

**Cycloaddition of 2-mercaptobenzaldehyde
with 5-arylidene-2-thioxooxazolidin-4-ones**

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S1. General

Commercially available reagents were used without additional purification. E. Merck Kieselgel 60 was used for column chromatography. 3-Phenyl-2-thioxooxazolidin-4-ones **2a-e** were synthesized according our previous work.^{S1}

Thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass-backed plates (MERCK). Visualization was performed using UV light (254 or 312 nm) or staining with KMnO₄.

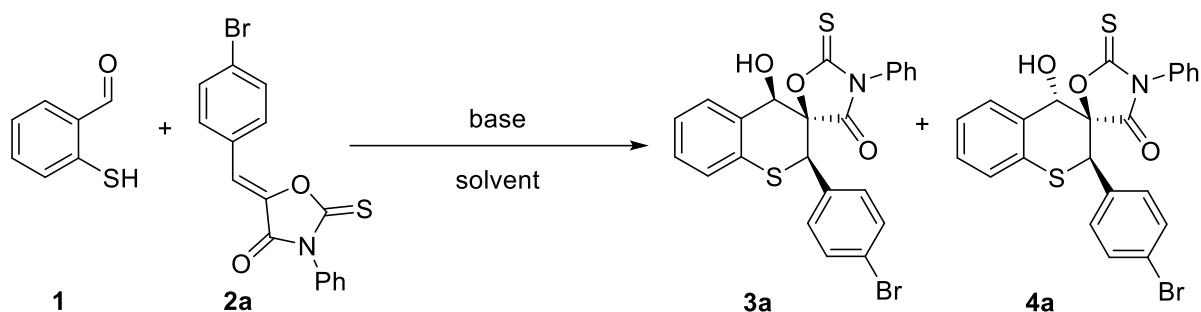
NMR spectra were recorded on a Bruker Avance III 800 (with a 5-mm CPTXI cryoprobe) and Bruker Fourier 300. Chemical shifts were reported relative to residue peaks of DMSO-d₆ (2.51 ppm: for ¹H and 39.5 ppm: for ¹³C).

Melting points were measured on a SMP 30 apparatus without correction.

High-resolution mass spectra (HRMS) spectra were recorded on AB Sciex TripleTOF® 5600+ System using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 5500 V); mass range from m/z 50 to m/z 3000; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 20 µl/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IUPAC compound names were generated using ChemDraw Software.

^{S1} I. V. Tiushina, A. I. Sokolov, A. Y. Smirnov, M. A. Dubinnyi, D. S. Ivanov, A. A. Korlyukov, A. A. Mikhaylov and M. S. Baranov, *ChemistrySelect*, 2024, **9**, e202400930; <https://doi.org/10.1002/slct.202400930>.

S2. Optimization of [4+2] cycloaddition reaction



A mixture of compound **1** (14 mg, 0.1 mmol) and **2a** (36 mg, 0.1 mmol) was dissolved in freshly distilled solvent (1 ml). Then base (10 mol %) was added, and the reaction mixture was stirred under the conditions listed in Table S1. After 4 hours of reaction, the solvents were removed in vacuum. For solutions in DMSO, DMF reaction mixtures were dissolved in 5 ml of EtOAc and washed with saturated KCl solution (5×3 ml). Next, the organic solutions were dried over Na₂SO₄ and similarly evaporated. Finally, all the residues were analyzed by ¹H NMR in DMSO-d₆. TMS signal was used as an internal standard - for all spectra its integral area was set on equal value. Initial integral area of aromatic signal from 6.50 ppm to 8.20 ppm was determined as 100%. The yields of components (presented on Scheme 2) were determined using the following integral areas:

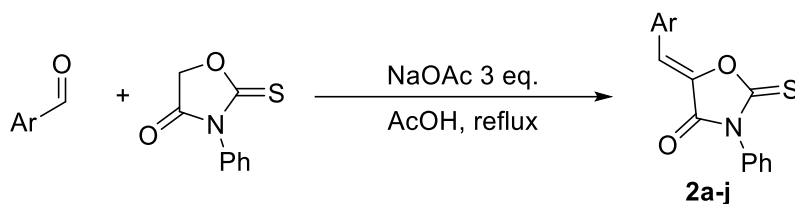
- doublet signal from 5.39 ppm to 5.42 ppm (1H) for product **3a**
- doublet signal from 5.24 ppm to 5.26 ppm (1H) for product **4a**

Results are presented in Table S1.

Table S1. Optimization of reaction conditions.

Entry	Solvent	Base	Conditions	Conversion (%)	Yield (%)	<i>dr</i> (3a/4a)
1	CH ₂ Cl ₂	DABCO	25°C	70	70	8.3:1
2	CH ₂ Cl ₂	K ₂ CO ₃	25°C	85	80	1:1
3	CH ₂ Cl ₂	DBU	25°C	85	50	2:1
4	CH ₂ Cl ₂	L-proline	25°C	65	70	1:3
5	CH ₂ Cl ₂	Pyridine	25°C	70	70	2:1
6	CH ₂ Cl ₂	DABCO	0°C	65	50	2:1
7	CH ₂ Cl ₂	DABCO	-30°C	55	60	2:1
8	PhMe	DABCO	25°C	90	75	4:1
9	PhCl	DABCO	25°C	90	60	6.6:1
10	CHCl ₃	DABCO	25°C	90	75	3.3:1
11	C ₂ H ₄ Cl ₂	DABCO	25°C	90	80	5.5:1
12	MeCN	DABCO	25°C	85	60	11:1
13	DMF	DABCO	25°C	80	50	17:1
14	(CF ₃) ₂ CHOH	DABCO	25°C	75	60	1.7:1
15	DMSO	DABCO	25°C	65	30	20:1
16	MeOH	DABCO	25°C	60	50	5:1
17	DMSO	DABCO	25°C Ar atm.	100	80	20:1
18	PhMe	L-proline	25°C	75	40	3:1
19	PhCl	L-proline	25°C	65	50	2:1
20	CHCl ₃	L-proline	25°C	70	70	1:2
21	C ₂ H ₄ Cl ₂	L-proline	25°C	100	50	1.5:1
22	MeCN	L-proline	25°C	85	60	1:1.2
23	DMF	L-proline	25°C	60	50	1.6:1
24	(CF ₃) ₂ CHOH	L-proline	25°C	60	40	1.6:1
25	DMSO	L-proline	25°C	75	50	2.2:1
26	MeOH	L-proline	25°C	60	40	1:5
27	MeOH	L-proline	25°C Ar atm.	100	80	1:5

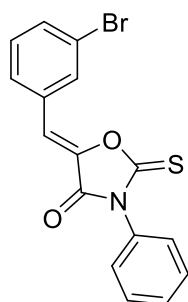
S3. General experimental procedure for the synthesis of compounds 2



An aromatic aldehyde (3 mmol), 3-phenyl-2-thioxooxazolidin-4-one (625 mg, 3.24 mmol) and anhydrous sodium acetate (738 mg, 9 mmol) were dissolved in glacial acetic acid (13 ml) in a round-bottom flask equipped with a condenser and a magnetic stirrer. The reaction mixture was refluxed for 22-32 hours until no starting material was observed. The progress of the reaction was monitored by TLC (EtOAc/Hex , v/v 1/2). After completion, the flask was cooled to a room temperature and poured into 250 ml of distilled water. If suspension was formed, solids were filtered off. The filter cake was washed successively with water (4x10 ml) and $\text{Et}_2\text{O/Hex}$ (v/v, 1/1, 1x10 ml). The crude product was purified by flash column chromatography (eluent – either DCM/Hex or DCM). Otherwise, the aqueous phase was neutralized with NaHCO_3 and extracted with $\text{CHCl}_3/\text{Pr}^i\text{OH}$ (v/v, 100/5). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (eluent – either DCM or DCM/MeOH , v/v, 100:2).

Products **2a-e**, **2g** were obtained in our previous work ^{S1}.

(Z)-5-(3-Bromobenzylidene)-3-phenyl-2-thioxooxazolidin-4-one (**2f**)



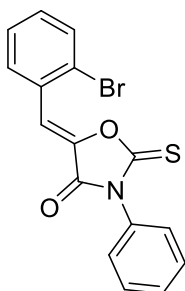
Yield: 60% (648 mg). Light yellow solid. m.p. 139-141 °C.

^1H NMR (300 MHz, CDCl_3) δ ppm: 7.95 - 8.01 (m, 1 H), 7.88 (d, $J=7.8$ Hz, 1 H), 7.53 - 7.64 (m, 4 H), 7.35 - 7.44 (m, 3 H), 6.76 (s, 1 H).

^{13}C NMR (75 MHz, CDCl_3) δ ppm: 181.8, 161.4, 139.5, 134.0, 133.8, 132.6, 132.0, 130.7, 129.9, 129.8, 129.6, 127.3, 123.2, 112.5.

HRMS (ESI) m/z : 359.9689 found (calcd for $\text{C}_{16}\text{H}_{11}\text{BrNO}_2\text{S}^+$, $[\text{M}+\text{H}]^+$ 359.9688).

(Z)-5-(2-Bromobenzylidene)-3-phenyl-2-thioxooxazolidin-4-one (2h)



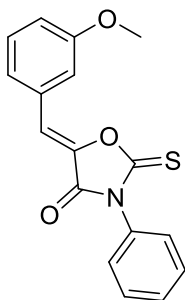
Yield: 83% (896 mg). Light yellow solid. m.p. 125-127 °C.

^1H NMR (300 MHz, CDCl_3): δ ppm 8.28 (dd, $J=7.9$, 1.6 Hz, 1 H), 7.70 (dd, $J=8.0$, 1.1 Hz, 1 H), 7.52 - 7.59 (m, 3 H), 7.40 - 7.48 (m, 3 H), 7.30 - 7.35 (m, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ ppm 182.0, 161.3, 139.8, 133.6, 132.3, 132.0, 131.9, 130.6, 129.9, 129.6, 128.1, 127.4, 126.5, 112.4.

HRMS (ESI) m/z : 359.9689 found (calcd for $\text{C}_{16}\text{H}_{11}\text{BrNO}_2\text{S}^+$, $[\text{M}+\text{H}]^+$ 359.9688).

(Z)-5-(3-Methoxybenzylidene)-3-phenyl-2-thioxooxazolidin-4-one (2i)



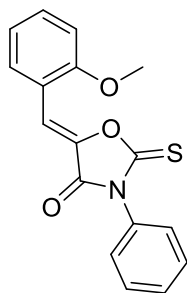
Yield: 71% (662 mg). Yellow solid. m.p. 157-159 °C.

^1H NMR (300 MHz, CDCl_3) δ ppm: 7.49 - 7.59 (m, 4 H), 7.39 - 7.45 (m, 4 H), 7.01 - 7.07 (m, 1 H), 6.83 (s, 1 H), 3.89 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3) δ ppm: 182.1, 161.7, 159.9, 138.9, 132.1, 131.9, 130.2, 129.8, 129.5, 127.4, 124.3, 117.2, 116.3, 114.6, 55.4.

HRMS (ESI) m/z : 312.0689 found (calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3\text{S}^+$, $[\text{M}+\text{H}]^+$ 312.0689).

(Z)-5-(2-Methoxybenzylidene)-3-phenyl-2-thioxooxazolidin-4-one



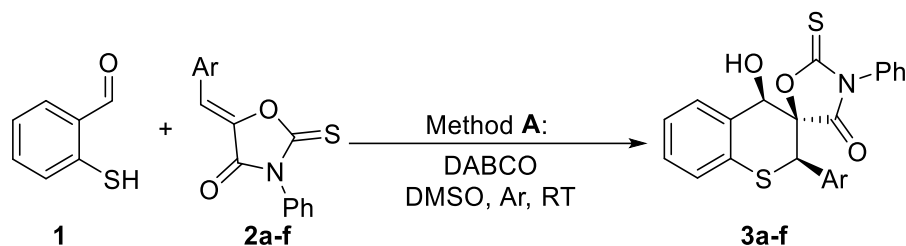
Yield: 75% (700 mg). Light yellow solid. m.p. 177-179 °C.

^1H NMR (300 MHz, CDCl_3): δ ppm 8.25 (dd, $J=7.8$, 1.6 Hz, 1 H), 7.50 - 7.60 (m, 3 H), 7.47 - 7.48 (m, 1 H), 7.35 - 7.47 (m, 3 H), 7.04 - 7.16 (m, 1 H), 6.96 (d, $J=8.1$ Hz, 1 H), 3.93 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ ppm 182.5, 161.7, 158.7, 138.5, 132.8, 132.3, 132.0, 129.7, 129.5, 127.4, 121.2, 119.8, 110.9, 109.2, 55.7.

HRMS (ESI) m/z : 312.0689 found (calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3\text{S}^+$, $[\text{M}+\text{H}]^+$ 312.0689).

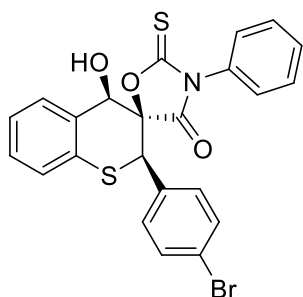
S4. General experimental procedures for the synthesis of compounds 3



Method A

A mixture of the 2-mercaptobenzaldehyde **1** (1 mmol) and a corresponding 3-phenyl-2-thioxooxazolidin-4-one **2** (1 mmol) was dissolved in freshly distilled DMSO (10 mL). Then DABCO (10 mol %) was added and the reaction mixture was stirred for 4 hours under argon atmosphere. The progress of the reaction was monitored by TLC and ^1H NMR. After the reaction completion, reaction mixtures were dissolved in 200 mL of EtOAc, washed with saturated KCl solution (10×30 mL) and dried over Na_2SO_4 . All volatiles were removed in vacuo and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 5:1).

(2'R*,4'R*,5S*)-2'-(4-Bromophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (**3a**)



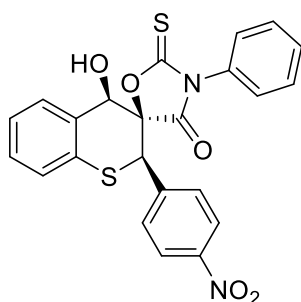
Yield 353 mg (71%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm: 7.69 (d, $J=8.4$ Hz, 2 H), 7.62 (d, $J=7.2$ Hz, 1 H), 7.45 - 7.50 (m, 4 H), 7.43 (br. s., 1 H), 7.21 - 7.31 (m, 3 H), 7.13 (d, $J=7.8$ Hz, 1 H), 6.44 - 6.68 (m, 2 H), 5.71 (s, 1 H), 5.41 (d, $J=7.9$ Hz, 1 H).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ ppm: 188.8, 171.4, 133.5, 132.5, 132.0, 131.8, 131.4, 131.3, 129.9, 129.6, 128.1, 127.7, 127.0, 125.0, 124.5, 123.0, 89.1, 69.1, 46.0.

HRMS (ESI) m/z : 497.9826 found (calcd for $\text{C}_{23}\text{H}_{17}\text{BrNO}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 497.9828).

(2'*R,4'*R**,5*S**)-4'-Hydroxy-2'-(4-nitrophenyl)-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (3b)**



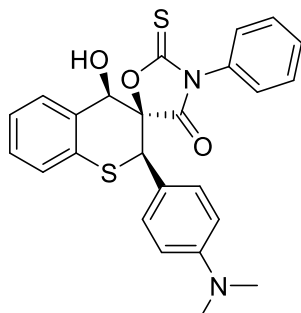
Yield 190 mg (41%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 8.32 - 8.34 (m, 2 H), 7.77 (d, $J=8.7$ Hz, 2 H), 7.65 (d, $J=7.6$ Hz, 1 H), 7.43 - 7.47 (m, 3 H), 7.27 - 7.33 (m, 3 H), 7.19 (d, $J=7.7$ Hz, 1 H), 6.64 (dd, $J=6.2, 3.0$ Hz, 2 H), 5.92 (s, 1 H), 5.42 (d, $J=7.6$ Hz, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.6, 171.3, 148.2, 140.6, 133.6, 131.7, 131.1, 130.7, 129.9, 129.7, 128.2, 127.7, 127.1, 125.2, 124.6, 124.1, 88.9, 69.4, 46.0.

HRMS (ESI) m/z : 465.0573 found (calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_5\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 465.0573).

(2'*R,4'*R**,5*S**)-2'-(4-Dimethylaminophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (3c)**



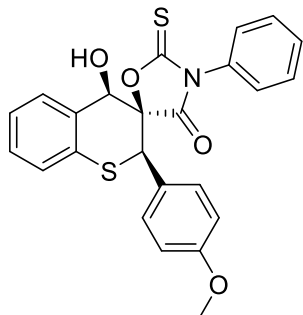
Yield 240 mg (52%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 7.58 - 7.63 (m, 1 H), 7.39 - 7.45 (m, 3 H), 7.26 - 7.29 (m, 3 H), 7.20 - 7.24 (m, 2 H), 6.99 (d, $J=7.8$ Hz, 1 H), 6.73 (d, $J=8.9$ Hz, 2 H), 6.57 (dd, $J=7.6, 1.6$ Hz, 2 H), 5.45 (s, 1 H), 5.39 (d, $J=7.6$ Hz, 1 H), 2.92 (s, 6 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 189.3, 171.8, 151.3, 133.6, 132.4, 132.1, 129.8, 129.7, 129.4, 127.9, 127.9, 127.7, 127.3, 124.6, 124.3, 119.2, 112.1, 89.8, 69.1, 46.4.

HRMS (ESI) m/z : 463.1148 found (calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 463.1145).

(2'R*,4'R*,5S*)-4'-Hydroxy-2'-(4-methoxyphenyl)-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (3d)



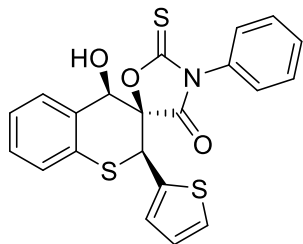
Yield 256 mg (57%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ ppm: 7.62 (d, $J=7.9$ Hz, 1 H), 7.44 - 7.47 (m, 3 H), 7.42 (d, $J=8.7$ Hz, 2 H), 7.29 (t, $J=7.2$ Hz, 1 H), 7.22 - 7.26 (m, 2 H), 7.04 (d, $J=7.7$ Hz, 1 H), 7.00 (d, $J=8.8$ Hz, 2 H), 6.58 (dd, $J=6.3, 2.7$ Hz, 2 H), 5.58 (s, 1 H), 5.40 (d, $J=7.7$ Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ ppm: 189.1, 171.6, 160.2, 133.6, 132.0, 131.9, 130.5, 129.8, 129.5, 128.0, 127.7, 127.1, 124.7, 124.6, 124.3, 114.3, 89.5, 69.1, 55.4, 46.1.

HRMS (ESI) m/z : 450.0827 found (calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 450.0828).

(2'S*,4'R*,5S*)-4'-Hydroxy-3-phenyl-2'-(thiophen-2-yl)-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (3e)



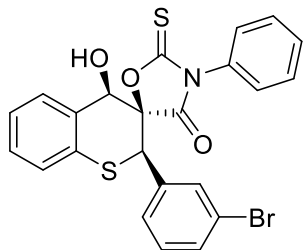
Yield 225 mg (53%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ ppm: 7.72 (dd, $J=4.9, 0.3$ Hz, 1 H), 7.62 (dd, $J=7.1, 0.6$ Hz, 1 H), 7.45 - 7.52 (m, 3 H), 7.19 - 7.31 (m, 4 H), 7.10 - 7.16 (m, 2 H), 6.70 (td, $J=3.7, 1.7$ Hz, 2 H), 6.11 (s, 1 H), 5.43 (d, $J=7.7$ Hz, 1 H).

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ ppm: 189.1, 171.4, 134.7, 133.5, 132.0, 131.5, 129.9, 129.6, 129.1, 128.4, 128.0, 127.8, 127.2, 127.1, 124.9, 124.0, 89.1, 69.0, 42.2.

HRMS (ESI) m/z : 426.0289 found (calcd for $\text{C}_{21}\text{H}_{16}\text{NO}_3\text{S}_3^+$, $[\text{M}+\text{H}]^+$ 426.0287).

(2'*R,4'*R**,5*S**)-2'-(3-Bromophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (3f)**



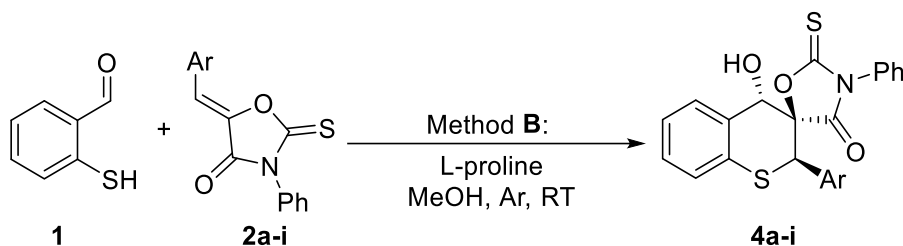
Yield 372 mg (75%), beige solid, m.p. over 250 °C with decomposition.

¹H NMR (300 MHz, DMSO-*d*₆) δ ppm: 7.67 - 7.75 (m, 2 H), 7.63 (dd, *J*=7.4, 0.6 Hz, 1 H), 7.44 - 7.52 (m, 5 H), 7.24 - 7.33 (m, 3 H), 7.15 (d, *J*=7.7 Hz, 1 H), 6.53 - 6.64 (m, 2 H), 5.73 (s, 1 H), 5.39 (d, *J*=7.7 Hz, 1 H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ ppm 188.8, 171.4, 135.7, 133.5, 132.6, 131.8, 131.8, 131.3, 131.2, 129.9, 129.6, 128.4, 128.1, 127.7, 127.0, 125.0, 124.5, 122.0, 89.1, 69.1, 46.0.

HRMS (ESI) *m/z*: 497.9826 found (calcd for C₂₃H₁₇BrNO₃S₂⁺, [M+H]⁺ 497.9828).

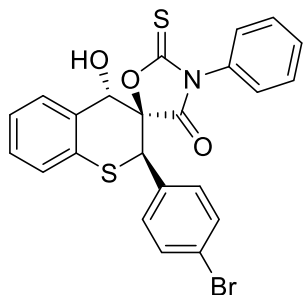
S5. General experimental procedures for the synthesis of compounds 4



Method B

A mixture of the 2-mercaptobenzaldehyde **1** (1 mmol) and a corresponding 3-phenyl-2-thioxooxazolidin-4-one **2** (1 mmol) was dissolved in freshly distilled MeOH (10 ml). Then L-proline (10 mol %) was added and the reaction mixture was stirred for 4 hours under argon atmosphere. The progress of the reaction was monitored by TLC and ^1H NMR. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 5:1).

(2'R*,4'S*,5S*)-2'-(4-Bromophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (**4a**)



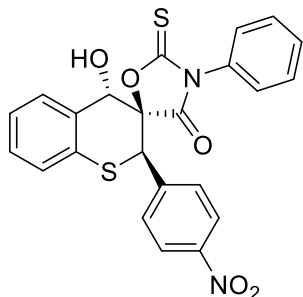
Yield 349 mg (70%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 7.67 (m, 2 H), 7.45 - 7.51 (m, 4 H), 7.43 (m, 2 H), 7.38 - 7.41 (m, 1 H), 7.34 - 7.38 (m, 1 H), 7.30 (td, $J=7.4$, 1.4 Hz, 1 H), 6.82 (d, $J=6.1$ Hz, 1 H), 6.79 (dd, $J=7.5$, 1.8 Hz, 2 H), 5.24 (d, $J=6.0$ Hz, 1 H), 5.14 (s, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.0, 170.2, 133.3, 132.7, 132.5, 132.1, 131.8, 131.7, 130.0, 129.8, 129.4, 128.5, 127.4, 126.1, 125.6, 122.8, 89.3, 69.2, 46.1.

HRMS (ESI) m/z : 497.9826 found (calcd for $\text{C}_{23}\text{H}_{17}\text{BrNO}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 497.9828).

(2'*R,4'*S**,5*S**)-4'-Hydroxy-2'-(4-nitrophenyl)-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4b)**



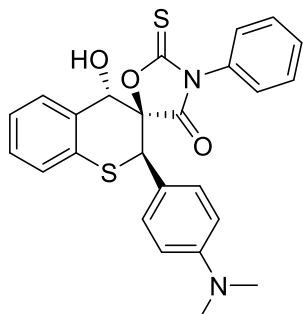
Yield 246 mg (53%), yellow solid, m.p. over 250 °C with decomposition.

¹H NMR (700 MHz, DMSO-*d*₆) δ ppm: 8.31 (d, *J*=8.7 Hz, 2 H), 7.76 (d, *J*=8.7 Hz, 2 H), 7.53 (d, *J*=7.4 Hz, 1 H), 7.44 - 7.49 (m, 3 H), 7.43 (d, *J*=7.4 Hz, 1 H), 7.38 (td, *J*=7.5, 1.1 Hz, 1 H), 7.33 (td, *J*=7.5, 1.1 Hz, 1 H), 6.94 (d, *J*=6.1 Hz, 1 H), 6.87 (dd, *J*=7.6, 1.7 Hz, 2 H), 5.30 (s, 1 H), 5.26 (d, *J*=6.0 Hz, 1 H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm: 187.8, 170.0, 148.0, 140.7, 133.6, 132.4, 132.0, 131.0, 129.8, 129.6, 129.5, 128.6, 127.4, 126.4, 126.0, 123.9, 89.7, 69.5, 46.6.

HRMS (ESI) *m/z*: 465.0573 found (calcd for C₂₃H₁₇N₂O₅S₂⁺, [M+H]⁺ 465.0573).

4-(2'*R,4'*S**,5*S**)-2'-(4-Dimethylaminophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4c)**



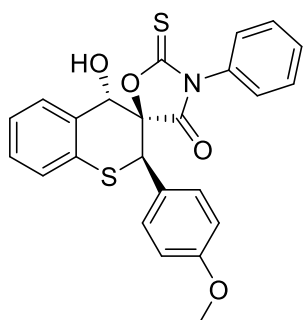
Yield 189 mg (41%), white solid, m.p. over 250 °C with decomposition.

¹H NMR (300 MHz, DMSO-*d*₆) δ ppm: 7.40 - 7.46 (m, 4 H), 7.31 - 7.36 (m, 2 H), 7.22 - 7.28 (m, 3 H), 6.65 - 6.76 (m, 5 H), 5.22 (d, *J*=6.0 Hz, 1 H), 5.04 (s, 1 H), 2.92 (s, 6 H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm: 188.4, 170.5, 151.1, 133.7, 133.0, 132.3, 130.6, 130.6, 130.2, 130.2, 129.6, 129.6, 129.3, 129.3, 128.5, 128.5, 127.6, 125.7, 125.7, 125.0, 125.0, 118.9, 112.1, 89.0, 69.0, 45.5.

HRMS (ESI) *m/z*: 463.1148 found (calcd for C₂₅H₂₃N₂O₃S₂⁺, [M+H]⁺ 463.1145).

(2'R*,4'S*,5S*)-4'-Hydroxy-2'-(4-methoxyphenyl)-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4d)



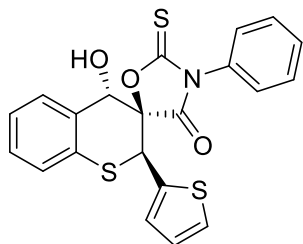
Yield 283 mg (63%), white solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, DMSO- d_6) δ ppm: 7.43 - 7.49 (m, 4 H), 7.41 (s, 1 H), 7.34 - 7.39 (m, 3 H), 7.24 - 7.30 (m, 1 H), 7.00 (d, $J=8.6$ Hz, 2 H), 6.70 - 6.79 (m, 3 H), 5.24 (d, $J=6.1$ Hz, 1 H), 5.10 (s, 1 H), 3.79 (s, 3 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.2, 170.4, 160.1, 133.3, 133.1, 132.2, 130.8, 130.4, 129.7, 129.4, 128.5, 127.4, 125.9, 125.3, 124.4, 114.2, 89.1, 69.1, 55.4, 45.6.

HRMS (ESI) m/z : 450.0827 found (calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 450.0828).

(2'S*,4'S*,5S*)-4'-Hydroxy-3-phenyl-2'-(thiophen-2-yl)-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4e)



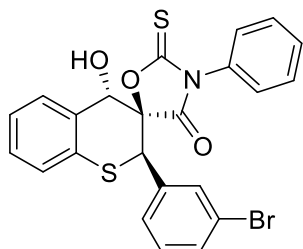
Yield 234 mg (55%), yellow solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, DMSO- d_6) δ ppm: 7.72 (d, $J=5.0$ Hz, 1 H), 7.42 - 7.50 (m, 4 H), 7.31 - 7.38 (m, 2 H), 7.23 - 7.30 (m, 2 H), 7.12 (dd, $J=4.9, 3.7$ Hz, 1 H), 6.79 - 6.87 (m, 2 H), 6.76 (d, $J=6.0$ Hz, 1 H), 5.64 (s, 1 H), 5.31 (d, $J=6.1$ Hz, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.2, 170.0, 134.8, 132.6, 132.2, 131.0, 129.8, 129.4, 128.7, 128.5, 127.5, 127.1, 125.3, 87.7, 68.7, 40.6.

HRMS (ESI) m/z : 426.0288 found (calcd for $\text{C}_{21}\text{H}_{16}\text{NO}_3\text{S}_3^+$, $[\text{M}+\text{H}]^+$ 426.0287).

(2'R*,4'S*,5S*)-2'-(3-Bromophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4f)



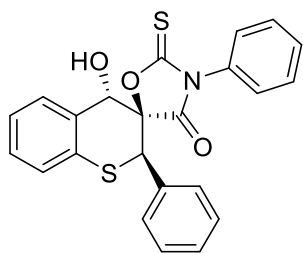
Yield 412 mg (83%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, DMSO- d_6): δ ppm 7.66 - 7.72 (m, 2 H), 7.41 - 7.50 (m, 6 H), 7.35 - 7.40 (m, 2 H), 7.25 - 7.33 (m, 1 H), 6.83 (d, J =5.9 Hz, 1 H), 6.72 - 6.79 (m, 2 H), 5.27 (d, J =5.9 Hz, 1 H), 5.20 (s, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6): δ ppm 188.0, 170.1, 135.7, 133.1, 132.6, 132.3, 132.2, 132.1, 131.0, 130.2, 129.8, 129.5, 128.8, 128.6, 127.4, 126.0, 125.5, 121.9, 88.9, 68.9, 45.8.

HRMS (ESI) m/z : 497.9824 found (calcd for $\text{C}_{23}\text{H}_{17}\text{BrNO}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 497.9828).

(2'R*,4'S*,5S*)-4'-Hydroxy-2',3-diphenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4g)



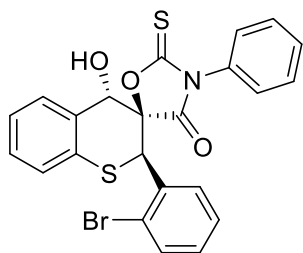
Yield 247 mg (59%), beige solid, m.p. over 250°C with decomposition.

^1H NMR (700 MHz, DMSO- d_6) δ ppm 7.46 - 7.50 (m, 4 H), 7.42 - 7.46 (m, 5 H), 7.34 - 7.39 (m, 2 H), 7.28 (td, J =7.2, 1.7 Hz, 1 H), 6.76 (d, J =6.2 Hz, 1 H), 6.69 (dd, J =6.4, 2.8 Hz, 2 H), 5.25 (d, J =6.0 Hz, 1 H), 5.13 (s, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.2, 170.3, 133.2, 133.0, 132.9, 132.1, 130.3, 129.7, 129.6, 129.5, 129.4, 128.9, 128.6, 127.4, 125.9, 125.4, 89.0, 69.1, 46.3.

HRMS (ESI) m/z : 420.0722 found (calcd for $\text{C}_{23}\text{H}_{18}\text{NO}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 420.0723).

(2'R*,4'S*,5S*)-2'-(2-Bromophenyl)-4'-hydroxy-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4h)



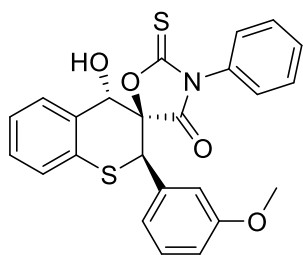
Yield 353 mg (71%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (300 MHz, DMSO- d_6) δ ppm: 7.73 - 7.78 (m, 2 H), 7.46 - 7.56 (m, 6 H), 7.36 - 7.43 (m, 3 H), 7.00 (d, J =6.0 Hz, 1 H), 6.89 (dd, J =7.1, 1.8 Hz, 2 H), 5.56 (s, 1 H), 5.28 (d, J =5.8 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 188.0, 170.0, 134.0, 133.3, 132.6, 132.5, 132.1, 131.3, 131.2, 129.8, 129.5, 129.5, 128.5, 128.5, 127.4, 126.6, 126.2, 124.2, 89.8, 70.2, 45.9.

HRMS (ESI) m/z : 497.9826 found (calcd for $\text{C}_{23}\text{H}_{17}\text{BrNO}_3\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 497.9828).

(2'R*,4'S*,5S*)-4'-Hydroxy-2'-(3-methoxyphenyl)-3-phenyl-2-thioxospiro[oxazolidine-5,3'-thiochroman]-4-one (4i)



Yield 364 mg (81%), beige solid, m.p. over 250 °C with decomposition.

^1H NMR (700 MHz, DMSO- d_6): δ ppm 7.43 - 7.49 (m, 4 H), 7.33 - 7.38 (m, 3 H), 7.26 - 7.29 (m, 1 H), 7.06 - 7.08 (m, 1 H), 7.01 - 7.05 (m, 2 H), 6.73 (d, $J=6.1$ Hz, 1 H), 6.64 - 6.73 (m, 2 H), 5.26 (d, $J=6.0$ Hz, 1 H), 5.14 (s, 1 H), 3.75 (s, 3 H).

^{13}C NMR (75 MHz, DMSO- d_6): δ ppm 188.3, 170.2, 159.3, 134.3, 133.0, 132.9, 132.2, 130.6, 129.9, 129.7, 129.4, 128.6, 127.4, 125.8, 125.3, 121.9, 115.6, 114.4, 88.6, 68.9, 55.2, 45.8.

HRMS (ESI) m/z : 450.0826 found (calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{S}_2^+$, $[\text{M}+\text{H}]^+$ 450.0828).

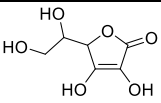
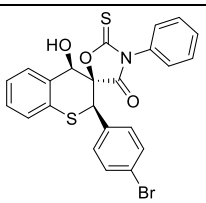
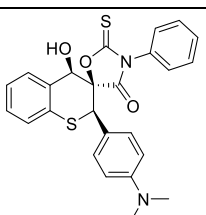
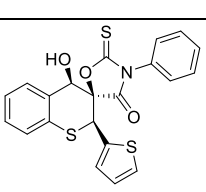
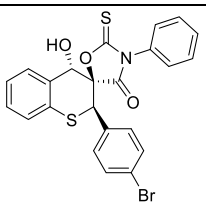
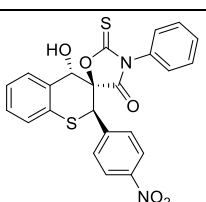
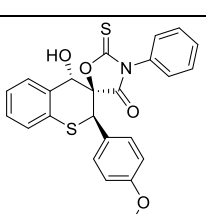
S6. DPPH Radical Scavenging Activity Assay

The free radical scavenging activity (RSA) of the compounds (**3a**, **3c**, **3e**, **4a**, **4b**, **4d**) was investigated using 0.2 mM solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in EtOH. The 0.2 mM solution of ascorbic acid in EtOH was used as a reference standard. The DPPH solution was added to the 2 mM solutions of the compounds (**3a**, **3c**, **3e**, **4a**, **4b**, **4d**) in EtOH in the ratio 1:1. The reaction mixtures were incubated in the dark for 20 min at 25°C. After that, the absorbance of the samples was measured on a Cary 100 Bio spectrophotometer (Varian, United States) at 517 nm. The ability of the compounds (**3a**, **3c**, **3e**, **4a**, **4b**, **4d**) to scavenge free radicals was calculated as follows (1):

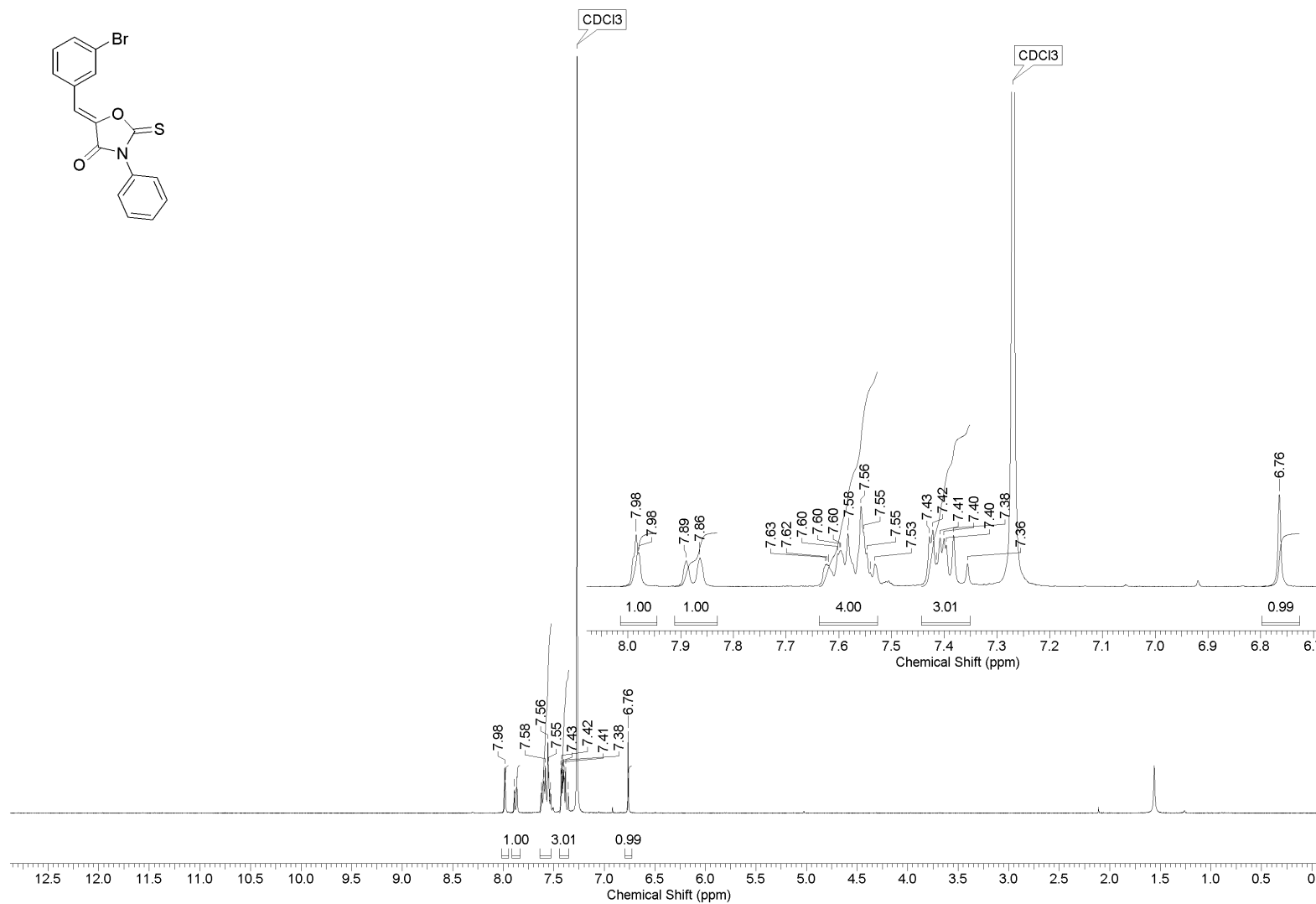
$$RSA = \frac{A_C - A_S}{A_C} \quad (1)$$

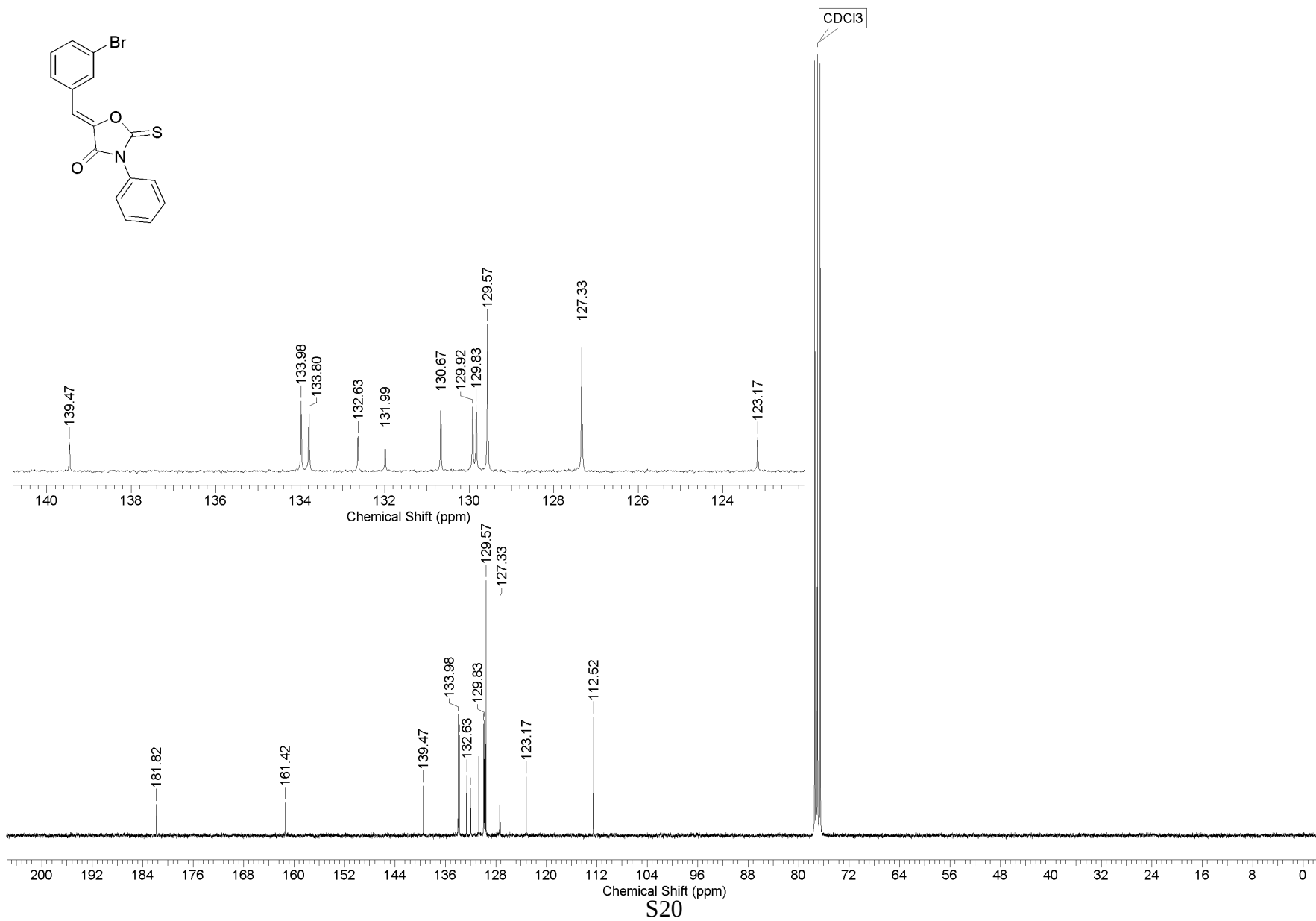
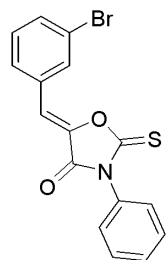
where A_C is the absorbance of the DPPH solution at 517 nm, A_S is the absorbance of the sample's solution at 517 nm.

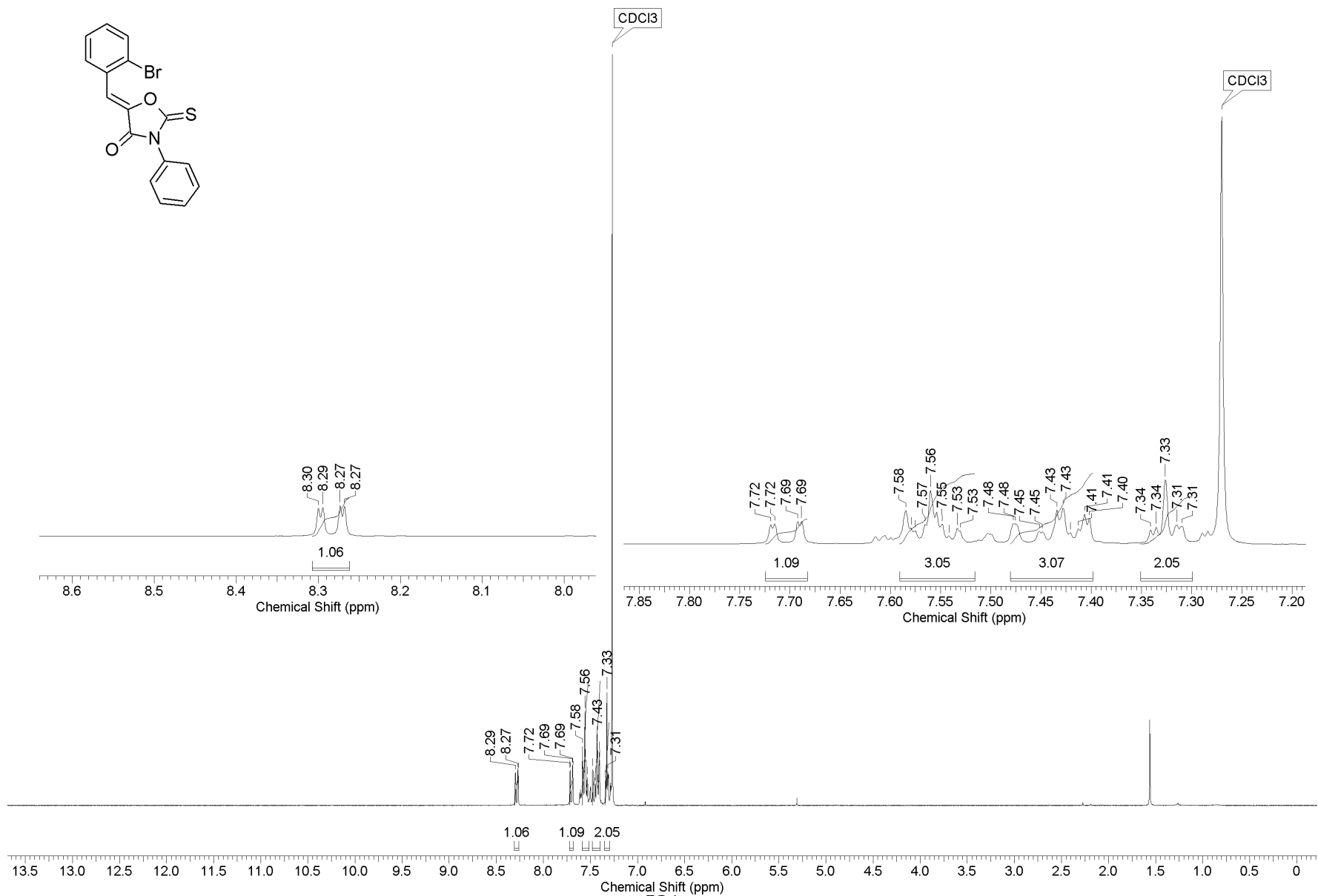
Table S2. The results of DPPH radical scavenging activity assay.

Compound	Structure	RSA
Ascorbic acid		0.941
3a		-0.028
3c		-0.008
3e		-0.001
4a		0.014
4b		0.033
4d		0.025

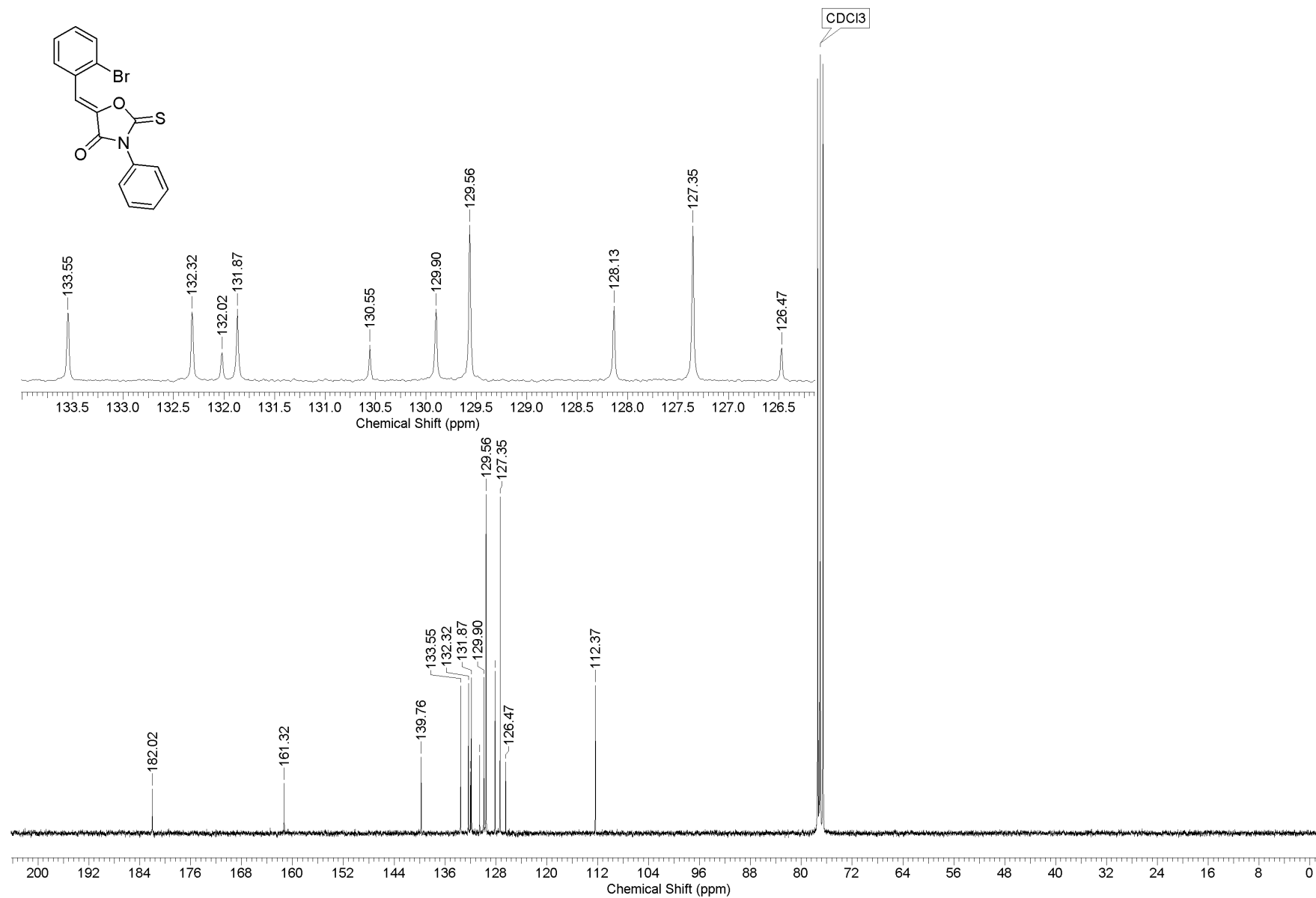
S7. Copies of ^1H and ^{13}C NMR spectra

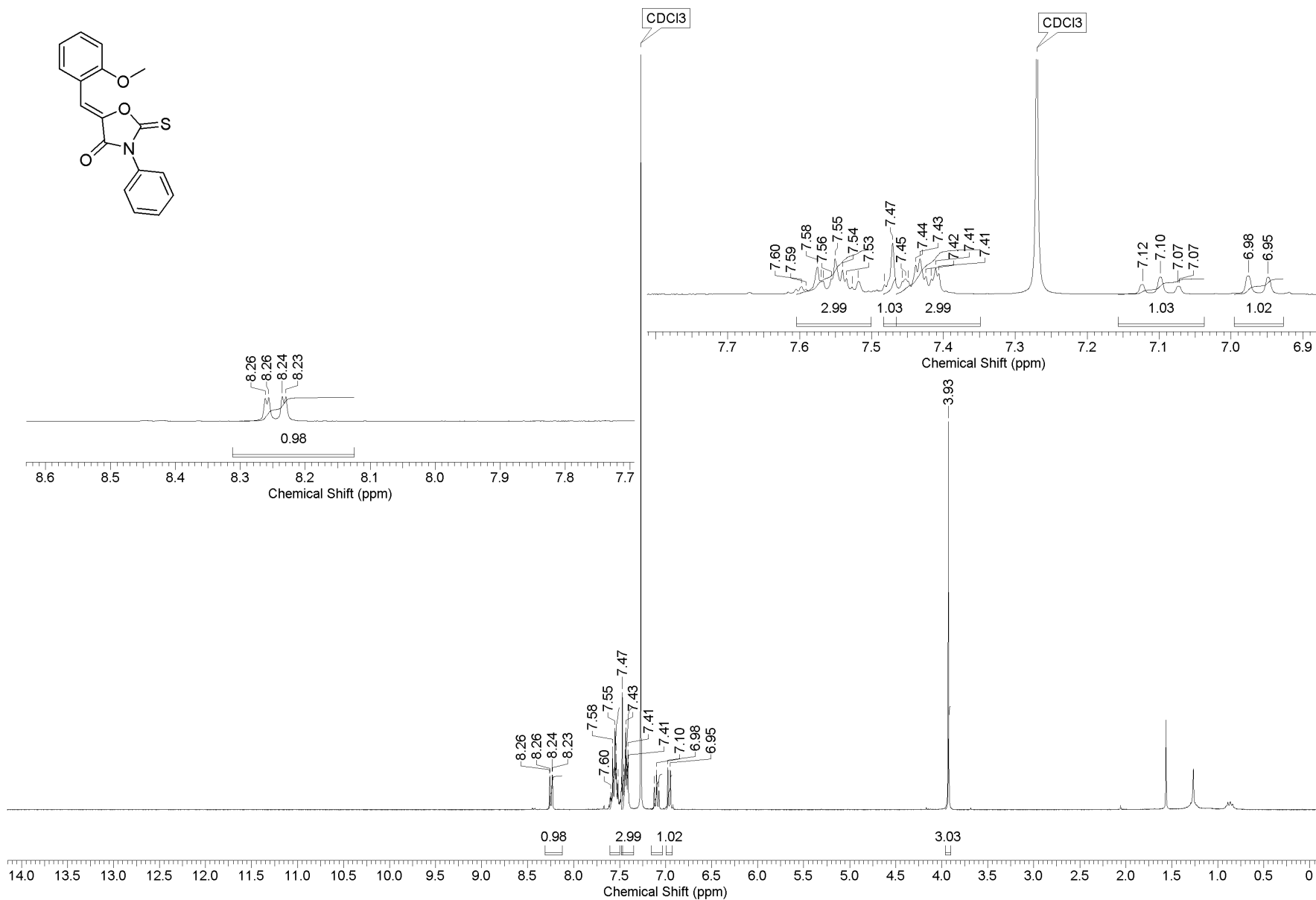
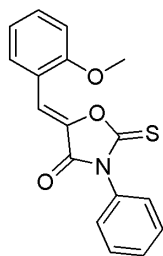




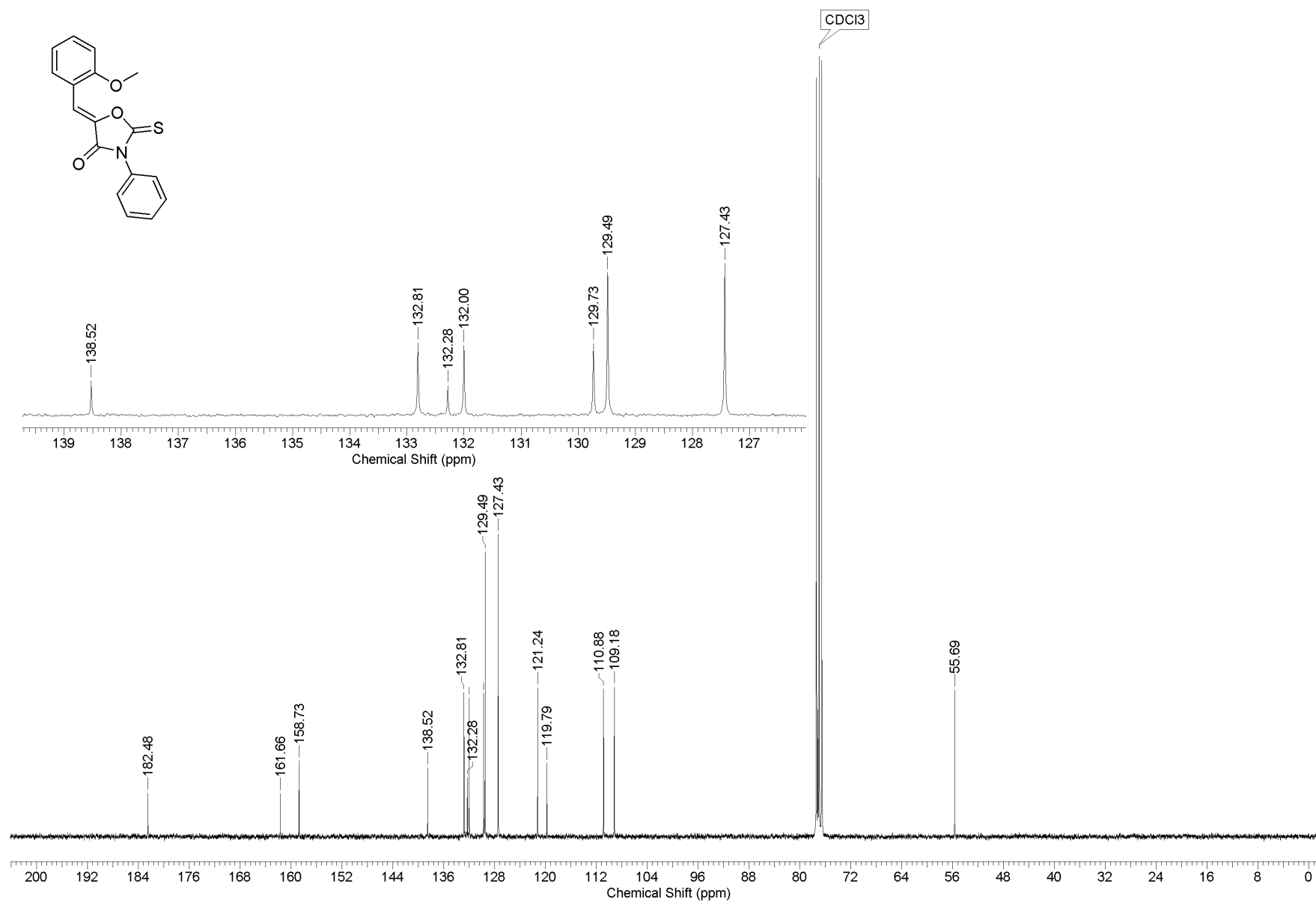
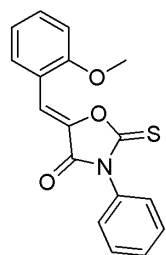


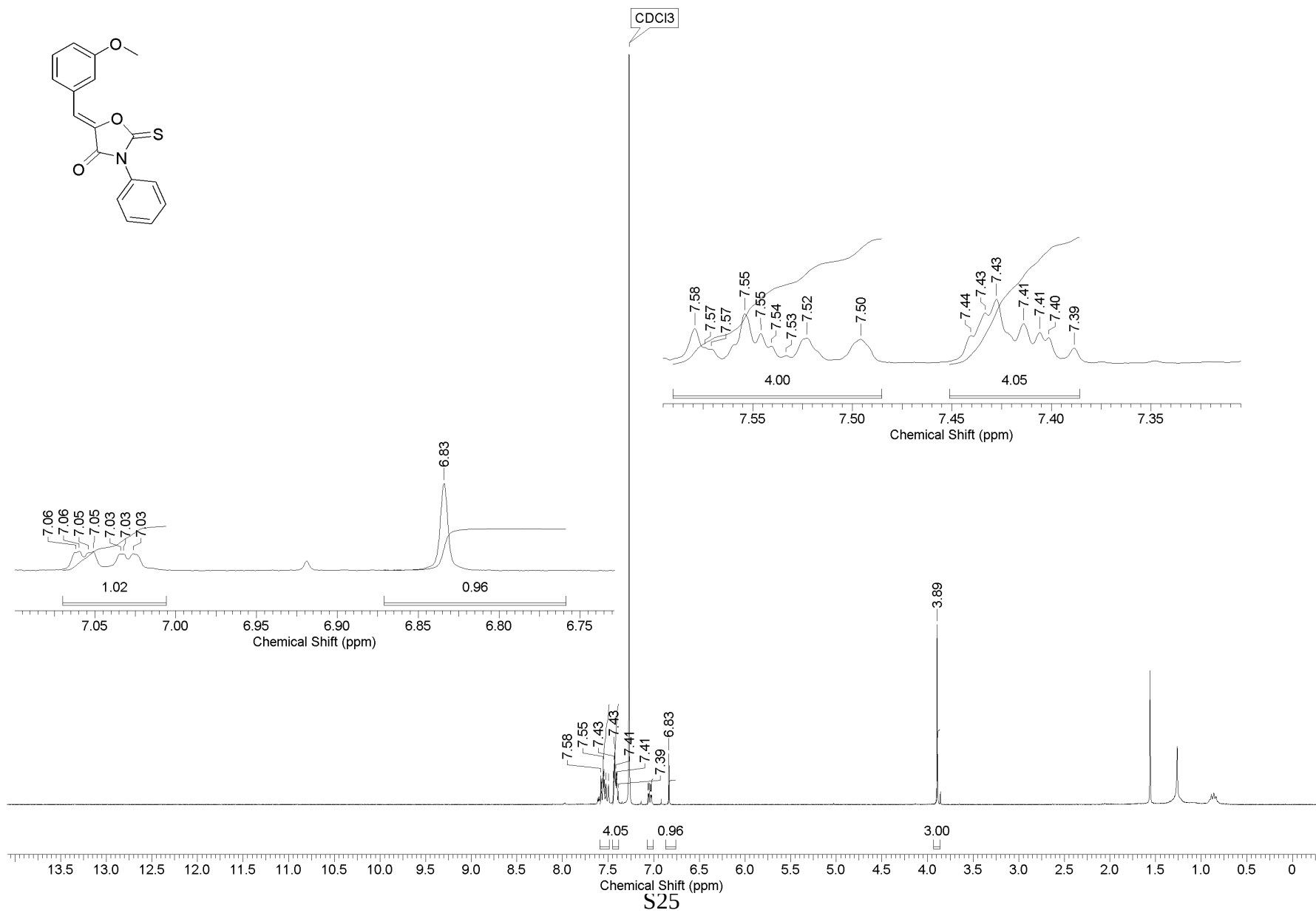
S21

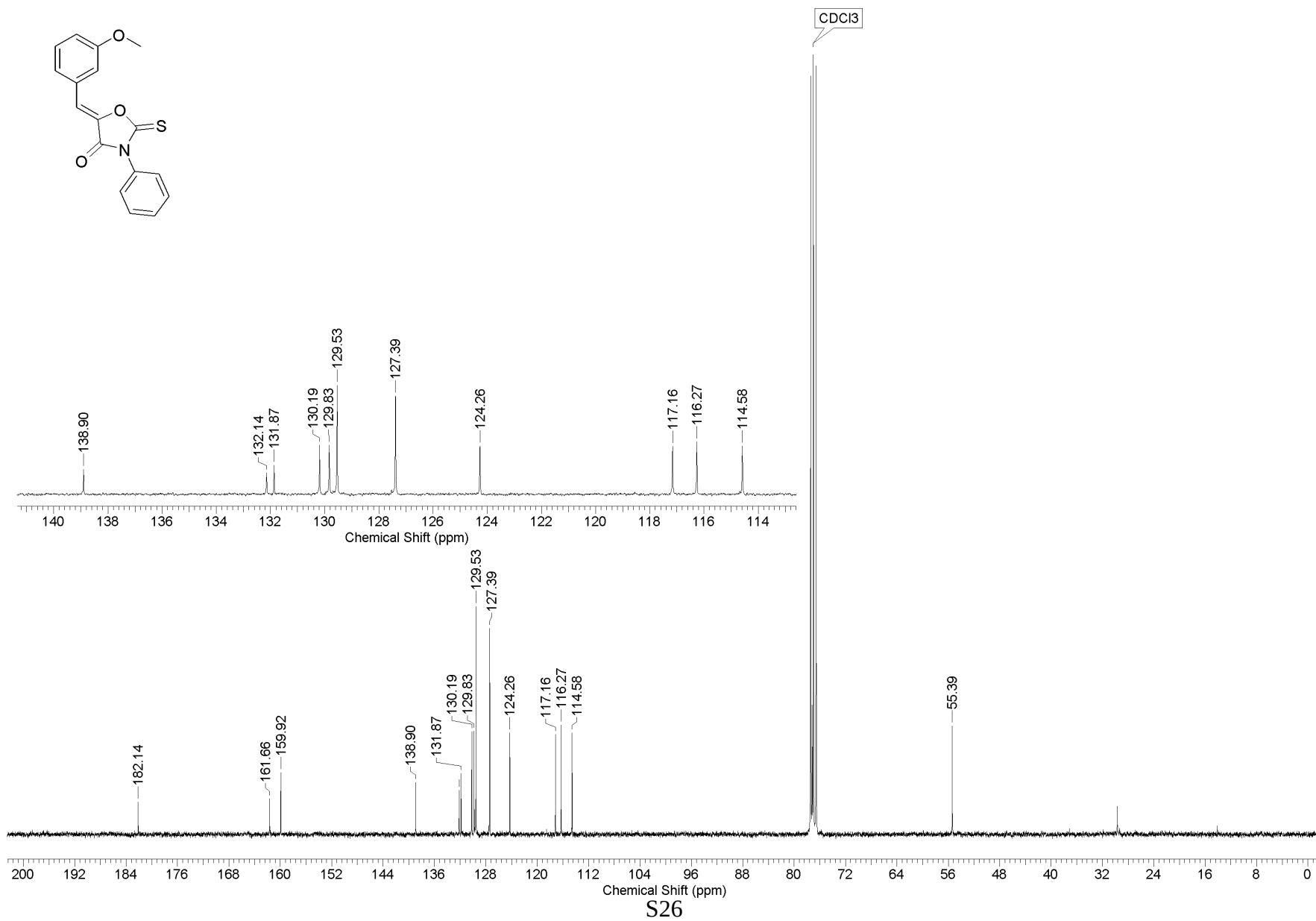
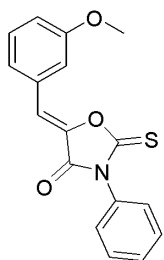


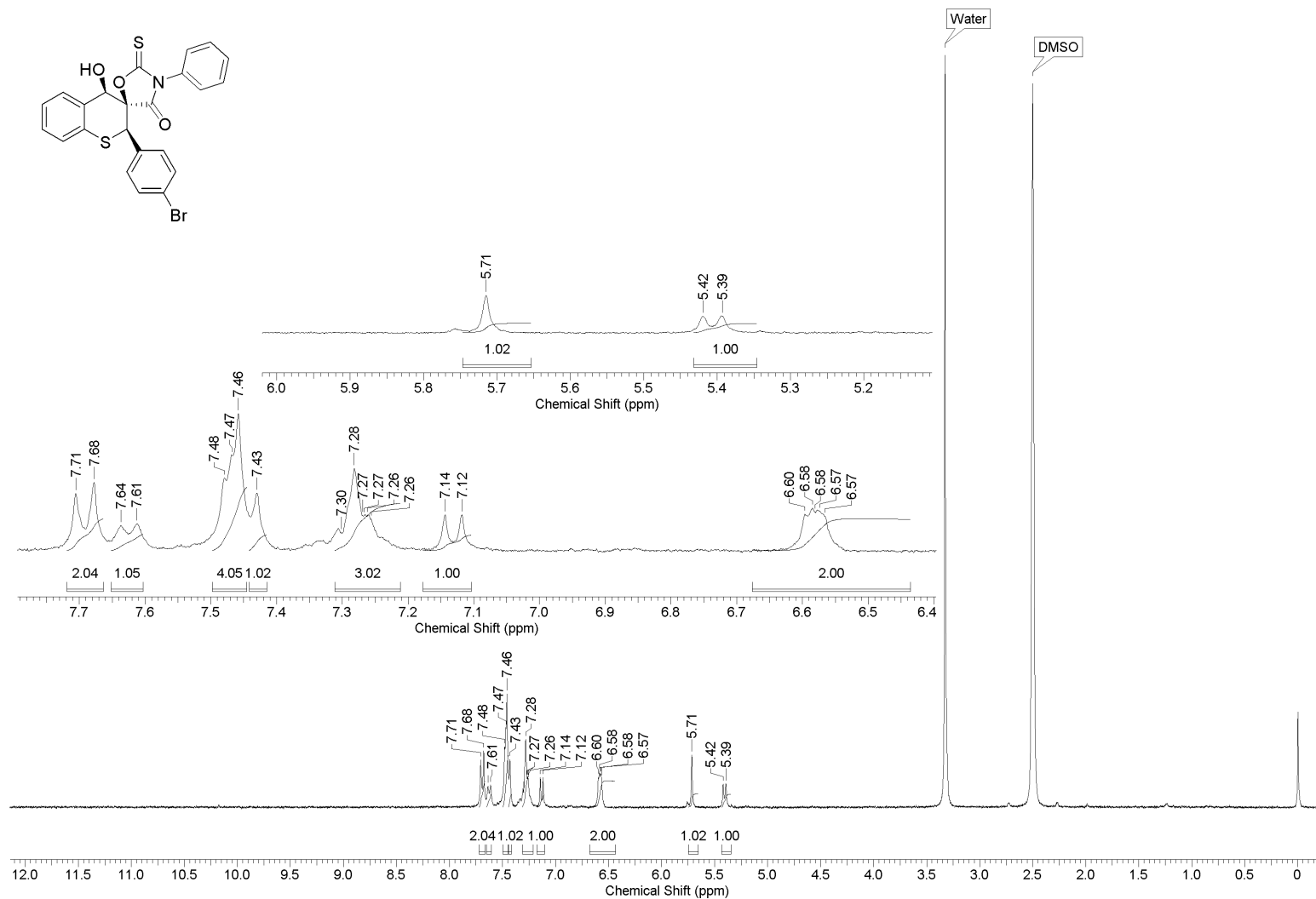


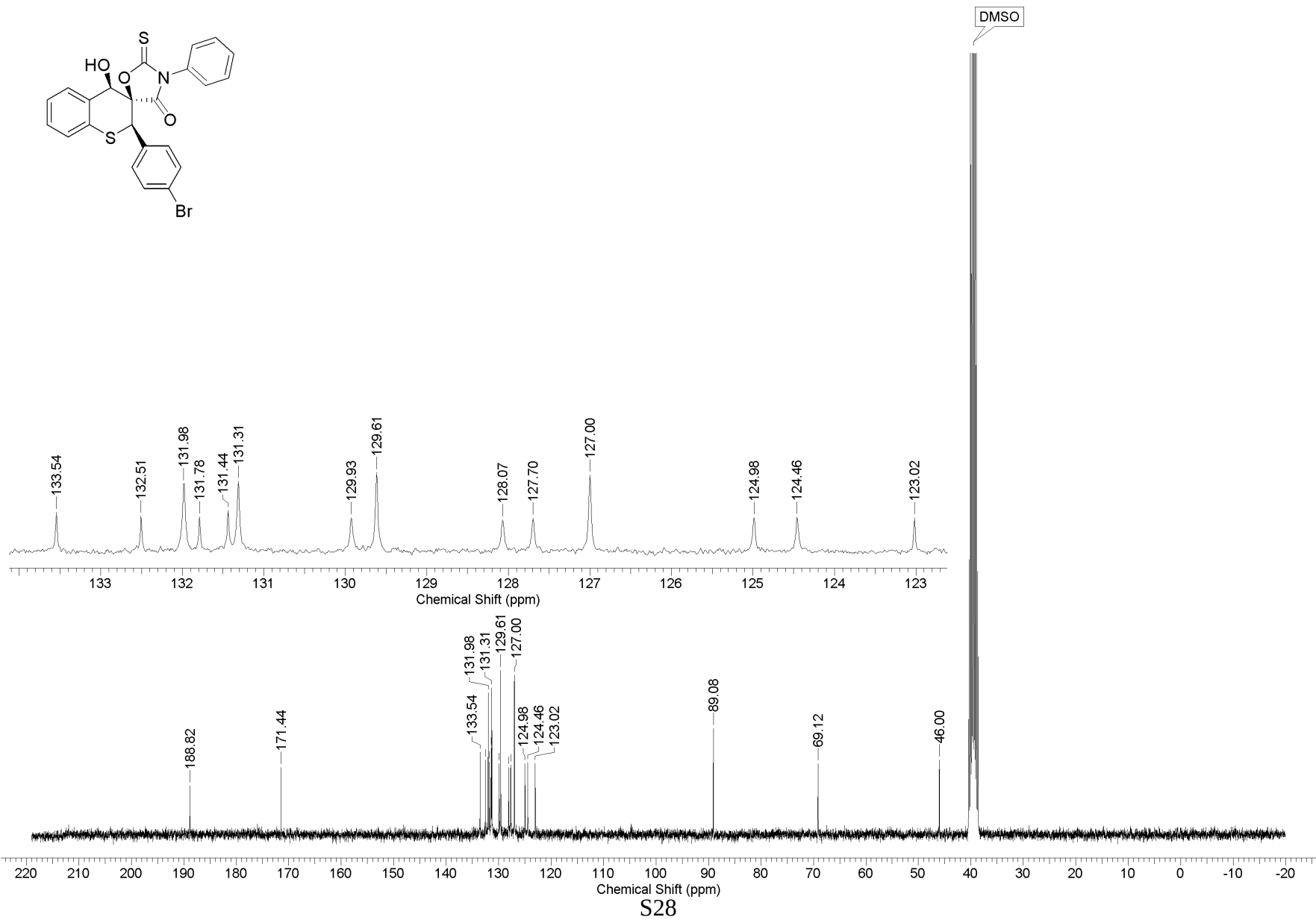
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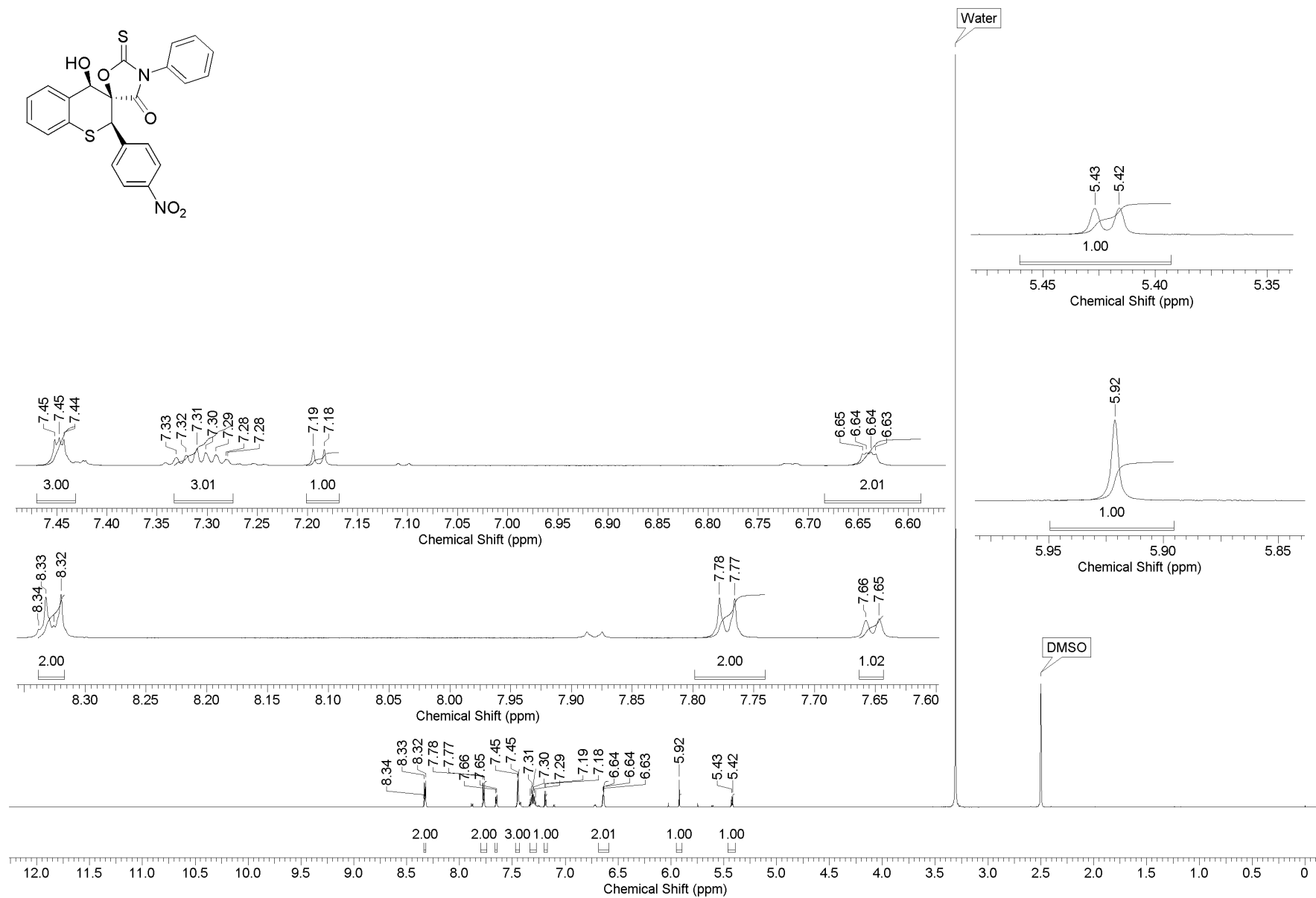
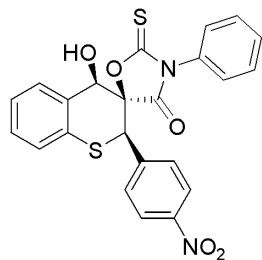


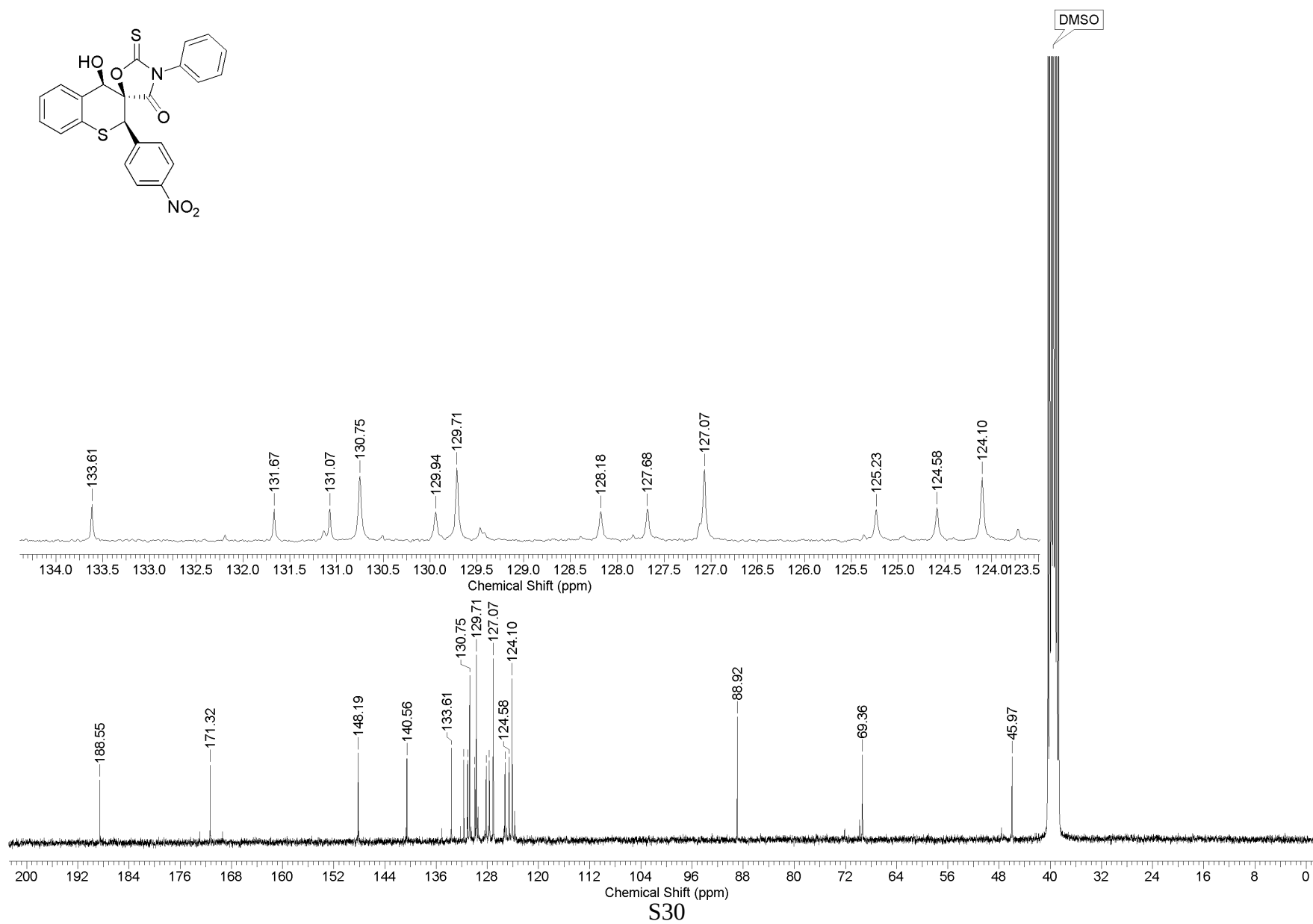
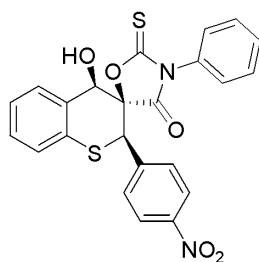


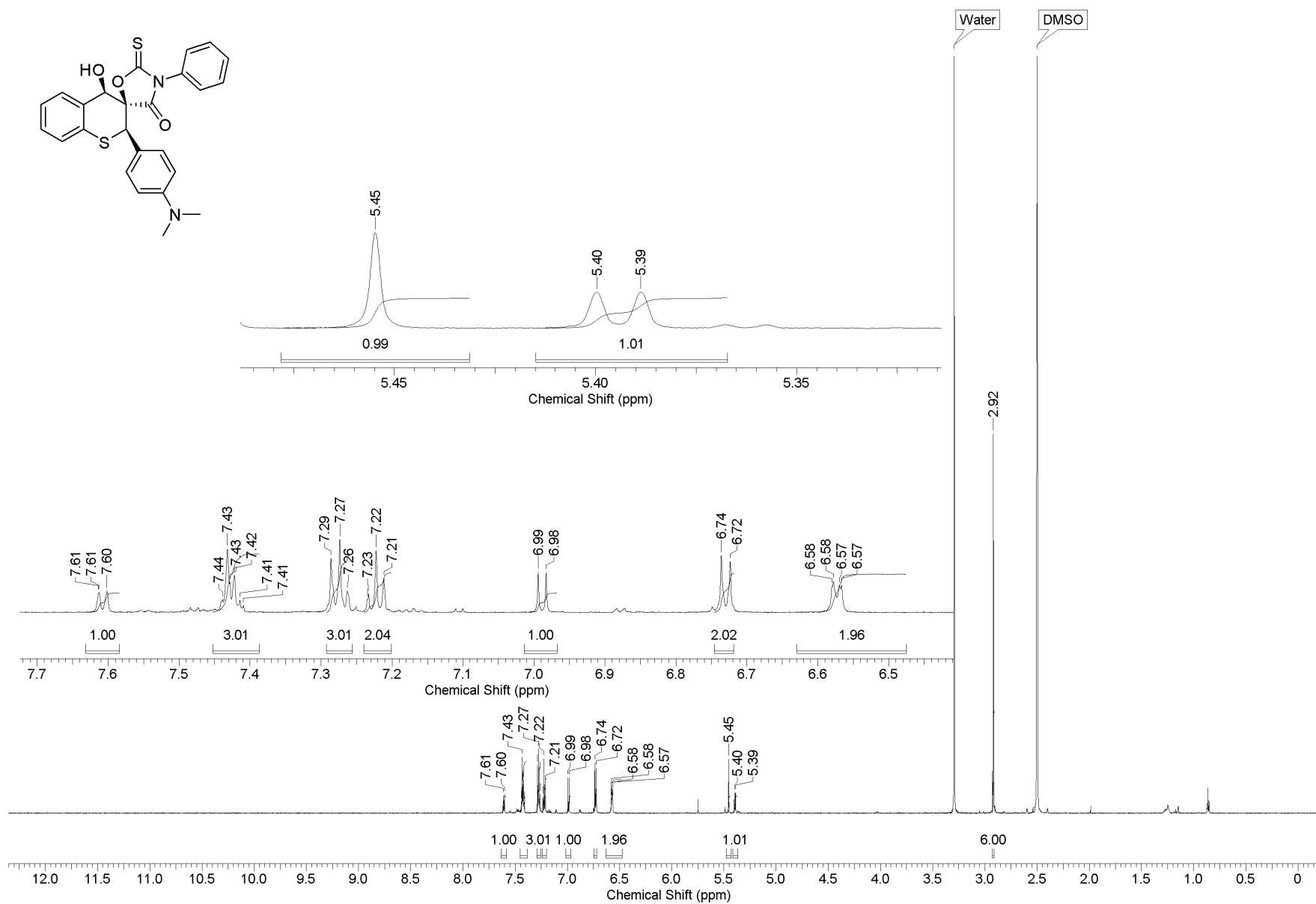
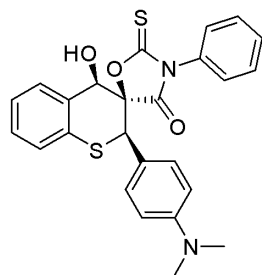




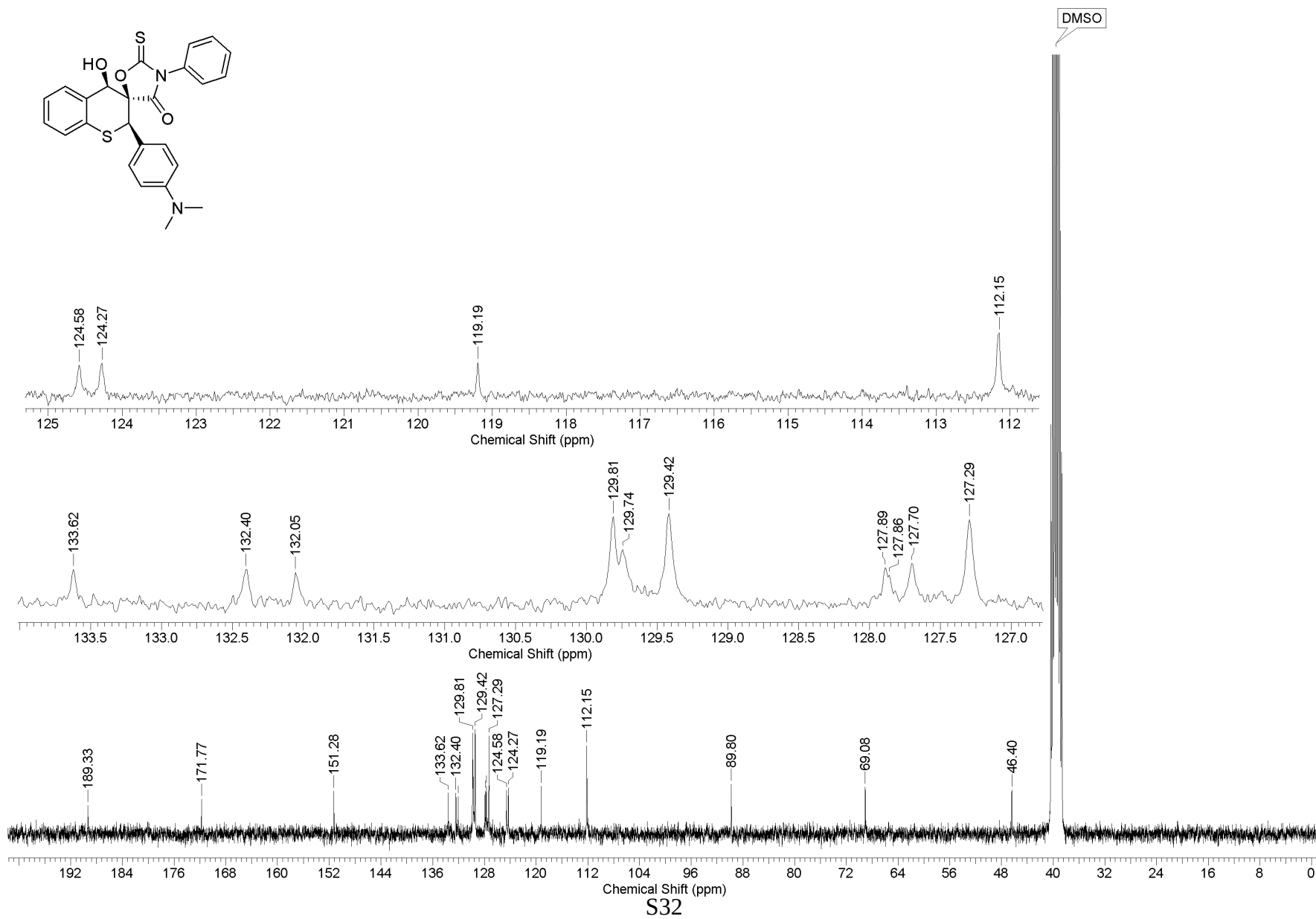
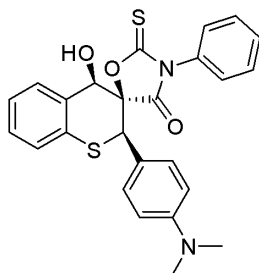


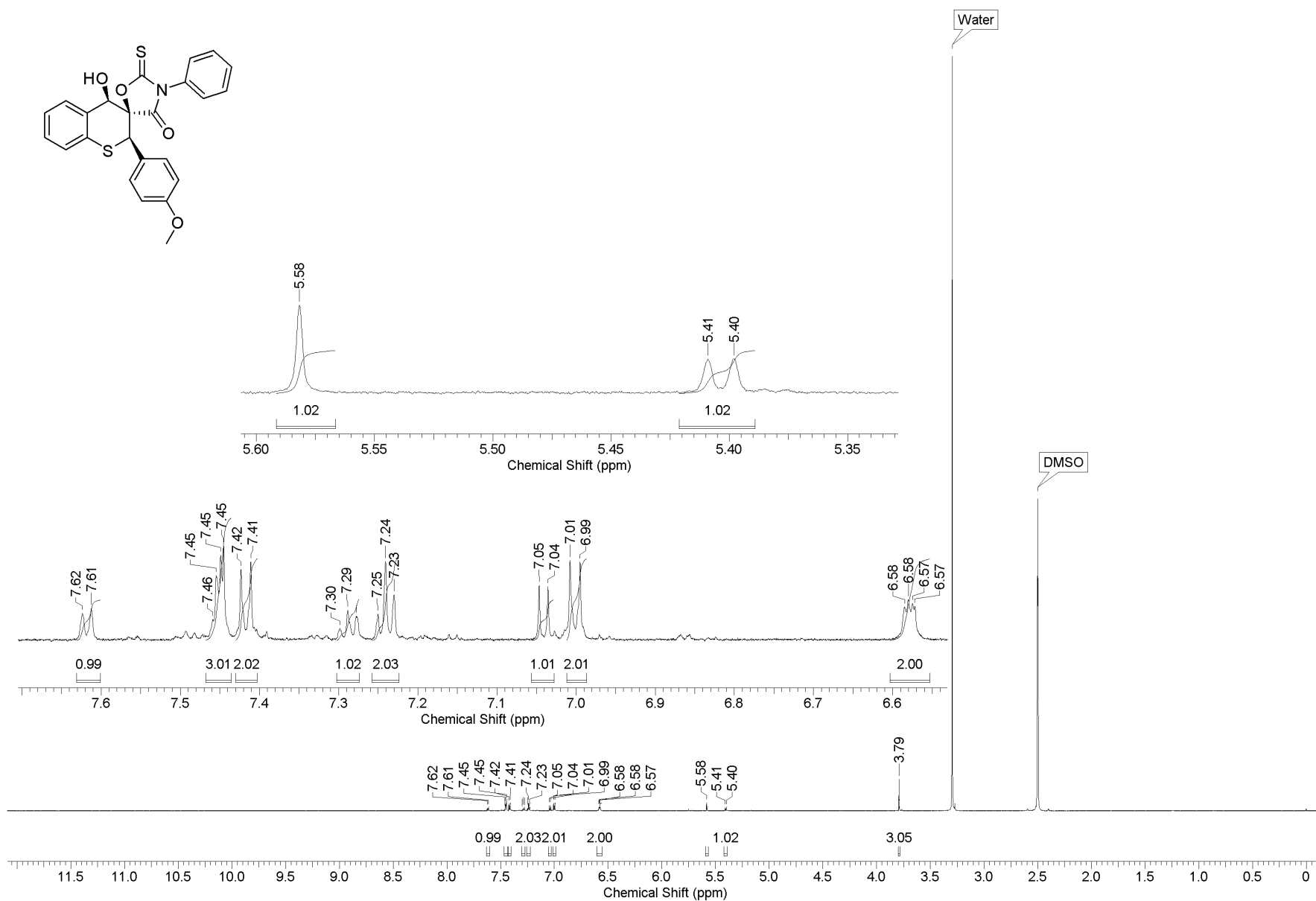
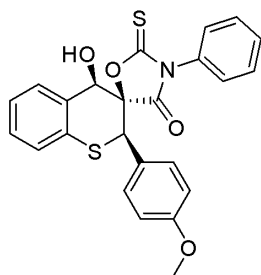




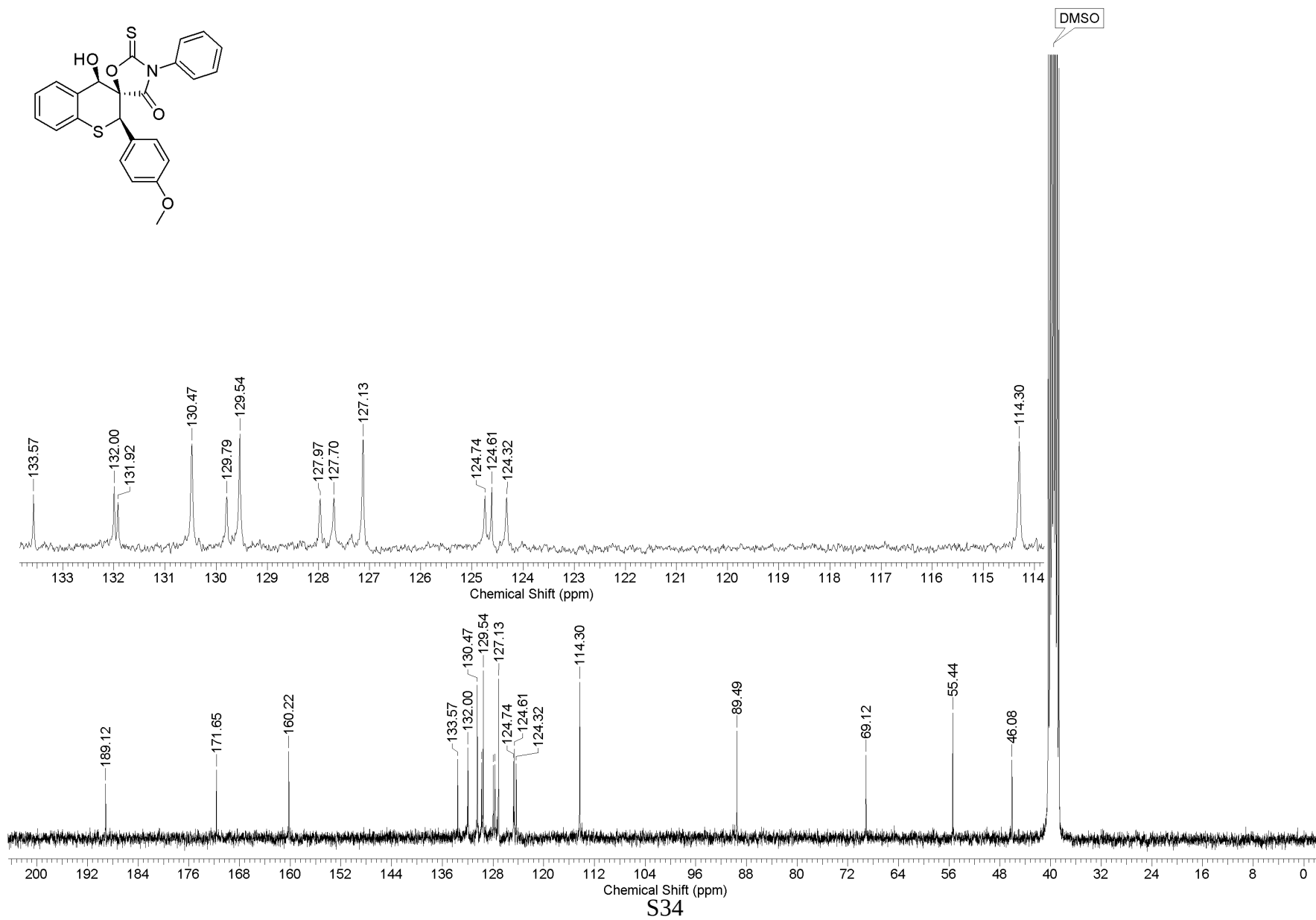
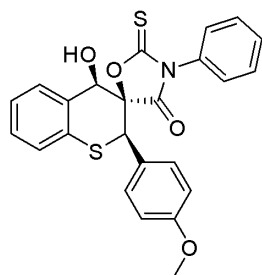


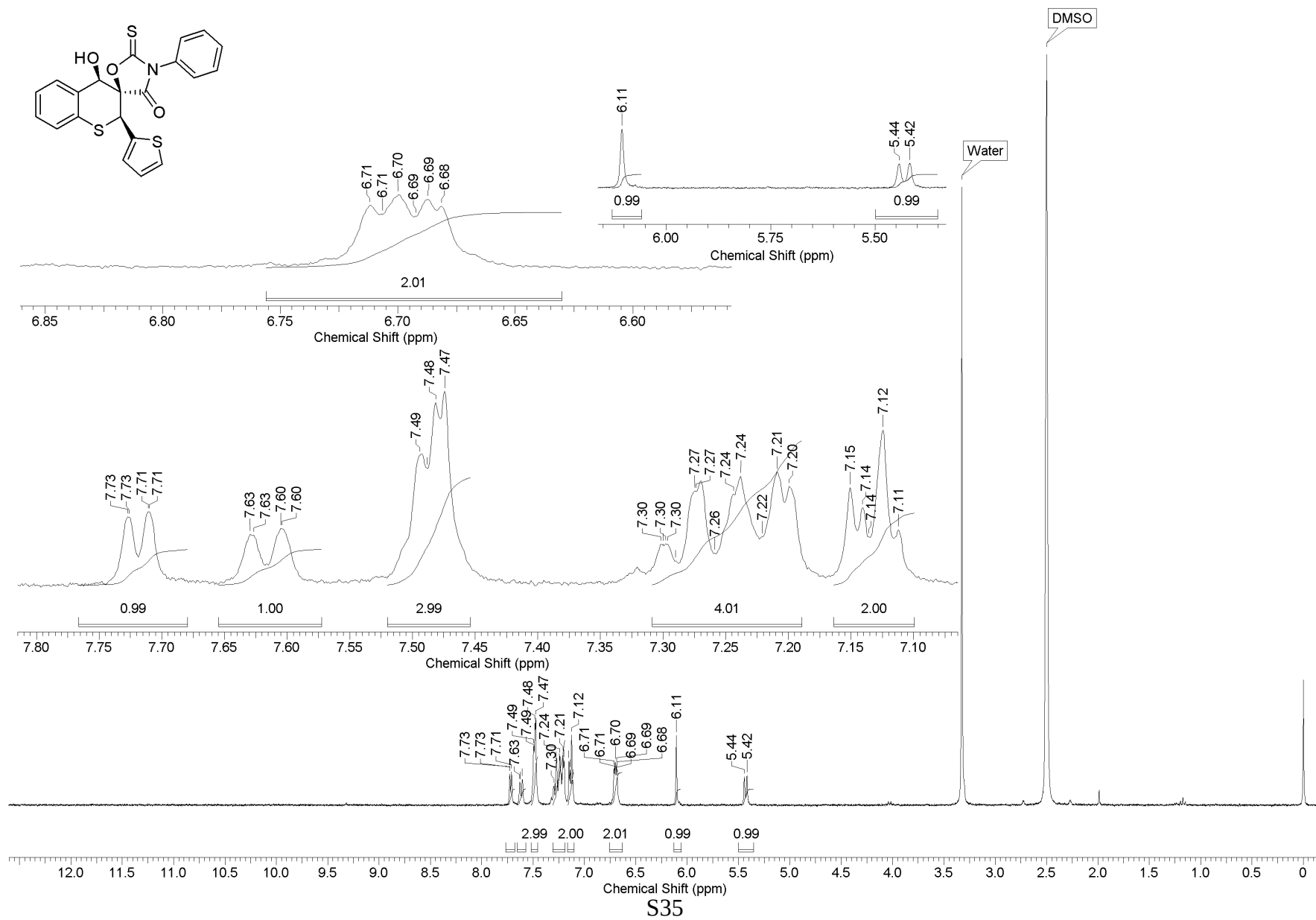
S31

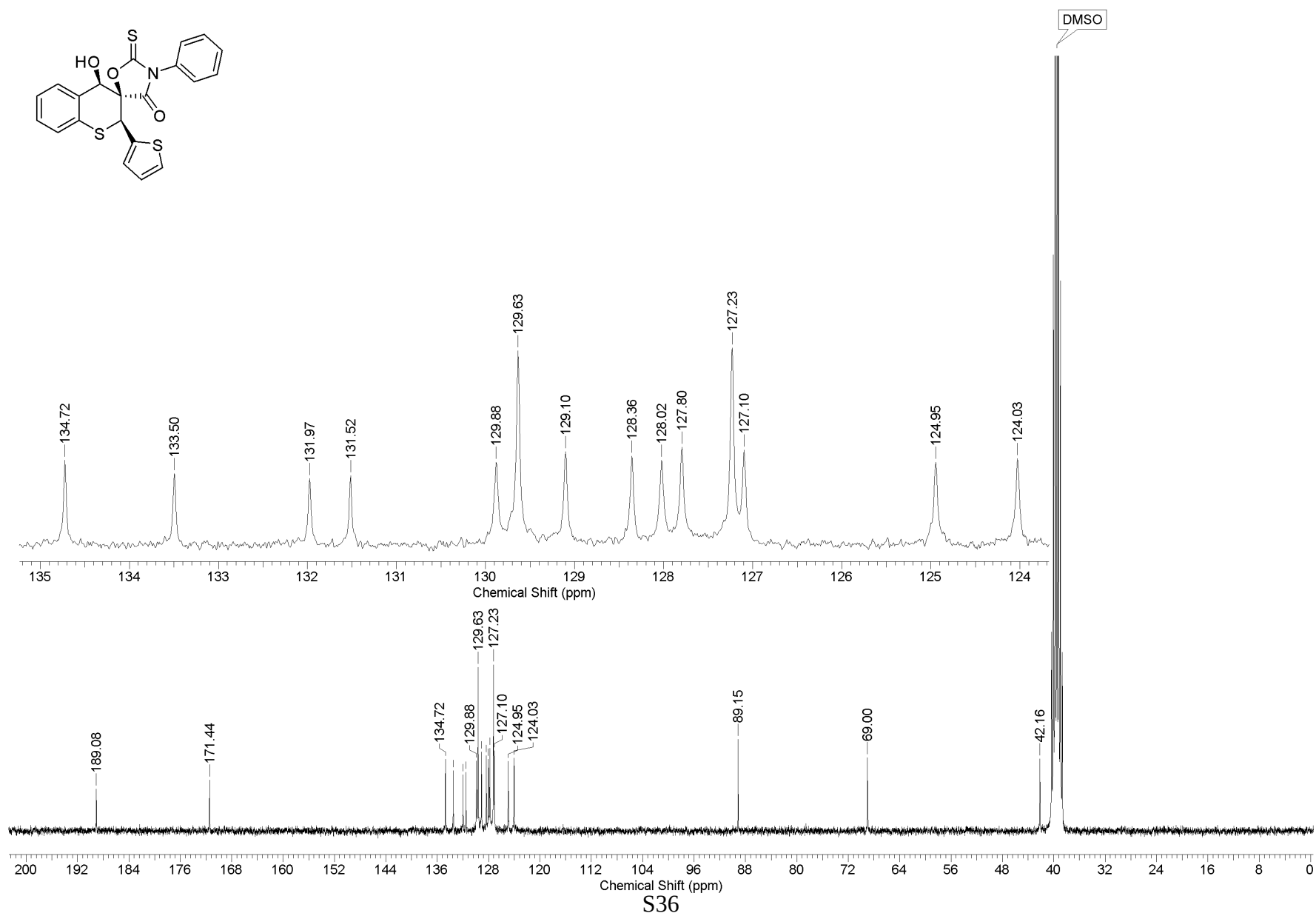
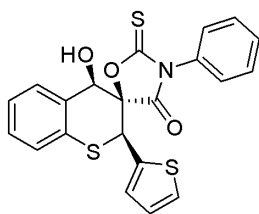


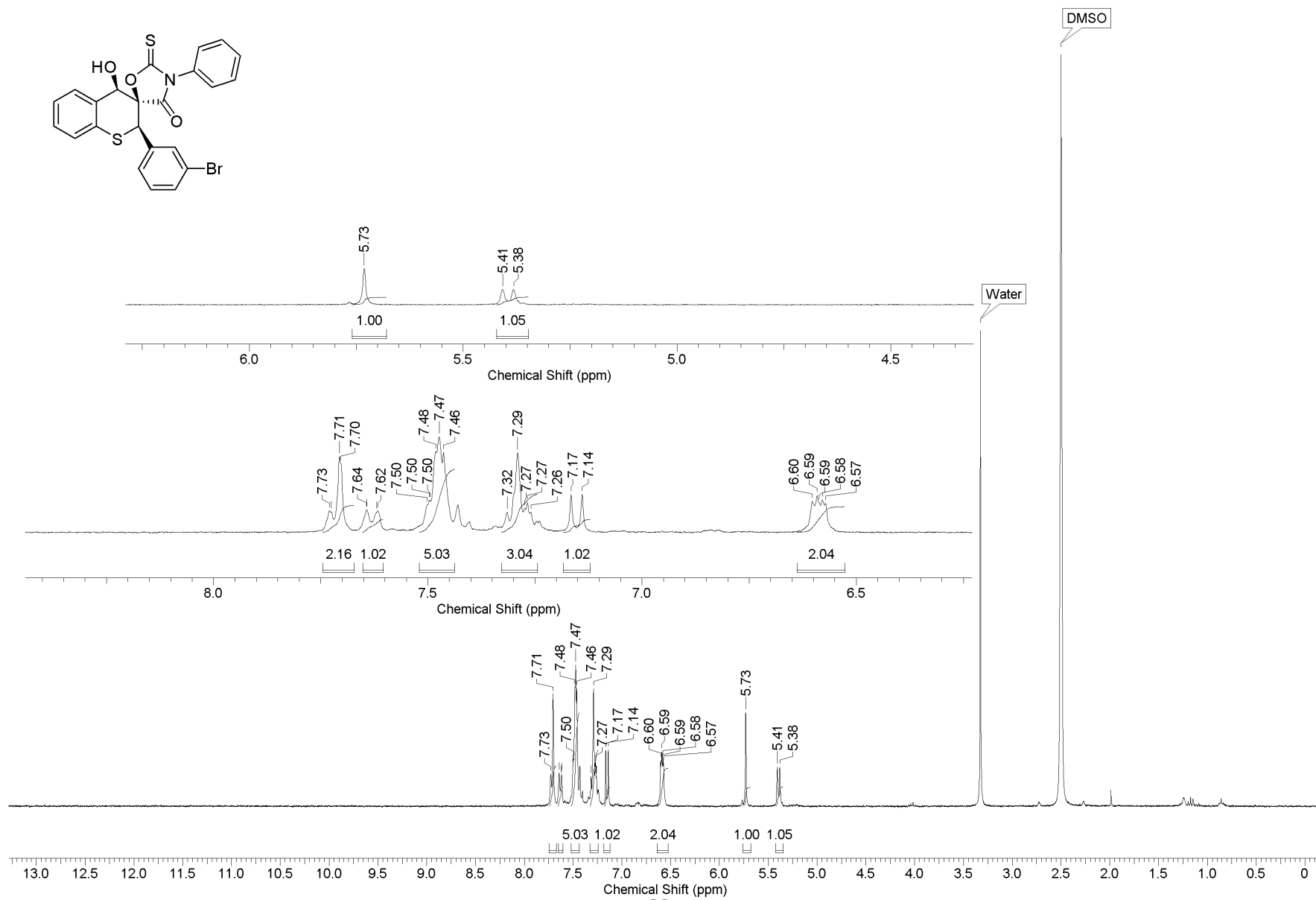
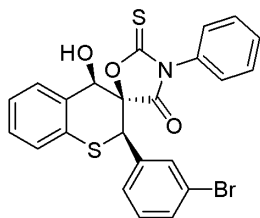


S33

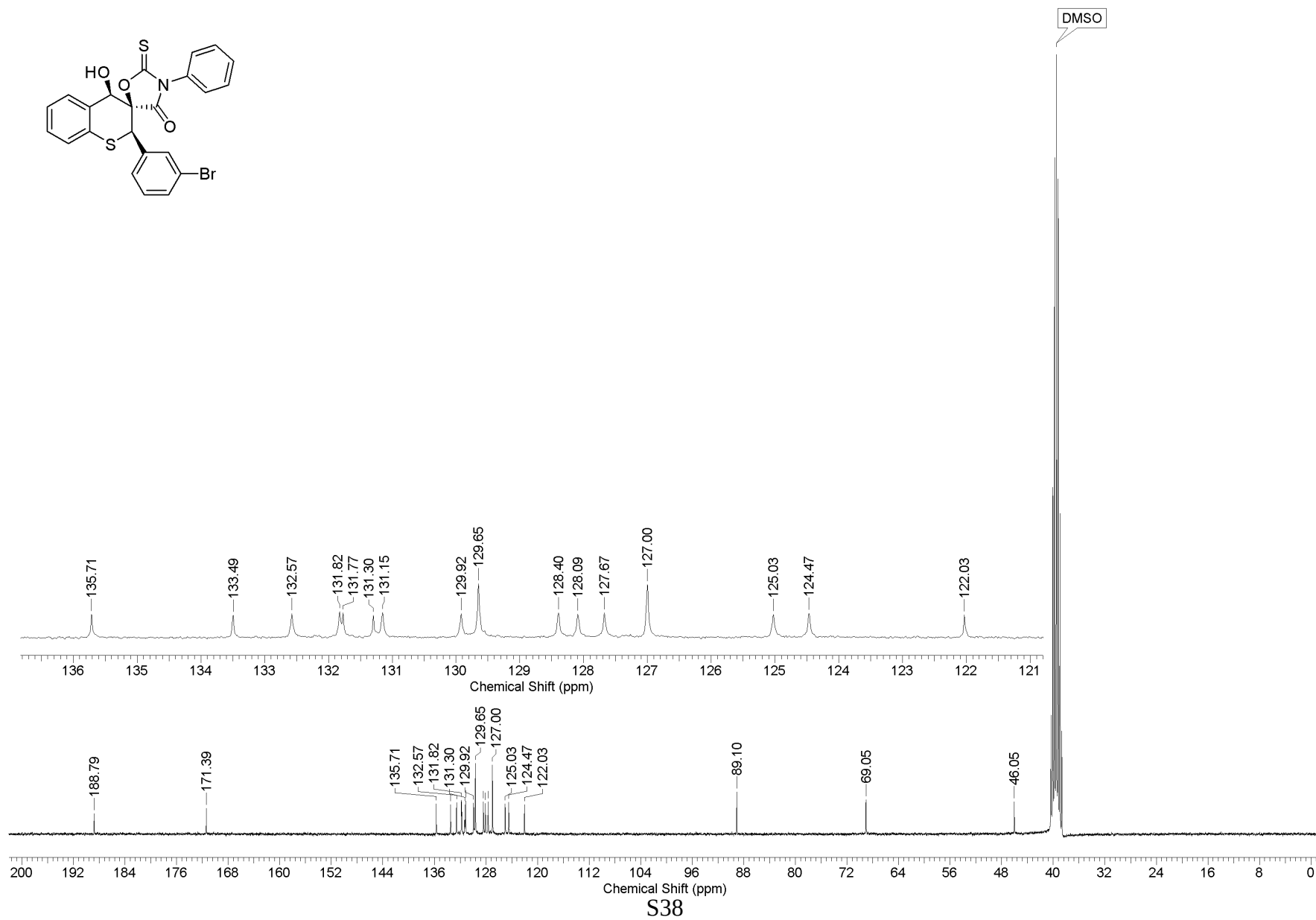


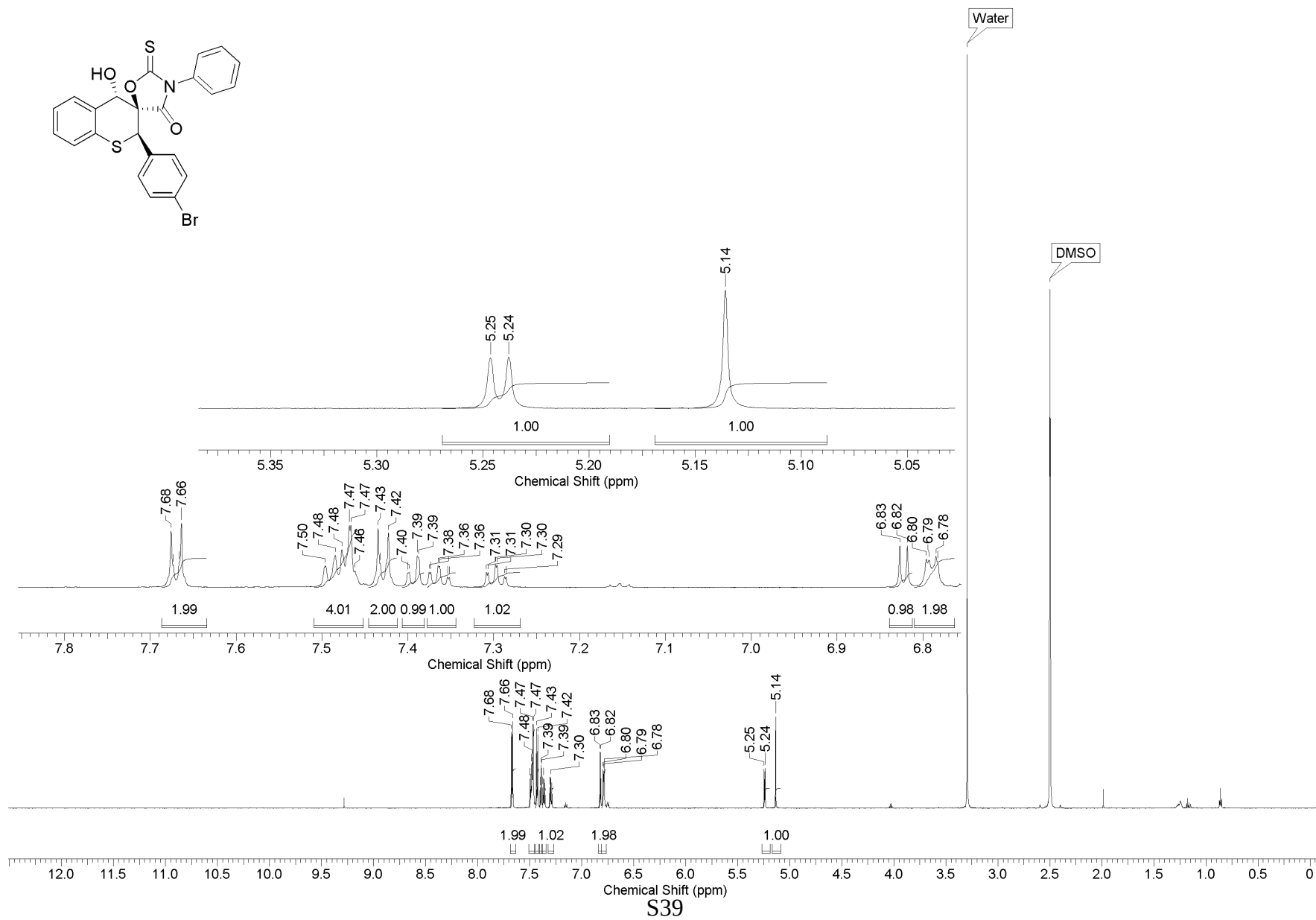
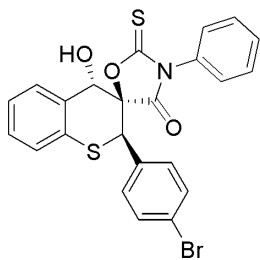


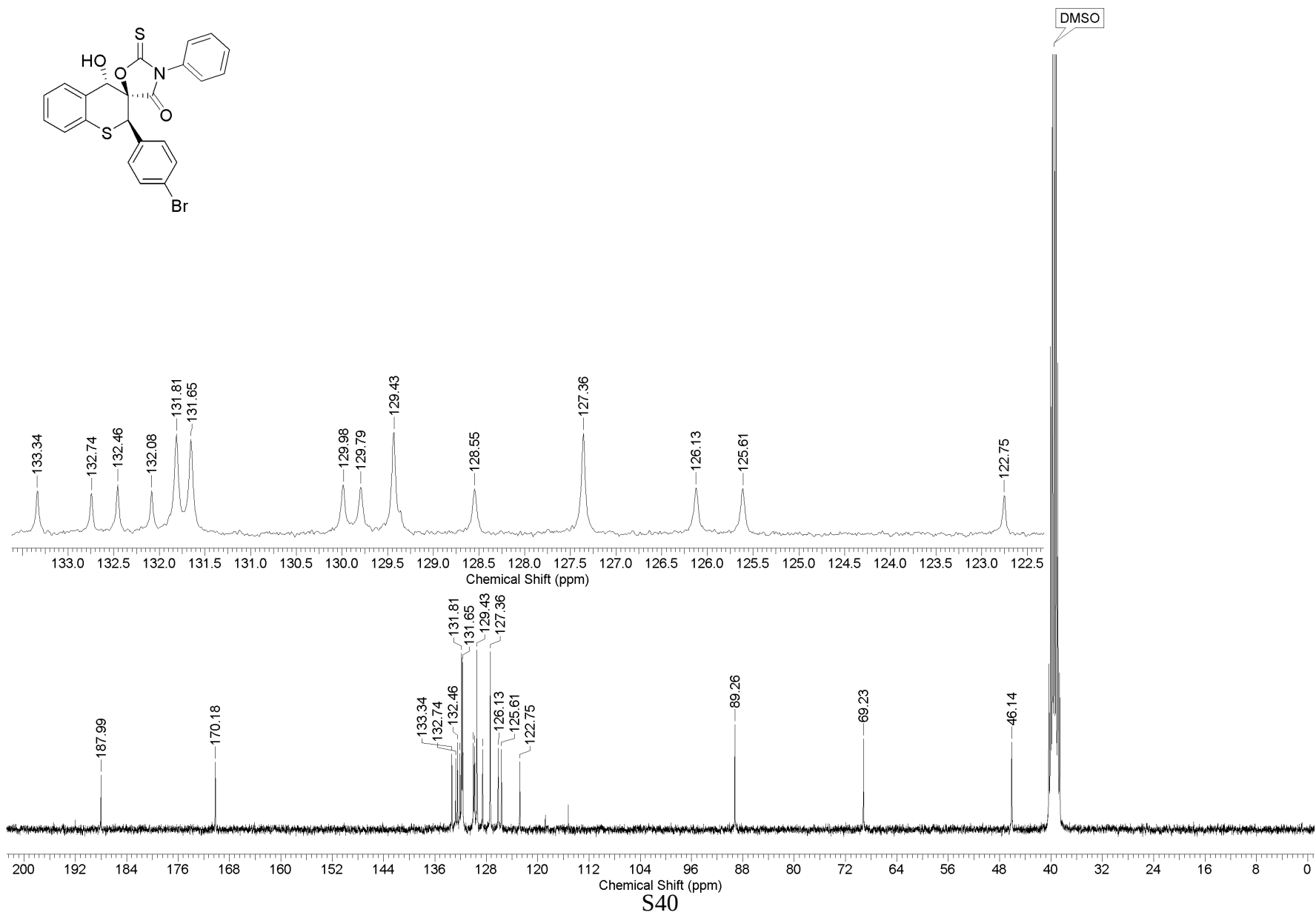
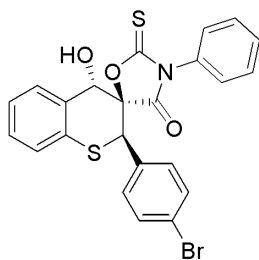


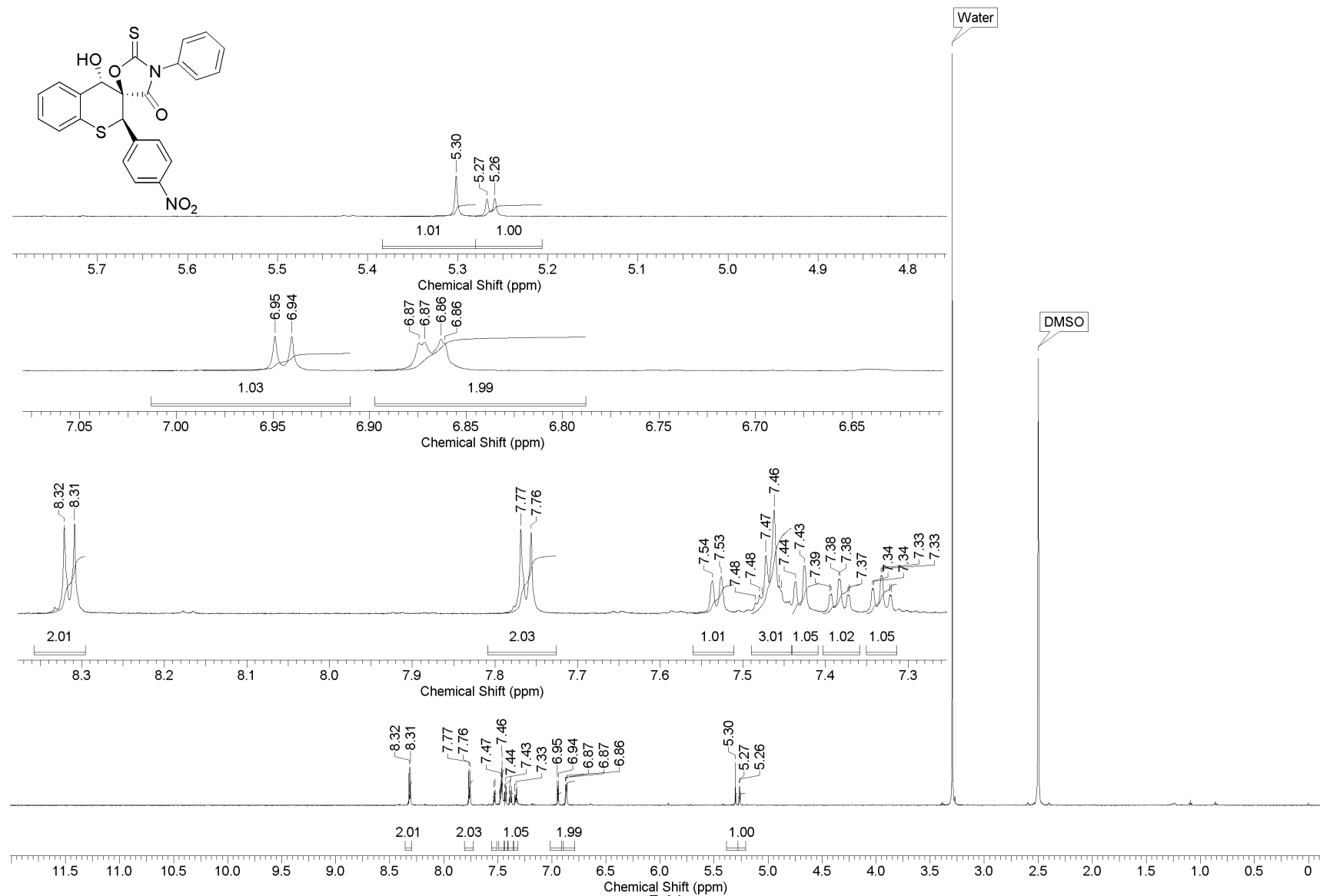


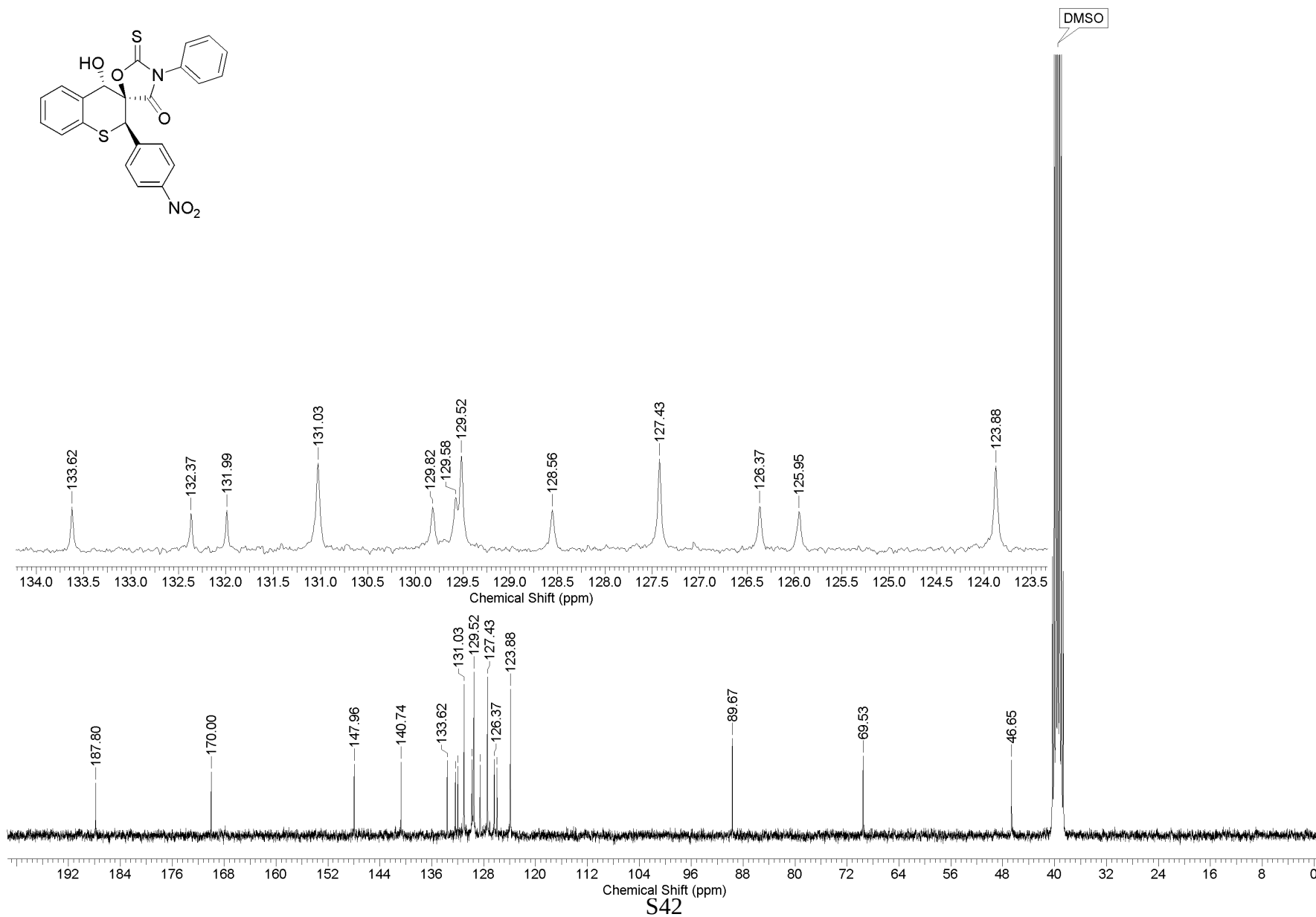
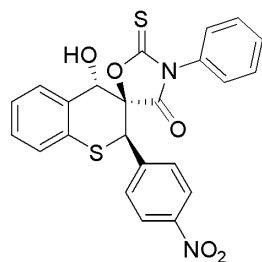
S37

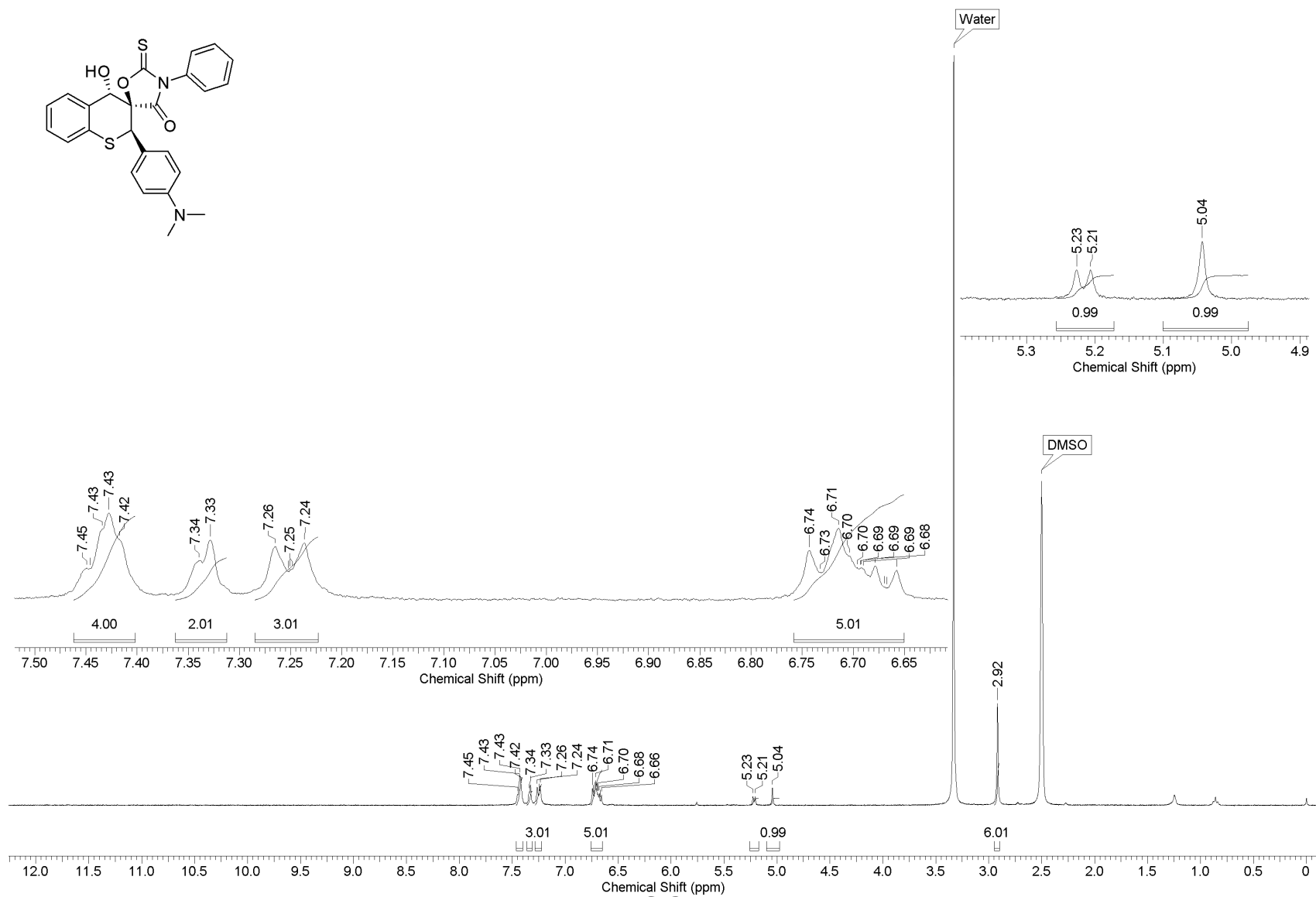
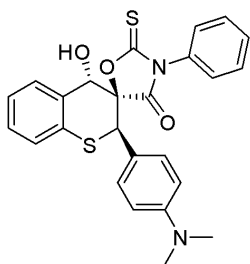


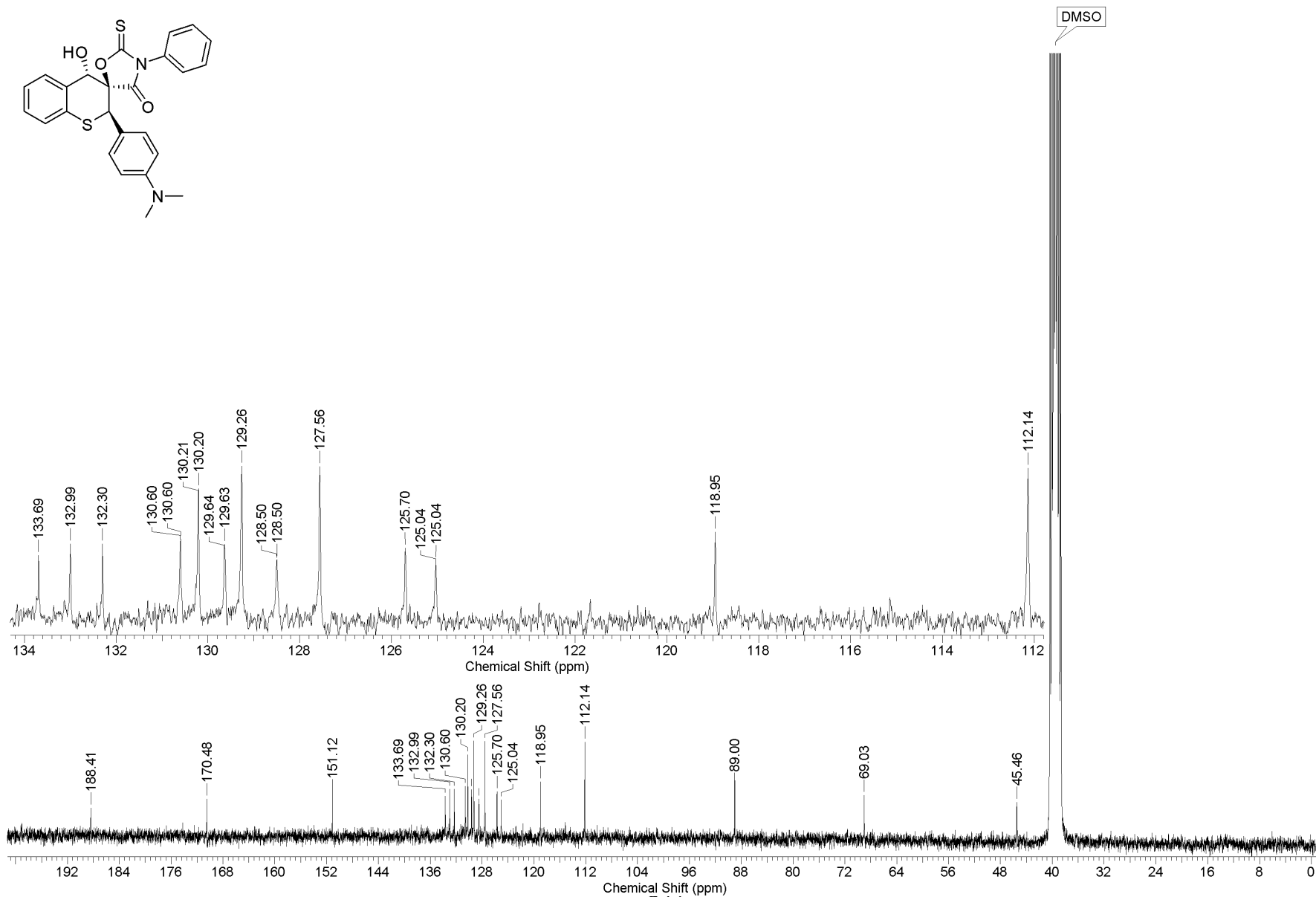
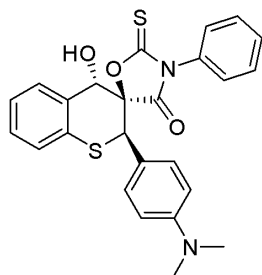


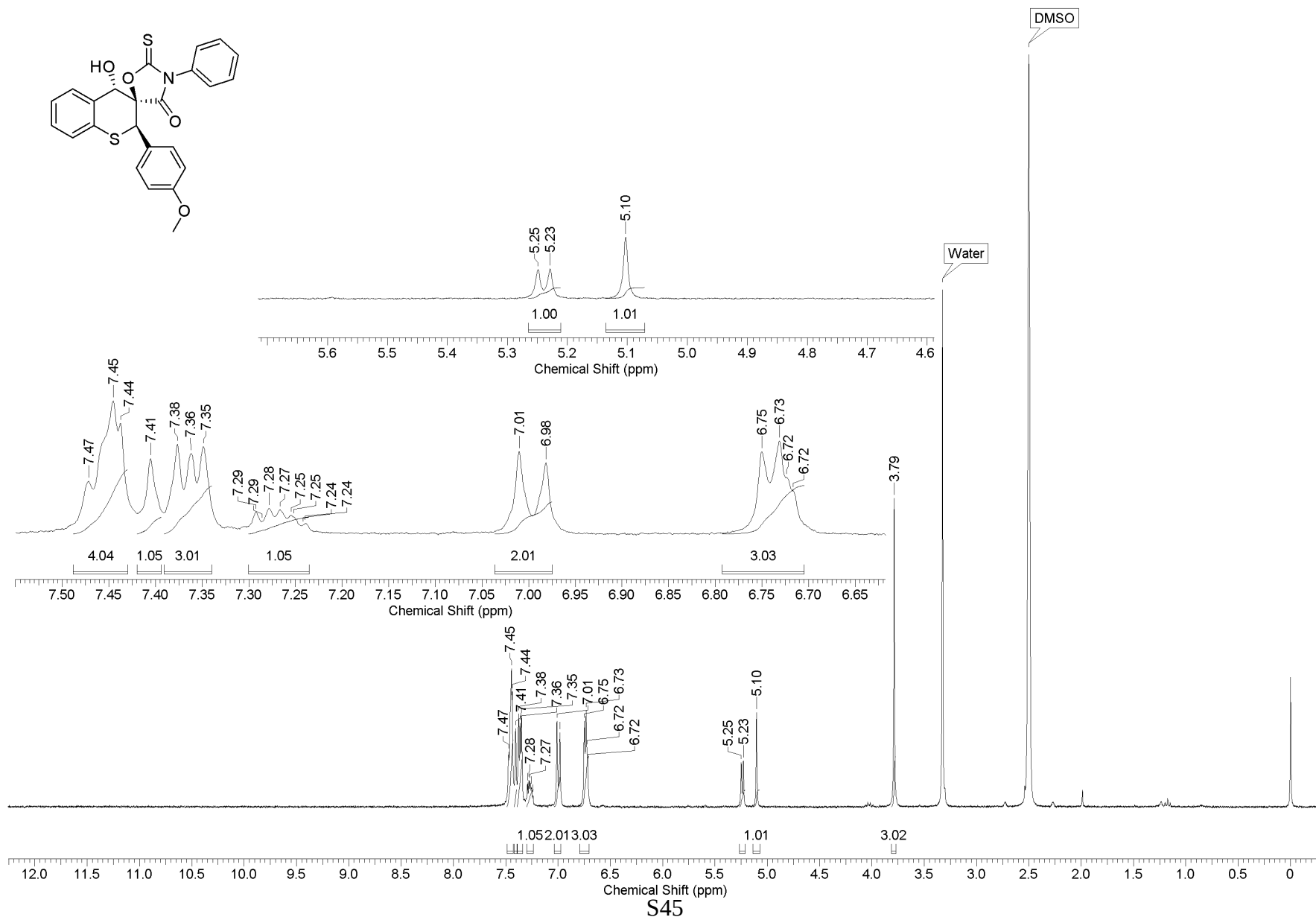
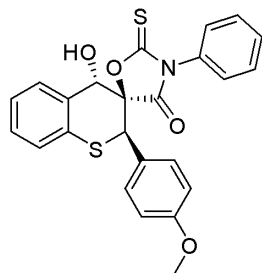


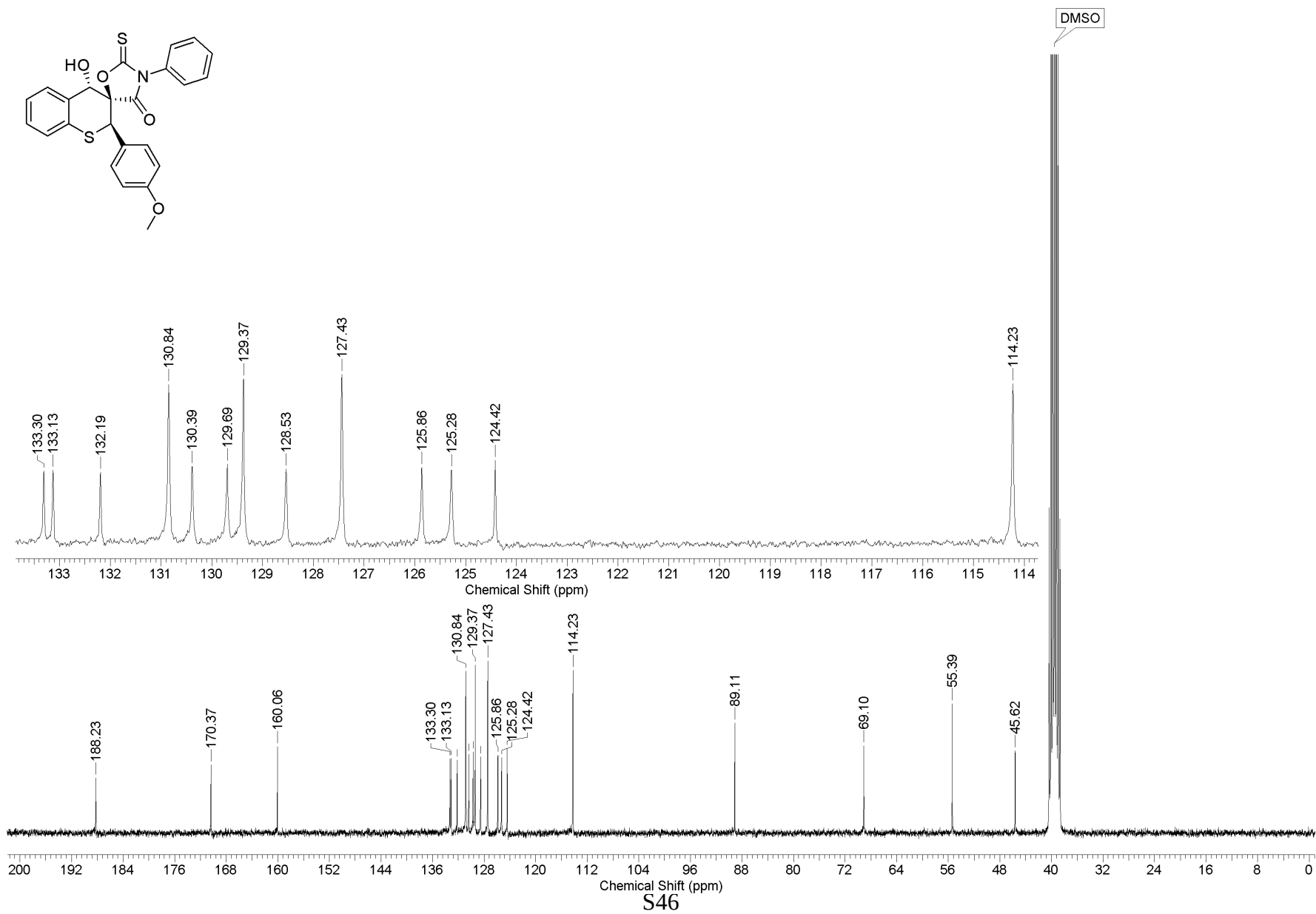
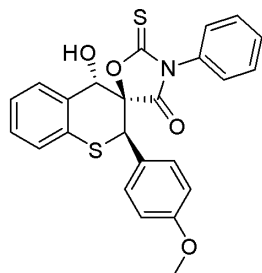


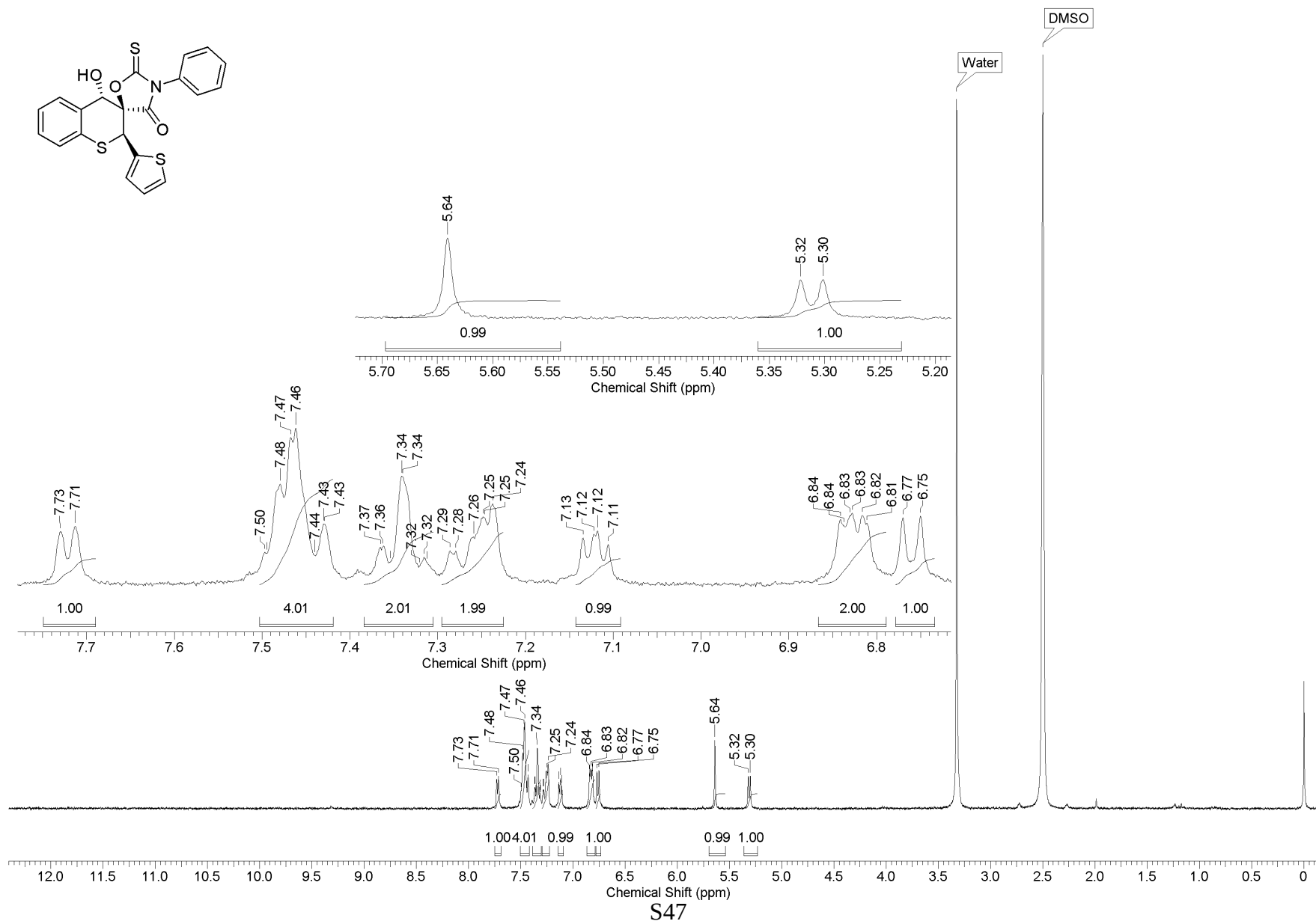
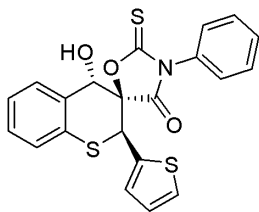


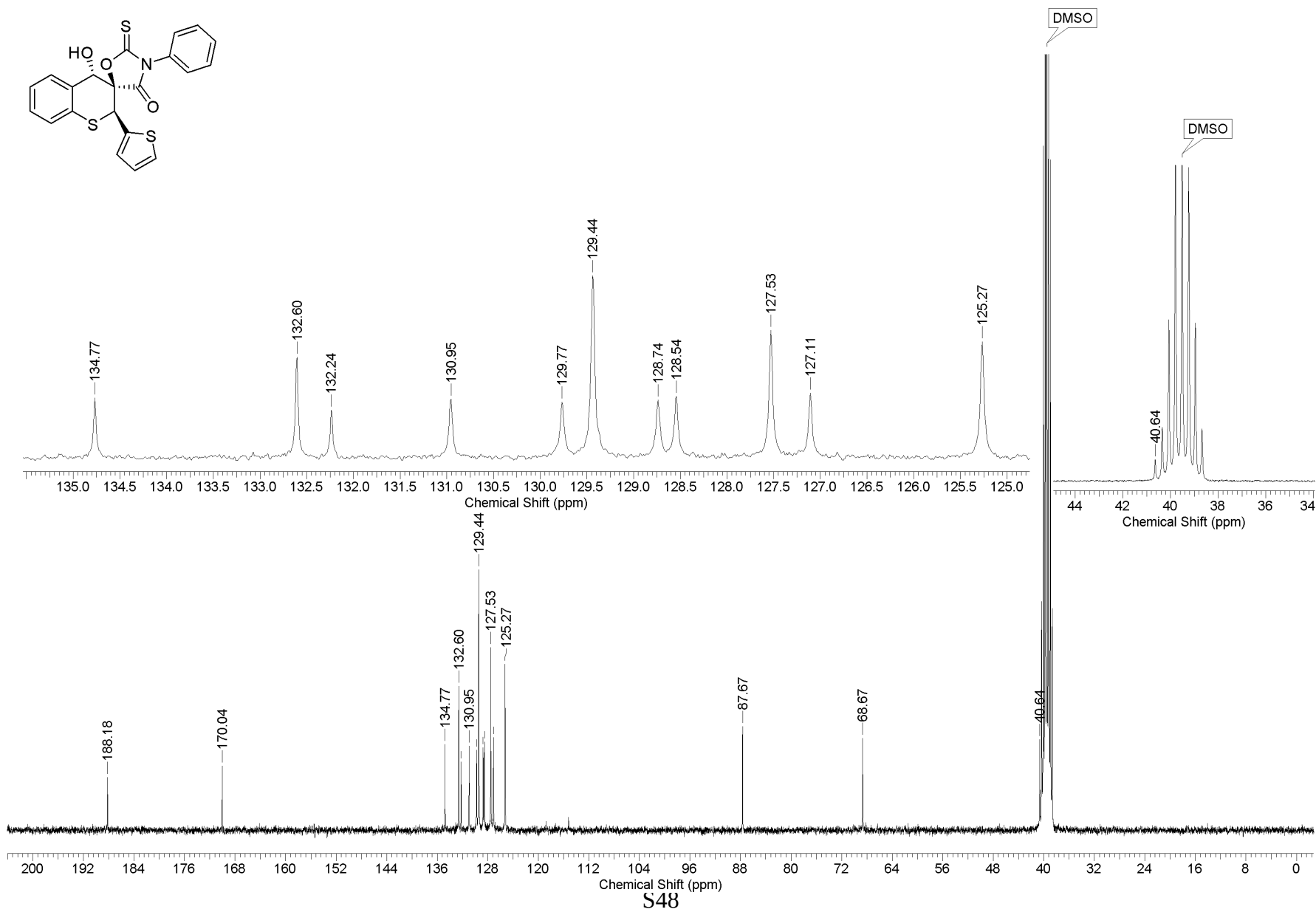


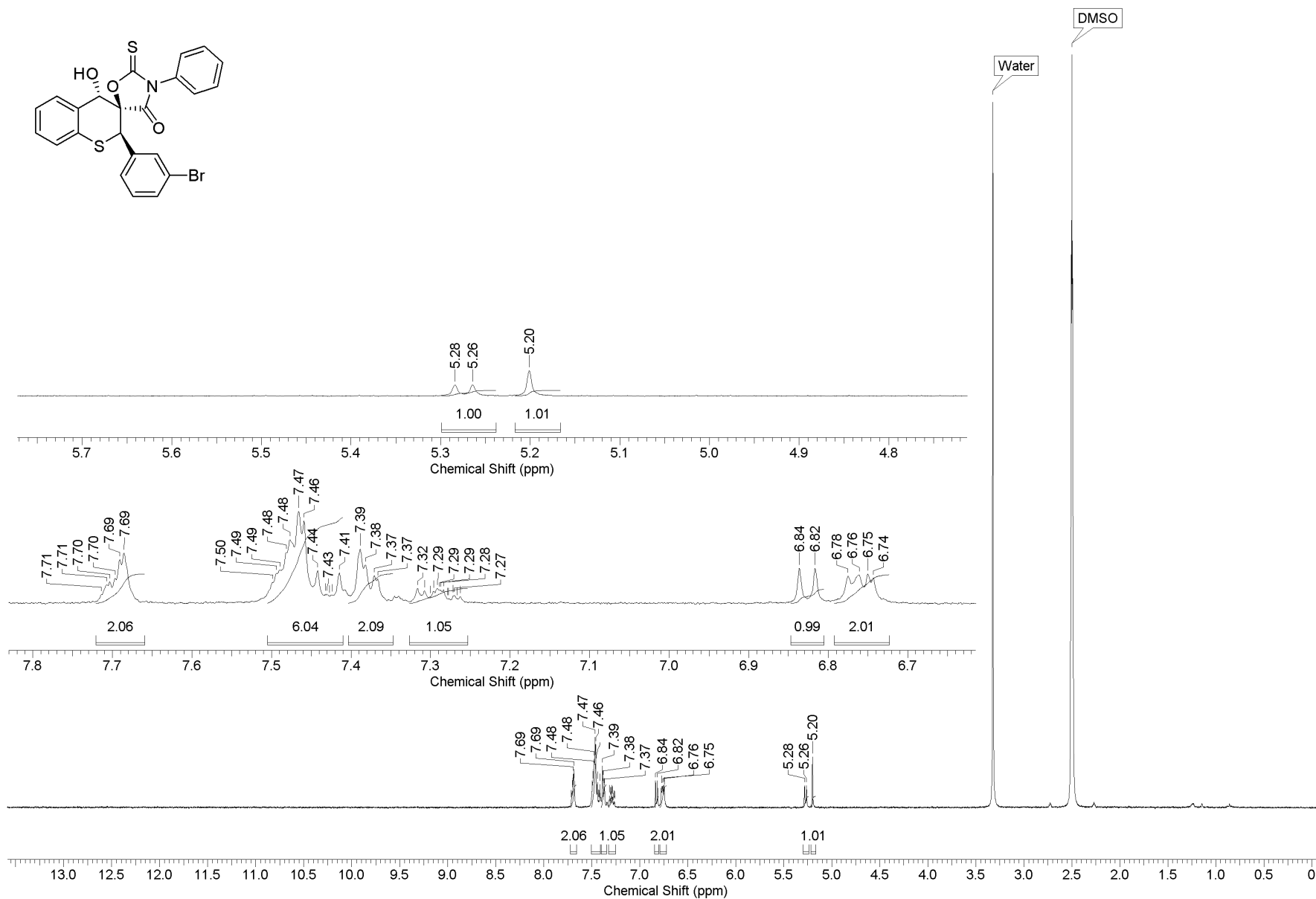
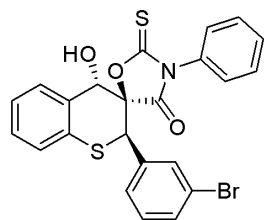


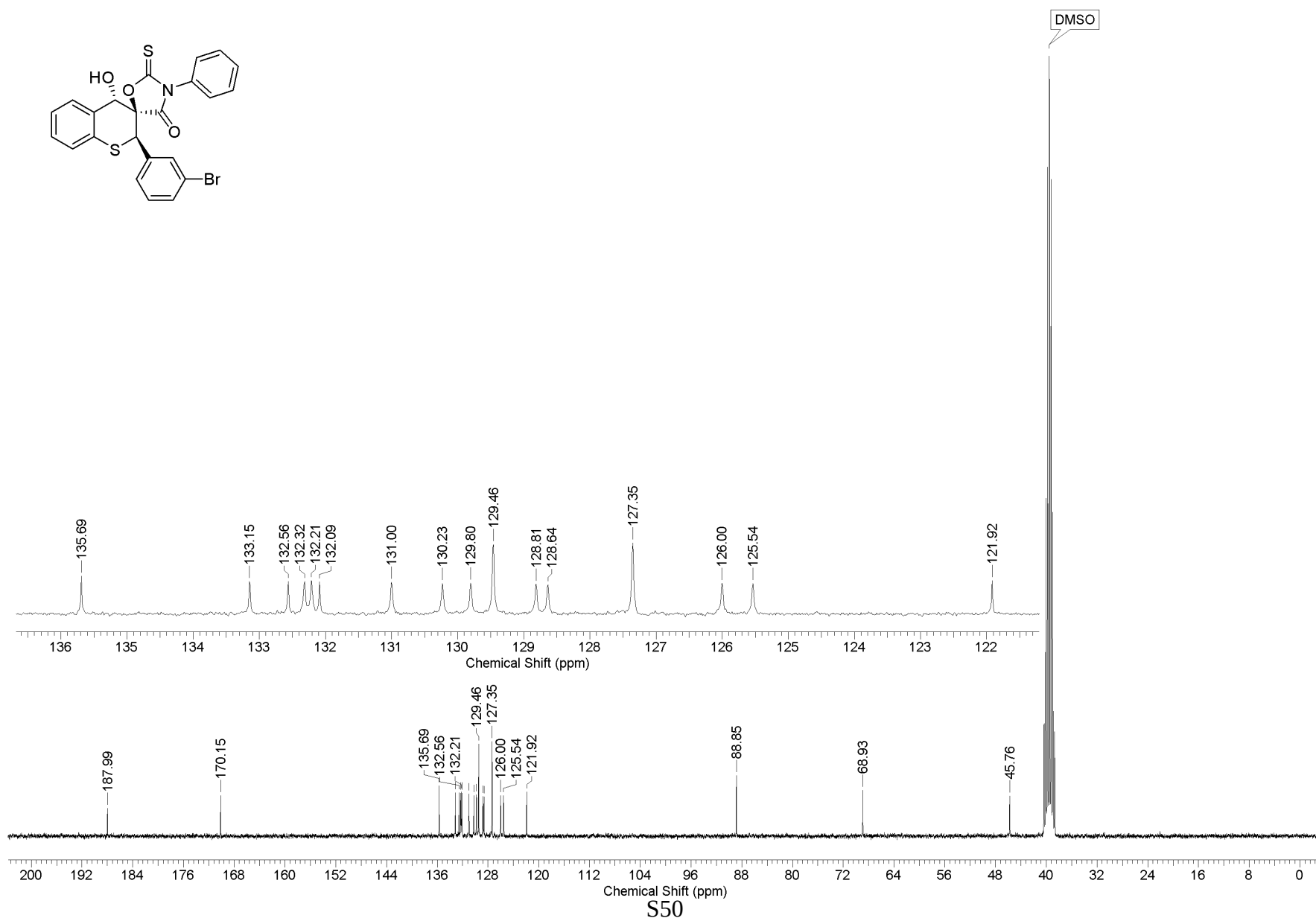
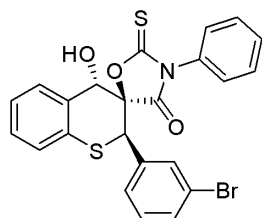


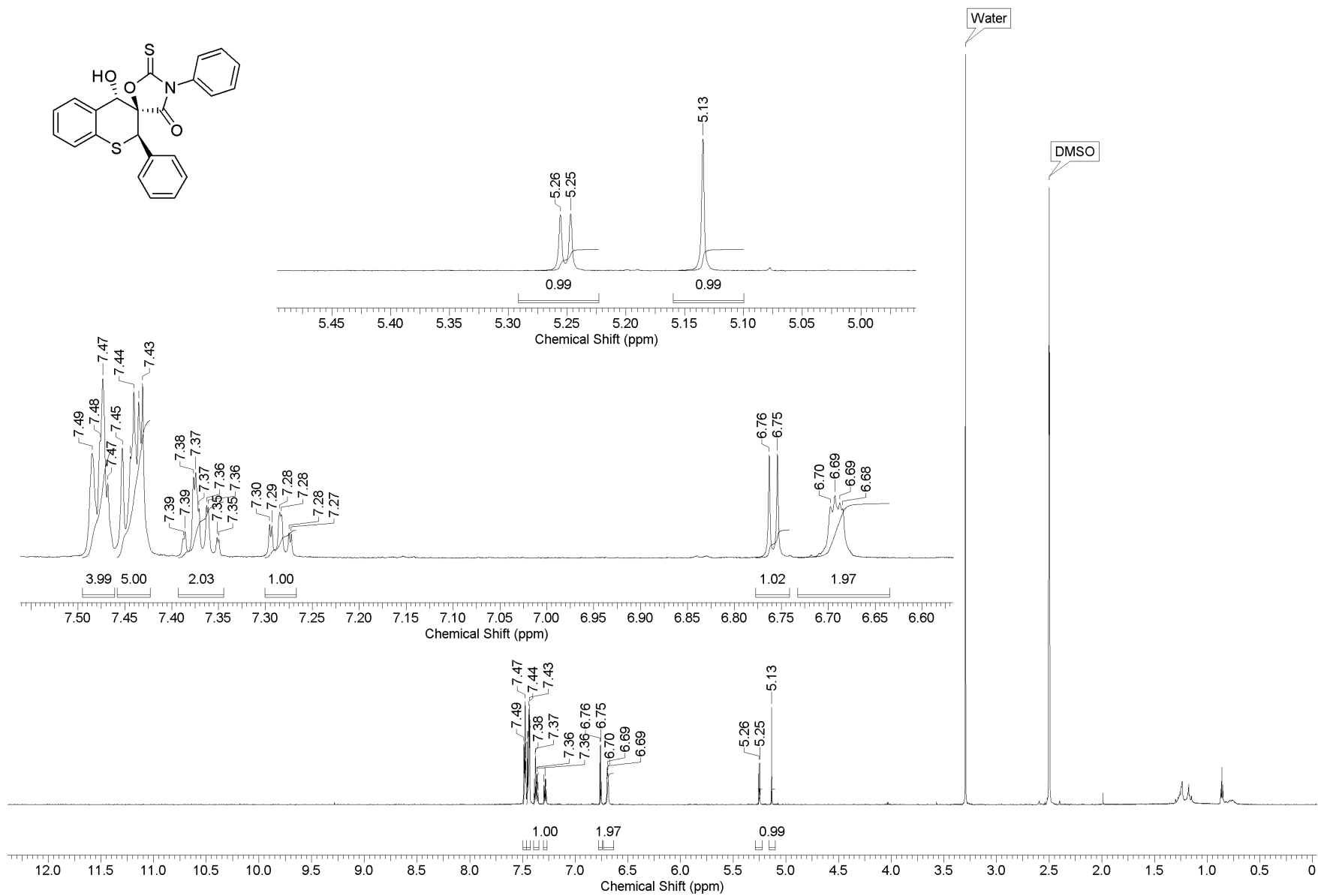


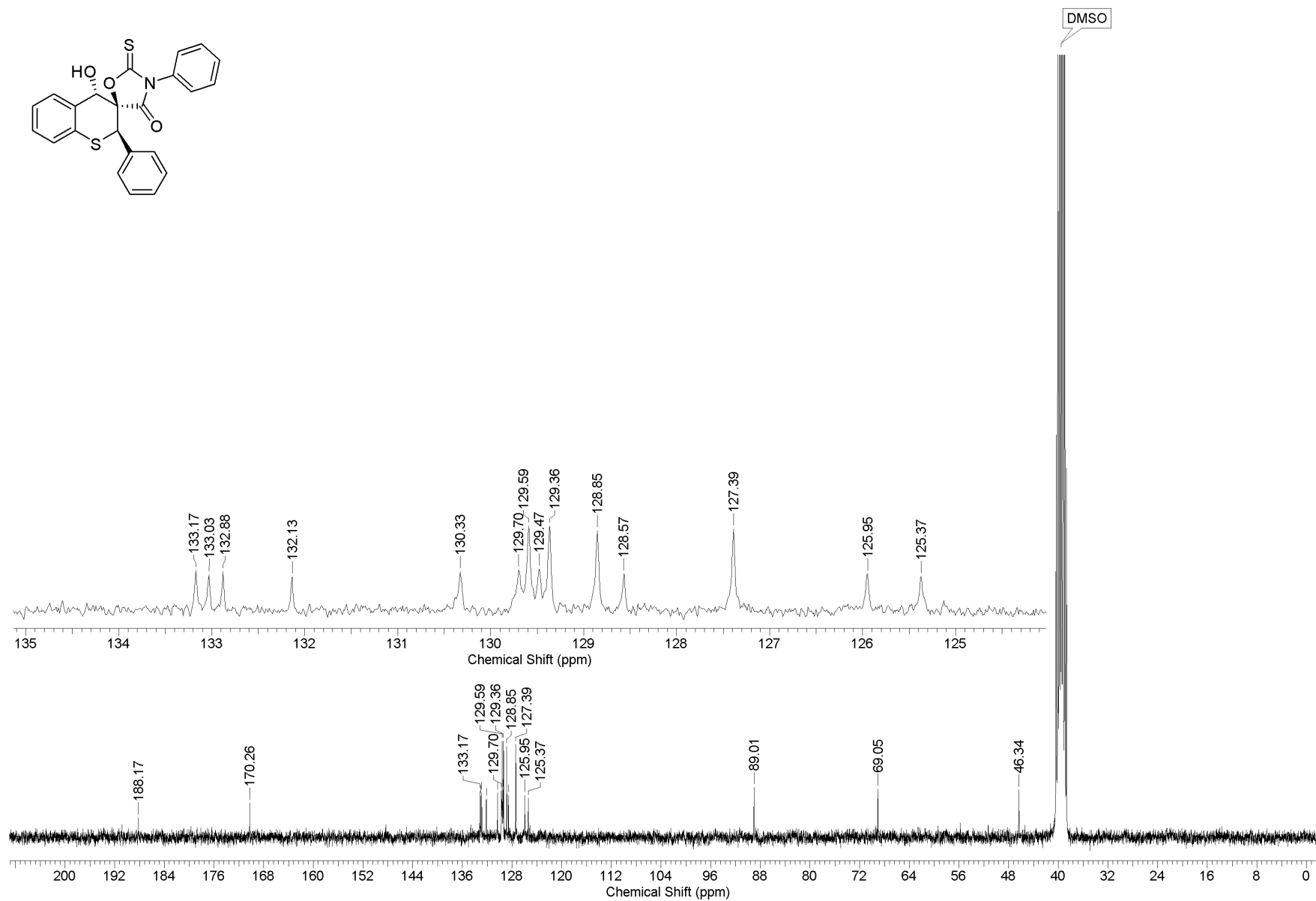
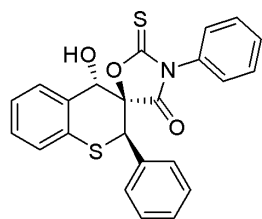




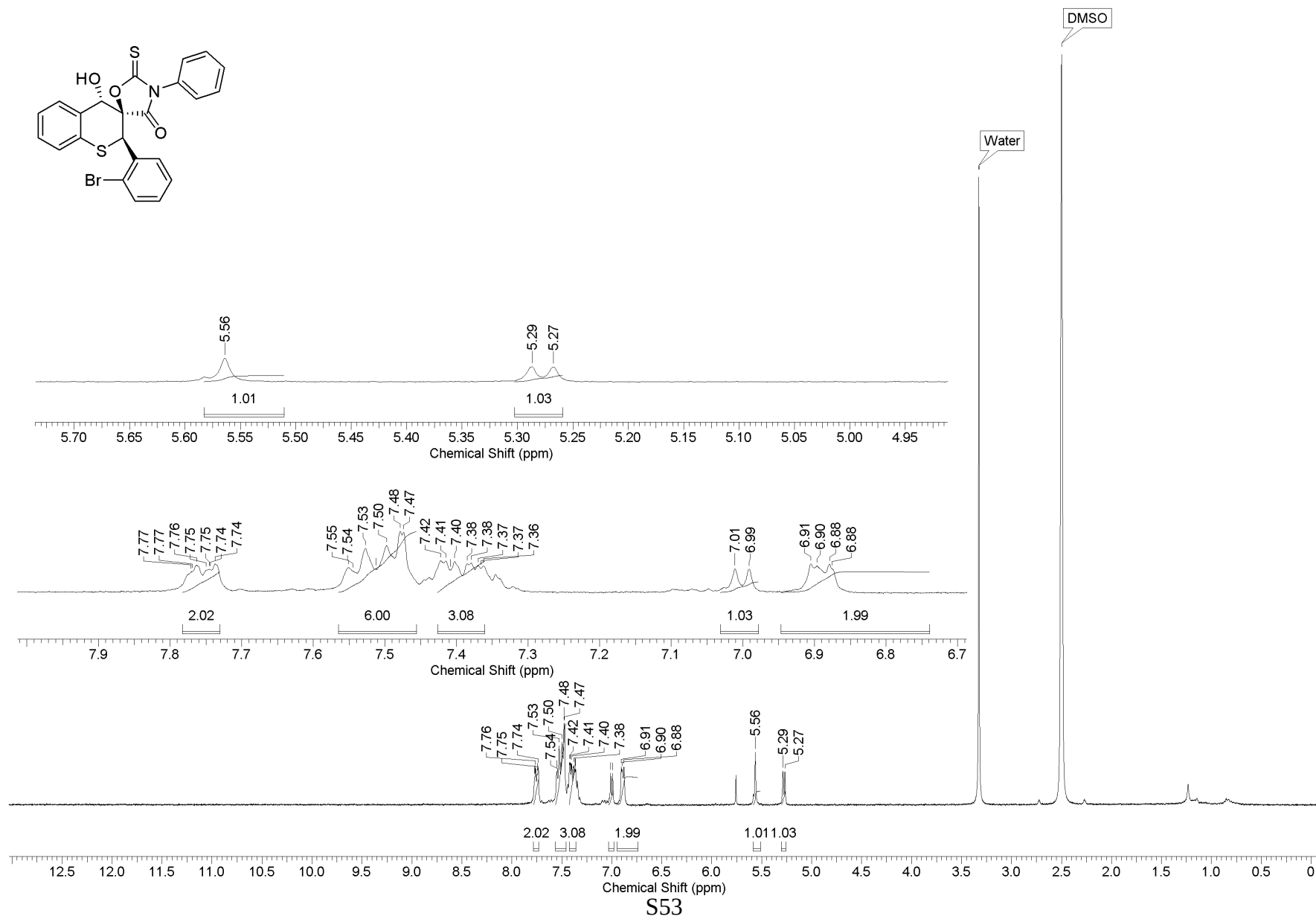
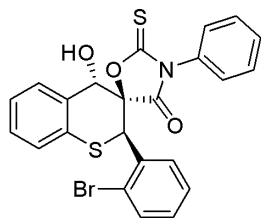




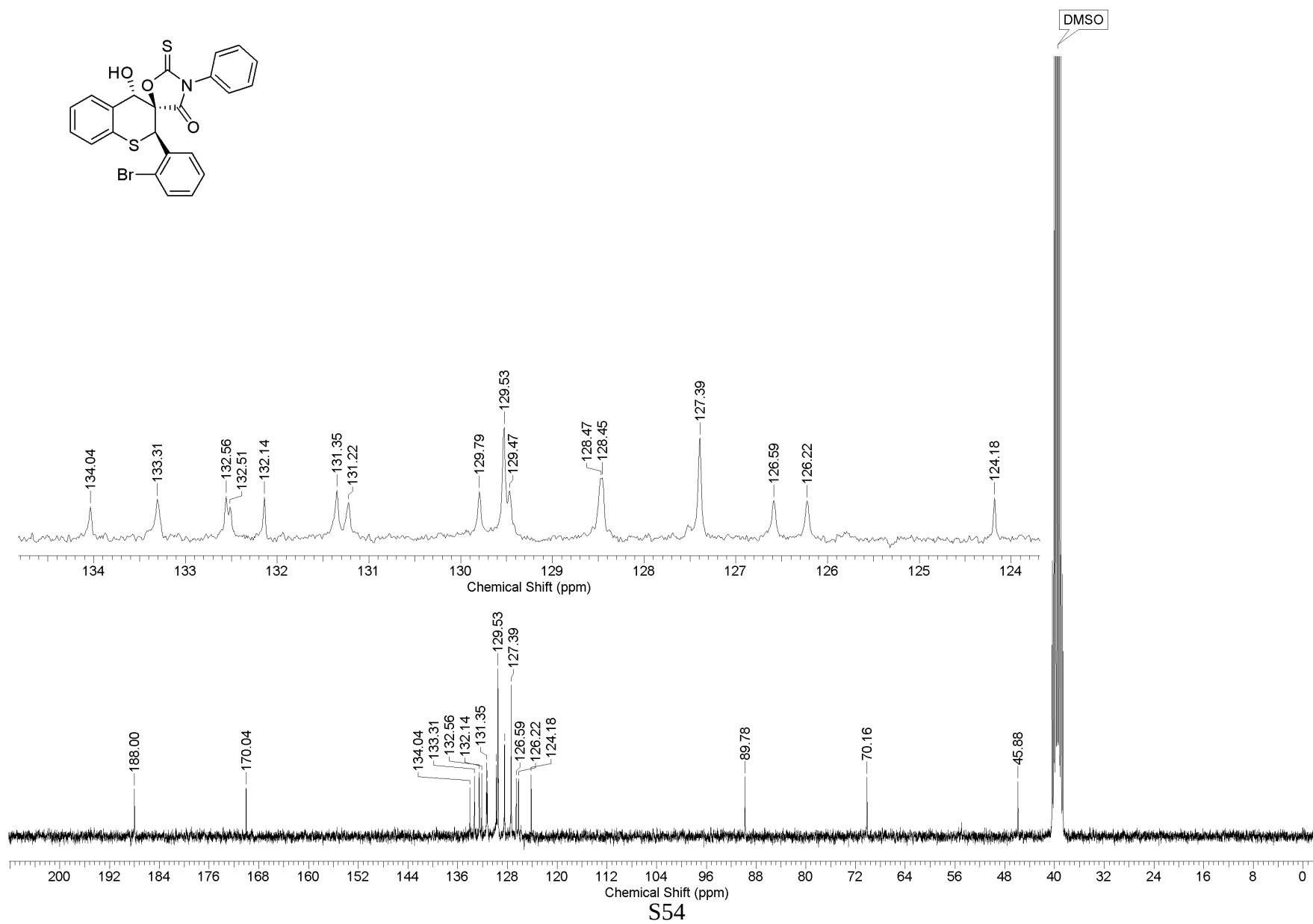
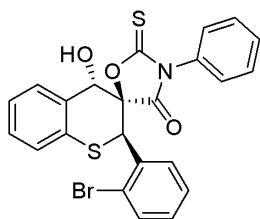


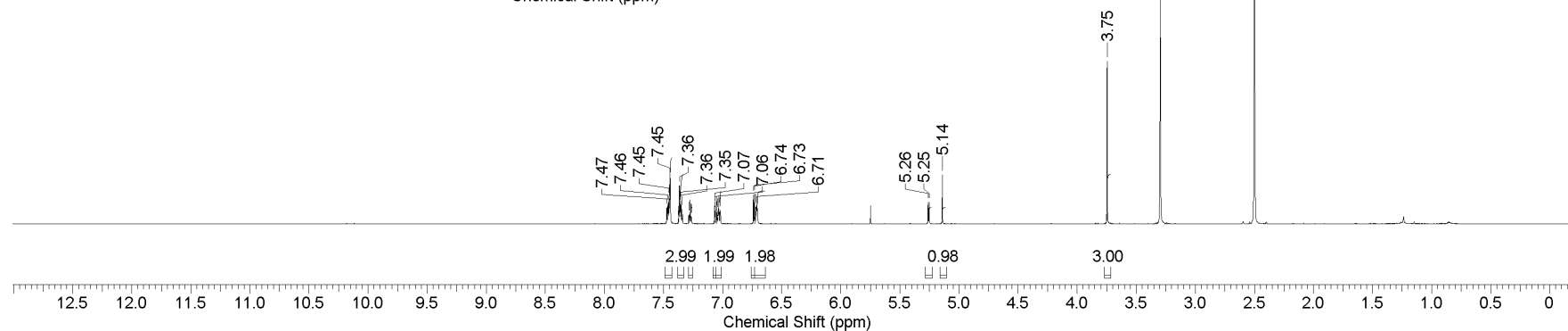
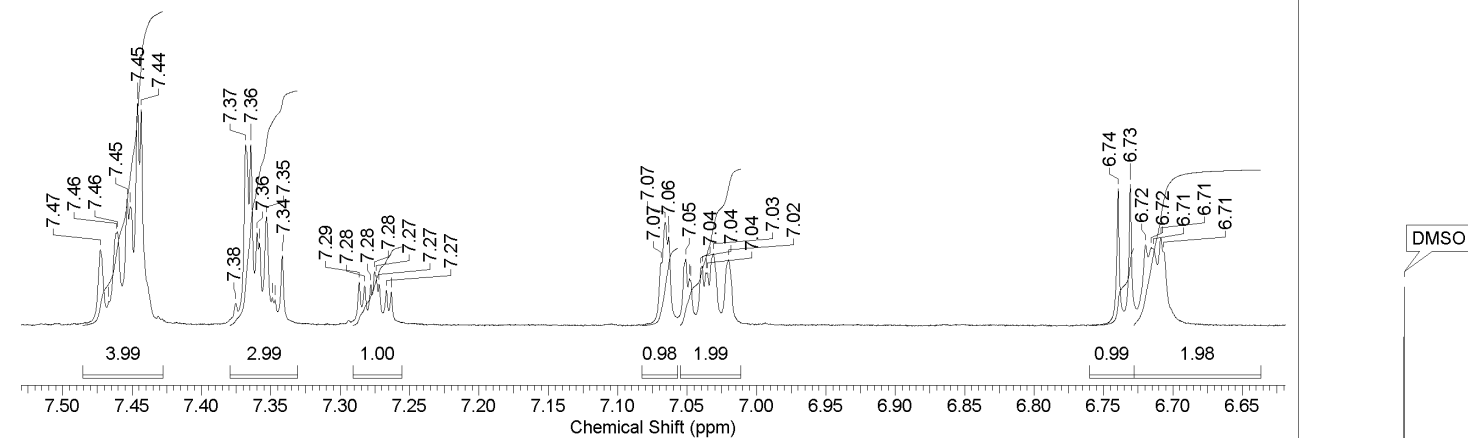
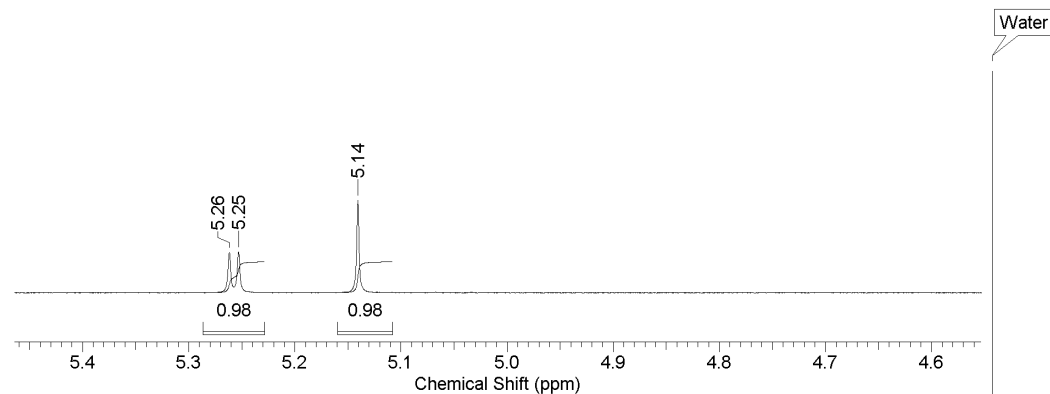
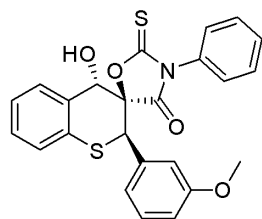


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