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Supporting Information for

The Involvement of the Trisulfur Radical Anion in Electron-Catalyzed Sulfur Insertion Reactions: Facile Synthesis of Benzothiazine Derivatives under Transition Metal-free Conditions

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Experimental Section

General

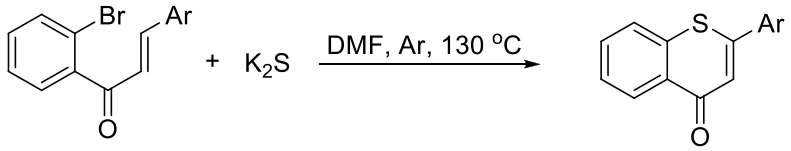
Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (^{1}H NMR) and 400 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. EPR spectra were recorded on a Bruker EXM-10/2 spectrophotometer. UV spectra were recorded on a UV1102 spectrophotometer. Raman spectra were recorded on a Horiba Jobin Yvon LabRam HR800 spectrophotometer. High resolution mass spectra were obtained using GCT-TOF instrument with ESI source or EI source.

Typical procedure for benzothiazine of K_2S with enaminones

1 **2** **3**

A mixture of enaminones **1** (0.5 mmol) and K_2S **2** (0.6 mmol) and DMF (3 mL) were added into a flask and stirred at 110 °C under Ar atmosphere. Then the mixture was vigorously stirred under reflux conditions monitored by TLC analysis (about 12 h). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product **3**.

Typical procedure for 2- aryl -4*H*-thiochromen-4-one Derivatives of K_2S with 2'-bromochalcones



4 **2a** **5**

A mixture of 2'-bromochalcones **4** (0.5 mmol) and K_2S **2** (0.6 mmol) and DMF (3 mL) were added into a flask and stirred at 110 °C under Ar atmosphere. Then the mixture was vigorously stirred under reflux conditions monitored by TLC analysis (about 12 h). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product **5**.

EPR Studies of Interaction between K_2S and DMF

A dried tube equipped with a stir bar was loaded with K_2S (0.50 mmol) in 3.0 mL DMF was stirred at 25 ℃. After 30 mins, the solution sample was taken out into a small tube

and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.852 GHz. Typical spectrometer parameters are shown as follows, scan range: 1000 G; center field set: 3400 G; scan time: 35 s.

EPR Studies of Interaction between K_2S and H_2O

A dried tube equipped with a stir bar was loaded with K_2S (0.50 mmol) in 3.0 mL H_2O was stirred at 25 ℃. After 30 mins, the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.852 GHz. Typical spectrometer parameters are shown as follows, scan range: 1000 G; center field set: 3400 G; scan time: 35 s.

UV spectra Studies of Interaction between K_2S and DMF

A dried tube equipped with a stir bar was loaded with K_2S (0.50 mmol) in 3.0 mL DMF was stirred at 25 ℃. Then, the solution sample was taken out into a small tube and analyzed by UV spectrometer operated. Typical spectrometer parameters are shown as follows, scan range: 400 nm; wavelength from 400 nm-800 nm; Scan speed: 800 nm/min

UV spectra Studies of Interaction between Na_2S, S and DMF

A dried tube equipped with a stir bar was loaded with Na_2S (0.50 mmol), S (0.50 mmol) in 3.0 mL DMF was stirred at 25 ℃. Then, the solution sample was taken out into a small tube and analyzed by UV spectrometer operated. Typical spectrometer parameters are shown as follows, scan range: 400 nm; wavelength from 400 nm-800 nm; Scan speed: 800 nm/min

Raman spectra Studies of Interaction between K_2S and DMF

A dried tube equipped with a stir bar was loaded with K_2S (0.50 mmol) in 3.0 mL DMF was stirred at 25 ℃. Then, the solution sample was taken out into a small tube and analyzed by Raman spectrometer operated. Typical spectrometer parameters are shown as follows, scan time: 50 s; wavelength 632.8 nm.

Raman spectra Studies of Interaction between Na_2S, S and DMF

A dried tube equipped with a stir bar was loaded with Na_2S (0.50 mmol), S (0.50 mmol) in 3.0 mL DMF was stirred at 25 ℃. Then, the solution sample was taken out into a small tube and analyzed by Raman spectrometer operated. Typical spectrometer parameters are shown as follows, scan time: 50 s; wavelength 632.8 nm.

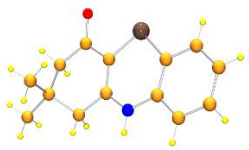


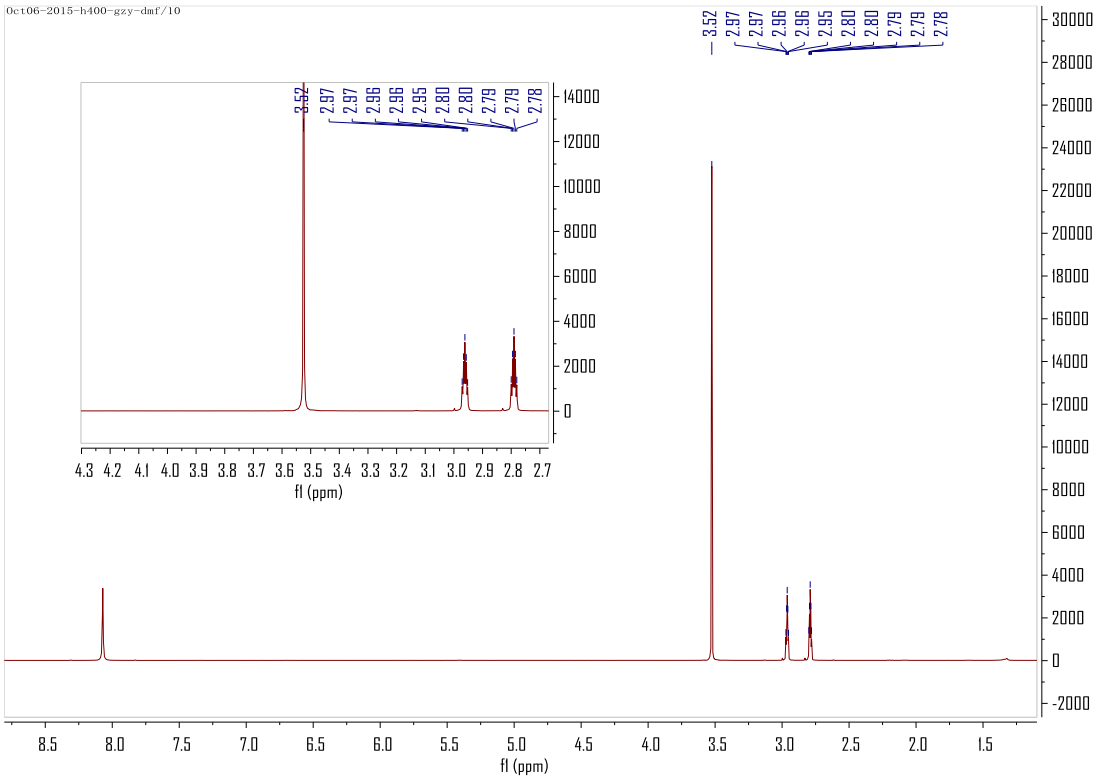
Figure 1 Crystal Structure of 3a

Screening of Reaction Conditions: Effects of Catalyst, Additive and Solvent[a]

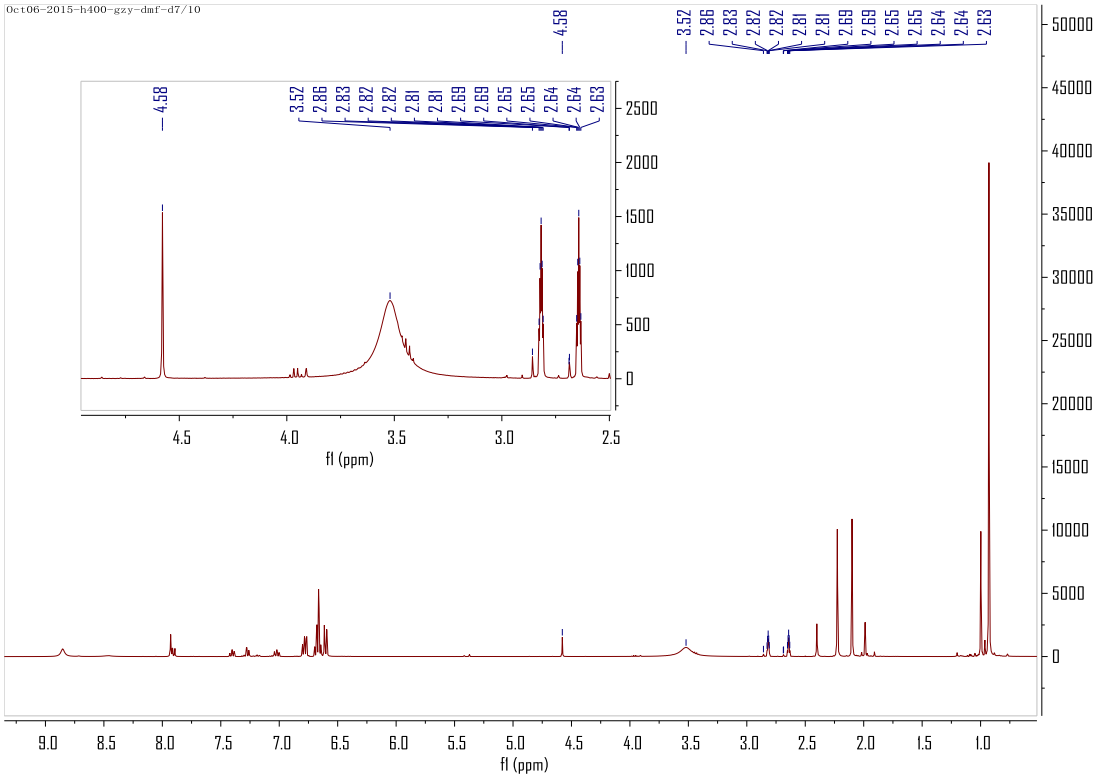
Entry	Cat. (10 mol%)	Solvent	Add. (x mol%)	T (℃)	Yield(%)[b]
1	CuI	DMF	I_2 (20)	110	65
2	$Cu(OAc)_2$	DMF	I_2 (20)	110	78
3	$CuCl_2$	DMF	I_2 (20)	110	58
4	Cu_2O	DMF	I_2 (20)	110	60
5	$CuBr_2$	DMF	I_2 (20)	110	38
6	CuBr	DMF	I_2 (20)	110	60
7	$CuSO_4$	DMF	I_2 (20)	110	50
8	$Cu(OAc)_2$	CH_3CN	I_2 (20)	110	39
9	$Cu(OAc)_2$	1,4-dioxene	I_2 (20)	110	39
10	$Cu(OAc)_2$	DCE	I_2 (20)	110	40
11	$Cu(OAc)_2$	THF	I_2 (20)	110	53
12	$Cu(OAc)_2$	Toluene	I_2 (20)	110	8
13	$Cu(OAc)_2$	DMSO	I_2 (20)	110	trace
14	$Cu(OAc)_2$	Xylene	I_2 (20)	110	trace
15	$Cu(OAc)_2$ (10)	DMF	-------	110	67
16	$Cu(OAc)_2$ (10)	DMF	I_2 (10)	110	56
17	$Cu(OAc)_2$ (10)	DMF	I_2 (30)	110	60
18	$Cu(OAc)_2$ (10)	DMF	-------	120	82
19	$Cu(OAc)_2$ (10)	DMF	-------	130	88
20	$Cu(OAc)_2$ (5)	DMF	-------	130	91
21	$Cu(OAc)_2$ (1)	DMF	-------	130	89
22	----------	DMF	-------	130	87(80)[c]

[a]Reaction Conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), solvent (3 mL) under air atmosphere. [b]The yields were determined by LC analysis using biphenyl as the internal standard. [c]Isolated yields.

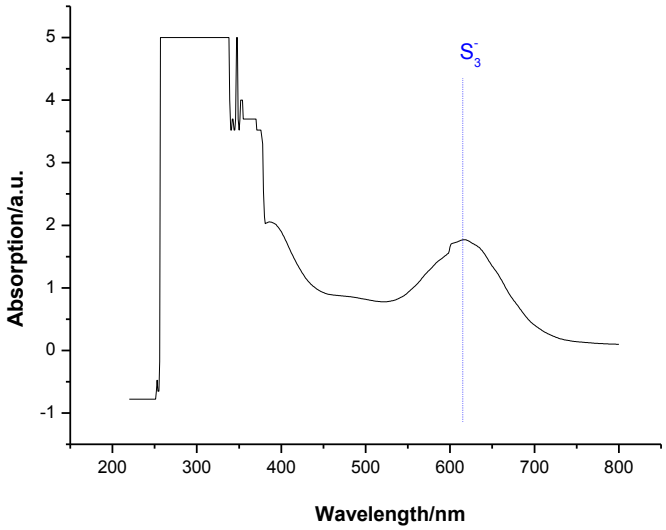
The ^{1}H NMR of d^7-DMF



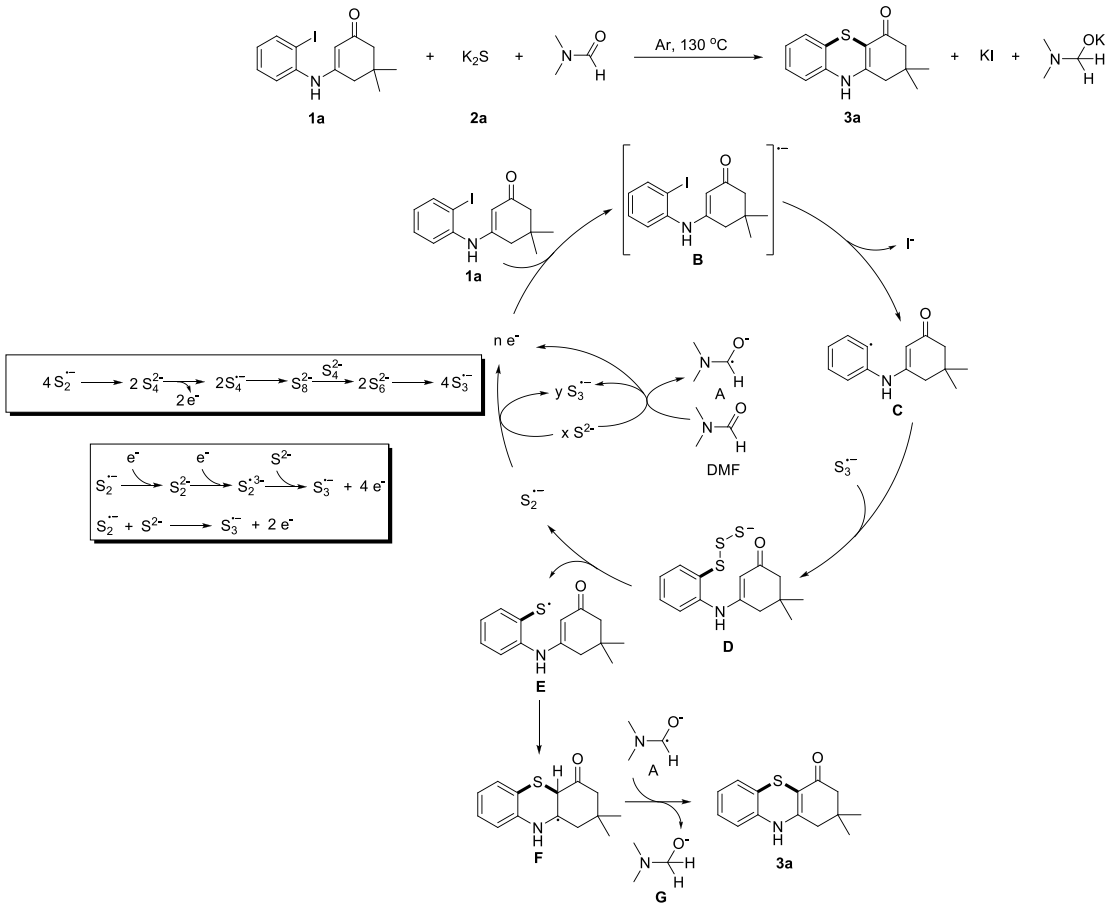
Crude ^{1}H NMR of the reaction of 1a with 2a in d^7-DMF

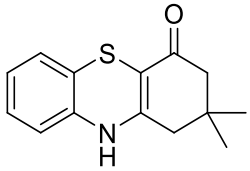


UV spectra studies of interaction between K_2S and DMF



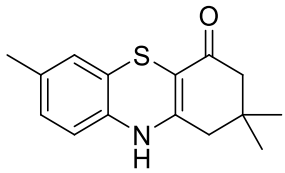
Plausible chemical balance and mechanism


Ar, 130 °C
1a
2a
3a
B
C
D
E
F
G
A
DMF
n e⁻
y S₃•⁻
x S²⁻
I⁻
S₂•⁻
S₃•⁻
4 S₂•⁻ → 2 S₄²⁻ → 2S₄•⁻ → S₈²⁻ → 2S₆²⁻ → 4S₃•⁻
2 e⁻
S₂•⁻ → S₂²⁻ → S₂•³⁻ → S₃•⁻ + 4 e⁻
S₂•⁻ + S²⁻ → S₃•⁻ + 2 e⁻



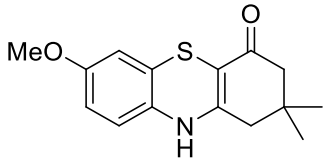
2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3a)

Yield=80%. Yellow solid. M.p. 254.4-255.7℃. IR 3247, 2955, 2927, 1611, 1522, 1468, 1306, 746 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.85 (s, 1H, N-H), 6.86 (t, *J* = 5.8 Hz, 1H, Ar-H), 6.78 – 6.67 (m, 2H, Ar-H), 6.54 (d, *J* = 7.6 Hz, 1H, Ar-H), 2.20 (s, 2H, -CH_2), 2.15 (s, 2H, -CH_2), 1.00 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, DMSO) δ 189.00, 154.43, 137.16, 127.36, 126.93, 125.02, 120.34, 116.19, 97.03, 50.20, 41.73, 31.97, 28.08 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{15}NOS$, 245.0874; found 245.0871.



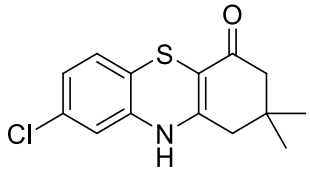
2,2,7-trimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3b)

Yield=95%. Yellow solid. M.p. 283.3-285.6℃. IR 3245, 2956, 2921, 1592, 1560, 1478, 1310, 814, 746 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.80 (s, 1H, N-H), 6.66 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.56 (s, 1H, Ar-H), 6.44 (d, *J* = 7.9 Hz, 1H, Ar-H), 2.19 (s, 2H, -CH_2), 2.13 (s, 2H, -CH_2), 2.07 (s, 3H, -CH_3), 0.99 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, DMSO) δ 188.26, 153.74, 133.93, 133.74, 127.08, 126.80, 119.73, 115.61, 96.06, 49.69, 41.25, 31.46, 27.60, 19.98 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{17}NOS$, 259.1031; found 259.1027.



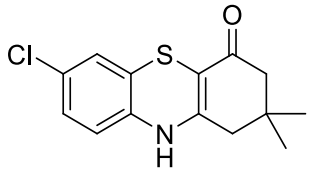
7-methoxy-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3c)

Yield=88%. Yellow solid. M.p. 270.1-273.3℃. IR 3242, 3031, 2965, 1604, 1561, 1478, 1355, 1070, 793 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 1H, N-H), 6.50 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.44 (dd, *J* = 8.7, 2.7 Hz, 1H, Ar-H), 6.37 (d, *J* = 2.7 Hz, 1H, Ar-H), 3.63 (s, 3H, -OMe), 2.19 (s, 2H, -CH_2), 2.13 (s, 2H, -CH_2), 0.99 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, DMSO) δ 187.97, 156.16, 153.60, 129.46, 121.48, 116.64, 112.09, 111.42, 94.88, 55.24, 49.69, 41.25, 31.45, 27.61 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{17}NO_2S$, $[M+H]^+$ 276.1058; found 276.1052.



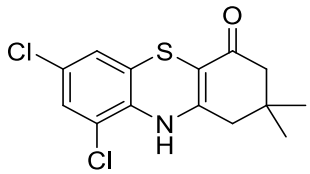
8-chloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3d)

Yield=65%. Yellow solid. M.p. 268.6-271.3℃. IR 3273, 2964, 2934, 1579, 1560, 1466, 1277, 860, 805 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.92 (s, 1H, N-H), 6.78 (dt, *J* = 14.4, 5.1 Hz, 2H, Ar-H), 6.56 (d, *J* = 1.9 Hz, 1H, Ar-H), 2.20 (s, 2H, -CH_2), 2.16 (s, 2H, -CH_2), 1.00 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 189.40, 154.00, 138.85, 131.22, 128.19, 124.36, 119.53, 115.54, 97.67, 50.13, 41.65, 32.03, 28.03 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}ClNOS$, 279.0485; found 279.0482.



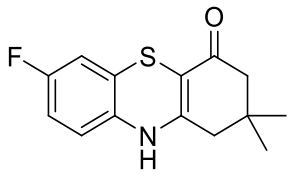
7-chloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3e)

Yield=81%. Brown solid. M.p. 268.6-271.3℃. IR 3272, 2958, 2908, 1579, 1467, 1380, 811, 664 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.96 (s, 1H, N-H), 6.97 – 6.77 (m, 2H, Ar-H), 6.52 (d, *J* = 8.4 Hz, 1H, Ar-H), 2.19 (s, 2H, -CH_2), 2.15 (s, 2H, -CH_2), 0.99 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 189.07, 154.23, 136.25, 128.25, 126.99, 126.10, 123.12, 117.28, 96.74, 50.11, 41.63, 31.98, 28.05 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}ClNOS$, 279.0485; found 279.0497.



7,9-dichloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3f)

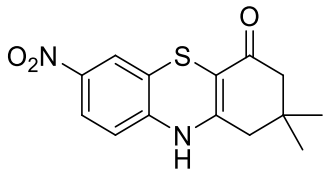
Yield=55%. Yellow solid. M.p. 193.2-195.1℃. IR 3270, 2954, 1588, 1486, 1266, 807, 638 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 7.98 (s, 1H, N-H), 7.18 (d, *J* = 2.3 Hz, 1H, Ar-H), 6.92 (d, *J* = 2.2 Hz, 1H, Ar-H), 2.42 (s, 2H, -CH_2), 2.19 (s, 2H, -CH_2), 0.99 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 190.14, 154.62, 133.38, 128.32, 127.27, 125.28, 125.23, 120.60, 99.15, 50.09, 41.46, 31.99, 28.00 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{13}Cl_2NOS$, $[M+H]^+$ 314.0173; found 314.0179.



7-fluoro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3g)

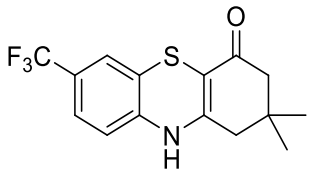
Yield=85%. Yellow solid. M.p. 268.6-271.3℃. IR 3274, 2956, 1593, 1476, 1344, 850, 807, 689 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.92 (s, 1H, N-H), 6.74 – 6.65 (m, 2H, Ar-H), 6.54 (dd, *J* = 9.4, 5.2 Hz, 1H, Ar-H), 2.19 (s, 2H, -CH_2), 2.15 (s, 2H, -CH_2), 1.00 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 188.91, 160.41, 158.01, 154.42, 133.55,

133.52, 123.08, 123.00, 117.22, 117.13, 113.99, 113.74, 113.46, 113.24, 95.73, 50.13, 41.66, 31.96, 28.06 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}FNOS$, $[M+H]^+$ 264.0858; found 264.0864.



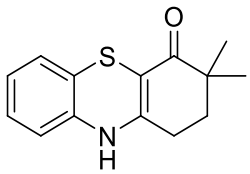
2,2-dimethyl-7-nitro-2,3-dihydro-1H-phenothiazin-4(10H)-one (3h)

Yield=92%. Purple solid. M.p. >300℃. IR 3270, 2966, 1590, 1473, 1332, 878, 714, 654 cm^{-1}. ^1H NMR (400 MHz, DMSO) δ 9.34 (s, 1H, N-H), 7.72 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 7.52 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.59 (d, *J* = 8.8 Hz, 1H, Ar-H), 2.19 (d, *J* = 3.9 Hz, 4H, -CH_2), 1.00 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 189.98, 152.99, 144.05, 143.67, 124.41, 122.38, 121.68, 115.55, 98.95, 50.04, 41.40, 32.06, 28.00 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}N_2O_3S$, $[M+H]^+$ 291.0803; found 291.0799.



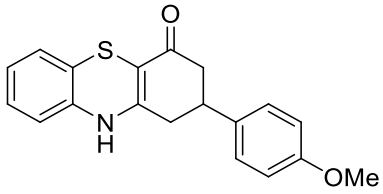
2,2-dimethyl-7-(trifluoromethyl)-2,3-dihydro-1H-phenothiazin-4(10H)-one (3i)

Yield=94%. Yellow solid. M.p. >300℃. IR 3260, 2958, 1596, 1569, 1479, 1305, 830, 704 cm^{-1}. ^1H NMR (400 MHz, DMSO) δ 9.11 (s, 1H, N-H), 7.20 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 6.64 (d, *J* = 8.2 Hz, 1H, Ar-H), 2.21 (s, 2H, -CH_2), 2.18 (s, 2H, -CH_2), 1.01 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 189.55, 154.03, 141.17, 125.55, 125.28, 124.96, 124.91, 124.87, 123.53, 123.50, 122.85, 122.14, 115.93, 97.93, 50.10, 41.55, 32.02, 28.01 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{14}F_3NOS$, $[M+H]^+$ 314.0826; found 314.0833.



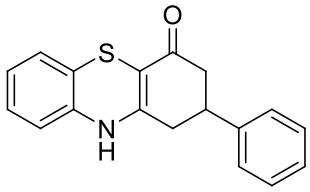
3,3-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3j)

Yield=96%. Yellow solid. M.p. 278.4-280.3℃. IR 3253, 2972, 1610, 1581, 1471, 1238, 747 cm^{-1}. ^1H NMR (400 MHz, DMSO) δ 8.87 (s, 1H, N-H), 6.86 (ddd, *J* = 8.0, 6.2, 3.6 Hz, 1H, Ar-H), 6.74 (dd, *J* = 7.4, 5.5 Hz, 2H, Ar-H), 6.55 (d, *J* = 7.8 Hz, 1H, Ar-H), 2.36 (t, *J* = 6.2 Hz, 2H, -CH_2), 1.69 (t, *J* = 6.2 Hz, 2H, -CH_2), 1.02 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 194.31, 154.87, 137.04, 127.28, 126.87, 124.85, 120.36, 115.99, 97.12, 34.06, 25.49, 25.29 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{15}NOS$, $[M+H]^+$ 246.0953; found 246.0957.



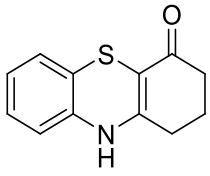
2-(4-methoxyphenyl)-2,3-dihydro-1H-phenothiazin-4(10H)-one (3k)

Yield=72%. Yellow solid. M.p. 285.8-287.3℃. IR 3245, 2941, 1580, 1565, 1468, 1248, 823, 752 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.97 (s, 1H, N-H), 7.24 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.89 (d, *J* = 7.9 Hz, 3H, Ar-H), 6.75 (d, *J* = 2.8 Hz, 2H, Ar-H), 6.55 (d, *J* = 7.5 Hz, 1H, Ar-H), 3.73 (s, 3H, -CH3), 2.76 – 2.28 (m, 5H, $-CH_2$, -CH). ^{13}C NMR (101 MHz, DMSO) δ 188.86, 158.46, 155.51, 137.09, 135.58, 128.34, 127.41, 126.96, 125.10, 120.32, 116.21, 114.34, 98.19, 55.49, 43.88, 37.35, 35.85 ppm. HRMS (ESI) m/z calculated for $C_{19}H_{17}NO_2S$, $[M+H]^+$ 324.1058; found 324.1042.



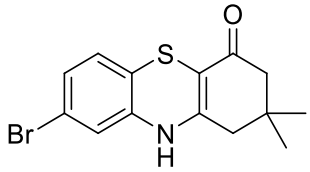
2-phenyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3l)

Yield=60%. Red solid. M.p. 241.2-243.1℃. IR 3253, 2954, 1582, 1565, 1470, 1246, 750, 699 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.99 (s, 1H, N-H), 7.34 (d, *J* = 4.1 Hz, 4H, Ar-H), 7.25 (dd, *J* = 8.3, 4.1 Hz, 1H, Ar-H), 6.94 – 6.83 (m, 1H, Ar-H), 6.76 (d, *J* = 4.0 Hz, 2H, Ar-H), 6.57 (s, 1H, Ar-H), 3.31 (dd, *J* = 20.3, 8.7 Hz, 1H, -CH), 2.74 – 2.57 (m, 2H, $-CH_2$), 2.53 – 2.43 (m, 2H, $-CH_2$). ^{13}C NMR (101 MHz, DMSO) δ 188.71, 155.46, 143.62, 137.07, 128.99, 127.42, 127.36, 127.18, 126.96, 125.12, 120.32, 116.24, 98.21, 43.59, 38.10, 35.55 ppm. HRMS (ESI) m/z calculated for $C_{18}H_{15}NOS$, $[M+H]^+$ 294.0953; found 294.0961.



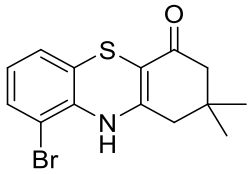
2,3-dihydro-1H-phenothiazin-4(10H)-one (3m)

Yield=47%. Yellow solid. M.p. 199.5-201.7℃. IR 3263, 2933, 1585, 1508, 1466, 1296, 737, 686 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.92 (s, 1H, N-H), 6.91 – 6.81 (m, 1H, Ar-H), 6.81 – 6.66 (m, 2H, Ar-H), 6.55 (d, *J* = 7.8 Hz, 1H, Ar-H), 2.33 (t, *J* = 6.1 Hz, 2H, $-CH_2$), 2.25 (t, *J* = 6.4 Hz, 2H, $-CH_2$), 1.89 – 1.75 (m, 2H, $-CH_2$). ^{13}C NMR (101 MHz, DMSO) δ 189.48, 156.47, 137.10, 127.32, 126.88, 124.95, 120.40, 116.11, 98.33, 36.61, 28.45, 20.60 ppm. HRMS (ESI) m/z calculated for $C_{12}H_{11}NOS$, $[M+H]^+$ 218.0640; found 218.0641.



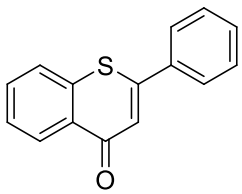
8-bromo-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3o)

Yield=80%. Yellow solid. M.p. 231.7-232-4℃. IR 3263, 2954, 1647, 1558, 1464, 1268, 877, 805 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 8.90 (s, 1H, N-H), 6.90 (dd, *J* = 8.2, 1.6 Hz, 1H, Ar-H), 6.72 – 6.63 (m, 2H, Ar-H), 2.18 (s, 2H, -CH_2), 2.15 (s, 2H, -CH_2), 0.99 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 188.88, 153.57, 138.54, 127.99, 126.78, 119.61, 118.70, 117.79, 97.14, 49.64, 41.16, 31.54, 27.54 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}BrNOS$, $[M+H]^+$ 324.0058; found 324.0059.



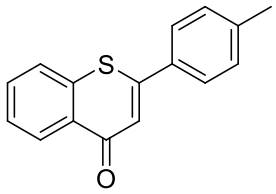
9-bromo-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3p)

Yield=68%. Yellow solid. M.p. >300℃. IR 3277, 2957, 1574, 1503, 1441, 1294, 763, 716 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 7.57 (s, 1H, N-H), 7.18 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar-H), 6.83 – 6.77 (m, 1H, Ar-H), 6.70 (t, *J* = 7.8 Hz, 1H, Ar-H), 2.44 (s, 2H, -CH_2), 2.19 (s, 2H, -CH_2), 0.99 (s, 6H, -CH3). ^{13}C NMR (101 MHz, DMSO) δ 190.16, 155.01, 135.19, 131.41, 126.61, 126.12, 123.01, 110.32, 99.77, 50.24, 41.64, 32.01, 28.00 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{14}BrNOS$, $[M+H]^+$ 324.0058; found 324.0059.



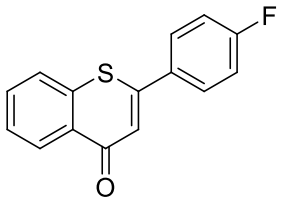
2-phenyl-4H-thiochromen-4-one (5a)

Yield=51%. Red solid. M.p. 105.5-106.9℃. IR 2923, 1618, 1587, 1435, 1332, 1099, 863, 758, 730, 695 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.70 – 7.44 (m, 8H, Ar-H), 7.24 (s, 1H, -CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.33, 152.84, 137.27, 136.05, 131.17, 130.38, 130.34, 128.82, 128.13, 127.34, 126.51, 126.02, 122.88, 122.85 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{10}OS$, $[M+H]^+$ 239.0531; found 239.0529.



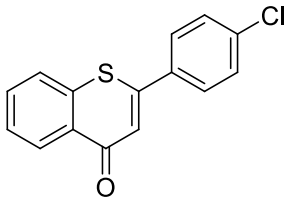
2-p-tolyl-4H-thiochromen-4-one (5b)

Yield=53%. Red solid. M.p. 106.7-108.3℃. IR 3028, 1604, 1587, 1507, 1431, 1336, 1131, 1103, 878, 775, 687 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 8.0, 1.4 Hz, 1H, Ar-H), 7.69 – 7.52 (m, 5H, Ar-H), 7.30 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.27 (s, 1H, -CH), 2.43 (s, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.38, 152.95, 152.92, 140.93, 137.31, 133.18, 131.10, 130.35, 129.52, 128.10, 127.26, 126.34, 125.99, 122.25, 20.91 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{12}OS$, $[M+H]^+$ 253.0687; found 253.0685.



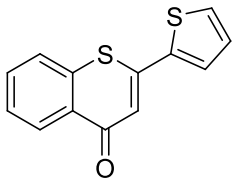
2-(4-fluorophenyl)-4H-thiochromen-4-one (5c)

Yield=50%. Red solid. M.p. 152.8-153.9℃. IR 1617, 1586, 1502, 1441, 1335, 1228, 1106, 1100, 847, 779, 743, 686 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 7.8, 1.3 Hz, 1H, Ar-H), 7.74 – 7.54 (m, 5H, Ar-H), 7.26 – 7.16 (m, 3H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.23, 165.13, 162.62, 151.70, 137.04, 132.20, 132.17, 131.30, 130.19, 128.57, 128.49, 128.17, 127.48, 125.98, 122.81, 116.12, 115.90 ppm. HRMS (ESI) m/z calculated for $C_{15}H_9FOS$, $[M+H]^+$ 257.0436; found 257.0442.



2-(4-chlorophenyl)-4H-thiochromen-4-one (5d)

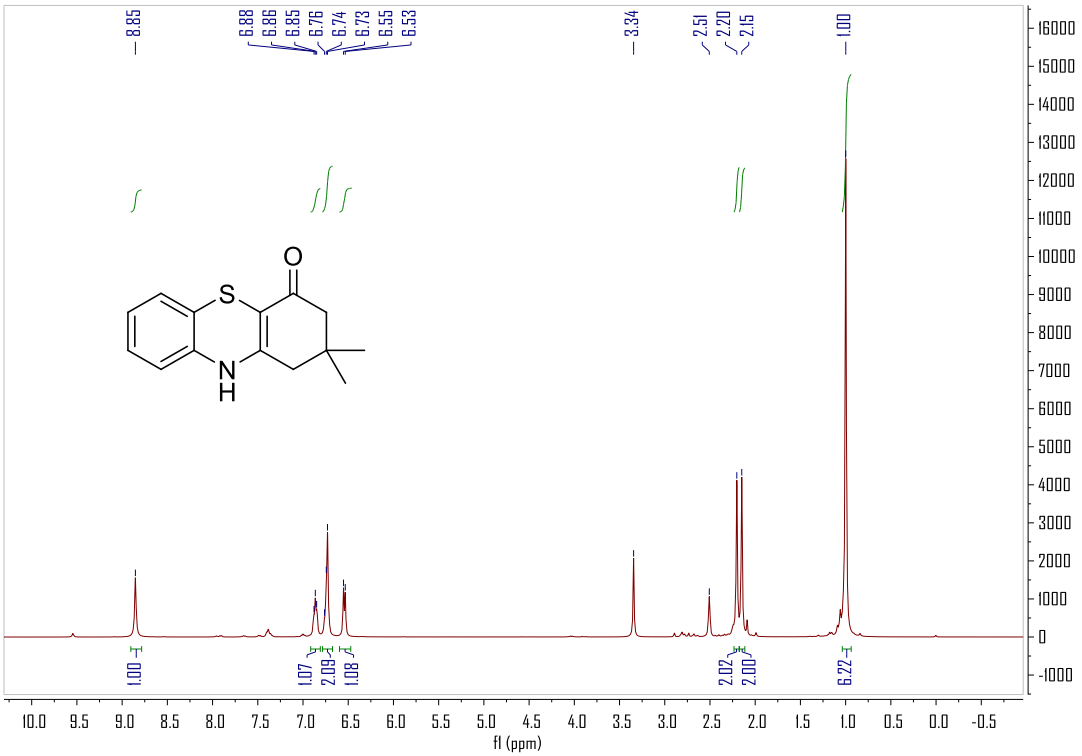
Yield=51%. Red solid. M.p. 160.8-162.6℃. IR 2161, 2028, 1629, 1589, 1485, 1327, 1088, 1010, 900, 828, 776, 707, 684 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.71 – 7.52 (m, 5H, Ar-H), 7.48 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.24 (s, 1H, -CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.21, 151.38, 136.94, 136.71, 134.46, 131.33, 130.26, 129.11, 128.19, 127.77, 127.52, 126.03, 123.00 ppm. HRMS (ESI) m/z calculated for $C_{15}H_9ClOS$, $[M+H]^+$ 273.0141; found 273.0147.

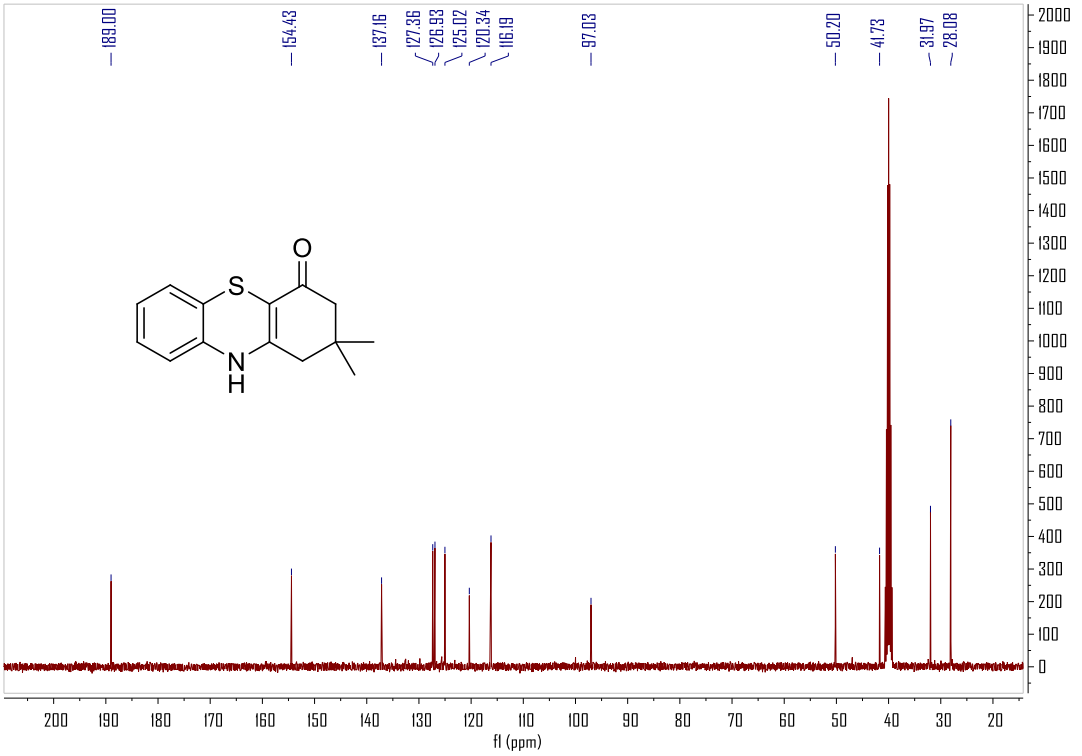


2-(thiophen-2-yl)-4H-thiochromen-4-one (5e)

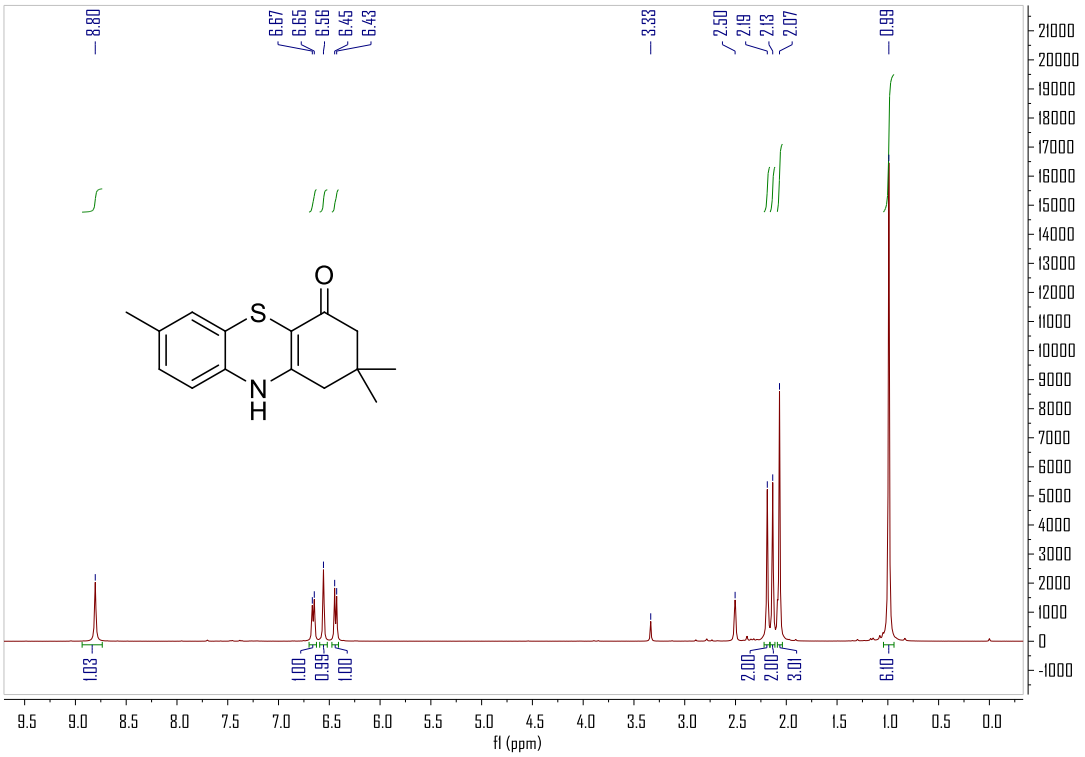
Yield=60%. Red solid. M.p. 97.8-99.1℃. IR 2161, 1610, 1585, 1544, 1417, 1321, 1228, 1098, 848, 825, 771, 718 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (dt, *J* = 8.0, 1.1 Hz, 1H, Ar-H), 7.63 – 7.59 (m, 2H, Ar-H), 7.56 – 7.50 (m, 3H, Ar-H), 7.27 (s, 1H, -CH), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.10, 145.26, 138.61, 136.36, 136.29, 131.29, 130.41, 128.81, 128.08, 128.06, 127.34, 126.88, 125.75, 120.82 ppm. HRMS (ESI) m/z calculated for $C_{13}H_8OS_2$, $[M+H]^+$ 245.0095; found 245.0105.

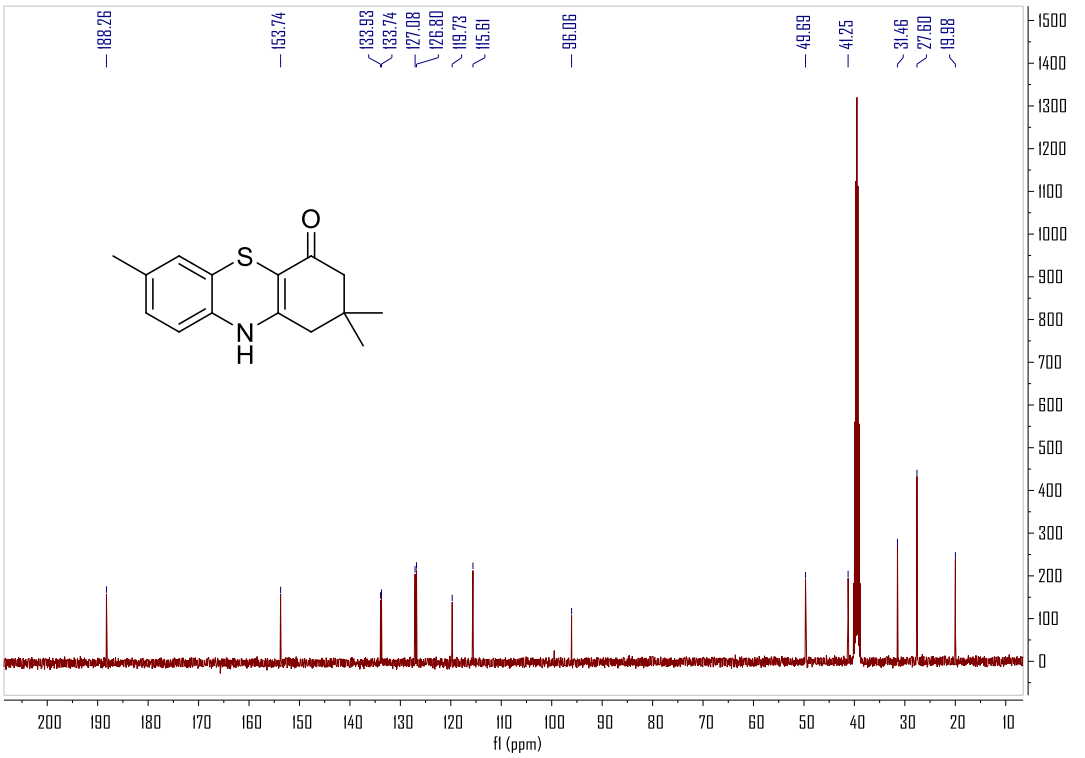
2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3a)



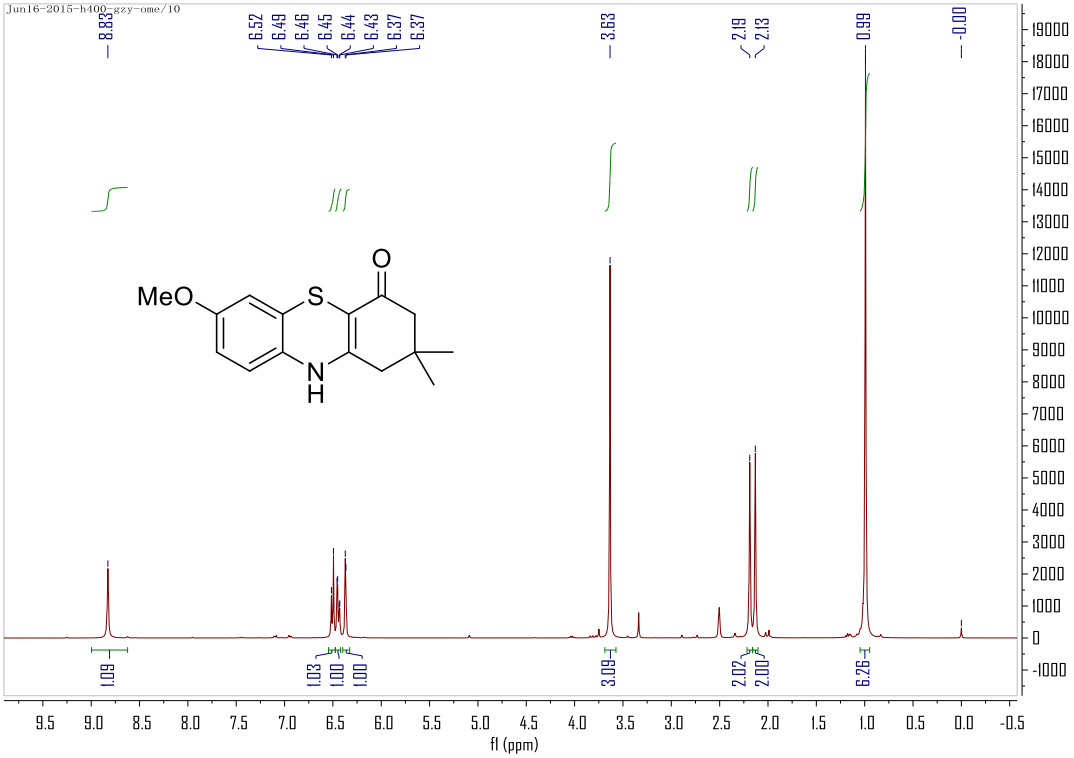


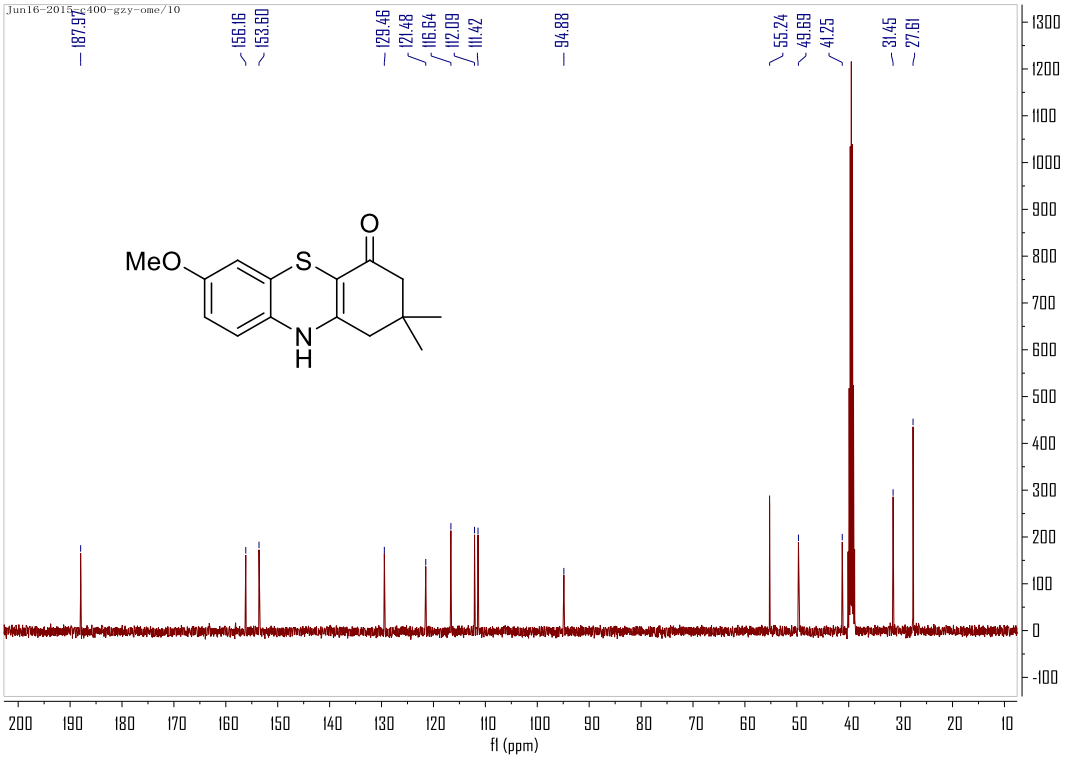
2,2,7-trimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3b)



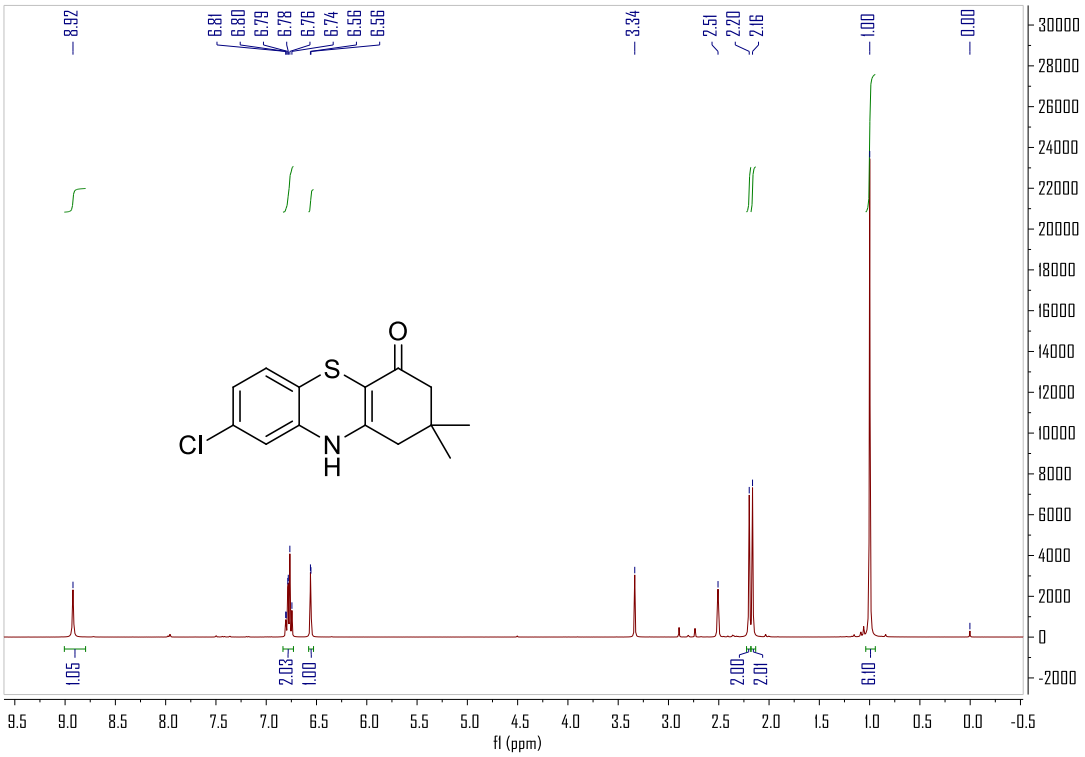


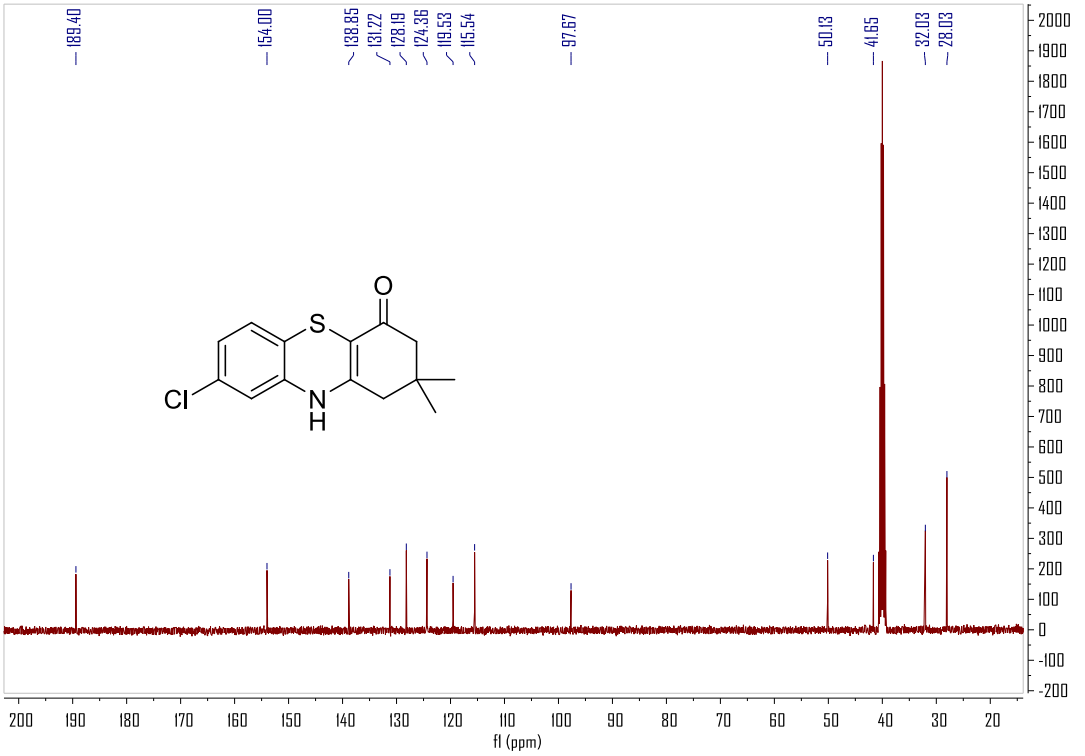
7-methoxy-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3c)



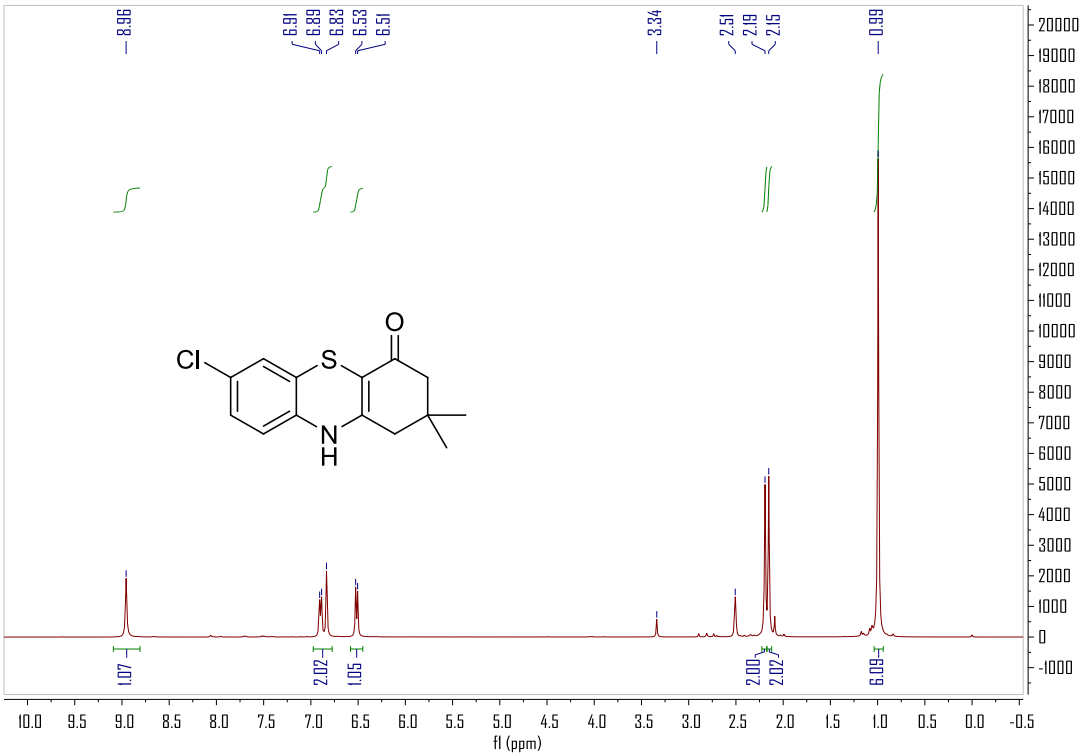


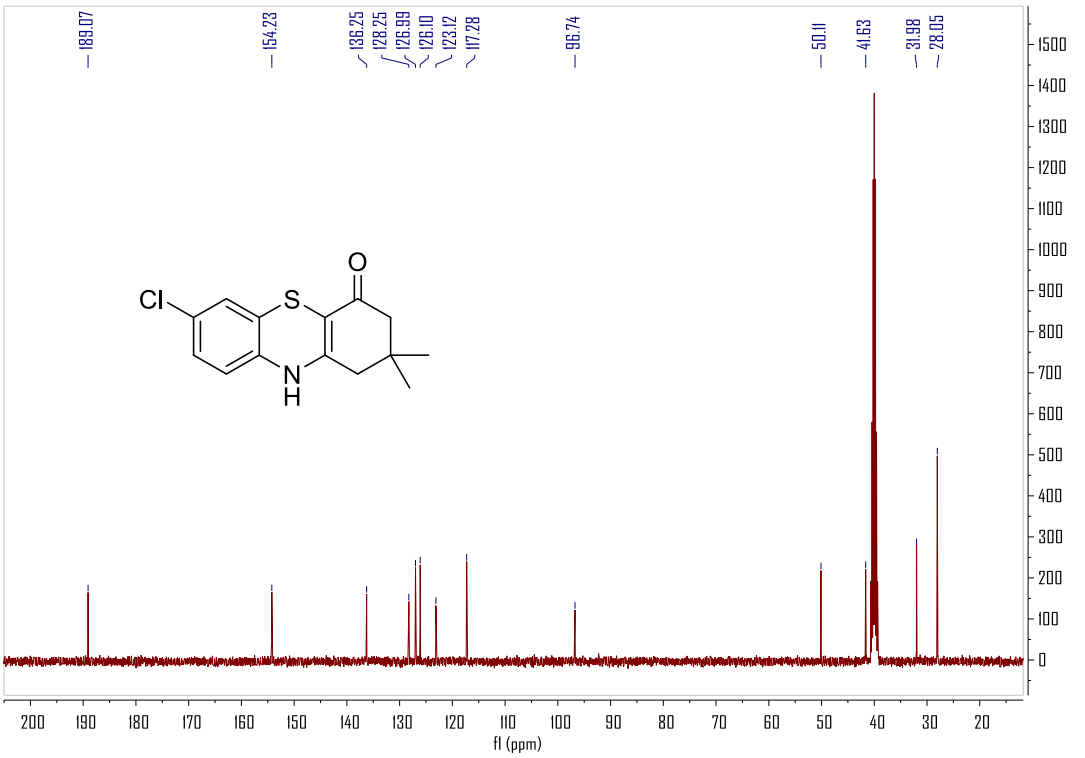
8-chloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3d)



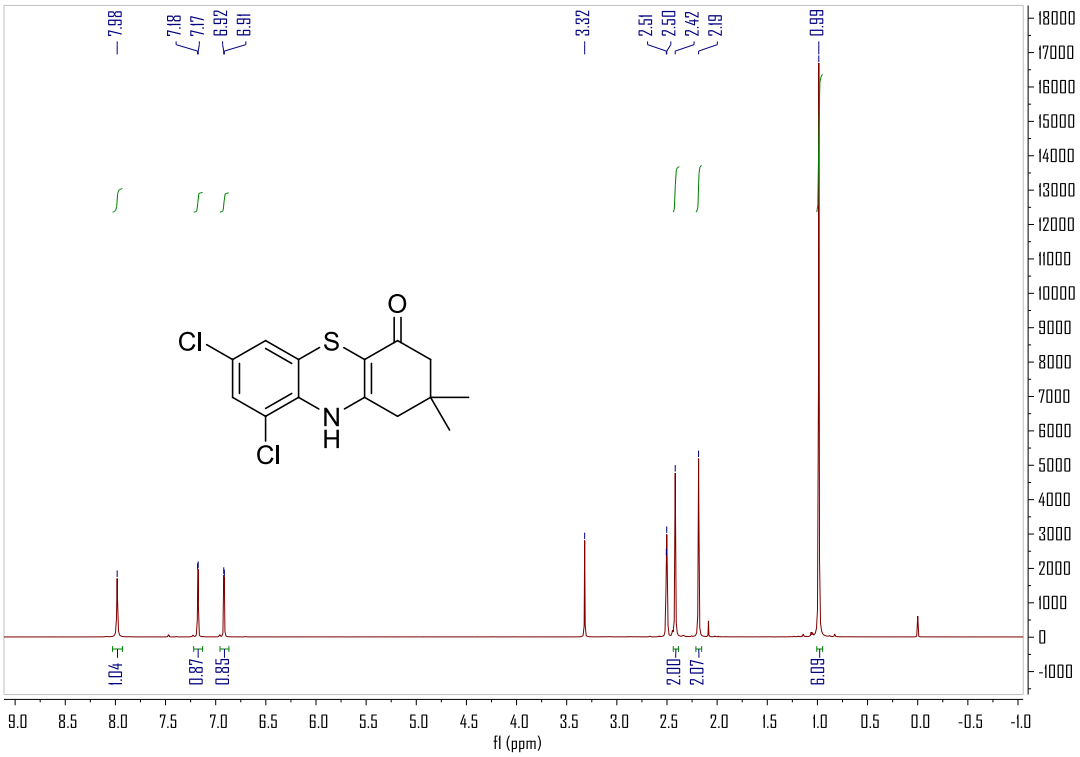


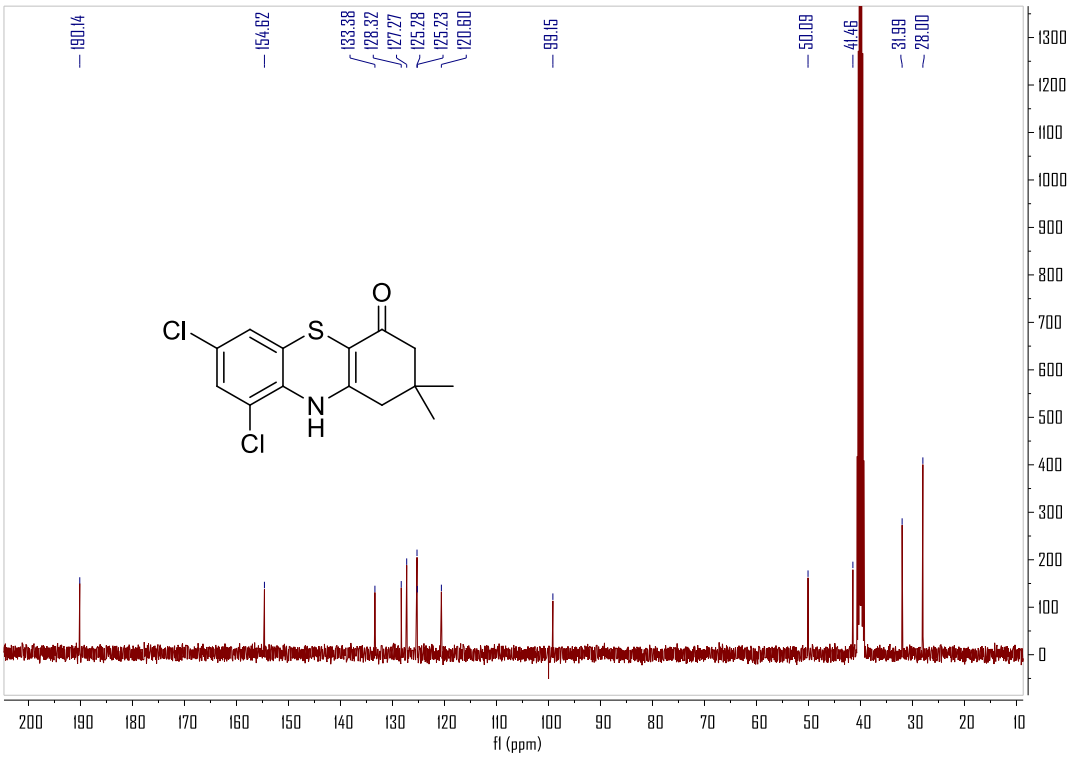
7-chloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3e)



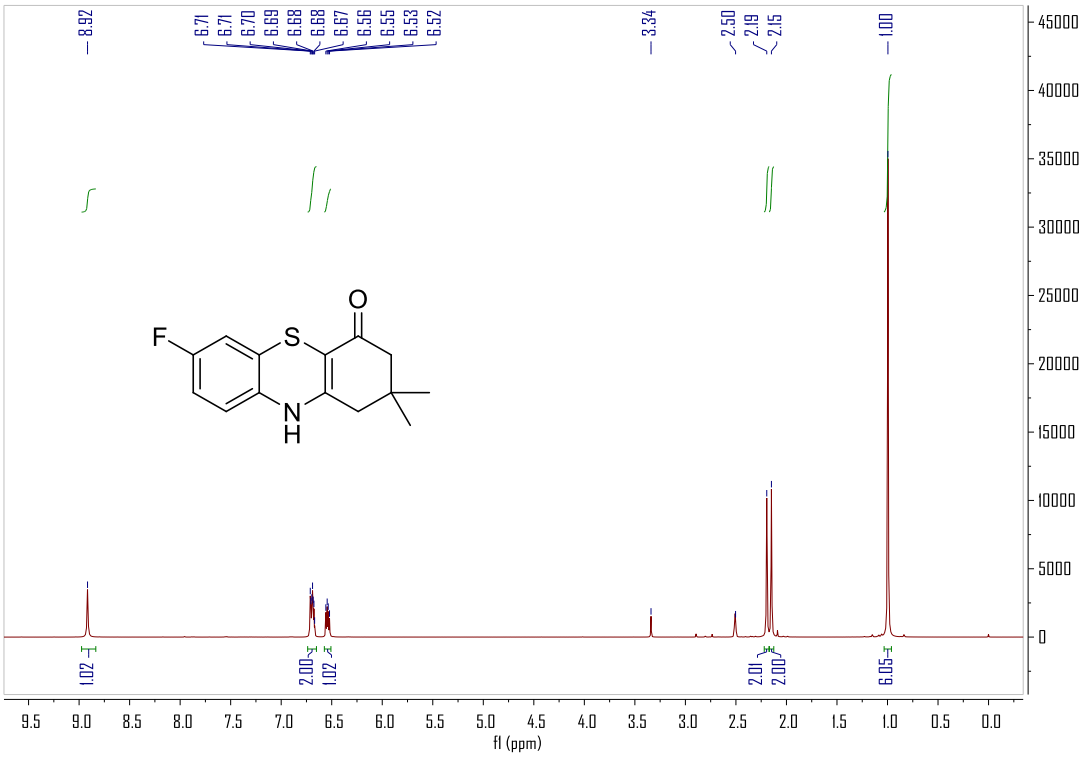


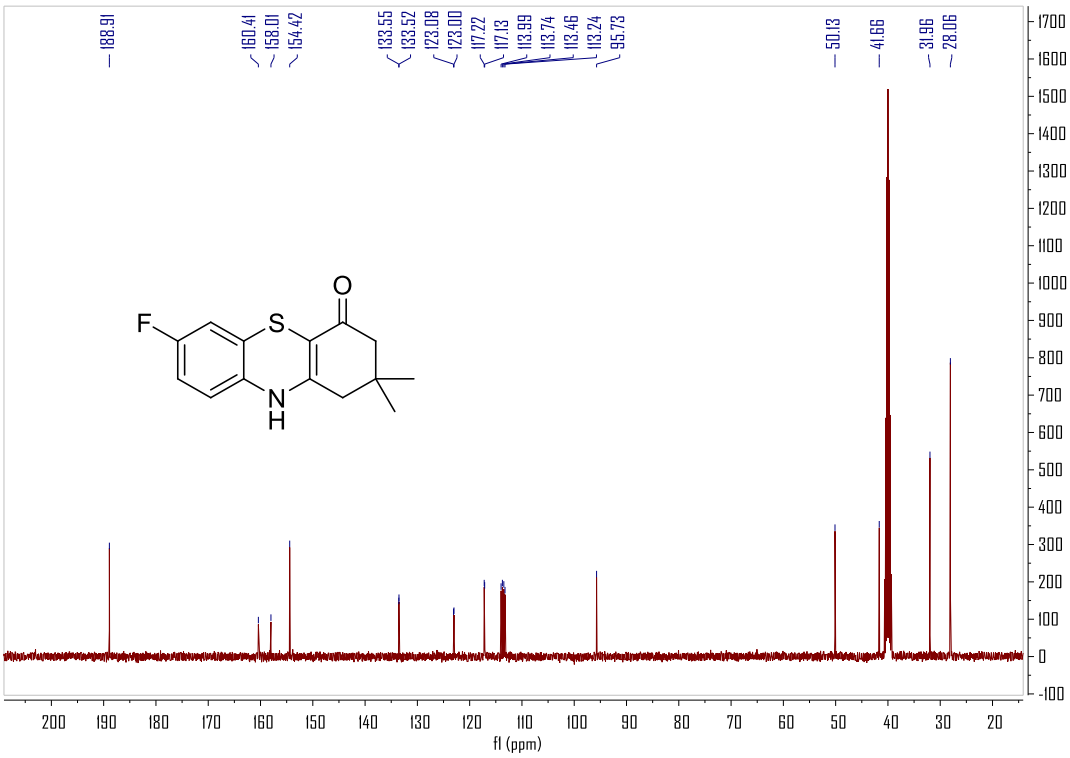
7,9-dichloro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3f)



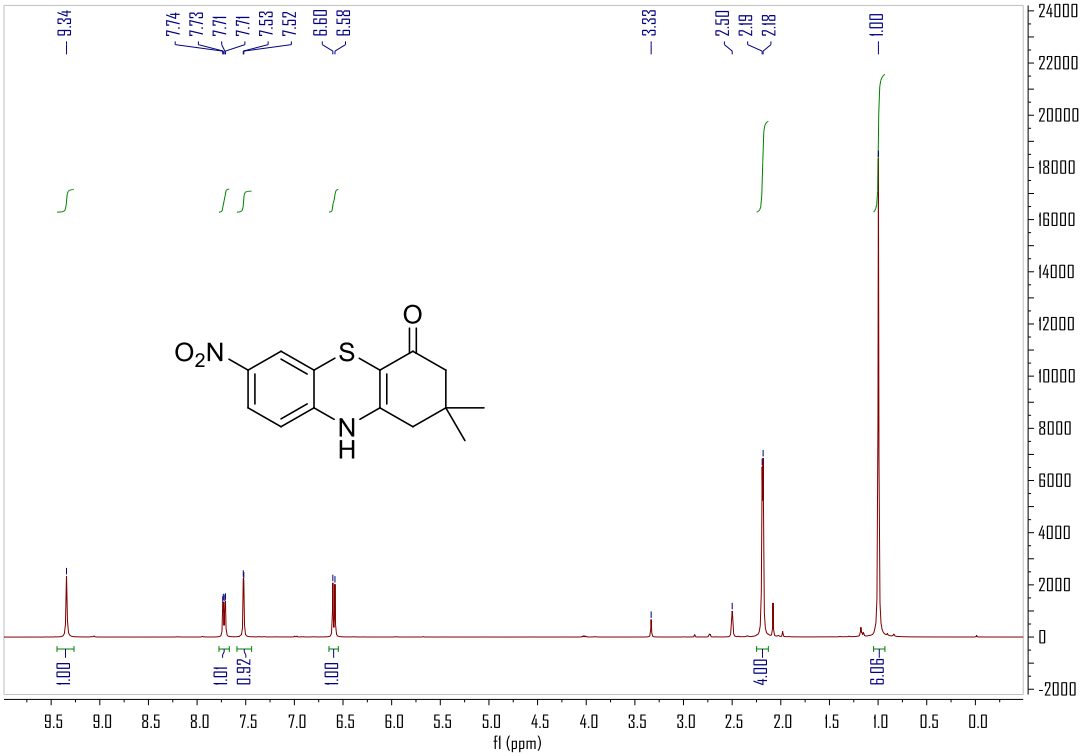


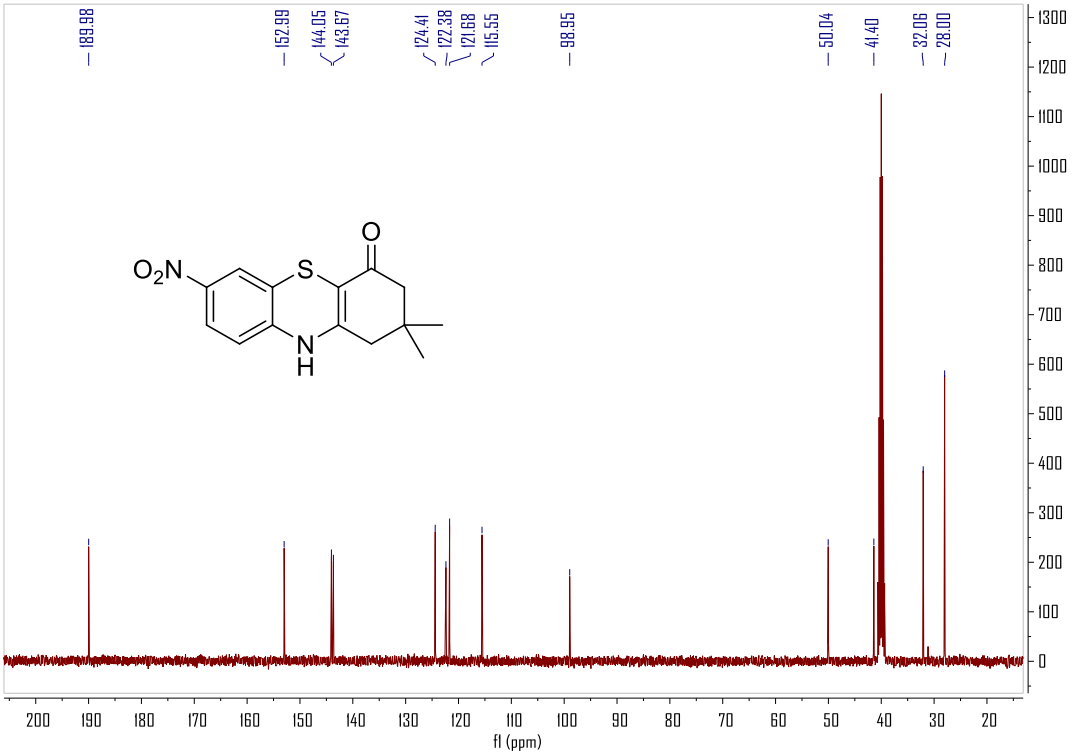
7-fluoro-2,2-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3g)



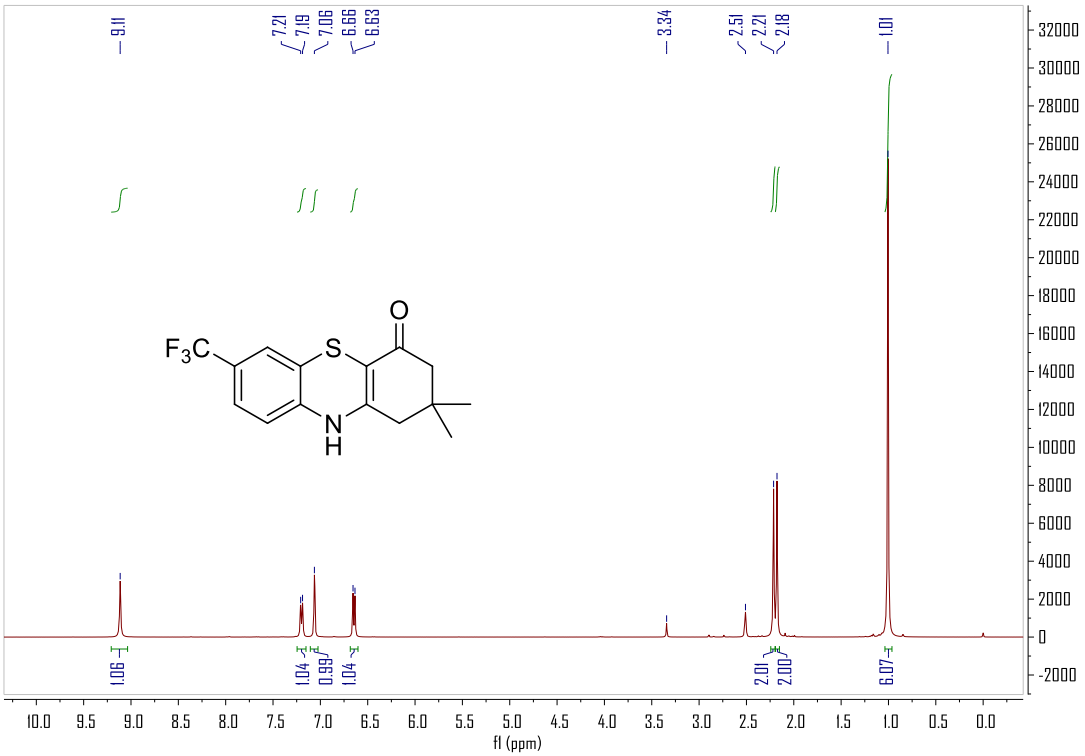


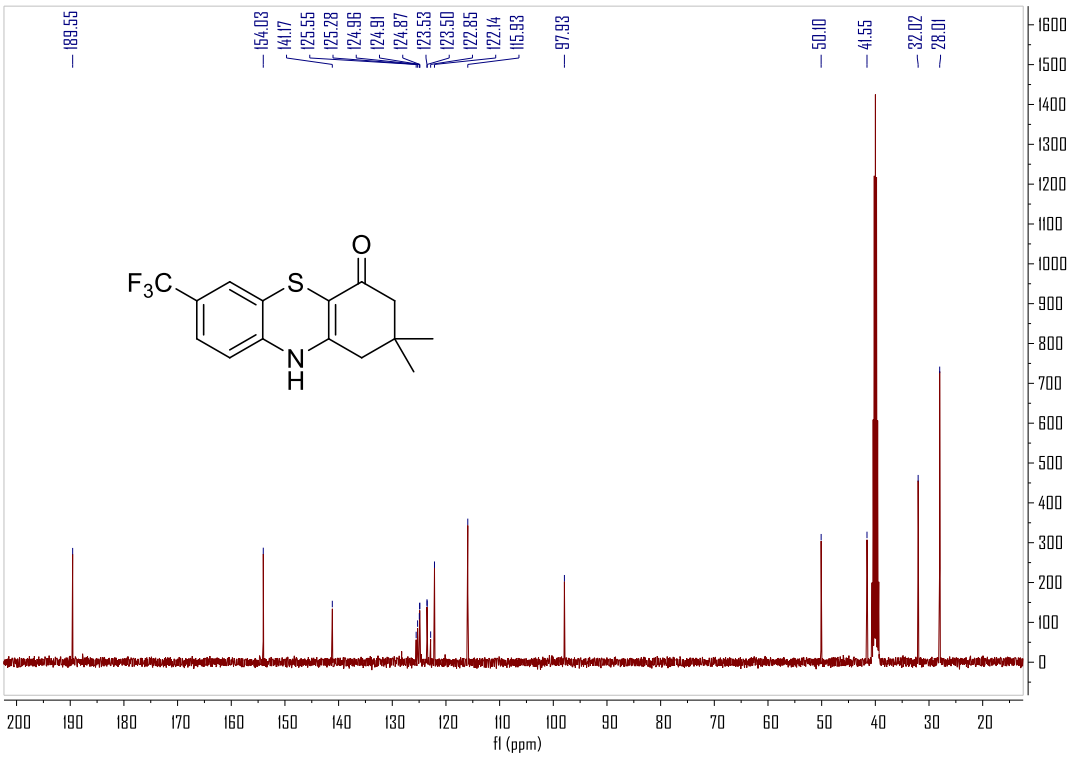
2,2-dimethyl-7-nitro-2,3-dihydro-1H-phenothiazin-4(10H)-one (3h)



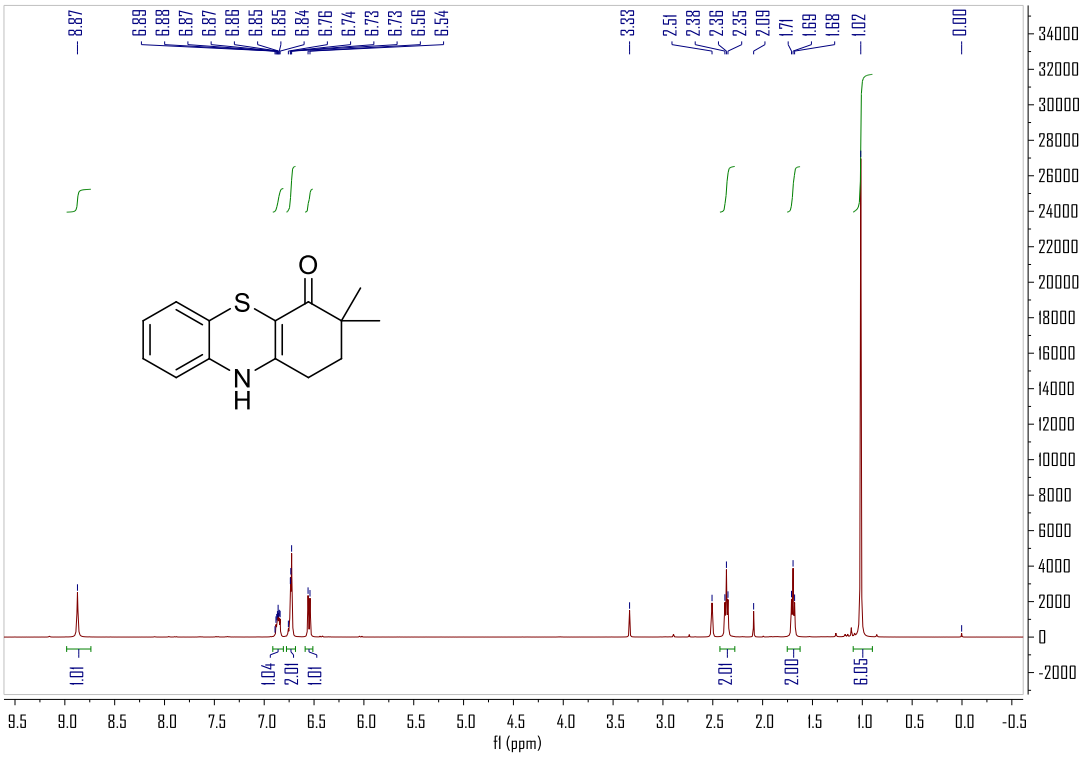


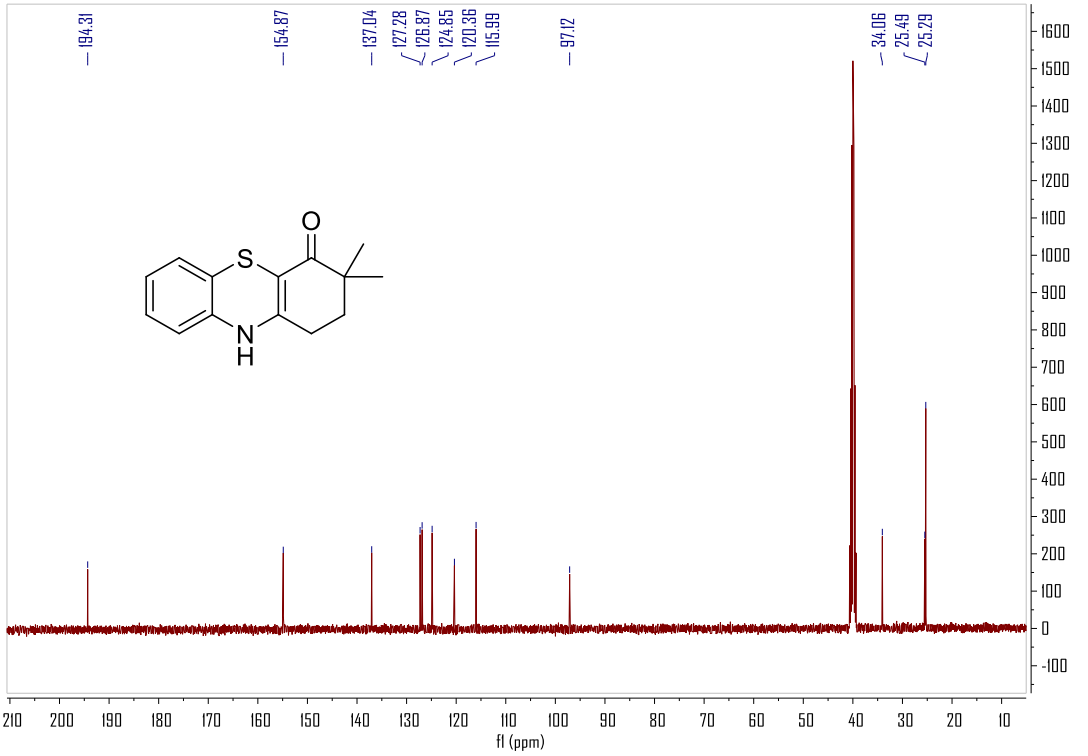
2,2-dimethyl-7-(trifluoromethyl)-2,3-dihydro-1H-phenothiazin-4(10H)-one (3i)



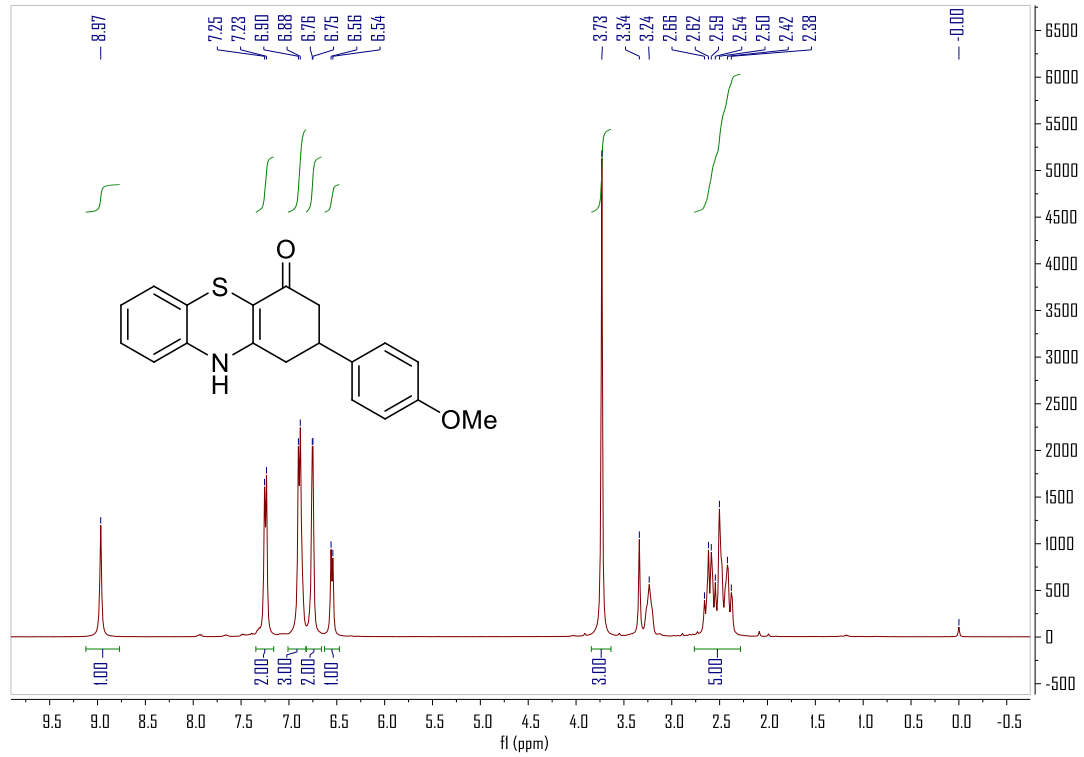


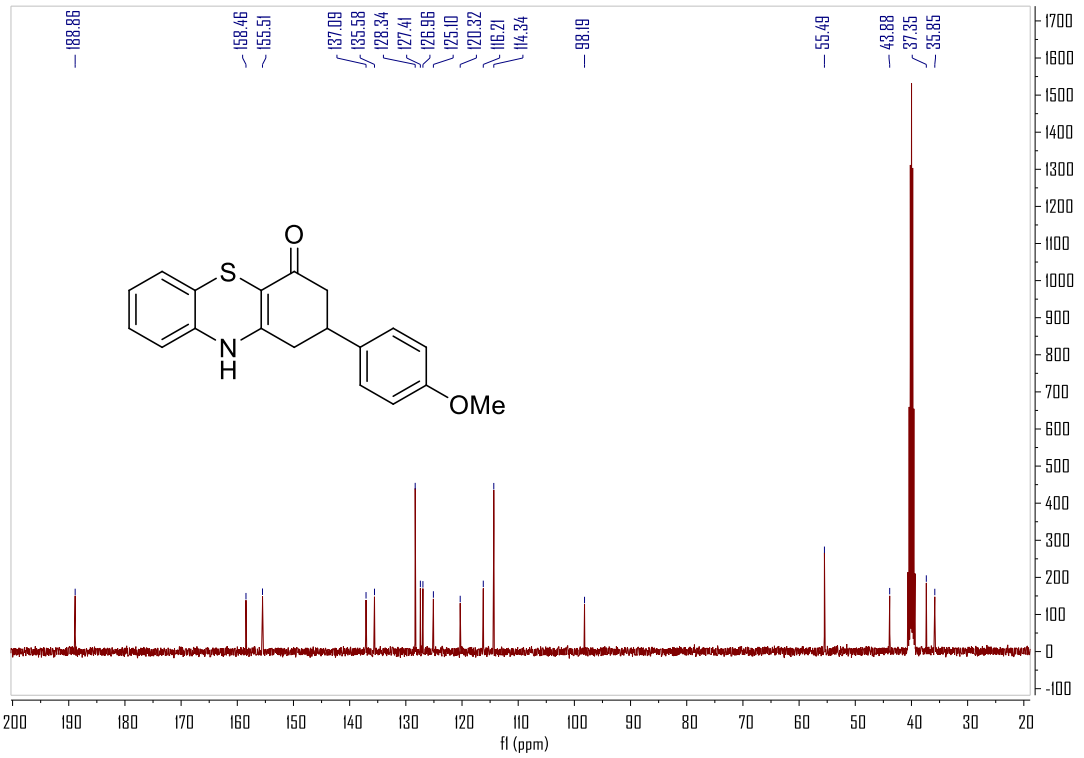
3,3-dimethyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3j)



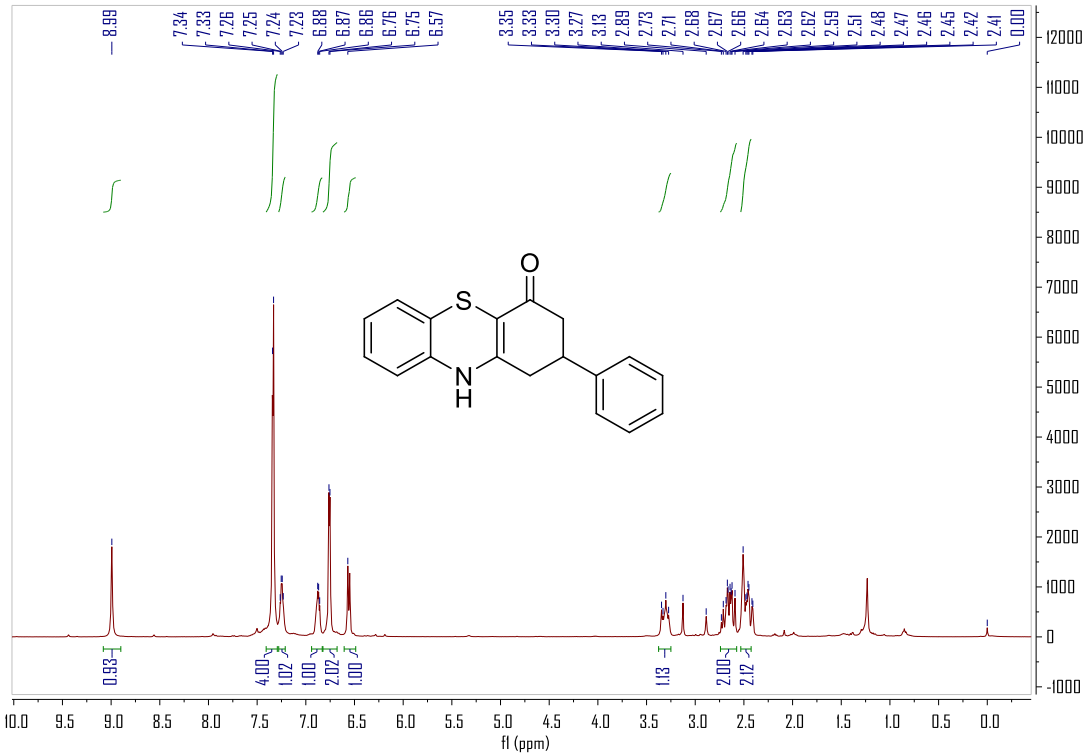


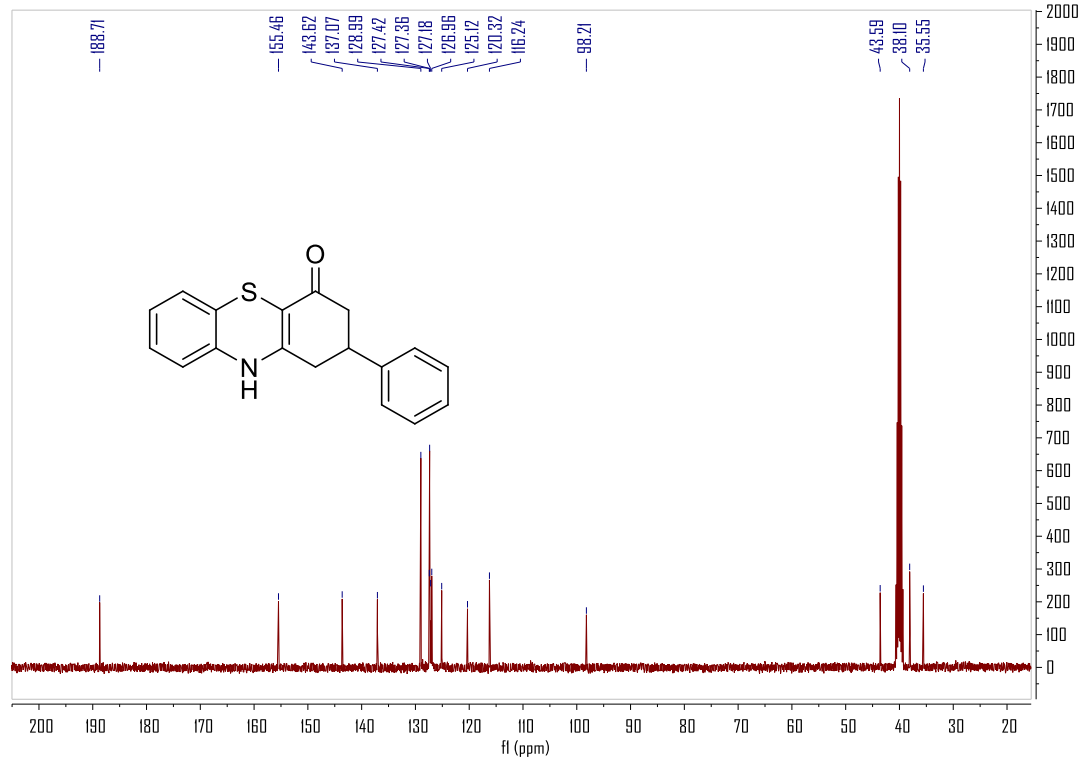
2-(4-methoxyphenyl)-2,3-dihydro-1H-phenothiazin-4(10H)-one (3k)



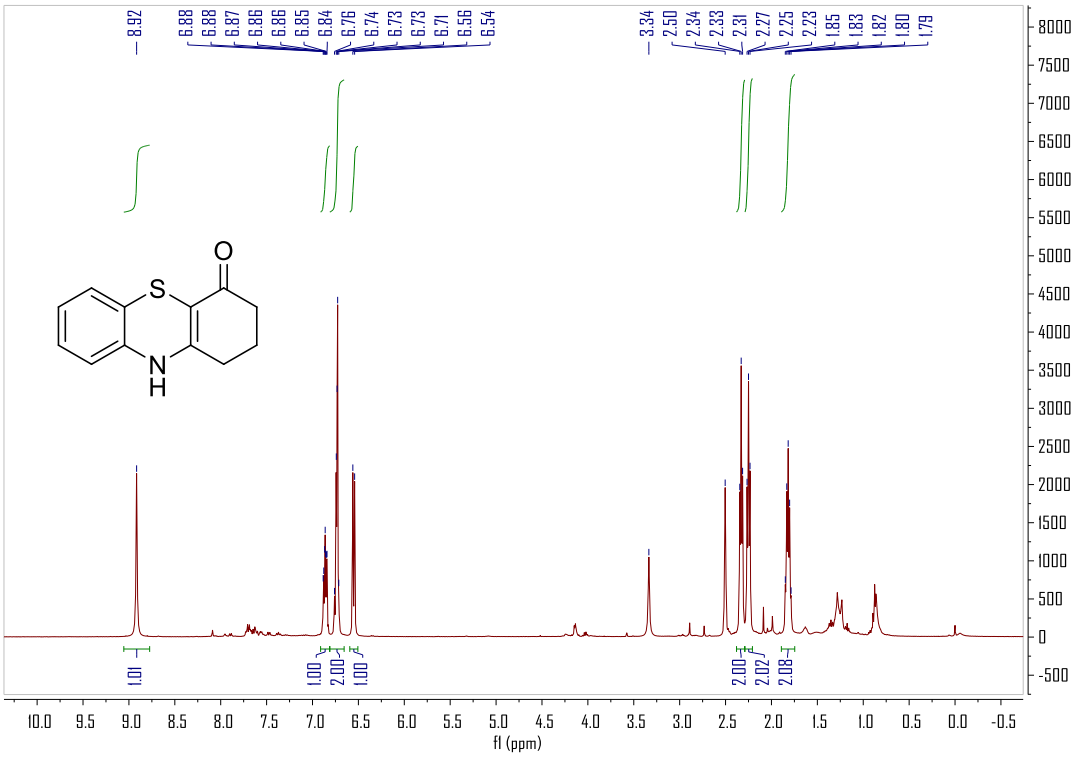


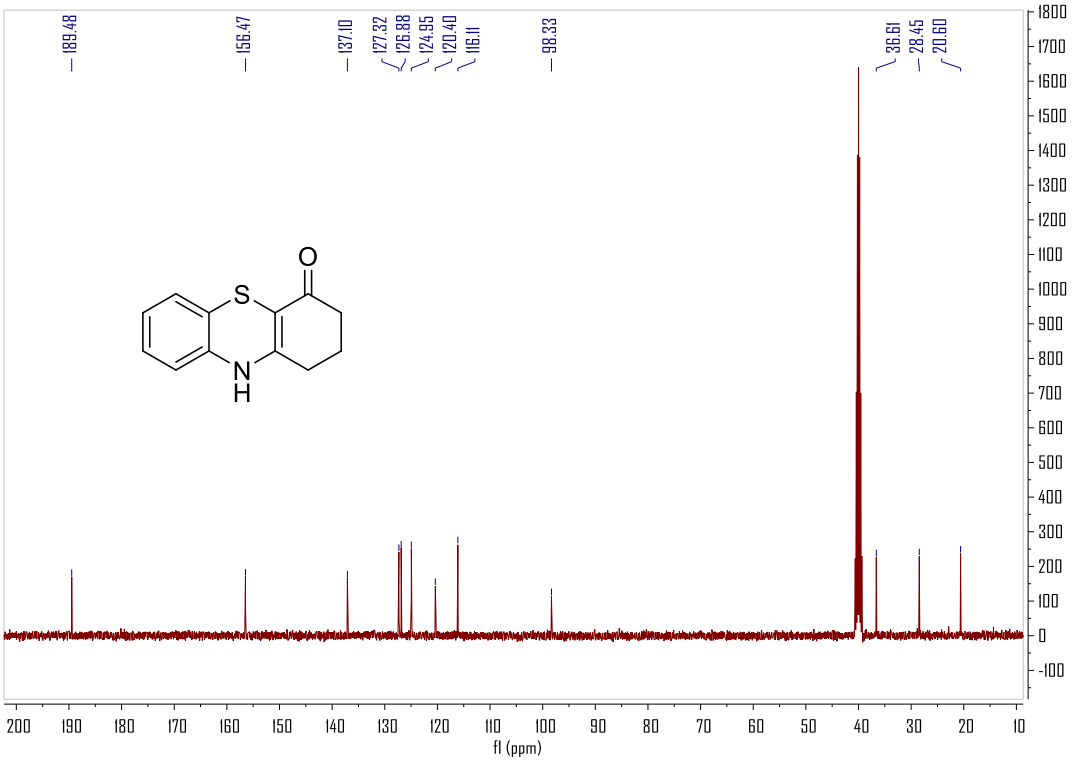
2-phenyl-2,3-dihydro-1H-phenothiazin-4(10H)-one (3l)





2,3-dihydro-1H-phenothiazin-4(10H)-one (3m)





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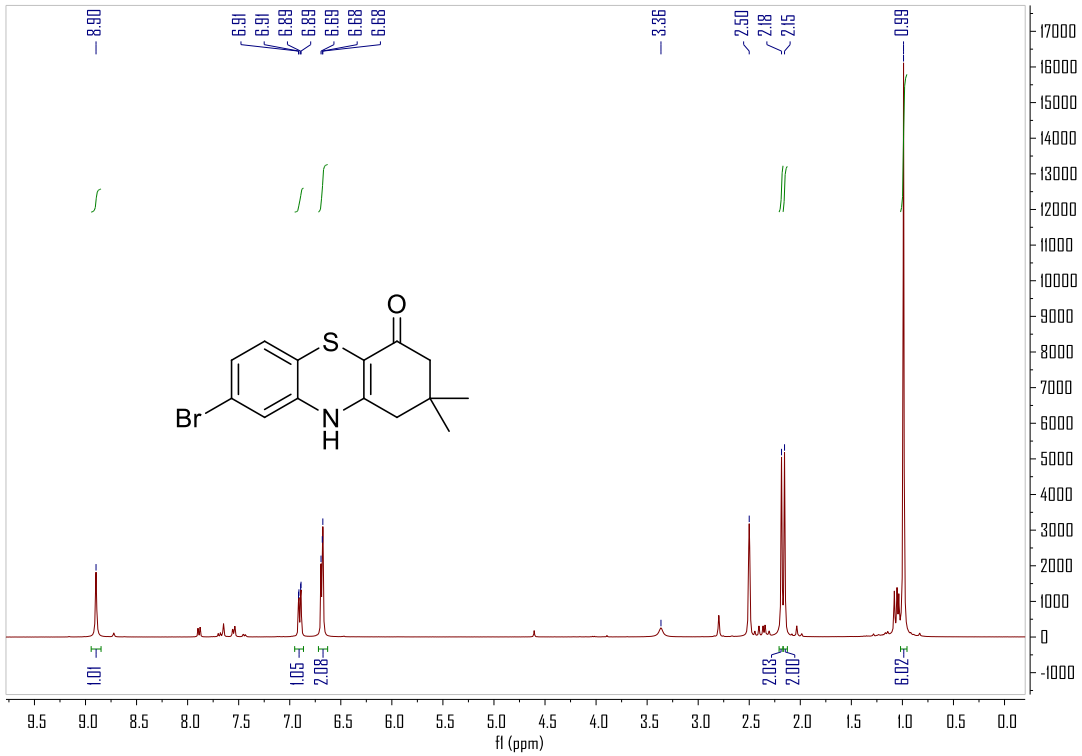

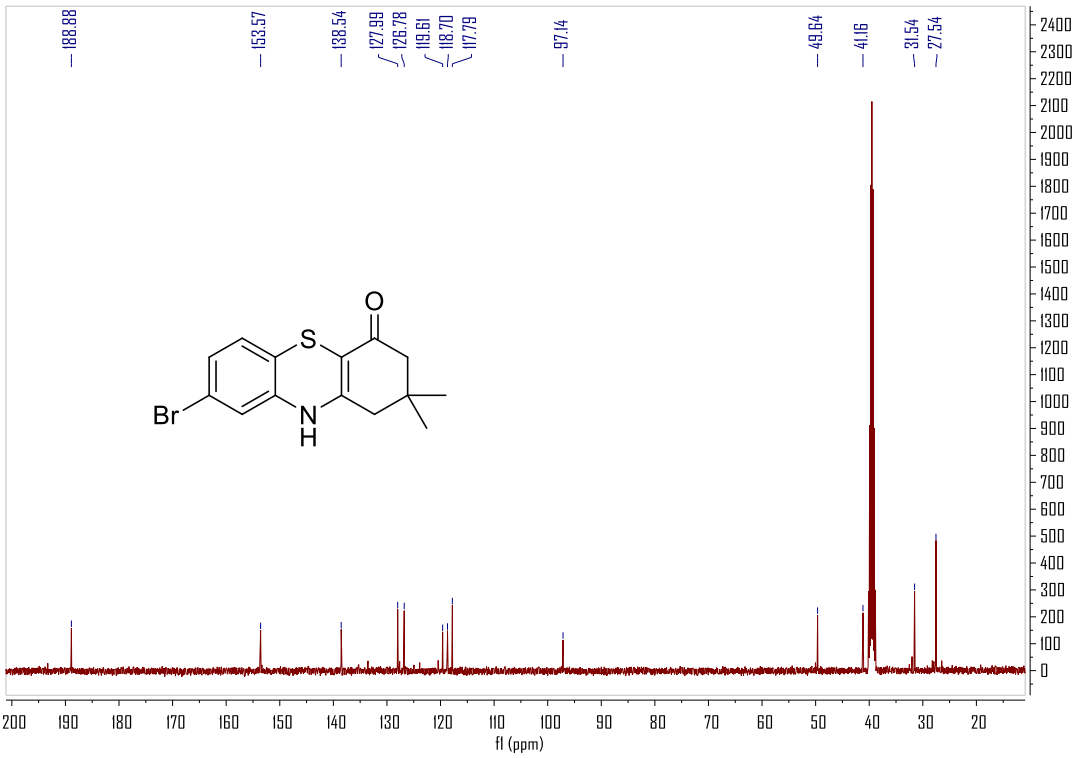

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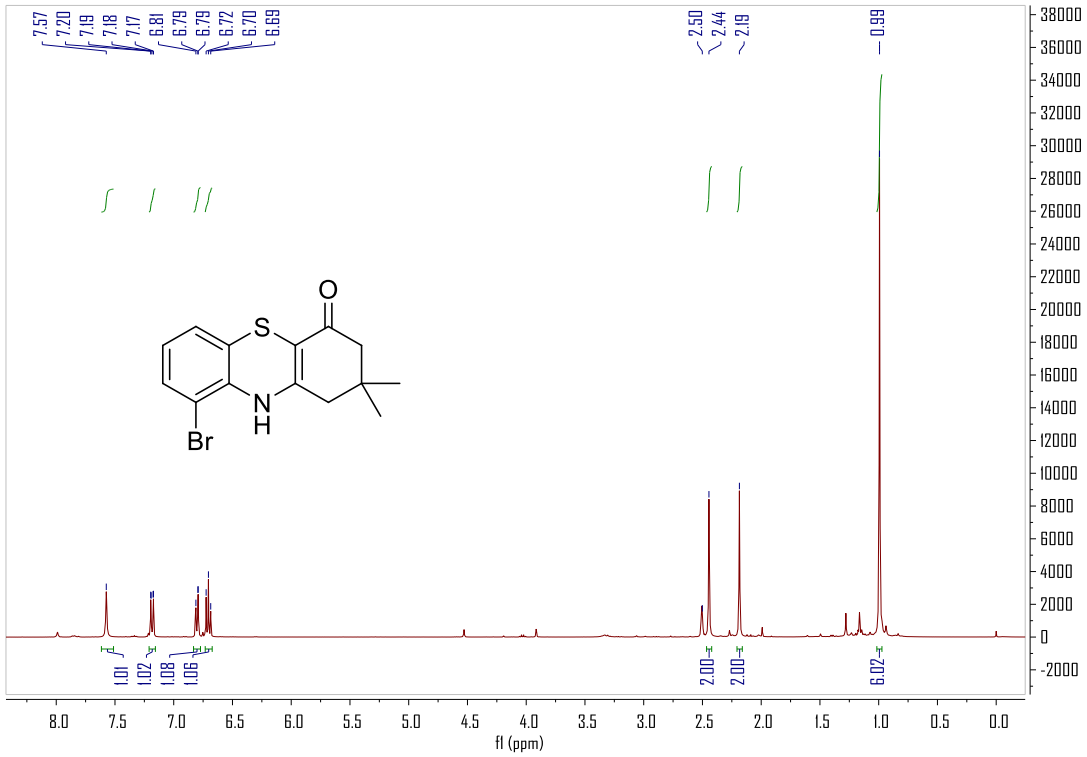

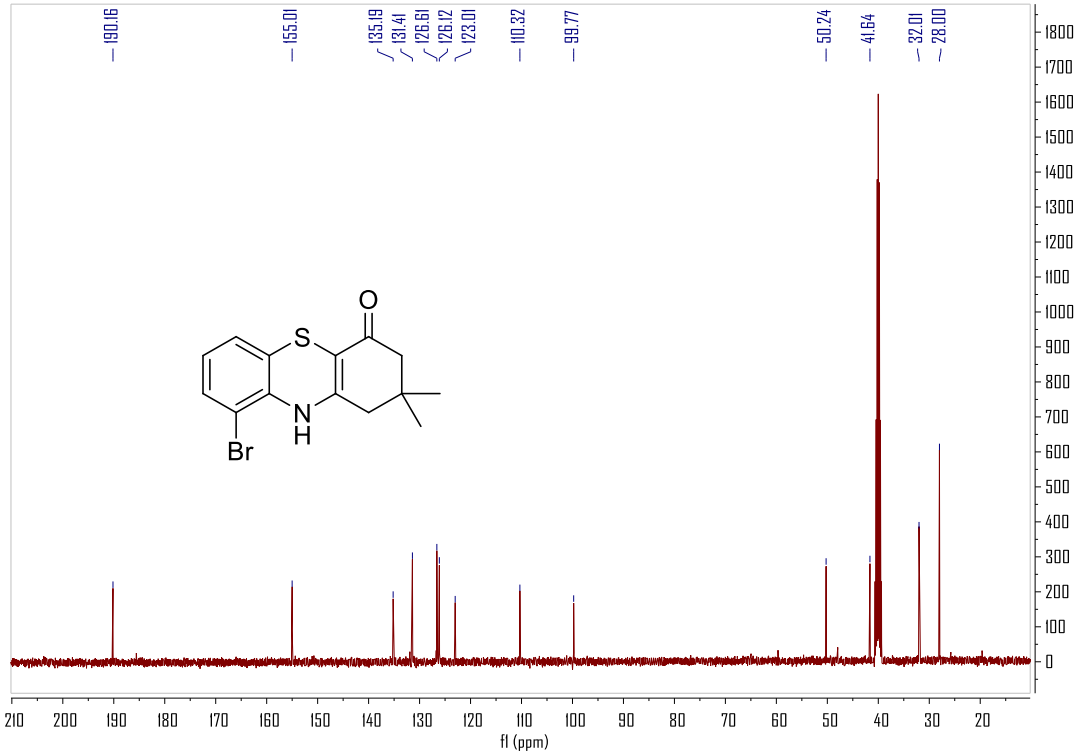

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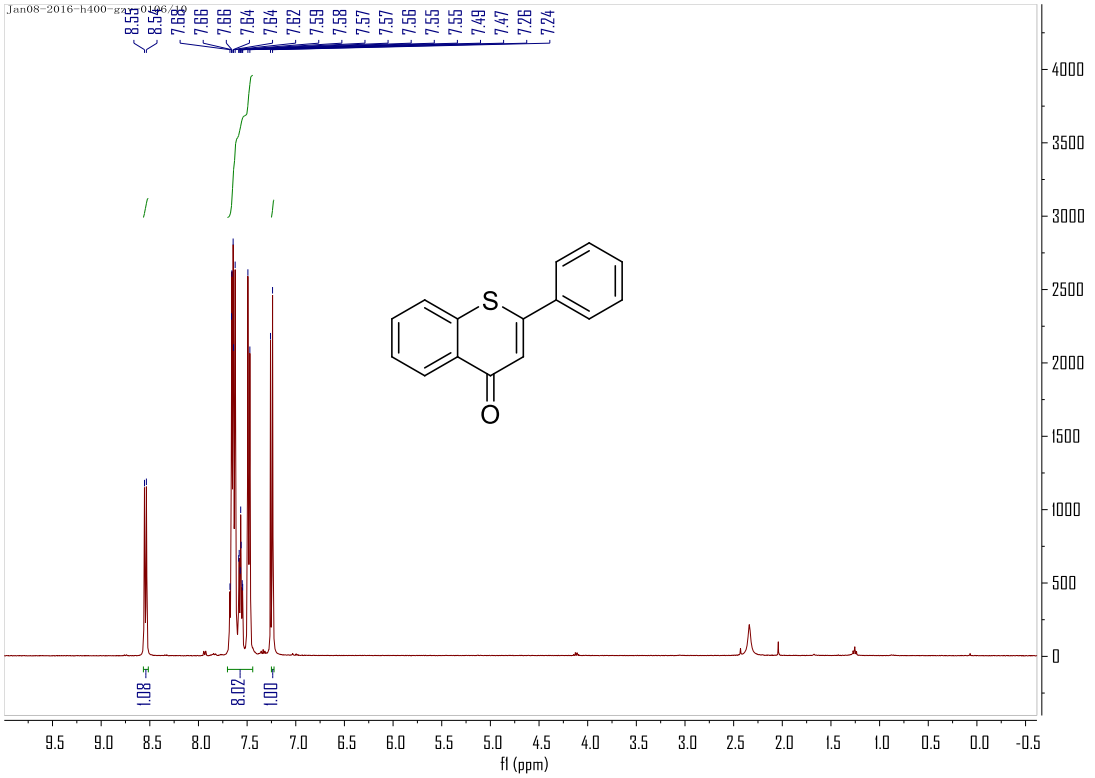

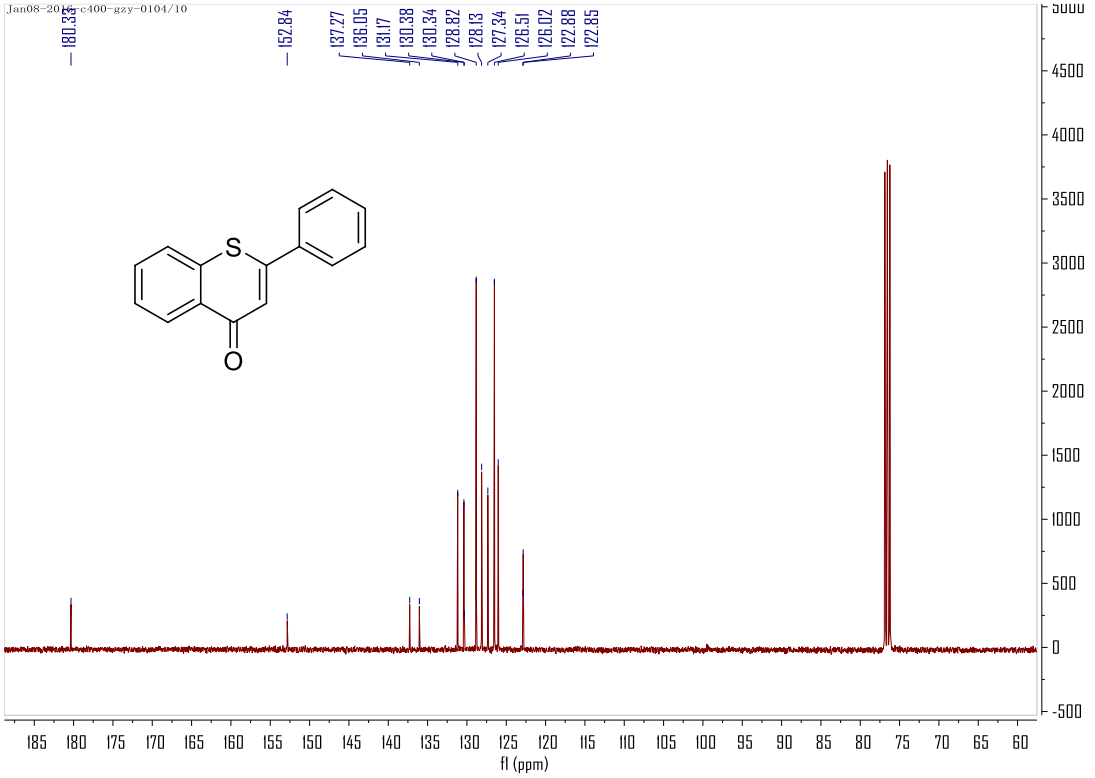

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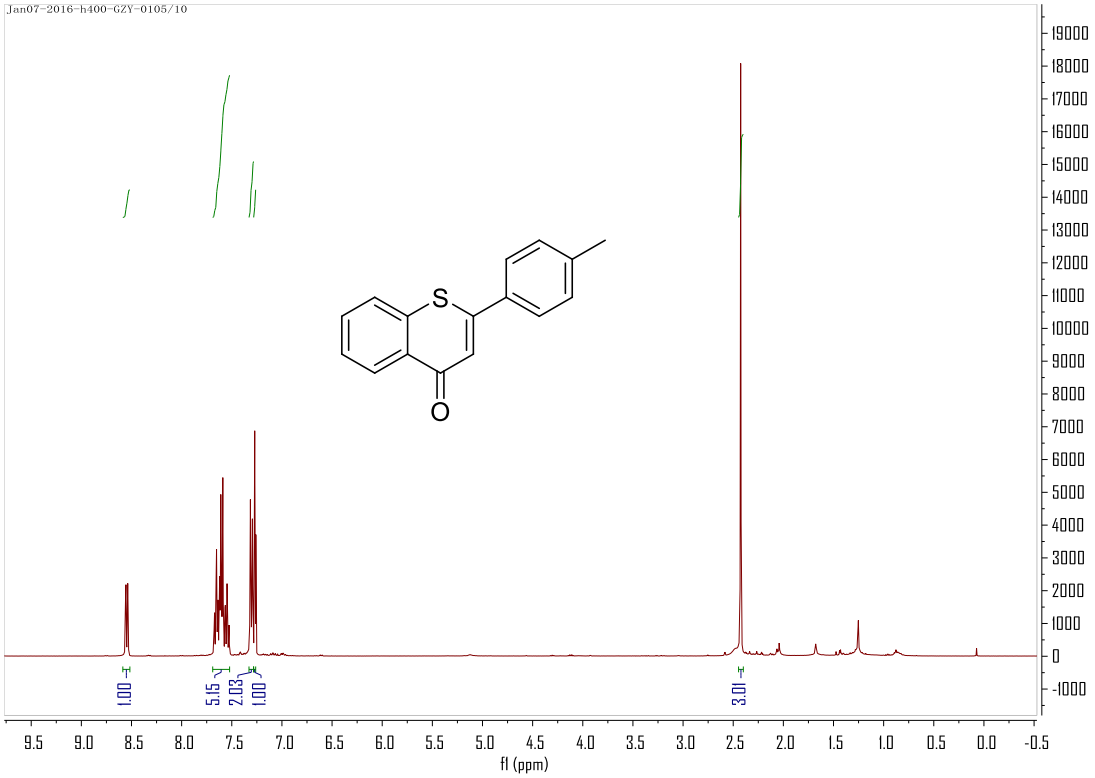

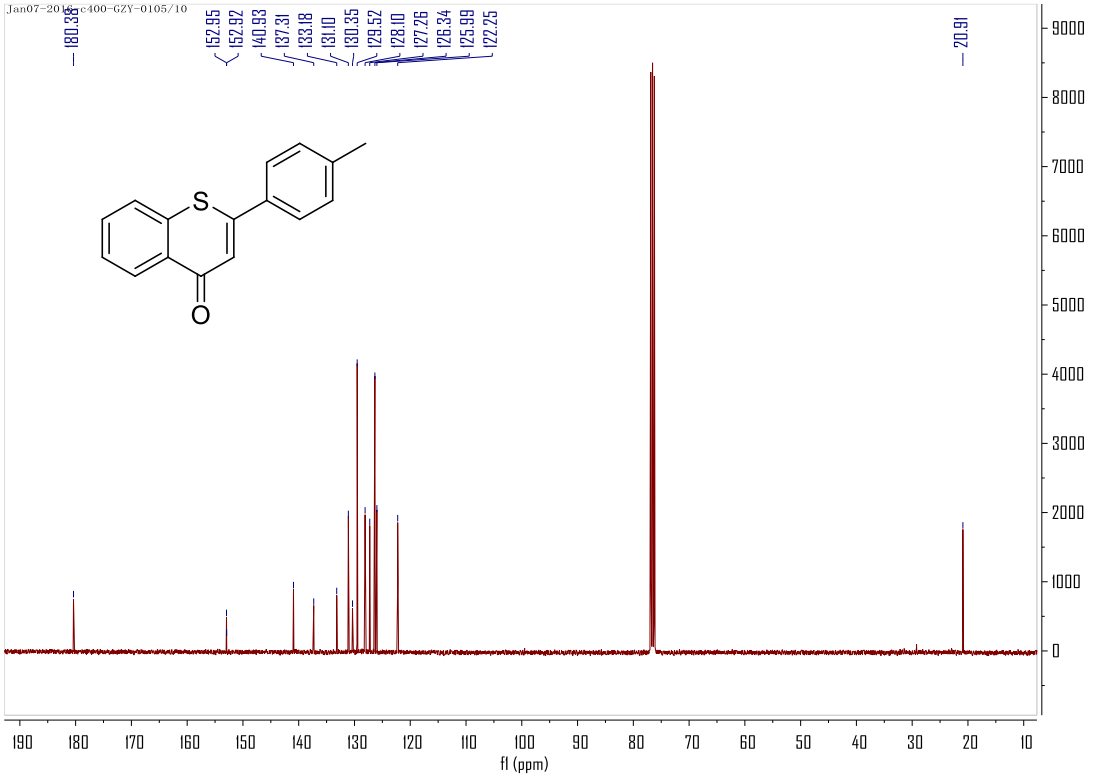

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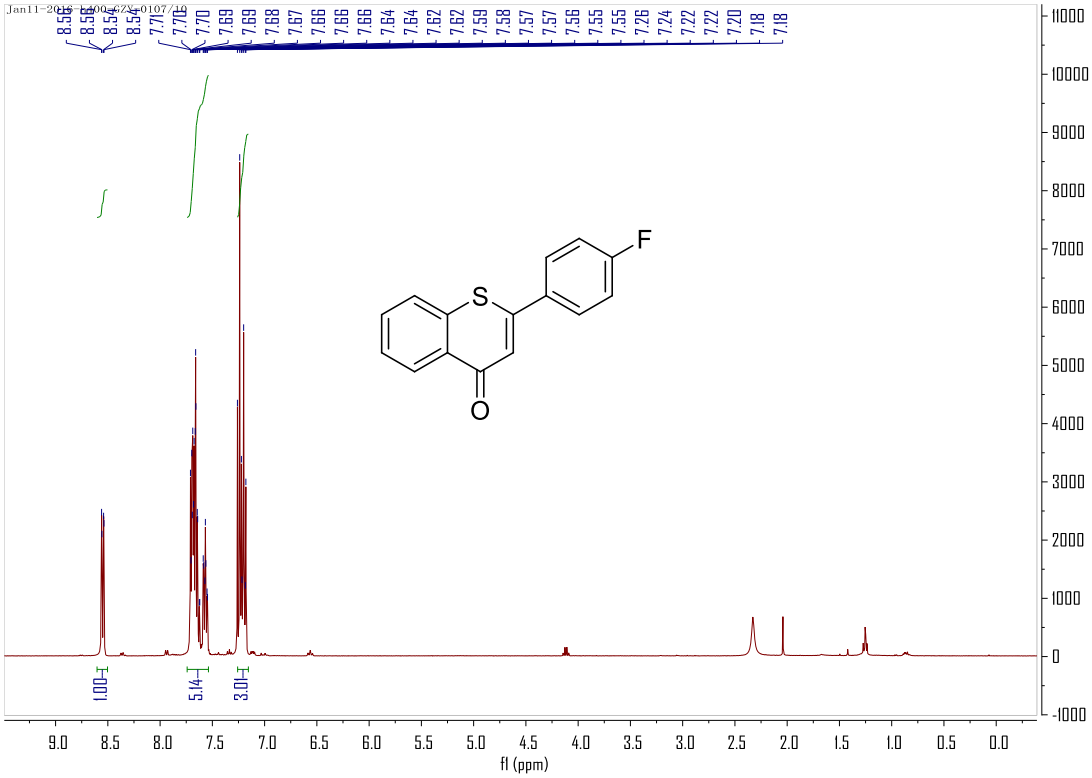

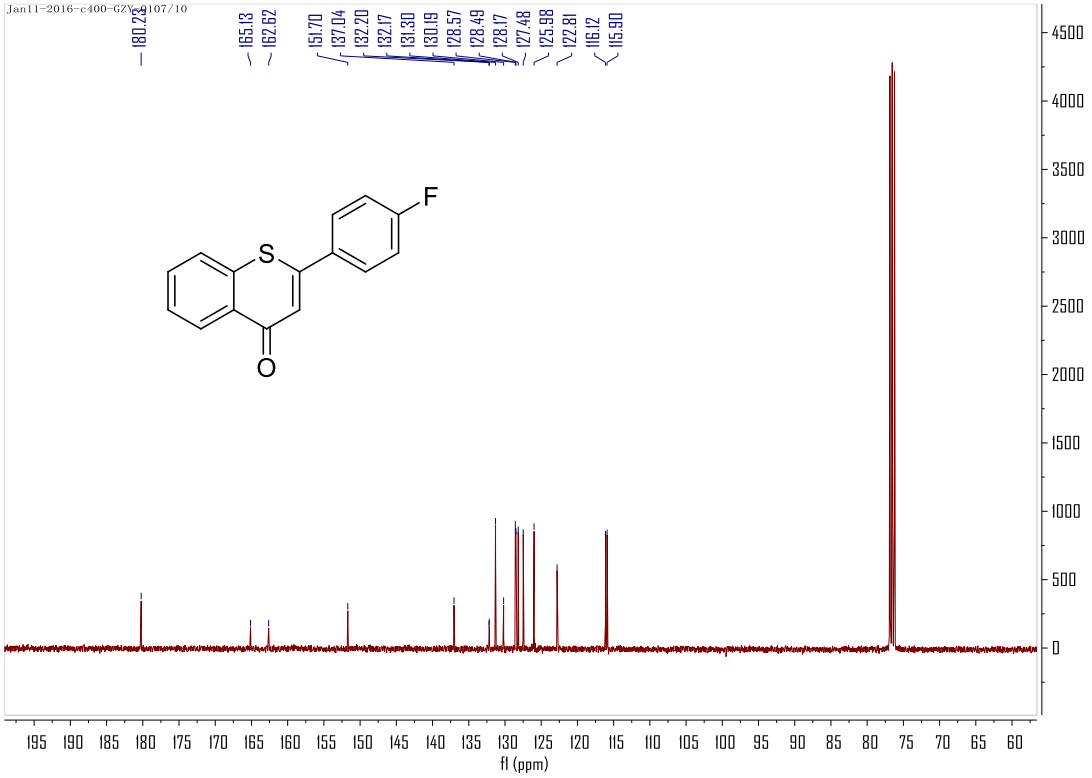

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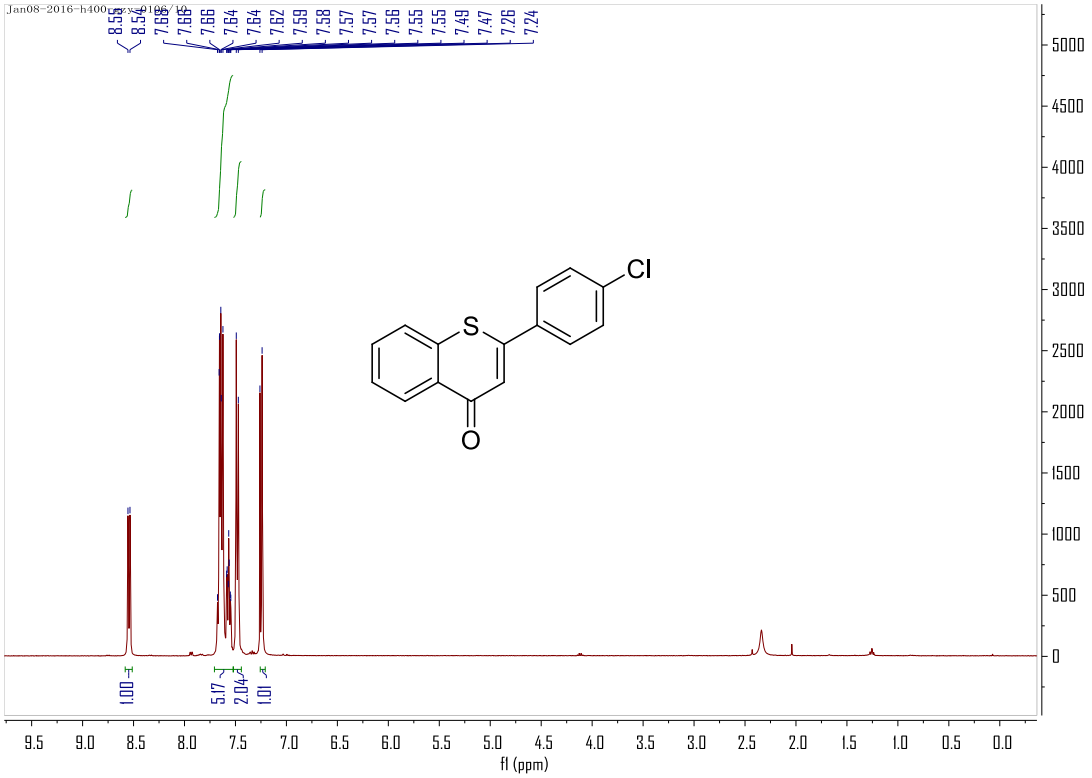

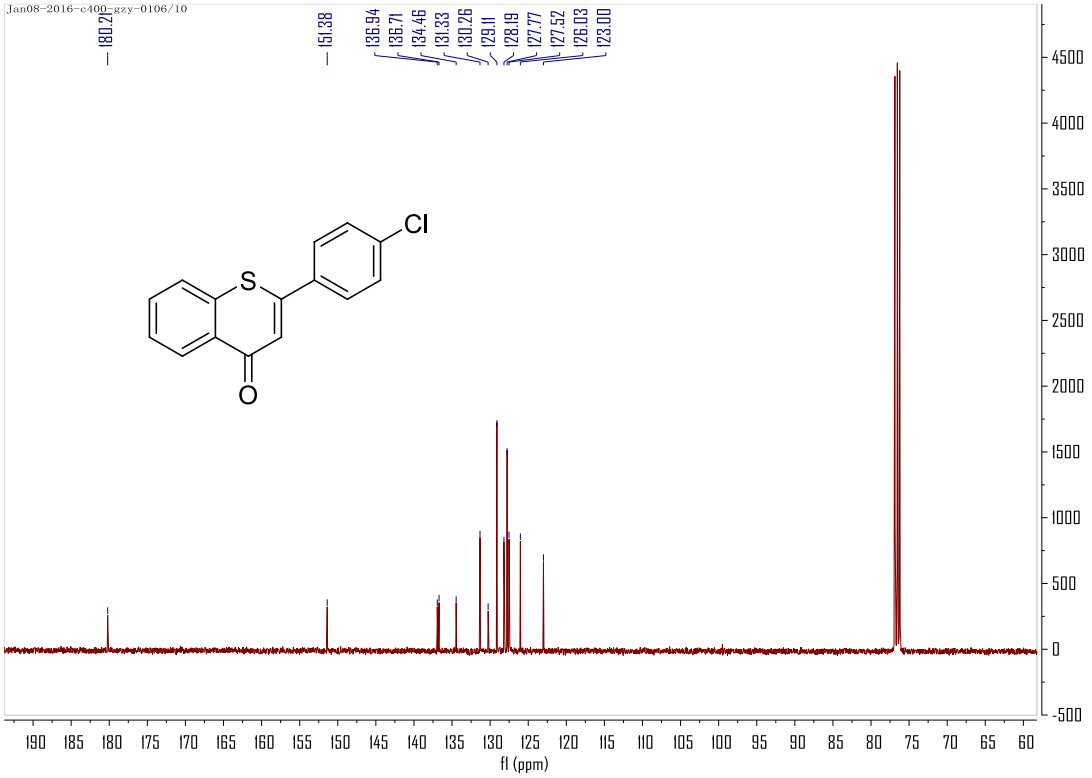

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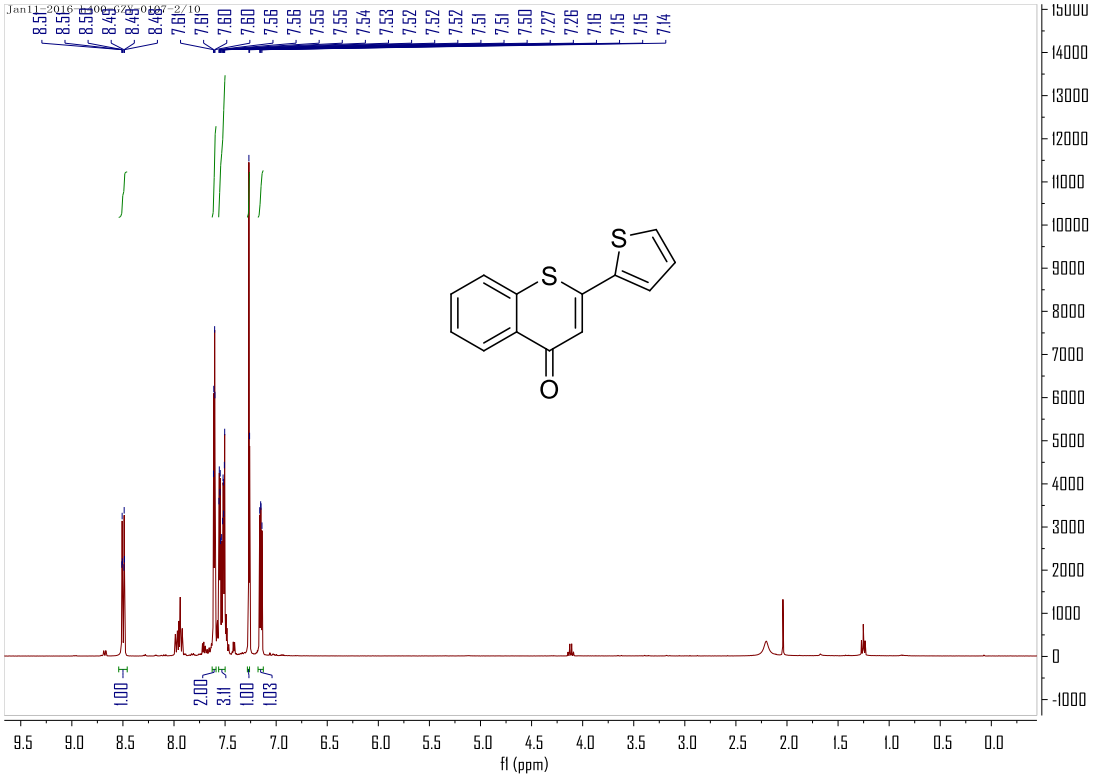

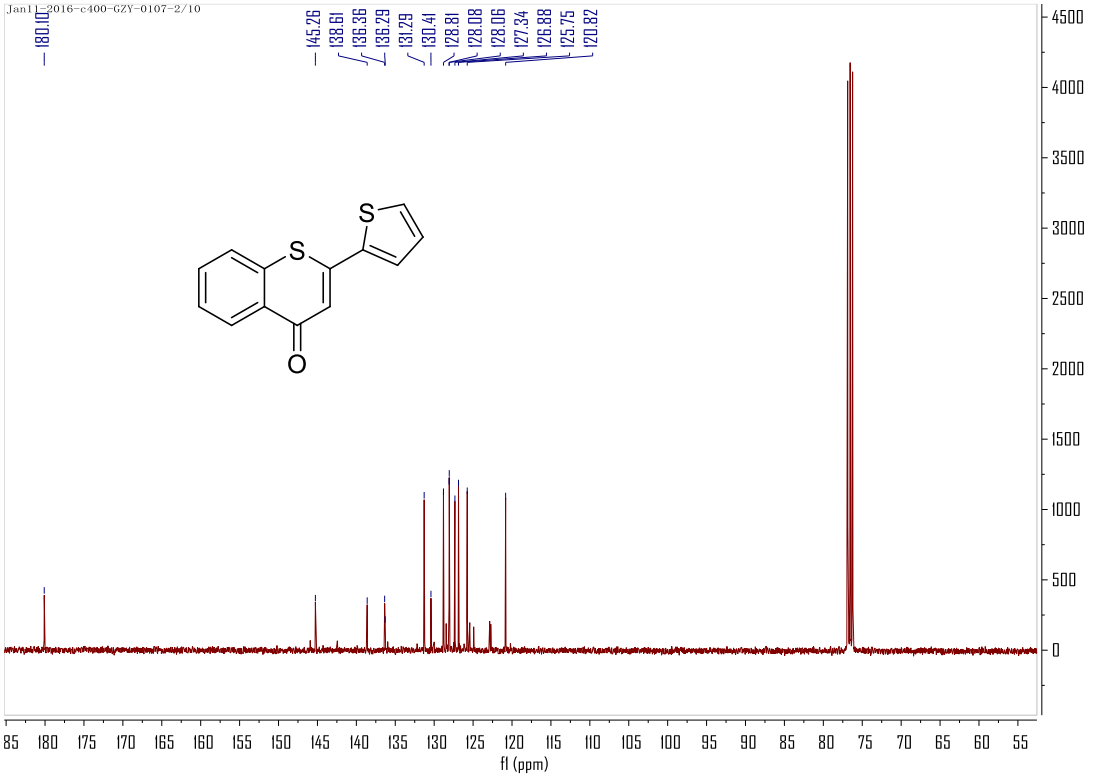

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O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann,
OLEX2: a complete structure solution, refinement and analysis program.
J. Appl. Cryst. (2009). 42, 339-341.
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O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann,
OLEX2: a complete structure solution, refinement and analysis program.
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C9 C8 S1 114.25(15) . . ?
O1 C9 C8 121.44(18) . . ?
O1 C9 C10 119.93(17) . . ?
C8 C9 C10 118.62(17) . . ?
C9 C10 H10A 108.8 . . ?
C9 C10 H10B 108.8 . . ?
C9 C10 C11 113.75(16) . . ?
H10A C10 H10B 107.7 . . ?
C11 C10 H10A 108.8 . . ?
C11 C10 H10B 108.8 . . ?
C10 C11 C12 107.97(16) . . ?
C13 C11 C10 109.82(17) . . ?
C13 C11 C12 110.60(16) . . ?
C13 C11 C14 109.41(16) . . ?
C14 C11 C10 110.58(15) . . ?
C14 C11 C12 108.44(16) . . ?
C7 C12 C11 113.94(16) . . ?
C7 C12 H12A 108.8 . . ?
C7 C12 H12B 108.8 . . ?
C11 C12 H12A 108.8 . . ?
C11 C12 H12B 108.8 . . ?
H12A C12 H12B 107.7 . . ?
C11 C13 H13A 109.5 . . ?
C11 C13 H13B 109.5 . . ?
C11 C13 H13C 109.5 . . ?
H13A C13 H13B 109.5 . . ?
H13A C13 H13C 109.5 . . ?
H13B C13 H13C 109.5 . . ?
C11 C14 H14A 109.5 . . ?

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  C11 C14 H14B 109.5 . . ?
  C11 C14 H14C 109.5 . . ?
  H14A C14 H14B 109.5 . . ?
  H14A C14 H14C 109.5 . . ?
  H14B C14 H14C 109.5 . . ?

loop_
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   _geom_hbond_distance_DA
   _geom_hbond_angle_DHA
   _geom_hbond_site_symmetry_A
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