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1. General

Commercially available reagents were used without additional purification. E. Merck Kieselgel 60 was used for column chromatography.

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 KMnO_4 .

NMR spectra were recorded on a 700 MHz Bruker Avance III NMR at 303K, Avance III 800 (with a 5-mm CPTXI cryoprobe) and Bruker Fourier 300. Chemical shifts were reported relative to residue peaks DMSO-d_6 (2.51 ppm for ^1H and 39.5 ppm for ^{13}C).

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

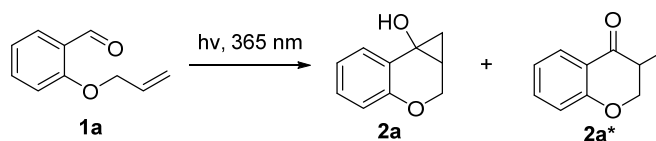
High-resolution mass spectra (HRMS) spectra were recorded on AB Sciex TripleTOF® 5600+ System using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 5500 V); mass range from m/z 50 to m/z 3000; external or internal calibration was done with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

Photoinduced processes were performed on EvoluChem™ PhotoRedOx box. 365 nm (LG, HCK1012-01-006, 25 mW/cm^2), 380 nm (LG, HCK1012-01-013, 8 mW/cm^2) and 405 nm (LG, HCK1012-01-010, 28 mW/cm^2) LED lamps from EvoluChem™ were used. This device is equipped with a fan to maintain room temperature during the irradiation process.

UV-VIS spectra were recorded on a Varian Cary 100 spectrophotometer.

2. Optimization of dihydrocyclopropa[*c*]chromen-7b(1*H*)-ol synthesis

Solvent screening



2-(Allyloxy)benzaldehyde **1a** (20 mg, 0.12 mmol) was dissolved in freshly distilled solvent (2.0 mL). Vials with obtained solutions were irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box with stirring. After 6 hours of irradiation, solvents were removed in vacuum (with the use of a rotary evaporator, the temperature in bath is not higher than 35 °C). For solutions in DMSO, DMF, DMAC and NMP reaction mixtures were dissolved in 10 mL of EtOAc and washed with saturated KCl solution (10×3 mL). Next, organic solutions were dried over Na₂SO₄ and similarly evaporated. Finally all residues were analyzed by ¹H NMR in DMSO-*d*₆.

The overall aromatic signal from 6.50 ppm to 8.50 ppm (4H) was used as a standard. The quantity of components was assessed using the following signals:

- singlet from 10.35 ppm to 10.50 ppm (1H) for the starting aldehyde **1a**.
- multiplet signal from 1.75 ppm to 1.88 ppm (1H) for product **2a**
- doublet from 1.04 ppm to 1.10 ppm (3H) for product **2a***

Results are presented in Table S1.

Table S1. Solvents screening results.

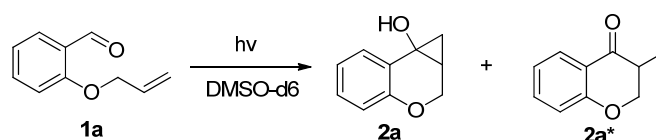
Entry	Solvent	2a , % ^a	2a* , % ^a	Remained 1a , % ^a
1	C ₂ H ₄ Cl ₂	0	17	8
2	CHCl ₃	0	14	46
3	MeOH	0	0	0
4	EtOH	0	0	0
5	<i>i</i> -PrOH	0	0	0
6	CF ₃ CH ₂ OH	0	0	95 ^b
7	(CF ₃) ₂ CHOH	0	0	100 ^b
8	THF	0	0	3
9	1,4-Dioxane	0	0	5
10	Et ₂ O	0	8	2
11	EtOAc	5	16	0
12	CH ₃ CN	0	7	5
13	C ₆ H ₆	0	10	0
14	Toluene	0	10	0
15	PhCl	0	14	0
16	Hexane	0	0	0
17	DMSO	53	4	3
18	DMF	0	0	0
19	DMAC	11	0	0
20	NMP	0	0	0
21	NEt ₃	0	6	0
22	DIPEA	0	9	0
23	Pyridine	0	12	0

a - measured in single experiment, error is about 5% based on integration accuracy in NMR spectra; b - almost no reaction.



Figure S1. Photochemical set-up. Solvent screening.

Various wavelength screening



Compound **1a** (15 mg) was dissolved in 3 mL of DMSO-*d*₆ in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.65 mL) was transferred to three argon fused NMR tubes and sealed. NMR tube with these solutions was irradiated with various LED lamp in EvoluChem™ PhotoRedOx box for 6 hours. The mixtures were analyzed by ¹H NMR as it was mentioned above.

Table S2. Wavelength screening results.

$h\nu$, nm	2a , %	1a , %
365	53	1
380	36	14
405	4	78

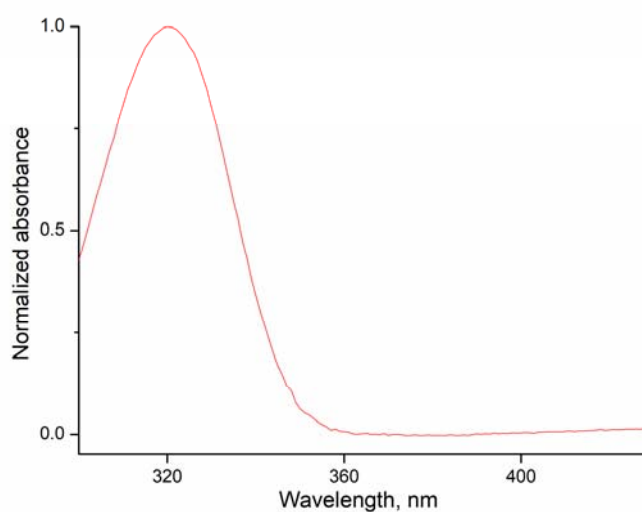


Figure S2. Normalized absorbance of **1a** in DMSO.

3. Kinetic study

Compound **1a** (10 mg) were dissolved in 2 mL of DMSO-*d*₆ in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.65 mL) was transferred to two argon fused NMR tubes and sealed. NMR tube with these solutions was irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box. The mixture was analyzed by ¹H NMR. One of two samples was wrapped in a foil and served as a blank standard confirming that the reaction does not proceed without irradiation at the similar conditions (solvent, time, temperature) (Figures S3 and S4).

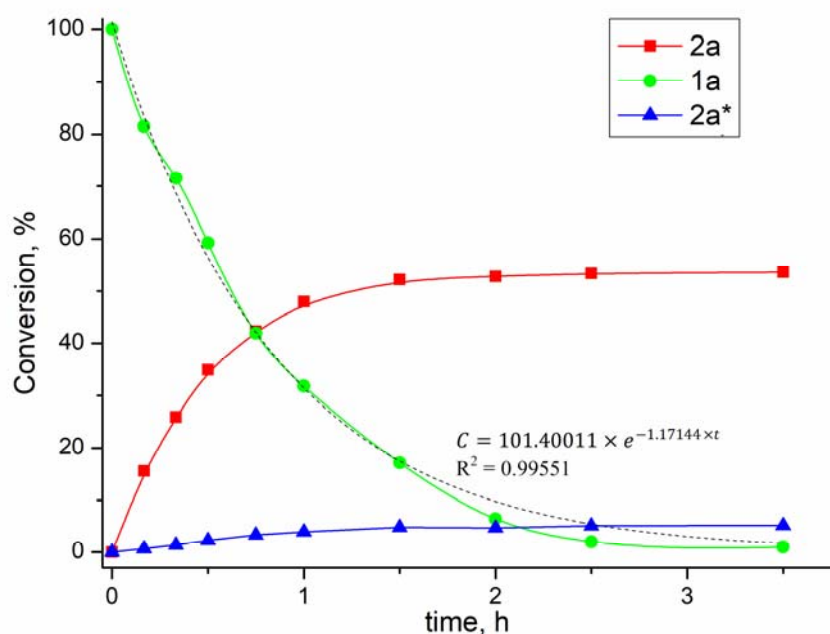


Figure S3. Kinetic study of compound **1a**.

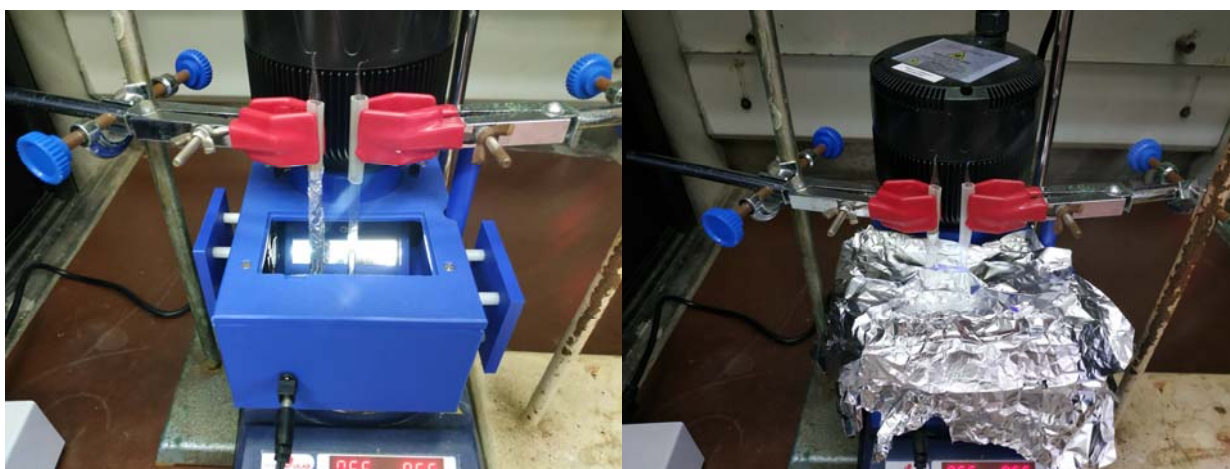
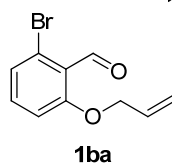
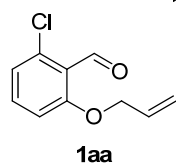
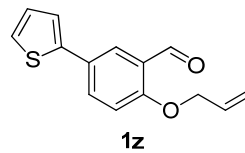
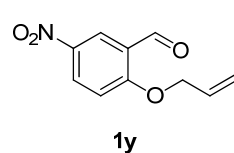
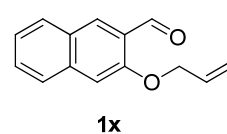
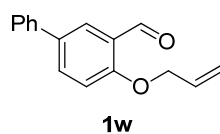
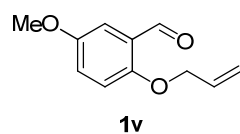
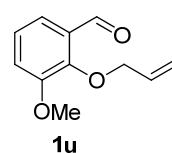
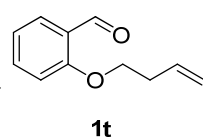
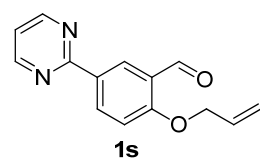
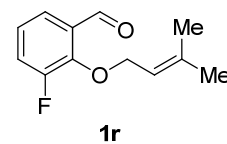
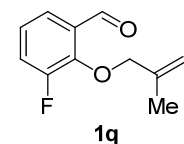
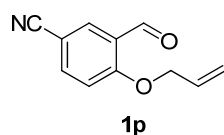
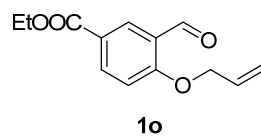
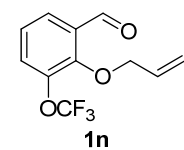
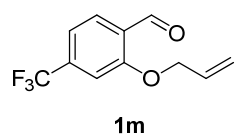
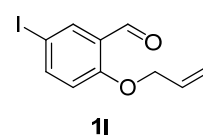
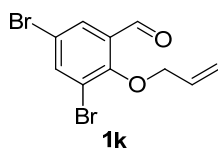
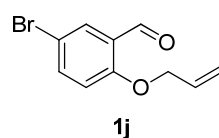
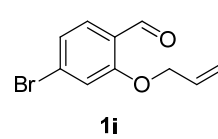
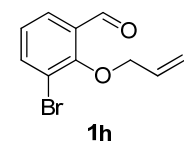
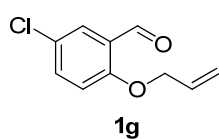
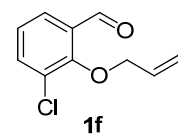
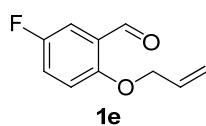
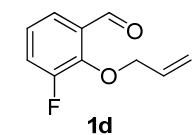
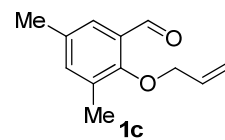
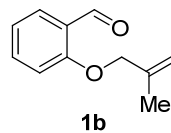
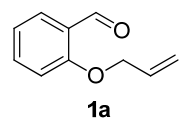
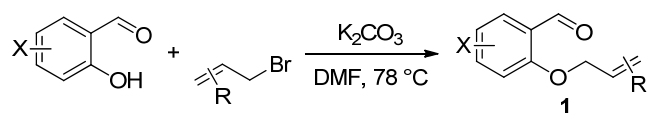


Figure S4. Photochemical set-up. Kinetic study.

4. Synthesis of the starting 2-(allyloxy)benzaldehydes (1)



General method

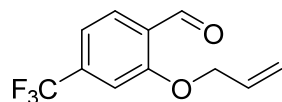
Mixture of the corresponding 2-hydroxybenzaldehyde (10 mmol), allylbromide (13 mmol) and K₂CO₃ (2.76 g, 20 mmol) in freshly distilled DMF (50 mL) was heated at 78°C for 12 h. EtOAc (200 mL) was added and the resulted mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na₂SO₄, all volatiles were removed in vacuo and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 50:1).

Aldehydes **1a-l**, **1o-p**, **1t-w** and **1y** were synthesized previously, the spectral properties corresponds to the literature data (Table S2).

Table S2. Starting aldehydes, references with preciously reported data.

Compounds	Reference
1a, 1e, 1h, 1j,	[¹]
1b, 1t	[²]
1c	[³]
1d	[⁴]
1f, 1g, 1k, 1l	[⁵]
1i	[⁶]
1o, 1aa	[⁷]
1p	[⁸]
1u	[⁹]
1v	[¹⁰]
1w	[¹¹]
1y	[¹²]
1ba	[¹³]

2-(Allyloxy)-4-(trifluoromethyl)benzaldehyde (1m)



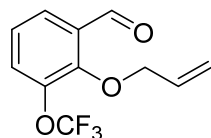
Yield 1.89 g (82%), yellowish viscous oil.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 4.86 (dt, $J=5.0, 1.6$ Hz, 2H), 5.33 (dq, $J=10.7, 1.5$ Hz, 1H), 5.49 (dq, $J=17.3, 1.7$ Hz, 1H), 6.07 - 6.13 (m, 1H), 7.42 (d, $J=8.0$ Hz, 1H), 7.53 (s, 1H), 7.88 (d, $J=8.0$ Hz, 1H), 10.44 (s, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 69.4, 111.1 (q, $J=3.9$ Hz), 117.3 (q, $J=3.9$ Hz), 118.0, 123.4 (q, $J=273.4$ Hz), 127.1, 129.0, 132.6, 135.1 (q, $J=32.1$ Hz), 160.3, 188.7.

HRMS (ESI-TOF) found, m/z : 231.0627 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}_2^+$. Calculated, m/z : 231.0627.

2-(Allyloxy)-3-(trifluoromethoxy)benzaldehyde (1n)



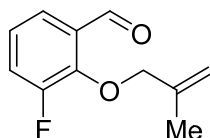
Yield 2.09 g (85%), yellowish viscous oil.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 4.68 (dt, $J=5.9, 1.2$ Hz, 2H), 5.26 - 5.33 (m, 1H), 5.40 (dq, $J=17.2, 1.5$ Hz, 1H), 6.05 - 6.13 (m, 1H), 7.39 (td, $J=8.0, 0.8$ Hz, 1H), 7.72 - 7.79 (m, 2H), 10.28 (d, $J=0.8$ Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 76.3, 119.2, 120.1 (q, $J=258.0$ Hz), 125.1, 127.0, 128.6, 131.0, 132.8, 141.8 (q, $J=1.7$ Hz), 152.9, 188.9.

HRMS (ESI-TOF) found, m/z : 247.0576 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}_3^+$. Calculated, m/z : 247.0577.

3-Fluoro-2-((2-methylallyl)oxy)benzaldehyde (1q)



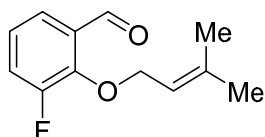
Yield 1.88 g (97%), yellowish viscous oil.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 1.82 (s, 3H), 4.65 (s, 2H), 5.00 (s, 1H), 5.10 (s, 1H), 7.26 (app td, $J=7.8, 4.7$ Hz, 1H), 7.56 (d, $J=7.6$ Hz, 1H), 7.62 (dd, $J=11.3, 8.2$ Hz, 1H), 10.30 (s, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 19.2, 78.3 (d, $J=5.7$ Hz), 114.1, 122.9 (d, $J=19.4$ Hz), 123.4 (d, $J=3.0$ Hz), 124.3 (d, $J=7.4$ Hz), 130.2 (d, $J=1.3$ Hz), 140.5, 148.4 (d, $J=11.0$ Hz), 154.8 (d, $J=248.0$ Hz), 188.7 (d, $J=3.0$ Hz).

HRMS (ESI-TOF) found, m/z : 195.0818 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_{12}\text{FO}_2^+$. Calculated, m/z : 195.0816.

3-Fluoro-2-((3-methylbut-2-en-1-yl)oxy)benzaldehyde (1r)



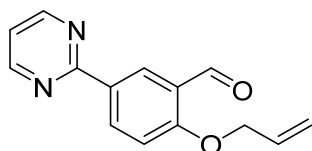
Yield 1.90 g (91%), yellowish viscous oil.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 1.57 (s, 3H), 1.70 (s, 3H), 4.71 (d, $J=7.4$ Hz, 2H), 5.45 - 5.53 (m, 1H), 7.25 (app td, $J=7.9, 4.8$ Hz, 1H), 7.53 (d, $J=7.8$ Hz, 1H), 7.58 - 7.65 (m, 1H), 10.25 (s, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.6, 25.3, 71.0, 118.9, 122.7 (d, $J=19.1$ Hz), 123.0 (d, $J=2.7$ Hz), 124.4 (d, $J=7.0$ Hz), 130.9 (d, $J=1.0$ Hz), 140.1, 148.4 (d, $J=11.4$ Hz), 155.3 (d, $J=247.3$ Hz), 188.9.

HRMS (ESI-TOF) found, m/z : 209.0970 $[\text{M}+\text{H}]^+$. $\text{C}_{12}\text{H}_{14}\text{FO}_2^+$. Calculated, m/z : 209.0972.

2-(Allyloxy)-5-(pyrimidin-2-yl)benzaldehyde (1s)



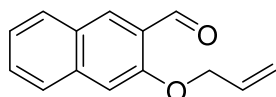
Yield 1.79 g (75%), yellowish solid, m. p. 109-111 °C.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 4.84 (d, $J=5.0$ Hz, 2H), 5.34 (dd, $J=10.6$, 1.4 Hz, 1H), 5.51 (dd, $J=17.3$, 1.6 Hz, 1H), 6.13 (dddd, $J=17.1$, 10.6, 5.2, 5.1 Hz, 1H), 7.40 (d, $J=9.0$ Hz, 1H), 7.43 (t, $J=4.8$ Hz, 1H), 8.63 (dd, $J=8.8$, 2.3 Hz, 1H), 8.75 (d, $J=2.3$ Hz, 1H), 8.89 (d, $J=4.8$ Hz, 2H), 10.46 (s, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 69.1, 114.1, 117.9, 119.6, 124.3, 127.5, 129.7, 132.7, 135.0, 157.7, 162.1, 162.2, 188.9.

HRMS (ESI-TOF) found, m/z : 241.0974 $[\text{M}+\text{H}]^+$. $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2^+$. Calculated, m/z : 241.0972.

3-(Allyloxy)-2-naphthaldehyde (1x)



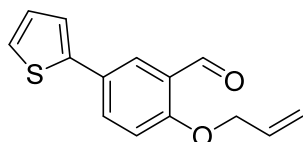
Yield 1.74 g (82%), white solid, m. p. 82-84 °C.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 4.91 (d, $J=5.2$ Hz, 2H), 5.33 (d, $J=10.5$ Hz, 1H), 5.48 (dd, $J=17.3$, 1.4 Hz, 1H), 6.11 - 6.18 (m, 1H), 7.47 (app t, $J=7.4$ Hz, 1H), 7.58 (d, $J=9.2$ Hz, 1H), 7.64 (app t, $J=7.7$ Hz, 1H), 7.94 (d, $J=8.0$ Hz, 1H), 8.26 (d, $J=9.2$ Hz, 1H), 9.10 (d, $J=8.6$ Hz, 1H), 10.83 (s, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 69.8, 114.9, 115.9, 118.0, 123.8, 124.6, 128.1, 128.5, 129.6, 130.6, 133.0, 137.7, 163.0, 191.2.

HRMS (ESI-TOF) found, m/z : 213.0910 $[\text{M}+\text{H}]^+$. $\text{C}_{14}\text{H}_{13}\text{O}_2^+$. Calculated, m/z : 213.0910.

2-(Allyloxy)-5-(thiophen-2-yl)benzaldehyde (1z)



Yield 2.31 g (95%), yellowish solid, m. p. 55-57 °C.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 4.79 (dt, $J=5.1$, 1.5 Hz, 2H), 5.32 (dq, $J=10.7$, 1.5 Hz, 1H), 5.49 (dq, $J=17.4$, 1.7 Hz, 1H), 6.08 - 6.15 (m, 1H), 7.13 (dd, $J=5.1$, 3.5 Hz, 1H), 7.30 (d, $J=8.8$ Hz, 1H), 7.49 (dd, $J=3.6$, 1.1 Hz, 1H), 7.53 (dd, $J=5.0$, 1.1 Hz, 1H), 7.88 (d, $J=2.5$ Hz, 1H), 7.95 (dd, $J=8.7$, 2.6 Hz, 1H), 10.42 (s, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 69.0, 114.8, 117.8, 123.5, 124.1, 124.5, 125.4, 126.7, 128.5, 132.9, 132.9, 141.9, 159.7, 188.8.

HRMS (ESI-TOF) found, m/z: 245.0633 $[\text{M}+\text{H}]^+$. $\text{C}_{14}\text{H}_{13}\text{O}_2\text{S}^+$. Calculated, m/z: 245.0631.

5. Synthesis of dihydrocyclopropa[*c*]chromen-7b(1*H*)-ol (2)

General method

Corresponding benzaldehyde **1** (1.0 mmol) was dissolved in freshly distilled (over CaH₂, under an inert atmosphere) DMSO (20 mL) in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. Obtained solutions were irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box with stirring.

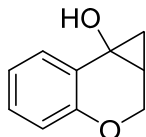
The process was carried out strictly with two samples at a time. This approach allowed us to claim approximately identical irradiation conditions for all samples, since the Schlenk vessels were installed symmetrically into the reactor each time.

The progress of the reaction was monitored by TLC and ¹H NMR (using technique reported in SI, Part 1). After the reaction completion, reaction mixtures were dissolved in 200 mL of EtOAc, washed with saturated KCl solution (10×30 mL) and dried over Na₂SO₄. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 5:1).



Figure S5. Photochemical set-up. Examples of large-scale reactions.

1a,2-Dihydrocyclopropa[c]chromen-7b(1H)-ol (2a)



Yield 84 mg (52%), yellowish viscous oil.

Reaction time ~ 12 h.

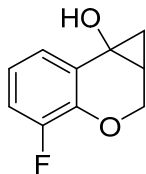
^1H NMR (800 MHz, DMSO- d_6) δ ppm: 0.92 (t, $J=5.5$ Hz, 1H), 1.21 (dd, $J=9.6$, 5.0 Hz, 1H), 1.81 - 1.86 (m, 1H), 3.77 (d, $J=10.5$ Hz, 1H), 4.16 (d, $J=9.8$ Hz, 1H), 6.20 (s, 1H), 6.76 (dd, $J=8.0$, 0.9 Hz, 1H), 6.96 (app td, $J=7.5$, 1.1 Hz, 1H), 7.06 (app td, $J=7.7$, 1.7 Hz, 1H), 7.55 (dd, $J=7.6$, 1.6 Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.5, 26.1, 49.9, 62.0, 116.3, 121.1, 125.0, 126.2, 130.9, 150.6.

The spectral properties corresponded to the literature data.^[14]

HRMS (ESI-TOF) found, m/z : 163.0755 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{11}\text{O}_2^+$. Calculated, m/z : 163.0754.

4-Fluoro-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2d)



Yield 127 mg (71%), colorless solid, m. p. 84-86 °C.

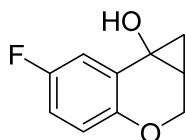
Reaction time ~ 4 h.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 0.98 (t, $J=5.8$ Hz, 1H), 1.26 (dd, $J=9.6$, 5.1 Hz, 1H), 1.87 - 1.92 (m, 1H), 3.81 (d, $J=10.5$ Hz, 1H), 4.26 (d, $J=10.5$ Hz, 1H), 6.34 (s, 1H), 6.94 (app td, $J=7.9$, 5.2 Hz, 1H), 7.00 (ddd, $J=10.8$, 8.3, 1.5 Hz, 1H), 7.36 (d, $J=7.8$ Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.9, 26.2, 49.9, 62.5, 113.0 (d, $J=18.4$ Hz), 120.4 (d, $J=3.0$ Hz), 120.8 (d, $J=7.7$ Hz), 133.9, 138.0 (d, $J=11.7$ Hz), 150.6 (d, $J=242.6$ Hz).

HRMS (ESI-TOF) found, m/z : 181.0657 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{FO}_2^+$. Calculated, m/z : 181.0659.

6-Fluoro-1a,2-dihydrocyclopropa[*c*]chromen-7b(1*H*)-ol (2e)



Yield 99 mg (55%), yellowish viscous oil.

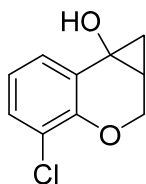
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.98 (t, $J=5.6$ Hz, 1H), 1.24 (dd, $J=9.5$, 5.1 Hz, 1H), 1.80 - 1.91 (m, 1H), 3.73 (d, $J=10.5$ Hz, 1H), 4.16 (d, $J=10.5$ Hz, 1H), 6.78 (dd, $J=8.7$, 4.9 Hz, 1H), 6.87 (app td, $J=8.6$, 3.1 Hz, 1H), 7.29 (dd, $J=9.4$, 3.1 Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.5, 26.1, 50.1, 62.2, 111.4 (d, $J=24.4$ Hz), 112.5 (d, $J=23.1$ Hz), 117.6 (d, $J=8.4$ Hz), 133.1 (d, $J=7.7$ Hz), 146.7 (d, $J=1.7$ Hz), 157.0 (d, $J=236.2$ Hz).

HRMS (ESI-TOF) found, m/z : 181.0658 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{FO}_2^+$. Calculated, m/z : 181.0659.

6-Chloro-1a,2-dihydrocyclopropa[*c*]chromen-7b(1*H*)-ol (2f)



Yield 149 mg (76%), yellowish viscous oil.

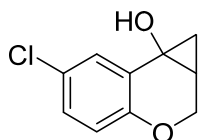
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.97 (t, $J=5.7$ Hz, 1H), 1.26 (dd, $J=9.5$, 5.1 Hz, 1H), 1.88 - 1.93 (m, 1H), 3.83 (d, $J=10.5$ Hz, 1H), 4.30 (d, $J=9.5$ Hz, 1H), 6.35 (s, 1H), 6.98 (app t, $J=7.8$ Hz, 1H), 7.21 (dd, $J=8.0$, 1.5 Hz, 1H), 7.52 (dd, $J=7.6$, 1.5 Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.8, 26.1, 50.0, 62.8, 120.4, 121.6, 123.9, 126.6, 133.1, 146.1.

HRMS (ESI-TOF) found, m/z : 197.0366 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{ClO}_2^+$. Calculated, m/z : 197.0364.

6-Chloro-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2g)



Yield 109 mg (56%), yellowish solid, m. p. 66-68 °C.

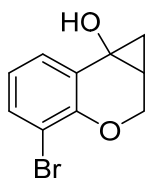
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.96 (t, $J=5.6$ Hz, 1H), 1.25 (dd, $J=9.6$, 5.1 Hz, 1H), 1.86 - 1.91 (m, 1H), 3.77 (d, $J=10.5$ Hz, 1H), 4.18 (d, $J=9.5$ Hz, 1H), 6.36 (s, 1H), 6.80 (d, $J=8.6$ Hz, 1H), 7.10 (dd, $J=8.6$, 2.7 Hz, 1H), 7.50 (d, $J=2.7$ Hz, 1 H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.7, 26.1, 50.0, 62.3, 118.2, 124.6, 125.1, 126.0, 133.2, 149.4.

HRMS (ESI-TOF) found, m/z: 197.0361 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{ClO}_2^+$. Calculated, m/z: 197.0364.

4-Bromo-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2h)



Yield 145 mg (61%), colorless viscous oil.

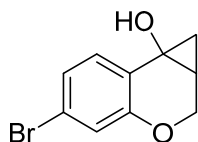
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.97 (t, $J=5.6$ Hz, 1H), 1.26 (dd, $J=9.5$, 5.1 Hz, 1H), 1.86 - 1.95 (m, 1H), 3.82 (d, $J=10.5$ Hz, 1H), 4.30 (d, $J=10.5$ Hz, 1H), 6.35 (s, 1H), 6.92 (app t, $J=7.7$ Hz, 1H), 7.35 (dd, $J=7.9$, 1.4 Hz, 1H), 7.56 (dd, $J=7.6$, 1.5 Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.7, 26.1, 50.0, 62.8, 110.0, 122.3, 124.6, 129.5, 133.0, 147.0.

HRMS (ESI-TOF) found, m/z: 240.9853 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{BrO}_2^+$. Calculated, m/z: 240.9859.

5-Bromo-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2i)



Yield 117 mg (49%), colorless solid, m. p. 91-93 °C.

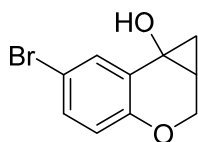
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.93 (t, $J=5.6$ Hz, 1H), 1.24 (dd, $J=9.5$, 5.0 Hz, 1H), 1.84 - 1.89 (m, 1H), 3.81 (d, $J=10.5$ Hz, 1H), 4.19 (d, $J=10.5$ Hz, 1H), 6.31 (s, 1H), 6.98 (d, $J=1.9$ Hz, 1H), 7.16 (dd, $J=8.2$, 2.1 Hz, 1H), 7.48 (d, $J=8.2$ Hz, 1H).

^{13}C NMR (75 MHz, DMSO- d_6) δ ppm: 17.7, 26.0, 49.8, 62.5, 118.1, 119.1, 124.0, 126.9, 130.6, 151.5.

HRMS (ESI-TOF) found, m/z: 240.9852 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{BrO}_2^+$. Calculated, m/z: 240.9859.

6-Bromo-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2j)



Yield 127 mg (53%), yellowish solid, m. p. 82-84 °C.

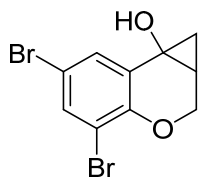
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.95 (t, $J=5.5$ Hz, 1H), 1.25 (dd, $J=9.5$, 5.1 Hz, 1H), 1.84 - 1.92 (m, 1H), 3.77 (d, $J=10.5$ Hz, 1H), 4.19 (d, $J=10.7$ Hz, 1H), 6.36 (s, 1H), 6.75 (d, $J=8.4$ Hz, 1H), 7.23 (dd, $J=8.5$, 2.6 Hz, 1H), 7.63 (d, $J=2.7$ Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.7, 26.1, 49.9, 62.2, 112.8, 118.7, 127.5, 128.9, 133.7, 149.9.

HRMS (ESI-TOF) found, m/z: 240.9855 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{BrO}_2^+$. Calculated, m/z: 240.9859.

4,6-Dibromo-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2k)



Yield 165 mg (52%), yellowish viscous oil.

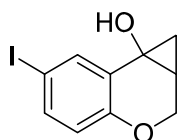
Reaction time ~ 4 h.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ ppm: 1.01 (t, $J=5.8$ Hz, 1H), 1.29 (dd, $J=9.5$, 5.3 Hz, 1H), 1.92 - 1.98 (m, 1H), 3.83 (d, $J=10.5$ Hz, 1H), 4.32 (d, $J=9.5$ Hz, 1H), 6.50 (br. s., 1H), 7.57 (d, $J=2.5$ Hz, 1H), 7.65 (d, $J=2.3$ Hz, 1H).

^{13}C NMR (176 MHz, $\text{DMSO-}d_6$) δ ppm: 18.0, 26.2, 50.0, 63.0, 111.1, 112.9, 127.1, 131.2, 135.0, 146.6.

HRMS (ESI-TOF) found, m/z : 318.8959 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_9\text{Br}_2\text{O}_2^+$. Calculated, m/z : 318.8964.

6-Iodo-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2l)



Yield 115 mg (40%), colorless solid, m. p. 60-62 °C.

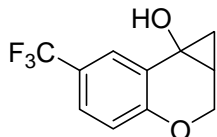
Reaction time ~ 4 h.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ ppm: 0.93 (t, $J=5.6$ Hz, 1H), 1.23 (dd, $J=9.5$, 5.1 Hz, 1H), 1.84 - 1.90 (m, 1H), 3.77 (d, $J=10.5$ Hz, 1H), 4.18 (d, $J=10.5$ Hz, 1H), 6.32 (s, 1H), 6.61 (d, $J=8.4$ Hz, 1H), 7.39 (dd, $J=8.3$, 2.2 Hz, 1H), 7.81 (d, $J=2.1$ Hz, 1H).

^{13}C NMR (176 MHz, $\text{DMSO-}d_6$) δ ppm: 17.7, 26.1, 49.6, 62.1, 84.2, 119.0, 133.4, 133.9, 134.8, 150.5.

HRMS (ESI-TOF) found, m/z : 288.9720 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_{10}\text{IO}_2^+$. Calculated, m/z : 288.9720.

6-(Trifluoromethyl)-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2m)



Yield 121 mg (53%), colorless solid, m. p. 75-77 °C.

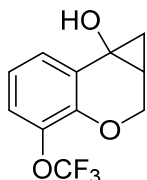
Reaction time ~ 4 h.

¹H NMR (700 MHz, DMSO-*d*₆) δ ppm: 1.03 (t, *J*=5.7 Hz, 1H), 1.30 (dd, *J*=9.6, 5.2 Hz, 1H), 1.94 - 1.98 (m, 1H), 3.84 (d, *J*=10.5 Hz, 1H), 4.24 (d, *J*=10.5 Hz, 1H), 6.44 (s, 1H), 7.08 (d, *J*=1.3 Hz, 1H), 7.33 (dd, *J*=7.9, 1.0 Hz, 1H), 7.76 (d, *J*=8.0 Hz, 1H).

¹³C NMR (176 MHz, DMSO-*d*₆) δ ppm: 18.0, 26.7, 50.1, 62.4, 113.1 (q, *J*=3.9 Hz), 117.7 (q, *J*=3.9 Hz), 124.1 (q, *J*=271.7 Hz), 126.0, 127.0 (q, *J*=32.1 Hz), 135.9, 150.8.

HRMS (ESI-TOF) found, *m/z*: 231.0625 [M+H]⁺. C₁₁H₁₀F₃O₂⁺. Calculated, *m/z*: 231.0627.

4-(Trifluoromethoxy)-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2n)



Yield 137 mg (56%), colorless viscous oil.

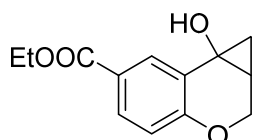
Reaction time ~ 4 h.

¹H NMR (700 MHz, DMSO-*d*₆) δ ppm: 0.97 (t, *J*=5.7 Hz, 1H), 1.29 (dd, *J*=9.5, 5.1 Hz, 1H), 1.89 - 1.94 (m, 1H), 3.78 (d, *J*=10.5 Hz, 1H), 4.30 (d, *J*=10.5 Hz, 1H), 6.39 (s, 1H), 7.05 (app t, *J*=8.0 Hz, 1H), 7.14 (d, *J*=8.2 Hz, 1H), 7.58 (dd, *J*=7.8, 1.3 Hz, 1H).

¹³C NMR (176 MHz, DMSO-*d*₆) δ ppm: 17.8, 26.1, 49.9, 62.6, 119.6, 120.2 (q, *J*=256.3 Hz), 121.1, 124.2, 134.0, 136.2, 142.8.

HRMS (ESI-TOF) found, *m/z*: 247.0575 [M+H]⁺. C₁₁H₁₀F₃O₃⁺. Calculated, *m/z*: 247.0577.

Ethyl 7b-hydroxy-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-6-carboxylate (2o)



Yield 116 mg (50%), yellow viscous oil.

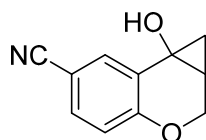
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.93 (t, $J=5.7$ Hz, 1H), 1.27 (dd, $J=9.6, 5.2$ Hz, 1H), 1.31 (t, $J=7.1$ Hz, 3H), 1.88 - 1.95 (m, 1H), 3.88 (d, $J=10.3$ Hz, 1H), 4.25 (d, $J=10.7$ Hz, 1H), 4.27 - 4.32 (m, 2H), 6.41 (s, 1H), 6.88 (d, $J=8.4$ Hz, 1H), 7.70 (dd, $J=8.4, 2.3$ Hz, 1H), 8.21 (d, $J=2.1$ Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 14.2, 17.9, 25.9, 49.8, 60.3, 62.6, 116.7, 122.8, 126.6, 127.9, 131.0, 154.7, 165.5.

HRMS (ESI-TOF) found, m/z : 235.0969 $[\text{M}+\text{H}]^+$. $\text{C}_{13}\text{H}_{15}\text{O}_4^+$. Calculated, m/z : 235.0965.

7b-Hydroxy-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-6-carbonitrile (2p)



Yield 82 mg (44%), colorless solid, m. p. 98-100 °C.

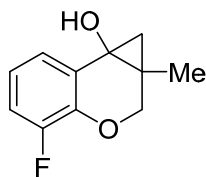
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.97 (t, $J=5.8$ Hz, 1H), 1.30 (dd, $J=9.6, 5.2$ Hz, 1H), 1.92 - 1.99 (m, 1H), 3.90 (d, $J=10.5$ Hz, 1H), 4.28 (d, $J=10.3$ Hz, 1H), 6.47 (s, 1H), 6.96 (d, $J=8.2$ Hz, 1H), 7.56 (dd, $J=8.2, 2.1$ Hz, 1H), 7.86 (d, $J=2.1$ Hz, 1H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 18.1, 26.1, 49.7, 62.7, 103.6, 117.8, 119.1, 129.1, 130.8, 132.6, 154.5.

HRMS (ESI-TOF) found, m/z : 188.0708 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_{10}\text{NO}_2^+$. Calculated, m/z : 188.0706.

4-Fluoro-1a-methyl-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2q)



Yield 137 mg (71%), colorless viscous oil.

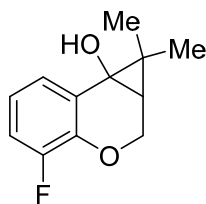
Reaction time ~ 4 h.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ ppm: 0.96 (d, $J=5.0$ Hz, 1H), 1.17 (d, $J=5.1$ Hz, 1H), 1.25 (s, 3H), 3.55 (d, $J=10.5$ Hz, 1H), 4.18 (d, $J=10.5$ Hz, 1H), 6.15 (s, 1H), 6.91 - 6.96 (m, 1H), 6.96 - 7.01 (m, 1H), 7.34 (d, $J=7.6$ Hz, 1H).

^{13}C NMR (176 MHz, $\text{DMSO-}d_6$) δ ppm: 13.0, 23.3, 29.3, 53.7 (d, $J=3.7$ Hz), 67.1, 112.8 (d, $J=18.1$ Hz), 120.2 (d, $J=2.7$ Hz), 120.9 (d, $J=7.4$ Hz), 134.1 (d, $J=1.3$ Hz), 138.5 (d, $J=11.7$ Hz), 150.5 (d, $J=242.6$ Hz).

HRMS (ESI-TOF) found, m/z : 195.0813 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_{12}\text{FO}_2^+$. Calculated, m/z : 195.0816.

4-Fluoro-1,1-dimethyl-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2r)



Yield 170 mg (82%), yellowish solid, m. p. 61-63 °C.

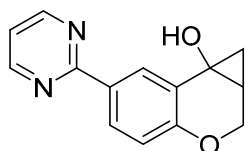
Reaction time ~ 4 h.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ ppm: 0.82 (s, 3H), 1.27 (s, 3H), 1.33 (d, $J=2.7$ Hz, 1H), 4.16 (dd, $J=11.3$, 3.6 Hz, 1H), 4.29 (d, $J=11.3$ Hz, 1H), 6.10 (s, 1H), 6.90 (app td, $J=8.0$, 5.1 Hz, 1H), 7.01 (ddd, $J=10.9$, 8.2, 1.2 Hz, 1H), 7.35 (d, $J=7.8$ Hz, 1H).

^{13}C NMR (176 MHz, $\text{DMSO-}d_6$) δ ppm: 16.1, 22.3, 28.4, 32.2, 54.9 (d, $J=3.3$ Hz), 61.4, 113.2 (d, $J=18.1$ Hz), 119.9 (d, $J=7.4$ Hz), 122.0 (d, $J=3.0$ Hz), 129.8 (d, $J=1.0$ Hz), 138.5 (d, $J=11.0$ Hz), 150.6 (d, $J=242.3$ Hz).

HRMS (ESI-TOF) found, m/z : 209.0966 $[\text{M}+\text{H}]^+$. $\text{C}_{12}\text{H}_{14}\text{FO}_2^+$. Calculated, m/z : 209.0972.

6-(Pyrimidin-2-yl)-1a,2-dihydrocyclopropa[c]chromen-7b(1H)-ol (2s)



Yield 113 mg (47%), yellowish solid, m. p. 156-156 °C.

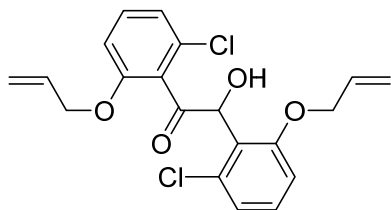
Reaction time ~ 4 h.

^1H NMR (700 MHz, DMSO- d_6) δ ppm: 0.96 (t, $J=5.6$ Hz, 1H), 1.27 (dd, $J=9.7, 5.1$ Hz, 1H), 1.87 - 1.92 (m, 1H), 3.88 (d, $J=10.3$ Hz, 1H), 4.25 (d, $J=10.5$ Hz, 1H), 6.39 (s, 1H), 6.89 (d, $J=8.4$ Hz, 1H), 7.37 (app t, $J=4.8$ Hz, 1H), 8.13 (dd, $J=8.4, 2.3$ Hz, 1H), 8.69 (d, $J=2.3$ Hz, 1H), 8.86 (d, $J=4.8$ Hz, 2H).

^{13}C NMR (176 MHz, DMSO- d_6) δ ppm: 17.8, 26.0, 50.0, 62.5, 116.6, 119.1, 125.1, 126.1, 130.3, 131.0, 153.1, 157.5, 163.3.

HRMS (ESI-TOF) found, m/z: 241.0974 $[\text{M}+\text{H}]^+$. $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2^+$. Calculated, m/z: 241.0972.

1,2-Bis(2-(allyloxy)-6-chlorophenyl)-2-hydroxyethan-1-one (3aa)



Yield 94 mg (49%), colorless viscous oil.

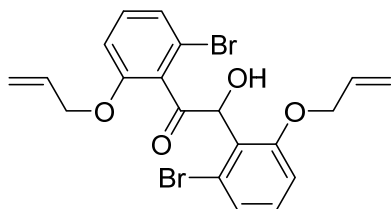
Reaction time ~ 4 h.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 4.41 - 4.60 (m, 4H), 5.17 - 5.28 (m, 2H), 5.29 - 5.44 (m, 3H), 5.89 - 5.99 (m, 2H), 6.26 (br. s., 1H), 6.87 - 6.96 (m, 3H), 6.99 (d, $J=8.4$ Hz, 1H), 7.21 - 7.25 (m, 1H), 7.29 - 7.34 (m, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 69.0, 69.2, 74.3 (br. s.), 111.1, 111.3, 117.3, 117.6, 121.4, 121.7 (br. s.), 123.7, 127.3, 130.1, 130.1, 131.3, 132.7, 133.0, 134.3 (br. s.), 156.0, 157.9, 199.0.

HRMS (ESI-TOF) found, m/z : 393.0652 $[\text{M}+\text{H}]^+$. $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{O}_4^+$. Calculated, m/z : 393.0655.

1,2-Bis(2-(allyloxy)-6-bromophenyl)-2-hydroxyethan-1-one (3ba)



Yield 57 mg (24%), colorless viscous oil.

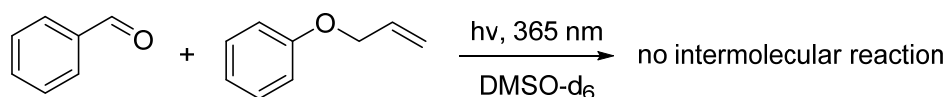
Reaction time ~ 4 h.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 4.41 - 4.60 (m, 4H), 5.18 (br. s., 1H), 5.24 (app t, $J=12.2$ Hz, 2H), 5.28 - 5.35 (m, 1H), 5.38 - 5.48 (m, 1H), 5.85 - 5.93 (m, 1H), 5.95 - 6.02 (m, 1H), 6.23 (br. s., 1H), 6.96 (d, $J=8.2$ Hz, 1H), 7.01 (d, $J=8.4$ Hz, 1H), 7.07 - 7.12 (m, 2H), 7.14 - 7.18 (m, 1H), 7.23 - 7.27 (m, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 68.9, 69.1, 71.5, 111.6, 112.0, 116.1, 117.4, 117.6, 118.7, 124.5, 124.8, 126.0, 128.9, 130.5, 131.7, 132.8, 133.1, 156.1, 156.5, 199.0.

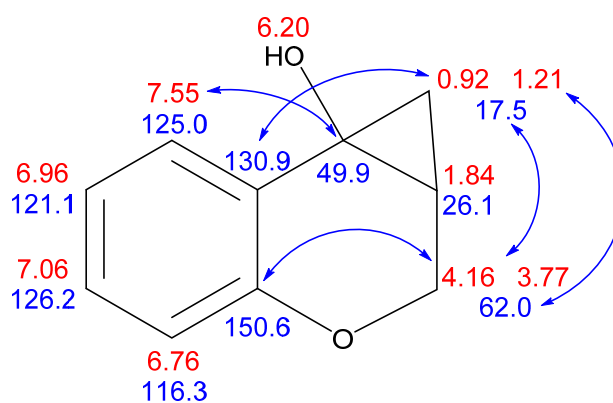
HRMS (ESI-TOF) found, m/z : 480.9636 $[\text{M}+\text{H}]^+$. $\text{C}_{20}\text{H}_{19}\text{Br}_2\text{O}_4^+$. Calculated, m/z : 480.9645.

6. Intermolecular study



Benzaldehyde (7 mg, 0.07 mmol) and allyloxybenzene (9 mg, 0.07 mmol) were dissolved in 1 mL of DMSO- d_6 in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, part of the solution (0.65 mL) was transferred to argon fused NMR tube and sealed. NMR tube with these solutions was irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box for 6 h. The mixture was analyzed by ^1H NMR.

7. 2D NMR data



Scheme S1. Results of 2D NMR study of compound **2a**. Chemical shifts ¹H (red), and ¹³C (blue) are indicated, the most important spin-spin interactions (HMBC) are marked with arrows. The spectra are presented in last part of SI.

8. Experiment with radical quenching reagents

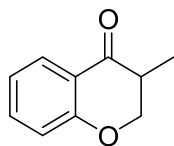
Compound **1a** (15 mg, 0.09 mmol) was dissolved in 3 mL of DMSO-*d*₆ in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.65 mL) were transferred to three argon fused NMR tubes and sealed. TEMPO (3 mg, 0.02 mmol) was added to one tube, BHT (4 mg, 0.02 mmol) was added to the second, and the third tube was used without additives. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in EvoluChem™ PhotoRedOx box for various time. The mixtures were analyzed by ¹H NMR.

Table S3. Experiment with radical quenching reagents results.

Time, hours	Blank sample		+ 1 eq. TEMPO		+1 eq. BHT	
	2a , %	1a , %	2a , %	1a , %	2a , %	1a , %
0.5	26	55	11	66	7	73
1	34	28	19	47	14	54
2	46	10	30	24	28	33
3	52	5	34	13	37	19

9. Further transformations

Hydrolysis of 2a to 3-methylchroman-4-one (2a)*



Compound **2a** (81 mg, 0.5 mmol) and TsOH·H₂O (95 mg, 0.5 mmol) were dissolved in mixture of THF (5 mL) and distilled water (0.5 ml). The resulted mixture was stirred overnight at 50 °C. EtOAc (100 mL) was added and the resulted mixture was washed with brine (3×20 mL). Organic layer was dried over anhydrous Na₂SO₄, all volatiles were removed in vacuo and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 20:1). Yield 49 mg (61%), colorless oil.

¹H NMR (800 MHz, CDCl₃) δ ppm: 1.24 (d, *J*=7.0 Hz, 3H), 2.84 - 2.92 (m, 1H), 4.17 (t, *J*=11.1 Hz, 1H), 4.51 (dd, *J*=11.2, 5.0 Hz, 1H), 6.97 (d, *J*=8.3 Hz, 1H), 7.01 – 7.05 (m, 1H), 7.45 - 7.50 (m, 1H), 7.91 (dd, *J*=7.8, 1.3 Hz, 1H).

¹³C NMR (201 MHz, CDCl₃) δ ppm: 10.7, 40.8, 72.2, 117.7, 120.6, 121.3, 127.4, 135.7, 161.7, 194.8.

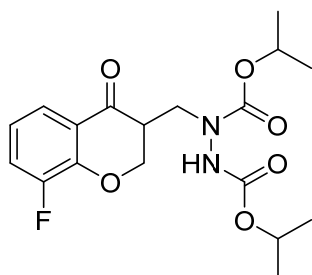
The spectral properties corresponded to the literature data.^[15]

HRMS (ESI-TOF) found, *m/z*: 163.0751 [M+H]⁺. C₁₀H₁₁O₂⁺. Calculated, *m/z*: 163.0754.

Synthesis of hydrazinedicarboxylates (4)

Mixture of the corresponding compound **2** (1 mmol), DIAD (242 mg, 1.2 mmol) and Cu(OAc)₂·H₂O (20 mg, 0.1 mmol) in freshly distilled DMSO (8 mL) was stirred at room temperature for 2 h. EtOAc (200 mL) was added and the resulted mixture was washed with saturated aqueous solution of KCl (5×50 mL). Organic layer was dried over anhydrous Na₂SO₄, all volatiles were removed in vacuo and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 4:1).

Diisopropyl 1-((8-fluoro-4-oxochroman-3-yl)methyl)hydrazine-1,2-dicarboxylate (4d)



Yield 240 mg (63%), white solid, m. p. 95-97 °C.

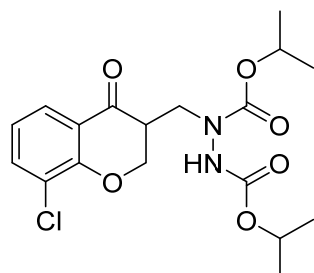
¹H NMR (800 MHz, DMSO-*d*₆) δ ppm: 1.01 - 1.30 (m, 12H), 3.14 (br. s., 1H), 3.74 (br. s., 1H), 4.43 - 4.58 (m, 1H), 4.63 - 4.90 (m, 3H), 6.99 - 7.11 (m, 1H), 7.47 - 7.61 (m, 2H), 8.92 - 9.46 (m, 1H).

¹³C NMR (201 MHz, DMSO-*d*₆) δ ppm: 20.8 - 22.6 (m), 43.7 - 44.6 (m), 46.1 - 47.0 (m), 68.4 (br. s.), 68.8 - 70.0 (m), 120.8 (d, *J*=6.5 Hz), 121.7 (d, *J*=17.2 Hz), 121.9 (br. s.), 122.5 (br. s.), 149.3 (d, *J*=11.2 Hz), 150.8 (d, *J*=246.2 Hz), 155.3 - 155.9 (m), 190.9.

HRMS (ESI-TOF) found, *m/z*: 383.1620 [M+H]⁺. C₁₈H₂₄FN₂O₆⁺. Calculated, *m/z*: 383.1613.

Diisopropyl 1-((8-chloro-4-oxochroman-3-yl)methyl)hydrazine-1,2-dicarboxylate

(4f)



Yield 277 mg (70%), white solid, m. p. 71-73 °C.

^1H NMR (800 MHz, DMSO- d_6) δ ppm: 1.12 - 1.22 (m, 12H) 3.15 (br. s., 1H), 3.66 - 3.80 (m, 1H), 4.44 - 4.54 (m, 1H), 4.70 - 4.84 (m, 3H), 7.08 (app t, $J=7.8$ Hz, 1H), 7.67 - 7.79 (m, 2H), 8.94 - 9.42 (m, 1H).

^{13}C NMR (201 MHz, DMSO- d_6) δ ppm: 21.0 - 22.3 (m), 43.2 - 44.3 (m), 45.4 - 47.1 (m), 68.4 (br. s.), 68.7 - 70.0 (m), 121.4, 121.7, 121.7 - 121.9 (m), 125.5, 135.8, 155.4 - 155.9 (m), 156.5, 191.1.

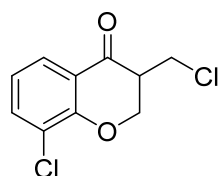
HRMS (ESI-TOF) found, m/z: 399.1320 $[\text{M}+\text{H}]^+$. $\text{C}_{18}\text{H}_{24}\text{ClN}_2\text{O}_6^+$. Calculated, m/z: 399.1317.

Chlorination of compound 2f

Compound **2f** (98 mg, 0.5 mmol) was added in argon to a solution of N-chlorosuccinimide (100 mg, 0.75 mmol), AgNO₃ (17 mg, 0.05 mmol) and K₂S₂O₈ (162 mg, 0.6 mmol) in C₂H₄Cl₂ (2 mL) and distilled water (2 mL) in a Schlenk flask. The resulted mixture was stirred for 3 h at room temperature. EtOAc (100 mL) was added and the resulted mixture was washed with brine (3×20 mL). Organic layer was dried over anhydrous Na₂SO₄, all volatiles were removed in vacuo.

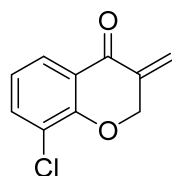
This reaction result in formation of compounds **5f** and **6f** mixture. Compound **5f** cannot be separated in pure form due to the rapid transformation to alkene **6f** on SiO₂. Thus, only ¹H NMR data are presented.

8-Chloro-3-(chloromethyl)chroman-4-one (5f)



¹H NMR (800 MHz, CDCl₃) δ ppm: 3.15 - 3.23 (m, 1H), 3.81 (dd, *J*=11.6, 8.5 Hz, 1H), 3.99 (dd, *J*=11.6, 4.0 Hz, 1H), 4.58 (t, *J*=11.1 Hz, 1H), 4.88 (dd, *J*=11.5, 4.9 Hz, 1H), 6.99 - 7.02 (m, 1H), 7.60 (dd, *J*=7.8, 1.6 Hz, 1H), 7.84 (dd, *J*=7.9, 1.5 Hz, 1H).

8-Chloro-3-methylenechroman-4-one (6f)



Was obtained after the flash chromatography (eluent – mixture of hexane and EtOAc, v/v 20:1) of abovementioned reaction mixture.

Yield 80 mg (82%), colorless viscous oil.

¹H NMR (800 MHz, CDCl₃) δ ppm: 5.13 (s, 2H), 5.65 (s, 1H), 6.36 (s, 1H), 7.00 – 7.04 (m, 1H), 7.59 (dd, *J*=7.7, 1.4 Hz, 1H), 7.93 (dd, *J*=7.9, 1.4 Hz, 1H).

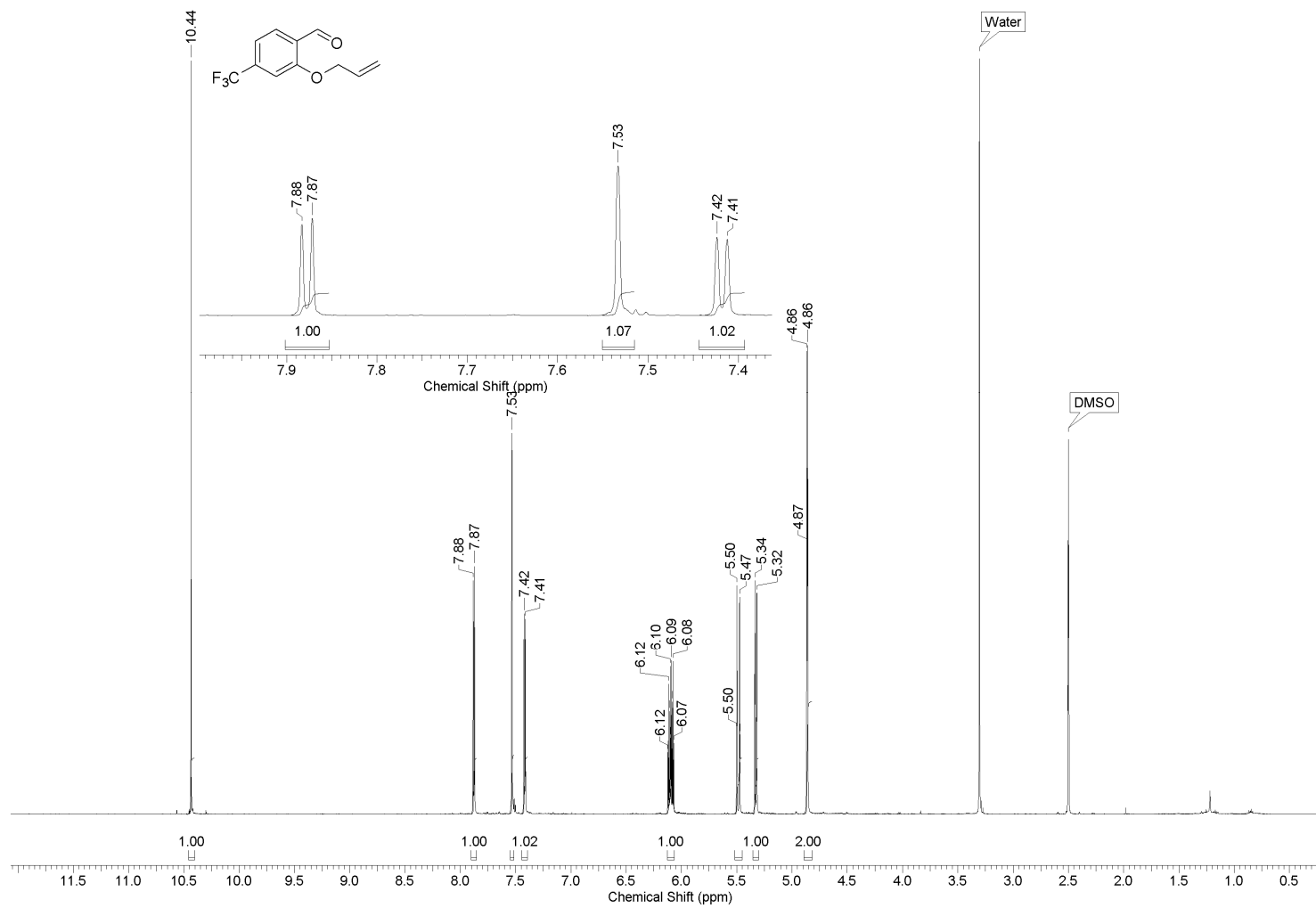
¹³C NMR (201 MHz, CDCl₃) δ ppm: 71.7, 122.0, 123.1, 123.38, 123.39, 126.6, 136.0, 137.9, 157.3, 181.3.

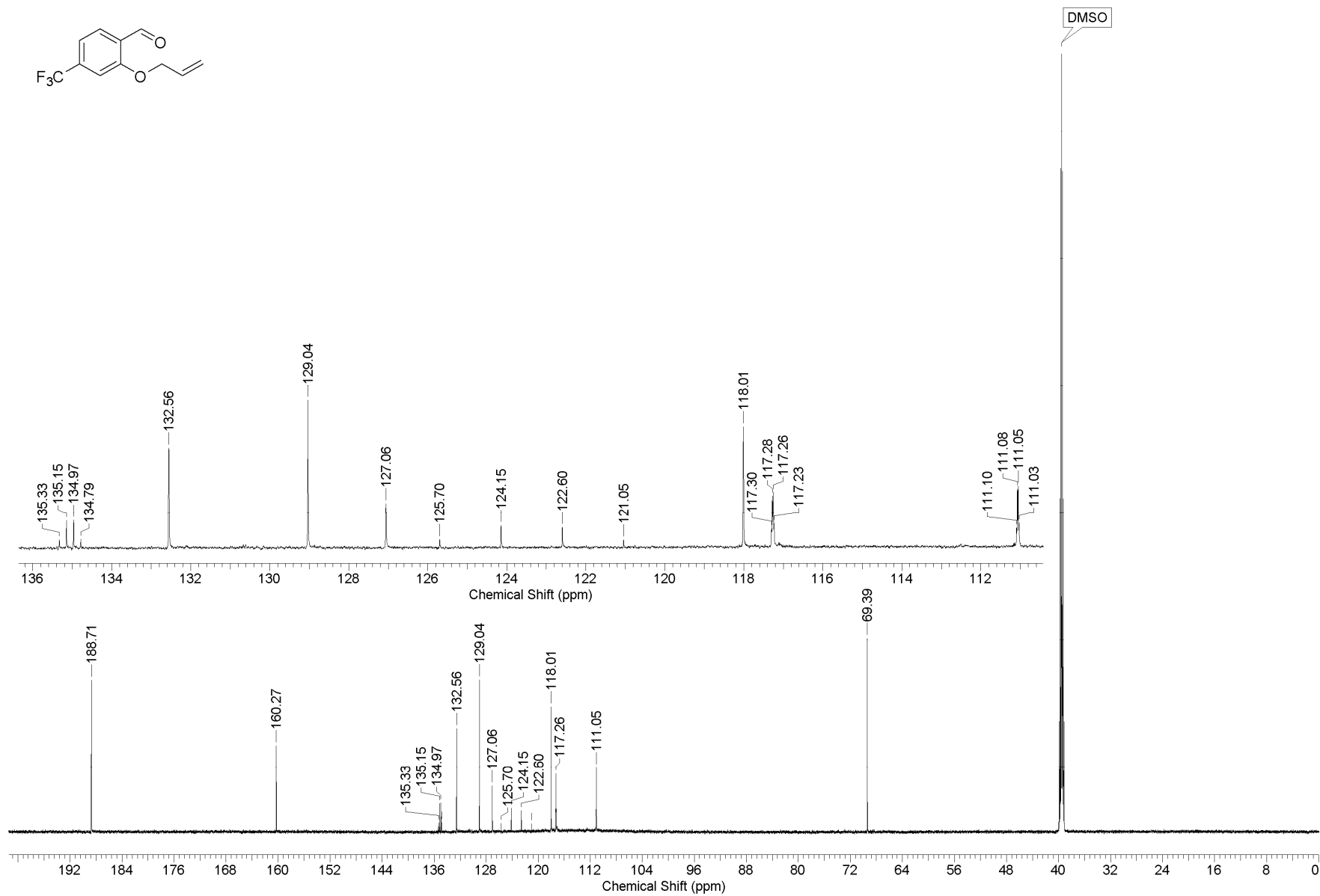
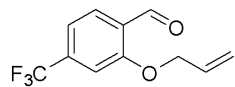
HRMS (ESI-TOF) found, *m/z*: 195.0207 [M+H]⁺. C₁₀H₈ClO₂⁺. Calculated, *m/z*: 195.0207.

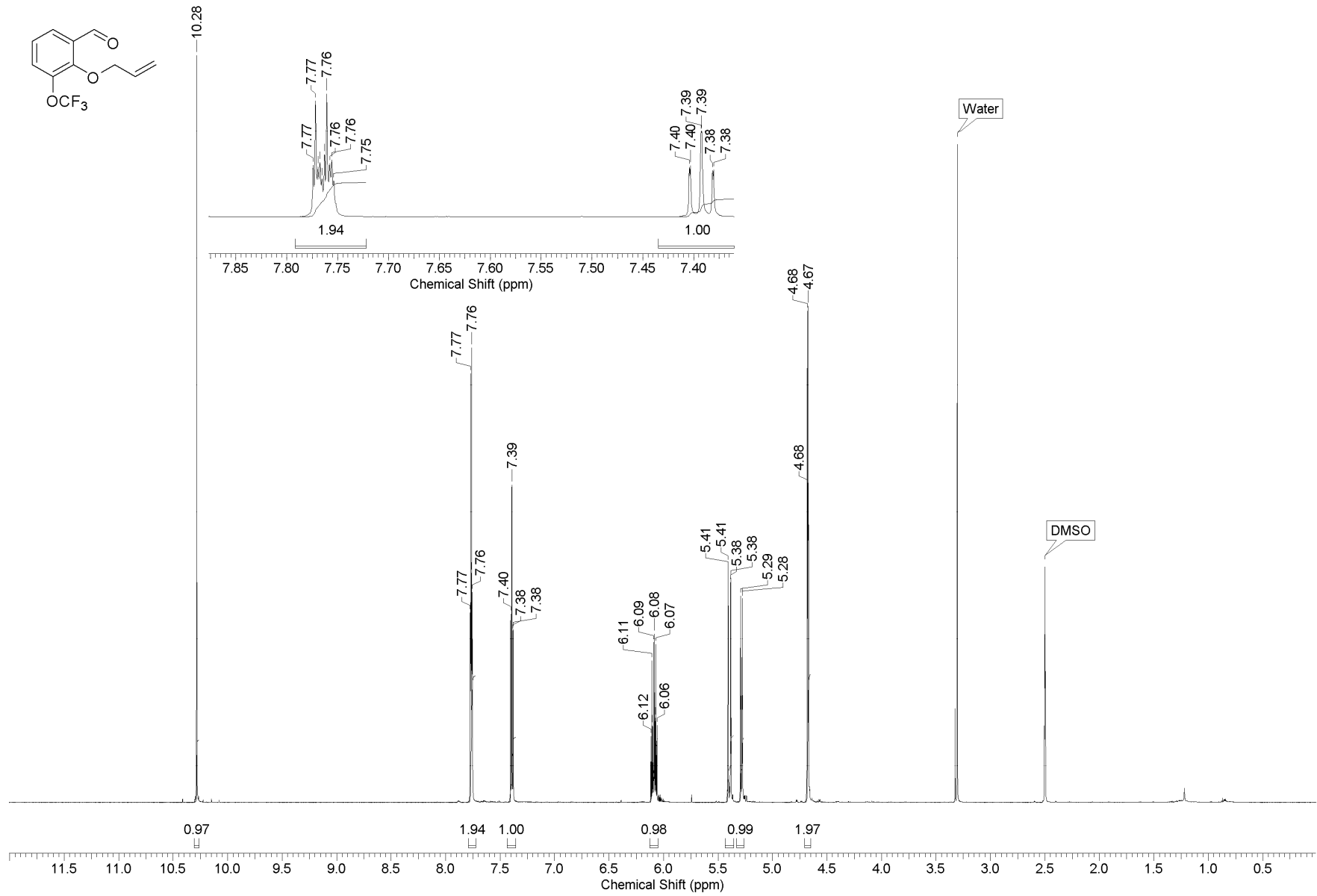
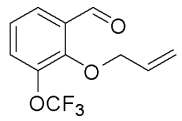
10. References

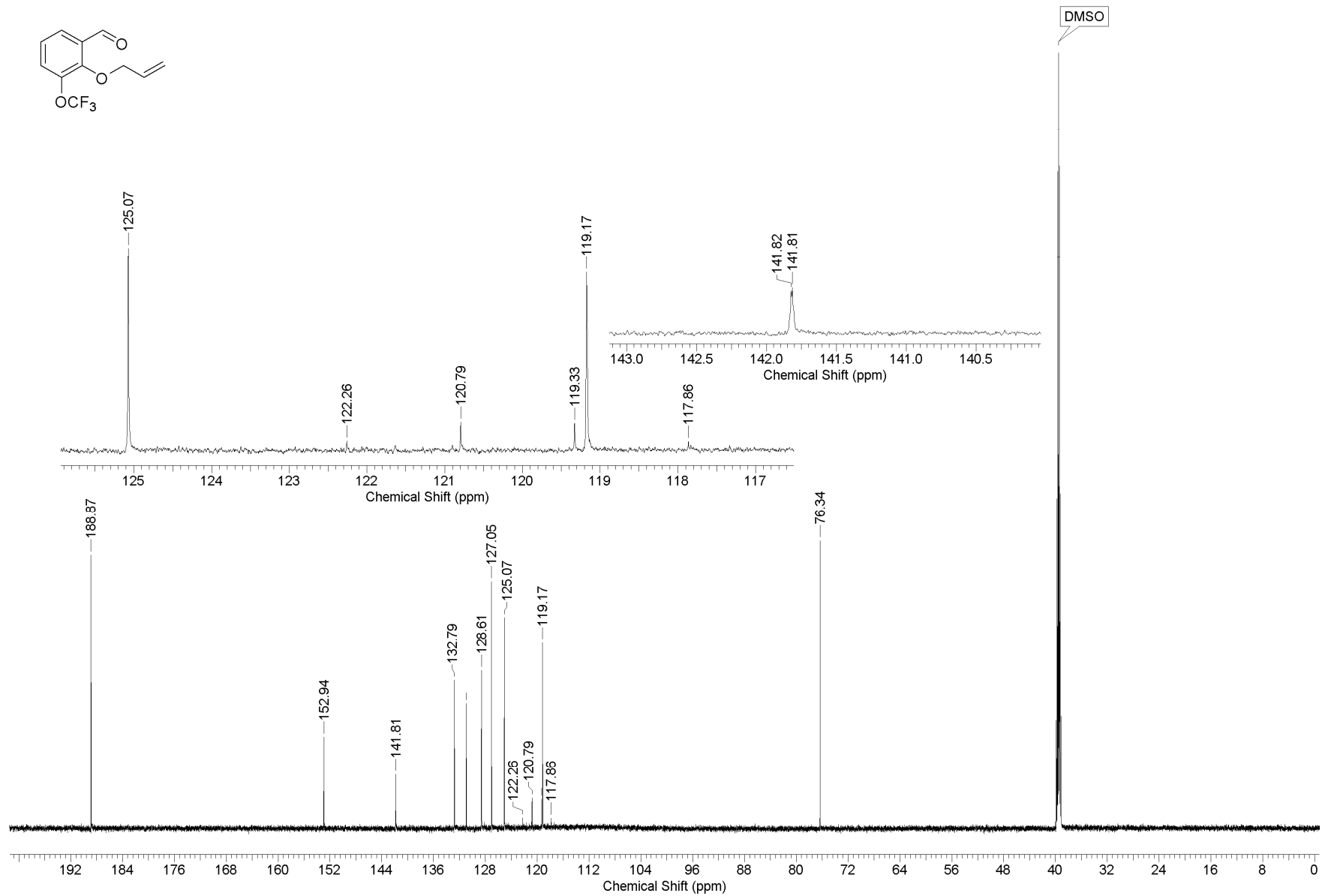
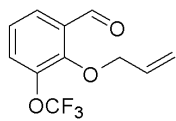
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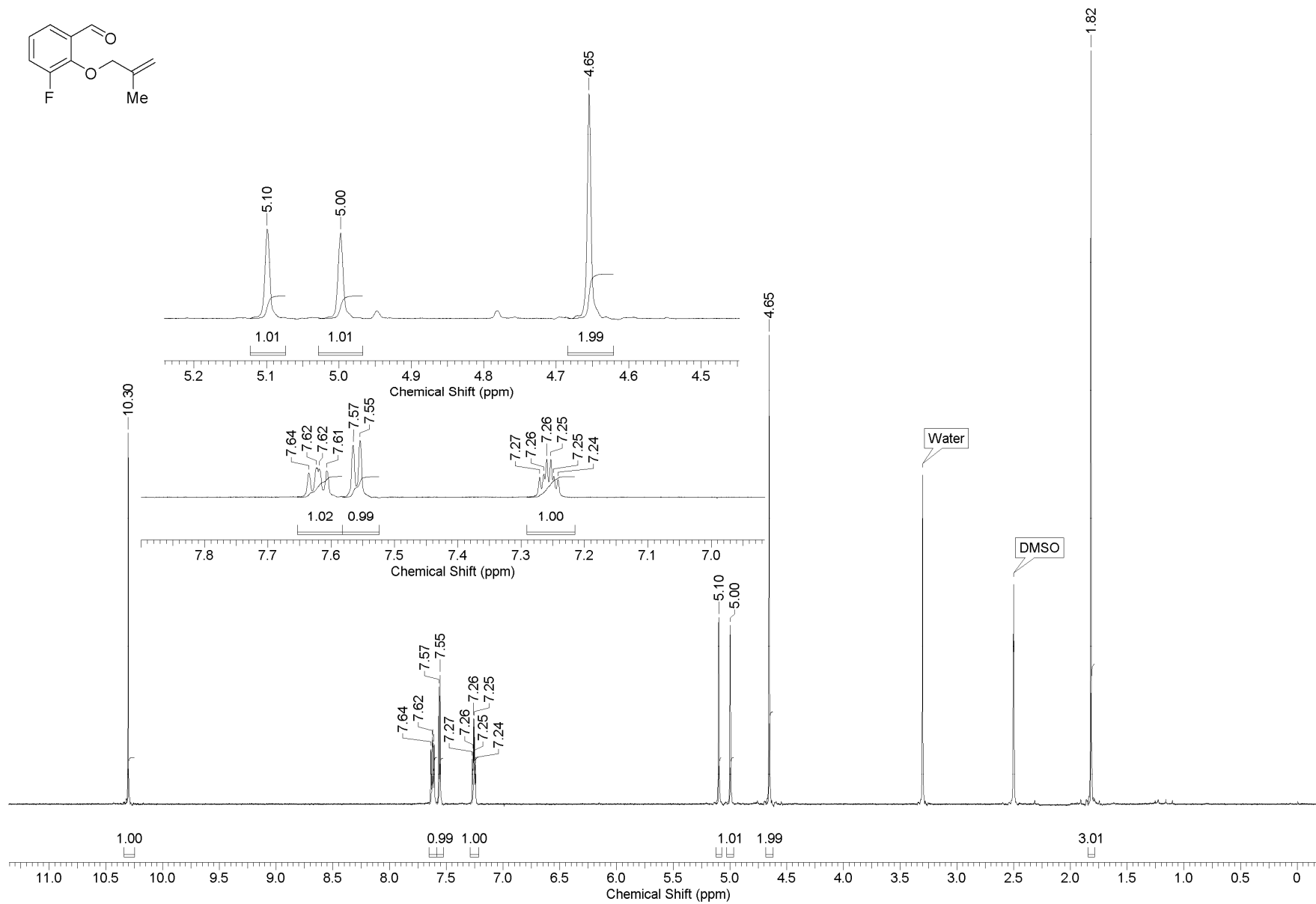
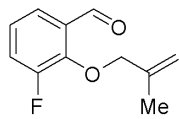
11. Copies of ^1H and ^{13}C NMR spectra

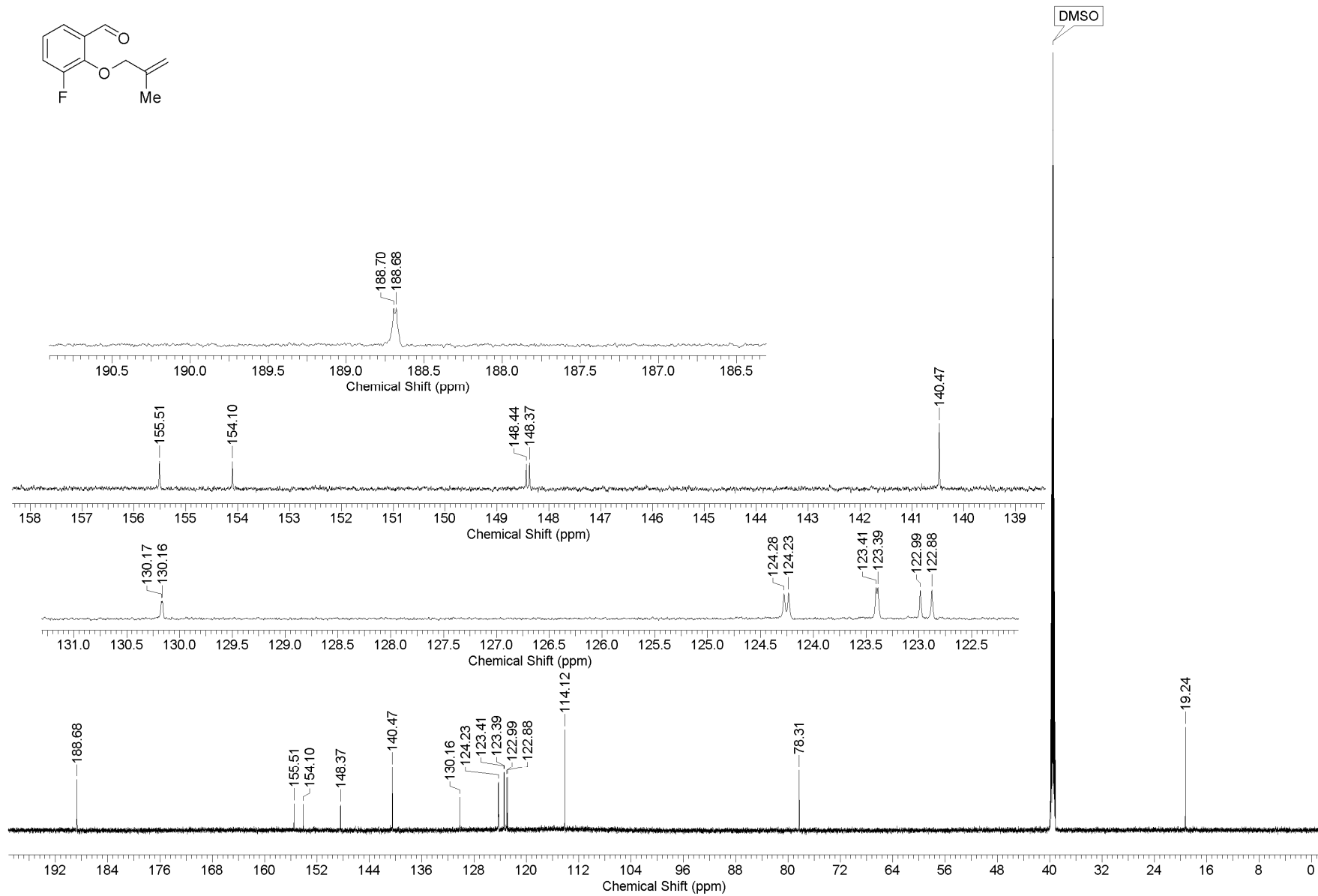
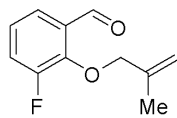


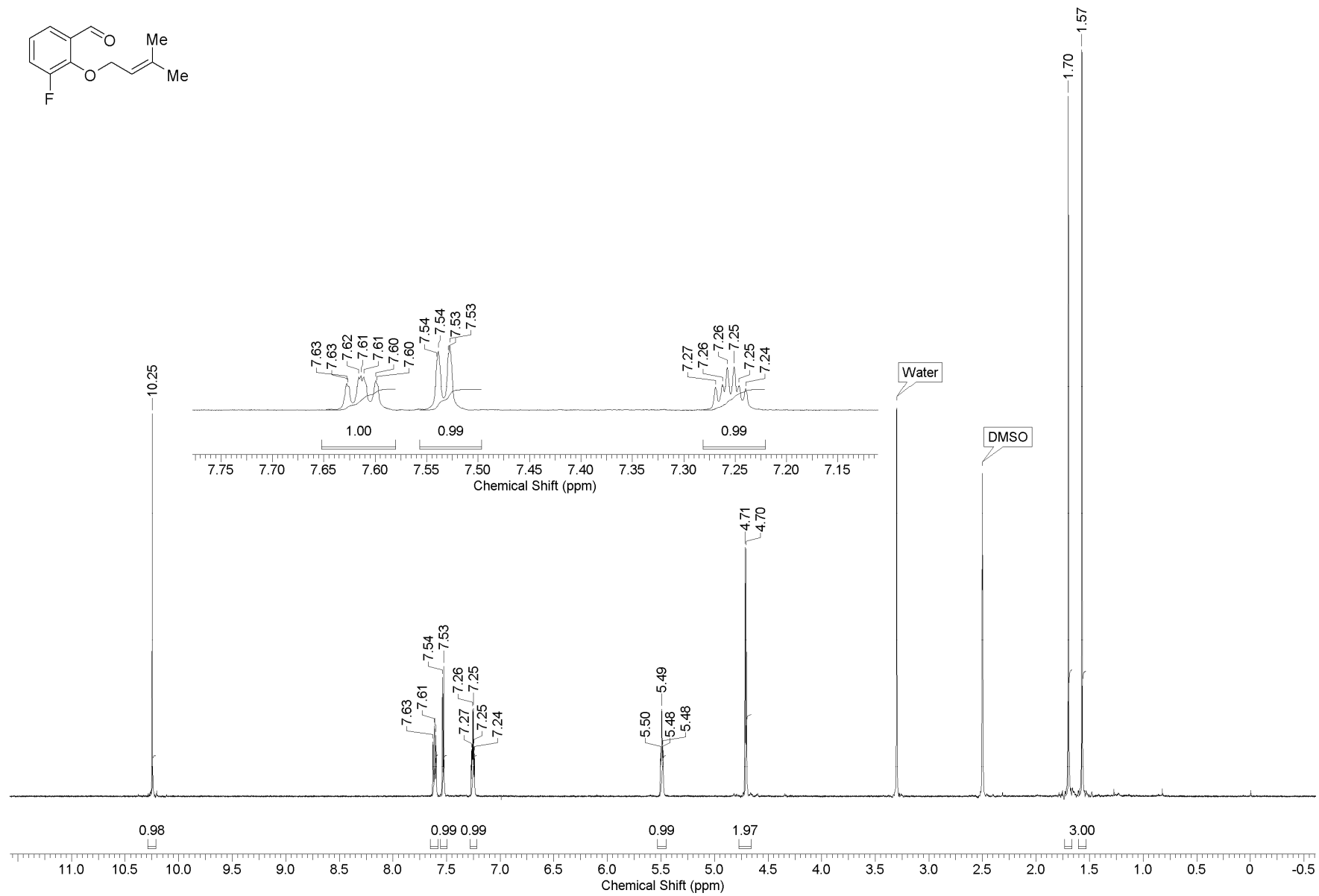
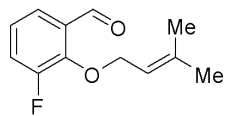




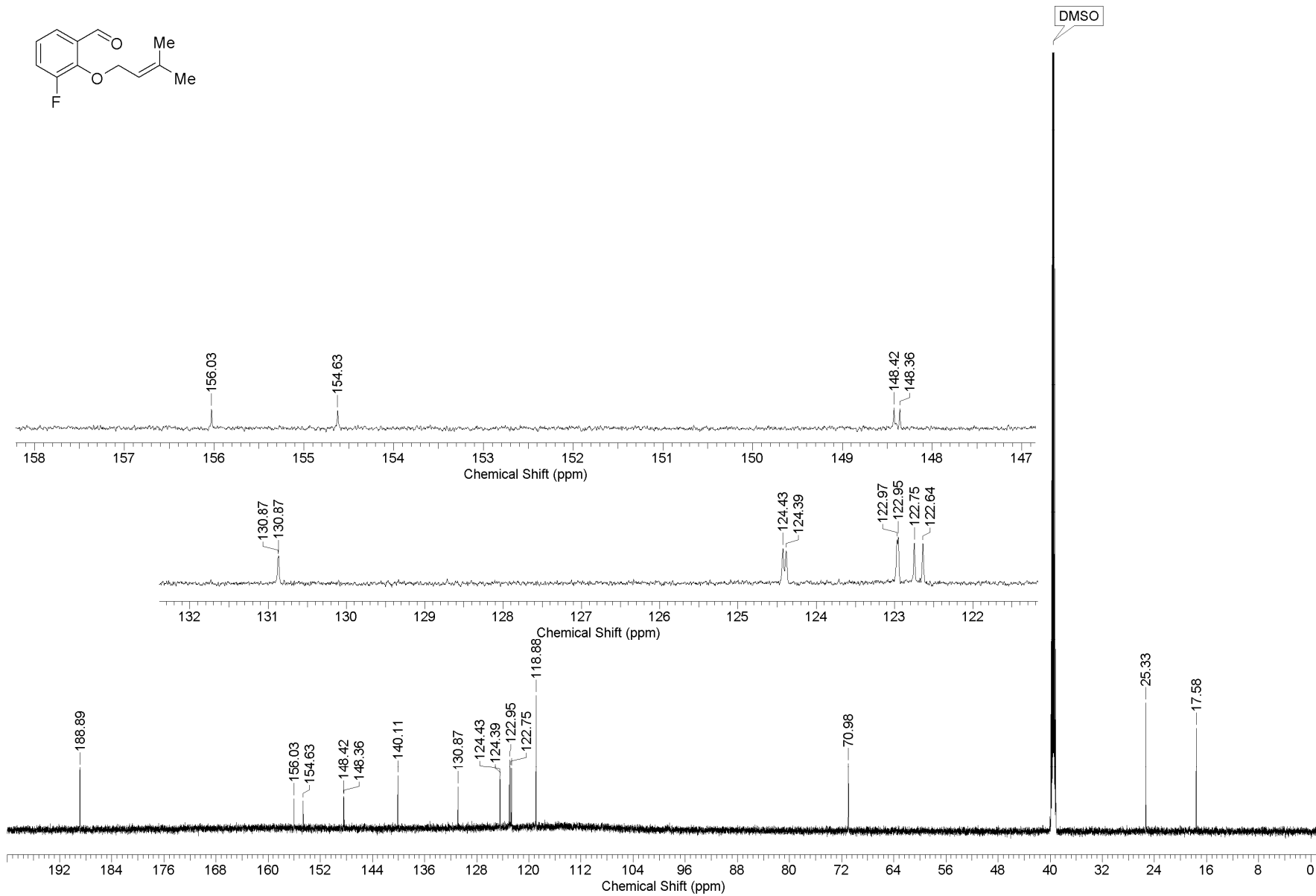
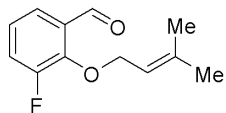


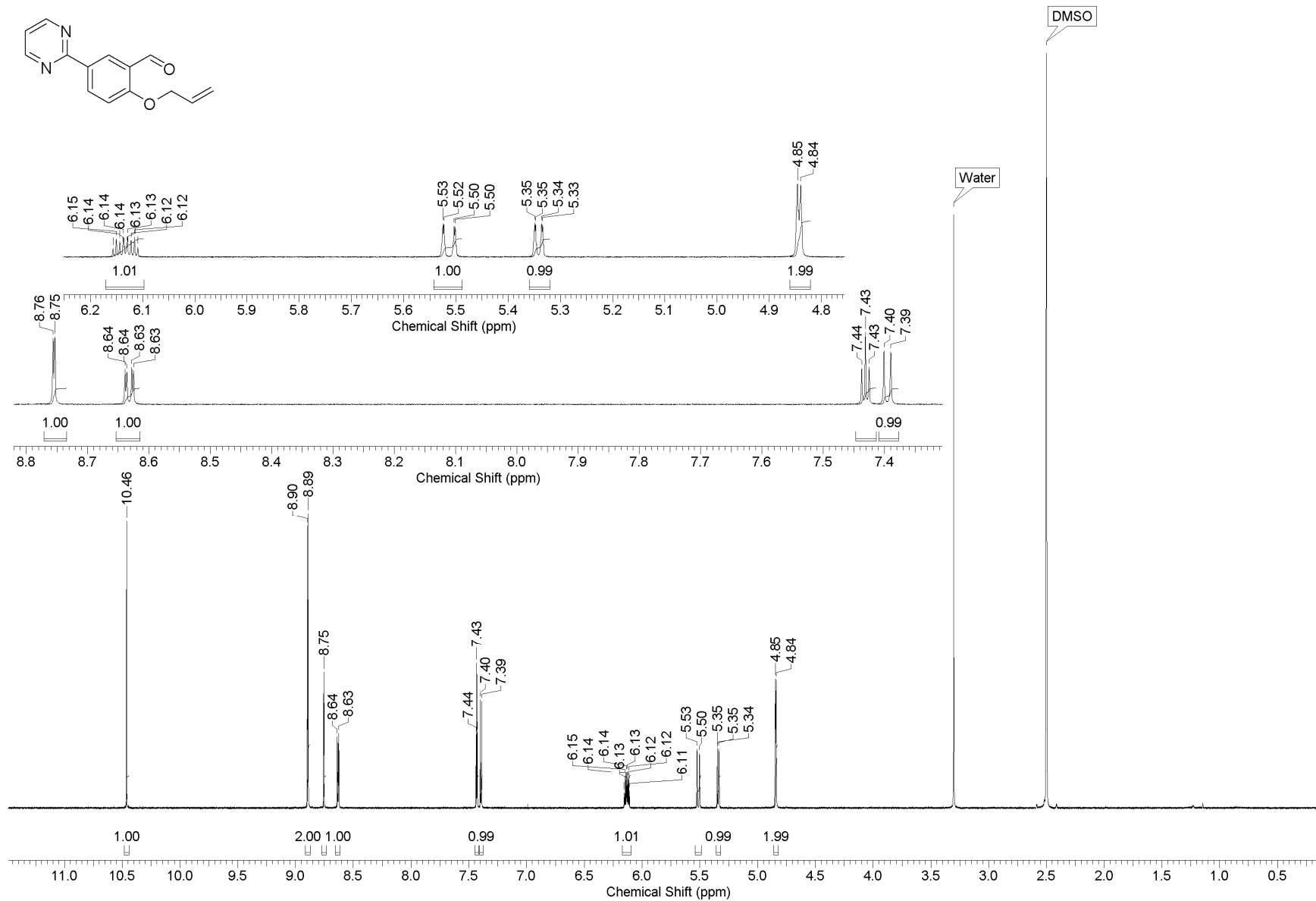
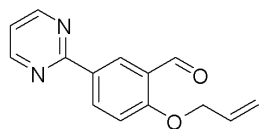


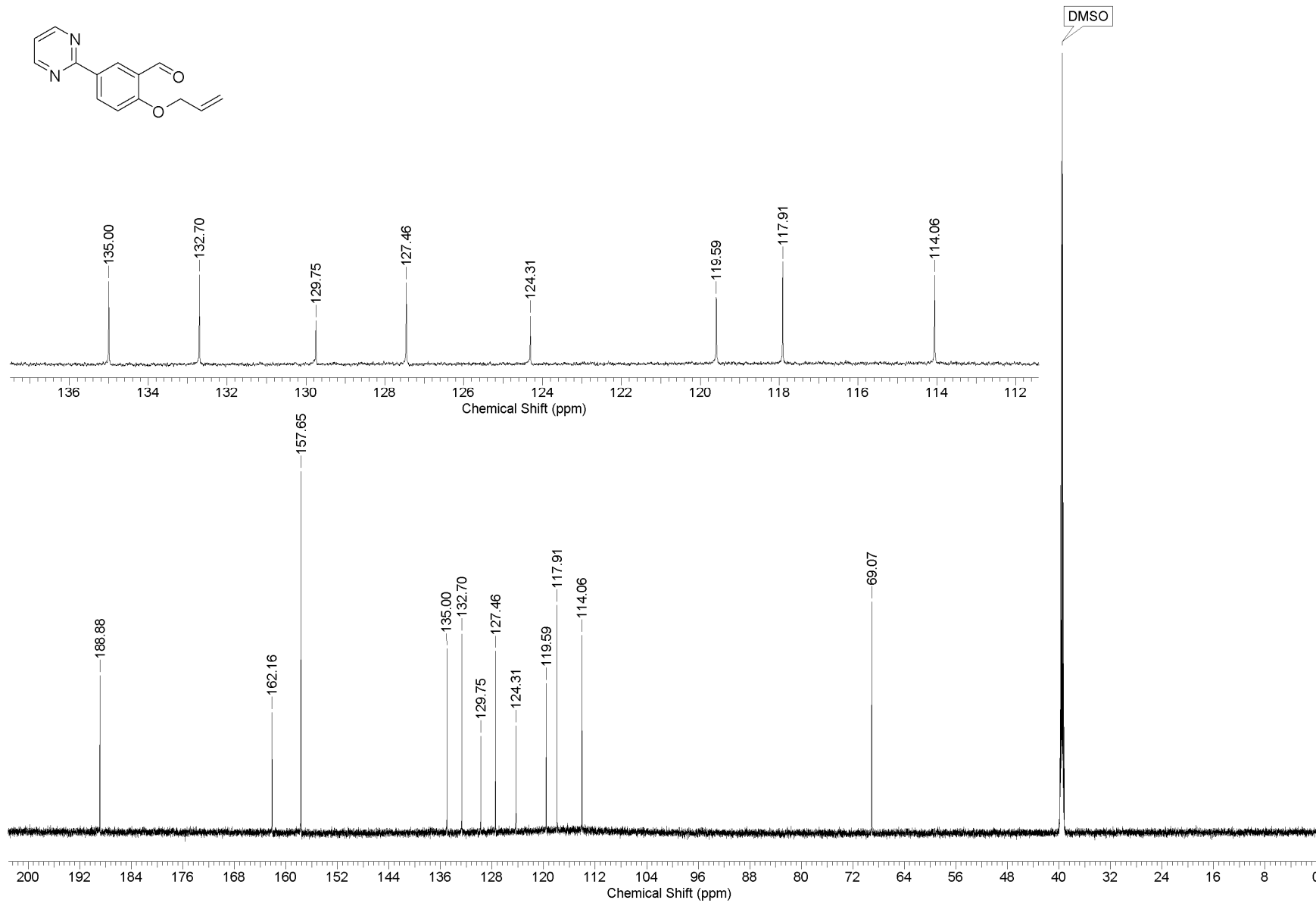
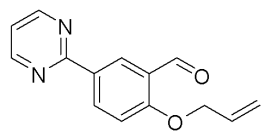


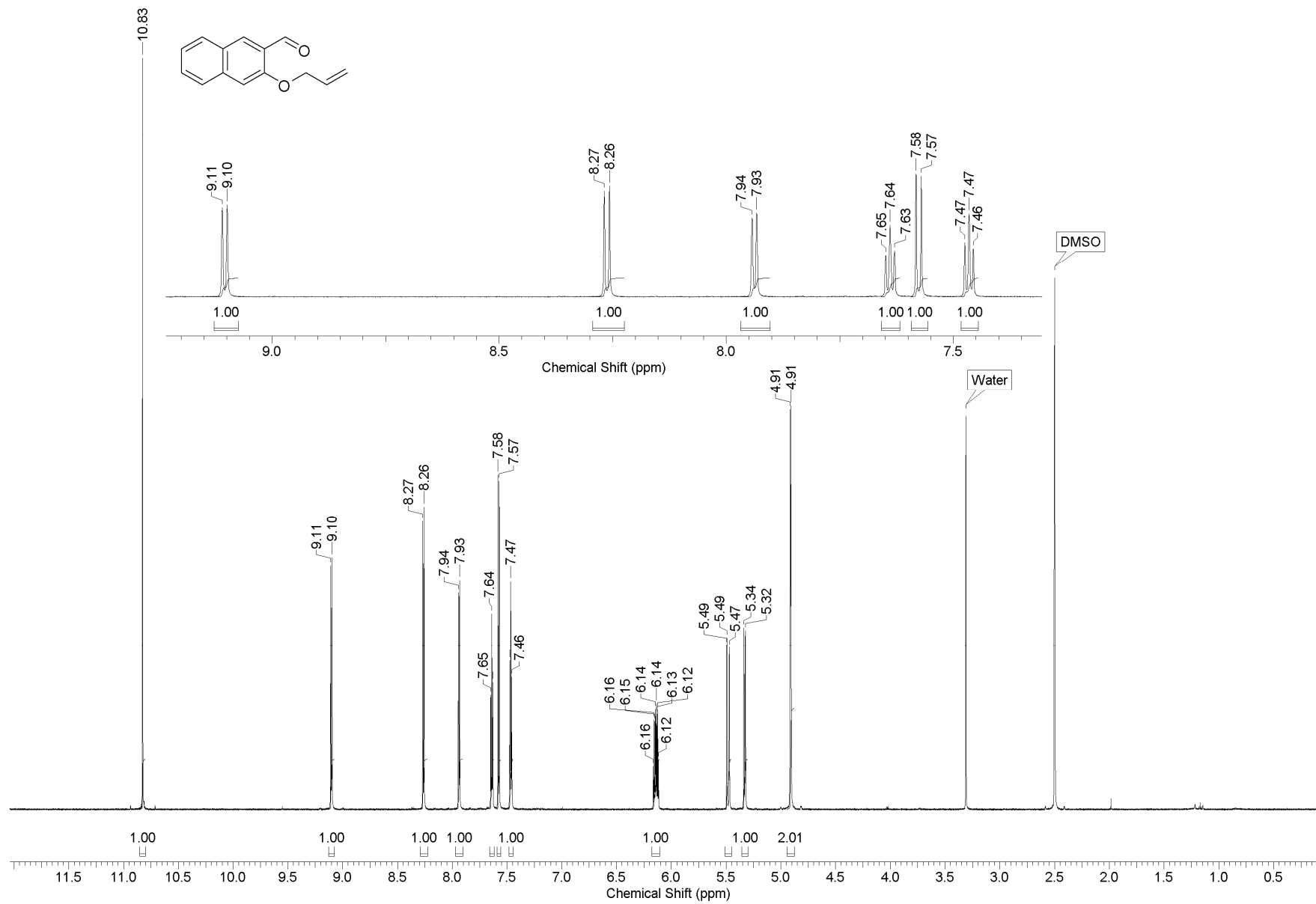


S38

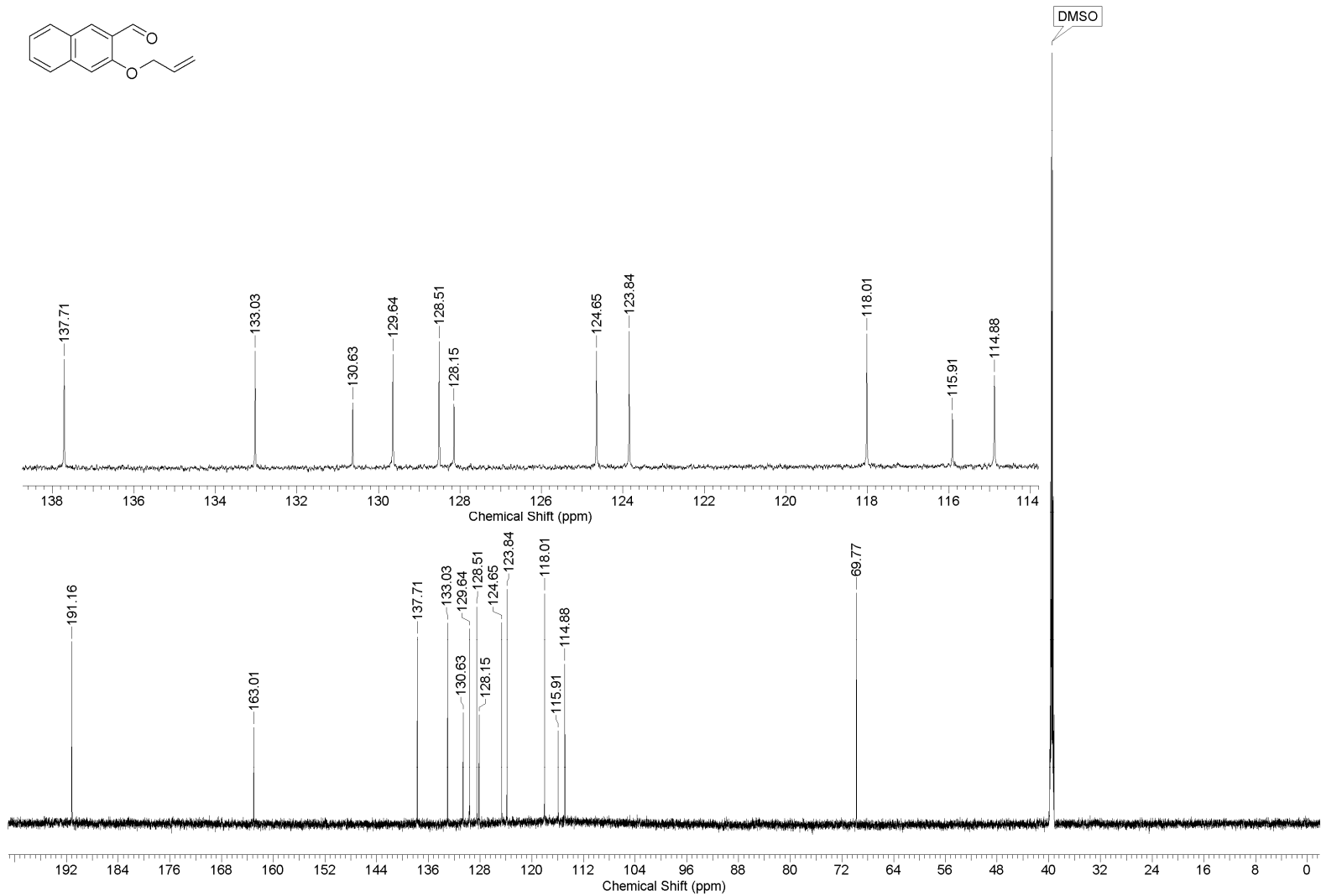
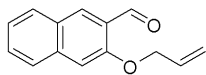


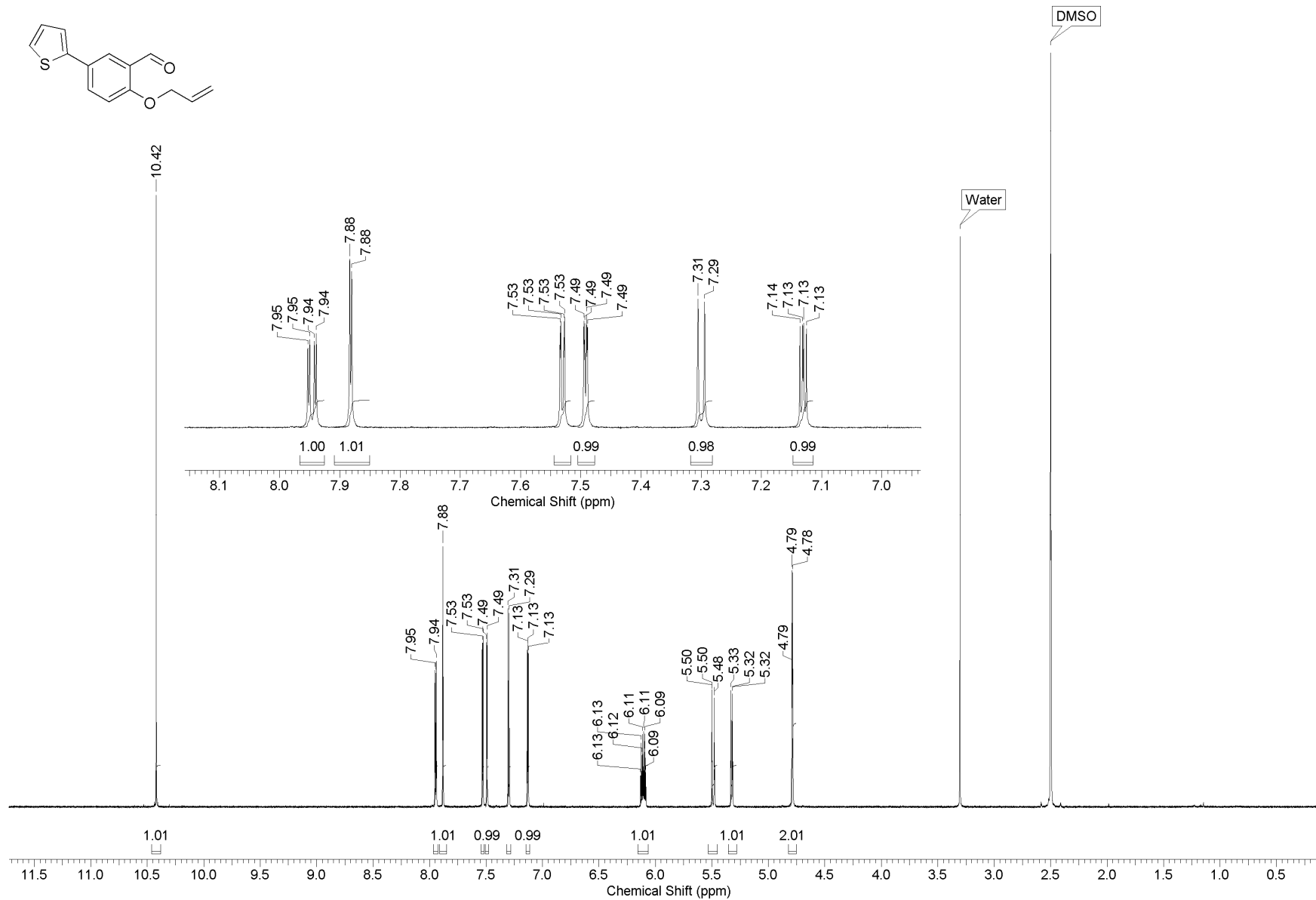
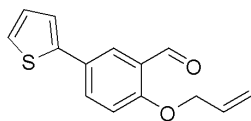


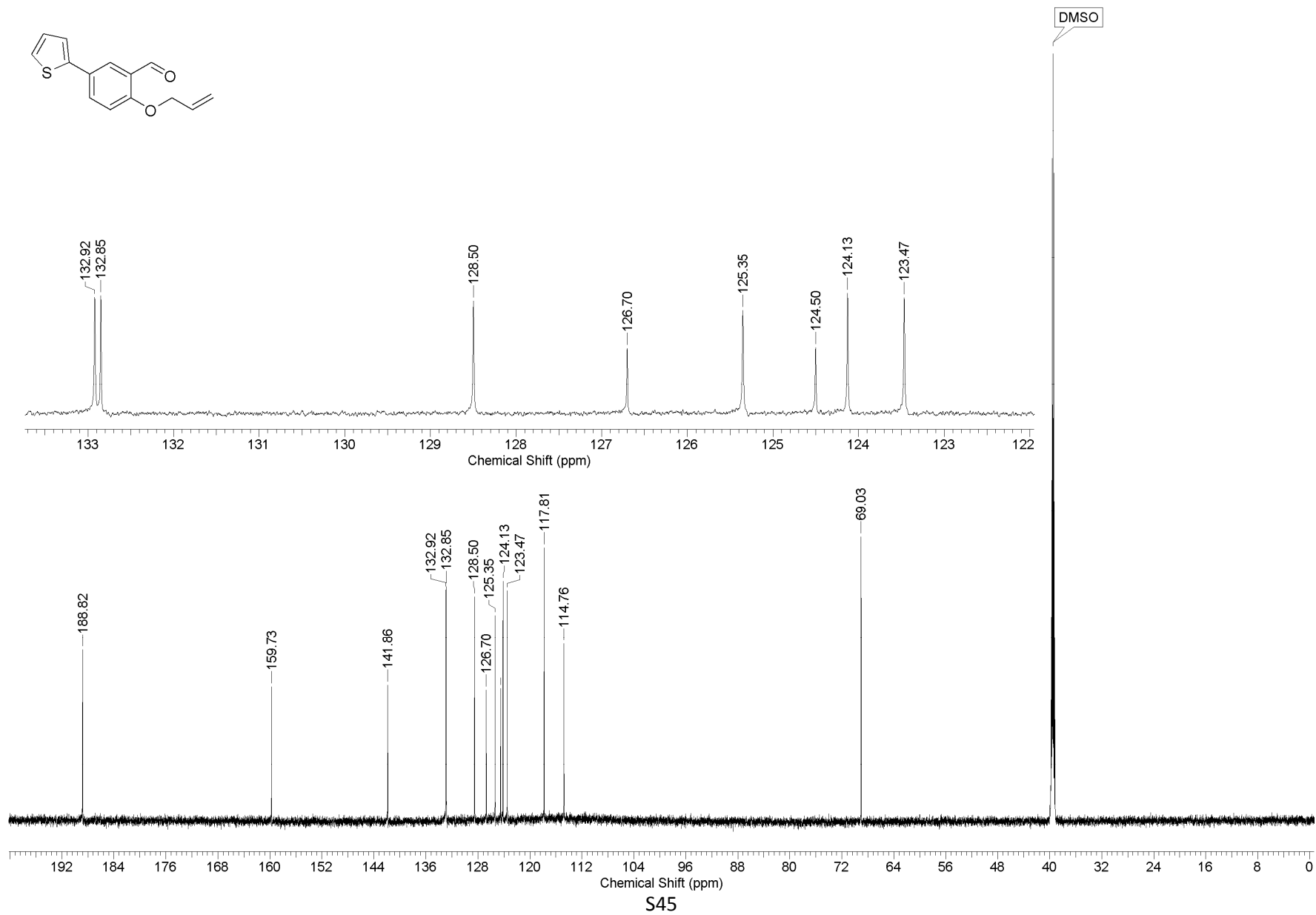
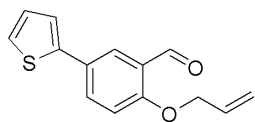


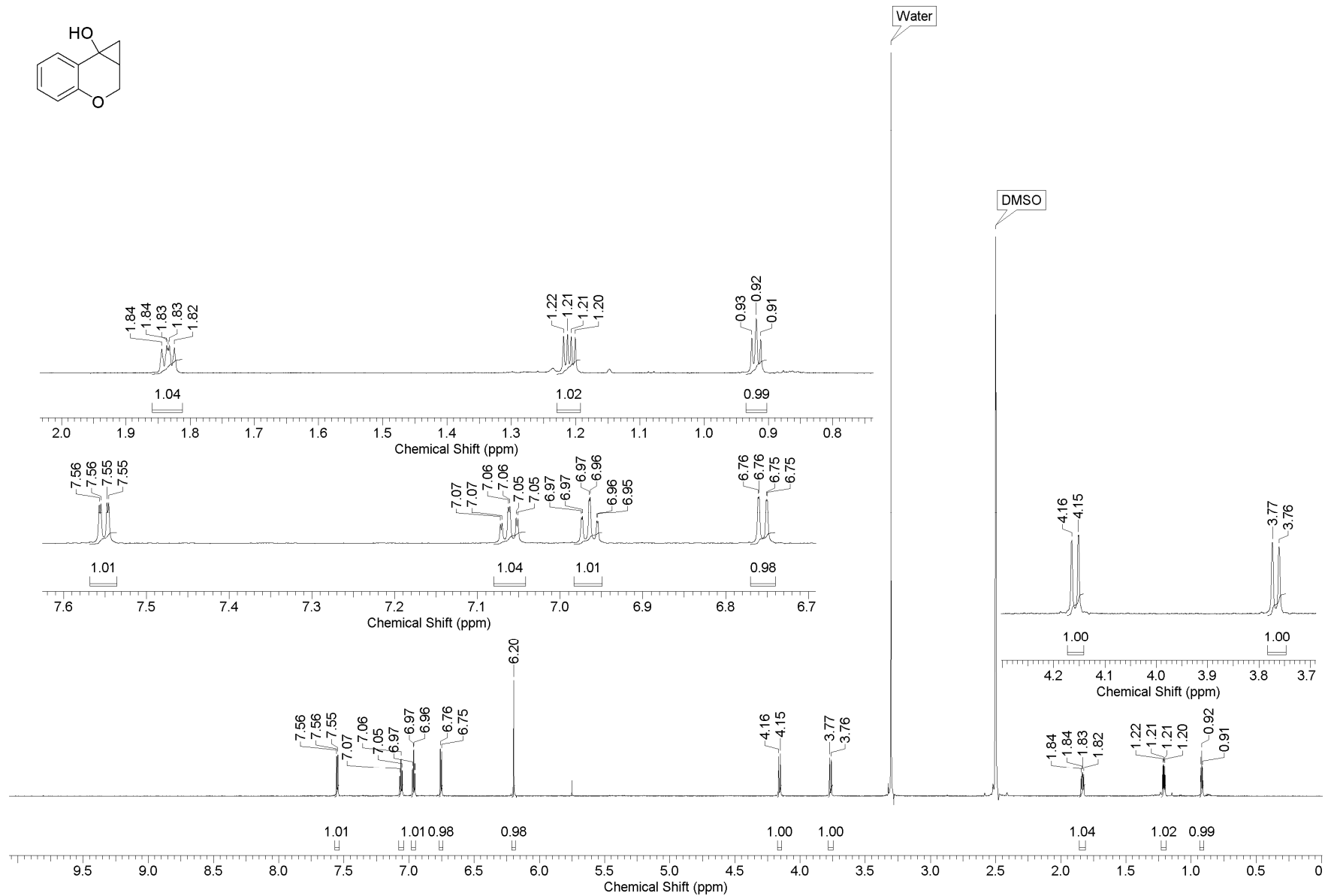
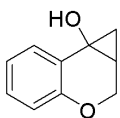


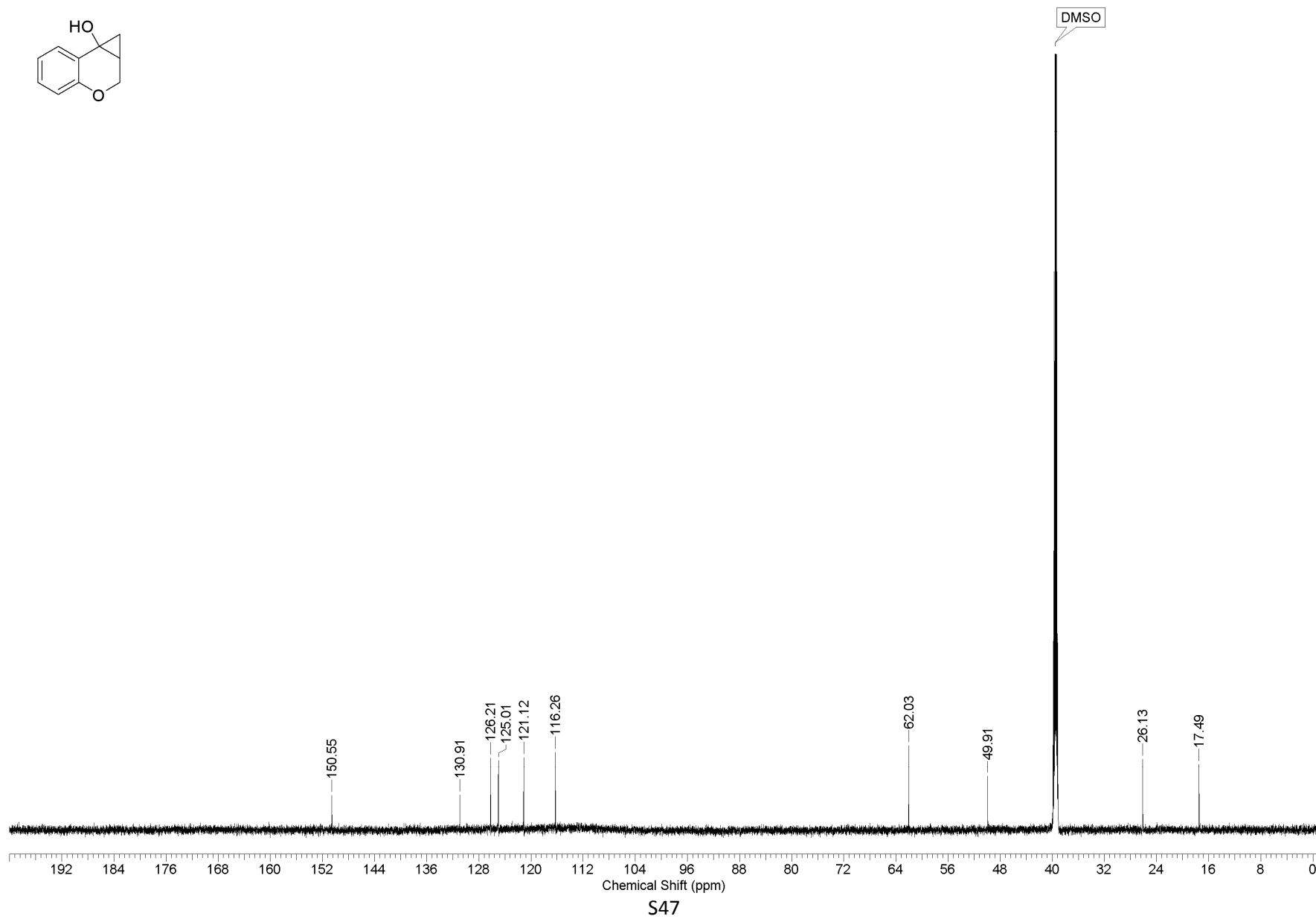
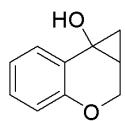
S42

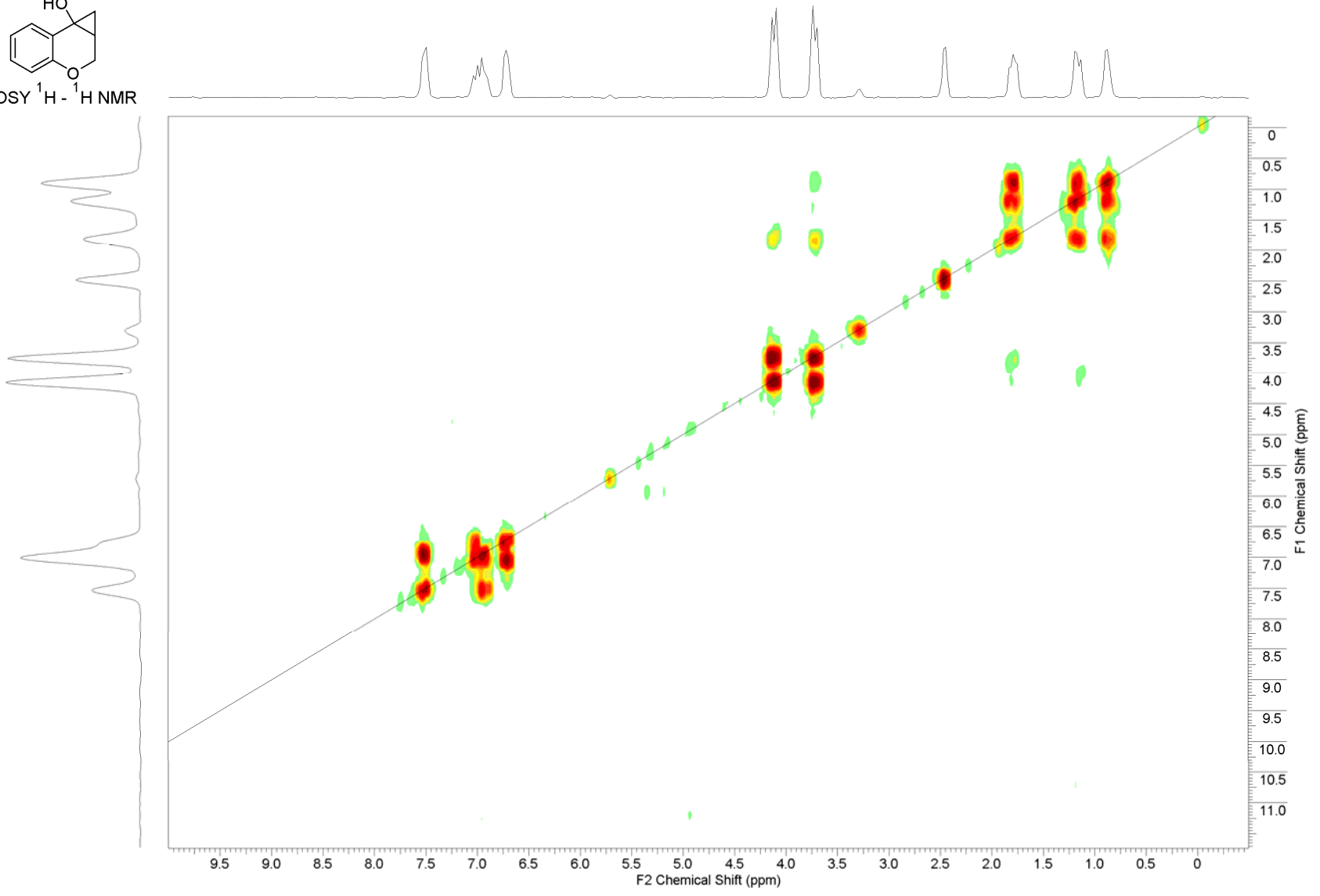
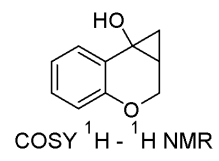


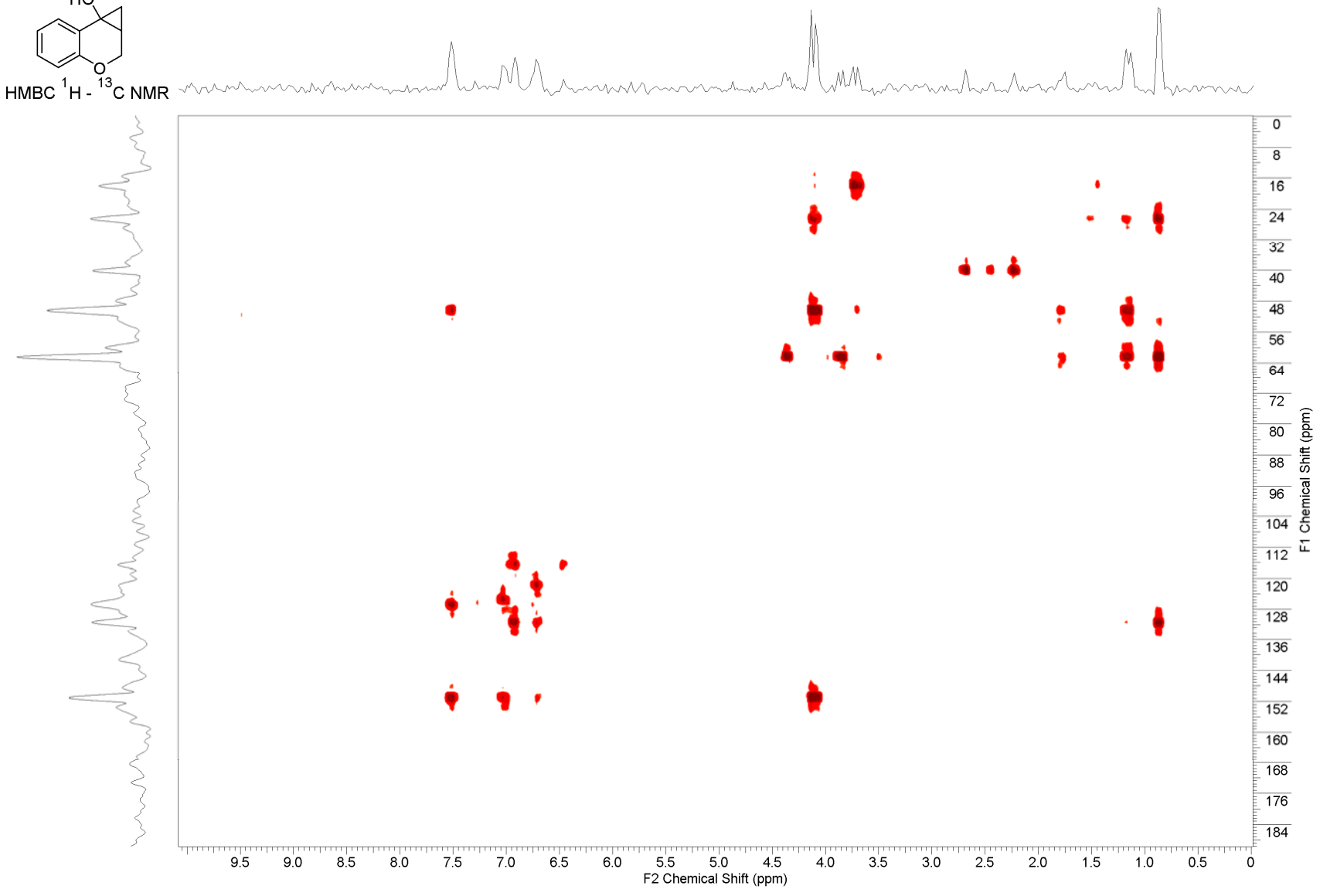
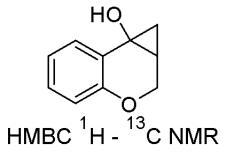


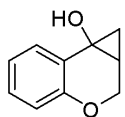




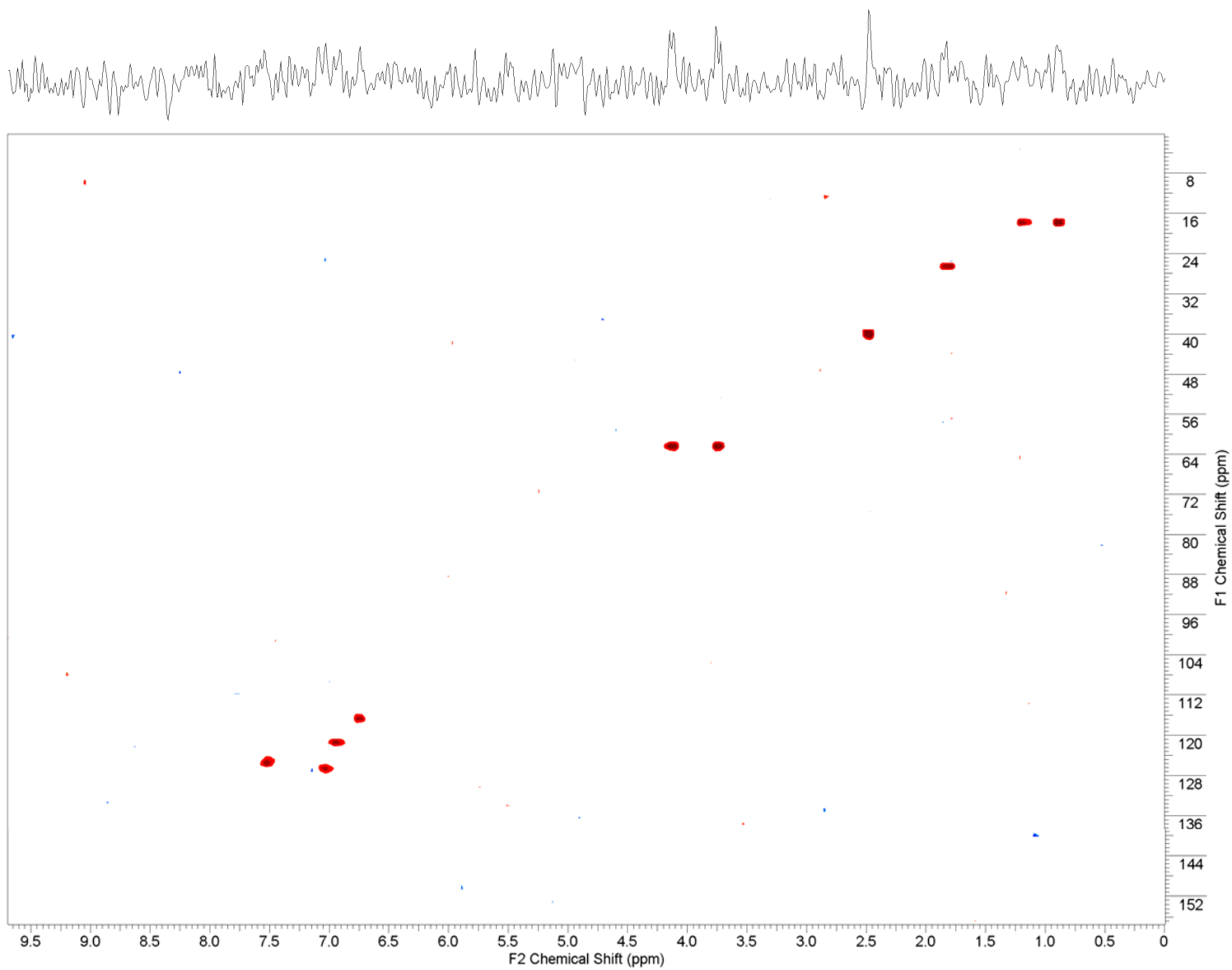




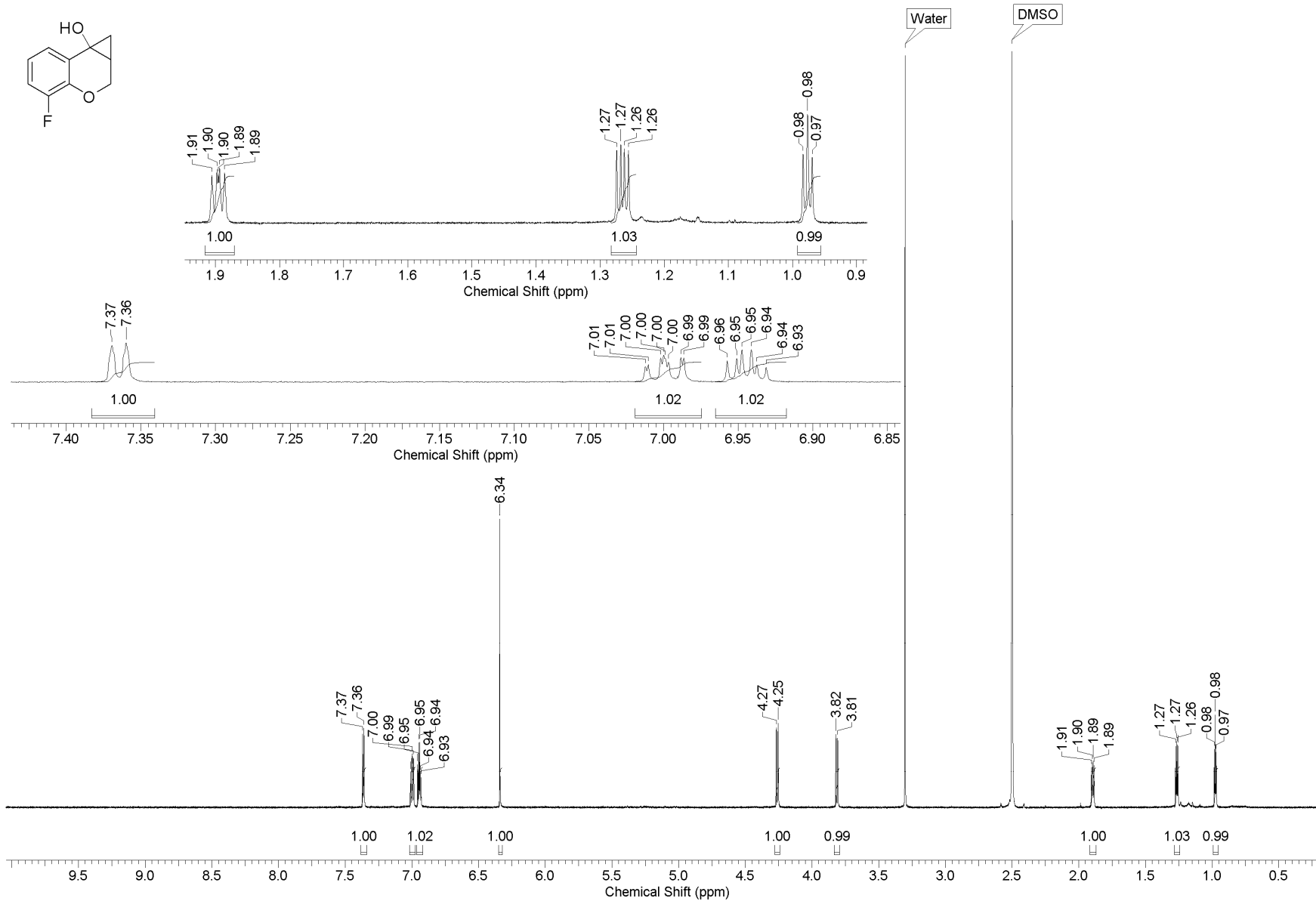
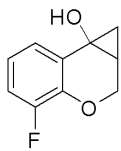




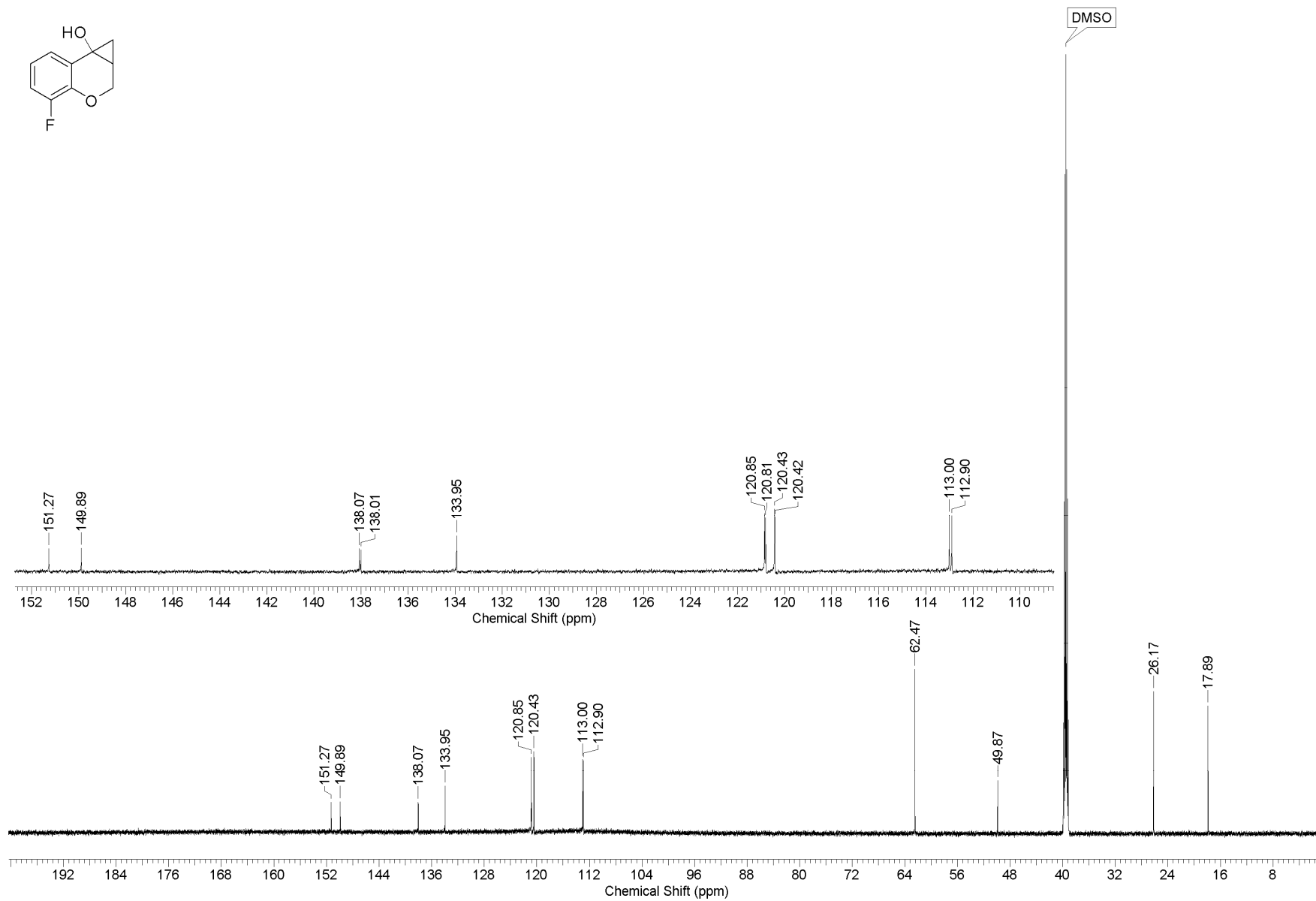
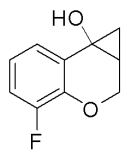
HSQC ^1H - ^{13}C NMR

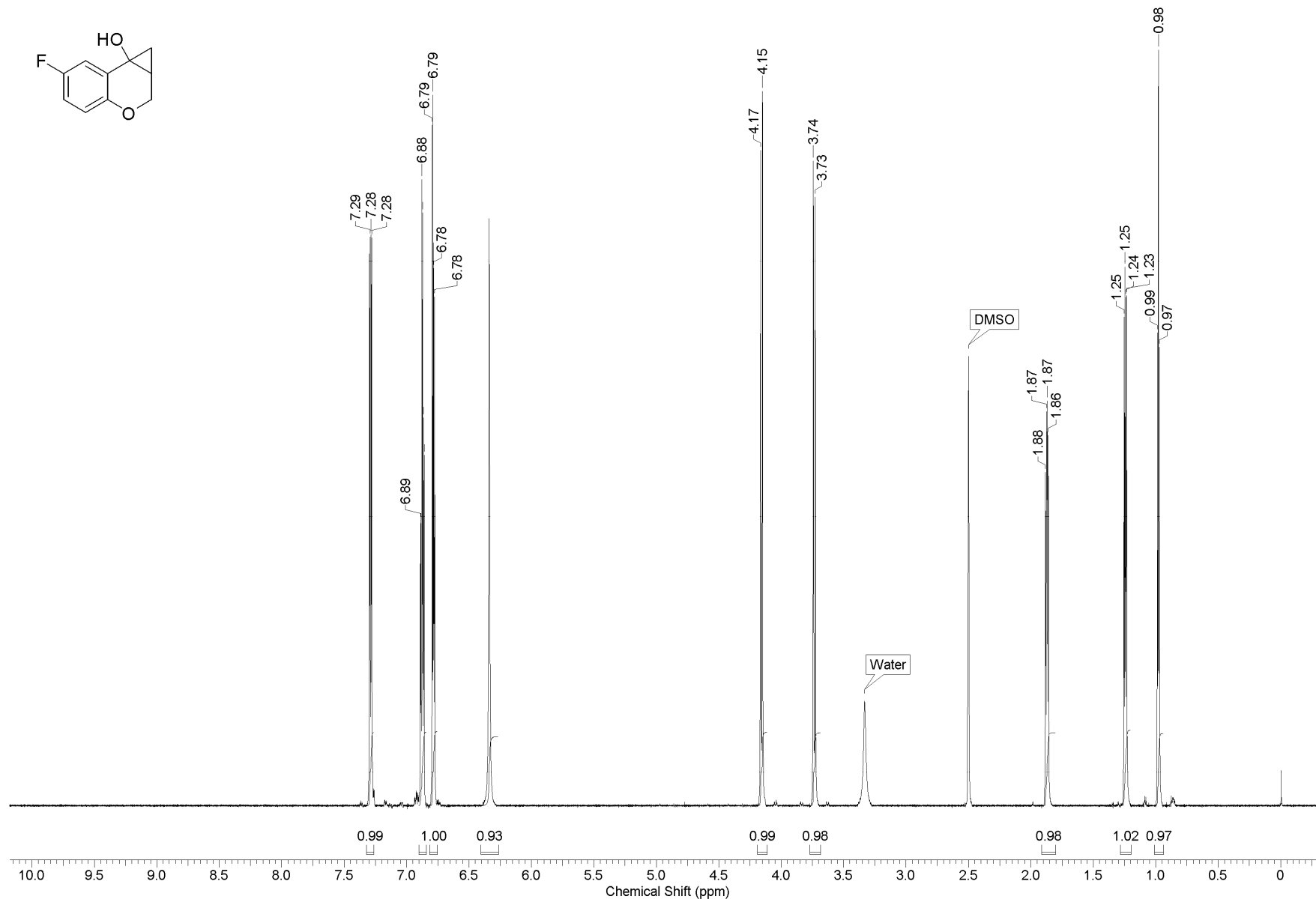
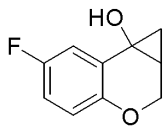


S50

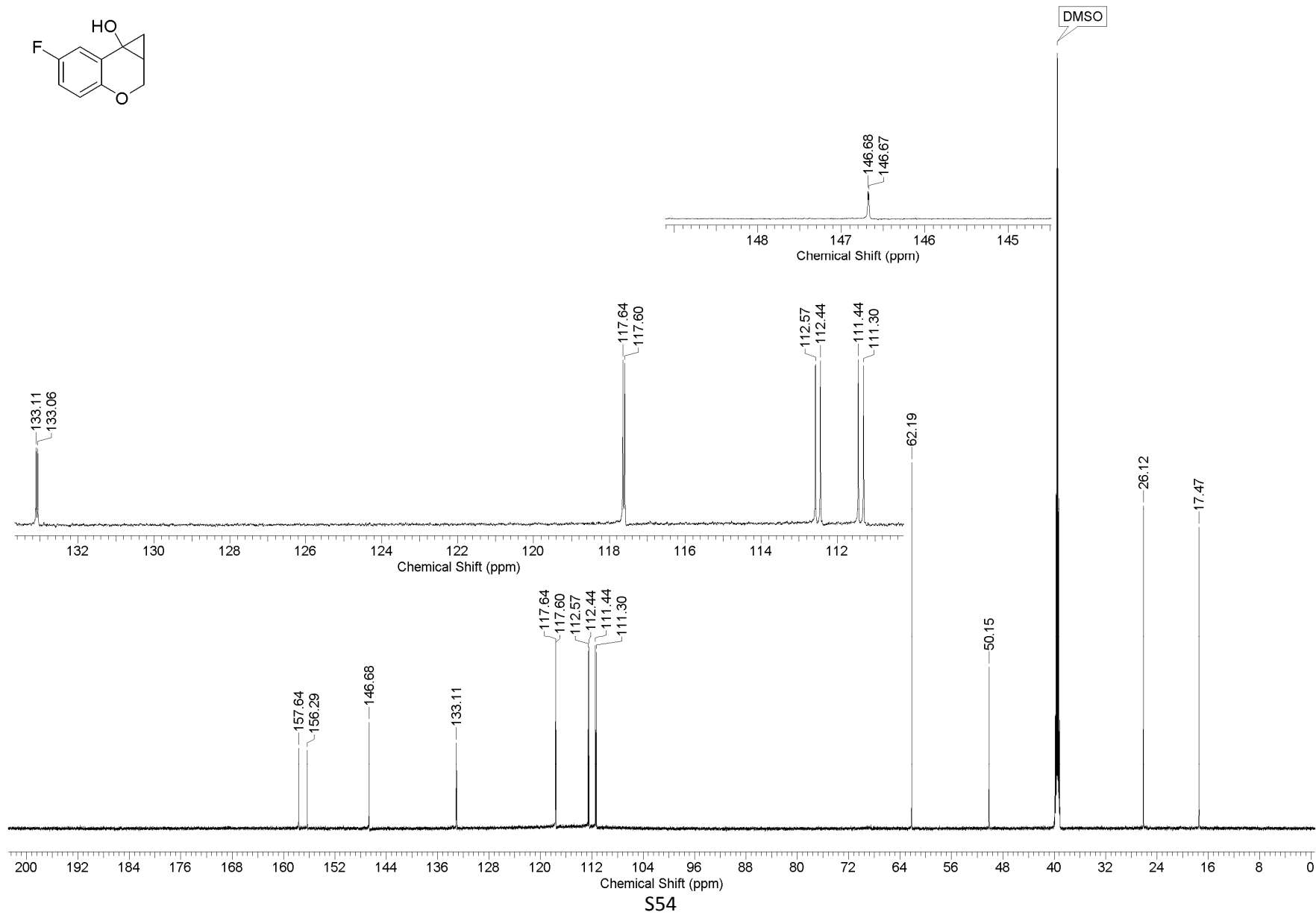
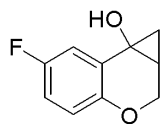


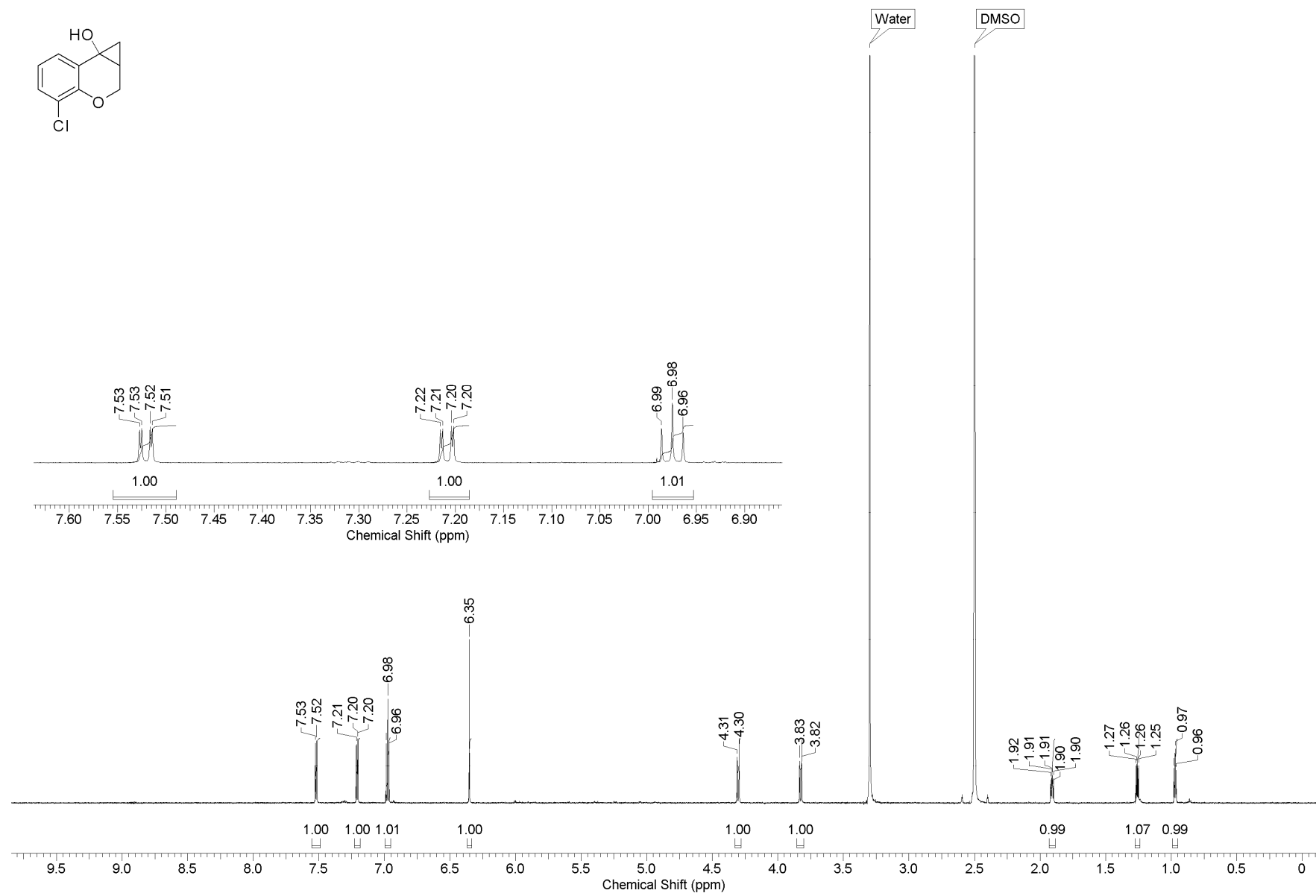
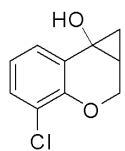
S51



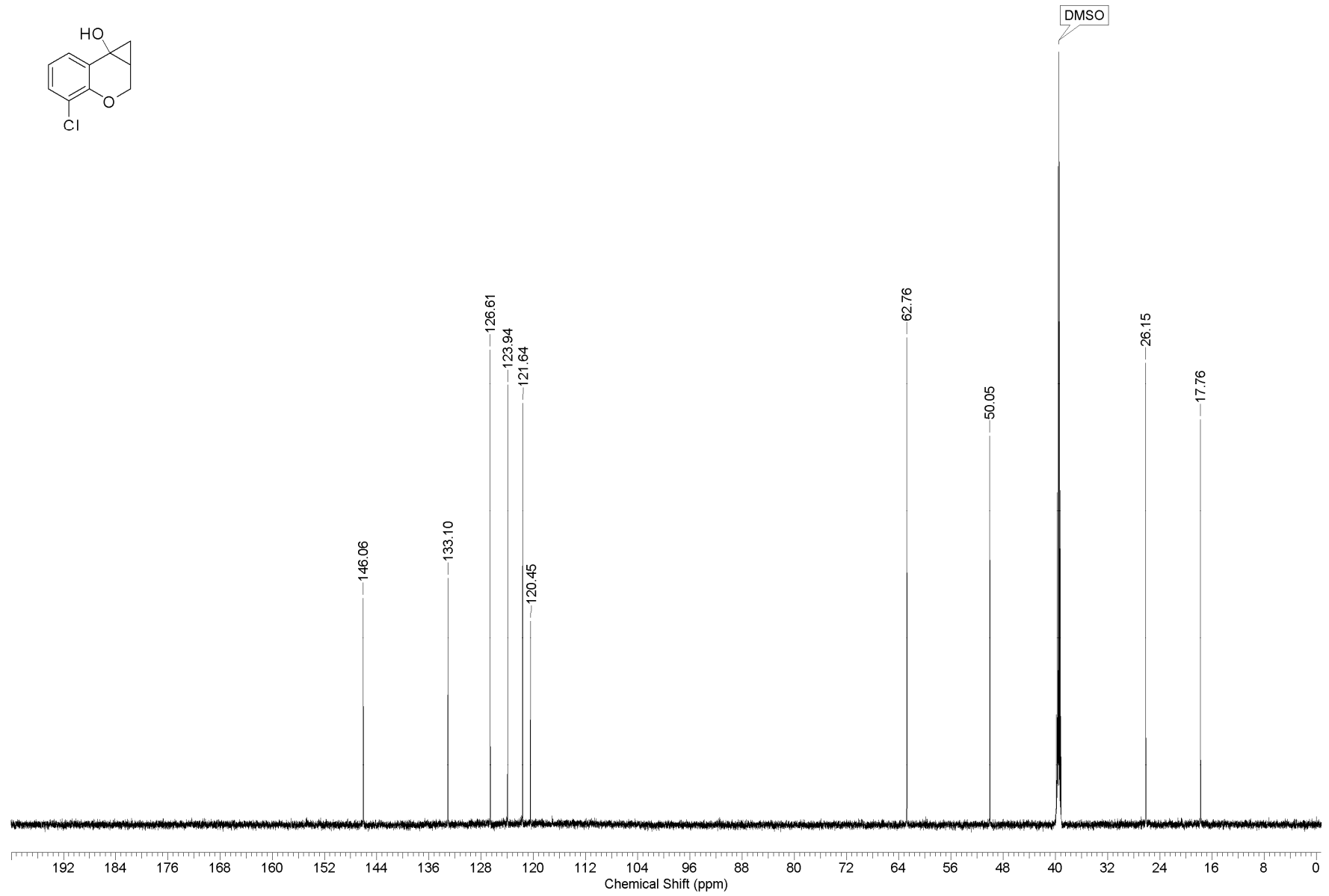
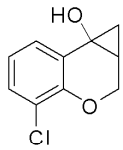


S53

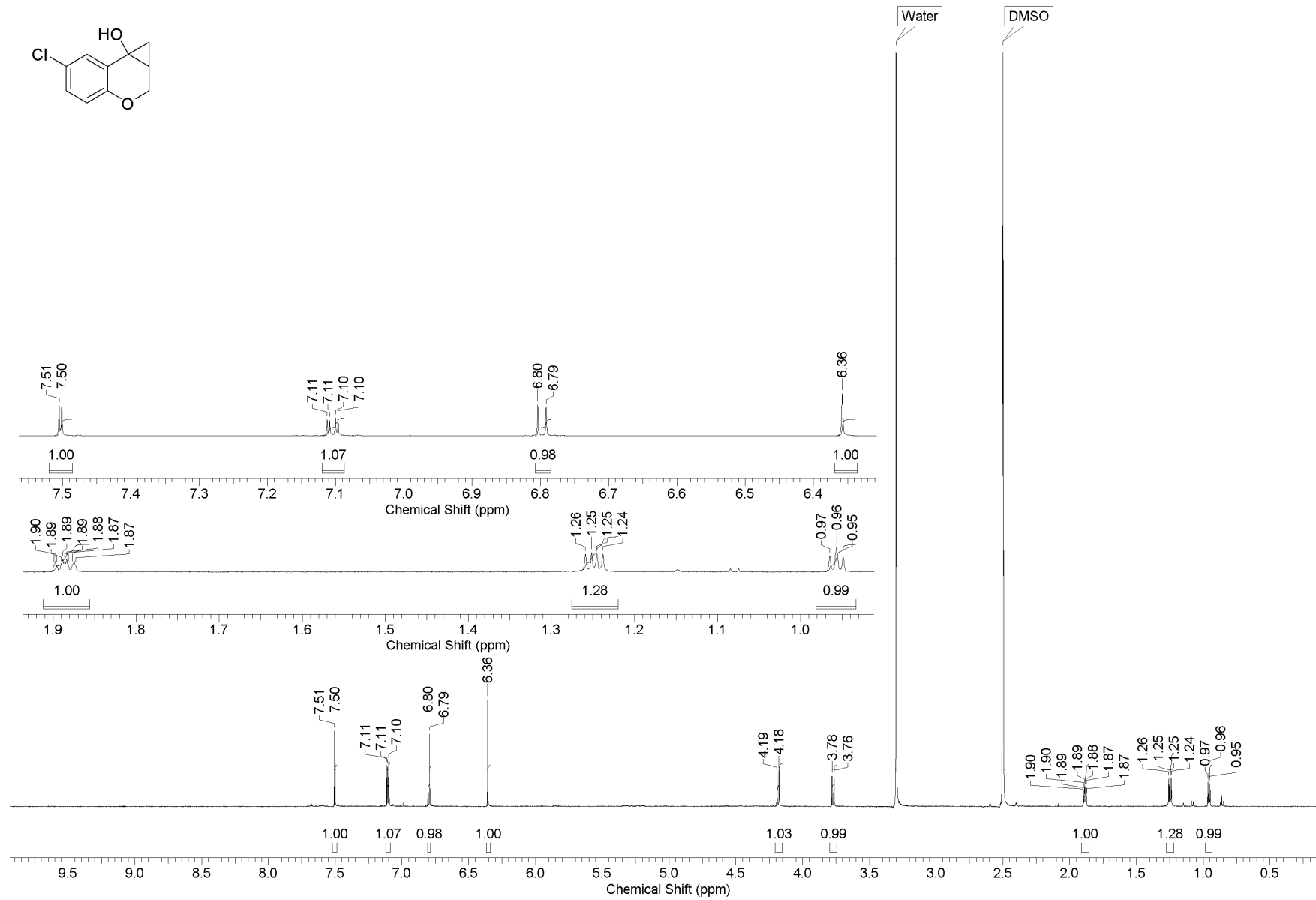
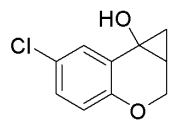




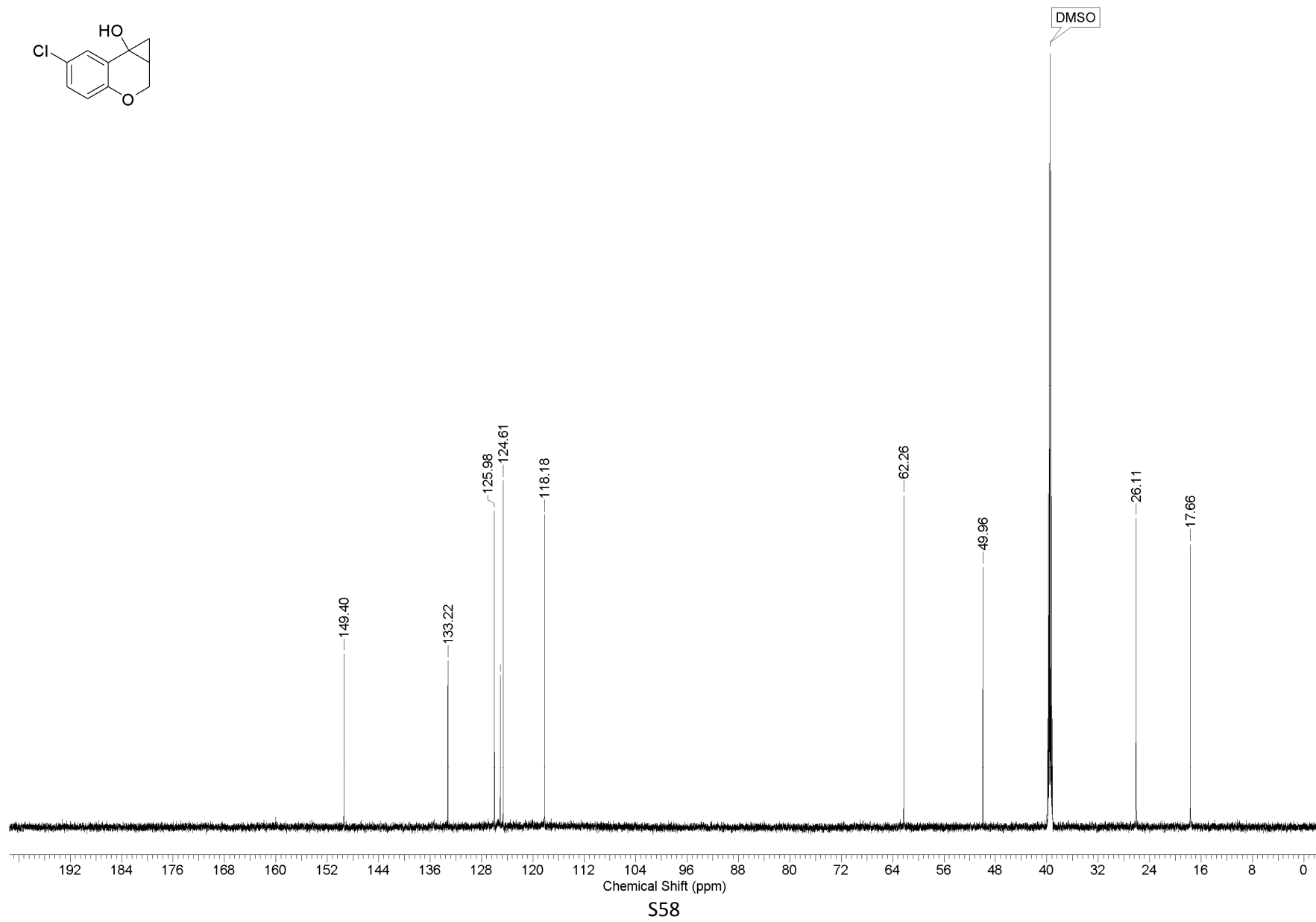
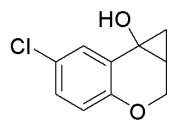
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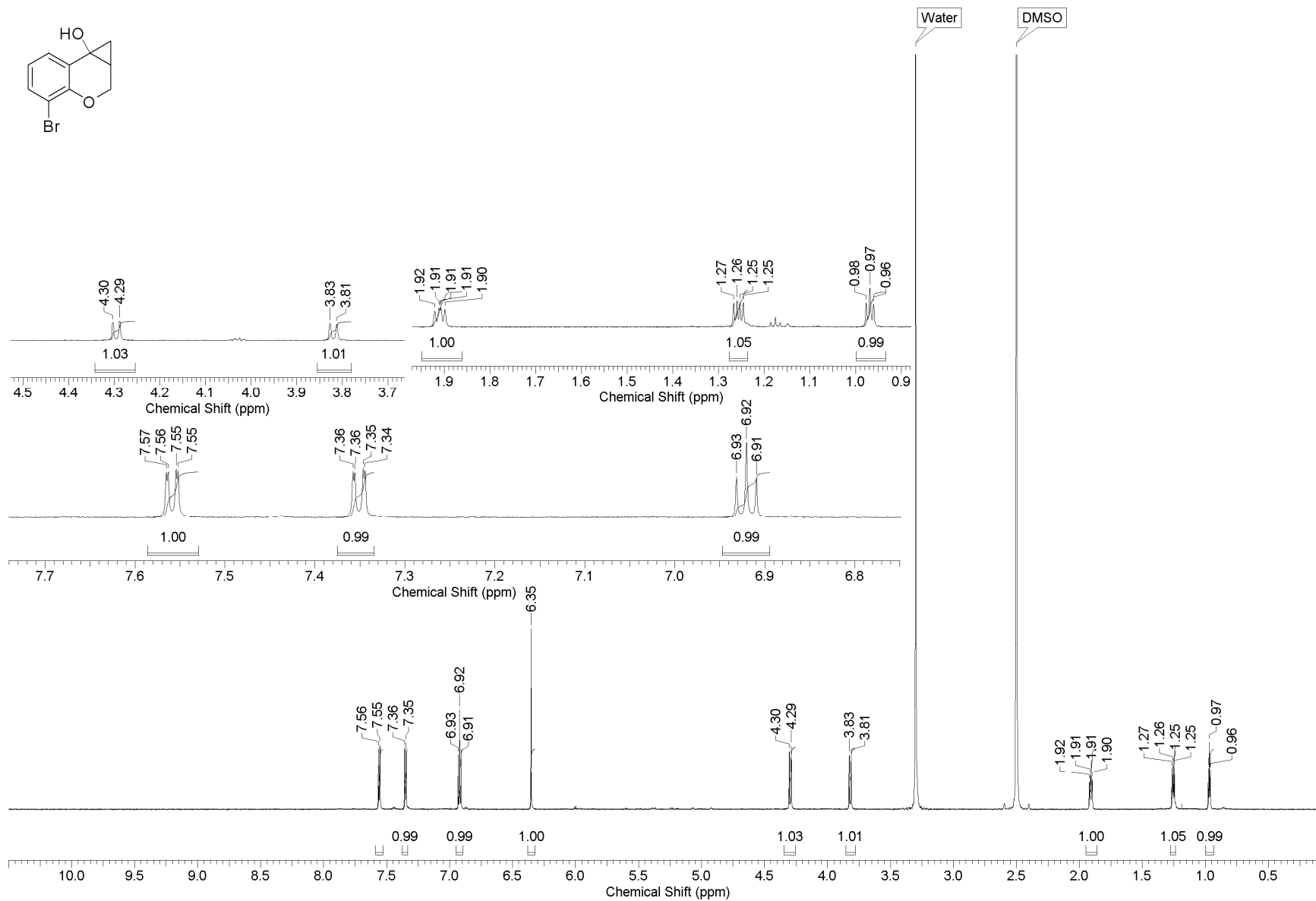
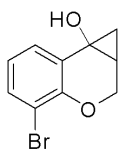


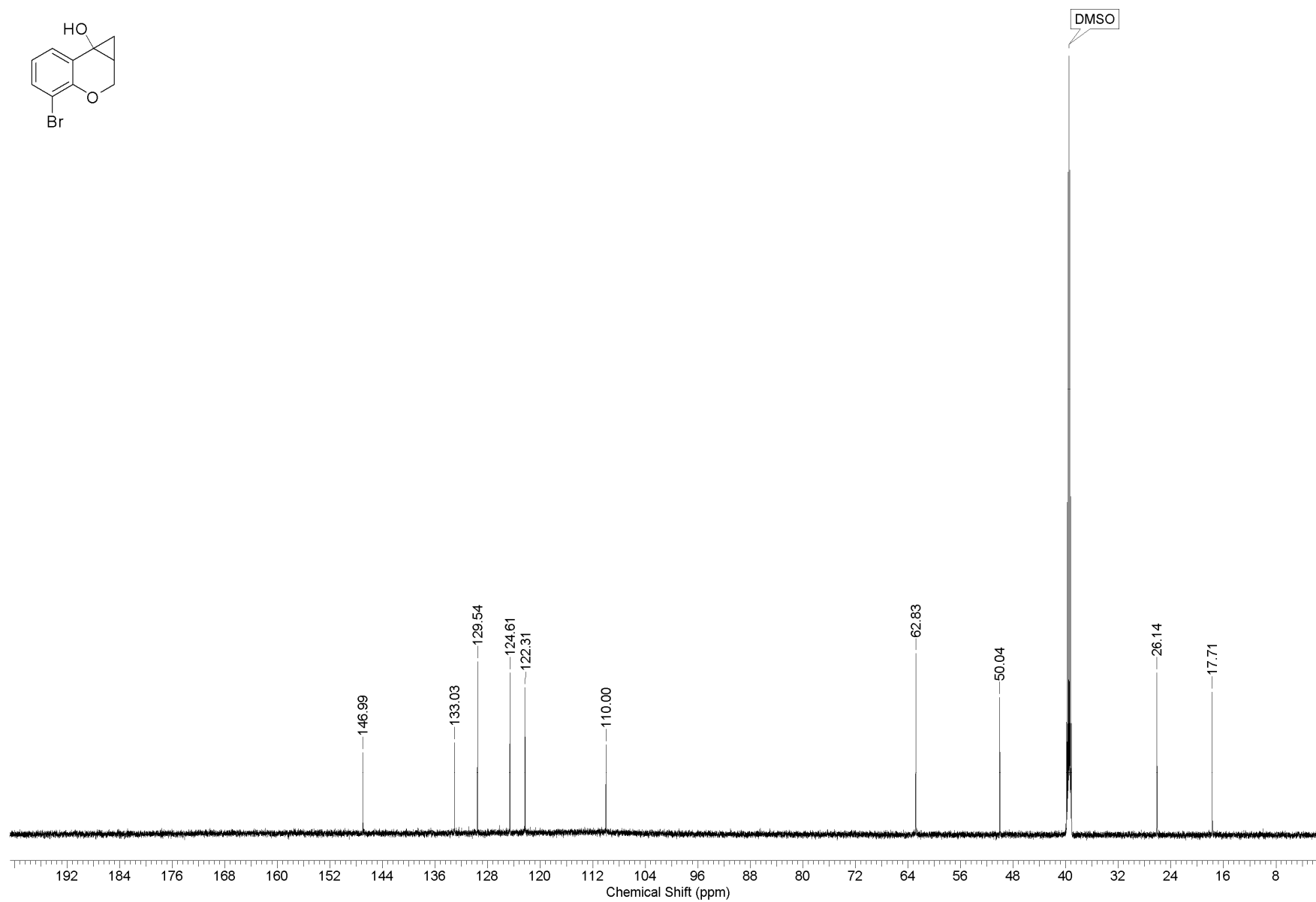
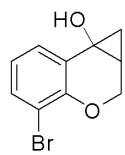
S56



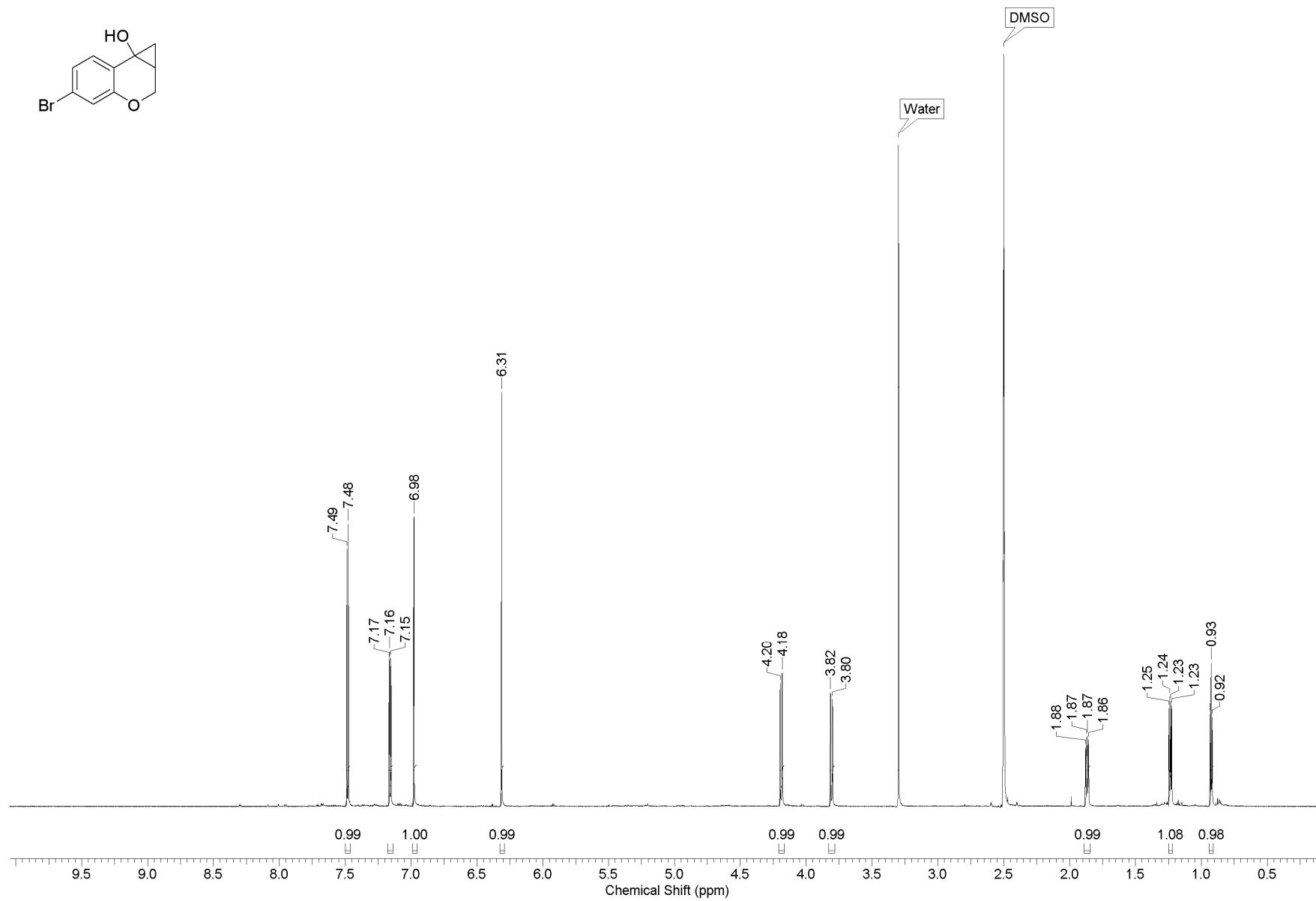
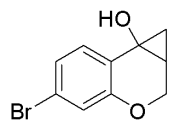
S57



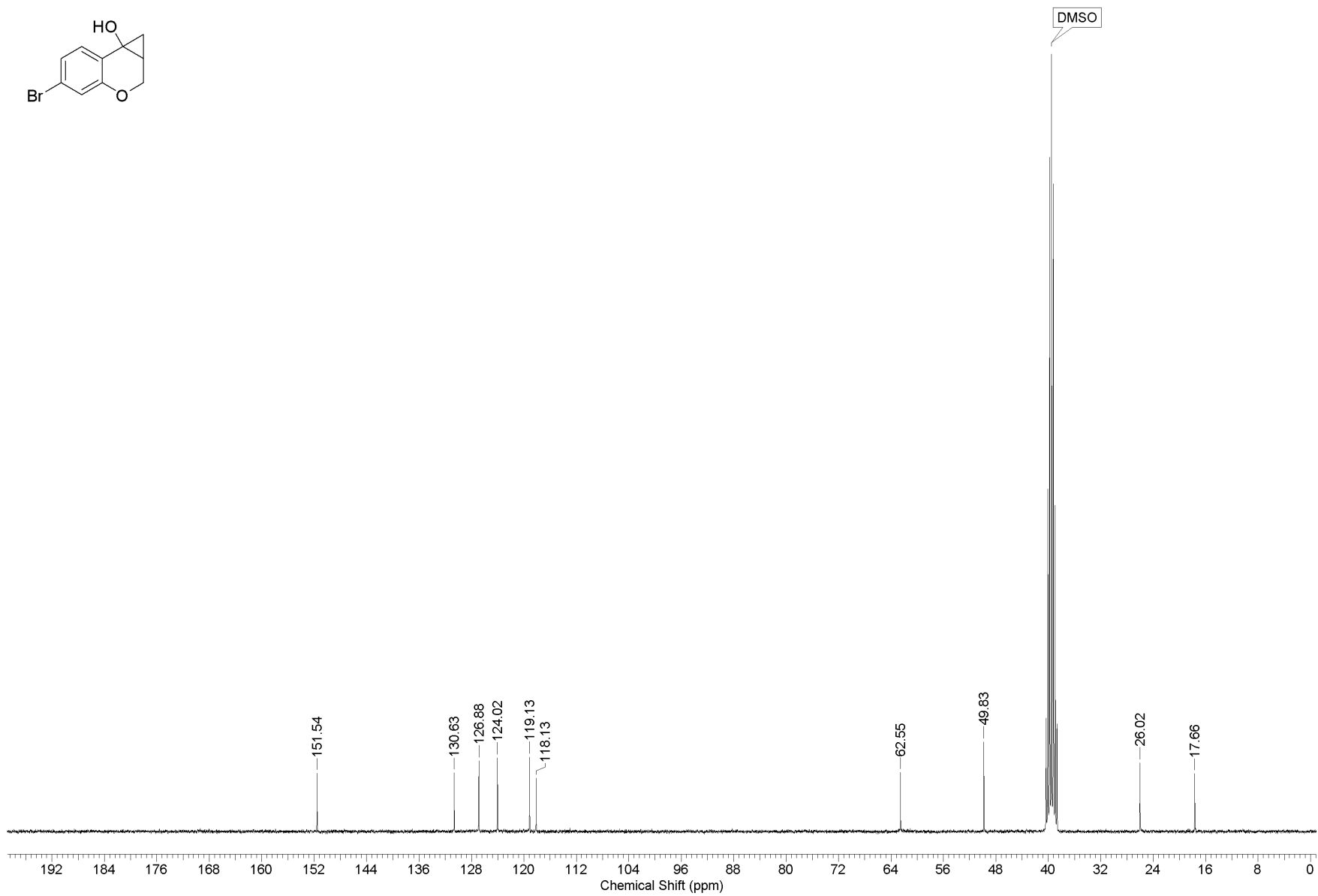
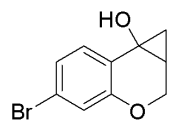


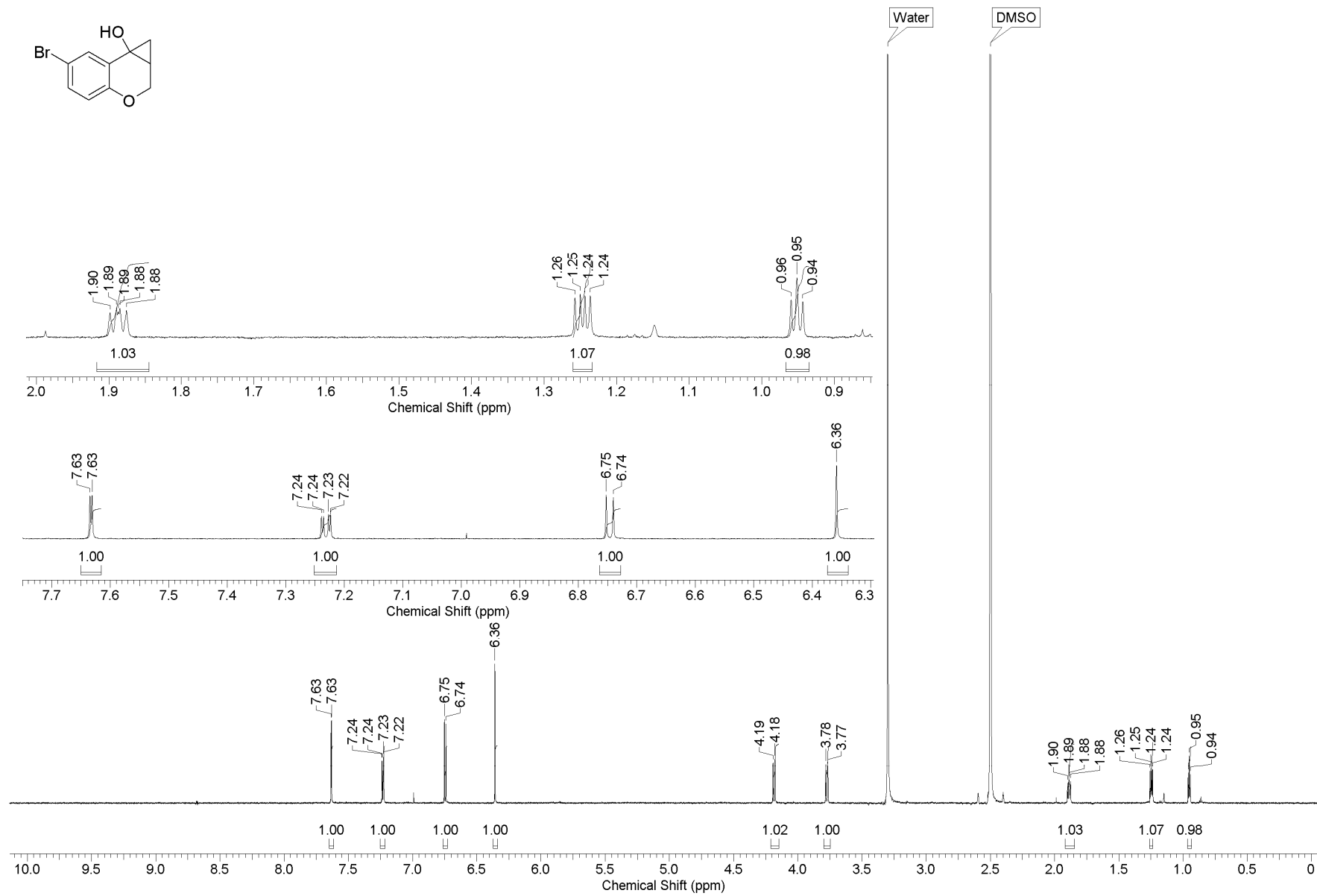
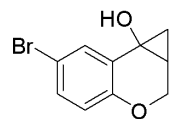


S60

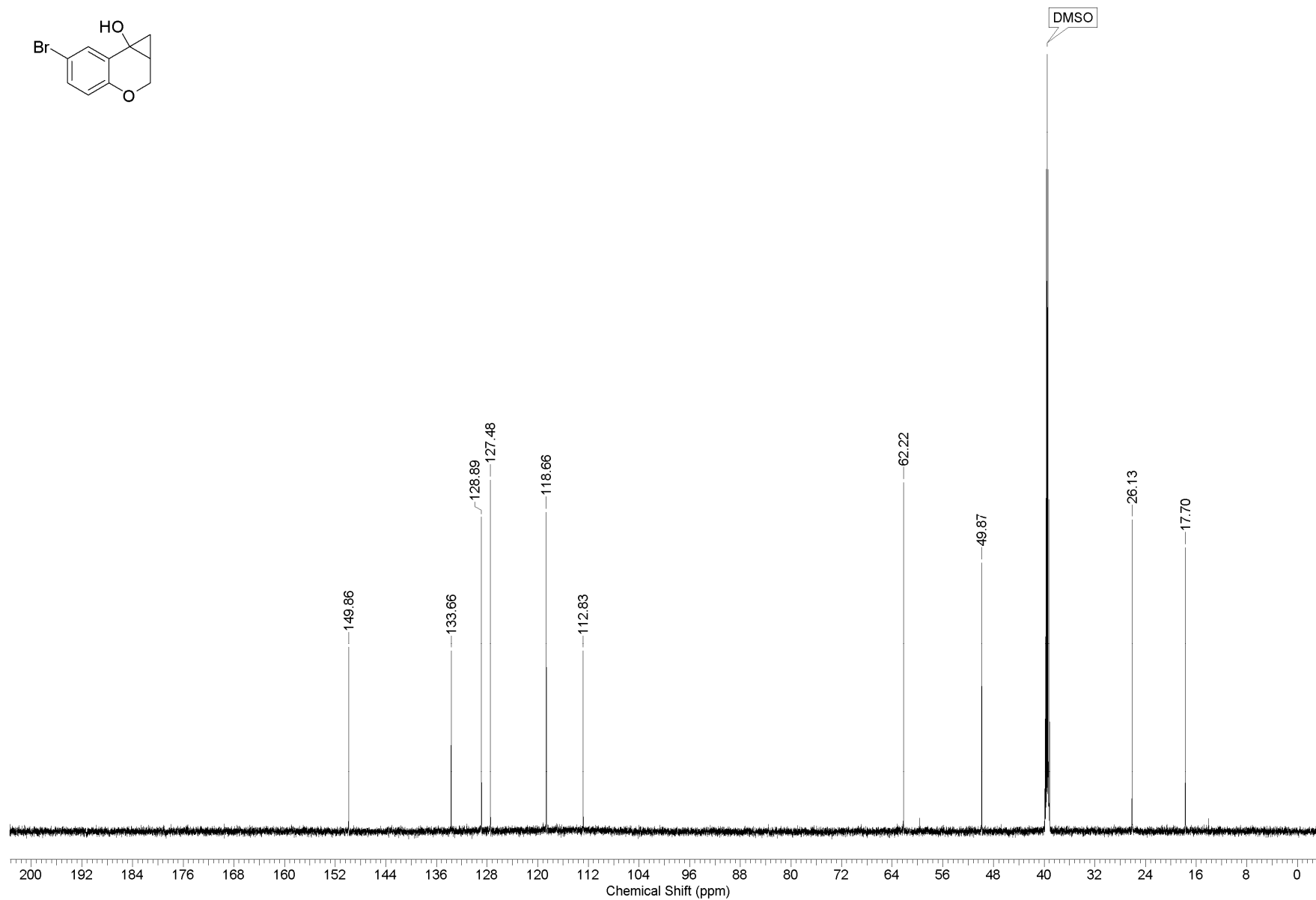
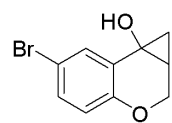


S61

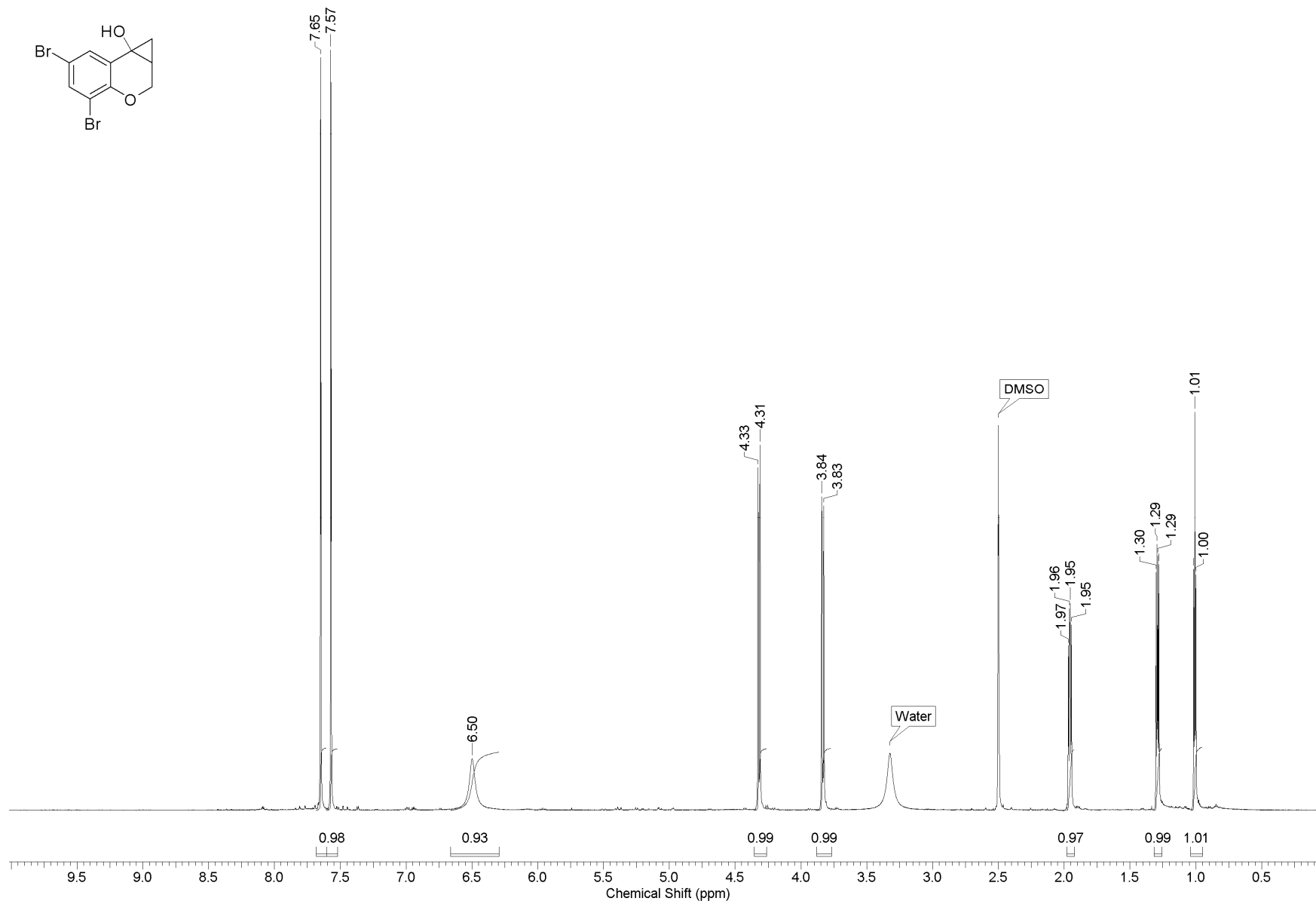
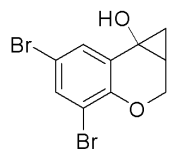




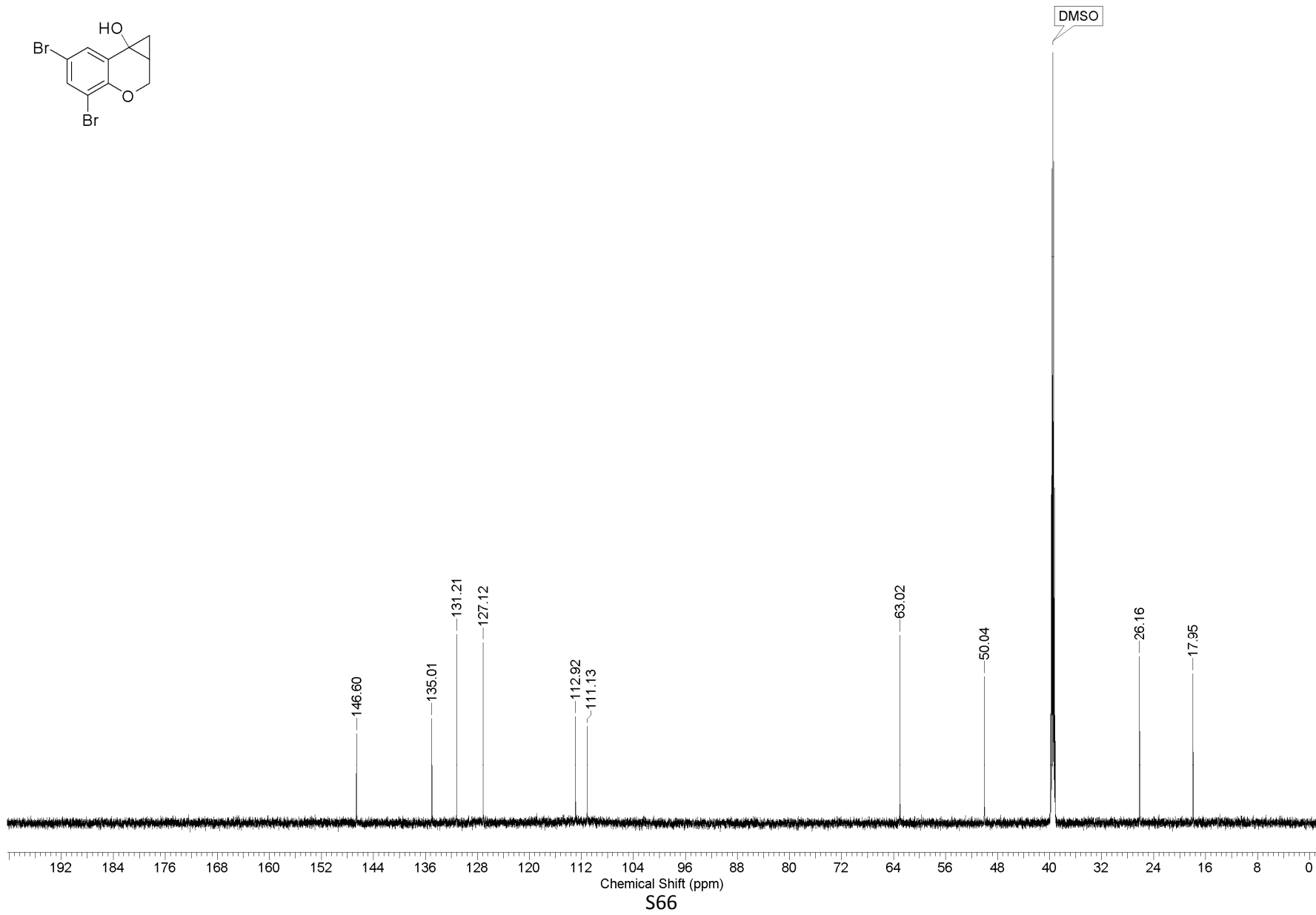
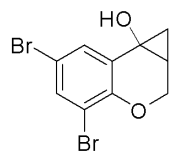
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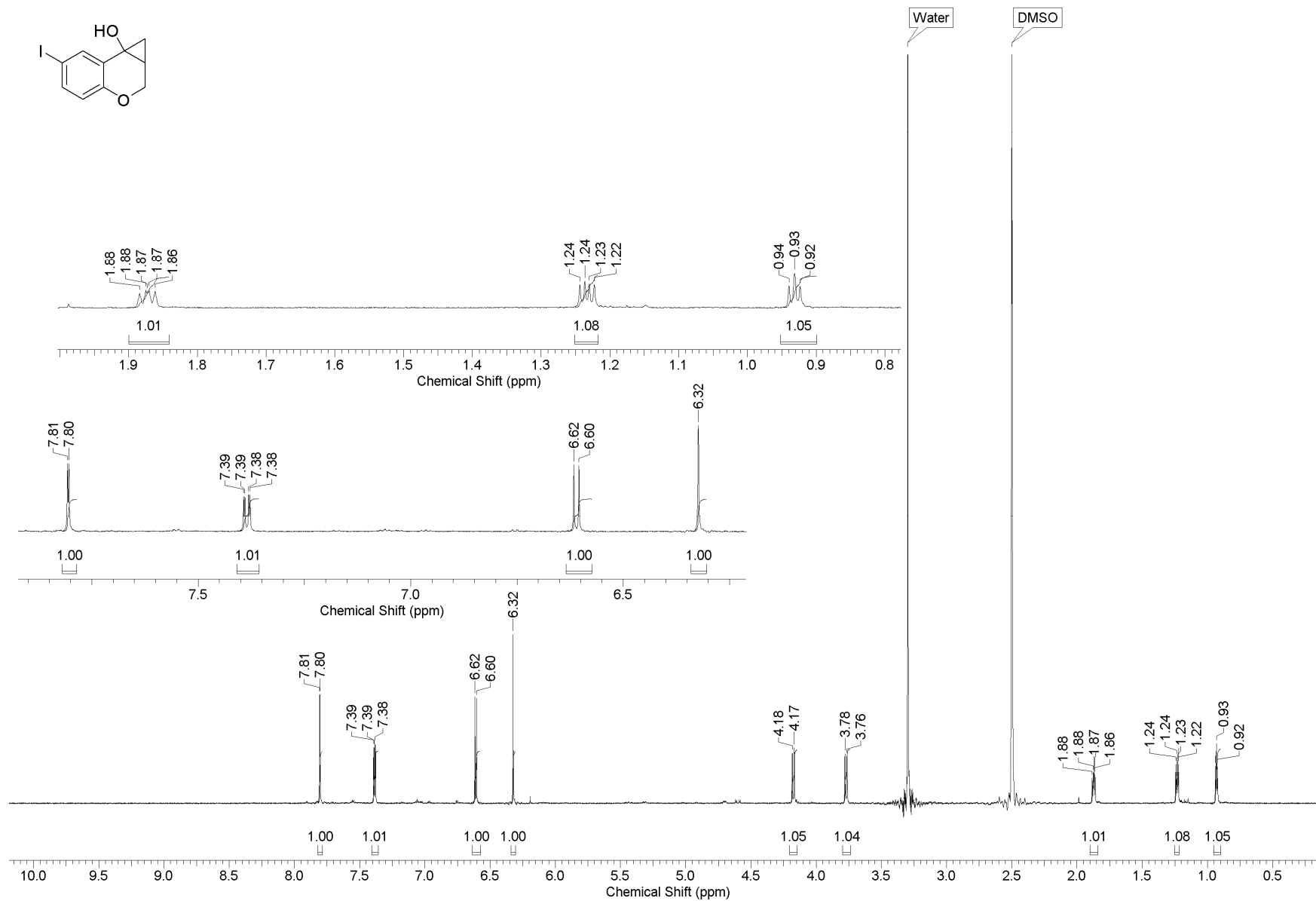
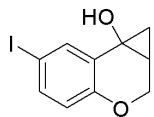


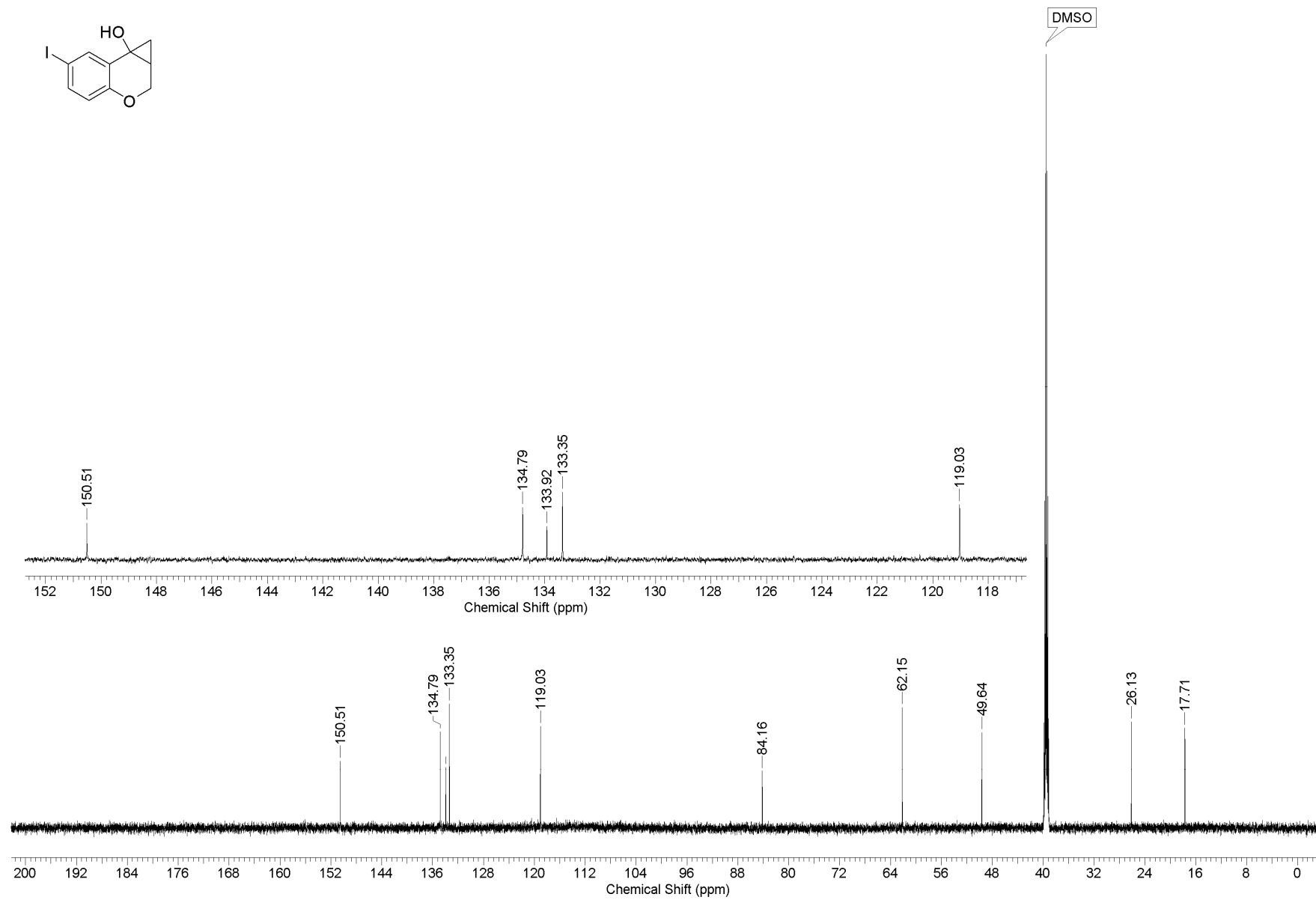
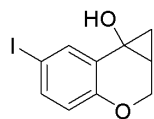
S64



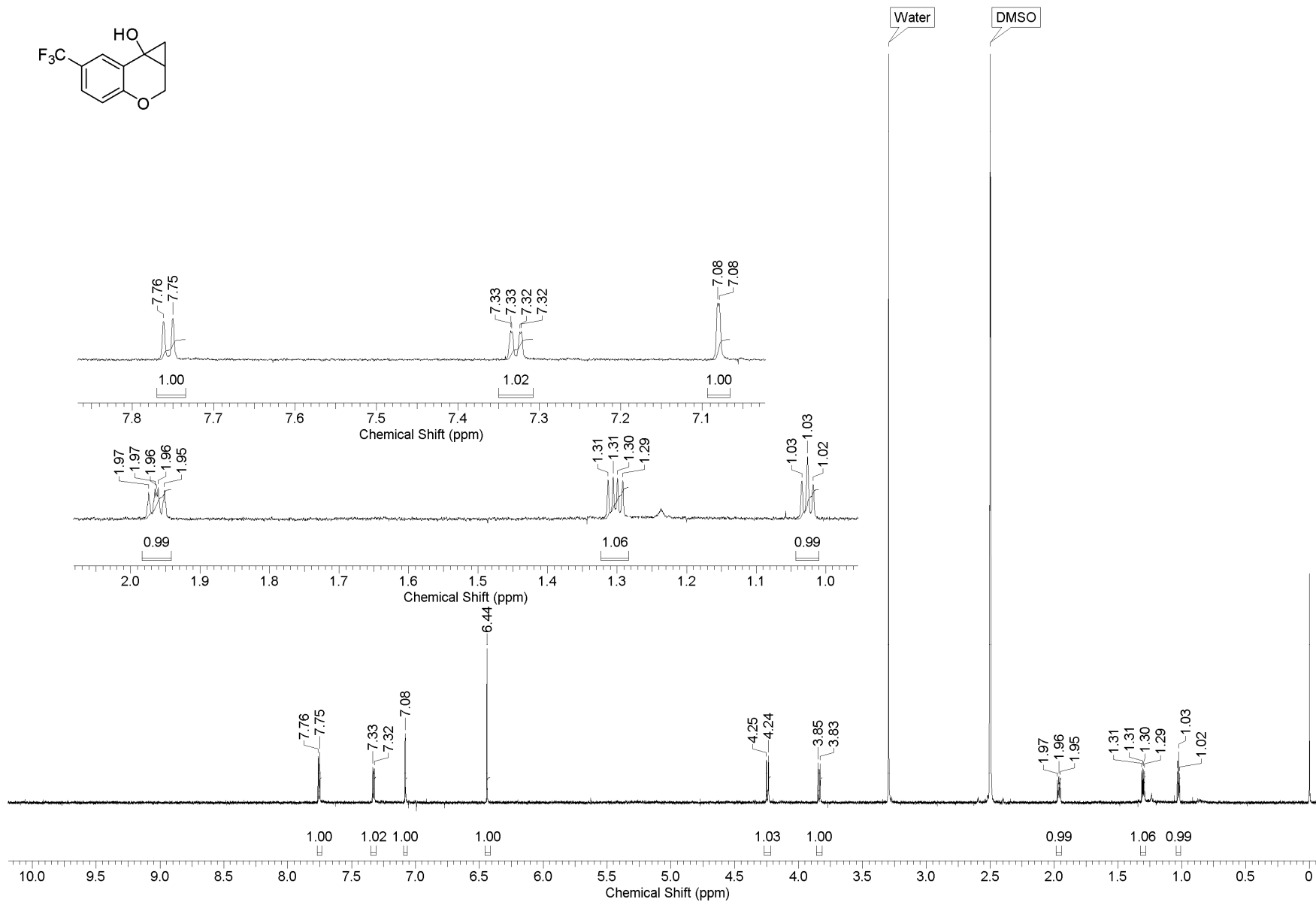
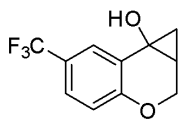
S65



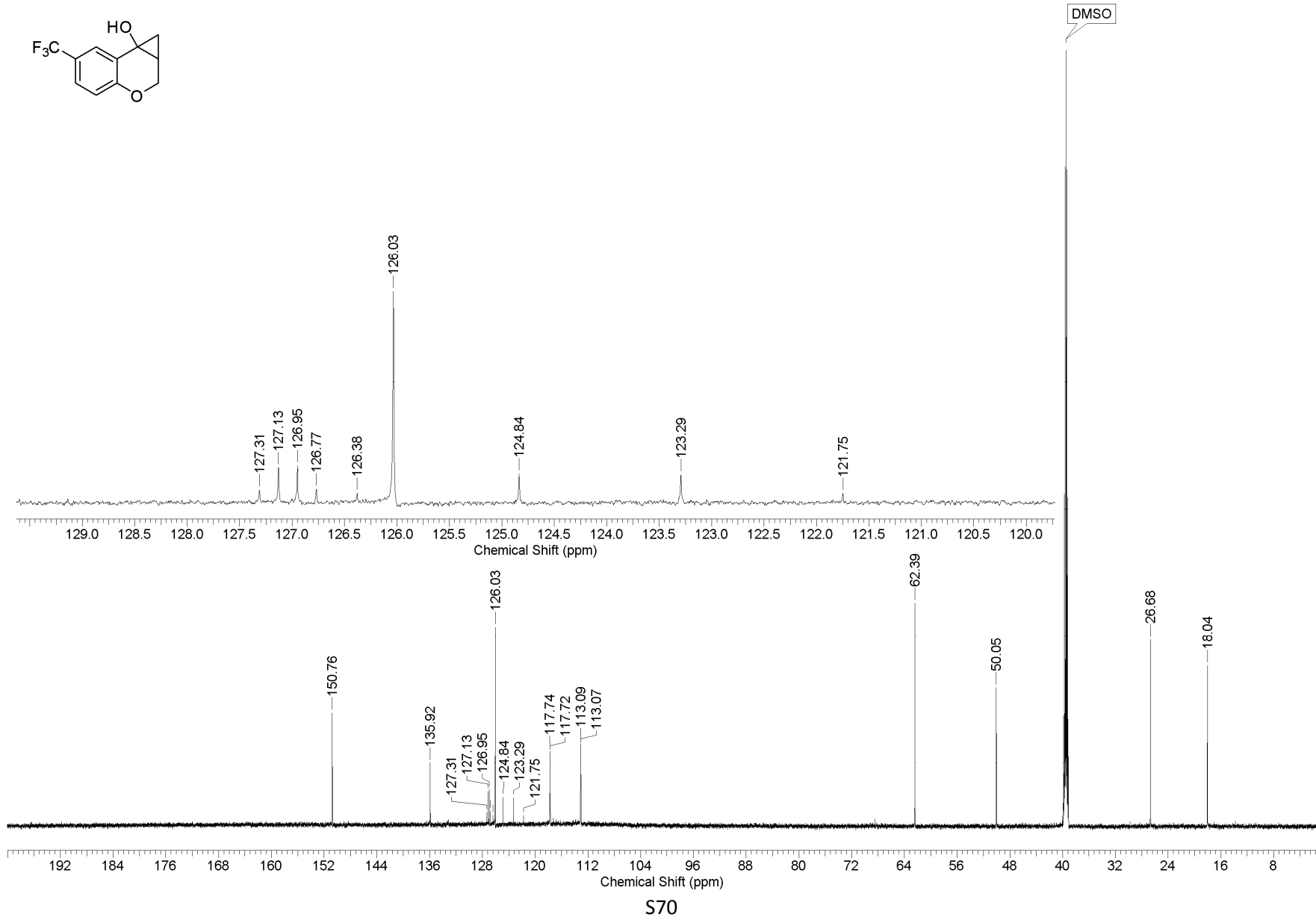
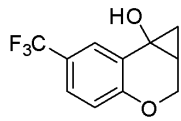


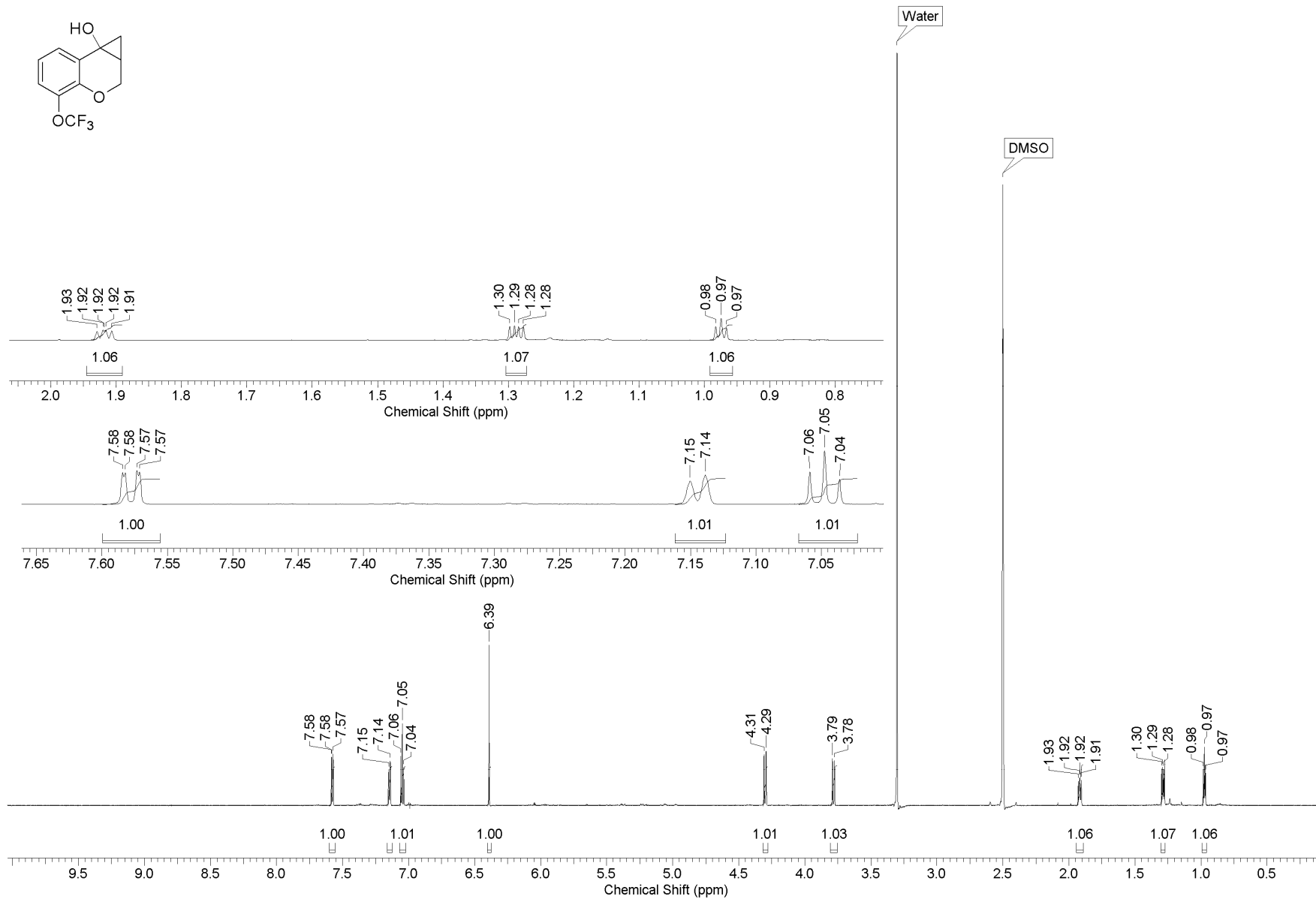
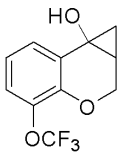


S68

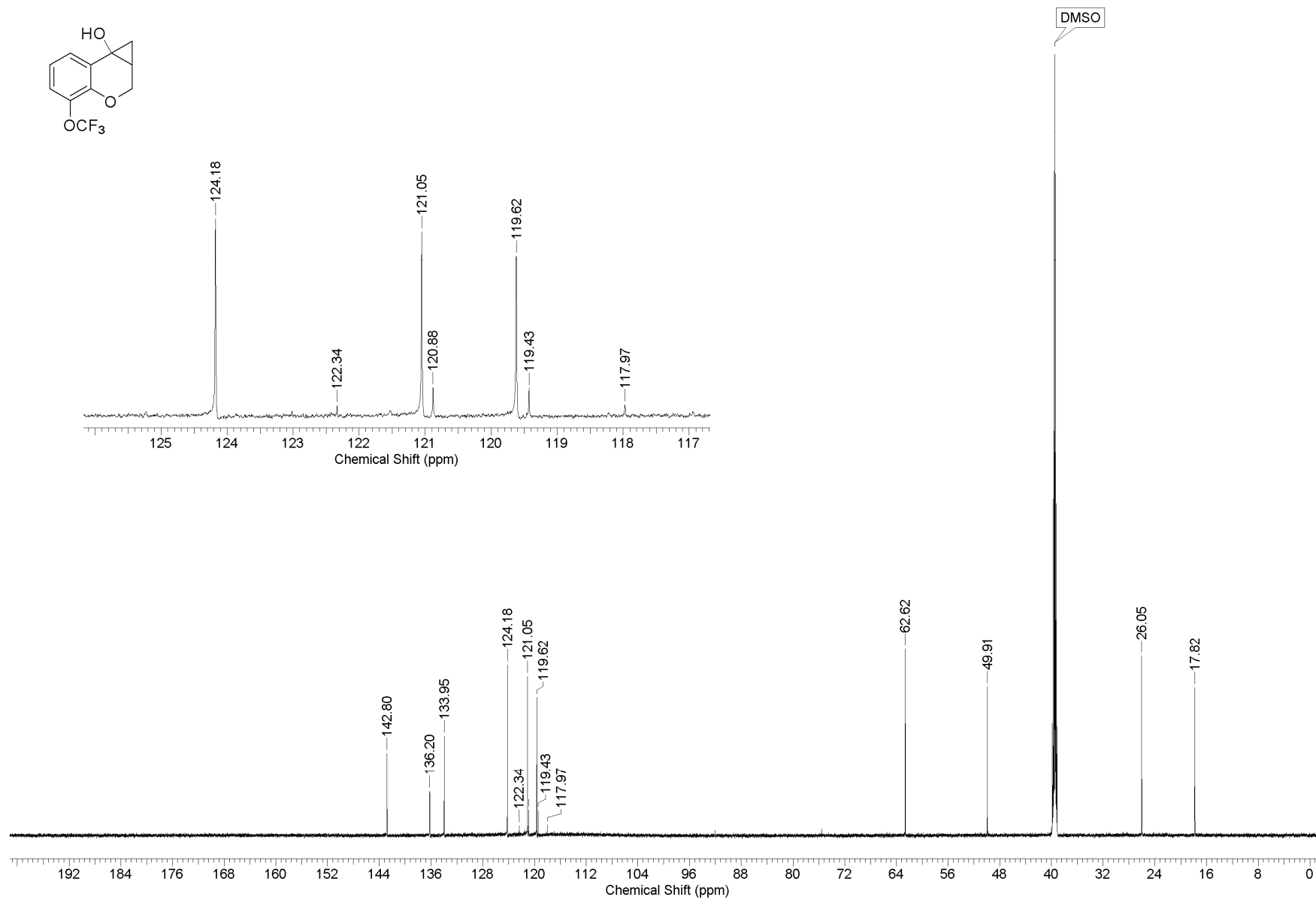
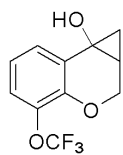


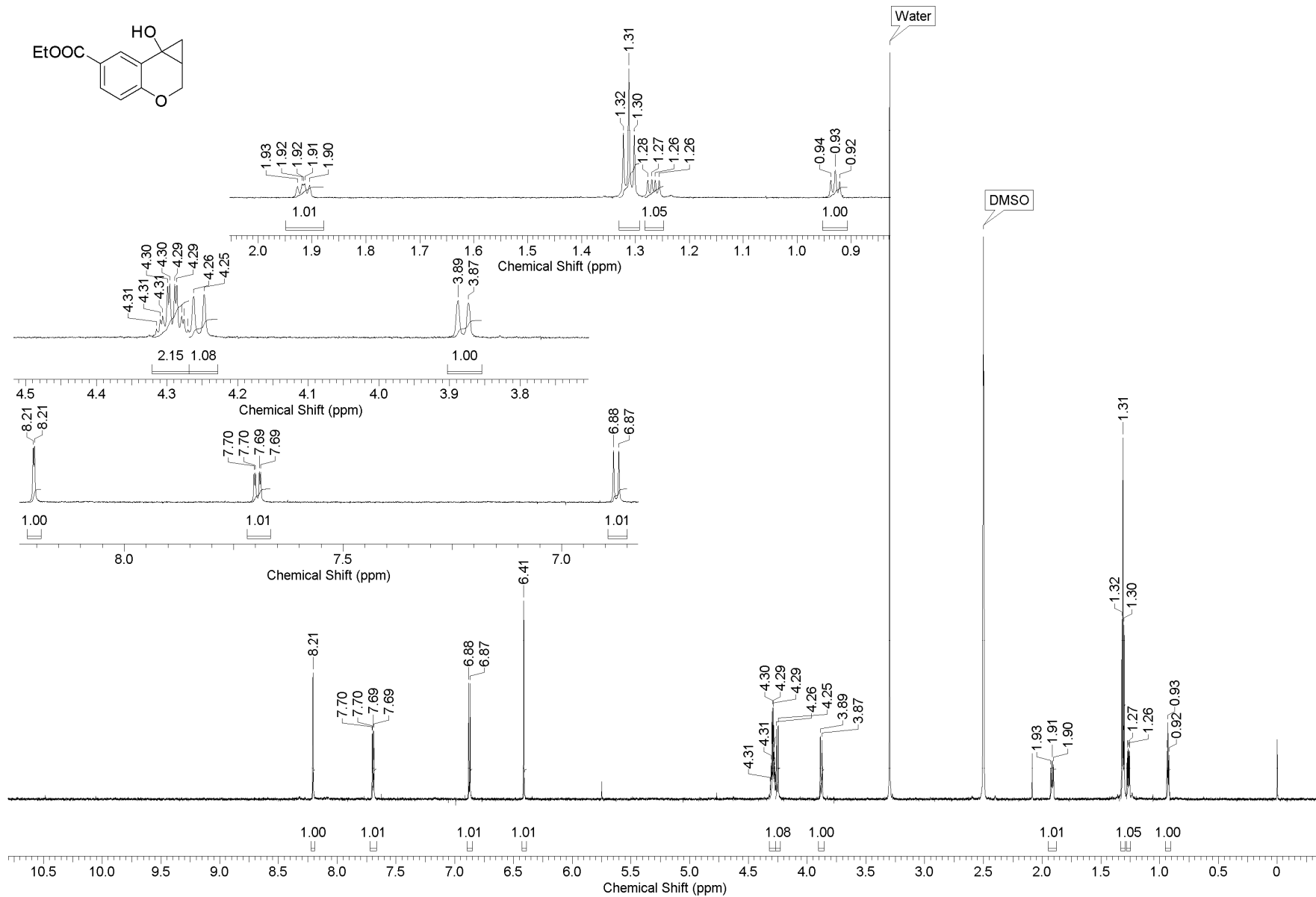
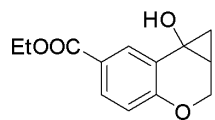
S69



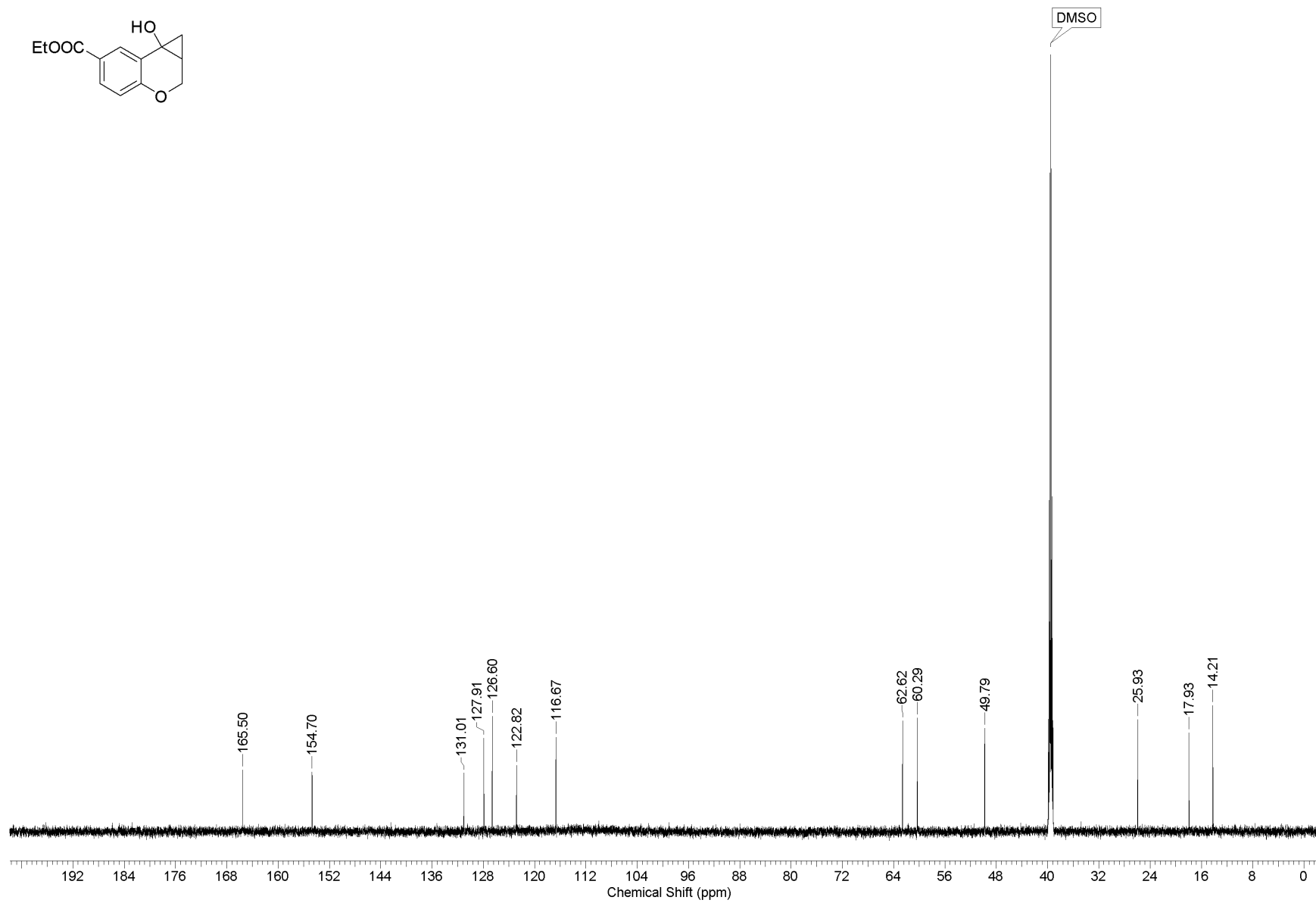
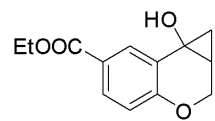


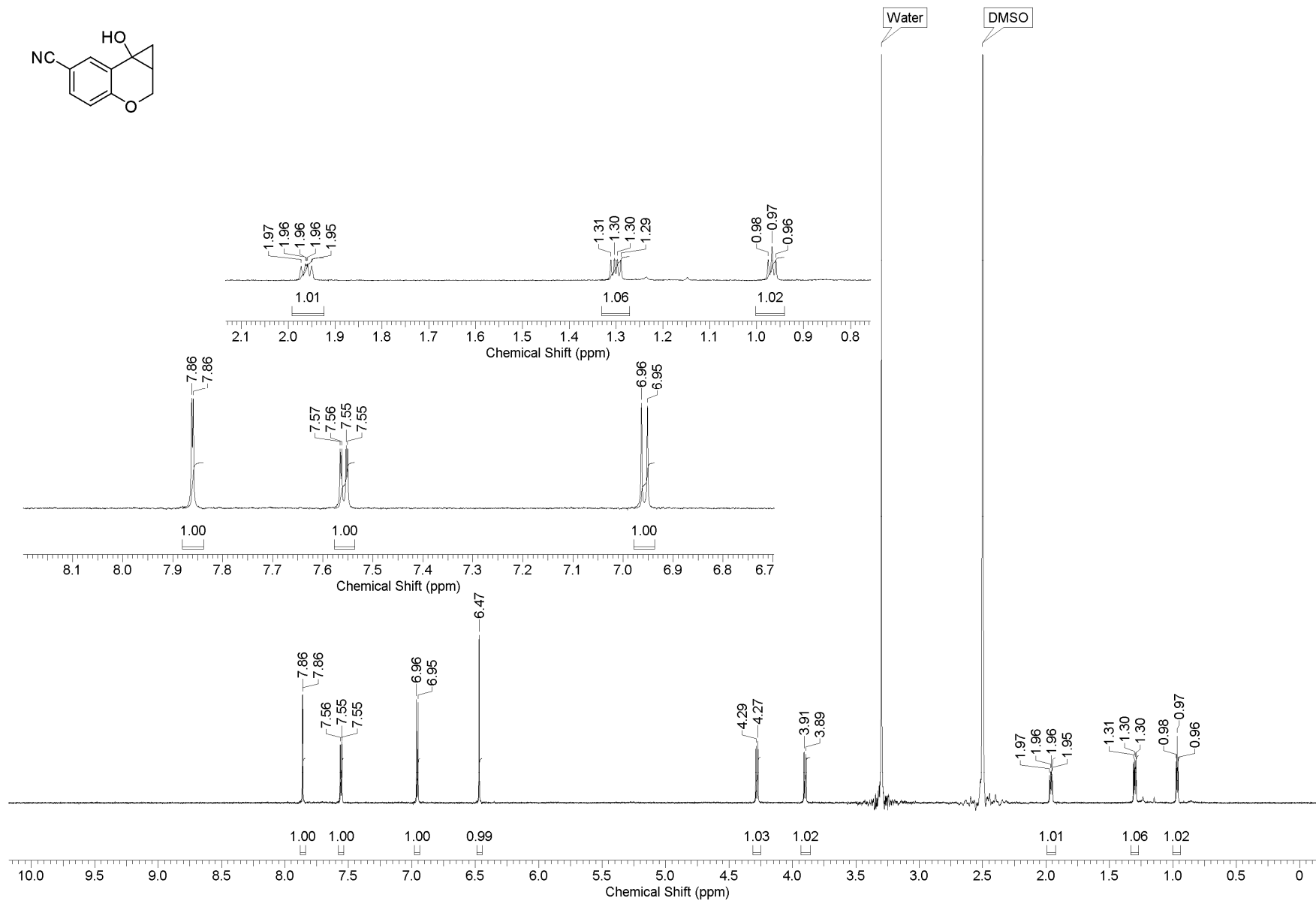
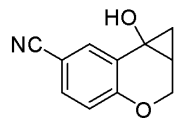
S71



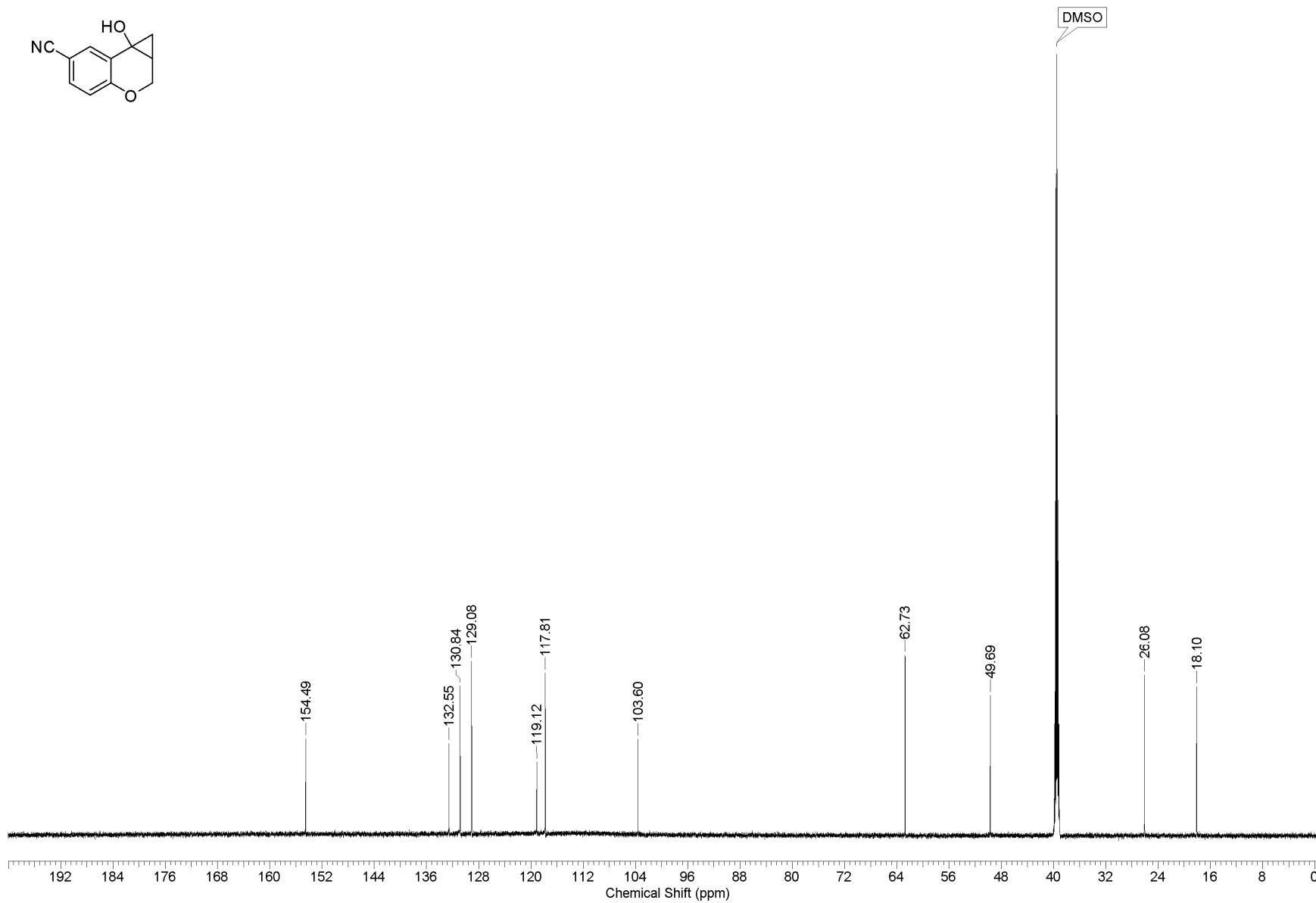
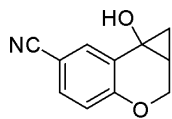


S73

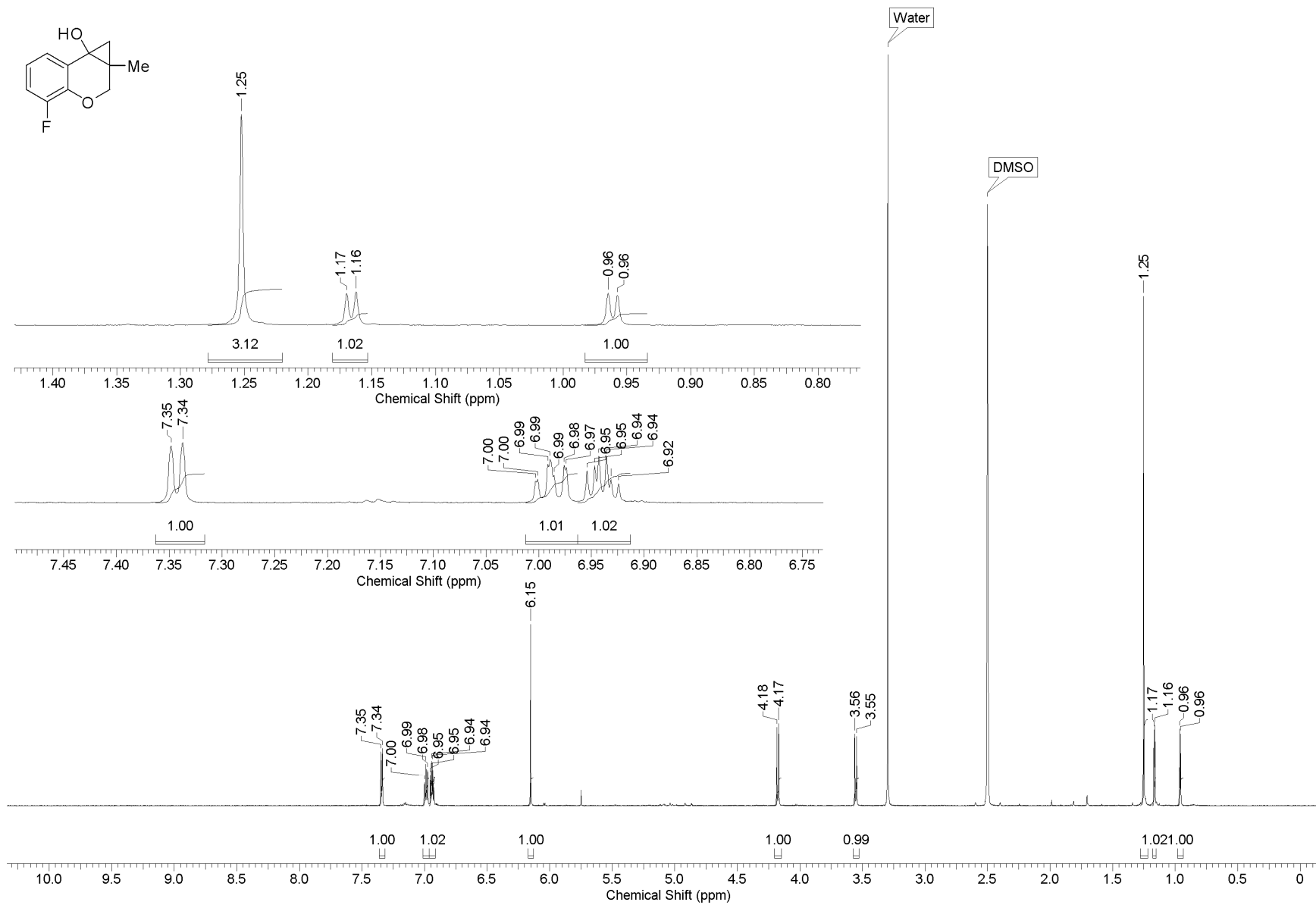
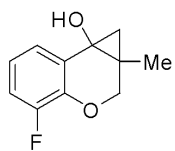


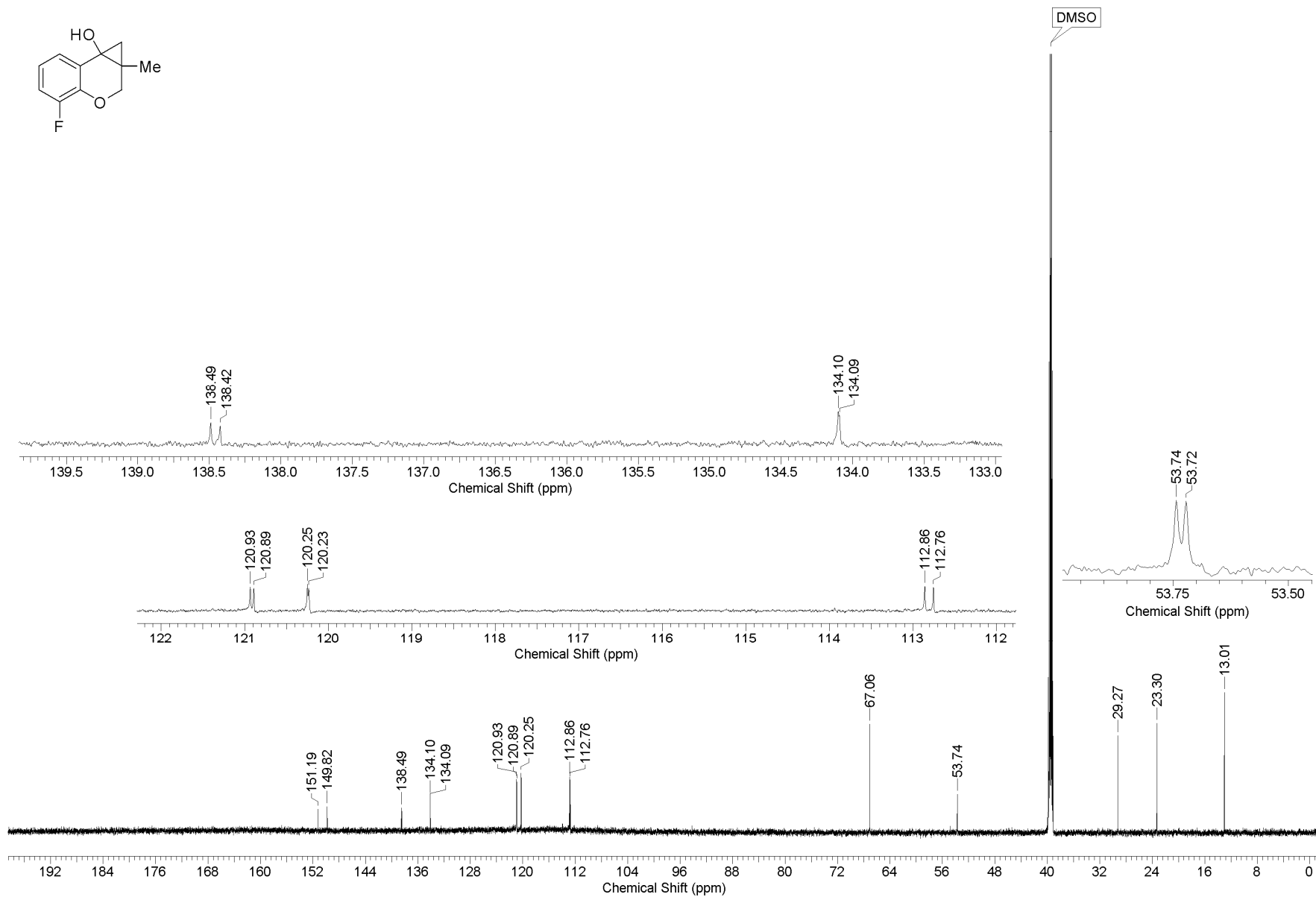
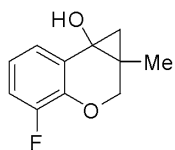


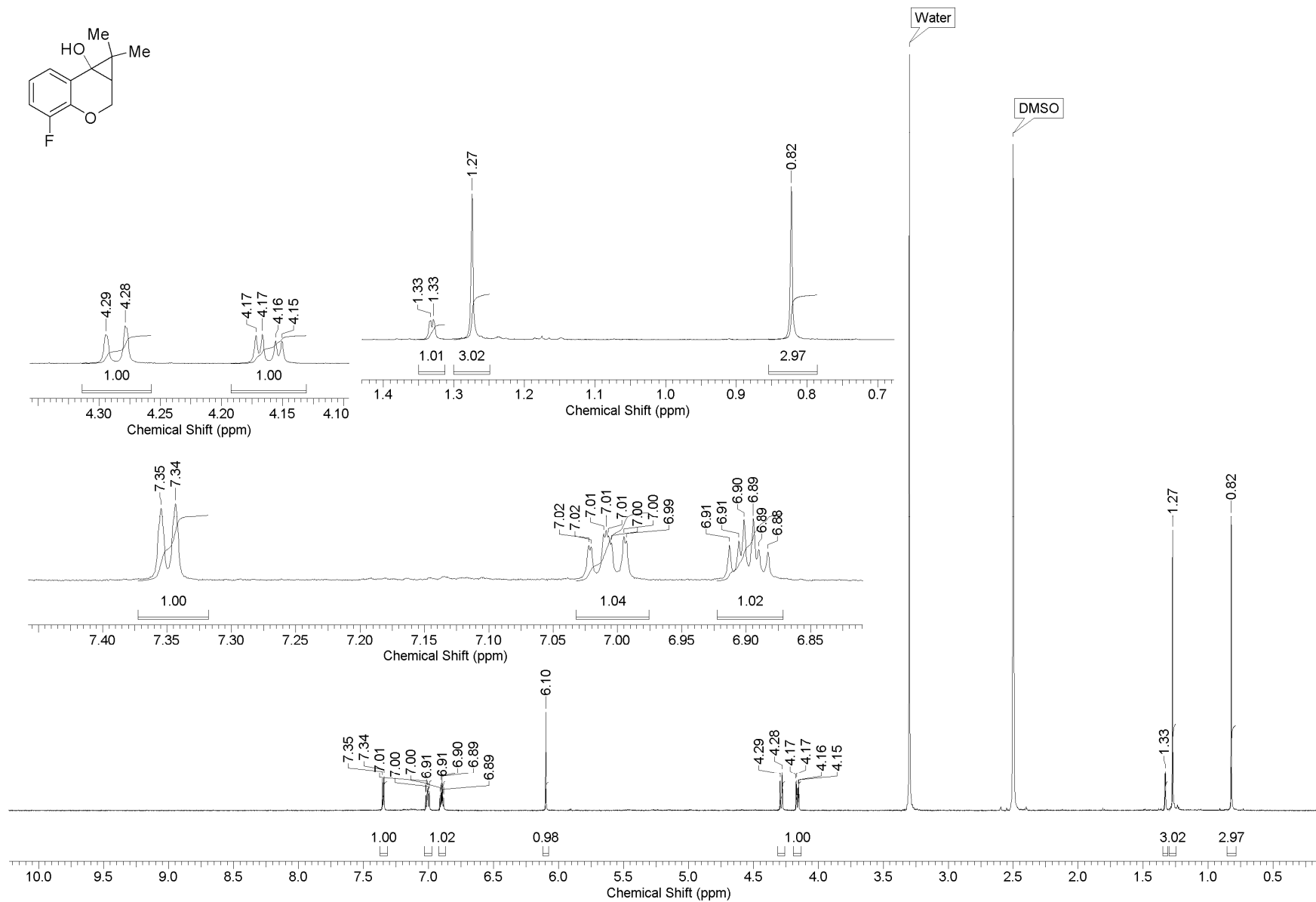
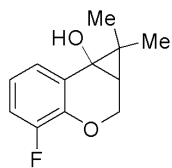
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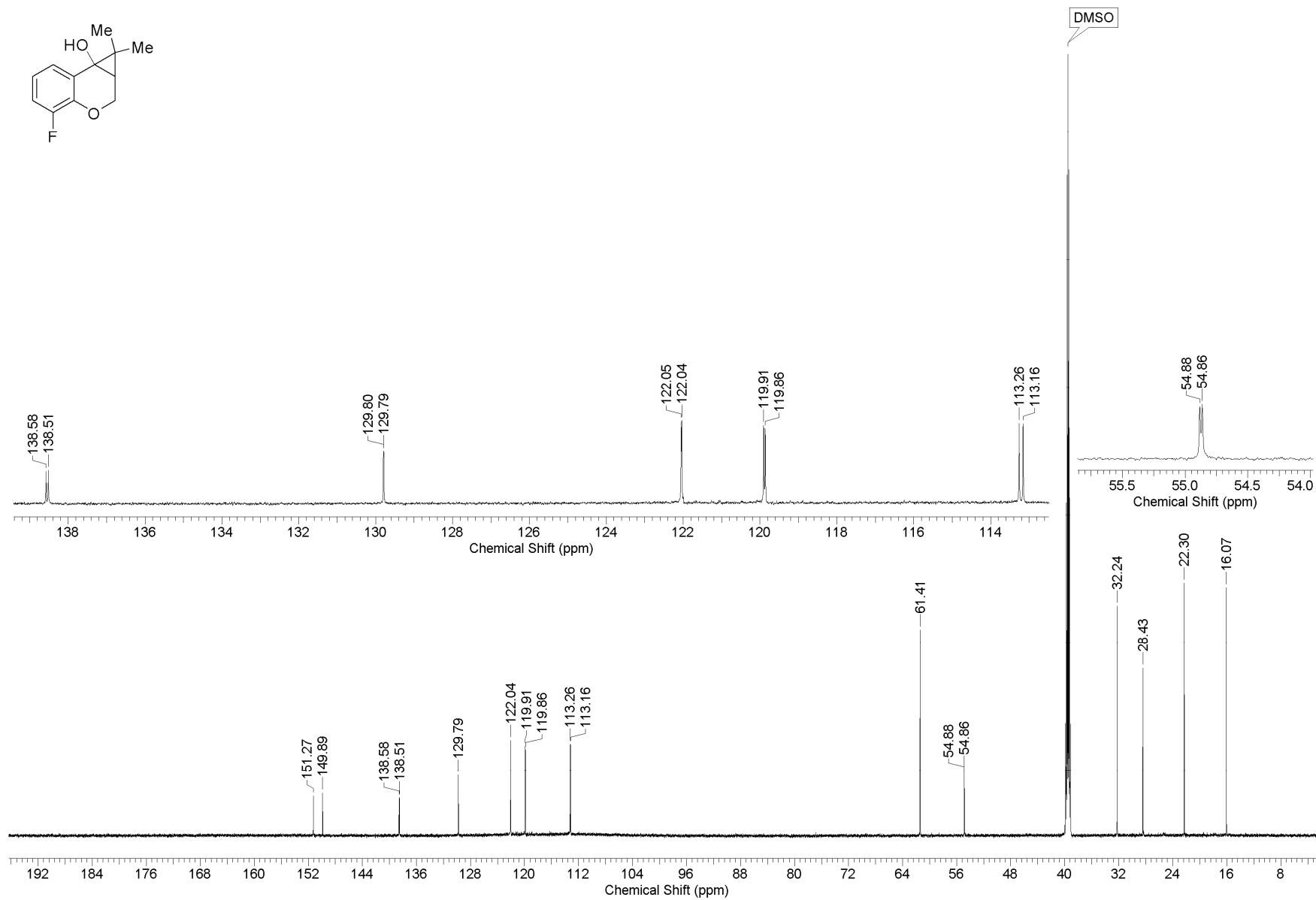
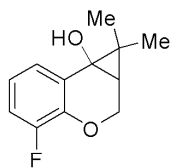


S76

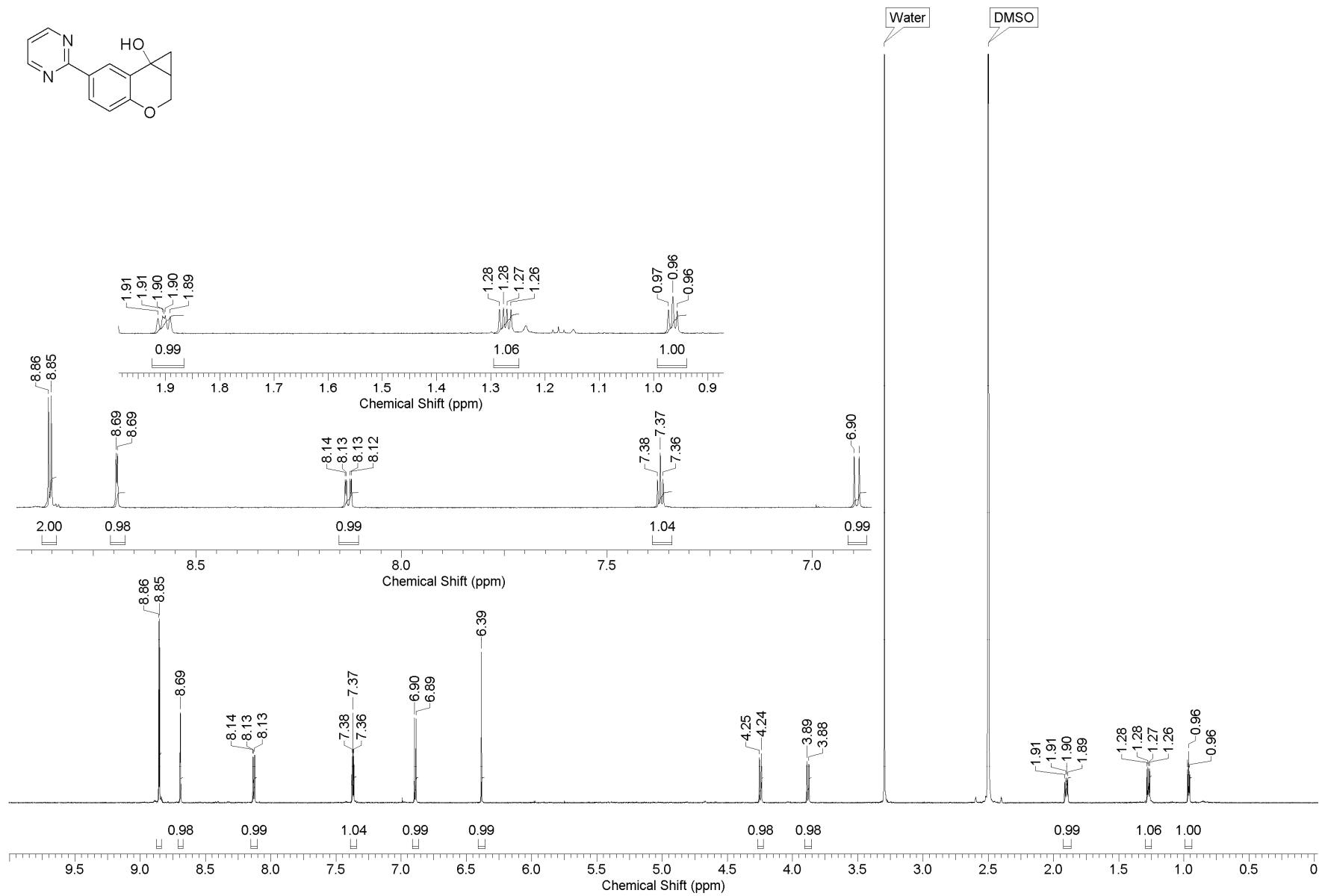
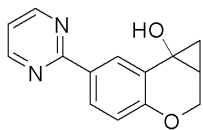




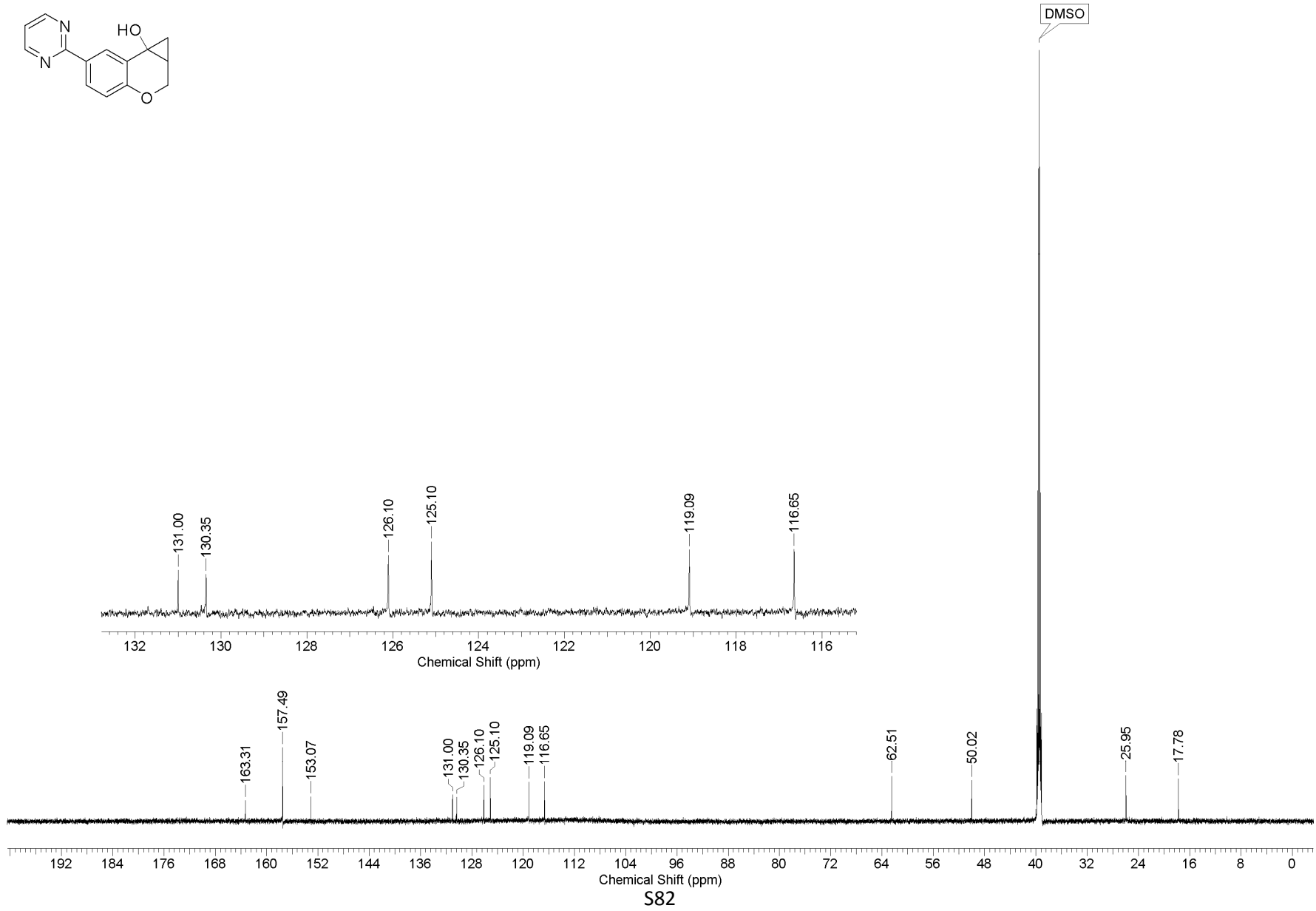
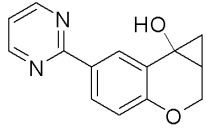


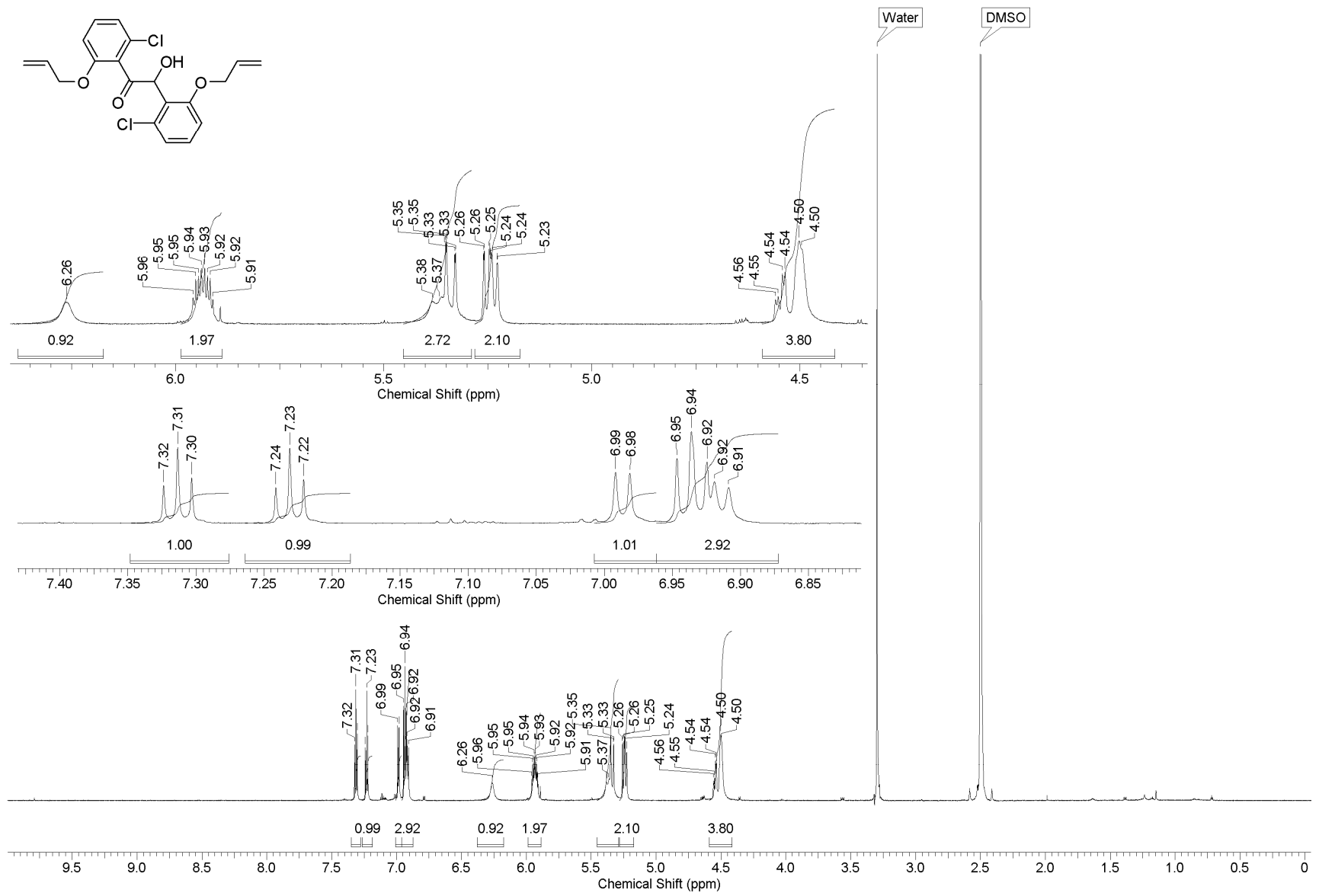
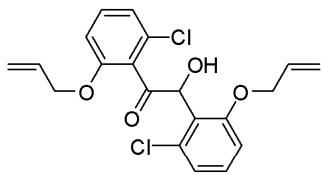


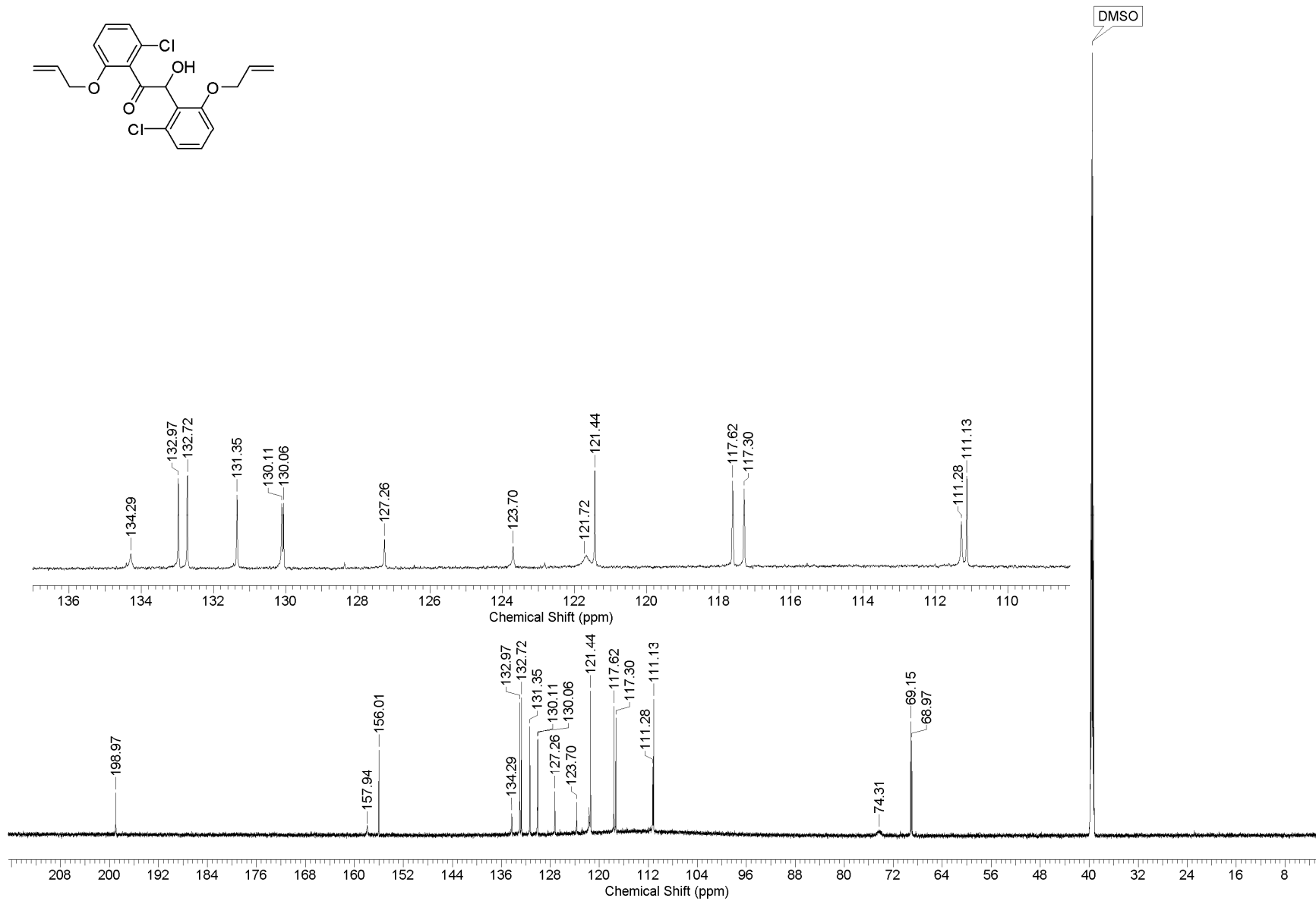
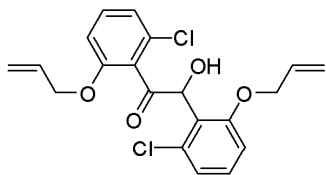
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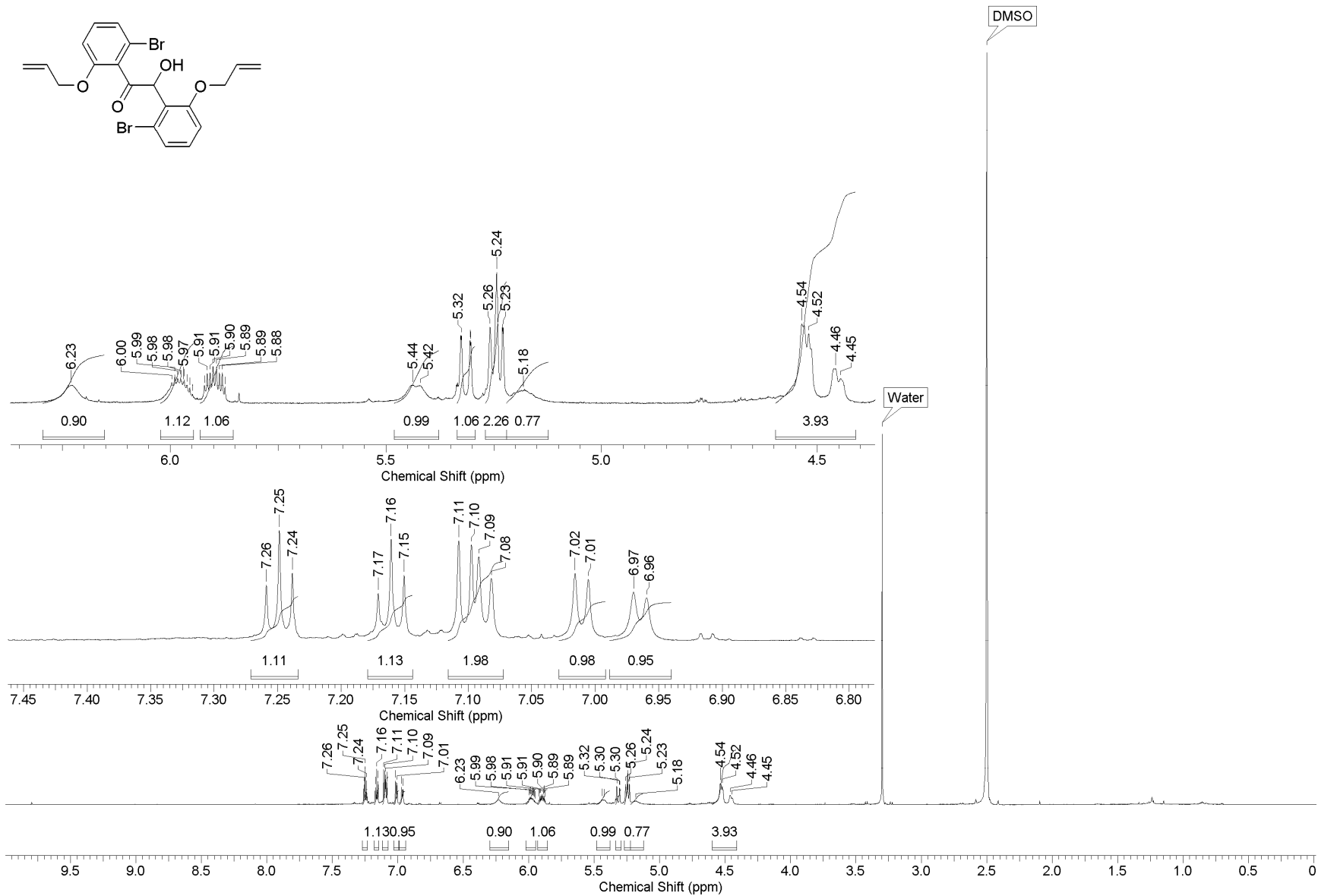
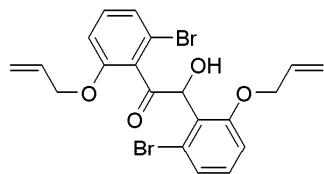


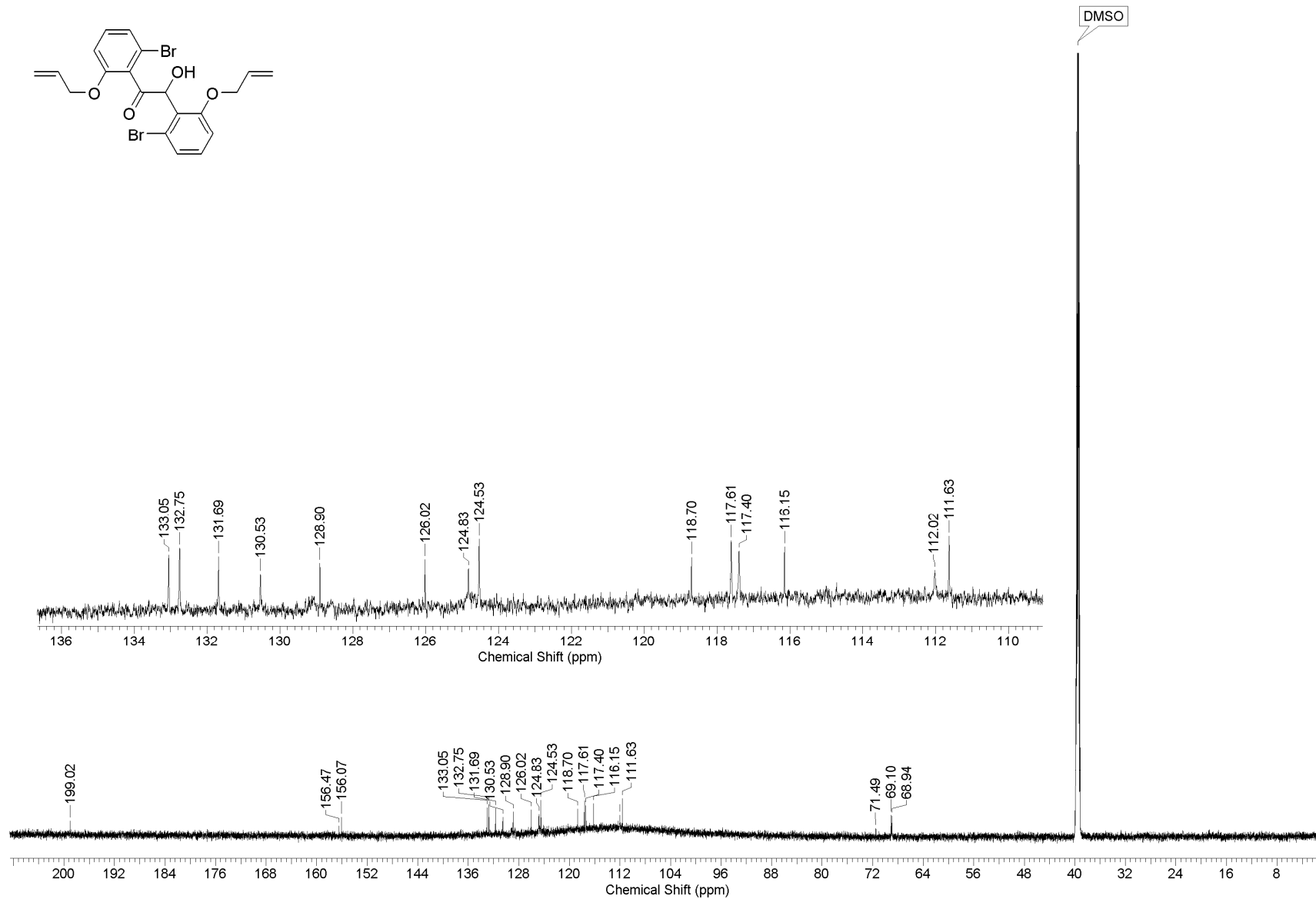
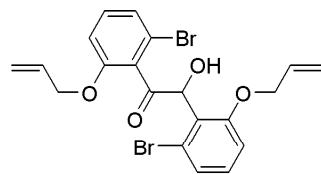
S81

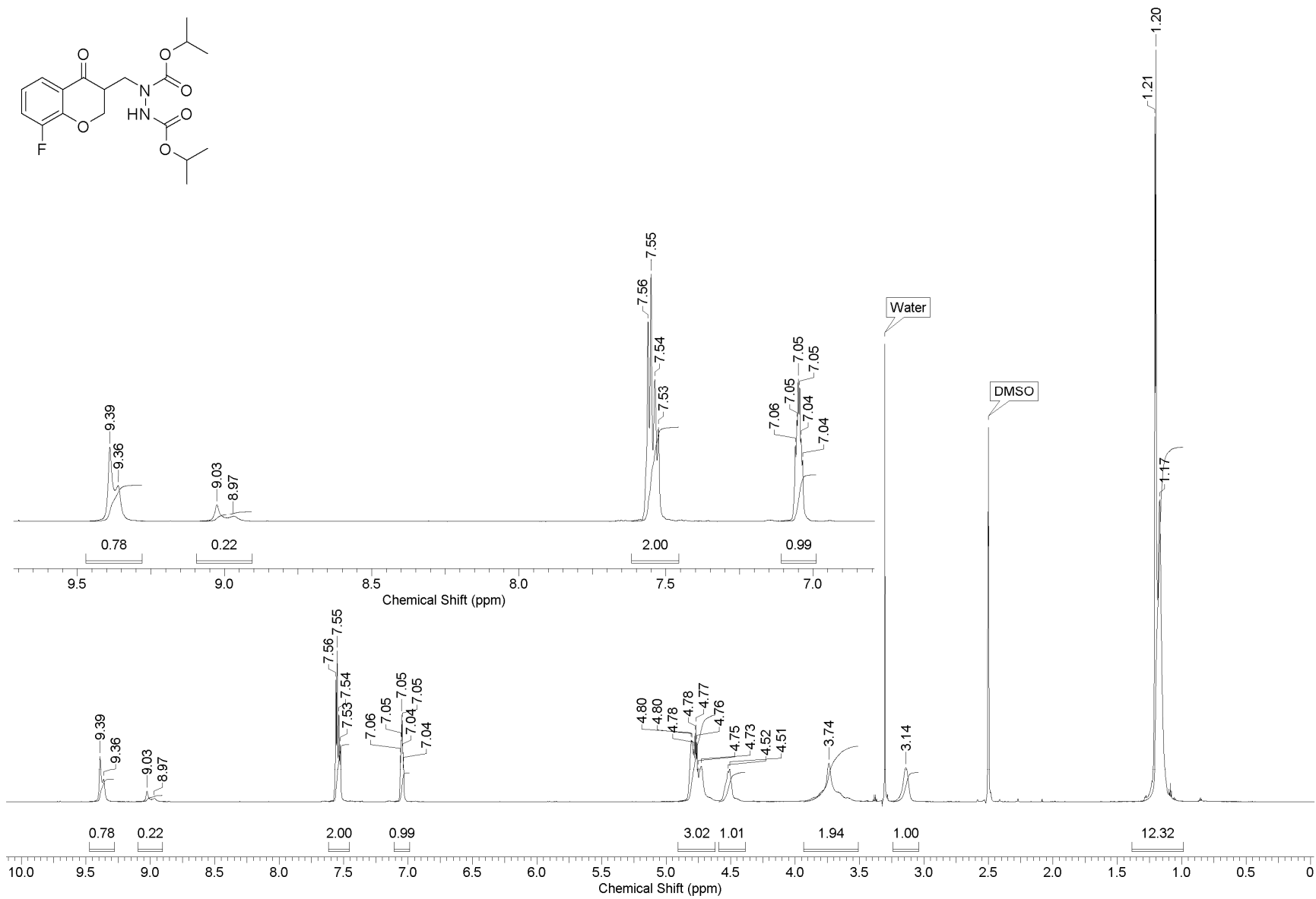
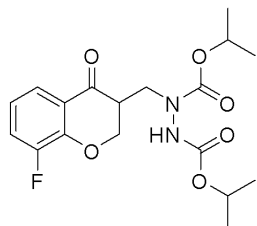


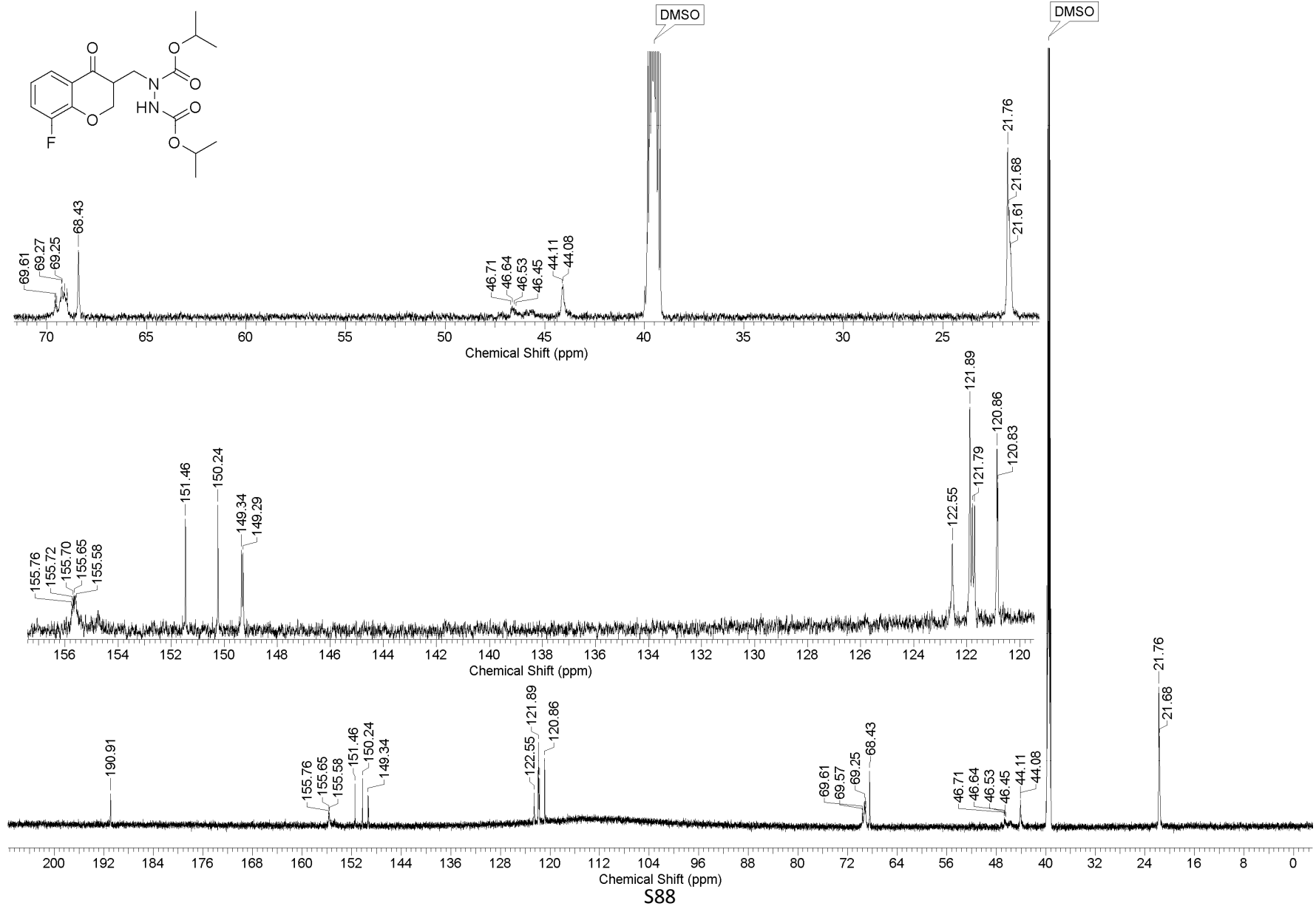


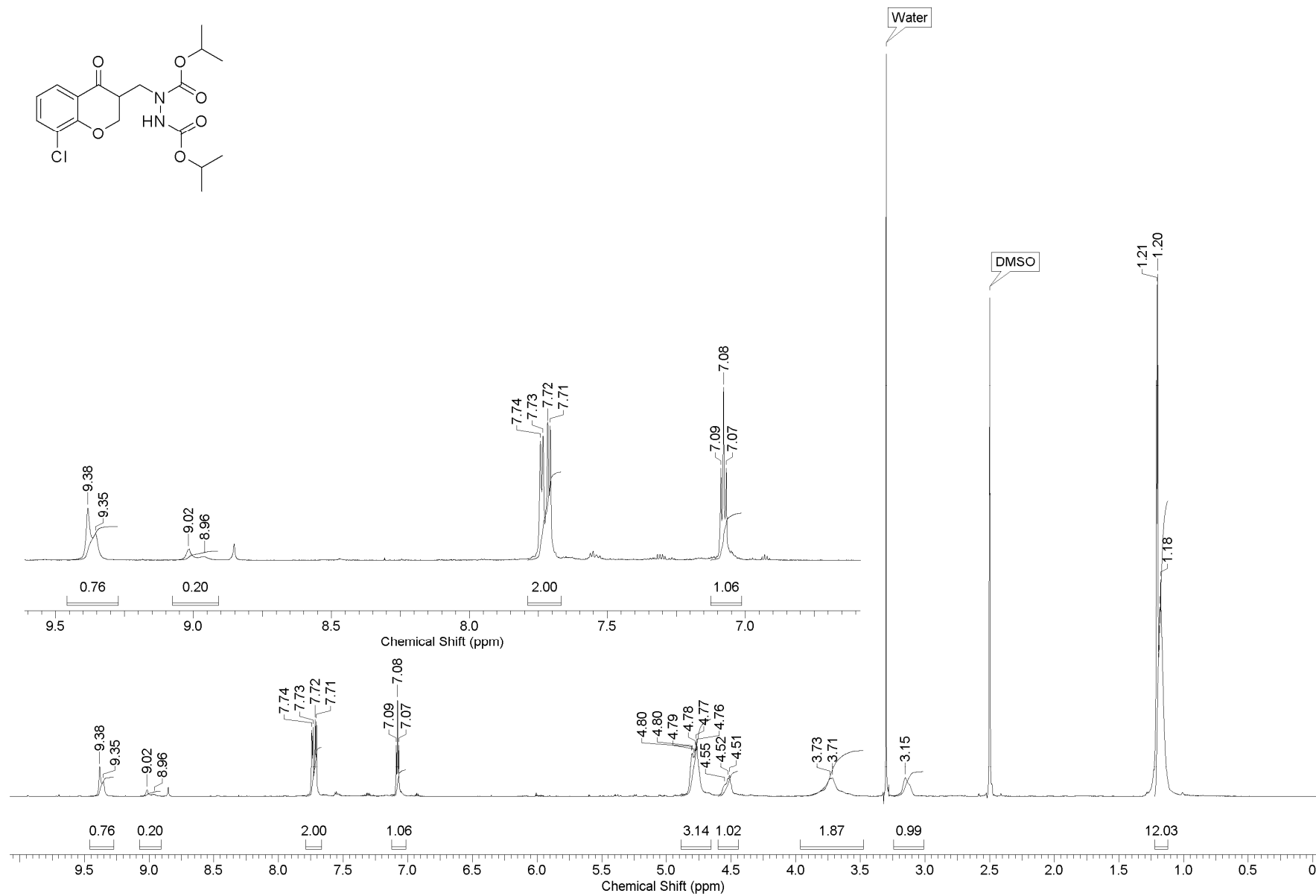
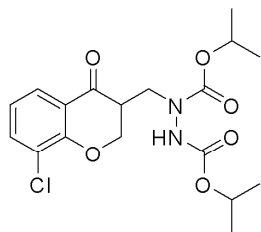




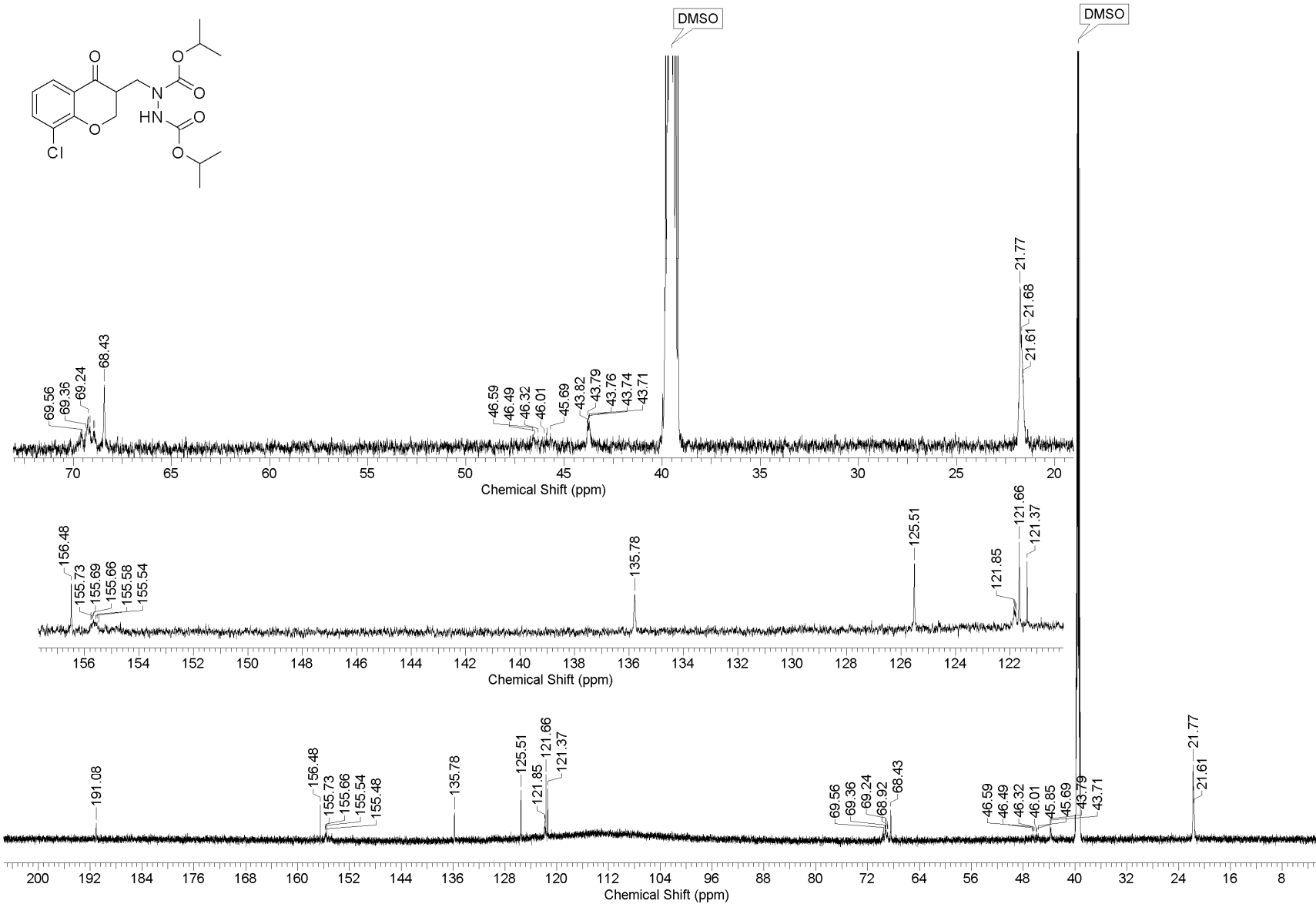
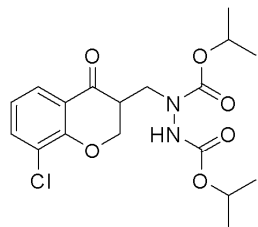


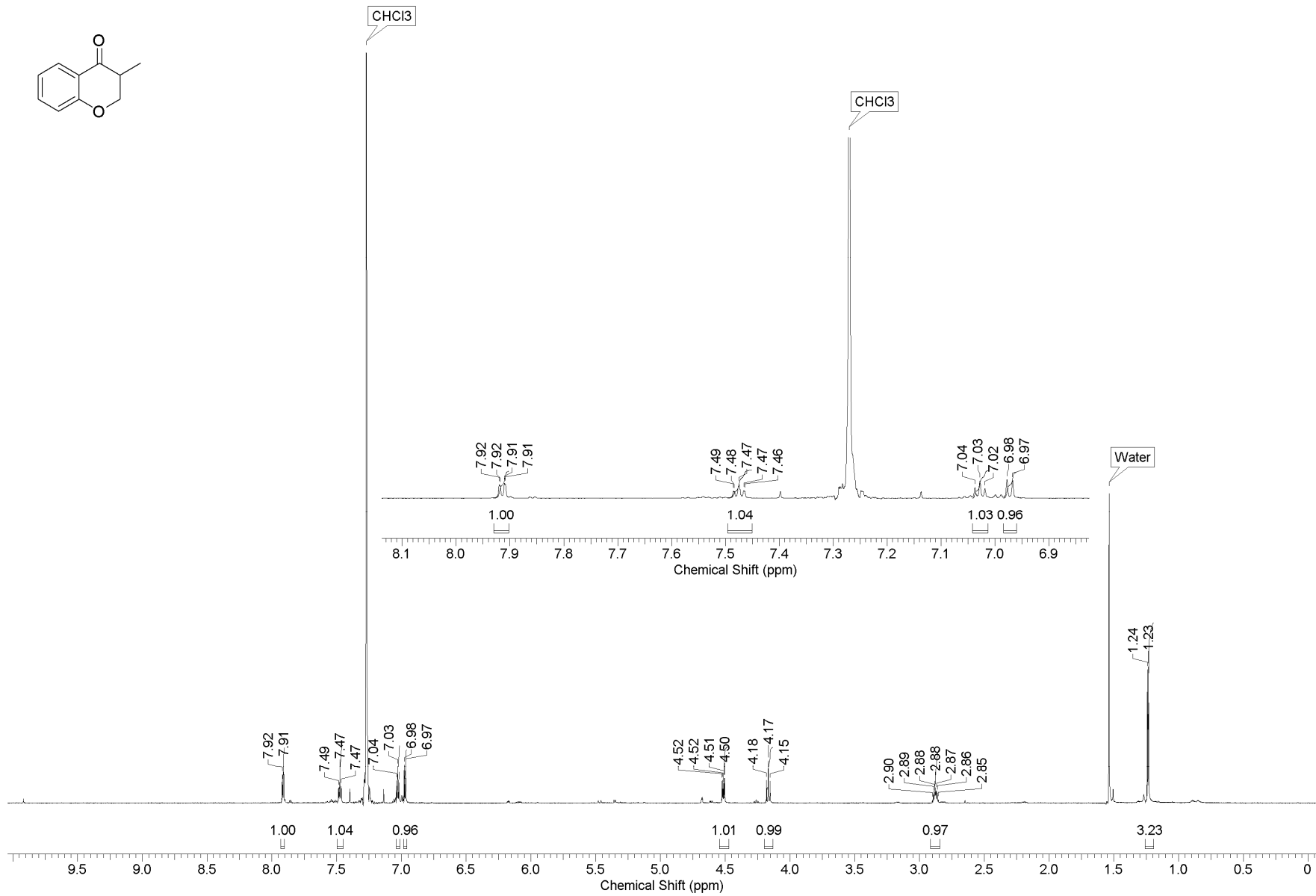
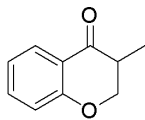






S89





S91

