed at reduced pressure. The resulting oil was dissolved in sat. aq. NH_4Cl solution and the solution was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by flash silica gel column chromatography (eluent, petroleum ether/ ethyl acetate: 10/1, v/v) to give desired products **2(a-m)**. The characterization data of the products matched with the literature reports.

2.3b General procedure for the synthesis of Phenyl dithiolanes[4] (2n-2p)



1) To a well-stirred suspension of 2,4-dione (1 equiv.), K_2CO_3 (2.5 equiv.) and TBAB (0.1 equiv.) in water at room temperature was added CS_2 (1.2 equiv.). After the reaction mixture was stirred for 1 h, alkyl bromide (1 equiv.) was added drop-wise within 15 min. The mixture was stirred for 8.0 h at room temperature. The resulting precipitate was filtered, washed with water and dried to afford a yellow solid. The crude product was directly used in the next step without further purification.

2) To a solution of above yellow solid (1 equiv.) in 50 mL of CH_2Cl_2 was added concentrated H_2SO_4 (4.0 equiv.) at 0^oC. The mixture was allowed to warm to room temperature and stirred for 10 h, and then poured into saturated NaCl ice-water under stirring. The mixture was neutralized with Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash silica gel column chromatography (eluent, petroleum ether/ ethyl acetate: 10/1, v/v) to give products **(2n-2p)**.

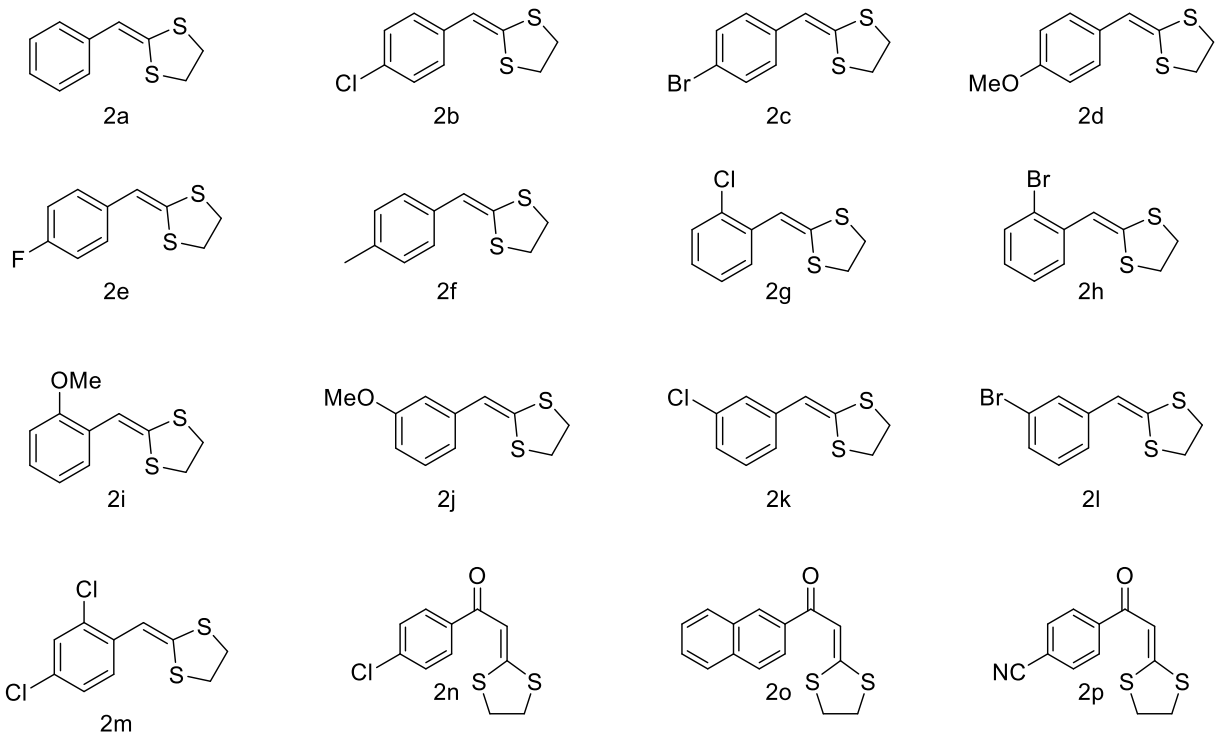
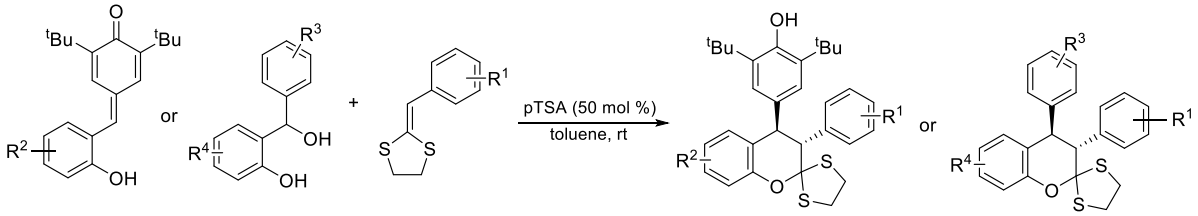


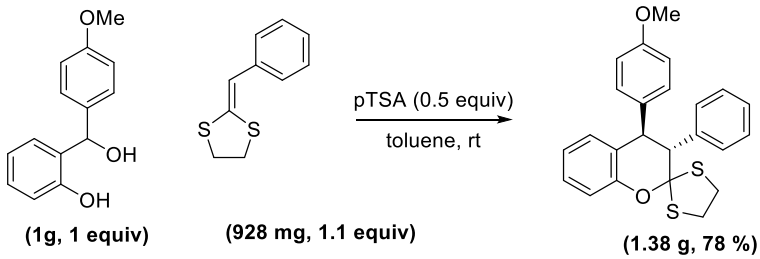
Figure-2: Synthesized phenyl dithiolanes

2.4 Synthesis of 3,4-diphenyl spiro [chroman-2,2'- [1,3] dithiolane]



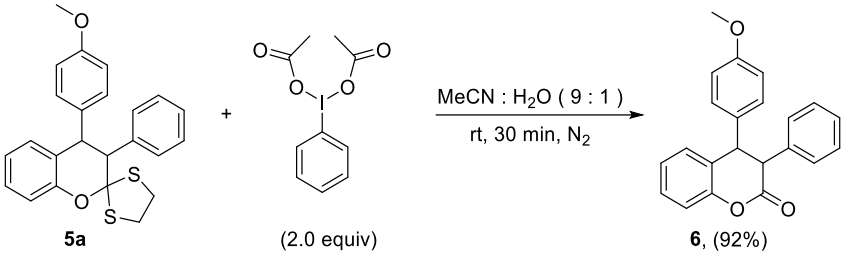
To an oven dried reaction vial charged with quinone methides (*ortho* and *para*) (1 equiv.), phenyl dithiolanes (1.1 equiv.), *p*-Toluenesulfonic acid (0.5 equiv.) dissolved in toluene (2 mL) was added and the reaction was stirred at ambient temperature. The reaction was monitored by thin layer chromatography and after the consumption of the quinone methide, solvent was removed under reduced pressure without work up to afford crude product. The crude product was purified by flash silica gel column chromatography (ethyl acetate in petroleum ether).

2.5 Gram-scale synthesis of 3,4-diphenyl spiro [chroman-2,2'- [1,3] dithiolane]



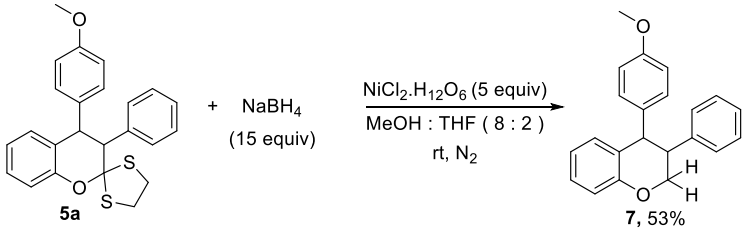
To an oven dried round bottom flask charged with *ortho* quinone methide (1 equiv, 4.34 mmol) and phenyl dithiolane (1.1 equiv., 4.8 mmol), *p*-toluenesulfonic acid (0.5 equiv.) dissolved in toluene (29 ml) was added and the reaction was stirred at ambient temperature. Reaction was monitored by thin layer chromatography and after the consumption of the quinone methide, solvent was removed under reduced pressure without work up to afford crude product. The crude product was purified by flash silica gel column chromatography (ethyl acetate in petroleum ether).

2.6 Synthesis of 4-(4-methoxyphenyl)-3-phenylchroman-2-one[5]



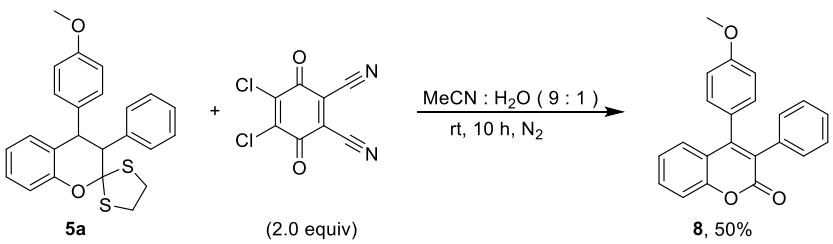
To a solution of **5a** (100 mg, 0.25 mmol) in MeCN/H_2O (9:1; 2 mL) was added PIDA (158 mg, 0.5 mmol) and the reaction mixture was stirred at room temperature under nitrogen atmosphere. After completion of reaction (confirmed by TLC), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and diluted with ethyl acetate (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (15 mL). The combined organic extracts were washed with saturated $NaHCO_3$ solution dried over anhydrous sodium sulfate and filtered. After removal of all the volatile components by evaporation, the residue was purified using silica gel column chromatography providing **6** as white crystalline solid.

2.7 Synthesis of 4-(4-methoxyphenyl)-3-phenylchroman[5]



To a solution of **5a** (100 mg, 0.25 mmol) in MeOH/THF (8:2; 2 mL) was added $NaBH_4$ (140 mg, 3.69 mmol) and $NiCl_2.6H_2O$ (292 mg, 1.23 mmol) the reaction mixture was stirred at room temperature under nitrogen atmosphere. After completion of reaction (confirmed by TLC), the reaction mixture was filtered through celite pad carefully and the filtrate was evaporated under vacuum. The crude product was dissolved in ethyl acetate then washed with water (10 ml) and brine solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (15 mL). The combined organic extracts were dried over sodium sulfate and filtered. After removal of all the volatile components by evaporation, the residue was purified using silica gel column chromatography providing **7** as a light-yellow paste.

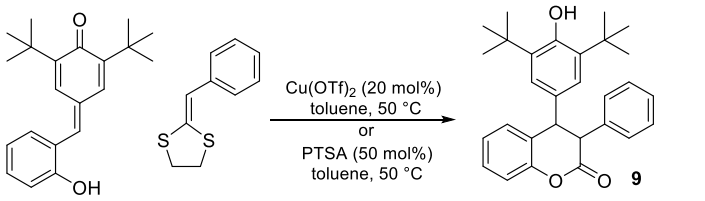
2.8. Synthesis of 4-(4-methoxyphenyl)-3-phenyl-2*H*-chromen-2-one



To a solution of **5a** (50 mg, 0.12 mmol) in MeCN/H_2O (9:1; 2 mL) was added DDQ (56 mg, 0.25 mmol) and the reaction mixture was stirred at room temperature under nitrogen atmosphere. After completion of reaction (confirmed by TLC), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and diluted with ethyl acetate (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (15 mL). The

combined organic extracts were washed with saturated $NaHCO_3$ solution dried over sodium sulfate and filtered. After removal of all the volatile components by evaporation, the residue was purified using silica gel column chromatography providing **8** as white crystalline solid.

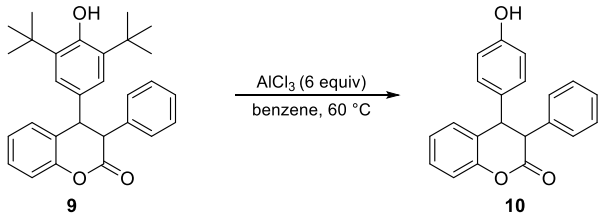
2.9. Synthesis of 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenylchroman-2-one (**9**):



with $Cu(OTf)_2$: 46%, *cis:trans* 1:6
with PTSA: 36%, *cis:trans* 1:8

To an oven dried reaction vial charged with *para* quinone methide **1a** (50 mg, 0.16 mmol), phenylene dithiolane **2a** (34 mg, 0.18 mmol), and $Cu(OTf)_2$ (0.2 equiv.) were dissolved in toluene (2 mL) and the reaction was stirred at 50 °C. The reaction was monitored by thin layer chromatography and after the consumption of the quinone methide, solvent was removed under reduced pressure without work up to afford crude product. The crude product **9** was purified by flash silica gel column chromatography (ethyl acetate in petroleum ether) to afford the product as white viscous solid (32 mg, 46% with $Cu(OTf)_2$; 25 mg, 36% with PTSA).

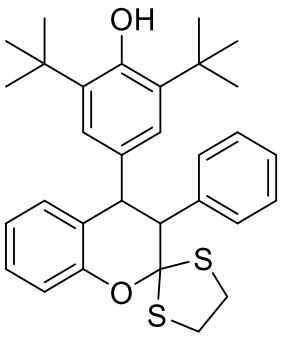
2.10. Synthesis of 4-(4-hydroxyphenyl)-3-phenylchroman-2-one (10):



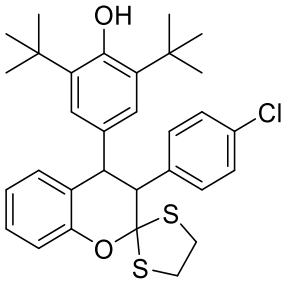
To an oven dried reaction vial equipped with magnetic stirrer bar, **9** (40mg, 0.093 mmol), $AlCl_3$ (75 mg, 0.560 mmol) were dissolved in 2 ml of benzene. The reaction mixture was heated at 60 °C for 2 h. After completion of reaction, the reaction mixture was quenched with water and partitioned in EtOAc/ water. The aqueous phase was extracted with EtOAc (x3). The combined organic layers were washed with saturated brine solution and dried over sodium sulphate, filtered and concentrated. The crude product was purified by flash column chromatography to afford the product (22 mg, 75%) yield.

3. Analytical data of synthesized products:

2,6-di-*tert*-Butyl-4-(3-phenylspiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3a) According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2a** (34 mg, 0.18 mmol) provided **3a** after flash column chromatography as light pink solid (58 mg, 71%). Mp = 182-184 °C, R_f = 0.6 (10% ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3637, 3418, 2956, 2853, 1736, 1452, 1156, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis*: *trans* = 1:3) δ 7.33 (d, *J* = 6.1 Hz, 1H), 7.20 – 7.18 (m, 3H), 7.11-7.00 (m, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.94-6.89 (m,1H), 6.64 (s, 2H), 4.97 (s, 0.36H), 4.95 (s, 1H), 4.88 (d, *J* = 6.5 Hz, 0.36H), 4.50 (d, *J* = 10.7 Hz, 1H), 3.78 (d, *J* = 10.8 Hz, 1H), 3.72 (d, *J* = 6.4 Hz, 0.46H), 3.70-3.63 (m, 0.67H), 3.55 – 3.50 (m, 1H), 3.48-3.44 (m, 1H), 3.42-3.32 (m, 0.54H), 3.23 (ddd, *J* = 11.3, 6.8, 5.3 Hz, 1H), 3.12 – 3.06 (m, 1H), 1.26 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.5, 153.3, 152.5, 152.2, 139.5, 139.3, 135.3, 135.1, 133.5, 130.8, 130.2, 129.9, 128.2, 127.9, 127.7, 127.5, 127.3, 127.2, 126.8, 126.5, 125.8, 123.9, 122.2, 121.9, 117.9, 117.8, 114.2, 110.7, 109.5, 57.7, 56.5, 49.8, 48.8, 39.6, 39.1, 38.5, 34.3, 34.2, 30.4, 29.8. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{31}H_{36}O_2S_2$ 504.2157, found 504.2167.

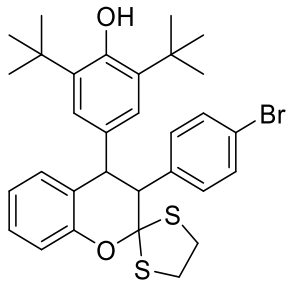


2,6-di-*tert*-Butyl-4-(3-(4-chlorophenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3b)



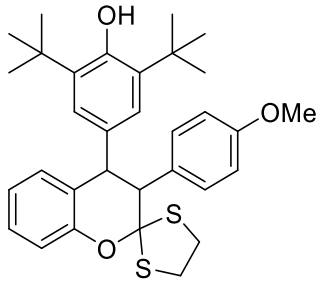
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2b** (41 mg, 0.18 mmol) provided **3b** after flash column chromatography as white solid (66 mg, 76%). Mp = 171-173 °C, R_f = 0.5 (10% ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3637, 3364, 2852, 1732, 1451, 1155, 855, 740. ^{1}H NMR (500 MHz, Chloroform-*d*)(mixture of diastereomers; *cis: trans* = 1:1.5) δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.20-7.15 (m, 3H), 7.05 – 7.02 (m, 1H), 6.97-6.89 (m, 3H), 6.61 (s, 2H), 5.01(s, 0.33H), 4.98 (s, 1H), 4.87 (d, *J* = 6.6 Hz, 0.33H), 4.44 (d, *J* = 11.2 Hz, 1H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.71(d, *J* = 3.6 Hz, 0.28H), 3.69-3.64 (m, 0.6H), 3.56 – 3.46 (m, 2H), 3.26 – 3.20 (m, 1H), 3.10-3.06 (m,1H), 1.27 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 152.8, 152.6, 152.0, 151.8, 137.3, 137.2, 134.9, 134.8, 132.6, 132.4, 130.6, 130.0, 129.6, 129.4, 127.7, 127.4, 127.2, 125.9, 125.1, 121.7, 121.4, 117.3, 117.25, 113.6, 109.9, 108.4, 56.4, 55.4, 49.4, 48.1, 39.0, 38.6, 38.5, 38.0, 33.7, 33.6, 29.8, 29.7. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{36}{}^{35}ClO_2S_2$ 539.1840, found 539.1845.

4-(3-(4-Bromophenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl)-2,6-di-*tert*-butylphenol (3c)



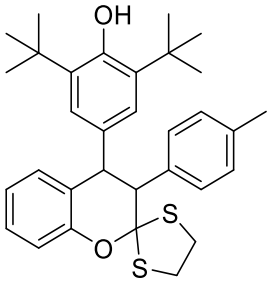
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2c** (48 mg, 0.18 mmol) provided **3c** after flash column chromatography as light brown solid (68 mg, 72%). Mp = 179-181 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1}= 3637, 3383, 2919, 2851, 1736, 1451, 1111, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:2) δ 7.32 – 7.30 (m, 2H), 7.24 – 7.16 (m, 2H), 7.05-7.01(m, 1H), 6.97 – 6.88 (m, 3H), 6.60 (s, 2H), 5.02 (s, 0.41H), 4.98 (s, 1H), 4.86 (d, *J* = 6.6 Hz, 0.34H), 4.43 (d, *J* = 11.2 Hz, 1H), 3.75 (d, *J* = 11.2 Hz, 1H), 3.69-3.64 (m,1H), 3.57 – 3.45 (m, 2H), 3.26 – 3.21 (m, 1H), 3.08 (ddd, *J* = 11.1, 6.4, 5.2 Hz, 1H), 1.27 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.3, 153.2, 152.6, 152.4, 138.4, 138.3, 135.5, 135.3, 132.9, 131.6, 130.7, 130.6, 130.3, 130.0, 128.3, 128.0, 126.5, 125.7, 122.4, 122.0, 121.5, 121.2, 117.9, 117.86, 114.2, 110.4, 108.9, 57.1, 56.0, 50.0, 48.7, 39.7, 39.3, 39.1, 38.6, 34.3, 34.2, 30.4, 30.3. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{36}{}^{79}BrO_2S_2$ 583.1335, found 583.1337.

2,6-di-*tert*-Butyl-4-(3-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3d)



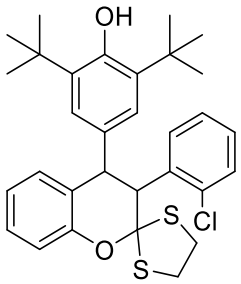
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2d** (40 mg, 0.18 mmol) provided **3d** after flash column chromatography as pale-yellow solid (54 mg, 63%). Mp = 170-172 °C, R_f = 0.3 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3638, 3394, 2920, 2851, 1737, 1451, 1110, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans*;1:1.3) δ 7.19 (dd, *J* = 15.0, 7.2 Hz, 2H), 7.05-6.99 (m,1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.93-6.88 (m, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 2H), 4.98 (s, 0.32H), 4.96 (s, 1H), 4.83 (d, *J* = 6.5 Hz, 0.30H), 4.44 (d, *J* = 10.8 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 0.58H), 3.67 (d, *J* = 10.6 Hz,1H), 3.55 – 3.44 (m, 2H), 3.23 (ddd, *J* = 11.3, 6.9, 5.1 Hz, 1H), 3.10 (ddd, *J* = 11.1, 6.1, 5.3 Hz, 1H), 1.26 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 158.7, 158.6, 153.5, 153.3, 152.4, 152.2, 135.2, 135.1, 133.6, 131.6, 131.5, 130.8, 130.5, 130.2, 128.1, 127.8, 126.8, 126.5, 125.8, 123.9, 122.1, 121.9, 117.9, 117.7, 113.0, 111.1, 109.8, 56.7, 55.7, 55.2, 55.1, 49.9, 48.8, 39.4, 39.2, 39.1, 38.5, 34.3, 34.2, 30.4, 30.3. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{32}H_{39}O_3S_2$ 535.2335 found 535.2319.

2,6-di-*tert*-Butyl-4-(3-*p*-tolyl spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3e)



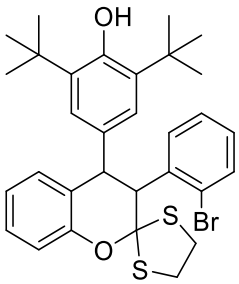
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2f** (37 mg, 0.18 mmol) provided **3e** after flash column chromatography as pale-yellow solid (56 mg, 67%). Mp = 163-165 °C, R_f = 0.4 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3639, 3392, 2919, 2851, 1736, 1451, 739.^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:1.3) δ 7.24-7.17 (m, 3H), 7.01 – 6.96 (m, 4H), 6.92 – 6.89 (m, 1H), 6.63 (s, 2H), 4.98 (s, 0.27H), 4.96 (s, 1H), 4.85 (d, *J* = 6.5 Hz, 0.28H), 4.47 (d, *J* = 10.6 Hz, 1H), 3.73 (d, *J* = 10.7 Hz, 1H), 3.69 (d, *J* = 6.2 Hz, 0.45H), 3.67-3.64 (m,0.29H), 3.57 – 3.52 (m, 1H), 3.49-3.45 (m, 1H), 3.40 (ddd, *J* = 10.9, 6.8, 5.3 Hz, 0.34H), 3.24 (ddd, *J* = 11.1, 7.1, 5.1 Hz, 1H), 3.16 – 3.11 (m, 1H), 2.28 (s, 3H), 2.21 (s, 1H), 1.26 (s, 18H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.5, 153.3, 152.4, 152.2, 136.8, 136.7, 136.6, 136.2, 135.2, 135.1, 133.6, 130.8, 130.4, 130.2, 128.4, 128.1, 127.8, 126.7, 126.5, 125.8, 122.1, 121.8, 117.9, 117.7, 110.8, 109.6, 57.3, 56.1, 50.0, 48.9, 39.5, 39.1, 39.09, 38.4, 34.3, 34.2, 30.3, 30.26, 21.2, 21.1. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{32}H_{38}O_2S_2$ 518.2313, found 518.2311.

2,6-di-*tert*-Butyl-4-(3-(2-chlorophenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3f)



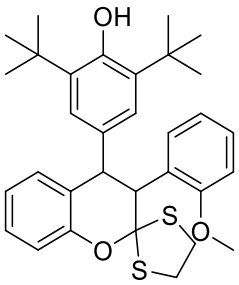
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2g** (41 mg, 0.18 mmol) provided **3f** after flash column chromatography as white solid (50 mg, 58%). Mp = 172-174 °C, R_f = 0.4 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3638, 3407, 2923, 2853, 1732, 1452, 1110, 740. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers ; *cis : trans* = 1:3) δ 7.91 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.08 – 7.05 (m, 1H), 6.98 – 6.87 (m, 3H), 6.72 (s, 2H), 4.95 (s, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 3.55 (ddd, *J* = 11.5, 7.1, 5.0 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.18 (ddd, *J* = 11.3, 6.9, 5.1 Hz, 1H), 3.08 (ddd, *J* = 11.4, 6.5, 5.0 Hz, 1H), 1.27 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.2, 152.4, 136.8, 136.3, 135.4, 132.4, 130.6, 129.6, 129.0, 128.1, 128.0, 126.7, 126.0, 125.9, 121.9, 117.9, 110.7, 50.7, 49.9, 39.4, 38.3, 34.3, 30.4, 30.3. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{36}{}^{35}ClO_2S_2$539.1840, found 539.1847.

4-(3-(2-Bromophenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl)-2,6-di-*tert*-butylphenol (3g)



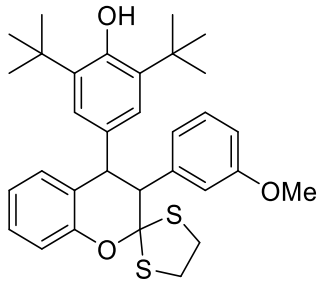
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2h** (48 mg, 0.18 mmol) provided **3g** after flash column chromatography as white solid (51 mg, 54 %). Mp = 195-197 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3636, 3415, 2922, 2852, 1735, 1450, 1120, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:3) δ 7.92 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.3 Hz, 0.18 H) 7.37 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.03 (m, 1H), 7.01 – 6.88 (m, 3H), 6.70 (s, 2H), 4.95 (s, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 3.71-3.62 (m, 0.40 H), 3.56 (ddd, *J* = 11.2, 6.9, 5.0 Hz, 1H), 3.45 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.20 – 3.04 (m, 2H), 1.27 (s, 18H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.3, 153.2, 152.5, 152.4, 138.7, 138.3, 135.3, 134.8, 132.6, 132.4, 132.3, 130.5, 130.3, 129.8, 128.6, 128.3, 128.2, 128.0, 127.9, 127.4, 126.7, 126.5, 125.9, 122.4, 121.9, 118.0, 117.9, 110.6, 108.9, 53.7, 52.6, 50.1, 47.8, 39.6, 39.5, 38.2, 34.3, 34.2, 30.3, 30.2. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{36}{}^{79}BrO_2S_2$ 583.1335, found 583.1328.

2,6-di-*tert*-Butyl-4-(3-(2-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3h)



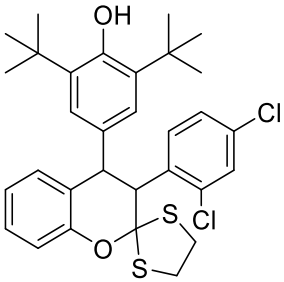
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2i** (40 mg, 0.18 mmol) provided **3h** after flash column chromatography as yellow solid (43 mg, 50 % yield). Mp = 184-186 °C, R_f = 0.7 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} =3638, 3425, 2922, 2852, 1736, 1451, 1114, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2) δ 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (d, *J* = 9.1 Hz,0.21H), 7.17 – 7.11 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 0.26 H), 6.97 – 6.88 (m, 4H), 6.82-6.78 (m, 0.3H), 6.71 – 6.67 (m, 3H), 6.52 (d, *J* = 7.9 Hz,0.26H), 4.95 (s,0.31H), 4.92 (s, 1H), 4.85 (d, *J* = 6.7 Hz, 0.23H), 4.68 (d, *J* = 11.3 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 0.22H), 4.43 (d, *J* = 11.2 Hz, 1H), 3.55 (s, 3H), 3.48-3.42 (m, 1H), 3.21 – 3.08 (m, 3H), 1.27 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 158.3, 157.8, 153.7, 152.6, 152.4, 135.3, 134.8, 133.7, 131.1, 130.6, 129.1, 129.0, 128.7, 128.6, 128.3, 128.2, 128.1, 127.2, 126.3, 124.4, 122.4, 122.0, 121.1, 120.4, 118.2, 118.0, 111.4, 111.0, 110.9, 110.0, 56.2, 56.0, 49.9, 48.9, 46.2, 45.4, 40.0, 39.4, 38.6, 34.6, 34.4, 34.3, 30.7, 30.1. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{32}H_{38}O_3S_2$ 534.2262, found 534.2214.

2,6-di-*tert*-Butyl-4-(3-(3-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3i)



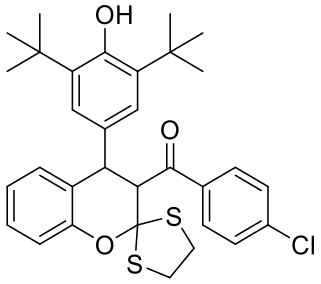
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2j** (40 mg, 0.18 mmol) provided **3i** after flash column chromatography as light brown solid (53 mg, 63% yield). Mp = 147-149 °C, R_f = 0.3 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3437,2957, 2919, 2852, 1763, 1435, 1156, 754. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* = 1:1.3) δ 7.23 – 7.15 (m, 1H), 7.06 (dt, *J* = 28.3, 8.4 Hz, 2H), 6.99 – 6.87 (m, 4H), 6.72 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.63 (s, 2H),4.99 (s, 0.29 H), 4.96 (s, 1H),4.86 (d, *J* = 6.6 Hz, 0.32 H), 4.46 (d, *J* = 10.8 Hz, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 3.69 (s, 3H), 3.56 – 3.46 (m, 2H),3.43-3.37 (m, 0.35 H), 3.29 – 3.23 (m, 1H), 3.20 – 3.10 (m, 1H), 1.26 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 159.0, 153.5, 153.3, 152.5, 152.2, 141.1, 140.5, 135.3, 135.2, 133.4, 130.7, 130.1, 128.5, 128.1, 127.9, 126.7, 126.4, 125.8, 122.1, 121.9, 117.9, 117.7, 112.6, 110.5, 109.3, 57.7, 55.2, 54.8, 50.1, 48.9, 39.7, 39.2, 39.0, 38.5, 34.24, 34.17, 30.4, 30.3.HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{32}H_{39}O_3S_2$ 535.2335 found 535.2311.

2,6-di-*tert*-Butyl-4-(3-(2,4-dichlorophenyl) spiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3j)



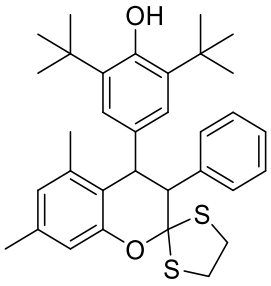
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2m** (47 mg, 0.18 mmol) provided **3j** after flash column chromatography as light-yellow solid (77 mg, 86% yield). Mp = 198-200 °C, R_f = 0.3 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3637, 3419, 2923, 2853, 1733, 1452, 1156, 740. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* = 1:3) δ 7.87 (d, *J* = 9.1 Hz, 1H), 7.43 (d, *J* = 9.1 Hz,0.18H), 7.19 (dt, *J* = 4.5, 2.0 Hz, 2H), 7.17 (d, *J* = 3.1 Hz, 0.25H), 7.10 – 7.03 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.88 (m, 2H), 6.70 (s, 2H), 5.00(s, 0.18H), 4.99 (s, 1H), 4.94 (d, *J* = 7.1 Hz, 0.18H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 7.1 Hz, 0.17 H), 4.41 (d, *J* = 11.6 Hz, 1H), 3.71 – 3.63 (m, 0.37 H), 3.59 – 3.54 (m, 1 H), 3.49 – 3.45 (m, 1H), 3.20 – 3.16 (m, 1H), 3.11 – 3.06 (m, 1H), 1.28 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) (mixture of diastereomers) δ 153.2, 153.0, 152.6, 152.5, 137.0, 135.5, 135.4, 133.4, 133.1, 131.9, 130.5, 130.4, 129.1, 128.8, 128.7, 128.4, 128.1, 127.0, 126.4, 126.2, 125.7, 122.6, 122.0, 118.1, 117.9, 110.4, 108.5, 50.3, 49.9, 49.5, 39.5, 39.3, 38.3, 34.3, 34.2, 30.3, 30.2.HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{35}{}^{35}Cl_2O_2S_2$ 573.1450, found 573.1450.

(4-Chlorophenyl) ((*3S,4S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-3-yl) methanone (3k)



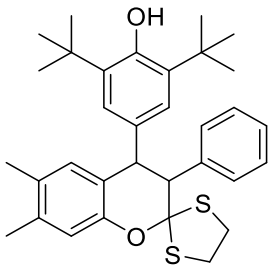
According to general procedure **2.4**, **1a** (50 mg, 0.16 mmol) and phenyl dithiolane **2n** (45 mg, 0.18 mmol) provided **3k** after flash column chromatography as light-yellow solid (59 mg, 65 % yield). Mp = 188-190 °C, R_f = 0.7 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} =3635, 3415, 2921, 2852, 1735, 1685, 1451, 1111, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:3) δ 7.52 – 7.48 (m, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 6.96 – 6.88 (m, 3H), 6.81 (s, 2H), 4.98 (s, 1H), 4.68 (s, 2H), 3.65 – 3.59 (m, 1H), 3.48 (ddd, *J* = 11.5, 9.2, 4.9 Hz, 1H), 3.38-3.33 (m,1H), 3.31 – 3.25 (m, 1H), 1.25 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 196.8, 153.1, 152.9, 139.1, 137.4, 136.2, 131.5, 130.0, 129.4, 128.5, 128.1, 126.0, 125.6, 122.2, 117.9, 105.9, 54.7, 48.1, 40.4, 37.4, 34.3, 30.3. HRMS (ESI) *m/z*: $[M+Na]^+$calcd for $C_{32}H_{35}{}^{35}ClNaO_3S_2$ 589.1608, found 589.1616.

2,6-di-*tert*-Butyl-4-(5,7-dimethyl-3-phenylspiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3l)



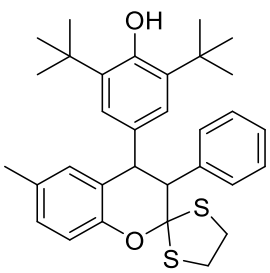
According to general procedure **2.4**, **1b** (50 mg, 0.15 mmol) and phenyl dithiolane **2a** (32 mg, 0.16 mmol) provided **3l** after flash column chromatography as yellow solid (56 mg, 71 % yield). Mp = 170-172 °C, R_f = 0.8 (15 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3639, 3375, 2919, 2851, 1736, 1435, 1120, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:3) δ 7.38 – 7.33 (m, 2H), 7.29 – 7.24 (m, 3H), 6.73 (s, 1H), 6.67 (s, 1H), 6.61 (s, 2H), 4.32 (d, *J* = 7.2 Hz, 1H), 3.80 (d, *J* = 7.2 Hz, 1H), 3.53 – 3.38 (m, 2H), 3.21 – 3.13 (m, 2H), 2.33 (s, 3H), 1.77 (s, 3H), 1.26 (s, 18H).^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.2, 152.0, 141.5, 138.7, 137.4, 135.3, 134.1, 129.4, 128.0, 127.4, 125.8, 124.8, 120.8, 116.5, 108.8, 59.6, 48.1, 39.1, 38.4, 34.3, 30.4, 21.2, 20.5. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{33}H_{40}O_2S_2$532.2470, found 532.2478.

2,6-di-*tert*-Butyl-4-(6,7-dimethyl-3-phenylspiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3m)



According to general procedure **2.4**, **1c** (50 mg, 0.15 mmol) and phenyl dithiolane **2a** (32 mg, 0.16 mmol) provided **3m** after flash column chromatography as yellow paste (57 mg, 73% yield). Mp = 160-163 °C, R_f = 0.8 (15 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3637, 3395, 2920, 2852, 1736, 1435, 1156, 738. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2.5) δ 7.32 – 7.27 (m, 1H), 7.19 – 7.14 (m, 3H), 7.10 – 7.04 (m, 1H), 6.84 (s, 0.31H), 6.79 – 6.70 (m, 2H), 6.63 (s, 2H), 6.53 (s, 0.24H), 4.95 (s, 0.27H), 4.93 (s, 1H), 4.82 (d, *J* = 6.6 Hz, 0.31H), 4.42 (d, *J* = 10.4 Hz, 1H), 3.72 (d, *J* = 10.5 Hz, 1H), 3.68 – 3.61 (m, 1H), 3.53 – 3.48 (m, 1H), 3.47 – 3.40 (m, 1H), 3.41 – 3.36 (m, 0.40H), 3.26 – 3.16 (m, 1H), 3.13 – 3.05 (m, 1H), 2.26 (s, 1H), 2.23 (s, 3H), 2.09 (s, 3H), 1.25 (s, 18H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) δ 152.3, 152.1, 151.5, 151.2, 139.8, 139.3, 136.6, 136.4, 135.2, 135.1, 133.7, 131.1, 130.6, 130.5, 130.5, 130.2, 127.11, 127.06, 126.3, 125.8, 123.5, 118.7, 118.6, 110.5, 109.4, 58.1, 56.9, 49.6, 48.4, 39.5, 39.01, 38.96, 38.3, 34.3, 34.2, 30.37, 30.35, 19.7, 18.9. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{33}H_{41}O_2S_2$ 533.2542, found 533.2543.

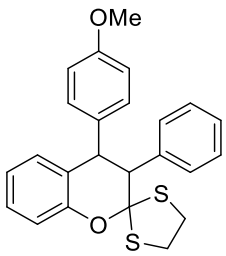
2,6-di-*tert*-butyl-4-(6-methyl-3-phenylspiro [chroman-2,2'- [1,3] dithiolane]-4-yl) phenol (3n)



According to general procedure **2.4**, **1d** (50 mg, 0.15 mmol) and phenyl dithiolane **2a** (33 mg, 0.17 mmol) provided **3n** after flash column chromatography as yellow paste (61 mg, 76% yield). R_f = 0.7 (15 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3638, 3416, 2957, 2853, 1435, 1120, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:1.1) δ 7.31 (s, 2H), 7.18 (d, *J* = 3.4 Hz, 3H), 7.02 (ddd, *J* = 37.8, 16.8, 7.7 Hz, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.62 (s, 2H), 4.96 (s, 0.31H), 4.95 (s, 1H), 4.85 (d, *J* = 6.6 Hz, 0.36H), 4.45 (d, *J* = 10.5 Hz, 1H), 3.73 (d, *J* = 10.5 Hz, 1H), 3.70 – 3.61 (m, 1H),3.53 (dd, *J* = 7.2, 4.1 Hz, 1H) 3.45 (ddd, *J* = 16.4, 10.8, 5.2 Hz, 2H), 3.21 (dt, *J* = 11.5, 5.9 Hz, 1H), 3.09 (dt, *J* = 10.8, 5.5 Hz, 1H), 2.20 (s, 3H), 1.25 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 152.4, 152.2, 151.5, 151.2, 139.7, 139.3, 135.23, 135.16, 133.7, 131.6, 131.2,

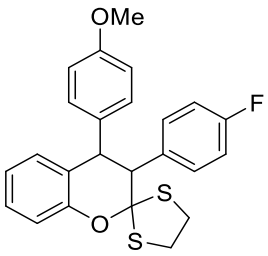
130.8, 130.3, 129.9, 128.9, 128.7, 127.7, 127.24, 127.16, 126.5, 126.2, 125.9, 123.4, 117.8, 117.6, 110.6, 109.4, 58.1, 56.8, 49.9, 48.8, 39.5, 39.1, 38.4, 34.3, 34.2, 30.4, 20.8. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{32}H_{38}O_2S_2$518.2313, found 518.2313.

4-(4-methoxyphenyl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5a)



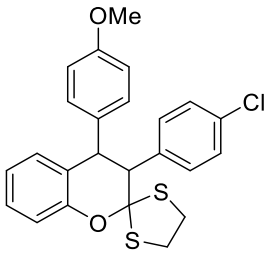
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2a** (65 mg, 0.33 mmol) provided **5a** after flash column chromatography as light-yellow solid (100 mg, 81% yield). Mp = 155-157 °C, R_f = 0.3 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3304, 3053, 2921, 2851, 1732, 1451, 1108, 737. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:4.7) δ 7.41 – 7.36 (m, 2H), 7.23 – 7.14 (m, 4H), 6.97 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.94 – 6.85 (m, 3H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.67(s, 1H), 6.65 (s, 1H), 4.94 (d, *J* = 6.6 Hz, 0.08 H), 4.58 (d, *J* = 11.0 Hz, 1H), 3.92 (d, *J* = 11.0 Hz, 1H), 3.72(s, 0.34 H), 3.70 (s, 3H), 3.53 – 3.42 (m, 2H), 3.21 – 3.16 (m, 1H), 3.02 (ddd, *J* = 11.2, 6.3, 5.1 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.2, 153.3, 138.8, 135.2, 130.6, 130.2, 130.0, 128.0, 127.8, 127.4, 126.9, 122.1, 118.0, 113.7, 111.0, 56.9, 55.2, 48.5, 39.1, 38.5. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{23}O_2S_2$ 407.1134, found 407.1138.

3-(4-fluorophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5b)



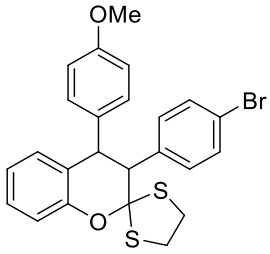
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2e** (71 mg, 0.33 mmol) provided **5b** after flash column chromatography as white solid, (115 mg, 89% yield). Mp = 160-162 °C, R_f = 0.6 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3453, 3053, 2924, 2852, 1732, 1451, 1177, 738. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2.7)δ 7.36 (s, 2H), 7.19-7.16 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.91-6.87 (m, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 2H), 4.53 (d, *J* = 11.3 Hz, 1H), 3.91 (d, *J* = 11.3 Hz, 1H), 3.71 (s, 3H), 3.53 – 3.43 (m, 2H), 3.21 – 3.16 (m, 1H), 3.03-2.99 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 246.0 Hz), 158.2, 153.1, 134.8, 134.4 (d, *J* = 3.1 Hz), 130.9 (d, *J* = 105.8 Hz), 130.0, 128.0, 126.7, 122.0, 117.9, 114.5 (d, *J* = 21.1 Hz), 113.7, 111.0, 56.1, 55.1, 48.6, 39.0, 38.5.^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.06 (tt, *J* = 9.1, 5.2 Hz).HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{22}FO_2S_2$ 425.1040, found 425.1031.

3-(4-Chlorophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5c)



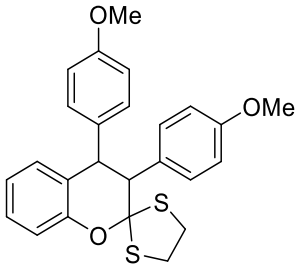
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2b** (76 mg, 0.33 mmol) provided **5c** after flash column chromatography as light pink solid (103 mg, 77% yield). Mp = 182-184°C, R_f = 0.4 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3053, 2925, 2853, 1735, 1451, 1177, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1 : 2.8) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.19 – 7.17 (m, 3H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.90 – 6.86 (m, 3H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.53 (d, *J* = 11.4 Hz, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 3.71 (s, 3H), 3.54 – 3.42 (m, 2H), 3.21 – 3.15 (m, 1H), 3.03 – 2.97 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.3, 153.1, 137.1, 134.7, 133.1, 131.4, 130.4, 130.1, 128.1, 127.9, 126.7, 122.1, 118.0, 113.8, 110.8, 56.3, 55.2, 48.5, 39.2, 38.6. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{22}{}^{35}ClO_2S_2$ 441.0744, found 441.0741.

3-(4-Bromophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5d)



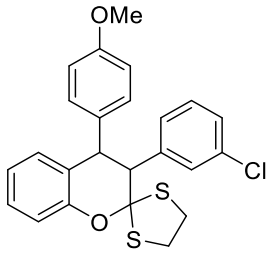
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2c** (91 mg, 0.33 mmol) provided **5d** after flash column chromatography as white solid (95 mg, 64% yield). Mp = 191-193 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} =3052, 2925, 2852, 1733, 1451, 1177, 738. ^{1}H NMR (400 MHz, Chloroform-*d*)(mixture of diastereomers; *cis:trans* = 1:3.2) δ 7.34 – 7.28 (m, 4H), 7.20-7.16 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.91 – 6.86 (m, 3H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.70 – 6.67 (m, 2H), 4.54 (d, *J* = 11.4 Hz, 1H), 3.90 (d, *J* = 11.4 Hz, 1H), 3.71 (s, 3H), 3.54 – 3.42 (m, 2H), 3.20 – 3.15 (m, 1H), 3.03 – 2.97 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.6, 153.4, 137.9, 134.9, 132.0, 131.1, 130.7, 130.4, 128.4, 127.0, 122.4, 121.7, 118.2, 114.1, 110.9, 56.6, 55.5, 48.8, 39.5, 38.9. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{22}{}^{79}BrO_2S_2$ 485.0239, found 485.0236.

3,4-Bis(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5e)



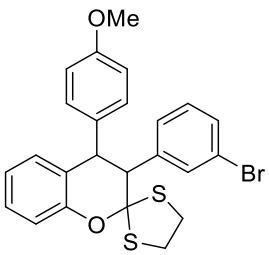
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2d** (75 mg, 0.33 mmol) provided **5e** after flash column chromatography as light-yellow solid (100 mg, 75% yield). Mp = 155-157 °C, R_f = 0.6 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1}= 3053, 2926, 2853, 1736, 1451, 1109, 738 .^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:3.5) δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.20-7.16 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.93 – 6.90 (m, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 4.55 (d, *J* = 11.1 Hz, 1H), 3.89 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.54 – 3.41 (m, 2H), 3.18 (ddd, *J* = 11.4, 6.7, 5.3 Hz, 1H), 3.05-3.00 (m, 1H).^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (major diastereomer) δ 158.6, 158.1, 153.2, 135.2, 131.0, 130.8, 130.5, 130.1, 127.9, 126.9, 121.9, 117.9, 113.6, 113.0, 111.4, 56.0, 55.1, 55.05, 48.5, 39.0, 38.4. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{25}H_{24}O_3S_2$436.1167, found 436.1150.

3-(3-chlorophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5f)



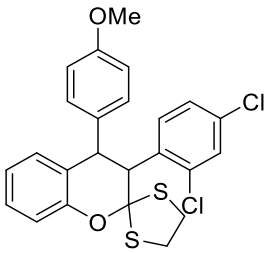
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2k** (76 mg, 0.33 mmol) provided **5f** after flash column chromatography as white solid (102 mg, 76% yield). Mp = 175-177 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1}= 3053, 2925, 2852, 1735, 1451, 1177, 738. ^{1}H NMR (400 MHz, Chloroform-*d*)(mixture of diastereomers; *cis : trans* = 1:3.3) δ 7.50 (s, 1H), 7.21 – 7.16 (m, 3H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.93 – 6.87 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.71 – 6.67 (m, 2H), 4.56 (d, *J* = 11.3 Hz, 1H), 3.91 (d, *J* = 11.3 Hz, 1H), 3.71 (s, 3H), 3.55 – 3.42 (m, 2H), 3.22 – 3.16 (m, 1H), 3.05 – 2.99 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.0, 152.8, 140.4, 134.2, 133.1, 130.1, 129.7, 128.5, 127.7, 127.2, 126.3, 121.8, 117.6, 113.5, 110.2, 56.2, 54.8, 48.2, 38.8, 38.3. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{24}H_{21}{}^{35}ClO_2S_2$440.0671, found 440.0663.

3-(3-bromophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5g)



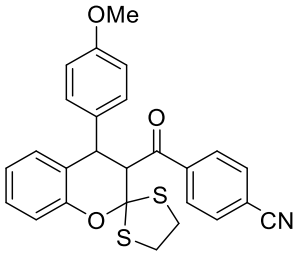
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2l** (91 mg, 0.33 mmol) provided **5g** after flash column chromatography as white solid (99 mg, 67% yield). Mp = 180-182 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3052, 2925, 2852, 1732, 1451, 1177, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:1.2) δ 7.66 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 1H), 7.08-7.04 (m, 1H), 7.00 – 6.97 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 6.9 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.57 (d, *J* = 11.3 Hz, 1H), 3.91 (d, *J* = 11.3 Hz, 1H), 3.71 (s, 3H), 3.54 – 3.41 (m, 2H), 3.19 (ddd, *J* = 11.4, 6.7, 5.1 Hz, 1H), 3.04 – 2.99 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 157.9, 152.7, 140.6, 134.2, 132.4, 130.1, 129.7, 128.8, 127.7, 126.2, 121.7, 121.4, 117.6, 113.5, 110.1, 56.1, 54.8, 48.1, 38.8, 38.2. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{22}{}^{79}BrO_2S_2$485.0239, found 485.0238.

3-(2,4-Dichlorophenyl)-4-(4-methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5h)



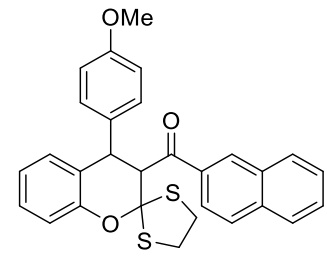
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2m** (88 mg, 0.33 mmol) provided **5h** after flash column chromatography as light-yellow paste (84 mg, 58% yield). Mp = 163-165 °C, R_f = 0.4 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3438, 2926, 2850, 1763, 1451, 1177. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers ; *cis : trans* = 1:4) δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.97-6.94 (m, 3H), 6.88-6.85 (m, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 3.72 (s, 3H), 3.55 (ddd, *J* = 11.6, 6.9, 5.0 Hz, 1H), 3.46-3.42 (m, 1H), 3.16 – 3.12 (m, 1H), 3.08-3.04 (m, 1H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) δ 158.7, 153.1, 137.3, 135.2, 134.0, 133.6, 130.5, 130.3, 129.3, 128.4, 126.8, 122.4, 118.2, 114.1, 110.9, 55.4, 49.9, 48.9, 39.7, 38.6. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{24}H_{20}{}^{35}Cl_2O_2S_2$ 474.0282, found 474.0290.

4-(4-(4-Methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-3-ylcarbonyl) benzonitrile (5i)



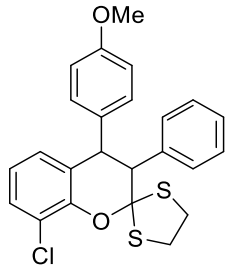
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2p** (83 mg, 0.33 mmol) provided **5i** after flash column chromatography as light-yellow paste (66 mg, 47% yield). Mp = 165-168 °C, R_f = 0.6 (25 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3387, 3054, 2919, 2851, 1735, 1467, 1177, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:2.5) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.20-7.16 (m, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.83 (d, *J* = 7.7 Hz,1H), 6.71 (d, *J* = 8.6 Hz, 2H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.8 Hz, 1H), 3.70 (s, 3H), 3.63-3.58 (m, 1H), 3.45 (ddd, *J* = 11.7, 9.2, 5.1 Hz, 1H), 3.35 – 3.30 (m, 1H), 3.27 – 3.21 (m, 1H). ^{13}C{^{1}H}NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 196.5, 159.2, 153.2, 153.1, 142.3, 132.8, 130.5, 130.3, 128.7, 128.6, 126.2, 122.8, 118.3, 118.2, 116.4, 114.6, 105.6, 55.6, 55.1, 46.9, 40.7, 37.5. HRMS (ESI) *m/z*: $[M+Na]^+$calcd for $C_{26}H_{21}NNaO_3S_2$ 482.0855, found 482.0852.

(4-(4-Methoxyphenyl) spiro [chroman-2,2'- [1,3] dithiolane]-3-yl) (naphthalen-2-yl) methanone (5j)



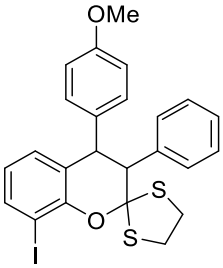
According to general procedure **2.4**, **4a** (70 mg, 0.30 mmol) and phenyl dithiolane **2o** (91 mg, 0.33 mmol) provided **5j** after flash column chromatography as light-yellow paste (37 mg, 25% yield). Mp = 176-178 °C, R_f = 0.5 (25 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3397, 2921, 2851, 1736, 1467, 1177, 740. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2) δ 8.18 (s, 1H), 7.84 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.80 – 7.76 (m, 2H), 7.58 – 7.45 (m, 3H), 7.19 – 7.14 (m,1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.95 – 6.81 (m, 3H), 6.68 – 6.66 (m, 1H), 5.10 (d, *J* = 7.8 Hz, 0.22H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.83 (d, *J* = 7.9 Hz, 0.20 H), 3.74 (s, 1H), 3.62 (s, 3H), 3.57 (dt, *J* = 10.4, 5.0 Hz, 1H), 3.51 – 3.39 (m, 1H), 3.34 – 3.29 (m, 1H), 3.27 – 3.21 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* = 1:2) δ 201.0, 173.5, 136.1, 135.5, 133.9, 132.4, 130.2, 130.1, 129.8 (2C), 129.1, 128.5, 128.4, 128.0, 127.7, 126.7, 126.4, 124.1, 122.3, 117.8, 114.7, 105.8, 55.1, 54.0, 46.4, 40.1, 37.1. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{29}H_{25}O_3S_2$ 485.1240, found 485.1231.

8-Chloro-4-(4-methoxyphenyl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5k)



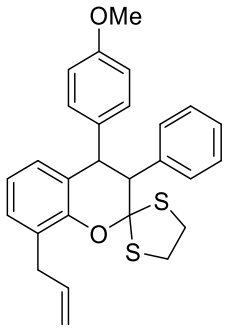
According to general procedure **2.4**, **4b** (70 mg, 0.3 mmol) and phenyl dithiolane **2a** (57 mg, 0.3 mmol) provided **5k** after flash column chromatography as white solid (80 mg, 69% yield). Mp= 200-202°C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3449, 3062, 2921, 2851, 1496, 1177, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1 : 4.6)(major diastereomer) δ 7.38 (d, *J* = 5.1 Hz, 2H), 7.27 – 7.21 (m, 4H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.83-6.79 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 4.59 (d, *J* = 11.3 Hz, 1H), 3.97 (d, *J* = 11.3 Hz, 1H),3.70 (s, 3H), 3.61 (ddd, *J* = 11.4, 7.0, 5.3 Hz, 1H), 3.52-3.46 (m, 1H), 3.26 – 3.20 (m, 1H), 3.15-3.10 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (major diastereomer) δ 158.3, 149.1, 138.1, 134.7, 130.0, 129.8, 129.1, 128.9, 128.4, 127.8, 127.5, 123.0, 122.0, 113.8, 111.6, 56.2, 55.1, 48.8, 38.8, 38.3. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{24}H_{21}{}^{35}ClO_2S_2$ 440.0671, found 440.0675.

8-Iodo-4-(4-methoxyphenyl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5l)



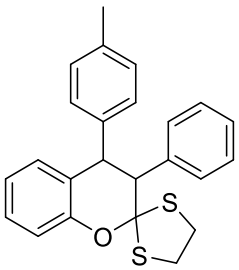
According to general procedure **2.4**, **4c** (70 mg,0.2 mmol) and phenyl dithiolane **2a** (42 mg, 0.22 mmol) provided **5l** after flash column chromatography as yellow solid (89 mg, 85% yield). Mp = 206-208 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3478, 3061, 2922, 2851, 1736, 1454, 1177, 736. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2) δ 7.72 (d, *J* = 8.7 Hz, 0.17H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.21 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.81 – 6.77 (m, 1H), 6.67 – 6.61 (m, 3H), 4.92 (d, *J* = 6.7 Hz, 0.09H), 4.57 (d, *J* = 11.3 Hz, 1H), 3.96 (d, *J* = 11.3 Hz, 1H), 3.71 (s, 0.42 H), 3.70 (s, 3H), 3.69 – 3.64 (m, 1H), 3.52 (dt, *J* = 10.7, 5.5 Hz, 1H), 3.28 – 3.16 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.3, 152.1, 138.1, 137.6, 134.7, 130.8, 130.1, 129.8, 128.5, 127.9, 127.6, 123.6, 113.8, 111.9, 87.0, 56.4, 55.2, 49.0, 38.7, 38.3. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{24}H_{22}IO_2S_2$ 533.0100, found 533.0096

4-(4-Methoxyphenyl)-3-phenyl-8-vinyl spiro [chroman-2,2'- [1,3] dithiolane] (5m)



According to general procedure **2.4**, **4d** (70mg, 0.26 mmol) and phenyl dithiolane **2a** (55 mg, 0.28 mmol) provided **5m** after flash column chromatography as pale-yellow solid (91 mg, 79% yield). Mp = 156-160°C, R_f = 0.5 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3396, 3056, 2919, 2851, 1735, 1452, 1177, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:2) δ 7.42 (d, *J* = 5.2 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.87-6.83 (m, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 2H), 6.09 (ddt, *J* = 16.6, 10.1, 6.6 Hz, 1H), 5.19 – 5.09 (m, 2H), 4.62 (d, *J* = 11.0 Hz, 1H), 3.96 (d, *J* = 11.0 Hz, 1H), 3.71 (s, 3H), 3.55(dt, *J* = 4.5, 2.7 Hz,1H), 3.51(dd, *J* = 6.7, 4.4 Hz,1H) 3.46 – 3.39 (m, 2H), 3.23 – 3.16 (m, 1H), 3.12-3.06 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* =1:2) δ 157.8, 150.8, 138.5, 136.7, 135.1, 129.8, 129.6, 128.5, 128.3, 127.9, 127.6, 127.4, 127.1, 127.0, 126.4, 121.4, 121.3, 115.3, 113.3, 112.8, 110.6, 109.1, 56.3, 55.6, 54.8, 48.4, 47.9, 39.1, 38.8, 38.4, 38.1, 34.3, 34.1. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{27}H_{26}O_2S_2$ 446.1374, found 446.1363.

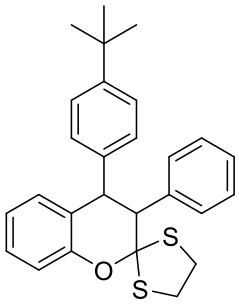
3-Phenyl-4-*p*-tolylspiro [chroman-2,2'- [1,3] dithiolane] (5n)



According to general procedure **2.4**, **4e** (70 mg, 0.33 mmol) and phenyl dithiolane **2a** (70 mg, 0.36 mmol) provided **5n** after flash column chromatography as white solid (106 mg, 83% yield). Mp = 155-157 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3336, 3029, 2919, 2850, 1736, 1451, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2.8) δ 7.41 (d, *J* = 5.0 Hz, 2H), 7.21 (t, *J* = 5.8 Hz, 4H),7.08 (d, *J* = 8 Hz, 0.27 H) 7.01 – 6.80 (m, 7H), 4.99 (d, *J* = 6.5 Hz, 0.08H), 4.63 (d, *J* = 10.9 Hz, 1H), 3.97 (d, *J* = 11.0 Hz, 1H), 3.80 (d, *J* = 6.6 Hz, 0.09H), 3.67 (tt, *J* = 10.7, 6.1 Hz, 0.22H), 3.48 (ddt, *J* = 22.2, 11.3, 5.4 Hz, 2H), 3.19 (dt, *J* = 11.6, 5.8 Hz, 1H), 3.02 (dt, *J* = 10.8, 5.6 Hz, 1H), 2.23 (s, 3H). ^{13}C{^{1}H}NMR(100 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:2.8) δ 153.3, 140.1, 140.0, 138.8, 138.7, 136.2, 136.1, 130.6, 130.0, 129.1, 129.0, 128.0, 127.71, 127.68, 127.38, 127.35,

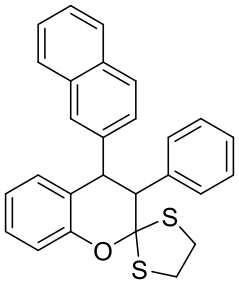
126.8, 126.7, 122.0, 118.0, 110.98, 110.95, 56.8, 56.2, 48.8, 48.4, 39.5, 39.0, 38.5, 21.1. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{24}H_{22}OS_2$ 390.1112, found 390.1100.

4-(4-*tert*-Butylphenyl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5o)



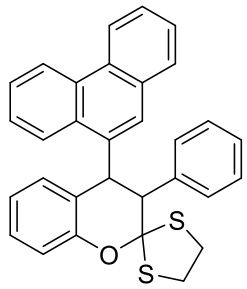
According to general procedure **2.4**, **4f** (70 mg, 0.27 mmol) and phenyl dithiolane **2a** (58 mg, 0.30 mmol) provided **5o** after flash column chromatography as white solid (97 mg, 82% yield). Mp = 172-175 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3390, 3053, 2920, 2851, 1735, 1452, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis : trans* = 1:2) δ 7.43 (d, *J* = 5.1 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.19 – 7.15 (m, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.89 (dd, *J* = 14.8, 7.2 Hz, 2H), 5.02 (d, *J* = 6.4 Hz, 0.16H) 4.64 (d, *J* = 10.5 Hz, 1H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.81(d, *J* = 6.7 Hz,0.14H), 3.54 – 3.43 (m, 2H), 3.23 – 3.15 (m, 1H), 3.07 – 3.00 (m, 1H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 153.6, 149.8, 149.6, 140.2, 139.2, 139.0, 131.0, 130.2, 129.7, 129.0, 128.5, 128.2, 127.9, 127.7, 127.6, 126.9, 125.4, 124.9, 122.5, 122.3, 118.2, 111.1, 57.1, 56.5, 49.0, 48.6, 39.8, 39.5, 39.3, 38.7, 34.7, 31.7, 30.1. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{27}H_{29}OS_2$433.1654, found 433.1651.

4-(Naphthalen-2-yl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5p)



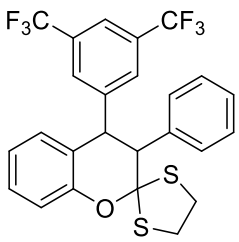
According to general procedure **2.4**, **4g** (70 mg, 0.28 mmol) and phenyl dithiolane **2a** (60 mg, 0.31 mmol) provided **5p** after flash column chromatography as white solid (94 mg, 79% yield). Mp = 200-202°C, R_f = 0.5 in 15 % ethyl acetate/ petroleum ether.IR: ν_{max}/cm^{-1} = 3443, 3053, 2924, 2852, 1735, 1451, 1107, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* = 1:2) δ 7.77 – 7.73 (m, 1H), 7.71 – 7.65 (m, 2H), 7.54 (s, 1H), 7.50 – 7.40 (m, 4H), 7.25 – 7.15 (m, 5H), 7.09 – 7.05 (m, 1H), 6.92 – 6.82 (m, 2H), 5.23(d, *J* = 6.6 Hz, 0.13H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.15 (d, *J* = 11.1 Hz, 1H), 3.95 (d, *J* = 6.7 Hz, 0.13H), 3.57 – 3.44 (m, 2H), 3.24 – 3.17 (m, 1H), 3.06 – 2.99 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers; cis: trans = 1:2) δ 153.3, 140.3, 138.5, 138.4, 133.2, 132.3, 130.7, 130.0, 128.7, 128.4, 128.3, 128.1, 127.7, 127.6, 127.4, 126.6, 126.4, 126.0, 125.7, 122.4, 122.1, 118.0, 111.0, 56.4, 56.2, 49.4, 48.9, 39.5, 39.3, 39.0, 38.5. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{27}H_{22}OS_2$426.1112, found 426.1115.

4-(Phenanthren-9-yl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5q)



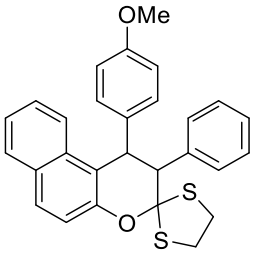
According to general procedure **2.4**, **4h** (70 mg, 0.23 mmol) and phenyl dithiolane **2a** (50 mg, 0.26 mmol) provided **5q** after flash column chromatography as yellow solid (85 mg, 77% yield). Mp = 165-168 °C, R_f = 0.5 (15% ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 2923, 1581, 1484, 1450, 749. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:3) δ 8.79 (d, *J* = 8.1 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.62 (dd, *J* = 17.2, 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 0.30H), 8.46 (d, *J* = 8.1 Hz, 0.18H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.79 (m, 0.29H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.1 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.57 – 7.51 (m,2 H), 7.46 – 7.42 (m, 2H), 7.35 (dd, *J* = 14.7, 7.8 Hz, 2H), 7.30 (d, *J* = 4.9 Hz, 2H), 7.19 (dd, *J* = 20.6, 7.7 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.90 (m, 0.47H), 6.85 (s, 0.15H), 6.78 (t, *J* = 8.2 Hz,0.21 H), 6.04 – 6.02 (m, 0.15H), 5.34 (d, *J* = 3.2 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 0.31H), 4.76 (d, *J* = 12.4 Hz, 0.32 H), 4.19 (d, *J* = 6.7 Hz, 0.21H), 4.15 (d, *J* = 3.6 Hz, 1H), 3.78 – 3.68 (m, 0.36 H), 3.66 – 3.57 (m, 0.47 H), 3.51 – 3.37 (m, 2H), 3.25 (dt, *J* = 12.8, 6.2 Hz, 0.39 H), 3.16 (dt, *J* = 11.0, 5.3 Hz, 1H), 3.07 (ddd, *J* = 10.7, 8.2, 5.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.1, 142.1, 138.2, 131.7, 131.3, 131.0, 131.0, 129.8, 129.6, 129.0, 128.9, 128.4 (2C), 127.9, 126.9, 126.8, 126.4, 124.1, 123.7, 123.6, 122.5, 118.4, 108.5, 55.9, 43.9, 39.9, 39.5, 38.8, 37.5. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{31}H_{25}OS_2$ 477.1341, found 477.1332.

4-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5r)



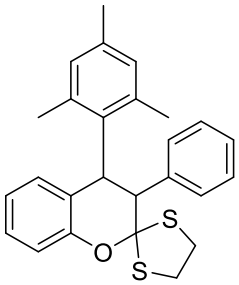
According to general procedure **2.4**, **4i** (70 mg, 0.21 mmol) and phenyl dithiolane **2a** (45 mg, 0.23 mmol) provided **5r** after flash column chromatography as pale-yellow solid (78 mg, 73% yield). Mp = 163-165 °C, R_f = 0.5 (10 % ethyl acetate in petroleum ether.). IR: ν_{max}/cm^{-1} = 3308, 3056, 2919, 2851, 1732, 1452, 1136, 739. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers ; *cis:trans* = 1:2) δ 7.62 (s, 1H), 7.40 (s, 2H), 7.31 (d, *J* = 9.6 Hz, 1H), 7.27 (s, 1H), 7.25 – 7.19 (m, 3H), 7.13 (dd, *J* = 13.1, 8.9 Hz, 1H), 7.03 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.99 – 6.92 (m, 1H), 6.79 (d, *J* = 8.9 Hz, 0.26 H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.15 (d, *J* = 6.7 Hz, 0.26H), 4.80 (d, *J* = 11.2 Hz, 1H), 3.85 (d, *J* = 11.2 Hz, 1H), 3.79 (d, *J* = 6.8 Hz, 0.25H), 3.74 – 3.63 (m, 0.49H), 3.57 – 3.40 (m, 2H), 3.23 (ddd, *J* = 11.3, 6.8, 5.0Hz, 1H), 3.06 (ddd, *J* = 10.9, 6.3, 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 153.6, 153.4, 145.9, 143.2, 137.4, 137.3, 131.4 (q, *J* = 33.3 Hz), 130.0, 129.6, 129.3, 129.2, 129.0, 128.5, 128.2, 128.0, 124.5, 124.3, 122.9, 122.5, 121.8, 121.4, 120.9, 118.6 , 110.5, 109.0, 57.1, 55.9, 49.5, 48.4, 39.6, 39.5, 39.3, 38.8. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{25}H_{19}F_6OS_2$ 513.0776, found 513.0784.

1-(4-Methoxyphenyl)-2-phenyl-1,2-dihydrospiro[benzo[f]chromene-3,2'- [1,3] dithiolane] (5s)



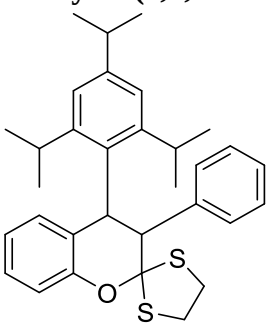
According to general procedure **2.4**, **4j** (70 mg, 0.25 mmol) and phenyl dithiolane **2a** (53 mg, 0.3 mmol) provided **5s** after flash column chromatography as light-yellow paste (89 mg, 78% yield). Mp = 100-102°C, R_f = 0.5 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} =3466, 3054, 2922, 2851, 1735, 1510, 738. ^{1}H NMR (400 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* = 1:3.5) δ 7.84 – 7.82 (m, 2H), 7.46-7.42 (m, 3H), 7.29 (d, *J* = 4.7 Hz, 4H), 7.25 (dd, *J* = 8.1, 1.3 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.92 (d, *J* = 5.3 Hz, 1H), 4.09 (d, *J* = 5.3 Hz, 1H), 3.73 (s, 3H), 3.54 (ddd, *J* = 10.5, 8.2, 5.2 Hz, 1H), 3.46-3.41 (m, 1H), 3.26 – 3.20 (m, 1H), 3.20 – 3.14 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.1, 152.2, 141.6, 136.1, 132.6, 130.4, 130.0, 129.5, 129.0, 128.6, 128.3, 127.7, 126.3, 124.7, 123.8, 119.5, 115.9, 113.5, 108.3, 59.1, 55.1, 46.0, 39.4, 38.3. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{28}H_{25}O_2S_2$ 457.1290, found 457.1294.

4-Mesityl-3-phenylspiro [chroman-2,2'- [1,3] dithiolane] (5t)



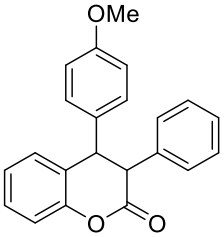
According to general procedure **2.4**, **4k** (70 mg, 0.3 mmol) and phenyl dithiolane **2a** (62 mg, 0.32 mmol) provided **5t** after flash column chromatography as white solid (107 mg, 88% yield). Mp = 175-178°C, R_f = 0.7 (15 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3363, 3029, 2919, 2851, 1735, 1450, 1106, 738.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.16 (m, 5H), 6.99 – 6.97 (m, 1H), 6.89 – 6.85 (m, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 15.2 Hz, 3H), 5.17 (d, *J* = 12.2 Hz, 1H), 4.40 (d, *J* = 12.2 Hz, 1H), 3.60 – 3.48 (m, 2H), 3.30 – 3.23 (m, 1H), 3.12 – 3.07 (m, 1H), 2.27 (s, 3H), 2.16 (s, 3H), 1.99 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 152.8, 138.4, 137.2, 135.9, 135.5, 134.8, 131.0, 128.6, 128.1, 127.2, 127.17, 127.1, 122.1, 117.5, 111.6, 51.7, 44.1, 38.5, 21.2, 20.6, 20.5. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{26}H_{26}OS_2$418.1425, found 418.1420.

3-Phenyl-4-(2,4,6-triisopropylphenyl) spiro [chroman-2,2'- [1,3] dithiolane] (5u)



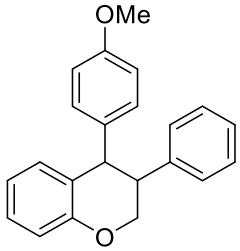
According to general procedure **2.4**, *ortho*-quinone methide **4l** (70 mg, 0.21 mmol) and phenyl dithiolane **2a** (46 mg, 0.24 mmol) provided **5u** after flash column chromatography as white solid (96 mg, 89% yield). Mp = 175-178°C, R_f = 0.8 (15% ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3444, 3053, 2959, 2851, 1736, 1452, 1115, 739. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.33 (m, 1H), 7.15 (d, *J* = 14.1 Hz, 5H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.79 – 6.76 (m, 2H), 5.27 (d, *J* = 11.8 Hz, 1H), 4.25 (d, *J* = 11.8 Hz, 1H), 3.61 – 3.49 (m, 1H), 3.20-3.12 (m, 1H), 3.01-2.94 (m, 1H), 2.82-2.75 (m, 1H), 1.33 – 1.30 (m, 5H), 1.23 – 1.18 (m, 10H), 0.77 (d, *J* = 6.6 Hz, 3H), 0.50 (d, *J* = 6.5 Hz, 3H).^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 152.6, 147.4, 147.0, 146.7, 138.2, 132.2, 129.5, 129.0, 128.1, 127.2, 126.9, 126.88, 125.7, 123.1, 122.1, 120.4, 117.7, 115.8, 111.6, 54.3, 42.3, 39.6, 38.8, 38.3, 35.5, 33.5, 29.4, 29.2, 26.0, 24.6, 23.63, 23.60, 23.1, 23.0. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{32}H_{38}OS_2$502.2364, found 502.2377.

4-(4-Methoxyphenyl)-3-phenylchroman-2-one (6)



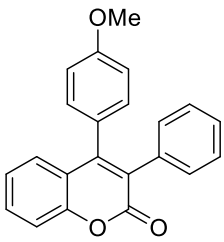
According to procedure **2.6**, **5a** provided **6** after flash column chromatography as white solid (75 mg, 92% yield). Mp = 138-140°C, R_f = 0.4 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3334, 2917, 2850, 1755, 1610, 1453. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.29 (m, 1H), 7.24 – 7.20 (m, 3H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.08 – 7.06 (m, 1H), 7.01 – 6.99 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.81 – 6.79 (m, 2H), 4.49 (d, *J* = 7.6 Hz, 1H), 4.20 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 168.7, 158.9, 151.3, 137.6, 136.0, 132.1, 130.4, 129.2, 129.0, 128.8, 127.7, 125.5, 124.9, 116.9, 114.4, 55.3, 53.5, 47.6. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{22}H_{18}O_3$330.1256, found 330.1253.

4-(4-methoxyphenyl)-3-phenylchroman (7)

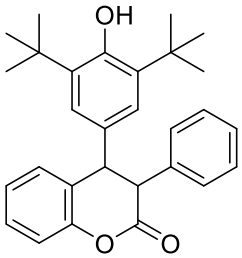


According to procedure **2.7**, **5a** provided **7** after flash column chromatography as light-yellow paste (41 mg, 53% yield). R_f = 0.5 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} = 3441, 2957, 1611, 1511, 755. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.92 (dd, *J* = 11.7, 8.5 Hz, 3H), 6.81 (d, *J* = 4.3 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.37 (dd, *J* = 10.9, 3.7 Hz, 1H), 4.28 – 4.24 (m, 2H), 3.75 (s, 3H), 3.32-3.27 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 158.3, 155.0, 140.5, 135.9, 130.8, 130.1, 128.7, 128.0, 127.7, 127.0, 126.2, 120.8, 116.7, 113.8, 69.9, 55.3, 48.3, 47.8. HRMS (ESI) *m/z*: $[M]^+$calcd for $C_{22}H_{20}O_2$316.1463, found 316.1421.

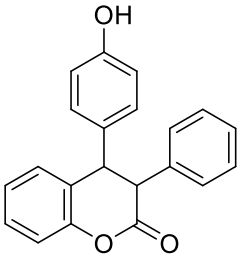
4-(4-Methoxyphenyl)-3-phenyl-2*H*-chromen-2-one (8)



According to procedure **2.8**, **5a** provided **8** after flash column chromatography as white solid (20 mg, 50 % yield). Mp = 188-190 °C, R_f = 0.2 (15 % ethyl acetate in petroleum ether).IR: ν_{max}/cm^{-1} =2962, 1719, 1512, 1451, 760. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53-7.49 (m, 1H), 7.40 (d, *J* = 8.4 Hz,1H), 7.26 (d, *J* = 18 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 3H), 7.11 (d, *J*= 9.1 Hz, 2H), 7.03-7.00 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.5, 159.6, 153.4, 151.6, 134.3, 131.5, 131.0, 130.7, 128.0, 127.95, 127.7, 127.1, 126.7, 124.2, 120.9, 116.9, 113.9, 55.4. HRMS (ESI) *m/z*: $[M+Na]^+$calcd for $C_{22}H_{16}NaO_3$351.0992, found 351.1005.

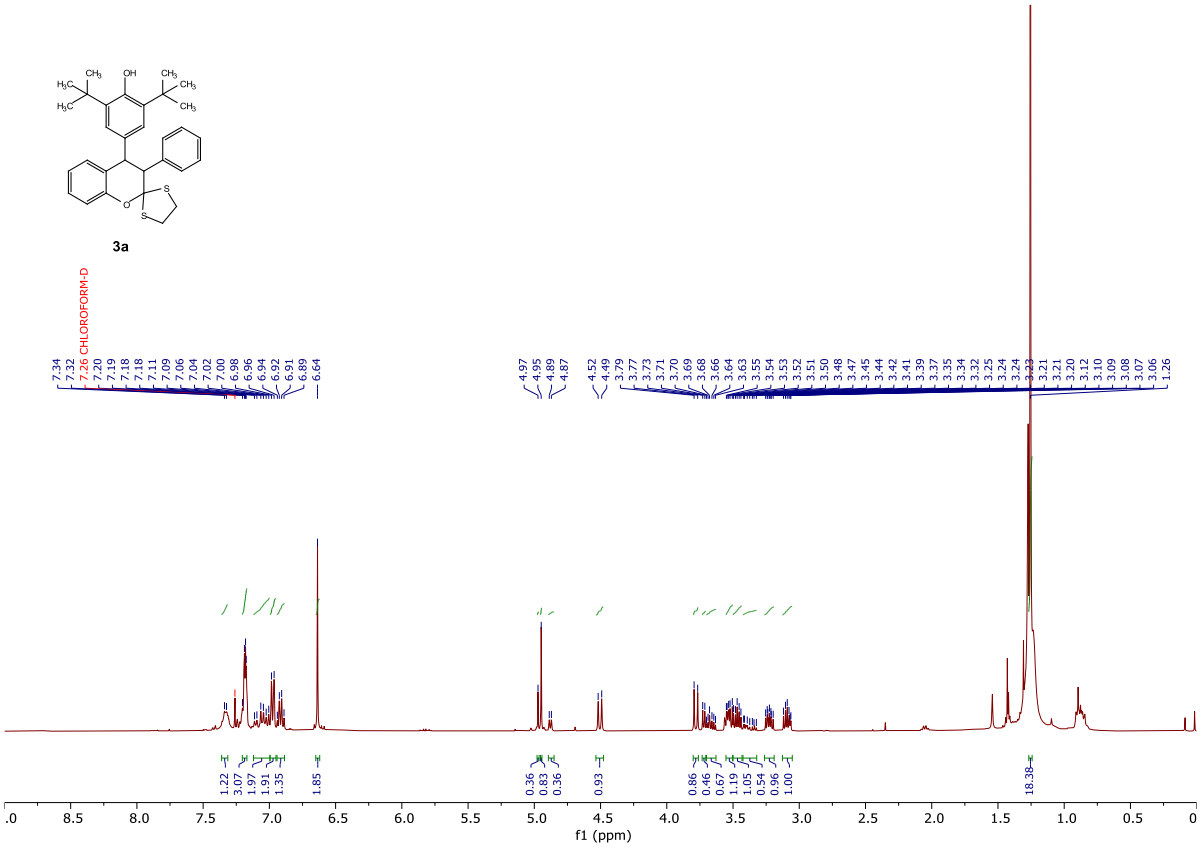


4-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-3-phenylchroman-2-one (9): According to the general procedure **2.9**, **1a** (50 mg, 0.16 mmol), phenyl dithiolane **2a** (34 mg, 0.18 mmol), provided **8** after flash column chromatography as white viscous solid (32 mg, 46%). R_f = 0.3 (10 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3636, 2957, 2870, 1768, 1457. ^{1}H NMR (500 MHz, Chloroform-*d*) (mixture of diastereomers; *cis: trans* 1:6) δ 7.33 – 7.29 (m, 1H), 7.23 – 7.15 (m, 4H), 7.10 (dd, *J* = 5.9, 3.7 Hz, 4H), 6.82 (s, 2H), 6.75 (d, *J* = 7.1 Hz, 0.37H), 5.11 (s, 1H), 4.40 (d, *J* = 6.3 Hz, 1H), 4.34 (d, *J* = 6.1 Hz, 0.23H), 4.25 (d, *J* = 6.1 Hz, 0.24H), 4.17 (d, *J* = 6.3 Hz, 1H), 1.35 (s, 18H), 1.26 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 168.7, 153.0, 151.4, 136.3, 135.7, 130.9, 130.2, 129.3, 128.8, 128.7, 128.1, 127.6, 125.5, 125.2, 124.9, 124.4, 116.8, 53.9, 48.6, 34.4, 34.2, 30.3, 30.1. HRMS (ESI) m/z: $[M+Na]^+$calcd for $C_{29}H_{32}NaO_3$ 451.2244; found 451.2243.

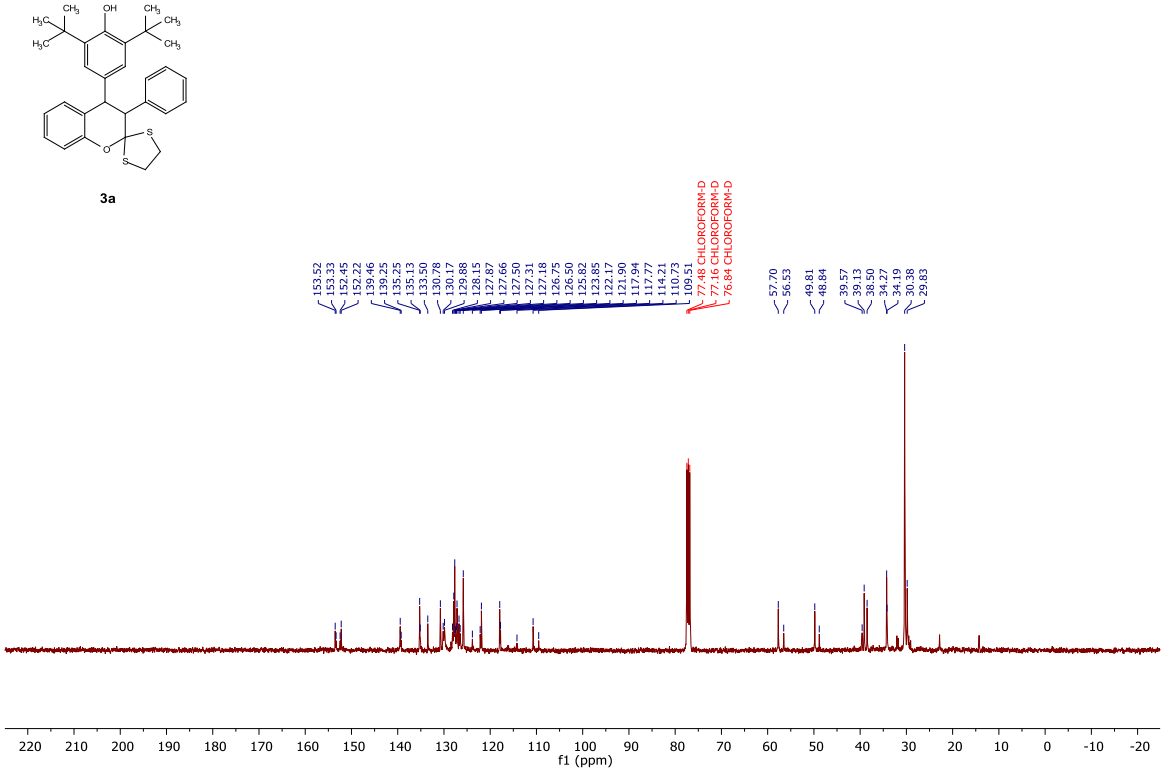


4-(4-Hydroxyphenyl)-3-phenylchroman-2-one (10): According to the general procedure **2.10, 9** provided **10** after flash column chromatography as white viscous solid (22 mg, 75%). R_f = 0.3 (20 % ethyl acetate in petroleum ether). IR: ν_{max}/cm^{-1} = 3398, 2957, 2870, 1752, 1454. ^1H NMR (396 MHz, Chloroform-*d*) (mixture of diastereomers; *cis:trans* 1:4) δ 7.34 – 7.28 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 3H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.84 – 6.80 (m, 0.40H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 1.4 Hz, 1H), 5.04 (s, 1H), 4.46 (d, *J* = 7.4 Hz, 1H), 4.36 (d, *J* = 6.2 Hz, 0.20H), 4.26 (d, *J* = 6.2 Hz, 0.20H), 4.19 (d, *J* = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) (mixture of diastereomers) δ 168.9, 155.0, 151.3, 135.9, 132.2, 129.3, 129.2, 129.0, 128.8, 128.2, 127.7, 125.3, 125.0, 116.9, 115.9, 53.6, 47.6.HRMS (ESI) m/z: $[M+Na]^+$calcd for $C_{21}H_{16}NaO_3$ 339.0992; found 339.0989.

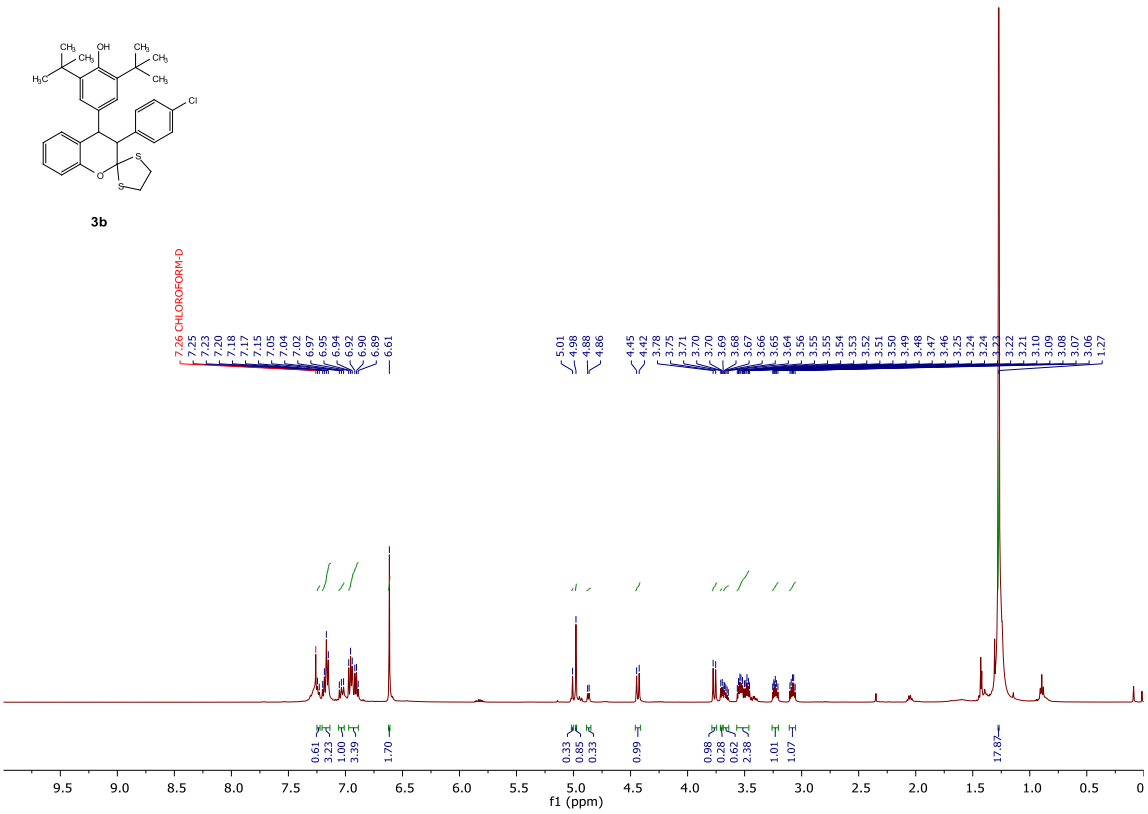
4. ^1H &^{13}C spectra:



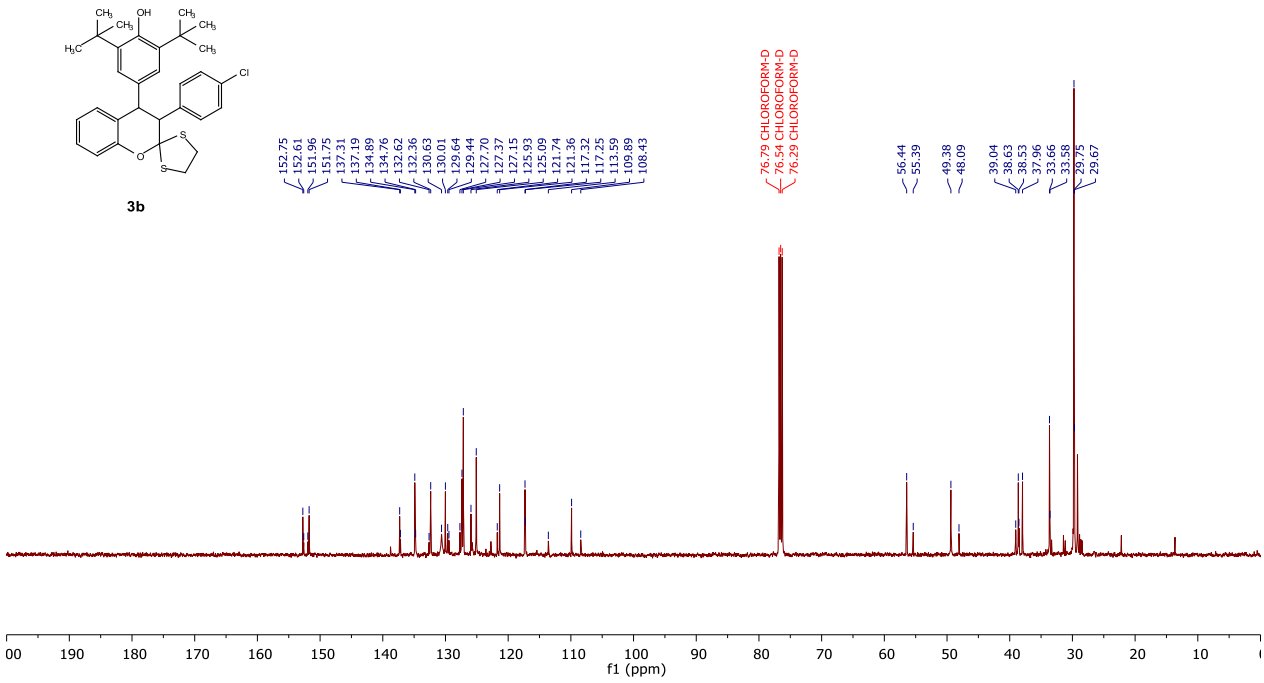
^{1}H NMR (400 MHz) spectrum of compound **3a** in $CDCl_3$



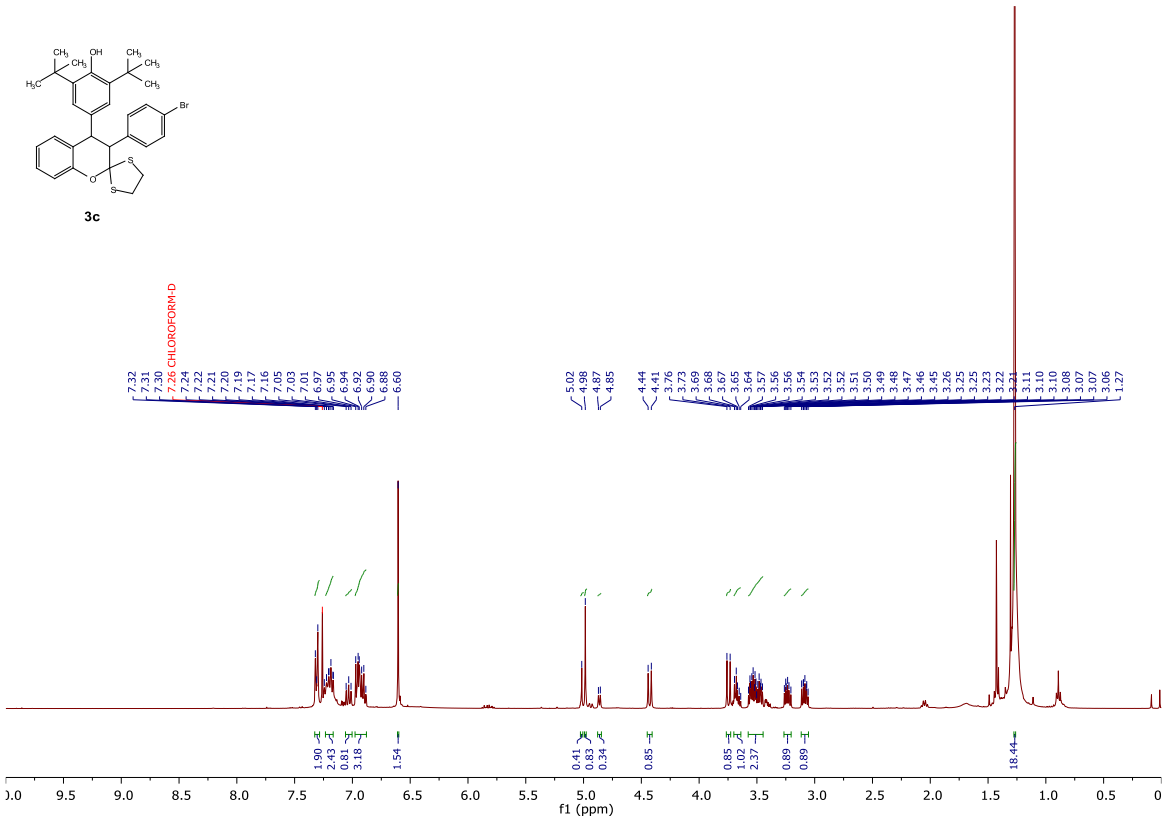
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3a** in $CDCl_3$



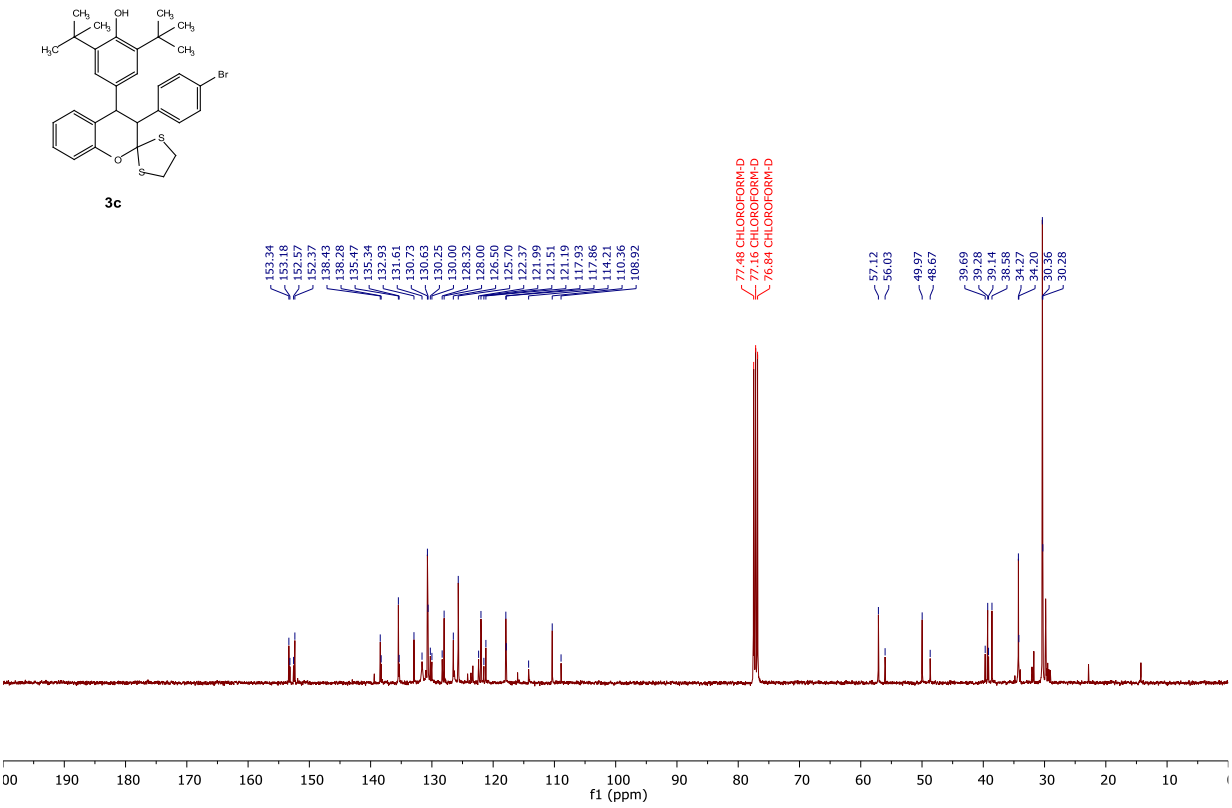
^{1}H NMR (500 MHz) spectrum of compound **3b** in $CDCl_3$



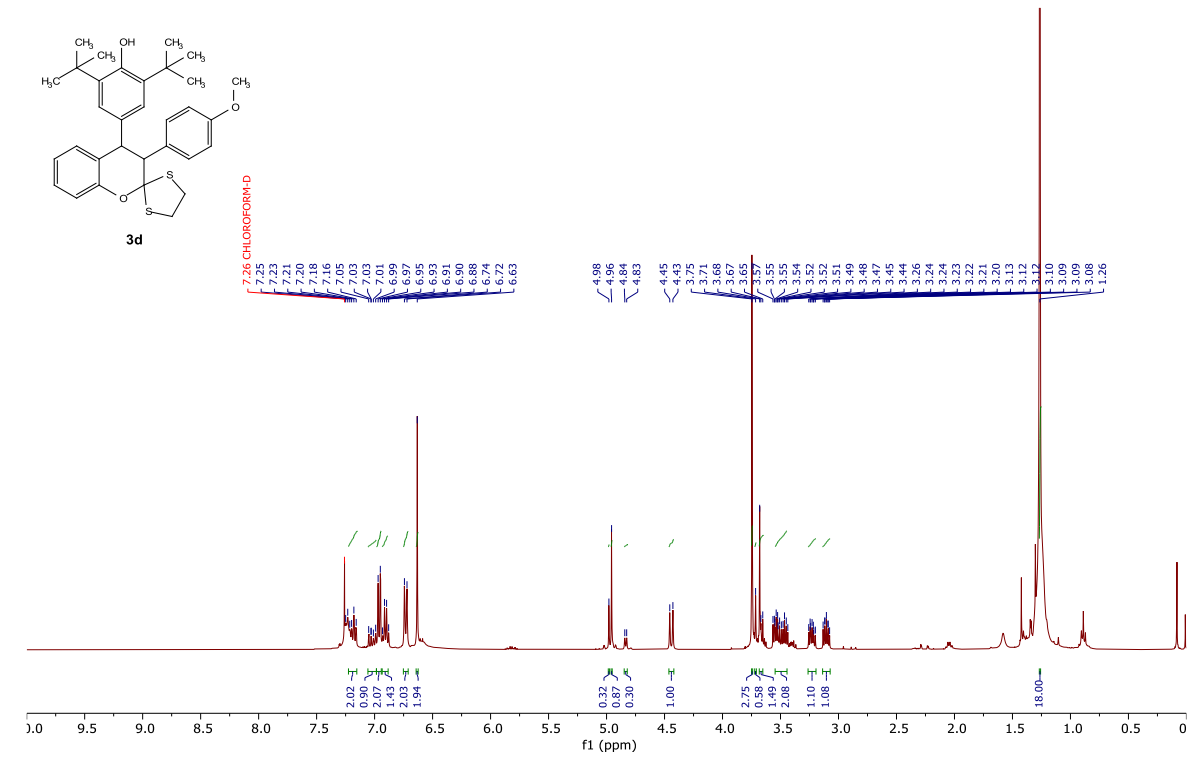
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3b** in $CDCl_3$



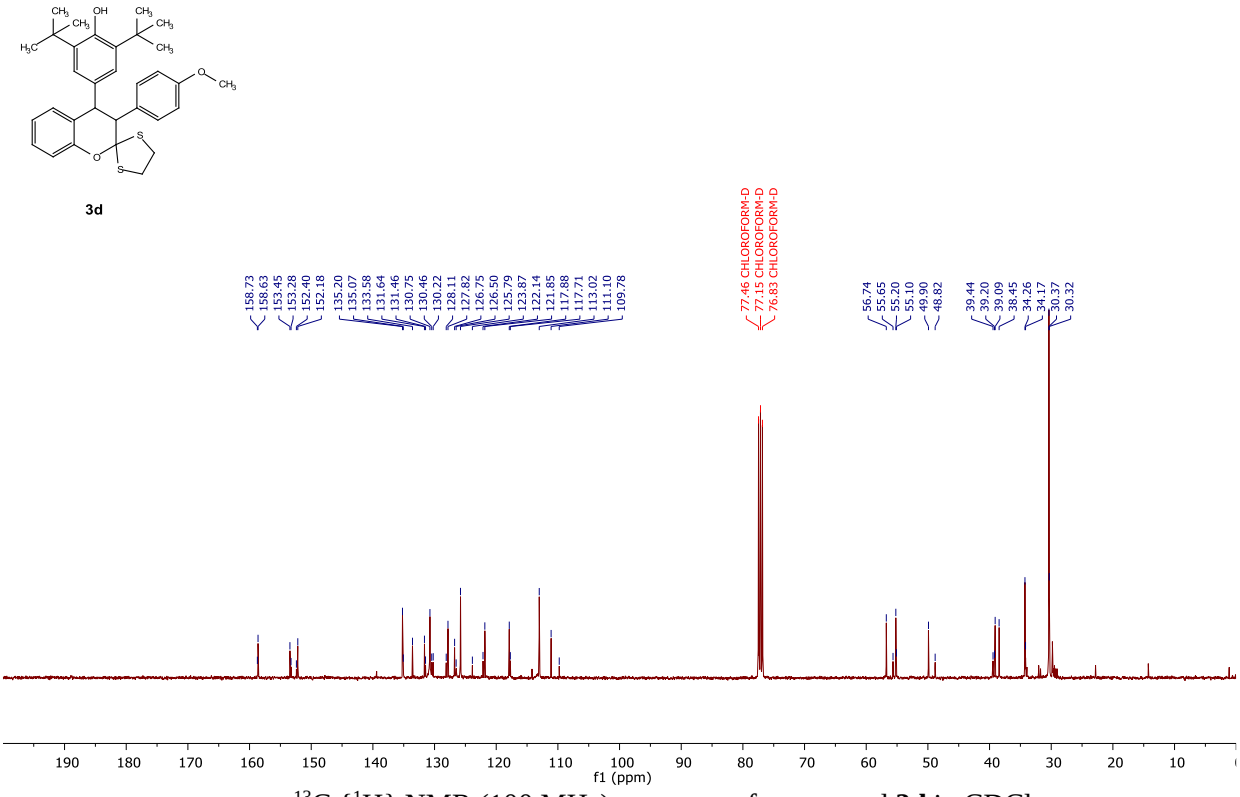
^{1}H NMR (400 MHz) spectrum of compound **3c** in $CDCl_3$



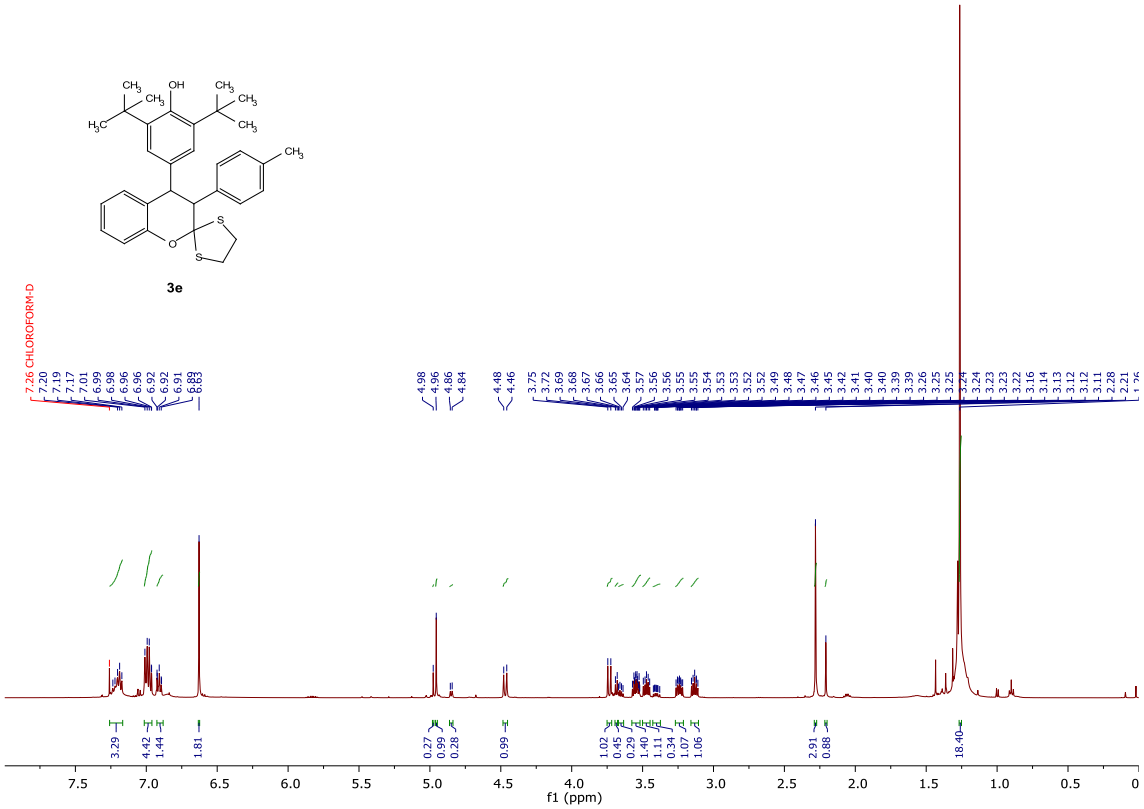
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3c** in $CDCl_3$



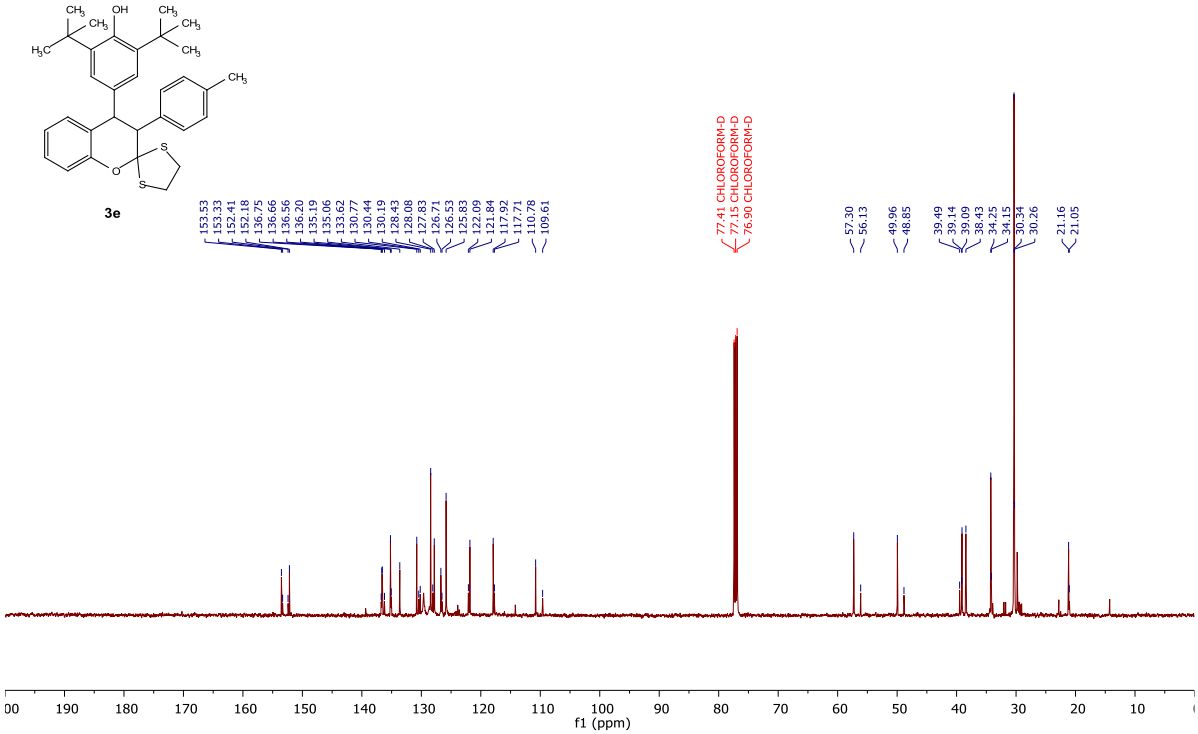
^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$



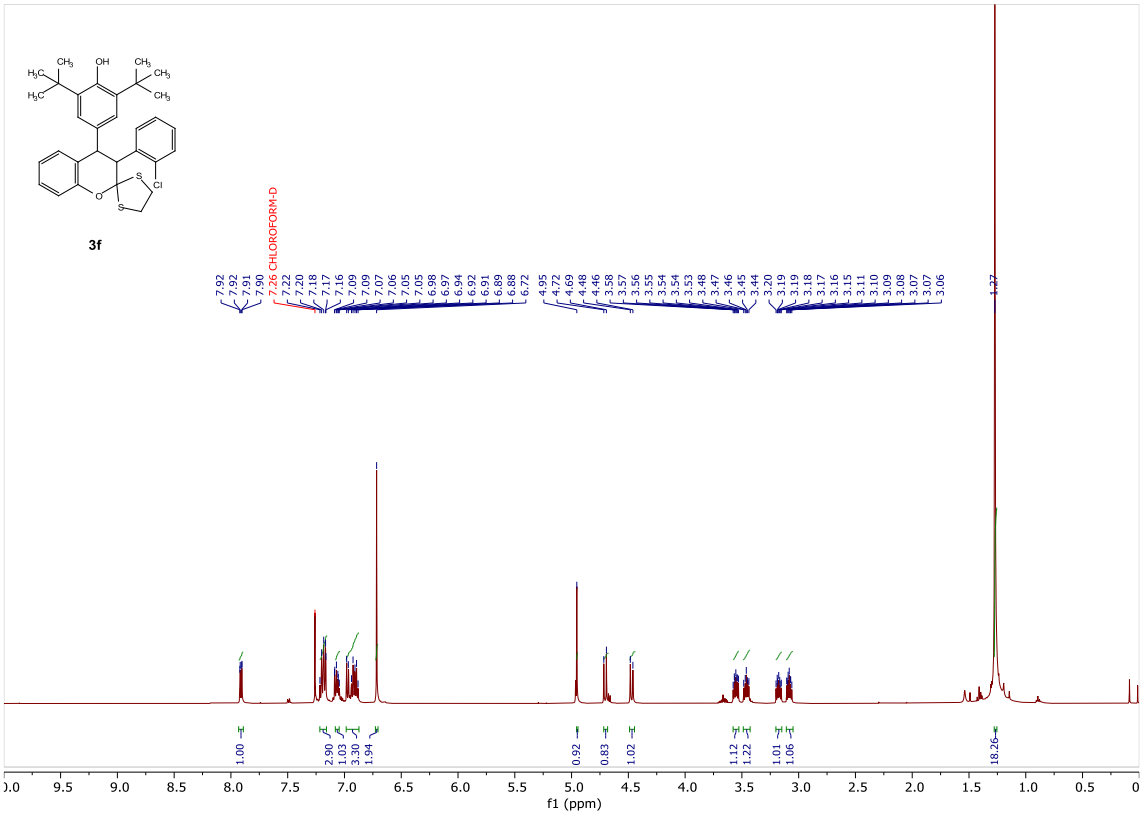
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3d** in $CDCl_3$



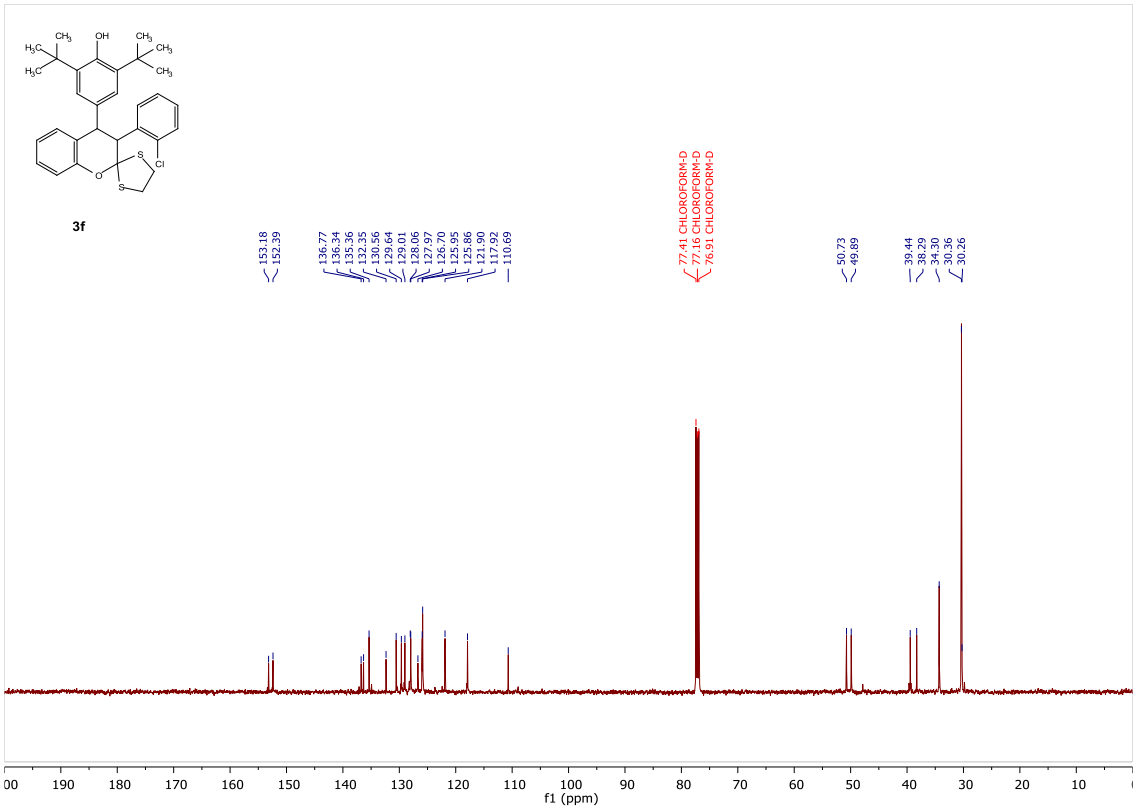
^{1}H NMR (500 MHz) spectrum of compound **3e** in $CDCl_3$



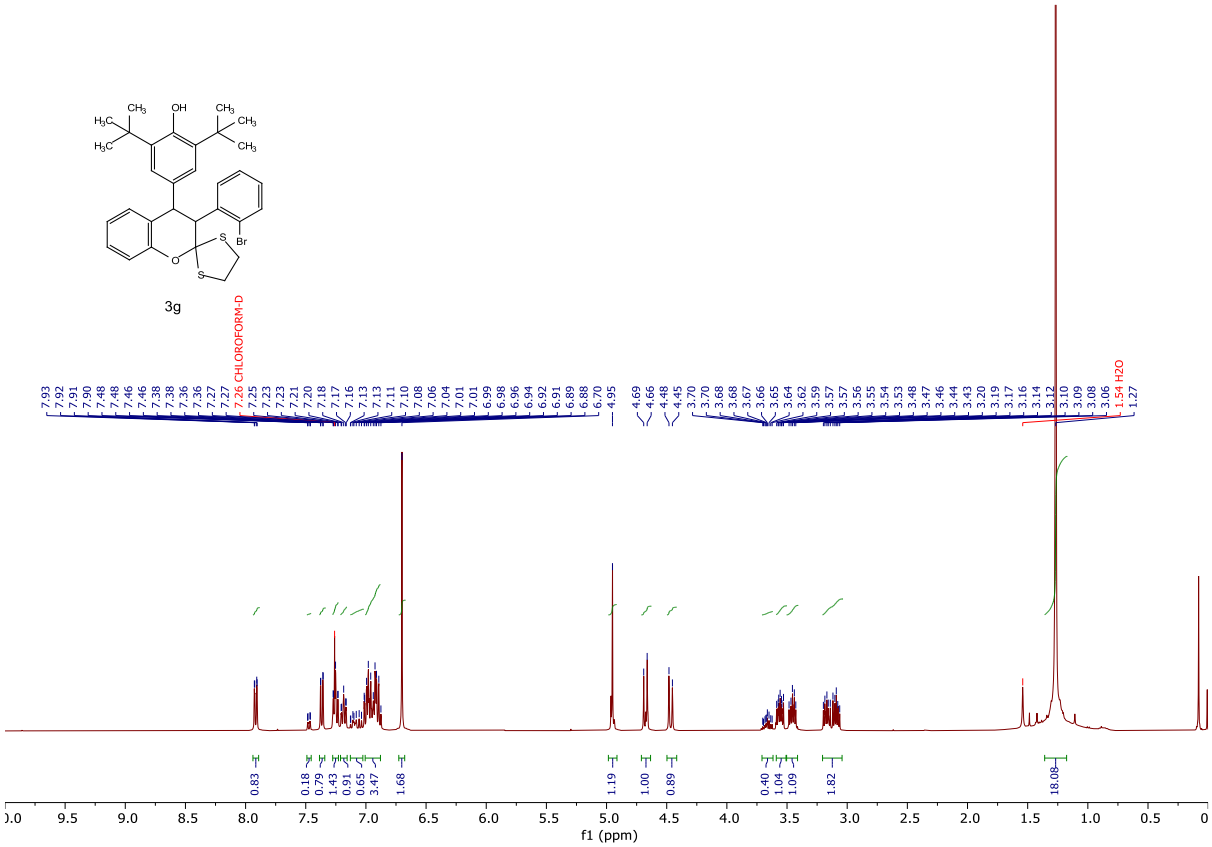
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3e** in $CDCl_3$



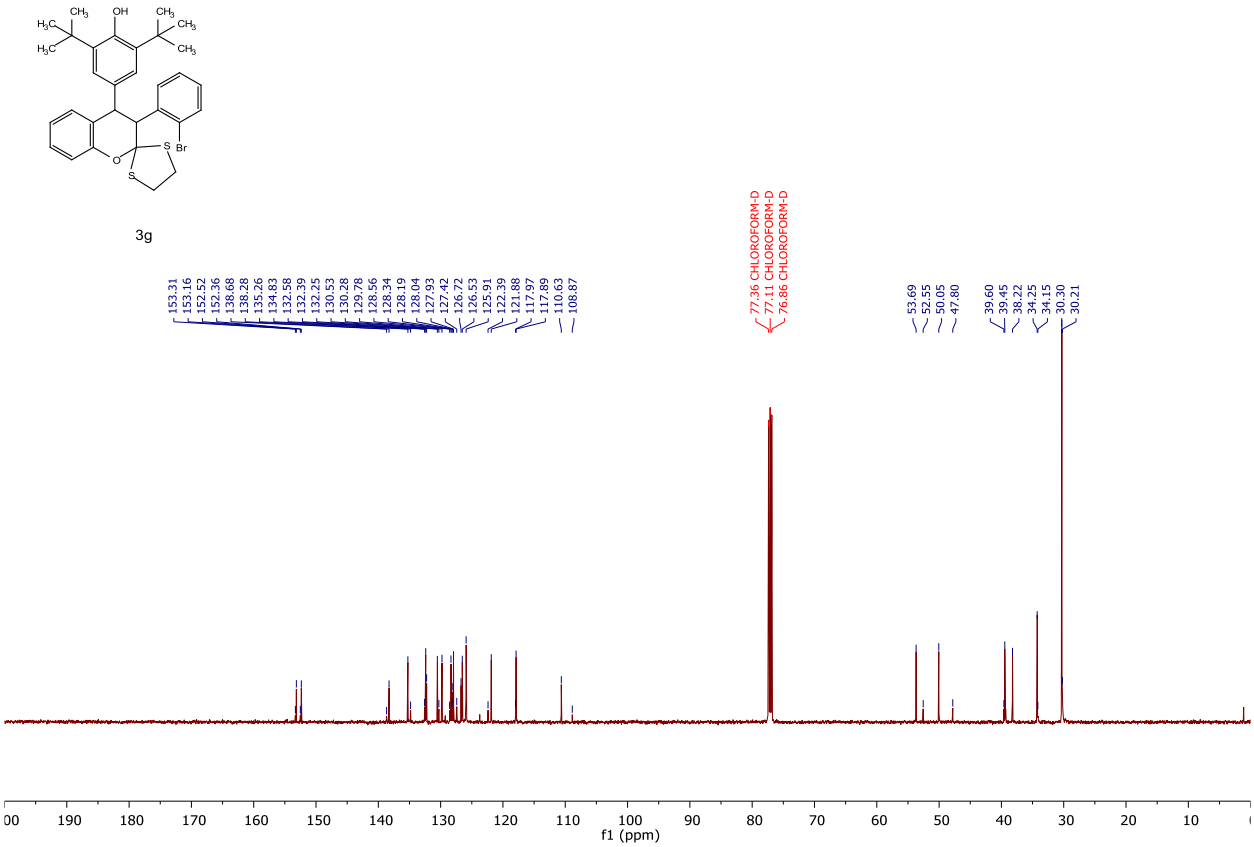
^{1}H NMR (500 MHz) spectrum of compound **3f** in $CDCl_3$



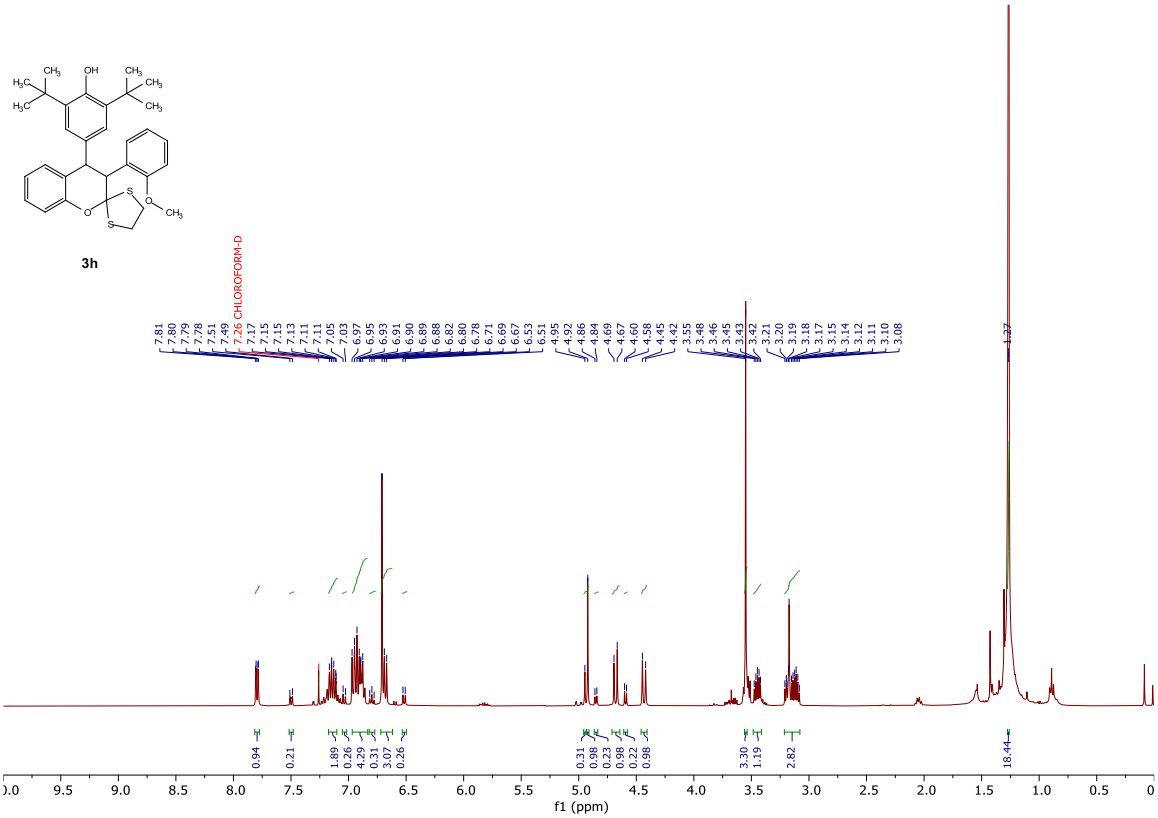
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3f** in $CDCl_3$



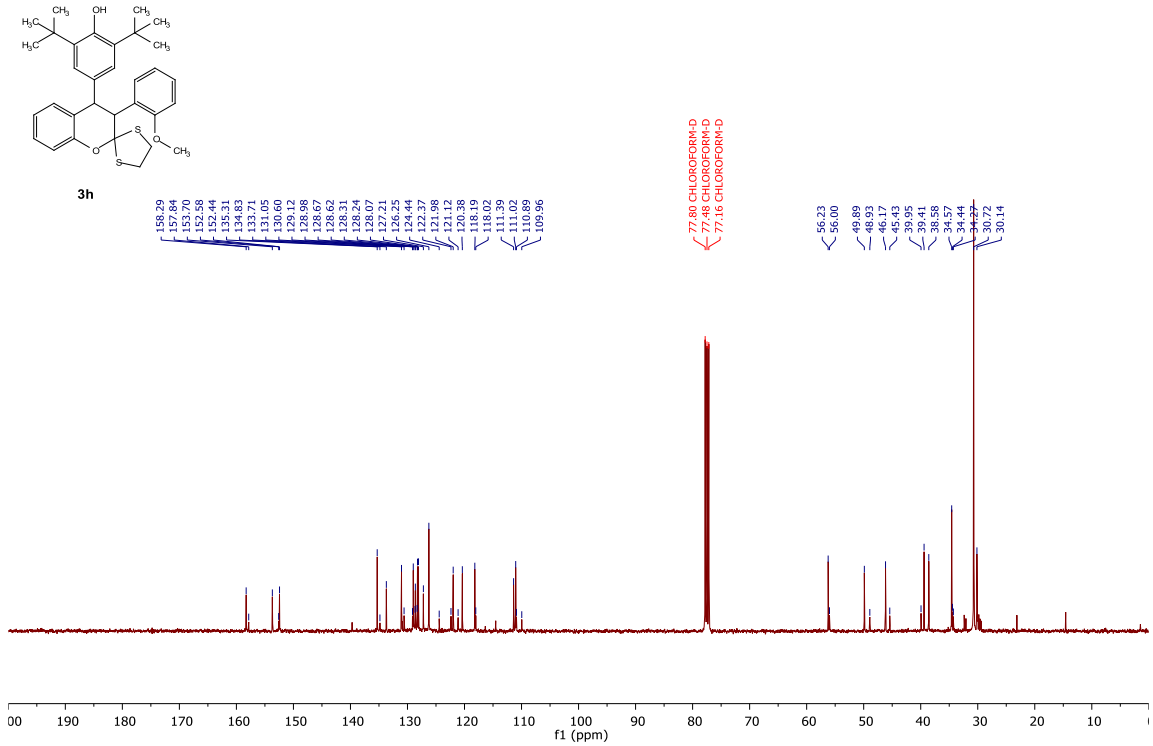
^{1}H NMR (400 MHz) spectrum of compound **3g** in $CDCl_3$



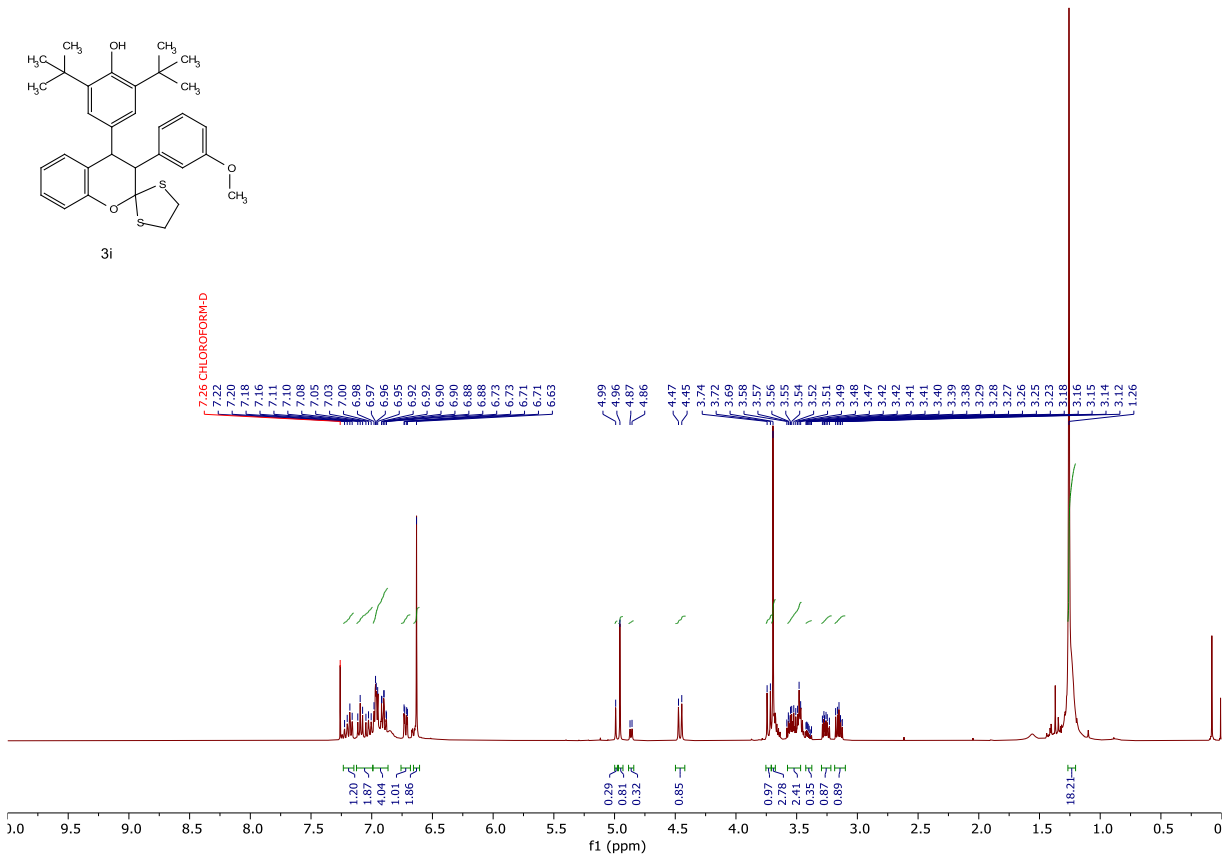
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3g** in $CDCl_3$



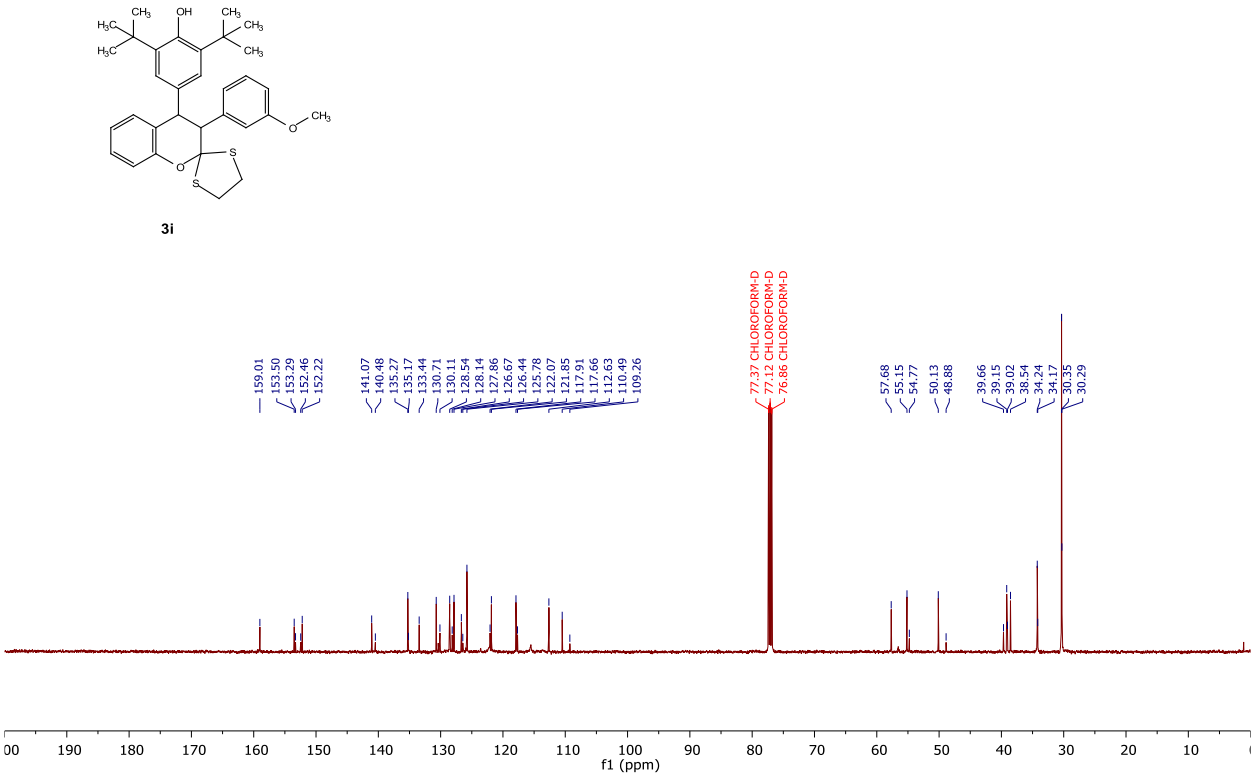
^{1}H NMR (400 MHz) spectrum of compound **3h** in $CDCl_3$



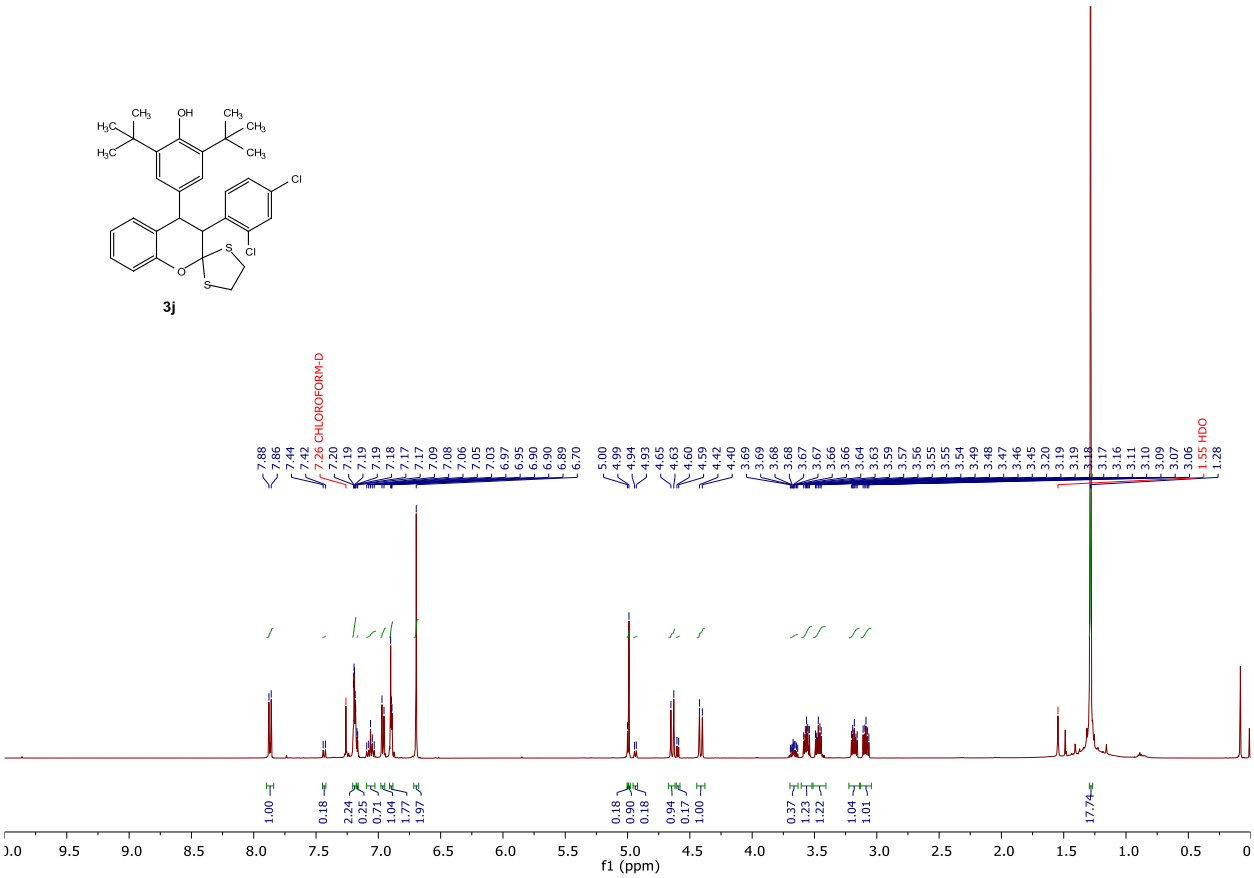
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3h** in $CDCl_3$



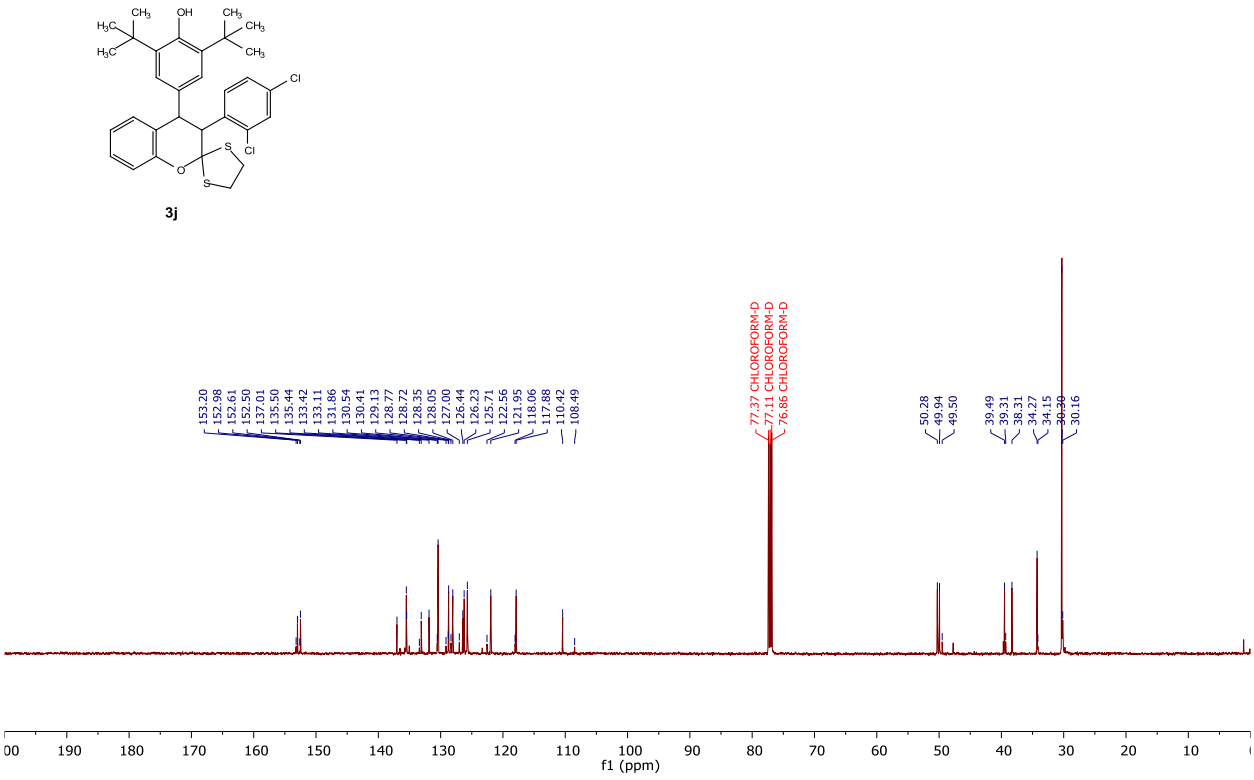
^{1}H NMR (400 MHz) spectrum of compound **3i** in $CDCl_3$



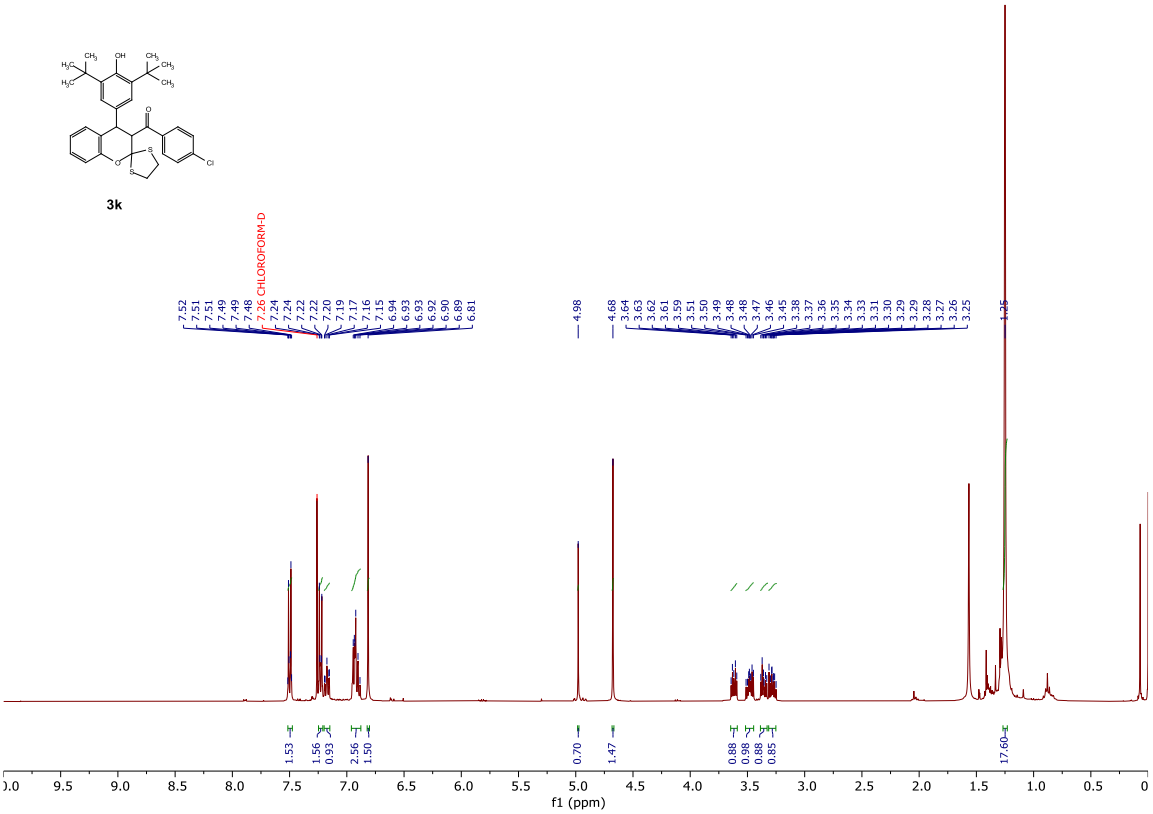
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3i** in $CDCl_3$



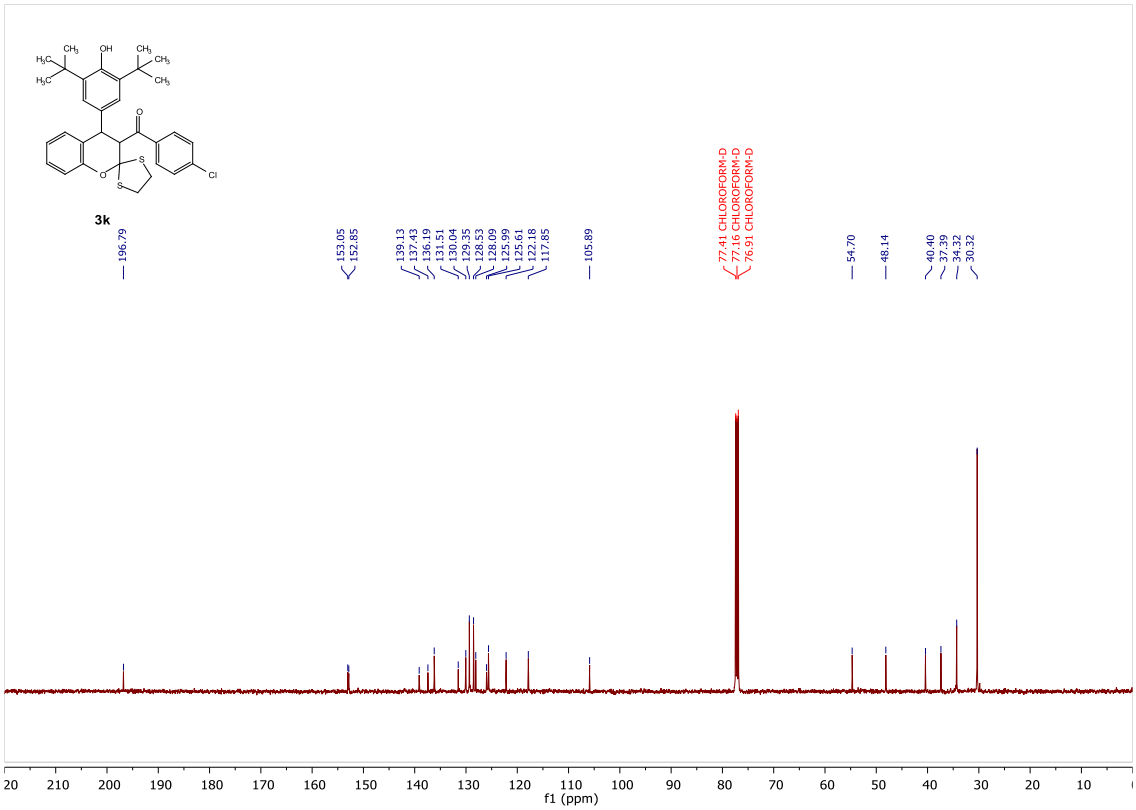
^{1}H NMR (500 MHz) spectrum of compound **3j** in $CDCl_3$



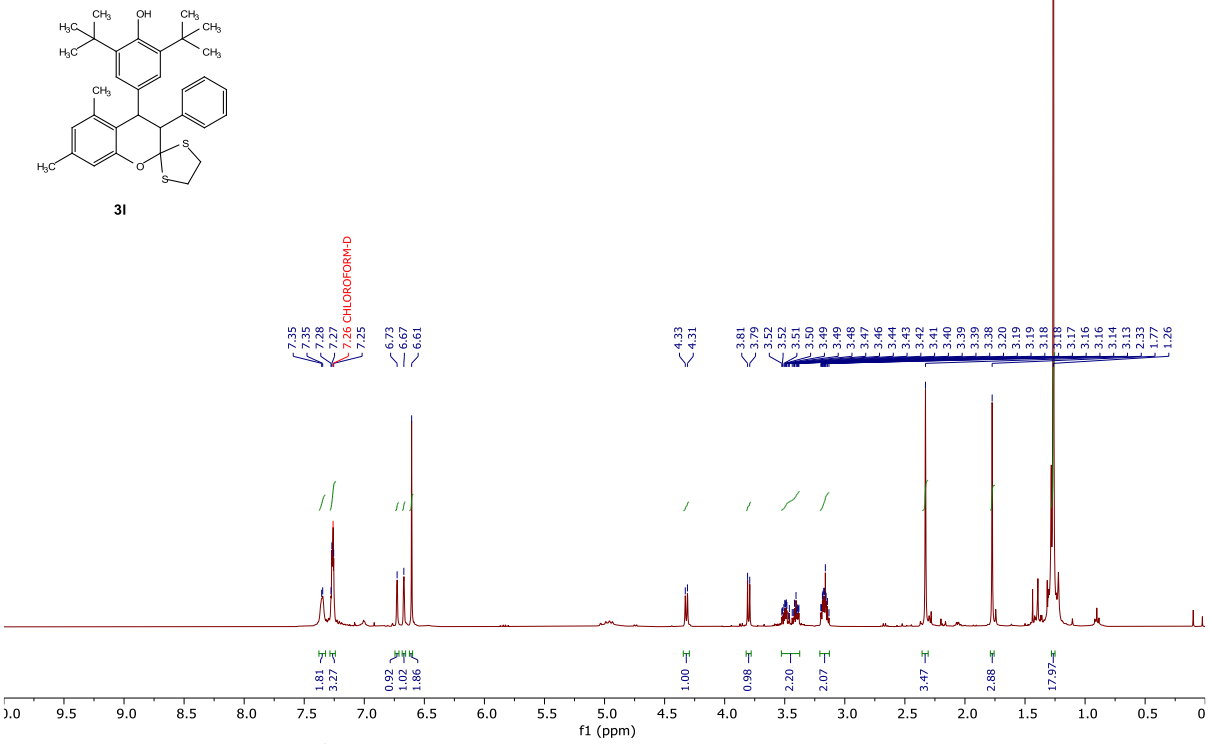
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3j** in $CDCl_3$



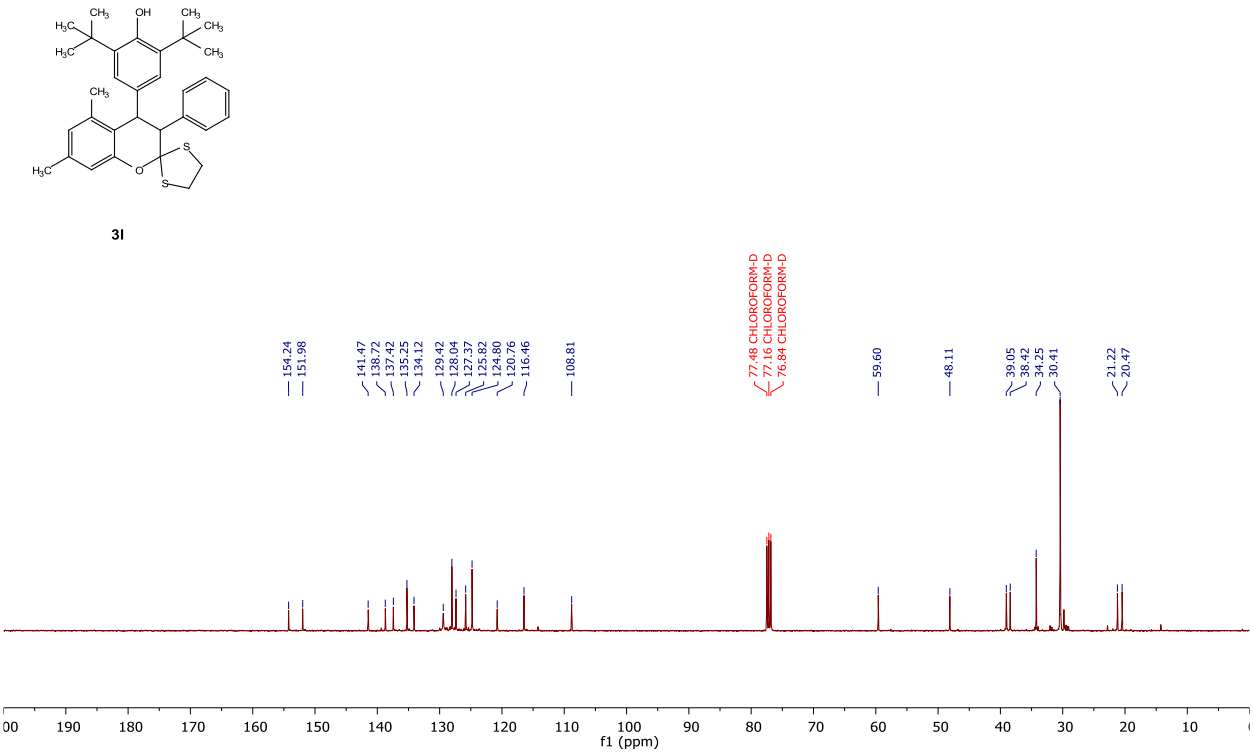
^{1}H NMR (400 MHz) spectrum of compound **3k** in $CDCl_3$



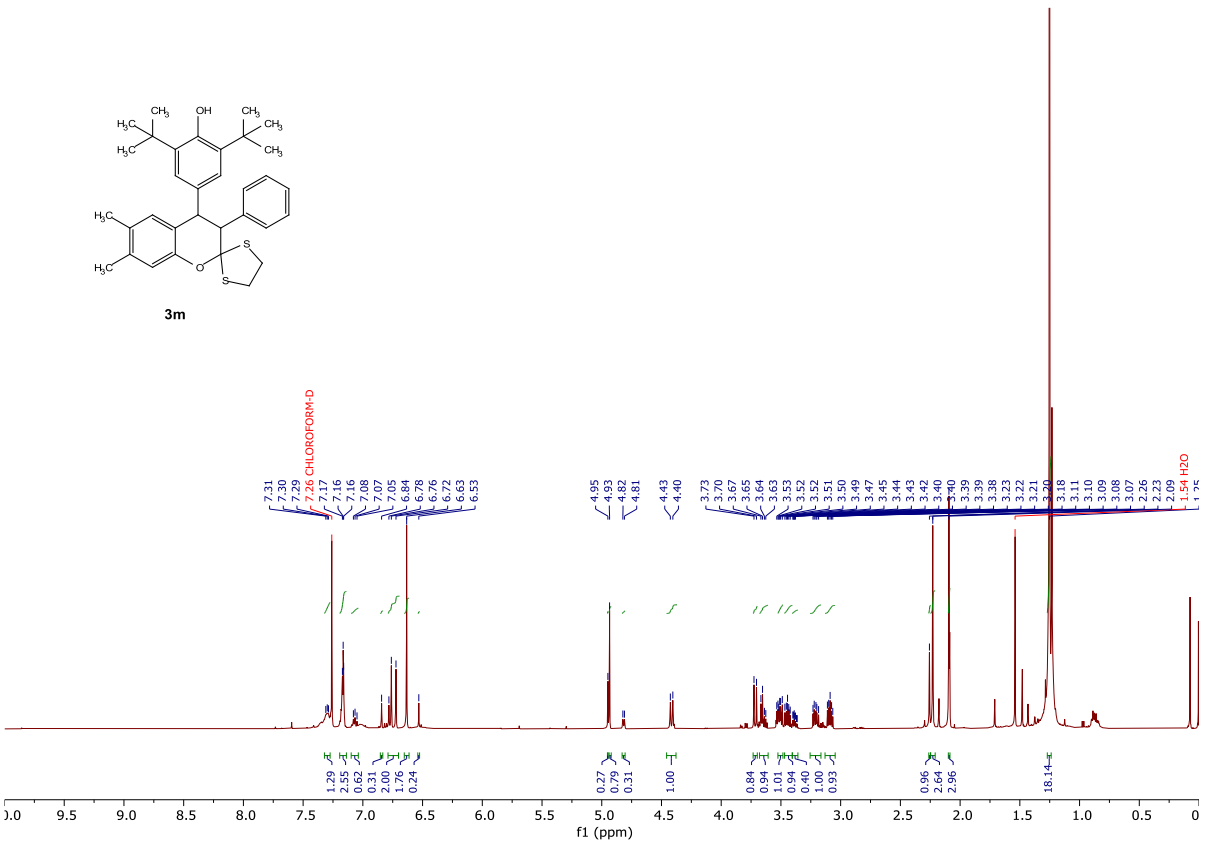
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3k** in $CDCl_3$



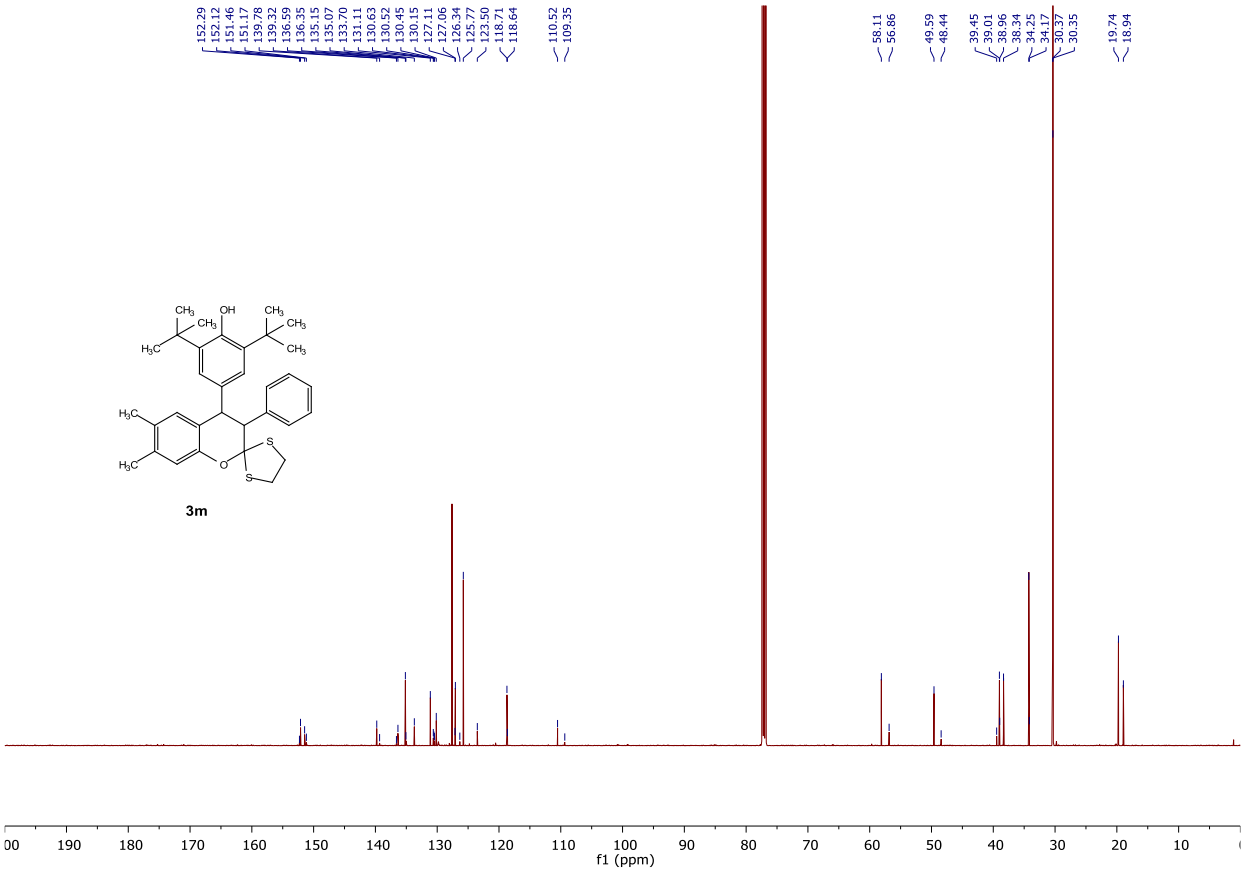
^{1}H NMR (400 MHz) spectrum of compound **3l** in $CDCl_3$



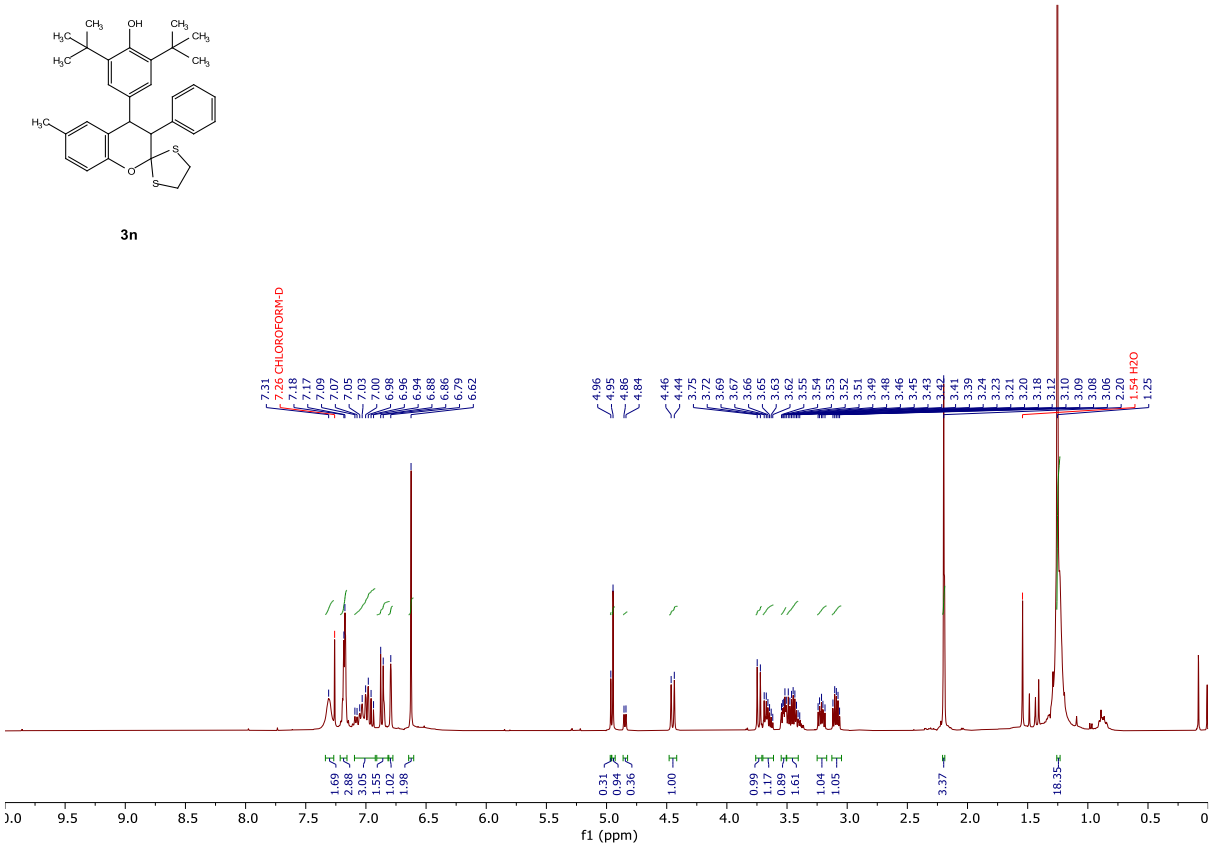
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3l** in $CDCl_3$



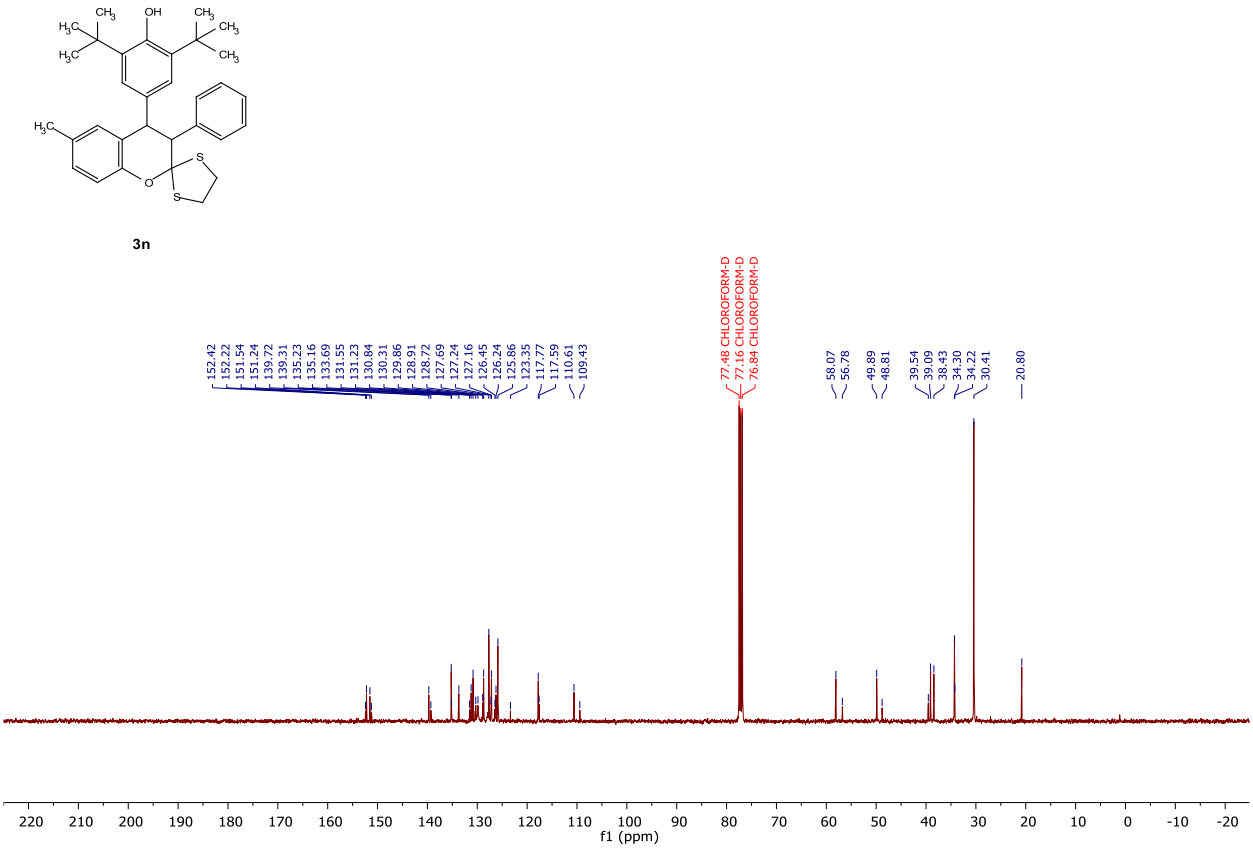
^{1}H NMR (500 MHz) spectrum of compound **3m** in $CDCl_3$



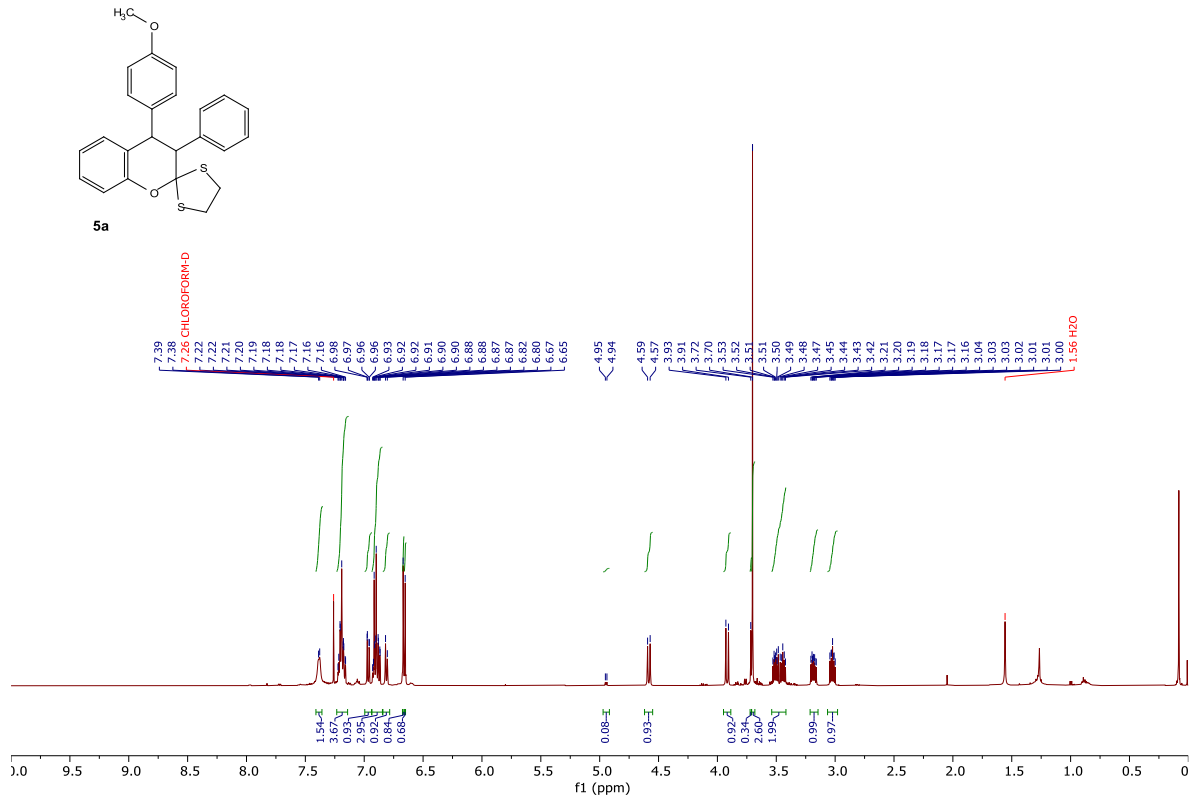
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3m** in $CDCl_3$



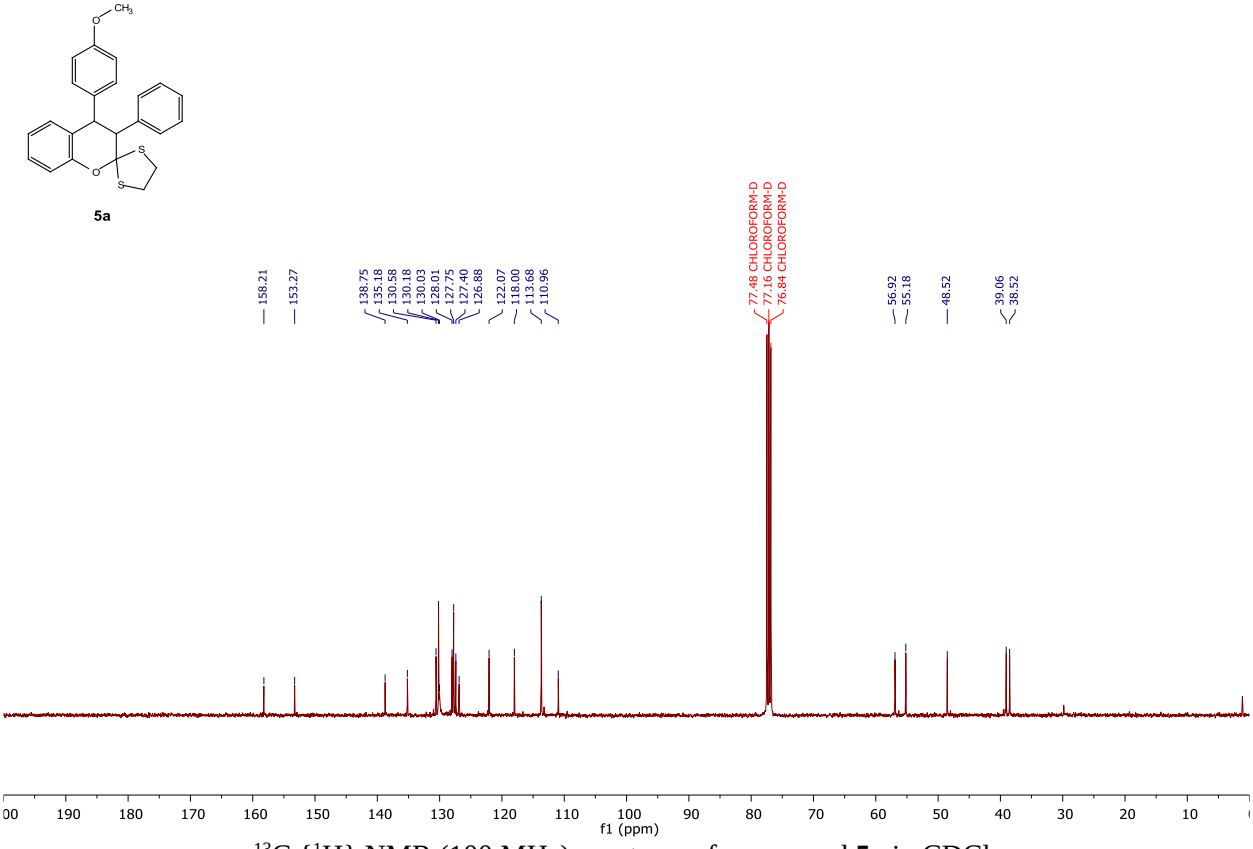
^{1}H NMR (400 MHz) spectrum of compound **3n** in $CDCl_3$



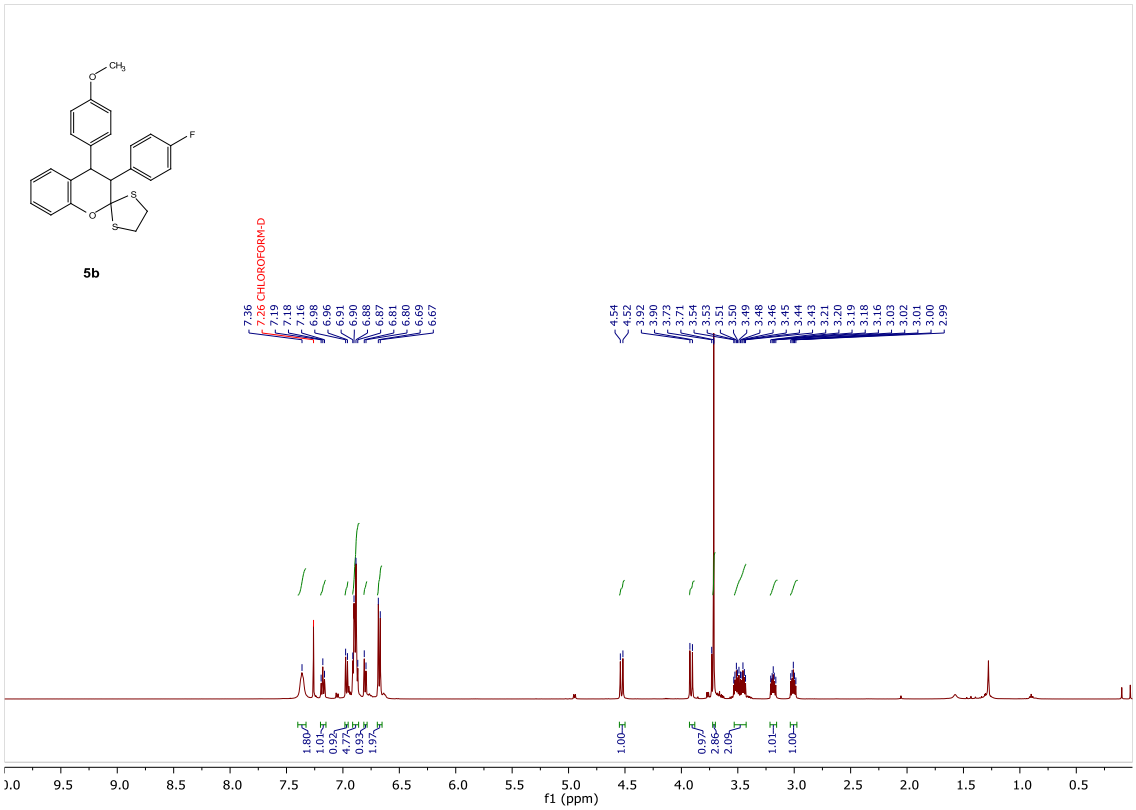
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3n** in $CDCl_3$



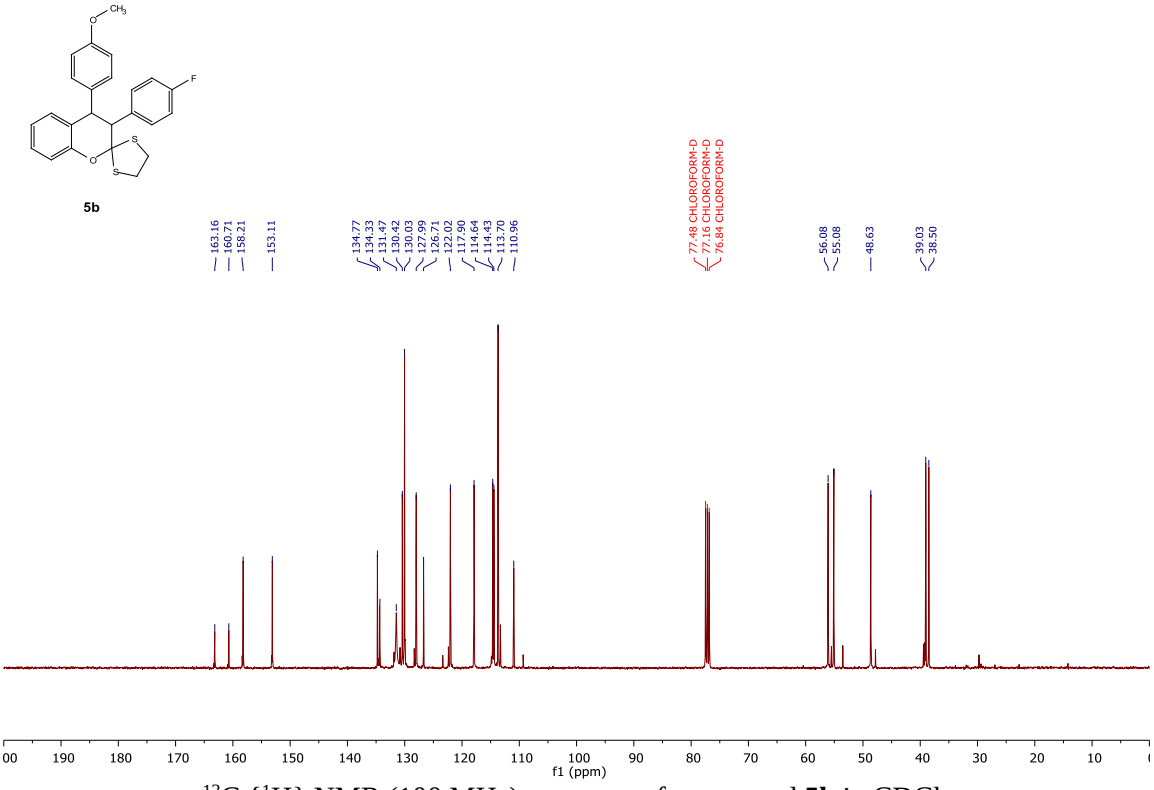
^{1}H NMR (500 MHz) spectrum of compound **5a** in $CDCl_3$



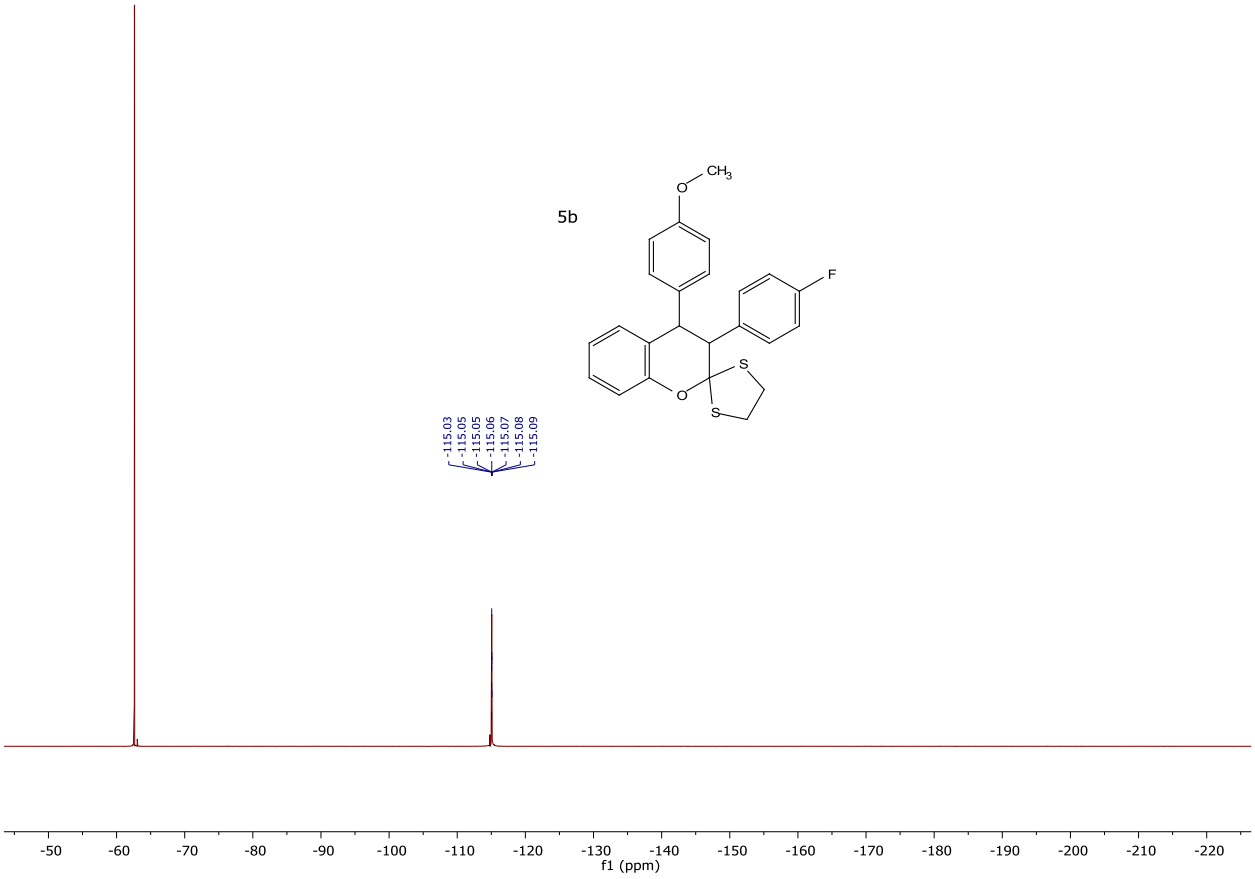
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5a** in $CDCl_3$



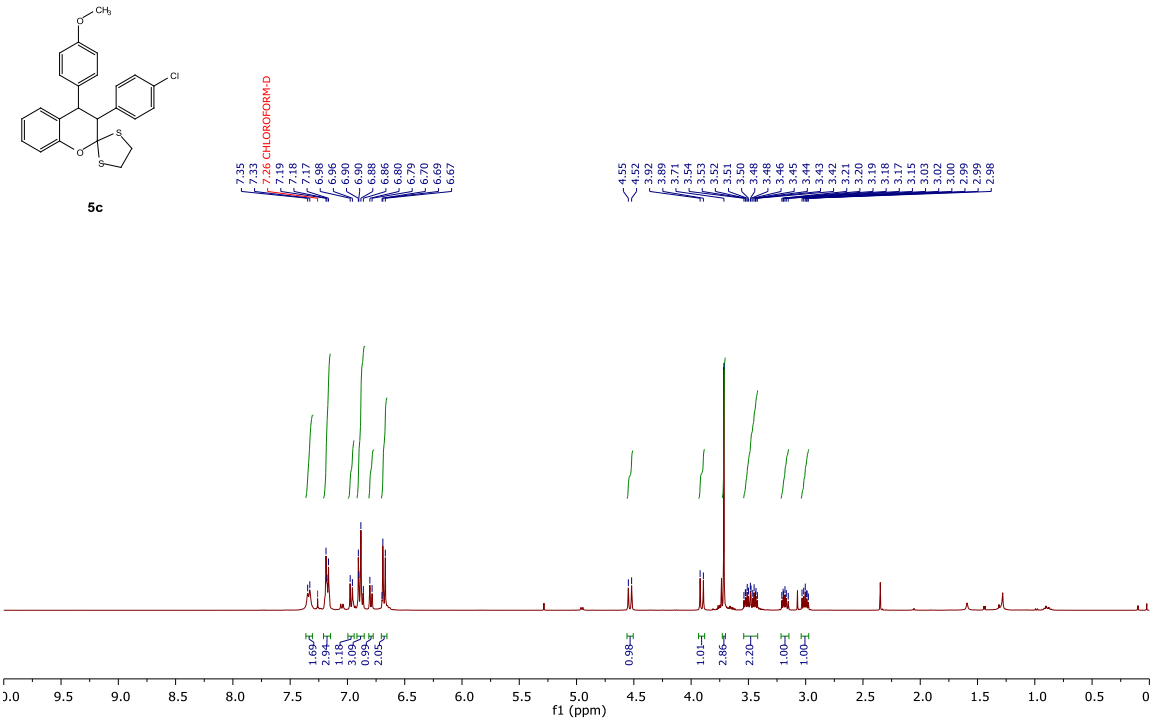
^{1}H NMR (500 MHz) spectrum of compound **5b** in $CDCl_3$



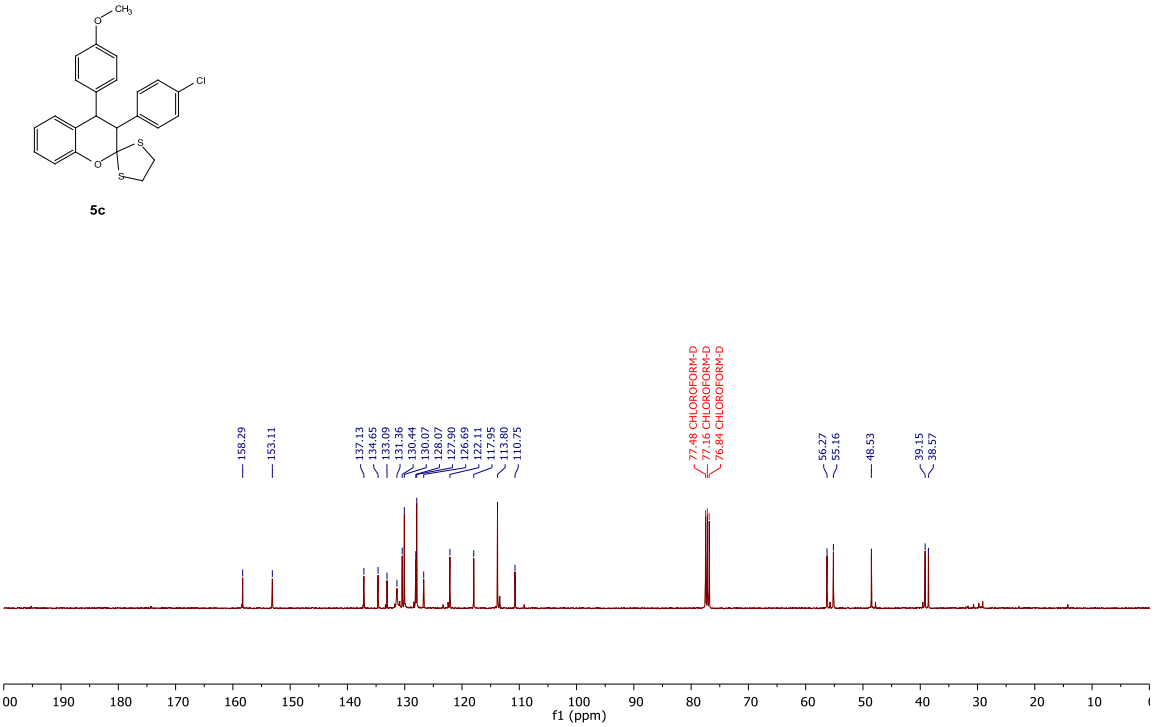
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5b** in $CDCl_3$



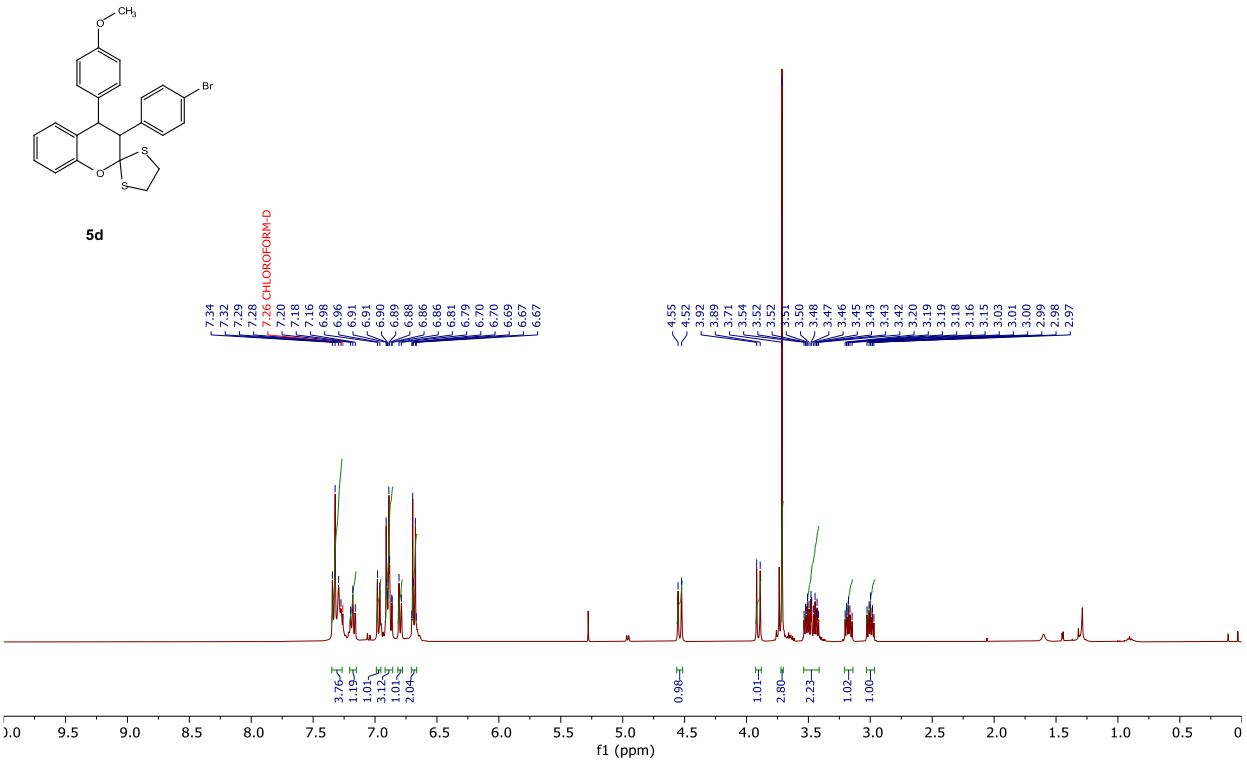
^{19}F NMR (471 MHz) spectrum of compound **5b** in $CDCl_3$ with $PhCF_3$ as reference



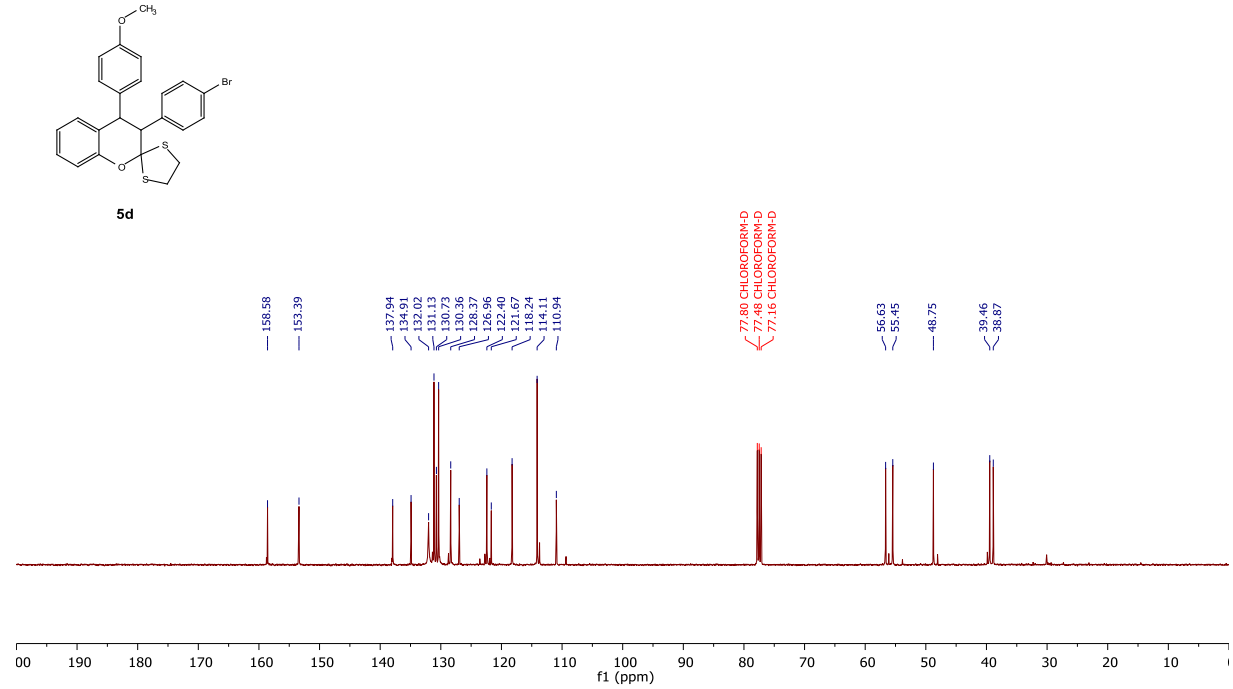
^{1}H NMR (400 MHz) spectrum of compound **5c** in $CDCl_3$



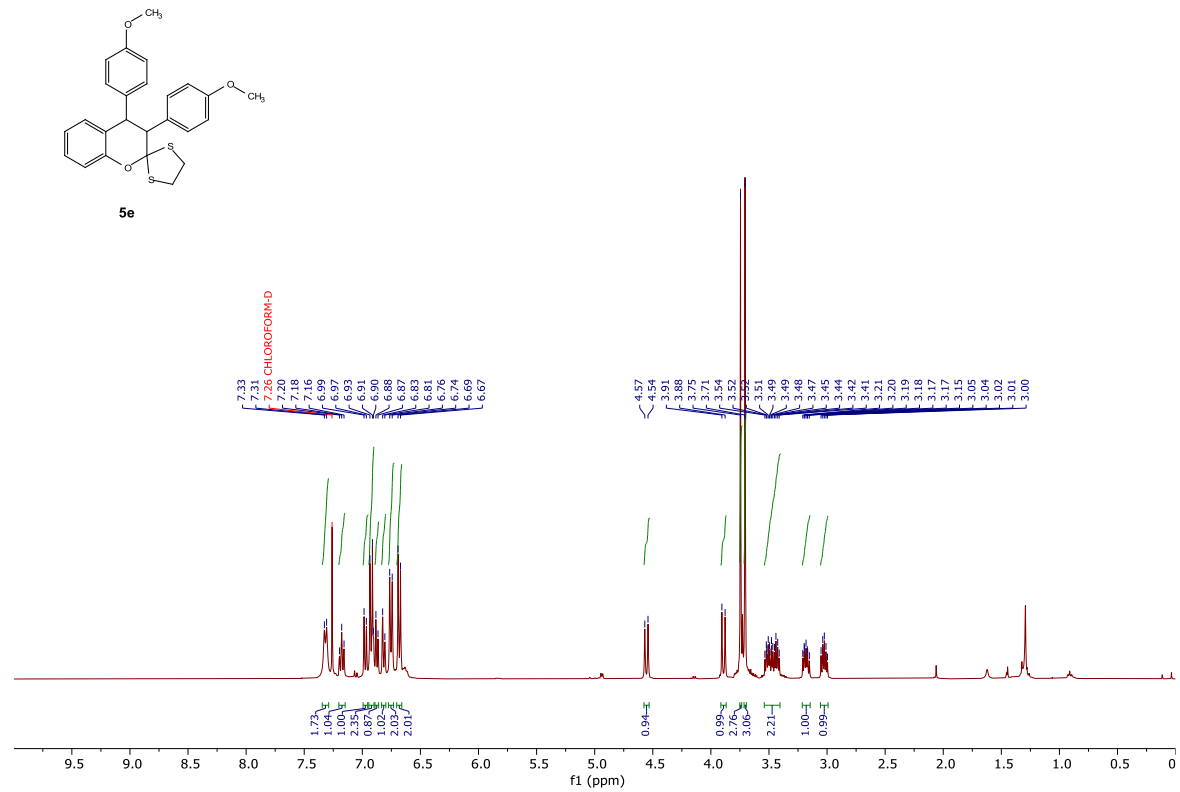
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5c** in $CDCl_3$



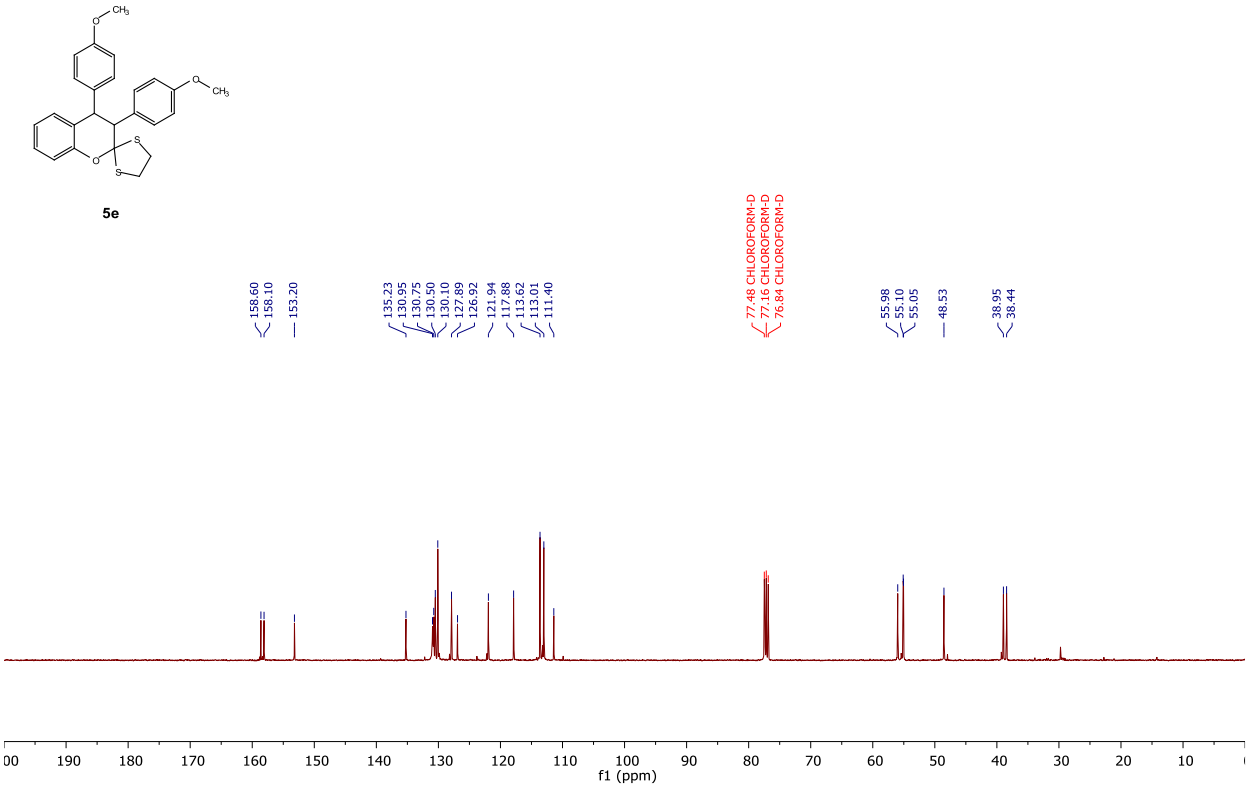
^{1}H NMR (400 MHz) spectrum of compound **5d** in $CDCl_3$



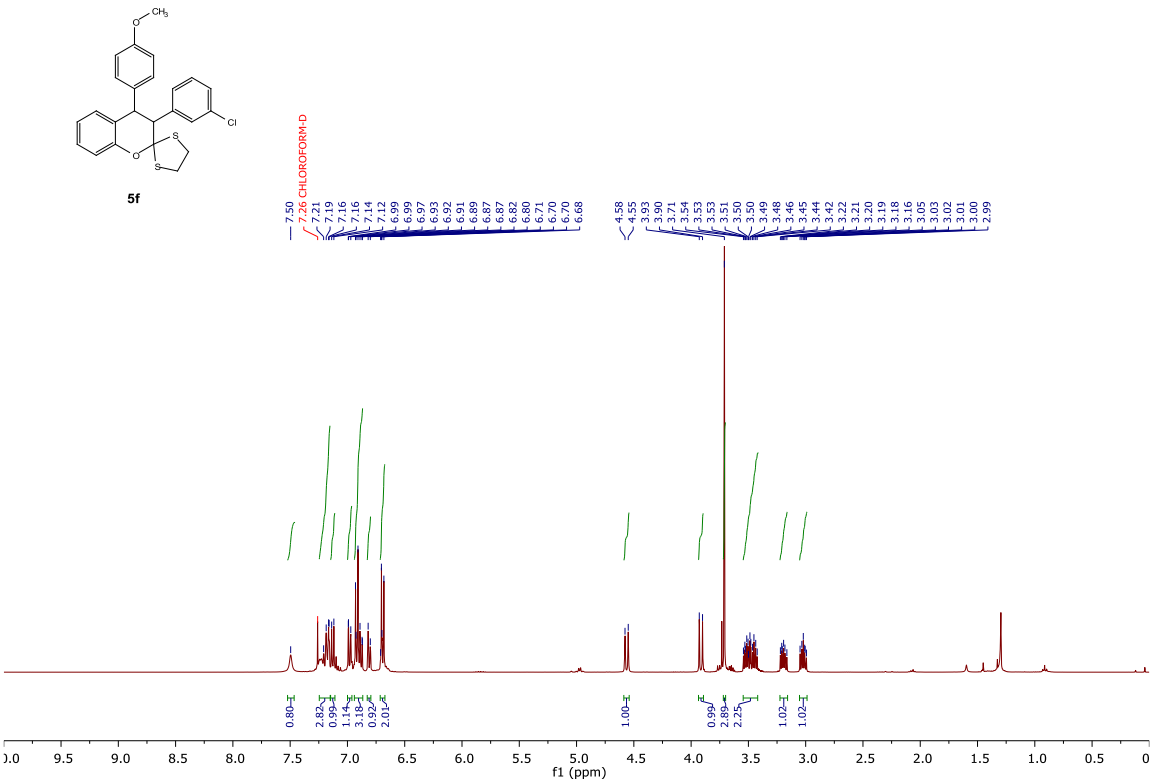
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5d** in $CDCl_3$



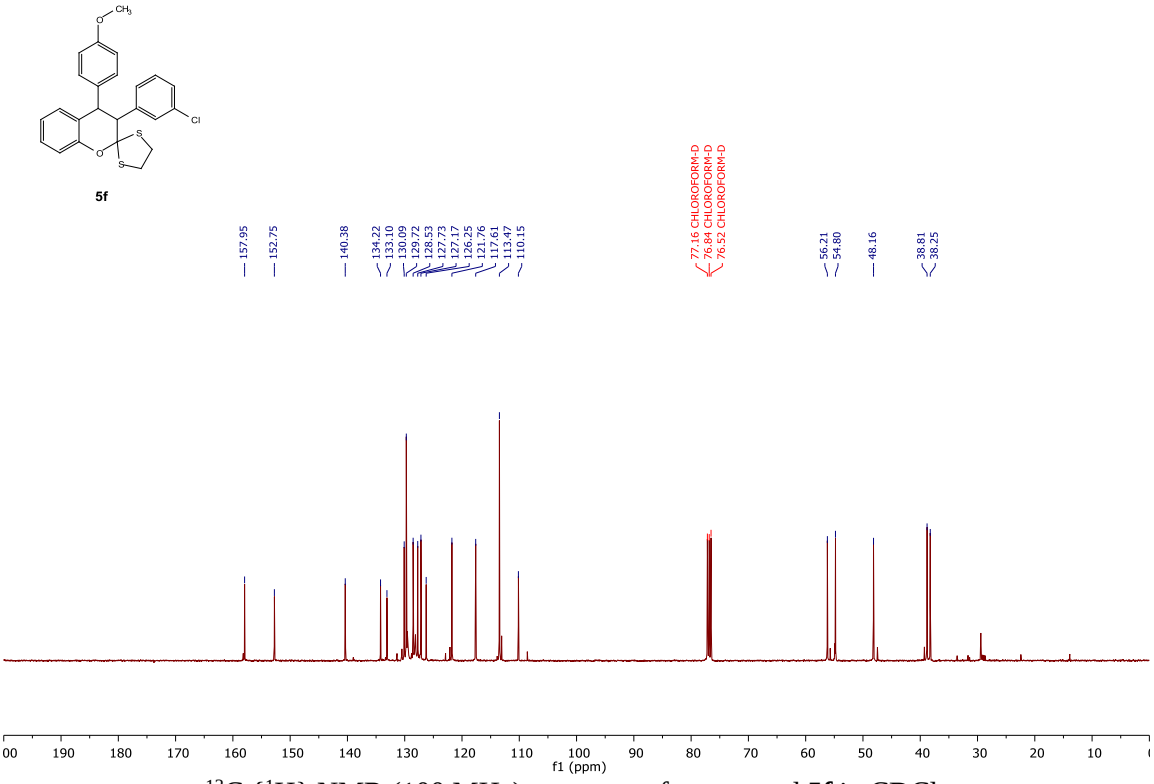
^{1}H NMR (400 MHz) spectrum of compound **5e** in $CDCl_3$



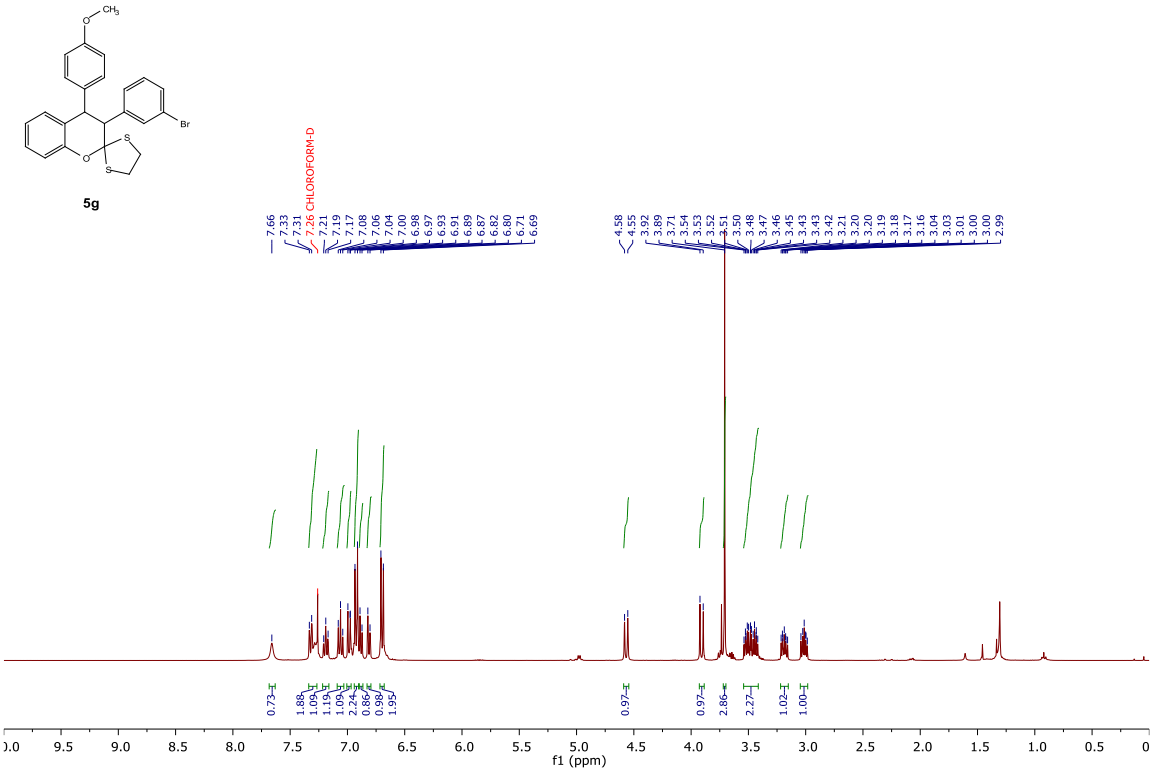
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5e** in $CDCl_3$



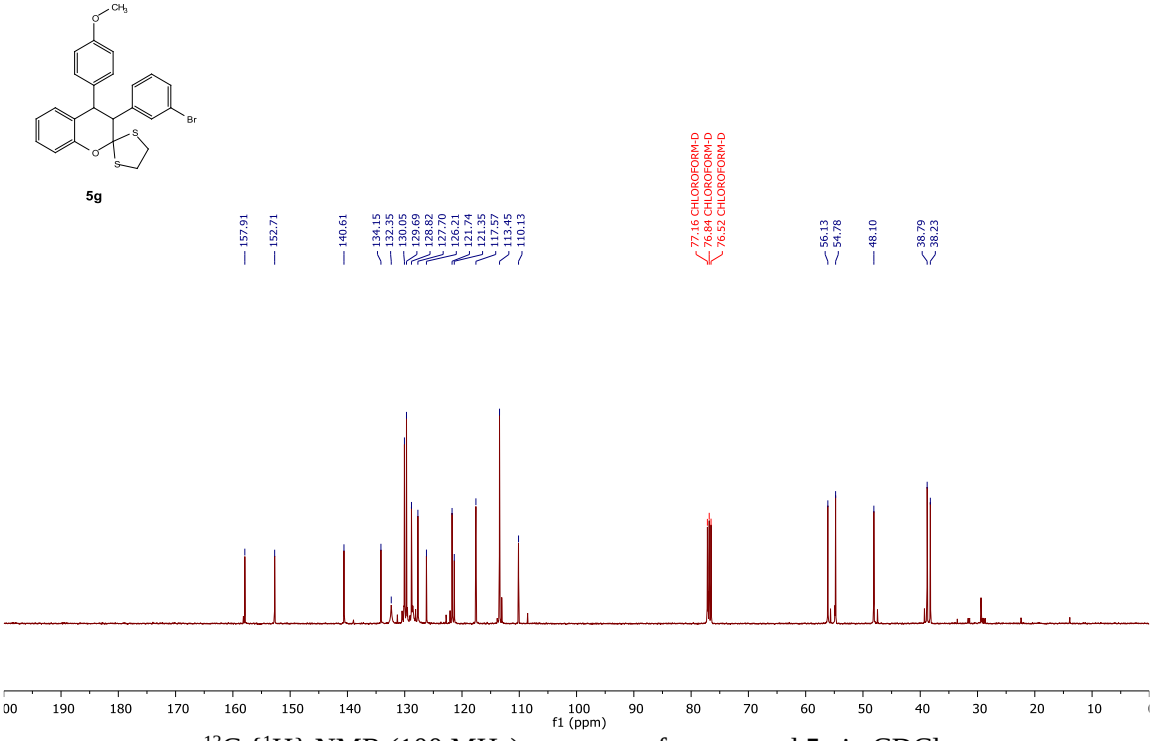
^{1}H NMR (400 MHz) spectrum of compound **5f** in $CDCl_3$



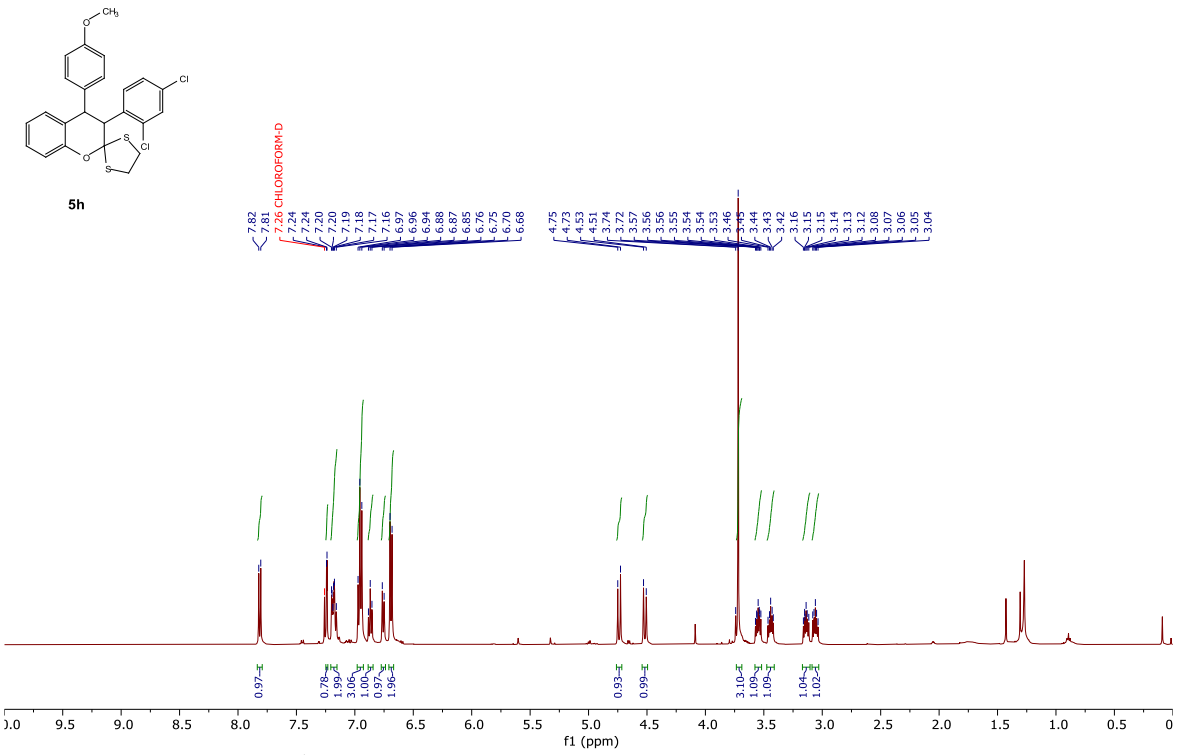
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5f** in $CDCl_3$



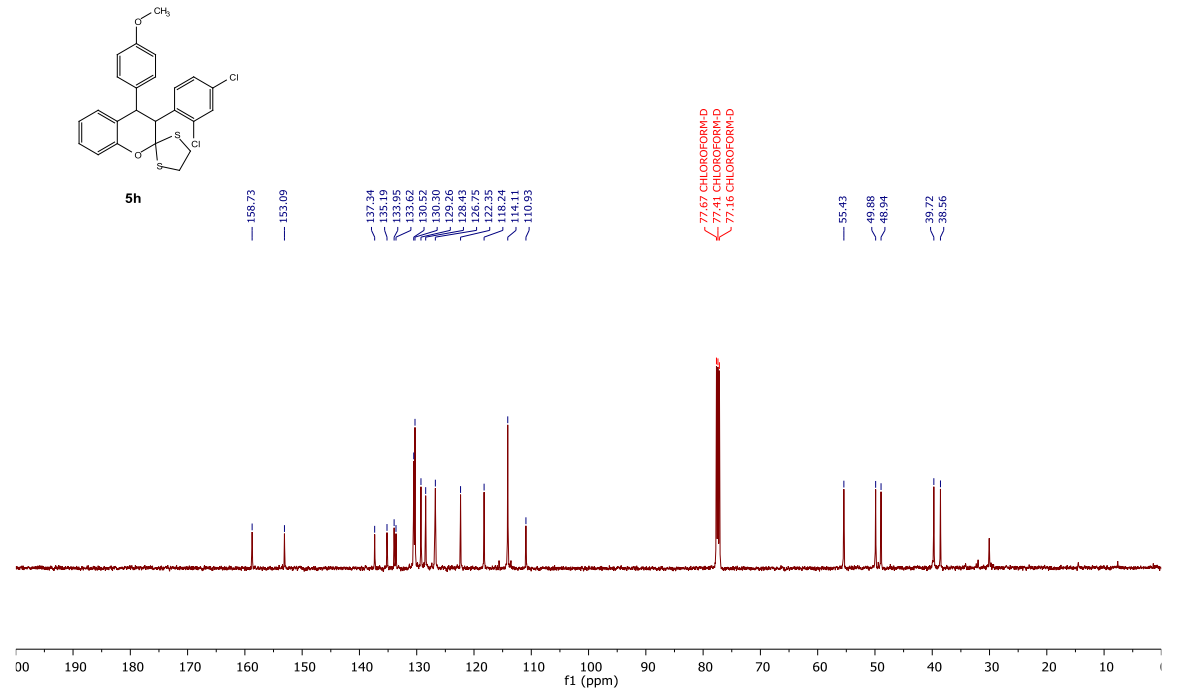
^{1}H NMR (400 MHz) spectrum of compound **5g** in $CDCl_3$



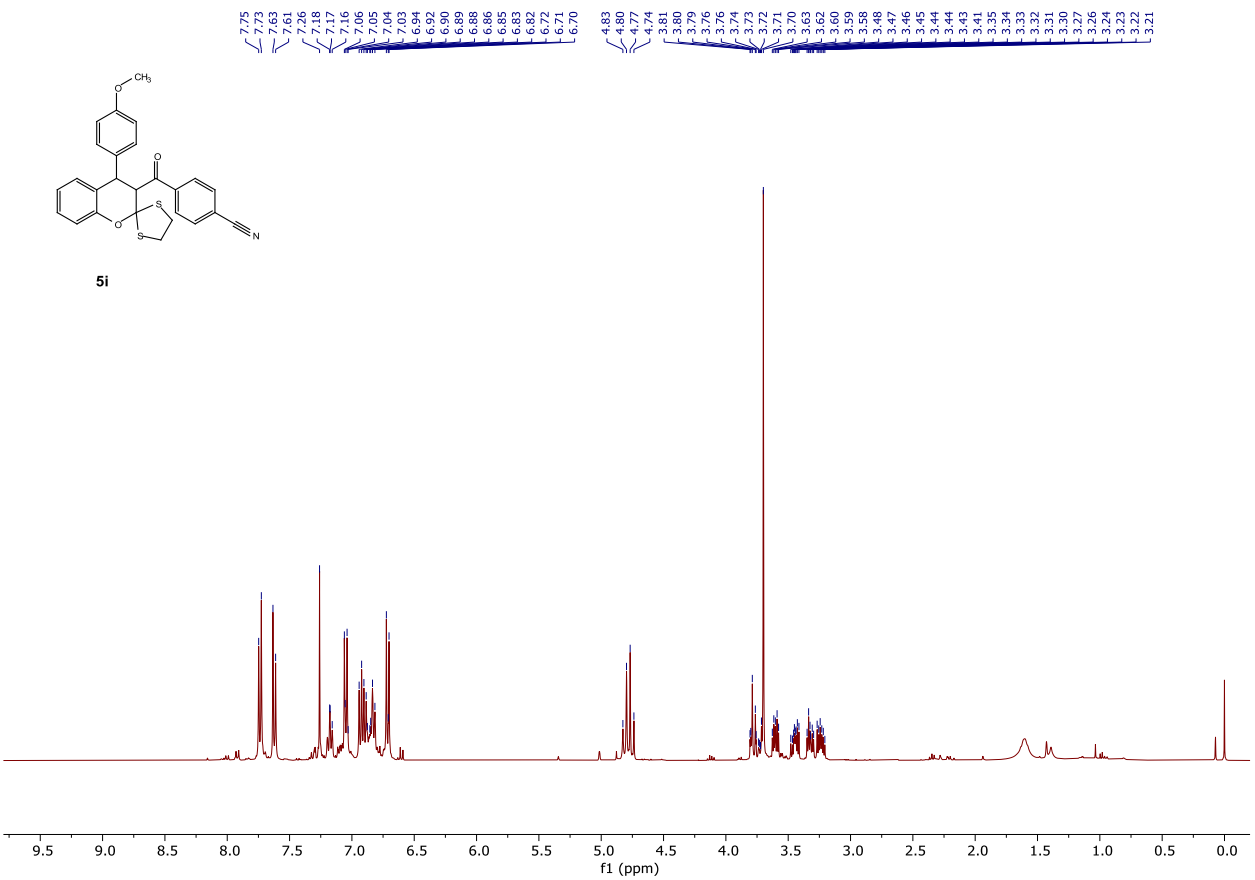
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5g** in $CDCl_3$



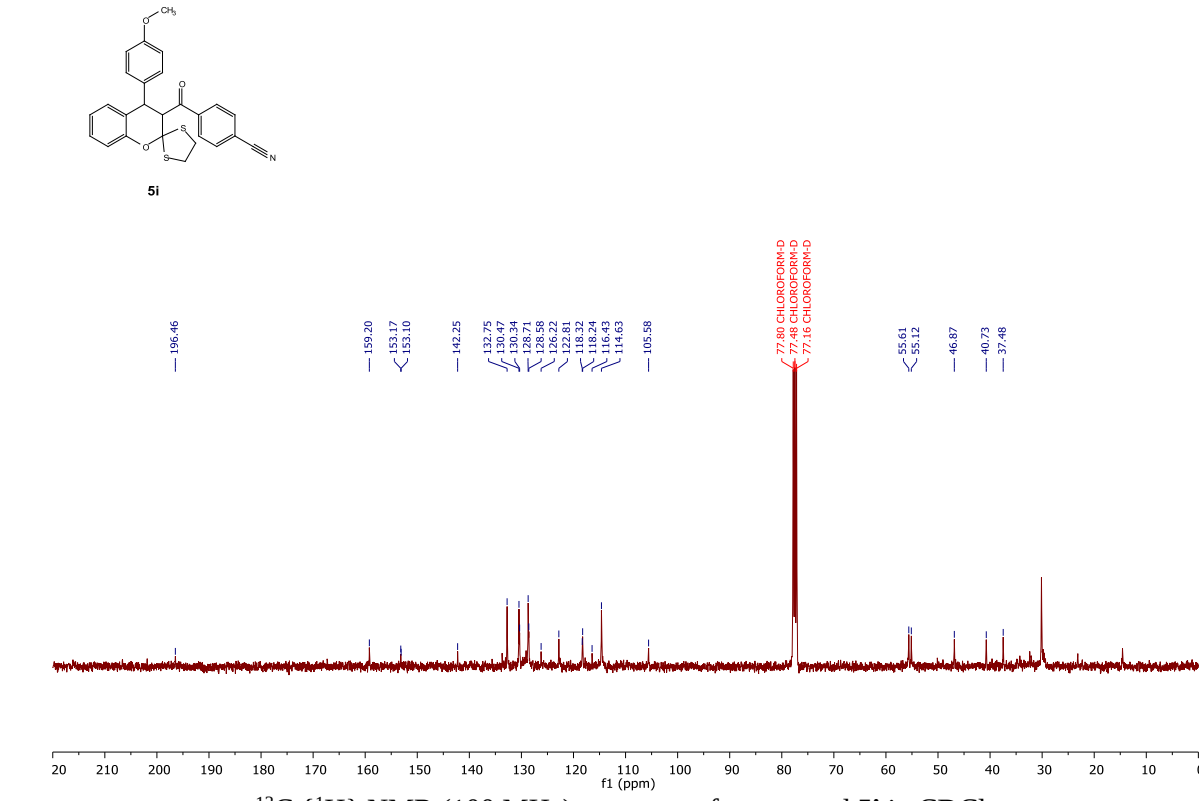
^{1}H NMR (500 MHz) spectrum of compound **5h** in $CDCl_3$



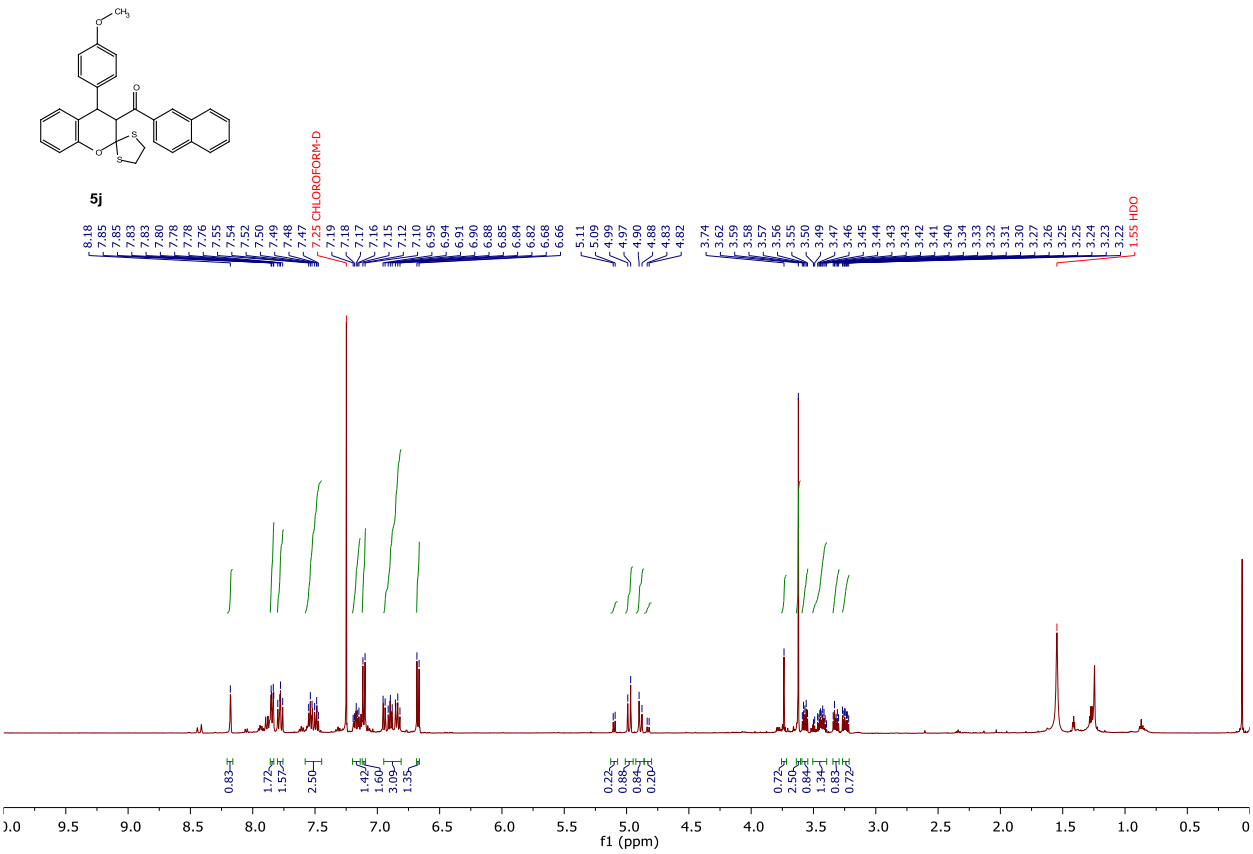
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5h** in $CDCl_3$



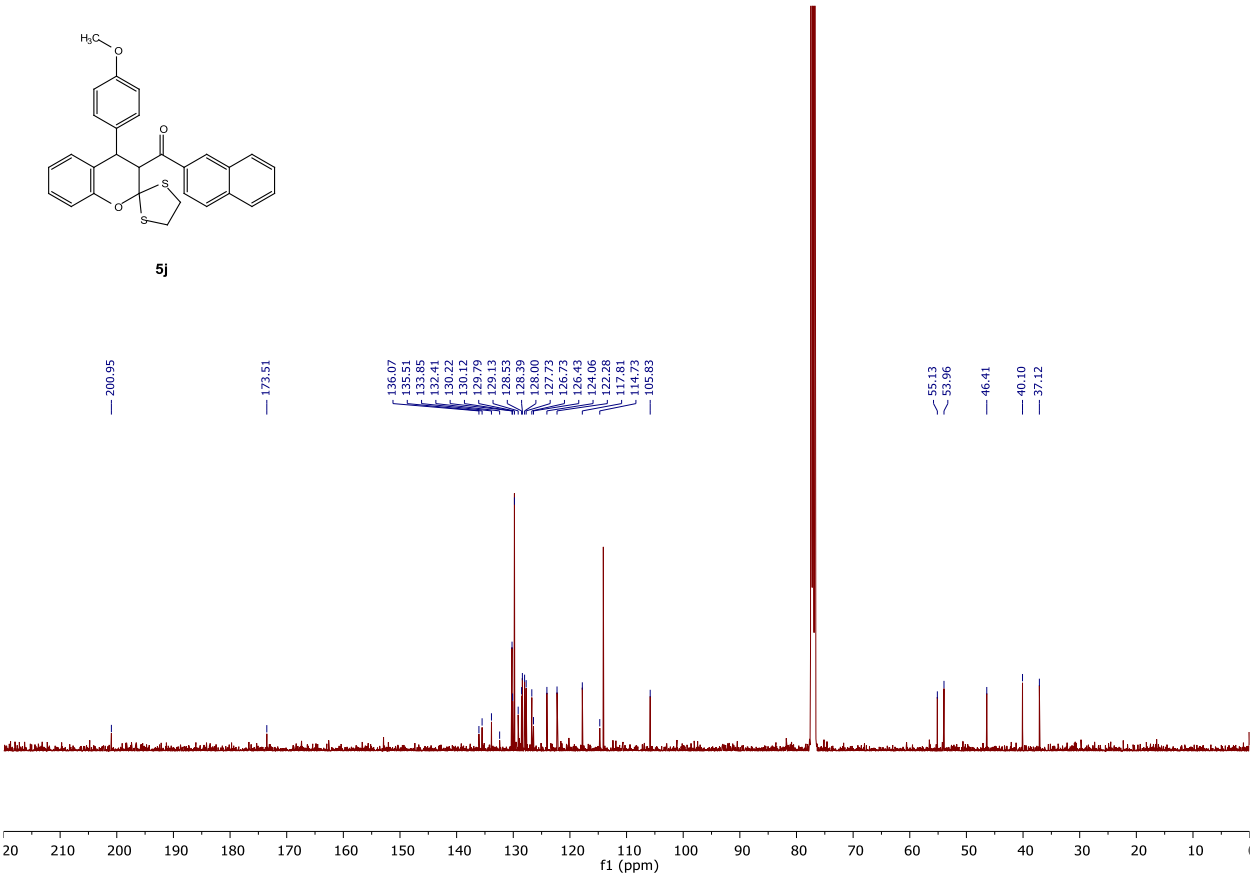
^{1}H NMR (400 MHz) spectrum of compound **5i** in $CDCl_3$



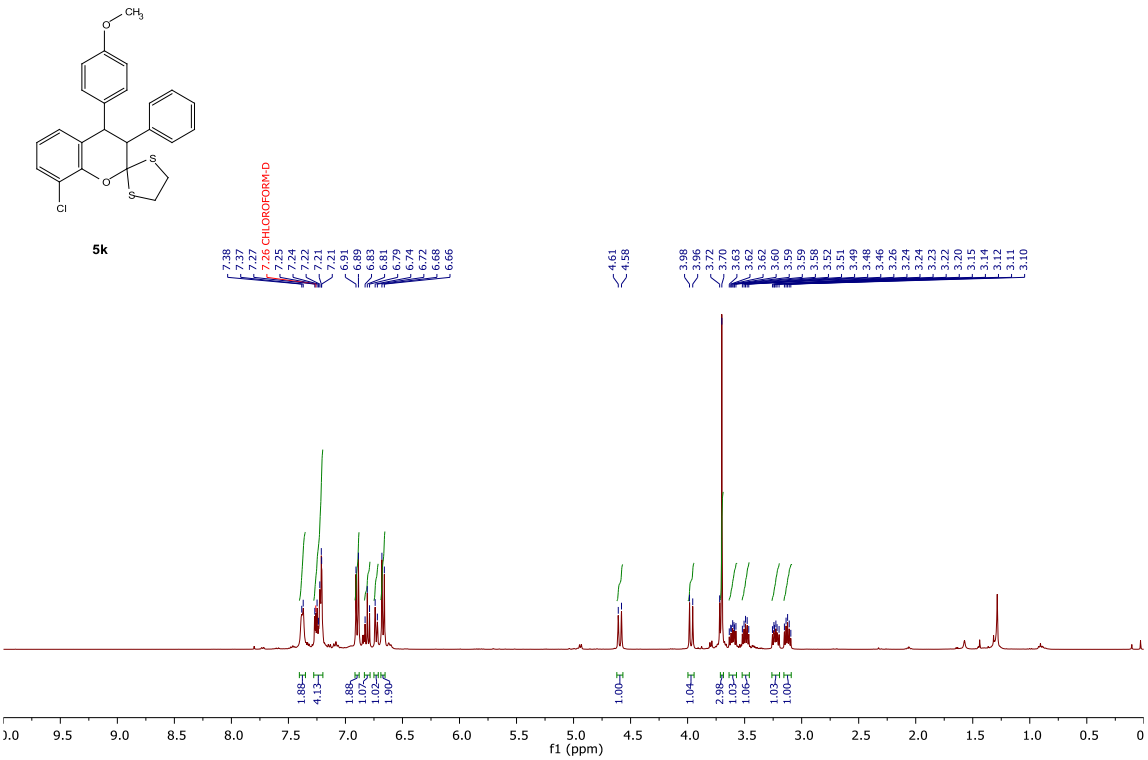
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5i** in $CDCl_3$



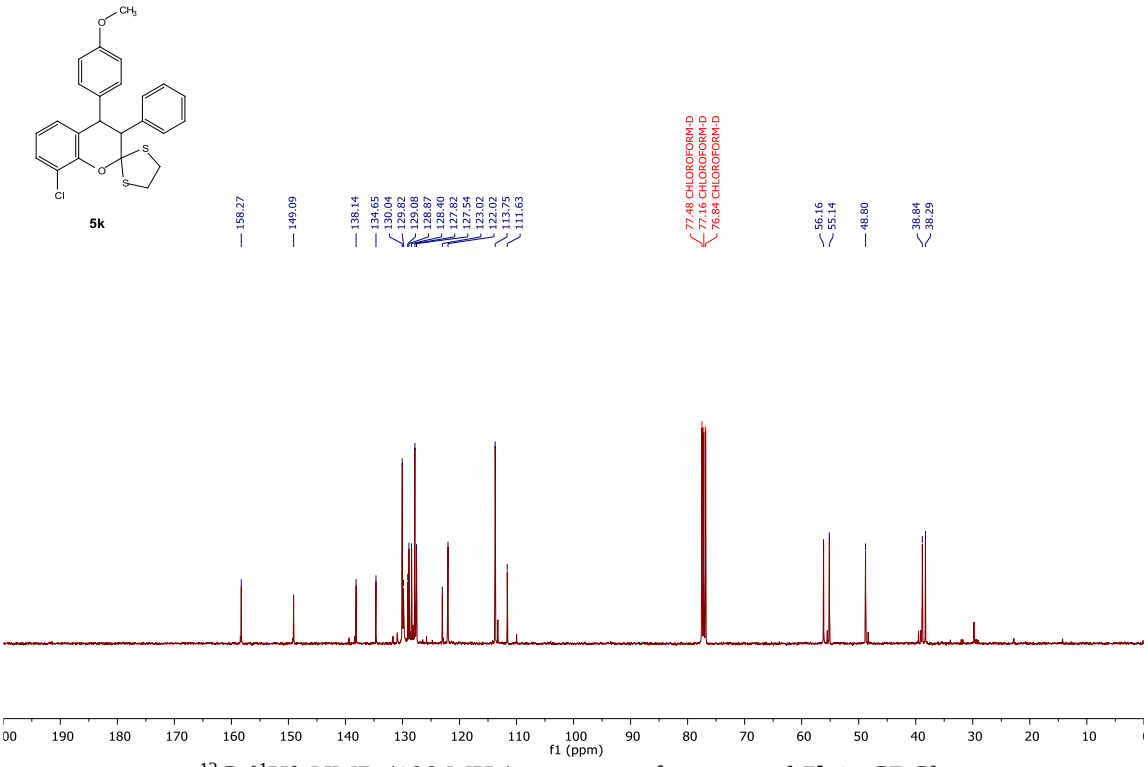
^{1}H NMR (500 MHz) spectrum of compound **5j** in $CDCl_3$



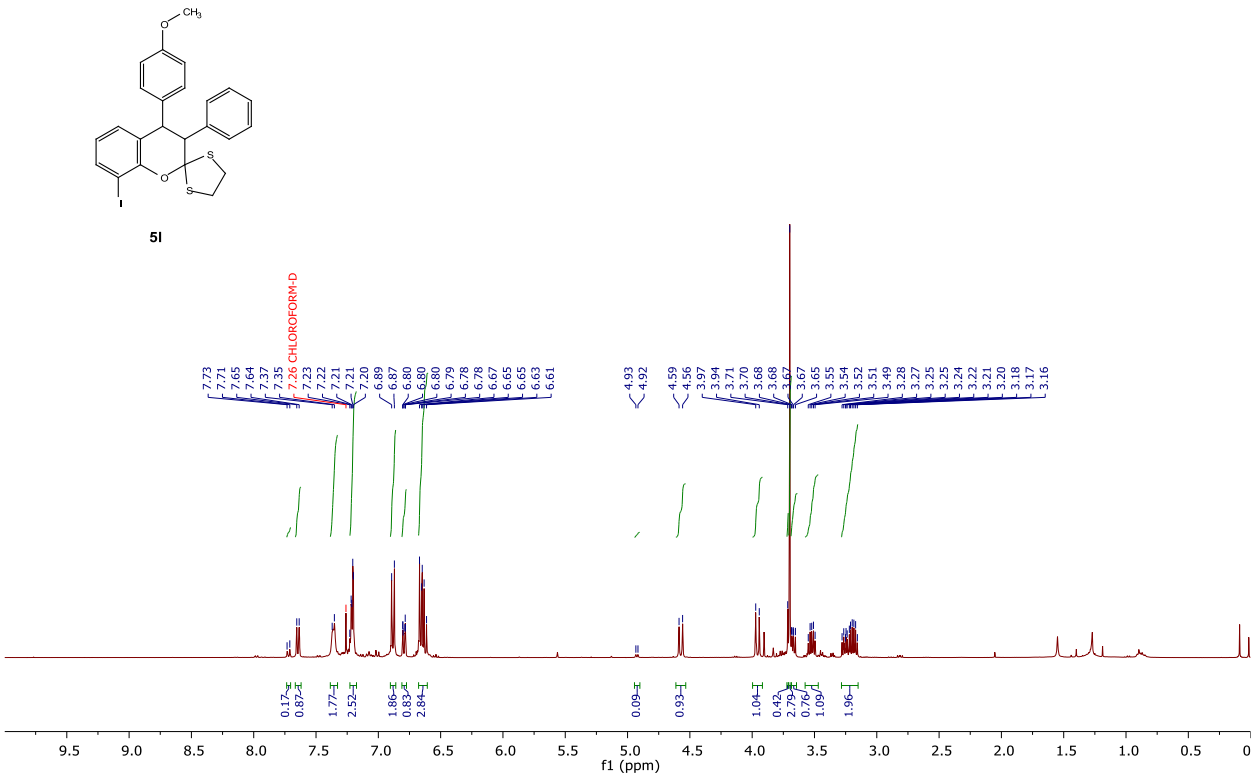
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5j** in $CDCl_3$



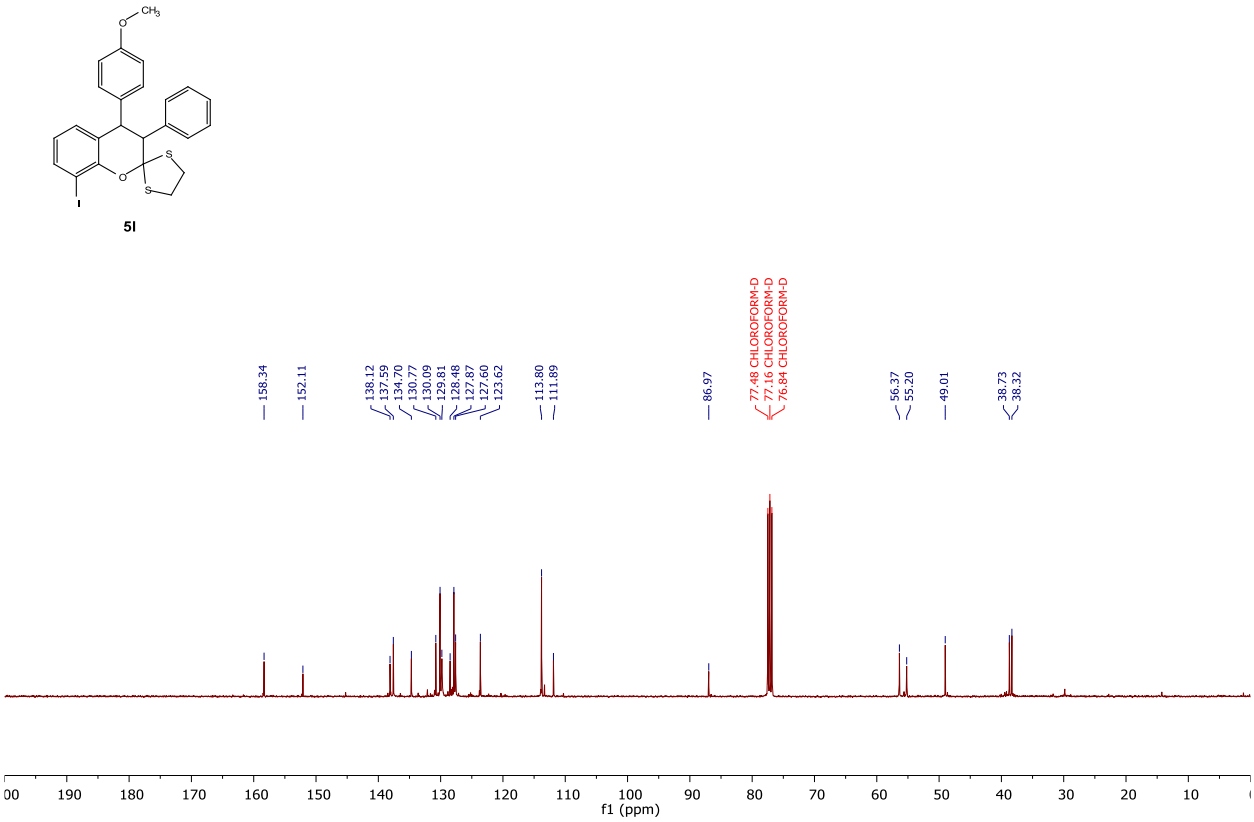
^{1}H NMR (400 MHz) spectrum of compound **5k** in $CDCl_3$



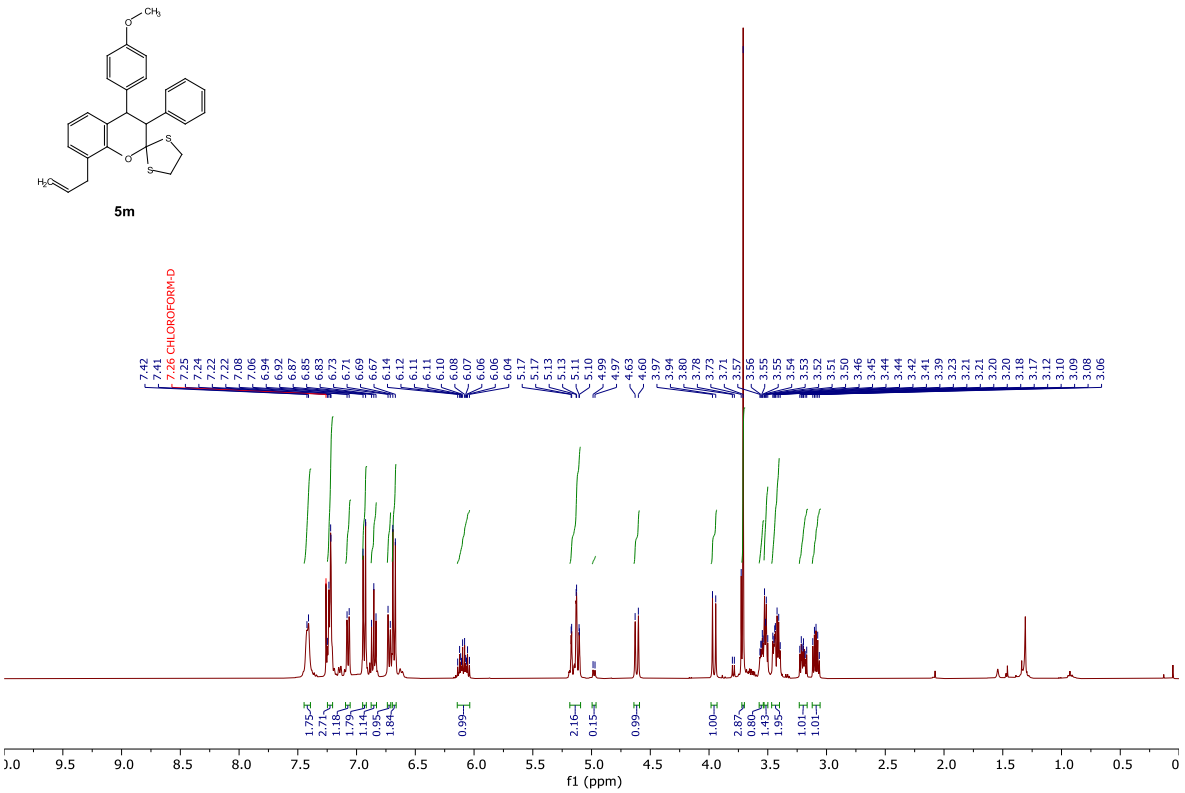
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5k** in $CDCl_3$



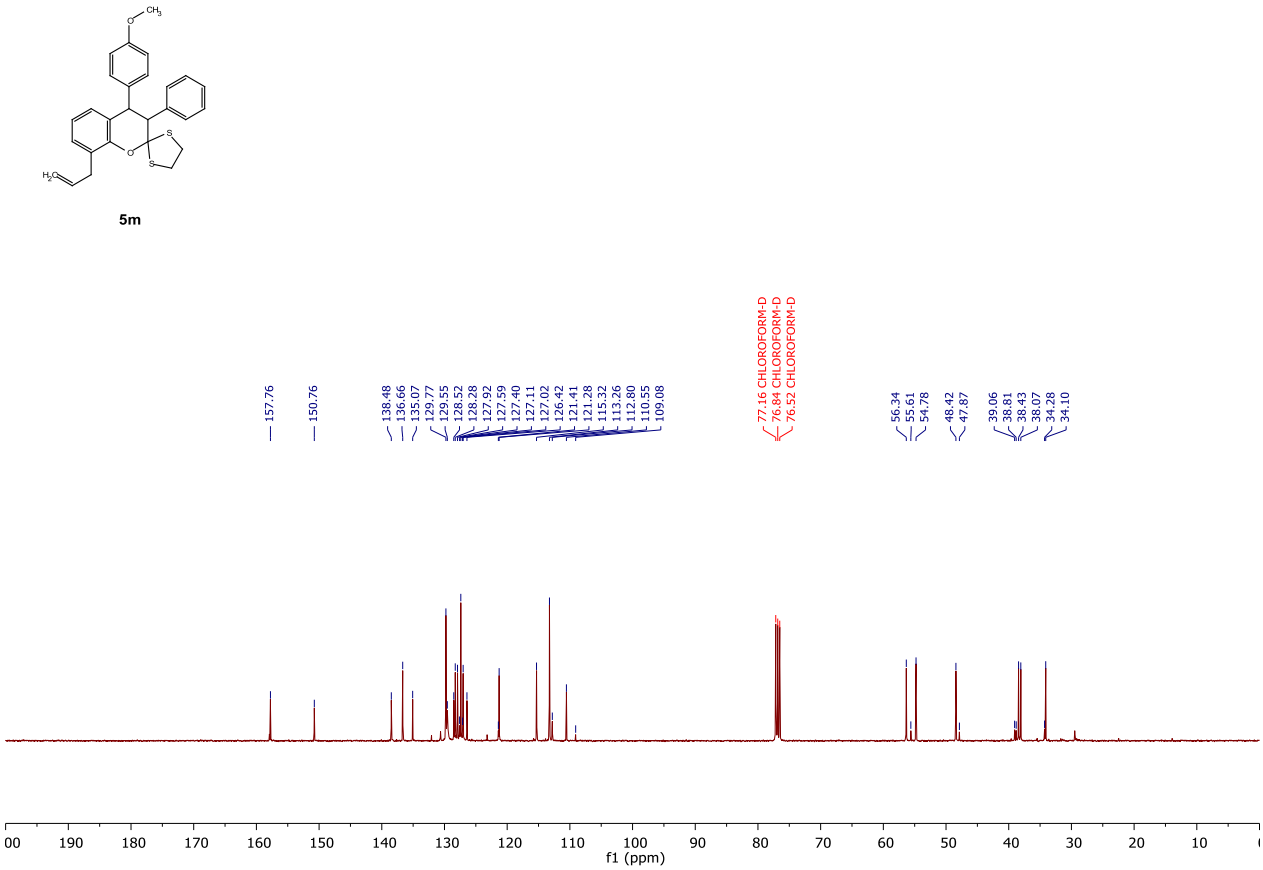
^{1}H NMR (396 MHz) spectrum of compound **5l** in $CDCl_3$



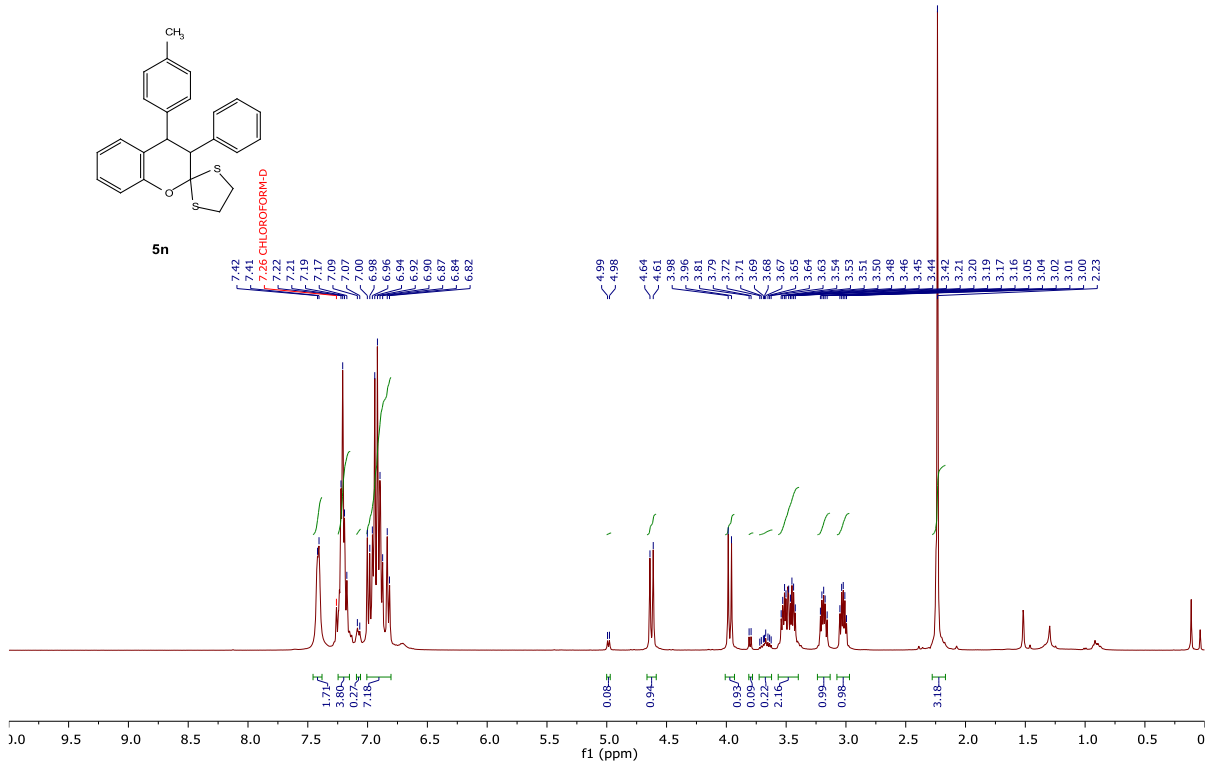
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5l** in $CDCl_3$



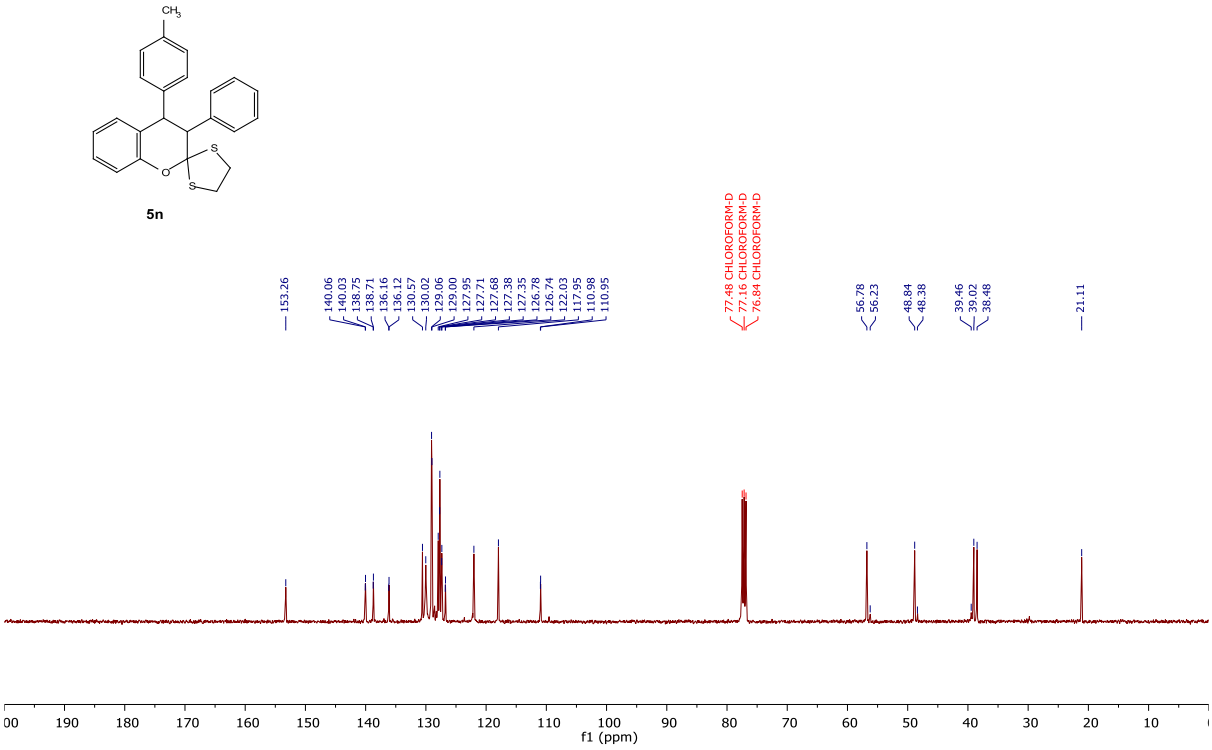
^{1}H NMR (400 MHz) spectrum of compound **5m** in $CDCl_3$



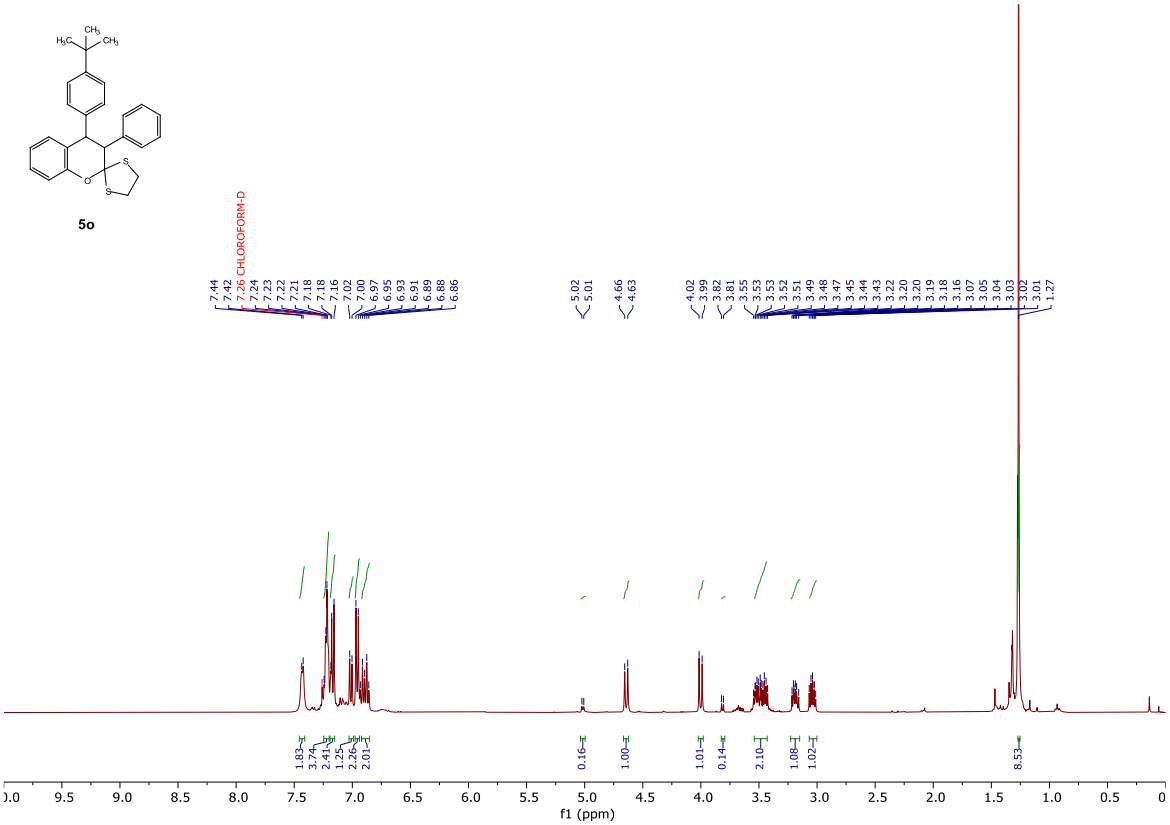
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5m** in $CDCl_3$



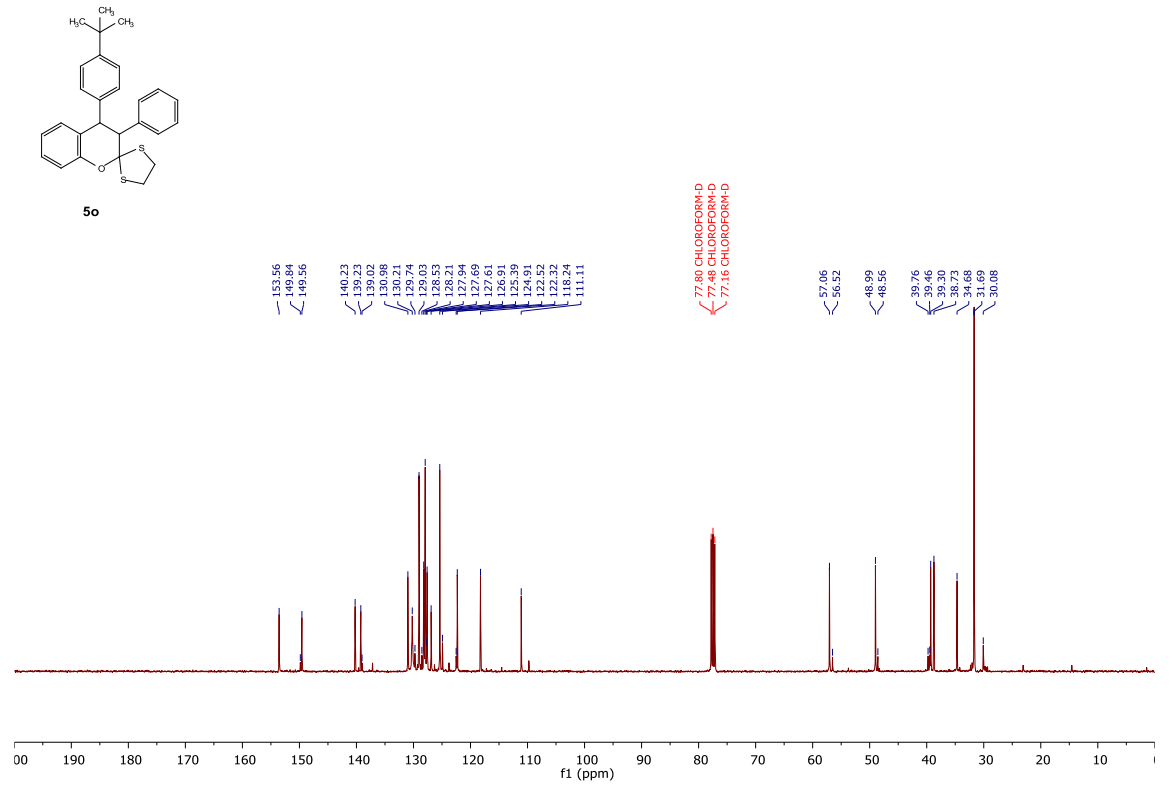
^{1}H NMR (400 MHz) spectrum of compound **5n** in $CDCl_3$



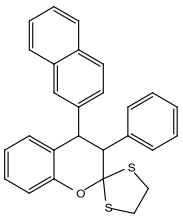
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5n** in $CDCl_3$



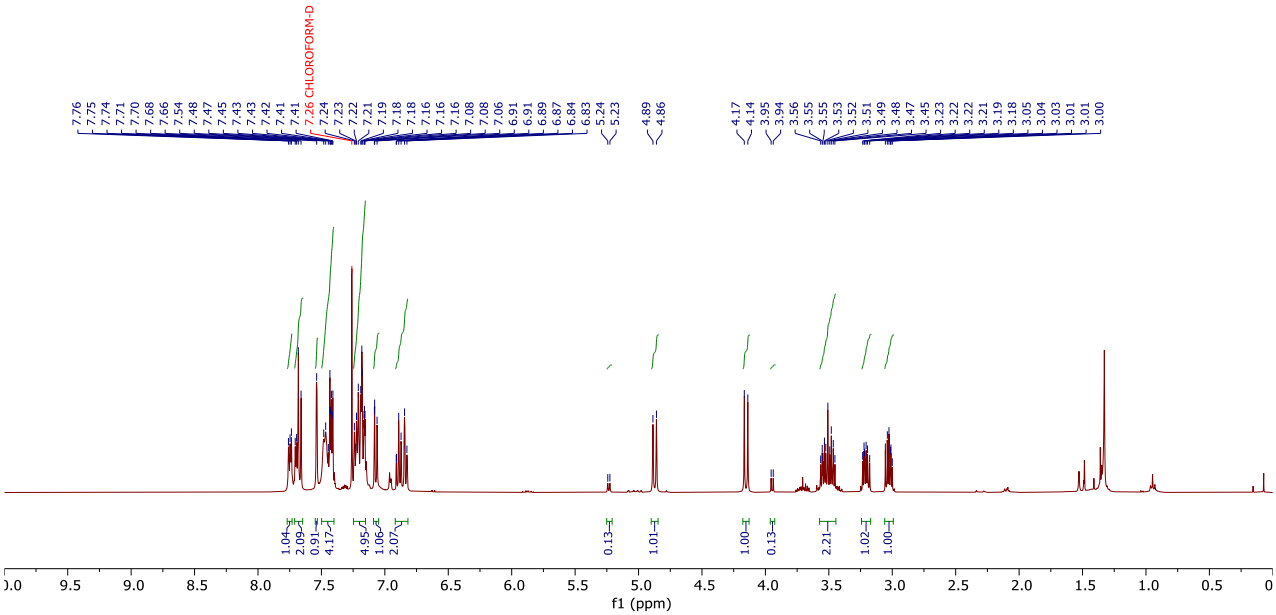
^{1}H NMR (400 MHz) spectrum of compound **5o** in $CDCl_3$



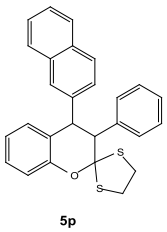
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5o** in $CDCl_3$



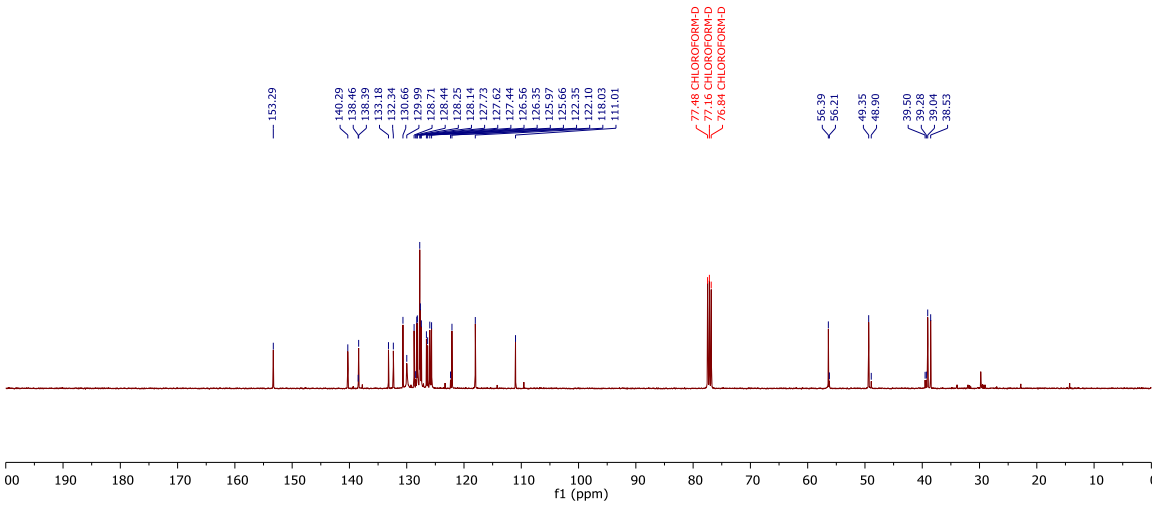
5p



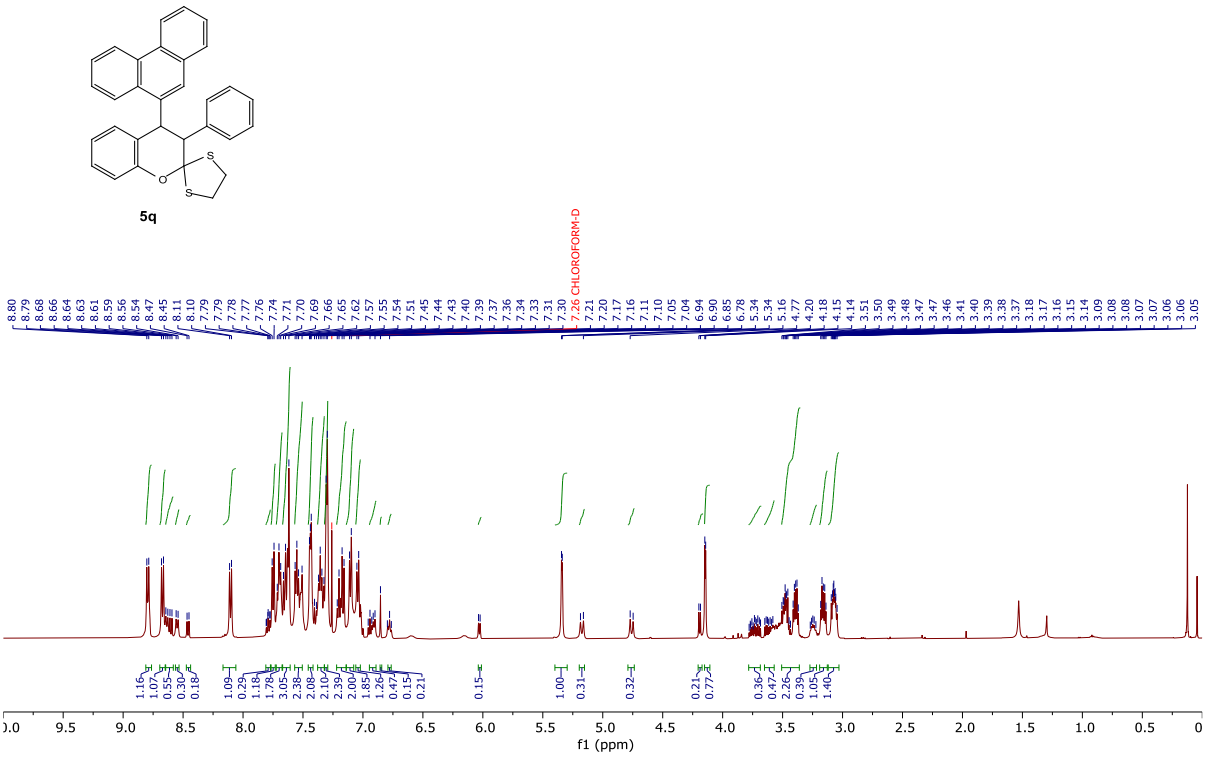
^{1}H NMR (400 MHz) spectrum of compound **5p** in $CDCl_3$



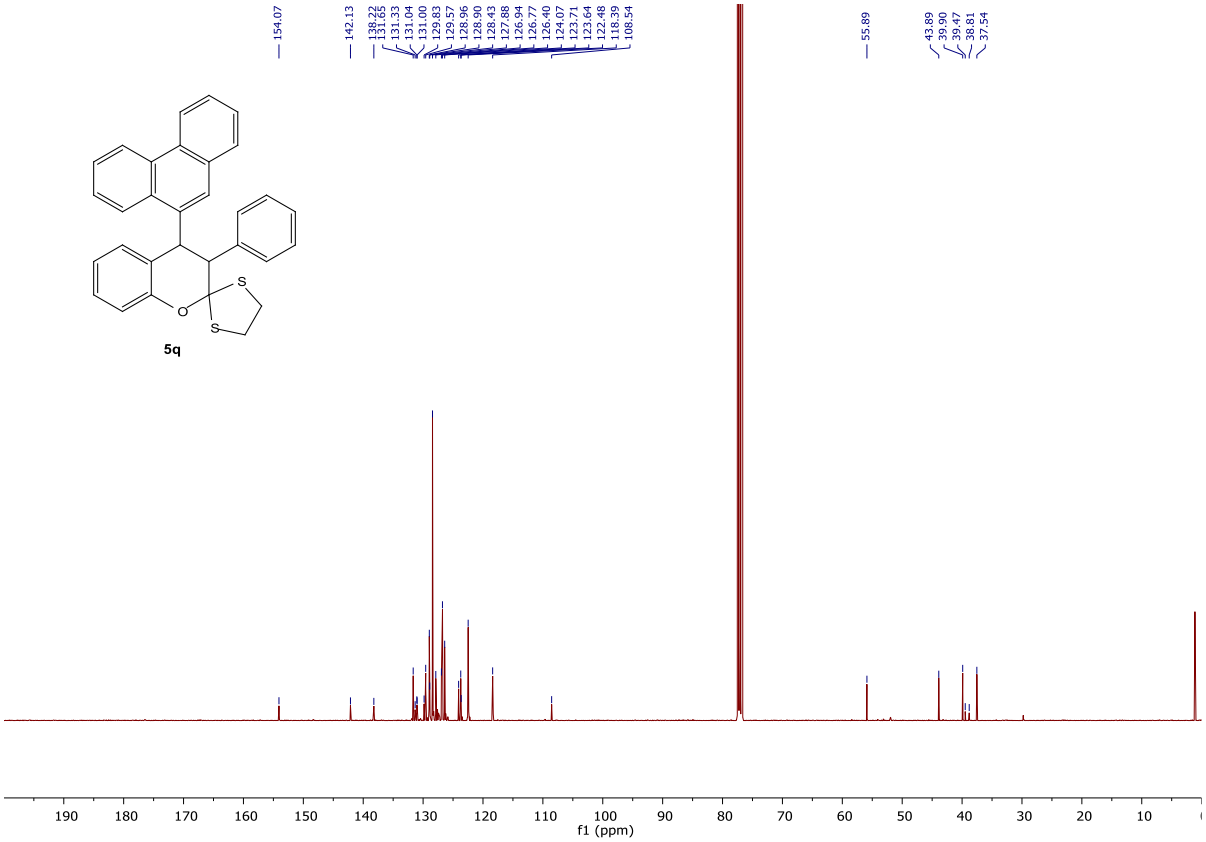
5p



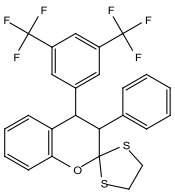
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5p** in $CDCl_3$



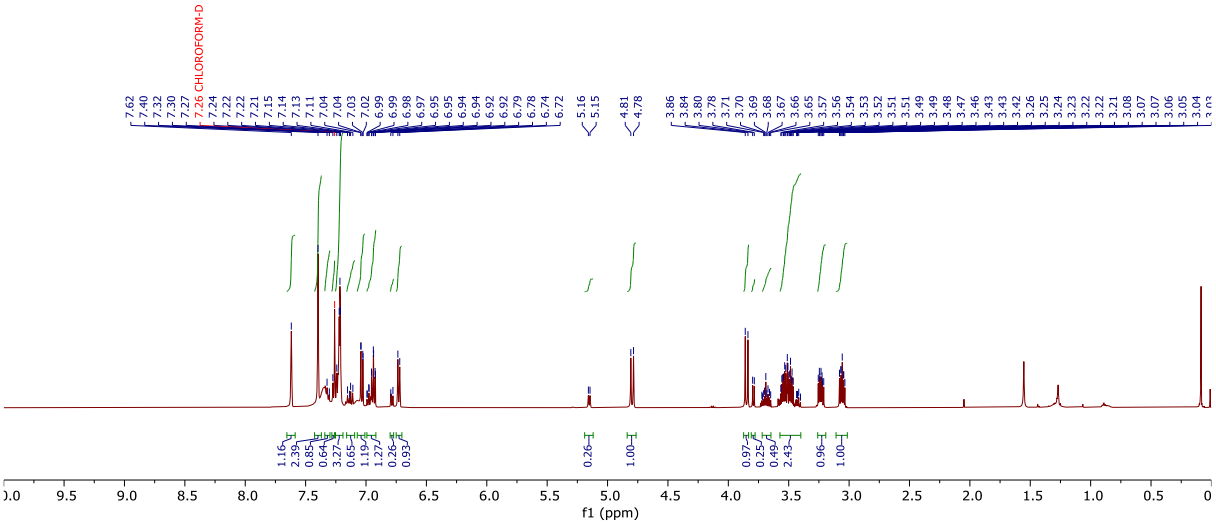
^{1}H NMR (500 MHz) spectrum of compound **5q** in $CDCl_3$



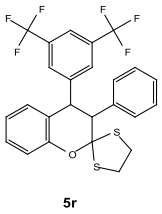
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5q** in $CDCl_3$



5r

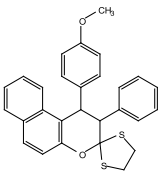


^{1}H NMR (500 MHz) spectrum of compound **5r** in $CDCl_3$

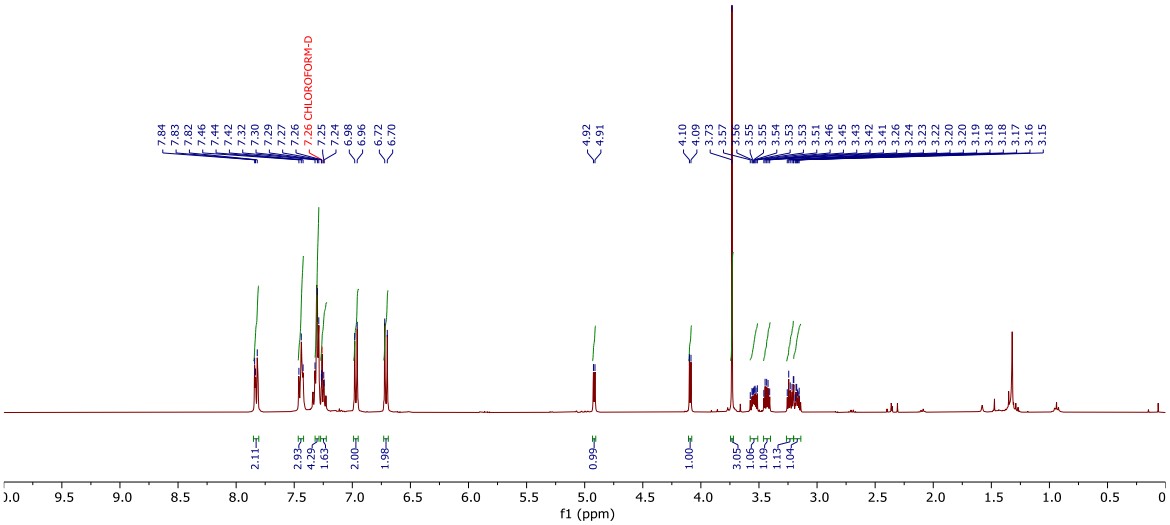


5r

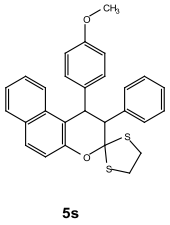
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5r** in $CDCl_3$



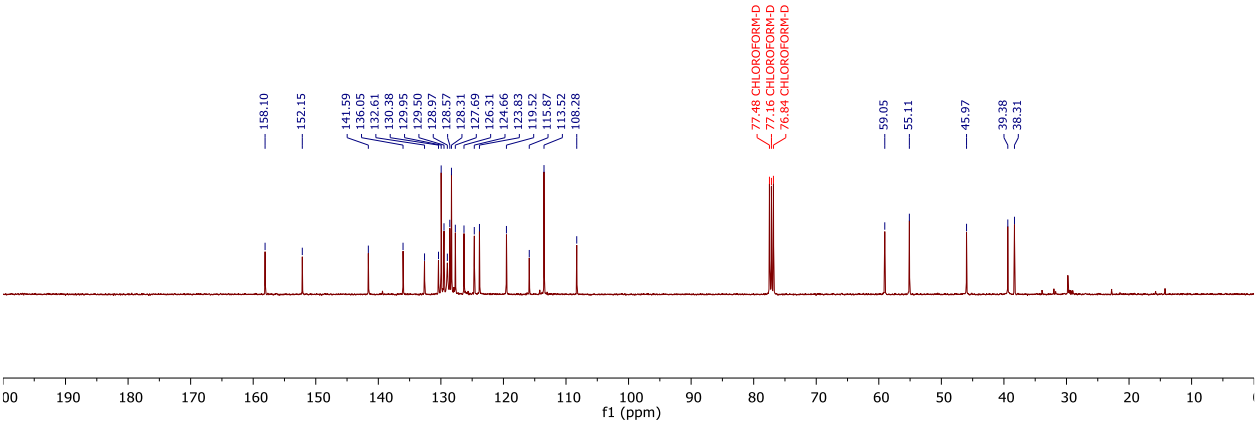
5s



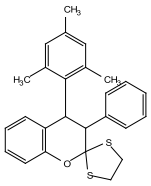
^{1}H NMR (400 MHz) spectrum of compound **5s** in $CDCl_3$



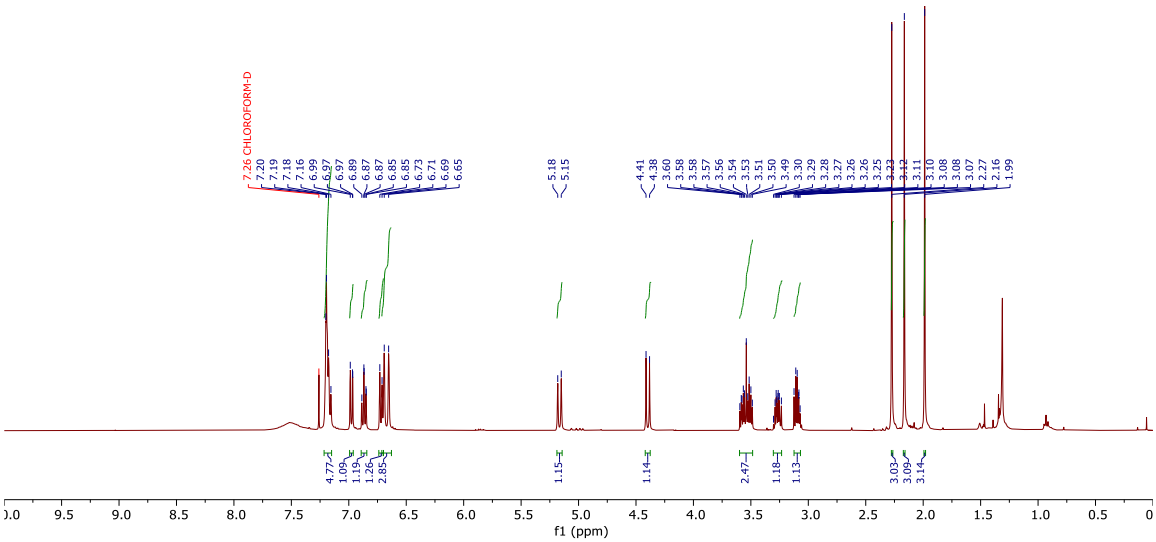
5s



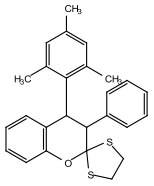
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5s** in $CDCl_3$



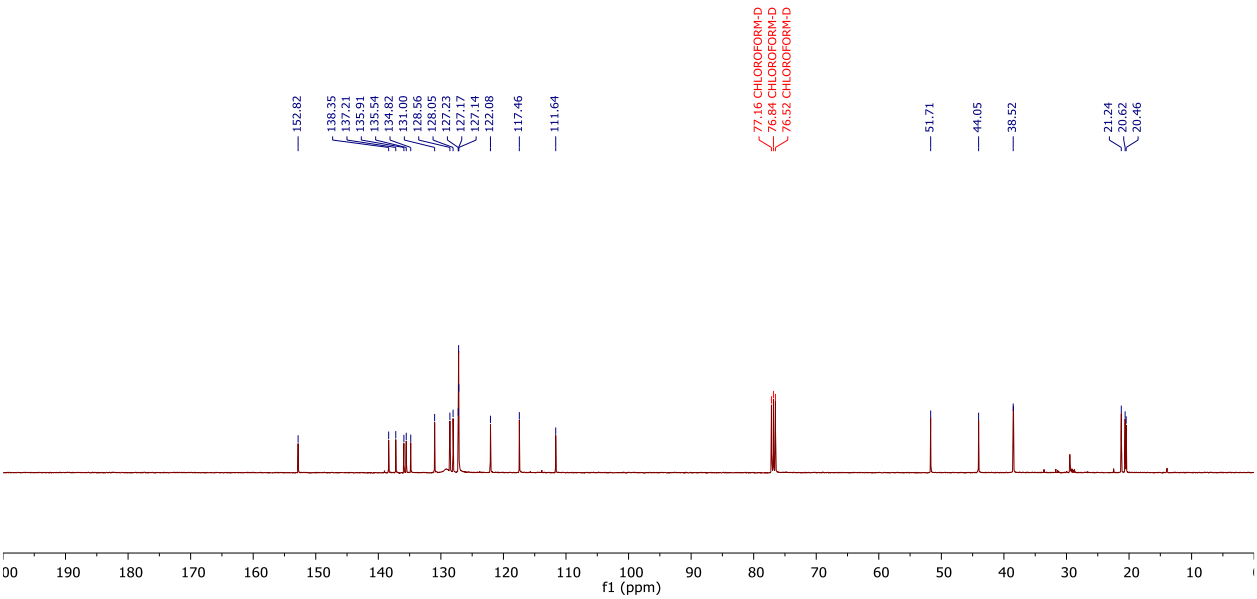
5t



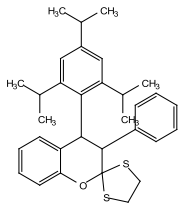
^{1}H NMR (400 MHz) spectrum of compound **5t** in $CDCl_3$



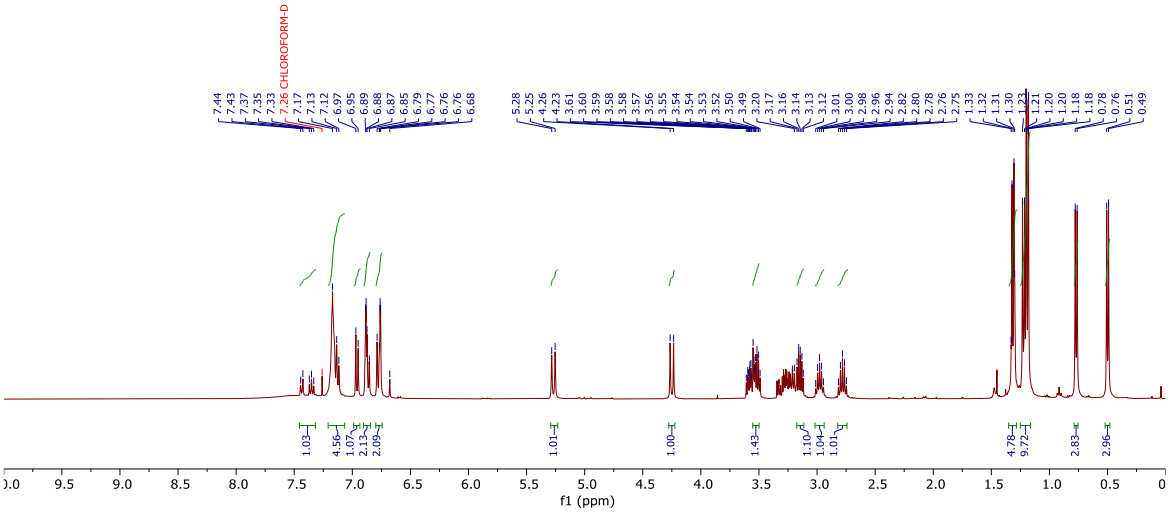
5t



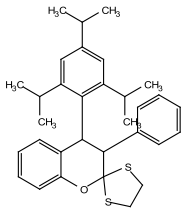
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5t** in $CDCl_3$



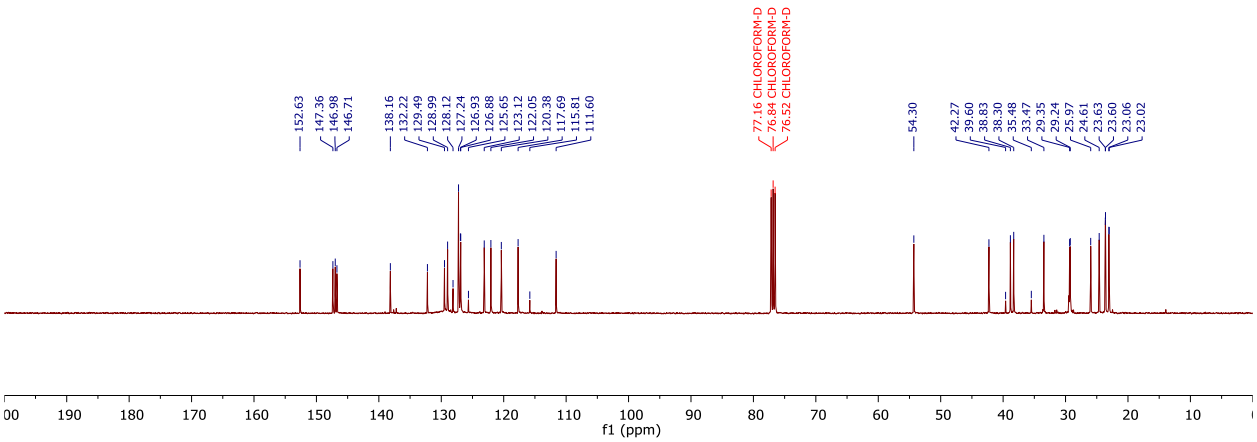
5u



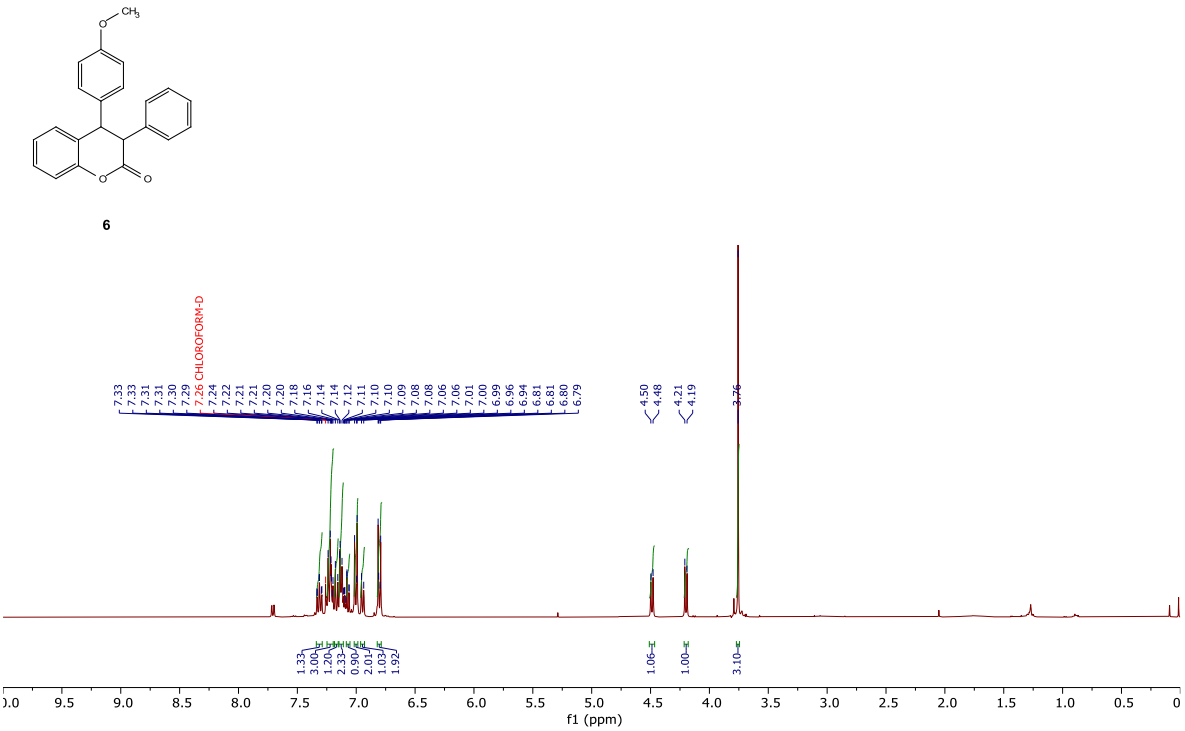
^{1}H NMR (400 MHz) spectrum of compound **5u** in $CDCl_3$



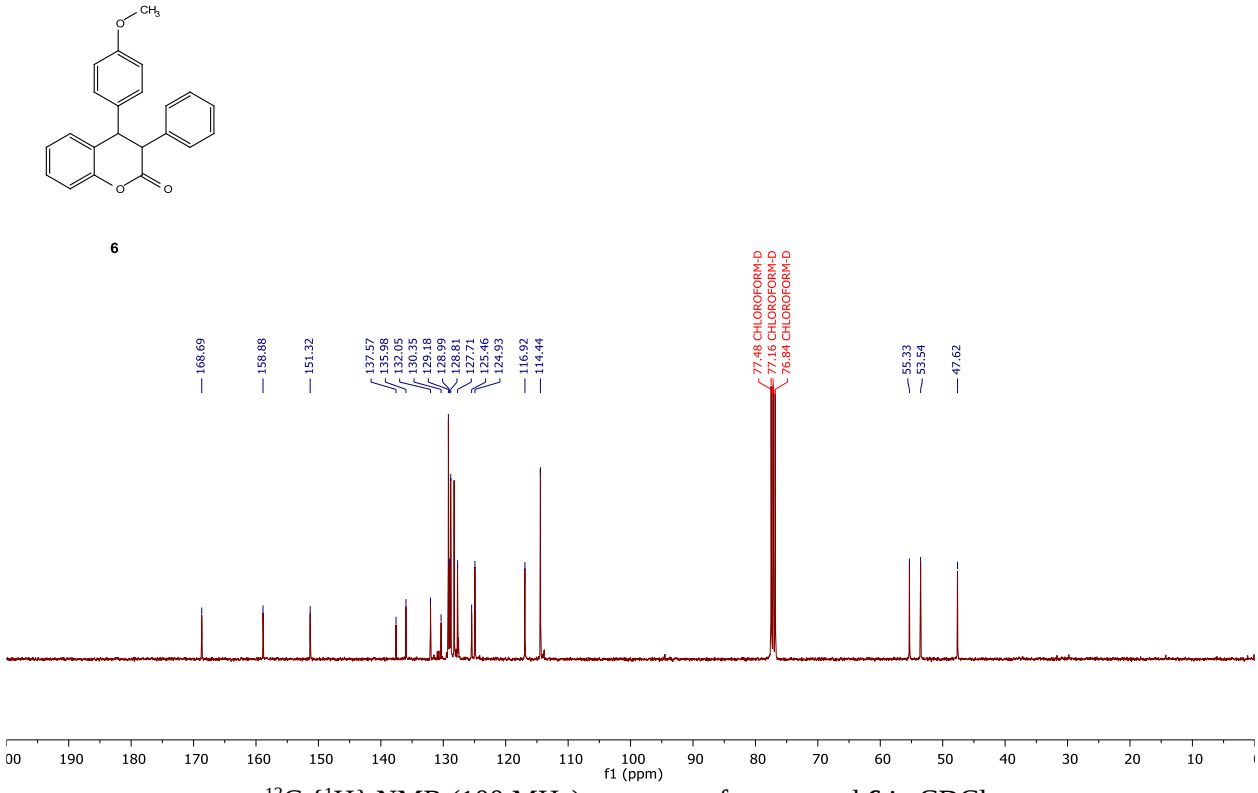
5u



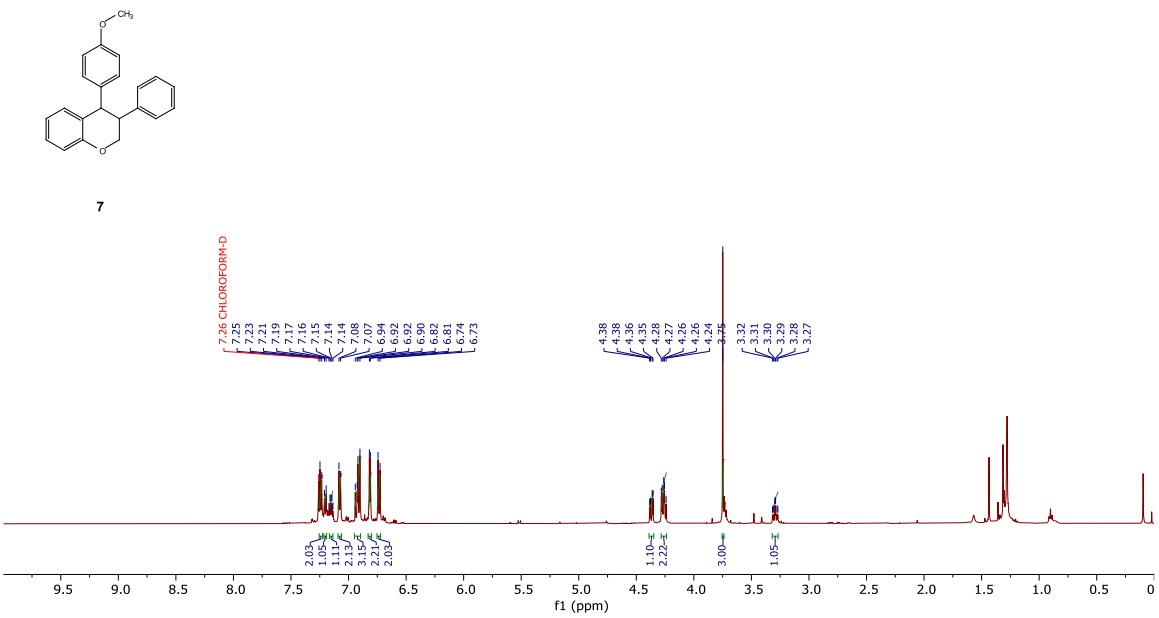
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5u** in $CDCl_3$



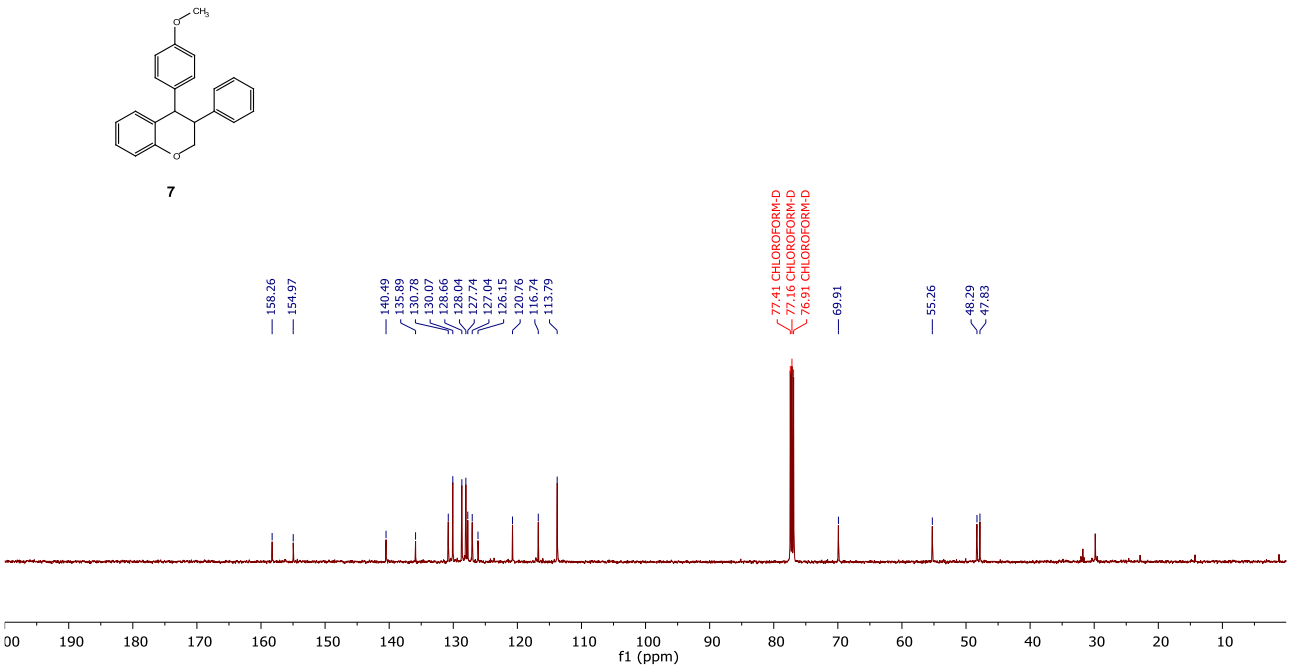
^{1}H NMR (400 MHz) spectrum of compound **6** in $CDCl_3$



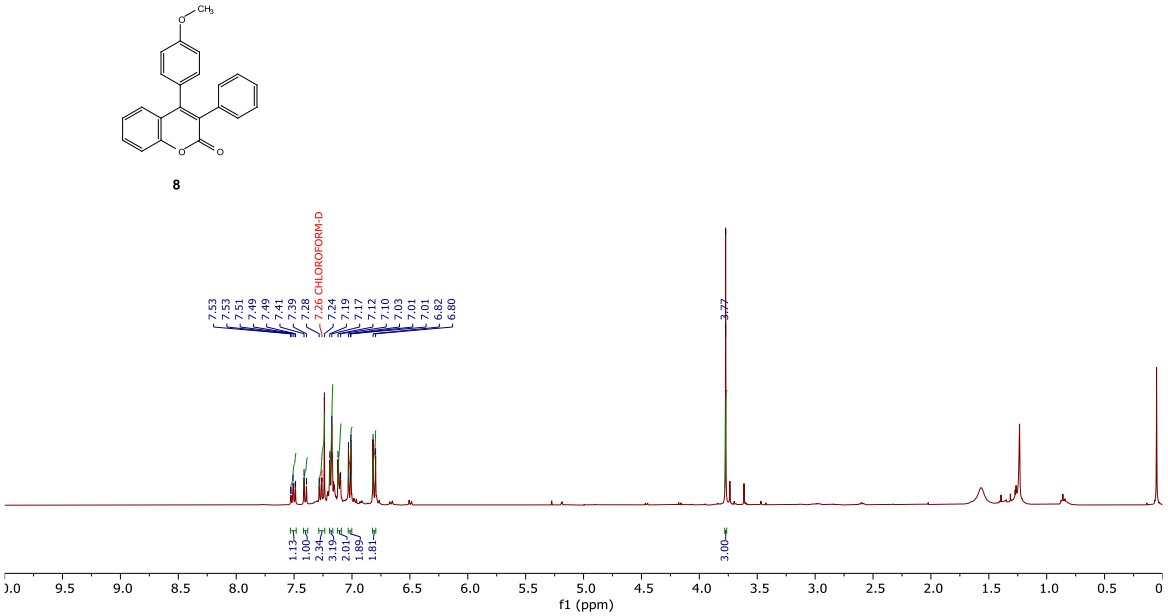
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **6** in $CDCl_3$



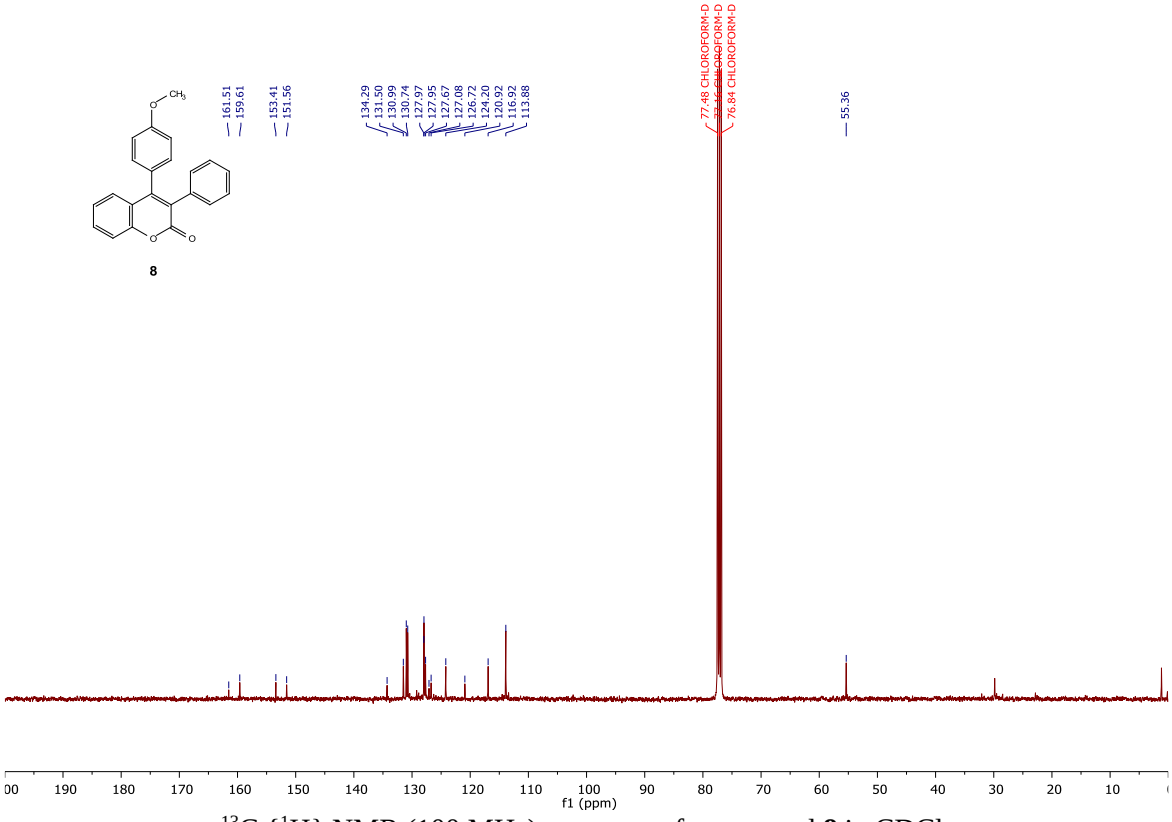
^{1}H NMR (500 MHz) spectrum of compound **7** in $CDCl_3$



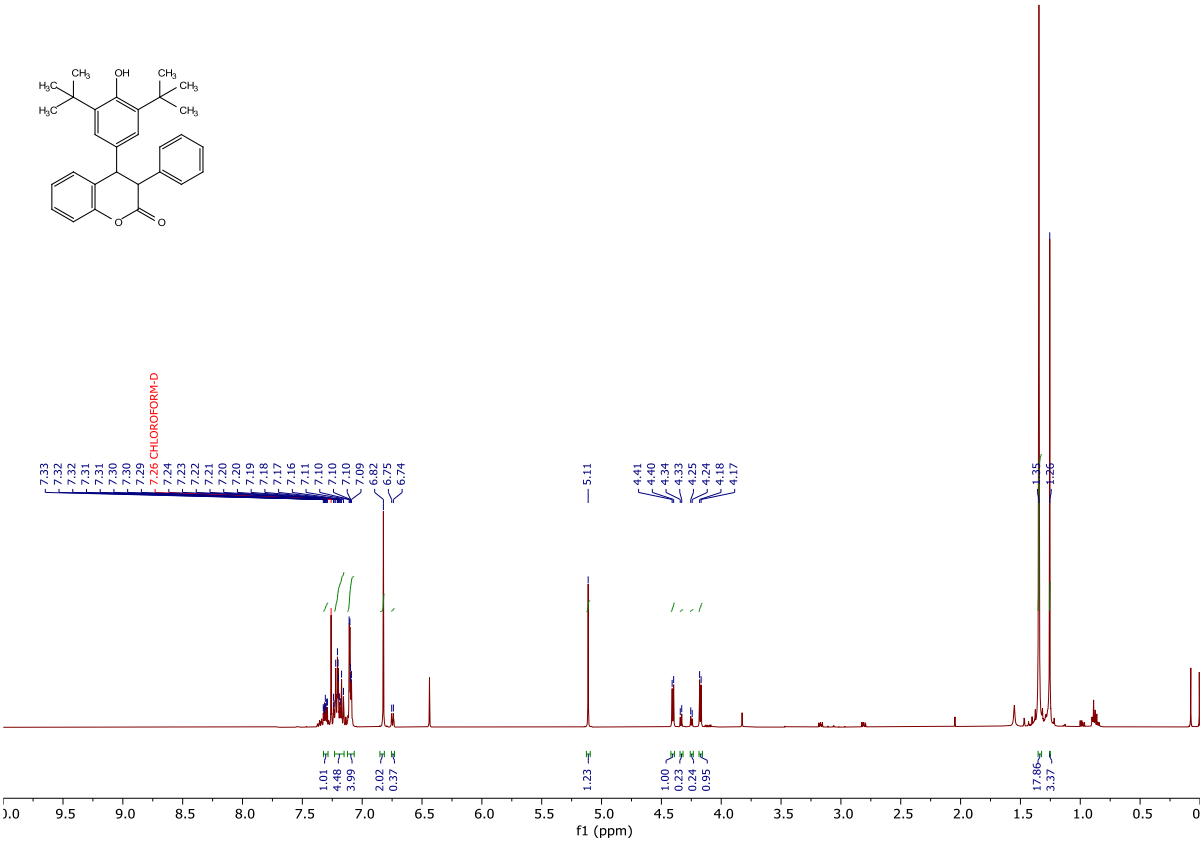
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **7** in $CDCl_3$



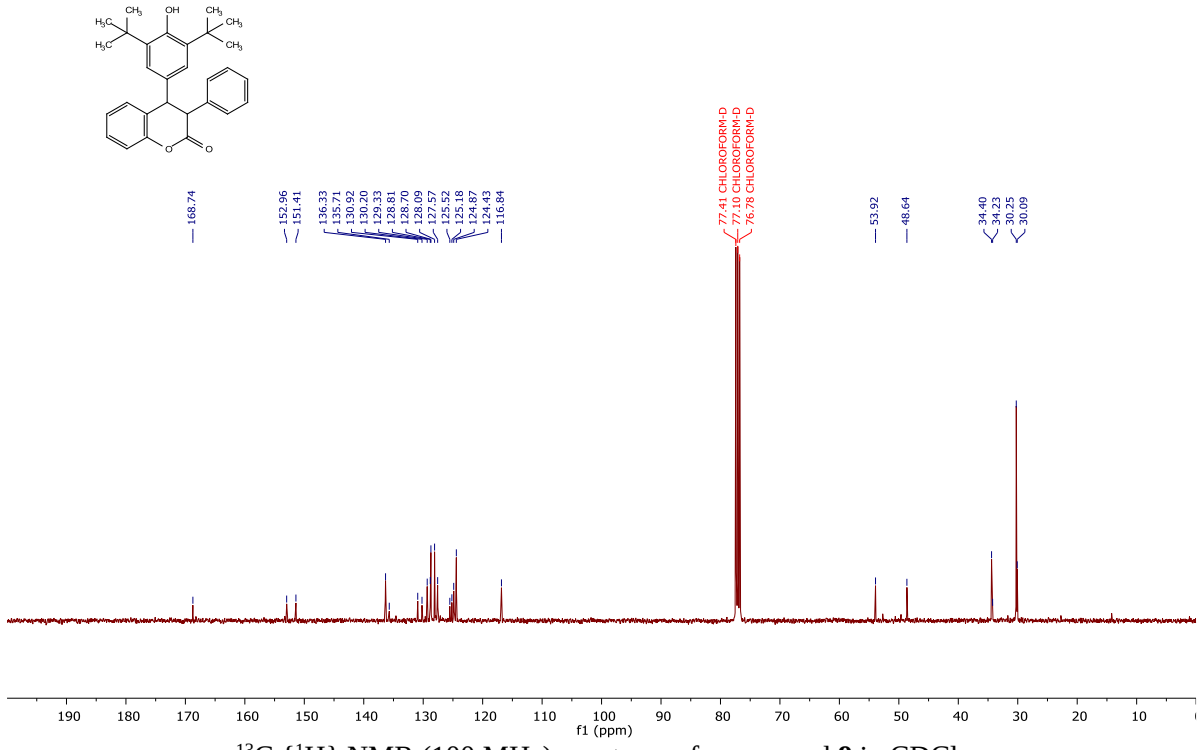
^{1}H NMR (400 MHz) spectrum of compound **8** in $CDCl_3$



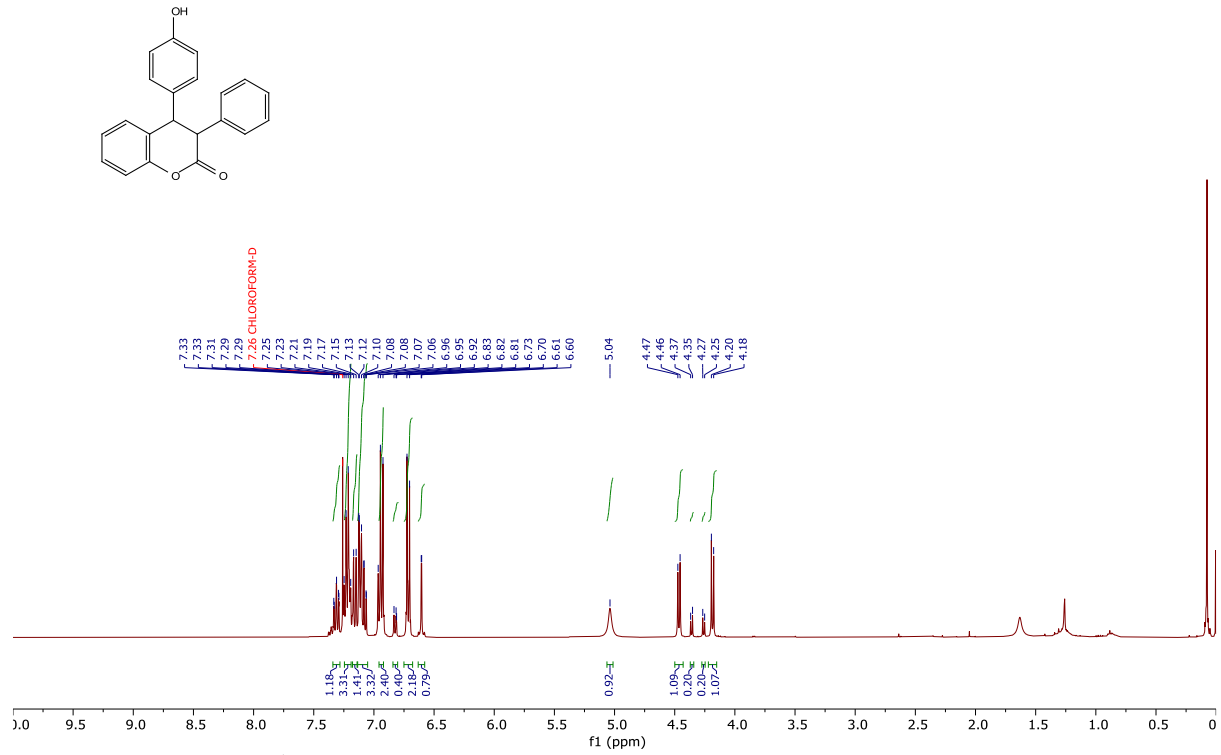
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **8** in $CDCl_3$



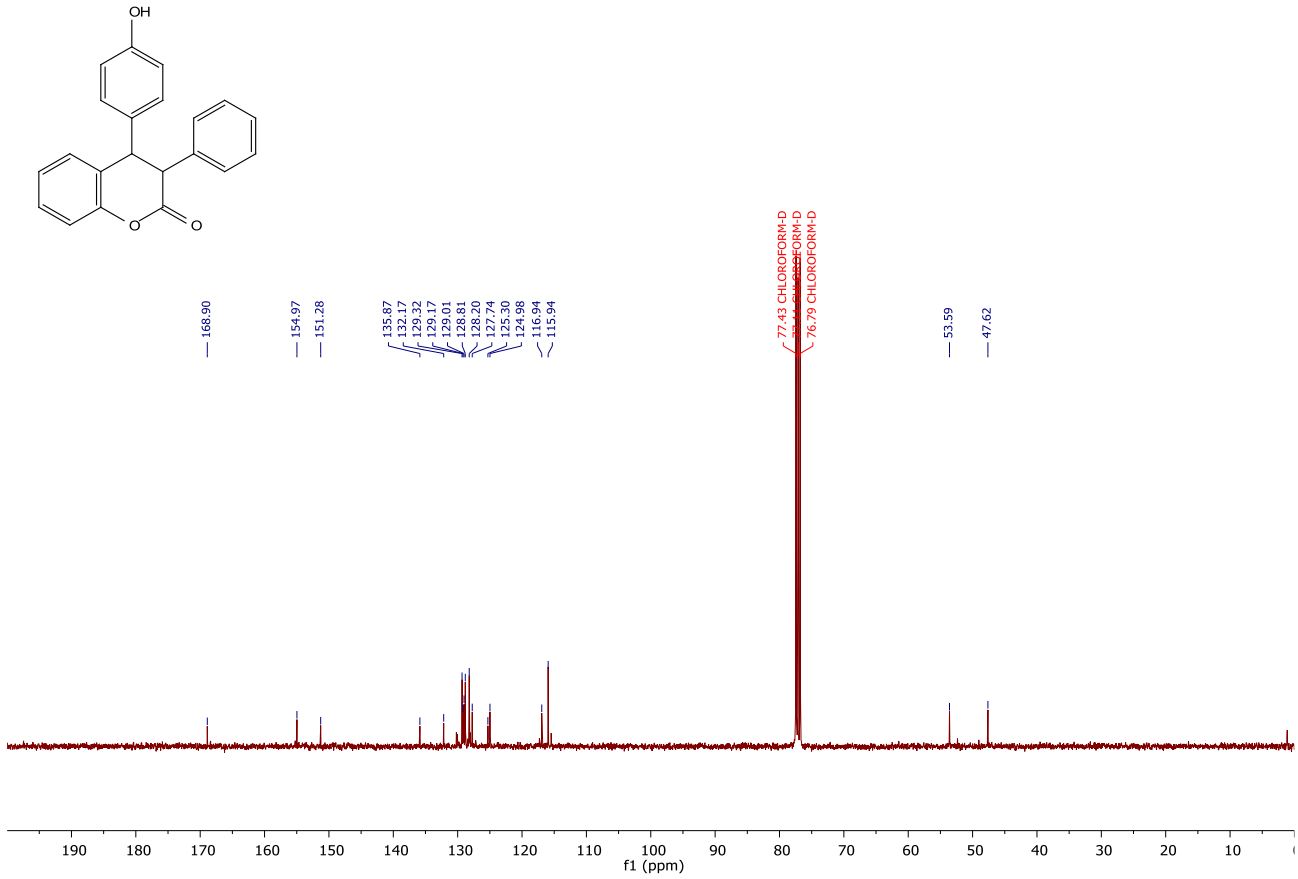
^{1}H NMR (500 MHz) spectrum of compound **9** in $CDCl_3$



^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **9** in $CDCl_3$

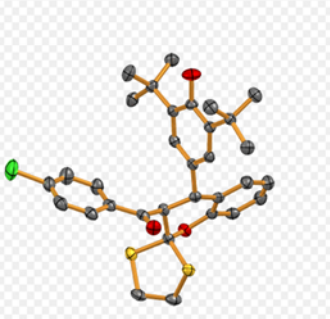


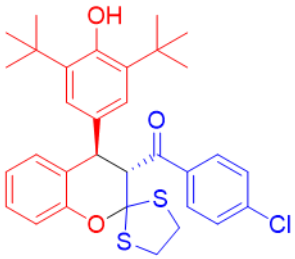
^{1}H NMR (396 MHz) spectrum of compound **10** in $CDCl_3$



^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **10** in $CDCl_3$

5. Crystal structure of 3k: (CCDC number 2126607)





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